Synthesis of Functionalized Quinolines, Flavones, Coumarins, Naphthoates and Phthalates by Site-Selective Suzuki-Miyaura Cross-Coupling Reactions

Dissertation

zur

Erlangung des akademischen Grades

doctor rerum naturalium (Dr. rer. nat.)

der Mathematisch-Naturwissenschaftlichen Fakultät

der Universität Rostock

vorgelegt von

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Rostock, 2012

urn:nbn:de:gbv:28-diss2012-0067-9

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Tag der Promotion: 19.06.2012

DEDICATION

“I feel a great pleasure to dedicate all of this work to ***Zakho University***, then to all my colleagues in the department of chemistry of Zakho University and to my dear mother, wife, son, brother and sister.

ACKNOWLEDGMENTS

When the letters gather to form a word of thanks for the basic ordinary person it will be an easy task, but it fails in front of a great God willing to give his blessing thankful worshiper the patience and perseverance, and to grow inside him the mind of an ambitious lover of science and learning. His great willing chose me to be one of those whom the Lord subservient to search for the correct information and the specific knowledge not only to achieve a scientific degree but also to provide such knowledge to those seeking it. So for the Almighty Lord loving all the gratefulness, love and obedience forever.

I would like to thank my supervisor Prof. Dr. Dr. h.c. Peter Langer for providing efficient guidance and energetic research environment during my whole Ph.D. I always found him ready to facilitate my research by effective discussions, reviving encouragements, unending trust, providing free hand in research and access to every possible facility.

Great thanks to Prof. Christian Vogel who supported me and provided good knowledge in carbohydrate chemistry.

I would like to thank the Iraqi cultural attaché in Germany Prof Dr. Salah M. Aliwi for his support and encouragement.

I wish to express my special gratitude to Dr. Martin Hein and Dr. Dirk Michalik for a number of nice talks about my research, to Dr. Holger Feist for his passion to deliver security instruction and making sure the security, to Dr. Alexander Villinger for his professional and accurate X-ray crystallographic analyses. I would also like to thank the members of the NMR, IR, UV, MS, and X-ray laboratories of the University of Rostock and of the Leibniz Institute for Catalysis Rostock.

I'd like to thank the technical and non-technical staff of the Institute of Chemistry, especially Anne Hallmann, Claudia Vinke and Jana Unger for their tremendous support during my stay.

I would like to take the opportunity to especially thank the DAAD Foundation for providing me a scholarship, deep gratitude for the contact person of Iraqi section Frau Steuernagel, Frau Sandra and the head master of Iraqi section Mr Alexander Haridi for their kindness. I want to thank all of my friends, for supporting me and for their

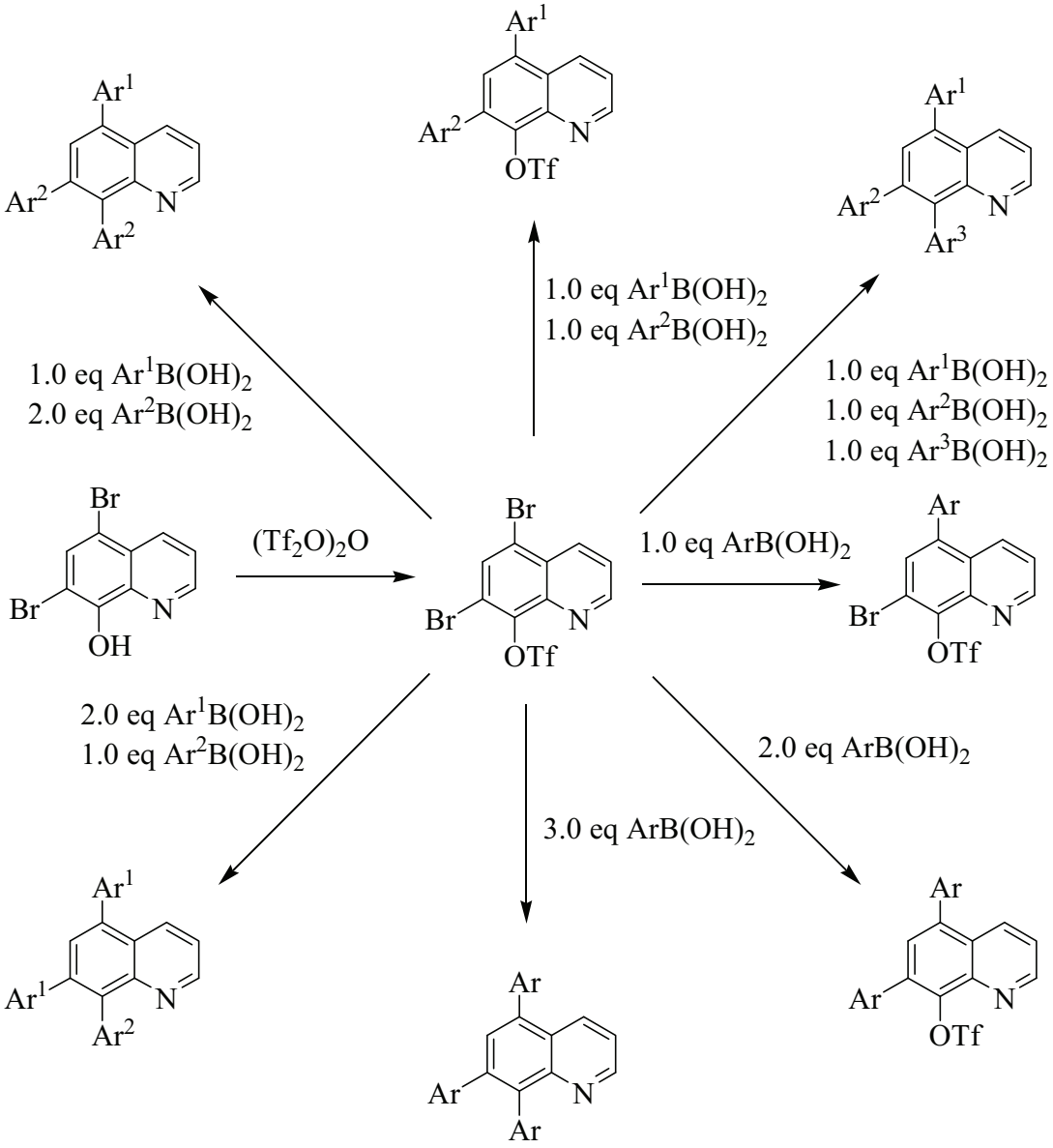
cordiality, especially Mr Friedrich Erben and Frau Verena Specowius and all Iraqi colleagues, Dr. Ahmad, Dhafer, Ghazwan and Omer.
Finally, I would like to thank my mother, who waits alone in Iraq for me to return with Ph.D.; from me all the love for her and a great thank to my wife Fadia who has supported me in all circumstances and my son Karas who gave me joy and hope to move on. Also I do not forget my brother Fadi and my sister Fadia who saved my life in Iraq.

Nadi

SUMMARY

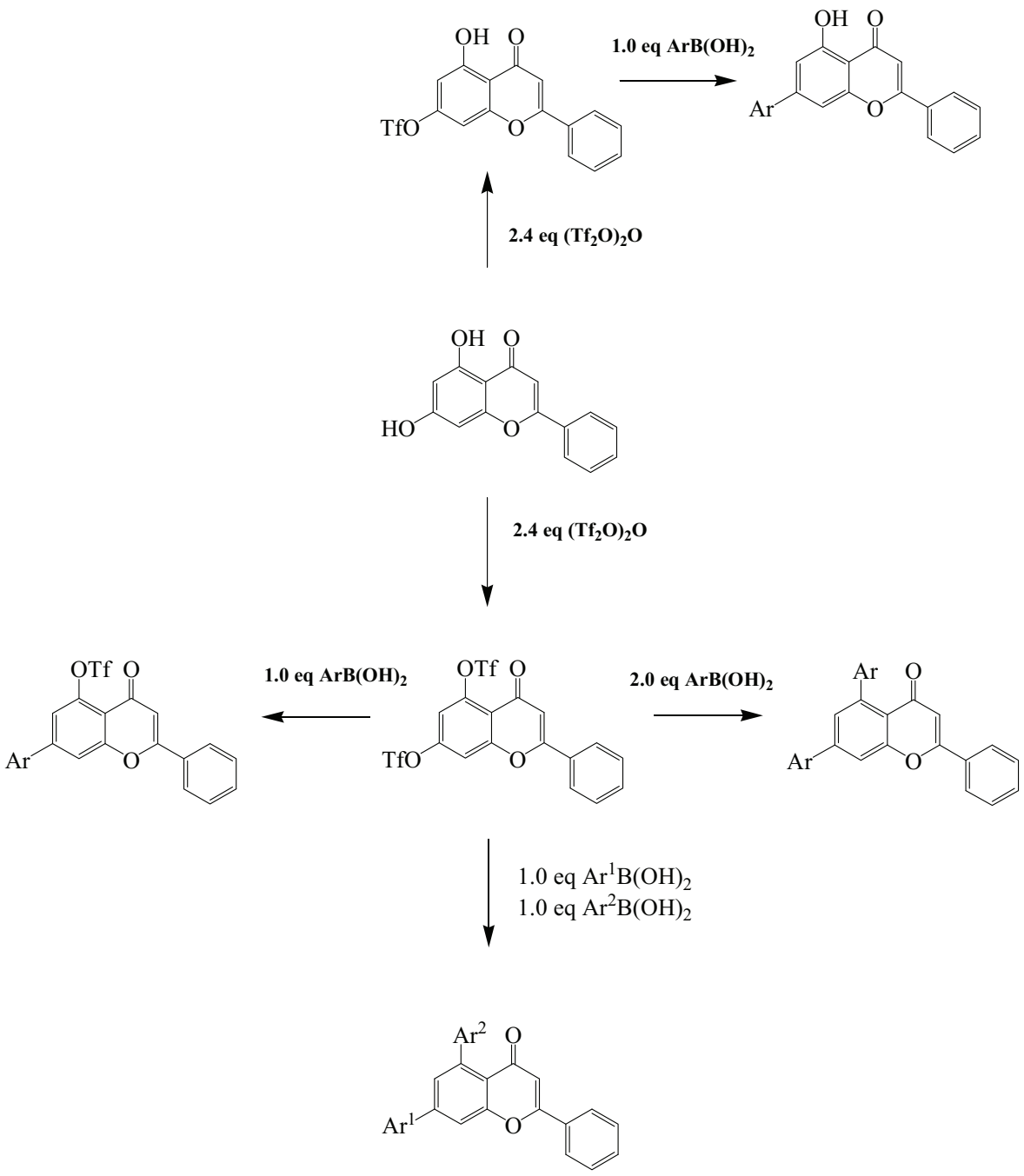
A significant part of this dissertation has been published (see list of publications). The task of my thesis was to study palladium(0)-catalyzed Suzuki cross-coupling reactions of various types of triflates or bromine compounds of different molecules (quinolines, flavones, coumarines, naphthaoates and tetrabromophthalates). The triflates are readily available from the corresponding hydroxy compounds. The issue of site-selectivity plays an important role in my thesis. In this context, steric and electronic parameters have been investigated.

I was studying palladium(0)-catalyzed Suzuki cross-coupling reactions of 5,7-dibromo-8-(trifluoromethanesulfonyloxy)quinoline. The reactions proceed with excellent site-selectivity. The first, second and third attack occur at positions 5, 7 and 8, respectively. The first attack occurs at position 5 (bromide) which is sterically less hindered than position 7 (bromide) (Scheme I). The second attack occurs at position 7 and the third attack occurs at position 8 (triflate).



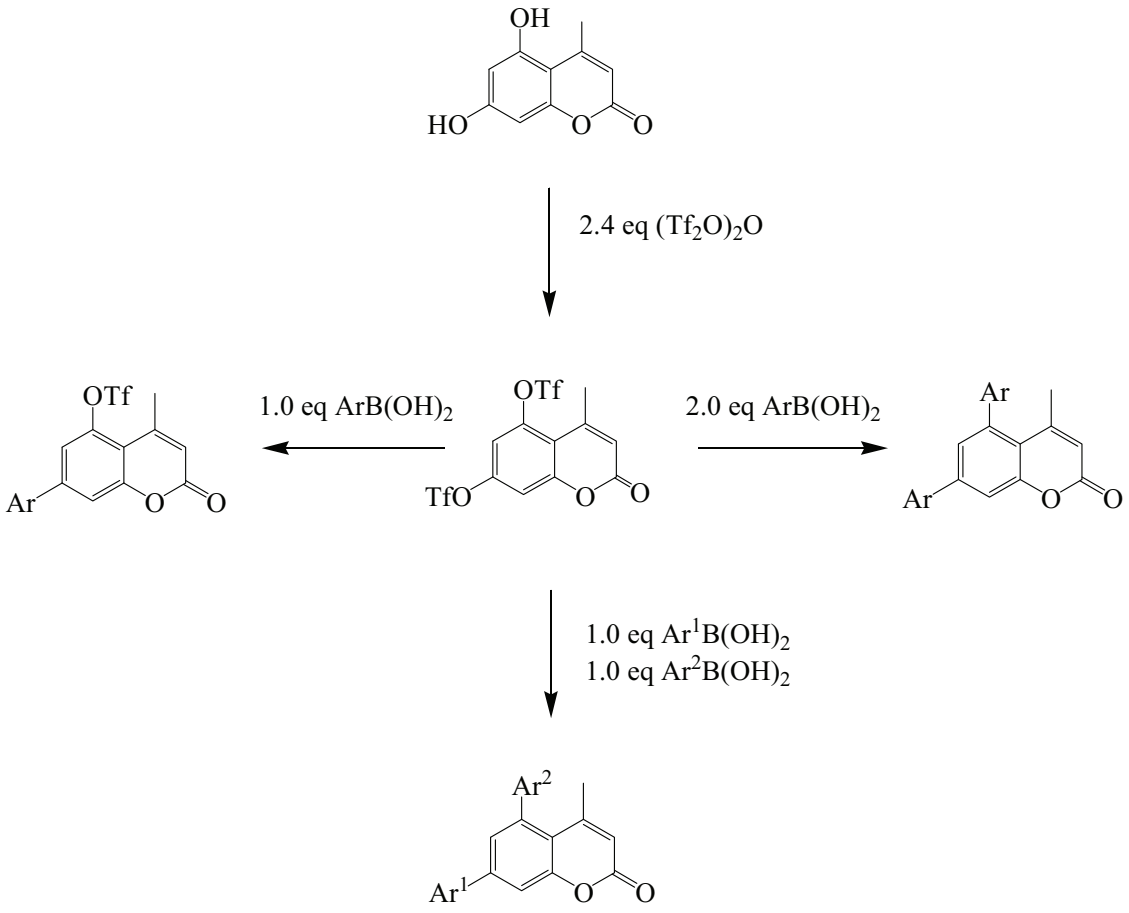
Scheme I

Suzuki-Miyaura reactions of the bis(triflate) of 5,7-dihydroxyflavone proceed with very good site-selectivity in favour of position 7 which is electronically less deficient and sterically less hindered than position 5 (Scheme II). The reaction of 5,7-dihydroxyflavone with one equivalent of triflic anhydride proceeds also with very good site-selectivity in favour of position 7. The subsequent Suzuki-Miyaura reaction of the product allows for the synthesis of 7-aryl-5-hydroxyflavones.


OH
O
TfO
O
1.0 eq ArB(OH)2
Ar
2.4 eq (Tf2O)2O
HO
OTf
1.0 eq ArB(OH)2
2.0 eq ArB(OH)2
1.0 eq Ar1B(OH)2
1.0 eq Ar2B(OH)2
Ar2
Ar1

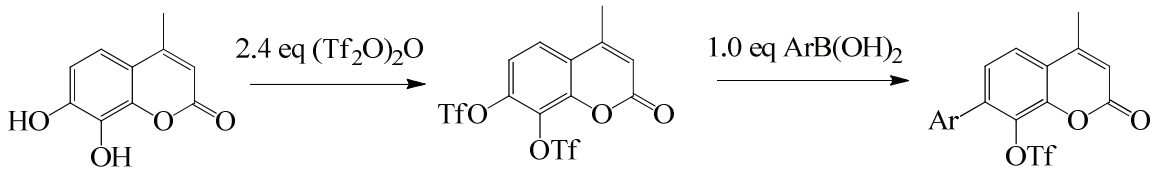
Scheme II

The palladium(0)-catalyzed Suzuki cross-coupling reaction of the bis(triflate) of 4-methyl-5,7-dihydroxycoumarin afforded various 4-methyl-5,7-diaryl-coumarins with very good site-selectivity. The first attack occurred at the sterically less hindered position C-7 (Scheme III).



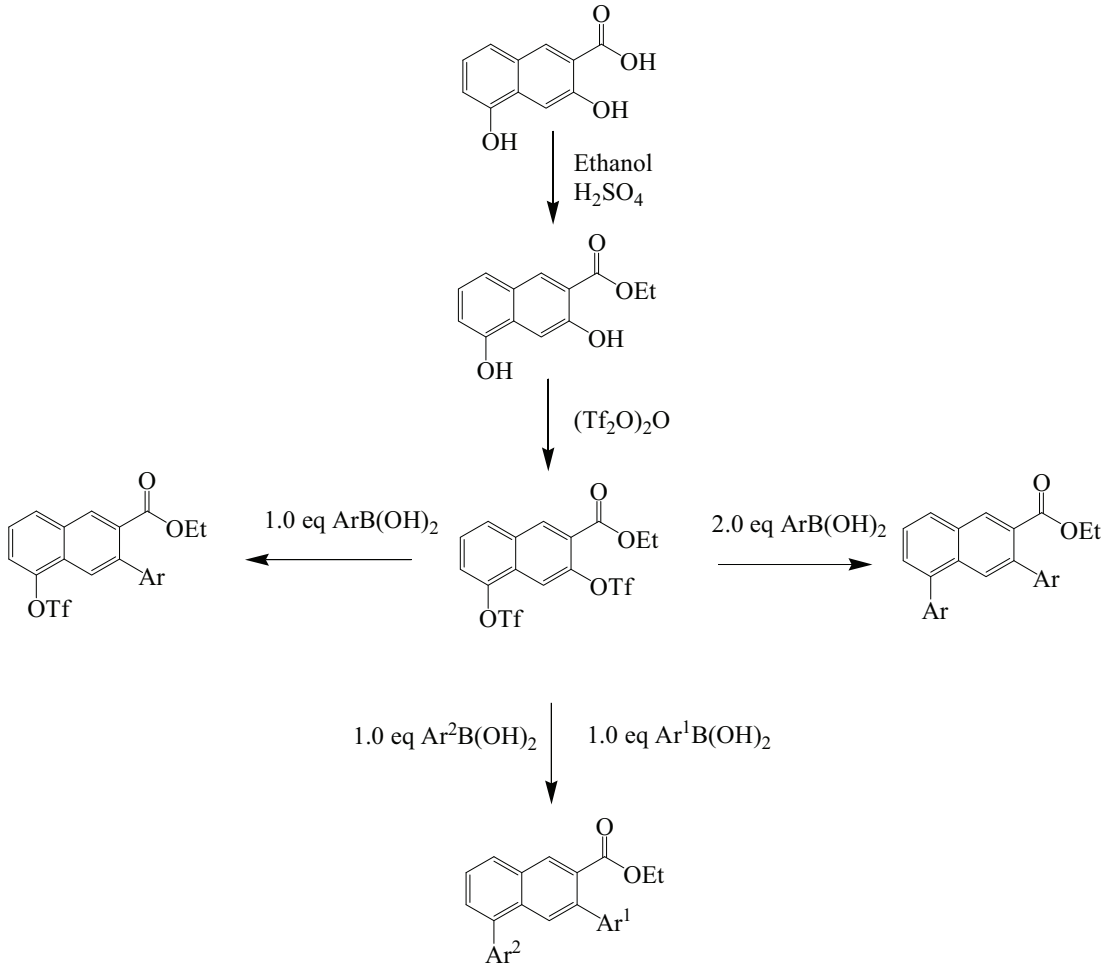
Scheme III

The palladium(0)-catalyzed Suzuki cross-coupling reaction of the bis(triflate) of 4-methyl-7,8-dihydroxycoumarin afforded various 4-methyl-7-aryl-8-(trifluoromethanesulfonate)coumarins (Scheme IV).



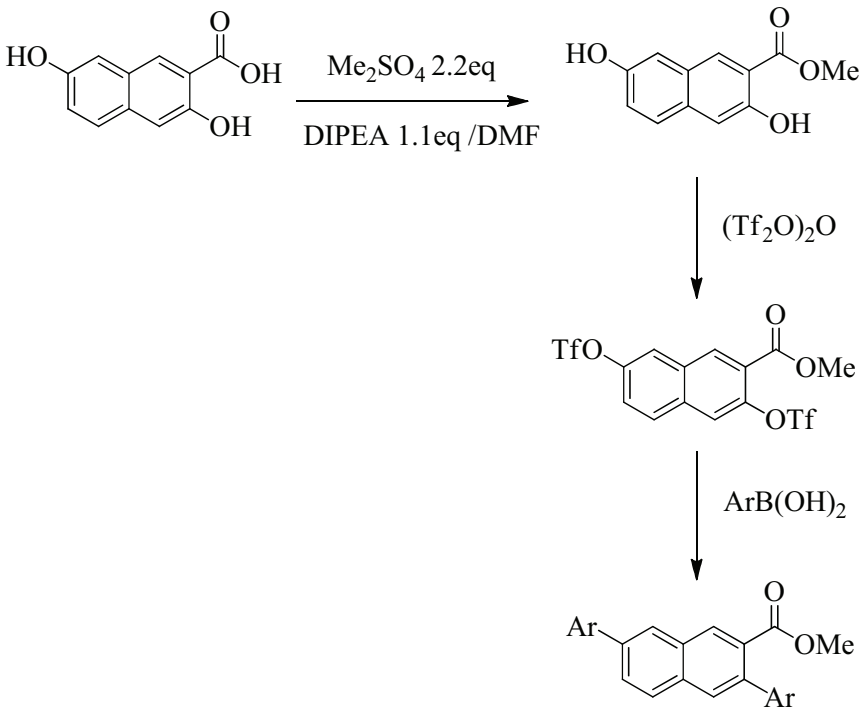
Scheme IV

The palladium(0)-catalyzed Suzuki cross-coupling reaction of the bis(triflates) of The ethyl 3,5- trifluoromethylsulfonyloxy-2-naphthoate afforded various 3,5-diaryl-2-naphthoates with very good siteselectivity (Scheme V). The first attack occurred at the sterically more hindered position C-3 which can be explained by the electronic influence of the ester group



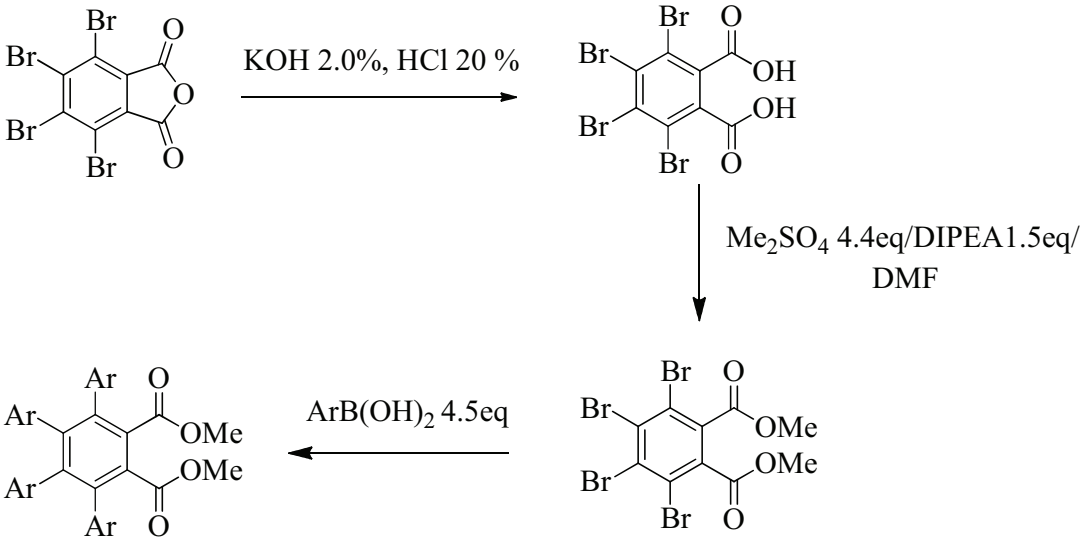
Scheme V

The palladium(0)-catalyzed Suzuki cross-coupling reaction of the bis(triflate) of methyl 3,7-trifluoromethylsulfonyloxy-2-naphthoate afforded various methyl-3,7-diaryl-2-naphthoates (Scheme VI).



Scheme VI

The palladium(0)-catalyzed Suzuki cross-coupling reaction of dimethyl tetrabromophthalate afforded various tetraarylphthalates in very good yields (Scheme VII).



Scheme VII

TABLE OF CONTENTS

Abbreviations

EtOAc	Ethylacetate
DMF	Dimethylformamide
DMSO	Dimethylsulfoxide
NEt_3	Triethylamine
Tf_2O	Trifluoromethanesulfonic Anhydride
THF	Tetrahydrofurane
DIPEA	Ethyldiisopropylamine
NMR	Nuclear Magnetic Resonance
HMQC	Heteronuclear Multiple Quantum Coherence
HMBC	Heteronuclear Multiple Bond Correlation
COSY	Correlated Spectroscopy
NOESY	Nuclear Overhauser and Exchange Spectroscopy
DEPT	Distortionless Enhancement by Polarisation Transfer
MS	Mass Spectrometry
EI	Electronic Impact
ESI	Electrospray Ionization
HRMS	High Resolution Mass Spectroscopy
IR	Infrared Spectroscopy
UV	Ultraviolet Spectroscopy
Ar	Aromatic
Ph	Phenyl
TLC	Thin Layer Chromatography
Sphos	2-Dicyclohexylphosphino-2',6'-dimethoxybiphenyl
Xphos	2-Dicyclohexylphosphino-2′,4′,6′-triisopropylbiphenyl
Hz	Hertz

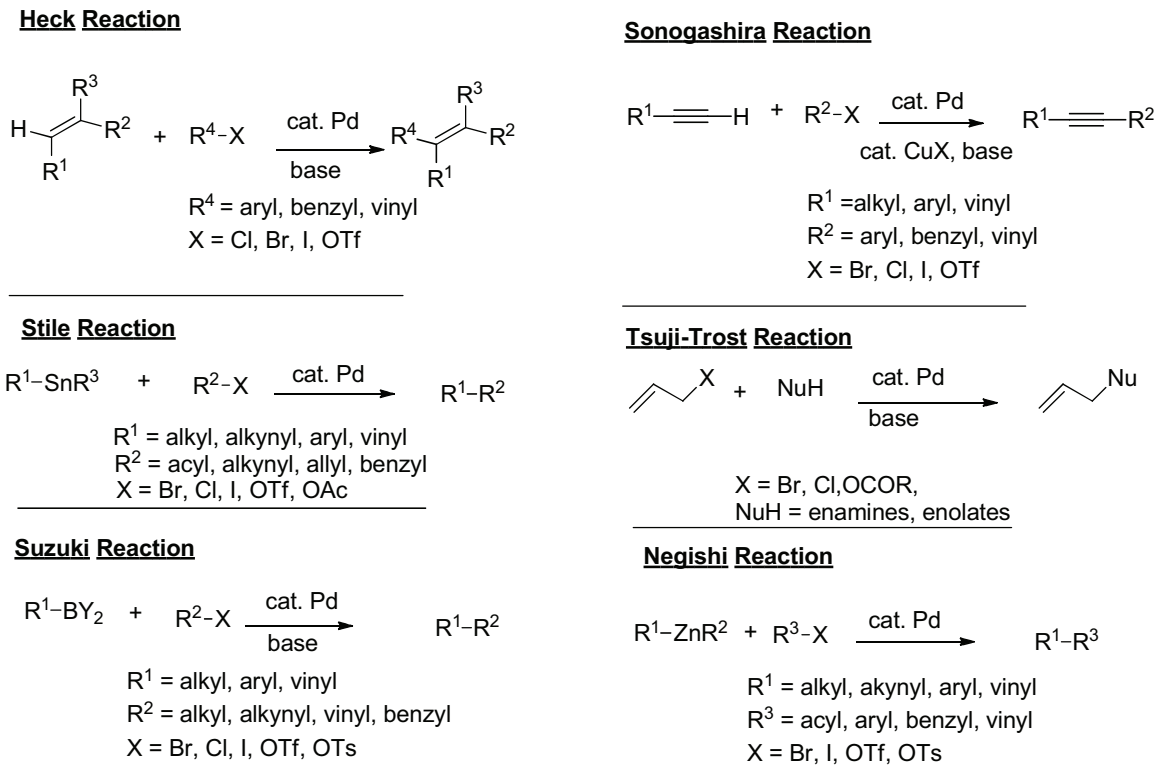
1. Introduction:

1.1 General introduction

Carbon-carbon bond–formation reactions have played a significant role in the development of organic chemistry. The importance of the synthesis of carbon-carbon bonds is reflected by the fact that Nobel Prizes in Chemistry have previously been given in this area: The Grignard reaction (1912), the Diels-Alder reaction (1950), the Wittig reaction (1979), and olefin metathesis to Y. Chauvin, R. H. Grubbs, and R. R. Schrock (2005). Palladium–catalysed cross coupling reactions (defined as transition-metal catalysed substitution of an organic halide or related electrophile by a nucleophile)[1] have been proved to be especially important, due to many benefits of these reactions, such as high productivity, atom economy, potential recycling of the catalyst and mild reaction conditions. They have been increasingly valuable, for example, in the pharmaceutical and fine chemical industries and natural product synthesis.[2-5] One event that stimulated research in palladium catalysis in organic chemistry was the discovery that ethylene is oxidized to acetaldehyde by air in a palladium-catalyzed reaction which became the industrially important Wacker process.[6] In 2010, the Nobel Prize in chemistry was awarded jointly to Richard F. Heck, Ei-ichi Negishi and Akira Suzuki for the development of methods for palladium-catalyzed cross-couplings synthesis.

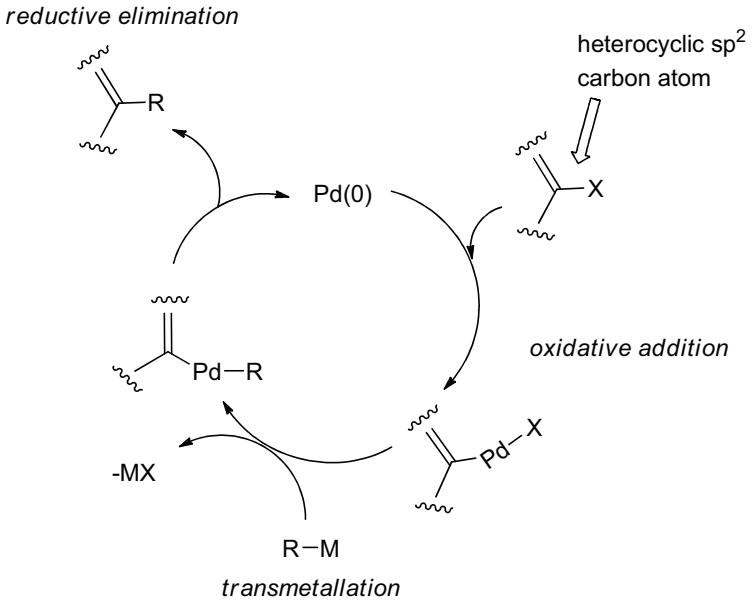
1.2 Palladium(0) Catalysis:

During recent decades an abundance of palladium (0)-catalysed coupling reactions has been developed; these coupling reactions have found widespread use in large areas of chemistry,[7] for example medicinal and pharmacological chemistry,[8] total synthesis, nanotechnology, and synthesis of advanced materials. Various types of palladium-catalyzed cross-coupling reactions[9,10] are known in organic synthesis, such as the Heck, Stille, Suzuki, Sonogashira, Tsuji-Trost and Negishi reactions (Scheme 1).



Scheme 1. palladium(0)-catalyzed cross-coupling reactions. (The picture was taken from *Angew. Chem. Ind. Ed.* **2005**, *44*, 4442).

Most of the coupling reactions presented above proceed in three steps (Scheme 2). Each cycle starts by oxidative addition of a palladium(0) species to an organohalide (I, Br, Cl) or a triflate or diazonium salt to generate an organo-palladium(II) species.[11,12] The second step of the reaction is the transmetallation process. In this process an organic moiety is transferred from a main group metal, *e.g.* Mg, Cu, Zn, Sn, B or Si, to a metal that is more electronegative, such as palladium, to give a diorganopalladium complex. In the last step of the reaction, this complex undergoes a reductive elimination to create a carbon-carbon bond and the palladium catalyst is regenerated.[13, 14]



Scheme 2. General mechanism for palladium(0)-catalyzed cross-coupling reactions. M = BY_2 (Suzuki), SnR_3, (Stille), ZnX (Negishi), MgX (Kumada) or SiR_3 (Hiyama) (picture was taken from *Tetrahedron*, **2005**, *61*, 2245).

1.3 Palladium-Catalyzed Suzuki-Miyaura Reaction:

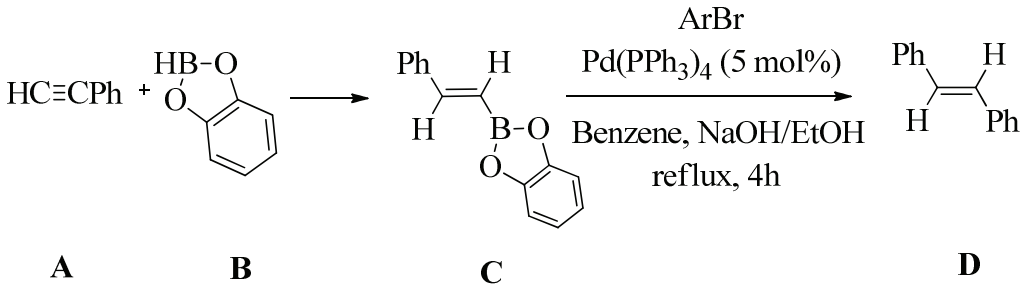
The Suzuki-Miyaura cross-coupling reaction is an extremely versatile methodology for the generation of carbon carbon $C(sp^2)$-$C(sp^2)$ bonds,[15] but more recently it was extended to accommodate carbon atoms in other hybridization states, such as sp^3.[16] Suzuki reactions are defined as Pd catalyzed cross–coupling reactions between organic electrophiles, such as aryl-, vinyl- or alkyl-halides, with organoboron compounds in the presence of a stoichiometric amount of base (Scheme 3).[17,18]

$$\text{R-X} \quad + \quad \text{R}_1\text{-BY}_2 \xrightarrow[\text{base}]{\text{Pd(0)}} \text{R-R}_1$$

R= alkyl, alkenyl, aryl, benzyl, vinyl
R_1= alkyl, alkynyl, aryl, vinyl
X= I, Br, Cl, OTf

Scheme 3. Palladium-catalysed Suzuki coupling.

Suzuki-Miyaura is widely used to synthesize poly-olefins, styrenes and substituted biphenyls. The first example of this reaction was reported in 1979 by Akira Suzuki and co-workers, The reaction of alkyne (**A)** with borate (**B)** in Benzene using 5 mol% of tetrakis(triphenylphosphine)palladium $Pd(PPh_3)_4$ gave (E)-1,2-diphenylethene (**D**) in decent yields (Scheme 4), This reaction was done in presence of base, such as sodium ethoxide in ethanol or sodium hydroxide in ethanol.[19, 20]

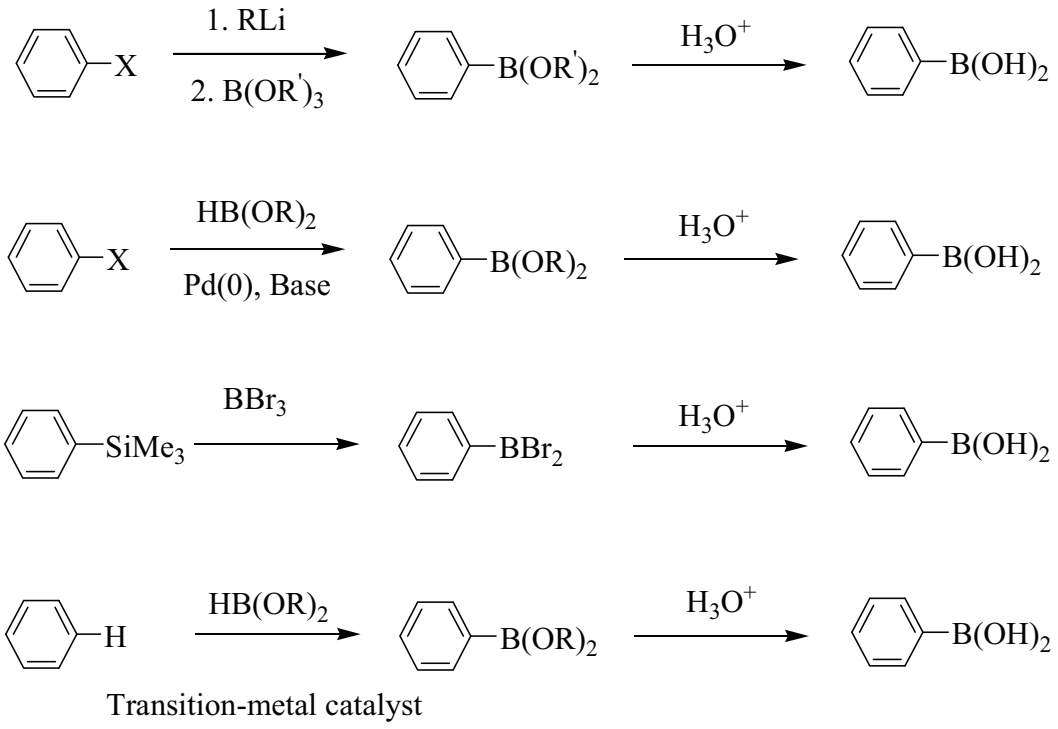


Scheme 4. An example of a Suzuki coupling reaction.

Organoboranes and boronic acids are attractive coupling partners, as they are widely commercially available. Moreover, they are generally relatively tolerant to air and moisture, tolerate a wide variety of functional groups, and are easy to handle. The by-products formed in coupling reactions of organoboranes are usually non-toxic and water soluble. All these fearures make organoboranes an attractive class of synthetic intermediate from an environmental point of view.[15] These interesting advantages make the Suzuki-Miyaura cross-coupling reaction an important tool in medicinal chemistry and also in the preparation of fine chemicals as well as in large scale pharmaceutical industry.[21]

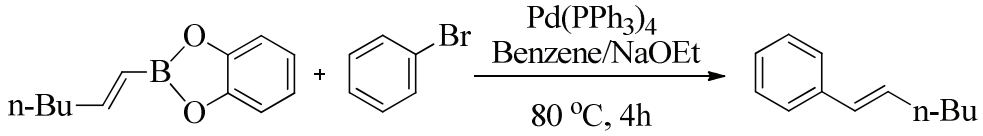
Several different organoboranes are used in transition-metal-catalyzed coupling reactions, for example, organoboronic acid, organoboronic esters and organotrifluoroborate salts which have gained popularity during the past few years, due to their low sensitivity to oxidation and nucleophilic substitutions. The trifluoroborate salts are easily prepared from their corresponding boronic acids or esters by treatment with an excess of KHF_2.[22,23,24] The most frequently employed reagents are organoboronic acids.

Organoboranes can be synthesized from different substrates, some examples are shown below (Scheme 5).



Scheme 5. Methods for the synthesis of boronic acids.

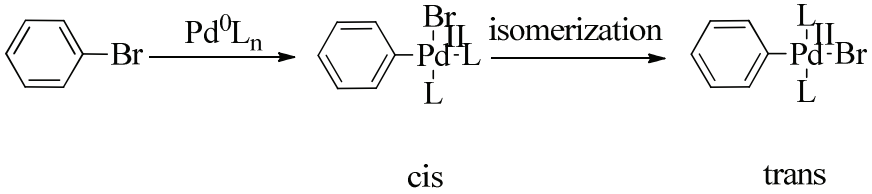
A Suzuki-Miyaura cross coupling reaction of organic halides and triflates with organoboronic esters can be exemplified by the reaction shown in Scheme 6.[19]



Scheme 6. Suzuki coupling reaction of a boronic ester and bromobenzene.

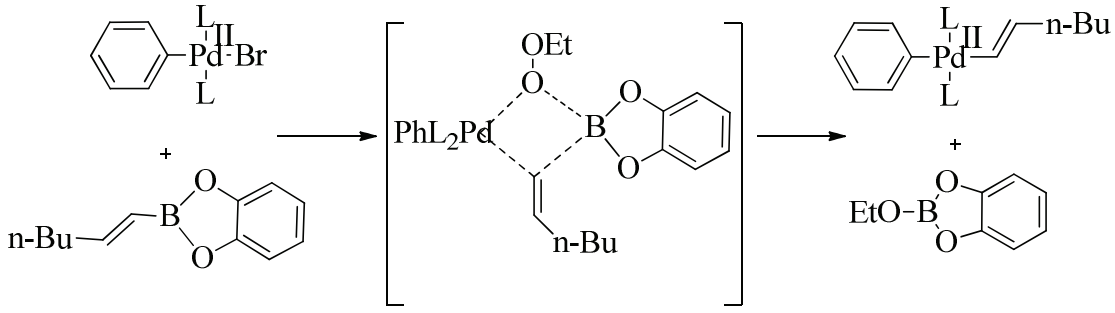
In the first step of the reaction, the oxidative addition of organic halides or triflates to the Pd(0) complex gives a stable *trans*- б-palladium (II) complex (Scheme 7).[25] The reaction

proceeds with complete retention of the stereochemistry for alkenyl halides and with inversion for allylic and benzylic halides. In the oxidative addition step of the Suzuki reaction, the reactivity of the reacting substrates has a vital role to play. Generally, the reactivity of various substrates is observed in the following order, Ar-I > Ar-OTf >Ar-Br > Ar-Cl and follows the bond strength of the C-X bond to be broken.[26,27,28] However, the reaction rate can also be influenced by electron–rich spectator ligands, which increase the nucleophilicity of the palladium center, or by introduction of electron–poor substituents to the aryl substrate.[29, 30]



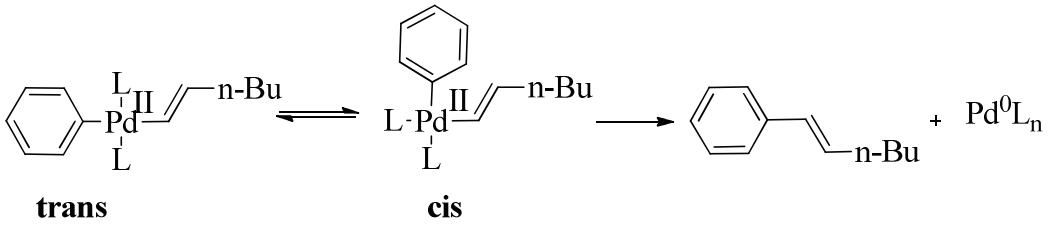
Scheme 7. Oxidative addition.

The next step is the transmetallation (Scheme 8)which is defined as a ligand exchange process between two metals, Pd(II) and M. The base supports the transmetallation step of the Suzuki reaction.[31] The presence of a base usually enhances the nucleophilicity of the organoborane compound by formation of an organoborate containing a tetravalent boron atom. Different types of bases are used in this reaction, e.g. potassium carbonate, potassium phosphate and cesium carbonate.



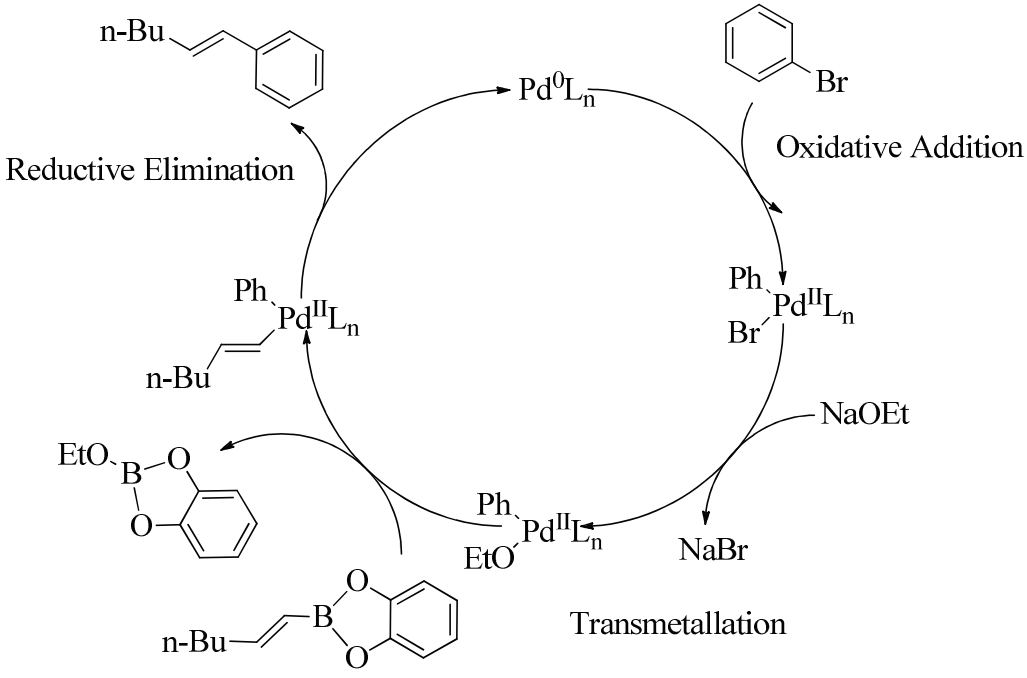
Scheme 8. Transmetallation processes.

The last step is the reductive elimination (Scheme 9) which can be considered to be the reverse process to the oxidative addition.[31] This step completes the catalytic cycle and releases Pd(0). Isomerization to the *cis* complex is required before the reductive elimination can occur.



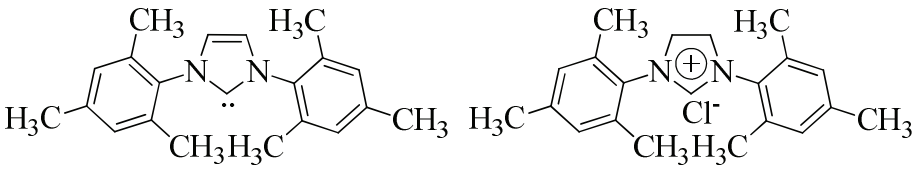
Scheme 9. Reductive elimination.

The complete catalytic cycle of Suzuki coupling reactions is shown below (Scheme 10).



Scheme 10. Catalytic cycle of Suzuki coupling reaction.

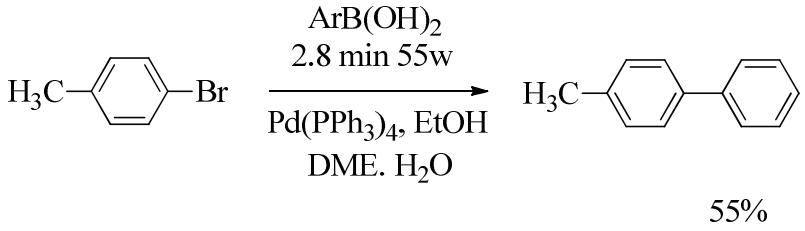
Several catalysts are used for this reaction, e.g. $Pd(PPh_3)_4$ and $Pd_2(dba)_3$, $Pd(PPh_3)_2Cl_2$ or $Pd(OAc)_2$ together with phosphine ligands (such as PPh_3, PCy_3, SPhos and XPhos).[32] N-Heterocyclic carbenes[33] (Figure 1) are also used as an alternative to phosphine ligands. The nucleophilic N-heterocyclic carbene **E** is the active ligand which is formed in situ from **F**.



E **F**

Figure 1. N-hetrocyclic carbine ligands.

Other factors, that also affect the rate of the reaction, are the variation of the solvent of the reaction[34] and the application of microwave which was reported for the first time by Hallberg an co-workers[35] in 1996 to enhance the rate of the carbon–carbon formation (Scheme 11). They confirmed that many metal-catalyzed reactions are completed within a few minutes. The reactions were carried out in water, ethylene glycol, or DMF, due to the ability of polar solvents to efficiently absorb microwave irradiation.



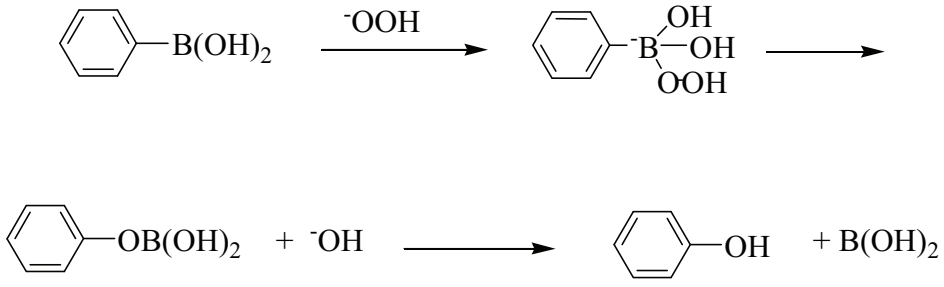
Scheme 11. Microwave-assisted Suzuki coupling reaction.

1.4 Side Reactions:

Organoboronic acids are relatively stable, due to the low polarity of the boron-carbon bond (electronegativity of boron 2.0 and carbon 2.5, according to the Pauling scale). Orrganoboronic acids are relatively unwilling to undergo transmetalation with palladium (electonegativity of 2.2). In order for arylboronic acids to become sufficiently reactive for efficient transmetallation with palladium, they require coordination of a base or Lewis base to form a tetracoordinated boronate anion which is more susceptible to transmetallation than the free boronic acid.[23]

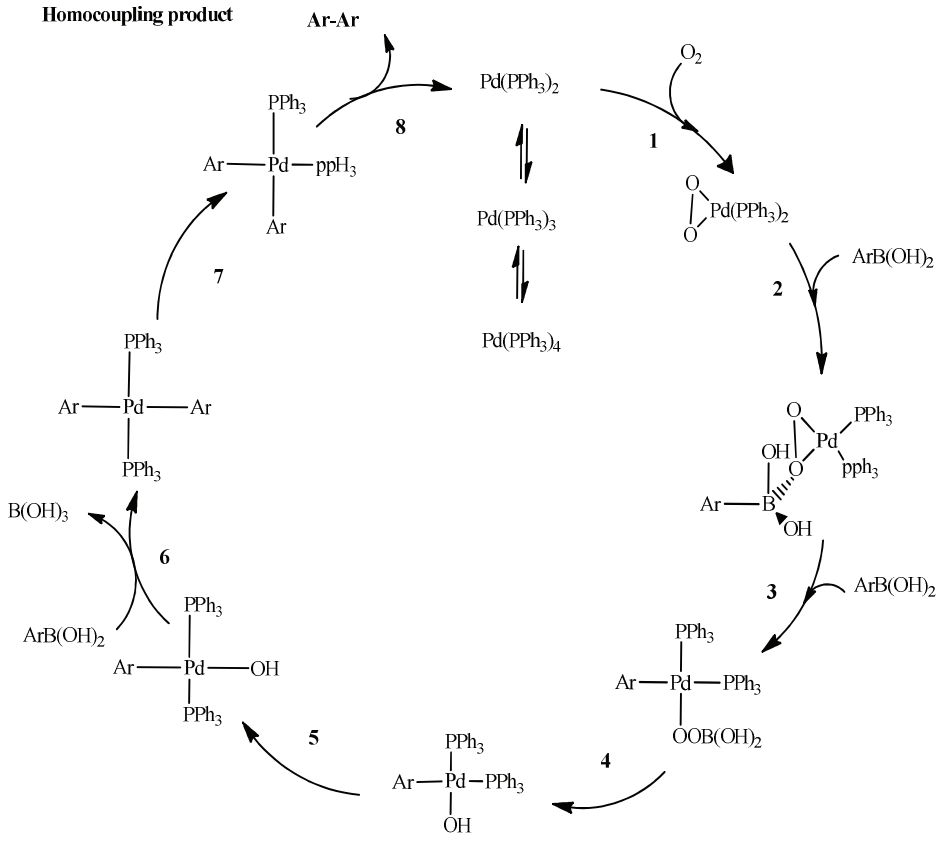
Although organoboronic acids are apparently stable, they often undergo side reactions during transition-metal-catalyzed coupling reactions. A public side reaction is the protodeboronation. Protodeboronation seldom occurs in the absence of transition metals under neutral conditions, even at high temperature.[36] In highly acidic or basic aqueous solutions, on the other hand, protodeboronation may be a fairly fast process.[37] Several metal ions, Pd(II), Ni(II), Zn(II), Ag(I), Cu(II), can induce protodeboronation in water by the formation of an aryl-metal intermediate.[38]

Other kinds of side reactions are the oxidation of the boronic acid to the corresponding alcohol. Challenger reported the formation of phenol by treating arylboronic acids with hydrogen peroxide in 1930,[39] and other oxidants, such as oxone[40] and sodium perborate.[41] (Scheme 12) explains the mechanism for the oxidation of boronic acid in aqueous solution.[42]



Scheme 12. Oxidation of boronic acids.

Biaryl formation by homocoupling of arylboronic acids is usually observed as a side reaction under palladium oxidative conditions. Moreno-Manas *et al.*[43] reported in their pioneering work on palladium-catalyzed homocoupling of arylboronic acids in 1996 and in 2005. Amatore and Jutad[44] published a thorough mechanistic investigation. Their investigation demonstrated that the reaction was catalyzed by palladium(II) and required dioxygen to form the active peroxo-palladium complex, $(\eta^2\text{-}O_2)PdL_2$, generated by reaction of dioxygen and palladium(0) (Scheme 13).

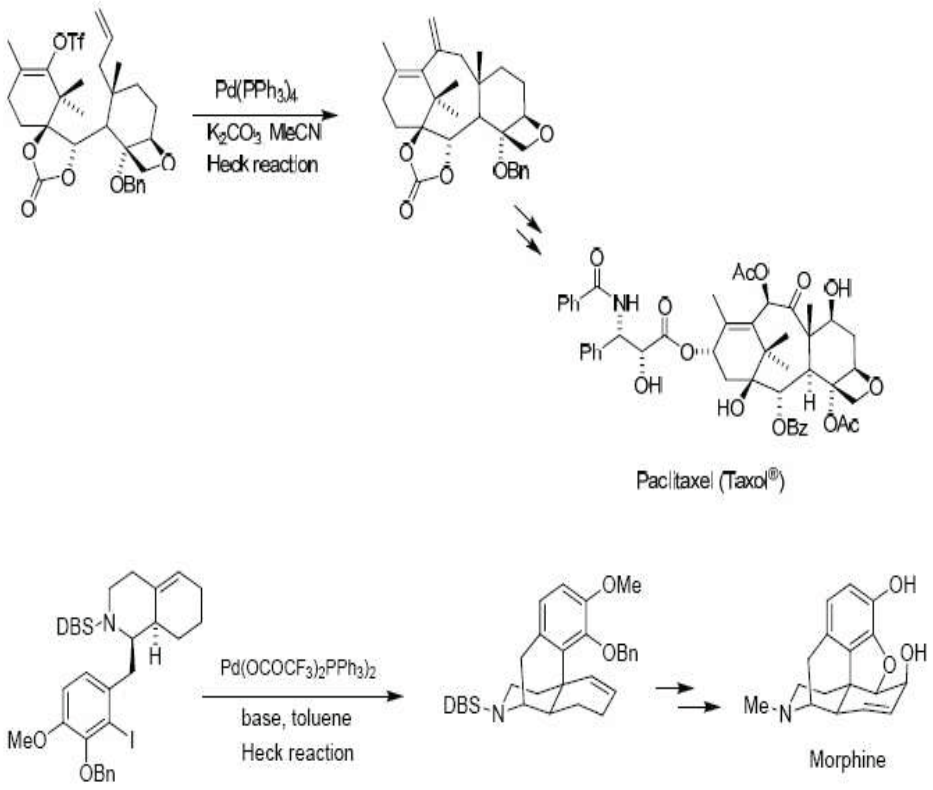


Scheme 13. Palladium-catalyzed homocoupling of arylboronic acids (*pictures were taken from refs.44*).

1.5 Application of Palladium-Catalyzed Cross Couplings:

The palladium-catalyzed carbon-carbon bond forming reactions developed by Heck, Negishi and Suzuki have had a large impact on synthetic organic chemistry and have found many applications in target oriented synthesis. These three cross-coupling reactions have been applied to the synthesis of a large number of natural products and biologically active compounds of complex molecular structures. They have also found applications in the fine chemical and pharmaceutical industries.

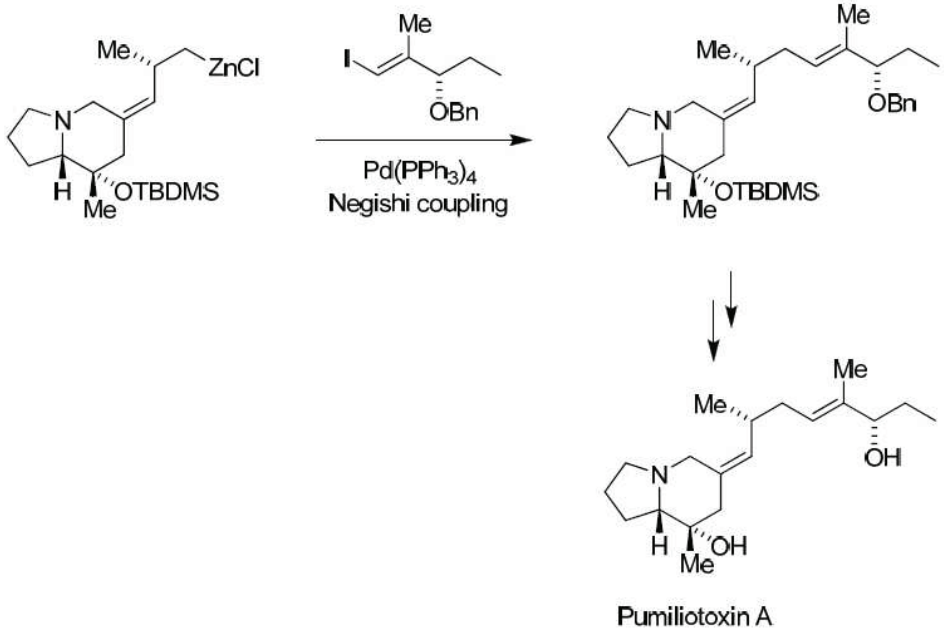
The Heck reaction has been used in more than 100 different syntheses of natural products and of biologically active compounds. Two examples are given in Scheme 14. The first example is given for the synthesis of Taxol®, where the Heck reaction was employed for creating the eight-membered ring.[45] The ring closure to complete the rigid tricyclic system is not trivial. In the other example, an intramolecular Heck-type coupling provides the morphine skeleton and the product is transformed to morphine in a few steps. [46]



Scheme 14. Example of the use of the Heck reaction in natural product syntheses *(pictures were taken from refs. 45 and 46).*

The Heck reaction has also been used as an important carbon-carbon bond forming step in the synthesis of other complex organic molecules, such as steroids,[47] strychnine,[48] and of the diterpenoid scopadulcic acid B[49] with cytotoxic and antitumor activity.

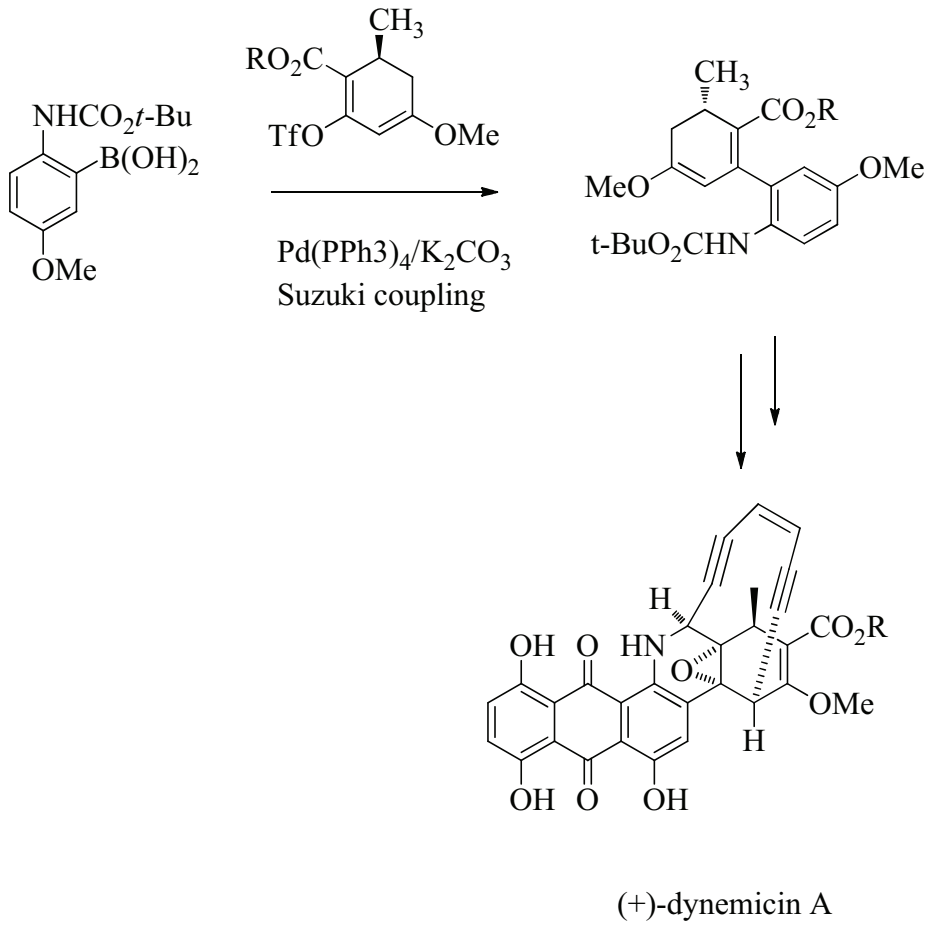
The Negishi and Suzuki reactions have also been frequently employed in natural product synthesis. Pumiliotoxin A is a toxic alkaloid found in the skin of frogs from the *Dendrobatidae* family that the frog uses for its defence. The total synthesis of pumiliotoxin A was performed via the use of a Negishi coupling in one of the key steps (Scheme 15).[50] It is interesting to note that an alkylzinc compound with ß-hydrogens is used in this reaction.



Scheme 15. The use of the Negishi coupling in the synthesis of Pumiliotoxin A *(picture was taken from ref. 50).*

An efficient synthesis of the potent natural antitumor agent (+)-dynemicin A involved a Suzuki coupling in one of the key carbon-carbon bond forming steps (Scheme 16).[51]

-



(+)-dynemicin A

Scheme 16. An efficient Suzuki coupling in the synthesis of (+)-dynemicin A *(picture was taken from ref. 51).*

Also the Suzuki reaction was used for preparing the antiviral bromoindole alkaloid dragmacidin F (Figure 2).[52]

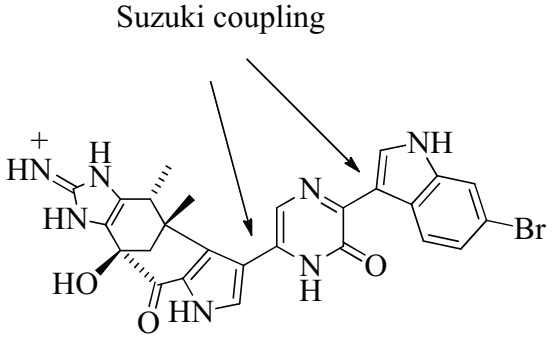


Figure 2. Synthesis of dragmacidin F (ref. 35) via palladium-catalyzed cross coupling.

1.6 Site-Selective Suzuki-Miyaura Cross-Coupling Reactions:

Recently, site-selective Suzuki coupling reactions became important. Complex compounds can be prepared by successive coupling reactions of substrates containing two or more possible reactive sites. The first attack usually occurs at the more electron deficient and less sterically hindered postion.[53,54]

In a couple of years, Prof. Peter Langer's research group studied site-selective Suzuki-Miyaura reactions of polyhalogenated heteroaromatic and aromatic compounds or their triflates. The site-selective Suzuki coupling reaction of indole (**G**) was found to be in favour of the 2-position (Figure 3). This is due to the fact that the electronic character of C-2 and C-3 appears to be sufficiently different because site-selective transformations are observed.[55] 2,3-Dibromoindenone (**H**) gives a very good site-selectivity. The first attack occurred at position 3.[56]

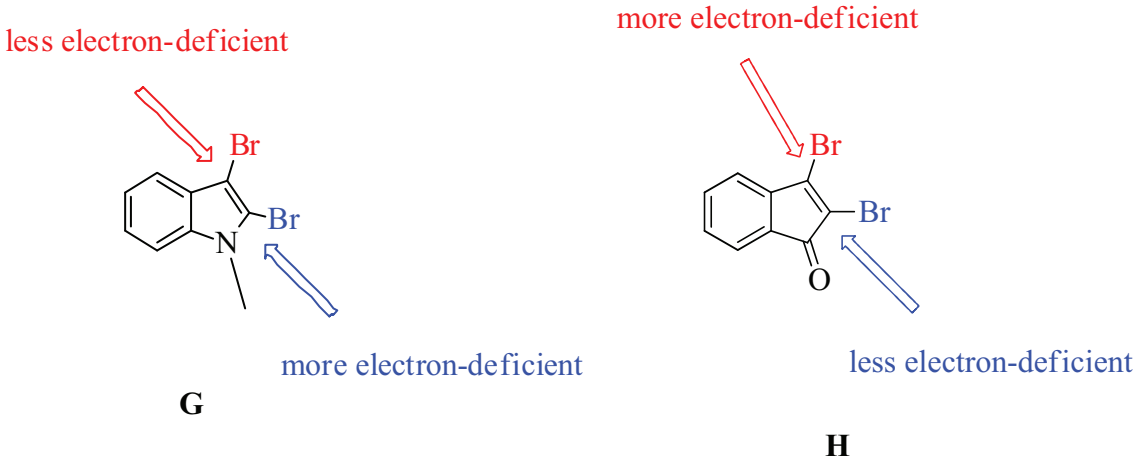


Figure 3. Possible explanation for the site-selectivity of **G** and **H.**

The substrates 2,3,4-tribromothiophene (**I**) and 2,3,5-tribromothiophene (**J**) showed a very good site selectivity. For compound **I**, the first coupling occurred at carbon atom C-2, the second coupling took place at carbon atom C-4. In case of **J**, the first coupling is preferred at carbon atom C-5 and the second one at carbon atom C-2. The selectivity can be explained based on the different electronic and steric properties of the three different C–Br bonds of **I** and **J** (Figure 4).[57]

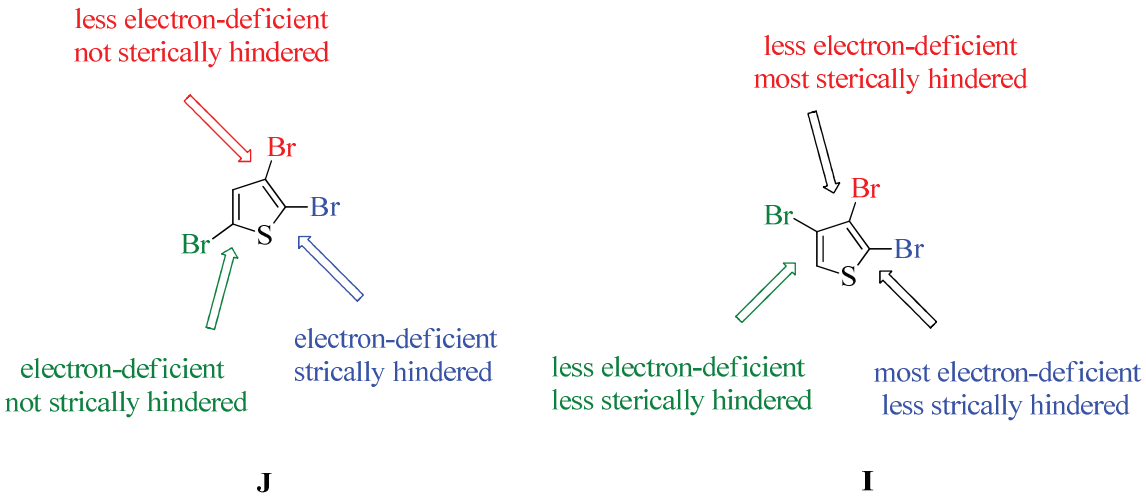
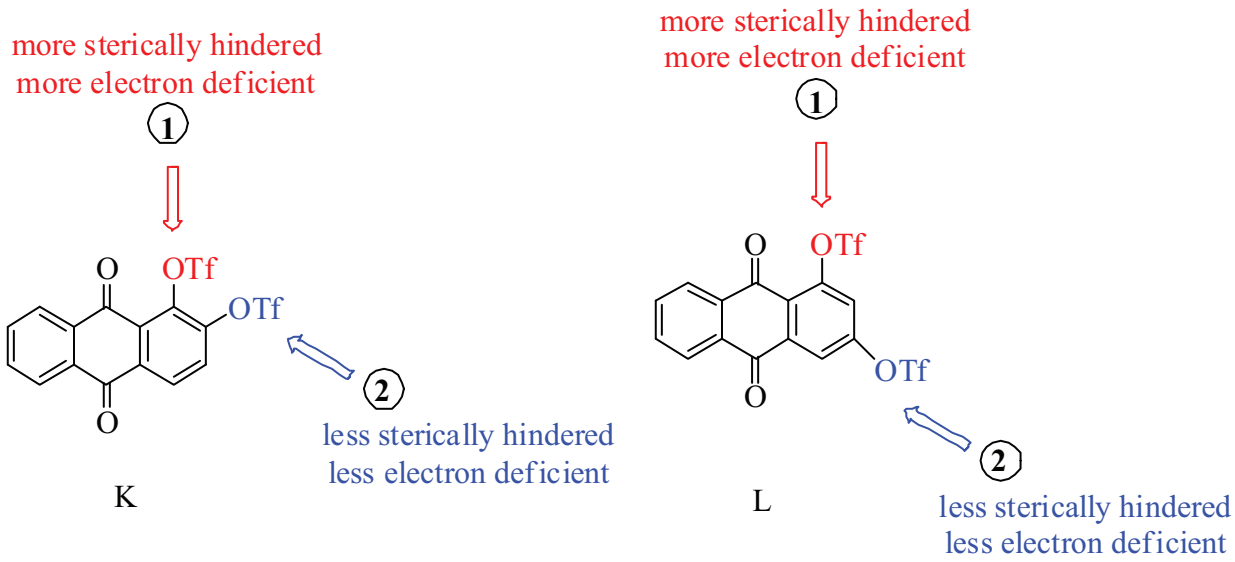


Figure 4. Possible explanation for the site-selectivity of **J** and **I.**

The Suzuki Miyaura reaction also provided excellent results for triflates. Their OH groups were converted into OTf groups by using triflic anhydride and subsequently the site-selectivity of Suzuki reactions was studied. The Langer group reported regioselective Suzuki-Miyaura cross coupling reactions of the bis(triflates) of many substrates. For example, for the bis(triflate) of 1,2-dihydroxyanthraquinone (**K**) and 1,3-dihydroxyanthraquinone (**L**),[58] the first attack occurs at position 1 which is more sterically hindered but more electron deficient. In case of phenyl 1,4-dihydroxynaphthoate (**M**), the first attack occurs at the more sterically hinderd and more electron deficient position 1.[59] For 7,8-dihydroxyflavone (**N**), the first attack of palladium(0)-catalyzed cross-coupling reactions generally occurs at the more electronical deficient and sterically less hindered position.[4,15] Position 7 of compound **N** is sterically less hindered than position 8. In addition, position 7 (located *meta* to the ether oxygen atom and *para* to the carbonyl group) is considerably more electron-deficient than position 1 (located *ortho* to the ether oxygen atom and *meta* to the carbonyl group).[60] The reactions of all mentioned substrates proceeded with excellent site-selectivities (Figure 5).



