UNIVERSITÄT ROSTOCK

Twofold Heck / 6π-Electrocyclization and Regioselective Palladium(0)-Catalyzed Reactions of Brominated Thiophenes, Pyrroles, Imidazoles and Indoles

DISSERTATION

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Eidesstattliche Erklärung

Hiermit erkläre ich, die vorliegende Dissertationsschrift eigenständig und nur unter Verwendung der angegebenen Hilfsmittel und Literaturquellen angefertigt zu haben.

Serge-Mithérand Tengho Toguem

Rostock, 14. September 2011

Affectionately Dedicated to

My Wife, Marie Chantal,

My Son, Ryan

My parents, Brothers and Sisters

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List of used abbreviations

Ac	Acetyl
Anal.	Elemental Analysis
Ar	Aryl
bp.	Boiling point
*n*BuLi	*n*-Butylithium
*n*Bu	*n*-Butyl
*t*Bu	*tert*-Butyl
*i*Bu	iso-Butyl
calcd	Calculated
CI	Chemical Ionization
CNS	Central nervous system
COSY	Correlated Spectroscopy
Cy	Cyclohexyl
dba	*trans*, *trans*-Dibenzylideneacetone
DEPT	Distortionless Enhancement by Polarisation Transfer
DMF	Dimethylformamide
EI	Electronic Ionization
equiv	Equivalent
ESI	Electrospray Ionization
Et	Ethyl
Et_2O	Diethyl ether
EtOAc	Ethylacetate
EtOH	Ethanol
GC	Gas Chromatography
Hex	Hexyl
HMBC	Heteronuclear Multiple Bond Correlation
HMQC	Heteronuclear Multiple Quantum Coherence
HRMS	High Resolution Mass Spectroscopy
IR	Infrared spectroscopy
L	Ligand
Me	Methyl

mp.	Melting point
MS	Mass Spectrometry
NEt_3	Triethylamine
NBS	*N*-Bromosuccinimide
NMR	Nuclear Magnetic Resolution
NOESY	Nuclear Overhauser and Exchange Spectroscopy
*n*Oct	*n*-Octyl
ORTEP	Oak Ridge Thermal Ellipsoid Plot
OTf	Triflate (trifluoromethanesulfonate)
Ph	Phenyl
PPAR	peroxisome proliferator-activated receptor
ppm	Parts per million
*i*Pr	*iso*-Propyl
r. t.	Room temperature
S-M	Suzuki-Miyaura
SPhos	2-Dicyclohexylphosphino-2',6'-dimethoxybiphenyl
TCHP	Tris(cyclohexyl) phosphane
Tf_2O	Trifluoromethanesulfonic anhydride
THF	Tetrahydrofurane
TLC	Thin Layer Chromatography
TMS	Tetramethylsilane
UV	Ultraviolet Spectroscopy
XPhos	2-Di-cyclohexylphosphino-2',4',6'-triisopropylbiphenyl

Abstract

This thesis presents site-selective Suzuki-Miyaura reactions of 2,3,5-tribromothiophene and 2,3,5-tribromo-*N*-methylpyrrole, which are controlled by steric and electronic parameters. The reactions proceed with very good site-selectivity in favour of position 5 which is more reactive than position 2, due to steric reasons. The second attack occurs at position 2 which is more electron deficient than position 3. The Suzuki reactions of 2,4,5-tribromothiophene provide a convenient and site-selective approach to 2,4-diaryl-3-bromothiophenes, 2,3,5-triarylthiophenes and 2,3,4-triarylthiophenes.

In this work, palladium-catalyzed Heck reactions of brominated thiophenes, *N*-methylimidazole, *N*-methylpyrrole and *N*-methylindole are also presented. The products were transformed by subsequent 6π-electrocyclization and dehydrogenation to functionalized benzothiophenes, dibenzothiophenes, benzimidazoles, indoles and carbazoles, respectively. The reactions were influenced by the temperature, the time of reaction, the choice of base, of catalyst and the solvent.

Im Rahmen der vorliegenden Arbeit wurden regioselektive Suzuki-Miyaura-Reaktionen von 2,3,5-Tribromthiophenen und 2,3,5-Tribrom-*N*-methylpyrrolen untersucht. Dabei stellen sterische und elektronische Parameter entscheidende Einflussfaktoren dar. Die Reaktionen verlaufen mit sehr guter Regioselektivität, wobei Position 5 bevorzugt angegriffen wird, da diese aufgrund sterischer Gründe reaktiver als Position 2 ist. Der zweite Angriff findet an Position 2 statt, da diese elektronenärmer als Position 3 ist. Die Suzuki-Reaktionen von 2,3,5-Tribromthiophenen stellt eine sehr effiziente regioselektive Methode zur Synthese von 2,4-Diaryl-3-bromthiophenen, 2,3,5-Triarylthiophenen und 2,3,4-Triarylthiophenen dar.

Außerdem wurden in der vorliegenden Arbeit palladiumkatalysierte Heck-Reaktionen von bromierten Thiophenen, *N*-Methylimidazolen, *N*-Methylpyrrolen und *N*-Methylindolen untersucht. Durch eine nachfolgende 6π-Elektrocyclisierung und anschließende Dehydrierung der synthetisierten Produkte konnten funktionalisierte Benzothiophene, Dibenzothiophene, Benzimidazole, Indole und Carbazole gewonnen werden. Die Reaktionen werden durch die Wahl von Reaktionszeit, Reaktionstemperatur, Base, Katalysator und Lösungsmittel beeinflusst.

GENERAL INTRODUCTION

Most drugs prescribed today for the treatment of diseases are organic compounds, while some are derived from natural sources. However, drugs from natural origins are small in quantity whereas synthetically produced ones are much more. Due to the occurence of natural products, often in very small quantities, it is difficult to investigate whether the compounds can be extracted and isolated from natural sources. Organic chemists can provide a solution to the problem by devising practicable laboratory syntheses. Sometimes, the chemical synthesis cost less than extraction of a product. The organic synthesis plays an important role in the preparation of biologically active compounds and natural products. Many methods have been developed for the synthesis of molecules that may have a pharmaceutical or therapeutic relevance. Among these methods, processes catalyzed by transition metals have received special attention.[1] Catalyzed coupling reactions by palladium are an effective tool for the formation of C-C bonds in organic chemistry.[2] The aromatic carbon-carbon coupling has recently emerged as an extremely important method for the preparation of complex organic molecules, such as pharmaceuticals[3]. Among the many coupling reactions commonly used, we cite the reactions such as Heck,[4] Suzuki,[5] Sonogashira[6] and Stille[7]. As most important representatives of this class of reactions, Heck and Suzuki couplings have been noted.

The Heck reaction, originally discovered independently by Mizoroki in 1971[4,8] and Heck in 1972,[4] is the chemical reaction between a halogenated derivative or triflate with an alkene in the presence of a base and a palladium catalyst to form substituted alkenes. It has been applied to a wide range of natural product syntheses and to the synthesis of biologically active molecules.[3,9] On the industrial front (scale), it has led to the production of naproxen commonly used as analgesic and anti-inflammatory agent[10] and of octyl methoxycinnamate used to reduce the appearance of scars.[11]

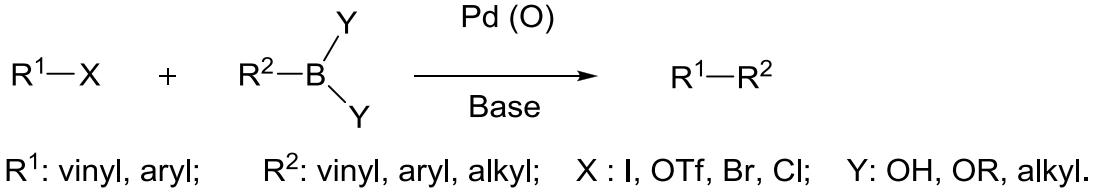
As for the Suzuki reaction, first published in 1979 by Akira Suzuki and Norio Miyaura, is the organic reaction of aryl- or vinyl-boronic acids with aryl or vinyl halides catalyzed by palladium (0).[5] This type of coupling has been used as a key step in the synthesis of a wide variety of natural and unnatural molecules (dendrimers, porphyrins and unusual amino acids and peptides).[3]

In the first part of the present work, the site-selectivity of tribromothiophene and tribromo-*N*-methylpyrrole in the Suzuki cross-coupling reaction has been studied. The Heck reaction has been used in the second part, to synthesize key intermediates for the preparation of functionalized benzothiophenes, benzimidazoles, indoles, carbazoles and dibenzo-thiophenes via 6π-electrocyclization and aromatization, catalyzed by palladium on charcoal, starting with dibromothiophene, tribromo-*N*-methylimidazole, tribromo-*N*-methylpyrrole, tetrabromo-*N*-methylpyrrole, tetrabromo-*N*-methylindole and tetrabromothiophene, respectively.

PART I Site-selective Palladium(0)-catalyzed coupling reactions of tribromo-substituted thiophenes and pyrroles

Introduction and background of Suzuki reaction

In 1979, Akira Suzuki reported the Palladium-catalyzed cross-coupling reaction of organoboronic acids with vinyl and aryl halides in the presence of base, a process known today as Suzuki reaction.[5] The reaction has later been extended to also include couplings with alkyl groups. It works also with pseudohalides like triflates according to the following reactivity order: R_2- I > R_2-OTf > R_2-Br >> R_2-Cl.



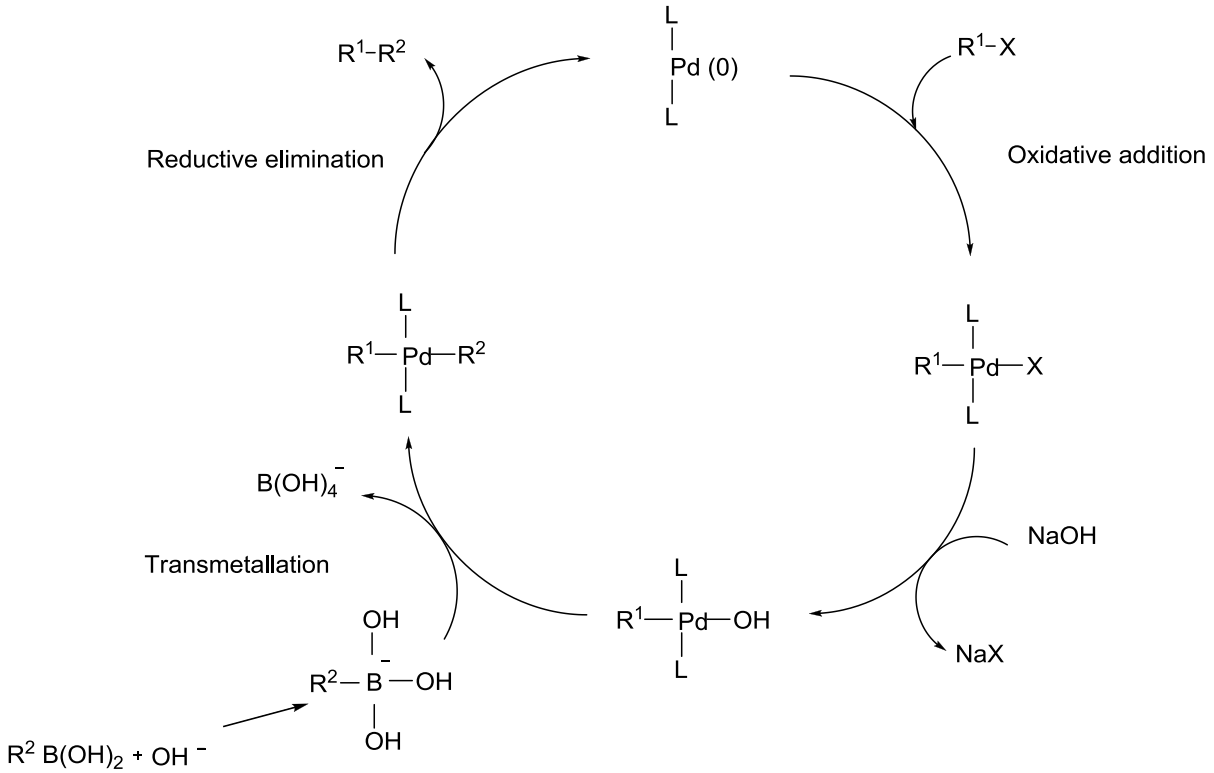
Scheme 1. Suzuki reaction

The Suzuki cross-coupling is one of the most efficient methods for the preparation of bi- or polyaryl compounds.[12] This reaction has been applied in wide areas (including herbicides and natural product syntheses).[3,13] The advantages include the use of boronic acids, which are easy to obtain, mostly non-toxic, air and moisture stable. In the same vein, the inorganic by-product is non-toxic and easily removed from the reaction.

The reaction is catalyzed by a palladium(0) complex formed from $Pd(OAc)_2$, $PdCl_2$, $Ph(PPh_3)_2Cl_2$, and $Pd(dba)_2$ as catalyst precursors. The phosphines are commonly used as ligands. The ligand has the role to stabilize the palladium catalyst. Traditionally, triarylphosphine/Pd complexes are employed as catalysts for the Suzuki reaction.[14] Buchwald and co-workers have developed electron-rich, bulky biphenylphosphine ligands, such as S-Phos, X-Phos, Dave-Phos, which give often a good yield. However, it has been shown that in some cases the reaction can be achieved by using palladium catalysts without a phosphine ligand.[15] The most commonly used bases in the Suzuki reaction are Na_2CO_3, K_2CO_3, NaOH, KOH, K_3PO_4, and Cs_2O_3. It has been found that the base is involved in the coordination

sphere of the palladium and the formation of the R^1-PdL_2-OR from R^1-PdL_2-X is known to accelerate the transmetallation step.[16]

The mechanism of the Suzuki cross-coupling reaction is given in the following scheme:



Scheme 2. Mechanism of the Suzuki palladium-catalyzed cross-coupling reactions

The first step of the catalytic cycle involves the oxidative addition of Pd(0) to the halide to form the organopalladium compound, which reacts with the base to give an intermediate. The intermediate via transmetallation with the boronate complex forms an organopalladium complex. The palladium(0) catalyst is regenerated in the reductive elimination step to form the desired product.

As one of the most commonly used methods of the formation of carbon-carbon bonds, the Suzuki reaction has been applied in the synthesis of many biologically active molecules,[17] useful materials[18] and in pharmaceutical industry.[19] For example, the Suzuki cross-coupling reaction of an isoquinolineboronic acid with a binaphthalene ditriflate gave the anti-HIV alkaloids michellamine A and B.[20]

It is good to notice that the Suzuki reaction can also be a regioselective reaction and it is thus interesting to study the site-selectivity for polyhalogenated compounds.

Site-selective Suzuki reactions

Polyhalogenated heterocycles are of considerable current interest as substrates in site-selective palladium(0)-catalyzed cross-coupling reactions.[21] The site-selectivity often relies on the different rates of oxidative additions of palladium(0) species to carbon-halide bonds and on steric parameters. Electron-poor are usually more reactive than electron-rich carbon atoms. This methodology is very practical and helpful in the total synthesis of natural compounds and pharmaceuticals.[22]

The reactivity order regarding the leaving group is I> OTf> Br>> Cl. This effect can be used to induce selectivity, but it is more difficult to synthesize starting materials with different halide groups than those with only one type of halogen atom. However, the problem of selectivity is more difficult to solve in this second case.

Several examples of regioselective cross-coupling reactions have been reported. For example, in the research group of Prof. Peter Langer, the synthesis of symmetrical and unsymmetrical mono-, di-, tri- and tetraaryl-pyrimidines by site-selective Suzuki cross-coupling reactions of 2,4,5,6-tetrachloropyrimidine was studied.[23] An excellent selectivity has also been observed for Suzuki-Miyaura reactions of the bis(triflate) of 1,2-dihydroxy-anthraquinone (alizarin).[24] The site-selectivity for tetrabromofuran, tetrabromo-thiophene, tribromopyrazole, and pentachloropyridine has also been reported.[25]

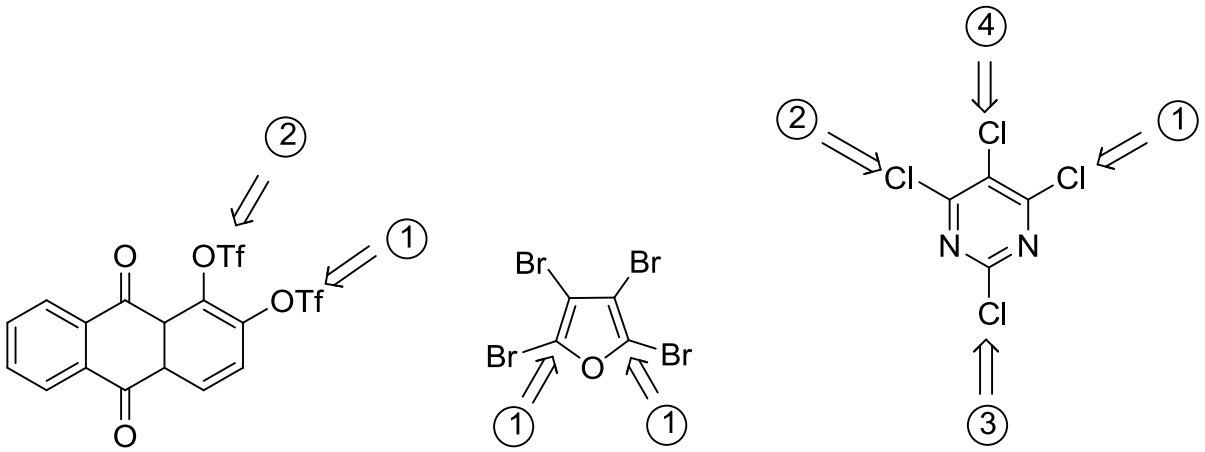


Figure 1. Site selective Suzuki cross-coupling reactions of the Langer group

It has been proved that the origin of selectivity in cross-coupling reactions is dominated by sterical and electronic effects. The presence of neighboring groups, such as ester, amino, imine, and hydroxyl, has a significant effect on the selectivity.

As part of my work, I studied the Suzuki reaction of tri-brominated thiophenes and *N*-methylpyrrole, which gave new functionalized derivatives of thiophene and pyrrole. The monoarylated compounds are used as starting materials in the second part of this work to perform the twofold Heck cross-coupling reaction of the corresponding substrates in good yields.

1 Site-selective Suzuki-Miyaura reactions of 2,3,5-tribromothiophene and 2,3,4-tribromothiophene

1.1 Introduction

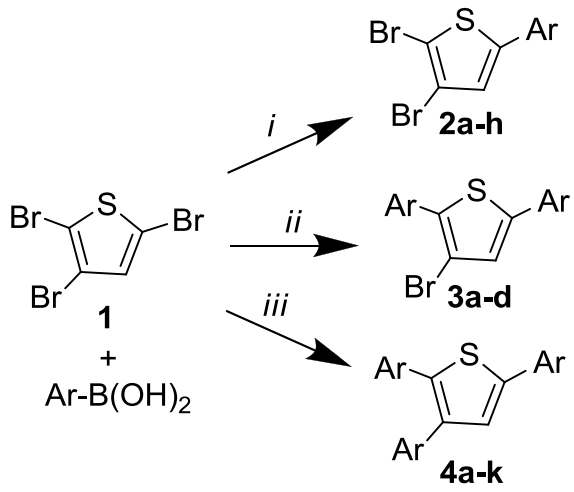
Thiophene derivatives are of special interest in organic chemistry. Aryl-substituted thiophenes are of significant relevance in medicinal chemistry.[26] Functionalized thiophenes also occur in a number of natural products.[27] Due to their electronic properties, such as luminescence, redox activity, nonlinear optical chromism and electron-transport, thiophenes are also important in the field of material sciences.[28] This includes, for example, dibenzothiophenes,[29] terthiophenes[30] and thienyl-diynes.[31]

Site-selective Sonogashira and Kumada reactions of the 2-position of 2,3- and 2,4-dibromothiophene have been studied.[32,33] Metal-halide exchange reactions[34] and Kumada cross-coupling reactions[33] of 2,3,5-tribromothiophene have been reported. In addition, an isolated example of a Stille coupling[35] and of a polymer synthesis have been reported.[36] 2,5-Disubstituted thiophenes were prepared by regioselective Sonogashira coupling reactions of 2,3,4,5-tetraiodothiophene[37] and 2,3,4,5-tetrabromothiophene.[38] In this chapter, I reported the first Suzuki-Miyaura reactions of 2,3,5-tribromothiophene and 2,3,4-tribromothiophene, which have not been reported to the date. The reaction of the latter with one, two and three equivalents of arylboronic acids afforded monoaryldibromothiophenes, diarylbromothiophenes and triarylthiophenes with very good site-selectivity, respectively.

1.2 Results and discussion

1.2.1 Site-selective Suzuki-Miyaura reactions of 2,3,5-tribromothiophene

The Suzuki-Miyaura reaction of commercially available 2,3,5-tribromothiophene (**1**) with various arylboronic acids (1.1 equiv.) afforded the 5-aryl-2,3-dibromothiophenes **2a-h** in 40-53% yield (Scheme 3, Table 1).



Scheme 3. Synthesis of **2a-h**, **3a-d** and **4a-k**. *Conditions: i*, **1** (1.0 equiv.), Ar-B(OH)$_2$ (1.1 equiv), Pd(PPh$_3$)$_4$ (5 mol-%), K$_2$CO$_3$ (2M), 1,4-dioxane / toluene = 1:1, 100 °C, 8 h (see Table 1); *ii*, **1** (1.0 equiv.), ArB(OH)$_2$ (2.2 equiv.), Pd(PPh$_3$)$_4$ (5 mol-%), K$_3$PO$_4$ (4.0 equiv.), 1,4-dioxane / toluene = 1:1), 100 °C, 12 h (see Table 2); *iii,* **1** (1.0 equiv.), ArB(OH)$_2$ (4.0 equiv.), Pd(PPh$_3$)$_4$ (10 mol-%), K$_2$CO$_3$ (2M), 1,4-dioxane, 90 °C, 8 h (see Table 3)

Table 1. Synthesis of 5-aryl-2,3-dibromothiophenes **2a-h**

2	Ar	% (**2**)[a]
a	4-MeC$_6$H$_4$	47
b	4-EtC$_6$H$_4$	53
c	4-*t*BuC$_6$H$_4$	51
d	3,5-Me$_2$C$_6$H$_3$	40
e	2,6-(MeO)C$_6$H$_3$	44
f	2-(MeO)C$_6$H$_4$	46
g	3-FC$_6$H$_4$	40
h	4-ClC$_6$H$_4$	45

[a] Yields of isolated products

The Suzuki-Miyaura reaction of **1** with 2.2 equiv. of arylboronic acids afforded the 2,5-diaryl-3-bromothiophenes **3a-d** in 45-67% yield (Scheme 3, Table 2). The reactions again proceeded with very good site-selectivity. The use of 4.0 equiv. of arylboronic acids resulted in the formation of 2,3,5-triarylthiophenes **4a-k** in very good yields (Scheme 3, Table 3).

Table 2. Synthesis of 2,5-diaryl-3-bromothiophenes **3a-d**

3	Ar	% (**3**)[a]
a	4-MeC_6H_4	55
b	4-EtC_6H_4	67
c	3,5-$Me_2C_6H_3$	49
d	3-FC_6H_4	45

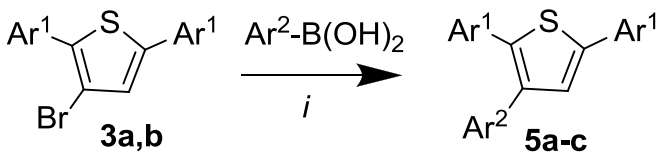
[a] Yields of isolated products

Table 3. Synthesis of 2,3,5-triarylthiophenes **4a-k**

4	Ar	% (**4**)[a]
a	4-MeC_6H_4	92
b	4-*t*BuC_6H_4	87
c	3,5-$Me_2C_6H_3$	78
d	3-FC_6H_4	76
e	2-$(MeO)C_6H_4$	81
f	2,5-$(MeO)_2C_6H_3$	91
g	4-vinylC_6H_4	88
h	4-ClC_6H_4	72
i	4-FC_6H_4	84
j	2,4-$(MeO)_2C_6H_3$	94
k	3,4-$(MeO)_2C_6H_3$	88

[a] Yields of isolated products

The Suzuki-Miyaura reaction of 2,5-diaryl-3-bromothiophenes **3a,b** with 2.0 equiv. of arylboronic acids afforded the 2,3,5-triarylthiophenes **5a-c** containing two different aryl groups (Scheme 4, Table 4).



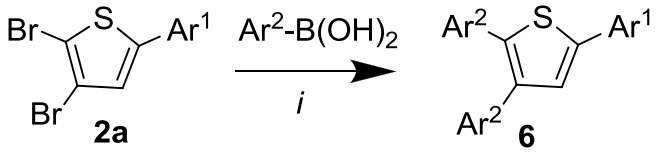
Scheme 4. Synthesis of **5a-c**. *Conditions*: *i*, **3a,b** (1.0 equiv), Ar^2-$B(OH)_2$ (2.0 equiv.), $Pd(PPh_3)_4$ (10 mol-%), K_3PO_4 (4.0 equiv), 1,4-dioxane / toluene = 1:1, 100 °C, 12 h

Table 4. Synthesis of 2,3,5-triarylthiophenes **5a-c**

5	Ar^1	Ar^2	% (**5**)[a]
a	4-MeC_6H_4	4-EtC_6H_4	92
b	4-EtC_6H_4	4-MeC_6H_4	87
c	4-EtC_6H_4	2-$(EtO)C_6H_4$	83

[a] Yields of isolated products

The Suzuki-Miyaura reaction of 5-aryl-2,3-dibromothiophenes **2a** with 3.0 equiv. of arylboronic acids afforded the 2,3,5-triarylthiophenes **6** containing two different aryl groups (Scheme 5, Table 5).



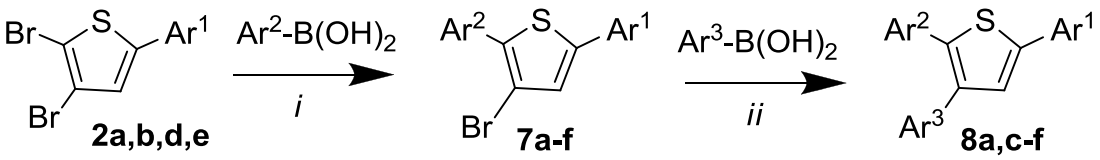
Scheme 5. Synthesis of **6**. *Conditions*: *i*, **2a** (1.0 equiv), Ar^2-$B(OH)_2$ (3.0 equiv.), $Pd(PPh_3)_4$ (10 mol-%), K_3PO_4 (4.0 equiv), 1,4-dioxane / toluene = 1:1, 100 °C, 12 h

Table 5. Synthesis of 2,3,5-triarylthiophenes **6**

	Ar^1	Ar^2	% (**6**)[a]
6	4-MeC_6H_4	4-$MeOC_6H_4$	84

[a] Yields of isolated products

The Suzuki reaction of 5-aryl-2,3-dibromothiophenes **2a,b,d,e** with 1.1 equivalent of arylboronic acids allows a site-selective synthesis of 2,5-diaryl-3-bromothiophenes **7a-f** containing two different aryl groups (scheme 6, Table 6). The employment of 2.0 equiv. of arylboronic acids to react with 1.0 equivalent of **7a,c-f** gave the 2,3,5-triarylthiophenes **8a,c-f** containing three different aryl groups in very good yields (Scheme 6, Table 7).



Scheme 6. Synthesis of **7a-f** and **8a,c-f**. *Conditions*: *i*, **2a,b,d,e** (1.0 equiv), Ar^2-$B(OH)_2$ (1.1 equiv.), $Pd(PPh_3)_4$ (10 mol-%), K_3PO_4 (4.0 equiv), 1,4-dioxane / toluene = 1:1, 100 °C, 12 h; *ii*, **7a,c-f** (1.0 equiv), Ar^3-$B(OH)_2$ (2.0 equiv.), $Pd(PPh_3)_4$ (10 mol-%), K_3PO_4 (4.0 equiv), 1,4-dioxane / toluene = 1:1, 100 °C, 12 h

Table 6. Synthesis of 2,5-diaryl-3-bromothiophenes **7a-f**

7	Ar^1	Ar^2	% (**7**) [a]
a	4-MeC_6H_4	2-(MeO)C_6H_4	58
b	4-EtC_6H_4	2-(MeO)C_6H_4	61
c	4-EtC_6H_4	2,6-$(MeO)_2C_6H_3$	43
d	3,5-$Me_2C_6H_3$	2-(MeO)C_6H_4	56
e	2,6-$(MeO)_2C_6H_3$	4-MeC_6H_4	67
f	2-(MeO)C_6H_4	4-MeC_6H_4	51

[a] Yields of isolated products

Table 7. Synthesis of 2,3,4-triarylthiophenes **8a,c-f**

8	Ar^1	Ar^2	Ar^3	% (**8**)[a]
a	4-MeC_6H_4	2-(MeO)C_6H_4	4-EtC_6H_4	77
b	4-EtC_6H_4	2,6-$(MeO)_2C_6H_3$	2-(EtO)C_6H_4	-[b]
c	4-EtC_6H_4	2-(MeO)C_6H_4	4-*t*BuC_6H_4	81
d	3,5-$Me_2C_6H_3$	2-(MeO)C_6H_4	4-EtC_6H_4	72
e	2,6-$(MeO)_2C_6H_3$	4-MeC_6H_4	4-EtC_6H_4	75
f	2-(MeO)C_6H_4	4-MeC_6H_4	2-(EtO)C_6H_4	64

[a] Yields of isolated products, [b] experiment was not carried out

In all reactions, the best yields were obtained when $Pd(PPh_3)_4$ was used as the catalyst. The use of other catalysts (such as $Pd(OAc)_2$ / X-Phos) proved to be less successful in terms of yield. All reactions were carried out at 90-100 °C. For the synthesis of **2a-h** and **4a-k,**

K_2CO_3 was used as the base. For the synthesis of **3a-d** and **5a-c**, K_3PO_4 was used as the base. 1,4-Dioxane or a 1:1 mixture of 1,4-dioxane and toluene was used as the solvent. The yields of products derived from arylboronic acids containing electron-donating and electron-withdrawing substituents are in a similar range. The yields of products **4a-k** and **5a-c**, where no issue of site-selectivity was present, were generally higher than those of **2a-h** and **3a-d**. Although products **2a-h** and **3a-d** were isolated in only moderate yields, the site-selectivities of all reactions were very good. In fact, inspection of selected crude spectra of **2** and **3** showed that significant amounts of other heterocyclic products were not formed. The moderate yields of the isolated products can be explained by practical problems during the chromatographic purification.

The structures of all products were established by spectroscopic methods. The structures of **2a**, **3a** and **4i** were independently confirmed by X-ray crystal structure analyses (Figures 2, 3, 4, 5 and 6).

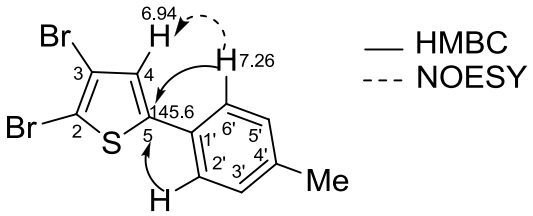


Figure 2. HMBC and NOESY correlations of **2a**

The structure of **2a** was established by 2D NMR using HMBC and NOESY correlations. In the HMBC spectrum, the phenyl protons resonating at δ 7.26 correlated with the quaternary carbon of the thiophene ring C-5 (δ 145.6). In the NOESY spectrum, an interaction between the phenyl proton δ 7.26 and the proton of the thiophene ring at δ 6.94 is observed.

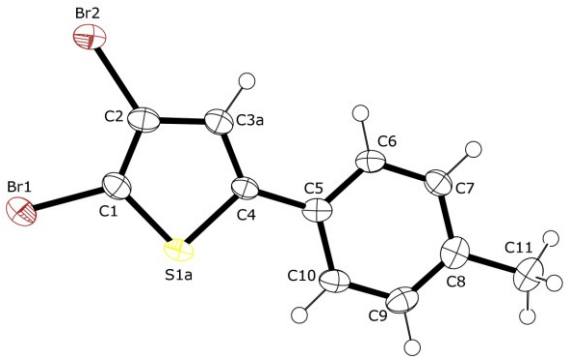


Figure 3. Crystal structure of **2a**

The crystal structure of **2a** showed that the phenyl ring is twisted slightly out of the plane of the thiophene (with torsion angles of 179.3(3)° for C6-C5-C4-S1a).

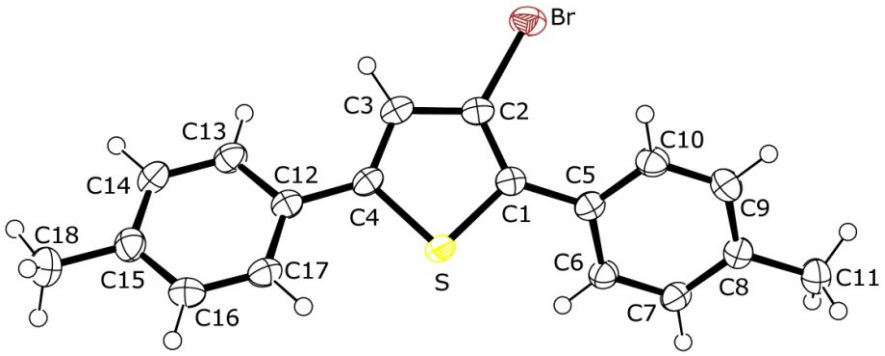


Figure 4. Crystal structure of **3a**

The crystal structure of **3a** showed that the phenyl ring are twisted slightly out of the plane of thiophene, with torsion angles of 34.5(2) and 23.4(2)° for C6-C5-C1-S and S-C4-C12-C17, respectively.

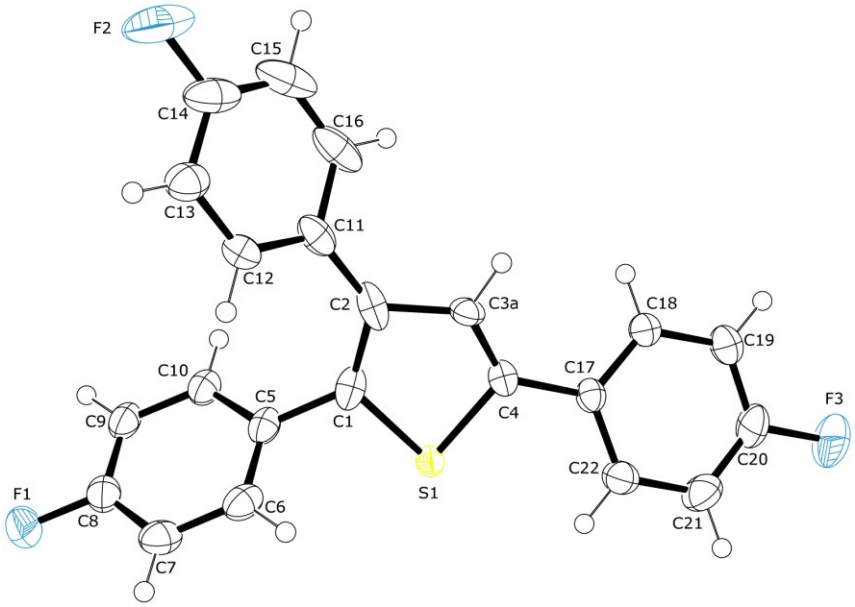


Figure 5. Crystal structure of **4i**

The crystal structure of **4i** showed that the phenyl rings are twisted slightly out of the plane of thiophene, with torsion angles of 160.63(10), 55.11(14) and 32.8(2)° for S1a-C4-C17-C18, S1a-C1-C5-C6 and C1-C2-C11-C12, respectively.

The regioselectivites reported herein can be explained based on the different electronic and steric properties of the three different C-Br bonds of **1**. Carbon atom C-5 is the most reactive position because of its electron-deficient character and because it is easily sterically accessible (Figure 6). From the electronic viewpoint, carbon C-2 is similar to C-5, but it is more sterically hindered because of the neighbourhood of the bromine atom attached to carbon C-3. The latter position is least reactive because of electronic reasons.

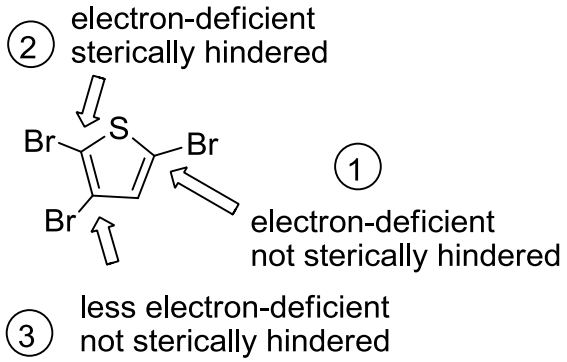
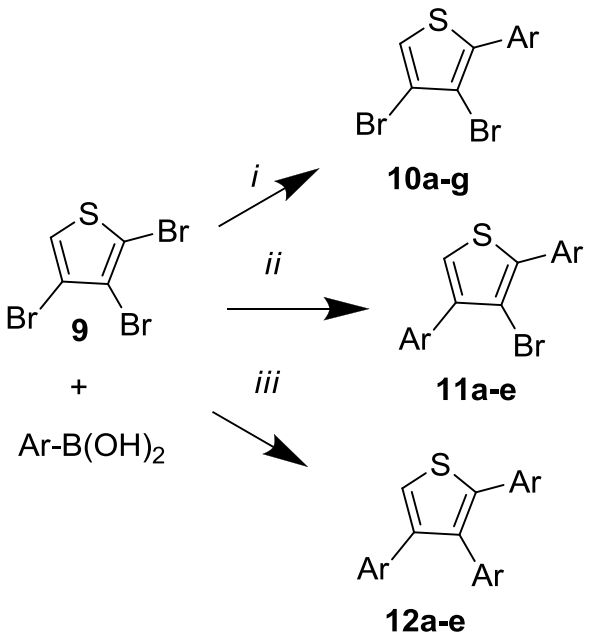


Figure 6. Possible explanation for the site-selectivity of the reactions of **1**

1.2.2 Site-selective Suzuki-Miyaura reactions of 2,3,4-tribromothiophene

The Suzuki-Miyaura reaction of commercially available 2,3,4-tribromothiophene (**9**) with various arylboronic acids (1.1 equiv.) afforded the 2-aryl-3,4-dibromothiophenes **10a-g** in 67-94% yield (Scheme 7, Table 8).

The Suzuki-Miyaura reaction of **9** with 2.1 equiv. of arylboronic acids afforded the 2,4-diaryl-3-bromothiophenes **11a-e** in 35-55% yield (Scheme 7, Table 9). The employment of 4.0 equiv. of arylboronic acids resulted in the formation of 2,3,4-triarylthiophenes **12a-e** in very good yields (Scheme 7, Table 10).



Scheme 7. Synthesis of **10a-g**, **11a-e** and **12a-e**. *Conditions*: *i*, **9** (1.0 equiv.), Ar-B(OH)$_2$ (1.1 equiv.), Pd(PPh$_3$)$_4$ (5 mol-%), K$_2$CO$_3$ (2M), 1,4-dioxane / toluene = 1:1, 100 °C , 5 h (see Table 8); *ii,* **9** (1.0 equiv.), Ar-B(OH)$_2$ (2.1 equiv.), Pd(PPh$_3$)$_4$ (6 mol-%), K$_3$PO$_4$ (4.0 equiv.), 1,4-dioxane / toluene = 1:1, 1mL of H$_2$O, 100 °C, 12 h, (see Table 9); *iii,* **9** (1.0 equiv.), Ar-B(OH)$_2$ (4.0 equiv.), Pd(PPh$_3$)$_4$ (6 mol-%), K$_2$CO$_3$ (2M),1,4-dioxane, 90 °C,12 h (see Table 10)

Table 8. Synthesis of 2-aryl-3,4-dibromothiophenes **10a-g**

10	Ar	% (**10**) [a]
a	4-MeC$_6$H$_4$	89
b	4-EtC$_6$H$_4$	87
c	4-*t*BuC$_6$H$_4$	94
d	2-(MeO)C$_6$H$_4$	85
e	2,6-(MeO)$_2$C$_6$H$_3$	67
f	3,5-Me$_2$C$_6$H$_3$	79
g	3-ClC$_6$H$_4$	67

[a] Yields of isolated products

Table 9. Synthesis of 3-bromo-2,4-diarylthiophenes **11a-e**

11	Ar	% (**11**) [a]
a	4-MeC_6H_4	55
b	4-EtC_6H_4	51
c	3,5-$Me_2C_6H_3$	46
d	4-*t*BuC_6H_4	49
e	3-ClC_6H_4	35

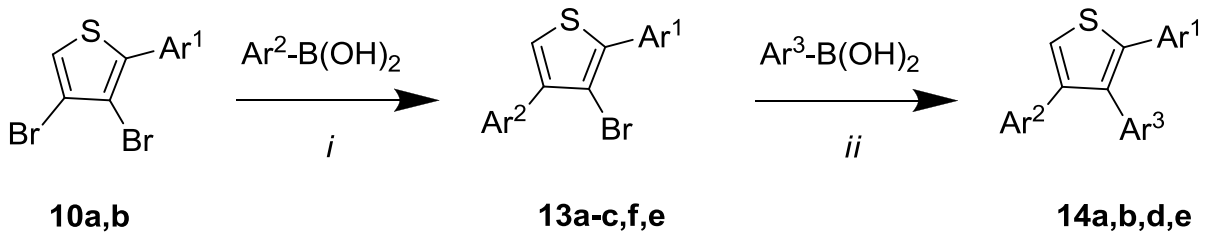
[a] Yields of isolated products

Table 10. Synthesis of 2,3,4-triarylthiophenes **12a-e**

12	Ar	% (**12**) [a]
a	4-MeC_6H_4	93
b	3,5-$Me_2C_6H_3$	86
c	4-*t*BuC_6H_4	94
d	4-(MeO)C_6H_4	96
e	4-ClC_6H_4	78

[a] Yields of isolated products

The Suzuki-Miyaura reaction of 2-aryl-3,4-dibromothiophenes **10a,b** with 1.1 equiv. of arylboronic acids resulted in site-selective formation of the 2,4-diarylthiophenes **13a-c,e,f** containing two different aryl groups (Scheme 8, Table 11). The reaction of 1.0 equiv. of **13a-e** with 2.0 equiv. of boronic acids allows the synthesis of 2,3,4-triarylthiophenes **14a,b,d,e** containing three different aryl groups (Scheme 8, Table 12).



10a,b **13a-c,f,e** **14a,b,d,e**

Scheme 8. Synthesis of **13a-f** and **14a-e**. *Conditions*: *i*, **10a,b** (1.0 equiv.), Ar^2-$B(OH)_2$ (1.1 equiv.), $Pd(PPh_3)_4$ (6 mol-%), K_3PO_4 (4.0 equiv.), 1,4-dioxane / toluene = 1:1, 1 mL of H_2O,

100 °C, 12 h; *ii*, **13a,b,d,e** (1.0 equiv), Ar^3-$B(OH)_2$ (2.0 equiv.), $Pd(PPh_3)_4$ (10 mol-%), K_3PO_4 (4.0 equiv), 1,4-dioxane / toluene = 1:1, 100 °C, 12 h

Table 11. Synthesis of 3-bromo-2,4-diarylthiophenes **13a-c,e,f**

13	Ar^1	Ar^2	% (**13**) [a]
a	4-MeC_6H_4	2-$(MeO)C_6H_4$	87
b	4-EtC_6H_4	2-$(MeO)C_6H_4$	81
c	4-EtC_6H_4	2,6-$(MeO)_2C_6H_3$	53
d	4-MeC_6H_4	4-EtC_6H_4	-[b]
e	4-MeC_6H_4	4-*t*BuC_6H_4	57
f	4-MeC_6H_4	2,6-$(MeO)_2C_6H_3$	46

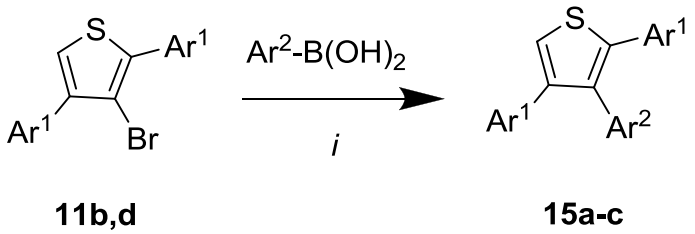
[a] Yields of isolated products; [b] complex mixture

Table 12. Synthesis of 2,3,4-triarylthiophenes **14a,b,d,e**

14	Ar^1	Ar^2	Ar^3	% (**14**)[a]
a	4-MeC_6H_4	2-$(MeO)C_6H_4$	2-$(EtO)C_6H_4$	92
b	4-EtC_6H_4	2-$(MeO)C_6H_4$	2-$(EtO)C_6H_4$	87
c	4-EtC_6H_4	2,6-$(MeO)_2C_6H_3$	2-$(EtO)C_6H_4$	-[b]
d	4-MeC_6H_4	4-EtC_6H_4	4-$(MeO)C_6H_4$	93
e	4-MeC_6H_4	4-*t*BuC_6H_4	4-$(MeO)C_6H_4$	96

[a] Yields of isolated products; [b] complex mixture

The Suzuki-Miyaura reaction of 3-bromo-2,4-diarylthiophene **11b,d** with 2.0 equiv. of arylboronic acids afforded the 2,3,4-triarylthiophenes **15a-c** containing two different aryl groups (Scheme 9, Table 13).



11b,d **15a-c**

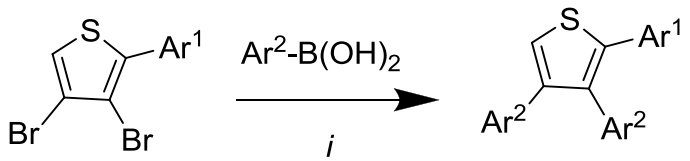
Scheme 9. Synthesis of **15a-c**. *Conditions*: *i*, **11b,d** (1.0 equiv), Ar^2-$B(OH)_2$ (2.0 equiv.), $Pd(PPh_3)_4$ (10 mol-%), K_3PO_4 (4.0 equiv), 1,4-dioxane / toluene = 1:1, 100 °C, 12 h

Table 13. Synthesis of 2,3,4-triarylthiophenes **15a-c**

15	Ar^1	Ar^2	% (**15**)[a]
a	4-EtC_6H_4	4-$(MeO)C_6H_4$	92
b	4-*t*BuC_6H_4	4-$(MeO)C_6H_4$	87
c	4-EtC_6H_4	2-$(MeO)C_6H_4$	80

[a] Yields of isolated products

The Suzuki-Miyaura reaction of 2-aryl-3,4-dibromothiophene **10a,c** with 3.0 equiv. of arylboronic acids afforded the 2,3,4-triarylthiophenes **16a-c** containing two different aryl groups (Scheme 10, Table 14).



10a,c **16a-c**

Scheme 10. Synthesis of **16a-c**. *Conditions*: *i*, **10a,c** (1.0 equiv), Ar^2-$B(OH)_2$ (3.0 equiv.), $Pd(PPh_3)_4$ (10 mol-%), K_3PO_4 (4.0 equiv), 1,4-dioxane / toluene = 1:1, 100 °C, 12 h

Table 14. Synthesis of 2,3,4-triarylthiophenes **16a-c**

16	Ar^1	Ar^2	% (**16**)[a]
a	4-MeC_6H_4	4-EtC_6H_4	92
b	4-MeC_6H_4	4-*t*BuC_6H_4	87
c	4-*t*BuC_6H_4	4-EtC_6H_4	83

[a] Yields of isolated products.

In all reactions, the best yields were obtained when $Pd(PPh_3)_4$ was used as the catalyst. The use of other catalysts (such as $Pd(OAc)_2$ / X-Phos) proved to be less successful in terms of yield. All reactions were carried out at 90-100 °C. For the synthesis of **10a-g** and **12a-e** K_2CO_3 and for the synthesis of **11a-e** and **13a-f**, K_3PO_4 was used as the base. 1,4-Dioxane or a 1:1 mixture of 1,4-dioxane and toluene was used as the solvent.

The structures of all products were established by spectroscopic methods (COSY, HMBC and NOESY).

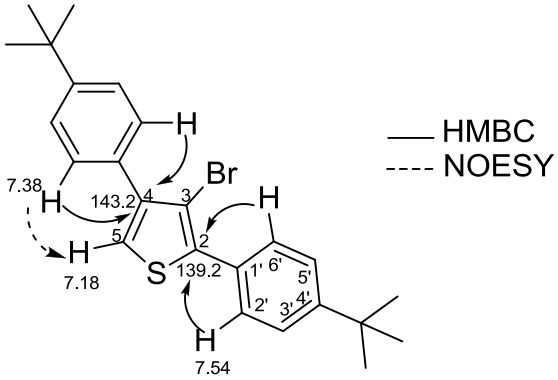


Figure 7. HMBC and NOESY correlations of **11d**

The structure of **11d** was established by 2D NMR using HMBC and NOESY correlations. In the HMBC spectrum, the phenyl protons δ 7.38 and δ 7.54 showed strong correlations with the quaternary carbons of the thiophene ring (C-2 δ 139.2 and C-5 δ 143.2). It was also observed in the NOESY spectrum an interaction between the phenyl proton δ 7.38 and the proton of the thiophene ring δ 7.18.

The structures of **11a**, and **12c** were independently confirmed by X-ray crystal structure analyses (Figures 8 and 9).

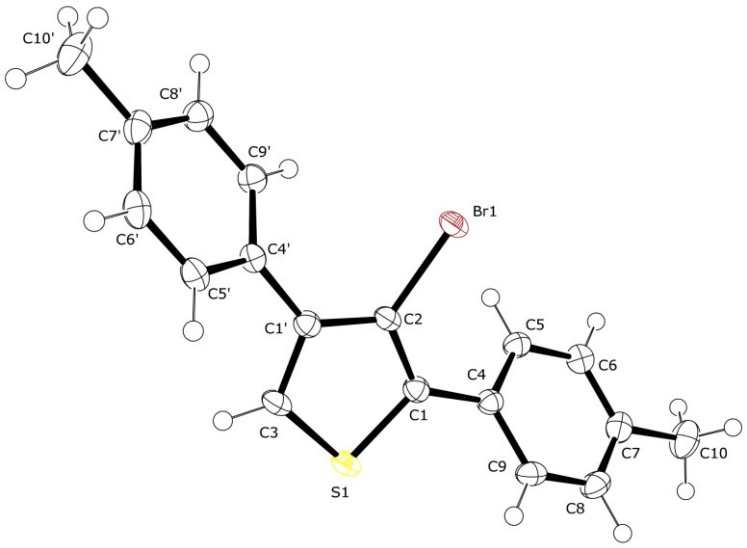


Figure 8. Crystal structure of **11a**

In the structure of **11a,** the two phenyl rings are twisted slightly out of the plane of thiophene, with torsion angles of 136.6 (2)° for S-C1-C4-C5.

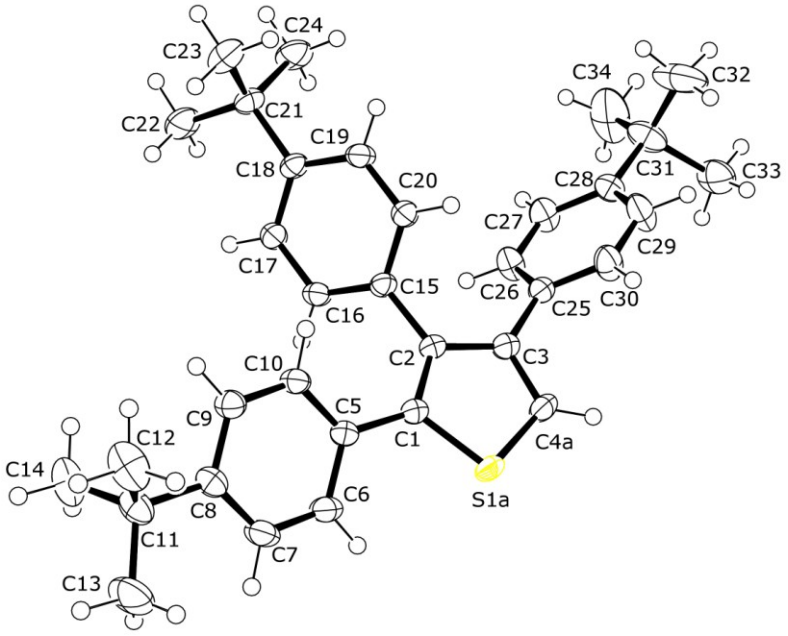


Figure 9. Crystal structure of **12c**

In the structure **12c**, the phenyl rings are also twisted slightly out of the plane of thiophene, with torsion angles of 143.51 (11), 127.12 (13) and 131.2 (4)° for S1a-C1-C5-C10, C1-C2-C15-C20 and C4a-C3-C25-C26, respectively.

The yields of 2-aryl-3,4-dibromothiophenes **10a-g** and of 2,3,4-triarylthiophenes **12a-e** were significantly higher than those of 2,4-diaryl-3-bromothiophenes **11a-e**. The high yields of **12a-e** can be explained by the fact that no issue of site-selectivity exists. The high yields show that the last step, the reaction of carbon atom C-3, must also proceed in good yields. The high yields of **10a-g** suggest that the rate of the reaction of carbon C-2 is considerably higher than that of carbon C-4. This can be explained by electronic reasons (Figure 10). Inspection of selected crude spectra of **10** and **11** showed that no significant amounts of other heterocyclic products were formed. The moderate yields of products **11** can be explained by practical problems during the chromatographic purification. In fact, the transformation of thiophenes **10** into **13** proceeded in very good yields (except for **13c,f** which are derived from sterically hindered 2,6-dimethoxyphenylboronic acid). These results suggest that the rate of the reaction

of carbon C-4 is considerably higher than that of carbon C-3. This can be explained by steric effects.

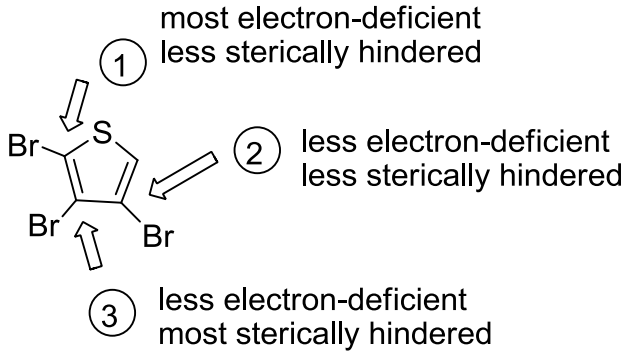


Figure 10. Possible explanation for the site-selectivity of the reactions of **9**

As discussed above, the regioselectivites reported herein can be explained based on the different electronic and steric properties of the three different C-Br bonds of **9**. Carbon atom C-2 is the most reactive position because of its electron-deficient character and because it is easily sterically accessible (Figure 10). From the electronic viewpoint, carbon C-3 is similar to C-4, but C-3 is more sterically hindered than C-4 because of the neighbourhood of two bromine atoms.

1.3 Conclusion

I have reported the first Suzuki-Miyaura reactions of 2,3,5-tribromothiophene and 2,3,4-tribromothiophene. The reaction with one, two and three equivalents of arylboronic acids resulted in formation of 5-aryl-2,3-dibromothiophenes, 2,5-diaryl-3-bromothiophenes, and 2,3,5-triarylthiophenes with very good site-selectivity.

2 Site-selective Suzuki-Miyaura reactions of 2,3,5-tribromo-*N*-methyl pyrrole

2.1 Introduction

The pyrrole system is of great importance in organic chemistry, due to its occurrence in many natural products and pharmacologically active molecules.[39] For example, a pyrrole core structure is present in marine natural products, such as the lamellarines (Figure 11), storniamide A, ningalin A and halitulin, which show considerable potential for the treatment of various cancers and AIDS.[40] Pyrroles also occur in the structure of atorvastatin (lipitor), an oral drug which lowers the level of cholesterol in the blood.[41] They are also found in the natural product porphobilinogen, a trisubstituted pyrrole which is a biosynthetic precursor of many natural products such as haemoglobin.[42] Structurally more simple pyrroles have been also isolated as natural products, e. g. pyrrolnitrin, isolated from *Pseudomonas pyrrocinia*, which possesses potent antifungal and antibiotic activities.[43]

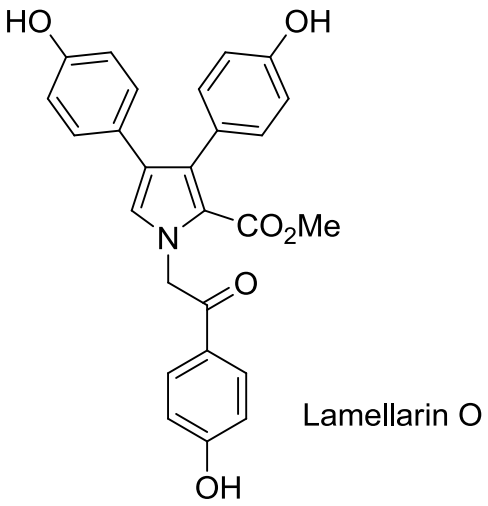


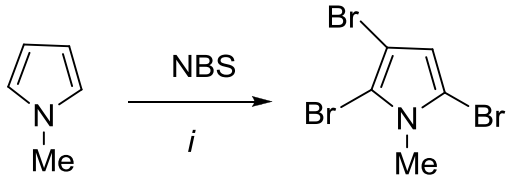
Figure 11. Structure of Lamellarin O

Schröter and Bach studied Suzuki-Miyaura (S-M) reactions of 2,3,4-tribromopyrrole-5-carboxylate and of 2,3-dibromo-5-nitropyrrole and observed site-selectivity in favour of position 2.[44] Handy and co-workers reported site-selective one-pot double S-M reactions of

4,5-dibromopyrroles using ligand free conditions.[45] Recently, Langer and coworkers have reported site-selective S-M reactions of various polyhalogenated heterocycles including tetrabromo-*N*-methylpyrrole. Herein, I studied what are, to the best of my knowledge, the first site-selective Suzuki-Miyaura reactions of 2,3,5-tribromo-*N*-methylpyrrole. These reaction provide a convenient approach to novel 5-aryl-2,3-dibromo-*N*-methylpyrroles, 2,5-diaryl-3-bromo-*N*-methylpyrroles and 2,3,5-triaryl-*N*-methylpyrroles.

2.2 Results and discussion

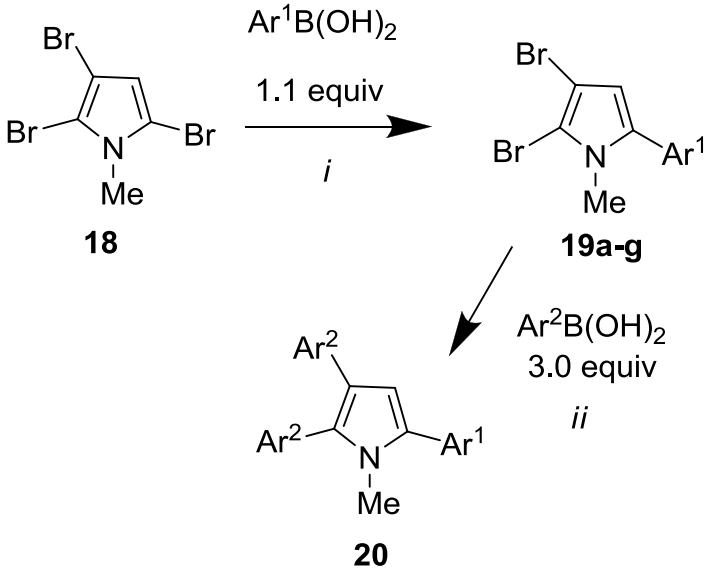
2,3,5-Tribromo-*N*-methylpyrrole **18** was prepared, following a known procedure,[46] by reaction of *N*-methylpryrrole (**17**) with NBS (3.1 equiv) in THF (Scheme 11).



17 **18** (88%)

Scheme 11. Synthesis of **18**. *Conditions*: **1** (1.0 equiv.), NBS (3.1 equiv), THF, -78 → 20 °C, 12 h

The S-M reaction of **18** with 1.1 equiv. of various arylboronic acids afforded the 5-aryl-2,3-dibromo-*N*-methylpyrroles **19a-g** in 41-82% yields (Scheme 12, Table 15). The reactions proceeded with very good site-selectivity in favour of position 5. The relatively low yield of **19a** can be explained by the steric hindrance of 2,6-di(methoxy)phenylboronic acid. Good yields were obtained for nearly all products when $Pd(PPh_3)_4$ (5 mol-%) and K_3PO_4 (4.0 equiv) were employed as the catalyst and as the base, respectively, when 1.1 equiv. of the boronic acid was used and when the reaction was carried out at 100 °C (8 h). The temperature should not be too high and the reaction time not too long to avoid multiple coupling. The employment of a solvent mixture dioxane/toluene proved to be important, due to reasons of solubility of the boronic acids. Analysis of the crude product mixture (GC-MS, ^{1}H NMR) shows that small amounts of products derived from double-coupling are present which could, however, be removed by chromatography. The structure of **19a** was independently confirmed by X-ray crystal structure analysis (Figure 12).



Scheme 12. Synthesis of **19a-g** and **20**. *Conditions*: *i,* **18** (1.0 equiv.), $Ar^1B(OH)_2$ (1.1 equiv.), $Pd(PPh_3)_4$ (5 mol-%), K_3PO_4 (4.0 equiv), 1,4-dioxane / toluene = 1:1, 100 °C, 8 h; *ii*, **19c** (1.0 equiv.), $Ar^2B(OH)_2$ (3 equiv.), $Pd(PPh_3)_4$ (5 mol-%), K_3PO_4(4.0 equiv.), toluene, 110 °C, 36 h

Table 15. Synthesis of 5-aryl-2,3-dibromo-*N*-methylpyrroles **19a-g**

19	Ar^1	*T* [°C]	*t* [h]	% (19)[a]
a	2,6-$(MeO)_2C_6H_3$	90	8	43
b	4-EtC_6H_4	100	6	73
c	4-*t*BuC_6H_4	90	8	64
d	2-$(MeO)C_6H_4$	90	8	61
e	3,5-$Me_2C_6H_3$	110	6	58
f	4-ClC_6H_4	100	8	41
g	4-MeC_6H_4	100	8	82

[a] Yields of isolated products

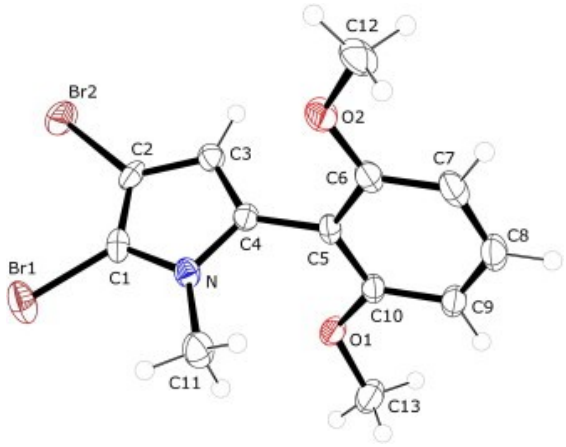


Figure 12. Ortep plot of **19a**

The crystal structure of **19a** showed that the phenyl ring is twisted slightly out of the plane of pyrrole, with torsion angles of 66.7 (4)° for C10-C5-C4-N1.

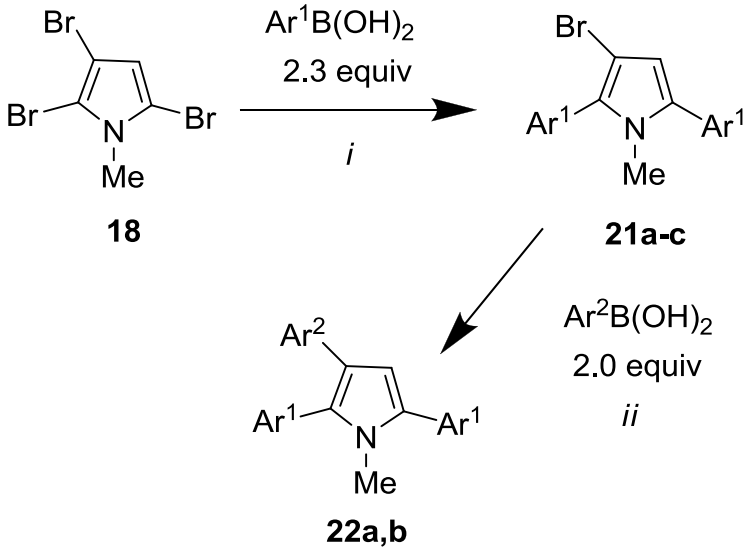
The S-M reaction of **19c** with 4-methoxyphenylboronic acid afforded the 2,3,5-triaryl-*N*-methylpyrrole **20a** in 74% yield (Scheme 12, Table 16). The best yield of this compound was obtained when an excess of the boronic acid was employed (3.0 equiv.) and when the reaction time was extended to 36 h and the temperature elevated to 110 °C. The yield of the one-pot synthesis of **20a** from **18** (sequential addition of the boronic acids) was less than the yield of the stepwise process. Therefore, the one-pot synthesis was not further studied.

Table 16. Synthesis of 2,3,5-triaryl-*N*-methylpyrrole **20**

	Ar^1	Ar^2	% (**20**)[a]
20	4-*t*BuC_6H_4	4-(MeO)C_6H_4	74

[a] Yields of isolated products

The S-M reaction of **18** with 2.3 equiv. of arylboronic acids gave the 2,5-diaryl-3-bromo-*N*-methylpyrroles **21a-c** in 37-58% yields (Scheme 13, Table 17). The reactions were carried out at 100 °C (12 h). The S-M reactions of **21b,c** with 2.0 equiv. of arylboronic acids afforded the 2,3,5-triaryl-*N*-methylpyrroles **22a,b** (Scheme 13, Table 18). Similar to the synthesis of **20a**, the yield of the one-pot synthesis of **22a** was lower compared to the stepwise synthesis. The structure of **22a** was independently confirmed by X-ray crystal structure analysis (Figure 13).



Scheme 13. Synthesis of **21a-c** and **22a,b.** *Conditions*: *i*, **18** (1.0 equiv), $Ar^1B(OH)_2$ (2.3 equiv.), $Pd(PPh_3)_4$ (5 mol-%), K_3PO_4 (4.0 equiv), 1,4-dioxane / toluene = 1:1, 100 °C, 12 h; *ii*, **21b,c** (1.0 equiv), $Ar^2B(OH)_2$ (2.0 equiv.), $Pd(PPh_3)_4$ (5 mol-%), K_3PO_4 (4.0 equiv), toluene, 110 °C, 36 h

Table 17. Synthesis of 2,5-diaryl-3-bromo-*N*-methylpyrroles **21a-c**

21	Ar^1	% (**21**)[a]
a	3,5-$Me_2C_6H_3$	42
b	4-*t*BuC_6H_4	37
c	4-(MeO)C_6H_4	58

[a] Yields of isolated products

Table 18. Synthesis of 2,3,5-triaryl-*N*-methylpyrroles **22a,b**

22	Ar^1	Ar^2	% (**22**)[a]
a	4-(MeO)C_6H_4	4-ClC_6H_4	72
b	4-*t*BuC_6H_4	2-(EtO)C_6H_3	83

[a] Yields of isolated products

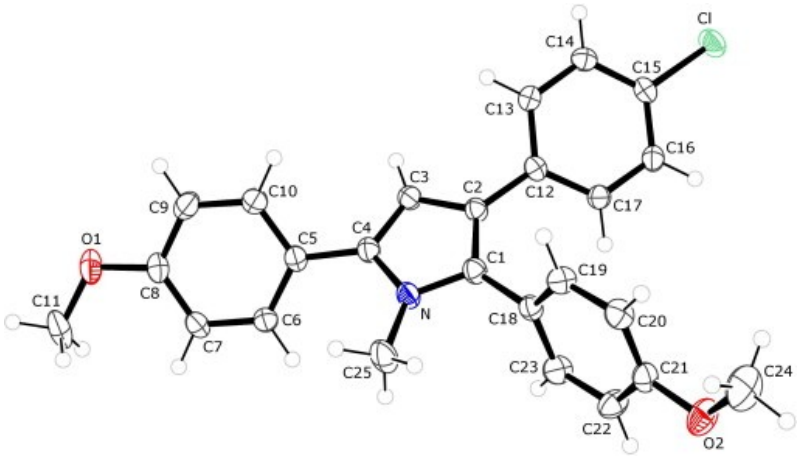
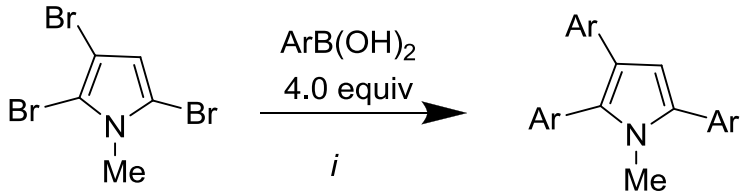


Figure 13. Crystal structure of **22a**

In the structure of **22a**, the phenyl ring at C2 is twisted from the plane of the pyrrole ring by 33.8(2)°. The phenyl rings at C1 and C4 are twisted slightly out of the plane of pyrrole, with torsion angles of 71.8 (19) and 142.4 (15)°, respectively.

The S-M reaction of **18** with 4.0 equiv. of arylboronic acids resulted in the formation of the 2,3,5-triarylpyrroles **23a-f** in 62-92% yields (Scheme 14, Table 19). The reactions were carried using $Pd(OAc)_2/P(Cy)_3$ (Cy = cyclohexyl) which gave better yields than $Pd(PPh_3)_4$.



18 **23a-f**

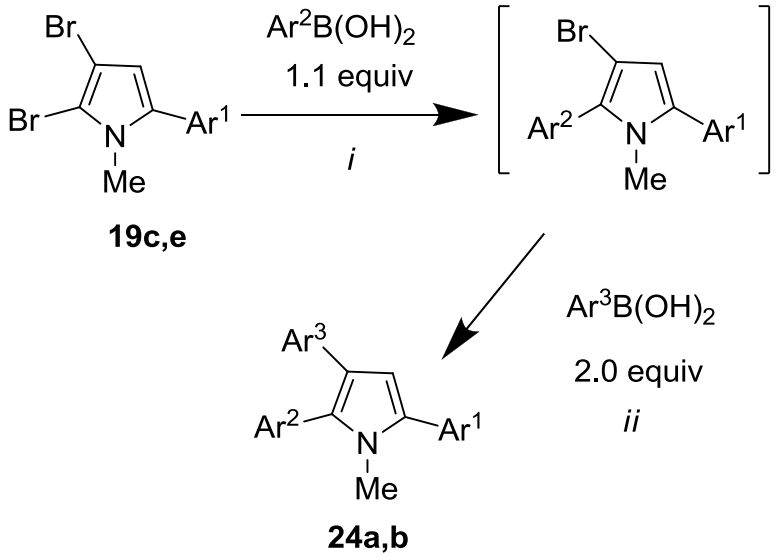
Scheme 14. Synthesis of **23a-f.** *Conditions*: *i,* 2 (1.0 equiv), Ar-$B(OH)_2$ (4.0 equiv), $Pd(OAc)_2$ (5 mol-%) / $P(Cy)_3$ (10 mol-%), K_3PO_4 (4.0 equiv), toluene, 110 °C, 36 h

Table 19. Synthesis of 2,3,5-triaryl-*N*-methylpyrroles **23a-f**

23	Ar	% (**23**)[a]
a	4-MeC_6H_4	68
b	4-$(MeO)C_6H_4$	89
c	3-$(MeO)C_6H_4$	76
d	4-*t*BuC_6H_4	72
e	2,3,4-$(MeO)_3C_6H_2$	92
f	3-FC_6H_4	62

[a] Yields of isolated products; Cy = cyclohexyl

The one-pot reaction of **19c,e** with two different arylboronic acids, which were sequentially added, gave the 2,3,5-triaryl-*N*-methylpyrrole **24a,b** containing three different aryl groups in moderate yields (Scheme 15, Table 20).



Scheme 15. Synthesis of **24a,b.** *Conditions*: *i*, **19c,e** (1.0 equiv), $Ar^2B(OH)_2$ (1.1 equiv.), $Pd(PPh_3)_4$ (5 mol-%), K_3PO_4 (4.0 equiv), 1,4-dioxane / toluene = 1:1, 100 °C, 6h; *ii*, $Ar^3B(OH)_2$ (2.0 equiv.), K_3PO_4 (2.0 equiv), 110 °C, 24 h.

Table 20. Synthesis of 2,3,5-triaryl-*N*-methylpyrroles **24a,b**

24	Ar^1	Ar^2	Ar^3	% (**24**)
a	4-*t*BuC_6H_4	2-(MeO)C_6H_4	4-Et C_6H_4	43
b	3,5-$Me_2C_6H_3$	2,6-$(MeO)_2C_6H_3$	4-Et C_6H_4	48

[a] Yields of isolated products

The structure of **21c** was established by 2D NMR using HMBC and NOESY correlations (Figure 14). In the HMBC spectrum, the phenyl protons δ 7.25 and δ 7.26 showed strong correlations with the quaternary carbons of the pyrrole ring C-2 and C-5. It is observed in the NOESY spectrum an interaction between phenyl proton δ 7.26 and the proton of the pyrrole ring δ 6.08.

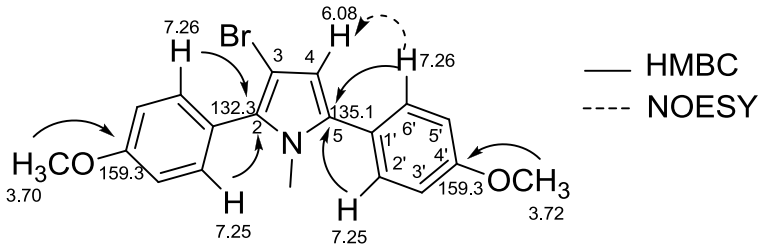


Figure 14. HMBC Correlations of **21c**

The site-selectivites can be explained by electronic and steric parameters.[21,47] Position 5 is most reactive because it is more electron deficient than position 3 and less sterically hinderd than position 2 (Figure 15). From the electronic viewpoint, positions 2 and 5 are similar.

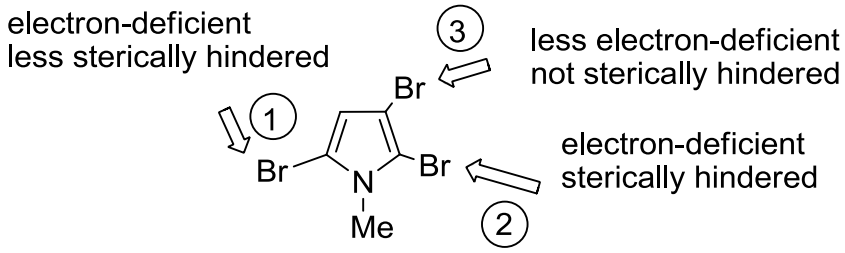


Figure 15. Possible explanation for the site-selectivity of the reactions of **18**

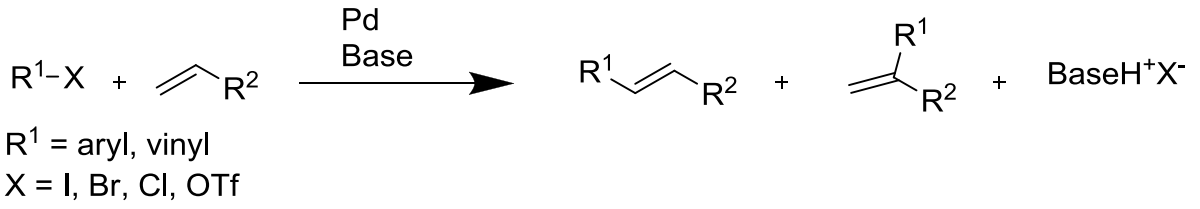
2.3 Conclusion

I have reported the first Suzuki-Miyaura reactions of 2,3,5-tribromo-*N*-methylpyrrole. The reaction provides a convenient and site-selective approach to various arylated pyrroles which are not readily available by other methods.

PART II Palladium-catalyzed Mizoroki-Heck reaction of bromo substituted thiophenes, pyrroles, imidazoles and indoles

Introduction and background of the Heck reaction

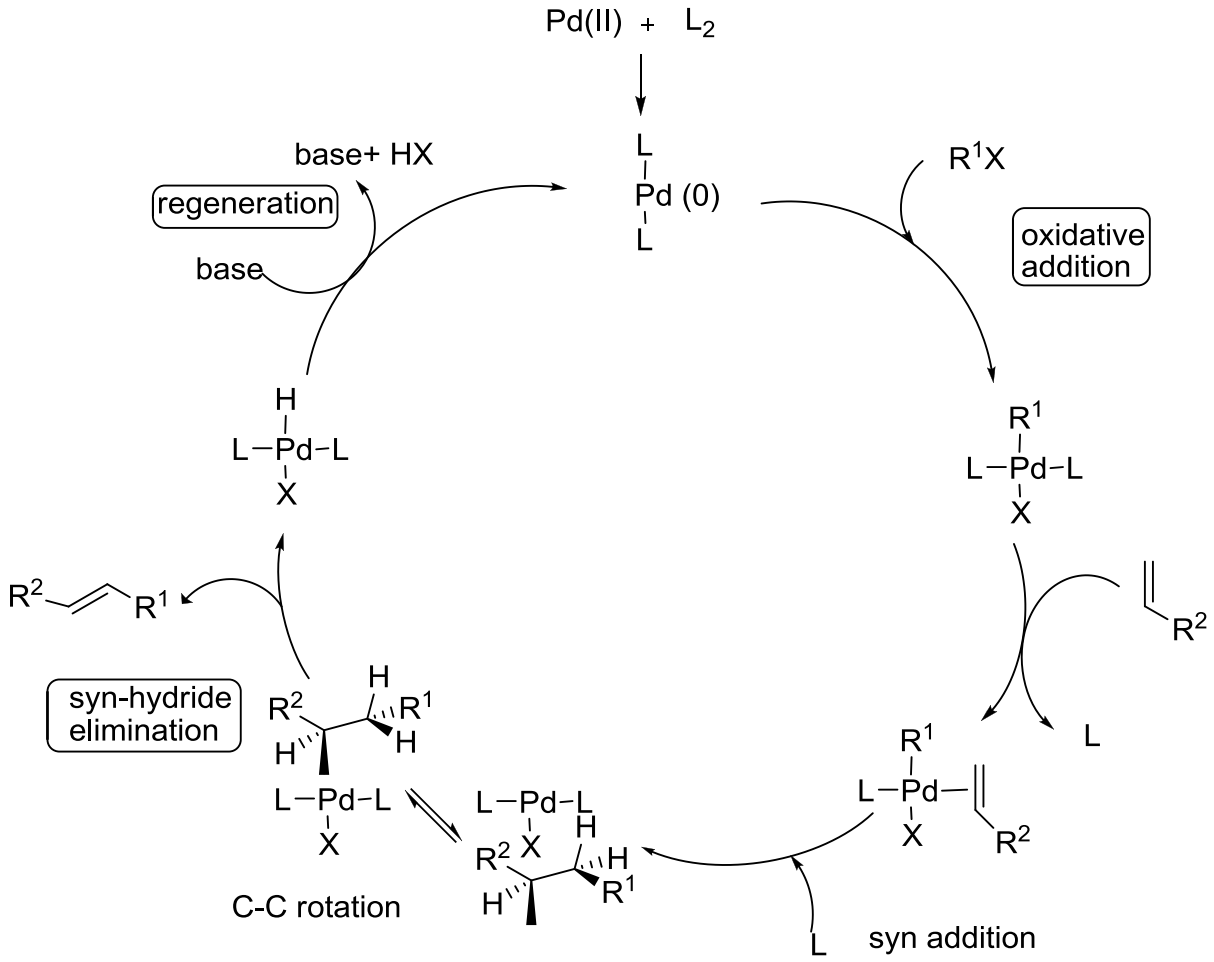
The palladium-catalyzed Mizoroki-Heck reaction is known as the most efficient route for the alkenylation or arylation of olefins.[4] It is one of the most powerful tools to make new C-C bonds, in the presence of an inorganic or organic base (triethylamine, sodium carbonate, potassium carbonate or sodium acetate) and palladium catalyst (Scheme 16).[4] The olefin contains at least one proton and is often electron-deficient such as an acrylate ester or an acrylonitrile. The halide or triflate is an aryl, benzyl, or vinyl compound. The catalyst can be tetrakis(triphenylphosphine)palladium(0), palladium chloride or palladium(II) acetate. During the past decades, the most common ligands used are phosphine-based ones. But due to the air and /or moisture sensitive nature of most phosphine-based ligands, in recent years, phosphine-free ligands have also been employed.[48] The Mizoroki-Heck reaction has been intensively developed from a synthetic and mechanistic view point, as expressed by the impressive number of reviews and book chapters.[49]



Scheme 16. Heck reaction

Reaction mechanism

In the preactivation step, the Pd(0) catalyst is formed by reduction of Pd(II) complexes and the following steps of the catalytic cycle were proposed:



Scheme 17. The catalytic cycle of the Heck reaction

The oxidative addition is the first step of the catalytic cycle, in which the C-X bond rupture is synchronized with the formation of Pd-C and Pd-X bonds. The trans-R^1PdXL_2, resulting from the oxidative addition, first coordinates to the alkene after dissociation of one phosphine and then undergoes a syn insertion to the alkene leading to a σ-alkenyl or σ-aryl-palladium(II) halide. The reaction of R^1PdXL_2 with an alkene, also referred to as carbo palladation, is at the origin of the regioselectivity of Mizoroki-Heck reactions.[50,51] After an internal C-C bond rotation, the syn elimination happened to give the new substituted alkene ($R^1CH=CHR^2$) and a hydridopalladium (II) halide. In the last step, the base is added to quench the hydrogen halide and to regenerate the active Pd(0) complex, which is ready to enter another catalytic cycle.

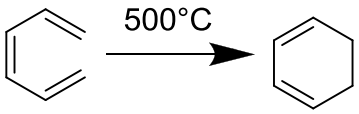
It is good to notice that besides the usual parameters of all reactions (temperature, solvent and concentration), other parameters may be varied (Pd precursors, ligands, bases, additives, etc.) to optimize Mizoroki-Heck reactions.

Electrocyclic reactions

In this work, the products obtained from the Heck reaction were cyclized via a 6π-electrocyclization process. In fact, the electrocyclic reaction is a pericyclic reaction which proceeds by formation of one new sigma bond across the ends of a conjugated polyene or reverse. This reaction follows different rules:

- All electrocyclic reactions follow the Woodward-Hoffmann rules,
- Thermal electrocyclic reactions involving $(4n + 2)$ π electrons are *disrotatory*,
- Thermal electrocyclic reactions involving $(4n)$ π electrons are *conrotatory*,
- In *conrotatory* reactions the two groups rotate in the *same* way: *both* clockwise or *both* anticlockwise,
- In *disrotatory* reactions, *one* group rotates *clockwise* and *one anticlockwise*[52].

As an classical and simple example of electrocyclic reaction, hexatriene is cyclized thermally to yield to cyclohexa-1,3-diene (Scheme 18).[53]

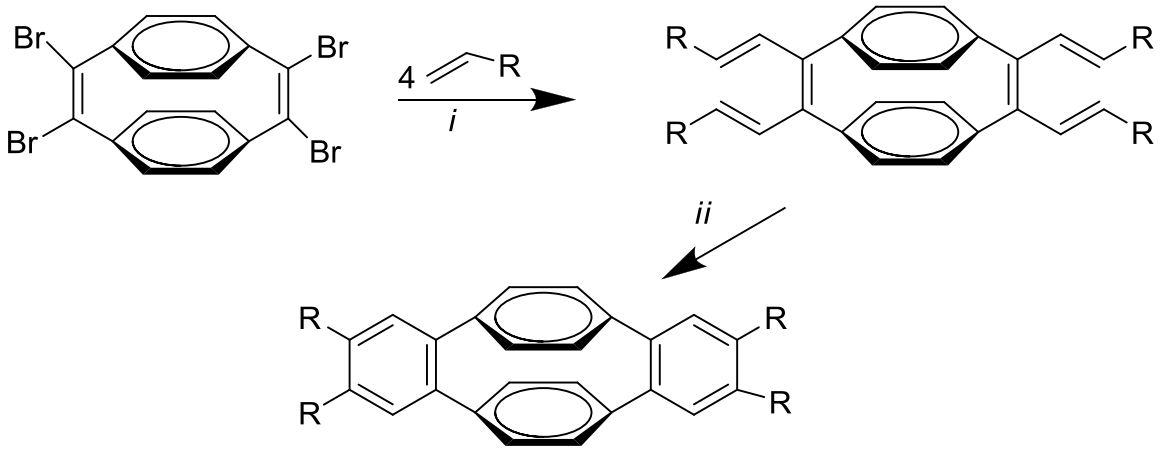


Scheme 18. Synthesis of cyclohexadiene by 6π-electrocyclization

The Heck cross-coupling reaction can provide easy access to various unsymmetrical 1,6-disubstituted 1,3,5-hexatrienes, which can be cyclized by 6π-electrocyclization to give the corresponding hexadienes.

Heck cross-coupling reaction and subsequent 6π-electrocyclization

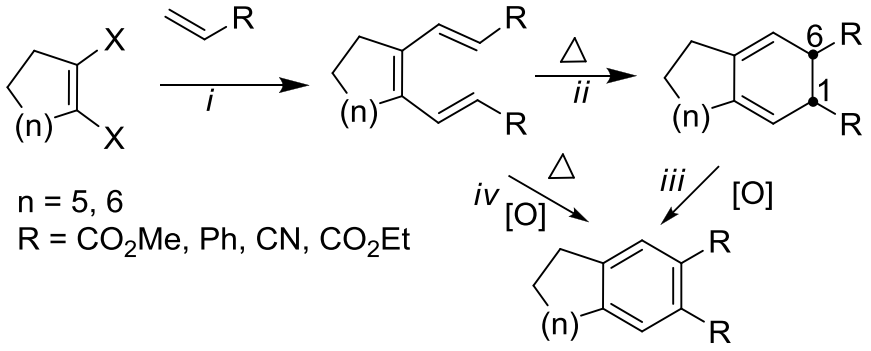
De Meijere and co-workers in 1987 reported the first twofold (and fourfold) Heck reactions, in which the 1,2,9,10-tetrabromo[2.2] paracyclophane-1,9-diene reacts with alkenes to give tetraalkenylated products in moderate yields. The thermal electrocyclization and subsequent dehydrogenation of tetraalkenylated products provided bis-benzoannelated [2.2] paracyclophanediene derivatives.[54]



R= H, $SiMe_3$, CHO, CO_2Me, Ph, 4-MeO_2C-C6H4, 4-F-C_6H_4, 4-t-Bu-C_6H_4, 4-Ph-C_6H_4

Scheme 19. Conditions: *i,* $Pd(OAc)_2$, Bu_4NBr, K_2CO_3 or $NaHCO_3$, DMF, 40-100 °C, 12 h to 5 days; *ii*, Pd/C (+O_2) or S_8, Xylene, 150 °C

Later in 1998, the same research group reported the twofold Heck-coupling reaction of 1,2-dihalocycloalkenes and subsequent 6π-electrocyclization of the resulting 1,2-dialkenyl-cycloalkenes to give ring-annelated cis-disubstituted cyclohexadienes (Scheme 20).[55]



Scheme 20. *Conditions*: *i*, $Pd(OAc)_2$, PPh_3, NEt_3 DMF, 90-100 °C; *ii*, xylene or (*n*-Bu_2O), 150 °C; *iii*, Pd/C (+O_2) or S, xylene, 150 °C; iv, Pd/C (+O_2) or S, xylene, 150 °C

The (*E,Z,E*)-1,3,5-hexatrienes were formed when 2.5 equiv of acrylate were added to dihalocycloalkenes. To perform the electrocyclization, the (*E,Z,E*)-1,3,5-hexatrienes were heated to 130-150 °C in deoxygenated xylene or dibutyl ether. The two substituents of the former 1- and 6-positions have a stereochemical *cis* relationship in the products due to the

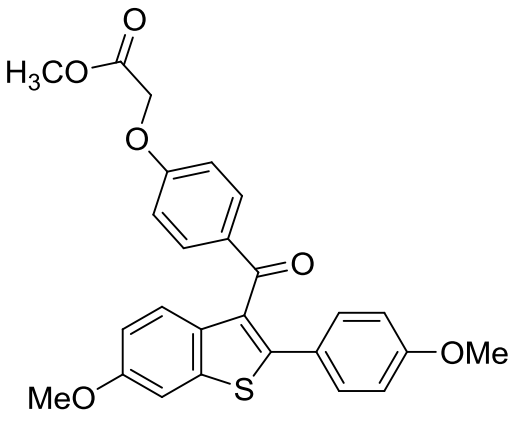
disrotatory ring closure under thermal conditions. The aromatized product was isolated when the solvent for chromatography and silica gel were not purged with nitrogen.

In my thesis I have studied ‘twofold Heck / 6π-electrocyclization’ as a useful method for the direct and convenient synthesis of functionalized benzothiophenes, benzimidazoles, indoles, carbazoles and dibenzothiophenes starting with dibromothiophenes, tribromo-*N*-methylimidazole, tribromo-*N*-methylpyrrole, tetrabromo-*N*-methylpyrrole, tetrabromo-*N*-methylindole and tetrabromothiophene.

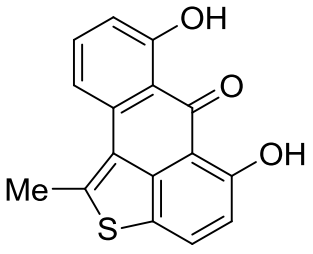
3 Synthesis of functionalized benzothiophenes by twofold Heck and subsequent 6π-electrocyclization reactions of 2,3-dibromothiophene, 4,5-dibromothiophene-2-carbaldehyde and 5-aryl-2,3-dibromothiophene

3.1 Introduction

Benzothiophenes are incorporated in many pharmaceuticals, such as raloxifene, zileuton and sertaconazole. It occurs also in some natural products, such as the antiangiogenic bryoanthrathiophene, which has an anti-angiogenesis effect.[56] Parent benzothiophene is present in coffee beans. Benzothiophenes are also used in crop-protection. For example, mobam (4-(*N*-methylcarbamoyl)benzo[*b*]-thiophene) represents a potent insecticide which inhibits, similar to its naphthalene analogue (1-(*N*-methylcarbamoyl) naphthalene), the enzyme acetylcholinesterase.[57] Benzothiophenes are often bioisosteric with naphthalenes and indoles. (Benzo[*b*]thien-3-yl)acetic acid accelerates, similar to its indole analogue, the growth of plants. 3-(2-aminoethyl)benzo[*b*]thiophene is known to stimulate the CNS. Its activity is even higher than that of the indole analogue tryptamine.[58] Last but not the least, benzothiophenes are present in many dyestuffs. Prominent examples are thioindigo and its derivatives. Benzothiophenes are synthetically available by condensation of thiophenolates or 2-formyl- or 2-acylthiophenolates with α-haloketones and subsequent cyclization.[59, 60]



(Benzo[b]thien-3-yl)acetic acid



Bryoanthrathiophene

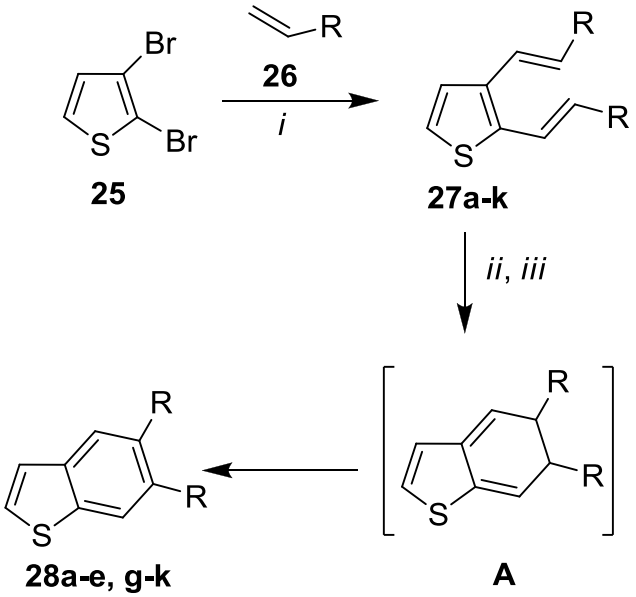
Figure 16. Structure of bryoanthrathiophene and (benzo[*b*]thien-3-yl)acetic acid

Sonogashira,[61] Kumada,[62] Suzuki[63] and Stille[64] coupling reactions of 2,3-dibromothiophene have been reported to regioselectively occur at position C-2. In this chapter, I report the first Heck reactions of 2,3-dibromothiophene, 4,5-dibromothiophenes-2-carbaldehyde and 5-aryl-2,3-dibromo thiophene to give 2,3-dialkenylthiophenes, 4,5-dialkenylthiophenes-2-carbaldehydes and 2,3-dialkenyl-5-arylthiophenes, respectively. Domino ′6π-electrocyclization/ dehydrogenation′ reactions[55, 65] of the products afforded functionalized benzothiophenes.

3.2 Results and discussion

3.2.1 Synthesis of benzothiophenes starting from 2,3-dibromothiophene

The Heck reaction of 2,3-dibromothiophene (**25**) with alkenes **26** (2.5 equiv.) afforded the 2,3-di(alkenyl)benzothiophenes **27a-k** in good yields (Scheme 21, Table 21). The best yields were obtained when the reactions were carried out using $Pd(OAc)_2$ (5 mol-%) and the biaryl monophosphine ligands SPhos or XPhos (10 mol-%) which were recently developed by Buchwald and coworkers (Figure 17).[66] The reactions were carried out in DMF at 120 °C for 12 h. The employment of $Pd(PPh_3)_4$ was less successful in terms of yield. Heating of a xylene solution of **27a-e** and **27g-k** in the presence of Pd/C resulted in the formation of benzothiophenes **28a-e** and **28g-k** in quantitative yields. The formation of the products can be explained by thermal 6π-electrocyclization to give intermediate **A** and subsequent dehydrogenation. During the optimization, it proved to be important to carry out the reaction at 200 °C. No conversion was observed at lower temperatures.



Scheme 21. Synthesis of **27a-k** and **28a-e,g-k** *Conditions*: *i*, **26** (2.5 equiv.), $Pd(OAc)_2$ (5 mol-%), SPhos or XPhos (10 mol-%), NEt_3, DMF, 120 °C, 48 h; *ii*, xylene, 200 °C, 24 h; *iii*, Pd/C (10 mol-%), xylene, 200 °C, 48 h

Table 21. Synthesis of **27a-k** and **28a-e,g-k**

27,28	R	% (**27**) [a]	% (**28**) [a]
a	CO_2Me	81 [b]	100
b	CO_2Et	90 [c]	100
c	CO_2iBu	86 [b]	100
d	CO_2nBu	93 [c]	100
e	CO_2nHex	92 [c]	100
f	CO_2tBu	89 [b]	- [d]
g	$CO_2[CH_2CH(Et)(CH_2)_3CH_3]$	85 [c]	100
h	4-tBuC_6H_4	94 [c]	100
i	4-(MeO)C_6H_4	83 [c]	100
j	4-MeC_6H_4	88[b]	94
k	4-ClC_6H_4	82[c]	- [d]

[a] Yields of isolated products; [b] XPhos was used; [c] SPhos was used; [d] experiment was not carried out

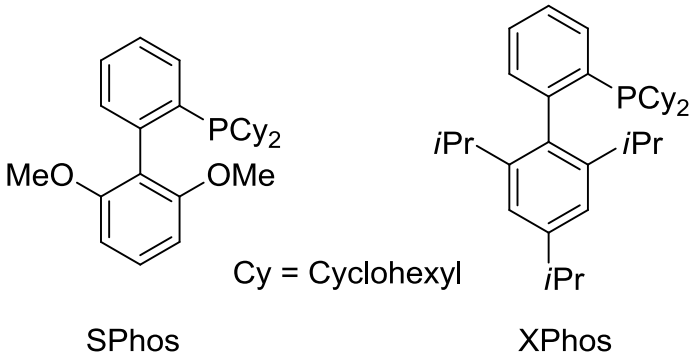
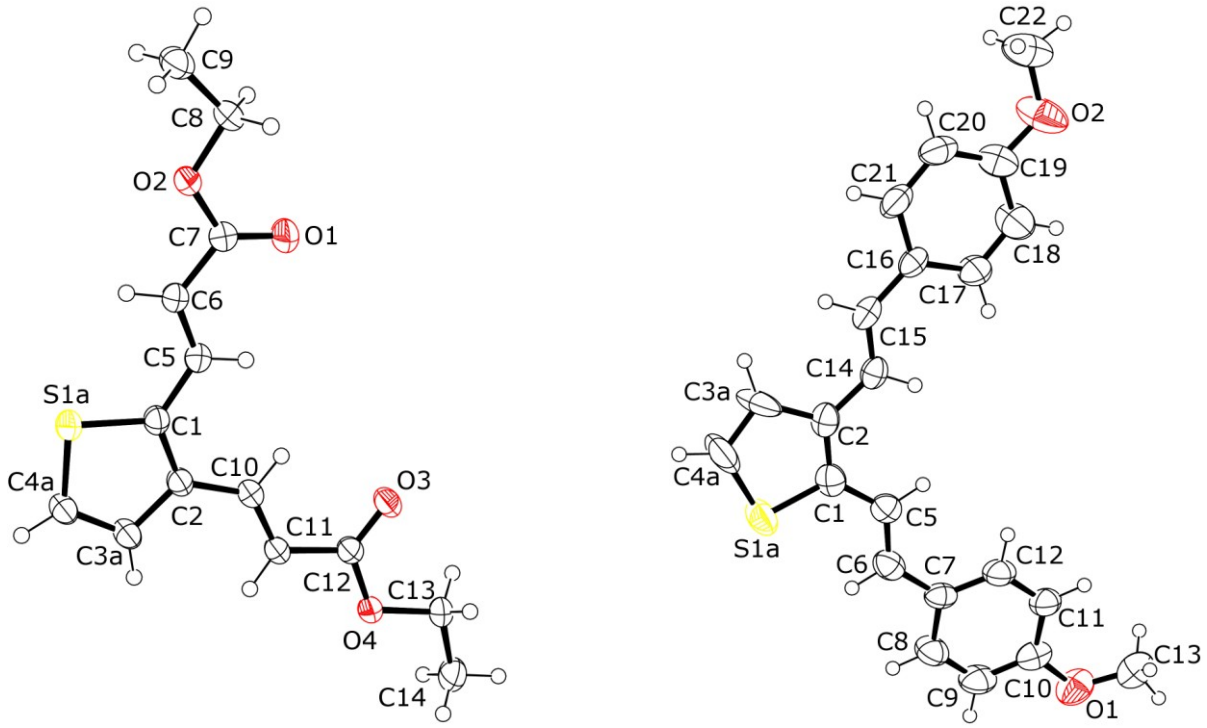


Figure 17. Biaryl monophosphine ligands developed by Buchwald and coworkers[66]

The structures of **27b** and **27i** were independently confirmed by X-ray crystal structure analysis (Figure 18).

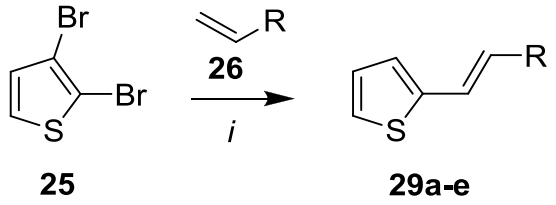


27b **27i**

Figure 18. Crystal structures of **27b** and **27i**

In both the structures **27b** and **27i**, the two alkenyl groups are in the same plane and almost in the plane of thiophene. The torsion angles between the thiophene ring and the alkenyl groups is 0.8 (2)° and 2.3 (4)° in structure **27b** and **27i**, respectively.

The Heck reaction of **25** with only one equivalent of alkenes **26** resulted in the formation of 2-alkenylthiophenes **29a-e** (Scheme 22, Table 22). The formation of these products can be explained by regioselective coupling of carbon atom C-2 of **25** with the acrylate and subsequent Pd(0)-catalyzed reduction.



Scheme 22. Synthesis of **29a-e**. Conditions: *i*,: **26** (1.0 equiv.), $Pd(OAc)_2$ (2.5-5 mol-%), SPhos or XPhos (5-10 mol-%), NEt_3, DMF, 120 °C, 24 h

Table 22. Synthesis of **29a-e**

29	R	% (**29**) [a]
a	CO_2Me	75 [b]
b	CO_2Et	78 [c]
c	CO_2iBu	74 [b]
d	CO_2tBu	87 [b]
e	CO_2nHex	76 [c]

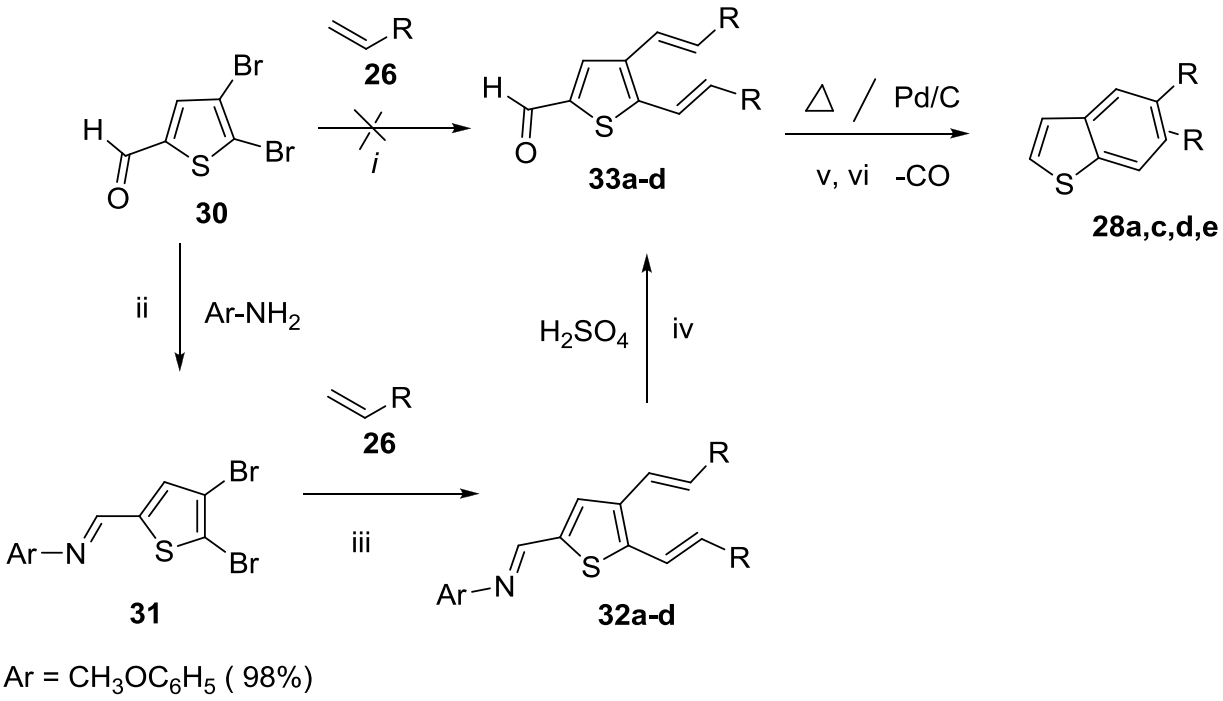
[a] Yields of isolated products; [b] XPhos was used; [c] SPhos was used

3.2.2 Synthesis of benzothiophenes starting from 4,5-dibromothiophene-2-carbaldhyde

The Heck reaction of commercially available 4,5-dibromothiophene-2-carbaldehyde (**30**) with 2.5 equivalents of alkenes **26** did not give the expected products **33**, but 5-alkenyl-4-aryl-*N*-[(4-bromothiophen-2-yl)methylenes]. The formation of these products can be

explained by regioselective coupling of carbon atom C-5 of **30** with the alkenes **26** and subsequent Pd(0)-catalyzed reduction of one C-Br bond. The reduction can be due to the presence of the aldehyde, an electron withdrawing group, which makes the molecule more active. To solve the problem, I have protected the aldehyde by making a Schiff base by reacting **30** with 1.5 equivalents of 4-methoxyaniline in glacial acetic acid to obtain (*E*)-4-Aryl-*N*-((4,5-dibromothiophen-2-yl)methylenes) **31** (Scheme 23).

The Heck reaction of **31** with alkenes **26** (2.5 equiv.) afforded compounds **32a-d** in 55-76% yield (Scheme 23, Table 23). The best yields were obtained when $Pd(OAc)_2$ (5 mol-%) with tris(cyclohexyl) phosphane [$P(Cy)_3$, 10 mol-%] was employed as the catalyst. The expected compounds **33a-d** were obtained with good yields after hydrolysis of the imino group of compounds **32a-d** to recover the aldehyde (deprotection) (Scheme 23, Table 24).



Ar = $CH_3OC_6H_5$ (98%)

Scheme 23. Synthesis of **31**, **32a-d, 33a-d** and **28a,c,d,e**. Conditions: *i*, **26** (2.5 equiv.), $Pd(OAc)_2$ (5 mol-%), SPhos, XPhos or $P(Cy)_3$ (10 mol-%), NEt_3 (8.0 equiv.), DMF, 90 °C, 12h; *ii*, 30 (1.0 equiv.), 4-methoxyaniline (1.5 equiv.), glacial acetic acid, 20°C, 15min; *iii*, **26** (2.5 equiv.), $Pd(OAc)_2$ (5 mol-%), $P(Cy)_3$ (10 mol-%), NEt_3 (8.0 equiv.), DMF, 90 °C, 12h;

iv, **32a-d**, dichloromethane, (H_2SO_4, 2.5M), 20°C, 20h ; *v*, **33a-d**, xylene, 200 °C, 24 h; *vi*, Pd/C (10 mol-%), xylene, 200 °C, 48 h

Table 23 Synthesis of **32a-d**

32	R	% (**32**) [a]
a	CO_2Me	62
b	CO_2*i*Bu	76
c	CO_2*n*Bu	55
d	CO_2*n*Hex	67

[a] Yields of isolated products

Table 24 Synthesis of **33a-d**

33	**32**	R	% (**33**) [a]
a	**a**	CO_2Me	98
b	**b**	CO_2*i*Bu	95
c	**c**	CO_2*n*Bu	92
d	**d**	CO_2*n*Hex	96

[a] Yields of isolated products

The compounds **28a,c,d,e** were formed after electrocyclization and aromatization of **33a-d**. The formation of **28a,c,d,e** can be explained by the thermal extrusion of CO.

The structures of **31** were independently confirmed by X-ray crystal structure analysis (Figure 19). The phenyl ring at C6 is twisted from the plane of the thiophene by -2.9 (9)°. The N-C5-C4 bond angle is 121.5 (3)°.

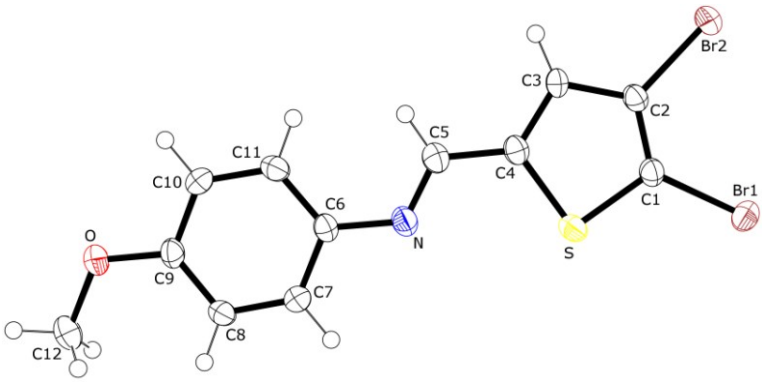
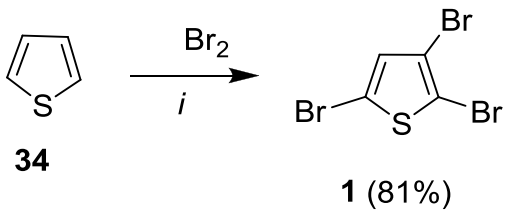


Figure 19. Crystal structures of **31**

3.2.3 Synthesis of benzothiophenes starting from 5-aryl-2,3-dibromothiophene

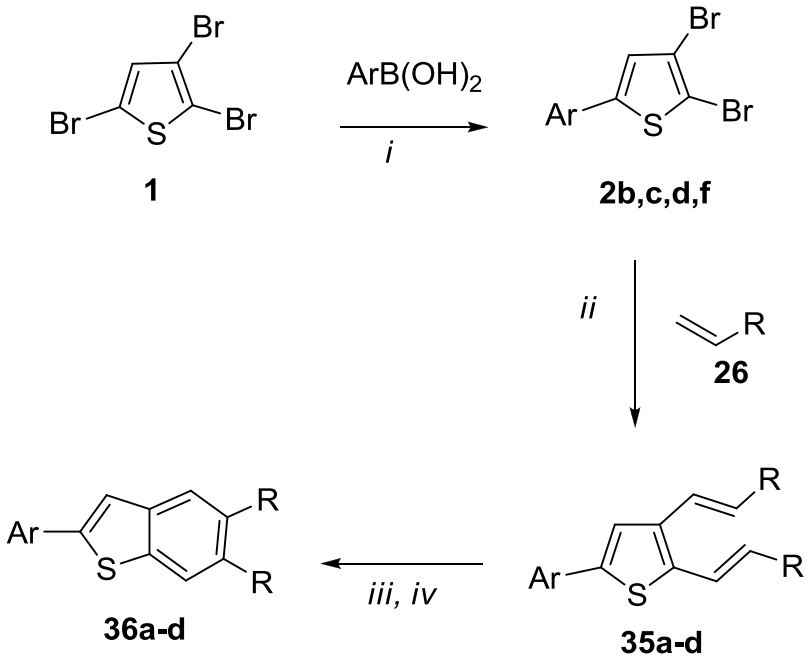
2,3,5-Tribromothiophene (**1**) was prepared by reaction of thiophene (**34**) with bromine (3.1 equiv.) in 81% yield (Scheme 24).[67] The Suzuki-Miyaura reaction of **1** with aryl boronic acids (1.1 equiv.) afforded the 5-aryl-2,3-dibromothiophenes **2a-d** (see chapter 1).



34 **1** (81%)

Scheme 24. Synthesis of 2,3,5-tribromothiophene **1**

The Heck reaction of **2b,c,d,f** with alkenes **26** afforded the 2-aryl-4,5-di(alkenyl) thiophenes **35a-d** in 52-91% yield (Scheme 25, Table 25). The reactions were carried out under the same conditions as the synthesis of **27a-k**. Products **35a-d** were transformed to the benzothiophene **36a-d** in 65-93% yield.



Scheme 25. Synthesis of **35a-d** and **36a-d**. *Conditions*: *i*, **1** (1.0 equiv.), $ArB(OH)_2$ (1.1 equiv.), $Pd(PPh_3)_4$ (5 mol-%), K_2CO_3 (2M), 1,4-dioxane / toluene = 1:1, 100 °C , 12 h; *ii*, **2b,c,d,f** (1 equiv), **26** (2.5 equiv.), $Pd(OAc)_2$ (5 mol-%), $P(Cy)_3$ (10 mol-%), NEt_3 (8.0 equiv.), DMF, 100 °C, 24 h; *iii*, **36a-d**, diphenylether, 200 °C, 24 h; *iv*, Pd/C (10 mol-%), diphenylether, 200 °C, 48 h

Table 25. Synthesis of **35a-d** and **36a-d**

2	**35,36**	Ar	R	% (**35**) [a]	% (**36**) [a]
b	**a**	4-EtC_6H_4	CO_2iBu	89	93
c	**b**	4-t-BuC_6H_4	CO_2nBu	75	82
d	**c**	3,5-$Me_2C_6H_3$	CO_2iBu	78	85
f	**d**	2-(MeO)C_6H_4	CO_2iBu	76	88

[a] Yields of isolated products

The structures of all products were established by spectroscopic methods. The structure of **36b** was independently confirmed by X-ray crystal structure analysis (Figure 20). The benzothiophene moiety is essentially planar. The phenyl ring at C1a is twisted slightly out of the plane of benzothiophene, with an torsion angle of -0.5 (5)°. The torsion angles between the benzothiophene and alkenyl groups are 19.7(8) and 66.1 (3)° for O5a-C21a-C7a-C8 and O3a- C16a-C6a-C7a, respectively.

