UNIVERSITÄT ROSTOCK

Synthesis of Highly Functionalized Carbacycles, Heterocycles and Silylium-Arene Adducts by Cyclocondensations, Palladium Catalyzed Cross-Coupling Reactions and Activation by $[Me_3Si]^+$ Cation.

DISSERTATION

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Muhammad Farooq Ibad geb. am 01. April 1982, Kunar Afghanistan

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Gutachter

1. Gutachter:
   Prof. Dr. Dr. h.c. Peter Langer,
   Institut für Chemie, Universität Rostock.
2. Gutachter:
   Prof. Dr. Axel Schulz
   Institut für Chemie, Universität Rostock.
3. Gutachter:
   Prof. Dr Manfred Braun
   Institut für Organische und Makromolekulare Chemie I,
   Heinrich-Heine-Universität Düsseldorf

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Muhammad Farooq Ibad

Rostock, 03. May 2012

Affectionately Dedicated to

My Father, Mother, Sweet Brother,

Sisters and My Own Family

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Table of Contents

Abbreviations

Å	Ångstrom
Ar	aryl
ATR	attenuated total reflectance
°C	Celsius
cm	centimeter
DEPT	Distortionless Enhancement by Polarisation Transfer
DFT	Density Functional Theory
DMAD	dimethyl acetylenedicarboxylate
DMF	dimethylformamide
DSC	Differential Scanning Calorimetry
EI	electron impact
ESI	electrospray ionization
Et	ethyl
Et_2O	diethyl ether
EtOAc	ethyl acetate
h	hour
Hz	Hertz
HRMS	High Resolution Mass Spectroscopy
IR	Infrared spectroscopy
LDA	lithium diisopropylamide
MS	Mass Spectrometry
m/z	Mass per charge
Me	methyl
Me_3SiOTf	trimethylsilyl trifluoromethanesulfonate
MHz	Megahertz
min	minute
mL	Millilitre
mmol	Millimole
mp	Melting point
NBO	Natural bond orbital

NMR	Nuclear Magnetic Resolution
Ph	Phenyl
T	Temperature
Tf_2O	trifluoromethanesulfonic anhydride
THF	tetrahydrofuran
TLC	Thin Layer Chromatography
TMS	trimethylsilane
TMSCl	trimethylsilyl chloride
TMSA	trimethylsilyl affinity
UV	Ultraviolet Spectroscopy

Summary

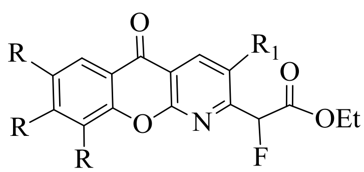
The Me_3SiOTf-mediated condensation of 1-ethoxy-2-fluoro-1,3-bis(trimethylsilyloxy) 1,3-dienes with 3-cyanochromones afforded 3-cyano-2-(4-ethoxy-3-fluoro-2,4-dioxobutyl)-chroman-4-ones. Their reaction with triethylamine afforded fluorinated azaxanthones or biaryls. The product distribution depends on the structure of the diene. The formation of the biaryls can be explained by an unprecedented domino "retro-Michael/aldol/fragmentation" reaction.

The [4+2] cycloaddition of 1-ethoxy-2-fluoro-1,3-bis(trimethylsilyloxy)-1,3-diene with dimethyl acetylenedicarboxylate (DMAD) afforded dimethyl 4-fluoro-3,5-dihydroxyphthalate. Site-selective Suzuki–Miyaura reactions of its bis(triflate) provide a convenient approach to 3,5-diaryl-4-fluorophthalates. The palladium(0)-catalyzed Suzuki cross-coupling reaction of the bis(triflates) of phenyl 1,4-dihydroxy-2-naphthoate afforded various 1,4-diaryl-2-naphthoates. The reactions proceeded with very good siteselectivity. Due to electronic reasons, the first attack occurred at the sterically more hindered position C-1. The Suzuki–Miyaura reaction of *N*-methyl-2,3-dibromoindole with two equivalents of boronic acids gave symmetrical 2,3-diarylindoles. The reaction with one equivalent of arylboronic acid resulted in site-selective formation of 2-aryl-3-bromoindoles. The one-pot reaction of 2,3-dibromoindole with two different arylboronic acids afforded unsymmetrical 2,3-diarylindoles containing two different aryl groups.

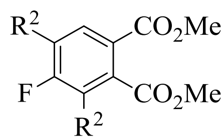
Furthermore the detailed experimental and theoretical study of the silylium arene adducts ($[Me_3Si\text{-}Ar][B(C_6F_5)_4]$) and the catalytic trimerisation of bissilylated diazomethane are studied. The decomposition of these salts to an interesting side product, the bissilylated fluoronium ion $[Me_3Si–F–SiMe_3]^+$, is studied. The side product was trapped with CS_2.

Aim and Purpose

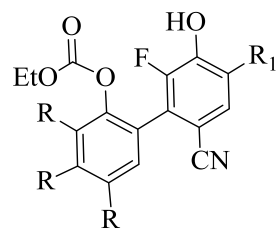
The aim of my PhD was the synthesis and characterization of new highly functionalized arenes (**Scheme 1,** species **A, B, C**) using a new domino reaction and a building block strategy. Fluorinated 1,3-dicarbonyl compounds were used as synthetic building blocks. They were characterized with traditional methods of analysis (Raman-/IR-/NMR spectroscopy, crystal structure analysis, elemental analysis, melting point / DSC).



A



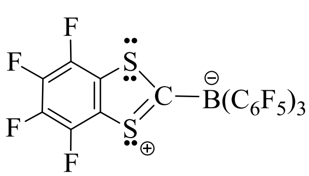
B



C

Scheme 1: Highly functionalized Arenes (R = Alkyl chains or halogen, R^1 = Aryl or hydroxyl).

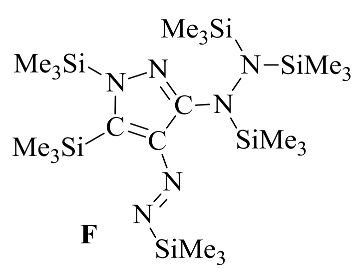
Next was planned to study theoretically and experimentally the behaviour of the super Lewis acid $[Me_3Si]^+$ with Lewis basic organic solvents (**Scheme 2,** species **D, E**) and small molecules (**Scheme 2,** species **F**).



D

$[Me_3Si.arene][B(C_6F_5)_4]$

E



F

Scheme 2. Heterocycles and trimethyl silyl arene adducts.

1. Synthesis of Highly Functionalized Biaryls by Condensation of 2-Fluoro-1,3-bis(silyloxy)-1,3-dienes with 3-Cyanochromones and Subsequent Domino "Retro-Michael / Aldol / Fragmentation" Reactions

1.1 Introduction

Since the discovery of fluorine (1886), a lot of interest in organofluorine molecules has emerged, due to the small size, high electronegativity, low polarizabilty and high ionization potential and liphphilicity of fluorine.

Fluorinated compounds are used in various types of molecules, e. g. in electronic materials, agrochemicals, and medicine or even in the process of separation of ^{235}U from ^{238}U for nuclear power stations. Teflon, a fluorine containing polymer, has a high thermal stability and inertness to a wide range of chemicals. The use of fluorinated medical drugs started with the synthesis of 5-fluorouracil,[1] an anti-tumor drug since 1957. About 20% of all pharmaceuticals, with even higher proportions for agrochemicals, contain fluorine.[2] Best selling fluorinated drugs are available in the market, such as the anti-depressant fluoxetine (Prozac), the anti-cholesterol atorvastatin (Lipitor) or the anti-bacterial ciprofloxacin (Ciprobay) shown in **Chart 1**.

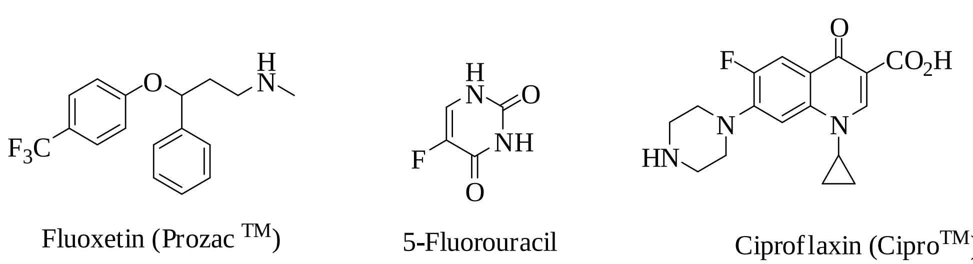


Chart 1. Popular Fluorinated Drugs.

The presence of even one fluorine atom in an organic compound alters significantly the electronic properties and reactivity from its counterpart without fluorine, with no significant steric effect. Despite the difference in size, fluorine (1.47 Å) is a good hydrogen (1.20 Å) mimic, which is extremely useful in medicinal chemistry.[3,4] The size of the CF_3 group is more close to an isopropyl and *tert*-butyl hroup than to a methyl group. The C-F bond is the strongest single bond in organic chemistry, with an electrostatic pair ($C^{\delta+}$ and $F^{\delta-}$) making fluorinated compounds resistant to metabolic degradation. True hydrogen bonding H····F is rare.[5]

Organofluorine compounds are very rare in nature. Fluoroacetate[6] is the first compound isolated in 1943, which further metabolizes in vivo forming fluorocitrate. Fluoroacetone[7] has been isolated from the plant *Acacia georginae.* Nucleocidin is a naturally occurring broad-spectrum antibiotic and was isolated in 1957 from the fermentation broth of the actinomycete *Streptomyces calvus*[8] shown in **Chart 2**.

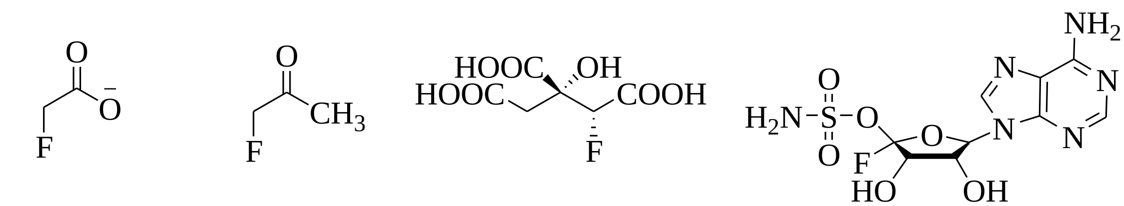


Chart 2. Fluorinated natural products.

Synthetically two major routes are used for the introduction of fluorine to organic molecules: I) the direct fluorination;[9-26] II) the building block method.[27-31] In direct fluorination reactions the fluorine is introduced directly at a specific position. These reactions can be categorized as nucleophilic, electrophilic, and electrochemical fluorinations. In the building block method fluorinated intermediates are used in cyclisation reactions. Mainly four major types of reagents can be used to transform fluorine-containing building blocks, namely: fluorine-substituted nucleophilic reagents, electrophilic reagents, radicals and carbenes. Some of the common fluorinated agents are shown below in **Chart 3.** Herein, I am going to discuss a new building block method for the synthesis of multifunctional organofluorine compounds.

1-Azaxanthones, studied by Ghosh and co-workers,[32] are of considerable pharmacological relevance. For example, they show anti-inflammatory activity and represent inhibitors of the passive cutaneous anaphylaxis.[33] The chemistry of 1,3-

bis(silyloxy)-1,3-butadienes[34,35] with chromone derivatives[36] has already been developed in the group of Professor Langer.

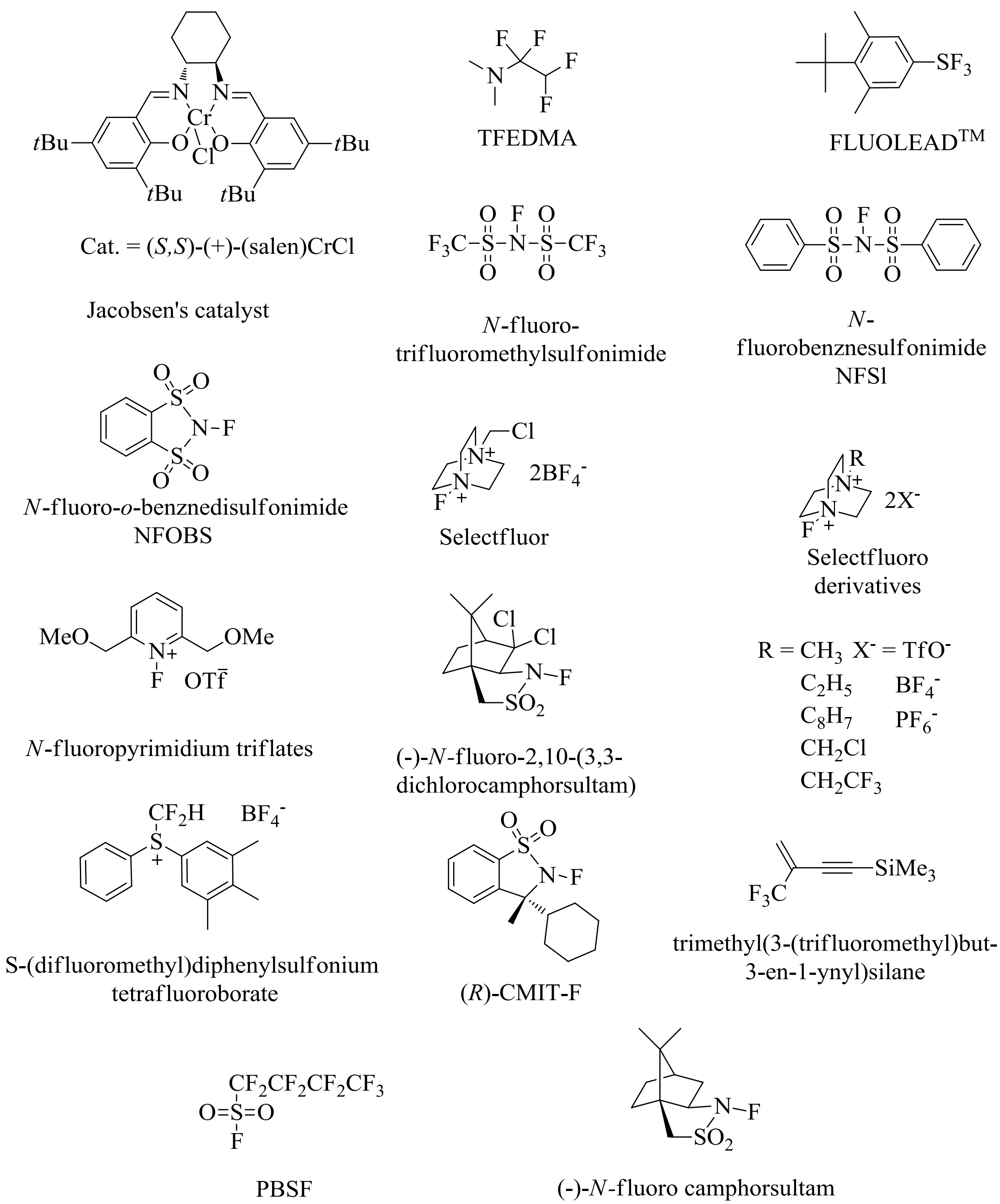
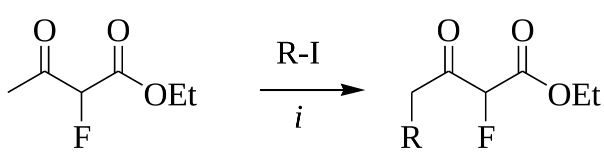


Chart 3. Fluorinating Agents.

While exploring the same chemistry toward fluoro-substituted 1,3-bis(silyloxy)-1,3-butadienes, for the first time, I have found, together with my colleague Dr. Obaid-ur-Rahman Abid (PhD thesis, Universität Rostock 2010), that the reaction of 3-cyanochromones with 2-fluoro-1,3-bis(silyloxy)-1,3-dienes gives rise to the unexpected formation of highly functionalized fluorinated biaryls. The outcome of these reactions shows the formation of newly highly substituted fluorinated biaryls. The reactions can be regarded as a new synthetic methodology for the buiding block synthesis in organofluoro chemistry. The products are not available by other methods. The formation of the products can be explained by a hitherto unprecedented domino “retro-Michael / aldol / fragmentation” reaction.

1.2 Synthesis of 2-fluoro-3-oxoesters

For this study I started the reaction of 3-cyanochromones with various 2-fluoro-3-oxoesters. The methodology[37] used for the synthesis of various 2-fluoro-3-oxoesters **1b-i** has not been applied until yet to the synthesis of the fluorinated derivatives. The reaction of commercially available ethyl 2-fluoroacetoacetate **1a** with benzyl bromide and various alkyl iodides afforded the 2-fluoro-3-oxoesters **1b-i** (**Scheme 3**, **Table 1**). The yield was found in the range 59-74% which is considered good for this type of reaction.



1a **1b-j**

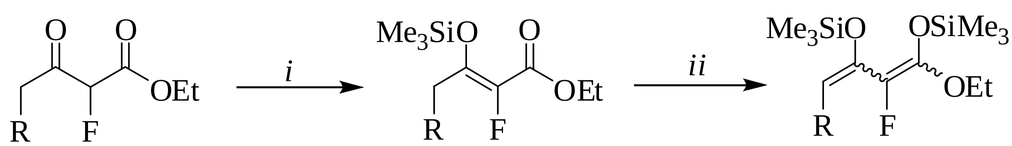
Scheme 3. Synthesis of **1b-i**: *i*: 1) LDA (2.3 equiv.), THF, −78 °C, 1 h; 2) BnBr or R-I, −78 → 20 °C, 14 h; 3) HCl (10%).

Table **1.** Synthesis of **1b-i**

1	**R**	**1 (%)**[a]
b	Bn	60
c	Me	59
d	*n*Pr	59
e	*n*Bu	63
f	*n*Pent	74
g	*n*Hex	64
h	*n*Hep	46
i	*n*Oct	62
j	*n*Dec	61

[a] yields of isolated products.

1.3 Synthesis of 1,3-Bis-Silyl Enol Ethers



1a-i **2a-i** **3a-i**

Scheme 4. Synthesis of **3a-i**: *i*: Me_3SiCl, NEt_3, benzene, 20 °C, 48 h; *ii*: 1) LDA, THF, −78 °C, 1 h; 2) Me_3SiCl, −78 → 20 °C, 14 h.

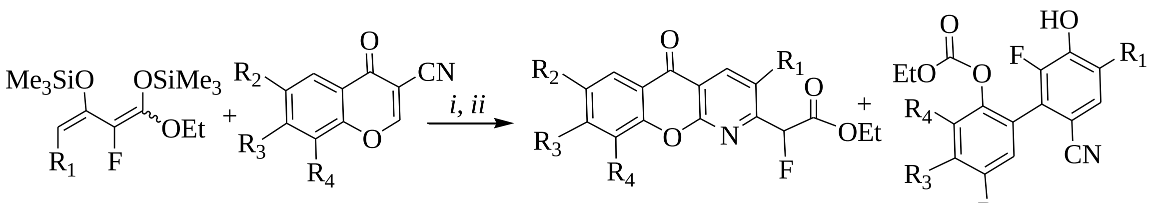
Silyl enol ethers **2a-i** were prepared by the silylation of **1a-j,** which are transformed into dienes (1-ethoxy-2-fluoro-1,3-bis(trimethylsilyloxy)-1,3-dienes) **3a-i** (**Scheme 4**, **Table 2**). Compounds **2b-i** and **3a-i** were prepared according to the procedures of Chan and Molander,[35] which were found suitable for fluorinated acetoacetates. The synthesis of **3a** has been previously reported.[38] Due to the unstable nature of the products; they were characterized only by ^1H NMR. All reactions were carried out on a 5 mmol scale. Dienes **3a-i** can be stored at −20 °C under inert atmosphere for several weeks.

Table 2. Synthesis of **3a-i**

2,3	R	2 (%)[a]	3 (%)[a]
a	H	81	94
b	Bn	83	91
c	Me	67	88
d	*n*Pr	82	90
e	*n*Bu	80	93
f	*n*Pent	65	89
g	*n*Hex	77	87
h	*n*Oct	84	94
i	*n*Dec	81	92

[a] yields of isolated products.

1.4 Synthesis of fluorinated biaryls and fluorinated azaxanthones



3a-i **4a-h** **5a-ab** **6a-ab**

Scheme 5. Synthesis of **5a-ai** and **6a-ai**; *i*, 1) Me_3SiOTf, 1 h, 20 °C; 2) CH_2Cl_2, 0 → 20 °C, 12 h; 3) HCl (10%); *ii*, 1) NEt_3, EtOH, 20 °C, 12 h; 2) HCl (10%).

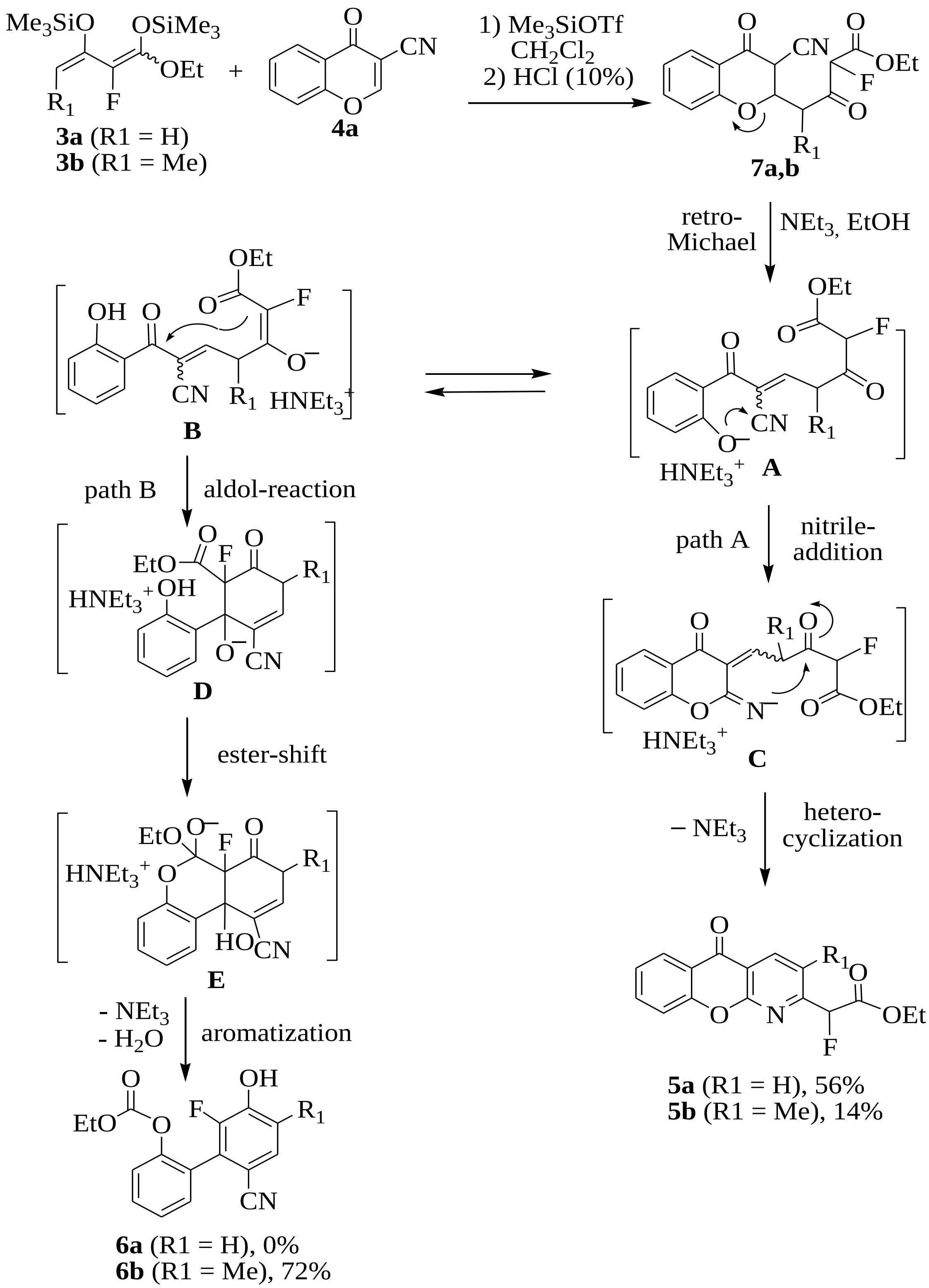
Two different results were found from the reaction of the resulted dienes **3** with 3-cyanochromones. Dienes **3b-i** resulted differently comparing, with in case of **3a** (**Scheme 5**). Reaction of unsubstituted **3a** with all types of 3-cyanochromones resulted in pure azaxanthone, no traces of biaryl product is found, while the reaction of parent 3-cyanochromone and of substituted cyanochromones (for electron-withdrawing, halogen substituents or electron donating alkyl groups) with substituted dienes **3b-i** mainly afforded the biaryls. Azaxanthones were isolated as side-products or not at all. The result is purely dependent on the chain elongation of the diene **3**.

Proposed mechanism

The proposed mechanism (**Scheme 6**) of the reaction can be explained as follows: the reaction of **3a** with 3-cyanochromone **4a** results in 3-cyano-2-(4-ethoxy-3-fluoro-2-4-dioxobutyl)chroman-4-one **7a** by action of Me_3SiOTf. Treatment of **7a** with triethylamine in ethanol afforded the fluorinated azaxanthone **5a** in 56%. Its formation has been reported to proceed by a domino “retro-Michael / nitrile-addition / heterocyclization” reaction (path A, **Scheme 6**). The retro-Michael reaction gave intermediate **A**. In the presence of triethylamine, it underwent a nitrile addition to give intermediate **C**. Heterocyclization of **C** gave **5a**.

When **4a** was reacted with diene **3b** (**Scheme 6**), a completely different product was obtained, namely fluorinated biaryl **6b** (72%). The isomeric azaxanthone **5b** was found in only 14%. The formation of **6b** can be explained by a domino “retro-Michael / aldol / 1,5-ester-shift” reaction (path B). A proton shift of intermediate **A** results in **B** which underwent an intramolecular aldol reaction to give **D**. An intramolecular ester shift (intermediate **E**) and following aromatization gave rise to the formation of **6b**. In this process, a direct aromatization during the intramolecular aldol reaction is not possible because of involvement of a quaternary carbon. But the aromatization took place because of the fragmentation.

I have concluded that the product distribution depends on the chain length of the diene. For this assumption, the substituents of the diene and of the chromone were systematically varied (**Scheme 5**, **Table 3**). In the result I found that the reaction of parent 3-cyanochromone and of the substituted cyanochromones with substituted dienes **3b-i** mainly afforded the biaryls, which were the main products in the reaction**.** Azaxanthones were isolated as side-products or not at all.



Scheme 6. Possible mechanisms of the formation of **5a** and **6b.**

Table 3. Synthesis of **5a-ai** and **6a-ab**

5,6	**3**	**4**	**R[1]**	**R[2]**	**R[3]**	**R[4]**	**5 (%)[a]**	**6 (%)[a,c]**
a	**a**	**a**	H	H	H	H	56	0
b	**c**	**a**	Me	H	H	H	14	72
c	**e**	**a**	*n*Bu	H	H	H	0	71
d	**f**	**a**	*n*Pent	H	H	H	13	72
e	**g**	**a**	*n*Hex	H	H	H	11	69
f	**c**	**b**	Me	Me	H	H	17	63
g	**g**	**b**	*n*Hex	Me	H	H	13	70
h	**a**	**c**	H	Me	Me	H	46	0
i	**d**	**c**	*n*Pr	Me	Me	H	14	71[c]
j	**f**	**c**	*n*Pent	Me	Me	H	12	71
k	**g**	**c**	*n*Hex	Me	Me	H	9	73
l	**h**	**c**	*n*Oct	Me	Me	H	14	67
m	**f**	**d**	*n*Pent	Me	H	Me	12	70
n	**g**	**d**	*n*Hex	Me	H	Me	10	66
o	**b**	**e**	Bn	Cl	H	H	0	68
p	**c**	**e**	Me	Cl	H	H	14	77
q	**e**	**e**	*n*Bu	Cl	H	H	0	72
r	**f**	**e**	*n*Pen	Cl	H	H	12	70
s	**g**	**e**	*n*Hex	Cl	H	H	10	70
t	**a**	**f**	H	Cl	H	Cl	35	0
u	**c**	**f**	Me	Cl	H	Cl	9	79
v	**a**	**g**	H	F	H	H	33	0
w	**c**	**g**	Me	F	H	H	11	73
x	**d**	**g**	*n*Pr	F	H	H	16	75[c]
y	**f**	**g**	*n*Pent	F	H	H	11	77
z	**g**	**g**	*n*Hex	F	H	H	7	73
aa	**c**	**h**	Me	Et	H	H	10	72
ab	**g**	**h**	*n*Hex	Et	H	H	12	70

[a] yields of isolated products; [c] compound is reported in the PhD thesis of Dr. Obaid-Ur-Rahman.

1.5 X-ray Analysis

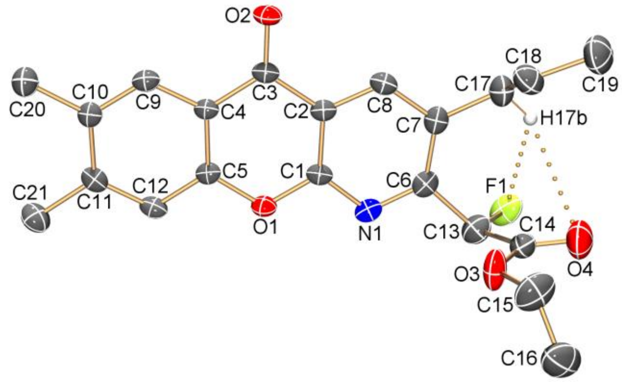


Figure 1. ORTEP drawing of the molecular structure of **5i** in the crystal. Thermal ellipsoids with 50% probability at 173 K. Except from H17b all other hydrogen atoms are omitted for clarity.

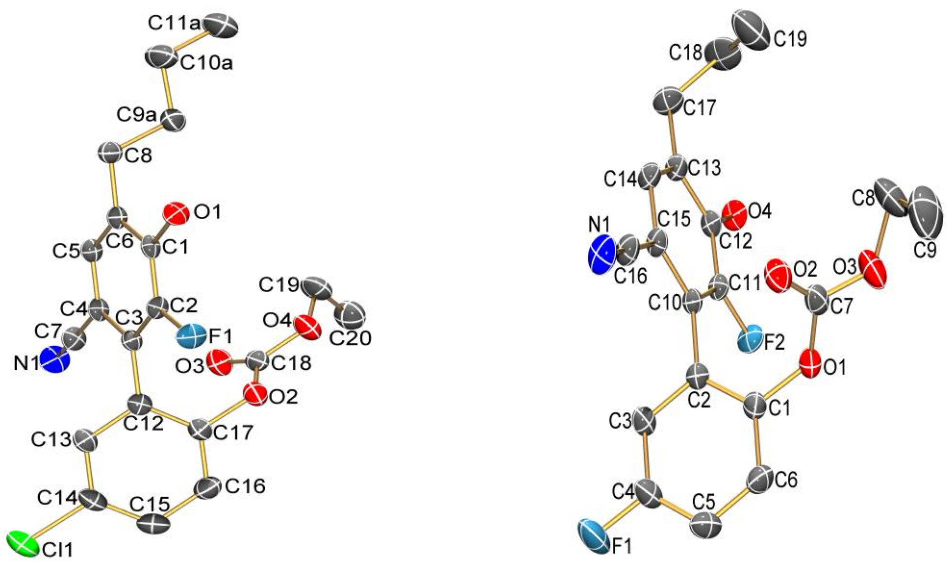


Figure 2. ORTEP drawing of the molecular structure of **6p** and **6x** in the crystal. Thermal ellipsoids with 50% probability at 173 K. Hydrogen atoms are omitted for clarity.

The monoclinic crystals of **5i** has a $P2_1$/c symmetry. The asymmetric unit contains a single molecule (**Figure 1**) which shows an intramolecular hydrogen bond between fluorine and hydrogen (2.431 Å) and oxygen and hydrogen (2.860 Å). The crystal contains a lot of intermolecular hydrogen bonding interactions between oxygen and nitrogen with hydrogens.

The monoclinic crystals of **6p** has $P2_1$/n symmetry. The crystal has two conformational isomers (**Figure 2**) in its asymmetric unit. No intramolecular hydrogen bonding can be found, but intermolecular hydrogen bonding interactions between oxygen, chlorine and nitrogen with hydrogens are present. The torsional angle between C2-C3-C12-C17 is -68.5(2)°. Compound **6x** crystallizes in monoclinic crystals with $P2_1$/c symmetry. The asymmetric unit has two molecules, which are conformational isomers of each other. The torsional angle between C1-C2-C10-C11 is 66.94 (14)°.

Compounds **5a**, **5h**, **5t** and **5v** are also reported in the thesis of Dr. Muhammad Adeel (PhD thesis, Universität Rostock 2009), but was found with wrong interpretation of data. Therefore, experiments were carried out again by me with correct interpretation of the data in Appendix.

1.6 Conclusions

In conclusion, a new building block strategy for the synthesis of multifunctional monofluorinated biaryls and fluorinated azaxanthones is developed. The behaviour of the reaction and its dependency on the effect of the chain length and change of the substituents of the 3-cyanochromone was studied. The proposed reaction mechanism is a domino ′retro-Michael / nitrile-addition / heterocyclization′ reaction for unsubstituted dienes. In contrast, for substituted homologues, a biaryl formation takes place which can be explained by an unprecedented domino ′retro-Michael / aldol / fragmentation′ reaction. Therefore, in conclusion, the steric affect of the fluorine atom attached to carbon atom C-2 of dienes **3** shows an important influence on the mechanism. From a preparative viewpoint, the reactions reported are useful as they allow a convenient approach to highly substituted fluorinated biaryls which are not readily available by other methods.

2. Synthesis of 3,5-Diaryl-4-fluorophthalates, 1,4-Diaryl-2-naphthoates, 1,4-Diethynyl -2-naphthoates and 2,3-Diarylindoles

To achieve the synthesis of biaryl and triaryl motifs in highly fuctionalized manner and in excellent yield, the use of highly reactive organolithium species is not suitable because it does not tolerate the presence of several functional groups, such as carbonyl, hydroxy and other groups. The use of Pd catalyzed carbon-carbon cross-coupling is one of the important transformations for this purpose. In carbon-carbon coupling, the three most important processes, the Heck reaction, the Suzuki-Miyaura coupling, and the Sonogashira reaction, are characteristically catalyzed by palladium and have been abundantly used in syntheses and widely studied in recent decades. Other methods, the Stille reaction, Kumada, Hiyama, and Negishi reaction, allylations including the Tsuji-Trost reaction, and relevant homocoupling processes are also studied and frequently used in natural product synthesis. For this great innovation of palladium-catalyzed C-C coupling reactions, it has been awarded the 2010 Nobel Prize in Chemistry to Professors Heck, Negishi, and Suzuki.

A lot of interest has been developed in the site selective Suzuki coupling of polyhaloginated substrates.[39] The site-selectivity is controlled by electronic and steric parameters.[40] Aromatic bis(triflates) have been also used for C-C cross coupling reactions via Suzuki reactions.[41]

The Suzuki-Miyaura coupling reaction is considered a significant tool for C-C bond formation in organic synthesis. It is normally catalyzed by palladium with diversified phosphine ligands, in the presence of suitable bases, such as carbonates, hydroxides, phosphates, or alkoxides.[42] This reaction is preferred on brominated and iodinated aromatic compounds over chlorinated, due to lower reactivity of the C–Cl bond in the oxidative addition step. A generally accepted reactivity order is I>Br>OTf>>Cl. These reactions follow mostly a similar mechanism. First oxidative addition takes place with the formation of organopalladium halides from organic halides or triflates with the Pd(0) complex. Then transmetallation takes place with nucleophilic compounds to give a diorganopalladium complex. The resultant complex undergoes a reductive elimination by formation of carbon-carbon bond and regeneration of the catalyst.

2.1 Synthesis of 3,5-Diaryl-4-fluorophthalates by [4+2] Cycloaddition of 1-Ethoxy-2-fluoro-1,3-bis(trimethylsilyloxy)-1,3-diene with Dimethyl Acetylenedicarboxylate and Subsequent Site-Selective Suzuki-Miyaura Reactions

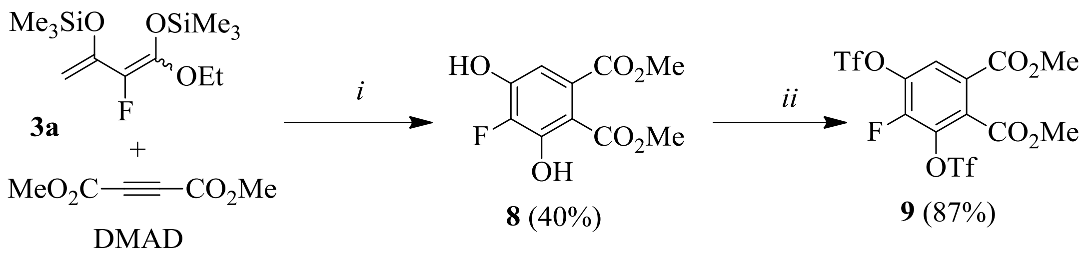
2.1.1 Introduction

Cyclization reactions of fluorinated building blocks provide a powerful alternative for the synthesis of fluorinated arenes and hetarenes. One important synthetic strategies reported for natural and unnatural carbocycles and heterocycles is the Diels–Alder (DA) reaction.[44] It takes place between diene and dienophile moieties with the formation of six-membered ring systems with excellent regio-, diastereo-, and enantioselective control. Schlosser et al.[45,46], Portella et al.[47] and Manzanares et al.[48] reported the synthesis of halogenated arenes by [4+2] cycloaddition. Recently, the Langer et al. has studied the synthesis of halogenated, especially fluorinated arenes and hetarenes based on formal [3+3], [3+2] and [4+2] cyclizations of 1,3-bis(silyloxy)-1,3-butadienes.[34,49,50]

The aim of my present work was the use of fluorinated bis(silyl enol ethers)[35] as synthetic building blocks in one-pot cyclizations. The synthesis of dimethyl 4-fluoro-3,5-dihydroxyphthalate was achieved by [4+2] cycloaddition of 1-ethoxy-2-fluoro-1,3-bis(trimethylsilyloxy)-1,3-diene with dimethyl acetylenedicarboxylate (DMAD). A following Suzuki-Miyaura reactions of the bis(triflate) of this product, with special emphasis on the issue of site-selectivity, resulted in a convenient approach to novel 3,5-diaryl-4-fluorophthalates which are not readily available by other methods.

2.1.2 Synthesis of dimethyl 4-fluoro-3,5-dihydroxyphthalate

1-Ethoxy-2-fluoro-1,3-bis(trimethylsilyloxy)-1,3-diene (**3a**) was obtained in two steps from ethyl 2-fluoroacetoacetate as described in chapter one (vide supra, **Scheme 4**). The [4+2] cycloaddition of **3a** with DMAD (dimethyl acetylenedicarboxylate) afforded dimethyl 4-fluoro-3,5-dihydroxyphthalate (**8**) (**Figure 3**) in 40 % yield (**Scheme 7**). The reaction was tried in scales from 1 mmol to 31 mmol and was found to proceed in good yields in all cases. The reaction of **8** with triflic anhydride resulted formation of its bis(triflate) **9** in 87 % yield.



Scheme 7. Synthesis of **8** and **9**. *i*: 1) **3a** (1.0 equiv.), DMAD (1.5 equiv.), −78 → 20 °C, 20 h; 2) HCl (10%); *ii*, 1) **8** (1.0 equiv), pyridine (4.0 equiv), CH_2Cl_2, -78 °C, 10 min; 2) Tf_2O (2.4 equiv), -78 → 0 °C, 4 h.

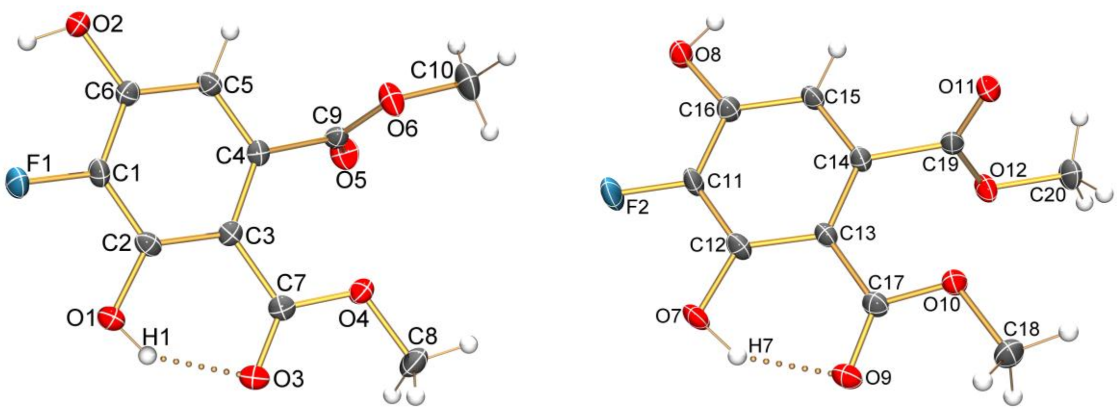
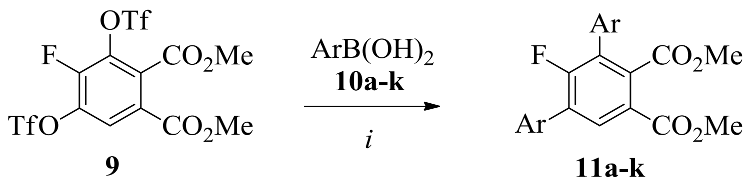


Figure 3. ORTEP drawing of the molecular structure of **8** in the crystal. Thermal ellipsoids with 50% probability at 173 K.

The colourless crystals of 4-fluoro-3,5-dihydroxyphthalate (**8**) have two molecules in their asymmetric unit, with monoclinic *C*2/c symmetry (**Figure 3**). Hydrogen bonding is found in the crystal lattice between oxygen and hydrogen, with lengths of 1.795 Å and 1.846 Å for intramolecular hydrogen bonding, while 1.915, 1.970 and 2.279 Å for intermolecular hydrogen bonding. No interaction between fluorine and hydrogen is found. The torsional angle for C19-C14-C13-C17 is 8.8 (2)°. The hydrogen atom attached to the O2 atom in the first molecule has a different orientation with respect to the hydrogen attached to the O8 atom in the second molecule.

2.1.3 Synthesis of functionalized bi- and triaryls.



Scheme 8. Synthesis of **11a-k**. *Conditions: i*, **9** (1.0 equiv), **10a-k** (2.3 equiv), K_3PO_4 (3.0 equiv), $Pd(PPh_3)_4$ (3 mol-%), 1,4-dioxane, 110 °C, 8 h.

Table 4. Synthesis and optimization of **11a**

Entry	Ligand	Solvent	Base	11a (%)[a]
a	$N(CH_2CH_2)OH$	Acetone	K_3PO_4	0
b	$N(CH_2CH_2)OH$	THF	K_3PO_4	0
c	$N(CH_2CH_2)OH$	Dioxane	K_2CO_3	0
d	XPhos	Dioxane	K_3PO_4	81
e	XPhos	Dioxane	K_2CO_3	74
f	XPhos	THF	K_3PO_4	69
g	SPhos	Dioxane	K_3PO_4	80
h	SPhos	Dioxane	K_2CO_3	73
i	SPhos	THF	K_3PO_4	77
j	$Pd(PPh_3)_4$	Dioxane	K_3PO_4	83
k	$Pd(PPh_3)_4$	Dioxane	K_2CO_3	66
l	$Pd(PPh_3)_4$	THF	K_3PO_4	76
m	$Pd(PPh_3)_4$	THF	K_2CO_3	55
n	$Pd(PPh_3)_4$	CH_2Cl_2	K_3PO_4	59
o	$Pd(PPh_3)_4$	Acetone	K_3PO_4	49
p	$Pd(PPh_3)_4$	1:1THF/Dioxane	K_3PO_4	53

[a] yields of isolated products.

The triflate **9** is subjected to Suzuki reactions which results in bi- and triaryls. Firstly, the reaction procedure was optimized, (**Scheme 8, Table 4)**. Reacions in the presence of triethanolamine as a ligand with $Pd(OAc)_2$ as a catalyst were unsuccessful. The use of XPhos[51] or SPhos[51] in the presence of $Pd(OAc)_2$ gave similar results in terms of yield as compared to $Pd(PPh_3)_4$ (3-4 mol-%) using 2.3 equivalent of arylboronic acids. However, the employment of $Pd(PPh_3)_4$ is significantly cheaper and easy to handle. Thus, $Pd(PPh_3)_4$ in the presence of K_3PO_4 and dioxane was used as a catalyst in the reactions (**Scheme 8**, **Table 5**).

Table 5. Synthesis of **11a-k**

10,11	**Ar**	**11 (%)[a]**
a	C_6H_5	83
b	$3\text{-}(C_6H_5)C_6H_4$	85
c	$4\text{-}MeC_6H_4$	79
d	$4\text{-}(C_2H_5)C_6H_4$	72
e	$3,5\text{-}Me_2C_6H_3$	77
f	$2\text{-}ClC_6H_4$	82
g	$3\text{-}ClC_6H_4$	63
h	$4\text{-}ClC_6H_4$	75
i	$3\text{-}FC_6H_4$	82
j	$4\text{-}FC_6H_4$	87
k	$4\text{-}(CF_3)C_6H_4$	67

[a] yields of isolated products.

The crystals of **11j** and **11k** are studied by X-ray crystallography (**Figure 4**). Compound **11j** is found to have a monoclinic $P2_1/c$ symmetry. The asymmetric unit contains a single molecule. Very strong intermolecular hydrogen bonding is found in the crystal lattice between oxygen, fluorine and hydrogen. For **11k** is found orthorhombic *P*bca symmetry. The asymmetric unit has a single molecule. Intermolecular hydrogen bonding is found in the crystal lattice between oxygen, fluorine and hydrogen atoms (2.509, 2.543, 2.567, 2.641, 2.659 and 2.661 Å). The CF_3 groups are in disordered form.

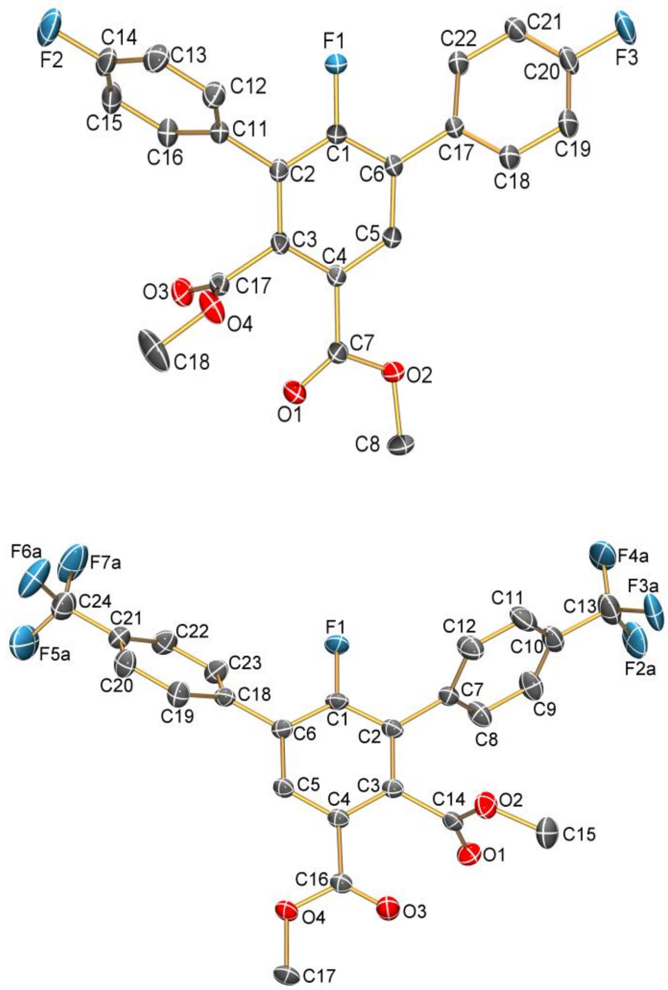
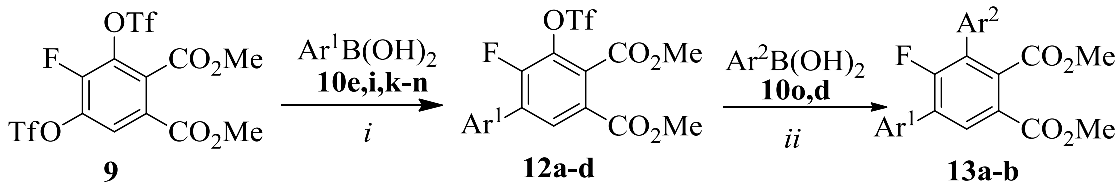


Figure 4. ORTEP drawing of the molecular structure of **11j** top and **11k** below in the crystal. Thermal ellipsoids with 50% probability at 173 K. Hydrogen atoms are omitted for clarity.

The 5-aryl-4-fluorophthalates **12a-d** were prepared by Suzuki reaction of **9** with boronic acids **10e,i,k,m** (1.1 equiv.) in good yields and with very good site-selectivity (**Scheme 9**, **Table 6**) The reaction was carried out using the optimized reaction conditions mentioned above, using $Pd(PPh_3)_4$ (3 mol-%) in 1,4-dioxane (90 °C, 9 h), K_3PO_4, and the boronic acid (1.1 equiv.). The formation of the opposite regioisomer was not observed under these conditions, but the use of other ligands resulted in formation of a mixture of isomers.



Scheme 9. Synthesis of **12a-d** and **13a-b**. *Conditions: i*) **9** (1.0 equiv.), **10e,i,k,m** (1.1 equiv.), K_3PO_4 (1.5 equiv.), $Pd(PPh_3)_4$ (3 mol-%), 1,4-dioxane, 90 °C, 9 h.

Table 6. Synthesis of **12a-d**

12	10	Ar^1	12 (%)[a]
a	**e**	3,5-$Me_2C_6H_3$	75
b	**i**	3-FC_6H_4	71
c	**k**	4-$(CF_3)C_6H_4$	68
d	**m**	4-$(OH)C_6H_4$	60

[a] yields of isolated products.

Table 7. Synthesis of **13a-b**

13	10	Ar^1	Ar^2	13 (%)[a]
a	**n,d**	2-$(EtO)C_6H_4$	4-EtC_6H_4	58
b	**k,o**	4-$(CF_3)C_6H_4$	3,4-$(MeO)_2C_6H_3$	51

[a] yields of isolated products.

The one-pot synthesis of 3,5-diaryl-4-fluorophthalates **13a-b**, containing two different aryl groups, were prepared directly from bis(triflate) **9** (**Scheme 9**, **Table 7**). In the first step, the Suzuki reaction of **9** with arylboronic acids **10e,i,k,m** (1.1 equiv.) was carried out at 90 °C for 9 h. In the second step, arylboronic acids **10o,d** (1.3 equiv.) were added (110 °C) to give products **13a,b** in acceptable yields.

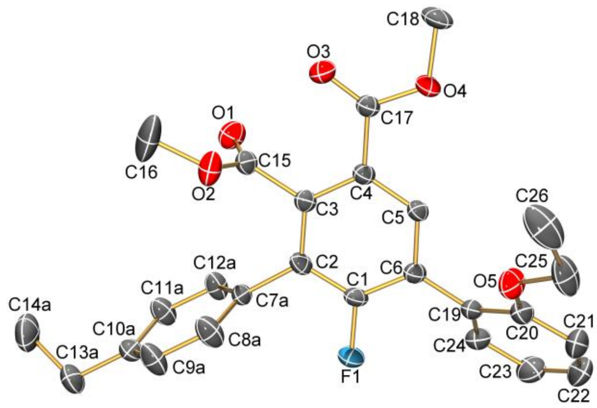


Figure 5. ORTEP drawing of the molecular structure of **13a** in the crystal. Thermal ellipsoids with 50% probability at 173 K. Hydrogen atoms are omitted for clarity.

The colourless crystals of **13a** were studied by X-ray crystallography (**Figure 5**). The structure clearly shows the first attack at the less sterically hindered position C6 and the second one at C2. The crystal structure is found to have an orthorhombic *P*bca symmetry. The asymmetric unit contains a single molecule. Strong intermolecular hydrogen bonding is found in the crystal lattice between oxygen, fluorine and hydrogen atoms.

2.1.4 Conclusions

In conclusion, dimethyl 4-fluoro-3,5-dihydroxyphthalate was synthesized by [4+2] cycloaddition of 1-ethoxy-2-fluoro-1,3-bis(trimethylsilyloxy)-1,3-diene with dimethyl acetylenedicarboxylate (DMAD). Its bis(triflate) is arylated by site-selective Suzuki-Miyaura reactions and allowed for a convenient approach to mono- and different diarylated 4-fluorophthalates. This methodology is proved to be a convenient method for preparing new organofluorine compounds which are not reported until yet.

2.2 Synthesis of 1,4-Diaryl-2-naphthoates and 1,4-Diethynyl-2-naphthoates by Site-Selective Suzuki-Miyaura and Sonogashira Reactions

2.2.1 Introduction

The naphthalene moiety has been used for a variety of applications. It has been used in industry, mostly in the synthesis of dyes, medicines, surfactants, photosynthetic compounds and in related organic chemistry, in organometallic chemistry, in biochemistry and in textile industry.[52] Several unique chemical and physical properties appear for peri-substituted naphthalenes.[53]

4-Hydroxy-3,5-dimethoxy-2-naphthaldehyde and 4-hydroxy-5-methoxy-2-naphthaldehye have been isolated from natural sources.[54] They exhibit marked pharmacological activities, like antimicrobial activities[55] and activity as antibody inhibitors.[56] Novel naphthalenyl-substituted 3*H*-1,2,3,5-oxathiadiazol-2-oxides have been reported to have antihyperglycemic activity. [57] The influence of naphthoate derivatives in biosynthetic pathways is of important consideration.[58] They are involved in the biosynthesis of the antitumor antibiotics azinomycin A (1) and B (2) (structurally unique natural products). [59] 1,4-Dihydroxy-2-naphthoate is involved in the shikimate pathway in the biosynthesis of ubiquinone and menaquinone (MK).[60]

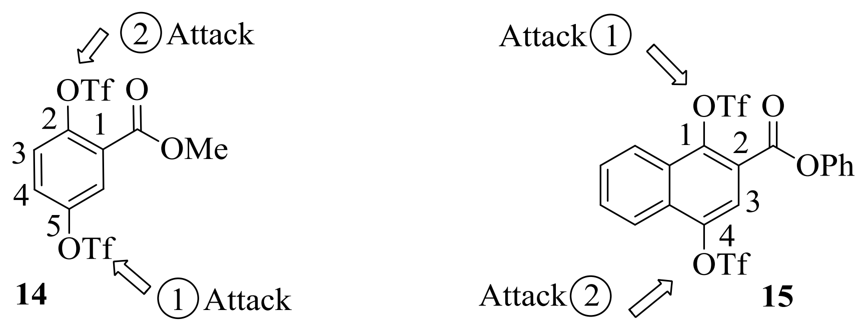
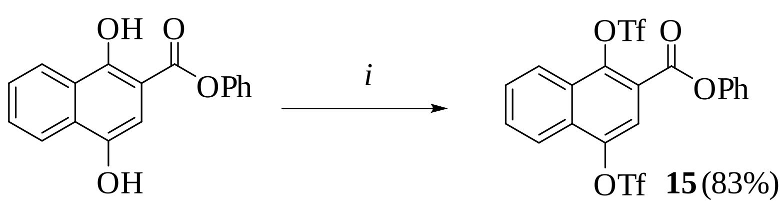


Chart 4. Observed site selective attacks**.**

We have earlier studied in our group the site-selective Suzuki-Miyaura (S-M) reactions of the bis(triflate) of methyl 2,5-dihydroxybenzoate **14** which proceeded in favour of position 5, presumably a result of steric effects (**Chart 4**).[61] We went to compare the site-selectivity of reactions of naphthoates **15** with that of benzoates **14**. We found clear difference in the site-selectivity between benzoate and naphthoate systems. The transition metal-catalyzed cross-coupling reactions on this and related naphthoate derivatives (including the corresponding dihalides) have, to the best of our knowledge, not been reported to date. A part of this work is already included in the thesis of my colleague Dr. Obaid-ur-Rahman. Herein, I report my own experimental work which is not included in the thesis of my colleague.

2.2.2 Synthesis of 1,4-diaryl-2-naphthoates

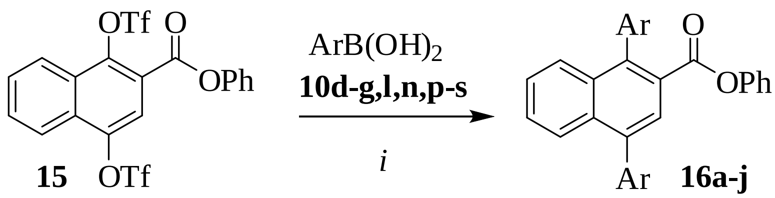
Starting with commercially available and inexpensive phenyl 1,4-dihydroxy-2-naphthoate this study was carried out. The starting material can be considered as a benzoannulated analogue of methyl 2,5-dihydroxybenzoate. Phenyl 1,4-dihydroxynaphthoate was treated with triflic anhydride to give its bis(triflate) **15** in 83% , (**Scheme 10**).



Scheme 10: Synthesis of **15**. *Conditions*: *i*: 1) phenyl 1,4-dihydroxy-2-naphthoate (1.0 equiv), pyridine (4.0 equiv), CH_2Cl_2, -78 °C, 10 min; 2) Tf_2O (2.4 equiv), -78→0 °C, 4 h.

The 1,4-diaryl-2-naphthoates **16a-j** in good yields (54-88%) were achieved by the Suzuki-Miyaura (S-M) reaction of **15** with boronic acids **10d-g,l,n,p-s** (2.4 equiv.) (**Scheme 11, Table 8**).

In a struggle to optimize the conditions of the reaction, I have found that $Pd(PPh_3)_4$ (3 mol-%) as catalyst, 2.4 equiv. boronic acid and 1,4-dioxane (at 110 °C, 8 h) and use of K_3PO_4 as the base gave good yields. While other ligands were also tried, as XPhos or SPhos in the presence of $Pd(OAc)_2$, worse results were obtained. The use of different types of arylboronic acids proved that electron-withdrawing gave better yields than electron-rich boronic acids.



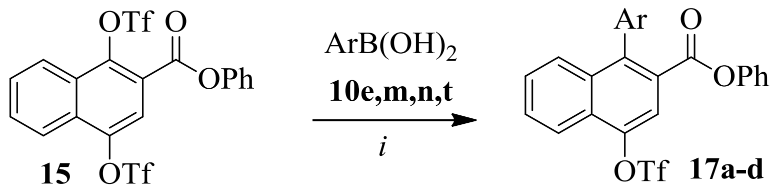
Scheme 11. Synthesis of **16a-j**. Conditions: *i*, **15** (1.0 equiv), **10d-g,l,n,p-s** (2.4 equiv.), K_3PO_4 (3.0 equiv.), $Pd(PPh_3)_4$ (3 mol-%), 1,4-dioxane, 110 °C, 8 h.

Table 8. Synthesis of **16a-j**

16	**10**	**Ar**	**16 (%)**[a]
a	**d**	4-$(C_2H_5)C_6H_4$	88
b	**e**	3,5-$(Me)_2C_6H_3$	71
c	**f**	2-ClC_6H_4	72
d	**g**	3-ClC_6H_4	77
e	**p**	2-FC_6H_4	77
f	**l**	3-$(CF_3)C_6H_4$	77
g	**q**	2-$(MeO)C_6H_4$	73
h	**n**	2-$(EtO)C_6H_4$	61
i	**r**	2,5-$(MeO)_2C_6H_3$	69
j	**s**	3-$(OH)C_6H_4$	54

[a] yields of isolated products.

Interesting results were found when reacting the educt with one equivalent of boronic acid. The reaction of **15** with boronic acids **10e,m,n,t** (1.1 equiv.) resulted in excellent site selectivity at carbon atom C-1 and afforded the 1-aryl-4-(trifluoromethylsulfonyloxy)-2-naphthoates **17a-d** (**Scheme 12**, **Table 9**).



Scheme 12. Synthesis of **17a-e**. *Conditions*: *i*, **15** (1.0 equiv.), **10e,m,n,t** (1.1 equiv.), K_3PO_4 (1.5 equiv.), $Pd(PPh_3)_4$ (3 mol-%), 1,4-dioxane, 95 °C, 8 h.

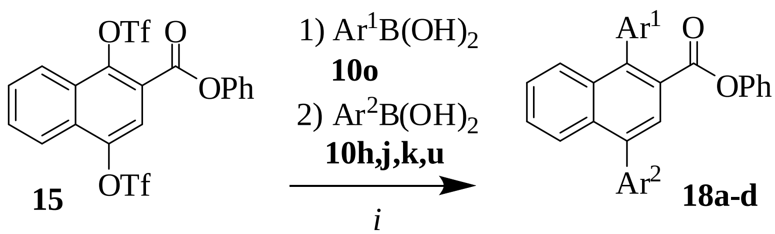
Table 9. Synthesis of **17a-d**

17	**10**	**Ar**	**17 (%)**[a]
a	**e**	3,5-$(Me)_2C_6H_3$	68
b	**n**	2-$(EtO)C_6H_4$	59
c	**m**	4-$(OH)C_6H_4$	52
d	**t**	2,6-$(MeO)_2C_6H_3$	33

[a] yields of isolated products.

Excellent site-selectivity was observed using $Pd(PPh_4)_3$ as catalyst. Small amounts of the bis-coupled product were observed by ^1H NMR and GC-MS of the crude product before the purification. The products were easily purified by chromatography. I have observed that **17d**, which is derived from the sterically hindered 2,6-dimethoxyarylboronic acid **10t**, did not give good yield , reported in thesis of Dr. Obaid-Ur-Rahman, while other reactions proceeded in good yields. Also the reactions were optimized with regard to temperature and it was found that double coupling can be avoided when the reaction proceeds at 80-95 °C instead of 110 °C. Using $Pd(OAc)_2$ with ligands XPhos or SPhos[51] resulted in a mixture of products.

The unsymmetrical 1,4-diaryl-2-naphthoates **18a-d** were isolated in 51-67% yields by the one-pot reaction of **15** with two different arylboronic acids. Firstly, the reaction was carried out with arylboronic acid (1.1 equiv.) at 95 °C instead of 110 °C for 7 hours heating and subsequent addition of the base and of the second arylboronic acid (**Scheme 13**, **Table 10**). I have observed that **18d**, which is derived from the sterically hindered 3-methoxyarylboronic acid **10,** has not resulted in good yield.



Scheme 13. Synthesis of **18a-d**. *Conditions: i*, 1) **15** (1.0 equiv.), **10o** (1.1 equiv.), K_3PO_4 (1.5 equiv.), $Pd(PPh_3)_4$ (3 mol-%), 1,4-dioxane, 95 °C, 7 h. 2) **10h,j,k,u** (1.3 equiv.), K_3PO_4 (1.5 equiv.), 110 °C, 8 h.

Table 10. Synthesis of **18a-d**

18	**10**	**Ar[1]**	**Ar[2]**	**18 (%)[a]**
a	**j,o**	4-FC_6H_4	3,4-$(MeO)_2C_6H_3$	54
b	**h,o**	4-ClC_6H_4	3,4-$(MeO)_2C_6H_3$	62
c	**k,o**	4-$(CF_3)C_6H_4$	3,4-$(MeO)_2C_6H_3$	51
d	**u,o**	3-$(MeO)C_6H_4$	3,4-$(MeO)_2C_6H_3$	46

[a] yields of isolated products.

The colourless crystals of **18b** (**Figure 6)** were studied by X-ray crystallography and the structure could be independently confirmed. The structure clearly shows the first attack at the less sterically hindered position C2 and then at C5. The crystal structure was found to show a monoclinic *P*21/c symmetry. The asymmetric unit contains a single molecule. Strong intermolecular hydrogen bonding is found in the crystal lattice between oxygen and hydrogen atoms (2.580 and 2.664 Å).

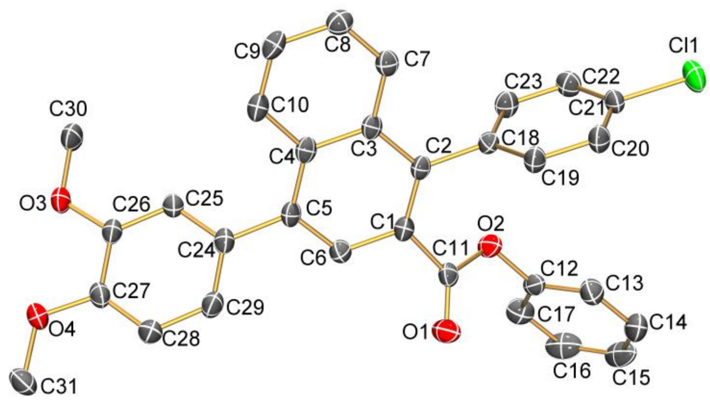
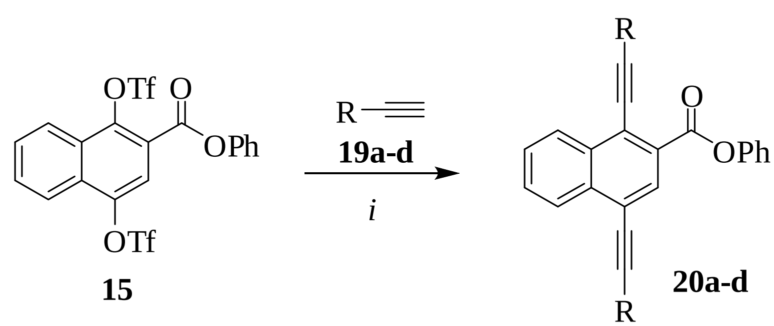


Figure 6: ORTEP drawing of the molecular structure of **18b** in the crystal. Thermal ellipsoids with 50% probability at 173 K. Hydrogen atoms are omitted for clarity.

2.2.3 Synthesis of 1,4-diethynyl -2-naphthoates



Scheme 14. Synthesis of **20a-d**. *Reagents and conditions:* **15** (1.0 equiv), **19a-d** (2.4 equiv), Dry CuI (20 mol%), $Pd(PPh_3)_4$ (10 mol %), Bu_4NI (300 mol %), Et_3N (2.5 equiv), DMF, 80 °C, 4 h.

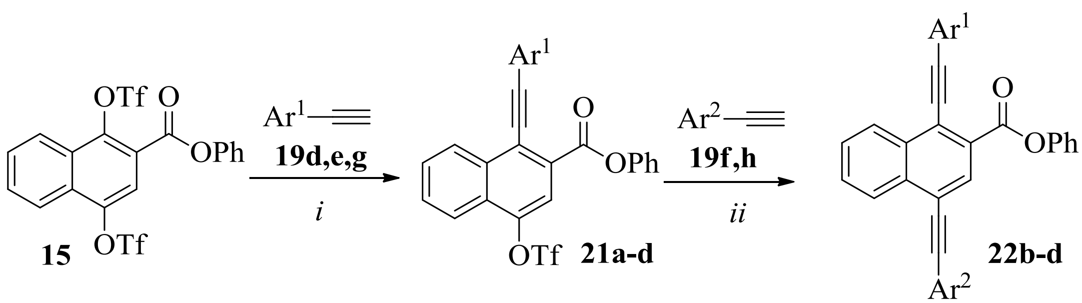
The same way as adopted for the S-M reaction, the Sonogoshira reaction of **15** with acetylenes **19a-d** (2.4 equiv.) resulted in the formation of the novel 1,4-bis(alkynyl)-2-naphthoates **20a-d** in 52-77% yields (**Scheme 14**, **Table 11**). The use of $Pd(PPh_3)_4$ as a catalyst resulted in good yields; DMF was found to be an appropriate solvent. I have observed here that not only electronic factors, but also steric factors reduce the yield as in the case of **20d**.

Table 11. Synthesis of **20a-d**

19,20	R	20 (%)[a]
a	cyclopentyl	67
b	3-Thienyl	59
c	n-Propyl	71
d	6-(MeO)-2-Naphthyl	52[b]

[a] yields of isolated products; [b] compound is reported in the thesis of Dr. Obaid-Ur-Rahman.

The Sonogoshira reaction of **15** with acetylene **19e** (1.1 equiv.) proceeded with good site-selectivity at carbon atom C-1 and afforded the 1-arylethynyl-4-(trifluoromethylsulfonyloxy)-2-naphthoate **21a** (**Scheme 15**, **Table 12**).



Scheme 15: Synthesis of **21a** and **22b-d**. *Conditions: i*, 1) **15** (1.0 equiv), **19d,e,g** (1.1 equiv), dry CuI (20 mol%), $Pd(PPh_3)_4$ (10 mol %), Bu_4NI (300 mol %), Et_3N (1.25 equiv), DMF, 60 °C, 3 h; 2) **19f,h** (1.3 equiv.), Et_3N (1.25 equiv), 80 °C, 4 h.

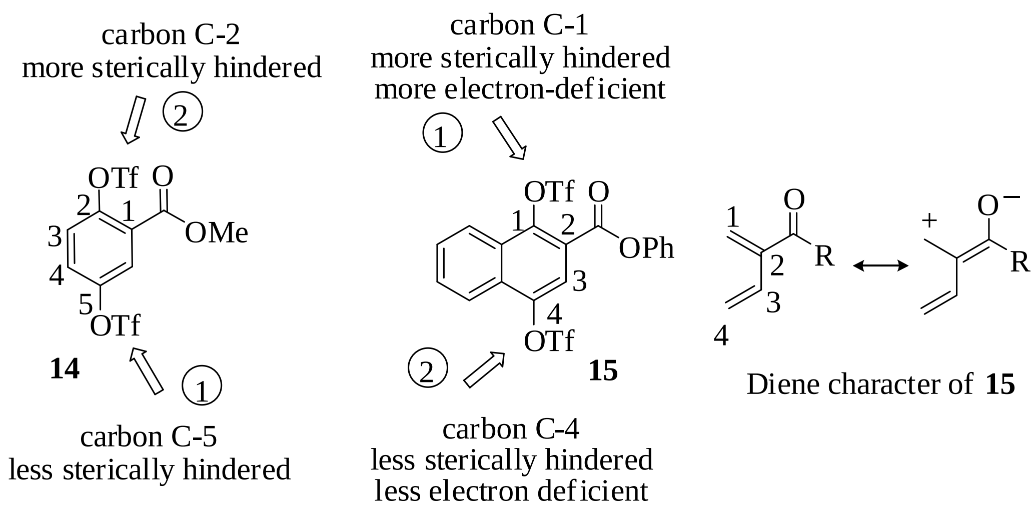
Processing the one-pot reaction of **15** with two different acetylenes, which were sequentially added, afforded the unsymmetrical 1,4-diarylethynyl-2-naphthoates **22b-d** in 54-58% yields (**Scheme 15**, **Table 12**). During the optimization, it was proved to be important for the first step of the one-pot procedure to employ only a slight excess of the acetylene (1.1 equiv.) and to carry out the reaction at 60 °C instead of 80 °C.

Table 12. Synthesis of **21a and 22a-c**

21,22	**19**	**Ar[1]**	**Ar[2]**	**21 (%)[a]**	**22 (%)[a]**
a	**e**	3-(MeO)C_6H_4	-	61	-
b	**g,h**	4-(MeO)C_6H_4	4-FC_6H_4	**--**	59
c	**d,f**	6-(MeO)-2-Naphthyl	4-MeC_6H_4	**--**	47
d	**e,f**	3-(MeO)C_6H_4	4-MeC_6H_4	**--**	58

[a] yields of isolated products, -- no product could be isolated, - not carried out.

2.2.4 Possible explanation for the site-selective reactions



Scheme 16. Possible explanation for the site-selective reactions of **15**.

In case of benzoate **14**,[61] it was observed that the S-M reaction prefers regioselective attack on the sterically less hindered carbon atom C-5, while the first attack occurs at the sterically more hindered position C-1 in case of naphthoate **15**. To explain the position to react regioselectively, the electronic factor is important (**Scheme 16**). The oxidative addition in the S-M reaction occurs first at the most electron deficient carbon atom.[62] In benzoate **14**, due to the *ortho* position to the ester group, carbon C-2 is the more electron deficient carbon atom than C-5. The same is true in naphthoate **15**, where C-1 is more electron defficient than C-4. Comparing both, one can suggest that the electron defficiency is more pronounced in napthoate moiety **15** because the non-substituted benzene moiety of naphthoate **15** represents a stable 6π aromatic system.

In contrast, the substitued aromatic ring system of **15**, contining ester and the triflate groups, shows a disturbed aromaticity. So we conclude that, due to the annulation of the stable unsubstituted benzene moiety, the aromaticity of the substituted benzene moiety should be more disturbed than the aromaticity of the benzene moiety of **14**. The substituted benzene moiety of **15** might thus be regarded as a cross-conjugated diene system (**Scheme 16**). Due to the π-acceptor effect of the ester group, the nucleophilic attack occurs at carbon atom C-1 of the diene system (conjugate addition).

2.2.5 Conclusions

A comparative study of the site-selective Suzuki-Miyaura (S-M) reactions and Sonogoshira reactions of the bis(triflate) of methyl 2,5-dihydroxybenzoate and of the bis(triflate) of phenyl 1,4-dihydroxynaphthoate has been carried out. In the bis(triflate) of phenyl 1,4-dihydroxynaphthoate, the first attack occurred at the sterically more hindered position C-1, while at the bis(triflate) of methyl 2,5-dihydroxybenzoate it occurred at position C-5. In case of the benzoate, the site selectivity is controlled by the steric effect of the ester group, while in case of the naphthoate the steric effect is also high, but the site-selectivity is controlled by the electronic effect.

2.3 One-Pot Synthesis of Unsymmetrical 2,3-Diarylindoles by Site-Selective Suzuki-Miyaura Reactions of *N*-Methyl-2,3-dibromoindol

2.3.1 Introduction

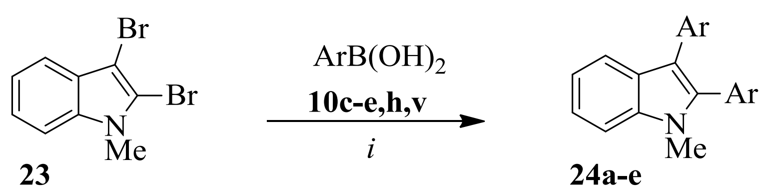
The substituted indole core is a structural component of agrochemicals, functional materials, of a broad number of biologically active compounds, and especially of many pharmaceutical agents.[63] Due to its capability of binding with many receptors with excellent affinity, indole is referred to as a "privileged structure".[64] Heteroarenes equipped with aryl groups (heterobiaryls) are often found in biologically active compounds, organic materials, and pharmaceuticals. They are structural motifs of a lot of biologically active compounds, such as novel COX-2 inhibitors for the treatment of arthritic pain.[65] 2,3-Bis(4-methoxyphenyl)indole (′indoxole′) has been shown to possess a stronger anti-inflammatory activity than common drugs, such as aspirin and indomethacin.[66] A lot of well-established classical methods have been applied for the synthesis and functionalization of indoles for over 100 years. All of those basic syntheses depend on some factors which include availability of the starting material and functional group tolerance. In some cases, specific substitution patterns remain difficult to obtain by standard indole-forming reactions; thus, new methodologies emerge.

Most of the work has been focused on the development of transition metal catalyzed reactions for the direct arylation of indoles.[67] A lot of impressive strategies have been developed to synthesize C2- and C3-functionalized indoles.[68] The traditional methods of their synthesis mostly involve multistep syntheses of the indole fragments.[68,69] Gribble and Liu reported the synthesis of symmetrical *N*-phenylsulfonyl-2,3-diarylindoles by twofold Suzuki-Miyaura reactions of 2,3-dihalo-*N*-(phenylsulfonyl)indoles.[70] But all attempts to develop site-selective reactions and to prepare mono-coupling products or unsymmetrical 2,3-diarylindoles, containing two different aryl groups, were unsuccessful. At the end, the regioselective synthesis of 2,3-disubstituted indoles remains a challenging problem in all the above mentioned classical approaches.

Recently, in our group, a new synthetic approach was developed for 2,3-di- and 2,3,6-tribromination of *N*-methylindole, which I further utilized for the one-pot synthesis of different diarylindoles based on site-selective Suzuki-Miyaura cross-coupling reactions.[71] In this regard, I have developed the first regioselective palladium (0)-catalyzed cross-coupling reactions of the 2,3-dibromoindoles and of 2,3,6-triarylindoles.

2.3.2 Synthesis of arylated indoles

2,3-Dibromo-*N*-methylindole (**23**) was synthesized as previously reported in Professor Langer's group.[71] The product was found to be sensitive to air and moisture. It can be stored at -30°C for more than three months under argon atmosphere.



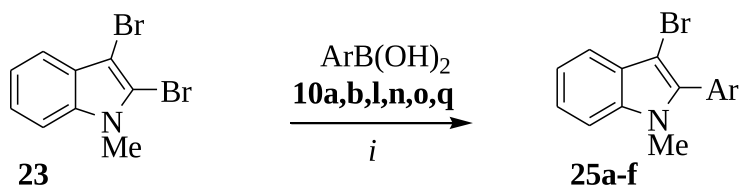
Scheme 17. Synthesis of **24a-e**. *Conditions: i*, **23** (1.0 equiv), Ar[1]-B(OH)$_2$ (2.3 equiv), K_3PO_4 (3.0 equiv), Pd(PPh$_3$)$_4$ (3 mol-%), 1,4-dioxane, 110 °C, 6 h.

Table 13. Synthesis of **24a-e**

24	10	Ar	24 (%)[a]
a	**c**	4-MeC$_6$H$_4$	90
b	**d**	4-EtC$_6$H$_4$	86
c	**e**	3,5-(Me)$_2$C$_6$H$_3$	90
d	**h**	4-ClC$_6$H$_4$	83
e	**v**	4-(*t*Bu)C$_6$H$_4$	79

[a] yields of isolated products.

The Suzuki-Miyaura reaction of **23** with aryl boronic acids **10c-e,h,v** (2.2 equiv.) afforded the formation of 2,3-diaryl-*N*-methylindoles **24a-e** in good yields (**Scheme 17**, **Table 13**). Good yields were obtained for both electron rich and electron deficient arylboronic acids, using 3 mol % of $Pd(PPh_3)_4$ and the solvent dioxane. The structures of all products were established by spectroscopic methods.



Scheme 18. Synthesis of **25a-f**. *Conditions: i*, **23** (1.0 equiv), Ar^1-$B(OH)_2$ (1.1 equiv), K_3PO_4 (1.5 equiv), $Pd(PPh_3)_4$ (3 mol %), 1,4-dioxane, 70 °C, 6 h.

The use of different conditions for the regioselective substitution showed a variety of results. Especially the use of undried solvents resulted in replacement of the bromine by a hydrogen atom at position 3 of **23** (**Scheme 20**, **Table 17**). Thus, care was taken to use dried solvents. It was found that dioxane and the base K_3PO_4 gave excellent yields of mono-coupling products and no formation of other isomers was observed. While in case of other solvents, such as dichloromethane, a mixture of products was observed. In case of THF and acetone, the other isomers were also observed by TLC. The use of $Pd(OAc)_2$ in the presence of XPhos or SPhos [51] gave similar results in terms of yield as $Pd(PPh_3)_4$ (3-4 mol.%). The $Pd(PPh_3)_4$ was thus used as a catalyst in all reactions **(Scheme 18**, **Table 14)**.

The Suzuki-Miyaura reaction of **23** with aryl boronic acids **10a,b,l,n,o,q** (1.0 equiv.) afforded the 2-aryl-3-bromo-1-methyl-1-*H*-indoles **25a-f** in good yields (**Scheme 18**, **Table 15**). The structures of all products were established by spectroscopic methods and the regioselectivity was independently confirmed with the help of the X-ray crystallography technique. Good yields were obtained for both electron rich and electron deficient arylboronic acids.

Table 14. Optimization of the synthesis of **25e**

25	Solvent	Base	25e (%)[a]
a	CH_2Cl_2	Et_3N	Mixture
b	CH_2Cl_2	K_3PO_4	41
c	CH_2Cl_2	K_2CO_3	33
d	THF	K_3PO_4	59
e	THF	K_2CO_3	53
f	Dioxane	K_3PO_4	79
g	Acetone	K_3PO_4	52
h	1:1, THF/Dioxane	K_3PO_4	53

[a] yields of isolated products.

Table 15. Synthesis of **25a-f**

25	10	Ar[1]	25 (%)[a]
a	**a**	C_6H_5	84
b	**b**	$3\text{-}(C_6H_5)C_6H_4$	77
c	**l**	$3\text{-}(CF_3)C_6H_4$	81
d	**n**	$2\text{-}(EtO)C_6H_4$	73
e	**o**	$3,4\text{-}(MeO)_2C_6H_3$	79
f	**q**	$2\text{-}(MeO)C_6H_4$	71

[a] yields of isolated products.

The colourless crystals of **25e** were measured and the regioselectivity or site selectivity was independently confirmed. The structure clearly proved the first attack at C1, which is the electronically preferable position. The crystal structure was found to have monoclinic *P*21/c space group. The asymmetric unit contains a single molecule (**Figure 7**).

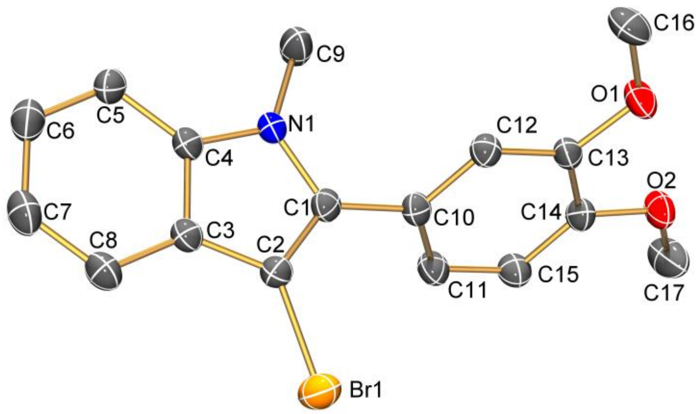
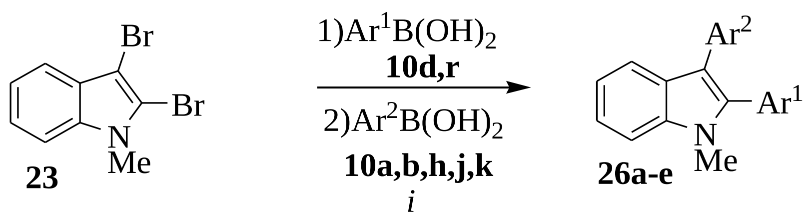


Figure 7. ORTEP drawing of the molecular structure of **25e** in the crystal. Thermal ellipsoids with 50% probability at 173 K. Hydrogen atoms are omitted for clarity.

The synthesis of **26a-e** was carried out by one-pot Suzuki-Miyaura reaction of **23** with arylboronic acid (1.0 equiv.) at 70°C for six hours. Then the addition of the next boronic acid (1.3 equiv.) was performed and the solution refluxed at 110 °C for 8 hours (**Scheme 19**, **Table 16**). The structures of all products were established by spectroscopic methods or by X-Ray crystallography. Good yields were obtained for both electron rich and electron deficient arylboronic acids.



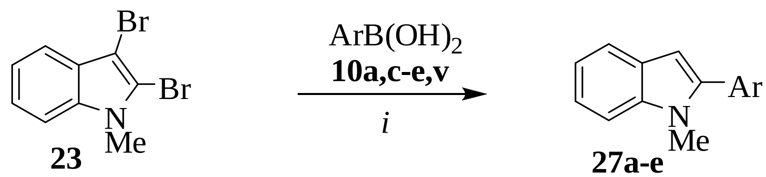
Scheme 19. Synthesis of **26**. *Conditions: i*, 1) **23** (1.0 equiv.), **10d,r** (1.1 equiv.), K_3PO_4 (1.5 equiv.), $Pd(PPh_3)_4$ (4 mol-%), 1,4-dioxane, 70 °C, 6 h; 2) **10a,b,h,j,k** (1.3 equiv.), K_3PO_4 (1.5 equiv.), 110°C, 8 h.

Table 16. Synthesis of **26a-e**

26	10	Ar[1]	Ar[2]	26 (%)[a]
a	**d,b**	4-$C_2H_5C_6H_4$	3-$(C_6H_5)C_6H_4$	71
b	**r,a**	2,5-$(MeO)_2C_6H_3$	C_6H_5	69
c	**r,h**	2,5-$(MeO)_2C_6H_3$	4-ClC_6H_4	59
d	**r,j**	2,5-$(MeO)_2C_6H_3$	2 or 4-FC_6H_4	71
e	**r,k**	2,5-$(MeO)_2C_6H_3$	4-$CF_3C_6H_4$	63

[a] yields of isolated products.

The use of undried solvents resulted in formation of a mixture of products, especially by loss of the bromine atom from position 3 of **23**. When the reaction was carried out in 1:1 dioxane/water it resulted in excellent yields of products with loss of the bromine atom (**Scheme 20**, **Table 17**).



23 **27a-e**

Scheme 20. Synthesis of **27a-e**. *Conditions:* 1) **23** (1.0 equiv.), **10a,c-e,v** (1.1 equiv.), K_3PO_4 (1.5 equiv.), $Pd(PPh_3)_4$ (4 mol-%), 1:1 (1,4-dioxane/water), 90°C, 6 h.

Crystal structures of **27a,b** were found to possess an orthorhombic *P*bca symmetry for **27a** and orthorhombic $P2_12_12_1$ symmetry for **27b**. The asymmetric units contain a single molecule. The molecular structures of crystals clearly show the loss of bromine at carbon C2.

Table 17. Synthesis of **27a-e**

27	**10**	**Ar[1]**	**27 (%)[a]**
a	**a**	C_6H_5	97
b	**c**	4-MeC_6H_4	92
c	**d**	4-EtC_6H_4	95
d	**e**	3,5-$Me_2C_6H_3$	83
e	**v**	4-(*t*Bu)C_6H_4	81

[a] yields of isolated products.

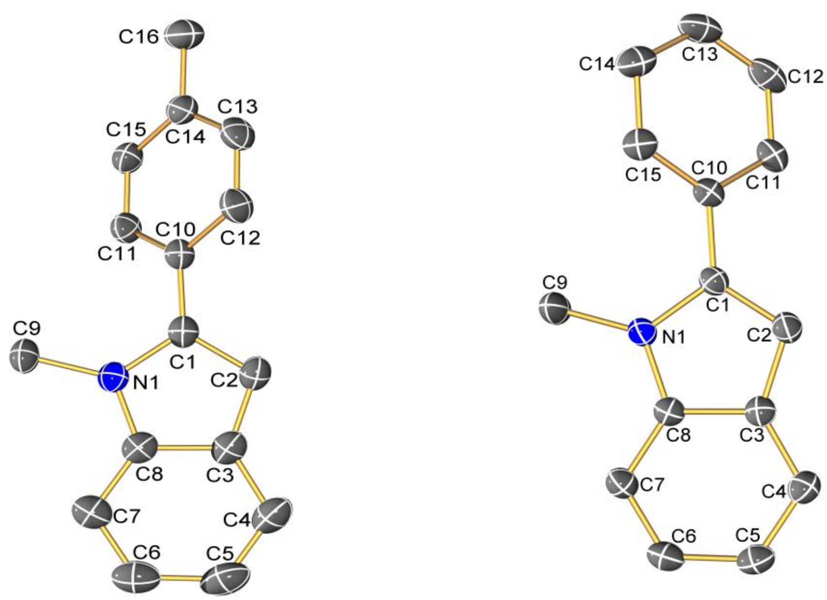
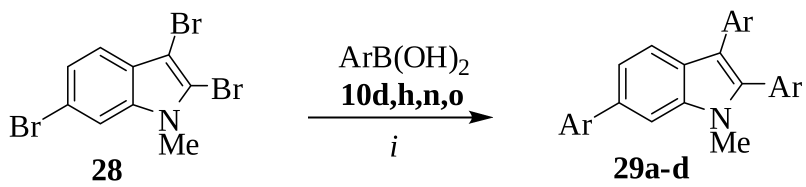


Figure 8. ORTEP drawing of the molecular structure of **27a** (left) and **27b** (right) in the crystal. Thermal ellipsoids with 50% probability at 173 K. Hydrogen atoms are omitted for clarity.

2,3,6-Tribromo-*N*-methylindole (**28**) was synthesized as previously reported in Professor Langer's group.[71] The compound was found to be stable and can be stored at room temperature for more than two months. The Suzuki-Miyaura reactions of **28** with one or two equivalents of arylboronic acids were studied, but all efforts resulted in the formation of mixtures of products. Monoarylated products could be separated in very small amounts, but I failed to optimize the reactions.



Scheme 21. Synthesis of **29**. *Conditions:* 1) **28** (1.0 equiv.), **10d,h,n,o** (3.3 equiv.), K_3PO_4 (4.5 equiv.), $Pd(PPh_3)_4$ (4 mol-%), 1,4-dioxane, 110°C, 8 h.

The reactions of **28** with aryl boronic acids **10d,h,n,o** (3.3 equiv.) afforded the 2,3,6-triaryl-*N*-methylindoles **29a-d** in good yields (**Scheme 21**, **Table 18**). The structures of all products were established by spectroscopic methods. The structures of **29a** and **29c** were independently confirmed by X-ray crystallography. The crystal structures were found to show monoclinic *P*21/n symmetry. The asymmetric unit contains single molecule. Good yields were obtained for both electron rich and electron poor arylboronic acids.

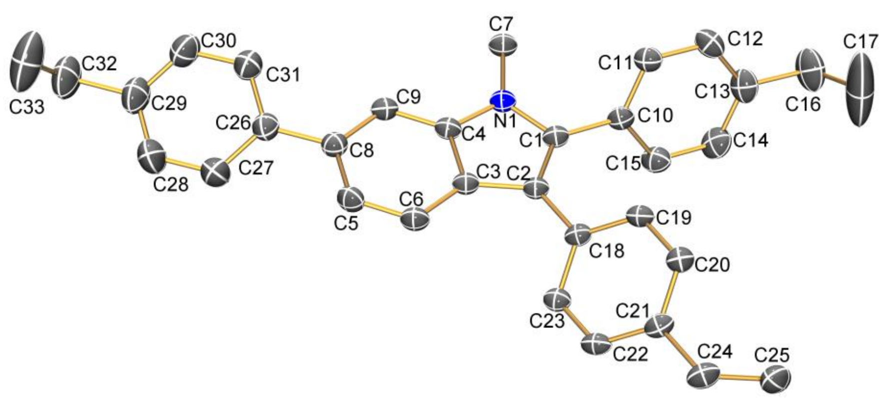


Figure 9. ORTEP drawing of the molecular structure of **29a** in the crystal. Thermal ellipsoids with 50% probability at 173 K. Hydrogen atoms are omitted for clarity.

Table 18. Synthesis of **29a-d**

29	**10**	Ar[1]	**29** (%)[a]
a	**d**	4-EtC_6H_4	94
b	**h**	4-ClC_6H_4	91
c	**n**	2-(EtO)C_6H_4	85
d	**o**	3,4-$(MeO)_2C_6H_3$	82

[a] yields of isolated products.

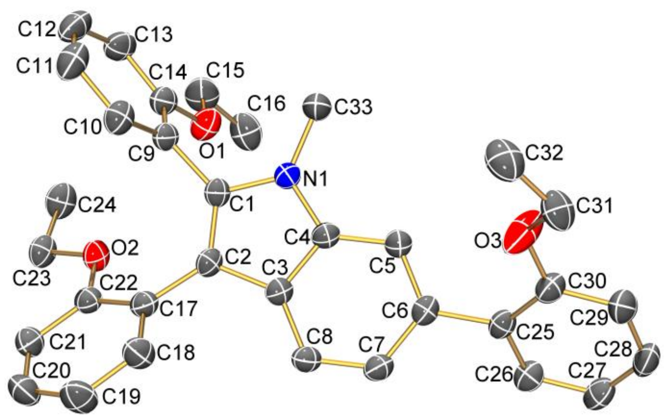


Figure 10. ORTEP drawing of the molecular structure of **29c** in the crystal. Thermal ellipsoids with 50% probability at 173 K. Hydrogen atoms are omitted for clarity.

2.3.3 Conclusions

In conclusion, symmetrical and unsymmetrical 2,3-diarylindoles by Suzuki-Miyaura reactions of *N*-methyl-2,3-dibromoindole were synthesized. The synthesis proved a convenient approach to mono- and diarylated-*N*-methyl indoles. The reaction in the presence of water resulted in loss of bromine from position 3. Reactions of *N*-methyl-2,3,6-tribromoindole were also studied. Monoarylated bromoindoles were found to be very sensitive to moisture and decompose very quickly with loss of bromine. The diarylated products are stable for several days at the air. The triarylated indoles are highly stable and can be stored for months.

3 Silylium - Arene Adducts: An Experimental and Theoritical Study

3.1 Introduction

Cations containing a tri-coordinate silicon atom, R_3Si^+ (where R is an alkyl or aryl group), are known as silylium (also silylenium or silicenium) ions.[72,73] A long debate concerning the existence of "naked" R_3Si^+ cations (**Charts 5** and **6**, species **A**),[74] free of interactions with counterions (**B**), neighboring groups (**E,F**) or solvent (**C** and **D**) was finally brought to an end with the isolation and full characterization of $[(Mes)_3Si][H\text{-}CB_{11}Me_5Br_6]\cdot C_6H_6$ (Mes = 2,4,6-trimethylphenyl) by the groups of Lambert and Reed in 2002.[75] The silylium ion in $[(Mes)_3Si][H\text{-}CB_{11}Me_5Br_6]$ was shown to be three-coordinate and planar and well separated from the carborane anions and benzene solvate molecules by means of single crystal X-ray studies. *Ortho*-methyl groups of the bulky mesityl substituents shield the silicon atom from the close approach of nucleophiles, while remaining innocent as electron donors themselves.[75]

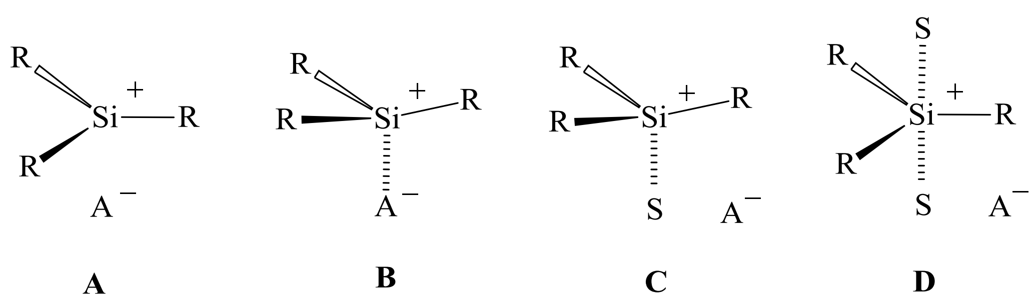
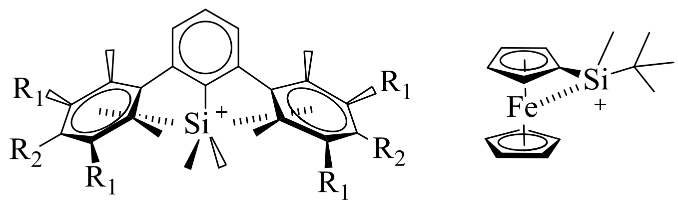


Chart 5. Silylium ions - **A**: naked, **B**: ion pair with strong cation-anion interactions, **C** and **D**: solvent complexes as cation (A^- = weakly coordinating anion, S = σ or π donor solvent).

Silylium ions with their electron sextet and empty p orbitals are electron deficient species and thus strong Lewis acids. Even relatively weak Lewis bases, such as π/σ-donor solvents (*e.g.* toluene,[76] CH_3CN,[77] etc.) form tetrahedral complexes with silylium ions.[76] In addition, intramolecular π coordination in silylium ions containing a 2,6-

diarylphenyl scaffold was observed which adopt the C_1-symmetric geometry of a Wheland-like complex (**Chart 6**, species **E**).[78]



E **F**

Chart 6. **E**: Intramolecular π coordination in silylium ions (R_1, R_2 = H, Me), **F**: ferrocene-based silylium ion intramolecularly stabilized by electron-rich Fe.

As silylium ions are highly reactive Lewis acids they are useful reagents in chemical synthesis.[79,80,81,82,83,84,85] Ozerov *et al.*[81] and Müller *et al.*[82] have utilized silylium ions as reactive catalysts for the activation of C–F bonds. The Ozerov group introduced a class of carborane-supported, highly electrophilic silylium compounds that act as long-lived catalysts for hydrodefluorination of trifluoromethyl and nonafluorobutyl groups by widely accessible silanes under mild conditions. The reactions are completely selective for aliphatic carbon-fluorine bonds in preference to aromatic carbon-fluorine bonds.[81b] Recently; Oestreich *et al.*[83] demonstrated that a tamed, ferrocene-based silylium ion (**Chart 6**, species **F**) catalyzes demanding Diels–Alder reactions in an unprecedented temperature range.

Both steric shielding of the empty orbital at the silicon atom,[78,86] and the clever design of weakly coordinating anions[87,88] allowed the structural determination of a silylium ion.[75] The first structurally characterized salt bearing a silylium cation, $[Et_3Si]^+[B(C_6F_5)_4]^-$·2(toluene) was reported by Lambert *et al.* in 1993.[76] The crystal structure of $[Et_3Si]^+[B(C_6F_5)_4]^-$·toluene revealed a silyl cation with significant coordination to a toluene molecule, which is the solvent for crystallization. The nature and extent of this coordination were controversial.[89] For a free R_3Si^+ cation, all three substituents should lie in a plane, and the average bond angle to the tricoordinate silicon should be 120°. However, for the Et_3Si^+-ion, the average angle was only 114° and thus

$[Et_3Si]^+[B(C_6F_5)_4]^-$·toluene should be regarded as a salt containing a solvent complex as cation of the type $[Et_3Si·toluene]^+$ (**Chart 5**, species **C**).

In contrast to the solid state, the free silylium cation in solution seems to be a fiction due to interaction with the solvent.[90] The question is how much silylium cation character (if any at all) can be retained in a solvent coordinated silylium cation.[91] There is computational evidence that even argon can be a ligand to Me_3Si^+.[74a]

Ever since the isolation of $[Et_3Si·toluene]^+$ no further solvent complex bearing a silylium solvent complex as cation of the type $[R_3Si·arene]^+$ (R = alkyl) has been isolated and structurally characterized. Recently, salts containing $[Me_3Si–X–SiMe_3]^+$ ions (X = halogen, pseudohalogen) were described,[92] which can also be considered as solvent complexes of $Me_3Si–X$ and $[Me_3Si]^+$. In these complexes the Me_3Si fragment has also almost completely lost its silylium character (strong deviation from planarity), since a stable covalently bonded tetracoordinated Si center is formed (**Chart 5**, species **C** with S = $Me_3Si–X$).[82,87b,92b,93]

Besides salts bearing $[R_3Si·arene]^+$ or $[Me_3Si–X–SiMe_3]^+$ ions (X = halogen), a frequently used reagent in silylation chemistry is $[Et_3Si^+][B(C_6F_5)_4]$, first reported by Lambert.[76b,94] Only recently, Reed and Nava proved that the commonly used triethylsilyl or trimethylsilyl perfluorotetraphenylborate salts, $[R_3Si^+][B(C_6F_5)_4]$, were misidentified.[95] All known alkyl substituted, formal "$[R_3Si^+][B(C_6F_5)_4]$" salts, prepared from R_3Si-H and $[Ph_3C][B(C_6F_5)_4]$, form $[B(C_6F_5)_4]$ salts containing a hydride-bridged silane adduct cation of the type $[R_3Si–H–SiR_3]^+$.

Since the silylium ion became a focus of attention especially in catalysis,[79,81,82,83,85] and there is still a lack of data with respect to silylium solvent complexes, we have studied in detail the structure, bonding and interaction of the Me_3Si^+ ion with differently substituted arenes of the type $R_nC_6H_{6-n}$, (R = H, Me, Et, Pr, and Bu; n = 0 – 6). By changing the substitution pattern and the size of the substituents (from small to bulky) we are able to discuss the steric and electronic influence on the solvent complex formation which is, in addition, supported by computational data. Furthermore, we show that isomerization may occur upon solvent complex formation when electron-rich *t*-Bu substituent.