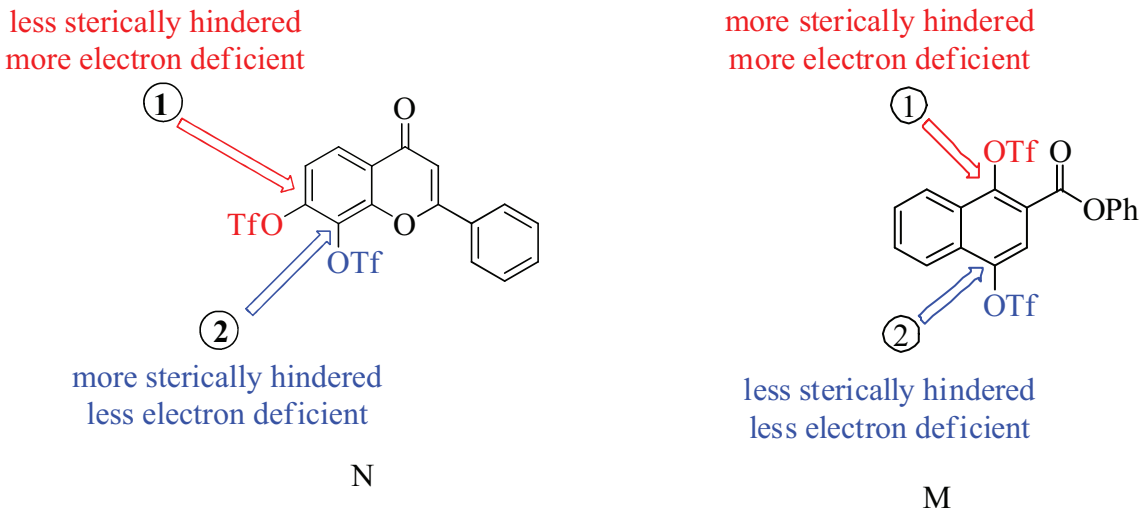


Figure 5. Possible explanation for the site-selectivity observed for **K, L, M,** and **N**.

2. Synthesis of Arylated Quinolines by Chemo- and Site-selective Suzuki-Miyaura Reactions of 5,7-Dibromo-8-(trifluoromethanesulfonyloxy)quinolone.

2 .1 Introduction:

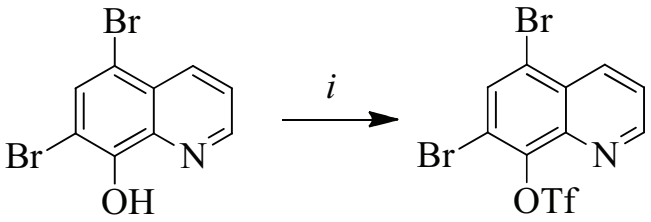
Quinoline derivatives are widely found in natural products[61] and bioactive molecules.[62] In fact, many of these derivatives exhibit important pharmacological activities, such as antiasthmatic, antiinflammatory and antimalarial activity[63], anti-cancer[64] and antibiotic activity.[65] Arylated quinolines represent an important subclass of quinolines. They were prepared by different classic reactions, such as the Skraup, Döbner-Miller, Conrad-Limpach, Friedländer and Pfitzinger syntheses.[66] Transition metal-catalyzed methods have also been developed as alternative methods for the construction of the quinoline framework.[67] For example, arylated quinolines were prepared by palladium catalyzed coupling of aryl triflates with organostannanes[68], and by nickel catalyzed reaction of arylzinc halides with quinoline nonaflates.[69] The Kumada–Tamao–Corriu reaction[70] was applied to the synthesis of 5-arylquinolines. Nickel catalyzed cross-coupling reactions of aryl quinoline carbamates with aryl boroxines have been used to prepare 5- and 6-arylquinoline derivatives.[71] Arylated quinolines were also synthesized by Suzuki-Miyaura reaction of 7-chloroquinolines with boronic acids.[72] A number of 5- and 7-arylquinolines were prepared by palladium catalyzed coupling of quinoline boronic esters with aryl halides.[73] Recently, 5,7-diarylquinolines were prepared by (non-selective) Suzuki-Miyaura reactions of dihalogenated quinolines.[74]

Site-selective palladium catalyzed cross-coupling reactions of polyhalogenated arenes and heteroarenes provide a convenient assembly of substituted benzene derivatives and heterocycles.[75,76] The first attack in such reactions usually occurs at the sterically less hindered and electronically more deficient position. Site-selective palladium catalyzed cross-coupling reactions and metal-halide exchange reactions of 2,4-dihaloquinolines were reported by Comins and coworkers.[77] Comins et al. also reported site-selective reactions of halogenated nicotine derivatives.[78] Tilley et al. reported site-selective Sonogashira reactions of 2,4-dibromopyridine.[79] A variety of cross-coupling reactions of 2,5-dibromopyridine and related substrates have been studied.[80] Handy and coworkers and Cid and coworkers reported Suzuki couplings of 2,5- and 2,3-dibromopyridine and of

several other heterocycles.[81] In all these reactions, the first reaction occurred at position C-2 which was explained by the effect of the lone pair of the nitrogen atom.

2.2 Results and Discussion:

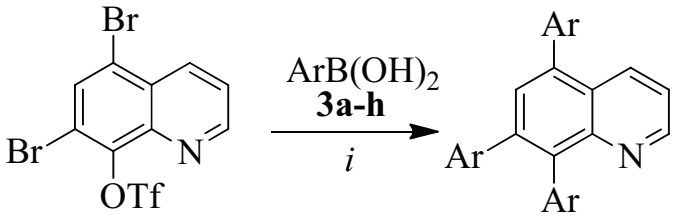
The reaction of commercially available 5,7-dibromo-8-hydroxyquinoline (**1**) with triflic anhydride afforded 5,7-dibromo-8-(trifluoromethanesulfonyloxy)-quinoline (**2**) in 80% yield (Scheme 17).



1 **2** (80%)

Scheme 17. Synthesis of **2**, *i*, 1) **1** (1.0 equiv), pyridine (4.0 equiv), CH_2Cl_2, -78 °C, 10 min; 2) Tf_2O (1.2 equiv), -78 → 0 °C, 4 h.

The reaction of **2** with three equivalents of arylboronic acids **3a-h** afforded the 5,7,8-triarylquinolines **4a-h** in 79-90% yield (Scheme 18, Table 1). The reactions were carried out under standard conditions for Suzuki-Miyaura reactions; $Pd(PPh_3)_4$ (3.0 mol-% for each cross-coupling step) was employed as the catalyst and an aqueous solution of K_2CO_3 was used as the base (dioxane, 135 °C, 8 h). Very good yields were obtained for both electron rich and poor arylboronic acids. The structure of **4a** was independently confirmed by X-ray crystal structure analysis (Figure 6).



2 **4a-h**

Scheme 18. Synthesis of **4a-h**. *Reagents and conditions: i*, **2** (1.0 equiv), **3a-h** (3.0 equiv.), $Pd(PPh_3)_4$ (9 mol-%), K_2CO_3 (2M, 1 mL), 1,4-dioxane, 135 °C, 8 h.

Table 1. Synthesis of **4a-h**

3	**4**	Ar	% (**4**) [a]
a	**a**	4-MeC_6H_4	90
b	**b**	3-MeC_6H_4	80
c	**c**	3,5-$Me_2C_6H_3$	85
d	**d**	4-EtC_6H_4	90
e	**e**	4-*t*BuC_6H_4	83
f	**f**	4-$(MeO)C_6H_4$	93
g	**g**	4-FC_6H_4	79
h	**h**	4-ClC_6H_4	80

[a] Yields of isolated products

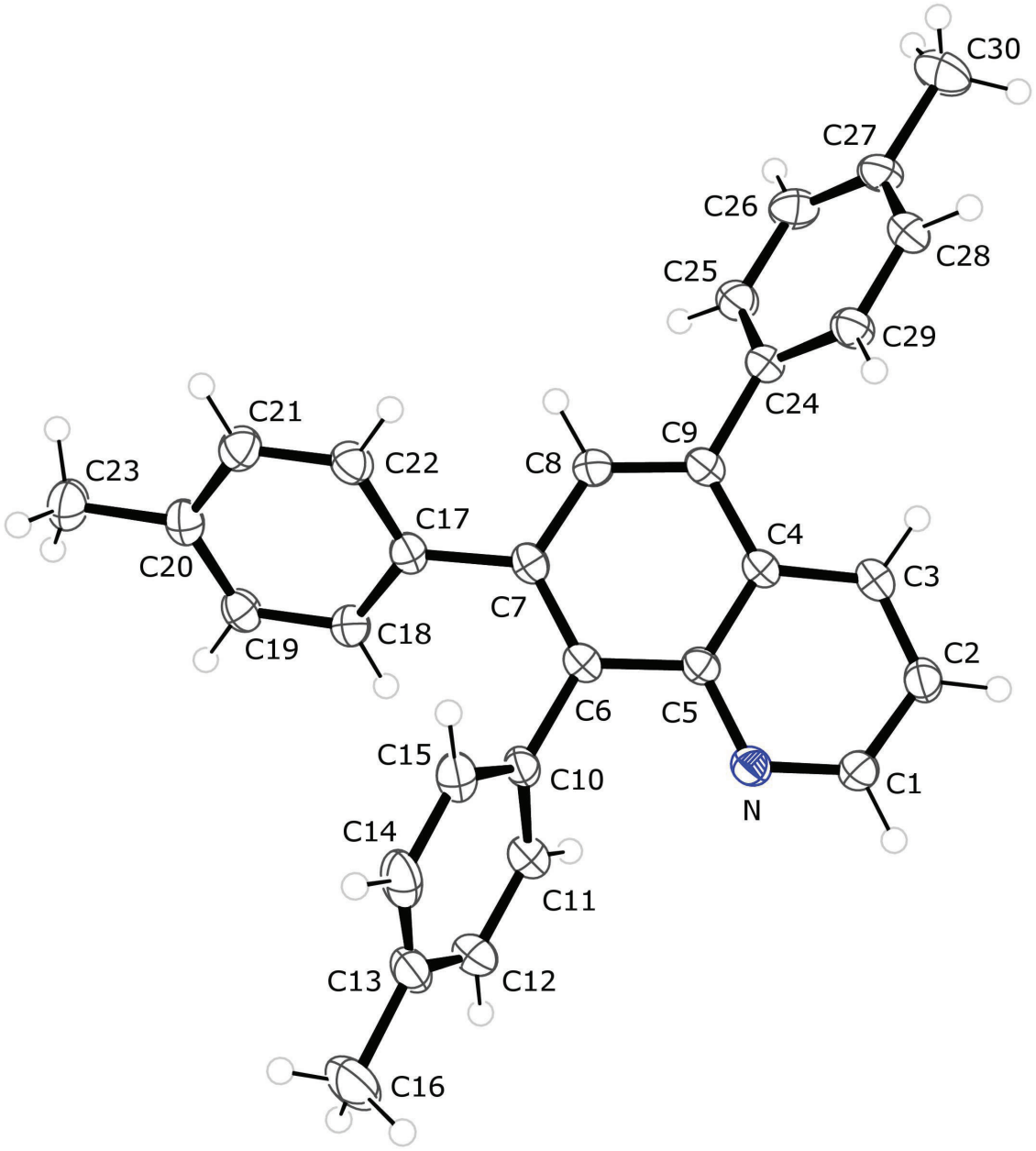
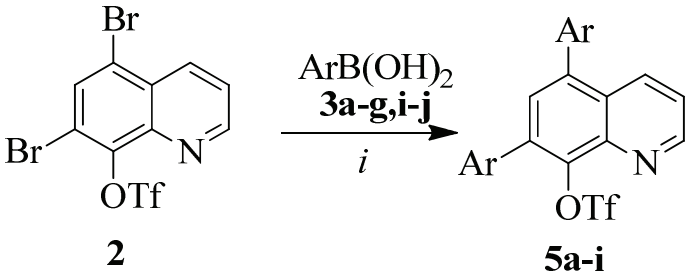


Figure 6. Molecular structure of **4a.**

The reaction of **2** with 2.0 equivalents of arylboronic acids **3a-g,i,j** gave 5,7-diarylquinolines **5a-i** in 75-90% yield (Scheme 3, Table 2). The reactions proceeded with excellent site-selectivity. The triflate group remained unattacked. During the optimization, it proved to be important to carry out the reaction at 90 °C instead of 135 °C and to use exactly 2.0 equiv. of the boronic acid. Both electron rich and poor

arylboronic acids could be successfully used. The structure of **5c** was independently confirmed by X-ray crystal structure analysis (Figure 7).



Scheme 19. Synthesis of **5a-i**. *Reagents and conditions: i*, **2** (1.0 equiv.), **3a-h,i-j** (2.0 equiv.), $Pd(PPh_3)_4$ (6 mol-%), K_2CO_3 (2M, 1.0 mL), 1,4-dioxane, 90 °C, 8 h.

Table 2. Synthesis of **5a-i**

3	**5**	Ar	% (**5**)[a]
a	**a**	4-MeC_6H_4	88
b	**b**	3-MeC_6H_4	85
c	**c**	3,5-$Me_2C_6H_3$	90
d	**d**	4-EtC_6H_4	89
e	**e**	4-*t*BuC_6H_4	80
f	**f**	4-(MeO)C_6H_4	83
g	**g**	4-FC_6H_4	80
i	**h**	3,4-$(MeO)_2C_6H_3$	82
j	**i**	3-$(F_3C)C_6H_4$	75

[a] Yields of isolated products

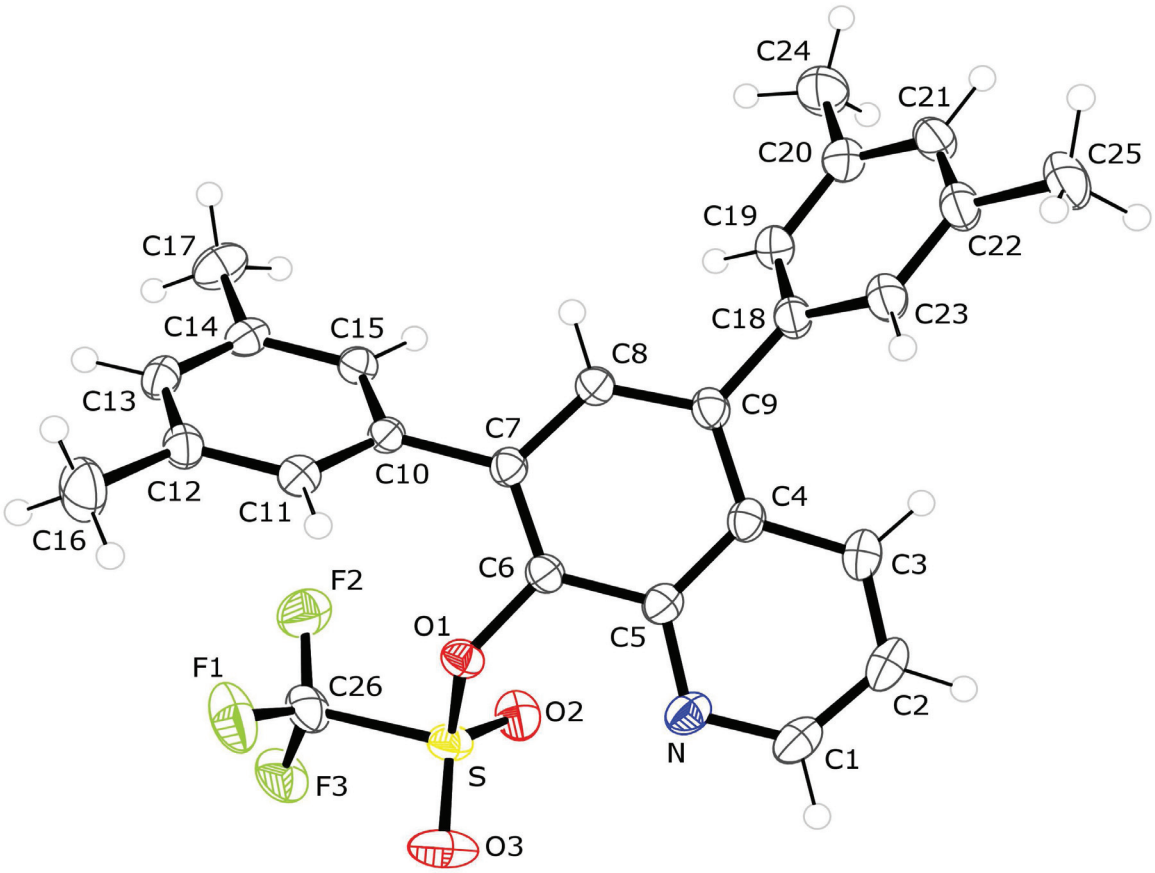
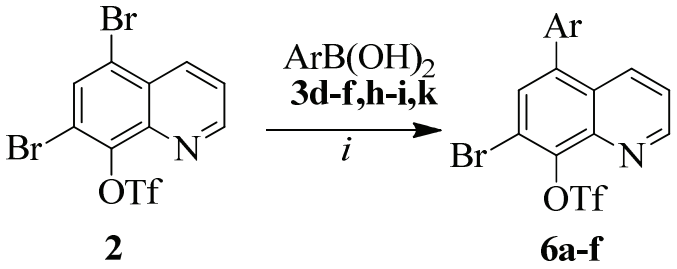


Figure 7. Molecular structure of **5c.**

The reaction of **2** with 1.0 equivalent of arylboronic acids **3d-f,h,i,k** afforded 5-arylquinolines **6a-f** in 60-85% yield with very good site-selectivity (Scheme 4, Table 3). It proved to be important to carry out the reaction at 65 °C (instead of 90 °C or 135 °C) and to use exactly 1.0 equiv. of the boronic acid. The yields of the products derived from electron rich arylboronic acids were higher compared to those derived from electron poor ones. The structure of **6a** was independently confirmed by X-ray crystal structure analysis (Figure 8).



2 **6a-f**

Scheme 20. Synthesis of **6a-f**. *Reagents and conditions: i*, **2** (1.0 equiv.), **3d-f,h,i,k** (1.0 equiv.), $Pd(PPh_3)_4$ (3 mol-%), K_2CO_3 (2M, 1.0 ml), 1,4-dioxane, 65°C, 12 h.

Table 3. Synthesis of **6a-f**

3	**6**	Ar	% (**6**)[a]
d	**a**	4-EtC_6H_4	80
e	**b**	4-*t*BuC_6H_4	80
f	**c**	4-$(MeO)C_6H_4$	95
h	**d**	4-ClC_6H_4	60
i	**e**	3,4-$(MeO)_2C_6H_3$	88
k	**f**	2,3,4-$(MeO)_3C_6H_2$	80

[a] Yields of isolated products

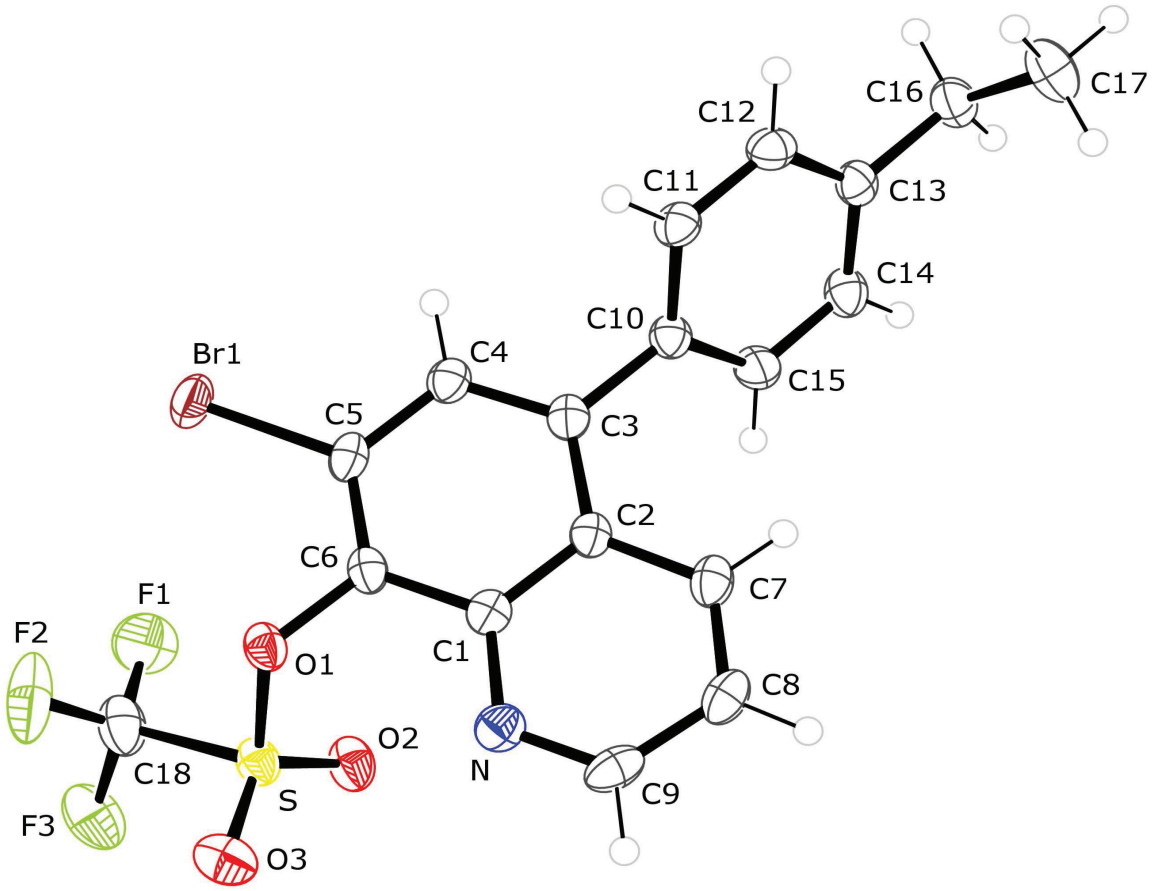
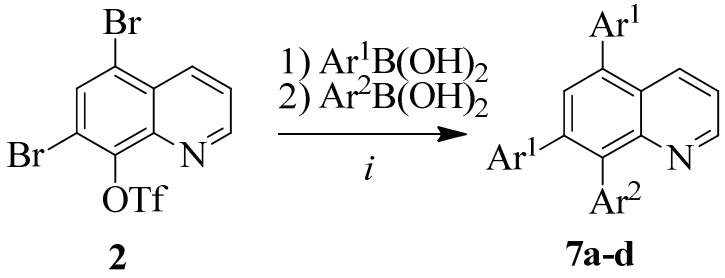


Figure 8. Molecular structure of **6a.**

The one-pot reaction of **2** with two different arylboronic acids was next studied. The reaction of **2** with 2.0 equivalents of an arylboronic acid and subsequent addition of a second arylboronic acid (1.0 equiv.) afforded the 5,7,8-triarylquinolines **7a-d** containing two different aryl groups in 79-82% yield (Scheme 21, Table 4). During the optimization it proved to be important to carry out the first step at 90 °C (as in the case of the synthesis of **5a-i**) and the second step at 135 °C. During the optimization of this one-pot reaction and of the reactions discussed below, it proved to be important to add a fresh portion of catalyst together with the second boronic acid. The structure of **7b** was independently confirmed by X-ray crystal structure analysis (Figure 9).



2 **7a-d**

Scheme 21. Synthesis of **7a-d**. *Reagents and conditions: i*, 1) **2** (1.0 equiv), $Ar^1(OH)_2$ (2.0 equiv.), $Pd(PPh_3)_4$ (6 mol-%), K_2CO_3 (2M, 1.0 mL), 1,4-dioxane, 90°C, 12 h; 2) $Ar^2(OH)_2$ (1.0 equiv.), $Pd(PPh_3)_4$ (3 mol-%), K_2CO_3 (2M, 0.5 mL), 135°C, 6 h.

Table 4. Synthesis of **7a-d**

3	**12**	Ar^1	Ar^2	% (**7**)[a]
c,f	**a**	3,5-$Me_2C_6H_3$	4-(MeO)C_6H_4	80
e,f	**b**	4-*t*BuC_6H_4	4-(MeO)C_6H_4	80
e,i	**c**	4-*t*BuC_6H_4	3,4-$(MeO)_2C_6H_3$	79
f,d	**d**	4-(MeO)C_6H_4	4-EtC_6H_4	82

[a] Yields of isolated products

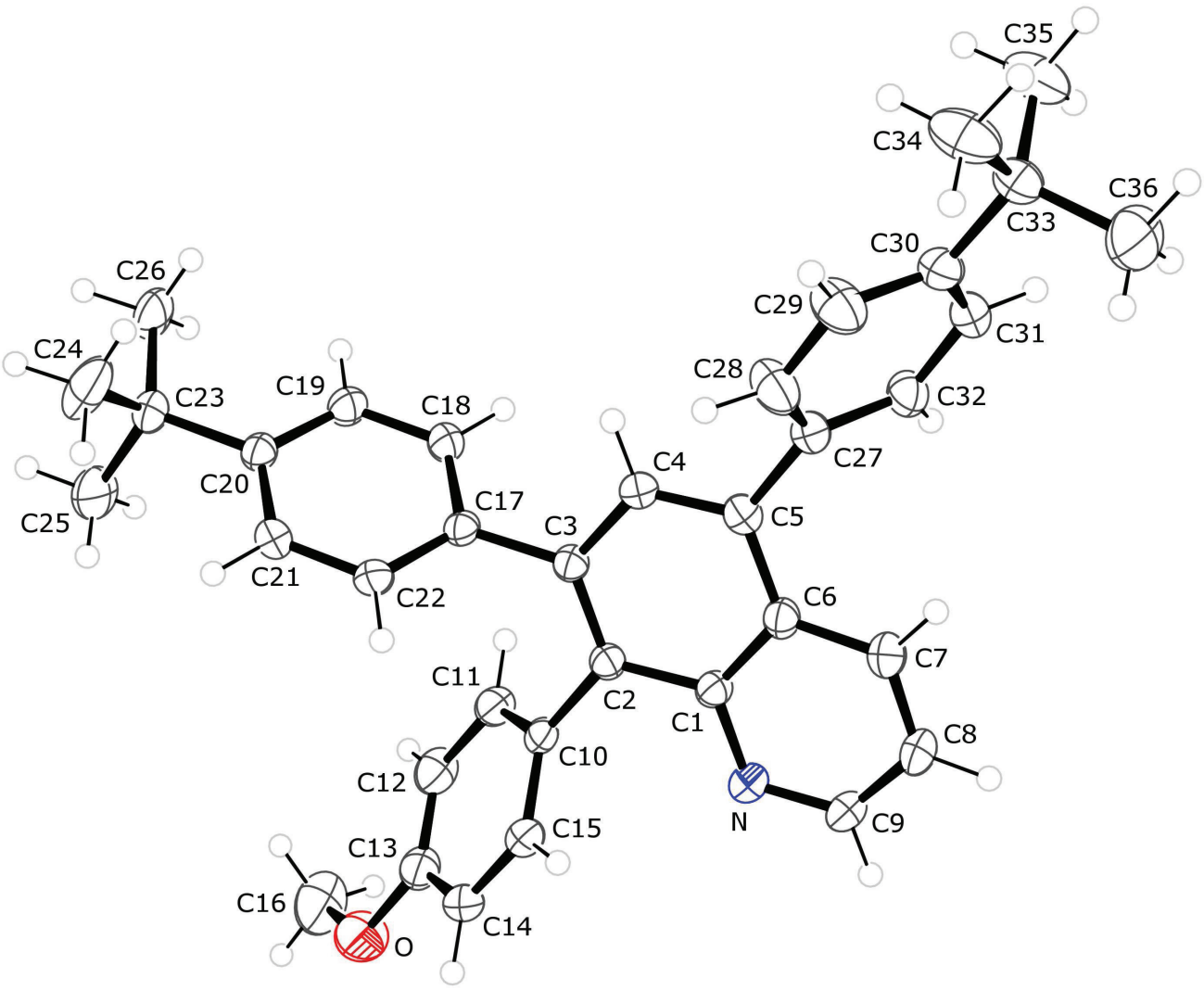
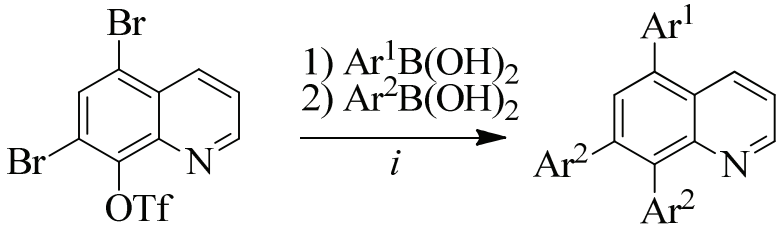


Figure 9. Molecular structure of **7b.**

The one-pot reaction of **2** with 1.0 equivalent of an arylboronic acid and 2.0 equivalents of a second arylboronic acid (sequential additon) resulted in the formation of 5,7,8-triarylquinolines **8a-c**. 5,7,8-Triarylquinolines **7a-d** and **8a-c** both contain two different aryl groups, but their substitution pattern is different (Scheme 22**,** Table 5). To obtain a good site-selectivity, it proved to be important to carry out the first step at 65 °C (as in the case of the synthesis of **6a-f**) and the second step at 135 °C.



2 **8a-c**

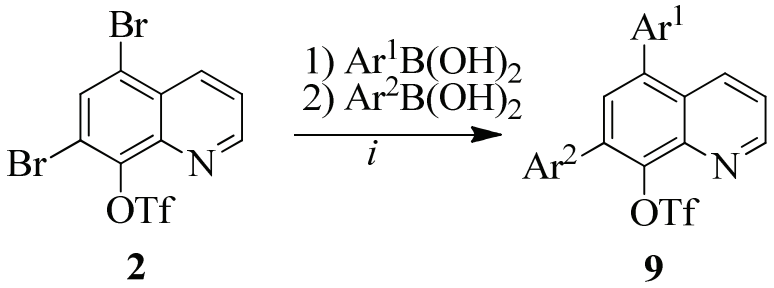
Scheme 22. Synthesis of **8a-c**. *Reagents and conditions: i*, 1) **2** (1.0 equiv), $Ar^1(OH)_2$ (1.0 equiv.), $Pd(PPh_3)_4$ (3 mol-%), K_2CO_3 (2M, 1.0 mL), 1,4-dioxane, 65°C, 12 h; 2) $Ar^2(OH)_2$ (2.0 equiv.), $Pd(PPh_3)_4$ (6 mol-%), K_2CO_3 (2M, 0.5 mL), 135°C, 6 h.

Table 5. Synthesis of **8a-c**

3	**8**	Ar^1	Ar^2	% (**8**)[a]
f,a	**a**	4-(MeO)C_6H_4	4-MeC_6H_4	85
f,h	**b**	4-(MeO)C_6H_4	4-ClC_6H_4	77
e,g	**c**	3,5-$Me_2C_6H_3$	4-FC_6H_4	70

[a] Yields of isolated products

The one-pot reaction of **2** with two different arylboronic acids (1.0 equivalent each, sequential addition) afforded the 5,7-diarylquinoline **9** in 87% yield (Scheme 7, Table 6). The first step was carried out at 65 °C, while the second step was carried out at 70 °C.



2 **9**

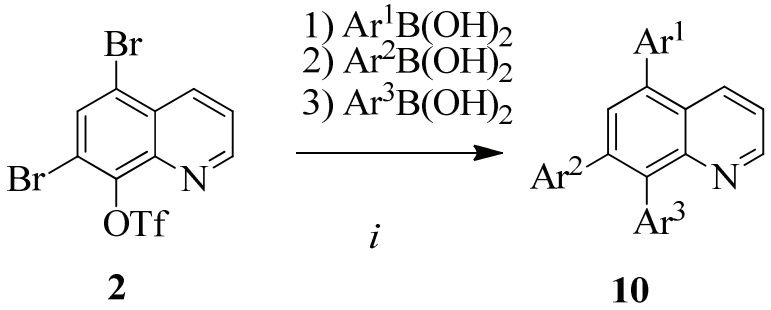
Scheme 23. Synthesis of **9**. *Reagents and conditions: i*, 1) **2** (1.0 equiv), $Ar^1(OH)_2$ (1.0 equiv.), $Pd(PPh_3)_4$ (3 mol-%), K_2CO_3 (2M, 1.0 mL), 1,4-dioxane, 65°C, 12 h; 2) $Ar^2(OH)_2$ (1.0 equiv.), $Pd(PPh_3)_4$ (3 mol-%), K_2CO_3 (2M, 0.5 mL), 70°C, 6 h.

Table 6. Synthesis of **9**

3	**9**	Ar^1	Ar^2	% (**9**)[a]
f,e	**a**	4-(MeO)C_6H_4	4-*t*BuC_6H_4	87

[a] Yields of isolated products

The one-pot reaction of **2** with three different arylboronic acids (1.0 equivalent each, sequential addition) gave 5,7,8-triarylquinoline **10**, containing three different aryl groups, in 79% yield (Scheme 8, Table 7). The first step was carried out at 65 °C, while the second step was carried out at 70 °C and the third step at 135 °C. This rather complex process demonstrates the efficiency and the excellent site-selectivity of the chemistry reported herein.



2 **10**

Scheme 24. Synthesis of **10**. *Reagents and conditions: i*, 1) **2** (1.0 equiv), $Ar^1(OH)_2$ (1.0 equiv.), $Pd(PPh_3)_4$ (3 mol-%), K_2CO_3 (2M, 1.0 mL), 1,4-dioxane, 65°C, 12 h; 2) $Ar^2(OH)_2$ (1.0 equiv.), $Pd(PPh_3)_4$ (3 mol-%), K_2CO_3 (2M, 0.5 mL), 70°C, 8 h; 3) $Ar^3(OH)_2$ (1.0 equiv.), $Pd(PPh_3)_4$ (3 mol-%), 135°C, 6 h.

Table 7. Synthesis of **10**

3	**10**	Ar^1	Ar^2	Ar^3	% (**10**)[a]
f,e,a	**a**	4-$(MeO)C_6H_4$	4-*t*-BuC_6H_4	4-MeC_6H_4	79

[a] Yields of isolated products

The Suzuki-Miyaura reactions of **2** proceed with excellent site-selectivity. The first, second and third attack occur at positions 5, 7 and 8, respectively. Aryl bromides usually undergo Suzuki-Miyaura reactions more rapidly than aryl triflates.[82] This reactivity order, which is different to other palladium(0) catalyzed reactions, can be explained by the high borane-halide affinity. Other parameters influence the selectivity as well. Therefore, the reactions reported herein follow the expected order of reactivity as the bromide positions are more reactive than the triflate position. In general, palladium catalyzed reactions of polyhalogenated substrates proceed by initial attack on the sterically less hindered and electronically more deficient position.[74] Position 5 is sterically less hindered than positions 7 and 8. Position 8 of parent quinoline is electronically more deficient than

positions 5 and 7. Thus, in case of a bromide located at position 8, the first attack would have been expected to occur at this position. Due to the presence of a triflate (instead of a bromide) located at C-8, the order of reactivity is changed. Positions 5 and 7 are electron deficient. In conclusion, the first attack occurs at position 5 (bromide) which is sterically less hindered than position 7 (bromide). The second attack occurs at position 7 and the third attack occurs at position 8 (triflate).

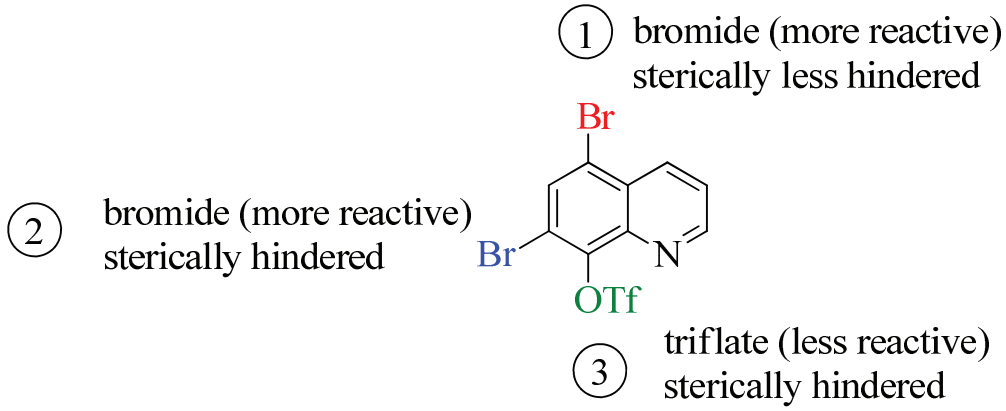


Figure 10. Possible explanation for the site-selectivity.

2.3 Conclusion:

In conclusion, I have reported an efficient synthesis of arylated quinolines by site-selective Suzuki-Miyaura reactions of 5,7-dibromo-8-(trifluoromethanesulfonyloxy)quinoline. The products reported herein are not readily available by other methods.

3. Efficient Synthesis of Arylated Flavones by Site-Selective Suzuki–Miyaura Cross-Coupling Reactions of the Bis(triflate) of 5,7-Dihydroxyflavone.

3.1 Introduction:

Flavones (2-arylchromones) are very important oxygenated heterocyclic compounds, which belong to the flavonoid group that occur naturally as secondary metabolites in fruits, vegetables, seeds and flowers. They play important roles in plant development, reproduction and defence and possess a wide range of biological and pharmaceutical activities. This includes antiviral, anti-inflammatory, hepatoprotective, antioxidant, antithrombotic, vasodilating and anticarcenogenic activity combining high efficiency and low toxicity.[83-88] Many studies have shown that chrysin has anti-inflammation, anti-cancer and anti-oxidation, and anti-HIV effects.[89] Natural anti-oxidant tangeretin shows significant protective effects against Parkinson's disease (Fig. 11).[90] The main synthetic methods include the Kostanecki reaction, Allan and Robinson synthesis, the Baker-Venkataraman rearrangement and several more methods.[91 -94] Only a few applications of palladium catalyzed cross coupling reactions to flavone-derived halides or triflates have been reported to date.[95] Langer *et al.* reported the synthesis of 7,8-diaryl-flavones by site-selective Suzuki-Miyaura reactions of the bis(triflate) of 7,8-dihydroxyflavone.[60] Herein, I report, for the first time, the synthesis of 5,7-diarylflavones by site-selective Suzuki–Miyaura reactions of the bis(triflate) of 5,7-dihydroxyflavone.

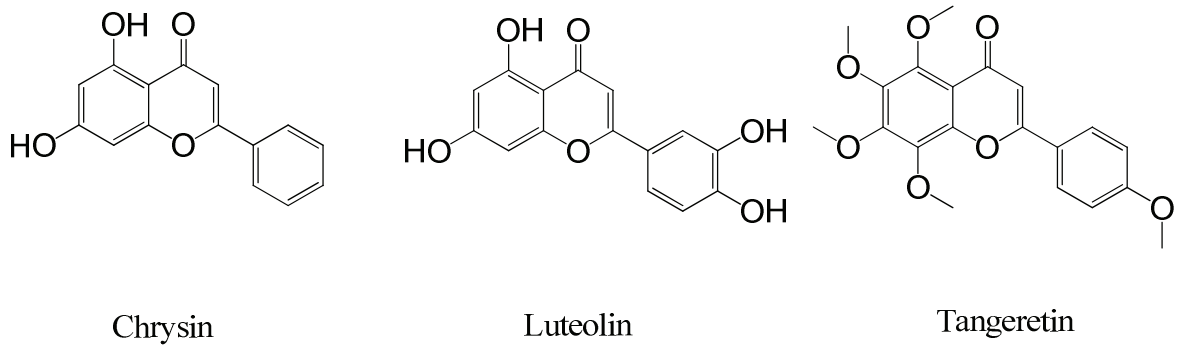
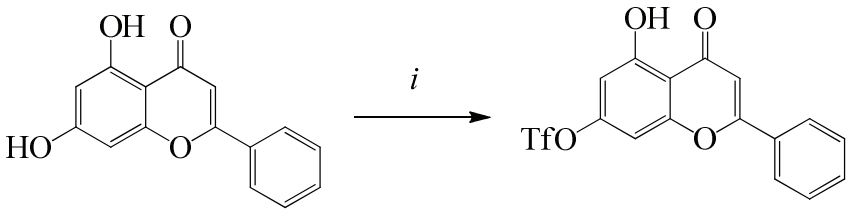


Figure 11. Some examples of flavones natural product.

3.2 Results and Discussion:

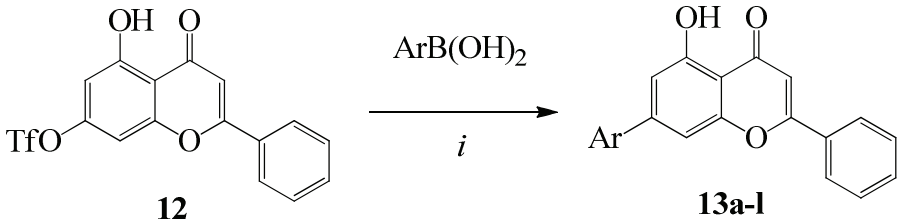
The reaction of 5,7-dihydroxyflavone **11** with triflic anhydride (2.4 equiv.) resulted in formation of the mono-triflate 1**2** in 80% yield (Scheme 24). The expected bis-triflate was not formed. The yield of 1**2** slightly dropped when only 1.2 equiv. of triflic anhydride was employed. The synthesis of **12** and a Stille reaction of the latter has been previously reported.[16] The difficulty to prepare the desired bis-triflate is in striking difference to the facile synthesis of the bis(triflate) of 7,8-dihydroxyflavone and might be explained by formation of a stable intramolecular hydrogen bond in case of **11**.



11 **12 (80 %)**

Scheme 24. Synthesis of **12**; *i*: 1) **11** (1.0 equiv.), pyridine (4.0 equiv.), CH_2Cl_2, 20 °C; 2) Tf_2O (2.4 equiv.), 20 °C, 4 h.

The Suzuki-Miayura reaction of mono-triflate **12** with various arylboronic acids **3** afforded the 7-aryl-5-hydroxyflavones **13a-l** in 75-90% yields (Scheme 25, Table 11). The reactions were carried out under standard conditions (3 mol-% of $Pd(PPh_3)_4$ as the catalyst, K_3PO_4 as the base, 1,4-dioxane, 80 °C). Very good yields were obtained both for electron rich and poor arylboronic acids. The yields for arylboronic acids containing an *ortho* substituent were slightly lower compared to those of other arylboronic acids, presumably due to steric effects.



12 **13a-l**

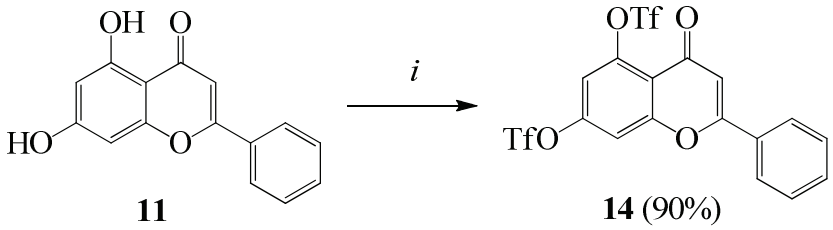
Scheme 25. Synthesis of **13a-l**. Conditions: *i*, **2** (1.0 equiv), **3a-l** (1.0 equiv.), K_3PO_4 (1.5 equiv.), $Pd(PPh_3)_4$ (3 mol-%), 1,4-dioxane, 80 °C, 4 h.

Table 11. Synthesis of **13a-l**

3	*13*	*Ar*	*13 (%)* [a]
a	**a**	4-MeC_6H_4	90
b	**b**	3-MeC_6H_4	85
c	**c**	3,5-MeC_6H_3	80
e	**d**	4-*t*BuC_6H_4	80
f	**e**	4-(MeO)C_6H_4	90
g	**f**	4-FC_6H_4	80
h	**g**	4-ClC_6H_4	86
i	**h**	3,4-(MeO)C_6H_3	85
j	**i**	4-$CF_3C_6H_4$	79
l	**j**	C_6H_5	80
m	**k**	2-ClC_6H_4	75
n	**l**	2-MeC_6H_4	77

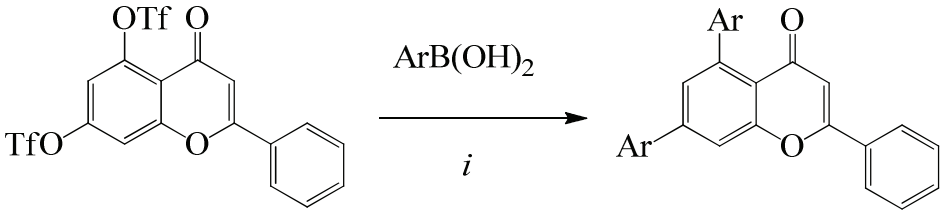
[a] Yields of isolated products

5,7-Bis(trifluoromethylsulfonyloxy)flavone **14** could be successfully prepared from **11** in 90% yield when the reaction was carried out at 40 °C instead of 20 °C (Scheme 26).



Scheme 26. Synthesis of **14**: *i*: 1) **11** (1.0 equiv), pyridine (4.0 equiv), CH_2Cl_2, 20 °C; 2) Tf_2O (2.4 equiv), 20 → 40 °C, 30 min.

The Suzuki-Miayura reaction of bis-triflate **14** with 2.0 equiv. of various arylboronic acids **3** afforded the 5,7-diarylflavones **15a-i** in 76-90% yields (Scheme 27, Table 12). The reactions had to be carried out at a higher temperature (115 °C), as compared to the synthesis of products **13**, to affect good yields. Very good yields were obtained for products derived from both electron rich and electron poor arylboronic acids.



14 **15a-i**

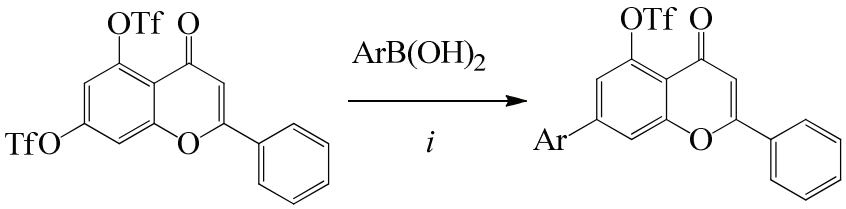
Scheme 27. Synthesis of **15a-i**. Conditions: *i*, **14** (1.0 equiv), $ArB(OH)_2$ (2.0 equiv.), K_3PO_4 (3.0 equiv.), $Pd(PPh_3)_4$ (6 mol-%), 1,4-dioxane, 115 °C, 6 h.

Table 12. Synthesis of **15a-i**

3	*15*	*Ar*	*15 (%)* [a]
a	**a**	4-MeC_6H_4	85
b	**b**	3-MeC_6H_4	80
c	**c**	3,5-MeC_6H_3	80
e	**d**	4-*t*BuC_6H_4	77
f	**e**	4-(MeO)C_6H_4	90
h	**f**	4-FC_6H_4	83
i	**g**	4-ClC_6H_4	85
j	**h**	4-$CF_3C_6H_4$	76
l	**i**	C_6H_5	81

[a] Yields of isolated products

The Suzuki-Miayura reaction of bis-triflate **14** with 1.0 equiv. of arylboronic acids **3** afforded the 7-aryl-5-(trifluorosulfonyloxy)flavones **16a-g** in 71-85% yields (Scheme 28, Table 13). The reactions had to be carried out at 70 °C instead of 115 °C to achieve good yields and to avoid the formation of 5,7-diarylflavones **6**.



14 **16a-g**

Scheme 28. Synthesis of **16a-g**. Conditions: *i*, **14** (1.0 equiv), $ArB(OH)_2$ (1.0 equiv.), K_3PO_4 (1.5 equiv.), $Pd(PPh_3)_4$ (3 mol-%), 1,4-dioxane, 70 °C, 9 h.

Table 13. Synthesis of **16a-g**

3	***16***	*Ar*	***16*** *(%)* [a]
b	**a**	3-MeC_6H_4	81
c	**b**	3,5-MeC_6H_3	85
e	**c**	4-*t*BuC_6H_4	71
f	**d**	4-(MeO)C_6H_4	83
g	**e**	4-FC_6H_4	80
h	**f**	4-ClC_6H_4	82
o	**g**	2-(MeO)C_6H_4	81

[a] Yields of isolated products

The structure of **16g** was independently confirmed by X-ray crystal structure analysis (Figure 12).

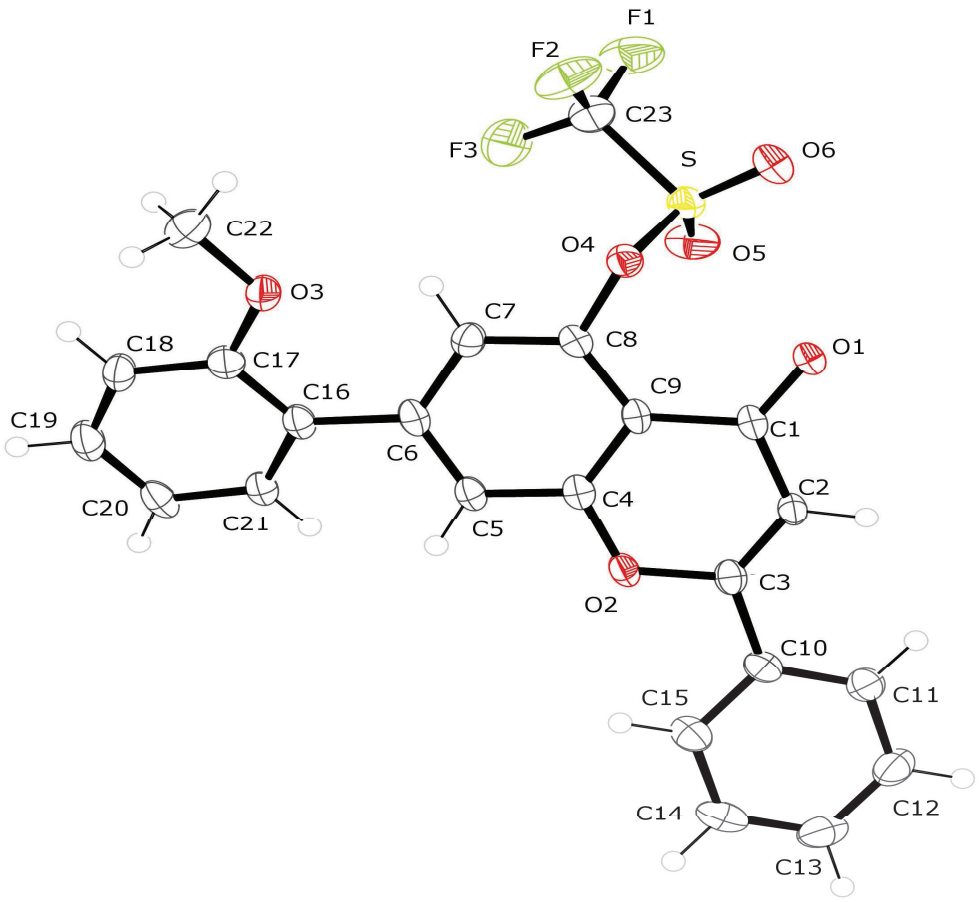


Figure 12. Ortep plot of **16g.**

The structure of compound **16f** was confirmed by a ^{1}H,^{1}H NOESY experment. The *ortho* protons of the 4-chlorophenyl group correlate with protons H-6 and H-8 of the flavone moiety (Figure13).

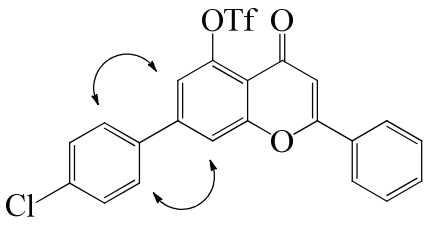
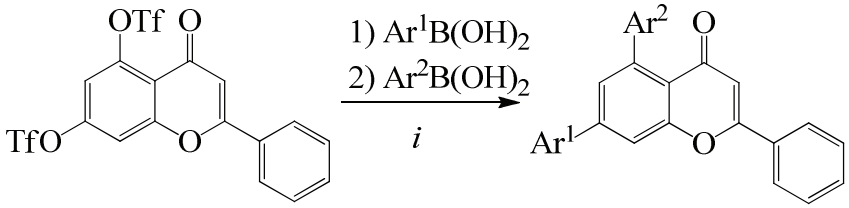


Figure 13. Diagnostic NOESY interactions of **16f.**

The one-pot Suzuki-Miayura reaction of bis-triflate **14** with two different arylboronic acids **3** (sequential addition of 1.0 equiv. of each boronic acid) afforded the 5,7-diarylflavones **17a,b** in 77-78% yields (Scheme 29, Table 14). The reactions were carried out at 70 °C for the first step (to avoid double coupling) and at 115 °C in the second step.



14 **17a,b**

Scheme 29. Synthesis of **17a,b**. Conditions: *i*, 1) **14** (1.0 equiv), $Ar^1B(OH)_2$ (1.0 equiv.), K_3PO_4 (1.5 equiv.), $Pd(PPh_3)_4$ (3 mol-%), 1,4-dioxane, 70 °C, 9 h; 2) $Ar^2B(OH)_2$ (1.0 equiv), K_3PO_4 (1.5 equiv.), $Pd(PPh_3)_4$ (3 mol-%), 1,4-dioxane, 115 °C.

Table 14. Synthesis of **17a,b**

3	*8*	*Ar¹*	*Ar²*	*% (17)*[a]
c,h	**a**	3,5-MeC_6H_3	4-ClC_6H_4	78
h,g	**b**	4-ClC_6H_4	4-FC_6H_4	77

[a] Yields of isolated products

The first attack of site-selective palladium catalyzed reactions usually occurs at the sterically less hindered or electronically more deficient position. The Suzuki-Miyaura reactions of the bis(triflates) of 1,2- and 1,3-dihydroxyanthraquinone[58] proceeds by initial attack at position 1 (next to the carbonyl group) which can be explained by the fact that position 1 is more electronically deficient than positions 2 and 3. In addition, a chelation of the catalyst by the carbonyl group might play a role. Therefore, it is unexpected that the Suzuki-Miyaura reactions of **5** proceed by initial attack at position 7 which is electronically less deficient and sterically less hindered than position 5. The regiodirecting effect of the carbonyl group of **5** seems to be less effective than in the case

of the bis(triflates) of 1,2- and 1,3-dihydroxyanthraquinone and the site-selectivity is controlled by steric parameters.

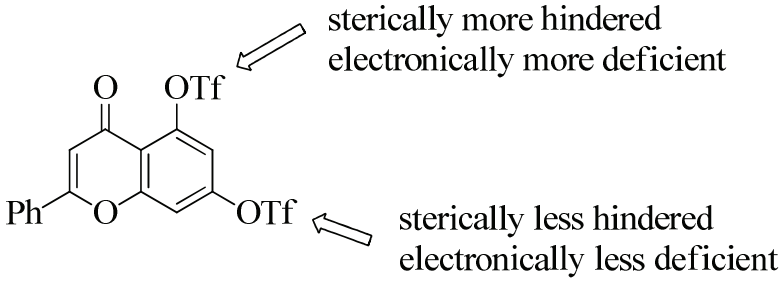


Figure 14. Possible explanation for the site-selectivity of the reactions of bis(triflate) **5.**

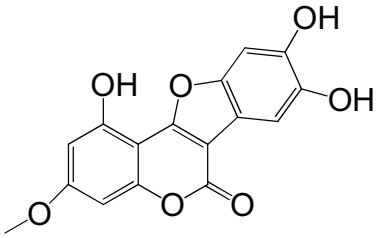
3.3 Conclusion:

In conclusion, 5,7-diarylflavones were prepared by Suzuki-Miyaura reactions of the bis(triflate) of 5,7-dihydroxyflavone. The reactions proceeded with very good site-selectivity first attack proceeded at position 7, due to steric reasons. The reaction of 5,7-dihydroxyflavone with one equivalent of triflic anhydride also proceeded with very good site-selectivity and allowed for the synthesis of 7-aryl-5-hydroxyflavones.

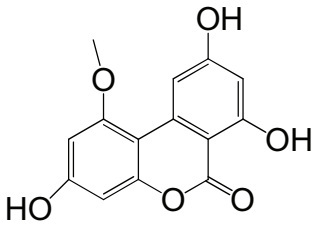
4. Efficient Synthesis of Arylated Coumarins by Site-Selective Suzuki–Miyaura Cross-Coupling Reactions of the Bis(triflate) of 4-Methyl-5,7-dihydroxycoumarin and 4-Methyl-7,8- dihydroxycoumarin.

4.1 Introduction:

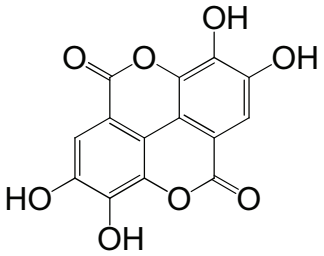
Coumarin and its derivatives are one of the important classes of heterocyclic compounds which occur in many natural products. For example, wedelolactone and other coumarines were isolated from the roots of *Hedysarum multijugum*, which is a plant in *Hedysarum Linn.* of the family *Leguminosae* used as a folk herbal drug in northwest China [96]. Many compounds were isolated from plants such as alternariol, umbelliferone (7-hydroxycoumarin), and others [97] (Fig. 15). Coumarin compounds are known to possess a wide range of biological activities, anti-HIV, anti-biotic, anti-fungal, anti-bacterial, anti-viral, anti-cancer, anti-clotting activity, and especially as anti- coagulants (Fig. 16).[98] In addition, they are widely used as additives in food, perfumes, agrochemicals, cosmetics, pharmaceuticals[99] and in the preparations of insecticides, optical brightening agents, and dispersed fluorescent and laser dyes.[100] Coumarins can be synthesized by various methods, such as Pechmann,[101] Perkin,[102] Knoevenagel,[103] and Wittig,[104] reactions. However, because of its simplicity and relatively inexpensive starting materials, the Pechmann reaction was widely used for the synthesis of coumarins and its derivatives. This method involves the reaction between phenol with β-ketoester in the presence of acidic catalysts.[105-110] Transition-metal-catalyzedreactions were applied to the synthesis of substituted coumarins at the 3- or 4-position. Zhen Yang *et al.* reported the synthesis of 4-substituted coumarins via palladium-catalyzed cross-couplings of 4-tosylcoumarins with terminal acetylenes and organozinc reagents.[111] Palladium-catalyzed site-selective cross-coupling reactions of 3-bromo-4-trifluormethylsulfonyloxycoumarin or 3-bromo-4-tosyloxycoumarin provide an efficient and facile route for the synthesis of 3,4-disubstituted coumarins.[112] Herein, I report a new and convenient synthesis of arylated coumarins by site-selective Suzuki–Miyaura cross-coupling reactions of the bis(triflate) of 4-methyl-5,7-dihydroxycoumarin. The products reported herein are not readily available by other methods.



Wedelolactone

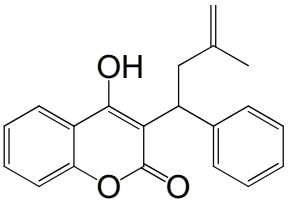


Alternariol

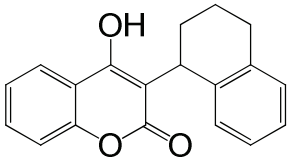


Ellagic acid

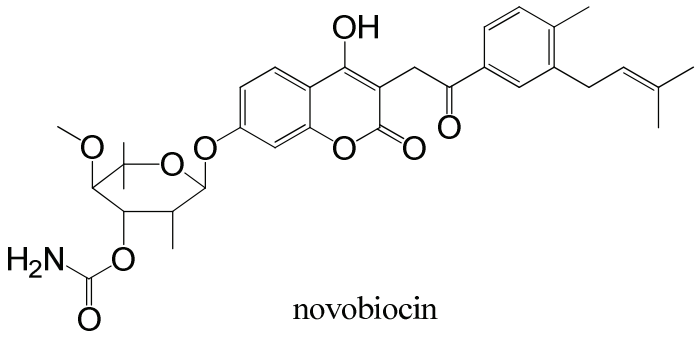
Figure 15. Natural occurring products.



Warfarin



Coumatetralyl

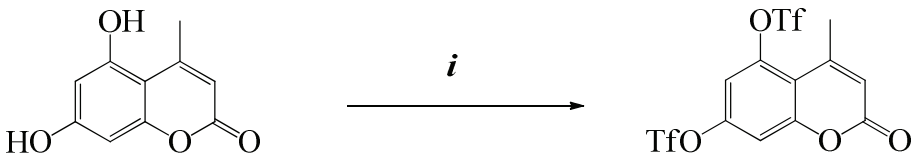


novobiocin

Figure 16. Coumarin-based biologically active compounds.

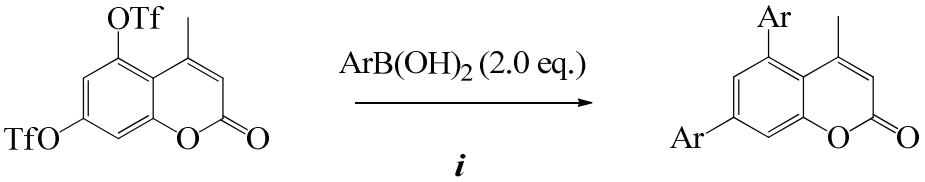
4.2 Result and Discussion:

4-Methyl-5,7-dihdroxycoumarin (**18**) was transformed to its bis(triflate) **19** in 75% yield (Scheme 30) by using triflic anhydride (2.4 equiv) and triethylamine (4.0 equiv). The addition of triflic anhydride was performed at -78 °C. The Suzuki-Miyaura reaction of **19** with arylboronic acids **3** (2.0 equiv.) afforded the 4-methyl-5,7-diarylcoumarines **20a-g** in 70-86% yield (Scheme 31, Table 15). Both electron-poor and electron-rich arylboronic acids could be successfully employed. The best yields were obtained by using $Pd(PPh_3)_4$ (3 mol-%) as the catalyst and K3PO4 (3.0 equiv.) as the base and mixture from (toluene /1,4-dioxane 1:1) at 105 °C for 8 h.



18 **19 (75%)**

Scheme 30**.** Synthesis of **19**: i, 1) **18** (1.0 equiv), Et_3N (4.0 equiv), CH_2Cl_2, 20 °C; 2) Tf_2O (2.4 equiv), -87°C→ 20 °C, 6 h.



19 **20a-g**

Scheme 31. Synthesis of **20a-g**. Conditions: *i*, **19** (1.0 equiv), **3** (2.0 equiv.), K_3PO_4 (3.0 equiv.), $Pd(PPh_3)_4$ (6 mol-%), (toluene /1,4-dioxane = 1:1), 105 °C, 8 h.

Table 15. Synthesis of **20a-g**

3	20	Ar	20 (%) [a]
a	**a**	4-MeC_6H_4	86
b	**b**	3,5-MeC_6H_3	81
f	**c**	4-$(MeO)C_6H_4$	83
g	**d**	4-FC_6H_4	74
h	**e**	4-ClC_6H_4	77
J	**f**	4-$CF_3C_6H_4$	70
l	**g**	C_6H_5	79

[a] Yields of isolated products

The structure of **20b** was independently confirmed by X-ray crystal structure analysis (fig 17).