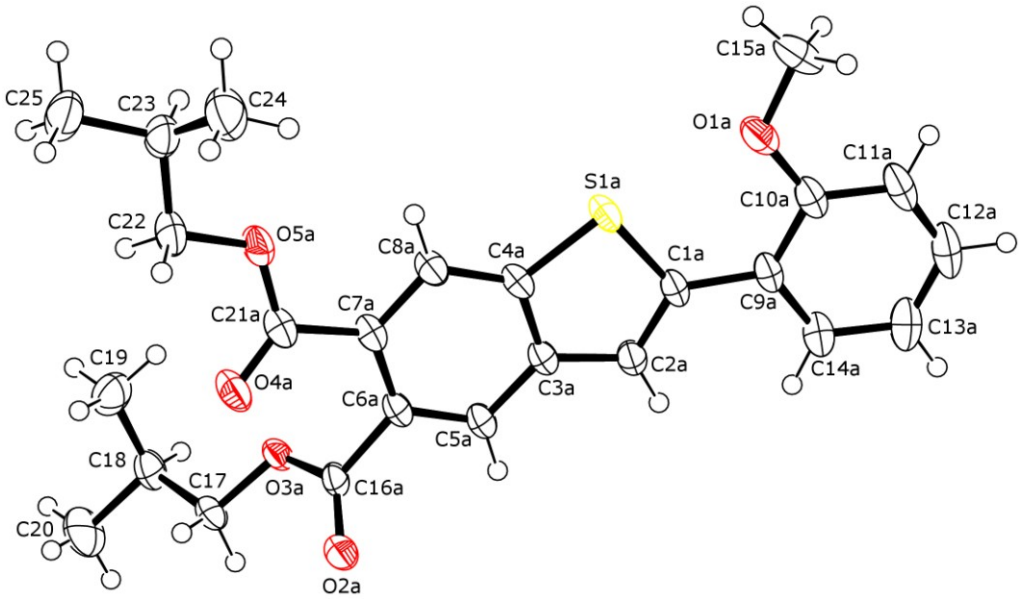


Figure 20. Crystal structure of **36b**

3.3 Conclusion

2,3-Dialkenylthiophenes, 4,5-dialkenylthiophene-2-carbaldehydes and 2,3-dialkenyl-5-arylthiophenes were prepared by the first Heck reactions of 2,3-dibromothiophenes, 4,5-dibromothiophene-2-carbaldehydes and 5-aryl-2,3-dibromothiophenes, respectively. Functionalized benzothiophenes were prepared by Pd/C-catalyzed domino ′6π-electrocyclization/dehydrogenation′ reactions of the 2,3-dialkenylthiophenes, 4,5-dialkenylthiophene-2-carbaldehydes and 2,3-dialkenyl-5-arylthiophenes. The reaction of 2,3-dibromothiophene with one equivalent of alkenes resulted in the formation of 2-alkenylthiophenes.

4 Synthesis of 2,5,6-trisubstituted benzimidazoles by Heck and subsequent 6π-electrocyclization / dehydrogenation reactions of 2,4,5-tribromo-*N*-methylimidazole and 2-aryl- or 2-alkyl-4,5-dibromo-*N*-methylimidazoles

4.1 Introduction

Benzimidazoles are of great relevance in medicinal chemistry and crop protection.[68] The benzimidazole moiety occurs in a number of natural products. The most prominent one is vitamin B_{12}. Benzimidazoles show a wide range of pharmacological activities and have been used, for example, as antifungals,[69] antibacterials,[69,70] anthelminthics,[71] 5-HT receptor antagonists,[72] and thrombin receptor antagonists.[73] Benzimidazole drugs (anthelmintics albendazole, fenbendazole, oxfenbendazole, thiabendazole, mebendazole and inhibitors of proton pump omeprazole, lansoprazole, pantoprazole) represent substances used in both human and veterinary medicine. The benzimidazole benomyl is a widely used plant fungicide.

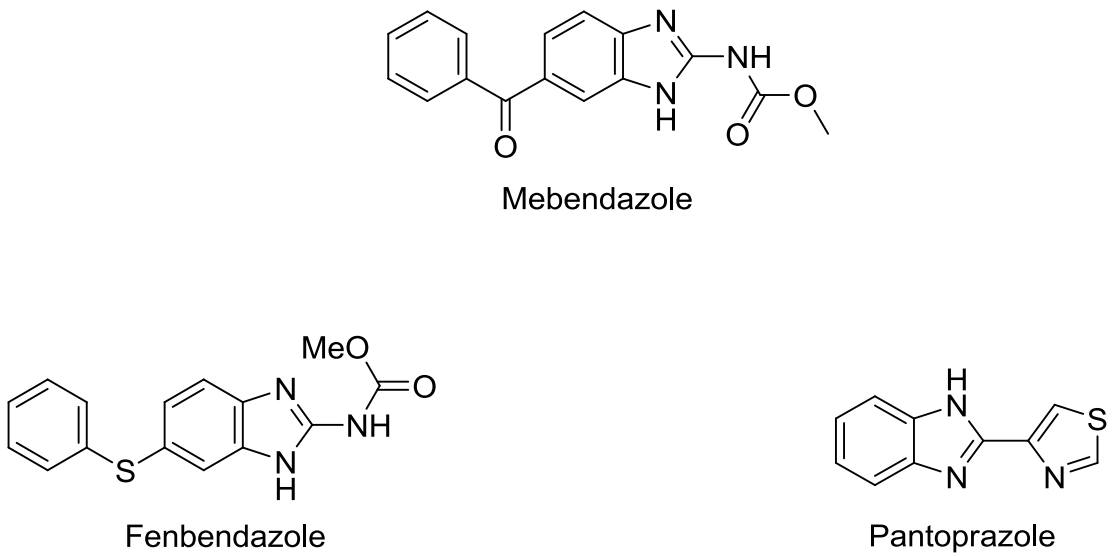
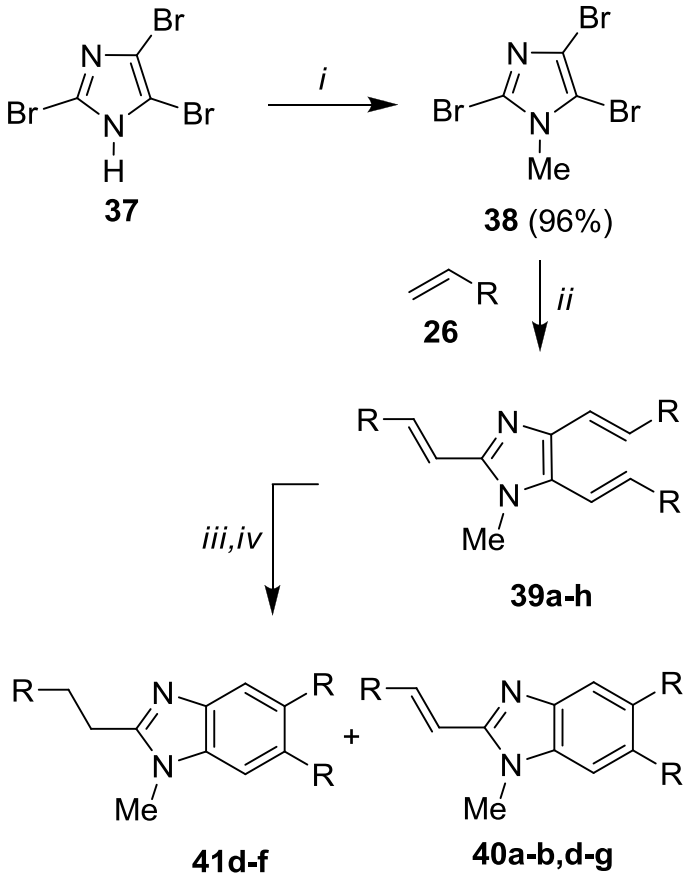


Figure 21. Some important benzimidazole derivatives

Suzuki-Miyaura, Negishi and Stille cross-coupling reactions of protected 2,4,5-tribromo- and 2,4,5-triiodoimidazole have been reported.[74] The first attack generally occurs at carbon atom C-2. Heck reactions of di- or tri-halogenated imidazoles have, to the best of our knowledge, not yet been reported. In this chapter, I developed a new synthesis of 2,5,6-trisubstituted benzimidazoles[75] by Heck reactions of 2,4,5-tribromo-*N*-methylimidazole and 2-aryl- or 2-alkyl-4,5-dibromo-*N*-methylimidazoles and subsequent domino ′6π-electro-cyclization / dehydrogenation′ reactions. The products are not readily available by other methods.

4.2 Results and discussion

Commercially available tribromoimidazole (**37**) was transformed into tribromo-*N*-methyl-imidazole (**38**) by reaction with potassium carbonate and methyl iodide in DMF (Scheme 26). The Heck reaction of **38** with alkenes **26** (3.3 equiv.) afforded the tri(alkenyl)-*N*-methyl-imidazoles **39a-h** in 46-86% yield (Table 26). The Heck reaction of **38** with styrene **26** gave product **39h**. The best yields were obtained when $Pd(OAc)_2$ (5 mol-%) in the presence of tris(cyclohexyl)phosphane ($P(Cy)_3$, 10 mol-%) was employed as the catalyst. During the optimization, the temperature also proved to be an important parameter. A clean transformation was observed when the reaction was carried out at 100 °C. Significant amounts of 2-alkenyl-4,5-dibromoimidazoles (0-10%) and of 2,5-di(alkenyl)-4-bromo-imidazoles (15-30%) were formed when the reactions were carried out at 90 °C.



Scheme 26. Synthesis of **39a-g**, **40a-b,d-g** and **41d-f**. *Conditions*: *i*, **37** (1 equiv), CH_3I (2 equiv), K_2CO_3 (2 equiv), DMF, 20 °C, 14 h; *ii*, **38** (1.0 equiv), **26** (3.3 equiv.), $Pd(OAc)_2$ (5 mol-%), $P(Cy)_3$ (10 mol-%), NEt_3, DMF, 100 °C, 24 h; *iii*, diphenylether, 200 °C, 24 h; *iv*, Pd/C (10 mol-%), diphenylether, 200 °C, 48 h

Heating of **39a,b** and **39d-g** in diphenyl ether for 24 h at 200 °C resulted in 6π-electrocyclization. Subsequent addition of Pd/C and heating for further 48 h at 200 °C afforded products **40a,b** and **40d-g**. Products **40a,b,g** were isolated in excellent yields. In case of **39c** and **39h**, the formation of a complex mixture was observed. In case of **40d-f**, considerable amounts of the hydrogenated products **41d-f** were formed. Their formation can be explained by formation of one equivalent of hydrogen during the Pd/C catalyzed dehydrogenation. The hydrogen thus formed reacts, again catalyzed by Pd/C, with the alkenyl group located at carbon atom C-2 to give products **41d-f**. It is surprising that the formation of hydrogenated products **41a,b,g** was not observed. This might be explained by the assumption that the electrocyclization, dehydrogenation and, thus, the formation of hydrogen, is slower for **39a,b,g** than for **39d-f**. Therefore, there is not sufficient time for the hydrogenation of

products **40a,b,g**. On the other hand, the formation of products **41a,b,g** was observed when the reaction time was extended.

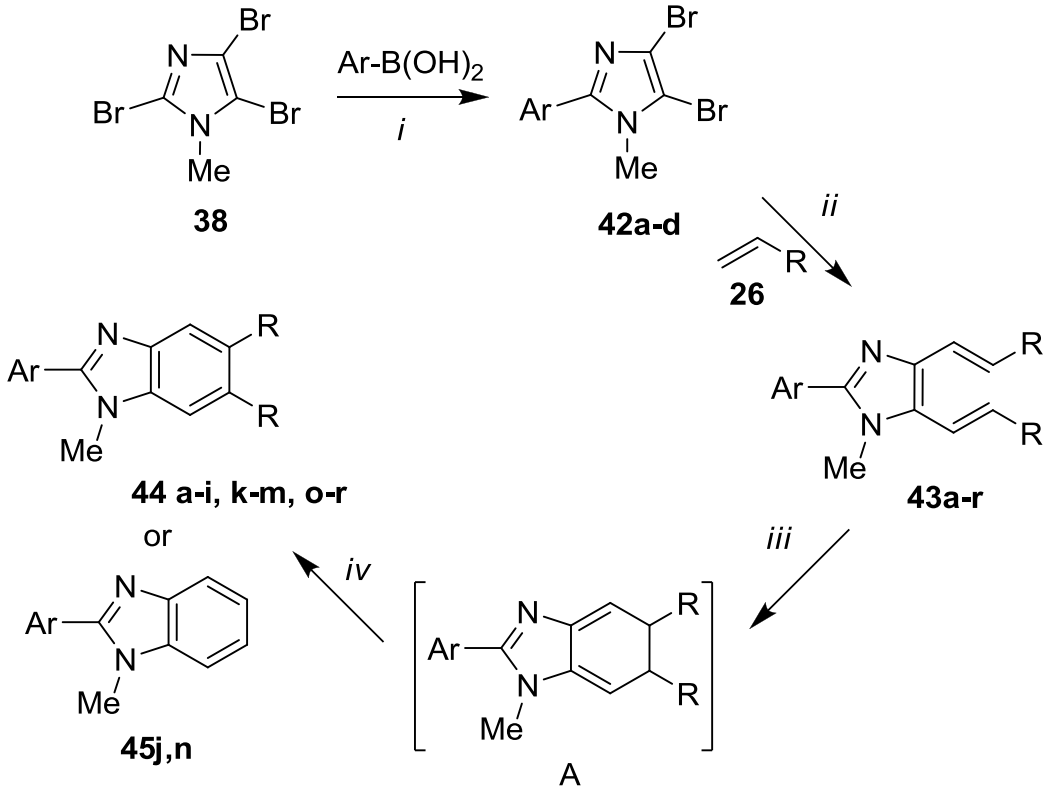
Table 26. Synthesis of **39a-h**, **40a,b,d-g** and **41d-f**

39,40,41	R	% (**39**) [a]	% (**40**) [a]	% (**41**)[a]
a	CO_2nBu	86	90	0
b	CO_2iBu	84	92	0
c	CO_2tBu	81	- [c]	- [c]
d	CO_2nHex	74	60	32
e	CO_2Et	73	48	40
f	CO_2Me	76	40	34
g	CO_2R [b]	82	88	0
h	MeC_6H_5	46	- [c]	- [c]

[a] Yields of isolated products; [b] R = $CH_2CH(Et)(CH_2)_3CH_3$; [c] formation of a complex mixture

The Suzuki-Miyaura reaction of tribromoimidazole **38** with different arylboronic acids afforded the 2-aryl-4,5-dibromoimidazoles **42a-d**[74] in 78-96% yield (Scheme 27, Table 27). The best yields for this transformation were obtained using $Pd(PPh_3)_4$ (5 mol-%) as the catalyst and an aqueous solution of K_2CO_3 (2 M) as the base (solvent: 1,4-dioxane / toluene).

The Heck reaction of **42a-d** with alkenes **26** afforded the 2-aryl-4,5-di(alkenyl) imidazoles **43a-r** in 52-91% yield (Scheme 27, Table 28). The reactions were carried out under the same conditions as the synthesis of **39a-g**. Products **43a-r** were transformed to benzimidazoles **44 a-i, k-m, o-r** in 65-93% yield.



Scheme 27. Synthesis of **42, 43a-r**, **44 a-i, k-m, o-r and 45j,n**. *Conditions*: *i*, **38** (1.0 equiv.), $ArB(OH)_2$ (1.1 equiv.), $Pd(PPh_3)_4$ (5 mol-%), K_2CO_3 (2M), 1,4-dioxane / toluene = 1:1, 100 °C , 12 h; *ii*, **42a-d** (1.0 equiv), **26** (2.5 equiv.), $Pd(OAc)_2$ (5 mol-%), $P(Cy)_3$ (10 mol-%), NEt_3 (8.0 equiv.), DMF, 100 °C, 24 h; *iii*, diphenylether, 200 °C, 24 h; *iv*, Pd/C (10 mol-%), diphenylether, 200 °C, 48 h

Table 27. Synthesis of **42a-d**[74]

42	Ar	% (**42**) [a]
a	4-$(MeO)C_6H_4$	78
b	4-MeC_6H_4	88
c	4-*t*BuC_6H_4	96
d	3,5-$Me_2C_6H_3$	90

[a] Yields of isolated products

Table 28. Synthesis of **43a-r, 44 a-i, k-m, o-r and 45j,n**

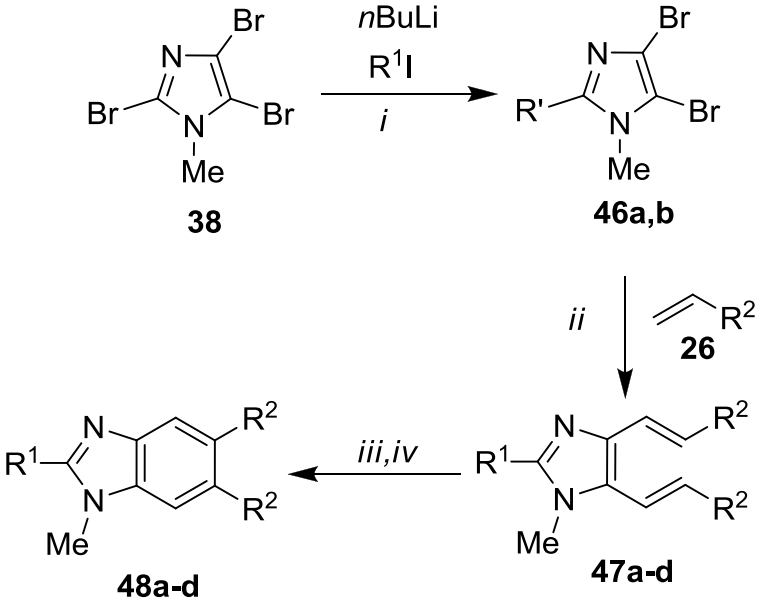
42	**43,44,45**	Ar	R	% (**43**)[a]	% (**44**)[a]	% (**45**)[a]
a	**a**	4-(MeO)C_6H_4	CO_2nBu	91	81	-[b]
a	**b**	4-(MeO)C_6H_4	CO_2iBu	85	77	-[b]
a	**c**	4-(MeO)C_6H_4	CO_2nHex	78	84	-[b]
a	**d**	4-(MeO)C_6H_4	4-MeC_6H_4	63	79	-[b]
a	**e**	4-(MeO)C_6H_4	4-tBuC_6H_4	52	71	-[b]
b	**f**	4-MeC_6H_4	4-(MeO)C_6H_4	-[c]	83	-[b]
b	**g**	4-MeC_6H_4	CO_2nHex	75	87	-[b]
b	**h**	4-MeC_6H_4	CO_2iBu	82	86	-[b]
b	**i**	4-MeC_6H_4	CO_2nBu	87	81	-[b]
b	**j**	4-MeC_6H_4	CO_2tBu	90	-[b]	82
c	**k**	4-tBuC_6H_4	4-(MeO)C_6H_4	64	65	-[b]
c	**l**	4-tBuC_6H_4	CO_2Et	81	93	-[b]
c	**m**	4-tBuC_6H_4	4-MeC_6H_4	56	77	-[b]
c	**n**	4-tBuC_6H_4	CO_2tBu	87	-[b]	65
c	**o**	4-tBuC_6H_4	CO_2nBu	87	85	-[b]
d	**p**	3,5-$Me_2C_6H_3$	CO_2nBu	74	90	-[b]
d	**q**	3,5-$Me_2C_6H_3$	4-tBuC_6H_4	65	72	-[b]
d	**r**	3,5-$Me_2C_6H_3$	CO_2iBu	75	83	-[b]

[a] Yields of isolated products, [b] compound was not formed, [c] compound was not isolated

The formation of **45j,n**, in which the ester groups were reduced, can be explained by the thermal extrusion of *tert*-butyl formate from intermediate A.

The monomethylation of tribromoimidazole **38** in the presence of *n*BuLi and R^1-I afforded the 2-alkyl-4,5-dibromoimidazoles **46a,b** in 78-89% yield (Scheme 28, Table 29). The reaction was done in DMF at room temperature with K_2CO_3 as a base.

The Heck reaction of **46a,b** with alkenes **26** afforded the 2-alkyl-4,5-di(alkenyl)imidazoles **47a-d** in 82-91% yield (Scheme 28 , Table 30). The reactions were carried out under the same conditions as the synthesis of **40a-h** and **43a-n**. Products **47a-d** were transformed to the benzimidazoles **48a-d** in 69-81% yield.



Scheme 28. Synthesis of **46a,b, 47a-d** and **48a-d**. *Conditions*: *i*, **2** (1.0 equiv.), *n*BuLi (1.2 equiv.), R^1I (2.0 equiv), -78° to 20 °C, 16h; *ii*, **46a,b** (1.0 equiv), **26** (2.5 equiv.), $Pd(OAc)_2$ (5 mol-%), $P(Cy)_3$ (10 mol-%), NEt_3 (8.0 equiv.), DMF, 100 °C, 24 h; *iii*, diphenylether, 200 °C, 24 h; *iv*, Pd/C (10 mol-%), diphenylether, 200 °C, 48 h

Table 29. Synthesis of **46a,b**

46	R^1	% (**46**) [a]
a	C_3H_7	78
b	C_4H_9	89

[a] Yields of isolated products

Table 30. Synthesis of **47a-d** and **48a-d**

46	**47, 48**	R^1	R^2	% (**47**)[a]	% (**48**)[a]
a	**a**	C_3H_7	CO_2nBu	91	81
b	**b**	C_4H_9	CO_2iBu	85	69
a	**c**	C_3H_7	CO_2iBu	89	85
b	**d**	C_4H_9	CO_2nBu	82	74

[a] Yields of isolated products

The structures of all products were established by spectroscopic methods. The structure of **44f** was independently confirmed by X-ray crystal structure analysis (Figure 22). The crystal structure of **44f** showed that the phenyl rings are twisted slightly out of the plane of benzimidazole, with torsion angles of 92.9(9), 49.3(3) and 41.9(3)° for N1-C1-C8a- C13a, C6-C5-C16-C17, C3-C4-C23-C28, respectively. The two phenyl rings at C4 and C5 are almost in the same plane.

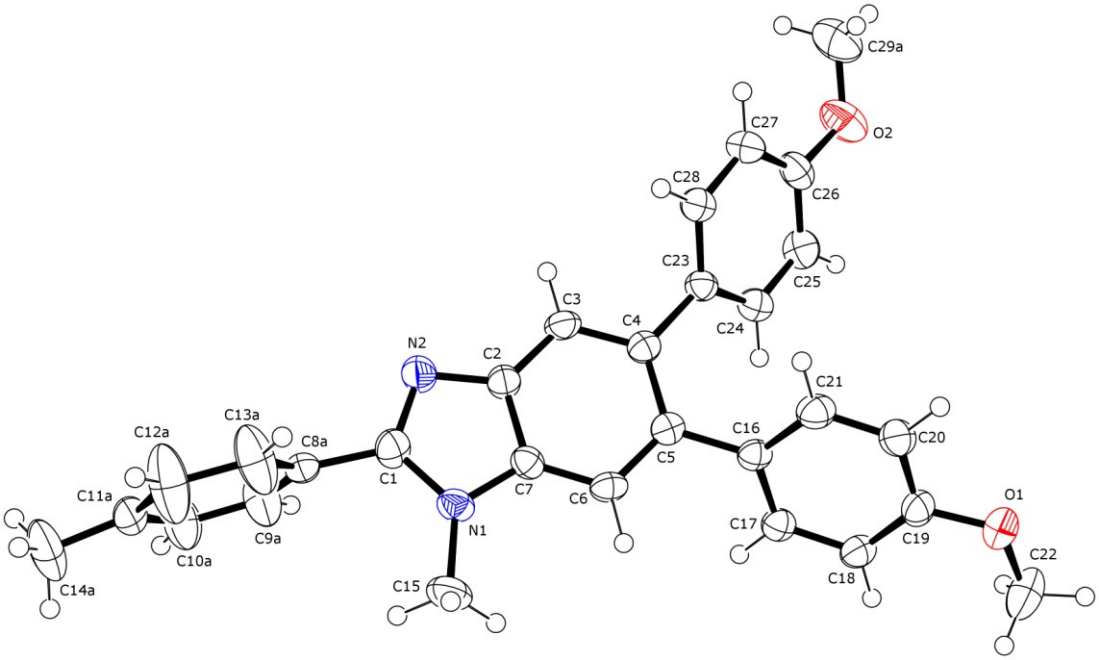


Figure 22. Crystal structure of **44f**

4.3 Conclusion

I have reported an efficient synthesis of 2,5,6-trisubstituted benzimidazoles by Heck reactions of 2,4,5-tribromo-*N*-methylimidazole, 2-aryl-4,5-dibromo-*N*-methyl-imidazoles and 2-alkyl-4,5-dibromo-*N*-methyl-imidazoles and subsequent 6π-electrocyclization/ dehydro-genation reactions.

5 Synthesis of 2,5,6-trisubstituted *N*-Methylindoles based on site-selective Suzuki-Miyaura cross-coupling, twofold Heck and 6π-electro cyclization / dehydrogenation reactions of 2,3,5-tribromo-*N*-methyl-pyrrole

5.1 Introduction

Indole derivatives are found in many natural, synthetic, agrochemical and pharmaceutical compounds.[76] For example, indole-3-carbinol, isolated from cruciferous vegetables, which works as antioxidant, shows chemopreventive and anticancer activities.[77] Indole derivatives influence the neurotransmitter serotonin,[78] act as potent anti-inflammatory agents,[79] neuroprotective agents affecting oxidative stress,[80] as hallucinogen agents,[81] potent PPAR-c binding agents with potential application for the treatment of osteoporosis,[82] and antimicrobial agents.[83] Indoles constitute a privileged scaffold capable of providing useful ligands for diverse receptors.[84] Indoles can be prepared by various classical methods, e. g. the Fischer indole synthesis, the Plieninger indole synthesis, the Madelung cyclization of *N*-acyl-*o*-toluidines, the Bischler indole synthesis, the Batcho-Leimgruber synthesis of indoles from *o*-nitrotoluenes and dimethylformamide acetals, and the reductive cyclization of *o*-nitrobenzyl ketones.[85] Most of the known methods allow to vary the substituents located at positions 2 and 3 of the indole moiety. Positions 5 and 6 are much more difficult to access.

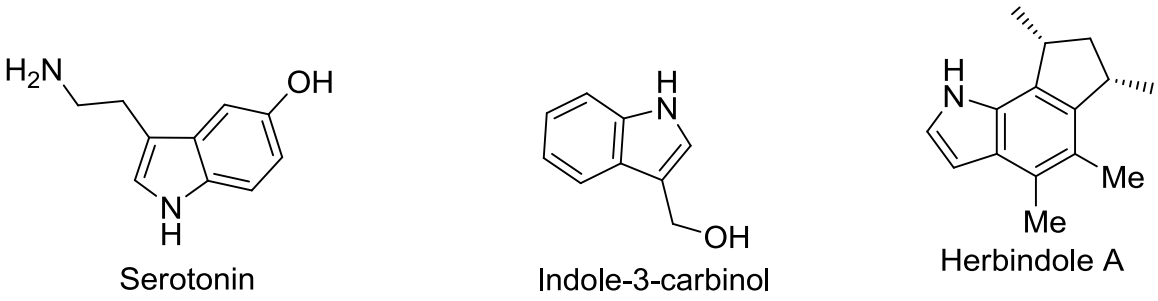
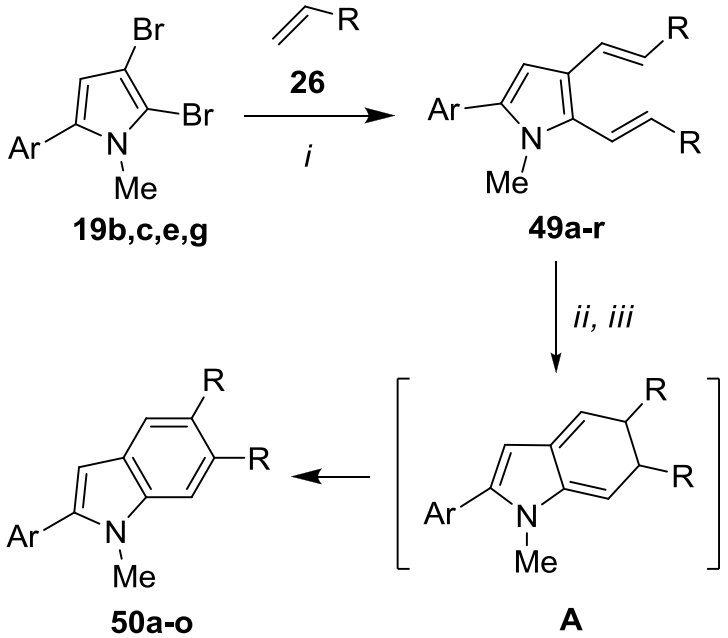


Figure 23. Some indole derivatives isolated from natural products

Due to the importance of indoles in organic and medicinal chemistry, I studied a new approach to 2,5,6-trisubstituted indoles based on the combination of hitherto unknown site-selective Suzuki-Miyaura reactions of 2,3,5-tribromo-*N*-methylpyrrole with twofold Heck and 6π-electrocyclization reactions. The building block strategy reported herein provides a powerful method for the synthesis of indoles which are not readily available by other methods.

5.2 Results and discussion

The Heck reaction of **19b,c,e,g** with alkenes **26** afforded the 5-aryl-2,3-di(alkenyl)-*N*-methylpyrroles **49a-r** in 47-76% yield (Scheme 29, Table 31). The best yields were obtained when the reactions were carried out using $Pd(OAc)_2$ (5 mol-%) as the catalyst in the presence of tricyclohexylphosphine ($P(Cy)_3$, 10 mol-%) (Table 32). The yields significantly dropped when $Pd(PPh_3)_4$ was employed.



Scheme 29. Synthesis of **49a-r** and **50a-o**. *i*, **19b,c,e,g** (1 equiv.), **26** (2.5 equiv.), $Pd(OAc)_2$ (5 mol-%), $P(Cy)_3$ (10 mol-%), NEt_3, DMF, 100 °C, 24 h; *ii*, diphenylether, 200 °C, 24 h; *iii*, Pd/C (10 mol-%), diphenylether, 200 °C, 48h

Table 31. Synthesis of **49a-r** and **50a-o**

19	**49,50**	Ar	R	% (**49**)[a]	% (**50**)[a]
g	**a**	4-MeC_6H_4	CO_2*i*Bu	72	91
g	**b**	4-MeC_6H_4	CO_2*n*Hex	75	80
b	**c**	4-EtC_6H_4	CO_2*n*Bu	63	76
b	**d**	4-EtC_6H_4	CO_2*i*Bu	69	72
b	**e**	4-EtC_6H_4	CO_2*n*Hex	60	90
b	**f**	4-EtC_6H_4	CO_2Et	47	69
b	**g**	4-EtC_6H_4	CO_2R [b]	61	94
b	**h**	4-EtC_6H_4	CO_2Me	58	74
c	**i**	4-*t*BuC_6H_4	CO_2Me	53	70
c	**j**	4-*t*BuC_6H_4	CO_2*i*Bu	76	77
c	**k**	4-*t*BuC_6H_4	CO_2*n*Bu	56	89
c	**l**	4-*t*BuC_6H_4	CO_2*n*Hex	71	81
c	**m**	4-*t*BuC_6H_4	CO_2Et	48	75
e	**n**	3,5-$Me_2C_6H_3$	CO_2R [b]	51	77
e	**o**	3,5-$Me_2C_6H_3$	CO_2*n*Bu	66	88
e	**p**	3,5-$Me_2C_6H_3$	Ph	-[c]	-[c]
b	**q**	4-EtC_6H_4	CO_2*t*Bu	65	-[c]
g	**r**	4-MeC_6H_4	CO_2*t*Bu	72	-[c]

[a] Yields of isolated products; [b] R = $CH_2CH(Et)(CH_2)_3CH_3$; [c] Compound was not isolated

The reactions were carried out at 100 °C in DMF. The yields dropped when the temperature was increased or decreased (Table 33). The employment of styrene **26** instead of acrylates proved to be unsuccessful, due to decomposition under the reaction conditions employed.

Table 32. Influence of the catalyst

Catalyst	% (**49d**)[a]	% (**49f**)[a]	% (**49k**)[a]
10 mol % $Pd(PPh_3)_4$	37	45	19
5 mol % $Pd(OAc)_2$			
10 mol % $P(Cy)_3$	69	47	56

[a] Yields of isolated products

Table 33. Influence of the temperature

T [°C]	% (**49a**)[a]	% (**49m**)[a]	% (**49k**)[a]
90	59	30	50
100	72	48	56
120	63	41	42

[a] Yields of isolated products

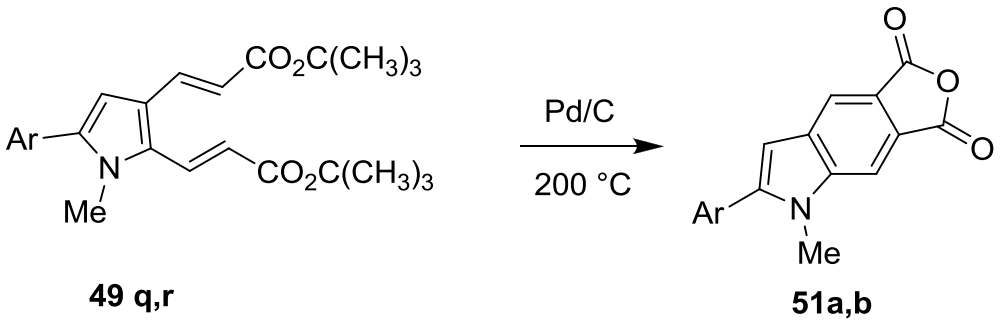
5-Aryl-2,3-di(alkenyl)-*N*-methylpyrroles **49a-o** were transformed into the indoles **50a-o** in 69-94% yield. The pyrroles were heated in diphenyl ether for 24 h at 200 °C. Subsequently, Pd/C was added and the mixture was heated for further 48 h at 200 °C. The indoles were formed by 6π-electrocyclization and subsequent dehydrogenation. The yields dropped when the reaction was carried out at 160 °C for 96 h instead of 200 °C for 72 h (Table 34).

Table 34. Influence of the temperature on the 6π-electrocyclisation

T [°C]	*t* [h]	% (**50a**)[a]	% (**50b**)[a]
160	96	63	71
200	72	91	80

[a] Yields of isolated products

Heating of **49q,r** in diphenyl ether for 12 hours at 200 °C resulted in 6π-electro-cyclization. Subsequent addition of Pd/C and heating for further 12 hours at 200 °C afforded products **51a,b** after another internal cyclisation (Scheme 30, Table 35).



49 q,r **51a,b**

Scheme 30. Synthesis of **51a,b**: Conditions, Pd/C, diphenylether, 200 °C, 24 h

Table 35. Synthesis of **51a,b**

51	Ar	% (**51**)[a]
a	4-EtC_6H_4	63
b	4-MeC_6H_4	72

[a] Yields of isolated products

5.3 Conclusion

I have reported an efficient synthesis of 2,5,6-trisubstituted indoles based on Suzuki and Heck reactions of 2,4,5-tribromo-*N*-methypyrrole and subsequent 6π-electrocyclization / dehydrogenation reactions. This methodology provides a convenient access to various indoles which are not readily available by other methods.

6 Synthesis of carbazoles and 1,2-dihydrocarbazoles by domino ′twofold Heck / 6π-electrocyclization′ reactions of tetrabromo-*N*-methylindole and tetrabromo-*N*-methylpyrrole

6.1 Introduction

Carbazole was isolated first from the anthracene fraction of coal tar by Graebe and Glaser in 1872.[86] Later, in 1987, Bhattacharyya and coworkers, reported isolation of carbazole from *glycomis pentaphylla,* a plant source.[87] The carbazole nucleus is found in many unnatural and natural products. Clausenapine,[88] 3-methylcarbazol,[89] mukonidine[90] and koenoline[91] are some carbazole derivatives found in the nature. The carbazole system occurs in several significant modern drugs, such as caprofen, which has been used for the treatment of arthritis in man and in animals, and carvedilol, which has been used for the treatment of hypertension.[92] Carbazoles have attracted much attention due to their biological and pharmacological activities.[93] Carbazoles and their related structures show antibiotic, anti-viral, anti-inflammatory, and anti-malarial activities.[94] 5,11-Dimethyl-6*H*-pyrido[4,3-*b*]carbazole (ellipticine), which is a natural plant product, has shown significant antitumor activity.[95] Bis(*O*-demethylmurrayafoline-A) shows cytotoxic activities against diverse human cancer cell lines[96] and exhibits moderate antimalarial activity.[97]

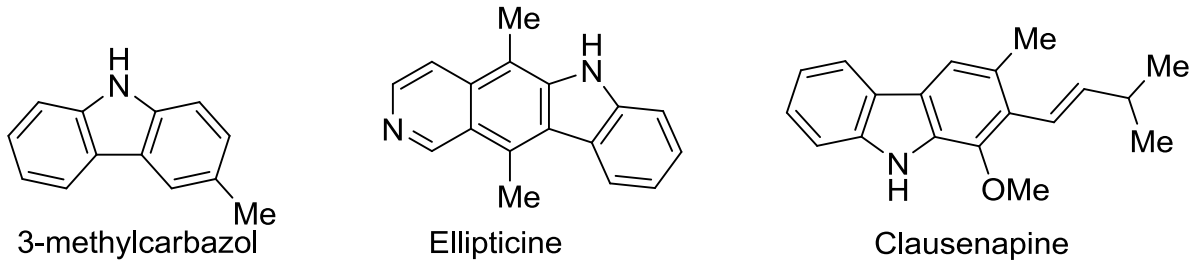


Figure 24. Carbazole derivatives isolated from natural products

The carbazol ring has been synthesized by different methods such as the method of Graebe and Ullmann, in which o-aminodiphenylamine is treated with nitrous acid giving 1-phenyl-1H-benzo[d][1,2,3]triazole, which loses nitrogen on heating to give cabazole.[98] By the

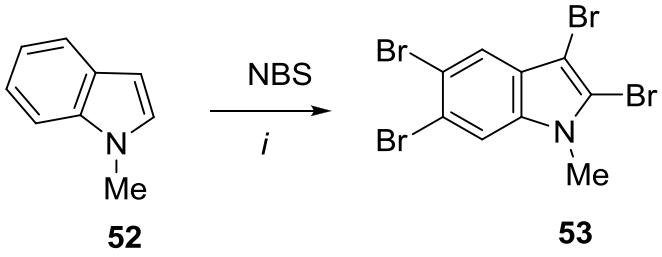
Fischer indole synthesis, tetrahydrocarbazole is obtained when cyclohexanone phenyl hydrazone is heated with dilute sulfuric acid.[99] Many other methods for the synthesis of carbazoles have been reported.[100] Recently Ackermann *et al.* have reported a proficient synthesis of carbazoles and other heterocycles by a new palladium-catalyzed domino ′N-H/C-H activation′ reaction of anilines with 1,2-dihaloalkenes.[101]

It occurred to me that ′twofold Heck / 6π-electrocyclization′ might provide a useful method for the direct and convenient synthesis of dihydrocarbazoles and carbazoles. Herein, I reported the synthesis of new carbazole derivatives from tetrabrominated *N*-methylindole and tetrabrominated *N*-methylpyrrole.

6.2 Result and discussion

6.2.1 Synthesis of carbazoles starting with *N*-methylindole

The reaction of *N*-methylindole (**52**) with NBS (5.0 equiv.) in THF (-78 °C, 1 h, then reflux for 4 h) afforded 2,3,5,6-tetrabromo- *N*-methylindole (**53**) in 78% yield (Scheme 31).[102]

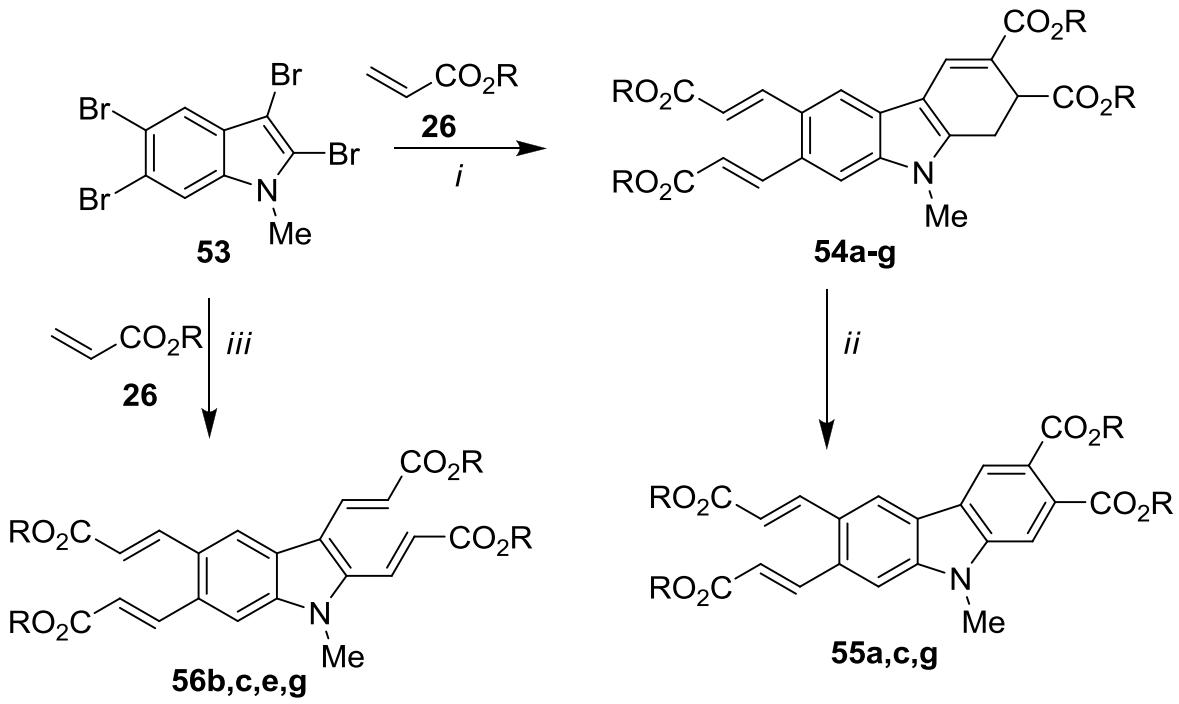


52 **53**

Scheme 31. Synthesis of 2,3,4,5-tetrabromo-*N*-methylpyrrole

The Heck cross-coupling reaction of 2,3,5,6-tetrabromoindole **53** with 5.0 equiv. of alkenes **26** (120 °C, 48 h) afforded the 6,7-di(alkenyl)-1,2-dihydrocarbazoles **54a-g** (Scheme 32, Table 36). The best yields were obtained when the reactions were carried out using $Pd(OAc)_2$ (5 mol-%) and the ligand SPhos (10 mol-%) (Table 38) which was developed by Buchwald and coworkers.

The Pd/C-catalyzed dehydrogenation of **54a,c,g** afforded the carbazoles **55a,c,g** in quantitative yield (Scheme 32). An electrocyclization involving the alkenyl groups attached to carbon atoms C-5 and C-6 was not observed. This can be explained by the aromaticity of the benzene ring which would be interrupetd by the electrocyclization. At lower temperature (90 °C) tetra-alkenylated indoles **56b,c,e,g** were also prepared successfully (Scheme 32, Table 36). Interestingly, due to the reduction of C-2 and C-3, by-product **57** (7 %) was isolated along with **56b** (Figure 25).



Scheme 32. Synthesis of **54a-g, 55a,c,g** and **56b,c,e,g**. *Conditions*: *i*, $Pd(OAc)_2$ (5 mol-%), SPhos (10 mol-%), NEt_3, DMF, 120 °C, 48 h; *ii*, Pd/C (10 mol-%), xylene, reflux, 2 d, *iii*, $Pd(OAc)_2$ (5 mol-%), SPhos (10 mol-%), NEt_3, DMF, 90 °C, 36 h

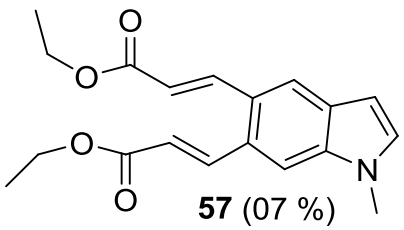


Figure 25. Structure of side product **57** derived from **56b**

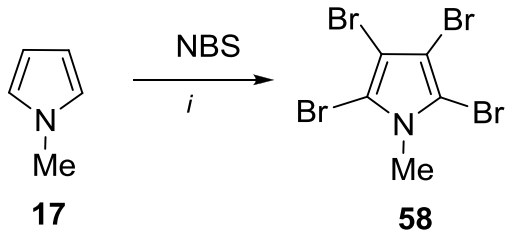
Table 36. Synthesis of **54a-g, 55a,c,g** and **56b,c,e,g**

54,55,56	R	% (**54**) [a]	% (**55**) [a]	% (**56**) [a]
a	Me	68	100	- [b]
b	Et	86	- [b]	76
c	*n*Bu	71	100	71
d	*i*Bu	72	- [b]	- [b]
e	*t*Bu	72	- [b]	88
f	*n*Hex	80	- [b]	- [b]
g	*2-Ethylhexyl*	71	100	75

[a] Yields of isolated products; [b] experiment was not carried out

6.2.2 Synthesis of carbazoles starting with *N*-methylpyrrole

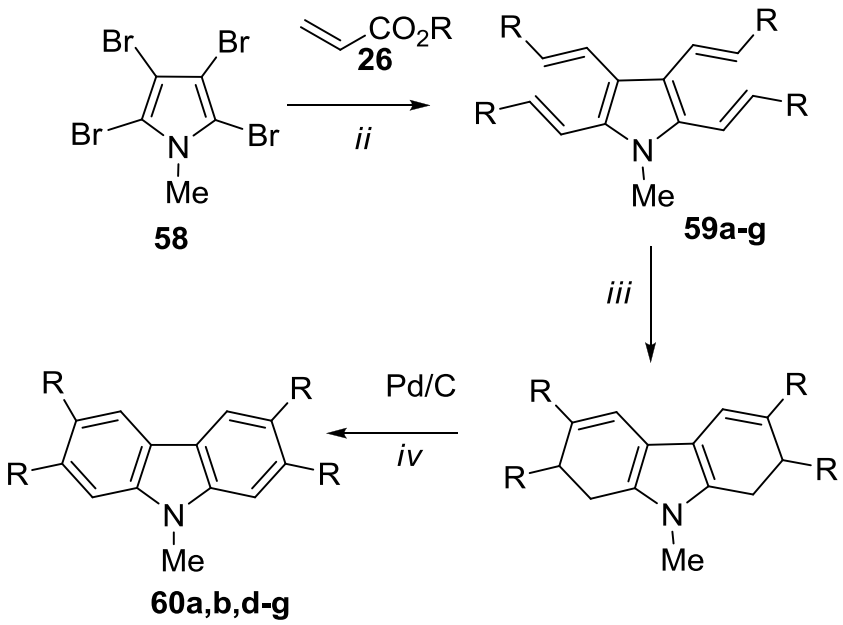
2,3,4,5-Tetrabromo-*N*-methylpyrrole **(58)** was prepared in 93% yield by reaction of *N*-methylpyrrole (**17**) with NBS (5.0 equiv.) in THF (-78°C, 12 h) (scheme 33).[46]



17 **58**

Scheme 33. Synthesis of 2,3,4,5-tetrabromo-*N*-methylpyrrole

The Heck reaction of **58** with alkenes **26** (5.0 equiv) afforded the tetra-alkenylated pyrroles **59a-g** in 52-75% yield (Scheme 34, Table 37). Good yields were obtained when the reactions were carried out using $Pd(OAc)_2$ (5 mol-%) as the catalyst in the presence of tricyclohexylphosphine ($P(Cy)_3$, 10 mol-%) or SPhos (10 mol-%) (Table 38). Tricyclo-hexylphosphine $P(Cy)_3$ was employed, due to its lower price as compared to SPhos. During the optimization, the temperature also proved to be an important parameter. A clean transformation was observed when the reaction was carried out at 90 °C.



Scheme 34. Synthesis of **59a-g** and **60a,b,d-g**. *Reagents and conditions*: *i*, ***58*** (1.0 equiv.), **26** (5.0 equiv.), $Pd(OAc)_2$ (5 mol-%), $P(Cy)_3$ (10 mol-%), Et_3N, DMF, 90 °C, 12 h; *ii*, diphenyl ether, 200 °C, 24 h; *iv*, Pd/C (10 mol-%), diphenylether, 200 °C, 48 h

Table 37. Synthesis of **59a-g** and **60a,b,d-g**

59,60	R	% (**59**) [a]	% (**60**) [a]
a	*n*Bu	65	75
b	*i*Bu	55	89
c	*t*Bu	71	- [b]
d	*n*Hex	73	80
e	Me	52	69
f	Et	69	63
g	2-Ethylhexyl	75	82
h	Ph	- [b]	- [c]

[a] Yields of isolated products; [b] No compounds were isolated; [c] experiment was not carried out

Table 38. Optimization of the reaction conditions for the synthesis **56c, 59a and 59e.**

Catalyst	% (**56c**)[a]	% (**59a**)[a]	% (**59e**)[a]
5 mol % $Pd(OAc)_2$ 10 mol % $P(Cy)_3$	61	65	52
5 mol % $Pd(OAc)_2$ 10 mol % SPhos	75	71	55

[a] Yields of isolated products

Tetra(alkenyl)-*N*-methyl pyrrole**s 59a-g** were transformed into the carbazoles **60a,b,d-g** in 63-89% yield. The pyrroles were heated in diphenyl ether for 24 h at 200 °C. Subsequently, Pd/C was added and the mixture was heated for further 48 h at 200 °C. The Carbazoles were formed by 6π-electrocyclization and subsequent dehydrogenation. Very low yields (Table 4) were observed when the reactions were carried out at 140 °C for 96 h instead of 200 °C for 72 h.

Table 39. Influence of the temperature on the 6π-electrocyclisation

T [°C]	*t* [h]	% (**60a**)[a]	% (**60f**)[a]
140	96	21	12
200	72	75	63

[a] Yields of isolated products

The employment of styrene instead of acrylates proved to be unsuccessful, due to decomposition under the reaction conditions employed.

6.3 Conclusion

I have reported the synthesis of tetra-alkenyl-*N*-methyl indoles and pyrroles by palladium(0)-catalyzed Heck cross-coupling reactions of tetrabromo-*N*-methylindole and –pyrrole, respectively. The reactions were carried out between 90-100 °C using $P(Cy)_3$ or the novel biaryl monophosphine ligand (SPhos) developed by Buchwald and coworkers. 1,2-Dihydrocarbazoles were formed by a domino ′twofold Heck / 6π-electrocyclization′ when the

reaction was carried out at 120 °C rather than 90 °C. Some of the 1,2-dihydrocarbazoles prepared were transformed, by Pd/C-catalyzed dehydrogenation, into the corresponding carbazoles in high yield. The tetra-alkenyl-*N*-methylpyrroles were transformed at 200 °C in diphenylether, by subsequent 6π-electrocyclization and aromatization to the corresponding carbazoles in good yield.

7 Synthesis and photophysical properties of dibenzothiophene by domino twofold (tetrafold) Heck / 6π-electrocyclization reactions of 2,3,4,5 -tetrabromothiophene

7.1 Introduction

Dibenzothiophene occurs naturally in the phenanthrene fraction of coal tar and was first isolated by Kruber.[103] Dibenzothiophene and its alkylated derivatives represent one of the most abundant types of sulfur-containing compounds in crude oil.[104] It has been shown that the dibenzothiophene derivatives, including 4,6-dimethyldibenzothiophene, possesses estrogenic activity.[105] Dibenzothiophenes, including derivatives of dibenzothiophene-3,7-diamine-5,5-dioxides are used as dyes and fluorescent whiteners.[106] Umemoto and coworkers have shown that 5-(trifluoromethyl)dibenzothiophenium salts are potentially usefull as electrophilic trifluoromethylating agents. Recently, dibenzothiophene derivatives were identified as new prototype semiconductors for organic field-effect transistors.[107] Many compounds including the dibenzothiophene system show antitumor,[108] genotoxic,[109] antiprotozoal,[110] antidiabetic[111] and antimicrobial[112] activities.

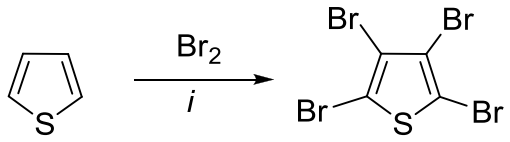
Dibenzothiophene was first synthetized by Stenhouse in 1870, by heating diphenyl sulfide in the presence of iron nails.[113] Later, a large number of methods for the synthesis of dibenzothiophenes have been reported. For example, the most general method for the synthesis of dibenzothiophenes is the cyclization of alpha-arylsulfanyl-cycloketones to give tetrahydro- or dihydrodibenzothiophenes, which are subsequently aromatized to form the desired products. That method can be inconvenient as it cannot be used to prepare dibenzothiophene derivatives with strong electron-withdrawing groups.[114] Recently, Nielsen and coworkers have reported a novel and efficient three-step protocol for synthesizing functionalized dibenzothiophenes from common starting materials and by using palladium-catalyzed carbon-carbon and carbon-sulfur bond formations.[115]

In this chapter, I developed a one-step and three-step synthesis of novel funtionalized dibenzothiophenes by domino tetrafold Heck reactions and subsquent 6π-electrocyclization reactions of 2,3,4,5-tetrabromothiophene .

7.2 Results and discussion

7.2.1 Synthesis of dibenzothiophenes

2,3,4,5-Tetrabromothiophene (**61**) was prepared in 81% yield by reaction of thiophene (**34**) with bromine (5.0 equiv.) in chloroform for 9 h (Scheme 35).[116]

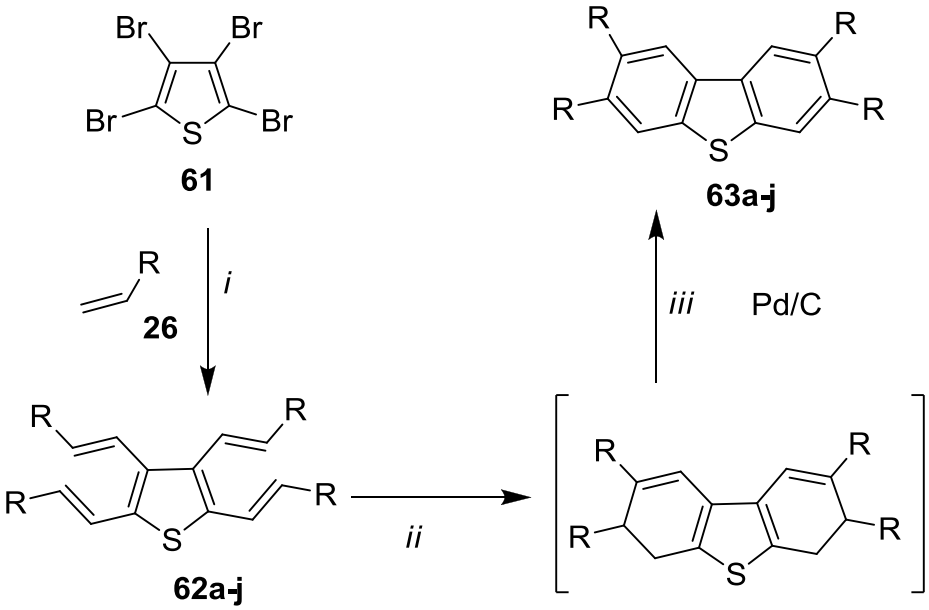


34 **61**

Scheme 35. Synthesis of 2,3,4,5-tetrabromothiophene. *Conditions*: *i*, 1) Br_2 (7.0 equiv., slow addition), 0 °C, $CHCl_3$, 2) reflux, 3 h; 3) NaOH, H_2O (2 M), reflux, 6 h

The Heck cross-coupling reaction of 2,3,4,5-tetrabromothiophene **61** with 5.0 equiv. of alkenes **26** (90 °C, 12 h) afforded the tetra-alkenylated thiophenes **62a-j** (Scheme 36, Table 40). The best yields were obtained when the reactions were carried out using $Pd(OAc)_2$ (3 mol-%), Na_2CO_3 and $P(Cy)_3$ (5 mol-%).

The Pd/C-catalyzed dehydrogenation of **62a-j** afforded the dibenzothiophenes **63a-j** in good yield (Scheme 36, Table 40).



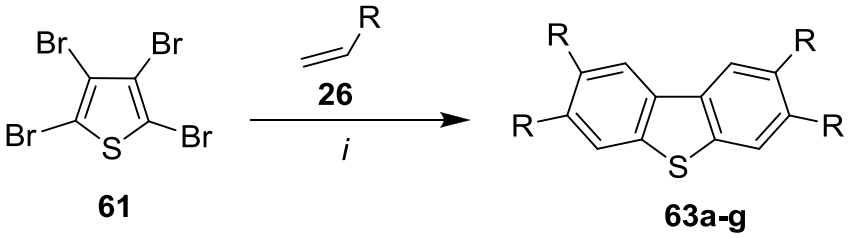
Scheme 36. Synthesis of **62a-j** and 6**3*a*-j**. *Reagents and conditions*: *i,* **61** (1 equiv), **26** (5.0 equiv.), $Pd(OAc)_2$ (3 mol-%), $P(Cy)_3$ (5 mol-%), Na_2CO_3, DMF, **90 °C**, 12 h; *ii*, diphenyl ether, 200 °C, 24 h; *iii*, Pd/C (10 mol-%), diphenylether, 200 °C, 48 h

Table 40. Synthesis of **62a-j** and **63a-j**

62,63	R	% (**62**) [a]	% (**63**) [a]
a	Me	71	60
b	Et	54	51
c	*n*Bu	51	59
d	*i*Bu	68	62
e	2-Ethylhexyl	52	70
f	*n*Hex	63	73
g	Ph	80	74
h	4-*t*BuC_6H_4	72	63
i	4-(MeO)C_6H_4	62	67
j	4-MeC_6H_4	78	59

[a] Yields of isolated products; [b] compound was not isolated

During the optimization, the temperature also proved to be an important parameter. When the Heck reactions of 2,3,4,5-tetrabromothiophenes with **26** (5.0 equiv.) were carried out at 140 °C for 24 h, compounds **63a-g** were formed in a one-step reaction with moderate yields (Scheme 37, Table 41).



Scheme 37. Synthesis of **63a-g**. *Reagents and conditions*: *i*, **61** (1 equiv), **26** (5.0 equiv), $Pd(OAc)_2$ (3 mol-%), $P(Cy)_3$ (5 mol-%), Na_2CO_3, DMF, 140 °C, 24 h

Table 41. Synthesis of **63a-g**

63	R	Base	solvent	*T* [°C]	*t* [h]	% (**63**) [a]
a	Me	Na_2CO_3	DMF	140	24	43
b	Et	Na_2CO_3	DMF	140	24	38
c	*n*Bu	K_2CO_3	DMF	120	24	40
d	*i*Bu	Na_2CO_3	DMF	140	24	52
e	2-Ethylhexyl	Na_2CO_3	DMF	120	24	36
f	*n*Hex	Na_2CO_3	DMF	140	24	40
g	ph	Na_2CO_3	DMF	140	36	48

[a] Yields of isolated products

The base plays also a very important role in the reaction (Table 42). The use of triethylamine as a base gave many products including mono-, di- and tri-alkenylated products, but not the products derived from fourfold Heck reactions. The reaction with Na_2CO_3 gave better yields than using K_2CO_3. No product or only trace amounts were observed when the reactions carried out in toluene and xylene.

Table 42. Optimization of reaction conditions

R	Base	solvent	*T* [°C]	*t* [h]	% (**62**)	% (**63**)
*i*Bu	Na_2CO_3	DMF	140	24	-[a]	52
*n*Bu	K_2CO_3	DMF	120	24	-[a]	40
*i*Bu	Et_3N	DMF	120	12	-[a]	-[a]
*n*Bu	Et_3N	DMF	90	24	-[a]	-[a]
*n*Bu	Na_2CO_3	toluene	110	24	-[a]	traces
2-Ethylhexyl	Na_2CO_3	xylene	150	12	-[a]	traces
iBu	K_3PO_4	DMF	140	24	-[a]	traces

[a] compounds were not isolated

7.2.2 UV analysis

To study the electronic properties of the synthesized compounds **62g**, **63g**, **63d**, **62d**, absorption spectroscopy was carried out. Representative UV-spectra of the different product classes (**62g**, **63g**, **63d**, **62d**) are shown in Figure 23 (in CH_2Cl_2).

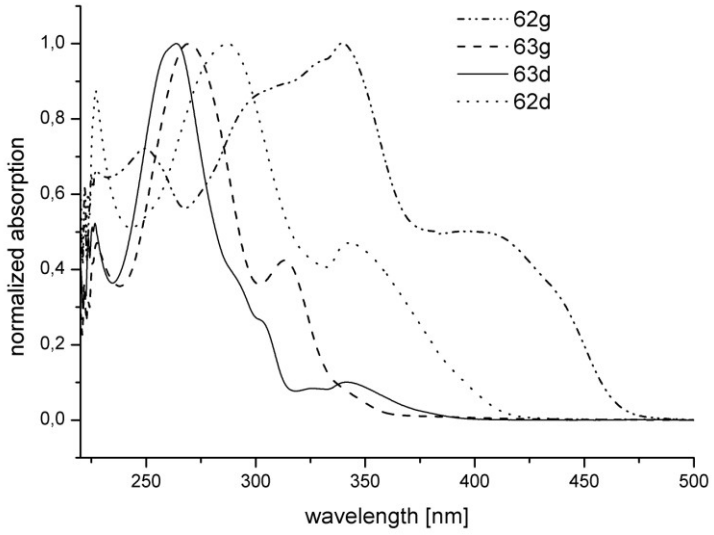


Figure 26. Normalized absorption spectra of compounds **62g, 63g, 63d** and **62d**

Compounds of **62g**, **63g** and **63d** have λ_{max}-values in the range of 260nm-290nm, while λ_{max} values of compounds **62d** are shifted about 80 nm to higher wavelengths. The transition with lowest energies $S_1 \leftarrow S_0$ belongs to the tetrastyryl derivatives (exemplarily

shown for **62g**). The alkenyl-derivatives absorb at lower energies than their corresponding dibenzothiophenes. This could be explained by hampered conjugation, due to steric hindrance by the phenyl- (**62g**) or ester-functions (**63d**), respectively. However, compound **62d** is shifted about 80nm to lower energies compared to **63g**, while **63d** is only shifted about 30 nm compared to **62g**.

Substituents located at the tetraphenyldibenzothiophenes (**63g, 63i** and **63j**) have a low impact on the absorption spectra (compare figure 26). Substituents at the phenyl group in the 4-positions lead to a slight shift of the λ_{max} to lower energies in accordance with their donor ability (Figure 27).

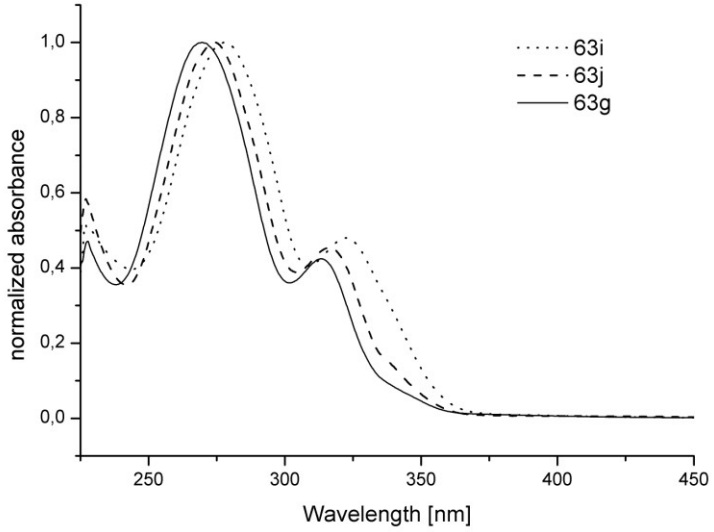


Figure 17. Normalized absorption spectra of compounds **63i, 63j** and **63g**

Table 43. General overview measurements of **63a, 63d, 63f, 63g, 63i, 63j 62c, 62d, 62e, 62g and 62j**

Compound	λ_{max} [nm]	Sh1 [nm]
63a	258	338
63d	264	342
63f	265	346
63g	270	313
63i	278	323

63j	274	316
62c	290	354
62d	287	343
62e	289	343
62g	340	401
62j	342	416

7.2.3 Fluorescence analysis

To study the electronic properties of the synthesized compounds, fluorescence spectroscopy was carried out. The fluorescence spectra were recorded on a Hitachi F-4010 fluorescence spectrometer in dichloromethane ($c \approx 10^{-3}$ - 10^{-4} mol/l; excitation wavelength: 250 nm).

Figure 28 shows the fluorescence spectra of three tetrastyrylthiophenes (**62g**, **62h** and **62i**).

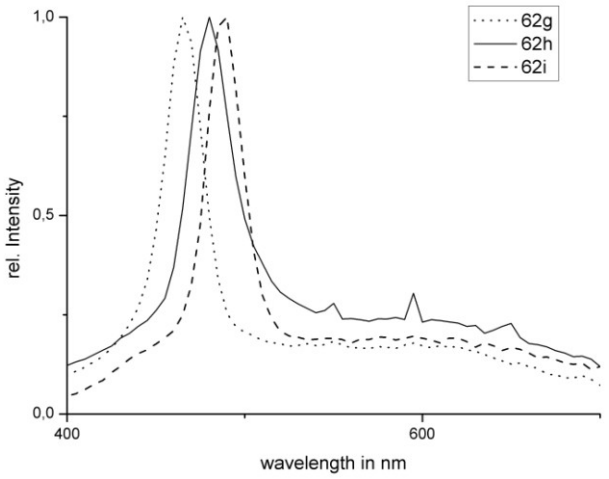


Figure 28. Fluorescence spectra of **62g**, **62h** and **62i**

The compounds have λ_{max}-values in the range of 465-490 nm (Table 44). The substitution of the phenyl group in 4-position leads to a shift of λ_{max} to lower energies, probably because the substituents are electron donating.

Table 44. Structure and λ_{max}-values of compounds **62g**, **62h** and **62i**

Compound	R	$\lambda_{max,\ emission}$
62g	H	465
62h	*t*-Butyl	480
62i	OMe	490

Figure 29 shows the fluorescence spectra of three tetrasubstituted dibenzothiophenes (**63d**, **63a** and **63i**).

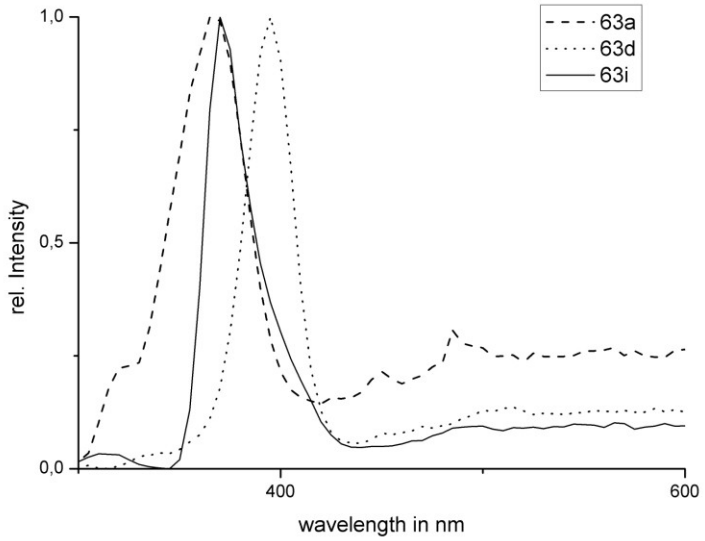


Figure 29. Fluorescence spectra of **63d**, **63a** and **63i**

The compounds have λ_{max}-values in the range of 365 nm-395 nm (Table 45). There seems to be a strong influence of the ester-group (*i*-Pr or Me, see Table 45) on the λ_{max}-value.

Table 45. Structure and λ_{max}-values of compounds **63d**, **63a** and **63i**

Compound	R	$\lambda_{max,\ emission}$
63d	COO(*i*-Pr)	395
63a	COOMe	365
63i	4-Methoxyphenyl	370

In Figure 30, the representative compounds **63i** and **62i** are compared to investigate the influence of cyclization on the fluorescence properties.

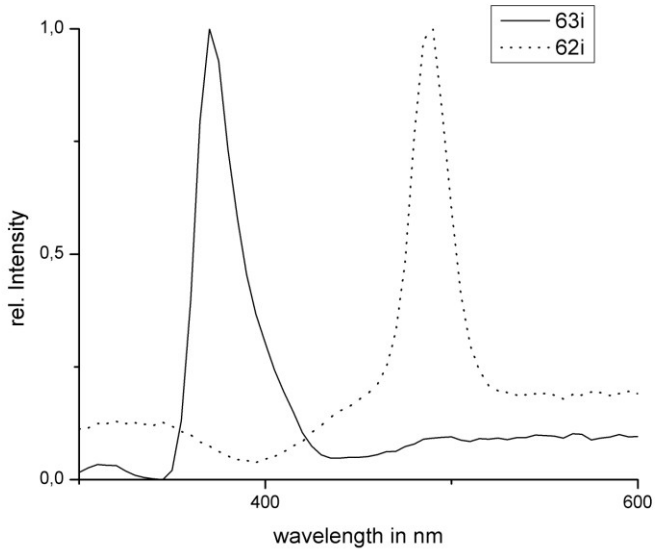


Figure 30. Comparison of **63i** and **62i**.

The cyclization causes a strong fluorescence shift of 120 nm towards higher energies. Table 46 shows a general overview about the values of the fluorescence measurement.

Table 46. General overview measurements of **63a**, **63d**, **63i**, **62g**, **62h**, **62i** and **62j**

Compound	$\lambda_{e,\,max}$ /nm
63a	365
63d	395
63i	370
62g	465
62h	480
62i	490
62j	480

7.3 Conclusion

I have reported the synthesis of tetra-alkenylthiophenes by palladium(0)-catalyzed fourfold Heck cross-coupling reactions of tetrabromothiophene. The reactions were carried out at 100 °C using $P(Cy)_3$ and Na_2CO_3. Tetra-alkenylthiophenes were transformed, by Pd/C-catalyzed dehydrogenation, into the corresponding dibenzothiophenes in good yield. The dibenzothiophenes were also obtained in one step by domino 'fourfold Heck-6π-electrocyclization' reactions of tetrabromothiophene when the reactions were carried out at 140 °C for 24 h. The UV and fluorescence analysis showed that the compounds absorb UV light and are fluorescent.

Appendix

8 Experimental section

8.1 Material and methods

8.1.1 General remarks

Reactions were carried out under inert atmosphere (Argon 4.6) in order to simultaneously exclude oxygen and water when appropriate. Schlenck techniques were applied. Solvents for reactions were dried and destilled by standard methods or purchased from Merck, Aldrich, Acros Organics, ABCR and others whenever exclusion of water was desired. Solvents for liquid chromatography and extraction were always destilled prior to use and partly reused after fractionating destillation (*n*-heptane, ethyl acetate).

8.1.2 Methods for compound characterization and analysis

NMR spectroscopy

Bruker AC 250, Bruker ARX 300, Bruker ARX 500, Bruker Avance 600. For NMR characterization the one-dimensional 1H NMR, proton-decoupled 13C NMR, and DEPT 135 spectra were collected. If necessary, other techniques (APT, NOESY, COSY, HMBC) were applied as well. All NMR spectra presented in this work were collected in CDCl3 solution. All chemical shifts are given in ppm.
References (1H NMR): TMS ($\delta = 0.00$) or residual $CHCl_3$ ($\delta = 7.26$) were taken as internal standard. When these reference peaks were superimposed by signals belonging to the compound under investigation a small amount of CH2Cl2 ($\delta = 5.30$) was added and taken as reference instead.
References (13C NMR): TMS ($\delta = 0.0$) or residual CHCl3 ($\delta = 77.0$) were taken as internal standard.

Multiplicities are given as follows: s = singlet, d = doublet, t = triplet, q = quartet, sep = septet, m = multiplet, br = broad signal. More complex coupling patterns are represented by combinations of the respective symbols. For example, td indicates a triplet of doublets with the larger coupling constant associated with the first symbol (here: triplet).

Infrared spectroscopy (IR)

Nicolet 205 FT-IR, Nicolet Protége 460 FT-IR. Peaks are given the following assignments: w = weak, m = medium, s = strong, br = broad.

Mass spektrometry (MS)

AMD MS40, Varian MAT CH 7, MAT 731 (EI, 70 eV), Intecta AMD 402 (EI, 70 eV and CI), Finnigan MAT 95 (CI, 200 eV).

High resolution mass spectrometry (HRMS)

Varian MAT 311, Intecta AMD 402.

Elemental analysis

LECO CHNS-932, Thermoquest Flash EA 1112.

Melting points

Micro heating table HMK 67/1825 Kuestner (Büchi Apparatus), Leitz Labolux 12 Pol with heating table Mettler FP 90. Melting points are uncorrected.

Rotation angles

LP (IBZ Meßtechnik, NaD = 589 nm).

X-ray structures

Bruker X8Apex diffractometer with CCD camera (Mo K_α radiation and graphite monochromator, λ= 0.71073 Å). The space group is determined by the XPREP program and the structures were solved via the SHELX-97 program package. Refinements were carried out according to the minimum square error method.

8.1.3 Chromatographic methods

Thin layer chromatography (TLC)

Merck Kieselgel 60 F254 on aluminium foil from Macherey-Nagel. Detection was carried out under UV light at 254 nm and 365 nm. As colourizing reagent the following mixtures were used: 1-2/100 p-Anisaldehyde or vanillin, 10/100 glacial acetic acid, 5/100 sulphuric acid, 83-84/100 methanol.

Column chromatography

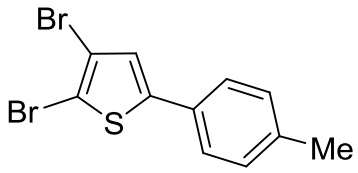
Column chromatography was performed with Merck Silica Gel 60 or Macherey-Nagel Silica Gel 60 (0.063-0.200 mm, 70-230 mesh). The finer Merck Silica Gel 60 (0.040-0.063 mm, 230 -400 mesh) was chosen when appropriate.

8.1.4 Procedures and spectroscopic data

General procedure for the synthesis of 2,3-Dibromo-5-arylthiophenes (2):

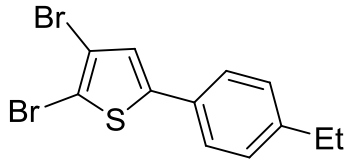
To a mixture of **1** (0.159 g, 0.5 mmol), arylboronic acid (0.55 mmol), $Pd(PPh_3)_4$ (29 mg, 5 mol-%) were added a mixture of 1,4-dioxane and toluene (1:1, 5 mL) and an aq solution of K_2CO_3 (2 mL, 2 M) under argon atmosphere. The reaction mixture was stirred at 100 °C for 8 h and was subsequently allowed to cool to 20 °C. The solution was poured into H_2O and CH_2Cl_2 (25 mL each) and the organic and the aqueous layer were separated. The latter was extracted with CH_2Cl_2 (3 × 25 mL), dried (Na_2SO_4), filtered, and concentrated in vacuo. The residue was purified by flash column chromatography (flash silica gel, *n*-heptane).

2,3-Dibromo-5-*p*-tolylthiophene (2a):



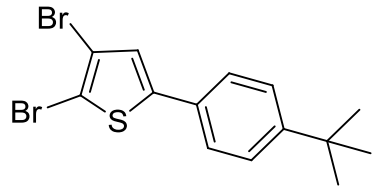
Starting with **1** (0.159 g, 0.5 mmol) and 4-tolylboronic acid (0.75 g, 0.55 mmol), **2a** was isolated (0.078 g, 47%) as a colorless solid, mp. = 83-85 °C. ^{1}H NMR (300 MHz, $CDCl_3$): δ = 2.26 (s, 3H, CH_3), 6.94 (s, 1H, ArH), 7.08 (d, 2H, *J* = 8.0 Hz, ArH), 7.26 (d, 2H, *J* = 8.2 Hz, ArH). ^{13}C NMR (62 MHz, $CDCl_3$): δ = 21.3 (CH_3), 109.4, 114.5 (CBr), 125.0, 125.3, 128.7, 129.4, 129.8 (CH), 130.0, 138.6, 145.6 (C). IR (KBr, cm^{-1}): *v* = 3091, 3019, 2918, 2852 (w), 1498 (m), 1433, 1118, 997, 821 (w), 801 (m), 550 (w). GC-MS (EI, 70 eV): m/z (%) = 334(53) [M^+ ($^{8'}$Br, $^{8'}$Br)], 332(100) [M^+ ($^{8'}$Br, Br)], 331(16), 330(49) [M^+ (Br, Br)], 172(35), 171(30), 86(11). HRMS (EI, 70 eV): calcd for $C_{11}H_8Br_2S$ [M^+ (Br, $^{8'}$Br)]: 331.86875; found: 331.86882.

2,3-Dibromo-5-(4-ethylphenyl)thiophene (2b):



Starting with **1** (0.159 g, 0.5 mmol)) and 4-ethylphenylboronic acid (0.083 g, 0.55 mmol), **2b** was isolated (0.092 g, 53%) as a colorless oil. ^{1}H NMR (300 MHz, $CDCl_3$): δ = 1.18 (t, 3H, *J* = 7.6 Hz, CH_3), 2.59 (q, 2H, *J* = 7.6 Hz, CH_2), 6.98 (s, 1H, $CH_{thiophene}$), 7.14 (d, 2H, *J* = 8.4 Hz, ArH), 7.33 (d, 2H, *J* = 8.3 Hz, ArH). ^{13}C NMR (62 MHz, $CDCl_3$): δ = 15.4 (CH_3), 28.6 (CH_2), 109.5, 114.5 (CBr), 125.1 (CH), 125.5 (2CH), 128.6 (2CH), 130.2, 145.0, 145.6 (C). IR (KBr, cm^{-1}): *v* = 3019, 2964, 2871 (w), 1495, 1430 (m), 1412, 1317, 1301, 1276, 1121, 955, 833, 810 (s), 769 (m), 685, 580, 553 (w). GC-MS (EI, 70 eV): m/z (%) = 348(43) [M^+ ($^{8'}$Br, $^{8'}$Br)], 346(82) [M^+ ($^{8'}$Br, Br)], 344(41) [M^+ (Br, Br)], 333(54), 331(100) [M^+], 329(50), 171(24), 85(11). HRMS (EI, 70 eV): calcd for $C_{12}H_{10}Br_2S$ [M^+ (Br, $^{8'}$Br)]: 345.88440; found: 345.88445.

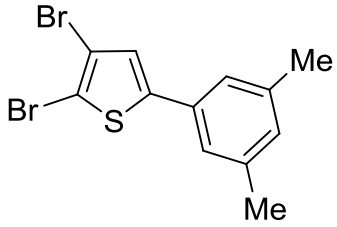
2,3-Dibromo-5-(4-*tert*-butylphenyl)thiophene (2c):



Starting with **1** (0.159 g, 0.5 mmol)) and 4-*tert*- butylphenyl boronic acid (0.098 g, 0.55 mmol), **2c** was isolated (0.096 g, 51%) as whitish semi solid. ^{1}H NMR (250 MHz, $CDCl_3$): δ = 1.26 (s, 9H, $3CH_3$), 6.98 (s, 1H, $CH_{thiophene}$), 7.34 (br, 4H, ArH). ^{13}C NMR (62 MHz, $CDCl_3$): δ = 31.2 ($3CH_3$), 34.7 (C), 109.5, 114.4 (CBr), 125.1 (CH), 125.2 (2CH), 126.1 (2CH), 129.9, 145.5, 151.9 (C). IR (KBr, cm^{-1}): *v* = 2958 (m), 2901, 2864, 1561, 1533 (w), 1497, 1460, 1432, 1408, 1362, 1306, 1267,

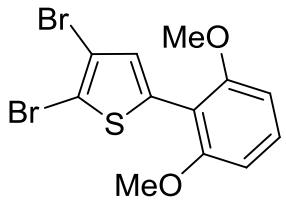
1200, 1109, 1016, 994, 834 (m), 810 (s), 731, 677 (m), 636, 610, 581 (w), 564 (s). GC-MS (EI, 70 eV): m/z (%) = 376(24) [M^+ ($^{8'}$Br, $^{8'}$Br)], 374(40) [M^+ ($^{8'}$Br, Br)], 372(21) [M^+ (Br, Br)], 361(54), 359(100) [M^+], 357(51), 331(16), 165(12). HRMS (EI, 70 eV): calcd for $C_{14}H_{14}Br_2S$ [M^+ (Br, $^{8'}$Br)]: 373.91570; found: 373.91523.

2,3-Dibromo-5-(3,5-dimethylphenyl)thiophene (2d):



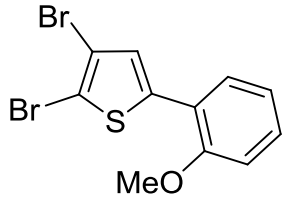
Starting with **1** (0.159 g, 0.5 mmol) and 3,5-dimethylphenyl boronic acid (0.083 g, 0.55 mmol), **2d** was isolated (0.069 g, 40%) as whitish semi solid. ^{1}H NMR (300 MHz, $CDCl_3$): δ = 2.25 (s, 6H, $2CH_3$), 6.88 (br, 1H, ArH), 6.98 (br, 1H, $CH_{thiophene}$), 7.01 (br, 2H, ArH). ^{13}C NMR (75 MHz, $CDCl_3$): δ = 21.3 ($2CH_3$), 109.7, 114.4 (CBr), 123.3 (2CH), 125.3, 130.3 (CH), 132.6 (C), 138.8 (2C), 145.7 (C). IR (KBr, cm^{-1}): ν = 3109 (w), 2919 (m), 2845 (w), 1602, 1464, 1305 (m), 1264, 1124, 1037 (w), 883, 844, 821 (s), 732 (m), 698 (s), 687 (m), 641, 568, 543 (w). GC-MS (EI, 70 eV): m/z (%) = 348(52) [M^+ ($^{8'}$Br, $^{8'}$Br)], 346(100) [M^+ (Br, $^{8'}$Br)], 344(49) [M^+ (Br, Br)], 171(14). HRMS (EI, 70 eV): calcd for $C_{12}H_{10}Br_2S$ [M^+ (Br, $^{8'}$Br)]: 346.88440; found: 346.88431.

2,3-Dibromo-5-(2,6-dimethoxyphenyl)thiophene (2e):



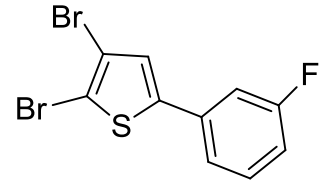
Starting with **1** (0.159 g, 0.5 mmol) and 2,6-dimethoxyphenylboronic acid (0.100 g, 0.55 mmol), **2e** was isolated (0.083 g, 44%) as a colorless oil. ^{1}H NMR (300 MHz, $CDCl_3$): δ = 3.80 (s, 6H, $2OCH_3$), 6.56 (d, 2H, J = 8.4 Hz, ArH), 7.14-7.19 (m, 1H, ArH), 7.35 (s, 1H, $CH_{thiophene}$). ^{13}C NMR (75 MHz, $CDCl_3$): δ = 55.9 ($2OCH_3$), 104.4 (2CH), 110.8 (C), 111.1, 112.7 (CBr), 129.3, 130.9 (CH), 136.0 (C), 157.5 (2C). IR (KBr, cm^{-1}): ν = 2999, 2931, 2833 (w), 1584 (m), 1469 (s), 1435, 1425 (w), 1312, 1292 (w), 1248 (s), 1206, 1192, 1151 (w), 1109 (s), 1037, 998, 947, 822, 813, 772 (m), 715 (s), 693, 684, 574, 539 (m). GC-MS (EI, 70 eV): m/z (%) = 380(52) [M^+ ($^{8'}$Br, $^{8'}$Br)], 378(100) [M^+ ($^{8'}$Br, Br)], 376(50) [M^+ (Br, Br)], 284(36), 282(37), 203(42), 149(11). HRMS (EI, 70 eV): calcd for $C_{12}H_{10}Br_2O_2S$ [M^+ (Br, $^{8'}$Br)]: 377.87423; found: 377.87420.

2,3-Dibromo-5-(2-methoxyphenyl)thiophene (2f):



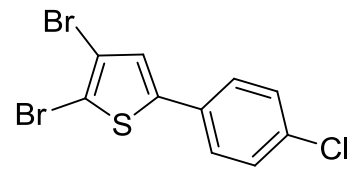
Starting with **1** (0.159 g, 0.5 mmol) and 2-methoxyphenylboronic acid (0.083 g, 0.55 mmol), **2f** was isolated (0.08 g, 46%) as a colorless oil. ^{1}H NMR (300 MHz, $CDCl_3$): δ = 3.85 (s, 3H, OCH_3), 6.88-6.94 (m, 2H, ArH), 7.17-7.24 (m, 2H, ArH and $CH_{thiophene}$), 7.47 (dd, 1H, J = 1.6, 7.8 Hz, ArH). ^{13}C NMR (62 MHz, $CDCl_3$): δ = 55.6 (OCH_3), 111.3 (CBr), 111.7 (CH), 113.5 (CBr), 121.0 (CH), 121.5 (C), 126.7, 127.1, 129.3 (CH), 140.5, 155.5 (C). IR (KBr, cm^{-1}): v = 3071, 2933, 2834, 1596, 1579 (w), 1519, 1483, 1455, 1433, 1323, 1293, 1270 (m), 1247 (s), 1178, 1159 (m), 1114 (s), 1052 (m), 1021 (s), 996, 818, 787 (m), 742 (s), 693, 582 (m). GC-MS (EI, 70 eV): m/z (%) = 350(51) [M^+ (^{81}Br, ^{81}Br)], 348(100) [M^+ (^{81}Br, Br)], 346(39) [M^+ (Br, Br)], 254(54), 252(53), 173(36), 145(25). HRMS (EI, 70 eV): calcd for $C_{11}H_8Br_2NOS$ [M^+ (Br, ^{81}Br)]: 347.86367; found: 347.86378.

2,3-Dibromo-5-(3-fluorophenyl)thiophene (2g):



Starting with **1** (0.159 g, 0.5 mmol) and 3-fluorophenyl boronic acid (0.077 g, 0.55 mmol), **2g** was isolated (0.067 g, 40%) as a white solid, mp. = 65-67 °C. ^{1}H NMR (300 MHz, $CDCl_3$): δ = 6.91-6.98 (m, 1H, ArH), 7.03 (s, 1H, $CH_{thiophene}$), 7.07-7.12 (m, 1H, ArH), 7.15-7.19 (m, 1H, ArH), 7.23-7.31 (m, 1H, ArH). ^{13}C NMR (62 MHz, $CDCl_3$): δ = 110.9 (CBr), 112.4 (d, $J_{F,C}$ = 23.1 Hz, CH), 114.8 (CBr), 115.4 (d, $J_{F,C}$ = 21.4 Hz, CH), 121.2 (d, $J_{F,C}$ = 3.0 Hz, CH), 126.3 (CH), 130.7 (d, $J_{F,C}$ = 8.7 Hz, CH), 134.6 (d, $J_{F,C}$ = 8.2 Hz, C), 143.8 (d, $J_{F,C}$ = 2.7 Hz, C), 163.1 (d, $J_{F,C}$ = 245.8 Hz, CF). ^{19}F NMR (282 MHz, $CDCl_3$): δ = -111.9 (ArF). IR (KBr, cm^{-1}): v = 2920, 2850, 1608, 1583, 1484, 1462, 1443, 1247, 1180, 1156, 1005, 985, 854, 821, 808 (m), 776, 673 (s), 607, 570 (m). GC-MS (EI, 70 eV): m/z (%) = 338(52) [M^+ (^{81}Br)], 336(100) [M^+ (Br)], 176(58), 132(15), 88(15). HRMS (EI, 70 eV): calcd for $C_{10}H_5Br_2FS$ [M^+ (Br)]: 335.84368; found: 335.84340.

2,3-Dibromo-5-(4-chlorophenyl)thiophene (2h):



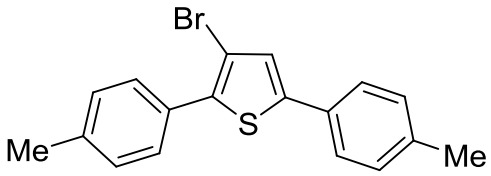
Starting with **1** (0.159 g, 0.5 mmol) and 4-chlorophenylboronic acid (0.086 g, 0.55 mmol), **2h** was isolated (0.079 g, 45%) as a white semi solid. ^{1}H NMR (300 MHz, $CDCl_3$): δ = 7.15 (s, 1H, $CH_{thiophene}$), 7.27-7.31 (m, 1H, ArH), 7.33 (dd, 1H, J = 2.1,

6.6 Hz, ArH), 7.41 (dd, 1H, J = 2.1, 6.6 Hz, ArH), 7.54 (dd, 1H, J = 2.0, 6.6 Hz, ArH). ^{13}C NMR (62 MHz, $CDCl_3$): δ = 110.5, 114.8 (CBr), 125.9 (CH), 126.6 (2CH), 129.3 (2CH), 131.2, 134.5, 144.0 (C). IR (KBr, cm^{-1}): ν = 3119, 2945, 2692 (w), 1479, 1454 (m), 1402, 1374, 1349 (w), 1317 (m), 1266, 1212, 1180, 1134 (w), 1086, 1006, 945 (m), 829, 821, 767 (s), 755, 735, 717, 700, 602, 574, 529 (m). GC-MS (EI, 70 eV): m/z (%) = 356(14) [M^+ (^{81}Br, ^{81}Br,^{37}Cl)], 354(69) [M^+ (^{81}Br, ^{81}Br, Cl); (Br, ^{81}Br,^{37}Cl)], 352(100) [M^+ (Br, ^{81}Br,^{35}Cl); (Br, Br,^{37}Cl)], 350(36) [M^+ (Br, Br, Cl)], 194(17), 192(51), 113(11). HRMS (EI, 70 eV): calcd for $C_{10}H_5Br_2ClS$ [M^+ (Br, ^{81}Br, Cl)]: 351.81413; found: 351.81418; [M^+ (Br, Br, ^{37}Cl)]: 351.81323; found: 351.81418.

Synthesis of 2,5-diaryl-3-bromothiophes (3):

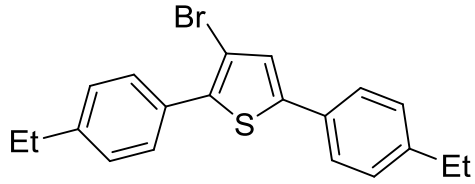
To a mixture of **1** (0.159 g, 0.5 mmol), aryl boronic acid (1.1 mmol), and $Pd(PPh_3)_4$ (29 mg, 5 mol-%) was added a mixture of 1,4-dioxane and toluene (1:1; 5 mL) and K_3PO_4 (4.0 equiv, 424 mg) under an argon atmosphere. The reaction mixture was stirred at 100 °C for 12 h and was subsequently allowed to cool to 20 °C. The solution was poured into H_2O and EtOAc (25 mL each) and the organic and the aqueous layers were separated. The latter was extracted with EtOAc (3 × 25 mL), dried (Na_2SO_4), filtered, and concentrated in vacuo. The residue was purified by flash column chromatography (flash silica gel, eluent: *n*-heptane/EtOAc).

3-Bromo-2,5-di-*p*-tolylthiophene (3a):



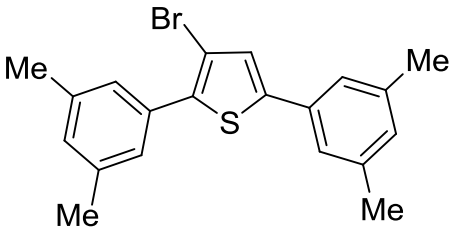
Starting with **1** (0.159 g, 0.5 mmol) and 4-methyl phenyl boronic acid (0.149 g, 1.1 mmol), **3a** was isolated (0.094 g, 55%) as yellowish solid, mp. = 101-103 °C. ^{1}H NMR (300 MHz, $CDCl_3$): δ = 2.29 (s, 3H, CH_3), 2.32 (s, 3H, CH_3), 7.10-7.13 (m, 3H, ArH and $CH_{thiophene}$), 7.16 (d, 2H, J = 8.0 Hz, ArH), 7.38 (d, 2H, J = 8.1 Hz, ArH), 7.50 (d, 2H, J = 8.1 Hz, ArH). ^{13}C NMR (62 MHz, $CDCl_3$): δ = 21.2, 21.3 (CH_3), 107.5 (CBr), 125.4 (2CH), 126.7 (C), 126.8 (CH), 128.7 (2CH), 129.3 (2CH), 129.7 (2CH), 130.0, 130.5, 138.1, 138.2, 143.0 (C). IR (KBr, cm^{-1}): ν = 3020, 2916, 1494, 1453, 1326, 1307,1186, 1112, 1019, 971, 943, 830 (w), 806 (s), 712, 697, 638, 624 (w), 609 (m), 566, 557 (w). GC-MS (EI, 70 eV): m/z (%) = 344(100) [M^+ (^{81}Br)], 342(98) [M^+ (Br)], 248(11). HRMS (EI, 70 eV): calcd for $C_{18}H_{15}BrS$ [(^{81}Br)]: 344.00519; found: 344.00415.

3-Bromo-2,5-bis(4-ethylphenyl)thiophene (3b):



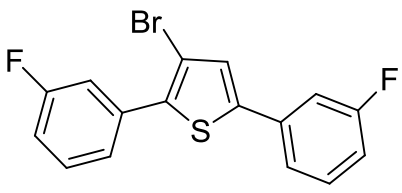
Starting with **1** (0.159 g, 0.5 mmol) and 4-ethyl phenylboronic acid (0.165 g, 1.1 mmol), **3b** was isolated (0.124 g, 67%) as a colorless solid, mp. = 49-50 °C. ^{1}H NMR (300 MHz, $CDCl_3$): δ = 1.17 (t, 3H, *J* = 7.6 Hz, CH_3), 1.19 (t, 3H, *J* = 7.6 Hz, CH_3), 2.59 (q, 2H, *J* = 7.6 Hz, CH_2), 2.61 (q, 2H, *J* = 7.6 Hz, CH_2), 7.12-7.15 (m, 3H, ArH and $CH_{thiophene}$), 7.18 (d, 2H, *J* = 8.3 Hz, ArH), 7.40 (dd, 2H, *J* = 1.8, 6.4 Hz, ArH), 7.53 (dd, 2H, *J* = 1.8, 6.4 Hz, ArH). ^{13}C NMR (62 MHz, $CDCl_3$): δ = 15.4, 15.5 (CH_3), 28.6, 28.7 (CH_2), 107.5 (CBr), 125.5 (2CH), 126.9 (CH), 128.0 (2CH), 128.5 (2CH), 128.8 (2CH), 130.3, 130.7, 136.9, 143.0, 144.4, 144.5 (C). IR (KBr, cm^{-1}): *v* = 3020, 2963, 2929 (w), 1495, 1453 (m),1411, 1324, 1185, 1117, 1050, 1019, 973 (w), 840 (m), 814 (s), 771, 609, 531 (m). GC-MS (EI, 70 eV): m/z (%) = 372(100) [M^+ (^{81}Br)], 370(99) [M^+ (Br)], 357(64), 355(64), 342(18), 340(17), 130(10). HRMS (EI, 70 eV): calcd for $C_{20}H_{19}BrS$ [M^+ (^{81}Br)]: 372.03649; found: 372.03628.

3-Bromo-2,5-bis(3,5-dimethylphenyl)thiophene (3c):



Starting with **1** (0.159 g, 0.5 mmol) and 3,5-dimethyl phenyl boronic acid (0.165 g, 1.1 mmol), **3c** was isolated (0.091 g, 49%) as a brown oil. ^{1}H NMR (250 MHz, $CDCl_3$): δ = 2.28 (s, 12H, $4CH_3$), 6.88 (br, 2H, ArH and $CH_{thiophene}$), 7.10 (br, 5H, ArH). ^{13}C NMR (62 MHz, $CDCl_3$): δ = 21.4 ($4CH_3$), 107.5 (CBr), 125.1 (5CH), 128.7 (2CH), 138.1 (6C), 141.5 (2C). IR (KBr, cm^{-1}): *v* = 3087, 2913, 2854 (w), 1596, 1454 (m), 1373 (w), 1321 (m), 1286, 1155, 1034, 993, 885 (w), 836, 816 (s), 775, 679, 666, 593 (m), 543 (w). GC-MS (EI, 70 eV): m/z (%) = 372(100) [M^+ (^{81}Br)], 370(92) [M^+ (Br)]. HRMS (EI, 70 eV): calcd for $C_{20}H_{19}BrS$ [(^{81}Br)]: 372.03649; found: 372.03657.

3-Bromo-2,5-bis(3-fluorophenyl)thiophene (3d):



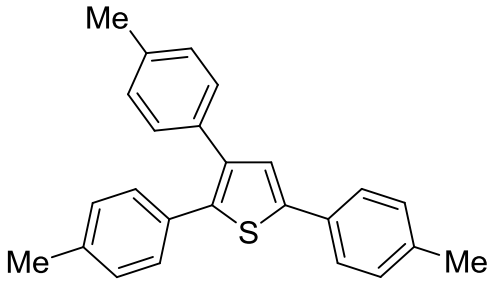
Starting with **1** (0.159 g, 0.5 mmol) and 3-fluorophenyl boronic acid (0.154 g, 1.1 mmol), **3d** was isolated (0.079 g, 45%) as a white solid, mp. = 54-56 °C. ^{1}H NMR (300 MHz, $CDCl_3$): δ = 6.90-7.04 (m, 2H, ArH), 7.18 (s, 1H,

$CH_{thiophene}$), 7.24-7.40 (m, 6H, ArH). ^{13}C NMR (62 MHz, $CDCl_3$): δ = 108.6 (CBr), 112.5 (d, $J_{F,C}$ = 23.0 Hz, CH), 115.2 (d, $J_{F,C}$ = 21.3 Hz, CH), 115.4 (d, $J_{F,C}$ = 21.2 Hz, CH), 115.7 (d, $J_{F,C}$ = 23.0 Hz, CH), 121.1 (d, $J_{F,C}$ = 3.0 Hz, CH), 124.5 (d, $J_{F,C}$ = 3.1 Hz, CH), 128.2 (CH), 130.2 (d, $J_{F,C}$ = 8.6 Hz, CH), 130.7 (d, $J_{F,C}$ = 8.6 Hz, CH), 134.5 (d, $J_{F,C}$ = 8.5 Hz, C), 135.0 (d, $J_{F,C}$ = 8.1 Hz, C), 136.4 (d, $J_{F,C}$ = 2.5 Hz, C), 142.2 (d, $J_{F,C}$ = 2.8 Hz, C), 162.6 (d, $J_{F,C}$ = 246.9 Hz, CF), 163.1 (d, $J_{F,C}$ = 246.9 Hz, CF). ^{19}F NMR (282 MHz, $CDCl_3$): δ = -112.2, -112.1 (ArF). IR (KBr, cm^{-1}): ν = 1608 (m), 1581 (s), 1483, 1470, 1436, 1262, 1247, 1174 (m), 1156 (s), 1141, 1075, 1015, 993, 872, 839, 825, 817 (m), 781, 770 (s), 703, 684 (m), 674 (s), 625, 606 (m). GC-MS (EI, 70 eV): m/z (%) = 352(100) [M^+ (^{81}Br)], 350(97) [M^+ (Br)], 270(25), 238(14), 227(15), 139(18). HRMS (EI, 70 eV): calcd for $C_{16}H_9BrF_2S$ [M^+ (^{81}Br)]: 351.95504; found: 351.95582.

Synthesis of 2,3,5-triarylthiophenes (4):

To a mixture of **1** (0.080 g, 0.25 mmol), arylboronic acid (1.0 mmol), $Pd(PPh_3)_4$ (57 mg, 10 mol-%) were added a mixture of 1,4-dioxane and toluene (1:1, 5 mL) and an aq solution of K_2CO_3 (2 mL, 2 M) under argon atmosphere. The reaction mixture was stirred at 90 °C for 8 h and was subsequently allowed to cool to 20 °C. The solution was poured into H_2O and CH_2Cl_2 (25 mL each) and the organic and the aqueous layer were separated. The latter was extracted with CH_2Cl_2 (3 × 25 mL), dried (Na_2SO_4), filtered, and concentrated in vacuo. The residue was purified by flash column chromatography (flash silica gel, *n*-heptane).

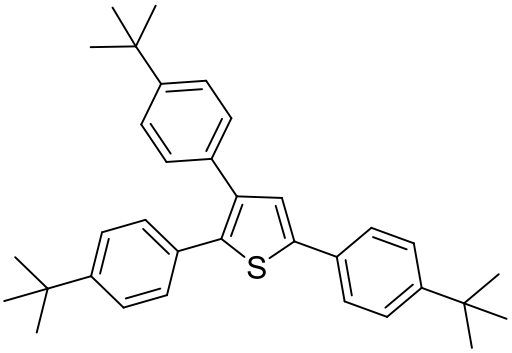
2,3,5-Tri-*p*-tolylthiophene (4a):



Starting with **1** (0.080 g, 0.25 mmol) and 4-methyl phenylboronic acid (0.136 g, 1.0 mmol), **4a** was isolated (0.081 g, 92%) as colorless solid, mp. = 125-126 °C. ^1H NMR (300 MHz, $CDCl_3$): δ = 2.38 (s, 3H, CH_3), 2.39 (s, 3H, CH_3), 2.41 (s, 3H, CH_3), 7.10-7.17 (m, 4H, ArH), 7.22-7.29 (m, 6H, ArH), 7.34 (s, 1H, $CH_{thiophene}$), 7.44 (dd, 2H, J = 1.7, 6.4 Hz, ArH). ^{13}C NMR (62 MHz, $CDCl_3$): δ = 21.2 ($3CH_3$), 125.5 (2CH), 126.1 (CH), 128.9 (2CH), 129.0 (2CH), 129.1 (2CH), 129.2 (2CH), 129.6 (2CH), 131.5, 131.4, 133.9, 136.5, 137.1, 137.2, 137.4, 138.5, 142.2 (C). IR (KBr, cm^{-1}): ν = 3023, 2915, 2855, 1512, 1497, 1443, 1309, 1183, 1118, 1035, 1017, 972,

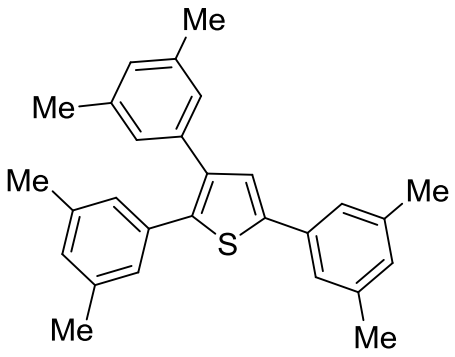
943, 848 (w), 819 (m), 806 (s), 781 (m), 715, 673, 576, 565 (w), 539 (m). GC-MS (EI, 70 eV): m/z (%) = 354(100) [M^+]. HRMS (EI, 70 eV): calcd for $C_{25}H_{22}S$ [M^+]: 354.14367; found: 354.14372.

2,3,5-Tris(4-*tert*-butylphenyl)thiophene (4b):



Starting with **1** (0.08 g, 0.25 mmol) and 4-*tert*-butylphenylboronic acid (0.178 g, 1.0 mmol), **4b** was isolated (0.104 g, 87%) as a white solid, mp. = 166-168 °C. ^{1}H NMR (300 MHz, $CDCl_3$): δ = 1.24 (s, 9H, $3CH_3$), 1.26 (s, 9H, $3CH_3$), 1.27 (s, 9H, $3CH_3$), 7.20 (br, 4H, ArH), 7.21-7.23 (m, 5H, ArH and $CH_{thiophene}$), 7.32 (d, 2H, J = 8.5 Hz, ArH), 7.44 (d, 2H, J = 8.3 Hz, ArH). ^{13}C NMR (62 MHz, $CDCl_3$): δ = 31.3 ($6CH_3$), 31.4 ($3CH_3$), 34.5, 34.6, 34.7 (C), 125.2 (2CH), 125.3 (4CH), 125.8 (2CH), 126.4 (CH), 128.5 (2CH), 128.6 (2CH), 131.5 (2C), 133.9, 137.3, 138.4, 141.9, 149.7, 150.2, 150.6 (C). IR (KBr, cm^{-1}): ν = 2957, 2949 (m), 2900, 2863, 1512, 1496, 1460, 1392 (w), 1360, 1267 (m), 1245, 1201, 1109, 1017, 977, 869 (w), 821 (s), 735, 719, 682, 670 (w), 568, 555, 540, 531 (m). GC-MS (EI, 70 eV): m/z (%) = 480(100) [M^+], 466(12), 465(48). HRMS (EI, 70 eV): calcd for $C_{34}H_{40}S$ [M^+]: 480.28452; found: 480.28478.

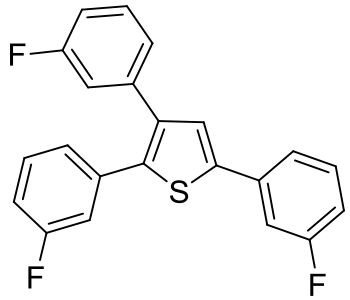
2,3,5-Tris(3,5-dimethylphenyl)thiophene (4c):



Starting with **1** (0.08 g, 0.25 mmol) and 3,5-dimethyl phenylboronic acid (0.150 g, 1.0 mmol), **4c** was isolated (0.077 g, 78%) as a white solid, mp. = 137-139 °C. ^{1}H NMR (300 MHz, $CDCl_3$): δ = 2.15 (s, 6H, $2CH_3$), 2.18 (s, 6H, $2CH_3$), 2.28 (s, 6H, $2CH_3$), 6.79 (br, 1H, ArH), 6.82 (br, 1H, ArH), 6.85 (br, 1H, ArH), 6.89 (br, 4H, ArH), 6.19 (br, 2H, ArH), 7.23 (s, 1H, $CH_{thiophene}$). ^{13}C NMR (62 MHz, $CDCl_3$): δ = 21.1 ($2CH_3$), 21.2 ($2CH_3$), 21.3 ($2CH_3$), 123.5 (2CH), 126.4 (CH), 126.7 (2CH), 126.8 (2CH), 128.5, 128.9, 129.2 (CH), 134.1, 134.2, 136.6 (C), 137.6 (2C), 137.7 (3C), 138.4 (2C), 138.8, 142.2 (C). IR (KBr, cm^{-1}): ν = 2918 (m), 2859 (w), 1599 (m), 1458, 1369, 1261, 1088 (w), 846 (s), 799, 755, 705, 687 (m), 666 (w). GC-MS (EI,

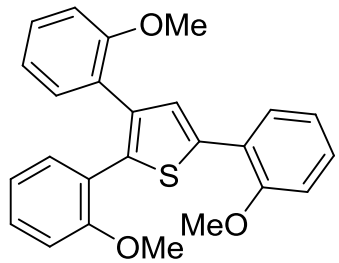
70 eV): m/z (%) = 396(100) [M^+]. HRMS (EI, 70 eV): calcd for $C_{28}H_{28}S$ [M^+]: 396.19062; found: 396.19064.

2,3,5-Tris(3-fluorophenyl)thiophene (4d):



Starting with **1** (0.080 g, 0.25 mmol) and 3-fluorophenyl boronic acid (0.140 g, 1.0 mmol), **4d** was isolated (0.069 g, 76%) as a colorless oil. ^{1}H NMR (300 MHz, $CDCl_3$): δ = 6.85-7.01 (m, 7H, ArH), 7.11-7.32 (m, 6H, ArH and $CH_{thiophene}$). ^{13}C NMR (75 MHz, $CDCl_3$): δ = 112.5 (d, $J_{F,C}$ = 22.9 Hz, CH), 114.3 (d, $J_{F,C}$ = 21.0 Hz, CH), 114.7 (d, $J_{F,C}$ = 21.1 Hz, CH), 114.8 (d, $J_{F,C}$ = 21.1 Hz, CH), 115.4 (d, $J_{F,C}$ = 21.8 Hz, CH), 115.5 (d, $J_{F,C}$ = 22.4 Hz, CH), 121.3 (d, $J_{F,C}$ = 2.9 Hz, CH), 124.8 (d, $J_{F,C}$ = 2.8 Hz, CH), 124.9 (d, $J_{F,C}$ = 2.8 Hz, CH), 126.9 (CH), 130.1 (d, $J_{F,C}$ = 8.4 Hz, CH), 130.2 (d, $J_{F,C}$ = 8.5 Hz, CH), 130.6 (d, $J_{F,C}$ = 8.6 Hz, CH), 135.6 (d, $J_{F,C}$ = 8.3 Hz, C), 135.8 (d, $J_{F,C}$ = 8.3 Hz, C), 137.6 (d, $J_{F,C}$ = 2.4 Hz, C), 138.1 (d, $J_{F,C}$ = 7.9 Hz, C), 138.4 (d, $J_{F,C}$ = 2.2 Hz, C), 142.0 (d, $J_{F,C}$ = 2.7 Hz, C), 162.7 (d, $J_{F,C}$ = 246.9 Hz, CF), 162.8 (d, $J_{F,C}$ = 246.3 Hz, CF), 163.6 (d, $J_{F,C}$ = 246.3 Hz, CF). IR (KBr, cm^{-1}): ν = 3069, 2925, 2853 (w), 1607, 1580 (s), 1474, 1439 (m), 1370 (w), 1266, 1257, 1185, 1170 (m), 1154 (s), 1076, 941, 873, 844, 831 (m), 776 (s), 693, 679 (m), 613 (w). GC-MS (EI, 70 eV): m/z (%) = 366(100) [M^+]. HRMS (EI, 70 eV): calcd for $C_{22}H_{13}F_3S$ [M^+]: 366.06846; found: 366.06837.

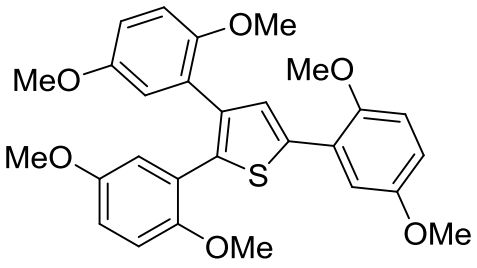
2,3,5-Tris(2-methoxyphenyl)thiophene (4e):



Starting with **1** (0.080 g, 0.25 mmol) and 2-methoxyphenyl boronic acid (0.152 g, 1.0 mmol), **4e** was isolated (0.081 g, 81%) as a white solid, mp. = 121-123 °C. ^{1}H NMR (300 MHz, $CDCl_3$): δ = 3.40 (s, 3H, OCH_3), 3.48 (s, 3H, OCH_3), 3.80 (s, 3H, OCH_3), 6.69-6.76 (m, 4H, ArH), 6.85-6.91 (m, 2H, ArH), 7.02 (dd, 1H, J = 1.5, 7.5 Hz, ArH). 7.01-7.17 (m, 4H, ArH), 7.50 (s, 1H, $CH_{thiophene}$), 7.59 (dd, 1H, J = 1.7, 7.6 Hz, ArH). ^{13}C NMR (62 MHz, $CDCl_3$): δ = 55.2, 55.3, 55.6 (OCH_3), 111.0, 111.2, 111.7, 120.3, 120.4, 120.9 (CH), 123.7, 124.4, 127.2 (C), 128.0, 128.1, 128.3, 128.7, 128.9, 131.0, 131.7 (CH), 135.7, 135.9, 137.5, 155.8, 156.5, 156.6 (C). IR (KBr, cm^{-1}): ν = 2998, 2930, 2833 (w), 1609 (m), 1571, 1532 (w), 1520, 1509, 1494, 1454, 1436, 1286 (m), 1244, 1173 (s), 1104 (m), 1029 (s), 952, 902, 876 (w), 824, 812

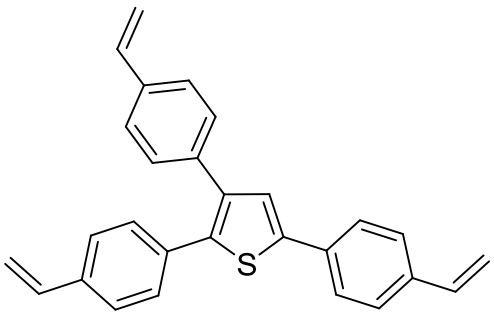
(s), 794, 785, 768, 750, 551 (m). GC-MS (EI, 70 eV): m/z (%) = 402(100) [M^+]. HRMS (EI, 70 eV): calcd for $C_{25}H_{22}O_3S$ [M^+]: 402.12842; found: 402.12834.

2,3,5-Tris(2,5-dimethoxyphenyl)thiophene (4f):



Starting with **1** (0.080 g, 0.25 mmol) and 2,5-dimethoxyphenylboronic acid (0.182 g, 1.0 mmol), **4f** was isolated (0.111 g, 91%) as a white solid, mp. = 138-140 °C. ^{1}H NMR (300 MHz, $CDCl_3$): δ = 3.45 (s, 3H, OCH_3), 3.49 (s, 3H, OCH_3), 3.53 (s, 3H, OCH_3), 3.54 (s, 3H, OCH_3), 3.74 (s, 3H, OCH_3), 3.81 (s, 3H, OCH_3), 6.65-6.75 (m, 7H, ArH), 6.84 (d, 1H, J = 8.9 Hz, ArH), 7.18 (s, 1H, $CH_{thiophene}$), 7.52 (s, 1H, ArH). ^{13}C NMR (62 MHz, $CDCl_3$): δ = 55.6, 55.7, 55.8, 56.0, 56.1, 56.6 (OCH_3), 112.5, 112.7, 113.1, 113.2, 113.5, 113.7, 114.3, 116.3, 116.6 (CH), 118.6, 120.7, 124.4, 124.9, 127.7 (C), 128.7 (CH), 135.8, 137.4, 150.2, 150.9, 153.2, 153.3, 153.7 (C). IR (KBr, cm^{-1}): ν = 2996, 2932, 2834 (w), 1606, 1573, 1494, 1452, 1413, 1304 (m), 1279, 1204, 1154 (s), 1124, 1091 (m), 1025 (s), 973, 908, 836, 825 (m), 811 (s), 792, 628, 566 (m). GC-MS (EI, 70 eV): m/z (%) = 492(100) [M^+], 446(11), 71(11), 57(17), 44(14). HRMS (EI, 70 eV): calcd for $C_{28}H_{28}O_6S$ [M^+]: 492.16011; found: 492.16048.