3.2 Synthesis of $[Me_3Si{\cdot}arene][B(C_6F_5)_4]$ salts (31a-k)

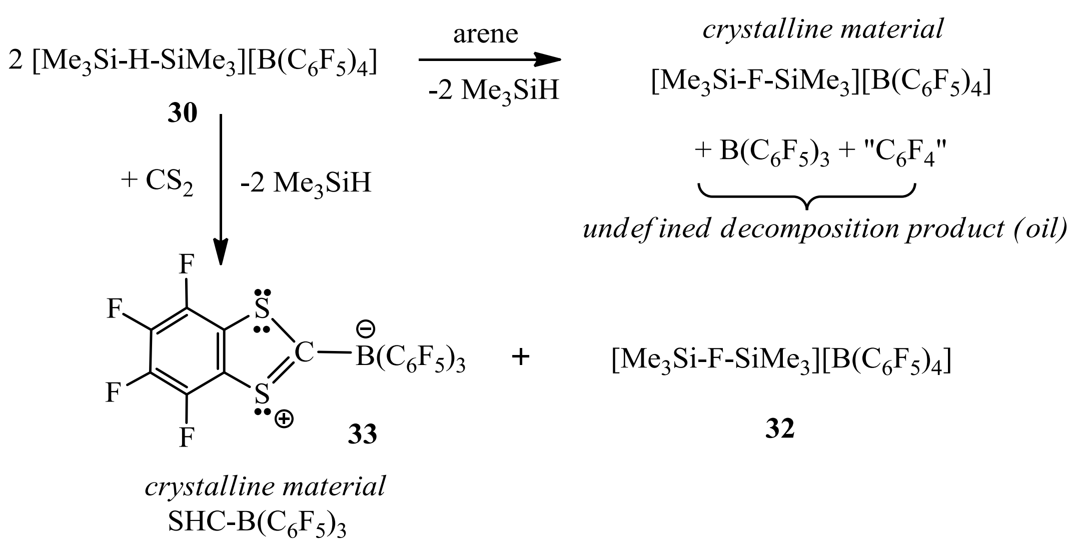
As Me_3Si^+ source always $[Me_3Si–H–SiMe_3][B(C_6F_5)_4]$ **(30)** was used and reacted with a large excess of arene solvent. These Me_3Si^+ transfer reactions can be considered as Lewis acid – Lewis base reaction (see below). The solvent coordinated $[Me_3Si{\cdot}arene][B(C_6F_5)_4]$ salts **(31a-k)** (arene = benzene, toluene, ethylbenzene, *n*-propylbenzene, *i*-propylbenzene, *o*-xylene, *m*-xylene, *p*-xylene, 1,2,3-trimethylbenzene, 1,2,4-trimethylbenzene, 1,3,5-trimethylbenzene, **Figures 11-17**) are easily obtained in 70-90 % yields by treatment of neat $[Me_3Si–H–SiMe_3][B(C_6F_5)_4]$ with the corresponding arene solvent at ambient temperatures (**Scheme 22**). It should be noted that it is difficult to obtain crystals suitable for a single crystal X-ray analysis due to the low solubility of $[Me_3Si{\cdot}arene][B(C_6F_5)_4]$ salts in the corresponding solvents. To avoid thermal decomposition, the mixtures were carefully warmed with stirring until two clear colorless layers were obtained. Slow cooling to ambient temperature resulted in the deposition of large crystals rather than needle like crystals or crystalline slurry.

$[Me_3Si{\cdot}arene][B(C_6F_5)_4]$ salts are air and moisture sensitive but stable under argon atmosphere over a long period as solid but slowly decompose in solution even at ambient temperatures. Colorless crystals and solutions of $[Me_3Si{\cdot}arene][B(C_6F_5)_4]$ salts quickly turn yellow if traces of moisture are present. All $[Me_3Si{\cdot}arene][B(C_6F_5)_4]$ salts can be prepared in bulk and are almost indefinitely stable when stored in a sealed tube. They are thermally stable up to over 80 °C. Between 88°C (benzene) and 118°C (1,2,3-trimethyl benzene), decomposition occurs, which is presumably triggered by the formation of $Me_3Si–F$. All $[Me_3Si{\cdot}arene][B(C_6F_5)_4]$ salts have been fully characterized by elemental analysis, Raman and IR spectroscopy and single crystal structure elucidation.

$$[Me_3Si\text{-}H\text{-}SiMe_3][B(C_6F_5)_4] \xrightarrow[\substack{-Me_3Si\text{-}H \\ 20\text{ - }80°C}]{\text{excess } \textit{arene}} [Me_3Si{\cdot}\textit{arene}][B(C_6F_5)_4]$$

Scheme 22. Synthesis of $[Me_3Si{\cdot}arene][B(C_6F_5)_4]$ (**31a-k**) salts.

An interesting side product the formation of bissilylated fluoronium ion[93] $[Me_3Si–F–SiMe_3]^+$ **(32)** was observed a few times and even co-crystallized with $[Me_3Si·arene][B(C_6F_5)_4]$ (arene = benzene, toluene) depending on the crystallization conditions (concentration, temperature and time). Obviously, especially the weakest bound solvent complexes with benzene and toluene (see **Section 3.5**) are reactive enough to degrade slowly the $[B(C_6F_5)_4]^-$ anion (**Scheme 23**) on gentle heating. A similar degradation of the $[B(C_6F_5)_4]^-$ ion has been reported before by Müller in naphthyl based silylium ions.[82] We assume that the degradation proceeds via abstraction of a F^- ion by the reactive Me_3Si^+ ion leading finally to the formation of the fluoronium salt $[Me_3Si–F–SiMe_3][B(C_6F_5)_4]$, $B(C_6F_5)_3$ and a reactive "C_6F_4" species. This assumption is supported by a trapping reaction with CS_2 as illustrated in **Scheme 23**.



Scheme 23. Degradation reaction of $[Me_3Si·arene][B(C_6F_5)_4]$ and trapping of C_6F_4 by SHC adduct formation (**33**) upon addition of CS_2.

Upon addition of CS_2 the formation of a formal *S*-heterocyclic carbene adduct, *SHC*-$B(C_6F_5)_3$, (**33**) was observed besides $[Me_3Si–F–SiMe_3][B(C_6F_5)_4]$, and $B(C_6F_5)_3$. By fractional crystallization *SHC*-$B(C_6F_5)_3$ could be isolated in small quantities and characterized by a single crystal X-ray analysis. To the best of our knowledge 1,3-dithiol-2-ylidenes (**Chart 7**, structure **A**), which can be regarded as *S*-heterocyclic carbenes

(*SHC*), are unknown since they immediately dimerize to well-known tetrathiafulvalenes (**B**).[96]

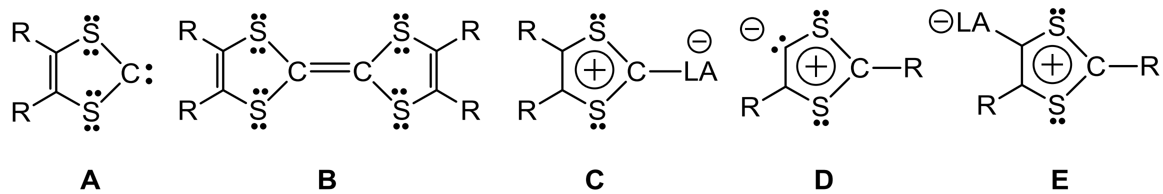
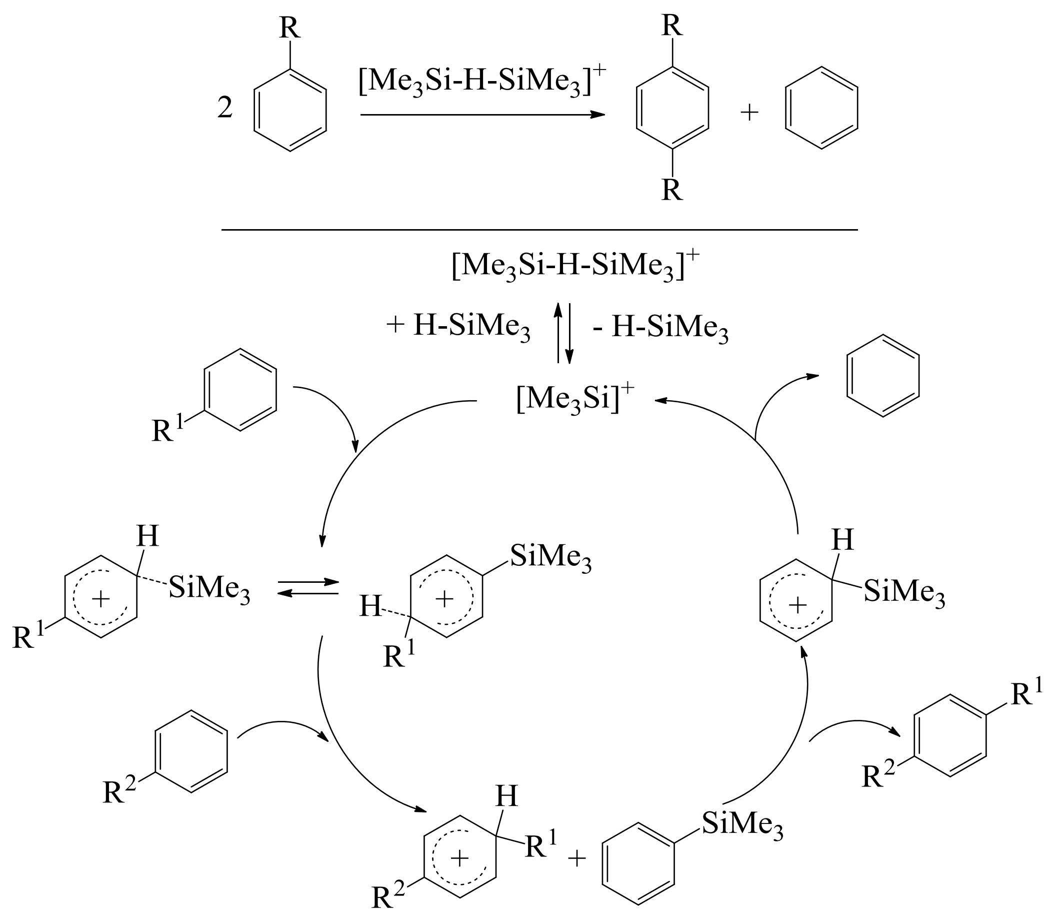


Chart 7. Structural framework of unknown SHCs = 1,3 dithiol-2-ylidenes (**A**), which dimerize to known tetrathiafulvalenes (**B**), adducts with Lewis acids (**C**), the unknown 1,3-dithiol-5-ylidene isomer (**D**) and their known adducts (**E**) (LA = Lewis acid).

The *SHC*-$B(C_6F_5)_3$ species is the first example of an *S*-heterocyclic carbene adduct complex with a Lewis acid.[97] Only recently Bertrand *et al.* reported on metal complexes (**E**) of the hitherto unknown 1,3-dithiol-5-ylidenes (**D**) which are isomers of *SHC* (**A**).[98]

3.3 Isomerization catalysed by silylium ions – Friedel-Crafts-catalysis

While the synthetic protocol described above worked nicely for benzene, toluene, ethylbenzene, *n*-propylbenzene, *i*-propylbenzene, *o*-xylene, *m*-xylene, *p*-xylene, 1,2,3-trimethylbenzene, 1,2,4-trimethylbenzene, 1,3,5-trimethylbenzene, the same route yielded in case of *tert.*-butylbenzene two major products $[Me_3Si–F–SiMe_3][B(C_6F_5)_4]$, which crystallizes first, and after concentration of the supernatant solution 1,4-di-*tert.*-butylbenzene (**31l**). Both products were identified by X-ray structure determination. This finding led to a detailed study of this isomerization reaction which can be referred to as a Fridel-Crafts type isomerization.[99] In the course of more than 120 years of Friedel-Crafts chemistry, two catalysts achieved preeminence: (i) anhydrous aluminum trichloride, which was introduced by Friedel and Crafts themselves and (ii) boron trifluoride or the more convenient etherate BF_3 complexes.[100] Since the 1960s, some superacid catalysts such as antimony pentafluoride gained significance.[101] Furthermore, the catalytic activity of superacids and metal triflate was intensively explored by Olah *et al.*[102] Now, we can show that [Me_3Si·arene][$B(C_6F_5)_4$] salts are convenient and effective new Friedel-Crafts catalysts, which catalysize in case of *tert.*-butylbenzene the isomerization affording 1,3-di-*tert*.-butylbenzene (8.47%), 1,4-di-*tert*.-butylbenzene (64.4%) and 1,3,5-tri-*tert*.-butylbenzene (27.2%) beside benzene as determined by GCMS. The overall isolated yield is about 5.3% (referring to *tert*.-butylbenzene) after three hours at ambient temperatures, or about 560 % (referring to [Me_3Si–H–$SiMe_3$][$B(C_6F_5)_4$]). This corresponds to a TON of about 7.0 (referring to [Me_3Si–H–$SiMe_3$][$B(C_6F_5)_4$], three hours reaction time). The long term stability was also studied. Even after three days the catalyst was still active. Interestingly, also at –80 °C isomerization was observed.



Scheme 24. Me_3Si^+ catalyzed isomerization reaction leading to the 1,4-substituted arene (**31m**) (R = *t*-Bu; counter ion = $[B(C_6F_5)_4]^-$).

The observation of predominant formation of 1,4-di-*tert*.-butylbenzene (**31l**) (64.4%) isomer can be explained only by intermolecular isomerization according to **Scheme 24**. Computations indicated that the silylium ion preferentially attacks at the *para* position (see Section **Computations** below).

Isomerization was only observed for the electon-rich *tert*.-butylbenzene. For instance in case of *n*-propylbenzene and *i*-propylbenzene no isomerization was observed even after refluxing for several days at high temperatures in a sealed tube (T = 160°C).

3.4 X-ray crystallography

The structures of [Me_3Si·arene][$B(C_6F_5)_4$] salts (arene = benzene, toluene, ethylbenzene, *n*-propylbenzene, *i*-propylbenzene, *o*-xylene, *m*-xylene, *p*-xylene, 1,2,3-trimethylbenzene, 1,2,4-trimethylbenzene, 1,3,5-trimethylbenzene) and the decomposition products [Me_3Si–F–$SiMe_3$][$B(C_6F_5)_4$] and *SHC*-$B(C_6F_5)_3$ have been determined with the help of Xray techneque. Tables A3.1-3.15 present the X-ray crystallographic data (see Appendix **A3**). Selected molecular parameters are listed in **Table 19**. X-ray quality crystals of all considered species were selected in Fomblin YR-1800 (Alfa Aesar) at ambient temperature. All samples were cooled to 173K during the measurement.

[Me_3Si·benzene][$B(C_6F_5)_4$](31a)

[Me_3Si·benzene][$B(C_6F_5)_4$] (**31a**) crystallizes solvent free from benzene in the monoclinic space group *P*2/c with four formula units per unit cell (**Figure 11**). Interestingly, slightly different cell and structural parameters are found for crystals from different experiments Depending on the crystallization conditions (time and temperature) the degradation product [Me_3Si–F–$SiMe_3$][$B(C_6F_5)_4$] co-crystallizes with [Me_3Si·benzene][$B(C_6F_5)_4$] forming mixed crystals of the type 0.76[Me_3Si·benzene][$B(C_6F_5)_4$] · 0.24[Me_3Si–F–$SiMe_3$][$B(C_6F_5)_4$]. Here, the position of one [Me_3Si–benzene]$^+$ cation was found to be partially occupied by a [Me_3Si–F–$SiMe_3$]$^+$ ion. The occupancy of each part was refined freely (0.525(2)/0.475(2)). Partly substitution of $[Me_3Si{\cdot}benzene]^+$ by $[Me_3Si–F–SiMe_3]^+$ ions leads to a change in the space group to $P2_1/c$ and eight formula units in the unit cell.

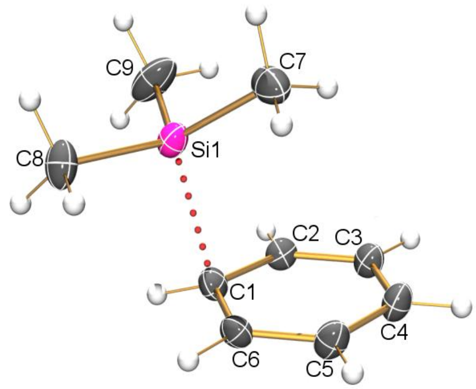


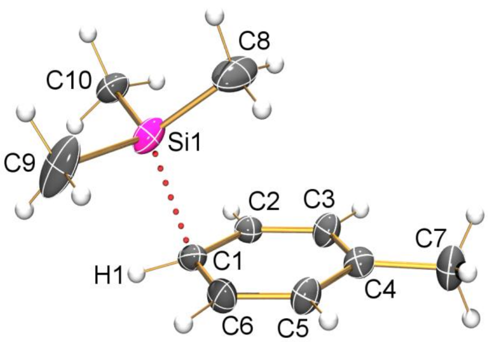
Figure 11. ORTEP drawing of the molecular structure of $[Me_3Si{\cdot}benzene]^+$ (**31a)**. Thermal ellipsoids with 30% probability at 173 K.

Although in all three structures the cations are well-separated from the $[B(C_6F_5)_4]$ anions, there are numerous very weak $H_{methyl,cation}{\cdots}C–F_{anion}$ and $H_{arene,cation}{\cdots}C–F_{anion}$ interactions. For instance 21 such contacts are found for all between 2.40 – 3.0 Å (*cf.* Σr_{vdW} (H···F) = 2.9 Å).[103]

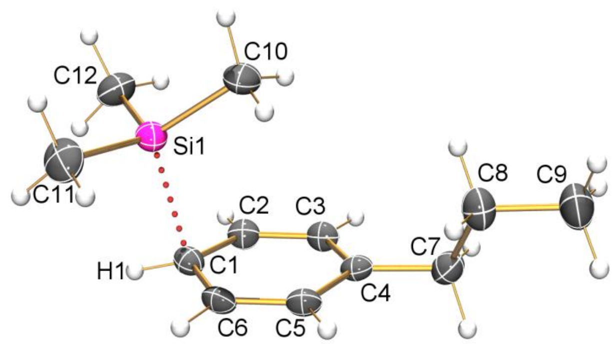
The silicon atom in the cations is tetracoordinated with bonding angles around the Si atoms between 341.7 and 343.1° displaying a strong deviation from planarity (360.0°) as well as from the value for an ideal tetrahedral environment (328.4°). Such relative large Σ<Si values[104] were reported for complexes between silylium ions with solvent molecules (341.4(5) and 342.6(5)° for $[Et_3Si{\cdot}toluene][B(C_6F_5)_4]$)[77], with anions (345.0(10) and 349.0(9)° for $[Et_3Si][Br_6CB_{11}H_6]$)[105] and for the bissilylated halonium ions (345-348° $[Me_3Si–X–SiMe_3][B(C_6F_5)_4]$, X = halogen).[92b] A second interesting aspect of the structure is the intriguingly large distance between silicon and the fourth coordination site, the solvent benzene (**Figure 11**). The coordination mode of this interaction is clearly η^1 rather than η^2 or η^6 (*cf.* Si–C1 2.174(2) *vs*. Si–C2 2.758(2), Si–C3 3.558(2), Si–C4 3.884, Si–C5 3.562, Si–C6 2.758 Å). The three slightly different Si–C1 distances illustrate both the huge influence of the environment due to a very flat

potential energy surface and manifest the error of structure elucidation. The observed value of 2.169(3)-2.183(4) Å is considerably larger than the sum of the C and Si covalent radii (1.91 Å;[93] *cf.* 2.18 in [Et_3Si·toluene][$B(C_6F_5)_4$])[76] but still much shorter than the sum of the van der Waals radii (3.8 Å).[106] As a consequence of the Si···C1 interaction, the trigonal planar environment around C1 changes to strongly distorted tetrahedral, leading to an out-of-plane position for H1 as displayed by the H1–C1–C2–C6 dihedral angle (**Table 19**).

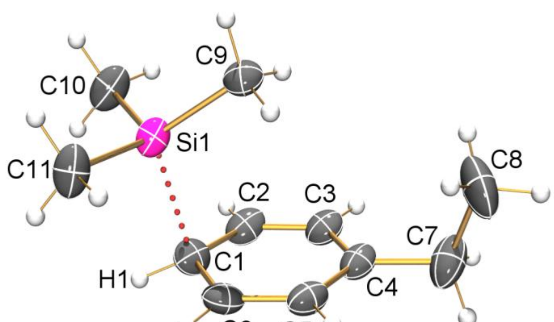
[$Me_3Si·RC_6H_5$][$B(C_6F_5)_4$] (31b-e)



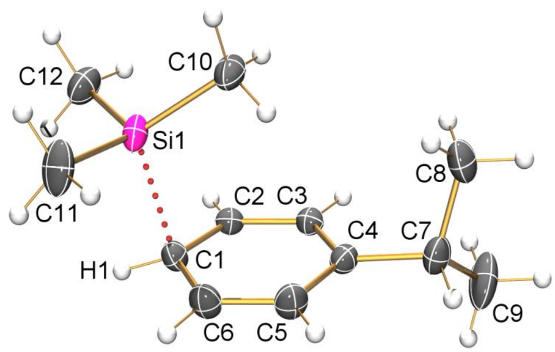
31b



31d



31c



31e

Figure 12. ORTEP drawing of the molecular structure of [Me_3Si·monosubstituted_arene]$^+$ (arene = toluene, *n*-propyl benzene, ethyl benzene and *i*-propyl benzene) (**31b-e**). Thermal ellipsoids with 30% probability at 173 K.

$[Me_3Si{\cdot}RC_6H_5][B(C_6F_5)_4]$ (R = Me, Et, *n*-Pr, *i*-Pr) (**31b-e**), crystallize from RC_6H_5 in the orthorhombic space groups *P*bca (R = Me), or the monoclinic space groups $P2_1$/n (Et) and $P2_1$/c (*n*-Pr, *i*-Pr) with either four (R = Et, *i*-Pr) or eight (R = Me, *n*-Pr) formula units per unit cell. Again, for the toluene species it was possible to isolate mixed crystals of the type $0.92[Me_3Si{\cdot}toluene][B(C_6F_5)_4] \cdot 0.08[Me_3Si–F–SiMe_3][B(C_6F_5)_4]$ besides pure $[Me_3Si{\cdot}toluene][B(C_6F_5)_4]$. Both sorts of crystals have almost identical cell data.

In all four alkyl-substituted benzene adducts (**Figure 12**) the silylium cation attacks in *para* position to the alkyl-substituent and slightly shorter Si···C1 distances compared to the unsubstituted $[Me_3Si{\cdot}benzene]^+$ ion are observed in accord with theoretical results (see Section **Computations**). In case of the derivatives with longer alkyl side chains, the beta C atom of the alkyl chain always adopts a *cis* position with respect to the silyl group. Similar to the $[Me_3Si{\cdot}benzene]^+$ ion, also all four alkyl substituted benzene cations display very weak $H_{methyl,cation}$···C–F_{anion} and $H_{arene,cation}$···C–F_{anion} interactions. Amongst these four salts only the ethyl derivative crystallizes with one solvent molecule (Et–C_6H_5) per cation.

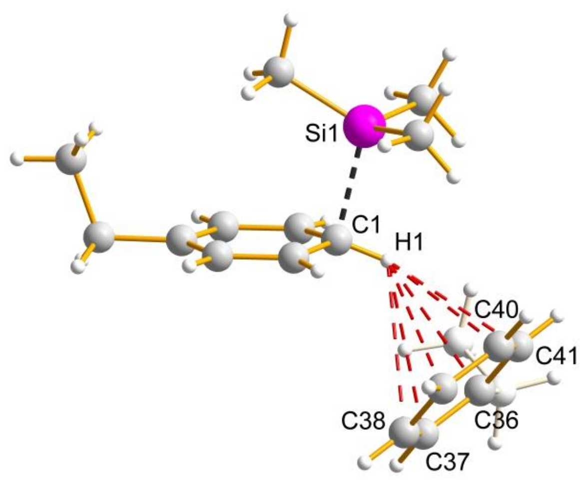


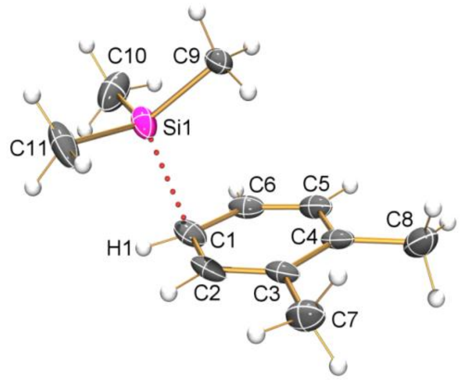
Figure 13. Short H1···C_{arene} distances (C36: 3.009, C37: 3.199, C38: 3.207, C39: 3.030, C40: 2.827, C41: 2.801 Å) in the ethyl benzene adduct (**31c**) indicating weak van der Waals interactions in η^6 fashion with one solvent molecule.

As can be seen from **Figure 13**, the solvent molecule is closely arranged to the cation and clearly directed towards the H1 proton in η^6 type coordination mode with $H_{arene,cation}\cdots C_{arene,solvent}$ distances between 2.80 and 3.20 Å (*cf.* Σr_{vdW} (H···C) = 3.1 Å).[103] This solvent···$H_{arene,cation}$ interaction is further supported by a significantly larger displacement of the H1 proton from the arene ring plane within the cation as indicated by the H1–C1–C2–C6 dihedral angle (–147.4 *vs.* < –155 for all other species). Furthermore, NPA partial charge calculations reveal that H1 carries the largest positive charge (**Table 20**) with 0.32*e* (*cf.* 0.23-0.27*e* for all other arene protons) and even the protons of the Me_3Si unit are less positive (0.27-0.29*e*). In the uncoordinated solvent the charges of all arene protons are all very similar and in the range 0.23-0.24*e*, displaying especially for H1 a large positive charge accumulation upon adduct formation. Comparison of the averaged C_{arene}–C_{arene} distances in the ethyl benzene cation and the uncoordinated solvent molecule displays a shorting of these distances by *ca.* 0.025 Å. An even stronger effect is found for the C_β–C_γ distance of the ethyl group which elongates by 0.049 Å in the cation which might partly be attributed to a stronger hypercongative effect of the C_β–C_γ σ bond with the π* bond system of the arene upon attack of the silylium cation in *para* position.

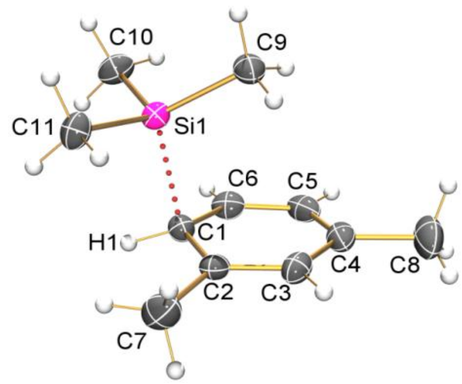
$[Me_3Si{\cdot}Me_2C_6H_4][B(C_6F_5)_4]$ (31f-h)

All three possible xylene derivatives (*ortho*, *meta*, and *para*) (**31f-h**) were synthesized (**Figure 14**). While *o*-xylene (1,2-dimethyl benzene) (**31f**) and *m*-xylene (1,3-dimethyl benzene) (**31g**) adducts crystallize in monoclinic space groups $P2_1/n$ and $P2_1/c$ with eight and four formula units, respectively, *p*-xylene (1,4-dimethyl benzene) (**31i**) crystallizes in the orthorhombic space group *P*bca with eight molecules per unit cell. In case of the *ortho*- and *para*-species solvent molecules are included in the unit cell. However, only for the *ortho*-species the η^6-coordination mode with the solvent - as described for $[Me_3Si{\cdot}EtC_6H_5][B(C_6F_5)_4]$ (**Figure 13**) was observed, again with a stronger displacement of the H1 proton and fairly short $H1_{arene,cation}\cdots C_{arene,solvent}$ distances (**Figure 15**).

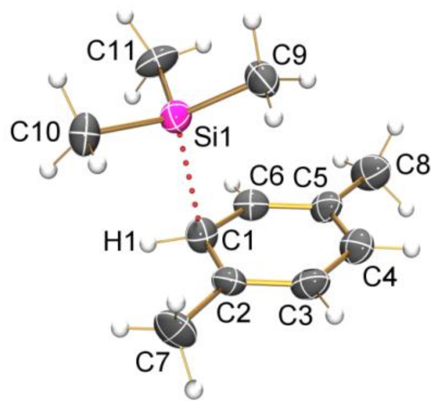
For the *p*-xylene species no such η^6-coordination arrangement was found and the shortest $H1{\cdots}C_{methyl}$ distance amounts to 3.592 Å which was observed between H1 and one methyl carbon atom of the solvent molecule (*cf.* shortest $H1_{arene,cation}{\cdots}C_{arene,solvent}$ 4.417 Å).



31f



31g



31h

Figure 14. ORTEP drawing of the molecular structure of $[Me_3Si{\cdot}disubstituted\_arene]^+$ (arene = 1,2-dimethyl benzene, 1,3-dimethyl benzene and 1,4-dimethyl benzene) (**31f-h**). Thermal ellipsoids with 30% probability at 173 K.

A comparison of the $Si{\cdots}C1$ distances with those of the benzene or mono-substituted species is not straightforward, since addition of the silyl group in *para* position is not feasible in *p*-xylene. Thus the most interesting question is the influence of the substitution pattern on the $Si{\cdots}C1$ distance within the group of xylene species. For the

1,2-substituted species clearly the position at C1 (equivalent to the C6 position, *para* to C1 and *meta* to C2/C5, Figure 13) is energetically favoured over all other possibilities which do allow a *para* position for the silyl group. The same argument holds for the 1,3-substituted cation where the position at C1 (equivalent to C5) represents the *ortho* position. In case of the 1,4-substituted species adduct formation in *para* position is rather unlikely due to steric repulsion with one methyl group in accord with theory (See section **Computations**). Hence, only *ortho* and *meta* positions are feasible (C1/C3/C5/C6 are equivalent, **Figure 14**). As a result the longest Si···C1 distance was found for *p*-xylene (2.167(5) Å, **Table 19**). The small difference between *o*- and *m*-xylene might be explained by the fact that in *o*-xylene the one *para* and one *meta* position is energetically favoured over one *para* and one *ortho* position.

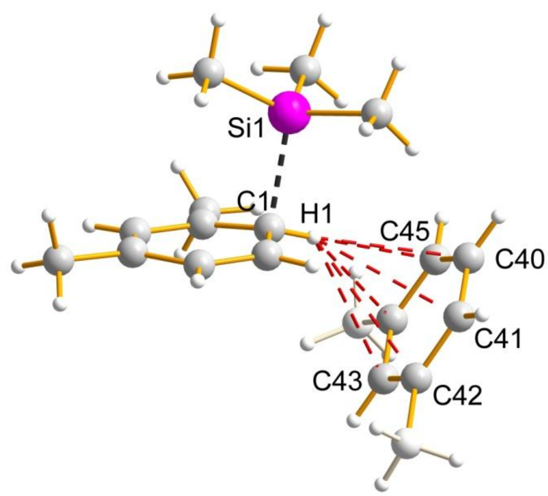
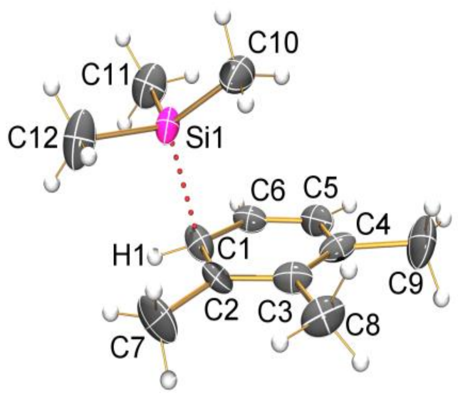


Figure 15. Short H1···$C_{arene,solvent}$ distances (C37: 3.176, C38: 3.115, C39: 2.953, C40: 2.885, C41: 2.963, C42: 3.127 Å) in the *meta*-xylene adduct (**31g**) indicating weak van der Waals interactions in η^6 fashion with one solvent molecule.

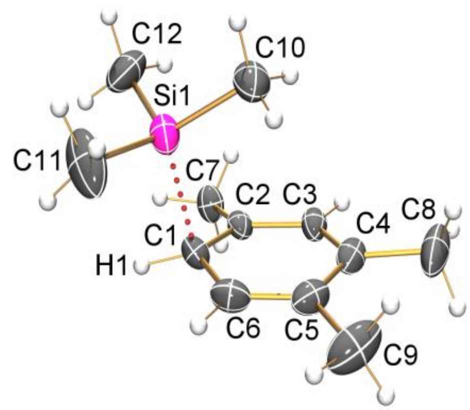
[$Me_3Si{\cdot}Me_3C_6H_3$][$B(C_6F_5)_4$] (**31i-k**)

In case of 1,2,3-trimethylbenzene three *para* positions are available (C1 equivalent to C5, and C6). The silylium ion prefers for energetic reasons **(**see Section

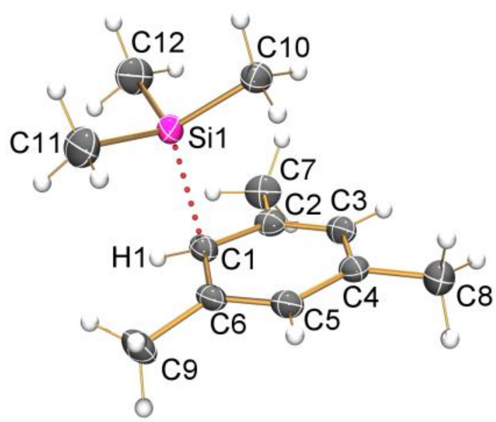
Computations) to attack position C1/C5 (one *para*, one *ortho* and one *meta* C atom) rather than C6 with one *para* and two *meta* carbon atoms. For 1,2,3-trimethylbenzene there are three different adduct ions possible: (i) attached to C1 with one *para*, *ortho* and *meta* position, (ii) attached to C3 with no *para* but two *ortho* and one *meta* position, and (iii) attached to C6 with one *ortho* and two *meta* positions. Since *para* position attack is preferred, the most stable isomer is the one where the silyl group attacks C1 in accord with theory. For mesitylene only one isomer is possible since all three hydrogen substituted arene carbon atoms are equivalent. Note: Adduct formation at an arene carbon atom attached to a methyl group is always unfavorable.



31i



31j



31k

Figure 16. ORTEP drawing of the molecular structure of $[Me_3Si{\cdot}trisubstituted\_arene]^+$ (arene = 1,2,3-trimethyl benzene, 1,2,4-trimethyl benzene and 1,3,5-trimethyl benzene) (**31i-k**). Thermal ellipsoids with 30% probability at 173 K.

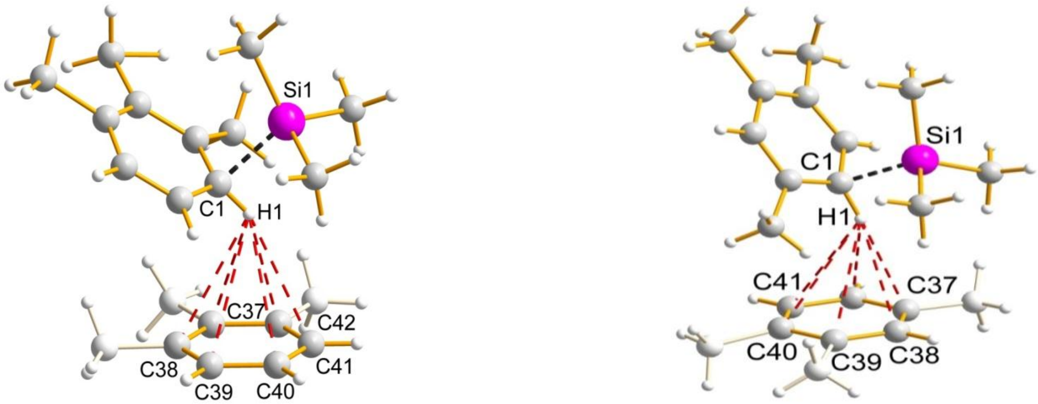


Figure 17. Short H1···$C_{arene,solvent}$ distances in 1,2,3-trimethyl benzene (**31i**, left)(C37: 2.999, C38: 3.141, C39: 3.216, C40: 3.013, C41: 3.154, C42: 3.013 Å) and 1,2,4-trimethyl benzene adduct (**31j**, right) (C37: 2.898, C38: 2.898, C39: 3.067, C40: 3.228, C41: 3.228, C42: 3.067 Å) indicating weak van der Waals interactions in η^6 fashion with one solvent molecule.

SHC-B(C_6F_5)$_3$ (33)

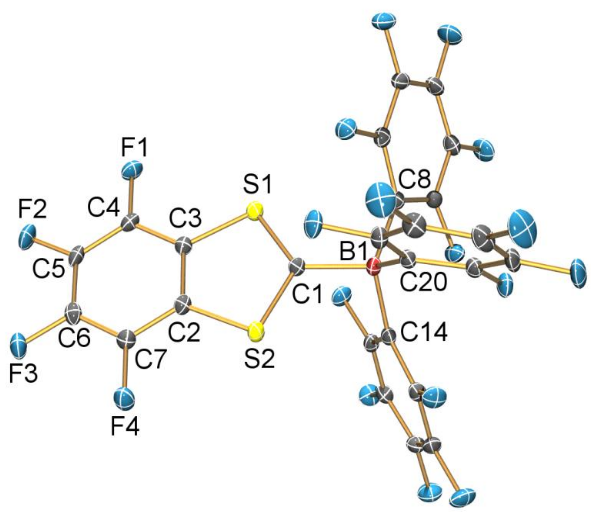


Figure 18. ORTEP drawing of the molecular structure of *SHC*–B(C_6F_5)$_3$ (**33**) in the crystal. Thermal ellipsoids with 30% probability at 173 K. Selected bond lengths (Å) and angles (°): S1–C1 1.669(2), S1–C3 1.728(2), S2–C1 1.691(2), S2–C2 1.735(2), C1–B1 1.660(2), C2–C7 1.390(3), C2–C3 1.393(2), C3–C4 1.394(2), C8–B1 1.652(3), C14–B1 1.654(3), C20–B1 1.639(3); C1–S1–C3 97.82(9), C1–S2–C2 97.18(8), B1–C1–S1

123.0(1), B1–C1–S2 121.0(1), S1–C1–S2 115.5(1), C7–C2–C3 120.0(2), C7–C2–S2 125.3(1), C3–C2–S2 114.6(1), C2–C3–C4 119.9(2), C2–C3–S1 114.8(1), C4–C3–S1 125.2(1), C3–S1–C1–B1 173.5(1), C3–S1–C1–S2 0.7(2), C2–S2–C1–B1 −174.0(1), C2–S2–C1–S1 −1.1(1), C1–S2–C2–C7 179.0(2), C1–S2–C2–C3 1.2(2).

SHC-B(C_6F_5)$_3$ crystallizes in the monoclinic space group $P2_1/n$ with eight formula unit per unit cell and two independent molecules. The planar *SHC* and the B(C_6F_5)$_3$ group (**Figure 18**) are connected by means of a strong B–C donor-acceptor bond that amounts to 1.660(2) Å (*cf.* Σr_{cov}(B–C) = 1.60 Å),[106] which is slightly longer than those found for the B–C_{C6F5} rings (C8–B1 1.652(3), C14–B1 1.654(3), C20–B1 1.639(3)Å).[107] The boron atom of the B(C_6F_5)$_3$ is tetracoordinated while the carbene carbon atom sits in an almost trigonal planar environment (B1–C1–S1 123.0(1), B1–C1–S2 121.0(1), S1–C1–S2 115.5(1)°). The coordination geometry around boron in the BC_4 core is slightly distorted with the smallest angle of 102.2(2), and the largest 114.7(1)°. Two sets of different S–C bond distances are found: (i) Two rather short bond lengths of S1–C1 1.669(2) and S2–C1 1.691(2) Å are determined for the bonds to the carbene carbon atom, while (ii) slightly larger distances (S1–C3 1.728(2) and S2–C2 1.735(2) Å) are found for the two other S–C_{ring} bonds. All four S–C bond lengths are considerably shorter than the sum of the covalent radii (Σr_{cov}(B–C) = 1.78 Å),[106] thus indicating partial double bond character within the five-membered C_3S_2 heterocycle.

Molecular structure of [Me_3Si–F–SiMe_3]$^+$ ions co-crystallized in [Me_3Si·benzene][B(C_6F_5)$_4$] and [Me_3Si·toluene][B(C_6F_5)$_4$]

While the molecular structure of the pure salt is ideal C_2 symmetric, the symmetry is decreased to C_1 for the fluoronium cations in the mixed crystals (**Table 19**). Thus slightly different Si–F bond distances are observed which range from 1.708(7) to 1.73(2) Å (*cf.* 1.753(9) Å for the pure salt). The largest difference is found for the Si–F–Si angles which are somewhat smaller for the cations in the mixed crystals (158/159 *vs*. 163°) which can be attributed to a very flat energy potential for the variation of the Si–F–Si angle.

Table 19. Selected structural data of experimentally observed $[Me_3Si–F–SiMe_3]^+$ ions.

$[Me_3Si–F–SiMe_3][B(C_6F_5)]$	*Si–F*	*Si–F–Si*	*Σ<Si*
$[Me_3Si·C_6H_6][B(C_6F_5)]^a$	1.708(7), 1.741(7)	159.0(6)	347.8, 347.9
$[Me_3Si·MeC_6H_5][B(C_6F_5)]^b$	1.73(2), 1.73(2)	158(2)	348.3, 348.0
pure salt [c]	1.753(9)	163.0(3)	348.0

[a] co-crystallized bis(trimethylsilyl) fluoronium ion taken from structure C, **Table 20** below, [b] co-crystallized bis(trimethylsilyl) fluoronium ion taken structure B , **Table 20** below, [c] taken from reference 93a.

3.5 Computations

Since very flat potential energy surfaces are observed for the systems $[Me_3Si·arene]^+$ with respect to C–Si–C and Si–C1–H1 angles and the Si···C1 distance, consistent trends are only obtained for isolated species in the gas phase when environmental effects are excluded. All calculations were carried out with the Gaussian 03 package of molecular orbital programs.[108] Structures were optimized within the DFT approach at the pbe1pbe level with an aug-cc-pVDZ basis set.[109] Vibrational frequencies were also computed, to include zero-point vibrational energies and thermal corrections in thermodynamic parameters and to characterize all structures as minima on the potential energy surface. A natural bond orbital analysis (NBO)[110] was performed at the same level, to study the charge distribution, bond polarization and hybridization effects.

Structure and isomers

It is common knowledge that a tetra-coordinated Si atom is tetrahedral and its tri-coordinated species trigonal planar.[72-87] However, the question arises what is the structure of a silylium derivative in which one coordination site is significantly weaker bound being in the range of a transition between a covalent bond and a van der Waals interactions. Of special interest is the effect of delocalization and substitution on the structure and energetics of the different possible isomers for the studied system

$[Me_3Si{\cdot}arene]^+$. Selected experimental and computed structural data (of the lowest-lying isomers) are given in **Tables 20** and **21**, respectively.

Table 20. Selected structural data of experimentally observed $[Me_3Si{\cdot}arene]^+$ ions.

Arene		**Si1···C1/Å**	**<Si/°**	**<H1-C1-C2-C6/°**
C_6H_6 (benzene)	A[a]	2.174(2)	341.7	-157.8
	B[a]	2.169(3)	341.8	-157.7
	C[b]	2.183(4)	343.1	-162.1
MeC_6H_5 (toluene)	A[a]	2.135(5)	341.0	-156.0
	B[b]	2.120(2)	340.7	-158.9
EtC_6H_5		2.140(3)	341.5	-147.4
n-PrC_6H_5		2.137(2)	340.9	-159.4
i-PrC_6H_5		2.169(2)	342.1	-155.9
1,2$Me_2C_6H_4$ (*o*-xylene)		2.137(3)	341.4	-158.0
1,3$Me_2C_6H_4$ (*m*-xylene)		2.148(2)	338.3	-148.9
1,4$Me_2C_6H_4$ (*p*-xylene)		2.167(5)	341.2	-155.6
1,2,3$Me_3C_6H_3$		2.129(5)	39.2	-154.2
1,2,4$Me_3C_6H_3$		2.121(3)	336.2	-155.2
1,3,5$Me_3C_6H_3$		2.139(2)	334.2	-150.0
		2.171(6)[c]	336.5[c]	

[a] two slightly different data sets, [b] mixed crystals with $[Me_3Si–F–SiMe_3]^+$ ions, [c] two independent molecules in the unit cell.

Comparison of our gas-phase geometry with the crystal structure shows a general agreement, within experimental errors. For instance according to **Table 20** the difference in the Si···C1 bond length scatters about 0.015 Å, the angle sum around Si about 1.4° and the dihedral H1-C1-C2-C6 angle about 4.4°.

Table 21. Theoretically obtained selected structural data (distances in Å, angles in °) of substituted $[Me_3Si·arene]^+$ and $[Me_3Si–H–SiMe_3]^+$ ions along with partial charges (in e) and the overall charge transfer (in e). TMSA values (ΔH_{298}).

cation[d]	**q_{Si}**	**Q_{CT}**[a]	**q_{H1}**	**d(Si···C1)**	**d(C···H1)**	**<Si**
$Me_3Si–H–SiMe_3$	1.816	0.330	–.340	-	-	348.1
C_6H_6_TMS[b]	1.922	0.275	0.315	2.1962	1.0952	342.4
1Me_C_6H_5_4TMS[c]	1.910	0.297	0.318	2.1464	1.0955	341.0
1,2Me_2_C_6H_4_4TMS[c]	1.912	0.301	0.318	2.1421	1.0956	340.5
1,3Me_2_C_6H_4_4TMS[c]	1.907	0.309	0.315	2.1323	1.0964	338.5
1,4Me_2_C_6H_4_2TMS[c]	1.915	0.296	0.313	2.1587	1.0962	338.7
1,2,3Me_3_C_6H_3_4TMS[c]	1.909	0.311	0.314	2.1296	1.0961	338.0
1,2,4Me_3_C_6H_3_5TMS[c]	1.908	0.313	0.315	2.1253	1.0964	337.7
1,3,5Me_3_C_6H_3_2TMS[c]	1.902	0.320	0.309	2.1258	1.0970	335.0
1,2,3,4Me_4_C_6H_2_5TMS[c]	1.909	0.316	0.314	2.1204	1.0964	337.4
1,2,3,5Me_4_C_6H_2_4TMS[c]	1.904	0.322	0.309	2.1230	1.0970	334.5
1,2,4,5Me_4_C_6H_2_3TMS[c]	1.910	0.312	0.308	2.1424	1.0970	334.8
1,2,3,4,5Me_5_C_6H_1_6TMS[c]	1.905	0.327	0.308	2.1130	1.0971	334.0
1Me_6_C_6_1TMS	1.923	0.318	-	2.1534	-	331.2
1Et_C_6H_5_4TMS[c]	1.910	0.299	0.318	2.1437	1.0955	340.7
1,3,5Et_3_C_6H_3_2TMS[c]	1.906	0.320	0.308	2.1222	1.0973	334.2
1*n*-Pr_C_6H_5_4TMS[c]	1.909	0.300	0.318	2.1422	1.0955	340.7
1*i*-Pr_C_6H_5_4TMS[c]	1.910	0.300	0.318	2.1419	1.0955	340.7
1,3,5*i*-Pr_3_C_6H_3_2TMS[c]	1.903	0.328	0.309	2.1119	1.0982	333.2
1*n*-Bu_C_6H_5_4TMS[c]	1.908	0.302	0.318	2.1381	1.0956	340.6
1*t*-Bu_C_6H_5_4TMS[c]	1.909	0.301	0.318	2.1394	1.0955	340.4

[a] $Q_{CT} = 1 - \Sigma q_i(SiMe_3)$, [b] TMS = trimethylsilyl, [c] only lowest-lying iomer is considered, [d] notation: xR_n_C_6H_n_yTMS with x and y = numerals describing the position in the arene, TMSA = trimethylsilyl affinity.

Table 22. TMSA values (ΔH_{298}) along with ΔE_0 and ΔG_{298} values (in kcal mol^{-1}) of substituted $[Me_3Si{\cdot}arene]^+$ and $[Me_3Si–X–SiMe_3]^+$ ions (X = H, F).

cation[a]	**ΔE_0**	**ΔH_{298}**	**ΔG_{298}**
TMS–H–TMS	34.53	31.30	23.23
TMS–F–TMS	38.02	34.79	26.79
C_6H_6_TMS	29.37	25.83	15.63
1Me_C_6H_5_4TMS	33.78	30.92	19.31
1,2Me$_2$_C_6H_4_4TMS	35.94	32.48	22.33
1,3Me$_2$_C_6H_4_4TMS	36.80	33.21	21.96
1,4Me$_2$_C_6H_4_2TMS	34.93	31.25	19.56
1,2,3Me$_3$_C_6H_3_4TMS	37.09	33.37	18.72
1,2,4Me$_3$_C_6H_3_5TMS	38.79	35.21	24.13
1,3,5Me$_3$_C_6H_3_2TMS	39.01	35.27	21.02
1,2,3,4Me$_4$_C_6H_2_5TMS	40.64	37.07	25.98
1,2,3,5Me$_4$_C_6H_2_4TMS	40.58	36.87	24.45
1,2,4,5Me$_4$_C_6H_2_3TMS	38.35	34.75	23.91
1,2,3,4,5Me$_5$_C_6H_1_6TMS	42.29	38.59	27.13
1Me$_6$_C_6_1TMS	40.61	36.51	22.71
1Et_C_6H_5_4TMS	34.35	30.81	20.83
1,3,5Et$_3$_C_6H_3_2TMS	40.04	36.19	23.81
1*n*-Pr_C_6H_5_4TMS	34.93	31.40	21.53
1*i*-Pr_C_6H_5_4TMS	34.92	31.30	21.47
1,3,5*i*-Pr$_3$_C_6H_3_2TMS	40.81	37.44	23.45
1*n*-Bu_C_6H_5_4TMS	35.41	31.80	21.48
1*t*-Bu_C_6H_5_4TMS	35.49	31.91	21.70

[a] notation: xR$_n$_C_6H_n_yTMS with x and y = numerals describing the position in the arene, TMS = trimethylsilyl, TMSA = trimethylsilyl affinity

All considered $[Me_3Si\cdot arene]^+$ are non-planar with Si···C1 distances between 2.196 ($[Me_3Si\cdot benzene]^+$) and 2.112 Å ($[Me_3Si\cdot 1,3,5\text{-}i Pr_3C_6H_3]^+$). More sensitive with respect to the substitution pattern is the angle sum around Si (Σ<Si) ranging between 342.4° ($[Me_3Si\cdot benzene]^+$) and 333.2° ($[Me_3Si\cdot 1,3,5\text{-}i Pr_3C_6H_3]^+$). In case of ($[Me_3Si\cdot C_6Me_6]^+$) an even smaller angle sum (Σ<Si) of 331.2° is computed due to steric repulsion between the methyl group attached to the arene C1 atom and the three methyl groups of the Si atom. In all other species the silylium ion is always attached to a C1 atom bearing a hydrogen atom. Only very minor changes are observed for the C1–H1 distances which only slightly increase upon substitution (1.095-1.099 Å).

In general, with increasing degree of substitution, the Si···C1 bond lengths decreases (C_6H_6: 2.196, $Me_1C_6H_5$: 2.132, $Me_2C_6H_4$: 2.132, $Me_3C_6H_3$: 2.125, $Me_4C_6H_2$: 2.123, and $Me_5C_6H_1$: 2.113 Å, **Table 21**), Σ<Si decreases (*cf.* 342.4, 341.0, 338.5, 335.0, 334.5, and 334.0°), while the C1–H1 bond lengths are almost not affected by the higher degree of substitution (*cf.* 1.0952, 1.0955, 1.0964, 1.0970, 1.0970, and 1.0971 Å). In Me_6C_6 the situation changes significantly since the C1 arene ring atom is now attached to a methyl group introducing steric strain which leads to longer Si···C1 bond but a smaller value for Σ<Si.

Substitution of the methyl group by ethyl, *n*-propyl, *i*-propyl, or *n*-butyl groups only marginally affects the structural data (**Table 12**); *e.g.* the Si···C1 distances slightly decreases along H (2.1962) < Me (2.1464) < Et (2.1437) < *n*-Pr (2.1422) < *n*-Bu (2.1394 Å).

While the interaction of the silylium ion with benzene and hexamethyl benzene gives only one species, in case of all other species of the type $Me_nC_6H_{6-n}$ (n = 0 - 6) in principle at least two different isomers should be observed since silylation of the corresponding substituted arene might occur at the carbon arene atom either attached to a hydrogen atom or a methyl (alkyl) group. Additionally, silylation can also occur either in *ortho*-, *meta*- or *para*-position of the carbon ring atom bearing a methyl group with the *para*-substituted isomer always being the lowest-lying isomer. For example, for toluene four different isomers have been calculated. The *para*-substituted isomer is energetically preferred over the *ortho*- and *meta*-compound by ΔG_{298} = 2.88 and 2.65 kcal mol^{-1}, respectively, in accord with the experimentally observed [Me_3Si·*para*-toluene]$^+$ species (**Figure 12**). The energy difference between both *ortho*- and *meta*-isomers is rather small (0.23 kcal mol^{-1}). The isomer with the silylium ion in 1 position (methyl and Me_3Si attached at C1, isomer 4) is always the highest-lying isomer (7.64 kcal mol^{-1}). The energetically preferred species always show the smallest Si···C1 distance (*para*: 2.146, *meta*: 2.173, *ortho*: 2.178, isomer 4: 2.283 Å).

A similar picture is found for all other $R_nC_6H_{6-n}$ (n = 0 - 6) (R = alkyl) species which we do not want to discuss here in detail. In **Tables 21** and **22** only data of the lowest-lying isomers are presented. The isomers with the Me_3Si group attached to a ring carbon atom bearing a methyl group is unfavoured by 4-7 kcal mol^{-1} with respect to the *para*-substituted species, while the *para*-substituted species is favoured by about 2 kcal mol^{-1} over the *meta*/*ortho*-species.

Energies and charge distribution

[Me_3Si·arene]$^+$ ions can be considered as solvent complexes between arene and [Me_3Si]$^+$. In these complexes the Me_3Si fragment has almost completely lost its silylium character (strong deviation from planarity, (**Tables 19-21**), since a stable bonded tetracoordinated Si center is formed. In this context and in analogy to the proton affinity, a trimethylsilylium affinity (TMSA) can be defined as the enthalpy change associated with the dissociation of the conjugated acid [eq.(1)]:[93a,111]

$$[Me_3Si \cdot B]^+_{(g)} \longrightarrow B_{(g)} + [Me_3Si]^+_{(g)} \quad : \quad \Delta H_{298} \quad (1)$$

TMSA values ($\Delta H_{(gas,\ 298\ K)}$) describe the energetics of the desilylation reaction of a trimethylsilylium ion donor in the gas phase at 298 K, and small gas phase TMSA values in comparison with that of un-substituted [Me_3Si·benzene]$^+$, can be regarded a measure of stabilization in substituted benzenes [eq.(2)].

$$[Me_3Si \cdot \text{benzene}]^+ \longrightarrow \text{benzene} + Me_3Si^+ \qquad (2)$$

Furthermore, with the help of TMSA values it is possible to decide if silylation transfer reactions are feasible *e.g.* between R–X and $[Me_3Si{\cdot}arene]^+$ (X = H, halogen, any basic center). Table **22** summarizes TMSA and Gibbs free energies of all considered $[Me_3Si{\cdot}arene]^+$ species (lowest-lying isomer) at 298 K along with those of B (= Me_3Si–X; X = H, halogen, and pseudohalogen) for comparison. The TMSA value of $[Me_3Si{\cdot}benzene]^+$ amounts to 25.83 kcal mol^{-1} which is, astonishingly, smaller than that of $[Me_3Si–H–SiMe_3]^+$ with 31.30 kcal mol^{-1} (*cf.* $TMSA_{halogen}$ between 31-35 kcal mol^{-1}). This means that $[Me_3Si{\cdot}benzene]^+$ is a stronger silylating agent than $[Me_3Si–H–SiMe_3]^+$ in the gas phase when solvent effects (liquid phase) or solid state effects (solid phase) are impossible. However, it can be assumed that in solution as well in the solid state interactions with the environment (as discussed before) stabilize $[Me_3Si{\cdot}benzene]^+$ relative to $[Me_3Si–H–SiMe_3]^+$. Taken the TMSA value for $[Me_3Si{\cdot}benzene]^+$ as reference all considered substituted benzene species possess larger TMSA values ranging between 30-39 kcal mol^{-1}. The small TMSA of $[Me_3Si{\cdot}benzene]^+$ and also $[Me_3Si{\cdot}toluene]^+$ (TMSA = 30.92 kcal mol^{-1}) may explain why fast degradation leading to the formation of a $[Me_3Si–F–SiMe_3]^+$ salt is observed (see Section **3.2**) Upon increasing substitution the TMSA value increases by at least 5 kcal mol^{-1} (*cf.* C_6H_6: 25.83, $Me_1C_6H_5$: 30.92, $Me_2C_6H_4$: 33.21, $Me_3C_6H_3$: 35.27, $Me_4C_6H_2$: 37.07, $Me_5C_6H_1$: 38.59 kcal mol^{-1}). Due to steric reasons in Me_6C_6 the TMSA value (36.51 kcal mol^{-1}) decreases compared to $Me_5C_6H_1$. This trend nicely corresponds to the trend discussed for the Si···C1 distances. Only small changes (30.92-31.80 kcal mol^{-1}) are computed when the methyl group is substituted by ethyl, *n*-propyl, *i*-propyl, *n*-butyl or *t*-butyl.

The Si···C1 bond in $[Me_3Si{\cdot}arene]^+$ ions might be regarded a donor-acceptor bond which can be characterized by the charge transfer from the arene into the Me_3Si^+ ion (**Table 21**), which becomes less positive. For the $[Me_3Si{\cdot}benzene]^+$ ion an overall charge transfer of 0.275*e* is found. The hydrogen atom attached to C1 suffers the largest loss of electron density upon complex formation (C_6H_6: q_{H1} = 0.237*e* *vs.* $[Me_3Si{\cdot}benzene]^+$: $q_{H1,cation}$ = 0.315*e*, *cf.* $q_{H2\text{-}6,cation}$ between 0.269 - 0.271*e*). A closer look into the charge transfer displays that the overall charge transfer can mainly be attributed to the arene hydrogen atoms (89.5%). With increasing degree of substitution the charge transfer slightly increases (*cf.* C_6H_6: 0.275, $Me_1C_6H_5$: 0.297, $Me_2C_6H_4$: 0.309, $Me_3C_6H_3$: 0.320,

$Me_4C_6H_2$: 0.322, $Me_5C_6H_1$: 0.327*e*). Substitution with a longer alkyl chain also only marginally increases the overall charge transfer (*cf.* $Me_1C_6H_5$: 0.297, $Et_1C_6H_5$: 0.299, *n*-$Pr_1C_6H_5$: 0.300, *n*-$Bu_1C_6H_5$: 0.302*e*).

It is interesting to mention that for the $[Me_3Si–H–SiMe_3]^+$ ion the charge transfer of 0.330*e* exclusively stems from the Me_3Si moiety of the $Me_3Si–H$ fragment. Moreover, the bridging H atoms becomes even more negative upon complex formation ($Me_3Si–H$: $q_H = –0.200$ *vs.* $[Me_3Si–H–SiMe_3]^+$: $q_{H,cation} = –0.340e$), which in turn means that the hydride character in $[Me_3Si–H–SiMe_3]^+$ is increased compared to $Me_3Si–H$. That also means that the Me_3Si moiety of the $Me_3Si−H$ fragment decreases its charge by 0.47*e* (= $0.33 + 0.14\ e = Q_{CT} + \Delta q_H$) upon complexation.

3.6 Conclusions

A simple synthetic route to solvent coordinated $[Me_3Si·arene][B(C_6F_5)_4]$ salts (arene = benzene, toluene, ethylbenzene, *n*-propylbenzene, *i*-propylbenzene, *o*-xylene, *m*-xylene, *p*-xylene, 1,2,3-trimethylbenzene, 1,2,4-trimethylbenzene, 1,3,5-trimethylbenzene) starting from $[Me_3Si−H−SiMe_3][B(C_6F_5)_4]$ have been described. This formal Lewis acid – Lewis base reaction allows preparation of large quantities in good yields. $[Me_3Si·arene][B(C_6F_5)_4]$ salts are air and moisture sensitive but stable under argon atmosphere over a long period as solid but slowly decompose in solution even at ambient temperatures. They are thermally stable up to over 80 °C. Between 88°C (benzene) and 118°C (1,2,3-trimethyl benzene, hemellitol), decomposition occurs, which is triggered by the formation of $Me_3Si–F$. Investigation of the degradation of $[Me_3Si·arene][B(C_6F_5)_4]$ revealed the formation of the fluoronium salt $[Me_3Si–F–SiMe_3][B(C_6F_5)_4]$, $B(C_6F_5)_3$ and a reactive "C_6F_4" species which could be trapped by CS_2. Upon addition of CS_2 the formation of a formal *S*-heterocyclic carbene adduct $C_6F_4CS_2$-$B(C_6F_5)_3$ was observed. The synthetic protocol described above does not work for *tert.*-butylbenzene. Here the formation of $[Me_3Si–F–SiMe_3][B(C_6F_5)_4]$ and 1,4-di-*tert.*-butylbenzene was observed, which can be referred to as a Fridel-Crafts type isomerization. Computations and Xray structure elucidation reveal a tetra-coordinated Si atom with a long Si···$C1_{arene}$ distance and an angle sum at Si considerably smaller than 360°. The Si···C1-coordination mode is always η^1 rather than η^2 or η^6. Due to very flat potential energy surfaces the molecular structure parameters (*e.g*. *d*(Si–C1), Σ<Si) of the $[Me_3Si{\cdot}arene]^+$ ion strongly depends on the magnitude of interactions with the environment such as anion-cation or cation-solvent interactions. If solvent molecules are in the proximity of the $[Me_3Si{\cdot}arene]^+$ ion, the solvent molecule is closely arranged to the cation and clearly directed towards the $H1_{cation}$ ring proton in η^6 type coordination mode with $H_{cation,arene}\cdots C_{solvent,arene}$ distances between 2.80 and 3.20 Å. These solvent-cation interaction is further supported by a significantly larger displacement of the $H1_{cation,arene}$ proton from the arene ring plane as indicated by the H1–C1–C2–C6 dihedral angle (-147 *vs.* -155° for all other non-solvate species). Furthermore, NPA partial charge calculations reveal that $H1_{cation,arene}$ always carries the largest positive charge within the ring (**Table 21**) with about 0.32*e* (*cf.* 0.23-0.27*e* for all other arene protons) and even the protons of the Me_3Si unit are less positive (0.27-0.29e).

Since very flat potential energy surfaces are observed for the systems [Me3Si·arene]+ with respect to C–Si–C and Si–C1–H1 angles and the donor-acceptor bond (Si…C1 distance), consistent structural trends are only obtained for isolated species in the gas phase when environmental effects are excluded. A systematic study of the influence of the arene substitution pattern in $[Me_3Si{\cdot}arene][B(C_6F_5)_4]$ (arene = $R_nC_6H_{6-n}$, R = H, Me, Et, Pr, and Bu; n = 0 - 6) shows the following general trends: (i) *para*-substitution with respect to the alkyl group is always favored over *ortho* or *meta* isomers (by *ca.* 2 kcal mol^{-1}). (ii) With increasing degree of substitution the shorter is the Si···C1 distance (between 2.196 $[Me_3Si{\cdot}benzene]^+$ - 2.113 Å $[Me_3Si{\cdot}Me_5C_6H_1]$), the larger is the overall charge transfer (between 0.275 $[Me_3Si{\cdot}benzene]^+$ - 0.327*e* $[Me_3Si{\cdot}Me_5C_6H_1]$), and the larger is the calculated TMSA value (between 25.83 $[Me_3Si{\cdot}benzene]^+$ - 38.59 kcal mol^{-1} $[Me_3Si{\cdot}Me_5C_6H_1]$). The TMSA values can be regarded a measure of stabilization in substituted benzenes. Furthermore, with the help of a TMSA scale it is possible to decide if silylation transfer reactions are feasible *e.g.* between R–X and $[Me_3Si{\cdot}arene]^+$ (X = H, halogen, any basic center). From this scale, it can be concluded that in the gas phase the strongest Me_3Si^+ transfer reagent is $[Me_3Si{\cdot}benzene]^+$, even stronger than $[Me_3Si–H–SiMe_3]^+$ (TMSA = 31.30 kcal mol^{-1}).

4. Catalytic Trimerisation of Bissilylated Diazomethane

4.1 Introduction

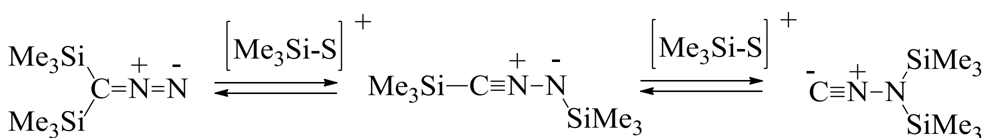
More than a decade after the first isolation and characterization of silylium ions,[86,112] their chemistry has been an area of rapid growth,[74b-d,104,113] since many applications due to the design of useful properties such as their enormous Lewis acidity and catalytic behavior have been expected.[79,81b,82,114]

The silylium ion $[Me_3Si]^+$ might be regarded as a sterically demanding big proton,[92b] and, similar to a proton, the bulky silylium ion is always solvated forming the $[Me_3Si_{(solv.)}]^+$ ion.[92b,76b,94,87a,115] For example, the full series of salts containing the bissilylated halonium/pseudohalonium cations $[Me_3Si–X–SiMe_3]^+$ (X = F, Cl, Br,[92b] and I; CN, N_3, OCN, SCN,[92a] CF_3SO_3)[116] were generated and fully characterized using the super Lewis acidic silylating media $Me_3Si–X$ and $[Me_3Si_{(solv.)}]^+$ salt.[92b] In view of the success of the pseudohalogen concept in super Lewis acidic silylating media,[92b] we were intrigued by the idea to utilize the enormous Lewis acidity of the $[Me_3Si]^+$ ion, to activate small molecules, such as bissilylated diazomethane, $(Me_3Si)_2CNN$, which can be considered as a pseudochalkogen.[117] To the best of our knowledge, salts containing silylated diazomethane cations, $[(Me_3Si)_2CNNSiMe_3]^+$ or $[Me_3SiCNN(SiMe_3)_2]^+$, respectively, have not yet been reported.

Diazomethane compounds are ambivalent reagents.[118,119] While electrophiles commonly attack at the nucleophilic C atom,[120] nucleophiles prefer the terminal N atom of diazomethane.[121] This ambivalent behavior was also observed in [3+2] cycloaddition reactions with dipolarophiles.[122] Herein, we report what is, to the best of our knowledge, the first trimerisation of a bissilylated diazomethane which provides, based on the use of $[Me_3SiCNN(SiMe_3)_2]^+$ as a catalyst, an efficient and facile synthesis of 4-diazenyl-3-hydrazinyl-1*H*-pyrazoles (**Scheme 26**).

Pyrazoles represent one of the most important classes of heterocyclic compounds.[123] Although a great variety of substituted pyrazoles are known, only a few examples of diazenyl- or hydrazinylpyrazoles have been described in the literature so far.[124] Likewise, di(hydrazinylidene)pyrazoles have only scarcely been reported in the literature.[125] To the best of our knowledge, trimerisation reactions of diazomethane or substituted diazomethanes have not yet been described. However, the dimerisations of ethyl diazoacetate[126a,b] and of a (diazomethylene)phosphorane[126c] were previously reported to yield 1,2,4,5-tetrazine derivatives.

4.2 Results and discussion

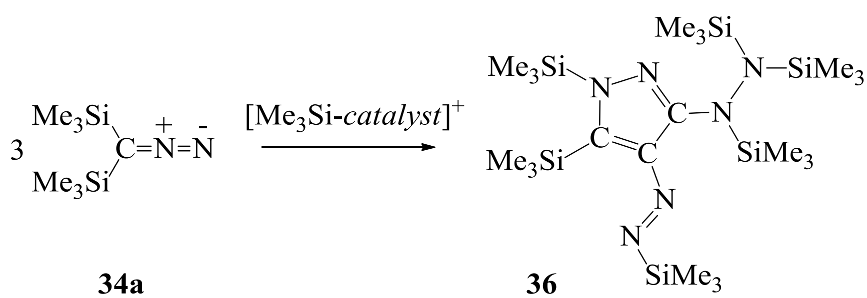


34a 34b 34c

Scheme 25. Isomerization of bissilylated diazomethane catalysed by $[Me_3Si\text{-}S]^+$ with S = isomer **34a, 34b or 34c**.[127]

For the molecule $(Me_3Si)_2CNN$, three acyclic constitutional isomers with a NNC unit can be formulated (**Scheme 25**): bis(trimethylsilyl)diazomethane (isomer **34a**)[128] and bis(trimethylsilyl)aminoisocyanide ($CNN(SiMe_3)_2$, isomer **34c**)[129] are experimenttally known but no structural data were available (**Figure 19**). Both compounds are thermally stable liquids and do not isomerize or show any other reactivity in pure form at 298 K. Bissilylated nitrilimine isomer **34b** is not known yet. Ever since the discovery of the first *C,N*-nitrilimines by Huisgen,[130] the development of their chemistry was hampered because of their potential instability and the lack of suitable preparative methods. Bertrand et al. have established efficient routes for preparing stable nitrilimines.[131,132,133] Moreover, the importance of steric hindrance was shown in the stabilization of *C,N*-nitrilimines. For instance, the reaction of BuLi with $R(H)CN_2$ followed by addition of R–Cl yields the bissilylated diazomethane R_2CNN for R = Me_3Si,[128] while the analogous reaction for the bulkier substituent R = $^iPr_3Si$ results in the formation of the thermally stable nitrilimine R–CNN–R, which only isomerizes to the carbodiimide R–NCN–R under photolytic conditions.[134]

Figure 19. ORTEP drawing of the molecular structure of $(Me_3Si)_2CNN$ (**34a**) (left) and $CNN(SiMe_3)_2$ (**34c**) (right) in the crystal. Thermal ellipsoids with 50% probability at 173 K. Hydrogen atoms omitted for clarity. Selected bond lengths (Å) and angles (°): $(Me_3Si)_2CNN$: N1–N2 1.135(2), N1–C1 1.312(2); C1–N1–N2 179.6(2); $CNN(SiMe_3)_2$: N1–N2 1.366(2), N2–C1 1.152(2); C1–N1–N2 177.7(2).



Scheme 26. Catalytic trimerisation of bissilylated diazomethane. [127]

The reaction of bis(trimethylsilyl)diazomethane $(Me_3Si)_2CNN$ (**34a**) with a $[Me_3Si_{(solv.)}]^+$-source was studied in two series of experiments. At first, the reaction was carried out in neat $(Me_3Si)_2CNN$ generating a super Lewis acidic silylating medium. However, upon addition of $[Me_3Si_{(solv.)}]^+$-salt (solv. = $HSiMe_3$) an immediate complex reaction contrary to the analogous reaction with Me_3Si–X (X = halogen, pseudohalogen) was observed resulting in a highly viscous reaction mixture. Thus *n*-pentane was added, since the work-up and isolation of the products is much easier due to a considerable decrease of the viscosity of the reaction mixture. It should be noted that the reaction in neat bis(trimethylsilyl)diazomethane yielded the same product. In a typical reaction set-up, to a stirred suspension of $[Me_3Si_{(solv.)}][B(C_6F_5)_4]$ in *n*-pentane, a mixture of liquid $(Me_3Si)_2CN_2$ (large excess) and *n*-pentane was added at –78 °C. The resulting suspension was allowed to warm to ambient temperature and stirred for 36 h.

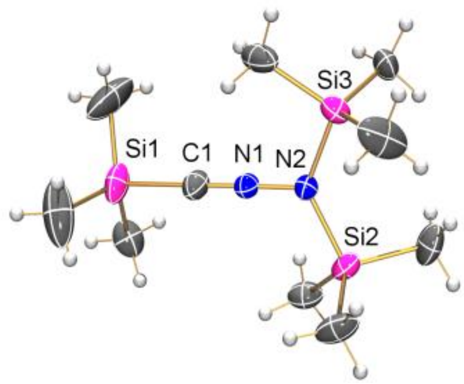


Figure 20. ORTEP drawing of the molecular structure of the $[(Me_3Si)CNN(SiMe_3)_2]^+$ ion in $[(Me_3Si)CNN(SiMe_3)_2]^+$ $[B(C_6F_5)_4]^-$ (**35**) in the crystal. Thermal ellipsoids with 50% probability at 173 K. Hydrogen atoms omitted for clarity. Selected bond lengths (Å) and angles (°): N1–N2 1.309(2), N1–C1 1.143(2), Si2–N2 1.818(1), Si3–N2 1.816(1), Si1–C1 1.897(2), C1–N1–N2 179.3(1), N1–N2–Si3 113.76(8), N1–N2–Si2 114.89(8), N1–C1–Si1 174.6(1), Si3–N2–Si2 131.34(6).

The reaction was followed by ^{1}H NMR experiments, and it was obvious, that diazomethane $(Me_3Si)_2CNN$ was involved in a more complex chemistry under these extreme Lewis acidic conditions beyond the simple formation of $[(Me_3Si)_2CNN(SiMe_3)]^+$ $[B(C_6F_5)_4]^-$ (**35**). Furthermore, these ^{1}H NMR experiments showed the exclusive and quantitative formation of pyrazole species 2 and the complete consumption of the starting material bis(trimethylsilyl)diazomethane. The end of the reaction is indicated by the deposition of the catalyst (**35**) as crystalline solid. Moreover, during the course of the reaction the color of the supernatant changed gradually from yellow to dark red. Thus, both the precipitate and the reaction solution were further studied. The supernatant was removed by filtration, and the brownish residue was washed with *n*-pentane. Recrystallization from a minimum of toluene at –25°C resulted in the deposition of

$[(Me_3Si)CNN(SiMe_3)_2][B(C_6F_5)_4]$ (**35**) as colourless crystals (49% yield based on $[Me_3Si_{(solv.)}][B(C_6F_5)_4]$; **Figure 20**). From the combined solutions of the filtration and washing process, the silylated 4-diazenyl-3-hydrazinyl-pyrazole species (**36**) was isolated as dark green crystals (**Scheme 26, Figure 21 left**). The overall isolated yield is about 51% (referring to $(Me_3Si)_2CNN$, which was used in a 22-fold excess both as reactant and solvent besides *n*-pentane) after 36 hours at ambient temperatures. Referring to $[Me_3Si_{(solv.)}][B(C_6F_5)_4]$) this trimerisation corresponds to a catalytic process with a TON of about 10.8.

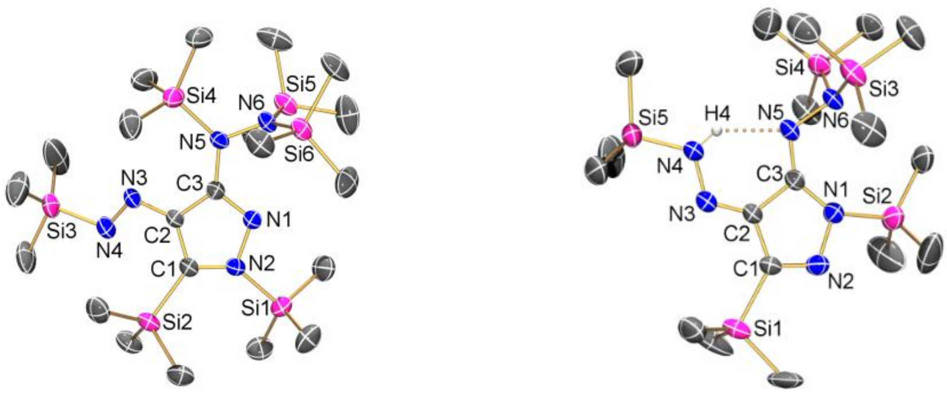


Figure 21. ORTEP drawing of the molecular structure of **36** (left) and **37** (right) in the crystal. Thermal ellipsoids with 50% probability at 173 K. Except from H4 all other hydrogen atoms are omitted for clarity. Selected bond lengths (Å): 2: N1–C3 1.324(3), N1–N2 1.400(2), N2–C1 1.355(2), N3–N4 1.272(2), N3–C2 1.389(3), N5–C3 1.387(2), N5–N6 1.455(2), C1–C2 1.398(3), C2–C3 1.425(3); 3: N1–C3 1.381(3), N1–N2 1.433(3), N2–C1 1.314(3), N3–C2 1.310(3), N3–N4 1.348(3), N5–C3 1.307(3), N5–N6 1.467(3), C1–C2 1.437(3), C2–C3 1.470(3).

DFT calculations (see below) indicated the catalytic formation of bis(trimethylsilyl)aminoisocyanide **34c** in the first reaction step (**Schemes 25** and **27**), in a second series of experiments isomeric **34c** was reacted with $[Me_3Si_{(solv.)}]^+$ under the same reaction conditions as discussed before for bis(trimethylsilyl)diazomethane (isomer **34a**). Indeed, the reaction of isomer **34c** with $[Me_3Si_{(solv.)}]^+$ resulted also in the exclusive formation of pyrazole species (**36**) besides $[(Me_3Si)CNN(SiMe_3)_2][B(C_6F_5)_4]$ (**35**) thus proving our computational results. Since now no isomerization step is needed prior to the C–C coupling step and [3+2] cyclization, this reaction is faster (12 h for a complete conversion). The long term activity and re-use of the catalyst was also studied. Even after 14 days and several re-uses the catalyst was still active as well as when the catalyst concentration was decreased to less than 1mol%. For instance, the reaction of aminoisocyanide **34c** afforded in three runs isolated yields of pyrazole species 2 between 74-82% when 1mol% catalysts was used displaying a constant activity over all runs. A TON of 230 was estimated (36h). After each cycle the amount of catalyst remained almost unchanged. The catalyst can always be recovered in good yields as crystalline material at the end of the reaction.

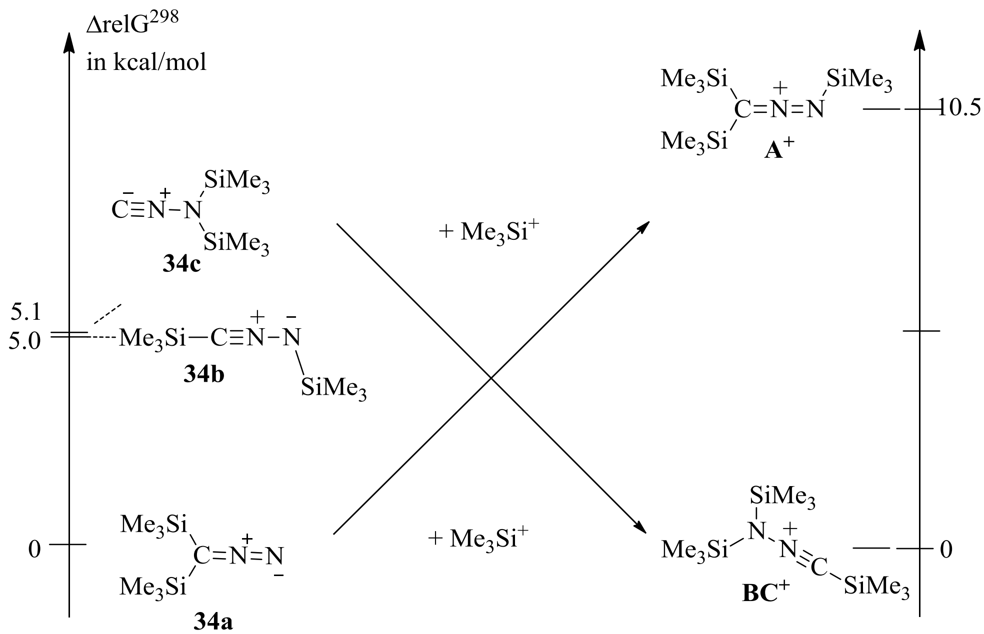
The salt $[(Me_3Si)CNN(SiMe_3)_2][B(C_6F_5)_4]$ (**35**) is extremely air and moisture sensitive, but stable under argon atmosphere over a long period as a solid. It is badly soluble in non-aromatic organic solvents and melts at 109°C (decomposition). Pyrazole species **36** is neither very air nor moisture sensitive, melts at 77°C and dissolves in almost all common organic solvents. One Me_3Si group can selectively be hydrolysed by addition of CF_3SO_3H or water/*n*-hexane to give pyrazole species **37** (**Figure 21** right). Compounds **35-37** are easily prepared in large scale and are stable when stored in a sealed tube and kept at ambient temperatures. All three compounds have been fully characterized. The IR and Raman data of $[(Me_3Si)CNN(SiMe_3)_2][B(C_6F_5)_4]$ **35** show a sharp band in the expected region[128,135] at 2215 (IR) and 2209 (Raman) cm^{-1}, respectively, which can be assigned to the stretching frequency $\nu_{CNN,as}$ (cf. 2041 (IR) in $(Me_3Si)_2CN_2$ and 2102 (Raman) cm^{-1} in $(Me_3Si)_2NNC$).

$[(Me_3Si)CNN(SiMe_3)_2][B(C_6F_5)_4]$ (**35**) crystallizes in the monoclinic space group $P2_1/c$ with four units per cell. As depicted in **Figure 20**, the cation adopts a C_1 symmetric structure with an almost linear CNN unit (C1–N1–N2 179.3(1)°, cf. 179.6(2) in $(Me_3Si)_2CNN$ and 177.7(2)° in $CNN(SiMe_3)_2$, (**Figure 19**), and a slightly bent Si1–C1–N1 angle of 174.6(1)° is found. The C–N bond length amounts to 1.143(2) Å, which nicely agrees with the sum of the covalent radii for a CN triple bond (Σr_{cov}(C≡N) = 1.14 Å;[106] cf. 1.152(2) in $CNN(SiMe_3)_2$ or 1.157(2) Å in $[Me_3Si{-}C{\equiv}N{-}SiMe_3]^+$).[92a] The N1–

N2 bond is rather long with 1.309(2) Å (cf. (Σr_{cov}(N=N) = 1.20, Σr_{cov}(N–N) = 1.42;[106] 1.135(2) in $(Me_3Si)_2CNN$ and 1.366(2) Å in $CNN(SiMe_3)_2$) indicating only partial double bond character. In accord with NBO analysis (NBO = natural bond orbital),[110] thus the best Lewis representation is those with a CN triple and a NN single bond according to $[Me_3Si–C≡N^+–N(SiMe_3)_2]^+$. The tri-coordinated N2 atom sits in a trigonal planar environment (Σ<N = 360.0°) with two small N1–N2–Si angles (113.76(8) and 114.89(8)°) and one large Si3–N2–Si2 angle of 131.34(6)°.

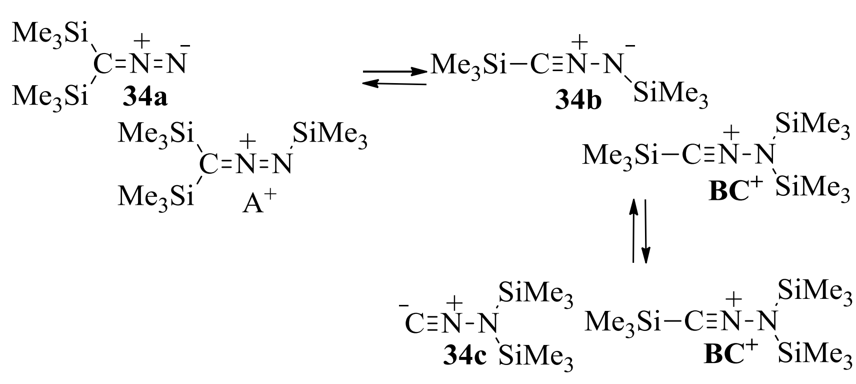
Both pyrazole species crystallize in the triclinic space group *P*-1 with two molecules per unit cell. As illustrated in **Figure 21** above, the major difference in the molecular structure of both species arises from an intramolecular hydrogen bond in **37** which forces a change of the configuration along the diazenyl substituent (cf. 2: N4 trans position to C3 vs. 3: N4 cis position to C3) allowing the formation of a six-membered ring closed by the H bridge. Furthermore, due to the hydrogen bond the amino nitrogen atom of the $(Me_3Si)_2N$ moiety pyramidalizes (Σ<N = 338.1°) since the nitrogen lone pair cannot be delocalized by hyperconjugation. Hyperconjugative effects are known to be responsible for the planarization of the amino nitrogen atom as found in **36**.[136] Both N atoms of the hydrazine substituent in **36** have a distorted trigonal-planar geometry (Σ<N = 359.4 and 359.7°) and both trigonal planes are almost perpendicular to each other (< Si4–N5–N6–Si6 93.8°). Both (amino)silyl groups adopt a staggered configuration in contrast to **37**, for which an eclipsed configuration is observed. While the N5–N6 bond lengths are similar in **36** (1.455(2) Å) and **37** (1.467(3) Å), the N3–N4 bond lengths of the diazenyl unit increases upon hydrogen bond formation in 3 (cf. 1.272(2) vs. 1.348(3) Å; Σr_{cov}(N=N) = 1.20, Σr_{cov}(N–N) = 1.42;[99] 1.247(3) Å in Ph–N=N–Ph).[137] The central five-membered pyrazole ring is planar (deviation from planarity less than 2°) with bond lengths and angles in the expected range.[138]

4.3 Computations

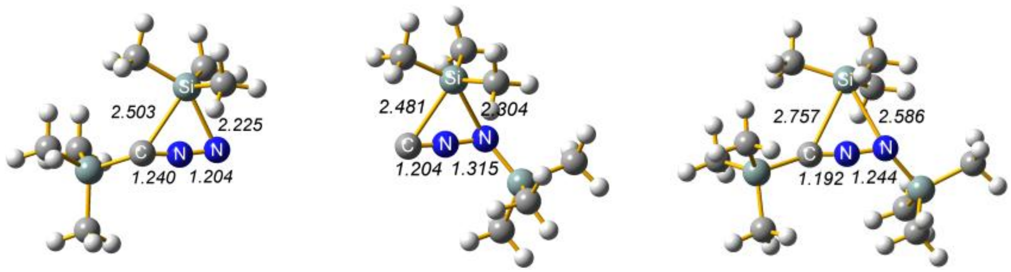


Scheme 27. Calculated relative free Gibbs energies of isomers of neutral $(Me_3Si)_2CNN$ (**34a**, **34b**, and **34c**) and cationic $[(Me_3Si)_3CNN]^+$ species ($\mathbf{A}^+$ and $\mathbf{BC}^+$). Higher-lying cyclic isomers are omitted for clarity.[117]

The astonishing isolation of $[Me_3SiCNN(SiMe_3)_2]^+$ ($\mathbf{BC}^+$) instead of isomeric $[(Me_3Si)_2CNNSiMe_3]^+$ ($\mathbf{A}^+$) as well as the isolation of the trimerisation product **36** prompted us to carry out quantum chemical calculations at the pbe1pbe/aug-cc-pwCVDZ level of theory to gain inside into the thermodynamics and kinetics of this complex reaction. In any case, the formation of pyrazole species **36**, starting from diazomethane, includes several successive reaction steps including (i) a C–C coupling, and (ii) a [3+2] cycloaddition reaction. Experimentally, it is known that pure $(Me_3Si)_2CNN$ is thermally stable for a long time. However, it is rearranged to bis(trimethylsilyl)carbodiimide, $Me_3Si–NCN–SiMe_3$, when it is heated in the presence of suitable catalysts such as Cu^{2+}.[128,135a] Thus, we studied the potential energy surface of neutral $(Me_3Si)_2CNN$ and cationic $[(Me_3Si)_3CNN]^+$ species always retaining the CNN unit. As depicted in **Scheme 27**, the diazomethane isomer **34a** is favoured by 5.0 and 5.1 kcal/mol over nitrilimine **34b** and aminoisocyanide C. Upon $[Me_3Si]^+$ addition this situation switches. Now isomer **BC⁺** generated from **34b** and **34c**, respectively, represents the lowest-lying isomer separated by 10.5 kcal/mol from cation **A⁺** in accord with our experimental observation. Considering the equilibrium of the isomerisation process, which includes both the neutral and the cationic species as catalyst according to **Scheme 26**, then the ΔG^{298} value is estimated to be –5.5 and 0.1 kcal/mol, respectively, displaying $[Me_3Si]^+$ exchange equilibria. It should be noted that an intrinsic 1,3-Me_3Si shift is rather unlikely, since the calculated barriers are 65.1 for the neutral (**A**, TS1; cf. 56.8 kcal/mol for the second 1,3-Me_3Si in **34b**, TS2) and 40.5 kcal/mol for the cationic species (**A⁺**, TS3), respectively (**Figure 22** below), which is in agreement with our experimental observations. These barriers dramatically decrease on solvation conditions as displayed by the study of the bimolecular reaction paths (**Scheme 28).** The exchange of a $[Me_3Si]^+$ ion between A^+/BC^+ and the neutral isomers (**34a, 34b** and **34c**) occurs almost barrier free (less than 10 kcal/mol) at ambient temperatures resulting in mono solvate formation of the type $[Me_3Si]^{+}\cdot 2$ S adduct (S = **34a**, **34b**, and **34c**). In case of **34a** and **34c**, these solvate adducts feature a trigonal planar $[Me_3Si]^+$ ion which is almost symmetrically stabilized by two S donor molecules (**Figure 22**). Therefore, it can be assumed that the initial reaction step for the trimerisation is the catalytic isomerisation of diazomethane **34a** and the cation **A⁺** in a bimolecular process as shown in **Scheme 28** generating the reactive species **B** and **C** besides **BC⁺**.



Scheme 28. Isomerization equilibria of bissilylated diazomethane catalysed by silylium ions.



TS1 TS2 TS3

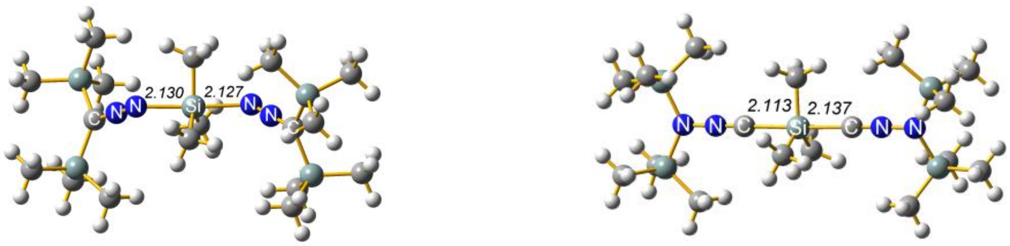
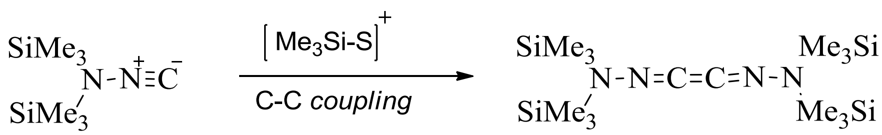


Figure 21. Top: Transition states for the intrinsic 1,3-Me_3Si shift in the neutral (TS 1 and 2) and cationic species (TS3); Bottom: stable $[Me_3Si]^{+}\cdot 2$ S adducts for S = $(Me_3Si)_2CNN$ (left) and $(Me_3Si)_2NNC$ (right), distances in Å.

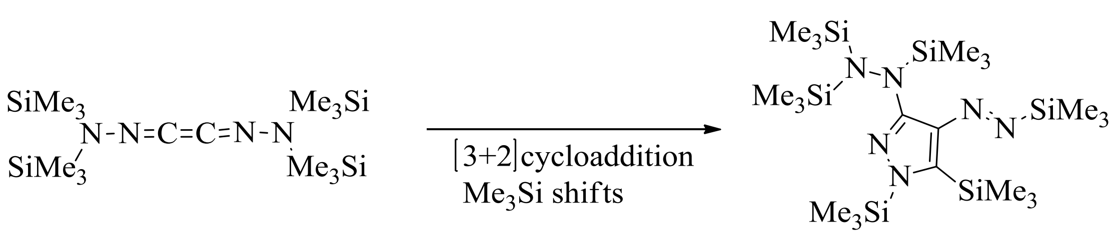
The trimethylsilylium affinity, which describes the enthalpy change associated with the dissociation of the conjugated acid,[111c] is largest for isomer B: 71.1 kcal/mol, followed by **34c**: 69.0 und **34a**: 53.1 kcal/mol (cf. 31.3 Me_3Si–H, 54.4 kcal/mol for Me_3Si–CN)[92a] indicating that $[Me_3SiCNN(SiMe_3)_2]^+$ (BC^+) is the most stable ion in the reaction mixture in accord with experiment. Once the isomerisation is triggered by the action of $[Me_3SiCNN(SiMe_3)_2]^+$, probably a C–C coupling reaction of aminoisocyanide **34c** occurs prior to the [3+2] cycloaddition as illustrated in **Schemes 29** and **30**, respectively. Since aminoisocyanide **34c** is thermally stable in pure state and reacts only when the catalyst BC^+ is present, it can be concluded that also the C–C coupling reactions is catalysed by silylium ions (e.g. $[Me_3SiCNN(SiMe_3)_2]^+$ + $CNN(SiMe_3)_2$ in **Scheme 29**). Interestingly according to in situ NMR experiments (see above) there is no experimental prove for the generation of such a dimer or any other species involved in the [3+2] cycloaddition. The fact, that only pyrazole species **36** is observed besides the starting material, indicates either a fast reaction on the NMR time scale or a very low concentration of the intermediates. Nevertheless, both reactions were calculated to be exothermic/exergonic with –19.8/–6.2 (**Scheme 29**) and –65.6/–44.1 kcal/mol (**Scheme 30**), respectively. Also the overall trimerisation process according to Scheme 1 is exothermic/exergonic with –67.0/–35.1 kcal/mol in the gas phase.



Scheme 29. Catalysed dimerization of aminoisocyanide **34c**.[125]

4.4. Conclusions

In conclusion we present an efficient and facile trimerisation reaction of bissilylated diazomethane which is triggered by the action of silylium ions to give exclusively 4-diazenyl-3-hydrazinyl-pyrazole. As catalyst the isonitrilium ion, $[(Me_3Si)CNN(SiMe_3)_2]^+$, was identified and fully characterized for the first time. The reaction is initiated by an isomerisation process followed by a C–C coupling reaction and a [3+2] cycloaddition to give finally the pyrazole derivative. From a mechanistic viewpoint, we report the first trimerisation of diazomethane derivatives which could also be extended to the aminoisocyanide isomer. This transformation can be regarded as a domino reaction.[139] From a practical viewpoint, the chemistry reported herein provides a facile approach to novel hydrazine-substituted pyrazoles which are of pharmacological relevance and not readily available by other methods.[140,141]



Scheme 30. [3+2] cycloaddition of nitrilimine **34b** and dimeric **34**c.[127]

5. Overall Conclusion

In conclusion, new building block strategies for the synthesis of multifunctional fluorinated arenes are developed. The behaviour of the reaction and its dependency on the effect of the chain length and change of the substituents is studied and very well optimized. This methodology is proved to be a convenient method for preparing new organofluorine compounds which are not reported until yet.

The site-selective Suzuki-Miyaura (S-M) reactions and Sonogoshira reactions for the comparative study of the bis(triflate) of methyl 2,5-dihydroxybenzoate and of the bis(triflate) of phenyl 1,4-dihydroxynaphthoate are studied. And the control of siteselectivity over steric effects and electronic effects for both compounds are clearly investigated. Symmetrical and unsymmetrical 2,3-diarylindoles by Suzuki-Miyaura reactions of *N*-methyl-2,3-dibromoindole are synthesized.

Enormous Lewis acidity of the $[Me_3Si]^+$ to activate small molecules is studied. A simple synthetic route to formal Lewis acid – Lewis base reaction, solvent coordinated $[Me_3Si{\cdot}arene][B(C_6F_5)_4]$ salts (arene = benzene, toluene, ethylbenzene, *n*-propylbenzene, *i*-propylbenzene, *o*-xylene, *m*-xylene, *p*-xylene, 1,2,3-trimethylbenzene, 1,2,4-trimethylbenzene, 1,3,5-trimethylbenzene) starting from $[Me_3Si{-}H{-}SiMe_3][B(C_6F_5)_4]$ have been described. The degradation product is traped with CS_2. Fridel-Crafts type isomerization was observed with *tert.*-butylbenzene. With computations and X-ray structure elucidation different theoretical studies were performed.

Similarly an efficient and facile domino trimerisation reaction of bissilylated diazomethane which is triggered by the action of silylium ions to give exclusively 4-diazenyl-3-hydrazinyl-pyrazole. As catalyst the isonitrilium ion, $[(Me_3Si)CNN(SiMe_3)_2]^+$, was identified and fully characterized for the first time. The reaction is initiated by an isomerisation process followed by a C–C coupling reaction and a [3+2] cycloaddition to give finally the pyrazole derivative.

Appendix

A1. Experimental Details

Equipment, Chemicals and Work Technique

NMR spectroscopy: ^{29}Si INEPT, proton decoupled ^{13}C NMR, DEPT 135, and ^{1}H NMR spectra were obtained on Bruker AC 250, Bruker ARX 300 or Bruker ARX 500 spectrometer and were referenced internally to the deuterated solvent (^{13}C, $CDCl_3$: $\delta_{reference}$ = 77.0 ppm, CD_2Cl_2: $\delta_{reference}$ = 54 ppm, $CDHCl_2$: $\delta_{reference}$ = 5.31 ppm, $(CHD_2)_2CO$: $\delta_{reference}$ 29.84 and 206.26 ppm, C_6HD_5: δ = 128.00 ppm) or to protic impurities in the deuterated solvent (^{1}H, $CHCl_3$: $\delta_{reference}$ = 7.26 ppm). $CDCl_3$ and CD_2Cl_2 were dried over P_4O_{10} and freshly distilled prior to use**.** Spectra were evaluated according to first order rule. All coupling constants are indicated as (*J*). All chemical shifts are given in ppm.

Characterization of the signal fragmentations are s = singlet, d = doublet, t = triplet, q = quartet, quint = quintet, sext = sextet, m = multiplet, brs = broad singlet, dd = double of doublet. A combination of the respective symbols represents more complex coupling patterns. For example, dd indicates a double of doublet.

Infrared Spectroscopy: Nicolet 6700 FT-IR spectrometer with a Smart Endurance ATR device was used. Abbreviations for signal allocations: w = weak, m = medium, s = strong, br = broadly, brw = broad and weak, brm = broad and medium.

Raman: Bruker VERTEX 70 FT-IR with RAM II FT-Raman module, equipped with a Nd: YAG laser (1064 nm) was used.

CHN analyses: C/H/N/S-Mikronalysator TruSpec-932 from Leco was used.

DSC: DSC 823e from Mettler-Toledo (Heating-rate 5 °C/min) was used. Melting points are corrected.

X-ray crystal structure analysis: Bruker X8Apex Diffractometer with CCD-Kamera (Mo-K_a und Graphit Monochromator, λ = 0.71073 Å) or Bruker Apex Kappa-II CCD diffractometer using graphite monochromated Mo Kα radiation (λ = 0.71073).

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.

Mass spectrometric data (MS): Masses were obtained by electron ionization (EI, 70 eV), chemical ionization (CI, isobutane) or electrospray ionization (ESI) using AMD MS40, AMD 402 (AMD Intectra), Varian MAT CH 7 or MAT 731.

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/or 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: 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.

Chemicals and work technique general information.

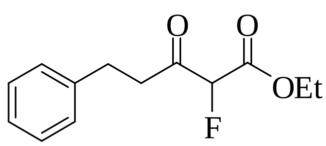
Nearly all reactions were carried out under oxygen- and moisture-free conditions under argon using standard Schlenk or drybox techniques. Solvents were freshly distilled by standard methods prior to use. Toluene and diethyl ether were dried over Na/benzophenone, *n*-hexane and *n*-pentane were dried over Na/benzophenone/tetraglyme. *n*-Heptane and trimethylchlorosilane (> 98 %, Aldrich), were freshly distilled prior to use. Lithium (99.9 %, powder), trimethylchloromethylsilane (97 %, ABCR), nBuLi (2.5 M, Acros) and magnesium sulfate $MgSO_4$ (98 %, VWR Prolabo) were used as received. Alumina (Aluminium oxide, basic Type T), was activated with triethylamine and dried in an oven at 120 °C for 36 hours). *p*-toluenesulfonylazide $MePhSO_2N_3$ and bis(trimethylsilyl)hydronium tetrakis(pentafluorophenyl)borate $[Me_3Si\text{-}H\text{-}SiMe_3][B(C_6F_5)_4]$ were prepared as previously reported.[76b,142] Trimethylsilyldiazomethane $(Me_3Si)CHN_2$ and bis(trimethylsilyl)diazomethane $(Me_3Si)_2CN_2$ have been reported in literature and were prepared by slightly modified procedures.[128,143] CH_2Cl_2 (anhydrous, 99.8 %), di*iso*propylamine (99 %) were purchased directly from ACROS and used without further purification.