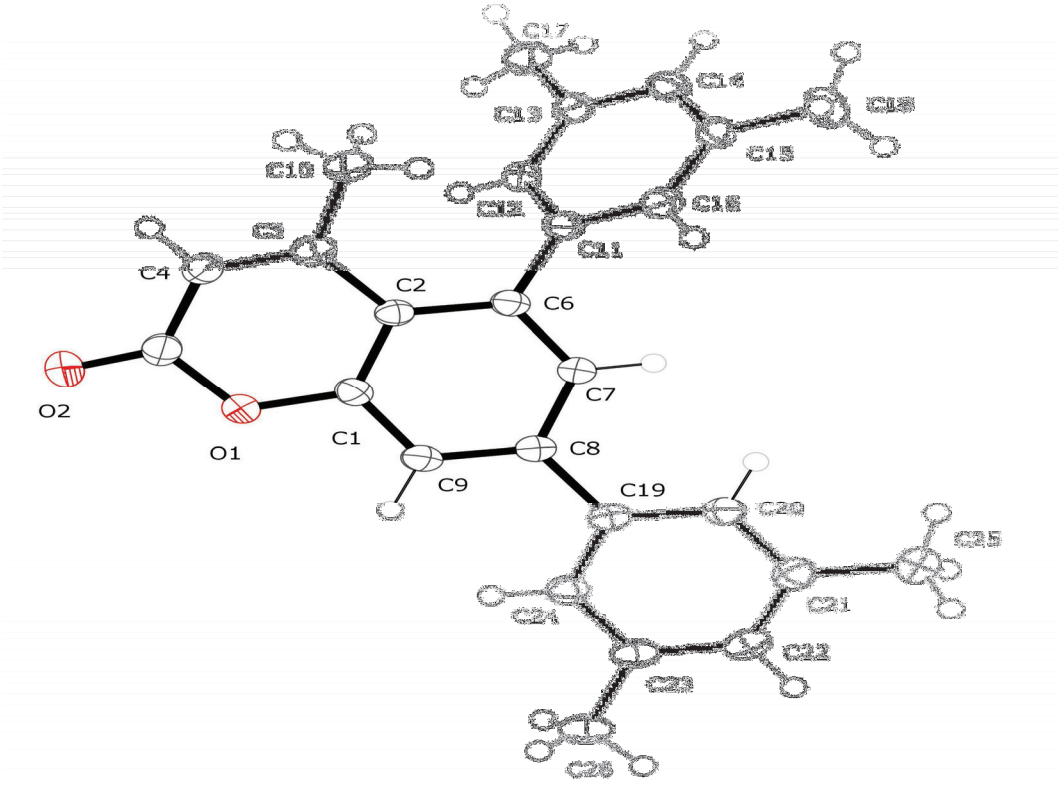
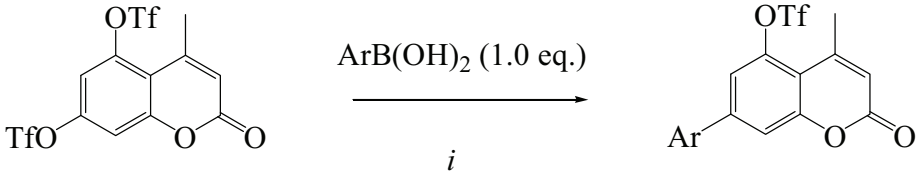


Figure 17. Molecular structure of **20b.**

The Suzuki-Miyaura reaction of **19** with arylboronic acids **3** (1.0 equiv.) afforded the 4-methyl-7-aryl-5-trifluorosulfonyloxy-coumarin **21a-f** in 60-80% yield with very good site-selectivity (Scheme 32, Table 16). During the optimization, it proved to be important to use exactly 1.0 equiv. of the arylboronic acid and to carry out the reaction at 70 instead of 105 °C and to use toluene as a solvent (reaction time 8 h). Both electron-poor and electron-rich arylboronic acids were successfully used.



19 **21a-f**

Scheme 32. Synthesis of **21a-f**. Conditions: *i*, **19** (1.0 equiv), **3** (1.0 equiv.), K_3PO_4 (1.0 equiv.), $Pd(PPh_3)_4$ (3 mol-%), Toluene, 70 °C, 8 h.

Table 16. Synthesis of **21a-f**

3	**21**	**Ar**	**21 (%)** [a]
a	**a**	4-MeC_6H_4	80
c	**b**	3,5-MeC_6H_3	77
d	**c**	4-EtC_6H_4	70
f	**d**	4-$(MeO)C_6H_4$	83
g	**e**	4-FC_6H_4	63
h	**f**	4-ClC_6H_4	60

[a] Yields of isolated products

The structure of product **21b** was elucidated by 2D NMR spectroscopy (NOESY, COSY, HMBC, HSQC). A NOESY correlation between hydrogen atoms H-6 and H-8 with the *ortho* protons of the 3,5-dimethylphenyl group is diagnostic.

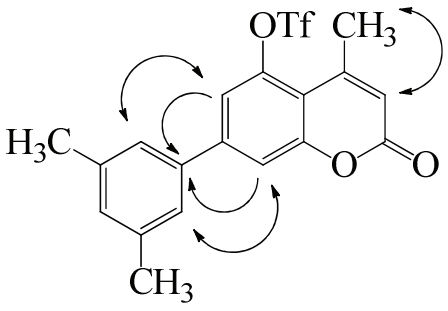
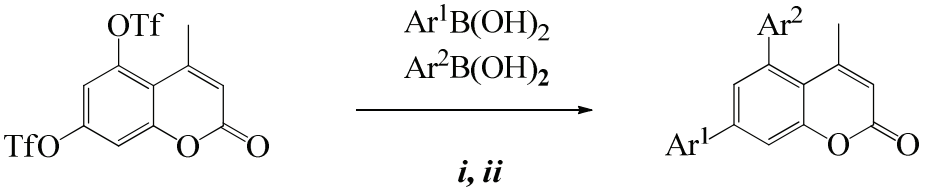


Figure 18. Important HMBC (single head arrows), NOESY (double head arrows) correlations of **21b.**

The one-pot Suzuki-Miayura reaction of bis-triflate **19** with two different arylboronic acids **3** (sequential addition of 1.0 equiv. of each boronic acid) afforded the 4-methyl-5,7-diarylcoumarin **22a-d** in 60-75% yields (Scheme 32, Table 17). The reactions were carried out at 70 °C for the first step (to avoid double coupling) and at 105 °C in the second step.



19 **22a-d**

Scheme 33. Synthesis of **22a-d**. Conditions: *i*, **19** (1.0 equiv), $Ar^1B(OH)_2$ (1.0 equiv.), K_3PO_4 (1.5 equiv.), $Pd(PPh_3)_4$ (3 mol-%), toluene, 70 °C 8 h. *ii,* $Ar^2B(OH)_2$ (1.0 equiv.), K_3PO_4 (1.5 equiv.), $Pd(PPh_3)_4$ (3 mol-%), 1,4-dioxane, 105 °C 8 h.

Table 17. Synthesis of **22a-d**

3	22	Ar^1	Ar^2	% (22)[a]
c,a	**a**	3,5-MeC_6H_3	4-MeC_6H_4	70
c,g	**b**	3,5-MeC_6H_3	4-FC_6H_4	60
a,h	**c**	4-MeC_6H_4	4-ClC_6H_4	62
f,a	**d**	4-(MeO)C_6H_4	4-MeC_6H_4	75

[a] Yields of isolated products

The structure of **22b** was independently confirmed by X-ray crystal structure analysis (Figure 19).

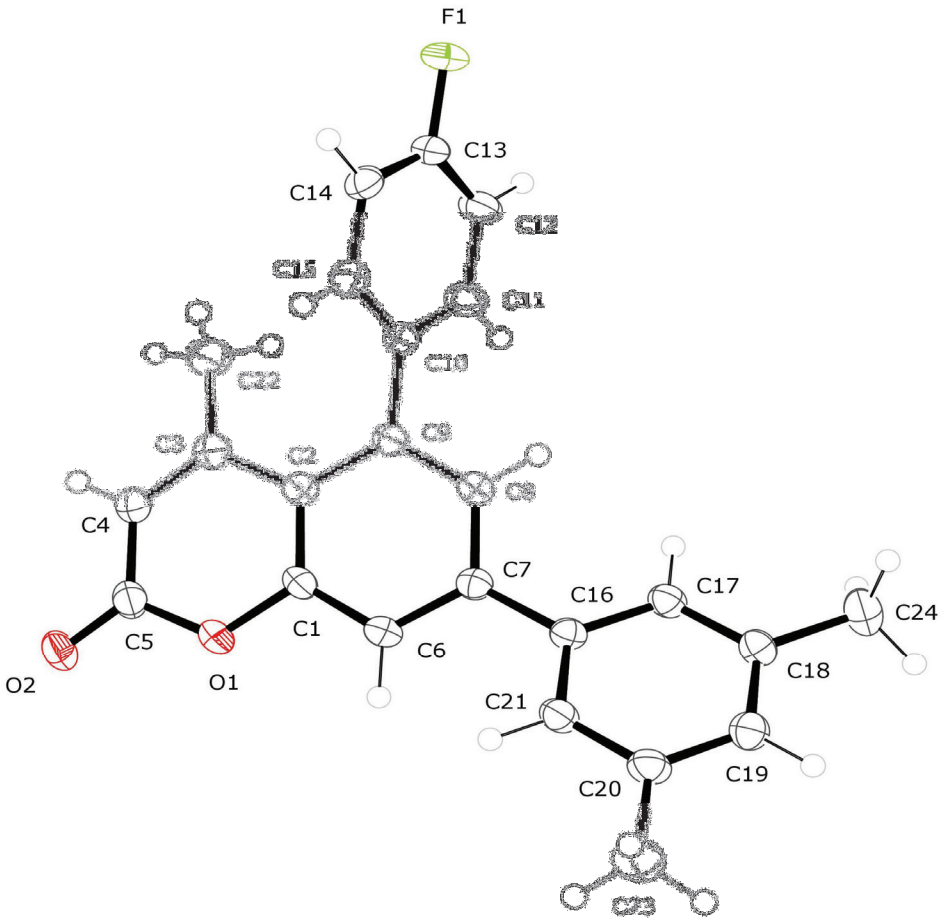


Figure 19. Molecular structure of **22b.**

Suzuki-Miyaura reactions of **19** proceed by initial attack at position 7 which is sterically less hindered than position 5 (Fig 20). Position 5 and 7 can be considered similar with regard to their electron density. Therefore, electronic factors are unlikely to play a role.

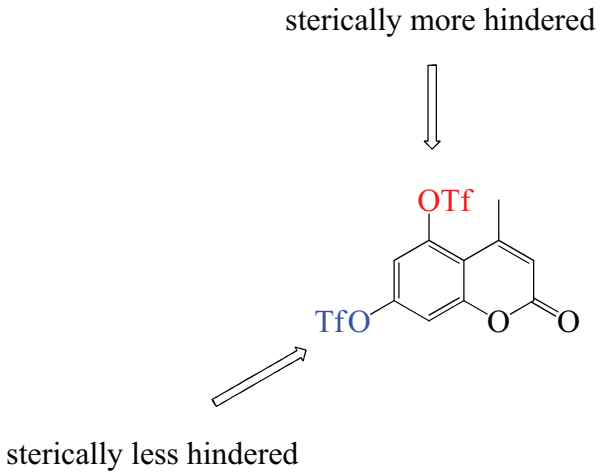
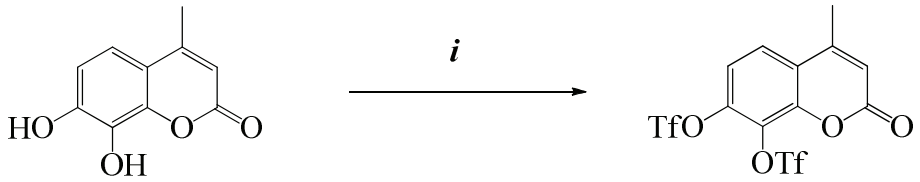


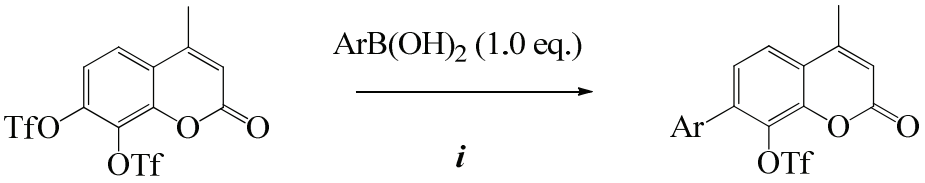
Figure 20. Possible explanation for the site-selectivity

4-Methyl-7,8-dihydroxycoumarin **23** was transformed into its bis(triflate) **24** in 80% yield (Scheme 31). The Suzuki-Miayura reaction of bis-triflate **24** with 1.0 equiv. of arylboronic acids **3** afforded the 7-aryl-5-(trifluorosulfonyloxy)coumarin **25a-g** in 70-80% yields (Scheme 34, Table 18). The reactions were carried out under standard conditions (3 mol-% of $Pd(PPh_3)_4$ as the catalyst, K_3PO_4 as the base, 1,4-dioxane, 80 °C for 7 h). During the optimization it was found that only electron rich arylboronic acids give good results and, in contrast, no reaction occurred with electron poor arylboronic acids, even when different solvents (1,4-dioxane, toluene, THF, MeOH), bases (K_3PO_4, K_2CO_3) and catalysts ($Pd(PPh_3)_2Cl_2$, $Pd(PPh_3)_4$ and $Pd(OAc)_2$ with S-Phos or X-Phos) were studied.



23 **24**

Scheme 34. Synthesis of **24** i: 1) **23** (1.0 equiv), Et_3N (4.0 equiv), CH_2Cl_2, 20 °C; 2) Tf_2O (2.4 equiv), -87°C→ 20 °C, 6 h.



24 **25a-g**

Scheme 35. Synthesis of **25a-g**. Conditions: *i*, **2** (1.0 equiv), **3a-f** (1.0 equiv.), K_3PO_4 (1.5 equiv.), $Pd(PPh_3)_4$ (3 mol-%), 1,4-dioxane, 80 °C, 8 h.

Table 18. Synthesis of **25a-g**

3	25	Ar	25 (%) [a]
a	**a**	4-MeC_6H_4	80
b	**b**	3-MeC_6H_4	80
c	**c**	3,5-MeC_6H_3	77
d	**d**	4-EtC_6H_4	70
e	**e**	4-*tBu*C_6H_4	83
f	**f**	4-(OMe)C_6H_4	83

[a] Yields of isolated products

The structure of **25e** was independently confirmed by X-ray crystal structure analysis (Figure 21).

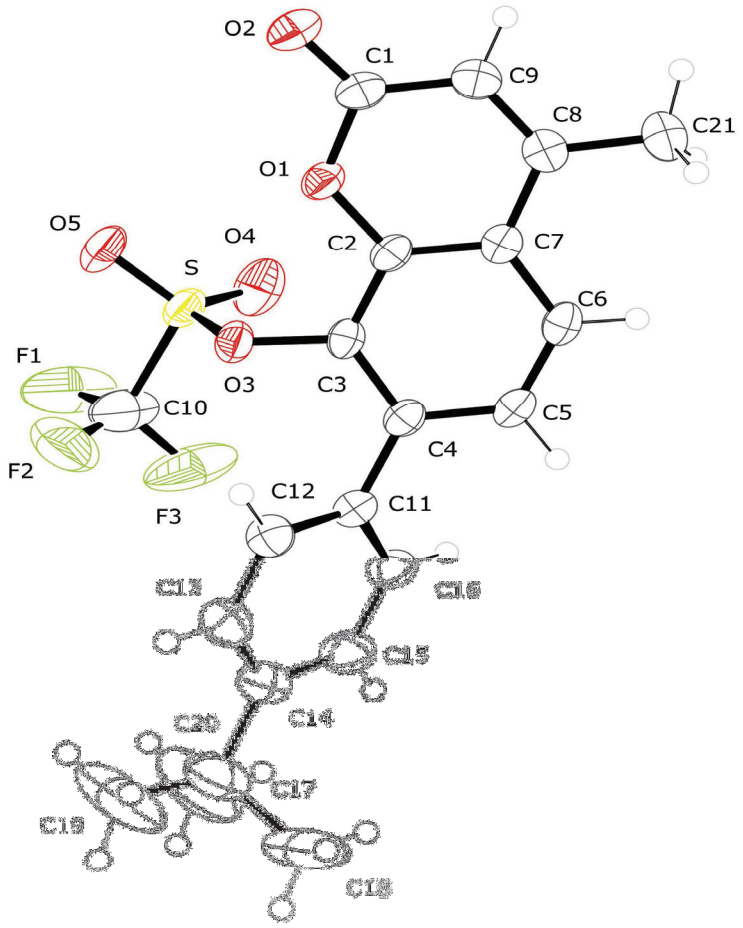


Figure 21. Molecular structure of **25e.**

The Suzuki-Miyaura reaction of bis-triflate **24** with 2.0 equiv. of arylboronic acids **3** to give the corresponding diaryls failed even when different solvents, bases and catalysts were studied. An increased temperature also did not allow the reaction to proceed. This might be due to high steric hindrance at position C8 and the electronically less deficient character of this position (Figure 21).

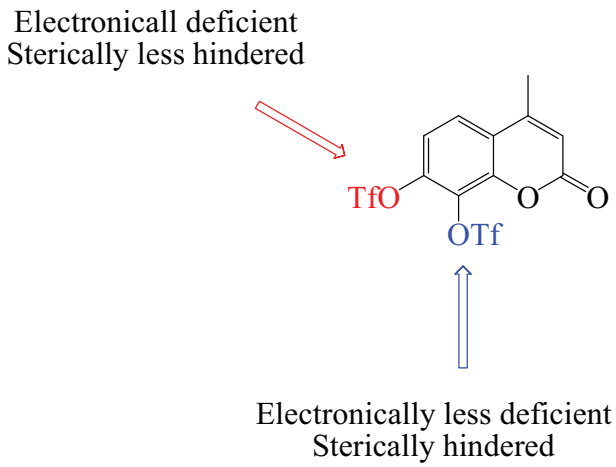


Figure 21. Possible explanation for the site-selectivity.

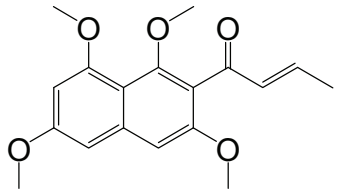
3.4 Conclusion:

I have synthesized 4-methyl-5,7-diarylcoumarins by Suzuki-Miyaura reactions of the bis(triflate) of 7,8-dihydroxycoumarine. The first attack proceeded with very good site-selectivity at position 7. I have also synthesized 4-methyl-7-aryl-8-(trifluorosulfonyloxy)coumarins, whereas the corresponding diaryl derivatives can not be obtained.

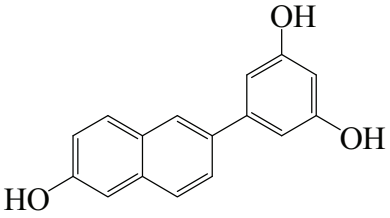
5. Synthesis of Ethyl 3,5-Diaryl-2-naphthaoates and Methyl 3,7-Diaryl-2-naphthaoates by Suzuki-Miyaura Cross-Coupling Reactions of Ethyl 3,5-Bis(trifluoromethylsulfonyloxy)-2-naphthoates and Methyl 3,5-B (trifluoromethylsulfonyloxy)-2-naphthoates.

5.1 Introduction:

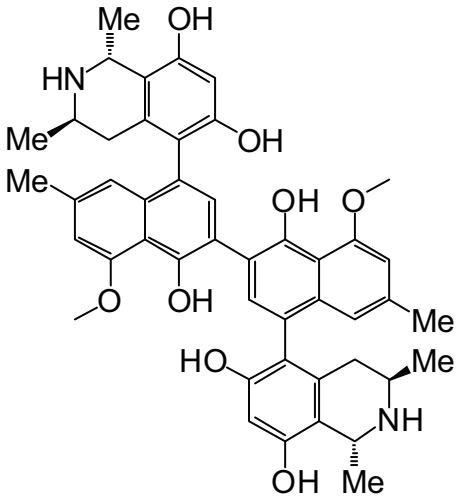
Substituted naphthalenes are important as drugs and lead structures in medicinal chemistry.[113] They also act as intermediates in the synthesis of organic dyes and surfactants. In the polymer industry they also serve in the function of supporting agents.[114] Naphthlene derivatives also exhibit marked pharmacological activities, like antimicrobial activities[115] and activity as antibody inhibitors.[116] Naphthalene derivatives are found in a number of natural sources, for example, guieranone A (Figure 22) which exhibited potent antifungal activity against *Cladosporium cucumerinum* and is the first naphthyl ketone derivative which has been isolated from the family *Combretaceae* from the leaves of *Guiera senegalensis*. Its structure was elucidated as (2*E*)-1-(1,3,6,8-tetramethoxy-2-naphthyl)but-2-en-1-one.[117] Michellamine A, isolated from *Ancistrocladus korupensis*, has attracted the scientific community primarily because of its antimalaria and anti-HIV activity.[118–120] Resveratrol is a naturally occurring potent anticancer drug, which, however, suffers from chemical and metabolic instability.[121] 5-(6-hydroxynaphthalen-2-yl)benzene-1,3-diol was found to be most active against human breast cancer cell line B. Konzik *et al.* have shown that the phenyl substituents of naphthalenes have a strong influence on their fungistatic activity.[122] Many methods are used to prepare substituted naphthalenes. For example, Baylis–Hillman adducts were used to prepare 2-substituted naphthalenes[123], or irradiation of 2-allylated acylbenzenes in DMF in the presence of potassium *tert*-butoxide.[124] Other methods, such as transition-metal-catalyzed [2+2+2] alkyne cyclizations[125] and the Lewis acid catalyzed cyclization of carbonyl compounds with alkynes and [4+2] cyclizations, have also been reported.[126]



Guieranone A



5-(6-Hydroxynaphthalen-2-yl)benzene-1,3-diol

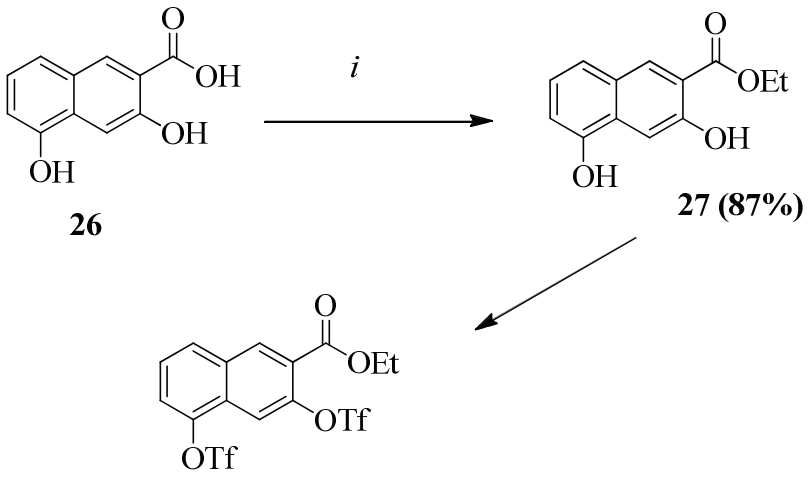


Michellamine A

Figure 22. Pharmacologically important naphthalene derivatives.

5.2 Result and Discussion:

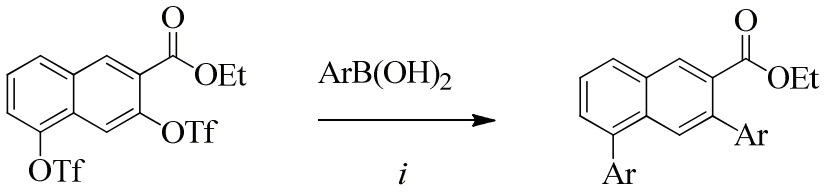
Ethyl 3,5-dihydroxynaphthoate (27) was prepared from the commercially available acid 26 (Scheme 36). The bis(triflate) 28 was prepared by reaction of **27** with triflic anhydride.



26 **27 (87%)** **28 (77%)**

Scheme 36. Synthesis of **28**; *i*, **26** (1.0 equiv), EtOH, H_2SO_4 conc. reflux, 6 h; *ii*: 1) **27** (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 Suzuki-Miyaura reaction of **28** with boronic acids **3** (2.4 equiv.), in the presence of $Pd(PPh_3)_4$ (6 mol-%) and K_3PO_4 (3.0 equiv.) in THF (reflux, 8 h), gave the 3,5-diaryl-2-naphthoates **29a-i** in 60-82% yields (Scheme 37, Table 19). The reactions were carried out under the conditions reported for related bis(triflates). Surprisingly, the yield of product **29d**, derived from the electron rich (nucleophilic) (4-methoxyphenyl)boronic acid (**3f**), was lower than the yields of the other products.



28 **29a-i**

Scheme 37. Synthesis of **29a-i**. *Reagents and conditions: i*, **28** (1.0 equiv), **3** (2.4 equiv.), $Pd(PPh_3)_4$ (6 mol-%), K_3PO_4 (3.0 equiv.), THF, 60 °C, 8 h.

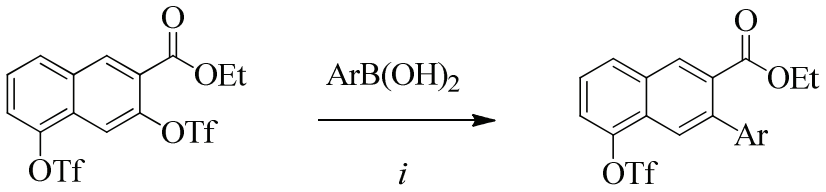
Table 19. Synthesis of **29a-i**

3	**29**	**Ar**	**29** (%) [a]
a	**a**	4-MeC_6H_4	76
c	**b**	3,5-MeC_6H_3	82
e	**c**	4-*tBu*C_6H_4	80
f	**d**	4-(MeO)C_6H_4	60
g	**e**	4-FC_6H_4	77
h	**f**	4-ClC_6H_4	76
j	**g**	4-(F_3C)C_6H_4	80
p	**h**	2,6-(MeO)C_6H_3	70
q	**i**	3-ClC_6H_4	81

[a] Yields of isolated products

The Suzuki reaction of **28** with boronic acids **3** (1.1 equiv.), in the presence of $Pd(PPh_3)_4$ (3 mol-%), afforded the 3-aryl-5-(trifluoromethylsulfonyloxy)-2-naphthoates **30a-f** in 63-

82% yield (Scheme 38, Table 20). All products were formed with very good site-selectivity at carbon atom C-3. The yield of product **30d**, derived from **3f**, was again relatively low compared to the yields of the other products. To avoid twofold coupling, it proved to be very important to carry out the reaction at 20 °C (instead of 60 °C). The pure products were isolated by chromatographic purification which was necessary to remove a small amount of bis-coupled product detected in the crude product mixture.



28 **30a-f**

Scheme 38. Synthesis of **30a-f**. *Reagents and conditions: i*, **28** (1.0 equiv.), **3** (1.0 equiv.), $Pd(PPh_3)_4$ (3 mol-%), K_3PO_4 (1.5 equiv.), THF, 20 °C, 12 h.

Table 20. Synthesis of **30a-f**

3	**30**	Ar	% (**30**)[a]
a	**a**	4-MeC_6H_4	70
c	**b**	3,5-MeC_6H_3	80
e	**c**	4-*t*BuC_6H_4	75
f	**d**	4-$(MeO)C_6H_4$	63
j	**e**	4-$(F_3C)C_6H_4$	65
q	**f**	3-ClC_6H_3	82

[a] Yields of isolated products

A ^1H, ^1H NOESY experiment was used to confirm the structure of compound **30a** (Figure 23).

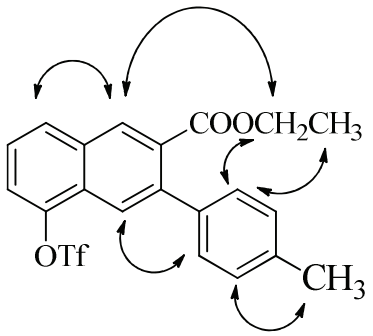
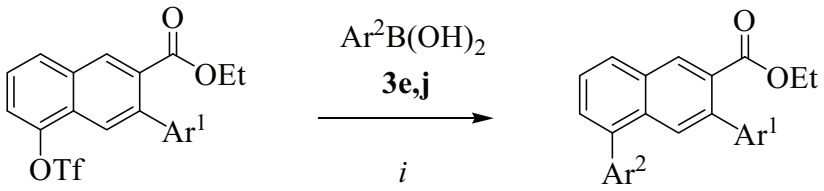


Figure 23. Relevant NOESY-correlation for Compound **30a.**

The Suzuki reaction of **30a** and **30c** with arylboronic acids **3e** and **4j** afforded the 3,5-diaryl-2-naphthoates **31a** and **31b** in 70 and 73% yield, respectively (Scheme 39, Table 21). During the optimization, it proved to be important to carry out the reaction at 60 °C (as for the synthesis of **30a-i**).



30a,c **31a,b**

Scheme 39. Synthesis of **31a,b**. *Reagents and conditions: i*, **30a,b** (1.0 equiv.), **3c,j** (1.0 equiv.), $Pd(PPh_3)_4$ (3 mol-%), K_3PO_4 (1.5 equiv.), THF, 60 °C, 8 h.

Table 21. Synthesis of **31a-b**

30	**3**	**31**	**Ar^1**	**Ar^2**	**31** (%)[a]
a	**e**	**a**	4-MeC_6H_4	4-*t*BuC_6H_4	70
c	**j**	**b**	4-*t*BuC_6H_4	4-$(F_3C)C_6H_4$	73

[a] Yields of isolated products

The Suzuki-Miyaura reaction of ethyl 3,5-trifluoromethylsulfonyloxy-2-naphthoate **28** occurs first at the sterically more hindered position C-3. This might be explained by electronic effects (Figure 24). The oxidative addition of the electron-rich palladium species usually occurs first at the most electron deficient carbon atom.[59] In case of **28**, carbon atom C-3 is more electron deficient than C-5, due to its location *ortho* to the ester group. In addition, the site-selectivity might be controlled by chelation of the catalyst to the carbonyl group. Handy and Zhang suggested a simple guide for the prediction of the site-selectivity of palladium(0) catalyzed cross-coupling reactions based on the ^{1}H NMR chemical shift values of the compound in which the halide atoms or the triflate groups of the substrate are replaced by hydrogen atoms.[127] This rule gives the correct prediction for site-selective Suzuki reactions of **28**.

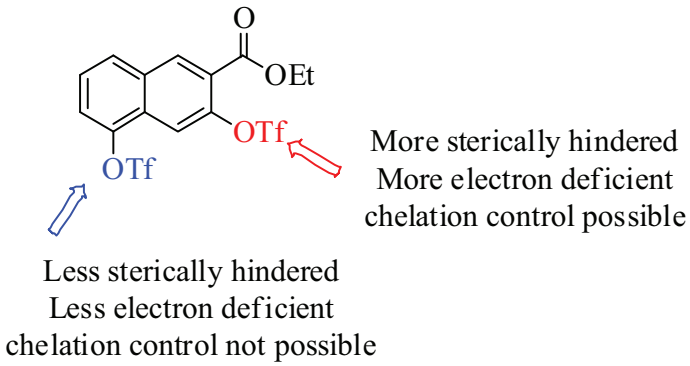
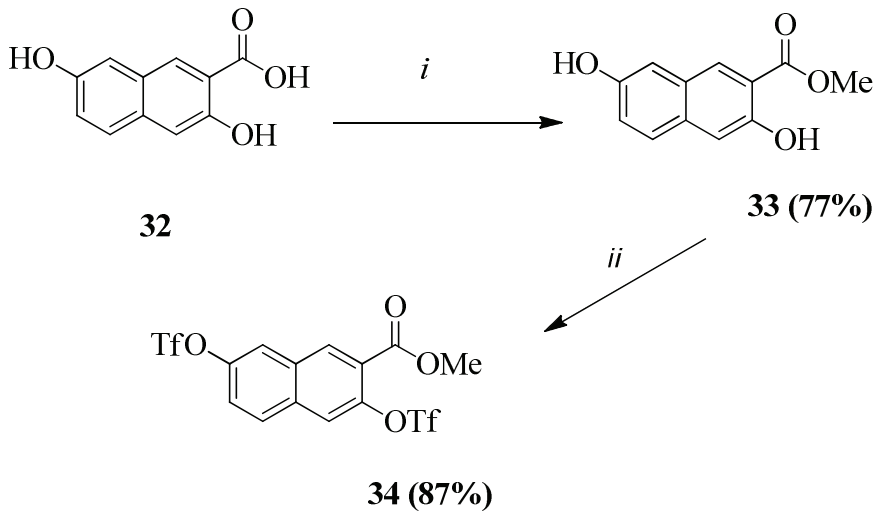


Figure 24. Possible explanation for the site-selectivity.

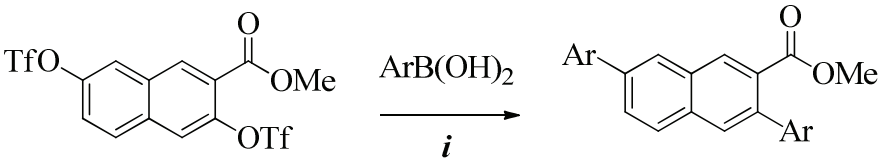
Methyl 3,7-dihydroxynaphthoate (**33**) was prepared from the commercially available acid **32** (Scheme 40). The bis(triflate) **34** was prepared by reaction of **33** with triflic anhydride.



32 **33 (77%)** **34 (87%)**

Scheme 40. Synthesis of **34**; *i*, **32** (1 equiv), (Me_2SO_4) (2.2 equiv) , DIPEA (1.1 equiv), DMF, 85 °C, 1 h. *ii*, **33** (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 Suzuki-Miyaura reaction of **33** with boronic acids **4a-i** (2.4 equiv.), in the presence of $Pd(PPh_3)_4$ (6 mol-%) and K_3PO_4 (3.0 equiv.) in 1,4-dioxane at room temperature for **3h**, gave the methyl 3,7-diaryl-2-naphthoates **34a-i** in 80-90% yields (Scheme 41, Table 22).



34 **35**

Scheme 41. Synthesis of **35a-i**. *Reagents and conditions: i*, **34** (1.0 equiv), **3** (2.4 equiv.), $Pd(PPh_3)_4$ (6 mol-%), K_3PO_4 (3.0 equiv.), 1,4-dioxane, 20 °C, 4 h.

Table 22. Synthesis of 35a-b

3	**35**	Ar	% (**35**)[a]
b	**a**	3-MeC_6H_4	81
c	**b**	3,5-$Me_2C_6H_3$	83
d	**c**	4-EtC_6H_4	77
f	**d**	4-$(MeO)C_6H_4$	85
g	**e**	4-FC_6H_4	75
h	**f**	4-ClC_6H_4	72
j	**g**	4-$(CF3)C_6H_4$	71
l	**h**	C_6H_6	74
q	**i**	3-ClC_6H_4	70

The structure of **35g** was independently confirmed by X-ray crystal structure analysis (Figure 25).

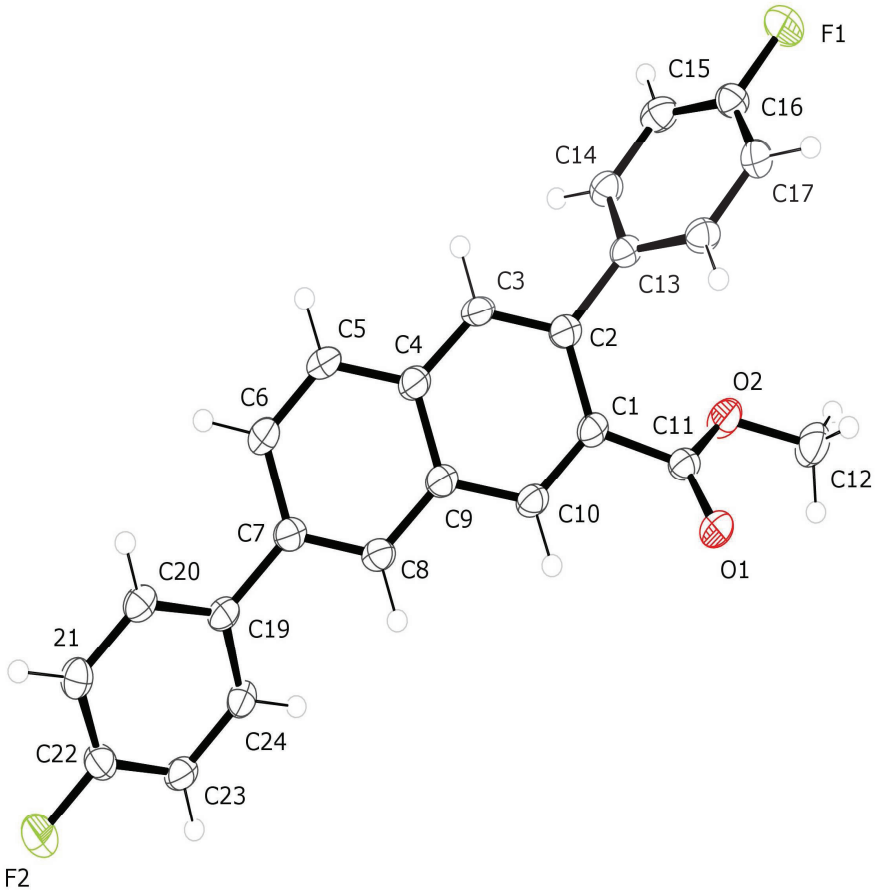


Figure 25. Molecular structure of **35g.**

5.3 Conclusion:

I have studied site-selective Suzuki-Miyaura reactions of the bis(triflate) of ethyl 3,5-trifluoromethylsulfonyloxy-2-naphthoate. The first attack occurred at the sterically more hindered position C-3. This method provides a conveniet access to aryl-substituted naphthalenes which are not readily available by other methods.

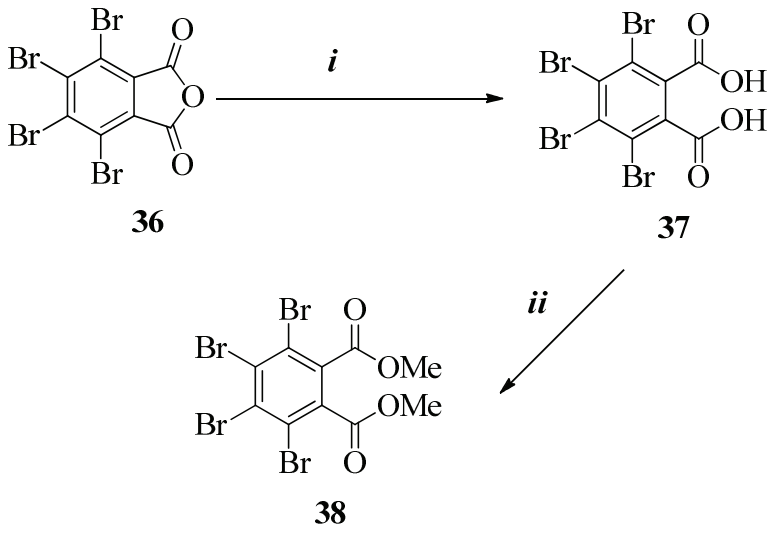
6. Arylation of dimethyl tetrabromophthalate by Suzuki–Miyaura cross-coupling reactions.

6.1 Introduction:

Aromatic skeletons are regarded as the essential structures of natural products, functional materials, and starting substrates of organic molecules. Phthalate esters (PAEs) are primarily used as plasticizers for polyvinyl chloride (PVC) resins, adhesives, and cellulose film coating. Other industrial applications include the manufacturing of cosmetics, insect repellents, insecticide carriers, and propellants.[127] Many methods were applied to prepare substituted phthalate compounds. For example, the Diels–Alder cycloaddition has been used as an efficient method,[128] Beller's reaction,[129] and transition metal–catalyzed [2 + 2+ 2] cycloadditions of alkynes.[130] Other kinds of substituted phthalates, for example, 4-hydroxy and 2,4-dihydroxy-homophthalate were prepared by [4+2] cycloaddition of 1,3-bis(silyoxy)-1,3-butadienes with dimethyl allene-1,3-dicarboxylate.[131]

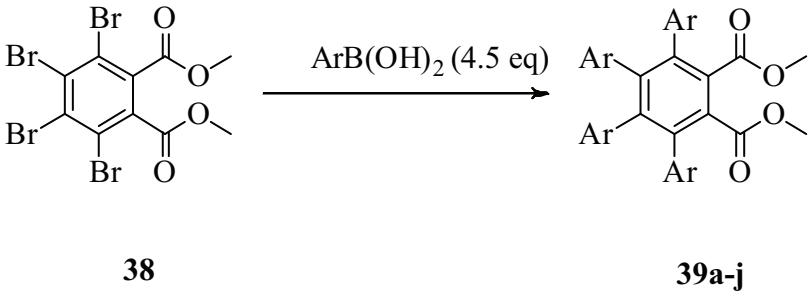
6.2 Result and discussion:

The commercially available tetrabromophthalic anhydride **36** was transferred to the corresponding acid **37** which was treated with Hünig's base (DIPEA) and dimethyl sulfate in *N,N*-dimethylformamide at 85 °C for 1 h to give dimethyl tetrabromophthalate **38** (Scheme 42).



Scheme 42. Synthesis of **38**; *i*: 1) **36** (1.0 equiv), KOH (2.0 %), reflux (30 min), HCl (20 %). *ii*: 1) **37** (1 equiv), (Me_2SO_4) (4.4 equiv), DIPEA (1.5 equiv), DMF, 85 °C, 1 h.

The Suzuki-Miyaura reaction of **38** with 4.5 equiv. of various arylboronic acids **3** afforded the dimethyl tetraarylphthalates **39a-j** in 90-72% yields (Scheme 43, Table 23). The reaction had to be carried out at higher temperature (130 °C). Very good yield were obtained for products derived from both electron poor and rich arylboronic acids.



Scheme 43. Synthesis of **39a-j**. *Reagents and conditions: i*, **3** (1.0 equiv), **4a-k** (4.5 equiv.), $Pd(PPh_3)_4$ (12 mol-%), K_2CO_3 (2M, 1 mL), 1,4-dioxane, 130 °C, 6 h.

Table23 . Synthesis of **39a- f**

3	**39**	**Ar**	**4** (%) [a]
a	**a**	4-MeC_6H_4	86
b	**b**	3-MeC_6H_4	85
c	**c**	3,5-MeC_6H_3	80
d	**d**	4-EtC_6H_4	79
e	**e**	4-*t*BuC_6H_4	88
f	**f**	4-(MeO)C_6H_4	90
g	**g**	4-FC_6H_4	79
h	**h**	4-ClC_6H_4	77
j	**i**	4-$CF_3C_6H_4$	73
l	**j**	C_6H_5	80

[a] Yields of isolated products

The structure of **39c** was independently confirmed by X-ray crystal structure analysis (Figure 26).

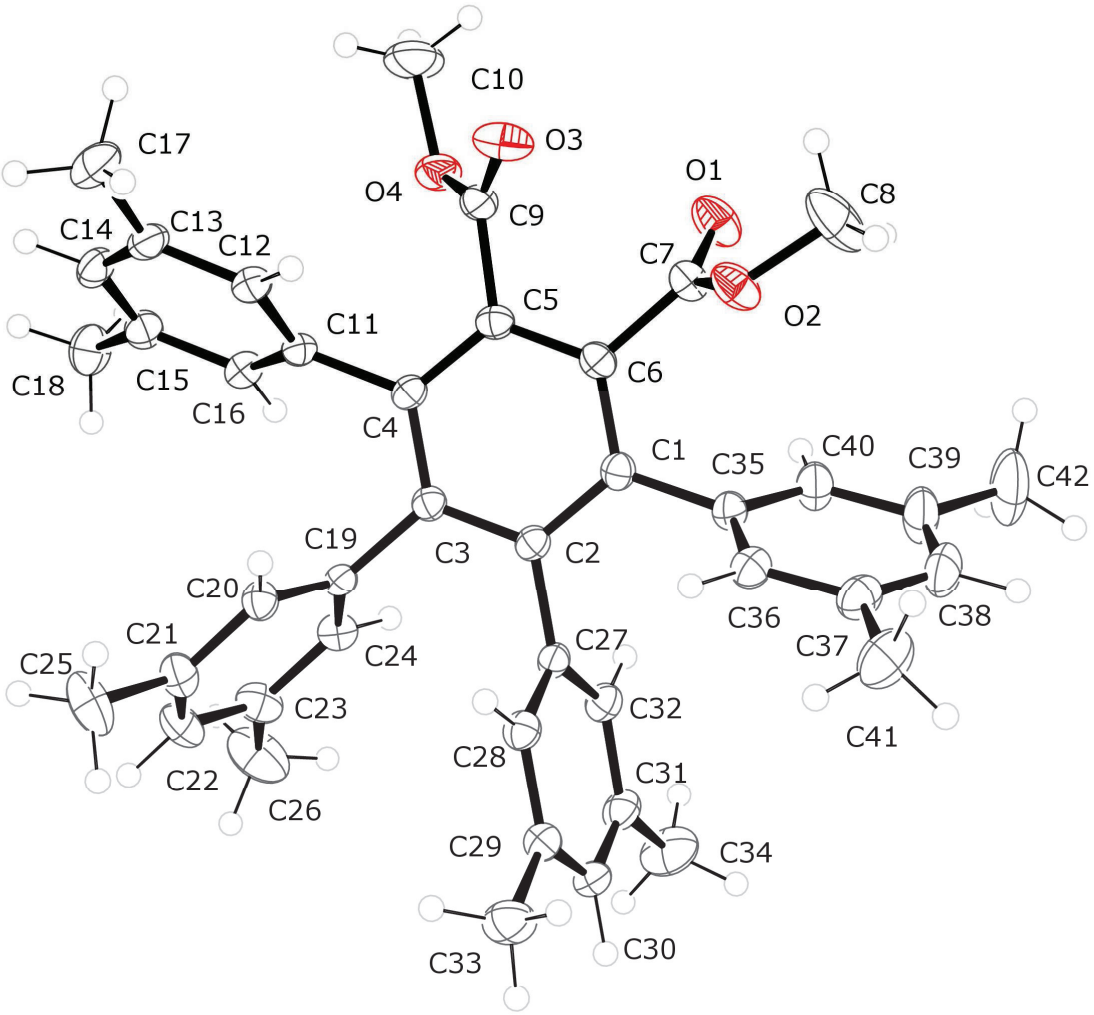


Figure 25. Molecular structure of **39c.**

Conclusion:

I have synthesized dimethyl tetraarylphthalates from dimethyl tetrabromophtahlate by Suzuki- Miyaura reactions. Both electron poor and rich arylboronic acids were successfully employed.

Abstract:

This PhD thesis includes regioselective palladium(0)-catalyzed Suzuki cross-coupling reactions of quinolines, flavones, coumarins, naphthaoates and phthalates. These classes of compounds are of pharmacological relevance. Suzuki cross-coupling reaction of 5,7-dibromo-8-(trifluoromethanesulfonyloxy)quinoline afforded arylated quinolines. The reactions proceeded with very good site-selectivity. The Suzuki-Miyaura reaction of the bis(triflates) of 5,7-dihydroxyflavone, 4-methyl-5,7-dihydroxycoumarin, 4-methyl-5,8-dihydroxycoumarin, ethyl 3,5-dihydroxy-2-naphthaoate and methyl 3,7-dihydroxy-2-naphthoate with different boronic acids gave the corresponding arylated derivatives, most of them with very good site-selectivity. The reaction of tetrabromophthalate with 4.5 equivalents of arylboronic acids gave tetraarylphthalates in very good yields.

Diese Dissertation umfasst Palladium(0)-katalysierte Suzuki-Kreuzkupplungsreaktionen von Chinolinen, Flavonen, Cumarinen, Naphthoaten und Phthalaten. Auf Grund der pharmakologischen Bedeutung dieser Substanzklassen wurden unter Anwendung der genannten Methodik neue Derivate synthetisiert. Suzuki-Kreuzkupplungsreaktionen von 5,7-Dibrom-8-(trifluormethansulfonyloxy)chinolin ergaben arylierte Chinoline. Die Reaktionen wiesen sich durch eine gute Regioselektivität aus. Die Suzuki-Miyaura-Reaktion der Bis-Triflate von 5,7-Dihydroxyflavon, 4-Methyl-5,7-dihydroxycumarin, 4-Methyl-5,8-dihydroxycumarin, Ethyl 3,5-dihydroxy-2-naphthoat und Methyl 3,7-dihydroxy-2-naphthoat mit unterschiedlichen Boronsäuren ergab die entsprechenden Arylderivate, den Großteil davon mit sehr guter Regioselektivität. Die Reaktion von Tetrabromphthalat mit 4.5 Äquivalenten unterschiedlicher Boronsäuren führte in sehr guten Ausbeuten zu Tetraarylphthalaten.

7.0 Experimental Section:

7.1 General: Equipment, Chemicals and Work Technique:

NMR Spectroscopy

Bruker AC 250, Bruker ARX 300, Bruker ARX 500. For NMR characterization the one-dimensional ^{1}H NMR, proton-decoupled ^{13}C NMR, and DEPT 135 spectra were collected. If necessary, other techniques (NOESY, COSY, HMQC, HMBC) were applied as well. All NMR spectra presented in this work were collected in $CDCl_3$ solution. All chemical shifts are given in ppm.

References (^{1}H NMR): TMS (δ = 0.00) or residual $CHCl_3$ (δ = 7.26) were taken as internal standard.

References (^{13}C NMR): TMS (δ = 0.0) or residual $CHCl_3$ (δ = 77.0) were taken as internal standard.

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

Infrared Spectroscopy (IR)

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

Mass Spektrometry (MS)

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

High Resolution Mass Spectrometry (HRMS)

Varian MAT 311, Intecta AMD 402.

Elemental Analysis

LECO CHNS-932, Thermoquest Flash EA 1112.

Melting Points

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

X-ray Structures

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

Thin Layer Chromatography (TLC)

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

Column Chromatography

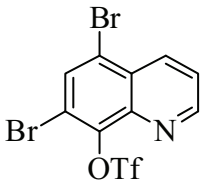
Column chromatography was performed with Merck Silica Gel 60 or Macherey-Nagel Silica Gel 60 (0.063-0.200 mm, 70-230 mesh). The finer Merck Silica Gel 60 (0.040-0.063 mm, 230-400 mesh) was chosen when appropriate.

Chemicals and work technique:

All solvents for using were distilled by standard methods. All reactions were carried out under an inert atmosphere, oxygen and humidity exclusion. All of the chemicals are standard, commercially available from Merck®, Aldrich®, Arcos® and others. The order of the characterized connections effected numerically, but does not correspond to the order in the main part of dissertation.

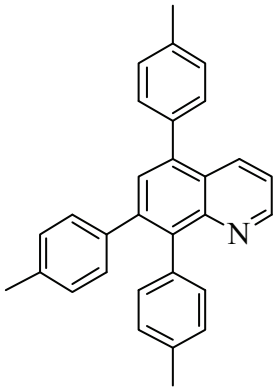
7.2 Procedures and Spectroscopic Data:

Synthesis of 5,7-Dibromo-8-(trifluoromethanesulfonyloxy)-quinoline (2): To a solution of 5,7-dibromo-8-hydroxyquinoline (**1**) (1.0 g, 3.30 mmol) in CH_2Cl_2 (40 mL) was added pyridine (0.97 mL, 13.4 mmol) at room temperature under an argon atmosphere. After 10 min, Tf_2O (0.6 mL, 3.9 mmol) was added at -78 °C. The mixture was allowed to warm to 20 °C and stirred overnight. The reaction mixture was filtered and the filtrate was concentrated in vacuo. The residue was purified by chromatography (flash silica gel, heptane-EtOAc) without aqueous work up to give **2** as a white solid (1.1 g, 80%); mp 119-120°C. ^{1}H-NMR (300 MHz, $CDCl_3$): δ = 7.54 (dd, J = 8.61, 4.23 Hz, 1H, ArH), 8.00 (s, 1H, ArH), 8.44 (dd, J = 8.58, 7.05 Hz, 1H, ArH), 8.97 (dd, J = 4.23, 2.67 Hz, 1H, ArH). ^{13}C-NMR (62.9 MHz, $CDCl_3$): δ = 117.6 (d, J = 320.9 Hz, CF_3), 114.9, 120.5 (C), 122.6 (CH), 126.8 (C), 132.3, 134.7 (CH), 140.8, 143.0 (C), 151 (CH). ^{19}F NMR (282 MHz, $CDCl_3$): δ = -72.36 (s, 3F, CF_3). IR (KBr, cm^{-1}): ν = 3084, 2961, 2919, 2850 (w), 1599, 1584, 1555, 1472, 1449 (w), 1420, 1405 (m), 1347, 1334, 1291, 1249 (w), 1229 (m), 1202, 1179, 1129, 1057 (s), 1035, 962, 933 (w), 873 (m), 825, 809, 784 (s), 765 (m), 692 (s), 641 (m), 609, 601, 584 (s), 584, 553, 546 (m). GC-MS (EI, 70 eV): *m/z* (%) =437 ([M]$^+$, [^{81}Br][^{81}Br], 13), 435 ([M]$^+$, [^{81}Br] [^{79}Br], 26), 433 ([M]$^+$, [^{79}Br] [^{79}Br], 13), 304 (49), 303 (10), 302 (100), 276 (37), 274 (73), 272 (39). HRMS (EI-TOF/MS): calcd for $C_{10}H_5Br_2F_3NO_3S$ ([M+H]$^+$,[^{81}Br][^{79}Br]): 435.8283; found 435.8290, calcd for $C_{10}H_5Br_2F_3NO_3S$ ([M+H]$^+$, [^{79}Br][^{79}Br]): 433.8304; found 433.8307.

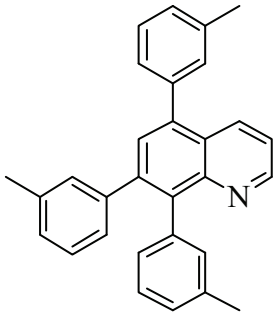


General Procedure for Suzuki–Miyaura Reactions: The reactions were carried out in a pressure tube. A solution of **2** (100 mg, 0.23 mmol), K_2CO_3 (2M, 1.0 mL), $Pd(PPh_3)_4$ (3 mol-% per cross-coupling) and arylboronic acid **3** (1.0 equiv. per cross-coupling) in 1,4-dioxane (3 mL) was stirred at 65-135 °C for 8-12 h under argon atmosphere. To the reaction mixture H_2O (20 mL) and CH_2Cl_2 (25 mL) were added at 20 °C. The organic and the aqueous layers were separated and the latter was extracted with CH_2Cl_2 (20 mL x 2). 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, heptane/EtOAc).

5,7,8-Tris(4-methylphenyl)quinoline (4a): Starting with **2** (100 mg, 0.23 mmol), **3a** (93 mg, 0.69 mmol), $Pd(PPh_3)_4$ (24 mg, 9 mol-%, 0.0207 mmol), K_2CO_3 (2M, 1.0 mL), and 1,4-dioxane (3 mL), **4a** was isolated as a white solid (82 mg, 90%). Reaction temperature: 135 °C for 8 h. M.p. 172-174 °C. ^{1}H NMR (300 MHz, $CDCl_3$): δ = 2.19 (s, 3H, CH_3), 2.25 (s, 3H, CH_3), 2.35 (s, 3H, CH_3), 6.90 (d, J = 7.90 Hz, 2H, ArH), 6.99-7.02 (m, 4H, ArH), 7.07-7.11 (m, 2H, ArH), 7.16-7.22 (m, 3H, ArH), 7.33 (d, J = 8.00 Hz, 2H, ArH), 7.51 (s, 1H, ArH), 8.20 (dd, J = 1.72, 8.50 Hz, 1H, ArH), 8.81 (dd, J = 1.72, 4.14 Hz, 1H, ArH). ^{13}C NMR (75.5 MHz, $CDCl_3$): δ = 21.1, 21.3, 21.4 ($3CH_3$), 120.4 (CH), 126.0 (C), 128.3, 128.5, 129.2, 129.9, 130.0, 130.0, 131.8, 134.1 (CH), 135.3, 136.0, 136.1, 136.5, 137.4, 137.9, 138.8, 139.4, 141.3, 147.5 (C), 150.1 (CH). IR (KBr, cm^{-1}): ν = 3042, 3013, 2954 (w), 2921, 2853 (m), 2728, 1612 (w), 1591 (m), 1571, 1551 (w), 1512 (m), 1491, 1442, 1414, 1389, 1378, 1349, 1335, 1308, 1259, 1212, 1183, 1164, 1111, 1092, 1033, 1019, 990, 975, 961, 950, 941, 904, 894, 879, 850, 843 (w), 829, 821, 788 (s), 729 (m), 714 (w), 692 (m), 666,653, 646, 635, 628, 606 (w), 560, 536 (m). GC-MS (EI, 70 eV): *m/z* (%) = 399 ($[M]^+$, 55), 398 (100), 384 (15), 308 (13). HRMS (EI, 70 eV): calcd for $C_{30}H_{26}N$ $[M+H]^+$: 400.2060; found: 400.2065.

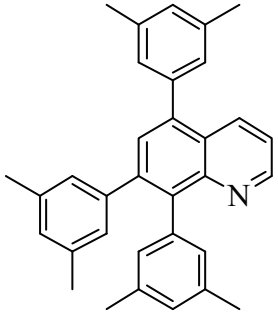


5,7,8-Tris(3-methylphenyl)quinoline (4b): Starting with **2** (100 mg, 0.23 mmol), **3b** (93 mg, 0.69 mmol), $Pd(PPh_3)_4$ (24 mg, 9 mol-%, 0.0207 mmol), K_2CO_3 (2M, 1.0 mL), and 1,4-dioxane (3 mL), **4e** was isolated as a white solid (73 mg, 80%). Reaction temperature: 135 °C for 8 h. M.p. 245-247 °C. ^{1}H NMR (300 MHz, $CDCl_3$): δ = 2.14 (s, 3H, CH_3), 2.19 (s, 3H, CH_3), 2.35 (s, 3H, CH_3), 6.85-6.89 (m, 2H, ArH), 6.94-6.97 (m, 3H, ArH), 6.99-7.00 (m,2H, ArH), 7.05 (m, 1H, ArH), 7.16-7.18 (m, 1H, ArH), 7.20 (dd, J = 4.11, 8.49 Hz, 1H, ArH), 7.26-7.30 (m, 3H, ArH), 7.55 (s, 1H, ArH), 8.21 (dd, J = 1.77, 8.49 Hz, 1H, ArH), 8.84 (dd, J = 1.82, 4.14 Hz, 1H, ArH). ^{13}C NMR (62.9 MHz, $CDCl_3$): δ = 20.2, 20.4, 20.4 ($3CH_3$), 119.3 (CH), 124.8 (C), 126.1, 126.1, 126.2, 126.4, 126.4, 127.3, 127.3, 127.9, 128.6, 129.7, 129.7, 131.5, 133.1 (CH), 135.5, 136.1, 137.0, 137.1, 137.2, 138.3, 138.5, 140.3, 140.4, 146.2 (C), 149.1 (CH). (IR (KBr, cm^{-1}): ν = 3079 (w), 3029, 2950, 2919, 1856 (m), 2731,



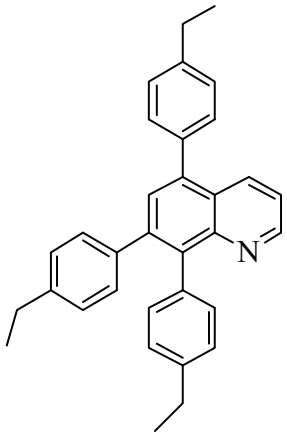
1933, 1864, 1784, 1713 (w), 1602, 1591, 1582 (m), 1554, 1499, 1487 (w), 1446 (m), 1376, 1349, 1337, 1307, 1261, 1216, 1166, 1155, 1114, 1092, 1011, 999, 979, 951, 907 (w), 895, 881, 856 (m), 826, 813 (w), 778 (s), 727 (m), 713, 702, 692 (s), 665, 657, 647, 620, 590, 553 (w). GC-MS (EI, 70 eV): *m/z* (%) = 399 ($[M]^+$, 55), 398 (100), 384 (24), 308 (13). HRMS (ESI-TOF/MS): calcd for. $C_{30}H_{26}N$ $[M+H]^+$: 400.2060; found: 400.2067.

5,7,8-Tris(3,5-dimethylphenyl)quinoline (4c): Starting with **2** (100 mg, 0.23 mmol), **3c**



(103 mg, 0.69 mmol), $Pd(PPh_3)_4$ (24 mg, 9 mol-%, 0.0207 mmol), K_2CO_3 (2M, 1.0 mL), and 1,4-dioxane (3 mL), **4c** was isolated as a white solid (86 mg, 85%). Reaction temperature: 135 °C for 8 h. M.p. 231-233 °C. ^{1}H NMR (300 MHz, $CDCl_3$): δ = 2.09 (s, 6H, $2CH_3$), 2.15 (s, 6H, $2CH_3$), 2.32(s, 6H, $2CH_3$), 6.70-6.72 (m, 3H, ArH), 6.79 (br s, 3H, ArH), 7.00 (s, 1H, ArH), 7.07 (br s, 2H, ArH), 7.20 (dd, *J* = 4.14, 8.49 Hz, 1H, ArH), 7.52 (s, 1H, ArH), 8.21 (dd, *J* = 1.77, 8.49 Hz, 1H, ArH), 8.84 (dd, *J* = 1.82, 4.14 Hz, 1H, ArH). ^{13}C NMR (62.9 MHz, $CDCl_3$): δ = 20.1, 20.3, 20.3 (CH_3), 119.2 (CH), 124.7 (C), 126.9, 126.9, 127.3, 128.1, 128.5, 128.6, 128.6, 133.1 (CH), 135.2, 135.7, 136.9, 137.0, 137.3, 138.4, 138.4, 140.3, 140.4, 146.3 (C), 149.0 (CH). (IR (KBr, cm^{-1}): *v* = 3025 (w), 2912, 2853 (m), 2732, 1955, 1921, 1888 (w), 1598, 1588 (s), 1556, 1538, 1501 (w), 1454 (m), 1395 (w), 1373, 1353, 1343 (m), 1300, 1291, 1260, 1222, 1189, 1165, 1157, 1088 (w), 1037 (m), 996, 982, 948, 934, 911, 903, 896, 877, 862 (w), 853, 845 (s), 822 (w), 797, 788 (s), 762, 738, 725 (m), 702, 690 (s), 657, 605, 592, 567, 558, 547, 535, 528 (w). GC-MS (EI, 70 eV): *m/z* (%) = 441 ($[M]^+$, 70), 440 (100), 427 (26), 426 (75), 336 (20). HRMS (ESI-TOF/MS): calcd for. $C_{33}H_{32}N$ $[M+H]^+$: 442.2529; found: 442.2528.

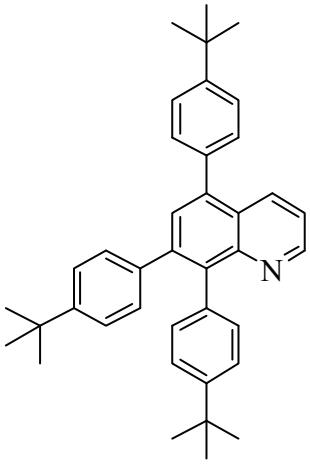
5,7,8-Tris(4-ethylphenyl)quinoline (4d): Starting with **2** (100 mg, 0.23 mmol), **3d** (103



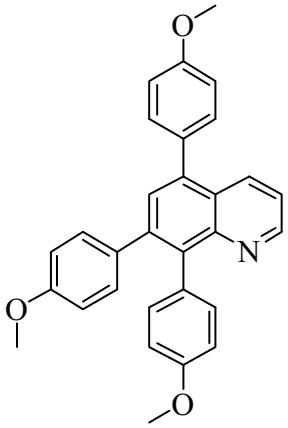
mg, 0.69 mmol), $Pd(PPh_3)_4$ (24 mg, 9 mol-%, 0.0207 mmol), K_2CO_3 (2M, 1.0 mL), and 1,4-dioxane (3 mL), **4d** was isolated as yellow oil (91 mg, 90%). Reaction temperature: 135 °C for 8 h. ^{1}H NMR (300 MHz, $CDCl_3$): δ = 1.10 (t, *J* = 7.56 Hz, 3H, CH_3), 1.16 (t, *J* = 7.56 Hz, 3H, CH_3), 1.23 (t, *J* = 7.56 Hz, 3H, CH_3), 2.46-2.70 (m, 6H, $3CH_2$), 6.93 (d, *J* = 8.40 Hz, 2H, ArH), 7.00-

7.04 (m, 4H, ArH), 7.09-7.13 (m, 2H, ArH), 7.20 (dd, J = 4.11, 8.49 Hz, 1H, ArH), 7.23 (d, J = 8.28 Hz, 2H, ArH), 7.36 (d, J = 8.16 Hz, 2H, ArH), 7.54 (s, 1H, ArH), 8.23 (dd, J = 1.83, 8.52 Hz, 1H, ArH), 8.82 (dd, J = 1.83, 4.14 Hz, 1H, ArH). ^{13}C NMR (75.4 MHz, $CDCl_3$): δ = 15.2, 15.3, 15.6 ($3CH_3$), 28.4, 28.6, 28.6 ($3CH_2$), 120.3 (CH), 126.0 (C), 127.0, 127.2, 128.0, 130.0, 130.0, 130.1, 131.8, 134.3 (CH), 135.4, 136.7, 137.9, 138.9, 139.5, 141.4, 142.2, 142.4, 143.7, 147.4 (C), 150.1 (CH). (IR (KBr, cm^{-1}): v = 3127, 3046, 3023 (w), 2961, 2929, 2870 (m), 1903, 1792, 1716, 1670, 1634, 1611 (w), 1591 (m), 1570 (w), 1512 (m), 1491 (w), 1453, 1446 (m), 1410, 1392, 1373, 1349, 1336, 1303, 1280, 1256, 1183, 1154, 1115, 1097, 1060, 1048, 1020 (w), 977 (m), 902, 880 (w), 827 (s), 792 (m), 732, 698, 668, 652, 630, 608, 570 (w). GC-MS (EI, 70 eV): *m/z* (%) = 441 ($[M]^+$, 61), 440 (100), 412 (28), 336 (15). HRMS (ESI-TOF/MS): calcd for. $C_{33}H_{32}N$ $[M+H]^+$: 442.2529; found: 442.2524.

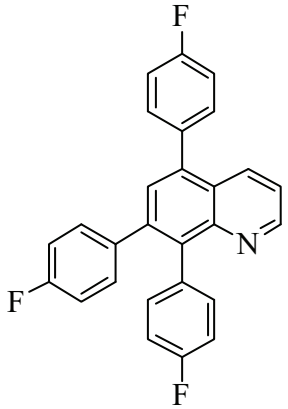
5,7,8-Tris(4-*tert*-butylphenyl)quinoline (4e): Starting with **2** (100 mg, 0.23 mmol), **3e** (122 mg, 0.69 mmol), $Pd(PPh_3)_4$ (24 mg, 9 mol-%, 0.0207 mmol), K_2CO_3 (2M, 1.0 mL), and 1,4-dioxane (3 mL), **4e** was isolated as a white solid (100 mg, 83%). Reaction temperature: 135 °C for 8 h. M.p. 245-247 °C. ^{1}H NMR (300 MHz, $CDCl_3$): δ = 1.15 (s, 9H, $3CH_3$) , 1.21 (s, 9H, $3CH_3$), 1.30 (s, 9H, $3CH_3$), 6.97 (d, J = 8.55 Hz, 2H, ArH), 7.04-7.10 (m, 4H, ArH), 7.19-7.21 (m, 3H, ArH), 7.35-7.44 (m, 4H, ArH), 7.57 (s, 1H, ArH), 8.25 (dd, J = 1.80, 8.52 Hz, 1H, ArH), 8.83 (dd, J =1.80, 4.14 Hz, 1H, ArH). ^{13}C NMR (75.4 MHz, $CDCl_3$): δ = 31.2, 31.4, 31.4 ($9CH_3$), 34.3, 34.4, 34.6 (C), 120.3, 124.3, 124.4, 125.4 (CH), 125.9 (C), 129.7, 129.8 (CH), 130.4, 131.6, 134.4 (CH), 135.3, 136.5, 136.5, 138.0, 138.6, 139.4, 141.7, 147.2, 149.0, 149.2 (C), 150.6 (CH). (IR (KBr, cm^{-1}): v = 3030 (w), 2955, 2901, 2865 (m), 1906, 1714, 1673, 1651, 1633, 1609, 1593, 1567, 1557 (w), 1510 (m), 1489 (w), 1461, 1445, 1391, 1361 (m), 1309 (w), 1268 (m), 1309 (w), 1268 (m), 1200, 1165, 1118, 1101, 1101, 1018, 977, 947, 923, 908, 890, 882 (w), 829, 818, 788 (s), 755, 746, 732, 721, 701, 669, 648, 637 (w), 623 (m), 590, 575, 538 (w). GC-MS (EI, 70 eV): *m/z* (%) = 525 ($[M]^+$, 75), 524 (100), 469 (18), 468 (45). HRMS (ESI-TOF/MS): calcd for. $C_{39}H_{43}N$ $[M+H]^+$: 526.3468; found: 526.3473.