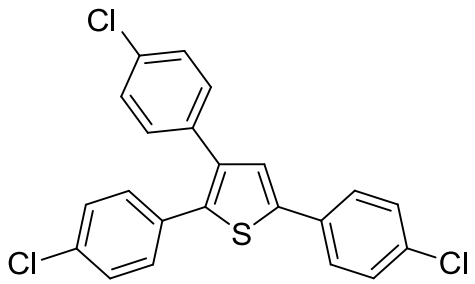
2,3,5-Tris(4-vinylphenyl)thiophene (4g):



Starting with **1** (0.080 g, 0.25 mmol) and 4-vinyl phenylboronic acid (0.148 g, 1.0 mmol), **4g** was isolated (0.086 g, 88%) as colorless solid, mp. = 156-158 °C. ^{1}H NMR (300 MHz, $CDCl_3$): δ = 5.15-5.21 (m, 3H, CH), 5.62-5.72 (m, 3H, CH), 6.55-6.69 (m, 3H, CH), 7.19-7.22 (m, 6H, ArH), 7.26-7.29 (m, 3H, ArH and $CH_{thiophene}$), 7.34 (d, 2H, J = 8.3 Hz, ArH), 7.51 (dd, 2H, J = 1.7, 6.7 Hz, ArH). ^{13}C NMR (62 MHz, $CDCl_3$): δ = 113.9, 114.0, 114.1 (CH_2), 125.6 (2CH), 126.3 (2CH), 126.4 (2CH), 126.5 (CH), 126.8 (2CH), 129.1 (2CH), 129.1 (2CH), 133.4, 133.6, 136.0 (C), 136.2, 136.3 (CH), 136.4 (C), 136.5 (CH), 136.7, 137.0, 137.8, 138.8, 142.3 (C). IR (KBr, cm^{-1}): ν = 1625, 1600, 1511, 1495, 1402, 1202, 1116 (w), 987, 899 (m), 824 (s), 703, 678, 563, 534 (m). GC-MS (EI, 70 eV): m/z

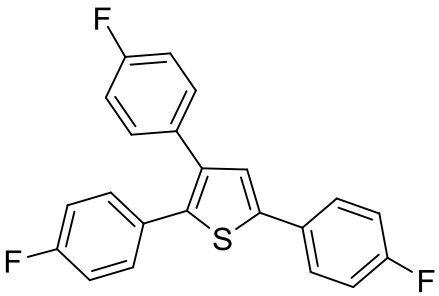
(%) = 390(100) [M^+], 173(13), 166(10). HRMS (EI, 70 eV): calcd for $C_{28}H_{22}S$ [M^+]: 390.14367; found: 390.14391.

2,3,5-Tris(4-chlorophenyl)thiophene (4h):



Starting with **1** (0.08 g, 1.0 mmol) and 4-chloro phenylboronic acid (0.156 g, 1.0 mmol), **4h** was isolated (0.074 g, 72%) as a brown oil. ^{1}H NMR (300 MHz, $CDCl_3$): δ = 7.12-7.15 (m, 4H, ArH), 7.17-7.22 (m, 5H, ArH and $CH_{thiophene}$), 7.28 (dd, 2H, J = 2.0, 6.7 Hz, ArH), 7.46 (dd, 2H, J = 2.1, 6.7 Hz, ArH). ^{13}C NMR (62 MHz, $CDCl_3$): δ = 126.5 (CH), 126.8 (2CH), 128.8 (2CH), 128.9 (2CH), 129.2 (2CH), 130.2 (2CH), 130.3 (2CH), 132.2, 132.2, 133.3, 133.7, 133.8, 134.5, 137.2, 138.2, 141.9 (C). IR (KBr, cm^{-1}): ν = 2921, 1905, 1546 (w), 1492, 1481 (m), 1454, 1395, 1303, 1247, 1210, 1114 (w), 1092, 1084, 1012 (m), 976, 952, 865, 852 (w), 833 (m), 816 (s), 738 (m), 715, 671, 628, 585, 565 (w). GC-MS (EI, 70 eV): m/z (%) = 420(6) [M^+ (^{37}Cl, ^{37}Cl, ^{37}Cl)], 418(38) [M^+ (Cl, ^{37}Cl, ^{37}Cl)], 416(96) [M^+ (Cl, Cl, ^{37}Cl)], 414(100) [M^+ (Cl, Cl, Cl)], 378(10), 346(11), 344(25), 308(13), 173(14), 172(29), 155(12), 154(19), 132(17). HRMS (EI, 70 eV): calcd for $C_{22}H_{13}Cl_3S$ [M^+ (Cl, Cl, ^{37}Cl)]: 415.97686 found: 415.97688.

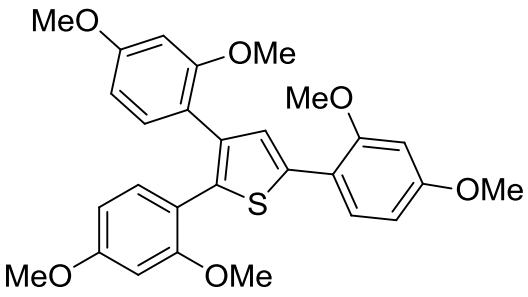
2,3,5-Tris(4-fluorophenyl)thiophene (4i):



Starting with **1** (0.080 g, 0.25 mmol) and 4-fluorophenyl boronic acid (0.140 g, 1.0 mmol), **4i** was isolated (0.077 g, 84%) as a colorless solid, mp. = 109-111 °C. ^{1}H NMR (300 MHz, $CDCl_3$): δ = 6.84-6.92 (m, 4H, ArH), 6.95-7.01 (m, 2H, ArH), 7.12-7.17 (m, 5H, ArH and $CH_{thiophene}$), 7.45-7.50 (m, 2H, ArH) . ^{13}C NMR (62 MHz, $CDCl_3$): δ = 115.5 (d, $J_{F,C}$ = 21.3 Hz, CH), 115.6 (d, $J_{F,C}$ = 21.3 Hz, CH), 116.0 (d, $J_{F,C}$ = 21.3 Hz, CH), 126.1 (CH), 127.3 (d, $J_{F,C}$ = 8.0 Hz, 3CH), 129.9 (d, $J_{F,C}$ = 3.5 Hz, C), 130.1 (d, $J_{F,C}$ = 3.5 Hz, C), 130.5 (d, $J_{F,C}$ = 8.0 Hz, 3CH), 130.8 (d, $J_{F,C}$ = 8.0 Hz, 3CH), 132.2 (d, $J_{F,C}$ = 3.4 Hz, C), 136.7, 138.0, 141.6 (C), 162.0 (d, $J_{F,C}$ = 246.9 Hz, CF), 162.3 (d, $J_{F,C}$ = 248.0 Hz, CF), 162.5 (d, $J_{F,C}$ = 247.7 Hz, CF). ^{19}F NMR (282 MHz, $CDCl_3$): δ = -113.8, -113.9, -114.7 (ArF). IR (KBr, cm^{-1}): ν = 2925, 2853 (w), 1610, 1580 (s), 1475, 1439 (m), 1370 (w), 1265, 1257, 1189, 1172 (m), 1150 (s), 1076, 941,

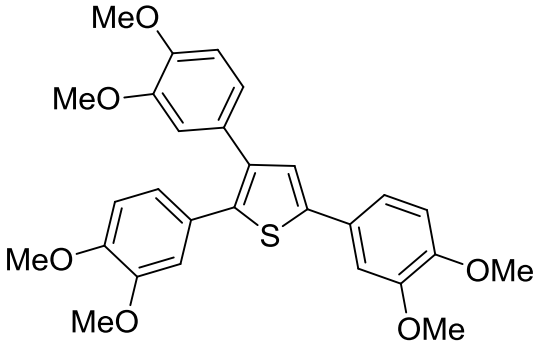
873, 844, 831 (m), 777 (s), 693, 679 (m), 613 (w). GC-MS (EI, 70 eV): m/z (%) = 366(100) [M^+]. HRMS (EI, 70 eV): calcd for $C_{22}H_{13}F_3S$ [M^+]: 366.06846; found: 366.06840.

2,3,5-Tris(2,4-dimethoxyphenyl)thiophene (4j):



Starting with **1** (0.080 g, 0.25 mmol) and 2,4-dimethoxyphenylboronic acid (0.182 g, 1.0 mmol), **4j** was isolated (0.115 g, 94%) as a violet oil, mp. = 125-126 °C. ^{1}H NMR (300 MHz, $CDCl_3$): δ = 3.48 (s, 3H, OCH_3), 3.54 (s, 3H, OCH_3), 3.71 (s, 6H, $2OCH_3$), 3.75 (s, 3H, OCH_3), 3.81 (s, 3H, OCH_3), 6.27-6.38 (m, 4H, ArH), 6.43-6.47 (m, 2H, ArH), 6.93 (d, 1H, J = 8.3 Hz, ArH), 7.04 (d, 1H, J = 8.0 Hz, ArH), 7.34 (s, 1H, $CH_{thiophene}$), 7.43 (d, 1H, J = 9.0 Hz, ArH). ^{13}C NMR (62 MHz, $CDCl_3$): δ = 55.2 ($2OCH_3$), 55.3 ($2OCH_3$), 55.4, 55.5 (OCH_3), 98.8 (2CH), 104.1 (2CH), 104.3, 105.0 (CH), 117.0, 117.3 (C), 120.1 (2C), 127.8, 129.1, 131.4, 132.2 (CH), 135.1 (2C), 156.8 (C), 157.6 (2C), 159.7 (3C). IR (KBr, cm^{-1}): ν = 2996, 2932, 2834 (w), 1606, 1573, 1494, 1452, 1413, 1304 (m), 1279, 1204, 1154 (s), 1124, 1091 (m), 1025 (s), 973, 908, 836, 825 (m), 811 (s), 792, 628, 566 (m). GC-MS (EI, 70 eV): m/z (%) = 492(100) [M^+], 477(11), 246(13), 151(17). HRMS (EI, 70 eV): calcd for $C_{28}H_{28}O_6S$ [M^+]: 492.16011; found: 492.16065.

2,3,5-Tris(3,4-dimethoxyphenyl)thiophene (4k):

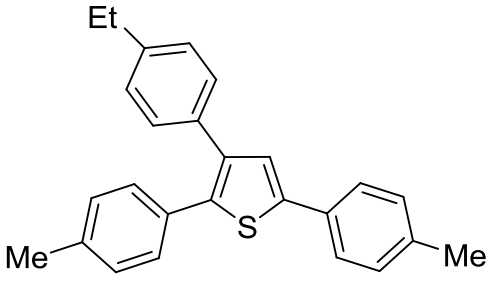


Starting with **1** (0.080 g, 0.25 mmol) and 3,4-dimethoxyphenylboronic acid (0.182 g, 1.0 mmol) , **4k** was isolated (0.108 g, 88%) as a pink semi solid. ^{1}H NMR (300 MHz, $CDCl_3$): δ = 3.45 (s, 3H, OCH_3), 3.49 (s, 3H, OCH_3), 3.53 (s, 3H, OCH_3), 3.54 (s, 3H, OCH_3), 3.74 (s, 3H, OCH_3), 3.81 (s, 3H, OCH_3), 6.65-6.66 (m, 1H, ArH), 6.67-6.72 (m, 4H, ArH), 6.73-6.75 (m, 2H, ArH), 6.84 (d, 1H, J = 8.9 Hz, ArH), 7.18 (s, 1H, $CH_{thiophene}$), 7.52 (s, 1H, ArH). ^{13}C NMR (75 MHz, $CDCl_3$): δ = 55.7, 55.8, 55.9, 55.9, 56.0, 56.0 (OCH_3), 109.1, 1121.1, 111.2, 111.6, 112.4, 112.5, 118.3, 121.4, 121.5, 125.5 (CH), 127.1, 127.3, 129.6, 136.5, 138.1, 141.8, 148.1, 148.5, 148.6, 148.7, 148.9, 148.3 (C). IR (KBr, cm^{-1}): ν = 2993, 2929, 2834 (w), 1610, 1576, 1494, 1452, 1412, 1307 (m), 1281, 1204,

1154 (s), 1122, 1090 (m), 1027 (s), 978, 908, 835, 825 (m), 812 (s), 792, 629, 564 (m). MS (EI, 70 eV): m/z (%) = 492(100) [M^+], 477(16), 181(10), 169(10), 131(12), 119(11), 71(10), 69(48), 57(16), 55(13), 44(30), 41(12). HRMS (EI, 70 eV): calcd for $C_{28}H_{28}O_6S$ [M^+]: 492.16011; found: 492.16075.

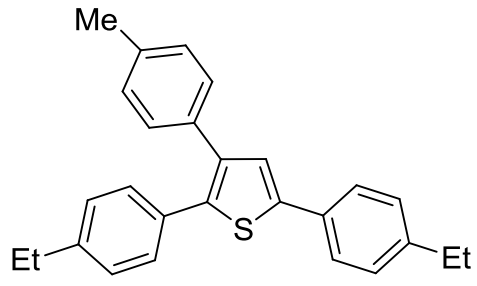
Synthesis of unsymmetrical 2,3,5-triarylbromothiophes (5):

3-(4-Ethylphenyl)-2,5-di-*p*-tolylthiophene (5a):



Starting with **3a** (0.086 g, 0.25 mmol) and 4-ethylphenylboronic acid (0.075 g, 0.5 mmol), **5a** was isolated (0.084 g, 92%) as yellowish semi solid. ^{1}H NMR (2500 MHz, $CDCl_3$): δ = 1.16 (t, 3H, *J* = 7.6 Hz, CH_3), 2.24 (s, 3H, CH_3), 2.28 (s, 3H, CH_3), 2.56 (q, 2H, *J* = 7.6 Hz, CH_2), 2.59 (q, 2H, *J* = 7.6 Hz, CH_2), 6.96-7.08 (m, 4H, ArH), 7.11-7.18 (m, 6H, ArH), 7.21 (s, 1H, $CH_{thiophene}$), 7.44 (d, 2H, *J* = 8.1 Hz, ArH). ^{13}C NMR (62 MHz, $CDCl_3$): δ = 15.4 (CH_3), 21.2 ($2CH_3$), 28.6 (CH_2), 125.5 (2CH), 126.1 (CH), 127.9 (2CH), 128.9 (2CH), 129.0 (2CH), 129.2 (2CH), 129.6 (2CH), 131.5, 131.6, 134.1, 137.1, 137.3, 137.4, 138.5, 142.2, 142.9 (C). IR (KBr, cm^{-1}): *ν* = 2963, 2916, 2852, 1512, 1497, 1455, 1184, 1120, 1016, 971 (w), 832, 819 (m), 809 (s), 769, 730, 717, 675, 634, 585, 540 (w). GC-MS (EI, 70 eV): m/z (%) = 368(100) [M^+], 353(15). HRMS (EI, 70 eV): calcd for $C_{26}H_{24}S$ [M^+]: 368.15932; found: 368.15939.

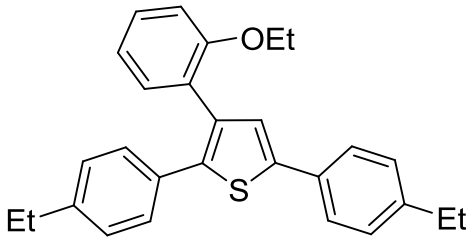
2,5-Bis(4-ethylphenyl)-3-*p*-tolylthiophene (5b)



Starting with **3b** (0.093 g, 0.25 mmol) and 4-methyl phenylboronic acid (0.068 g, 0.5 mmol), **5b** was isolated (0.083 g, 87%) as a brown semi solid. ^{1}H NMR (300 MHz, $CDCl_3$): δ = 1.16 (t, 3H, *J* = 7.7 Hz, CH_3), 1.19 (t, 3H, *J* = 7.7 Hz, CH_3), 2.28 (s, 3H, CH_3), 2.56 (q, 2H, *J* = 7.6 Hz, CH_2), 2.59 (q, 2H, *J* = 7.6 Hz, CH_2), 7.01-7.05 (m, 4H, ArH), 7.13-7.19 (m, 6H, ArH), 7.21 (s, 1H, $CH_{thiophene}$), 7.48 (d, 2H, *J* = 8.1 Hz, ArH). ^{13}C NMR (75 MHz, $CDCl_3$): δ = 15.3, 15.5, 21.2 (CH_3), 28.5, 28.6 (CH_2), 125.6 (2CH), 126.1 (CH), 127.9 (2CH), 128.4 (2CH), 128.9 (2CH), 129.0 (2CH), 129.1 (2CH), 131.8 (2C), 133.9, 136.5, 137.3, 138.5, 142.2, 143.4, 143.8 (C). IR (KBr, cm^{-1}): *ν* =

3022, 2961, 2920, 2852, 1513, 1497, 1453, 1182, 1117, 1019, 979 (w), 825 (m), 811 (s), 783 (m), 719, 675, 635, 569 (w), 534 (m). GC-MS (EI, 70 eV): m/z (%) = 382(100) [M^+], 367(32). HRMS (EI, 70 eV): calcd for $C_{27}H_{26}S$ [M^+]: 382.17497; found: 382.17515.

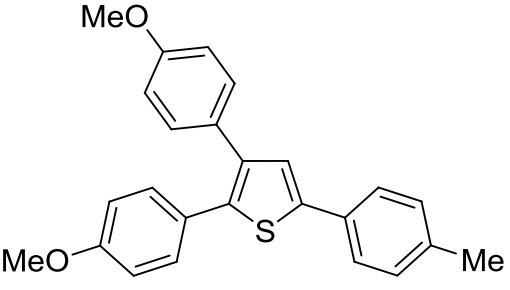
3-(2-Ethoxyphenyl)-2,5-bis(4-ethylphenyl)thiophene (5c):



Starting with **3b** (0.093 g, 0.25 mmol) and 2-ethoxy phenylboronic acid (0.083 g, 0.5 mmol), **5c** was isolated (0.085 g, 83%) as a brown oil. ^{1}H NMR (300 MHz, $CDCl_3$): δ = 0.98 (t, 3H, *J* = 7.0 Hz, CH_3), 1.16 (t, 3H, *J* = 7.6 Hz, CH_3), 1.18 (t, 3H, *J* = 7.6 Hz, CH_3), 2.50 (q, 2H, *J* = 7.6 Hz, CH_2), 2.58 (q, 2H, *J* = 7.6 Hz, CH_2), 3.73 (q, 2H, *J* = 7.0 Hz, OCH_2), 6.77-6.85 (m, 2H, ArH), 6.96 (d, 2H, *J* = 8.3 Hz, ArH), 7.11-7.17 (m, 6H, ArH), 7.23 (s, 1H, $CH_{thiophene}$), 7.47 (d, 2H, *J* = 1.8, 6.5 Hz, ArH). ^{13}C NMR (62 MHz, $CDCl_3$): δ = 14.4 (CH_3), 15.5 ($2CH_3$), 28.5, 28.6 (CH_2), 63.7 (OCH_2), 112.4, 120.5 (CH), 125.5 (2CH), 126.4 (C), 127.3 (CH), 127.7 (2CH), 127.9 (2CH), 128.3 (2CH), 128.5, 131.7 (CH), 132.0, 132.7, 134.8, 138.8, 141.2, 143.1, 143.5, 156.2 (C). IR (KBr, cm^{-1}): *v* = 3020, 2961, 2927, 2870, 1597, 1579, 1548 (w), 1505, 1489, 1474, 1450, 1439 (m), 1412, 1389, 1372, 1281 (w), 1241, 1119, 1044 (m), 1020, 978, 924 (m), 825, 747 (s), 704, 676, 648, 634, 601, 575 (w). GC-MS (EI, 70 eV): m/z (%) = 412(100) [M^+], 293(16). HRMS (EI, 70 eV): calcd for $C_{28}H_{28}OS$ [M^+]: 412.18554; found: 412.18582.

Synthesis of unsymmetrical 2,3,5-triarylbromothiophes (6):

2,3-Bis(4-methoxyphenyl)-5-*p*-tolylthiophene (6):

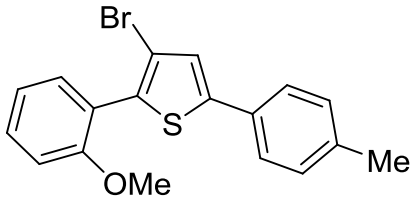


Starting with **2a** (0.083 g, 0.25 mmol) and 4-methoxyphenylboronic acid (0.114 g, 0.75 mmol), **6** was isolated (0.081 g, 84%) as a brown oil. ^{1}H NMR (300 MHz, $CDCl_3$): δ = 2.29 (s, 3H, CH_3), 3.72 (s, 3H, OCH_3), 3.73 (s, 3H, OCH_3), 6.73 (dd, 2H, *J* = 2.1, 6.8 Hz, ArH), 6.76 (dd, 2H, *J* = 2.1, 6.8 Hz, ArH), 7.10-7.13 (m, 2H, ArH), 7.15-7.18 (m, 4H, ArH), 7.20 (s, 1H, $CH_{thiophene}$), 7.44 (d, 2H, *J* = 1.9, 6.5 Hz, ArH). ^{13}C NMR (62 MHz, $CDCl_3$): δ = 21.2 (CH_3), 55.2 ($2OCH_3$), 113.8 (2CH), 113.9 (2CH), 125.4 (2CH), 125.9 (CH), 126.9, 129.3 (C), 129.6 (2CH), 130.1

(2CH), 130.3 (2CH), 131.5, 136.6, 137.3, 137.8, 141.8, 158.5, 158.9 (C). IR (KBr, cm^{-1}): ν = 2996, 2952, 2928, 2832 (w), 1605 (m), 1570, 1550 (w), 1511 (m), 1496 (s), 1454, 1438, 1288 (m), 1240, 1173 (s), 1109, 1095 (w), 1030 (s), 974, 865 (w), 824, 808, 793 (s), 730, 677, 627 (w), 584, 561, 545, 528 (m). GC-MS (EI, 70 eV): m/z (%) = 386(100) [M^+], 371(22). HRMS (EI, 70 eV): calcd for $C_{25}H_{22}O_2S$ [M^+]: 386.13350; found: 386.13293.

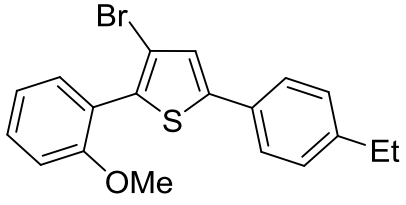
Synthesis of unsymmetrical 2,5-diaryl-3-bromothiophes (7):

3-Bromo-2-(2-methoxyphenyl)-5-*p*-tolylthiophene (7a):



Starting with **2a** (0.166 g, 0.5 mmol) and 2-methoxy phenylboronic acid (0.083 g, 0.55 mmol), **7a** was isolated (0.104 g, 58%) as a brown oil. ^{1}H NMR (300 MHz, $CDCl_3$): δ = 2.28 (s, 3H, CH_3), 3.76 (s, 3H, OCH_3), 6.88-6.96 (m, 2H, ArH), 7.09 (d, 2H, J = 7.9 Hz, ArH), 7.12 (s, 1H, $CH_{thiophene}$), 7.26-7.31 (m, 1H, ArH), 7.36-7.39 (m, 3H, ArH). ^{13}C NMR (62 MHz, $CDCl_3$): δ = 20.2 (CH_3), 54.6 (OCH_3), 109.3 (CBr), 110.3, 119.3 (CH), 120.6 (C), 124.4 (2CH), 124.6 (CH), 128.6 (2CH), 129.1 (CH), 129.6 (C), 131.2 (CH), 132.2, 136.9, 143.0, 156.0 (C). IR (KBr, cm^{-1}): ν = 3057, 2998, 2833, 1597, 1577, 1540, 1513 (w), 1486, 1462, 1431 (m), 1325, 1277 (w), 1250 (s), 1178, 1161 (w), 1113, 1049, 1023, 972, 825 (m), 805 (s), 787 (m), 747 (s), 698, 664, 623, 565, 541 (w). GC-MS (EI, 70 eV): m/z (%) = 360(83) [M^+ (^{81}Br)], 358(83) [M^+ (Br)], 264(100) [M^+], 263(21). HRMS (EI, 70 eV): calcd for $C_{18}H_{15}BrOS$, [M^+ (Br)]: 358.00215; found: 358.00228.

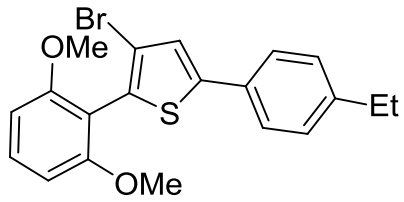
3-Bromo-5-(4-ethylphenyl)-2-(2-methoxyphenyl)thiophene (7b):



Starting with **2b** (0.173 g, 0.5 mmol) and 2-methoxyphenyl boronic acid (0.083 g, 0.55 mmol), **7b** was isolated (0.114 g, 61%) as a brown oil. ^{1}H NMR (300 MHz, $CDCl_3$): δ = 1.17 (t, 3H, J = 7.5 Hz, CH_3), 2.58 (q, 2H, J = 7.6 Hz, CH_2), 3.77 (s, 3H, OCH_3), 6.88-6.97 (m, 2H, ArH), 7.11-7.15 (m, 3H, ArH and $CH_{thiophene}$), 7.27-7.32 (m, 1H, ArH), 7.37-7.42 (m, 3H, ArH). ^{13}C NMR (62 MHz, $CDCl_3$): δ = 15.5 (CH_3), 28.6 (CH_2), 55.7 (OCH_3), 110.3 (CBr), 111.3, 120.4 (CH), 121.6 (C), 125.6 (2CH), 125.7 (CH), 128.5 (2CH), 130.2 (CH), 130.9 (C), 132.2 (CH), 133.3, 144.1, 144.3, 157.1 (C). IR (KBr, cm^{-1}): ν = 3058, 2960, 2928, 2833, 1597, 1577, 1539, 1513 (w),

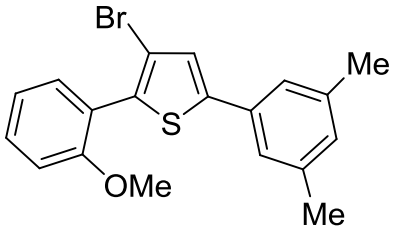
1487, 1461, 1431 (m), 1414, 1325, 1296 (w), 1277 (m), 1251 (s), 1179, 1161, 1116, 1049, 1024, 973 (m), 816 (s), 790 (m), 748 (s), 698, 663, 623, 590, 574 (w). GC-MS (EI, 70 eV): m/z (%) = 374(100) [M^+ (^{81}Br)], 372(99) [M^+ (Br)], 359(21), 357(20), 278(42), 264(16), 263(61), 234(10). HRMS (EI, 70 eV): calcd for $C_{19}H_{17}BrOS$, [M^+ (^{81}Br)]: 374.01575; found: 374.01498.

3-Bromo-2-(2,6-dimethoxyphenyl)-5-(4-ethylphenyl)thiophene (7c):



Starting with **2b** (0.173 g, 0.5 mmol) and 2,6-dimethoxy phenylboronic acid (0.100 g, 0.55 mmol), **7c** was isolated (0.087 g, 43%) as a brown oil. ^{1}H NMR (300 MHz, $CDCl_3$): δ = 1.17 (t, 3H, *J* = 7.7 Hz, CH_3), 2.57 (q, 2H, *J* = 7.7 Hz, CH_2), 3.72 (s, 6H, $2OCH_3$), 6.55 (d, 1H, *J* = 8.4 Hz, ArH), 7.11 (d, 2H, *J* = 8.4 Hz, ArH), 7.41(s, 1H, $CH_{thiophene}$), 7.24 (m, 1H, ArH), 7.39-7.42 (m, 2H, ArH), 7.54 (d, 1H, *J* = 8.2 Hz, ArH). ^{13}C NMR (62 MHz, $CDCl_3$): δ = 15.4 (CH_3), 28.6 (CH_2), 56.1 ($2OCH_3$), 104.1 (2CH), 106.2 (CBr), 112.2 (C), 125.5 (2CH), 127.9 (CH), 128.4 (2CH), 130.7 (CH), 131.2, 132.8, 144.1, 144.6 (C), 158.9 (2C). IR (KBr, cm^{-1}): *v* = 2958, 2930, 2835 (w), 1582 (m), 1469 (s), 1429 (m), 1411, 1320, 1297, 1284 (w), 1249 (s), 1199 (w), 1104 (s), 1033, 972, 945 (w), 836, 827, 810, 775, 741, 722, 693, 636, 539 (m). GC-MS (EI, 70 eV): m/z (%) = 404(100) [M^+ (^{81}Br)], 402(90) [M^+ (Br)], 389(18), 387(20), 308(32), 293(37), 278(21). HRMS (EI, 70 eV): calcd for $C_{20}H_{19}BrO_2S$, [M^+ (^{81}Br)]: 404.02632; found: 404.02590.

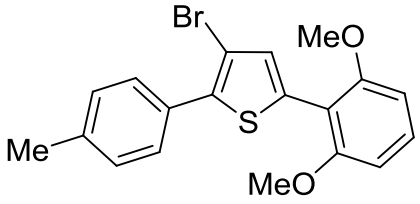
3-Bromo-5-(3,5-dimethylphenyl)-2-(2-methoxyphenyl)thiophene (7d):



Starting with **2d** (0.173 g, 0.5 mmol) and 2-methoxy phenylboronic acid (0.083 g, 0.55 mmol), **7d** was isolated (0.104 g, 56%) as a brown oil. ^{1}H NMR (300 MHz, $CDCl_3$): δ = 2.25 (s, 6H, $2CH_3$), 3.77 (s, 3H, OCH_3), 6.86 (br, 1H, ArH), 6.89-6.96 (m, 2H, ArH), 7.11 (br, 2H, ArH), 7.24 (s, 1H, $CH_{thiophene}$), 7.26-7.32 (m, 1H, ArH), 7.35-7.40 (m, 1H, ArH). ^{13}C NMR (75 MHz, $CDCl_3$): δ = 20.3 ($2CH_3$), 54.6 (OCH_3), 109.2 (CBr), 110.3, 119.3 (CH), 121.0 (C), 122.4 (2CH), 125.0, 128.7, 129.1, 131.2 (CH), 132.2, 137.0 (C), 137.5 (2C), 143.1, 156.0 (C). IR (KBr, cm^{-1}): *v* = 3058, 2960, 2928, 2833, 1597, 1577, 1539, 1513 (w), 1487, 1461, 1431 (m), 1414, 1325, 1296 (w), 1277 (m), 1251 (s), 1179, 1161, 1116, 1049, 1024, 973 (m), 816 (s),

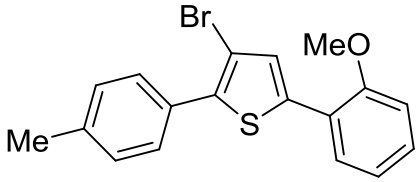
790 (m), 748 (s), 698, 663, 623, 590, 574 (w). GC-MS (EI, 70 eV): m/z (%) = 374(85) [M^+ (^{81}Br)], 372(89) [M^+ (Br)], 279(22), 278(100). HRMS (EI, 70 eV): calcd for $C_{19}H_{17}BrOS$, [M^+ (^{81}Br)]: 374.01575; found: 374.01414.

3-Bromo-5-(2,6-dimethoxyphenyl)-2-*p*-tolylthiophene (7e):



Starting with **2e** (0.189 g, 0.5 mmol) and 4-methylphenyl boronic acid (0.074 g, 0.55 mmol), **7e** was isolated (0.130 g, 67%) as a brown oil. ^{1}H NMR (300 MHz, $CDCl_3$): δ = 2.31 (s, 3H, CH_3), 3.79 (s, 6H, 2OCH_3), 6.54 (d, 2H, *J* = 8.4 Hz, ArH), 7.13-7.19 (m, 3H, ArH), 7.41(s, 1H, $CH_{thiophene}$), 7.52 (dd, 2H, *J* = 1.8, 6.4 Hz, ArH). ^{13}C NMR (62 MHz, $CDCl_3$): δ = 21.3 (CH_3), 55.9 (2OCH_3), 104.4 (2CH), 106.1 (CBr), 111.2 (C), 128.9 (2CH), 129.0 (CH), 129.1 (2CH), 130.4 (C), 132.8 (CH), 133.3, 137.7, 137.8 (C), 157.8 (2C). IR (KBr, cm^{-1}): *v* = 3002, 2929, 2834 (w), 1592 (m), 1538, 1512 (w), 1470 (s), 1428 (m), 1318, 1305, 1286 (w), 1250 (s), 1203, 1172 (w), 1106 (s), 1030, 971, 823, 808, 776, 720, 687, 633, 610, 565, 526 (m). GC-MS (EI, 70 eV): m/z (%) = 390(100) [M^+ (^{81}Br)], 388(97) [M^+ (Br)], 295(12), 294(54), 279(41). HRMS (EI, 70 eV): calcd for $C_{19}H_{17}BrO_2S$, [M^+ (^{81}Br)]: 390.01067; found: 390.01055.

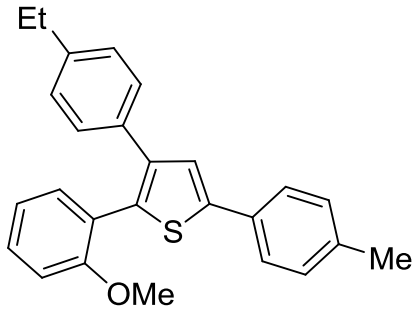
3-Bromo-5-(2-methoxyphenyl)-2-*p*-tolylthiophene (7f):



Starting with **2f** (0.174 g, 0.5 mmol) and 4-methyl phenylboronic acid (0.075 g, 0.55 mmol), **7f** was isolated (0.091 g, 51%) as a brown oil. ^{1}H NMR (300 MHz, $CDCl_3$): δ = 2.29 (s, 3H, CH_3), 3.84 (s, 3H, OCH_3), 6.87-6.93 (m, 2H, ArH), 7.13 (d, 2H, *J* = 7.7 Hz, ArH), 7.18-7.21 (m, 1H, ArH), 7.36(s, 1H, $CH_{thiophene}$), 7.49-7.52 (m, 3H, ArH). ^{13}C NMR (62 MHz, $CDCl_3$): δ = 20.3 (CH_3), 54.5 (OCH_3), 105.9 (CBr), 110.6, 120.0 (CH), 121.0 (C), 126.7 (CH), 127.7 (2CH), 127.9 (CH), 128.2 (2CH), 128.3 (CH), 129.2, 136.8, 137.0, 137.3, 154.7 (C). IR (KBr, cm^{-1}): *v* = 3020, 2918, 2834, 1595, 1578, 1535, 1510 (w), 1484, 1461, 1433 (m), 1329, 1296 (w), 1249 (s), 1179, 1114, 1052 (m), 1021 (s) 973 (m), 808, 747 (s), 715, 702, 642, 613, 571, 541 (w). GC-MS (EI, 70 eV): m/z (%) = 360(100) [M^+ (^{81}Br)], 358(97) [M^+ (Br)], 265(18), 264(99), 263(16). HRMS (EI, 70 eV): calcd for $C_{18}H_{15}BrOS$, [M^+ (Br)]: 358.00215; found: 358.00174.

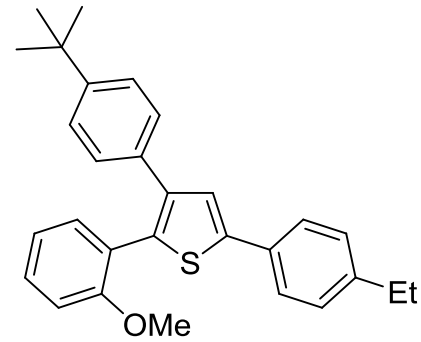
Synthesis of unsymmetrical 2,3,5-triarylbromothiophes (8):

3-(4-Ethylphenyl)-2-(2-methoxyphenyl)-5-*p*-tolylthiophene (8a):



Starting with **7a** (0.090 g, 0.25 mmol) and 4-ethylphenyl boronic acid (0.075 g, 0.5 mmol), **8a** was isolated (0.074 g, 77%) as a brown oil. ^{1}H NMR (300 MHz, $CDCl_3$): δ = 1.13 (t, 3H, *J* = 7.6 Hz, CH_3), 2.29 (s, 3H, CH_3), 2.53 (q, 2H, *J* = 7.6 Hz, CH_2), 3.45 (s, 3H, OCH_3), 6.77-6.80 (m, 2H, ArH), 6.99 (d, 2H, *J* = 8.2 Hz, ArH), 7.11 (d, 3H, *J* = 8.0 Hz, ArH), 7.16-7.22 (m, 3H, ArH), 7.29 (s, 1H, $CH_{thiophene}$), 7.46 (d, 2H, *J* = 8.1 Hz, ArH). ^{13}C NMR (62 MHz, $CDCl_3$): δ = 14.5 (CH_3), 20.2 (CH_3), 27.5 (CH_2), 54.2 (OCH_3), 110.4, 119.5 (CH), 122.4 (C), 123.8 (CH), 124.6 (2CH), 126.5 (2CH), 127.0 (2CH), 128.1 (CH), 128.5 (2CH), 130.6 (C), 131.3 (CH), 131.7, 133.8, 136.2, 139.4, 141.5, 142.0, 155.9 (C). IR (KBr, cm^{-1}): *v* = 3019, 2960, 2927, 2832, 1596, 1577, 1549 (w), 1504, 1489, 1461, 1431 (m), 1368, 1275 (w), 1249 (s), 1179, 1118, 1048, 1023, 828 (m), 809 (s), 790 (m), 748 (s), 680, 584, 530 (w). GC-MS (EI, 70 eV): m/z (%) = 384(100) [M^+], 340(11). HRMS (EI, 70 eV): calcd for $C_{26}H_{24}OS$ [M^+]: 384.15424; found: 384.15385.

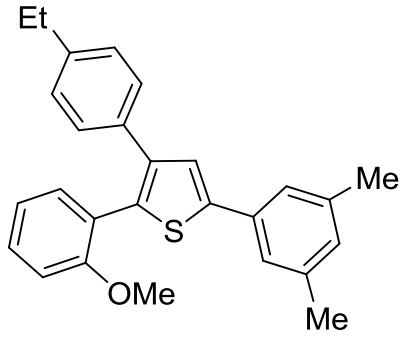
3-(4-*tert*-Butylphenyl)-5-(4-ethylphenyl)-2-(2-methoxyphenyl)thiophene (8c):



Starting with **7c** (0.093 g, 0.25 mmol) and 4-*tert*-butyl phenylboronic acid (0.089 g, 0.5 mmol), **8c** was isolated (0.086 g, 81%) as a brown oil. ^{1}H NMR (300 MHz, $CDCl_3$): δ = 1.18 (t, 3H, *J* = 7.7 Hz, CH_3), 1.21 (s, 9H, $3CH_3$), 2.58 (q, 2H, *J* = 7.5 Hz, CH_2), 3.39 (s, 3H, OCH_3), 6.76 (d, 1H, *J* = 8.2 Hz, ArH), 6.79-6.84 (m, 1H, ArH), 7.11-7.14 (m, 4H, ArH), 7.16-7.19 (m, 3H, ArH), 7.21-7.23 (m, 1H, ArH), 7.30 (s, 1H, $CH_{thiophene}$), 7.47 (d, 2H, *J* = 1.8, 6.5 Hz, ArH). ^{13}C NMR (62 MHz, $CDCl_3$): δ = 14.4 (CH_3), 28.6 (CH_2), 30.3 ($3CH_3$), 33.4 (C), 54.1 (OCH_3), 111.4, 119.5 (CH), 122.5 (C), 123.8 (CH), 123.9 (2CH), 124.7 (2CH), 126.6 (2CH), 127.3 (2CH), 128.1 (CH), 130.9 (C), 131.3 (CH), 131.8, 133.6, 139.2, 142.0, 142.5, 148.4, 155.8 (C). IR (KBr, cm^{-1}): *v* = 2959, 2930, 2901, 2832, 1503 (w), 1489, 1461 (m), 1431, 1361, 1275 (w), 1251 (m), 1202, 1179, 1160, 1116, 1088, 1049 (m), 1024 (s), 976, 907 (w), 821, 749, 730 (s),

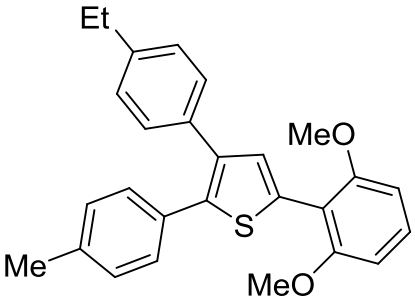
696, 647, 593 (w), 566 (m). GC-MS (EI, 70 eV): m/z (%) = 426(100) [M^+], 412(13), 411(39). HRMS (EI, 70 eV): calcd for $C_{29}H_{30}OS$ [M^+]: 426.20119; found: 426.20134.

5-(3,5-Dimethylphenyl)-3-(4-ethylphenyl)-2-(2-methoxyphenyl)thiophene (8d):



Starting with **7d** (0.093 g, 0.25 mmol) and 4-ethylphenyl boronic acid (0.075 g, 0.5 mmol), **8d** was isolated (0.072 g, 72%) as a brown oil. ^{1}H NMR (300 MHz, $CDCl_3$): δ = 1.13 (t, 3H, *J* = 7.7 Hz, CH_3), 2.27 (s, 6H, $2CH_3$), 2.53 (q, 2H, *J* = 7.6 Hz, CH_2), 3.45 (s, 3H, OCH_3), 6.77-6.81 (m, 2H, ArH), 6.84 (br, 1H, ArH), 6.90 (d, 1H, *J* = 7.9 Hz, ArH), 6.98 (d, 2H, *J* = 8.1 Hz, ArH), 7.11 (dd, 2H, *J* = 1.8, 6.3 Hz, ArH), 7.17-7.21 (m, 3H, ArH), 7.30 (s, 1H, $CH_{thiophene}$). ^{13}C NMR (62 MHz, $CDCl_3$): δ = 15.5 (CH_3), 21.3 ($2CH_3$), 28.5 (CH_2), 55.3 (OCH_3), 111.4, 120.5 (CH), 122.5 (C), 123.6 (2CH), 125.1 (CH), 127.5 (2CH), 128.0 (2CH), 129.2 (2CH), 132.3 (CH), 134.3, 134.9 (C), 138.3 (2C), 140.4, 142.5, 143.2, 156.9 (2C). IR (KBr, cm^{-1}): *ν* = 3020, 2959, 2925, 2833, 1596, 1577, 1549 (w), 1505, 1479, 1463, 1431 (m), 1370, 1275 (w), 1250 (s), 1179, 1120, 1048, 1023, 828 (m), 809 (s), 792 (m), 748 (s), 680, 584 (w). GC-MS (EI, 70 eV): m/z (%) = 398(100) [M^+]. HRMS (EI, 70 eV): calcd for $C_{27}H_{26}OS$ [M^+]: 398.16989; found: 398.16929.

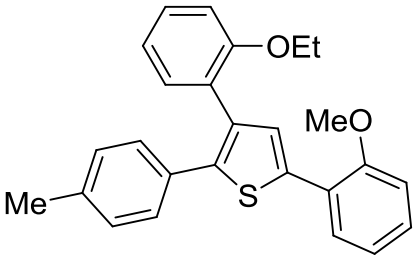
5-(2,6-Dimethoxyphenyl)-3-(4-ethylphenyl)-2-*p*-tolylthiophene (8e):



Starting with **7e** (0.097 g, 0.25 mmol) and 4-ethylphenyl boronic acid (0.075 g, 0.5 mmol), **8e** was isolated (0.077 g, 75%) as a brown oil. ^{1}H NMR (300 MHz, $CDCl_3$): δ = 1.17 (t, 3H, *J* = 7.7 Hz, CH_3), 2.24 (s, 3H, CH_3), 2.56 (q, 2H, *J* = 7.5 Hz, CH_2), 3.78 (s, 6H, $2OCH_3$), 6.58 (d, 2H, *J* = 8.4 Hz, ArH), 6.98 (d, *J* = 8.2 Hz, 2H, ArH), 7.03 (d, 2H, *J* = 8.0 Hz, ArH), 7.15-7.21 (m, 5H, ArH), 7.45 (s, 1H, $CH_{thiophene}$). ^{13}C NMR (62 MHz, $CDCl_3$): δ = 14.3 (CH_3), 20.2 (CH_3), 27.5 (CH_2), 54.9 ($2OCH_3$), 103.3 (2CH), 111.3, 120.8 (C), 126.6 (2CH), 127.5 (CH), 128.0 (2CH), 128.1 (2CH), 128.2 (2CH), 130.8 (C), 131.5 (CH), 133.6, 135.5, 135.7, 137.0, 141.3 (C), 156.6 (2C). IR (KBr, cm^{-1}): *ν* = 2960, 2929, 2834 (w), 1581 (m), 1512 (w), 1469 (s), 1430 (m), 1248 (s), 1214, 1201, 1183, 1170 (w), 1105 (s), 1031, 1020 (m), 974, 946 (w), 906, 830 (m),

812 (s), 778 (m), 724 (s), 647, 597, 567, 541 (w). GC-MS (EI, 70 eV): m/z (%) = 414(100) [M^+]. HRMS (EI, 70 eV): calcd for $C_{27}H_{26}O_2S$ [M^+]: 414.16480; found: 414.16368.

3-(2-Ethoxyphenyl)-5-(2-methoxyphenyl)-2-*p*-tolylthiophene (8f):

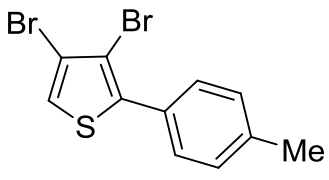


Starting with **7f** (0.090 g, 0.25 mmol) and 2-ethoxyphenyl boronic acid (0.083 g, 0.5 mmol), **8f** was isolated (0.064 g, 64%) as a brown oil. ^{1}H NMR (300 MHz, $CDCl_3$): δ = 1.01 (t, 3H, *J* = 7.0 Hz, CH_3), 2.21 (s, 3H, CH_3), 3.75 (q, 2H, *J* = 6.9 Hz, OCH_2), 3.85 (s, 3H, OCH_3), 6.78-6.94 (m, 2H, ArH), 6.89 (d, 2H, *J* = 7.9 Hz, ArH), 6.93 (d, 2H, *J* = 7.9 Hz, ArH), 7.11-7.19 (m, 5H, ArH), 7.46 (s, 1H, $CH_{thiophene}$), 7.59 (d, 1H, *J* = 1.6, 8.2 Hz, ArH). ^{13}C NMR (75 MHz, $CDCl_3$): δ = 13.5 (CH_3), 20.1 (CH_3), 54.5 (OCH_3), 62.7 (CH_2), 110.6, 111.4, 119.4, 119.9 (CH), 122.4, 125.6 (C), 127.0 (3CH), 127.1, 127.3 (CH), 127.8 (2CH), 129.0, 130.8 (CH), 131.6, 132.7, 135.3, 135.5, 138.7, 154.7, 155.2 (C). IR (KBr, cm^{-1}): *ν* = 2961, 1595, 1485, 1412 (w), 1258 (s), 1086 (m), 1017, 795 (s), 745, 705 (w). GC-MS (EI, 70 eV): m/z (%) = 400(100) [M^+], 295(20). HRMS (EI, 70 eV): calcd for $C_{26}H_{24}O_2S$ [M^+]: 400.14915; found: 400.14881.

General Procedure for the Synthesis of 2-Aryl-3,4-dibromothiophenes (10):

To a mixture of **9** (0.159 g, 0.5 mmol), arylboronic acid (0.55 mmol), $Pd(PPh_3)_4$ (29 mg, 5 mol-%) were added a mixture of 1,4-dioxane and toluene (1:1, 5 mL) and an aq solution of K_2CO_3 (2 mL, 2 M) under argon atmosphere. The reaction mixture was stirred at 100 °C for 5 h and was subsequently allowed to cool to 20 °C. The solution was poured into H_2O and CH_2Cl_2 (25 mL each), and the organic and the aqueous layer were separated. The latter was extracted with CH_2Cl_2 (3 × 25 mL), dried (Na_2SO_4), filtered, and concentrated in vacuo. The residue was purified by flash column chromatography (flash silica gel, heptanes).

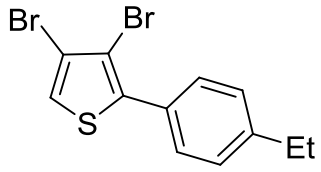
3,4-Dibromo-2-*p*-tolylthiophene (10a):



Starting with **9** (0.159 g, 0.5 mmol) and 4-methylphenylboronic acid (0.074 g, 0.55 mmol), **10a** was isolated (0.147 g, 89%) as a white solid, mp. = 78-80 °C. ^{1}H NMR (300 MHz, $CDCl_3$): δ = 2.32 (s, 3H, CH_3), 7.17 (d, 2H, *J* = 7.9 Hz, ArH), 7.27 (s, 1H,

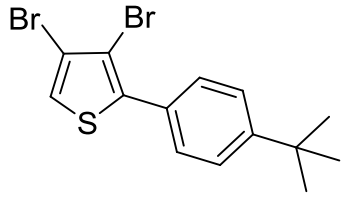
$CH_{thiophene}$), 7.42 (dd, 2H, J = 1.7, 6.4 Hz, ArH). ^{13}C NMR (75 MHz, $CDCl_3$): δ = 21.3 (CH_3), 111.0, 114.6 (CBr), 122.0 (CH), 128.9 (2CH), 129.4 (2CH), 130.1, 139.0, 139.7 (C). IR (KBr, cm^{-1}): v = 3011, 2914, 1486 , 1409, 1378, 1313 (w), 1303 (m), 1180, 1106, 1019, 874 (m), 729 (s), 707, 646 (w), 530 (m). GC-MS (EI, 70 eV): m/z (%) = 334(53) [M^+ ($^{8'}$Br, $^{8'}$Br)], 332(100) [M^+ ($^{8'}$Br, Br)], 330(51) [M^+ (Br, Br)], 172(48), 171(31). HRMS (EI, 70 eV): calcd for $C_{11}H_8Br_2S$ (M^+, [Br, $^{8'}$Br]): 331.86875; found: 331.86649.

2-(4-Ethylphenyl)thiophene (10b):



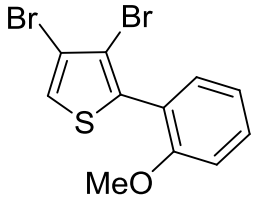
Starting with **9** (0.159 g, 0.5 mmol) and 4-ethylphenylboronic acid (0.083 g, 0.55 mmol), **10b** was isolated (0.150 g, 87%) as whitish oil. ^1H NMR (300 MHz, $CDCl_3$): δ =1.32 (t, J = 7.6 Hz, 3H, CH_3), 2.75 (q, 2H, J = 7.6 Hz, CH_2), 7.32 (d, 2H, J = 8.4 Hz, ArH), 7.38 (s, 1H, $CH_{thiophene}$), 7.58 (d, 2H, J = 8.3 Hz, ArH). ^{13}C NMR (62 MHz, $CDCl_3$): δ = 15.4 (CH_3), 28.7 (CH_2), 111.0, 114.7 (CBr), 122.0 (CH), 128.2 (2CH), 128.9 (2CH), 130.3, 139.7, 145.7 (C). IR (KBr, cm^{-1}): v = 3107 (w), 3020 (w), 2961 (m), 2927 (m), 2630 (w), 2306 (w), 1903 (w), 1524 (w), 1484 (m), 1308 (w), 1126 (w), 963 (w), 877 (s), 828 (s), 785 (m), 722 (s), 645 (w), 585 (m), 539 (m). GC-MS (EI, 70 eV): m/z (%) = 348(44) [M^+ (^{81}Br, ^{81}Br)], 346(83) [M^+ (^{81}Br, Br)], 344(41) [M^+ (Br, Br)], 333(54), 331(100), 329(50), 186(11), 171(38), 13(11). HRMS (EI, 70 eV): calcd for $C_{12}H_{10}Br_2S$ [M^+ (Br, ^{81}Br)]: 345.88440; found: 345.8845.

3,4-Dibromo-2-(4-*tert*-butylphenyl)thiophene (10c):



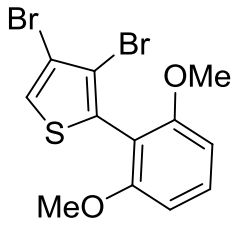
Starting with **9** (0.159 g, 0.5 mmol)) and 4-*tert*- butylphenyl boronic acid (0.098 g, 0.55 mmol), **10c** was isolated (0.176 g, 94%) as a white solid, mp. = 93-94 °C. ^1H NMR (300 MHz, $CDCl_3$): δ = 1.28 (s, 9H, $3CH_3$), 7.27 (s, 1H, $CH_{thiophene}$), 7.38 (dd, J = 2.1, 2H, 6.6 Hz, ArH), 7.48 (dd, 2H, J = 2.2, 6.5 Hz, ArH). ^{13}C NMR (62 MHz, $CDCl_3$): δ = 31.2 ($3CH_3$), 34.8 (C), 110.9, 114.7 (CBr), 122.0 (CH), 125.6 (2CH), 128.6 (2CH), 130.0, 139.6, 152.0 (C). IR (KBr, cm^{-1}): v = 3019, 2953, 2860, 1485 , 1456, 1406, 1390, 1303, 1267, 1107, 1020 (w), 879 (m), 828 (s), 765, 736 (m), 727 (s), 690 (m), 562 (s). GC-MS (EI, 70 eV): m/z (%) = 376(21) [M^+ ($^{8'}$Br, $^{8'}$Br)], 374(40) [M^+ ($^{8'}$Br, Br)], 372(20) [M^+ (Br, Br)], 361(53), 359(100) [M^+], 357(50), 331(15). HRMS (EI, 70 eV): calcd for $C_{14}H_{14}Br_2S$ [M^+ (Br, $^{8'}$Br)]: 373.91570; found: 373.91523.

3,4-Dibromo-2-(2-methoxyphenyl)thiophene (10d):



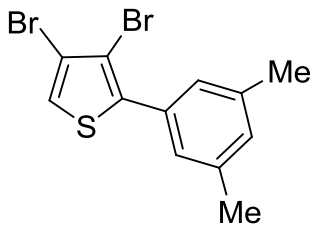
Starting with **9** (0.159 g, 0.5 mmol) and 2-methoxyphenylboronic acid (0.084 g, 0.55 mmol), **10d** was isolated (0.148 g, 85%) as whitish oil. ^{1}H NMR (300 MHz, $CDCl_3$): δ = 3.76 (s, 3H, OCH_3), 6.89-6.97 (m, 2H, ArH), 7.27 (dd, 1H, *J* = 1.7, 7.6 Hz, ArH), 7.30-7.36 (m, 2H, ArH and $CH_{thiophene}$). ^{13}C NMR (62 MHz, $CDCl_3$): δ = 55.6 (OCH_3), 111.3 (CH), 111.5, 111.6 (CBr), 121.4 (CH), 121.6 (C), 122.8, 130.7, 132.1 (CH), 135.9, 157.0 (C). IR (KBr, cm^{-1}): *ν* = 3104, 2934, 2833, 1596, 1578, 1518 (w), 1480, 1460, 1433, 1312, 1291, 1276 (m), 1247 (s), 1178, 1161, 1115, 1048 (m), 1022 (s), 970, 935 (w), 878 (s), 844, 795 (m), 748, 716 (s), 630, 571 (m). GC-MS (EI, 70 eV): m/z (%) = 350(52) [M^+ ($^{8'}$Br, $^{8'}$Br)], 348(100) [M^+ ($^{8'}$Br, Br)], 346(50) [M^+ (Br, Br)], 254(66), 252(66), 188(52), 187(36), 173(16), 145(30). HRMS (EI, 70 eV): calcd for $C_{11}H_8Br_2OS$ [M^+ (Br, $^{8'}$Br)]: 347.86367; found: 347.86314.

3,4-Dibromo-2-(2,6-dimethoxyphenyl)thiophene (10e):



Starting with **9** (0.159 g, 0.5 mmol) and 2,6-dimethoxyphenylboronic acid (0.100 g, 0.55 mmol), **10e** was isolated (0.127 g, 67%) as a white solid, mp. = 106-108 °C. ^{1}H NMR (250 MHz, $CDCl_3$): δ = 3.70 (s, 6H, $2OCH_3$), 6.55 (d, 2H, *J* = 8.4 Hz, ArH), 7.29 (t, 1H, *J* = 8.3 Hz, ArH), 7.36 (s, 1H, $CH_{thiophene}$). ^{13}C NMR (62 MHz, $CDCl_3$): δ = 55.0 ($2OCH_3$), 102.9 (2CH), 109.0 (C), 112.0, 114.0 (CBr), 122.3 (C), 122.3, 130.9 (CH), 157.7 (2C). IR (KBr, cm^{-1}): *ν* = 3102, 3003, 2963, 2836 (w), 1579 (m), 1469 (s), 1430 (m), 1303, 1284 (w), 1250 (s), 1210, 1172, 1150 (w), 1101 (s), 1027, 875, 786, 765, 722, 704, 694, 604, 595, 539 (m). GC-MS (EI, 70 eV): m/z (%) = 380(54) [M^+ ($^{8'}$Br, $^{8'}$Br)], 378(100) [M^+ ($^{8'}$Br, Br)], 376(49) [M^+ (Br, Br)], 284(42), 282(40), 269(22), 267(24), 218(43), 204(10). HRMS (EI, 70 eV): calcd for $C_{12}H_{10}Br_2O_2S$ [M^+ (Br, $^{8'}$Br)]: 377.87423; found: 377.87406.

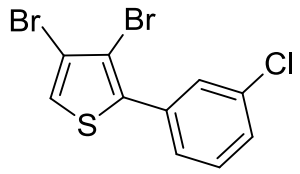
3,4-Dibromo-2-(3,5-dimethylphenyl)thiophene (10f):



Starting with **9** (0.159 g, 0.5 mmol) and 3,5-dimethylphenylboronic acid (0.083 g, 0.55 mmol), **10f** was isolated (0.136 g, 79%) as a colorless oil. ^{1}H NMR (300 MHz, $CDCl_3$): δ = 2.28 (s, 3H, CH_3), 2.29 (s, 3H, CH_3), 6.96 (br, 1H, ArH), 7.12 (br, 2H, ArH), 7.26 (s, 1H, $CH_{thiophene}$). ^{13}C NMR (62 MHz, $CDCl_3$): δ = 21.3 ($2CH_3$),

111.0, 114.6 (CBr), 122.0 (CH), 126.7 (2CH), 130.6 (CH), 132.7 (C), 138.3 (2C), 139.9 (C). IR (KBr, cm^{-1}): ν = 3107 (w), 2917 (m), 2854 (w), 1600, 1462, 1307 (m), 1264, 1126, 1037 (w), 883, 846, 821 (s), 731 (m), 699 (s), 683 (m), 642, 567, 543 (w). GC-MS (EI, 70 eV): m/z (%) = 348(52) [M^+ ($^{8'}$Br, $^{8'}$Br)], 346(100) [M^+ ($^{8'}$Br, Br)], 344(51) [M^+ (Br, Br)], 331(11), 186(30), 185(14), 171(20). HRMS (EI, 70 eV): calcd for $C_{12}H_{10}Br_2S$ [M^+ (Br, $^{8'}$Br)]: 346.88440; found: 346.88334.

3,4-Dibromo-2-(3-chlorophenyl)thiophene (10g):

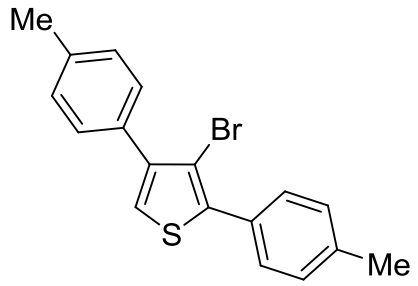


Starting with **9** (0.159 g, 0.5 mmol) and 3-chlorophenylboronic acid (0.086 g, 0.55 mmol), **10g** was isolated (0.117 g, 67%) as as a white solid, mp. = 67-69 °C. ^{1}H NMR (300 MHz, $CDCl_3$): δ = 7.29-7.31 (m, 2H, ArH), 7.32 (s, 1H, $CH_{thiophene}$), 7.39-7.43 (m, 1H, ArH), 7.52-7.53 (m, 1H, ArH). ^{13}C NMR (62 MHz, $CDCl_3$): δ = 112.1, 115.0 (CBr), 122.8 (CH), 127.2, 128.8, 128.9, 129.9 (CH), 134.8, 137.8, 141.6 (C). IR (KBr, cm^{-1}): ν = 3103, 2922, 2851 (w), 1593, 1562, 1463 (m), 1425, 1385 (w), 1307 (m), 1260, 1164, 1095 (w), 1078, 995 (m), 877, 766, 737, 682 (s), 636 (m). GC-MS (EI, 70 eV): m/z (%) = 356(16) [M^+ ($^{8'}$Br, $^{8'}$Br,^{37}Cl)], 354(72) [M^+ ($^{8'}$Br, $^{8'}$Br, Cl); (Br, $^{8'}$Br,^{37}Cl)], 352(100) [M^+ (Br, $^{8'}$Br,^{35}Cl); (Br, Br,^{37}Cl)], 350(43) [M^+ (Br, Br, Cl)], 194(16), 192(41), 113(12). HRMS (EI, 70 eV): calcd for $C_{10}H_5Br_2ClS$ [M^+ (Br, $^{8'}$Br, Cl)]: 351.81413; found: 351.81376; [M^+ (Br, Br, ^{37}Cl)]: 351.81323; found: 351.81476.

Synthesis of 2,4-diaryl-3-bromothiophenes (11):

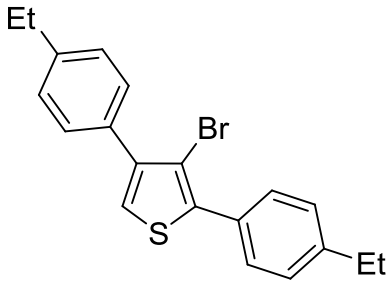
To a mixture of **9** (0.159 g, 0.5 mmol), aryl boronic acid (1.1 mmol), and $Pd(PPh_3)_4$ (35mg, 6 mol-%) was added a mixture of 1,4-dioxane and toluene (1:1; 5 mL), K_3PO_4 (4.0 equiv, 424 mg) and 1mL of H_2O, under an argon atmosphere. The reaction mixture was stirred at 100 °C for 12 h and was subsequently allowed to cool to 20 °C. The solution was poured into H_2O and EtOAc (25 mL each) and the organic and the aqueous layers were separated. The latter was extracted with EtOAc (3 × 25 mL), dried (Na_2SO_4), filtered, and concentrated in vacuo. The residue was purified by flash column chromatography (flash silica gel, eluent: heptanes/EtOAc).

3-Bromo-2,4-di-*p*-tolylthiophene (11a):



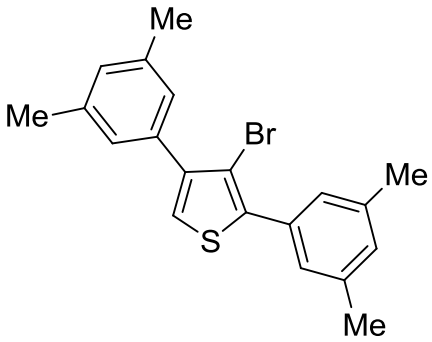
Starting with **9** (0.159 g, 0.5 mmol) and 4-methylphenyl boronic acid (0.149 g, 1.1 mmol), **11a** was isolated (0.095 g, 55%) as yellowish solid, mp. = 122-124 °C. ^{1}H NMR (300 MHz, $CDCl_3$): δ = 2.32 (br, 6H, $2CH_3$), 7.14-7.18 (m, 5H, ArH and $CH_{thiophene}$), 7.32 (dd, 2H, J = 1.7, 6.3 Hz, ArH), 7.47 (dd, 2H, J = 1.7, 6.5 Hz, ArH). ^{13}C NMR (62 MHz, $CDCl_3$): δ = 21.3, 21.4 (CH_3), 108.9 (CBr), 121.6 (CH), 128.9 (2CH), 129.1 (2CH), 129.2 (2CH), 129.3 (2CH), 130.5, 130.7, 133.3, 137.6, 138.3, 143.3 (C). IR (KBr, cm^{-1}): v = 2960 (m), 2864, 1521, 1493, 1456, 1361, 1200, 1109, 1021, 963, 892 (w), 832 (m), 815, 797, 742 (s), 722, 707 (m), 684, 675, 640, 602 (w), 582, 566, 541, 528 (m). GC-MS (EI, 70 eV): m/z (%) = 344(100) [M^+ (^{81}Br)], 342(97) [M^+ (Br)], 248(26), 247(15). HRMS (EI, 70 eV): calcd for $C_{18}H_{15}BrS$ [(^{81}Br)]: 344.00519; found: 344.00529.

3-Bromo-2,4-bis(4-ethylphenyl)thiophene (11b):



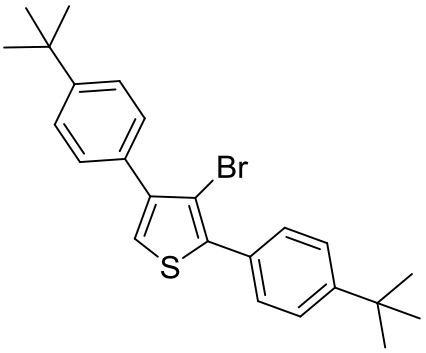
Starting with **9** (0.159 g, 0.5 mmol) and 4-ethylphenylboronic acid (0.165 g, 1.1 mmol), **11b** was isolated (0.095 g, 51%) as a whitish oil. ^{1}H NMR (300 MHz, $CDCl_3$): δ = 1.20 (t, 3H, J = 7.6 Hz, CH_3), 1.21 (t, 3H, J = 7.6 Hz, CH_3), 2.59-2.267 (m, 4H, $2CH_2$), 7.18-7.22 (m, 5H, ArH and $CH_{thiophene}$), 7.37 (dd, 2H, J = 1.9, 6.3 Hz, ArH), 7.51 (dd, 2H, J = 1.8, 6.4 Hz, ArH). ^{13}C NMR (62 MHz, $CDCl_3$): δ = 15.3, 15.4 (CH_3), 28.6, 28.7 (CH_2), 108.8 (CBr), 121.6 (CH), 127.6 (2CH), 128.0 (2CH), 129.2 (2CH), 129.4 (2CH), 130.9, 133.5, 139.3, 143.3, 143.8, 144.6 (C). IR (KBr, cm^{-1}): v = 3100, 3021 (w), 2961, 2927 (m), 1536, 1513 (w), 1491, 1453 (m), 1410, 1334, 1184, 1115, 1049, 1020, 964 (w), 894 (m), 828 (s), 792, 751, 726 (m), 678, 641, 539 (w). GC-MS (EI, 70 eV): m/z (%) = 372(100) [M^+ (^{81}Br)], 370(97) [M^+ (Br)], 357(64), 355(64), 247(19), 171(12), 170(11). HRMS (EI, 70 eV): calcd for $C_{20}H_{19}BrS$ [M^+ (^{81}Br)]: 372.03649; found: 372.03594.

3-Bromo-2,4-bis(3,5-dimethylphenyl)thiophene (11c):



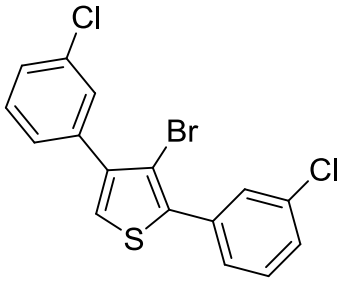
Starting with **9** (0.159 g, 0.5 mmol) and 3,5-dimethyl phenyl boronic acid (0.165 g, 1.1 mmol), **11c** was isolated (0.086 g, 46%) as a yellowish solid, mp. = 80-82 °C. ^{1}H NMR (300 MHz, $CDCl_3$): δ = 2.29 (s, 12H, $4CH_3$), 6.94 (br, 2H, ArH), 7.04 (br, 2H, ArH), 7.13 (s, 1H, $CH_{thiophene}$), 7.18 (br, 2H, ArH). ^{13}C NMR (75 MHz, $CDCl_3$): δ = 21.3 ($2CH_3$), 21.4 ($2CH_3$), 108.8 (CBr), 121.8 (CH), 127.2 (2CH), 127.3 (2CH), 129.5, 130.1 (CH), 133.5, 136.1 (C), 137.7 (2C), 138.1 (2C), 139.5, 143.5 (C). IR (KBr, cm^{-1}): ν = 3092, 2913, 2853 (w), 1598 (m), 1454, 1374, 1336, 1036, 941, 903 (w), 847, 827 (s), 757 (m), 699 (s), 677, 667 (m), 542, 536 (w). GC-MS (EI, 70 eV): m/z (%) = 372(100) [M^+ (^{81}Br)], 371(23), 370(96) [M^+ (Br)], 276(16), 275(12). HRMS (EI, 70 eV): calcd for $C_{20}H_{19}BrS$ [M^+ (^{81}Br)]: 372.03649; found: 372.03590.

3-Bromo-2,4-bis(4-*tert*-butylphenyl)thiophene (11d):



Starting with **9** (0.159 g, 0.5 mmol) and 4-*tert*-butylphenylboronic acid (0.195 g, 1.1 mmol), **11d** was isolated (0.105 g, 49%) as a white solid, mp. = 144-146 °C. ^{1}H NMR (300 MHz, $CDCl_3$): δ = 1.27 (s, 9H, $9CH_3$), 1.28 (s, 9H, $9CH_3$), 7.15 (s, 1H, $CH_{thiophene}$), 7.36-7.39 (m, 6H, ArH), 7.37 (dd, 2H, J = 2.0, 6.5 Hz, ArH). ^{13}C NMR (62 MHz, $CDCl_3$): δ = 31.3 ($3CH_3$), 31.4 ($3CH_3$), 34.6, 34.7 (C), 108.8 (CBr), 121.8 (CH), 125.1 (2CH), 125.5 (2CH), 128.9 (2CH), 129.1 (2CH), 130.7, 133.2, 139.2, 143.2, 150.7, 151.4 (C). IR (KBr, cm^{-1}): ν = 2958 (m), 2900, 2863, 1537, 1489, 1460, 1392 (w), 1361 (m), 1267, 1201, 1115, 1017 (w), 896 (m), 832 (s), 778, 756, 732 (m), 684 (w), 575, 562 (m). GC-MS (EI, 70 eV): m/z (%) = 428(65) [M^+ (^{81}Br)], 426(64) [M^+ (Br)], 413(100), 411(98), 171(12), 170(11), 57(25). HRMS (EI, 70 eV): calcd for $C_{24}H_{27}BrS$ [M^+ (^{81}Br)]: 428.09909; found: 428.09834.

3-Bromo-2,4-bis(3-chlorophenyl)thiophene (11e):

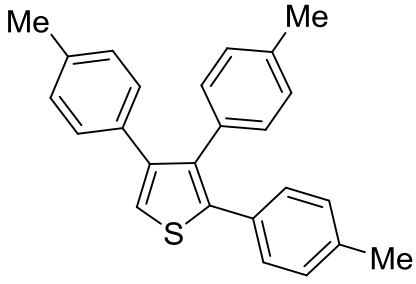


Starting with **9** (0.159 g, 0.5 mmol) and 3-chlorophenylboronic acid (0.171 g, 1.1 mmol), **11e** was isolated (0.128 g, 67%) as a white solid, mp. = 162-164 °c. ^{1}H NMR (300 MHz, $CDCl_3$): δ = 7.26-7.46 (m, 8H, ArH and $CH_{thiophene}$), 7.57 (s, 1H, ArH). ^{13}C NMR (75 MHz, $CDCl_3$): δ = 109.3 (CBr), 123.3 (CH), 127.5, 127.6, 128.1, 128.6, 129.4, 129.4, 129.5, 129.8 (CH), 134.1, 134.5, 135.0, 137.4, 138.0, 142.1 (C). IR (KBr, cm^{-1}): ν = 3062, 1928, 1681 (w), 1595, 1565, 1462, 1435, 1415, 1332, 1296 (m), 1226, 1163 (w), 1092, 1077, 996, 915, 876, 802 (m), 772, 740, 690, 683 (s), 646 (m), 626, 591, 534 (w). GC-MS (EI, 70 eV): m/z (%) = 388(08) [M^+ (^{81}Br, ^{37}Cl, ^{37}Cl)], 386(50) [M^+ (Br, ^{37}Cl, ^{37}Cl)] or [M^+ (^{81}Br, Cl, ^{37}Cl)], 384(100) [M^+ (Br, Cl, ^{37}Cl)] or [M^+ (^{81}Br, Cl, Cl)], 382(59) [M^+ (Br, Cl, Cl)], 270(12), 268(31), 232(10). HRMS (EI, 70 eV): calcd for $C_{16}H_9BrCl_2S$ [M^+ (Br, Cl, ^{37}Cl)]: 383.89504; found: 383.89549; [M^+ (^{81}Br, Cl, Cl)]: 383.89594; found: 383.89549.

Synthesis of 2,3,4-triarylthiophenes (12):

To a mixture of **9** (0.080 g, 0.25 mmol), arylboronic acid (1.0 mmol), $Pd(PPh_3)_4$ (35 mg, 6 mol-%) were added a mixture of 1,4-dioxane and toluene (1:1, 5 mL) and an aq solution of K_2CO_3 (2 mL, 2 M) under argon atmosphere. The reaction mixture was stirred at 90 °C for 12 h and was subsequently allowed to cool to 20 °C. The solution was poured into H_2O and CH_2Cl_2 (25 mL each) and the organic and the aqueous layer were separated. The latter was extracted with CH_2Cl_2 (3 × 25 mL), dried (Na_2SO_4), filtered, and concentrated in vacuo. The residue was purified by flash column chromatography (flash silica gel, *n*-heptane).

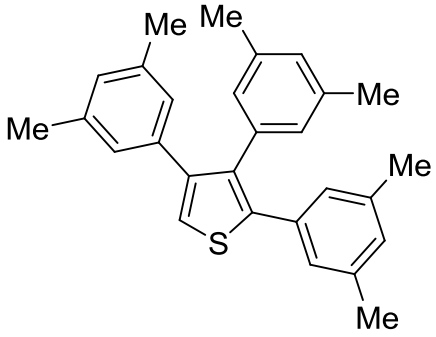
2,3,4-Tri-*p*-tolylthiophene (12a):



Starting with **9** (0.08 g, 0.25 mmol) and 4-methylphenyl boronic acid (0.136 g, 1.0 mmol), **12a** was isolated (0.082 g, 93%) as a white solid, mp. = 122-124 °C. ^{1}H NMR (250 MHz, $CDCl_3$): δ = 2.22 (s, 9H, $3CH_3$), 6.81 (dd, 2H, J = 2.1, 6.4 Hz, ArH), 6.87-6.96 (m, 8H, ArH), 7.02 (dd, 2H, J = 1.9, 6.3 Hz, ArH), 7.15 (s, 1H, $CH_{thiophene}$). ^{13}C NMR (62 MHz, $CDCl_3$): δ = 20.0, 20.1, 20.2 (CH_3), 120.2 (CH), 127.6

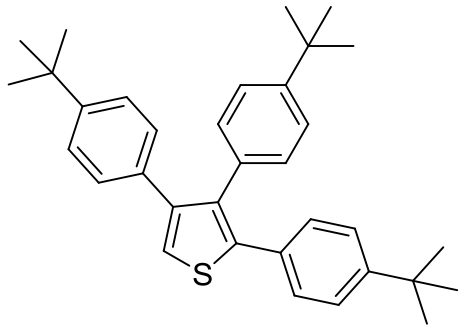
(2CH), 127.7 (2CH), 127.8 (2CH), 127.9 (2CH), 128.1 (2CH), 129.7 (2CH), 130.9, 132.2, 133.2, 135.1, 135.2, 135.8, 135.9, 139.3, 142.7 (C). IR (KBr, cm^{-1}): ν = 3019, 2962, 2919, 2964, 1512, 1494, 1361, 1264, 1111, 1020 (w), 904 (m), 818 (s), 803, 753, 746, 726 (m), 647, 617, 572 (w), 545 (m). GC-MS (EI, 70 eV): m/z (%) = 354(100) [M^+], 339(12), 324(11). HRMS (EI, 70 eV): calcd for $C_{25}H_{22}S$ [M^+]: 354.14367; found: 354.14355.

2,3,4-Tris(3,5-dimethylphenyl)thiophene (12b):



Starting with **9** (0.08 g, 0.25 mmol) and 3,5-dimethyl phenylboronic acid (0.150 g, 1.0 mmol), **12b** was isolated (0.085 g, 86%) as a white solid, mp. = 113-115 °C. ^{1}H NMR (300 MHz, $CDCl_3$): δ = 2.06 (s, 6H, $2CH_3$), 2.11 (s, 12H, $4CH_3$), 6.56 (br, 2H, ArH), 6.66 (br, 2H, ArH), 6.72-6.74 (m, 3H, ArH), 6.77 (s, 2H, ArH), 7.15 (s, 1H, $CH_{thiophene}$). ^{13}C NMR (75 MHz, $CDCl_3$): δ = 20.1 ($2CH_3$), 20.2 ($4CH_3$), 120.0 (CH), 125.8 (2CH), 126.0 (2CH), 127.0, 127.1 (CH), 127.6 (2CH), 127.7 (CH), 133.5, 135.1, 135.8 (C), 135.9 (2C), 136.0 (2C), 136.4 (2C), 136.5, 139.3, 142.9 (C). IR (KBr, cm^{-1}): ν = 3004 (w), 2916 (m), 2856 (w), 1598 (m), 1455, 1375, 1260, 1080, 1036, 909 (w), 845 (s), 799, 754, 705, 698 (m), 667, 540 (w). GC-MS (EI, 70 eV): m/z (%) = 396(100) [M^+]. HRMS (EI, 70 eV): calcd for $C_{28}H_{28}S$ [M^+]: 396.19062; found: 396.19030.

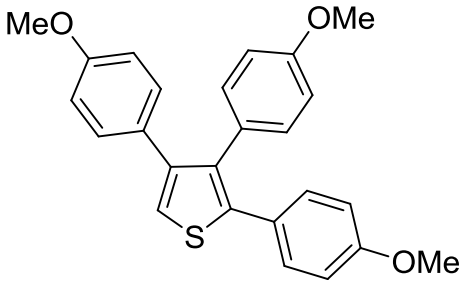
2,3,4-Tris(4-*tert*-butylphenyl)thiophene (12c):



Starting with **9** (0.08 g, 0.25 mmol) and 4-*tert*-butyl phenylboronic acid (0.178 g, 1.0 mmol), 12c was isolated (0.112 g, 94%) as a white solid, mp. = 168-170 °C. ^{1}H NMR (300 MHz, $CDCl_3$): δ = 1.20 (s, 9H, $3CH_3$), 1.21 (s, 9H, $3CH_3$), 1.22 (s, 9H, $3CH_3$), 6.87 (dd, 2H, J = 2.0, 6.5 Hz, ArH), 6.94 (dd, 2H, J = 2.0, 6.6 Hz, ArH), 7.06 (dd, 2H, J = 2.1, 6.5 Hz, ArH), 7.10 (dd, 4H, J = 2.0, 6.5 Hz, ArH), 7.13 (dd, 2H, J = 2.1, 6.5 Hz, ArH), 7.16 (s, 1H, $CH_{thiophene}$). ^{13}C NMR (62 MHz, $CDCl_3$): δ = 31.2 ($3CH_3$), 31.3 ($3CH_3$), 31.4 ($3CH_3$), 34.3, 34.4, 34.5 (C), 121.1 (CH), 124.7 (2CH), 124.8 (2CH), 125.1 (2CH), 128.5 (2CH), 128.7 (2CH), 130.4 (2CH), 131.8, 133.3, 134.2, 137.1, 140.2, 143.8, 149.3, 149.5, 149.9 (C). IR (KBr, cm^{-1}): ν = 2959 (m), 2900, 2864, 1520, 1493, 1460 (w), 1360, 1266 (m), 1199, 1110, 1021, 904 (w), 831

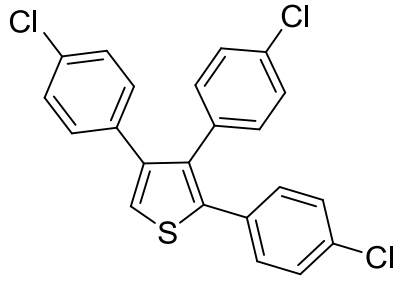
(s), 795, 757, 721, 684, 602, 580, 563, 542 (m). GC-MS (EI, 70 eV): m/z (%) = 480(100) [M^+], 466(26), 465(73), 57(14). HRMS (EI, 70 eV): calcd for $C_{34}H_{40}S$ [M^+]: 480.28452; found: 480.28570.

2,3,4-Tris(4-methoxyphenyl)thiophene (12d):



Starting with **9** (0.08 g, 0.25 mmol) and 4-methoxy phenyl boronic acid (0.152 g, 1.0 mmol), **12d** was isolated (0.096 g, 96%) as a white solid, mp. = 137-139 °C. ^{1}H NMR (300 MHz, $CDCl_3$): δ = 3.69 (s, 3H, OCH_3), 3.70 (s, 6H, $2OCH_3$), 6.63-6.70 (m, 6H, ArH), 6.84 (dd, 2H, *J* = 2.1, 6.6 Hz, ArH), 6.95 (dd, 2H, *J* = 2.1, 6.7 Hz, ArH), 7.06 (dd, 2H, *J* = 2.1, 6.7 Hz, ArH), 7.09 (s, 1H, $CH_{thiophene}$). ^{13}C NMR (62 MHz, $CDCl_3$): δ = 55.0, 55.1, 55.2 (OCH_3), 113.4 (2CH), 113.6 (2CH), 113.7 (2CH), 120.4 (CH), 127.3, 128.6, 129.8 (C), 130.1 (2CH), 130.5 (2CH), 132.0 (2CH), 136.3, 139.9, 143.3, 158.3, 158.4, 158.7 (C). IR (KBr, cm^{-1}): *ν* = 2998, 2930, 2833 (w), 1609 (m), 1571, 1532 (w), 1520, 1509, 1494, 1454, 1436, 1286 (m), 1244, 1173 (s), 1104 (m), 1029 (s), 952, 902, 876 (w), 824, 812 (s), 794, 785, 768, 750, 551 (m). GC-MS (EI, 70 eV): m/z (%) = 402(100) [M^+]. HRMS (EI, 70 eV): calcd for $C_{25}H_{22}O_3S$ [M^+]: 402.12897; found: 402.12812.

2,3,4-Tris(4-chlorophenyl)thiophene (12e):

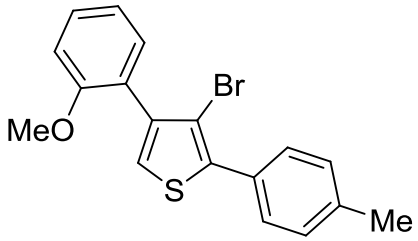


Starting with **9** (0.08 g, 0.25 mmol) and 4-chlorophenyl boronic acid (0.156 g, 1.0 mmol), **12e** was isolated (0.081 g, 78%) as a white solid, mp. = 238-240 °C. ^{1}H NMR (300 MHz, $CDCl_3$): δ = 6.82 (dd, 2H, *J* = 1.9, 6.5 Hz, ArH), 6.92 (dd, 2H, *J* = 1.9, 6.5 Hz, ArH), 7.02 (dd, 2H, *J* = 2.0, 6.6 Hz, ArH), 7.07-7.16 (m, 6H, ArH), 7.22 (s, 1H, $CH_{thiophene}$). ^{13}C NMR (62 MHz, $CDCl_3$): δ = 122.7 (CH), 128.4 (2CH), 128.7 (4CH), 130.2 (2CH), 130.5 (2CH), 132.0 (2CH), 132.5, 133.1, 133.2, 133.6, 133.9, 134.9, 136.2, 139.9, 142.4 (C). IR (KBr, cm^{-1}): *ν* = 1595, 1567, 1529, 1503 (w), 1490, 1478 (m), 1395, 1278, 1176 (w), 1089, 1013, 905 (m), 824 (s), 790, 755, 736, 711 (m), 676, 636, 580, 569 (w). GC-MS (EI, 70 eV): m/z (%) = 420(6) [M^+ (^{37}Cl, ^{37}Cl, ^{37}Cl)], 418(39) [M^+ (Cl, ^{37}Cl, ^{37}Cl)], 416(100) [M^+ (Cl, Cl, ^{37}Cl)], 414(99) [M^+ (Cl, Cl, Cl)], 346(14), 344(31), 309(10), 154(31), 153(14).

HRMS (EI, 70 eV): calcd for $C_{22}H_{13}Cl_3S$ [M^+ (Cl, Cl, ^{37}Cl)]: 415.97686 found: 415.97670. Anal. calcd for $C_{22}H_{13}Cl_3S$: C, 63.55; H, 3.15; S, 7.71. Found: C, 63.39; H, 3.25; S, 6.10.

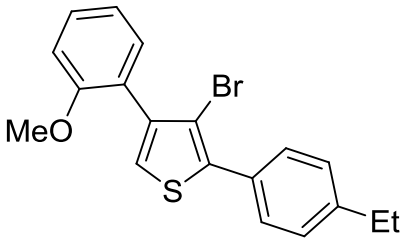
Synthesis of unsymmetrical 2,4-diaryl-3-bromothiophes (13):

3-Bromo-4-(2-methoxyphenyl)-2-*p*-tolylthiophene (13a):



Starting with **10a** (0.165 g, 0.5 mmol) and 2-methoxy phenyl boronic acid (0.083 g, 0.55 mmol), **13a** was isolated (0.155 g, 87%) as whitish solid, mp. = 80-82 °C. ^{1}H NMR (300 MHz, $CDCl_3$): δ = 2.32 (s, 3H, CH_3), 3.75 (s, 3H, OCH_3), 6.90-6.97 (m, 2H, ArH), 7.15-7.20 (m, 4H, ArH and $CH_{thiophene}$), 7.25-7.28 (m, 1H, ArH), 7.30-7.33 (m, 1H, ArH), 7.51 (dd, 1H, *J* = 1.7, 6.3 Hz, ArH). ^{13}C NMR (62 MHz, $CDCl_3$): δ = 21.3 (CH_3), 55.6 (OCH_3), 110.4 (CBr), 111.0, 120.3, 122.5 (CH), 125.3 (C), 129.1 (2CH), 129.2 (2CH), 129.6 (CH), 130.8 (C), 131.7 (CH), 138.1, 138.2, 140.2, 157.2 (C). IR (KBr, cm^{-1}): *v* = 3022, 2926, 2825, 1598, 1578, 1536, 1507 (w), 1478, 1457, 1427 (m), 1341, 1295, 1272 (w), 1239 (s), 1172, 1161, 1122, 1090, 1046 (m), 1025 (s), 890, 816, 787 (m), 763, 753, 727 (s), 694, 675, 631, 567, 539 (m). GC-MS (EI, 70 eV): m/z (%) = 360(100) [M^+ (^{81}Br)], 358(92) [M^+ (Br)], 279(21), 264(43), 246(17), 234(15), 221(12), 205(13), 202(14), 189(11), 117(12). HRMS (EI, 70 eV): calcd for $C_{18}H_{15}BrOS$, [M^+ (Br)]: 358.00215; found: 358.00153.

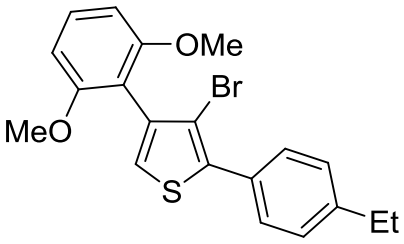
3-Bromo-2-(4-ethylphenyl)-4-(2-methoxyphenyl)thiophene (13b):



Starting with **10b** (0.173 g, 0.5 mmol) and 2-methoxyphenyl boronic acid (0.083 g, 0.55 mmol), **13b** was isolated (0.151 g, 81%) as a brownish oil. ^{1}H NMR (300 MHz, $CDCl_3$): δ = 1.19 (t, 3H, *J* = 7.6 Hz, CH_3), 2.60 (q, 2H, *J* = 7.6 Hz, CH_2), 3.72 (s, 3H, OCH_3), 6.88-6.95 (m, 2H, ArH), 7.16-7.21 (m, 4H, ArH and $CH_{thiophene}$), 7.25-7.32 (m, 1H, ArH), 7.53 (d, 2H, *J* = 8.2 Hz, ArH). ^{13}C NMR (62 MHz, $CDCl_3$): δ = 14.3 (CH_3), 27.6 (CH_2), 54.5 (OCH_3), 109.3 (CBr), 110.0, 119.2, 121.5 (CH), 124.2 (C), 126.9 (2CH), 128.3 (2CH), 128.5 (CH), 129.9 (C), 130.7 (CH), 137.2, 139.2, 143.3, 156.2 (C). IR (KBr, cm^{-1}): *v* = 3098, 2960, 2929, 2832, 1600, 1579, 1537, 1513 (w), 1483, 1459, 1432 (m), 1373, 1335, 1291 (w), 1273 (m), 1243 (s), 1178, 1160, 1121, 1091, 1047, 1024, 893, 832, 798 (m), 749

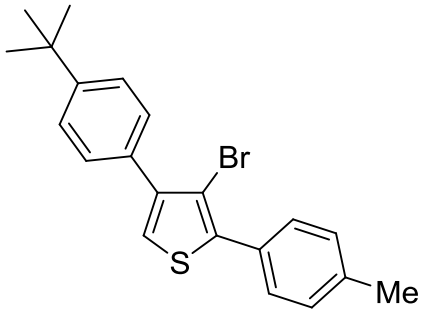
(s), 632, 571 (m). GC-MS (EI, 70 eV): m/z (%) = 374(100) [M^+ (^{81}Br)], 373(23), 372(97) [M^+ (Br)], 359(15), 357(15), 293(18), 278(17), 264(23), 263(51), 247(16), 234(11), 231(11), 202(14), 189(11). HRMS (EI, 70 eV): calcd for $C_{19}H_{17}BrOS$, [M^+ (^{81}Br)]: 374.01575; found: 374.01516.

3-Bromo-4-(2,6-dimethoxyphenyl)-2-(4-ethylphenyl)thiophene (13c):



Starting with **10b** (0.173 g, 0.5 mmol) and 2,6-dimethoxy phenyl boronic acid (0.100 g, 0.55 mmol), **13c** was isolated (0.106 g, 53%) as brownish oil. ^{1}H NMR (300 MHz, $CDCl_3$): δ = 1.19 (t, 3H, *J* = 7.6 Hz, CH_3), 2.60 (q, 2H, *J* = 7.6 Hz, CH_2), 3.68 (s, 6H, $2OCH_3$), 6.56 (d, 2H, *J* = 8.4 Hz, ArH), 7.18 (d, 2H, *J* = 8.3 Hz, ArH), 7.11 (s, 1H, $CH_{thiophene}$), 7.21-7.27 (m, 2H, ArH), 7.56 (dd, 1H, *J* = 1.8, 6.4 Hz, ArH). ^{13}C NMR (62 MHz, $CDCl_3$): δ = 14.3 (CH_3), 27.6 (CH_2), 54.9 ($2OCH_3$), 103.0 (2CH), 110.2 (CBr), 112.8 (C), 122.0 (CH), 126.8 (2CH), 128.2 (2CH), 128.8 (CH), 130.1, 134.8, 136.5, 143.1 (C), 157.5 (2C). IR (KBr, cm^{-1}): *v* = 3000, 2960, 2931, 2834 (w), 1585 (m), 1469 (s), 1430 (m), 1329, 1285 (w), 1247 (s), 1207, 1171, 1150 (w), 1105 (s), 1108, 1033, 892, 831, 778, 752, 722, 695, 540 (m). GC-MS (EI, 70 eV): m/z (%) = 404(100) [M^+ (^{81}Br)], 402(94) [M^+ (Br)], 323(22), 308(21), 293(30), 278(19), 201(11), 147(10). HRMS (EI, 70 eV): calcd for $C_{20}H_{19}BrO_2S$, [M^+ (^{81}Br)]: 404.02632; found: 404.02691.

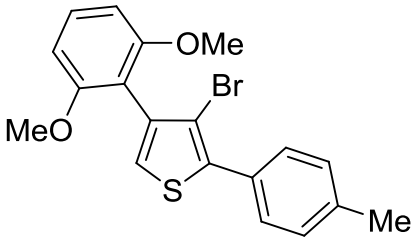
3-Bromo-4-(4-*tert*-butylphenyl)-2-*p*-tolylthiophene (13e):



Starting with **10a** (0.166 g, 0.5 mmol) and 4-*tert*-butyl phenyl boronic acid (0.098 g, 0.55 mmol), **13e** was isolated (0.110 g , 57%) as a white solid, mp. = 81-83 °C.^{1}H NMR (300 MHz, $CDCl_3$): δ = 1.28 (s, 9H, $3CH_3$), 2.31 (s, 3H, CH_3), 7.15-7.18 (m, 3H, ArH and $CH_{thiophene}$), 7.37 (br, 4H, ArH), 7.47 (d, 2H, *J* = 8.0 Hz, ArH). ^{13}C NMR (75 MHz, $CDCl_3$): δ = 21.4 (CH_3), 31.4 ($3CH_3$), 34.7 (C), 108.9 (CBr), 121.7 (CH), 125.1 (2CH), 128.9 (2CH), 129.3 (2CH), 129.4 (2CH), 130.8, 133.2, 138.3, 139.3, 143.2, 150.7 (C). IR (KBr, cm^{-1}): *v* = 2957 (m), 2902, 2862, 1536 (w), 1492 (m), 1472, 1461, 1392, 1361, 1336, 1306, 1267, 1114, 1018 (w), 895, 831 (m), 818 (s), 798, 759 (m), 735 (s), 714, 588, 570, 558 (m). GC-MS (EI, 70 eV): m/z

(%) = 386(64) [M^+ (^{81}Br)], 384(60) [M^+ (Br)], 371(100) [M^+], 369(96), 290(14), 275(10), 171(14). HRMS (EI, 70 eV): calcd for $C_{21}H_{21}BrS$ [M^+ (^{81}Br)]: 386.05214; found: 386.05169.

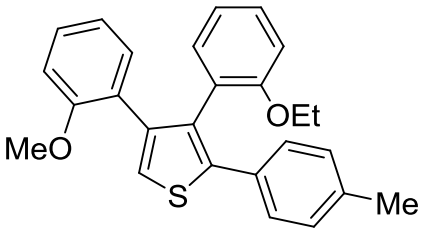
3-Bromo-4-(2,6-dimethoxyphenyl)-2-*p*-tolylthiophene (13f):



Starting with **10a** (0.166 g, 0.5 mmol) and 2,6-dimethoxy phenyl boronic acid (0.100 g, 0.55 mmol), **13f** was isolated (0.089 g, 46%) as a brownish oil. ^{1}H NMR (300 MHz, $CDCl_3$): δ = 2.30 (s, 3H, CH_3), 3.68 (s, 3H, OCH_3), 3.70 (s, 3H, OCH_3), 6.56 (d, 2H, *J* = 8.4 Hz, ArH), 7.11 (s, 1H, $CH_{thiophene}$), 7.13-7.16 (m, 2H, ArH), 7.21-7.27 (m, 2H, ArH), 7.53 (dd, 1H, *J* = 1.7, 6.5 Hz, ArH). ^{13}C NMR (62 MHz, $CDCl_3$): δ = 20.3 (CH_3), 54.9 ($2OCH_3$), 103.0 (2CH), 110.2 (CBr), 112.8 (C), 122.0 (CH), 128.0 (2CH), 128.1 (2CH), 128.7 (CH), 128.8, 129.9, 134.8, 136.8 (C), 157.5 (2C). IR (KBr, cm^{-1}): *v* = 3099, 2927, 2829 (w), 1585, 1469, 1427 (m), 1334, 1299, 1282 (w), 1248 (s), 11198, 1182, 1171 (w), 1112 (s), 1076, 1034, 1019 889, 823, 800, 775, 761, 714, 595, 541 (m). GC-MS (EI, 70 eV): m/z (%) = 390(100) [M^+ (^{81}Br)], 388(94) [M^+ (Br)], 309(22), 294(30), 279(11), 276(11), 263(14), 221(10), 187(11), 147(13). HRMS (EI, 70 eV): calcd for $C_{19}H_{17}BrO_2S$, [M^+ (^{81}Br)]: 390.01067; found: 390.01087.

Synthesis of unsymmetrical 2,3,4-triarylthiophenes (14):

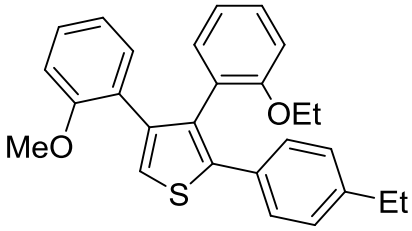
3-(2-Ethoxyphenyl)-4-(2-methoxyphenyl)-2-*p*-tolylthiophene (14a):



Starting with **13a** (0.090 g, 0.25 mmol) and 2-ethoxy phenyl boronic acid (0.083 g, 0.5 mmol), **14a** was isolated (0.092 g, 92%) as a brown oil. ^{1}H NMR (300 MHz, CDCl3): δ = 0.85 (t, 3H, *J* = 7.0 Hz, CH_3), 2.19 (s, 3H, CH_3), 3.33 (s, 3H, OCH_3), 3.44-3.51 (m, 2H, CH_2O), 6.61 (t, 2H, *J* = 7.6 Hz, ArH), 6.70-6.76 (m, 1H, ArH), 6.78-6.81 (m, 1H, ArH), 6.90 (d, 2H, *J* = 8.0 Hz, ArH), 6.98-7.01 (m, 1H, ArH), 7.02 (m, 5H, ArH), 7.20 (s, 1H, $CH_{thiophene}$). ^{13}C NMR (75 MHz, CDCl3): δ = 14.4, 21.2 (CH_3), 54.9 (OCH_3), 63.1 (CH_2O), 110.5, 111.4, 119.8, 119.9, 122.0 (CH), 126.2, 126.7 (C), 128.0, 128.2 (CH), 128.4 (2CH), 128.8 (2CH), 131.3, 132.2 (CH), 134.7 (C), 136.5 (2C), 139.9, 140.8, 156.4, 156.6 (C). IR (KBr, cm^{-1}): v = 3051, 2975, 2921, 2831, 1598, 1579, 1539 (w), 1500, 1483, 1446, 1433, 1260 (m), 1240 (s), 1178,

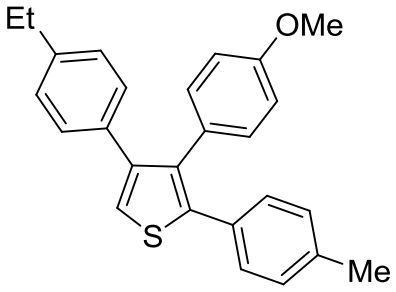
1159 (w), 1116, 1043, 1026 (m), 926, 900 (w), 808 (m), 746 (s), 658 (w), 633 (m), 573, 561 (w). GC-MS (EI, 70 eV): m/z (%) = 400(100) [M^+], 295(15). HRMS (EI, 70 eV): calcd for $C_{26}H_{24}O_2S$ [M^+]: 400.14915; found: 400.14894.

3-(2-Ethoxyphenyl)-2-(4-ethylphenyl)-4-(2-methoxyphenyl)thiophene (14b):



Starting with **13b** (0.093 g, 0.25 mmol) and 2-ethoxyphenyl boronic acid (0.083 g, 0.5 mmol), **14b** was isolated (0.090 g, 87%) as a brown oil. ^{1}H NMR (300 MHz, CDCl3): δ = 0.85 (t, 3H, *J* = 7.0 Hz, CH_3), 1.09 (t, 3H, *J* = 7.6 Hz, CH_3), 2.49 (q, 2H, *J* = 7.6 Hz, CH_2), 3.31 (s, 3H, OCH_3), 3.43-3.52 (m, 2H, CH_2O), 6.57 (m, 3H, ArH), 6.70-6.76 (m, 1H, ArH), 6.79 (dd, 1H, *J* = 1.7, 7.7 Hz, ArH), 6.93 (d, 2H, *J* = 8.3 Hz, ArH), 6.99 (dd, 1H, *J* = 1.8, 7.5 Hz, ArH), 7.04-7.09 (m, 4H, ArH), 7.19 (s, 1H, $CH_{thiophene}$). ^{13}C NMR (62 MHz, CDCl3): δ = 13.2, 14.2 (CH_3), 27.5 (CH_2), 53.8 (OCH_3), 62.0 (CH_2O), 109.4, 110.3, 118.7, 113.9, 120.9 (CH), 125.2, 125.7 (C), 126.5 (2CH), 126.9, 127.2 (CH), 127.3 (2CH), 130.3, 131.1 (CH), 132.0, 133.5, 138.8, 139.8, 141.8, 155.3, 155.5 (C). IR (KBr, cm^{-1}): v = 2961, 2928, 2831, 1598, 1579 (w), 1500, 1483, 1457, 1446, 1260 (m), 1240 (s), 1178, 1159 (w), 1117, 1046, 1026 (m), 926, 900 (w), 834, 814 (m), 746 (s), 658, 623, 567, 532 (w). GC-MS (EI, 70 eV): m/z (%) = 414(100) [M^+], 295(10). HRMS (EI, 70 eV): calcd for $C_{27}H_{26}O_2S$ [M^+]: 414.16480; found: 414.16509.

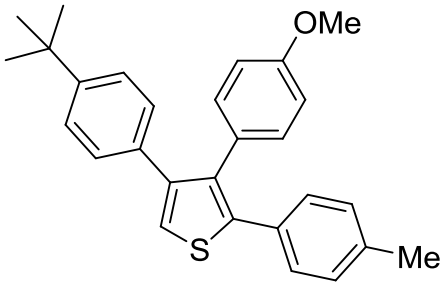
4-(4-Ethylphenyl)-3-(4-methoxyphenyl)-2-*p*-tolylthiophene (14d):



Starting with **13d** (0.089 g, 0.25 mmol) and 4-methoxy phenyl boronic acid (0.076 g, 0.5 mmol), **14d** was isolated (0.089 g, 93%) as a white solid, mp. = 125-127 °C. ^{1}H NMR (300 MHz, CDCl3): δ = 1.14 (t, 3H, *J* = 7.6 Hz, CH_3), 2.22 (s, 3H, CH_3), 2.53 (q, 2H, *J* = 7.6 Hz, CH_2), 3.69 (s, 3H, OCH_3), 6.64 (d, 2H, *J* = 8.7 Hz, ArH), 6.84 (d, 2H, *J* = 8.6 Hz, ArH), 6.93-6.96 (m, 6H, ArH), 7.02 (d, 2H, *J* = 8.1 Hz, ArH), 7.14 (s, 1H, $CH_{thiophene}$). ^{13}C NMR (62 MHz, CDCl3): δ = 15.3, 21.2 (CH_3), 28.5 (CH_2), 55.1 (OCH_3), 113.5 (2CH), 121.2 (CH), 127.4 (2CH), 128.5 (C), 128.8 (2CH), 128.9 (2CH), 129.2 (2CH), 131.9 (2CH), 135.5, 136.8 (C), 136.8 (2C), 140.2, 142.5, 143.7, 158.3 (C). IR (KBr, cm^{-1}): v = 2964, 2930, 2831 (w), 1607 (m), 1573, 1540 (w), 1512, 1495, 1460 (m), 1440, 1376, 1361 (w), 1284 (m), 1241 (s), 1170, 1034, 1020, 904 (m), 826, 820, 804 (s), 778, 754, 728, 711,

647, 564, 548, 528 (m). GC-MS (EI, 70 eV): m/z (%) = 384(100) [M^+]. HRMS (EI, 70 eV): calcd for $C_{26}H_{24}OS$ [M^+]: 384.15424; found: 384.15413.

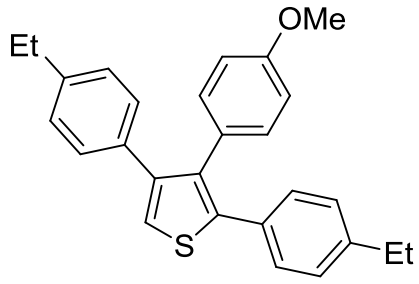
4-(4-*tert*-Butylphenyl)-3-(4-methoxyphenyl)-2-*p*-tolylthiophene (14e):



Starting with **13e** (0.096 g, 0.25 mmol) and 4-methoxy phenylboronic acid (0.076 g, 0.5 mmol), **14e** was isolated (0.099 g, 96%) as a brown oil. ^{1}H NMR (250 MHz, $CDCl_3$): δ = 1.21 (s, 9H, $3CH_3$), 2.21 (s, 3H, CH_3), 3.68 (s, 3H, OCH_3), 6.63 (d, *J* = 8.8 Hz, 2H, ArH), 6.85 (d, 2H, *J* = 8.8 Hz, ArH), 6.92-6.97 (m, 4H, ArH), 7.02 (d, 2H, *J* = 8.1 Hz, ArH), 7.11-7.15 (m, 3H, ArH and $CH_{thiophene}$). ^{13}C NMR (62 MHz, $CDCl_3$): δ = 20.1 (CH_3), 30.3 ($3CH_3$), 33.3 (C), 54.0 (OCH_3), 112.5 (2CH), 120.2 (CH), 123.8 (2CH), 127.5 (2CH), 127.6 (C), 127.9 (2CH), 128.1 (2CH), 130.9 (2CH), 133.1, 135.6 (C), 135.8 (2C), 139.1, 142.6, 148.4, 157.3 (C). IR (KBr, cm^{-1}): *ν* = 2952, 2902, 2835 (w), 1608 (m), 1573, 1537 (w), 1512, 1495, 1462 (m), 1439, 1360, 1282 (w), 1243 (s), 1173, 1031, 1020 (m), 904 (w), 820, 803 (s), 756, 726, 567, 565, 553, 544 (m). GC-MS (EI, 70 eV): m/z (%) = 412(100) [M^+], 398(17), 397(56). HRMS (EI, 70 eV): calcd for $C_{28}H_{28}OS$ [M^+]: 412.18554; found: 412.18562.

Synthesis of unsymmetrical 2,3,4-triarylthiophenes (15):

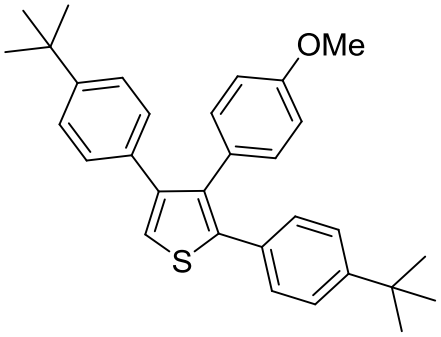
2,4-Bis(4-ethylphenyl)-3-(4-methoxyphenyl)thiophene (15a):



Starting with **11b** (0.093 g, 0.25 mmol) and 4-methoxy phenylboronic acid (0.076 g, 0.5 mmol), **15a** was isolated (0.091 g, 92%) as a whitish semi solid. ^{1}H NMR (250 MHz , $CDCl_3$): δ = 1.13 (t, 6H, *J* = 7.8 Hz, $2CH_3$), 2.52 (q, 4H, *J* = 7.6 Hz, $2CH_2$), 3.68 (s, 3H, OCH_3), 6.64 (d, 2H, *J* = 8.7 Hz, ArH), 6.85 (d, 2H, *J* = 8.7 Hz, ArH), 6.95-6.98 (m, 6H, ArH), 7.05 (d, 2H, *J* = 8.1 Hz, ArH), 7.14 (s, 1H, $CH_{thiophene}$). ^{13}C NMR (62 MHz, $CDCl_3$): δ = 15.2, 15.3 (CH_3), 28.5 ($2CH_2$), 55.1 (OCH_3), 113.5 (2CH), 121.2 (CH), 127.4 (2CH), 127.8 (2CH), 128.6 (C), 128.9 (2CH), 129.2 (2CH), 131.9 (2CH), 132.1, 134.5, 136.6, 140.2, 142.5, 143.1, 143.8, 158.3 (C). IR (KBr, cm^{-1}): *ν* = 2960, 2929, 2855 (w), 1607 (m), 1573, 1538 (w), 1511, 1495, 1460, 1435 (m), 1407, 1375, 1330 (w), 1284 (m), 1241 (s),

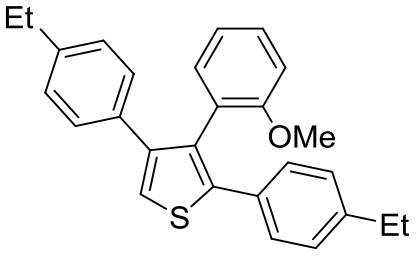
1171, 1116, 1101, 1071, 1035, 1020 (m), 963, 904, 868 (w), 825, 805 (s), 784, 754, 736, 720, 694, 617, 588, 567, 547 (m). GC-MS (EI, 70 eV): m/z (%) = 398(100) [M^+], 383(14). HRMS (EI, 70 eV): calcd for $C_{27}H_{26}OS$ [M^+]: 398.16989; found: 398.16960.

2,4-Bis(4-*tert*-butylphenyl)-3-(4-methoxyphenyl)thiophene (15b):



Starting with **11d** (0.106 g, 0.25 mmol) and 4-methoxy phenylboronic acid (0.076 g, 0.5 mmol), **15b** was isolated (0.098 g, 87%) as yellowish semi solid. ^{1}H NMR (300 MHz, $CDCl_3$): δ = 1.21 (s, 18H, $6CH_3$), 3.70 (s, 3H, OCH_3), 6.65 (d, 2H, *J* = 8.8 Hz, ArH), 6.87 (d, 2H, *J* = 8.8 Hz, ArH), 6.96 (d, 2H, *J* = 8.3 Hz, ArH), 7.06 (dd, 2H, *J* = 1.8, 6.8 Hz, ArH) 7.12-7.17 (m, 5H, ArH and $CH_{thiophene}$). ^{13}C NMR (62 MHz, $CDCl_3$): δ = 31.2 ($3CH_3$), 31.3 ($3CH_3$), 34.4, 34.5 (C), 55.1 (OCH_3), 113.5 (2CH), 121.2 (CH), 124.8 (2CH), 125.2 (2CH), 127.7 (C), 128.5 (2CH), 128.8 (2CH), 131.8 (C), 132.0 (2CH), 134.2, 137.0, 140.1, 143.7, 149.4, 149.9, 158.3 (C). IR (KBr, cm^{-1}): *v* = 2957 (m), 2902, 2864, 2831, 1607, 1537 (w), 1513, 1461, 1361, 1267 (m), 1241 (s), 1173, 1106, 1032, 1017 (m), 905, 875 (w), 831 (s), 802, 730, 722 (m), 688, 644, 600 (w), 579, 566, 547 (m) . GC-MS (EI, 70 eV): m/z (%) = 454(100) [M^+], 440(22), 439(62), 212(12). HRMS (EI, 70 eV): calcd for $C_{31}H_{34}OS$ [M^+]: 454.23249; found: 454.23281.

2,4-Bis(4-ethylphenyl)-3-(2-methoxyphenyl)thiophene (15c):

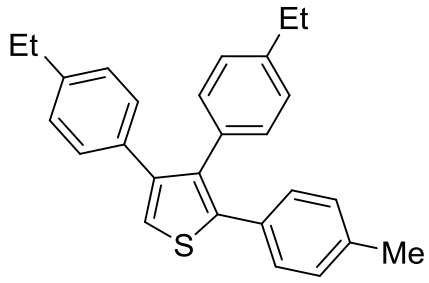


Starting with **11b** (0.093 g, 0.25 mmol) and 2-methoxy phenylboronic acid (0.076 g, 0.5 mmol), **15c** was isolated (0.079 g, 80%) as yellowish semi solid. ^{1}H NMR (300 MHz , $CDCl_3$): δ = 1.10 (t, 3H, *J* = 7.6 Hz, CH_3), 1.11 (t, 3H, *J* = 7.6 Hz, CH_3), 2.49 (q, 2H, *J* = 7.7 Hz, CH_2), 2.50 (q, 2H, *J* = 7.5 Hz, CH_2), 3.18 (s, 3H, OCH_3), 6.64-6.74 (m, 2H, ArH), 6.87 (dd, 1H, *J* = 1.8, 7.4 Hz, ArH), 6.93-6.96 (m, 6H, ArH), 7.06 (dd, 2H, *J* = 1.8, 6.3 Hz, ArH), 7.09-7.13 (m, 1H, ArH), 7.16 (s, 1H, $CH_{thiophene}$). ^{13}C NMR (62 MHz, $CDCl_3$): δ = 14.3, 14.5 (CH_3), 27.4 ($2CH_2$), 54.0 (OCH_3), 110.3, 119.5, 119.6 (CH), 124.7 (C), 126.2 (2CH), 126.6 (2CH), 127.0 (2CH), 127.5 (CH), 127.6 (2CH), 131.4 (C), 131.5 (CH), 132.5, 134.0, 139.9, 141.3, 142.0, 143.2, 156.5 (C). IR (KBr, cm^{-1}): *v* = 3054, 2963, 2929, 2835, 1598, 1579, 1537, 1503 (w), 1485, 1461, 1455, 1432 (m), 1411, 1283 (w),

1262, 1244, 1237 (m), 1178, 1158 (w), 1062, 1049 (m), 1022 (s), 974, (w), 904 (m), 832, 761, 744 (s), 657, 569, 529 (m). GC-MS (EI, 70 eV): m/z (%) = 398(100) [M^+], 383(17). HRMS (EI, 70 eV): calcd for $C_{27}H_{26}OS$ [M^+]: 398.16989; found: 398.16971.