Procedures and Spectroscopic Data

General procedure for the synthesis of 2-fluoro-3-oxoesters (1b-j).

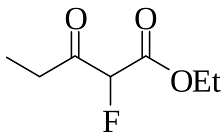
A THF solution of LDA was prepared from di*iso*propylamine (2.5 equiv.), *n*BuLi (2.5 equiv.) and THF (2.5 mL per 1 mmol of *n*BuLi) and the bright yellow reaction mixture was stirred at 0 °C for 30 minutes. To the solution was added ethyl-2-fluoro-acetoacetate **1a** (1.0 equiv.) at 0 °C. After stirring for 1 hour at 0 °C, bromomethylbenzene or alkyl iodides (1.2 equiv.) were added at -78 °C. The solution was allowed to warm up to room temperature during 14 hours with stirring. Hydrochloric acid (10%) was added to the solution and the organic and the aqueous layer were separated. The latter was extracted with diethylether (3 x 25 mL). The combined organic layers were dried (Na_2SO_4), filtered and the filtrate was concentrated *in vacuo*. The residue was purified by column chromatography (silica gel, *n*-heptane/EtOAc = 10:1).

Ethyl 2-fluoro-3-oxo-5-phenylpentanoate (1b): Starting with di*iso*propylamine

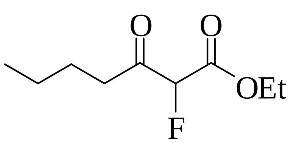


(3.5 mL, 25.0 mmol), *n*BuLi (9.8 mL, 25.0 mmol), THF (25 mL), **1a** (1.3 mL, 10.0 mmol) and benzyl bromide (1.44 mL, 12.0 mmol), **1b** was isolated as a brown liquid (1.431 g, 60 %). ^{1}H NMR (300.13 MHz, $CDCl_3$): δ = 1.27 (t, J = 7.2 Hz, 3H, CH_3), 2.90-3.04 (m, 4H, $2CH_2$), 4.25 (dq, J = 7.2 Hz, J_{FH} = 1.9 Hz, 2H, OCH_2), 5.18 (d, J_{FH} = 49.3 Hz, 1H, FCH), 7.16-7.30 (m, 5H, ArH). ^{13}C NMR (75.46 MHz, $CDCl_3$): δ = 13.9 (CH_3), 28.6 (d, J_{FC} = 2.2 Hz, CH_2), 40.0 (CH_2), 62.7 (OCH_2), 91.4 (d, J_{FC} = 198.1 Hz, FCH), 126.3 (ArCH), 128.3 (2ArCH), 128.5 (2ArCH), 140.1 (ArC), 163.9 (d, J_{FC} = 23.7 Hz, C=O), 200.3 (d, J_{FC} = 23.1 Hz, C=O). ^{19}F NMR (282.40 MHz, $CDCl_3$): δ = -194.94 (FCH). IR (ATR, 32 scans, cm^{-1}): 3063 (w), 3028 (w), 2983 (w), 2939 (w), 2872 (w), 1757 (m), 1731 (s), 1604 (w), 1497 (m), 1454 (m), 1399 (w), 1370 (m), 1329 (w), 1263 (m), 1208 (m), 1129 (w), 1095 (w), 1018 (s). GCMS (EI, 70 eV, m/z > 5 %): 238 (1) $[M]^+$, 200 (21), 145 (21), 144 (18), 133 (45), 105 (95), 104 (10), 103 (12), 91 (100), 78 (10), 77 (15). HRMS (EI): calculated for $C_{13}H_{15}FO_3$ $[M]^+$ is 238.099970, found 238.100389.

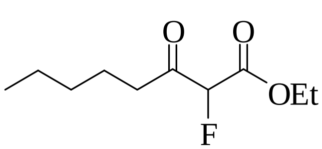
Ethyl 2-fluoro-3-oxopentanoate (1c): Starting with di*iso*propylamine (3.5 mL, 25.0 mmol), *n*BuLi (9.8 mL, 25.0 mmol), THF (25 mL), **1a** (1.3 mL, 10.0 mmol) and methyl iodide (0.75 mL, 12.0 mmol), **1c** was isolated as a colourless liquid (0.96 g, 59 %).^{1}H NMR (250 MHz, $CDCl_3$): δ = 1.09 (t, J = 7.2 Hz, 3H, CH_3), 1.30 (t, J = 7.2 Hz, 3H, OCH_2CH_3), 2.54-2.80 (m, 2H, CH_2), 4.29 (q, J = 7.2 Hz, 2H, OCH_2), 5.20 (d, J_{FH} = 49.3 Hz, 1H, FCH). ^{13}C NMR (75.46 MHz, $CDCl_3$): δ = 6.7 (CH_3), 14.0 (OCH_2CH_3), 31.9 (CH_2), 62.6 (OCH_2), 91.3 (d, J_{FC} = 197.5 Hz, FCH), 164.2 (d, J_{FC} = 24.2 Hz, C=O), 201.8 (d, J_{FC} = 23.1 Hz, C=O). ^{19}F NMR (282.40 MHz, $CDCl_3$): δ = -195.16 (FCH). IR (ATR, 32 scans, cm^{-1}): 2984 (w), 2944 (w), 2911 (w), 2885 (w), 1758 (s), 1731 (s), 1461 (w), 1408 (w), 1371 (w), 1330 (w), 1272 (w), 1238 (w), 1210 (w), 1136 (m), 1098 (m), 1020 (m). MS (EI, 70 eV, m/z > 5 %): 162 ($[M]^+$, 1), 78 (15), 57 (100), 29 (37). HRMS (EI): calculated for $C_7H_{11}FO_3$ $[M]^+$ is 162.068670, found 162.069142.



Ethyl 2-fluoro-3-oxoheptanoate (1d): Starting with di*iso*propylamine (3.5 mL, 25.0 mmol), *n*BuLi (9.8 mL, 25.0 mmol), THF (25 mL), **1a** (1.3 mL, 10.0 mmol) and propyl iodide (1.17 mL, 12.0 mmol), **1d** was isolated as a colourless liquid (1.11 g, 59 %). ^{1}H NMR (300.13 MHz, $CDCl_3$): δ = 0.89 (t, J = 7.2 Hz, 3H, CH_3), 1.28-1.37 (m, 5H, CH_2, OCH_2CH_3), 1.53-1.63 (m, 2H, CH_2), 2.61-2.68 (m, 2H, CH_2), 4.28 (q, J = 7.2 Hz, 2H, OCH_2), 5.18 (d, J_{FH} = 49.5 Hz, 1H, FCH). ^{13}C NMR (75.46 MHz, $CDCl_3$): δ = 13.7 (CH_3), 14.0 (OCH_2CH_3), 22.0 (CH_2), 24.7 (d, J_{FC} = 1.6 Hz, CH_2), 38.1 (CH_2), 62.6 (OCH_2), 91.3 (d, J_{FC} = 197.5 Hz, FCH), 164.2 (d, J_{FC} = 24.2 Hz, C=O), 201.3 (d, J_{FC} = 23.1 Hz, C=O). IR (ATR, 32 scans, cm^{-1}): $\tilde{\nu}$ = 2961 (w), 2937 (w), 2875 (m), 1758 (m), 1731 (s), 1467 (w), 1403 (w), 1371 (m), 1329 (w), 1260 (m), 1211 (m), 1136 (m), 1098 (m), 1020 (s). MS (EI, 70 eV, m/z > 5 %): 190 ($[M]^+$, 1), 85 (100), 57 (77), 41 (29), 29 (26). HRMS (EI): calculated for $C_9H_{15}FO_3$ $[M]^+$ is 190.099970, found 190.100499.

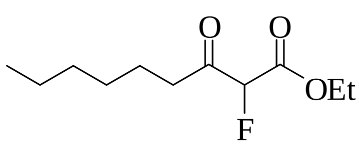


Ethyl 2-fluoro-3-oxooctanoate (1e): Starting with di*iso*propylamine (3.5 mL, 25.0 mmol), *n*BuLi (9.8 mL, 25.0 mmol), THF (25 mL), **1a** (1.3 mL, 10.0 mmol) and butyl iodide (1.37 mL, 12.0 mmol), **1e** was isolated as a colourless liquid (1.28 g, 63 %). ^{1}H NMR



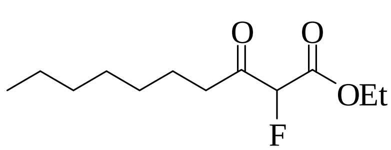
(300.13 MHz, $CDCl_3$): δ = 0.81 (t, J = 6.9 Hz, 3H, CH_3), 1.14-1.27 (m, 7H, $2CH_2$, OCH_2CH_3), 1.49-1.59 (m, 2H, CH_2), 2.54-2.61 (m, 2H, CH_2), 4.29 (q, J = 7.2 Hz, 2H, OCH_2), 5.18 (d, J_{FH} = 49.5 Hz, 1H, FCH). ^{13}C NMR (75.46 MHz, $CDCl_3$): δ = 13.8 (CH_3), 14.0 (OCH_2CH_3), 22.2 (CH_2), 22.3 (d, J_{FC} = 1.6 Hz, CH_2), 31.0, 38.4 (CH_2), 62.6 (OCH_2), 91.3 (d, J_{FC} = 198.1 Hz, FCH), 164.2 (d, J_{FC} = 24.2 Hz, C=O), 201.4 (d, J_{FC} = 23.1Hz, C=O). ^{19}F NMR (282.40 MHz, $CDCl_3$): δ = -195.74 (FCH). IR (ATR, 32 scans, cm^{-1}): $\tilde{\nu}$ = 2958 (w), 2934 (w), 2873 (w), 1758 (m), 1732 (s), 1467 (w), 1403 (w), 1371 (m), 1328 (w), 1270 (w), 1257 (w), 1206 (m), 1136 (m), 1095 (m), 1019 (s). MS (EI, 70 eV, m/z > 5 %): 204 ($[M]^+$, 1), 99 (100), 71 (42), 55 (10), 43 (48), 41 (13), 29 (13). HRMS (EI): calculated for $C_{10}H_{17}FO_3$ $[M]^+$ is 204.115620, found 204.115740.

Ethyl 2-fluoro-3-oxononanoate (1f): Starting with di*iso*propylamine (3.5 mL, 25.0 mmol), *n*BuLi (9.8 mL, 25.0 mmol), THF (25 mL), **1a** (1.3 mL, 10.0 mmol) and pentyl iodide (1.57 mL, 12.0 mmol), **1f** was isolated as a yellow liquid (1.61 g, 74 %).



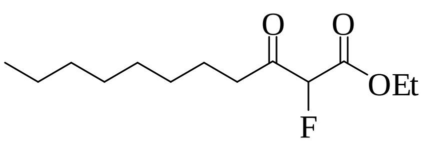
^{1}H NMR (300.13 MHz, $CDCl_3$): δ = 0.81 (t, J = 7.2 Hz, 3H, CH_3), 1.18-1.27 (m, 9H, $3CH_2$, OCH_2CH_3), 1.49-1.59 (m, 2H, CH_2), 2.56-2.62 (m, 2H, CH_2), 4.24 (q, J = 7.2 Hz, 2H, OCH_2), 5.14 (d, J_{FH} = 49.5 Hz, 1H, FCH). ^{13}C NMR (75.46 MHz, CDCl3): δ =13.9 (CH_3), 14.0 (OCH_2CH_3), 22.4 (CH_2), 22.6 (d, J_{FC} = 1.6 Hz, CH_2), 28.6 , 31.4, 38.4 (CH_2), 62.6 (OCH_2), 91.3 (d, J_{FC} = 198.3 Hz, FCH), 164.2 (d, J_{FC} = 24.1 Hz, C=O), 201.4 (d, J_{FC} = 22.8 Hz, C=O). ^{19}F NMR (282.40 MHz, $CDCl_3$): δ = -194.71 (FCH). IR (ATR, 32 scans, cm^{-1}): $\tilde{\nu}$ = 2957 (w), 2931 (w), 2859 (w), 1759 (m), 1732 (s), 1467 (m), 1402 (w), 1371 (m), 1328 (w), 1266 (m), 1204 (m), 1136 (m), 1095 (m), 1019 (s). MS (EI, 70 eV, m/z > 5 %): 218 ($[M]^+$, 1), 113 (100), 85 (28), 57 (12), 55 (11), 43 (50), 41 (16), 29 (12). HRMS (ESI-TOF/MS): calculated for $C_{11}H_{19}FNaO_3$ $[M+Na]^+$ is 241.121040, found 241.120840.

Ethyl 2-fluoro-3-oxodecanoate (1g): Starting with di*iso*propylamine (3.5 mL, 25.0 mmol), *n*BuLi (9.8 mL, 25.0 mmol), THF (25 mL), **1a** (1.3 mL, 10.0 mmol) and hexyl iodide (1.77 mL, 12.0 mmol), **1g** was isolated as a yellow liquid (1.48 g, 64 %).



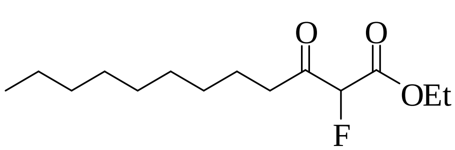
^{1}H NMR (300.13 MHz, $CDCl_3$): δ = 0.85 (t, J = 6.8 Hz, 3H, CH_3), 1.24-1.32 (m, 11H, 4CH$_2$, OCH$_2$CH_3), 1.54-1.63 (m, 2H, CH$_2$), 2.60-2.67 (m, 2H, CH$_2$), 4.28 (q, J = 7.0 Hz, 2H, OCH$_2$), 5.17 (d, J_{FH} = 49.5 Hz, 1H, FCH). ^{13}C NMR (75.46 MHz, CDCl3): δ = 13.9 (CH$_3$), 14.0 (OCH$_2$$CH_3$), 22.5 (CH$_2$), 22.6 (d, J_{FC} = 1.4 Hz, CH$_2$), 28.8, 28.9, 31.5, 38.4 (CH$_2$), 62.5 (OCH$_2$), 91.3 (d, J_{FC} = 198.1 Hz, FCH), 164.2 (d, J_{FC} = 24.2 Hz, C=O), 201.3 (d, J_{FC} = 22.6 Hz, C=O). ^{19}F NMR (282.40 MHz, CDCl$_3$,): δ = -194.75 (FCH). IR (ATR, 32 scans, cm^{-1}): $\tilde{\nu}$ = 2956 (w), 2928 (m), 2857 (m), 1759 (m), 1732 (s), 1466 (m), 1403 (w), 1371 (m), 1328 (w), 1264 (m), 1206 (w), 1136 (m), 1095 (m), 1019 (s). MS (EI, 70 eV, m/z > 5 %): 232 ([M]$^+$, 1), 127 (99), 57 (100), 55 (20), 43 (26), 41 (25), 29 (19). HRMS Pos (ESI): calculated for $C_{12}H_{21}FNaO_3$ [M+Na]$^+$ is 255.136690, found 255.136700.

Ethyl 2-fluoro-3-oxoundecanoate (1h): Starting with di*iso*propylamine (3.5 mL, 25.0 mmol), *n*BuLi (9.8 mL, 25.0 mmol), THF (25 mL), **1a** (1.3 mL, 10.0 mmol) and heptyl iodide (1.98 mL, 12.0 mmol), **1h** was isolated as a yellow liquid (1.12 g, 46 %).



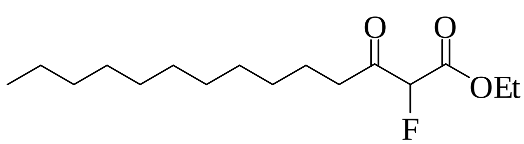
^{1}H NMR (250.13 MHz, CDCl$_3$): δ = 0.86 (t, J = 6.9 Hz, 3H, CH$_3$), 1.25-1.34 (m, 13H, 5CH$_2$, OCH$_2$CH_3), 1.56-1.62 (m, 2H, CH$_2$), 2.60-2.68 (m, 2H, CH$_2$), 4.29 (q, J = 7.1 Hz, 2H, OCH$_2$), 5.18 (d, J_{FH} = 49.5 Hz, 1H, FCH). ^{13}C NMR (75.46 MHz, CDCl$_3$): δ = 14.0 (CH$_3$), 14.0 (OCH$_2$$CH_3$), 22.6, (d, J_{FC} = 1.8 Hz, CH$_2$), 22.7, 28.9, 29.0, 29.2, 31.7, 38.4 (CH$_2$), 62.6 (OCH$_2$), 91.3 (d, J_{FC} = 198.1 Hz, FCH), 164.2 (d, J_{FC} = 23.7 Hz, C=O), 201.4 (d, J_{FC} = 23.7 Hz, C=O). ^{19}F NMR (282.40 MHz, CDCl$_3$): δ = -195.73 (FCH). IR (ATR, 32 scans, cm^{-1}): $\tilde{\nu}$ = 2925 (s), 2855 (s), 1759 (s), 1732 (s), 1466 (m), 1402 (w), 1371 (m), 1328 (w), 1261 (m), 1207 (w), 1136 (m), 1096 (m), 1019 (s). MS (EI, 70 eV, m/z > 5 %): 246 ([M]$^+$, 1), 141 (100), 81 (12), 71 (48), 57 (53), 55 (24), 43 (32), 41 (27), 29 (21). HRMS (EI): calculated mass for $C_{13}H_{23}FO_3$ [M]$^+$ is 246.162570, found 246.161883.

Ethyl 2-fluoro-3-oxododecanoate (1i): Starting with di*iso*propylamine (3.5 mL, 25.0 mmol), *n*BuLi (9.8 mL, 25.0 mmol), THF (25 mL), **1a** (1.3 mL, 10.0 mmol) and octyl iodide (2.17 mL, 12.0 mmol), **1i** was isolated as a yellow liquid (1.613 g, 62 %).



^{1}H NMR (250 MHz, CDCl$_3$): δ = 0.87 (t, J = 6.7 Hz, 3H, CH$_3$), 1.25-1.34 (m, 15H, $6CH_2$, $OCH_2C\mathit{H_3}$), 1.57-1.63 (m, 2H, CH_2), 2.61-2.69 (m, 2H, CH_2), 4.30 (q, J = 7.2 Hz, 2H, OCH_2), 5.19 (d, J_{FH} = 49.3 Hz, 1H, FCH). ^{13}C NMR (75.46 MHz, $CDCl_3$): δ = 13.9 (CH_3), 14.0 ($OCH_2\mathit{C}H_3$), 22.61 (CH_2), 22.65 (d, J_{FC} = 1.8 Hz, CH_2), 28.9, 29.1, 29.2, 29.3, 31.8, 38.4 (CH_2), 62.6 (OCH_2), 91.3 (d, J_{FC} = 197.5 Hz, FCH), 164.2 (d, J_{FC} = 23.9 Hz, C=O), 201.3 (d, J_{FC} = 22.9 Hz, C=O). ^{19}F NMR (282.40 MHz, $CDCl_3$): δ = -194.76 (FCH). IR (ATR, 32 scans, cm^{-1}): $\tilde{\nu}$ = 2925 (s), 2855 (s), 1759 (s), 1732 (s), 1466 (m), 1402 (w), 1371 (m), 1328 (w), 1261 (m), 1207 (w), 1136 (m), 1096 (m), 1019 (s). MS (EI, 70 eV, m/z > 5 %): 260 ($[M]^+$, 0.10), 242 (0.10), 156 (13), 155 (100), 95 (17), 85 (33), 81 (14), 71 (48), 69 (14), 57 (38), 55 (26), 43 (41), 41 (28), 29 (18). HRMS Pos (ESI) calcd for $C_{14}H_{26}FO_3$ $[M+H]^+$ is 261.18605 found 261.18582. HRMS Neg (ESI) calcd for $C_{14}H_{24}FO_3$ $[M-H]^-$ is 259.171500 found 259.172070.

Ethyl 2-fluoro-3-oxotetradecanoate (1j): Starting with di*iso*propylamine (3.5 mL, 25.0 mmol), *n*BuLi (9.8 mL, 25.0 mmol), THF (25 mL), **1a** (1.3 mL, 10.0 mmol) and decyl iodide (2.56 mL, 12.0 mmol), **1i** was isolated as a yellow liquid (1.756 g, 61 %). ^{1}H NMR (250 MHz, $CDCl_3$): δ = 0.87 (t, J = 6.8 Hz, 3H, CH_3), 1.25-1.34 (m, 19H, $8CH_2$, $OCH_2C\mathit{H_3}$), 1.55-1.62 (m, 2H, CH_2), 2.61-2.68 (m, 2H, CH_2), 4.29 (q, J = 7.1 Hz, 2H, OCH_2), 5.18 (d, J_{FH} = 49.5 Hz, 1H, FCH). ^{13}C NMR (75.46 MHz, $CDCl_3$): δ = 14.00 ($2CH_3$), 22.6 (d, J_{FC} = 1.8 Hz, CH_2), 22.7, 28.9, 29.2, 29.3, 29.4 (CH_2), 29.5 ($2CH_2$), 31.9, 38.4 (CH_2), 62.6 (OCH_2), 91.3 (d, J_{FC} = 197.8 Hz, FCH), 164.2 (d, J_{FC} = 24.2 Hz, C=O), 201.4 (d, J_{FC} = 22.7 Hz, C=O). ^{19}F NMR (282 .40 MHz, $CDCl_3$): δ = -194.73 (FCH). IR (ATR, 32 scans, cm^{-1}): $\tilde{\nu}$ = 2931 (s), 2852 (s), 1756 (s), 1731 (s), 1473 (m), 1408 (w), 1373 (m), 1327 (w), 1263 (m), 1205 (w), 1133 (m), 1091 (m), 1017 (s). MS (EI, 70 eV, m/z > 5 %): 288 ($[M]^+$, 0.08), 259 (23), 183 (13), 182 (100), 94 (17), 85 (33), 81 (14), 71 (48), 69 (14), 57 (38), 55 (26), 43 (41), 41 (28), 29 (18). HRMS (EI) calcd for $C_{16}H_{29}FO_3$ $[M]^+$ is 288.209520 found 288.208990.



General procedure for the synthesis of ethyl-2-fluoro-3-[(trimethylsilyl)oxy]-alk-2-enoates (2a-i).

Compounds **2a-i** was prepared according to the procedures of Chan and Molander.[35] To a benzene solution of β-ketoesters **1a-i** (1.0 equiv.) triethylamine (1.5 equiv.) was added. After stirring for 1h at 20 °C, TMSCl (1.5 equiv.) was added dropwise at 20 °C. After stirring for 48 h, the precipitated salts were filtered off and the filtrate was concentrated *in vacuo* to give silyl enol ethers **2a-i**.

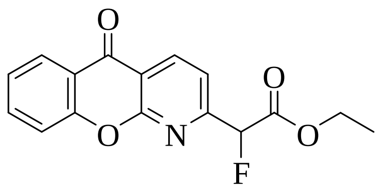
General procedure for the synthesis of 1-ethoxy-2-fluoro-1,3-bis(trimethylsilyloxy)-1,3-dienes 3a-i.

To a THF-solution of LDA, {prepared by addition of *n*BuLi (1.5 equiv., 15 % or 2.5 M solution in *n*-hexane) to a THF-solution of diisopropylamine (1.5 equiv.) at 0 °C and stirring for 20 min}, at –78 °C was added a THF-solution of silyl enol ether **2a-i** (1.0 equiv.). After stirring for 1h at –78 °C, TMSCl (1.5 equiv.) was added. The temperature of the solution was allowed to rise to ambient temperature during 2 h and the solution was stirred for 1h at 20 °C. The solvent was removed *in vacuo* and *n*-hexane was added to the residue. The precipitated lithium chloride was removed by filtration under inert atmosphere and the solvent of the filtrate was removed *in vacuo* to give 1,3-bis-silyl enol ethers **3a-i**.

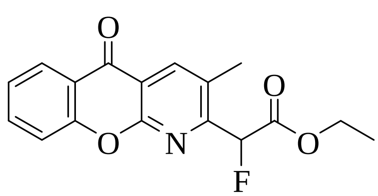
General procedure for the synthesis of azaxanthones (5) and biaryls (6).

To 4-oxo-4*H*-chromen-3-carbonitrile **4** (1.0 equiv.) was added Me_3SiOTf (1.3 equiv.) and CH_2Cl_2 (1 mL) at 20 °C. After stirring for 1 hour, CH_2Cl_2 (10 mL) and 1-ethoxy-2-fluoro-1,3-bis(trimethylsilyloxy)-1,3-diene **3** (1.3 equiv.) were added at 0 °C. The mixture was stirred for 12 hours at 20 °C and subsequently poured into hydrochloric acid (10%). The organic and the aqueous layer were separated and the latter was extracted with CH_2Cl_2 (3 x 100 mL). The combined organic layers were washed with water, dried (Na_2SO_4), filtered and the filtrate was concentrated *in vacuo*. The residue was dissolved in ethanol (10 mL), triethylamine (2.0 equiv.) was added and the solution was stirred for 12 hours at 20 °C. To the solution were subsequently added an aqueous solution of hydrochloric acid (1 M) and ether (50 mL). The organic and the aqueous layer were separated and the latter was extracted with diethylether (3 x 100 mL). The combined organic layers were washed with water, dried (Na_2SO_4), filtered and the filtrate was concentrated *in vacuo*. The residue was purified by column chromatography (silica gel, *n*-heptane/EtOAc = 10:1).

Ethyl 2-fluoro-2-(5-oxo-5*H*-chromeno[2,3-*b*]pyridin-2-yl)acetate (5a): Starting with 4-oxo-4*H*-chromen-3-carbonitrile **4a** (171 mg, 1.0 mmol), Me_3SiOTf (288 mg, 0.23 mL, 1.30 mmol), **3a** (380 mg, 1.30 mmol), CH_2Cl_2 (9 mL), EtOH (10 mL), and triethylamine (202 mg, 0.28 mL, 2 mmol), **5a** was isolated as a white solid (168 mg, 56 %), mp = 147-148 °C. ^{1}H NMR (250.13 MHz, $CDCl_3$): δ = 1.23 (t, *J*= 7.2 Hz, 3H, CH_3), 4.18-4.31 (m, 2H, OCH_2), 5.82 (d, J_{FH} = 47.5 Hz, 1H, FCH), 7.35-7.41 (m, 1H, ArH), 7.54-7.63 (m, 2H, ArH), 7.70-7.77 (m, 1H, ArH), 8.22 (dd, *J* = 6.4, 1.6 Hz, 1H, ArH), 8.72 (d, *J* = 8.7 Hz, 1H, ArH). ^{13}C NMR (62.90 MHz, $CDCl_3$): δ = 14.0 (CH_3), 63.1 (OCH_2), 89.4 (d, J_{FC} = 187 Hz, FCH), 116.9 (C), 118.0 (d, J_{FC} = 5.28 Hz, CH), 118.5 (CH), 121.5 (C), 124.9, 126.7, 135.9, 138.9 (CH), 155.6 (C), 158.2 (d, J_{FC} = 25.0 Hz, C), 159.6 (C), 166.1 (d, J_{FC} = 25.6 Hz, C=O), 177.0 (C=O). ^{19}F NMR (235 MHz, $CDCl_3$): δ = -187.79 (FCH). IR (ATR, 32 scans, cm^{-1}): $\tilde{\nu}$ = 3071 (w), 2980 (w), 2868 (w), 1757 (s), 1669 (s), 1600 (m), 1397 (s), 1205 (s), 1087 (s), 753 (s). GCMS (EI, 70 eV, m/z > 5 %): 301 ($[M]^+$, 41), 229 (100), 200 (31), 146 (8). HRMS (EI) calculated for $C_{16}H_{12}FNO_4$ $[M]^+$ is 301.074490, found 301.074205.

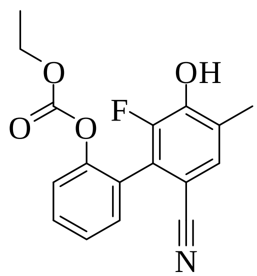


Ethyl 2-fluoro-2-(3-methyl-5-oxo-5*H*-chromeno[2,3-*b*]pyridin-2-yl)acetate (5b): Starting with 4-oxo-4*H*-chromen-3-carbonitrile **4a** (171 mg, 1.0 mmol), Me_3SiOTf (288 mg, 0.23 mL, 1.30 mmol), **3c** (398 mg, 1.30 mmol), CH_2Cl_2 (9 mL), EtOH (10 mL), and triethylamine (202 mg, 0.28 mL, 2 mmol), **5b** was isolated as white solid (44 mg, 14 %), mp = 107-109 °C. ^{1}H NMR (300.13 MHz, $CDCl_3$): δ = 1.22 (t, *J* = 7.2 Hz, 3H, CH_3), 2.50 (d, J_{FH} = 2.1 Hz, 3H, CH_3), 4.21-4.32 (m, 2H, OCH_2), 6.03 (d, J_{FH} = 47.4 Hz, 1H, FCH), 7.34 (dt, *J* = 7.2, 1.1 Hz, 1H, ArH), 7.52 (dd, *J* = 8.4, 0.6 Hz, 1H, ArH), 7.70 (dt, *J* = 7.2, 1.7 Hz, 1H, ArH), 8.21 (dd, *J* = 8.0, 1.6 Hz, 1H, ArH), 8.46 (s, 1H, ArH). ^{13}C NMR (62.89 MHz, $CDCl_3$):



δ = 13.1 (CH_3), 16.2 (d, J_{FC} = 2.6 Hz, CH_3), 61.3 (OCH_2), 87.6 (d, J_{FC} = 188.7 Hz, FCH), 115.8 (d, J_{FC} = 1.8 Hz, C), 117.5 (CH), 120.5 (C), 123.7, 125.7 (CH), 129.4 (C), 134.8, 138.8 (CH), 154.8 (C), 154.9 (d, J_{FC} = 19.5 Hz, C), 156.8 (C), 165.7 (d, J_{FC} = 25.7 Hz, C=O), 176.2 (C=O). ^{19}F NMR (282.40 MHz, $CDCl_3$): δ = -185.70 (FCH). IR (ATR, 32 scans, cm^{-1}): $\tilde{\nu}$ = 3114 (w), 3078 (w), 3054 (w), 2985 (w), 2965 (w), 2941 (w), 1766 (s), 1760 (s), 1665 (s), 1605 (s), 1471 (m), 1434 (s), 1371 (m), 1338 (w), 1312 (m), 1292 (w), 1255 (w), 1202 (s), 1168 (w), 1149 (w), 1097 (m), 1055 (s), 1000 (m), 956 (w), 941 (w), 765 (m), 756 (s), 696 (w), 597 (m). GCMS (EI, 70 eV, m/z > 5 %): 317 ([M+2]$^+$, 2), 316 ([M+1]$^+$, 16), 315 ([M]$^+$, 94), 270 (6), 269 (19), 244 (10), 243 (70), 242 (100), 241 (15), 214 (10), 140 (5), 139 (4), 29 (10). HRMS (EI) calculated for $C_{17}H_{14}FNO_4$ [M]$^+$ is 315.090140, found 315.089755.

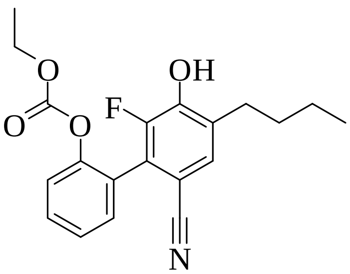
6'-Cyano-2'-fluoro-3'-hydroxy-4'-methylbiphenyl-2-yl ethyl carbonate (6b): Starting



with 4-oxo-4*H*-chromen-3-carbonitrile **4a** (171mg, 1.0 mmol), Me_3SiOTf (288 mg, 0.23 mL, 1.30 mmol), **3c** (398 mg, 1.30 mmol), CH_2Cl_2 (9 mL), EtOH (10 mL), and triethylamine (202 mg, 0.28 mL, 2 mmol), **6b** was isolated as yellowish white solid (226 mg, 72 %), mp = 123-125 °C. ^{1}H NMR (300 MHz, $(CD_3)_2CO$): δ = 1.15 (t, J = 7.1 Hz, 3H, CH_3), 2.33 (d, J_{FH} = 0.7 Hz, 3H, CH_3), 4.12 (q, J = 7.1 Hz, 2H, OCH_2), 7.40-7.46 (m, 2H, ArH), 7.48-7.52 (m, 2H, ArH), 7.57 (dt, J = 7.1, 2.0 Hz, 1H, ArH), 9.61 (brs, 1H, OH). ^{13}C NMR (75.47 MHz, $(CD_3)_2CO$): δ = 14.0 (CH_3), 15.4 (d, J_{FC} = 2.8 Hz, CH_3), 65.2 (OCH_2), 104.1 (d, J_{FC} = 4.1 Hz, C), 117.8 (d, J_{FC} = 3.7 Hz, C), 123.0 (CH), 125.8 (C), 126.8 (CH), 126.9 (d, J_{FC} = 19.4 Hz, C), 129.2 (d, J_{FC} = 3.6 Hz, C), 131.2 (CH), 131.3 (d, J_{FC} = 3.1 Hz, CH), 132.1 (CH), 147.9 (d, J_{FC} = 15 Hz, C-OH), 148.9 (d, J_{FC} = 240 Hz, C), 149.6 (C), 153.1 (C=O). ^{19}F NMR (282.40 MHz, $(CD_3)_2CO$): δ = 40.62 (ArF). IR (ATR, 32 scans, cm^{-1}): $\tilde{\nu}$ = 3218 (br), 2993 (w), 2925 (w), 2235 (m), 1759 (s), 1667 (w), 1614 (m), 1573 (w), 1483 (m), 1466 (m), 1428 (w), 1381 (w), 1368 (m), 1321 (m), 1293 (w), 1270 (m), 1243 (s), 1205 (s), 1159 (m), 1111 (w), 1060 (m), 1032 (m), 997 (m), 982 (m), 945 (w), 891 (m), 821 (m), 775 (m), 764 (s), 690 (m), 669 (w), 647 (w), 576 (w). GCMS (EI, 70 eV, m/z > 5 %): 315 ([M]$^+$, 1), 298 (2), 256 (45), 244 (15), 243 (100), 242 (10), 222 (10), 216

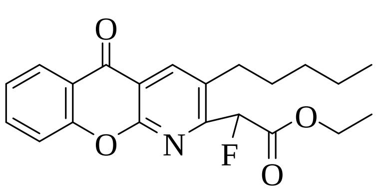
(8), 215 (14), 166 (6), 140 (6), 29 (7). HRMS (EI) calculated for $C_{17}H_{14}FNO_4$ $[M]^+$ is 315.09014, found 315.089341.

4'-Butyl-6'-cyano-2'-fluoro-3'-hydroxybiphenyl-2-yl ethyl carbonate (6c): Starting



with 4-oxo-4*H*-chromen-3-carbonitrile **4a** (171 mg, 1.0 mmol), Me_3SiOTf (288 mg, 0.23 mL, 1.30 mmol), **3e** (450 mg, 1.30 mmol), CH_2Cl_2 (9.0 mL), EtOH (10 mL), and triethylamine (202 mg, 0.28 mL, 2 mmol), **6c** was isolated as a colourless gel, (244 mg, 71 %), mp = (253, 71%). ^{1}H NMR (300.13 MHz, $CDCl_3$): δ = 0.88 (t, *J* = 7.20 Hz, 3H, CH_3), 1.1 (t, *J* = 7.7 Hz, 3H, CH_3), 1.25-1.37 (m, 2H, CH_2), 1.48-1.58 (m, 2H, CH_2), 2.59 (t, *J* = 7.7 Hz, 2H, CH_2), 4.08 (q, *J* = 7.2 Hz, 2H, OCH_2), 6.19 (brs, 1H, OH), 7.25 (s, 1H, ArH), 7.26-7.35 (m, 3H, ArH), 7.41 (dt, *J* = 8.7, 2.1 Hz, 1H, ArH). ^{13}C NMR (75.47 MHz, $CDCl_3$): δ = 13.9, 14.0 (CH_3), 22.4 (CH_2), 29.1 (d, J_{FC} = 2.3 Hz, CH_2), 31.2 (CH_2), 65.0 (OCH_2), 104.1 (d, J_{FC} = 4.4 Hz, C), 117.3 (d, J_{FC} = 3.9 Hz, C), 122.3 (CH), 124.4 (C), 126.0 (d, J_{FC} = 17.6 Hz, C), 126.3 (CH), 130.3 (d, J_{FC} = 3.0 Hz, CH), 130.7, 131.4 (CH), 132.4 (d, J_{FC} = 2.3 Hz, C), 146.1 (d, J_{FC} = 15 Hz, C-OH), 147.9 (d, J_{FC} = 239 Hz, C), 148.6 (C), 152.7 (C=O). ^{19}F NMR (282.40 MHz, $CDCl_3$): δ = -138.4 (ArF). IR (ATR, 32 scans, cm^{-1}): $\tilde{\nu}$ = 3248 (br), 2951 (m), 2926 (m), 2854 (m), 2234 (m), 1753 (s), 1615 (w), 1606 (w), 1480 (m), 1459 (m), 1432 (m), 1247 (s), 1197 (s), 1055 (m), 1035 (m), 949 (m), 888 (m), 873 (m), 817 (m), 651 (w), 600 (w), 582 (w). MS (EI, 70 eV, m/z > 5 %): 357 ($[M]^+$, 2), 313 (7), 298 (51), 268 (20), 242 (100), 224 (5). HRMS (EI) calculated for $C_{20}H_{20}FNO_4$ $[M]^+$ is 357.13709, found 357.136810.

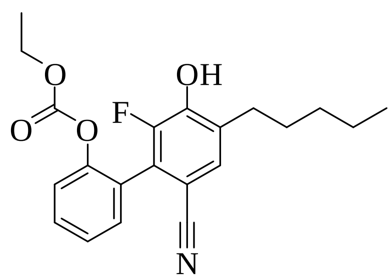
Ethyl 2-fluoro-2-(5-oxo-3-pentyl-5*H*-chromeno[2,3-*b*]pyridin-2-yl)acetate (5d):



Starting with 4-oxo-4*H*-chromen-3-carbonitrile **4a** (171 mg, 1.0 mmol), Me_3SiOTf (288 mg, 0.23 mL, 1.30 mmol), **3f** (471 mg, 1.30 mmol), CH_2Cl_2 (9 mL), EtOH (10 mL), and triethylamine (202 mg, 0.28 mL, 2 mmol), **5d** was isolated as yellowish white solid (48 mg, 13 %), mp = 76-78 °C. ^{1}H NMR (300.13 MHz, $CDCl_3$): δ = 0.85 (t, *J* = 6.9 Hz, 3H, CH_3), 1.23 (t, *J* = 7.2 Hz, 3H, CH_3), 1.31-1.37 (m, 4H, $2CH_2$), 1.60-1.70 (m, 2H, CH_2), 2.77-2.83 (m, 2H, CH_2), 4.21-

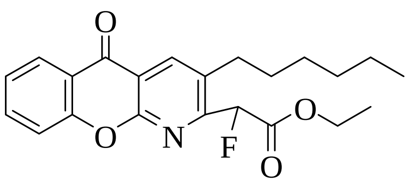
4.33 (m, 2H, OCH_2), 6.07 (d, J_{FH} = 47.5 Hz, 1H, FCH), 7.36 (dt, J = 7.1, 1.1 Hz, 1H, ArH), 7.53 (dd, J = 8.3, 0.8 Hz, 1H, ArH), 7.71 (dt, J = 7.2, 1.8 Hz, 1H, ArH), 8.24 (dd, J = 8.0, 1.3 Hz, 1H, ArH), 8.53 (s, 1H, ArH). ^{13}C NMR (75.47 MHz, $CDCl_3$): δ = 13.9, 14.1 (CH_3), 22.4 (CH_2), 30.6 (d, J_{FC} = 1.5 Hz, CH_2), 30.6, 31.5 (CH_2), 62.3 (OCH_2), 87.9 (d, J_{FC} = 188 Hz, FCH), 117.1 (d, J_{FC} = 2.0 Hz, C), 118.6 (CH), 121.5 (C), 124.7, 126.7 (CH), 135.4 (C), 135.8, 138.9 (CH), 155.5 (d, J_{FC} = 19.0 Hz, C), 155.9, 157.8 (C), 167.0 (d, J_{FC} = 25.8 Hz, C=O), 177.4 (C=O). ^{19}F NMR (282.40 MHz, $CDCl_3$): δ = -182.17 (FCH). IR (ATR, 32 scans, cm^{-1}): $\tilde{\nu}$ = 3048 (w), 2956 (w), 2927 (w), 2873 (w), 2857 (w), 1721 (s), 1665 (s), 1601 (s), 1559 (w), 1467 (s), 1425 (s), 1371 (m), 1275 (s), 1203 (s), 1019 (s), 958 (m) 760 (m), 636, 532.). GCMS (EI, 70 eV, m/z > 5 %): 371 ($[M]^+$, 19), 329 (21), 328 (100), 267 (14), 266 (86), 256 (4), 243 (17), 242 (49), 241 (10), 236 (6), 210 (9), 29 (7). HRMS (EI) calculated for $C_{21}H_{22}FNO_4$ $[M]^+$ is 371.152740 found 371.152296.

6'-Cyano-2'-fluoro-3'-hydroxy-4'-pentylbiphenyl-2-yl ethyl carbonate (6d). Starting



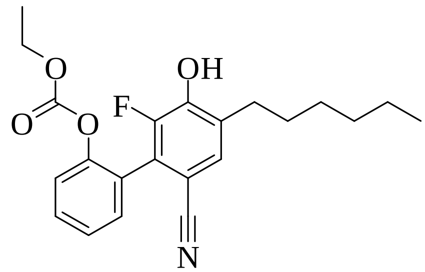
with 4-oxo-4*H*-chromen-3-carbonitrile **4a** (171 mg, 1.0 mmol), Me_3SiOTf (288 mg, 0.23 mL, 1.30 mmol), **3f** (471 mg, 1.30 mmol), CH_2Cl_2 (9 mL), EtOH (10 mL), and triethylamine (202 mg, 0.28 mL, 2 mmol), **6d** was isolated as a yellowish white solid (267 mg, 72 %), mp = 104-106 °C. ^{1}H NMR (300.13 MHz, $CDCl_3$): δ = 0.86 (t, J = 6.7 Hz, 3H, CH_3), 1.15 (t, J = 7.1 Hz, 3H, CH_3), 1.27-1.32 (m, 4H, $2CH_2$), 1.52-1.62 (m, 2H, CH_2), 2.61 (t, J = 7.3 Hz, 2H, CH_2), 4.11 (q, J = 7.1 Hz, 2H, OCH_2), 6.07 (brs, 1H, OH), 7.27 (s, 1H, ArH), 7.29-7.36 (m, 3H, ArH), 7.44 (dt, J = 7.0, 2.1 Hz, 1H, ArH). ^{13}C NMR (75.47 MHz, $CDCl_3$): δ = 12.8, 12.9 (CH_3), 21.4, 27.7 (CH_2), 28.3 (d, J_{FC} = 2.2 Hz, CH_2), 30.4 (CH_2), 63.9 (OCH_2), 103.3 (d, J_{FC} = 4.7 Hz, C), 116.3 (d, J_{FC} = 3.9 Hz, C), 121.2 (CH), 123.3 (C), 124.9 (d, J_{FC} = 18.0 Hz, C), 125.2 (CH), 129.2 (d, J_{FC} = 3.0 Hz, CH), 129.7, 130.3 (CH), 131.4 (d, J_{FC} = 2.1 Hz, C), 144.9 (d, J_{FC} = 15 Hz, C-OH), 146.8 (d, J_{FC} = 239 Hz, C), 147.5 (C), 151.6 (C=O). ^{19}F NMR (282.40 MHz, $CDCl_3$): δ = -138.69 (ArF). IR (ATR, 32 scans, cm^{-1}): $\tilde{\nu}$ = 3248 (br), 2956 (w), 2927 (w), 2857 (w), 2235 (m), 1753 (s), 1714 (w), 1614 (m), 1607 (m), 1570 (w), 1481(m), 1459 (m), 1433 (m), 1395 (w), 1373 (m), 1321 (m), 1281 (m), 1246 (s), 1196 (s), 1152 (m), 1105 (m), 1096 (m), 1056 (m), 1035 (m), 997 (m) 949 (m), 925 (w), 902 (m), 884 (w), 859 (w), 817 (m), 775 (m), 767 (m), 747 (m), 684 (m), 650 (m), 602 (m), 582 (w), 569 (m), 556 (m), 533 (m). GCMS (EI, 70 eV, m/z > 5 %): 373 ($[M+2]^+$, 1), 372 $(M+1]^+$, 3), 371 ($[M]^+$, 19), 329 (21), 328 (100), 267 (14), 266 (86), 256 (4), 243 (17), 242 (49), 241 (10), 236 (6), 210 (9), 29 (7). HRMS (ESI) calculated for $C_{21}H_{23}FNO_4$ $[M+H]^+$ is 372.1606, found 372.1605.

Ethyl 2-fluoro-2-(3-hexyl-5-oxo-5*H*-chromeno[2,3-*b*]pyridin-2-yl)acetate (5e):

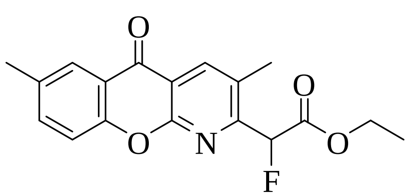


Starting with 34-oxo-4*H*-chromen-3-carbonitrile **4a** (171 mg, 1.0 mmol), Me_3SiOTf (288 mg, 0.23 mL, 1.30 mmol), **3g** (489 mg, 1.30 mmol), CH_2Cl_2 (9 mL), EtOH (10 mL), and triethylamine (202 mg, 0.28 mL, 2 mmol), **5e** was isolated as white solid (41 mg, 11 %), mp = 76-78 °C. ^{1}H NMR (300.13 MHz, $CDCl_3$): δ = 0.83 (t, *J* = 7.0 Hz, 3H, CH_3), 1.23 (t, *J* = 7.1 Hz, 3H, CH_3), 1.24-1.37 (m, 6H, $3CH_2$), 1.58-1.69 (m, 2H, CH_2), 2.76-2.82 (m, 2H, CH_2), 4.21-4.33 (m, 2H, OCH_2), 6.07 (d, J_{FH} = 47.6 Hz, 1H, FCH), 7.35 (dt, *J* = 7.2, 1.1 Hz, 1H, ArH), 7.53 (dd, *J* = 8.3, 0.5 Hz, 1H, ArH), 7.71 (dt, *J* = 7.2, 1.7 Hz, 1H, ArH), 8.23 (dd, *J* = 8.0, 1.6 Hz, 1H, ArH), 8.52 (s, 1H, ArH). ^{13}C NMR (62.89 MHz, $CDCl_3$): δ = 14.0, 14.1 (CH_3), 22.5, 29.0 (CH_2), 30.6 (d, J_{FC} = 1.3 Hz, CH_2), 30.9, 31.5 (CH_2), 62.2 (OCH_2), 87.9 (d, J_{FC} = 189 Hz, FCH), 117.0 (d, J_{FC} = 1.6 Hz, C), 118.5 (CH), 121.5 (C), 124.7, 126.7 (CH), 135.3 (C), 135.8, 138.9 (CH), 155.5 (d, J_{FC} = 19.0 Hz, C), 155.8, 157.7 (C), 166.9 (d, J_{FC} = 25.8 Hz, C=O), 177.3 (C=O). ^{19}F NMR (282.40 MHz, $CDCl_3$): δ = -182.15 (FCH). IR (ATR, 32 scans, cm^{-1}): $\tilde{\nu}$ = 3064 (w), 3051 (w), 2985 (w), 2952 (m), 2920 (m), 2850 (m), 1754 (w), 1735 (s), 1666 (s), 1602 (s), 1562 (w), 1468 (s), 1427 (s), 1368 (m), 1327 (m), 1316 (m), 1271 (m), 1254 (m), 1228 (m), 1203 (m), 1154 (w), 1122 (w), 1082 (w), 1061 (m), 1030 (s), 960 (s), 868 (m) 848 (m), 777 (m), 761 (s), 724 (w), 699 (m), 662 (m), 637 (m), 573 (w). GCMS (EI, 70 eV, m/z > 5 %): 386 ($[M+1]^+$, 1), 385 ($[M]^+$, 3), 329 (10), 328 (50), 281 (19), 280 (100), 254 (21), 243 (10), 242 (32), 241 (6), 29 (5). HRMS Pos (ESI) calculated for $C_{22}H_{25}FNO_4$ $[M+H]^+$ is 386.1762, found 386.1771.

6'-Cyano-2'-fluoro-4'-hexyl-3'-hydroxybiphenyl-2-yl ethyl carbonate (6e): Starting with 4-oxo-4*H*-chromen-3-carbonitrile **4a** (171 mg, 1.0 mmol), Me_3SiOTf (288 mg, 0.23 mL, 1.30 mmol), **3g** (489 mg, 1.30 mmol), CH_2Cl_2 (9 mL), EtOH (10 mL), and triethylamine (202 mg, 0.28 mL, 2 mmol), **6e** was isolated as yellowish white solid (266 mg, 69 %), mp = 88-90 °C. ^{1}H NMR (300.13 MHz, $CDCl_3$): δ = 0.84 (t, J = 7.0 Hz, 3H, CH_3), 1.14 (t, J = 7.2 Hz, 3H, CH_3), 1.23-1.35 (m, 6H, 3CH_2), 1.50-1.60 (m, 2H, CH_2), 2.60 (t, J = 7.6 Hz, 2H, CH_2), 4.10 (q, J = 7.0 Hz, 2H, OCH_2), 6.27 (brs, 1H, OH), 7.26-7.29 (m, 2H, ArH), 7.31-7.36 (m, 2H, ArH), 7.42 (dt, J = 7.0, 2.0 Hz, 1H, ArH). ^{13}C NMR (62.89 MHz, $CDCl_3$): δ = 12.9, 13.0 (CH_3), 21.5, 27.9, 28.0 (CH_2), 28.4 (d, J_{FC} = 2.3 Hz, CH_2), 30.6 (CH_2), 64.0 (OCH_2), 103.1 (d, J_{FC} = 4.5 Hz, C), 116.4 (d, J_{FC} = 3.8 Hz, C), 121.3 (CH), 123.4 (C), 125.0 (d, J_{FC} = 17.8 Hz, C), 125.3 (CH), 129.2 (d, J_{FC} = 3.0 Hz, CH), 129.7, 130.4 (CH), 131.5 (d, J_{FC} = 2.4 Hz, C), 145.1 (d, J_{FC} = 14.8 Hz, C-OH), 146.8 (d, J_{FC} = 239 Hz, C), 147.6 (C), 151.7 (C=O). ^{19}F NMR (282.40 MHz, $CDCl_3$): δ = -138.28 (ArF). IR (ATR, 32 scans, cm^{-1}): $\tilde{\nu}$ = 3251 (br), 2956 (w), 2923 (m), 2853 (w), 2234 (m), 1753 (s), 1614 (m), 1606 (m), 1571 (w), 1511 (w), 1481 (m), 1459 (m), 1431 (m), 1397 (w), 1374 (m), 1284 (m), 1250.13 (s), 1197 (s), 1152 (m), 1107 (m), 1056 (m), 1036 (m), 997 (m), 959 (w), 882 (w), 818 (m), 761 (m), 682 (w), 601 (w), 556 (w). GCMS (EI, 70 eV, m/z > 5 %): 385 ($[M]^+$, 2), 369 (12), 341 (7), 327 (9), 326 (57), 313 (6), 298 (7), 296 (8), 284 (6), 271 (8), 270 (17), 257 (28), 256 (100), 244 (13), 243 (68), 242 (66), 228 (10), 226 (9), 224 (10), 223 (7), 221 (5), 207 (10), 184 (5), 170 (5), 43 (6), 41 (6), 29 (5). HRMS Pos (ESI) calculated for $C_{22}H_{25}FNO_4$ $[M+H]^+$ is 386.1762, found 386.1765.

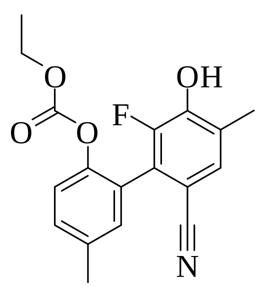


Ethyl 2-(3,7-dimethyl-5-oxo-5*H*-chromeno[2,3-*b*]pyridin-2-yl)-2-fluoroacetate (5f): Starting with 6-methyl-4-oxo-4*H*-chromene-3-carbonitrile **4b** (185mg, 1.0 mmol), Me_3SiOTf (288 mg, 0.23 mL, 1.30 mmol), **3c** (398 mg, 1.30 mmol), CH_2Cl_2 (9 mL), EtOH (10 mL), and triethylamine (202 mg, 0.28 mL, 2 mmol), **5f** was isolated as yellowish white semisolid (56 mg, 17 %). ^{1}H NMR (300.13 MHz, $CDCl_3$): δ = 1.32 (t, J = 7.2 Hz, 3H, CH_3), 2.47



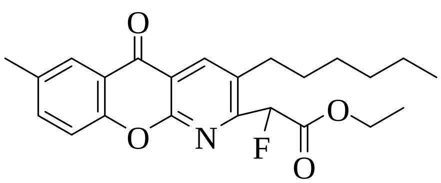
(s, 3H, CH_3), 2.58 (dd, J_{FH} = 2.2, 0.7 Hz, 3H, CH_3), 4.28-4.44 (m, 2H, OCH_2), 6.13 (d, J_{FH} = 48 Hz, 1H, FCH), 7.48 (d, J = 8.3 Hz, 1H, ArH), 7.58 (dd, J = 8.5, 1.9 Hz, 1H, ArH), 8.05 (d, J = 1.7 Hz, 1H, ArH), 8.54 (s, 1H, ArH). ^{13}C NMR (62.89 MHz, $CDCl_3$): δ = 14.0 (CH_3), 17.1 (d, J_{FC} = 1.7 Hz, CH_3), 20.7 (CH_3), 60.3 (OCH_2), 88.6 (d, J_{FC} = 188.6 Hz, FCH), 116.7 (d, J_{FC} = 1.8 Hz, C), 118.2 (CH), 121.1 (C), 125.9 (CH), 130.1, 134.0 (C), 137.0, 139.7 (CH), 153.9 (C), 155.6 (d, J_{FC} = 19.2 Hz, C), 157.8 (C), 166.7 (d, J_{FC} = 25.6 Hz, C=O), 177.1 (C=O). ^{19}F NMR (282.40 MHz, $CDCl_3$): δ = -185.65 (FCH). IR (ATR, 32 scans, cm^{-1}): $\tilde{\nu}$ = 3061 (w), 2995 (w), 2922 (w), 2873 (w), 1763 (s), 1740 (m), 1674 (s), 1633 (w), 1618 (m), 1606 (m), 1564 (w), 1488 (m), 1442 (m), 1417 (m), 1367 (m), 1343 (m), 1333 (m), 1299 (s), 1208 (s), 1150 (w), 1140 (m), 1116 (m), 1052 (s), 1015 (s), 952 (m), 925 (m), 910 (w), 854 (m), 831 (m), 799 (m), 781 (s), 764 (m), 754 (m), 708 (w), 698 (m), 656 (m), 641 (m), 558 (m), 536 (s). GCMS (EI, 70 eV, m/z > 5 %): 330 ($[M+1]^+$, 18), 329 ($[M]^+$, 90), 284 (6), 283 (17), 258 (11), 257 (76), 256 (100), 255 (19), 237 (7), 228 (12), 29 (8). HRMS (EI) calculated for $C_{18}H_{16}FNO_4$ $[M]^+$ is 329.10579, found 329.104969.

6'-Cyano-2'-fluoro-3'-hydroxy-4',5-dimethylbiphenyl-2-yl ethyl carbonate (6f):



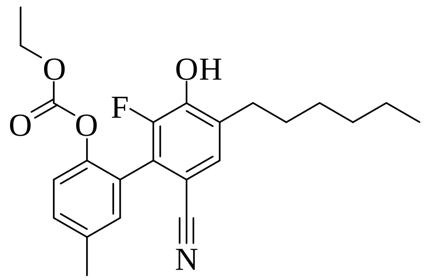
Starting with 6-methyl-4-oxo-4*H*-chromene-3-carbonitrile **4b** (185 mg, 1.0 mmol), Me_3SiOTf (288 mg, 0.23 mL, 1.30 mmol), **3c** (398 mg, 1.30 mmol), CH_2Cl_2 (9 mL), EtOH (10 mL), and triethylamine (202 mg, 0.28 mL, 2 mmol), **6f** was isolated as yellowish white semisolid (207 mg, 63 %). ^{1}H NMR (300 MHz, $(CD_3)_2CO$): δ = 0.82 (t, J = 6.8 Hz, 3H, CH_3), 2.19 (s, 3H, $ArCH_3$), 2.29 (s, 3H, $ArCH_3$), 4.06 (q, J = 7.1 Hz, 2H, OCH_2), 6.37 (brs, 1H, OH), 7.10 (d, J = 1.9 Hz, 1H, ArH), 7.13-7.21 (m, 2H, ArH), 7.23 (d, J = 1.3 Hz, 1H, ArH). ^{13}C NMR (62.89 MHz, $CDCl_3$): δ = 14.3(CH_3), 15.6, 15.7 ($ArCH_3$), 65.3 (OCH_2), 104.4 (d, J_{FC} = 4.5 Hz, C), 119.0 (d, J_{FC} = 3.8 Hz, C), 123.0 (CH), 123.0 (C), 126.1 (d, J_{FC} = 18.1 Hz, C), 130.1 (d, J_{FC} = 3.0 Hz, CH), 131.9, 132.5 (CH), 133.0 (d, J_{FC} = 2.4 Hz, C), 136.0 (C), 146.9 (d, J_{FC} = 15.0 Hz, C-OH), 147.4 (C), 148.9 (d, J_{FC} = 239 Hz, C), 153.5 (C=O); ^{19}F NMR (282 MHz, $(CD_3)_2CO$): δ = 40.56 (ArF). IR (ATR, 32 scans, cm^{-1}): $\tilde{\nu}$ = 3270 (br), 2987 (w), 2920 (w), 2239 (m), 1764 (s), 1621 (w), 1558 (m), 1487 (m), 1464 (m), 1444 (w), 1389 (m), 1368 (m), 1321 (m), 1305 (w), 1276 (w), 1262 (m), 1243 (s), 1225 (s), 1197 (s), 1148 (m), 1126 (m), 1094 (m), 1051 (m), 1040 (m), 1015 (w), 974 (m), 959 (m), 895 (m),879 (m), 825 (m), 810 (m), 779 (m), 759 (w), 738 (w), 703 (w), 667 (m), 633 (br), 596 (w), 580 (m), 561 (w), 546 (m). GCMS (EI, 70 eV, m/z > 5 %): 330 ($[M+1]^+$, 1), 329 ($[M]^+$, 3), 271 (8), 270 (38), 258 (17), 257 (100), 256 (21), 241 (9), 240 (12), 229 (9), 228 (13). HRMS (ESI) calculated for $C_{18}H_{17}FNO_4$ $[M+H]^+$ is 330.1136 found 330.1139.

Ethyl 2-fluoro-2-(3-hexyl-7-methyl-5-oxo-5*H*-chromeno[2,3-*b*]pyridin-2-yl)acetate



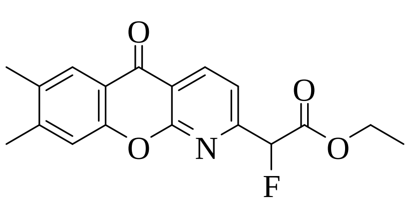
(5g): Starting with 6-methyl-4-oxo-4*H*-chromene-3-carbonitrile **4b** (185 mg, 1.0 mmol), Me_3SiOTf (288 mg, 0.23 mL, 1.30 mmol), **3g** (489 mg, 1.30 mmol), CH_2Cl_2 (9 mL), EtOH (10 mL), and triethylamine (202 mg, 0.28 mL, 2 mmol), **5g** was isolated as white solid (53 mg, 13 %), mp = 80-82 °C. ^{1}H NMR (300.13 MHz, $CDCl_3$): δ = 0.82 (t, J = 7.0 Hz, 3H, CH_3), 1.22 (t, J = 7.1 Hz, 3H, CH_3), 1.24-1.37 (m, 6H, $3CH_2$), 1.58-1.67 (m, 2H, CH_2), 2.40 (s, 3H, $ArCH_3$), 2.76-2.82 (m, 2H, CH_2), 4.21-4.33 (m, 2H, OCH_2), 6.06 (d, J_{FH} = 47.6 Hz, FCH), 7.41 (d, J = 8.5 Hz, 1H, ArH), 7.50 (dd, J = 8.6, 2.0 Hz, 1H, ArH), 8.0 (d, J = 1.0 Hz, 1H, ArH), 8.51 (s, 1H, ArH). ^{13}C NMR (62.89 MHz, $CDCl_3$): δ = 13.0, 13.1 (CH_3), 19.8 ($ArCH_3$), 21.5, 28.1 (CH_2), 29.6 (d, J_{FC} = 1.2 Hz, CH_2), 29.9, 30.5 (CH_2), 61.2 (OCH_2), 86.9 (d, J_{FC} = 189 Hz, FCH), 116.0 (d, J_{FC} = 1.9 Hz, C), 117.3 (CH), 120.1 (C), 125.0 (CH), 133.6, 134.1(C), 136.0, 137.9 (CH), 153.1 (C), 154.4 (d, J_{FC} = 18.7 Hz, C), 156.8 (C), 166.0 (d, J_{FC} = 25.8 Hz, C=O), 176.4 (C=O). ^{19}F NMR (282.40 MHz, $CDCl_3$): δ = -182.09 (FCH). IR (ATR, 32 scans, cm^{-1}): $\tilde{\nu}$ = 3074 (w), 3051 (w), 3022 (w), 2951 (w), 2922 (m), 2855 (w), 1734 (s), 1663 (s), 1619 (m), 1603 (s), 1560 (w), 1488 (m), 1445 (m), 1428 (s), 1324 (m), 1307 (m), 1272 (s), 1255 (s), 1229 (m), 1207 (m), 1140 (m), 1082 (m), 1061 (m), 1030 (m), 969 (w), 953 (w) 831 (m), 790 (m), 772 (m), 739 (m), 703 (w), 640 (m), 543 (m). GCMS (EI, 70 eV, m/z > 5 %): 401 ($[M+2]^+$, 0.5), 400 ($[M+1]^+$, 1), 399 ($[M]^+$, 4), 343 (10), 342 (47), 295 (22), 294 (100), 268 (24), 257 (12), 256 (33), 255 (5), 224 (5), 29 (5). HRMS Pos (ESI) calculated for $C_{23}H_{27}FNO_4$ $[M+H]^+$ is 400.1919, found 400.1919.

6'-Cyano-2'-fluoro-4'-hexyl-3'-hydroxy-5-methylbiphenyl-2-yl ethyl carbonate (6g):



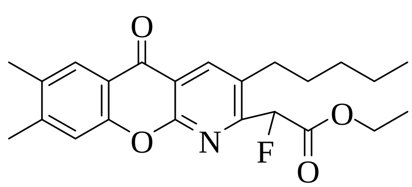
Starting with 6-methyl-4-oxo-4*H*-chromene-3-carbonitrile **4b** (185 mg, 1.0 mmol), Me_3SiOTf (288 mg, 0.23 mL, 1.30 mmol), **3g** (489 mg, 1.30 mmol), CH_2Cl_2 (9 mL), EtOH (10 mL), and triethylamine (202 mg, 0.28 mL, 2 mmol), **6g** was isolated as yellowish white solid (279 mg, 70 %), mp = 103-105 °C. ^{1}H NMR (300.13 MHz, $CDCl_3$): δ = 0.82 (t, J = 6.8 Hz, 3H, CH_3), 1.11 (t, J = 7.2 Hz, 3H, CH_3), 1.21-1.30 (m, 6H, 3CH_2), 1.53 (p, J = 7.2 Hz, 2H, CH_2), 2.29 (s, 3H, ArCH_3), 2.57 (d, J = 7.6 Hz, 2H, CH_2), 4.06 (q, J = 7.1 Hz, 2H, OCH_2), 6.37 (brs, 1H, OH), 7.10 (d, J = 1.9 Hz, 1H, ArH), 7.13-7.21 (m, 2H, ArH), 7.23 (d, J = 1.3 Hz, 1H, ArH). ^{13}C NMR (62.89 MHz, $CDCl_3$): δ = 12.9, 13.0 (CH_3), 14.3 (ArCH_3), 19.7 (CH_2), 21.5, 27.9, 28.0 (CH_2), 28.3 (d, J_{FC} = 2.3 Hz, CH_2), 30.6 (CH_2), 63.9 (OCH_2), 103.0 (d, J_{FC} = 4.5 Hz, C), 116.4 (d, J_{FC} = 3.8 Hz, C), 120.9 (CH), 123.0 (C), 125.1 (d, J_{FC} = 18.1 Hz, C), 129.1 (d, J_{FC} = 3.0 Hz, CH), 130.2, 130.7 (CH), 131.3 (d, J_{FC} = 2.4 Hz, C), 135.0 (C), 145.1 (d, J_{FC} = 15.0 Hz, C-OH), 145.4 (C), 146.9 (d, J_{FC} = 239 Hz, C), 151.9 (C=O). ^{19}F NMR (282.40 MHz, $CDCl_3$): δ = -138.19 (ArF). IR (ATR, 32 scans, cm^{-1}): $\tilde{\nu}$ = 3283 (br), 2951 (w), 2925 (w), 2856 (W), 2231 (m), 1760 (s), 1614 (w), 1576 (w), 1462 (m), 1448 (m), 1441 (m), 1390 (w), 1368 (w), 1329 (w), 1296 (m), 1265 (w), 1237 (s), 1195 (s), 1140 (m), 1096 (m), 1049 (m), 1020 (w), 973 (m), 878 (w), 828 (m), 775 (m), 745 (w), 697 (w), 632 (br), 578 (m). GCMS (EI, 70 eV, m/z > 5 %): 400 ($[M+1]^+$, 1), 399 ($[M]^+$, 2), 355 (11), 341 (13), 340 (57), 327 (14), 326 (7), 310 (12), 298 (10), 284 (20), 282 (9), 271 (31), 270 (100), 258 (11), 257 (67), 256 (51), 242 (11), 238 (11), 29 (9). HRMS (EI) calculated for $C_{23}H_{26}FNO_4$ $[M]^+$ is 399.18404, found 399.185087.

Ethyl 2-(7,8-dimethyl-5-oxo-5*H*-chromeno[2,3-*b*]pyridin-2-yl)-2-fluoroacetate (5h):



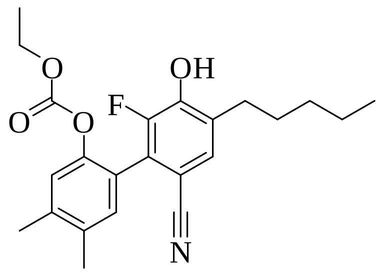
Starting with 6,7-dimethyl-4-oxo-4*H*-chromene-3-carbonitrile **4c** (198 mg, 1.0 mmol), Me_3SiOTf (288 mg, 0.235 mL, 1.30 mmol), **3a** (380 mg, 1.30 mmol), CH_2Cl_2 (9 mL), EtOH (10 mL), and triethylamine (202 mg, 0.28 mL, 2 mmol), **5h** was isolated as a yellow solid (151 mg, 46 %), mp = 134-136°C. ^{1}H NMR (250.13 MHz, $CDCl_3$): δ = 1.22 (t, J= 7.1 Hz, 3H, CH_3), 2.29 (s, 3H, CH_3), 2.34 (s, 3H, CH_3), 4.16-4.30 (m, 2H, OCH_2), 5.89 (d, 1H, J_{FH} = 47.5 Hz, FCH), 7.27 (s, 1H, ArH), 7.57 (d, J= 7.9 Hz, 1H, ArH), 7.92 (s, 1H, ArH), 8.70 (d, J = 7.9 Hz, 1H, ArH). ^{13}C NMR (62.89 MHz, $CDCl_3$): δ = 14.0 (CH_3), 19.2, 20.7 ($ArCH_3$), 62.5 (OCH_2), 89.4 (d, J_{FC} = 188.1 Hz, FCH), 116.9 (C), 117.7 (d, J_{FC} = 5.12 Hz, 1H, CH), 118.6 (CH), 119.3 (C), 126.3 (CH), 134.2 (C), 138.8 (CH), 146.8, 154.1 (C), 157.9 (d, J_{FC} = 24.3 Hz, C), 159.6 (d, J_{FC} = 2.3 Hz, C), 166.4 (d, J_{FC} = 25.7 Hz, C=O), 176.7 (C=O). ^{19}F NMR (282.40 MHz, $CDCl_3$): δ = -181.09 (FCH). IR (ATR, 32 scans, cm^{-1}): $\tilde{\nu}$ = 3067 (w), 2958 (w), 2920 (w), 1745 (s), 1658 (s), 1625 (s), 1602 (s), 1582 (m), 1562 (m), 1460 (m), 1422 (s), 1398 (s), 1367 (s), 1275 (s), 1207 (s), 1184 (s), 1089 (s), 1010 (s), 870 (s), 791 (s), 761 (m), 601 (m). GCMS (EI, 70 eV, m/z > 5 %): 329 ($[M]^+$, 65), 330 (13), 329 (65), 258 (16), 257 (100), 256 (45), 228 (42), 214 (5), 213 (10), 184 (3), 128 (4), 91 (4), 77 (3), 29 (16). HRMS (EI) calculated for $C_{18}H_{16}NFO_4$ $[M]^+$ is 329.10579, found 329.105736.

Ethyl 2-(7,8-dimethyl-5-oxo-3-pentyl-5*H*-chromeno[2,3-*b*]pyridin-2-yl)-2-fluoroacetate (5j):



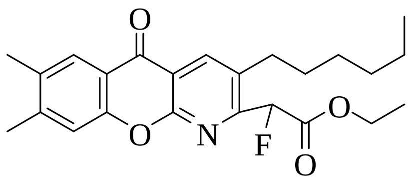
Starting with 6,7-dimethyl-4-oxo-4*H*-chromene-3-carbonitrile **4c** (199 mg, 1.0 mmol), Me_3SiOTf (288 mg, 0.23 mL, 1.30 mmol), **3f** (471 mg, 1.30 mmol), CH_2Cl_2 (9 mL), EtOH (10 mL), and triethylamine (202 mg, 0.28 mL, 2 mmol), **5j** was isolated as yellowish white semisolid (48 mg, 12 %). ^{1}H NMR (300.13 MHz, $CDCl_3$): δ = 0.94 (t, J = 7.0 Hz, 3H, CH_3), 1.32 (t, J = 7.1 Hz, 3H, CH_3), 1.37-1.46 (m, 4H, $2CH_2$), 1.68-1.79 (m, 2H, CH_2), 2.40 (s, 3H, $ArCH_3$), 2.45 (s, 3H, $ArCH_3$), 2.85-2.91 (m, 2H, CH_2), 4.28-4.45 (m, 2H, OCH_2), 6.15 (d, J_{FH} = 48 Hz, FCH), 7.38 (s, 1H, ArH), 8.05 (s, 1H, ArH), 8.61 (s, 1H, ArH). ^{13}C NMR (75.47 MHz, $CDCl_3$): δ = 14.0, 14.1 (CH_3), 19.2, 20.7 ($ArCH_3$), 22.4, 30.6, 30.7, 31.6 (CH_2), 62.2 (OCH_2), 88.0 (d, J_{FC} = 188.7 Hz, FCH), 117.2 (d, J_{FC} = 1.7 Hz, C), 118.7 (CH), 119.3 (C), 126.3 (CH), 134.0, 135.0 (C), 138.9 (CH), 146.8, 154.4 (C), 155.1 (d, J_{FC} = 18.7 Hz, C), 157.8 (C), 167.2 (d, J_{FC} = 25.9 Hz, C=O), 177.2 (C=O). ^{19}F NMR (282.40 MHz, $CDCl_3$): δ = -181.98 (FC). IR (ATR, 32 scans, cm^{-1}): $\tilde{\nu}$ = 3048 (w), 2956 (m), 2925 (m), 2873 (m), 2856 (m), 1767 (s), 1659 (s), 1625 (s), 1601 (s), 1555 (w), 1464 (m), 1424 (s), 1372 (m), 1340 (m), 1296 (m), 1276 (m), 1255 (m), 1215 (s), 1165 (m), 1138 (m), 1093 (m), 1066 (s), 1055 (m), 1016 (m), 953 (m), 897 (m), 859 (m), 802 (m), 789 (m), 771 (m), 741 (m), 728 (m), 705 (m), 663 (m), 606 (m), 582 (m), 550 (m). GCMS (EI, 70 eV, m/z > 5 %): 400 ($[M+1]^+$, 10), 399 ($[M]^+$, 21), 357 (7), 356 (100), 295 (10), 294 (85), 283 (9), 282 (25), 271 (17), 270 (38), 29 (5). HRMS (EI) calculated for $C_{23}H_{26}FNO_4$ $[M]^+$ is 399.18404, found 399.182860.

6'-Cyano-2'-fluoro-3'-hydroxy-4,5-dimethyl-4'-pentylbiphenyl-2-yl ethyl carbonate (6j): Starting with 6,7-dimethyl-4-oxo-4*H*-chromene-3-carbonitrile **4c** (199 mg, 1.0 mmol), Me_3SiOTf (288 mg, 0.23 mL, 1.30 mmol), **3f** (471 mg, 1.30 mmol), CH_2Cl_2 (9 mL), EtOH (10 mL), and triethylamine (202 mg, 0.28 mL, 2 mmol), **6j** was isolated as yellowish white semisolid (283 mg, 71 %).



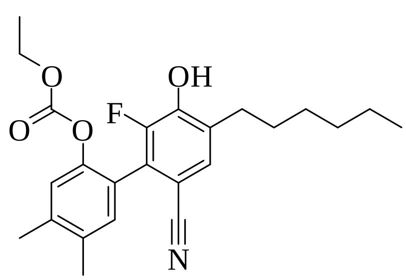
^{1}H NMR (300.13 MHz, $CDCl_3$): δ = 0.94 (t, J = 6.8 Hz, 3H, CH_3), 1.24 (t, J = 7.2 Hz, 3H, CH_3), 1.34-1.42 (m, 4H, $2CH_2$), 1.61-1.71 (m, 2H, CH_2), 2.31 (s, 3H, $ArCH_3$), 2.34 (s, 3H, $ArCH_3$), 2.70 (dd, J = 8.6, 6.7 Hz, 2H, CH_2), 4.18 (q, J = 7.0 Hz, 2H, OCH_2), 5.98 (brs, 1H, OH), 7.16 (d, J = 2.5 Hz, 1H, ArH), 7.17 (s, 1H, ArH), 7.34 (d, J = 1.5 Hz, 1H, ArH). ^{13}C NMR (75.47 MHz, $CDCl_3$): δ = 13.9, 14.1 (CH_3), 19.2, 19.9 ($ArCH_3$), 22.4, 28.8 (CH_2), 29.3 (d, J_{FC} = 2.3 Hz, CH_2), 31.2 (CH_2), 64.8 (OCH_2), 104.6 (d, J_{FC} = 4.6 Hz, C), 117.6 (d, J_{FC} = 4.0 Hz, C), 121.3 (C), 123.1 (CH), 126.2 (d, J_{FC} = 18 Hz, C), 130.1 (d, J_{FC} = 3.2 Hz, CH), 131.9 (CH), 132.1 (d, J_{FC} = 2.3 Hz, C), 134.8, 139.6 (C), 146.0 (d, J_{FC} = 15.1 Hz, C-OH), 146.4 (C), 148.0 (d, J_{FC} = 239 Hz, C), 152.0 (C=O). ^{19}F NMR (282.40 MHz, $(CD_3)_2CO$): δ = -139.18 (ArF). IR (ATR, 32 scans, cm^{-1}): $\tilde{\nu}$ = 3306 (br), 2955 (m), 2926 (m), 2859 (m), 2224 (m), 1762 (s), 1663 (w), 1611 (m), 1516 (m), 1485 (m), 1444 (s), 1387 (m), 1368 (m), 1224 (s), 1184 (s), 1094 (m), 1049 (s), 1001 (s), 886 (m), 860 (m), 778 (m), 737 (m), 662 (w), 606 (s), 580 (m). GCMS (EI, 70 eV, m/z > 5 %): 399 ($[M]^+$, 6), 355 (13), 354 (5), 341 (18), 340 (64), 327 (39), 310 (24), 298 (10), 285 (21), 284 (63), 282 (10), 272 (12), 271 (40), 270 (100), 256 (18), 254 (14), 253 (6), 252 (8), 240 (6), 209 (6), 207 (11), 191 (7), 177 (7), 44 (12), 29 (13). HRMS (EI) calculated for $C_{23}H_{26}FNO_4$ $[M]^+$ is 399.18404, found 399.183733.

Ethyl 2-fluoro-2-(3-hexyl-7,8-dimethyl-5-oxo-5*H*-chromeno[2,3-*b*]pyridin-2-yl)acetate (5k):



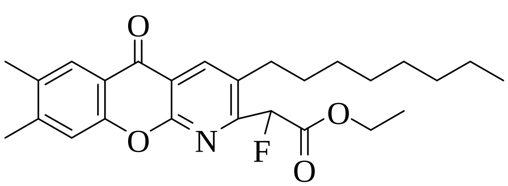
Starting with 6,7-dimethyl-4-oxo-4*H*-chromene-3-carbonitrile **4c** (199 mg, 1.0 mmol), Me_3SiOTf (288 mg, 0.23 mL, 1.30 mmol), **3g** (489 mg, 1.30 mmol), CH_2Cl_2 (9 mL), EtOH (10 mL), and triethylamine (202 mg, 0.28 mL, 2 mmol), **5k** was isolated as yellowish white solid (37 mg, 9 %), mp = 90-92 °C. ^{1}H NMR (300.13 MHz, $CDCl_3$): δ = 0.82 (t, *J* = 7.0 Hz, 3H, CH_3), 1.22 (t, *J* = 7.1 Hz, 3H, CH_3), 1.23-1.37 (m, 6H, $3CH_2$), 1.57-1.66 (m, 2H, CH_2), 2.29 (s, 3H, $ArCH_3$), 2.33 (s, 3H, $ArCH_3$), 2.75-2.81 (m, 2H, CH_2), 4.21-4.33 (m, 2H, OCH_2), 6.05 (d, J_{FH} = 47.7 Hz, CH), 7.27 (s, 1H, ArH), 7.93 (s, 1H, ArH), 8.50 (s, 1H, ArH). ^{13}C NMR (62.89 MHz, $CDCl_3$): δ = 13.0, 13.1 (CH_3), 18.2, 19.7 ($ArCH_3$), 21.5, 28.1 (CH_2), 29.6 (d, J_{FC} = 1.2 Hz, CH_2), 29.9, 30.5 (CH_2), 61.2 (OCH_2), 86.9 (d, J_{FC} = 188.8 Hz, FCH), 116.1 (d, J_{FC} = 2.0 Hz, C), 117.6 (CH), 118.3 (C), 125.3 (CH), 132.9, 134.0 (C), 137.8 (CH), 145.7, 153.3 (C), 154.0 (d, J_{FC} = 18.9 Hz, C), 156.7 (C), 166.1 (d, J_{FC} = 25.8 Hz, C=O), 176.1 (C=O). ^{19}F NMR (282.40 MHz, $CDCl_3$): δ = -181.96 (FCH). IR (ATR, 32 scans, cm^{-1}): $\tilde{\nu}$ = 3048 (w), 2983 (w), 2951 (m), 2923 (m), 2852 (m), 1764 (s), 1659 (s), 1625 (m), 1600 (s), 1556 (w), 1464 (m), 1443 (m), 1424 (s), 1372 (m), 1338 (m), 1299 (w), 1273 (w), 1258 (m), 1215 (s), 1166 (w), 1092 (m), 1069 (m), 1053 (m), 1017 (m), 965 (w), 860 (m) 801 (m), 769 (m), 721 (m), 603 (w). GCMS (EI, 70 eV, m/z > 5 %): 414 ($[M+1]^+$, 1), 413 ($[M]^+$, 4), 412 (2), 357 (12), 356 (49), 309 (23), 308 (100), 282 (20), 271 (9), 270 (27), 238 (5), 29 (4). HRMS Pos (ESI) calculated for $C_{24}H_{29}FNO_4$ $[M+H]^+$ is 414.2075, found 414.2086.

6'-Cyano-2'-fluoro-4'-hexyl-3'-hydroxy-4,5-dimethylbiphenyl-2-yl ethyl carbonate (6k):



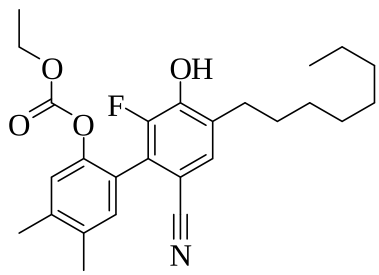
Starting with 6,7-dimethyl-4-oxo-4*H*-chromen-3-carbonitrile **4c** (199 mg, 1.0 mmol), Me_3SiOTf (288 mg, 0.23 mL, 1.30 mmol), **3g** (489 mg, 1.30 mmol), CH_2Cl_2 (9 mL), EtOH (10 mL), and triethylamine (202 mg, 0.28 mL, 2 mmol), **6k** was isolated as yellowish white solid (301 mg, 73 %), mp = 128-130 °C. ^{1}H NMR (300.13 MHz, $CDCl_3$): δ = 0.84 (t, *J* = 6.7 Hz, 3H, CH_3), 1.14 (t, *J* = 7.2 Hz, 3H, CH_3), 1.23-1.32 (m, 6H, $3CH_2$), 1.55 (p, *J* = 7.5 Hz, 2H, CH_2), 2.21 (s, 3H, $ArCH_3$), 2.24 (s, 3H, $ArCH_3$), 2.59 (t, J = 7.8 Hz, 2H, CH_2), 4.08 (q, J = 7.1 Hz, 2H, OCH_2), 6.27 (brs, 1H, OH), 7.06 (s, 1H, ArH), 7.08 (s, 1H, ArH), 7.24 (s, 1H, ArH). ^{13}C NMR (62.89 MHz, $CDCl_3$): δ = 12.9, 13.0 (CH_3), 18.1, 18.8 ($ArCH_3$), 21.5, 27.9, 28.0 (CH_2), 28.3 (d, J_{FC} = 2.3 Hz, CH_2), 30.6 (CH_2), 63.8 (OCH_2), 103.3 (d, J_{FC} = 4.6 Hz, C), 116.6 (d, J_{FC} = 4.0 Hz, C), 120.3 (C), 122.1 (CH), 125.2 (d, J_{FC} = 18 Hz, C), 129.1 (d, J_{FC} = 3.2 Hz, CH), 130.9 (CH), 131.1 (d, J_{FC} = 2.3 Hz, C), 133.8, 138.6 (C), 145.0 (d, J_{FC} = 15.1 Hz, C-OH), 145.4 (C), 147.0 (d, J_{FC} = 239 Hz, C), 152.0 (C=O). ^{19}F NMR (282.40 MHz, $CDCl_3$): δ = -138.47 (ArF). IR (ATR, 32 scans, cm^{-1}): $\tilde{\nu}$ = 3286 (br), 2954 (w), 2924 (m), 2857 (w), 2231 (m), 1763 (s), 1611 (m), 1580 (w), 1516 (w), 1488 (m), 1437 (s), 1387 (w), 1369 (m), 1325 (w), 1294 (m), 1227 (s), 1180 (s), 1094 (m), 1049 (m), 1003 (m), 980 (m), 886 (w), 853 (w), 642 (br), 584 (w), 570 (w). GCMS (EI, 70 eV, m/z > 5 %): 413 ($[M]^+$, 6), 369 (15), 355 (16), 354 (67), 341 (16), 324 (12), 312 (11), 299 (10), 298 (23), 296 (10), 285 (32), 284 (100), 272 (13), 271 (70), 270 (67), 256 (14), 254 (10), 252 (11), 29 (9). HRMS (EI) calculated for $C_{24}H_{28}FNO_4$ $[M]^+$ is 413.19969, found 413.199288.

Ethyl 2-(7,8-dimethyl-3-octyl-5-oxo-5*H*-chromeno[2,3-*b*]pyridin-2-yl)-2-fluoroacetate (5l): Starting with 6,7-dimethyl-4-oxo-4*H*-chromene-3-carbonitrile **4c** (199 mg, 1.0 mmol), Me_3SiOTf (288 mg, 0.23 mL, 1.30 mmol), **3h** (526 mg, 1.30 mmol), CH_2Cl_2 (9 mL), EtOH (10 mL), and triethylamine (202 mg, 0.28 mL, 2 mmol), **5l** was isolated as yellowish white semisolid (62 mg, 14 %).

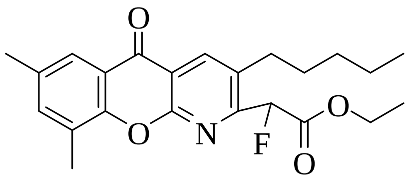


^{1}H NMR (300.13 MHz, $CDCl_3$): δ = 0.91 (t, J = 6.8 Hz, 3H, CH_3), 1.32 (t, J = 7.2 Hz, 3H, CH_3), 1.28-1.49 (m, 10H, $5CH_2$), 1.68-1.78 (m, 2H, CH_2) 2.39 (s, 3H, $ArCH_3$), 2.44 (s, 3H, $ArCH_3$), 2.83-2.89 (m, 2H, CH_2), 4.29-4.41 (m, 2H, OCH_2), 6.13 (d, J_{FH} = 47.8 Hz, 1H, CH), 7.38 (s, 1H, ArH), 8.34 (s, 1H, ArH), 8.59 (s, 1H, ArH). ^{13}C NMR (62.89 MHz, $CDCl_3$): δ = 14.0, 14.1(CH_3), 19.2, 20.7 ($ArCH_3$), 22.6, 29.1, 29.3, 29.4 (CH_2), 30.6 (d, J_{FC} = 1.4 Hz, CH_2), 31.0, 31.8 (CH_2), 62.2 (OCH_2), 87.9 (d, J_{FC} = 188.6 Hz, FCH), 117.2 (d, J_{FC} = 1.8 Hz, C), 118.6 (CH), 119.3 (C), 126.3 (CH), 134.0, 135.0 (C), 138.8 (CH), 146.7, 154.4 (C), 155.0 (d, J_{FC} = 18.8 Hz, C), 157.8 (C), 167.1 (d, J_{FC} = 26.1 Hz, C=O), 177.2 (C=O). ^{19}F NMR (282.40 MHz, $CDCl_3$): δ = -181.97 (FCH). IR (ATR, 32 scans, cm^{-1}): $\tilde{\nu}$ = 3094 (w), 2953 (m), 2923 (m), 2854 (m), 1762 (m), 1742 (m), 1665 (s), 1624 (s), 1605 (s), 1554 (m), 1463 (s), 1441 (s), 1424 (s), 1371 (m), 1339 (m), 1274 (m), 1255 (m), 1206 (s), 1165 (m), 1138 (m), 1072 (m), 1021 (m), 967 (m), 941 (m), 898 (w), 860 (m), 798 (m) 757 (m), 738 (m),706 (m), 677 (m), 611 (m), 604 (m), 586 (w), 555 (w). GCMS (EI, 70 eV, m/z > 5 %): 441 ($[M]^+$, 9), 358 (8), 357 (12), 356 (37), 337 (14), 336 (100), 283 (7), 282 (19), 280 (11), 271 (15), 270 (32), 269 (7), 238 (11). HRMS (EI) calculated for $C_{26}H_{33}FNO_4$ $[M+H]^+$ is 442.23881, found 442.23886.

6'-Cyano-2'-fluoro-3'-hydroxy-4,5-dimethyl-4'-octylbiphenyl-2-yl ethyl carbonate (6l): Starting with 6,7-dimethyl-4-oxo-4*H*-chromene-3-carbonitrile **4c** (199 mg, 1.0 mmol), Me_3SiOTf (288 mg, 0.23 mL, 1.30 mmol), **3h** (526 mg, 1.30 mmol), CH_2Cl_2 (9 mL), EtOH (10 mL), and triethylamine (202 mg, 0.28 mL, 2 mmol), **6l** was isolated as semi solid (295 mg, 67 %). ^{1}H NMR (300.13 MHz, $CDCl_3$): δ = 0.91 (t, *J* = 6.8 Hz, 3H, CH_3), 1.24 (t, *J* = 7.0 Hz, 3H, CH_3), 1.28-1.43 (m, 8H, $4CH_2$), 1.60-1.70 (m, 4H, $2CH_2$), 2.32 (s, 3H, $ArCH_3$), 2.34 (s, 3H, $ArCH_3$), 2.70 (dd, *J* = 8.9, 6.6 Hz, 2H, CH_2), 4.18 (q, *J* = 7.0 Hz, 2H, OCH_2), 5.85 (brs, 1H, OH), 7.16 (s, 1H, ArH), 7.17 (s, 1H, ArH), 7.34 (d, *J* = 1.5 Hz, 1H, ArH). ^{13}C NMR (62.89 MHz, $CDCl_3$): δ = 14.0, 14.1 (CH_3), 19.2, 19.9 ($ArCH_3$), 22.6, 29.1, 29.2, 29.3 (CH_2), 29.4 ($2CH_2$), 31.8 (CH_2), 64.8 (OCH_2), 104.7 (d, J_{FC} = 5.0 Hz, C), 117.5 (d, J_{FC} = 4.0 Hz, C), 121.2 (C), 123.1 (CH), 126.2 (d, J_{FC} = 18.3 Hz, C), 130.2 (d, J_{FC} = 3.2 Hz, CH), 131.9 (CH), 132.0 (d, J_{FC} = 2.3 Hz, C), 134.8, 139.7 (C), 145.7 (d, J_{FC} = 15.1 Hz, C-OH), 146.4 (C), 147.9 (d, J_{FC} = 238.5 Hz, C), 152.9 (C=O). ^{19}F NMR (282.40 MHz, $CDCl_3$): δ = -139.34 (ArF). IR (ATR, 32 scans, cm^{-1}): $\tilde{\nu}$ = 3305 (br), 2953 (m), 2923 (m), 2854 (m), 2225 (w), 1762 (s), 1665 (w), 1612 (m), 1514 (w), 1484 (m), 1444 (m), 1387 (w), 1368 (m), 1224 (s), 1184 (s), 1093 (m), 1048 (m), 1002 (m), 886 (m), 864 (m), 778 (m), 737 (m), 722 (m), 665 (w), 606 (m), 581 (w). GCMS (EI, 70 eV, m/z > 5 %): 442 ($[M+1]^+$, 2), 441 ($[M]^+$, 4), 397 (17), 383 (13), 382 (51), 369 (11), 368 (11), 354 (12), 352 (15), 340 (15), 326 (12), 312 (15), 299 (18), 298 (19), 296 (20), 285 (33), 284 (86), 272 (18), 271 (100), 270 (36), 256 (9), 254 (10), 250.13 (7), 29 (10). HRMS (EI) calculated mass for $C_{26}H_{32}FNO_4$ $[M]^+$ is 441.23099, found 441.232117.

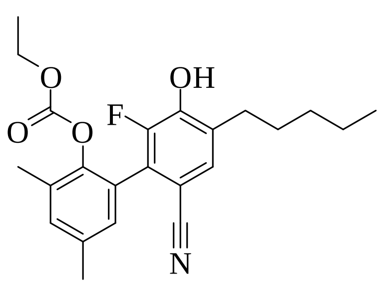


Ethyl 2-(7,9-dimethyl-5-oxo-3-pentyl-5*H*-chromeno[2,3-*b*]pyridin-2-yl)-2-fluoroacetate (5m):



Starting with 6,8-dimethyl-4-oxo-4*H*-chromene-3-carbonitrile **4d** (199 mg, 1.0 mmol), Me_3SiOTf (288 mg, 0.23 mL, 1.30 mmol), **3f** (471 mg, 1.30 mmol), CH_2Cl_2 (9 mL), EtOH (10 mL), and triethylamine (202 mg, 0.28 mL, 2 mmol), **5m** was isolated as white solid (48 mg, 12 %), mp = 104-106 °C. ^1H NMR (300.13 MHz, $CDCl_3$): δ = 0.85 (t, J = 7.2 Hz, 3H, CH_3), 1.24 (t, J = 7.1 Hz, 3H, CH_3), 1.30-1.36 (m, 4H, $2CH_2$), 1.60-1.67 (m, 2H, CH_2), 2.36 (s, 3H, $ArCH_3$), 2.50 (s, 3H, $ArCH_3$), 2.75-2.81 (m, 2H, CH_2), 4.24-4.32 (m, 2H, OCH_2), 6.07 (d, J_{FH} = 47.9 Hz, CH), 7.36 (s, 1H, ArH), 7.85 (s, 1H, ArH), 8.51 (s, 1H, ArH). ^{13}C NMR (75.47 MHz, $CDCl_3$): δ = 12.9, 13.0 (CH_3), 14.9, 19.7 ($ArCH_3$), 21.4 (CH_2), 29.5 (d, J_{FC} = 1.3 Hz, CH_2), 29.6, 30.5 (CH_2), 61.3 (OCH_2), 87.1 (d, J_{FC} = 188 Hz, FCH), 115.7 (d, J_{FC} = 2.0 Hz, C), 120.0 (C), 122.5 (CH), 126.6, 132.9, 134.0 (C), 137.1, 137.7 (CH), 151.5 (C), 154.2 (d, J_{FC} = 19.1 Hz, C), 156.7 (C), 166.1 (d, J_{FC} = 25.4 Hz, C=O), 176.7 (C=O). ^{19}F NMR (282 MHz, CDCl3): δ = -181.97 (FCH). IR (ATR, 32 scans, cm^{-1}): $\tilde{\nu}$ = 3050 (w), 3013 (w), 2954 (w), 2925 (m), 2871 (w), 2857 (w), 1750 (w), 1724 (s), 1666 (s), 1607 (m), 1598 (m), 1562 (w), 1477 (m), 1427 (s), 1371 (m), 1343 (w), 1326 (m), 1313 (m), 1296 (w), 1261 (s), 1238 (m), 1196 (m), 1152 (m), 1114 (w), 1069 (w), 1023 (s), 951 (w), 869 (w), 792 (m), 768 (m), 659 (w), 555 (w). GCMS (EI, 70 eV, m/z > 5 %): 400 ($[M+1]^+$, 7), 399 ($[M]^+$, 25), 357 (23), 356 (100), 295 (19), 294 (89), 282 (33), 271 (12), 270 (44), 238 (8), 29 (7). HRMS (EI) calculated for $C_{28}H_{36}FNO_4$ $[M]^+$ is 399.18404, found 399.184778.

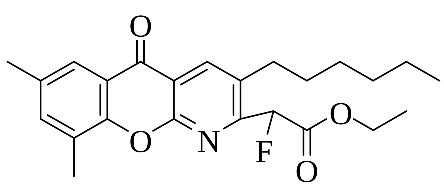
6'-Cyano-2'-fluoro-3'-hydroxy-3,5-dimethyl-4'-pentylbiphenyl-2-yl ethyl carbonate (6m):



Starting with 6,8-dimethyl-4-oxo-4*H*-chromene-3-carbonitrile **4d** (199 mg, 1.0 mmol), Me_3SiOTf (288 mg, 0.23 mL, 1.30 mmol), **3f** (471 mg, 1.30 mmol), CH_2Cl_2 (9 mL), EtOH (10 mL), and triethylamine (202 mg, 0.28 mL, 2 mmol), **6m** was isolated as yellowish white solid (279 mg, 70 %), mp = 114-116 °C. ^1H NMR (300.13 MHz, $CDCl_3$): δ = 0.85 (t, J = 6.8 Hz, 3H, CH_3), 1.04 (t, J = 7.1 Hz, 3H, CH_3), 1.12-1.29 (m, 4H, $2CH_2$), 1.55 (p, J = 7.3 Hz, 2H, CH_2), 2.18 (s, 3H, $ArCH_3$), 2.28 (s, 3H, $ArCH_3$), 2.59 (t, 2H, J = 7.7 Hz,

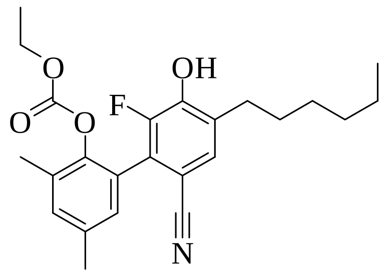
CH_2), 4.02 (q, *J* = 7.1 Hz, 2H, OCH_2), 6.10 (brs, 1H, OH), 6.94 (s, 1H, ArH), 7.08 (s, 1H, ArH), 7.19 (s, 1H, ArH). ^{13}C NMR (62.89 MHz, $CDCl_3$): δ = 13.0 (2CH_3), 15.2, 19.7 ($ArCH_3$), 21.5, 27.8 (CH_2), 28.3 (d, J_{FC} = 2.3 Hz, CH_2), 30.5 (CH_2), 63.8 (OCH_2), 103.6 (d, J_{FC} = 4.6 Hz, C), 116.4 (d, J_{FC} = 3.7 Hz, C), 123.7 (C), 125.5 (d, J_{FC} = 18 Hz, C), 128.2 (CH), 129.0 (d, J_{FC} = 3.0 Hz, CH), 129.8, 131.1, 132.3, 135.0 (C), 144.6 (d, J_{FC} = 15 Hz, C), 146.8 (d, J_{FC} = 239 Hz, C), 151.4 (C=O). ^{19}F NMR (282.40 MHz, $CDCl_3$): δ = -138.40 (ArF). IR (ATR, 32 scans, cm^{-1}): $\tilde{\nu}$ = 3297 (br), 2957 (w), 2927 (m), 2858 (m), 2230 (m), 1763 (s), 1661 (w), 1605 (w), 1580 (w), 1466 (m), 1446 (m), 1369 (m), 1330 (w), 1304 (w), 1245 (s), 1195 (s), 1146 (m), 1094 (m), 1052 (m), 995 (m), 973 (m), 903 (w), 859 (m), 781 (m), 733 (w), 666 (w), 645 (w), 565 (w). GCMS (EI, 70 eV, m/z > 5 %): 399 ($[M]^+$, 7), 356 (5), 355 (21), 354 (5), 341 (21), 340 (93), 328 (13), 327 (58), 326 (12), 313 (3), 312 (8), 311 (8), 310 (35), 299 (5), 298 (13), 286 (6), 285 (32), 284 (98), 271 (50), 270 (100), 268 (5), 257 (7), 256 (22), 252 (17), 250.13 (11), 208 (5), 43 (7), 29 (14). HRMS (EI) calculated mass for $C_{23}H_{26}FNO_4$ $[M]^+$ is 399.18404, found 399.183995.

Ethyl 2-fluoro-2-(3-hexyl-7,9-dimethyl-5-oxo-5*H*-chromeno[2,3-*b*]pyridin-2-yl)acetate (5n): Starting with 6,8-dimethyl-4-oxo-4*H*-chromene-3-carbonitrile **4d** (199 mg, 1.0 mmol), Me_3SiOTf (288 mg, 0.23 mL, 1.30 mmol), **3g** (489 mg, 1.30 mmol), CH_2Cl_2 (9 mL), EtOH (10 mL), and triethylamine (202 mg, 0.28 mL, 2 mmol), **5n** was isolated as white solid (41 mg, 10 %), mp = 79-81 °C. ^{1}H NMR (300.13 MHz, $CDCl_3$): δ = 0.82 (t, *J* = 7.1 Hz, 3H, CH_3), 1.24 (t, *J* = 7.2 Hz, 3H, CH_3), 1.25-1.37 (m, 6H, 3CH_2), 1.58-1.66 (m, 2H, CH_2), 2.34 (s, 3H, $ArCH_3$), 2.49 (s, 3H, $ArCH_3$), 2.75-2.81 (m, 2H, CH_2), 4.24-4.32 (m, 2H, OCH_2), 6.07 (d, J_{FH}= 47.4 Hz, FCH), 7.34 (s, 1H, ArH), 7.84 (s, 1H, ArH), 8.50 (s, 1H, ArH). ^{13}C NMR (62.89 MHz, $CDCl_3$): δ = 13.0, 13.1 (CH_3), 15.0, 19.7 ($ArCH_3$), 21.5, 28.1 (CH_2), 29.6 (d, J_{FC} = 1.3 Hz, CH_2), 29.9, 30.5 (CH_2), 61.2 (OCH_2), 87.1 (d, J_{FC} = 189 Hz, FCH), 115.8 (d, J_{FC} = 2.0 Hz, C), 120.0 (C), 122.6 (CH), 126.7, 132.9, 134.0 (C), 137.1, 137.8 (CH), 151.5 (C), 154.3 (d, J_{FC} = 19.3 Hz, C), 156.7 (C), 166.1 (d, J_{FC} = 25.6 Hz, C=O), 176.7 (C=O). ^{19}F NMR (282 MHz, $CDCl_3$): δ = -181.96 (FCH). IR (ATR, 32 scans, cm^{-1}): $\tilde{\nu}$ = 2953 (m), 2920 (m), 2854 (m), 1762 (s), 1755 (s), 1667 (s), 1599



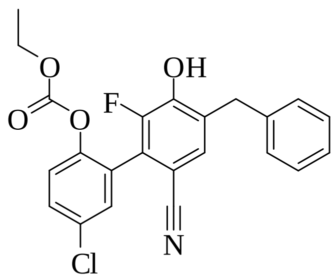
(s), 1468 (m), 1437 (s), 1426 (s), 1371 (m), 1344 (w), 1305 (m), 1271 (w), 1213 (s), 1202 (s), 1110 (w), 1061 (s), 1019 (w), 941 (w), 886 (w), 848 (w), 799 (m) 771 (m), 681 (m), 585 (m), 531 (w). GCMS (EI, 70 eV, m/z > 5 %): 413 ($[M]^+$, 5), 357 (14), 356 (47), 309 (20), 308 (100), 282 (20), 271 (10), 270 (30). HRMS Pos (ESI) calculated mass for $C_{24}H_{29}FNO_4$ $[M+H]^+$ is 414.2075, found 414.2081.