5,7,8-Tris(4-methoxyphenyl)quinoline (4f): Starting with **2** (100 mg, 0.23 mmol), **3f** (104 mg, 0.69 mmol), $Pd(PPh_3)_4$ (24 mg, 9 mol-%, 0.0207 mmol), K_2CO_3 (2M, 1.0 mL), and 1,4-dioxane (3 mL), **4f** was isolated as a white solid (95 mg, 93%). Reaction temperature: 135 °C for 8 h. M.p. 149-151 °C. ^{1}H NMR (300 MHz, $CDCl_3$): δ = 3.67 (s, 3H, OCH_3), 3.72 (s, 3H, OCH_3), 3.79 (s, 3H,OCH_3), 6.66 (d, J = 8.76 Hz, 2H, ArH), 6.76 (d, J = 8.73 Hz, 2H, ArH), 6.95 (d, J = 8.70 Hz, 2H, ArH), 7.03 (d, J = 8.76 Hz, 2H, ArH), 7.12 (d, J = 8.76 Hz, 2H, ArH), 7.20 (dd, J = 4.11, 8.19 Hz, 1H, ArH), 7.37 (d, J = 8.76 Hz, 2H, ArH), 7.50 (s, 1H, ArH), 8.20 (dd, J = 1.77, 8.52 Hz, 1H, ArH), 8.83 (dd, J = 1.77, 4.11 Hz, 1H, ArH). ^{13}C NMR (62.9 MHz, $CDCl_3$): δ = 55.1, 55.1, 55.4 (OCH_3), 113.1, 113.3, 114.0, 120.3 (CH), 126.0 (C), 129.9 (CH), 130.5 (C), 131.2, 131.2 (CH), 131.8 (C), 133.0 (CH), 134.1 (C), 134.2 (CH), 137.3, 139.1, 141.0 147.5 (C), 150.1 (CH), 158.2, 158.2, 159.3 (C). (IR (KBr, cm^{-1}): ν = 3034, 2999, 2925, 2900 (w), 2829 (m), 1607 (s), 1574, 1554 (w), 1509 (s), 1491, 1460, 1450, 1439 (m), 1410, 1392, 1348, 1338, 1304 (w), 1288, 1238, 1173, 1107, 1028 (s), 974 (m), 954, 933, 903, 880 (w), 826, 819, 802, 795 (s), 736, 713, 702, 675, 654, 643, 624 (w), 573, 553, 538 (w). GC-MS (EI, 70 eV): *m/z* (%) = 447 ($[M]^+$, 70), 432 (9), 340 (13). HRMS (ESI-TOF/MS): calcd for. $C_{30}H_{26}N\,O_3$ $[M+H]^+$: 448.1907; found: 448.1905.

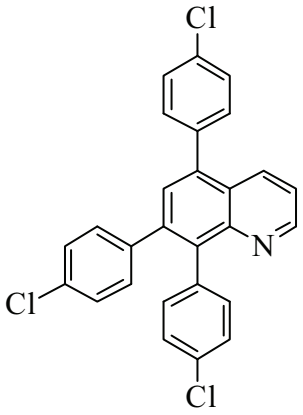


5,7,8-Tris(4-fluorophenyl)quinoline (4g): Starting with **2** (100 mg, 0.23 mmol), **3g** (96 mg, 0.69 mmol), $Pd(PPh_3)_4$ (24 mg, 9 mol-%, 0.0207 mmol), K_2CO_3 (2M, 1.0 mL), and 1,4-dioxane (3 mL), **4g** was isolated as a white solid (74 mg, 79%). Reaction temperature: 135 °C for 8 h. M.p. 222-224 °C. ^{1}H NMR (300 MHz, $CDCl_3$): δ = 6.79-6,94 (m, 4H, ArH), 7.02-7.07 (m, 2H, ArH), 7.10-7.16 (m, 4H, ArH), 7.28 (dd, J = 4.14, 8.49 Hz, 1H, ArH), 7.41 (m, 2H, ArH), 7.47 (s, 1H, ArH), 8.15 (dd, J = 1.77, 8.52 Hz, 1H, ArH), 8.83 (dd, J = 1.77, 4.11 Hz, 1H, ArH). ^{13}C NMR (62.9 MHz, $CDCl_3$): δ = 114 (d, J = 21.4 Hz), 115.0 (d, J = 21.4 Hz), 115.6 (d, J = 21.4 Hz), 120.9 (CH), 126.1 (C), 129.6, 131.5 (d, J = 1.7 Hz), 131.7 (d, J = 1.7 Hz), 133.3, 133.5 (CH), 133.6 (d, J = 3.5 Hz) (C), 134.0 (CH), 135.0 (d, J = 3.5 Hz), 137.1 (d, J = 3.5 Hz), 137.4, 138.9,



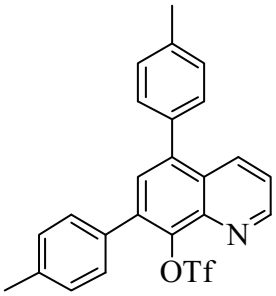
140.5, 147.1 (C), 150.4 (CH), 161.7 (d, J = 246.9 Hz) (CF), 161.8 (d, J = 246.0 Hz) (CF), 162.6 (d, J = 247.4 Hz) (CF). ^{19}F NMR (282.4, MHz): δ = -144.1, -115.5, -155.3. (IR (KBr, cm^{-1}): v = 3038, 2929, 2859, 1892 (w), 1604 (m), 1558 (w), 1507 (s), 1490 (m), 1448, 1404, 1390, 1351, 1337, 1295 (w), 1218, 1156 (s), 1094, 1087 (m), 1038 (w), 1014, 976 (m), 956, 939, 907, 899, 882 (w), 827, 815, 797 (s), 734 (m), 725, 713, 695, 669, 655, 644, 621 (w), 603, 560, 536 (m). GC-MS (EI, 70 eV): *m/z* (%) = 411 ([M]$^+$, 44), 410 (100). HRMS (EST-TOF/MS): calcd for. $C_{27}H_{17}F_3N$ [M+H]$^+$: 412.1308; found: 412.1301.

5,7,8-Tris(4-chlorophenyl)quinoline (4h): Starting with **2** (100 mg, 0.23 mmol), **3h** (108 mg, 0.69 mmol), $Pd(PPh_3)_4$ (24 mg, 9 mol-%, 0.0207 mmol), K_2CO_3 (2M, 1.0 mL), and 1,4-dioxane (3 mL), **4h** was isolated as a white solid (84 mg, 80%). Reaction temperature: 135 °C for 8 h. M.p. 223-225°C. ^{1}H NMR (300 MHz, $CDCl_3$): δ = 7.00 (d, J = 8.58 Hz, 2H, ArH), 7.09-7.12 (m, 4H, ArH), 7,20 (d, J = 8.52 Hz, 2H, ArH), 7.28 (dd, J = 4.14, 8.52 Hz, 1H, ArH), 7.35-7.40 (m, 4H, ArH), 7.45 (s, 1H, ArH), 8.15 (dd, J = 1.77, 8.52 Hz, 1H, ArH), 8.85 (dd, J = 1.77, 4.14 Hz, 1H, ArH).

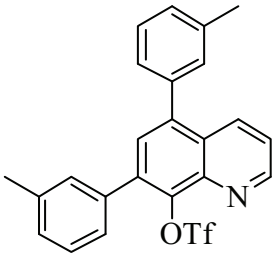


^{13}C NMR (75.4 MHz, $CDCl_3$): δ = 120.0 (CH), 124.9 (C), 126.9, 127.2, 127.3, 127.8, 128.3 (CH), 128.9 (C), 130.2 (CH), 131.9, 132.0 (C), 132.2, 132.8 (CH), 133.1, 135.1, 136.3, 137.9, 138.3, 139.1, 145.9 (C), 49.5 (CH). (IR (KBr, cm^{-1}): v = 3042, 3027, 2923, 2852, 1640, 1626, 1620 (w), 1593 (m), 1571, 1547, 1536, 1529, 1510 (w), 1491, 1483 (s), 1468, 1445, 1389, 1349, 1335, 1298, 1262, 1176, 1166 (w), 1087 (s), 1037 (w), 1013 (s), 975 (m), 903, 877, 848 (w), 817 (s), 792, 769 (m), 761 (w), 735 (s), 700, 670, 663, 650, 640, 608, 588, 570, 562, 548 (w). GC-MS (EI, 70 eV): *m/z* (%) = 460 ([M+H]$^+$, [^{35}Cl] [^{35}Cl] [^{35}Cl] , 100), 459 ([M]$^+$ [^{35}Cl] [^{35}Cl] [^{35}Cl] , 43), 458 (95), 424 (18), 350 (10). HRMS (ESI-TOF/MS): calcd for $C_{27}H_{17}Cl_3N$ ([M+H]$^+$, [^{35}Cl] [^{35}Cl] [^{35}Cl]): 460.0421; found: 460.0421.

5,7-Bis(4-methylphenyl)-8-(trifluoromethanesulfonyloxy)quinoline (5a): Starting with **2** (100 mg, 0.23 mmol), **3a** (62 mg, 0.46 mmol), $Pd(PPh_3)_4$ (15 mg, 6 mol-%, 0.0138 mmol), K_2CO_3 (2M, 1.0 mL), and 1,4-dioxane (3 mL), **5a** was isolated as a white solid (92 mg, 88 %). Reaction temperature: 90 °C for 8 h. M.p. 152-154°C. ^{1}H NMR (300 MHz, $CDCl_3$): δ = 2.36 (s, 3H, CH_3), 2.38 (s, 3H, CH_3), 7.22-7.24 (m, 3H, ArH), 7.27-7.29 (m, 3H, ArH), 7.38 (dd, J = 4.17, 8.58 Hz, 1H, ArH), 7.44 (d, J = 8.13 Hz, 2H, ArH), 7.50 (s, 1H, ArH), 8.20 (dd, J = 1.59, 8.58 Hz, 1H, ArH), 8.99 (dd, J = 1.59, 4.17 Hz, 1H, ArH). ^{13}C NMR (62.9 MHz, $CDCl_3$): δ = 20.2, 20.3 (CH_3), 118.7 (q, J = 320.6 Hz, CF_3), 120.9 (CH), 125.9 (C), 128.3, 128.3, 128.4, 128.7 (CH), 131.4 (C), 133.0 (CH), 133.4, 134.0, 137.1, 137.6, 139.3, 140.6, 141.0 (C), 150.0 (CH). ^{19}F NMR (282.4, MHz): δ = -74.86. (IR (KBr, cm^{-1}): ν = 3058, 3031 (w), 2960, 2922 (m), 2860, 1911, 1800, 1732, 1656, 1615, 1598, 1561, 1514, 1488, 1454 (w), 1416 (s), 1392 (m), 1349, 1338, 1308 (w), 1259, 1240 (m), 1219, 1201 (s), 1187 (m), 1171, 1152 (m), 1135 (s), 1102, 1090, 1042 (m), 1033, 1018 (s), 966, 945, 937, 902 (w), 846, 822, 791 (s), 765 (m), 732, 723, 699, 680, 667, 642, 631 (w), 603 (s), 573 (m), 556, 550 (w). GC-MS (EI, 70 eV): *m/z* (%) = 457 ($[M]^+$, 14), 429 (26), 356 (11), 355 (36), 341 (10), 325 (81), 324 (100), 295 (20). HRMS (EI, 70 eV): calcd for $C_{24}H_{18}F_3NO_3S$ $[M]^+$: 457.0954; found: 457.0961.

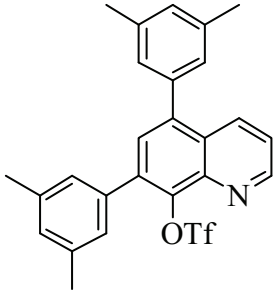


5,7-Bis(3-methylphenyl)-8-(trifluoromethanesulfonyloxy)quinoline (5b): Starting with **2** (100 mg, 0.23 mmol), **3b** (63 mg, 0.46 mmol), $Pd(PPh_3)_4$ (15 mg, 6 mol-%, 0.0138 mmol), K_2CO_3 (2M, 1.0 mL), and 1,4-dioxane (3 mL), **5b** was isolated as a white solid (89 mg, 85 %). Reaction temperature: 90 °C for 8 h. M.p. 183-184 °C.^{1}H NMR (300 MHz, $CDCl_3$): δ = 2.35 (s, 3H, CH_3), 2.37 (s, 3H, CH_3), 7.19-7.22 (m, 4H, ArH), 7.27-7.33 (m, 3H, ArH), 7.37-7.42 (m, 2H, ArH), 7.52 (s, 1H, ArH), 8.20 (dd, J = 1.52, 8.58 Hz, 1H, ArH), 8.98 (dd, J = 1.55, 4.17 Hz, 1H, ArH). ^{13}C NMR (75.4 MHz, $CDCl_3$): δ = 20.3, 20.4 (CH_3), 117.2 (q, J = 316.3 Hz, CF_3), 121.0, 125.6, 125.9, 126.0, 127.4, 127.5, 127.9, 128.2, 128.3, 129.2 (CH), 129.5, 133.0 (C), 133.4 (CH), 134.2, 136.9, 137.2, 137.4, 139.4, 140.6, 141.1 (C), 150.0 (CH). ^{19}F NMR (282.4, MHz): δ = -74.93. (IR (KBr, cm^{-1}): ν = 3034, 2954, 2923, 2855, 1595, 1583,



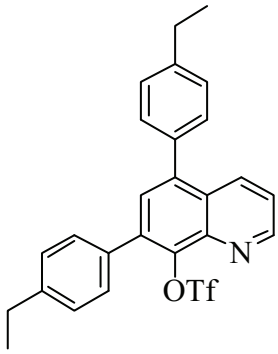
1562, 1494, 1483, 1444 (w), 1417 (s), 1401, 1392, 1347, 1336, 1263 (w), 1244, 1205 (m), 1194 (s), 1159 (w), 1140 (s), 1109, 1097 (w), 1047, 1039 (s), 964, 886 (w), 866, 821, 808, 781 (s), 764 (m), 728, 714, 708 (w), 695 (s), 677, 666, 658 (w), 646, 614 (m), 594 (s), 570 (m), 531 (w). GC-MS (EI, 70 eV): *m/z* (%) = 457 ($[M]^+$, 9), 325 (25), 324 (100), 352 (100). HRMS (ESI-TOF/MS): calcd for $C_{24}H_{19}F_3NO_3S$ $[M+H]^+$: 458.1032; found: 458.1042.

5,7-Bis(3,5-dimethylphenyl)-8-(trifluoromethanesulfonyloxy)quinoline (5c): Starting



with **2** (100 mg, 0.23 mmol), **3c** (69 mg, 0.46 mmol), $Pd(PPh_3)_4$ (15 mg, 6 mol-%, 0.0138 mmol), K_2CO_3 (2M, 1.0 mL), and 1,4-dioxane (3 mL), **5c** was isolated as a white solid (100 mg, 90 %). Reaction temperature: 90 °C for 8 h. M.p. 183-184 °C. ^{1}H NMR (300 MHz, $CDCl_3$): δ = 2.29 (s, 6H, $2CH_3$), 2.30 (s, 6H, $2CH_3$), 7.00 (br s, 3H, ArH), 7.02 (s, 1H, ArH), 7.15 (br s, 2H, ArH), 7.35 (dd, J = 4.12, 8.50 Hz, 1H, ArH), 7.50 (s, 1H, ArH), 8.18 (dd, J = 1.50, 8.50 Hz, 1H, ArH), 8.95 (dd, J = 1.51, 4.12 Hz, 1H, ArH). ^{13}C NMR (75.4 MHz, $CDCl_3$): δ = 20.1, 20.2 ($4CH_3$), 117.5 (q, J = 320.4 Hz, CF_3), 120.9 (CH_2), 125.8 (C), 126.3, 126.7, 128.1, 128.7, 129.1 (CH), 133.1 (C), 133.5 (CH), 134.1, 136.9, 137.1, 137.2, 139.5, 140.5, 141.0 (C), 149.9 (CH). ^{19}F NMR (282.4, MHz): δ = -75.1. IR (KBr, cm^{-1}): ν = 3018, 2957, 2918, 2855, 1614 (w), 1595 (m), 1573, 1563, 1556, 1536, 1531, 1493, 1485, 1485, 1461, 1454 (w), 1417 (s), 1392 (m), 1376, 1345, 1260, 1250, 1238 (w), 1210, 1192 (s), 1159 (w), 1139 (s), 1119 (m), 1055 (s), 967, 941, 914, 900, 887 (s), 871, 846, 812, 790, 775, 761 (s), 717 (m), 695 (s), 684, 664, 651 (m), 633 (w), 604 (s), 593 (m), 575 (s), 563, 544 (w). GC-MS (EI, 70 eV): *m/z* (%) = 485 ($[M]^+$, 8), 353 (26), 352 (100), 328 (27), 326 (27). HRMS (EI, 70 eV): calcd for $C_{26}H_{22}FN_3O_3S$ $[M]^+$: 485.1267; found: 485.1282.

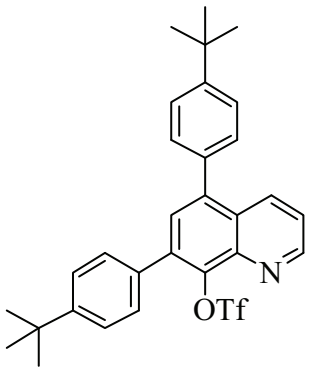
5,7-Bis(4-ethylphenyl)-8-(trifluoromethanesulfonyloxy)quinoline (5d): Starting with



2 (100 mg, 0.23 mmol), **3d** (69 mg, 0.46 mmol), $Pd(PPh_3)_4$ (15 mg, 6 mol-%, 0.0138 mmol), K_2CO_3 (2M, 1.0 mL), and 1,4-dioxane (3 mL), **5d** was isolated as a white solid (99 mg, 89 %). Reaction temperature: 90 °C for 8 h. M.p. 146-148 °C. ^{1}H NMR (300 MHz, $CDCl_3$): δ = 1.20 (t, J = 7.59 Hz, 3H, CH_3), 1.23 (t, J = 7.56 Hz, 3H, CH_3), 2.60-2.70 (m, 4H, $2CH_2$), 7.22-7.25 (m, 4H,

ArH), 7.29-7.32 (m, 2H, ArH), 7.36 (dd, J = 4.17, 8.58 Hz, 1H, ArH), 7.46 (d, J = 8.25 Hz, 2H, ArH), 7.50 (s, 1H, ArH), 8.20 (dd, J = 1.62, 8.58 Hz, 1H, ArH), 8.96 (dd, J = 1.59, 4.17 Hz, 1H, ArH). ^{13}C NMR (75.4 MHz, $CDCl_3$): δ = 15.5, 15.5 (CH_3), 28.6, 28.7 (CH_2), 118.7 (q, J = 320.6 Hz, CF_3), 122.0 (CH), 126.9 (C), 128.1, 128.2, 129.4, 129.6, 129.9 (CH), 132.7, 134.1 (C), 134.5 (CH), 135.3, 140.4, 141.7, 142.1, 144.5, 145.1 (C), 151.0 (CH). ^{19}F NMR (282.4, MHz): δ = -74.93. (IR (KBr, cm^{-1}): v = 3028 (w), 2965, 2933 (m), 1981, 1911, 1799 (w), 1616, 1597, 1557, 1514, 1487, 1454 (w), 1414 (s), 1392 (m), 1349, 1338, 1240 (w), 1217, 1202, 1186 (s), 1170, 1151 (m), 1135 (s), 1105, 1061 (w), 1042, 1033, 1017 (m), 964, 948, 939, 902, 884 (w), 845, 838, 829, 822, 789 (s), 763 (m), 738, 715, 701, 680, 669, 642, 631 (w), 602 (s), 577 (m), 558 (w). GC-MS (EI, 70 eV): *m/z* (%) = 485 ([M]$^+$, 32), 354 (16), 353 (82), 352 (100), 337 (16), 325 (10), 324 (46), 308 (41), 293 (13). HRMS (EI, 70 eV): calcd for $C_{26}H_{22}F_3NO_3S$ [M]$^+$: 485.1267; found: 485.1264.

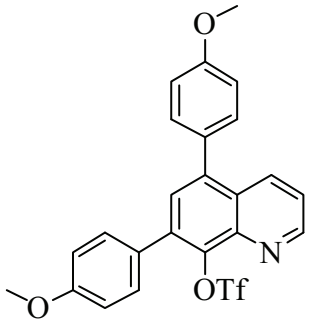
5,7-Bis(4-*tert*-butylphenyl) -8-(trifluoromethanesulfonyloxy)quinoline (5e): Starting



with **2** (100 mg, 0.23 mmol), **3e** (78 mg, 0.46 mmol), $Pd(PPh_3)_4$ (15 mg, 6 mol-%, 0.0132 mmol), K_2CO_3 (2M, 1.0 mL), and 1,4-dioxane (3 mL), **5e** was isolated as colorless solid (99 mg, 80%). Reaction temperature: 90 °C for 8 h. M.p. 150-152 °C. ^{1}H-NMR (300 MHz, $CDCl_3$): = 1.30 (s, 9H, $3CH_3$), 1.33 (s, 9H, $3CH_3$), 7.33-7.36 (m, 2H, ArH), 7.40 (dd, J = 8.61, 4.23 Hz, 1H, ArH), 7.45-7.48 (m, 6H, ArH), 7.54 (s, 1H, ArH), 8.24 (dd, J = 8.55, 7.11 Hz, 1H, ArH), 8.99 (dd, J = 4.05, 2.67 Hz, 1H, ArH). ^{13}C-NMR (62.9 MHz, $CDCl_3$): = 31.2, 31.35 ($6CH_3$), 34.7 (C), 118.5 (q, J = 320.5 Hz, CF_3), 121.9, 125.4, 125.6 (CH), 126.9 (C), 129.3, 129.6 (CH), 132.3 (C), 134.0, 134.5 (CH), 134.8, 135.0, 140.3, 141.7, 142.1 (C), 151.0 (CH), 151.3, 151.9 (C). ^{19}F NMR (282 MHz, $CDCl_3$): = -75.06 (s, 3F, CF_3). IR (KBr, cm^1): v = 3037 (w), 2952, 2924, 2903, 2866 (m), 1619, 1596, 1568, 1555, 1513, 1485, 1454 (w), 1416 (s), 1392 (m), 1363, 1342, 1311, 1266, 1241 (w), 1220, 1203 (s), 1170, 1153 (m), 1135 (s), 1106, 1097, 1065 (w), 1043, 1034, 1021, 1014 (m), 968, 940, 922, 900, 880 (w), 849 (m), 838, 828, 793 (s), 774, 763, 755, 747, 723, 706, 687, 665, 642, 631 (w), 607, 597 (s), 577, 563, 555, 540, 529 (w).

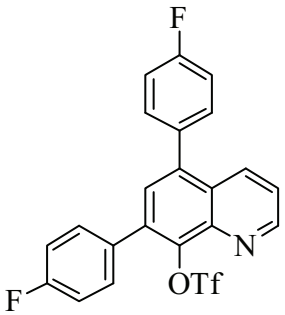
GC-MS (EI, 70 eV): *m/z* (%) = 541 ([M]$^+$, 4), 353 (22), 352 (100), 336 (14). HRMS (EI, 70 eV): calcd for $C_{30}H_{30}F_3N\,O_3S$ [M]$^+$: 541.1893; found: 541.1884.

5,7-Bis(4-methoxyphenyl)-8-(trifluoromethanesulfonyloxy)quinoline (5f): Starting



with **2** (100 mg, 0.23 mmol), **3f** (69 mg, 0.46 mmol), $Pd(PPh_3)_4$ (15 mg, 6 mol-%, 0.0138 mmol), K_2CO_3 (2M, 1.0 mL), and 1,4-dioxane (3 mL), **5f** was isolated as a white solid (93 mg, 83 %). Reaction temperature: 90 °C for 8 h. M.p. 148-150 °C. ^{1}H NMR (300 MHz, $CDCl_3$): δ = 3.79 (s, 3H, OCH_3), 3.81 (s, 3H, OCH_3), 6.93-6.98 (m, 4H, ArH), 7.32 (d, *J* = 8.70 Hz, 2H, ArH), 7.36 (dd, *J* = 4.17, 8.61 Hz, 1H, ArH), 7.46-7.49 (m, 3H, ArH), 8.18 (dd, *J* = 1.56, 8.58 Hz, 1H, ArH), 8.96 (dd, *J* = 1.53, 4.17 Hz, 1H, ArH). ^{13}C NMR (75.4 MHz, $CDCl_3$): δ = 55.3, 55.4 (OCH_3), 114.1, 114.1 (CH), 118.3 (q, *J* = 316.3 Hz, CF_3), 121.9 (CH), 126.9, 127.7 (C), 129.3 (CH), 130.3 (C), 130.9, 131.0 (CH), 133.7 (C), 134.4 (CH), 140.0, 141.8, 141.9 (C), 151.0 (CH), 159.7, 160.0 (C). ^{19}F NMR (282.4, MHz): δ = -74.90. (IR (KBr, cm^{-1}): ν = 3056, 3033, 2923, 2848 (w), 1607 (s), 1574, 1562 (w), 1513 (s), 1488, 1464, 1452 (w), 1423, 1417 (s), 1403, 1395 (m), 1339, 1306 (w), 1291 (s), 1274 (w), 1258, 1241, 1207, 1190, 1178 (s), 1152 (w), 1139 (s), 1152 (m), 1139 (s), 1118, 1108, 1049 (m), 1024 (s), 1006 (m), 950, 938, 890, 881 (w), 851, 834, 825, 789 (s), 763, 740, 730, 722, 706, 678, 670, 646, 623 (w), 602, 577, 551, 527 (s). GC-MS (EI, 70 eV): *m/z* (%) = 358 (25), 357 (100), 342 (26). HRMS (ESI-TOF/MS): calcd for $C_{24}H_{19}F_3N\,O_5S$ [M+H]$^+$: 490.0931; found: 490.0943.

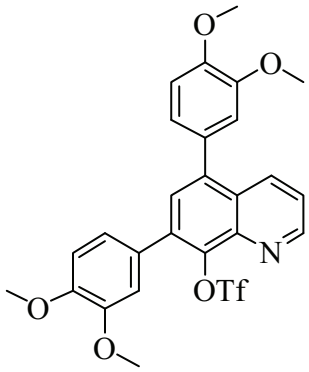
5,7-Bis(4-fluorophenyl)-8-(trifluoromethanesulfonyloxy)quinoline (5g): Starting with



2 (100 mg, 0.23 mmol), **3g** (64 mg, 0.46 mmol), $Pd(PPh_3)_4$ (15 mg, 6 mol-%, 0.0138 mmol), K_2CO_3 (2M, 1 mL), and 1,4-dioxane (3 mL), **5g** was isolated as a white solid (85 mg, 80 %). Reaction temperature: 90 °C for 8 h. M.p. 201-203 °C. ^{1}H NMR (300 MHz, $CDCl_3$): δ = 7.10-7.13 (m, 2H, ArH), 7.14-7.7.18 (m, 2H, ArH), 7.36-7.38 (m, 2H, ArH), 7.40-7.44 (dd, *J* = 4.14, 8.58 Hz, 1H, ArH), 7.46 (s, 1H, ArH), 7.49-7.54 (m, 2H, ArH), 8.13 (dd, *J* = 1.59, 8.58 Hz, 1H, ArH), 9.00 (dd, *J* = 1.59, 4.23 Hz, 1H, ArH). ^{13}C NMR (75.4 MHz, $CDCl_3$): δ =

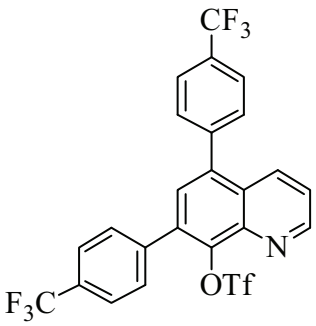
114.8 (d, $J_{F,C}$ = 21.5 Hz), 114.9 (d, $J_{F,C}$ = 21.5 Hz) (CH), 117.2 (q, J = 320.7 Hz, CF_3), 121.4 (CH), 126.0 (C), 128.2 (CH), 130.2 (d, $J_{F,C}$ = 3.3 Hz) (C), 130.4 (d, $J_{F,C}$ = 7.8 Hz), 130.5 (d, $J_{F,C}$ = 7.8 Hz) (CH), 131.9, 132.7 (d, $J_{F,C}$ = 3.3 Hz) (C), 133.1 (CH), 138.3, 140.5, 141.3 (C), 150.3 (CH), 161.8 (d, J = 246.7 Hz) (CF), 162.0 (d, J = 248.2 Hz) (CF), (IR (KBr, cm^{-1}): ν = 3076, 2959, 2923, 2853, 1619.3 (w), 1600 (m), 1564 (w), 1511(s), 1490, 1456 (m), 1423 (s), 1406, 1394, 1340 (m), 1301, 1282, 1259 (w), 1227, 1187, 1162, 1155, 1137 (s), 1113, 1096, 1048 (m), 1033, 1012 (s), 971, 946, 938, 899, 886, 853 (w), 834, 821, 809, 789 (s), 765 (w), 737, 724, 707, 680, 664, 627, 608, 601, 573, 549 (m), 532 (w). GC-MS (EI, 70 eV): *m/z* (%) = 465 ($[M]^+$, 6), 333 (24), 332 (100), 303 (14). HRMS (EI, 70 eV): calcd for $C_{22}H_{12}F_5N\,O_3S$ $[M]^+$: 465.0453; found: 465.0463.

5,7-Bis(3,4-dimethoxyphenyl)-8-(trifluoromethanesulfonyloxy)quinoline (5h):



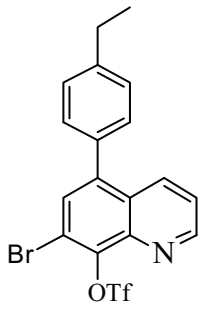
Starting with **2** (100 mg, 0.23 mmol), **3i** (84 mg, 0.46 mmol), $Pd(PPh_3)_4$ (15 mg, 6 mol-%, 0.0138 mmol), K_2CO_3 (2M, 1.0 mL), and 1,4-dioxane (3 mL), **5h** was isolated as a white solid (103 mg, 82 %). Reaction temperature: 90 °C for 8 h. M.p. 200 -202 °C. ^{1}H NMR (300 MHz, $CDCl_3$): δ = 3.38 (s, 3H, OCH_3), 3.85 (s, 3H, OCH_3), 3.88 (s, 3H, OCH_3), 3.89 (s, 3H, OCH_3), 6.91-6.96 (m, 4H, ArH), 7.09-7.13 (m, 2H, ArH), 7.40 (dd, J = 4.17, 8.58 Hz, 1H, ArH), 7.52 (s, 1H, ArH), 8.22 (dd, J = 1.62, 8.58 Hz, 1H, ArH), 8.98 (dd, J = 1.62, 4.17 Hz, 1H, ArH). ^{13}C NMR (75.4 MHz, $CDCl_3$): δ = 55.9, 55.9, 56.0, 56.0 ($4OCH_3$), 110.2, 110.2, 111.7, 112.0 (CH), 117.2 (q, J = 320.6 Hz, CF_3), 121.0, 121.3 (CH), 125.9, 126.9 (C), 128.1, 129.5 (CH), 132.7 (C), 133.4 (CH), 139.1, 140.7, 140.8, 147.9, 148.0, 148.2, 148.5 (C), 150.1 (CH). ^{19}F NMR (282.4, MHz): δ = -74.90. (IR (KBr, cm^{-1}): ν = 3015, 3001, 2953, 2838, 1619, 1597, 1583, 1562 (w), 1513 (s), 1487, 1463, 1443 (m), 1412 (s), 1394 (m), 1351, 1321, 1288 (w), 1268, 1242 (m), 1220, 1195 (s), 1175 (m), 1133 (s), 1106, 1042 (m), 1025 (s), 974, 944, 925, 903, 978 (w), 853, 831 (m), 818, 792, 763 (s), 732, 718, 707, 681, 671 (w), 630, 611, 596 (m), 566, 546, 536 (w). GC-MS (EI, 70 eV): *m/z* (%) = 549 ($[M]^+$, 17), 417 (12), 416 (49), 385 (24), 384 (10), 277 (100). HRMS (ESI-TOF/MS): calcd for $C_{26}H_{23}F_3N\,O_7S$ $[M+H]^+$: 550.1142; found: 550.1144.

5,7-Bis(3-trifluoromethylphenyl)-8-(trifluoromethanesulfonyloxy)quinoline (5i):



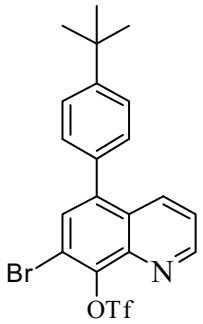
Starting with **2** (100 mg, 0.23 mmol), **3j** (87 mg, 0.46 mmol), $Pd(PPh_3)_4$ (15 mg, 6 mol-%, 0.0138 mmol), K_2CO_3 (2M, 1.0 mL), and 1,4-dioxane (3 mL), **5i** was isolated as a white solid (97 mg, 75 %). Reaction temperature: 90 °C for 8 h. M.p. 150-152 °C. NMR (300 MHz, $CDCl_3$): δ = 7.48 (dd, J = 4.17, 8.61 Hz, 1H, ArH), 7.52 (s, 1H, ArH), 7.59-7.63 (m, 3H, ArH), 7.67-7.75 (m, 4H, ArH), 7.82 (br s, 1H, ArH), 8.10 (dd, J = 1.56, 8.65 Hz, 1H, ArH), 8.83 (dd, J = 1.56, 4.17 Hz, 1H, ArH). ^{13}C NMR (75. 4 MHz, $CDCl_3$): δ = 118.2 (q, J = 320.7 Hz, CF_3), 120.2 (q, J = 270.7 Hz, CF_3), 120.8 (q, J = 273.0 Hz, CF_3), 123.0 (CH), 125.3 (q, J = 3.7 Hz), 125.6 (q, J = 3.7 Hz), 126.5 (q, J = 3.7 Hz), 126.6 (q, J = 3.7 Hz) (CH), 128.9, 129.3, 129.3 (CH), 131.3 (q, $J_{F,C}$ = 32.4 Hz), 131.4 (q, $J_{F,C}$ = 32.4 Hz), 132.4 (C), 132.9, 133.2, 133.8 (CH), 138.4, 139.1, 141.5, 142.9 (C), 151.7 (CH). (IR (KBr, cm^{-1}): ν = 3051, 3030, 2924, 2854, 1615, 1596, 1497 (w), 1419 (s), 1403, 1391, 1352 (w), 1327 (s), 1281 (w), 1242 (m), 1223 (s), 1168, 1160 (m), 1118 (s), 1097, 1073, 1047, 1038 (m), 1000, 962, 931, 917, 902, 893 (w), 848, 807, 801, 784, 765 (s), 740 (m), 702 (s), 690, 665, 654, 615, 602, 594 (m), 567, 546 (w). GC-MS (EI, 70 eV): *m/z* (%) = 565 ([M]$^+$, 11), 432 (100), 111 (11). HRMS (EI, 70 eV): calcd for. $C_{24}H_{12}F_9N\,O_3S$ [M]$^+$: 565.0389; found: 565.0387.

5-(4-Ethylphenyl)-7-bromo-8-(trifluoromethanesulfonyloxy)quinoline (6a): Starting with **2** (100 mg, 0.23 mmol), **3d** (34 mg, 0.23 mmol), $Pd(PPh_3)_4$ (8 mg, 3 mol-%, 0.0069 mmol), K_2CO_3 (2M, 1.0 mL), and 1,4-dioxane (3 mL), **6a** was isolated as a white solid (84 mg, 80 %). Reaction temperature: 65 °C for 12 h. M.p. 108-109 °C. ^{1}H NMR (300 MHz, $CDCl_3$): δ = 1.24 (t, J = 7.62 Hz, 3H, CH_3), 2.68 (q, J = 7.50 Hz, 2H, CH_2), 7.24-7.27 (m, 4H, ArH), 7.39 (dd, J = 4.12 ,8.61 Hz, 1H, ArH), 7.62 (s, 1H, ArH), 8.16 (dd, J = 1.6, 8.6 Hz, 1H, ArH), 8.92 (dd, J = 1.5, 4.1 Hz, 1H, ArH). ^{13}C NMR (75.4 MHz, $CDCl_3$): δ = 15.5 (CH_3), 28.6 (CH_2), 114.4 (C), 117.6 (q, J = 320.4 Hz, CF_3), 121.4 (CH), 126.0 (C), 127.3, 128.3, 129.6 (CH), 133.0 (C), 133.8 (CH), 140.4, 140.7, 142.3, 143.9 (C), 150.3 (CH). ^{19}F NMR (282.4, MHz): δ = -72.4. IR (KBr, cm^{-1}): ν = 3040,



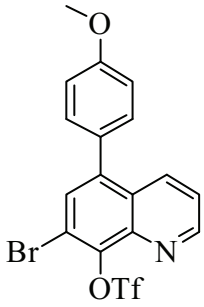
3024, 2965, 2934, 2874 (w), 1608, 1601, 1588, 1568, 1514, 1462, 1449 (w), 1423 (s), 1388, 1351, 1314, 1259 (w), 1232 (m), 1214, 1194, 1183, 1131 (s), 1120 (m), 1053(s), 1040 (m), 1020, 991, 969, 953, 940, 881, 864 (w), 832, 818 (s), 791, 779, 763 (m), 720, 707(w), 693 (m), 667 (w), 648 (s), 628 (w), 616, 592 (s), 569 (m), 543 (w). GC-MS (EI, 70 eV): *m/z* (%) = 458 ([M]$^+$, [^{79}Br], 21), 329 (28), 328 (100), 283 (16), 204 (13), 190 (10), HRMS (EI, 70 eV): calcd for $C_{18}H_{13}BrF_3NS$ ([M]$^+$, [^{79}Br]): 458.9746; found: 458.9756.

5-(4-*tert*-Butylphenyl)-7-bromo-8-(trifluoromethanesulfonyloxy)quinoline (6b):



Starting with **2** (100 mg, 0.23 mmol), **3e** (39 mg, 0.23 mmol), $Pd(PPh_3)_4$ (8 mg, 3 mol-%, 0.0066 mmol), K_2CO_3 (2M, 1 mL), and 1,4-dioxane (2 mL), **6b** was isolated as a colorless solid (90 mg, 80%). Reaction temperature: 65 °C for 12 h. M.p. 111-113 °C. ^{1}H-NMR (300 MHz, $CDCl_3$): δ = 1.33 (s, 9H, $3CH_3$), 7.28-7.32 (m, 2H, ArH), 7.41 (dd, J = 8.64, 4.17 Hz, 1H, ArH), 7.45-7-50 (m, 2H, ArH), 7.65 (s, 1H, ArH), 8.20 (dd, J = 8.61, 6.99 Hz, 1H, ArH), 8.95 (dd, J = 4.17, 2.58 Hz, 1H, ArH). ^{13}C-NMR (62.9 MHz, $CDCl_3$): δ = 30.31 ($3CH_3$), 33.75 (C), 114.4 (q, J = 320.5 Hz, CF_3), 121.3, 124.7 (CH), 126.0 (C), 128.5, 129.6 (CH), 132.8 (C), 133.8 (CH), 140.3, 140.8, 142.3 (C), 150.3 (CH), 150.8, 151.2 (C). ^{19}F NMR (282 MHz, $CDCl_3$): δ = -72.49 (s, 3F, CF_3). IR (KBr, cm^1): ν = 2956 (m), 2922 (s), 2852 (m), 1743, 1728, 1693, 1665, 1630, 1602, 1589, 1515 (w), 1462, 1451 (m), 1426 (s), 139, 1376, 1307, 1261 (w), 1241 (m), 1209 (s), 1183 (m), 1136 (s), 1103 (w), 1055 (s), 1034 (w), 1019, 942, 881, 865 (w), 832 (s), 788, 766, 754, 746, 720, 697, 684, 644, 619, 613 (w), 599 (s), 565, 541 (w). HRMS (EI, 70 eV): calcd for $C_{20}H_{18}BrF_3NO_3S$ ([M]$^+$, [^{79}Br]): 488.0137; found: 488.0145.

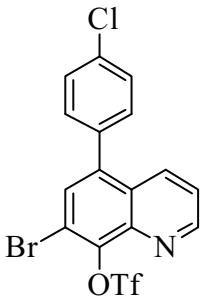
5-(4-Methoxyphenyl)-7-bromo-8-(trifluoromethanesulfonyloxy)quinoline (6c):



Starting with **2** (100 mg, 0.23 mmol), **3i** (35 mg, 0.23 mmol), $Pd(PPh_3)_4$ (8 mg, 3 mol-%, 0.0069 mmol), K_2CO_3 (2M, 1.0 mL), and 1,4-dioxane (3 mL), **6c** was isolated as a white solid (100 mg, 95 %). Reaction temperature: 65 °C for 12 h. M.p. 148-150 °C. ^{1}H NMR (300 MHz, $CDCl_3$): δ = 3.82 (s, 3H, OCH_3), 6.98 (d, J = 8.73 Hz, 2H, ArH), 7.28 (d, J = 8.73 Hz, 2H, ArH), 7.40 (dd, J = 4.17, 8.61 Hz, 1H, ArH), 7.61 (s, 1H, ArH), 8.16 (dd, J = 1.59, 8.61 Hz, 1H, ArH), 8.94 (dd, J = 1.56, 4.14 Hz, 1H,

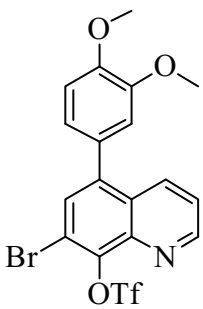
ArH). ^{13}C NMR (62.9 MHz, $CDCl_3$): δ = 55.4 (OCH_3), 114.2 (CH), 115.4 (C), 118.7(q, J = 320.8 Hz, CF_3), 122.4 (CH), 127.1, 129.0 (C), 130.6, 130.9, 134.7 (CH), 141.1, 141.8, 143.2 (C), 151.3 (CH), 160.0 (C). ^{19}F NMR (282.4, MHz): δ = -72.48. (IR (KBr, cm^{-1}): ν = 3053, 3022, 2961, 2852 (w), 1609, 1600, 1591 (m), 1555 (w), 1514 (m), 1485, 1463, 1450, 1438 (w), 1420 (s), 1403, 1389 (m), 1352, 1314, 1305, 1295, 1269 (w), 1248, 1242, 1205, 1178, 1137 (s), 1118, 1111, 1049 (m), 1039, 1029 (s), 975, 964, 943, 934, 894, 880, 864 (w), 840, 822 (s), 809 (m), 788 (s), 765 (m), 734, 712 (w), 701 (m), 667 (w), 647, 614 (m), 596 (s), 570, 550, 527 (w). GC-MS (EI, 70 eV): *m/z* (%) = 461([M]$^+$, [^{79}Br], 14), 330 (100), 328 (98), 300 (25), 249 (12). HRMS (EI, 70 eV): calcd for $C_{18}H_{14}Br\,F_3N\,O_5S$ ([M]$^+$, [^{79}Br]): 460.9539; found: 460.9535.

5-(4-Chlorophenyl)-7-bromo-8-(trifluoromethanesulfonyloxy)quinoline (6d):



Starting with **2** (100 mg, 0.23 mmol), **3h** (36 mg, 0.23 mmol), $Pd(PPh_3)_4$ (8 mg, 3 mol-%, 0.0069 mmol), K_2CO_3 (2M, 1.0 mL), and 1,4-dioxane (3 mL), **6d** was isolated as a white solid (64 mg, 60 %). Reaction temperature: 65 °C for 12 h. M.p. 106-107 °C.^{1}H NMR (300 MHz, $CDCl_3$): δ = 7.28-7.31 (m, 2H, ArH), 7.40-7.43 (m, 2H, ArH), 7.45 (d, J = 2.1 Hz, 1H, ArH), 7.62 (s, 1H, ArH), 8.06 (dd, J = 1.5, 8.6 Hz, 1H, ArH), 8.95 (dd, J = 1.5, 4.1 Hz, 1H, ArH). ^{13}C NMR (75.4 MHz, $CDCl_3$): δ = 114.4 (C), 118.5 (q, $J_{F,C}$ = 320.9 Hz, CF_3), 121.7 (CH), 125.8 (C), 128.1, 129.7, 130.0, 133.3 (CH), 134.0, 134.1, 138.9, 140.7, 142.7 (C), 150.5 (CH). IR (KBr, cm^{-1}): ν = 3033, 2961, 2917, 2849 (w), 1598, 1589 (m), 1558 (w), 1498, 1481, 1452 (m), 1421, 1404 (s), 1355, 1314, 1299, 1260, 1243 (w), 1220, 1201, 1186, 1136, 1117, 1085, 1054, 1041, 1013 (s), 975, 961, 951, 938 (w), 890 (m), 840, 827, 799, 787 (s), 768, 752, 721, 699, 678 (m), 661 (w), 640 (m), 624 (w), 612, 593, 578 (s), 565, 540 (w). GC-MS (EI, 70 eV): *m/z* (%) = 465 ([M]$^+$, [^{79}Br] [^{35}Cl], 21), 336 (52), 335 (31), 334 (100), 333 (23), 332 (95), 308 (23), 307 (13), 306 (89), 304 (76), 253 (12). HRMS (EI, 70 eV): calcd for $C_{16}H_8BrClFN\,O_3S$ ([M]$^+$, [^{79}Br] [^{35}Cl]): 464.9043; found: 464.9052.

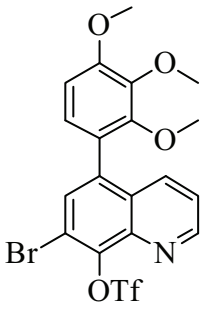
5-(3,4-Dimethoxyphenyl)-7-bromo-8-(trifluoromethanesulfonyloxy)quinoline (6e):



Starting with **2** (100 mg, 0.23 mmol), **3i** (42 mg, 0.23 mmol), $Pd(PPh_3)_4$ (8 mg, 3 mol-%, 0.0069 mmol), K_2CO_3 (2M, 1.0 mL), and 1,4-dioxane (3 mL), **6e** was isolated as a white solid (99 mg, 88 %). Reaction

temperature: 65 °C for 12 h. M.p. 106-107 °C. ^{1}H NMR (300 MHz, $CDCl_3$): δ = 3.83 (s, 3H, OCH_3), 3.88 (s, 3H, OCH_3), 6.85 (d, J = 1.7Hz, 1H, ArH), 6.90 (d, J = 1.83 Hz, 1H, ArH), 6.92 (s, 1H, ArH), 7.40 (dd, J = 4.17, 8.61 Hz, 1H, ArH), 7.62 (s, 1H,ArH), 8.17 (dd, J = 1.62, 8.61 Hz, 1H, ArH), 8.92 (dd, J = 1.59, 4.17 Hz, 1H, ArH). ^{13}C NMR (62.9 MHz, $CDCl_3$): δ = 56.0, 56.0 (OCH_3), 111.2, 112.8 (CH), 115.4 (C), 118.6 (q, J = 320.8 Hz, CF_3), 122.3, 122.4, 127.2, 129.2 (CH), 130.5 (C), 134.7 (CH), 141.2, 141.7, 143.2, 149.1, 149.4, 151.3 (C). ^{19}F NMR (282.4, MHz): δ = -72.50. (IR (KBr, cm^{-1}): ν = 3075, 3007, 2961, 2837, 1603, 1587, 1573, 1566, 1547 (w), 1515 (m), 1489, 1468, 1462, 1450, 1440 (w), 1415 (s), 1391 (m), 1352, 1328, 1314, 1286 (w), 1247, 1215, 1182 (s), 1155 (m), 1135 (s), 1114 (m), 1050, 1040, 1028 (s), 977 (m), 952, 903 (w), 883, 868 (m), 827, 815, 801, 782, 762 (s), 710, 699 (m), 667, 655 (w), 646, 608, 588 (m), 564, 544 (w). GC-MS (EI, 70 eV): *m/z* (%) = 491 ([M]$^{+}$, ^{79}Br, 25), 360 (100), 332 (16), 330 (16). HRMS (ESI-TOF/MS): calcd for $C_{18}H_{14}BrF_3N\ O_5S$ ([M+H]$^{+}$, [^{79}Br]): 491.9732; found: 491.9723.

5-(2,3,4-Trimethoxyphenyl)-7-bromo-8-(trifluoromethanesulfonyloxy)quinoline (6f):



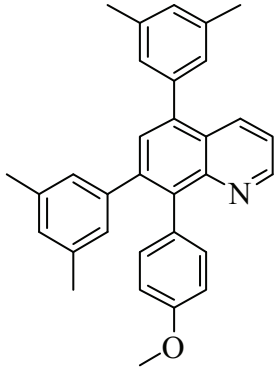
Starting with **2** (100 mg, 0.23 mmol), **3k** (49 mg, 0.23 mmol), $Pd(PPh_3)_4$ (8 mg, 3 mol-%, 0.0069 mmol), K_2CO_3 (2M, 1.0 mL), and 1,4-dioxane (3 mL), **6f** was isolated as a white solid (95 mg, 80 %). Reaction temperature: 65 °C for 12 h. M.p. 144-146 °C .^{1}H NMR (300 MHz, $CDCl_3$): δ = 3.48 (s, 3H, OCH_3), 3.86 (s, 3H, OCH_3), 3.87 (s, 3H, OCH_3), 6.72 (d, J = 8.61 Hz, 1H, ArH), 6.85 (d, J = 8.52 Hz, 1H, ArH), 7.35 (dd, J = 4.20, 8.58 Hz, 1H, ArH), 7.60 (s, 1H, ArH), 7.91 (dd, J = 1.62, 8.58 Hz, 1H, ArH), 8.90 (dd, J = 1.59, 4.17 Hz, 1H, ArH). ^{13}C NMR (62.9 MHz, $CDCl_3$): δ = 56.1, 61.0, 61.2 (OCH_3), 107.2 (CH), 115.2 (C), 118.6 (q, J = 320.7 Hz, CF_3), 122.2 (CH), 123.2 (C), 125.7 (CH), 127.8 (C), 131.2, 135.2 (CH), 138.0, 141.4, 142.2, 143.5 (C), 151.3 (CH), 151.5, 154.6 (C). ^{19}F NMR (282.4, MHz): δ = -72.48. (IR (KBr, cm^{-1}): ν = 2993, 2937, 2838 (w), 1596 (m), 1569 (w), 1500, 1482, 1464, 1453 (m), 1436 (w), 1415 (s), 1390 (m), 1356, 1330 (w), 1296 (m), 1269, 1247 (w), 1223, 1204, 1178, 1128, 1094, 1054 (s), 1029, 1012, 973, 913, 880, 872 (m), 823, 817, 805 (s), 787 (m), 765, 718, 697, 682 (w), 646 (s), 626, 592 (m), 562, 544, 535 (w). GC-MS (EI, 70 eV): *m/z* (%) = 521

([M]$^+$, [^{79}Br], 39), 390 (96), 389 (60), 388 (100). HRMS (EI, 70 eV): calcd for C19H15BrF3N O_6S ([M]$^+$, [^{79}Br]): 520.9750; found: 520.9753.

General Procedure for the Synthesis of 7a-d:

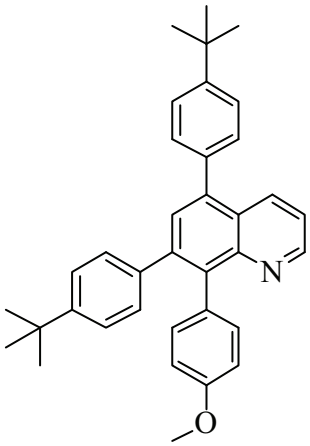
The reaction was carried out in a pressure tube. To a dioxane suspension (3 mL) of (**2**) (100 mg, 0.23 mmol), arylboronic acid $Ar^1B(OH)_2$ (0.46 mmol) and $Pd(PPh_3)_4$ (6 mol%) was added K_2CO_3 (2M, 1.0 mL), and the resultant solution was degassed by bubbling argon through the solution for 10 min. The mixture was heated at 90 °C under argon atmosphere for 12 h. The mixture was cooled to 20 °C. Arylboronic acid $Ar^2B(OH)_2$ (0.23 mmol), $Pd(PPh_3)_4$ (3 mol%), K_3CO_3 (2M, 0.5 mL) and dioxane (1 mL) were added. The reaction mixture was heated under an argon atmosphere for 6 h at 135 °C and then diluted with H_2O and extracted with CH_2Cl_2 (3 × 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, heptane/EtAOc).

5,7-Bis(3,5-dimethylphenyl)-8-(4-methoxyphenyl)quinoline (7a): Starting with **2** (100 mg, 0.23 mmol), **3c** (69 mg, 0.46 mmol) and $Pd(PPh_3)_4$ (15 mg, 6 mol-%, 0.0138 mmol) was added K_2CO_3 (2M, 1.0 mL). **3f** (35 mg, 0.23 mmol), $Pd(PPh_3)_4$ (8 mg, 3 mol-%, 0.0069 mmol), K_2CO_3 (2M, 0.5 mL), 1,4-dioxane (1 mL). **7a** was isolated as a white solid (81 mg, 80 %); mp 192-194 °C. ^{1}H NMR (300 MHz, $CDCl_3$): δ = 2.10 (s, 6H, $2CH_3$), 2.32 (s, 6H, $2CH_3$), 3.72 (s, 3H, OCH_3), 6.73 (br s, 3H, ArH), 6.77 (d, J = 8.76 Hz, 2H, ArH), 7.01 (s, 1H, ArH), 7.07 (br s, 2H, ArH), 7.12 (d, J = 8.55 Hz, 2H, ArH), 7.22 (dd, J = 4.11, 8.49 Hz, 1H, ArH), 7.5 (s, 1H, ArH), 8.23 (dd, J = 1.80, 8.49 Hz, 1H, ArH), 8.85 (dd, J = 1.83, 4.11 Hz, 1H, ArH). ^{13}C NMR (75.4 MHz, $CDCl_3$): δ = 21.2, 21.4 ($4CH_3$), 55.2 (OCH_3), 133.0, 120.3 (CH), 126.0 (C), 128.0, 128.0, 128.1, 129.2, 129.8 (CH), 130.5 (C), 133.0, 134.3 (CH), 137.1, 137.5, 138.0, 139.4, 139.6, 141.5, 141.6, 147.4 (C), 150.1 (CH), 158.3 (C). (IR (KBr, cm^{-1}): ν = 3009, 2954 (w), 2910 (m), 2857, 2836 (w), 1600, 1585 (m), 1552 (w), 1510, 1500 (m), 1462, 1442, 1394, 1342, 1302 (w), 1288 (m), 1275 (w), 1238 (s), 1188 (w), 1172 (s), 1160 (w), 1105 (m), 1054 (w), 1032 (s), 977, 949, 938, 922, 907, 896, 889 (w), 847, 828 (s), 806, 814 (w), 789, 773 (s), 731 (m), 718 (w), 711, 694 (s), 669, 661, 646, 637, 620, 593, 575, 552, 539 (w). GC-MS (EI, 70 eV): *m/z* (%) =

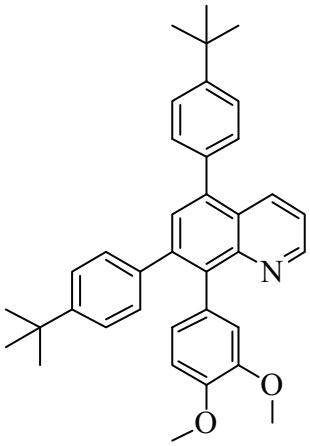


444 ([M+H]$^+$, 20), 443 ([M]$^+$, 75), 442 (100), 428 (25). HRMS (ESI-TOF/MS): calcd for $C_{32}H_{30}NO$ [M+H]$^+$: 444.2319 found 444.2320.

5,7-Bis(4-*tert*-butylphenyl)-8-(4-methoxyphenyl)quinoline (7b): Starting with **2** (100 mg, 0.23 mmol), **3e** (81 mg, 0.46 mmol) and $Pd(PPh_3)_4$ (15 mg, 6 mol-%, 0.0138 mmol) was added K_2CO_3 (2M, 1.0 mL). **3f** (35 mg, 0.23 mmol), $Pd(PPh_3)_4$ (8 mg, 3 mol-%, 0.0069 mmol), K_2CO_3 (2M, 0.5 mL), 1,4-dioxane (1 mL). **7b** was isolated as a white solid (91 mg, 80 %); mp 299-300 °C. ^{1}H NMR (300 MHz, $CDCl_3$): δ = 1.20 (s, 9H, $3CH_3$), 1,35 (s, 9H, $3CH_3$), 3.74 (s, OCH_3), 6.77 (d, J = 8.7 Hz, 2H, ArH), 7.04 (d, J = 8.5 Hz, 2H, ArH), 7.13-7.17 (m, 4H, ArH), 7.24 (dd, J = 4.1, 8.5 Hz, 1H, ArH), 7.38-7.47 (m, 4H, ArH), 7.57 (s, 1H, ArH), 8.27 (dd, J = 1.7, 8.5 Hz, 1H, ArH), 8.86 (dd, J = 1.6, 4.0 Hz, 1H, ArH). ^{13}C NMR (75.4 MHz, $CDCl_3$): δ 31.3, 31.4 ($6CH_3$), 34.4, 34.6 (C), 55.1 (OCH_3), 113.0, 120.3, 124.6, 125.4, 125.4 (CH), 125.9 (C), 129.7, 129.8, 130.1 (CH), 130.3 (C), 133.1, 134.4 (CH), 136.4, 137.3, 138.6, 139.3, 141.3, 147.3, 149.3 (C), 150.0 (CH), 150.6, 158.2 (C). IR (KBr, cm^{-1}): ν = 3029 (w), 2959 (m), 2864, 1976, 1887 (w), 1610, 1593, 1574, 1568 (m), 1552, 1538 (w), 1512 (s), 1489 (m), 1462, 1456 (m), 1440 (w), 1991, 1361 (m), 1348, 1305 (w), 1291 (m), 1267 (w), 1244 (s), 1201 (w), 1176 (m), 1116, 1109, 1102, 1088 (w), 1038, 1016, 975 , 670, 644 (w), 632, 596, 573, 559 (m), 540, 530 (w). GC-MS (EI, 70 eV): *m/z* (%) = 499 ([M]$^+$, 75), 498 (100), 366 (14). HRMS (ESI-TOF/MS): calcd for $C_{36}H_{38}NO$ [M+H]$^+$: 500.2948; found: 500.2946.

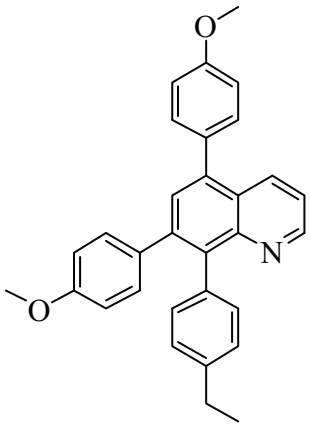


5,7-Bis(4-*tert*-butylphenyl)-8-(3,4-dimethoxyphenyl)quinoline (7c): Starting with **2** (100 mg, 0.23 mmol), **3e** (81 mg, 0.46 mmol) and $Pd(PPh_3)_4$ (15 mg, 6 mol-%, 0.0138 mmol) was added K_2CO_3 (2M, 1.0 mL). **3i** (42 mg, 0.23 mmol), $Pd(PPh_3)_4$ (8 mg, 3 mol-%, 0.0069 mmol), K_2CO_3 (2M, 0.5 mL), 1,4-dioxane (1 mL). **7c** was isolated as a white solid (96 mg, 79 %); mp 210-212 °C. ^{1}H NMR (300 MHz, $CDCl_3$): δ = 1.34 (s, 9H, $3CH_3$), 1.46 (s, 9H, $3CH_3$) , 3.62 (s, 3H, OCH_3), 3.9 (s, 3H, OCH_3), 6.76 (s, 1H, ArH), 6.94 (d, J = 8.25 Hz, 1H, ArH), 7.06 (d, J = 8.22 Hz,



1H, ArH), 7.17-7.29 (m, 4H, ArH), 7.37 (dd, J = 4.05, 8.46 Hz, 1H, ArH), 7.51-7,60 (m, 4H, ArH), 7.72 (s, 1H, ArH), 8.39 (m, 1H, ArH), 9.00 (dd J = 1.44, 2.58 Hz, 1H, ArH). ^{13}C NMR (75.4 MHz, $CDCl_3$): δ = 31.3, 31.4 ($6CH_3$), 34.4, 34.7 (C), 55.6, 55.7 (OCH_3), 110.3, 115.7, 120.4, 124.7, 125.1, 125.4 (CH), 126.0 (C), 129.6, 129.8, 130.0 (CH), 130.4 (C), 134.3 (CH), 136.4, 137.4, 138.8, 139.4, 141.3, 147.3, 147.6, 148.0, 149.4, 150.2 (C), 150.6 (CH). (IR (KBr, cm^{-1}): ν = 3061, 3032 (w), 2951, 2933 (m), 2830, 1908 (w), 1591 (m), 1567, 1548 (w), 1510 (s), 1489 (m), 1464 (s), 1456, 1438, 1412, 1386, 1361, 1349 (m), 1316, 1289 (w), 1260, 1251, 1238, 1211, 1172, 1164, 1145 (s), 1115, 1103 (m), 1045 (w), 1029 (s), 935, 920, 892, 886, 860, 847 (w), 837, 830, 823 (m), 803, 798 (s), 767, 760, 744, 729, 705, 673, 655, 639, 931 (w), 603, 571 (s), 540 (w). (GC-MS (EI, 70 eV): *m/z* (%) = 529 ($[M]^+$, 36), 528 (37), 514 (9). HRMS (ESI-TOF/MS): calcd for $C_{37}H_{40}NO_2$ $[M+H]^+$: 530.3054; found: 530.3059.

5,7-Bis(4-methoxyphenyl)-8-(4-ethylphenyl)quinoline (7d): Starting with **2** (100 mg, 0.23 mmol), **3f** (70 mg, 0.46 mmol) and $Pd(PPh_3)_4$ (15 mg, 6 mol-%, 0.0138 mmol) was added K_2CO_3 (2M, 1.0 mL). **3d** (35 mg, 0.23 mmol), $Pd(PPh_3)_4$ (8 mg, 3 mol-%, 0.0069 mmol), K_2CO_3 (2M, 0.5 mL), 1,4-dioxane (1 mL). **7d** was isolated as a white solid (84 mg, 82 %); mp 154-156 °C. ^{1}H NMR (300 MHz, $CDCl_3$): δ = 1.18 (t, J = 7.59 Hz, 3H, CH_3), 2.58 (q, J = 7.56, 15.15 Hz, 2H, CH_2), 3.68 (s, 3H, OCH_3), 3.81 (s, 3H, OCH_3), 6.67 (d, J = 8.82 Hz, 2H, ArH), 6.97 (d, J = 8,73 Hz, 2H, ArH), 7.04 (d, J = 8.79 Hz, 2H, ArH), 7.07-713 (m, 4H, ArH), 7.22 (dd, J = 4.14, 8.49 Hz, 1H, ArH), 7.39 (d, J = 8.73 Hz, 2H, ArH), 7.52 (s, 1H, ArH), 8.22 (dd, J = 1.77, 8.52 Hz, 1H, ArH), 8.85 (dd, J = 1.77, 4.1 Hz, 1H, ArH). ^{13}C NMR (75.4 MHz, $CDCl_3$): δ = 15.1 (CH_3), 28.6 (CH_2), 55.1, 55.4 (OCH_3), 113.2, 113.9, 120.3 (CH), 126.0 (C), 127.1, 129.9, 131.2, 131.2, 131.8 (CH), 134.0 (C), 134.2 (CH), 135.4, 137.7, 139.1, 141.0, 142.2, 147.3 (C), 150.1 (CH), 185.2, 159.3 (C). (IR (KBr, cm^{-1}): ν = 2997 (w), 2956, 2925, 1607 (m), 1592, 1575 (w), 1510 (s), 1491, 1460, 1440, 1409, 1392, 1348, 1336, 1303 (w), 1289 (m), 1241, 1174 (s), 1108 (w), 1029 (s), 976 (m), 901, 880 (w), 826 (s), 791 (m), 730, 715, 698, 669, 645, 624, 607, 563 (w). (GC-MS (EI, 70 eV): *m/z* (%) =



445 ([M]$^+$, 66), 444 (100), 416 (26), 338 (12). HRMS (ESI-TOF/MS): calcd for $C_{31}H_{28}NO_2$ [M+H]$^+$: 446.2115; found: 446.2112.

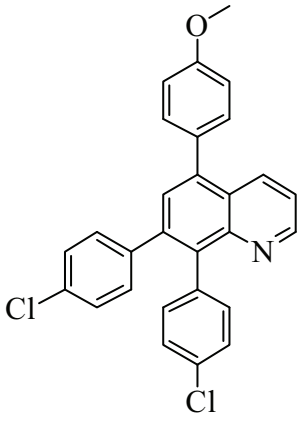
General Procedure for the Synthesis of 8a-c:

The reaction was carried out in a pressure tube. To a dioxane suspension (3 mL) of **2** (100 mg, 0.23 mmol), arylboronic acid $Ar^1B(OH)_2$ (0.23 mmol) and $Pd(PPh_3)_4$ (3 mol%) was added K_2CO_3 (2M, 1.0 mL), and the resultant solution was degassed by bubbling argon through the solution for 10 min. The mixture was heated at 65 °C under an argon atmosphere for 12 h. The mixture was cooled to 20 °C. Arylboronic acid $Ar^2B(OH)_2$ (0.46 mmol), $Pd(PPh_3)_4$ (6 mol%), K_3CO_3 (2M, 0.5 mL) and dioxane (1 mL) were added. The reaction mixture was heated under an argon atmosphere for 6 h at 135 °C. Then diluted with H_2O and extracted with CH_2Cl_2 (3 × 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, heptane/EtAOc).

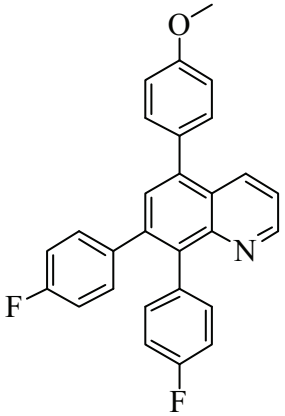
5-(4-Methoxyphenyl)-7,8-bis(4-methylphenyl)quinoline (8a): Starting with **2** (100 mg, 0.23 mmol), **3f** (35 mg, 0.23 mmol) and $Pd(PPh_3)_4$ (8 mg, 3mol-%, 0.0069 mmol), K_2CO_3 (2M, 1.0 mL), **3a** (62 mg, 0.46 mmol), $Pd(PPh_3)_4$ (15 mg, 6 mol-%, 0.0138 mmol), K_2CO_3 (2M, 0.5 mL) and 1,4-dioxane (1 mL). **8a** was isolated as a white solid (81 mg, 85 %); mp 188-190 °C. ^{1}H NMR (300 MHz, $CDCl_3$): δ = 2.19 (s, 3H, CH_3), 2.25 (s, 3H, CH_3), 3.78 (s, 3H, OCH_3), 6.90 (d, J = 8.0Hz, 2H, ArH), 6.95 (d, J = 8.7 Hz, 2H, ArH), 6.99-7.03 (m, 4H, ArH), 7.08 (d, J = 8.1 Hz, 2H, ArH), 7.20 (dd, J = 4.1, 8.5 Hz, 1H, ArH), 7.37 (d, J = 8.7 Hz, 2H, ArH), 7.50 (s, 1H, ArH), 8.20 (dd, J = 1.8, 8.5 Hz, 1H, ArH), 8.82 (dd, J = 1.8, 4.1 Hz). ^{13}C NMR (75.4 MHz, $CDCl_3$): δ = 21.1, 21.4 (CH_3), 55.4 (OCH_3), 114.0, 120.4 (CH), 126.0 (C), 128.3, 128.5, 129.9, 130.0, 131.2, 131.8, 134.1 (CH), 135.2, 136.0, 136.1, 137.8, 138.7, 139.1, 141.3, 147.5 (C), 150.1 (CH), 159.3 (C). IR (KBr, cm^{-1}): ν = 2919, 2833 (w), 1607, 1590 (m), 1570, 1558 (w), 1512 (s), 1490, 1440 (m), 1416 (w), 1391 (m), 1350, 1337, 1303 (w), 1290 (m), 1245, 1176 (s), 1162 (w), 1108 (m), 1094 (w), 1024 (s), 975 (m), 937, 907, 880 (w), 834, 811, 791 (s), 736 (w), 726 (m), 713, 694, 667, 655, 636, 627 (w), 605, 571 (m), 539 (w). GC-

MS (EI, 70 eV): *m/z* (%) = 415 ($[M]^+$, 62), 414 (100), 400 (15), 370 (10). HRMS (ESI-TOF/MS): calcd for $C_{30}H_{26}NO$ $[M+H]^+$: 416.2009; found: 416.2018.