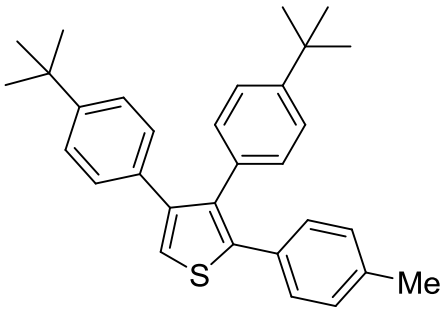
Synthesis of unsymmetrical 2,3,4-triarylthiophenes (16):

3,4-Bis(4-ethylphenyl)-2-*p*-tolylthiophene (16a):



Starting with **10a** (0.083 g, 0.25 mmol) and 4-ethyl phenyl boronic acid (0.112 g, 0.75 mmol), **16a** was isolated (0.088 g, 92%) as a brownish oil. ^{1}H NMR (300 MHz, $CDCl_3$): δ = 1.12 (t, 3H, *J* = 7.6 Hz, CH_3), 1.13 (t, 3H, *J* = 7.6 Hz, CH_3), 2.21 (s, 3H, CH_3), 2.52 (q, 4H, *J* = 7.8 Hz, $2CH_2$), 6.84 (d, 2H, *J* = 8.2 Hz, ArH), 6.90-6.94 (m, 8H, ArH), 7.02 (d, 2H, *J* = 8.2 Hz, ArH), 7.14 (s, 1H, $CH_{thiophene}$). ^{13}C NMR (62 MHz, $CDCl_3$): δ = 15.2, 15.3 (CH_3), 21.2 (CH_3), 28.4, 28.5 (CH_2), 121.2 (CH), 127.4 (2CH), 127.5 (2CH), 128.9 (2CH), 129.0 (2CH), 129.2 (2CH), 130.7 (2CH), 131.9, 133.4, 134.5, 136.8, 137.0, 140.3 (C), 142.5 (2C), 143.8 (C). IR (KBr, cm^{-1}): *ν* = 2966, 2928, 2852, 1538, 1512, 1494, 1452, 1374, 1115, 1019, 961, 904 (w), 829, 817, 803 (s), 753, 733 (m), 709, 645, 615 (w), 586, 570, 550, 528 (m). GC-MS (EI, 70 eV): m/z (%) = 382(100) [M^+]. HRMS (EI, 70 eV): calcd for $C_{27}H_{26}S$ [M^+]: 382.17497; found: 382.17547.

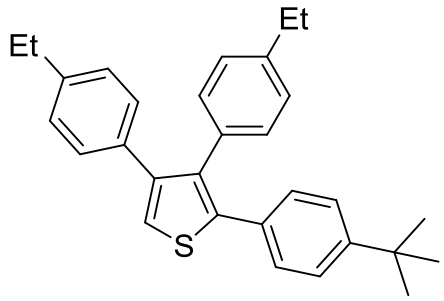
3,4-Bis(4-*tert*-butylphenyl)-2-*p*-tolylthiophene (16b):



Starting with **10a** (0.083 g, 0.25 mmol) and 4-*tert*-butyl phenyl boronic acid (0.133 g, 0.75 mmol), **16b** was isolated (0.095 g, 87%) as whitish solid, mp. = 184-186 °C. ^{1}H NMR (300 MHz, $CDCl_3$): δ = 1.20 (s, 18H, $6CH_3$), 2.22 (s, 3H, CH_3), 6.86 (dd, 2H, *J* = 2.0, 6.6 Hz, ArH), 6.91-6.96 (m, 4H, ArH), 7.02 (dd, 2H, *J* = 1.7, 6.3 Hz, ArH), 7.08-7.13 (m, 4H, ArH) 7.24 (s, 1H, $CH_{thiophene}$). ^{13}C NMR (62 MHz, $CDCl_3$): δ = 21.2 (CH_3), 31.3 ($3CH_3$), 31.4 ($3CH_3$), 34.4, 34.5 (C), 121.1 (CH), 124.7 (2CH), 124.9 (2CH), 128.5 (2CH), 128.9 (2CH), 129.1 (2CH), 130.4 (2CH), 131.9, 133.2, 134.1, 136.8, 137.1, 140.3, 143.8, 149.4, 149.5 (C). IR (KBr, cm^{-1}): *ν* = 2959, 2901, 2864 (m), 1520, 1492, 1434, 1392 (w), 1360, 1264, 1200, 1192, 1111,

1089, 1068, 1017 (m), 965, 944 (w), 906, 877 (m),832, 822, 803 (s), 777, 761 (m), 740, 694 (s), 640, 607, 579, 568, 556, 540 (m). GC-MS (EI, 70 eV): m/z (%) = 438(100) [M^+], 424(24), 423(71), 204(11), 57(14). HRMS (EI, 70 eV): calcd for $C_{31}H_{34}S$ [M^+]: 438.23757; found: 438.23746.

2-(4-*tert*-Butylphenyl)-3,4-bis(4-ethylphenyl)thiophene (16c):

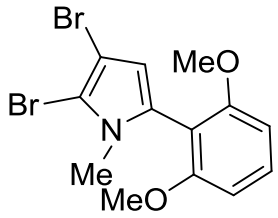


Starting with **10c** (0.094 g, 0.25 mmol) and 4-ethyl phenyl boronic acid (0.112 g, 0.75 mmol), **16c** was isolated (0.088 g, 83%) as whitish solid, mp. = 125-127 °C. ^{1}H NMR (300 MHz, $CDCl_3$): δ = 1.13 (t, 3H, *J* = 7.6 Hz, CH_3), 1.14 (t, 3H, *J* = 7.6 Hz, CH_3), 1.21 (s, 9H, $3CH_3$), 2.53 (q, 2H, *J* = 7.6 Hz, CH_2), 2.54 (q, 2H, *J* = 7.6 Hz, CH_2), 6.85 (dd, 2H, *J* = 2.0, 6.3 Hz, ArH), 6.92-6.93 (m, 6H, ArH), 7.06 (dd, 2H, *J* = 2.1, 6.6 Hz, ArH), 7.12-7.17 (m, 3H, ArH and $CH_{thiophene}$). ^{13}C NMR (62 MHz, $CDCl_3$): δ = 15.2, 15.3 (CH_3), 28.4, 28.5 (CH_2), 31.3 ($3CH_3$), 34.5 (C), 121.2 (CH), 125.1 (2CH), 127.3 (2CH), 127.5 (2CH), 128.8 (2CH), 128.9 (2CH), 130.7 (2CH), 131.8, 133.5, 134.5, 137.0, 140.3 (C), 142.5 (2C), 143.8, 149.9 (C). IR (KBr, cm^{-1}): *ν* = 2962 (m), 2925, 2871, 1538, 1493, 1455, 1360, 1266, 1116, 1017, 936, 904 (m), 829 (s), 802, 760, 750, 698, 571, 559 (m). GC-MS (EI, 70 eV): m/z (%) = 424(100) [M^+], 410(28), 409(87). HRMS (EI, 70 eV): calcd for $C_{30}H_{32}S$ [M^+]: 424.22192; found: 424.22141.

General procedure for synthesis of 5-aryl-2,3-dibromo-*N*-methylpyrroles (19):

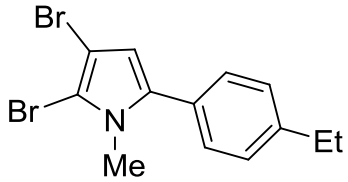
To a mixture of **18** (0.159 g, 0.5 mmol), aryl boronic acid (0.55 mmol), and $Pd(PPh_3)_4$ (29 mg, 5 mol-%) was added a mixture of 1,4-dioxane and toluene (1:1; 5 mL) and K_3PO_4 (4.0 equiv, 424 mg) under an argon atmosphere. The reaction mixture was stirred at 100 °C for 8 h and was subsequently allowed to cool to 20 °C. The solution was poured into H_2O and EtOAc (25 mL each) and the organic and the aqueous layers were separated. The latter was extracted with EtOAc (3 × 25 mL), dried (Na_2SO_4), filtered, and concentrated in vacuo. The residue was purified by flash column chromatography (flash silica gel, eluent: *n*-heptane).

2,3-Dibromo-5-(2,6-dimethoxyphenyl)-1-methyl-1*H*-pyrrole (19a):



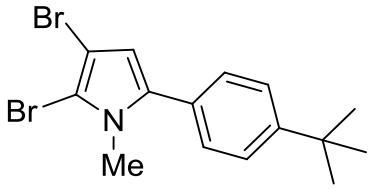
Starting with **18** (0.159 g, 0.5 mmol) and 2,6-dimethoxylphenyl boronic acid (0.100 g, 0.55 mmol), **19a** was isolated (0.080 g, 43%) as a white solid, mp. = 128-130°C. ^{1}H NMR (300 MHz, acetone-d_6): δ = 3.18 (s, 3H, NCH_3), 3.61 (s, 6H, $2OCH_3$), 5.97 (s, 1H, $CH_{pyrrole}$), 6.60 (d, 2H, J = 8.4 Hz, ArH), 7.25 (t, 1H, J = 8.4 Hz, ArH). ^{13}C NMR (62 MHz, , acetone-d_6): δ = 34.4 (NCH_3), 56.1 ($2OCH_3$), 97.4, 103.1 (CBr), 104.9 (2CH), 110.0 (C), 112.8 (CH), 128.7 (C), 131.7 (CH), 160.2 (2C). IR (KBr, cm^{-1}): ν = 3003, 2936, 2834 (w), 1598, 1588 (m), 1472 (s), 1454, 1439 (m), 1430 (s), 1377, 1314, 1298, 1288 (m), 1250 (s), 1207, 1150 (m), 1102 (s), 1050, 1027, 1004, 945 (m), 782 (s), 761 (m), 734 (s), 712, 687, 600, 568 (m). GC-MS (EI, 70 eV): m/z (%) = 377(49) [M^+ (^{81}Br, ^{81}Br)], 375(100) [M^+ (^{81}Br, Br)], 373(51) [M^+ (Br, Br)], 296(13), 294(20), 281(10), 279(11), 266(13), 264(15), 215(17), 200(14), 148(23), 146(21). HRMS (EI, 70 eV): calcd for $C_{13}H_{13}Br_2NO_2$ [M^+ (Br, ^{81}Br)]: 374.92871; found: 374.92931.

2,3-Dibromo-5-(4-ethylphenyl)-1-methyl-1*H*-pyrrole (19b):



Starting with **18** (0.159 g, 0.5 mmol) and 4-ethylphenyl boronic acid (0.082 g, 0.55 mmol), **19b** was isolated (0.125 g, 73%) as a colorless oil. ^{1}H NMR (250 MHz, acetone-d_6): δ = 1.23 (t, 3H, J = 7.5 Hz, CH_3), 2.68 (q, 2H, J = 7.4 Hz, CH_2), 3.61 (s, 3H, NCH_3), 6.28 (s, 1H, $CH_{pyrrole}$), 7.32 (br, 4H, ArH). ^{13}C NMR (62 MHz, acetone-d_6): δ = 15.9 (CH_3), 29.1 (CH_2), 35.3 (NCH_3), 98.5, 105.4 (CBr), 111.3 (CH), 129.0 (2CH), 129.7 (2CH), 130.4, 137.5, 145.0 (C). IR (KBr, cm^{-1}): ν = 3018, 2961, 2869 (w), 1496, 1457 (s), 1437, 1375 (m), 1318 (s), 1216, 1184, 1135 (w), 1089 (m), 1059, 1008 (w), 943 (m), 833, 774 (s), 744, 667, 619 (w), 600, 560, 530 (m). GC-MS (EI, 70 eV): m/z (%) = 345(49) [M^+ (^{81}Br, ^{81}Br)], 343(100) [M^+ (^{81}Br, Br)], 341(51) [M^+ (Br, Br)], 330(32), 328(63), 326(34). HRMS (EI, 70 eV): calcd for $C_{13}H_{13}Br_2N$ [M^+ (Br, Br)]: 340.94093; found: 340.94196.

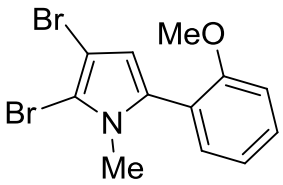
2,3-Dibromo-5-(4-*tert*-butylphenyl)-1-methyl-1*H*-pyrrole (19c):



Starting with **18** (0.159 g, 0.5 mmol) and 4-*tert*-butylphenyl boronic acid (0.098 g, 0.55 mmol), **19c** was isolated (0.118 g, 64%) as a colorless oil. ^{1}H NMR (250 MHz, acetone-d_6): δ = 1.34 (s, 9H, $3CH_3$), 3.61 (s, 3H, NCH_3), 6.29 (s, 1H,

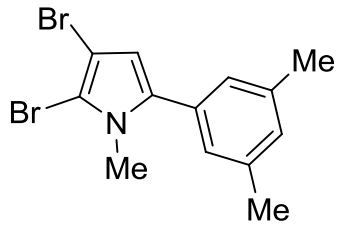
$CH_{pyrrole}$), 7.34 (d, 2H, J = 8.6 Hz, ArH), 7.49 (d, 2H, J = 8.6 Hz, ArH). ^{13}C NMR (62 MHz, acetone-d_6): δ = 31.6 ($3CH_3$), 35.2 (C), 35.4 (NCH_3), 98.5, 105.5 (CBr), 111.3 (CH), 126.4 (2CH), 129.4 (2CH), 130.2, 137.4, 151.7 (C). IR (KBr, cm^{-1}): v = 2959 (m), 2903, 2866, 1697, 1606, 1537 (w), 1499, 1456, 1362, 1318, 1265, 1109, 1086, 1017, 946 (m), 837, 779 (s), 741, 595, 574, 555 (m). GC-MS (EI, 70 eV): m/z (%) = 373(36) [M^+ ($^{8'}$Br, $^{8'}$Br)], 371(73) [M^+ ($^{8'}$Br, Br)], 369(36) [M^+ (Br, Br)], 358(49), 356(100), 354(53). HRMS (EI, 70 eV): calcd for $C_{15}H_{17}Br_2N$ [M^+ (Br, $^{8'}$Br)]: 370.97018; found: 370.97046.

2,3-Dibromo-5-(2-methoxyphenyl)-1-methyl-1*H*-pyrrole (19d):



Starting with **18** (0.159 g, 0.5 mmol) and 2-methoxyphenylboronic acid (0.083 g, 0.55 mmol), **19d** was isolated (0.105 g, 61%) as a colourless oil. ^{1}H NMR (300 MHz, acetone-d_6): δ = 3.32 (s, 3H, NCH_3), 3.72 (s, 3H, OCH_3), 6.13 (s, 1H, $CH_{pyrrole}$), 6.85-6.93 (m, 2H, ArH), 7.11 (dd, 1H, J = 1.6, 7.5 Hz, ArH), 7.26-7.32 (m, 1H, ArH). ^{13}C NMR (75 MHz, , acetone-d_6): δ = 34.6 (NCH_3), 55.5 (OCH_3), 97.7, 104.4 (CBr), 110.9, 111.3, 120.8 (CH), 121.2 (C), 130.2, 132.3 (CH), 132.7, 157.3 (C). IR (KBr, cm^{-1}): v = 3120, 2943, 2833, 1601, 1577, 1541 (w), 1486, 1459, 1452, 1430 (m), 1376 (w), 1317, 1292, 1275 (m), 1243 (s), 1178, 1161, 1116, 1086, 1050, 1023, 1006, 946 (m), 748 (s), 669, 601, 577 (w). GC-MS (EI, 70 eV): m/z (%) = 347(50) [M^+ ($^{8'}$Br, $^{8'}$Br)], 345(100) [M^+ ($^{8'}$Br, Br)], 343(51) [M^+ (Br, Br)], 289(12), 266(16), 264(22), 251(24), 249(25), 184(36), 170(13), 148(16), 127(12), 115(16). HRMS (EI, 70 eV): calcd for $C_{12}H_{11}Br_2NO$ [M^+ (Br, $^{8'}$Br)]: 344.91814; found: 344.91909.

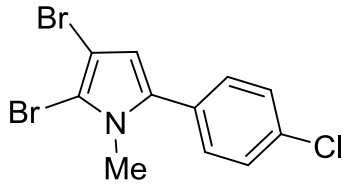
2,3-Dibromo-5-(3,5-dimethylphenyl)-1-methyl-1*H*-pyrrole (19e):



Starting with **18** (0.159 g, 0.5 mmol) and 3,5-dimethylphenyl boronic acid (0.082 g, 0.55 mmol), **19e** was isolated (0.099 g, 58%) as a colourless oil. ^{1}H NMR (300 MHz, acetone-d_6): δ = 2.21 (s, 3H, CH_3), 2.22 (s, 3H, CH_3), 3.50 (s, 3H, NCH_3), 6.16 (s, 1H, $CH_{pyrrole}$), 6.92 (s, 3H, ArH). ^{13}C NMR (75 MHz, acetone-d_6): δ = 21.3 ($2CH_3$), 35.4 (NCH_3), 98.4, 105.5 (CBr), 111.3 (CH), 127.4 (2CH), 130.3 (CH), 132.9, 137.7 (C), 138.9 (2C). IR (KBr, cm^{-1}): v = 3120, 2947, 2915, 2855 (w), 1600, 1466, 1450, 1372, 1322, 1302, 1273 (m), 1205, 1181 (w), 1086, 1036, 950 (m), 899 (w), 851, 840, 775, 695 (s), 663, 602 (m). GC-MS (EI, 70 eV): m/z (%) = 345(49) [M^+ ($^{8'}$Br,

$^{8'}$Br)], 34(100) [M^+ ($^{8'}$Br, Br)], 341(52) [M^+ (Br, Br)], 183(10), 168(13). HRMS (EI, 70 eV): *m/z* [M^+ (Br, $^{8'}$Br)] calcd for $C_{13}H_{13}Br_2N$: 342.93888; found: 342.939847.

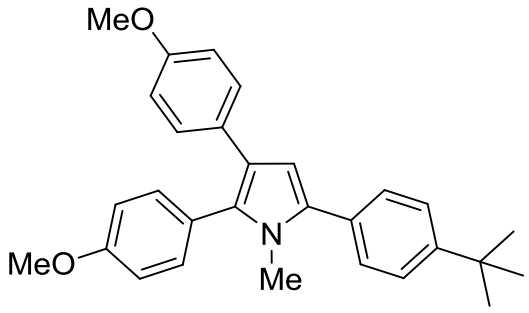
2,3-Dibromo-5-(4-chlorophenyl)-1-methyl-1*H*-pyrrole (19f):



Starting with **18** (0.159 g, 0.5 mmol) and 4-chlorophenyl boronic acid (0.086 g, 0.55 mmol), **19f** was isolated (0.072 g, 41%) as a colourless oil. ^{1}H NMR (300 MHz, , acetone-d_6): δ = 3.50 (s, 3H, NCH_3), 6.23 (s, 1H, $CH_{pyrrole}$), 7.32-7.34 (m, 4H, ArH). ^{13}C NMR (62 MHz, acetone-d_6): δ = 35.5 (NCH_3), 98.7, 106.5 (CBr), 111.9 (CH), 129.6 (2CH), 131.2 (2CH), 131.7, 134.2, 136.0 (C). IR (KBr, cm^{-1}): *v* = 3103, 2922, 2851 (w), 1593, 1562, 1463 (m), 1425, 1385 (w), 1307 (m), 1260, 1164, 1095 (w), 1078, 995 (m), 877, 766, 737, 682 (s), 636 (m).. GC-MS (EI, 70 eV): m/z (%) = 354(10) [M^+ ($^{8'}$Br, $^{8'}$Br,^{37}Cl)], 352(66) [M^+ ($^{8'}$Br, $^{8'}$Br, Cl); (Br, $^{8'}$Br, ^{37}Cl)], 350(100) [M^+ (Br, $^{8'}$Br,Cl); (Br, Br,^{37}Cl)], 348(37) [M^+ (Br, Br, Cl)], 273(39), 272(11), 271(33), 230(11), 175(10). HRMS (EI, 70 eV): calcd for $C_{11}H_8Br_2ClNS$ [M^+ ($^{8'}$Br, $^{8'}$Br, ^{35}Cl)]: 350.86656; found: 350.87303; [M^+ (Br, $^{8'}$Br, ^{37}Cl)]: 350.86566; found: 350.81418.

Synthesis of unsymmetrical 2,4,5-triarylmethyl-1*H*-pyrroles (20):

5-(4-*tert*-Butylphenyl)-2,3-bis(4-methoxyphenyl)-1-methyl-1*H*-pyrrole (20):



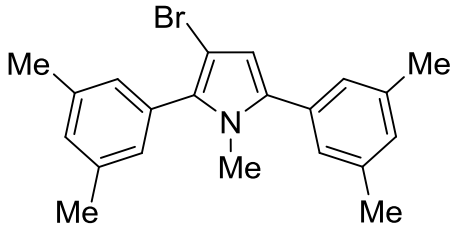
Starting with **19c** (0.093 g, 0.25 mmol) and 4-methoxyphenylboronic acid (0.114 g, 0.75 mmol) , **20a** was isolated (0.077 g, 74%) as a yellowish oil. ^{1}H NMR (300 MHz, $CDCl_3$): δ = 1.29 (s, 9H, $3CH_3$), 3.30 (s, 3H, NCH_3), 3.68 (s, 3H, OCH_3), 3.76 (s, 3H, OCH_3), 6.33 (s, 1H, $CH_{pyrrole}$), 6.67 (dd, 2H, *J* = 2.1, 6.8 Hz, ArH), 6.85 (dd, 2H, *J* = 2.1, 6.7 Hz, ArH), 7.07 (dd, 2H, *J* = 2.2, 6.7 Hz, ArH), 7.20 (dd, 2H, *J* = 2.2, 6.7 Hz, ArH), 7.36 (br, 4H, ArH). ^{13}C NMR (75 MHz, $CDCl_3$): δ = 31.4 ($3CH_3$), 33.6 (NCH_3), 34.6 (C), 55.1, 55.2 (OCH_3), 108.2 (CH), 113.6 (2CH), 114.0 (2CH), 122.1 (C), 125.3 (2CH), 125.6 (C), 128.5 (2CH), 128.8 (2CH), 129.3, 130.6, 131.4 (C), 132.4 (2CH), 135.2, 149.8, 157.3, 159.0 (C). IR (KBr, cm^{-1}): v = 2951, 2903, 2831, 1606, 1574, 1554 (w), 1514, 1496, 1455, 1439, 1287 (m), 1247, 1239, 1170 (s), 1105, 1037, 1011 (m), 831, 807, 801 (s), 766, 584, 558 (m). GC-MS (EI, 70 eV): m/z (%)

= 425(100) [M^+], 411(10), 410(36). HRMS (EI, 70 eV): calcd for $C_{29}H_{31}NO_2$ [M^+]: 425.23493; found: 425.23416.

Synthesis of 2,5-diaryl-3-bromo-*N*-methylpyrroles (21):

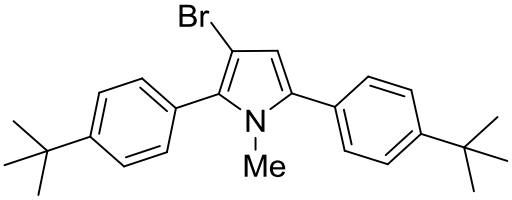
To a mixture of **18** (0.159 g, 0.5 mmol), aryl boronic acid (1.15 mmol) and $Pd(PPh_3)_4$ (29 mg, 5 mol-%) was added a mixture of 1,4-dioxane and toluene (1:1; 5 mL) and K_3PO_4 (4.0 equiv, 424 mg) under an argon atmosphere. The reaction mixture was stirred at 100 °C for 12 h and was subsequently allowed to cool to 20 °C. The solution was poured into H_2O and EtOAc (25 mL each) and the organic and the aqueous layers were separated. The latter was extracted with EtOAc (3 × 25 mL), dried (Na_2SO_4), filtered, and concentrated in vacuo. The residue was purified by flash column chromatography (flash silica gel, eluent: heptanes/EtOAc).

3-Bromo-2,5-bis(3,5-dimethylphenyl)-1-methyl-1*H*-pyrrole (21a):



Starting with **18** (0.159 g, 0.5 mmol) and 3,5-dimethyl phenyl boronic acid (0.172 g, 1.15 mmol), **21a** was isolated (0.077 g , 42%) as a colorless oil. ^{1}H NMR (300 MHz, acetone-d_6): δ = 2.34 (s, 3H, CH_3), 2.34 (s, 3H, CH_3), 2.35 (s, 3H, CH_3), 2.36 (s, 3H, CH_3), 3.48 (s, 3H, NCH_3), 6.26 (s, 1H, $CH_{pyrrole}$), 7.00 (s, 1H, ArH), 7.04 (s, 1H, ArH), 7.10 (s, 4H, ArH). ^{13}C NMR (75 MHz, acetone-d_6): δ = 21.3 ($2CH_3$), 21.4 ($2CH_3$), 35.0 (NCH_3), 95.9 (CBr), 111.4 (CH), 127.4 (2CH), 129.1 (2CH), 129.8, 130.2 (CH), 132.2, 133.3, 134.1, 136.9 (C), 138.6 (2C), 138.8 (2C). IR (KBr, cm^{-1}): v = 3005, 2918, 2856, 1711, 1679, 1663 (w), 1600, 1462 (m), 1376, 1330, 1270, 1191, 1038, 900 (w), 854, 841 (m), 780, 696, 659 (w). GC-MS (EI, 70 eV): m/z (%) = 369(100) [M^+ (^{81}Br)], 367(99) [M^+ (Br)], 272(10). HRMS (EI, 70 eV): *m/z* [M^+ (Br)] calcd for $C_{21}H_{22}BrN$: 367.09301; found: 367.09300.

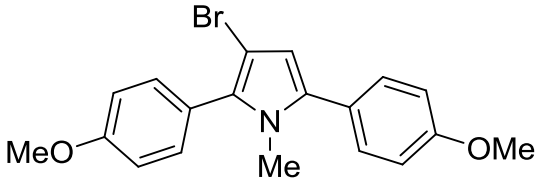
3-Bromo-2,5-bis(4-*tert*-butylphenyl)-1-methyl-1*H*-pyrrole (21b):



Starting with **18** (0.159 g, 0.5 mmol) and 4-*tert*-butylphenyl boronic acid (0.204 g, 1.15 mmol), **21b** was isolated (0.078 g, 37%) as brownish oil. ^{1}H NMR (250 MHz, acetone-d_6): δ = 1.20 (s, 9H, $3CH_3$), 1.21 (s, 9H, $3CH_3$), 3.34 (s, 3H, NCH_3), 6.15 (s, 1H, $CH_{pyrrole}$), 7.26 (d, 2H, *J* = 8.7 Hz, ArH), 7.27 (d, 2H, *J* = 8.7 Hz, ArH), 7.29 (m, 2H, ArH), 7.39 (d, 2H, *J* = 8.7 Hz, ArH). ^{13}C NMR (62 MHz, acetone-d_6): δ = 31.7 ($6CH_3$),

35.1 (NCH_3), 35.3 (2C), 96.1 (CBr), 111.4 (CH), 126.1 (2CH), 126.3 (2CH), 129.3 (2CH), 129.4, 130.6 (C), 131.0 (2CH), 133.8, 136.6, 151.1, 151.4 (C). IR (KBr, cm^{-1}): ν = 2957 (m), 2902, 2866, 1736 (w), 1496, 1460, 1361, 1322, 1264 (m), 1241, 1226, 1201 (w), 1111, 1016, 944 (m), 836 (s), 780 (m), 736 (s), 704 (m), 679, 632, 614 (w), 562 (s). GC-MS (EI, 70 eV): m/z (%) = 425(98) [M^+ (^{81}Br)], 423(100) [M^+ (Br)], 410(60), 409(17), 408(59), 314(12). HRMS (EI, 70 eV): calcd for $C_{25}H_{30}BrN$ [M^+ (Br)]: 423.15561; found: 423.15524.

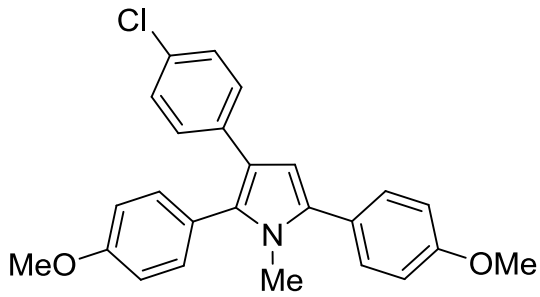
3-Bromo-2,5-bis(4-methoxyphenyl)-1-methyl-1*H*-pyrrole (21c):



Starting with **18** (0.159 g, 0.5 mmol) and 4-methoxyphenylboronic acid (0.204 g, 1.15 mmol), **21c** was isolated (0.107 g, 58%) as brownish oil. ^{1}H NMR (250 MHz, acetone-d_6): δ = 3.31 (s, 3H, NCH_3), 3.70 (s, 3H, OCH_3), 3.72 (s, 3H, OCH_3), 6.08 (s, 1H, $CH_{pyrrole}$), 6.87 (d, 2H, J = 8.9 Hz, ArH), 6.90 (d, 2H, J = 8.9 Hz, ArH), 7.25 (d, 2H, J = 8.9 Hz, ArH), 7.26 (d, 2H, J = 8.9 Hz, ArH). ^{13}C NMR (62 MHz, acetone-d_6): δ = 34.7 (NCH_3), 55.6 ($2OCH_3$), 95.8 (CBr), 110.8 (CH), 114.7 (2CH), 114.8 (2CH), 124.5, 125.9 (C), 130.9 (2CH), 132.6 (2CH), 133.2, 136.1, 160.2, 160.4 (C). IR (KBr, cm^{-1}): ν = 3117, 2934, 2834 (w), 1609, 1552 (m), 1494 (s), 1463, 1439 (m), 1411, 1320, 1320 (w), 1284, 1245, 1172 (s), 1107 (m), 1028 (s), 998, 940 (m), 831 (s), 797, 776, 665, 644, 593, 535 (m). MS (EI, 70 eV): m/z (%) = 373(100) [M^+ (^{81}Br)], 371(199) [M^+ (Br)], 358(44), 356(44), 293(19), 278(14). HRMS (EI, 70 eV): calcd for $C_{19}H_{18}BrNO_2$ [M^+ (Br)]: 371.05154; found: 371.05125.

Synthesis of unsymmetrical 2,4,5-triarylmethyl-1*H*-pyrroles (22):

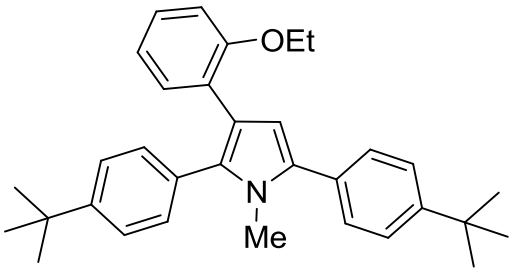
3-(4-Chlorophenyl)-2,5-bis(4-methoxyphenyl)-1-methyl-1*H*-pyrrole (22a):



Starting with **21c** (0.093 g, 0.25 mmol) and 4-chlorophenylboronic acid (0.074 g, 0.50 mmol), **22a** was isolated (0.072 g, 72%) as a yellowish solid, mp.= 165-166 °C. ^{1}H NMR (300 MHz, $CDCl_3$): δ = 3.32 (s, 3H, NCH_3), 3.74 (s, 3H, OCH_3), 3.75 (s, 3H, OCH_3), 6.29 (s, 1H, $CH_{pyrrole}$), 6.83 (dd, J = 2.1, 6.7 Hz, 2H, ArH), 6.88 (dd, J = 2.1, 6.7 Hz, 2H, ArH), 7.04 (br, 4H, ArH), 7.15 (dd, J = 2.1, 6.7 Hz, 2H, ArH), 7.31 (dd, J = 2.1, 6.9 Hz, 2H, ArH). ^{13}C NMR

(62 MHz, $CDCl_3$): δ = 33.4 (NCH_3), 55.2, 55.3 (OCH_3), 107.7 (CH), 113.9 (2CH), 114.2 (2CH), 121.1, 125.2, 125.8 (C), 128.2 (2CH), 128.8 (2CH), 130.1 (2CH), 130.6, 131.8 (C), 132.3 (2CH), 135.2 (2C), 158.9, 159.2 (C). IR (KBr, cm^{-1}): v = 2955, 2924, 2852, 1721 (w), 1668 (m), 1595 (s), 1572, 1509, 1490, 1461, 1422, 1307, 1286 (m), 1238, 1165 (s), 1114, 1014, 833, 821, 758, 607, 590 (m). GC-MS (EI, 70 eV): m/z (%) = 403(100) [M^+], 390(13), 388(34). HRMS (ESI): calcd for $C_{25}H_{23}ClNO_2$ [M+H]$^+$: 404.1412; found: 404.1410.

2,5-Bis(4-*tert*-butylphenyl)-3-(2-ethoxyphenyl)-1-methyl-1*H*-pyrrole (22b):



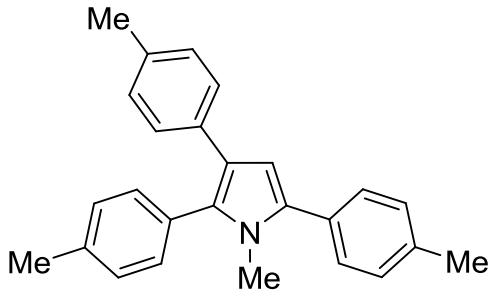
Starting with **21b** (0.106 g, 0.25 mmol) and 2-ethoxyphenylboronic acid (0.083 g, 0.50 mmol), **22b** was isolated (0.096 g, 83%) as a yellowish semi solid. ^{1}H NMR (300 MHz, $CDCl_3$): δ = 1.08 (t, 3H, *J* = 7.0 Hz, CH_3), 1.23 (s, 9H, $3CH_3$), 1.28 (s, 9H, $3CH_3$), 3.46 (s, 3H, NCH_3), 3.75 (q, 2H, *J* = 7.0 Hz, OCH_2), 6.43 (s, 1H, $CH_{pyrrole}$), 6.67-6.74 (m, 2H, ArH), 6.99-7.06 (m, 2H, ArH), 7.13 (dd, 2H, *J* = 1.9, 6.6 Hz, ArH), 7.23 (dd, 2H, *J* = 2.0, 6.6 Hz, ArH), 7.37 (br, 4H, ArH). ^{13}C NMR (75 MHz, $CDCl_3$): δ = 14.6 (CH_3), 31.3 ($3CH_3$), 31.4 ($3CH_3$), 34.4 (NCH_3), 34.5, 34.6 (C), 63.3 (OCH_2), 110.7, 111.9 (CH), 119.0 (C), 120.1 (CH), 125.0 (2CH), 125.3 (2CH), 126.0 (C), 126.6 (CH), 128.5 (2CH), 130.0 (2CH), 130.8, 130.9 (C), 131.9 (CH), 133.5, 135.1, 149.4, 149.5, 155.9 (C). IR (KBr, cm^{-1}): v = 3085, 2960, 2866, 1659, 1597, 1552, 1461, 1455, 1391, 1361 (w), 1267, 1237, 1121, 1109, 1040 (m), 1014, 920 (w), 837, 746, 566 (m). GC-MS (EI, 70 eV): m/z (%) = 465(100) [M^+], 450(20). HRMS (ESI): calcd for $C_{33}H_{40}NO$ [M+H]$^+$: 466.3104; found: 466.3108.

Synthesis of 2,3,5-triaryl-*N*-methylpyrroles (23):

In a pressure tube (glass bomb) a suspension of $Pd(OAc)_2$ (12 mg, 0.05 mmol, 5 mol-%) and $P(Cy)_3$ (10 mol-%) in toluene (5 mL) was purged with Argon and stirred at 20 °C to give a brownish solution. To the stirred solution were added **18** (0.159 g, 0.5 mmol), arylboronic acid (2.0 mmol), and K_3PO_4 (4.0 equiv, 424 mg) under argon atmosphere. The reaction mixture was stirred at 110 °C for 36 h and was subsequently allowed to cool to 20 °C. The solution was poured into H_2O and EtOAc (25 mL each) and the organic and the aqueous layer were separated. The latter was extracted with EtOAc (3 × 25 mL), dried (Na_2SO_4), filtered,

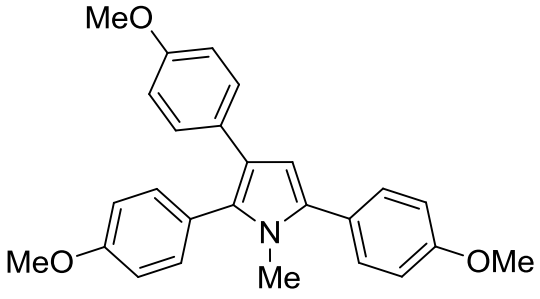
and concentrated *in vacuo*. The residue was purified by flash column chromatography (flash silica gel, eluent: heptanes/EtOAc).

1-Methyl-2,3,5-tri-*p*-tolyl-1*H*-pyrrole (23a):



Starting with **18** (0.159 g, 0.5 mmol) and 4-methyl phenylboronic acid (0.272 g, 2.0 mmol), **23a** was isolated (0.119 g, 68%) as a brownish oil. ^{1}H NMR (300 MHz, acetone-d_6): δ = 2.09 (s, 3H, CH_3), 2.23 (s, 6H, $2CH_3$), 3.30 (s, 3H, NCH_3), 6.26 (s, 1H, $CH_{pyrrole}$), 6.82 (d, 2H, J = 8.0 Hz, ArH), 6.95 (dd, 2H, J = 1.8, 6.4 Hz, ArH), 7.09 (br, 4H, ArH), 7.11 (d, 2H, J = 7.9 Hz, ArH), 7.23 (dd, 1H, J = 1.9, 6.3 Hz, ArH), 7.28 (dd, 1H, J = 1.8, 6.2 Hz, ArH). ^{13}C NMR (75 MHz, acetone-d_6): δ = 21.0, 21.2, 21.3 (CH_3), 34.0 (NCH_3), 109.6 (CH), 128.4 (2CH), 129.3 (2CH), 129.5 (2CH), 130.0 (2CH), 130.1 (2CH), 131.2, 131.5, 131.7 (C), 131.8 (2CH), 132.8, 134.9. 135.0, 136.1, 137.2, 138.0 (C). IR (KBr, cm^{-1}): v = 3019, 2918, 2855, 1699, 1606, 1555 (w), 1519, 1497, 1444, 1376, 1179, 1109, 1018 (m), 942 (w), 820, 788 (s), 762 (m), 672, 612, 563 (w). GC-MS (EI, 70 eV): m/z (%) = 351(100) [M^+]. HRMS (EI, 70 eV): calcd for $C_{26}H_{25}N$ [M^+]: 351.19815; found: 351.19776.

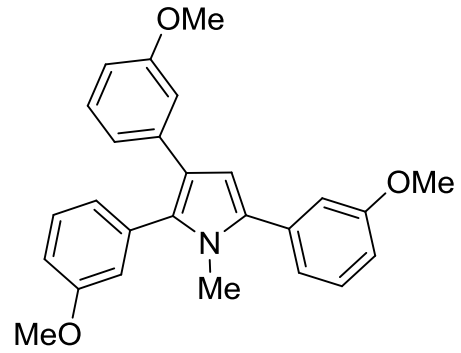
2,3,5-Tris(4-methoxyphenyl)-1-methyl-1*H*-pyrrole (23b):



Starting with **18** (0.159 g, 0.5 mmol) and 4-methoxyphenylboronic acid (0.304 g, 2.0 mmol), **23b** was isolated (0.177 g, 89%) as a brownish oil. ^{1}H NMR (300 MHz, acetone-d_6): δ = 3.30 (s, 3H, NCH_3), 3.59 (s, 3H, OCH_3), 3.71 (s, 6H, $2OCH_3$), 6.19 (s, 1H, $CH_{pyrrole}$), 6.60 (dd, 2H, J = 2.1, 6.7 Hz, ArH), 6.84 (dd, 2H, J = 2.1, 6.7 Hz, ArH), 6.88 (dd, 2H, J = 2.2, 6.8 Hz, ArH), 6.98 (dd, 2H, J = 2.1, 6.7 Hz, ArH), 7.12 (dd, 2H, J = 2.1, 6.7 Hz, ArH), 7.31 (dd, 2H, J = 2.1, 6.7 Hz, ArH). ^{13}C NMR (62 MHz, acetone-d_6): δ = 33.7 (NCH_3), 55.4, 55.5, 55.5 (OCH_3), 108.5 (CH), 114.3 (2CH), 114.7 (2CH), 114.8 (2CH), 122.7, 126.7, 127.1 (C), 129.3 (2CH), 130.4 (C), 130.7 (2CH), 131.8 (C), 133.1 (2CH), 135.5, 158.4, 159.8, 160.1 (C). IR (KBr, cm^{-1}): v = 3004, 2952, 2930, 2833, 1608, 1600, 1574, 1562 (w), 1517, 1497, 1461, 1440 (m), 1373, 1343, 1304 (w), 1285

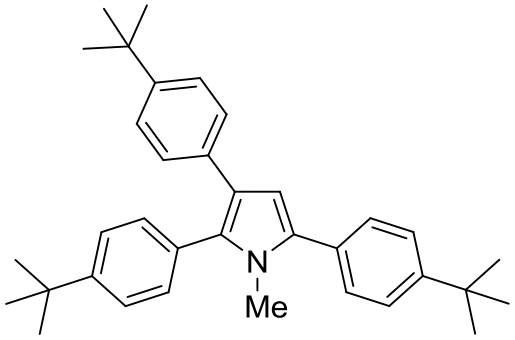
(m), 1239, 1170 (s), 1108 (m), 1026, 832 (s), 806, 790 (m), 752, 650 (w), 585, 534 (m). GC-MS (EI, 70 eV): m/z (%) = 399(100) [M^+], 384 (35). HRMS (EI, 70 eV): calcd for $C_{26}H_{25}NO_3$ [M^+]: 399.18290; found: 399.18262.

2,3,5-Tris(3-methoxyphenyl)-1-methyl-1*H*-pyrrole (23c):



Starting with **18** (0.159 g, 0.5 mmol) and 2-methoxy phenyl boronic acid (0.304 g, 2.0 mmol), **23c** was isolated (0.152 g, 76%) as brown oil. ^{1}H NMR (300 MHz, acetone-d_6): δ = 3.33 (s, 3H, NCH_3), 3.42 (s, 3H, OCH_3), 3.59 (s, 3H, OCH_3), 3.69 (s, 3H, OCH_3), 6.37 (s, 1H, $CH_{pyrrole}$), 6.45-6.49 (m, 1H, ArH), 6.61-6.63 (m, 1H, ArH), 6.67-6.71 (m, 1H, ArH), 6.72-6.81 (m, 4H, ArH), 6.90 (d, 1H, J = 8.0 Hz, ArH), 6.94-6.97 (m, 2H, ArH), 7.15-7.22 (m, 2H, ArH). ^{13}C NMR (62 MHz, acetone-d_6): δ = 34.1 (NCH_3), 55.1, 55.5, 55.6 (OCH_3), 109.5, 111.7, 113.4, 111.8, 114.3, 114.9, 117.4, 120.8, 121.7 (CH), 123.3 (C), 124.2, 129.8, 130.4, 130.5 (CH), 133.3, 135.5, 135.6, 136.1, 138.9, 160.5, 160.8, 160.9 (C). IR (KBr, cm^{-1}): v = 3010, 2954, 2932, 2834, 1605, 1603, 1574, 1562 (w), 1517, 1497, 1461, 1440 (m), 1373, 1343, 1307 (w), 1285 (m), 1243, 1170 (s), 1108 (m), 1028, 832 (s), 806, 790 (m), 752, 650 (w), 585, 534 (m). GC-MS (EI, 70 eV): m/z (%) = 399(100) [M^+]. HRMS (EI, 70 eV): calcd for $C_{26}H_{25}NO_3$ [M^+]: 399.18290; found: 399.18281.

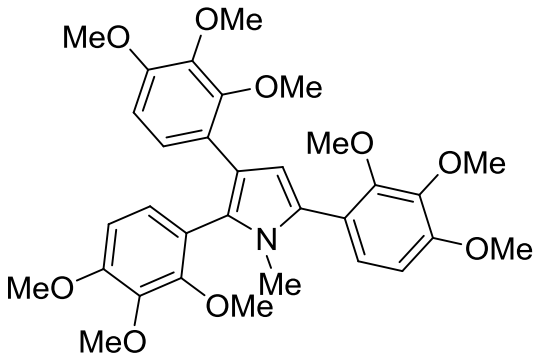
2,3,5-Tris(4-*tert*-butylphenyl)-1-methyl-1*H*-pyrrole (23d):



Starting with **18** (0.159 g, 0.5 mmol) and 4-*tert*-butylphenylboronic acid (0.356 g, 2.0 mmol), **23d** was isolated (0.171 g, 72%) as a brownish oil. ^{1}H NMR (300 MHz, acetone-d_6): δ = 1.20 (s, 27H, $9CH_3$), 3.44 (s, 3H, NCH_3), 6.07 (s, 1H, $CH_{pyrrole}$), 7.26 (dd, 5H, J = 2.3, 6.4 Hz, ArH), 7.30-7.33 (m, 7H, ArH). ^{13}C NMR (62 MHz, acetone-d_6): δ = 31.7 ($9CH_3$), 34.7 (NCH_3), 35.1 (3C), 109.2 (CH), 126.2 (6CH), 129.0 (6CH), 131.9 (3C), 137.4 (3C), 150.2 (3C). IR (KBr, cm^{-1}): v = 2951 (m), 2901, 2863, 1495, 1444 (w), 1362, 1266 (m), 1246, 1184 (w), 1110, 1014 (m), 834 (s), 794 (m), 767 (s), 733, 697 (m), 673, 622

(w). GC-MS (EI, 70 eV): m/z (%) = 477(100) [M^+], 463(11), 462(40). HRMS (EI, 70 eV): calcd for $C_{35}H_{43}N$ [M^+]: 477.33900; found: 477.33899.

1-Methyl-2,3,5-tris(2,3,4-trimethoxyphenyl)-1*H*-pyrrole (23e):

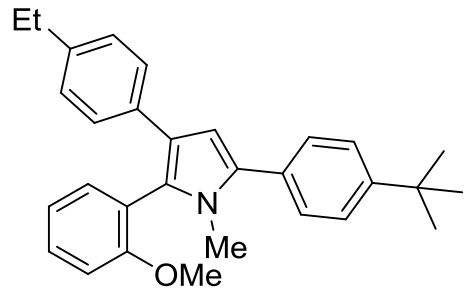


Starting with **18** (0.160 g, 0.5 mmol) and 2,3,4-trimethoxyphenyl boronic acid (0.424 g, 2.0 mmol) , **23e** was isolated (0.266 g, 92%) as a brownish oil. ^{1}H NMR (300 MHz, acetone-d_6): δ = 3.10 (s, 3H, NCH_3), 3.52, 3.53, 3.54, 3.60, 3.61, 3.67, 3.68, 3.71, 3.74 (s, 3H, OCH_3), 6.20 (s, 1H, $CH_{pyrrole}$), 6.39 (d, 1H, *J* = 8.7 Hz, ArH), 6.55 (d, 1H, *J* = 8.7 Hz, ArH), 6.57 (d, 1H, *J* = 8.7 Hz, ArH), 6.66 (d, 1H, *J* = 8.5 Hz, ArH), 6.70 (d, 1H, *J* = 8.6 Hz, ArH), 6.92 (d, 1H, *J* = 8.5 Hz, ArH). ^{13}C NMR (62 MHz, acetone-d_6): δ = 32.9 (NCH_3), 56.1, 56.2, 56.4, 60.4, 60.6, 60.7, 60.8, 61.0, 61.1 (OCH_3), 108.1, 108.2, 108.5, 111.0 (CH), 119.2, 120.9, 121.6, 125.1 (C), 126.0, 127.0, 128.1 (CH), 128.9, 131.2, 143.4, 143.5, 143.6, 152.7, 152.8, 153.1, 153.6, 154.7, 154.8 (C). IR (KBr, cm^{-1}): v = 2931, 2871, 2835, 1737, 1600, 1558 (w), 1499, 1484, 1459, 1430, 1405 (w), 1346 (w), 1286 (s), 1252, 1227, 1203, 1166 (m), 1094, 1079 (s), 1054 (m), 1009 (s), 985 (m), 914, 878, 855, 834 w), 793 (m), 744, 720 (w), 689 (m). MS (EI, 70 eV): m/z (%) = 579(100) [M^+], 208(12). HRMS (EI, 70 eV): calcd for $C_{32}H_{37}NO_9$ [M^+]: 579.24628; found: 579.24647.

One-pot Synthesis of unsymmetrical 2,4,5-triarylmethyl-1*H*-pyrroles (24):

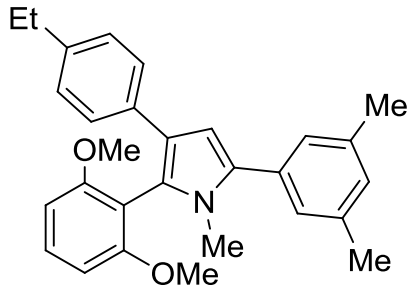
To a mixture of **19** (0.5 mmol), aryl boronic acid (0.55 mmol), and $Pd(PPh_3)_4$ (29 mg, 5 mol-%) was added a mixture of 1,4-dioxane and toluene (1:1; 5 mL) and K_3PO_4 (424 mg, 2.0 mmol) under an argon atmosphere. The reaction mixture was stirred at 100 °C. After for 6 h, was added the second aryl boronic acid (1.0 mmol) and K_3PO_4 (212mg, 1.0 mmol). The mixture was heated at 110 °C under Argon atmosphere for 24 h. The solution was poured into H_2O and EtOAc (25 mL each) and the organic and the aqueous layers were separated. The latter was extracted with EtOAc (3 × 25 mL), dried (Na_2SO_4), filtered, and concentrated *in vacuo*. The residue was purified by flash column chromatography (flash silica gel, eluent: heptanes/EtOAc).

5-(4-*tert*-Butylphenyl)-3-(4-ethylphenyl)-2-(2-methoxyphenyl)-1-methyl-1*H*-pyrrole (24a):



Starting with **19c** (0.186 g, 0.5 mmol), 2-methoxy phenyl boronic acid (0.084 g, 0.55 mmol) and 4-ethylphenyl boronic acid (0.150 g, 1.0 mmol), **24a** was isolated (0.091 g, 43%) as a brownish oil. ^{1}H NMR (250 MHz, acetone-d_6): δ = 0.99 (t, 3H, J = 7.6 Hz, CH_3), 1.19 (s, 9H, $3CH_3$), 2.36 (q, 2H, J = 7.6 Hz, CH_2), 3.20 (s, 3H, NCH_3), 3.63 (s, 3H, OCH_3), 6.32 (s, 1H, $CH_{pyrrole}$), 6.80 (d, 2H, J = 8.0 Hz, ArH), 6.92-7.00 (m, 5H, ArH), 7.20-7.24 (m, 1H, ArH), 7.26-7.32 (m, 4H, ArH). ^{13}C NMR (62 MHz, acetone-d_6): δ = 16.1 (CH_3), 29.0 (CH_2), 31.7 ($3CH_3$), 33.1 (NCH_3), 35.1 (C), 55.8 (OCH_3), 108.6, 112.4, 121.5 (CH), 123.3, 123.4 (C), 126.2 (2CH), 127.9 (2CH), 128.3 (2CH), 129.1 (2CH), 129.5 (C), 130.7 (CH), 131.8 (C), 134.2 (CH), 135.3, 135.4, 141.3, 150.3, 159.6 (C). IR (KBr, cm^{-1}): ν = 2958, 2930 (m), 2867, 2833, 1611, 1578, 1555, 1511 (w), 1491, 1460, 1431 (m), 1407, 1373, 1361, 1341, 1289 (w), 1240 (s), 1178, 1116, 1052, 1022 (m), 1004, 944 (w), 835, 792, 750 (s), 716, 676, 621, 598 (w), 559, 537 (m). GC-MS (EI, 70 eV): m/z (%) = 423(100) [M^+], 409 (11), 408(33), 183(14). HRMS (ESI): calcd for $C_{30}H_{34}NO$ $[M+H]^+$: 424.26349; found: 424.26434.

2-(2,6-Dimethoxyphenyl)-5-(3,5-dimethylphenyl)-3-(4-ethylphenyl)-1-methyl-1*H*-pyrrole (24b):



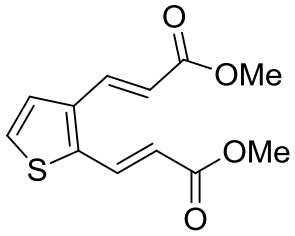
Starting with **19e** (0.171 g, 0.5 mmol), 2,6-dimethoxy phenyl boronic acid (0.100 g, 0.55 mmol) and 4-ethyl phenyl boronic acid (0.150 g, 1.0 mmol), **24b** was isolated (0.102 g, 48%) as a brownish oil. ^{1}H NMR (300 MHz, acetone-d_6): δ = 1.09 (t, 3H, J = 7.6 Hz, CH_3), 2.28 (s, 6H, $2CH_3$), 2.47 (q, 2H, J = 7.6 Hz, CH_2), 3.28 (s, 3H, NCH_3), 3.52 (s, 6H, $2OCH_3$), 6.45 (s, 1H, $CH_{pyrrole}$), 6.52 (d, 2H, J = 8.3 Hz, ArH), 6.84 (br, 1H, ArH), 7.89 (d, 2H, J = 8.2 Hz, ArH), 7.05-7.07 (m, 4H, ArH), 7.18-7.27 (m, 1H, ArH). ^{13}C NMR (62 MHz, acetone-d_6): δ = 15.6 (CH_3), 21.4 ($2CH_3$), 28.6 (CH_2), 32.5 (NCH_3), 55.9 ($2OCH_3$), 104.5 (2CH), 107.9 (CH), 111.4, 123.0, 123.8 (C), 126.3 (2CH), 126.7 (2CH), 127.3 (2CH), 128.1, 130.0 (CH), 133.8, 134.9, 135.0 (C), 137.6 (2C), 140.4 (C), 159.7 (2C). IR (KBr, cm^{-1}): ν = 2999, 2959, 2929, 2834 (w), 1599, 1583, 1469, 1430 (m), 1406, 1372,

1340, 1294 (w), 1247 (s), 1182 (w), 1103 (s), 1028, 833, 784, 735, 698, 650, 630, 595, 537 (m). GC-MS (EI, 70 eV): m/z (%) = 425(100) [M^+]. HRMS (ESI): calcd for $C_{29}H_{32}NO_2$ $[M+H]^+$: 426.24276; found: 426.24233.

General procedure A for the di(alkenyl)thiophene (27), (32), (**33)** and (**35)**:

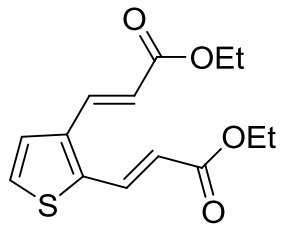
In a pressure tube (glass bomb) a suspension of $Pd(OAc)_2$ (12 mg, 0.05 mmol, 5 mol-%) and L [XPhos, SPhos or $P(Cy)_3$] (10 mol-%) in DMF (5 mL) was purged with Argon and stirred at 20 °C to give a yellowish or brownish clear solution. To the stirred solution were added 2,3-dibromothiophene (**25**), **31a,b** or 5-Aryl-2,3-dibromothiophene (**2b,c,d,f**) (1.0 mmol), NEt_3 (1.1 mL, 8.0 mmol) and an alkene (1.25 equiv per Br). The reaction mixture was stirred at 100-120 °C for 24-48 h. The solution was cooled to 20 °C, poured into H_2O and CH_2Cl_2 (25 mL each), and the organic and the aqueous layer were separated. The latter was extracted with CH_2Cl_2 (3 × 25 mL). The combined organic layers were washed with H_2O (3 × 20 mL), dried (Na_2SO_4), and concentrated *in vacuo*. The residue was purified by chromatography (flash silica gel, heptanes/EtOAc).

(2*E*,2'*E*)-Dimethyl-3,3'-(thiophene-2,3-diyl)diacrylate (27a):



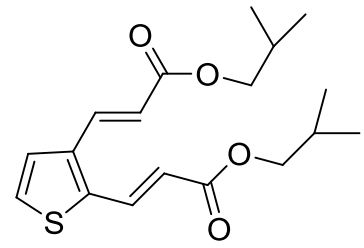
Product **27a** was prepared starting with **25** (242 mg, 1.0 mmol), methyl acrylate (0.23 mL, 2.5 mmol), $Pd(OAc)_2$ (11 mg, 5 mol-%), XPhos (10 mol %), NEt_3 (1.10 mL, 8.0 mmol), DMF (5 mL) at 120 °C for 48 h following general procedure A, as a brown oil (204 mg, 81%). ^{1}H NMR (300 MHz, $CDCl_3$): δ = 3.74 (s, 3H, OCH_3), 3.75 (s, 3H, OCH_3), 6.22 (d, 1H, J = 15.5 Hz, CH), 6.24 (d, 1H, J = 15.8 Hz, CH), 7.18 (d, 1H, J = 5.5 Hz, ArH), 7.25 (d, 1H, J = 5.3 Hz, ArH), 7.79 (d, 1H, J = 15.8 Hz, CH), 7.94 (d, 1H, J = 15.6 Hz, CH). ^{13}C NMR (62 MHz, $CDCl_3$): δ = 51.8, 51.9 (OCH_3), 118.8, 120.0, 126.4, 127.8, 133.7, 134.7 (CH), 138.2, 139.8 (C), 166.7, 167.1 (CO). IR (KBr, cm^{-1}): ν = 3110, 2950, 2923 (w), 1705 (s), 1631 (m), 1513 (w), 1427, 1308, 1270 (m), 1190, 1170, 1159 (s), 1110, 1009 (m), 972, 805 (s), 724, 709, 612, 575, 535 (m). GC-MS (EI, 70 eV): *m/z* (%) = 252(30) $[M]^+$, 221(13), 193(45), 192(22), 177(22), 161(58), 149(26), 135(13), 134(100), 133(18), 89(19), 67(13). HRMS (EI, 70 eV): calcd for $C_{12}H_{12}O_4S$ $[M]^+$: 252.04508; found: 252.04533.

(2*E*,2'*E*)-Diethyl-3,3'-(thiophene-2,3-diyl)diacrylate (27b):



Product **27b** was prepared starting with **25** (242 mg, 1.0 mmol), ethyl acrylate (0.27 mL, 2.5 mmol), $Pd(OAc)_2$ (11 mg, 5 mol %), SPhos (10 mol %), NEt_3(1.10 mL, 8.0 mmol), DMF (5 mL) at 120 °C for 48 h following general procedure A, as a brown semi solid (252 mg, 90%). ^{1}H NMR (300 MHz, $CDCl_3$): δ = 1.26 (t, 3H, J = 7.1 Hz, CH_3), 1.27 (t, 3H, J = 7.1 Hz, CH_3), 4.20 (q, 2H, J = 7.1 Hz, CH_2O), 4.21 (q, 2H, J = 7.1 Hz, CH_2O), 6.23 (d, 1H, J = 15.5 Hz, CH), 6.24 (d, 1H, J = 15.8 Hz, CH), 7.18 (d, 1H, J = 5.6 Hz, ArH), 7.24 (d, 1H, J = 5.3 Hz, ArH), 7.79 (d, 1H, J = 15.8 Hz, CH), 7.93 (d, 1H, J = 15.5 Hz, CH). ^{13}C NMR (62 MHz, $CDCl_3$): δ = 14.3 ($2CH_3$), 60.6, 60.7 (CH_2O), 119.2, 120.4, 126.4, 127.7, 133.5, 134.5 (CH), 138.2, 139.8 (C), 166.3, 166.7 (CO). IR (KBr, cm^{-1}): ν = 3095, 2985, 2939, 2872 (w), 1697 (s), 1621 (m), 1505, 1471, 1443, 1394 (w), 1369, 1315, 1298, 1278, 1254, 1212 (m), 1176 (s), 1110, 1028, 976, 956, 868, 851 (m), 831, 808 (w), 771, 764, 718, 701, 664, 627, 582 (m). GC-MS (EI, 70 eV): *m/z* (%) = 280(24) $[M]^+$, 235(11), 207(31), 206(15), 179(21), 178(08), 163(45), 162(07), 161(34), 136(12), 135(100), 134(44), 91(16), 89(13), 29(19). HRMS (EI, 70 eV): calcd for $C_{14}H_{16}O_4S$ $[M]^+$: 280.07638; found: 280.07680.

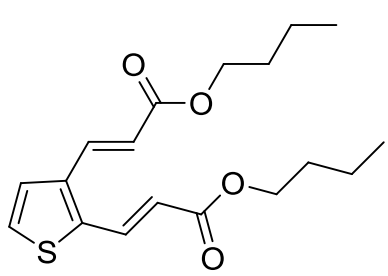
(2*E*,2'*E*)-Isobutyl-3,3'-(thiophene-2,3-diyl)diacrylate (27c):



Product **27c** was prepared starting with **25** (242 mg, 1.0 mmol), *iso*-butyl acrylate (0.36 mL, 2.5 mmol), $Pd(OAc)_2$ (11 mg, 5 mol %), XPhos (10 mol %), NEt_3(1.10 mL, 8.0 mmol), DMF (5 mL) at 120 °C for 48 h following general procedure A, as a brown oil (288 mg, 86%). ^{1}H NMR (250 MHz, $CDCl_3$): δ = 0.92 (d, 12H, J = 6.7 Hz, $4CH_3$), 1.89-1.98 (m, 2H, CH), 3.92 (d, 2H, J = 6.7 Hz, CH_2O), 3.93 (d, 2H, J = 6.7 Hz, CH_2O), 6.23 (d, 1H, J = 15.5 Hz, CH), 6.25 (d, 1H, J = 15.7 Hz, CH), 7.19 (d, 1H, J = 5.4 Hz, ArH), 7.25 (d, 1H, J = 5.4 Hz, ArH), 7.79 (d, 1H, J = 15.8 Hz, CH), 7.93 (d, 1H, J = 15.6 Hz, CH)). ^{13}C NMR (75 MHz, $CDCl_3$): δ = 19.1 ($4CH_3$), 27.8 (2CH), 70.8, 70.9 (CH_2O), 119.2, 120.4, 126.4, 127.7, 133.5, 134.5 (CH), 138.2, 139.8 (C), 166.4, 166.8 (CO). IR (KBr, cm^{-1}): ν = 3106, 2959, 2873 (w), 1704, 1619 (s), 1508, 1468, 1393, 1375, 1342 (w), 1311, 1266, 1237, 1201 (m), 1154 (s), 1018, 967, 852 (m), 832, 750 (w), 709 (m), 665, 620, 586, 533 (w). GC-MS (EI, 70 eV): *m/z* (%) = 336(25) $[M]^+$, 263(19), 180(15), 179(100), 178(36), 163(82), 162(12), 161(42),

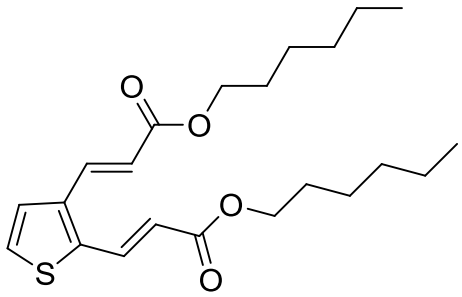
135(83), 134(59), 91(13), 57(80), 41(34). HRMS (EI, 70 eV): calcd for $C_{18}H_{24}O_4S$ $[M]^+$: 336.13898; found: 336.13894.

(2*E*,2'*E*)-Dibutyl-3,3'-(thiophene-2,3-diyl)diacrylate (27d):



Product **27d** was prepared starting with **25** (242 mg, 1.0 mmol), *n*-butyl acrylate (0.36 mL, 2.5 mmol), $Pd(OAc)_2$ (11 mg, 5 mol %), SPhos (10 mol %), NEt_3 (1.10 mL, 8.0 mmol), DMF (5 mL) at 120 °C for 48 h following general procedure A, as a brown oil (312 mg, 93%). ^{1}H NMR (300 MHz, $CDCl_3$): δ = 0.90 (t, 6H, *J* = 7.4 Hz, $2CH_3$), 1.32-1.40 (m, 4H, $2CH_2$), 1.59-1.64 (m, 4H, $2CH_2$), 4.14 (t, 2H, *J* = 6.7 Hz, CH_2O), 4.15 (t, 2H, *J* = 6.7 Hz, CH_2O), 6.21 (d, 1H, *J* = 15.5 Hz, CH), 6.24 (d, 1H, *J* = 15.8 Hz, CH), 7.18 (d, 1H, *J* = 5.3 Hz, ArH), 7.24 (d, 1H, *J* = 5.4 Hz, ArH), 7.78 (d, 1H, *J* = 15.8 Hz, CH), 7.93 (d, 1H, *J* = 15.6 Hz, CH)). ^{13}C NMR (62 MHz, $CDCl_3$): δ = 13.7 ($2CH_3$), 19.2 ($2CH_2$), 30.7 ($2CH_2$), 64.5, 64.6 (CH_2O), 119.3, 120.4, 126.4, 127.7, 133.5, 134.4 (CH), 138.2, 139.8 (C), 166.4, 166.8 (CO). IR (KBr, cm^{-1}): ν = 2957, 2931, 2872 (w), 1704 (s), 1619 (m), 1509, 1463, 1433, 1383, 1354 (w), 1309, 1276, 1238, 1202 (m), 1159 (s), 1061, 1024, 968, 853, 751, 710 (m), 665, 619, 584 (w). GC-MS (EI, 70 eV): *m/z* (%) = 336(26) $[M]^+$, 263(11), 235(15), 234(10), 180(12), 179(94), 178(32), 163(62), 162(11), 161(45), 135(100), 134(50), 91(14), 57(56), 41(33), 29(21). HRMS (EI, 70 eV): calcd for $C_{18}H_{24}O_4S$ $[M]^+$: 336.13898; found: 336.13896.

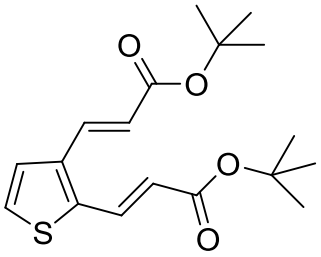
(2*E*,2'*E*)-Dihexyl-3,3'-(thiophene-2,3-diyl)diacrylate (27e):



Product **27e** was prepared starting with **25** (242 mg, 1.0 mmol), hexyl acrylate (2.5 mmol), $Pd(OAc)_2$ (11 mg, 5 mol %), SPhos (10 mol %), NEt_3(1.10 mL, 8.0 mmol), DMF (5 mL) at 120 °C for 48 h following general procedure A, as a brown oil (360 mg, 92%). ^{1}H NMR (300 MHz, $CDCl_3$): δ = 0.83 (t, 6H, *J* = 6.9 Hz, $2CH_3$), 1.22-1.37 (m, 12H, $6CH_2$), 1.58-1.68 (m, 4H, $2CH_2$), 4.13 (t, 2H, *J* = 6.8 Hz, CH_2O), 4.14 (t, 2H, *J* = 6.8 Hz, CH_2O), 6.22 (d, 1H, *J* = 15.5 Hz, CH), 6.24 (d, 1H, *J* = 15.8 Hz, CH), 7.18 (d, 1H, *J* = 5.3 Hz, ArH), 7.24 (d, 1H, *J* = 5.4

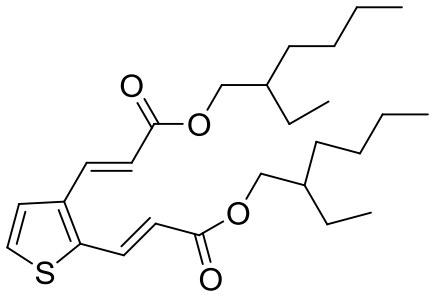
Hz, ArH), 7.78 (d, 1H, J = 15.8 Hz, CH), 7.93 (d, 1H, J = 15.5 Hz, CH)). ^{13}C NMR (62 MHz, $CDCl_3$): δ = 14.0 ($2CH_3$), 22.5 ($2CH_2$), 25.6 ($2CH_2$), 28.7 ($2CH_2$), 31.4 ($2CH_2$), 64.9, 65.0 (CH_2O), 119.3, 120.4, 126.4, 127.6, 133.5, 134.4 (CH), 138.2, 139.8 (C), 166.4, 166.8 (CO). IR (KBr, cm^{-1}): ν = 2954, 2927, 2857 (w), 1707 (s), 1620 (m), 1510, 1465, 1434, 1379 (w), 1309, 1267, 1240, 1201 (m), 1160 (s), 1058, 1013, 970 (m), 906 (w), 854 (m), 834, 750 (w), 710 (m), 665, 620, 586 (w). GC-MS (EI, 70 eV): *m/z* (%) = 392(07) $[M]^+$, 263(32), 262(18), 205(16), 180(14), 179(100), 178(29), 161(44), 135(35), 134(16), 91(07), 57(07), 41(46). HRMS (EI, 70 eV): calcd for $C_{22}H_{32}O_4S$ $[M]^+$: 392.20158; found: 392.20182.

(2*E*,2'*E*)-*tert*-Butyl-3,3'-(thiophene-2,3-diyl)diacrylate (27f):



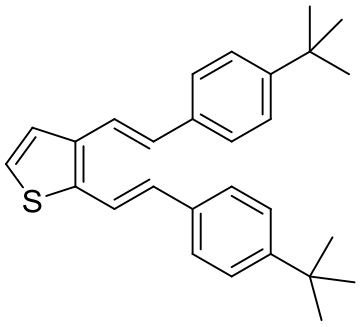
Product **27f** was prepared starting with **25** (242 mg, 1.0 mmol), *tert*-butyl acrylate (0.36 mL, 2.5 mmol), $Pd(OAc)_2$ (11 mg, 5 mol %), XPhos (10 mol %), NEt_3(1.10 mL, 8.0 mmol), DMF (5 mL) at 120 °C for 48 h following general procedure A, as yellowish solid (299 mg, 89%), mp. = 85-87 °C. ^{1}H NMR (300 MHz, $CDCl_3$): δ = 1.45 (s, 9H, $3CH_3$), 1.46 (s, 9H, $3CH_3$), 6.13 (d, 1H, J = 15.5 Hz, CH), 6.16 (d, 1H, J = 15.7 Hz, CH), 7.15 (d, 1H, J = 5.3 Hz, ArH), 7.20 (d, 1H, J = 5.4 Hz, ArH), 7.68 (d, 1H, J = 15.7 Hz, CH), 7.84 (d, 1H, J = 15.6 Hz, CH)). ^{13}C NMR (75 MHz, $CDCl_3$): δ = 28.2 ($6CH_3$), 80.1, 80.7 (C-O), 121.1, 122.2, 126.4, 127.3, 132.7, 133.6 (CH), 138.0, 139.6 (C), 165.6, 166.1 (CO). IR (KBr, cm^{-1}): ν = 2976, 2932, 2872 (w), 1700 (s), 1617 (m), 1506, 1474, 1456, 1432, 1390 (w), 1364, 1313, 1275, 1249, 1199 (m), 1137 (s), 1039 (m), 999 (w), 971, 960, 911, 849 (m), 787 (w), 754, 727, 712, 694, 662, 621, 582 (m). GC-MS (EI, 70 eV): *m/z* (%) = 336(05) $[M]^+$, 263(04), 224(41), 180(14), 179(50), 178(30), 163(19), 162(10), 161(34), 136(10), 135(100), 134(42), 91(23), 57(64), 41(72), 29(21). HRMS (ESI): calcd for $C_{18}H_{24}NaO_4S$ $[M+Na]^+$: 359.12875; found: 359.12877.

(2*E*,2'*E*)-Bis(2-ethylhexyl)-3,3'-(thiophene-2,3-diyl)diacrylate (27g):



Product **27g** was prepared starting with **25** (242 mg, 1.0 mmol), 2-ethylhexyl acrylate (0.52 mL, 2.5 mmol), $Pd(OAc)_2$ (11 mg, 5 mol %), SPhos (10 mol %), NEt_3 (1.10 mL, 8.0 mmol), DMF (5 mL) at 120 °C for 48 h following general procedure A, as a brown oil (380 mg, 85%). ^{1}H NMR (300 MHz, $CDCl_3$): δ = 0.85 (t, 12H, *J* = 7.1 Hz, $4CH_3$), 1.17-1.38 (m, 16H, CH-Aliphatic), 1.55-1.61 (m, 2H, CH), 4.02-4.07 (m, 4H, $2CH_2O$), 6.22 (d, 1H, *J* = 15.5 Hz, CH), 6.24 (d, 1H, *J* = 15.8 Hz, CH), 7.19 (d, 1H, *J* = 5.4 Hz, ArH), 7.24 (d, 1H, *J* = 5.3 Hz, ArH), 7.78 (d, 1H, *J* = 15.8 Hz, CH), 7.93 (d, 1H, *J* = 15.5 Hz, CH)). ^{13}C NMR (75 MHz, $CDCl_3$): δ = 11.0 ($2CH_3$), 14.0 ($2CH_3$), 23.0 ($2CH_2$), 23.8, 23.9 (CH_2), 28.9 ($2CH_2$), 30.4, 30.5 (CH_2), 38.8 (2CH), 67.2 ($2CH_2O$), 119.3, 120.5, 126.4, 127.6, 133.5, 134.4 (CH), 138.2, 139.8 (C), 166.5, 166.9 (CO). IR (KBr, cm^{-1}): ν = 2957, 2927, 2858 (w), 1708 (s), 1621 (m), 1510, 1461, 1379 (w), 1308, 1267, 1241 (m), 1161 (s), 1028, 970 (m), 854, 833, 750, 710, 665, 620, 586 (w). GC-MS (EI, 70 eV): *m/z* (%) = 448(04) $[M]^+$, 207(24), 180(17), 179(100), 178(31), 161(30), 135(19), 134(11), 71(23), 57(31), 43(20). HRMS (EI, 70 eV): calcd for $C_{26}H_{40}O_4S$ $[M]^+$: 448.26418; found: 448.26485.

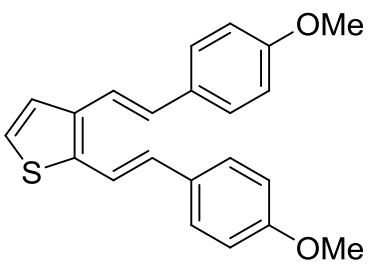
2,3-Bis(4-*tert*-butylstyryl)thiophene (27h):



Product **27h** was prepared starting with **25** (242 mg, 1.0 mmol), 4-*tert*-butyl styrene (0.45 mL, 2.5 mmol), $Pd(OAc)_2$ (11 mg, 5 mol %), SPhos (10 mol %), NEt_3 (1.10 mL, 8.0 mmol), DMF (5 mL) at 120 °C for 48 h following general procedure A, as a brown solid (376 mg, 94%), mp.= 171-174 °C. ^{1}H NMR (300MHz, $CDCl_3$): δ = 1.25 (s, 9H, $3CH_3$), 1.26 (s, 9H, $3CH_3$), 6.83 (d, 1H, *J* = 15.9 Hz, CH), 6.88 (d, 1H, *J* = 16.1 Hz, CH), 7.04 (d, 1H, *J* = 5.3 Hz, ArH), 7.15-7.22 (m, 3H, ArH), 7.28-7.32 (m, 4H, ArH), 7.35-7.39 (m, 4H, ArH). ^{13}C NMR (62 MHz, $CDCl_3$): δ = 31.3 ($6CH_3$), 34.6, 34.7 (C), 119.0, 120.3, 123.6 (CH), 125.7 (4CH), 126.0 (CH), 126.2 (4CH), 129.0, 129.5 (CH), 134.4, 134.8, 136.8, 138.4, 150.8, 150.9 (C). IR (KBr, cm^{-1}): ν = 3028 (w), 2957 (m), 2864, 1903, 1605, 1515, 1504, 1462, 1409, 1391 (w), 1361, 1268 (m), 1246, 1199, 1107, 1015 (w), 953, 940, 852, 827, 809 (m), 741 (w), 714 (m), 665 (w), 635 (m), 610 (w), 558 (s). GC-MS (EI, 70 eV): *m/z* (%) =

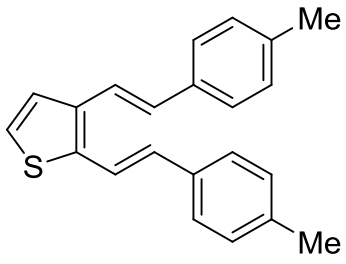
400(100) $[M]^+$, 385(27), 343(15), 287(10), 254(11), 253(42), 209(14), 185(36), 157(20), 147(20), 91(12), 57(47). HRMS (EI, 70 eV): calcd for $C_{28}H_{32}S$ $[M]^+$: 400.22192; found: 400.22190.

2,3-Bis(4-methoxystyryl)thiophene (27i):



Product **27i** was prepared starting with **25** (242 mg, 1.0 mmol), 4-methoxy styrene (0.33 mL, 2.5 mmol), $Pd(OAc)_2$ (11 mg, 5 mol %), SPhos (10 mol %), NEt_3 (1.10 mL, 8.0 mmol), DMF (5 mL) at 120 °C for 48 h following general procedure A, as a brown oil (289 mg, 83%). ^{1}H NMR (300 MHz, $CDCl_3$): δ = 3.69 (s, 6H, $2OCH_3$), 6.74-6.80 (m, 6H, 4ArH and 2CH), 6.97 (d, 1H, J = 5.3 Hz, ArH), 7.06 (d, 1H, J = 16.1 Hz, CH), 7.12 (d, 1H, J = 5.4 Hz, ArH), 7.21 (d, 1H, J = 15.9 Hz, CH), 7.33 (dd, 4H, J = 2.8, 8.8 Hz, ArH). ^{13}C NMR (62 MHz, $CDCl_3$): δ = 55.3 ($2OCH_3$), 114.2 (2CH), 114.3 (2CH), 117.7, 119.0, 123.3, 125.9 (CH), 127.6 (2CH), 127.7 (2CH), 128.6, 129.0 (CH), 130.0, 130.3, 136.5, 138.2, 159.3, 159.4 (C). IR (KBr, cm^{-1}): v = 3030, 2963, 2834 (w), 1597 (m), 1573 (w), 1510, 1505 (m), 1462, 1455, 1440, 1435, 1410, 1303, 1283 (w), 1246, 1172 (s), 1107, 1093 (w), 1024, 967, 957, 946, 931, 849, 812, 804, 778, 765, 726, 704, 631 (m). GC-MS (EI, 70 eV): *m/z* (%) = 348(100) $[M]^+$, 347(10), 240(10), 227(39), 225(10), 121(51). HRMS (EI, 70 eV): calcd for $C_{22}H_{20}O_2S$ $[M]^+$: 348.11785; found: 348.11778.

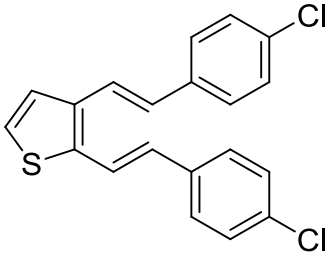
2,3-Bis(4-methylstyryl)thiophene (27j):



Product **27j** was prepared starting with **25** (242 mg, 1.0 mmol), 4-methyl styrene (2.5 mmol), $Pd(OAc)_2$ (11 mg, 5 mol %), XPhos (10 mol %), NEt_3 (1.10 mL, 8.0 mmol), DMF (5 mL) at 120 °C for 48 h following general procedure A, as a brown semi solid (278 mg, 88 %). ^{1}H NMR (250 MHz, $CDCl_3$): δ = 2.28 (s, 6H, $2CH_3$), 6.83 (d, 1H, J = 15.9 Hz, CH), 6.85 (d, 1H, J = 16.1 Hz, CH), 7.03 (d, 1H, J = 5.4 Hz, ArH), 7.09 (d, 4H, J = 7.8 Hz, ArH), 7.16-7.22 (m, 2H, ArH), 7.30-7.37 (m, 5H, 3ArH and 2CH). ^{13}C NMR (62 MHz, $CDCl_3$): δ = 21.2 ($2CH_3$), 118.8, 119.9, 123.6, 125.9 (CH), 126.4 (4CH), 129.1 (CH), 129.4 (4CH), 129.6 (CH), 134.4, 134.7, 136.7, 137.6, 137.7, 138.4 (C). IR (KBr, cm^{-1}): v = 3123, 2916, 2853, 1609, 1511, 1440, 1377, 1259, 1180, 1091, 1017 (w), 957 (s), 938, 905, 850, 829 (m), 800, 729 (s), 707, 637 (m). GC-MS (EI, 70 eV): *m/z* (%) = 316(100) $[M]^+$, 315(11), 301(22), 225(17), 224(12),

212(10), 211(62), 209(12). HRMS (EI, 70 eV): calcd for $C_{22}H_{20}S$ $[M]^+$: 316.12802; found: 316.12823.

2,3-Bis(4-chlorostyryl)thiophene (27k):

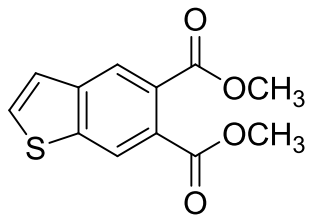


Product **27k** was prepared starting with **25** (242 mg, 1.0 mmol), 4-chloro styrene (0.32 mL, 2.5 mmol), $Pd(OAc)_2$ (11 mg, 5 mol-%), SPhos (10 mol %), NEt_3 (1.10 mL, 8.0 mmol), DMF (5 mL) at 120 °C for 48 h following general procedure A, as a brown solid (292 mg, 82%), mp.= 106-108 °C. ^{1}H NMR (300 MHz, $CDCl_3$): δ = 6.80 (d, 1H, J = 15.7 Hz, CH), 6.81 (d, 1H, J = 16.1 Hz, CH), 7.07 (d, 1H, J = 5.2 Hz, ArH), 7.14-7.29 (m, 7H, 5ArH and 2CH), 7.33-7.36 (dd, 4H, J = 3.2, 8.3 Hz, ArH). ^{13}C NMR (75 MHz, $CDCl_3$): δ = 119.9, 121.1, 124.3, 125.9 (CH), 127.6 (4CH), 128.0, 128.6 (CH), 128.9 (2CH), 129.0 (2CH), 133.3, 133.4, 135.5, 135.9, 136.8, 138.5 (C). IR (KBr, cm^{-1}): ν = 3093, 3037, 2990, 2851, 1622, 1613, 1565, 1510 (w), 1488 (m), 1439, 1401, 1328, 1255, 1245, 1178, 1103 (w), 1087, 1009, 957, 939, 852, 829 (m), 806 (s), 729, 705, 690, 636 (m), 592 (w). GC-MS (EI, 70 eV): *m/z* (%) = 356 (70) [M^+ (^{37}Cl, ^{37}Cl)], 356 (100) [M^+ (^{35}Cl,^{37}Cl)], 321(15), 320(13), 286(12), 252(13), 245(24), 231(99), 210(27), 142(14), 125(19). HRMS (EI, 70 eV): calcd for $C_{20}H_{14}Cl_2S$ [M^+ (Cl, ^{37}Cl)]: 354.00313; found: 354.00225.

General procedure B for the synthesis of Benzothiophenes (28) and (36):

A xylene or diphenylether solution (3 mL) of **27a-e**, **h-l** or **35a-d** (0.5 mmol) was stirred at 200 °C for 24 h in a pressure tube. The solution was allowed to cool to 20 °C and Pd/C (30 mg, 10 mol %) was added. The solution was stirred at 200 °C for 48 h under argon atmosphere. The reaction mixture was filtered and the filtrate was concentrated in vacuo. The residue was purified by chromatography (flash silica gel, heptanes/EtOAc).

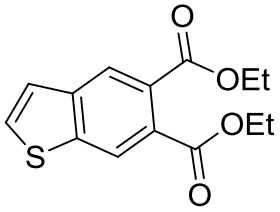
Dimethyl benzo[*b*]thiophene-5,6-dicarboxylate (28a):



Compound **28a** was prepared starting with **27a** (100 mg, 0.39 mmol), following the general procedure B, as a brown highly viscous oil (99 mg, 100%). ^{1}H NMR (300 MHz, $CDCl_3$): δ = 3.86 (s, 6H, OCH_3), 7.34 (d, 1H, J = 5.4 Hz, ArH), 7.59 (d, 1H, J = 5.5 Hz, ArH), 8.10 (s, 1H, ArH), 8.20 (s, 1H, ArH)). ^{13}C NMR (75

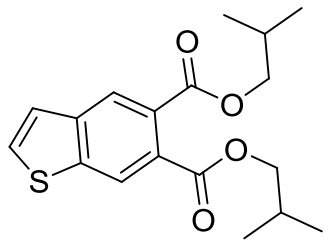
MHz, $CDCl_3$): δ = 51.7, 51.7 (OCH_3), 122.9, 124.1, 123.5 (CH), 126.2, 127.4 (C), 129.8 (CH), 139.9, 140.6 (C), 167.0, 167.4 (CO). IR (KBr, cm^{-1}): ν = 2950, 2925, 2852, 1840, 1780 (w), 1716 (s), 1601, 1545, 1491 (w), 1433 (m), 1400, 1356 (w), 1316, 1277, 1263, 1246, 1220, 1198, 1124, 1099, 1075 (m), 1009, 968, 893, 836, 787, 777, 759, 736, 703, 651, 628, 604, 530 (w). GC-MS (EI, 70 eV): *m/z* (%) = 250(40) $[M]^+$, 220(13), 219(100), 133(12). HRMS (EI, 70 eV): calcd for $C_{12}H_{10}O_4S$ $[M]^+$: 250.02943; found: 250.02983.

Diethyl benzo[*b*]thiophene-5,6-dicarboxylate (28b):



Compound **28b** was prepared starting with **27b** (100 mg, 0.36 mmol), following the general procedure B, as a brown highly viscous oil (99 mg, 100%). ^1H NMR (300 MHz, $CDCl_3$): δ = 1.32 (t, 6H, J = 7.1 Hz, $2CH_3$), 1.32 (q, 4H, J = 7.1 Hz, $2OCH_2$), 7.34 (d, 1H, J = 5.4 Hz, ArH), 7.58 (d, 1H, J = 5.4 Hz, ArH), 8.10 (s, 1H, ArH), 8.20 (s, 1H, ArH). ^{13}C NMR (62 MHz, $CDCl_3$): δ = 14.1 ($2CH_3$), 61.6, 61.7 (OCH_2), 123.8, 124.1, 124.5 (CH), 127.7, 128.8 (C), 130.6 (CH), 140.8, 141.5 (C), 167.5, 168.0 (CO). IR (KBr, cm^{-1}): ν = 2979, 2933, 2903, 2871 (w), 1714 (s), 1622, 1600, 1544, 1490, 1463, 1449, 1388 (w), 1365, 1313 (m), 1273, 1241 (s), 1191, 1173, 1120, 1095, 1073, 1018 (m), 972, 907, 854, 804 (w), 774, 755, 701 (m), 649, 607, 545 (w). GC-MS (EI, 70 eV): *m/z* (%) = 278(30) $[M]^+$, 233(20), 206(15), 205(100), 121(12). HRMS (EI, 70 eV): calcd for $C_{14}H_{14}O_4S$ $[M]^+$: 278.06073; found: 278.06090.

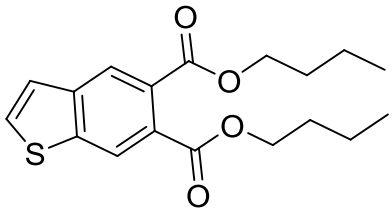
Diisobutyl benzo[*b*]thiophene-5,6-dicarboxylate (28c):



Compound **28c** was prepared starting with **27c** (100 mg, 0.30 mmol), following the general procedure B, as a brown oil (99 mg, 100%). ^1H NMR (300 MHz, $CDCl_3$): δ = 0.93 (d, 6H, J = 6.7 Hz, $2CH_3$), 0.94 (d, 6H, J = 6.7 Hz, $2CH_3$), 1.91-2.06 (m, 2H, CH), 4.05 (d, 4H, J = 6.8 Hz, $2CH_2O$), 7.35 (dd, 1H, J = 0.7, 5.6 Hz, ArH), 7.58 (d, 1H, J = 5.5 Hz, ArH), 8.10 (s, 1H, ArH), 8.20 (s, 1H, ArH). ^{13}C NMR (62 MHz, $CDCl_3$): δ = 19.1 ($2CH_3$), 19.2 ($2CH_3$), 27.7, 27.8 (CH), 71.8, 71.9 (CH_2O), 123.8, 124.0, 124.4 (CH), 127.8, 128.9 (C), 130.6 (CH), 140.8, 141.5 (C), 167.6, 168.3 (CO). IR (KBr, cm^{-1}): ν = 3106, 2958, 2873 (w), 1716 (s), 1626, 1601, 1545, 1490, 1468 (w), 1448, 1452, 1405, 1392, 1392, 1375, 1341 (m), 1314, 1271, 1239, 1190, 1167, 1119, 1097, 1073 (s), 1005, 982, 945, 904, 785, 775, 754, 702 (m), 682, 653, 626 (w). GC-MS (EI, 70 eV): *m/z* (%)

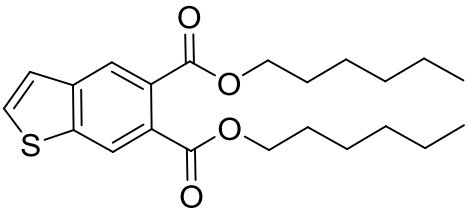
= 334(8) $[M]^+$, 222(57), 206(17), 205(100), 178(15), 160(06). HRMS (EI, 70 eV): calcd for $C_{18}H_{22}O_4S$ $[M]^+$: 334.12388; found: 334.12360.

Dibutyl benzo[*b*]thiophene-5,6-dicarboxylate (28d):



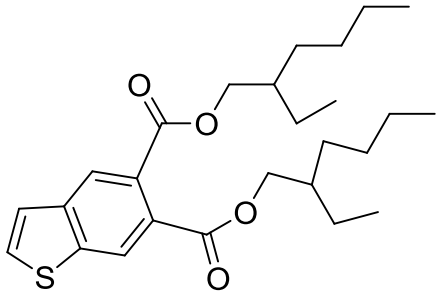
Compound **28d** was prepared starting with **27d** (100 mg, 0.30 mmol), following the general procedure B, as a brown oil (99 mg, 100%). ^{1}H NMR (300 MHz, $CDCl_3$): δ = 0.90 (t, 6H, J = 7.4 Hz, $2CH_3$), 1.32-1.42 (m, 4H, $2CH_2$), 1.62-1.71 (m, 4H, $2CH_2$), 4.26 (t, 4H, J = 6.7 Hz, $2CH_2O$), 7.35 (dd, 1H, J = 0.6, 5.4 Hz, ArH), 7.57 (d, 1H, J = 5.4 Hz, ArH), 8.09 (s, 1H, ArH), 8.19 (s, 1H, ArH)). ^{13}C NMR (62 MHz, $CDCl_3$): δ = 13.7 ($2CH_3$), 19.2 ($2CH_2$), 30.6 ($2CH_2$), 65.5, 65.6 (CH_2O), 123.8, 124.1, 124.4 (CH), 127.8, 128.8 (C), 130.6 (CH), 140.8, 141.5 (C), 167.6, 168.1 (CO). IR (KBr, cm^{-1}): ν = 2957, 2930, 2871 (w), 1717 (s), 1625, 1600, 1543, 1490, 1452, 1405, 1381 (w), 1314 (m), 1273 (s), 1241, 1190, 1119, 1096, 1074 (m), 1018, 961, 942, 903, 840 (w), 775, 754, 736, 700 (m), 651, 545 (w). GC-MS (EI, 70 eV): *m/z* (%) = 334(11) $[M]^+$, 222(27), 206(13), 205(100), 178(11). HRMS (EI, 70 eV): calcd for $C_{18}H_{22}O_4S$ $[M]^+$: 334.12333; found: 334.12338.

Dihexyl benzo[*b*]thiophene-5,6-dicarboxylate (28e):



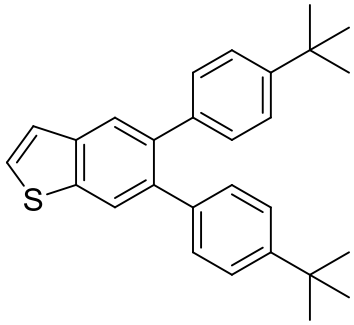
Compound **28e** was prepared starting with **27e** (100 mg, 0.26 mmol), following the general procedure B, as a brown oil (99 mg, 100%). ^{1}H NMR (300 MHz, $CDCl_3$): δ = 0.80-0.85 (m, 6H, $2CH_3$), 1.18-1.40 (m, 12H, $6CH_2$), 1.63-1.72 (m, 4H, $2CH_2$), 4.25 (q, 4H, J = 6.8 Hz, $2OCH_2$), 7.35 (dd, 1H, J = 0.5, 5.5 Hz, ArH), 7.58 (d, 1H, J = 5.5 Hz, ArH), 8.10 (s, 1H, ArH), 8.20 (s, 1H, ArH)). ^{13}C NMR (62 MHz, $CDCl_3$): δ = 14.0 ($2CH_3$), 22.5 ($2CH_2$), 25.6 ($2CH_2$), 28.5 ($2CH_2$), 31.5 ($2CH_2$) 65.8, 65.9 (OCH_2), 123.8, 124.1, 124.4 (CH), 127.8, 128.8 (C), 130.5 (CH), 140.8, 141.5 (C), 167.6, 168.0 (CO). IR (KBr, cm^{-1}): ν = 2953, 2926, 2856 (w), 1720 (s), 1624, 1601, 1544, 1490, 1465, 1455, 1378, 1314 (w), 1272, 1241, 1189, 1167, 1120, 1097, 1074 (m), 993, 904, 837, 776, 755, 724, 701, 652 (w). GC-MS (EI, 70 eV): *m/z* (%) = 390(7) $[M]^+$, 222(23), 206(13), 205(100). HRMS (EI, 70 eV): calcd for $C_{22}H_{30}O_4S$ $[M]^+$: 390.18593; found: 390.18607.

Bis(2-ethylhexyl) benzo[*b*]thiophene-5,6-dicarboxylate (28g):



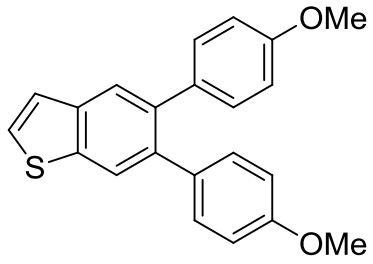
Compound **28g** was prepared starting with **27g** (100 mg, 0.26 mmol), following the general procedure B, as a brown oil (99 mg, 100%). ^{1}H NMR (300 MHz, $CDCl_3$): δ = 0.77-0.88 (m, 12H, $4CH_3$), 1.25-1.41 (m, 16H, CH-Aliphatic), 1.59-1.65 (m, 2H, CH), 4.15-4.18 (m, 4H, $2CH_2O$), 7.33 (d, 1H, J = 5.4 Hz, ArH), 7.56 (d, 1H, J = 5.4 Hz, ArH), 8.07 (s, 1H, ArH), 8.17 (s, 1H, ArH)). ^{13}C NMR (62 MHz, $CDCl_3$): δ = 11.0 ($2CH_3$), 14.1 ($2CH_3$), 23.0 ($2CH_2$), 23.8 ($2CH_2$), 29.0 ($2CH_2$), 30.4 ($2CH_2$), 38.7, 38.8 (CH), 68.1, 68.2 (CH_2O), 123.7, 124.1, 124.4 (CH), 127.9, 129.0 (C), 130.5 (CH), 140.8, 141.5 (C), 167.7, 168.1 (CO). IR (KBr): v = 2956, 2927 (m), 2858 (w), 1720 (s), 1625, 1459, 1379, 1313 (w), 1270 (s), 1240, 1190, 1167, 1120, 1097, 1073, 774, 701 (m), 654, 544 (w) cm^{-1}. GC-MS (EI, 70 eV): *m/z* (%) = 446(02) $[M]^+$, 223(27), 222(41), 205(100), 57(10). HRMS (EI, 70 eV): calcd for $C_{26}H_{38}O_4S$ $[M]^+$: 446.24853; found: 446.24915.

5,6-Bis(4-*tert*-butylphenyl)benzo[*b*]thiophene (28h):



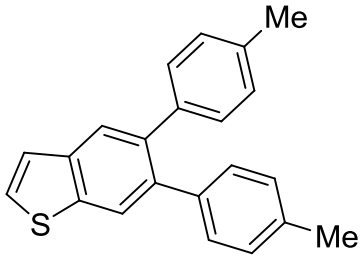
Compound **28h** was prepared starting with **27h** (100 mg, 0.25 mmol), following the general procedure B, as a brown highly viscous oil (99 mg, 100%). ^{1}H NMR (300 MHz, $CDCl_3$): δ = 1.21 (s, 18H, $6CH_3$), 7.01 (d, 4H, J = 8.3 Hz, ArH), 7.13 (d, 4H, J = 8.1 Hz, ArH), 7.26 (d, 1H, J = 5.3 Hz, ArH), 7.36 (d, 1H, J = 5.4 Hz, ArH), 7.77 (s, 1H, ArH), 7.83 (s, 1H, ArH). ^{13}C NMR (62 MHz, $CDCl_3$): δ = 31.4 ($6CH_3$), 34.4 (2C), 123.7, 123.9 (CH), 124.6 (4CH), 125.1, 126.9 (CH), 129.6 (2CH), 129.7 (2CH), 137.6, 137.7, 138.6, 138.7, 138.8, 138.9 (C), 149.2, 149.3 (C).). IR (KBr, cm^{-1}): v = 3026, 2958, 2902, 2864, 2245, 1906, 1602, 1514, 1449, 1408, 1390 (w), 1361 (m), 1320, 1307 (w), 1267 (m), 1200, 1181, 1111, 1085, 1085, 1058, 1038, 1014, 960, 907, 894, 876 (w), 834 (s), 776, 762 (w), 731, 719 (m), 683, 661, 646, 633 (w), 602, 562 (m). GC-MS (EI, 70 eV): *m/z* (%) = 398(100) $[M]^+$, 384(25), 383(84), 184(12), 156(16), 57(29). HRMS (EI, 70 eV): calcd for $C_{28}H_{30}S$ $[M]^+$: 398.20627; found: 398.20642.

5,6-Bis(4-methoxyphenyl)benzo[*b*]thiophene (28i):



Compound **28i** was prepared starting with **27i** (100 mg, 0.29 mmol), following the general procedure B, as a brown highly viscous oil (99 mg, 100%). ^{1}H NMR (300 MHz, $CDCl_3$): δ = 3.69 (s, 6H, $2OCH_3$), 6.7 (dd, 4H, J = 1.3, 8.6 Hz, ArH), 7.01 (dd, 4H, J = 1.9, 8.7 Hz, ArH), 7.25 (d, 1H, J = 5.4 Hz, ArH), 7.35 (d, 1H, J = 5.4 Hz, ArH), 7.72 (s, 1H, ArH), 7.78 (s, 1H, ArH). ^{13}C NMR (75 MHz, $CDCl_3$): δ = 55.2 ($2OCH_3$), 113.4 (4CH), 123.7, 123.9, 125.1, 126.9 (CH), 131.0 (2CH), 131.1 (2CH), 134.1, 134.3, 137.2, 137.3, 138.8, 138.9 (C), 158.2, 158.3 (C-O). IR (KBr, cm^{-1}): ν = 3132, 2952, 2929, 2833, 2540, 1712 (w), 1607 (m), 1574 (w), 1484, 1449, 1439 (m), 1415, 1390, 1319 (w), 1286 (m), 1240, 1173 (s), 1107 (m), 1087, 1085 (w), 1044, 1025 (m), 958 (w), 905 (m), 830 (s), 801, 759, 730, 716 (m), 683, 670, 657, 628, 603 (w), 585, 546, 534 (m). GC-MS (EI, 70 eV): *m/z* (%) = 346(100) $[M]^+$, 271(12). HRMS (EI, 70 eV): calcd for $C_{22}H_{18}O_2S$ $[M]^+$: 346.10220; found: 346.10260.

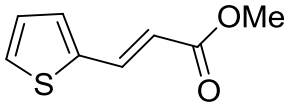
5,6-Di-*p*-tolylbenzo[*b*]thiophene (28j):



Compound **28j** was prepared starting with **27j** (100 mg, 0.32 mmol), following the general procedure B, as a brown highly viscous oil (99 mg, 100%). ^{1}H NMR (250 MHz, $CDCl_3$): δ = 2.23 (s, 6H, $2CH_3$), 6.94 (d, 4H, J = 7.3 Hz, ArH), 6.99 (d, 4H, J = 8.2 Hz, ArH), 7.25 (d, 1H, J = 5.4 Hz, ArH), 7.35 (d, 1H, J = 5.5 Hz, ArH), 7.74 (s, 1H, ArH), 7.79 (s, 1H, ArH). ^{13}C NMR (62 MHz, $CDCl_3$): δ = 21.2 ($2CH_3$), 123.7, 124.0, 125.3, 127.0 (CH), 128.6 (4CH), 129.9 (2CH), 130.0 (2CH), 135.9, 136.0, 137.5, 137.6, 138.7 (C), 138.8 (2C), 138.9 (C). IR (KBr, cm^{-1}.): ν = 3020, 2916, 2848 (w), 1512 (m), 1484 (w), 1448 (m), 1409, 1319, 1181, 1110, 1087, 1057, 1036, 1018, 943, 894, 875 (m), 814 (s), 758, 724, 657, 583, 526 (w). GC-MS (EI, 70 eV): *m/z* (%) = 314(100) $[M]^+$, 299(42), 298(19), 285(10), 284(28). HRMS (EI, 70 eV): calcd for $C_{22}H_{18}S$ $[M]^+$: 314.11237; found: 314.11245.

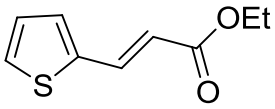
Synthesis of 2-alknylthiophene (29):

(*E*)-Methyl-3-(thiophen-2-yl)acrylate (29a):



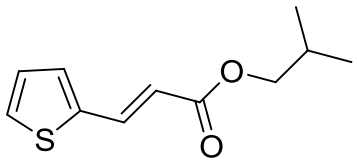
Product **29a** was prepared starting with **25** (242 mg, 1.0 mmol), methyl acrylate (0.09 mL, 1.0 mmol), $Pd(OAc)_2$ (11 mg, 5 mol %), XPhos (10 mol %), NEt_3 (1.10 mL, 8.0 mmol), DMF (5 mL) at 120 °C for 24 h following general procedure A, as a brown oil (126 mg, 75%). ^{1}H NMR (230) MHz, $CDCl_3$): δ = 3.71 (s, 3H, OCH_3), 6.18 (d, 1H, J = 15.9 Hz, CH), 7.18-7.27 (m, 2H, ArH), 7.40-7.42 (m, 1H, ArH), 7.60 (d, 1H, J = 15.9 Hz, CH). ^{13}C NMR (62 MHz, $CDCl_3$): δ = 51.6 (OCH_3), 117.4, 125.1, 126.9, 128.1 (CH), 137.5 (C), 138.3 (CH), 167.6 (CO). IR (KBr, cm^{-1}): v = 3098, 29993, 2946, 2841 (w), 1703, 1699, 1632 (s), 1515 (w), 1435 (m), 1392, 1370 (w), 1306, 1275, 1247, 1197 (m), 1168 (s), 1054, 1043, 1012, 979, 922, 865, 842, 828 (m), 793 (s), 754, 736, 725, 666, 608, 590 (m). GC-MS (EI, 70 eV): *m/z* (%) = 168(62) $[M]^+$, 138(10), 137(100), 110(08), 109(42), 65(16). HRMS (EI, 70 eV): calcd for $C_8H_8O_2S$ $[M]^+$: 168.02395; found: 168.02367.

(*E*)-Ethyl-3-(thiophen-2-yl)acrylate (29b):



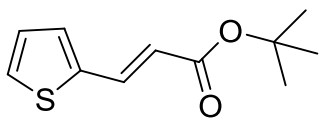
Product **29b** was prepared starting with **25** (242 mg, 1.0 mmol), ethyl acrylate (0.11 mL, 1.0 mmol), $Pd(OAc)_2$ (11 mg, 5 mol %), SPhos (10 mol %), NEt_3 (1.10 mL, 8.0 mmol), DMF (5 mL) at 120 °C for 24 h following general procedure A, as a brown oil (141 mg, 78%). ^{1}H NMR (300 MHz, $CDCl_3$): δ = 1.26 (t, 3H, J = 7.1 Hz, CH_3), 4.18 (q, 2H, J = 7.1 Hz, CH_2O), 6.18 (d, 1H, J = 15.9 Hz, CH), 7.19-7.26 (m, 2H, ArH), 7.40-7.42 (m, 1H, ArH), 7.59 (d, 1H, J = 15.9 Hz, CH). ^{13}C NMR (62 MHz, $CDCl_3$): δ = 14.3 (CH_3), 60.4 (CH_2O), 117.9, 125.1, 126.9, 127.9, 138.0 (CH), 137.6 (C), 167.2 (CO). IR (KBr, cm^{-1}): v = 3098, 2978, 2927, 2853 (w), 1703 (s), 1632 (m), 1518, 1463, 1444, 1392, 1365 (w), 1302, 1276, 1244, 1204 (m), 1152 (s), 1094, 1033, 975, 863, 828, 783, 700, 666, 605, 592 (m). GC-MS (EI, 70 eV): *m/z* (%) = 182(46) $[M]^+$, 154(11), 138(12), 137(100), 110(20), 109(37), 65(16). HRMS (EI, 70 eV): calcd for $C_9H_{10}O_2S$ $[M]^+$: 182.03960; found: 182.03963.

(*E*)-Isobutyl-3-(thiophen-2-yl)acrylate (29c):



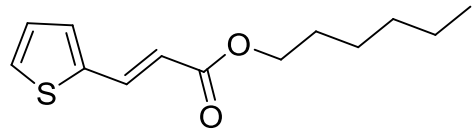
Product **29c** was prepared starting with **25** (242 mg, 1.0 mmol), *iso*-butyl acrylate (0.14 mL, 1.0 mmol), $Pd(OAc)_2$ (11 mg, 5 mol %) , XPhos (10 mol %), NEt_3(1.10 mL, 8.0 mmol), DMF (5 mL) at 120 °C for 24 h following general procedure A, as a brown highly viscous oil (155 mg, 74%). ^{1}H NMR (250 MHz, $CDCl_3$): δ = 0.90 (d, 6H, J = 6.7 Hz, $2CH_3$), 1.85-2.01 (m, 1H, CH), 3.91 (d, 2H, J = 6.7 Hz, CH_2O), 6.20 (d, 1H, J = 15.9 Hz, CH), 7.18-7.25 (m, 2H, ArH), 7.40-7.42 (m, 1H, ArH), 7.59 (d, 1H, J = 15.9 Hz, CH). ^{13}C NMR (75 MHz, $CDCl_3$): δ = 19.2 ($2CH_3$), 27.9 (CH), 70.6 (CH_2O), 117.9, 125.2, 126.9, 127.9 (CH), 137.6 (C), 138.0 (CH), 167.3 (CO). IR (KBr): ν = 3098, 2958, 2931, 2872 (w), 1704 (s), 1632 (m), 1518, 1468, 1426, 1394, 1375, 1342 (w), 1305, 1276, 1203 (m), 1151 (s), 1084 (w), 1013, 974 (m), 867, 859, 828 (w), 783 (m), 699, 667 (w), 605 (m), 569, 537 (w) cm^{-1}. GC-MS (EI, 70 eV): *m/z* (%) = 210 ($[M]^+$, 12), 154 (71), 138 (10), 137 (100), 112 (12), 109 (31), 65 (13), 39 (08). HRMS (EI, 70 eV): calcd for $C_{11}H_{14}O_2S$ $[M]^+$: 210.07090; found: 210.07110.

(*E*)-*tert*-Butyl-3-(thiophen-2-yl)acrylate (29d):



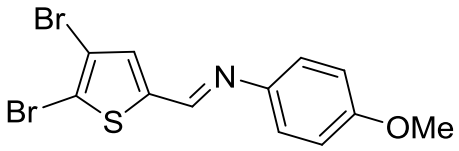
Product **29d** was prepared starting with **25** (242 mg, 1.0 mmol), *tert*-butyl acrylate (0.14 mL, 1.0 mmol), $Pd(OAc)_2$ (11 mg, 5 mol %), XPhos (10 mol %), NEt_3 (1.10 mL, 8.0 mmol), DMF (5 mL) at 120 °C for 24 h following general procedure A, as a brown oil (182 mg, 87%). ^{1}H NMR (300 MHz, $CDCl_3$): δ = 1.45 (s, 9H, $3CH_3$), 6.12 (d, 1H, J = 15.9 Hz, CH), 7.18-7.25 (m, 2H, ArH), 7.36-7.39 (m, 1H, ArH), 7.59 (d, 1H, J = 16.0 Hz, CH). ^{13}C NMR (75 MHz, $CDCl_3$): δ = 28.2 ($3CH_3$), 80.4 (C-O), 119.9, 125.2, 126.8, 127.4, 137.1 (CH), 137.8 (C), 166.6 (CO). IR (KBr, cm^{-1}): ν = 3098, 2976, 2927, 2855 (w), 1705 (s), 1633 (m), 1518, 1455, 1392 (w), 1366, 1309, 1281 (m), 1248, 1219 (w), 1148 (s), 1085, 1041, 978, 855, 829, 787, 702, 665, 606, 529 (w). GC-MS (EI, 70 eV): *m/z* (%) = 210(16) $[M]^+$, 154(100), 137(57), 126(10), 112(30), 109(21), 65(12), 57(20), 41(14). HRMS (EI, 70 eV): calcd for $C_{11}H_{14}O_2S$ $[M]^+$: 210.07090; found: 210.07071.

(*E*)-Hexyl-3-(thiophen-2-yl)acrylate (29e):



Product **29e** was prepared starting with **25** (242 mg, 1.0 mmol), hexyl acrylate (1.0 mmol), $Pd(OAc)_2$ (11 mg, 5 mol %), SPhos (10 mol %), NEt_3 (1.10 mL, 8.0 mmol), DMF (5 mL) at 120 °C for 24 h following general procedure A, as a brown oil (180 mg, 76%). ^{1}H NMR (300 MHz, $CDCl_3$): δ = 0.83 (t, 3H, J = 6.8 Hz, CH_3), 1.21-1.29 (m, 6H, $3CH_2$), 1.54-1.64 (m, 2H, CH_2), 4.11 (t, 2H, J = 6.8 Hz, CH_2O), 6.19 (d, 1H, J = 15.9 Hz, CH), 7.18-7.25 (m, 2H, ArH), 7.40-7.42 (m, 1H, ArH), 7.59 (d, 1H, J = 15.9 Hz, CH). ^{13}C NMR (62 MHz, $CDCl_3$): δ = 14.0 (CH_3), 22.5, 25.6, 28.7, 31.4 (CH_2), 64.7 (CH_2O), 118.0, 125.1, 126.9, 127.9 (CH), 137.6 (C), 138.0 (CH), 167.3 (CO). IR (KBr, cm^{-1}): ν = 3098, 2953, 2927, 2856 (w), 1707 (s), 1632 (m), 1518, 1465, 1391, 1379 (w), 1302, 1276, 1245, 1203 (m), 1162 (s), 1112, 1082, 976 (m), 908, 867, 860, 829 (w), 784, 711 (m), 668 (w), 605 (m). GC-MS (EI, 70 eV): *m/z* (%) = 238(12) $[M]^+$, 155(16), 154(100), 138(10), 137(81), 112(13), 110(12), 109(32), 65(14). HRMS (EI, 70 eV): calcd for $C_{13}H_{18}O_2S$ $[M]^+$: 238.10220; found: 238.10245

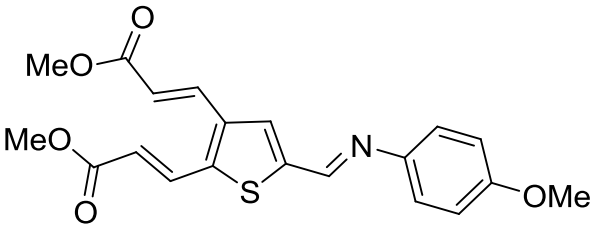
Synthesis of (*E*)-*N*-[(4,5-dibromothiophen-2-yl)methylene]-4-methoxyaniline (31):



A mixture of 4,5-dibromothiophene-2-carbaldehyde **(30)** (269 mg, 1.0 mmol), 4-methoxy aniline (184 mg, 1.5 mmol) in glacial acetic acid (5 mL) was stirred at room temperature for 15 min to give a greenish precipitate. Then it was filtered and washed with ethanol to give the pure imine **31** (365 mg, 98.00 %), mp. = 136-137 °C. ^{1}H NMR (300 MHz, $CDCl_3$): δ = 3.75 (s, 3H, OCH_3), 6.83 (dd, 2H, J = 2.1, 6.8 Hz, ArH), 7.12 (s, 1H, ArH), 7.14 (dd, 2H, J = 2.1, 6.8 Hz, ArH), 8.33 (s, 1H, N=CH). ^{13}C NMR (62 MHz, $CDCl_3$): δ = 55.5 (OCH_3), 114.5 (2CH), 122.5 (2CH), 132.8 (CH), 143.1 (2C-Br), 144.0 (2C), 148.2 (CH), 158.9 (C-O). IR (KBr, cm^{-1}): ν = 2932, 2834 (w), 1614, 1579, 1519, 1502, 1463, 1427, 1417, 1287 (m), 1239 (s), 1200, 1183, 1159, 1118 (m), 1030 (s), 991, 950 (m), 827 (s), 770, 665, 636, 582 (m), 546 (w). GC-MS (EI, 70 eV): *m/z* (%) = 377(53) [M^+ (^{81}Br, ^{81}Br)], 375(100) [M^+ (Br, ^{81}Br)], 373(52) [M^+ (Br, Br)], 360(93), 358(47), 172(19), 92(12), 77(12), 64(11). HRMS (EI, 70 eV): calcd for $C_{12}H_9Br_2NOS$ [M^+ (Br, ^{81}Br)]$^+$: 374.87456; found: 374.87422.