6'-Cyano-2'-fluoro-4'-hexyl-3'-hydroxy-3,5-dimethylbiphenyl-2-yl ethyl carbonate



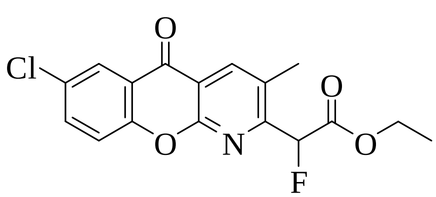
(6n): Starting with 6,8-dimethyl-4-oxo-4*H*-chromene-3-carbonitrile **4d** (199 mg, 1.0 mmol), Me_3SiOTf (288 mg, 0.23 mL, 1.30 mmol), **3g** (489 mg, 1.30 mmol), CH_2Cl_2 (9 mL), EtOH (10 mL), and triethylamine (202 mg, 0.28 mL, 2 mmol), **6n** was isolated as a white solid (273 mg, 66 %), mp = 134-136 °C. ^1H NMR (300.13 MHz, $CDCl_3$): δ = 0.84 (t, J = 6.8 Hz, 3H, CH_3), 1.07 (t, J = 7.1 Hz, 3H, CH_3), 1.20-1.32 (m, 6H, $3CH_2$), 1.55 (p, J = 7.6 Hz, 2H, CH_2), 2.19 (s, 3H, $ArCH_3$), 2.29 (s, 3H, $ArCH_3$), 2.60 (t, J = 7.9 Hz, 2H, CH_2), 4.03 (q, J = 7.1 Hz, 2H, OCH_2), 6.16 (brs, 1H, OH), 6.95 (d, J = 1.4 Hz, 1H, ArH), 7.09 (d, J = 1.2 Hz, 1H, ArH), 7.24 (d, J = 1.3 Hz, 1H, ArH). ^{13}C NMR (62.89 MHz, $CDCl_3$): δ = 12.9, 13.1 (CH_3), 15.1, 19.8 ($ArCH_3$), 21.6, 28.0, 28.1 (CH_2), 28.3 (d, J_{FC} = 2.3 Hz, CH_2), 30.6 (CH_2), 63.8 (OCH_2), 103.5 (d, J_{FC} = 4.4 Hz, C), 116.4 (d, J_{FC} = 3.9 Hz, C), 123.7 (C), 125.4 (d, J_{FC} = 18.1 Hz, C), 128.2 (CH), 129.0 (d, J_{FC} = 3.1 Hz, CH), 129.7 (C), 131.2 (d, J_{FC} = 2.3 Hz, C), 132.3 (CH), 135.0, 144.0 (C), 145.0 (d, J_{FC} = 15 Hz, C-OH), 146.7 (d, J_{FC} = 239 Hz, C), 151.4 (C=O). ^{19}F NMR (282.40 MHz, $CDCl_3$): δ = -138.23 (ArF). IR (ATR, 32 scans, cm^{-1}): $\tilde{\nu}$ = 3295 (br), 2955 (w), 2926 (w), 2858 (w), 2230 (w), 1764 (s), 1738 (w), 1614 (w), 1575 (w), 1483 (m), 1469 (m), 1447 (m), 1435 (m), 1368 (m), 1331 (w), 1302 (m), 1291 (m), 1249 (s), 1197 (s), 1147 (s), 1096 (m), 1052 (m), 995 (m), 974 (m), 904 (m), 860 (m), 801 (w), 781 (m), 754 (w), 726 (w), 646 (br), 594 (m). GCMS (EI, 70 eV, m/z > 5 %): 413 ($[M]^+$, 3), 355 (11), 354 (40), 341 (22), 340 (10), 324 (17), 313 (7), 312 (12), 299 (9), 298 (21), 285 (32), 284 (100), 272 (17), 271 (64), 270 (43), 256 (18), 250.13 (8), 206 (5), 29 (11). HRMS Pos (ESI) calculated mass for $C_{24}H_{29}FNO_4$ $[M+H]^+$ is 414.2075, found 414.2083.

4'-Benzyl-5-chloro-6'-cyano-2'-fluoro-3'-hydroxybiphenyl-2-yl ethyl carbonate (6o):



Starting with 6-chloro-4-oxo-4*H*-chromene-3-carbonitrile **4e** (205 mg, 1.0 mmol), Me_3SiOTf (288 mg, 0.23 mL, 1.30 mmol), **3b** (497 mg, 1.30 mmol), CH_2Cl_2 (9.0 mL), EtOH (10 mL), and triethylamine (202 mg, 0.28 mL, 2 mmol), **6o** was isolated as a reddish solid (290 mg, 68 %), mp = 121-123°C. ^{1}H NMR (300.13 MHz, $CDCl_3$): δ = 1.08 (t, *J* = 7.2 Hz, 3H, CH_3), 3.92 (d, J_{FH} = 2.3 Hz, 2H, $ArCH_2$), 4.05 (q, *J* = 7.1 Hz, 2H, OCH_2), 6.49 (brs, 1H, OH), 7.13-7.28 (m, 8H, ArH), 7.35 (dd, *J* = 8.6, 2.5 Hz, 1H, ArH). ^{13}C NMR (75.47 MHz, $CDCl_3$): δ = 14.0 (CH_3), 34.1 (d, J_{FC} = 2.1 Hz, CH_2), 64.3 (OCH_2), 103.2 (d, J_{FC} = 4.0 Hz, C), 115.9 (C), 122.7 (CH), 124.2 (d, J_{FC} = 17.4 Hz, C), 124.8 (C), 125.8 (CH), 127.8 (2CH), 127.9 (2CH), 129.6 (d, J_{FC} = 2.6 Hz, CH), 12.7, 130.1 (CH), 130.6 (C), 130.7 (d, J_{FC} = 2.0 Hz, C), 137.2 (C), 145.1 (d, J_{FC} = 15 Hz, C-OH), 146.2 (C), 146.9 (d, J_{FC} = 240 Hz, C), 151.5 (C=O). ^{19}F NMR (282.40 MHz, $CDCl_3$): δ = -137.4 (ArF). IR (ATR, 32 scans, cm^{-1}): $\tilde{\nu}$ = 3294 (br), 2932 (w), 2226 (m), 1762 (s), 1614 (w), 1476 (m), 1444 (s), 1388 (m), 1369 (m), 1242 (s), 1203 (s), 1152 (s), 1092 (m), 994 (m), 873 (m), 777 (m), 659 (w), 561 (w). GCMS (EI, 70 eV, m/z > 5 %): 425 ($[M]^+$, ^{35}Cl, 2), 381 (14), 366 (26), 353 (100), 352 (49), 336 (14), 258 (15), 184 (4), 135 (3), 91 (82). HRMS (EI) calculated for $C_{23}H_{17}ClFNO_4$ ($[M]^+$, ^{35}Cl) or [M^+, ^{35}Cl] is 425.08247, found 425.082079.

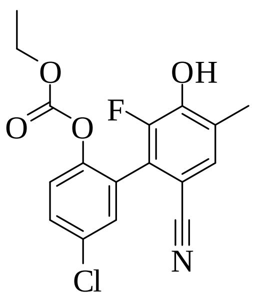
Ethyl 2-(7-chloro-3-methyl-5-oxo-5*H*-chromeno[2,3-*b*]pyridin-2-yl)-2-fluoroacetate (5p):



Starting with 6-chloro-4-oxo-4*H*-chromene-3-carbonitrile **4e** (205 mg, 1.0 mmol), Me_3SiOTf (288 mg, 0.23 mL, 1.30 mmol), **3c** (398 mg, 1.30 mmol), CH_2Cl_2 (9 mL), EtOH (10 mL), and triethylamine (202 mg, 0.28 mL, 2 mmol), **5p** was isolated as white solid (50 mg, 14 %), mp = 169-171 °C. ^{1}H NMR (300.13 MHz, $CDCl_3$): δ = 1.23 (t, *J* = 7.1Hz, 3H, CH_3), 2.50 (d, J_{FH} = 2.1 Hz, 3H, CH_3), 4.21-4.33 (m, 2H, OCH_2), 6.03 (d, J_{FH} = 47.7 Hz, CH), 7.48 (d, *J* = 8.9 Hz, 1H, ArH), 7.63 (dd, *J* = 8.9, 2.6 Hz, 1H, ArH), 8.16 (d, *J* = 2.6 Hz, 1H, ArH), 8.46 (s, 1H, ArH). ^{13}C NMR (75.47 MHz, $CDCl_3$): δ = 13.0 (CH_3), 16.1 (d, J_{FC} = 2.6 Hz, CH_3), 61.3 (OCH_2), 87.5 (d, J_{FC} = 189 Hz, FCH), 115.4 (d, J_{FC} = 1.8 Hz, C), 119.2 (CH), 121.3 (C), 125.0 (CH), 129.5, 129.7 (C), 134.8, 138.8 (CH), 153.0 (C), 155.2

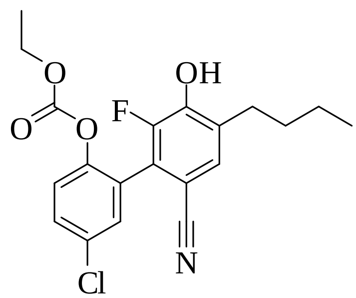
(d, J_{FC} = 19.6 Hz, C), 156.6 (C), 165.5 (d, J_{FC} = 25.6 Hz, C=O), 175.1 (C=O). ^{19}F NMR (282 MHz, $CDCl_3$): δ = -185.77 (FCH). IR (ATR, 32 scans, cm^{-1}): $\tilde{\nu}$ = 3088 (w), 3051 (w), 2988 (w), 1754 (s), 1734 (w), 1695 (w), 1663 (s), 1605 (s), 1556 (m), 1467 (m), 1444 (s), 1417 (m), 1368 (m), 1296 (m), 1283 (m), 1250.13 (s),1211 (s), 1113 (s), 1012 (m) 842 (s), 719 (m), 633 (m), 540 (m). GCMS (EI, 70 eV, m/z > 5 %): 352 ($[M+1]^+$, ^{37}Cl, 4), 351 ($[M]^+$, ^{37}Cl, 30), 350 ($[M+1]^+$, ^{35}Cl, 15), 349 ($[M]^+$, ^{35}Cl, 86), 303 (21), 279 (20), 278 (45), 277 (72), 276 (100), 275 (18), 257 (8), 256 (7), 126 (7), 29 (18). HRMS (EI) calculated for $C_{17}H_{13}ClFNO_4$ ($[M]^+$, ^{35}Cl) is 349.05117, found 349.050212.

5-Chloro-6'-cyano-2'-fluoro-3'-hydroxy-4'-methylbiphenyl-2-yl ethyl carbonate



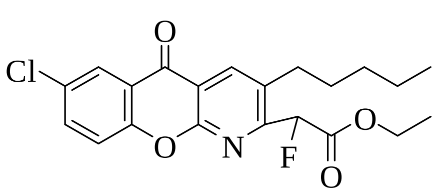
(6p): Starting with 6-chloro-4-oxo-4*H*-chromene-3-carbonitrile **4e** (205 mg, 1.0 mmol), Me_3SiOTf (288 mg, 0.23 mL, 1.30 mmol), **3c** (398 mg, 1.30 mmol), CH_2Cl_2 (9 mL), EtOH (10 mL), and triethylamine (202 mg, 0.28 mL, 2 mmol), **6p** was isolated as white solid (271 mg, 77 %), mp = 182-183 °C. ^{1}H NMR (300.13 MHz, $(CD_3)_2CO$): δ = 1.01 (t, J = 7.2 Hz, 3H, CH_3), 2.19 (s, 3H, CH_3), 3.98 (q, J = 7.1, 2H, OCH_2), 7.33-7.37 (m, 2H, ArH), 7.44-7.49 (m, 2H, ArH), 9.56 (brs, 1H, OH). ^{13}C NMR (75.47 MHz, $(CD_3)_2CO$): δ = 14.2, (CH_3), 15.7 (d, J_{FC} = 2.9 Hz, $ArCH_3$), 65.7 (OCH_2), 104.2 (d, J_{FC} = 3.9 Hz, C), 117.8 (d, J_{FC} = 3.7 Hz, C), 125.1 (CH), 125.7 (d, J_{FC} = 17.3 Hz, C), 127.9 (C), 130.0 (d, J_{FC} = 3.6 Hz, C), 131.3 (CH), 131.6 (d, J_{FC} = 3.0 Hz, CH), 131.9 (CH), 147.2 (C), 148.2 (d, J_{FC} = 14.9 Hz, C-OH), 148.7 (C), 149.0 (d, J_{FC} = 240 Hz, C), 153.1 (C=O). ^{19}F NMR (282.40 MHz, $(CD_3)_2CO$): δ = 40.69 (ArF). IR (ATR, 32 scans, cm^{-1}): $\tilde{\nu}$ = 3261 (br), 2962 (w), 2238 (m), 1769 (s), 1621 (w), 1556 (w), 1486 (m), 1464 (m), 1391 (m), 1368 (m), 1323 (m), 1220 (s), 1203 (s), 1157 (s), 1123 (m), 1093 (m), 1049 (m), 973 (m), 873 (m), 829 (w), 777 (m), 660 (w), 581 (w), 546 (w). GCMS (EI, 70 eV, m/z > 5 %): 349 ($[M]^+$, ^{35}Cl, 1), 292 (10), 291 (7), 290 (34), 279 (34), 278 (18), 277 (100), 260 (10), 241 (9), 214 (8), 164 (6), 29 (5). HRMS Pos (ESI) calculated for $C_{17}H_{14}ClFNO_4$ ($[M+H]^+$, ^{35}Cl) is 350.0589, found 350.0590

4'-Butyl-5-chloro-6'-cyano-2'-fluoro-3'-hydroxybiphenyl-2-yl ethyl carbonate (6q):



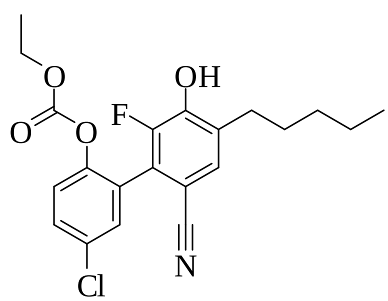
Starting with 6-chloro-4-oxo-4*H*-chromene-3-carbonitrile **4e** (205 mg, 1.0 mmol), Me_3SiOTf (288 mg, 0.23 mL, 1.30 mmol), **3e** (452 mg, 1.30 mmol), CH_2Cl_2 (9.0 mL), EtOH (10 mL), and triethylamine (202 mg, 0.28 mL, 2 mmol), **6q** was isolated as white crystals (266 mg, 68 %), mp = 129-130°C. ^{1}H NMR (300.13 MHz, $CDCl_3$): δ = 0.87 (t, *J* = 7.3 Hz, 3H, CH_3), 1.12 (t, J_{FC} = 7.1 Hz, 3H, CH_3), 1.24-1.37 (m, 2H, CH_2), 1.47-1.57 (m, 2H, CH_2), 2.60 (dt, J_{HH} = 7.5 Hz, J_{FH} = 2.5 Hz, 2H, CH_2), 4.08 (q, *J* = 7.2, 2H, OCH_2), 6.39 (brs, 1H, OH), 7.22-7.25 (m, 2H, ArH), 7.30 (d, *J* = 2.5 Hz, CH), 7.37 (dd, *J* = 8.7, 2.6 Hz, 1H, ArH). ^{13}C NMR (75.47 MHz, $CDCl_3$): δ = 13.8, 13.9 (CH_3), 22.4 (CH_2), 29.1 (d, J_{FC} = 2.2 Hz, CH_2), 31.2 (CH_2), 65.3 (OCH_2), 103.9 (d, J_{FC} = 4.2 Hz, C), 117.1 (d, J_{FC} = 3.7 Hz, C), 123.7 (CH), 124.6 (d, J_{FC} = 17.5 Hz, C), 126.0 (C), 130.3 (d, J_{FC} = 3.1 Hz, CH), 130.7, 131.2 (CH), 131.6 (C), 133.1 (d, J_{FC} = 2.5 Hz, C), 146.3 (d, J_{FC} = 15 Hz, C-OH), 147.2 (C), 147.9 (d, J_{FC} = 240 Hz, C), 152.5 (C=O). ^{19}F NMR (282.40 MHz, $CDCl_3$): δ = -138.0 (ArF). IR (ATR, 32 scans, cm^{-1}): $\tilde{\nu}$ = 3265 (br), 2957 (m), 2928 (m), 2235 (m), 1758 (s), 1614 (w), 1603, (w), 1476 (m), 1460 (m), 1370 (m), 1260 (s), 1243 (s), 1199 (s), 1154 (s), 1092 (m), 1048 (m), 995 (m), 973 (m), 892 (m), 820 (m), 662 (w), 638 (w), 582 (w). MS (EI, 70 eV, m/z > 5 %): 391 ([M]$^+$, ^{35}Cl, 2), 347 (7), 319 (40), 302 (20), 276 (100), 258 (7), 242 (5), 193 (5), 57 (6), 41 (8). HRMS (EI) calculated for $C_{20}H_{19}ClFNO_4$ ([M]$^+$, ^{35}Cl) is 391.09812, found 391.097933.

Ethyl 2-(7-chloro-5-oxo-3-pentyl-5*H*-chromeno[2,3-*b*]pyridin-2-yl)-2-fluoroacetate



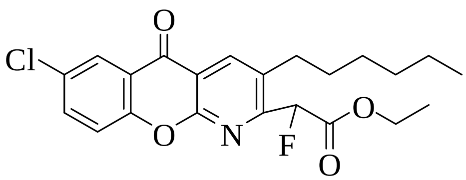
(5r): Starting with 6-chloro-4-oxo-4*H*-chromene-3-carbonitrile **4e** (205 mg, 1.0 mmol), Me_3SiOTf (288 mg, 0.23 mL, 1.30 mmol), **3f** (471 mg, 1.30 mmol), CH_2Cl_2 (9 mL), EtOH (10 mL), and triethylamine (202 mg, 0.28 mL, 2 mmol), **5r** was isolated as a white solid (49 mg, 12 %), mp = 129-131 °C. ^{1}H NMR (300.13 MHz, $CDCl_3$): δ = 0.85 (t, *J* = 7.1 Hz, 3H, CH_3), 1.23 (t, *J* = 7.2 Hz, 3H, CH_3), 1.28-1.36 (m, 4H, 2CH_2), 1.55-1.68 (m, 2H, CH_2), 2.77-2.88 (m, 2H, CH_2), 4.22-4.34 (m, 2H, OCH_2), 6.06 (d, J_{FH} = 47.3 Hz, FCH), 7.48 (d, *J* = 8.9 Hz, 1H, ArH), 7.65 (dd, *J* = 9.0, 2.6 Hz, 1H, ArH), 8.19 (d, *J* = 2.5 Hz, 1H, ArH), 8.51 (s, 1H, ArH). ^{13}C NMR (62.89 MHz, $CDCl_3$): δ = 13.9, 14.1 (CH_3), 22.4 (CH_2), 30.6 ($2CH_2$), 31.5 (CH_2), 62.3 (OCH_2), 87.8 (d, J_{FC} = 188.3 Hz, FCH), 116.7 (d, J_{FC} = 1.9 Hz, C), 120.3 (CH), 122.4 (C), 126.0 (CH), 130.6, 135.8 (C), 135.9, 139.0 (CH), 154.2 (C), 155.9 (d, J_{FC} = 19.0 Hz, C), 157.6 (C), 166.8 (d, J_{FC} = 26 Hz, C=O), 176.3 (C=O). ^{19}F NMR (282.40 MHz, $CDCl_3$): δ = -182.26 (FCH). IR (ATR, 32 scans, cm^{-1}): $\tilde{\nu}$ = 3091 (w), 3052 (w), 2953 (w), 2926 (w), 2870 (w), 1731 (s), 1666 (s), 1602 (s), 1557 (m), 1468 (s), 1449 (s), 1427 (s), 1394 (w), 1369 (m), 1326 (m), 1294 (m), 1263 (s), 1239 (s), 1240 (s), 1206 (s), 1113 (m), 1070 (m), 1058 (m), 1023 (s) 835 (s), 719 (s), 638 (m), 542 (m). GCMS (EI, 70 eV, m/z > 5 %). 407 ([M]$^+$, ^{37}Cl, 7), 406 ([M]$^+$+1, ^{35}Cl, 5), 405 ([M]$^+$, ^{35}Cl, 18), 365 (7), 364 (34), 363 (20), 362 (96), 302 (35), 301 (20), 300 (100), 290 (16), 289 (7), 288 (38), 278 (18), 277 (17), 276 (54), 275 (9), 244 (7), 29 (13). HRMS (EI) calculated for $C_{21}H_{21}ClFNO_4$ ([M]$^+$, ^{35}Cl) is 405.11377, found 405.114494.

5-Chloro-6'-cyano-2'-fluoro-3'-hydroxy-4'-pentylbiphenyl-2-yl ethyl carbonate (6r):



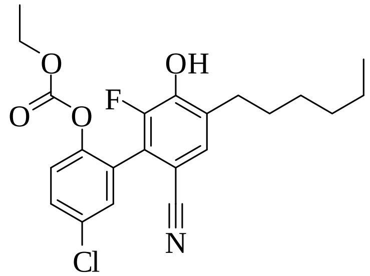
Starting with 6-chloro-4-oxo-4*H*-chromene-3-carbonitrile **4e** (205 mg, 1.0 mmol), Me_3SiOTf (288 mg, 0.23 mL, 1.30 mmol), **3f** (471 mg, 1.30 mmol), CH_2Cl_2 (9 mL), EtOH (10 mL), and triethylamine (202 mg, 0.28 mL, 2 mmol), **6r** was isolated as a white solid (283 mg, 70 %), mp = 78-80 °C. ^{1}H NMR (300.13 MHz, $CDCl_3$): δ = 0.84 (t, J = 6.8 Hz, 3H, CH_3), 1.14 (t, J = 7.1 Hz, 3H, CH_3), 1.25-1.33 (m, 4H, $2CH_2$), 1.55 (p, J = 7.4 Hz, CH_2), 2.59 (dt, J_{HH} = 7.7 Hz, J_{FH}= 2.2 Hz, 2H, CH_2), 4.09 (q, J = 7.2 Hz, 2H, OCH_2), 6.51 (brs, 1H, OH), 7.25 (d, J = 6.4 Hz, 1H, ArH), 7.26 (s, 1H, ArH), 7.31 (d, J = 2.5 Hz, CH), 7.38 (dd, J = 8.8, 2.5 Hz, 1H, ArH). ^{13}C NMR (62.89 MHz, $CDCl_3$): δ = 12.9 ($2CH_3$), 21.4, 27.7 (CH_2), 28.3 (d, J_{FC} = 2.3 Hz, CH_2), 30.4 (CH_2), 64.2 (OCH_2), 102.9 (d, J_{FC} = 4.2 Hz, C), 116.1 (d, J_{FC} = 3.8 Hz, C), 122.6 (CH), 123.6 (d, J_{FC} = 17.4 Hz, C), 124.9 (C), 129.2 (d, J_{FC} = 3.0 Hz, CH), 129.6, 130.1 (CH), 130.6 (C), 132.1 (d, J_{FC} = 2.5 Hz, C), 145.2 (d, J_{FC} = 14.2 Hz, C-OH), 146.2 (C), 146.7 (d, J_{FC} = 240 Hz, C), 151.5 (C=O). ^{19}F NMR (282.40 MHz, $CDCl_3$): δ = -138.01 (ArF). IR (ATR, 32 scans, cm^{-1}): $\tilde{\nu}$ = 3232 (br), 2956 (w), 2929 (w), 2858 (w), 2227 (w), 1759 (m), 1603 (w), 1545 (w), 1477 (m), 1444 (m), 1369 (m), 1244 (s), 1206 (s), 1154 (m), 1115 (w), 995 (m), 884 (w), 823 (w), 777 (w), 661 (w), 575 (w). GCMS (EI, 70 eV, m/z > 5 %): 407 ([M]$^+$,^{37}Cl, 9), 406 ([M+1]$^+$, ^{35}Cl, 6), 405 ([M]$^+$, ^{35}Cl, 35), 346 (13), 333 (14), 318 (19), 316 (34), 304 (17), 291 (32), 277 (38), 276 (100), 207 (42), 164 (7), 44 (17), 29 (22). HRMS Pos (ESI) calculated for $C_{21}H_{22}ClFNO_4$ ([M+H]$^+$, ^{35}Cl) is 406.121600, found 406.125100.

Ethyl 2-(7-chloro-3-hexyl-5-oxo-5*H*-chromeno[2,3-*b*]pyridin-2-yl)-2-fluoroacetate



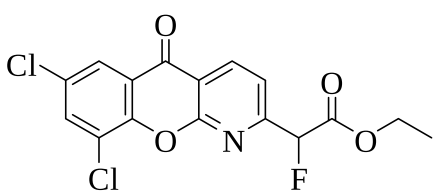
(5s): Starting with 6-chloro-4-oxo-4*H*-chromene-3-carbonitrile **4e** (205 mg, 1.0 mmol), Me_3SiOTf (288 mg, 0.23 mL, 1.30 mmol), **3g** (489 mg, 1.30 mmol), CH_2Cl_2 (9 mL), EtOH (10 mL), and triethylamine (202 mg, 0.28 mL, 2 mmol), **5s** was isolated as a white solid (42 mg, 10 %), mp = 123-125 °C. ^{1}H NMR (300.13 MHz, $CDCl_3$): δ = 0.83 (t, J = 7.2 Hz, 3H, CH_3), 1.23 (t, J = 7.1 Hz, 3H, CH_3), 1.24-1.38 (m, 6H, 3CH_2), 1.59-1.67 (m, 2H, CH_2), 2.77-2.83 (m, 2H, CH_2), 4.21-4.33 (m, 2H, OCH_2), 6.06 (d, J_{FH} = 47.6 Hz, FCH), 7.49 (d, J = 9.0 Hz, 1H, ArH), 7.64 (dd, J = 8.9, 2.6 Hz, 1H, ArH), 8.18 (d, J = 2.5 Hz, 1H, ArH), 8.51 (s, 1H, ArH). ^{13}C NMR (62.89 MHz, $CDCl_3$): δ = 13.0, 13.1 (CH_3), 21.5, 28.0 (CH_2), 29.6 (d, J_{FC} = 1.4 Hz, CH_2), 29.9, 30.5 (CH_2), 61.3 (OCH_2), 86.7 (d, J_{FC} = 189.2 Hz, FCH), 115.7 (d, J_{FC} = 1.8 Hz, C), 119.3 (CH), 121.4 (C), 125.0 (CH), 129.6, 134.8 (C), 134.9, 138.0 (CH), 153.2 (C), 154.9 (d, J_{FC} = 19.0 Hz, C), 156.6 (C), 165.9 (d, J_{FC} = 25.8 Hz, C=O), 175.3 (C=O). ^{19}F NMR (282.40 MHz, $CDCl_3$): δ = -182.25 (FCH). IR (ATR, 32 scans, cm^{-1}): $\tilde{\nu}$ = 3089 (w), 2995 (w), 2950 (w), 2856 (w), 1734 (s), 1667 (s), 1601 (s), 1557 (m), 1470 (s), 1451 (s), 1369 (m), 1266 (s), 1252 (s), 1170 (s), 1026 (m) 720 (m), 638 (m), 542 (m). GCMS (EI, 70 eV, m/z > 5 %): 419 ([M]$^+$, ^{35}Cl, 2), 364 (14), 362 (41), 316 (34), 314 (100), 288 (20), 278 (10), 277 (10), 276 (29), 272 (6), 29 (7). HRMS Pos (ESI) calculated for $C_{22}H_{24}ClFNO_4$ ([M+H]$^+$, ^{35}Cl) is 420.1372, found 420.1379.

5-Chloro-6'-cyano-2'-fluoro-4'-hexyl-3'-hydroxybiphenyl-2-yl ethyl carbonate (6s): Starting with 6-chloro-4-oxo-4*H*-chromene-3-carbonitrile **4e** (205 mg, 1.0 mmol), Me_3SiOTf (288 mg, 0.23 mL, 1.30 mmol), **3g** (489 mg, 1.30 mmol), CH_2Cl_2 (9 mL), EtOH (10 mL), and triethylamine (202 mg, 0.28 mL, 2 mmol), **6s** was isolated as a white



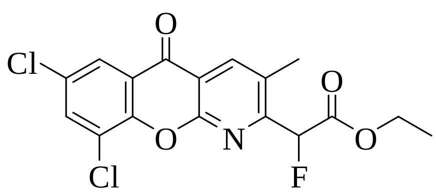
solid (293 mg, 70 %), mp = 85-87 °C. ^{1}H NMR (300.13 MHz, $CDCl_3$): δ = 0.84 (t, *J* = 6.8 Hz, 3H, CH_3), 1.14 (t, *J* = 7.1Hz, 3H, CH_3), 1.20-1.34 (m, 6H, 3CH_2), 1.54 (p, *J* = 7.3 Hz, CH_2), 2.57-2.62 (m, 2H, CH_2), 4.09 (q, *J* = 7.1 Hz, 2H, OCH_2), 6.50 (brs, 1H, OH), 7.24-7.27 (m, 2H, ArH), 7.31 (d, *J* = 2.5 Hz, CH), 7.38 (dd, *J* = 8.7, 2.6 Hz, 1H, ArH). ^{13}C NMR (62.89 MHz, $CDCl_3$): δ = 12.9, 13.0 (CH_3), 21.5 (CH_2), 27.9 (2CH_2), 28.4 (d, J_{FC} = 2.2 Hz, CH_2), 64.2 (OCH_2), 102.7 (d, J_{FC} = 4.1 Hz, C), 116.0 (d, J_{FC} = 3.7 Hz, C), 122.6 (CH), 123.6 (d, J_{FC} = 17.4 Hz, C), 124.9 (C), 129.2 (d, J_{FC} = 3.0 Hz, CH), 129.6, 130.1 (CH), 130.5 (C), 132.1 (d, J_{FC} = 2.6 Hz, C), 145.3 (d, J_{FC} = 14.7 Hz, C-OH), 146.1 (C), 146.7 (d, J_{FC} = 241 Hz, C), 151.5 (C=O). ^{19}F NMR (282.40 MHz, $CDCl_3$): δ = -137.8 (ArF). IR (ATR, 32 scans, cm^{-1}): $\tilde{\nu}$ = 3315 (br), 2923 (m), 2857 (w), 2229 (w), 1767 (m), 1613 (w), 1569 (w), 1478 (m), 1391 (w), 1369 (m), 1239 (s), 1202 (s), 1117 (w), 996 (m), 870 (w), 835 (w), 779 (m), 682 (w), 591 (w), 559 (w). GCMS (EI, 70 eV, m/z > 5 %): 419 ($[M]^+$, ^{35}Cl, 2), 375 (8), 361 (10), 360 (49), 330 (14), 304 (22), 290 (100), 279 (22), 278 (27), 276 (50), 258 (14), 193 (6), 43 (11), 29 (13). HRMS Pos (ESI) calculated mass for $C_{22}H_{24}ClFNO_4$ ($[M+H]^+$, ^{35}Cl) is 420.1372, found 420.1381.

Ethyl 2-(7,9-dichloro-5-oxo-5*H*-chromeno[2,3-*b*]pyridin-2-yl)-2-fluoroacetate (5t):



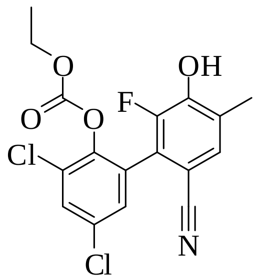
Starting with 6,8-dichloro-4-oxo-4*H*-chromene-3-carbonitrile **4f** (240 mg, 1.0 mmol), Me_3SiOTf (288 mg, 0.23 mL, 1.30 mmol), **3a** (380 mg, 1.30 mmol), CH_2Cl_2 (9.0 mL), EtOH (10 mL), and triethylamine (202 mg, 0.28 mL, 2 mmol), **5t** was isolated as a yellow solid (130 mg, 35 %), mp = 164-166°C. ^{1}H NMR (250.13 MHz, $CDCl_3$): δ = 1.24 (t, *J* = 7.1 Hz, 3H, CH_3), 4.18-4.31 (m, 2H, OCH_2), 5.94 (d, J_{FH} = 47.4 Hz, FCH), 7.67 (d, *J* = 8.0 Hz, 1H, ArH), 7.76 (d, *J* = 2.6 Hz, 1H, ArH), 8.08 (d, *J* = 2.5 Hz, 1H, ArH), 8.70 (d, *J* = 8.0 Hz, 1H, ArH). ^{13}C NMR (75.47 MHz, $CDCl_3$): δ = 14.0 (CH_3), 62.7 (OCH_2), 89.3 (d, J_{FC} = 187.7 Hz, FCH), 116.3 (C), 118.9 (d, J_{FC} = 5.2 Hz, CH), 123.3 (C), 124.7 (CH), 124.8, 130.6 (C), 135.8, 139.1 (CH), 150.1 (C), 159.1 (d, J_{FC} = 2.2 Hz, C), 159.4 (d, J_{FC} = 24.7 Hz, C), 166.2 (d, J_{FC} = 25.3 Hz, C=O), 175.47 (C=O). ^{19}F NMR (282.40 MHz, $CDCl_3$): δ = -

187.54 (FCH). IR (ATR, 32 scans, cm^{-1}): $\tilde{\nu}$ = 3082 (w), 2987 (w), 2906 (w), 1745 (s), 1668 (s), 1608 (m), 1577 (m), 1459 (m), 1386 (s), 1311 (m), 1238 (s), 1176 (m), 1086 (s), 1019 (m), 888 (m), 776 (s), 731 (m), 674 (m), 563 (m). GCMS (EI, 70 eV, m/z > 5 %): 371 ([M]$^+$, ^{37}Cl, 26), 370 ([M+1]$^+$, ^{35}Cl, 7), 369 ([M]$^+$, ^{35}Cl, 40), 301 (12), 300 (13), 299 (66), 298 (35), 297 (100), 296 (32), 270 (12), 268 (18), 108 (5), 97 (5), 57 (5), 29 (29). HRMS (EI) calculated for $C_{16}H_{10}Cl_2FNO_4$ ([M]$^+$, ^{35}Cl) is 368.99654, found 368.995651.



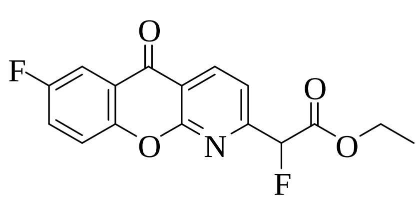
Ethyl 2-(7,9-dichloro-3-methyl-5-oxo-5*H*-chromeno[2,3-*b*]pyridin-2-yl)-2-fluoroacetate (5u): Starting with 6,8-dichloro-4-oxo-4*H*-chromene-3-carbonitrile **4f** (240 mg, 1.0 mmol), Me_3SiOTf (288 mg, 0.23 mL, 1.30 mmol), **3c** (398 mg, 1.30 mmol), CH_2Cl_2 (9 mL), EtOH (10 mL), and triethylamine (202 mg, 0.28 mL, 2 mmol), **5u** was isolated as yellowish white solid (35 mg, 9 %), mp = 180-182 °C. ^{1}H NMR (300.13 MHz, $CDCl_3$): δ = 1.24 (t, J = 7.1 Hz, 3H, CH_3), 2.50 (d, J_{FH} = 2.4 Hz, 3H, CH_3), 4.24-4.32 (m, 2H, OCH_2), 6.05 (d, J_{FH} = 47.3 Hz, FCH), 7.74 (d, J = 2.5 Hz, 1H, ArH), 8.06 (d, J = 2.5 Hz, 1H, ArH), 8.43 (s,1H, ArH). ^{13}C NMR (62.89 MHz, $CDCl_3$): δ =13.1 (CH_3), 16.2 (d, J_{FC} = 3.1 Hz, 3H CH_3), 61.5 (OCH_2), 87.9 (d, J_{FC} = 188.8 Hz, FC), 115.1 (d, J_{FC} = 1.8 Hz, C), 122.2 (C), 123.6 (CH), 123.7, 129.2, 130.6 (C), 134.6, 138.9 (CH), 149.2 (C), 155.8 (d, J_{FC} = 20.0 Hz, C), 156.3 (C), 165.5 (d, J_{FC} = 25.5 Hz, C=O), 174.6 (C=O). ^{19}F NMR (282.40 MHz, $CDCl_3$): δ = -186.01 (FCH). IR (ATR, 32 scans, cm^{-1}): $\tilde{\nu}$ = 3073 (w), 2991 (w), 1767 (w), 1746 (w), 1714 (s), 1681 (s), 1610 (s), 1593 (m), 1554 (m), 1462 (m), 1444 (s), 1395 (m), 1374 (m), 1304 (m), 1285 (w), 1268 (s), 1230 (s), 1181 (m), 1088 (w), 1012 (m), 986 (w), 952 (w), 910 (w), 888 (m), 850 (m), 792 (m) 726 (s), 577 (m), 566 (m). GCMS (EI, 70 eV, m/z > 5 %): 387 ([M]$^+$, $^{37}Cl_2$, 11), 386 ([M+1]$^+$, ^{37}Cl^{35}Cl, 12), 385 ([M]$^+$,^{37}Cl^{35}Cl, 61), 384 ([M+1]$^+$, $^{35}Cl_2$, 17), 383 ([M]$^+$, $^{35}Cl_2$, 93), 339 (15), 338 (7), 337 (26), 335 (7), 315 (9), 314 (20), 313 (59), 312 (76), 311 (100), 310 (99), 309 (20), 293 (9), 292 (9), 291 (13), 290 (7), 276 (10), 97 (6), 29 (22). HRMS (EI) calculated for $C_{17}H_{12}Cl_2FNO_4$ ([M]$^+$, $^{35}Cl_2$) is 383.01219, found 383.011920.

3,5-Dichloro-6'-cyano-2'-fluoro-3'-hydroxy-4'-methylbiphenyl-2-yl ethyl carbonate



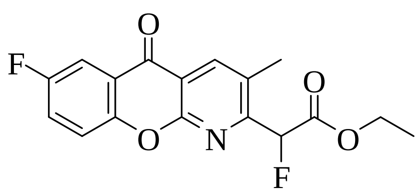
(6u): Starting with 6,8-dichloro-4-oxo-4*H*-chromene-3-carbonitrile **4f** (240 mg, 1.0 mmol), Me_3SiOTf (288 mg, 0.23 mL, 1.30 mmol), **3c** (398 mg, 1.30 mmol), CH_2Cl_2 (9 mL), EtOH (10 mL), and triethylamine (202 mg, 0.28 mL, 2 mmol), **6u** was isolated as yellowish white solid (301 mg, 79 %), mp = 137-139 °C. ^{1}H NMR (300.13 MHz, $(CD_3)_2CO$): δ = 1.14 (t, J = 7.1 Hz, 3H, CH_3), 2.33 (d, J_{FH} = 0.7 Hz, 3H, $ArCH_3$), 4.15 (q, J = 7.2, 2H, OCH_2), 7.52 (d, J = 1.5 Hz, 1H, ArH), 7.60 (d, J = 2.5 Hz, 1H, ArH), 7.80 (d, J = 2.5 Hz, 1H, ArH), 9.82 (brs, 1H, OH). ^{13}C NMR (75.47 MHz, $(CD_3)_2CO$): δ = 13.9 (CH_3), 15.5 (d, J_{FC} = 2.8 Hz, $ArCH_3$), 22.3 (CH_2), 31.4 (d, J_{FC} = 2.5 Hz, CH_2), 66.2 (OCH_2), 104.0 (d, J_{FC} = 3.8 Hz, C), 117 (d, J_{FC} = 3.9 Hz, C), 124.5 (d, J_{FC} = 17.5 Hz, C), 129.4, 130.0 (C), 130.3 (d, J_{FC} = 3.8 Hz, C), 130.7 (CH), 131.4 (d, J_{FC} = 3.1 Hz, CH), 131.5 (CH), 144.9, 147.1 (C), 148.0 (d, J_{FC} = 14.7 Hz, C-OH), 148.8 (d, J_{FC} = 243 Hz, C), 151.6 (C=O). ^{19}F NMR (282.40 MHz, $(CD_3)_2CO$): δ = 39.03 (ArF). IR (ATR, 32 scans, cm^{-1}): $\tilde{\nu}$ = 3292 (br), 3082 (w), 2988 (w), 2944 (w), 2911 (w), 2232 (w), 1748 (s), 1611 (w), 1592 (w), 1562 (w), 1504 (w), 1471 (m), 1447 (m), 1434 (w), 1390 (m), 1370 (m), 1318 (w), 1267 (s), 1255 (s), 1213 (s), 1155 (s), 1116 (w), 1099 (w), 1036 (s), 992 (s), 903 (m), 884 (m), 869 (m), 851 (m), 783 (s), 754 (w), 731 (m), 639 (br), 567 (m). GCMS (EI, 70 eV, m/z > 5 %): 385 ($[M]^+$,$^{37}Cl^{35}Cl$, 5), 383 ($[M]^+$, $^{35}Cl_2$, 5), 326 (11), 324 (15), 315 (13), 313 (67), 311 (100), 292 (6), 276 (11), 275 (13), 248 (7), 207 (5), 29 (13). HRMS Pos (ESI) calculated for $C_{17}H_{13}Cl_2FNO_4$ ($[M+H]^+$, $^{35}Cl_2$) is 384.0200, found 384.0209.

Ethyl 2-fluoro-2-(7-fluoro-5-oxo-5*H*-chromeno[2,3-*b*]pyridin-2-yl)acetate (5v):



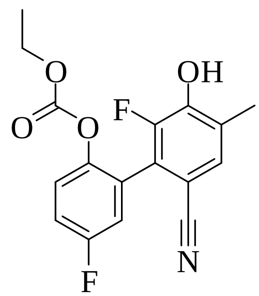
Starting with 6-fluoro-4-oxo-4*H*-chromene-3-carbonitrile **4g** (184 mg, 1.0 mmol), Me_3SiOTf (288 mg, 0.23 mL, 1.30 mmol), **3a** (380 mg, 1.30 mmol), CH_2Cl_2 (9.0 mL), EtOH (10 mL), and triethylamine (202 mg, 0.28 mL, 2 mmol), **5v** was isolated as a crystalline solid (105 mg, 33 %), mp = 134-136°C**.** ^{1}H NMR (250.13 MHz, $CDCl_3$): δ = 1.23 (t, J = 7.1 Hz, 3H, CH_3), 4.17-4.31 (m, 2H, OCH_2), 5.90 (d, J_{FH} = 47.4 Hz, FCH), 7.41-7.59 (m, 2H, ArH), 7.63 (d, J = 7.9 Hz, 1H, ArH), 7.86 (dd, J = 7.9, 3.0 Hz, 1H, ArH), 8.72 (d, J = 8.0 Hz, 1H, ArH). ^{13}C NMR (75.47 MHz, $CDCl_3$): δ = 14.0 (CH_3), 62.6 (OCH_2), 89.3 (d, J_{FC} = 188.3 Hz, FCH), 111.6 (d, J_{FC} = 23.8 Hz, CH), 116.1 (C), 118.3 (d, J_{FC} = 5.3 Hz, CH), 120.6 (d, J_{FC} = 8.0 Hz, CH), 122.5 (d, J_{FC} = 7.5 Hz, C), 124.0 (d, J_{FC} = 25.2 Hz, CH), 139.0 (CH), 151,8 (d, J_{FC} = 1.8 Hz, C), 158.8 (d, J_{FC} = 24.5 Hz, C), 159.2 (d, J_{FC} = 246.7 Hz, ArFC), 159.5 (d, J_{FC} = 2.2 Hz, C) 166.2 (d, J_{FC} = 25.2 Hz, C=O), 176.4 (d, J_{FC} = 2.4 Hz, C=O). ^{19}F NMR (282.40 MHz, $CDCl_3$): δ = -115.3 (ArF), 187.9 (FCH). IR (ATR, 32 scans, cm^{-1}): $\tilde{\nu}$ = 3072 (w), 2978 (w), 2926 (w), 1752 (s), 1672 (s), 1592 (s), 1566 (m), 1484 (s), 1447 (s), 1395 (s), 1243 (m), 1208 (s), 1140 (s), 888 (m). GCMS (EI, 70 eV, m/z > 5 %): 319 ($[M]^+$, 42), 247 (52), 218 (26), 164 (7), 123 (4), 94 (5), 82 (5), 29 (22). HRMS (EI) calculated for $C_{16}H_{11}F_2NO_4$ $[M]^+$ is 319.06507, found 319.065232.

Ethyl 2-fluoro-2-(7-fluoro-3-methyl-5-oxo-5*H*-chromeno[2,3-*b*]pyridin-2-yl)acetate



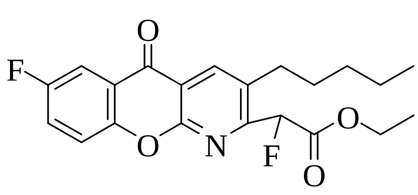
(5w): Starting with 6-fluoro-4-oxo-4*H*-chromene-3-carbonitrile **4g** (189 mg, 1.0 mmol), Me_3SiOTf (288 mg, 0.23 mL, 1.30 mmol), **3c** (398 mg, 1.30 mmol), CH_2Cl_2 (9 mL), EtOH (10 mL), and triethylamine (202 mg, 0.28 mL, 2 mmol), **5w** was isolated as white solid (37 mg, 11 %), mp = 150-151 °C. ^{1}H NMR (300.13 MHz, $CDCl_3$): δ = 1.22 (t, *J* = 7.2 Hz, 3H, CH_3), 2.50 (d, J_{FH} = 1.69 Hz, 3H, $ArCH_3$), 4.19-4.35 (m, 2H, OCH_2), 6.04 (d, J_{FH} = 47.4 Hz, CH), 7.39-7.46 (m, 1H, ArH), 7.53 (dd, *J* = 9.0, 4.12 Hz, 1H, ArH), 7.83 (dd, *J* = 7.9, 3.0 Hz, 1H, ArH), 8.45 (s, 1H, ArH). ^{13}C NMR (75.47 MHz, $CDCl_3$): δ = 14.0 (CH_3), 17.2 (d, J_{FC} = 2.6 Hz, $ArCH_3$), 62.4 (OCH_2), 88.5 (d, J_{FC} = 188.5 Hz, FCH), 111.5 (d, J_{FC} = 23.7 Hz, CH), 116.0 (C), 120.6 (d, J_{FC} = 8.3 Hz, CH), 122.4 (d, J_{FC} = 7.3 Hz, C), 123.9 (d, J_{FC} = 25.2 Hz, CH), 130.7 (C),139.8 (CH), 151,9 (d, J_{FC} = 1.5 Hz, C), 156.3 (d, J_{FC} = 19.7 Hz, C), 157.7 (C), 159.1 (d, J_{FC} = 247 Hz, ArFC), 166.6 (d, J_{FC} = 25.6 Hz, C=O), 176.5 (d, J_{FC} = 2.0 Hz, C=O). ^{19}F NMR (282.40 MHz, $CDCl_3$): δ = -115.7, 185.8 (FCH). IR (ATR, 32 scans, cm^{-1}): $\tilde{\nu}$ = 3147 (w), 3099 (w), 3056 (w), 2988 (w), 2943 (w), 2915 (w), 1759 (s), 1665 (s), 1624 (w), 1607 (m), 1593 (m), 1563 (w), 1481 (s), 1453 (s), 1424 (s), 1369 (m), 1284 (m), 1250.13 (s), 1207 (m), 1102 (m), 1073 (m), 1010 (m), 930 (w), 841 (s), 789 (m), 771 (s), 639 (m), 555 (m). GCMS (EI, 70 eV, m/z > 5 %): 334 ($[M+1]^+$, 17), 333 ($[M]^+$, 83), 287 (15), 262 (8), 261 (66), 260 (100), 259 (17), 241 (7), 240 (7), 157 (4), 29 (9). HRMS (EI) calculated for $C_{21}H_{21}F_2NO_4$ $[M]^+$ is 333.08072, found 333.080897.

6'-Cyano-2',5-difluoro-3'-hydroxy-4'-methylbiphenyl-2-yl ethyl carbonate (6w):



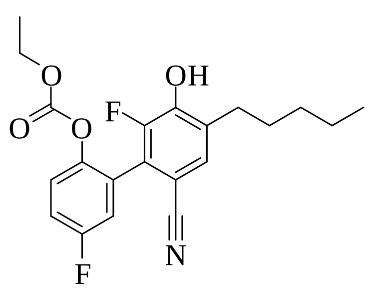
Starting with 6-fluoro-4-oxo-4*H*-chromene-3-carbonitrile **4g** (189 mg, 1.0 mmol), Me_3SiOTf (288 mg, 0.23 mL, 1.30 mmol), **3c** (398 mg, 1.30 mmol), CH_2Cl_2 (9 mL), EtOH (10 mL), and triethylamine (202 mg, 0.28 mL, 2 mmol), **6w** was isolated as a white solid (243 mg, 73 %), mp = 155-157 °C. ^{1}H NMR (300 MHz, $(CD_3)_2CO$): δ = 1.16 (t, J = 7.1 Hz, 3H, CH_3), 2.36 (s, 3H, $ArCH_3$), 4.13 (q, J = 7.1 Hz, 2H, OCH_2), 7.35-7.42 (m, 2H, ArH), 7.48-7.54 (m, 2H, ArH), 9.72 (brs, 1H, OH). ^{13}C NMR (62.89 MHz, $(CD_3)_2CO$): δ = 14.2 (CH_3), 15.7 (d, J_{FC} = 2.6 Hz, $ArCH_3$), 65.6 (OCH_2), 104.2 (d, J_{FC} = 4.1 Hz, C), 117.7 (C), 118.0 (d, J_{FC} = 23.5 Hz, CH), 118.8 (d, J_{FC} = 24.7 Hz, CH), 125.2 (d, J_{FC} = 8.9 Hz, CH), 125.9, (d, J_{FC} = 17.4 Hz, C), 127.8 (d, J_{FC} = 8.9 Hz, C), 129.9 (d, J_{FC} = 3.7 Hz, C), 131.6 (d, J_{FC} = 3.0 Hz, CH), 146.1 (d, J_{FC} = 2.9 Hz, C), 148.2 (d, J_{FC} = 14.9 Hz, C-OH), 149.1 (d, J_{FC} = 240 Hz, C), 153.3 (C=O), 160.6 (d, J_{FC} = 245 Hz, C). ^{19}F NMR (282.40 MHz, $(CD_3)_2CO$): δ = 40.65, 59.82 (ArF). IR (ATR, 32 scans, cm^{-1}): $\tilde{\nu}$ = 3266 (br), 3085 (w), 2990 (w), 2942 (w), 2240 (m), 2140 (w), 1770 (s), 1618 (w), 1593 (w), 1557 (m), 1510 (w), 1485 (m), 1467 (w), 1408 (w), 1369 (m), 1322 (m), 1249 (m), 1226 (s), 1179 (s), 1144 (m), 1111 (w), 1094 (m), 1052 (m), 1036 (m), 973 (m), 946 (w), 896 (m), 874 (m), 833 (m), 779 (s), 667 (m), 631 (br), 587 (w). GCMS (EI, 70 eV, m/z > 5 %): 289 (4), 274 (45), 262 (18), 261 (100), 245 (9), 244 (15), 242 (9), 233 (12), 232 (10), 213 (5), 185 (5), 184 (5), 29 (6). HRMS Pos (ESI) calculated for $C_{17}H_{14}F_2NO_4$ $[M+H]^+$ is 334.0885, found 334.0889.

Ethyl 2-fluoro-2-(7-fluoro-5-oxo-3-pentyl-5*H*-chromeno[2,3-*b*]pyridin-2-yl)acetate (5y):



Starting with 6-fluoro-4-oxo-4*H*-chromene-3-carbonitrile **4g** (189 mg, 1.0 mmol), Me_3SiOTf (288 mg, 0.23 mL, 1.30 mmol), **3f** (471 mg, 1.30 mmol), CH_2Cl_2 (9 mL), EtOH (10 mL), and triethylamine (202 mg, 0.28 mL, 2 mmol), **5y** was isolated as yellow crystals (43 mg, 11 %), mp = 107-109 °C. ^{1}H NMR (300.13 MHz, $CDCl_3$): δ = 0.85 (t, J = 7.2 Hz, 3H, CH_3), 1.23 (t, J = 7.1 Hz, 3H, CH_3), 1.31-1.36 (m, 4H, $2CH_2$), 1.61-1.69 (m, 2H, CH_2), 2.75-2.86 (m, 2H, CH_2), 4.22-4.34 (m, 2H, OCH_2), 6.06 (d, J_{FH} = 47.8 Hz, FCH), 7.41-7.47 (m, 1H, ArH), 7.55 (dd, J = 9.2, 4.1 Hz, 1H, ArH), 7.87 (dd, J = 8.0, 3.1 Hz, 1H, ArH), 8.52 (s, 1H, ArH). ^{13}C NMR (62.89 MHz, $CDCl_3$): δ = 12.9, 13.1 (CH_3), 21.4, 29.6 (CH_2), 30.5 ($2CH_2$), 61.3 (OCH_2), 86.8 (d, J_{FC} = 189.2 Hz, FCH), 110.5 (d, J_{FC} = 23.9 Hz, CH), 115.2 (C), 119.6 (d, J_{FC} = 8.0 Hz, CH), 121.4 (d, J_{FC} = 7.2 Hz, C), 123.0 (d, J_{FC} = 25.3 Hz, CH), 134.6 (C), 137.9 (CH), 151.0 (d, J_{FC} = 1.8 Hz, C), 154.9 (d, J_{FC} = 19.0 Hz, C), 156.7 (C), 158.1 (d, J_{FC} = 246.8 Hz, ArFC), 165.9 (d, J_{FC} = 25.6 Hz, C=O), 175.7 (d, J_{FC} = 2.6 Hz, C=O). ^{19}F NMR (282.40 MHz, $CDCl_3$): δ = -115.75 (ArF), 182.27 (FCH). IR (ATR, 32 scans, cm^{-1}): $\tilde{\nu}$ = 3090 (w), 2954 (m), 2927 (m), 2870 (w), 2854 (w), 1731 (s), 1666 (s), 1603 (s), 1562 (w), 1481 (s), 1455 (s), 1424 (s), 1370 (m), 1264 (s), 1245 (s), 1203 (m), 1023 (m), 951 (m), 881 (m), 835 (m), 786 (s), 637 (m), 557 (m). GCMS (EI, 70 eV, m/z > 5 %): 389 ($[M]^+$, 20), 347 (18), 346 (98), 285 (19), 284 (100), 272 (45), 261 (16), 260 (57), 256 (7), 254 (8), 29 (8). HRMS (EI) calculated for $C_{21}H_{21}F_2NO_4$ $[M]^+$ is 389.143320, found 389.143205.

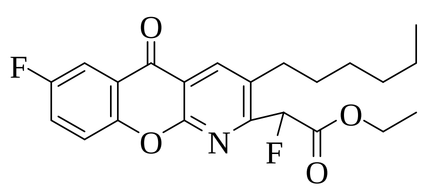
6'-Cyano-2',5-difluoro-3'-hydroxy-4'-pentylbiphenyl-2-yl ethyl carbonate (6y):



Starting with 6-fluoro-4-oxo-4*H*-chromene-3-carbonitrile **4g** (189 mg, 1.0 mmol), Me_3SiOTf (288 mg, 0.23 mL, 1.30 mmol), **3f** (471 mg, 1.30 mmol), CH_2Cl_2 (9 mL), EtOH (10 mL), and triethylamine (202 mg, 0.28 mL, 2 mmol), **6y** was isolated as yellow crystals (299 mg, 77 %), mp = 91-93 °C. ^{1}H NMR (300.13 MHz, $CDCl_3$): δ = 0.85 (t, J = 6.8 Hz, 3H, CH_3), 1.14 (t, J = 7.1 Hz, 3H, CH_3), 1.26-1.34 (m, 4H, $2CH_2$), 1.56 (p, J = 7.4 Hz, 2H, CH_2), 2.60 (t, J = 7.5 Hz, 2H, CH_2), 4.09 (q, J = 7.0 Hz, 2H, OCH_2), 6.29 (brs, 1H, OH), 7.05 (dd, J = 8.3, 3.2 Hz, 1H, ArH), 7.08-7.15 (m, 1H, ArH), 7.25-7.29 (m, 2H, ArH). ^{13}C NMR (75.47 MHz, $CDCl_3$): δ = 12.8 ($2CH_3$), 21.3, 27.6 (CH_2), 28.3 (d, J_{FC} = 2.3 Hz, CH_2), 30.4 (CH_2), 64.1 (OCH_2), 102.8 (d, J_{FC} = 4.2 Hz, C), 116.0 (d, J_{FC} = 3.8 Hz, C), 116.3 (d, J_{FC} = 23.3 Hz, CH), 117.0 (d, J_{FC} = 24.5 Hz, CH), 122.8 (d, J_{FC} = 8.8 Hz, CH), 123.7, (d, J_{FC} = 18.4 Hz, C), 124.9 (d, J_{FC} = 8.4 Hz, C), 129.2 (d, J_{FC} = 2.9 Hz, CH), 131.9 (d, J_{FC} = 2.5 Hz, C), 143.6 (d, J_{FC} = 3.1 Hz, C), 145.2 (d, J_{FC} = 14.8 Hz, C-OH), 146.7 (d, J_{FC} = 240 Hz, C), 151.7 (C=O), 158.7 (d, J_{FC} = 247

Hz, C). ^{19}F NMR (282.40 MHz, $CDCl_3$): δ = -115.40, -138.17 (ArF). IR (ATR, 32 scans, cm^{-1}): $\tilde{\nu}$ = 3295 (br), 2960 (w), 2928 (w), 2860 (w), 2234 (w), 1758 (s), 1612 (w), 1592 (w), 1574 (w), 1485 (m), 1456 (m), 1368 (w), 1305 (m), 1260 (m), 1243 (s), 1220 (s), 1180 (s), 1138 (m), 1100 (m), 1055 (w), 996 (m), 888 (m), 791 (m), 634 (br), 563 (w). GCMS (EI, 70 eV, m/z > 5 %): 331 (15), 330 (64), 317 (19), 300 (26), 288 (11), 275 (33), 274 (100), 261 (49), 260 (88), 242 (14), 212 (4), 211 (14), 202 (5), 195 (3), 182 (5), 41 (5), 29 (13). HRMS (EI) calculated for $C_{21}H_{21}F_2NO_4$ $[M]^+$ is 389.14332, found 389.142894.

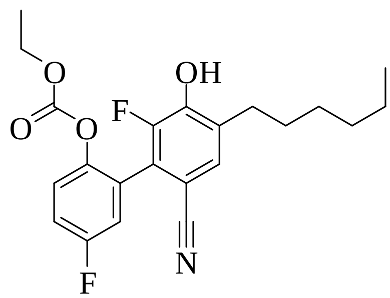
Ethyl 2-fluoro-2-(7-fluoro-3-hexyl-5-oxo-5*H*-chromeno[2,3-*b*]pyridin-2-yl)acetate



(5z): Starting with 6-fluoro-4-oxo-4*H*-chromene-3-carbonitrile **4g** (189 mg, 1.0 mmol), Me_3SiOTf (288 mg, 0.23 mL, 1.30 mmol), **3g** (489 mg, 1.30 mmol), CH_2Cl_2 (9 mL), EtOH (10 mL), and triethylamine (202 mg, 0.28 mL, 2 mmol), **5z** was isolated as white solid (28 mg, 7 %), mp = 125-127 °C. ^{1}H NMR (300.13 MHz, $CDCl_3$): δ = 0.83 (t, J = 7.2Hz, 3H, CH_3), 1.23 (t, J = 7.2Hz, 3H, CH_3), 1.24-1.38 (m, 6H, $3CH_2$), 1.59-1.67 (m, 2H, CH_2), 2.77-2.83 (m, 2H, CH_2), 4.21-4.33 (m, 2H, OCH_2), 6.06 (d, J_{FH} = 47.9 Hz, FCH), 7.40-7.47 (m, 1H, ArH), 7.55 (dd, J = 9.2, 4.1 Hz, 1H, ArH), 7.88 (dd, J = 8.1, 3.0 Hz, 1H, ArH), 8.51 (s, 1H, ArH). ^{13}C NMR (75.47 MHz, $CDCl_3$): δ = 12.95, 13.0 (CH_3), 21.4, 28.0 (CH_2), 29.6 (d, J_{FC} = 1.4 Hz, CH_2), 29.8, 30.7 (CH_2), 61.3 (OCH_2), 86.7 (d, J_{FC} = 189.0 Hz, FCH), 110.5 (d, J_{FC} = 24.0 Hz, CH), 115.1 (C), 119.6 (d, J_{FC} = 7.6 Hz, CH), 121.4 (d, J_{FC} = 7.0 Hz, C), 122.9 (d, J_{FC} = 25.3 Hz, CH), 134.6 (C), 137.9 (CH), 150.9 (d, J_{FC} = 1.6 Hz, C), 154.9 (d, J_{FC} = 19.05 Hz, C), 156.6 (C), 158.0 (d, J_{FC} = 246.7 Hz, ArFC), 165.8 (d, J_{FC} = 25.8 Hz, C=O), 175.7 (d, J_{FC} = 2.2 Hz, C=O). ^{19}F NMR (282.40 MHz, $CDCl_3$): δ = -115.7 (ArF), 182.3 (FCH). IR (ATR, 32 scans, cm^{-1}): $\tilde{\nu}$ = 3092 (w), 3074 (w), 2991 (w), 2951 (w), 2925 (m), 2853 (w), 1736 (s), 1666 (s), 1622 (w), 1604 (m), 1563 (w), 1482 (s), 1456 (s), 1425 (s), 1369 (m), 1345 (w), 1328 (m), 1304 (w), 1284 (m), 1264 (s), 1254 (s), 1242 (m), 1206 (m), 1194 (m), 1145 (w), 1078 (w), 1057 (m), 1028 (s), 956 (w), 932 (w), 881 (w), 778 (s), 746 (w) 725 (m), 637 (m), 560 (m). GCMS (EI, 70 eV, m/z > 5 %): 403 ($[M]^+$, 3), 347 (9), 346 (43), 299 (20), 298 (100), 272 (23), 261 (10), 260 (29), 259

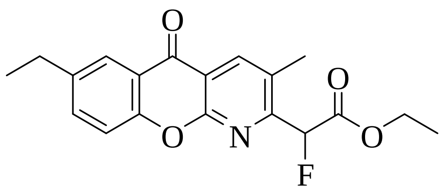
(7), 29 (5). HRMS (EI) calculated for $C_{22}H_{23}F_2NO_4$ $[M]^+$ is 403.15897, found 403.158852.

6'-Cyano-2',5-difluoro-4'-hexyl-3'-hydroxybiphenyl-2-yl ethyl carbonate (6z):



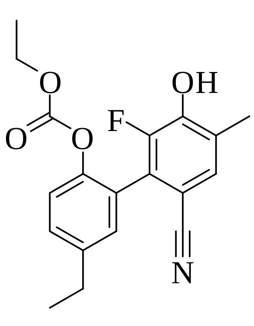
Starting with 6-fluoro-4-oxo-4*H*-chromene-3-carbonitrile **4g** (189 mg, 1.0 mmol), Me_3SiOTf (288 mg, 0.23 mL, 1.30 mmol), **3g** (489 mg, 1.30 mmol), CH_2Cl_2 (9 mL), EtOH (10 mL), and triethylamine (202 mg, 0.28 mL, 2 mmol), **6x** was isolated as yellowish white solid (294 mg, 73 %), mp = 82-84 °C. ^{1}H NMR (300.13 MHz, $CDCl_3$): δ = 0.84 (t, J = 7.0 Hz, 3H, CH_3), 1.13 (t, J = 7.1 Hz, 3H, CH_3), 1.20-1.35 (m, 6H, $3CH_2$), 1.55 (p, J = 7.1 Hz, 2H, CH_2), 2.59 (t, J = 7.4 Hz, 2H, CH_2), 4.09 (q, J = 7.1 Hz, 2H, OCH_2), 6.41 (brs, 1H, OH), 7.05 (dd, = 8.3, 3.1 Hz,1H, ArH), 7.08-7.14 (m, 1H, ArH), 7.25-7.29 (m, 2H, ArH). ^{13}C NMR (75.47 MHz, $CDCl_3$): δ = 12.8, 12.9 (CH_3), 21.4 (CH_2), 27.9 ($2CH_2$), 28.3 (d, J_{FC} = 2.3 Hz, CH_2), 30.5 (CH_2), 64.1 (OCH_2), 102.8 (d, J_{FC} = 4.2 Hz, C), 116.0 (d, J_{FC} = 3.9 Hz, C), 116.3 (d, J_{FC} = 23.3 Hz, CH), 117.0 (d, J_{FC} = 24.4 Hz, CH), 122.8 (d, J_{FC} = 8.8 Hz, CH), 123.7, (d, J_{FC} = 16.2 Hz, C), 124.9 (d, J_{FC} = 8.8 Hz, C), 129.1 (d, J_{FC} = 2.9 Hz, CH), 131.9 (d, J_{FC} = 2.6 Hz, C), 143.6 (d, J_{FC} = 3.1 Hz, C), 145.2 (d, J_{FC} = 15 Hz, C-OH), 146.7 (d, J_{FC} = 240 Hz, C), 151.7 (C=O), 158.7 (d, J_{FC} = 247 Hz, C). ^{19}F NMR (282.40 MHz, $CDCl_3$): δ = -115.39, -138.13 (ArF). IR (ATR, 32 scans, cm^{-1}): $\tilde{\nu}$ = 3218 (br), 2956 (w), 2930 (w), 2857 (w), 2236 (w), 1755 (s), 1612 (w), 1593 (w), 1573 (w), 1511 (w), 1483 (m), 1465 (m), 1402 (w), 1368 (m), 1330 (w), 1293 (w), 1278 (w), 1259 (m), 1240 (s), 1216 (s), 1181 (s), 1142 (m), 1104 (w), 1098 (w), 1058 (m), 995 (m), 897 (w), 879 (m), 838 (m), 814 (w), 778 (m), 688 (m), 665 (br), 590 (w), 552 (w). GCMS (EI, 70 eV, m/z > 5 %): 403 ($[M]^+$, 2), 345 (11), 344 (52), 314 (12), 302 (10), 289 (9), 288 (19), 275 (30), 274 (100), 262 (10), 261 (67), 260 (47), 242 (12), 240 (8), 233 (5), 43 (7), 29 (9). HRMS Pos (ESI) calculated for $C_{22}H_{24}F_2NO_4$ $[M+H]^+$ is 404.1668, found 404.1675.

Ethyl 2-(7-ethyl-3-methyl-5-oxo-5*H*-chromeno[2,3-*b*]pyridin-2-yl)-2-fluoroacetate (5aa):



Starting with 6-ethyl-4-oxo-4*H*-chromene-3-carbonitrile **4h** (199 mg, 1.0 mmol), Me_3SiOTf (288 mg, 0.23 mL, 1.30 mmol), **3c** (398 mg, 1.30 mmol), CH_2Cl_2 (9 mL), EtOH (10 mL), and triethylamine (202 mg, 0.28 mL, 2 mmol), **5aa** was isolated as yellowish white solid (34 mg, 10 %), mp = 103-104 °C. ^1H NMR (300.13 MHz, $CDCl_3$): δ = 1.19 (t, *J* = 7.3 Hz, 6H, $2CH_3$), 2.47 (d, J_{FH} = 1.8 Hz, 3H, $ArCH_3$), 2.66 (q, *J* = 7.6 Hz, 2H, $ArCH_2$), 4.20-4.29 (m, 2H, OCH_2), 6.01 (d, J_{FH} = 47.2 Hz, FCH), 7.40 (d, *J* = 8.5 Hz, 1H, ArH), 7.50 (dd, *J* = 8.6, 2.3 Hz, 1H, ArH), 7.97 (d, *J* = 2.0 Hz, 1H, ArH), 8.43 (s, 1H, ArH). ^{13}C NMR (62.89 MHz, $CDCl_3$): δ = 13.0 (CH_3), 14.3 ($ArCH_2CH_3$), 16.1 (d, J_{FC} = 2.5 Hz, $ArCH_3$), 27.1 ($ArCH_2$), 61.2 (OCH_2), 87.5 (d, J_{FC} = 188.8 Hz, FCH), 115.7 (d, J_{FC} = 1.8 Hz, C), 117.3 (CH), 120.1 (C), 123.7 (CH), 129.1 (C), 134.9, 138.7 (CH), 139.8, 153.1 (C), 154.6 (d, J_{FC} = 19.7 Hz, C), 156.8 (C), 165.7 (d, J_{FC} = 25.9 Hz, C=O), 176.2 (C=O). ^{19}F NMR (282.40 MHz, $CDCl_3$): δ = -185.65 (FCH). IR (ATR, 32 scans, cm^{-1}): $\tilde{\nu}$ = 3091 (w), 3052 (w), 2971 (m), 2936 (w), 2877 (w), 1746 (w), 1728 (s), 1660 (s), 1606 (s), 1590 (m), 1558 (w), 1489 (m), 1452 (s), 1417 (s), 1368 (m), 1348 (w), 1303 (s), 1278 (s), 1235 (s), 1209 (s), 1192 (m), 1153 (m), 1143 (m), 1104 (m), 1024 (m), 965 (w), 941 (w), 844 (s), 801 (m), 786 (m), 751 (m), 698 (w), 552 (m). GCMS (EI, 70 eV, m/z > 5 %): 344 ($[M+1]^+$, 20), 343 ($[M]^+$, 100), 297 (20), 272 (11), 271 (74), 270 (93), 256 (14), 255 (19), 254 (10), 242 (13), 240 (7), 227 (9), 133 (4), 128 (4), 29 (10). HRMS (EI) calculated for $C_{19}H_{18}FNO_4$ $[M]^+$ is 343.121440, found 343.120972.

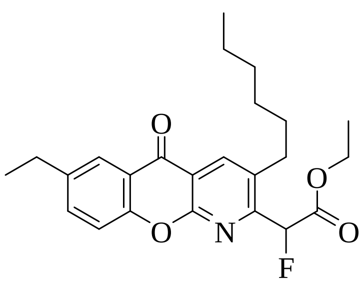
6'-Cyano-5-ethyl-2'-fluoro-3'-hydroxy-4'-methylbiphenyl-2-yl ethyl carbonate (6aa)



Starting with 6-ethyl-4-oxo-4*H*-chromene-3-carbonitrile **4h** (199 mg, 1.0 mmol), Me_3SiOTf (288 mg, 0.23 mL, 1.30 mmol), **3c** (398 mg, 1.30 mmol), CH_2Cl_2 (9 mL), EtOH (10 mL), and triethylamine (202 mg, 0.28 mL, 2 mmol), **6aa** was isolated as white solid (247 mg, 72 %), mp = 104-106 °C. ^1H NMR (300.13 MHz, $(CD_3)_2CO$): δ = 1.15 (t, *J* = 7.1 Hz, 3H, CH_3), 1.26 (t, *J* = 7.6 Hz, 3H, CH_3), 2.33 (d, J_{FH} ,= 0.7 Hz, 3H, $ArCH_3$), 2.73 (q, *J* = 7.7 Hz, 2H, $ArCH_2$), 4.11 (q, *J* = 7.1 Hz, 2H, OCH_2), 7.32 (d, *J* = 5.1 Hz, 1H, ArH), 7.34 (s, 1H, ArH), 7.40 (dd, *J* =

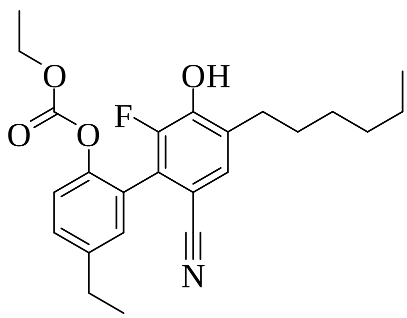
8.6, 2.1 Hz, 1H, ArH), 7.47 (d, *J* = 1.4 Hz, 1H, ArH), 9.61 (brs, 1H, OH). ^{13}C NMR (62.89 MHz, $(CD_3)_2CO$): δ = 14.1 (CH_3), 15.5 (d, J_{FC} = 2.8 Hz, CH_3), 15.8 ($ArCH_3$), 28.6 ($ArCH_2$), 65.1 (OCH_2), 104.3 (d, J_{FC} = 4.4 Hz, C), 117.9 (d, J_{FC} = 3.8 Hz, C), 122.9 (CH), 125.5 (C), 127.3 (d, J_{FC} = 17.8 Hz, C), 129.1 (d, J_{FC} = 3.6 Hz, CH), 130.5, 131.3 (CH), 131.4 (d, J_{FC} = 2.4 Hz, C), 142.8, 147.6 (C), 147.9 (d, J_{FC} = 15.1 Hz, C-OH), 149.0 (d, J_{FC} = 240 Hz, C), 153.3 (C=O). ^{19}F NMR (282.40 MHz, $(CD_3)_2CO$): δ = 40.68 (ArF). IR (ATR, 32 scans, cm^{-1}): $\tilde{\nu}$ = 3218 (br), 2964 (w), 2929 (w), 2871 (w), 2233 (m), 1755 (s), 1714 (w), 1615 (m), 1573 (w), 1483 (m), 1471 (m), 1435 (w), 1404 (w), 1368 (w), 1318 (m), 1297 (m), 1247 (s), 1206 (s), 1196 (s), 1145 (m), 1120 (m), 1054 (m), 1033 (m), 994 (w), 977 (m), 895 (m), 835 (m), 779 (m), 769 (w), 689 (m), 674 (w), 658 (w), 592 (w). GCMS (EI, 70 eV, m/z > 5 %): 344 ([M+1]$^+$, 1), 343 ([M]$^+$, 2), 285 (9), 284 (48), 272 (9), 271 (53), 270 (22), 257 (16), 256 (100), 254 (15), 242 (6), 241 (5), 236 (5), 29 (7). HRMS (ESI) calculated mass for $C_{19}H_{19}FNO_4$ [M+H]$^+$ is 344.1293, found 344.1294.

Ethyl 2-(7-ethyl-3-hexyl-5-oxo-5*H*-chromeno[2,3-*b*]pyridin-2-yl)-2-fluoroacetate



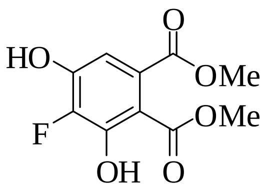
(5ab): Starting with 6-ethyl-4-oxo-4*H*-chromene-3-carbonitrile **4h** (199 mg, 1.0 mmol), Me_3SiOTf (288 mg, 0.23 mL, 1.30 mmol), **3g** (489 mg, 1.30 mmol), CH_2Cl_2 (9 mL), EtOH (10 mL), and triethylamine (202 mg, 0.28 mL, 2 mmol), **5ab** was isolated as yellowish white semisolid (49 mg, 12 %). ^{1}H NMR (300.13 MHz, $CDCl_3$): δ = 0.82 (t, *J* = 7.2 Hz, 3H, CH_3), 1.20-1.38 (m, 12H), 1.59-1.67 (m, 2H, CH_2), 2.70 (q, *J* = 7.6 Hz, 2H, CH_2), 2.76-2.82 (m, 2H, CH_2), 4.21-4.33 (m, 2H, OCH_2), 6.06 (d, J_{FH} = 47.6 Hz, FCH), 7.44 (d, *J* = 8.6 Hz, 1H, ArH), 7.54 (dd, *J* = 8.6, 2.2 Hz, 1H, ArH), 8.03 (d, *J* = 2.0 Hz, 1H, ArH), 8.51 (s, 1H, ArH). ^{13}C NMR (62.89 MHz, $CDCl_3$): δ = 13.0, 13.1 (CH_3), 14.4 (CH_3), 21.5, 27.2 (CH_2), 29.6 (d, J_{FC} = 1.2 Hz, CH_2), 29.9, 30.5 (CH_2), 61.2 (OCH_2), 86.8 (d, J_{FC} = 188.5 Hz, FCH), 116.0 (d, J_{FC} = 1.9 Hz, C), 117.4 (CH), 120.2 (C), 123.8 (CH), 134.1 (C), 135.0, 137.9 (CH), 139.9, 153.2 (C), 154.3 (d, J_{FC} = 18.8 Hz, C), 156.8 (C), 166.0 (d, J_{FC} = 25.9 Hz, C=O), 176.4 (C=O). ^{19}F NMR (282.40 MHz, $CDCl_3$): δ = -182.09 (FCH). IR (ATR, 32 scans, cm^{-1}): $\tilde{\nu}$ = 2959 (m), 2928 (m), 2857 (m), 1764 (m), 1665 (s), 1619 (m), 1605 (s), 1590 (m), 1559 (w), 1487 (m), 1452 (s), 1421 (s), 1370 (m), 1340 (w), 1300 (m), 1275 (m), 1219 (s), 1205 (s), 1135 (w), 1092 (m), 1066 (m), 1019 (m), 958 (w), 940 (w), 907 (w), 828 (m), 799 (m) 749 (m), 700 (w), 579 (w). GCMS (EI, 70 eV, m/z > 5 %): 413 ($[M]^+$, 5), 357 (11), 356 (45), 309 (19), 308 (100), 282 (18), 270 (26), 266 (5), 255 (6), 254 (7), 29 (5). HRMS (EI) calculated for $C_{24}H_{28}FNO_4$ $[M]^+$ is 413.199690, found 413.199222.

6'-Cyano-5-ethyl-2'-fluoro-4'-hexyl-3'-hydroxybiphenyl-2-yl ethyl carbonate (6ab):



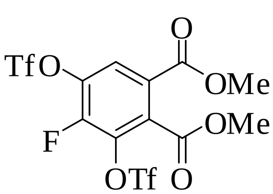
Starting with 6-ethyl-4-oxo-4*H*-chromene-3-carbonitrile **4h** (199 mg, 1.0 mmol), Me_3SiOTf (288 mg, 0.23 mL, 1.30 mmol), **3g** (489 mg, 1.30 mmol), CH_2Cl_2 (9 mL), EtOH (10 mL), and triethylamine (202 mg, 0.28 mL, 2 mmol), **6ab** was isolated as yellowish white solid (289 mg, 70 %), mp = 78-80 °C. ^{1}H NMR (300.13 MHz, $CDCl_3$): δ = 0.83 (t, *J* = 6.9 Hz, 3H, CH_3), 1.13 (t, *J* = 7.1 Hz, 3H, CH_3), 1.18 (t, *J* = 7.7 Hz, 3H, CH_3), 1.21-1.36 (m, 6H, $3CH_2$), 1.54 (p, *J* = 7.2 Hz, 2H, CH_2), 2.54-2.65 (m, 4H, $2CH_2$), 4.07 (q, *J* = 7.1 Hz, 2H, OCH_2), 6.22 (brs, 1H, OH), 7.14 (d, *J* = 1.8 Hz, 1H, ArH), 7.16-7.22 (m, 2H, ArH), 7.24 (d, *J* = 1.4 Hz, 1H, ArH), ^{13}C NMR (62.89 MHz, $CDCl_3$): δ = 12.9, 13.0, 14.3 (CH_3), 21.5, 27.2, 28.0, 28.1 (CH_2), 28.3 (d, J_{FC} = 2.3 Hz, CH_2), 30.6 (CH_2), 63.9 (OCH_2), 103.3 (d, J_{FC} = 4.5 Hz, C), 116.5 (d, J_{FC} = 3.8 Hz, C), 121.0 (CH), 123.0 (C), 125.3 (d, J_{FC} = 17.9 Hz, C), 129.1 (CH), 129.2 (d, J_{FC} = 3.0 Hz, CH), 129.6 (CH), 131.3 (d, J_{FC} = 2.4 Hz, C), 141.2 (C), 145.0 (d, J_{FC} = 15.0 Hz, C-OH), 145.5 (C), 146.7 (d, J_{FC} = 239 Hz, C), 151.9 (C=O). ^{19}F NMR (282.40 MHz, $CDCl_3$): δ = -138.42 (ArF). IR (ATR, 32 scans, cm^{-1}): $\tilde{\nu}$ = 3299 (br), 2962 (w), 2926 (m), 2858 (w), 2230 (m), 1760 (s), 1610 (w), 1575 (w), 1511 (w), 1483 (m), 1454 (s), 1406 (w), 1391 (w), 1367 (m), 1326 (w), 1294 (m), 1241 (s), 1203 (s), 1193 (s), 1140 (m), 1120 (m), 1096 (m), 1050 (m), 1001 (w), 973 (m), 894 (w), 878 (w), 826 (m), 775 (m), 633 (br), 610 (m), 577 (m). GCMS (EI, 70 eV, m/z > 5 %): 413 ($[M]^+$, 3), 370 (5), 369 (13), 355 (14), 354 (62), 341 (15), 340 (8), 327 (10), 326 (30), 325 (12), 324 (18), 313 (9), 312 (11), 299 (18), 298 (22), 285 (42), 284 (100), 282 (10), 272 (15), 271 (79), 270 (25), 256 (8), 254 (11), 252 (13), 250.13 (9), 208 (11), 178 (7), 177 (7), 29 (15). HRMS (EI) calculated for $C_{24}H_{28}FNO_4$ $[M]^+$ is 413.199690, found 413.199583.

Synthesis of dimethyl 4-fluoro-3,5-dihydroxyphthalate (8).



Diene **3a** (9.0 g, 30.8 mmol) was added to DMAD (6.5 g, 5.5 mL, 46.2 mmol) at –78 °C. The mixture was allowed to warm up to 20 °C during 20h with stirring. To the mixture was added hydrochloric acid (10 %) (50 mL). The organic and the aqueous layer were separated and the latter was extracted with CH_2Cl_2 (50 mL). The combined organic layers were dried (Na_2SO_4), filtered and the filtrate was concentrated *in vacuo*. The residue was purified by column chromatography (silica gel, *n*-heptane/EtOAc = 10:1) to give **8** as a crystalline colourless solid (3.0 g, 40 %), mp = 140-142 °C. ^{1}H NMR (250.13 MHz, $CDCl_3$): δ = 3.87 (s, 3H, OCH_3), 3.90 (s, 3H, OCH_3), 6.15 (s, 1H, OH), 6.60 (d, 1H, J_{FH} = 7.5 Hz, ArH), 10.96 (s, 1H, OH). ^{13}C NMR (75.47 MHz, $CDCl_3$): δ = 52.8, 53.0 (OCH_3), 104.6 (C), 108.4 (CH), 131.6 (d, J_{FC} = 4.5 Hz, C), 140.5 (d, J_{FC} = 239 Hz, CF), 148.3 (d, J_{FC} = 11.7 Hz, C-OH), 151.1 (d, J_{FC} = 11.0 Hz, C-OH), 168.6 (C=O), 168.8 (d, J_{FC} = 3.0 Hz, C=O). ^{19}F NMR (282.40 MHz, $CDCl_3$): δ = -160.80 (ArF). IR (ATR, 32 scans, cm^{-1}): $\tilde{\nu}$ = 3292 (m), 2962 (w), 2859 (w), 1716 (s), 1682 (s), 1621 (s), 1599 (s), 1515 (w), 1434 (s), 1325 (s), 1236(s), 1093(s), 933(w). GCMS (EI, 70 eV, m/z > 5 %): 244 ([M]$^+$, 24), 212 (53), 181 (11), 154 (100), 126 (12), 97 (9). HRMS (EI) calculated for $C_{10}H_9FO_6$ [M]$^+$ is 244.037770, found 244.037617.

Synthesis of dimethyl 4-fluoro-3,5-bis(trifluoromethylsulfonyloxy)phthalate (9).

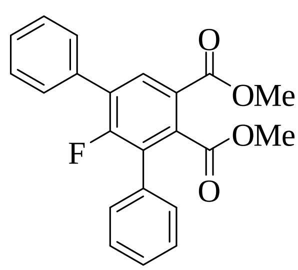


To a solution of dimethyl 4-fluoro-3,5-dihydroxyphthalate **8** (2.00 g, 8.0 mmol) in CH_2Cl_2 (80 mL) was added pyridine (2.6 mL, 32.0 mmol) at –78 °C under an argon atmosphere. After 10 min stirring, Tf_2O (3.2 mL, 19.2 mmol), was added at -78 °C. The mixture was allowed to warm up to 0 °C and stirred for 4h. The reaction mixture was filtered and the filtrate was concentrated *in vacuo*. The products of the reaction mixture were isolated by rapid column chromatography (flash silica gel, *n*-heptanes/EtOAc = 20:1), giving **9** as viscous colourless liquid (3.54 g, 87 %). ^{1}H NMR (300.13 MHz, $CDCl_3$): δ = 3.87 (s, 3H, OCH_3), 3.90 (s, 3H, OCH_3), 7.96 (d, J_{FH} = 6.4 Hz, 1H, ArH). ^{13}C NMR (75.47 MHz, $CDCl_3$): δ = 52.6, 52.7 (OCH_3), 117.5 (q, J_{FC} = 321 Hz, CF_3), 117.6 (q, J_{CF} = 321 Hz, CF_3), 124.3 (brs, CH), 124.9 (d, J_{FC} = 5.0 Hz, C), 130.9 (C), 133.8 (d, J_{FC} = 13.2 Hz, C), 136.7 (d, J_{FC} = 12.2 Hz, C), 148.0 (d, J_{FC} = 268 Hz, CF), 161 (CO), 161.4 (d, J_{FC} = 1.6 Hz, CO). ^{19}F NMR (282.40 MHz, $CDCl_3$): δ = -129.34 (qq, J_{FCF3} = 14.3, 5.1 Hz, ArF), -72.81 (d, J_{FCF3}= 5.1 Hz, CF_3), -72.51 (d, J_{FCF3} = 14.31 Hz, CF_3). IR (ATR, 32 scans, cm^{-1}): $\tilde{\nu}$= 2960 (w), 2922 (w), 1739 (s), 1616 (w), 1595 (w), 1502 (w), 1426 (s), 1326 (m), 1209 (s), 1128 (m), 1045 (m), 1011 (s), 971 (s), 887 (m), 821 (m), 787 (s), 750 (m), 736 (m), 650 (w), 601 (s). GCMS (EI, 70 eV, m/z > 5 %): 508 ([M]+, 12), 477 (100), 439 (5), 413 (44), 349 (52), 283 (33), 253 (6), 222 (19), 183 (16), 155 (14), 127 (4), 81 (8), 69 (63), 59 (15), 45 (4). HRMS (EI) calculated for $C_{12}H_7F_7O_{10}S_2$ $[M]^+$ is 507.936340, found 507.936470.

General procedure for suzuki-miyaura reactions of 11a-k,12a-e.

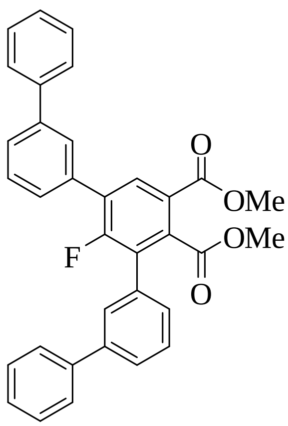
A 1,4-dioxane solution (4 mL per 3 mmol of **9**) of **9**, K_3PO_4, $Pd(PPh_3)_4$ and arylboronic acid **10** were stirred at 110 °C (for compound 11) and 90 °C (for compound 12) for 8h, in a pressure tube. After cooling to 20 °C, a saturated aqueous solution of NH_4Cl was added. The organic and the aqueous layers were separated and the latter was extracted with CH_2Cl_2 (3 x 25 mL). The combined organic layers were dried (Na_2SO_4), filtered and the filtrate was concentrated *in vacuo*. The residue was purified by column chromatography (flash silica gel, *n*-heptanes/EtOAc = 10:1).

Dimethyl 4-fluoro-3,5-bis(phenyl)phthalate (11a): Starting with **9** (152 mg, 0.3 mmol),

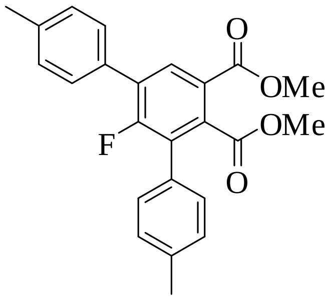


K_3PO_4 (191 mg, 0.9 mmol), $Pd(PPh_3)_4$ (3 mol %), **10a** (85 mg, 0.7 mmol) and 1,4-dioxane (4 mL), **11a** was isolated as colourless crystals (90.7 mg, 83 %), mp = 130-132 °C. ^{1}H NMR (300.13 MHz, $CDCl_3$): δ =3.67 (s, 3H, OCH_3) , 3.95 (s, 3H, OCH_3), 7.40-7.54 (m, 8H, ArH), 7.60-7.64 (m, 2H, ArH), 8.19 (d, J_{FC} = 5 Hz, 1H, ArH). ^{13}C NMR (62.89 MHz, $CDCl_3$): δ = 52.4, 52.7 (OCH_3), 123.7 (d, J_{FC} = 4.1 Hz, C), 128.2 (2CH), 128.5 (d, J_{FC} = 1.4 Hz, 2CH), 128.6 (2CH), 129.1 (d, J_{FC} = 3.2 Hz, 2CH), 129.2 (d, J_{FC} = 16 Hz, C), 129.7 (d, J_{FC} = 1.4 Hz, 2CH), 130.3 (d, J_{FC} = 16 Hz, C), 132.1 (C), 132.2 (d, J_{FC} = 5 Hz, CH), 134.2 (d, J_{FC} = 1.4 Hz, C), 136.9 (d, J_{FC} = 3.7 Hz, C), 158.9 (d, J_{FC} = 256 Hz, CF), 165.2 (CO), 167.7 (d, J_{FC} = 2.7 Hz, CO). ^{19}F NMR (282.40 MHz, $CDCl_3$): δ = -111.34 (ArF). IR (ATR, 32 scans, cm^{-1}): $\tilde{\nu}$= 3058 (w), 3003 (w), 2948 (m), 2849 (w), 1737 (s), 1720 (s), 1598 (m), 1579 (m), 1563 (m), 1499 (m), 1443 (m), 1429 (m), 1406 (m), 1344 (m), 1291 (m), 1283 (m), 1273 (s), 1247 (s), 1220 (s), 1200 (s), 1148 (s), 1072 (s), 1028 (m), 996 (m), 968 (m), 928 (m), 916 (m), 858 (m), 824 (m), 795 (m), 783 (m), 772 (m), 762 (m), 745 (m), 709 (s), 698 (s), 673 (m), 633 (m), 608 (m), 590 (w). GCMS (EI, 70 eV, m/z > 5 %): 365 ($[M+1]^+$, 14), 364 ($[M]^+$, 59), 334 (23), 333 (100), 301 (19), 274 (5), 246 (12), 245 (10), 244 (12), 233 (7), 122 (5). HRMS (EI): calculated for $C_{22}H_{17}FO_4$ $[M]^+$ is 364.11054, found 364.110399.

Dimethyl 3,5-bis(3-biphenyl)-4-fluorophthalate (11b): Starting with **9** (152 mg, 0.3 mmol), K_3PO_4 (191 mg, 0.9 mmol), $Pd(PPh_3)_4$ (3 mol %), **10b** (138.6 mg, 0.7 mmol) and 1,4-dioxane (4 mL), **11b** was isolated as viscous gel (131.7 mg, 85 %). ^{1}H NMR (300.13 MHz, $CDCl_3$): δ = 3.70 (s, 3H, OCH_3) , 3.97 (s, 3H, OCH_3), 7.38-7.53 (m, 7H, ArH), 7.56-7.61 (m, 3H, ArH), 7.61-7.71 (m, 7H, ArH), 7.84 (d, *J* = 1.1 Hz, 1H, ArH), 8.26 (d, J_{FC} = 7.0 Hz, 1H, ArH). ^{13}C NMR (75.47 MHz, $CDCl_3$): δ = 52.6, 52.8 (OCH_3), 123.8 (d, J_{FC} = 4.4 Hz, C), 127.2 (2CH), 127.3 (3CH), 127.4, 127.5, 127.6 (CH), 128.0 (t, J_{FC} = 3.3 Hz, 2CH), 128.6 (d, J_{FC} = 4.4 Hz, 2CH), 128.7 (CH), 128.8, 128.9 (2CH), 129.1 (CH), 129.2 (d, J_{FC} = 21 Hz, C), 130.3 (d, J_{FC} = 16 Hz, C), 132.3 (d, J_{FC} = 5 Hz, CH), 132.6, 134.6 (C), 137.0 (d, J_{FC} = 3.3 Hz, C), 140.5, 140.7, 141.1, 141.9 (C), 159.1 (d, J_{FC} = 256 Hz, CF), 165.2 (CO), 167.8 (d, J_{FC} = 2.8 Hz, CO). ^{19}F NMR (282 MHz, $CDCl_3$): δ = -111.01 (ArF). IR (ATR, 32 scans, cm^{-1}): $\tilde{\nu}$ = 3371 (br), 3068 (w), 2960 (w), 2926 (w), 2854 (w), 1596 (m), 1476 (m), 1461 (m), 1429 (m), 1302 (m), 1261 (s), 1197 (m), 1161 (m), 1125 (m), 1086 (s), 1025 (s), 883 (m), 792 (m), 757 (s), 732 (m), 697 (s), 668 (m), 616 (m). GCMS (EI, 70 eV, m/z > 5 %): 518 ($[M+2]^+$, 7), 517 ($[M+1]^+$, 37), 516 ($[M]^+$, 100), 486 (14), 485 (38), 472 (18), 459 (6), 454 (20), 453 (54), 398 (7), 368 (20), 328 (8), 198 (10), 197 (42), 170 (26), 135 (36), 97 (9), 57 (15), 44 (44). HRMS (EI): calculated for $C_{34}H_{25}FO_4$ $[M]^+$ is 516.173140, found 516.173579.

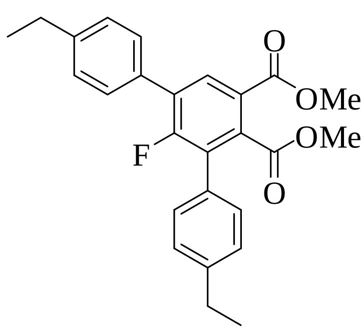


Dimethyl 4-fluoro-3,5-bis(4-methylphenyl)phthalate (11c): Starting with **9** (152 mg, 0.3 mmol), K_3PO_4 (191 mg, 0.9 mmol), $Pd(PPh_3)_4$ (3 mol %), **10c** (138.6 mg, 0.7 mmol) and 1,4-dioxane (4 mL), **11c** was isolated as semi solid gel (93 mg, 79 %). ^{1}H NMR (300.13 MHz, $CDCl_3$): δ = 2.43 (s, 3H, $ArCH_3$), 2.44 (s, 3H, $ArCH_3$), 3.69 (s, 3H,



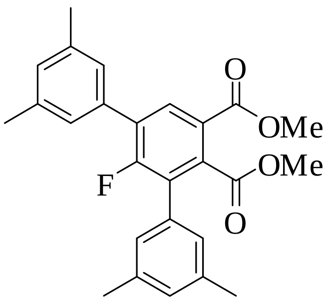
OCH_3), 3.94 (s, 3H, OCH_3), 7.25-7.32 (m, 6H, ArH), 7.51 (dd, J = 8.1, 1.7 Hz, 2H, ArH), 8.15 (d, J_{FC} = 7.2 Hz, 1H, ArH). ^{13}C NMR (62.89 MHz, $CDCl_3$): δ = 20.2, 20.3 ($ArCH_3$), 51.3, 51.6 (OCH_3), 122.6 (d, J_{FC} = 4.1 Hz, C), 127.9 (4CH), 128.0 (d, J_{FC} = 15 Hz, C), 128.1 (C), 128.3, 128.5 (2CH), 129.2 (d, J_{FC} = 16 Hz, C), 130.3 (d, J_{FC} = 1.4 Hz, C), 130.9 (d, J_{FC} = 5 Hz, CH), 135.6 (d, J_{FC} = 3.7 Hz, C), 137.3, 137.5 (C), 158.1 (d, J_{FC} = 256 Hz, CF), 164.3 (CO), 166.8 (d, J_{FC} = 3.2 Hz, CO). ^{19}F NMR (282.40 MHz, $CDCl_3$): δ = -111.34 (ArF). IR (ATR, 32 scans, cm^{-1}): $\tilde{\nu}$ = 3027 (w), 2995 (w), 2947 (m), 2919 (m), 2851 (m), 1737 (s), 1716 (s), 1614 (m), 1514 (m), 1447 (m), 1428 (s), 1391 (m), 1344 (m), 1272 (s), 1247 (s), 1221 (s), 1197 (s), 1145 (s), 1113 (m), 1069 (s), 1020 (m), 1002 (m), 968 (m), 951 (m), 926 (m), 915 (m), 862 (m), 843 (m), 824 (m), 817 (s), 803 (m), 793 (s), 773 (m), 760 (s), 723 (m), 684 (m), 644 (m), 625 (m), 593 (m), 566 (m). GCMS (EI, 70 eV, m/z > 5 %): 393 ($[M+1]^+$, 24), 392 ($[M]^+$, 91), 362 (26), 361 (100), 330 (8), 329 (32), 302 (5), 274 (10), 273 (20), 260 (5), 259 (8), 258 (6), 257 (12), 239 (5). HRMS (EI): calculated for $C_{24}H_{21}FO_4$ $[M]^+$ is 392.14184, found 392.141789.

Dimethyl 3,5-bis(4-ethylphenyl)-4-fluorophthalate (**11d**): Starting with **9** (152 mg, 0.3 mmol), K_3PO_4 (191 mg, 0.9 mmol), $Pd(PPh_3)_4$ (3 mol %), **10d** (105 mg, 0.7 mmol) and 1,4-dioxane (4 mL), **11d** was isolated as colourless solid (91 mg, 72 %), mp = 151-153 °C. ^{1}H NMR ($CDCl_3$, 300.13MHz): δ = 1.19 (t, J = 7.5 Hz, 3H, CH_3), 1.20 (t, J = 7.5 Hz, 3H, CH_3), 2.62 (q, J = 7.6 Hz, 2H, CH_2), 2.63 (q, J = 7.6 Hz, 2H, CH_2), 3.56 (s, 3H, OCH_3), 3.83 (s, 3H, OCH_3), 7.16-7.23 (m, 6H, ArH). ^{13}C NMR (75.47 MHz, $CDCl_3$): δ = 15.3, 15.5 (CH_3), 28.6 ($2CH_2$), 52.4, 52.6 (OCH_3), 123.6 (d, J_{CF} = 4.4 Hz, C), 127.7, 128.2 (2CH), 129.0 (d, J_{FC} = 2.8 Hz, 2CH), 129.3 (C), 129.6 (d, J_{FC} = 1.2 Hz, 2CH), 130.2 (d, J_{FC} = 15.9 Hz, C), 131.5 (C), 131.9 (d, J_{FC} = 5.5 Hz, CH), 136.6 (d, J_{FC} = 3.8 Hz, C), 144.7 (d, J_{FC} = 23.7 Hz, C), 159.1 (d, J_{FC} = 256 Hz, CF), 165.4 (CO), 167.9 (d, J_{FC} = 2.7 Hz, CO). ^{19}F NMR (282.40 MHz, $CDCl_3$): δ = -111.4 (ArF). IR (ATR, 32 scans, cm^{-1}): $\tilde{\nu}$ = 3037 (w), 3002 (w), 2961 (m), 2947 (m), 2931 (m), 2671(w), 1739 (m), 1717 (s), 1613 (w), 1514 (m), 1429 (m), 1396 (m), 1345 (m),1274 (m), 1247 (m), 1219

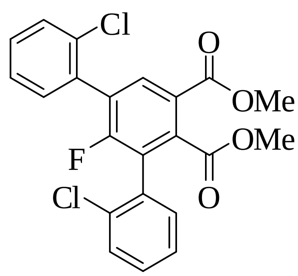


(s), 1146 (m), 1118 (m), 1069 (m), 1020 (m), 1003 (m), 968 (m), 848 (m), 835 (m), 794 (m), 683 (m), 575 (m), 531 (m). GCMS (EI, 70 eV, m/z > 5 %): 421 ($[M+1]^+$, 28), 420 ($[M]^+$, 100), 405 (20), 389 (52), 373 (3), 357 (18), 329 (7), 315 (2), 301(4), 287 (5), 273 (6), 272 (5), 259 (4), 257 (6), 252 (2), 244 (3), 195 (7), 170 (2), 143 (3), 135 (3), 129 (2), 77 (1), 59 (1), 29 (2). HRMS (EI) calculated for $C_{26}H_{25}FO_4$ $[M]^+$ is 420.17314, found 420.173423.