5-(4-Methoxyphenyl)-7,8-bis(4-chlorophenyl)quinoline (8b): Starting with **2** (100 mg, 0.23 mmol), **3f** (35 mg, 0.23 mmol) and $Pd(PPh_3)_4$ (8 mg, 3mol-%, 0.0069 mmol), K_2CO_3 (2M, 1.0 mL), **3h** (72 mg, 0.46 mmol), $Pd(PPh_3)_4$ (15 mg, 6 mol-%, 0.0138 mmol), K_2CO_3 (2M, 0.5 mL) and 1,4-dioxane (1 mL). **8b** was isolated as a white solid (81 mg, 77 %); mp 202-204 °C. ^{1}H NMR (250 MHz, $CDCl_3$): δ = 3.81 (s, 3H, OCH_3), 6.96-7.04 (m, 4H, ArH), 7.11 (d, *J* = 8.05 Hz, 2H, ArH), 7.14-7.19 (m, 4H, ArH), 7.28 (dd, *J* = 4.15, 8.50 Hz, 1H, ArH), 7.35 (d, *J* = 8.67 Hz, 2H, ArH), 7.46 (s, 1H, ArH), 8.24 (dd, *J* = 1.77, 8.52 Hz, 1H, ArH), 8.84 (dd, *J* = 1.75, 4,12 Hz, 1H, ArH). ^{13}C NMR (62. 9 MHz, $CDCl_3$): δ = 55.42 (OCH_3), 114.0, 120.8 (CH), 126.3, 126.4 (C), 127.9, 128.2, 129.3, 131.1, 131.3 (CH), 132.9, 132.9 (C), 133.2, 134.4 (CH), 136.3, 136.6, 139.6, 140.0, 140.1, 147.0 (C), 150.4 (CH), 159.4 (C). (IR (KBr, cm^{-1}): *v* = 2928, 2833, 1895 (w), 1608, 1593 (m), 1569, 1553 (w), 1513, 1487 (s), 1461, 1448, 1439, 1415 (w), 1391 (m), 1349, 1338, 1304 (w), 1290 (m), 1242 (s), 1175 (m), 1165, 1105 (w), 1085 (s), 1030 (m), 1013 (s), 975 (m), 906, 878 (w), 817, 794 (s), 769, 755 (w), 734 (m), 725, 696, 684, 665, 629, 613 (w), 583, 572, 554 (m). GC-MS (EI, 70 eV): *m/z* (%) = 455 ($[M]^+$, [^{35}Cl] [^{35}Cl] , 56), 454 (100), 410 (8). HRMS (ESI-TOF/MS): calcd for $C_{28}H_{19}Cl_2NO$ ($[M+H]^+$, [^{35}Cl] [^{35}Cl]): 456.0821; found: 456.0844.



5-(3,5-Dimethylphenyl)-7,8-bis(4-fluorophenyl)quinoline (8c): Starting with **2** (100 mg, 0.23 mmol), **3e** (35 mg, 0.23 mmol) and $Pd(PPh_3)_4$ (8 mg, 3mol-%, 0.0069 mmol), K_2CO_3 (2M, 1.0 mL), **3g** (65 mg, 0.46 mmol), $Pd(PPh_3)_4$ (15 mg, 6 mol-%, 0.0138 mmol), K_2CO_3 (2M, 0.5 mL) and 1,4-dioxane (1 mL). **8c** was isolated as a white solid (67 mg, 70%); mp 202-204 °C. ^{1}H NMR (250 MHz, $CDCl_3$): δ = 2.34 (s, 6H, $2CH_3$), 6.80-6.83 (m, 2H, ArH), 6.89-6.95 (m, 2H, ArH), 7.00-7.08 (m, 5H, ArH), 7.12-7.17 (m, 2H, ArH), 7.27 (dd, *J* = 4.14, 8.50 Hz, 1H, ArH), 7.49 (s, 1H, ArH), 8.25 (dd, *J* = 1.77, 8.52 Hz, 1H, ArH), 8.84 (dd, *J* = 1.75, 4,14 Hz, 1H, ArH). ^{13}C NMR (62. 9 MHz,

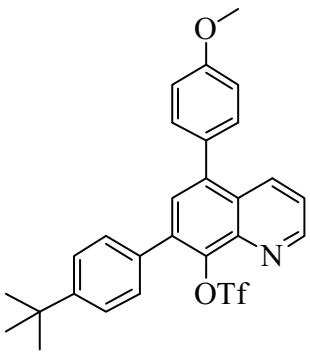


$CDCl_3$): δ = 113.6 (d, $J_{F,C}$ = 21.4 Hz), 113.8 (d, $J_{F,C}$ = 21.4 Hz), 120.7 (CH), 125.1 (C), 126.8, 128.3, 128.4, 130.5 (d, $J_{F,C}$ = 8.0 Hz), 132.4 (d, $J_{F,C}$ = 8.0 Hz) (CH), 132.8 (d, $J_{F,C}$ = 3.4 Hz) (C), 133.4 (CH), 135.9, 136.2, 136.3 (d, $J_{F,C}$ = 3.4 Hz), 137.0, 137.9, 139.3, 139.4, 146.0 (C), 149.3 (CH), 160.6 (d, $J_{F,C}$ = 246.2 Hz) (CF), 160.7 (d, $J_{F,C}$ = 246.2 Hz) (CF). ^{19}F NMR (282.4, MHz): δ = -115.5, -115.7. (IR (KBr, cm^{-1}): ν = 3067, 2918 (w), 1601, 1596, 1584 (m), 1556, 1538 (w), 1506, 1497 (s), 1470, 1450, 1417 (w), 1392 (m), 1376, 1345, 1296, 1260 (w), 1214, 1160, 1155 (s), 1121, 1101, 1088, 1044, 1014, 996, 978, 946, 910, 898 (w), 854 (m), 831, 799, 791 (s), 776 (w), 730 (m), 710, 698, 690, 665, 651 (w), 629, 594, 564, 551, 530 (m). GC-MS (EI, 70 eV): *m/z* (%) = 421 ($[M]^+$, 49), 420 (100). HRMS (ESI-TOF/MS): calcd for $C_{29}H_{22}F_2N$ $[M+H]^+$: 422.1715; found: 422.1713.

General Procedure for the Synthesis of 9:

The reaction was carried out in a pressure tube. To a dioxane suspension (3 mL) of **2** (100 mg, 0.23 mmol), arylboronic acid $Ar^1B(OH)_2$ (0.23 mmol) and $Pd(PPh_3)_4$ (3 mol%) was added K_2CO_3 (2M, 1.0 mL), and the resulting solution was degassed by bubbling argon through the solution for 10 min. The mixture was heated at 65 °C under an argon atmosphere for 12 h. The mixture was cooled to 20 °C. Arylboronic acid $Ar^2B(OH)_2$ (0.23 mmol), $Pd(PPh_3)_4$ (3 mol%), K_3CO_3 (2M, 0.5 mL) and dioxane (1 mL) were added. The reaction mixture was heated under an argon atmosphere for 6 h at 70 °C. Then diluted with H_2O and extracted with CH_2Cl_2 (3 × 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, heptane/EtAOc).

5-(4-Methoxyphenyl)-7-(4-*tert*-butylphenyl)-8-(trifluoromethanesulfonyloxy)-quinoline (9): Starting with **2** (100 mg, 0.23 mmol), **3f** (35 mg, 0.23 mmol) and



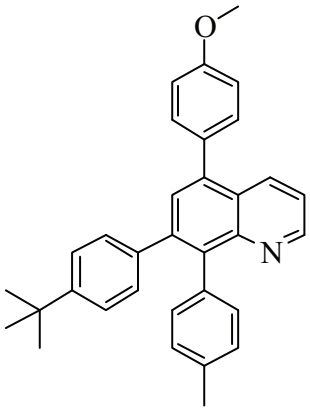
$Pd(PPh_3)_4$ (8 mg, 3 mol-%, 0.0069 mmol), K_2CO_3 (2M, 1.0 mL). **3e** (40 mg, 0.23 mmol), $Pd(PPh_3)_4$ (8 mg, 3 mol-%, 0.0069 mmol), K_2CO_3 (2M, 0.5 mL), 1,4-dioxane (1 mL). **9** was isolated as a white solid (91 mg, 87 %); mp 180-182 °C. ^{1}H NMR (300 MHz, $CDCl_3$): δ = 1.30 (s, 9H, $3CH_3$), 3.82 (s, 3H, OCH_3), 6.97 (d, J = 8.7 Hz, 2H, ArH), 7.33 (d, J = 8.7 Hz, 2H, ArH), 7,38 (dd, J = 4.2, 8.5 Hz, 1H, ArH), 7.43-7.49 (m, 4H, ArH), 7.51 (s, 1H, ArH), 8.20 (dd, J =1.6, 8.6 Hz, 1H, ArH), 8.98 (dd, J = 1.5, 4.1

Hz, 1H, ArH). ^{13}C NMR (75.4 MHz, $CDCl_3$): δ = 30.2 (CH_3), 33.7 (C), 54.3 (OCH_3), 113.1 (CH), 117.2 (q, J = 320.4 Hz, CF_3), 120.9, 124.4 (CH), 125.9 (C), 128.2 (CH), 129.2 (C), 130.0 (CH), 131.3, 133.0 (C), 139.0, 140.7, 141.0 (C), 149.9, 150.9 (CH), 158.6 (C). IR (KBr, cm^{-1}): ν = 3041 (w), 2959, 2923 (m), 2850, 1737 (w), 1609 (m), 1575 (w), 1514 (m), 1487, 1461, 1452 (w), 1414 (s), 1393 (m), 1363, 1340, 1290 (w), 1244, 1213 (s), 1181, 1174 (m), 1155 (w), 1134 (m), 1114 (w), 1044, 1033, 1022 (m), 944, 924, 907 (w), 851, 830, 791 (s), 765, 757, 747, 734, 703, 680, 670, 632 (w), 608, 596, 573, 562 (m), 534 (w). GC-MS (EI, 70 eV): *m/z* (%) = 515 ([M]$^+$, 44), 368 (20), 383 (34), 368 (20), 352 (11), 326 (100), 282 (16). HRMS (ESI-TOF/MS): calcd for $C_{27}H_{25}F_3NO_4S$ [M+H]$^+$: 516.1451; found: 516.1460.

General Procedure for the Synthesis of 10:

The reaction was carried out in a pressure tube. To a 1,4-dioxane suspension (3 mL) of **2** (100 mg, 0.23 mmol), arylboronic acid $Ar^1B(OH)_2$ (0.23 mmol) and $Pd(PPh_3)_4$ (3 mol%) was added K_2CO_3 (2M, 1.0 mL), and the resultant solution was degassed by bubbling argon through the solution for 10 min. The mixture was heated at 65 °C under an argon atmosphere for 12 h. The mixture was cooled to 20 °C. Arylboronic acid $Ar^2B(OH)_2$ (0.23 mmol), $Pd(PPh_3)_4$ (3 mol%), K_3CO_3 (2M, 0.5 mL) and dioxane (1 mL) were added. The mixture was heated at 70 °C under an argon atmosphere for 8 h. The mixture was cooled to 20 °C. Arylboronic acid $Ar^3B(OH)_2$ (0.23 mmol), $Pd(PPh_3)_4$ (3 mol%), K_3CO_3 (2M, 0.5 mL) and dioxane (1 mL) were added. The reaction mixture was heated under an argon atmosphere for 6 h at 130 °C and then diluted with H_2O and extracted with CH_2Cl_2 (3 × 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, heptane/EtAOc).

5-(4-Methoxyphenyl)-7-(4-*tert*-butylphenyl)-8-(4-methylphenyl)quinoline (10):



Starting with **2** (100 mg, 0.23 mmol), **3f** (35 mg, 0.23 mmol) and $Pd(PPh_3)_4$ (8 mg, 3 mol-%, 0.0069 mmol), K_2CO_3 (2M, 1.0 mL). **3e** (40 mg, 0.23 mmol), $Pd(PPh_3)_4$ (8 mg, 3 mol-%, 0.0069 mmol), K_2CO_3 (2M, 0.5 mL), 1,4-dioxane (1 mL), **3a** (31 mg, 0.23 mmol) and $Pd(PPh_3)_4$ (8 mg, 3 mol-%, 0.0069 mmol), K_2CO_3 (2M, 0.5 mL), 1,4-dioxane (1 mL), **10** was

isolated as a white solid (91 mg, 87%); mp 180-182 °C. ^{1}H NMR (300 MHz, $CDCl_3$): δ = 1.19 (s, 9H, $3CH_3$), 2.27 (s, 3H, CH_3), 3.8 (s, 3H, OCH_3), 6.95 (d, J = 8.7 Hz, 2H, ArH), 7.00-7.06 (m, 4H, ArH), 7.08-7.14 (m, 4H, ArH), 7.21 (dd, J =4.1, 8.5 Hz, 1H, ArH), 7.37 (d, J = 8.6 Hz, 2H, ArH), 7.53 (s, 1H, ArH), 8.21 (dd, J = 1.6, 8.5 Hz, 1H, ArH), 8.82 (dd, J = 1.6, 4.0 Hz, 1H, ArH). ^{13}C NMR (75.4 MHz, $CDCl_3$): δ = 21.4 (CH_3), 31.3 ($3CH_3$), 34.4 (C), 55.4 (OCH_3), 113.9, 120.3, 124.6 (CH), 126.0 (C), 128.2, 129.7, 130.0, 131.2, 131.8, 134.1 (CH), 135.1, 135.9, 137.7, 138.6, 139.0, 141.2, 147.4, 149.3 (C), 150.1 (CH), 159.2 (C). IR (KBr, cm^{-1}): ν = 3128, 3029 (w), 2959 (m), 2902, 2864, 2834 (w), 1608 (m), 1592, 1569, 1556 (w), 1512 (s), 1490, 1461, 1455, 1440, 1391 (m), 1360, 1350, 1304 (w), 1289 (m), 1243 (s), 1202 (w), 1176 (m), 1163 (w), 1109 (w), 1089 (w), 1026, 975 (m), 906, 881 (w), 833, 826, 813, 795 (s), 757, 747, 734, 722, 701, 690, 668, 652, 629 (w), 598, 572, 543 (m). GC-MS (EI, 70 eV): *m/z* (%) = 457 ($[M]^+$, 65), 442 (15), 400 (10). HRMS (ESI-TOF/MS): calcd for $C_{33}H_{32}NO$ $[M+H]^+$: 458.2478; found: 458.2479.

5-Hydroxy-4-oxo-2-phenyl-4*H*-chromen-7-yl trifluoromethanesulfonate (12): To a solution of **11** (1.0 g, 3.93 mmol) in CH_2Cl_2 (40 mL) was added pyridine (1.3 mL, 15.72 mmol) and the solution was stirred at room temperature. To the solution was added Tf_2O (1.5 mL, 9.43 mmol) at room temperature and stirred for 4 h. The reaction mixture was filtered and the filtrate was concentrated in vacuo. The product 1**2** was isolated by rapid column chromatography (flash silica gel, heptane–EtOAc) as a yellow solid (1.2 g, 80 %); mp: 75-77 ^{o}C. ^{1}H NMR (300 MHz, $CDCl_3$): δ = 6.64 (d, J = 2.2 Hz, 1H, ArH), 6.69 (s, 1H), 6.88 (d, J = 2.2 Hz, 1H, ArH), 7.44-7.52 (m, 3H, ArH), 7.76-7.80 (m, 2H, ArH), 12.84 (br s , 1H, OH). ^{13}C-NMR (62.9 MHz, $CDCl_3$): δ = 99.8, 104.0, 105.3 (CH), 109.3 (C), 117.6 (d, $J_{F,C}$ = 320.9 Hz, CF_3), 125.2, 128.2 (CH), 129.3 ,(C), 131.5 (CH), 152.2, 155.6, 161.5, 164.2 (C), 181.5 (CO). ^{19}F NMR (282 MHz, $CDCl_3$): δ = -72.64 (s, 3F, CF_3). IR (KBr, cm^{-1}): ν = 3099, 3082, 3063 (w), 1650 (m), 1614, 1582, 1485 (s), 1415 (m), 1420 (s), 1371, 1337 (m), 1324 (w), 1298 (m), 1282 (w), 1264 (m), 1253, 1242 (w), 1229 (m), 1208, 1185, 1128, 1096 (s), 1034 (w), 1020 (s), 1001, 992 (w), 973 (s), 935, 908 (w), 857 (s), 842 (w), 825, 769, 721, 684, 664, 650 (s), 635, 612 (m), 596 (s), 566, 540 (m). GC-MS (EI, 70 eV): *m/z* (%) = 387 ($[M+H]^+$, 20),

386 ([M]$^+$, 100), 225 (77), 207 (12), 123 (31), 77 (10). HRMS (EI, 70 eV): calcd for $C_{16}H_9O_6F_3S$ [M]$^+$: 386.00664, found 386.006622.

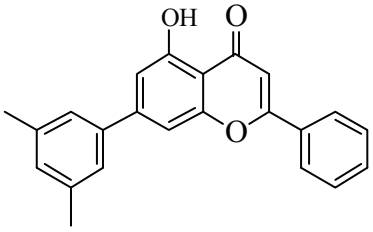
General Procedure for synthesis 13a-l: A 1,4-dioxane solution (3 mL) of **12** (80 mg, 0.207 mmol), K_3PO_4 (65 mg, 0.304 mmol) , [$Pd(PPh_3)_4$] (7 mg, 3 mol%, 0.006 mmol), and arylboronic acid **3** (0.207 mmol), was stirred at 80 °C for 4 h. After cooling to 20 °C, distilled water was added, the organic and the aqueous layers 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 column chromatography.

5-Hydroxy-2-phenyl-7-(*p*-tolyl)-4*H*-chromen-4-one (13a): Starting with **12** (80 mg, 0.207 mmol), **3a** (28 mg, 0.207 mmol), $Pd(PPh_3)_4$ (7 mg, 3 mol%, 0.006 mmol), K_3PO_4 (65 mg, 0.304 mmol), and 1,4-dioxane (3 mL), **13a** was isolated as a yellow solid (61 mg, 90%); mp 204-206 °C. ^{1}H NMR (300 MHz, $CDCl_3$): δ = 2.32 (s, 3H, CH_3), 6.63 (s, 1H), 6.95 (d, J = 1.5 Hz, 1H, ArH), 7.11 (d, J = 1.5 Hz, 1H, ArH), 7.16-7.20 (m, 2H, ArH), 7.43-7.47 (m, 5H, ArH), 7.81-7.84 (m, 2H, ArH), 12.45 (br s, 1H, OH). ^{13}C-NMR (75.4 MHz, $CDCl_3$): δ = 21.2 (CH_3), 104.2, 105.1 (CH), 108.5 (C), 108.8, 125.3, 126.0, 128.0, 128.7 (CH), 130.2 (C), 130.9 (CH), 135.3, 137.9, 147.4, 155.6, 159.7, 163.5 (C), 182.1 (CO). IR (KBr, cm^{-1}): ν = 3074, 2918, 2855, 1894 (w), 1658, 1614, 1591(s), 1564, 1556, 1538 (w), 1519, 1486 (m), 1450, 1430, 1409, 1359 (s), 1344, 1309, 1294 (w), 1272 (m), 1254, 1211, 1201, 1189, 1159, 1124 (w), 1093, 1051, 1031 (m), 998 (s), 957, 938 (w), 864 (s), 838 (w), 803 (s), 774 (w), 763 (s), 727, 684 (m), 674 (s), 654, 645, 633, 623, 600, 563 (m), 531 (s). GC-MS (EI, 70 eV): *m/z* (%) = 329 ([M+H]$^+$, 22), 328 ([M]$^+$, 100), 300 (12), 155 (10). HRMS (EI, 70 eV): calcd for $C_{22}H_{16}O_3$ [M]$^+$: 328.10940, found 328.109336.

5-Hydroxy-2-phenyl-7-(*m*-tolyl)-4*H*-chromen-4-one (13b): Starting with **12** (80 mg, 0.207 mmol), **3b** (28 mg, 0.207 mmol), $Pd(PPh_3)_4$ (7 mg, 3 mol%, 0.006 mmol), K_3PO_4 (65 mg, 0.304 mmol), and 1,4-dioxane (3 mL), **13b** was isolated as a yellow solid (57 mg, 85%); mp 186-188 °C. ^{1}H NMR (300 MHz, $CDCl_3$): δ = 2.33 (s, 3H,CH_3), 6.62 (s, 1H), 6.94 (d, J = 1.5 Hz, 1H,

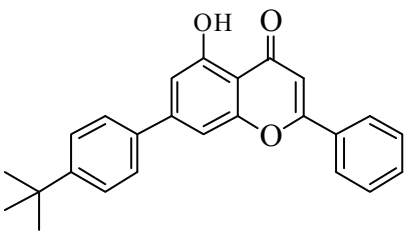
ArH), 7.10 (d, J = 1.5 Hz, 1H, ArH), 7.12-7.15 (m, 1H, ArH), 7.23-7.28 (m, 1H, ArH), 7.35-7.39 (m, 2H, ArH), 7.40-7.49 (m, 3H, ArH), 7.79-7.83 (m, 2H, ArH), 12.44 (br s, 1H, OH). ^{13}C-NMR (62.9 MHz, $CDCl_3$): δ = 20.4 (CH_3), 104.5, 105.0 (CH), 108.6 (C), 109.0, 123.3, 125.3, 126.9, 127.8, 128.0, 128.5 (CH), 130.2 (C), 130.9 (CH), 137.6, 138.1, 147.6, 155.5 159.6, 163.5 (C), 182.1 (CO). IR (KBr, cm^{-1}) : v = 3067, 2916, 2850, 2791 (m), 1652, 1615, 1591 (s), 1568, 1556, 1537, 1504 (w), 1494, 1482 (m), 1450, 1411, 1398, 1362 (s), 1342, 1312 (w), 1294 (m), 1270, 1254, 1237, 1205 (m), 1179, 1166, 1159 (w), 1120, 1094, 1054, 1032, 1011, 999 (m), 965, 938, 920 (w), 907, 899, 861, 827, 809, 793 (m), 761 (s), 725, 700, 691, 684 (w), 673 (s), 654, 643 (w), 634 (s), 619, 607, 576, 545 (w). GC-MS (EI, 70 eV): *m/z* (%) = 329 ([M+H]$^+$, 22), 328 ([M]$^+$, 100). HRMS (EI, 70 eV): calcd for $C_{22}H_{16}O_3$ [M]$^+$: 328.10940, found 328.109336.

7-(3,5-Dimethylphenyl)-5-hydroxy-2-phenyl-4*H*-chromen-4-one (13c): Starting with



12 (80 mg, 0.207 mmol), **3c** (31 mg, 0.207 mmol), $Pd(PPh_3)_4$ (7 mg, 3 mol%, 0.006 mmol), K_3PO_4 (65 mg, 0.304 mmol), and 1,4-dioxane (3 mL), **13c** was isolated as a yellow solid (56 mg, 80%); mp 169-171 °C. ^{1}H NMR (300 MHz, $CDCl_3$): δ = 2.29 (s, 6H, 2CH_3), 6.61 (s, 1H), 6.93 (d, J = 1.5 Hz, 1H, ArH), 6.96 (s, 1H, ArH), 7.10 (d, J = 1.5 Hz, ArH), 7.15 (br s, 2H, ArH), 7.40-7.45 (m, 3H, ArH), 7.79-7.82 (m, 2H, ArH), 12.4 (br s, 1H, OH). ^{13}C-NMR (75.4 MHz, $CDCl_3$): δ = 21.4 (2CH_3), 105.5, 106.1 (CH), 109.6 (C), 110.1, 125.1, 126.4, 129.1, 130.5 (CH), 131.2 (C), 131.9 (CH), 138.5, 139.2, 148.8, 156.5, 160.7, 164.5 (C), 183.1 (CO). IR (KBr, cm^{-1}): v = 3066, 3023, 2917, 2863, 2796 (w), 1657, 1619 (s), 1592 (m), 1556, 1537 (w), 1491 (m), 1449 (s), 1414 (m), 1384 (w), 1295 (m), 1260 (s), 1219 (w), 1200 (m), 1177, 1160 (w), 1119, 1095, 1033, 1022, 999 (m), 968, 950 (w), 903 (m), 891 (w), 845, 820, 795 (s), 780, 771 (w), 761 (s), 721, 701 (w), 672, 663, 635 (s), 585 (m), 558, 546 (w). GC-MS (EI, 70 eV): *m/z* (%) = 343 ([M+H]$^+$, 28), 342 ([M]$^+$, 100), 314 (6). HRMS (EI, 70 eV): calcd for $C_{23}H_{18}O_3$ [M]$^+$: 342.12505, found 342.125397.

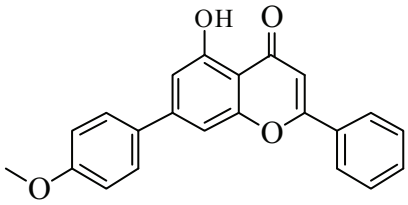
7-(4-*tert*-Butylphenyl)-5-hydroxy-2-phenyl-4*H*-chromen-4-one (13d): Starting with



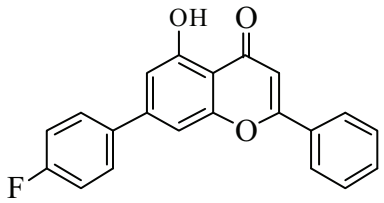
12 (80 mg, 0.207 mmol), **3e** (37 mg, 0.207 mmol), $Pd(PPh_3)_4$ (7 mg, 3 mol%, 0.006 mmol), K_3PO_4 (65 mg,

0.304mmol), and 1,4-dioxane (3 mL), **13d** was isolated as a yellow solid (61 mg, 80 %); mp 196-198 °C. ^{1}H NMR (300 MHz, $CDCl_3$): δ = 1.27 (s, 9H, $3CH_3$), 6.6 (s, 1H), 6.95 (d, J = 1.5 Hz, ArH), 7.10 (d, J = 1.5 Hz, 1H, ArH), 7.38-7.44 (m, 5H, ArH), 7.47-7.50 (m, 2H, ArH), 7.78-7.81 (m, 2H, ArH), 12.45 (br s, 1H, OH). ^{13}C-NMR (75.4 MHz, $CDCl_3$): δ = 31.3 ($3CH_3$), 34.7 (C), 105.3, 106.1 (CH), 109.5 (C), 109.9, 126.0, 126.4, 126.9, 129.1 (CH), 131.2 (C), 131.9 (CH), 136.2, 148.4, 152.1, 156.6, 160.7, 164.5 (C), 183.1 (CO). IR (KBr, cm^{-1}): ν = 3063, 2962, 2902, 2859 (w), 1646 (m), 1608 (s), 1590 (m), 1558, 1522, 1505, 1494, 1472, 1464 (w), 1450 (m), 1428, 1397, 1362, 1352, 1313, 1294 (w), 1263, 1205 (s), 1159, 1118, 1096, 1075, 1050, 1032, 1017 (w), 1002, 997 (m), 985, 970, 926, 910 (w), 868 (m), 859, 849, 841 (w), 827, 822 (s), 791 (m), 760 (s), 743, 733 (m), 717, 685 (w), 676 (s), 657, 644, 634, 625, 619, 607, 591 (w), 551 (m). GC-MS (EI, 70 eV): *m/z* (%) = 371 ($[M+H]^+$, 20), 370 ($[M]^+$, 100), 356 (26), 355 (100), 127 (12). HRMS (EI, 70 eV): calcd for $C_{25}H_{22}O_3$ $[M]^+$: 370.15635, found 370.155853.

5-Hydroxy-7-(4-methoxyphenyl)-2-phenyl-4*H*-chromen-4-one (13e): Starting with **12** (80 mg, 0.207 mmol), **3f** (31 mg, 0.207 mmol), $Pd(PPh_3)_4$ (7 mg, 3 mol%, 0.006 mmol), K_3PO_4 (65 mg, 0.304 mmol), and 1,4-dioxane (3 mL), **13e** was isolated as a yellow solid (64 mg, 90%); mp 173-175 °C. ^{1}H NMR (300 MHz, $CDCl_3$): δ = 3.78 (s, 3H, OCH_3), 6.63 (s, 1H), 6.89-6.92 (m, 3H, ArH), 7.09 (d, J = 1.5 Hz, 1H, ArH), 7.42-7.45 (m, 3H, ArH), 7.45 (d, J = 6.7 Hz, 2H, ArH), 7.80-7.90 (m, 2H, ArH), 12.45 (br s, 1H, OH). ^{13}C-NMR (75.4 MHz, $CDCl_3$): δ = 55.4 (OCH_3), 104.9, 106.1 (CH), 109.3 (C), 109.5, 114.4, 126.3, 128.4, 129.1 (CH), 131.3, 131.5 (C), 131.9 (CH), 148.1, 156.4, 160.4, 160.7, 164.5 (C), 183.1 (CO). IR (KBr, cm^{-1}): ν = 3068, 3046, 2995, 2978, 1941, 2914, 2894, 1836 (w), 1656, 1606, 1592 (s), 1572, 1558 (m), 1539 (w), 1519, 1490, 1450, 1433, 1417, 1402, 1361, 1345, 1294, 1272 (m), 1253 (s), 1214, 1203 (w), 1177 (s), 1122, 1115, 1095, 1051 (w), 1034 (s), 1013 (w), 999 (m), 955, 929 (w), 858 (m), 842 (w), 821, 797, 764 (s), 728, 722, 685 (w), 675 (s), 655, 643, 619 (w), 603 (m), 566 (w), 534 (m). GC-MS (EI, 70 eV): *m/z* (%) = 345 ($[M+H]^+$, 24), 344 ($[M]^+$, 100), 301 (8). HRMS (EI, 70 eV): calcd for $C_{22}H_{16}O_4$ $[M]^+$: 344.10431, found 344.104996.

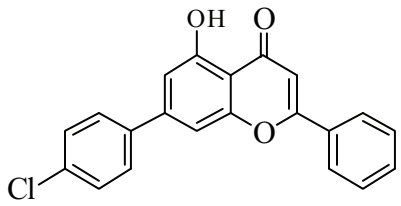


7-(4-Fluorophenyl)-5-hydroxy-2-phenyl-4*H*-chromen-4-one (13f): Starting with **12**



(80 mg, 0.207 mmol), **3g** (29 mg, 0.207 mmol), $Pd(PPh_3)_4$ (7 mg, 3 mol%, 0.006 mmol), K_3PO_4 (65 mg, 0.304 mmol), and 1,4-dioxane (3 mL), **13f** was isolated as a yellow solid (55 mg, 80%); mp 214-216 °C. ^{1}H NMR (300 MHz, $CDCl_3$): δ = 6.66 (s, 1H), 6.92 (d, J = 1.5 Hz, 1H, ArH), 7.06-7.12 (m, 3H, ArH), 7.45-7.50 (m, 3H, ArH), 7.51-7.56 (m, 2H, ArH), 7.83-7.86 (m, 2H, ArH), 12.4 (br s, 1H, OH). ^{13}C-NMR (62.9 MHz, $CDCl_3$): δ = 105.4, 106.2 (CH), 109.6 (C), 110.0, 116.0 (d, J = 21.6 Hz, (CH)), 126.4, 129.0 (d, J = 8.2 Hz, (CH)), 129.1 (CH), 131.1 (C), 132.0 (CH), 135.4 (d, J = 3.2 Hz), 147.4, 156.6, 160.8 (C), 163.2 (d, $J_{F,C}$ = 248.9 Hz) (CF), 164.6 (C), 183.1 (CO). ^{19}F NMR (282 MHz, $CDCl_3$): = -112.90. IR (KBr, cm^{-1}): v = 3074, 3056, 1885 (w), 1657, 1619, 1600 (s), 1568, 1556 (w), 1517, 1490, 1450, 1434, 1410 (s), 1398 (w), 1359 (m), 1346, 1300, 1293 (w), 1270 (m), 1254 (w), 1235, 1215, 1202, 1163 (m), 1123, 1095, 1050, 1032, 1015 (w), 999 (s), 952, 937 (w), 909, 862 (s), 842 (w), 817, 807, 798 (s), 775 (w), 764 (s), 727, 718, 684 (w), 674 (s), 654 (m), 641, 632, 618 (w), 600 (m), 561 (w), 533 (s). GC-MS (EI, 70 eV): *m/z* (%) = 333 ($[M+H]^+$, 20), 332 ($[M]^+$, 100), 304 (11), 202 (10), 152 (12). HRMS (EI, 70 eV): calcd for $C_{21}H_{13}FO_3$ $[M]^+$: 332.08432, found 332.084347.

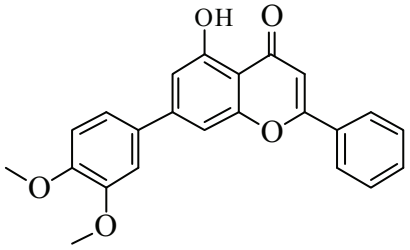
7-(4-Chlorophenyl)-5-hydroxy-2-phenyl-4*H*-chromen-4-one (13g): Starting with **12**



(80 mg, 0.207 mmol), **3h** (32 mg, 0.207 mmol), $Pd(PPh_3)_4$ (7 mg, 3 mol%, 0.006 mmol), K_3PO_4 (65 mg, 0.304 mmol), and 1,4-dioxane (3 mL), **13g** was isolated as a yellow solid (62 mg, 86%); mp 217-219°C. ^{1}H NMR (250 MHz, $CDCl_3$): δ = 6.68 (s, 1H), 6.94 (d, J = 1.5 Hz, 1H, ArH), 7.12 (d, J = 1.5 Hz, 1H, ArH), 7.35-7.40 (m, 2H, ArH), 7.48-7.52 (m, 5H, ArH), 7.83-7.87 (m, 2H, ArH), 12.5 (br s, 1H, OH). ^{13}C-NMR (62.9 MHz, $CDCl_3$): δ = 105.4, 106.2 (CH), 109.8 (C), 109.9, 126.4, 128.5, 129.1, 129.2 (CH), 131.1(C), 132.1 (CH), 135.0, 137.7, 147.2, 156.6, 160.9, 164.7 (C), 183.1 (CO). IR (KBr, cm^{-1}): v = 3071, 3053, 1900 (w), 1656, 1619 (s), 1593 (m), 1572, 1557 (w), 1504, 1494, 1485, 1477, 1450, 1430, 1408 (m), 1393 (w), 1356, 1294, 1267, 1216, 1203 (m), 1188, 1160, 1123, 1108 (m), 1093 (s), 1052, 1032, 1015, 1000 (m), 969, 956, 943 (w), 909 (m), 889 (w), 862 (s), 840 (w), 814 (s), 790 (m),

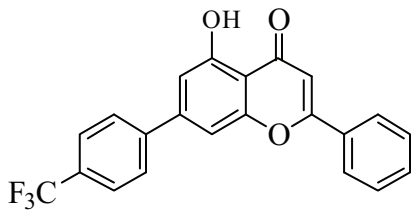
764 (s), 737, 720, 715 (w), 673 (s), 655, 639, 631, 618 (m), 607 (w), 584, 534 (s). GC-MS (EI, 70 eV): *m/z* (%) = 350 ($[M]^+$, ^{37}Cl, 34), 349 ($[M+H]^+$, ^{35}Cl, 24), 348 ($[M]^+$, ^{35}Cl, 100), 155 (11). HRMS (EI, 70 eV): calcd for $C_{21}H_{13}{}^{37}ClO_3$ $[M]^+$: 350.05182, found 350.052887, calcd for $C_{21}H_{13}{}^{35}ClO_3$ $[M]^+$: 348.05477 found 348.055573.

5-Hydroxy-7-(3,4-dimethoxyphenyl)-2-phenyl-4*H*-chromen-4-one (13h): Starting



with **12** (80 mg, 0.207 mmol), **3i** (38 mg, 0.207 mmol), $Pd(PPh_3)_4$ (7 mg, 3 mol%, 0.006 mmol), K_3PO_4 (65 mg, 0.304 mmol), and 1,4-dioxane (3 mL), **13h** was isolated as a yellow solid (65 mg, 85%); mp 198-200 °C. ^{1}H NMR (300 MHz, $CDCl_3$): δ = 3.85 (s, 3H, OCH_3), 3.87 (s, 3H, OCH_3), 6.62 (s, 1H), 6.87 (d, J = 8.3 Hz, 1H, ArH), 6.92 (d, J = 1.4, 1H, ArH), 7.05-7.08 (m, 2H, ArH), 7.13 (dd, J = 2.0, 8.3 Hz, 1H, ArH), 7.43-7.47 (m, 3H, ArH), 7.80-7.84 (m, 2H, ArH), 12.4 (br s, 1H, OH). ^{13}C-NMR (75.4 MHz, $CDCl_3$): δ = 56.0, 56.0 ($2OCH_3$), 105.0, 106.1 (CH), 109.3 (C), 109.6, 110.2, 111.4, 119.9, 126.4, 129.1 (CH), 131.2, 131.9 (C), 132.0 (CH), 148.3, 149.3, 149.9, 156.6, 160.7, 164.5 (C), 183.1 (CO). IR (KBr, cm^{-1}): ν = 3436, 3070, 3000, 2937, 2916, 2837 (w), 1651, 1608, 1587 (s), 1522 (m), 1492 (s), 1468 (w), 1450, 1434 (s), 1398 (w), 1347 (s), 1322, 1301, 1291 (w), 1252, 1247 (s), 1218, 1203, 1192 (w), 1170 (m), 1129, 1096 (s), 1049 (w), 1018, 1006, 999 (7), 973, 949, 923, 904 (w), 864, 837 (m), 820, 802, 769 (s), 726 (w), 682, 672 (s), 663, 650, 621, 607, 580, 569 (w). GC-MS (EI, 70 eV): *m/z* (%) = 375 ($[M+H]^+$, 20), 374 ($[M]^+$, 100), 332 (13), 331 (26), 238 (11). HRMS (EI, 70 eV): calcd for $C_{23}H_{18}O_5$ $[M]^+$: 374.11488, found 374.1143136.

5-Hydroxy-2-phenyl-7-[4-(trifluoromethyl)phenyl]-4*H*-chromen-4-one (13i):



Starting with **12** (80 mg, 0.207 mmol), **3j** (39 mg, 0207 mmol), $Pd(PPh_3)_4$ (7 mg, 3 mol%, 0.006 mmol), K_3PO_4 (65 mg, 0.304 mml), and 1,4-dioxane (3 mL), **13i** was isolated as a yellow solid (62 mg, 79%); mp 215-217 °C. ^{1}H NMR (300 MHz, $CDCl_3$): δ = 6.67 (s, 1H), 6.95 (br s, 1H, ArH), 7.13 (br s, 1H, ArH), 7.45-7.48 (m, 3H, ArH), 7.65 (br s, 4H, ArH), 7.82-7.85 (m, 2H, ArH), 12.51 (br s, 1H, OH). ^{13}C-NMR (75.4 MHz, $CDCl_3$): δ = 105.8, 106.2 (CH), 110.2 (C), 110.3 (CH), 122.2 (q, $J_{F,C}$ = 320.3 Hz, CF_3), 125.9 (q, J = 3.7 Hz) (CH), 126.4, 129.1 (CH), 130.5,

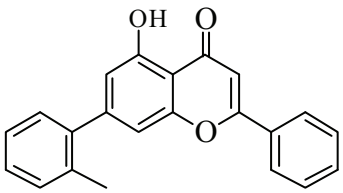
131.0 (C), 142.8, 146.8, 156.6, 161.0, 164.8 (C), 183.1 (CO). ^{19}F NMR (282 MHz, $CDCl_3$): = -62.60. IR (KBr, cm^{-1}): ν = 3060, 2922, 2850, 2803 (w), 1650, 1611, 1589 (s), 1557, 1523 (w), 1484, 1450, 1433, 1410, 1355, 1325, 1296, 1284, 1267 (s), 1249, 1214, 1203 (m), 1167, 1108, 1098, 1068 (s), 1049, 1032, 1015, 997 (m), 975, 958, 930, 906 (w), 845 (m), 822, 766 (s), 754, 724, 699 (w), 686, 676, 656, 633 (s), 611, 593, 580 (w), 531 (m). GC-MS (EI, 70 eV): *m/z* (%) = 383 ($[M+H]^+$, 18), 382 ($[M]^+$, 100), 252 (10), 177 (8). HRMS (EI, 70 eV): calcd for $C_{22}H_{13}F_3O_3$ $[M]^+$: 382.08113, found 382.080944.

5-Hydroxy-2,7-diphenyl-4*H*-chromen-4-one (13j): Starting with **12** (80 mg, 0.207 mmol), **3l** (25 mg, 0.207 mmol), $Pd(PPh_3)_4$ (7 mg, 3 mol%, 0.006 mmol), K_3PO_4 (65 mg, 0.304 mmol), and 1,4-dioxane (3 mL), **13j** was isolated as a yellow solid (mg, 80%); mp 186-188 °C. ^{1}H NMR (300 MHz, $CDCl_3$): δ = 6.62 (s, 1H), 6.94 (d, J = 1.5 Hz, 1H, ArH), 7.11 (d, J = 1.5 Hz, 1H, ArH), 7.30-7,36 (m, 3H, ArH), 7.41-7.48 (m, 3H, ArH), 7.52-7.55 (m, 2H, ArH), 7.79-7.782 (m, 2H, ArH), 12.46 (br s, 1H, OH). ^{13}C-NMR (62.9 MHz, $CDCl_3$): δ = 105.6, 106.1 (CH), 109.7 (C), 110.1; 126.4, 127.3, 128.8, 129.0, 129.1 (CH), 131.2 (C), 132.0 (CH), 139.2, 148.5, 156.6, 160.8, 164.6 (C), 183.1 (CO). IR (KBr, cm^{-1}) : ν = 3075, 3053, 3032, 2926, 2852, 2797 (w), 1656, 1651, 1613, 1593 (s), 1537 (w), 1508 (m), 1496 (w), 1482, 1450, 1420, 1402, 1361, 1346 (s), 1296 (m), 1270 (s), 1251 (w), 1217, 1207, 1199, 1186 (m), 1160 (w), 1121, 1094, 1075, 1052, 1032, 1002, 997 (m), 946 (w), 910, 903 (m), 872 (w), 850 (s), 835, 825, 794 (m), 752, 727, 684, 674, 654, 639, 630 (s), 616, 575 (w), 535 (m). GC-MS (EI, 70 eV): *m/z* (%) = 315 ($[M+H]^+$, 20), 314 ($[M]^+$, 100), 184 (8). HRMS (EI, 70 eV): calcd for $C_{21}H_{14}O_3$ $[M]^+$: 314.09375, found 314.093679.

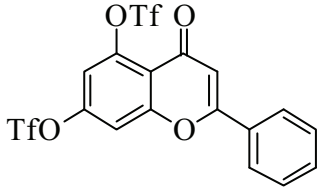
5-Hydroxy-7-(2-chlorophenyl)-2-phenyl-4*H*-chromen-4-one (13k): Starting with **12** (80 mg, 0.207 mmol), **3m** (32 mg, 0.207 mmol), $Pd(PPh_3)_4$ (7 mg, 3 mol%, 0.006 mmol), K_3PO_4 (65 mg, 0.304 mmol), and 1,4-dioxane (3 mL), **13k** was isolated as a yellow solid (54 mg, 75%); mp 186-188 °C. ^{1}H NMR (250 MHz, $CDCl_3$): δ = 6.68 (s, 1H), 6.80 (d, J = 1.4 Hz, 1H, ArH), 7.02 (d, J = 1.4 Hz, 1H, ArH), 7.25-7.29 (m, 3H, ArH), 7.43-7.46 (m, 4H, ArH), 7.81-7.85 (m, 2H, ArH), 12.50 (br s, 1H, OH). ^{13}C-NMR (62.9 MHz, $CDCl_3$): δ = 106.2, 108.3 (CH), 110.0 (C), 112.8, 126.4, 127.0,

129.1, 129.5, 130.2, 130.9, 131.1 (CH), 132.0, 132.1, 138.9, 146.7, 155.9, 160.2, 164.7 (C), 183.3 (CO). IR (KBr, cm^{-1}) : ν = 2956, 2851(w), 1657, 1609, 1591 (s), 1573, 1556, 1503, 1492, 1462 (m), 1450, 1421, 1396, 1359 (s), 1341 (w), 1296 (s), 1268 (w), 1255, 1246, 1211, 1196, 1186 (s), 1156, 1119, 1095 (m), 1078, 1067 (w), 1043 (s), 1034 (w), 998 (m), 970, 954, 921, 907, 869, 861 (w), 844 (s), 828, 817, 766, 751 (s), 734, 727, 713 (m), 690, 681, 673, 656, 627 (m), 579 (w), 545 (m). GC-MS (EI, 70 eV): *m/z* (%) = 350 ($[M]^+$, ^{37}Cl, 35), 349 ($[M+H]^+$, ^{35}Cl, 20), 348 ($[M]^+$, ^{35}Cl, 100), 218 (10), 155 (14). HRMS (EI, 70 eV): calcd for $C_{21}H_{13}{}^{37}ClO_3$ $[M]^+$: 350.05182, found 350.052314, calcd for $C_{21}H_{13}{}^{35}ClO_3$ $[M]^+$: 348.05477 found 348.054378.

5-Hydroxy-2-phenyl-7-(*o*-tolyl)-4*H*-chromen-4-one (13l): Starting with **12** (80 mg, 0.207 mmol), **3n** (28 mg, 0.207 mmol), $Pd(PPh_3)_4$ (7 mg, 3mol%, 0.006 mmol), K_3PO_4 (65 mg, 0.304 mmol), and 1,4-dioxane (3 mL), **13l** was isolated as a yellow solid (52 mg, 77%); mp 150-152 °C. ^1H NMR (250 MHz, $CDCl_3$): δ = 2.33 (s, 3H, CH_3), 6.60 (s, 1H), 6.93 (d, J = 1.4 Hz, 1H, ArH), 7.09 (d, J = 1.4 Hz, 1H, ArH), 7.11-7.14 (m, 1H, ArH), 7.22-7.28(m, 1H, ArH), 7.31-7.34 (m, 2H, ArH), 7.41-7.43 (m, 3H, ArH), 7.78-7.81 (m, 2H, ArH), 12.4 (br s, 1H, OH). ^{13}C-NMR (62.9 MHz, $CDCl_3$): δ= 105.5, 106.1 (CH), 109.6 (C), 110.1, 124.3, 126.3, 128.0, 128.8, 129.0, 129.6 (CH), 131.2 (C), 131.9 (CH), 138.6, 139.2, 148.6, 156.5, 160.7, 164.5 (C), 183.1 (CO). IR (KBr, cm^{-1}): ν = 3068, 2916 (w), 1652, 1615 (s), 1591 (m), 1568, 1556, 1537, 1519, 1504 (w)1494, 1482, 1450, 1411, 1362 (m), 1343, 1312, 1295 (w), 1271, 1255, 1237, 1206 (m), 1167, 1159, 1120, 1054, 1033 (w), 1011, 999 (m), 965, 938, 921 (w), 908, 899, 860, 827, 809, 794 (m), 761 (s), 725, 700, 691, 685 (w), 673 (s), 654, 643 (w), 634 (m), 619, 608, 576, 545 (w). GC-MS (EI, 70 eV): *m/z* (%) = 329 ($[M+H]^+$, 24), 328 ($[M]^+$, 100), 300 (9). HRMS (EI, 70 eV): calcd for $C_{22}H_{16}O_3$ $[M]^+$: 328.10940, found 328.109232.



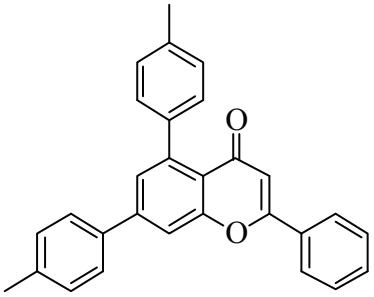
4-Oxo-2-phenyl-4*H*-chromene-5,7-diyl-bis(trifluoromethanesulfonate) (14): To a solution of **11** (0.5 g, 1.96 mmol) in CH_2Cl_2 (20 mL) was added pyridine (0.6 mL, 7.86 mmol) and the solution was stirred at room temperature. To the solution was added Tf_2O (0.8 mL, 4.72 mmol) and the solution was stirred at room



temperature for 10 min. Subsequently, the solution was stirred at 40 °C for 30 min. After cooling, the reaction mixture was concentrated in vacuo. Product **14** was isolated by rapid column chromatography (flash silica gel, heptane–EtOAc) as a white solid (0.90 g, 90%); mp 182-184 °C. ^{1}H NMR (300 MHz, $CDCl_3$): δ = 6.76 (s, 1H), 7.07 (d, J = 2.2 Hz, 1H, ArH), 7.47-7.52 (m, 3H, ArH), 7.55 (d, J = 2.2 Hz, 1H, ArH), 7.80-7.83 (m, 2H, ArH). ^{13}C- NMR (75.4 MHz, $CDCl_3$): δ = 109.0, 112.3, 113.2 (CH), 117.7 (C), 118.6 (q, J_{CF} = 320 Hz, CF_3), 118.7 (q, J_{CF} = 320 Hz, CF_3), 126.4, 129.3 (CH), 130 (C), 132.5 (CH), 147.8, 150.8, 157.4, 163.4 (C), 174.6 (CO). ^{19}F NMR (282.4 MHz. $CDCl_3$): = -72.27 (3F, CF_3), -72.96 (3F, CF_3). IR (KBr, cm^{-1}): ν = 3111, 3093, 3068, 2958, 2924, 2855 (w), 1651, 1617 (s), 1572, 1496, 1467, 1450 (w), 1427, 1363 (s), 1338, 1301, 1279 (w), 1248, 1216, 1202, 1135, 1129, 1097 (s), 1067, 1035 (m), 1006, 972 (s), 929 (w), 892, 872, 848, 812 (s), 782 (w), 773 (s), 761, 713, 705, 689 (m), 680 (w), 661 (m), 650, 641 (w), 612 (s), 596 (w), 586 (s), 569, 545 (m). GC-MS (EI, 70 eV): *m/z* (%) = 519 ($[M+H]^+$, 23), 518 ($[M]^+$, 100), 454 (12). HRMS (EI, 70 eV): calcd for $C_{17}H_8F_6O_8S_2$ $[M]^+$: 517.95593, found 517.95651.

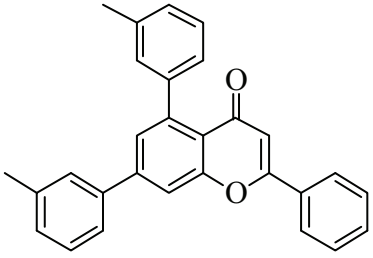
General Procedure for synthesis 15a-i, 16a-g: A 1,4-dioxane solution (3 mL) of **14**, K_3PO_4, [$Pd(PPh_3)_4$], and arylboronic acid **3** was stirred at 70 or 115 °C for 6-9 h. After cooling to 20 °C, distilled water was added, the organic and the aqueous layers were separated, and the latter was extracted 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 column chromatography.

2-Phenyl-5,7-di(*p*-tolyl)-4*H*-chromen-4-one (15a): Starting with **14** (75 mg, 0.145 mmol), **3a** (39 mg, 0.29 mmol), $Pd(PPh_3)_4$ (10 mg, 6 mol%, 0.009 mmol), K_3PO_4 (92 mg, 0.435 mmol), and 1,4-dioxane (3 mL), **15a** was isolated as a white solid (49 mg, 85%). Reaction temperature: 115 °C for 6 h. M.p. 236-238 °C. ^{1}H NMR (300 MHz, $CDCl_3$): δ = 2.32 (s, 3H, CH_3), 2.34 (s, 3H, CH_3), 6.6 (s, 1H), 7.13-7.16 (m, 3H, ArH), 7.19-7.22 (m, 3H, ArH), 7.36 (d, J = 1.8 Hz, 1H, ArH), 7.42-7.44 (m, 3H, ArH), 7.52 (d, J = 8.1 Hz, 2H, ArH), 7.66 (d, J = 1.8 Hz, 1H, ArH), 7.83-7.86 (m, 2H,ArH). ^{13}C-NMR (62.9 MHz, $CDCl_3$): δ = 21.2, 21.3 (CH_3), 108.9, 114.9 (CH), 119.8 (C), 126.1,

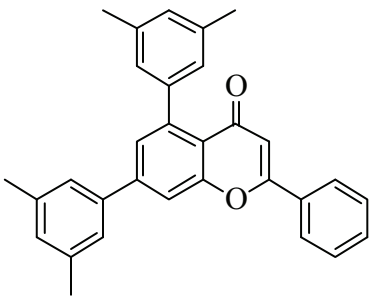


127.1, 127.1, 128.2, 128.6, 128.9, 129.8, 131.3 (CH), 131.7, 135.8, 136.8, 138.8, 143.5, 145.1, 157.9, 161.7 (C), 178.0 (CO). IR (KBr, cm^{-1}): ν = 3063, 2915, 2858 (w), 1643, 1605 (s), 1574, 1552, 1537 (w), 1519, 1495, 1484, 1463, 1448, 1423 (w), 1372 (s), 1311, 1286, 1271, 1225, 1203, 1191 (w), 1138, 1108 (m), 1081, 1064 (w), 1033, 1023, 1015, 965, 941 (w), 929, 909, 877, 861 (m), 843 (w), 809, 773 (s), 725, 711 (w), 692, 678 (s), 645, 616, 603, 596 (m), 568 (w), 546 (s). GC-MS (EI, 70 eV): *m/z* (%) = 403 ($[M+H]^+$, 11), 402 ($[M]^+$, 43), 401 (100). HRMS (EI, 70 eV): calcd for $C_{29}H_{21}O_2$ $[M-H]^+$: 401.15361 , found 401.1534321.

2-Phenyl-5,7-di(*m*-tolyl)-4*H*-chromen-4-one (15b): Starting with **14** (75 mg, 0.145 mmol), **3b** (39 mg, 0.29 mmol), $Pd(PPh_3)_4$ (10 mg, 6 mol%, 0.009 mmol), K_3PO_4 (92 mg, 0.435 mmol), and 1,4-dioxane (3 mL), **15b** was isolated as a white solid (46 mg, 80%). Reaction temperature: 115 °C for 6 h. M.p. 122-124 °C.^{1}H NMR (300 MHz, $CDCl_3$): δ = 2.33 (s, 3H, CH_3), 2.34 (s, 3H, CH_3), 6.60 (s, 1H), 7.09-7.16 (m, 5H, ArH), 7.20-7.30 (m, 2H, ArH), 7.36 (d, J = 1.8 Hz, 1H, ArH), 7.40-7.44 (m, 5H, ArH), 7.69 (d, J = 1.8 Hz, 1H, ArH), 7.83-7.86 (m, 2H, ArH). ^{13}C-NMR (75.4 MHz, $CDCl_3$): δ = 21.5, 21.5 ($2CH_3$), 108.9, 115.4, 124.4, 126.0, 126.2, 127.3, 127.9, 128.1, 129.0, 129.3, 129.56, 131.4 (CH), 131.7, 137.0, 138.7, 138.7, 141.3, 143.7, 145.3, 157.8, 161.8 (C), 178.0 (CO). IR (KBr, cm^{-1}): ν = 3068; 3060; 3033; 2952 (m), 2920, 2852 (m), 1642 (s), 1622 (w), 1602 (s), 1574, 1557 (w), 1495, 1462, 1447 (m), 1371 (s), 1302, 1286, 1260, 1193, 1169 (w), 1130 (m), 1106, 1091, 1078, 1063, 1041, 1028, 998, 971, 948, 928, 900 (w), 876, 862, 854, 820, 790 (m), 780, 770 (s), 717 (m) 687, 676 (s) 646, 635, 631 (m), 612, 587, 578, 556 (w). GC-MS (EI, 70 eV): *m/z* (%) = 403 ($[M+H]^+$, 12), 402 ($[M]^+$, 38), 401 (100), 201 (18), 185 (10). HRMS (EI, 70 eV): calcd for $C_{29}H_{21}O_2$ $[M-H]^+$: 401.15361, found 401.153486.

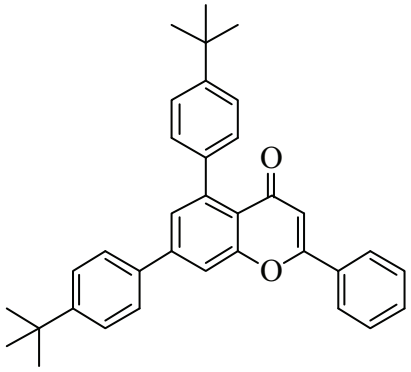


5,7-Bis(3,5-dimethylphenyl)-2-phenyl-4*H*-chromen-4-one (15c): Starting with **14** (75 mg, 0.145 mmol), **3c** (93 mg, 0.29 mmol), $Pd(PPh_3)_4$ (10 mg, 6 mol%, 0.009 mmol), K_3PO_4 (92 mg, 0.435 mmol), and 1,4-dioxane (3 mL), **15c** was isolated as a white solid (49 mg, 80%). Reaction temperature: 115 °C for 6 h. M.p. 171-173 °C. ^{1} H NMR (300 MHz, $CDCl_3$): δ = 2.29 (s,



6H, 2CH_3), 2.30 (s, 6H, 2CH_3), 6.62 (s, 1H), 6.93-6.97 (m, 4H, ArH), 7.23 (br s, 2H, ArH), 7.35 (d, J = 1.8 Hz, 1H, ArH), 7.41-7.45 (m, 3H, ArH), 7.67 (d, J = 1.8 Hz, 1H, ArH), 7.84-7.87 (m, 2H, ArH). ^{13}C-NMR (74.5 MHz, $CDCl_3$): δ = 21.3, 21.4 (CH3), 108.9, 115.2 (CH), 119.9 (C), 125.2, 126.1, 126.5, 127.4, 128.9, 129.0, 130.3, 131.3 (CH), 131.7, 136.8, 138.6, 138.7, 141.3, 143.7, 145.4, 157.7 (C), 161.7 (CO). IR (KBr, cm^{-1}): v = 3062, 3006, 2914, 2858, 2732 (w), 1645, 1597 (s), 1574, 1557 (w), 1483 (m), 1463 (w), 1447 (m), 1433 (w), 1371 (s), 1304, 1284, 1262, 1246, 1231, 1188, 1157 (w), 1137, 1110, 1062 (m), 1029, 1012, 998, 983, 954, 925, 911, 901, 868 (w), 846 (s), 790 (m), 765 (s), 746 (m), 707 (w), 690, 680 (s), 645, 637, 617, 586 (m), 563, 541, 531 (w). GC-MS (EI, 70 eV): *m/z* (%) = 430 ([M]$^+$, 25), 429 (100), 416 (9), 199 (43). HRMS (EI, 70 eV): calcd for $C_{31}H_{25}O_2$ [M-H]$^+$: 429.18491, found 429.184637.

5,7-Bis(4-*tert*-butylphenyl)-2-phenyl-4*H*-chromen-4-one (15d): Starting with **14** (75 mg, 0.145 mmol), **3e** (52 mg, 0.29 mmol), $Pd(PPh_3)_4$ (10 mg, 6 mol%, 0.009 mmol), K_3PO_4 (92 mg, 0.435 mml), and 1,4-dioxane (3 mL), **15d** was isolated as a white solid (54 mg, 77%). Reaction temperature: 115 °C for 6 h. M.p. 204-206 °C.[1] H NMR (300 MHz, $CDCl_3$): δ = 1.29 (s, 9H, 3CH_3), 1.31 (s, 9H, 3CH_3), 6.62 (s, 1H), 7.25 (d, J = 8.4 Hz, 2H, ArH), 7.36 (d, J = 8.4 Hz, 2H, ArH), 7.41 (d, J = 1.8 Hz, 1H, ArH), 7.55 (d, J = 8.5 Hz, 2H, ArH), 7.69 (d, J = 1.7 Hz, 1H, ArH), 7.84-7.87 (m, 2H, ArH). ^{13}C- NMR (75.4 MHz, $CDCl_3$): δ = 31.3, 31.4 (6CH_3), 34.6, 34.7 (C), 108.8, 115.0, 124.4 (CH), 125.6 (C), 126.0, 126.2, 127.0, 127.4, 128.5, 129.0, 131.4 (CH), 131.7, 135.8, 138.3, 143.6, 145.1, 149.8, 152.0, 157.9, 161.9 (C), 178.1 (CO). IR (KBr, cm^{-1}): v = 3071, 3039 (w), 2957, 2947 (m), 2900, 2863 (w), 1644, 1604 (s), 1576, 1548 (w), 1520 (m), 1496 (w), 1462, 1449, 1422 (m), 1402 (w), 1375 (s), 1318, 1309, 1287 (w), 1268 (m), 1211, 1193, 1157, 1144 (w), 1108 (m), 1081, 1064, 1034, 1023, 1012, 999, 970, 942 (w), 929, 909, 873, 863, 843 (m), 825 (s), 815 (m), 769 (s), 750, 740, 729 (w), 693, 679 (s), 659, 644, 613, 604, 588 (w), 566 (m), 545, 535 (w). GC-MS (EI, 70 eV): *m/z* (%) = 487 ([M+H]$^+$, 17), 486 ([M]$^+$, 57), 485 (100), 471 (26), 455 (12). HRMS (EI, 70 eV): calcd for $C_{35}H_{33}O_2$ [M-H]$^+$: 485.24751, found 485.247625.

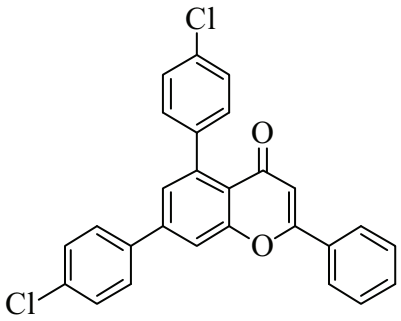


5,7-Bis(4-methoxyphenyl)-2-phenyl-4*H*-chromen-4-one (15e): Starting with **5** (75 mg, 0.145 mmol), **3f** (44 mg, 0.29 mmol), $Pd(PPh_3)_4$ (10 mg, 6 mol%, 0.009 mmol), K_3PO_4 (92 mg, 0,435 mmol), and 1,4-dioxane (3 mL), **6e** was isolated as a white solid (56 mg, 90%). Reaction temperature: 115 °C for 6 h. M.p. 211-212 °C. ^{1}H NMR (300 MHz, $CDCl_3$): δ = 3.75 (s, 3H, OCH_3), 3.77 (s, 3H, OCH_3), 6.57 (s, 1H), 6.87 (d, J = 8.7 Hz, 2H, ArH), 6.90 (d, J = 8.8 Hz, 2H, ArH), 7.24 (d, J = 8.7 Hz, 2H, ArH), 7.31 (d, J = 1.8 Hz, 1H, ArH), 7.40-7.43 (m, 3H, ArH), 7.55 (d, J = 8.8 Hz, 2H, ArH), 7.60 (d, J = 1.8 Hz, 1H, ArH), 7.81-7.84(m, 2H, ArH). ^{13}C- NMR (75.4 MHz, $CDCl_3$): δ = 55.2, 55.4 (OCH_3), 108.9, 113.0, 114.4, 114.5 (CH), 119.5 (C), 126.1, 127.0, 128.4, 129.0, 130.0 (CH), 131.1 (C), 131.3 (CH), 131.7, 133.6, 143.2, 144.7, 158.0, 158.9, 160.3, 161.6 (C), 178.1 (CO). IR (KBr, cm^{-1}): v = 3066, 3011, 2957, 2933, 2904, 2836 (w), 1643, 1600 (s), 1576, 1552 (m), 1511 (s), 1461, 1448, 1427 (m), 1371 (s), 1346, 1313 (w), 1291, 1282, 1254 (m), 1236 (s), 1205 (m), 1183, 1176 (s), 1157 (w), 1139 (m), 1116 (w), 1106 (m), 1080, 1062 (w), 1028, 1018 (s), 954 (w), 927, 907, 878, 857, 838 (m), 825 (s), 807, 793 (m), 770 (s), 730 (m), 693, 677 (s), 645, 616, 596, 550, 535 (m). GC-MS (EI, 70 eV): *m/z* (%) = 435($[M+H]^+$, 15), 434 ($[M]^+$, 61), 433 (100), 390 (10), 217 (7). HRMS (EI, 70 eV): calcd for $C_{29}H_{21}O_4$ $[M-H]^+$: 433.14344, found 433.1143348.

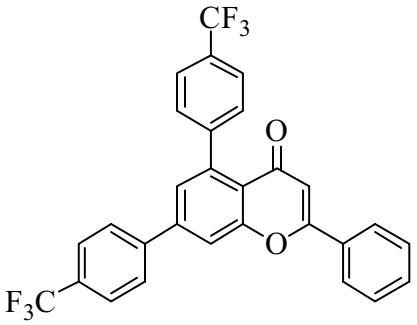
5,7-Bis(4-fluorophenyl)-2-phenyl-4*H*-chromen-4-one (15f): Starting with **14** (75 mg, 0.145 mmol), **3h** (41 mg, 0.29 mmol), $Pd(PPh_3)_4$ (10 mg, 6 mol%, 0.009 mmol), K_3PO_4 (92 mg, 0.345 mml), and 1,4-dioxane (3 mL), **15f** was isolated as a white solid (49 mg, 83%). Reaction temperature: 115 °C for 6 h. M.p. 213-215 °C. ^{1}H NMR (250 MHz, $CDCl_3$): δ = 6.63 (s, 1H), 7.06 (dt, J = 8.7, 17.2 Hz, 4H, ArH), 7.23-7.29 (m, 3H, ArH), 7.44-7.47 (m, 3H, ArH), 7.59 (dd, J = 5.2, 8.8 Hz, 2H, ArH), 7.67 (d, J = 1.6 Hz, 1H, ArH), 7.83-7.87 (m, 2H, ArH). ^{13}C-NMR (62.9 MHz, $CDCl_3$): δ = 108.9, 114.5 (d, J = 21.5 Hz), 115.6, 115.2 (d, J = 21.4 Hz) (CH), 119.9 (C), 126.1, 127.2, 129.0, 129.1 (d, J = 8.0 Hz),130.4 (d, J = 8.0 Hz) (CH), 131.4 (C), 131.5 (CH), 134.8 (d, J = 3.3

Hz), 136.9 (d, J = 3.3 Hz), 142.6, 144.2, 157.8, 162.0 (C), 162.3 (d, $J_{F,C}$ = 245.9 Hz) (CF), 163.3 (d, $J_{F,C}$ = 249.1 Hz) (CF)), 175.8 (CO). ^{19}F NMR (282 MHz, $CDCl_3$): = -115.4, -112.7. IR (KBr, cm^{-1}): v = 3065, 2919, 2852, 1894, 1743 (w), 1644 (s), 1621 (m), 1606 (s), 1576, 1555 (m), 1509 (s), 1466, 1448, 1425 (m), 1402 (w), 1369 (s), 1346, 1305, 1287, 1271, 1260 (w), 1216 (s), 1189 (w), 1157, 1138 (s), 1108, 1092, 1081, 1054, 1034, 1020, 1012, 1000, 984, 965 (w), 927 (m), 908, 895 (w), 873 (m), 858 (w), 829 (s), 790 (m), 771 (s), 742, 730, 721 (w), 694, 685, 674 (s), 647, 636 (w), 616, 603, 594, 566, 547 (m). GC-MS (EI, 70 eV): *m/z* (%) = 411 ($[M+H]^+$, 9), 410 ($[M]^+$, 44), 409 (100), 251 (7). HRMS (EI, 70 eV): calcd for $C_{27}H_{15}F_2O_2$ $[M-H]^+$: 409.10346, found 409.103561.