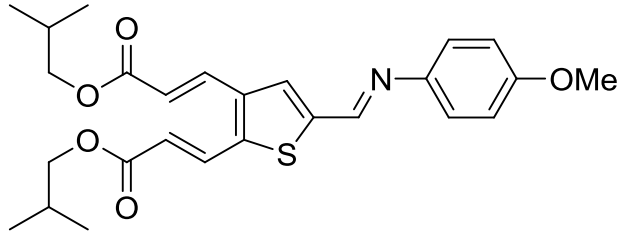
Synthesis of 2,3-di(alkenyl)thiophenes (32):

(2*E*,2'*E*)-Dimethyl-3,3'-{5-[(*E*)-(4-methoxyphenylimino)methyl]thiophene-2,3-diyl} diacrylate (32a):



Product **32a** was prepared starting with **31** (186 mg, 0.5 mmol), methyl acrylate (0.12 mL, 1.25 mmol), $Pd(OAc)_2$ (6 mg, 5 mol-%), $P(Cy)_3$ (10 mol-%), NEt_3 (0.55 mL, 4.0 mmol) , DMF (5 mL) at 90 °C for 12 h following general procedure A, as a brown oil (119 mg, 62%). ^{1}H NMR (300 MHz, $CDCl_3$): δ = 3.75 (s, 9H, $3OCH_3$), 6.25 (d, 1H, J = 16.4 Hz, CH), 6.31 (d, 1H, J = 16.4 Hz, CH), 6.85 (d, 2H, J = 9.0 Hz, ArH), 7.15 (d, 2H, J = 9.0 Hz, ArH), 7.46 (s, 1H, ArH), 7.76 (d, 1H, J = 15.7 Hz, CH), 7.92 (d, 1H, J = 15.3 Hz, CH), 8.44 (s, 1H, N=CH). ^{13}C NMR (75 MHz, $CDCl_3$): δ = 51.9, 52.0, 55.5 (OCH_3), 114.5 (2CH), 120.2, 120.3 (CH), 122.6 (2CH), 129.1, 133.4, 134.3 (CH), 138.5 (C), 142.2 (C-N), 143.2, 144.4 (C) 149.0 (CH), 159.1 (C-O), 166.6, 167.0 (CO). IR (KBr, cm^{-1}): ν = 2957, 2935, 2830 (w), 1709, 1637 (m), 1614 (s), 1574, 1508, 1453, 1440, 1386, 1367, 1304, 1291 (m), 1243, 1171, 1162 (s), 1120, 1108 (m),1022, 970 (s), 864 (m), 832 (s), 795, 780, 732, 705, 678, 599, 554, 537 (m). GC- MS (EI, 70 eV): *m/z* (%) = 385(60) [M^+], 383(19), 326(79), 327(100), 310(35), 294(60), 267(16), 252(27), 162(12), 147(20), 134(35). HRMS (EI, 70 eV): calcd for $C_{20}H_{19}NO_5S$ $[M]^+$: 385.09784; found: 385.09850.

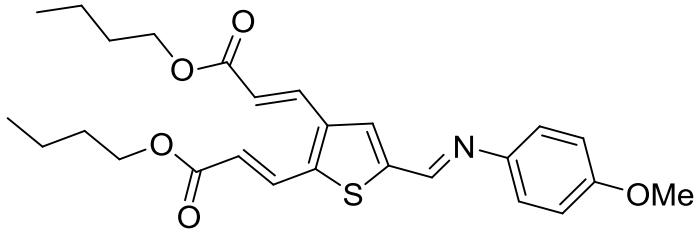
(2*E*,2'*E*)-Isobutyl-3,3'-{5-[(*E*)-(4-methoxyphenylimino)methyl]thiophene-2,3-diyl} diacrylate (32b):



Product **32b** was prepared starting with **31** (186 mg, 0.5 mmol), *iso*-butyl acrylate (0.18 mL, 1.25 mmol), $Pd(OAc)_2$ (6 mg, 5 mol %), $P(Cy)_3$ (10 mol %), NEt_3 (0.55 mL, 4.0 mmol), DMF (5 mL) at 90 °C for 12 h following general procedure A, as a brown oil (178 mg, 76%). ^{1}H NMR (300 MHz, $CDCl_3$): δ = 0.92 (dd, 12H, J = 0.8, 6.7 Hz, $4CH_3$), 1.92-1.98 (m, 2H, CH), 3.76 (s, 3H, OCH_3), 3.92 (dd, 4H, J = 1.9, 6.7 Hz, $2CH_2O$), 6.31 (t, 2H, J = 15.8 Hz, CH), 6.85 (dd, 2H, J = 2.1, 6.8 Hz, ArH), 7.18 (dd, 2H, J = 2.2, 6.8

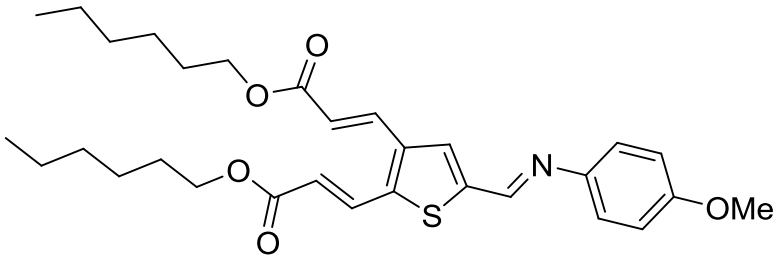
Hz, ArH), 7.49 (s, 1H, ArH), 7.76 (d, 1H, J = 15.8 Hz, CH), 7.92 (d, 1H, J = 15.5 Hz, CH), 8.45 (s, 1H, N=CH). ^{13}C NMR (75 MHz, $CDCl_3$): δ = 18.1 ($4CH_3$), 26.8 (2CH), 54.5 (OCH_3), 69.9, 70.0 (CH_2O), 113.5 (2CH), 119.7, 119.8 (CH), 121.6 (2CH), 128.2, 132.2, 133.1 (CH), 137.4 (C), 141.2 (C-N), 142.2, 143.3 (C) 148.0 (CH), 158.0 (C-O), 165.2, 165.6 (CO). IR (KBr, cm^{-1}): v = 2960, 2873, 2835 (w), 1692 (s), 1608, 1574, 1501, 1465, 1393, 1377, 1367 (m), 1343, 1305 (w), 1282, 1268 (m), 1246, 1234 (s), 1199, 1178 (m), 1166, 1156 (s), 1109 (m), 1024, 1014 (s), 967, 951, 930, 908, 856, 843 (m), 827 (s), 779, 735, 712, 664, 636, 617, 599, 553, 535 (m). MS (EI, 70 eV): *m/z* (%) = 469(100) [M^+], 343(15), 312(21), 296(16), 294(10), 268(26), 252(10), 134(17), 78(12), 63(14), 57(32). HRMS (EI, 70 eV): calcd for $C_{26}H_{31}NO_5S$ [$M]^+$: 469.19175; found: 469.19242.

(2*E*,2'*E*)-Dibutyl-3,3'-{5-[(*E*)-(4-methoxyphenylimino)methyl]thiophene-2,3-diyl}diacrylate (32c):



Product **32c** was prepared starting with **31** (186 mg, 0.5 mmol), *n*-butyl acrylate (0.18 mL, 1.25 mmol), $Pd(OAc)_2$ (6 mg, 5 mol %), $P(Cy)_3$ (10 mol %), NEt_3 (0.55 mL, 4.0 mmol), DMF (5 mL) at 90 °C for 12 h following general procedure A, as a brown oil (128 mg, 55%). ^{1}H NMR (300 MHz, $CDCl_3$): δ = 0.90 (t, 6H, J = 7.4 Hz, $2CH_3$), 1.30-1.43 (m, 4H, $2CH_2$), 1.57-1.68 (m, 4H, $2CH_2$), 3.76 (s, 3H, OCH_3), 4.15 (t, 2H, J = 6.7 Hz, CH_2O), 4.16 (t, 2H, J = 6.7 Hz, CH_2O), 6.27 (d, 1H, J = 15.9 Hz, CH), 6.32 (d, 1H, J = 15.6 Hz, CH), 6.85 (dd, 2H, J = 2.8, 9.0 Hz, ArH), 7.14-7.20 (m, 2H, ArH), 7.51 (s, 1H, ArH), 7.76 (d, 1H, J = 15.8 Hz, CH), 7.92 (d, 1H, J = 15.5 Hz, CH), 8.45 (s, 1H, N=CH). ^{13}C NMR (75 MHz, $CDCl_3$): δ = 13.7 ($2CH_3$), 19.2 ($2CH_2$), 30.7 ($2CH_2$), 55.5 (OCH_3), 64.7, 64.8 (CH_2O), 114.4 (2CH), 120.8, 122.4 (CH), 122.6 (2CH), 129.2, 133.2, 134.1 (CH), 138.4 (C), 142.3 (C-N), 143.3, 144.3 (C) 149.1 (CH), 159.1 (C-O), 166.3, 166.7 (CO). IR (KBr, cm^{-1}): v = 2956, 2869, 2835 (w), 1698, 1613 (s), 1557, 1529 (w), 1503, 1455, 1392 (m), 1281, 1242 (s), 1202 (m), 1164 (s), 1108, 1064, 1031 (m), 963 (s), 933, 858 (m), 833 (s), 800, 780, 739, 713, 666, 601, 555, 531 (m). MS (EI, 70 eV): *m/z* (%) = 469(100) [M^+], 343(15), 312(20), 296(15), 294(10), 268(27), 252(10), 134(19), 78(14), 63(15), 57(15). HRMS (EI, 70 eV): calcd for $C_{26}H_{31}NO_5S$ [$M]^+$: 469.19175; found: 469.19256.

(2*E*,2'*E*)-dihexyl 3,3'-{5-[(*E*)-(4-methoxyphenylimino)methyl]thiophene-2,3-diyl}diacrylate (32d):

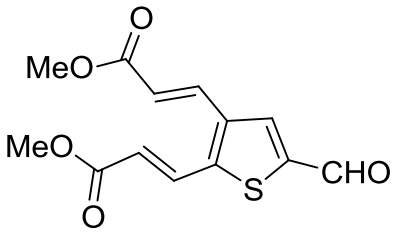


Product **32d** was prepared starting with **31** (186 mg, 0.5 mmol), *n*-hexyl acrylate (0.22 mL, 1.25 mmol), $Pd(OAc)_2$ (6 mg, 5 mol %), $P(Cy)_3$ (10 mol %), NEt_3 (0.55 mL, 4.0 mmol), DMF (5 mL) at 90 °C for 12 h following general procedure A, as a brown oil (176 mg, 67%). ^{1}H NMR (300 MHz, $CDCl_3$): δ = 0.83 (t, 6H, *J* = 6.7 Hz, $2CH_3$), 1.23-1.35 (m, 12H, $6CH_2$), 1.59-1.67 (m, 4H, $2CH_2$), 3.76 (s, 3H, OCH_3), 4.14 (t, 2H, *J* = 6.8 Hz, CH_2O), 4.15 (t, 2H, *J* = 6.8 Hz, CH_2O), 6.27 (d, 1H, *J* = 16.4 Hz, CH), 6.33 (d, 1H, *J* = 15.7 Hz, CH), 6.85 (d, 2H, *J* = 8.9 Hz, ArH), 7.17-7.20 (m, 2H, ArH), 7.48 (s, 1H, ArH), 7.75 (d, 1H, *J* = 15.8 Hz, CH), 7.92 (d, 1H, *J* = 15.5 Hz, CH), 8.45 (s, 1H, N=CH). ^{13}C NMR (75 MHz, $CDCl_3$): δ = 14.0 ($2CH_3$), 22.5 ($2CH_2$), 25.6 ($2CH_2$), 28.6, 28.7 (CH_2), 31.4 ($2CH_2$), 55.5 (OCH_3), 65.0, 65.1 (CH_2O), 114.5 (2CH), 120.8 (2CH), 122.6 (2CH), 129.2, 133.2, 134.1 (CH), 138.4 (C), 142.3 (C-N), 143.3, 144.3 (C) 149.1 (CH), 159.0 (C-O), 166.3, 166.7 (CO). IR (KBr, cm^{-1}): *v* = 2954, 2927, 2857 (w), 1695, 1612 (s), 1575, 1529 (w), 1502, 1454 (m), 1268, 1237, 1165, 1158 (s), 1015, 969, 827, 779 (m), 711, 662, 601 (w), 553, 533 (m). MS (EI, 70 eV): *m/z* (%) = 525(100) [M^+], 312(22), 296(19), 294(10), 268(29), 252(10), 134(22), 43(44), 41(12). HRMS (EI, 70 eV): calcd for $C_{30}H_{39}NO_5S$ $[M]^+$: 525.25435; found: 525.25419.

General procedure C for the synthesis of 2,3-di(alkenyl)-5-formylthiophene (33):

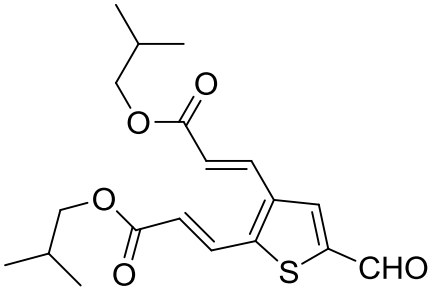
In a pressure tube (glass bomb), to a mixture of compounds **32a-e** (0.5 mmol) and dichloromethane (1mL) were added H_2SO_4 (4mL, 2.5M). The reaction mixture was stirred at room temperature for 20 h. The solution was poured into H_2O and CH_2Cl_2 (25 mL each) and the organic and the aqueous layer were separated. The latter was extracted with CH_2Cl_2 (3 × 25 mL), dried (Na_2SO_4), filtered, and concentrated *in vacuo*.

(2*E*,2'*E*)-Dimethyl-3,3'-(5-formylthiophene-2,3-diyl)diacrylate (33a):



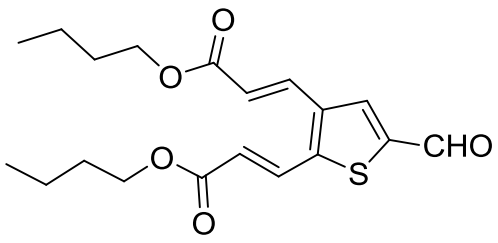
Compound **33a** was prepared starting with **32a** (192 mg, 0.50 mmol), following the general procedures C, as a brown solid (137 mg, 98%), mp.= 142-145 °C. ^{1}H NMR (300 MHz, $CDCl_3$): δ = 3.77 (s, 6H, $2CH_3O$), 6.32 (d, 1H, J = 15.8 Hz, CH), 6.40 (d, 1H, J = 15.6 Hz, CH), 7.75 (d, 1H, J = 15.9 Hz, CH), 7.82 (s, 1H, ArH), 7.92 (d, 1H, J = 15.7 Hz, CH), 9.85 (s, 1H, O=CH). ^{13}C NMR (62 MHz, $CDCl_3$): δ = 51.1, 51.2 (CH_3O), 120.4, 121.5, 131.9, 132.8, 133.1 (CH), 137.3, 142.4, 145.3 (C), 165.0, 165.6 (CO), 181.6 (O=CH). IR (KBr, cm^{-1}): ν = 3084, 2958, 2922, 2850 (w), 1708, 1668, 1620 (s), 1442, 1472, 1302, 1276, 1242, 1212 (m), 1191, 1160 (s), 1031, 1015 (m), 966 (s), 915, 863, 853, 730, 685, 663, 607, 538 (m). GC-MS (EI, 70 eV): *m/z* (%) = 280(47) [M^+], 249(23), 221(100), 220(47), 205(47), 189(80), 177(46), 161(75), 149(23), 134(64), 89(39), 67(17), 59(41). HRMS (EI, 70 eV): calcd for $C_{13}H_{12}O_5S$ [$M]^+$: 280.04000; found: 280.04067.

(2*E*,2'*E*)-Isobutyl-3,3'-(5-formylthiophene-2,3-diyl)diacrylate (33b):



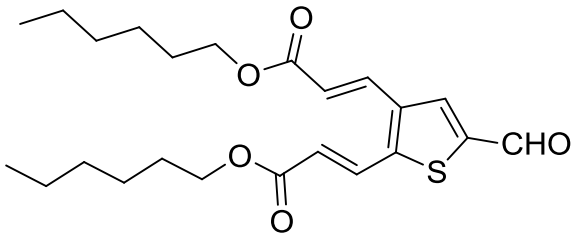
Compound **33c** was prepared starting with **32b** (234 mg, 0.50 mmol), following the general procedures C, as a brown oil (172 mg, 95%). ^{1}H NMR (300 MHz, $CDCl_3$): δ = 0.92 (d, 12H, J = 6.7 Hz, $4CH_3$), 1.88-2.02 (m, 2H, CH), 3.95 (d, 4H, J = 6.7 Hz, $2CH_2O$), 6.33 (d, 1H, J = 15.8 Hz, CH), 6.41 (d, 1H, J = 15.6 Hz, CH), 7.74 (d, 1H, J = 15.8 Hz, CH), 7.84 (s, 1H, ArH), 7.92 (d, 1H, J = 15.6 Hz, CH), 9.85 (s, 1H, O=CH). ^{13}C NMR (75 MHz, $CDCl_3$): δ = 19.1 ($4CH_3$), 27.8 (2CH), 71.1, 71.3 (CH_2O), 121.9, 122.9, 132.7, 133.6, 134.3 (CH), 138.3, 143.3, 146.3 (C), 165.6, 166.2 (CO), 182.6 (O=CH). IR (KBr, cm^{-1}): ν = 2978, 2926, 2848 (w), 1708, 1671 (s), 1625, 1449, 1375, 1279, 1240 (m), 1176, 1157, 1031 (s), 968, 954, 854, 677 (m). GC-MS (EI, 70 eV): *m/z* (%) = 364(20) [M^+], 291(18), 208 (22), 207 (100), 191(72), 163(61), 135(33), 91(11), 89(15), 57(75), 41(37), 29(18). HRMS (EI, 70 eV): calcd for $C_{19}H_{24}O_5S$ [$M]^+$: 364.13390; found: 364.13470.

(2*E*,2'*E*)-Dibutyl-3,3'-(5-formylthiophene-2,3-diyl)diacrylate (33c):



Compound **33c** was prepared starting with **32c** (234 mg, 0.50 mmol), following the general procedures C, as a brown oil (167 mg, 92%). ^{1}H NMR (300 MHz, $CDCl_3$): δ = 0.90 (t, 6H, J = 7.4 Hz, $2CH_3$), 1.33-1.40 (m, 4H, $2CH_2$), 1.59-1.66 (m, 4H, $2CH_2$), 4.15 (t, 2H, J = 6.8 Hz, CH_2O), 4.17 (t, 2H, J = 6.7 Hz, CH_2O), 6.32 (d, 1H, J = 15.8 Hz, CH), 6.39 (d, 1H, J = 15.6 Hz, CH), 7.74 (d, 1H, J = 15.9 Hz, CH), 7.82 (s, 1H, ArH), 7.90 (d, 1H, J = 15.6 Hz, CH), 9.84 (s, 1H, O=CH). ^{13}C NMR (62 MHz, $CDCl_3$): δ = 13.7 ($2CH_3$), 19.0, 19.1 (CH_2), 30.6, 30.7 (CH_2), 64.9, 65.1 (CH_2O), 121.9, 123.0, 132.7, 133.6, 134.2 (CH), 138.3, 143.2, 146.3 (C), 165.7, 166.3 (CO), 182.5 (O=CH). IR (KBr, cm^{-1}): ν = 2957, 2930, 2871 (w), 1705, 1671 (s), 1621, 1443, 1308, 1274, 1242 (m), 1162 (s), 1061, 1025, 967, 856, 661, 600 (m). GC-MS (EI, 70 eV): *m/z* (%) = 364(06) [M^+], 263(35), 262(19), 207(100), 189(40), 163(15), 161(15), 135(28), 91(11), 57(23), 41(25), 29(21). HRMS (EI, 70 eV): calcd for $C_{19}H_{24}O_5S$ [M]$^+$: 364.13390; found: 364.13398.

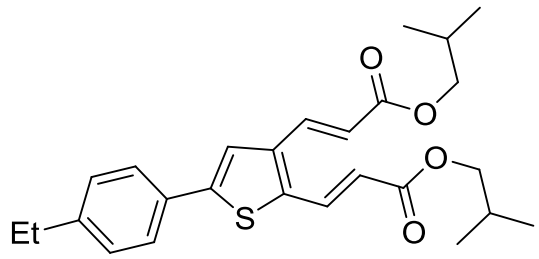
(2*E*,2'*E*)-Dihexyl-3,3'-(5-formylthiophene-2,3-diyl)diacrylate (33d):



Compound **33d** was prepared starting with **32d** (262 mg, 0.50 mmol), following the general procedures C, as a brown oil (201 mg, 96%). ^{1}H NMR (300 MHz, $CDCl_3$): δ = 0.29 (t, 6H, J = 6.8 Hz, $2CH_3$), 0.69-0.81 (m, 12H, $6CH_2$), 1.07-1.12 (m, 4H, $2CH_2$), 3.61 (t, 4H, J = 6.8 Hz, $2CH_2O$), 5.78 (d, 1H, J = 15.8 Hz, CH), 5.85 (d, 1H, J = 15.6 Hz, CH), 7.20 (d, 1H, J = 15.8 Hz, CH), 7.29 (s, 1H, ArH), 7.37 (d, 1H, J = 15.6 Hz, CH), 9.30 (s, 1H, O=CH). ^{13}C NMR (62 MHz, $CDCl_3$): δ = 14.0 ($2CH_3$), 22.5 ($2CH_2$), 25.5 ($2CH_2$), 28.5, 28.6 (CH_2), 31 ($2CH_2$), 65.2, 65.4 (CH_2O), 121.9, 123.0, 132.7, 133.6, 134.2 (CH), 138.3, 143.2, 146.3 (C), 165.6, 166.2 (CO), 182.5 (O=CH). IR (KBr, cm^{-1}): ν = 2953, 2926, 2855 (w), 1707, 1670 (s), 1622, 1443, 1305, 1271, 1243 (m), 1163 (s), 966, 857 (m), 725, 684 (w), 661 (m), 601 (w). GC-MS (EI, 70 eV): *m/z* (%) = 420(04) [M^+], 291(32), 233(20), 207(100), 189(37), 163(11), 135(18), 43(49), 41(16). HRMS (EI, 70 eV): calcd for $C_{23}H_{32}O_5S$ [M]$^+$: 420.19650; found: 420.19703.

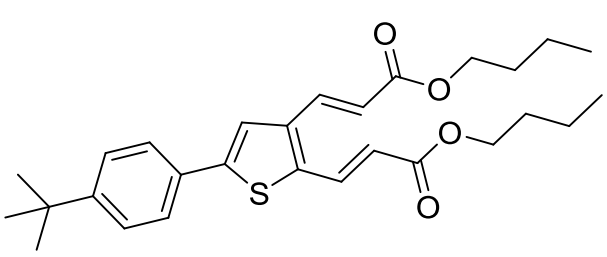
Synthesis of 2,3-di(alkenyl)-5-arylthiophene (35):

(2*E*,2'*E*)-Isobutyl-3,3'-(5-(4-ethylphenyl)thiophene-2,3-diyl)diacrylate (35a):



Product **35a** was prepared starting with **2b** (173 mg, 0.5 mmol), *iso*-butyl acrylate (0.18 mL, 1.25 mmol), $Pd(OAc)_2$ (6 mg, 5 mol %), $P(Cy)_3$ (10 mol %), NEt_3 (0.55 mL, 4.0 mmol), DMF (5 mL) at 100 °C for 24 h following general procedure A, as a brown oil (196 mg, 89%). ^{1}H NMR (300 MHz, $CDCl_3$): δ = 0.90 (d, 6H, J = 6.7 Hz, $2CH_3$), 0.91 (d, 6H, J = 6.7 Hz, $2CH_3$), 1.17 (t, 3H, J = 7.6 Hz, CH_3), 1.87-2.01 (m, 2H, 2CH), 2.58 (q, 2H, J = 7.6 Hz, CH_2), 3.92 (d, 2H, J = 6.7 Hz, CH_2O), 3.93 (d, 2H, J = 6.7 Hz, CH_2O), 6.20 (d, 1H, J = 15.4 Hz, CH), 6.29 (d, 1H, J = 15.7 Hz, CH), 7.15 (d, 2H, J = 8.2 Hz, ArH), 7.37 (s, 1H, ArH), 7.42 (d, 2H, J = 8.2 Hz, ArH), 7.76 (d, 1H, J = 16.0 Hz, CH), 7.91 (d, 1H, J = 15.4 Hz, CH). ^{13}C NMR (62 MHz, $CDCl_3$): δ = 14.3 (CH_3), 18.1 ($4CH_3$), 26.8 (2CH), 27.6 (CH_2), 69.8 ($2CH_2O$), 117.4, 119.4, 120.1(CH), 125.0 (2CH), 127.6 (2CH), 129.2 (C), 132.4, 133.4 (CH), 137.5, 138.2, 144.4, 145.3 (C), 165.5, 165.8 (CO). IR (KBr, cm^{-1}): v = 2960, 2933, 2872 (w), 1702 (s), 1622 (m), 1504, 1468, 1417, 1392, 1375 (w), 1303, 1271, 1246, 1220 (m), 1156 (s), 1019, 969, 823 (m), 774, 713, 680, 614, 550 (w). MS (EI, 70 eV): *m/z* (%) = 440(51) [M^+], 367(16), 283(53), 265(46), 239(57), 223(23), 221(12), 207(21), 169(13), 149(12), 133(15), 111(18), 97(26), 83(28), 69(69), 57(100), 44(68). HRMS (EI, 70 eV): calcd for $C_{26}H_{32}O_4S$ [M]$^+$: 440.20158; found: 440.20124.

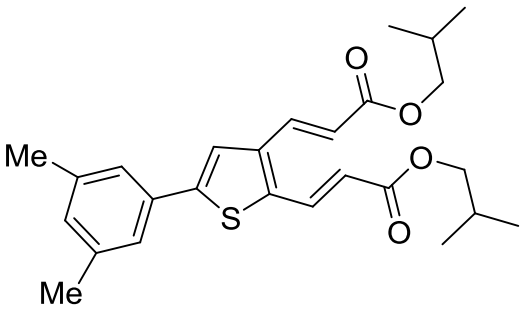
(2*E*,2'*E*)-Dibutyl-3,3'-[5-(4-*tert*-butylphenyl)thiophene-2,3-diyl]diacrylate (35b):



Product **35b** was prepared starting with **2c** (187 mg, 0.5 mmol), *n*-butyl acrylate (0.18 mL, 1.25 mmol), $Pd(OAc)_2$ (6 mg, 5 mol %), $P(Cy)_3$ (10 mol %), NEt_3 (0.55 mL, 4.0 mmol), DMF (5 mL) at 100 °C for 24 h following general procedure A, as a brown oil (176 mg, 75%). ^{1}H NMR (300 MHz, $CDCl_3$): δ = 0.89 (t, 6H, J = 6.8 Hz, $2CH_3$), 1.26 (s, 9H, $3CH_3$), 1.32-1.40 (m, 4H, $2CH_2$), 1.57-1.67 (m, 4H, $2CH_2$), 4.14 (t, 2H, J = 6.8 Hz, CH_2O), 4.16 (t, 2H, J = 6.7 Hz, CH_2O), 6.20 (d, 1H, J = 15.6 Hz, CH), 6.29 (d, 1H, J = 15.8 Hz, CH), 7.33-7.36 (m, 3H, ArH), 7.45 (d, 2H, J = 8.4 Hz, ArH), 7.77 (d, 1H, J = 15.9 Hz, CH), 7.92 (d, 1H, J = 15.3 Hz, CH). ^{13}C NMR (75 MHz,

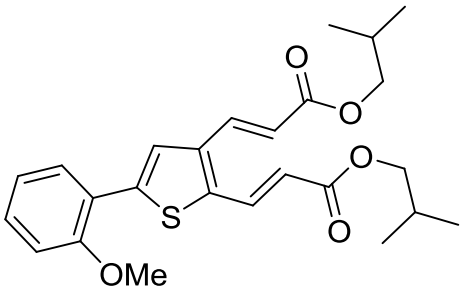
$CDCl_3$): δ = 13.8 ($2CH_3$), 19.2 ($2CH_2$), 30.8 ($2CH_2$), 31.2 ($3CH_3$), 34.8 (C), 64.6, 64.7 (CH_2O), 118.5, 120.5, 121.2 (CH), 125.8 (2CH), 126.1 (2CH), 130.0 (C), 133.5, 134.5 (CH), 138.6, 139.3, 146.2, 152.4 (C), 166.6, 166.9 (CO). IR (KBr, cm^{-1}): v = 2957, 2932, 2871 (w), 1714 (m), 1695 (s), 1613 (m), 1504, 1456, 1391, 1361 (w), 1271, 1251, 1228 (m), 1163 (s), 1113, 1064, 1026, 968, 823 (m), 739, 607, 529 (w). MS (EI, 70 eV): *m/z* (%) = 468(26) $[M]^+$, 367(10), 366(18), 351(16), 322(12), 311(36), 293(23), 267(47), 251(22), 237(15), 223(12), 211(13), 91(27), 69(15), 66(12), 57(100), 44(48), 41(68). HRMS (ESI): calcd for $C_{28}H_{37}O_4S$ $[M+H]^+$: 469.2407; found: 469.2405

(2*E*,2'*E*)-Isobutyl 3,3'-[5-(3,5-dimethylphenyl)thiophene-2,3-diyl]diacrylate (35c):



Product **35c** was prepared starting with **2d** (173 mg, 0.5 mmol), *iso*-butyl acrylate (0.18 mL, 1.25 mmol), $Pd(OAc)_2$ (6 mg, 5 mol %), $P(Cy)_3$ (10 mol %), NEt_3 (0.55 mL, 4.0 mmol), DMF (5 mL) at 100 °C for 24 h following general procedure A, as a brown oil (171 mg, 78%). ^1H NMR (300 MHz, $CDCl_3$): δ = 0.91 (d, 6H, J = 6.7 Hz, $2CH_3$), 0.92 (d, 6H, J = 6.7 Hz, $2CH_3$), 1.88-2.02 (m, 2H, 2CH), 2.28 (s, 6H, 2 CH_3), 3.93 (d, 2H, J = 6.7 Hz, CH_2O), 3.94 (d, 2H, J = 6.7 Hz, CH_2O), 6.22 (d, 1H, J = 15.5 Hz, CH), 6.32 (d, 1H, J = 15.8 Hz, CH), 6.92 (s, 1H, ArH), 7.15 (s, 2H, ArH), 7.37 (s, 1H, ArH), 7.78 (d, 1H, J = 15.8 Hz, CH), 7.93 (d, 1H, J = 15.5 Hz, CH). ^{13}C NMR (75 MHz, $CDCl_3$): δ = 19.2 ($4CH_3$), 21.3 ($2CH_3$), 27.9 (2CH), 70.8 (CH_2O), 70.9 (CH_2O), 118.5, 120.4, 121.5 (CH), 123.9 (2CH), 130.7 (CH), 132.6 (C), 133.5 134.5 (CH), 138.7 (C), 138.8 (2C), 139.2, 146.5 (C), 166.5, 166.8 (CO). IR (KBr, cm^{-1}): v = 2958 (m), 2872 (w), 1705 (s), 1615, 1602 (m), 1530 (w), 1467, 1375, 1309, 1265, 1240, 1213 (m), 1155 (s), 1021, 967, 829, 687 (m), 598, 541 (w). GC- MS (EI, 70 eV): *m/z* (%) = 440(34) $[M]^+$, 339(14), 338(16), 309(11), 283(65), 265(51), 240(18), 239(100), 238(30), 224(18), 91(16), 57(94), 44(63), 41(51). HRMS (ESI): calcd for $C_{26}H_{33}O_4S$ $[M+H]^+$: 441.2094; found: 441.2090.

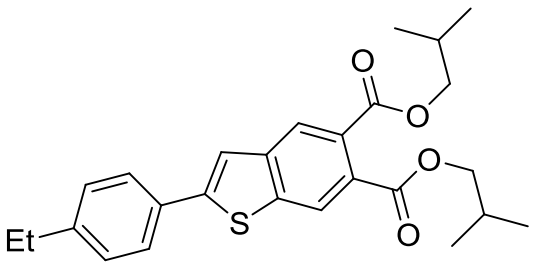
(2*E*,2'*E*)-Isobutyl-3,3'-[5-(2-methoxyphenyl)thiophene-2,3-diyl]diacrylate (35d):



Product **35d** was prepared starting with **2f** (174 mg, 0.5 mmol), *iso*-butyl acrylate (0.18 mL, 1.25 mmol), $Pd(OAc)_2$ (6 mg, 5 mol %), $P(Cy)_3$ (10 mol %), NEt_3 (0.55 mL, 4.0 mmol), DMF (5 mL) at 100 °C for 24 h following general procedure A, as a brown oil (168 mg, 76%). ^{1}H NMR (300 MHz, $CDCl_3$): δ = 0.91 (d, 12H, *J* = 6.8 Hz, $4CH_3$), 1.86-2.01 (m, 2H, 2CH), 3.86 (s, 3H, OCH_3), 3.92 (d, 2H, *J* = 6.6 Hz, CH_2O), 3.93 (d, 2H, *J* = 6.6 Hz, CH_2O), 6.23 (d, 1H, *J* = 15.3 Hz, CH), 6.28 (d, 1H, *J* = 15.3 Hz, CH), 6.88-6.94 (m, 2H, ArH), 7.20-7.26 (m, 1H, ArH), 7.52-7.58 (m, 2H, ArH), 7.78 (d, 1H, *J* = 15.7 Hz, CH), 7.93 (d, 1H, *J* = 15.6 Hz, CH). ^{13}C NMR (75 MHz, $CDCl_3$): δ = 18.2 ($4CH_3$), 26.8 (2CH), 54.6 (OCH_3), 69.7, 69.8 (CH_2O), 110.7, 117.0, 118.9, 120.0 (CH), 120.6 (C), 122.8, 127.2, 128.9, 132.7, 133.7 (CH), 136.9, 138.1, 140.6, 154.9 (C), 165.6, 165.9 (CO). IR (KBr, cm^{-1}): *v* = 3099, 2957, 2844 (w), 1692 (s), 1605, 1462 (m), 1441, 1393, 1375, 1342 (w), 1268, 1253, 1240, 1210 (s), 1179, 1162, 1115 (m), 1024, 970 (s), 950, 846 (m), 744 (s), 717, 683, 603 (w). MS (EI, 70 eV): *m/z* (%) = 442(11) $[M]^+$, 285(57), 269(13), 267(25), 243(11), 241(54), 57(100), 41(42). HRMS (ESI): calcd for $C_{25}H_{31}O_5S$ $[M+H]^+$: 443.1887; found: 443.1876.

Synthesis of benzothiophenes (36):

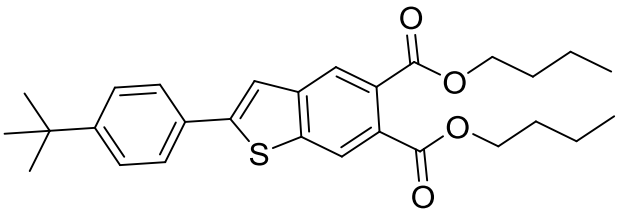
Diisobutyl-2-(4-ethylphenyl)benzo[*b*]thiophene-5,6-dicarboxylate (36a):



Compound **36a** was prepared starting with **35a** (100 mg, 0.23 mmol), following the general procedure B, as a brown semi solid (92 mg, 93%). ^{1}H NMR (300 MHz, $CDCl_3$): δ = 0.92 (d, 6H, *J* = 6.8 Hz, $2CH_3$), 0.93 (d, 6H, *J* = 6.7 Hz, $2CH_3$), 1.18 (t, 3H, *J* = 7.6 Hz, CH_3), 1.92-2.05 (m, 2H, 2CH), 2.60 (q, 2H, *J* = 7.6 Hz, CH_2), 4.03 (d, 2H, *J* = 6.7 Hz, CH_2O), 4.04 (d, 2H, *J* = 6.7 Hz, CH_2O), 7.18 (d, 2H, *J* = 8.8 Hz, ArH), 7.47 (s, 1H, ArH), 7.54 (dd, 2H, *J* = 1.7, 6.6 Hz, ArH), 7.98 (s, 1H, ArH), 8.13 (s, 1H, ArH). ^{13}C NMR (62 MHz, $CDCl_3$): δ = 15.4 (CH_3), 19.2 ($4CH_3$), 27.7, 27.8 (CH), 28.7 (CH_2), 71.8 ($2CH_2O$), 118.7, 123.5, 123.9 (CH), 126.6 (2CH), 127.3 (C), 128.6 (2CH), 129.4, 130.8, 140.9, 142.2, 145.6, 149.0 (C), 167.5, 168.2 (CO). IR (KBr, cm^{-1}): *v* = 2958, 2873 (m), 1721,

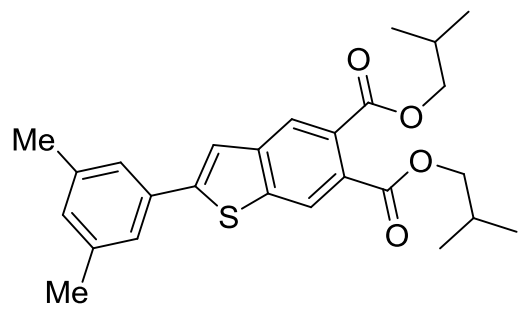
1708 (s), 1593, 1552, 1526 (w), 1495, 1469 (m), 1419, 1403, 1392 (w), 1371, 1303 (m), 1281, 1254, 1229, 1179, 1119, 1090 (s), 1013, 982, 945, 898, 888, 832 (m), 818 (s), 780, 719, 691 (m), 657, 634, 590, 549 (w). GC- MS (EI, 70 eV): *m/z* (%) = 438(69) $[M]^+$, 382(16), 326(24), 310(22), 309(100), 221(13). HRMS (EI, 70 eV): calcd for $C_{26}H_{30}O_4S$ $[M]^+$: 438.18593; found: 438.18532.

Dibutyl-2-(4-*tert*-butylphenyl)benzo[*b*]thiophene-5,6-dicarboxylate (36b):



Compound **36b** was prepared starting with **35b** (100 mg, 0.21 mmol), following the general procedure B, as a yellowish solid (81 mg, 82%), mp. 56-58 °C. ^{1}H NMR (250 MHz, $CDCl_3$): δ = 0.89 (t, 6H, *J* = 7.3 Hz, $2CH_3$), 1.28 (s, 9H, $3CH_3$), 1.34-1.43 (m, 4H, $2CH_2$), 1.61-1.72 (m, 4H, $2CH_2$), 4.25 (t, 2H, *J* = 6.7 Hz, CH_2O), 4.26 (t, 2H, *J* = 6.7 Hz, CH_2O), 7.39 (dd, 2H, *J* = 1.9, 6.6 Hz ArH), 7.48 (s, 1H, ArH), 7.58 (dd, 2H, *J* = 1.9, 6.6 Hz, ArH), 7.99 (s, 1H, ArH), 8.13 (s, 1H, ArH). ^{13}C NMR (62 MHz, $CDCl_3$): δ = 13.7 ($2CH_3$), 19.2 ($2CH_2$), 30.6, 30.7 (CH_2), 31.2 ($3CH_3$), 34.8 (C), 65.6 ($2CH_2O$), 118.7, 123.6, 123.9 (CH), 126.1 (2CH), 126.4 (2CH), 127.2, 129.3, 130.6, 140.9, 142.2, 148.9, 152.5 (C), 167.5, 168.2 (CO). IR (KBr, cm^{-1}): *v* = 2955, 2927, 2869 (m), 1709 (s), 1650, 1625, 1595, 1497, 1460, 1390, 1359 (w), 1330 (m), 1306, 1284, 1258, 1239 (s), 1189, 1122 (m), 1094 (s), 1060, 1017, 834, 819, 778 (m), 729, 719, 578 (w), 532 (m). GC- MS (EI, 70 eV): *m/z* (%) = 466(100) $[M]^+$, 452(20), 451(67), 410(11), 395(23), 337(62), 321(14), 250(13). HRMS (ESI): calcd for $C_{28}H_{35}O_4S$ $[M+H]^+$: 467.2251; found: 467.2256. Anal. calcd for $C_{28}H_{34}O_4S$: C, 72.07; H, 7.34; S, 6.87. Found: C, 72.08; H, 7.52; S, 6.88.

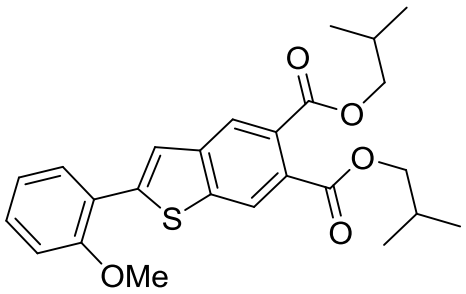
Diisobutyl-2-(3,5-dimethylphenyl)benzo[*b*]thiophene-5,6-dicarboxylate (36c):



Compound **36c** was prepared starting with **35c** (100 mg, 0.23 mmol), following the general procedure B, as a white solid (84 mg, 85%), mp. 66-68 °C. ^{1}H NMR (300 MHz, $CDCl_3$): δ = 0.93 (d, 6H, *J* = 6.7 Hz, $2CH_3$), 0.94 (d, 6H, *J* = 6.7 Hz, $2CH_3$), 1.92-2.08 (m, 2H, 2CH), 2.29 (s, 6H, $2CH_3$), 4.03 (d, 2H, *J* = 6.7 Hz, CH_2O), 4.04 (d, 2H, *J* = 6.7 Hz, CH_2O), 6.94 (s, 1H, ArH), 7.17 (s, 2H, ArH), 7.49 (s, 1H, ArH), 7.99 (s, 1H, ArH), 8.13 (s, 1H, ArH). ^{13}C NMR (62

MHz, $CDCl_3$): δ = 18.2 ($4CH_3$), 20.3 ($2CH_3$), 26.7, 26.8 (CH), 70.8 ($2CH_2O$), 118.0, 122.5, 123.0 (CH), 123.5 (2CH), 126.3, 128.3 (C), 129.8 (CH), 132.2 (C), 137.7 (2C), 140.0, 141.0, 148.2 (C), 166.5, 167.1 (CO). IR (KBr, cm^{-1}): v = 2957, 2924, 2871 (m), 1716 (s), 1600, 1514, 1487 (w), 1468 (m), 1405, 1392, 1376, 1344 (w), 1305, 1273, 1261 (m), 1236 (s), 1180, 1163, 1120, 1091, 1012, 979, 946, 899, 843, 816, 781, 748, 721, 690, 681, 603 (m). GC-MS (EI, 70 eV): *m/z* (%) = 438(57) $[M]^+$, 382(12), 326(26), 310(22), 309(100), 236(14). HRMS (ESI): calcd for $C_{26}H_{31}O_4S$ $[M+H]^+$: 439.1938; found: 439.1944. Anal. calcd for $C_{26}H_{30}O_4S$: C, 71.20; H, 6.89; S, 7.31. Found: C, 71.08; H, 7.13; S, 7.47.

Diisobutyl-2-(2-methoxyphenyl)benzo[*b*]thiophene-5,6-dicarboxylate (36d):



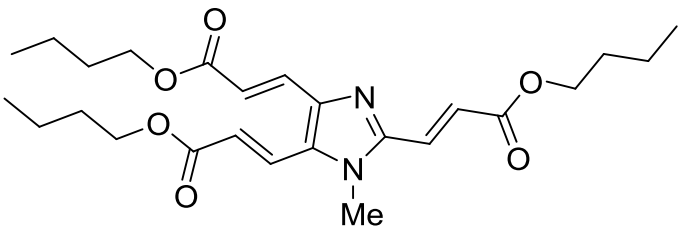
Compound **36d** was prepared starting with **35d** (100 mg, 0.23 mmol), following the general procedure B, as yellowish solid (87 mg, 88%), mp. 96-98 °C. ^1H NMR (300 MHz, $CDCl_3$): δ = 0.93 (d, 12H, J = 6.7 Hz, $4CH_3$), 1.92-2.06 (m, 2H, 2CH), 3.89 (s, 3H, OCH_3), 4.03 (d, 2H, J = 6.7 Hz,CH_2O), 4.04 (d, 2H, J = 6.7 Hz, CH_2O), 6.93-6.99 (m, 2H, ArH), 7.24-7.29 (m, 1H, ArH), 7.63 (dd, 1H, J = 1.5, 7.7 Hz, ArH), 7.73 (s, 1H, ArH), 8.02 (s, 1H, ArH), 8.14 (s, 1H, ArH). ^{13}C NMR (62 MHz, $CDCl_3$): δ = 19.2 ($4CH_3$), 27.8 (2CH), 55.6 (OCH_3), 71.8 ($2CH_2O$), 111.8, 121.1, 122.0 (CH), 122.3 (C), 123.2, 124.0 (CH), 127.2, 128.9 (C), 129.3, 130.1 (CH), 141.3, 141.5, 144.6, 156.4 (C), 167.7, 168.3 (CO). IR (KBr, cm^{-1}): v = 2955, 2928, 2872 (w), 1707 (s), 1627, 1594, 1579, 1547, 1509, 1481 (w), 1468, 1458 (m), 1435, 1408, 1376, 1341 (w), 1307, 1283, 1267 (m), 1252, 1242 (s), 1167, 1125, 1101, 1025, 982, 906, 833, 772 (m), 755 (s), 735, 690 (m), 594, 548 (w). GC- MS (EI, 70 eV): *m/z* (%) = 440(63) $[M]^+$, 384(12), 328(13), 312(20), 311(100). HRMS (ESI): calcd for $C_{25}H_{29}O_5S$ $[M+H]^+$: 441.1730; found: 441.1738. Anal. calcd for $C_{25}H_{28}O_5S$: C, 68.16; H, 6.41; S, 7.28. Found: C, 68.15; H, 6.55; S, 7.48.

General procedure D for the synthesis of compounds 39, 43 and 47:

In a pressure tube (glass bomb) a suspension of $Pd(OAc)_2$ (12 mg, 0.05 mmol, 5 mol%) and $P(Cy)_3$ (28.04 mg, 0.10 mmol, 10 mol%) in DMF (5 mL) was purged with Argon and stirred at 20 °C to give a yellowish or brownish clear solution. To the stirred solution were added **38**, **42a-d or 46a,b** (1.0 mmol), Et_3N (1.1 mL, 8.0 mmol) and the alkene (1.25 equiv. per bromine atom of the substrate). The reaction mixture was stirred at 100 °C for 24 h. The solution was

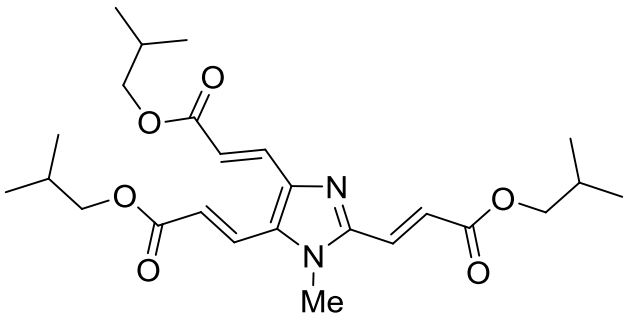
cooled to 20 °C, poured into a mixture of H_2O and CH_2Cl_2 (25 mL each), and the organic and the aqueous layer were separated. The latter was extracted with CH_2Cl_2 (3 × 25 mL). The combined organic layers were washed with H_2O (3 × 20 mL), dried (Na_2SO_4), and concentrated *in vacuo*. The residue was purified by chromatography (flash silica gel, heptanes-EtOAc).

(2*E*,2'*E*,2''*E*)-Tributyl-3,3',3''-(1-methyl-1*H*-imidazole-2,4,5-triyl)triacrylate (39a):



Product **39a** was prepared starting with **38** (318 mg,1.0 mmol), *n*-butyl acrylate (0.47 mL, 3.3 mmol), $Pd(OAc)_2$ (11 mg, 5 mol %), $P(Cy)_3$ (10 mol %), NEt_3 (1.10 mL, 8.0 mmol), DMF (5 mL) at 100 °C for 24 h following general procedure D, as a brown oil (395 mg, 86%). ^{1}H NMR (250 MHz, $CDCl_3$): δ = 0.88 (t, 6H, *J* = 7.3 Hz, $2CH_3$), 0.90 (t, 3H, *J* = 7.2 Hz, CH_3), 1.32-1.41 (m, 6H, $3CH_2$), 1.55-1.66 (m, 6H, $3CH_2$), 3.69 (s, 3H, NCH_3), 4.14 (t, 2H, *J* = 6.5 Hz, CH_2O), 4.15 (t, 2H, *J* = 6.6 Hz, CH_2O), 4.16 (t, 2H, *J* = 6.4 Hz, CH_2O), 6.23 (d, 1H, *J* = 16.1 Hz, CH), 6.78 (d, 1H, *J* = 15.3 Hz, CH), 6.95 (d, 1H, *J* = 15.4 Hz, CH), 7.43 (d, 1H, *J* = 15.3 Hz, CH), 7.55 (d, 1H, *J* = 16.2 Hz, CH), 7.62 (d, 1H, *J* = 15.4 Hz, CH). ^{13}C NMR (62 MHz, $CDCl_3$): δ = 13.7 ($3CH_3$), 19.1 (CH_2), 19.2 ($2CH_2$), 30.6, 30.7, 30.8 (CH_2), 31.6 (NCH_3), 64.4, 64.8, 64.9 (OCH_2), 120.5, 121.5, 124.6, 127.2, 128.3 (CH), 130.7 (C), 133.0 (CH), 140.3, 146.1 (C), 166.2, 166.4, 167.2 (CO). IR (KBr, cm^{-1}): ν = 2957, 2932, 2872 (w), 1705 (s), 1625, 1457 (m), 1392 (w), 1299 (m), 1272, 1160 (s), 1062, 1022, 964 (m), 867, 739, 661 (w). GC-MS (EI, 70 eV): *m/z* (%) = 460(18) $[M]^+$, 387(19), 359(45), 329(14), 303(100), 285(74), 259(38), 229(21), 185(40), 157(28), 57(14), 44(34). HRMS (EI, 70 eV): *m/z* calcd for $C_{25}H_{36}N_2O_6$ $[M]^+$: 460.25679; found: 460.25633.

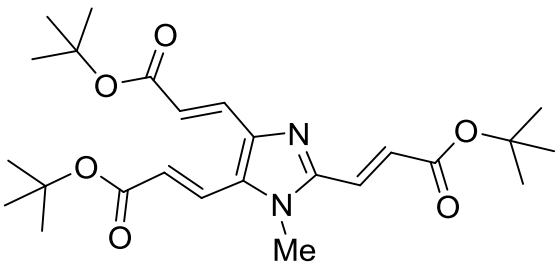
(2*E*,2'*E*,2''*E*)-Isobutyl-3,3',3''-(1-methyl-1*H*-imidazole-2,4,5-triyl)triacrylate (39b):



Product **39b** was prepared starting with **38** (318 mg, 1.0 mmol), *iso*-butyl acrylate (0.47 mL, 3.3 mmol), $Pd(OAc)_2$ (11 mg, 5 mol %), $P(Cy)_3$ (10 mol %), NEt_3 (1.10 mL, 8.0 mmol), DMF (5 mL) at 100 °C for 24 h following general procedure D, as a brown oil (386 mg, 84%). ^{1}H NMR (250 MHz, $CDCl_3$): δ = 0.90 (d, 12H, *J*

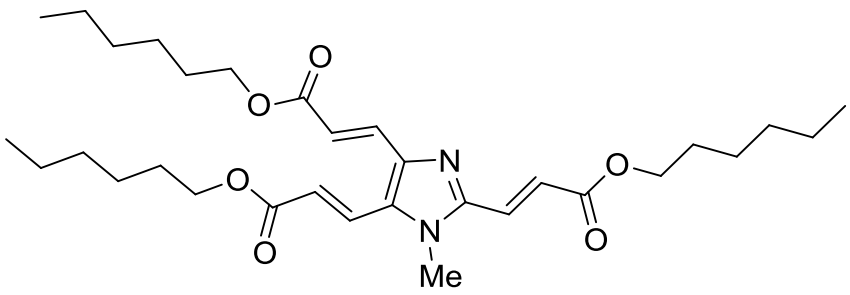
= 6.7 Hz, 4CH_3), 0.91 (d, 6H, *J* = 6.7 Hz, 2CH_3), 1.88-1.98 (m, 3H, 3CH), 3.69 (s, 3H, NCH_3), 3.91 (d, 2H, *J* = 6.3 Hz, CH_2O), 3.93 (d, 2H, *J* = 6.6 Hz, CH_2O), 3.94 (d, 2H, *J* = 6.3 Hz, CH_2O), 6.24 (d, 1H, *J* = 16.0 Hz, CH), 6.77 (d, 1H, *J* = 15.5 Hz, CH), 6.97 (d, 1H, *J* = 15.4 Hz, CH), 7.43 (d, 1H, *J* = 15.4 Hz, CH), 7.56 (d, 1H, *J* = 16.2 Hz, CH), 7.63 (d, 1H, *J* = 15.4 Hz, CH). ^{13}C NMR (62 MHz, $CDCl_3$): δ = 19.0 (2CH_3), 19.1 (4CH_3), 27.7 (2CH), 27.8 (CH), 31.6 (NCH_3), 70.6, 70.0, 71.1 (OCH_2), 120.5, 121.4, 124.6, 127.2, 128.3 (CH), 130.7 (C), 133.0 (CH), 140.2, 146.1 (C), 166.2, 166.3, 167.1 (CO). IR (KBr, cm^{-1}): ν = 2959, 2874 (w), 1706 (s), 1625, 1463 (m), 1394, 1370, 1342 (w), 1303 (m), 1272, 1242, 1154 (s), 1009, 964 (m), 867, 744, 704, 553 (w). GC-MS (EI, 70 eV): *m/z* (%) = 460(15) $[M]^+$, 387(18), 359(16), 303(100), 285(47), 259(20), 229(12), 203(18), 185(23), 157(17), 57(11), 41(11). HRMS (ESI): *m/z* calcd for $C_{25}H_{37}N_2O_6$ $[M+H]^+$: 461.2646; found: 461.2648.

(2*E*,2'*E*,2''*E*)-*tert*-butyl-3,3',3''-(1-methyl-1*H*-imidazole-2,4,5-triyl)triacrylate (39c):



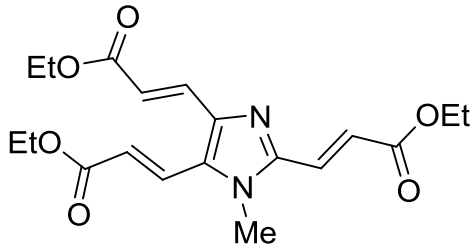
Product **39c** was prepared starting with **38** (318 mg, 1.0 mmol), *tert*-butyl acrylate (0.47 mL, 3.3 mmol), $Pd(OAc)_2$ (11 mg, 5 mol %), $P(Cy)_3$ (10 mol %), NEt_3 (1.10 mL, 8.0 mmol), DMF (5 mL) at 100 °C for 24 h following general procedure D, as a brown oil (372 mg, 81%). ^{1}H NMR (250 MHz, $CDCl_3$): δ = 1.44 (s, 18H, 6CH_3), 1.46 (s, 9H, 3CH_3), 3.65 (s, 3H, NCH_3), 6.15 (d, 1H, *J* = 16.1 Hz, CH), 6.70 (d, 1H, *J* = 15.3 Hz, CH), 6.85 (d, 1H, *J* = 15.3 Hz, CH), 7.33 (d, 1H, *J* = 15.4 Hz, CH), 7.44 (d, 1H, *J* = 16.1 Hz, CH), 7.55 (d, 1H, *J* = 15.3 Hz, CH). ^{13}C NMR (62 MHz, $CDCl_3$): δ = 28.0 (3CH_3), 28.1 (3CH_3), 28.2 (3CH_3), 31.4 (NCH_3), 80.3, 81.1, 81.2 (C-O), 122.1, 123.3, 126.0, 126.4, 127.4 (CH), 130.5 (C), 132.3 (CH), 139.9, 145.9 (C), 165.4, 166.5, 166.5 (CO). IR (KBr, cm^{-1}): ν = 2975, 2931 (w), 1701 (s), 1627, 1456 (m), 1392 (w), 1366, 1304, 1279, 1255 (m), 1139 (s), 956, 855, 848 (m), 760, 744, 708, 630, 539 (w). MS (EI, 70 eV): *m/z* (%) = 460(23) $[M]^+$, 404(10), 247(11), 204(14), 203(100), 185(26), 157(16), 56(34), 41(62). HRMS (EI, 70 eV): *m/z* calcd for $C_{25}H_{36}N_2O_6$ $[M]^+$: 460.25679; found: 460.25587.

(2*E*,2'*E*,2''*E*)-Trihexyl-3,3',3''-(1-methyl-1*H*-imidazole-2,4,5-triyl)triacrylate (39d):



Product **39d** was prepared starting with **38** (318 mg, 1.0 mmol), *n*-hexyl acrylate (0.58 mL, 3.3 mmol), $Pd(OAc)_2$ (11 mg, 5 mol %) , $P(Cy)_3$ (10 mol %), NEt_3 (1.10 mL, 8.0 mmol), DMF (5 mL) at 100 °C for 24 h following general procedure D, as a brown oil (402 mg, 74%). ^{1}H NMR (250 MHz, $CDCl_3$): δ = 0.83 (t, 9H, *J* = 6.6 Hz, $3CH_3$), 1.24-1.34 (m, 18H, $9CH_2$), 1.56-1.65 (m, 6H, $3CH_2$), 3.69 (s, 3H, NCH_3), 4.09-4.17 (m, 6H, $3OCH_2$), 6.22 (d, 1H, *J* = 16.1 Hz, CH), 6.78 (d, 1H, *J* = 15.3 Hz, CH), 6.94 (d, 1H, *J* = 15.3 Hz, CH), 7.42 (d, 1H, *J* = 15.3 Hz, CH), 7.55 (d, 1H, *J* = 16.5 Hz, CH), 7.57 (d, 1H, *J* = 15.5 Hz, CH). ^{13}C NMR (62 MHz, $CDCl_3$): δ = 13.9 ($3CH_3$), 22.5 ($3CH_2$), 25.5 (CH_2), 25.6 ($2CH_2$), 28.5, 28.6, 28.7 (CH_2), 31.3 (CH_2), 31.4 ($2CH_2$), 31.6 (NCH_3), 64.6, 65.1, 65.2 (OCH_2), 120.5, 121.4, 124.6, 127.2, 128.3 (CH), 130.7 (C), 133.0 (CH), 140.3, 146.1 (C), 166.2, 166.3, 167.1 (CO). IR (KBr, cm^{-1}): *v* = 2954, 2928, 2857 (w), 1707 (s), 1695, 1457, 1299 (m), 1272, 1161 (s), 1060 (w), 964 (m), 910, 867, 728, 663, 611 (w). MS (EI, 70 eV): *m/z* (%) = 544(49) $[M]^+$, 443(17), 417(100), 389(10), 331(41), 315(24), 287 (58), 231(14), 203(30), 185(35), 55(20), 44(43). HRMS (ESI): *m/z* calcd for $C_{31}H_{49}N_2O_6$ $[M+H]^+$: 545.3585; found: 545.3591.

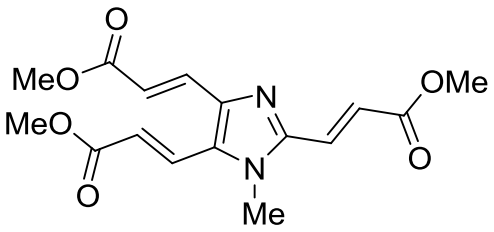
(2*E*,2'*E*,2''*E*)-Triethyl-3,3',3''-(1-methyl-1*H*-imidazole-2,4,5-triyl)triacrylate (39e):



Product **39e** was prepared starting with **38** (318 mg, 1.0 mmol), ethyl acrylate (0.36 mL, 3.3 mmol), $Pd(OAc)_2$ (11 mg, 5 mol %), $P(Cy)_3$ (10 mol %), NEt_3 (1.10 mL, 8.0 mmol), DMF (5 mL) at 100 °C for 24 h following general procedure D, as a yellow solid (275 mg, 73%), mp. 129-131 °C. ^{1}H NMR (250 MHz, $CDCl_3$): δ = 1.25 (t, 3H, *J* = 7.1 Hz, CH_3), 1.26 (t, 3H, *J* = 7.1 Hz, CH_3), 1.27 (t, 3H, *J* = 7.2 Hz, CH_3), 3.68 (s, 3H, NCH_3), 4.15-4.22 (m, 6H, OCH_2), 6.20 (d, 1H, *J* = 16.2 Hz, CH), 6.74 (d, 1H, *J* = 15.3 Hz, CH), 6.91 (d, 1H, *J* = 15.3 Hz, CH), 7.41 (d, 1H, *J* = 15.3 Hz,

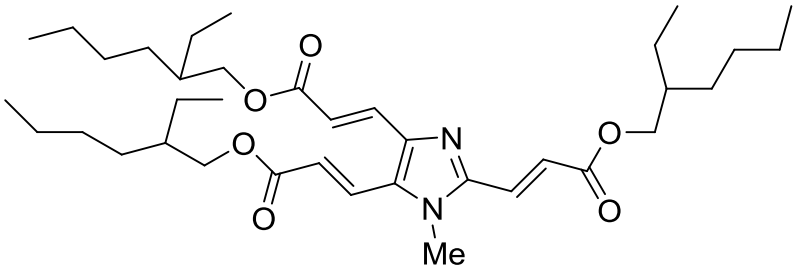
CH), 7.54 (d, 1H, J = 16.1 Hz, CH), 7.60 (d, 1H, J = 15.3 Hz, CH). ^{13}C NMR (62 MHz, $CDCl_3$): δ = 14.1, 14.2, 14.3 (CH_3), 31.6 (NCH_3), 60.4, 60.9, 61.0 (OCH_2), 120.4, 121.4, 124.5, 127.2, 128.2 (CH), 130.7 (C), 133.0 (CH), 140.3, 146.1 (C), 166.1, 166.2, 167.0 (CO). IR (KBr, cm^{-1}): ν = 3046, 2980, 2938, 2873, 1733 (w), 1695, 1619 (s), 1514 (w), 1461, 1391, 1363 (m), 1298, 1270, 1170, 1151 (s), 1115, 1095 (m), 1025, 962 (s), 932, 871, 850, 743, 709 (m), 676, 662, 613 (w). GC-MS (EI, 70 eV): *m/z* (%) = 376(90) $[M]^+$, 332(11), 333(51), 303(50), 275(14), 257(50), 231(83), 229(21), 185(100), 184(11), 157(52), 156(19). HRMS (ESI): *m/z* calcd for $C_{19}H_{25}N_2O_6$ $[M+H]^+$: 377.1707; found: 377.1711.

(2*E*,2'*E*,2''*E*)-Trimethyl-3,3',3''-(1-methyl-1*H*-imidazole-2,4,5-triyl)triacrylate (39f):



Product **39f** was prepared starting with **38** (318 mg, 1.0 mmol), methyl acrylate (0.30 mL, 3.3 mmol), $Pd(OAc)_2$ (11 mg, 5 mol %), $P(Cy)_3$ (10 mol-%), NEt_3 (1.10 mL, 8.0 mmol), DMF (5 mL) at 100 °C for 24 h following general procedure D, as a yellow clear highly viscous oil (254 mg, 76%). ^{1}H NMR (250 MHz, $CDCl_3$): δ = 3.70 (s, 3H, NCH_3), 3.72, 3.75, 3.76 (s, 3H, OCH_3), 6.20 (d, 1H, J = 16.2 Hz, CH), 6.74 (d, 1H, J = 15.4 Hz, CH), 6.91 (d, 1H, J = 15.3 Hz, CH), 7.41 (d, 1H, J = 15.3 Hz, CH), 7.53 (d, 1H, J = 16.2 Hz, CH), 7.57 (d, 1H, J = 15.4 Hz, CH). ^{13}C NMR (75 MHz, $CDCl_3$): δ = 31.7 (NCH_3), 51.7 (OCH_3), 52.0 ($2OCH_3$), 120.0, 121.0, 124.1, 127.4, 128.4 (CH), 130.7 (C), 133.1 (CH), 140.3, 146.1 (C), 166.5, 166.6, 167.4 (CO). IR (KBr, cm^{-1}): ν = 3041, 2991, 2948, 2847 (w), 1708, 1695, 1622 (s), 1519 (w), 1431, 1411, 1306 (m), 1279, 1261, 1193, 1165 (s), 1065, 1034, 1014, 984 (m), 959 (s), 931, 879, 869, 811, 748, 713, 700, 665, 611 (m). GC-MS (EI, 70 eV): *m/z* (%) = 334(74) $[M]^+$, 303(41), 276(13), 275(82), 244(16), 243(100), 231(27), 216(12), 215(18), 199(17), 185(28), 184(10), 171(25), 157(44), 156(21). HRMS (EI, 70 eV): *m/z* calcd for $C_{16}H_{18}N_2O_6$ $[M]^+$: 334.11594; found: 334.11621.

(2*E*,2'*E*,2''*E*)-Tris(2-ethylhexyl)-3,3',3''-(1-methyl-1*H*-imidazole-2,4,5-triyl)triacrylate (39g):

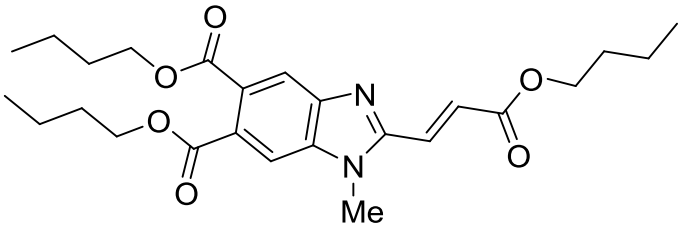


Product **39g** was prepared starting with **38** (318 mg, 1.0 mmol), 2-ethylhexyl acrylate (0.69 mL, 3.3 mmol), $Pd(OAc)_2$ (11 mg, 5 mol %), $P(Cy)_3$ (10 mol %), NEt_3 (1.10 mL, 8.0 mmol), DMF (5 mL) at 100 °C for 24 h following general procedure D, as a brown oil (515 mg, 82%). ^{1}H NMR (250 MHz, $CDCl_3$): δ = 0.81-0.89 (m, 18H, $6CH_3$), 1.25-1.39 (m, 24H, $12CH_2$), 1.53-1.62 (m, 3H, 3CH), 3.69 (s, 3H, NCH_3), 4.03-4.09 (m, 6H, $3OCH_2$), 6.23 (d, 1H, *J* = 16.1 Hz, CH), 6.80 (d, 1H, *J* = 15.4 Hz, CH), 6.97 (d, 1H, *J* = 15.3 Hz, CH), 7.44 (d, 1H, *J* = 15.4 Hz, CH), 7.55 (d, 1H, *J* = 16.1 Hz, CH), 7.63 (d, 1H, *J* = 15.4 Hz, CH). ^{13}C NMR (75 MHz, $CDCl_3$): δ = 10.9, 11.0, 11.1 (CH_3), 14.1 ($3CH_3$), 22.9 ($3CH_2$), 23.7, 23.8, 23.9 (CH_2), 28.9 ($2CH_2$), 29.0 (CH_2), 30.3, 30.4, 30.5 (CH_2), 31.6 (NCH_3), 38.8, 38.8, 38.9 (CH), 66.9, 67.4, 67.6 (OCH_2), 120.6, 121.6, 124.7, 127.2, 128.3 (CH), 130.7 (C), 133.0 (CH), 140.3, 146.1 (C), 166.4, 166.6, 167.3 (CO). IR (KBr, cm^{-1}): *v* = 2957, 2928, 2858 (w), 1708, 1625, 1458 (m), 1379 (w), 1299, 1271 (m), 1162 (s), 964 (m), 868, 729, 704, 663 (w). MS (EI, 70 eV): *m/z* (%) = 628(100) $[M]^+$, 501(20), 499(22), 475(13), 473(74), 471(18), 446(18), 361(13), 359(22), 343(19), 333(24), 317(65), 315(44), 231(18), 203(27), 118(11), 185(20), 133(16), 117(14), 83(24), 81(11), 70(25), 66(11), 55(44), 44(89), 41(40). HRMS (EI, 70 eV): *m/z* calcd for $C_{37}H_{60}N_2O_6$ $[M]^+$: 628.44459; found: 628.44336.

General procedure E for the synthesis of Benzimidazoles 40, 41, 44, 45 and 48:

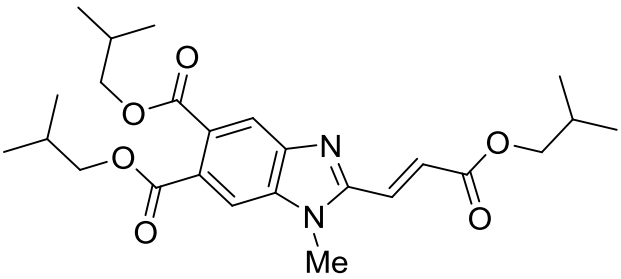
A diphenylether solution (3 mL) of **39a-g, 43a-r, 47a-d** (0.5 mmol) was stirred at 200 °C for 24 h in a pressure tube. The solution was allowed to cool to 20 °C and Pd/C (30 mg, 10 mol %) was added. The solution was stirred at 200 °C for 48 h under argon atmosphere. The reaction mixture was filtered and the filtrate was concentrated in vacuo. The residue was purified by chromatography (flash silica gel, heptanes/EtOAc).

(*E*)-Dibutyl-2-(3-butoxy-3-oxoprop-1-enyl)-1-methyl-1*H*-benzo[*d*]imidazole-5,6-dicarboxylate (40a):



Compound **40a** was prepared starting with **39a** (100 mg, 0.22 mmol), following the general procedures E, as a brown oil (89 mg, 90%). ^{1}H NMR (300 MHz, $CDCl_3$): δ = 0.89 (t, 9H, J = 7.3 Hz, $3CH_3$), 1.33-1.41 (m, 6H, $3CH_2$), 1.61-1.70 (m, 6H, $3CH_2$), 3.86 (s, 3H, NCH_3), 4.19 (t, 2H, J = 6.7 Hz, CH_2O), 4.26 (t, 4H, J = 6.5 Hz, $2CH_2O$), 7.15 (d, 1H, J = 15.5 Hz, CH), 7.62 (d, 1H, J = 15.5 Hz, CH), 7.66 (s, 1H, ArH), 8.06 (s, 1H, ArH). ^{13}C NMR (62 MHz, $CDCl_3$): δ = 13.6 (CH_3), 13.7 ($2CH_3$), 19.0, 19.1, 19.2 (CH_2), 30.4 (NCH_3), 30.5 (CH_2), 30.6 ($2CH_2$), 65.0, 65.5, 65.7 (CH_2O), 111.2, 121.6 (CH), 127.7 (2CH), 127.7, 128.2, 136.9, 143.9, 151.3 (C), 165.9, 167.7, 168.0 (CO). IR (KBr, cm^{-1}): ν = 2957 (m), 2932, 2872 (w), 1710 (s), 1634, 1618, 1463, 1388, 1340, 1294 (m), 1252, 1209, 1170, 1102 (s), 1060, 1033, 1020, 964, 949, 899, 870, 843, 786, 746, 737 (m), 697, 608 (w). GC-MS (EI, 70 eV): *m/z* (%) = 458(18) $[M]^+$, 385(19), 330(12), 329(100), 328(33), 273(27), 272(12). HRMS (EI, 70 eV): *m/z* calcd for $C_{25}H_{34}N_2O_6$ $[M]^+$: 458.24114; found: 458.24011.

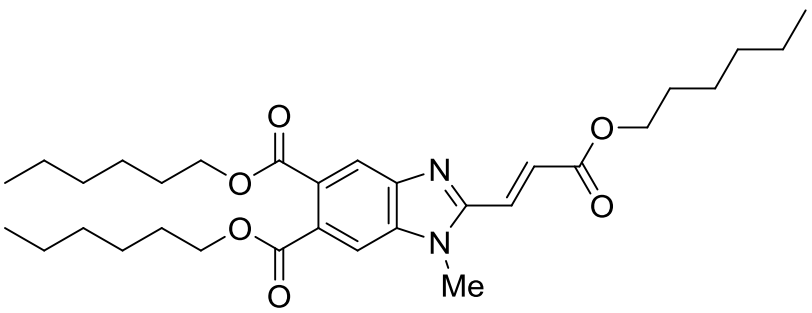
(*E*)-Diisobutyl-2-(3-isobutoxy-3-oxoprop-1-enyl)-1-methyl-1*H*-benzo[*d*]imidazole-5,6-dicarboxylate (40b):



Compound **40b** was prepared starting with **39b** (100 mg, 0.22 mmol), following the general procedures E, as a brown oil (89 mg, 90%). ^{1}H NMR (300 MHz, $CDCl_3$): δ = 0.92 (d, 6H, J = 6.5 Hz, $2CH_3$), 0.93 (d, 6H, J = 6.7 Hz, $2CH_3$), 0.94 (d, 6H, J = 6.5 Hz, $2CH_3$), 1.94-2.02 (m, 3H, 3CH), 3.87 (s, 3H, NCH_3), 3.97 (d, 2H, J = 6.6 Hz, CH_2O), 4.04 (d, 2H, J = 6.6 Hz, CH_2O), 4.05 (d, 2H, J = 6.6 Hz, CH_2O), 7.19 (d, 1H, J = 15.5 Hz, CH), 7.64 (d, 1H, J = 15.5 Hz, CH), 7.67 (s, 1H, ArH), 8.10 (s, 1H, ArH). ^{13}C NMR (75 MHz, $CDCl_3$): δ = 18.0 ($2CH_3$), 18.1 ($2CH_3$), 18.2 ($2CH_3$), 26.7 (CH), 26.8 (2CH), 29.4 (NCH_3), 70.3, 70.7, 71.0 (CH_2O), 110.2 (2CH), 120.7, 126.7 (CH), 126.7, 127.5, 136.0, 142.9, 150.3 (C), 164.9, 166.6, 167.1 (CO). IR (KBr, cm^{-1}): ν = 2959 (m), 2930, 2873 (w), 1713 (s), 1634, 1620 (w), 1468, 1377, 1341, 1289 (m), 1252, 1210, 1170, 1101 (s), 1034, 1009, 983, 947,

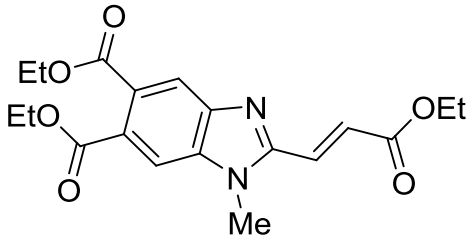
900, 786 (m). GC-MS (EI, 70 eV): *m/z* (%) = 458(18) $[M]^+$, 385(19), 330(12), 329(100), 328(33), 273(27), 272(12). HRMS (EI, 70 eV): *m/z* calcd for $C_{25}H_{34}N_2O_6$ $[M]^+$: 458.24114; found: 458.24011.

(*E*)-Dihexyl-2-(3-(hexyloxy)-3-oxoprop-1-enyl)-1-methyl-1*H*-benzo[*d*]imidazole-5,6-dicarboxylate (40d):



Compound **40d** was prepared starting with **39d** (100 mg, 0.18 mmol), following the general procedures E, as a brown oil (59 mg, 60%). ^{1}H NMR (250 MHz, $CDCl_3$): δ = 0.80-0.86 (m, 9H, $3CH_3$), 1.25-1.33 (m, 18H, $9CH_2$), 1.59-1.71 (m, 6H, $3CH_2$), 3.87 (s, 3H, NCH_3), 4.15-4.28 (m, 6H, $3CH_2O$), 7.17 (d, 1H, J = 15.4 Hz, CH), 7.63 (d, 1H, J = 15.5 Hz, CH), 7.68 (s, 1H, ArH), 8.08 (s, 1H, ArH). ^{13}C NMR (62 MHz, $CDCl_3$): δ = 14.0 ($3CH_3$), 22.5 ($3CH_2$), 25.5, 25.6, 25.7 (CH_2), 28.5 (CH_2), 28.6 ($2CH_2$), 29.7, 30.4, 31.4 (CH_2), 30.5 (NCH_3), 65.4, 65.8, 66.1 (CH_2O), 111.2, 121.7 (CH), 127.7 (2C), 127.8, 128.3 (CH), 137.0, 143.9, 151.4 (C), 166.0, 167.7, 168.1 (CO). IR (KBr, cm^{-1}): ν = 2956, 2932, 2872 (w), 1712 (s), 1636, 1616, 1463, 1389, 1290 (m), 1254, 1170, 1103 (s), 1060, 1035, 1020, 962, 949, 899, 870, 845, 786, 746, 733 (m), 697 (w). MS (EI, 70 eV): *m/z* (%) = 542(09) $[M]^+$, 441(11), 415(20), 358(58), 357(100), 273(18), 69(18), 57(10), 55(13), 44(24), 41(13). HRMS (ESI): *m/z* calcd for $C_{31}H_{47}N_2O_6$ $[M+H]^+$: 543.3429; found: 543.3431.

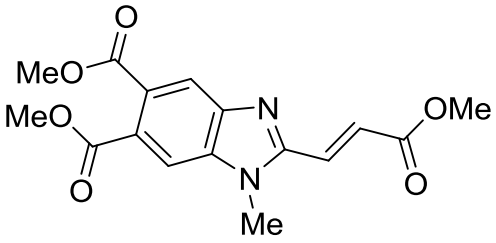
(*E*)-Diethyl-2-(3-ethoxy-3-oxoprop-1-enyl)-1-methyl-1*H*-benzo[*d*]imidazole-5,6-dicarboxylate (40e):



Compound **40e** was prepared starting with **39e** (100 mg, 0.27 mmol), following the general procedures E, as a brown oil (47 mg, 48%). ^{1}H NMR (300 MHz, $CDCl_3$): δ = 1.29 (t, 3H, J = 7.1 Hz, CH_3), 1.32 (t, 6H, J = 7.1 Hz, $2CH_3$), 3.87 (s, 3H, NCH_3), 4.25 (q, 2H, J = 7.1 Hz, CH_2O), 4.28-4.37 (m, 4H, $2CH_2O$), 7.16 (d, 1H, J = 15.5 Hz, CH), 7.63 (d, 1H, J = 15.5 Hz, CH), 7.69 (s, 1H, ArH), 8.08 (s, 1H, ArH). ^{13}C NMR (62 MHz, $CDCl_3$): δ = 14.1 (CH_3), 14.2 ($2CH_3$), 30.4 (NCH_3), 61.2, 61.6,

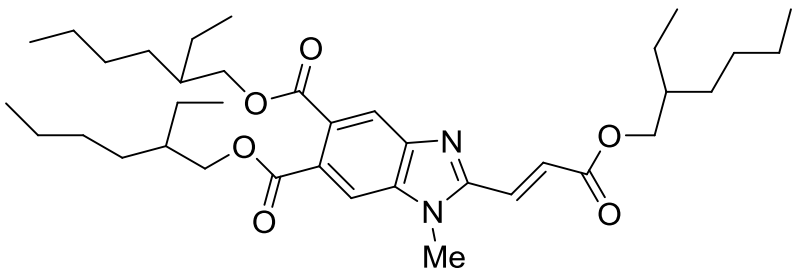
61.8 (CH_2O), 111.3, 121.7 (CH), 127.8 (2CH), 128.1 (2C), 137.0, 144.0, 151.3 (C), 165.8, 167.7, 167.9 (CO). IR (KBr, cm^{-1}): ν = 2956, 2932, 2872 (w), 1712 (s), 1636, 1616, 1463, 1389, 1290 (m), 1254, 1170, 1103 (s), 1060, 1035, 1020, 962, 949, 899, 870, 845, 786, 746, 733 (m), 697 (w). GC-MS (EI, 70 eV): *m/z* (%) = 374(40) $[M]^+$, 329(18), 302(35), 303(100), 273(29), 207(23), 32(12). HRMS (EI, 70 eV): *m/z* calcd for $C_{19}H_{22}N_2O_6$ $[M]^+$: 374.14724; found: 374.14642.

(*E*)-Dimethyl-2-(3-methoxy-3-oxoprop-1-enyl)-1-methyl-1*H*-benzo[*d*]imidazole-5,6-dicarboxylate (40f):



Compound **40f** was prepared starting with **39f** (100 mg, 0.30 mmol), following the general procedures E, as a brown oil (39 mg, 40%). ^1H NMR (300 MHz, $CDCl_3$): δ = 3.79 (s, 3H, NCH_3), 3.87 (s, 9H, $3CH_3O$), 7.17 (d, 1H, *J* = 15.3 Hz, CH), 7.64 (d, 1H, *J* = 15.5 Hz, CH), 7.70 (s, 1H, ArH), 8.07 (s, 1H, ArH). ^{13}C NMR (62 MHz, $CDCl_3$): δ = 30.4 (NCH_3), 52.3, 52.7, 52.8 (CH_3O), 111.4, 121.7 (CH), 126.3 (C), 127.3 (CH), 125.5 (C), 128.0 (CH), 134, 144.1, 151.4 (C), 165.4, 166.3, 168.3 (CO). IR (KBr, cm^{-1}): ν = 2954, 2923, 2851 (w), 1725, 1707 (s), 1643, 1621, 1429, 1393, 1359, 1345, 1306 (m), 1257, 1226, 1170, 1101, 1037, 968 (s), 892, 877, 815, 776, 744, 733 (m), 692, 619, 578 (w). GC-MS (EI, 70 eV): *m/z* (%) = 332(48) $[M]^+$, 310(100), 273(32). HRMS (EI, 70 eV): *m/z* calcd for $C_{16}H_{16}N_2O_6$ $[M]^+$: 332.10029; found: 332.09953.

(*E*)-Bis(2-ethylhexyl)-2-[3-(2-ethylhexyloxy)-3-oxoprop-1-enyl]-1-methyl-1*H*-benzo[*d*] imidazole-5,6-dicarboxylate (40g):

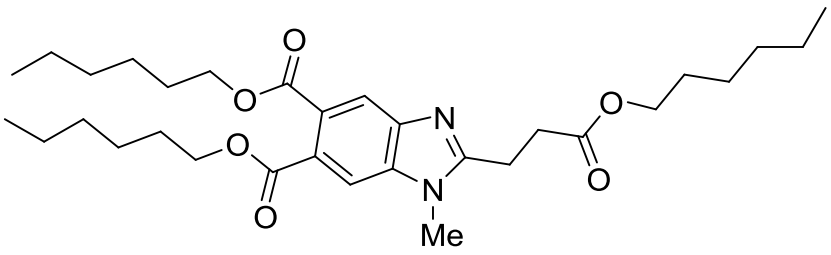


Compound **40g** was prepared starting with **39g** (100 mg, 0.16 mmol), following the general procedures E, as a brown oil (87 mg, 88%). ^1H NMR (300 MHz, $CDCl_3$): δ = 0.82-.088 (m, 18H, $6CH_3$), 1.25-1.40 (m, 24H, $12CH_2$), 1.57-1.66 (m, 3H, 3CH), 3.87 (s, 3H, NCH_3), 4.09-4.19 (m, 6H, $3CH_2O$), 7.19 (d, 1H, *J* = 15.4 Hz, CH), 7.63 (s, 1H, ArH), 7.64 (d, 1H, *J* = 15.8 Hz, CH), 8.09 (s, 1H, ArH). ^{13}C NMR (62 MHz, $CDCl_3$): δ = 10.9

(CH_3), 11.0 ($2CH_3$), 14.0 ($3CH_3$), 23.0 ($3CH_2$), 23.8 ($3CH_2$), 28.9 ($3CH_2$), 30.3 (NCH_3), 30.4 ($3CH_2$), 38.7 (CH), 38.8 (2CH) 67.6, 68.0, 68.4 (OCH_2), 111.1, 121.7 (CH), 127.7, 127.8 (CH), 127.8, 128.7, 137.0, 143.8, 151.3 (C), 166.1, 167.5, 168.3 (CO). IR (KBr, cm^{-1}): ν = 2956, 2926, 2858 (m), 1712 (s), 1630 (w), 1459, 1380, 1339, 1296 (m), 1255, 1208, 1113, 1100 (s), 1032, 965, 785 (m), 745, 727 (w). MS (EI, 70 eV): *m/z* (%) = 626(06) $[M]^+$, 515(13), 471(17), 402(45), 385(100), 290(11), 273(30), 69(15), 57(22), 43(17), 41(15). HRMS (ESI): *m/z* calcd for $C_{37}H_{59}N_2O_6$ $[M+H]^+$: 627.4368; found: 627.4372.

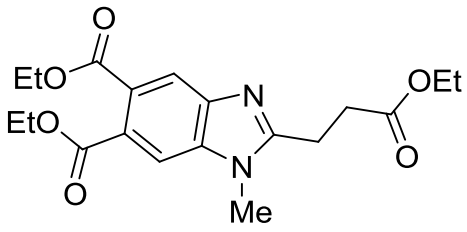
Synthesis of Benzimidazoles (41):

Dihexyl-2-(3-(hexyloxy)-3-oxopropyl)-1-methyl-1*H*-benzo[*d*]imidazole-5,6-dicarboxylate (41d):



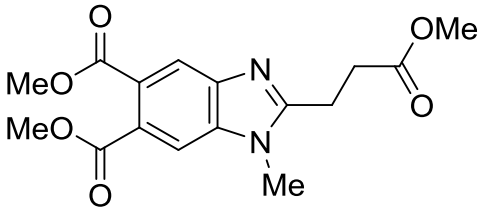
Compound **41d** was prepared starting with **39d** (100 mg, 0.18 mmol), following the general procedures E, as a brown oil (31 mg, 32%). ^1H NMR (250 MHz, $CDCl_3$): δ = 0.80 (t, 3H, *J* = 6.7 Hz, CH_3), 0.83 (t, 6H, *J* = 6.7 Hz, $2CH_3$), 1.19-1.34 (m, 18H, $9CH_2$), 1.47-1.59 (m, 2H, CH_2), 1.61-1.72 (m, 4H, $2CH_2$), 2.97 (t, 2H, *J* = 6.5 Hz, CH_2), 3.11 (t, 2H, *J* = 6.6 Hz, CH_2), 3.74 (s, 3H, NCH_3), 4.00 (t, 2H, *J* = 6.7 Hz, OCH_2), 4.22 (t, 2H, *J* = 6.7 Hz, OCH_2), 4.24 (t, 2H, *J* = 6.7 Hz, OCH_2), 7.59 (s, 1H, ArH), 7.99 (s, 1H, ArH). ^{13}C NMR (62 MHz, $CDCl_3$): δ = 13.9 (CH_3), 14.0 ($2CH_3$), 22.4 (CH_2), 22.5 ($3CH_2$), 25.5, 25.6, 25.7 (CH_2), 28.5 ($2CH_2$), 28.6 (CH_2), 30.1 (NCH_3), 31.2, 31.4 (CH_2), 31.5 ($2CH_2$), 65.0, 65.6, 65.9 (OCH_2), 110.4, 120.6 (CH), 126.5, 127.0, 136.8, 143.5, 157.3 (C), 168.0, 168.4, 172.5 (CO). IR (KBr, cm^{-1}): ν = 2954, 2928 (m), 2857 (w), 1715 (s), 1622, 1511 (w), 1465, 1334 (m), 1252, 1204, 1173, 1151 (s), 1024, 984, 785 (m), 725, 612 (w). GC-MS (EI, 70 eV): *m/z* (%) = 544(21) $[M]^+$, 416(38), 415(100), 359(39), 331(13), 229(13). HRMS (EI, 70 eV): *m/z* calcd for $C_{31}H_{48}N_2O_6$ $[M]^+$: 544.35069; found: 544.34919.

Diethyl-2-(3-ethoxy-3-oxopropyl)-1-methyl-1*H*-benzo[*d*]imidazole-5,6-dicarboxylate (41e):



Compound **41e** was prepared starting with **39e** (100 mg, 0.27 mmol), following the general procedures E, as a brown oil (39 mg, 40%). ^{1}H NMR (250 MHz, $CDCl_3$): δ = 1.16 (t, 3H, J = 7.1 Hz, CH_3), 1.29 (t, 3H, J = 7.1 Hz, CH_3), 1.30 (t, 3H, J = 7.1 Hz, CH_3), 2.94 (t, 2H, J = 6.6 Hz, CH_2), 3.09 (t, 2H, J = 6.4 Hz, CH_2), 3.72 (s, 3H, NCH_3), 4.06 (q, 2H, J = 7.0 Hz, CH_2O), 4.24-4.34 (m, 4H, $2CH_2O$), 7.59 (s, 1H, ArH), 7.96 (s, 1H, ArH). ^{13}C NMR (62 MHz, $CDCl_3$): δ = 14.1 ($3CH_3$), 22.4 (CH_2), 30.0 (NCH_3), 31.1 (CH_2), 60.7, 61.3, 61.5 (OCH_2), 110.5, 120.5 (CH), 126.4, 126.6, 136.7, 143.5, 157.3 (C), 168.0, 168.2, 172.3 (CO). IR (KBr, cm^{-1}): v = 2956, 2929 (m), 2858 (w), 1716 (s), 1513 (w), 1467, 1334 (m), 1255, 1206, 1173, 1152 (s), 1024, 984, 786 (m), 725, 612 (w). GC-MS (EI, 70 eV): *m/z* (%) = 376(40) $[M]^+$, 329(18), 302(35), 303(100), 273(29), 207(23), 32(12). HRMS (EI, 70 eV): *m/z* calcd for $C_{19}H_{24}N_2O_6$ $[M]^+$: 376.16344; found: 376.16442.

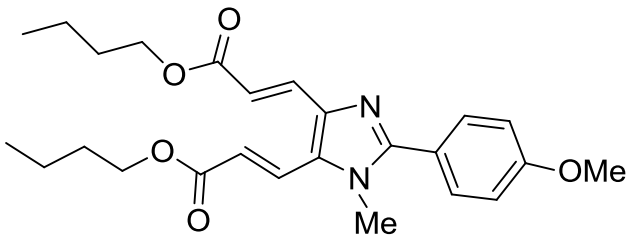
Dimethyl-2-(3-methoxy-3-oxopropyl)-1-methyl-1*H*-benzo[*d*]imidazole-5,6-dicarboxylate (41f):



Compound **41f** was prepared starting with **39f** (100 mg, 0.30 mmol), following the general procedures E, as a white semi solid (33 mg, 34%). ^{1}H NMR (300 MHz, $CDCl_3$): δ = 2.98 (t, 2H, J = 7.0 Hz, CH_2), 3.12 (t, 2H, J = 7.0 Hz, CH_2), 3.63 (s, 3H, NCH_3), 3.75 (s, 3H, OCH_3), 3.85 (s, 3H, OCH_3), 3.86 (s, 3H, OCH_3), 7.62 (s, 1H, ArH), 7.98 (s, 1H, ArH). ^{13}C NMR (62 MHz, $CDCl_3$): δ = 22.4 (CH_2), 30.1 (NCH_3), 30.9 (CH_2), 52.0 (OCH_3), 52.5 (OCH_3), 52.6 (OCH_3), 110.6, 120.7 (CH), 126.24, 126.28, 136.8, 143.7, 157.3 (C), 168.5, 168.6, 172.8 (CO). IR (KBr, cm^{-1}): v = 2997, 2948, 2843 (w), 1727, 1713 (s), 1622, 1581, 1510, 1488 (w), 1431, 1368, 1339 (m), 1254 (s), 1229, 1219, 1190, 1153, 1101, 1041, 970 (m), 888, 887, 830, (w), 783 (m), 680, 669, 620, 570 (w). GC-MS (EI, 70 eV): *m/z* (%) = 334(12) $[M]^+$, 303(24), 276(18), 275(100). HRMS (EI, 70 eV): *m/z* calcd for $C_{16}H_{18}N_2O_6$ $[M]^+$: 334.11594; found: 334.11537.

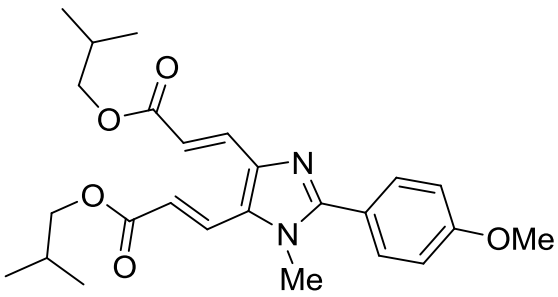
Synthesis of 4,5-di(alkenyl)-2-aryl-*N*-methyl imidazol (43):

(2*E*,2'*E*)-Dibutyl-3,3'-(2-(4-methoxyphenyl)-1-methyl-1*H*-imidazole-4,5-diyl)diacrylate (43a):



Product **43a** was prepared starting with **42a** (346 mg, 1.0 mmol), *n*-butyl acrylate (0.36 mL, 2.5 mmol), $Pd(OAc)_2$ (11 mg, 5 mol %), $P(Cy)_3$ (10 mol %), NEt_3 (1.10 mL, 8.0 mmol), DMF (5 mL) at 100 °C for 24 h following general procedure D, as a yellow highly viscous oil (400 mg, 91%). ^{1}H NMR (300 MHz, $CDCl_3$): δ = 0.87 (t, 3H, J = 7.4 Hz, CH_3), 0.90 (t, 3H, J = 7.3 Hz, CH_3), 1.31-1.41 (m, 4H, $2CH_2$), 1.55-1.65 (m, 4H, $2CH_2$), 3.64 (s, 3H, NCH_3), 3.78 (s, 3H, OCH_3), 4.12 (t, 2H, J = 6.6 Hz, CH_2O), 4.16 (t, 2H, J = 6.7 Hz, CH_2O), 6.20 (d, 1H, J = 16.1 Hz, CH), 6.77 (d, 1H, J = 15.3 Hz, CH), 6.92 (dd, 2H, J = 2.0, 6.8 Hz, ArH), 7.48 (dd, 2H, J = 2.1, 6.8 Hz, ArH), 7.62 (d, 1H, J = 16.1 Hz, CH), 7.69 (d, 1H, J = 15.3 Hz, CH). ^{13}C NMR (75 MHz, $CDCl_3$): δ = 13.7 ($2CH_3$), 19.2 ($2CH_2$), 30.7, 30.8 (CH_2), 33.9 (NCH_3), 55.4 (OCH_3), 64.2, 64.8 (CH_2O), 114.2 (2CH), 119.1, 119.4 (CH), 121.6 (C), 129.1 (CH), 130.0 (C), 130.7 (2CH), 133.5 (CH), 139.7, 152.1, 160.8 (C), 166.7, 167.5 (CO). IR (KBr, cm^{-1}): ν = 2957, 2933, 2871 (w), 1694 (s), 1622, 1612 (m), 1578, 1531 (w), 1456, 1443 (m), 1387, 1338 (w), 1278 (m), 1249, 1158 (s), 1114, 1065, 1024, 965, 835 (m), 815, 793 (w), 741 (m), 695, 638, 620, 536 (w). GC-MS (EI, 70 eV): *m/z* (%) = 440(30) $[M]^+$, 339(25), 338(20), 284(22), 283(100), 281(12), 266(14), 265(71), 240(18), 239(96), 237(17), 41(11). HRMS (EI, 70 eV): *m/z* calcd for $C_{25}H_{32}N_2O_5$ $[M]^+$: 440.23057; found: 440.22968.

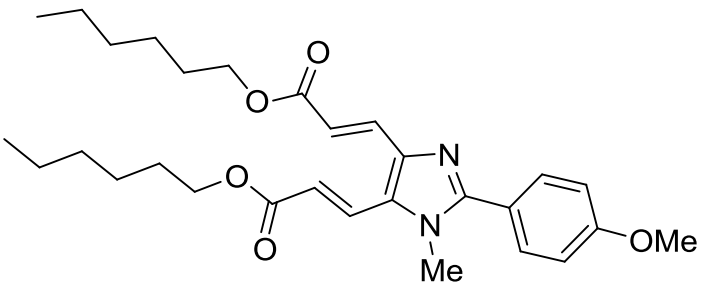
(2*E*,2'*E*)-Isobutyl-3,3'-(2-(4-methoxyphenyl)-1-methyl-1*H*-imidazole-4,5-diyl)diacrylate (43b):



Product **43b** was prepared starting with **42a** (346 mg, 1.0 mmol), *iso*-butyl acrylate (0.36 mL, 2.5 mmol) , $Pd(OAc)_2$ (11 mg, 5 mol %), $P(Cy)_3$ (10 mol %), NEt_3 (1.10 mL, 8.0 mmol), DMF (5 mL) at 100 °C for 24 h following general procedure D, as a brown oil (374 mg, 85%). ^{1}H NMR (300 MHz, $CDCl_3$): δ = 0.90 (d, 6H, J = 6.8 Hz, $2CH_3$), 0.92 (d, 6H,

J = 6.8 Hz, 2CH_3), 1.88-2.00 (m, 2H, 2CH), 3.65 (s, 3H, NCH_3), 3.79 (s, 3H, OCH_3), 3.91 (d, 2H, J = 6.6 Hz, CH_2O), 3.94 (d, 2H, J = 6.7 Hz, CH_2O), 6.23 (d, 1H, J = 16.1 Hz, CH), 6.80 (d, 1H, J = 15.3 Hz, CH), 6.94 (dd, 2H, J = 1.9, 6.8 Hz, ArH), 7.49 (dd, 2H, J = 2.1, 6.8 Hz, ArH), 7.64 (d, 1H, J = 16.1 Hz, CH), 7.71 (d, 1H, J = 15.3 Hz, CH). ^{13}C NMR (75 MHz, $CDCl_3$): δ = 19.1 (2CH_3), 19.2 (2CH_3), 27.8, 27.9 (CH), 33.8 (NCH_3), 55.4 (OCH_3), 70.5, 71.0 (CH_2O), 114.2 (2CH), 119.2, 119.4 (CH), 121.6 (C), 129.2 (CH), 130.0 (C), 130.7 (2CH), 133.5 (CH), 139.7, 152.1, 160.8 (C), 166.7, 167.5 (CO). IR (KBr, cm^{-1}): ν = 2958 (m), 2873, 2838 (w), 1703 (s), 1624, 1611 (m), 1577, 1533 (w), 1481, 1454, 1440, 1392, 1376 (m), 1279 (m), 1249, 1154 (s), 1111, 1059, 1024, 1009, 967, 835, 791, 741, 699 (m), 614, 603, 536 (w). GC-MS (EI, 70 eV): *m/z* (%) = 440(30) $[M]^+$, 338(13), 284(18), 283(100), 281(11), 265(52), 240(16), 239(70). HRMS (ESI): *m/z* calcd for $C_{25}H_{33}N_2O_5$ $[M+H]^+$: 441.2384; found: 441.2392.

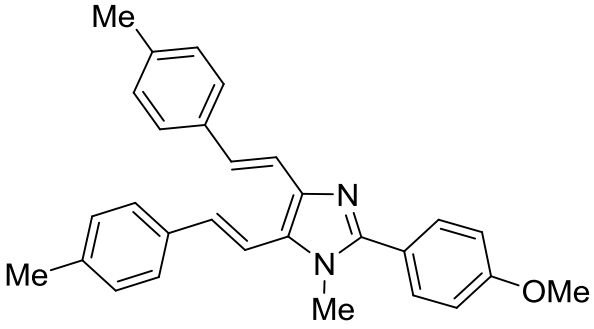
(2*E*,2'*E*)-Dihexyl-3,3'-[2-(4-methoxyphenyl)-1-methyl-1*H*-imidazole-4,5-diyl]diacrylate (43c):



Product **43c** was prepared starting with **42a** (346 mg, 1.0 mmol), *n*-hexyl acrylate (0.44 mL, 2.5 mmol), $Pd(OAc)_2$ (11 mg, 5 mol %), $P(Cy)_3$ (10 mol %), NEt_3 (1.10 mL, 8.0 mmol), DMF (5 mL) at 100 °C for 24 h following general procedure D, as yellowish solid (385 mg, 78%), mp. 95-97 °C. ^{1}H NMR (250 MHz, $CDCl_3$): δ = 0.81 (t, 3H, J = 6.6 Hz, CH_3), 0.83 (t, 3H, J = 6.5 Hz, CH_3), 1.18-1.34 (m, 12H, 6CH_2), 1.55-1.67 (m, 4H, 2CH_2), 3.64 (s, 3H, NCH_3), 3.78 (s, 3H, OCH_3), 4.11 (t, 2H, J = 6.7 Hz, CH_2O), 4.14 (t, 2H, J = 6.8 Hz, CH_2O), 6.20 (d, 1H, J = 16.1 Hz, CH), 6.77 (d, 1H, J = 15.4 Hz, CH), 6.92 (dd, 2H, J = 2.1, 6.8 Hz, ArH), 7.48 (dd, 2H, J = 1.9, 6.9 Hz, ArH), 7.63 (d, 1H, J = 16.1 Hz, CH), 7.69 (d, 1H, J = 15.3 Hz, CH). ^{13}C NMR (75 MHz, $CDCl_3$): δ = 14.0 (2CH_3), 22.5 (2CH_2), 25.6 (2CH_2), 28.7 (2CH_2), 31.4, 31.5 (CH_2), 33.9 (NCH_3), 55.4 (OCH_3), 64.5, 65.1 (CH_2O), 114.2 (2CH), 119.1, 119.4 (CH), 121.6 (C), 129.1 (CH), 130.0 (C), 130.7 (2CH), 133.5 (CH), 139.7, 152.1, 160.8 (C), 166.7, 167.5 (CO). IR (KBr, cm^{-1}): ν = 2953, 2928, 2856, 1716 (w), 1695, 1624 (s), 1578, 1531 (w), 1474, 1463 (m), 1388, 1338 (w), 1294 (m), 1283, 1251, 1170 (s), 1112, 1021, 964, 868, 835 (m), 815, 792, 742, 698, 602, 539 (w). GC-MS (EI, 70 eV): *m/z* (%) = 494(33) $[M]^+$, 326(12), 310(19),

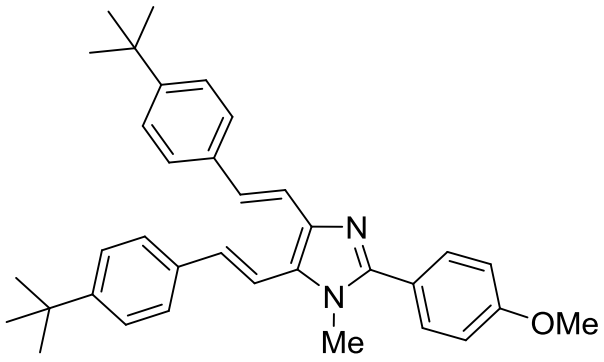
309(100), 281(10). HRMS (EI, 70 eV): *m/z* calcd for $C_{29}H_{40}N_2O_5$ $[M]^+$: 496.29317; found: 496.29374.

2-(4-Methoxyphenyl)-1-methyl-4,5-bis(4-methylstyryl)-1*H*-imidazole (43d):



Product **43d** was prepared starting with **42a** (346 mg, 1.0 mmol), 4-methyl styrene (0.33 mL, 2.5 mmol) , $Pd(OAc)_2$ (11 mg, 5 mol %), $P(Cy)_3$ (10 mol %), NEt_3 (1.10 mL, 8.0 mmol), DMF (5 mL) at 100 °C for 24 h following general procedure D, as a brown oil (264 mg, 63%). ^{1}H NMR (300 MHz, $CDCl_3$): δ = 2.25 (s, 3H, CH_3), 2.31 (s, 3H, CH_3), 3.58 (s, 3H, NCH_3), 3.78 (s, 3H, OCH_3), 6.80 (d, 1H, J = 16.3 Hz, CH), 6.86-6.95 (m, 4H, ArH and CH), 7.04 (d, 2H, J = 8.0 Hz, ArH), 7.12 (d, 2H, J = 7.1 Hz, ArH), 7.33-7.38 (m, 4H, ArH and CH), 7.44 (dd, 1H, J = 2.2, 6.4 Hz, ArH), 7.52 (dd, 2H, J = 2.0, 6.8 Hz, ArH). ^{13}C NMR (75 MHz, $CDCl_3$): δ = 21.2, 21.3 (CH_3), 33.2 (NCH_3), 55.4 (OCH_3), 114.0 (CH), 114.1 (2CH), 114.4, 118.5 (CH), 122.9 (C), 126.3 (3CH), 127.9 (CH), 129.2 (2CH), 129.5 (2CH), 130.6 (2CH), 131.9 (CH), 134.5, 135.3, 136.8, 137.9 (C), 138.0 (2C), 149.2, 160.3 (C). IR (KBr, cm^{-1}): v = 2955 (w), 1608, 1509, 1465 (w), 1394, 1362, 1305 (w), 1248 (s), 1173, 1111, 1031, 948, 838, 816, 805 (m), 728, 623, 541 (w). GC-MS (EI, 70 eV): *m/z* (%) = 420(100) $[M]^+$, 419(35), 329(11), 253(10), 207(65), 148(15), 44(13), 32(12). HRMS (ESI): *m/z* calcd for $C_{29}H_{29}N_2O$ $[M+H]^+$: 421.2274; found: 421.2274.

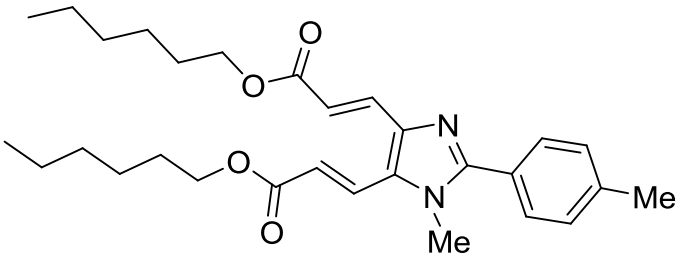
4,5-Bis(4-*tert*-butylstyryl)-2-(4-methoxyphenyl)-1-methyl-1*H*-imidazole (43e):



Product **43e** was prepared starting with **42a** (346 mg, 1.0 mmol), 4-*tert*-butyl styrene (0.45 mL, 2.5 mmol) , $Pd(OAc)_2$ (11 mg, 5 mol %), $P(Cy)_3$ (10 mol %), NEt_3 (1.10 mL, 8.0 mmol), DMF (5 mL) at 100 °C for 24 h following general procedure D, as a brown oil (262 mg, 52%). ^{1}H NMR (300 MHz, $CDCl_3$): δ = 1.24 (s, 9H, $3CH_3$), 1.27 (s, 9H, $3CH_3$), 3.58 (s, 3H, NCH_3), 3.77 (s, 3H, OCH_3), 6.86 (d, 2H, J = 16.3 Hz, CH), 6.92 (d, 2H, J = 8.8 Hz, ArH), 7.12 (d, 2H, J =

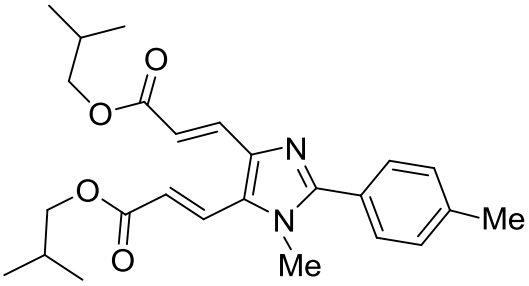
16.0 Hz, CH), 7.26 (d, 2H, J = 8.3 Hz, ArH), 7.34 (d, 2H, J = 8.5 Hz, ArH), 7.37-7.41 (m, 4H, ArH), 7.51 (d, 2H, J = 8.8 Hz, ArH). ^{13}C NMR (62 MHz, $CDCl_3$): δ = 30.2 ($3CH_3$), 30.3 ($3CH_3$), 32.0 (NCH_3), 33.5, 33.7 (C), 54.3 (OCH_3), 113.0 (2CH), 113.6, 117.8 (CH), 121.9 (C), 124.4 (2CH), 124.7 (2CH), 125.0 (2CH), 125.1 (2CH), 126.7 (CH), 129.3 (C), 129.5 (2CH), 130.9 (CH), 133.5, 134.3, 136.9, 148.1, 149.0, 150.2, 159.2 (C). IR (KBr, cm^{-1}): v = 2959 (w), 1611, 1508, 1465 (m), 1394, 1362, 1305 (w), 1248 (s), 1173, 1111, 1031, 948, 838, 816, 805 (m), 728, 623, 541 (w). HRMS (ESI): *m/z* calcd for $C_{35}H_{41}N_2O$ $[M+H]^+$: 505.3213; found: 505.3212.

(2*E*,2'*E*)-Dihexyl-3,3'-(1-methyl-2-*p*-tolyl-1*H*-imidazole-4,5-diyl)diacrylate (43g):



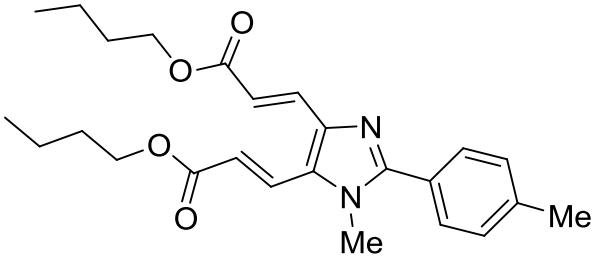
Product **43g** was prepared starting with **42b** (330 mg, 1.0 mmol), *n*-hexyl acrylate (0.44 mL, 2.5 mmol) , $Pd(OAc)_2$ (11 mg, 5 mol %), $P(Cy)_3$ (10 mol %), NEt_3 (1.10 mL, 8.0 mmol), DMF (5 mL) at 100 °C for 24 h following general procedure D, as a brown oil (360 mg, 75%). ^{1}H NMR (300 MHz, $CDCl_3$): δ = 0.82 (t, 3H, J = 6.8 Hz, CH_3), 0.84 (t, 3H, J = 6.7 Hz, CH_3), 1.21-1.33 (m, 12H, $6CH_2$), 1.58-1.67 (m, 4H, $2CH_2$), 2.35 (s, 3H, CH_3), 3.65 (s, 3H, NCH_3), 4.11 (t, 2H, J = 6.7 Hz, CH_2O), 4.15 (t, 2H, J = 6.8 Hz, CH_2O), 6.22 (d, 1H, J = 16.1 Hz, CH), 6.79 (d, 1H, J = 15.3 Hz, CH), 7.22 (d, 2H, J = 7.9 Hz, ArH), 7.44 (dd, 2H, J = 1.7, 6.5 Hz, ArH), 7.64 (d, 1H, J = 16.2 Hz, CH), 7.70 (d, 1H, J = 15.3 Hz, CH). ^{13}C NMR (62 MHz, $CDCl_3$): δ = 14.0 ($2CH_3$), 21.4 (CH_3), 22.5 ($2CH_2$), 25.6 ($2CH_2$), 28.7 ($2CH_2$), 31.4 ($2CH_2$), 33.8 (NCH_3), 64.5, 65.1 (CH_2O), 119.3, 119.5 (CH), 126.4 (C), 129.1 (3CH), 129.5 (2CH), 130.1 (C), 133.5 (CH), 139.7, 140.0, 152.2 (C), 166.6, 167.5 (CO). IR (KBr, cm^{-1}): v = 2953, 2925, 2855 (m), 1705 (s), 1624, 1452, 1277 (m), 1163 (s), 1056, 1018, 970 (m), 913, 865, 848 (w), 823 (m), 790, 734, 611 (w). GC-MS (EI, 70 eV): *m/z* (%) = 480(18) $[M]^+$, 351(21), 268(14), 267(100), 265(10), 249(54), 224(15), 223(80), 221(15), 207(28), 43(13). HRMS (ESI): *m/z* calcd for $C_{29}H_{41}N_2O_4$ $[M+H]^+$: 481.3061; found: 481.3064.

(2*E*,2'*E*)-Isobutyl-3,3'-(1-methyl-2-*p*-tolyl-1*H*-imidazole-4,5-diyl)diacrylate (43h):



Product **43h** was prepared starting with **42b** (330 mg, 1.0 mmol), *iso*-butyl acrylate (0.36 mL, 2.5 mmol) , $Pd(OAc)_2$ (11 mg, 5 mol %), $P(Cy)_3$ (10 mol %), NEt_3 (1.10 mL, 8.0 mmol), DMF (5 mL) at 100 °C for 24 h following general procedure D, as a brown oil (347 mg, 82%). ^{1}H NMR (300 MHz, $CDCl_3$): δ = 0.89 (d, 6H, J = 6.9 Hz, $2CH_3$), 0.91 (d, 6H, J = 7.0 Hz, $2CH_3$), 1.86-1.97 (m, 2H, 2CH), 2.33 (s, 3H, CH_3), 3.64 (s, 3H, NCH_3), 3.90 (d, 2H, J = 6.6 Hz, CH_2O), 3.94 (d, 2H, J = 6.8 Hz, CH_2O), 6.23 (d, 1H, J = 16.1 Hz, CH), 6.80 (d, 1H, J = 15.3 Hz, CH), 7.21 (d, 2H, J = 7.8 Hz, ArH), 7.42 (d, 2H, J = 8.0 Hz, ArH), 7.63 (d, 1H, J = 16.1 Hz, CH), 7.70 (d, 1H, J = 15.3 Hz, CH). ^{13}C NMR (62 MHz, $CDCl_3$): δ = 19.0 ($2CH_3$), 19.1 ($2CH_3$), 21.4 (CH_3), 27.7, 27.8 (CH), 33.8 (NCH_3), 70.4, 71.0 (CH_2O), 119.3, 119.4 (CH), 126.1 (C), 129.0 (2CH), 129.1 (CH), 129.4 (2CH), 130.1 (C), 133.5 (CH), 139.6, 140.0, 152.1 (C), 166.6, 167.4 (CO). IR (KBr, cm^{-1}): v = 2958, 2873 (w), 1704 (s), 1624, 1467, 1453, 1376, 1276, 1244 (m), 1149 (s), 1111, 967, 822 (m), 734, 700, 615 (w). GC-MS (EI, 70 eV): *m/z* (%) = 424(18) $[M]^+$, 323(11), 268(19), 267(100), 249(45), 223 (71), 221(14), 207(12). HRMS (EI, 70 eV): *m/z* calcd for $C_{25}H_{32}N_2O_4$ $[M]^+$: 424.23566; found: 424.23506.