Dimethyl 4-fluoro-3,5-bis(3,5-dimethylphenyl)phthalate (11e): Starting with **9** (152 mg, 0.3 mmol), K_3PO_4 (191 mg, 0.9 mmol), $Pd(PPh_3)_4$ (3 mol %), **10e** (105 mg, 0.7 mmol) and 1,4-dioxane (4mL), **11e** was isolated as colourless crystals (97 mg, 77 %), mp = 150-152 °C. ^{1}H NMR (300.13 MHz, $CDCl_3$): δ = 2.38 (s, 6H, $2ArCH_3$), 2.41 (s, 6H, $2ArCH_3$), 3.70 (s, 3H, OCH_3) , 3.95 (s, 3H, OCH_3), 7.03 (s, 2H, ArH), 7.06 (s, 1H, ArH), 7.09 (s, 1H, ArH), 7.22 (s, 2H, ArH), 8.13 (d, J_{FC} = 7.2 Hz, 1H, ArH). ^{13}C NMR (75.47 MHz, $CDCl_3$): δ = 21.29, 21.33 ($2ArCH_3$), 52.2, 52.6 (OCH_3), 123.5 (d, J_{FC} = 4.4 Hz, C), 126.8, 126.9 (CH), 127.3 (2CH), 129.4 (d, J_{FC} = 20.4 Hz, C), 130.1, 130.2 (CH), 130.5 (d, J_{FC} = 16.5 Hz, C), 131. 9 (C), 132.0 (d, J_{FC} = 5.5 Hz, CH), 134.1 (d, J_{FC} = 1.1 Hz, C), 136.5 (d, J_{FC} = 3.3 Hz, C), 137.6, 138.2 (2C), 159.0 (d, J_{FC} = 256 Hz, CF), 165.4 (CO), 167.8 (d, J_{FC} = 2.2 Hz, CO). ^{19}F NMR (282.40 MHz, $CDCl_3$): δ = -110.88 (ArF). IR (ATR, 32 scans, cm^{-1}): $\tilde{\nu}$ = 3005 (w), 2954 (m), 2919 (m), 2857 (w), 1738 (s), 1722 (s), 1600 (m), 1425 (s), 1394 (m), 1385 (m), 1350 (m), 1298 (m), 1267 (s), 1247 (s), 1223 (s), 1204 (s), 1164 (m), 1145 (s), 1103 (m), 1031 (m), 1012 (m), 974 (m), 921 (m), 901 (m), 870 (m), 851 (s), 815 (m), 794 (s), 768 (s), 739 (m), 701 (s), 691 (m), 673 (m), 663 (m), 634 (m), 600 (m), 580 (w), 559 (m), 549 (m), 531 (m). GCMS (EI, 70 eV, m/z > 5 %): 422 ($[M+2]^+$, 4), 421 ($[M+1]^+$, 28), 420 ($[M]^+$, 100), 390 (23), 389 (86), 358 (10), 357 (39), 301 (11), 287 (7). HRMS Pos (ESI): calculated for $C_{26}H_{26}FO_4$ $[M+H]^+$ is 421.1809, found: 421.1809.

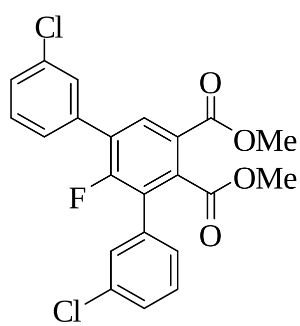


Dimethyl 3,5-bis(2-chlorophenyl)-4-fluorophthalate (11f): Starting with **9** (152 mg, 0.3 mmol), K_3PO_4 (191 mg, 0.9 mmol), $Pd(PPh_3)_4$ (3mol %), **10f** (109.5 mg, 0.7 mmol) and 1,4-dioxane (4 mL), **11f** was isolated as viscous gel (106.5 mg, 82 %). ^{1}H NMR



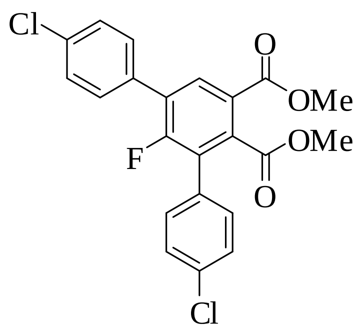
(300.13 MHz, $CDCl_3$): δ =3.65 (s, 3H, OCH_3) , 3.93 (s, 3H, OCH_3), 7.34-7.42 (m, 6H, ArH), 7.49-7.55 (m, 2H, ArH), 8.12 (d, J_{FC} = 6.8 Hz, ArH). ^{13}C NMR (75.47 MHz, $CDCl_3$): δ = 52.4 , 52.7 (OCH_3), 123.5 (d, J_{FC} = 4.1 Hz, C), 126.2 (d, J_{FC} = 18 Hz, C), 126.4, 126.8 (CH), 128.2 (d, J_{FC} = 18 Hz, C), 129.4, 129.8, 130.0, 130.2 (CH), 131.0 (C), 131.5 (2CH), 133.2, 133.7 (C), 133.8 (d, J_{FC} = 5 Hz, CH), 134.5 (C), 137.6 (d, J_{FC} = 3.6 Hz, C), 159.1 (d, J_{FC} = 257 Hz, CF), 165.0 (CO), 167.1 (d, J_{FC} = 2.7 Hz, CO). ^{19}F NMR (282.40 MHz, $CDCl_3$): δ = -104.98 (ArF). IR (ATR, 32 scans, cm^{-1}): $\tilde{\nu}$= 3060 (w), 2998 (w), 2951 (m), 2926 (w), 2851 (w), 1725 (s), 1567 (m), 1481 (m), 1455 (m), 1428 (m), 1409 (m), 1345 (m), 1276 (s), 1245 (s), 1220 (s), 1197 (m), 1147 (m), 1128 (m), 1091 (m), 1047 (m), 998 (m), 973 (m), 949 (w), 919 (m), 855 (m), 830 (m), 795 (m), 782 (m), 752 (s), 738 (s), 728 (m), 719 (m), 696 (m), 678 (m), 643 (w), 628 (m), 612 (m), 540 (m). GCMS (EI, 70 eV, m/z > 5 %): 401 (10), 400 (8), 399 (44), 398 (26), 397 (100), 351 (11), 244 (8). HRMS Pos (ESI): calculated for $C_{22}H_{16}Cl_2FO_4$ $[M+H]^+$ is 433.04042, found 433.03984.

Dimethyl 3,5-bis(3-chlorophenyl)-4-fluorophthalate (11g): Starting with **9** (152 mg, 0.3 mmol), K_3PO_4 (191 mg, 0.9 mmol), $Pd(PPh_3)_4$ (3mol %), **10g** (109.5 mg, 0.7 mmol) and 1,4-dioxane (4 mL), **11g** was isolated as viscous gel (81.9 mg, 63 %). ^{1}H NMR (300.13 MHz, $CDCl_3$): δ =3.69 (s, 3H, OCH_3) , 3.93 (s, 3H, OCH_3), 7.27 (dt, J = 6.1, 1.7 Hz, 1H, ArH), 7.34-7.48 (m, 6H, ArH), 8.12 (t, J_{FC} = 1.3 Hz, ArH), 8.14 (d, J = 7.2 Hz, 1H, ArH). ^{13}C NMR (75.47 MHz, $CDCl_3$): δ = 52.6 , 52.8 (OCH_3), 124.0 (d, J_{FC} = 4.4 Hz, C), 127.2 (d, J_{FC} = 3.3 Hz, CH), 127.8 (d, J_{FC} = 20 Hz, C), 127.9, 128.8, 128.9 (CH), 129.0 (d, J_{FC} = 15 Hz, C), 129.1 (d, J_{FC} = 3.3 Hz, CH), 129.5, 129.8, 130.0 (CH), 132.4 (d, J_{FC} = 5 Hz, CH), 133.5, 134.2, 134.7, 135.6 (C), 137.3 (d, J_{FC} = 3.3 Hz, C), 158.7 (d, J_{FC} = 257 Hz, CF), 165.0 (CO), 167.2 (d, J_{FC} = 2.8 Hz, CO). ^{19}F NMR (282.40 MHz, $CDCl_3$): δ = -110.94 (ArF). IR (ATR, 32 scans, cm^{-1}): $\tilde{\nu}$= 3066 (w), 2998 (w), 2951 (m), 2848 (w), 1725 (s), 1595 (m), 1566 (m), 1480 (m), 1433 (m), 1389 (m), 1340 (m), 1276 (s), 1264 (s), 1248 (s), 1220 (s), 1197 (m), 1149 (s), 1097 (m), 1082 (m), 1070 (s), 1006 (m), 977 (m), 824 (m),

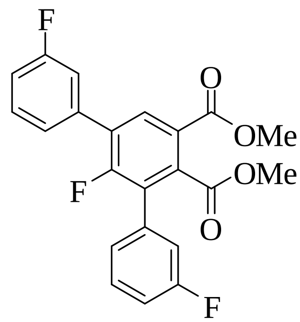


884 (m), 854 (m), 788 (s), 749 (m), 695 (s), 679 (m), 632 (m), 620 (m), 599 (w), 542 (w). GCMS (EI, 70 eV, m/z > 5 %): 436 ($[M]^+$, $^{37}Cl_2$, 6), 435 ($[M+1]^+$, ^{37}Cl, 7), 434 ($[M]^+$, ^{37}Cl, 32), 433 ($[M+1]^+$, ^{35}Cl, 12), 432 ($[M]^+$, ^{35}Cl, 48), 405 (12), 404 (15), 403 (68), 402 (24), 401 (100), 371 (8), 369 (12), 280 (7), 244 (15), 198 (9), 122 (6). HRMS (EI): calculated for $C_{22}H_{15}Cl_2FO_4$ $[M]^+$ is 432.03259, found 432.032778.

Dimethyl 3,5-bis(4-chlorophenyl)-4-fluorophthalate (11h): Starting with **9** (152 mg, 0.3 mmol), K_3PO_4 (191 mg, 0.9 mmol), $Pd(PPh_3)_4$ (3 mol %), **10h** (109.5 mg, 0.7 mmol) and 1,4-dioxane (4 mL), **11h** was isolated as colourless crystals (97.5 mg, 75 %), mp = 172-174 °C. ^{1}H NMR (300.13 MHz, $CDCl_3$): δ =3.70 (s, 3H, OCH_3) , 3.95 (s, 3H, OCH_3), 7.30 (d, J = 11 Hz, 1H, ArH), 7.35 (s, 1H, ArH), 7.42-7.55 (m, 6H, ArH), 8.15 (d, J_{FC} = 7.2 Hz, 1H, ArH). ^{13}C NMR (75.47 MHz, $CDCl_3$): δ = 52.6, 52.8 (OCH_3), 124.0 (d, J_{FC} = 4.4 Hz, C), 128.1 (d, J_{FC} = 20 Hz, C), 128.2 (C), 128.6, 129.0 (2CH), 129.2 (d, J_{FC} = 15.4 Hz, C), 130.3 (d, J_{FC} = 2.8 Hz, 2CH), 131.0 (2CH), 132.2 (d, J_{FC} = 5 Hz, CH), 132.3 (C), 134.9 (2C), 137.1 (d, J_{FC} = 3.3 Hz, C), 158.7 (d, J_{FC} = 257 Hz, CF), 165.0 (CO), 167.4 (d, J_{FC} = 2.8 Hz, CO). ^{19}F NMR (282.40 MHz, $CDCl_3$): δ = -111.25 (ArF). IR (ATR, 32 scans, cm^{-1}): $\tilde{\nu}$ = 3039 (w), 3003 (w), 2952 (m), 2923 (m), 2851 (m), 1723 (s), 1681 (m), 1594 (m), 1574 (m), 1556 (m), 1494 (m), 1486 (m), 1430 (m), 1386 (m), 1344 (m), 1294 (m), 1264 (s), 1245 (s), 1219 (s), 1199 (m), 1149 (m), 1103 (m), 1090 (s), 1068 (s), 1027 (m), 1014 (s), 1004 (m), 995 (m), 969 (m), 915 (m), 862 (m), 845 (m), 831 (m), 817 (s), 794 (s), 776 (m), 763 (m), 739 (s), 719 (m), 694 (m), 668 (m), 661 (m), 616 (m), 587 (m), 558 (w). GCMS (EI, 70 eV, m/z > 5 %): 436 ($[M]^+$, $^{37}Cl_2$, 8), 435 ($[M+1]^+$, ^{37}Cl, 11), 434 ($[M]^+$, ^{37}Cl, 45), 433 ($[M+1]^+$, ^{35}Cl, 17), 432 ($[M]^+$, ^{35}Cl, 67), 405 (12), 404 (15), 403 (67), 402 (24), 401 (100), 371 (8), 369 (11), 314 (6), 280 (7), 244 (14), 242 (6), 199 (18), 122 (6). HRMS Pos (ESI): calculated for $C_{22}H_{16}Cl_2FO_4$ $[M+H]^+$ is 433.04042, found 433.03987.

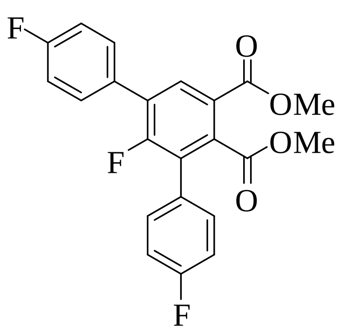


Dimethyl 4-fluoro-3,5-bis(3-fluorophenyl)phthalate (11i): Starting with **9** (152 mg, 0.3 mmol), K_3PO_4 (191 mg, 0.9 mmol), $Pd(PPh_3)_4$ (3mol %), **10i** (98 mg, 0.7 mmol) and 1,4-dioxane (4 mL), **11i** was isolated as colourless crystals (98.5 mg, 82 %), mp = 92-94 °C.



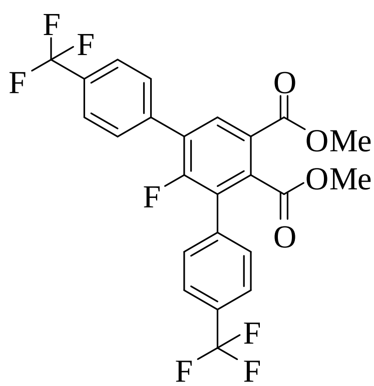
^{1}H NMR (300.13 MHz, $CDCl_3$): δ =3.70 (s, 3H, OCH_3), 3.95 (s, 3H, OCH_3), 7.12-7.20 (m, 4H, ArH), 7.30-7.49 (m, 4H, ArH), 7.86 (d, J_{FH} = 6.6 Hz, 1H, ArH). ^{13}C NMR (75.47 MHz, $CDCl_3$): δ = 52.6, 52.8 (OCH_3), 115.6 (d, J_{FC} = 20.9 Hz, CH), 115.7 (d, J_{FC} = 20.9 Hz, CH), 116.2 (dd, J_{FC} = 23.1, 3.3 Hz, CH), 116.9 (dd, J_{FC} = 22.6, 1.1 Hz, CH), 124.0 (d, J_{FC} = 4.4 Hz, C), 124.8 (t, J_{FC} = 3 Hz, CH), 125.5 (dd, J_{FC} = 3.3, 1.1 Hz, CH), 128.1 (d, J_{FC} = 20 Hz, C), 129.2 (d, J_{FC} = 15.4, 2.7 Hz, C), 129.8 (d, J_{FC} = 8.3 Hz, CH), 130.3 (d, J_{FC} = 8.3 Hz, CH), 132.4 (d, J_{FC} = 5 Hz, CH), 133.8 (d, J_{FC} = 8.3 Hz, C), 135.9 (d, J_{FC} = 8.3, 1.1 Hz, C), 137.2 (d, J_{FC} = 3.3 Hz, C), 158.7 (d, J_{FC} = 257 Hz, C), 162.4 (d, J_{FC} = 247 Hz, C), 162.8 (d, J_{FC} = 246 Hz, C), 164.9 (CO), 167.3 (d, J_{FC} = 2.8 Hz, CO).^{19}F NMR (282.40 MHz, $CDCl_3$): δ = -111.08, -112.39, -112. 78 (ArF). IR (ATR, 32 scans, cm^{-1}): $\tilde{\nu}$ = 3070 (w), 3003 (w), 2953 (m), 2845 (w), 1737 (s), 1720 (s), 1613 (m), 1607 (m), 1583 (s), 1491 (m), 1439 (m), 1428 (m), 1395 (m), 1343 (m), 1294 (s), 1282 (s), 1263 (m), 1238 (s), 1223 (s), 1193 (s), 1184 (s), 1155 (m), 1133 (m), 1084 (m), 1075 (m), 1062 (m), 1041 (m), 1012 (m), 973 (m), 943 (m), 927 (m), 901 (m), 887 (s), 834 (m), 802 (m), 787 (s), 774 (m), 757 (m), 711 (s), 696 (s), 674 (m), 653 (w), 636 (w), 628 (m), 609 (m), 561 (m), 544 (w). GCMS (EI, 70 eV, m/z > 5 %): 401 ($[M+1]^+$, 10), 400 ($[M]^+$, 43), 370 (23), 369 (100), 337 (9), 282 (9), 280 (6), 269 (6), 262 (6). HRMS (EI): calculated for $C_{22}H_{15}F_3O_4$ $[M]^+$ is 400.091695, found: 400.091973.

Dimethyl 4-fluoro-3,5-bis(4-fluorophenyl)phthalate (11j): Starting with **9** (152 mg, 0.3 mmol), K_3PO_4 (191 mg, 0.9 mmol), $Pd(PPh_3)_4$ (3mol %), **10j** (98 mg, 0.7 mmol) and 1,4-dioxane (4 mL), **11j** was isolated as colourless crystals (104.5 mg, 87 %), mp = 108-111 °C.



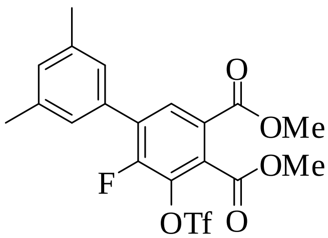
^{1}H NMR (500 MHz, $CDCl_3$): δ =3.69 (s, 3H, OCH_3), 3.95 (s, 3H, OCH_3), 7.13-7.22 (m, 4H, ArH), 7.39 (t, J_{FH} = 6.7 Hz, 2H, ArH), 7.58 (t, J_{FH} = 6.2 Hz, 2H, ArH), 8.15 (d, J_{FH} = 7.0 Hz, 1H, ArH). ^{13}C NMR (75.47 MHz, $CDCl_3$): δ = 52.5, 52.7 (OCH_3), 123.8 (d, J_{FC} = 4.4 Hz, C), 115.3 (d, J_{FC} = 22.0 Hz, 2CH), 115.7 (d, J_{FC} = 22.0 Hz, 2CH), 127.8 (d, J_{FC} = 3.3 Hz, C), 128.2 (d, J_{FC} = 20.4 Hz, C), 129.3 (d, J_{FC} = 16 Hz, C), 129.9 (d, J_{FC} = 2.2, 1.1 Hz, C), 130.8 (d, J_{FC} = 3.3 Hz, CH), 130.9 (d, J_{FC} = 3.3 Hz, CH), 131.5 (d, J_{FC} = 8.3 Hz, 2CH), 132.2 (d, J_{FC} = 5 Hz, CH), 137.0 (d, J_{FC} = 3.3 Hz, C), 158.8 (d, J_{FC} = 255 Hz, C), 162.8 (d, J_{FC} = 248 Hz, C), 162.9 (d, J_{FC} = 249 Hz, C), 165.0 (CO), 167.5 (d, J_{FC} = 2.8 Hz, CO). ^{19}F NMR (282.40 MHz, $CDCl_3$): δ = -111.50, -112.70, -112. 79 (ArF). IR (ATR, 32 scans, cm^{-1}): $\tilde{\nu}$ = 3070 (w), 3003 (w), 2955 (w), 2925 (w), 2850 (w), 1738 (s), 1727 (s), 1590 (w), 1557 (w), 1513 (w), 1495 (w), 1439 (m), 1425 (m), 1379 (w), 1356 (m), 1325 (s), 1261 (s), 1249 (s), 1237 (s), 1201 (m), 1183 (m), 1162 (s), 1147 (m), 1118 (s), 1094 (s), 1074 (s), 1066 (s), 986 (m), 965 (m), 930 (m), 912 (m), 899 (m), 881 (m), 840 (m), 806 (s), 791 (s), 783 (s), 762 (m), 704 (s), 690 (m), 665 (s), 585 (m), 565 (m). GCMS (EI, 70 eV, m/z > 5 %): 401 ($[M+1]^+$, 14), 400 ($[M]^+$, 62), 370 (22), 369 (100), 337 (10), 282 (12), 269 (7), 262 (7), 85 (6), 84 (18), 83 (9), 81 (7), 69 (15), 65 (13), 57 (14), 55 (12), 51 (7), 49 (20), 44 (33), 43 (12), 41 (14). HRMS (EI): calculated for $C_{22}H_{15}F_3O_4$ $[M]^+$ is 400.09170, found 400.091847.

Dimethyl 4-fluoro-3,5-bis(4-trifluoromethylphenyl)phthalate (11k): Starting with **9** (152 mg, 0.3 mmol), K_3PO_4 (191 mg, 0.9 mmol), $Pd(PPh_3)_4$ (3mol %), **10k** (133 mg, 0.7 mmol) and 1,4-dioxane (4 mL), **11k** was isolated as colourless crystals (100.5 mg, 67 %), mp = 117-119 °C. ^{1}H NMR (500 MHz, $CDCl_3$): δ =3.69 (s, 3H, OCH_3), 3.96 (s, 3H, OCH_3), 7.53 (s, 1H, ArH), 7.56 (s, 1H, ArH), 7.71-7.79 (m, 6H, ArH), 8.22 (d, J_{FH} = 7.0 Hz, 1H, ArH). ^{13}C NMR (75.47 MHz, $CDCl_3$): δ = 52.7, 52.9 (OCH_3), 123.9 (q, J_{FC} = 272 Hz, $2CF_3$), 124.2 (d, J_{FC} = 4.4 Hz, C), 125.2 (q, J_{FC} = 3.5 Hz, 2CH), 125.7 (q, J_{FC} = 3.9 Hz, 2CH), 128.0 (d, J_{FC} = 20 Hz, C), 129.1 (d, J_{FC} = 15 Hz, C), 129.5 (d, J_{FC} = 3.3 Hz, 2CH), 130.2 (d, J_{FC} = 1.1 Hz, 2CH), 130.6 (q, J_{FC} = 6.6 Hz, C), 131.1 (q, J_{FC} = 6.6 Hz, C), 132.7 (d, J_{FC} = 5 Hz, CH), 135.5, 137.4 (C), 137.5 (d, J_{FC} = 5 Hz, C), 158.7 (d, J_{FC} = 257 Hz, C), 164.8 (CO), 167.1 (d, J_{FC} = 2.2 Hz, CO). ^{19}F NMR (282.40 MHz, $CDCl_3$): δ = -62.76, -62.77 ($ArCF_3$), -111.27 (ArF). IR (ATR, 32 scans, cm^{-1}): $\tilde{\nu}$ = 3002 (w), 2963 (w), 2849 (w), 1726 (s), 1620 (m), 1086 (m), 1519 (w), 1440 (m), 1433 (m), 1406 (m), 1321 (s), 1298 (s), 1277 (s), 1245 (s), 1221 (s), 1201 (m), 1137 (s), 1126 (s), 1107 (s), 1076 (s), 1061 (s), 1017 (s), 994 (m), 967 (m), 918 (m), 858 (m), 851 (m), 841 (m), 828 (m), 805 (w), 796 (m), 767 (m), 758 (m), 748 (m), 738 (m), 705 (s), 677 (m), 657 (m), 627 (m), 604 (m), 589 (w). GCMS (EI,

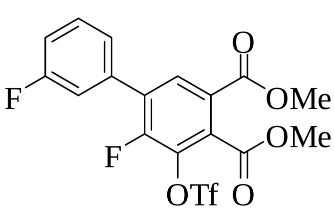


70 eV, m/z > 5 %): 501 ($[M+1]^+$, 3), 500 ($[M]^+$, 10), 470 (9), 469 (36), 122 (9), 121 (100), 93 (17), 86 (11), 85 (6), 84 (18), 83 (9), 81 (7), 69 (15), 65 (13), 57 (14), 55 (12), 51 (7), 49 (20), 44 (33), 43 (12), 41 (14). HRMS (EI): calculated for $C_{24}H_{15}F_7O_4$ $[M]^+$ is 500.08531, found 500.085593.

Dimethyl 4-fluoro-3-(trifluoromethylsulfonyloxy)-5-(3,5-dimethylphenyl)phthalate (12a): Starting with **9** (152 mg, 0.3 mmol), K_3PO_4 (95 mg, 0.45 mmol), $Pd(PPh_3)_4$ (3 mol %), **10e** (50 mg, 0.33 mmol) and 1,4-dioxane (4 mL), **12a** was isolated as a colourless solid (104 mg, 75 %), mp = 79-80 °C. ^{1}H NMR (300.13 MHz, $CDCl_3$): δ = 2.31 (brs, 6H, $2CH_3$), 3.85 (s, 3H, OCH_3) , 3.92 (s, 3H, OCH_3), 7.02 (s, 1H, ArH), 7.06 (s, 2H, ArH), 8.01 (d, J_{FH} = 6.6 Hz, ^{1}H, ArH). ^{13}C NMR (62.89 MHz, $CDCl_3$): δ = 20.3 ($2CH_3$), 52.1, 52.3 (OCH_3), 117.5 (q, J_{FC} = 321 Hz, CF_3), 124.4 (d, J_{FC} = 4.4 Hz, C), 125.6 (d, J_{FC} = 2.75, 2CH), 128.8 (C), 130.1 (CH), 130.9 (d, J_{FC} = 4.6 Hz, CH), 131.1 (d, J_{FC} = 1.8 Hz, C), 131.9 (d, J_{FC} = 13 Hz, C), 133.3 (d, J_{FC} = 17 Hz, C), 137.6 (s, 2C), 152.3 (d, J_{FC} = 261 Hz, C), 162.7 (d, J_{FC} = 2.7 Hz, CO). 163.1 (CO). ^{19}F NMR (282.40 MHz, $CDCl_3$): δ = -72.58 (d, J = 13.4 Hz, 3F, CF_3), -122.34 (q, J = 13.4 Hz, ArF). IR (ATR, 32 scans, cm^{-1}): $\tilde{\nu}$ = 2959 (w), 2921 (w), 1737 (s), 1729 (s), 1620 (w), 1602 (w), 1495 (w), 1428 (s), 1408 (m), 1343 (m), 1275 (s), 1205 (s), 1133 (m), 1006 (m), 945 (m), 854 (m), 813 (s), 757 (m), 731 (m), 598 (s), 532 (s). GCMS (EI, 70 eV, m/z > 5 %): 466 ($[M+2]^+$, 8), 465 ($[M+1]^+$, 21), 464 ($[M]^+$, 100), 433 (35), 369 (16), 331 (6), 303 (10), 272 (9), 242 (15), 214 (10), 185 (6), 160 (7), 69 (5). HRMS Pos (ESI): calculated for $C_{19}H_{17}F_4O_7S$ $[M+H]^+$ is 465.06256, found: 465.06268.

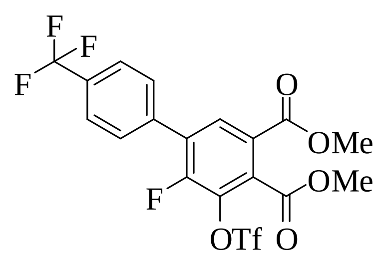


Dimethyl 4-fluoro-3-(trifluoromethylsulfonyloxy)-5-(3-fluorophenyl)phthalate (12b): Starting with **9** (152 mg, 0.3 mmol), K_3PO_4 (95 mg, 0.45 mmol), $Pd(PPh_3)_4$ (3 mol %), **10i** (46 mg, 0.33 mmol) and 1,4-dioxane (4 mL), **12b** was isolated as a colourless oil (97 mg, 71 %). ^{1}H NMR (300.13 MHz, $CDCl_3$): δ = 3.94 (s, 3H, OCH_3) , 4.02 (s, 3H, OCH_3), 7.15-7.25 (m, 1H, ArH), 7.26-7.36 (m, 2H, ArH), 7.45-7.53 (m, 1H, ArH), 8.13 (d, J_{FH} = 6.8 Hz, 1H, ArH). ^{13}C NMR (62.89 MHz, $CDCl_3$): δ = 53.2, 53.4 (OCH_3), 116.0 (dd, J_{FC} = 22.9, 3.2 Hz, CH), 116.5 (d, J_{FC} = 21.1 Hz, CH), 118.5 (q,



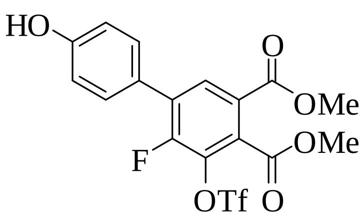
J_{FC} = 321 Hz, CF_3), 124.7 (t, J_{FC} = 3.2 Hz, CH), 125.6 (d, J_{FC} = 4.6 Hz, C), 130.1 (d, J_{FC} = 8.2 Hz, CH), 130.2 (d, J_{FC} = 8.2 Hz, C), 131.1 (dd, J_{FC} = 11.9, 2.3 Hz, C), 131.8 (d, J_{FC} = 4.1 Hz, CH), 134.1 (dd, J_{FC} = 8.2, 1.4 Hz, C), 134.4 (d, J_{FC} = 16.9 Hz, C), 153.3 (d, J_{FC} = 263 Hz, C), 162.8 (d, J_{FC} = 248 Hz, C), 163.4 (d, J_{FC} = 2.7 Hz, CO), 163.8 (d, J_{FC} = 0.92 Hz, CO). ^{19}F NMR (282.40 MHz, $CDCl_3$): δ = -72.54 (d, *J* = 14.3 Hz, CF_3), -111.63 (ArF), -122.31 (q, *J* = 14.3 Hz, ArF). IR (ATR, 32 scans, cm^{-1}): $\tilde{\nu}$ = 3074 (w), 2957 (w), 2848 (w), 1732 (s), 1614 (m), 1589 (m), 1502 (w), 1478 (w), 1427 (s), 1410 (s), 1336 (s), 1281 (s), 1263 (s), 1242 (s), 1210 (s), 1182 (s), 1164 (s), 1131 (s), 1106 (s), 1076 (m), 1023 (s), 992 (s), 955 (m), 929 (m), 880 (m), 823 (s), 785 (s), 759 (s), 744 (s), 708 (m), 694 (m), 670 (m), 639 (m), 598 (s), 542 (w). GCMS (EI, 70 eV, m/z > 5 %): 456 ($[M+2]^+$, 8), 455 ($[M+1]^+$, 20), 454 ($[M]^+$, 100), 424 (17), 423 (88), 360 (12), 359 (12), 321 (14), 293 (18), 277 (12), 262 (12), 261 (10), 232 (43), 231 (13), 204 (19), 175 (31), 151 (9), 69 (12). HRMS (EI): calculated for $C_{17}H_{11}F_5O_7S$ $[M]^+$ is 454.01402, found 454.014199.

Dimethyl 4-fluoro-5-(4-trifluoromethylphenyl)-3-(trifluoromethylsulfonyloxy) phthalate (12c): Starting with **9** (152 mg, 0.3 mmol), K_3PO_4 (95 mg, 0.45 mmol), $Pd(PPh_3)_4$ (3 mol %), **10k** (63 mg, 0.33 mmol) and 1,4-dioxane (4 mL), **12c** was isolated as a colourless solid (103 mg, 68 %), mp = 74-77 °C. ^{1}H NMR (500 MHz, $CDCl_3$): δ =3.95 (s, 3H, OCH_3) , 4.03 (s, 3H, OCH_3), 7.69 (d, *J* = 7.9 Hz, 2H, ArH), 7.79 (d, *J* = 8.2 Hz, 2H, ArH), 8.15 (d, J_{FH} = 6.6 Hz, 1H, ArH). ^{13}C NMR (75.47 MHz, $CDCl_3$): δ = 53.3, 53.5 (OCH_3), 118.5 (q, J_{FC} = 321 Hz, CF_3), 123.7 (q, J_{FC} = 272 Hz, CF_3), 125.8 (d, J_{FC} = 4.4 Hz, C), 126.0 (q, J_{FC} = 3.7 Hz, 2CH), 129.4 (d, J_{FC} = 3.3 Hz, 2CH), 131.0 (d, J_{FC} = 13 Hz, C), 131.2 (C), 131.6 (d, J_{FC} = 34 Hz, C), 131.9 (d, J_{FC} = 4.4 Hz, CH), 134.4 (d, J_{FC} = 16.5 Hz, C), 135.8 (C), 153.4 (d, J_{FC} = 262 Hz, C), 163.4 (d, J_{FC} = 2.8 Hz, CO), 163.7 (d, J_{FC} = 1.1 Hz, CO). ^{19}F NMR (282.40 MHz, $CDCl_3$): δ = -62.91 ($ArCF_3$), 72.47 (d, *J* = 13.3 Hz, CF_3), -122.23 (q, *J* = 13.3 Hz, ArF). IR (ATR, 32 scans, cm^{-1}): $\tilde{\nu}$ = 2959 (w), 2923 (w), 2853 (w), 1744 (s), 1726 (s), 1620 (m), 1586 (w), 1565 (w), 1429 (s), 1401 (s), 1367 (w), 1322 (s), 1295 (m), 1273 (s), 1257 (m), 1235 (s), 1207 (s), 1183 (m), 1171 (s), 1132 (m), 1112 (s), 1067 (s),



1019 (s), 985 (m), 931 (m), 915 (m), 848 (s), 800 (m), 790 (s), 763 (m), 749 (s), 705 (m), 670 (w), 661 (w), 649 (w), 635 (w), 619 (m), 600 (s), 577 (m), 554 (w). GCMS (EI, 70 eV, m/z > 5 %): 506 ($[M+2]^+$, 6), 505 ($[M+1]^+$, 17), 504 ($[M]^+$, 82), 485 (13), 475 (7), 474 (17), 473 (100), 410 (16), 409 (86), 371 (12), 355 (9), 343 (18), 341 (11), 340 (7), 327 (13), 315 (7), 313 (5), 312 (9), 311 (9), 283 (7), 282 (41), 281 (12), 269 (6), 254 (22), 225 (18), 213 (5), 206 (5), 201 (7), 157 (7), 69 (10). HRMS Pos (ESI): calculated for $C_{18}H_{11}F_7O_7S$ $[M]^+$ is 504.01082, found 504.011134.

Dimethyl 4-fluoro-3-(trifluoromethylsulfonyloxy)-5-(4-hydroxyphenyl)phthalate

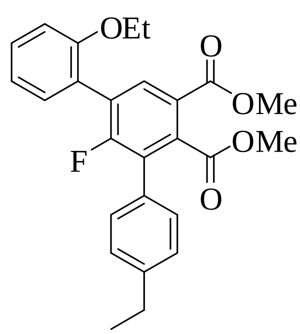


(12d): Starting with **9** (152 mg, 0.3 mmol), K_3PO_4 (95 mg, 0.45 mmol), $Pd(PPh_3)_4$ (3 mol %), **10m** (45.5 mg, 0.33 mmol) and 1,4-dioxane (4 mL), **12e** was isolated as a colourless solid (92.2 mg, 60 %), mp = 110-112 °C. ^{1}H NMR (300.13 MHz, $CDCl_3$): δ =3.91 (s, 3H, OCH_3) , 3.99 (s, 3H, OCH_3), 7.08 (d, J_{FH} = 6.4 Hz, 1H, ArH), 7.38-7.42 (m, 2H, ArH), 7.65-7.69 (m, 2H, ArH), 10.55 (s, 1H, ArOH). ^{13}C NMR (75.47 MHz, $CDCl_3$): δ = 52.9, 53.3 (OCH_3), 119.5 (d, J_{FC} = 2.7 Hz, CH), 121.8 (2CH), 118.7 (q, J_{FC} = 321 Hz, CF_3), 129.0 (C), 130.9 (d, J_{FC} = 3.3 Hz, 2CH), 130.4 (d, J_{FC} = 5 Hz, C), 131.6 (d, J_{FC} = 11 Hz, C), 134.0 (C), 148.8 (d, J_{FC} = 251 Hz, C), 149.8 (C), 150.3 (d, J_{FC} = 14 Hz, C), 168.1 (CO), 168.6 (d, J_{FC} = 3.30 Hz, CO). ^{19}F NMR (282.40 MHz, $CDCl_3$): δ = -72.73 (CF_3), -136.44 (ArF). IR (ATR, 32 scans, cm^{-1}): $\tilde{\nu}$ = 2955 (w), 2923 (w), 2852 (w), 1731 (w), 1682 (m), 1620 (w), 1510 (m), 1497 (m), 1422 (s), 1398 (m), 1370 (m), 1325 (m), 1248 (s), 1203 (s), 1168 (m), 1134 (s), 1018 (m), 999 (m), 934 (w), 881 (s), 843 (s), 801 (m), 789 (m), 779 (m), 755 (m), 744 (m), 724 (m), 705 (m), 604 (m), 573 (w). GCMS (EI, 70 eV, m/z > 5 %): 453 ($[M+1]^+$, 3), 422 (8), 421 (32), 363 (13), 362 (100), 288 (15), 287 (11), 260 (11), 259 (50), 201 (15), 135 (8), 134 (77), 125 (8), 121 (20), 57 (9), 43 (9). HRMS (EI): calculated mass for $C_{17}H_{12}F_4O_8S$ $[M]^+$ is 452.01835, found 452.018664.

General procedure for the synthesis of 13a,b.

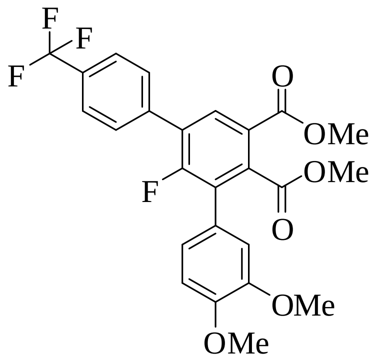
The reactions were carried out in pressure tube. To a dioxane suspension (4 mL) of **9** (228 mg, 0.45 mmol), $Pd(PPh_3)_4$ (3 mol %) and $Ar^1B(OH)_2$ (0.5 mmol) was added K_3PO_4 (143 mg, 0.67 mmol), was added and the resultant solution was degassed by bubbling argon through the solution for 10 minutes. The mixture was heated at 90 ˚C under argon atmosphere for 9 hours. The mixture was cooled to 20 °C. $Ar^2B(OH)_2$ (0.6 mmol) and K_3PO_4 (143 mg, 0.67 mmol) were added. The reaction mixtures were heated under Argon atmosphere for 6 hours at 110 ˚C. Then the reaction mixture was diluted with water and extracted with CH_2Cl_2 (3 x 25 mL). The combined organic layers were dried (Na_2SO_4), filtered and the filtrate was concentrated *in vacuo*. The residue was purified by flash chromatography (flash silica gel, heptanes/EtOAc = 10:1).

Dimethyl 5-(2-ethoxyphenyl)-3-(4-ethylphenyl)-4-fluorophthalate 13a: Starting with

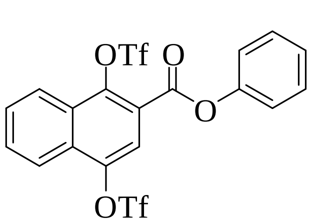


9 (228 mg, 0.45 mmol), K_3PO_4 (286 mg, 1.34 mmol), $Pd(PPh_3)_4$ (3 mol %), **10n** (83 mg, 0.5 mmol), 1,4-dioxane (4 mL), and **10d** (90 mg, 0.6 mmol), **13a** was isolated as transparent crystals (113.8 mg, 58%) mp = 104-106°C. ^{1}H NMR ($CDCl_3$, 300.13 MHz): δ = 1.15-1.25 (m, 6H, $2CH_3$), 2.61 (q, J = 7.5 Hz, 2H, CH_2), 3.57 (s, 3H, OCH_3) , 3.78 (s, 3H, OCH_3), 3.95 (q, J = 7.0 Hz, 2H, OCH_2), 6.87 (d, J = 8.4 Hz, 1H, ArH), 6.93 (dt, J = 7.5 Hz, 1H, ArH), 7.14-7.30 (m, 6H, ArH), 7.98 (d, J_{FH} = 6.7 Hz, 1H, ArH). ^{13}C NMR (62.89 MHz, $CDCl_3$): δ = 14.7, 15.2 (CH_3), 28.6 (CH_2), 52.3, 52.5 (OCH_3), 64.0 (OCH_2), 112.1, 120.5 (CH), 122.9, 123.0, 123.7 (C), 127.6 (2CH), 127.8 (d, J_{FC} = 19 Hz, C), 128.5 (d, J_{FC} = 20.7 Hz, C), 129.4, 129.5, 130.1 (CH), 131.0 (d, J_{FC} = 1.4 Hz, CH), 133.3 (d, J_{FC} = 5.6 Hz, CH), 136.8 (d, J_{FC} = 4.1 Hz, C), 144.3, 156.3 (C), 159.6 (d, J_{FC} = 256 Hz, CF), 165.5 (C=O), 168.1 (d, J_{FC} = 2.7 Hz, C=O). ^{19}F NMR (282.40 MHz, $CDCl_3$): δ = -106.42 (ArF). IR (ATR, 32 scans, cm^{-1}): $\tilde{\nu}$ = 2973 (w), 2944 (w), 2929 (w), 2881 (w), 1724 (brs), 1609 (w), 1580 (w), 1563 (w), 1516 (w), 1497 (m), 1451 (m), 1428 (m), 1390 (m), 1341 (m), 1273 (s), 1249 (s), 1215 (s), 1149 (s), 1123 (m), 1067 (m), 1041 (s), 969 (m), 919 (m), 858 (w), 839 (w), 793 (m), 754 (s), 689 (m), 611 (m), 537 (w). GCMS (EI, 70 eV, m/z > 5 %): 438 ($[M+2]^+$, 5), 437 ($[M +1]^+$, 30), 436 ($[M]^+$, 100), 405 (19), 376 (30), 361 (16), 348 (20), 317 (20), 289 (9), 271 (9), 244 (5), 171 (3), 29 (4). HRMS (EI) calculated for $C_{26}H_{25}FO_5$ $[M]^+$ is 436.16805, found 436.168135.

Dimethyl 4-fluoro-5-(4-trifluoromethylphenyl)-3-(3,4-dimethoxyphenyl)phthalate (13b): Starting with 9 (228 mg, 0.45 mmol), K_3PO_4 (286 mg, 1.34 mmol), $Pd(PPh_3)_4$ (3 mol %), **10k** (95 mg, 0.5 mmol), 1,4-dioxane (4 mL), and **10o** (109 mg, 0.6 mmol), **13b** was isolated as colourless solid (113 mg, 51 %), mp = 135-137 °C. ^{1}H NMR (300.13 MHz, $CDCl_3$): δ = 3.72 (s, 3H, OCH_3), 3.91 (s, 3H, OCH_3), 3.95 (s, 3H, OCH_3), 3.96 (s, 3H, OCH_3), 6.94 (s, 1H, ArH), 6.97 (s, 2H, ArH), 7.71-7.78 (m, 4H, ArH), 8.16 (d, J_{FH} = 7.2 Hz, 1H, ArH). ^{13}C NMR (75.47 MHz, $CDCl_3$): δ = 52.6, 52.8, 55.8, 55.9 (OCH_3), 110.8, 112.9, 122.3 (CH), 123.9 (C), 123.9 (d, J_{FC} = 9 Hz, C), 124.0 (q, J_{FC} = 272 Hz, CF_3), 125.6 (q, J_{FC} = 3.7 Hz, 2CH), 128.8 (d, J_{FC} = 15.6 Hz, C), 129.2 (d, J_{FC} = 20.6 Hz, C), 129.4 (d, J_{FC} = 3.2 Hz, 2CH), 130.3 (d, J_{FC} = 9.6 Hz, C), 131.8 (d, J_{FC} = 4.6 Hz, CH), 137.7 (C), 137.8 (d, J_{FC} = 3.7 Hz, C), 148.6, 149.3 (C), 159.0 (d, J_{FC} = 256 Hz, C), 164.9 (CO), 167.6 (d, J_{FC} = 2.7 Hz, CO).^{19}F NMR (282.40 MHz, $CDCl_3$): δ = -62.70 ($ArCF_3$), -111.26 (ArF). IR (ATR, 32 scans, cm^{-1}): $\tilde{\nu}$ = 3005 (w), 2924 (br), 2840 (w), 1739 (s), 1725 (s), 1619 (w), 1605 (m), 1589 (m), 1522 (m), 1462 (m), 1447 (m), 1431 (m), 1411 (m), 1387 (m), 1346 (m), 1327 (s), 1290 (s), 1274 (m), 1264 (s), 1243 (s), 1213 (s), 1162 (s), 1144 (s), 1112 (s), 1079 (s), 1066 (s), 1037 (w), 1027 (s), 1019 (s), 975 (m), 918 (m), 866 (m), 847 (s), 833 (m), 807 (m), 793 (s), 769 (m), 763 (m), 752 (m), 742 (m), 699 (s), 676 (m), 661 (m), 648 (m), 634 (m), 625 (m), 609 (m), 581 (m), 543 (m). GCMS (EI, 70 eV, m/z > 5 %): 494 ($[M+2]^+$, 5), 493 ($[M+1]^+$, 28), 492 ($[M]^+$, 100), 461 (10), 246 (5), 231 (5). HRMS (EI) calculated for $C_{25}H_{20}F_4O_6$ $[M]^+$ is 492.11905, found 492.119098.



Synthesis of phenyl 1,4-bis(trifluoromethylsulfonyloxy)-2-naphthoate (15): To a solution of **14** (2800 mg, 10 mmol) in CH_2Cl_2 (100 mL) was added pyridine (3.2 ml, 40 mmol) at –78 °C under an argon atmosphere. After 10 minutes, Tf_2O (2.4 equiv) was added at -78 °C. The mixture was allowed to warm up to 0 °C and stirred for 4 hours. The reaction mixture was filtered and the filtrate was concentrated *in vacuo*. **15** was isolated by rapid column chromatography (flash silica gel, heptanes/EtOAc = 20:1) as white powder (4515 mg, 83 %), mp 100-101 °C. ^{1}H NMR

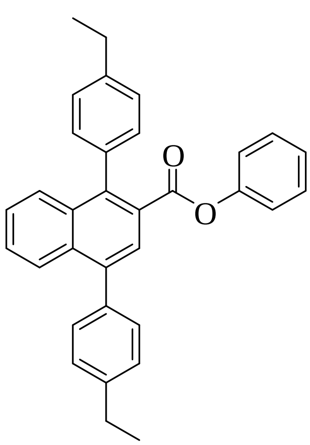


(300.13 MHz, $CDCl_3$): δ = 7.20-7.27 (m, 3H, ArH), 7.36-7.41 (m, 2H, ArH), 7.75-7.85 (m, 2H, ArH), 8.08 (s, 1H, ArH), 8.12 (dd, *J* = 7.1, 1.8 Hz, 1H, ArH), 8.24 (d, *J* = 7.9 Hz, 1H, ArH). ^{13}C NMR (62.89 MHz, $CDCl_3$): δ = 118.5 (CH), 118.6 (q, J_{FC} = 321 Hz, CF_3), 118.7 (q, J_{FC} = 321 Hz, CF_3), 121.2 (C), 121.4 (2CH), 121.5, 123.1, 126.6 (CH), 127.9, 129.6 (C), 129.7 (2CH), 129.9, 131.4 (CH), 144.0, 144.2, 150.2 (C), 161.9 (C=O). ^{19}F NMR (282.40 MHz. $CDCl_3$): δ = -72.27 (3F, CF_3), -72.96 (3F, CF_3). IR (ATR, 32 scans, cm^{-1}): $\tilde{\nu}$ = 3068 (w), 1733(m), 1589 (w), 1482 (w), 1427 (s), 1358 (m), 1347 (m), 1247 (m), 1203 (s), 1130 (s), 1045 (m), 1018 (m), 936 (m), 873 (s), 761 (s), 641 (s), 597 (s). MS (EI, 70 eV, m/z > 5 %): 544 ($[M]^+$, 10), 453 (16), 452 (22), 451 (100), 318 (64), 234 (3), 186 (19), 185 (97), 157 (47), 129 (16), 101 (18), 75 (5), 69 (8), 64 (9), 51. HRMS (EI) calculated for $C_{19}H_{10}F_6O_8S_2$ $[M^+]$ is 543.97158, found 543.970512.

General procedure for synthesis of 16a-j and 17a-e.

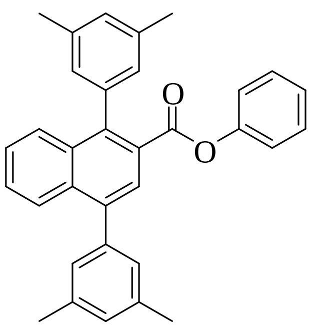
A 1,4-dioxane solution (4 mL per 0.5 mmol of **15**) of **15**, K_3PO_4, $Pd(PPh_3)_4$ and arylboronic acid **10** were stirred at 110 °C for 8 hours (for compounds **16a-j)** or 95 °C for 7 hours (for compounds **17a-e**) in pressure tube. After cooling to 20 °C, a saturated aqueous solution of NH_4Cl was added. The organic and the aqueous layer were separated and the latter was extracted with CH_2Cl_2. The combined organic layers were dried (Na_2SO_4), filtered and the filtrate was concentrated *in vacuo*. The residue was purified by flash chromatography (silica gel, EtOAc / heptanes = 10:1).

Phenyl 1,4-bis(4-ethylphenyl)-2-naphthoate (16a): Starting with **15** (272 mg, 0.5 mmol), K_3PO_4 (318 mg, 1.5 mmol), $Pd(PPh_3)_4$ (3 mol %), **10d** (179 mg, 1.2 mmol) and 1,4-dioxane (4 mL), **16a** was isolated as viscous gel (200 mg, 88 %). ^{1}H NMR (300.13 MHz, $CDCl_3$): δ = 1.25 (t, *J* = 7.6 Hz, 3H, CH_3), 1.26 (t, *J* = 7.6 Hz, 3H, CH_3), 2.65-2.72 (m, 4H, $2CH_2$), 6.64-6.70 (m, 2H, ArH), 7.02-7.09 (m, 1H, ArH), 7.14-7.31 (m, 8H, ArH), 7.34-7.44 (m, 4H, ArH), 7.66 (dd, *J* = 8.1, 1.2 Hz, 1H, ArH), 7.88 (s, 1H, ArH), 7.93 (dd, *J* = 8.0, 1.2 Hz, 1H, ArH). ^{13}C NMR (62.89 MHz, $CDCl_3$): δ = 15.6, 15.8 (CH_3), 28.7, 28.8 (CH_2), 121.5 (2CH), 125.6, 126.2, 126.3, 126.4 (CH), 127.7 (2CH), 127.78 (C), 127.9 (2CH), 128.2 (CH), 129.1 (2CH),

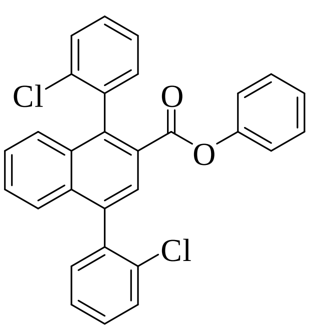


129.7 (CH), 130.0, 130.1 (2CH), 133.1, 133.3, 136.2, 137.2, 140.2, 140.7, 143.6, 143.7, 150.8 (C), 167.1 (C=O). IR (ATR, 32 scans, cm^{-1}): $\tilde{\nu}$ = 3024 (w), 2962 (m), 2928 (w), 2871 (w), 1711 (s), 1591 (m), 1512 (m), 1487 (m), 1455 (m), 1379 (m), 1368 (m), 1344 (m), 1240 (s), 1214 (s), 1190 (s), 1162 (s), 1140 (s), 1098 (s), 1070 (m), 1021 (m), 985 (m), 964 (m), 900 (m), 824 (s), 763 (s), 746 (s), 687 (s), 598 (m) 533 (m). MS (EI, 70 eV, m/z > 5 %): 456 ($[M]^+$, 8), 364 (42), 363 (100), 335 (15), 334 (16), 319 (17), 318 (14), 289 (15), 145 (13). HRMS (EI) calculated for $C_{33}H_{28}O_2$ $[M]^+$ is 456.20838, found 456.209388.

Phenyl 1,4-bis(3,5-dimethylphenyl)-2-naphthoate (16b): Starting with **15** (272 mg, 0.5 mmol), K_3PO_4 (318 mg, 1.5 mmol), $Pd(PPh_3)_4$ (3 mol %), **10e** (180 mg, 1.2 mmol) and 1,4-dioxane (4 mL), **16b** was isolated as colorless crystals (162 mg, 71 %), mp = 80-81 °C. ^{1}H NMR (300.13 MHz, $CDCl_3$): δ = 2.30 (s, 6H, $2CH_3$), 2.34 (s, 6H, $2CH_3$), 6.70-6.73 (m, 2H, ArH), 6.98-7.23 (m, 9H, ArH), 7.32-7.44 (m, 2H, ArH), 7.68 (d, *J* = 8.4 Hz, 1H, ArH), 7.86 (s, 1H, ArH), 7.91(d, *J* = 8.1 Hz, 1H, ArH). ^{13}C NMR (62.89 MHz, $CDCl_3$): δ = 21.6 ($4ArCH_3$), 121.6 (2CH), 125.8, 126.3, 126.5, 126.6 (CH), 127.6 (C), 127.7 (CH), 128.0, 128.1 (2CH), 128.5, 129.3 (CH), 129.4 (2CH), 129.5 (CH), 133.2, 133.5 (C), 137.7, 138.1 (2C), 138.9, 140.1, 140.6, 141.2, 151.0 (C), 167.4 (C=O). IR (ATR, 32 scans, cm^{-1}): $\tilde{\nu}$ = 3026 (w), 2916 (w), 2860 (w), 1732(s), 1598 (m), 1487 (m), 1370 (m), 1216 (s), 1185 (s), 1160 (s), 1105 (s), 1038 (m), 848 (m), 762 (s), 704 (s), 687 (m). GCMS (EI, 70 eV, m/z > 5 %): 456 ($[M]^+$, 2), 364 (30), 363 (100), 320 (5), 289 (5), 215 (2), 151 (3), 145 (3), 65 (1). HRMS (ESI): calculated for $C_{33}H_{29}O_2$ $[M+H]^+$ is 457.21621, found 457.21598.

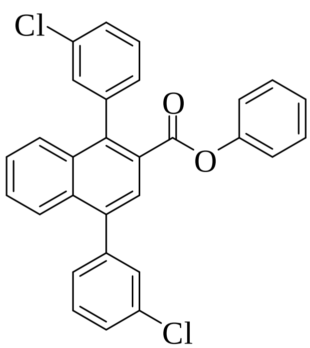


Phenyl 1,4-bis(2-chlorophenyl)-2-naphthoate (16c): Starting with **15** (272 mg, 0.5 mmol), K_3PO_4 (318 mg, 1.5 mmol), $Pd(PPh_3)_4$ (3 mol %), **10f** (187 mg, 1.2 mmol) and 1,4-dioxane (4 mL), **16c** was isolated as colorless crystals (168 mg, 72 %), mp = 172-174 °C. ^{1}H NMR (250.13 MHz, $CDCl_3$): δ = 6.80-6.86 (m, 2H, ArH), 7.02-7.08 (m, 1H, ArH), 7.16-7.22 (m, 2H, ArH), 7.26-7.53 (m, 12H, ArH), 8.03 (s, 1H, ArH). ^{13}C NMR (75.47 MHz, $CDCl_3$): δ = 121.5 (2CH), 125.8, 126.3 (CH), 126.5 (C), 126.6, 126.9, 127.0, 127.2,

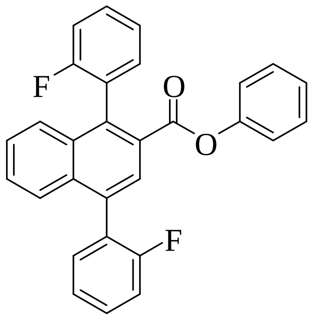


127.8, 128.4, 129.2 (CH), 129.3 (2CH), 129.4, 129.5, 129.7, 131.4, 132.3 (CH), 132.4, 133.7, 134.1, 134.2, 137.9, 138.1, 138.5, 139.9, 150.8 (C), 165.6 (C=O). IR (ATR, 32 scans, cm^{-1}): $\tilde{\nu}$ = 3057 (w), 2915 (w), 2861 (w), 1747(w), 1592 (m), 1564 (m), 1509 (w), 1482 (m), 1453 (m), 1434 (m), 1379 (m), 1232 (m), 1208 (m), 1187 (s), 1160 (s), 1152 (s), 1101 (s), 1054 (m), 1034 (m), 981 (m), 895 (m), 762 (s), 745 (s), 731 (s), 690 (m), 608 (m), 561 (m). GCMS (EI, 70 eV, m/z > 5 %): 468 ($[M]^+$, ^{35}Cl, 1), 379 (12), 378 (16), 377 (67), 376 (26), 375 (100), 342 (6), 340 (18), 312 (16), 277 (16), 276 (40), 274 (12), 138 (6), 65 (5). HRMS (EI) calculated for C_{29} $H_{18}Cl_2O_2$ $[M]^+$ is 468.06868, found 468.06784.

Phenyl 1,4-bis(3-chlorophenyl)-2-naphthoate (16d): Starting with **15** (272 mg, 0.5 mmol), K_3PO_4 (318 mg, 1.5 mmol), $Pd(PPh_3)_4$ (3 mol %), **10g** (187 mg, 1.2 mmol) and 1,4-dioxane (4 mL), **16d** was isolated as colorless crystals (180 mg, 77 %), mp = 124-125 °C. ^1H NMR (250.13 MHz, $CDCl_3$): δ = 6.75-6.82 (m, 2H, ArH), 7.04-7.0 (m, 14H, ArH), 7.81-7.88 (m, 1H, ArH), 7.93-7.97 (m, 1H, ArH). ^{13}C NMR (75.47 MHz, $CDCl_3$): δ = 121.4 (2CH), 125.9, 126.0, 126.6 (CH), 127.0 (C), 127.1, 127.9, 128.0, 128.1, 128.2, 128.3, 128.4 (CH), 129.4 (2CH), 129.5, 129.8, 129.9, 130.1 (CH), 132.9, 133.2, 134.2, 134.5, 139.3, 140.3, 140.7, 141.6, 150.6 (C), 166.3 (C=O). IR (ATR, 32 scans, cm^{-1}): $\tilde{\nu}$ = 3061 (w), 2923 (w), 2851 (w), 2720 (w), 1747 (m), 1590 (m), 1563 (m), 1487 (m), 1478 (m), 1375 (m), 1341 (m), 1244 (m), 1213 (s), 1190 (s), 1161 (m), 1092 (s), 1079 (m), 1026 (m), 995 (m), 886 (w), 800 (w), 780 (s), 758 (s), 735 (s), 688 (s), 610 (m), 555 (m). GCMS (EI, 70 eV, m/z > 5 %): 468 ($[M]^+$, 2), 379 (12), 378 (17), 377 (67), 376 (27), 375 (100), 342 (7), 340 (20), 312 (23), 277 (10), 276 (32), 138 (6), 65 (5). HRMS (EI) calculated for $C_{29}H_{18}Cl_2O_2$ $[M]^+$ is 468.06784, found 468.068942.

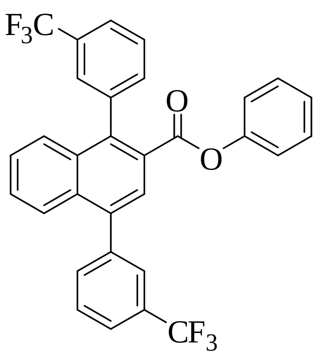


Phenyl 1,4-bis(2-fluorophenyl)-2-naphthoate (16e): Starting with **15** (272 mg, 0.5 mmol), K_3PO_4 (318 mg, 1.5 mmol), $Pd(PPh_3)_4$ (3 mol %), **10p** (168 mg, 1.2 mmol) and 1,4-dioxane (4 mL), **16e** was isolated as colorless crystals (168 mg, 77 %), mp = 137-139 °C. ^1H NMR (250.13 MHz, $CDCl_3$): δ = 6.80-6.84 (m, 2H, ArH), 7.03-7.30 (m, 9H, ArH), 7.32-7.49 (m, 4H, ArH), 7.56 (d, J = 8.2 Hz, 1H, ArH), 7.68 (d, J = 8.2 Hz, 1H, ArH), 8.08 (s, 1H, ArH). ^{13}C NMR (75.47 MHz, $CDCl_3$): δ = 115.6 (d, J_{FC} = 22.0 Hz,

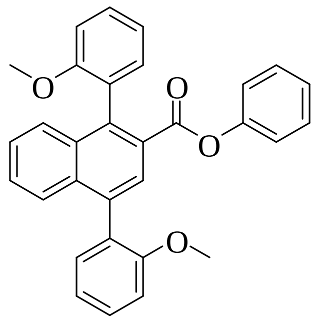


CH), 115.8 (d, J_{FC} = 22.0 Hz, CH), 121.4 (2CH), 124.0 (d, J_{FC} = 3.0 Hz, CH), 124.4 (d, J_{FC} = 3.0 Hz, CH), 125.8, 126.2 (CH), 127.0 (C), 127.07 (CH), 127.2, 127.3 (C), 127.6, 127.8, 128.4 (CH), 129.4 (2CH), 129.9 (d, J_{FC} = 7.7 Hz, CH), 130.1 (d, J_{FC} = 7.7 Hz, CH), 131.8 (d, J_{FC} = 2.3 Hz, CH), 132.4 (CH), 132.8, 133.7, 134.9, 136.3, 150.7 (C), 160.1 (d, J_{FC} = 247 Hz, CF), 160.2 (d, J_{FC} = 247 Hz, CF), 166.5 (C=O). ^{19}F NMR (282.40 MHz, $CDCl_3$): δ = -113.58, -114.37 (ArF). IR (ATR, 32 scans, cm^{-1}): $\tilde{\nu}$ = 3068 (w), 2924 (w), 1750 (m), 1593 (m), 1574 (m), 1568 (m), 1492 (m), 1455 (m), 1381 (m), 1344 (m), 1241 (m), 1211 (m), 1186 (s), 1161 (s), 1149 (s), 1111 (m), 1089 (m), 983 (m), 896 (m), 749 (s), 688 (m), 607 (m). GCMS (EI, 70 eV, m/z, > 5 %): 436 ([M]$^+$, 2), 344 (25), 343 (100), 314 (7), 294 (21), 220 (4). HRMS (EI) calculated for $C_{29}H_{18}F_2O_2$ [M$^+$] is 436.12694, found 436.127214.

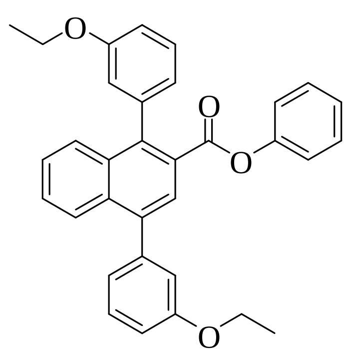
Phenyl 1,4-bis[3-(trifluoromethyl)phenyl]-2-naphthoate (16f): Starting with **15** (272 mg, 0.5 mmol), K_3PO_4 (318 mg, 1.5 mmol), $Pd(PPh_3)_4$ (3 mol %), **10l** (228 mg, 1.2 mmol) and 1,4-dioxane (4 mL), **16f** was isolated as colorless crystals (206 mg, 77 %). Mp = 124-126 °C. ^{1}H NMR (300.13 MHz, $CDCl_3$): δ = 6.71-6.74 (m, 2H, ArH), 7.00-7.66 (m, 13H, ArH), 7.74 (brs, 1H, ArH), 7.78 (dd, J = 8.4, 1.1 Hz, 1H, ArH), 7.99 (s, 1H, ArH). ^{13}C NMR (75.47 MHz, $CDCl_3$): δ = 121.4 (2CH), 124.3 (q, J_{FC} = 272 Hz, CF_3), 124.4 (q, J_{FC} = 272 Hz, CF_3), 124.8 (q, J_{FC} = 3.7 Hz, CH), 124.9 (q, J_{FC} = 3.7 Hz, CH), 126.0, 126.1 (CH), 126.7 (q, J_{FC} = 3.7 Hz, CH), 126.9 (CH), 127.0 (q, J_{FC} = 3.7 Hz, CH), 127.3 (C), 127.5, 128.2, 128.8, 128.9, 129.3 (CH), 129.6 (2CH), 131.0 (q, J_{FC} = 32.4 Hz, C), 131.3 (q, J_{FC} = 32.4 Hz, C), 133.1, 133.3 (C), 133.4, 133.6 (CH), 139.6, 139.9, 140.6, 140.7, 150.7 (C), 166.3 (C=O). ^{19}F NMR (282.40 MHz, $CDCl_3$): δ = -62.33, -62.39 (CF_3). IR (ATR, 32 scans, cm^{-1}): $\tilde{\nu}$ = 3071 (w), 2925 (w), 2853 (w), 1744 (m), 1592 (w), 1491 (w), 1322 (s), 1313 (m), 1210 (m), 1163 (m), 1119 (s), 1069 (s), 901 (m), 803 (m), 702 (s), 685 (s), 592 (w). MS (EI, 70 eV, m/z, > 5 %): 536 ([M]$^+$, 1), 444 (29), 443 (100), 395 (7), 346 (12), 270 (2), 269 (2), 65 (2). HRMS (EI) calculated for $C_{31}H_{18}F_6O_2$ [M]$^+$ is 536.12055 found, 536.12087.



Phenyl 1,4-bis(2-methoxyphenyl)-2-naphthoate (16g): Starting with **15** (272 mg, 0.5 mmol), K_3PO_4 (318 mg, 1.5 mmol), $Pd(PPh_3)_4$ (3 mol %), **10q** (182 mg, 1.2 mmol) and 1,4-dioxane (4 mL), **16g** was isolated as viscous gel (168 mg, 73 %), mp = 124-126 °C. ^{1}H NMR (300.13 MHz, $CDCl_3$): δ = 3.58 (s, 3H, OCH_3), 3.61 (s, 3H, OCH_3), 6.72-6.76 (m, 2H, ArH), 6.91-7.04 (m, 5H, ArH), 7.09-7.21 (m, 3H, ArH), 7.25-7.36 (m, 5H, ArH), 7.53-7.58 (m, 2H, ArH), 7.96 (s, 1H, ArH). ^{13}C NMR (62.89 MHz, $CDCl_3$): δ = 55.6, 55.7 (OCH_3), 110.1, 111.0, 120.5, 120.7, 120.8 (CH), 121.5 (2CH), 125.6, 126.2, 127.2, 127.4 (CH), 127.5 (C), 127.9 (CH), 128.1, 128.9 (C), 129.2 (2CH), 129.4, 131.2, 131.4, 132.1 (CH), 132.8, 134.1, 137.0, 138.4, 150.1, 157.3, 157.4 (C), 166.6 (C=O). IR (ATR, 32 scans, cm^{-1}): $\tilde{\nu}$ = 3062 (w), 3021 (w), 2929 (w), 2829 (w), 1741 (s), 1590 (m), 1581 (m), 1564 (m), 1493 (s), 1456 (m), 1434 (m), 1370 (m), 1343 (m), 1295 (m), 1272 (m), 1245 (s), 1227 (m), 1184 (s), 1162 (s), 1148 (s), 1130 (m), 1119 (m), 1106 (m), 1089 (s), 1046 (s), 1023 (s), 981 (m), 938 (w), 917 (m), 896 (m), 834 (w), 798 (m), 750 (s), 741 (s), 688 (s), 609 (m), 551 (m). GCMS (EI, 70 eV, m/z > 5 %): 460 ($[M]^+$, 2), 368 (27), 367 (100), 324 (5), 308 (5), 281 (5). HRMS (EI) calculated for $C_{31}H_{24}O_4$ $[M]^+$ is 460.16691, found 460.167581.

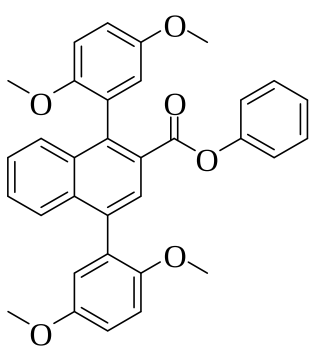


Phenyl 1,4-bis(3-ethoxyphenyl)-2-naphthoate (16h): Starting with **15** (272 mg, 0.5 mmol), K_3PO_4 (318 mg, 1.5 mmol), $Pd(PPh_3)_4$ (3 mol %), **10n** (199 mg, 1.2 mmol) and 1,4-dioxane (4 mL), **16h** was isolated as colorless solid (149 mg, 61 %), mp = 69-71 °C. ^{1}H NMR (300.13 MHz, $CDCl_3$): δ = 0.92-1.05 (m, 6H, $2CH_3$), 3.81-3.95 (m, 4H, $2OCH_2$), 6.75-6.77 (m, 2H, ArH), 6.92-7.06 (m, 5H, ArH), 7.15-7.24 (m, 3H, ArH), 7.25-7.36 (m, 5H, ArH), 7.56-7.63 (m, 2H, ArH), 7.97 (s, 1H, ArH). ^{13}C NMR (62.89 MHz, $CDCl_3$): δ = 14.5, 14.6 (CH_3), 63.9, 64.1 (OCH_2), 112.3, 112.6, 120.4, 120.7 (CH), 121.5 (2CH), 125.5, 126.0, 126.8, 127.1, 127.2 (CH), 127.3 (C), 128.0 (CH), 128.6 (C), 129.1 (CH), 129.2 (2CH), 129.3 (CH), 129.4 (C), 131.5, 132.1 (CH), 132.7, 134.0, 137.0, 138.4, 151.0, 156.6, 156.8 (C), 166.8 (C=O). IR (ATR, 32 scans, cm^{-1}): $\tilde{\nu}$ = 3063 (m), 2978 (m), 2925 (m), 2874 (m), 2854 (m), 1732 (s), 1592 (m), 1579

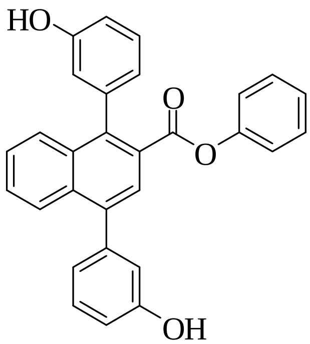


(m), 1489 (s), 1444 (s), 1411 (m), 1377 (m), 1347 (m), 1288 (m), 1224 (s), 1188 (s), 1161 (s), 1122 (m), 1112 (m), 1089 (s), 1043 (s), 982 (m), 925 (m), 897 (m), 835 (m), 797 (m), 748 (s), 712 (m), 687 (m), 647 (m), 623 (w), 609 (m), 548 (w). MS (EI, 70 eV, m/z, > 5 %): 488 ($[M]^+$, 4), 397 (5), 396 (30), 395 (100), 368 (11), 367 (41), 366 (5), 340 (6), 339 (24), 338 (6), 337 (7), 321 (12), 295 (5), 294 (6), 292 (11), 276 (10), 252 (5), 202 (5). HRMS (EI) calculated mass for $C_{33}H_{28}O_4$ $[M]^+$ is 488.19821, found 488.198613.

Phenyl 1,4-bis(2,5-dimethoxyphenyl)-2-naphthoate (16i): Starting with **15** (272 mg, 0.5 mmol), K_3PO_4 (318 mg, 1.5 mmol), $Pd(PPh_3)_4$ (3 mol %), **10r** (218 mg, 1.2 mmol) and 1,4-dioxane (4 mL), **16i** was isolated as colorless crystals (179 mg, 69 %), mp = 175-177 °C. ^{1}H NMR (300.13 MHz, $CDCl_3$): δ = 3.54 (s, 3H, OCH_3), 3.57 (s, 3H, OCH_3), 3.65 (s, 3H, OCH_3), 3.69 (s, 3H, OCH_3), 6.74-6.80 (m, 3H, ArH), 6.86 (s, 2H, ArH), 6.88 (s, 2H, ArH), 6.90 (s, 1H, ArH), 7.01-7.06 (m, 1H, ArH), 7.16-7.21 (m, 2H, ArH), 7.28-7.38 (m, 2H, ArH), 7.57-7.60 (m, 2H, ArH), 7.99 (s, 1H, ArH). ^{13}C NMR (75.47 MHz, $CDCl_3$): δ = 54.7 ($2OCH_3$), 55.2, 55.3 (OCH_3), 111.1, 111.2, 112.9, 113.2, 115.9, 116,5 (CH), 120.4 (2CH), 124.5, 125.3, 125.6, 125.9 (CH), 126.1 (C), 126.4, 126.8 (CH), 127.8 (C), 128.1 (2CH), 128.6, 131.5, 132.7, 135.9, 137.1, 149.8, 150.4, 150.6, 152.4, 152.6(C), 165.3 (C=O). IR (ATR, 32 scans, cm^{-1}): $\tilde{\nu}$ = 3068 (w), 2942 (w), 2827 (w), 1741 (s), 1588 (m), 1497 (s), 1461 (m), 1441 (m), 1417 (m), 1369 (m), 1347 (m), 1302 (m), 1280 (m), 1268 (m), 1254 (m), 1220 (s), 1189 (s), 1093 (s), 1038 (s), 1024 (s), 1000 (m), 884 (m), 799 (m), 774 (m), 692 (s), 638 (m), 588 (m). MS (EI, 70 eV, m/z, > 5 %): 521 ($[M+1]^+$, 11), 520 ($[M]^+$, 36), 429 (16), 427 (100), 413 (11), 412 (47), 397 (19), 396 (23),381 (8), 262 (13), 206 (22), 183 (9), 94 (8). HRMS (EI) calculated for $C_{33}H_{28}O_6$ $[M]^+$ is 520.18804, found 520.188872.

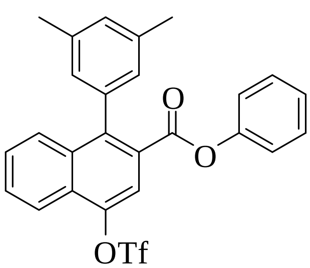


Phenyl 1,4-bis(3-hydroxyphenyl)-2-naphthoate (16j): Starting with **15** (272 mg, 0.5 mmol), K_3PO_4 (318 mg, 1.5 mmol), $Pd(PPh_3)_4$ (3 mol %), **10s** (167 mg, 1.2 mmol) and 1,4-dioxane (4 mL), **16j** was isolated as colourless solid (117 mg, 54 %). ^{1}H NMR (250.13 MHz, $(CD_3)_2CO$): δ = 6.67-6.69 (m, 1H, ArH), 6.70-6.72 (m, 1H, ArH), 6.75 (dt, J = 7.6, 1.3 Hz, 1H, ArH), 6.79-6.80 (m, 2H, ArH), 6.81-6.83 (m, 1H, ArH), 6.86 (dt, J = 7.6, 1.3 Hz, 1H, ArH), 6.90 (t, J = 1.8 Hz, 1H, ArH), 6.95-7.01 (m, 1H, ArH), 7.09-7.23



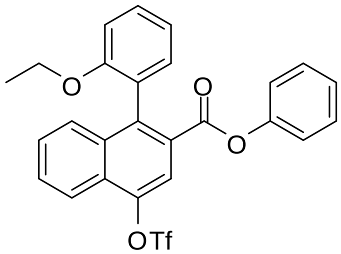
(m, 4H, ArH), 7.34 (m, 1H, ArH), 7.40 (m, 1H, ArH), 7.62 (dd, *J* = 7.9, 1.3 Hz, 1H, ArH), 7.71 (s, 1H, ArH), 7.85 (dd, *J* = 7.9, 1.3 Hz, 1H, ArH), 8.38 (s, 1H, ArOH), 8.40 (s, 1H, ArOH). ^{13}C NMR (62.89 MHz, $(CD_3)_2CO$): δ= 115.7, 115.8, 117.8, 118.0, 122.1, 122.3 (CH), 122.5 (2CH), 126.5, 126.6, 127.0, 127.7, 128.7, 128.8 (CH), 128.9 (C), 130.1 (2CH), 130.3, 130.6 (CH), 133.6, 133.8, 140.9, 141.0, 141.1, 142.0, 151.9, 158.2, 158.5 (C), 167.7 (C=O). IR (ATR, 32 scans, cm^{-1}): 3421-2633 (br), 3068 (w), 2930 (w), 2839 (w), 1723 (m), 1589 (w), 1515 (s), 1427 (m), 1365 (m), 1238 (s), 1220 (s), 1193 (s), 1187 (s), 1013 (s), 966 (m), 923 (w), 761 (m), 687 (m), 597 (w). MS (EI, 70 eV, m/z > 5 %): 432 (1) (M^+), 340 (23), 339 (100), 338 (30), 310 (7), 281 (5), 263 (5), 189 (5), 94 (21), 66 (7), 65 (8). HRMS (EI) calculated mass for $C_{29}H_{20}O_4$ $[M]^+$ is 432.13561, found 432.136252.

Phenyl 4-(trifluoromethylsulfonyloxy)-1-(3,5-dimethylphenyl)-2-naphthoate (17a):



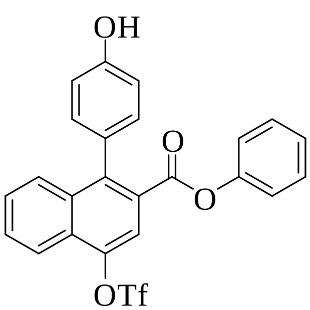
Starting with **15** (272 mg, 0.5 mmol), K_3PO_4 (160 mg, 0.75 mmol), $Pd(PPh_3)_4$ (3 mol %), **10e** (82 mg, 0.55 mmol) and 1,4-dioxane (4 mL), **17a** was isolated as colorless crystals (170 mg, 68 %), mp = 98-100 °C. ^{1}H NMR (300.13 MHz, $CDCl_3$): δ = 2.48 (s, 6H, $2CH_3$), 6.92-6.96 (m, 2H, ArH), 7.12 (s, 2H, ArH), 7.21-7.44 (m, 4H, ArH), 7.65 (dt, *J* = 8.0, 1.1 Hz, 1H, ArH), 7.83 (dt, *J* = 8.0, 1.1 Hz, 1H, ArH), 7.88 (d, *J* = 8.5 Hz, 1H, ArH), 8.18 (s, 1H, ArH), 8.29 (d, *J* = 8.4 Hz, 1H, ArH). ^{13}C NMR (75.47 MHz, $CDCl_3$): δ = 21.4 ($2CH_3$), 117.9 (CH), 118.9 (q, J_{FC} = 321 Hz, CF_3), 120.9 (CH), 121.4 (2CH), 126.1 (CH), 127.4 (C), 127.6 (2CH), 128.0 (C), 128.3, 128.9 (CH), 129.5 (2CH), 129.7, 129.9 (CH), 134.5, 137.5 (C), 137.9 (2C), 143.2, 144.9, 150.7 (C), 165.5 (C=O). ^{19}F NMR (282.40 MHz, $CDCl_3$): δ = -73.06 (3F, CF_3). IR (ATR, 32 scans, cm^{-1}): $\tilde{\nu}$ = 3030 (w), 2922 (w), 2853 (w), 1731 (m), 1598 (w), 1508 (w), 1491 (w), 1366 (w), 1243 (m), 1214 (s), 1189 (s), 1138 (s), 1009 (m), 858 (m), 762 (m), 687 (m), 598 (m). MS (EI, 70 eV, m/z > 5 %): 500 ($[M]^+$, 1), 408 (28), 407 (100), 406 (35), 275 (12), 274 (71), 273 (23), 259 (34), 231 (23), 203 (14), 202 (22), 94 (2), 65 (4). HRMS (ESI) calculated for $C_{26}H_{20}F_3O_5S$ $[M+H]^+$ is 501.0978, found 501.0980.

Phenyl 1-(2-ethoxyphenyl)-4-(trifluoromethylsulfonyloxy)-2-naphthoate (17b):



Starting with **15** (272 mg, 0.5 mmol), K_3PO_4 (160 mg, 0.75 mmol), $Pd(PPh_3)_4$ (3 mol %), **10b** (91 mg, 0.55 mmol) and 1,4-dioxane (4 mL), **17b** was isolated as colorless crystals (150 mg, 59 %), mp = 87-89 °C; ^{1}H NMR (300.13 MHz, $CDCl_3$): δ = 0.98 (t, J = 7.0 Hz, 3H, CH_3), 3.86 (q, J = 7.0 Hz, 2H, OCH_2), 6.76-6.80 (m, 2H, ArH), 6.94 (d, J = 8.0 Hz, 1H, ArH), 7.00 (dt, J = 7.4, 1.0 Hz, 1H, ArH), 7.06-7.38 (m, 5H, ArH), 7.46 (dt, J = 8.0, 1.2 Hz, 1H, ArH), 7.61 (d, J = 8.4 Hz, 1H, ArH), 7.66 (dt, J = 7.6, 1.2 Hz, 1H, ArH), 8.04 (s, 1H, ArH), 8.10 (d, J = 8.4 Hz, 1H, ArH); ^{13}C NMR (75.47 MHz, $CDCl_3$): δ = 14.7 (CH_3), 64.1 (OCH_2), 112.3, 118.3 (CH), 119.0 (q, J_{FC} = 321 Hz, CF_3), 120.6, 121.0 (CH), 121.4 (2CH), 126.0 (CH), 126.9, 127.7 (C), 128.1 (CH), 128.3 (C), 128.7 (CH), 129.5 (2CH), 129.7, 129.9, 131.3 (CH), 134.6, 140.3, 145.0, 150.8, 156.6 (C), 165.2 (C=O); ^{19}F NMR (282.40 MHz, $CDCl_3$): δ = -73.16 (3F, CF_3); IR (ATR, 32 scans, cm^{-1}): $\tilde{\nu}$ = 3063 (w), 2926 (w), 2854 (w), 1744 (m), 1598 (w), 1491 (m), 1421 (m), 1332 (w), 1244 (m), 1201 (s), 1185 (s), 1127 (s), 1012 (s), 925 (m), 843 (m), 753 (s), 724 (s), 687 (m), 607 (s); GCMS (EI, 70 eV, m/z > 5 %): 516 ($[M]^+$, 7), 424 (19), 423 (90), 396 (19), 395 (100), 263 (16), 262 (78), 261 (20), 234 (26), 233 (25), 205 (28), 176 (17), 65 (6); HRMS (EI) calculated for $C_{26}H_{19}F_3O_6S$, $[M]^+$ is 516.08490, found 516.08473.

Phenyl 4-(trifluoromethylsulfonyloxy)-1-(4-hydroxyphenyl)-2-naphthoate (17c):



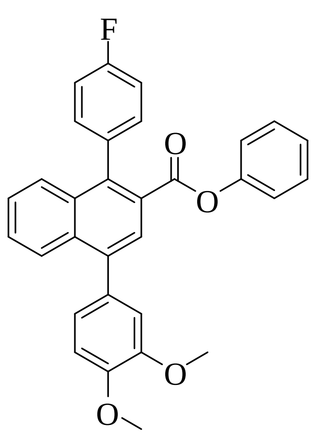
Starting with **15** (272 mg, 0.5 mmol), K_3PO_4 (160 mg, 0.75 mmol), $Pd(PPh_3)_4$ (3 mol %), **10m** (76 mg, 0.55 mmol) and 1,4-dioxane (4 mL), **17c** was isolated as colorless crystals (127 mg, 52 %), mp = 117-119 °C. ^{1}H NMR (250.13 MHz, $CDCl_3$): δ = 4.28 (brs, 1H, OH), 6.77-6.84 (m, 4H, ArH), 7.08-7.25 (m, 5H, ArH), 7.47 (dt, J = 8.8, 2.0 Hz, 1H, ArH), 7.63-7.69 (m, 2H, ArH), 7.96 (s, 1H, ArH), 8.09 (d, J = 8.0 Hz, 1H, ArH). ^{13}C NMR (62.89 MHz, $CDCl_3$): δ = 115.5 (2CH), 117.9 (CH), 119.0 (q, J_{FC} = 321 Hz, CF_3), 121.1 (CH),121.4 (2CH), 126.3 (CH), 127.6, 128.2 (C), 128.4, 128.8 (CH), 129.5 (C), 129.6 (2CH), 129.8 (CH), 131.1 (2CH), 134.9, 142.8, 145.0, 150.6, 156.0 (C), 165.9 (C=O). ^{19}F NMR

(282.40 MHz, $CDCl_3$): δ = -73.07 (3F, CF_3). IR (ATR, 32 scans, cm^{-1}): $\tilde{\nu}$ = 3421-2633 (br), 3069 (w), 2927 (w), 2852 (w), 1723 (m), 1589 (w), 1515 (w), 1427 (m), 1335 (m), 1240 (m), 1212 (s), 1193 (s), 1135 (s), 1013 (s), 966 (m), 830 (s), 750 (m), 642 (s), 594 (s). GCMS (EI, 70 eV, m/z > 5 %): 478 ($[M]^+$, 11), 386 (28), 385 (100), 326 (4), 283 (5), 270 (6), 192 (7), 135 (3). HRMS (ESI) calculated for $C_{24}H_{16}F_3O_6S$ $[M+H]^+$ is 489.0614, found 489.0616.

General procedure for the synthesis of 18a-c.

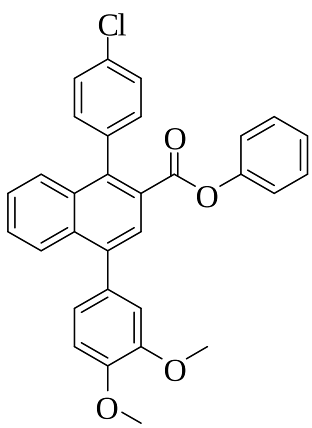
The reaction was carried out in a pressure tube. To a dioxane suspension (4 mL) of **15** (272 mg, 0.5 mmol), $Pd(PPh_3)_4$ (3 mol %) and $Ar^1B(OH)_2$ (0.55 mmol) was added K_3PO_4 (159 mg, 0.75 mmol) and the solution was degassed by bubbling argon through the solution for 10 minutes. The mixture was heated at 95 °C under argon atmosphere for 7 hours. The mixture was cooled to 20 °C and $Ar^2B(OH)_2$ (0.65 mmol) and K_3PO_4 (159 mg, 0.75 mmol) were added. The reaction mixture was heated under Argon atmosphere for 6 hours at 110 °C, then diluted with water and extracted with CH_2Cl_2 (3 x 25 mL). The combined organic layers were dried (Na_2SO_4), filtered and the filtrate was concentrated *in vacuo*. The residue was purified by flash chromatography (silica gel, EtOAc / heptanes = 10:2).

Phenyl 1-(4-fluorophenyl)-4-(3,4-dimethoxyphenyl)-2-naphthoate (18a): Starting with **15** (272 mg, 0.5 mmol), K_3PO_4 (318 mg, 1.5 mmol), $Pd(PPh_3)_4$ (3 mol %), **10j** (77 mg, 0.55 mmol), 1,4-dioxane (4 mL), and **10o** (118 mg, 0.65 mmol), **18a** was isolated as colourless crystals (129 mg, 54 %), mp = 136-138 °C. ^1H NMR (300.13 MHz, $CDCl_3$): δ = 3.84 (s, 3H, OCH_3), 3.89 (s, 3H, OCH_3), 6.75-6.78 (m, 2H, ArH), 6.95 (d, *J* = 8.1 Hz, 1H, ArH), 7.00 (d, *J* = 1.8 Hz, 1H, ArH), 7.04 (dd, *J* = 8.0, 1.9 Hz, 1H, ArH), 7.07-7.24 (m, 6H, ArH), 7.35-7.48 (m, 3H, ArH), 7.57 (dd, *J* = 8.4, 0.9 Hz, 1H, ArH), 7.95 (s, 1H, ArH), 7.96 (dd, *J* = 7.6, 0.8 Hz, 1H, ArH). ^{13}C NMR (62.89 MHz, $CDCl_3$): δ = 56.2 ($2OCH_3$), 111.4, 113.5 (CH), 114.8 (d, J_{FC} = 21.3 Hz, CH), 117.3 (d, J_{FC} = 21.3 Hz, CH), 121.5 (2CH), 122.6 (CH), 125.9 (d, J_{FC} = 3.0 Hz, CH), 126.0, 126.4, 126.5, 127.0 (CH), 127.2 (C), 128.1 (2CH), 129.5 (2CH),

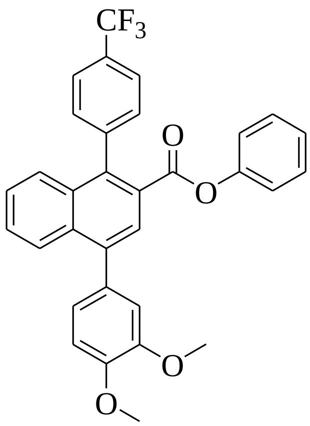


129.9 (d, J_{FC} = 8.4 Hz, CH), 132.5, 133.0, 133.7, 139.7, 140.8 (C), 141.3 (d, J_{FC} = 7.9 Hz, CH), 149.0, 149.1, 150.8 (C), 162.8 (d, J_{FC} = 247 Hz, CF), 166.7 (C=O). ^{19}F NMR (282.40 MHz, $CDCl_3$): δ = -113.35 (ArF). IR (ATR, 32 scans, cm^{-1}): $\tilde{\nu}$ = 3058 (w), 2956 (w), 2831 (w), 1723 (m), 1580 (w), 1460 (m), 1381 (w), 1242 (m), 1216 (s), 1187 (s), 1141 (s), 1097 (m), 934 (w), 815 (w), 742 (s), 688 (m), 593 (w). GCMS (EI, 70 eV, m/z > 5 %): 478 (M^+, 11), 386 (28), 385 (100), 326 (4), 283 (5), 270 (6), 192 (7), 135 (3). HRMS (EI) calculated for $C_{31}H_{23}FO_4$ $[M]^+$ is 478.15749, found 478.15783.

Phenyl 1-(4-chlorophenyl)-4-(3,4-dimethoxyphenyl)-2-naphthoate (18b): Starting with **15** (272 mg, 0.5 mmol), K_3PO_4 (318 mg, 1.5 mmol), $Pd(PPh_3)_4$ (3 mol %), **10h** (86 mg, 0.55 mmol),), 1,4-dioxane (4 mL), and **10o** (118 mg, 0.65 mmol), **18b** was isolated as colourless crystals (153 mg, 62 %), mp = 181-183 °C. ^{1}H NMR (300.13 MHz, $CDCl_3$): δ = 3.84 (s, 3H, OCH_3), 3.89 (s, 3H, OCH_3), 6.76-6.79 (m, 2H, ArH), 6.95 (d, J = 8.1 Hz, 1H, ArH), 7.00-7.11 (m, 3H, ArH), 7.19-7.30 (m, 4H, ArH), 7.35-7.42 (m, 3H, ArH), 7.46 (dt, J = 6.9, 1.5 Hz, 1H, ArH), 7.55 (dd, J = 8.2, 0.9 Hz, 1H, ArH), 7.95 (d, J = 7.7 Hz, 1H, ArH), 7.96 (s, 1H, ArH). ^{13}C NMR (75.47 MHz, $CDCl_3$): δ = 56.2 ($2OCH_3$), 111.4, 113.5 (CH), 121.5 (2CH), 122.6, 126.0, 126.4, 126.6, 127.0 (CH), 127.2 (C), 128.1, 128.6, 129.6, 131.4 (2CH), 132.5, 133.2, 133.8, 133.9, 137.6, 140.0, 140.7, 149.0, 149.1, 150.8 (C), 166.7 (C=O). IR (ATR, 32 scans, cm^{-1}): $\tilde{\nu}$ = 3055 (w), 2959 (w), 2832 (w), 1728 (s), 1597 (w), 1516 (m), 1408 (w), 1317 (w), 1243 (m), 1211 (m), 1192 (s), 1142 (s), 1099 (s), 925 (w), 813 (m), 741 (s), 687 (m), 593 (w). GCMS (EI, 70 eV, m/z > 5 %): 494 ($[M]^+$, 14), 403 (35), 402 (29), 401 (100), 367 (15), 366 (56), 263 (6), 250.13 (7), 125 (5). HRMS (EI) calculated for $C_{31}H_{23}ClO_4$ $[M^+]$ is 494.12794, found 494.12780.



Phenyl 1-[4-(trifluoromethyl)phenyl]-4-(3,4-dimethoxyphenyl)-2-naphthoate (18c): Starting with **15** (272 mg, 0.5 mmol), K_3PO_4 (318 mg, 1.5 mmol), $Pd(PPh_3)_4$ (3 mol %), **10k** (104 mg, 0.55 mmol), 1,4-dioxane (4 mL), and **10o** (118 mg, 0.65 mmol), **18c** was isolated as colourless crystals (134 mg, 51 %), mp = 163-165 °C. ^{1}H NMR (250.13 MHz, $CDCl_3$): δ = 3.85 (s, 3H, OCH_3), 3.90 (s, 3H, OCH_3), 6.70-6.73 (m, 2H, ArH), 6.96 (d, J = 8.2 Hz, 1H, ArH), 7.01-7.11 (m, 3H, ArH), 7.17-7.24 (m, 2H, ArH), 7.40 (dd, J = 7.3,

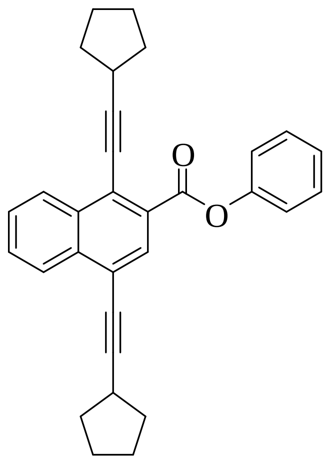


2.4 Hz, 1H, ArH), 7.44-7.50 (m, 4H, ArH), 7.68-7.71 (m, 2H, ArH), 7.95-7.99 (m, 1H, ArH), 8.0 (s, 1H, ArH). ^{13}C NMR (75.47 MHz, $CDCl_3$): δ = 56.0, 56.1 (OCH_3), 111.3, 113.3 (CH), 121.2 (2CH), 122.4 (CH), 124.3 (q, J_{FC} = 272 Hz, CF), 125.2 (q, J_{FC} = 3.8 Hz, 2CH), 125.9, 126.4, 126.5 (CH), 126.8 (C), 126.9, 127.8, 128.1 (CH), 129.4 (2CH), 129.9 (q, J_{FC} = 32.5 Hz, C), 130.3 (2CH), 132.3, 132.8, 133.7, 139.7, 140.9, 143.1, 148.9, 149.0, 150.5 (C), 166.2 (C=O). ^{19}F NMR (282.4 MHz. $CDCl_3$): δ = -62.38 (3F, $ArCF_3$). IR (ATR, 32 scans, cm^{-1}): $\tilde{\nu}$ =3065 (w), 2966 (w), 2838 (w), 1712 (m), 1597 (w), 1515 (m), 1406 (w), 1320 (m), 1239 (m), 1212 (m), 1159 (s), 1101 (s), 1023 (m), 923 (w), 775 (m), 744 (m), 685 (m), 623 (m), 549 (w). MS (EI, 70 eV, m/z > 5 %): 528 ($[M]^+$, 18), 436 (27), 435 (100), 376 (4), 333 (4), 252 (3), 207 (3), 153 (3), 94 (18), 69 (13), 60 (25), 43 (29). HRMS (EI) calculated for $C_{32}H_{23}F_3O_4$ $[M]^+$ is 528.15430, found 528.154433.

General procedure for synthesis of 20a-c and 21a.

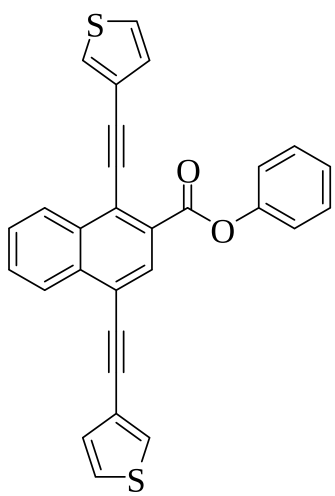
The reaction was carried out in a pressure tube under argon atmosphere. To a DMF suspension of **15** (272 mg, 0.5 mmol), $Pd(PPh_3)_4$ and Bu_4NI was added CuI after 10 minutes stirring. After next 10 minues stirring triethylamine, was added and followed by drop wise addition of alkyne. The reaction mixture was stirred at temperature of 80 °C (compound **20a-d)** or 60 °C (compound **21a)** for 4 hours respectively, under argon atmosphere. After cooling to 20 °C, 20 mL distilled water was added to the reaction mixture and the aqueous layer was extracted with CH_2Cl_2 (3 × 20 mL). The combined organic layers were dried (Na_2SO_4), filtered and the filtrate was concentrated *in vacuo*. The residue was purifed by flash chromatography (silica gel, heptanes / EtOAc = 20:1).

Phenyl 1,4-bis(cyclopentylethynyl)-2-naphthoate (20a): Starting with **15** (272 mg, 0.50 mmol), DMF (2.5 mL), Pd $(PPh_3)_4$ (**10** mol %), dry CuI (20 mol %), triethylamine (126 mg, 1.25 mmol), Bu_4NI (553 mg, 1.5mmol) and **19a** (112 mg, 1.2 mmol), **20a** was isolated as brown solid (145 mg, 67 %), mp = 79-80 °C. ^{1}H NMR (300.13 MHz, $CDCl_3$): δ = 1.48-1.79 (m, 13H), 1.92-2.00 (m, 3H), 2.93 (p, J = 6.9 Hz, 2H), 7.14-7.20 (m, 3H, ArH), 7.31-7.37 (m, 2H, ArH), 7.53-7.60 (m, 2H, ArH), 8.13 (s, 1H, ArH), 8.26 (dd, J =

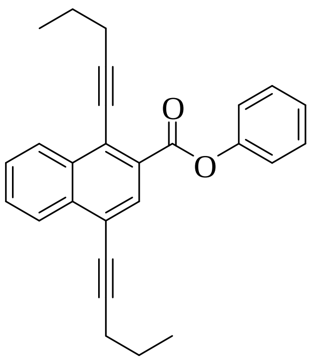


7.2, 2.1 Hz, 1H, ArH), 8.48 (dd, J = 7.2, 2.2 Hz, 1H, ArH). ^{13}C NMR (75.47 MHz, $CDCl_3$): δ = 25.3 ($4CH_2$), 31.3, 31.7 (CH), 34.1, 34.2 ($2CH_2$), 76.8, 77.8, 102.0, 109.2 (≡C), 121.7 (C), 121.9 (2CH), 123.7 (C), 126.0, 126.7, 127.7, 128.3, 128.9 (CH), 129.1 (C), 129.6 (2CH), 130.0 (CH), 133.9, 134.8, 151.2 (C), 165.3 (C=O). IR (ATR, 32 scans, cm^{-1}): $\tilde{\nu}$ = 3058 (w), 2950 (w), 2866 (w), 2117 (w), 1738 (m), 1591 (w), 1492 (m), 1370 (w), 1228 (m), 1186 (s), 1161 (s), 1143 (s), 1091 (m), 895 (m), 841 (w), 758 (s), 745 (m), 688 (m), 551 (w). GCMS (EI, 70 eV, m/z > 5 %): 432 ($[M]^+$, 7), 340 (27), 339 (100), 239 (5). HRMS (EI) calculated for $C_{31}H_{28}O_2$ $[M]^+$ is 432.20838, found 432.20857.