5,7-Bis(4-chlorophenyl)-2-phenyl-4*H*-chromen-4-one (15g): Starting with **14** (75 mg, 0.145 mmol), **3i** (45 mg, 0.29 mmol), $Pd(PPh_3)_4$ (10 mg, 6 mol%, 0.009 mmol), K_3PO_4 (92 mg, 0.435 mmol), and 1,4-dioxane (3 mL), **15g** was isolated as a yellow solid (54 mg, 85%). Reaction temperature: 115 °C for 6 h. M.p. 280-282 °C. ^{1}H NMR (300 MHz, $CDCl_3$): δ = 6.66 (s, 1H), 7.23 (d, J = 8.6 Hz, 2H, ArH), 7.29-7.33 (m, 3H, ArH), 7.40 (d, J = 8.6 Hz, 2H, ArH), 7.44-7.49 (m, 3H, ArH), 7.55 (d, J = 8.6 Hz, 2H, ArH), 7.7 (d, J = 1.8 Hz, 1H, ArH), 7.83-7.87 (m, 2H, ArH). ^{13}C-NMR (62.9 MHz, $CDCl_3$): δ = 108.9, 115.8, 126.2, 127.0, 127.7, 128.6, 129.1, 129.3, 130.1, 131.6 (CH), 131.6, 133.4, 135.2, 137.0, 139.4, 142.5, 144.1, 157.8, 162.2 (C), 177.8 (CO). IR (KBr, cm^{-1}): v = 3061, 2954, 2922, 2852 (w), 1639, 1605 (s), 1574, 1552 (w), 1503, 1496, 1463, 1448, 1423 (m), 1398 (w), 1372 (s), 1311, 1287, 1257, 1212, 1190, 1110 (w), 1087 (s), 1064, 1033, 1019, 1014 (w), 1008 (m), 964, 937 (w), 927, 908, 878, 865 (m), 845, 834 (w), 818, 808, 775 (s), 732, 712 (w), 692, 678, 650 (s), 634, 609, 601, 585, 538 (m). GC-MS (EI, 70 eV): *m/z* (%) = 445 ($[M+H]^+$, $[^{35}Cl]$ $[^{37}Cl]$, 12), 444 ($[M]^+$, $[^{35}Cl]$ $[^{37}Cl]$, 23), 443 ($[M+H]^+$, $[^{35}Cl]$ $[^{35}Cl]$, 68), 442 ($[M]^+$, $[^{35}Cl]$ $[^{35}Cl]$, 36), 441 (100). HRMS (EI, 70 eV): calcd for $C_{27}H_{15}Cl_2O_2$ ($[M-H]^+$, $[^{35}Cl]$ $[^{37}Cl]$): 443.04141, found 443.041464, calcd for $C_{27}H_{15}Cl_2O_2$ ($[M-H]^+$, $[^{35}Cl]$ $[^{35}Cl]$): 441.04436, found 441.044306.

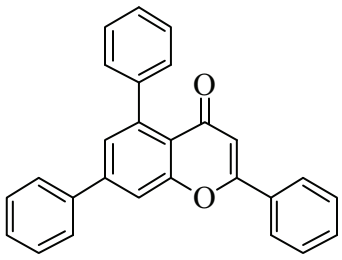


2-Phenyl-5,7-bis[4-(trifluoromethyl)phenyl]-4*H*-chromen-4-one (15h): Starting with



14 (75 mg, 0.145 mmol), **3j** (55 mg, 0.29 mmol), $Pd(PPh_3)_4$ (10 mg, 6 mol%, 0.009 mmol), K_3PO_4 (92 mg, 0.435 mL), and 1,4-dioxane (3 mL), **15h** was isolated as a yellow solid (56 mg, 76%). Reaction temperature: 115 °C for 6 h. M.p. 308-310 °C. ^{1}H NMR (300 MHz, $CDCl_3$): δ = 6.64 (s, 1H), 7.35 (br s, 1H, ArH), 7.41-7.49 (m, 5H, ArH), 7.62 (d, J = 7.8 Hz, 2H, ArH), 7.68-7.76 (m, 4H, ArH), 7.80 (br s, 1H, ArH), 7.88-7.89 (br m, 2H, ArH). ^{13}C- NMR (75.4 MHz, $CDCl_3$): δ = 108.8, 116.7 (CH), 120.6 (q, J_{CF} = 270 Hz, CF_3), 120.8 (q, J_{CF} = 270 Hz, CF_3), 124.5 (q, J_{CF} = 3.7 Hz, CH), 126.1 (q, J_{CF} = 3.7 Hz, CH), 126.3, 127.1, 127.7, 129.0, 129.1 (CH), 131.8 (C), 131.8 (CH), 136.2, 138.9, 142.0, 144.1, 149.8, 152.0, 157.9, 162.5 (C), 177.7 (CO). ^{19}F NMR (282.4 MHz. $CDCl_3$): δ = -62.39 (3F, CF_3), -62.63 (3F, CF_3). IR (KBr, cm^{-1}): ν = 3069 (w), 1645, 1606 (s), 1578, 1556 (m), 1536, 1498 (w), 1470, 1452, 1427 (m), 1406 (w), 1375, 1320 (s), 1291, 1260, 1195 (w), 1170, 1163, 1152, 1102, 1066 (s), 1035 (w9, 1012 (s), 955, 948 (w), 929 (m), 909, 884 (w), 871, 854 (m), 831, 773 (s), 740 (w), 693, 681, 671 (s), 650, 641, 621 (w), 598, 584 (m), 533 (w). GC-MS (EI, 70 eV): *m/z* (%) = 511 ($[M+H]^+$, 9), 510 ($[M]^+$, 44), 509 (100). HRMS (EI, 70 eV): calcd for $C_{29}H_{16}F_6O_2$ $[M-H]^+$: 510.11541, found 510.117632.

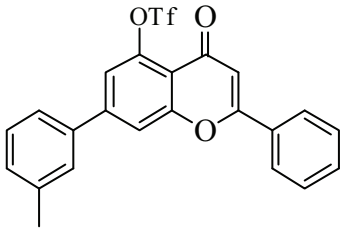
2,5,7-Triphenyl-4-*H*-chromen-4-one (15i): Starting with **14** (75 mg, 0.145 mmol), **3l**



(35 mg, 0.29 mmol), $Pd(PPh_3)_4$ (10 mg, 6 mol%, 0.009 mmol), K_3PO_4 (92 mg, 0,435 mmol), and 1,4-dioxane (3 mL), **15i** was isolated as a white solid (43 mg, 80%). Reaction temperature: 115 °C for 6 h. M.p. 194-195 °C.[1] H NMR (300 MHz, $CDCl_3$): δ = 6.60 (s, 1H), 7.30-7.45 (m, 12H, ArH), 7.60-7.63 (m, 2H, ArH), 7.71 (d, J = 1.8 Hz, 1H, ArH), 7.84-7.87 (m, 2H, ArH). ^{13}C-NMR (75.4 MHz, $CDCl_3$): δ = 108.9, 115.5 (CH), 120.0 (C), 126.2, 127.2, 127.3, 127.5, 128.7, 128.8, 129.0, 129.1, 131.4 (CH), 131.6, 138.7, 141.3, 143.6, 145.2, 157.8, 161.9 (C), 178.0 (CO). IR (KBr, cm^{-1}): ν = 3059, 3030 (w), 1644, 1606, 1598 (s), 1574, 1556 (m), 1537 (w), 1503, 1495, 1464, 1448 (s), 1440 (m), 14150, 1393 (w), 1372 (s), 1310, 1287, 1207, 1192, 1157 (w), 1139, 1109 (m), 1079, 1072, 1064, 1039, 1030

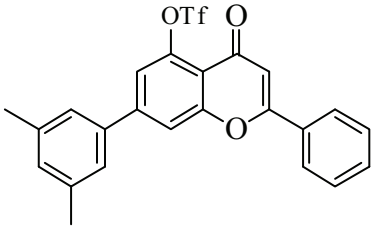
(w), 1016 (m), 999, 975 (w), 929, 906, 872 (m), 843, 789 (w), 760 (s), 710 (m), 690 (s), 646, 627, 614, 604, 583 (w), 569, 534 (m). GC-MS (EI, 70 eV): *m/z* (%) = 374 ($[M]^+$, 38), 373 (100), 215 (5). HRMS (EI, 70 eV): calcd for $C_{24}H_{17}F_3O_5S$ $[M-H]^+$: 373.12231, found 373.121759.

4-Oxo-2-phenyl-7-(*m*-tolyl)-4*H*-chromen-5-yl trifluoromethanesulfonate (16a):



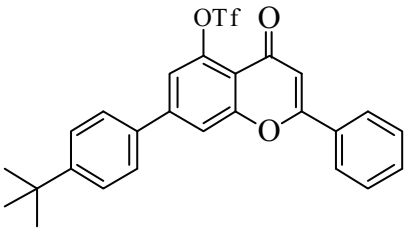
Starting with **14** (75 mg, 0.145 mmol), **3b** (22 mg, 0.145 mmol), $Pd(PPh_3)_4$ (5 mg, 3mol%, 0.004 mmol), K_3PO_4 (46 mg, 0,217 mmol), and 1,4-dioxane (3 mL), **16a** was isolated as a white solid (58 mg, 85%). Reaction temperature: 70 °C for 9 h. M.p. 218-221°C. ^{1}H NMR (300 MHz, $CDCl_3$): δ = 2.38 (s, 3H, CH_3), 6.70 (s, 1H), 7.21-7.24 (m, 1H, ArH), 7.30-7.36 (m, 4H, ArH), 7.44-7.48 (m, 3H, ArH), 7.72 (J = 1.8 Hz, 1H, ArH), 7.81-7.84 (m, 2H, ArH). ^{13}C-NMR (75.4 MHz, $CDCl_3$): δ = 108.8 (CH), 116.1 (C), 116.6, 117.7 (CH), 118.9 (q, $J_{F,C}$ = 320.1 Hz, CF_3), 124.3, 126.3, 127.9, 129.1, 129.3, 130.4 (CH), 130.8 (C), 132.0, 137.2 (CH), 139.2, 147.0, 157.3, 162.8 (C), 175.8 (CO). ^{19}F NMR (282 MHz, $CDCl_3$): = -73.3. IR (KBr, cm^{-1}): ν = 3061, 2955 (w), 2921 (m), 2852 (w), 1647, 1626, 1614 (s), 1579, 1552 (w), 1495 (m), 1468 (w), 1449 (m), 1430 (s), 1392 (m), 1368 (s), 1348, 1303, 1287 (w), 1246 (m), 1217, 1193, 1137 (s), 1112 (m), 1080 (w), 1066, 1033 (m), 981 (s), 938, 926, 905, 886 (w), 867, 834, 796, 786, 768, 760 (s), 711 (w), 687 (s), 666, 647 (m), 637 (w), 609, 585, 577 (s), 533 (w). GC-MS (EI, 70 eV): *m/z* (%) = 461 ($[M+H]^+$, 25), 460 ($[M]^+$, 100), 368 (32), 299 (26), 228 (9). HRMS (EI, 70 eV): calcd for $C_{23}H_{15}F_3O_5S$ $[M]^+$: 460.06346, found 460.063561.

7-(3,5-Dimethylphenyl)-4-oxo-2-phenyl-4*H*-chromen-5-yl trifluoromethanesulfonate (16b):

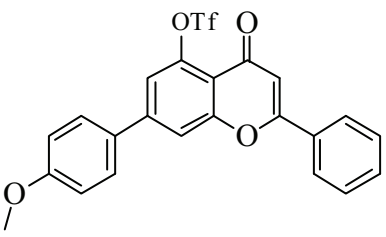


Starting with **14** (75 mg, 0.145 mmol), **3c** (22 mg, 0.145 mmol), $Pd(PPh_3)_4$ (5 mg, 3mol%, 0.004 mmol), K_3PO_4 (46 mg, 0,217 mmol), and 1,4-dioxane (3 mL), **16b** was isolated as a white solid (58 mg, 85%). Reaction temperature: 70 °C for 9 h. M.p. 218-221°C. ^{1}H NMR (300 MHz, $CDCl_3$): δ = 2.34 (s, 3H, $6CH_3$), 6.70 (s, 1H), 7.05 (br, 1H, ArH), 7.15 (br, 2H, ArH), 7.32 (br, 1H, ArH), 7.45-7.49 (m, 3H, ArH), 7.72 (d, J = 1.6 Hz, 1H, ArH), 7.821-7.85 (m, 2H, ArH). ^{13}C-NMR (74.5 MHz, $CDCl_3$): δ = 21.3 ($2CH_3$), 108.7 (CH),

116.0 (C), 116.3 (CH), 117.3 (q, $J_{F,C}$ = 320.1 Hz, CF_3), 117.7, 125.0, 126.2, 129.1 (CH), 130.8 (C), 131.3, 132.0 (CH), 137.2, 139.1, 146.9, 147.2, 157.3, 162.8 (C), 175.8 (CO). ^{19}F NMR (282 MHz, $CDCl_3$): = -73.3. IR (KBr, cm^{-1}): ν = 3063, 2916, 2859 (w), 1639, 1630, 1611 (s), 1579, 1493 (w), 1449 (m), 1425 (s), 1394 (w), 1369 (s), 1348, 1298, 1284, 1249 (w), 1231 (m), 1201, 1138 (s), 1116 (m), 1077 (w), 1064, 1031, 1008 (m), 978 (s), 949, 924, 908, 895, 868, 857, 850 (w), 828, 768, 758 (s), 734, 711, 701 (w), 685, 675, 665 (m), 653 (w), 614, 588 (s), 569, 541 (w). GC-MS (EI, 70 eV): *m/z* (%) = 475 ($[M+H]^+$, 25), 474 ($[M]^+$, 100), 382 (29), 313 (25). HRMS (EI, 70 eV): calcd for $C_{24}H_{17}F_3O_5S$ $[M]^+$: 474.07433, found 474.072983.

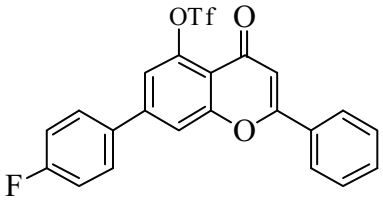
7-(4-*tert*-Butylphenyl)-4-oxo-2-phenyl-4*H*-chromen-5-yl trifluoromethanesulfonate (16c): 

Starting with **14** (75 mg, 0.145 mmol), **3e** (26 mg, 0.145 mmol), $Pd(PPh_3)_4$ (5 mg, 3mol%, 0.004 mmol), K_3PO_4 (46 mg, 0.217 mmol), and 1,4-dioxane (3 mL), **16c** was isolated as a white solid (51 mg, 71%). Reaction temperature: 70 °C for 9 h. M.p. 185-188 °C.^{1}H NMR (300 MHz, $CDCl_3$): δ = 1.3 (s, 9H, $3CH_3$), 6.71 (s, 1H), 7.35 (br s, 1H, ArH), 7.45-7.54 (m, 7H, ArH), 7.74 (d, J = 1.5 Hz, 1H, ArH), 7.83-7.86 (m, 2H, ArH). ^{13}C-NMR (62.9 MHz, $CDCl_3$): δ = 31.21 ($3CH_3$), 34.8 (C), 108.3, 116.2, 117.5 (CH), 118.7 (q, $J_{F,C}$ = 322.1 Hz, CF_3), 126.3, 126.4, 126.9, 129.1 (CH), 130.9 (C), 131.9 (CH), 134.3, 146.7, 147.0 153.1, 157.4, 162.8 (C), 175.8 (CO). ^{19}F NMR (282 MHz, $CDCl_3$): = -73.3. IR (KBr, cm^{-1}): ν = 3063, 2962, 2866, 2252 (w), 1643, 1630, 1613 (s), 1577, 1546, 1523, 1494, 1474 (w), 1449 (m), 1242 (s), 1400 (m), 1369 (s), 1346, 1301, 1285, 1269 (w), 1242 (m), 1230 (w), 1205, 1137 (s), 1117, 1106, 1065, 1055, 1031 (m), 1016, 1001 (w), 981, 903 (s), 879 (w), 833, 810, 767, 761 (s), 746 (w), 730, 721, 707, 686, 676, 647 (m), 613, 595, 588 (s), 569, 558, 546, 527 (w). GC-MS (EI, 70 eV): *m/z* (%) = 503 ($[M+H]^+$, 11), 502 ($[M]^+$, 40), 487 (27), 488 (100), 326 (10). HRMS (EI, 70 eV): calcd for $C_{26}H_{21}F_3O_5S$ $[M]^+$: 502.10563, found 502.105916.

7-(4-Methoxyphenyl)-4-oxo-2-phenyl-4*H*-chromen-5-yl trifluoromethanesulfonate (16d): 

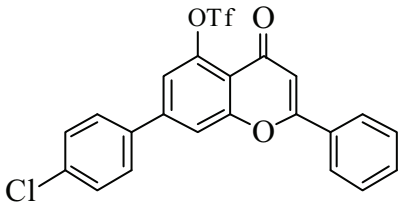
Starting with **14** (75 mg, 0.145 mmol), **3f** (22 mg, 0.145 mmol), $Pd(PPh_3)_4$ (5 mg, 3mol%, 0.004 mmol), K_3PO_4 (46 mg, 0.217 mmol), and 1,4-dioxane (3 mL),

16d was isolated as a white solid (57 mg, 83%). Reaction temperature: 70 °C for 9 h. M.p. 214-216 °C. ^{1}H NMR (300 MHz, $CDCl_3$): δ = 3.78 (s, 3H, OCH_3), 6.71 (s, 1H), 6.98 (d, J = 8.8 Hz, ArH), 730 (br, 1H, ArH), 7.46-7.53 (m, 5H, ArH), 7.70 (d, J = 1.5 Hz, 1H, ArH), 7.82-7.85 (m, 2H, ArH). ^{13}C-NMR (62.9 MHz, $CDCl_3$): δ = 55.4 (OCH_3), 108.7, 114.8, 115.6, 117.1 (CH), 118.7 (q, $J_{F,C}$ = 320.1 Hz, CF_3), 126.2, 128.4, 129.1 (CH), 129.9, 130.9 (C), 131.9 (CH), 146.4, 147.1, 157.4, 160.9, 162.7 (C), 175.8 (CO). ^{19}F NMR (282 MHz, $CDCl_3$): = -73.3. IR (KBr, cm^{-1}): ν = 3062, 3006, 2963, 2836 (w), 1647, 1629, 1604 (s), 1578, 1549 (w), 1523 (s), 1495, 1476, 1450 (w), 1429 (s), 1402 (m), 1371 (s), 1346, 1298, 1285 (w), 1257, 1244, 1212, 1201, 1192, 1182 (m), 1161 (w), 1139 (s), 1116, 1090, 1078, 1065, 1054, 1031 (m), 1009, 1001 (w), 982 (s), 923 (w), 904 (s), 877, 866 (w), 822 (s), 797, 789, 766 (m), 732, 713 (w), 686, 676 (m), 657, 645, 613 (w), 604, 586 (s), 569, 549, 528 (w). GC-MS (EI, 70 eV): *m/z* (%) = 477 ([M+H]$^+$, 26), 476 ([M]$^+$, 100), 369 (12), 315 (22). HRMS (EI, 70 eV): calcd for $C_{23}H_{15}F_3O_6S$ [M]$^+$:476.05359, found 476.052814.

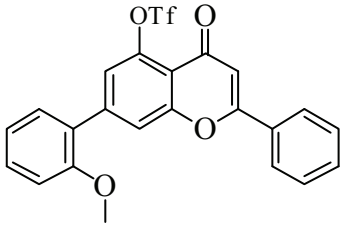
7-(4-Fluorophenyl)-4-oxo-2-phenyl-4*H*-chromen-5-yl trifluoromethanesulfonate (16e): 

Starting with **14** (75 mg, 0.145 mmol), **3g** (20 mg, 0.145 mmol), $Pd(PPh_3)_4$ (5 mg, 3mol%, 0.004 mmol), K_3PO_4 (46 mg, 0,217 mmol), and 1,4-dioxane (3 mL), **16e** was isolated as a white solid (53 mg, 80%). Reaction temperature: 70 °C for 9 h. M.p. 188-189°C.^{1}H NMR (300 MHz, $CDCl_3$): δ = 6.71 (s, 1H), 7.12-7.15 (m, 1H, ArH), 7.29 (br, 1H, ArH), 7.45-7.50 (m, 4H, ArH), 7.52-7.57 (m, 2H, ArH), 7.70 (d, J = 1.5 Hz, 1H ArH), 7.81-7.84 (m, 2H, ArH). ^{13}C-NMR (74.5 MHz, $CDCl_3$): δ = 108.8, 116.3 (d, J = 21.6 Hz), 116.4, 117.5 (CH), 118.2 (q, $J_{F,C}$ = 321.1 Hz, CF_3), 126.3, 129.1 (d, J = 8.2 Hz), 129.2 (CH), 130.7 (C), 132.1 (CH), 133.4 (d, J = 3.3 Hz), 145.7, 147.1, 157.4, 162.8 (C), 163.7 (d, $J_{F,C}$ = 248.9 Hz) (CF), 175.6 (CO). ^{19}F NMR (282 MHz, $CDCl_3$): = -111.2, -73.3. IR (KBr, cm^{-1}): ν = 3067, 2956, 2922, 2852 (w), 1648, 1627, 1613 (s), 1601 (m), 1578, 1549 (w), 1518 (s), 1495, 1473, 1451 (w), 1431, 1420 (s), 1394 (m), 1372 (s), 1344, 1306, 1288 (w), 1241 (m), 1199 (s), 1161 (m), 1140, 1134 (s), 1116 (m), 1103, 1081 (w), 1068, 1054, 1030 (m), 1014, 1001 (w), 984 (s), 930 (w), 904 (s), 882, 873 (w), 833, 821, 800 (s), 777, 770, 760 (m), 722, 709, 695, 688, 678, 649, 637, 614 (w), 602, 586 (s), 569, 546, 528 (w). GC-MS (EI, 70 eV): *m/z*

(%) = 465 ([M+H]$^+$, 25), 464 ([M]$^+$, 100), 400 (9), 372 (40), 303 (25), 246 (10). HRMS (EI, 70 eV): calcd for $C_{22}H_{12}F_4O_5S$ [M]$^+$:464.03359, found 464.033814.

7-(4-Chlorophenyl)-4-oxo-2-phenyl-4*H*-chromen-5-yl trifluoromethanesulfonate (16f): 

Starting with **5** (75 mg, 0.145 mmol), **3h** (22 mg, 0.145 mmol), $Pd(PPh_3)_4$ (5 mg, 3mol%, 0.004 mmol), K_3PO_4 (46 mg, 0,217 mmol), and 1,4-dioxane (3 mL), **16f** was isolated as a white solid (57 mg, 82%). Reaction temperature: 70 °C for 9 h. M.p. 249-252 °C.^{1}H NMR (300 MHz, $CDCl_3$): δ = 6.72 (s, 1H), 7.30 (br, 1H, ArH), 7.42-7.52 (m, 7H, ArH), 7.72 (d, J = 1.6 Hz, 1H, ArH), 7.82-7.85 (m, 2H, ArH). ^{13}C-NMR (62.9 MHz, $CDCl_3$): δ = 108.8, 116.3, 116.5, 117.5 (CH), 118.2 (q, $J_{F,C}$ = 320.7 Hz, CF_3), 126.2, 128.4, 129.1, 129.6 (CH), 130.7 (C), 132.1 (CH), 135.6, 136.0, 145.5, 147.2, 157.4, 162.9 (C), 175.6 (CO). ^{19}F NMR (282 MHz, $CDCl_3$): = -73.32. IR (KBr, cm^{-1}): ν = 3116, 3063, 2956, 2922, 2852 (w), 1647, 1626, 1614 (s), 1593, 1579, 1574, 1548 (w), 1505, 1494 (m), 1470, 1449 (w), 1432 (s), 1413, 1388 (m), 1367 (s), 1343, 1301, 1282, 1257 (w), 1244, 1214, 1202, 1192, 1183, 1140 (s), 1116, 1091, 1077, 1065, 1053, 1035, 1011, 1001 (m), 982 (s), 922 (w), 901, 870 (s), 842 (w), 820 (s), 779 (w), 767 (s), 730 (w), 711, 686, 678, 664 (m), 654, 645 , 633 (w), 612, 588 (s), 565, 532 (m). GC-MS (EI, 70 eV): *m/z* (%) = 483 ([M+H]$^+$, ^{37}Cl, 8), 482 ([M]$^+$, ^{37}Cl, 41), 481 ([M+H]$^+$, ^{35}Cl, 24), 480 ([M]$^+$, ^{35}Cl, 100), 390 (13), 319 (23). HRMS (EI, 70 eV): calcd for $C_{22}H_{12}{}^{35}ClF_3O_5S$ [M]$^+$: 480:00406, found 480.003734.

7-(2-Methoxyphenyl)-4-oxo-2-phenyl-4*H*-chromen-5-yl trifluoromethanesulfonate (16g): 

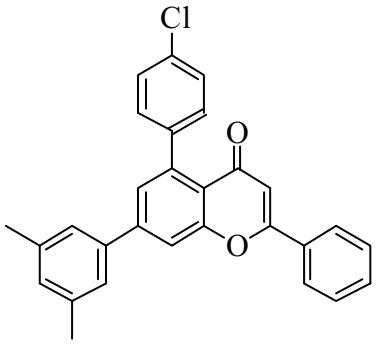
Starting with **14** (75 mg, 0.145 mmol), **3o** (22 mg, 0.145 mmol), $Pd(PPh_3)_4$ (5 mg, 3mol%, 0.004 mmol), K_3PO_4 (46 mg, 0,217 mmol), and 1,4-dioxane (3 mL), **16g** was isolated as a white solid (55 mg, 81%). Reaction temperature: 70 °C for 9 h. M.p. 218-220°C. H NMR (300 MHz, $CDCl_3$): δ = 3.79 (s, 3H, OCH_3), 6.71 (s, 1H), 6.95-6.98 (m, 1H, ArH), 6.99-7.04 (m, 1H, ArH), 7.29-7.33 (m, 1H, ArH), 7.36-7.39 (m, 2H, ArH), 7.42-7.49 (m, 3H, ArH), 7.70 (d, J = 1.8 Hz, 1H, ArH), 7.81-7.84 (m, 2H, ArH). ^{13}C-NMR (74.5 MHz, $CDCl_3$): δ = 55.5 (OCH_3), 108.8, 111.5 (CH), 116.0 (C), 118.2 (q, $J_{F,C}$ = 285.2 Hz, CF_3), 119.1, 120.5, 121.2, 126.3 (CH), 126.5 (C), 129.1, 130.4, 130.9 (CH); 131.0 (C), 131.9 (CH),

144.6, 146.1, 156.4, 156.8, 162.7 (C), 175.9 (CO). ^{19}F NMR (282 MHz, $CDCl_3$): = -73.4. IR (KBr, cm^{-1}): ν = 3075, 3061, 3011 (w), 2922 (m), 2851 (w), 1647, 1627, 1613, 1598 (s), 1598, 1579 (m), 1544 (w), 1495, 1467, 1450 (m), 1440 (w), 1420, 1405, 1369 (s), 1308 (w), 1266 (m), 1238, 1201, 1190 (s), 1166 (w), 1143, 1134, 1110 (s), 1072, 1066, 1058, 1044 (w), 1029, 1022 (m), 1000 (w), 979 (s), 941 (w), 899, 877 (s), 861, 852 (w), 814 (s), 786, 779, 769 (w), 752 (s), 713 (w), 690 (s), 672, 647, 623 (w), 611, 587 (s), 568, 551 (w). GC-MS (EI, 70 eV): *m/z* (%) = 478 ($[M+1]^+$, 9), 477 ($[M]^+$, 26), 476 (100). HRMS (EI, 70 eV): calcd for $C_{23}H_{15}F_3O_6S$: 476.05359, found 476.053485.

General Procedure for the Synthesis of 17a,b:

The reaction was carried out in a pressure tube. To a 1,4-dioxane suspension (3 mL) of **14** (75 mg, 0.145 mmol), arylboronic acid $Ar^1B(OH)_2$ (0.145 mmol) and $Pd(PPh_3)_4$ (3 mol%) was added K_3PO_4 (46 mg, 0.217 mmol), and the resultant solution was degassed by bubbling argon through the solution for 10 min. The mixture was heated at 70 °C under an argon atmosphere for 9 h. The mixture was cooled to 20 °C. Arylboronic acid $Ar^2B(OH)_2$ (0.145 mmol), $Pd(PPh_3)_4$ (3 mol%), K_3PO_4 (46 mg, 0.75 mmol) and dioxane (2 mL) were added. The reaction mixtures were heated under an argon atmosphere for 6 h at 115 °C. Then diluted with H_2O and extracted with CH_2Cl_2 (3 × 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, heptane/EtAOc).

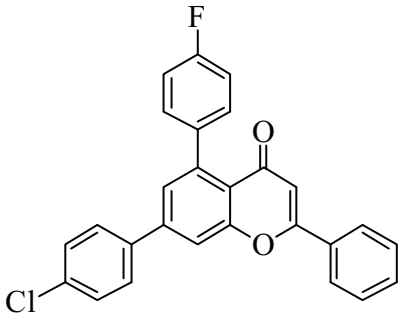
5-(4-Chlorophenyl)-7-(3,5-dimethylphenyl)-2-phenyl-4*H*-chromen-4-one (17a):



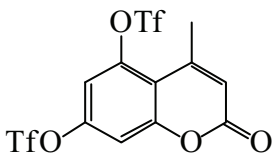
Starting with **14** (75 mg, 0.145 mmol), **3c** (22 mg, 0.145 mmol), $Pd(PPh_3)_4$ (5 mg, 3mol%, 0.004 mmol), K_3PO_4 (46 mg, 0.217 mmol), and 1,4-dioxane (3 mL), **3h (**23 mg, 0.145 mmol), $Pd(PPh_3)_4$ (5 mg, 3mol%, 0.004 mmol), K_3PO_4 (46 mg, 0.217 mmol), **17a** was isolated as a white solid (49 mg, 78%); mp 226-227°C. ^{1}H NMR (300 MHz, $CDCl_3$): δ = 2.33 (s, 6H, $2CH_3$), 6.64 (s, 1H), 7.01 (br s, 1H, ArH), 7.23-7.27 (m, 4H, ArH), 7.29-7.31 (m, 2H, ArH), 7.33 (d, J = 1.8 Hz, 1H, ArH), 7.45-7.47 (m, 3H, ArH), 7.73 (d, J = 1.8 Hz, 1H, ArH), 7.86-7.89 (m, 2H, ArH). ^{13}C-NMR (74.5 MHz, $CDCl_3$): δ = 21.3 ($2CH_3$), 107.7, 114.7 (CH), 118.7 (C), 124.1, 125.2, 126.3, 126.6, 128.0, 129.1, 129.5, 130.5 (CH), 132.2, 137.4, 137.7, 138.7, 141.1,

144.7, 156.7, 161.0 (C), 177.0 (CO). IR (KBr, cm^{-1}): ν = 3058, 2961, 2915, 2852 (w), 1640, 1606 (s), 1575, 1557 (w), 1495 (m), 1480 (w), 1447 (m), 1401 (w), 1371 (s), 1324, 1303 (w), 1288, 1261 (m), 1203, 1187, 1140, 1109, 1101 (w), 1085, 1055 (m), 1029 (w), 1014 (m), 999, 949 (w), 920, 880, 872 (m), 850, 823 (s), 788 (w), 767 (s), 733, 713 (w), 690, 680, 638 (s), 599, 283 (w), 537 (s). GC-MS (EI, 70 eV): *m/z* (%) = 438 ($[M]^+$, ^{37}Cl, 16), 437 ($[M+H]^+$, ^{35}Cl, 41), 436 ($[M]^+$, ^{35}Cl, 46), 435 (100). HRMS (EI, 70 eV): calcd for $C_{29}H_{20}{}^{35}Cl\,O_2$ $[M-H]^+$: 435.11463, found 435.11470.

7-(4-Chlorophenyl)-5-(4-fluorophenyl)-2-phenyl-4*H*-chromen-4-one (17b): Starting with **14** (75 mg, 0.145 mmol), **3h** (20 mg, 0.145 mmol), $Pd(PPh_3)_4$ (5 mg, 3mol%, 0.004 mmol), K_3PO_4 (46 mg, 0.217 mmol), and 1,4-dioxane (3 mL), **3g (**23 mg, 0.145 mmol), $Pd(PPh_3)_4$ (5 mg, 3mol%, 0.004 mmol), K_3PO_4 (46 mg, 0.217 mmol), **17b** was isolated as a white solid (47 mg, 77%); mp 256-258 °C. ^{1}H NMR (300 MHz, $CDCl_3$): δ = 6.63 (s, 1H), 6.99-7.06 (m, 2H, ArH), 7.24-7.28 (m, 2H, ArH), 7.30 (d, J = 1.8 Hz, 1H, ArH), 7.38 (d, J = 7.5 Hz, 2H, ArH), 7.43-7.47 (m, 3H, ArH), 7.55 (d, J = 8.6 Hz, 2H, ArH), 7.68 (d, J = 1.8 Hz, 1H, ArH), 7.84-7.87 (m, 2H, ArH). ^{13}C- NMR (62.9 MHz, $CDCl_3$): δ = 108.9, 114.5 (d, $J_{F,C}$ = 21.5Hz) , 115.6 (CH), 120.3(C), 126.2, 127.1, 128.5, 129.0, 129.3, 130.4 (d, $J_{F,C}$ = 8.0 Hz) (CH), 131.4 (C), 131.6 (CH), 135.1, 136.9 (d, $J_{F,C}$ = 3.4 Hz), 137.0, 142.7, 144.0, 157.8, 162.0 (C), 162.3 (d, $J_{F,C}$ = 246.1 Hz, CF), 177.9 (CO). IR (KBr, cm^{-1}): ν = 3062 (m), 1639 (s), 1622 (w), 1606 (s), 1575, 1553 (m), 1503, 1463, 1449, 1424 (m), 1374 (s), 1311 (w), 1288, 1272 (m), 1257 (w), 1215 (s), 1189 (m), 1157 (s), 1140, 1110, 1091 (s), 1065, 1034, 1021 (w), 1009 (s), 999, 982, 958 (w), 934, 929, 909 (m), 872, 830, 821 (s), 811 (m), 797 (w), 775 (s), 733, 723 (w), 693, 679 (s), 656, 648, 638, 621, 600 (w), 585, 553, 541 (m). GC-MS (EI, 70 eV): *m/z* (%) = 428 ($[M]^+$, ^{37}Cl, 15), 427 ($[M+H]^+$, ^{35}Cl, 46), 426 ($[M]^+$, ^{35}Cl, 49), 425 (100), 388 (11), 386 (17), 384 (23). HRMS (EI, 70 eV): calcd for $C_{27}H_{15}ClF\,O_2$ ($[M-H]^+$, ^{35}Cl): 425.07391, found 425.073196.



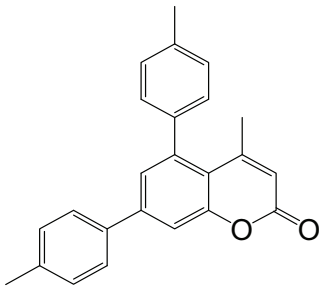
4-Methyl-2-oxo-2*H*-chromene-5,7-diyl bis(trifluoromethanesulfonate) (19)|: To a solution of 4-methyl-5,7-dihydroxycoumarine (**18**) (0.5 g, 2.60 mmol) in CH_2Cl_2 (30 mL) was added triethylamine (0.36 mL,



10.4 mmol) at room temperature under an argon atmosphere. After 10 min, Tf_2O (1.0 mL, 6.2 mmol) was added at -78 °C. The mixture was allowed to warm to 20 °C and stirred for 6 h. The reaction mixture was filtered and the filtrate was concentrated in vacuo. The residue was purified by chromatography (flash silica gel, heptane-EtOAc) without aqueous work up to give **19** as a white solid (0.9 g, 75%); mp 131-132°C. ^{1}H NMR (300 MHz, $CDCl_3$): δ = 2.56 (d, J = 1.3 Hz, CH_3), 6.32 (d, J = 1.3 Hz, 1H), 7.19 (d, J = 2.5 Hz, 1H, ArH), 7.28 (d, J = 2.5 Hz, 1H, ArH). ^{13}C NMR (75.46 MHz, $CDCl_3$): δ = 21.9 (CH_3), 110.0, 110.6 (CH), 113.1 (C), 117.3 (q, $J_{F,C}$ = 320.0 Hz, CF_3), 117.6 (q, $J_{F,C}$ = 320.0 Hz, CF_3), 118.1 (CH), 144.8, 147.9, 148.5, 154.5 (C), 156.4 (CO). ^{19}F NMR (282.4, MHz): δ = -72.6, -72.2. . IR (KBr, cm^1): ν = 3181, 3111, 3084, 3065, 3020, 2935, 1795 (w), 1728, 1615 (s), 1566, 1547, 1530, 1476, 1454 (w), 1434, 1415 (s), 1379, 1359 (m), 1326, 1285 (w), 1244, 1235, 1218, 1202, 1132, 1124 (s), 1071 (m), 1052, 1006, 993 (s), 898, 878, 870 (m), 834, 796 (s), 771 (w), 759, 730, 707, 659 (m), 610, 589, 579 (s), 550, 538 (w). GC-MS (EI, 70 eV): *m/z* (%) = 457 ($[M+H]^+$, 13), 456 ($[M]^+$, 100), 323 (25), 295 (79), 231 (47), 203 (22), 162 (30), 134 (37). HRMS (EI, 70 eV) calcd for $C_{12}H_6F_6O_8S_2$ $[M]^+$: 455.94028; found: 455.941352.

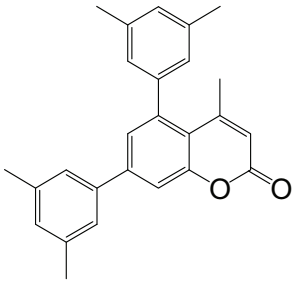
General Procedure for synthesis 20a-g: A solution of **19** (80 mg, 0.175 mmol), K_3PO_4 (3.0 equiv.), $Pd(PPh_3)_4$ (6 mmol-%) and arylboronic acid **3** (2.0 equiv.) in toluene-1,4-dioxane (1:1 4 mL) was stirred at 105 °C for 8 h under argon atmosphere. To the reaction mixture H_2O (20 mL) and CH_2Cl_2 (25 mL) were added at 20 °C. The organic and the aqueous layers were separated and the latter was extracted with CH_2Cl_2 (2 x 20 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, heptane/EtOAc).

4-Methyl-5,7-di-*p*-tolyl-2*H*-chromen-2-one (20a): Starting with **19** (80 mg, 0.175 mmol), **3a** (47 mg, 0.35 mmol), $Pd(PPh_3)_4$ (12 mg, 6 mol-%, 0.0105 mmol), K_3PO_4 (111 mg, 0.525 mmol), and Toluene-1,4-dioxane (1:1 4 mL), **20a** was isolated as a white solid (51 mg, 86%); mp 176-177°C. ^{1}H NMR (300 MHz, $CDCl_3$): δ = 1.70 (d, J = 1.2 Hz, CH_3), 2.31 (s, 3H, CH_3), 2.35 (s, 3H, CH_3), 6.07 (d, J = 1.2 Hz, CH_3), 7.10-7.18 (m, 5H, ArH), 7.23 (d, J = 2.0 Hz, ArH), 7.43-7.47 (m, 3H, ArH). ^{13}C NMR (75.46



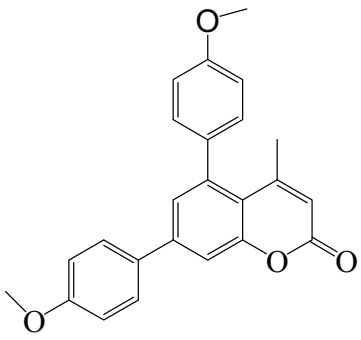
MHz, $CDCl_3$): δ = 21.1, 21.2, 24.0 (CH_3), 114.1, 116.3 (CH), 117.1 (C), 126.3, 126.9, 128.7, 129.1, 129.7 (CH), 135.6, 137.8, 138.6, 139.1, 142.1, 142.8, 153.9, 154.9 (C), 160.5 (CO). IR (KBr, cm^1): ν = 3024, 2968, 2923, 2854, 1921, 1858, 1789, 1754 (w), 1719 (s), 1613 (m), 1601 (s), 1574, 1557, 1519, 1513, 1488, 1465 (w), 1439 (m), 1417, 1392, 1376, 1355, 1308, 1295, 1259, 1239, 1212 (w), 1194 (m), 1181, 1137, 1109, 1083, 1041, 1024, 1014 (w), 962 (s), 894, 881, 867 (w), 856 (s), 838 (w), 827, 814 (s), 778, 733, 721, 707, 673, 644, 631, 614, 605, 575, 552, 544 (w). GC-MS (EI, 70 eV): *m/z* (%) = 341 ($[M+H]^+$, 26), 340 ($[M]^+$, 100), 339 (11), 312 (34), 311 (13), 297 (22), 252 (12). HRMS (EI, 70 eV) calcd for $C_{24}H_{20}O_2$ $[M]^+$: 340.14578; found: 340.145833.

5,7-Bis(3,5-dimethylphenyl)-4-methyl-2*H*-chromen-2-one (20b): Starting with **19** (80 mg, 0.175 mmol), **3c** (53 mg, 0.35 mmol), $Pd(PPh_3)_4$ (12 mg, 6 mol-%, 0.0105 mmol), K_3PO_4 (111 mg, 0.525 mmol), and Toluene-1,4-dioxane (1:1 4 mL), **20b** was isolated as a white solid (58 mg, 90%); mp 172-174 °C.

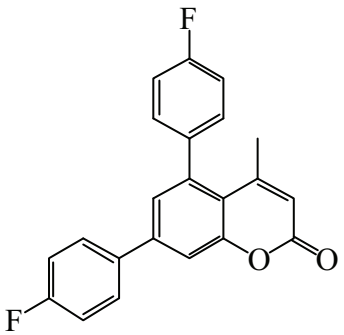


^1H NMR (300 MHz, $CDCl_3$): δ = 1.73 (d, J = 1.2 Hz, 3H, CH_3), 2.28 (s, 12H, $4CH_3$), 6.07 (d, J = 1.2 Hz, 1H), 6.87 (br s, 2H, ArH), 6.96 (d, J = 8.4 Hz, 2H, ArH), 7.17 (br s, 2H, ArH), 7.23 (d, J = 1.9 Hz, 1H, ArH), 7.47 (d, J = 1.9 Hz, 1H, ArH). ^{13}C NMR (75.47 MHz, $CDCl_3$): δ = 21.3 ($2CH_3$), 21.4 ($2CH_3$), 24.0 (CH_3), 114.3, 116.3 (CH), 117.1 (C), 125.0, 126.3, 127.1, 129.4, 130.2 (CH), 137.6, 138.5, 138.6, 141.9, 142.2, 143.1, 154.0, 154.8 (C), 160.5 (CO). IR (KBr, cm^1): ν = 2951, 2915, 2853 (w), 1721, 1708, 1594 (s), 1538, 1484, 1463 (w), 1438 (m), 1386 (w), 1354, 1344, 1304, 1294 (m), 1231, 1182, 1137 (s), 1058 (w), 1045, 977 (s), 950, 913, 859, 886, 868, 853 (w), 844 (s), 803, 767, 755, 744 (w), 717, 707, 697 (m), 665 (w), 650 (s), 619, 588, 569, 554, 530 (w). GC-MS (EI, 70 eV): *m/z* (%) = 369 ($[M+H]^+$, 27), 368 ($[M]^+$, 100), 353 (14), 340 (33), 325 (27), 310 (9). HRMS (EI, 70 eV) calcd for $C_{26}H_{24}O_2$ $[M]^+$: 368.17708; found: 368.177505.

5,7-Bis(4-methoxyphenyl)-4-methyl-2*H*-chromen-2-one (20c): Starting with **19** (80 mg, 0.175 mmol), **3f** (53 mg, 0.35 mmol), $Pd(PPh_3)_4$ (12 mg, 6mol-%, 0.0105 mmol), K_3PO_4 (111 mg, 0.525 mmol), and Toluene-1,4-dioxane (1:1 4 mL), **20c** was isolated as a white solid (54 mg, 83%); mp 132-134 °C. ^{1}H NMR (300 MHz, $CDCl_3$): δ = 1.71 (d, J = 1.2 Hz, 3H, CH_3), 3.76 (s, 3H, OCH_3), 3.79 (s, 3H, OCH_3), 6.05 (d, J = 1.2 Hz, 1H), 6.88 (m, 4H, ArH), 7.14 (d, J = 8.7 Hz, 2H, ArH), 7.22 (d, J = 2.0 Hz, 1H, ArH), 7.42 (d, J = 2.0 Hz, 1H, ArH), 7.50 (d, J = 8.8 Hz, 2H, ArH). ^{13}C NMR (75.46 MHz, $CDCl_3$): δ = 24.0 (CH_3), 55.3, 55.4 (OCH_3), 113.4, 113.7, 114.5, 116.1 (CH), 117.0 (C), 126.2, 128.2, 130.3 (CH), 130.9, 134.3, 141.7, 142.5 153.9, 155.0, 159.4, 160.1 (C), 160.6 (CO). IR (KBr, cm^1): ν = 3040, 2998, 2964, 2931, 2906, 2834, 1900, 1864, 1790 (w), 1722, 1715, 1597 (s), 1557, 1538 (m), 1514 (s), 1462, 1435 (m), 1514 (s), 1462, 1435 (m), 1393, 1378, 1351, 1309 (m), 1292, 1240 (s), 1195, 1177, 1138, 1110 (m), 1085 (w), 1032 (s), 1019 (m), 965, 942, 914, 894, 873, 849 (w), 830 (s), 793, 774, 738, 730, 718 (w), 706 (m), 672, 649, 629, 612, 603, 585, 546 (w). GC-MS (EI, 70 eV): *m/z* (%) = 373 ($[M+H]^+$, 24), 372 ($[M]^+$, 100), 371 (13), 344 (17), 329 (12). HRMS (EI, 70 eV) calcd for $C_{24}H_{20}O_4$ $[M]^+$: 372.13561; found: 372.135278.

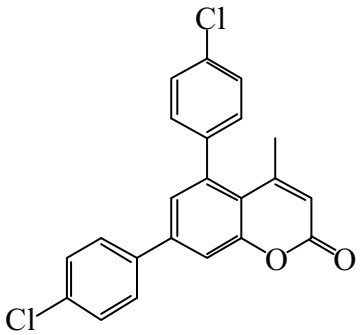


5,7-Bis(4-fluorophenyl)-4-methyl-2*H*-chromen-2-one (20d): Starting with **19** (80 mg, 0.175 mmol), **3g** (49 mg, 0.35 mmol), $Pd(PPh_3)_4$ (12 mg, 6 mol-%, 0.0105 mmol), K_3PO_4 (111 mg, 0.525 mmol), and Toluene-1,4-dioxane (1:1 4 mL), **20d** was isolated as a white solid (45 mg, 74%); mp 178-180 °C. ^{1}H NMR (300 MHz, $CDCl_3$): δ = 1.70 (d, J = 1.1 Hz, 3H, CH_3), 6.11 (d, J = 1.2 Hz, 1H), 7.03-7.10 (m, 4H, ArH), 7.19 (d, J = 2.0 Hz, 1H, ArH), 7.21-7.26 (m, 2H, ArH), 7.45 (d, J = 2.0 Hz, 1H, ArH), 7.50-7.55 (m, 2H, ArH). ^{13}C NMR (75.46 MHz, $CDCl_3$): δ = 24.1(CH_3), 114.7, 115.0 (d, J_{CF} = 21.5 Hz), 116.0 (d, J_{CF} = 21.5 Hz), 116.9 (CH), 125.3, 127.8 (d, J_{CF} = 8.2 Hz), 129.7 (d, J_{CF} = 8.2 Hz) (CH), 133.5 (d, J_{CF} = 3.2Hz), 136.7 (d, J_{CF} = 3.2Hz), 139.9, 140.9, 152.2, 153.9 (C), 159.1 (CO), 163.2 (d, J_{CF} = 247.9 Hz) (CF), 163.8 (d, J_{CF} =

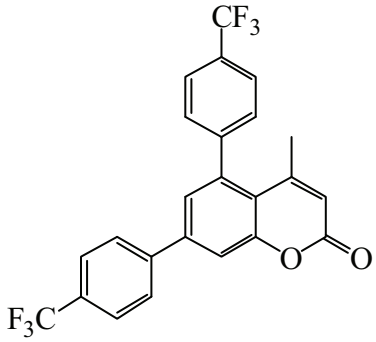


249.4 Hz) (CF). ^{19}F NMR (282 MHz, $CDCl_3$): = -113.5, -113.0. IR (KBr, cm^{-1}): ν = 3067, 2927, 2851, 1897 (w), 1723 (s), 1699, 1683, 1652 (w), 1594 (s), 1558, 1539 (w), 1511 (s), 1463 (w), 1435, 1426, 1404, 1384, 1349 (m), 1321, 1299 (w), 1216, 1196 (s), 1159, 1135 (m), 1118, 1096, 1063, 1025, 1013, 998, 967, 939, 912, 891, 880, 853 (w), 830 (s), 801, 791 (m), 765, 736, 707, 692, 668, 646, 626 (w), 609, 601 (m), 572, 551, 543, 528 (w). GC-MS (EI, 70 eV): *m/z* (%) = 349 ($[M+H]^+$, 22), 348 ($[M]^+$, 100), 321 (11), 320 (52), 319 (40), 288 (11), 275 (14), 270 (10). HRMS (EI, 70 eV) calcd for $C_{22}H_{14}O_2F_2$ $[M]^+$: 348.09564; found: 348.095528.

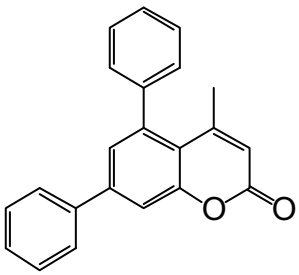
5,7-Bis(4-chlorophenyl)-4-methyl-2*H*-chromen-2-one (20e): Starting with **19** (80 mg, 0.175 mmol), **3h** (55 mg, 0.35 mmol), $Pd(PPh_3)_4$ (12 mg, 6 mol-%, 0.0105 mmol), K_3PO_4 (111 mg, 0.525 mmol), and Toluene-1,4-dioxane (1:1 4 mL), **20e** was isolated as a white solid (54 mg, 77%); mp 173-174 °C. ^{1}H NMR (300 MHz, $CDCl_3$): δ = 1.72 (d, J = 1.0 Hz, 3H, CH_3), 6.11 (d, J = 1.2 Hz, 1H), 7.17 (d, J = 1.8 Hz, 1H, ArH), 7.21 (d, J = 8.0 Hz, 2H, ArH), 7.34 (br d, J = 8.0 Hz, 4H, ArH), 7.45-7.48 (m, 3H, ArH). ^{13}C NMR (75.46 MHz, $CDCl_3$): δ = 24.2 (CH_3), 114.8, 117.0 (CH), 117.4 (C), 126.1, 128.3, 128.3, 129.2, 130.5 (CH), 134.3, 134.9, 136.7, 140.2, 140.8, 141.7, 153.0, 154.9 (C), 159.9 (CO). IR (KBr, cm^{-1}): ν = 3041, 2974, 2927, 2849, 1905, 1789 (w), 1721 (s), 1681,1651(w), 1602 (m), 1573, 1556, 1537 (w), 1495(s), 1463 (w), 1435 (m), 1397 (w), 1385 (m), 1347(s), 1311 , 1295, 1258 (w), 1235, 1196 (m), 1258 (w), 1235, 1196, 1137,1100 (m), 1085(s), 1028 (m), 1011, 964 (s), 946 (w), 915, 893, 879, 849 (m), 744 (w), 733, 717, 705, 695 (m), 649, 636, 626 (w), 598, 552 (m). GC-MS (EI, 70 eV): *m/z* (%) =382 ($[M]^+$, [^{35}Cl] [^{37}Cl], 64), 381 ($[M+H]^+$, [^{35}Cl] [^{35}Cl], 30), 380 ($[M]^+$, [^{35}Cl] [^{35}Cl], 100), 354 (23), 353 (16), 351 (14), 345 (15), 317 (29), 282 (12). HRMS (EI, 70 eV) calcd for $C_{22}H_{14}Cl_2O_2$ ($[M]^+$, [^{35}Cl] [^{37}Cl]): 382.03359; found: 382.033630. calcd for $C_{22}H_{14}Cl_2O_2$ ($[M]^+$, [^{35}Cl] [^{35}Cl]): 380.03654; found: 380.036187.



4-Methyl-5,7-bis(4-trifluoromethylphenyl)-2*H*-chromen-2-one (20f): Starting with **19** (80 mg, 0.175 mmol), **3j** (67 mg, 0.35 mmol), $Pd(PPh_3)_4$ (12 mg, 6 mol-%, 0.0105 mmol), K_3PO_4 (111 mg, 0.525 mmol), and Toluene-1,4-dioxane (1:1 4 mL), **20f** was isolated as a white solid (55 mg, 70%); mp 214-216 °C. ^{1}H NMR (300 MHz, $CDCl_3$): δ = 1.70 (d, J = 1.2 Hz, 3H, CH_3), 6.16 (d, J = 1.2 Hz, 1H), 7.23 (d, J = 2.0 Hz, 1H, ArH), 7.43 (d, J = 8.0 Hz, 2H, ArH), 7.55 (d, J = 1.2 Hz, 1H, ArH), 7.64-7.66 (m, 6H, ArH). ^{13}C NMR (75.46 MHz, $CDCl_3$): δ = 24.2 (CH_3), 115.6, 117.6 (CH), 117.8 (C), 125.7 (q, $J_{F,C}$ = 272.45 Hz, CF_3), 125.8 (q, $J_{F,C}$ = 272.47 Hz, CF_3), 125.2 (q, J = 3.7 Hz), 126.1 (q, J = 3.7 Hz) (CH), 126.2 (C), 127.5, 129.6 (CH), 130.8 (d, J = 32.8 Hz), 131.0 (d, J = 32.8 Hz), 140.6, 141.6, 141.7 (d, J = 1.1 Hz), 145.3 (J = 32.8 Hz), 152.6, 155.0 (C), 159.7 (CO). ^{19}F NMR (282 MHz, $CDCl_3$): -62.6, -62.4. IR (KBr, cm^{-1}): ν = 3092, 3058, 2983, 2936, 1929, 1789 (w), 1721, 1614, 1605 (s), 1578, 1542, 1525, 1473, 1441, 1407, 1392, 1380 (w), 1322 (s), 1236, 1199, 1192 (w), 1163, 1132 (m), 1115, 1104, 1067 (s), 1028 (w), 1013, 964, 960 (m), 915, 893, 876, 860 (w), 843 (s), 768, 754, 727, 708, 697, 669, 645, 607 (w), 595, 589 (m), 549, 541 (w). GC-MS (EI, 70 eV): *m/z* (%) = 449 ($[M+H]^+$, 26), 448 ($[M]^+$, 100), 447 (11), 429 (15), 421 (14), 420 (56), 351 (34). HRMS (EI, 70 eV) calcd for $C_{24}H_{14}F_6O_2$ $[M]^+$: 448.08925; found: 448.089094.



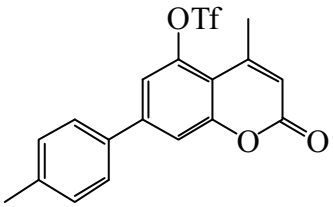
4-Methyl-5,7-diphenyl-2*H*-chromen-2-one (20g): Starting with **19** (80 mg, 0.175 mmol), **3l** (43 mg, 0.35 mmol), $Pd(PPh_3)_4$ (12 mg, 6 mol-%, 0.0105 mmol), K_3PO_4 (111 mg, 0.525 mmol), and Toluene-1,4-dioxane (1:1 4 mL), **20g** was isolated as a white solid (43 mg, 79%); mp 178-180 °C. ^{1}H NMR (300 MHz, $CDCl_3$): δ = 1.69 (d, J = 1.2 Hz, 3H, CH_3), 6.09 (d, J = 1.2 Hz, 1H), 7.23-7.27 (m, 4H, ArH), 7.30-7.39 (m, 5H, ArH), 7.50 (d, J = 1.9 Hz, 1H, ArH), 7.54-7.57 (m, 2H, ArH). ^{13}C NMR (75.46 MHz, $CDCl_3$): δ = 22.9 (CH_3), 113.6, 115.6 (CH), 116.2 (C), 125.4, 126.1, 126.9, 127.0, 127.5, 128.0, 128.1 (CH), 137.4, 140.9, 141.0, 141.9, 152.6, 153.9 (C), 159.3 (CO). IR (KBr, cm^{-1}): ν = 3059, 2962, 2929 (w), 1716, 1699 (s), 1651, 1645 (w), 1596 (s), 1557, 1538, 1519, 1503, 1494, 1463



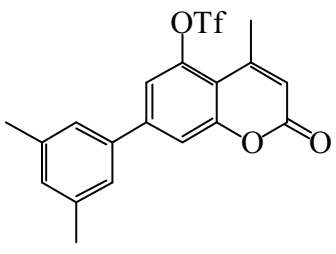
(w), 1435 (m), 1396, 1378 (w), 1353 (m), 1295, 1259, 1243, 1209, 1196 (w), 1136 (m), 1118, 1084, 1072, 1029, 999 (w), 960 (m), 907 (w), 868, 848, 816, 777 (m), 760 (s), 731 (w), 705, 692 (s), 666, 644, 618, 60, 565, 553, 546 (w). GC-MS (EI, 70 eV): *m/z* (%) = 313 ($[M+H]^+$, 24), 312 ($[M]^+$, 100), 311 (15), 284 (47), 319 (40), 283 (38), 252 (13), 239 (22). HRMS (EI, 70 eV) calcd for $C_{22}H_{16}O_2$ $[M]^+$: 312.11448; found: 312.114464.

General Procedure for synthesis 21a-f: A solution of **19** (80 mg, 0.175 mmol), K_3PO_4 (1.5 equiv.), $Pd(PPh_3)_4$ (3 mmol-%) and arylboronic acid **3** (1.0 equiv.) in toluene (3 mL) was stirred at 70 °C for 8 h under argon atmosphere. To the reaction mixture H_2O (20 mL) and CH_2Cl_2 (25 mL) were added at 20 °C. The organic and the aqueous layers were separated and the latter was extracted with CH_2Cl_2 (2 x 20 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, heptane/EtOAc).

4-Methyl-2-oxo-7-(*p*-tolyl)-2*H*-chromen-5-yl trifluoromethanesulfonate (21a): Starting with **19** (80 mg, 0.175 mmol), **3a** (24 mg, 0.175 mmol), $Pd(PPh_3)_4$ (6 mg, 3 mol-%, 0.00525 mmol), K_3PO_4 (55mg, 0.262 mL), and Toluene (3 mL), **21a** was isolated as a white solid (55 mg, 80%); mp 135-136 °C. ^{1}H NMR (300 MHz, $CDCl_3$): δ = 2.35 (s, 3H, CH_3), 2.56 (d, J = 1.2 Hz, 3H, CH_3), 6.24 (d, J = 1.2 Hz, 1H), 7.23 (d, J = 8.0 Hz, 2H, ArH), 7.41 (d, J = 1.8 Hz, 1H, ArH), 7.42 (d, J = 8.0 Hz, 2H, ArH), 7.49 (d, J = 1.8 Hz, 1H, ArH). ^{13}C NMR (75.47 MHz, $CDCl_3$): δ = 21.2, 22.9 (CH_3), 112.3 (C), 115.0, 116.0, 117.7 (CH), 118.4 (q, $J_{F,C}$ = 318.8 Hz, CF_3), 126.8, 130.1 (CH), 134.2, 139.8, 144.8, 145.7, 149.6, 155.3 (C), 159.0 (CO). ^{19}F NMR (282.4, MHz): δ = -72.6. IR (KBr, cm^1): ν = 3071, 3053, 3033, 2923, 2852, 1914, 1803 (w), 1735, 1613 (s), 1577, 1529, 1482, 1452 (w), 1424 (m), 1398 (s), 1386, 1364, 1292 (m), 1206, 1179, 1133 (s), 1089 (m), 1039, 926, 880, 869, 813, 787, 764, 758 (s), 735, 712, 703, 690 (w), 656 (m), 640, 633, 617 (w), 601, 574 (m), 548, 539 (w). GC-MS (EI, 70 eV): *m/z* (%) = 399 ($[M+H]^+$, 19), 398 ($[M]^+$, 100), 265 (16), 238 (17), 237 (85), 209 (34), 165 (32). HRMS (EI, 70 eV) calcd for $C_{18}H_{13}F_3O_5S$ $[M]^+$: 398.04303; found: 398.04309.

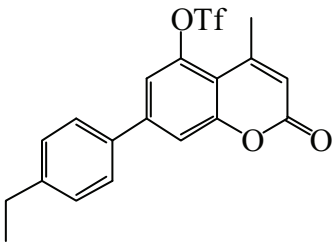


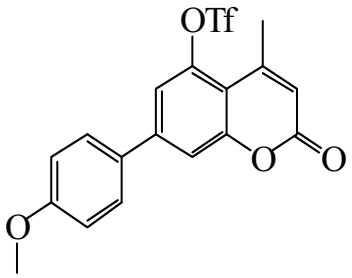
7-(3,5-Dimethylphenyl)-4-methyl-2-oxo-2*H*-chromen-5-yl trifluoromethanesulfonate (21b): Starting with **19** (80 mg, 0.175 mmol), **3c** (26 mg, 0.175 mmol), $Pd(PPh_3)_4$ (6 mg, 3 mol-%, 0.00525 mmol),



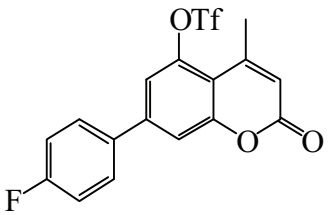
K_3PO_4 (55 mg, 0.262 mmol), and Toluene (3 mL), **21b** was isolated as a white solid (54 mg, 77%); mp 155-157 °C. ^{1}H NMR (300 MHz, $CDCl_3$): δ = 2.33 (s, 6H, CH_3), 2.56 (d, J = 1.2 Hz, CH_3), 6.25 (d, J = 1.2 Hz, 1H), 7.03 (br s, 1H, ArH), 7.11 (br s, 2H, ArH), 7.41 (d, J = 1.7 Hz, 1H, ArH), 7.50 (d, J = 1.7 Hz, 1H, ArH). ^{13}C NMR (62.9 MHz, $CDCl_3$): δ = 21.3 ($2CH_3$) , 22.8 (CH_3), 112.3 (C), 115.4, 116.3, 117.8 (CH), 118.5 (q, $J_{F,C}$ = 318.8 Hz, CF_3), 124.8, 131.1 (CH), 137.1, 139.0, 145.2, 145.6, 149.6, 155.1 (C), 158.9 (CO). ^{19}F NMR (282.4, MHz): δ = -72.8. IR (KBr, cm^1): ν = 3367, 2920, 2845, 2735, 2655, 1788 (w), 1712, 1739, 1614, 1596 (s), 1539, 1495, 1450 (w), 1418 (s), 1393, 1384, 1360, 1337, 1376, 1306 (w), 1208 (s), 1179 (m), 1136 (s), 1117, 1101 (m), 1063 (w), 1040, 993, 957 (s), 893, 873 (m),844, 830 (s), 777 (w), 756 (m), 733, 702, 689, 670, 646, 628 (w), 616, 590 (m), 570, 546 (w). GC-MS (EI, 70 eV): *m/z* (%) = 313 ($[M+H]^+$, 21), 412 ($[M]^+$, 100), 279 (17), 251 (88), 235 (11), 179 (13), 165 (23). HRMS (EI, 70 eV) calcd for $C_{19}H_{15}F_3O_5S$ $[M]^+$: 412.05868; found: 412.058864.

7-(4-Ethylphenyl)-4-methyl-2-oxo-2*H*-chromen-5-yl trifluoromethanesulfonate (21c): Starting with **19** (80 mg, 0.175 mmol), **3d** (26 mg, 0.175 mmol), $Pd(PPh_3)_4$ (6 mg, 3 mol-%, 0.00525 mmol), K_3PO_4 (55 mg, 0.262 mmol), and Toluene (3 mL), **21c** was isolated as a white solid (50 mg, 70%); mp 89-91 °C. ^{1}H NMR (300 MHz, $CDCl_3$): δ = 1.26 (t, J = 6.7 Hz, 3H, CH_3), 2.56 (d, J = 1.2 Hz, 3H, CH_3), 2.61 (q, J = 6.7 Hz, 2H, CH_2), 6.24 (d, J = 1.2 Hz, 1H, ArH), 7.26 (d, J = 8.2 Hz, 2H, ArH), 7.42-7.47 (m, 3H, ArH), 7.50 (d, J = 1.8 Hz, ArH). ^{13}C NMR (75.47 MHz, $CDCl_3$): δ = 15.4, 22.9 (CH_3), 29.7 (CH_2), 112.3 (C), 115.1, 116.1, 116.3, 117.7 (CH), 118.6 (q, $J_{F,C}$ = 320.6 Hz, CF_3), 127.0, 128.9 (CH), 134.4, 144.9, 145.7, 146.1, 149.7, 155.3 (C), 159.0 (CO). ^{19}F NMR (282 MHz, $CDCl_3$): -72.8. IR (KBr, cm^{-1}): ν = 3459, 3075, 3041 (w), 2963, 2918, 2849 (m), 2353, 1804 (w), 1737, 1614 (s), 1573, 1525, 1494, 1484, 1455 (w), 1408, 1396 (s), 1386, 1359, 1289 (m), 1207, 1176, 1137 (s), 1090 (w), 1034, 998, 969, 926, 877 (m), 854 (w), 822 (s), 762, 735, 700, 687, 628, 613 (w), 593, 578 (m), 542 (w). GC-MS (EI, 70 eV): *m/z* (%) = 413 ($[M+H]^+$, 21), 412 ($[M]^+$, 100), 279 (14), 251 (84), 223 (14), 333 (31), 165 (24). HRMS (EI, 70 eV) calcd for $C_{19}H_{15}O_5F_3S$ $[M]^+$: 412.0568, found 412.058786.



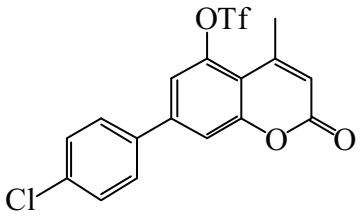
7-(4-Methoxyphenyl)-4-methyl-2-oxo-2*H*-chromen-5-yl trifluoromethanesulfonate (21d): 

Starting with **19** (80 mg, 0.175 mmol), **3f** (26 mg, 0.175 mmol), $Pd(PPh_3)_4$ (6 mg, 3 mol-%, 0.00525 mmol), K_3PO_4 (55 mg, 0.262 mmol), and Toluene (3 mL), **21d** was isolated as a white solid (60 mg, 83%); mp 142-144 °C. ^{1}H NMR (300 MHz, $CDCl_3$): δ = 2.55 (d, J = 1.2 Hz, 3H, CH_3), 3.79 (s, 1H, OCH_3), 6.22 (d, J = 1.2 Hz, 1H), 6.94 (d, J = 8.8 Hz, 2H, ArH), 7.38 (d, J = 1.7 Hz, 1H, ArH), 7.45-7.48 (m, 3H, ArH). ^{13}C NMR (75.46 MHz, $CDCl_3$): δ = 22.9 (CH_3), 55.4 (OCH_3), 111.9 (C), 114.6, 114.8, 115.7, 117.5 (CH), 120.6 (q, $J_{F,C}$ = 320.1 Hz, CF_3), 128.2 (CH), 129.3, 144.4, 145.7, 149.7, 155.3, 159.0 (C), 160.9 (CO). ^{19}F NMR (282 MHz, $CDCl_3$): = -72.8. IR (KBr, cm^{-1}): ν = 3080, 2979, 2936, 2916, 2836, 1903, 1807 (w), 1727 (s), 1650, 1643 (w), 1615, 1601, 1522 (s), 1485, 1469 (w), 1453, 1409, 1385, 1364, 1298, 1284 (m), 1253, 1202, 1185, 1135 (s), 1119, 1091 (m), 1053 (w), 1037, 1021, 999, 928, 878, 863, 827, 816 (s), 786, 765 (m), 737, 723, 690 (w) ,653, 638, 612 (m) , 578 (s) , 553, 537 (w). GC-MS (EI, 70 eV): *m/z* (%) = 415 ($[M+H]^+$, 18), 414 ($[M]^+$, 91), 254 (17), 253 (100), 225 (25), 165 (12). HRMS (EI, 70 eV) calcd for $C_{18}H_{13}F_3O_6S$ $[M]^+$: 414.03794; found: 414.038064.