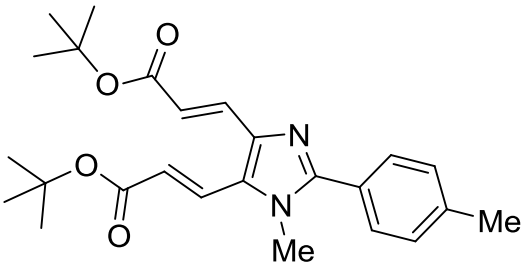
(2*E*,2'*E*)-Dibutyl-3,3'-(1-methyl-2-*p*-tolyl-1*H*-imidazole-4,5-diyl)diacrylate (43i):



Product **43i** was prepared starting with **42b** (330 mg, 1.0 mmol), *n*-butyl acrylate (0.36 mL, 2.5 mmol) , $Pd(OAc)_2$ (11 mg, 5 mol %), $P(Cy)_3$ (10 mol %), NEt_3 (1.10 mL, 8.0 mmol), DMF (5 mL) at 100 °C for 24 h following general procedure D, as a brown oil (369 mg, 87%). ^{1}H NMR (300 MHz, $CDCl_3$): δ = 0.88 (t, 3H, J = 7.4 Hz, CH_3), 0.90 (t, 3H, J = 7.3 Hz, CH_3), 1.31-1.41 (m, 4H, $2CH_2$), 1.55-1.66 (m, 4H, $2CH_2$), 2.34 (s, 3H, CH_3), 3.65 (s, 3H, NCH_3), 4.13 (t, 2H, J = 6.6 Hz, CH_2O), 4.16 (t, 2H, J = 6.6 Hz, CH_2O), 6.22 (d, 1H, J = 16.2 Hz, CH), 6.78 (d, 1H, J = 15.3 Hz, CH), 7.22 (d, 2H, J = 7.9 Hz, ArH), 7.44 (dd, 2H, J = 1.8, 6.3 Hz, ArH), 7.64 (d, 1H, J = 16.2 Hz, CH), 7.70 (d, 1H, J = 15.3 Hz, CH). ^{13}C NMR (62 MHz, $CDCl_3$): δ = 13.7 ($2CH_3$), 19.2 ($2CH_2$), 21.4 (CH_3), 30.7, 30.8 (CH_2), 33.8 (NCH_3), 64.2, 64.8 (CH_2O), 119.3, 119.5 (CH), 126.4 (C), 129.1 (3CH), 129.5 (2CH), 130.1 (C), 133.5

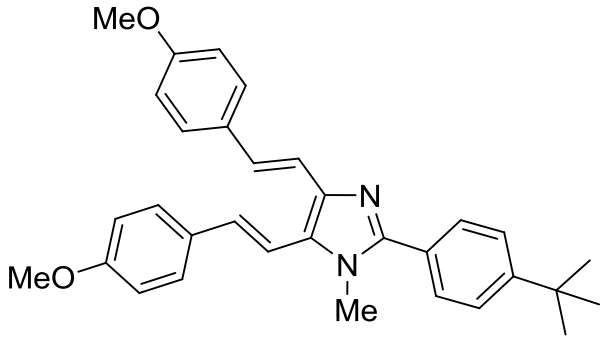
(CH), 139.7, 140.0, 152.2 (C), 166.6, 167.5 (CO). IR (KBr, cm^{-1}): ν = 2956, 2931, 2871 (w), 1701, 1623 (s), 1451 (m), 1381 (w), 1276 (s), 1258 (m), 1159, 1148 (s), 1118, 1059, 1018, 967 (m), 864, 847 (w), 822, 734 (m), 700, 610 (w). GC-MS (EI, 70 eV): *m/z* (%) = 424(26) $[M]^+$, 323(35), 322(13), 268(17), 267(100), 265(14), 250(10), 249(59), 224(14), 223(94), 221(17). HRMS (ESI): *m/z* calcd for $C_{25}H_{33}N_2O_4$ $[M+H]^+$: 425.2435; found: 425.2443.

(2*E*,2'*E*)-*tert*-Butyl-3,3'-(1-methyl-2-*p*-tolyl-1*H*-imidazole-4,5-diyl)diacrylate (43j):



Product **43j** was prepared starting with **42b** (330 mg, 1.0 mmol), *tert*-butyl acrylate (0.36 mL, 2.5 mmol) , $Pd(OAc)_2$ (11 mg, 5 mol %), $P(Cy)_3$ (10 mol %), NEt_3 (1.10 mL, 8.0 mmol), DMF (5 mL) at 100 °C for 24 h following general procedure D, as whitish solid (381 mg, 90%), mp. = 126-126 °C. ^1H NMR (300 MHz, $CDCl_3$): δ = 1.44 (s, 9H, $3CH_3$), 1.47 (s, 9H, $3CH_3$), 2.34 (s, 3H, CH_3), 3.63 (s, 3H, NCH_3), 6.16 (d, 1H, *J* = 16.1 Hz, CH), 6.72 (d, 1H, *J* = 15.4 Hz, CH), 7.22 (d, 2H, *J* = 8.0 Hz, ArH), 7.43 (d, 2H, *J* = 8.1 Hz, ArH), 7.53 (d, 1H, *J* = 16.2 Hz, CH), 7.62 (d, 1H, *J* = 15.3 Hz, CH). ^{13}C NMR (75 MHz, $CDCl_3$): δ = 21.4 (CH_3), 28.2 ($6CH_3$), 33.6 (NCH_3), 80.1, 81.1 (C), 121.3, 121.6 (CH), 126.5 (C), 128.3 (CH), 129.1 (2CH), 129.4 (2CH), 130.0 (C), 132.7 (CH), 139.3, 139.9, 151.8 (C), 166.9, 166.9 (CO). IR (KBr, cm^{-1}): ν = 2974, 2928, 2869 (w), 1698, 1623 (m), 1520, 1480 (w), 1452 (m), 1391 (w), 1365, 1299, 1278, 1255 (m), 1136 (s), 1057, 969, 886, 854, 822, 761, 733 (m). MS (EI, 70 eV): *m/z* (%) = 424(16) $[M]^+$, 267(15), 224(19), 223(100), 221(16), 56(12), 41(22). HRMS (ESI): *m/z* calcd for $C_{25}H_{33}N_2O_4$ $[M+H]^+$: 425.24348; found: 425.24384.

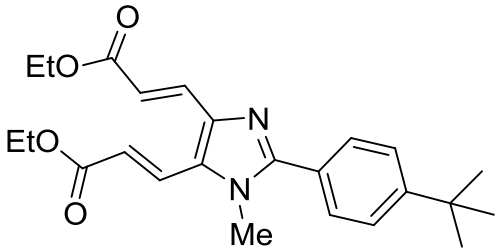
2-(4-*tert*-Butylphenyl)-4,5-bis(4-methoxystyryl)-1-methyl-1*H*-imidazole (43k):



Product **43k** was prepared starting with **42c** (372 mg, 1.0 mmol), 4-methoxy styrene (0.33 mL, 2.5 mmol) , $Pd(OAc)_2$ (11 mg, 5 mol %), $P(Cy)_3$ (10 mol %), NEt_3 (1.10 mL, 8.0 mmol), DMF (5 mL) at 100 °C for 24 h following general procedure D, as a brown oil (305 mg, 64%). ^1H NMR (300 MHz, $CDCl_3$): δ = 1.27 (s, 9H, $3CH_3$), 3.60 (s, 3H, NCH_3), 3.72 (s, 3H,

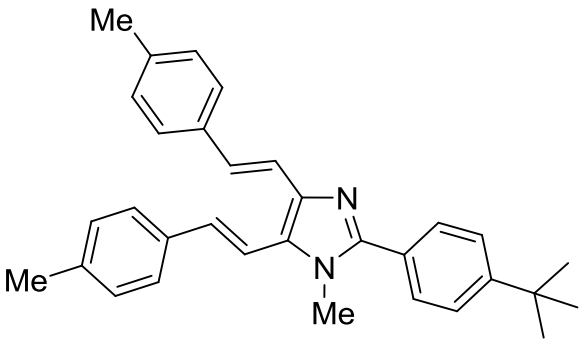
OCH_3), 3.76 (s, 3H, OCH_3), 6.77-6.79 (m, 5H, ArH and CH), 6.85 (d, 1H, J = 8.6 Hz, ArH), 7.02 (d, 2H, J = 16.0 Hz, CH), 7.37-7.42 (m, 6H, ArH and CH), 7.51 (d, 2H, J = 8.3 Hz, ArH). ^{13}C NMR (62 MHz, $CDCl_3$): δ = 31.2 ($3CH_3$), 33.1 (NCH_3), 34.8 (C), 55.3, 55.4 (OCH_3), 113.3 (CH), 114.0 (2CH), 114.3 (3CH), 125.5 (CH), 125.6 (2CH), 127.5 (2CH), 127.6 (2CH), 128.8 (2CH), 129.7, 130.1 (C), 131.0 (2C), 131.6 (CH), 137.8, 149.1, 152.2, 158.8, 159.6 (C). IR (KBr, cm^{-1}): v = 2954 (w), 1603, 1509, 1462 (m), 1394, 1362, 1303 (w), 1246 (s), 1173, 1111, 1031, 948, 837, 816, 802 (m), 728, 623, 540 (w). GC-MS (EI, 70 eV): *m/z* (%) = 478(100) $[M]^+$, 476(48), 461(11), 371(13), 174(16), 44(10). HRMS (ESI): *m/z* calcd for $C_{32}H_{35}N_2O_2$ $[M+H]^+$: 479.2693; found: 479.2693.

(2*E*,2'*E*)-Diethyl-3,3'-(2-(4-*tert*-butylphenyl)-1-methyl-1*H*-imidazole-4,5-diyl)diacrylate (43l):



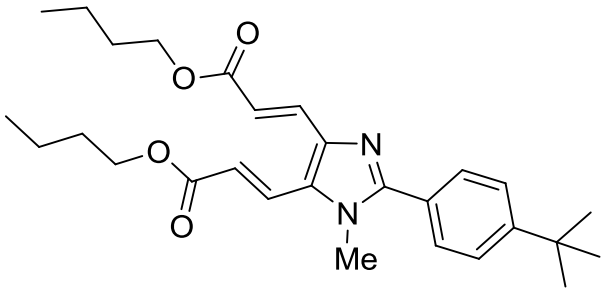
Product **43l** was prepared starting with **42c** (372 mg, 1.0 mmol), ethyl acrylate (0.27 mL, 2.5 mmol), $Pd(OAc)_2$ (11 mg, 5 mol %), $P(Cy)_3$ (10 mol %), NEt_3 (1.10 mL, 8.0 mmol), DMF (5 mL) at 100 °C for 24 h following general procedure D, as a brown oil (301 mg, 81%). ^{1}H NMR (300 MHz, $CDCl_3$): δ = 1.23 (t, 6H, J = 7.2 Hz, $2CH_3$), 1.27 (s, 9H, $3CH_3$), 3.66 (s, 3H, NCH_3), 4.17 (q, 2H, J = 7.2 Hz, CH_2O), 4.20 (q, 2H, J = 7.2 Hz, CH_2O), 6.21 (d, 1H, J = 16.3 Hz, CH), 6.77 (d, 1H, J = 15.4 Hz, CH), 7.42 (d, 2H, J = 8.0 Hz, ArH), 7.47 (d, 2H, J = 8.4 Hz, ArH), 7.64 (d, 1H, J = 16.2 Hz, CH), 7.69 (d, 1H, J = 15.3 Hz, CH). ^{13}C NMR (62 MHz, $CDCl_3$): δ = 14.3 ($2CH_3$), 31.1 ($3CH_3$), 33.9 (NCH_3), 34.8 (C), 60.3, 60.8 (CH_2O), 119.1, 119.4 (CH), 125.7 (2CH), 126.3 (C), 128.9 (2CH), 129.1 (CH), 130.0 (C), 133.5 (CH), 139.8, 152.2, 153.1 (C), 166.5, 167.4 (CO). IR (KBr, cm^{-1}): v = 2958, 2903, 2868 (w), 1701, 1624 (s), 1479, 1451 (m), 1391 (w), 1364 (m), 1277, 1261, 1151 (s), 1111, 1094, 1028, 1015, 967 (m), 917, 892 (w), 839, 728 (m), 671, 645 (w), 610, 558 (m). GC-MS (EI, 70 eV): *m/z* (%) = 410(46) $[M]^+$, 338(25), 337(100), 336(24), 321(15), 309(21), 293(63), 291(88), 277(17), 265(73), 249(52). HRMS (EI, 70 eV): *m/z* calcd for $C_{24}H_{30}N_2O_4$ $[M]^+$: 410.22001; found: 410.21940.

2-(4-*tert*-Butylphenyl)-1-methyl-4,5-bis(4-methylstyryl)-1*H*-imidazole (43m):



Product **43m** was prepared starting with **42c** (372 mg, 1.0 mmol), 4-methylstyrene (0.33 mL, 2.5 mmol), $Pd(OAc)_2$ (11 mg, 5 mol %), $P(Cy)_3$ (10 mol %), NEt_3 (1.10 mL, 8.0 mmol), DMF (5 mL) at 100 °C for 24 h following general procedure D, as a brown oil (249 mg, 56%). ^{1}H NMR (300 MHz, $CDCl_3$): δ = 1.27 (s, 9H, $3CH_3$), 2.25 (s, 3H, CH_3), 2.30 (s, 3H, CH_3), 3.60 (s, 3H, NCH_3), 6.86 (d, 2H, J = 14.3 Hz, CH), 7.03 (d, 2H, J = 8.0 Hz, ArH), 7.08-7.15 (m, 3H, ArH and CH), 7.34 (dd, 4H, J = 1.4, 8.0 Hz, ArH), 7.39-7.46 (m, 3H, ArH and CH), 7.51 (dd, 2H, J = 1.9, 6.6 Hz, ArH). ^{13}C NMR (62 MHz, $CDCl_3$): δ = 21.2, 21.3 (CH_3), 31.3 ($3CH_3$), 33.1 (NCH_3), 34.8 (C), 114.4, 118.6 (CH), 125.5 (CH), 125.6 (2CH), 126.3 (3CH), 127.6 (C), 128.0 (CH), 128.8 (2CH), 129.3 (2CH), 129.5 (2CH), 129.9 (C), 131.9 (CH), 134.5, 135.3, 136.8, 137.9, 138.1, 149.3, 152.2 (C). IR (KBr, cm^{-1}): v = 3019, 2957, 2864, 1510, 1477, 1446, 1362, 1266 (w), 1111, 1014, 954, 838, 802, 728 (m), 624, 612, 556 (w). GC-MS (EI, 70 eV): *m/z* (%) = 446(09) $[M]^+$, 444(100), 429(28), 215(13). HRMS (ESI): *m/z* calcd for $C_{32}H_{35}N_2$ $[M+H]^+$: 447.2795; found: 447.2801.

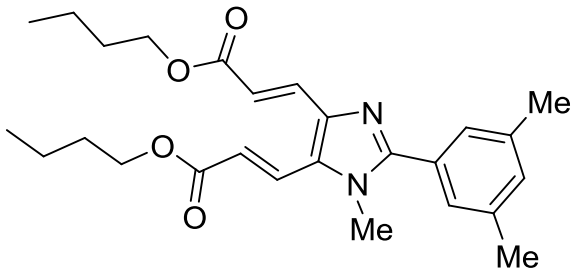
(2*E*,2'*E*)-Dibutyl-3,3'-(2-(4-*tert*-butylphenyl)-1-methyl-1*H*-imidazole-4,5-diyl)diacrylate (43o):



Product **43o** was prepared starting with **42c** (372 mg, 1.0 mmol), *n*-butylacrylate (0.36 mL, 2.5 mmol) , $Pd(OAc)_2$ (11 mg, 5 mol %), $P(Cy)_3$ (10 mol %), NEt_3 (1.10 mL, 8.0 mmol), DMF (5 mL) at 100 °C for 24 h following general procedure D, as a brown oil (405 mg, 87%). ^{1}H NMR (300 MHz, $CDCl_3$): δ = 0.86 (t, 3H, J = 7.4 Hz, CH_3), 0.89 (t, 3H, J = 7.4 Hz, CH_3), 1.27 (s, 9H, $3CH_3$), 1.31-1.43 (m, 4H, $2CH_2$), 1.55-1.67 (m, 4H, $2CH_2$), 3.66 (s, 3H, NCH_3), 4.12 (t, 2H, J = 6.5 Hz, CH_2O), 4.15 (t, 2H, J = 6.7 Hz, CH_2O), 6.22 (d, 1H, J = 16.2 Hz, CH), 6.78 (d, 1H, J = 15.3 Hz, CH), 7.42 (d, 2H, J = 8.5 Hz, ArH), 7.47 (d, 2H, J = 8.6 Hz, ArH), 7.64 (d, 1H, J = 16.2 Hz, CH), 7.70 (d, 1H, J = 15.3 Hz, CH). ^{13}C NMR (62 MHz, $CDCl_3$): δ = 13.7 ($2CH_3$), 19.2 ($2CH_2$), 30.7, 30.8 (CH_2),

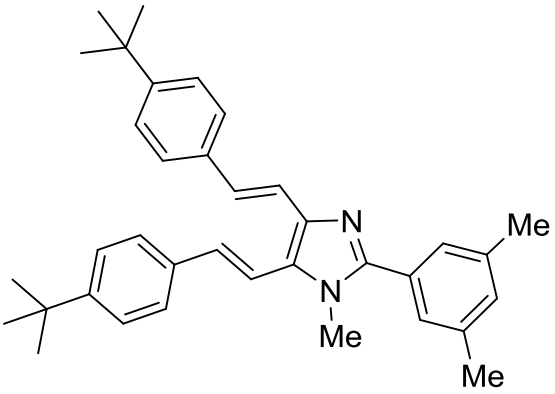
31.2 ($3CH_3$), 33.8 (NCH_3), 34.8 (C), 64.2, 64.7 (CH_2O), 119.2, 119.4 (CH), 125.7 (2CH), 126.3 (C), 128.9 (2CH), 129.1 (CH), 130.0 (C), 133.5 (CH), 139.7, 152.2, 153.1 (C), 166.6, 167.5 (CO). IR (KBr, cm^{-1}): ν = 2956, 2934, 2870 (w), 1705, 1624 (s), 1480, 1453 (m), 1383, 1362 (w), 1277, 1159 (s), 1113, 1061, 1014, 969, 840 (m), 728, 613, 559 (w). GC-MS (EI, 70 eV): *m/z* (%) = 466(20) $[M]^+$, 365(32), 309(100), 291(65), 265(64), 249(133). HRMS (EI, 70 eV): *m/z* calcd for $C_{28}H_{38}N_2O_4$ $[M]^+$: 466.28261; found: 466.28365.

(2*E*,2'*E*)-Dibutyl-3,3'-(2-(3,5-dimethylphenyl)-1-methyl-1*H*-imidazole-4,5-diyl)diacrylate (43p):



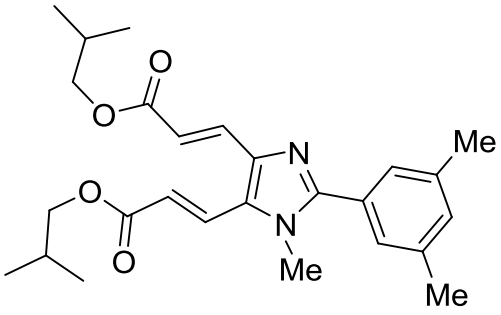
Product **43p** was prepared starting with **42d** (344 mg, 1.0 mmol), *n*-butyl acrylate (0.36 mL, 2.5 mmol) , $Pd(OAc)_2$ (11 mg, 5 mol %), $P(Cy)_3$ (10 mol %), NEt_3 (1.10 mL, 8.0 mmol), DMF (5 mL) at 100 °C for 24 h following general procedure D, as a brown oil (324 mg, 74%). ^1H NMR (250 MHz, $CDCl_3$): δ = 0.87 (t, 3H, *J* = 7.2 Hz, CH_3), 0.90 (t, 3H, *J* = 7.2 Hz, CH_3), 1.30-1.41 (m, 4H, $2CH_2$), 1.54-1.66 (m, 4H, $2CH_2$), 2.29 (s, 6H, $2CH_3$), 3.64 (s, 3H, NCH_3), 4.11 (t, 2H, *J* = 6.6 Hz, CH_2O), 4.16 (t, 2H, *J* = 6.7 Hz, CH_2O), 6.22 (d, 1H, *J* = 16.2 Hz, CH), 6.79 (d, 1H, *J* = 15.4 Hz, CH), 7.03 (s, 1H, ArH), 7.14 (s, 2H, ArH), 7.63 (d, 1H, *J* = 15.8 Hz, CH), 7.69 (d, 1H, *J* = 15.2 Hz, CH). ^{13}C NMR (62 MHz, $CDCl_3$): δ = 13.7 ($2CH_3$), 19.2 ($2CH_2$), 21.3 ($2CH_3$), 30.7 ($2CH_2$), 33.8 (NCH_3), 64.2, 64.7 (CH_2O), 119.3, 119.5 (CH), 126.9 (2CH), 129.0 (C), 129.1 (CH), 130.0 (C), 131.5, 133.5 (CH), 138.4 (2C), 139.6, 152.4 (C), 166.6, 167.5 (CO). IR (KBr, cm^{-1}): ν = 2956 (m), 2931, 2871 (w), 1703 (s), 1624, 1605 (m), 1514, (w), 1456 (m), 1381, 1387 (w), 1292, 1274, 1256, 1197 (m), 1160 (s), 1097, 1063, 1023 (w), 969, 854 (m), 783, 757, 735, 695, 666, 620, 545 (w). GC-MS (EI, 70 eV): *m/z* (%) = 438(24) $[M]^+$, 337(29), 336(11), 282(19), 281(100), 279(14), 264(13), 263(65), 238(17), 237(94), 235(18). HRMS (ESI): *m/z* calcd for $C_{26}H_{35}N_2O_4$ $[M+H]^+$: 439.2591; found: 439.2595.

4,5-Bis(4-*tert*-butylstyryl)-2-(3,5-dimethylphenyl)-1-methyl-1*H*-imidazole (43q):



Product **43q** was prepared starting with **42q** (344 mg, 1.0 mmol), 4-*tert*-butylstyrene (0.45 mL, 2.5 mmol) , $Pd(OAc)_2$ (11 mg, 5 mol %), $P(Cy)_3$ (10 mol %), NEt_3 (1.10 mL, 8.0 mmol), DMF (5 mL) at 100 °C for 24 h following general procedure D, as a brown oil (326 mg, 65%). ^{1}H NMR (300 MHz, $CDCl_3$): δ = 1.23 (s, 9H, $3CH_3$), 1.26 (s, 9H, $3CH_3$), 2.28 (s, 6H, $2CH_3$), 3.58 (s, 3H, NCH_3), 6.86 (d, 2H, J = 15.1 Hz, CH), 6.94-6.97 (m, 3H, ArH), 7.09-7.11 (m, 2H, ArH), 7.14-7.19 (m, 2H, ArH and CH), 7.22-7.28 (m, 2H, ArH), 7.35-7.40 (m, 5H, ArH). ^{13}C NMR (62 MHz, $CDCl_3$): δ = 21.2 ($2CH_3$), 31.3 ($6CH_3$), 33.1 (NCH_3), 34.5, 34.7 (C), 114.6, 118.8 (CH), 125.5 (2CH), 125.8 (2CH), 126.1 (2CH), 126.2 (2CH), 126.4 (CH), 126.9 (2CH), 127.8 (CH), 130.0, 130.3 (C), 130.7 (CH), 132.0, 134.5, 135.4, 138.0 (C), 138.2 (2C), 150.0, 151.3 (C). IR (KBr, cm^{-1}): ν = 2952, 2921 (m), 2863 (w), 1602, 1462, 1455, 1361, 1107, 955 (m), 852, 817 (s), 791, 690 (m), 559 (s). MS (EI, 70 eV): *m/z* (%) = 502(100) $[M]^+$, 501(49), 448(19), 433(14), 371(40), 357(10), 343(20), 161(13), 146(23), 133(12), 97(11), 69(18), 57(25), 44(12). HRMS (ESI): *m/z* calcd for $C_{36}H_{43}N_2$ $[M+H]^+$: 503.3421; found: 503.3422.

(2*E*,2'*E*)-Isobutyl-3,3'-[2-(3,5-dimethylphenyl)-1-methyl-1*H*-imidazole-4,5-diyl] diacrylate (43r):

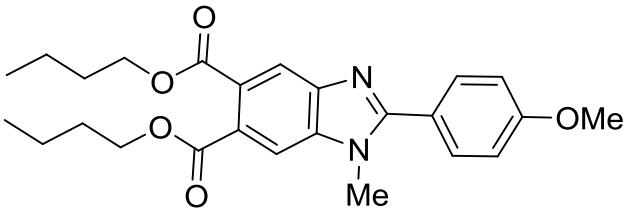


Product **43r** was prepared starting with **42d** (344 mg, 1.0 mmol), *iso*-butyl acrylate (0.36 mL, 2.5 mmol) , $Pd(OAc)_2$ (11 mg, 5 mol %), $P(Cy)_3$ (10 mol %), NEt_3 (1.10 mL, 8.0 mmol), DMF (5 mL) at 100 °C for 24 h following general procedure D, as a brown oil (328 mg, 75%). ^{1}H NMR (300 MHz, $CDCl_3$): δ = 0.88 (d, 6H, J = 6.7 Hz, $2CH_3$), 0.91 (d, 6H, J = 6.7 Hz, $2CH_3$), 1.86-1.99 (m, 2H, 2CH), 2.28 (s, 6H, $2CH_3$), 3.64 (s, 3H, NCH_3), 3.89 (d, 2H, J = 6.6 Hz, CH_2O), 3.93 (d, 2H, J = 6.7 Hz, CH_2O), 6.23 (d, 1H, J = 16.2 Hz, CH), 6.80 (d, 1H, J = 15.4 Hz, CH), 7.02 (s, 1H, ArH), 7.14 (s, 2H, ArH), 7.63 (d, 1H, J = 16.2 Hz, CH), 7.70 (d, 1H, J = 15.4 Hz, CH). ^{13}C NMR (62 MHz, $CDCl_3$): δ = 19.0 ($2CH_3$), 19.1

($2CH_3$), 21.2 ($2CH_3$), 27.7, 27.8 (CH), 33.7 (NCH_3), 70.4, 70.9 (CH_2O), 119.3, 119.4 (CH), 126.9 (2CH), 129.0 (C), 129.1 (CH), 130.0 (C), 131.5, 133.5 (CH), 138.4 (2C), 139.6, 152.4 (C), 166.6, 167.4 (CO). IR (KBr, cm^{-1}): ν = 2958, 2873 (w), 1704 (s), 1624, 1604, 1468 (m), 1392 (w), 1376 (m), 1340 (w), 1288, 1274, 1258, 1240, 1197 (m), 1154 (s), 1111, 969, 854 (m), 785, 735, 695, 547 (w). GC-MS (EI, 70 eV): *m/z* (%) = 438(18) $[M]^+$, 282(19), 281(100), 263(44), 238(11), 237(62), 235(11). HRMS (ESI): *m/z* calcd for $C_{26}H_{35}N_2O_4$ $[M+H]^+$: 439.2591; found: 439.2594.

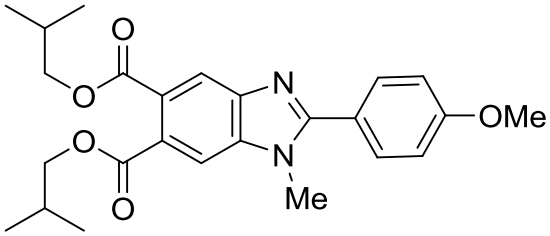
Synthesis of Benzimidazoles (44)

Dibutyl-2-(4-methoxyphenyl)-1-methyl-1*H*-benzo[*d*]imidazole-5,6-dicarboxylate (44a):



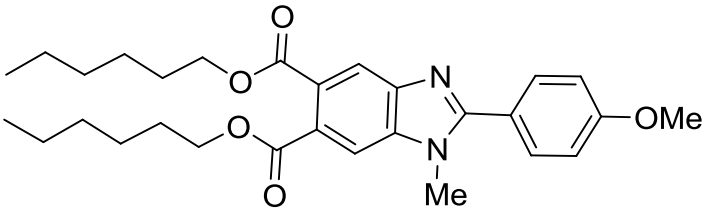
Compound **44a** was prepared starting with **43a** (100 mg, 0.23 mmol), following the general procedure E, as a brown highly viscous oil (80 mg, 81%). ^1H NMR (300 MHz, $CDCl_3$): δ = 0.89 (t, 6H, *J* = 7.3 Hz, $2CH_3$), 1.31-1.43 (m, 4H, $2CH_2$), 1.61-1.70 (m, 4H, $2CH_2$), 3.79 (s, 3H, OCH_3), 3.80 (s, 3H, NCH_3), 4.25 (t, 4H, *J* = 6.7 Hz, $2CH_2O$), 6.96 (dd, 2H, *J* = 2.0, 6.9 Hz, ArH), 7.64 (dd, 2H, *J* = 2.0, 6.5 Hz, ArH), 7.65 (s, 1H, ArH), 8.05 (s, 1H, ArH). ^{13}C NMR (62 MHz, $CDCl_3$): δ = 12.7 ($2CH_3$), 18.1, 18.2 (CH_2), 29.5, 29.6 (CH_2), 31.1 (NCH_3), 54.4 (OCH_3), 64.3, 64.6 (CH_2O), 111.0 (CH), 113.3 (2CH), 119.9 (CH), 120.5, 125.9, 126.1 (C), 129.9 (2CH), 136.5, 143.0, 156.0, 160.3 (C), 167.1, 167.3 (CO). IR (KBr, cm^{-1}): ν = 2957, 2932, 2872 (w), 1713 (s), 1609 (m), 1577, 1532 (w), 1478, 1463, 1438 (m), 1381, 1358 (w), 1327, 1306, 1271 (m), 1245, 1174 (s), 1099, 1059, 1024, 962, 943, 836, 782, 740 (m), 661, 638, 588, 549 (w). GC-MS (EI, 70 eV): *m/z* (%) = 438(45) $[M]^+$, 310(19), 309(100), 308(12). HRMS (EI, 70 eV): *m/z* calcd for $C_{25}H_{30}N_2O_5$ $[M]^+$: 438.21492; found: 438.21393.

Diisobutyl-2-(4-methoxyphenyl)-1-methyl-1*H*-benzo[*d*]imidazole-5,6-dicarboxylate (44b):



Compound **44b** was prepared starting with **43b** (100 mg, 0.23 mmol), following the general procedure E, as a brown oil (77 mg, 77%). ^{1}H NMR (300 MHz, $CDCl_3$): δ = 0.93 (d, 6H, J = 6.7 Hz, $2CH_3$), 0.94 (d, 6H, J = 6.7 Hz, $2CH_3$), 1.93-2.03 (m, 2H, 2CH), 3.82 (s, 3H, NCH_3), 3.83 (s, 3H, OCH_3), 4.04 (d, 2H, J = 6.6 Hz, CH_2O), 4.05 (d, 2H, J = 6.7 Hz, CH_2O), 6.99 (dd, 2H, J = 2.0, 6.8 Hz, ArH), 7.65-7.68 (m, 3H, ArH), 8.1 (s, 1H, ArH). ^{13}C NMR (62 MHz, $CDCl_3$): δ = 18.1 ($2CH_3$), 18.2 ($2CH_3$), 26.7, 26.8 (CH), 31.1 (NCH_3), 54.4 (OCH_3), 70.6, 70.9 (CH_2O), 110.0 (CH), 113.3 (2CH), 119.9 (CH), 120.5, 126.0, 126.2 (C), 129.9 (2CH), 136.6, 142.9, 156.0, 160.3 (C), 167.0, 167.4 (CO). IR (KBr, cm^{-1}): v = 2957 (m), 2927, 2872 (w), 1714 (s), 1609 (m), 1578, 1533 (w), 1479, 1465, 1438, 1376, 1327 (m), 1248, 1175, 1099, 1027 (s), 984, 836, (m), 782 (s), 741 (m), 699, 661, 589 (w). GC-MS (EI, 70 eV): *m/z* (%) = 438(46) $[M]^+$, 326(17), 310(20), 309(100). HRMS (EI, 70 eV): *m/z* calcd for $C_{25}H_{30}N_2O_5$ $[M]^+$: 438.21492; found: 438.21400.

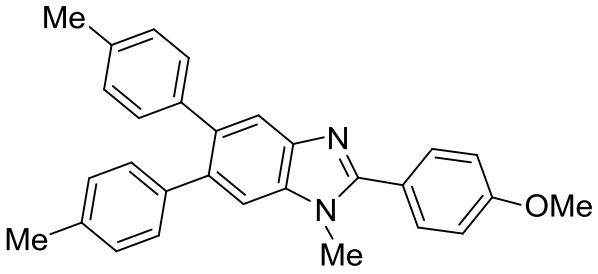
Dihexyl-2-(4-methoxyphenyl)-1-methyl-1*H*-benzo[*d*]imidazole-5,6-dicarboxylate (44c):



Compound **44c** was prepared starting with **43c** (100 mg, 0.20 mmol), following the general procedure E, as a brown highly viscous oil (83 mg, 84%). ^{1}H NMR (300 MHz, $CDCl_3$): δ = 0.83 (t, 6H, J = 6.9 Hz, $2CH_3$), 1.20-1.36 (m, 12H, $6CH_2$), 1.63-1.73 (m, 4H, $2CH_2$), 3.81 (s, 3H, OCH_3), 3.82 (s, 3H, NCH_3), 4.24 (t, 2H, J = 6.6 Hz, CH_2O), 4.25 (t, 2H, J = 6.8 Hz, CH_2O), 6.98 (dd, 2H, J = 2.0, 6.8 Hz, ArH), 7.64-7.67 (m, 3H, ArH), 8.07 (s, 1H, ArH). ^{13}C NMR (75 MHz, $CDCl_3$): δ = 14.0 ($2CH_3$), 22.6 ($2CH_2$), 25.6, 25.7, 28.5, 28.6 (CH_2), 31.5 ($2CH_2$), 32.1 (NCH_3), 55.4 (OCH_3), 65.7, 65.9 (CH_2O), 111.0 (CH), 114.3 (2CH), 120.9 (CH), 121.5, 127.0, 127.1 (C), 131.0 (2CH), 137.6, 144.0, 157.0, 161.3 (C), 168.1, 168.4 (CO). IR (KBr, cm^{-1}): v = 2953, 2927, 2856 (w), 1713 (s), 1609 (m), 1577, 1532 (w), 1479, 1465, 1438, 1379, 1358, 1327, 1269 (m), 1246, 1220, 1174, 1024 (s), 981, 836, 783, 741 (m), 661, 606, 588 (w). GC-MS (EI, 70 eV): *m/z* (%) = 494(36) $[M]^+$, 326(12),

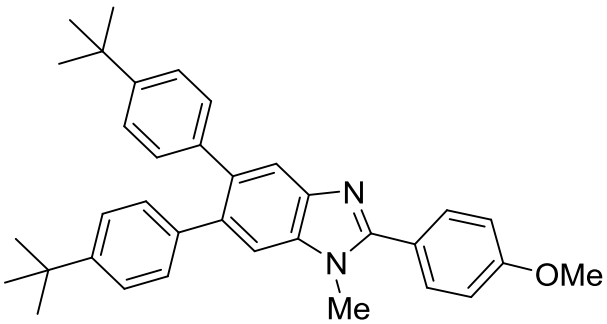
309(100), 308(20), 281(11), 207(14). HRMS (EI, 70 eV): *m/z* calcd for $C_{29}H_{38}N_2O_5$ $[M]^+$: 494.27752; found: 494.27654.

2-(4-Methoxyphenyl)-1-methyl-5,6-di-*p*-tolyl-1*H*-benzo[*d*]imidazole (44d):



Compound **44d** was prepared starting with **43d** (100 mg, 0.24 mmol), following the general procedure E, as a brown semi solid (78 mg, 79%). ^{1}H NMR (300 MHz, $CDCl_3$): δ = 2.25 (s, 3H, CH_3), 2.26 (s, 3H, CH_3), 3.80 (s, 3H, OCH_3), 3.82 (s, 3H, NCH_3), 6.94-7.04 (m, 10H, ArH), 7.29 (s, 1H, ArH), 7.67 (dd, 2H, *J* = 2.0, 6.8 Hz, ArH), 7.75 (s, 1H, ArH). ^{13}C NMR (62 MHz, $CDCl_3$): δ = 21.1 (2CH_3), 31.8 (NCH_3), 55.4 (OCH_3), 111.2 (CH), 114.2 (2CH), 121.0 (CH), 122.4 (C), 128.5 (2CH), 128.6 (2CH), 130.0 (2CH), 130.1 (2CH), 130.8 (2CH), 135.5, 135.8, 135.9, 136.1, 139.3 (C), 139.5 (2C), 142.2, 154.5, 160.9 (C). IR (KBr, cm^{-1}): *v* = 3019, 2918, 2950, 1715, 1659 (w), 1608 (m), 1576, 1531 (w), 1514, 1466, 1434, 1415, 1377, 1291 (m), 1249, 1173 (s), 1109, 1023 (m), 963, 946, 907, 882 (w), 835 (m), 818 (s), 789 (m), 724 (s), 678, 646, 625 (w), 608 (m), 566, 539 (w). GC-MS (EI, 70 eV): *m/z* (%) = 418(100) $[M]^+$, 417(31), 403(10). HRMS (ESI): calcd for $C_{29}H_{27}N_2O$ $[M+H]^+$: 419.2118; found: 419.2119.

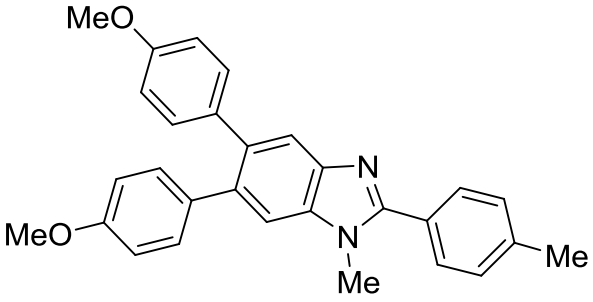
5,6-Bis(4-*tert*-butylphenyl)-2-(4-methoxyphenyl)-1-methyl-1*H*-benzo[*d*]imidazole (44e):



Compound **44e** was prepared starting with **43e** (100 mg, 0.20 mmol), following the general procedure E, as a brown solid (70 mg, 71%), mp. 152-154 °C. ^{1}H NMR (300 MHz, $CDCl_3$): δ = 1.22 (s, 9H, 3CH_3), 1.23 (s, 9H, 3CH_3), 3.79 (s, 3H, OCH_3), 3.81 (s, 3H, NCH_3), 6.98 (dd, 2H, *J* = 1.9, 6.9 Hz, ArH), 7.03 (dd, 2H, *J* = 1.6, 6.6 Hz, ArH), 7.04 (s, 1H, ArH), 7.11-7.17 (m, 5H, ArH), 7.32 (s, 1H, ArH), 7.66 (dd, 2H, *J* = 2.0, 6.8 Hz, ArH), 7.78 (s, 1H, ArH). ^{13}C NMR (75 MHz, $CDCl_3$): δ = 31.4 (6CH_3), 31.8 (NCH_3), 34.3, 34.4 (C), 55.4 (OCH_3), 111.1 (CH), 114.2 (2CH), 120.9 (CH), 122.5 (C), 124.5 (2CH), 124.6 (2CH), 129.8 (2CH), 130.0 (2CH), 130.9 (2CH), 136.1 (2C), 136.3, 139.2, 139.5, 142.3, 148.8, 149.0, 154.5, 160.9 (C). IR (KBr,

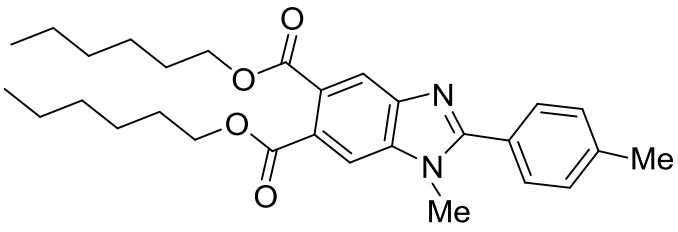
cm^{-1}): ν = 2955 (m), 2902, 2864, 1609, 1576, 1511 (w), 1467, 1435 (m), 1379, 1361, 1291 (w), 1250 (s), 1174, 1110, 1025 (m), 907, 883 (w), 832 (s), 790, 728, 666, 622, 572, 564, 554 (m). HRMS (ESI): calcd for $C_{35}H_{39}N_2O$ $[M+H]^+$: 503.3057; found: 503.3058.

5,6-Bis(4-methoxyphenyl)-1-methyl-2-*p*-tolyl-1*H*-benzo[*d*]imidazole (44f):



Compound **44f** was prepared starting with **43f** (100 mg, 0.23 mmol), following the general procedure E, as a a browm oil (82 mg, 83%). ^{1}H NMR (300 MHz, $CDCl_3$): δ = 2.35 (s, 3H, CH_3), 3.69 (s, 3H, OCH_3), 3.70 (s, 3H, OCH_3), 3.77 (s, 3H, NCH_3), 6.68 (d, 2H, J = 8.9 Hz, ArH), 6.69 (d, 2H, J = 8.9 Hz, ArH), 7.02 (d, 2H, J = 8.7 Hz, ArH), 7.23-7.26 (m, 3H, ArH), 7.59 (d, 2H, J = 8.1 Hz, ArH), 7.73 (s, 1H, ArH). ^{13}C NMR (62 MHz, $CDCl_3$): δ = 21.4 (CH_3), 31.8 (NCH_3), 55.1, 55.2 (OCH_3), 111.1 (CH), 113.2 (2CH), 113.3 (2CH), 121.0 (CH), 125.3 (C), 129.3 (2CH), 129.4 (2CH), 131.2 (2CH), 131.3 (2CH), 134.8, 134.9, 135.6, 135.8, 136.1, 139.9, 142.3, 154.7, 158.0, 158.1 (C). IR (KBr, cm^{-1}): ν = 2953, 2922, 2852 (w), 1606, 1513, 1464, 1435, 1379, 1286 (m), 1243, 1173 (s), 1106, 1080, 1032, 921, 880 (m), 826 (s), 773, 655, 606, 547 (m). GC-MS (EI, 70 eV): *m/z* (%) = 434(12) $[M]^+$, 433(100), 201(23), 173(24), 166(24). HRMS (EI, 70 eV): calcd for $C_{29}H_{26}N_2O_2$ $[M]^+$: 434.19888; found: 434.19812.

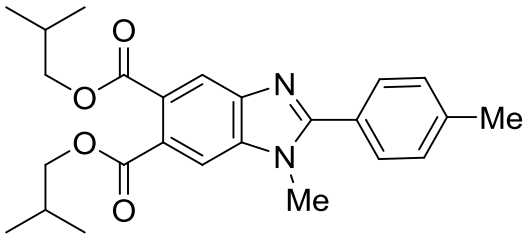
Dihexyl-1-methyl-2-*p*-tolyl-1*H*-benzo[*d*]imidazole-5,6-dicarboxylate (44g):



Compound **44g** was prepared starting with **43g** (100 mg, 0.21 mmol), following the general procedure E, as a brown oil (86 mg, 87%). ^{1}H NMR (300 MHz, $CDCl_3$): δ = 0.82 (t, 3H, J = 6.9 Hz, CH_3), 0.83 (t, 3H, J = 6.8 Hz, CH_3), 1.25-1.38 (m, 12H, $6CH_2$), 1.63-1.73 (m, 4H, $2CH_2$), 2.37 (s, 3H, CH_3), 3.83 (s, 3H, NCH_3), 4.24 (t, 2H, J = 6.7 Hz, CH_2O), 4.25 (t, 2H, J = 6.9 Hz, CH_2O), 7.27 (d, 2H, J = 7.9 Hz, ArH), 7.60 (d, 2H, J = 8.1 Hz, ArH), 7.68 (s, 1H, ArH), 8.08 (s, 1H, ArH). ^{13}C NMR (62 MHz, $CDCl_3$): δ = 14.0 ($2CH_3$), 21.5 (CH_3), 22.5 ($2CH_2$), 25.6, 25.7 (CH_2), 28.5, 28.6 (CH_2), 31.5 ($2CH_2$), 32.1 (NCH_3), 65.7, 65.9 (CH_2O), 111.1, 121.1 (CH), 126.3, 127.0, 127.1 (C), 129.3 (2CH), 129.5

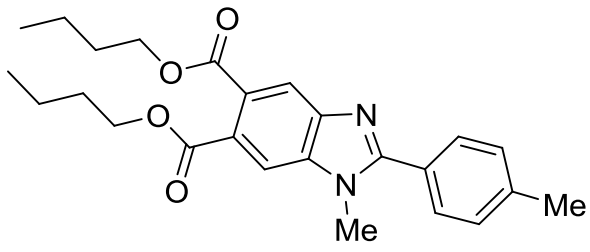
(2CH), 137.5, 140.7, 144.0, 157.2 (C), 168.1, 168.4 (CO). IR (KBr, cm^{-1}): ν = 2952, 2925, 2856 (m), 1713 (s), 1615, 1577 (w), 1466, 1379, 1357, 1326 (m), 1270, 1243, 1220 (s), 1194, 1117 (m), 1099 (s), 1018 (m), 982, 951, 892 (w), 823, 783, 730 (m), 627, 583 (w). GC-MS (EI, 70 eV): *m/z* (%) = 478(61) $[M]^+$, 394(21), 310(44), 294(43), 293(100), 292(46), 265(13). HRMS (EI, 70 eV): *m/z* calcd for $C_{29}H_{38}N_2O_4$ $[M]^+$: 478.28261; found: 478.28202. Anal. calcd for $C_{29}H_{38}N_2O_4$: C, 72.77; H, 8.00; N, 5.85. Found: C, 72.42; H, 8.49; N, 5.58.

Diisobutyl-1-methyl-2-*p*-tolyl-1*H*-benzo[*d*]imidazole-5,6-dicarboxylate (44h):



Compound **44h** was prepared starting with **43h** (100 mg, 0.24 mmol), following the general procedure E, as a brown oil (85 mg, 86%). ^{1}H NMR (300 MHz, $CDCl_3$): δ = 0.93 (d, 6H, *J* = 6.7 Hz, $2CH_3$), 0.94 (d, 6H, *J* = 6.7 Hz, $2CH_3$), 1.95-2.04 (m, 2H, 2CH), 2.38 (s, 3H, CH_3), 3.84 (s, 3H, NCH_3), 4.04 (d, 2H, *J* = 6.6 Hz, CH_2O), 4.05 (d, 2H, *J* = 6.8 Hz, CH_2O), 7.28 (d, 2H, *J* = 8.0 Hz, ArH), 7.60 (d, 3H, *J* = 8.1 Hz, ArH), 7.7 (s, 1H, ArH), 8.1 (s, 1H, ArH). ^{13}C NMR (62 MHz, $CDCl_3$): δ = 19.1 ($2CH_3$), 19.2 ($2CH_3$), 21.5 (CH_3), 27.7, 27.8 (CH), 30.9 (NCH_3), 71.6, 71.9 (CH_2O), 111.0, 121.2 (CH), 126.3, 127.0, 127.1 (C), 129.3 (2CH), 129.5 (2CH), 137.5, 140.7, 144.0, 157.1 (C), 168.1, 168.3 (CO). IR (KBr, cm^{-1}): ν = 2957, 2927 (m), 2872 (w), 1716 (s), 1603, 1511, 1465, 1376, 1327 (m), 1246, 1175, 1100, 1032, 1017 (s), 985, 823, 783, 731 (m). GC-MS (EI, 70 eV): *m/z* (%) = 422(27) $[M]^+$, 310(30), 293(100), 265(11). HRMS (EI, 70 eV): *m/z* calcd for $C_{25}H_{30}N_2O_4$ $[M]^+$: 422.22001; found: 422.22021.

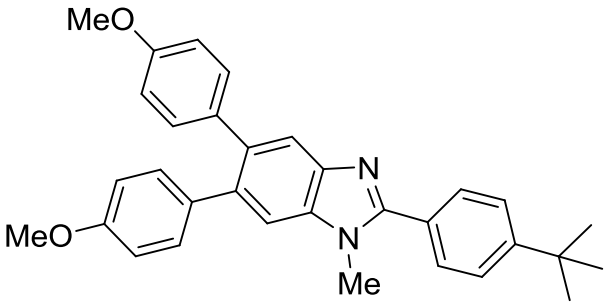
Dibutyl-1-methyl-2-*p*-tolyl-1*H*-benzo[*d*]imidazole-5,6-dicarboxylate (44i):



Compound **44i** was prepared starting with **43i** (100 mg, 0.24 mmol), following the general procedure E, as a yellow solid (80 mg, 81%), mp. 88-90 °C. ^{1}H NMR (300 MHz, $CDCl_3$): δ = 0.88 (t, 6H, *J* = 7.4 Hz, $2CH_3$), 1.31-1.45 (m, 4H, $2CH_2$), 1.61-1.71 (m, 4H, $2CH_2$), 2.35 (s, 3H, CH_3), 3.80 (s, 3H, NCH_3), 4.25 (t, 4H, *J* = 6.7 Hz, $2CH_2O$), 7.24 (d, 2H, *J* = 8.1 Hz, ArH), 7.57 (d, 2H, *J* = 8.1 Hz, ArH), 7.66 (s, 1H, ArH), 8.07 (s, 1H, ArH). ^{13}C NMR (62 MHz, $CDCl_3$): δ = 13.7 ($2CH_3$), 19.1, 19.2 (CH_2), 21.4 (CH_3), 30.5, 30.6 (CH_2), 32.1 (NCH_3), 65.3, 65.6 (CH_2O), 111.1, 121.0 (CH), 126.3,

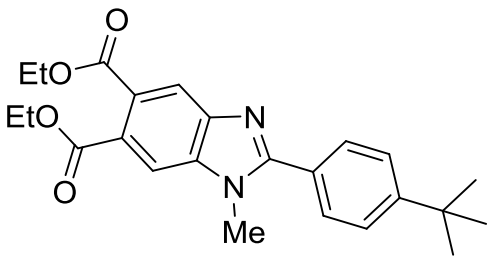
127.0, 127.1 (C), 129.3 (2CH), 129.5 (2CH), 137.5, 140.7, 144.0, 157.1 (C), 168.1, 168.3 (CO). IR (KBr, cm^{-1}): ν = 2957 (m), 2933, 2872 (w), 1715, 1700 (s), 1614, 1479, 1464, 1441, 1391, 1380, 1357 (m), 1329, 1275, 1257, 1239, 1219, 1209, 1197, 1122, 1098 (s), 1061, 1037, 1018, 963, , 902, 887, 832, 822, 783, 730 (m), 703, 673, 602, 586, 552 (w). GC-MS (EI, 70 eV): *m/z* (%) = 422(31) $[M]^+$, 310(13), 294(19), 295(100), 292(14). HRMS (EI, 70 eV): *m/z* calcd for $C_{25}H_{30}N_2O_4$ $[M]^+$: 422.22001; found: 422.22049. Anal. calcd for $C_{25}H_{30}N_2O_4$: C, 71.07; H, 7.16; N, 6.63. Found: C, 70.42; H, 7.25; N, 6.26.

2-(4-*tert*-Butylphenyl)-5,6-bis(4-methoxyphenyl)-1-methyl-1*H*-benzo[*d*]imidazole (44k):



Compound **44k** was prepared starting with **43k** (100 mg, 0.21 mmol), following the general procedure E, as a yellow solid (64 mg, 65%), mp. 190-192 °C. ^{1}H NMR (300 MHz, $CDCl_3$): δ = 1.30 (s, 9H, $3CH_3$), 3.70 (s, 3H, OCH_3), 3.71 (s, 3H, OCH_3), 3.81 (s, 3H, NCH_3), 6.69 (d, 2H, *J* = 8.7 Hz, ArH), 6.70 (d, 2H, *J* = 8.7 Hz, ArH), 7.03 (d, 2H, *J* = 8.6 Hz, ArH), 7.04 (d, 2H, *J* = 8.6 Hz, ArH), 7.28 (s, 1H, ArH), 7.47 (d, 2H, *J* = 8.5 Hz, ArH), 7.65 (d, 2H, *J* = 8.4 Hz, ArH), 7.74 (s, 1H, ArH). ^{13}C NMR (62 MHz, $CDCl_3$): δ = 31.2 ($3CH_3$), 31.8 (NCH_3), 34.9 (C), 55.1, 55.2 (OCH_3), 111.1 (CH), 113.2 (2CH), 113.3 (2CH), 121.1 (CH), 125.7 (2CH), 127.3 (C), 129.1 (2CH), 131.2 (2CH), 131.3 (2CH), 134.8, 134.9, 135.5, 135.8, 136.1, 142.4, 153.0, 154.7, 158.0, 158.1 (C). IR (KBr, cm^{-1}): ν = 2952, 2961, 2833, 1607, 1556 (w), 1513, 1462, 1456, 1435 (m), 1404, 1380, 1361, 1287, 1266 (w), 1243, 1172 (m), 1110 (w), 1041, 1032, 1023, 1014 (w), 829 (s), 807 (m), 776, 730, 713, 699, 655, 646, 626 (w), 577, 547, 535 (m). GC-MS (EI, 70 eV): *m/z* (%) = 476(100) $[M]^+$, 461(14), 365(31), 185(15), 183(20), 44(30), 43(13). HRMS (ESI): calcd for $C_{32}H_{33}N_2O_2$ $[M+H]^+$: 477.2537; found: 477.2540.

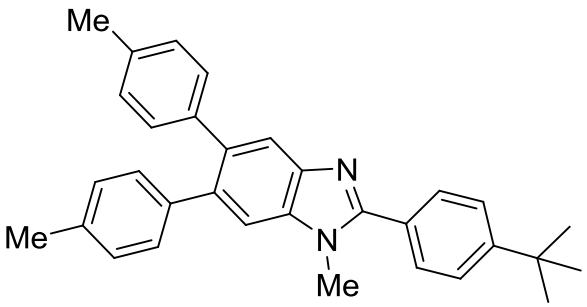
Diethyl-2-(4-*tert*-butylphenyl)-1-methyl-1*H*-benzo[*d*]imidazole-5,6-dicarboxylate (44l):



Compound **44l** was prepared starting with **43l** (100 mg, 0.24 mmol), following the general procedure E, as a brown oil (92 mg, 93%). ^{1}H NMR (250 MHz, $CDCl_3$): δ = 1.29 (s, 9H, $3CH_3$), 1.30 (t, 6H, *J* = 7.2 Hz, $2CH_3$), 3.83 (s, 3H, NCH_3), 4.31 (q, 2H, *J* = 7.1

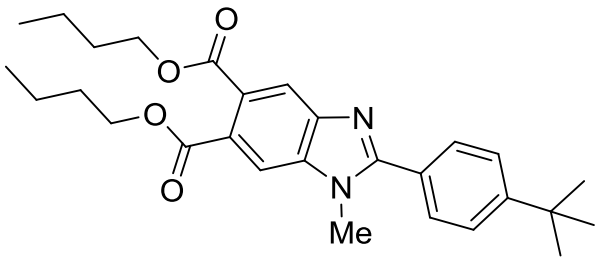
Hz, CH_2O), .432 (q, 2H, J = 7.1 Hz, CH_2O), 7.48 (d, 2H, J = 8.5 Hz, ArH), 7.63 (d, 2H, J = 8.4 Hz, ArH), 7.69 (s, 1H, ArH), 8.07 (s, 1H, ArH). ^{13}C NMR (62 MHz, $CDCl_3$): δ = 14.1 ($2CH_3$), 31.2 ($3CH_3$), 32.1 (NCH_3), 34.9 (C), 61.4, 61.6 (CH_2O), 111.1, 121.0 (CH), 125.8 (2CH), 126.3, 126.8, 127.1 (C), 129.2 (2CH), 137.5, 144.1, 153.8, 157.1 (C), 168.1, 168.2 (CO). IR (KBr, cm^{-1}): ν = 2956 (m), 2903, 2867 (w), 1712 (s), 1614 (m), 1578 (w), 1475, 1463, 1443, 1391, 1367 (m), 1326, 1266, 1246, 1219, 1200 (s), 1172 (m), 1116, 1098, 1039, 1014 (s), 893, 843, 823, 784, 728, 711 (m), 676, 640, 613, 590, 558 (w). GC-MS (EI, 70 eV): *m/z* (%) = 408(100) $[M]^+$, 394(13), 393(49), 363(13), 336(15), 335(62), 248(11), 146(15). HRMS (EI, 70 eV): *m/z* calcd for $C_{24}H_{28}N_2O_4$ $[M]^+$: 408.20436; found: 408.20359.

2-(4-*tert*-Butylphenyl)-1-methyl-5,6-di-*p*-tolyl-1*H*-benzo[*d*]imidazole (44m):



Compound **44m** was prepared starting with **43m** (100 mg, 0.22 mmol), following the general procedure E, as a brown oil (76 mg, 77%). ^{1}H NMR (300 MHz, $CDCl_3$): δ = 1.29 (s, 9H, $3CH_3$), 2.22 (s, 3H, CH_3), 2.23 (s, 3H, CH_3), 3.79 (s, 3H, NCH_3), 6.92-6.97 (m, 4H, ArH), 7.01(d, 4H, J = 7.9 Hz, ArH), 7.28 (s, 1H, ArH), 7.46 (d, 2H, J = 8.4 Hz, ArH), 7.64 (d, 2H, J = 8.4 Hz, ArH), 7.75 (s, 1H, ArH). ^{13}C NMR (62 MHz, $CDCl_3$): δ = 21.1 ($2CH_3$), 31.2 ($3CH_3$), 31.8 (NCH_3), 34.9 (C), 111.3, 121.3 (CH), 125.7 (2CH), 127.3 (C), 128.5 (2CH), 128.6 (2CH), 129.1 (2CH), 130.1 (2CH), 130.2 (2CH), 135.5, 135.7, 135.9 (C), 136.2 (2C), 139.4, 139.6, 142.5, 153.1, 154.7 (C). IR (KBr, cm^{-1}): ν = 2957, 2928 (m), 2871 (w), 1716 (s), 1598 (w), 1495, 1455, 1300 (m), 1283, 1283, 1238, 1177, 1117, 1091 (s), 1060, 1018, 961, 941, 898, 819, 778, 695 (m), 633, 635, 577 (w). MS (EI, 70 eV): *m/z* (%) = 444(100) $[M]^+$, 429(20), 91(19). HRMS (EI, 70 eV): calcd for $C_{32}H_{32}N_2$ $[M]^+$: 444.25600; found: 444.25609.

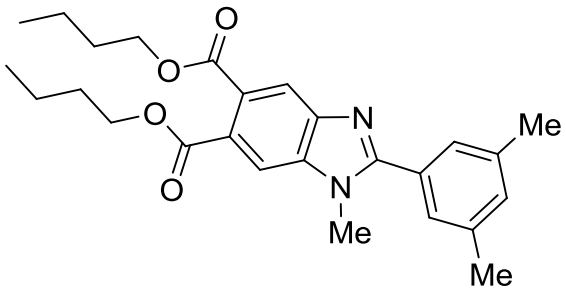
Dibutyl-2-(4-*tert*-butylphenyl)-1-methyl-1*H*-benzo[*d*]imidazole-5,6-dicarboxylate (44o):



Compound **44o** was prepared starting with **43o** (100 mg, 0.21 mmol), following the general procedure E, as colorless oil (84 mg, 85%). ^{1}H NMR (300 MHz, $CDCl_3$): δ = 0.89 (t, 6H, J = 7.3 Hz, $2CH_3$), 1.29 (s, 9H,

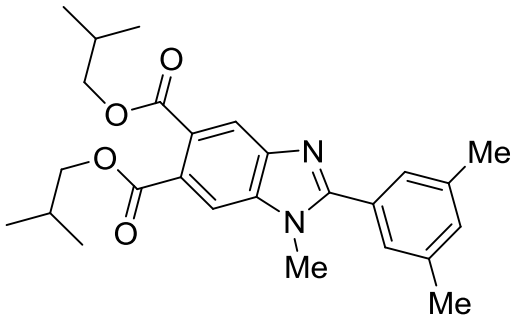
$3CH_3$), 1.33-1.42 (m, 4H, $2CH_2$), 1.61-1.71 (m, 4H, $2CH_2$), 3.83 (s, 3H, NCH_3), 4.25 (t, 4H, J = 6.7 Hz, $2CH_2O$), 7.47 (d, 2H, J = 8.3 Hz, ArH), 7.63 (d, 2H, J = 8.3 Hz, ArH), 7.67 (s, 1H, ArH), 8.07 (s, 1H, ArH). ^{13}C NMR (62 MHz, $CDCl_3$): δ = 13.7 ($2CH_3$), 19.1, 19.2 (CH_2), 30.5, 30.6 (CH_2), 31.2 ($3CH_3$), 32.1 (NCH_3), 34.9 (C), 65.3, 65.6 (CH_2O), 111.1, 121.0 (CH), 125.8 (2CH), 126.3, 127.0, 127.1 (C), 129.2 (2CH), 137.5, 144.0, 153.8, 157.1 (C), 168.1, 168.3 (CO). IR (KBr, cm^{-1}): ν = 2956 (m), 2934, 2870 (w), 1713 (s), 1616, 1578, 1555 (w), 1463, 1435, 1386, 1359 (m), 1326, 1267, 1244, 1218, 1220, 1117, 1098 (s), 1060, 1033, 1013 (w), 961, 943, 893 (w), 840, 784 (m), 752, 711, 614, 560 (w). MS (EI, 70 eV): *m/z* (%) = 464(45) $[M]^+$, 408(13), 352(11), 337 (13), 336(21), 335(100), 334(18), 319(21), 248(13), 247(12). HRMS (ESI): calcd for $C_{28}H_{37}N_2O_4$ $[M+H]^+$: 465.2748; found: 465.2750. Anal. calcd for $C_{28}H_{36}N_2O_4$: C, 72.39; H, 7.81; N, 6.03. Found: C, 72.45; H, 7.80; N, 5.45.

Dibutyl-2-(3,5-dimethylphenyl)-1-methyl-1*H*-benzo[*d*]imidazole-5,6-dicarboxylate (44p):



Compound **44p** was prepared starting with **43p** (100 mg, 0.23 mmol), following the general procedure E, as whitish solid (89 mg, 90%), mp. 80-81 °C. ^{1}H NMR (250 MHz, $CDCl_3$): δ = 0.89 (t, 6H, J = 7.3 Hz, $2CH_3$), 1.33-1.47 (m, 4H, $2CH_2$), 1.61-1.72 (m, 4H, $2CH_2$), 2.32 (s, 6H, $2CH_3$), 3.82 (s, 3H, NCH_3), 4.25 (t, 4H, J = 6.6 Hz, $2CH_2O$), 7.08 (s, 1H, ArH), 7.29 (s, 2H, ArH), 7.67 (s, 1H, ArH), 8.07 (s, 1H, ArH). ^{13}C NMR (62 MHz, $CDCl_3$): δ = 13.7 ($2CH_3$), 19.1, 19.2 (CH_2), 21.3 ($2CH_3$), 30.5, 30.6 (CH_2), 32.1 (NCH_3), 65.3, 65.6 (CH_2O), 111.1, 121.1 (CH), 127.1 (C), 127.1 (2CH), 129.0 (C), 132.0 (CH), 137.5 (C), 138.5 (3C), 144.0, 157.3 (C), 168.1, 168.3 (CO). IR (KBr, cm^{-1}): ν = 2954, 2931, 2871 (m), 1710 (s), 1619, 1602, 1577, 1504 (w), 1467, 1457, 1442, 1394, 1359, 1331 (m), 1265, 1249, 1237, 1224 (s), 1108, 1061, 1037 (m), 1018, 946, 906 (w), 888, 850, 784, 728 (m), 688, 658, 591 (w). GC-MS (EI, 70 eV): *m/z* (%) = 436(32) $[M]^+$, 324(13), 308(20), 307(100), 306(13). HRMS (EI, 70 eV): *m/z* calcd for $C_{26}H_{32}N_2O_4$ $[M]^+$: 436.23566; found: 436.23489. Anal. calcd for $C_{26}H_{32}N_2O_4$: C, 71.53; H, 7.39; N, 6.42. Found: C, 71.01; H, 7.51; N, 5.73.

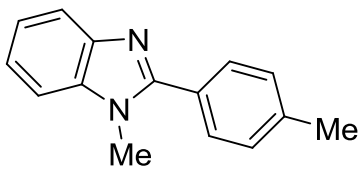
Diisobutyl-2-(3,5-dimethylphenyl)-1-methyl-1*H*-benzo[*d*]imidazole-5,6-dicarboxylate (44r):



Compound **44r** was prepared starting with **43r** (100 mg, 0.23 mmol), following the general procedure E, as whistish solid (82 mg, 83%), mp. 100-101 °C. ^{1}H NMR (300 MHz, $CDCl_3$): δ = 0.92 (d, 6H, J = 6.7 Hz, $2CH_3$), 0.93 (d, 6H, J = 6.7 Hz, $2CH_3$), 1.92-2.05 (m, 2H, 2CH), 2.32 (s, 6H, $2CH_3$), 3.83 (s, 3H, NCH_3), 4.03 (d, 4H, J = 6.2 Hz, $2CH_2O$), 7.09 (s, 1H, ArH), 7.30 (s, 2H, ArH), 7.68 (s, 1H, ArH), 8.1 (s, 1H, ArH). ^{13}C NMR (62 MHz, $CDCl_3$): δ = 19.1 ($2CH_3$), 19.2 ($2CH_3$), 21.3 ($2CH_3$), 27.7, 27.8 (CH), 32.1 (NCH_3), 71.6, 71.9 (CH_2O), 110.1, 121.1 (CH), 127.0 (C), 127.1 (2CH), 127.3, 129.0 (C), 132.1 (CH), 137.5 (C), 138.5 (2C), 143.9, 157.3 (C), 167.9, 168.4 (CO). IR (KBr, cm^{-1}): v = 2960 (m), 2916, 2873 (w), 1712 (s), 1621, 1604, 1578, 1516, 1483 (w), 1468, 1392, 1371, 1321 (m), 1256, 1200 (s), 1134, 1120 (m), 1100, 1093, 1034 (s), 982, 947, 927, 900, 853, 786, 774, 728, 696 (m), 681, 645, 620, 529 (w). MS (EI, 70 eV): *m/z* (%) = 436(71) $[M]^+$, 380(27), 325(15), 324(76), 323(18), 308(40), 307(100), 280(13), 279(24), 263(12), 57(14). HRMS (ESI): calcd for $C_{26}H_{33}N_2O_4$ $[M+H]^+$: 437.2435; found: 437.2435. Anal. calcd for $C_{26}H_{32}N_2O_4$: C, 71.53; H, 7.39; N, 6.42. Found: C, 71.33; H, 7.56; N, 5.76.

Synthesis of Benzimidazol (45):

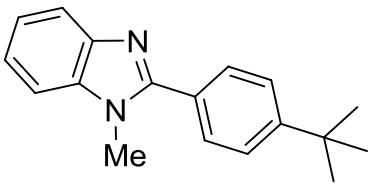
1-Methyl-2-*p*-tolyl-1*H*-benzo[*d*]imidazole (45j):



Compound **45j** was prepared starting with **43j** (100 mg, 0.24 mmol), following the general procedure E, as a brown solid (42 mg, 82%), mp. 108-110 °C. ^{1}H NMR (300 MHz, $CDCl_3$): δ = 2.37 (s, 3H, CH_3), 3.79 (s, 3H, NCH_3), 7.22-7.27 (m, 4H, ArH), 7.29-7.34 (m, 1H, ArH), 7.59 (dd, 2H, J = 1.7, 6.5 Hz, ArH), 7.73-7.79 (m, 1H, ArH). ^{13}C NMR (62 MHz, $CDCl_3$): δ = 21.4 (CH_3), 31.7 (NCH_3), 109.6, 119.6, 122.5, 122.7 (CH), 126.9 (C), 129.3 (2CH), 129.4 (2CH), 136.4, 140.0, 142.4, 153.8 (C). IR (KBr, cm^{-1}): v = 3039, 2923, 2855, 1481 (w), 1453, 1437, 1322, 1288, 1248 (m), 1181, 1097, 1052, 1018, 899 (w), 819 (m), 747 (s), 729 (m), 640, 590, 570, 528 (w). GC-MS (EI, 70 eV): *m/z* (%) =

222(72) $[M]^+$, 221(100) 206(11). HRMS (EI, 70 eV): *m/z* calcd for $C_{15}H_{14}N_2$ $[M]^+$: 222.11570; found: 222.11534.

2-(4-*tert*-Butylphenyl)-1-methyl-1*H*-benzo[*d*]imidazole (45n):

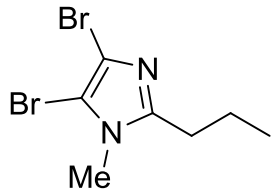


Compound **45n** was prepared starting with **43n** (100 mg, 0.21 mmol), following the general procedure E, as a brown semi solid (36 mg, 65%). ^{1}H NMR (250 MHz, $CDCl_3$): δ = 1.30 (s, 9H, $3CH_3$), 3.81 (s, 3H, NCH_3), 7.22-7.34 (m, 3H, ArH), 7.47 (d, 2H, J = 8.4 Hz, ArH), 7.64 (d, 2H, J = 8.4 Hz, ArH), 7.72-7.78 (m, 1H, ArH). ^{13}C NMR (62 MHz, $CDCl_3$): δ = 30.2 ($3CH_3$), 30.7 (NCH_3), 33.8 (C), 108.5, 118.6, 121.4, 121.7 (CH), 124.6 (2CH), 126.0 (C), 128.2 (2CH), 135.5, 141.7, 152.1, 152.8 (C). IR (KBr, cm^{-1}): ν = 2955 (w), 2922 (m), 2854, 1487 (w), 1467, 1458, 1434, 1408, 1379, 1324, 1247, 1112, 1005, 836, 817, 743 (m), 731 (s), 723, 598, 544 (m). GC-MS (EI, 70 eV): *m/z* (%) = 264(64) $[M]^+$, 263(19), 250(19), 249(100). HRMS (EI, 70 eV): *m/z* calcd for $C_{18}H_{20}N_2$ $[M]^+$: 264.16210; found: 264.16199.

General procedure for 2-alkenyl-4,5-dibromo-*N*-methylimidazol (46):

To a THF solution (15 mL) of *n*BuLi (2.5 M in *n*-hexane, 0.5 mL, 1.2 mmol) was added and tribromo-*N*-methylimidazol (**38**) (0.319 g, 1.0 mmol) at -78 °C under Argon atmosphere and the mixture was stirred for 1 h. To the stirred solution were added (2.0 mmol) of 1-iodoalkane. After stirring for 16 h, a saturated aqueous solution of Na_2SO_4 (10 mL) was added to the solution. The aqueous and the organic layer were separated. The organic layer was dried (Na_2SO_4), filtered and concentrated *in vacuo*. The residue was purified by flash column chromatography (fine flash silica gel, *n*-heptane).

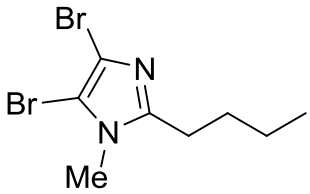
4,5-Dibromo-1-methyl-2-propyl-1*H*-imidazole (46a):



Compound **46b** was prepared starting with **38** (319 mg, 1.0 mmol), nBuLi (0.5mL , 1.2 mmol)and 1-Iodopropane (0.19 mL, 2.0 mmol), as a brown oil (220 mg, 78 %). ^{1}H NMR (300 MHz, $CDCl_3$): δ = 0.92 (t, 3H, J = 7.4 Hz, CH_3), 1.60-1.73 (m, 2H, CH_2), 2.60 (t, 2H, J = 7.8 Hz, CH_2), 3.46 (s, 3H, NCH_3). ^{13}C NMR (75 MHz, $CDCl_3$): δ = 13.8 (CH_3), 21.0, 29.9 (CH_2), 32.6 (NCH_3), 103.0, 114.9 (CBr), 149.4 (C). IR (KBr, cm^{-1}): ν =

2962, 2932 (m), 2872 (w), 1501, 1451, 1432, 1400, 1382 (m), 1351, 1277 (w), 1223 (s), 1098, 1079 (m), 972 (s), 908, 812 (w), 750, 666 (m), 566 (w). GC-MS (EI, 70 eV): *m/z* (%) = 284(16) [M^+ (^{81}Br, ^{81}Br)], 282(28) [M^+ (Br, ^{81}Br)], 280(15) [M^+ (Br, Br)], 267(16), 256(49), 254(100), 251(25), 212(13), 134(16), 132(20), 122(15), 120(14). HRMS (ESI): *m/z* calcd for $C_7H_{11}Br_2N_2$ $[M+H]^+$: 282.92632; found: 282.92588.

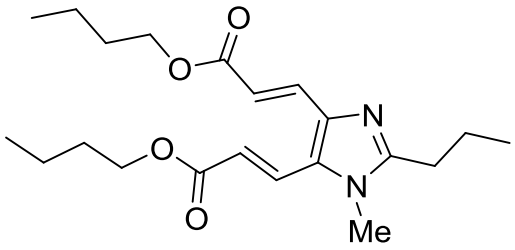
4,5-Dibromo-2-butyl-1-methyl-1*H*-imidazole (46b):



Compound **46b** was prepared starting with **38** (319 mg, 1.0 mmol), nBuLi (0.5 mL , 1.1 mmol)and 1-Iodobutane (0.23 mL, 2.0 mmol), as a brown oil (263 mg, 89 %). ^{1}H NMR (300 MHz, $CDCl_3$): δ = 0.87 (t, 3H, *J* = 7.3 Hz, CH_3), 1.26-1.39 (m, 2H, CH_2), 1.56-1.67 (m, 2H, CH_2), 2.60 (t, 2H, *J* = 7.8 Hz, CH_2), 3.47 (s, 3H, NCH_3). ^{13}C NMR (75 MHz, $CDCl_3$): δ = 13.7 (CH_3), 22.3, 27.7, 29.6 (CH_2), 32.5 (NCH_3), 102.9, 114.9 (CBr), 149.5 (C). IR (KBr, cm^{-1}): ν = 2954, 2929 (m), 2869 (w), 1505, 1452, 1399 (m), 1378, 1324, 1282 (w), 1226 (s), 1077 (m), 971 (s), 932, 809, 730, 715, 666, 644, 572 (w). GC-MS (EI, 70 eV): *m/z* (%) = 298(08) [M^+ (^{81}Br, ^{81}Br)], 296(19) [M^+ (Br, ^{81}Br)], 294(09) [M^+ (Br, Br)], 267(18), 265(10), 254(100), 252(51), 134(11), 132(12). HRMS: *m/z* calcd for $C_8H_{12}Br_2N_2$ [M^+ (Br, ^{81}Br)]$^+$: 295.93413; found: 295.93371.

Synthesis of tri(alkenyl)imidazol (47):

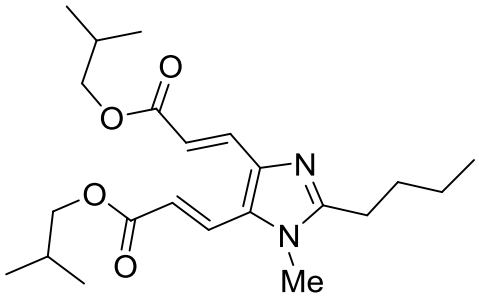
(2*E*,2'*E*)-Dibutyl-3,3'-(1-methyl-2-propyl-1*H*-imidazole-4,5-diyl)diacrylate (47a):



Product **47a** was prepared starting with **46a** (282 mg, 1.0 mmol), *n*-butyl acrylate (0.36 mL, 2.5 mmol), $Pd(OAc)_2$ (11 mg, 5 mol %), $P(Cy)_3$ (10 mol %), NEt_3 (1.10 mL, 8.0 mmol), DMF (5 mL) at 100 °C for 24 h following general procedure D, as a brown oil (343 mg, 91%). ^{1}H NMR (300 MHz, $CDCl_3$): δ = 0.88 (t, 3H, *J* = 7.3 Hz, CH_3), 0.89 (t, 3H, *J* = 7.3 Hz, CH_3), 0.95 (t, 3H, *J* = 7.4 Hz, CH_3), 1.31-1.43 (m, 4H, $2CH_2$), 1.57-1.77 (m, 6H, $3CH_2$), 2.62 (t, 2H, *J* = 7.4 Hz, CH_2), 3.55 (s, 3H, NCH_3), 4.12 (t, 2H, *J* = 6.6 Hz, CH_2O), 4.15 (t, 2H, *J* = 6.7 Hz, CH_2O), 6.15 (d, 1H, *J* = 16.2 Hz, CH), 6.67 (d, 1H, *J* = 15.3 Hz, CH), 7.56 (d, 1H, *J* = 16.1 Hz, CH), 7.63 (d, 1H, *J* = 15.3 Hz, CH). ^{13}C NMR (75 MHz, $CDCl_3$): δ = 12.7 ($2CH_3$), 12.9 (CH_3), 18.2 ($2CH_2$), 20.1, 28.2, 29.7, 29.8 (CH_2), 30.7

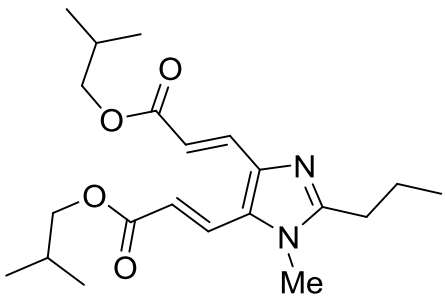
(NCH_3), 63.2, 63.7 (OCH_2), 117.8, 117.9 (CH), 127.9 (C), 128.1, 132.6 (CH), 137.8, 151.9 (C), 165.7, 166.6 (CO). IR (KBr, cm^{-1}): ν = 2956, 2931, 2872 (w), 1703 (s), 1624 (m), 1514 (w), 1459 (m), 1392, 1379, 1343 (w), 1294, 1275, 1257 (m), 1148 (s), 1062, 1022, 968 (m), 865, 849, 735, 701 (w). GC-MS (EI, 70 eV): *m/z* (%) = 376(32) $[M]^+$, 303(19), 275(21), 219(44), 203(29), 201(22), 176(11), 175(100), 174(11), 146(13), 145(13). HRMS (ESI): *m/z* calcd for $C_{21}H_{33}O_4N_2$ $[M+H]^+$: 377.24348; found: 377.24365.

(2*E*,2'*E*)-Isobutyl-3,3'-(2-butyl-1-methyl-1*H*-imidazole-4,5-diyl)diacrylate (47b):



Product **47b** was prepared starting with **46b** (296 mg, 1.0 mmol), *iso*-butyl acrylate (0.36 mL, 2.5 mmol), $Pd(OAc)_2$ (11 mg, 5 mol %), $P(Cy)_3$ (10 mol %), NEt_3 (1.10 mL, 8.0 mmol), DMF (5 mL) at 100 °C for 24 h following general procedure D, as a brown oil (331 mg, 85%). ^{1}H NMR (250 MHz, $CDCl_3$): δ = 0.85-0.92 (m, 15H, $5CH_3$), 1.29-1.44 (m, 2H, CH_2), 1.59-1.71 (m, 2H, CH_2), 1.83-1.99 (m, 2H, 2CH), 2.64 (t, 2H, J = 7.5 Hz, CH_2), 3.55 (s, 3H, NCH_3), 3.90 (d, 2H, J = 6.8 Hz, CH_2O), 3.92 (d, 2H, J = 6.9 Hz, CH_2O), 6.16 (d, 1H, J = 16.2 Hz, CH), 6.69 (d, 1H, J = 15.4 Hz, CH), 7.57 (d, 1H, J = 16.1 Hz, CH), 7.65 (d, 1H, J = 15.3 Hz, CH). ^{13}C NMR (62 MHz, $CDCl_3$): δ = 13.7 (CH_3), 19.0 ($2CH_3$), 19.1 ($2CH_3$), 22.5, 27.1 (CH_2), 27.7, 27.8 (CH), 29.8 (CH_2), 31.7 (NCH_3), 70.4, 70.9 (OCH_2), 118.7 (2CH), 128.9 (C), 129.1, 133.6 (CH) 138.8, 153.0 (C), 166.7, 166.5 (CO). IR (KBr, cm^{-1}): ν = 2960, 2929, 2873 (w), 1710 (s), 1626, 1460 (m), 1395, 1369, 1342 (w), 1276, 1245 (m), 1145 (s), 1011, 967 (m), 895, 702 (w). GC-MS (EI, 70 eV): *m/z* (%) = 390(44) $[M]^+$, 361(15), 348(94), 317(41), 289(21), 274(13), 233(49), 217(39), 215(22), 189(100), 173(21), 159(13), 145(20), 131(11), 57(13), 41(15). HRMS (EI, 70 eV): *m/z* calcd for $C_{22}H_{34}N_2O_4$ $[M]^+$: 390.25131; found: 390.25087.

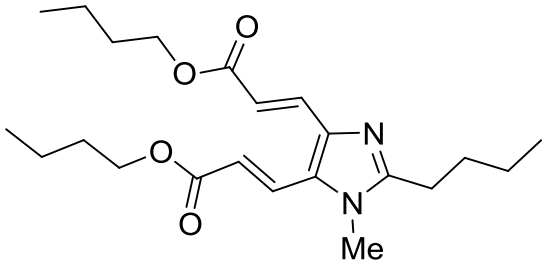
(2*E*,2'*E*)-Isobutyl-3,3'-(1-methyl-2-propyl-1*H*-imidazole-4,5-diyl)diacrylate (47c):



Product **47c** was prepared starting with **46a** (282 mg, 1.0 mmol), *iso*-butyl acrylate (0.36 mL, 2.5 mmol), $Pd(OAc)_2$ (11 mg, 5 mol %), $P(Cy)_3$ (10 mol %), NEt_3 (1.10 mL, 8.0 mmol), DMF (5 mL) at 100 °C for 24 h following general procedure D, as a brown oil (335 mg, 89%). ^{1}H NMR (250 MHz, $CDCl_3$): δ = 0.89 (d,

6H, J = 6.6 Hz, $2CH_3$), 0.91 (d, 6H, J = 6.8 Hz, $2CH_3$), 0.96 (t, 3H, J = 7.2 Hz, CH_3), 1.64-1.76 (m, 2H, CH_2), 1.84-1.99 (m, 2H, 2CH), 2.63 (t, 2H, J = 7.6 Hz, CH_2), 3.55 (s, 3H, NCH_3), 3.90 (d, 2H, J = 6.8 Hz, CH_2O), 3.93 (d, 2H, J = 7.0 Hz, CH_2O), 6.16 (d, 1H, J = 16.2 Hz, CH), 6.69 (d, 1H, J = 15.3 Hz, CH), 7.57 (d, 1H, J = 16.6 Hz, CH), 7.65 (d, 1H, J = 15.4 Hz, CH). ^{13}C NMR (62 MHz, $CDCl_3$): δ = 12.9 (CH_3), 18.1 ($2CH_3$), 18.2 ($2CH_3$), 20.2 (CH_2), 26.7, 26.8 (CH), 28.3 (CH_2), 30.7 (NCH_3), 69.4, 70.0 (OCH_2), 117.8 (2CH), 127.9 (C), 128.1, 132.6 (CH), 137.8, 151.9 (C), 165.7, 166.5 (CO). IR (KBr, cm^{-1}): v = 2958, 2928, 2872 (w), 1705 (s), 1625, 1461 (m), 1394, 1369, 1342 (w), 1276, 1242 (m), 1148 (s), 1010, 967 (m), 895, 702, 533 (w). GC-MS (EI, 70 eV): *m/z* (%) = 376(29) $[M]^+$, 303(25), 275(20), 219(41), 203(29), 201(18), 175(100), 174(12), 146(15), 145(11), 57(13), 41(10). HRMS (ESI): *m/z* calcd for $C_{21}H_{33}N_2O_4$ $[M+H]^+$: 377.24348; found: 377.24422.

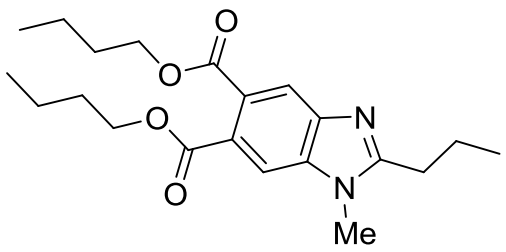
(2*E*,2'*E*)-Dibutyl-3,3'-(2-butyl-1-methyl-1*H*-imidazole-4,5-diyl)diacrylate (47d):



Product **47d** was prepared starting with **46b** (296 mg, 1.0 mmol), *n*-butyl acrylate (0.36 mL, 2.5 mmol), $Pd(OAc)_2$ (11 mg, 5 mol %), $P(Cy)_3$ (10 mol %), NEt_3 (1.10 mL, 8.0 mmol), DMF (5 mL) at 100 °C for 24 h following general procedure D, as a brown oil (319 mg, 82%). ^{1}H NMR (300 MHz, $CDCl_3$): δ = 0.87 (t, 3H, J = 7.3 Hz, CH_3), 0.88 (t, 3H, J = 7.3 Hz, CH_3), 0.89 (t, 3H, J = 7.3 Hz, CH_3), 1.30-1.40 (m, 6H, $3CH_2$), 1.54-1.68 (m, 6H, $3CH_2$), 2.63 (t, 2H, J = 7.5 Hz, CH_2), 3.54 (s, 3H, NCH_3), 4.12 (t, 2H, J = 6.6 Hz, CH_2O), 4.15 (t, 2H, J = 6.7 Hz, CH_2O), 6.14 (d, 1H, J = 16.1 Hz, CH), 6.67 (d, 1H, J = 15.3 Hz, CH), 7.55 (d, 1H, J = 16.1 Hz, CH), 7.63 (d, 1H, J = 15.3 Hz, CH). ^{13}C NMR (62 MHz, $CDCl_3$): δ = 13.6 ($2CH_3$), 13.7 (CH_3), 19.1 ($2CH_2$), 22.5, 27.1, 29.7, 30.7, 30.8 (CH_2), 31.7 (NCH_3), 64.1, 64.7 (OCH_2), 118.7, 118.8 (CH), 128.9 (C), 129.1, 133.6 (CH), 138.8, 153.0 (C), 166.7, 167.5 (CO). IR (KBr, cm^{-1}): v = 2956, 2931, 2872 (w), 1703 (s), 1624 (m), 1514 (w), 1459 (m), 1392, 1379, 1343 (w), 1294, 1275, 1257 (m), 1148 (s), 1062, 1022, 968 (m), 865, 849, 735, 701 (w). GC-MS (EI, 70 eV): *m/z* (%) = 390(43) $[M]^+$, 361(15), 359(14), 349(13), 348(64), 347(21), 346(77), 317(27), 289(24), 259(24), 246(11), 233(53), 217(31), 215(23), 190(18), 189(100), 187(10), 174(12), 173(19), 159(12), 146(22), 145(20), 131(11), 57(11), 41(17). HRMS (EI, 70 eV): *m/z* calcd for $C_{22}H_{34}N_2O_4$ $[M]^+$: 390.25131; found: 390.25143.

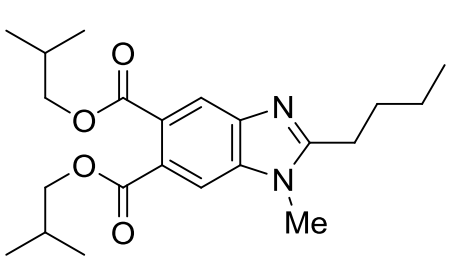
Synthesis of Benzimidazol (48):

Dibutyl-1-methyl-2-propyl-1*H*-benzo[*d*]imidazole-5,6-dicarboxylate (48a):



Compound **48a** was prepared starting with **47a** (100 mg, 0.26 mmol), following the general procedure E, as a brown oil (80 mg, 81%). ^{1}H NMR (300 MHz, $CDCl_3$): δ = 0.89 (t, 6H, J = 7.3 Hz, $2CH_3$), 1.00 (t, 3H, J = 7.1 Hz, CH_3), 1.33-1.42 (m, 4H, $2CH_2$), 1.61-1.71 (m, 4H, $2CH_2$), 1.82-1.90 (m, 2H, CH), 2.86 (t, 2H, J = 7.4 Hz, CH_2), 3.72 (s, 3H, NCH_3), 4.24 (t, 2H, J = 6.6 Hz, CH_2O), 4.25 (t, 2H, J = 6.7 Hz, CH_2O), 7.61 (s, 1H, ArH), 8.03 (s, 1H, ArH). ^{13}C NMR (62 MHz, $CDCl_3$): δ = 12.7 ($2CH_3$), 12.9 (CH_3), 18.2 ($2CH_2$), 19.8, 28.7 (CH_2), 29.5 (NCH_3), 29.5, 29.6 (CH_2), 64.4, 64.7 (CH_2O), 109.6, 119.2 (CH), 126.0, 126.1, 135.4, 141.5, 157.6 (C), 166.9, 167.3 (CO). IR (KBr, cm^{-1}): ν = 2958, 2929 (m), 2872 (w), 1714 (s), 1620, 1579, 1510 (w), 1455, 1388, 1359, 1330 (m), 1252, 1205, 1009 (s), 1060, 1032, 961, 943, 894, 784, 746 (m), 682, 613, 543 (w). GC-MS (EI, 70 eV): *m/z* (%) = 374(08) $[M]^+$, 347(22), 346(100), 290(23), 245(63). HRMS (ESI): *m/z* calcd for $C_{21}H_{31}N_2O_4$ $[M+H]^+$: 375.22783; found: 375.22849.

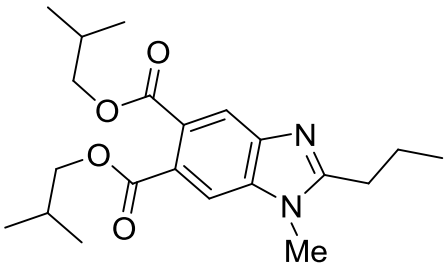
Diisobutyl-2-butyl-1-methyl-1*H*-benzo[*d*]imidazole-5,6-dicarboxylate (48b):



Compound **48b** was prepared starting with **47b** (100 mg, 0.29 mmol), following the general procedure E, as a brown solid (68 mg, 69%), mp.= 96-98 °C. ^{1}H NMR (300 MHz, $CDCl_3$): δ = 0.91 (t, 3H, J = 7.4 Hz, CH_3), 0.92 (d, 6H, J = 6.7 Hz, $2CH_3$), 0.93 (d, 6H, J = 6.7 Hz, $2CH_3$), 1.34-1.47 (m, 2H, CH_2), 1.74-1.85 (m, 2H, CH_2), 1.91-2.05 (m, 2H, 2CH), 2.83 (t, 2H, J = 7.6 Hz, CH_2), 3.70 (s, 3H, NCH_3), 4.02 (d, 2H, J = 6.7 Hz, CH_2O), 4.03 (d, 2H, J = 6.7 Hz, CH_2O), 7.58 (s, 1H, ArH), 8.03 (s, 1H, ArH). ^{13}C NMR (62 MHz, $CDCl_3$): δ = 13.8 (CH_3), 19.1 ($2CH_3$), 19.2 ($2CH_3$), 22.5, 27.3 (CH_2), 27.7, 27.8 (CH), 29.4 (CH_2), 30.1 (NCH_3), 71.5, 71.8 (CH_2O), 110.3, 120.6 (CH), 126.4, 126.9, 136.8, 143.6, 159.0 (C), 168.0, 168.6 (CO). IR (KBr, cm^{-1}): ν = 2957, 2927 (m), 2872 (w), 1713 (s), 1620, 1578, 1504, 1482 (w), 1467, 1456, 1444, 1396, 1377, 1367, 1339 (m), 1256, 1233, 1216, 1103 (s), 1033, 985 (m), 946, 888 (w), 781 (m), 733, 639, 611, 575 (w). GC-MS (EI, 70 eV): *m/z* (%) = 388(3)

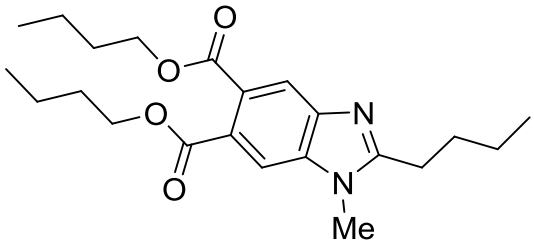
$[M]^+$, 359(13), 347(19), 346(100), 259(32). HRMS (EI, 70 eV): *m/z* calcd for $C_{22}H_{32}N_2O_4$ $[M]^+$: 388.23566; found: 388.23532.

Diisobutyl-1-methyl-2-propyl-1*H*-benzo[*d*]imidazole-5,6-dicarboxylate (48c):



Compound **48c** was prepared starting with **47c** (100 mg, 0.26 mmol), following the general procedure E, as whitish semi solid (84 mg, 85%).^{1}H NMR (300 MHz, $CDCl_3$): δ = 0.91 (d, 6H, *J* = 6.7 Hz, $2CH_3$), 0.92 (d, 6H, *J* = 6.7 Hz, $2CH_3$), 0.98 (t, 3H, *J* = 7.4 Hz, CH_3), 1.77-1.90 (m, 2H, CH_2), 1.93-2.04 (m, 2H, CH), 2.81 (t, 2H, *J* = 7.4 Hz, CH_2), 3.69 (s, 3H, NCH_3), 4.01 (d, 2H, *J* = 6.6 Hz, CH_2O), 4.02 (d, 2H, *J* = 6.7 Hz, CH_2O), 7.58 (s, 1H, ArH), 8.02 (s, 1H, ArH). ^{13}C NMR (62 MHz, $CDCl_3$): δ = 13.9 (CH_3), 19.1 ($2CH_3$), 19.2 ($2CH_3$), 20.7 (CH_2), 27.7, 27.8 (CH), 29.4 (CH_2), 30.1 (NCH_3), 71.5, 71.8 (CH_2O), 110.3, 120.5 (CH), 126.5, 126.9, 136.7, 143.4, 158.8 (C), 167.9, 168.5 (CO). IR (KBr, cm^{-1}): *v* = 2958 (m), 2872 (w), 1726, 1708 (s), 1620, 1574, 1504, 1484 (w), 1463, 1440, 1377, 1360, 1332, 1278 (m), 1250, 1229, 1208, 1101 (s), 1035, 990 (m), 948, 875 (w), 784 (m), 736, 636, 576 (w). MS (EI, 70 eV): *m/z* (%) = 374(10) $[M]^+$, 347(22), 346(100), 290(74), 246(22), 245(96), 234(27), 231(20), 217(10), 216(19). HRMS (EI, 70 eV): *m/z* calcd for $C_{21}H_{30}N_2O_4$ $[M]^+$: 374.22001; found: 374.21979.

Dibutyl-2-butyl-1-methyl-1*H*-benzo[*d*]imidazole-5,6-dicarboxylate (48d):



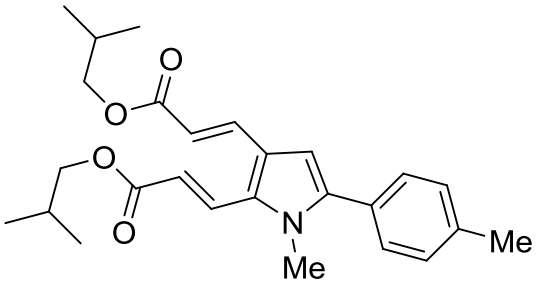
Compound **48d** was prepared starting with **47d** (100 mg, 0.26 mmol), following the general procedure E, as a brown oil (73 mg, 74%). ^{1}H NMR (300 MHz, $CDCl_3$): δ = 0.89 (t, 6H, *J* = 7.3 Hz, $2CH_3$), 0.91 (t, 3H, *J* = 7.3 Hz, CH_3), 1.30-1.45 (m, 6H, $3CH_2$), 1.60-1.70 (m, 4H, $2CH_2$), 1.73-1.83 (m, 2H, CH_2), 2.81 (t, 2H, *J* = 7.5 Hz, CH_2), 3.69 (s, 3H, NCH_3), 4.23 (t, 2H, *J* = 6.5 Hz, CH_2O), 4.24 (t, 2H, *J* = 6.8 Hz, CH_2O), 7.58 (s, 1H, ArH), 7.99 (s, 1H, ArH). ^{13}C NMR (62 MHz, $CDCl_3$): δ = 13.7 ($3CH_3$), 19.1, 19.2, 22.5, 27.3, 29.4 (CH_2), 30.0 (NCH_3), 30.5, 30.6 (CH_2), 65.3, 65.5 (CH_2O), 110.3, 120.4 (CH), 126.5, 12679, 136.7, 143.5, 158.9 (C), 168.1, 168.4 (CO). IR (KBr, cm^{-1}): *v* = 2959, 2928 (m), 2872 (w), 1716 (s), 1620, 1579, 1511 (w), 1455, 1388, 1360, 1331 (m), 1252, 1205, 1010 (s), 1061, 1032, 961, 944, 894, 784, 747 (m), 682, 614, 543 (w). GC-MS (EI, 70 eV):

m/z (%) = 388(3) $[M]^+$, 359(13), 347(19), 346(100). HRMS (EI, 70 eV): *m/z* calcd for $C_{22}H_{32}N_2O_4$ $[M]^+$: 388.23566; found: 388.23512.

General procedure F for synthesis of 2,3-Di(alkenyl)pyrroles 49:

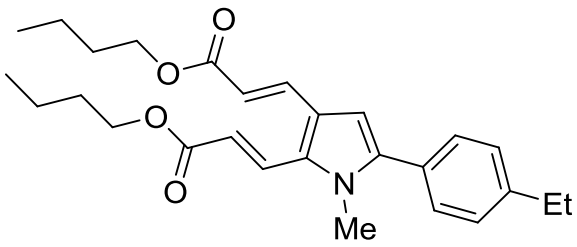
In a pressure tube (glass bomb) a suspension of $Pd(OAc)_2$ (12 mg, 0.05 mmol, 5 mol%) and $P(Cy)_3$ (28.04 mg, 0.10 mmol, 10 mol%) in DMF (5 mL) was purged with Argon and stirred at 20 °C to give a yellowish or brownish clear solution. To the stirred solution were added **19b,c,e,g** (1.0 mmol), Et_3N (1.1 mL, 8.0 mmol) and the alkene **26** (2.5 equiv). The reaction mixture was stirred at 100 °C for 24 h. The solution was cooled to 20 °C, poured into H_2O and CH_2Cl_2 (25 mL each), and the organic and the aqueous layers were separated. The latter was extracted with CH_2Cl_2 (3 × 25 mL). The combined organic layers were washed with H_2O (3 × 20 mL), dried (Na_2SO_4), and concentrated *in vacuo*. The residue was purified by chromatography (flash silica gel, eluent: heptanes-EtOAc).

(2*E*,2'*E*)-Isobutyl-3,3'-(1-methyl-5-*p*-tolyl-1*H*-pyrrole-2,3-diyl)diacrylate (49a):



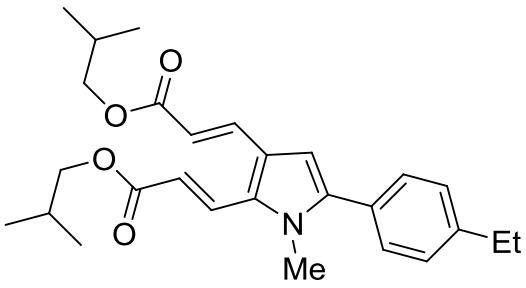
Compound **49a** was prepared starting with **19g** (329 mg, 1.0 mmol) and *iso*-butyl acrylate **26** (0.36 mL, 2.5 mmol), following the general procedure F, as a brown oil (304 mg, 72%). ^1H NMR (300 MHz, $CDCl_3$): δ = 0.91 (d, 6H, *J* = 6.7 Hz, $2CH_3$), 0.92 (d, 6H, *J* = 6.7 Hz, $2CH_3$), 1.91-1.97 (m, 2H, 2CH), 2.33 (s, 3H, CH_3), 3.57 (s, 3H, NCH_3), 3.91 (d, 2H, *J* = 6.8 Hz, CH_2O), 3.93 (d, 2H, *J* = 6.9 Hz, CH_2O), 6.10 (d, 1H, *J* = 16.0 Hz, CH), 6.18 (d, 1H, *J* = 15.6 Hz, CH), 6.42 (s, 1H, $CH_{pyrrole}$), 7.18-7.20 (m, 4H, ArH), 7.71 (d, 1H, *J* = 16.0 Hz, CH), 7.78 (d, 1H, *J* = 15.7 Hz, CH). ^{13}C NMR (62 MHz, $CDCl_3$): δ = 19.2 ($4CH_3$), 21.3 (CH_3), 27.8, 27.9 (CH), 33.8 (NCH_3), 70.4, 70.8 (CH_2O), 107.7, 116.5, 117.5 (CH), 123.7, 128.6 (C), 129.0 (2CH), 129.4 (2CH), 130.9 (C), 131.0, 136.3 (CH), 138.3, 140.7 (C), 167.2, 167.5 (CO). IR (KBr, cm^{-1}): *v* = 2959, 2872 (w), 1703, 1615 (m), 1565 (w), 1468, 1454, 1375, 1283, 1243, 1222 (m), 1151 (s), 1016, 969 (m), 852, 824, 798, 657 (w). MS (EI, 70 eV): *m/z* (%) = 423(48) $[M]^+$, 350(16), 322(28), 266(100), 250(39), 248(32), 222(89), 57(34), 4 (18). HRMS (ESI): calcd for $C_{26}H_{34}NO_4$ $[M+H]^+$: 424.2482; found: 424.2475.

(2*E*,2'*E*)-Dibutyl-3,3'-(5-(4-ethylphenyl)-1-methyl-1*H*-pyrrole-2,3-diyl)diacrylate (49c):



Compound **49c** was prepared starting with **19b** (343mg, 1.0 mmol) and *n*-butyl acrylate **26** (0.36 mL, 2.5 mmol), following the general procedure F, as a brown oil (275 mg, 63%). ^{1}H NMR (300 MHz, $CDCl_3$): δ = 0.89 (t, 3H, *J* = 7.3 Hz, CH_3), 0.90 (t, 3H, *J* = 7.3 Hz, CH_3), 1.21 (t, 3H, *J* = 7.6 Hz, CH_3), 1.33-1.41 (m, 4H, $2CH_2$), 1.57-1.65 (m, 4H, $2CH_2$), 2.63 (q, 2H, *J* = 7.6 Hz, CH_2), 3.57 (s, 3H, NCH_3), 4.13 (t, 4H, *J* = 6.8 Hz, $2CH_2O$), 6.09 (d, 1H, *J* = 16.0 Hz, CH), 6.17 (d, 1H, *J* = 15.6 Hz, CH), 6.41 (s, 1H, $CH_{pyrrole}$), 7.18-7.22 (m, 4H, ArH), 7.70 (d, 1H, *J* = 16.0 Hz, CH), 7.77 (d, 1H, *J* = 15.7 Hz, CH). ^{13}C NMR (75 MHz, $CDCl_3$): δ = 13.8 ($2CH_3$), 15.4 (CH_3), 19.1, 19.2 (CH_2), 28.6, 30.8, 30.9 (CH_2), 33.9 (NCH_3), 64.2, 64.5 (CH_2O), 107.7, 116.5, 117.5 (CH), 123.8 (C), 128.2 (2CH), 128.8 (C), 129.1 (2CH), 130.9 (C), 131.0, 136.3 (CH), 140.8, 144.6 (C), 167.3, 167.6 (CO). IR (KBr, cm^{-1}): ν = 3003, 2964, 2872 (w), 1711, 1691 (s), 1610 (m), 1502 (w), 1470, 1452, 1432, 1374, 1282 (m), 1254, 1241, 1217, 1163, 1033, 966, 848, 835, 802 (s), 775, 722, 689, 670, 632, 609, 535 (m). GC-MS (EI, 70 eV): *m/z* (%) = 437(84) $[M]^+$, 364(22), 336(100), 306(28), 280(89), 262(77), 235(67), 207(46), 124(15), 41(20). HRMS (EI, 70 eV): calcd for $C_{27}H_{35}NO_4$ $[M]^+$: 437.25606; found: 437.25602.

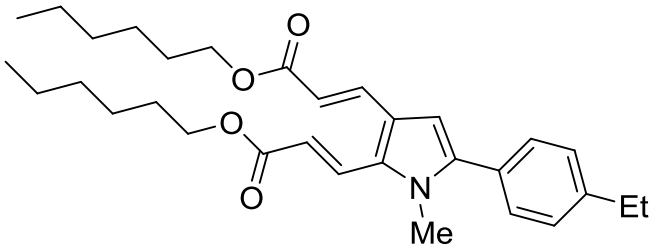
(2*E*,2'*E*)-Isobutyl-3,3'-[5-(4-ethylphenyl)-1-methyl-1*H*-pyrrole-2,3-diyl]diacrylate (49d):



Compound **49d** was prepared starting with **19b** (343mg, 1.0 mmol) and *iso*-butyl acrylate **26** (0.36 mL, 2.5 mmol), following the general procedure F, as a brown oil (301 mg, 69%). ^{1}H NMR (300 MHz, $CDCl_3$): δ = 0.90 (d, 6H, *J* = 6.7 Hz, $2CH_3$), 0.91 (d, 6H, *J* = 6.7 Hz, $2CH_3$), 1.20 (t, *J* = 7.6 Hz, 3H, CH_3), 1.87-1.99 (m, 2H, 2CH), 2.62 (q, 2H, *J* = 7.6 Hz, CH_2), 3.57 (s, 3H, NCH_3), 3.90 (d, 2H, *J* = 6.8 Hz, CH_2O), 3.92 (d, 2H, *J* = 6.8 Hz, CH_2O), 6.10 (d, 1H, *J* = 16.0 Hz, CH), 6.18 (d, 1H, *J* = 15.6 Hz, CH), 6.42 (s, 1H, $CH_{pyrrole}$), 7.20-7.25 (m, 4H, ArH), 7.71 (d, 1H, *J* = 16.0 Hz, CH), 7.78 (d, 1H, *J* = 15.7 Hz, CH). ^{13}C NMR (75 MHz, $CDCl_3$): δ = 15.4 (CH_3), 19.2 ($4CH_3$), 27.8, 27.9 (CH), 28.6 (CH_2), 33.9 (NCH_3), 70.4, 70.8 (CH_2O), 107.7, 116.5, 117.5 (CH), 123.7 (C), 128.2 (2CH), 129.0 (C), 129.1 (2CH), 130.9 (C), 131.1, 136.3 (CH), 140.7, 144.6 (C), 167.2, 167.5 (CO). IR (KBr, cm^{-1}): ν = 2959 (m), 2932, 2872 (w),

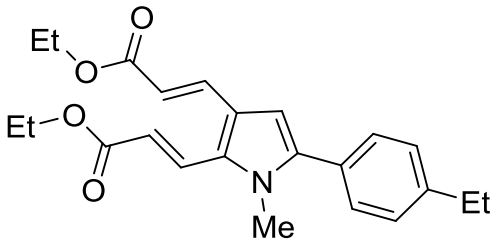
1699, 1615 (s), 1548, 1504 (w), 1468, 1453 (m), 1424, 1392 (w), 1368, 1284, 1260, 1241, 1220 (m), 1148 (s), 1015, 966, 839, 799 (m), 773, 723, 703, 672, 610, 533 (w). MS (EI, 70 eV): *m/z* (%) = 437(07) $[M]^+$, 280(14), 236(11), 66(13), 44(16), 43(100), 42(30), 41(55). HRMS (EI, 70 eV): calcd for $C_{27}H_{35}NO_4$ $[M]^+$: 437.25606; found: 437.25529.

(2*E*,2'*E*)-Dihexyl-3,3'-[5-(4-ethylphenyl)-1-methyl-1*H*-pyrrole-2,3-diyl]diacrylate (49e):



Compound **49e** was prepared starting with **19b** (343mg, 1.0 mmol) and *n*-hexyl acrylate **26** (0.44 mL, 2.5 mmol), following the general procedure F, as a brown oil (296 mg, 60%). ^{1}H NMR (250 MHz, $CDCl_3$): δ = 0.82 (t, 3H, *J* = 7.9 Hz, CH_3), 0.83 (t, 3H, *J* = 7.1 Hz, CH_3), 1.17-1.32 (m, 15H, $6CH_2$ and CH_3), 1.56-1.67 (m, 4H, $2CH_2$), 2.63 (q, 2H, *J* = 7.6 Hz, CH_2), 3.57 (s, 3H, NCH_3), 4.11 (t, 2H, *J* = 6.7 Hz, CH_2O), 4.13 (t, 2H, *J* = 6.7 Hz, CH_2O), 6.09 (d, 1H, *J* = 16.0 Hz, CH), 6.17 (d, 1H, *J* = 15.6 Hz, CH), 6.41 (s, 1H, $CH_{pyrrole}$), 7.18-7.23 (m, 4H, ArH), 7.70 (d, 1H, *J* = 16.1 Hz, CH), 7.77 (d, 1H, *J* = 15.8 Hz, CH). ^{13}C NMR (62 MHz, $CDCl_3$): δ = 14.0 ($2CH_3$), 15.4 (CH_3), 22.5 ($2CH_2$), 25.6 ($2CH_2$), 28.6 (CH_2), 28.7 ($2CH_2$), 31,5 ($2CH_2$), 33.9 (NCH_3), 64.4, 64.8 (CH_2O), 107.7, 116.5, 117.5 (CH), 123.7 (C), 128.2 (2CH), 128.8 (C), 129.1 (2CH), 129.1 (C), 131.0, 136.3 (CH), 140.7, 144.6 (C), 167.2, 167.6 (CO). IR (KBr, cm^{-1}): *v* = 2954 (w), 2927 (m), 2856 (w), 1701, 1615 (m), 1549, 1504 (w), 1454 (m), 1377 (w), 1273, 1244, 1220 (m), 1150 (s), 1060, 1012, 969, 837, 798 (m), 725, 672, 606, 533 (w). MS (EI, 70 eV): *m/z* (%) = 493(84) $[M]^+$, 392(12), 365(12), 364(53), 281(16), 280(100), 264(35), 262(37), 237(11), 236(72), 235(30), 220(17), 43(28). HRMS (EI, 70 eV): calcd for $C_{31}H_{43}NO_4$ $[M]^+$: 493.31866; found: 493.31916.

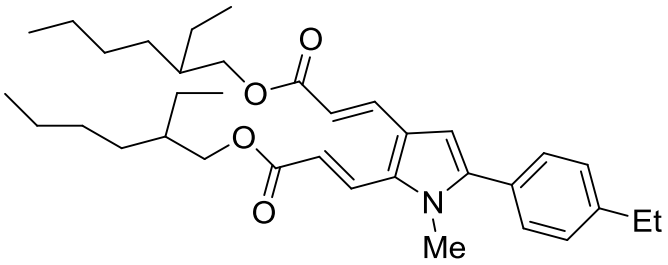
(2*E*,2'*E*)-Diethyl-3,3'-[5-(4-ethylphenyl)-1-methyl-1*H*-pyrrole-2,3-diyl]diacrylate (49f):



Compound **49f** was prepared starting with **19b** (343mg, 1.0 mmol) and ethyl acrylate **26** (0.27 mL, 2.5 mmol), following the general procedure F, as a brown oil (179 mg, 47%). ^{1}H NMR (300 MHz, $CDCl_3$): δ = 1.21 (t, 3H, *J* = 7.6 Hz, CH_3), 1.26 (t, 3H, *J* = 7.1 Hz, CH_3), 1.27 (t, 3H, *J* = 7.2 Hz, CH_3), 2.63 (q, 2H, *J* = 7.6 Hz, CH_2), 3.57 (s,

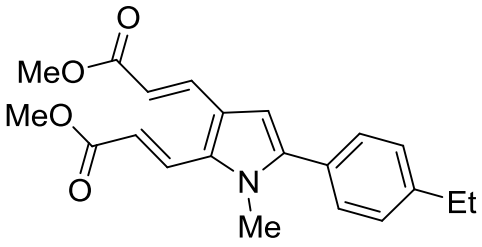
3H, NCH_3), 4.19 (q, 2H, J = 7.2 Hz, OCH_2), 4.20 (q, 2H, J = 7.1 Hz, OCH_2), 6.09 (d, 1H, J = 16.0 Hz, CH), 6.17 (d, 1H, J = 15.6 Hz, CH), 6.41 (s, 1H, $CH_{pyrrole}$), 7.18-7.21 (m, 4H, ArH), 7.71 (d, 1H, J = 16.1 Hz, CH), 7.77 (d, 1H, J = 15.7 Hz, CH). ^{13}C NMR (75 MHz, $CDCl_3$): δ = 14.4 ($2CH_3$), 15.4 (CH_3), 28.6 (CH_2), 34.0 (NCH_3), 60.2, 60.6 (OCH_2), 107.7, 116.5, 117.5 (CH), 123.8 (C), 128.2 (2CH), 128.8 (C), 129.1 (2CH), 129.1 (C), 131.0, 136.3 (CH), 140.8, 144.7 (C), 167.2, 167.5 (CO). IR (KBr, cm^{-1}): ν = 2964, 2931, 2872 (w), 1698, 1614 (s), 1504 (w), 1453, 1365, 1260, 1220 (m), 1149 (s), 1094, 1034, 967, 838, 797 (m), 771, 724, 603, 532 (w). MS (EI, 70 eV): *m/z* (%) = 381(64) $[M]^+$, 336(14), 309(21), 308(90), 307(13), 280(24), 262(77), 235(100), 220(67), 204(20). HRMS (EI, 70 eV): calcd for $C_{23}H_{27}NO_4$ $[M]^+$: 381.19346; found: 381.19387.