Phenyl 1,4-bis(thiophen-3-ylethynyl)-2-naphthoate (20b): Starting with **15** (272 mg, 0.50 mmol), DMF (2.5 mL), Pd $(PPh_3)_4$ (**10** mol %), dry CuI (20 mol %), triethylamine (126 mg, 1.25 mmol), Bu_4NI (553 mg, 1.5 mmol) and **19b** (130 mg, 1.2 mmol), **20b** was isolated as light brown solid (136 mg, 59 %), mp = 164-166 °C. ^{1}H NMR (300.13 MHz, $CDCl_3$): δ = 7.17-7.27 (m, 7H, ArH), 7.33-7.39 (m, 2H, ArH), 7.53 (dd, J = 2.9, 1.2 Hz, 1H), 7.57 (dd, J = 2.9, 1.2 Hz, 1H), 7.60-7.65 (m, 2H, ArH), 8.34 (s, 1H, ArH), 8.37 (dd, J = 7.2, 2.1 Hz, 1H, ArH), 8.59 (dd, J = 7.2, 2.1 Hz, 1H, ArH). ^{13}C NMR (62.89 MHz, $CDCl_3$): δ = 86.0 (C), 86.6 (C), 91.9 (C), 98.6 (≡C), 121.5 (C), 121.9 (2CH), 122.1, 122.4, 123.6 (C), 125.8, 125.9, 126.2, 126.8, 128.2, 128.4 (CH), 129.1 (C), 129.4, 129.6 (CH), 129.8 (2CH), 130.0 (CH), 130.1 (2CH), 130.6 (CH), 133.5, 134.5, 151.2 (C), 164.8 (C=O). IR (ATR, 32 scans' cm^{-1}): $\tilde{\nu}$ = 3065 (w), 2921 (w), 2852 (w), 2204 (w), 1711 (s), 1583 (w), 1492 (w), 1365 (m), 1240 (w), 1190 (s), 1165 (m), 1124 (m), 1070 (m), 941 (m), 832 (m), 772 (s), 750 (s), 687 (s), 620 (s), 561 (m). MS (EI, 70 eV, m/z > 5 %): 460 ($[M]^+$, 33), 369 (28), 368 (48), 367 (100), 340 (13), 339 (39), 338 (31), 293 (11), 261 (4), 184 (2), 169 (9), 125 (2), 94 (12), 69 (4), 44 (9). HRMS (EI) calculated for $C_{29}H_{16}O_2S_2$ $[M]^+$ is 460.05862, found 460.05926.

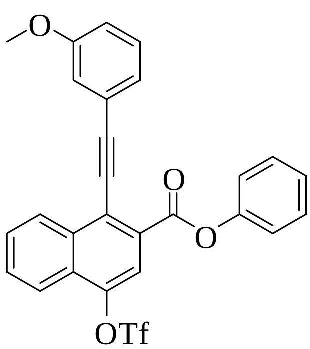


Phenyl 1,4-di(pent-1-yn-1-yl)-2-naphthoate (20c): Starting with **15** (272 mg, 0.50



mmol), DMF (2.5mL), Pd $(PPh_3)_4$ (**10** mol %), dry CuI (20 mol %), triethylamine (126 mg, 1.25 mmol), Bu_4NI (553 mg, 1.5 mmol) and **19c** (82 mg, 1.1 mmol), **20c** was isolated as light brown solid (135 mg, 71 %), mp = 77-78 °C. ^{1}H NMR (300.13 MHz, $CDCl_3$): δ = 1.00 (t, *J* = 7.4 Hz, 3H, CH_3), 1.05 (t, *J* = 7.4 Hz, 3H, CH_3), 1.61-1.70 (m, 4H), 2.49 (t, *J* = 7.1 Hz, 2H, CH_2), 2.53 (t, *J* = 7.1 Hz, 2H, CH_2), 7.17-7.22 (m, 3H, ArH), 7.33-7.39 (m, 2H, ArH), 7.56-7.60 (m, 2H, ArH), 8.16 (s, 1H, ArH), 8.30 (dd, *J* = 7.2, 2.1 Hz, 1H, ArH), 8.52 (dd, *J* = 7.3, 2.1 Hz, 1H, ArH). ^{13}C NMR (62.89 MHz, $CDCl_3$): δ = 13.9, 14.0 (CH_3), 22.0, 22.4 (CH_2), 22.5 ($2CH_2$), 77.2, 78.4, 97.7, 104.9 (≡C), 121.8 (C), 121.9 (2CH), 123.8 (C), 126.1, 126.8, 127.8, 128.4, 129.0 (CH), 129.2 (C), 129.7 (2CH), 130.1 (CH), 134.0, 134.8, 151.3 (C), 165.2 (C=O). IR (ATR, 32 scans, cm^{-1}): $\tilde{\nu}$ = 3057 (w), 2931 (w), 2870 (w), 2213 (w), 1742 (s), 1590 (w), 1491 (m), 1370 (m), 1227 (m), 1187 (s), 1142 (s), 1084 (s), 900 (m), 838 (m), 758 (s), 744 (s), 688 (s), 620 (m), 553 (w). MS (EI, 70 eV, m/z > 5 %): 380 ($[M]^+$, 4), 288 (17), 287 (100), 229 (5), 215 (10), 202 (13), 189 (5), 94 (9), 69 (9), 57 (11), 43 (21). HRMS (EI) calculated for $C_{27}H_{24}O_2$ $[M]^+$ is 380.17708 found 380.17763.

Phenyl 4-(trifluoromethylsulfonyloxy)-1-[(3-methoxyphenyl)ethynyl]-2-naphthoate



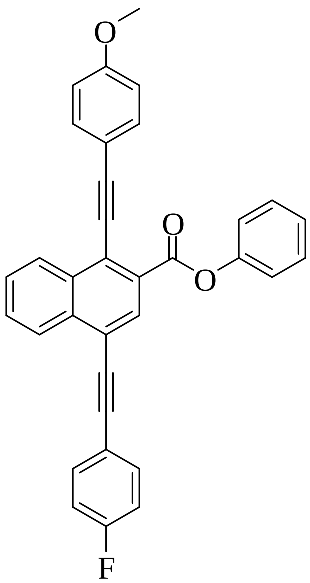
(21a): Starting with **15** (272 mg, 0.50 mmol), DMF (2.5mL), Pd $(PPh_3)_4$ (5 mol %), dry CuI (10 mol %), triethylamine (63 mg, 0.62 mmol), Bu_4NI (276 mg, 0.75mmol) and **19e** (73 mg, 0.55 mmol), **21a** was isolated as light yellow solid (160 mg, 61 %), mp = 82-84 °C. ^{1}H NMR (300.13 MHz, $CDCl_3$): δ = 3.67 (s, 3H, OCH_3), 6.87 (dd, *J* = 7.7, 2.6 Hz, 1H, ArH), 7.02-7.27 (m, 6H, ArH), 7.37-7.42 (m, 2H, ArH), 7.74-7.78 (m, 2H, ArH), 8.09 (dd, *J* = 7.1, 1.6 Hz, 1H, ArH), 8.10 (s, 1H, ArH), 8.69-8.72 (m, 1H, ArH). ^{13}C NMR (75.47 MHz, $CDCl_3$): δ = 55.5 (OCH_3), 84.8, 103.9 (≡C), 116.4, 116.7, 118.7 (CH), 119.0 (q, J_{FC} = 321 Hz, CF_3), 121.5 (CH), 121.9 (2CH), 123.7, 124.5 (C), 124.8, 126.4 (CH), 128.3 (C), 128.6 (CH), 129.2 (C), 129.3, 129.8 (CH), 129.9 (2CH), 130.6

(CH), 135.2, 144.9, 151.0, 159.7 (C), 163.8 (C=O). ^{19}F NMR (282.40 MHz, $CDCl_3$): δ = -73.03 (3F, CF_3). IR (ATR, 32 scans, cm^{-1}): $\tilde{\nu}$ = 3068 (w), 2964 (w), 2834 (w), 2196 (w), 1737 (m), 1574 (m), 1486 (m), 1329 (w), 1247 (m), 1200 (s), 1183 (s), 1136 (s), 1126 (s), 1010 (s), 909 (m), 847 (s), 755 (s), 647 (s), 590 (s). GCMS (EI, 70 eV, m/z > 5 %): 526 ($[M]^+$, 46), 435 (21), 434 (67), 433 (100), 369 (11), 301 (32), 300 (85), 272 (62), 244 (11), 213 (17), 201 (18), 200 (20), 94 (14), 64 (5). HRMS (EI) calculated for $C_{27}H_{17}F_3O_6S$, $[M]^+$ is 526.06925, found 526.06948.

General procedure for synthesis of 22b-d.

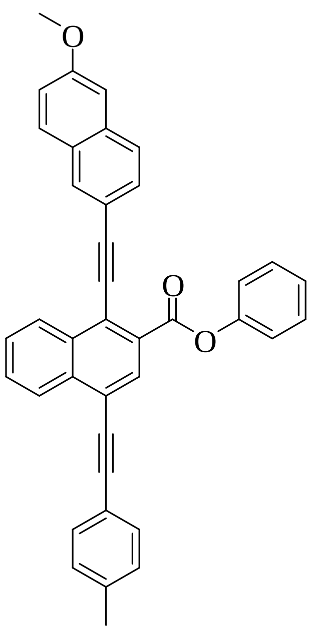
The reaction was carried out in a pressure tube under argon atmosphere. To a DMF suspension of **15** (272 mg, 0.5 mmol), $Pd(PPh_3)_4$ (10 mol %) and Bu_4NI (300 mol %) was added dry CuI (20 mol %) after stirring for 10 minutes. After 10 minutes stirring, triethylamine (126 mg, 1.25 mmol) was added followed by slow addition of Ar^1-alkyne (0.55 mmol). The reaction mixture was stirred at temperature of 60 °C for 3 hours under argon atmosphere. The reaction mixture was cooled to 20 °C and further triethylamine (126 mg, 1.25 mmol) was added followed by slow addition of Ar^2-alkyne (0.65 mmol). The reaction mixture was heated under Argon atmosphere for 4 hours at 80 °C. After cooling to 20 °C, distilled water (25 mL) was added and the reaction mixture was extracted with CH_2Cl_2 (3 × 20 mL). The combined organic layers were dried (Na_2SO_4), filtered and the filtrate was concentrated *in vacuo*. The residue was purifed by chromatography (silica gel, heptanes / EtOAc = 20:1).

Phenyl 4-[(4-fluorophenyl)ethynyl]-1-[(4-methoxyphenyl)ethynyl]-2-naphthoate (22b): Starting with **15** (272 mg, 0.50 mmol), DMF (2.5 mL), Pd $(PPh_3)_4$ (10 mol %), dry CuI (20 mol %), triethylamine (126 mg, 1.25 mmol), Bu_4NI (553 mg, 1.5 mmol), **19g** (73 mg, 0.55 mmol), and **19h** (78 mg, 0.65 mmol), **22b** was isolated as greenish yellow solid (146 mg, 59 %), mp = 161-163 °C. ^{1}H NMR (300.13 MHz, $CDCl_3$): δ = 3.73 (s, 3H, OCH_3), 6.79 (td, J = 8.9, 2.0 Hz, 2H, ArH), 6.98-7.04 (m, 2H, ArH), 7.19-7.26 (m, 3H, ArH), 7.34-7.40 (m, 2H, ArH), 7.48 (td, J = 8.9, 2.0 Hz, 2H, ArH), 7.52-7.65 (m, 4H, ArH), 8.34 (s, 1H, ArH), 8.37 (dd, J = 7.2, 2.2 Hz, 1H, ArH), 8.64 (dd, J = 7.2, 2.2 Hz, 1H, ArH). ^{13}C NMR (75.47 MHz, $CDCl_3$): δ = 55.5 (OCH_3), 85.4 (C), 86.8 (C) 95.4 (C), 104.1 (≡C), 114.3 (2CH), 115.3 (C), 116.0 (d, J_{FC} = 22.2 Hz, 2CH), 119.2 (d, J_{FC} = 3.6



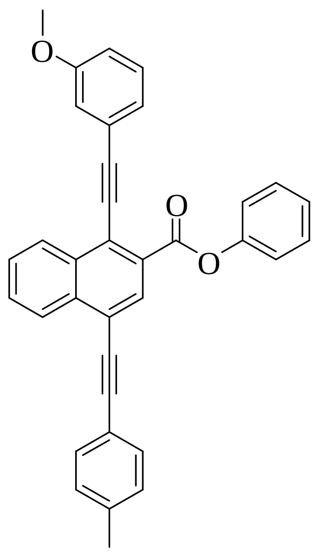
Hz, C), 120.9 (C), 122.0 (2CH), 124.2 (C), 126.2, 126.7, 128.1, 128.5 (CH), 128.7 (C), 129.4 (CH), 129.8 (2CH), 130.7 (CH), 133.6 (C), 133.8 (2CH), 133.9 (d, J_{FC} = 8.0 Hz, 2CH), 134.5, 151.2, 160.5 (C), 163.0 (d, J_{FC} = 250.13 Hz, CF), 164.8 (C=O). ^{19}F NMR (282.40 MHz. $CDCl_3$): δ = -109.93 (ArF). IR (ATR, 32 scans, cm^{-1}): $\tilde{\nu}$ = 3062 (w), 2915 (w), 2837 (w), 2202 (w), 1714 (s), 1602 (m), 1504 (m), 1463 (m), 1391 (w), 1245 (m), 1227 (m), 1189 (s), 1151 (m), 1029 (m), 932 (w), 829 (s), 759 (s), 742 (m), 691 (m), 532 (m). MS (EI, 70 eV, m/z > 5 %): 496 ($[M]^+$, 13), 405 (11), 404 (27), 403 (100), 375 (23), 332 (14), 331 (41), 329 (10), 166 (8), 94 (22), 69 (7), 66 (8), 65 (7), 43 (7). HRMS (EI) calculated for $C_{34}H_{21}FO_3$ $[M]^+$ is 496.14692, found 496.14719.

Phenyl 1-[(6-methoxynaphthalen-2-yl)ethynyl]-4-(*p*-tolylethynyl)-2-naphthoate (22c): Starting with **15** (272 mg, 0.50 mmol), DMF (2.5 mL), Pd $(PPh_3)_4$ (10 mol %), dry CuI (20 mol %), triethylamine (126 mg, 1.25 mmol), Bu_4NI (553 mg, 1.5mmol), **19d** (100 mg, 0.55 mmol) and **19f** (76 mg, 0.65 mmol), **22c** was isolated as yellow solid (127 mg, 47 %), mp = 204-206 °C. ^{1}H NMR (300.13 MHz, $CDCl_3$): δ = 2.29 (s, 3H, CH_3), 3.81 (s, 3H, OCH_3), 6.99-7.28 (m, 8H, ArH), 7.36-7.65 (m, 8H, ArH), 7.94 (s, 1H, ArH), 8.35 (s, 1H, ArH), 8.40 (dd, J = 7.7, 2.7 Hz, 1H, ArH), 8.68 (dd, J = 7.7, 2.8 Hz, 1H, ArH). ^{13}C NMR (75.47 MHz, $CDCl_3$): δ = 21.8 (CH_3), 55.5 (OCH_3), 86.2, 86.6, 97.0, 104.3 (≡C), 106.1 (CH), 118.1 (C), 119.7 (CH), 120.0, 121.6 (C), 122.0 (2CH), 123.7 (C), 126.2, 126.8, 127.1, 128.2, 128.4 (CH), 128.6, 129.0 (C), 129.2, 129.3 (CH), 129.5 (2CH), 129.7 (CH), 129.8 (2CH), 130.6 (CH), 131.9 (2CH), 132.2 (CH), 133.6, 134.6, 134.8, 139.3, 151.3, 158.8 (C), 164.8 (C=O). IR (ATR, 32 scans, cm^{-1}): $\tilde{\nu}$ = 3054 (w), 2945 (w), 2847 (w), 2200 (w), 1724 (s), 1628 (m), 1565 (m), 1487 (m), 1395 (m), 1331 (w), 1261 (m), 1190 (s), 1160 (s), 1132 (s), 1026 (m), 935 (w), 850 (m), 809 (s), 772 (s), 733 (m), 687 (m), 564 (w). MS (EI, 70 eV, m/z > 5 %): 542 ($[M]^+$, 18), 451 (11), 450 (31), 449 (100), 421 (22), 377 (19), 363



(13), 188 (15), 187 (13), 130 (18), 94 (27), 66 (9), 55 (6), 43 (8). HRMS (EI) calculated for $C_{39}H_{26}O_3$ $[M]^+$ is 542.18765, found 542.18762.

Phenyl 1-[(3-methoxyphenyl)ethynyl]-4-(*p*-tolylethynyl)-2-naphthoate (22d): Starting

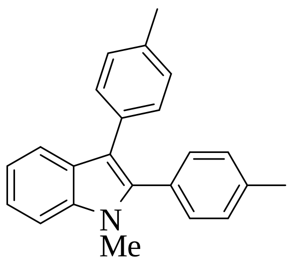


with **15** (272 mg, 0.50 mmol), DMF (2.5 mL), Pd $(PPh_3)_4$ (10 mol %), dry CuI (20 mol %), triethylamine (126 mg, 1.25 mmol), Bu_4NI (553 mg, 1.5 mmol), **19e** (73 mg, 0.55 mmol) and **19f** (75 mg, 0.65 mmol), **22d** was isolated as green crystals (143 mg, 58 %), mp = 148-149 °C. ^1H NMR (300 MHz, $CDCl_3$): δ = 2.29 (s, 3H, CH_3), 3.62 (s, 3H, OCH_3), 6.79-7.26 (m, 9H, ArH), 7.32-7.38 (m, 2H, ArH), 7.46 (td, *J* = 8.1, 1.7 Hz, 2H, ArH), 7.60-7.64 (m, 2H, ArH), 8.33 (s, 1H, ArH), 8.39 (dd, *J* = 7.1, 2.1 Hz, 1H, ArH), 8.61 (dd, *J* = 7.1, 2.1 Hz, 1H, ArH); ^{13}C NMR (75.47 MHz, $CDCl_3$): δ = 21.8 (CH_3), 55.4 (OCH_3), 86.1, 86.4, 97.1, 103.2 (≡C), 116.1, 116.5 (CH), 120.0, 121.9 (C), 122.0 (2CH), 123.2, 124.2 (C), 124.7, 126.1, 126.8, 128.2, 128.3 (CH), 129.3 (C), 129.4 (CH), 129.5 (2CH), 129.7 (CH), 129.8 (2CH), 130.5 (CH), 131.9 (2CH), 133.6, 134.5, 139.3, 151.2, 159.6 (C), 164.9 (C=O); IR (ATR, 32 scans, cm^{-1}): $\tilde{\nu}$ = 3055 (w), 2962 (w), 2832 (w), 2200 (w), 1740 (m), 1592 (m), 1488 (m), 1389 (w), 1332 (w), 1259 (m), 1198 (s), 1160 (s), 1132 (s), 1032 (s), 933 (m), 896 (m), 807 (m), 786 (s), 752 (s), 687 (s), 549 (w); MS (EI, 70 eV): m/z (%): 492 (M^+, 5), 399 (33), 378 (10), 4286 (37), 285 (100), 257 (16), 226 (15), 214 (22), 213 (46), 107 (7), 94 (14), 71 (5), 57 (8), 44 (11), 43 (14); HRMS (EI) calcd for $C_{35}H_{24}O_3$ $[M^+]$ is 492.17200, found 492.17119.

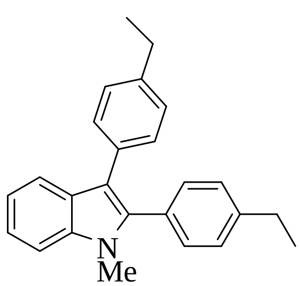
General procedure for the synthesis of 24a-e, 25a-f, and 27a-e.

The reaction was carried out in a pressure tube. A 1,4-dioxane (for compounds **24** and **25**) or 1:1 dioxane/water (for compounds **27**) solution (4 mL) of **23**, K_3PO_4, $Pd(PPh_3)_4$ and arylboronic acid **10** was stirred at 110 °C (for compounds **24**), 70 °C (for compounds **25**) or 90 °C (for compounds **27**) for 6 hours (for compounds **24**, **25** and **27**). After cooling to 20 °C, a saturated aqueous solution of NH_4Cl was added. The organic and the aqueous layer were separated and the latter was extracted with CH_2Cl_2 (3 x 30 mL). The combined organic layers were dried (Na_2SO_4), filtered and the filtrate was concentrated *in vacuo*. The residue was purified by flash chromatography (silica gel, heptanes).

1-Methyl-2,3-di-*p*-tolyl-1*H*-indole (24a): Starting with **23** (289 mg, 1.0 mmol), **10c** (313 mg, 2.3 mmol), K_3PO_4 (446 mg, 2.1mmol), $Pd(PPh_3)_4$ (3 mol %), and 1,4-dioxane (4 mL), **24a** was isolated as a colourless oil. (280 mg, 90 %). ^{1}H NMR (250.13 MHz, $CDCl_3$): δ = 3.28 (s, 3H, CH_3), 2.36 (s, 3H, CH_3), 3.63 (s, 3H, NCH_3), 7.05-7.27 (m, 10H, ArH), 7.45 (dt, *J* = 8.0, 0.9 Hz, 1H, ArH), 7.67 (dt, *J* = 8.0, 0.9 Hz, 1H, ArH). ^{13}C NMR (62.89 MHz, $(CD_3)_2CO$): δ = 21.2, 21.3 (CH_3), 31.1 (NCH_3), 110.7 (CH), 115.3 (C), 119.9, 120.7, 122.7 (CH), 128.1 (C), 129.7 (2CH), 129.9 (2CH), 130.1 (C), 130.5, 131.9 (2CH), 133.4, 135.6, 138.3, 138.4, 138.7 (C). IR (ATR, 32 scans, cm^{-1}): $\tilde{\nu}$ = 3044 (w), 3015 (m), 2942 (m), 2914 (m), 2860 (w), 1904 (w), 1613 (w), 1564 (w), 1553 (m), 1519 (m), 1494 (w), 1480 (m), 1464 (m), 1446 (m), 1428 (m), 1414 (w), 1366 (m), 1326 (m), 1258 (m), 1232 (m), 1182 (m), 1150 (m), 1089 (m), 1018 (m), 940 (m), 858 (m), 825 (s), 816 (s), 802 (s), 773 (m), 747 (s), 738 (s), 719 (s), 694 (m), 652 (m), 627 (s), 561 (m), 540 (m). GCMS (EI, 70 eV, m/z > 5 %): 312 ($[M+1]^+$, 26), 311 ($[M]^+$, 100), 295 (8), 281 (8), 140 (8), 139 (6). HRMS (EI) calculated for $C_{23}H_{21}N$ $[M]^+$ is 311.16685, found 311.166454.

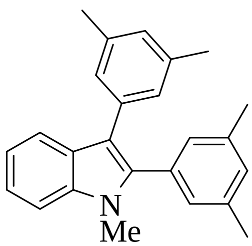


2,3-Bis(4-ethylphenyl)-1-methyl-1*H*-indole (24b): Starting with **23** (289 mg, 1.0 mmol), **10d** (262 mg, 2.3 mmol), K_3PO_4 (446 mg, 2.1mmol), $Pd(PPh_3)_4$ (3 mol %), and 1,4-dioxane (4 mL), **24b** was isolated as a yellowish oil (291 mg, 86 %). ^{1}H NMR (300.13 MHz, $CDCl_3$): δ = 1.01 (t, *J* = 7.5 Hz, 3H, CH_3), 1.05 (t, *J* = 7.5 Hz, 3H, CH_3), 2.40 (q, *J* = 7.5 Hz, 2H, CH_2), 2.48 (q, *J* = 7.5 Hz, 2H, CH_2), 3.42 (s, 3H, NCH_3), 6.90-6.96 (m, 3H, ArH), 7.02-7.10 (m, 7H, ArH), 7.25 (d, *J* = 8.2 Hz, 1H, ArH), 7.51 (d, *J* = 7.8 Hz, 1H, ArH). ^{13}C NMR (75.47 MHz, $CDCl_3$): δ = 15.8, 16.0 (CH_3), 29.1, 29.2 (CH_2), 31.2 (NCH_3), 110.7 (CH), 115.4 (C), 120.0, 121.0, 123.0 (CH), 128.1 (C), 128.5, 128.7 (2CH), 130.3 (C), 130.6, 132.0 (2CH), 133.7, 138.3, 138.4, 142.0, 144.9 (C). IR (ATR, 32 scans, cm^{-1}): $\tilde{\nu}$ = 3047 (w), 3022 (w), 2961 (s), 2928 (w), 1797 (w), 1765 (w), 1726 (w), 1519 (m),

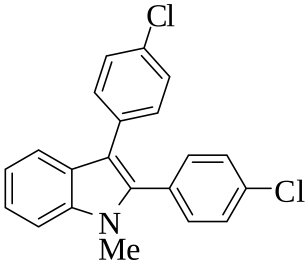


1463 (s), 1362 (m), 1325 (m), 1257 (m), 1131 (w), 1115 (w), 1089 (m), 1060 (w), 1017 (m), 967 (w), 923 (w), 869 (m), 836 (s), 801 (w), 740 (s), 652 (w), 629 (m), 545 (m). MS (EI, 70 eV, m/z > 5 %): 340 ($[M+1]^+$, 28), 339 ($[M]^+$, 100), 324 (34), 309 (5), 294 (5), 281 (5), 278 (4), 146 (5). HRMS (EI) calculated for $C_{25}H_{25}N$ $[M]^+$ is 339.19815, found 339.197901.

2,3-Bis(3,5-dimethylphenyl)-1-methyl-1*H*-indole (24c): Starting with **23** (289 mg, 1.0 mmol), **10e** (345 mg, 2.3 mmol), K_3PO_4 (446 mg, 2.1 mmol), $Pd(PPh_3)_4$ (3 mol %), and 1,4-dioxane (4 mL), **24c** was isolated as a colourless crystals (305 mg, 90 %), mp = 108-109 °C. ^{1}H NMR (300.13 MHz, $CDCl_3$): δ = 2.22 (s, 6H, $2CH_3$), 2.30 (s, 6H, $2CH_3$), 3. 64 (s, 3H, NCH_3), 6.82 (d, *J* = 0.8 Hz, 1H, ArH), 6.97 (s, 2H, ArH), 7.03 (s, 2H, ArH), 7.06 (s, 1H, ArH), 7.11-7.16 (m, 1H, ArH), 7.25 (ddd, *J* = 8.2, 7.0, 1.2 Hz, 1H, ArH), 7.46 (dt, *J* = 8.3, 0.9 Hz, 1H, ArH), 7.73 (dt, *J* = 7.8, 0.9 Hz, 1H, ArH). ^{13}C NMR (62.89 MHz, $(CD_3)_2CO$): δ = 21.3, 21.4 ($2ArCH_3$), 31.1 (NCH_3), 110.6 (CH), 115.5 (C), 120.1, 120.7, 122.6, 127.9 (CH), 128.1 (C), 128.4, 129.7 (2CH), 130.4 (CH), 132.9, 136.2 (C), 137.9 (2C), 138.3 (C), 138.5 (2C), 138.7 (C). IR (ATR, 32 scans, cm^{-1}): $\tilde{\nu}$ = 3026 (w), 2912 (m), 2857 (m), 2728 (w), 2687 (w), 1783 (m), 1598 (m), 1573 (m), 1549 (m), 1538 (m), 1519 (w), 1480 (m), 1467 (m), 1435 (m), 1392 (m), 1379 (m), 1366 (m), 1323 (m), 1288 (m), 1237 (m), 1196 (m), 1153 (m), 1132 (m), 1101 (m), 1036 (m), 1015 (m), 997 (m), 966 (m), 948 (m), 914 (m), 903 (m), 889 (m), 862 (m), 845 (m), 836 (m), 781 (m), 738 (s), 702 (s), 693 (s), 666 (m), 648 (m), 603 (m), 588 (m), 567 (m), 541(m). MS (EI, 70 eV, m/z > 5 %): 340 ($[M+1]^+$, 30), 339 ($[M]^+$, 100), 308 (5). HRMS (EI) calculated for $C_{25}H_{25}N$ $[M]^+$ is 339.19815, found 339.198033.

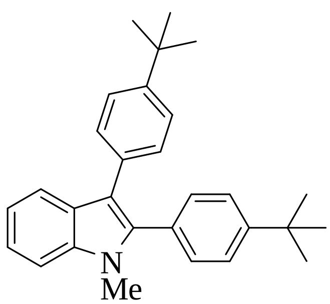


2,3-Bis(4-chlorophenyl)-1-methyl-1*H*-indole (24d): Starting with **23** (289 mg, 1.0 mmol), **10h** (360 mg, 2.3 mmol), K_3PO_4 (446 mg, 2.1 mmol), $Pd(PPh_3)_4$ (3 mol %), and 1,4-dioxane (4 mL), **24d** was isolated as a yellowish oil (292 mg, 83 %).^{1}H NMR (300.13 MHz, $CDCl_3$,): δ = 3.68 (s, 3H, NCH_3), 7.12-7.18 (m, 1H, ArH), 7.23-7.32 (m, 5H, ArH), 7.35-7.40 (m, 2H, ArH), 7.44-7.51 (m, 2H, ArH), 7.51 (d, *J* = 8.0 Hz, 1H, ArH), 7.67 (d, *J* =

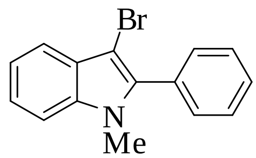


7.8 Hz, 1H, ArH). ^{13}C NMR (75.47 MHz, $CDCl_3$): δ = 31.2 (CH_3), 110.9 (CH), 114.7 (C), 119.8, 121.3, 123.3 (CH), 127.5 (C), 129.3, 129.6 (2CH), 131.3, 131.8 (C), 132.1, 133.7 (2CH), 134.8, 134.9, 137.4, 138.5 (C). IR (ATR, 32 scans, cm^{-1}): $\tilde{\nu}$ = 3078 (w), 3051 (w), 2919 (m), 2850 (m), 1916 (w), 1894 (w), 1567 (w), 1538 (m), 1496 (m), 1478 (m), 1464 (m), 1456 (m), 1430 (m), 1410 (m), 1389 (m), 1364 (m), 1326 (m),12 97 (w), 1257 (m), 1233 (m), 1177 (w), 1152 (m), 1135 (w), 1121 (w), 1106 (w), 1088 (s), 1044 (m), 1011 (s), 967 (m), 938 (m), 930 (m), 856 (m), 846 (m), 836 (m), 830 (m), 820 (s), 794 (m), 761 (w), 743 (s), 727 (s), 719 (s), 705 (m), 688 (m), 666 (m), 644 (m), 622 (m), 607 (m), 578 (m), 557 (m), 540 (m). MS (EI, 70 eV, m/z > 5 %): 354 ($[M+1]^+$, ^{37}Cl, 15), 353 ($[M]^+$, ^{37}Cl, 67), 352 ($[M+1]^+$, ^{35}Cl, 24), 351 ($[M]^+$, ^{35}Cl, 100), 315 (9), 314 (5), 301 (6), 266 (7), 265 (6), 140 (17), 139 (13). HRMS (EI): calculated for $C_{21}H_{15}Cl_2N$ $[M]^+$ is 351.05761, found 351.057126.

2,3-Bis(4-*tert*-butylphenyl)-1-methyl-1*H*-indole (24e): Starting with **23** (289 mg, 1.0 mmol), **10v** (409 mg, 2.3 mmol), K_3PO_4 (446 mg, 2.1 mmol), $Pd(PPh_3)_4$ (3 mol %), and 1,4-dioxane (4 mL), **24e** was isolated as a greenish oil (313 mg, 79 %). ^{1}H NMR (250.13 MHz, $CDCl_3$): δ = 1.18 (s, 9H, $[C(CH_3)_3]$, 1.23 (s, 9H, $[C(CH_3)_3]$, 3.52 (s, 3H, NCH_3), 6.39-7.54 (m, 12H, ArH). ^{13}C NMR (62.89 MHz, $CDCl_3$): δ = 31.1 (NCH_3), 31.6 (s, 3C, $C(CH_3)_3$), 31.7 (s, 3C, $C(CH_3)_3$), 34.9, 35.2 ($C(CH_3)_3$), 110.6 (CH), 116.9 (C), 120.0, 120.7, 122.7 (CH), 125.8, 126.1 (2CH), 126.8, 128.1 (C), 130.2, 131.7 (2CH), 133.9 (C), 138.3 (2C), 149.9, 150.8 (C). IR (ATR, 32 scans, cm^{-1}): $\tilde{\nu}$ = 3052 (w), 2954 (m), 2928 (m), 2903 (m), 2865 (m), 1716 (m), 1661 (m), 1651 (m), 1606 (m), 1520 (m), 1464 (s), 1392 (m), 1362 (s), 1326 (m), 1266 (m), 1233 (s), 1201 (m), 1150 (m), 1109 (m), 1086 (m), 1016 (m), 941 (m), 932 (m), 880 (w), 861 (m), 838 (m), 823 (m), 795 (w), 763 (w), 737 (s), 711 (m), 699 (m), 651 (m), 633 (m), 619 (m), 601 (m), 552 (m). MS (EI, 70 eV, m/z > 5 %): 396 ($[M+1]^+$, 32), 395 ($[M]^+$, 100), 380 (59), 350 (6), 183 (9), 154 (15). HRMS (EI) calculated for $C_{29}H_{33}N$ $[M]^+$ is 395.26075, found 395.260299.

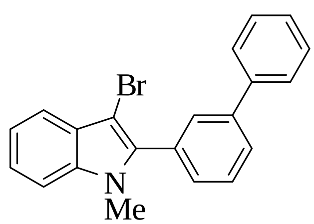


3-Bromo-1-methyl-2-phenyl-1*H*-indole (25a): Starting with **23** (289 mg, 1.0 mmol), **10a** (134 mg, 1.1 mmol), K_3PO_4 (318 mg, 1.5 mmol), $Pd(PPh_3)_4$ (3 mol %), and 1,4-



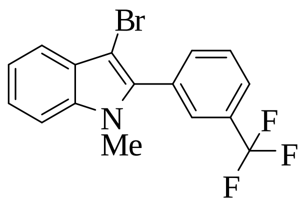
dioxane (4 mL), **25a** was isolated as a brownish oil (240 mg, 84 %). ^{1}H NMR (300.13 MHz, $CDCl_3$): δ = 3.68 (s, 3H, NCH_3), 7.18-7.23 (m, 1H, ArH), 7.26-7.32 (m, 1H, ArH), 7.48 (dt, *J* = 8.1, 0.8 Hz, 1H, ArH), 7.48-7.57 (m, 6H, ArH). ^{13}C NMR (62.89 MHz, $CDCl_3$): δ = 32.0 (NCH_3), 90.0 (C), 111.2, 119.6, 121.4, 123.7 (CH), 128.0 (C), 129.4 (2CH), 129.7 (CH), 131.3 (C), 131.6 (2CH), 137.9, 139.0 (C). IR (ATR, 32 scans, cm^{-1}): $\tilde{\nu}$ = 3055 (m), 3028 (m), 2937 (m), 2880 (w), 2836 (m), 1887 (w), 1714 (w), 1651 (w), 1604 (m), 1574 (m), 1479 (m), 1462 (s), 1441 (m), 1428 (m), 1380 (m), 1356 (m), 1339 (m), 1320 (m), 1234 (m), 1214 (m), 1176 (m), 1154 (m), 1127 (m), 1103 (m), 1074 (m), 1022 (m), 1010 (m), 968 (w), 944 (m), 921 (m), 828 (m), 792 (m), 735 (s), 697 (s), 677 (m), 614 (m), 583 (m), 547 (m). MS (EI, 70 eV, m/z > 5 %): 288 ($[M+1]^+$, ^{81}Br, 18), 287 ($[M]^+$, ^{81}Br, 100), 286 ($[M+1]^+$, ^{79}Br, 20), 285 ($[M]^+$, ^{79}Br, 98), 206 (7), 205 (21), 204 (35), 191 (13), 190 (12), 178 (8), 176 (7), 164 (6), 163 (6), 102 (14). HRMS (EI) calculated for $C_{15}H_{12}BrN$ $[M]^+$ is 285.01476, found 285.014285.

2-(Biphenyl-3-yl)-3-bromo-1-methyl-1*H*-indole (25b): Starting with **23** (289 mg, 1.0 mmol), **10b** (218 mg, 1.1 mmol), K_3PO_4 (318 mg, 1.5 mmol), $Pd(PPh_3)_4$ (3 mol %), and 1,4-dioxane (4 mL), **25b** was isolated as a yellowish oil (279 mg, 77 %). ^{1}H NMR (250.13 MHz, $CDCl_3$): δ = 3.70 (s, 3H, NCH_3), 7.24 (td, *J* = 6.9, 1.1 Hz, 1H, ArH), 7.32 (td, *J* = 6.9, 1.1 Hz, 1H, ArH) 7.38-7.42 (m, 1H, ArH), 7.46-7.67 (m, 6H, ArH), 7.72-7.80 (m, 3H, ArH), 7.87 (t, *J* = 1.5 Hz, 1H, ArH). ^{13}C NMR (62.89 MHz, $(CD_3)_2CO$): δ = 32.1 (NCH_3), 90.3 (C), 111.2, 119.7, 121.4, 123.8 (CH), 127.9 (2CH), 128.0 (C), 128.1, 128.6 (CH), 129.9 (2CH), 130.0, 130.1, 130.4 (CH), 131.9, 137.9, 138.8, 141.2, 142.1 (C). IR (ATR, 32 scans, cm^{-1}): $\tilde{\nu}$ = 3055 (m), 3028 (m), 2922 (m), 2851 (m), 1949 (w), 1884 (w), 1712 (w), 1599 (m), 1574 (m), 1537 (m), 1500 (w), 1462 (s), 1450 (m), 1430 (m), 1412 (m), 1355 (m), 1338 (m), 1321 (m), 1234 (m), 1204 (m), 1154 (m), 1103 (m), 1019 (w), 1011 (m), 945 (m), 899 (m), 854 (m), 806 (m), 737 (s), 699 (s), 671 (m), 638 (m), 613 (m), 586 (m), 548 (m). MS (EI, 70 eV, m/z > 5 %): 364 ($[M+1]^+$, ^{81}Br, 22), 363 ($[M]^+$, ^{81}Br, 100), 362 ($[M+1]^+$, ^{79}Br, 24), 361 ($[M]^+$, ^{79}Br, 100),

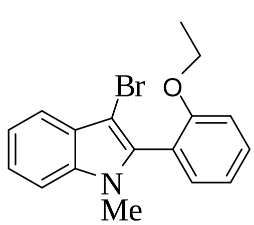


281 (10), 280 (20), 267 (7), 266 (6), 204 (8), 181 (5), 180 (5), 133 (7), 120 (5). HRMS (EI) calculated for $C_{16}H_{14}BrNO$ $[M]^+$ is 361.04606, found 361.045430.

3-Bromo-2-(3-(trifluoromethyl)phenyl)-1-methyl-1*H*-indole (25c): Starting with **23** (289 mg, 1.0 mmol), **10l** (209 mg, 1.1 mmol), K_3PO_4 (318 mg, 1.5 mmol), $Pd(PPh_3)_4$ (3 mol %), and 1,4-dioxane (4 mL), **25c** was isolated as a yellowish oil (287 mg, 81 %). ^{1}H NMR (300 MHz, $(CD_3)_2CO$): δ = 3.73 (s, 3H, NCH_3), 7.21-7.26 (m, 1H, ArH), 7.30-7.36 (m, 1H, ArH), 7.51 (dt, *J* = 8.3, 0.8 Hz, 1H, ArH), 7.56 (dq, *J* = 7.9, 0.6 Hz, 1H, ArH), 7.79-7.89 (m, 3H, ArH), 7.94-7.95 (m, 1H, ArH). ^{13}C NMR (62.89 MHz, $(CD_3)_2CO$): δ = 32.1 (NCH_3), 111.3, 119.8, 121.6 (CH), 123.4 (C), 124.2 (CH), 125.2 (q, J_{FC} = 271 Hz, $ArCF_3$), 126.3 (q, J_{FC} = 3.9 Hz, CH, ArH), 127.8 (C), 128.2 (q, J_{FC} = 3.9 Hz, CH, ArCH), 130.5 (CH), 131.2 (q, J_{FC} = 32 Hz, ArC), 132.4 (C), 135.4 (d, *J* = 1.1 Hz, CH, ArH), 137.2, 138.0 (C). ^{19}F NMR (282.40 MHz, $(CD_3)_2CO$): δ = -114.49 (3F, CF_3). IR (ATR, 32 scans, cm^{-1}): $\tilde{\nu}$ = 3056 (m), 2940 (m), 1613 (m), 1592 (m), 1574 (m), 1462 (m), 1423 (m), 1380 (m), 1356 (m), 1340 (m), 1321 (s), 1310 (s), 1278 (m), 1235 (m), 1211 (m), 1165 (s), 1120 (s), 1105 (s), 1095 (s), 1073 (s), 1052 (m), 1010 (m), 946 (m), 926 (w), 907 (m), 858 (m), 808 (m), 781 (w), 770 (w), 737 (s), 701 (s), 694 (s), 651 (m), 643 (m), 608 (w), 586 (m), 547 (m). MS (EI, 70 eV, m/z > 5 %): 356 ($[M+1]^+$, ^{81}Br, 18), 355 ($[M]^+$, ^{81}Br, 98), 354 ($[M+1]^+$, ^{79}Br, 20), 353 ($[M]^+$, ^{79}Br, 100), 274 (6), 273 (14), 272 (15), 205 (10), 204 (23), 190 (5). HRMS (EI) calculated for $C_{16}H_{11}BrF_3N$ $[M]^+$ is 353.00215, found 353.001842.

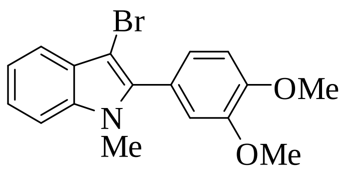


3-Bromo-2-(2-ethoxyphenyl)-1-methyl-1*H*-indole (25d): Starting with **23** (289 mg, 1.0 mmol), **10n** (182.6 mg, 1.1 mmol), K_3PO_4 (318 mg, 1.5 mmol), $Pd(PPh_3)_4$ (3 mol %), and 1,4-dioxane (4 mL), **25d** was isolated as a brownish oil (241 mg, 73 %). ^{1}H NMR (300.13 MHz, $CDCl_3$): δ = 1.21 (t, *J* = 7.7 Hz, 3H, CH_3), 2.63 (q, *J* = 7.6 Hz, 2H, OCH_2), 3.64 (s, 3H, NCH_3), 7.02-7.07 (m, 1H, ArH), 7.12-7.18 (m, 1H, ArH), 7.19-7.28 (m, 3H, ArH), 7.32-7.36 (m, 2H, ArH), 7.54 (dt, *J* = 7.9, 0.9 Hz, 1H, ArH). ^{13}C NMR (62.89 MHz, $CDCl_3$): δ = 15.5 (CH_3), 28.7 (CH_2), 31.1 (NCH_3), 101.2 (C), 109.6, 119.8, 120.4, 121.5 (CH), 128.0 (2CH), 128.0 (C), 129.4 (2CH), 130.2, 138.3, 141.7, 144.0 (C).

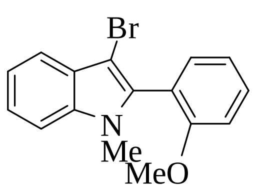


IR (ATR, 32 scans, cm^{-1}): $\tilde{\nu}$ = 3049 (m), 3023 (m), 2963 (m), 2929 (m), 2873 (m), 1916 (w), 1609 (m), 1543 (m), 1495 (m), 1462 (s), 1429 (s), 1412 (m), 1374 (m), 1357 (s), 1337 (s), 1313 (s), 1238 (m), 1213 (m), 1163 (m), 1129 (m), 1116 (m), 1099 (m), 1063 (w), 1050 (w), 1004 (m), 966 (w), 945 (w), 924 (w), 895 (w), 837 (s), 792 (s), 783 (s), 749 (s), 733 (s), 700 (m), 666 (m), 623 (w), 586 (m), 568 (m), 546 (m). MS (EI, 70 eV, m/z > 5 %): 315 (95), 313 (100), 300 (40), 299 (42), 235 (5), 204 (10).

3-Bromo-2-(3,4-dimethoxyphenyl)-1-methyl-1*H*-indole (25e): Starting with **23** (289 mg, 1.0 mmol), **10o** (200 mg, 1.1 mmol), K_3PO_4 (318 mg, 1.5 mmol), $Pd(PPh_3)_4$ (3 mol %), and 1,4-dioxane (4 mL), **25e** was isolated as a yellowish solid (272 mg, 79 %), mp = 146-148 °C. ^{1}H NMR (300.13 MHz, $CDCl_3$): δ = 3.59 (s, 3H, NCH_3), 3.84 (s, 3H, OCH_3), 3.87(s, 3H, OCH_3), 6.93-6.95 (m, 2H, ArH), 7.11-7.27 (m, 4H, ArH), 7.50-7.53 (m, 1H, ArH). ^{13}C NMR (62.89 MHz, $CDCl_3$): δ = 30.6 (CH_3), 54.9, 55.0 (OCH_3), 88.9 (C), 108.6, 109.9, 112.8, 118.2, 119.5, 121.7 (CH), 121.8 (C), 122.4 (CH), 126.1, 135.7, 137.0, 147.8, 148.4 (C). IR (ATR, 32 scans, cm^{-1}): $\tilde{\nu}$ = 3052 (w), 2960 (w), 2924 (W), 1607 (w), 1584 (w), 1502 (m), 1462 (m), 1445 (m), 1404 (w), 1379 (w), 1339 (w), 1317 (w), 1257 (s), 1239 (s), 1168 (m), 1136 (s), 1022 (s), 945 (m), 911 (w), 858 (m), 812 (m), 777 (w), 750 (s), 654 (m), 575 (w), 547 (w). MS (EI, 70 eV, m/z > 5 %): 348 ($[M+1]^+$, ^{81}Br, 18), 347 ($[M]^+$, ^{81}Br, 100), 346 ($[M+1]^+$, ^{79}Br, 19), 345 ($[M]^+$, ^{79}Br, 98), 302 (5), 302 (5), 300 (4), 251 (5), 223 (24), 180 (10), 152 (7), 102 (5). HRMS (EI) calculated for $C_{17}H_{16}Br^{79}NO_2$ $[M]^+$ is 345.03589, found 345.035679.



3-Bromo-2-(2-methoxyphenyl)-1-methyl-1*H*-indole (25f): Starting with **23** (289 mg, 1.0 mmol), **10q** (167 mg, 1.1 mmol), K_3PO_4 (318 mg, 1.5 mmol), $Pd(PPh_3)_4$ (3 mol %), and 1,4-dioxane (4 mL), **25f** was isolated as a yellowish oil (224 mg, 71 %). ^{1}H NMR (300.13 MHz, $CDCl_3$): δ = 3.39 (s, 3H, CH_3), 3.62 (s, 3H, NCH_3), 6.95 (td, *J* = 7.5, 0.9 Hz, 1H, ArH), 6.98-7.04 (m, 2H, ArH), 7.07-7.12 (m, 1H, ArH), 7.21 (dd, *J* = 7.6, 1.7 Hz, 1H, ArH), 7.27 (dt, *J* = 8.1, 0.8 Hz, 1H, ArH), 7.31-7.37 (m, 2H, ArH). ^{13}C NMR (62.89 MHz, $(CD_3)_2CO$): δ = 31.6 (NCH_3), 55.9 (OCH_3), 90.3 (C), 110.8, 112.3, 119.4 (CH), 120.1 (C), 120.9, 121.4, 123.3 (CH), 127.9 (C), 132.0, 133.8 (CH), 136.7, 137.5,

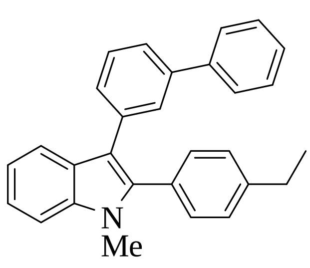


158.9 (C). IR (ATR, 32 scans, cm^{-1}): $\tilde{\nu}$ = 3052 (w), 3002 (w), 2929 (m), 2835 (m), 2716 (w), 2555 (w), 1604 (m), 1579 (m), 1545 (m), 1461 (s), 1434 (s), 1379 (m), 1362 (m), 1338 (m), 1321 (m), 1294 (m), 1278 (m), 1246 (s), 1232 (s), 1209 (m), 1179 (m), 1154 (m), 1118 (m), 1103 (m), 1054 (m), 1021 (m), 1011 (m), 945 (m), 837 (w), 779 (w), 734 (s), 668 (m), 618 (m), 592 (m), 565 (m). MS (EI, 70 eV, m/z > 5 %): 318 ($[M+1]^+$, ^{81}Br, 18), 317 ($[M]^+$, ^{81}Br, 98), 316 ($[M+1]^+$, ^{79}Br, 20), 315 ($[M]^+$, ^{79}Br, 98), 237 (11), 236 (56), 235 (9), 234 (15), 222 (12), 221 (47), 220 (58), 219 (12), 218 (11), 208 (12), 206 (12), 205 (15), 204 (22), 193 (16), 192 (14), 191 (12), 178 (9), 177 (9), 165 (22), 118 (13), 102 (13). HRMS (EI) calculated for $C_{16}H_{14}BrNO$ $[M]^+$ is 315.02533, found 315.024969.

General procedure for the synthesis of 26a-e.

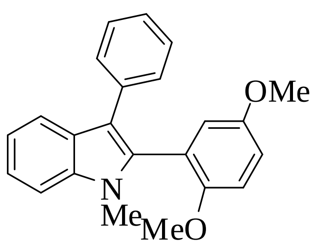
The reaction was carried out in pressure tube. To a dioxane suspension (4 mL) of **23** (215 mg, 0.75 mmol), $Pd(PPh_3)_4$ (3 mol %) and $Ar^1B(OH)_2$ (0.82 mmol) was added K_3PO_4 (234 mg, 1.1 mmol) and the solution was degassed by bubbling argon through the solution for 10 minutes. The mixture was heated at 70 °C under argon atmosphere for 6 hours. The mixture was cooled to 20 °C. To the solution was added $Ar^2B(OH)_2$ (0.90 mmol) and K_3PO_4 (254 mg, 1.2 mmol) and the solution was degassed again. The reaction mixture was heated under argon atmosphere for 8 hours at 110 °C. After cooling to 20 °C, the solution was diluted with water and extracted with CH_2Cl_2 (3 x 25 mL). The combined organic layers were dried (Na_2SO_4), filtered and the filtrate was concentrated *in vacuo*. The residue was purified by flash chromatography (silica gel, heptanes).

3-(Biphenyl-3-yl)-2-(4-ethylphenyl)-1-methyl-1*H*-indole (26a): Starting with **23** (215 mg, 0.75 mmol), **10d** (123 mg, 0.82 mmol), **10b** (178 mg, 0.9 mmol), K_3PO_4 (488 mg, 2.3 mmol), $Pd(PPh_3)_4$ (4 mol %) and 1,4-dioxane (4 mL), **26a** was isolated as a brownish oil. (206 mg, 71 %).^{1}H NMR (300 MHz, $(CD_3)_2CO$): δ = 1.29 (t, *J* = 7.6 Hz, 3H, CH_3), 2.73 (q, *J* = 7.6 Hz, 2H, CH_2), 3.70 (s, 3H, NCH_3), 7.14-7.20 (m, 1H, ArH), 7.24-7.43 (m, 14H, ArH), 7.51 (dt, *J* = 8.1, 1 Hz, 1H, ArH), 7.81 (dt, *J* = 7.9, 0.9 Hz, 1H, ArH). ^{13}C NMR (62.89 MHz, $(CD_3)_2CO$,): δ = 16.1 (CH_3), 29.3 (CH_2), 31.1 (NCH_3), 110.8 (CH), 115.2 (C), 119.9, 121.0, 122.8, 124.8 (CH),

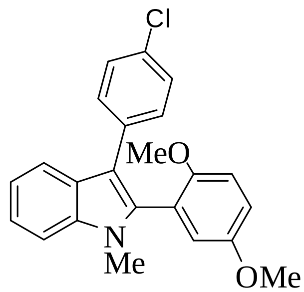


127.7 (2CH), 127.7 (C), 128.0 (CH), 128.9 (2CH), 129.2, 129.3 (CH), 129.6 (2CH), 129.7 (CH), 130.4 (C), 132.1 (2CH), 136.9, 138.4, 139.0, 141.6, 142.1, 145.4 (C). IR (ATR, 32 scans, cm^{-1}): $\tilde{\nu}$ = 3400 (br), 3051 (m), 3025 (m), 2962 (m), 2928 (m), 2871 (m), 1710 (m), 1650 (w), 1643 (w), 1609 (m), 1599 (m), 1582 (m), 1518 (w), 1493 (m), 1463 (s), 1428 (m), 1410 (m), 1363 (s), 1325 (m), 1261 (m), 1247 (m), 1218 (m), 1182 (m), 1152 (w), 1131 (m), 1115 (m), 1088 (m), 1049 (w), 1016 (m), 974 (w), 918 (w), 897 (m), 879 (m), 856 (m), 834 (s), 812 (s), 799 (m), 784 (m), 742 (s), 699 (s), 648 (m), 630 (m), 615 (m), 578 (m), 567 (m), 548 (m). MS (EI, 70 eV, m/z > 5 %): 388 ($[M+1]^+$, (32), 387 ($[M]^+$, 100), 372 (5), 357 (5), 343 (6). HRMS (EI) calculated for $C_{29}H_{25}N$ $[M]^+$ is 387.19815, found 387.198028.

2-(2,5-Dimethoxyphenyl)-1-methyl-3-phenyl-1*H*-indole (26b): Starting with **23** (215 mg, 0.75 mmol), **10r** (150 mg, 0.82 mmol), **10a** (110 mg, 0.9 mmol), K_3PO_4 (488 mg, 2.3 mmol), $Pd(PPh_3)_4$ (4 mol %) and 1,4-dioxane (4 mL), **26b** was isolated as a colourless oil (177 mg, 69 %). ^{1}H NMR (250.13 MHz, $CDCl_3$): δ = 3.40 (s, 3H, NCH_3), 3.44 (s, 3H, OCH_3), 3.52 (s, 3H, OCH_3), 6.54 (d, *J* = 3.1 Hz, 1H, ArH), 6.77-6.82 (m, 1H, ArH), 6.87-6.98 (m, 3H, ArH), 7.04-7.18 (m, 5H, ArH), 7.28 (d, *J* = 8.3 Hz, 1H, ArH), 7.56 (d, *J* = 7.8 Hz, 1H, ArH). ^{13}C NMR (62.9 MHz, $CDCl_3$): δ = 30.7 (NCH_3), 55.9, 56.3 (OCH_3), 110.5, 113.3 (CH), 115.7 (C), 115.8, 119.5, 119.8, 120.6 (CH), 122.5 (C), 122.6, 126.2 (CH), 127.7 (C), 129.0, 130.1 (2CH), 135.7, 136.7, 138.1, 153.7, 154.4 (C). IR (ATR, 32 scans, cm^{-1}): $\tilde{\nu}$ = 3051 (w), 2936 (w), 2832 (w), 1736 (w), 1712 (w), 1602 (w), 1549 (w), 1502 (m), 1485 (m), 1463 (m), 1366 (m), 1273 (m), 1225 (m), 1210 (m), 1039 (m), 1020 (m), 941 (w), 918 (w), 876 (w), 805 (w), 772 (m), 735 (s), 700 (s), 616 (w), 570 (w), 531 (w). MS (EI, 70 eV, m/z > 5 %): 345 ($[M+2]^+$, 3), 344 ($[M+1]^+$, 24), 343 ($[M]^+$, 100), 342 (15), 297 (6), 230 (5), 220 (5), 156 (7). HRMS (EI) calculated for $C_{23}H_{21}NO_2$ $[M]^+$ is 343.15668, found 343.156270.

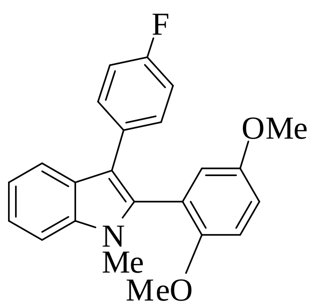


3-(4-Chlorophenyl)-2-(2,5-dimethoxyphenyl)-1-methyl-1*H*-indole (26c): Starting with **23** (215 mg, 0.75 mmol), **10r** (150 mg, 0.82 mmol), **10h** (141 mg, 0.9 mmol), K_3PO_4 (488 mg, 2.3 mmol), $Pd(PPh_3)_4$ (4 mol %) and 1,4-dioxane (4 mL), **26c** was isolated as a



colourless oil (167 mg, 59 %). [1]H NMR (300.13 MHz, $CDCl_3$): δ = 3.58 (s, 3H, OCH_3), 3.65 (s, 3H, NCH_3), 3.71 (s, 3H, OCH_3), 6.71 (d, *J* = 3 Hz, 1H, ArH), 7.01 (dd, *J* = 9.0, 3.0 Hz, 1H, ArH), 7.08-7.16 (m, 2H, ArH), 7.22-7.26 (m, 1H, ArH), 7.28-7.32 (m, 4H, ArH), 7.47 (dt, *J* = 8.0, 1.0 Hz, 1H, ArH), 7.70 (dt, *J* = 8.0, 1.0 Hz, 1H, ArH). ^{13}C NMR (62.89 MHz, $(CD_3)_2CO$): δ = 30.1 (N*C*H_3), 55.9, 56.3 (OCH_3), 110.6, 113.3 (CH), 114.3 (C), 116.0, 119.4, 119.6, 120.8 (CH), 122.2 (C), 122.7 (CH), 127.5 (C), 129.1 (2CH), 131.4 (C), 131.5 (2CH), 135.6, 136.0, 138.1, 153.6, 154.4, (C). IR (ATR, 32 scans, cm^{-1}): $\tilde{\nu}$ = 3047 (w), 2921 (m), 2851 (m), 1732 (w), 1667 (w), 1609 (w), 1544 (w), 1499 (m), 1483 (m), 1463 (m), 1431 (m), 1417 (m), 1366 (m), 1326 (m), 1302 (m), 1274 (m), 1263 (m), 1225 (s), 1209 (s), 1178 (m), 1150 (m), 1133 (m), 1091 (s), 1038 (s), 1013 (s), 934 (m), 912 (m), 879 (m), 866 (m), 835 (m), 810 (s), 761 (m), 732 (s), 719 (m), 712 (m), 699 (m), 675 (m), 649 (m), 630 (m), 603 (m), 585 (m), 571 (m), 551 (m). MS (EI, 70 eV, m/z > 5 %): 380 ($[M+1]^+$, ^{37}Cl, 8), 379 ($[M]^+$, ^{37}Cl, 35), 378 ($[M+1]^+$, ^{35}Cl, 30), 377 ($[M]^+$, ^{35}Cl, 100), 376 (14), 327 (6), 241 (6), 133 (9), 127 (6). HRMS (EI) calculated for $C_{23}H_{20}ClNO_2$ $[M]^+$ is 377.11771, found 377.117256.

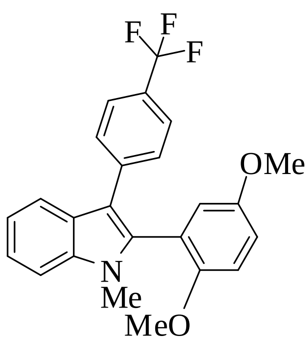
3-(4-fluorophenyl)-2-(2,5-Dimethoxyphenyl)-1-methyl-1*H*-indole (26d): Starting with



23 (215 mg, 0.75 mmol), **10r** (150 mg, 0.82 mmol), **10j** (126 mg, 0.9 mmol), K_3PO_4 (488 mg, 2.3 mmol), $Pd(PPh_3)_4$ (4 mol %) and 1,4-dioxane (4 mL), **26d** was isolated as a yellowish oil (192 mg, 71 %). [1]H NMR (300 MHz, $(CD_3)_2CO$): δ = 3.58 (s, 3H, OCH_3), 3.63 (s, 3H, OCH_3), 3.69 (s, 3H, NCH_3), 6.73 (d, *J* = 3.0 Hz, 1H, ArH), 6.97-7.08 (m, 4H, ArH), 7.12-7.17 (m, 1H, ArH), 7.26 (td, *J* = 7.6, 1.0 Hz, 1H, ArH), 7.30-7.38 (m, 2H, ArH), 7.47 (d, *J* = 8.3 Hz, 1H, ArH), 7.72 (d, *J* = 7.7 Hz, 1H, ArH). ^{13}C NMR (62.89 MHz, $(CD_3)_2CO$): δ = 30.8 (NCH_3), 55.9, 56.3 (OCH_3), 110.6, 113.3 (CH), 114.7 (C), 115.7 (d, J_{FC} = 21.4 Hz, 2CH), 116.0, 119.5, 119.7, 120.7 (CH), 122.3 (C), 122.7 (CH), 127.7 (C), 131.7 (d, J_{FC} = 7.8 Hz, 2CH), 132.9 (d, J_{FC} = 3.0 Hz, C), 135.7, 138.1, 153.7, 154.4 (C), 161.9 (d, J_{FC} = 242 Hz, C). ^{19}F NMR (282.40 MHz, $CDCl_3$): δ = -112.53 (ArF). IR (ATR, 32 scans, cm^{-1}):

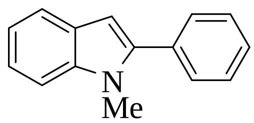
$\tilde{\nu}$ = 3046 (w), 2997 (w), 2934 (m), 2832 (m), 1712 (w), 1608 (w), 1589 (w), 1549 (m), 1508 (s), 1487 (s), 1463 (s), 1431 (s), 1417 (m), 1366 (m), 1326 (m), 1301(m), 1273 (m), 1212 (s), 1179 (m), 1155 (m), 1133 (m), 1089 (m), 1038 (s), 1019 (m), 941 (m), 911 (m), 877 (m), 839 (m), 821 (m), 785 (m), 762 (w), 734 (s), 719 (m), 693 (m), 678 (m), 673 (m), 651 (m), 633 (m), 609 (m), 589 (m), 574 (m), 559 (s). MS (EI, 70 eV, m/z > 5 %): 362 ($[M+1]^+$, 26), 361 ($[M]^+$, 100), 360 (16), 347 (8), 329 (5), 315 (7), 272 (5), 259 (5), 248 (9), 238 (6). HRMS (EI) calculated for $C_{29}H_{25}N$ $[M]^+$ is 361.14726, found 361.147102.

3-[4-(trifluoromethyl)phenyl]-2-(2,5-Dimethoxyphenyl)-1-methyl-1*H*-indole (26e):



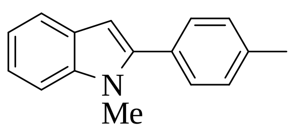
Starting with **23** (215 mg, 0.75 mmol), **10r** (150 mg, 0.82 mmol), **10k** (171 mg, 0.9 mmol), K_3PO_4 (488 mg, 2.3 mmol), $Pd(PPh_3)_4$ (4 mol %) and 1,4-dioxane (4 mL), **26e** was isolated as a yellowish oil (194 mg, 63 %). ^{1}H NMR (300.13 MHz, $CDCl_3$): δ = 3.61 (s, 3H, OCH_3), 3.65 (s, 3H, OCH_3), 3.71 (s, 3H, NCH_3), 6.74 (d, *J* = 3.2 Hz, 1H, ArH), 7.05 (d, *J* = 3.2 Hz, 1H, ArH), 7.10-7.21 (m, 2H, ArH), 7.29 (ddd, *J* = 8.1, 7.0, 1.1 Hz, 1H, ArH), 7.50-7.62 (m, 5H, ArH), 7.79 (d, *J* = 7.7 Hz, 1H, ArH). ^{13}C NMR (62.89 MHz, $(CD_3)_2CO$): δ = 30.8 (NCH_3), 55.9, 56.3 (OCH_3), 110.8, 113.4 (CH), 114.2 (C), 116.2, 119.3, 119.5, 121.1 (CH), 122.0 (C), 122.9 (CH), 123.5 (C), 125.6 (q, J_{FC} = 271 Hz, ArCF_3), 125.9 (q, J_{FC} = 3.8 Hz, 2CH, C), 127.4 (q, J_{FC} = 32 Hz, C), 130.2 (2CH), 136.6, 138.2 (C), 141.1 (d, *J* = 1.4 Hz, C), 153.6, 154.5 (C). ^{19}F NMR (282.40 MHz, Acetone): δ = -114.49 ($ArCF_3$). IR (ATR, 32 scans, cm^{-1}): $\tilde{\nu}$ = 3057 (w), 2953 (m), 2921 (m), 2852 (m), 1732 (w), 1613 (m), 1574 (w), 1566 (w), 1549 (m), 1494 (w), 1465 (m), 1435 (w), 1415 (w), 1394 (w), 1367 (w), 1320 (s), 1260 (m), 1190 (w), 1166 (m), 1106 (s), 1090 (s), 1064 (s), 1014 (m), 961 (m), 941 (m), 930 (m), 863 (m), 851 (m), 833 (m), 802 (m), 768 (m), 748 (m), 734 (s), 695 (m), 674 (m), 650 (m), 631 (m), 597 (m), 574 (m), 557 (m).

1-Methyl-2-phenyl-1*H*-indole (27a): Starting with **23** (289 mg, 1.0 mmol), **10a** (134 mg, 1.1 mmol), K_3PO_4 (318 mg, 1.5 mmol), $Pd(PPh_3)_4$ (3 mol %), 1,4-dioxane (2 mL) and H_2O (2mL) **27a** was isolated as a colourless crystals (201 mg, 97 %), mp = 93-95 °C.



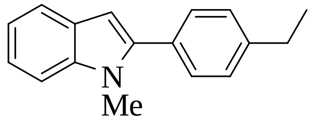
^{1}H NMR (300 MHz, $(CD_3)_2CO$): δ = 3.77 (s, 3H, NCH_3), 6.55 (d, J = 0.8 Hz, 1H, ArH), 7.05-7.11 (m, 1H, ArH), 7.17-7.23 (m, 1H, ArH), 7.37-7.61 (m, 7H, ArH). ^{13}C NMR ($(CD_3)_2CO$, 62.89 MHz): δ = 31.5 (NCH_3), 102.2, 110.7, 120.5, 121.1, 122.3 (CH), 129.0 (C), 129.5, 130.1 (2CH), 133.8, 139.5, 142.3 (C). IR (ATR, 32 scans, cm^{-1}): $\tilde{\nu}$ = 3053 (m), 3026 (m), 2919 (m), 2850 (m), 1601 (m), 1539 (w), 1464 (s), 1433 (m), 1382 (m), 1366 (m), 1340 (m), 1319 (m), 1307 (m), 1241 (m), 1233 (m), 1207 (m), 1178 (m), 1168 (m), 1147 (m), 1129 (m), 1119 (m), 1100 (m), 1074 (m), 1035 (w), 1007 (m), 996 (w), 988 (w), 975 (w), 924 (m), 893 (w), 842 (m), 796 (m), 765 (s), 747 (s), 731 (s), 700 (s), 672 (m), 659 (m), 616 (m), 582 (m), 576 (m), 532 (s). MS (EI, 70 eV, m/z > 5 %): 208 ($[M+1]^+$, 16), 207 ($[M]^+$, 100), 206 (44), 204 (10), 165 (10). HRMS (EI) calculated for $C_{15}H_{13}N$ $[M]^+$ is 207.10425, found 207.103624.

1-Methyl-2-*p*-tolyl-1*H*-indole (27b): Starting with **23** (289 mg, 1.0 mmol), **10c** (149 mg, 1.1 mmol), K_3PO_4 (318 mg, 1.5 mmol), $Pd(PPh_3)_4$ (3 mol %), 1,4-dioxane (2 mL) and H_2O (2 mL) **27b** was isolated as a colourless crystals (203 mg, 92%), mp 88-89 °C.



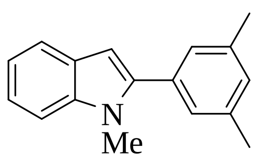
^{1}H NMR (250.13 MHz, $(CD_3)_2CO$): δ = 2.39 (s, 3H, ArCH_3), 3.74 (s, 3H, NCH_3), 6.50 (d, J = 0.8 Hz, 1H, ArH), 7.06 (td, J = 6.9, 1.1 Hz, 1H, ArH), 7.18 (td, J = 6.9, 1.1 Hz, 1H, ArH), 7.29-7.39 (m, 2H, ArH), 7.42-7.48 (m, 2H, ArH), 7.72-7.80 (m, 3H, ArH), 7.56 (dt, J = 8.0, 0.9 Hz, 1H, ArH). ^{13}C NMR (62.89 MHz, $(CD_3)_2CO$): δ = 21.2 (CH_3), 31.4 (NCH_3), 101.9, 110.6, 120.4, 121.0, 122.2 (CH), 129.1 (C), 130.0, 130.1 (2CH), 130.9, 138.5, 139.4, 142.4 (C). IR (ATR, 32 scans, cm^{-1}): $\tilde{\nu}$ = 3051 (m), 3018 (m), 2920 (m), 2853 (m), 2726 (w), 1925 (w), 1907 (w), 1755 (w), 1607 (w), 1495 (w), 1477 (w), 1462 (m), 1432 (w), 1409 (w), 1382 (m), 1366 (m), 1337 (m), 1317 (m), 1305 (m), 1239 (m), 1219 (m), 1189 (w), 1026 (w), 1006 (m), 955 (m), 918 (m), 895 (w), 826 (m), 773 (s), 749 (s), 734 (s), 716 (m), 666 (m), 636 (m), 623 (w), 581 (m), 556 (s), 526 (m). MS (EI, 70 eV, m/z > 5 %): 222 ($[M+1]^+$, 18), 221 ($[M]^+$, 100), 220 (38), 205 (10), 204 (14), 178 (6), 110 (8). HRMS (EI) calculated for $C_{16}H_{15}N$ $[M]^+$ is 221.11990, found 221.119448.

2-(4-Ethylphenyl)-1-methyl-1*H*-indole (27c): Starting with **23** (289 mg, 1.0 mmol), **10d** (165 mg, 1.1 mmol), K_3PO_4 (318 mg, 1.5 mmol), $Pd(PPh_3)_4$ (3 mol %), 1,4-dioxane (2



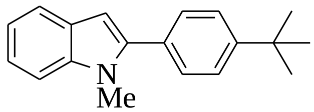
mL) and H_2O (2 mL) **27c** was isolated as a colourless solid (223 mg, 95 %), mp = 133-135 °C. ^{1}H NMR ($CDCl_3$, 300 MHz): δ = 1.19 (t, *J* = 7.6 Hz, 3H, CH_3), 2.61 (q, *J* = 7.6 Hz, 2H, CH_2), 3.60 (s, 3H, NCH_3), 7.00-7.05 (m, 1H, ArH), 7.10-7.24 (m, 4H, ArH), 7.29-7.34 (m, 2H, ArH), 7.31 (dt, *J* = 8.1, 1.7 Hz, 1H, ArH). ^{13}C NMR (62.89 MHz, $(CD_3)_2CO$): δ = 15.6 (CH_3), 28.8 (CH_2), 31.2 (NCH_3), 109.7, 119.9, 120.5, 121.6 (CH), 128.1 (2CH), 128.2 (C), 129.5 (2CH), 130.7, 138.1, 138.4, 141.9, 144.2 (C). IR (ATR, 32 scans, cm^{-1}): $\tilde{\nu}$ = 3045 (w), 3024 (w), 2960 (m), 2922 (m), 2852 (m), 1682 (w), 1598 (m), 1567 (w), 1504 (w), 1495 (w), 1463 (m), 1455 (m), 1432 (m), 1409 (m), 1385 (m), 1362 (m), 1325 (m), 1310 (m), 1250.13 (m), 1228 (m), 1183 (m), 1149 (m), 1132 (m), 1115 (m), 1093 (m), 1085 (m), 1053 (m), 1018 (m), 1001 (m), 970 (m), 955 (m), 922 (m), 901 (m), 856 (m), 834 (m), 801 (m), 763 (s), 755 (s), 738 (s), 707 (s), 701 (s), 670 (m), 646 (m), 614 (m), 598 (m), 575 (m), 567 (m), 547 (m). MS (EI, 70 eV, m/z > 5 %): 236 ($[M+1]^+$, 19), 235 ($[M]^+$, 100), 234 (9), 221 (11), 220 (62), 218 (6), 205 (10), 204 (21), 178 (5), 110 (6), 102 (5). HRMS (EI) calculated for $C_{17}H_{17}N$ $[M]^+$ is 235.13555, found 235.135424.

2-(3,5-Dimethylphenyl)-1-methyl-1*H*-indole (27d): Starting with **23** (289 mg, 1.0 mmol), **10e** (165 mg, 1.1 mmol), K_3PO_4 (318 mg, 1.5 mmol), $Pd(PPh_3)_4$ (3 mol %), 1,4-dioxane (2 mL) and H_2O (2 mL) **27d** was isolated as a yellowish gel (195 mg, 83 %). ^{1}H NMR (300.13 MHz, $CDCl_3$): δ = 2.22 (s, 6H, $2CH_3$), 3. 60 (s, 3H, NCH_3), 6.35 (d, *J* = 0.8 Hz, 1H, ArH), 6.89-6.94 (m, 2H, ArH), 7.00-7.06 (m, 3H, ArH), 7.25 (dd, *J* = 8.1, 0.8 Hz, 1H, ArH), 7.41 (dt, *J* = 7.7, 1 Hz, 1H, ArH). ^{13}C NMR (62.89 MHz, $(CD_3)_2CO$): δ = 21.4 (2Ar*C*H_3), 31.5 (NCH_3), 102.0, 110.6, 120.4, 121.0, 122.2 (CH), 127.9 (2CH), 129.1 (C), 130.3 (CH), 133.6 (C), 138.8 (2C), 139.5, 142.6 (C). IR (ATR, 32 scans, cm^{-1}): $\tilde{\nu}$ = 3052 (w), 2919 (m), 2853 (m), 2725 (w), 1599 (m), 1537 (m), 1465 (s), 1432 (m), 1376 (m), 1362 (m), 1338 (m), 1312 (s), 1281 (w), 1262 (w), 1230 (m), 1162 (m), 1146 (m), 1129 (m), 1099 (m), 1074 (m), 1036 (m), 1009 (m), 960 (w), 946 (w), 922 (w), 903 (m), 857 (m), 772 (s), 748 (s), 731 (s), 700 (s), 666 (s), 608 (w), 584 (m), 576 (m), 548 (m), 536 (m). MS (EI, 70 eV, m/z > 5 %): 236 ($[M+1]^+$, 19), 235 ($[M]^+$, 100), 234 (30), 220 (8), 219 (8), 218



(11), 217 (5), 205 (6), 204 (14). HRMS (EI) calculated mass for $C_{17}H_{17}N$ $[M]^+$ is 235.13555, found 235.135292.

2-(4-*Tert*-butylphenyl)-1-methyl-1*H*-indole (27e): Starting with **23** (289 mg, 1.0 mmol), **10v** (196 mg, 1.1 mmol), K_3PO_4 (318 mg, 1.5 mmol), $Pd(PPh_3)_4$ (3 mol %), 1,4-dioxane (2 mL) and H_2O (2 mL) **27e** was isolated as a yellowish solid (213 mg, 81 %), mp = 108-110 °C.

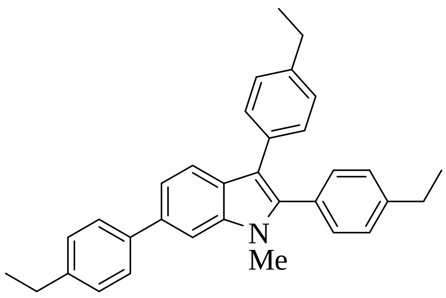


^1H NMR (300.13 MHz, $CDCl_3$): δ = 1.37 (s, 3H, CH_3), 3.76 (s, 3H, NCH_3), 6.51 (s, 1H, ArH), 7.03-7.09 (m, 1H, ArH), 7.14-7.21 (m, 1H, ArH), 7.48 (dt, *J* = 8.2, 0.8 Hz, 1H, ArH), 7.49-7.57 (m, 5H, ArH). ^{13}C NMR (62.89 MHz, $CDCl_3$): δ = 31.5 (NCH_3), 31.6 (CH_3), 35.2 (C), 101.9, 110.6, 120.4, 121.0, 122.2 (CH), 126.3 (2CH), 129.1 (C), 129.8 (2CH), 130.9, 139.5, 142.3, 151.6 (C). IR (ATR, 32 scans, cm^{-1}): $\tilde{\nu}$ = 3049 (w), 2954 (w), 2901 (w), 2860 (w), 1613 (w), 1494 (w), 1463 (m), 1454 (m), 1430 (w), 1406 (w), 1358 (m), 1336 (m), 1317 (w), 1266 (w), 1242 (w), 1216 (w), 1196 (w), 1165 (w), 1120 (m), 1098 (m), 1023 (w), 1004 (m), 922 (w), 846 (m), 840 (m), 794 (m), 782 (m), 747 (s), 736 (s), 671 (w), 589 (m), 559 (m), 542 (m). MS (EI, 70 eV, m/z > 5 %): 264 ($[M+1]^+$, 20), 263 ($[M]^+$, 100), 249 (19), 248 (85), 233 (18), 232 (7), 220 (8), 218 (6), 217 (5), 204 (9), 110 (19), 109 (7), 102 (6). HRMS (EI): calculated for $C_{19}H_{21}N$ $[M]^+$ is 263.16685, found 263.166607.

General procedure for the synthesis of 29a-d.

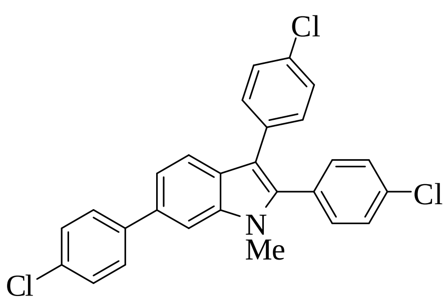
The reaction was carried out in a pressure tube. The mixure of **28**, THF (4 mL), H_2O (2 mL), K_2CO_3, $Pd(PPh_3)_4$ and arylboronic acid **10** was stirred at 110 °C for 8 hours. After cooling to 20 °C, a saturated aqueous solution of NH_4Cl was added. The organic and the aqueous layer were separated and the latter was extracted with CH_2Cl_2. The combined organic layers were dried (Na_2SO_4), filtered and the filtrate was concentrated in vacuo. The residue was purified by flash chromatography (silica gel, heptanes).

2,3,6-Tris(4-ethylphenyl)-1-methyl-1*H*-indole (29a): (Starting with **28** (184 mg, 0.5 mmol), **10d** (247.5 mg, 1.65 mmol), K_2CO_3 (276 mg, 2.0 mmol), $Pd(PPh_3)_4$ (4 mol-%) THF (4 mL), and H_2O (2 mL) **29a** was isolated as a colourless crystals (208 mg, 94 %), mp = 154-156 °C. ^1H NMR (300.13 MHz, $CDCl_3$): δ = 1.29 (t, *J* = 7.5 Hz, 3H, CH_3), 1.32 (t, *J* = 7.5 Hz, 3H, CH_3), 1.34 (t, *J* = 7.5 Hz, 3H, CH_3), 2.69 (q, *J* = 7.5 Hz, 2H,



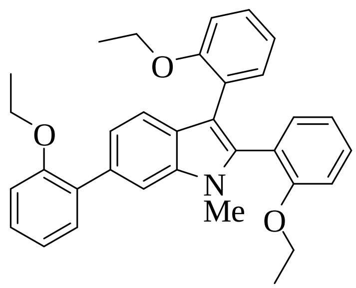
CH_2), 2.74 (q, *J* = 7.5 Hz, 2H, CH_2), 2.76 (q, *J* = 7.6 Hz, 2H, CH_2), 3.74 (s, 3H, NCH_3), 7.02-7.05 (m, 2H, ArH), 7.12-7.19 (m, 6H, ArH), 7.21-7.23 (m, 2H, ArH), 7.34 (dd, *J* = 8.3, 1.5 Hz, 1H, ArH), 7.49 (d, *J* = 0.9 Hz, 1H, ArH), 7.56 (m, 2H, ArH), 7.74 (d, *J* = 8.3 Hz, 1H, ArH). ^{13}C NMR (62.89 MHz, $CDCl_3$): δ = 15.3, 15.3, 15.7 (CH_3), 28.5, 28.5, 28.7 (CH_2), 31.0 (NCH_3), 107.9 (CH), 114.8 (C), 119.8 (2CH), 126.3 (C), 127.4, 127.7, 127.9, 128.2 (2CH), 129.2 (C), 129.7, 131.0 (2CH), 132.5, 135.6, 137.8, 138.2, 140.0, 141.2, 142.7, 144.0 (C). IR (ATR, 32 scans, cm^{-1}): $\tilde{\nu}$ = 3020 (w), 2962 (m), 2922 (m), 2871 (m), 2852 (m), 1915 (w), 1886 (w), 1800 (w), 1651 (w), 1609 (m), 1566 (w), 1545 (m), 1517 (m), 1464 (m), 1429 (m), 1410 (m), 1393 (m), 1374 (m), 1318 (m), 1278 (m), 1257 (m), 1228 (m), 1206 (w), 1119 (m), 1088 (m), 1060 (m), 1047 (m), 944 (m), 856 (m), 822 (s), 806 (s), 783 (m), 754 (m), 730 (m), 700 (w), 688 (w), 641 (w), 629 (m), 611 (m), 584 (m), 536 (m). MS (EI, 70 eV, m/z > 5 %): 445 ([M+2]$^+$, 12), 444 ([M+1]$^+$, 43), 443 ([M]$^+$, 100), 429 (9), 428 (12), 200 (11), 192 (37), 191 (23), 184 (37), 178 (13), 171 (10). HRMS (EI) calculated for $C_{33}H_{33}N$ [M]$^+$ is 443.26075, found 443.260766.

2,3,6-Tris(4-chlorophenyl)-1-methyl-1*H*-indole (29b): Starting with **28** (184 mg, 0.5 mmol), **10h** (258 mg, 1.65 mmol), K_2CO_3 (276 mg, 2.0 mmol), $Pd(PPh_3)_4$ (4 mol %) THF (4 mL), and H_2O (2 mL) **29b** was isolated as white powder (210 mg, 91 %), mp = 198-200 °C. ^{1}H NMR (300.13 MHz, $CDCl_3$,): δ = 3.74 (s, 3H, NCH_3), 7.22-7.32 (m, 6H, ArH), 7.35-7.48 (m, 5H, ArH), 7.58 (d, *J* = 1.1 Hz, 1H, ArH), 7.63-7.67 (m, 2H, ArH), 7.49 (dd, *J* = 8.3, 0.6 Hz, 1H, ArH). ^{13}C NMR (62.89 MHz, $CDCl_3$): δ = 31.1 (NCH_3), 108.9 (CH), 114.4 (C), 119.8, 120.2, 126.3 (C), 128.6 (4CH), 128.9, 129.0 (2CH), 129.8 (C), 130.9 (2CH), 131.7 (C), 132.3 (2CH), 132.9, 133.2, 134.6, 134.9, 137.4, 137.9, 140.6 (C). IR (ATR, 32 scans, cm^{-1}): $\tilde{\nu}$ = 3078 (w), 3030 (w), 2930 (w), 1538 (w), 1496 (m), 1463 (m), 1427 (m), 1396 (m), 1370 (m), 1334 (m), 1315 (m), 1299 (w), 1254 (m), 1234 (m), 1177 (w), 1163 (w), 1089 (s), 1013 (m), 958 (w), 946 (m), 854 (m), 831 (m), 812 (s), 760 (m), 747 (m), 733 (m), 721 (m),

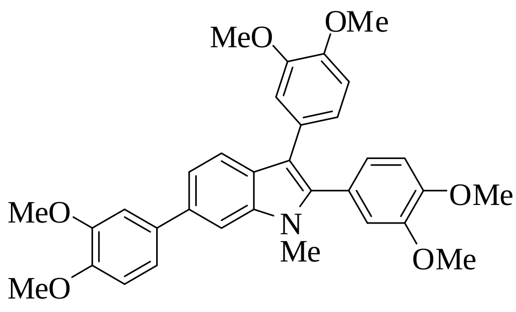


706 (m), 662 (m), 644 (m), 626 (w), 615 (m), 584 (m). MS (EI, 70 eV, m/z > 5 %): 465 (30), 464 (25), 463 (100), 465 (30), 461 (99), 376 (5), 178 (12), 177 (6), 170 (6), 69 (5), 44 (6), 43 (5). HRMS (EI) calculated for $C_{27}H_{18}ClN$ $[M]^+$ is 461.04993 found, 461.049515.

2,3,6-Tris(2-ethoxyphenyl)-1-methyl-1*H*-indole (29c): Starting with **28** (184 mg, 0.5 mmol), **10n** (274 mg, 1.65 mmol), K_2CO_3 (276 mg, 2.0 mmol), $Pd(PPh_3)_4$ (4 mol %) THF (4 mL), and H_2O (2 mL) **29c** was isolated as white powder (209 mg, 85 %), mp = 166 °C. ^{1}H NMR (300.13 MHz, $CDCl_3$): δ = 1.19 (brs, 3H, CH_3), 1.32 (t, *J* = 7.0 Hz, 3H, CH_3), 1.40 (t, *J* = 7.0 Hz, 3H, CH_3), 3.68 (s, 3H, NCH_3), 3.97-4.04 (m, 2H, $ArOCH_2$), 4.10 (q, *J* = 7.0 Hz, 4H, $2ArOCH_2$), 6.83-6.91 (m, 3H, ArH), 6.97 (d, *J* = 7.9 Hz, 1H, ArH), 7.02-7.22 (m, 4H, ArH), 7.28-7.34 (m, 3H, ArH), 7.38 (dd, *J* = 8.2, 1.4 Hz, 1H, ArH), 7.52 (dd, *J* = 7.6, 1.7 Hz, 1H, ArH), 7.60 (d, *J* = 8.3 Hz, 1H, ArH), 7.63 (d, *J* = 0.8 Hz, 1H, ArH). ^{13}C NMR (262.89 MHz, $CDCl_3$): δ = 14.5, 14.7, 14.9 (CH_3), 30.9 (NCH_3), 63.4 ($2CH_2$), 64.1 (CH_2), 110.2, 111.5 (2CH), 112.0 (C), 112.9 (2CH), 120.0, 120.2, 120.8, 121.3 (CH), 121.9, 125.0, 126.6 (C), 127.0, 127.7, 129.4 (CH), 131.3 (2CH), 131.8, 132.5, 132.6, 133.2, 136.3, 137.1, 156.1 (C). IR (ATR, 32 scans, cm^{-1}): $\tilde{\nu}$ = 3045 (w), 2978 (m), 2922 (m), 2874 (m), 1595 (w), 1577 (m), 1554 (m), 1499 (m), 1467 (m), 1451 (m), 1439 (m), 1387 (m), 1371 (m), 1333 (m), 1312 (m), 1281 (s), 1239 (s), 1158 (m), 1117 (s), 1084 (m), 1040 (s), 950 (m), 921 (m), 850 (m), 814 (m), 794 (m), 748 (s), 721 (s), 698 (m), 681 (m), 642 (m), 633 (m), 601 (m), 545 (m). MS (EI, 70 eV, m/z > 5 %): 493 ($[M+2]^+$, 7), 492 ($[M+1]^+$, 37), 491 ($[M]^+$, 100), 433 (9), 29 (5). HRMS (EI) calculated for $C_{33}H_{33}NO_3$ $[M]^+$ is 491.24550, found 491.245592.



2,3,6-Tris(3,4-dimethoxyphenyl)-1-methyl-1*H*-indole (29d): Starting with **28** (184 mg, 0.5 mmol), **10o** (274 mg, 1.65 mmol), K_2CO_3 (276 mg, 2.0 mmol), $Pd(PPh_3)_4$ (4 mol %) THF (4 mL), and H_2O (2 mL) **29d** was isolated as a white powder, (221 mg, 85 %), mp = 176 °C. ^{1}H NMR (300.13 MHz, $CDCl_3$): δ = 3.72 (s,



3H, NCH_3), 3.78 (s, 6H, $2ArOCH_3$), 3.91 (s, 3H, $ArOCH_3$), 3.96 (s, 3H, $ArOCH_3$), 3.98 (s, 3H, $ArOCH_3$), 4.03 (s, 3H, $ArOCH_3$), 6.86-6.89 (m, 3H, ArH), 6.95-6.98 (m, 3H, ArH), 7.02 (d, J = 8.3 Hz, 1H, ArH), 7.27-7.31 (m, 2H, ArH), 7.44 (dd, J = 8.3, 1.5 Hz, 1H, ArH), 7.18 (d, J = 0.9 Hz, 1H, ArH), 7.85 (d, J = 8.3 Hz, 1H, ArH). ^{13}C NMR (62.89 MHz, $(CD_3)_2CO$): δ = 30.9 (NCH_3), 55.6, 55.8 ($ArOCH_3$), 55.9, 56.0 ($2ArOCH_3$), 107.7, 110.9, 111.0, 111.1, 111.6, 113.1, 114.2 (CH), 114.5 (C), 119.58, 119.6, 119.9, 121.8, 123.6 (CH), 124.4, 126.0, 127.9, 135.5, 135.6, 137.7, 137.9, 147.0, 148.2, 148.5, 148.7, 148.9, 149.1 (C). IR (ATR, 32 scans, cm^{-1}): $\tilde{\nu}$ = 3644 (br), 3068 (w), 2999 (m), 2923 (m), 2839 (m), 1731 (w), 1605 (w), 1585 (m), 1552 (m), 1607 (w), 1517 (m), 1501 (m), 1486 (m), 1462 (m), 1444 (m), 1421 (m), 1403 (m), 1387 (m), 1369 (m), 1333 (m), 1315 (m), 1301 (m), 1274 (s), 1227 (s), 1169 (m), 1132 (s), 1094 (m), 1064 (m), 1021 (s), 982 (m), 933 (m), 910 (m), 867 (m), 842 (m), 815 (s), 806 (m), 790 (s), 761 (s), 751 (s), 697 (m), 655 (m), 642 (m), 622 (m), 612 (m), 591 (m), 580 (m), 570 (m). MS (EI, 70 eV, m/z > 5 %): 541 ($[M+2]^+$, 7), 540 ($[M+1]^+$, 34), 539 (M^+, 100), 270 (3). HRMS (EI) calculated mass for $C_{33}H_{33}NO_6$ [M^+] is 539.23024, found 539.231334.

General procedure for the synthesis of trimethylsilicenium-arene salts [Me_3Si·*arene*][$B(C_6F_5)_4$] (31a-k).

To neat bis(trimethylsilyl)hydronium tetrakis(pentafluorpheny-l)borate [Me_3Si-H-$SiMe_3$][$B(C_6F_5)_4$] (**30**) (0.413 g, 0.5 mmol), a minimum of the corresponding arene (3-5 mL) was added at ambient temperatures with stirring, followed by gently heating up to 80 °C, until a clear colourless solution and an oiled out layer is obtained. Slow cooling to ambient temperatures over a period of one hour results in the deposition of colourless crystals. Removal of excess arene by decantation and drying *in vacuo* gives the corresponding trimethylsilicenium-*arene* tetrakis(pentafluorophenyl)borate [Me_3Si–*arene*][$B(C_6F_5)_4$] (**31a-k**; *arene* = benzene, toluene, ethylbenzene, *n*-propylbenzene, *i*-propylbenzene, *o*-xylene, *m*-xylene, *p*-xylene, 1,2,3-trimethylbenzene, 1,2,4-trimethylbenzene, 1,3,5-trimethylbenzene) as a colourless solid in good yield (70 - 90%).

Crystals of **c, g,h,i** and **j** contain one equivalent of the arene solvent per formula unit, crystals of **k** contain 0.75 equivalents of the arene solvent per formula unit. Crystals suitable for X-ray crystallographic analysis were obtained directly from the above reaction solutions.

[Me_3Si·*benzene*][$B(C_6F_5)_4$] (31a)

Mp = 88 °C (dec.). Anal. calc. % ([C_6H_6–$SiMe_3$][$B(C_6F_5)_4$]) (found): C, 47.73 (45.98); H, 1.82 (1.45). IR (ATR, 16 scans, cm^{-1}): 3113 (w), 3092 (w), 3034 (w), 2996 (w), 2914 (w), 1643 (m), 1600 (w), 1588 (w), 1556 (w), 1513 (s), 1455 (s), 1412 (m), 1383 (m), 1372 (m), 1342 (m), 1321 (m), 1271 (m), 1180 (w), 1164 (w), 1082 (s), 1034 (w), 1022 (w), 972 (s), 912 (w), 869 (m), 856 (w), 813 (m), 770 (m), 755 (m), 737 (m), 728 (w), 698 (m), 683 (m), 662 (s), 623 (m), 611 (w), 603 (w), 573 (m).

[Me_3Si·*toluene*][$B(C_6F_5)_4$] (31b)

Mp = 108 °C (dec.). Anal. calc. % ([C_7H_8–$SiMe_3$][$B(C_6F_5)_4$], (found): C, 48.36 (48.01); H, 2.03 (1.76). IR (ATR, 16 scans, cm^{-1}): 3092 (w), 3014 (w), 2979 (w), 2914 (w), 2042 (w), 2016 (w), 1987 (w), 1644 (m), 1598 (w), 1556 (w), 1513 (s), 1456 (s), 1413 (m), 1380 (m), 1321 (m), 1271 (m), 1261 (m), 1216 (w), 1190 (w), 1179 (w), 1145 (w), 1082 (s), 1022 (w), 998 (m), 972 (s), 918 (w), 865 (m), 820 (s), 799 (s), 774 (s), 755 (s), 735 (w), 727 (w), 694 (m), 683 (m), 659 (s), 624 (m), 610 (w), 603 (w), 573 (m).

[Me_3Si·*ethylbenzene*][$B(C_6F_5)_4$] · ethylbenzene (31c)

Mp = 112 °C (dec.). Anal. calc. % ([C_8H_{10}–$SiMe_3$][$B(C_6F_5)_4$] C_8H_{10}), (found): C, 53.54 (53.35); H, 3.03 (3.13). IR (ATR, 16 scans, cm^{-1}): 3084 (w), 3063 (w), 3028 (w), 2969 (w), 2936 (w), 2913 (w), 2877 (w), 1643 (m), 1615 (w), 1597 (w), 1562 (w), 1556 (w), 1512 (s), 1456 (s), 1412 (m), 1382 (m), 1374 (m), 1341 (w), 1327 (w), 1270 (m), 1263 (m), 1186 (w), 1082 (s), 1037 (w), 1031 (w), 973 (s), 923 (w), 907 (w), 863 (m), 809 (m), 773 (s), 770 (s), 755 (s), 726 (m), 700 (m), 683 (m), 660 (s), 623 (m), 610 (m), 603 (m), 573 (m), 558 (m).

[Me_3Si·*n-propylbenzene*][$B(C_6F_5)_4$] (31d)

Mp = 87 °C (dec.). Anal. calc. % ([C_9H_{12}–$SiMe_3$][$B(C_6F_5)_4$]), (found): C, 49.56 (47.46); H, 2.43 (2.00). IR (ATR, 16 scans, cm^{-1}): 3089 (w), 3009 (w), 2973 (w), 2939 (w), 2879 (w), 1644 (m), 1644 (w), 1610 (w), 1595 (w), 1563 (w), 1556 (w), 1513 (s), 1456 (s), 1412 (m), 1381 (m), 1375 (m), 1322 (m), 1271 (m), 1188 (w), 1180 (w), 1162 (w), 1144 (w), 1082 (s), 1028 (w), 1011 (w), 972 (s), 921 (m), 909 (w), 861 (m), 811 (m), 774 (s), 769 (s), 755 (s), 726 (m), 711 (w), 683 (m), 661 (s), 623 (m), 611 (m), 603 (m), 573 (m).

[Me_3Si·*i-propylbenzene*][B(C_6F_5)$_4$] (31e)

Mp = 95°C (dec.). Anal. calc. % ([C_9H_{12}–$SiMe_3$][B(C_6F_5)$_4$]), (found): C, 49.56 (49.12); H, 2.43 (2.13). IR (ATR, 16 scans, cm^{-1}): 3099 (w), 3014 (w), 3013 (w), 2974 (w), 2936 (w), 2914 (w), 2875 (w), 1644 (m), 1611 (w), 1595 (w), 1557 (w), 1557 (w), 1512 (s), 1457 (s), 1413 (m), 1381 (m), 1375 (m), 1367 (m), 1325 (w), 1271 (m), 1261 (m), 1192 (w), 1164 (w), 1080 (s), 1048 (w), 1029 (w), 998 (m), 974 (s), 922 (m), 908 (w), 865 (m), 853 (m), 834 (w), 808 (s), 774 (s), 768 (s), 756 (s), 725 (m), 702 (w), 683 (m), 660 (s), 622 (m), 611 (m), 603 (m), 573 (m), 563 (w), 538 (m).

[Me_3Si·*o-xylene*][B(C_6F_5)$_4$] (31f)

Mp = 91°C, (106 °C, dec.). Anal. calc. % ([C_8H_{10}–$SiMe_3$][B(C_6F_5)$_4$]), (found): C, 48.97 (48.40); H, 2.23 (1.80). IR (ATR, 16 scans, cm^{-1}): 3013 (w), 2975 (w), 2915 (w), 2874 (w), 1644 (m), 1595 (w), 1556 (w), 1512 (s), 1455 (s), 1412 (m), 1381 (m), 1374 (m), 1321 (w), 1270 (m), 1262 (m), 1188 (w), 1179 (w), 1161 (w), 1081 (s), 1035 (w), 972 (s), 938 (m), 895 (w), 858 (m), 823 (m), 801 (m), 773 (s), 768 (s), 755 (s), 727 (m), 696 (m), 683 (s), 661 (s), 622 (m), 610 (m), 603 (m), 573 (w).

[Me_3Si·*m-xylene*][B(C_6F_5)$_4$] · *m*-xylene (31g)

Mp = 104 °C (dec.). Anal. calc. % ([C_8H_{10}–$SiMe_3$][B(C_6F_5)$_4$]), (found): C, 48.97 (50.64); H, 2.23 (2.59). IR (ATR, 16 scans, cm^{-1}): 3013 (w), 2950 (w), 2918 (w), 2864 (w), 2734 (w), 1644 (m), 1620 (w), 1601 (w), 1558 (w), 1512 (s), 1455 (s), 1412 (m), 1374 (m), 1341 (w), 1325 (w), 1300 (w), 1270 (m), 1205 (w), 1176 (w), 1158 (w), 1144 (w), 1082 (s), 1031 (w), 998 (m), 972 (s), 924 (m), 907 (m), 862 (m), 818 (m), 808 (m), 773 (s), 756 (s), 727 (m), 715 (w), 692 (m), 683 (s), 660 (s), 624 (m), 610 (m), 603 (m), 574 (m), 543 (w), 530 (w).

[Me_3Si·*p-xylene*][B(C_6F_5)$_4$] · *p*-xylene (31h)

Mp = 95 °C (dec.). Anal. calc. % (found): C, 48.97 (48.75); H, 2.23 (2.29). IR (ATR, 16 scans, cm^{-1}): 2995 (w), 2974 (w), 2961 (w), 2923 (w), 2872 (w), 1643 (m), 1622 (w), 1613 (w), 1600 (w), 1556 (w), 1512 (s), 1456 (s), 1412 (m), 1380 (m), 1375 (m), 1323 (w), 1270 (m), 1211 (w), 1183 (w), 1145 (w), 1081 (s), 1038 (w), 1030 (w), 995 (m), 974 (s), 924 (m), 904 (m), 861 (m), 821 (m), 802 (s), 773 (s), 755 (s), 725 (m), 703 (w), 682 (s), 659 (s), 622 (m), 610 (m), 602 (m), 573 (m), 553 (w), 544 (w).

[Me3Si·*1,2,3-trimethylbenzene*][B(C_6F_5)$_4$] · 1,2,3-trimethylbenzene (31i)

Mp = 118 °C (dec.). Anal. calc. % ([C_9H_{12}–$SiMe_3$][B(C_6F_5)$_4$] · C_9H_{12}), (found): C, 54.45 (54.25); H, 3.35 (2.61). IR (ATR, 16 scans, cm^{-1}): 3066 (w), 3041 (w), 3013 (w), 2944 (w), 2916 (w), 2871 (w), 2732 (w), 1643 (m), 1606 (w), 1586 (w), 1512 (s), 1456 (s), 1412 (m), 1375 (m), 1328 (w), 1270 (s), 1176 (w), 1082 (s), 1033 (w), 973 (s), 926 (m), 907 (w), 857 (m), 816 (m), 802 (m), 773 (s), 756 (s), 726 (m), 708 (m), 683 (m), 659 (s), 624 (m), 610 (m), 602 (m), 573 (m), 538 (m).

[Me_3Si·*1,2,4-trimethylbenzene*][B(C_6F_5)$_4$] · 1,2,4-trimethylbenzene (31j)

Mp = 115 °C (dec.). Anal. calc. % ([C_9H_{12}–$SiMe_3$][B(C_6F_5)$_4$] · C_9H_{12}), (found): C, 54.45 (53.19); H, 3.35 (2.61). IR (ATR, 16 scans, cm^{-1}): 2962 (w), 2943 (w), 2925 (w), 2873 (w), 2735 (w), 1643 (m), 1620 (w), 1604 (w), 1556 (w), 1512 (s), 1457 (s), 1413 (m), 1375 (m), 1320 (w), 1271 (s), 1259 (m), 1154 (w), 1082 (s), 1030 (w), 974 (s), 924 (w), 908 (w), 872 (m), 853 (m), 815 (s), 773 (s), 756 (s), 726 (m), 695 (w), 683 (s), 660 (m), 622 (m), 610 (m), 602 (m), 573 (m), 540 (m).