7-(4-Fluorophenyl)-4-methyl-2-oxo-2*H*-chromen-5-yl trifluoromethanesulfonate (21e): 

Starting with **19** (80 mg, 0.175 mmol), **3g** (25 mg, 0.175 mmol), $Pd(PPh_3)_4$ (6 mg, 3 mol-%, 0.00525 mmol), K_3PO_4 (55 mg, 0.262 mmol), and Toluene (3 mL), **21e** was isolated as a white solid (44 mg, 63%); mp 116-118 °C. ^{1}H NMR (300 MHz, $CDCl_3$): δ = 2.57 (d, J = 1.2 Hz, 3H, CH_3), 6.26 (d, J = 1.2 Hz, 1H), 7.10-7.16 (m, 2H, ArH), 7.38 (d, J = 1.7 Hz, 1H, ArH), 7.46 (d, J = 1.7 Hz, 1H, ArH), 7.48-7.53 (m, 2H, ArH). ^{13}C NMR (75.46 MHz, $CDCl_3$): δ = 22.9 (CH_3), 112.6 (C), 115.3, 116.1, 116.6 (d, J = 21.6 Hz), 118.0 (CH), 120.5 (q, $J_{F,C}$ = 321.1 Hz, CF_3), 128.8 (d, J = 8.2 Hz) (CH), 133.3 (d, J = 3.3 Hz), 143.7, 145.7, 149.5, 155.3 (C), 158.8 (CO), 165.3 (d, $J_{F,C}$ = 248.9 Hz) (CF). ^{19}F NMR (282 MHz, $CDCl_3$): = -111.4, -72.8. IR (KBr, cm^{-1}): ν = 3066, 3012, 2990, 2943, 2923, 2853, 1911, 1805 (w), 1738, 1732, 1614, 1601 (s), 1538 (w), 1522 (s), 1484, 1449 (w), 1418, 1407, 1393, 1382 (s), 1360 (m), 1335, 1293, 1276, 1247 (w), 1227, 1213, 1181, 1166, 1135 (s), 1108, 1090

(m), 1035, 995, 927, 877 (s), 855 (w), 835, 820, 797, 764 (s), 735, 691, 651, 638, 625, 613 (m), 586, 579 (s), 549, 541 (w). GC-MS (EI, 70 eV): *m/z* (%) = 403 ($[M+H]^+$, 18), 402 ($[M]^+$, 100), 269 (22), 242 (12), 241 (82), 213 (47), 183 (28), 170 (14), 165 (19). HRMS (EI, 70 eV) calcd for $C_{17}H_{10}F_4O_5S$ $[M]^+$: 402.01796; found: 402.017961.

7-(4-Chlorophenyl)-4-methyl-2-oxo-2*H*-chromen-5-yl trifluoromethanesulfonate (21f): 

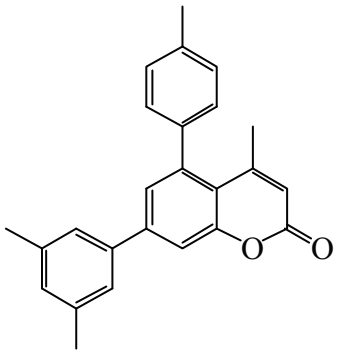
Starting with **19** (80 mg, 0.175 mmol), **3h** (27 mg, 0.175 mmol), $Pd(PPh_3)_4$ (6 mg, 3 mol-%, 0.00525 mmol), K_3PO_4 (55 mg, 0.262 mmol), and Toluene (3 mL), **21f** was isolated as a white solid (44 mg, 60%); mp 134-1135 °C. ^{1}H NMR (300 MHz, $CDCl_3$): δ = 2.57 (d, J = 1.2 Hz, 3H, CH_3), 6.27 (d, J = 1.2 Hz, 1H), 7.39-7.48 (m, 6H, ArH). ^{13}C NMR (62.9 MHz, $CDCl_3$): δ = 22.8 (CH_3), 112.8 (C), 115.3, 116.1, 118.1 (CH), 118.4 (q, $J_{F,C}$ = 320.6 Hz, CF_3), 128.2, 129.6 (CH), 135.5, 135.9, 143.5, 145.7, 149.5, 155.3 (C), 158.7 (CO). ^{19}F NMR (282.4, MHz): δ = -72.8. IR (KBr, cm^1): ν = 3079, 3064, 2920, 2849 (w), 1737, 1731, 1614 (s), 1591, 1573, 1537 (w), 1504 (m), 1476, 1453, 1420, 1398 (m), 1384 (s), 1361, 1335, 1306, 1291 (w), 1216 (s), 1186, 1178, 1132 , 1110, 1090 (m), 1037 (s), 1009 (w), 996 (s), 945 (w), 923, 879, 871 (m), 812 (s), 768, 739, 729, 705, 677, 645, 633, 614, (m), 580, 567, 543 (m). GC-MS (EI, 70 eV): *m/z* (%) = 420 ($[M]^+$, ^{37}Cl, 38), 419 ($[M+H]^+$, ^{35}Cl, 19), 418 ($[M]^+$, ^{35}Cl, 100), 285 (21), 259 (25), 258 (13), 257 (78), 229 (38), 194 (10). HRMS (EI, 70 eV) calcd for $C_{17}H_{10}O_5ClF_3S$ ($[M]^{+,\,37}$Cl): 419.98546; found: 419.986233. calcd for $C_{17}H_{10}O_5ClF_3S$ ($[M]^{+,\,35}$Cl): 417.98841; found: 417.988532.

General Procedure for the Synthesis of 22a-d:

The reaction was carried out in a pressure tube. To a toluene suspension (3 mL) of **19** (80 mg, 0.175 mmol), arylboronic acid $Ar^1B(OH)_2$ (0.175 mmol) and $Pd(PPh_3)_4$ (3 mol%) was added K_3PO_4 (55 mg, 0.262 mmol), and the resulting solution was degassed by bubbling argon through the solution for 10 min. The mixture was heated at 70 °C under an argon atmosphere for 8 h. The mixture was cooled to 20 °C. Arylboronic acid $Ar^2B(OH)_2$ (0.175 mmol), $Pd(PPh_3)_4$ (3 mol%), K_3PO_4 (55 mg, 0.262 mmol) and 1,4-dioxane (3 mL) were added. The reaction mixtures were heated under an argon atmosphere for 8 h at 105 °C. They were diluted with H_2O and extracted with CH_2Cl_2 (3 × 25 mL). The combined organic layers were dried (Na_2SO_4), filtered and the filtrate was

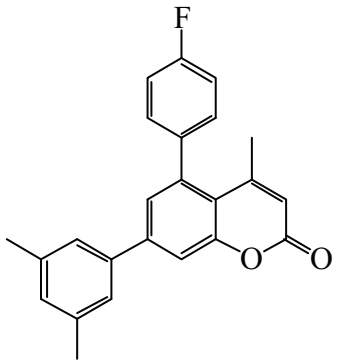
concentrated in vacuo. The residue was purified by flash chromatography (silica gel, heptane/EtAOc).

7-(3,5-Dimethylphenyl)-4-methyl-5-(*p*-tolyl)-2*H*-chromen-2-one (22a): Starting with



19 (80 mg, 0.175 mmol), **3c** (26 mg, 0.175 mmol), $Pd(PPh_3)_4$ (6 mg, 3mol%, 0.00525 mmol), K_3PO_4 (55 mg, 0.262 mmol), and toluene (3 mL), **3a (**24 mg, 0.175 mmol), $Pd(PPh_3)_4$ (6 mg, 3mol%, 0.00525 mmol), K_3PO_4 (55 mg, 0.262 mmol), and 1,4-dioxin (3 mL), **22a** was isolated as a white solid (43 mg, 70%); mp 256-258 °C. ^{1}H NMR (300 MHz, $CDCl_3$): δ = 1.72 (d, J = 1.2 Hz, 3H, CH_3), 2.29 (s, 6H, $2CH_3$), 2.36 (s, 3H, CH_3), 6.09 (d, J = 1.2 Hz, 1H), 6.96 (s, 1H, ArH), 7.15-7.17 (m, 6H, ArH), 7.24 (d, J = 2.0 Hz, 1H, ArH), 7.49 (d, d, J = 2.0 Hz, 1H, ArH). ^{13}C NMR (75.47 MHz, $CDCl_3$): δ = 21.2 (CH_3), 21.3 ($2CH_3$), 24.0 (CH_3), 114.4, 116.4 (CH), 117.2 (C), 125.0, 126.6, 128.7, 129.1, 130.2 (CH), 137.8, 138.5, 138.6, 139.1, 141.9, 143.2, 153.9, 154.8 (C), 160.6 (CO). IR (KBr, cm^{-1}): ν = 3030, 2974, 2917, 2850, 2733, 1798 (w), 1724, 1704 (s), 1613 (m), 1598 (s), 1537 (w), 1514 (m), 1484, 1463 (w), 1440, 1435 (m), 1386, 1377 (w), 1350 (m), 1320, 1311, 1295, 1281, 1247, 1228, 1203, (w), 1136 (m), 1112, 1089, 1056 (w), 1030 (m), 994, 971, 948, 921 (w), 899 (m), 887, 868 (w), 842, 824 (s), 766, 732, 717 (w), 702 (m), 684, 671, 649, 633, 613, 601, 571 (w), 558 (m), 536 (w). GC-MS (EI, 70 eV): *m/z* (%) = 355 ($[M+H]^+$, 27), 354 ($[M]^+$, 100), 353 (10), 326 (34), 325 (11), 311 (22). HRMS (EI, 70 eV) calcd for $C_{25}H_{22}O_2$ $[M]^+$: 354.16143, found 354.161234.

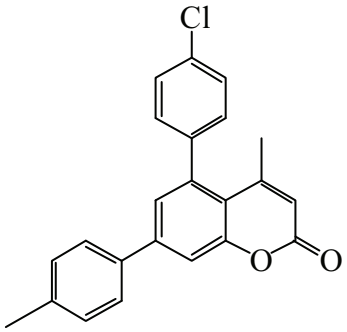
7-(3,5-Dimethylphenyl)-5-(4-fluorophenyl)-4-methyl-2*H*-chromen-2-one (22b):



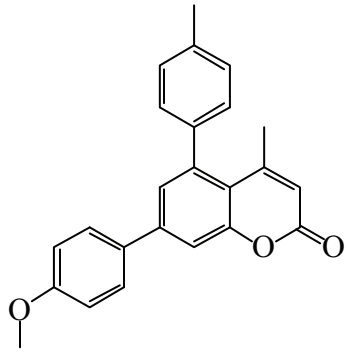
Starting with **19** (80 mg, 0.175 mmol), **3c** (26 mg, 0.175 mmol), $Pd(PPh_3)_4$ (6 mg, 3mol%, 0.00525 mmol), K_3PO_4 (55 mg, 0.262 mmol), and toluene (3 mL), **3ag (**25 mg, 0.175 mmol), $Pd(PPh_3)_4$ (6 mg, 3mol%, 0.00525 mmol), K_3PO_4 (55 mg, 0.262 mmol), and 1,4-dioxin (3 mL), **22b** was isolated as a white solid (38 mg, 60%); mp 256-258 °C.^{1}H NMR (300 MHz, $CDCl_3$): δ = 1.70 (d, J = 1.0 Hz, 3H, CH_3), 2.29 (s, 6H, $2CH_3$), 6.10 (d, J = 1.1 Hz,1H), 6.97 (s, 1H, ArH), 7.02-7.08 (m, 2H, ArH), 7.16 (br

s, 2H, ArH), 7.20-7.26 (m, 3H, ArH). ^{13}C NMR (75.47 MHz, $CDCl_3$): δ = 21.3 ($2CH_3$), 24.1 (CH_3), 114.8, 115.0 (d, J = 21.4 Hz), 116.7 (CH), 117.2 (C), 125.0, 126.6, 130.3, 130.8 (J = 8.4 Hz) (CH), 138.0 (d, J = 3.6 Hz), 138.3, 138.7, 140.7, 143.3, 153.3, 154.9 (C), 160.3 (CO), 164.2 (d, $J_{F,C}$ = 248.0 Hz) (CF). IR (KBr, cm^1): ν = 3107, 3070, 3041, 2972, 2916, 2850, 2732 (w), 1726, 1705 (s), 1673, 1668, 1651, 1614 (w), 1597 (s), 1557, 1538 (w), 1508 (s), 1484, 1471, 1455 (w), 1440 (m), 1402 (w), 1389, 1379, 1353, 1299 (m), 1250 (w), 1218, 1189, 1153, 1139 (s), 1092, 1057, 1031 (m), 1014, 971, 947 (w), 903, 889, 878, 871, 860 (w), 838 (s), 809, 767, 736, 719, 671, 651, 632, 609 (w), 563, 552 (m), 538 (w). GC-MS (EI, 70 eV): *m/z* (%) = 359 ($[M+H]^+$, 26), 358 ($[M]^+$, 100), 357 (17), 331 (10), 330 (46), 329 (26), 271 (12), 270 (11). HRMS (EI, 70 eV) calcd for $C_{24}H_{19}FO_2$ $[M]^+$: 358.13636; found: 358.136337.

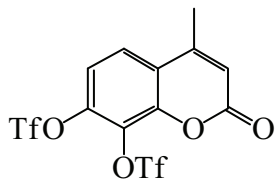
5-(4-Chlorophenyl)-4-methyl-7-(*p*-tolyl)-2*H*-chromen-2-one (22c): Starting with **19** (80 mg, 0.175 mmol), **3a** (24 mg, 0.175 mmol), $Pd(PPh_3)_4$ (6 mg, 3mol%, 0.00525 mmol), K_3PO_4 (55 mg, 0.262 mmol), and toluene (3 mL), **3h (**27 mg, 0.175 mmol), $Pd(PPh_3)_4$ (6 mg, 3mol%, 0.00525 mmol), K_3PO_4 (55 mg, 0.262 mmol), and 1,4-dioxin (3 mL), **22c** was isolated as a white solid (38 mg, 62%); mp 256-258 °C. ^{1}H NMR (300 MHz, $CDCl_3$): δ = 1.71 (d, J = 1.1 Hz, 3H, CH_3), 2.32 (s, 3H, CH_3), 6.10 (d, J = 1.2 Hz, 1H), 7.17-7.21 (m, 5H, ArH), 7.33 (d, J = 8.4 Hz, 2H, ArH), 7.45 (d, J = 8.1 Hz, 2H, ArH), 7.50 (d, J = 1.9 Hz, 1H, ArH). ^{13}C NMR (75.47 MHz, $CDCl_3$): δ = 21.2, 24.2 (CH_3), 114.6, 116.6 (CH), 116.9 (C), 126.1, 126.9, 128.3, 129.8, 130.5 (CH),134.2, 135.3, 138.8, 140.4, 140.5, 143.0, 153.2, 154.9 (C), 160.3 (CO). IR (KBr, cm^{-1}): ν = 3350, 3028, 2921, 2855, 2732, 2386, 1904, 1856, 1784 (w), 1728, 1704, 1600 (s), 1537 (w), 1517, 1491, 1465, 1440, 1390, 1378, 1353, 1297 (m), 1264, 1234 (w), 1191, 1137 (m), 1115 (w), 1086 (s), 1048, 1031 (w), 1015, 962 (s), 892, 877, 851, 833 (m), 814 (s), 789, 771, 743, 726, 709, 697, 664, 642 (w), 608, 553 (m). GC-MS (EI, 70 eV): *m/z* (%) = 362 ($[M]^+$,^{37}Cl , 35), 361 ($[M+H]^+$, ^{35}Cl ,28), 360 ($[M]^+$, ^{35}Cl ,100), 359 (13), 334 (14), 333 (12), 332 (36), 297 (18), 253 (14), 252 (18), 240 (10). HRMS (EI, 70 eV) calcd for $C_{23}H_{17}ClO_2$ ($[M]^+$, ^{37}Cl): 362.08821; found: 362.08868. calcd for $C_{23}H_{17}ClO_2$ ($[M]^+$, ^{35}Cl): 360.09116; found: 360.091032.



7-(4-Methoxyphenyl)-4-methyl-5-(*p*-tolyl)-2*H*-chromen-2-one (22d). Starting with **19** (80 mg, 0.175 mmol), **3f** (27 mg, 0.175 mmol), $Pd(PPh_3)_4$ (6 mg, 3mol%, 0.00525 mmol), K_3PO_4 (55 mg, 0.262 mmol), and toluene (3 mL), **3a (**23 mg, 0.175 mmol), $Pd(PPh_3)_4$ (6 mg, 3mol%, 0.00525 mmol), K_3PO_4 (55 mg, 0.262 mmol), and 1,4-dioxin (3 mL), **22d** was isolated as a white solid (47 mg, 75%); mp 256-258 °C. ^{1}H NMR (300 MHz, $CDCl_3$): δ = 1.73 (d, J = 1.2 Hz, 3H, CH_3), 2.32 (s, 3H, CH_3), 3.80 (s, 3H, OCH_3), 6.09 (d, J = 1.2 Hz, 1H), 6.88 (d, J = 8.7 Hz, 2H, ArH), 7.15-7.20 (m, 4H, ArH), 7.26 (d, J = 2.0 Hz, 1H, ArH), 7.45-7.49 (m, 3H, ArH). ^{13}C NMR (75.47 MHz, $CDCl_3$): δ = 21.1, 24.1 (CH_3), 55.3 (OCH_3), 113.4, 114.1, 116.3 (CH), 117.3 (C), 126.5, 126.9, 129.7, 130.3 (CH), 134.3, 135.6, 138.6, 141.7, 142.8, 153.9, 154.9, 159.4 (C), 160.5 (CO). IR (KBr, cm^1): ν = 3029, 2927, 2852, 2836 (w), 1725 (s), 1642 (w), 1599 (s), 1574, 1536 (w), 1510 (s), 1464, 1439, 1391, 1379, 1354, 1286 (m), 1243 (s), 1191, 1176, 1137 (s), 1108, 1084 (w), 1032 (s), 1017 (w), 963 (s), 893, 875, 853, 834 (w), 816 (s), 795, 778, 726, 714, 672, 648 (w), 613, 582, 555 (w). GC-MS (EI, 70 eV): *m/z* (%) = 357 ($[M+H]^+$, 26), 356 ($[M]^+$, 100), 355 (11), 328 (26). HRMS (EI, 70 eV) calcd for $C_{24}H_{20}O_3$ $[M]^+$: 356.14070; found: 356.140927.



4-Methyl-2-oxo-2*H*-chromene-7,8-diyl bis(trifluoromethanesulfonate) (24):

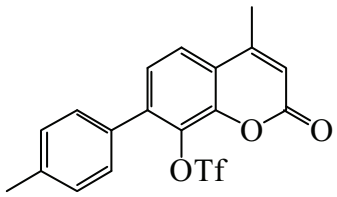


To a solution of 4-methyl-7,8-dihydroxy-2*H*-chromen-2-one (**23**) (0.5 g, 2.60 mmol) in CH_2Cl_2 (30 mL) was added triethylamine (0.36 mL, 10.4 mmol) at room temperature under an argon atmosphere. After 10 min, Tf_2O (1.0 mL, 6.2 mmol) was added at -78 °C. The mixture was allowed to warm to 20 °C and stirred for 6 h. The reaction mixture was filtered and the filtrate was concentrated in vacuo. The residue was purified by chromatography (flash silica gel, heptanes-EtOAc) without aqueous work up to give **24** as a white solid (0.9 g, 80%); mp 128-1130°C. ^{1} H NMR (300 MHz, $CDCl_3$): δ = 2.41 (d, J = 1.3 Hz, 3H, CH_3), 6.34 (d, J = 1.3 Hz, 1H, CH), 7.34 (d, J = 9.0 Hz, 1H, ArH), 7.63 (d, J = 9.0 Hz, 1H, ArH). ^{13}C-NMR (62.9 MHz, $CDCl_3$): δ =18.8 (CH_3) , 116.7, 117.6 (CH), 118.5 (q, J_{CF} = 320.0 Hz, CF_3), 119.5 (q, J_{CF} = 317.0 Hz, CF_3) 121.4(C)

124.5 (CH), 128.2, 142.7, 146.9, 150.7 (C), 156.7 (CO). ^{19}F NMR (282 MHz, $CDCl_3$): = -72.4, -72.7. IR (KBr, cm^{-1}): ν = 3126, 3105, 3085 (w), 1737, 1731 (s), 1681, 1630 (w), 1610, 1574, 1496 (m), 1429, 1382, 1369 (s), 1274 (w), 1210, 1191 (s), 1160 (w), 1127, 1041, 1006, 946, 871, 836, 831, 789, 758, 745, 692, 637, 621, 592, 583 (s), 551 (w). GC-MS (EI, 70 eV): *m/z* (%) = 457 ($[M+H]^+$, 9), 456 ($[M]^+$, 61), 323 (25), 300 (11), 259 (37), 231 (100), 175 (14). HRMS (EI, 70 eV): calcd for $C_{12}H_6F_6O_8S_2$ $[M]^+$: 455. 94028, found 455.940627.

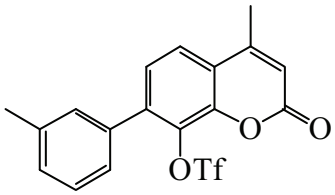
General Procedure for synthesis 25a-f: A solution of **24** (80 mg, 0.175 mmol), K_3PO_4 (1.5 equiv.), $Pd(PPh_3)_4$ (3 mmol-%) and arylboronic acid **3** (1.0 equiv.) in 1,4-dioxane (3 mL) was stirred at 80 °C for 8 h under argon atmosphere. To the reaction mixture H_2O (20 mL) and CH_2Cl_2 (25 mL) were added at 20 °C. The organic and the aqueous layers were separated and the latter was extracted with CH_2Cl_2 (2 x 20 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, heptane/EtOAc).

4-Methyl-2-oxo-7-(*p*-tolyl)-2*H*-chromen-8-yl trifluoromethanesulfonate (25a):



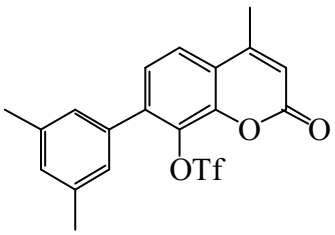
Starting with **24** (80 mg, 0.175 mmol), **3a** (24 mg, 0.175 mmol), $Pd(PPh_3)_4$ (6 mg, 3 mol-%, 0.00525 mmol), K_3PO_4 (55mg, 0.262 mL), and 1,4-dioxane (3 mL), **25a** was isolated as a white solid (55 mg, 80%); mp 152-154 °C.^{1}H NMR (300 MHz, $CDCl_3$): δ = 2.35 (s, 3H, CH_3), 2.40 (d, J = 1.2 Hz, 3H, CH_3), 6.28 (d, J = 1.2 Hz, 1H, CH) 7.22 (d, J = 8.0Hz, 2H, ArH), 7.28 (d, J = 8.3 Hz, 1H, ArH), 7.34 (d, J = 8.0 Hz, 2H, ArH), 7.56 (d, J = 8.3 Hz, 1H, ArH). ^{13}C-NMR (75.4 MHz, $CDCl_3$): δ = 18.7, 21.3 (CH_3), 155.5 (CH), 118.2 (q, J_{CF} = 320.0 Hz, CF_3), 120.4 (C), 123.8, 125.9, 129.1, 129.5 (CH), 131.6, 133.8, 139.1, 139.3, 146.0, 151.6 (C), 158.1 (CO). ^{19}F NMR (282 MHz, $CDCl_3$): = -73.4. IR (KBr, cm^{-1}): ν = 3038, 2957, 2925, 2854 (w), 1738, 1614 (s), 1573, 1542, 1521, 1493, 1455 (w), 1417 (s), 1403, 1388, 1369 (m), 1336, 1315, 1292, 1269, 1244 (w), 1228, 1207, 1190, 1181, 1124, 1107 (s), 1039, 1020, 1001 (w), 954, 934, 852 (s), 830, 809 (m), 797 (s), 773 (w), 762, 745, 721 (s), 666, 657, 641, 616, 598, 579 (m), 540, 530 (w). GC-MS (EI, 70 eV): *m/z* (%) = 399 ($[M+H]^+$, 10), 398 ($[M]^+$, 51), 266 (17), 265 (100), 209 (9), 166 (17), 165 (30). HRMS (EI, 70 eV): calcd for $C_{18}H_{13}F_3O_5S$ $[M]^+$: 398.04303, found 398.042958.

4-Methyl-2-oxo-7-(*m*-tolyl)-2*H*-chromen-8-yl trifluoromethanesulfonate (25b):



Starting with **24** (80 mg, 0.175 mmol), **3b** (24 mg, 0.175 mmol), $Pd(PPh_3)_4$ (6 mg, 3 mol-%, 0.00525 mmol), K_3PO_4 (55mg, 0.262 mL), and 1,4-dioxane (3 mL), **25b** was isolated as a white solid (55 mg, 80%); mp 152-154 °C. ^{1}H NMR (300 MHz, $CDCl_3$): δ = 2.34 (s, 3H, CH_3), 2.40 (d, J = 1.2 Hz, 3H, CH_3), 6.28 (d, J = 1.2, 1H, CH), 7.20-7.24 (br m, 3H, ArH), 7.27-7.33 (m, 2H, ArH), 7.57 (d, J = 8.3 Hz, 1H, ArH). ^{13}C-NMR (62.9 MHz, $CDCl_3$): δ = 18.7, 21.3 (CH_3), 114.6 (CH), 117.2 (q, J_{CF} = 320.0 Hz, CF_3), 119.7 (C), 122.7, 124.8, 125.3, 127.6, 128.8 (CH), 132.8, 133.4, 137.5, 138.1, 145.0, 150.6 (C), 157.0 (CO). ^{19}F NMR (282 MHz, $CDCl_3$): = -73.6. IR (KBr, cm^{-1}): v = 3065, 2960, 2922, 2858, 2801 (w), 1740 (s), 1698 (w), 1619 (s), 1587, 1557, 1544, 1505, 1483 (w), 1423, 1408 (s), 1384, 1364 (m), 1330, 1290 (w), 1247 (m), 1219, 1200, 1174, 1137, 1126, 1112 (s), 1034, 1024, 999 (w), 964 (m), 947 (s), 896 (w), 859 (s), 838, 828 (w), 801, 790, 773, 763, 745 (s), 718, 703 (m), 688, 667, 659 (w), 630, 601, 586 (s), 553, 543 (w). GC-MS (EI, 70 eV): *m/z* (%) = 399 ($[M+H]^+$, 12), 398 ($[M]^+$, 56), 266 (18), 265 (100), 166 (13), 165 (26). HRMS (EI, 70 eV): calcd for $C_{18}H_{13}F_3O_5S$ $[M]^+$: 398.04303, found 398.042259.

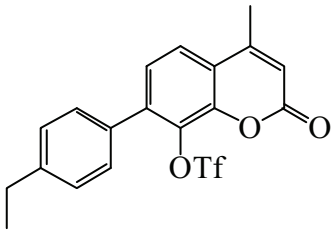
7-(3,5-Dimethylphenyl)-4-methyl-2-oxo-2*H*-chromen-8-yl trifluoromethanesulfonate (25c):



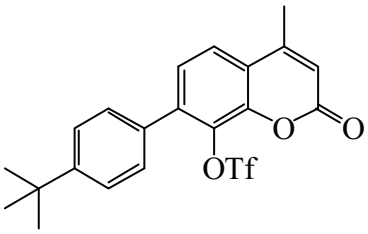
Starting with **24** (80 mg, 0.175 mmol), **3c** (26 mg, 0.175 mmol), $Pd(PPh_3)_4$ (6 mg, 3 mol-%, 0.00525 mmol), K_3PO_4 (55 mg, 0.262 mmol), and 1,4-dioxane (3 mL), **25c** was isolated as a white solid (54 mg, 77%); mp 180-181 °C. ^{1}H NMR (300 MHz, $CDCl_3$): δ = 2.30 (s, 6H, $2CH_3$), 2.40 (d, J = 1.2 Hz, 3H, CH_3), 6.27 (d, J = 1.2 Hz, 1H, CH), 7.04 (br m, 3H, ArH), 7.30 (d, J = 8.3 Hz, 1H, ArH), 7.55 (d, J = 8.3 Hz, 1H, ArH). ^{13}C-NMR (62.9 MHz, $CDCl_3$): δ = 18.7, 21.3 (CH_3), 115.5 (CH), 118.2 (q, J_{CF} = 320.0 Hz, CF_3), 120.4 (C), 123.7, 125.8, 127.0, 130.7 (CH), 133.8, 134.3, 138.4, 139.2, 146.0, 151.6 (C), 158.1 (CO). ^{19}F NMR (282 MHz, $CDCl_3$): = -73.6. IR (KBr, cm^{-1}): v = 3081, 3006, 2922, 2864, 2737 (w), 1740 (s), 1698, 1650 (w), 1619, 1604 (s), 1545, 1504 (w), 1423, 1406, 1384, 1365 (s), 1339, 1304, 1247 (w), 1202 (s), 1138, 1130, 1118 (s), 1035 (m), 968 (w), 944, 856, 824, 800 (s), 775 (w), 762, 733, 720 (m), 703, 669, 661 (w), 636, 603, 591, 579 (m), 547, 537 (w). GC-MS (EI, 70 eV): *m/z*

(%) = 413 ([M+H]$^+$, 10), 412 ([M]$^+$, 47), 280 (19), 279 (100), 264 (11), 165 (17). HRMS (EI, 70 eV): calcd for $C_{19}H_{15}F_3O_5S$ [M]$^+$: 412.05868, found 412.058493.

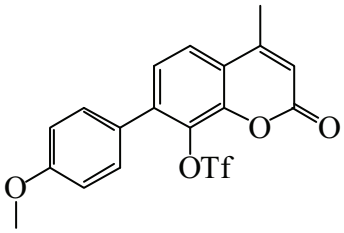
7-(4-Ethylphenyl)-4-methyl-2-oxo-2*H*-chromen-8-yl trifluoromethanesulfonate (25d): Starting with **24** (80 mg, 0.175 mmol), **3d** (26 mg, 0.175 mmol), $Pd(PPh_3)_4$ (6 mg, 3 mol-%, 0.00525 mmol), K_3PO_4 (55 mg, 0.262 mmol), and 1,4-dioxane (3 mL), **25d** was isolated as a white solid (50 mg, 70%); mp 129-131 °C. ^{1}H NMR (300 MHz, $CDCl_3$): δ = 1.21 (t, , J = 7.5 Hz, 3H, CH_3), 2.41 (d, J = 1.2 Hz, 3H, CH_3), 2.65 (q, J = 7.5 Hz, 2H, CH_2), 6.28 (d, J = 1.2 Hz, 1H, CH), 7.25 (d, J = 8.3 Hz, 2H, ArH), 7.30 (d, J = 8.3 Hz, 1H, ArH), 7.35 (d, J = 8.2 Hz, 2H, ArH), 7.55 (d, J = 8.3 Hz; 1H, ArH). ^{13}C-NMR (75.4 MHz, $CDCl_3$): δ = 15.4, 18.8 (CH_3), 18.6 (CH_2), 115.6 (CH), 118.2 (q, J_{CF} = 320.0 Hz, CF_3), 120.4 (C), 123.7, 125.9, 128.3, 129.2 (CH), 131.8, 133.8, 139.2, 145.6, 146.0, 151.6 (C), 158.1 (CO). ^{19}F NMR (282 MHz, $CDCl_3$): = -73.5. IR (KBr, cm^{-1}): ν = 3065, 3045, 3027, 2975, 2935, 2866 (w), 1739, 1621 (s), 1567, 1542, 1519, 1462 (w), 1430, 1413 (s), 1384, 1365 (m), 1325, 1293, 1279 (w), 1246, 1218 (m), 1200, 1171, 1136, 1122, 1105 (s), 1062, 1032, 1024, 1016 (w), 953 (m), 935, 856, 823, 802 (s), 775 (w), 762 (m), 748, 730, 715, 663, 645, 622, 598, 582, 563, 546 (m). GC-MS (EI, 70 eV): *m/z* (%) = 413 ([M+H]$^+$, 14), 412 ([M]$^+$, 74), 280 (16), 279 (91), 252 (17), 251 (100), 222 (11), 195 (12), 165 (34), 152 (10). HRMS (EI, 70 eV): calcd for $C_{19}H_{15}F_3O_5S$ [M]$^+$: 412.05868, found 412.058432.



7-[4-(*tert*-Butyl)phenyl]-4-methyl-2-oxo-2*H*-chromen-8-yl trifluoromethanesulfonate (25e): Starting with **24** (80 mg, 0.175 mmol), **3e** (31 mg, 0.175 mmol), $Pd(PPh_3)_4$ (6 mg, 3 mol-%, 0.00525 mmol), K_3PO_4 (55 mg, 0.262 mmol), and 1,4-dioxane (3 mL), **25e** was isolated as a white solid (60 mg, 83%); mp 148-150°C. ^{1}H NMR (300 MHz, $CDCl_3$): δ = 1.29 (s, 9H, $3CH_3$), 2.40 (d, J = 1.2 Hz, 3H, CH_3), 6.28 (d, J = 1.2 Hz, 1H, CH), 7.30 (d, J = 8.3 Hz, 1H, ArH), 7.35 (d, J = 8.3 Hz, 2H, ArH),7.44 (d, J = 8.5 Hz, 1H, ArH), 7.56 (d, J = 8.3 Hz, 1H, ArH). ^{13}C-NMR (75.4 MHz, $CDCl_3$): δ = 17.7 (CH_3), 30.2 ($3CH_3$), 33.7 (C), 114.5 (CH), 117.1 (q, J_{CF} = 320.0 Hz, CF_3), 119.4 (C), 122.7, 124.7, 124.8, 127.9 (CH), 130.5, 132.8, 138.1, 145.0, 150.6, 151.5 (C), 157.0 (CO). ^{19}F NMR (282 MHz, $CDCl_3$): = -73.6. IR (KBr,

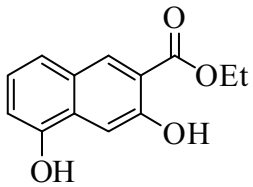


cm^{-1}): ν = 3082, 3050, 2961, 2906, 2868 (w), 1737, 1618 (s), 1595, 1519 (w), 1421 (s), 1397, 1383, 1364 (m), 1329, 1318, 1290, 1268 (w), 1246 (m), 1224, 1203, 1193, 1136, 1114, 1097 (s), 1062, 1024, 1014, 1000 (w), 952, 931, 862, 848, 829, 802 (s), 760, 718, 712 (m), 598 (s), 564 (m), 548 (w). GC-MS (EI, 70 eV): *m/z* (%) = 441 ([M+H]$^+$, 10), 440 ([M]$^+$, 44), 426 (13), 292 (15), 277 (28), 251 (100). HRMS (EI, 70 eV): calcd for $C_{21}H_{19}F_3O_5S$ [M]$^+$: 440.08998, found 440.089328.

7-(4-Methoxyphenyl)-4-methyl-2-oxo-2*H*-chromen-8-yl trifluoromethanesulfonate (25f): 

Starting with **24** (80 mg, 0.175 mmol), **3f** (26 mg, 0.175 mmol), $Pd(PPh_3)_4$ (6 mg, 3 mol-%, 0.00525 mmol), K_3PO_4 (55 mg, 0.262 mmol), and 1,4-dioxane (3 mL), **25f** was isolated as a white solid (60 mg, 83%); mp 148-150°C. ^{1}H NMR (300 MHz, $CDCl_3$): δ = 2.40 (d, J = 1.2 Hz, 3H, CH_3), 3.80 (s, 3H, OCH_3), 6.27 (d, J = 1.2 Hz, 1H, CH), 6.94 (d, J = 8.8 Hz, 2H, ArH), 7.28 (d, J = 8.3 Hz, 1H, ArH), 7.38 (d, J = 8.8 Hz, 2H, ArH), 7.54 (d, J = 8.3 Hz, 1H, ArH). ^{13}C-NMR (62.9 MHz, $CDCl_3$): δ = 17.7 (CH_3), 54.3 (OCH_3), 113.3, 114.4 (CH), 118.2 (q, J_{CF} = 320.0 Hz, CF_3), 119.2 (C), 122.7, 124.7 (CH), 125.8 (C), 129.6 (CH), 132.8, 137.8, 145.0, 150.5 (C), 157.1 (C), 159.3 (CO). ^{19}F NMR (282 MHz, $CDCl_3$): = -73.4. IR (KBr, cm^{-1}): ν = 3092, 3052, 2962, 2916, 2840 (w), 1756, 1742, 1611 (s), 1580, 1542 (w), 1521, 1493 (m), 1465, 1456, 1444, 1430 (w), 1417, 1384 (s), 1366 (m), 1328, 1310 (w), 1299, 1282 (m), 1252, 1218, 1204, 1180, 1131, 1122, 1112, 1037, 956, 933, 855, 840, 821, 800 (s), 773 (w), 762, 749, 726, 708 (m), 665 (w), 616, 598, 580 (s), 541 (m). GC-MS (EI, 70 eV): *m/z* (%) = 415 ([M+H]$^+$, 9), 414 ([M]$^+$, 42), 282 (18), 281 (100), 253 (11). HRMS (EI, 70 eV): calcd for $C_{18}H_{13}F_3O_6S$ [M]$^+$: 414.03794; found 414.038072.

Ethyl 3,5-dihydroxy-2-naphthoate (27): To a solution of **26** (1.00 g, 4.9 mmol) in absolute ethanol (20 ml) was added carefully H_2SO_4 conc. (1 ml). The reaction mixture was heated under reflux for 6 h and poured into H_2O (250 ml). A saturated aqueous solution of $NaHCO_3$ (100 ml) was added and the mixture was extracted with CH_2Cl_2 (3 x 50 ml). The aqueous and the organic layer were separated and the latter was dried (Na_2SO_4) and filtered. The filtrate was concentrated in vacuo. The residue was purified by column chromatography (flash silica gel, heptane/EtOAc) to give **27** as a yellow solid (0.88 g,

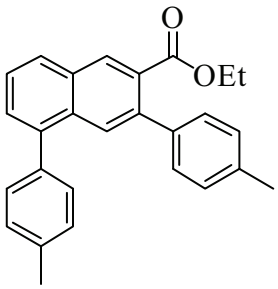


77%). ^{1}H NMR (300 MHz, $CDCl_3$): δ = 1.41 (t, J = 7.1 Hz, 3H, CH_3), 4.42 (q, J = 7.1 Hz, 2H, CH_2), 5.20 (s, 1H, OH), 6.78 (dd, J = 0.8, 7.4 Hz, 1H, ArH), 7.09 (t, J = 8.3 Hz, 1H, ArH), 7.34 (d, J = 8.4 Hz, 1H, ArH), 7.55 (s, 1H, ArH), 8.39 (s, 1H, ArH), 10.46 (s, 1H, OH). ^{13}C NMR (75.5 MHz, $CDCl_3$): δ = 14.2 (CH_3), 61.8 (CH_2O), 106.2, 111.1 (CH), 114.8 (C), 121.8, 123.7 (CH), 128.2, 129.0 (C), 132.1 (CH), 150.0, 156.1 (C), 169.8 (CO). IR (KBr, cm): v = 1671 (s), 1633, 1579 (w), 1528 (m), 1478, 1469, 1454, 1396 (w), 1370 (m), 1324 (w), 1289 (m), 1274, 1222, 1161, 1105 (s), 1066, 1058 (w), 1003 (s), 964, 926, 911 (w), 871, 791 (s), 761 (m), 741 (s), 719, 671, 657 (m), 594 (w), 580 (s), 547 (m). GC-MS (EI, 70 eV): *m/z* (%) = 232 ([M]$^+$, 46), 187 (18), 186 (100), 158 (60), 130 (19). HRMS (EI, 70 eV) calcd for $C_{13}H_{12}O_4$ [M]$^+$: 232.07301; found: 232.07313.

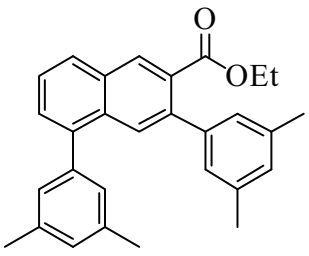
Ethyl 3,5-bis(trifluoromethylsulfonyloxy)-2-naphthoate (28): To a CH_2Cl_2 solution (65 ml) of **27** (1.50 g, 6.4 mmol) was added pyridine (2.0 ml, 25.8 mmol) and the solution was stirred at 20 °C for 10 min under Argon atmosphere. Then Tf_2O (2.6 mL, 15.3 mmol) was added at –78 °C and the reaction mixture was allowed to warm to room temperature and was stirred for 14 h. The reaction mixture was filtered and the filtrate was concentrated in vacuo. The product **28** was isolated by column chromatography (flash silica gel, heptane/EtOAc) as a colourless solid (2.80 g, 87%); mp 75-77 ^{o}C. ^{1}H NMR (300 MHz, $CDCl_3$): δ = 1.31 (t, J = 7.1 Hz, 3H, CH_3), 4.35 (q, J = 7.1, 2H, CH_2), 7.43-7.51 (m, 2H, ArH), 7.77 (s, 1H, ArH), 7.80 (d, J = 7.5 Hz, 1H, ArH), 8.50 (s, 1H, ArH). ^{13}C NMR (62.9 MHz, $CDCl_3$): δ = 12.8 (CH_3), 61.5 (CH_2), 113.8 (CH), 117.7 (q, $J_{F,C}$ = 320.2 Hz, CF_3), 117.9 (q, $J_{F,C}$ = 320.8 Hz, CF_3), 120.6 (CH), 123.3 (C), 126.7 (CH), 126.8 (C), 128.4 (CH), 131.6 (C), 133.7 (CH), 143.6, 145.2 (C), 162.1 (CO). ^{19}F NMR (282.4, MHz): δ = -73.6, -73.3. IR (KBr, cm^{1}): v = 1708 (s), 1640, 1606, 1501,1476, 1458 (w), 1426, 1395 (s), 1375, 1322, 1302 (w), 1274, 1242 (m), 1200 (s), 1161 (m), 1128 (s), 1094 (m), 1078, 1058 (s), 1018, 974 (m), 946 (s), 905 (s), 886 (m), 869, 814, 805 (s), 781 (m), 766 (s), 746, 720, 709 (m), 674, 651, 614, 595, 576 (s), 574, 529 (m). GC-MS (EI, 70 eV): *m/z* (%) = 496 ([M]$^+$, 32), 451 (11), 364 (09), 363 (61), 291 (11). HRMS (EI, 70 eV): calcd for $C_{15}H_{10}F_6O_8S_2$ [M]$^+$: 495.97158; found: 495.97131.

General procedure for the synthesis of products 29a-i and 30a-f by Suzuki–Miyaura reactions: A suspension of 2**8** (100 mg, 0.2 mmol), K_3PO_4 (1.5 mmol per cross-coupling step), $Pd(PPh_3)_4$ (3 mol-% per cross-coupling step) and of the arylboronic acid (1.1-2.4 equiv. per cross-coupling step) in THF (4 ml) was stirred at 20-60 °C for 8-12 h. To the reaction mixture were added H_2O (25 mL) and CH_2Cl_2 (25 ml) at 20 °C. The organic and the aqueous layers were separated and the latter was extracted with CH_2Cl_2 (2 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.

Ethyl 3,5-bis(4-methylphenyl)-2-naphthoate (29a): Starting with **28** (100 mg, 0.2 mmol), 4-methylphenylboronic acid **3a** (64 mg, 0.48 mmol), $Pd(PPh_3)_4$ (14 mg, 6 mol-%), K_3PO_4 (127 mg, 0.6 mmol) and THF (4 mL), **29a** was isolated as a yellow oil (58 mg, 76%). ^{1}H NMR (300 MHz, $CDCl_3$): δ = 0.97 (t, J = 7.1 Hz, 3H, CH_3), 2.25 (s, 3H, CH_3), 2.29 (s, 3H, CH_3), 4.06 (q, J = 7.1 Hz, 2H, CH_2O), 7.05 (d, J = 7.5 Hz, 2H, ArH), 7.10-7.13 (m, 3H, ArH),7.16 (s, 1H, ArH), 7.26 (d, J = 8.0 Hz, 2H, ArH), 7.37 (dd, J = 1.5, 7.1 Hz, 1H, ArH),7.4 (t, J = 8.0 Hz, 1H, ArH), 7.79-7.81 (m, 2H, ArH), 8.3 (s, 1H, ArH). ^{13}C NMR (62.9 MHz, $CDCl_3$): δ = 13.8 (CH_3), 21.2, 21.3 ($2CH_3$), 61.0 (CH_2O), 125.0 (CH), 126.7, 126.9 (C), 127.4, 127.6, 127.9, 128.0, 128.4, 128.7, 130.0 (CH), 131.0 (C), 131.6 (CH), 135.5, 136.0, 136.1, 137.6, 137.8, 139.2 (C), 167.6 (CO). IR (KBr, cm^{-1}): ν = 1713 (s), 1619, 1589, 1566 (w), 1512 (m), 1478 (w), 1443 (m), 1389 (w), 1366, 1297 (m), 1269, 1235 (s), 1211 (w), 1192 (s), 1211(w), 1192(s), 1173, 1121, 1111 (m), 1086 (s), 1052 (w), 1022 (s), 984(m), 944, 919, 902, 863, 849 (w), 816, 797 (s), 780, 752 (m), 722, 702, 684, 658, 644, 608, 593 (w), 563, 532 (m). GC-MS (EI, 70 eV): *m/z* (%) = 380 ([M]$^+$, 100), 335 (13), 317 (11), 292 (9). HRMS (EI, 70 eV) calcd for $C_{27}H_{24}O_2$ [M]$^+$: 380.17708; found: 380.17674.

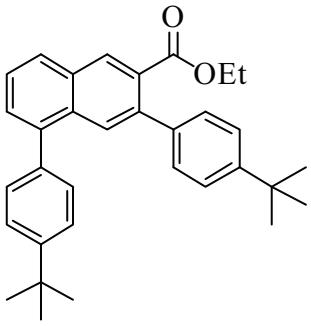


Ethyl 3,5-bis(3,5-dimethylphenyl)-2-naphthoate (29b): Starting with **28** (100 mg, 0.2 mmol), 3,5-dimethylphenylboronic acid **3c** (72 mg, 0.48 mmol), $Pd(PPh_3)_4$ (14 mg, 6 mol-%), K_3PO_4 (127 mg, 0.6 mmol) and THF (4 mL), **10c** was isolated as a colourless solid (67 mg, 82%); mp 89-90 °C. ^{1}H NMR (300 MHz, $CDCl_3$): δ =



0.96 (t, J = 6.0, 3H, CH_3) , 2.22 (s, 6H, $2CH_3$), 2.27 (s, 6H, $2CH_3$), 4.07 (q, J = 6.0 Hz, 2H, CH_2O), 6.85 (b, 3H, ArH), 6.93 (s, 1H, ArH), 7.01 (b, 2H, ArH), 7.35 (dd, J = 1.5, 7.1 Hz, 1H, ArH), 7.43 (t, J = 6.0 Hz, 1H, ArH), 7.79-7.82 (m, 2H, ArH), 8.20 (s, 1H, ArH). ^{13}C NMR (62.9 MHz, $CDCl_3$): δ = 13.7 (CH_3), 21.3, 21.4 (CH_3), 61.0 (CH_2O), 126.0, 126.5, 127.8, 127.9, 128.0, 128.5, 128.8, 129.0 (CH), 129.7 (C), 130.8 (CH), 131.9, 132.6, 137.3, 137.8, 138.7, 140.0, 140.6, 141.6 (C), 169.0 (CO). IR (KBr, cm^{-1}): ν = 1718 (s), 1620 (w), 1598 (m), 1462, 1443 (m), 1389 (s), 1369 (m), 1316, 1295(w), 1265, 1248, 1195 (s), 1126 (w), 1106 (s), 1052, 1052, 1023 (m),970, 950, 917, 893, 870 (s), 845, 812 (s), 798, 775, 763, 754 (m), 719 (s), 705 (m), 686 (s), 656 (w), 619 (m), 588, 568, 557, 536, 528 (w). GC-MS (EI, 70 eV): *m/z* (%) = 408 ($[M]^+$, 100), 363 (17). HRMS (EI, 70 eV): calcd for $C_{29}H_{28}O_2$ $[M]^+$: 408.20838; found: 408.20727.

Ethyl 3,5-bis(4-*tert*-butylphenyl)-2-naphthoate (29c): Starting with **28** (100 mg, 0.2 mmol), 4-*tert*-butylphenylboronic acid **3e** (86 mg, 0.48 mmol), $Pd(PPh_3)_4$ (14 mg, 6 mol-%), K_3PO_4 (127 mg, 0.6 mmol) and THF (4 mL), **29c** was isolated as a colourless solid (74 mg, 80%); mp. 239-238 °C. ^{1}H NMR (300 MHz, $CDCl_3$): δ = 0.87 (t, J = 7.1 Hz, CH_3), 1.25 (s, 9H, $3CH_3$), 1.30 (s, 9H, $3CH_3$), 4.05 (q, J = 7.1 Hz, CH_2O), 7.19 (d, J = 8.5 Hz, 2H, ArH), 7.31 (d, J = 8.3 Hz, 2H, ArH), 7.34-7.48 (m, 5H, ArH), 7.82 (d, J = 7.7, 1H, ArH), 7.90 (s, 1H, ArH), 7.90 (s, 1H, ArH), 8.32 (s, 1H, ArH). ^{13}C NMR (75.5 MHz, $CDCl_3$): δ = 13.6 (CH_3), 31.2, 31.5 ($3CH_3$), 33.4, 33.5 (C), 61.0 (CH_2O), 123.8, 124.3, 125.1, 126.6, 126.9, 127.3, 128.1, 128.5 (CH), 128.7, 129.9 (C), 130.9 (CH), 131.5, 136.1, 137.4, 137.8, 139.2, 148.8, 149.2 (C), 168.0 (CO). IR (KBr, cm^{-1}): ν = 1723 (s), 1687, 1671, 1653, 1638, 1619, 1575, 1560, 1543, 1525 (w), 1508, 1476, 1461, 1443, 1397, 1361 (m), 1297 (s), 1262 (s), 1242, 1189, 1172 (m), 1127 (w), 1104 (m),1081 (s), 1053, 1024, 984 (m), 947, 928 (w), 904 (m), 876, 853 (w), 832, 824 (m), 800 (s), 787, 750 (m), 699, 666, 641, 634 (w), 597, 571 (m), 531 (w). GC-MS (EI, 70 eV): *m/z* (%) = 464 ($[M]^+$, 100), 449 (83), 347 (07), 217 (17). HRMS (EI, 70 eV): calcd for $C_{33}H_{36}O_2$ $[M]^+$: 464.27098; found: 464.27024.



Ethyl 3,5-bis(4-methoxyphenyl)-2-naphthoate (29d): Starting with **28** (100 mg, 0.2 mmol), 4-methoxyphenylboronic acid **3f** (73 mg, 0.48 mmol), $Pd(PPh_3)_4$ (14 mg, 6 mol-%), K_3PO_4 (127 mg, 0.6 mmol) and THF (4 mL), **29d** was isolated as a yellow oil (49 mg, 60%). ^{1}H NMR (300 MHz, $CDCl_3$): δ = 1.01 (t, J = 7.1 Hz, 3H, CH_3), 3.73 (s, 3H, CH_3O), 3.77 (s, 3H, CH_3O), 4.09 (q, J = 7.1 Hz, 2H, CH_2O), 6.79-6.81 (m, 2H, ArH), 6.84-6.89 (m, 2H, ArH), 7.14-7.19 (m, 2H, ArH), 7.29-7.34 (m, 2H, ArH), 7.39 (dd, J = 1.4, 7.0 Hz, 1H, ArH), 7.45 (t, J = 7.7 Hz, 1H, ArH), 7.80-7.83 (m, 2H, ArH), 8.30 (s, 1H,ArH). ^{13}CNMR (62.9 MHz, $CDCl_3$): δ = 13.9 (CH_3), 55.3, 55.2 (2 CH_3O), 61.0 (CH_2O), 113.4, 113.9, 126.1, 127.7, 127.8, 129.0 (CH), 129.5 (C), 129.6, 131.0, 131.1 (CH), 131.9, 132.4, 132.7, 134.2, 138.3, 139.9, 158.8, 159.0 (C), 168.8 (CO). IR (KBr, cm^{-1}): ν = 1713, 1607 (s), 1573 (w), 1510 (s), 1480,1453, 1438 (m), 1411, 1389, 1366 (w), 1270, 1236, 1192, 1172 (s), 1122, 1108, 1087, 1030 (m), 982, 919, 901, 850 (w), 830, 800, 786 (m), 753, 730, 703, 684, 658, 641, 594 (w), 573, 545 (m). GC-MS (EI, 70 eV): *m/z* (%) = 412 ([M]$^+$, 100), 384 (17), 367 (16), 349 (10). HRMS (EI, 70 eV): calcd for $C_{27}H_{24}O_4$ [M]$^+$: 412.16691; found: 412.16641.

Ethyl 3,5-bis(4-fluorophenyl)-2-naphthoate (29e): Starting with **28** (100 mg, 0.2 mmol), 4-fluorophenylboronic acid **3g** (67 mg, 0.48 mmol), $Pd(PPh_3)_4$ (14 mg, 6 mol-%), K_3PO_4 (127 mg, 0.6 mmol) and THF (4 mL), **29e** was isolated as a yellow solid (60 mg, 77%); mp 89-90 ^{o}C. ^{1}H NMR (300 MHz, $CDCl_3$): δ = 0.9 (t, J = 7.1 Hz, 3H, CH_3), 4.06 (q, J = 7.1 Hz, 2H, CH_2O), 6.92-6.99 (m, 2H, ArH), 7.02-7.09 (m, 2H, ArH), 7.13-7.21 (m, 2H, ArH), 7.30-7.35 (m, 2H, ArH), 7.38 (dd J = 1.3, 7.1 Hz, 1H, ArH), 7.46 (t, J = 8.0 Hz, 1H, ArH) , 7.67 (s, 1H, ArH), 7.84 (d, J = 8.0 Hz, 1H, ArH), 8.35 (s, 1H, ArH). ^{13}CNMR (62.9 MHz, $CDCl_3$): δ = 13.8 (CH_3), 61.1 (CH_2O), 115.2 (d, J = 21.4 Hz), 115.4 (d, J = 21.4 Hz), 126.3, 127.6, 128.4, 129.4, 130.1 (d, J = 8.0 Hz), 131.4, 131.4 (d, J = 8.0 Hz) (CH), 132.0, 132.5, 135.9 (d, J = 3.3 Hz), 137.7 (d, J = 3.3 Hz), 138.0, 139.2 (C), 162.1 (d, $J_{F,C}$ = 246.2 Hz) (CF), 162.4 (d, $J_{F,C}$ = 246.8 Hz) (CF), 168.3 (CO). ^{19}F NMR (282 MHz, $CDCl_3$): = -115.07, -114.85. IR (KBr, cm^{-1}): ν = 1716 (s), 1670, 1661, 1653, 1638, 1621

(w), 1603 (m), 1560, 1543 (w), 1508 (s), 1480, 1453, 1443 (m), 1404, 1390, 1367 (w), 1269, 1219, 1193 (s), 1174 (m), 1157 (s), 1122 (w), 1090 (s), 1053 (w), 1016 (m), 985, 921, 901, 854 (w), 836, 798 (s), 781, 753 (m), 723, 701, 685, 657, 641, 605, 591 (w), 561, 537 (m). GC-MS (EI, 70 eV): *m/z* (%) = 388 ($[M]^+$, 100), 343 (29), 325 (16), 294 (16). HRMS (EI, 70 eV): calcd for $C_{25}H_{18}F_2O_2$ $[M]^+$: 388.12694; found: 388.12670.

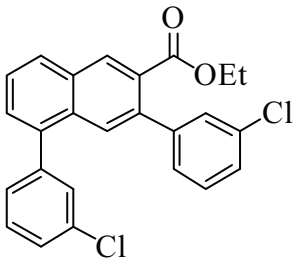
Ethyl 3,5-bis(4-chlorophenyl)-2-naphthoate (29f): Starting with **28** (100 mg, 0.2 mmol), 4-chlorophenylboronic acid **3h** (75 mg, 0.48 mmol), $Pd(PPh_3)_4$ (14 mg, 6 mol-%), K_3PO_4 (127 mg, 0.6 mmol) and THF (4 mL), **29f** was isolated as a colourless solid (64 mg, 76%); mp 104-106 °C. ^{1}H NMR (300 MHz, $CDCl_3$): δ = 1.0 (t, *J* = 7.1 Hz, 3H, CH_3), 4.07 (q, *J* = 7.1 Hz, 2H, CH_2O), 7.12-7.13 (m, 1H, ArH), 7.22-7.27 (m, 3H, ArH), 7.30-7.32 (m, 4H, ArH), 7.38 (dd, *J* = 1.1, 7.0 Hz, 1H, ArH), 7.41 (t, *J* = 8.0 Hz, 1H, ArH), 7.66 (s, 1H, ArH), 7.85 (d, *J* = 8.1 Hz, 1H, ArH), 8.37 (s,1H, ArH). ^{13}CNMR (62.9 MHz, $CDCl_3$): δ = 13.8 (CH_3), 61.2 (CH_2O), 126.4, 127.5, 128.1, 128.6, 128.7 (CH), 129.2 (C), 129.3, 129.9, 131.1, 131.6 (CH), 132.1, 132.3, 133.2, 133.7, 138.0, 138.3, 139.0, 140.1 (C), 168.1 (CO). IR (KBr, cm^{-1}): *v* = 1714 (s), 1682, 1622, 1596, 1493 (w), 1480, 1472, 1454, 1443 (m), 1397, 1363, 1352, 1310 (w), 1278, 1246, 1191 (s), 1174 (w), 1126 (m), 1089 (s), 1054, 1023 (w), 1013, 985 (s), 969, 958, 929, 918 (w), 902, 896 (m), 866 (w), 850, 836, 824, 819 (m), 797, 786 (s), 754, 743, 735 (m), 721, 693, 663, 635, 624, 597, 583 (w), 569, 531 (m). GC-MS (EI, 70 eV): *m/z* (%) = 420 ($[M]^+$, ^{35}Cl, 100), 340 (15), 276 (34), 138 (15). HRMS (EI, 70 eV): calcd for $C_{25}H_{18}Cl_2O_2$ ($[M]^+$, ^{35}Cl): 420.06784; found: 420.06781.

Ethyl 3,5-bis(4-trifluoromethylphenyl)-2-naphthoate (29g). Starting with **28** (100 mg, 0.2 mmol), 4- trifluoromethylboronic acid **3j** (91 mg, 0.48 mmol), $Pd(PPh_3)_4$ (14 mg, 6 mol-%), K_3PO_4 (127 mg, 0.6 mmol) and THF (4 mL), **29g** was isolated as a yellow solid (78 mg, 80%); mp 123-125 °C. ^{1}H NMR (300 MHz, $CDCl_3$): δ = 0.96 (t, *J* = 7.1 Hz, 3H, CH_3), 4.06 (q, *J* = 7.1 Hz, 2H, CH_2O), 7.32 (d, *J* = 8, 2H, ArH), 7.44 (dd, *J* = 1.2, 7.1 Hz, 1H, ArH), 7.49-7.58 (m, 5H, ArH), 7.64-7.67 (m, 3H, ArH), 7.93 (d, *J* = 8.1 Hz, 1H, ArH), 8.46 (s,

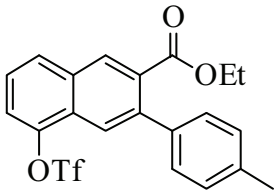
1H, ArH). ^{13}C NMR (62.9 MHz, $CDCl_3$): δ = 13.6 (CH_3), 61.2 (CH_2O), 118.2 (q, J_{CF} = 320.3 Hz, CF_3), 122.0 (q, J_{CF} = 272.4 Hz, CF_3), 124.9 (q, J_{CF} = 3.7 Hz), 125.5 (q, J_{CF} = 3.7 Hz) (CH), 126.6, 127.4, 128.9 (CH), 129.0, 129.0 (C), 129.1 (CH), 129.5 (C), 129.6, 130.2, 131.9 (CH), 132.0, 132.3, 138.1, 138.8, 143.5, 145.3 (C), 167.7 (CO). ^{19}F NMR (282 MHz, $CDCl_3$): δ = -62.69, -62.37. IR (KBr, cm-1): *v* = 1721 (s), 1615 (m), 1592, 1573, 1474, 1455, 1446, 1407, 1365, 1356 (w), 1319 (s), 1283 (m), 1247, 1192, 1177, 1156 (m), 1115, 1105, 1093, 1063, 1017 (s), 986 (m), 968, 931, 919, 905, 897, 867 (w), 851, 841, 832, 800, 789 (m), 774, 751,719, 704, 689, 648, 639, 619, 591, 579, 561 (w). GC-MS (EI, 70 eV): *m/z* (%) = 488 ([M]+,100), 489 ([M+H]+,29), 443 (37), 423 (23), 346 (18), 276 (11). HRMS (EI, 70 eV): calcd for $C_{27}H_{18}F_6O_2$ [M]+: 488.12055; found: 488.12080.

Ethyl 3,5-bis(2,6-dimethoxyphenyl)-2-naphthoate (29h): Starting with **28** (100 mg, 0.2 mmol), 2,6-dimethoxyphenylboronic acid **3p** (87 mg, 0.48 mmol), $Pd(PPh_3)_4$ (14 mg, 6 mol-%), K_3PO_4 (127 mg, 0.6 mmol) and THF (4 mL), **29h** was isolated as a colourless solid (66 mg, 70%); mp 212-214 °C. ^{1}H NMR (300 MHz, $CDCl_3$): *δ* = 0.95 (t, *J* = 7.1 Hz, 3H, CH_3), 3.53 (s, 6H, $2CH_3O$), 3.54 (s, 6H, $2CH_3O$), 4.03 (q, *J* = 7.1 Hz, 2H, CH_2O), 6.50 (d, *J* = 8.3 Hz, 2H, ArH), 7.11-7.26 (m, 2H, ArH), 7.31 (s, 1H, ArH), 7.33 (dd, *J* = 1.7, 7.6 Hz, 1H, ArH), 7.47 (t, *J* = 7.1Hz, 1H, ArH), 7.85 (d, *J* = 8.2 Hz, 1H,ArH), 8.44 (s, 1H, ArH). ^{13}C NMR (62.9 MHz, $CDCl_3$): *δ* = 13.8 (CH_3), 55.8, 55.9 (4 CH_3O), 60.30 (CH_2O), 104.1, 104.2 (CH), 117.3, 120.2 (C), 125.8, 128.2, 128.3, 129.1 (CH), 129.7 (C), 129.8, 129.9 (CH), 130.0 (C), 130.9 (CH), 131.9, 132.6, 133.9, 157.5, 158.4 (C), 167.9 (CO). IR (KBr, cm^{-1}): *v* = 1715 (s), 1679, 1621 (w), 1587, 1467 (s), 1428 (m), 1391, 1367, 1310, 1296, 1284 (w), 1265 (m), 1243 (s), 1188, 1168 (m), 1145 (w), 1101, 1074 (s), 1035, 1028, 978 (m), 952, 938, 916, 909, 900, 884, 873, 845 (w), 808 (m), 789 (w), 778 (m), 760, 746 (w), 725 (s), 696, 683, 671, 636, 601, 588, 566, 540 (w). GC-MS (EI, 70 eV): *m/z* (%) = 472 ($[M]^+$, 100), 413 (25), 321 (17). HRMS (EI, 70 eV): calcd for $C_{29}H_{28}O_6$ $[M]^+$: 472.18804; found: 472.18810.

Ethyl 3,5-bis(3-chlorophenyl)-2-naphthoate (29i): Starting with **28** (100 mg, 0.2 mmol), 3-chlorophenylboronic acid **3q** (75 mg, 0.48 mmol), $Pd(PPh_3)_4$ (14 mg, 6 mol-%), K_3PO_4 (127 mg, 0.6 mmol) and THF (4 mL), **29i** was isolated as a yellow oil (68 mg, 81%). ^1H NMR (300 MHz, $CDCl_3$): δ = 0.98 (t, J = 7.1 Hz, 3H, CH_3), 4.08 (q, J = 7.1 Hz, 2H, CH_2O), 7.16-7.21 (m, 3H, ArH), 7.23-7.31 (m, 4H, ArH), 7.36-7.38 (m, 1H, ArH), 7.40 (dd, J = 1.3, 7.2 Hz, 1H, ArH), 7.47 (t, J = 8.1 Hz, 1H, ArH), 7.67 (s, 1H, ArH), 7.87 (d, J = 8.1 Hz, 1H, ArH), 8.38 (s, 1H, ArH). ^{13}CNMR (62.9 MHz, $CDCl_3$): δ = 13.0 (CH_3), 60.1 (CH_2O), 125.4, 125.8, 126.0, 126.3, 126.7, 127.0, 127.7, 127.7, 128.1, 128.3, 128.6, 128.8 (CH), 130.6 (C), 131.1 (CH), 132.7, 133.4, 136.7, 137.8, 140.6, 142.4 (C), 166.9 (CO). IR (KBr, cm^{-1}): ν = 1713 (s), 1621 (w), 1592, 1563, 1470, 1442 (m), 1408, 1367, 1297 (w), 1269, 1234, 1192 (s), 1176, 1127 (m), 1088, 1078, 1019 (s), 997 (m), 940, 921 (w), 883 (m), 854, 833, 805 (w), 782, 754, 747, 696, 689 (s), 677, 604, 556 (w). GC-MS (EI, 70 eV): m/z (%) = 420 ($[M]^+$, ^{35}Cl, 100), 375 (29), 312 (24), 276 (48). HRMS (EI, 70 eV): calcd for $C_{25}H_{18}Cl_2O_2$ ($[M]^+$, ^{35}Cl): 420.06784; found: 420.06670.

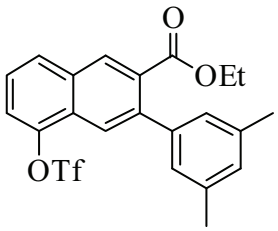


Ethyl 3-(4-methylphenyl)-5-(trifluoromethylsulfonyloxy)-2-naphthoate (30a): Starting with **28** (100 mg, 0.2 mmol), 4-methylphenylboronic acid **3a** (27 mg, 0.2 mmol), $Pd(PPh_3)_4$ (7 mg, 3 mol-%), K_3PO_4 (63 mg, 0.3 mmol) and THF (4 mL), **30a** was isolated as a yellow oil (61 mg, 70%). ^1H NMR (300 MHz, $CDCl_3$): δ = 1.00 (t, J = 7.1 Hz, 3H, CH_3), 2.3 (s, 3H, ArH), 4.11 (q, J = 7.1 Hz, 2H, CH_2O), 7.16-7.24 (m, 4H, ArH), 7.50-7.43 (m, 2H, ArH), 7.88 (dd, J = 2.0, 7.0 Hz, 1H, ArH), 7.96 (s, 1H, ArH), 8.30 (s, 1H, ArH). ^{13}C NMR (62.9 MHz, $CDCl_3$): δ = 13.7, 21.2 (CH_3), 61.4 (CH_2O), 118.7 (q, $J_{F,C}$ = 320.4 Hz, CF_3), 119.8, 122.3, 125.8 (CH), 127.1 (C), 128.4, 129.0, 130.4 (CH), 131.6, 132.9, 137.4, 137.7, 140.8, 145.4 (C), 168.2 (CO). ^{19}F NMR (282.4 MHz, $CDCl_3$): δ = -73.09. IR (KBr, cm^{-1}): ν = 1713 (s), 1638, 1602, 1563, 1517, 1487, 1475, 1446 (w), 1416 (s), 1399, 1382, 1367, 1320, 1306 (w), 1277, 1254, 1241 (m), 1206, 1199 (s), 1156 (w), 1138, 1100 (s), 1063 (w), 1027 (m), 1007 (s), 967 (w), 955 (m), 885 (s), 840 (w), 817, 796 (s), 779, 764, 744 (m), 728, 713, 696, 660 (w), 636 (m), 597 (s), 572, 558, 540



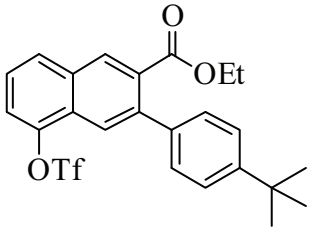
(w). GC-MS (EI, 70 eV): *m/z* (%) = 438 ([M]$^+$, 35), 305 (100), 202(10), 189 (10). HRMS (EI, 70 eV): calcd for $C_{21}H_{17}F_3O_5S$ [M]$^+$: 438.07433; found: 438.07449.