(2*E*,2'*E*)-Bis(2-ethylhexyl)-3,3'-[5-(4-ethylphenyl)-1-methyl-1*H*-pyrrole-2,3-diyl] diacrylate (49g):



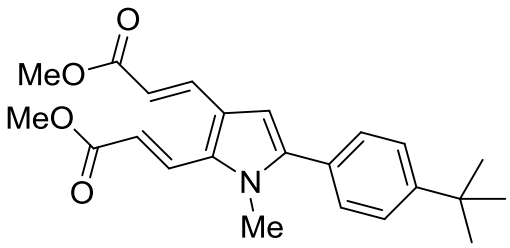
Compound **49g** was prepared starting with **19b** (343mg, 1.0 mmol) and 2-ethylhexyl acrylate **26** (0.52 mL, 2.5 mmol), following the general procedure F, as a brown oil (334 mg, 61%). ^{1}H NMR (300 MHz, $CDCl_3$): δ = 0.81-0.89 (m, 15H, $5CH_3$), 1.25-1.37 (m, 16H, $8CH_2$), 1.52-1.62 (m, 2H, 2CH), 2.63 (q, 2H, J = 7.6 Hz, CH_2), 3.58 (s, 3H, NCH_3), 4.00-4.07 (m, 4H, $2CH_2O$), 6.10 (d, 1H, J = 16.0 Hz, CH), 6.18 (d, 1H, J = 15.6 Hz, CH), 6.42 (s, 1H, $CH_{pyrrole}$), 7.21-7.24 (m, 4H, *A*rH), 7.71 (d, 1H, J = 16.0 Hz, CH), 7.78 (d, 1H, J = 15.7 Hz, CH). ^{13}C NMR (75 MHz, $CDCl_3$): δ = 11.0, 11.1 (CH_3), 14.1 ($2CH_3$), 15.4 (CH_3), 23.0 ($2CH_2$), 23.9, 24.0 (CH_2), 28.6 (CH_2), 30.0 ($2CH_2$), 30.4, 30.5 (CH_2), 33.8 (NCH_3), 38.9 (2CH), 66.7, 67.2 (CH_2O), 107.7, 116.6, 117.6 (CH), 123.7 (C), 128.2 (2CH), 128.8 (C), 129.1 (2CH), 130.3 (CH), 131.0 (C), 136.2 (CH), 140.7, 144.6 (C), 167.4, 167.7 (CO). IR (KBr, cm^{-1}): ν = 2956, 2926, 2857, 1727, 1704, 1616, 1456 (m), 1378 (w), 1273, 1222 (m), 1152 (s), 1031, 1015, 970, 837 (m), 795, 772, 726, 529 (w). MS (EI, 70 eV): *m/z* (%) = 549(24) $[M]^+$, 392(19), 368(14), 367(54), 280(54), 255(63), 238(100), 211(33), 198(14), 71(21), 57(40). HRMS (EI, 70 eV): calcd for $C_{35}H_{51}NO_4$ $[M]^+$: 549.38181; found: 549.38164.

(2*E*,2'*E*)-Dimethyl-3,3'-[5-(4-ethylphenyl)-1-methyl-1*H*-pyrrole-2,3-diyl]diacrylate (49h):



Compound **49h** was prepared starting with **19b** (343mg, 1.0 mmol) and methyl acrylate **26** (0.23 mL, 2.5 mmol), following the general procedure F, as a yellow solid (204 mg, 58%), mp. = 125-127 °C. ^{1}H NMR (300 MHz, $CDCl_3$): δ = 1.20 (t, 3H, J = 7.6 Hz, CH_3), 2.62 (q, 2H, J = 7.6 Hz, CH_2), 3.57 (s, 3H, NCH_3), 3.71 (s, 3H, OCH_3), 3.74 (s, 3H, OCH_3), 6.08 (d, 1H, J = 16.0 Hz, CH), 6.16 (d, 1H, J = 15.6 Hz, CH), 6.41 (s, 1H, $CH_{pyrrole}$), 7.18-7.21 (m, 4H, ArH), 7.71 (d, 1H, J = 16.3 Hz, CH), 7.76 (d, 1H, J = 16.2 Hz, CH). ^{13}C NMR (75 MHz, $CDCl_3$): δ = 14.4 (CH_3), 27.6 (CH_2), 33.0 (NCH_3), 50.5 (OCH_3), 50.7 (OCH_3), 106.7, 115.1, 116.0 (CH), 122.8 (C), 127.2 (2CH), 127.7 (C), 128.1 (2CH), 129.9 (C), 130.1, 135.4 (CH), 139.9, 143.7 (C), 166.5, 166.9 (CO). IR (KBr, cm^{-1}): ν = 3003, 2964, 2928 (w), 1711, 1691 (s), 1622, 1611 (m), 1502 (w), 1471, 1452, 1432, 1425, 1374, 1282 (m), 1254, 1241, 1217, 1162 (s), 1117, 1063, 1052 (m), 1033, 956, 848, 835, 802 (s), 775, 722, 702, 652, 608, 535 (m). GC-MS (EI, 70 eV): *m/z* (%) = 353(49) $[M]^+$, 322(16), 320(10), 295(14), 294(99), 293(11), 281(15), 279(12), 278(11), 263(20), 262(100), 236(11), 135(48), 234(24), 232(12), 221(14), 220(49), 209(12), 208(18), 207(71), 205(12), 204(21), 178(10), 44(23), 32(18). HRMS (EI, 70 eV): calcd for $C_{21}H_{23}NO_4$ $[M]^+$: 353.16216; found: 353.16297.

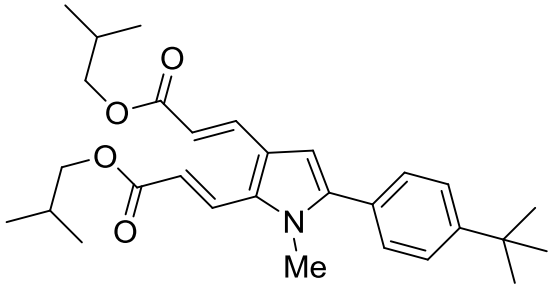
(2*E*,2'*E*)-Dimethyl-3,3'-[5-(4-*tert*-butylphenyl)-1-methyl-1*H*-pyrrole-2,3-diyl]diacrylate (49i):



Compound **49i** was prepared starting with **19c** (371 mg, 1.0 mmol) and methyl acrylate **26** (0.23 mL, 2.5 mmol), following the general procedure F, as a brown oil (202 mg, 53%). ^{1}H NMR (300 MHz, $CDCl_3$): δ = 1.28 (s, 9H, $3CH_3$), 3.58 (s, 3H, NCH_3), 3.71 (s, 3H, OCH_3), 3.74 (s, 3H, OCH_3), 6.08 (d, 1H, J = 16.0 Hz, CH), 6.17 (d, 1H, J = 15.7 Hz, CH), 6.41 (s, 1H, $CH_{pyrrole}$), 7.23 (dd, 2H, J = 2.1, 6.5 Hz, ArH), 7.39 (dd, 2H, J = 1.8, 6.6 Hz, ArH), 7.71 (d, 1H, J = 16.1 Hz, CH), 7.77 (d, 1H, J = 16.0 Hz, CH). ^{13}C NMR (62 MHz, $CDCl_3$): δ = 31.3 ($3CH_3$), 34.0 (NCH_3), 34.7 (C), 51.5, 51.7 (OCH_3), 107.7, 116.1, 117.0 (CH), 123.8 (C), 125.6 (2CH), 128.6 (C), 128.8 (2CH), 131.0 (C), 131.2, 136.4 (CH), 140.9, 151.5 (C), 167.5, 167.9 (CO). IR (KBr, cm^{-1}): ν = 2950, 2905, 2868 (w), 1708, 1616

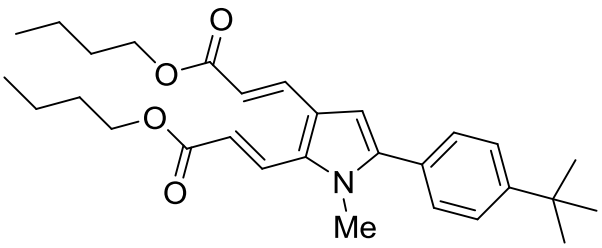
(s), 1550, 1502 (w), 1455, 1432 (m), 1364 (w), 1303, 1266, 1222, 1191 (m), 1156 (s), 1037, 1014 (w), 969 (m), 936 (w), 841, 800 (m), 729, 605, 558 (w). MS (EI, 70 eV): *m*/*z* (%) = 381(49) [M^+], 323(20), 322(100), 290(46), 263(10), 248(23), 234(28), 69(18), 57(22), 44(48), 41(11). HRMS (EI, 70 eV): calcd for $C_{23}H_{27}NO_4$ [M]$^+$: 381.19346; found: 381.19290.

(2*E*,2'*E*)-Isobutyl-3,3'-[5-(4-*tert*-butylphenyl)-1-methyl-1*H*-pyrrole-2,3-diyl]diacrylate (49j):



Compound **49j** was prepared starting with **19c** (371 mg, 1.0 mmol) and *iso*-butyl acrylate **26** (0.36 mL, 2.5 mmol), following the general procedure F, as a brown oil (353 mg, 76%). ^{1}H NMR (300 MHz, $CDCl_3$): δ = 0.91 (d, 6H, *J* = 6.8 Hz, $2CH_3$), 0.92 (d, 6H, *J* = 6.7 Hz, $2CH_3$), 1.29 (s, 9H, $3CH_3$), 1.87-1.99 (m, 2H, 2CH), 3.56 (s, 3H, NCH_3), 3.91 (d, 2H, *J* = 6.9 Hz, CH_2O), 3.93 (d, 2H, *J* = 6.8 Hz, CH_2O), 6.11 (d, 1H, *J* = 16.0 Hz, CH), 6.18 (d, 1H, *J* = 15.6 Hz, CH), 6.43 (s, 1H, $CH_{pyrrole}$), 7.25 (d, 2H, *J* = 8.5 Hz, ArH), 7.40 (d, 2H, *J* = 8.5 Hz, ArH), 7.72 (d, 1H, *J* = 16.0 Hz, CH), 7.79 (d, 1H, *J* = 15.7 Hz, CH). ^{13}C NMR (75 MHz, $CDCl_3$): δ = 19.2 ($4CH_3$), 27.8, 27.9 (CH), 31.3 ($3CH_3$), 33.9 (NCH_3), 34.7 (C), 70.4, 70.8 (CH_2O), 107.8, 116.5, 117.5 (CH), 123.7 (C), 125.6 (2CH), 128.6 (C), 128.8 (2CH), 131.0 (C), 131.1, 136.3 (CH), 140.7, 151.5 (C), 167.3, 167.6 (CO). IR (KBr, cm^{-1}): ν = 2957 (m), 2871 (w), 1704, 1616 (m), 1462, 1455, 1375, 1367, 1267, 1243, 1222 (m), 1149 (s), 1110, 1013, 968, 839, 794 (m), 742, 722, 666, 610, 558 (w). MS (EI, 70 eV): *m*/*z* (%) = 465(41) [M^+], 364(38), 309(18), 310(100), 292(18), 290(23), 266(15), 264(37), 248(15), 57(18). HRMS: *m*/*z* calcd for $C_{29}H_{39}NO_4$ [M^+]: 465.28736; found: 465.28617.

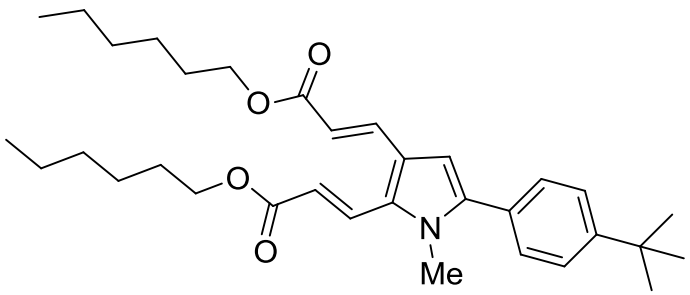
(2*E*,2'*E*)-Dibutyl-3,3'-[5-(4-*tert*-butylphenyl)-1-methyl-1*H*-pyrrole-2,3-diyl]diacrylate (49k):



Compound **49k** was prepared starting with **19c** (371 mg, 1.0 mmol) and *n*-butyl acrylate **26** (0.36 mL, 2.5 mmol), following the general procedure F, as a brown oil (260 mg, 56%). ^{1}H NMR (300 MHz, $CDCl_3$): δ = 0.89 (t, 3H, *J* = 7.3 Hz, CH_3), 0.90 (t, 3H, *J* = 7.2 Hz, CH_3), 1.28 (s, 9H, $3CH_3$), 1.33-1.40 (m, 4H,

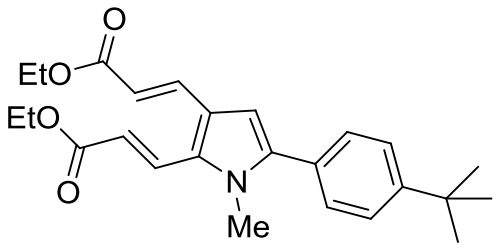
$2CH_2$), 1.57-1.65 (m, 4H, $2CH_2$), 3.58 (s, 3H, NCH_3), 4.12 (t, 2H, J = 6.8 Hz, CH_2O), 4.15 (t, 2H, J = 6.8 Hz, CH_2O), 6.09 (d, 1H, J = 16.0 Hz, CH), 6.17 (d, 1H, J = 15.6 Hz, CH), 6.41 (s, 1H, $CH_{pyrrole}$), 7.24 (dd, 2H, J = 1.8, 6.5 Hz, ArH), 7.39 (dd, 2H, J = 2.0, 6.4 Hz, ArH), 7.71 (d, 1H, J = 16.0 Hz, CH), 7.76 (d, 1H, J = 15.7 Hz, CH). ^{13}C NMR (75 MHz, $CDCl_3$): δ = 12.7 ($2CH_3$), 18.1, 18.2 (CH_2), 29.7, 29.8 (CH_2), 30.3 ($3CH_3$), 32.9 (NCH_3), 33.7 (C), 63.1, 63.5 (CH_2O), 106.7, 115.5, 116.5 (CH), 122.7 (C), 124.6 (2CH), 127.5 (C), 127.8 (2CH), 130.0 (C), 130.1, 135.3 (CH), 139.7, 150.5 (C), 166.3, 166.6 (CO). IR (KBr, cm^{-1}): ν = 2956 (m), 2932, 2870 (w), 1700, 1616 (s), 1454, 1363, 1267, 1245, 1221 (m), 1150 (s), 1063, 1023, 968, 839, 799, 730 (m), 647, 605, 557 (w). GC-MS (EI, 70 eV): *m/z* (%) = 465(45) $[M]^+$, 463(11), 364(47), 308(100), 290(77), 264(22), 248(24), 234(10), 57(10). HRMS (EI, 70 eV): calcd for $C_{29}H_{39}NO_4$ $[M]^+$: 465.28736; found: 465.28768. Anal. calcd for $C_{29}H_{39}NO_4$: C, 75.13; H, 8.04; N, 3.02. Found: C, 75.53; H, 8.18; S, 2.70.

(2*E*,2'*E*)-Dihexyl-3,3'-[5-(4-*tert*-butylphenyl)-1-methyl-1*H*-pyrrole-2,3-diyl]diacrylate (49l):



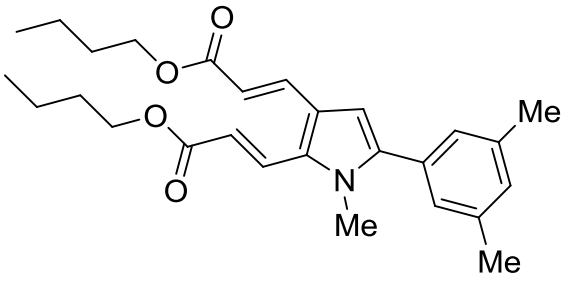
Compound **49l** was prepared starting with **19c** (371mg, 1.0 mmol) and *n*-hexyl acrylate **26** (0.44 mL, 2.5 mmol), following the general procedure F, as a brown oil (369 mg, 71%). ^{1}H NMR (500 MHz, $CDCl_3$): δ = 0.80-0.85 (m, 6H, $2CH_3$), 1.17-1.33 (m, 17H, $4CH_2$ and $3CH_3$), 1.50-1.58 (m, 4H, $2CH_2$), 1.59-1.67 (m, 4H, $2CH_2$), 3.58 (s, 3H, NCH_3), 4.10-4.16 (m, 4H, $2CH_2O$), 6.09 (d, 1H, J = 16.0 Hz, CH), 6.17 (d, 1H, J = 15.6 Hz, CH), 6.42 (s, 1H, $CH_{pyrrole}$), 7.24 (d, 2H, J = 8.4 Hz, ArH), 7.39 (d, 2H, J = 8.4 Hz, ArH), 7.70 (d, 1H, J = 16.0 Hz, CH), 7.78 (d, 1H, J = 15.6 Hz, CH). ^{13}C NMR (125 MHz, $CDCl_3$): δ = 13.9, 14.00 (CH_3), 22.5 ($2CH_2$), 25.7 ($2CH_2$), 28.7 (CH_2), 31.3 (CH_3), 31.5 ($2CH_2$), 33.9 (NCH_3), 34.7 (C), 64.5, 64.8 (CH_2O), 107.7, 116.5, 117.5 (CH), 123.8, 125.4 (C), 125.6 (2CH), 128.8 (2CH), 130.9 (C), 131.0, 136.3 (CH), 140.7, 151.5 (C), 167.6, 167.6 (CO). IR (KBr, cm^{-1}): ν = 2953, 2927, 2857 (w), 1703, 1617 (m), 1548, 1502 (w), 1454, 1267, 1245 (m), 1153 (s), 1057, 1010, 970, 840, 800 (m), 724, 607, 558 (w). MS (EI, 70 eV): *m/z* (%) = 519(10) $[M]^+$, 392(69), 309(19), 308(100), 292(23), 290(33), 282(15), 264(43), 248(19), 236(14), 234(11), 157(10), 69(21), 66(15), 57(18), 44(24), 41(16). HRMS (EI, 70 eV): calcd for $C_{33}H_{45}NO_4$ $[M]^+$: 519.33431; found: 519.33507.

(2*E*,2'*E*)-diethyl-3,3'-(5-(4-*tert*-butylphenyl)-1-methyl-1*H*-pyrrole-2,3-diyl)diacrylate (49m):



Compound **49m** was prepared starting with **19c** (371 mg, 1.0 mmol) and ethyl acrylate **26** (0.27 mL, 2.5 mmol), following the general procedure F, as a brown oil (196 mg, 48%). ^{1}H NMR (300 MHz, $CDCl_3$): δ = 1.27-1.30 (m, 15H, $5CH_3$), 3.58 (s, 3H, NCH_3), 4.14-4.23 (m, 4H, $2CH_2O$), 6.09 (d, 1H, J = 15.9 Hz, CH), 6.17 (d, 1H, J = 15,6 Hz, CH), 6.41 (s, 1H, $CH_{pyrrole}$), 7.24 (d, 2H, J = 8,5 Hz, ArH), 7.39 (d, 2H, J = 8,4 Hz, ArH), 7.71 (d, 1H, J = 16.0 Hz, CH), 7.78 (d, 1H, J = 15,6 Hz, CH). ^{13}C NMR (62 MHz, $CDCl_3$): δ = 13.4 ($2CH_3$), 30.2 ($3CH_3$), 33.0 (NCH_3), 33.7 (C), 59.2, 59.5 (CH_2O), 106.7, 115.4, 116.4 (CH), 122.8, 124.4 (C), 124.6 (2CH), 127.5 (C), 127.8 (2CH), 130.0, 135.3 (CH), 139.7, 150.5 (C), 166.2, 166.5 (CO). IR (KBr, cm^{-1}): ν = 2958, 2903, 2867 (w), 1700, 1615 (s), 1453, 1364, 1299, 1260 (m), 1149 (s), 1110, 1094, 1034, 968, 839, 798, 728 (m), 603, 556 (w). MS (EI, 70 eV): m/z (%) = 409(43) [M^+], 337(20), 336(100), 308(13), 292(20), 290(38), 264(17), 263(32), 248(29), 234(12). HRMS: m/z calcd for $C_{25}H_{31}NO_4$ [M^+]: 409.22476; found: 409.222406.

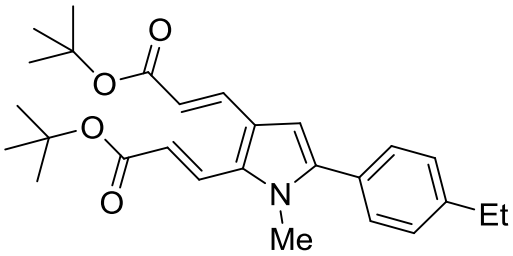
(2*E*,2'*E*)-Dibutyl-3,3'-(5-(3,5-dimethylphenyl)-1-methyl-1*H*-pyrrole-2,3-diyl)diacrylate (49o):



Compound **49o** was prepared starting with **19e** (343 mg, 1.0 mmol) and *n*-butyl acrylate **26** (0.36 mL, 2.5 mmol), following the general procedure F, as a brown oil (288 mg, 66%). ^{1}H NMR (300 MHz, $CDCl_3$): δ = 0.89 (t, 3H, J = 7.4 Hz, CH_3), 0.90 (t, 3H, J = 7.3 Hz, CH_3), 1.30-1.41 (m, 4H, $2CH_2$), 1.57-1.65 (m, 4H, $2CH_2$), 2.29 (s, 6H, $2CH_3$), 3.57 (s, 3H, NCH_3), 4.12 (t, 2H, J = 6.8 Hz, CH_2O), 4.15 (t, 2H, J = 6.6 Hz, CH_2O), 6.09 (d, 1H, J = 16.0 Hz, CH), 6.17 (d, 1H, J = 15.6 Hz, CH), 6.41 (s, 1H, $CH_{pyrrole}$), 6.92 (br, 2H, ArH), 6.95 (br, 1H, ArH), 7.70 (d, 1H, J = 16.0 Hz, CH), 7.77 (d, 1H, J = 15.7 Hz, CH). ^{13}C NMR (62 MHz, $CDCl_3$): δ = 13.8 ($2CH_3$), 19.2 ($2CH_2$), 21.3 ($2CH_3$), 30.8 ($2CH_2$), 33.9 (NCH_3), 64.1, 64.5 (CH_2O), 107.8, 116.5, 117.5 (CH), 123.7 (C), 126.9 (2CH), 130.0, 130.9 (CH), 131.0, 131.4 (C), 136.3 (CH), 138.3 (2C), 140.9 (C), 167.3, 167.6 (CO). IR (KBr, cm^{-1}): ν = 2956, 2931, 2871 (w),

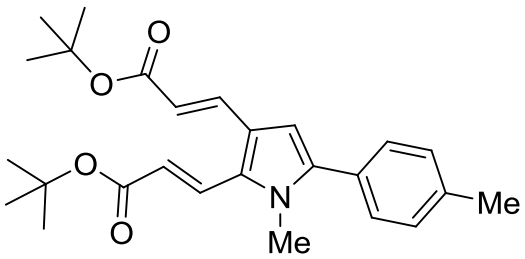
1700, 1615, 1456 (m), 1378 (w), 1300, 1274, 1257, 1238 (m), 1149 (s), 1160, 1023, 968, 851, 799 (m), 738 (w), 701 (m), 670, 632, 545 (w). GC-MS (EI, 70 eV): *m/z* (%) = 437(38) $[M]^+$, 336(44), 335(33), 281(19), 280(100), 279(13), 263(17), 262(84), 236(34), 235(26), 234(13), 221(15). HRMS (EI, 70 eV): calcd for $C_{27}H_{35}NO_4$ $[M]^+$: 437.25606; found: 437.25671.

(2*E*,2'*E*)-*tert*-butyl-3,3'-[5-(4-ethylphenyl)-1-methyl-1*H*-pyrrole-2,3-diyl]diacrylate (49q):



Compound **49q** was prepared starting with **19b** (343mg, 1.0 mmol) and *tert*-butyl acrylate **26** (0.36 mL, 2.5 mmol), following the general procedure F, as a brown oil (284 mg, 65%). ^{1}H NMR (300 MHz, $CDCl_3$): δ = 1.20 (t, 3H, *J* = 7.6 Hz, CH_3), 1.46 (s, 9H, $3CH_3$), 1.47 (s, 9H, $3CH_3$), 2.62 (q, 2H, *J* = 7.6 Hz, CH_2), 3.55 (s, 3H, NCH_3), 6.04 (d, 1H, *J* = 15.9 Hz, CH), 6.10 (d, 1H, *J* = 15.6 Hz, CH), 6.40 (s, 1H, $CH_{pyrrole}$), 7.18-7.22 (m, 4H, ArH), 7.60 (d, 1H, *J* = 16.0 Hz, CH), 7.71 (d, 1H, *J* = 15.6 Hz, CH). ^{13}C NMR (75 MHz, $CDCl_3$): δ = 15.4 (CH_3), 28.2 ($3CH_3$), 28.3 ($3CH_3$), 28.6 (CH_2), 33.7 (NCH_3), 80.0, 80.5 (C), 107.6, 118.1, 119.5 (CH), 123.4 (C), 128.2 (2CH), 129.0 (C), 129.1 (2CH), 130.2 (CH), 131.0 (C), 135.6 (CH), 140.3, 144.5 (C), 166.5, 167.0 (CO). IR (KBr, cm^{-1}): ν = 2970, 2930, 2873 (w), 1696, 1615 (s), 1470, 1453 (m), 1390 (w), 1365, 1305, 1277, 1253 (m), 1134 (s), 969, 839, 799, 763, 730 (m), 692, 614, 531 (w). MS (EI, 70 eV): *m/z* (%) = 437(30) $[M]^+$, 280(100), 264(11), 236(37), 220(14). HRMS (EI, 70 eV): calcd for $C_{27}H_{35}NO_4$ $[M]^+$: 437.25606; found: 437.25616.

(2*E*,2'*E*)-*tert*-butyl-3,3'-(1-methyl-5-*p*-tolyl-1*H*-pyrrole-2,3-diyl)diacrylate (49r):



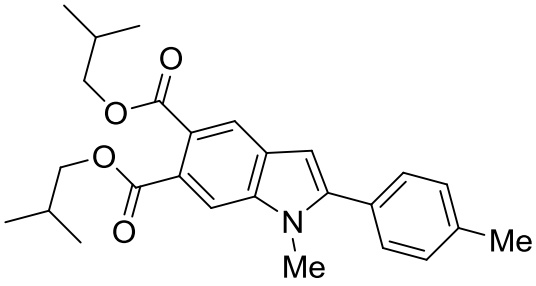
Compound **49r** was prepared starting with **19g** (329 mg, 1.0 mmol) and *tert*-butyl acrylate **26** (0.36 mL, 2.5 mmol), following the general procedure F, as a brown oil (304 mg, 72%). ^{1}H NMR (300 MHz, $CDCl_3$): δ = 1.46 (s, 9H, $3CH_3$), 1.47 (s, 9H, $3CH_3$), 2.33 (s, 3H, CH_3), 3.55 (s, 3H, NCH_3), 6.04 (d, 1H, *J* = 16.0 Hz, CH), 6.10 (d, 1H, *J* = 15.7 Hz, CH), 6.39 (s, 1H, $CH_{pyrrole}$), 7.18 (br, 4H, ArH), 7.60 (d, 1H, *J* = 16.0 Hz, CH), 7.70 (d, 1H, *J* = 15.6 Hz, CH). ^{13}C NMR (62 MHz, $CDCl_3$): δ = 21.2 (CH_3), 28.2 ($6CH_3$), 33.7 (NCH_3), 80.0, 81.0 (C), 107.5, 118.1,

119.5 (CH), 123.4, 128.8 (C), 129.0 (2CH), 129.3 (2CH), 130.1 (CH), 131.0 (C), 135.5 (CH), 138.2, 140.2 (C), 166.5, 167.0 (CO). IR (KBr, cm^{-1}): ν = 2974, 2926, 2868 (w), 1696, 1614 (m), 1503, 1471 (w), 1453 (m), 1424, 1390 (w), 1365, 1305, 1277, 1254 (m), 1225, 1201 (w), 1134 (s), 969, 853, 823, 797 (m), 764, 734, 594 (w). MS (EI, 70 eV): *m/z* (%) = 423(20) $[M]^+$, 267(20), 266(100), 250(13), 248(13), 222(45), 221(15), 207(12), 57(22), 41(21). HRMS (EI, 70 eV): calcd for $C_{26}H_{33}NO_4$ $[M]^+$: 423.24041; found: 423.24040.

General procedure G for synthesis of Indoles 50 and 51:

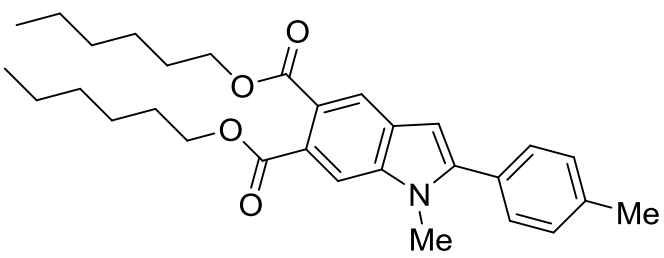
A diphenyl ether solution (3 mL) of **49a-o,q,r** (0.25 mmol) was stirred at 200 °C for 24 h in a pressure tube. The solution was allowed to cool to 20 °C and Pd/C (30 mg, 10 mol %) was added. The solution was stirred at 200 °C for 48 h under an argon atmosphere. The reaction mixture was filtered and the filtrate was concentrated *in vacuo*. The residue was purified by chromatography (flash silica gel, eluent: heptanes-EtOAc).

Diisobutyl-1-methyl-2-*p*-tolyl-1*H*-indole-5,6-dicarboxylate (50a):



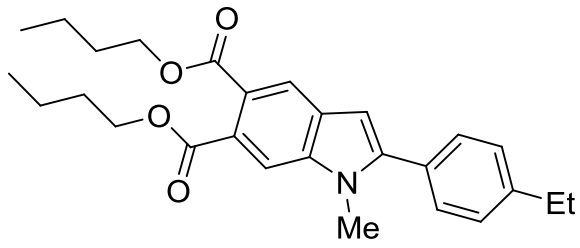
Compound **50a** was prepared starting with **49a** (100 mg, 0.24 mmol), following the general procedure G, as a brown oil (90 mg, 91%). ^{1}H NMR (300 MHz, $CDCl_3$): δ = 0.92 (d, 6H, *J* = 6.7 Hz, $2CH_3$), 0.93 (d, 6H, *J* = 6.7 Hz, $2CH_3$), 1.92-2.05 (m, 2H, 2CH), 2.36 (s, 3H, CH_3), 3.70 (s, 3H, NCH_3), 4.02 (d, 2H, *J* = 6.7 Hz, CH_2O), 4.03 (d, 2H, *J* = 6.7 Hz, CH_2O), 6.53 (s, 1H, $CH_{pyrrole}$), 7.22 (d, 2H, *J* = 7.9 Hz, ArH), 7.31 (dd, 2H, *J* = 1.8, 6.5 Hz, ArH), 7.66 (s, 1H, ArH), 7.94 (s, 1H, ArH). ^{13}C NMR (75 MHz, $CDCl_3$): δ = 19.3 ($4CH_3$), 21.3 (CH_3), 27.8, 27.9 (CH), 31.4 (NCH_3), 71.4, 71.6 (CH_2O), 102.6, 111.2, 122.1 (CH), 124.3, 125.7, 128.8, 129.1 (C), 129.3 (2CH), 129.4 (2CH), 138.3, 138.6, 145.1 (C), 168.8, 169.0 (CO). IR (KBr, cm^{-1}): ν = 2958, 2930, 2872 (w), 1710 (s), 1610, 1495 (w), 1469 (m), 1429, 1394 (w), 1376, 1359, 1340 (m), 1260, 1233 (s), 1214, 1157 (m), 1104 (s), 1037, 1023, 986, 907, 823, 784, 779, 729 (m), 672, 646, 569, 545 (w). GC-MS (EI, 70 eV): *m/z* (%) = 421(80) $[M]^+$, 309(13), 293(22), 292(100), 219(14). HRMS (EI, 70 eV): calcd for $C_{26}H_{31}NO_4$ $[M]^+$: 421.22476; found: 421.22551.

Dihexyl-1-methyl-2-*p*-tolyl-1*H*-indole-5,6-dicarboxylate (50b):



Compound **50b** was prepared starting with **49b** (100 mg, 0.21 mmol), following the general procedure G, as a brown oil (79 mg, 80%). ^{1}H NMR (300 MHz, $CDCl_3$): δ = 0.82 (t, 6H, J = 7.0 Hz, $2CH_3$), 1.22-1.37 (m, 12H, $6CH_2$), 1.63-1.72 (m, 4H, $2CH_2$), 2.34 (s, 3H, CH_3), 3.69 (s, 3H, NCH_3), 4.22 (t, 2H, J = 6.8 Hz, CH_2O), 4.24 (t, 2H, J = 6.8 Hz, CH_2O), 6.51 (s, 1H, $CH_{pyrrole}$), 7.20 (d, 2H, J = 8.0 Hz, ArH), 7.31 (d, 2H, J = 8.1 Hz, ArH), 7.65 (s, 1H, ArH), 7.92 (s, 1H, ArH). ^{13}C NMR (62 MHz, $CDCl_3$): δ = 14.0 ($2CH_3$), 21.3 (CH_3), 22.6 ($2CH_2$), 25.7 ($2CH_2$), 28.6, 28.7 (CH_2), 31.5 (NCH_3), 31,4 ($2CH_2$), 65.5, 65.7 (CH_2O), 102.6, 111.1, 122.1 (CH), 124.2, 125.6, 128.8, 129.1 (C), 129.2 (2CH), 129.4 (2CH), 138.2, 138.6, 145.1 (C), 168.9, 169.0 (CO). IR (KBr, cm^{-1}): v = 2952, 2924 (m), 2855 (w), 1711 (s), 1610, 1547 (w), 1495, 1456, 1379, 1360, 1339 (m), 1254, 1234, 1156, 1104 (s), 1033, 1021, 984, 894, 823, 780, 741, 720 (m), 671, 625, 600, 572, 543 (w). GC-MS (EI, 70 eV): *m/z* (%) = 477(78) $[M]^+$, 293(22), 294(100), 219(18), 41(11). HRMS (ESI): calcd for $C_{30}H_{40}NO_4$ $[M+H]^+$: 478.2952; found: 478.2958.

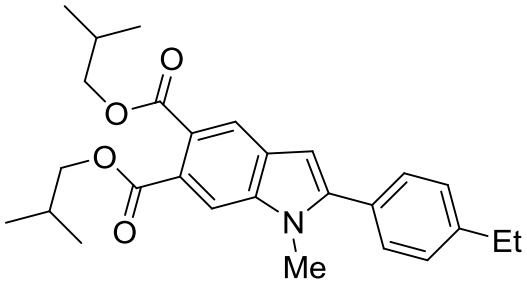
Dibutyl-2-(4-ethylphenyl)-1-methyl-1*H*-indole-5,6-dicarboxylate (50c):



Compound **50c** was prepared starting with **49c** (100 mg, 0.23 mmol), following the general procedure G, as a brown oil (75 mg, 76%). ^{1}H NMR (300 MHz, $CDCl_3$): δ = 0.90 (t, 6H, J = 7.4 Hz, $2CH_3$), 1.23 (t, 3H, J = 7.6 Hz, CH_3), 1.35-1.43 (m, 4H, $2CH_2$), 1.62-1.72 (m, 4H, $2CH_2$), 2.66 (q, 2H, J = 7.6 Hz, CH_2), 3.72 (s, 3H, NCH_3), 4.24 (t, 2H, J = 6.7 Hz, CH_2O), 4.26 (t, 2H, J = 6.7 Hz, CH_2O), 6.53 (s, 1H, $CH_{pyrrole}$), 7.25 (d, 2H, J = 8.3 Hz, ArH), 7.35 (dd, 2H, J = 1.8, 6.5 Hz, ArH), 7.66 (s, 1H, ArH), 7.93 (s, 1H, ArH). ^{13}C NMR (75 MHz, $CDCl_3$): δ = 13.8 ($2CH_3$), 15.5 (CH_3), 19.3 ($2CH_2$), 28.7, 30.7, 30.8 (CH_2), 31.5 (NCH_3), 65.2, 65.4 (CH_2O), 102.6, 111.2, 122.1 (CH), 124.2, 125.6 (C), 128.2 (2CH), 129.1 (C), 129.3 (2CH), 129.3, 138.0, 144.9, 145.2 (C), 168.9, 169.0 (CO). IR (KBr, cm^{-1}): v = 2957 (m), 2871 (w), 1711 (s), 1611, 1562, 1494 (w), 1456 (m), 1430, 1382 (w), 1360, 1340 (m), 1254, 1233 (s), 1209, 1157 (m), 1103 (s), 1060, 1036, 1021 (m), 962, 944, 897 (w), 837, 784, 740 (m), 700, 671, 599, 543 (w). GC-MS (EI, 70 eV):

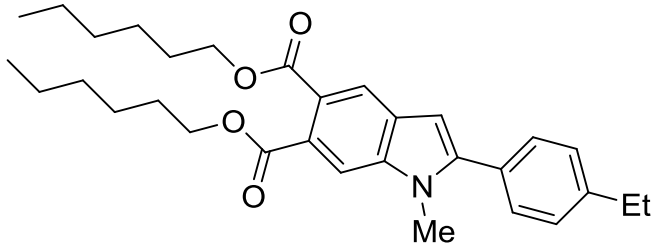
m/z (%) = 435(100) $[M]^+$, 307(17), 306(78). HRMS (EI, 70 eV): calcd for $C_{27}H_{33}NO_4$ $[M]^+$: 435.24041; found: 435.23989.

Diisobutyl-2-(4-ethylphenyl)-1-methyl-1*H*-indole-5,6-dicarboxylate (50d):



Compound **50d** was prepared starting with **49d** (100 mg, 0.23 mmol), following the general procedure G, as a yellow oil (71 mg, 72%). ^{1}H NMR (300 MHz, $CDCl_3$): δ = 0.92 (d, 6H, *J* = 6.7 Hz, $2CH_3$), 0.93 (d, 6H, *J* = 6.7 Hz, $2CH_3$), 1.22 (d, 3H, *J* = 7.6 Hz, CH_3), 1.92-2.05 (m, 2H, 2CH), 2.65 (q, 2H, *J* = 7.6 Hz, CH_2), 3.71 (s, 3H, NCH_3), 4.01 (d, 2H, *J* = 6.6 Hz, CH_2O), 4.03 (d, 2H, *J* = 6.7 Hz, CH_2O), 6.53 (s, 1H, $CH_{pyrrole}$), 7.24 (d, 2H, *J* = 8.1 Hz, ArH), 7.34 (d, 2H, *J* = 8.1 Hz, ArH), 7.66 (s, 1H, ArH), 7.94 (s, 1H, ArH). ^{13}C NMR (62 MHz, $CDCl_3$): δ = 15.4 (CH_3), 19.3 ($4CH_3$), 27.7, 27.8 (CH), 28.7 (CH_2), 31.4 (NCH_3), 71.4, 71.6 (CH_2O), 102.6, 111.1, 122.1 (CH), 124.2, 125.7, 128.2 (C), 128.2 (2CH), 129.0 (C), 129.3 (2CH), 138.2, 144.9, 145.2 (C), 168.8, 169.0 (CO). IR (KBr, cm^{-1}): *v* = 2959, 2930, 2872 (w), 1711 (s), 1610, 1494 (w), 1469 (m), 1429, 1394 (w), 1376, 1360, 1340 (m), 1254, 1232 (s), 1209, 1156 (m), 1104 (s), 1037, 1024, 986, 837, 783, 731 (m), 671, 626, 586, 546 (w). GC-MS (EI, 70 eV): *m/z* (%) = 435(84) $[M]^+$, 323(12), 307(20), 306(100), 233(14), 218(10). HRMS (EI, 70 eV): calcd for $C_{27}H_{33}NO_4$ $[M]^+$: 435.24041; found: 435.24055.

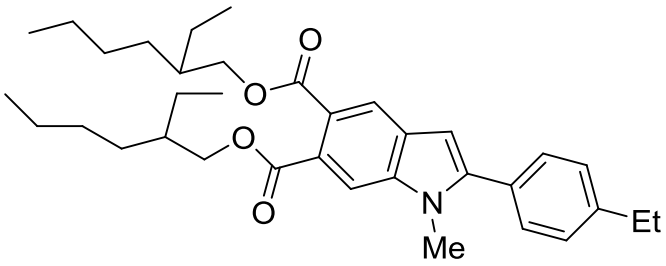
Dihexyl-2-(4-ethylphenyl)-1-methyl-1*H*-indole-5,6-dicarboxylate (50e):



Compound **50e** was prepared starting with **49e** (100 mg, 0.20 mmol), following the general procedure G, as a brown oil (89 mg, 90%). ^{1}H NMR (300 MHz, $CDCl_3$): δ = 0.82 (t, 6H, *J* = 7.0 Hz, $2CH_3$), 1.18-1.38 (m, 15H, $6CH_2$ and CH_3), 1.63-1.72 (m, 4H, $2CH_2$), 2.65 (q, 2H, *J* = 7.6 Hz, CH_2), 3.71 (s, 3H, NCH_3), 4.22 (t, 2H, *J* = 6.8 Hz, CH_2O), 4.24 (t, 2H, *J* = 6.8 Hz, CH_2O), 6.53 (s, 1H, $CH_{pyrrole}$), 7.24 (d, 2H, *J* = 8.2 Hz, ArH), 7.35 (dd, 2H, *J* = 1.8, 6.6 Hz, ArH), 7.66 (s, 1H, ArH), 7.92 (s, 1H, ArH). ^{13}C NMR (62 MHz, $CDCl_3$): δ = 14.0 ($2CH_3$), 15.4 (CH_3), 22.6 ($2CH_2$), 25.6, 25.7, 28.6 (CH_2), 28.7 ($2CH_2$), 31.4 (NCH_3), 31,5 ($2CH_2$), 65.5, 65.7 (CH_2O), 102.6, 111.1, 122.1 (CH), 124.2,

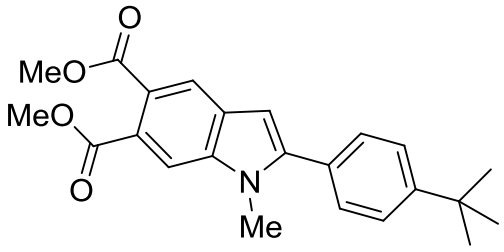
125.6 (C), 128.2 (2CH), 129.1 (C), 129.3 (2CH), 129.3, 138.2, 144.9, 145.1 (C), 168.9, 169.0 (CO). IR (KBr, cm^{-1}): ν = 2957, 2927 (m), 2856 (w), 1712 (s), 1611, 1494 (w), 1456 (m), 1430, 1379 (w), 1360, 1340 (m), 1253, 1233 (s), 1209, 1157 (m), 1104 (s), 1034, 1021 (m), 894 (w), 837, 784 (m), 726, 671, 586, 546 (w). GC-MS (EI, 70 eV): *m/z* (%) = 491(58) $[M]^+$, 407(13), 323(10), 307(18), 306(100), 305(42), 233(26), 218(11), 56(19), 55(15). HRMS (EI, 70 eV): calcd for $C_{31}H_{41}NO_4$ $[M]^+$: 491.30301; found: 491.30315.

Bis(2-ethylhexyl)-2-(4-ethylphenyl)-1-methyl-1*H*-indole-5,6-dicarboxylate (50g):



Compound **50g** was prepared starting with **49g** (100 mg, 0.18 mmol), following the general procedure G, as a brown oil (93 mg, 94%). ^{1}H NMR (300 MHz, $CDCl_3$): δ = 0.82 (t, 9H, *J* = 6.9 Hz, $3CH_3$), 0.86 (t, 6H, *J* = 7.5 Hz, $2CH_3$), 1.26-1.40 (m, 16H, $8CH_2$), 1.59-1.68 (m, 2H, 2CH), 2.65 (q, 2H, *J* = 7.6 Hz, CH_2), 3.71 (s, 3H, NCH_3), 4.14-4.18 (m, 4H, $2CH_2O$), 6.54 (s, 1H, $CH_{pyrrole}$), 7.24 (d, 2H, *J* = 8.1 Hz, ArH), 7.34 (d, 2H, *J* = 8.1 Hz, ArH), 7.65 (s, 1H, ArH), 7.92 (s, 1H, ArH). ^{13}C NMR (62 MHz, $CDCl_3$): δ = 11.0 ($2CH_3$), 14.1 ($2CH_3$), 15.4 (CH_3), 23.0 ($2CH_2$), 23.8 ($2CH_2$), 28.7 (CH_2), 29.0 ($2CH_2$), 30.5 ($2CH_2$), 31.4 (NCH_3), 38.7, 38.8 (CH), 67.8, 68.0 (CH_2O), 102.6, 111.1, 122.1 (CH), 124.3, 125.8 (C), 128.2 (2CH), 129.0, 129.1 (C), 129.3 (2CH), 138.2, 144.9, 145.1 (C), 168.8, 169.1 (CO). IR (KBr, cm^{-1}): ν = 2957, 2926 (m), 2857 (w), 1712 (s), 1611, 1563, 1494 (w), 1458, 1378, 1361, 1340 (m), 1257, 1232 (s), 1209, 1157 (m), 1104 (s), 1037, 1023 (m), 960, 896 (w), 837, 785 (m), 741, 671, 586, 547 (w). MS (EI, 70 eV): *m/z* (%) = 547(78) $[M]^+$, 435(17), 323(31), 307(22), 306(100), 305(31), 234(14), 233(30), 218(12), 70(16), 57(35). HRMS (ESI): calcd for $C_{35}H_{50}NO_4$ $[M+H]^+$: 548.3734; found: 548.3739.

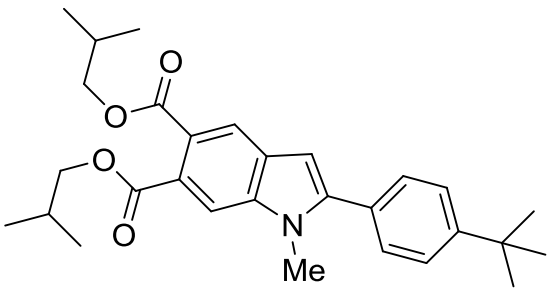
Dimethyl-2-(4-*tert*-butylphenyl)-1-methyl-1*H*-indole-5,6-dicarboxylate (50i):



Compound **50i** was prepared starting with **49i** (100 mg, 0.26 mmol), following the general procedure G, as a brown oil (69 mg, 70%). ^{1}H NMR (300 MHz, $CDCl_3$): δ = 1.31 (s, 9H, $3CH_3$), 3.73 (s, 3H, NCH_3), 3.84 (s, 3H, CH_3O), 3.86 (s, 3H, CH_3O), 6.54 (s, 1H, $CH_{pyrrole}$), 7.37 (d, 2H, *J* = 8.5 Hz, ArH), 7.44 (d, 2H, *J* = 8.5 Hz, ArH), 7.66 (s, 1H, ArH),

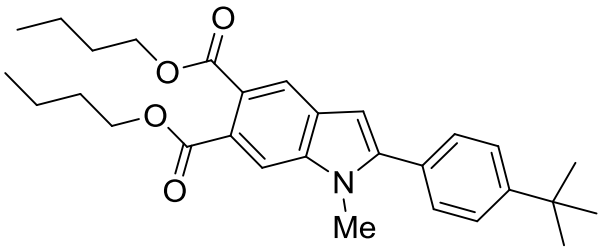
7.94 (s, 1H, ArH). ^{13}C NMR (62 MHz, $CDCl_3$): δ = 31.3 ($3CH_3$), 31.5 (NCH_3), 34.8 (C), 52.4, 52.5 (CH_3O), 102.7, 111.3, 122.2 (CH), 123.8, 124.9 (C), 125.6 (2CH), 128.7 (C), 129.1 (2CH), 129.2, 138.3, 145.3, 151.8 (C), 169.2, 169.3 (CO). IR (KBr, cm^{-1}): ν = 3141, 3033 (w), 2949 (m), 1714 (s), 1611, 1558, 1493 (w), 1432, 1404, 1361, 1340 (m), 1260, 1236 (s), 1190, 1157 (m), 1106 (s), 1042, 972 (m), 888 (w), 839, 783, 738 (m), 670,599, (w), 564 (m). GC-MS (EI, 70 eV): *m/z* (%) = 379(100) $[M]^+$, 365(12), 364(46), 348(31), 334(54), 153(13). HRMS (EI, 70 eV): calcd for $C_{23}H_{25}NO_4$ $[M]^+$: 379.17781; found: 379.17794.

Diisobutyl-2-(4-*tert*-butylphenyl)-1-methyl-1*H*-indole-5,6-dicarboxylate (50j):



Compound **50j** was prepared starting with **49j** (100 mg, 0.22 mmol), following the general procedure G, as a yellow oil (76 mg, 77%). ^{1}H NMR (300 MHz, $CDCl_3$): δ = 0.92 (d, 6H, J = 6.7 Hz, $2CH_3$), 0.93 (d, 6H, J = 6.7 Hz, $2CH_3$), 1.30 (s, 9H, $3CH_3$), 1.92-2.05 (m, 2H, 2CH), 3.72 (s, 3H, NCH_3), 4.02 (d, 2H, J = 6.7 Hz, CH_2O), 4.04 (d, 2H, J = 6.7 Hz, CH_2O), 6.54 (s, 1H, $CH_{pyrrole}$), 7.36 (d, 2H, J = 8.6 Hz, ArH), 7.44 (d, 2H, J = 8.6 Hz, ArH), 7.67 (s, 1H, ArH), 7.94 (s, 1H, ArH). ^{13}C NMR (62 MHz, $CDCl_3$): δ = 19.3 ($4CH_3$), 27.7, 27.8 (CH), 31.3 ($3CH_3$), 31.5 (NCH_3), 34.7 (C), 71.4, 71.6 (CH_2O), 102.6, 111.1, 122.1 (CH), 124.2 (C), 125.6 (2CH), 125.7, 128.8 (C), 129.1 (2CH), 129.1, 138.3, 145.1, 151.8 (C), 168.8, 169.0 (CO). IR (KBr, cm^{-1}): ν = 2957 (m), 2871 (w), 1712 (s), 1611, 1558, 1495 (w), 1468 (m), 1429, 1394 (w), 1376, 1361, 1340 (m), 1260, 1233 (s), 1210, 1157 (m), 1105 (s), 1037, 987 (m), 907 (w), 839, 783, 732 (m), 673, 626, 608 (w), 565 (m). GC-MS (EI, 70 eV): *m/z* (%) = 463(100) $[M]^+$, 407(12), 335(26), 334(64), 333(23), 247(12). HRMS (EI, 70 eV): calcd for $C_{29}H_{37}NO_4$ $[M]^+$: 463.27171; found: 463.27044.

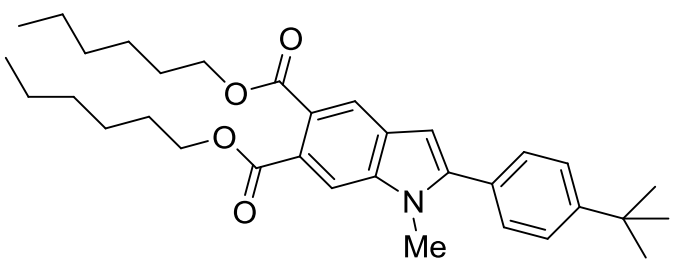
Dibutyl-2-(4-*tert*-butylphenyl)-1-methyl-1*H*-indole-5,6-dicarboxylate (50k):



Compound **50k** was prepared starting with **49k** (100 mg, 0.22 mmol), following the general procedure G, as a yellow oil (88 mg, 89%). ^{1}H NMR (250 MHz, $CDCl_3$): δ = 0.89 (t, 6H, J = 8.7 Hz, $2CH_3$), 1.29 (s, 9H, $3CH_3$), 1.33-1.42 (m, 4H, $2CH_2$), 1.61-1.72 (m, 4H, $2CH_2$), 3.71 (s, 3H, NCH_3), 4.23 (t, 2H, J = 6.7

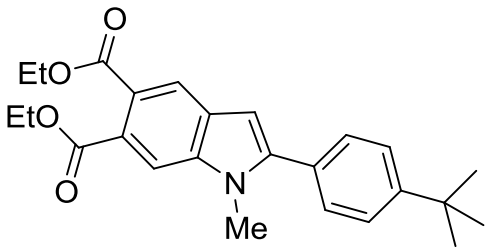
Hz, CH_2O), 4.25 (t, 2H, J = 6.7 Hz, CH_2O), 6.52 (s, 1H, $CH_{pyrrole}$), 7.36 (d, 2H, J = 8.4 Hz, ArH), 7.43 (d, 2H, J = 8.5 Hz, ArH), 7.65 (s, 1H, ArH), 7.92 (s, 1H, ArH). ^{13}C NMR (75 MHz, $CDCl_3$): δ = 12.8 ($2CH_3$), 18.2 ($2CH_2$), 29.6, 29.7 (CH_2), 30.3 ($3CH_3$), 30.5 (NCH_3), 33.7 (C), 64.1, 64.3 (CH_2O), 101.5, 110.1, 121.1 (CH), 123.2, 124.5 (C), 124.6 (2CH), 127.8 (C), 128.0 (2CH), 128.0, 137.2, 144.1, 150.7 (C), 167.8, 168.0 (CO). IR (KBr, cm^{-1}): v = 2956 (m), 2870 (w), 1711 (s), 1611, 1562, 1494 (w), 1475, 1461 (m), 1430, 1390 (w), 1360, 1339 (m), 1256, 1243 (s), 1209, 1157 (m), 1103 (s), 1060, 1036, 1004 (m), 962, 944, 896 (w), 839, 783, 736 (m), 672, 625, 602, 565 (w). GC-MS (EI, 70 eV): m/z (%) = 463(100) $[M]^+$, 448(13), 407(10), 355(14), 334(54), 318(13), 290(11). HRMS (EI, 70 eV): calcd for $C_{29}H_{37}NO_4$ $[M]^+$: 463.27171; found: 463.27286.

Dihexyl-2-(4-*tert*-butylphenyl)-1-methyl-1*H*-indole-5,6-dicarboxylate (50l):



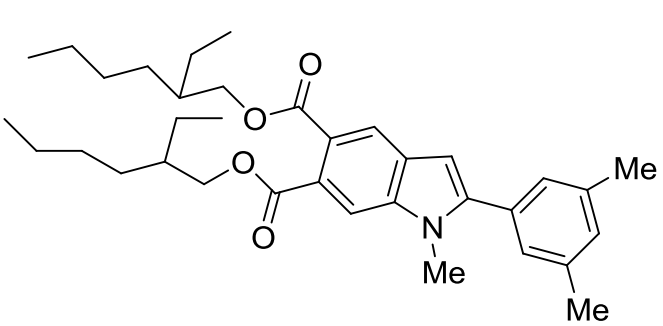
Compound **50l** was prepared starting with **49l** (100 mg, 0.19 mmol), following the general procedure G, as a brown oil (80 mg, 81%). ^{1}H NMR (300 MHz, $CDCl_3$): δ = 0.83 (t, 6H, J = 6.7 Hz, $2CH_3$), 1.24-1.31 (m, 21H, $6CH_2$ and $3CH_3$), 1.63-1.73 (m, 4H, $2CH_2$), 3.73 (s, 3H, NCH_3), 4.23 (t, 2H, J = 6.8 Hz, CH_2O), 4.25 (t, 2H, J = 6.8 Hz, CH_2O), 6.54 (s, 1H, $CH_{pyrrole}$), 7.37 (dd, 2H, J = 2.0, 6.6 Hz, ArH), 7.44 (dd, 2H, J = 2.1, 6.5 Hz, ArH), 7.67 (s, 1H, ArH), 7.93 (s, 1H, ArH). ^{13}C NMR (62 MHz, $CDCl_3$): δ = 14.0 ($2CH_3$), 22.6 ($2CH_2$), 25.7 ($2CH_2$), 28.6, 28.7 (CH_2), 31.3 ($3CH_3$), 31.4 (NCH_3), 31.5 ($2CH_2$), 34.7 (C), 65.5, 65.7 (CH_2O), 102.7, 111.1, 122.1 (CH), 124.2, 125.6 (C), 125.6 (2CH), 128.8, 129.1 (C), 129.1 (2CH), 138.3, 145.1, 151.8 (C), 168.9, 169.0 (CO). IR (KBr, cm^{-1}): v = 2953, 2927 (m), 2856 (w), 1712 (s), 1611, 1494 (w), 1458, 1361, 1340 (m), 1255, 1234 (s), 1157 (m), 1106 (s), 1077, 1021 (m), 894 (w), 839, 784 (m), 697, 565 (w). MS (EI, 70 eV): m/z (%) = 519(100) $[M^+]$, 335(10), 334(49), 69(15), 69(15), 43(28). HRMS (EI, 70 eV): calcd for $C_{33}H_{45}NO_4$ $[M]^+$: 519.33431; found: 519.33467.

Diethyl-2-(4-*tert*-butylphenyl)-1-methyl-1*H*-indole-5,6-dicarboxylate (50m):



Compound **50m** was prepared starting with **49m** (100 mg, 0.24 mmol), following the general procedure G, as brownish solid (74 mg, 75%), mp. 113-115 °C. ^{1}H NMR (250 MHz, $CDCl_3$): δ = 1.29-1.34 (m, 15H, $5CH_3$), 3.73 (s, 3H, NCH_3), 4.29 (q, 2H, J = 7.0 Hz, CH_2O), 4.30 (q, 2H, J = 7.1 Hz, CH_2O), 6.53 (s, 1H, $CH_{pyrrole}$), 7.37 (d, 2H, J = 8,4 Hz, ArH), 7.44 (d, 2H, J = 8,4 Hz, ArH), 7.68 (s, 1H, ArH), 7.94 (s, 1H, ArH). ^{13}C NMR (62 MHz, $CDCl_3$): δ = 13.2 ($2CH_3$), 30.2 ($3CH_3$), 30.5 (NCH_3), 33.7 (C), 60.2, 61.3 (CH_2O), 101.6, 110.2, 121.1 (CH), 123.2, 124.4 (C), 124.6 (2CH), 127.8 (C), 128.0 (2CH), 128.1, 137.3, 144.1, 150.8 (C), 167.8, 167.9 (CO). IR (KBr, cm^{-1}): ν = 2956 (m), 2853 (w), 1713 (s), 1611, 1560, 1494 (w), 1475, 1463 (m), 1430, 1392 (w), 1370, 1338 (m), 1255, 1235 (s), 1209, 1157 (m), 1103 (s), 1042, 1021 (m), 841, 784 (m), 737, 646, 604 (w), 566 (m). GC-MS (EI, 70 eV): *m/z* (%) = 407(100) $[M]^+$, 392(24), 334(30), 144(13). HRMS (EI, 70 eV): calcd for $C_{25}H_{29}NO_4$ $[M]^+$: 407.20911; found: 407.20967.

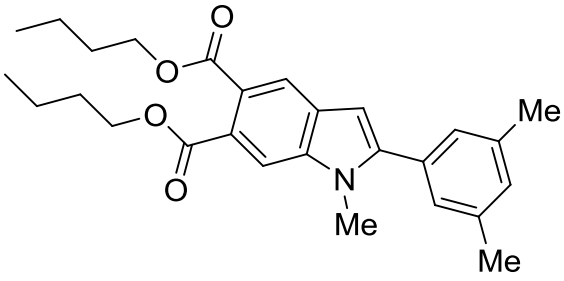
Bis(2-ethylhexyl)-2-(3,5-dimethylphenyl)-1-methyl-1*H*-indole-5,6-dicarboxylate (50n):



Compound **50n** was prepared starting with **49n** (100 mg, 0.18 mmol), following the general procedure G, as a brown oil (76 mg, 77%). ^{1}H NMR (300 MHz, $CDCl_3$): δ = 0.82 (t, 6H, J = 7.0 Hz, $2CH_3$), 0.86 (t, 6H, J = 7.5 Hz, $2CH_3$), 1.26-1.43 (m, 16H, $8CH_2$), 1.58-1.66 (m, 2H, 2CH), 2.31 (s, 6H, $2CH_3$), 3.70 (s, 3H, NCH_3), 4.13-4.18 (m, 4H, $2CH_2O$), 6.52 (s, 1H, $CH_{pyrrole}$), 7.00 (s, 1H, ArH), 7.03 (s, 2H, ArH), 7.65 (s, 1H, ArH), 7.92 (s, 1H, ArH). ^{13}C NMR (62 MHz, $CDCl_3$): δ = 11.0 ($2CH_3$), 14.1 ($2CH_3$), 21.3 ($2CH_3$), 23.0 ($2CH_2$), 23.8 ($2CH_2$), 28.9 ($2CH_2$), 30.5 ($2CH_2$), 31.4 (NCH_3), 38.7, 38.8 (CH), 67.8, 68.0 (CH_2O), 102.6, 111.1, 122.1 (CH), 124.3, 125.8 (C), 127.2 (2CH), 129.0 (C), 130.3 (CH), 131.6, 138.2 (C), 138.3 (2C), 145.3 (C), 168.8, 169.1 (CO). IR (KBr, cm^{-1}): ν = 2955, 2925 (m), 2857 (w), 1712 (s), 1602, 1536 (w), 1460, 1379, 1361, 1338 (m), 1257, 1228 (s), 1155 (m), 1104 (s), 1076, 1032 (m), 995, 959, 897 (w), 853, 785, 785, 731, 703 (m), 670, 642, 543 (w). GC-MS (EI, 70 eV): *m/z* (%) = 547(64) $[M]^+$, 324(21), 323(100), 307(88), 306(99), 290 (13), 279(19), 261(21), 250(13), 234(49), 222(18), 218(23), 208(15),

191(15), 116(10), 83(13), 70(26), 57(71), 43(21). HRMS (ESI): calcd for $C_{35}H_{50}NO_4$ $[M+H]^+$: 548.3734; found: 548.3744.

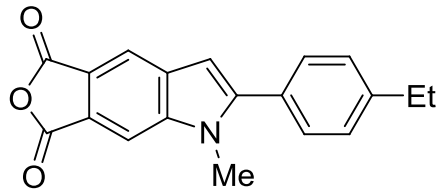
Dibutyl-2-(3,5-dimethylphenyl)-1-methyl-1*H*-indole-5,6-dicarboxylate (50o):



Compound **50o** was prepared starting with **49o** (100 mg, 0.23 mmol), following the general procedure G, as a brown oil (87 mg, 88%). ^{1}H NMR (300 MHz, $CDCl_3$): δ = 0.89 (t, 6H, J = 7.4 Hz, $2CH_3$), 1.32-1.44 (m, 4H, $2CH_2$), 1.60-1.71 (m, 4H, $2CH_2$), 2.31 (s, 6H, $2CH_3$), 3.70 (s, 3H, NCH_3), 4.23 (t, 2H, J = 6.7 Hz, CH_2O), 4.25 (t, 2H, J = 6.7 Hz, CH_2O), 6.51 (s, 1H, $CH_{pyrrole}$), 6.99 (s, 1H, ArH), 7.03 (s, 2H, ArH), 7.65 (s, 1H, ArH), 7.92 (s, 1H, ArH). ^{13}C NMR (75 MHz, $CDCl_3$): δ = 13.8 ($2CH_3$), 19.3 ($2CH_2$), 21.4 ($2CH_3$), 30.7, 30.8 (CH_2), 31.5 (NCH_3), 65.2, 65.4 (CH_2O), 102.7, 111.2, 122.1 (CH), 124.2, 125.6 (C), 127.2 (2CH), 129.1 (C), 130.3 (CH), 131.6, 138.3 (C), 138.3 (2C), 145.3 (C), 168.9, 169.0 (CO). IR (KBr, cm^{-1}): ν = 2956, 2930, 2871 (w), 1710 (s), 1601, 1534 (w), 1456, 1383, 1360, 1337 (m), 1255, 1224 (s), 1155 (m), 1104 (s), 1060, 1032 (m), 944, 897 (w), 852, 784, 733, 703, 669 (m), 642, 543 (w). GC-MS (EI, 70 eV): *m/z* (%) = 435(100) $[M]^+$, 307(22), 306(97), 305(12), 233(13). HRMS (EI, 70 eV): calcd for $C_{27}H_{33}NO_4$ $[M]^+$: 435.24041; found: 435.24084.

Synthesis of furo[3,4-*f*]indole (51):

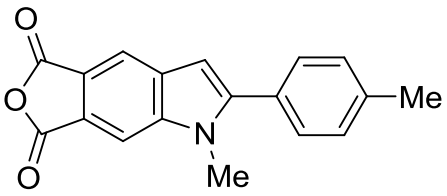
2-(4-Ethylphenyl)-1-methyl-1*H*-furo[3,4-*f*]indole-5,7-dione (51a):



Compound **51a** was prepared starting with **49q** (100 mg, 0.23 mmol), following the general procedure G, as yellowish oil (44 mg, 63%). ^{1}H NMR (300 MHz, $CDCl_3$): δ = 1.24 (t, 3H, J = 7.6 Hz, CH_3), 2.69 (q, 2H, J = 7.6 Hz, CH_2), 3.82 (s, 3H, NCH_3), 6.73 (s, 1H, $CH_{pyrrole}$), 7.30 (d, 2H, J = 8.2 Hz, ArH), 7.38 (dd, 2H, J = 1.8, 6.4 Hz, ArH), 7.88 (s, 1H, ArH), 8.12 (s, 1H, ArH). ^{13}C NMR (75 MHz, $CDCl_3$): δ = 15.4 (CH_3), 28.7 (CH_2), 31.9 (NCH_3), 104.5, 107.6, 118.8 (CH), 122.2, 123.2, 127.9 (C), 128.5 (2CH), 129.4 (2CH), 133.7, 141.3, 145.9, 148.1 (C), 164.3, 164.5 (CO). IR (KBr, cm^{-1}): ν = 3032, 2965, 2921, 2851 (w), 1829 (m), 1748 (s), 1594, 1587 (m), 1565, 1541 (w), 1485, 1459, 1435, 1401, 1357, 1260, 1241, 1209, 1165,

1135, 1021 (m), 878, 838, 802,736 (s), 717, 639, 632 (m), 584 (s), 542 (m). GC-MS (EI, 70 eV): *m/z* (%) = 305(100) $[M]^+$, 234(15), 233(80), 218(27), 109(12). HRMS (ESI): calcd for $C_{19}H_{16}NO_3$ $[M+H]^+$: 306.11247; found: 306.11168.

1-Methyl-2-*p*-tolyl-1H-furo[3,4-*f*]indole-5,7-dione (51b):

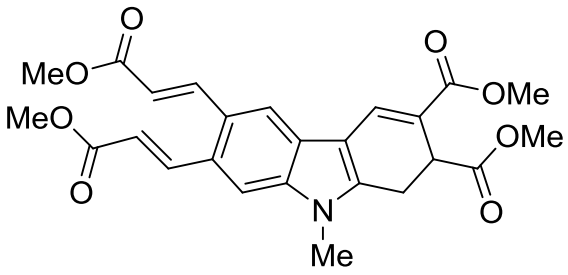


Compound **51b** was prepared starting with **49r** (100 mg, 0.24 mmol), following the general procedure G, as yellowish solid (51 mg, 72%), mp 240-242 °C. ^{1}H NMR (300 MHz, $CDCl_3$): δ = 2.39 (s, 3H, CH_3), 3.81 (s, 3H, NCH_3), 6.73 (s, 1H, $CH_{pyrrole}$), 7.28 (d, 2H, *J* = 8.0 Hz, ArH), 7.35 (d, 2H, *J* = 8.1 Hz, ArH), 7.87 (s, 1H, ArH), 8.11 (s, 1H, ArH). ^{13}C NMR (62 MHz, $CDCl_3$): δ = 20.4 (CH_3), 30.9 (NCH_3), 103.4, 106.6, 117.8 (CH), 121.1, 122.2, 126.7 (C), 128.3 (2CH), 128.6 (2CH), 132.6, 138.6, 140.2, 147.0 (C), 163.3, 163.5 (CO). IR (KBr, cm^{-1}): *v* = 3093, 3044, 2946, 2852 (w), 1828, 1805 (m), 1749 (s), 1693, 1588, 1481, 1463, 1434, 1401, 1359, 1261, 1135, 1059 (m), 889, 814, 785, 734 (s), 723, 712, 677 (m), 637 (s), 609 (m), 584 (s), 541 (m). GC-MS (EI, 70 eV): *m/z* (%) = 291(100) $[M]^+$, 220(16), 219(90), 218(15), 109(12). HRMS (ESI): calcd for $C_{18}H_{14}NO_3$ $[M+H]^+$: 292.09682; found: 292.09706.

General procedure H for synthesis of 2,3-dihydrocarbazoles (54), 2,3,5,6-tetraalkenyl-*N*-methylindole (56) and 2,3,4,5-tetraalkenyl-*N*-methylpyrrole (59):

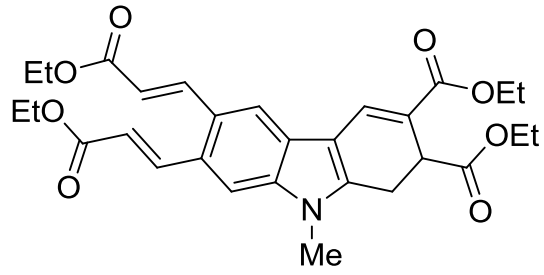
In a pressure tube (glass bomb) a suspension of $Pd(OAc)_2$ (12 mg, 0.05 mmol) and SPhos or $P(Cy)_3$ (10 mol %) in DMF (5 mL) was purged with argon and stirred at 20 °C to get a yellowish or brownish transparent solution. To the stirred solution were added the brominated indole **53** or pyrrole **58** (1.0 mmol), NEt_3 (1.1 mL, 8.0 mmol) and the alkene **26** (1.25 equiv per Br). The reaction mixture was stirred at 90-120 °C for 12-48 h. The solution was cooled to 20 °C, poured into H_2O and CH_2Cl_2 (25 mL each), and the organic and the aqueous layer were separated. The latter was extracted with CH_2Cl_2 (3×25 mL). The combined organic layers were washed with H_2O (3×20 mL), dried (Na_2SO_4), and concentrated *in vacuo*. The residue was purified by chromatography (flash silica gel, heptanes/EtOAc).

Dimethyl-6,7-bis[(*E*)-3-methoxy-3-oxoprop-1-enyl]-9-methyl-2,9-dihydro-1*H*-carbazole-2,3-dicarboxylate (54a):



Product **54a** was prepared starting with **53** (446 mg, 1.0 mmol), 2-ethylhexyl acrylate (0.5 mL, 5.0 mmol), $Pd(OAc)_2$ (11 mg, 5 mol %), SPhos (10 mol %), NEt_3 (1.10 mL, 8.0 mmol), DMF (5 mL) at 120 °C for 48 h following general procedure H, as a yellow highly viscous oil (316 mg, 68%). ^{1}H NMR (300 MHz, $CDCl_3$): δ = 3.01-3.61 (m, $2H_{\alpha/\beta}$, C-1), 3.52 (s, 3H, NCH_3), 3.62 (s, 3H, OCH_3), 3.71 (s, 6H, 2 OCH_3), 3.81 (s, 3H, OCH_3), 4.01 (br d, 1H, J = 7.2 Hz, C-2), 6.42 (d, 1H, J = 15.6 Hz, CH), 6.43 (d, 1H, J = 15.6 Hz, CH), 7.32 (s, 1H, ArH), 7.71 (s, 1H, ArH), 7.82 (s, 1H, CH), 8.02 (d, 1H, J = 15.8 Hz, CH), 8.03 (d, 1H, J = 15.7 Hz, CH). ^{13}C NMR (62 MHz, $CDCl_3$): δ = 23.9 (CH_2), 30.0 (NCH_3), 38.6 (C(4)H), 51.6, 51.7, 51.8, 52.6 (CH_3O), 108.5 (CH), 109.7 (C), 117.1 (CH), 117.3 (C), 119.1, 119.2 (CH), 126.4, 127.8, 128.3 (C), 131.4 (CH), 138.8 (C), 142.6, 142.7 (CH), 142.9 (C), 167.0, 167.1, 167.3, 173.4 (CO). IR (KBr, cm^{-1}): ν = 2950, 2921, 2851 (w), 1693, 1625, 1602, 1525, 1433, 1365 (s), 1310, 1271, 1228, 1189, 1162, 1088 (m), 1035, 972, 912, 919, 853, 802, 775, 725 (s). GC-MS (EI, 70 eV): *m*/*z* (%) = 467(75) [M^+], 434(38), 405(100), 374(59), 347(26), 316(15). HRMS (ESI): *m*/*z* calcd for $C_{25}H_{25}NNaO_8$ $[M+Na]^+$: 490.14724; found: 490.14693.

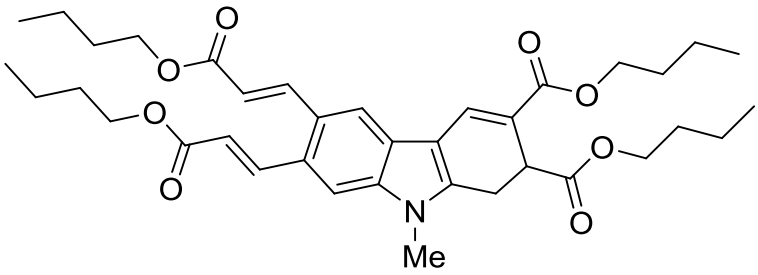
Diethyl-6,7-bis[(*E*)-3-ethoxy-3-oxoprop-1-enyl]-9-methyl-2,9-dihydro-1*H*-carbazole-2,3-dicarboxylate (54b):



Compound **54b** was synthesized starting with **53** (446 mg, 1.0 mmol), following general procedure H, as a yellow highly viscous oil (450 mg, 86%). ^{1}H NMR (250 MHz, $CDCl_3$): δ = 1.10 (t, 3H, J = 7.0 Hz, CH_3), 1.30 (t, 6H, J = 7.1 Hz, $2CH_3$), 1.30 (t, 3H, J = 7.0 Hz, CH_3), 3.00 (dd, $1H_\alpha$, J = 8.8, 17.1 Hz, H-1), 3.60 (dd, $1H_\beta$, J = 2.3, 17.1 Hz, H-1), 3.70 (s, 3H, NCH_3), 3.90-4.00 (m, 2H, CH_2O), 4.10 (dd, $1H_\alpha$, J = 2.6, 9.0 Hz, H-2), 4.20-4.30 (m, 6H, $3CH_2O$), 6.20 (d, 1H, J = 15.7 Hz, CH), 6.30 (d, 1H, J = 15.7 Hz, CH), 7.40 (s, 1H, ArH), 7.70 (s, 1H, ArH), 7.80 (s, 1H, H-4), 8.00 (d, 1H, J = 15.8 Hz, CH), 8.10 (d, 1H, J = 15.8 Hz, CH). ^{13}C NMR (62 MHz, $CDCl_3$): δ = 14.0 (CH_3), 14.3 ($2CH_3$), 14.5 (CH_3), 23.8 (CH_2), 30.0 (NCH_3), 38.8

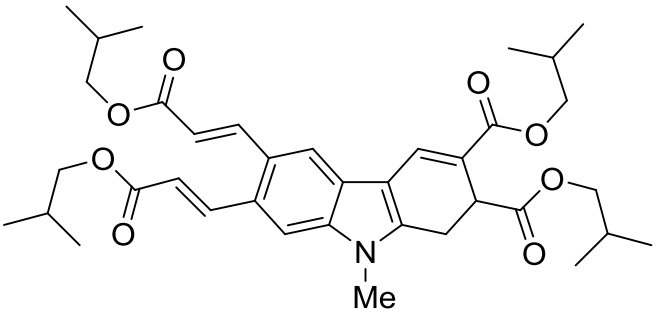
(CH, C-2), 60.4, 60.5, 60.5, 61.3 (CH_2O), 108.6 (CH), 109.8 (C), 117.3 (CH), 118.0 (C), 119.6, 119.8 (CH), 126.4, 127.9, 128.8 (C), 130.8 (CH), 138.8 (C), 142.5, 142.6 (CH), 142.7 (C), 166.6, 166.7, 166.9, 172.9 (CO). IR (KBr, cm^{-1}): ν = 2989, 2934, 2903 (w), 1694, 1625, 1604 9 (s), 1528, 1477, 1464, 1446, 1392, 1367 (m), 1274, 1220, 1158 (s), 1111, 1092, 1034, 973, 914, 855 (m), 777 (w), 727 (m), 660, 646, 612, 558 (w). GC–MS (EI, 70 eV): *m*/*z* (%) = 523(100) [M^+], 478(18), 450(88), 404(84), 375(23), 332(22), 303(34), 275(25), 231(51), 217(9). HRMS (EI, 70 eV): calcd for $C_{29}H_{33}NO_8$ [M^+]: 523.22062; found: 523.22073.

Dibutyl-6,7-bis[(*E*)-3-butoxy-3-oxoprop-1-enyl]-9-methyl-2,9-dihydro-1*H*-carbazole-2,3-dicarboxylate (54c):



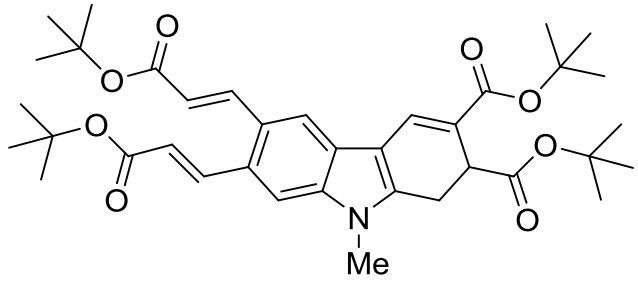
Product **54c** was prepared starting with **53** (446 mg, 1.0 mmol), *n*-butyl acrylate (0.70 mL, 5.0 mmol), $Pd(OAc)_2$ (11 mg, 5 mol %), SPhos (10 mol %), NEt_3 (1.10 mL, 8.0 mmol), DMF (5 mL) at 120 °C for 48 h following general procedure H, as a yellow highly viscous oil (450 mg, 71%). ^{1}H NMR (300 MHz, $CDCl_3$): δ = 0.9 (t, 3H, *J* = 7.2 Hz, CH_3), 0.9 (t, 3H, *J* = 7.4 Hz, CH_3), 0.9 (t, 6H, *J* = 7.3 Hz, $2CH_3$), 1.3-1.4 (m, 8H, $4CH_2$), 1.6–1.7 (m, 8H, $4CH_2$), 3.0 (dd, $1H_\alpha$, *J* = 8.5, 17.3, Hz, C-1), 3.6 (dd, $1H_\beta$, *J* = 2.0, 17.2 Hz, C-1), 3.7 (s, 3H, NCH_3), 4.0 (dd, 1H, *J* = 2.0, 8.8 Hz, C-2), 4.1 (t, 4H, *J* = 6.7 Hz, $2CH_2O$), 4.2 (t, 4H, *J* = 6.7 Hz, $2CH_2O$), 6.2 (d, 1H, *J* = 15.5 Hz, CH), 6.3 (d, 1H, *J* = 16.4 Hz, CH), 7.4 (s, 1H, ArH), 7.8 (s, 1H, ArH), 7.8 (s, 1H, C-4), 8.0 (d, 1H, *J* = 16.4 Hz, CH), 8.0 (d, 1H, *J* = 15.5 Hz, CH). ^{13}C NMR (62 MHz, $CDCl_3$): δ = 13.6 (CH_3), 13.7 ($2CH_3$), 13.8 (CH_3), 18.9 (CH_2), 19.2 ($2CH_2$), 19.3 (CH_2), 23.8 (CH_2), 30.0 (NCH_3), 30.4 (CH_2), 30.8 ($2CH_2$), 30.9 (CH_2), 38.8 (CH, C-2), 64.4 (CH_2O), 64.5 ($2CH_2O$), 65.2 (CH_2O), 108.6 (CH), 109.9 (C), 117.4 (CH), 118.2 (C), 119.7, 119.9 (CH), 126.4, 128.0, 128.5 (C), 130.7 (CH), 138.8 (C), 142.6, 142.7 (CH) 142.8 (C), 166.7, 166.8, 167.0, 172.9 (CO). IR (KBr, cm^{-1}): ν = 2932 (w), 1698, 1624, 1604, 1528 (s), 1464 (m), 1700, 1622 (s), 1548, 1380, 1287, 1274, 1243, 1213 (m), 1168 (s), 1062, 1025, 965, 864 (m), 780, 738, 721, 549 (w). MS (EI, 70 eV): *m*/*z* (%) = 635(12) [$M]^+$, 591(2), 531(7), 380(24), 379(100), 304(5), 215(20), 67(12). HRMS: *m*/*z* calcd for $C_{37}H_{49}NO_8$ [$M]^+$: 635.34527; found: 635.34556.

Di(isobutyl)-6,7-bis[(*E*)-3-isobutoxy-3-oxoprop-1-enyl]-9-methyl-2,9-dihydro-1*H*-carbazole-2,3-dicarboxylate (54d):



Compound **54d** was synthesized starting with **53** (455 mg, 1.0 mmol) and *iso*-butyl acrylate (0.72 mL, 5.0 mmol) following general procedure H, as a yellow highly viscous oil (455 mg, 72%). ^{1}H NMR (250 MHz, $CDCl_3$): δ = 0.70 (d, 6H, J = 6.9 Hz, $2CH_3$), 0.90-1.00 (m, 18H, $6CH_3$), 1.70-1.80 (m, 3H, CH), 1.90-2.00 (m, 1H, CH), 3.00 (dd, $1H_\alpha$, J = 8.6, 17.2 Hz, H-1), 3.60 (dd, $1H_\beta$, J = 1.8, 17.3 Hz, H-1), 3.60-3.70 (m, 5H, NCH_3 and CH_2O), 3.90-4.00 (m, 6H, $3CH_2O$), 4.00-4.10 (dd, $1H_\alpha$, J = 1.6, 8.4 Hz, H-2), 6.20 (d, 1H, J = 15.6 Hz, CH), 6.30 (d, 1H, J = 15.6 Hz, CH), 7.40 (s, 1H, ArH), 7.70 (s, 1H, ArH), 7.80 (s, 1H, H-4), 8.10 (d, 2H, J = 15.6 Hz, CH). ^{13}C NMR (75 MHz, $CDCl_3$): δ = 18.7 (CH_3), 18.8 (CH_3), 19.2 ($4CH_3$), 19.3 ($2CH_3$), 23.7 (CH_2), 27.6 (CH), 27.8 (2CH), 27.9 (CH), 30.0 (NCH_3), 38.7 (CH, C-2), 70.5, 70.6, 70.7, 71.2 (CH_2O), 108.6 (CH), 109.8 (C), 117.3 (CH), 118.2 (C), 119.6, 119.8 (CH), 126.4, 127.9, 128.3 (C), 130.5 (CH), 138.8 (C), 142.5, 142.6 (CH), 142.9 (C), 166.6, 166.7, 166.9, 172.8 (CO). IR (KBr, cm^{-1}): ν = 2958, 2932, 2873 (w), 1702, 1692 (s), 1623, 1605, 1528, 1483, 1468, 1393, 1375, 1342, 1287, 1271 (m), 1219, 1163 (s), 1084, 1035, 980 (m), 945, 908, 884, 863, 778, 729, 645, 613, 572 (w). GC-MS (EI, 70 eV): m/z (%) = 635(100) [M^+], 578(27), 498(55), 409(43), 375(32), 333(51), 288(16), 275(33), 196(22), 173(77). HRMS (EI, 70 eV): calcd for $C_{37}H_{49}NO_8$ [M^+]: 635.34582; found: 635.34571.

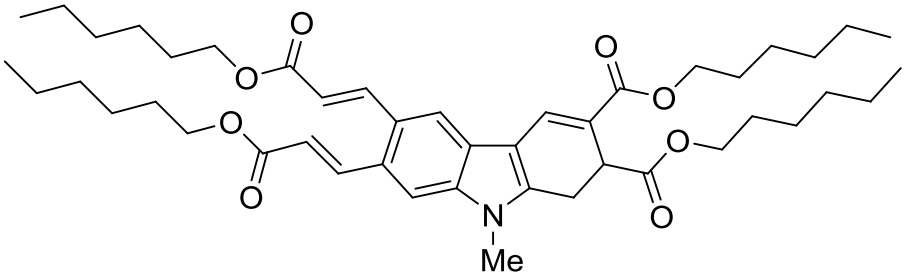
Di(*tert*-butyl)-6,7-bis[(*E*)-3-*tert*-butoxy-3-oxoprop-1-enyl]-9-methyl-2,9-dihydro-1*H*-carbazole-2,3-dicarboxylate (54e):



Compound **54e** was synthesized starting with **53** (446 mg, 1.0 mmol), following general procedure H, as a yellow highly viscous oil (463 mg, 72%). ^{1}H NMR (250 MHz, $CDCl_3$): δ = 1.30 (s, 9H, $3CH_3$), 1.50 (s, 18H, $6CH_3$), 1.50 (s, 9H, $3CH_3$), 3.00 (dd, $1H_\alpha$, J = 8.9, 17.2 Hz, H-1), 3.50 (dd, $1H_{\beta,}$, J = 2.2, 17.2 Hz, H-1), 3.70 (s, 3H, NCH_3), 3.90 (dd, $1H_\alpha$, J = 2.2, 8.6 Hz, H-2), 6.20 (d, 1H, J = 15.5 Hz, CH), 6.30 (d, 1H, J

= 15.5 Hz, CH), 7.40 (s, 1H, ArH), 7.70 (s, 1H, ArH), 7.80 (s, 1H, H-4), 7.90 (d, 1H, J = 15.7 Hz, CH), 8.00 (d, 1H, J = 15.7 Hz, CH). ^{13}C NMR (75 MHz, $CDCl_3$): δ = 23.6 (CH_2), 27.9 ($3CH_3$), 28.1 (CH_3), 28.3 ($6CH_3$), 28.4 ($2CH_3$), 30.0 (NCH_3), 39.5 (C(2)H), 80.1, 80.4, 80.5, 81.3 (C), 108.4 (CH), 109.7 (C), 117.2 (CH), 120.3 (C), 121.3, 121.6 (CH), 126.4, 127.9, 128.4 (C), 129.3(CH), 138.7 (C), 141.8, 141.9 (CH), 142.6 (C), 166.0, 166.1, 166.4, 172.1 (CO). IR (KBr, cm^{-1}): v = 2977, 2929 (w), 1713 (s), 1611, 1530, 1478, 1455, 1392, 1367, 1285, 1256, 1221 (m), 1152 (s), 1089, 979, 847, 794, 530 (w). MS (EI, 70 eV): m/z (%) = 635(15) [M^+], 634(10), 577(46), 562(100), 259(25), 225(50), 181(97), 63(37). HRMS (EI, 70 eV): calcd for $C_{37}H_{49}NO_8$ [M^+]: 635.34582; found: 635.34535.

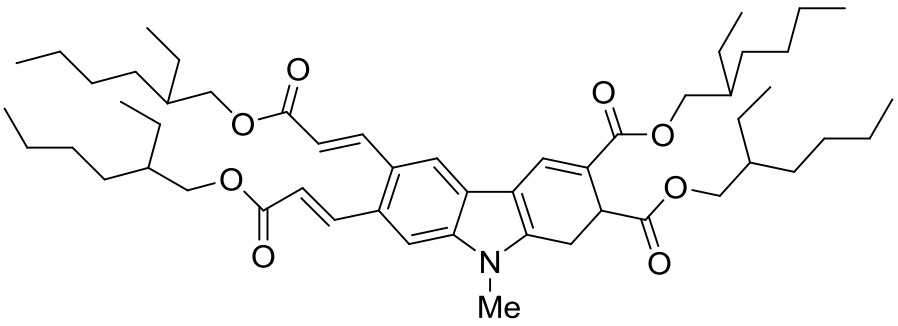
Dihexyl-6,7-bis[(*E*)-3-(hexyloxy)-3-oxoprop-1-enyl]-9-methyl-2,9-dihydro-1*H*-carbazole-2,3-dicarboxylate (54f):



Product **54f** was prepared starting with **53** (446 mg, 1.0 mmol), *n*-hexyl acrylate (0.9 mL, 5.0 mmol), $Pd(OAc)_2$ (11 mg, 5 mol %), SPhos (10 mol %), NEt_3 (1.10 mL, 8.0 mmol), DMF (5 mL) at 120 °C for 48 h following general procedure H, as a yellow highly viscous oil (598 mg, 80%). ^{1}H NMR (300 MHz, $CDCl_3$): δ = 0.81-0.93 (m, 12H, CH_3), 1.32-1.41 (m, 16H, $8CH_2$), 1.61-1.72 (m, 16H, $8CH_2$), 3.00 (dd, $1H_\alpha$, J = 8.5, 17.1 Hz, C-1); 3.61 (dd, $1H_\beta$, J = 2.1, 17.1 Hz, C-1), 3.82 (s, 3H, NCH_3), 3.91 (dd, $1H_\alpha$, J = 1.7, 6.7 Hz, C-2), 4.12-4.22 (m, 8H, $4CH_2O$), 6.31 (d, 2H, J = 16.0 Hz, CH), 7.30 (s, 1H, ArH), 7.49 (s, 1H, ArH), 8.01 (s, 1H, C-4), 8.02 (d, 2H, J = 16.0 Hz, CH). ^{13}C NMR (62.9 MHz, $CDCl_3$): δ = 14.0 ($4CH_3$), 22.5 ($4CH_2$), 25.7 ($3CH_2$), 28.4 (CH_2), 28.7 ($2CH_2$), 28.8, 29.7 (CH_2), 30.1 (NCH_3), 31.2 (CH_2), 31.5 ($3CH_2$), 31.6 (CH_2), 33.3 (C(2)H), 64.5, 64.8, 64.8, 65.4 (CH_2O), 108,9 (CH), 109.6, 112.8 (C), 120.0, 120.4, 120.5 (CH), 127.4, 128.1, 129.6 (C), 136.6 (CH), 138.6, 138.7 (C), 142,5, 142.6 (CH), 166.6, 166.8, 168.0, 172.8 (CO). IR (KBr, cm^{-1}): v = 2953, 2926, 2856 (w), 1701, 1622, 1605 (s), 1551, 1527, 1465, 1455, 1378, 1337 (w), 1242 (m), 1159 (s), 973, 908, 849, 728, 674, 648, 605 (w). MS (EI, 70 eV): m/z (%) = 747(10) [M^+], 596(11), 595(31),

594(37), 595(100), 492(20), 465(16), 464(33), 463(68), 407(07), 380(30), 362(35), 336(13), 355(18), 278(13), 251(13), 234(23). HRMS: *m*/*z* calcd for $C_{45}H_{65}NO_8$ [M^+]: 747.47047; found: 747.46850.

Bis(2-ethylhexyl)-6,7-bis[(*E*)-3-(2-ethylhexyloxy)-3-oxoprop-1-enyl]-9-methyl-2,9-dihydro-1*H*-carbazole-2,3-dicarboxylate (54g):

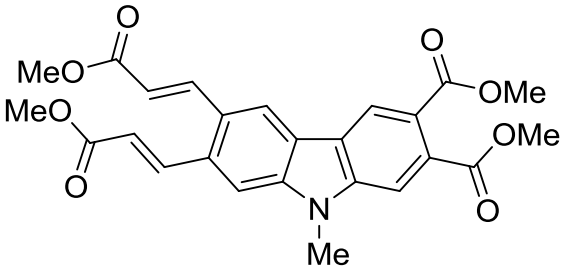


Product **54g** was prepared starting with **53** (446 mg, 1.0 mmol), 2-ethylhexyl acrylate (1.10 mL, 5.0 mmol), $Pd(OAc)_2$ (11 mg, 5 mol %), SPhos (10 mol %), NEt_3 (1.10 mL, 8.0 mmol), DMF (5 mL) at 120 °C for 48 h following general procedure H, as a yellow highly viscous oil (618 mg, 72%). ^{1}H NMR (300 MHz, $CDCl_3$): δ = 0.82-0.93 (m, 24H, $8CH_3$), 1.21-1.43 (m, 32H, Aliphatic), 1.51-1.62 (m, 4H, CH-aliphatic), 2.98-3.06 (m, $1H_\alpha$, C-1), 3.58-3.64 (m, $1H_\beta$, C-1), 3.71 (s, 3H, NCH_3), 3.82 (m, $1H_\alpha$, C-2), 4.12 (dd, 8H, J = 2.4, 5.8 Hz, $4CH_2O$), 6.32 (d, 1H, J = 15.7 Hz, CH), 6.33 (d, 1H, J = 15.7 Hz, CH), 7.41 (s, 1H, ArH), 7.72 (s, 1H, ArH), 7.83 (s, 1H, C(4)), 8.01 (d, 1H, J = 15.7 Hz, CH), 8.12 (d, 1H, J = 15.7 Hz, CH). ^{13}C NMR (62 MHz, $CDCl_3$): δ = 10.9 (CH_3), 11.0 ($3CH_3$), 14.1 ($4CH_3$), 23.0 ($5CH_2$), 23.9 ($4CH_2$), 29.0 ($4CH_2$), 29.7 ($2CH_2$), 30.1 (NCH_3), 30.5 ($2CH_2$), 31.2, 38.6, 38.7 (CH), 38.9 (CH(2)), 38.9 (CH), 67.0, 67.1, 67.3, 67.5 (CH_2O), 108.6 (CH), 110.0 (C), 117.3 (CH), 118.0 (C), 119.7, 120.0 (CH), 126.4, 128.0, 128.5 (C), 130.5 (CH), 138.8 (C), 142.5, 142.6 (CH), 142.8 (C), 166.8, 166.9, 167.0, 173.0 (CO). IR (KBr, cm^{-1}): ν = 2928, 2925, 2858 (w), 1703 (s), 1631, 1605, 1528, 1460, 1380, 1265, 1220 (m), 1161 (s), 1113, 1085, 1031, 974 (m), 852, 773, 730, 695, 645, 609 (w). MS (EI, 70 eV): *m*/*z* (%) = 859(12) [M^+], 699(10), 590(11), 588(11), 572(11), 460(5), 83(20), 71(22), 70(11), 69(16), 57(100), 44(93). HRMS: *m*/*z*calcd for $C_{53}H_{81}NO_8$ [M^+]: 859.596901; found: 859.59567.

General procedure I for the transformation of 1,2-dihydrocarbazoles (54) to carbazoles (55):

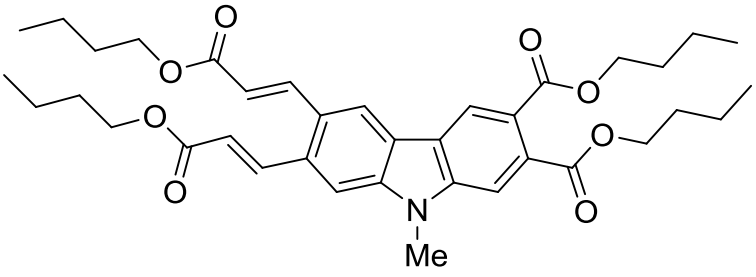
To solution of xylene (5 mL) were added the 1,2-dihydrocarbazole (**54**) (0.25 mmol) and Pd/C (10 mg, 10 mol %). The solution was stirred under reflux for 48 h under argon atmosphere. The reaction mixture was filtered and the filtrate was concentrated *in vacuo.*

Dimethyl-6,7-bis[(*E*)-3-methoxy-3-oxoprop-1-enyl]-9-methyl-9*H*-carbazole-2,3-dicarboxylate (55a):



Compound **55a** was synthesized starting with **54a** (100 mg, 0.22 mmol), following general procedure I, as a yellow highly viscous oil (99 mg, 100%). ^{1}H NMR (300 MHz, $CDCl_3$): δ = 3.54 (s, 3H, CH_3), 3.64 (s, 3H, CH_3), 3.74 (s, 6H, $2CH_3$), 3.77 (s, 3H, CH_3), 6.3 (d, 1H, J = 15.6 Hz, CH), 6.4 (d, 1H J = 16.3 Hz, CH), 7.4 (s, 1H, ArH), 7.5 (s, 1H, ArH), 8.0 (d, 1H, J = 15.6 Hz, CH), 8.1 (d, 1H, J = 15.6 Hz, CH), 8.5 (s, 2H, ArH). ^{13}C NMR (75 MHz, $CDCl_3$): δ = 29.6 (NCH_3), 52.5, 52.6, 52.8, 52.9 (CH_3O), 107.9, 109.4, 119.6, 120.2, 122.7, 122.9 (CH), 123.1, 123.8, 124.5, 125.5, 126.0, 126.9, 128.9, 133.7 (C), 142.0, 142.4 (CH), 166.7, 167.1, 167.8, 169.4 (CO). IR (KBr, cm^{-1}): v = 3089 (w), 1652 (s), 1455, 1277 (m), 1097, 1060 (s), 912 (w), 845, 798, 699 (s). GC-MS (EI, 70 eV): m/z (%) = 465(53) [M^+], 434(31), 405(100), 374(83). HRMS: m/z calcd for $C_{25}H_{23}NO_8$ [M^+]: 465.14181; found: 465.141506.

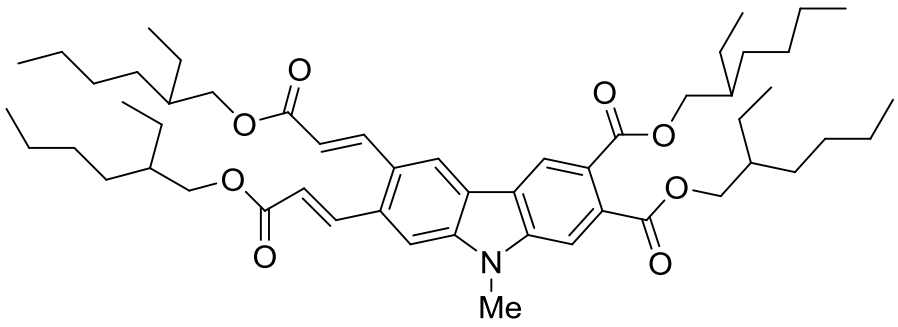
Dibutyl-6,7-bis[(*E*)-3-butoxy-3-oxoprop-1-enyl]-9-methyl-9*H*-carbazole-2,3-dicarboxylate (55c):



Compound **55c** was synthesized starting with **54c** (100 mg, 0.16 mmol), following general procedure I, as a yellow highly viscous oil (98 mg, 100%). ^{1}H NMR (300 MHz, $CDCl_3$): δ = 0.9 (t, 3H, J =7.3 Hz, CH_3), 0.9 (t, 3H, J = 7.3 Hz, CH_3), 0.9 (t, 3H, J = 7.5 Hz, CH_3), 0.9 (t, 3H, J = 7.3 Hz, CH_3), 1.3-1.4 (m, 8H, $4CH_2$), 1.6-1.7 (m, 8H, $4CH_2$), 3.7 (s, 3H, NCH_3), 4.1 (t, 4H, J = 6.7 Hz, $2CH_2O$), 4.2 (t, 2H, J = 7.1 Hz, CH_2O), 4.3 (t, 2H, J = 6.9 Hz, CH_2O), 6.3

(d, 1H, J = 15.9 Hz, CH), 6.4 (d, 1H, J = 15.9 Hz, CH), 7.4 (s, 1H, ArH), 7.4 (s, 1H, ArH), 8.0 (d, 1H, J = 15.2 Hz, CH), 8.1 (d, 1H, J = 15.8 Hz, CH), 8.1 (s, 1H, ArH), 8.3 (s, 1H, ArH). ^{13}C NMR (75.5 MHz, $CDCl_3$): δ = 13.7 ($3CH_3$), 13.7 (CH_3), 19.2 (CH_2), 19.2 ($2CH_2$), 19.3 (CH_2), 29.5 (NCH_3), 30.6 (CH_2), 30.7 ($2CH_2$), 30.8 (CH_2), 64.5, 64.6, 65.4, 65.8 (CH_2O), 107.7, 109.2, 119.8, 120.0, 121.8, 122.5 (CH), 122.5, 122.9, 123.6, 126.8, 132.4, 133.6 (C), 141.6, 142.0 (CH), 142.7 (2C), 166.3, 166.7, 167.2, 168.9 (CO). IR (KBr, cm^{-1}): ν = 2957, 2932, 2872 (w), 1705 (s), 1623, 1596, 1561, 1463 (m), 1387, 1341 (w), 1262, 1226, 1162, 1107 (s), 1080, 1063, 1021, 967 (m), 906, 856, 774, 737, 713, 659, 618, 594 (w). MS (EI, 70 eV): m/z (%) = 633(24) [M^+], 560(09), 531(69), 507(100), 458(29), 378(41), 302(28). HRMS (ESI): m/z calcd for $C_{37}H_{48}NO_8$ $[M+H]^+$: 634.33744; found: 634.33799.

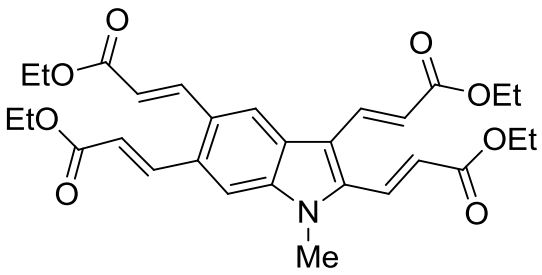
Bis(2-ethylhexyl)-6,7-bis[(*E*)-3-(2-ethylhexyloxy)-3-oxoprop-1-enyl]-9-methyl-9*H*-carbazole-2,3-dicarboxylate (55g):



Compound **55g** was synthesized starting with **54g** (100 mg, 0.12 mmol), follow ing general proce dure I, as a yellow highly viscous oil (99 mg, 100%). ^{1}H NMR (300 MHz, $CDCl_3$): δ = 0.8-0.9 (m, 24H, $8CH_3$), 1.2-1.4 (m, 32H, CH-aliphatic), 1.6-1.7 (m, 4H, aliphatic), 3.9 (s, 3H, NCH_3), 4.1 (dd, 4H, J = 2.6, 5.7 Hz, $2CH_2O$), 4.2 (dd, 4H, J = 2.6, 5.7 Hz, $2CH_2O$), 6.4 (d, 1H, J = 15.7 Hz, CH), 6.4 (d, 1H, J = 15.7 Hz, CH), 7.5 (s, 1H, ArH), 7.6 (s, 1H, ArH), 8.1 (d, 1H, J = 15.7 Hz, CH), 8.2 (d, 1H, J = 15.8 Hz, CH), 8.3 (s, 1H, ArH), 8.5 (s, 1H, ArH). ^{13}C NMR (62.9 MHz, $CDCl_3$): δ = 10.9 ($3CH_3$), 11.0 (CH_3), 14.1 ($4CH_3$), 23.0 ($2CH_2$), 23.7 ($2CH_2$), 23.8 ($2CH_2$), 23.9 ($2CH_2$), 28.9 ($2CH_2$), 29.0 ($2CH_2$), 29.6 (NCH_3), 30.4 ($2CH_2$), 30.5 ($2CH_2$), 30.9, 38.5, 38.7, 38.8, (CH), 67.1, 67.3, 68.1, 68.5 (CH_2O), 107.8, 109.4, 120.1, 120.3, 122.0, 122.7 (CH), 122.9, 123.1, 123.8, 127.0, 132.7, 133.8 (C), 141.8, 142.2 (CH), 142.8, 142.9 (C), 166.5, 166.8, 167.4, 169.1 (CO). IR (KBr, cm^{-1}): ν = 2927(w), 1712, 1624, 1601, 1562, 1459, 1379, 1260, 1229, 1165, 1108, 1081, 1015, 975, 858, 774, 726, 615 (s). GC-MS (EI^+, 70 eV): m/z (%) = 857(23) [M^+], 699(23), 588(27), 346(18), 302(29). HRMS: m/z calcd for $C_{53}H_{79}NO_8$ [M^+]: 857.5806; found: 857.5803.

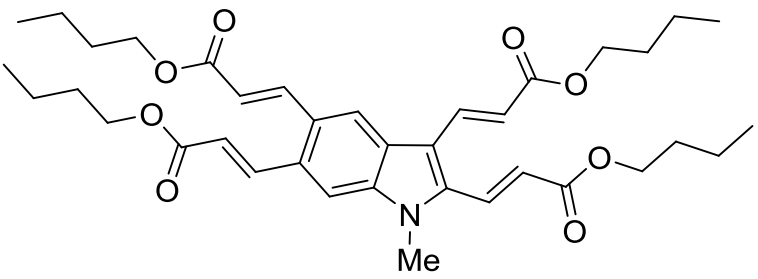
Synthesis of 2,3,5,6-tetra(alkenyl)-*N*-methylindoles (56):

(2*E*,2′*E*,2″*E*,2‴*E*)-Tetraethyl-3, 3′,3″,3‴-(1-methyl-1*H*-indole-2,3,5,6-tetrayl) tetraacrylate (56b):



Product 56b was prepared starting with 53 (446 mg, 1.0 mmol), ethyl acrylate (0.6 mL, 5.0 mmol), Pd(OAc)2 (11 mg, 5 mol %), SPhos (10 mol %), NEt_3 (1.10 mL, 8.0 mmol), DMF (5 mL) at 90 °C for 36 h following general procedure H, as a yellow highly viscous oil (397 mg, 76%). ^{1}H NMR (300 MHz, $CDCl_3$): δ = 1.3 (t, 6H, J = 6.8 Hz, $2CH_3$), 1.3 (t, 6H, J = 7.0 Hz, $2CH_3$), 3.8 (s, 3H, NCH_3), 4.2-4.3 (m, 8H, $4CH_2O$), 6.2 (d, 1H, J = 15.8 Hz, CH), 6.3 (d, 1H, J = 15.7 Hz, CH), 6.3 (d, 1H, J = 15.4 Hz, CH), 6.4 (d, 1H, J = 16.0 Hz, CH), 7.4 (s, 1H, ArH), 7.8 (d, 1H, J = 16.0 Hz, CH), 7.9 (d, 1H, J = 16.0 Hz, CH), 8.0 (s, 1H, ArH), 8.0 (d, 1H, J = 15.8 Hz, CH), 8.1 (d, 1H, J = 15.8 Hz, CH). ^{13}C NMR (62 MHz, $CDCl_3$): δ = 13.2 (CH_3), 13.3 ($2CH_3$), 13.4 (CH_3), 30.4 (NCH_3), 59.5, 59.6, 59.7, 60.2 (CH_2O), 107.9 (CH), 113.2 (C), 116.7, 119.4, 119.7, 120.1, 125.1, (CH), 125.7, 127.8 (C), 129.3 (CH), 130.0 (C), 134.7 (CH), 138.1, 138.4 (C), 141.2, 141.3 (CH), 164.7, 165.4, 165.6, 166.5 (CO). IR (KBr, cm^{-1}): v = 2979, 2930, 2872 (w), 1704, 1613 (s), 1463, 1445, 1367 (m), 1259, 1160, 1093, 1028, 974, 855 (s), 809, 785, 770, 727, 702, 607 (m). GC-MS (EI, 70 eV): m/z (%) = 523(100) [M^+], 477(18), 452(88), 402(84), 375(23), 350(70). HRMS: m/z calcd for $C_{29}H_{33}NO_8$ [M^+]: 523.22062; found: 523.22073.

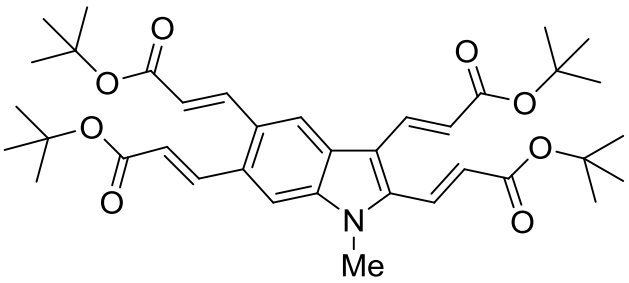
(2*E*,2′*E*,2″*E*,2‴*E*)-Tetrabutyl-3,3′,3″,3‴-(1-methyl-1*H*-indole-2,3,5,6-tetrayl)tetraacrylate (56c):



Product **56c** was prepared starting with **53** (446 mg, 1.0 mmol), *n*-butyl acrylate (0.70 mL, 5.0 mmol), $Pd(OAc)_2$ (11 mg, 5 mol %), SPhos (10 mol %), NEt_3 (1.10 mL, 8.0 mmol), DMF (5 mL) at 90 °C for 36 h following general procedure I, as a yellow highly viscous oil (450 mg, 71%). ^{1}H NMR (300 MHz, $CDCl_3$): δ = 0.8-0.9 (m, 12H, $4CH_3$), 1.3-1.5 (m, 8H, $4CH_2$), 1.6-1.7 (m, 8H, $4CH_2$), 3.7 (s, 3H, NCH_3), 4.1 (t, 4H, J = 6.9 Hz, $2CH_2O$), 4.2 (t,

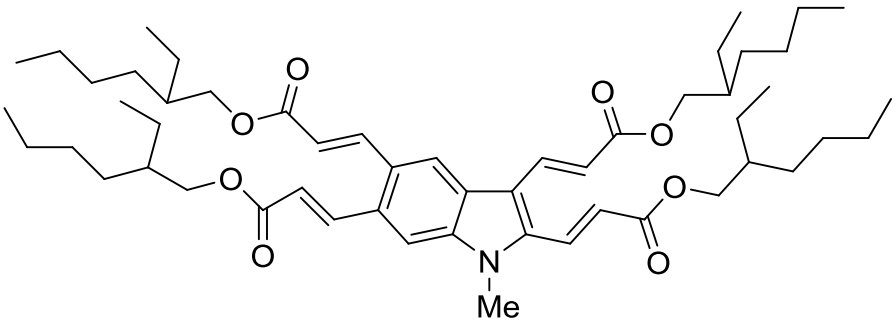
4H, *J* = 6.9 Hz, $2CH_2O$), 6.2 (d, 1H, *J* = 16.4 Hz, CH), 6.2 (d, 1H, *J* = 15.4 Hz, CH), 6.3 (d, 1H, *J* = 15.8 Hz, CH), 6.4 (d, 1H, *J* = 16.2 Hz, CH), 7.4 (s, 1H, ArH), 7.7 (d, 1H, *J* = 16.2 Hz, CH), 7.8 (d, 1H, *J* = 16.2 Hz, CH), 7.9 (s, 1H, ArH), 8.0 (d, 1H, *J* = 15.4 Hz, CH), 8.0 (d, 1H, *J* = 15.4 Hz, CH). ^{13}C NMR (75.5 MHz, $CDCl_3$): δ = 13.7 (CH_3), 13.7 ($2CH_3$), 13.8 (CH_3), 19.1, 19.1, 19.2, 19.2, 30.6, 30.7, 30.8, 30.8 (CH_2), 31.4 (NCH_3), 64.4, 64.5, 64.5, 65.0 (CH_2O), 108.9 (CH), 114.1 (C), 117.6, 120.3, 120.6, 121.0, 125.9 (CH), 126.6, 128.6 (C), 130.3 (CH), 130.9 (C), 135.5 (CH), 139.0, 139.3, 142.0, 142.1 (C), 165.7, 166.3, 166.6, 167.4 (CO). IR (KBr, cm^{-1}): *v* = 2932 (w), 1699, 1622, 1548 (s), 1463 (m), 1416, 1379, (s), 1273 (m), 1243, 1212, 1168, 1062, 1025, 956, 864, 780 (s), 738 (m), 694, 647, 588 (s). MS (EI, 70 eV): *m*/*z* (%) = 635(100) [M^+], 591(18), 562(16), 534(14), 509(14), 507(11), 478(33), 460(46), 431(11), 360(11), 334(12), 304(13), 260(19), 231(15), 57(21). HRMS: *m*/*z* calcd for $C_{37}H_{49}NO_8$ [M^+]: 635.34527; found: 635.34554.

(2*E*,2'*E*,2''*E*,2'''*E*)-*tert*-butyl-3,3',3'',3'''-(1-methyl-1*H*-indole-2,3,5,6-tetrayl) tetraacrylate (56e):



Product **56e** was prepared starting with **53** (446 mg, 1.0 mmol), *tert*-butyl acrylate (0.7 mL, 5.0 mmol), $Pd(OAc)_2$ (11 mg, 5 mol %), SPhos (10 mol %), NEt_3 (1.10 mL, 8.0 mmol), DMF (5 mL) at 90 °C for 36 h following general procedure H, as a yellow highly viscous oil (559 mg, 88%). ^{1}H NMR (300 MHz, $CDCl_3$): δ = 1.5 (s, 9H, $3CH_3$), 1.5 (s, 9H, $3CH_3$), 1.5 (s, 9H, $3CH_3$), 1.5 (s, 9H, $3CH_3$), 3.8 (s, 3H, CH_3N), 6.2 (d, 1H, *J* = 16.1 Hz, CH), 6.3 (d, 1H, *J* = 15.7 Hz, CH), 6.3 (d, 1H, *J* = 15.7 Hz, CH), 6.4 (d, 1H, *J* = 16.0 Hz, CH), 7.4 (s, 1H, ArH), 7.7 (d, 1H, *J* = 16.0 Hz, CH), 7.8 (d, 1H, *J* = 16.0 Hz, CH), 7.9 (d, 1H, *J* = 15.8 Hz, CH), 8.0 (d, 1H, *J* = 14.2 Hz, CH), 8.0 (s, 1H, ArH). ^{13}C NMR (62 MHz, $CDCl_3$): δ = 28.1 ($3CH_3$), 28.2 ($6CH_3$), 28.3 ($3CH_3$), 30.9 (NCH_3), 80.4, 80.6, 80.7, 81.5 (CO), 108.7 (CH), 114,1 (C), 119.3, 120.5, 122.6, 122.7 (CH), 126.6 (C), 127.7 (CH), 128.8 (C), 129.6 (CH), 131.0 (C), 134.9 (CH) 139.0, 139.3 (C), 141.5 (2CH), 165.0, 165.7, 165.9, 166.9 (CO). IR (KBr, cm^{-1}): *v* = 2976, 2931 (w), 1694, 1621, 1548, 1475, 1455, 1390, 1365, 1289, 1254, 1217, 1140, 965, 846, 764 (s). MS (EI, 70 eV): *m*/*z* (%) = 635(15) [M^+], 579(04), 523(07), 478(17), 766(20), 304(28). HRMS: *m*/*z* calcd for $C_{37}H_{49}NO_8$ [M^+]: 635.34582; found: 635.34532.