[Me_3Si·*1,3,5-trimethylbenzene*][B(C_6F_5)$_4$] · 1,3,5-trimethylbenzene (31k)

Mp = 89 °C (116°C, dec.). Anal. calc. % ([C_9H_{12}–$SiMe_3$][B(C_6F_5)$_4$] · C_9H_{12}) (found): C, 53.34 (53.47); H, 3.14 (2.61). IR (ATR, 16 scans, cm^{-1}): 3011 (w), 2953 (w), 2916 (w), 2862 (w), 1643 (m), 1622 (w), 1600 (m), 1556 (w), 1512 (s), 1457 (s), 1412 (m), 1381 (m), 1374 (m), 1338 (w), 1293 (w), 1272 (m), 1259 (m), 1161 (w), 1153 (w), 1082 (s), 1032 (w), 999 (m), 975 (s), 933 (m), 917 (m), 853 (m), 841 (m), 815 (s), 773 (s), 755 (s), 726 (m), 683 (s), 660 (s), 631 (m), 611 (m), 603 (m), 573 (m), 537 (m).

Attempted synthesis of trimethylsilicenium-*tert.*-butylbenzene tetrakis(pentafluoro-phenyl)borate [Me_3Si–*tert.*-butylbenzene][$B(C_6F_5)_4$].

Procedure 1

To neat bis(trimethylsilyl)hydronium tetrakis(pentafluorophenyl)borate [Me_3Si-H-$SiMe_3$][$B(C_6F_5)_4$] (**30**) (0.413 g, 0.5 mmol), *tert.*-butylbenzene (5mL) was added dropwise at ambient temperatures with stirring, followed by gently heating to 80 °C, until a clear colourless solution and an oiled out layer is obtained. Slow cooling to ambient temperatures over a period of one hour results in the deposition of colourless crystals which could be identified as bis(trimethylsilyl)fluoronium tetrakis(pentafluorophenyl)borate [Me_3Si–F–$SiMe_3$][$B(C_6F_5)_4$] by a xray structure determination[80b]. The supernatant was concentated *in vacuo* and stored at 25°C for 12 hours which results in the deposition of colourless crystals, which could be identified as 1,4-di-*tert.*-butylbenzene by a xray structure determination.

Procedure 2

To neat bis(trimethylsilyl)hydronium tetrakis(pentafluorophenyl)borate [Me_3Si-H-$SiMe_3$][$B(C_6F_5)_4$] (**30**) (0.250.13 g, 0.30mmol), *tert.*-butylbenzene (5mL) was added dropwise at ambient temperatures. After stirring for three hours, a clear colourless solution and a pale-brownish precipitate are obtained. The supernatant is removed by decantation and the residue is washed with *n*-hexane (5mL). The liquid fractions are combined and all volatile compounds are removed *in vaccuo* resulting in a brownish solid surrounded by oil. Column chromatography (silica gel, *n*-heptane) resulted in slightly oily colurless crystalline residue. The residue could be identified as a mixture of 1,3-di-*tert*.-butylbenzene (8.47%), 1,4-di-*tert*.-butylbenzene (64.4%) and 1,3,5-tri-*tert*.-butylbenzene (27.2%) by GCMS. The overall isolated yield is about 5.3% (referring to *tert*.-butylbenzene), or about 560 % (referring to [Me_3Si-H-$SiMe_3$][$B(C_6F_5)_4$]). This corresponds to a TON of about 7.0 in three hours (referring to [Me_3Si-H-$SiMe_3$][$B(C_6F_5)_4$]).

1,4-di-*tert.*-butylbenzene (31l)

^{1}H NMR (300.13 MHz, $CDCl_3$): δ = 1.31 (s, 18H, $C(CH_3)_3$), 7.32 (s, 4H, CH). ^{13}C NMR (62.90 MHz, $CDCl_3$): δ = 31.4 (s, 6C, C(*C*$H_3)_3$), 34.2 (s, 2C, *C*$(CH_3)_3$), 124.9 (4CH), 148.0 (2C). GCMS (EI, m/z > 5 %): 57 (7) $[C_4H_9]^+$, 91 (5) $[C_7H_7]^+$, 145 (7) $[M -3Me]^+$, 160 (11) $[M -2Me]^+$, 175 (100) $[M -Me]^+$, 190 (15) $[M]^+$.

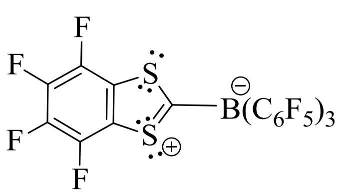
1,3,5-tri-*tert.*-butylbenzene

^{1}H NMR (300.13 MHz, $CDCl_3$): δ = 1.34 (s, 27H, $C(CH_3)_3$), 7.22 (s, 3H, CH). ^{13}CNMR (62.90 MHz, $CDCl_3$) δ = 31.6 (s, 9C, C(*C*$H_3)_3$), 35.0 (s, 3C, *C*$(CH_3)_3$), 119.5 (s, 3C, 3CH), 149.9 (3C). GCMS (EI, m/z > 5 %): 57 (13) $[C_4H_9]^+$, 231 (100) $[M -Me]^+$, 246 (12) $[M]^+$.

Attempted isomerization of *iso*-propylbenzene (cymene) with bis(trimethylsilyl)-hydronium tetrakis(pentafluorophenyl)borate.

To neat bis(trimethylsilyl)hydronium tetrakis(pentafluorophenyl)borate $[Me_3Si\text{-}H\text{-}SiMe_3][B(C_6F_5)_4]$ (**30**) (0.083 g, 0.1 mmol), *iso*-propylbenzene (2mL) was added dropwise at ambient temperatures with stirring, followed by heating to 160 °C. The resulting clear champaign coloured solution is refluxed for 48 hours and is slowly cooled to 5 °C over a period of three hours, resulting in the deposition of colourless needle-like crystals which could be identified as tris(pentafluorophenyl)borane $B(C_6F_5)_3$ by a xray structure determination[144]. The supernatant was washed with aqueous NaOH (0.1M) and dried with $MgSO_4$. A GCMS analysis showed no conversion of the *i*-propylbenzene.

Thermal decomposition of bis(trimethylsilyl)hydronium tetrakis(pentafluorophenyl)borate $[Me_3Si\text{-}H\text{-}SiMe_3][B(C_6F_5)_4]$ (33) in CS_2.



To neat bis(trimethylsilyl)hydronium tetrakis(pentafluorophenyl)borate $[Me_3Si\text{-}H\text{-}SiMe_3][B(C_6F_5)_4]$ (**30**) (0.100 g, 0.1 mmol), carbon disulfide CS_2 (2mL) was added dropwise at ambient temperatures with stirring, followed by heating to 160 °C, resulting in clear yellowish solution and a brownish oil. The mixture is slowly cooled to 5 °C over a period of three hours, resulting in the deposition of colourless needle-like crystals which could be identified as tris(pentafluorophenyl)borane $B(C_6F_5)_3$ by a xray structure determination[144]. The supernatant was filtered, fully concentrated and the remaining yellowish oil was left at 5°C for one week which resulted in colourless crystals of (perfluorobenzo[d][1,3]dithiol-1-ium-2-yl)tris(perfluorophenyl)borate $[(C_6F_4)S_2C\text{-}B(C_6F_5)_3]$ (**33**) and little precipitate of other borates. Again dissolving the crystal in dichloromethane and fully concentrating, after one week at 5°C resulted in a single big crystal.

Synthesis of trimethylsilyldiazomethane $(Me_3Si)CHN_2$.

$$(Me_3Si)CH_2Cl \xrightarrow[Et_2O]{\text{1) 2Li} \quad \text{2) } p\text{-TosN}_3} (Me_3Si)CHN_2 + p\text{-TosNHLi} + LiCl$$

To a stirred suspension of powdered lithium (0.999g, 144mmol) in diethyl ether (50mL), trimethylchloromethylsilane $(Me_3Si)CH_2Cl$ (4.393g, 36.0mmol) was added dropwise by syringe at -23°C. The mixture was stirred for 1.5 hours at this temperature and further 30 minutes at ambient temperature. The grey suspension was filtered (F4) and the resulting colourless solution was added dropwise to a stirred solution of *p*-tosylazide (7.099g, 36.0mmol) in diethyl ether (100mL) at 0°C. The yellowish suspension was stirred for six hours at this temperature and further 16 hours at ambient temperature. After filtration (F4), the resulting bright yellow-green solution was washed with slightly alkaline water and dried over $MgSO_4$. After filtration (F4) the majority of diethyl ether was removed by distillation through a 15 cm vigreux-column in which the heating temperature was never raised above 43°C. After maximum removal of diethyl ether, a NMR spectrum was recorded from which the % yield was calculated as (1.638g, 40%). For complete removal of diethyl ether, *n*-hexane (20mL) was added and the solution was distilled with gradual increase of temperature from 53°C to 63°C within seven hours, until no further diethyl ether was distilling out, resulting in a yellowish solution of trimethylsilyldiazomethane $(Me_3Si)CHN_2$ in *n*-hexane.

^{1}H NMR (250.13 MHz, Et_2O/CD_2Cl_2): 0.14 (s, 9H, $Si(CH_3)_3$), 2.63 (s, 1H, CH). ^{13}C NMR (62.89 MHz, Et_2O/CD_2Cl_2): 0.3 (s, 3C, $Si(CH_3)_3$), 21.2 (CH). $^{29}Si\{^{1}H\}$ NMR (49.69 MHz, Et_2O/CD_2Cl_2): -1.05 (m, $J(^{1}H\text{-}^{29}Si)$ = 6.66Hz, 1.22Hz). GCMS (EI, m/z > 10 %): 43 (100) $[MeN_2$ or $CH_2NNH]^+$, 45 (32) $[MeSiH_2, MeNNH_2]^+$, 53 (15) $[C_2HN_2]^+$, 55 (12) $[C_2H_3N_2]^+$, 58 (80) $[N_2SiH_2]^+$, 59 (33) $[Me_2SiH]^+$, 73 (30) $[Me_3Si]^+$, 99 (65) $[M - Me]^+$, 114 (85) $[M]^+$. HRMS Neg (ESI-TOF): calculated mass for $C_4H_9N_2Si$ is 113.05405, found 113.05422.

Synthesis of bis(trimethylsilyl)diazomethane $(Me_3Si)_2CN_2$ (34a).

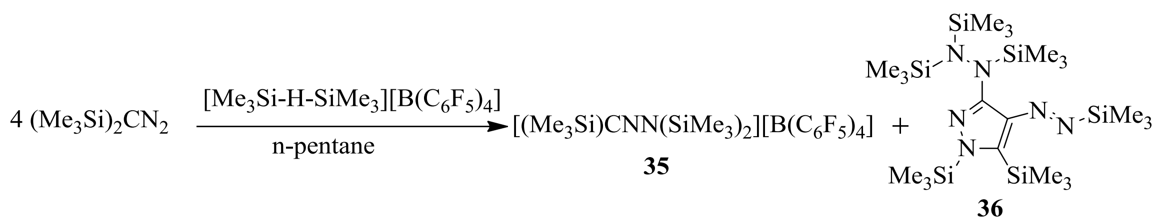
$$(Me_3Si)CHN_2 \xrightarrow[n\text{-hexane}]{\text{1) n-BuLi} \quad \text{2) } Me_3SiCl} \underset{\mathbf{34a}}{(Me_3Si)_2CN_2} + BuH + LiCl$$

To a stirred solution of trimethylsilyldiazomethane $(Me_3Si)CHN_2$ (**34a**) (1.638g, 14.34mmol) in *n*-hexane (20 mL) at -100 °C, nBuLi (2.5M, 14.34mmol) was added dropwise over a period of one hour. The resulting reddish solution was stirred for 15 minutes at this temperature. Trimethylsilyl chloride Me_3SiCl was added dropwise by syringe at -80 °C, resulting in a brownish suspension which was slowly warmed to ambient temperature over 1.5 hours. After further two hours at room temperature, the suspension was filtered (F4) and the solvent was removed *in vacuo*. The resulting red coloured liquid was distilled in high vacuum, and purified by column chromatography on basic Alumina, which yielded 1.524g, (57%) of bis(trimethylsilyl)diazomethane $(Me_3Si)_2CN_2$ (**34a**) as an yellowish liquid.

^{1}H NMR ($CDCl_3$, 300.13 MHz): 0.17 (s, 18H, $Si(CH_3)_3$). ^{13}C NMR (75.47 MHz, $CDCl_3$): -0.33 (s, 6C, $Si(CH_3)_3$), 16.5 (s, CN_2). $^{29}Si\{^{1}H\}$ NMR (59.63 MHz, $CDCl_3$): 1.22 (m, $J(^{1}H\text{-}^{29}Si)$ = 6.60Hz). IR (ATR, 16 scans, cm^{-1}): 3256 (w), 2956 (m), 2900 (w), 2442 (w), 2041 (s), 1510 (w), 1444 (w), 1405 (w), 1250.13 (s), 1225 (s), 1174 (w), 1132 (w), 1029 (w), 971 (m), 926 (s), 834 (s), 819 (s), 755 (s), 712 (w), 689 (m), 637 (m), 622 (m), 565 (m), 536 (m). GCMS (EI, m/z, >10 %): 43 (13) $[MeN_2$ or $CH_2NNH]^+$, 45 (13) $[MeNNH_2, MeSiH_2]^+$, 59 (29) $[Me_2SiH]^+$, 73 (100) $[Me_3Si]^+$, 83 (39) $[C_2H_3N_2Si]^+$, 85

(19) $[C_2H_5N_2Si]^+$, 143 (98) $[C_4H_{11}N_2Si_2]^+$, 144 (17) $[C_4H_{12}N_2Si_{2\ isotopic}]^+$, 171 (13) $[M\text{-}CH_3]^+$, 186 (39) $[M]^+$, 187 (8) $[M_{isotopic}]^+$.

Synthesis of *N*-bis(trimethylsilyl)amino-trimethylsilylisonitrilium tetrakis(pentafluorophenyl)borate $[(Me_3Si)CNN(SiMe_3)_2][B(C_6F_5)_4]$ (35) and 4-(trimethylsilyl)diazenyl-3-[*N*,*N*',*N*'-tris(trimethylsilyl)]hydrazinyl-1*H*-pyrazole (36).



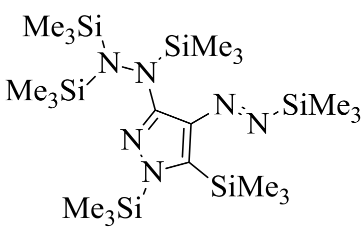
To a stirred suspension of trimethylsilicenium tetrakis(pentafluorophenyl)borate $[Me_3Si][B(C_6F_5)_4]$ (0.053 mmol, 0.040g) in *n*-pentane (2 mL), a solution of bis(trimethylsilyl) diazomethane $(Me_3Si)_2CN_2$ (1.06 mmol, 0.197g) in *n*-pentane (2 mL) was added at -78 °C. The resulting suspension was allowed to warm to ambient temperature. Stirring for 36 hours resulted in the deposition of crystals while the colour of the supernatant changed gradually from yellow to dark red. The supernatant was removed by filtration (F4), and the brownish residue was washed three times with *n*-pentane (3mL). Recrystallization from a minimum of toluene at -25°C resulted in the deposition of colourless crystals. Removal of supernatant by decantation and drying *in vacuo* yielded 0.022g (0.02 mmol, 49% yield based on 0.05 mmol $[Me_3Si\text{-}H\text{-}SiMe_3][B(C_6F_5)_4]$) of *N*,*N*-bis(trimethylsilyl)amino-trimethylsilylisonitrilium tetrakis-(pentafluorophenyl)borate $[(Me_3Si)CNN(SiMe_3)_2][B(C_6F_5)_4]$ (**35**) as colourless crystals.

The solutions from filtration and washing were combined and the solvent was removed *in vacuo*, resulting in a dark red solution. Storage at -5°C for one week, led to the deposition of greenish crystals. Removal of supernatant and drying *in vacuo* yielded 0.097g (0.17 mmol, 51%) of 4-(trimethylsilyl)diazenyl-3-[*N*,*N*',*N*'-tris(trimethylsilyl)]-hydrazinyl-1H-pyrazole (**36**) as dark green crystals.

***N,N*-bis(trimethylsilyl)amino-trimethylsilylisonitrilium tetrakis(pentafluorophenyl)-borate [$(Me_3Si)CNN(SiMe_3)_2$][$B(C_6F_5)_4$] (35).**

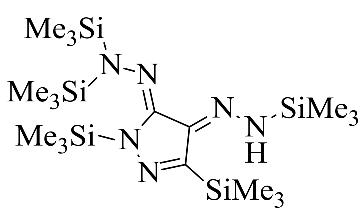
Mp = 109°C. Anal. calc. % (found): C 43.51 (43.75); H 2.90 (2.85); N 2.98 (2.86). IR (ATR, 16 scans, cm^{-1}): 3374 (w), 3224 (w), 2962 (w), 2912 (w), 2327 (w), 2215 (m), 1643 (m), 1600 (w), 1556 (w), 1512 (s), 1460 (s), 1413 (m), 1382 (m), 1374 (m), 1340 (w), 1261 (m), 1167 (m), 1081 (s), 976 (s), 923 (w), 907 (w), 855 (s), 822 (s), 773 (m), 768 (m), 756 (s), 726 (m), 700 (w), 683 (m), 660 (m), 643 (m) 626 (m), 611 (m), 602 (m), 573 (m). Raman (1500 mW, 25 °C, 800 scans, cm^{-1}): = 2970 (4), 2910 (10), 2209 (9), 1643 (3), 1598 (1), 1576 (1), 1536 (1), 1513 (1), 1454 (1), 1417 (1), 1375 (2), 1314 (1), 1276 (1), 1263 (1), 1125 (1), 1106 (1), 976 (1), 960 (1), 945 (1), 862 (1), 845 (1), 820 (3), 771 (1), 757 (1), 733 (1), 700 (1), 685 (1), 661 (1), 643 (5), 628 (5), 584 (7), 509 (2), 491 (5), 476 (4), 448 (6), 422 (4), 394 (5), 371 (1), 359 (1), 348 (1), 320 (1), 287 (1), 265 (1), 244 (1), 206 (1), 186 (2), 157 (1), 119 (1). MS (CI+, *iso*butane): 259 [$(SiMe_3)_3CN_2$]$^+$, 187 [$(SiMe_3)_2CN_2$+H]$^+$.

4-(Trimethylsilyl)diazenyl-3-[*N*,*N*',*N*'-tris(trimethylsilyl)]hydrazinyl-1*H*-pyrazole



(36). Mp = 77 °C. Anal. calc. % (found): C 45.10 (44.45); H 9.73 (9.03); N 15.03 (14.28). ^{1}H NMR (300.13 MHz, CD_2Cl_2): 0.15 (s, 18H, $Si(CH_3)_3$), 0.16 (s, 9H, $Si(CH_3)_3$), 0.28 (s, 9H, $Si(CH_3)_3$), 0.32 (s, 9H, $Si(CH_3)_3$), 0.48 (s, 9H, $Si(CH_3)_3$). ^{13}C NMR (62.89 MHz, CD_2Cl_2): -3.35 (s, 3C, $Si(CH_3)_3$), -0.21 (s, 3C, $Si(CH_3)_3$), 0.08 (s, 6C,($Si(CH_3)_3)_2$), 0.11 (s, 3C, $Si(CH_3)_3$), 0.29 (s, 3C, $Si(CH_3)_3$), 137.29 (C), 146.91(C), 158.15 (C). ^{29}Si{^{1}H} NMR (49.69 MHz, CD_2Cl_2): -13.39 (m,1Si, $J(^1H-^{29}Si)$ = 6.82 Hz), 6.22 (m, 1Si, $J(^1H-^{29}Si)$ = 6.79Hz), 8.94 (m, 2Si, $J(^1H-^{29}Si)$ = 6.65Hz), 11.31 (m, 1Si, $J(^1H-^{29}Si)$ = 6.59Hz), 17.15 (m,1Si, $J(^1H-^{29}Si)$ = 6.71Hz); IR (ATR, 16 scans): 2956 (m), 2899 (m), 2864 (w), 1603 (w), 1574 (w), 1565 (w), 1521 (w), 1510 (w), 1490 (m), 1454 (m), 1388 (m), 1363 (m), 1298 (w), 1279 (m), 1245 (s), 1178 (m), 1142 (w), 1103 (w), 1074 (m), 1022 (w), 1004 (w), 981(w), 939 (m), 875 (m), 832 (s), 822 (s), 753 (s), 726 (m), 890 (m), 632 (m), 621 (m), 561 (w), 532 (m). Raman (1500 mW, 25 °C, 1209 scans, cm^{-1}): 2957 (3), 2903 (10), 1490 (2), 1453 (2), 1388 (7), 1364 (9), 1282 (5), 1245 (1), 1103 (1), 1080 (1), 1006 (1), 964 (2), 946 (1), 878 (1), 838 (1), 748 (1), 726 (1), 693 (3), 610 (3), 535 (1), 472 (1), 454 (1), 407 (1), 376 (1), 351 (1), 340 (1), 308 (1), 256 (1), 204 (1), 182 (1), 114 (1). MS (CI+, *iso*butane): 558 $[M]^+$, 543 $[M-CH_3]^+$, 486 $[M-SiMe_3]^+$. UV-VIS (25 °C, CH_2Cl_2, nm): 556, 393, 321, 255.

(4Z,5Z)-5-[bis(trimethylsilyl)hydrazin-1-ylidene]-1,3-bis(trimethylsilyl)-4-(2-trimethylsilyl)hydrazin-1-ylidene)pyrazole (37).



4-(Trimethylsilyl)diazenyl-3-[*N*,*N'*,*N'*-tris(tri-methylsilyl)]-hydrazinyl-1*H*-pyrazole (**36**) (0.179 mmol, 0.1g) is dissolved in destilled (but not anhydrous) *n*-hexane (3 mL) at ambient temperature with stirring. The resulting orange solution is stirred for 15 minutes. Concentration to an approximate volume of 0.5 mL and storage at 5 °C resulted in the deposition of yellowish crystals. Removal of supernatant and drying *in vacuo* yielded 0.085 g (97%) of (4Z,5Z)-5-[bis(trimethylsilyl)hydrazin-1-ylidene]-1,3-bis(trimethylsily- l)-4-(2-trimethylsilyl)hydrazine-1-ylidene)pyrazole (**37**) as yellow crystals.

According to NMR studies at ambient temperature, in solution an equilibrium between two tautomeres can be observed (assigned **37A** and **37B**). The ratio at 25°C is 62.3% **37A** and 37.7 % **37B**.

^{1}H NMR (25 °C, CD_6Cl_6, 300.13 MHz): **37A**: 0.15 (s, 18H, $Si(CH_3)_3$), 0.27 (s, 9H, $Si(CH_3)_3$), 0.42 (s, 18H, $Si(CH_3)_3$), 0.52 (s, 9H, $Si(CH_3)_3$), 10.16 (s, 1H, NH); **37B**: 0.17 (s, 18H, $Si(CH_3)_3$), 0.28 (s, 9H, $Si(CH_3)_3$), 0.41 (s, 9H, $Si(CH_3)_3$), 0.56(s, 9H, $Si(CH_3)_3$), 12.49 (s, 1H, NH). ^{13}C NMR (25 °C, CD_6Cl_6, 62.89 MHz): **37A**: -2.84 (s, 3C, $Si(CH_3)_3$), -1.84 (s, 3C, $Si(CH_3)_3$), -1.02 (s, 6C, $(Si(CH_3)_3)_2$); **37B**: -2.86 (s, 3C, $Si(CH_3)_3$), -2.44 (s, 3C, $Si(CH_3)_3$), -1.89 (s, 3C, $Si(CH_3)_3$), -0.57 (s, 6C, $(Si(CH_3)_3)_2$); not assigned: 1.68 (s, $Si(CH_3)_3$), 141.1 (C), 156.1 (C), 156.3 (C), 158.5 (C), 160.9 (C); IR (ATR, 16 scans): 2956 (m), 2899 (m), 2855 (w), 1573 (m), 1563 (m), 1520 (m), 1465 (m), 1405 (m), 1345 (w), 1325 (w), 1300 (m), 1245 (s), 1179 (s), 1076 (m), 1050 (m), 982 (m), 961 (m), 930 (m), 898 (m), 870 (m), 828 (s), 818 (s), 753 (s), 693 (m), 662 (m), 628 (s), 601 (m); Raman (1500 mW, 25 °C, 800 scans, cm^{-1}): = 2960 (5), 2900 (10), 1562 (1), 1522 (1), 1466 (4), 1411 (1), 1345 (1), 1300 (1), 1250.13 (1), 1179 (1), 1076 (1), 983 (1), 963 (1), 941 (1), 898 (1), 843 (1), 763 (1), 694 (1), 663 (1), 634 (2), 601 (1), 531 (1), 462 (1), 435 (1), 357 (1), 318 (1), 303 (1), 235 (1), 177 (1), 117 (1). MS (CI+, *iso*butane): 486 $[M]^+$, 471 $[M-CH_3]^+$, 413 $[M-SiMe_3]^+$.

A2. Crystallographic details

	5i	**6p**	**6x**
Chem. Formula	$C_{21}H_{22}FNO_4$	$C_{20}H_{19}FNO_4$	$C_{19}H_{17}F_2NO_4$
Form. Wght. [g mol^{-1}]	371.40	391.81	361.34
Colour	yellow	Colourless	Colourless
Cryst. system	Monoclinic	Monoclinic	Monoclinic
Space group	*P*2/c	*P*2/n	*P*2/c
a [Å]	17.319(5)	21.1169(11)	9.8175(6)
b [Å]	8.507(5)	8.7948(4)	8.9019(5)
c [Å]	12.752(5)	21.9674(11)	20.8901(13)
α [°]	90.00	90.00	90.00
β [°]	100.116(5)	109.408(5)	102.246(1)
γ [°]	90.00	90.00	90.00
V [Å^3]	1849.6(14)	3847.9(3)	1784.14(19)
Z	4	8	4
$\rho_{calc.}$ [g cm^{-3}]	1.334	1.353	1.345
μ [mm^{-1}]	0.099	0.233	0.108
$\lambda_{MoK\alpha}$ [Å]	0.71073	0.71073	0.71073
T [K]	173(2)	173(2)	173(2)
Measured reflections	15937	36097	19596
Independent reflections	4445	9239	5185
Reflections with $I > 2\sigma(I)$	2031	5912	4030
$R_{int.}$	0.1236	0.0424	0.0262
F(000)	784	1632	752
R_1 (R [$F^2 > 2\sigma(F^2)$])	0.061	0.051	0.0422
wR_2 (F^2)	0.125	0.147	0.1181
GooF	0.862	1.052	1.085
Parameters	294	514	255

Crystallographic Details

	8	**11j**	**11k**
Chem. Formula	$C_{10}H_9FO_6$	$C_{22}H_{15}F_3O_4$	$C_{24}H_{15}F_7O_4$
Form. Wght. [g mol^{-1}]	244.17	400.34	500.36
Colour	Colourless	Colourless	Colourless
Cryst. system	Monoclinic	Monoclinic	Orthorhombic
Space group	*C*2/c	*P*2/c	*P*bca
a [Å]	34.95(2)	11.2876(4)	14.6096(7)
b [Å]	5.020(4)	10.5937(4)	10.4889(5)
c [Å]	25.73(2)	15.6094(5)	27.9680(14)
α [°]	90.00	90.00	90.00
β [°]	117.26(4)	101.81(2)	90.00
γ [°]	90.00	90.00	90.00
V [$Å^3$]	4012(5)	1827.01(11)	4285.8(4)
Z	16	4	8
$\rho_{calc.}$ [g cm^{-3}]	1.617	1.455	1.551
μ [mm^{-1}]	0.144	0.120	0.145
$\lambda_{MoK\alpha}$ [Å]	0.71073	0.71073	0.71073
T [K]	173(2)	173(2)	173(2)
Measured reflections	36048	20026	39658
Independent reflections	5800	5289	5640
Reflections with $I > 2\sigma(I)$	3811	4220	4024
$R_{int.}$	0.0467	0.0382	0.0450
F(000)	2016	824	2032
R_1 (R [$F^2 > 2\sigma(F^2)$])	0.0421	0.045	0.0485
wR_2 (F^2)	0.117	0.0130	0.147
GooF	1.012	1.066	1.090
Parameters	327	264	374

Crystallographic Details

	13a	**18b**	**25e**
Chem. Formula	$C_{26}H_{25}FO_5$	$C_{31}H_{23}ClO_4$	$C_{17}H_{16}BrNO_2$
Form. Wght. [g mol^{-1}]	436.46	494.94	346.22
Colour	Colourless	Colourless	Colourless
Cryst. system	Orthorhombic	Monoclinic	Monoclinic
Space group	*P*bca	$P2_1$/c	*P*2/c
a [Å]	10.517(7)	14.293(3)	9.2672(6)
b [Å]	19.433(13)	10.183(2)	17.6014(10)
c [Å]	22.175(16)	17.953(4)	10.3376(7)
α [°]	90.00	90.00	90.00
β [°]	90.00	109.38(3)	116.008(1)
γ [°]	90.00	90.00	90.00
V [Å^3]	4532(5)	2464.9(9)	1515.46(17)
Z	8	4	4
$\rho_{calc.}$ [g cm^{-3}]	1.279	1.334	1.517
μ [mm^{-1}]	0.093	0.191	2.716
$\lambda_{MoK\alpha}$ [Å]	0.71073	0.71073	0.71073
T [K]	173(2)	173(2)	173(2)
Measured reflections	24458	20673	16062
Independent reflections	5430	5547	4339
Reflections with $I > 2\sigma(I)$	3829	4203	3456
$R_{int.}$	0.0485	0.0339	0.0284
F(000)	1840	1032	704
R_1 (R [$F^2 > 2\sigma(F^2)$])	0.0468	0.0512	0.0372
wR_2 (F^2)	0.1389	0.144	0.121
GooF	1.058	1.055	1.070
Parameters	314	327	193

Crystallographic Details

	27a	**27b**	**29a**
Chem. Formula	$C_{15}H_{13}N$	$C_{16}H_{15}N$	$C_{33}H_{33}N$
Form. Wght. [g mol^{-1}]	207.26	221.29	443.60
Colour	Colourless	Colourless	Colourless
Cryst. system	Orthorhombic	Orthorhombic	Orthorhombic
Space group	*P*bca	$P2_12_12_1$	$P2_1$/n
a [Å]	8.1615(4)	9.9040(8)	6.0548(2)
b [Å]	15.7033(7)	17.2477(15)	33.0630(11)
c [Å]	17.0073(8)	7.1529(6)	12.5289(4)
α [°]	90.00	90.00	90.00
β [°]	90.00	90.00	91.42(2)
γ [°]	90.00	90.00	90.00
V [Å^3]	2179.70(18)	1221.87(18)	2507.39(14)
Z	8	4	4
$\rho_{calc.}$ [g cm^{-3}]	1.263	1.203	1.175
μ [mm^{-1}]	0.073	0.073	0.067
$\lambda_{MoK\alpha}$ [Å]	0.71073	0.71073	0.71073
T [K]	173(2)	173(2)	173(2)
Measured reflections	23625	13856	23374
Independent reflections	3175	3547	5724
Reflections with $I > 2\sigma(I)$	2522	3139	4370
$R_{int.}$	0.0327	0.0225	0.0319
F(000)	880	472	9552
R_1 (R [$F^2 > 2\sigma(F^2)$])	0.0416	0.0395	0.0511
wR_2 (F^2)	0.117	0.112	0.144
GooF	1.064	1.053	1.074
Parameters	146	156	333

Crystallographic Details

	29c
Chem. Formula	$C_{33}H_{33}NO_3$
Form. Wght. [g mol^{-1}]	491.60
Colour	Colourless
Cryst. system	Orthorhombic
Space group	$P2_1$/n
a [Å]	13.4397(5)
b [Å]	14.7058(6)
c [Å]	14.1954(6)
α [°]	90.00
β [°]	111.10(2)
γ [°]	90.00
V [Å^3]	2617.41(18)
Z	4
$\rho_{calc.}$ [g cm^{-3}]	1.248
μ [mm^{-1}]	0.079
$\lambda_{MoK\alpha}$ [Å]	0.71073
T [K]	173(2)
Measured reflections	6299
Independent reflections	6299
Reflections with $I > 2\sigma(I)$	4613
$R_{int.}$	0.0295
F(000)	1048
R_1 (R [$F^2 > 2\sigma(F^2)$])	0.0458
wR_2 (F^2)	0.132
GooF	1.101
Parameters	358

Crystallographic Details

	31a1	**31a2**	**31a3**
	benzene	**benzene**	**benzene/fluoronium**
Chem. Formula	$C_{33}H_{15}BF_{20}Si$	$C_{33}H_{15}BF_{20}Si$	$C_{33.79}H_{17.21}BF_{20.24}Si_{1.24}$
Form. Wght. [g mol^{-1}]	830.35	830.35	853.22
Colour	Colourless	Colourless	Colourless
Cryst. system	Monoclinic	Monoclinic	Monoclinic
Space group	*P*2/c	*P*2/c	$P2_1$/c
a [Å]	19.7871(5)	19.7831(8)	9.2012(2)
b [Å]	8.1334(2)	8.1266(3)	44.1297(10)
c [Å]	20.1056(5)	20.0827(9)	16.8661(4)
α [°]	90.00	90.00	90.00
β [°]	95.9430(10)	95.903(2)	97.4720(10)
γ [°]	90.00	90.00	90.00
V [Å^3]	3218.33(14)	3211.6(2)	6790.3(3)
Z	4	4	8
$\rho_{calc.}$ [g cm^{-3}]	1.714	1.717	1.669
μ [mm^{-1}]	0.216	0.216	0.216
$\lambda_{MoK\alpha}$ [Å]	0.71073	0.71073	0.71073
T [K]	173(2)	173(2)	173(2)
Measured reflections	36846	32831	73759
Independent reflections	7775	7013	15492
Reflections with $I > 2\sigma(I)$	4853	4152	8576
$R_{int.}$	0.0432	0.0597	0.0547
F(000)	1648	1648	3395
R_1 (R [$F^2 > 2\sigma(F^2)$])	0.0429	0.0456	0.0613
wR_2 (F^2)	0.1074	0.1167	0.1408
GooF	1.024	0.949	1.047
Parameters	504	504	1120

Crystallographic Details

	31b1	**31b2**	**31c**
	toluene	**toluene/fluoronium**	**ethylbenzene**
Chem. Formula	$C_{34}H_{17}BF_{20}Si$	$C_{33.69}H_{17.08}BF_{20.08}Si_{1.08}$	$C_{43}H_{29}BF_{20}Si$
Form. Wght. [g mol^{-1}]	844.38	844.40	964.56
Colour	Colourless	Colourless	Colourless
Cryst. system	Orthorhombic	Orthorhombic	Monoclinic
Space group	*P*bca	*P*bca	$P2_1$/n
a [Å]	17.0809(11)	17.0523(4)	14.9264(5)
b [Å]	18.9831(12)	18.9850(5)	17.9423(7)
c [Å]	20.8630(14)	20.8924(5)	16.8793(6)
α [°]	90.00	90.00	90.00
β [°]	90.00	90.00	114.239(2)
γ [°]	90.00	90.00	90.00
V [Å^3]	6764.8(8)	6763.7(7)	4122.0(3)
Z	8	8	4
$\rho_{calc.}$ [g cm^{-3}]	1.658	1.658	1.554
μ [mm^{-1}]	0.207	0.210	0.180
$\lambda_{MoK\alpha}$ [Å]	0.71073	0.71073	0.71073
T [K]	173(2)	173(2)	173(2)
Measured reflections	20211	58168	40808
Independent reflections	3151	7754	9302
Reflections with $I > 2\sigma(I)$	2012	5237	5224
$R_{int.}$	0.1167	0.0408	0.0510
F(000)	3360	3360	1944
R_1 (R [$F^2 > 2\sigma(F^2)$])	0.0398	0.0385	0.0473
wR_2 (F^2)	0.0895	0.0960	0.1245
GooF	0.964	1-035	1.003
Parameters	514	553	595

Crystallographic Details

	31d	**31e**	**31f**
	***n*-propylbenzene**	***i*-propylbenzene**	***o*-xylene**
Chem. Formula	$C_{36}H_{21}BF_{20}Si$	$C_{36}H_{21}BF_{20}Si$	$C_{35}H_{19}BF_{20}Si$
Form. Wght. [g mol^{-1}]	872.43	872.43	858.40
Colour	Colourless	Colourless	Colourless
Cryst. system	Monoclinic	Monoclinic	Monoclinic
Space group	$P2_1$/c	$P2_1$/c	$P2_1$/n
a [Å]	22.1413(7)	10.4308(3)	17.2347(6)
b [Å]	16.9067(5)	21.5092(7)	12.7041(4)
c [Å]	18.9409(6)	16.7513(5)	31.2332(10)
α [°]	90.00	90.00	90.00
β [°]	92.1760(10)	106.562(2)	94.0110(10)
γ [°]	90.00	90.00	90.00
V [Å^3]	7085.2(4)	3602.37(19)	6821.8(4)
Z	8	4	8
$\rho_{calc.}$ [g cm^{-3}]	1.636	1.609	1.672
μ [mm^{-1}]	0.200	0.197	0.207
$\lambda_{MoK\alpha}$ [Å]	0.71073	0.71073	0.71073
T [K]	173(2)	173(2)	173(2)
Measured reflections	80226	68458	73754
Independent reflections	17010	10970	14852
Reflections with $I > 2\sigma(I)$	11545	7995	9101
$R_{int.}$	0.0309	0.0270	0.0485
F(000)	3488	1744	3424
R_1 (R [$F^2 > 2\sigma(F^2)$])	0.0408	0.0457	0.0399
wR_2 (F^2)	0.1102	0.1364	0.0999
GooF	1.051	1.094	1.034
Parameters	1061	532	1045

Crystallographic Details

	31g	**31h**	**31i**
	***m*-xylene**	***p*-xylene**	**123-trimethyl**
Chem. Formula	$C_{43}H_{29}BF_{20}Si$	$C_{43}H_{29}BF_{20}Si$	$C_{45}H_{33}BF_{20}Si$
Form. Wght. [g mol^{-1}]	964.56	964.56	992.61
Colour	Colourless	Colourless	Colourless
Cryst. system	Monoclinic	Orthorhombic	Monoclinic
Space group	$P2_1/c$	*P*bca	$P2_1/c$
a [Å]	14.4403(7)	16.6384(11)	14.3401(7)
b [Å]	18.1650(9)	20.3523(11)	19.2559(10)
c [Å]	17.1757(8)	24.3708(15)	16.8610(8)
α [°]	90.00	90.00	90.00
β [°]	114.6820(10)	90.00	113.164(2)
γ [°]	90.00	90.00	90.00
V [Å^3]	4093.7(3)	8252.7(9)	4280.5(4)
Z	4	8	4
$\rho_{calc.}$ [g cm^{-3}]	1.565	1.553	1.540
μ [mm^{-1}]	0.182	0.180	0.176
$\lambda_{MoK\alpha}$ [Å]	0.71073	0.71073	0.71073
T [K]	173(2)	173(2)	173(2)
Measured reflections	47417	27624	35188
Independent reflections	9858	5320	7489
Reflections with $I > 2\sigma(I)$	6311	3208	4257
$R_{int.}$	0.0410	0.0866	0.0628
F(000)	1944	3888	2008
R_1 (R [$F^2 > 2\sigma(F^2)$])	0.0456	0.0510	0.0423
wR_2 (F^2)	0.1183	0.1378	0.1029
GooF	1.064	1.023	0.947
Parameters	597	598	682

Crystallographic Details

	31j	**31k**	**31l**
	124-trimethyl	**135-trimethyl**	**14-ditertbutyl**
Chem. Formula	$C_{45}H_{33}BF_{20}Si$	$C_{42.75}H_{30}BF_{20}Si$	$C_{14}H_{22}$
Form. Wght. [g mol^{-1}]	992.61	962.57	190.32
Colour	Colourless	Colourless	Colourless
Cryst. System	Monoclinic	Triclinic	Monoclinic
Space group	$P2_1$/c	P-1	$P2_1$/n
a [Å]	14.8417(11)	11.3883(3)	6.3310(4)
b [Å]	18.3481(13)	16.9060(5)	10.0315(6)
c [Å]	17.1252(11)	22.5187(6)	9.7425(6)
α [°]	90.00	85.8830(10)	90.00
β [°]	113.424(4)	84.9900(10)	95.923(4)
γ [°]	90.00	72.9010(10)	90.00
V [Å^3]	4279.2(5)	4123.2(2)	615.44(7)
Z	4	4	2
$\rho_{calc.}$ [g cm^{-3}]	1.541	1.551	1.027
μ [mm^{-1}]	0.176	0.180	0.057
$\lambda_{MoK\alpha}$ [Å]	0.71073	0.71073	0.71073
T [K]	173(2)	173(2)	173(2)
Measured reflections	46330	93718	9901
Independent reflections	9335	18887	1950
Reflections with $I > 2\sigma(I)$	4677	12728	1406
$R_{int.}$	0.0618	0.0310	0.0347
F(000)	2008	1942	212
R_1 (R [$F^2 > 2\sigma(F^2)$])	0.0444	0.0517	0.0498
wR_2 (F^2)	0.1069	0.1469	0.1439
GooF	0.903	1.068	1.047
Parameters	724	1270	67

Crystallographic Details

	35	**36**	**37**
Chem. Formula	$C_{10}H_{27}N_2Si_3^{+}\cdot C_{24}BF_{20}^{-}$	$C_{21}H_{54}N_6Si_6$	$C_{18}H_{46}N_6Si_5$
Form. Wght. [g mol^{-1}]	938.66	559.24	487.06
Colour	Colourless	Green	Yellow
Cryst. system	Monoclinic	Triclinic	Triclinic
Space group	$P2_1/c$	P-1	P-1
a [Å]	16.8725(9)	11.9027(6)	10.3442(4)
b [Å]	12. 8944(7)	13.7351(7)	12.3935(4)
c [Å]	19.1131(11)	21.8917(11)	14.0201(5)
α [°]	90.00	84.898(2)	107.678(2)
β [°]	104.297(2)	86.585(2)	90.213(2)
γ [°]	90.00	79.752(2)	112.531(2)
V [Å^3]	4029.5(4)	3504.4(3)	615.44(7)
Z	4	4	2
$\rho_{calc.}$ [g cm^{-3}]	1.547	1.060	1.032
μ [mm^{-1}]	0.24	0.257	0.243
$\lambda_{MoK\alpha}$ [Å]	0.71073	0.71073	0.71073
T [K]	173(2)	173(2)	173(2)
Measured reflections	66871	79279	21027
Independent reflections	14516	17485	5791
Reflections with $I > 2\sigma(I)$	10359	12007	4066
$R_{int.}$	0.0204	0.0463	0.0380
$F(000)$	1888	1224	532
R_1 (R [$F^2 > 2\sigma(F^2)$])	0.0420	0.0485	0.0507
wR_2 (F^2)	0.1216	0.1347	0.1211
GooF	1.080	1.073	1.048
Parameters	550	17485	309

A3. Selected interatomic distances, bond angles and dihedral angles

Numbering scheme of **31a**.

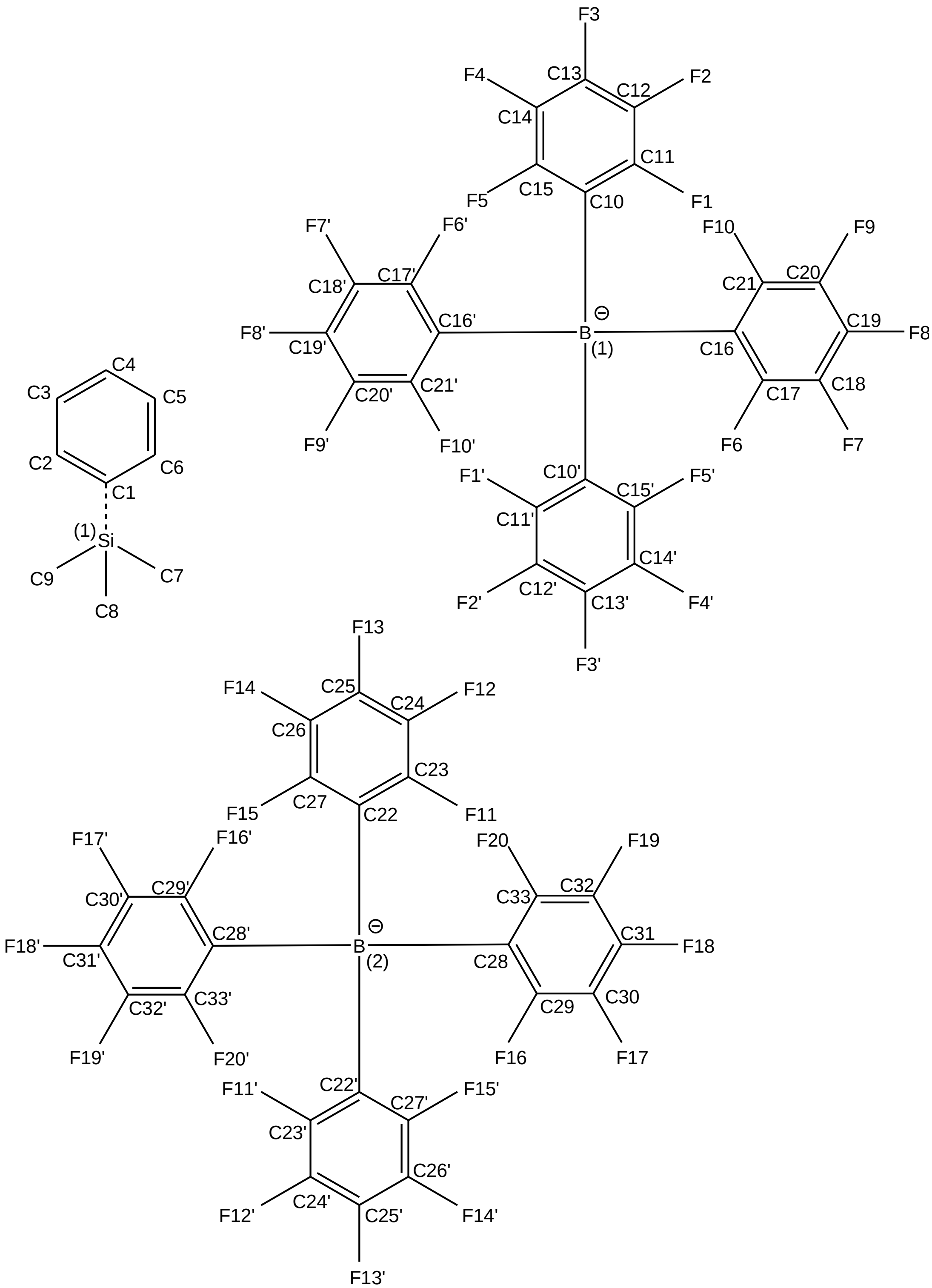


Table A3.1. Selected bond lengths (Å), angles and torsion angles (°) of **31a**.

Si1—C8	1.836 (2)	**C2—C1—H1**	116.7 (13)
Si1—C9	1.839 (2)	**Si1—C1—H1**	93.0 (14)
Si1—C7	1.843 (2)	**C3—C2—C1**	120.19 (19)
Si1—C1	2.174 (2)	**C2—C3—C4**	119.40 (18)
C1—C6	1.408 (3)	**C5—C4—C3**	121.6 (2)
C1—C2	1.411 (3)	**C6—C5—C4**	119.83 (19)
C1—H1	0.94 (2)	**C5—C6—C1**	119.41 (18)
C2—C3	1.361 (3)	**C8—Si1—C1—C6**	−66.33 (15)
C3—C4	1.383 (3)	**C9—Si1—C1—C6**	175.38 (15)
C4—C5	1.381 (3)	**C7—Si1—C1—C6**	53.72 (16)
C5—C6	1.372 (3)	**C8—Si1—C1—C2**	172.16 (14)
C8—Si1—C9	113.79 (12)	**C9—Si1—C1—C2**	53.87 (17)
C8—Si1—C7	113.20 (10)	**C7—Si1—C1—C2**	−67.79 (16)
C9—Si1—C7	114.71 (13)	**C6—C1—C2—C3**	−5.1 (3)
C8—Si1—C1	102.76 (10)	**Si1—C1—C2—C3**	99.56 (19)
C9—Si1—C1	102.52 (10)	**C1—C2—C3—C4**	2.5 (3)
C7—Si1—C1	108.35 (9)	**C2—C3—C4—C5**	0.3 (3)
C6—C1—C2	119.36 (19)	**C3—C4—C5—C6**	−0.6 (3)
C6—C1—Si1	98.46 (14)	**C4—C5—C6—C1**	−2.0 (3)
C2—C1—Si1	98.32 (13)	**C2—C1—C6—C5**	4.8 (3)
C6—C1—H1	120.0 (13)	**Si1—C1—C6—C5**	−99.79 (19)

Numbering scheme of **31a (2)**.

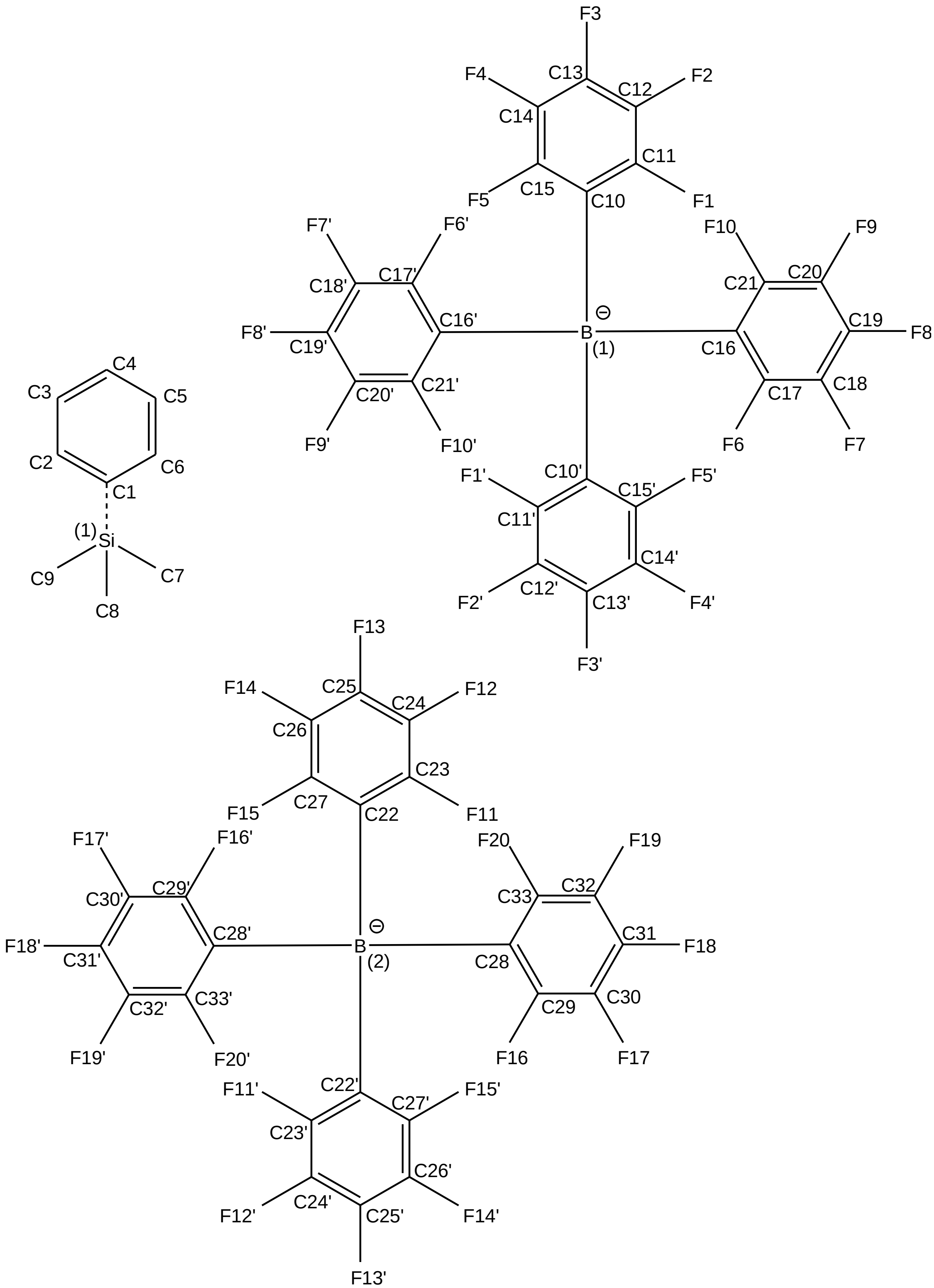


Table A3.2. Selected bond lengths (Å), angles and torsion angles (°) of **31a(2)**.

Si1—C8	1.835 (2)	**C6—C1—H1**	120.2 (16)
Si1—C7	1.839 (3)	**Si1—C1—H1**	92.8 (18)
Si1—C9	1.840 (3)	**C3—C2—C1**	120.3 (2)
Si1—C1	2.169 (3)	**C2—C3—C4**	119.3 (2)
C1—C2	1.407 (3)	**C5—C4—C3**	121.5 (2)
C1—C6	1.409 (3)	**C6—C5—C4**	119.9 (2)
C1—H1	0.91 (3)	**C5—C6—C1**	119.4 (2)
C2—C3	1.366 (3)	**C8—Si1—C1—C2**	172.11 (16)
C3—C4	1.389 (3)	**C7—Si1—C1—C2**	−67.85 (18)
C4—C5	1.380 (3)	**C9—Si1—C1—C2**	53.7 (2)
C5—C6	1.376 (3)	**C8—Si1—C1—C6**	−66.23 (18)
C8—Si1—C7	113.20 (12)	**C7—Si1—C1—C6**	53.81 (19)
C8—Si1—C9	114.03 (13)	**C9—Si1—C1—C6**	175.31 (18)
C7—Si1—C9	114.60 (14)	**C6—C1—C2—C3**	−5.2 (4)
C8—Si1—C1	102.65 (11)	**Si1—C1—C2—C3**	99.7 (2)
C7—Si1—C1	108.46 (11)	**C1—C2—C3—C4**	2.2 (4)
C9—Si1—C1	102.36 (12)	**C2—C3—C4—C5**	1.0 (4)
C2—C1—C6	119.5 (2)	**C3—C4—C5—C6**	−1.2 (4)
C2—C1—Si1	98.32 (16)	**C4—C5—C6—C1**	−1.8 (4)
C6—C1—Si1	98.60 (16)	**C2—C1—C6—C5**	4.9 (4)
C2—C1—H1	116.4 (17)	**Si1—C1—C6—C5**	−99.8 (2)

Numbering scheme of **31a(3)**.

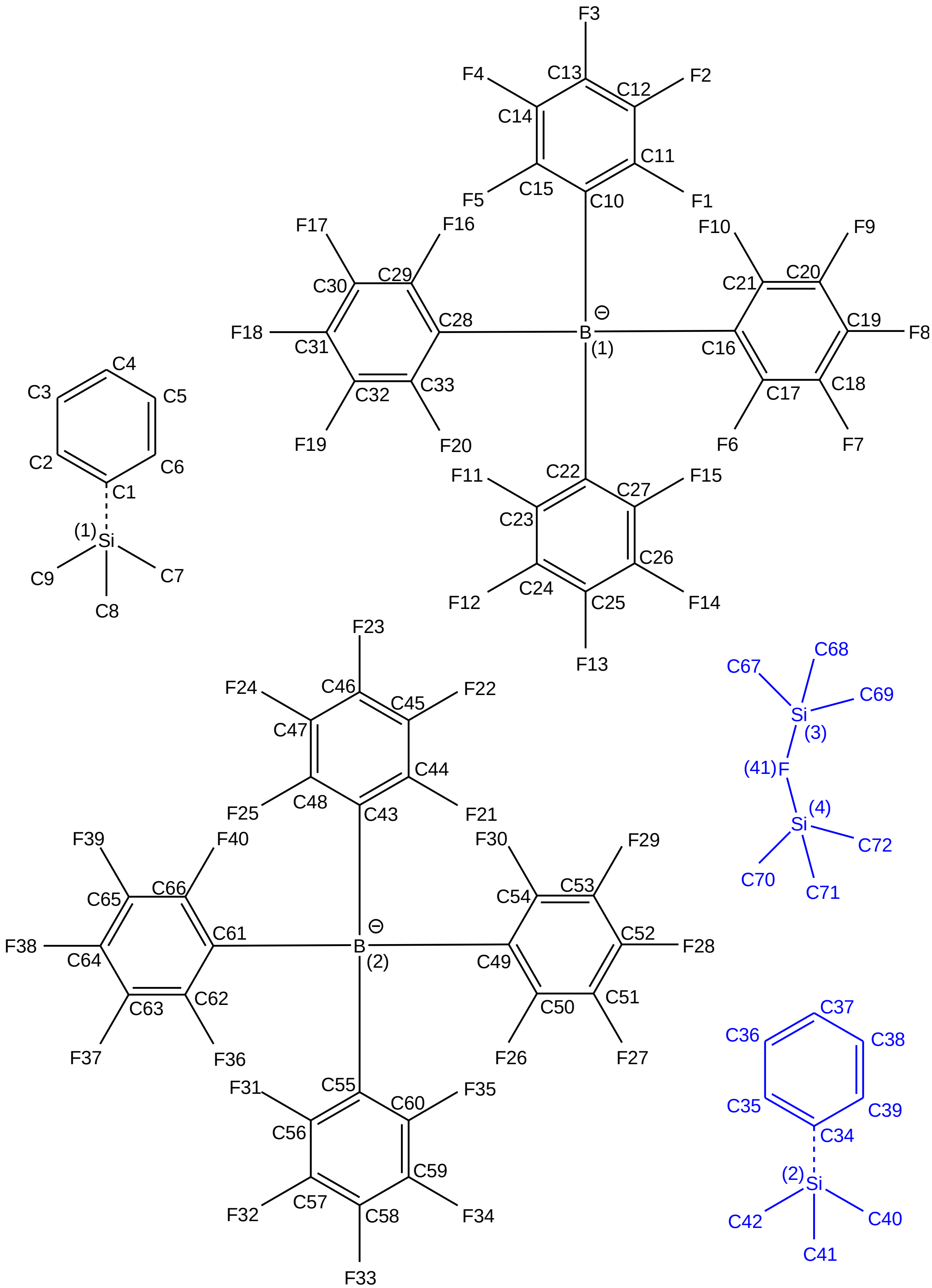


Table A3.3. Selected bond lengths (Å), angles and torsion angles (°) of **31a(3)**.

Si1—C9	1.827 (3)	**C35—C34—H34**	112 (3)
Si1—C7	1.830 (3)	**C39—C34—H34**	125 (4)
Si1—C8	1.842 (3)	**Si2—C34—H34**	93 (3)
Si1—C1	2.183 (4)	**C34—C35—C36**	121.8 (9)
C1—C2	1.383 (6)	**C35—C36—C37**	117.5 (8)
C1—C6	1.422 (6)	**C38—C37—C36**	120.3 (8)
C1—H1	1.03 (5)	**C39—C38—C37**	121.4 (9)
C2—C3	1.370 (5)	**C38—C39—C34**	119.8 (7)
C3—C4	1.370 (5)	**Si4—F41—Si3**	159.0 (6)
C4—C5	1.367 (6)	**F41—Si3—C69**	101.5 (5)
C5—C6	1.361 (6)	**F41—Si3—C67**	102.5 (9)
Si2—C42	1.784 (8)	**C69—Si3—C67**	115.5 (11)
Si2—C41	1.810 (11)	**F41—Si3—C68**	101.4 (5)
Si2—C40	1.838 (8)	**C69—Si3—C68**	114.4 (6)
Si2—C34	2.209 (7)	**C67—Si3—C68**	117.9 (11)
C34—C35	1.373 (13)	**F41—Si4—C71**	101.8 (5)
C34—C39	1.427 (10)	**F41—Si4—C72**	101.3 (7)
C34—H34	1.18 (7)	**C71—Si4—C72**	115.4 (9)
C35—C36	1.393 (12)	**F41—Si4—C70**	102.2 (7)
C36—C37	1.411 (11)	**C71—Si4—C70**	116.1 (6)
C37—C38	1.393 (13)	**C72—Si4—C70**	116.4 (9)
C38—C39	1.334 (12)	**C9—Si1—C1—C2**	59.6 (3)
F41—Si4	1.708 (7)	**C7—Si1—C1—C2**	−63.5 (3)
F41—Si3	1.741 (7)	**C8—Si1—C1—C2**	175.0 (3)
Si3—C69	1.759 (11)	**C9—Si1—C1—C6**	−179.9 (3)
Si3—C67	1.80 (2)	**C7—Si1—C1—C6**	57.0 (3)
Si3—C68	1.810 (14)	**C8—Si1—C1—C6**	−64.5 (3)
Si4—C71	1.747 (11)	**C6—C1—C2—C3**	−4.0 (6)

Si4—C72	1.852 (16)	**Si1—C1—C2—C3**	101.3 (4)
Si4—C70	1.897 (19)	**C1—C2—C3—C4**	1.8 (6)
C9—Si1—C7	115.52 (18)	**C2—C3—C4—C5**	0.1 (6)
C9—Si1—C8	111.87 (16)	**C3—C4—C5—C6**	0.5 (7)
C7—Si1—C8	115.73 (17)	**C4—C5—C6—C1**	−2.8 (7)
C9—Si1—C1	103.23 (17)	**C2—C1—C6—C5**	4.5 (6)
C7—Si1—C1	108.59 (17)	**Si1—C1—C6—C5**	−100.3 (4)
C8—Si1—C1	99.78 (17)	**C42—Si2—C34—C35**	−50.6 (7)
C2—C1—C6	118.2 (4)	**C41—Si2—C34—C35**	−173.9 (8)
C2—C1—Si1	98.4 (3)	**C40—Si2—C34—C35**	70.3 (6)
C6—C1—Si1	99.2 (3)	**C42—Si2—C34—C39**	70.5 (6)
C2—C1—H1	120 (3)	**C41—Si2—C34—C39**	−52.8 (7)
C6—C1—H1	120 (3)	**C40—Si2—C34—C39**	−168.6 (5)
Si1—C1—H1	88 (3)	**C39—C34—C35—C36**	−5.5 (13)
C3—C2—C1	120.8 (4)	**Si2—C34—C35—C36**	99.1 (9)
C4—C3—C2	119.5 (4)	**C34—C35—C36—C37**	4.3 (13)
C5—C4—C3	121.6 (4)	**C35—C36—C37—C38**	−1.4 (12)
C6—C5—C4	119.7 (4)	**C36—C37—C38—C39**	−0.2 (14)
C5—C6—C1	120.1 (4)	**C37—C38—C39—C34**	−0.9 (14)
C42—Si2—C41	114.8 (6)	**C35—C34—C39—C38**	3.8 (12)
C42—Si2—C40	115.6 (4)	**Si2—C34—C39—C38**	−100.5 (8)
C41—Si2—C40	112.7 (5)	**Si4—F41—Si3—C69**	172.8 (14)
C42—Si2—C34	109.8 (4)	**Si4—F41—Si3—C67**	53.2 (18)
C41—Si2—C34	104.1 (5)	**Si4—F41—Si3—C68**	−69.1 (16)
C40—Si2—C34	97.8 (4)	**Si3—F41—Si4—C71**	95.7 (15)
C35—C34—C39	119.0 (8)	**Si3—F41—Si4—C72**	−145.0 (16)
C35—C34—Si2	98.0 (6)	**Si3—F41—Si4—C70**	−24.5 (16)
C39—C34—Si2	98.7 (5)		

(i) −x+2, −y, −z+2.

Numbering scheme of **31b**.

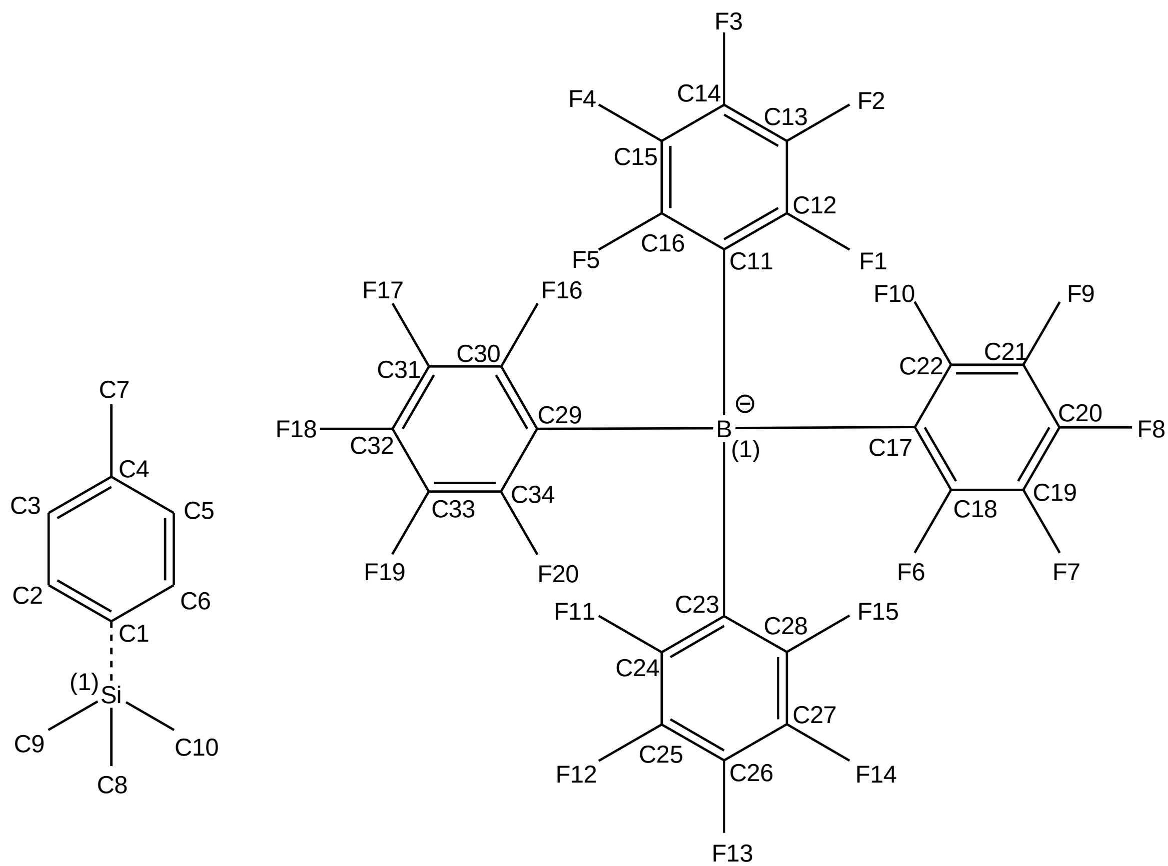


Table A3.4. Selected bond lengths (Å), angles and torsion angles (°) of **31b**.

Si1—C8	1.809 (6)	**C3—C2—C1**	120.5 (6)
Si1—C10	1.839 (5)	**C2—C3—C4**	121.2 (5)
Si1—C9	1.851 (6)	**C3—C4—C5**	119.3 (5)
Si1—C1	2.135 (5)	**C3—C4—C7**	120.8 (5)
C1—C2	1.418 (7)	**C5—C4—C7**	119.9 (6)
C1—C6	1.418 (7)	**C6—C5—C4**	120.7 (5)
C1—H1	1.05 (6)	**C5—C6—C1**	120.6 (5)
C2—C3	1.357 (7)	**C8—Si1—C1—C2**	−61.1 (5)
C3—C4	1.384 (7)	**C10—Si1—C1—**	59.5 (5)
C4—C5	1.394 (7)	**C9—Si1—C1—C2**	175.6 (4)
C4—C7	1.503 (7)	**C8—Si1—C1—C6**	59.4 (4)
C5—C6	1.359 (7)	**C10—Si1—C1—**	179.9 (4)
C8—Si1—C10	113.2 (3)	**C9—Si1—C1—C6**	−64.0 (4)
C8—Si1—C9	116.2 (3)	**C6—C1—C2—C3**	−5.5 (8)
C10—Si1—C9	111.6 (3)	**Si1—C1—C2—C3**	101.1 (5)
C8—Si1—C1	108.5 (3)	**C1—C2—C3—C4**	3.1 (8)
C10—Si1—C1	103.6 (2)	**C2—C3—C4—C5**	−1.0 (8)
C9—Si1—C1	102.2 (3)	**C2—C3—C4—C7**	177.0 (5)
C2—C1—C6	117.5 (6)	**C3—C4—C5—C6**	1.4 (8)
C2—C1—Si1	100.3 (3)	**C7—C4—C5—C6**	−176.5 (5)
C6—C1—Si1	99.6 (4)	**C4—C5—C6—C1**	−4.1 (8)
C2—C1—H1	118 (3)	**C2—C1—C6—C5**	6.0 (8)
C6—C1—H1	120 (3)	**Si1—C1—C6—C5**	−101.0 (5)
Si1—C1—H1	92 (3)		

Numbering scheme of **31b (2)**.

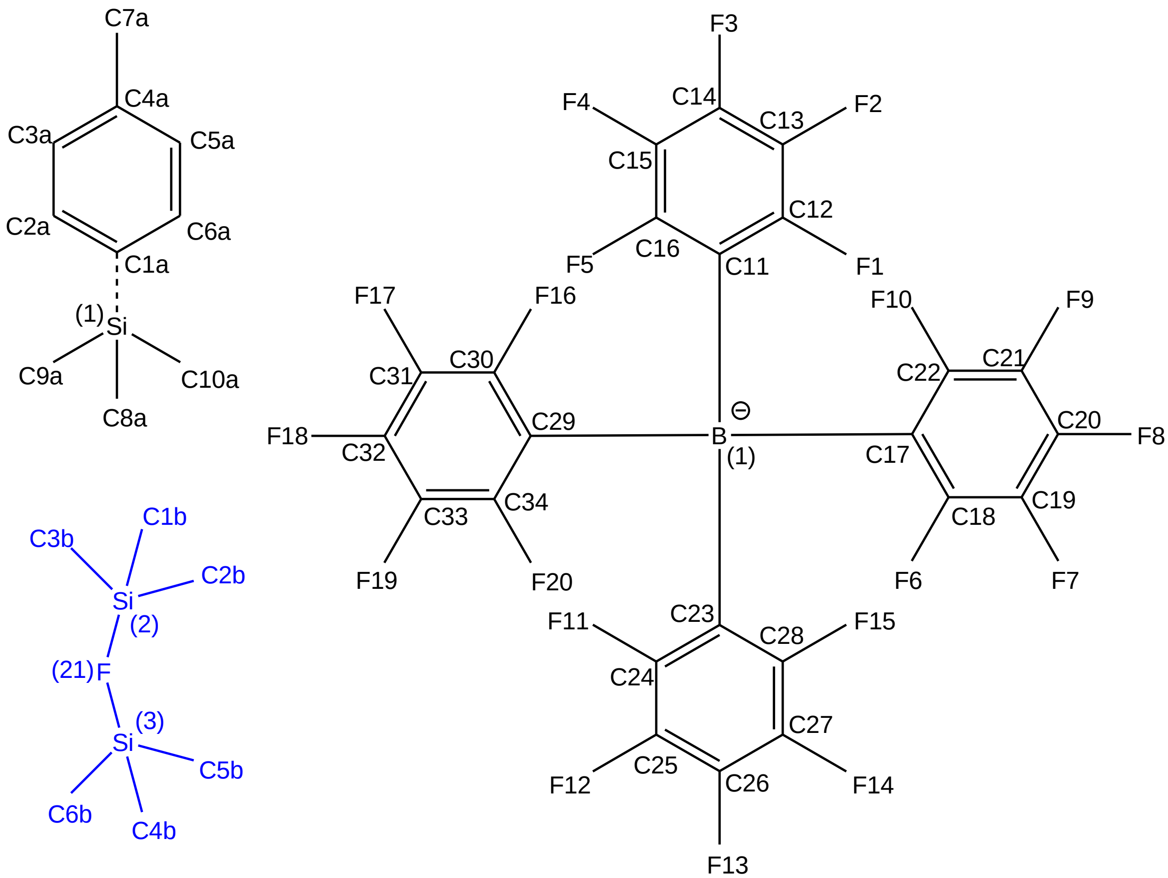


Table A3.5. Selected bond lengths (Å), angles and torsion angles (°) of **31b (2)**.

C1A—C6A	1.402 (3)	**C9A—Si1—C1A**	104.06 (10)
C1A—C2A	1.405 (3)	**C10A—Si1—C1A**	102.50 (13)
C1A—Si1	2.120 (2)	**Si3—F21—Si2**	158 (2)
C1A—H1A	0.95 (2)	**F21—Si2—C1B**	105.5 (17)
C2A—C3A	1.373 (3)	**F21—Si2—C2B**	101.6 (13)
C3A—C4A	1.396 (3)	**C1B—Si2—C2B**	114.2 (12)
C4A—C5A	1.394 (3)	**F21—Si2—C3B**	97.5 (15)
C4A—C7A	1.497 (3)	**C1B—Si2—C3B**	117.2 (14)

C5A—C6A	1.368 (3)	**C2B—Si2—C3B**	116.9 (13)
Si1—C8A	1.834 (3)	**F21—Si3—C4B**	95.6 (16)
Si1—C9A	1.843 (3)	**F21—Si3—C5B**	106.7 (15)
Si1—C10A	1.852 (3)	**C4B—Si3—C5B**	121.4 (19)
F21—Si3	1.73 (2)	**F21—Si3—C6B**	103.4 (16)
F21—Si2	1.73 (2)	**C4B—Si3—C6B**	115 (2)
Si2—C1B	1.814 (17)	**C5B—Si3—C6B**	111.6 (19)
Si2—C2B	1.822 (15)	**C6A—C1A—C2A—C3A**	−5.5 (3)
Si2—C3B	1.826 (17)	**Si1—C1A—C2A—C3A**	102.6 (2)
Si3—C4B	1.88 (2)	**C1A—C2A—C3A—C4A**	3.0 (3)
Si3—C5B	1.90 (2)	**C2A—C3A—C4A—C5A**	−0.3 (3)
Si3—C6B	1.90 (2)	**C2A—C3A—C4A—C7A**	177.4 (2)
C6A—C1A—C2A	118.77 (19)	**C3A—C4A—C5A—C6A**	0.2 (3)
C6A—C1A—Si1	101.00 (14)	**C7A—C4A—C5A—C6A**	−177.6 (2)
C2A—C1A—Si1	99.29 (15)	**C4A—C5A—C6A—C1A**	−2.8 (3)
C6A—C1A—H1A	119.7 (14)	**C2A—C1A—C6A—C5A**	5.4 (3)
C2A—C1A—H1A	118.0 (15)	**Si1—C1A—C6A—C5A**	−101.74 (19)
Si1—C1A—H1A	88.3 (14)	**C6A—C1A—Si1—C8A**	61.88 (18)
C3A—C2A—C1A	120.3 (2)	**C2A—C1A—Si1—C8A**	−60.03 (19)
C2A—C3A—C4A	120.6 (2)	**C6A—C1A—Si1—C9A**	−58.93 (18)
C5A—C4A—C3A	118.8 (2)	**C2A—C1A—Si1—C9A**	179.16 (18)
C5A—C4A—C7A	120.4 (2)	**C6A—C1A—Si1—C10A**	−174.53 (15)
C3A—C4A—C7A	120.7 (2)	**C2A—C1A—Si1—C10A**	63.56 (17)
C6A—C5A—C4A	121.2 (2)	**Si3—F21—Si2—C1B**	−176 (5)
C5A—C6A—C1A	120.14 (19)	**Si3—F21—Si2—C2B**	−56 (5)
C8A—Si1—C9A	113.36 (17)	**Si3—F21—Si2—C3B**	63 (5)
C8A—Si1—C10A	116.48 (16)	**Si2—F21—Si3—C4B**	148 (5)
C9A—Si1—C10A	110.90 (14)	**Si2—F21—Si3—C5B**	−87 (5)
C8A—Si1—C1A	108.14 (11)	**Si2—F21—Si3—C6B**	31 (6)

Numbering scheme of 31**c**.

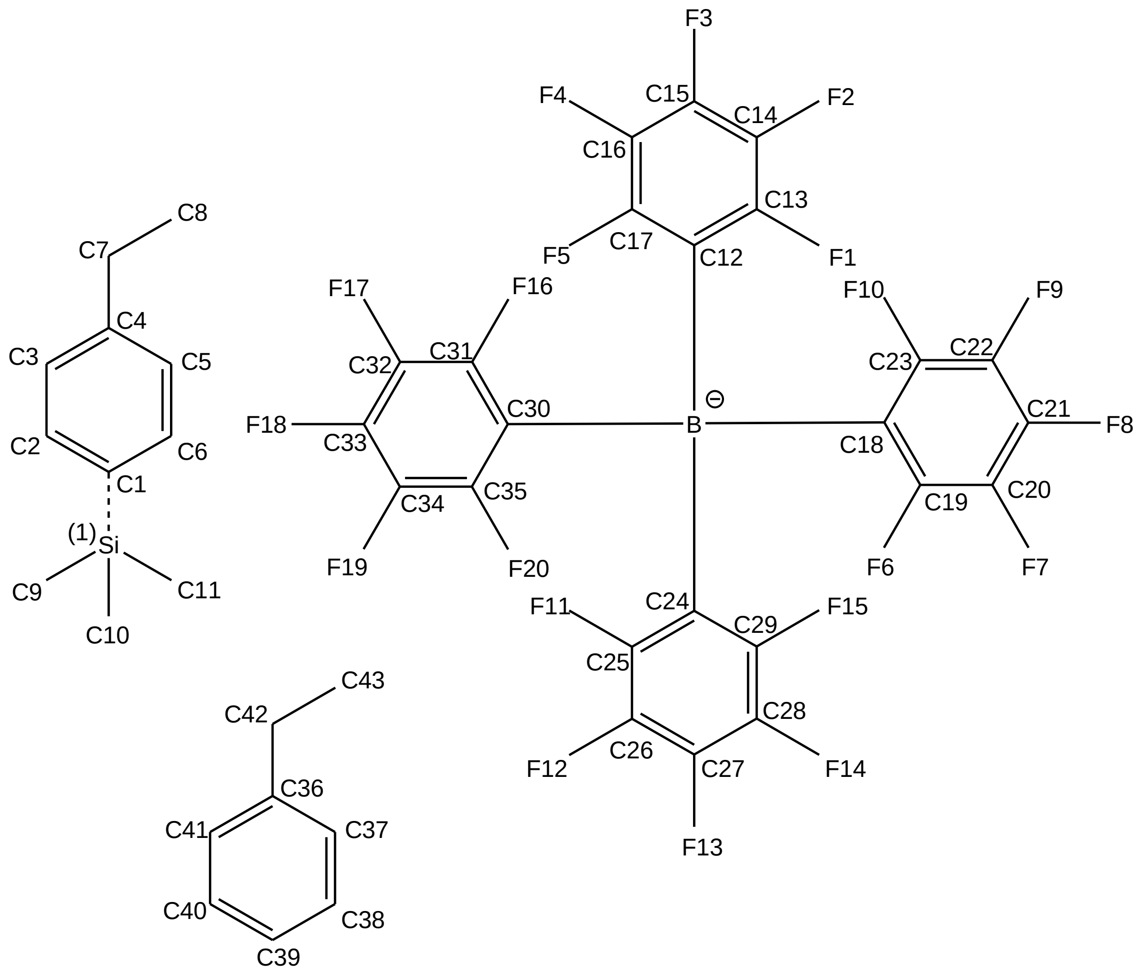


Table A3.6. Selected bond lengths (Å), angles and torsion angles (°) of **31c**.

Si1—C9	1.834 (3)	**C5—C6—C1**	119.6 (3)
Si1—C11	1.838 (3)	**C8—C7—C4**	111.8 (3)
Si1—C10	1.842 (3)	**C37—C36—C41**	118.2 (3)
Si1—C1	2.140 (3)	**C37—C36—C42**	120.9 (4)
C1—C6	1.416 (4)	**C41—C36—C42**	120.9 (4)
C1—C2	1.418 (4)	**C36—C37—C38**	120.5 (3)
C1—H1	1.00 (3)	**C39—C38—C37**	120.3 (4)
C2—C3	1.372 (4)	**C40—C39—C38**	119.3 (4)
C3—C4	1.384 (4)	**C39—C40—C41**	121.0 (4)

C4—C5	1.393 (4)	**C40—C41—C36**	120.5 (3)
C4—C7	1.492 (4)	**C43—C42—C36**	114.8 (3)
C5—C6	1.373 (4)	**C9—Si1—C1—C6**	61.7 (2)
C7—C8	1.484 (5)	**C11—Si1—C1—C6**	−60.5 (2)
C36—C37	1.363 (5)	**C10—Si1—C1—C6**	−177.0 (2)
C36—C41	1.375 (4)	**C9—Si1—C1—C2**	−59.4 (2)
C36—C42	1.519 (5)	**C11—Si1—C1—C2**	178.5 (2)
C37—C38	1.393 (5)	**C10—Si1—C1—C2**	61.9 (2)
C38—C39	1.352 (5)	**C6—C1—C2—C3**	−6.6 (4)
C39—C40	1.350 (6)	**Si1—C1—C2—C3**	99.1 (3)
C40—C41	1.373 (5)	**C1—C2—C3—C4**	2.9 (4)
C42—C43	1.436 (6)	**C2—C3—C4—C5**	0.7 (4)
C9—Si1—C11	114.96 (14)	**C2—C3—C4—C7**	−178.9 (3)
C9—Si1—C10	114.20 (16)	**C3—C4—C5—C6**	−0.4 (4)
C11—Si1—C10	112.36 (15)	**C7—C4—C5—C6**	179.2 (3)
C9—Si1—C1	109.07 (13)	**C4—C5—C6—C1**	−3.5 (4)
C11—Si1—C1	102.33 (16)	**C2—C1—C6—C5**	6.9 (4)
C10—Si1—C1	102.35 (14)	**Si1—C1—C6—C5**	−99.5 (3)
C6—C1—C2	118.4 (3)	**C3—C4—C7—C8**	98.0 (4)
C6—C1—Si1	98.75 (19)	**C5—C4—C7—C8**	−81.7 (4)
C2—C1—Si1	100.0 (2)	**C41—C36—C37—C38**	0.7 (5)
C6—C1—H1	113.8 (16)	**C42—C36—C37—C38**	−179.8 (3)
C2—C1—H1	120.1 (16)	**C36—C37—C38—C39**	−0.4 (5)
Si1—C1—H1	99.2 (2)	**C37—C38—C39—C40**	−0.6 (6)
C3—C2—C1	120.2 (3)	**C38—C39—C40—C41**	1.5 (6)
C2—C3—C4	120.7 (3)	**C39—C40—C41—C36**	−1.2 (5)
C3—C4—C5	119.6 (3)	**C37—C36—C41—C40**	0.2 (5)
C3—C4—C7	120.7 (3)	**C42—C36—C41—C40**	−179.4 (3)
C5—C4—C7	119.7 (3)	**C37—C36—C42—C43**	85.2 (6)
C6—C5—C4	121.1 (3)	**C41—C36—C42—C43**	−95.3 (5)

Numbering scheme of **31d**.

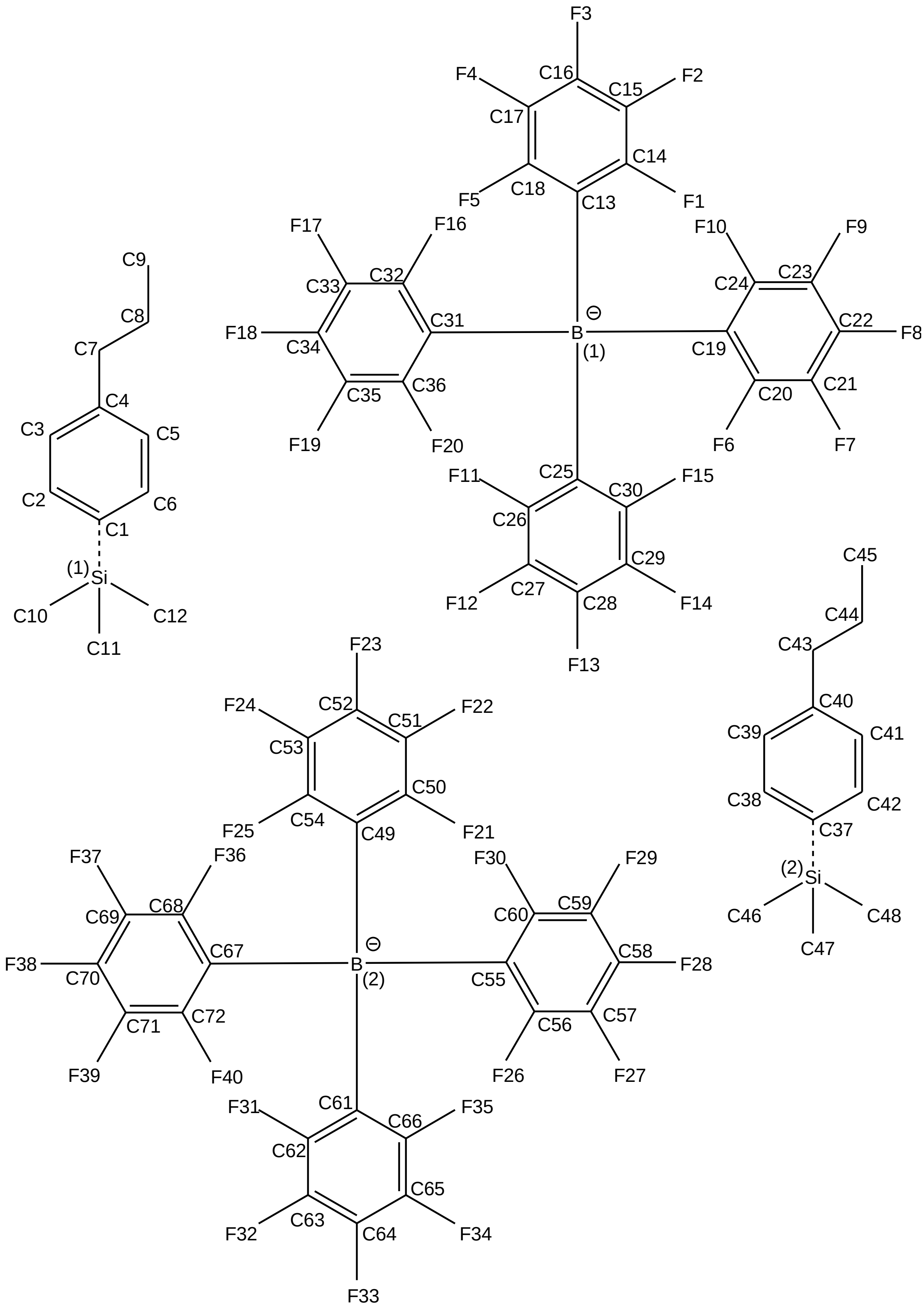


Table A3.7. Selected bond lengths (Å), angles and torsion angles (°) of **31d**.

Si1—C11	1.836 (2)	**C48—Si2—C37**	103.18 (10)
Si1—C12	1.838 (2)	**C42—C37—C38**	117.93 (19)
Si1—C10	1.839 (2)	**C42—C37—Si2**	100.79 (13)
Si1—C1	2.137 (2)	**C38—C37—Si2**	98.34 (13)
C1—C6	1.409 (3)	**C42—C37—H37**	119.6 (13)
C1—C2	1.411 (3)	**C38—C37—H37**	118.7 (1)
C1—H1	0.97 (2)	**Si2—C37—H37**	90.3 (12)
C2—C3	1.372 (3)	**C39—C38—C37**	120.11 (18)
C3—C4	1.397 (3)	**C38—C39—C40**	121.35 (18)
C4—C5	1.400 (3)	**C41—C40—C39**	118.77 (19)
C4—C7	1.498 (3)	**C41—C40—C43**	120.7 (2)
C5—C6	1.371 (3)	**C39—C40—C43**	120.5 (2)
C7—C8	1.518 (3)	**C42—C41—C40**	120.92 (19)
C8—C9	1.514 (3)	**C41—C42—C37**	120.56 (18)
Si2—C47	1.829 (2)	**C40—C43—C44**	113.5 (2)
Si2—C46	1.838 (2)	**C43—C44—C45**	115.6 (2)
Si2—C48	1.846 (2)	**C11—Si1—C1—C6**	−62.83 (16)
Si2—C37	2.139 (2)	**C12—Si1—C1—C6**	179.60 (15)
C37—C42	1.409 (3)	**C10—Si1—C1—C6**	58.14 (16)
C37—C38	1.413 (3)	**C11—Si1—C1—C2**	176.13 (15)
C37—H37	0.92 (2)	**C12—Si1—C1—C2**	58.56 (16)
C38—C39	1.362 (3)	**C10—Si1—C1—C2**	−62.91 (17)
C39—C40	1.393 (3)	**C6—C1—C2—C3**	−6.6 (3)
C40—C41	1.388 (3)	**Si1—C1—C2—C3**	99.90 (18)
C40—C43	1.495 (3)	**C1—C2—C3—C4**	2.3 (3)
C41—C42	1.367 (3)	**C2—C3—C4—C5**	2.0 (3)

C43—C44	1.497 (3)	**C2—C3—C4—C7**	−177.59 (17)
C44—C45	1.501 (3)	**C3—C4—C5—C6**	−1.9 (3)
C11—Si1—C12	112.94 (13)	**C7—C4—C5—C6**	177.65 (17)
C11—Si1—C10	113.49 (12)	**C4—C5—C6—C1**	−2.5 (3)
C12—Si1—C10	114.44 (13)	**C2—C1—C6—C5**	6.7 (3)
C11—Si1—C1	103.46 (10)	**Si1—C1—C6—C5**	−99.81 (17)
C12—Si1—C1	102.35 (9)	**C3—C4—C7—C8**	116.2 (2)
C10—Si1—C1	108.81 (9)	**C5—C4—C7—C8**	−63.3 (2)
C6—C1—C2	118.25 (19)	**C4—C7—C8—C9**	−179.42 (19)
C6—C1—Si1	99.64 (12)	**C47—Si2—C37—C42**	−57.10 (17)
C2—C1—Si1	99.61 (12)	**C46—Si2—C37—C42**	63.61 (17)
C6—C1—H1	120.8 (12)	**C48—Si2—C37—C42**	−175.36 (15)
C2—C1—H1	117.6 (12)	**C47—Si2—C37—C38**	−177.75 (15)
Si1—C1—H1	89.1 (12)	**C46—Si2—C37—C38**	−57.05 (16)
C3—C2—C1	120.35 (18)	**C48—Si2—C37—C38**	63.99 (16)
C2—C3—C4	120.89 (17)	**C42—C37—C38—C39**	−7.1(3)
C3—C4—C5	118.85 (18)	**Si2—C37—C38—C39**	99.82 (19)
C3—C4—C7	121.39 (17)	**C37—C38—C39—C40**	4.0 (3)
C5—C4—C7	119.76 (17)	**C38—C39—C40—C41**	0.5 (3)
C6—C5—C4	120.73 (18)	**C38—C39—C40—C43**	−177.7 (2)
C5—C6—C1	120.56 (17)	**C39—C40—C41—C42**	−1.7 (3)
C4—C7—C8	112.71 (16)	**C43—C40—C41—C42**	176.5 (2)
C9—C8—C7	113.2 (2)	**C40—C41—C42—C37**	−1.6 (3)
C47—Si2—C46	113.08 (12)	**C38—C37—C42—C41**	6.0 (3)
C47—Si2—C48	112.85 (12)	**Si2—C37—C42—C41**	−99.59 (19)
C46—Si2—C48	114.04 (12)	**C41—C40—C43—C44**	−71.9 (3)
C47—Si2—C37	104.67 (10)	**C39—C40—C43—C44**	106.3 (3)
C46—Si2—C37	107.92 (9)	**C40—C43—C44—C45**	−173.0 (2)

Numbering scheme of **31e**.

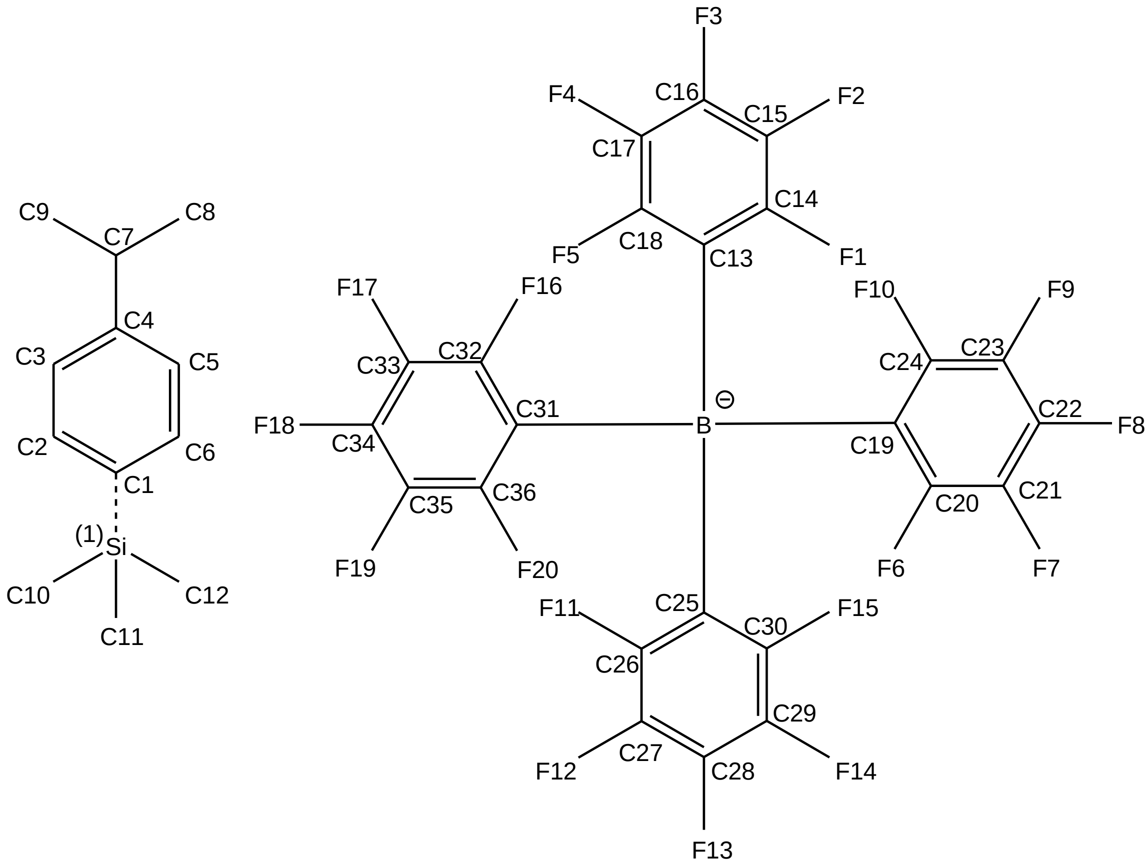


Table A3.8. Selected bond lengths (Å), angles and torsion angles (°) of **31e.**

Si1—C10	1.835 (2)	**C2—C3—C4**	120.51 (16)
Si1—C12	1.836 (2)	**C5—C4—C3**	119.23 (16)
Si1—C11	1.837 (2)	**C5—C4—C7**	119.35 (16)
Si1—C1	2.1687 (19)	**C3—C4—C7**	121.39 (16)
C1—C2	1.408 (2)	**C6—C5—C4**	120.80 (17)
C1—C6	1.409 (3)	**C5—C6—C1**	120.28 (17)
C1—H1	0.94 (3)	**C4—C7—C9**	113.40 (18)
C2—C3	1.374 (2)	**C4—C7—C8**	109.41 (16)
C2—H2	0.9500	**C9—C7—C8**	111.1 (2)

C3—C4	1.397 (2)	**C10—Si1—C1—C2**	−54.73 (15)
C3—H3	0.9500	**C12—Si1—C1—C2**	67.75 (14)
C4—C5	1.393 (3)	**C11—Si1—C1—C2**	−175.56 (13)
C4—C7	1.512 (3)	**C10—Si1—C1—C6**	65.82 (15)
C5—C6	1.370 (3)	**C12—Si1—C1—C6**	−171.70 (14)
C7—C9	1.518 (3)	**C11—Si1—C1—C6**	−55.01 (14)
C7—C8	1.524 (3)	**C6—C1—C2—C3**	−6.4 (3)
C10—Si1—C12	115.99 (12)	**Si1—C1—C2—C3**	97.89 (15)
C10—Si1—C11	113.44 (12)	**C1—C2—C3—C4**	2.4 (2)
C12—Si1—C11	112.62 (11)	**C2—C3—C4—C5**	1.8 (3)
C10—Si1—C1	108.70 (8)	**C2—C3—C4—C7**	−176.19 (16)
C12—Si1—C1	100.99 (9)	**C3—C4—C5—C6**	−1.9 (3)
C11—Si1—C1	103.42 (11)	**C7—C4—C5—C6**	176.16 (19)
C2—C1—C6	118.49 (16)	**C4—C5—C6—C1**	−2.2 (3)
C2—C1—Si1	98.16 (11)	**C2—C1—C6—C5**	6.3 (3)
C6—C1—Si1	98.42 (13)	**Si1—C1—C6—C5**	−97.8 (2)
C2—C1—H1	120.6 (16)	**C5—C4—C7—C9**	132.6 (2)
C6—C1—H1	116.7 (16)	**C3—C4—C7—C9**	−49.4 (3)
Si1—C1—H1	94.1 (16)	**C5—C4—C7—C8**	−102.7 (2)
C3—C2—C1	120.36 (15)	**C3—C4—C7—C8**	75.2 (2)

Numbering scheme of **31f**.

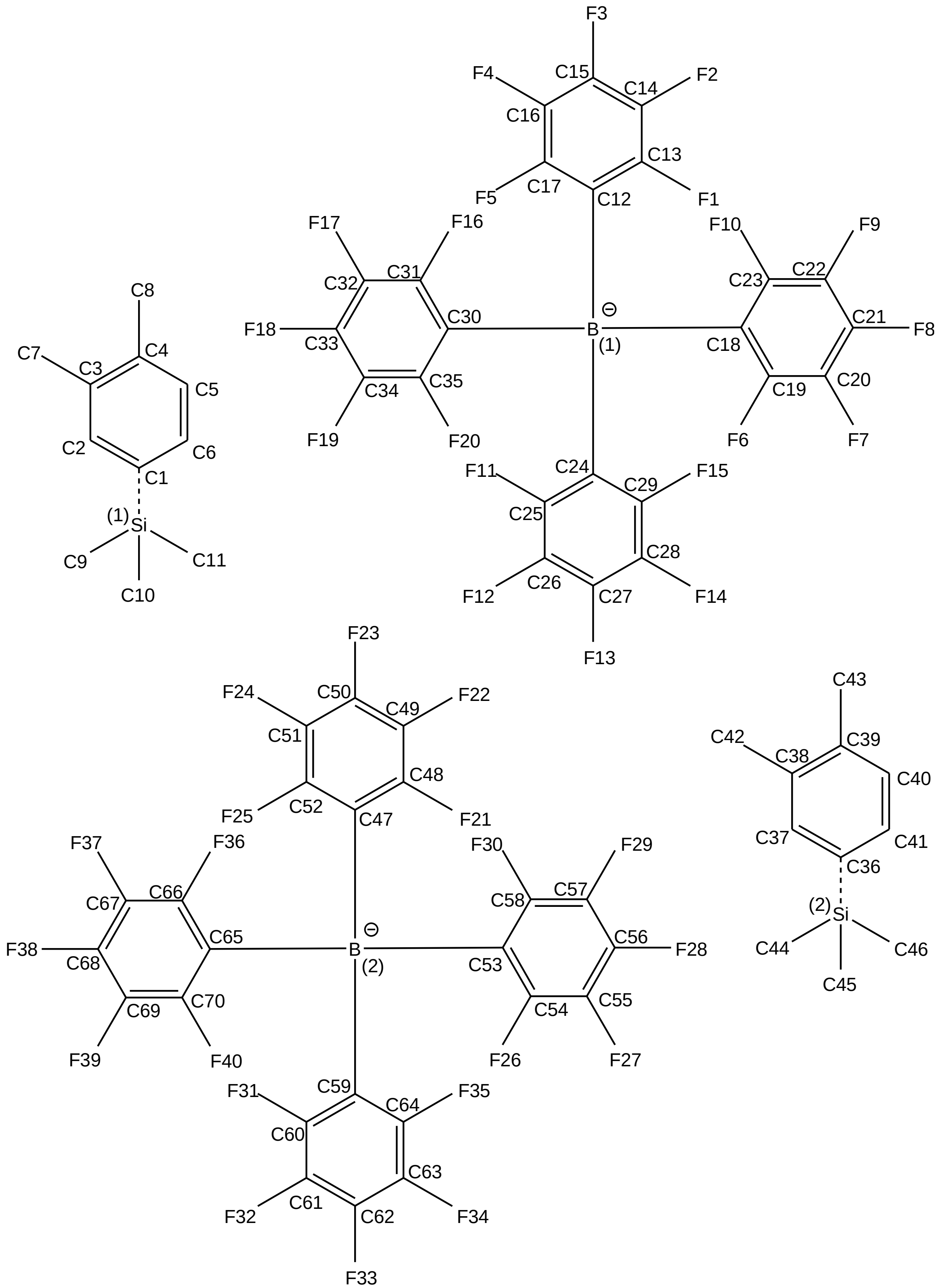


Table A3.9. Selected bond lengths (Å), angles and torsion angles (°) of **31f**.

Si1—C9	1.824 (2)	**C45—Si2—C36**	102.00 (10)
Si1—C11	1.836 (3)	**C37—C36—C41**	117.9 (2)
Si1—C10	1.849 (3)	**C37—C36—Si2**	99.98 (14)
Si1—C1	2.137 (3)	**C41—C36—Si2**	99.95 (13)
C1—C6	1.414 (3)	**C37—C36—H36**	118.7 (12)
C1—C2	1.424 (3)	**C41—C36—H36**	118.1 (13)
C1—H1	0.98 (2)	**Si2—C36—H36**	93.1 (12)
C2—C3	1.364 (3)	**C38—C37—C36**	122.6 (2)
C2—H2	0.9500	**C37—C38—C39**	118.2 (2)
C3—C4	1.409 (3)	**C37—C38—C42**	120.78 (19)
C3—C7	1.505 (3)	**C39—C38—C42**	121.0 (2)
C4—C5	1.395 (3)	**C40—C39—C38**	120.1 (2)
C4—C8	1.499 (3)	**C40—C39—C43**	119.9 (2)
C5—C6	1.368 (3)	**C38—C39—C43**	120.0 (2)
Si2—C44	1.835 (2)	**C41—C40—C39**	121.1 (2)
Si2—C46	1.837 (2)	**C40—C41—C36**	119.9 (2)
Si2—C45	1.844 (2)	**C9—Si1—C1—C6**	−55.3 (2)
Si2—C36	2.139 (2)	**C11—Si1—C1—C6**	−176.38 (18)
C36—C37	1.412 (3)	**C10—Si1—C1—C6**	65.9 (2)
C36—C41	1.414 (3)	**C9—Si1—C1—C2**	66.03 (2)
C36—H36	0.95 (2)	**C11—Si1—C1—C2**	−55.1 (2)
C37—C38	1.374 (3)	**C10—Si1—C1—C2**	−172.83 (18)
C37—H37	0.9500	**C6—C1—C2—C3**	4.2 (3)
C38—C39	1.407 (3)	**Si1—C1—C2—C3**	−102.9 (2)
C38—C42	1.508 (3)	**C1—C2—C3—C4**	−1.1 (3)
C39—C40	1.404 (3)	**C1—C2—C3—C7**	−179.2 (2)

C39—C43	1.499 (3)	**C2—C3—C4—C5**	0.0 (3)
C40—C41	1.371 (3)	**C7—C3—C4—C5**	178.1 (2)
C9—Si1—C11	113.99 (11)	**C2—C3—C4—C8**	−179.0 (2)
C9—Si1—C10	114.62 (13)	**C7—C3—C4—C8**	−0.9 (3)
C11—Si1—C10	112.75 (15)	**C3—C4—C5—C6**	−2.2 (3)
C9—Si1—C1	107.23 (11)	**C8—C4—C5—C6**	176.8 (2)
C11—Si1—C1	104.10 (13)	**C4—C5—C6—C1**	5.4 (3)
C10—Si1—C1	102.72 (12)	**C2—C1—C6—C5**	−6.2 (3)
C6—C1—C2	117.8 (3)	**Si1—C1—C6—C5**	103.5 (2)
C6—C1—Si1	98.53 (15)	**C44—Si2—C36—C37**	−70.81 (16)
C2—C1—Si1	103.05 (16)	**C46—Si2—C36—C37**	52.05 (17)
C6—C1—H1	123.0 (14)	**C45—Si2—C36—C37**	168.35 (16)
C2—C1—H1	115.1 (14)	**C44—Si2—C36—C41**	50.10 (17)
Si1—C1—H1	88.7 (14)	**C46—Si2—C36—C41**	172.96 (15)
C3—C2—C1	122.1 (2)	**C45—Si2—C36—C41**	−70.73 (17)
C2—C3—C4	118.8 (2)	**C41—C36—C37—C38**	−4.0 (3)
C2—C3—C7	120.5 (2)	**Si2—C36—C37—C38**	103.01 (19)
C4—C3—C7	120.7 (2)	**C36—C37—C38—C39**	1.7 (3)
C5—C4—C3	119.8 (2)	**C36—C37—C38—C42**	−179.4 (2)
C5—C4—C8	120.0 (2)	**C37—C38—C39—C40**	−0.2 (3)
C3—C4—C8	120.3 (2)	**C42—C38—C39—C40**	−179.13 (19)
C6—C5—C4	121.6 (2)	**C37—C38—C39—C43**	179.67 (19)
C5—C6—C1	119.6 (2)	**C42—C38—C39—C43**	0.8 (3)
C44—Si2—C46	116.22 (10)	**C38—C39—C40—C41**	1.1 (3)
C44—Si2—C45	115.19 (12)	**C43—C39—C40—C41**	−178.8 (2)
C46—Si2—C45	111.80 (11)	**C39—C40—C41—C36**	−3.4 (3)
C44—Si2—C36	105.84 (9)	**C37—C36—C41—C40**	4.7 (3)
C46—Si2—C36	103.81 (9)	**Si2—C36—C41—C40**	−102.28 (19)

Numbering scheme of **31g**.

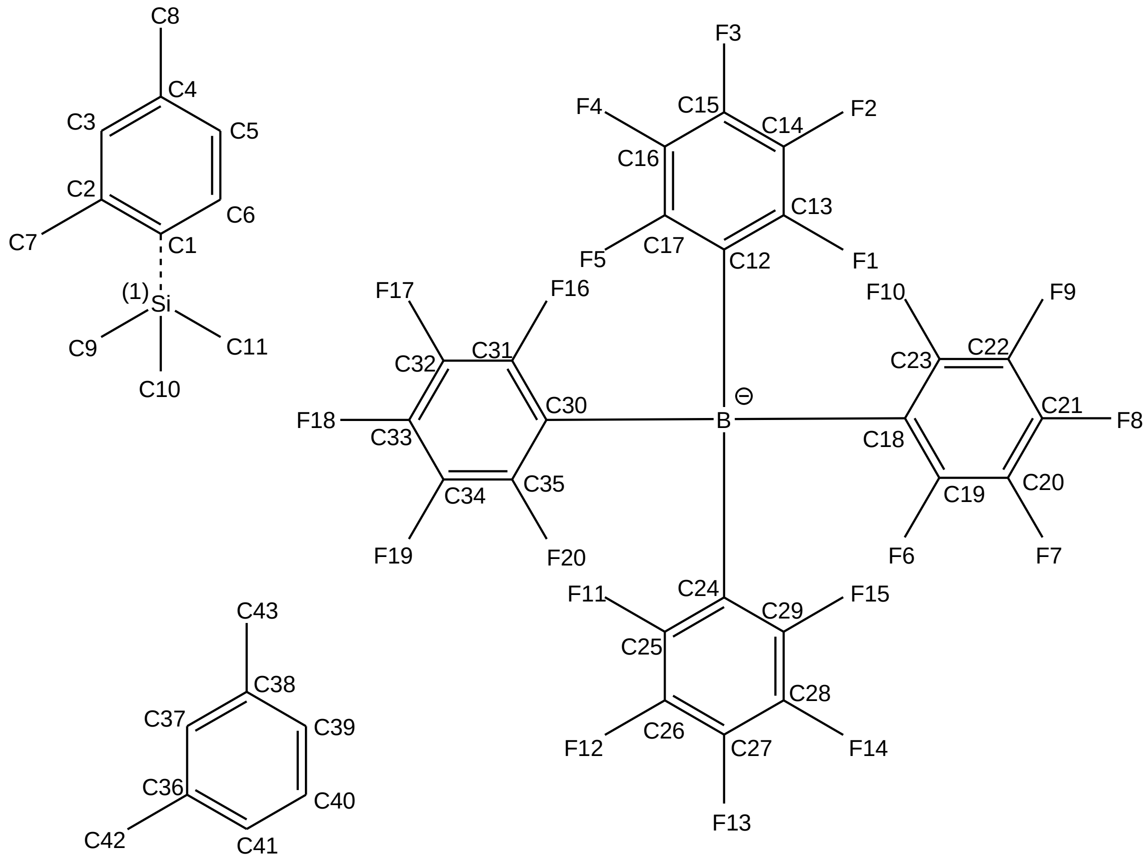


Table A3.10. Selected bond lengths (Å), angles and torsion angles (°) of **31g**.

Si1—C11	1.842 (2)	**C5—C6—C1**	119.6 (2)
Si1—C10	1.842 (2)	**C37—C36—C41**	118.1 (2)
Si1—C9	1.846 (2)	**C37—C36—C42**	120.5 (2)
Si1—C1	2.148 (2)	**C41—C36—C42**	121.4 (2)
C1—C2	1.409 (3)	**C36—C37—C38**	122.2 (2)
C1—C6	1.419 (3)	**C39—C38—C37**	117.6 (2)
C1—H1	0.98 (3)	**C39—C38—C43**	121.2 (2)
C2—C3	1.378 (3)	**C37—C38—C43**	121.2 (2)
C2—C7	1.486 (3)	**C40—C39—C38**	121.0 (2)

C3—C4	1.385 (3)	**C39—C40—C41**	120.3 (2)
C4—C5	1.394 (4)	**C40—C41—C36**	120.8 (2)
C4—C8	1.506 (4)	**C11—Si1—C1—C2**	179.65 (17)
C5—C6	1.373 (3)	**C10—Si1—C1—C2**	−64.46 (17)
C36—C41	1.389 (3)	**C9—Si1—C1—C2**	57.96 (18)
C36—C42	1.504 (3)	**C11—Si1—C1—C6**	57.68 (18)
C37—C38	1.402 (3)	**C10—Si1—C1—C6**	173.56 (16)
C38—C39	1.387 (3)	**C9—Si1—C1—C6**	−64.01 (18)
C38—C43	1.500 (4)	**C6—C1—C2—C3**	11.2 (3)
C39—C40	1.370 (4)	**Si1—C1—C2—C3**	−95.3 (2)
C40—C41	1.377 (4)	**C6—C1—C2—C7**	−166.7 (2)
C11—Si1—C10	110.65 (12)	**Si1—C1—C2—C7**	86.9 (2)
C11—Si1—C9	113.89 (13)	**C1—C2—C3—C4**	−5.5 (3)
C10—Si1—C9	113.78 (11)	**C7—C2—C3—C4**	172.4 (2)
C11—Si1—C1	103.24 (10)	**C2—C3—C4—C5**	−1.9 (4)
C10—Si1—C1	104.74 (11)	**C2—C3—C4—C8**	179.0 (2)
C9—Si1—C1	109.58 (10)	**C3—C4—C5—C6**	3.4 (4)
C2—C1—C6	119.1 (2)	**C8—C4—C5—C6**	−177.5 (2)
C2—C1—Si1	100.41 (14)	**C4—C5—C6—C1**	2.4 (4)
C6—C1—Si1	98.94 (15)	**C2—C1—C6—C5**	−9.7 (3)
C2—C1—H1	113.4 (15)	**Si1—C1—C6—C5**	97.6 (2)
C6—C1—H1	120.5 (15)	**C41—C36—C37—C38**	0.2 (4)
Si1—C1—H1	97.2 (14)	**C42—C36—C37—C38**	−178.8 (2)
C3—C2—C1	118.8 (2)	**C36—C37—C38—C39**	−0.2 (4)
C3—C2—C7	121.2 (2)	**C36—C37—C38—C43**	177.6 (3)
C1—C2—C7	120.0 (2)	**C37—C38—C39—C40**	0.4 (4)
C2—C3—C4	121.7 (2)	**C43—C38—C39—C40**	−177.4 (3)
C3—C4—C5	119.2 (2)	**C38—C39—C40—C41**	−0.7 (4)

C3—C4—C8	120.7 (3)	**C39—C40—C41—C36**	0.8 (4)
C5—C4—C8	120.0 (3)	**C37—C36—C41—C40**	−0.6 (4)
C6—C5—C4	120.7 (2)	**C42—C36—C41—C40**	178.5 (2)

Numbering scheme of **31h**.

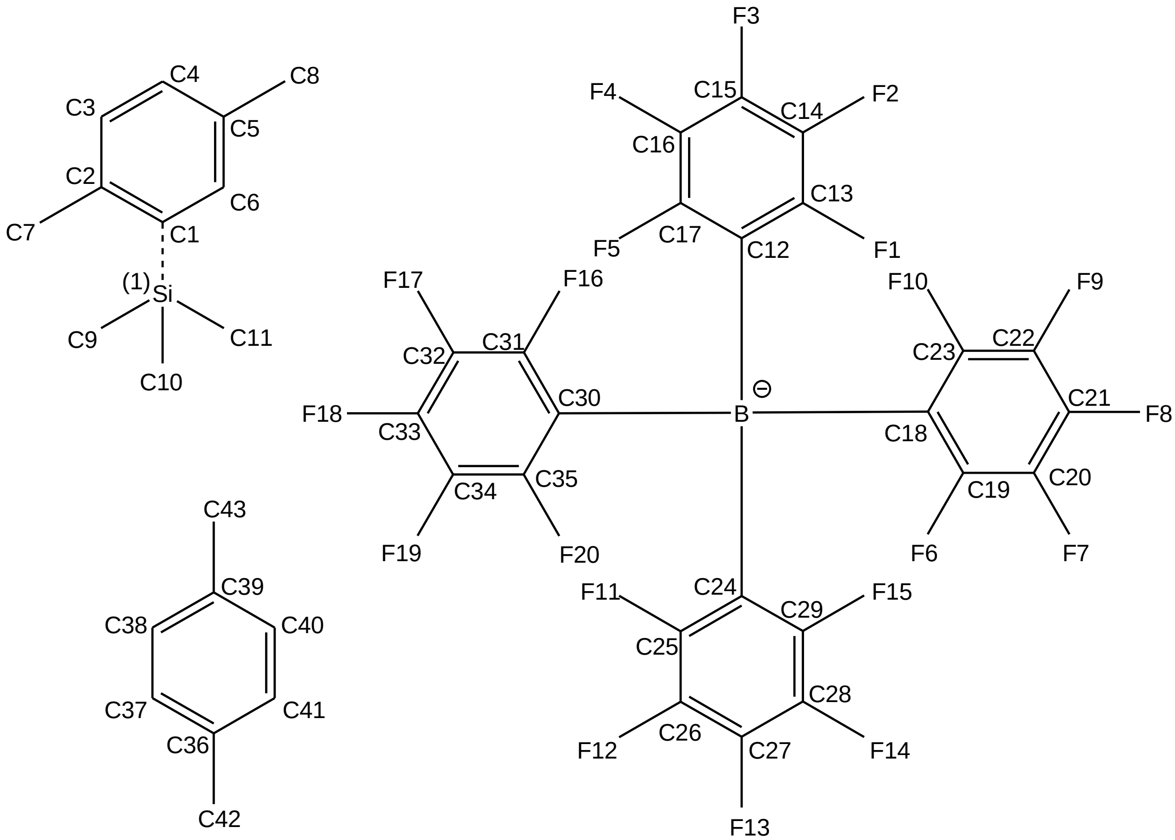


Table A3.11. Selected bond lengths (Å), angles and torsion angles (°) of **31h**.

Si1—C9	1.824 (5)	**C3—C2—C7**	119.0 (5)
Si1—C10	1.838 (5)	**C1—C2—C7**	123.9 (5)
Si1—C11	1.840 (5)	**C4—C3—C2**	121.5 (5)
Si1—C1	2.167 (5)	**C3—C4—C5**	122.1 (5)
C1—C2	1.388 (7)	**C6—C5—C4**	116.6 (5)
C1—C6	1.417 (7)	**C6—C5—C8**	120.4 (5)
C1—H1	1.02 (5)	**C4—C5—C8**	123.0 (5)
C2—C3	1.387 (7)	**C5—C6—C1**	121.7 (5)
C2—C7	1.500 (7)	**C37—C36—C41**	116.6 (6)
C3—C4	1.379 (7)	**C37—C36—C42**	121.3 (5)
C4—C5	1.399 (7)	**C41—C36—C42**	122.1 (5)
C5—C6	1.368 (7)	**C36—C37—C38**	122.9 (5)
C5—C8	1.479 (7)	**C37—C38—C39**	119.8 (5)
C36—C37	1.373 (7)	**C40—C39—C38**	117.1 (6)
C36—C41	1.382 (7)	**C40—C39—C43**	122.2 (6)
C36—C42	1.506 (8)	**C38—C39—C43**	120.7 (6)
C37—C38	1.385 (7)	**C41—C40—C39**	122.2 (6)
C38—C39	1.391 (7)	**C40—C41—C36**	121.4 (6)
C39—C40	1.383 (8)	**C9—Si1—C1—C2**	49.7 (4)
C39—C43	1.501 (9)	**C10—Si1—C1—C2**	−70.5 (4)
C40—C41	1.366 (9)	**C11—Si1—C1—C2**	171.8 (4)
C36—C37	1.373 (7)	**C9—Si1—C1—C6**	−73.1 (4)
C36—C41	1.382 (7)	**C10—Si1—C1—C6**	166.7 (3)
C36—C42	1.506 (8)	**C11—Si1—C1—C6**	49.0 (4)
C37—C38	1.385 (7)	**C6—C1—C2—C3**	9.0 (7)
C38—C39	1.391 (7)	**Si1—C1—C2—C3**	−94.8 (5)

C39—C40	1.383 (8)	**C6—C1—C2—C7**	−172.7 (5)
C39—C43	1.501 (9)	**Si1—C1—C2—C7**	83.5 (5)
C40—C41	1.366 (9)	**C1—C2—C3—C4**	−3.9 (7)
C36—C37	1.373 (7)	**C7—C2—C3—C4**	177.8 (5)
C36—C41	1.382 (7)	**C2—C3—C4—C5**	−1.1 (8)
C36—C42	1.506 (8)	**C3—C4—C5—C6**	0.8 (7)
C37—C38	1.385 (7)	**C3—C4—C5—C8**	−178.8 (5)
C38—C39	1.391 (7)	**C4—C5—C6—C1**	4.5 (7)
C9—Si1—C10	113.0 (2)	**C8—C5—C6—C1**	−175.9 (5)
C9—Si1—C11	115.1 (3)	**C2—C1—C6—C5**	−9.7 (8)
C10—Si1—C11	113.1 (3)	**Si1—C1—C6—C5**	98.3 (5)
C9—Si1—C1	108.5 (2)	**C41—C36—C37—C38**	1.0 (8)
C10—Si1—C1	103.4 (2)	**C42—C36—C37—C38**	−179.4 (5)
C11—Si1—C1	102.3 (2)	**C36—C37—C38—C39**	−0.5 (7)
C2—C1—C6	120.4 (5)	**C37—C38—C39—C40**	0.3 (8)
C2—C1—Si1	102.8 (3)	**C37—C38—C39—C43**	−179.8 (5)
C6—C1—Si1	95.1 (3)	**C38—C39—C40—C41**	−0.6 (10)
C2—C1—H1	118 (3)	**C43—C39—C40—C41**	179.4 (7)
C6—C1—H1	117 (3)	**C39—C40—C41—C36**	1.2 (11)
Si1—C1—H1	93 (3)	**C37—C36—C41—C40**	−1.3 (10)
C3—C2—C1	117.0 (5)	**C42—C36—C41—C40**	179.1 (7)

Numbering scheme of **31i**.

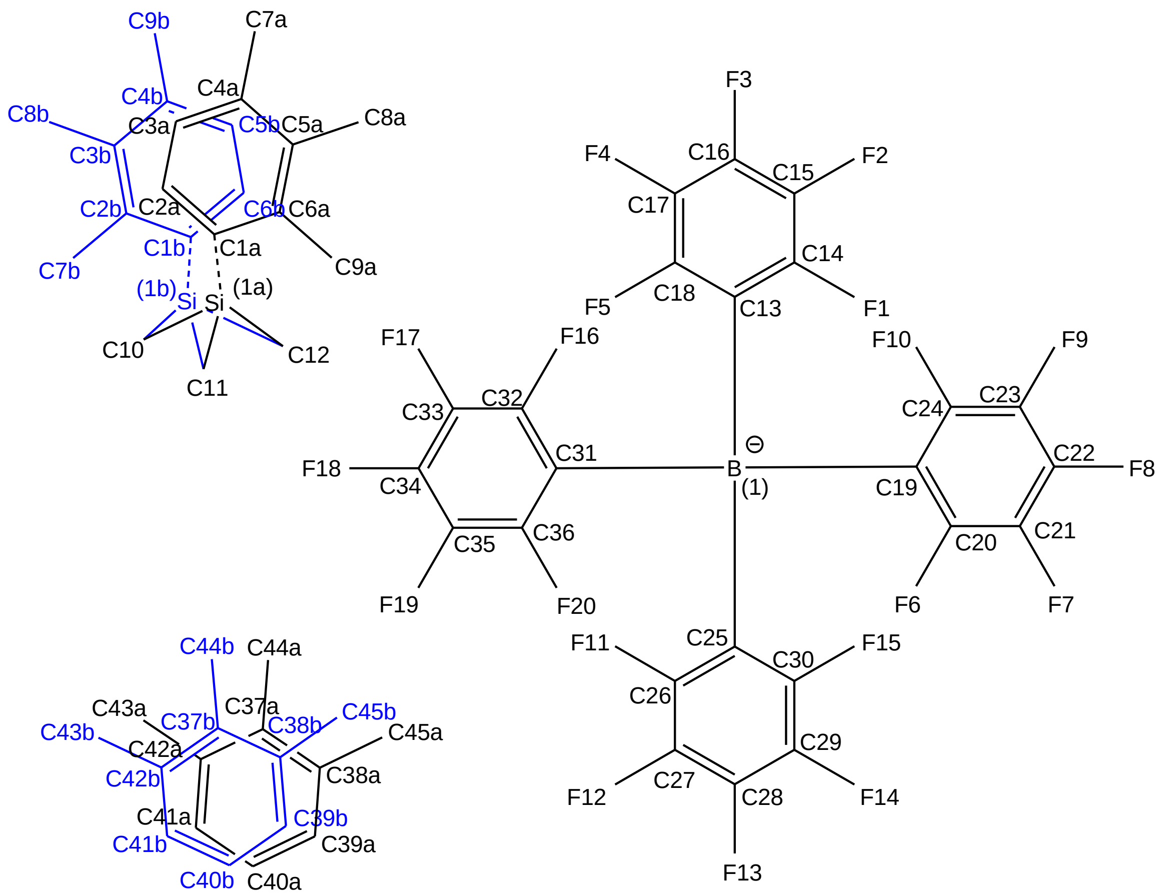


Table A3.12. Selected bond lengths (Å), angles and torsion angles (°) of **31i**.

Si1A—C10	1.795 (7)	**C3A—C2A—C1A**	118.7 (8)
Si1A—C11	1.821 (6)	**C2A—C3A—C4A**	118.2 (11)
Si1A—C12	1.875 (7)	**C5A—C4A—C3A**	125.7 (18)
Si1A—C1A	2.129 (5)	**C5A—C4A—C7A**	118.5 (14)
C1A—C6A	1.396 (11)	**C3A—C4A—C7A**	115.8 (17)
C1A—C2A	1.439 (16)	**C4A—C5A—C6A**	117.4 (10)
C2A—C3A	1.357 (7)	**C4A—C5A—C8A**	121.2 (11)
C3A—C4A	1.39 (2)	**C6A—C5A—C8A**	121.4 (6)
C4A—C5A	1.35 (2)	**C1A—C6A—C5A**	118.3 (8)

C4A—C7A	1.58 (2)	**C1A—C6A—C9A**	119.1 (8)
C5A—C6A	1.418 (8)	**C5A—C6A—C9A**	122.5 (6)
C5A—C8A	1.519 (8)	**C2B—C1B—C6B**	118 (3)
C6A—C9A	1.517 (6)	**C2B—C1B—Si1B**	103.6 (16)
Si1B—C1B	2.131 (9)	**C6B—C1B—Si1B**	104.1 (12)
C1B—C2B	1.41 (4)	**C1B—C2B—C7B**	119.0 (15)
C1B—C6B	1.52 (2)	**C1B—C2B—C3B**	123 (2)
C2B—C7B	1.532 (12)	**C7B—C2B—C3B**	117.4 (18)
C2B—C3B	1.54 (5)	**C8B—C3B—C4B**	129 (4)
C3B—C8B	1.39 (5)	**C8B—C3B—C2B**	121 (3)
C3B—C4B	1.43 (5)	**C4B—C3B—C2B**	109 (3)
C4B—C5B	1.357 (17)	**C5B—C4B—C3B**	126 (2)
C4B—C9B	1.546 (16)	**C5B—C4B—C9B**	122.8 (13)
C5B—C6B	1.375 (15)	**C3B—C4B—C9B**	111 (2)
C37A—C38A	1.3900	**C4B—C5B—C6B**	126.6 (12)
C37A—C40A	1.3900	**C5B—C6B—C1B**	113 (2)
C37A—C44A	1.491 (10)	**C38A—C37A—C40A**	120.0
C38A—C39A	1.3900	**C38A—C37A—C44A**	116.6 (10)
C38A—C45A	1.504 (9)	**C40A—C37A—C44A**	123.4 (10)
C39A—C41A	1.3900	**C39A—C38A—C37A**	120.0
C41A—C42A	1.3900	**C39A—C38A—C45A**	115.7 (7)
C42A—C40A	1.3900	**C37A—C38A—C45A**	124.3 (7)
C40A—C43A	1.494 (9)	**C38A—C39A—C41A**	120.0
C37B—C38B	1.3900	**C42A—C41A—C39A**	120.0
C37B—C42B	1.3900	**C40A—C42A—C41A**	120.0
C37B—C44B	1.485 (11)	**C42A—C40A—C37A**	120.0
C38B—C39B	1.3900	**C42A—C40A—C43A**	120.1 (7)
C38B—C45B	1.513 (10)	**C37A—C40A—C43A**	119.9 (7)

C39B—C40B	1.3900	**C38B—C37B—C42B**	120.0
C40B—C41B	1.3900	**C38B—C37B—C44B**	122.5 (12)
C41B—C42B	1.3900	**C42B—C37B—C44B**	117.5 (12)
C42B—C43B	1.506 (10)	**C37B—C38B—C39B**	120.0
C10—Si1A—C11	117.1 (4)	**C37B—C38B—C45B**	119.9 (8)
C10—Si1A—C12	112.2 (3)	**C39B—C38B—C45B**	120.1 (8)
C11—Si1A—C12	109.9 (3)	**C40B—C39B—C38B**	120.0
C10—Si1A—C1A	111.1 (5)	**C39B—C40B—C41B**	120.0
C11—Si1A—C1A	100.1 (3)	**C40B—C41B—C42B**	120.0
C12—Si1A—C1A	105.2 (5)	**C41B—C42B—C37B**	120.0
C6A—C1A—C2A	121.2 (13)	**C41B—C42B—C43B**	115.3 (8)
C6A—C1A—Si1A	98.7 (5)	**C37B—C42B—C43B**	124.7 (8)
C2A—C1A—Si1A	98.3 (6)		

Numbering scheme of **31j**.

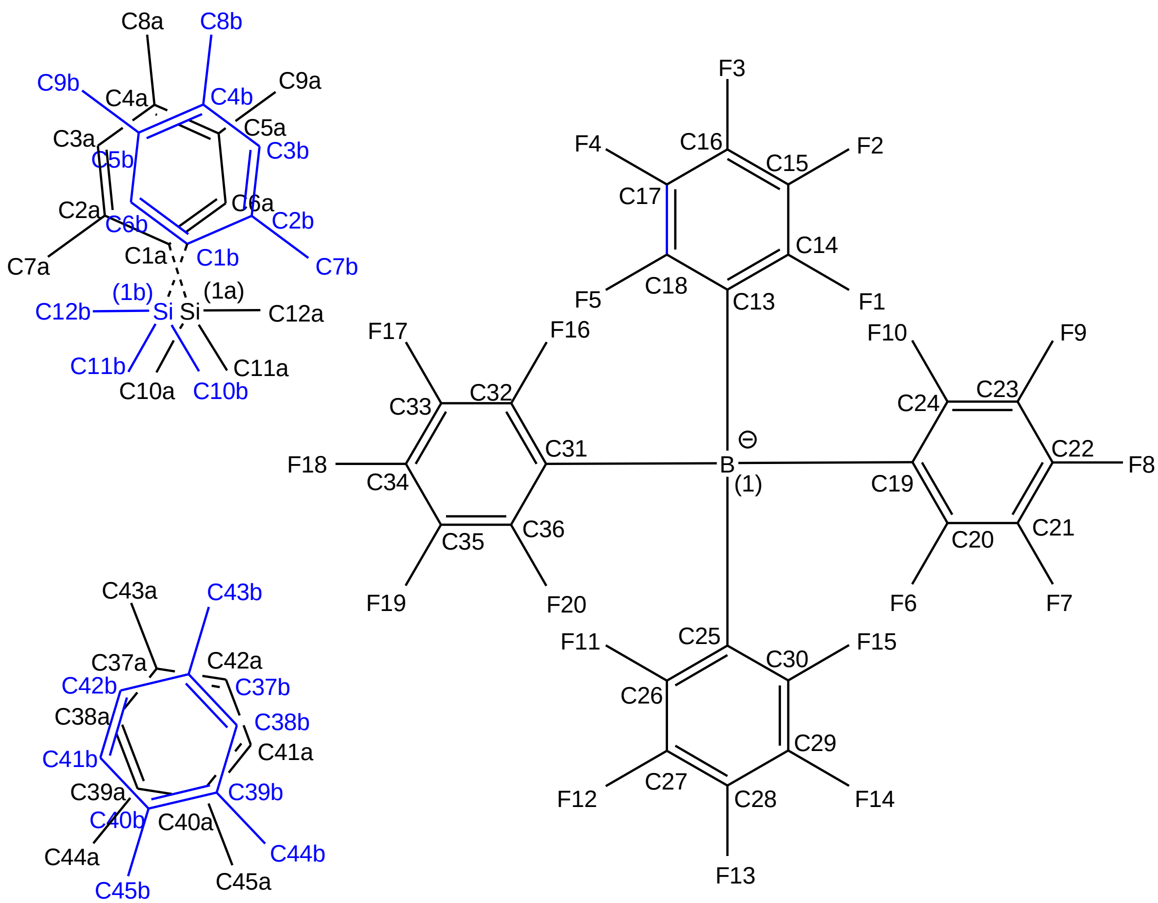


Table A3.13. Selected bond lengths (Å), angles and torsion angles (°) of **31j**.

Si1A—C11A	1.833 (4)	**C38A—C37A—C43A**	118.9 (7)
Si1A—C10A	1.843 (3)	**C42A—C37A—C43A**	121.1 (7)
Si1A—C12A	1.853 (4)	**C39A—C38A—C37A**	120.0
Si1A—C1A	2.121 (3)	**C38A—C39A—C40A**	120.0
C1A—C2A	1.399 (5)	**C38A—C39A—C44A**	125.0 (9)
C1A—C6A	1.439 (5)	**C40A—C39A—C44A**	114.7 (9)
C1A—H1A	1.01 (2)	**C41A—C40A—C39A**	120.0
C2A—C3A	1.382 (4)	**C41A—C40A—C45A**	112.5 (9)
C2A—C7A	1.461 (4)	**C39A—C40A—C45A**	126.4 (9)

C3A—C4A	1.388 (4)	**C42A—C41A—C40A**	120.0
C4A—C5A	1.379 (5)	**C41A—C42A—C37A**	120.0
C4A—C8A	1.487 (4)	**C37B—C42B—C41B**	120.0
C5A—C6A	1.377 (5)	**C38B—C37B—C42B**	120.0
C5A—C9A	1.512 (5)	**C38B—C37B—C43B**	119.4 (8)
Si1B—C10B	1.829 (16)	**C42B—C37B—C43B**	120.6 (8)
Si1B—C12B	1.832 (17)	**C37B—C38B—C39B**	120.0
Si1B—C11B	1.842 (16)	**C40B—C39B—C38B**	120.0
Si1B—C1B	2.139 (17)	**C40B—C39B—C44B**	116.8 (10)
C1B—C2B	1.406 (19)	**C38B—C39B—C44B**	122.4 (10)
C1B—C6B	1.459 (19)	**C39B—C40B—C41B**	120.0
C1B—H1B	1.0000	**C39B—C40B—C45B**	126.9 (10)
C1B—H1A	1.05 (4)	**C41B—C40B—C45B**	112.9 (10)
C2B—C3B	1.368 (17)	**C40B—C41B—C42B**	120.0
C2B—C7B	1.420 (15)	**C11A—Si1A—C1A—C2A**	171.8 (3)
C3B—C4B	1.378 (16)	**C10A—Si1A—C1A—C2A**	−67.6 (4)
C4B—C5B	1.375 (17)	**C12A—Si1A—C1A—C2A**	54.3 (3)
C4B—C8B	1.504 (16)	**C11A—Si1A—C1A—C6A**	−66.0 (3)
C5B—C6B	1.405 (17)	**C10A—Si1A—C1A—C6A**	54.6 (4)
C5B—C9B	1.505 (18)	**C12A—Si1A—C1A—C6A**	176.6 (3)
C37A—C38A	1.3900	**C6A—C1A—C2A—C3A**	−11.9 (5)
C37A—C42A	1.3900	**Si1A—C1A—C2A—C3A**	95.2 (4)
C37A—C43A	1.516 (7)	**C6A—C1A—C2A—C7A**	164.9 (3)
C38A—C39A	1.3900	**Si1A—C1A—C2A—C7A**	−88.0 (4)
C39A—C40A	1.3900	**C1A—C2A—C3A—C4A**	5.5 (5)
C39A—C44A	1.54 (2)	**C7A—C2A—C3A—C4A**	−171.5 (3)
C40A—C41A	1.3900	**C2A—C3A—C4A—C5A**	4.2 (5)
C40A—C45A	1.551 (15)	**C2A—C3A—C4A—C8A**	−178.2 (3)
C41A—C42A	1.3900	**C3A—C4A—C5A—C6A**	−7.1 (5)

C42B—C37B	1.3900	**C8A—C4A—C5A—C6A**	175.4 (3)
C42B—C41B	1.3900	**C3A—C4A—C5A—C9A**	172.9 (3)
C37B—C38B	1.3900	**C8A—C4A—C5A—C9A**	−4.6 (5)
C37B—C43B	1.512 (10)	**C4A—C5A—C6A—C1A**	0.4 (5)
C38B—C39B	1.3900	**C9A—C5A—C6A—C1A**	−179.6 (3)
C39B—C40B	1.3900	**C2A—C1A—C6A—C5A**	9.3 (5)
C39B—C44B	1.484 (18)	**Si1A—C1A—C6A—C5A**	−99.4 (3)
C40B—C41B	1.3900	**C10B—Si1B—C1B—C2B**	60 (2)
C40B—C45B	1.47 (3)	**C12B—Si1B—C1B—C2B**	−178.5 (16)
C11A—Si1A—C10A	112.8 (3)	**C11B—Si1B—C1B—C2B**	−61 (2)
C11A—Si1A—C12A	111.1 (3)	**C10B—Si1B—C1B—C6B**	−63 (2)
C10A—Si1A—C12A	112.3 (3)	**C12B—Si1B—C1B—C6B**	58.6 (17)
C11A—Si1A—C1A	103.6 (2)	**C11B—Si1B—C1B—C6B**	176 (2)
C10A—Si1A—C1A	109.6 (3)	**C6B—C1B—C2B—C3B**	8 (3)
C12A—Si1A—C1A	106.9 (2)	**Si1B—C1B—C2B—C3B**	−95.3 (17)
C2A—C1A—C6A	119.0 (3)	**C6B—C1B—C2B—C7B**	−164 (2)
C2A—C1A—Si1A	101.8 (3)	**Si1B—C1B—C2B—C7B**	93 (2)
C6A—C1A—Si1A	98.8 (2)	**C1B—C2B—C3B—C4B**	4 (3)
C2A—C1A—H1A	119.5 (14)	**C7B—C2B—C3B—C4B**	176 (2)
C6A—C1A—H1A	116.9 (14)	**C2B—C3B—C4B—C5B**	−13 (4)
Si1A—C1A—H1A	90.8 (14)	**C2B—C3B—C4B—C8B**	176 (2)
C3A—C2A—C1A	117.3 (3)	**C3B—C4B—C5B—C6B**	11 (4)
C3A—C2A—C7A	120.5 (3)	**C8B—C4B—C5B—C6B**	−179 (3)
C1A—C2A—C7A	122.1 (3)	**C3B—C4B—C5B—C9B**	172 (2)
C2A—C3A—C4A	123.1 (3)	**C8B—C4B—C5B—C9B**	−17 (4)
C5A—C4A—C3A	119.5 (3)	**C4B—C5B—C6B—C1B**	0 (4)
C5A—C4A—C8A	121.0 (3)	**C9B—C5B—C6B—C1B**	−160 (2)
C3A—C4A—C8A	119.5 (3)	**C2B—C1B—C6B—C5B**	−9 (4)
C6A—C5A—C4A	119.4 (3)	**Si1B—C1B—C6B—C5B**	94 (3)

C6A—C5A—C9A	120.9 (4)	**C42A—C37A—C38A—C39A**	0.0
C4A—C5A—C9A	119.7 (4)	**C43A—C37A—C38A—C39A**	−178.6 (7)
C5A—C6A—C1A	120.5 (3)	**C37A—C38A—C39A—C40A**	0.0
C10B—Si1B—C12B	114.6 (18)	**C37A—C38A—C39A—C44A**	172.5 (13)
C10B—Si1B—C11B	114.2 (18)	**C38A—C39A—C40A—C41A**	0.0
C12B—Si1B—C11B	112.6 (17)	**C44A—C39A—C40A—C41A**	−173.3 (12)
C10B—Si1B—C1B	107.9 (17)	**C38A—C39A—C40A—C45A**	167.0 (14)
C12B—Si1B—C1B	103.4 (12)	**C44A—C39A—C40A—C45A**	−6.3 (12)
C11B—Si1B—C1B	102.8 (13)	**C39A—C40A—C41A—C42A**	0.0
C2B—C1B—C6B	121.2 (18)	**C45A—C40A—C41A—C42A**	−168.7 (12)
C2B—C1B—Si1B	97.2 (14)	**C40A—C41A—C42A—C37A**	0.0
C6B—C1B—Si1B	97.4 (16)	**C38A—C37A—C42A—C41A**	0.0
C2B—C1B—H1B	112.8	**C43A—C37A—C42A—C41A**	178.6 (8)
C6B—C1B—H1B	112.8	**C41B—C42B—C37B—C38B**	0.0
Si1B—C1B—H1B	112.8	**C41B—C42B—C37B—C43B**	179.2 (8)
C3B—C2B—C1B	116.5 (15)	**C42B—C37B—C38B—C39B**	0.0
C3B—C2B—C7B	117.6 (15)	**C43B—C37B—C38B—C39B**	−179.2 (8)
C1B—C2B—C7B	125.4 (16)	**C37B—C38B—C39B—C40B**	0.0
C2B—C3B—C4B	125.3 (16)	**C37B—C38B—C39B—C44B**	169.0 (15)
C5B—C4B—C3B	116.4 (15)	**C38B—C39B—C40B—C41B**	0.0
C5B—C4B—C8B	123.7 (16)	**C44B—C39B—C40B—C41B**	−169.6 (15)
C3B—C4B—C8B	119.2 (17)	**C38B—C39B—C40B—C45B**	174.8 (16)
C4B—C5B—C6B	123.7 (16)	**C44B—C39B—C40B—C45B**	5.2 (16)
C4B—C5B—C9B	111.0 (16)	**C39B—C40B—C41B—C42B**	0.0
C6B—C5B—C9B	122.6 (17)	**C45B—C40B—C41B—C42B**	−175.5 (14)
C5B—C6B—C1B	115.2 (18)	**C37B—C42B—C41B—C40B**	0.0
C38A—C37A—C42A	120.0		

Numbering scheme of **31k**.

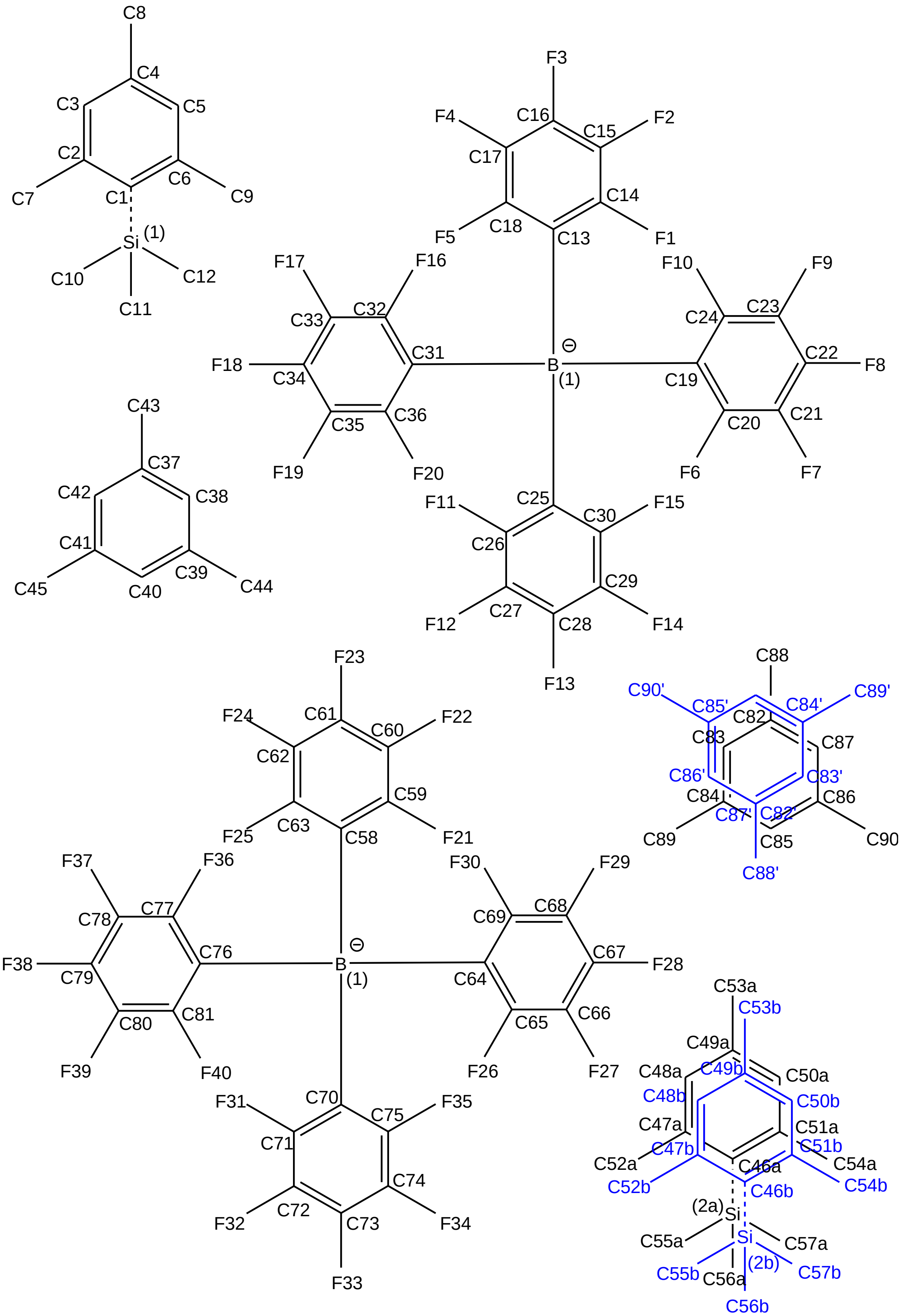


Table A3.14. Selected bond lengths (Å), angles and torsion angles (°) of **31k**.

Si1—C12	1.799 (3)	**C57B—Si2B—C46B**	100.5 (10)
Si1—C10	1.823 (2)	**C55B—Si2B—C46B**	110.1 (9)
Si1—C11	1.847 (3)	**C56B—Si2B—C46B**	106.8 (10)
Si1—C1	2.139 (2)	**C47B—C46B—C51B**	119 (2)
C1—C6	1.431 (3)	**C47B—C46B—Si2B**	104.8 (14)
C1—C2	1.433 (3)	**C51B—C46B—Si2B**	104 (2)
C1—H1	0.99 (3)	**C47B—C46B—H46**	122 (3)
C2—C3	1.373 (4)	**C51B—C46B—H46**	96 (3)
C2—C7	1.500 (4)	**Si2B—C46B—H46**	110 (3)
C3—C4	1.385 (4)	**C46B—C47B—C48B**	112.0 (19)
C4—C5	1.401 (3)	**C46B—C47B—C52B**	117.6 (18)
C4—C8	1.499 (4)	**C48B—C47B—C52B**	127.5 (17)
C5—C6	1.371 (3)	**C49B—C48B—C47B**	136.5 (19)
C6—C9	1.502 (3)	**C53B—C49B—C48B**	129 (3)
C37—C42	1.383 (3)	**C53B—C49B—C50B**	129 (3)
C37—C38	1.390 (3)	**C48B—C49B—C50B**	103 (2)
C37—C43	1.517 (4)	**C51B—C50B—C49B**	125 (3)
C38—C39	1.392 (3)	**C50B—C51B—C46B**	117 (3)
C39—C40	1.391 (3)	**C50B—C51B—C54B**	101 (3)
C39—C44	1.508 (3)	**C46B—C51B—C54B**	138 (4)
C40—C41	1.387 (3)	**C83—C82—C87**	120.0
C41—C42	1.387 (3)	**C83—C82—C88**	124.3 (10)
C41—C45	1.504 (3)	**C87—C82—C88**	115.7 (10)
Si2A—C55A	1.794 (9)	**C82—C83—C84**	120.0
Si2A—C56A	1.865 (12)	**C83—C84—C85**	120.0
Si2A—C57A	1.883 (8)	**C83—C84—C89**	118.5 (13)

Si2A—C46A	2.171 (6)	**C85—C84—C89**	121.4 (13)
C46A—C47A	1.468 (13)	**C86—C85—C84**	120.0
C46A—C51A	1.480 (11)	**C87—C86—C85**	120.0
C46A—H46	1.21 (5)	**C87—C86—C90**	126.6 (10)
C47A—C48A	1.317 (10)	**C85—C86—C90**	113.4 (10)
C47A—C52A	1.494 (11)	**C86—C87—C82**	120.0
C48A—C49A	1.386 (14)	**C12—Si1—C1—C6**	−164.32
C49A—C50A	1.331 (15)	**C10—Si1—C1—C6**	71.21 (18)
C49A—C53A	1.551 (17)	**C11—Si1—C1—C6**	−50.8 (2)
C50A—C51A	1.407 (11)	**C12—Si1—C1—C2**	73.8 (2)
C51A—C54A	1.50 (3)	**C10—Si1—C1—C2**	−50.65
Si2B—C57B	1.743 (16)	**C11—Si1—C1—C2**	−172.71
Si2B—C55B	1.95 (2)	**C6—C1—C2—C3**	−12.2 (3)
Si2B—C56B	1.98 (2)	**Si1—C1—C2—C3**	94.0 (2)
Si2B—C46B	2.093 (19)	**C6—C1—C2—C7**	167.2 (2)
C46B—C47B	1.39 (3)	**Si1—C1—C2—C7**	−86.7 (2)
C46B—C51B	1.428 (19)	**C1—C2—C3—C4**	5.3 (3)
C46B—H46	1.11 (5)	**C7—C2—C3—C4**	−174.1 (2)
C47B—C48B	1.41 (3)	**C2—C3—C4—C5**	1.4 (3)
C47B—C52B	1.52 (3)	**C2—C3—C4—C8**	−180.0 (2)
C48B—C49B	1.31 (4)	**C3—C4—C5—C6**	−1.0 (3)
C49B—C53B	1.25 (4)	**C8—C4—C5—C6**	−179.7 (2)
C49B—C50B	1.65 (4)	**C4—C5—C6—C1**	−5.9 (3)
C50B—C51B	1.33 (3)	**C4—C5—C6—C9**	171.6 (2)
C51B—C54B	1.51 (6)	**C2—C1—C6—C5**	12.5 (3)
C82—C83	1.3900	**Si1—C1—C6—C5**	−92.9 (2)
C82—C87	1.3900	**C2—C1—C6—C9**	−165.0 (2)
C82—C88	1.498 (17)	**Si1—C1—C6—C9**	89.5 (2)

C83—C84	1.3900	**C42—C37—C38—C39**	−1.6 (3)
C84—C85	1.3900	**C43—C37—C38—C39**	176.8 (2)
C84—C89	1.521 (13)	**C37—C38—C39—C40**	0.5 (3)
C85—C86	1.3900	**C37—C38—C39—C44**	179.4 (2)
C86—C87	1.3900	**C38—C39—C40—C41**	1.3 (3)
C86—C90	1.479 (14)	**C44—C39—C40—C41**	−177.5 (2)
C12—Si1—C10	114.73	**C39—C40—C41—C42**	−1.9 (3)
C12—Si1—C11	106.93	**C39—C40—C41—C45**	177.2 (2)
C10—Si1—C11	112.57	**C38—C37—C42—C41**	1.0 (3)
C12—Si1—C1	105.90	**C43—C37—C42—C41**	−177.4 (2)
C10—Si1—C1	109.92	**C40—C41—C42—C37**	0.7 (3)
C11—Si1—C1	106.25	**C45—C41—C42—C37**	−178.4 (2)
C6—C1—C2	119.4 (2)	**C55A—Si2A—C46A—C47A**	−49.5 (8)
C6—C1—Si1	99.65 (15)	**C56A—Si2A—C46A—C47A**	−167.7 (9)
C2—C1—Si1	98.44 (14)	**C57A—Si2A—C46A—C47A**	69.7 (7)
C6—C1—H1	116.9 (15)	**C55A—Si2A—C46A—C51A**	72.0 (8)
C2—C1—H1	116.8 (14)	**C56A—Si2A—C46A—C51A**	−46.3 (10)
Si1—C1—H1	98.4 (14)	**C57A—Si2A—C46A—C51A**	−168.9 (7)
C3—C2—C1	118.1 (2)	**C51A—C46A—C47A—C48A**	−11.6 (10)
C3—C2—C7	120.9 (2)	**Si2A—C46A—C47A—C48A**	90.5 (6)
C1—C2—C7	121.0 (2)	**C51A—C46A—C47A—C52A**	170.2 (8)
C2—C3—C4	122.1 (2)	**Si2A—C46A—C47A—C52A**	−87.7 (7)
C6—C1—H1	116.9 (15)	**C46A—C47A—C48A—C49A**	12.8 (8)
C2—C1—H1	116.8 (14)	**C52A—C47A—C48A—C49A**	−169.0 (5)
C3—C4—C5	119.4 (2)	**C47A—C48A—C49A—C50A**	−7.9 (9)
C3—C4—C8	121.0 (2)	**C47A—C48A—C49A—C53A**	179.7 (6)
C5—C4—C8	119.6 (2)	**C48A—C49A—C50A—C51A**	0.9 (13)
C6—C5—C4	121.3 (2)	**C53A—C49A—C50A—C51A**	173.4 (9)

C5—C6—C1	118.6 (2)	**C49A—C50A—C51A—C46A**	0.2 (16)
C5—C6—C9	120.7 (2)	**C49A—C50A—C51A—C54A**	164.7 (17)
C1—C6—C9	120.6 (2)	**C47A—C46A—C51A—C50A**	5.0 (14)
C42—C37—C38	118.4 (2)	**Si2A—C46A—C51A—C50A**	−98.2 (11)
C42—C37—C43	120.7 (2)	**C47A—C46A—C51A—C54A**	−162.2
C38—C37—C43	120.9 (2)	**Si2A—C46A—C51A—C54A**	94.6 (15)
C37—C38—C39	121.2 (2)	**C57B—Si2B—C46B—C47B**	97.5 (18)
C40—C39—C38	118.6 (2)	**C55B—Si2B—C46B—C47B**	−20 (2)
C40—C39—C44	120.3 (2)	**C56B—Si2B—C46B—C47B**	−138.7
C38—C39—C44	121.1 (2)	**C57B—Si2B—C46B—C51B**	−137 (2)
C41—C40—C39	121.4 (2)	**C55B—Si2B—C46B—C51B**	105 (2)
C42—C41—C40	118.3 (2)	**C56B—Si2B—C46B—C51B**	−13 (2)
C42—C41—C45	120.7 (2)	**C51B—C46B—C47B—C48B**	−33 (3)
C40—C41—C45	121.0 (2)	**Si2B—C46B—C47B—C48B**	82.4 (14)
C37—C42—C41	122.1 (2)	**C51B—C46B—C47B—C52B**	164.9 (19)
C55A—Si2A—C56A	109.4 (7)	**Si2B—C46B—C47B—C52B**	−79.8 (19)
C55A—Si2A—C57A	111.2 (4)	**C46B—C47B—C48B—C49B**	21.4 (19)
C56A—Si2A—C57A	115.9 (7)	**C52B—C47B—C48B—C49B**	−178.7
C55A—Si2A—C46A	110.2 (3)	**C47B—C48B—C49B—C53B**	174 (2)
C56A—Si2A—C46A	105.9 (4)	**C47B—C48B—C49B—C50B**	−3.6 (16)
C57A—Si2A—C46A	103.9 (4)	**C53B—C49B—C50B—C51B**	−180 (3)
C47A—C46A—C51A	119.9 (9)	**C48B—C49B—C50B—C51B**	−3 (3)
C47A—C46A—Si2A	98.2 (5)	**C49B—C50B—C51B—C46B**	−10 (5)
C51A—C46A—Si2A	96.3 (8)	**C49B—C50B—C51B—C54B**	−173 (3)
C47A—C46A—H46	131 (2)	**C47B—C46B—C51B—C50B**	29 (4)
C51A—C46A—H46	108 (2)	**Si2B—C46B—C51B—C50B**	−86 (4)
Si2A—C46A—H46	85 (2)	**C47B—C46B—C51B—C54B**	−177 (4)
C48A—C47A—C46A	118.0 (8)	**Si2B—C46B—C51B—C54B**	67 (5)

C48A—C47A—C52A	120.6 (7)	**C87—C82—C83—C84**	0.0
C46A—C47A—C52A	121.3 (7)	**C88—C82—C83—C84**	−178.2 (9)
C47A—C48A—C49A	121.0 (7)	**C82—C83—C84—C85**	0.0
C50A—C49A—C48A	123.3 (11)	**C82—C83—C84—C89**	179.2 (13)
C50A—C49A—C53A	117.4 (11)	**C83—C84—C85—C86**	0.0
C48A—C49A—C53A	118.8 (10)	**C89—C84—C85—C86**	−179.2
C49A—C50A—C51A	121.9 (12)	**C84—C85—C86—C87**	0.0
C50A—C51A—C46A	114.7 (12)	**C84—C85—C86—C90**	178.6 (7)
C50A—C51A—C54A	130.2 (11)	**C85—C86—C87—C82**	0.0
C46A—C51A—C54A	113.5 (9)	**C90—C86—C87—C82**	−178.4 (8)
C57B—Si2B—C55B	111.3 (10)	**C83—C82—C87—C86**	0.0
C57B—Si2B—C56B	118.1 (12)	**C88—C82—C87—C86**	178.4 (8)
C55B—Si2B—C56B	109.5 (11)		

Numbering scheme of **31l**.

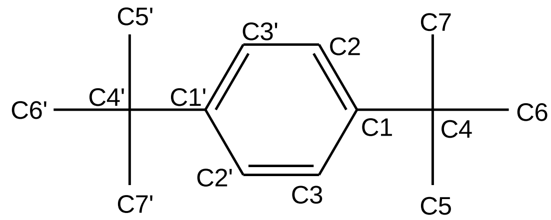


Table A3.15. Selected bond lengths (Å), angles and torsion angles (°) of **31l**.

C1—C3	1.3910 (12)	**C7—C4—C6**	108.53 (9)
C1—C2	1.3930 (12)	**C1—C4—C5**	109.98 (8)
C1—C4	1.5296 (12)	**C7—C4—C5**	107.92 (9)
C2—C3^{i}	1.3902 (13)	**C6—C4—C5**	109.01 (10)
C3—C2^{i}	1.3902 (13)	**C3—C1—C2—C3^{i}**	0.30 (15)
C4—C7	1.5311 (14)	**C4—C1—C2—C3^{i}**	179.23 (9)
C4—C6	1.5326 (16)	**C2—C1—C3—C2^{i}**	−0.30 (15)
C4—C5	1.5334 (16)	**C4—C1—C3—C2^{i}**	−179.19 (9)
C3—C1—C2	116.59 (8)	**C3—C1—C4—C7**	−8.82 (14)
C3—C1—C4	123.17 (8)	**C2—C1—C4—C7**	172.32 (9)
C2—C1—C4	120.24 (8)	**C3—C1—C4—C6**	111.50 (11)
C3^{i}—C2—C1	121.95 (8)	**C2—C1—C4—C6**	−67.36 (12)
C2^{i}—C3—C1	121.46 (8)	**C3—C1—C4—C5**	−129.02 (11)
C1—C4—C7	112.30 (8)	**C2—C1—C4—C5**	52.12 (12)
C1—C4—C6	109.03 (8)		

Symmetry code: (i) −x, −y+1, −z.

Numbering scheme of $(Me_3Si)_2CNN$ **(34a)**.

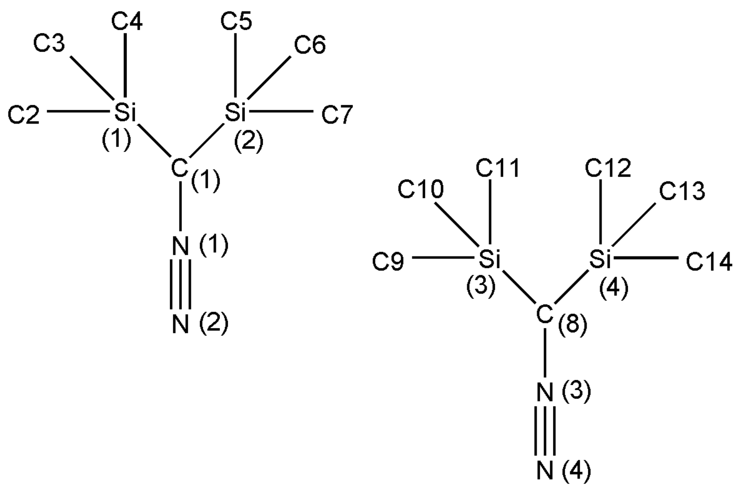


Table A3.16. Selected bond lengths (Å), angles and torsion angles (°) of $(Me_3Si)_2CNN$ (**34a**).

Si1—C3	1.837 (2)	**C10—Si3—C9**	108.92 (8)
Si1—C2	1.849 (2)	**C11—Si3—C9**	110.47 (9)
Si1—C4	1.851 (2)	**C14—Si4—C12**	110.68 (11)
Si1—C1	1.8552 (14)	**C14—Si4—C13**	110.30 (10)
Si2—C1	1.8515 (14)	**C12—Si4—C13**	109.77 (10)
Si2—C5	1.8536 (15)	**C14—Si4—C8**	109.69 (8)
Si2—C6	1.8582 (17)	**C12—Si4—C8**	107.95 (8)
Si2—C7	1.8597 (17)	**C13—Si4—C8**	108.38 (7)
N1—N2	1.1349 (18)	**N4—N3—C8**	179.41 (18)
N1—C1	1.3121 (17)	**N3—C8—Si3**	115.60 (10)
Si3—C8	1.8494 (13)	**N3—C8—Si4**	115.58 (10)
Si3—C10	1.8539 (15)	**Si3—C8—Si4**	128.57 (7)
Si3—C11	1.8583 (16)	**N2—N1—C1—Si2**	−84 (25)
Si3—C9	1.8618 (15)	**N2—N1—C1—Si1**	98 (25)

Si4—C14	1.8468 (19)	**C5—Si2—C1—N1**	−117.59 (12)
Si4—C12	1.8506 (19)	**C6—Si2—C1—N1**	120.27 (12)
Si4—C13	1.8508 (17)	**C7—Si2—C1—N1**	1.54 (13)
Si4—C8	1.8527 (14)	**C5—Si2—C1—Si1**	59.18 (12)
N3—N4	1.1377 (19)	**C6—Si2—C1—Si1**	−62.96 (12)
N3—C8	1.3090 (17)	**C7—Si2—C1—Si1**	178.31 (10)
C3—Si1—C2	108.42 (13)	**C3—Si1—C1—N1**	−52.41 (16)
C3—Si1—C4	111.80 (16)	**C2—Si1—C1—N1**	66.54 (14)
C2—Si1—C4	108.72 (14)	**C4—Si1—C1—N1**	−174.57 (15)
C3—Si1—C1	109.26 (9)	**C3—Si1—C1—Si2**	130.80 (15)
C2—Si1—C1	110.06 (9)	**C2—Si1—C1—Si2**	−110.25 (13)
C4—Si1—C1	108.56 (9)	**C4—Si1—C1—Si2**	8.64 (17)
C1—Si2—C5	109.94 (7)	**N4—N3—C8—Si3**	−113 (16)
C1—Si2—C6	110.26 (8)	**N4—N3—C8—Si4**	72 (16)
C5—Si2—C6	110.55 (8)	**C10—Si3—C8—N3**	−123.57 (12)
C1—Si2—C7	106.96 (7)	**C11—Si3—C8—N3**	−3.90 (14)
C5—Si2—C7	109.77 (9)	**C9—Si3—C8—N3**	116.65 (12)
C6—Si2—C7	109.29 (9)	**C10—Si3—C8—Si4**	50.36 (11)
N2—N1—C1	179.60 (18)	**C11—Si3—C8—Si4**	170.04 (10)
N1—C1—Si2	115.06 (10)	**C9—Si3—C8—Si4**	−69.42 (11)
N1—C1—Si1	114.36 (10)	**C14—Si4—C8—N3**	93.64 (13)
Si2—C1—Si1	130.51 (8)	**C12—Si4—C8—N3**	−27.03 (14)
C8—Si3—C10	109.03 (7)	**C13—Si4—C8—N3**	−145.88 (13)
C8—Si3—C11	107.23 (7)	**C14—Si4—C8—Si3**	−80.29 (12)
C10—Si3—C11	110.52 (8)	**C12—Si4—C8—Si3**	159.03 (11)
C8—Si3—C9	110.67 (7)	**C13—Si4—C8—Si3**	40.19 (12)

Numbering scheme of $(Me_3Si)_2NNC$ (**34c**).

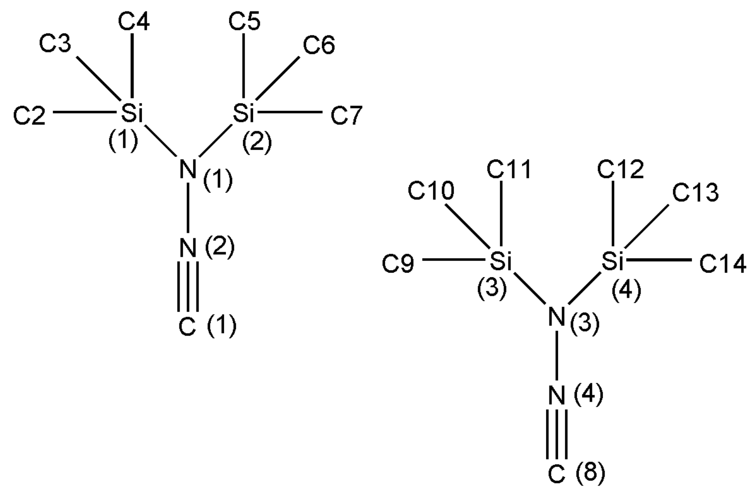


Table A3.17. Selected bond lengths (Å), angles and torsion angles (°) of $(Me_3Si)_2NNC$(**34c**).

Si1—N1	1.7765 (14)	**C11—Si3—C9**	112.10 (11)
Si1—C2	1.842 (2)	**C10—Si3—C9**	109.17 (11)
Si1—C4	1.849 (2)	**N3—Si4—C14**	106.32 (8)
Si1—C3	1.8525 (19)	**N3—Si4—C13**	109.91 (8)
Si2—N1	1.7740 (14)	**C14—Si4—C13**	111.13 (9)
Si2—C6	1.8457 (18)	**N3—Si4—C12**	109.52 (8)
Si2—C5	1.8487 (17)	**C14—Si4—C12**	110.00 (9)
Si2—C7	1.8506 (18)	**C13—Si4—C12**	109.89 (9)
N1—N2	1.3664 (18)	**N4—N3—Si4**	115.49 (10)
N2—C1	1.152 (2)	**N4—N3—Si3**	111.22 (10)
Si3—N3	1.7782 (14)	**Si4—N3—Si3**	133.19 (8)
Si3—C11	1.8378 (19)	**C8—N4—N3**	178.36 (18)
Si3—C10	1.8393 (19)	**C6—Si2—N1—N2**	50.23 (13)
Si3—C9	1.845 (2)	**C5—Si2—N1—N2**	169.97 (11)

Si4—N3	1.7780 (14)	**C7—Si2—N1—N2**	−69.38 (13)
Si4—C14	1.8463 (18)	**C6—Si2—N1—Si1**	−137.76 (11)
Si4—C13	1.8493 (19)	**C5—Si2—N1—Si1**	−18.01 (13)
Si4—C12	1.8561 (18)	**C7—Si2—N1—Si1**	102.64 (12)
N3—N4	1.3608 (18)	**C2—Si1—N1—N2**	2.13 (15)
N4—C8	1.153 (2)	**C4—Si1—N1—N2**	120.37 (13)
N1—Si1—C2	107.44 (8)	**C3—Si1—N1—N2**	−118.12 (14)
N1—Si1—C4	108.32 (8)	**C2—Si1—N1—Si2**	−169.63 (12)
C2—Si1—C4	109.53 (10)	**C4—Si1—N1—Si2**	−51.39 (13)
N1—Si1—C3	109.48 (9)	**C3—Si1—N1—Si2**	70.11 (14)
C2—Si1—C3	110.69 (10)	**Si2—N1—N2—C1**	−8 (5)
C4—Si1—C3	111.28 (11)	**Si1—N1—N2—C1**	178 (100)
N1—Si2—C6	107.53 (7)	**C14—Si4—N3—N4**	−6.49 (14)
N1—Si2—C5	107.63 (7)	**C13—Si4—N3—N4**	113.88 (13)
C6—Si2—C5	111.08 (9)	**C12—Si4—N3—N4**	−125.30 (13)
N1—Si2—C7	108.44 (8)	**C14—Si4—N3—Si3**	177.66 (12)
C6—Si2—C7	110.59 (9)	**C13—Si4—N3—Si3**	−61.97 (14)
C5—Si2—C7	111.41 (9)	**C12—Si4—N3—Si3**	58.85 (14)
N2—N1—Si2	112.08 (10)	**C11—Si3—N3—N4**	−178.07 (13)
N2—N1—Si1	116.04 (10)	**C10—Si3—N3—N4**	60.86 (14)
Si2—N1—Si1	131.45 (8)	**C9—Si3—N3—N4**	−57.31 (15)
C1—N2—N1	177.70 (19)	**C11—Si3—N3—Si4**	−2.09 (16)
N3—Si3—C11	106.44 (8)	**C10—Si3—N3—Si4**	−123.16 (12)
N3—Si3—C10	108.03 (8)	**C9—Si3—N3—Si4**	118.67 (14)
C11—Si3—C10	112.52 (10)	**Si4—N3—N4—C8**	172 (78)
N3—Si3—C9	108.39 (8)	**Si3—N3—N4—C8**	−11 (7)

Numbering scheme of **35**.

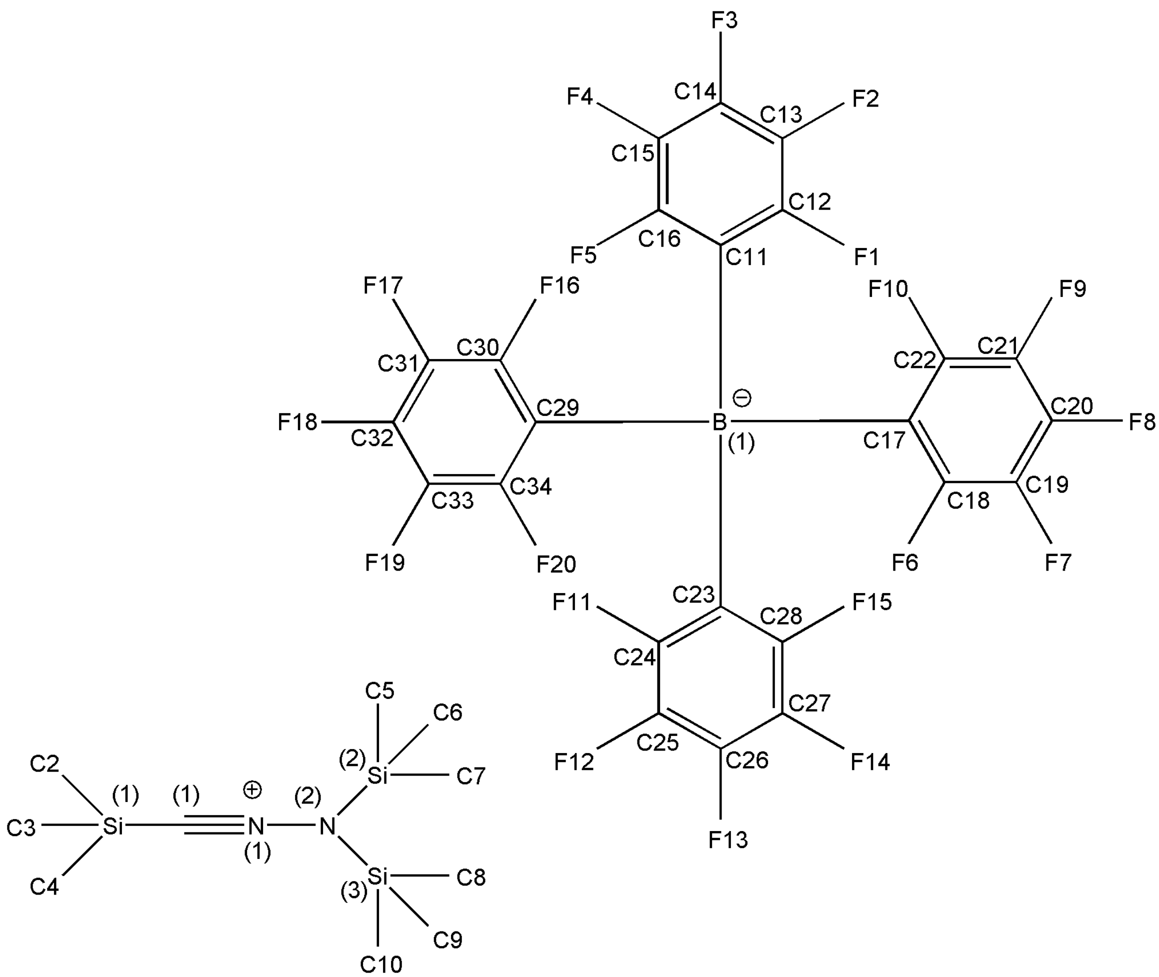


Table A3.18. Selected bond lengths (Å), angles and torsion angles (°) of **35**.

Si2—N2	1.8182 (11)	**C2—Si1—C4**	116.64 (16)
Si2—C6	1.8418 (15)	**C3—Si1—C1**	103.18 (8)
Si2—C7	1.8423 (18)	**C2—Si1—C1**	105.11 (10)
Si2—C5	1.8546 (18)	**C4—Si1—C1**	103.35 (11)
Si3—N2	1.8157 (11)	**N1—N2—Si3**	113.76 (8)
Si3—C10	1.8466 (16)	**N1—N2—Si2**	114.89 (8)
Si3—C9	1.8486 (16)	**Si3—N2—Si2**	131.34 (6)

Si3—C8	1.8487 (18)	**C1—N1—N2**	179.27 (13)
Si1—C3	1.8295 (18)	**N1—C1—Si1**	174.58 (14)
Si1—C2	1.842 (2)	**C10—Si3—N2—N1**	28.81 (11)
Si1—C4	1.847 (3)	**C9—Si3—N2—N1**	−90.50 (11)
Si1—C1	1.8973 (15)	**C8—Si3—N2—N1**	149.29 (10)
N2—N1	1.3090 (15)	**C10—Si3—N2—Si2**	−152.14 (9)
N1—C1	1.1427 (18)	**C9—Si3—N2—Si2**	88.55 (11)
N2—Si2—C6	108.65 (6)	**C8—Si3—N2—Si2**	−31.66 (11)
N2—Si2—C7	105.66 (8)	**C6—Si2—N2—N1**	−105.27 (10)
C6—Si2—C7	113.73 (10)	**C7—Si2—N2—N1**	132.34 (12)
N2—Si2—C5	105.05 (6)	**C5—Si2—N2—N1**	12.95 (11)
C6—Si2—C5	110.46 (8)	**C6—Si2—N2—Si3**	75.68 (10)
C7—Si2—C5	112.72 (11)	**C7—Si2—N2—Si3**	−46.70 (13)
N2—Si3—C10	105.41 (6)	**C5—Si2—N2—Si3**	−166.10 (9)
N2—Si3—C9	107.97 (6)	**Si3—N2—N1—C1**	−2 (14)
C10—Si3—C9	111.53 (9)	**Si2—N2—N1—C1**	178 (100)
N2—Si3—C8	105.78 (7)	**N2—N1—C1—Si1**	−67 (15)
C10—Si3—C8	113.47 (8)	**C3—Si1—C1—N1**	41.5 (14)
C9—Si3—C8	112.13 (9)	**C2—Si1—C1—N1**	160.5 (14)
C3—Si1—C2	113.36 (11)	**C4—Si1—C1—N1**	−76.7 (14)
C3—Si1—C4	113.27 (11)		

Numbering scheme of **36**.

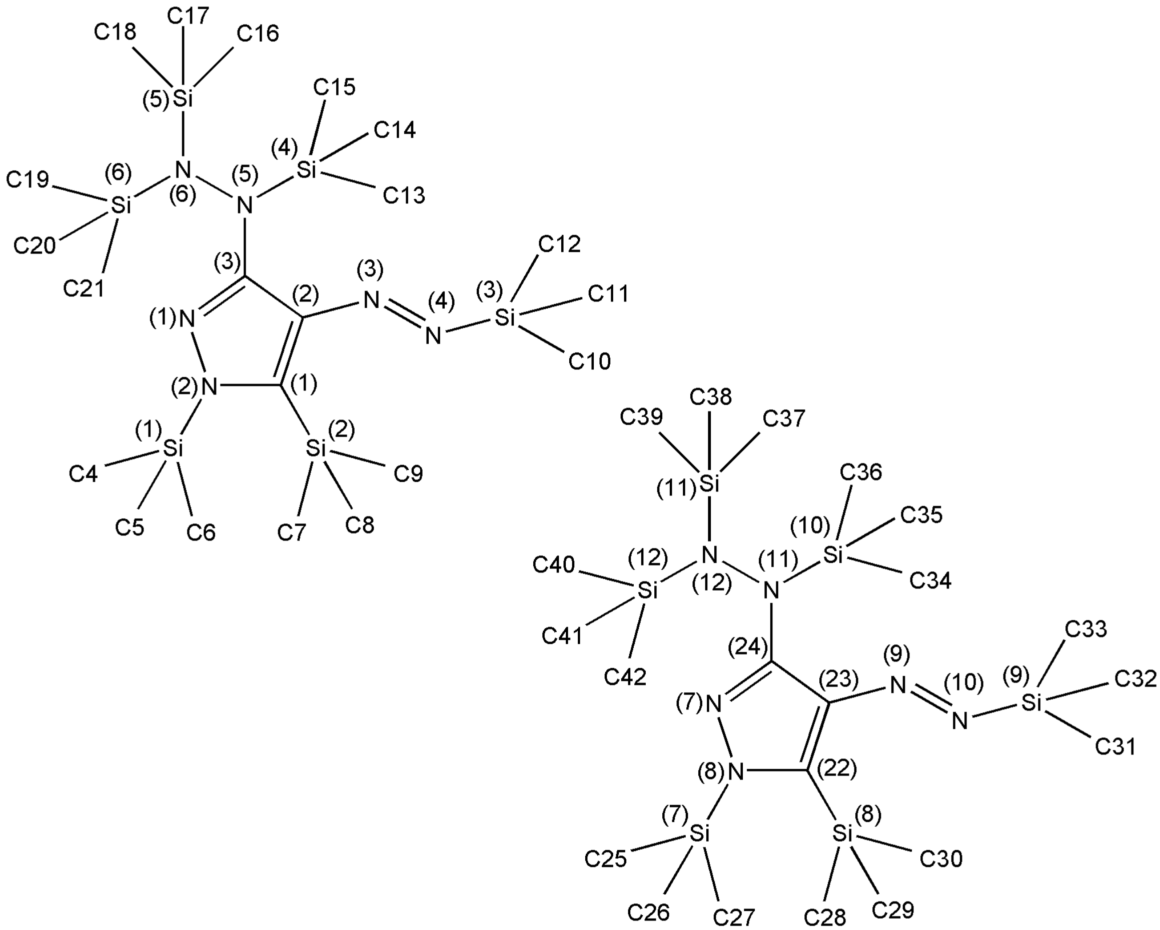


Table A3.19. Selected bond lengths (Å), angles and torsion angles (°) of **36**.

Si1—N2	1.8000 (18)	**Si7—N8**	1.7948 (15)
Si1—C4	1.849 (2)	**Si7—C26**	1.850 (2)
Si1—C5	1.852 (3)	**Si7—C25**	1.853 (2)
Si1—C6	1.866 (2)	**Si7—C27**	1.854 (2)
Si2—C8	1.863 (2)	**Si8—C29**	1.857 (2)
Si2—C7	1.867 (2)	**Si8—C30**	1.869 (2)
Si2—C9	1.869 (2)	**Si8—C28**	1.869 (2)
Si2—C1	1.8956 (19)	**Si8—C22**	1.8956 (18)

Si3—N4	1.7874 (19)	**Si9—N10**	1.7893 (17)
Si3—C12	1.832 (3)	**Si9—C33**	1.833 (3)
Si3—C11	1.844 (3)	**Si9—C32**	1.841 (3)
Si3—C10	1.848 (2)	**Si9—C31**	1.856 (3)
Si4—N5	1.7710 (18)	**Si10—N11**	1.7643 (16)
Si4—C14	1.859 (3)	**Si10—C35**	1.859 (2)
Si4—C13	1.860 (3)	**Si10—C36**	1.861 (2)
Si4—C15	1.869 (2)	**Si10—C34**	1.866 (2)
Si5—N6	1.7486 (18)	**Si11—N12**	1.7442 (16)
Si5—C16	1.853 (2)	**Si11—C39**	1.850 (2)
Si5—C17	1.860 (3)	**Si11—C38**	1.857 (2)
Si5—C18	1.861 (3)	**Si11—C37**	1.870 (2)
Si6—N6	1.7470 (18)	**Si12—N12**	1.7445 (16)
Si6—C21	1.859 (2)	**Si12—C40**	1.853 (2)
Si6—C19	1.865 (3)	**Si12—C42**	1.862 (2)
Si6—C20	1.874 (2)	**Si12—C41**	1.871 (2)
N1—C3	1.324 (3)	**N7—C24**	1.320 (2)
N1—N2	1.400 (2)	**N7—N8**	1.396 (2)
N2—C1	1.355 (2)	**N8—C22**	1.364 (2)
N3—N4	1.272 (2)	**N9—N10**	1.272 (2)
N3—C2	1.389 (3)	**N9—C23**	1.395 (2)
N5—C3	1.387 (2)	**N11—C24**	1.380 (2)
N5—N6	1.455 (2)	**N11—N12**	1.4634 (19)
C1—C2	1.398 (3)	**C22—C23**	1.396 (2)
C2—C3	1.425 (3)	**C23—C24**	1.430 (2)
N2—Si1—C4	107.35 (10)	**N8—Si7—C26**	109.74 (9)
N2—Si1—C5	109.57 (10)	**N8—Si7—C25**	106.52 (9)
C4—Si1—C5	109.43 (13)	**C26—Si7—C25**	110.18 (11)

N2—Si1—C6	109.97 (10)	**N8—Si7—C27**	109.45 (9)
C4—Si1—C6	107.31 (13)	**C26—Si7—C27**	113.50 (10)
C5—Si1—C6	113.04 (13)	**C25—Si7—C27**	107.20 (12)
C8—Si2—C7	108.36 (12)	**C29—Si8—C30**	113.43 (11)
C8—Si2—C9	112.18 (12)	**C29—Si8—C28**	108.04 (11)
C7—Si2—C9	103.32 (12)	**C30—Si8—C28**	103.05 (10)
C8—Si2—C1	114.80 (10)	**C29—Si8—C22**	113.70 (9)
C7—Si2—C1	107.79 (10)	**C30—Si8—C22**	108.95 (9)
C9—Si2—C1	109.67 (10)	**C28—Si8—C22**	109.06 (9)
N4—Si3—C12	111.01 (12)	**N10—Si9—C33**	110.71 (10)
N4—Si3—C11	108.85 (12)	**N10—Si9—C32**	108.86 (11)
C12—Si3—C11	112.1 (2)	**C33—Si9—C32**	113.30 (16)
N4—Si3—C10	102.85 (11)	**N10—Si9—C31**	104.47 (11)
C12—Si3—C10	109.97 (18)	**C33—Si9—C31**	109.58 (17)
C11—Si3—C10	111.74 (13)	**C32—Si9—C31**	109.55 (15)
N5—Si4—C14	110.77 (12)	**N11—Si10—C35**	110.01 (10)
N5—Si4—C13	110.48 (11)	**N11—Si10—C36**	109.08 (9)
C14—Si4—C13	112.20 (14)	**C35—Si10—C36**	107.40 (11)
N5—Si4—C15	109.14 (10)	**N11—Si10—C34**	110.27 (10)
C14—Si4—C15	106.63 (13)	**C35—Si10—C34**	112.90 (12)
C13—Si4—C15	107.46 (13)	**C36—Si10—C34**	107.04 (12)
N6—Si5—C16	110.79 (10)	**N12—Si11—C39**	114.65 (10)
N6—Si5—C17	109.39 (11)	**N12—Si11—C38**	109.36 (9)
C16—Si5—C17	108.65 (14)	**C39—Si11—C38**	106.34 (12)
N6—Si5—C18	110.82 (11)	**N12—Si11—C37**	107.69 (9)
C16—Si5—C18	108.77 (13)	**C39—Si11—C37**	107.38 (11)
C17—Si5—C18	108.35 (15)	**C38—Si11—C37**	111.46 (11)
N6—Si6—C21	109.27 (10)	**N12—Si12—C40**	110.92 (9)

N6—Si6—C19	115.45 (10)	**N12—Si12—C42**	110.00 (10)
C21—Si6—C19	106.77 (13)	**C40—Si12—C42**	108.94 (12)
N6—Si6—C20	107.44 (10)	**N12—Si12—C41**	110.27 (10)
C21—Si6—C20	110.07 (12)	**C40—Si12—C41**	109.86 (11)
C19—Si6—C20	107.79 (13)	**C42—Si12—C41**	106.75 (12)
C3—N1—N2	105.68 (15)	**C24—N7—N8**	105.91 (14)
C1—N2—N1	111.96 (15)	**C22—N8—N7**	111.97 (14)
C1—N2—Si1	135.16 (13)	**C22—N8—Si7**	134.42 (12)
N1—N2—Si1	110.63 (12)	**N7—N8—Si7**	111.57 (11)
N4—N3—C2	113.86 (16)	**N10—N9—C23**	114.05 (16)
N3—N4—Si3	116.57 (14)	**N9—N10—Si9**	114.92 (13)
C3—N5—N6	114.27 (16)	**C24—N11—N12**	113.89 (14)
C3—N5—Si4	127.07 (13)	**C24—N11—Si10**	128.02 (12)
N6—N5—Si4	118.39 (12)	**N12—N11—Si10**	117.96 (11)
N5—N6—Si6	117.60 (12)	**N11—N12—Si11**	117.25 (11)
N5—N6—Si5	113.46 (12)	**N11—N12—Si12**	114.14 (11)
Si6—N6—Si5	128.29 (10)	**Si11—N12—Si12**	128.13 (9)
N2—C1—C2	105.47 (16)	**N8—C22—C23**	105.21 (15)
N2—C1—Si2	127.51 (15)	**N8—C22—Si8**	127.76 (13)
C2—C1—Si2	124.43 (15)	**C23—C22—Si8**	124.76 (13)
N3—C2—C1	128.06 (17)	**N9—C23—C22**	128.17 (16)
N3—C2—C3	124.86 (17)	**N9—C23—C24**	124.86 (16)
C1—C2—C3	106.73 (17)	**C22—C23—C24**	106.73 (15)
N1—C3—N5	121.04 (17)	**N7—C24—N11**	121.54 (16)
N1—C3—C2	110.01 (17)	**N7—C24—C23**	110.00 (16)
N5—C3—C2	128.95 (18)	**N11—C24—C23**	128.46 (16)
C3—N1—N2—C1	0.3 (2)	**C24—N7—N8—C22**	0.7 (2)
C3—N1—N2—Si1	165.86 (13)	**C24—N7—N8—Si7**	−165.47 (12)

C2—N3—N4—Si3	177.68 (13)	**C23—N9—N10—Si9**	−176.79 (12)
C3—N5—N6—Si6	−80.68 (18)	**C24—N11—N12—Si11**	83.68 (17)
Si4—N5—N6—Si6	93.79 (15)	**Si10—N11—N12—Si11**	−92.32 (13)
C3—N5—N6—Si5	90.86 (17)	**C24—N11—N12—Si12**	−89.07 (16)
Si4—N5—N6—Si5	−94.67 (14)	**Si10—N11—N12—Si12**	94.92 (13)
N1—N2—C1—C2	2.2 (2)	**N7—N8—C22—C23**	−3.1 (2)
Si1—N2—C1—C2	−158.55 (16)	**Si7—N8—C22—C23**	158.75 (15)
N1—N2—C1—Si2	−160.03 (14)	**N7—N8—C22—Si8**	160.19 (14)
Si1—N2—C1—Si2	39.2 (3)	**Si7—N8—C22—Si8**	−37.9 (3)
N4—N3—C2—C1	−9.0 (3)	**N10—N9—C23—C22**	7.7 (3)
N4—N3—C2—C3	163.29 (19)	**N10—N9—C23—C24**	−165.92 (17)
N2—C1—C2—N3	169.77 (19)	**N8—C22—C23—N9**	−170.35 (17)
Si2—C1—C2—N3	−27.3 (3)	**Si8—C22—C23—N9**	25.7 (3)
N2—C1—C2—C3	−3.6 (2)	**N8—C22—C23—C24**	4.15 (19)
Si2—C1—C2—C3	159.30 (14)	**Si8—C22—C23—C24**	−159.81 (13)
N2—N1—C3—N5	178.06 (16)	**N8—N7—C24—N11**	−178.56 (16)
N2—N1—C3—C2	−2.6 (2)	**N8—N7—C24—C23**	2.0 (2)
N6—N5—C3—N1	9.1 (3)	**N12—N11—C24—N7**	−9.6 (2)
Si4—N5—C3—N1	−164.78 (16)	**Si10—N11—C24—N7**	165.90 (14)
N6—N5—C3—C2	−170.08 (19)	**N12—N11—C24—C23**	169.68 (17)
Si4—N5—C3—C2	16.0 (3)	**Si10—N11—C24—C23**	−14.8 (3)
N3—C2—C3—N1	−169.66 (18)	**N9—C23—C24—N7**	170.76 (17)
C1—C2—C3—N1	4.0 (2)	**C22—C23—C24—N7**	−4.0 (2)
N3—C2—C3—N5	9.6 (3)	**N9—C23—C24—N11**	−8.6 (3)
C1—C2—C3—N5	−176.74 (19)	**C22—C23—C24—N11**	176.66 (18)

Numbering scheme of **36b**.

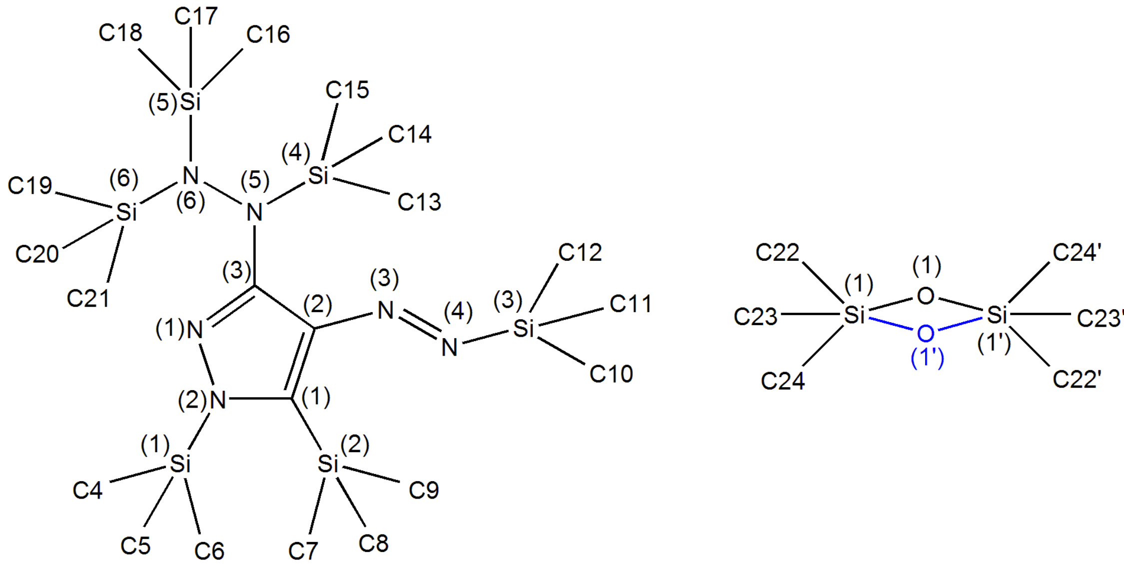


Table A3.20. Selected bond lengths (Å), angles and torsion angles (°) of **36b**.

N1—C3	1.3246 (17)	**Si5—N6—Si6**	128.25 (6)
N1—N2	1.3965 (14)	**N2—C1—C2**	105.18 (10)
N2—C1	1.3637 (16)	**N2—C1—Si2**	127.92 (9)
N2—Si1	1.7917 (11)	**C2—C1—Si2**	124.60 (10)
N3—N4	1.2711 (15)	**N3—C2—C1**	128.02 (11)
N3—C2	1.3975 (16)	**N3—C2—C3**	124.74 (11)
N4—Si3	1.7877 (12)	**C1—C2—C3**	106.81 (11)
N5—C3	1.3882 (15)	**N1—C3—N5**	121.68 (11)
N5—N6	1.4611 (14)	**N1—C3—C2**	109.88 (11)
N5—Si4	1.7647 (11)	**N5—C3—C2**	128.43 (11)
N6—Si5	1.7490 (12)	**O1—Si7—C23**	122.9 (2)
N6—Si6	1.7519 (11)	**O1^{i}—Si7—C23**	94.9 (2)
Si1—C6	1.8491 (16)	**O1—Si7—C22**	94.5 (2)
Si1—C5	1.8501 (18)	**O1^{i}—Si7—C22**	119.1 (2)

Si1—C4	1.8509 (19)	**C23—Si7—C22**	111.2 (2)
Si2—C8	1.8605 (16)	**O1—Si7—C24**	105.5 (2)
Si2—C9	1.8708 (16)	**O1^{i}—Si7—C24**	109.5 (2)
Si2—C7	1.8764 (16)	**C23—Si7—C24**	111.27 (16)
Si2—C1	1.8971 (13)	**C22—Si7—C24**	110.1 (2)
Si3—C10	1.8497 (17)	**Si7—O1—Si7^{i}**	149.4 (2)
Si3—C11	1.8504 (19)	**C3—N1—N2—C1**	−0.20 (14)
Si3—C12	1.8509 (19)	**C3—N1—N2—Si1**	165.61 (9)
Si4—C13	1.8623 (17)	**C2—N3—N4—Si3**	−179.82 (9)
Si4—C14	1.8627 (17)	**C3—N5—N6—Si5**	90.72 (11)
Si4—C15	1.8695 (15)	**Si4—N5—N6—Si5**	−94.90 (9)
Si5—C18	1.8549 (17)	**C3—N5—N6—Si6**	−81.91 (12)
Si5—C17	1.8597 (19)	**Si4—N5—N6—Si6**	92.46 (10)
Si5—C16	1.8697 (17)	**N1—N2—C1—C2**	2.71 (14)
Si6—C19	1.8559 (17)	**Si1—N2—C1—C2**	−158.85 (10)
Si6—C21	1.8620 (18)	**N1—N2—C1—Si2**	−160.48 (9)
Si6—C20	1.8700 (15)	**Si1—N2—C1—Si2**	37.96 (19)
C1—C2	1.4009 (17)	**N4—N3—C2—C1**	−9.60 (19)
C2—C3	1.4281 (17)	**N4—N3—C2—C3**	161.87 (12)
Si7—O1	1.612 (4)	**N2—C1—C2—N3**	168.69 (12)
Si7—O1^{i}	1.623 (4)	**Si2—C1—C2—N3**	−27.41 (19)
Si7—C23	1.810 (3)	**N2—C1—C2—C3**	−4.00 (14)
Si7—C22	1.833 (3)	**Si2—C1—C2—C3**	159.91 (9)
Si7—C24	1.836 (3)	**N2—N1—C3—N5**	178.34 (11)
O1—Si7^{i}	1.623 (4)	**N2—N1—C3—C2**	−2.41 (14)
C3—N1—N2	106.00 (10)	**N6—N5—C3—N1**	14.17 (17)
C1—N2—N1	111.95 (10)	**Si4—N5—C3—N1**	−159.65 (10)
C1—N2—Si1	134.02 (9)	**N6—N5—C3—C2**	−164.93 (12)

N1—N2—Si1	111.90 (8)	**Si4—N5—C3—C2**	21.26 (19)
N4—N3—C2	114.07 (11)	**N3—C2—C3—N1**	−168.88 (12)
N3—N4—Si3	114.73 (9)	**C1—C2—C3—N1**	4.11 (15)
C3—N5—N6	114.07 (10)	**N3—C2—C3—N5**	10.3 (2)
C3—N5—Si4	127.06 (9)	**C1—C2—C3—N5**	−176.70 (12)
N6—N5—Si4	118.60 (8)	**C23—Si7—O1—Si7^{i}**	26.6 (9)
N5—N6—Si5	113.53 (8)	**C22—Si7—O1—Si7^{i}**	145.5 (8)
N5—N6—Si6	117.73 (8)	**C24—Si7—O1—Si7^{i}**	−102.2 (8)

(i) z+2. −*x*+1, −*y*, −*z*+1.

Numbering scheme of **37**.

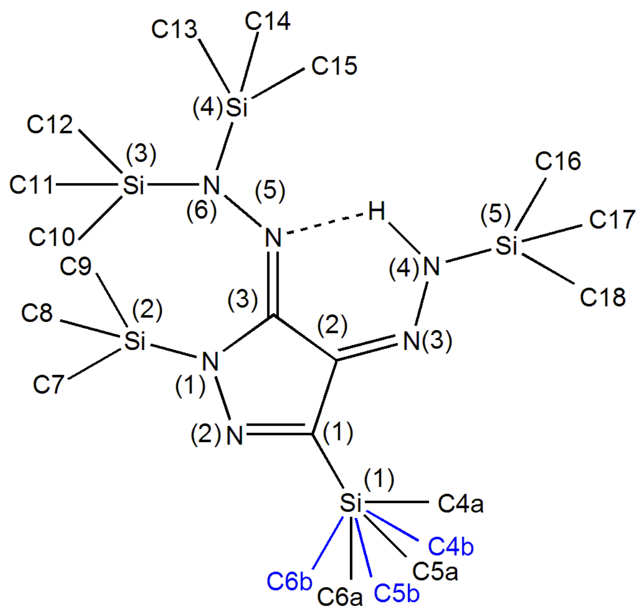


Table A3.21. Selected bond lengths (Å), angles and torsion angles (°) of **37**.

Si1—C4B	1.79 (2)	**N3—N4—H4**	115.3 (19)
Si1—C5A	1.790 (10)	**Si5—N4—H4**	125.6 (19)
Si1—C6B	1.79 (3)	**C3—N5—N6**	116.67 (19)
Si1—C4A	1.862 (14)	**N5—N6—Si4**	104.67 (14)
Si1—C6A	1.868 (14)	**N5—N6—Si3**	107.12 (14)
Si1—C1	1.870 (2)	**Si4—N6—Si3**	126.29 (12)
Si1—C5B	1.983 (17)	**N2—C1—C2**	109.4 (2)
Si2—N1	1.792 (2)	**N2—C1—Si1**	120.66 (18)
Si2—C9	1.835 (3)	**C2—C1—Si1**	129.88 (18)
Si2—C7	1.841 (4)	**N3—C2—C1**	123.4 (2)
Si2—C8	1.844 (4)	**N3—C2—C3**	130.3 (2)
Si3—N6	1.760 (2)	**C1—C2—C3**	106.2 (2)
Si3—C10	1.855 (3)	**N5—C3—N1**	135.0 (2)

Si3—C11	1.864 (3)	**N5—C3—C2**	119.3 (2)
Si3—C12	1.865 (3)	**N1—C3—C2**	105.67 (19)
Si4—N6	1.755 (2)	**C3—N1—N2—C1**	1.2 (3)
Si4—C15	1.850 (3)	**Si2—N1—N2—C1**	−170.32 (17)
Si4—C13	1.858 (3)	**C2—N3—N4—Si5**	173.39 (18)
Si4—C14	1.867 (3)	**C3—N1—N2—C1**	1.2 (3)
Si5—N4	1.740 (2)	**C3—N5—N6—Si4**	122.48 (19)
Si5—C18	1.845 (3)	**C3—N5—N6—Si3**	−101.4 (2)
Si5—C16	1.848 (3)	**N1—N2—C1—C2**	0.3 (3)
Si5—C17	1.859 (4)	**N1—N2—C1—Si1**	177.59 (16)
N1—C3	1.381 (3)	**N4—N3—C2—C1**	−179.6 (2)
N1—N2	1.433 (3)	**N4—N3—C2—C3**	−1.5 (4)
N2—C1	1.314 (3)	**N2—C1—C2—N3**	176.8 (2)
N3—C2	1.310 (3)	**Si1—C1—C2—N3**	−0.1 (4)
N3—N4	1.348 (3)	**N2—C1—C2—C3**	−1.7 (3)
N4—H4	0.84 (3)	**Si1—C1—C2—C3**	−178.60 (18)
N5—C3	1.307 (3)	**N6—N5—C3—N1**	0.0 (4)
N5—N6	1.467 (3)	**N6—N5—C3—C2**	177.71 (19)
C1—C2	1.437 (3)	**N2—N1—C3—N5**	175.8 (3)
C2—C3	1.470 (3)	**Si2—N1—C3—N5**	−18.4 (5)
C3—N1—N2	108.97 (18)	**N2—N1—C3—C2**	−2.2 (2)
C3—N1—Si2	144.72 (16)	**Si2—N1—C3—C2**	163.6 (2)
N2—N1—Si2	105.32 (15)	**N3—C2—C3—N5**	5.6 (4)
C1—N2—N1	109.67 (19)	**C1—C2—C3—N5**	−176.0 (2)
C2—N3—N4	118.33 (19)	**N3—C2—C3—N1**	−176.0 (2)
N3—N4—Si5	118.51 (16)	**C1—C2—C3—N1**	2.4 (2)

Curriculum Vitae

Personal Data.

Name :	Muhammad farooq Ibad
Nationality :	Afghan
Email :	Farooq_ebad@yahoo.com

Academics.

2006-2008	Studied M.phil. leading to Phd in ICCBS University of Karachi, Pakistan.
2004	MSc. Chemistry in Institute of Chemical Sciences (previously Department of Chemistry) University of Peshawar, NWFP Pakistan.
2002	BSc. in natural sciences Govt. Post Graduate Collage Charsada, NWFP, Pakistan.
2000	FSc. Pre Medical Govt. Post Graduate Collage Charsada, NWFP, Pakistan.
1998	SSc. Shabqadar Model High School, Shabqadar, NWFP, Pakistan

Scholarships awarded

1. Scholarship Awarded by DAAD as doctoral researcher for the year 2008 to 2012 at Universität Rostock, Germany.

2. Junior research fellowship awarded by International Center for Chemical Sciences, H.E.J. Research Institute of Chemistry, University of Karachi, Pakistan. 2006-2008.

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