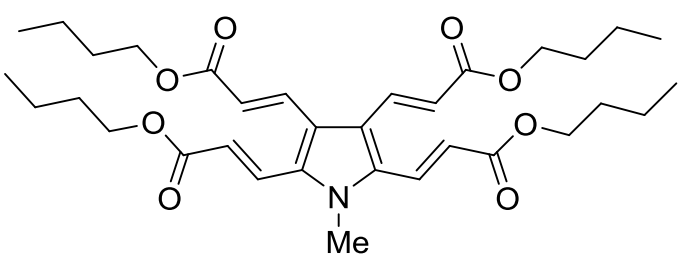
(2*E*,2′*E*,2″*E*,2‴*E*)-Tetrakis(2-ethylhexyl)-3,3′,3″,3‴-(1-methyl-1*H*-indole-2,3,5,6-tetrayl) tetraacrylate (56g):



Product **56g** was prepared starting with **53** (446 mg, 1.0 mmol), 2-ethylhexyl acrylate (1.10 mL, 5.0 mmol), $Pd(OAc)_2$ (11 mg, 5 mol %), SPhos (10 mol %), NEt_3 (1.10 mL, 8.0 mmol), DMF (5 mL) at 90 °C for 36 h following general procedure H, as a yellow highly viscous oil (645 mg, 75%). ^{1}H NMR (300 MHz, $CDCl_3$): δ = 0.81-0.92 (m, 24H, $8CH_3$), 1.23-1.44 (m, 32H, CH_2-aliphatic), 1.52-1.61 (m, 4H, CH), 3.83 (s, 3H, NCH_3), 4.01-4.12 (m, 8H, $4CH_2O$), 6.21 (d, 1H, J = 16.1 Hz, CH), 6.32 (d, 1H, J = 15.6 Hz, CH), 6.33 (d, 1H, J = 15.7 Hz, CH), 6.41 (d, 1H, J = 16.0 Hz, CH), 7.52 (s, 1H, ArH), 7.74 (d, 1H, J = 16.0 Hz, CH), 7.81 (d, 1H, J = 16.0 Hz, CH), 8.01 (s, 1H, ArH), 8.02 (d, 2H, J = 16.0 Hz, CH). ^{13}C NMR (75.5 MHz, $CDCl_3$): δ = 10.9 (CH_3), 11.0 ($3CH_3$), 14.0 ($4CH_3$), 22.9 ($4CH_2$), 23.7 (CH_2), 23.8 ($2CH_2$), 23.9, 28.1, 28.9 (CH_2), 29.0 ($2CH_2$), 30.3 (CH_2), 30.4 ($2CH_2$), 30.5 (CH_2), 31.3 (NCH_3), 38.8 (CH), 38.9 (3CH), 66.9, 67.0, 67.1, 67.6 (CH_2O), 108.9 (CH), 114.1 (C), 117.8, 120.4, 120.7, 121.0, 125.9 (CH), 126.7, 128.8 (C), 130.4 (CH), 131.0 (C), 135.5 (CH), 139.0, 139.4 (C), 142.1, 142.2 (CH), 165.8, 166.4, 166.6, 167.5 (CO). IR (KBr, cm^{-1}): v = 2957, 2927, 2872, 2858 (w), 1706, 1691, 1624 (s), 1600, 1548, 1460, 1379, 1283, 1254, 1215 (w), 1164 (s), 1029, 970, 864 (m), 769, 727, 695, 639, 595 (w). MS (EI, 70 eV): m/z (%) = 859(46) [M^+], 703(11), 701(14), 591(13), 590(32), 571(11), 572(28), 543(15), 460(14), 432(21), 431(13), 416(10), 414(13), 304(19), 276(19), 71(31), 70(20), 57(100), 44(19), 43(44). HRMS (ESI): m/z calcd for $C_{53}H_{82}NO_8$ [M^++H]: 860.6035; found: 860.6029.

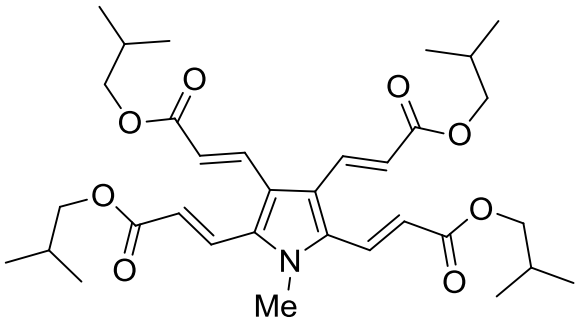
Synthesis of 2,3,4,5-tetra(alkenyl)-*N*-methyl pyrrole (59):

(2*E*,2'*E*,2''*E*,2'''*E*)-Tetrabutyl-3,3',3'',3'''-(1-methyl-1*H*-pyrrole-2,3,4,5-tetrayl)tetraacrylate (59a):



Product **59a** was prepared starting with **58** (392 mg, 1.0 mmol), *n*-butyl acrylate (0.72 mL, 5.0 mmol), $Pd(OAc)_2$ (11 mg, 5 mol %) , $P(Cy)_3$ (10 mol %), NEt_3 (1.10 mL, 8.0 mmol), DMF (5 mL) at 90 °C for 12 h following general procedure H, as a brown oil (380 mg, 65%). ^{1}H NMR (300 MHz, $CDCl_3$): δ = 0.89 (t, 12H, J = 7.4 Hz, $4CH_3$), 1.30-1.40 (m, 8H, $4CH_2$), 1.58-1.65 (m, 8H, $4CH_2$), 3.71 (s, 3H, NCH_3), 4.14 (t, 4H, J = 6.7 Hz, $2CH_2O$), 4.16 (t, 4H, J = 6.7 Hz, $2CH_2O$), 6.02 (d, 2H, J = 16.0 Hz, 2CH), 6.12 (d, 2H, J = 16.1 Hz, 2CH), 7.58 (d, 2H, J = 16.1 Hz, 2CH), 7.65 (d, 2H, J = 16.0 Hz, 2CH). ^{13}C NMR (62 MHz, $CDCl_3$): δ = 13.7 ($2CH_3$), 13.8 ($2CH_3$), 19.1 ($2CH_2$), 19.2 ($2CH_2$), 30.6 ($2CH_2$), 30.7 ($2CH_2$), 34.2 (NCH_3), 64.5 ($2CH_2O$), 64.8 ($2CH_2O$), 121.9 (2CH), 122.2 (2C), 122.5 (2CH), 130.5 (2CH), 132.8 (2C), 135.7 (2CH), 166.4 (2CO), 166.6 (2CO). IR (KBr, cm^{-1}): v = 2957, 2933 (m), 2872 (w), 1705 (s), 1618 (m), 1453, 1383 (w), 1278, 1247 (m), 1161 (s), 1062, 1023, 964, 858, 735 (m), 653, 611 (w). MS (EI, 70 eV): *m/z* (%) = 585(44) $[M]^+$, 512 (12), 484(21), 428(12), 410(100), 354(14), 310(30), 254(22), 252(15), 226(17), 182(17), 173(11), 57(23), 41(17). HRMS (EI, 70 eV): calcd for $C_{33}H_{47}NO_8$ $[M^+]$: 585.32962; found: 585.32935.

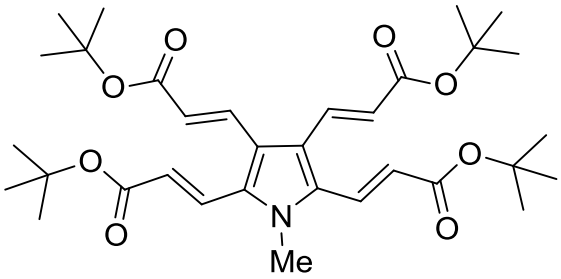
(2*E*,2'*E*,2''*E*,2'''*E*)-Isobutyl-3,3',3'',3'''-(1-methyl-1*H*-pyrrole-2,3,4,5-tetrayl) tetraacrylate (59b):



Product **59b** was prepared starting with **58** (392 mg, 1.0 mmol), *iso*-butyl acrylate (0.72 mL, 5.0 mmol), $Pd(OAc)_2$ (11 mg, 5 mol %), $P(Cy)_3$ (10 mol %), NEt_3 (1.10 mL, 8.0 mmol), DMF (5 mL) at 90 °C for 12 h following general procedure H, as a brown oil (322 mg, 55%). ^{1}H NMR (250 MHz, $CDCl_3$): δ = 0.90 (d, 24H, J = 6.7 Hz, $8CH_3$), 1.87-1.99 (m, 4H, 4CH), 3.72 (s, 3H, NCH_3), 3.91 (d, 4H, J = 6.6 Hz, $2CH_2O$), 3.93 (d, 4H, J = 6.9 Hz, $2CH_2O$), 6.03 (d, 2H, J = 16.0 Hz, 2CH), 6.14 (d, 2H, J

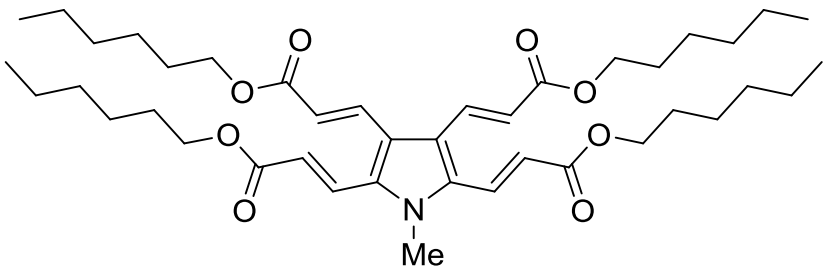
= 16.2 Hz, 2CH), 7.60 (d, 2H, J = 16.3 Hz, 2CH), 7.67 (d, 2H, J = 16.1 Hz, 2CH). ^{13}C NMR (62 MHz, $CDCl_3$): δ = 18.1 ($4CH_3$), 18.2 ($4CH_3$), 26.8 (4CH), 33.1 (NCH_3), 69.7 ($2CH_2O$), 70.0 ($2CH_2O$), 120.9 (2CH), 121.2 (2C), 121.5 (2CH), 129.6 (2CH), 131.8 (2C), 134.7 (2CH), 165.3 (2CO), 165.5 (2CO). IR (KBr, cm^{-1}): v = 2958 (m), 2873 (w), 1701 (s), 1617, 1468, 1376, 1283, 1242 (m), 1155 (s), 1016, 973, 863, 705, 537 (m). MS (EI, 70 eV): *m/z* (%) = 585(76) $[M]^+$, 512(26), 484(30), 428(26), 412(34), 410(100), 384(10), 354(32), 310(61), 254(39), 226(18), 210(34), 182(18), 57(63), 41(23). HRMS (EI, 70 eV): calcd for $C_{33}H_{47}N\,O_8$ $[M]^+$: 585.32962; found: 585.11000.

(2*E*,2'*E*,2''*E*,2'''*E*)-*tert*-Butyl-3,3',3'',3'''-(1-methyl-1*H*-pyrrole-2,3,4,5-tetrayl)tetra acrylate (59c):



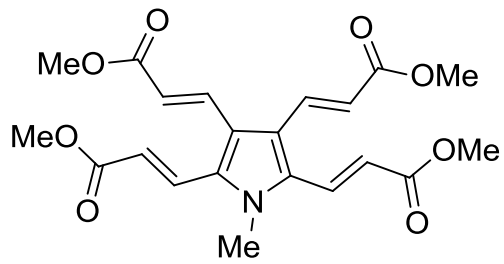
Product **59c** was prepared starting with **58** (392 mg, 1.0 mmol), *tert*-butyl acrylate (0.72 mL, 5.0 mmol), $Pd(OAc)_2$ (11 mg, 5 mol %), $P(Cy)_3$ (10 mol %), NEt_3 (1.10 mL, 8.0 mmol), DMF (5 mL) at 90 °C for 12 h following general procedure H, as a brown oil (322 mg, 55%). ^{1}H NMR (250 MHz, $CDCl_3$): δ = 1.46 (br, 36H, $12CH_3$), 3.68 (s, 3H, NCH_3), 5.94 (d, 2H, J = 16.0 Hz, 2CH), 6.03 (d, 2H, J = 16.1 Hz, 2CH), 7.50 (d, 2H, J = 16.2 Hz, 2CH), 7.55 (d, 2H, J = 16.0 Hz, 2CH). ^{13}C NMR (62 MHz, $CDCl_3$): δ = 28.1 ($6CH_3$), 28.2 ($6CH_3$), 34.2 (NCH_3), 80.4 (2C), 81.0 (2C), 122.1 (2C), 123.3 (2CH), 124.0 (2CH), 129.9 (2CH), 132.6 (2C), 134.9 (2CH), 165.6 (2CO), 165.9 (2CO). IR (KBr, cm^{-1}): v = 2975, 2930, 2871 (w), 1702, 1620 (m), 1474, 1455, 1390 (w), 1366, 1280, 1253 (m), 1140 (s), 971, 949, 847, 767, 730 (m). MS (EI, 70 eV): *m/z* (%) = 585(04) $[M]^+$, 287(24), 233(79), 199(12), 173(100), 121(32), 114(49), 82(29), 71(21), 58(60), 44(44), 41(84). HRMS (ESI): calcd for $C_{33}H_{47}NNa\,O_8$ $[M]^+$: 608.3194; found: 608.3204.

(2*E*,2'*E*,2''*E*,2'''*E*)-Tetrahexyl-3,3',3'',3'''-(1-methyl-1*H*-pyrrole-2,3,4,5-tetrayl)tetraacrylate (59d):



Product **59d** was prepared starting with **58** (392 mg, 1.0 mmol), *n*-hexyl acrylate (0.88 mL, 5.0 mmol), $Pd(OAc)_2$ (11 mg, 5 mol %), $P(Cy)_3$ (10 mol %), NEt_3 (1.10 mL, 8.0 mmol), DMF (5 mL) at 90 °C for 12 h following general procedure H, as a brown oil (508 mg, 73%). ^{1}H NMR (300 MHz, $CDCl_3$): δ = 0.83 (t, 12H, *J* = 7.0 Hz, $4CH_3$), 1.22-1.34 (m, 24H, $12CH_2$), 1.58-1.65 (m, 8H, $4CH_2$), 3.71 (s, 3H, NCH_3), 4.12 (t, 4H, *J* = 6.7 Hz, $2CH_2O$), 4.14 (t, 4H, *J* = 6.7 Hz, $2CH_2O$), 6.02 (d, 2H, *J* = 16.0 Hz, 2CH), 6.12 (d, 2H, *J* = 16.1 Hz, 2CH), 7.58 (d, 2H, *J* = 16.1 Hz, 2CH), 7.66 (d, 2H, *J* = 16.0 Hz, 2CH). ^{13}C NMR (62 MHz, $CDCl_3$): δ = 13.0 ($4CH_3$), 22.5 ($4CH_2$), 24.6 ($4CH_2$), 27.6 ($4CH_2$), 30.4($2CH_2$), 30.5 ($2CH_2$), 33.2 (NCH_3), 63.8 ($2CH_2O$), 64.1 ($2CH_2O$), 120.9 (2CH), 121.3 (2C), 121.5 (2CH), 129.5 (2CH), 131.8 (2C), 134.7 (2CH), 165.4 (2CO), 165.6 (2CO). IR (KBr, cm^{-1}): *v* = 2953, 2927 (m), 2857 (w), 1706, 1618 (m), 1466, 1380 (w), 1279, 1247 (m), 1161 (s), 1057, 967, 858 (m), 725, 611 (w). MS (EI, 70 eV): *m/z* (%) = 697(84) $[M]^+$, 695(20), 596(12), 568(21), 484(16), 482(22), 466(100), 382(17), 380(12), 354(15), 338(21), 296(20), 270(10), 252(30), 226(21), 210(10), 182(16), 173(18), 114(10), 56(21), 43(68). HRMS (ESI): calcd for $C_{41}H_{64}NO_8$ $[M+H]^+$: 698.4626; found: 698.4609.

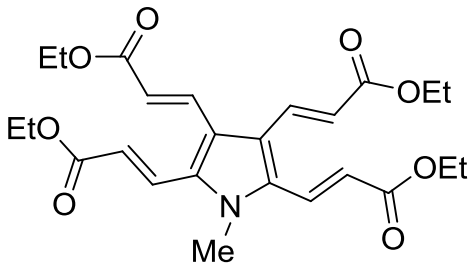
(2*E*,2'*E*,2''*E*,2'''*E*)-Tetramethyl-3,3',3'',3'''-(1-methyl-1*H*-pyrrole-2,3,4,5-tetrayl) tetraacrylate (59e):



Product **59e** was prepared starting with **58** (392 mg, 1.0 mmol), methyl acrylate (0.45 mL, 5.0 mmol), $Pd(OAc)_2$ (11 mg, 5 mol %), $P(Cy)_3$ (10 mol %), NEt_3 (1.10 mL , 8.0 mmol), DMF (5 mL) at 90 °C for 12 h following general procedure H, as a brown oil (216 mg, 52%). ^{1}H NMR (250 MHz, $CDCl_3$): δ = 3.70 (s, 3H, NCH_3), 3.73 (s, 6H, $2OCH_3$), 3.75 (s, 6H, $2OCH_3$), 6.01 (d, 2H, *J* = 16.0 Hz, 2CH), 6.12 (d, 2H, *J* = 16.2 Hz, 2CH), 7.58 (d, 2H, *J* = 16.2 Hz, 2CH), 7.64 (d, 2H, *J* = 16.0 Hz, 2CH). ^{13}C NMR (62 MHz, $CDCl_3$): δ = 34.2 (NCH_3), 51.7 ($2OCH_3$), 51.9 ($2OCH_3$), 121.6 (2CH), 122.1 (2CH), 122.2 (2C), 130.7 (2CH), 132.8 (2C), 135.8 (2CH), 166.6 (2CO), 166.9 (2CO). IR (KBr, cm^{-1}): *v* =

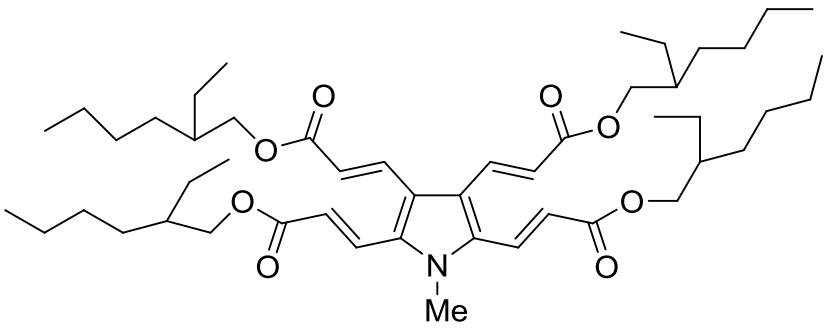
2998, 2952, 2849 (w), 1704 (s), 1620, 1432 (m), 1279, 1191, 1165 (s), 1103, 1016 (m), 963 (s), 890, 853, 728, 715 (m). MS (EI, 70 eV): *m/z* (%) = 417(29) $[M]^+$, 358 (32), 327(17), 326(100), 324(13), 298(14), 282(15), 266(17), 240(10), 239(13), 208(15), 181(16), 180(13). HRMS (ESI): calcd for $C_{21}H_{24}NO_8$ $[M+H]^+$: 418.1496; found: 418.1501.

(2*E*,2'*E*,2''*E*,2'''*E*)-Tetraethyl -3,3',3'',3'''-(1-methyl-1*H*-pyrrole-2,3,4,5-tetrayl)tetraacrylate (59f):



Product **59f** was prepared starting with **58** (392 mg, 1.0 mmol), ethyl acrylate (5.0 mmol), $Pd(OAc)_2$ (11 mg, 5 mol %), $P(Cy)_3$ (10 mol %), NEt_3 (1.10 mL, 8.0 mmol), DMF (5 mL) at 90 °C for 12 h following general procedure H, as brownish solid (326 mg, 69%), mp 97-99 °C. ^{1}H NMR (250 MHz, $CDCl_3$): δ = 1.26 (t, 6H, *J* = 7.1 Hz, $2CH_3$), 1.27 (t, 6H, *J* = 7.1 Hz, $2CH_3$), 3.71 (s, 3H, NCH_3), 4.15-4.25 (m, 8H, $4CH_2O$), 6.01 (d, 2H, *J* = 16.0 Hz, 2CH), 6.12 (d, 2H, *J* = 16.1 Hz, 2CH), 7.58 (d, 2H, *J* = 16.2 Hz, 2CH), 7.65 (d, 2H, *J* = 16.0 Hz, 2CH). ^{13}C NMR (75 MHz, $CDCl_3$): δ = 14.3 ($4CH_3$), 34.2 (NCH_3), 60.6 ($2CH_2O$), 60.9 ($2CH_2O$), 121.9 (2CH), 122.3 (2C), 122.5 (2CH), 130.6 (2CH), 132.8 (2C), 135.7 (2CH), 166.3 (2CO), 166.6 (2CO). IR (KBr, cm^{-1}): *v* = 2981, 1936, 2873 (w), 1710, 1620 (s), 1450, 1392 (w), 1364, 1277 (m), 1255, 1161, 1031, 968 (s), 933, 853, 727 (m), 649 (w). MS (EI, 70 eV): *m/z* (%) = 471(15) $[M]^+$, 428(14), 400(35), 356(17), 354(100), 352(23), 326(35), 282(41), 254(38), 225(12), 210(24), 181(37), 169(15), 131(17), 119(17), 97(11), 83(13), 69(65), 57(22), 44(27), 41(14). HRMS (EI, 70 eV): calcd for $C_{25}H_{31}NO_8$ $[M^+]$: 471.18877; found: 471.18739.

(2*E*,2'*E*,2''*E*,2'''*E*)-Tetrakis(2-ethylhexyl)-3,3',3'',3'''-(1-methyl-1*H*-pyrrole-2,3,4,5-tetrayl)tetraacrylate (59g):

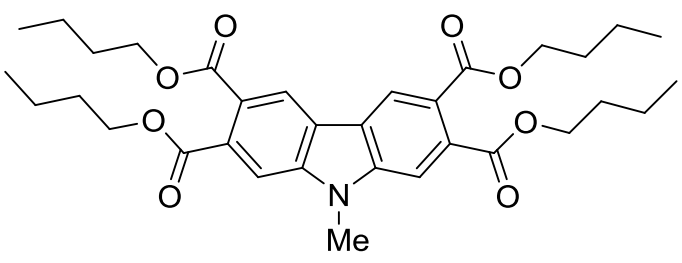


Product **59g** was prepared starting with **58** (392 mg, 1.0 mmol), 2-ethylhexyl acrylate (1.1 mL, 5.0 mmol), $Pd(OAc)_2$ (11 mg, 5 mol %), $P(Cy)_3$ (10 mol %), NEt_3 (1.10 mL, 8.0 mmol), DMF (5 mL) at 90 °C for 12 h following general procedure H, as a brown oil (607 mg, 75%). ^{1}H NMR (250 MHz, $CDCl_3$): δ = 0.82-0.88 (m, 24H, $8CH_3$), 1.17-1.28 (m, 24H, $12CH_2$), 1.29-1.36 (m, 8H, $4CH_2$), 1.54-1.61 (m, 4H, 4CH), 3.71 (s, 3H, NCH_3), 4.02-4.08 (m, 8H, $4CH_2O$), 6.01 (d, 2H, J = 16.0 Hz, 2CH), 6.12 (d, 2H, J = 16.1 Hz, 2CH), 7.59 (d, 2H, J = 16.2 Hz, 2CH), 7.65 (d, 2H, J = 16.2 Hz, 2CH). ^{13}C NMR (62 MHz, $CDCl_3$): δ = 10.9 ($4CH_3$), 14.0 ($4CH_3$), 22.9 ($4CH_2$), 23.8 ($4CH_2$), 28.9 ($4CH_2$), 30.4 ($4CH_2$), 34.2 (NCH_3), 38.8 (4CH), 67.1 ($2CH_2O$), 67.5 ($2CH_2O$), 121.9 (2CH), 122.2 (2C), 122.6 (2CH), 130.5 (2CH), 132.8 (2C), 135.6 (2CH), 166.4 (2CO), 166.6 (2CO). IR (KBr, cm^{-1}): ν = 2956, 2927 (m), 2858 (w), 1708 (s), 1619 (m), 1459, 1380 (w), 1278, 1244 (m), 1163 (s), 1028, 966 (m), 858, 769, 727 (w). MS (EI, 70 eV): *m/z* (%) = 809(25) $[M]^+$, 627(18), 522(22), 499(13) 498(41), 410(16), 358(18), 340(11), 228(11), 83(15), 71(31), 70(20), 57(100), 55(25), 44(21), 43(39), 41(27). HRMS (ESI): calcd for $C_{49}H_{80}NO_8$ $[M+H]^+$: 810.5878; found: 810.5873.

General procedure J for synthesis of Carbazol (60):

A diphenyl ether solution (3 mL) of **59a**-**g** (0.25 mmol) was stirred at 200 °C for 24 h in a pressure tube. The solution was allowed to cool to 20 °C and Pd/C (30 mg, 10 mol %) was added. The solution was stirred at 200 °C for 48 h under an argon atmosphere. The reaction mixture was filtered and the filtrate was concentrated *in vacuo*. The residue was purified by chromatography (flash silica gel, eluent: heptanes-EtOAc).

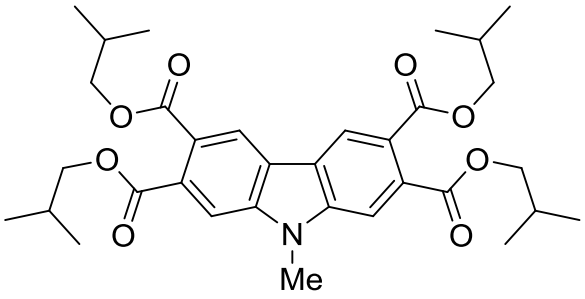
Tetrabutyl-9-methyl-9*H*-carbazole-2,3,6,7-tetracarboxylate (60a):



Compound **60a** was synthesized starting with **59a** (100 mg, 0.17 mmol), following general procedure J, as brown oil (74 mg, 75%). ^{1}H NMR (300 MHz, $CDCl_3$): δ = 0.90 (t, 6H, J = 7.4 Hz, $2CH_3$), 0.92 (t, 6H, J = 7.3 Hz, $2CH_3$), 1.33-1.48 (m, 8H, $4CH_2$), 1.64-1.75 (m, 8H, $4CH_2$), 3.86 (s, 3H, NCH_3), 4.28 (t, 4H, J = 6.7 Hz, $2CH_2O$), 4.30 (t, 4H, J = 6.7 Hz, $2CH_2O$), 7.62 (s, 2H, ArH), 8.50 (s, 2H, ArH). ^{13}C NMR (75 MHz, $CDCl_3$): δ = 13.7 ($2CH_3$), 13.8 ($2CH_3$), 19.2 ($2CH_2$), 19.3 ($2CH_2$), 29.8 (NCH_3), 30.6 ($2CH_2$), 30.8 ($2CH_2$), 65.5 ($2CH_2O$), 65.9 ($2CH_2O$),

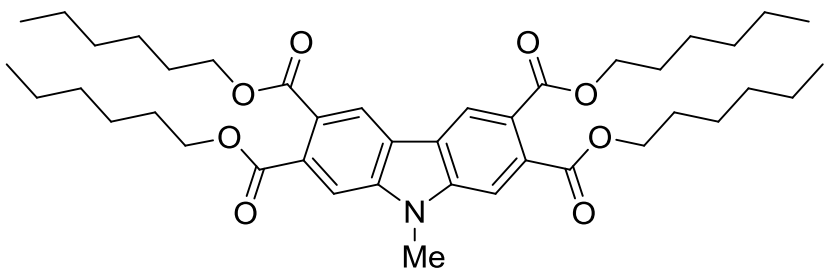
109.7 (2CH), 123.0 (2CH), 123.1 (4C), 132.6 (2C), 142.8 (2C), 167.3 (2CO), 168.8 (2CO). IR (KBr, cm^{-1}): ν = 2957, 2932 (m), 2872 (w), 1712 (s), 1634, 1601, 1563 (w), 1457 (m), 1384, 1340 (w), 1254, 1230, 1107, 1084, 1074 (s), 1018, 961, 784 (m), 681, 603 (w). MS (EI, 70 eV): *m/z* (%) = 581(100) $[M]^+$, 525(12), 453(23), 422(85), 396(21), 340(11), 322(25), 173(11). HRMS (ESI): calcd for $C_{33}H_{44}NO_8$ $[M+H]^+$: 582.3061; found: 582.3064.

Tetraisobutyl-9-methyl-9*H*-carbazole-2,3,6,7-tetracarboxylate (60b):



Compound **60b** was synthesized starting with **59b** (100 mg, 0.17 mmol), following general procedure J, as a brown oil (88 mg, 89%). ^{1}H NMR (300 MHz, $CDCl_3$): δ = 0.94 (d, 12H, *J* = 6.6 Hz, $4CH_3$), 0.95 (d, 12H, *J* = 6.6 Hz, $4CH_3$), 1.96-2.06 (m, 4H, 4CH), 3.89 (s, 3H, NCH_3), 4.07 (d, 4H, *J* = 6.7 Hz, $2CH_2O$), 4.08 (d, 4H, *J* = 6.7 Hz, $2CH_2O$), 7.65 (s, 2H, ArH), 8.54 (s, 2H, ArH). ^{13}C NMR (75 MHz, $CDCl_3$): δ = 18.2 ($4CH_3$), 18.3 ($4CH_3$), 26.7 (2CH), 26.8 (2CH), 28.8 (NCH_3), 70.8 ($2CH_2O$), 71.1 ($2CH_2O$), 108.8 (2CH), 122.0 (2CH), 122.1 (2C), 122.3 (2C), 131.6 (2C), 141.8 (2C), 166.3 (2CO), 167.8 (2CO). IR (KBr, cm^{-1}): ν = 2958 (m), 2873 (w), 1713 (s), 1634, 1602 (w), 1467, 1377 (m), 1257, 1229, 1108 (s), 1085, 1035, 1008, 988, 945, 783 (m). GC-MS (EI, 70 eV): *m/z* (%) = 581(84) $[M]^+$, 525(19), 469(17), 452(100), 413(12), 396(30), 357(14), 340(30), 322(38), 251(24), 57(55), 41(70). HRMS (EI, 70 eV): calcd for $C_{33}H_{43}NO_8$ $[M]^+$: 581.29832; found: 581.29761.

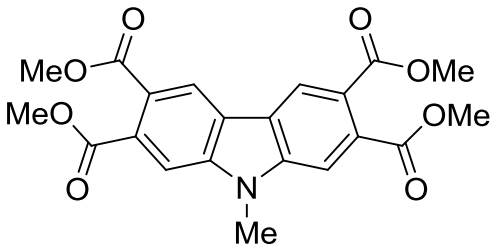
Tetrahexyl-9-methyl-9*H*-carbazole-2,3,6,7-tetracarboxylate (60d):



Compound **60d** was synthe sized starting with **59d** (100 mg, 0.14 mmol), follo wing general procedure J, as yellow oil (79 mg, 80%). ^{1}H NMR (300 MHz, $CDCl_3$): δ = 0.82 (t, 6H, *J* = 7.3 Hz, $2CH_3$), 0.84 (t, 6H, *J* = 7.0 Hz, $2CH_3$), 1.25-1.40 (m, 24H, $12CH_2$), 1.63-1.76 (m, 8H, $4CH_2$), 3.87 (s, 3H, NCH_3), 4.27 (t, 4H, *J* = 6.8 Hz, $2CH_2O$), 4.29 (t, 4H, *J* = 6.8 Hz, $2CH_2O$), 7.62 (s, 2H, ArH), 8.52 (s, 2H, ArH). ^{13}C NMR (75 MHz, $CDCl_3$): δ = 13.0 ($4CH_3$), 21.5 ($4CH_2$), 24.6 ($2CH_2$), 24.7 ($2CH_2$), 27.5 ($2CH_2$), 27.6 ($2CH_2$), 28.8 (NCH_3), 30.4($2CH_2$), 30.5 ($2CH_2$), 64.8 ($2CH_2O$), 65.2

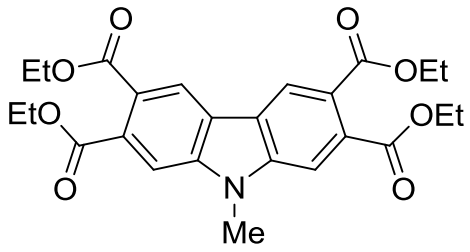
(2CH_2O), 108.7 (2CH), 122.0 (2CH), 122.1 (2C), 122.2 (2C), 131.6 (2C), 141.8 (2C), 166.3 (2CO), 167.8 (2CO). IR (KBr, cm^{-1}): v = 2953, 2927 (m), 2856 (w), 1713 (s), 1635, 1602, 1460, 1390, 1341 (w), 1256, 1230, 1108 (s), 1085, 992 (m), 899, 866 (w), 784 (m), 725, 604 (w). MS (EI, 70 eV): *m/z* (%) = 693(80) $[M]^+$, 609(14), 508(70), 424(26), 339(15), 322(34), 251(12), 173(11), 149(11), 147(12), 135(16), 133(15), 125(12), 123(13), 119(16), 111(13), 109(23), 107(18), 105(14), 97(15), 81(32), 69(27), 55(39), 43(100). HRMS (ESI): calcd for $C_{41}H_{60}NO_8$ $[M+H]^+$: 694.4313; found: 694.4313. Anal. calcd for $C_{41}H_{59}NO_8$: C, 70.97; H, 8.57; N, 2.02. Found: C, 70.42; H, 8.53; N, 2.19.

Tetramethyl-9-methyl-9*H*-carbazole-2,3,6,7-tetracarboxylate (60e):



Compound **60e** was synthesized starting with **59e** (100 mg, 0.24 mmol), following general procedure J, as a yellow oil (68 mg, 69%). ^1H NMR (300 MHz, $CDCl_3$): δ = 3.85 (s, 3H, NCH_3), 3.89 (s, 6H, 2OCH_3), 3.91 (s, 6H, 2OCH_3), 7.62 (s, 2H, ArH), 8.51 (s, 2H, ArH). ^{13}C NMR (75 MHz, $CDCl_3$): δ = 29.8 (NCH_3), 52.6 (2OCH_3), 52.9 (2OCH_3), 109.8 (2CH), 122.7 (2C), 123.2 (2C), 123.3 (2CH), 132.3 (2C), 142.8 (2C), 167.6 (2CO), 169.2 (2CO). IR (KBr, cm^{-1}): v = 2959, 2910, 2834 (w), 1614, 1579, 1519, 1502, 1463, 1427, 1417, 1287 (m), 1239 (s), 1200, 1183, 1165, 1159, 1118 (w), 1030 (s), 991, 950 (m), 827 (s), 770, 708, 665, 636, 582 (m), 546 (s). GC-MS (EI, 70 eV): *m/z* (%) = 413(799 $[M]^+$, 383(22), 382(100), 336(15), 265(13), 176(16). HRMS (EI, 70 eV): calcd for $C_{21}H_{19}NO_8$ $[M]^+$: 413.11052; found: 413.11033.

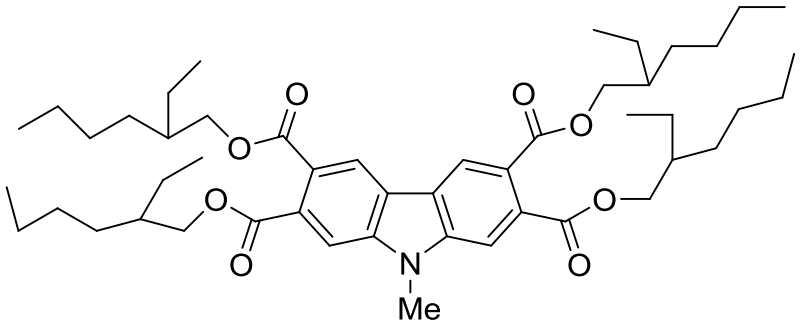
Tetraethyl-9-methyl-9*H*-carbazole-2,3,6,7-tetracarboxylate (60f):



Compound **60f** was synthesized starting with 59f (100 mg, 0.21 mmol), following general procedure J, as whitish solid (62 mg, 63%), mp 120-122 °C. ^1H NMR (300 MHz, $CDCl_3$): δ = 1.34 (t, 6H, J = 7.2 Hz, 2CH_3), 1.36 (t, 6H, J = 7.1 Hz, 2CH_3), 3.87 (s, 3H, NCH_3), 4.34 (q, 4H, J = 7.1 Hz, 2CH_2O), 4.35 (q, 4H, J = 7.1 Hz, 2CH_2O), 7.62 (s, 2H, ArH), 8.52 (s, 2H, ArH). ^{13}C NMR (75 MHz, $CDCl_3$): δ = 14.1 (2CH_3), 14.3 (2CH_3), 29.8 (NCH_3), 61.5 (2CH_2O), 61.9 (2CH_2O), 109.7 (2CH), 123.0 (2CH), 123.1 (4C), 132.5 (2C), 142.8 (2C), 167.2 (2CO), 168.8 (2CO). IR (KBr, cm^{-1}): v = 2979, 2929 (w), 1709 (s), 1635, 1600, 1563

(w), 1463, 1443, 1367 (m), 1251, 1229, 1213, 1107, 1084, 1073, 1013 (s), 949, 900, 872, 772 (m), 654, 616, 559 (w). MS (EI, 70 eV): *m/z* (%) = 469(100) $[M]^+$, 424(19), 396(88), 368(12), 322(21), 251(14). HRMS (EI, 70 eV): calcd for $C_{25}H_{27}NO_8$ $[M]^+$: 469.17312; found: 469.17296.

Tetrakis(2-ethylhexyl)-9-methyl-9*H*-carbazole-2,3,6,7-tetracarboxylate (60g):



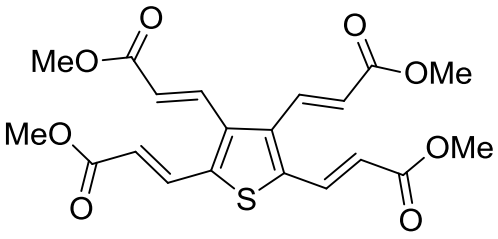
Compound **60g** was synthesized starting with **59g** (100 mg, 0.12 mmol), following general procedure J, as a yellow oil (81 mg, 82%). ^{1}H NMR (300 MHz, $CDCl_3$): δ = 0.83-0.92 (m, 24H, $8CH_3$), 1.27-1.45 (m, 32H, $16CH_2$), 1.61-1.72 (m, 4H, 4CH), 3.88 (s, 3H, NCH_3), 4.16-4.23 (m, 8H, $4CH_2O$), 7.62 (s, 2H, ArH), 8.52 (s, 2H, ArH). ^{13}C NMR (75 MHz, $CDCl_3$): δ = 10.9 ($2CH_3$), 11.0 ($2CH_3$), 14.1 ($4CH_3$), 23.0 ($4CH_2$), 23.8 ($2CH_2$), 23.9 ($2CH_2$), 28.9 ($2CH_2$), 29.0 ($2CH_2$), 29.8 (NCH_3), 30.4 ($2CH_2$), 30.5 ($2CH_2$), 38.7 (2CH), 38.9 (2CH), 68.2 ($2CH_2O$), 68.6 ($2CH_2O$), 109.7 (2CH), 123.0 (2CH), 123.1 (2C), 123.3 (2C), 132.7 (2C), 142.8 (2C), 167.4 (2CO), 168.9 (2CO). IR (KBr, cm^{-1}): ν = 2956, 2926, 2858 (m), 1713 (s), 1634, 1601 (w), 1458, 1379 (m), 1260, 1229, 1109 (s), 1084, 1000, 772 (m), 725, 625 (w). MS (EI, 70 eV): *m/z* (%) = 805(100) $[M]^+$, 693(18), 581(15), 564(99), 452(32), 357(26), 340(30), 322(27), 71(16), 57(34), 55(17), 43(21), 41(17). HRMS (EI, 70 eV): calcd for $C_{49}H_{75}NO_8$ $[M]^+$: 805.54872; found: 805.55104.

General procedure K for synthesis of 2,3,4,5-tetra(alkenyl)thiophenes (62):

A pressure tube (glass bomb) a suspension of $Pd(OAc)_2$ (3.4 mg, 0.03 mmol, 3 mol%) and $P(Cy)_3$ (5 mol%) in DMF (5 mL) was purged with Argon and stirred at 20 °C to give a yellowish clear solution. To the stirred solution were added **61** (200 mg, 0.5 mmol), Na_2CO_3 (216 mg, 4.0 mmol) and the alkene (1.25 equiv per bromine atom of the substrate). The reaction mixture was stirred at 90-100 °C for 12 h. The solution was poured into H_2O, brine,

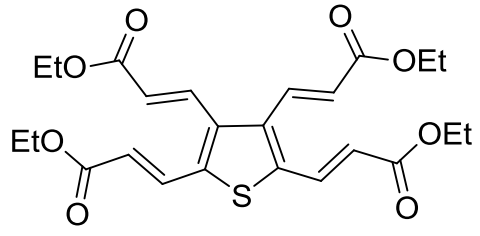
and EtOAc (25 mL each) and the organic and the aqueous layers were separated. The latter was extracted with EtOAc (3 × 25mL), dried (Na_2SO_4), filtered, and concentrated in vacuo. The residue was purified by flash column chromatography (flash silica gel, eluent: *n*-heptane-EtOAc).

(2*E*,2'*E*,2''*E*,2'''*E*)-Tetramethyl-3,3',3'',3'''-(thiophene-2,3,4,5-tetrayl)tetraacrylate (62a):



Product **62a** was prepared starting with **61** (200 mg, 0.5 mmol), methylacrylate (0.23 mL, 2.5 mmol), $Pd(OAc)_2$ (3.4 mg, 3 mol %), $P(Cy)_3$ (5 mol %), Na_2CO_3 (216 mg, 4.0 mmol), DMF (5 mL) at 90 °C for 12 h according to general procedure K, as yellowish solid (149 mg, 71%), mp 80-82 °C. ^{1}H NMR (300 MHz, $CDCl_3$): δ = 3.75 (s, 6H, $2OCH_3$), 3.77 (s, 6H, $2OCH_3$), 6.04 (d, 2H, J = 16.0 Hz, 2CH), 6.28 (d, 2H, J = 15.7 Hz, 2CH), 7.61 (d, 2H, J = 16.0 Hz, 2CH), 7.76 (d, 2H, J = 15.7 Hz, 2CH). ^{13}C NMR (62 MHz, $CDCl_3$): δ = 52.0 ($2OCH_3$), 52.1 ($2OCH_3$), 121.1 (2CH), 125.8 (2CH), 133.8 (2CH), 135.4 (2CH), 138.3 (2C), 139.0 (2C), 166.0 (2CO), 166.2 (2CO). IR (KBr, cm^{-1}): ν = 3000, 2952, 2921, 2848 (w), 1710 (s), 1615, 1432, 1306 (m), 1267, 1192, 1164 (s), 1081, 1018 (m), 964 (s), 919, 852, 801, 735, 701, 657, 575 (m). MS (EI, 70 eV): *m/z* (%) = 420(28) $[M]^+$, 389(12), 361(25), 360(33), 331(10), 330(18), 329(100), 327(16), 302(10), 301(20), 297(15), 285(30), 270(10), 269(29), 242(16), 211(23), 198(11), 184(29), 183(12), 139(11), 59(18). HRMS (EI, 70 eV): calcd for $C_{20}H_{20}O_8S$ $[M]^+$: 420.08734; found: 420.08705.

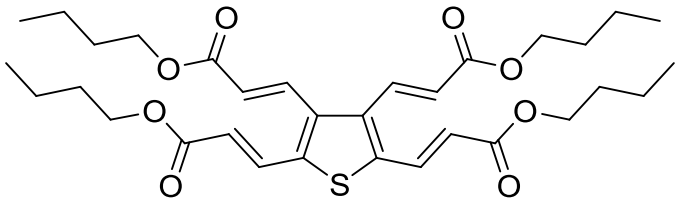
(2*E*,2'*E*,2''*E*,2'''*E*)-Tetraethyl-3,3',3'',3'''-(thiophene-2,3,4,5-tetrayl)tetraacrylate (62b):



Product **62b** was prepared starting with **61** (200 mg, 0.5 mmol), ethyl acrylate (0.27 mL, 2.5 mmol), $Pd(OAc)_2$ (3.4 mg, 3 mol %), $P(Cy)_3$ (5 mol %), Na_2CO_3 (216 mg, 4.0 mmol), DMF (5 mL) at 90 °C for 12 h according to general procedure K, as brownish oil (129 mg, 54%). ^{1}H NMR (300 MHz, $CDCl_3$): δ = 1.27 (t, 6H, J = 7.1 Hz, $2CH_3$), 1.28 (t, 6H, J = 7.1 Hz, $2CH_3$), 4.20 (q, 4H, J = 7.1 Hz, $2CH_2O$), 4.22 (q, 4H, J = 7.1 Hz, $2CH_2O$), 6.04 (d, 2H, J = 16.0 Hz, 2CH), 6.27 (d, 2H, J = 15.7 Hz, 2CH), 7.60 (d, 2H, J = 16.0 Hz, 2CH), 7.76 (d, 2H, J = 15.7 Hz, 2CH). ^{13}C NMR (62 MHz, $CDCl_3$): δ = 14.2

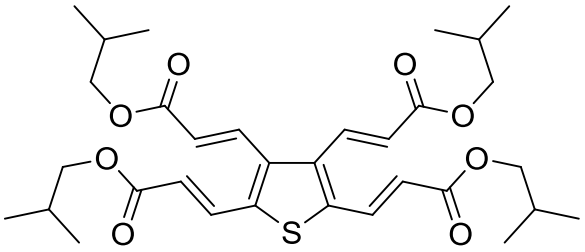
($2CH_3$), 14.2 ($2CH_3$), 60.9 ($2CH_2O$), 61.0 ($2CH_2O$), 121.4 (2CH), 126.2 (2CH), 133.7 (2CH), 135.2 (2CH), 138.3 (2C), 138.9 (2C), 165.7 (2CO), 165.8 (2CO). IR (KBr, cm^{-1}): ν = 2980, 2936, 2904, 2872 (w), 1708 (s), 1617 (m), 1547, 1498, 1464, 1445, 1391 (w), 1365, 1301 (m), 1266, 1162 (s), 1094 (m), 1029, 960 (s), 917, 856 (m), 810, 784 (w), 729 (m), 699, 613, 575, 552 (w). MS (EI, 70 eV): *m/z* (%) = 476(25) $[M]^+$, 474(11), 431(15), 403(27), 402(37), 385(11), 359(23), 357(100), 355(22), 329(25), 313(14), 311(11), 285(74), 257(43), 241(15), 239(17), 213(55), 185(52), 171(12), 139(15), 44(42). HRMS (ESI): calcd for $C_{24}H_{28}NaO_8S$ $[M+Na]^+$: 499.13971; found: 499.13974.

(2*E*,2'*E*,2''*E*,2'''*E*)-Tetrabutyl-3,3',3'',3'''-(thiophene-2,3,4,5-tetrayl)tetraacrylate (62c)



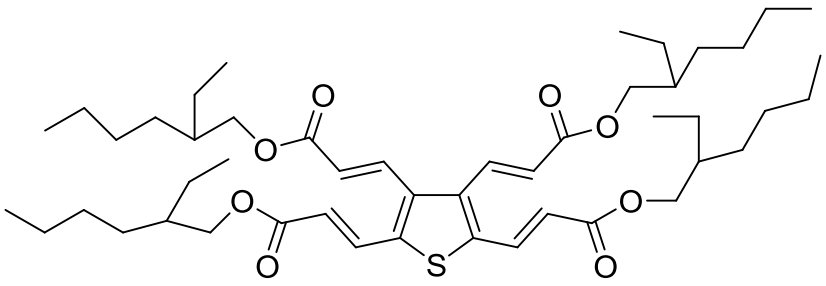
Product **62c** was prepared starting with **61** (200 mg, 0.5 mmol), *n*-butyl acrylate (0.36 mL, 2.5 mmol), $Pd(OAc)_2$ (3.4 mg, 3mol%), $P(Cy)_3$ (5 mol %), Na_2CO_3 (216 mg, 4.0 mmol), DMF (5 mL) at 90 °C for 12 h according to general procedure K, as brownish oil (150 mg, 51%). ^{1}H NMR (300 MHz, $CDCl_3$): δ = 0.90 (t, 12H, *J* = 7.2 Hz, $4CH_3$), 1.30-1.43 (m, 8H, $4CH_2$), 1.57-1.67 (m, 8H, $4CH_2$), 4.14 (t, 4H, *J* = 6.7 Hz, $2CH_2O$), 4.16 (t, 4H, *J* = 6.7 Hz, $2CH_2O$), 6.04 (d, 2H, *J* = 16.2 Hz, 2CH), 6.27 (d, 2H, *J* = 15.7 Hz, 2CH), 7.59 (d, 2H, *J* = 16.0 Hz, 2CH), 7.76 (d, 2H, *J* = 15.5 Hz, 2CH). ^{13}C NMR (75 MHz, $CDCl_3$): δ = 13.7 ($4CH_3$), 19.2 ($4CH_2$), 30.6 ($2CH_2$), 30.7 ($2CH_2$), 64.8 ($2CH_2O$), 64.9 ($2CH_2O$), 121.5 (2CH), 126.2 (2CH), 133.7 (2CH), 135.3 (2CH), 138.3 (2C), 138.9 (2C), 165.7 (2CO), 165.9 (2CO). IR (KBr, cm^{-1}): ν = 2958 (m), 2933, 2872 (w), 1710 (s), 1617 (m), 1458, 1383 (w), 1302 (m), 1257, 1161 (s), 1062, 1023, 962, 855 (m), 734, 576 (w). MS (EI, 70 eV): *m/z* (%) = 588(25) $[M]^+$, 515(12), 488(10), 487(25), 486(48), 431(18), 415(30), 414(24), 413(100), 387(11), 357(20), 329(11), 313(85), 257(47), 255(20), 229(14), 213(59), 211(12), 185(20), 57(97), 44(19), 41(70). HRMS (EI, 70 eV): calcd for $C_{32}H_{44}O_8S$ $[M]^+$: 588.27514; found: 588.27510.

(2*E*,2'*E*,2''*E*,2'''*E*)-Isobutyl-3,3',3'',3'''-(thiophene-2,3,4,5-tetrayl)tetraacrylate (62d):



Product **62d** was prepared starting with **61** (200 mg, 0.5 mmol), *iso*-butyl acrylate (0.36 mL, 2.5 mmol), $Pd(OAc)_2$ (3.4 mg, 3 mol %), $P(Cy)_3$ (5 mol %), Na_2CO_3 (216 mg, 4.0 mmol), DMF (5 mL) at 90 °C for 12 h according to general procedure B, as brownish oil (199 mg, 68%). ^{1}H NMR (300 MHz, $CDCl_3$): δ = 0.91 (d, 24H, J = 6.7 Hz, $8CH_3$), 1.89-1.99 (m, 4H, 4CH), 3.92 (d, 4H, J = 6.6 Hz, $2CH_2O$), 3.94 (d, 4H, J = 6.7 Hz, $2CH_2O$), 6.06 (d, 2H, J = 16.0 Hz, 2CH), 6.29 (d, 2H, J = 15.5 Hz, 2CH), 7.61 (d, 2H, J = 16.0 Hz, 2CH), 7.78 (d, 2H, J = 15.6 Hz, 2CH). ^{13}C NMR (62 MHz, $CDCl_3$): δ = 19.0 ($4CH_3$), 19.1 ($4CH_3$), 27.7 (2CH), 27.8 (2CH), 71.0 ($2CH_2O$), 71.1 ($2CH_2O$), 121.4 (2CH), 126.1 (2CH), 133.6 (2CH), 135.3 (2CH), 138.3 (2C), 138.9 (2C), 165.7 (2CO), 165.9 (2CO). IR (KBr, cm^{-1}): ν = 2959 (m), 2874 (w), 1713 (s), 1620, 1469, 1369, 1306 (m), 1207, 1162 (s), 1015, 967, 944 (m), 857, 778, 576 (w). MS (EI, 70 eV): *m/z* (%) = 588(12) $[M]^+$, 487(10), 486(18), 455(11), 431(15), 429(21), 415(22), 413(43), 411(16), 360(12), 357(17), 355(19), 329(13), 316(11), 313(40), 301(13), 299(30), 257(38), 255(36), 229(13), 213(27), 211(10), 185(15), 184(11), 57(100), 56(13), 44(56), 41(77), 39(18). HRMS (ESI): calcd for $C_{32}H_{45}O_8S$ $[M+H]^+$: 589.28297; found: 589.28149.

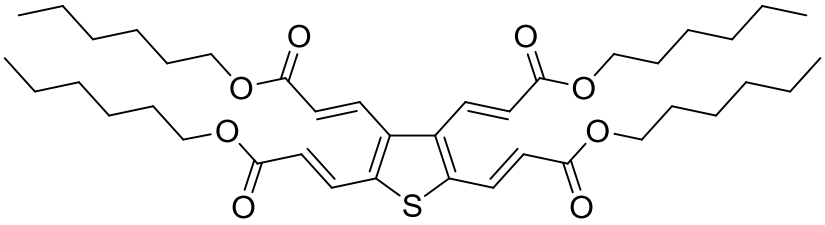
(2*E*,2'*E*,2''*E*,2'''*E*)-Tetrakis(2-ethylhexyl) 3,3',3'',3'''-(thiophene-2,3,4,5-tetrayl) tetraacrylate (62e):



Product **62e** was prepared starting with **61** (200 mg, 0.5 mmol), 2-ethylhexyl acrylate (0.52 mL, 2.5 mmol), $Pd(OAc)_2$ (3.4 mg , 3 mol %), $P(Cy)_3$ (5 mol %), Na_2CO_3 (216 mg, 4.0 mmol), DMF (5 mL) at 90 °C for 12 h according to general procedure K, as brownish oil (211 mg, 52%). ^{1}H NMR (300 MHz, $CDCl_3$): δ = 0.81-0.88 (m, 24H, $8CH_3$), 1.25-1.41 (m, 32H, $16CH_2$), 1.56-1.62 (m, 4H, 4CH), 4.04-4.08 (m, 8H, $4CH_2O$), 6.04 (d, 2H, J = 16.0 Hz,

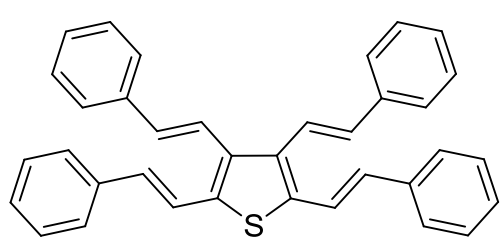
2CH), 6.28 (d, 2H, J = 15.6 Hz, 2CH), 7.59 (d, 2H, J = 16.0 Hz, 2CH), 7.77 (d, 2H, J = 15.6 Hz, 2CH). ^{13}C NMR (75 MHz, $CDCl_3$): δ = 10.9 ($2CH_3$), 11.0 ($2CH_3$), 14.0 ($4CH_3$), 22.9 ($4CH_2$), 23.8 ($2CH_2$), 23.9 ($2CH_2$), 28.9 ($4CH_2$), 30.4 ($2CH_2$), 30.5 ($2CH_2$), 38.7 (2CH), 38.8 (2CH), 67.4 ($2CH_2O$), 67.6 ($2CH_2O$), 121.5 (2CH), 126.2 (2CH), 133.6 (2CH), 135.2 (2CH), 138.4 (2C), 138.9 (2C), 165.8 (2CO), 166.0 (2CO). IR (KBr, cm^{-1}): ν = 2956, 2927 (m), 2858 (w), 1713 (s), 1618 (m), 1460, 1379 (w), 1302, 1261 (m), 1164 (s), 1080 (w), 1027, 965 (m), 856, 772, 726, 576 (w). MS (EI, 70 eV): *m/z* (%) = 812(11) $[M]^+$, 654(17), 543(15), 541(21), 527(23), 525(38), 523(11), 413(13), 411(11), 385(12), 369(21), 301(24), 299(25), 273(12), 257(31), 255(13), 213(11), 71(73), 70(20), 57(100), 55(31), 44(14), 43(59), 41(32). HRMS (ESI): calcd for $C_{48}H_{77}O_8S$ $[M+H]^+$: 813.53337; found: 813.53293.

(2*E*,2'*E*,2''*E*,2'''*E*)-Tetrahexyl-3,3',3'',3'''-(thiophene-2,3,4,5-tetrayl)tetraacrylate (62f):



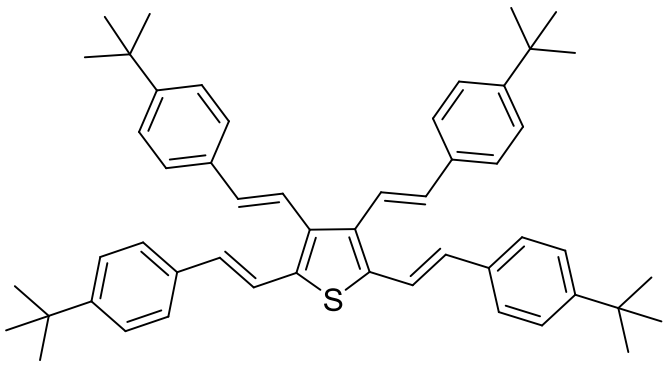
Product **62f** was prepared starting with **61** (200 mg, 0.5 mmol), *n*-hexyl acrylate (0.44 mL, 2.5 mmol), Pd $(OAc)_2$ (3.4 mg, 3 mol %), $P(Cy)_3$ (5 mol %), Na_2CO_3 (216 mg, 4.0 mmol), DMF (5 mL) at 90 °C for 12 h according to general procedure K, as brownish oil (220 mg, 63%). ^{1}H NMR (300 MHz, $CDCl_3$): δ = 0.83 (t, 12H, J = 6.7 Hz, $4CH_3$), 1.25-1.37 (m, 24H, $12CH_2$), 1.60-1.69 (m, 8H, $4CH_2$), 4.13 (t, 4H, J = 6.7 Hz, $2CH_2O$), 4.15 (t, 4H, J = 6.8 Hz, $2CH_2O$), 6.04 (d, 2H, J = 16.0 Hz, 2CH), 6.27 (d, 2H, J = 15.6 Hz, 2CH), 7.59 (d, 2H, J = 16.0 Hz, 2CH), 7.74 (d, 2H, J = 15.6 Hz, 2CH). ^{13}C NMR (62 MHz, $CDCl_3$): δ = 14.0 ($4CH_3$), 22.5 ($4CH_2$), 25.6 ($4CH_2$), 28.5 ($2CH_2$), 28.6 ($2CH_2$), 31.4 ($4CH_2$), 65.1 ($2CH_2O$), 65.2 ($2CH_2O$), 121.4 (2CH), 126.2 (2CH), 133.7 (2CH), 135.2 (2CH), 138.3 (2C), 138.9 (2C), 165.7 (2CO), 165.9 (2CO). IR (KBr, cm^{-1}): ν = 2954, 2926, 2856 (w), 1712, 1617 (m), 1465, 1457, 1379 (w), 1302, 1259 (m), 1162 (s), 1061, 1013 (w), 964 (m) 905, 855, 778, 724, 576 (w). MS (EI, 70 eV): *m/z* (%) = 700(13) $[M]^+$, 571(15), 570(30), 569(15), 511(23), 485(43), 469(67), 467(34), 427(11), 385(12), 383(27), 341(44), 299(45), 257(30), 255(40), 229(11), 213(19), 85(10), 57(13), 43(100), 41(13). HRMS (ESI): calcd for $C_{40}H_{60}N_aO_8S$ $[M+N_a]^+$: 723.39011; found: 723.38923.

2,3,4,5-Tetrastyrylthiophene (62g):



Product **62g** was prepared starting with **61** (200 mg, 0.5 mmol), styrene (0.33 mL, 2.5 mmol), $Pd(OAc)_2$ (3.4 mg, 3 mol %), $P(Cy)_3$ (5 mol %), Na_2CO_3 (216 mg, 4.0 mmol), DMF (5 mL) at 100 °C for 12 h according to general procedure K, as a brown solid (197 mg, 80%), mp 162-164 °C. ^{1}H NMR (300 MHz, $CDCl_3$): δ = 6.74 (d, 2H, J = 16.3 Hz, 2CH), 6.93 (d, 2H, J = 16.1 Hz, CH), 7.07 (d, 2H, J = 16.3 Hz, CH), 7.10-7.17 (m, 6H, ArH and 2CH), 7.19-7.23 (m, 4H, ArH), 7.25-7.29 (m, 6H, ArH), 7.37-7.43 (m, 6H, ArH). ^{13}C NMR (62 MHz, $CDCl_3$): δ = 120.8 (2CH), 122.2 (2CH), 126.4 (4CH), 126.5 (4CH), 127.8 (2CH), 127.9 (2CH), 128.8 (8CH), 129.5 (2CH), 134.7 (2CH), 136.7 (2C), 137.1 (2C), 137.3 (2C), 137.4 (2C). IR (KBr, cm^{-1}): ν = 3026, 2921, 2850, 1595, 1489, 1445, 1178, 1154, 1072, 1025, 969 (w), 942, 740 (m), 688 (s), 648, 580, 550 (w). MS (EI, 70 eV): *m/z* (%) = 492(100) $[M]^+$, 490(30), 488(25), 401(25), 324(13), 167(14), 115(11), 91(32), 44(13). HRMS (EI, 70 eV): calcd for $C_{36}H_{28}S$ $[M]^+$: 492.19062; found: 492.18969.

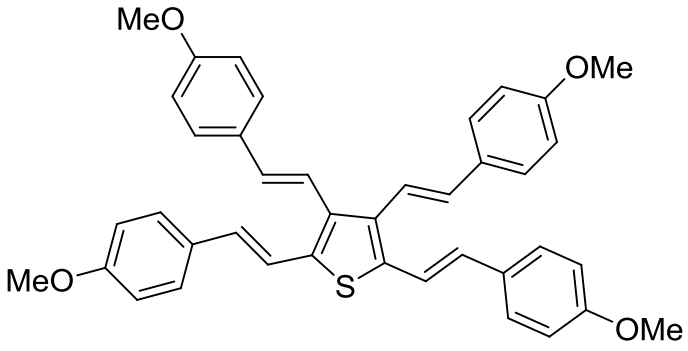
2,3,4,5-Tetrakis(4-*tert*-butylstyryl)thiophene (62h):



Product **62h** was prepared starting with **61** (200 mg, 0.5 mmol), 4-*tert*-butyl styrene (0.45 mL, 2.5 mmol), $Pd(OAc)_2$ (3.4 mg, 3 mol %), $P(Cy)_3$ (5 mol %), Na_2CO_3 (216 mg, 4.0 mmol), DMF (5 mL) at 100 °C for 12 h according to general procedure K, as brownish solid (258 mg, 72%). ^{1}H NMR (250 MHz, $CDCl_3$): δ = 1.24 (s, 18H, $6CH_3$), 1.27 (s, 18H, $6CH_3$), 6.70 (d, 2H, J = 16.3 Hz, 2CH), 6.90 (d, 2H, J = 16.0 Hz, 2CH), 7.02 (d, 2H, J = 16.3 Hz, 2CH), 7.27-7.34 (m, 18H, ArH and 2CH). ^{13}C NMR (62 MHz, $CDCl_3$): δ = 31.2 ($6CH_3$), 31.3 ($6CH_3$), 34.6 (2C), 34.7 (2C), 120.3 (2CH), 121.6 (2CH), 125.7 (8CH), 126.2 (4CH), 126.3 (4CH), 129.0 (2CH), 134.3 (2CH), 134.4 (2C), 134.7 (2C), 136.5 (2C), 137.3 (2C), 150.9 (2C), 151.1 (2C). IR (KBr, cm^{-1}): ν = 3026 (w), 2957 (m), 2902, 2865, 1513, 1462, 1408, 1392 (w), 1361, 1267, 1108 (m), 1014 (w), 948, 937, 823, 812 (m), 698, 6330, 572 (w), 555 (s). MS (EI, 70 eV): *m/z* (%) = 716(100)

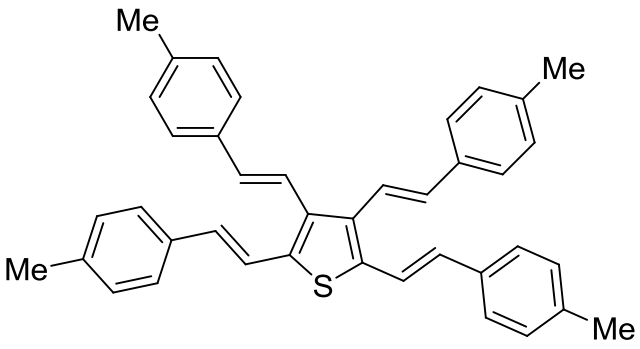
$[M]^+$, 715(23), 714(42), 713(12), 712(21), 424(12), 277(13), 43(28), 42(12), 41(28), 39(10). HRMS (EI, 70 eV): calcd for $C_{52}H_{60}S$ $[M]^+$: 716.44102; found: 716.43964.

2,3,4,5-Tetrakis(4-methoxystyryl)thiophene (62i):



Product **62i** was prepared starting with **61** (200 mg, 0.5 mmol), 4-methoxy styrene (0.33 mL, 2.5 mmol), $Pd(OAc)_2$ (3.4 mg, 3 mol %), $P(Cy)_3$ (5 mol %), Na_2CO_3 (216 mg, 4.0 mmol), DMF (5 mL) at 100 °C for 12 h according to general procedure K, as a brown solid (190 mg, 62%), mp 150-152 °C. ^{1}H NMR (300 MHz, $CDCl_3$): δ = 3.74 (s, 6H, $2CH_3O$), 3.76 (s, 6H, $2CH_3O$), 6.67 (d, 2H, J = 16.2 Hz, 2CH), 6.79 (d, 4H, J = 9.0 Hz, ArH), 6.81-6.88 (m, 6H, ArH and CH), 6.91 (d, 2H, J = 16.3 Hz, CH), 7.20 (d, 2H, J = 16.0 Hz, CH), 7.32 (d, 4H, J = 8.8 Hz, ArH), 7.35 (d, 4H, J = 8.7 Hz, ArH). ^{13}C NMR (75 MHz, $CDCl_3$): δ = 55.3 ($2CH_3O$), 55.4 ($2CH_3O$), 114.2 (4CH), 114.3 (4CH), 119.2 (2CH), 120.5 (2CH), 127.6 (4CH), 127.7 (4CH), 128.5 (2CH), 130.1 (2C), 130.3 (2C), 133.8 (2CH), 136.1 (2C), 137.1 (2C), 159.3 (2C), 159.5 (2C). IR (KBr, cm^{-1}): ν = 3028, 2953, 2930, 2833 (w), 1600 (m), 1573 (w), 1508 (s), 1461, 1455, 1439 (m), 1418 (w), 1302 (m), 1286, 1272 (w), 1241, 1171 (s), 1108 (m), 1029 (s), 969 (m), 941 (s), 848, 812, 766, 731, 608 (m), 580 (w). MS (EI, 70 eV): *m/z* (%) = 612(100) $[M]^+$, 611(15), 610(31), 493(10), 491(17), 121(29), 44(15), 43(16). HRMS (EI, 70 eV): calcd for $C_{40}H_{36}O_4S$ $[M]^+$: 612.23288; found: 612.23136.

2,3,4,5-Tetrakis(4-methylstyryl)thiophene (62j):



Product **62j** was prepared starting with **61** (200 mg, 0.5 mmol), 4-methyl styrene (0.33 mL, 2.5 mmol), $Pd(OAc)_2$ (3.4 mg, 3 mol %), $P(Cy)_3$ (5 mol %), Na_2CO_3 (216 mg, 4.0 mmol), DMF (5 mL) at 100 °C for 12 h according to general procedure K, as a brown solid (213 mg, 78%), mp. 178-180 °C. ^{1}H NMR (300 MHz, $CDCl_3$): δ = 2.27 (s, 6H, $2CH_3$), 2.30 (s, 6H,

$2CH_3$), 6.69 (d, 2H, J = 16.3 Hz, 2CH), 6.88 (d, 2H, J = 15.9 Hz, 2CH), 6.98-7.04 (m, 2H, 2CH), 7.05 (d, 4H, J = 8.6 Hz, ArH), 7.09 (d, 4H, J = 8.3 Hz, ArH), 7.10-7.16 (m, 2H, 2CH), 7.28 (d, 4H, J = 7.0 Hz, ArH), 7.31 (d, 4H, J = 7.5 Hz, ArH). ^{13}C NMR (62 MHz, $CDCl_3$): δ = 20.2 ($4CH_3$), 119.0 (2CH), 120.4 (2CH), 125.3 (4CH), 125.4 (4CH), 128.1 (2CH), 128.4 (8CH), 133.3 (2CH), 133.4 (2C), 133.6 (2C), 135.4 (2C), 136.2 (2C), 136.6 (2C), 136.8 (2C). IR (KBr, cm^{-1}): v = 3021, 2919, 2851, 1731, 1613, 1511, 1453, 1376 (w), 1259, 1179 (m), 1031, 1017, 945, 934 (s), 869, 849 (m), 798 (s), 700, 547 (m). MS (EI, 70 eV): *m/z* (%) = 548(100) $[M]^+$, 546(17), 445(13), 443(19), 105(16), 44(46), 43(15). HRMS (EI, 70 eV): calcd for $C_{40}H_{36}S$ $[M]^+$: 548.25322; found: 548.25237.

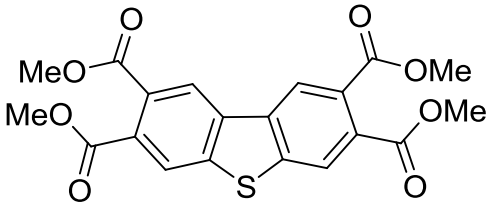
General procedure L for synthesis of dibenzothiophenes (63):

A pressure tube (glass bomb) a suspension of $Pd(OAc)_2$ (3.4 mg, 0.03 mmol, 3 mol%) and $P(Cy)_3$ (5 mol%) in DMF (5 mL) was purged with Argon and stirred at 20 °C to give a yellowish clear solution. To the stirred solution were added **61** (200 mg, 0.5 mmol), Na_2CO_3 (216 mg, 4.0 mmol) and the alkene or styrene (5.0 equiv per bromine atom of the substrate). The reaction mixture was stirred at 140 °C for 24-36h. The solution was poured into H_2O, brine and EtOAc (25 mL each) and the organic and the aqueous layers were separated. The latter was extracted with EtOAc (3 × 25mL), dried (Na_2SO_4), filtered, and concentrated in vacuo. The residue was purified by flash column chromatography (flash silica gel, eluent: *n*-heptane- EtOAc).

General procedure M for synthesis of dibenzothiophenes (63):

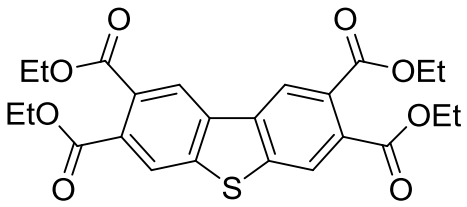
A diphenyl ether solution (3 mL) of **62a-j** was stirred at 200 °C for 24 h in a pressure tube. The solution was allowed to cool to 20 °C and Pd/C (30 mg, 10 mol %) was added. The solution was stirred at 200 °C for 48 h under an argon atmosphere. The reaction mixture was filtered and the filtrate was concentrated in vacuo. The residue was purified by chromatography (flash silica gel, eluent: heptanes-EtOAc).

Tetramethyl dibenzo[*b*,*d*]thiophene-2,3,7,8-tetracarboxylate (63a):



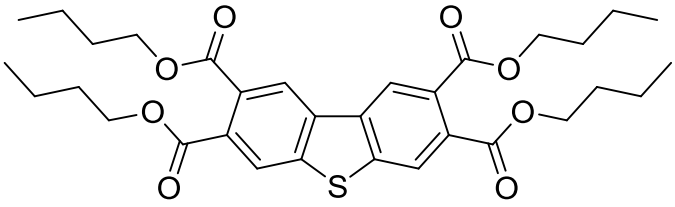
Product **63a** was prepared starting with **62a** (100 mg, 0.24 mmol), following general procedure M, as whitish solid (59 mg, 60%), mp. = 146-148 °C. ^{1}H NMR (300 MHz, $CDCl_3$): δ = 3.90 (s, 6H, $2CH_3O$), 3.92 (s, 6H, $2CH_3O$), 8.15 (s, 2H, ArH), 8.54 (s, 2H, ArH). ^{13}C NMR (62 MHz, $CDCl_3$): δ = 51.9 ($2CH_3O$), 52.0 ($2CH_3O$), 122.4 (2CH), 122.8 (2CH), 127.5 (2C), 130.6 (2C), 134.9 (2C), 142.3 (2C), 166.4 (2CO), 166.7 (2CO). IR (KBr, cm^{-1}): ν = 2999, 2951, 2923, 2850 (w), 1716 (s), 1600, 1548, 1465 (w), 1431 (m), 1351, 1316 (w), 1270, 1243 (m), 1191 (m), 1123, 1094 (s), 1012, 962, 896, 881, 820, 781, 746 (m), 609, 575 (w). GC-MS (EI, 70 eV): *m/z* (%) = 416(57) $[M]^+$, 386(21), 385(100), 339(11), 268(13). HRMS (EI, 70 eV): calcd for $C_{20}H_{16}O_8S$ $[M]^+$: 416.05604; found: 416.05600.

Tetraethyl dibenzo[*b*,*d*]thiophene-2,3,7,8-tetracarboxylate (63b):



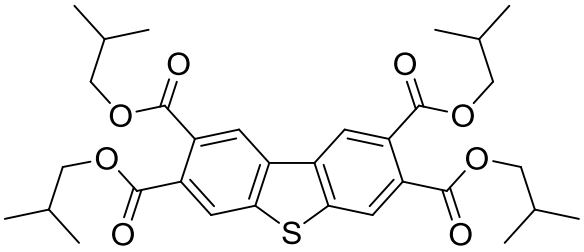
Product **63b** was prepared starting with **62b** (100 mg, 0.21 mmol), following general procedure M, as a light yellow semi solid (50 mg, 51%). ^{1}H NMR (300 MHz, $CDCl_3$): δ = 1.34 (t, 6H, J = 7.1 Hz, $2CH_3$), 1.36 (t, 6H, J = 7.1 Hz, $2CH_3$), 4.36 (q, 4H, J = 7.1 Hz, $2CH_2O$), 4.37 (q, 4H, J = 7.1 Hz, $2CH_2O$), 8.16 (s, 2H, ArH), 8.54 (s, 2H, ArH). ^{13}C NMR (62 MHz, $CDCl_3$): δ = 14.1 ($2CH_3$), 14.2 ($2CH_3$), 61.9 ($2CH_2O$), 62.0 ($2CH_2O$), 123.3 (2CH), 123.7 (2CH), 129.0 (2C), 131.9 (2C), 135.9 (2C), 143.1 (2C), 167.1 (2CO), 167.2 (2CO). IR (KBr, cm^{-1}): ν = 2979, 2936, 2905, 2874 (w), 1732, 1707 (s), 1607, 1550, 1470, 1446, 1419, 1384 (w), 1365, 1314 (m), 1271, 1258, 1241, 1223 (s), 1172, 1118 (m), 1092, 1077, 1029, 1019 (s), 896, 872, 849, 779, 744 (m), 721, 664, 625, 614, 591, 540 (w). GC-MS (EI, 70 eV): *m/z* (%) = 472(95) $[M]^+$, 427(20), 400(26), 399(100), 371(12), 325(19), 254(15). HRMS (EI, 70 eV): calcd for $C_{24}H_{24}O_8S$ $[M]^+$: 472.11864; found: 472.11846. Anal. calcd for $C_{24}H_{24}O_8S$: C, 61.01; H, 5.12; S, 6.79. Found: C, 60.88; H, 5.66; S, 6.90.

Tetrabutyl dibenzo[*b*,*d*]thiophene-2,3,7,8-tetracarboxylate (63c):



Product **63c** was prepared starting with **61** (200 mg, 0.5 mmol), n-butyl acrylate (0.36 mL, 2.5 mmol), $Pd(OAc)_2$ (3.4 mg, 3 mol %), $P(Cy)_3$ (5 mol %), Na_2CO_3 (216 mg, 4.0 mmol), DMF (5 mL) at 140 °C for 24 h according to general procedure L, as brownish oil (117 mg, 40%). ^{1}H NMR (300 MHz, $CDCl_3$): δ = 0.91 (t, 6H, J = 7.3 Hz, $2CH_3$), 0.92 (t, 6H, J = 7.4 Hz, $2CH_3$), 1.35-1.45 (m, 8H, $4CH_2$), 1.64-1.75 (m, 8H, $4CH_2$), 4.30 (t, 4H, J = 6.7 Hz, $2CH_2O$), 4.31 (t, 4H, J = 6.7 Hz, $2CH_2O$), 8.15 (s, 2H, ArH), 8.52 (s, 2H, ArH). ^{13}C NMR (75 MHz, $CDCl_3$): δ = 12.7 ($4CH_3$), 18.2 ($4CH_2$), 29.5 ($2CH_2$), 29.6 ($2CH_2$), 64.9 ($2CH_2O$), 65.0 ($2CH_2O$), 122.3 (2CH), 122.7 (2CH), 128.1 (2C), 130.9 (2C), 134.9 (2C), 142.0 (2C), 166.2 (2CO), 166.3 (2CO). IR (KBr, cm^{-1}): v = 2953, 2925, 2856 (m), 1716 (s), 1608, 1547, 1466, 1379 (m), 1268, 1240, 1119, 1097 (s), 991, 897, 781 (m), 746, 600, 542 (w). MS (EI, 70 eV): *m/z* (%) = 584(39) $[M]^+$, 528(10), 457(10), 456(31), 457(100), 399(50), 360(17), 343(27), 342(12), 325(27), 254(12), 57(14), 44(16), 41(21). HRMS (ESI): calcd for $C_{32}H_{41}O_8S$ $[M+H]^+$: 585.2516; found: 585.2517.

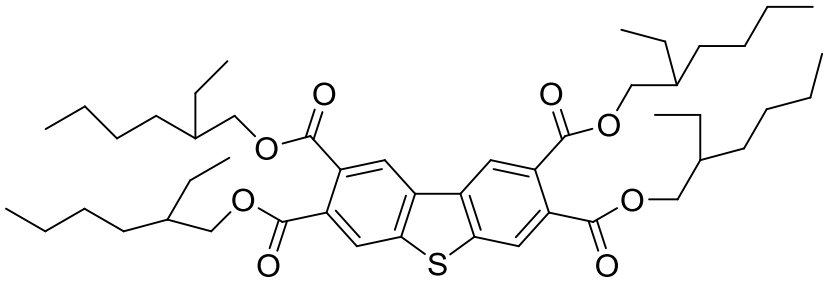
Tetraisobutyl dibenzo[*b*,*d*]thiophene-2,3,7,8-tetracarboxylate (63d):



Product **63d** was prepared starting with **61** (200 mg, 0.5 mmol), iso-butyl acrylate (0.36 mL, 2.5 mmol), $Pd(OAc)_2$ (3.4 mg, 3 mol %) , $P(Cy)_3$ (5 mol %), Na_2CO_3 (216 mg, 4.0 mmol), DMF (5 mL) at 140 °C for 24 h according to general procedure L, as yellowish semi solid (152 mg, 52%). ^{1}H NMR (300 MHz, $CDCl_3$): δ = 0.94 (d, 12H, J = 6.7 Hz, $4CH_3$), 0.96 (d, 12H, J = 6.7 Hz, $4CH_3$), 1.96-2.07 (m, 4H, 4CH), 4.07 (d, 4H, J = 6.7 Hz, $2CH_2O$), 4.08 (d, 4H, J = 6.7 Hz, $2CH_2O$), 8.16 (s, 2H, ArH), 8.51 (s, 2H, ArH). ^{13}C NMR (62 MHz, $CDCl_3$): δ = 19.2 ($8CH_3$), 27.7 (4CH), 72.1 ($2CH_2O$), 72.2 ($2CH_2O$), 123.2 (2CH), 123.8 (2CH), 129.2 (2C), 131.9 (2C), 135.9 (2C), 143.0 (2C), 167.2 (4CO). IR (KBr, cm^{-1}): v = 2959 (m), 2874 (w), 1719 (s), 1609, 1548, 1521 (w), 1468 (m), 1418, 1393, 1376, 1324 (w), 1266, 1237 (s), 1161 (m), 1122 (s), 1097, 1006, 981, 944 (m), 895, 823, 807 (w), 779 (m), 759, 707, 621, 569 (w). MS (EI, 70 eV): *m/z* (%) = 584(41) $[M]^+$, 456(43), 455(100), 400(11), 399(57), 361(12), 360(78), 342(12), 325(42),

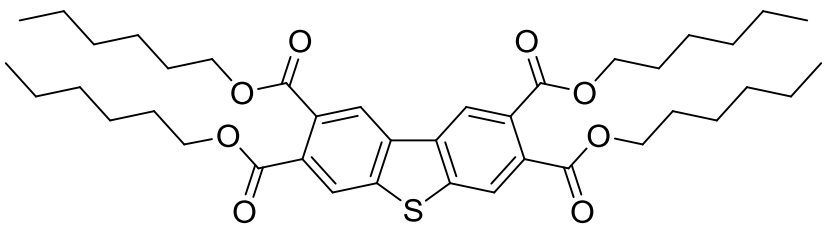
254(21), 57(66), 56(11), 41(50). HRMS (ESI): calcd for $C_{32}H_{41}O_8S$ $[M+H]^+$: 585.25167; found: 585.25244.

Tetrakis(2-ethylhexyl) dibenzo[*b*,*d*]thiophene-2,3,7,8-tetracarboxylate (63e):



Product **63e** was prepared starting with **62e** (100 mg, 0.12 mmol), following general procedure M, as brownish oil (69 mg, 70%). ^{1}H NMR (300 MHz, $CDCl_3$): δ = 0.84-0.91 (m, 24H, $8CH_3$), 1.27-1.45 (m, 32H, $16CH_2$), 1.61-1.71 (m, 4H, 4CH), 4.19-4.24 (m, 8H, $4CH_2O$), 8.15 (s, 2H, ArH), 8.48 (s, 2H, ArH). ^{13}C NMR (62 MHz, $CDCl_3$): δ = 11.0 ($4CH_3$), 14.0 ($4CH_3$), 23.0 ($4CH_2$), 23.7 ($2CH_2$), 23.8 ($2CH_2$), 28.9 ($4CH_2$), 30.4 ($4CH_2$), 38.8 (4CH), 68.6 ($4CH_2O$), 123.1 (2CH), 123.7 (2CH), 129.3 (2C), 131.9 (2C), 135.9 (2C), 143.0 (2C), 167.3 (2CO), 167.3 (2CO). IR (KBr, cm^{-1}): ν = 2956, 2926, 2858 (w), 1721 (s), 1608, 1549 (w), 1460, 1379, 1314 (m), 1265, 1236, 1122, 1097 (s), 1004, 957, 894 (w), 776 (m), 517 (w). MS (EI, 70 eV): *m/z* (%) = 808(2) $[M]^+$, 568(19), 567(57), 473(15), 456(11), 455(41), 360(68), 343(38), 325(23), 216(17), 112(24), 83(14), 71(48), 57(100), 43(60), 41(36). HRMS (EI, 70 eV): calcd for $C_{48}H_{72}O_8S$ $[M]^+$: 808.49424; found: 808.49384.

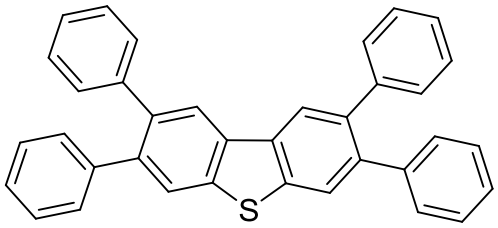
Tetrahexyl dibenzo[*b*,*d*]thiophene-2,3,7,8-tetracarboxylate (63f):



Product **63f** was prepared starting with **61** (200 mg, 0.5 mmol), *n*-hexyl acrylate (0.44 mL, 2.5 mmol), $Pd(OAc)_2$ (3.4 mg, 3 mol %), $P(Cy)_3$ (5 mol %), Na_2CO_3 (216 mg, 4.0 mmol), DMF (5 mL) at 140 °C for 24 h according to general procedure L, as brownish semi solid (139 mg, 40%). ^{1}H NMR (300 MHz, $CDCl_3$): δ = 0.83 (t, 6H, J = 6.8 Hz, $2CH_3$), 0.84 (t, 6H, J = 6.9 Hz, $2CH_3$), 1.24-1.31 (m, 16H, $8CH_2$), 1.33-1.40 (m, 8H,

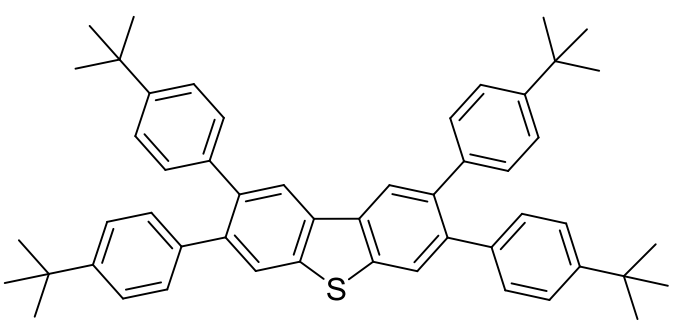
4CH_2), 1.65-1.77 (m, 8H, 4CH_2), 4.28 (t, 4H, J = 6.8 Hz, 2CH_2O), 4.30 (t, 4H, J = 6.8 Hz, 2CH_2O), 8.15 (s, 2H, ArH), 8.52 (s, 2H, ArH). ^{13}C NMR (62 MHz, $CDCl_3$): δ = 14.0 (4CH_3), 22.5 (4CH_2), 25.6 (4CH_2), 28.5 (2CH_2), 28.6 (2CH_2), 31.5 (4CH_2), 66.2 (2CH_2O), 66.3 (2CH_2O), 123.2 (2CH), 123.7 (2CH), 129.1 (2C), 131.9 (2C), 135.9 (2C), 143.0 (2C), 167.2 (2CO), 167.3 (2CO). IR (KBr, cm^{-1}): ν = 2953, 2925, 2856 (m), 1716 (s), 1608, 1547, 1466, 1379 (m), 1268, 1240, 1119, 1097 (s), 991, 897, 781 (m), 746, 600, 542 (w). MS (EI, 70 eV): *m/z* (%) = 696(11) $[M]^+$, 512(26), 511(100), 428(12), 427(50), 360(13), 343(29), 342(12), 325(47), 290(15), 258(12), 69(12), 55(25), 43(62). HRMS (EI, 70 eV): calcd for $C_{40}H_{56}O_8S$ $[M]^+$: 696.36904; found: 696.36962. Anal. calcd for $C_{40}H_{56}O_8S$: C, 68.93; H, 8.10; S, 4.60. Found: C, 69.17; H, 8.57; S, 4.99.

2,3,7,8-Tetraphenyldibenzo[*b*,*d*]thiophene (63g):



Product **63g** was prepared starting with **62g** (100 mg, 0.20 mmol), following general procedure M, as a yellow solid (73 mg, 74%), mp. = 228-230 °C. ^{1}H NMR (300 MHz, $CDCl_3$): δ = 7.16 (br, 20H, ArH), 7.83 (s, 2H, ArH), 8.11 (s, 2H, ArH. ^{13}C NMR (75 MHz, $CDCl_3$): δ = 123.6 (2CH), 124.6 (2CH), 126.6 (2CH), 126.8 (2CH), 128.0 (8CH), 130.1 (4CH), 130.2 (4CH), 134.8 (2C), 137.9 (2C), 139.3 (2C), 139.9 (2C), 141.3 (2C), 141.6 (2C). IR (KBr, cm^{-1}): ν = 3079, 3055, 2921, 2851, 1598, 1493 (w), 1457 (m), 1441, 1403, 1305, 1262, 1178, 1089, 1072, 966 (w), 905, 882, 764 (m), 728, 695 (s), 670, 648, 603, 585 (m). MS (EI, 70 eV): *m/z* (%) = 488(100) $[M]^+$, 312(13), 299(18), 71(10), 57(15), 43(15). HRMS (EI, 70 eV): calcd for $C_{36}H_{24}S$ $[M]^+$: 488.15932; found: 488.15903.

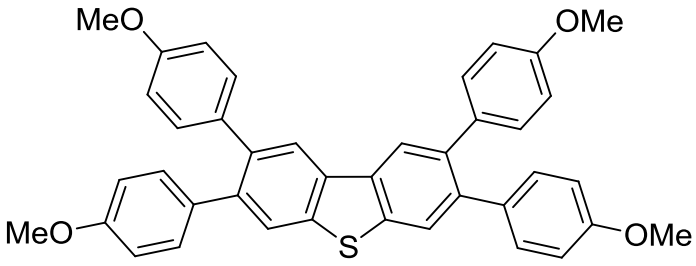
2,3,7,8-Tetrakis(4-*tert*-butylphenyl)dibenzo[*b*,*d*]thiophene (63h):



Product **63h** was prepared starting with **62h** (100 mg, 0.14 mmol), following general procedure M, as a yellow solid (62 mg, 63%), mp.= 92-94°C. ^{1}H NMR (300 MHz, $CDCl_3$): δ = 1.23 (s, 36H, 12 CH_3), 7.07 (d, 8H, J = 8.3 Hz, ArH), 7.17 (d, 8H, J = 8.3 Hz, 2CH), 7.80 (s,

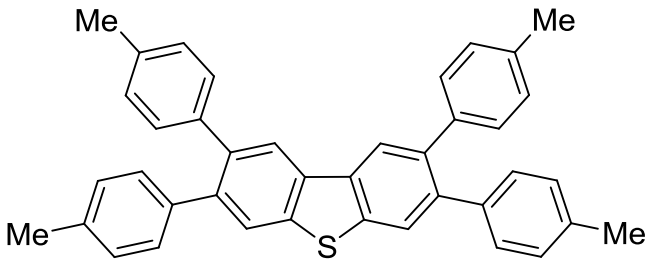
2H, ArH), 8.09 (s, 2H, ArH). ^{13}C NMR (62 MHz, $CDCl_3$): δ = 31.4 ($12CH_3$), 34.4 (2C), 34.5 (2C), 123.5 (2CH), 124.4 (2CH), 124.7 (8CH), 129.6 (4CH), 129.7 (4CH), 134.7 (2C), 137.7 (2C), 138.4 (2C), 138.6 (2C), 134.9 (2C), 139.7 (2C), 149.3 (2C), 149.5 (2C). IR (KBr, cm^{-1}): ν = 2955 (m), 2902, 2864, 1515, 1506 (w), 1456, 1361, 1267 (m), 1200 (w), 1111 (m), 1014, 884 (m), 831 (s), 761, 710, 626 (w), 601, 562 (m). MS (EI, 70 eV): *m/z* (%) = 712(100) $[M]^+$, 697(13), 424(13), 341(21), 71(10), 69(14), 57(68), 55(11), 43(11), 41(14). HRMS (EI, 70 eV): calcd for $C_{52}H_{56}S$ $[M]^+$: 712.40972; found: 712.40988.

2,3,7,8-Tetrakis(4-methoxyphenyl)dibenzo[*b*,*d*]thiophene (63i):



Product **63i** was prepared starting with **62i** (100 mg, 0.16 mmol), following general procedure M, as whitish solid (65 mg, 67%), mp. = 269-271 °C. ^{1}H NMR (300 MHz, $CDCl_3$): δ = 3.71 (s, 12H, $4OCH_3$), 6.71 (dd, 8H, *J* = 1.7, 8.6 Hz, ArH), 7.06 (dd, 8H, *J* = 1.4, 8.6 Hz, 2CH), 7.76 (s, 2H, ArH), 8.03 (s, 2H, ArH). ^{13}C NMR (75 MHz, $CDCl_3$): δ = 54.2 ($4OCH_3$), 112.4 (4CH), 112.5 (4CH), 122.3 (2CH), 123.3 (2CH), 130.0 (4CH), 130.1 (4CH), 132.8 (2C), 133.1 (2C), 133.5 (2C), 136.2 (2C), 137.8 (2C), 138.3 (2C), 157.3 (2C), 157.4 (2C). IR (KBr, cm^{-1}): ν = 3034, 2952, 2831 (w), 1606 (m), 1574 (w), 1510 (s), 1455, 1439 (m), 1420, 1398 (w), 1290 (m), 1242, 1174 (s), 1107, 1045, 1023 (m), 957, 936, 882 (w), 827 (s), 799, 785, 733, 678, 642, 598, 585, 573 (m). MS (EI, 70 eV): *m/z* (%) = 608(100) $[M]^+$, 579(30), 578(77), 44(12). HRMS (EI, 70 eV): calcd for $C_{40}H_{32}O_4S$ $[M]^+$: 608.20158; found: 608.20256.

2,3,7,8-Tetra-*p*-tolyldibenzo[*b*,*d*]thiophene (63j):



Product **63j** was prepared starting with **62j** (100 mg, 0.18 mmol), following general procedure C, as whitish solid (58 mg, 59%). mp. = 82-84 °C. ^{1}H NMR (300 MHz, $CDCl_3$): δ = 2.25 (s, 12H, $4CH_3$), 6.98 (d, 8H, *J* = 8.1 Hz, ArH), 7.05 (d, 8H, *J* = 8.1 Hz, 2CH), 7.78 (s, 2H, ArH), 8.06 (s, 2H, ArH). ^{13}C NMR (62 MHz, $CDCl_3$): δ = 20.1 ($4CH_3$), 122.5 (2CH), 123.4 (2CH), 127.7 (8CH), 128.8 (4CH), 128.9

(4CH), 133.6 (2C), 135.0 (2C), 135.2 (2C), 136.6 (2C), 137.5 (2C), 137.7 (2C), 137.9 (2C), 138.7 (2C). IR (KBr, cm^{-1}): ν = 3021, 2918, 2852, 1513, 1455, 1376, 1259, 1183, 1109, 1018, 881 (w), 815 (s), 724 (m), 660, 641, 599, (w), 578 (m). MS (EI, 70 eV): *m/z* (%) = 544(65) $[M]^+$, 515(15), 514(39), 432(38), 404(62), 327(100), 285(23), 271(29), 257(11), 112(21), 105(33), 85(11), 83(14), 71(27), 57(42), 43(27), 41(16). HRMS (EI, 70 eV): calcd for $C_{40}H_{32}S$ $[M]^+$: 544.22192; found: 544.22257.

8.2 Crystallographic Data

Table 47. Crystal data and structure refinement for **2a**.

Identification code	is_st2081	
Empirical formula	$C_{11}H_8Br_2S$	
Formula weight	332.05	
Temperature	173 (2) K	
Wavelength	0.71073 Å	
Crystal system	Monoclinic	
Space group (H.-M.)	P 21/n	
Space group (Hall)	-P 2yn	
Unit cell dimensions	*a* = 7.5006 (5) Å	α= 90.00°.
	b = 11.4919 (8) Å	β = 97.945 (4)°.
	c = 25.8482 (17) Å	γ = 90.00°.
Volume	2206.6 (3) $Å^3$	
Z	8	
Density (calculated)	1.999 Mg/m^3	
Absorption coefficient	7.491 mm^{-1}	
F(000)	1280	
Crystal size	0.86 × 0.26 × 0.04 mm^3	
Θ range for data collection	3.55 to 27.49°	
Index ranges	-9≤h≤9, -14≤k≤14, -33≤l≤33	
Reflections collected	38013	
Independent reflections	5029 [R(int) = 0.0761]	
Completeness to Θ = 29.00°	99.4%	
Absorption correction	multi-scan	
Max. and min. transmission	0.0599 and 0.7537	
Refinement method	Full-matrix least-squares on F^2	
Data / restraints / parameters	3602 / 2 / 268	
Goodness-of-fit on F^2	1.074	
Final R indices [I>2σ(I)]	R1 = 0.0429, wR2 = 0.0987	
R indices (all data)	R1 = 0.0743, wR2 = 0.1066	
Largest diff. peak and hole	0.822 and -0.802 $e.Å^{-3}$	

Table 48. Crystal data and structure refinement for **3a**.

Identification code	av_st208-2	
Empirical formula	$C_{18}H_{15}BrS$	
Formula weight	343.27	
Temperature	173 (2) K	
Wavelength	0.71073 Å	
Crystal system	Monoclinic	
Space group (H.-M.)	P -1	
Space group (Hall)	-P 1	
Unit cell dimensions	*a* = 8.515 (4) Å	α= 90.00°.
	b = 9.856 (6) Å	β = 105.959 (13)°.
	c = 9.983 (5) Å	γ = 90.00°.
Volume	746.9 (7) $Å^3$	
Z	2	
Density (calculated)	1.526 Mg/m^3	
Absorption coefficient	2.878 mm^{-1}	
F(000)	348	
Crystal size	0.48 × 0.28 × 0.04 mm^3	
Θ range for data collection	4.25 to 30.00°	
Index ranges	-11≤h≤11, -13≤k≤13, -13≤l≤14	
Reflections collected	15327	
Independent reflections	4278 [R(int) = 0.0352]	
Completeness to Θ = 29.00°	98.2%	
Absorption correction	multi-scan	
Max. and min. transmission	0.3388 and 0.8936	
Refinement method	Full-matrix least-squares on F^2	
Data / restraints / parameters	3480 / 0 / 183	
Goodness-of-fit on F^2	1.061	
Final R indices [I>2σ(I)]	R1 = 0.0333, wR2 = 0.0884	
R indices (all data)	R1 = 0.0466, wR2 = 0.0927	
Largest diff. peak and hole	0.687 and -0.412 $e.Å^{-3}$	

Table 49. Crystal data and structure refinement for **4i**.

Identification code	is_st203	
Empirical formula	$C_{22}H_{13}F_3S$	
Formula weight	366.38	
Temperature	173 (2) K	
Wavelength	0.71073 Å	
Crystal system	Monoclinic	
Space group (H.-M.)	P 21/n	
Space group (Hall)	-P 2yn	
Unit cell dimensions	a = 6.186 (5) Å	α= 90.00°.
	b = 24.301 (16) Å	β = 92.74 (3)°.
	c = 11.336 (8) Å	γ = 90.00°.
Volume	1702 (2) $Å^3$	
Z	4	
Density (calculated)	1.430 Mg/m^3	
Absorption coefficient	0.223 mm^{-1}	
F(000)	752	
Crystal size	0.63 × 0.44 × 0.34 mm^3	
Θ range for data collection	1.98 to 29.00°	
Index ranges	-8≤h≤8, -33≤k≤33, -15≤l≤15	
Reflections collected	17349	
Independent reflections	4497 [R(int) = 0.0348]	
Completeness to Θ = 29.00°	99.2%	
Absorption correction	multi-scan	
Max. and min. transmission	0.8724 and 0.9281	
Refinement method	Full-matrix least-squares on F^2	
Data / restraints / parameters	3820 / 0 / 248	
Goodness-of-fit on F^2	1.048	
Final R indices [I>2σ(I)]	R1 = 0.0410, wR2 = 0.0994	
R indices (all data)	R1 = 0.0507, wR2 = 0.1037	
Largest diff. peak and hole	0.349 and -0.274 e.$Å^{-3}$	

Table 50. Crystal data and structure refinement for **11a**.

Identification code	is_st327-1	
Empirical formula	$C_{18}H_{15}BrS$	
Formula weight	343.27	
Temperature	173 (2) K	
Wavelength	0.71073 Å	
Crystal system	Orthorhombic	
Space group (H.-M.)	P n m a	
Space group (Hall)	-P 2ac 2n	
Unit cell dimensions	a = 7.4143 (15) Å	α = 90.00°.
	b = 17.139 (3) Å	β = 90.00°.
	c = 11.617 (2) Å	γ = 90.00°.
Volume	1476.1 (5) $Å^3$	
Z	4	
Density (calculated)	1.545 Mg/m^3	
Absorption coefficient	2.913 mm^{-1}	
F(000)	696	
Crystal size	1.00 × 0.26 × 0.18 mm^3	
Θ range for data collection	4.76 to 32.50°.	
Index ranges	-11≤h≤ 10, -25≤k≤ 13, -17≤l≤ 16	
Reflections collected	11430	
Independent reflections	2724 [R(int) = 0.0343]	
Completeness to Θ = 29.00°	99.2%	
Absorption correction	multi-scan	
Max. and min. transmission	0.1587 and 0.6222	
Refinement method	Full-matrix least-squares on F^2	
Data / restraints / parameters	2210 / 0/ 98	
Goodness-of-fit on F^2	1.038	
Final R indices [I>2σ(I)]	R1 = 0.0299, wR2 = 0.0803	
R indices (all data)	R1 = 0.0435, wR2 = 0.0837	
Largest diff. peak and hole	0.743 and -0.352 $e.Å^{-3}$	

Table 51. Crystal data and structure refinement for **12c**.

Identification code	is_st3113	
Empirical formula	$C_{34}H_{40}S$	
Formula weight	480.72	
Temperature	173 (2) K	
Wavelength	0.71073 Å	
Crystal system	Triclinic	
Space group (H.-M.)	P -1	
Space group (Hall)	-P 1	
Unit cell dimensions	*a* = 9.302 (5) Å	α= 105.606 (12)°.
	b = 12.594 (7) Å	β = 95.188 (14)°.
	c = 13.009 (7) Å	γ = 97.384 (19)°.
Volume	1443.0 (13) $Å^3$	
Z	2	
Density (calculated)	1.106 Mg/m^3	
Absorption coefficient	0.131 mm^{-1}	
F(000)	520	
Crystal size	0.50 × 0.26 × 0.18 mm^3	
Θ range for data collection	2.23 to 29.00°	
Index ranges	-12≤h≤12, -17≤k≤17, -17≤l≤17	
Reflections collected	28799	
Independent reflections	7630 [R(int) = 0.0399]	
Completeness to Θ = 29.00°	99.2%	
Absorption correction	multi-scan	
Max. and min. transmission	0.9372 and 0.9767	
Refinement method	Full-matrix least-squares on F^2	
Data / restraints / parameters	5662 / 0 / 363	
Goodness-of-fit on F^2	1.095	
Final R indices [I>2σ(I)]	R1 = 0.0489, wR2 = 0.1359	
R indices (all data)	R1 = 0.0698, wR2 = 0.1459	
Largest diff. peak and hole	0.743 and -0.352 $e.Å^{-3}$	

Table 52. Crystal data and structure refinement for **19a**.

Identification code	is_st319	
Empirical formula	$C_{13}H_{13}Br_2NO_2$	
Formula weight	375.06	
Temperature	173 (2) K	
Wavelength	0.71073 Å	
Crystal system	Orthorhombic	
Space group (H.-M.)	*P* 21 21 21	
Space group (Hall)	P 2ac 2ab	
Unit cell dimensions	*a* = 7.807 (4) Å	α= 90.00°.
	b = 7.859 (4) Å	β = 90.00°.
	c = 22.553 (12) Å	γ = 90.00°.
Volume	1383.7 (13) $Å^3$	
Z	4	
Density (calculated)	1.800 Mg/m^3	
Absorption coefficient	5.851 mm^{-1}	
F(000)	736	
Crystal size	0.26 × 0.15 × 0.07 mm^3	
Θ range for data collection	2.74 to 30.02°	
Index ranges	-9≤h≤10, -11≤k≤10, -29≤l≤31	
Reflections collected	8845	
Independent reflections	3926 [R(int) = 0.0322]	
Completeness to Θ = 29.00°	98.8%	
Absorption correction	multi-scan	
Max. and min. transmission	0.3115 and 0.6848	
Refinement method	Full-matrix least-squares on F^2	
Data / restraints / parameters	3150 / 0 / 166	
Goodness-of-fit on F^2	1.001	
Final R indices [I>2σ(I)]	R1 = 0.0347, wR2 = 0.0682	
R indices (all data)	R1 = 0.0510, wR2 = 0.0712	
Largest diff. peak and hole	0.932 and -0.746 e.$Å^{-3}$	

Table 53. Crystal data and structure refinement for **22a**.

Identification code	ch_st541	
Empirical formula	$C_{25}H_{22}ClNO_2$	
Formula weight	403.89	
Temperature	173 (2) K	
Wavelength	0.71073 Å	
Crystal system	Triclinic	
Space group (H.-M.)	P -1	
Space group (Hall)	-P 1	
Unit cell dimensions	*a* = 12.3435 (2) Å	α= 106.070 (1)°.
	b = 14.5892 (2) Å	β = 97.205 (1)°.
	c = 18.5121 (3) Å	γ = 101.973 (1)°.
Volume	3073.88 (8) $Å^3$	
Z	6	
Density (calculated)	1.309 Mg/m^3	
Absorption coefficient	0.208 mm^{-1}	
F(000)	1272	
Crystal size	0.31 × 0.30 × 0.12 mm^3	
Θ range for data collection	1.88 to 30.00°	
Index ranges	-17≤h≤16, -20≤k≤20, -25≤l≤26	
Reflections collected	64412	
Independent reflections	17700 [R(int) = 0.0344]	
Completeness to Θ = 29.00°	98.7%	
Absorption correction	multi-scan	
Max. and min. transmission	0.9384 and 0.9755	
Refinement method	Full-matrix least-squares on F^2	
Data / restraints / parameters	11998 / 0 / 793	
Goodness-of-fit on F^2	1.036	
Final R indices [I>2σ(I)]	R1 = 0.0463, wR2 = 0.1088	
R indices (all data)	R1 = 0.0819, wR2 = 0.1191	
Largest diff. peak and hole	0.335 and -0.352 $e.Å^{-3}$	

Table 54. Crystal data and structure refinement for **27b.**

Identification code	av_st962	
Empirical formula	$C_{14}H_{16}O_4S$	
Formula weight	280.33	
Temperature	173 (2) K	
Wavelength	0.71073 Å	
Crystal system	Monoclinic	
Space group (H.-M.)	P 21/n	
Space group (Hall)	-P 2yn	
Unit cell dimensions	*a* = 7.998 (8) Å	α= 90.00°.
	b = 13.898 (13) Å	β = 91.13 (2)°.
	c = 12.924 (13) Å	γ = 90.00°.
Volume	1436 (2) $Å^3$	
Z	4	
Density (calculated)	1.296 Mg/m^3	
Absorption coefficient	0.232 mm^{-1}	
F(000)	592	
Crystal size	0.40 × 0.30 × 0.27 mm^3	
Θ range for data collection	2.15 to 28.00°	
Index ranges	-9≤h≤10, -18≤k≤18, -17≤l≤17	
Reflections collected	28799	
Independent reflections	3441 [R(int) = 0.0285]	
Completeness to Θ = 29.00°	99.4%	
Absorption correction	multi-scan	
Max. and min. transmission	0.9129 and 0.9400	
Refinement method	Full-matrix least-squares on F^2	
Data / restraints / parameters	2700 / 3 / 184	
Goodness-of-fit on F^2	1.062	
Final R indices [I>2σ(I)]	R1 = 0.0420, wR2 = 0.1199	
R indices (all data)	R1 = 0.0575, wR2 = 0.1280	
Largest diff. peak and hole	0.350 and -0.253 $e.Å^{-3}$	

Table 55. Crystal data and structure refinement for **27i**.

Identification code	av_st106	
Empirical formula	$C_{22}H_{20}O_2S$	
Formula weight	348.44	
Temperature	173 (2) K	
Wavelength	0.71073 Å	
Crystal system	Monoclinic	
Space group (H.-M.)	P 21/c	
Space group (Hall)	-P 2ybc	
Unit cell dimensions	*a* = 6.1658 (5) Å	α= 90.00°.
	b = 8.2731 (8) Å	β = 92.852 (3)°
	c = 35.418 (3) Å	γ = 90.00°.
Volume	1804.5 (3)Å^3	
Z	4	
Density (calculated)	1.283 Mg/m^3	
Absorption coefficient	0.191 mm^{-1}	
F(000)	736	
Crystal size	0.24 × 0.14 × 0.05 mm^3	
Θ range for data collection	4.19 to 22.95°	
Index ranges	-6≤h≤5, -8≤k≤9, -33≤l≤38	
Reflections collected	9310	
Independent reflections	2451 [R(int) = 0.0592]	
Completeness to Θ = 29.00°	98.0%	
Absorption correction	multi-scan	
Max. and min. transmission	0.9556 and 0.9905	
Refinement method	Full-matrix least-squares on F^2	
Data / restraints / parameters	1552 / 4 / 243	
Goodness-of-fit on F^2	1.006	
Final R indices [I>2σ(I)]	R1 = 0.0469, wR2 = 0.1006	
R indices (all data)	R1 = 0.0953, wR2 = 0.1140	
Largest diff. peak and hole	0.165 and -0.197 e.Å^{-3}	

Table 56. Crystal data and structure refinement for **31**.

Identification code	is_st150	
Empirical formula	$C_{12}H_9Br_2NOS$	
Formula weight	375.08	
Temperature	173 (2) K	
Wavelength	0.71073 Å	
Crystal system	Monoclinic	
Space group (H.-M.)	P 21/n	
Space group (Hall)	-P 2yn	
Unit cell dimensions	*a* = 11.5759 (6) Å	α= 90.00°.
	b = 10.4612 (6) Å	β = 115.361 (1)°.
	c = 11.8700 (7) Å	γ = 90.00°.
Volume	1298.90 (13) $Å^3$	
Z	4	
Density (calculated)	1.918 Mg/m^3	
Absorption coefficient	6.383 mm^{-1}	
F(000)	728	
Crystal size	0.30 × 0.29 × 0.26 mm^3	
Θ range for data collection	4.03 to 30.00°	
Index ranges	-15≤h≤16, -14≤k≤14, -16≤l≤15	
Reflections collected	14885	
Independent reflections	3774 [R(int) = 0.0972]	
Completeness to Θ = 29.00°	99.7%	
Absorption correction	multi-scan	
Max. and min. transmission	0.2504 and 0.2876	
Refinement method	Full-matrix least-squares on F^2	
Data / restraints / parameters	2938 / 0 / 155	
Goodness-of-fit on F^2	1.005	
Final R indices [I>2σ(I)]	R1 = 0.0311, wR2 = 0.0762	
R indices (all data)	R1 = 0.0435, wR2 = 0.0784	
Largest diff. peak and hole	1.230 and -0.689 e.$Å^{-3}$	

Table 57. Crystal data and structure refinement for **36b**.

Identification code	ch_st592	
Empirical formula	$C_{25}H_{28}O_5S$	
Formula weight	440.53	
Temperature	173 (2) K	
Wavelength	0.71073 Å	
Crystal system	Triclinic	
Space group (H.-M.)	P -1	
Space group (Hall)	-P 1	
Unit cell dimensions	*a* = 10.2275 (3) Å	α= 69.527 (1)°.
	b = 11.3135 (3) Å	β = 66.716 (1)°.
	c = 11.4252 (3)Å	γ = 80.957 (1)°
Volume	1137.35 (5) $Å^3$	
Z	2	
Density (calculated)	1.286 Mg/m^3	
Absorption coefficient	0.176 mm^{-1}	
F(000)	468	
Crystal size	0.35 × 0.31 × 0.24 mm^3	
Θ range for data collection	2.05 to 29.93°	
Index ranges	-14≤h≤14, -15≤k≤15, -16≤l≤16	
Reflections collected	23380	
Independent reflections	6502 [R(int) = 0.0184]	
Completeness to Θ = 29.00°	98.6%	
Absorption correction	multi-scan	
Max. and min. transmission	0.9410 and 0.9590	
Refinement method	Full-matrix least-squares on F^2	
Data / restraints / parameters	5481 / 12 / 344	
Goodness-of-fit on F^2	1.035	
Final R indices [I>2σ(I)]	R1 = 0.0402, wR2 = 0.1033	
R indices (all data)	R1 = 0.0497, wR2 = 0.1074	
Largest diff. peak and hole	0.330 and -0.228 e.$Å^{-3}$	

Table 58. Crystal data and structure refinement for **44f.**

Identification code	av_st504	
Empirical formula	$C_{29}H_{26}N_2O_2$	
Formula weight	434.52	
Temperature	173 (2) K	
Wavelength	0.71073Å	
Crystal system	Triclinic	
Space group (H.-M.)	P -1	
Space group (Hall)	-P 1	
Unit cell dimensions	a = 9.9187 (3)Å	α = 98.132 (2)°.
	b = 13.2291 (4)Å	β = 99.594 (2)°.
	c = 18.0652 (6)Å	γ = 96.469 (2)°.
Volume	2291.13 (12) $Å^3$	
Z	4	
Density (calculated)	1.260Mg/m^3	
Absorption coefficient	0.08 mm^{-1}	
F(000)	920	
Crystal size	0.64 × 0.13 × 0.09mm^3	
Θ range for data collection	2.10 to 26.00°.	
Index ranges	-12≤h≤ 9, -14≤k≤ 16, -21≤l≤ 22	
Reflections collected	36320	
Independent reflections	8982 [R(int) = 0.0615]	
Completeness to Θ = 29.00°	99.7%	
Absorption correction	multi-scan	
Max. and min. transmission	0.9510 and 0.9929	
Refinement method	Full matrix	
Data / restraints / parameters	4537 / 1/ 624	
Goodness-of-fit on F^2	0.921	
Final R indices [I>2σ(I)]	R1 = 0.0545, wR2 = 0.1057	
R indices (all data)	R1 = 0.1482, wR2 = 0.1259	
Largest diff. peak and hole	0.216 and -0.196e.$Å^{-3}$	

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