Ethyl 3-(3,5-dimethylphenyl)-5-(trifluoromethylsulfonyloxy)-2-naphthoate (30b):



Starting with **28** (100 mg, 0.2 mmol), 3,5-dimethyllboronic acid **3 c** (30 mg, 0.2 mmol), $Pd(PPh_3)_4$ (7 mg, 3 mol-%), K_3PO_4 (63 mg, 0.3 mmol) and THF (4 mL), **30b** was isolated as a yellow oil (73 mg, 80%). ^{1}H NMR (300 MHz, $CDCl_3$): δ = 0.99 (t, J = 7.1 Hz, 3H, CH_3), 2.30 (s, 6H, $2CH_3$), 4.01 (q, J = 7.1 Hz, 2H, CH_2O), 6.94-6.97 (m, 3H, ArH), 7.43-7.51 (m, 2H, ArH), 7.88 (dd, J = 2.0, 7.0 Hz, 1H, ArH), 7.96 (s, 1H, ArH), 8.28 (s, 1H, ArH). ^{13}C NMR (62.9 MHz, $CDCl_3$): δ = 13.6 (CH_3), 21.2 (2 CH_3), 61.3 (CH_2O), 118.6 (q, $J_{F,C}$ = 320.5 Hz, CF_3), 119.7, 122.2 (CH), 125.8 (C), 126.3 (CH), 127.0 (C), 128.8, 129.2, 130.2, 131.8 (CH), 132.9, 137.7, 140.4, 140.9, 145.5 (C), 168.3 (CO). ^{19}F NMR (282.4 MHz, $CDCl_3$): δ = -73.06. IR (KBr, cm^{-1}): ν = 1717 (s), 1635 (w), 1597(m), 1562, 1455, 1447 (w), 1420 (s), 1367, 1322, 1300 (w), 1270 (m), 1246, 1198 (s), 1198 (s), 1156 (w), 1137 (s), 1105, 1074, 1049 (m), 1020, 991, 966 (w), 886 (m), 859, 848 (w), 813 (m), 765, 742, 712, 687, 648, 625 (w), 599 (m), 534 (w). GC-MS (EI, 70 eV): *m/z* (%) = 452 ([M]$^+$, 34), 319 (100), 202 (10). HRMS (EI, 70 eV): calcd for $C_{22}H_{19}F_3O_5S$ [M]$^+$: 452.08998; found: 452. 08986.

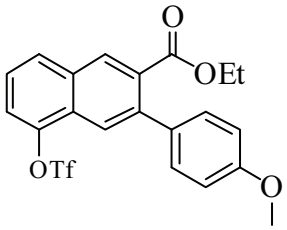
Ethyl 3-(4-*tert*-butylphenyl)-5-(trifluoromethylsulfonyloxy)-2-naphthoate (30c):



Starting with **28** (100 mg, 0.2 mmol), 4-*tert*-butylphenylboronic acid **3e** (36 mg, 0.2 mmol), $Pd(PPh_3)_4$ (7 mg, 3 mol-%), K_3PO_4 (63 mg, 0.3 mmol) and THF (4 mL), **30c** was isolated as a colourless solid (73 mg, 75%); mp 124-126 ^{o}C. ^{1}H NMR (300 MHz, $CDCl_3$): δ = 0.89 (t, J = 7.1 Hz, 3H, CH_3), 1.30 (s, 9H, $3CH_3$), 4.06 (q, J = 7.1 Hz, 2H, CH_2O), 7.27 (d, J = 8.7 Hz, 2H, ArH), 7.39 (d, J = 8.5 Hz, 2H, ArH), 7.46-7.48 (m, 2H, ArH), 7.88 (dd, J = 0.5, 7.0 Hz, 1H, ArH), 7.99 (s, 1H, ArH), 8.30 (s, 1H, ArH). ^{13}C NMR (75.5 MHz, $CDCl_3$): δ = 13.5 (CH_3), 31.3 ($3CH_3$), 34.6 (C), 61.3 (CH_2O), 118.7 (q, $J_{F,C}$ = 320.5 Hz, CF_3), 119.7, 122.3, 125.2, 125.8 (CH), 127.1 (C), 128.1, 129.0, 130.4 (CH), 131.8, 133.0, 137.6, 140.7, 145.4, 150.6 (C), 168.0 (CO). ^{19}F NMR (282.4 MHz, $CDCl_3$): δ = -73.07. IR (KBr, cm^{-1}): ν = 1708 (s), 1636, 1600, 1562, 1518, 1477, 1462 (w), 1446 (m), 1395 (s), 1366 (m),

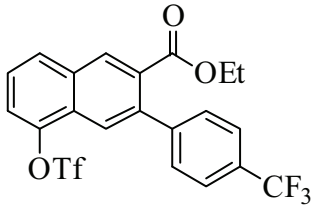
1318, 1309 (w), 1277, 1259, 1241 (m), 1213, 1202, 1192, 1153, 1130, 1120, 1099 (s), 1060, 1022 (m), 1007, 958 (s), 922 (w), 898 (m), 885 (s), 847, 842 (m), 815, 799 (s), 784, 766, 744, 736, 714, 693 (m), 655 (s), 633 (m), 603, 583, 572 (s), 552 (m). GC-MS (EI, 70 eV): *m/z* (%) = 480 ([M]$^+$, 54), 465 (68), 347 (100), 332 (73). HRMS (EI, 70 eV): calcd for $C_{24}H_{23}F_3O_5S$ [M]$^+$: 480.12128; found: 480.12190.

Ethyl 3-(4-methoxyphenyl)-5-(trifluoromethylsulfonyloxy)-2-naphthoate (30d):



Starting with **28** (100 mg, 0.2 mmol), 4-methoxyboronic acid **3f** (30 mg, 0.2 mmol), $Pd(PPh_3)_4$ (7 mg, 3 mol-%), K_3PO_4 (63 mg, 0.3 mmol) and THF (4 mL), **30d** was isolated as a yellow oil (57 mg, 63%). ^{1}H NMR (300 MHz, $CDCl_3$): δ = 1.38 (t, J = 7.1 Hz, 3H, CH_3), 3.83 (s, 3H, CH_3O), 4.42 (q, J = 7.1 Hz, 2H, CH_2O), 6.97-7.00 (m, 2H, ArH), 7.18 , 7.51-7.54 (m, 2H, ArH), 7.53 (dd, J = 1.5, 7.1 Hz, 1H, ArH), 7.58 (t, J = 7.8 Hz, 1H, ArH), 7.77 (s, 1H, ArH), 7.89 (d, J = 7.8 Hz, 1H, ArH), 8.61 (s, 1H, ArH). ^{13}C NMR (62.9 MHz, $CDCl_3$): δ = 14.1 (CH_3), 55.3 (CH_3O), 62.1 (CH_2O), 114.1 (CH), 118.6 (q, $J_{F,C}$ = 321.1 Hz, CF_3), 119.7 (CH), 122.2 (C), 127.6, 128.2, 130.2, 130.8 (CH), 131.1, 131.9, 133.5 (C), 134.9 (CH), 140.2, 145.0, 159.5 (C), 163.9 (CO). ^{19}F NMR (282.4 MHz, $CDCl_3$): δ = -73.20. IR(KBr, cm^{-1}): ν = 1716 (s), 1621 (m), 1592, 1574, 1553, 1514 (w), 1496 (m), 1467, 1453, 1440 (w), 1410, 1397 (s), 1365, 1354, 1315, 1305 (w), 1276, 1245, 1206, 1177, 1137, 1109 (s), 1059 (w), 1044 (m), 1030 (s), 1014, 1008 (m), 966, 960, 945, 939 (w), 929, 906 (m), 881, 823, 802 (s), 788, 775, 767 (m), 752 (s), 719 (m), 684 (w), 669 (m), 639 (w), 607, 587, 572 (m), 546, 538 (w). GC-MS (EI, 70 eV): *m/z* (%) = 454 ([M]$^+$, 75), 275 (100), 248 (19), 205 (13), 176 (23). HRMS (EI, 70 eV): calcd for $C_{21}H_{17}F_3O_6S$ [M]$^+$: 454.06925; found: 454.06977.

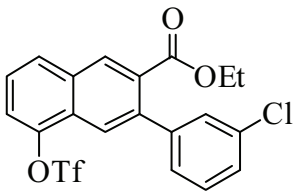
Ethyl 3-(4-trifluoromethylphenyl)-5-(trifluoromethylsulfonyloxy)-2-naphthoate (30e):



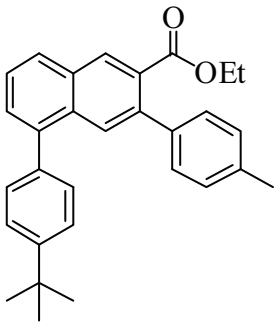
Starting with **28** (100 mg, 0.2 mmol), 4-trifluoromethylphenylboronic acid **3j** (38 mg, 0.2 mmol), $Pd(PPh_3)_4$ (7 mg, 3 mol-%), K_3PO_4 (63 mg, 0.3 mmol) and THF (4 mL), **30e** was isolated as a yellow oil (64 mg, 65%). ^{1}H NMR (300 MHz, $CDCl_3$): δ = 1.39 (t, J = 7.1 Hz, 3H, CH_3), 4.44 (q, J = 7.1 Hz, 2H, CH_2O), 7.51 (d, J = 7.9, 2H, ArH), 7.56 (dd, J = 1.2, 7.1 Hz, 1H, ArH), 7.61-7.66 (m, 2H, ArH), 7.73 (d, J = 8.0, 2H, ArH), 7.97 (d, J = 8.1, 1H,

ArH), 8.66 (s,1H, ArH). ^{13}C NMR (75.4 MHz, $CDCl_3$): δ = 14.1 (CH_3), 62.32 (CH_2O), 117.0 (q, $J_{F,C}$ = 321.0 Hz, CF_3), 119.1 (CH), 122.7 (C), 123.1 (q, $J_{F,C}$ = 271.3 Hz, CF_3), 125.6 (q, J = 3.8 Hz) (CH), 126.0 (C), 127.6, 129.3, 130.1, 130.4 (CH), 131.8, 132.9 (C), 135.1 (CH), 138.9, 142.5, 145.3 (C), 163.7 (CO). ^{19}F NMR (282.4 MHz, $CDCl_3$): δ = -73.24, -62.55. IR (KBr, cm^{-1}): ν = 1720 (s), 1681,1619, 1596, 1500, 1481, 1455 (w), 1425 (s), 1408 (m), 1367, 1354 (s), 1425 (s), 1408 (m), 1367, 1354 (w), 1327, 1284, 1277 (s), 1249, 1240 (m), 1199 (s), 1157 (m), 1133, 1126, 1104, 1069, 1045, 1015 (s), 952 (w), 940, 907 (m), 849, 883 (s), 842 (m), 826, 801 (s), 773, 765, 757, 724 (m), 706 (w), 662, 647, 635 (m), 608, 598, 585 (s), 544 (w). GC-MS (EI, 70 eV): *m/z* (%) = 492 ([M]$^+$, 54), 313 (100), 257 (36). HRMS (EI, 70 eV): calcd for $C_{21}H_{14}F_6O_5S$ [M]$^+$: 492.04606; found: 492.04653.

Ethyl 3-(3-chlorophenyl)-5-(trifluoromethylsulfonyloxy)-2-naphthoate (30f): Starting with **28** (100 mg, 0.2 mmol), 3-chlorophenylboronic acid **3q** (31 mg, 0.2 mmol), $Pd(PPh_3)_4$ (7 mg, 3 mol-%), K_3PO_4 (63 mg, 0.3 mmol) and THF (4 mL), **30f** was isolated as a colourless solid (75 mg, 82%); mp 102-103 °C. ^{1}H NMR (300 MHz, $CDCl_3$): δ = 1.01 (t, J = 7.1 Hz, 3H, CH_3), 4.11 (q, J = 7.1 Hz, 2H, CH_2O), 7.18-7.23 (m, 1H, ArH), 7.30-7.32 (m, 3H, ArH), 7.51 (d, J = 2.5 Hz, 1H, ArH), 7.52 (s, 1H, ArH), 7.90-7.93 (m, 2H, ArH), 8.38 (s, 1H, ArH). ^{13}C NMR (62.9 MHz, $CDCl_3$): δ = 13.7 (CH_3), 61.5 (CH_2O), 119.3 (q, $J_{F,C}$ = 320.6 Hz, CF_3), 120.1, 122.6, 126.3, 126.7 (CH), 127.1 (C), 127.7, 128.6, 129.0, 129.4, 131.1 (CH), 133.2, 134.0, 139.3, 142.5, 145.4 (C) , 167.5 (CO). ^{19}F NMR (282.4 MHz, $CDCl_3$): δ = -73.03. IR (KBr, cm^{-1}): ν = 1712 (s), 1639 (w), 1593, 1567 (m), 1475 (w), 1443 (m), 1414 (s), 1396, 1368 (m), 1302, 1280 (w), 1258, 1240 (m), 1211, 1199 (s), 1157 (w), 1135 (m), 1106, 1092, 1064 (m), 1016 (s), 959, 923, 914, 897 (w), 880 (s), 842 (w), 818, 793, 786 (s), 758, 741, 715, 706, 684, 670 (w), 642 (m), 618 (w), 600 (s), 575, 555 (w). GC-MS (EI, 70 eV): *m/z* (%) = 458 ([M]$^+$, 31), 325 (100), 245 (9), 217 (13). HRMS (EI, 70 eV): calcd for $C_{20}H_{14}ClF_3O_5S$ [M]$^+$: 458.01971; found: 458.01984.

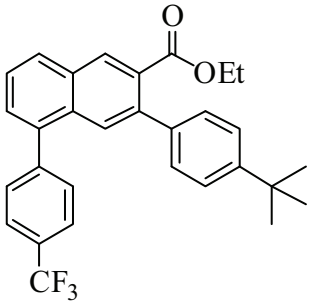


Ethyl 3-(4-methylphenyl)-5-(4-*tert*-butylphenyl)-2-naphthoate (31a): Starting with



30a (100 mg, 0.23 mmol), $Pd(PPh_3)_4$ (7 mg, 3 mol-%), K_3PO_4 (63 mg, 0.3 mmol), 4-*tert*-butylphenylboronic acid **3e** (41 mg, 0.23 mmol) and THF (4 mL), **31a** was isolated as a colourless solid (67 mg, 70%). Reaction temperature: 60 °C for 12 h. M.P. 142-145 °C. ^{1}H NMR (300 MHz, $CDCl_3$): δ = 1.00 (t, J = 7.1 Hz, 3H, CH_3), 1.30 (s, 9H, $3CH_3$), 2.29 (s, 3H, CH_3), 4.08 (q, J = 7.1 Hz, 2H, CH_2O), 7.09-7.11 (m, 2H, ArH), 7.14-7.17 (m, 2H, ArH), 7.32-7.36 (m, 2H, ArH), 7.38-7.41 (m, 2H, ArH), 7.42 (d, J , 1.6 Hz, 1H, ArH), 7.48 (t, , J = 7.7 Hz, 1H, ArH), 7.84 (dd, J = 1.2, 7.6 Hz, 1H, ArH), 7.87 (s, 1H, ArH), 8.33 (s, 1H,ArH). ^{13}C NMR (62.9 MHz, $CDCl_3$): δ = 13.6 (CH_3), 21.1 (CH_3), 31.4 ($3CH_3$), 33.5 (C), 61.0 (CH_2O), 124.3, 125.1, 126.8, 126.9, 127.5, 127.6, 128.1 (CH), 128.4 (C), 128.5, 130 (CH), 130.9, 131.5, 135.6, 136.0, 137.6, 137.9, 139.2, 149.2 (C), 167.7 (CO). IR (KBr, cm^{-1}): ν = 1702 (s), 1621, 1589, 1510, 1471, 1453, 1441, 1393, 1366 (w), 1277, 1266 (s), 1238, 1194 (m), 1129 (w), 1106, 1096, 1025, 1016 (m), 985, 973, 937, 908, 897, 865, 853 (w), 833 (m), 801 (s), 784, 755 (m), 724, 699, 666, 645, 637 (w), 607, 597 (m), 565 (s). GC-MS (EI, 70 eV): *m/z* (%) = 422 ([M]$^+$,100), 407 (36). HRMS (EI, 70 eV): calcd for $C_{30}H_{30}O_2$ [M]$^+$: 422.22403; found: 422.22406.

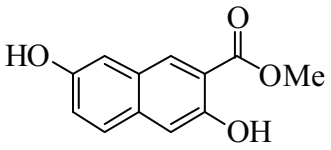
Ethyl 3-(4-*tert*-butylphenyl)-5-(4-trifluoromethylphenyl)-2-naphthoate (31b):



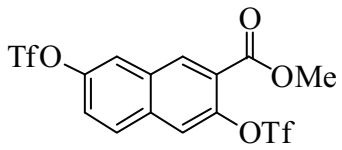
Starting with **30c** (100 mg, 0.2 mmol), $Pd(PPh_3)_4$ (7 mg, 3 mol-%), K_3PO_4 (63 mg, 0.3 mmol), 4-(trifluoromethyl)phenylboronic acid **3j** (41 mg) and THF (4 mL), **31b** was isolated as a colourless solid (72 mg, 73%). Reaction temperature: 60 °C for 12 h. M.P. 212-214 °C. ^{1}H NMR (300 MHz, $CDCl_3$): δ = 0.88 (t, J = 7.1 Hz, 3H, CH_3), 1.26 (s, 9H, $3CH_3$), 4.05 (q, J = 7.1 Hz, 2H, CH_2O), 7.18-7.19 (m, 2H, ArH), 7.33 (d, J = 8.4 Hz, 2H, ArH), 7.42 (d, J = 1.2, 7.1 Hz, 1H, ArH), 7.52-7.55 (m, 3H, ArH), 7.67 (d, J = 8.1 Hz, 2H, ArH), 7.73 (s, 1H, ArH), 7.92 (d, J = 8.1, 1H, ArH), 8.35 (s, 1H, ArH). ^{13}C NMR (62.9 MHz, $CDCl_3$): δ = 13.5 (CH_3), 31.3 ($3CH_3$), 34.5 (C), 61.0 (CH_2O), 122.4 (q, $J_{F,C}$ = 272.2 Hz, CF_3), 124.9, 125.4 (q, J = 3.8 Hz), 126.0, 127.0, 128.2, 128.9, 129.1 (CH), 129.7 (q, J_{CF} = 32.3 Hz), 130.2 (C), 130.3, 131.0 (CH), 132.0, 132.1, 138.5, 138.7,

139.1, 143.8, 150.1 (C), 168.8 (CO). ^{19}F NMR (282.4 MHz, $CDCl_3$): δ = -62.4. IR (KBr, cm^{-1}): ν = 1715 (s), 1616, 1591, 1514, 1475, 1454, 1403, 1365 (w), 1322, 1269 (s), 1238, 1194 (m), 1163, 1122, 1107, 1089, 1066, 1017 (s), 985 (m), 921 (w), 901, 854 (m), 839, 800 (s), 786, 752 (m), 707, 652, 640 (w), 610, 587, 570 (m), 534 (w). GC-MS (EI, 70 eV): *m/z* (%) = 476 ($[M]^+$, 53), 462 (32), 461 (100). HRMS (EI, 70 eV): calcd for $C_{30}H_{27}F_3O_2$ $[M]^+$: 476.19577; found: 476.19558.

Methyl 3,7-dihydroxy-2-naphthoate (33): To a solution of 3,7-dihydroxy-2-naphthoic acid **32** (2.0 g, 9.79 mmol) in (30 mL) DMF, dimethyl sulfate (2.76 g, 21.93 mmol) and *N,N*-diisopropylethylamine (1.4 g, 10.76 mmol) were added. The reaction mixture was heated for 1 h at 85 °C. After cooling to room temperature, it was poured in a crash ice the white solid precipitate was filtered and the filtered was concentrated in vacuo. The product **33** was isolated by column chromatography (flash silica gel, heptane/EtOAc) as a yellow solid (1.6 g, 77%); mp 101-102 °C. ^{1}H NMR (300 MHz, $CDCl_3$): δ = 3.95 (s, 3H, OCH_3), 4.79 (s, 1H, OH), 7.04-7.05 (m, 1H, ArH), 7.08 (dd, *J* = 2.4, 8.8 Hz, 1H, ArH), 7.20 (s, 1H, ArH), 7.55 (d, *J* = 8.9 Hz, 1H, ArH), 8.25 (s, 1H, ArH), 10.19 (s, 1H, OH). ^{13}C NMR (62.90 MHz, $CDCl_3$): = 52.5 (OCH_3), 110.1, 111.8 (CH), 114.6 (C), 121.6 (CH), 127.7 (C), 128.1, 130.3 (CH), 133.4, 151.7, 154.7 (C), 170.2 (CO). IR (KBr, cm^1): ν = 3328 (m), 3038, 3003, 2953 (w), 1681 (m), 1651, 1633, 1609, 1576, 1556 (w), 1531 (m), 1505, 1479, 1462 (w), 1441, 1392, 1345, 1263, 1214 (s), 1180, 1147, 1130, 1072 (m), 1012, 969 (w), 944, 903, (w), 860 (s), 836, 812 (m), 783 (s), 746 (w), 716 (s), 665, 620, 610 (w), 587, 550 (w). GC-MS (EI, 70 eV): *m/z* (%) = 219 ($[M+H]^+$, 8), 218 ($[M]^+$, 52), 187 (17), 186 (100), 185 (10), 159 (10), 158 (80), 130 (45), 102 (20). HRMS (EI, 70 eV) calcd for $C_{12}H_{10}O_4$ $[M]^+$: 218.0579; found: 218.0599.



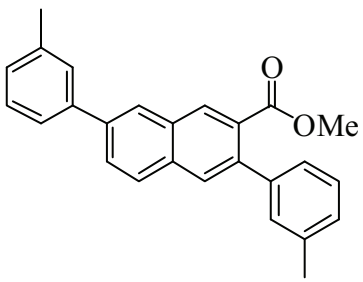
Methyl 3,7-bis(4-(trifluoromethyl)sulfonyloxyphenyl)-2-naphthoate (34): To a CH_2Cl_2 solution (46 ml) of **33** (1.0 g, 4.6 mmol) was added pyridine (1.5 ml, 18.4 mmol) and the solution was stirred at 20 °C for 10 min under argon atmosphere. Then Tf_2O (1.8 mL, 11.0 mmol) was added at –78 °C and the reaction mixture was allowed to warm to room temperature and was stirred for 14 h. The reaction mixture was filtered and the



filtrate was concentrated in vacuo. The product **34** was isolated by column chromatography (flash silica gel, heptane/EtOAc) as a colourless solid (1.9 g, 87%); mp 75-77 °C. ^{1}H NMR (300 MHz, $CDCl_3$): δ = 4.06 (s, 3H, OCH_3), 7.47-7.70 (m, 1H, ArH), 7.85 (s, 1H, ArH), 7.94 (d, J = 2.3 Hz, 1H, ArH), 8.03 (d, J = 9.0 Hz, 1H, ArH), 8.72 (s, 1H, ArH). ^{13}C NMR (62.90 MHz, $CDCl_3$ = 52.99 (OCH_3), 117.7 (q, $J_{F,C}$ = 320.2 Hz, CF_3), 117.9 (q, $J_{F,C}$ = 320.8 Hz, CF_3), 120.4, 121.2, 123.6 (CH), 130.5 (C), 130.5 (CH), 131.8, 133.8 (C), 134.6 (CH), 145.5, 148.3 (C), 163.7 (CO). IR (KBr, cm^1): ν = 3070, 2963 (w), 1713 (s), 1678, 1633 (w), 1599 (m), 1502, 1461, 1443 (w), 1426, 1398 (s), 1365, 1309 (m), 1276 (s), 1249 (m),1203, 1131, 1116, 1048 (s), 965 (w), 937, 909, 937, 909, 845, 813, 795 (s), 779, 766, 754, 739 (m), 697 (w), 676 (m), 650, 609, (s), 597, 582 (m), 565 (w). GC-MS (EI, 70 eV): *m/z* (%) = 483 ($[M+H]^+$, 10), 482 ($[M]^+$, 61), 451 (16), 350 (14), 349 (100), 257 (24), 129 (17). HRMS (ESI-TOF/MS) calcd for $C_{14}H_9F_6O_8S_2$ $[M+H]^+$: 482.96375; found: 482.96348.

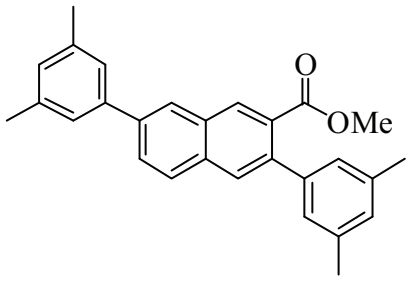
General Procedure for the synthesis of 35a-j: A solution of **34** (75mg, 0.155 mmol), K_3PO_4 (3.0 equiv.), $Pd(PPh_3)_4$ (6 mmol-%) and arylboronic acid **3** (2.0 equiv.) in 1,4-dioxane (3 mL) was stirred at room temperature for 4 h under argon atmosphere. To the reaction mixture H_2O (20 mL) and CH_2Cl_2 (25 mL) were added. The organic and the aqueous layers were separated and the latter was extracted with CH_2Cl_2 (2 x 20 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, heptane/EtOAc).

Methyl 3,7-di-*m*-tolyl-2-naphthoate (35a): Starting with **34** (75 mg, 0.155 mmol), **3b** (42 mg, 0.31 mmol), $Pd(PPh_3)_4$ (10.7 mg, 6 mol-%, 0.0093 mmol), K_3PO_4 (98.5 mg, 0.465 mmol), and 1,4-dioxane (3 mL), **35a** was isolated as a white solid (46 mg, 81%), mp 132-134 °C**.** ^{1}H NMR (300 MHz, $CDCl_3$): δ = 2.33 (s, 3H, CH_3), 2.36 (s, 3H, CH_3)3.61 (s, 3H, OCH_3), 7.08-7.16 (m, 4H, ArH), 7.19-7.31 (m, 2H, ArH), 7.42 (d, J = 7.3 Hz, 2H, ArH), 7.71-7.75 (m, 2H, ArH), 7.79 (d, J = 8.6 Hz, 1H, ArH), 8.00 (br s, 1H, ArH), 8.32 (s, 1H, ArH). ^{13}C NMR (62.9 MHz, $CDCl_3$): = 21.5, 21.6 (CH_3), 52.0 (OCH_3), 125.6,

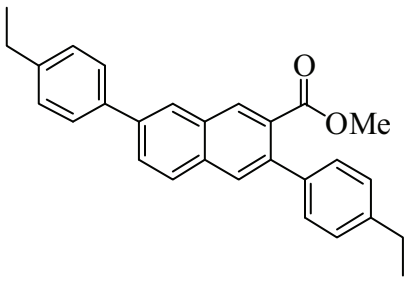


126.2, 127.9, 128.0, 128.1, 128.2, 128.4, 128.8, 129.1, 129.4 (CH), 129.6 (C), 131.1 (CH), 131.8, 133.4, 138.5, 138.8, 139.5, 140.5, 141.3 (C), 169.1 (CO). IR (KBr, cm^{1}): ν = 3453, 3022, 2946, 2920, 2853, 2731, 1934, 1868, 1783 (w), 1719 (s), 1630 (w), 1597, 1582, 1482, 1454, 1432 (m), 1400, 1376, 1315 (w), 1278, 1253, 1219 (s), 1193, 1169, 1147 (m), 1089 (s), 1038, 1022, 999, 987, 965, 940 (w), 914, 893 (m), 847, 818, 802 (w), 781 (s), 762, 731, 709 (w), 692 (s), 673, 647, 625, 609, 566 (w). GC-MS (EI, 70 eV): *m/z* (%) = 367 ($[M+H]^+$, 27), 366 ($[M]^+$, 100), 335 (16), 317 (12). HRMS (EI, 70 eV) calcd for $C_{26}H_{22}O_2$ $[M]^+$: 366.16143; found: 366.161284.

Methyl 3,7-bis(3,5-dimethylphenyl)-2-naphthoate (35b): Starting with **34** (75 mg, 0.155 mmol), **3c** (47 mg, 0.31 mmol), $Pd(PPh_3)_4$ (10.7 mg, 6 mol-%, 0.0093 mmol), K_3PO_4 (98.5 mg, 0.465 mmol), and 1,4-dioxane (3 mL), **35b** was isolated as a white solid (50 mg, 83%), mp 175-176 °C**.** ^{1}H NMR (300 MHz, $CDCl_3$): δ = 2.28 (s, 6H, $2CH_3$), 2.32 (s, 6H, $2CH_3$), 3.62 (s, 3H, OCH_3), 6.92 (br s, 1H, ArH), 6.95 (br s, 3H, ArH), 7.24 (br s, 2H, ArH), 7.70-7.74 (m, 2H, ArH), 7.78-7.80 (d, J = 8.6 Hz, 1H, ArH), 7.99 (br s, 1H, ArH), 8.29 (s, 1H, ArH). ^{13}C NMR (75.46 MHz, $CDCl_3$): = 21.3, 21.4 ($4CH_3$), 52.0 (OCH_3), 125.3, 126.1, 126.3, 128.0, 128.1, 128.8, 129.3 (CH), 129.7 (C), 130.9 (CH), 131.7, 133.4, 137.5, 138.4, 138.8, 139.5, 140.5, 141.2 (C), 169.2 (CO). IR (KBr, cm^{1}): ν = 3453, 3026, 2986, 2944, 2914, 2857, 1935, 1841, 1787 (w), 1734 (s), 1693 (w), 1589 (m), 1496, 1454, 1443, 1430, 1397, 1375, 1462, 1325 (w), 1282 (m), 1268, 1258 (s), 1226, 1203, 1192, 1147 (m), 1100 (s), 1047 (m), 969, 943 (w), 922 (s), 897, 943 (w), 922, 897 (m), 852 (s), 833, 8220, 792 (m), 771, 760, 734, 721, 702 (w), 689 (s),637, 622, 608, 574, 559, 543, 535 (w). GC-MS (EI, 70 eV): *m/z* (%) = 395 ($[M+H]^+$, 30), 394 ($[M]^+$, 100), 363 (13). HRMS (EI, 70 eV) calcd for $C_{28}H_{26}O_2$ $[M]^+$: 394.19273; found: 394.192591.

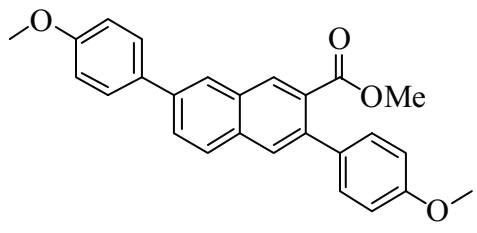


Methyl 3,7-bis(4-ethylphenyl)-2-naphthoate (35c): Starting with **34** (75 mg, 0.155 mmol), **3d** (47 mg, 0.31 mmol), $Pd(PPh_3)_4$ (10.7 mg, 6 mol-%, 0.0093 mmol), K_3PO_4 (98.5 mg, 0.465 mmol), and 1,4-dioxane (3 mL), **35c** was isolated as a white

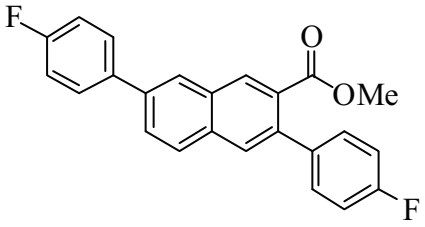


solid (47 mg, 77%), mp 89-89 °C. ^{1}H NMR (300 MHz, $CDCl_3$): δ = 1.21 (t, J = 7.2 Hz, 6H, $2CH_3$), 2.63 (q, J = 7.3 Hz, 4H, $2CH_2$), 3.63 (s, 3H, OCH_3), 7.14-7.19 (m, 2H, ArH), 7.23-7.26 (m, 5H, ArH), 7.56 (d, J = 7.55 Hz, 1H, ArH), 7.72-7.75 (m, 2H, ArH), 7.80 (d, J = 8.6 Hz, 1H, ArH), 8.00 (br s, 1H, ArH), 8.23 (s, 1H, ArH). ^{13}C NMR (62.90 MHz, $CDCl_3$) = 14.4, 14.5 ($2CH_3$), 27.5, 28.6 ($2CH_2$), 52.0 (OCH3), 124.8, 126.2, 126.5, 126.8, 127.1, 127.4, 127.5, 128.3 (CH), 128.5 (C), 130.0 (CH), 130.7, 132.3, 136.8, 137.6, 137.6, 138.2, 142.0, 142.8 (C), 168.1 (CO). IR (KBr, cm^1): ν = 3051, 3021, 2960, 2926, 2870, 1908, 1798 (w), 1733, 1719 (s), 1650, 1630, 1597, 1565 (w), 1513, 1489, 1454, 1431 (m), 1401, 1372, 1318 (w), 1282, 1268, 1252, 1414 (s), 1183, 1149 (m), 1117 (w), 1095, 1084 (s), 1049, 1022, 1016, 991, 964, 949 (w), 918, 899 (m), 836, 815, 802, 787 (s), 764, 734, 698, 653, 641, 618 (w), 601 (m), 572, 553, 536 (w). GC-MS (EI, 70 eV): *m/z* (%) = 395 ([M+H]$^+$, 29), 394 ([M]$^+$, 100), 379 (25). HRMS (EI, 70 eV) calcd for $C_{28}H_{26}O_2$ [M]$^+$: 398.15126; found: 398.151064.

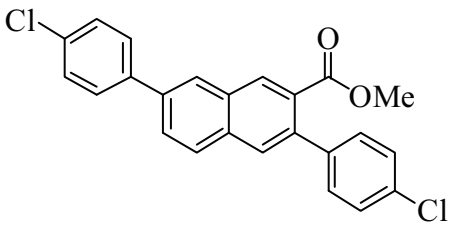
Methyl 3,7-bis(4-methoxyphenyl)-2-naphthoate (35d): Starting with **34** (75 mg, 0.155 mmol), **3f** (47 mg, 0.31 mmol), $Pd(PPh_3)_4$ (10.7 mg, 6 mol-%, 0.0093 mmol), K_3PO_4 (98.5 mg, 0.465 mmol), and 1,4-dioxane (3 mL), **35d** was isolated as a white solid (52 mg, 85%), mp 174-175 °C. ^{1}H NMR (300 MHz, $CDCl_3$): δ = 3.64 (s, 3H, OCH_3), 3.77 (s, 3H, OCH_3), 3.78 (s, 3H, OCH_3), 6.87 (d, J = 8.7 Hz, 2H, ArH), 6.94 (d, J = 8.7 Hz, 2H, ArH), 7.25 (d, J = 8.7 Hz, 2H, ArH), 7.56 (d, J = 8.7 Hz, 2H, ArH), 7.68-7.72 (m, 2H, ArH), 7.79 (d, J = 8.4 Hz, 1H, ArH), 7.95 (br s, 1H, ArH),i 8.29 (s, 1H, ArH). ^{13}C NMR (75.46 MHz, $CDCl_3$): = 52.1, 55.3, 55.4 (OCH_3), 113.6, 114.4, 115.4, 127.7, 128.1, 128.4, 129.3, 129.6, 130.9 (CH), 131.7, 133.0, 133.2, 133.8, 138.1, 138.9, 158.9, 159.5 (C), 169.2 (CO). IR (KBr, cm^1): ν = 3037, 3007, 2962, 2936, 2836, 1908, 1893 (w), 1722 (s), 1681, 1651, 1644, 1638 (w), 1608 (m), 1571 (w), 1513, 1489, 1416, 1452, 1430 (m), 1402, 1376, 1357, 1322, 1304 (m), 1283, 1274, 1262, 1241, 1209, 1174 (s), 1143, 1109, 1091,1082, 1038 (m), 1024 (s), 989, 955, 938, 881 (w), 833, 819, 805, 791 (s), 777, 762 (m), 734, 723, 700, 687, 653, 636, 617 (w), 596, 589, 565, 551, 540 (m). GC-MS (EI, 70 eV): *m/z* (%) = 399 ([M+H]$^+$, 23), 398 ([M]$^+$, 100), 384 (10). HRMS (EI, 70 eV) calcd for $C_{26}H_{22}O_4$ [M]$^+$: 398.15126; found: 398.151064.



Methyl 3,7-bis(4-fluorophenyl)-2-naphthoate (35e): Starting with **34** (75 mg, 0.155 mmol), **3g** (43 mg, 0.31 mmol), $Pd(PPh_3)_4$ (10.7 mg, 6 mol-%, 0.0093 mmol), K_3PO_4 (98.5 mg, 0.465 mmol), and 1,4-dioxane (3 mL), **35e** was isolated as a white solid (43 mg, 75%), mp 132-134 °C**.** ^{1}H NMR (300 MHz, $CDCl_3$): δ = 3.64 (s, 3H, OCH_3), 7.00-7.16 (m, 4H, ArH), 7.25-7.30 (m, 2H, ArH), 7.55-7.60 (m,2H, ArH), 7.69-7.71 (m, 2H, ArH), 7.82 (d, J = 8.9 Hz, 1H, ArH), 7.96 (br s, 1H, ArH), 8.32 (s, 1H, ArH). ^{13}C NMR (75.46 MHz, $CDCl_3$): = 52.1 (OCH_3), 115.0 (d, J = 21.7 Hz), 115.9 (d, J = 21.7 Hz), 126.1, 127.9, 128.3, 128.9 (d, J = 8.0 Hz), 129.5, 130.1 (d, J = 8.0 Hz), 131.3 (CH), 131.8, 133.4, 136.6 (d, J = 21.7 Hz), 137.4 (d, J = 21.7 Hz), 137.9, 138.6 (C), 163.9 (d, $J_{F,C}$ = 246.6 Hz) (CF), 164.4 (d, $J_{F,C}$ = 246.6 Hz) (CF). 168.8 (CO). IR (KBr, cm^1): ν = 3409, 3078, 3056, 3039, 2954, 2918, 2849, 1897 (w), 1711 (s), 1673, 1651, 1631, 1604 (w), l508, 1487 (m), 1462 (w), 1434 (s), 1398, 1376, 1319, 1299 (w), 1279, 1258, 1216 (s), 1178, 1160, 1151, 1094 (m), 1030, 1013 (w), 1094 (s), 1030, 1013, 991, 956, 944, 929, 908, 903, 890 (w), 836, 808 (s), 781, 763, 729, 718, 700, 686, 652, 636, 612 (w), 603, 589, 560, 536 (m). GC-MS (EI, 70 eV): *m/z* (%) = 375([M+H]$^+$, 26), 374 ([M]$^+$, 100), 343 (26), 325 (17), 314 (14), 412 (13), 294 (14). HRMS (EI, 70 eV) calcd for $C_{24}H_{16}F_2O_2$ [M]$^+$: 374.11129; found: 374.110959.

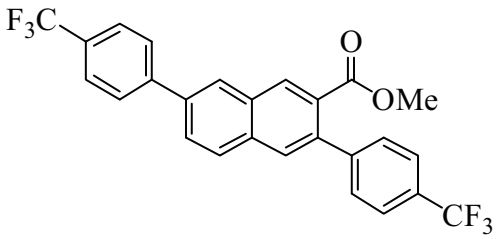


Methyl 3,7-bis(4-chlorophenyl)-2-naphthoate (35f): Starting with **34** (75 mg, 0.155 mmol), **3h** (48 mg, 0.31 mmol), $Pd(PPh_3)_4$ (10.7 mg, 6 mol-%, 0.0093 mmol), K_3PO_4 (98.5 mg, 0.465 mmol), and 1,4-dioxane (3 mL), **35f** was isolated as a white solid (45 mg, 72%), mp 152-154 °C**.** ^{1}H NMR (300 MHz, $CDCl_3$): δ = 3.64 (s, 3H, OCH_3), 7.22 (d, J = 8.7, 2H, ArH), 7.30 (d, J = 8.7, 2H, ArH), 7.36 (d, J = 8.7, 2H, ArH), 7.53 (d, J = 8.7, 2H, ArH), 7.67-7.70 (m, 2H, ArH), 7.80 (d, J = 8.7, 1H, ArH), 7.97 (br s, 1H, ArH), 8.36 (s, 1H, ArH). ^{13}C NMR (62.90 MHz, $CDCl_3$): ^{13}C NMR (62.90 MHz, $CDCl_3$ = 52.2 (OCH_3), 126.2, 127.7, 128.2, 128.4, 128.5, 129.1, 129.5, 129.8, 131.5 (CH), 131.8, 133.3, 133.5, 133.9, 137.8, 138.4, 139.8 (C), 168.4 (CO). IR (KBr, cm^1): ν = 3434, 3082, 3055, 3031, 2950, 2921, 2848, 1910 (w), 1721 (s), 1681, 1667, 1650,1644,

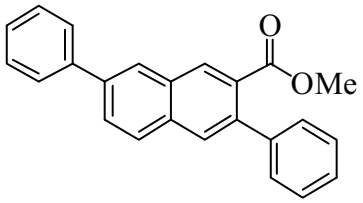


1631, 1573, 1565, 1556 (w), 1484, 1455, 1435 (m), 1374, 1357, 1317 (w), 1279, 1246, 1215 (s), 1189, 1177, 1149 (w), 1085 (s), 1010, 989 (m), 957, 946 (w), 917, 892 (m), 832, 815, 803 (s), 781, 758, 732 (m), 721, 682, 665, 645, 646, 599, 575, 564 (w). GC-MS (EI, 70 eV): *m/z* (%) = 409 ($[M+H]^+$, ^{35}Cl, ^{37}Cl, 17), 408 ($[M]^+$, ^{35}Cl, ^{37}Cl, 68), 407 ($[M+H]^+$, $^{35}Cl_2$, 26), 406 ($[M]^+$, $^{35}Cl_2$, 100), 375 (14), 342 (14), 340 (141), 312 (20), 276 (26), 186 (12). HRMS (EI, 70 eV) calcd for $C_{24}H_{16}O_2Cl_2$ ($[M]^+$, ^{35}Cl, ^{37}Cl): 408.04924; found: 408.049594. calcd for $C_{24}H_{16}O_2Cl_2$ ($[M]^+$, $^{35}Cl_2$): 406.05219, found: 406.0051426.

Methyl 3,7-bis[4-(trifluoromethyl)phenyl]-2-naphthoate (35g): Starting with **34** (75 mg, 0.155 mmol), **3j** (59 mg, 0.31 mmol), $Pd(PPh_3)_4$ (10.7 mg, 6 mol-%, 0.0093 mmol), K_3PO_4 (98.5 mg, 0.465 mmol), and 1,4-dioxane (3 mL), **35g** was isolated as a white solid (52 mg, 71%), mp 161-164 °C**.** ^{1}H NMR (300 MHz, $CDCl_3$): δ = 3.64 (s, 3H, OCH_3), 7.42 (d, *J* =8.0 Hz, 2H, ArH), 7.58-7.64 (m, 4H, ArH), 7.72-7.77 (m, 4H, ArH), 7.85 (d, *J* = 8.6 Hz, 1H, ArH), 8.05 (br s, 1H, ArH), 8.44 (s, 1H, ArH).^{13}C NMR (75.46 MHz, $CDCl_3$): = 52.2 (OCH_3), 125.0 (q, *J* = 3.7 Hz), 125.9 (q, *J* = 3.7 Hz), 126.0 (q, $J_{F,C}$ = 272.0 Hz, CF_3), 126.1 (q, $J_{F,C}$ = 271.4 Hz, CF_3), 126.9, 127.6, 127.9, 128.7, 128.9 (CH), 129.6 (d, *J* = 32.8 Hz) (C), 129.8 (CH) 130.0 (d, *J* = 32.8 Hz) (C), 131.9 (CH), 132.0, 133.7, 138.1, 138.4, 143.8 (d, *J* = 1.1 Hz), 145.0 (*J* = 1.1 Hz) (C),168.1 (CO) .IR (KBr, cm^1): ν = 3051, 3010, 2954, 2975, 118, 2849, 2640, 1922 (w), 1699 (s), 1633, 1615, 1601, 1537, 1519, 1489, 1453, 1438, 1425, 1407, 1377 (w), 1322 (s), 1284, 1269, 1217 (m), 1189 (w), 1160, 1154, 1098, 1067 (s), 1018, 995, 966, 959, 933, 898 (m), 844, 813 (s), 786, 764, 750, 743, 689, 686, 642, 634,620 (w), 608 (m), 596, 566 (w). GC-MS (EI, 70 eV): *m/z* (%) = 475 ($[M+H]^+$, 28), 474 ($[M]^+$, 100), 443(35),423 (11), 346 (19). HRMS (ESI-TOF/MS) calcd for $C_{26}H_{16}F_6O_2$ $[M+H]^+$: 474.10490; found: 474.104997.

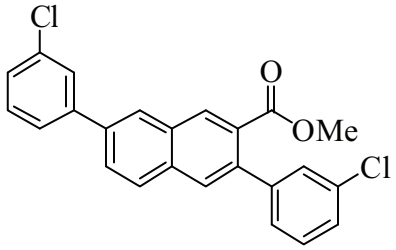


Methyl 3,7-diphenyl-2-naphthoate (35h): Starting with **34** (75 mg, 0.155 mmol), **3l** (38 mg, 0.31 mmol), $Pd(PPh_3)_4$ (10.7 mg, 6 mol-%, 0.0093 mmol), K_3PO_4 (98.5 mg, 0.465 mmol), and 1,4-dioxane (3 mL), **35h** was isolated as a white solid (39 mg, 74%), mp 132-134 °C**.** ^{1}H NMR (300



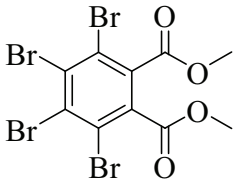
MHz, $CDCl_3$): δ = 3.60 (s, 3H, OCH_3), 7.27-7.42 (m, 8H, ArH), 7.59-7.63 (m, 2H, ArH), 7.72-7.75 (m, 2H, ArH), 7.814 (d, *J* = 8.7 Hz, 1H, ArH), 8.01 (br s, 1H, ArH), 8.34 (s, 1H, ArH). ^{13}C NMR (75.46 MHz, $CDCl_3$): = 52.0 (OCH_3), 126.2, 127.1, 127.4, 127.7, 128.0, 128.0, 128.3, 128.5, 128.9, 129.5 (CH), 129.5(C), 131.2 (CH), 131.8, 133.5, 138.8, 139.4, 140.5, 141.4 (C), 169.0 (CO). IR (KBr, cm^1): *v* = 3433, 3080, 3056, 3027, 2952, 2921, 2849 (w), 1726 (s), 1682, 1650, 1642, 1632, 1596, 1574, 1556, 1537, 1510, 1485, 1462, 1441 (w), 1429 (m), 1407, 1378, 1312 (w), 1279, 1266, 1246, 1212, 1176 (m), 1152 (w), 1093, 1075 (m), 1030, 1000, 989, 963, 925, 918, 905 (w), 896 (m), 848, 838, 817, 799, 780 (w), 764, 751, 691, 707 (s), 673 (m), 631, 616, 601, 582, 550 (w). GC-MS (EI, 70 eV): *m/z* (%) = 339 ([M+H]$^+$, 23), 338 ([M]$^+$, 100), 384 (10). HRMS (EI, 70 eV) calcd for $C_{24}H_{18}O_2$ [M]$^+$: 338.13013; found: 338.130534.

Methyl 3,7-bis(3-chlorophenyl)-2-naphthoate (35i): Starting with **34** (75 mg, 0.155 mmol), **3q** (48 mg, 0.31 mmol), $Pd(PPh_3)_4$ (10.7 mg, 6 mol-%, 0.0093 mmol), K_3PO_4 (98.5 mg, 0.465 mmol), and 1,4-dioxane (3 mL), **35i** was isolated as a white solid (44 mg, 70%), mp 88-89 °C**.** ^{1}H NMR (300 MHz, $CDCl_3$): δ = 3.64 (s, 3H, OCH_3), 7.13-7.19 (m, 1H, ArH), 7,24-7.29 (m, 3H, ArH), 7.32-7.33 (m, 1H, ArH), 7.47 (dt, *J* = 1.5, 7.3 Hz, 1H, ArH), 7.59 (t, *J* = 1.5 Hz, 1H, ArH), 7.68-7.71 (m, 2H, ArH), 7.82 (d, *J* = 8.6 Hz, 2H, ArH), 7.98 (br s, 1H, ArH), 8.36 (s, 1H, ArH). ^{13}C NMR (75.46 MHz, $CDCl_3$): = 52.2 (OCH_3), 124.4, 125.4, 125.8, 126.2, 126.4, 126.7, 126.7, 127.5, 127.5, 128.1, 128.5, 129.1, 130.6 (CH), 130.8, 132.5, 132.9, 133.8, 136.7, 137.2, 141.1, 142.1 (C), 167.2 (CO). IR (KBr, cm^1): *v* = 3435, 3016, 3017 (w), 2953, 2912, 1851 (m), 1722 (s), 1632 (w), 1592, 1564 (s), 1495 (w), 1473, 1431, 1417 (m), 1378, 1358, (w), 1315 (m), 1310 (w), 1276, 1259, 1245, 1213 (s), 1184, 1152 (m), 1097, 1091, 1080 (s), 1040, 1005, 1000, 955, 937, 923, 909 895 (w), 870 (s), 831 (w), 807, 786 (m), 772 (s), 761 (m), 746, 704, 682, 676, (s), 662 (m), 622, 609, 596, 577, 544, 532 (w). GC-MS (EI, 70 eV): *m/z* (%) = 409 ([M+H]$^+$, ^{35}Cl, ^{37}Cl, 17), 408 ([M]$^+$, ^{35}Cl, ^{37}Cl, 68), 407 ([M+H]$^+$, $^{35}Cl_2$, 26), 406 ([M]$^+$, $^{35}Cl_2$, 100), 377 (15), 375 (23), 342 (10), 340 (28), 274 (10), 185 (11). HRMS (EI, 70 eV) calcd for $C_{24}H_{16}O_2Cl_2$ ([M]$^+$, ^{35}Cl, ^{37}Cl):



408.04924; found: 408.050190. calcd for $C_{24}H_{16}O_2Cl_2$ ($[M]^+$, $^{35}Cl_2$): 406.05219, found: 406.052385.

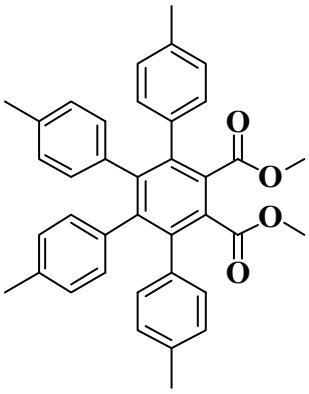
Synthesis of Dimethyl 3,4,5,6-tetrabromophthalate (38):

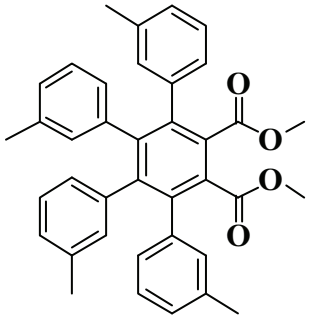


To a KOH solution (2%, 50 ml), **36** (0.5 g, 0.107 mmol) was added. The reaction mixture was reflux for 30 min. After cooling to room temperature HCl (20%, 50 ml) was added, the white precipitate was filtered and dried to give **37** (0.5 g, 96%). Then dimethyl sulfate (0.58 g, 4.5 mmol) and *N,N*-diisopropylethylamine (0.2 g, 1.56 mmol) were added to a solution of **37** (0.5 g, 1.04 mmol) in DMF (50 ml). The reaction mixture was heated for 1 h at 85 °C. After cooling to room temperature, the reaction mixture was poured into crashed ice. The precipitated white solid was filtered and dried in oven to give **38** (0.5 g, 94 %), mp 106-108 °C. NMR (300 MHz, $CDCl_3$): δ = 3.41 (s, 6H, $2OCH_3$). ^{13}C-NMR (62.9 MHz, $CDCl_3$): δ= 53.4 (OCH_3), 102.7, 132.3, 135.1, 135.1 (C), 165.1 (CO). IR (KBr, cm^{-1}): ν = 3046, 3017, 2955, 2845 (m), 1744, 1721 (s), 1682, 1532, 1506 (w), 1483, 1432, 1367, 1330 (m), 1255, 1236, 1221, 1147 (s), 1084 (m), 962 (s), 873 (w), 858 (s), 804 (m), 792 (w), 630, 619, 552 (m). GC-MS (EI, 70 eV): *m/z* (%) = 510 ($[M+1]^+$, [$^{79}Br_2$] [$^{81}Br_2$], 45), 508 ($[M+1]^+$, [^{79}Br] [^{79}Br] [^{79}Br] [^{81}Br], 29), 506 ($[M+1]^+$, [^{79}Br] [^{79}Br] [^{79}Br] [^{79}Br], 6), 483 (17), 481 (85), 480 (10), 479 (100), 477 (86), 475 (18). HRMS (EI, 70 eV): calcd for $C_{10}H_6O_4Br_4$ ($[M]^+$, [^{79}Br] [^{79}Br] [^{79}Br] [^{79}Br]): 505.69941, found 505.700002, calcd for $C_{10}H_6O_4Br_4$ ($[M]^+$, [^{79}Br] [^{79}Br] [^{79}Br] [^{81}Br]) : 507.69736, found 507.697997, calcd for $C_{10}H_6O_4Br_4$ ($[M]^+$, [$^{79}Br_2$] [$^{81}Br_2$]): 509.69532, found 509.6961.

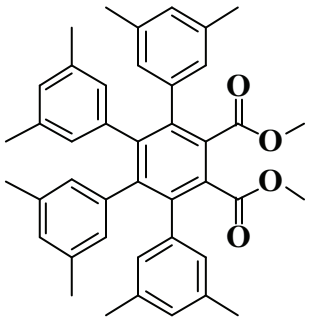
General Procedure for the synthesis of 39a-j:

A solution of **38** (75 mg, 0.147 mmol), K_2CO_3 (2M, 1.0 mL), $Pd(PPh_3)_4$ (12 mol-%) and of arylboronic acid **3** (4.5 equiv.) in 1,4-dioxane (4 mL) was stirred at 130 °C for 6 h under argon atmosphere. To the reaction mixture H_2O (20 mL) and CH_2Cl_2 (25 mL) were added at 20 °C. The organic and the aqueous layers were separated and the latter was extracted with CH_2Cl_2 (2 x 20 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, heptane/EtOAc).

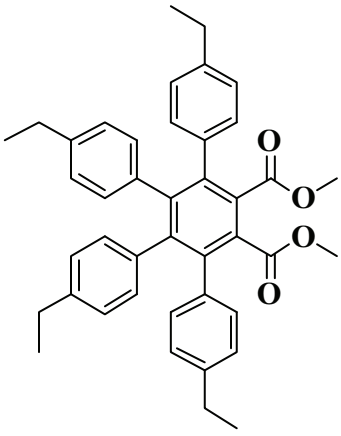
Dimethyl 3,4,5,6-tetra(*p*-tolyl)phthalate (39a): Starting with **38** (75 mg, 0.147 mmol), 
3a (90 mg, 0.661 mmol), $Pd(PPh_3)_4$ (20 mg, 12 mol%, 0.0207 mmol), K_2CO_3 (2M, 1.0 mL), and 1,4-dioxane (3 mL), **39a** was isolated as a white solid (70 mg, 86%); mp 245-247 °C. ^{1}H NMR (300 MHz, $CDCl_3$): δ = 2.01 (s, 6H, $2CH_3$), 2.15 (s, 6H, $2CH_3$), 3.41 (s, 6H, $2OCH_3$), 6.43 (d, J = 7.8 Hz, 4H, ArH), 6.57 (d, J = 7.8 Hz, 4H, ArH), 6.82 (s, 8H, ArH). ^{13}C-NMR (62.9 MHz, $CDCl_3$): δ = 21.0, 21.7 (CH_3), 52.1 (OCH_3), 127.5, 128.0, 129.5, 130.7 (CH), 132.0, 135.0, 135.8, 135.9, 136.0, 139.1, 143.3 (C), 168.9 (CO). IR (KBr, cm^{-1}): v = 3024, 2952, 2920, 2863, 2732, 1897 (w), 1738, 1727 (s), 1650, 1613, 1567, 1550 (w), 1513 (m), 1435 (s), 1419, 1392 (w), 1340, 1247, 1221, 1210, 1189, 1171 (s), 1149, 1111, 1060 (m), 1038, 1019 (w), 969 (s), 907, 890, 878, 858 , 839, 829, 814 (w), 806 (m), 791 (s), 756 (w), 727 (s), 694, 674, 660, 638, 612, 560 (w), 541 (m). GC-MS (EI, 70 eV): *m/z* (%) = 555 ($[M+1]^+$, 51), 554 ($[M]^+$, 100), 491 (24), 464 (18), 433 (9), 262 (8). HRMS (EI, 70 eV): calcd for $C_{38}H_{34}O_4$ ($[M]^+$: 554.24516, found 554.245113.

Dimethyl 3,4,5,6-tetra(*m*-tolyl)phthalate (39b): Starting with **38** (75 mg, 0.147 mmol), 
3b (90 mg, 0.661 mmol), $Pd(PPh_3)_4$ (20 mg, 12 mol%, 0.0207 mmol), K_2CO_3 (2M, 1.0 mL), and 1,4-dioxane (4 mL), **39b** was isolated as a white solid (69 mg, 85%); mp 170-173 °C.^{1}H NMR (300 MHz, $CDCl_3$): δ = 1.90 (s, 6H, $2CH_3$), 2.08 (s, 6H, $2CH_3$), 3.41 (s, 6H, $2OCH_3$), 6.40-6.46 (m, 4H, ArH), 6.55-6.65 (m, 4H, ArH), 6.73-6.82 (m, 6H, ArH), 6.89-6.97 (m, 2H, ArH). ^{13}C-NMR (74.4 MHz, $CDCl_3$): δ = 21.0, 21.2 (CH_3), 52.1 (OCH_3), 126.4, 126.8, 127.1, 127.4, 127.9, 130.5, 130.5, 131.7 (CH), 131.8, 135.9, 136.6, 138.5, 138.7, 139.1, 143.3 (C), 168.8 (CO). IR (KBr, cm^{-1}): v = 3098, 3015, 2947, 2919, 2861, 2733 (w), 1740, 1724 (s), 1605 (m), 1584, 1548, 1488 (w), 1435 (m), 1398, 1377 (w), 1344 (m), 1259, 1212, 1195, 1180, 1167, 1151 (s), 1136, 1095 (w), 1069 (m), 1038, 1000, 975, 934, 906, 883, 936, 816 (w), 779 (s), 719 (w), 707 (s), 642, 591, 576, 555 (w). GC-MS (EI, 70 eV): *m/z* (%) = 555 ($[M+H]^+$, 38), 554($[M]^+$, 100), 491 (30). HRMS (EI, 70 eV): calcd for $C_{38}H_{34}O_4$ $[M]^+$: 554.24516, found 554.244093.

Dimethyl 3,4,5,6-tetra(3,5-dimethylphyenyl)phthalate (39c): Starting with **3** (75 mg, 0.147 mmol), **3c** (99 mg, 0.661 mmol), $Pd(PPh_3)_4$ (20 mg, 12 mol%, 0.0207 mmol), K_2CO_3 (2M, 1.0 mL), and 1,4-dioxane (4 mL), **39c** was isolated as a white solid (71 mg, 80%); mp 205-207 °C. ^{1}H NMR (300 MHz, $CDCl_3$): δ = 1.87 (s, 12H, $4CH_3$), 2.04 (s, 12H, $4CH_3$), 3.42 (s, 6H, $2OCH_3$), 6.23 (br s, 4H, ArH), 6.35 (br s, 2H, ArH), 6.57 (br s, 4H, ArH), 6.61 (br s, 2H, ArH). ^{13}C-NMR (62.9 MHz, $CDCl_3$): δ = 20.8, 21.0 (CH_3), 52.0 (OCH_3), 127.0, 127.6, 128.0, 128.7 (CH), 131.4, 135.4, 136.2, 138.4, 138.6, 139.0, 143.5 (C), 168.9 (CO). IR (KBr, cm^{-1}): ν = 3022, 3002, 2943, 29181, 2730 (w), 1738, 1722, 1600 (s), 1556, 1545 (w), 1434, 1428, 1377, 1355, 1297 (m), 1282 (w), 1246, 1208, 1197 (s), 1157, 1145, 1104, 1099, 1026 (m), 996, 975, 946, 907, 901, 891, 874, 860 (w), 870, 860 (m), 841 (s), 821 (w), 808 (m), 799, 764, 727, 719, 711 (w), 700 (s), 653, 613, 591, 569, 540 (w). GC-MS (EI, 70 eV): *m/z* (%) = 611 ([M+H], 38), 610 ($[M]^+$, 100), 609 (50), 548 (20), 547 (59), 546 (47), 519 (9). HRMS (EI, 70 eV): calcd for $C_{42}H_{42}O_4$ ($[M]^+$: 610.30776, found 610.308341.

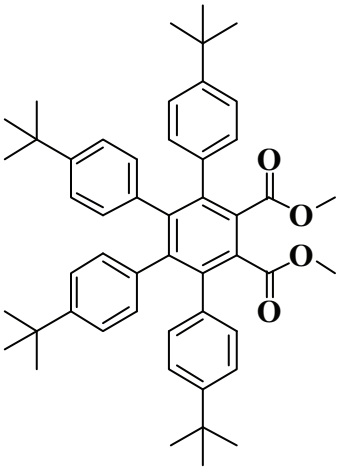


Dimethyl 3,4,5,6-tetra(4-ethylphenyl)phthalate (39d): Starting with **3** (75 mg, 0.147 mmol), **3d** (99 mg, 0.661 mmol), $Pd(PPh_3)_4$ (20 mg, 12 mol%, 0.0207 mmol), K_2CO_3 (2M, 1.0 mL), and 1,4-dioxane (4 mL), **39d** was isolated as a yellow solid (79 mg, 88%); mp 132-134 °C. ^{1}H NMR (300 MHz, $CDCl_3$): δ = 0.90-0.95 (m, 6H, $2CH_3$), 1.03-1.09 (m, 6H, $2CH_3$), 2.29 (q, J = 7.5, 15.1 Hz, 4H, $2CH_2$), 2.45 (q, J = 7.5, 15.1 Hz, 6H, $2CH_3$), 3.39 (s, 6H, $2OCH_3$), 6.47 (d, J = 8.1 Hz, 4H, ArH), 6.58 (d, J = 8.1 Hz, ArH), 6.84 (s, 8H, ArH). ^{13}C-NMR (74.4 MHz, $CDCl_3$): δ = 15.4, 15.5 (CH_3), 28.3, 28.4 (CH_2), 52.1 (OCH_3), 126.1, 126.7, 129.6, 130.8 (CH), 132.0, 136.1, 136.2, 139.1, 141.5, 142.4, 143.5 (C), 169.0 (CO). IR (KBr, cm^{-1}): ν = 3437, 3084, 3048, 3021 (w), 2960, 2929 (m), 2870, 1901 (w), 1725 (s), 1611, 1569, 1551, 1541 (w), 1514, 1451, 1435 (m), 1408, 1400, 1372 (w), 1326 (s), 1280 (w), 1234 (s), 1206, 1189, 1165, 1156, 1114 (m), 1061 (s), 1049, 1023 (m), 967 (s), 943, 908, 883 (w), 858, 842 (s), 831, 819, 813, 797 (m), 777, 764 (w), 733 (m), 685 (w), 675,

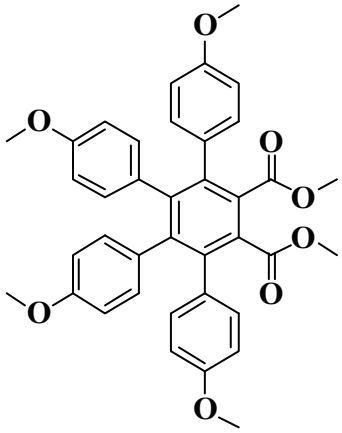


653, 635, 613, 584 (w). GC-MS (EI, 70 eV): *m/z* (%) = 610 ($[M]^+$, 100), 547 (8), 516 (9). HRMS (EI, 70 eV): calcd for $C_{38}H_{34}O_4$ $[M]^+$: 610.30776, found 610.307662.

Dimethyl 3,4,5,6-tetra(4-*tert*-butylphenyl)phthalate (39e): Starting with **38** (75 mg, 0.147 mmol), **3e** (117 mg, 0.661 mmol), $Pd(PPh_3)_4$ (20 mg, 12 mol%, 0.0207 mmol), K_2CO_3 (2M, 1.0 mL), and 1,4-dioxane (4 mL), **39e** was isolated as a white solid (93 mg, 88%); mp 217-219 °C. ^{1}H NMR (300 MHz, $CDCl_3$): δ = 1.01 (s, 18H, $6CH_3$), 1.13 (s, 18H, $6CH_3$), 3.39 (s, 6H, $2OCH_3$), 6.47 (d, *J* = 8.5 Hz, 4H, ArH), 6.74 (d, *J* = 8.5 Hz, 4H, ArH), 6.84 (d, *J* = 8.5 Hz, 4H, ArH), 7.02 (d, *J* = 8.5 Hz, 4H, ArH). ^{13}C-NMR (74.4 MHz, $CDCl_3$): δ = 31.1, 31.2 (CH_3), 34.1, 34.3 (C), 52.1 (OCH_3), 123.3, 124.0, 129.4, 130.5 (CH), 131.7, 135.8, 135.9, 139.2, 143.6, 148.32, 149.2 (C), 169.0 (CO) IR (KBr, cm^{-1}): ν = 3031 (w), 2951 (s), 2902, 2866 (w), 1727 (s), 1689, 1651, 1610, 1567, 1556 (w), 1511 (m), 1475, 1460 (w), 1436, 1392, 1361, 1341, 1332, 1269 (m), 1240, 1223, 1199, 1172, 1165 (s), 1122, 1105 (m), 1066, 1016, 972 (s), 951, 934, 921, 893, 883 (w), 863, 849, 837, 819, 787 (m), 767, 758, 742, 733, 700, 678, 657, 647 (w), 622, 572 (s), 531 (w). GC-MS (EI, 70 eV): *m/z* (%) = 723 ($[M+H]^+$, 47), 722 ($[M]^+$, 100), 676 (11), 661 (12), 531 (23), 489 (11), 475 (14). HRMS (EI, 70 eV): calcd for $C_{50}H_{58}O_4$ $[M]^+$: 722.43296, found 722.433526.

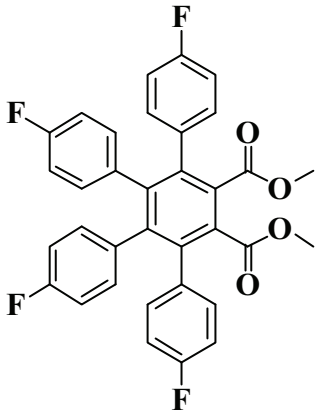


Dimethyl 3,4,5,6-tetra(4-methoxyphenyl)phthalate (39f): Starting with **38** (75 mg, 0.147 mmol), **3f** (100 mg, 0.661 mmol), $Pd(PPh_3)_4$ (20 mg, 12 mol%, 0.0207 mmol), K_2CO_3 (2M, 1.0 mL), and 1,4-dioxane (4 mL), **39f** was isolated as a white solid (81 mg, 90%); mp 253-255 °C. ^{1}H NMR (300 MHz, $CDCl_3$*):* δ = 3.43 (s, 6H, $2OCH_3$), 3.54 (s, 6H, $2OCH_3$), 3.64 (s, 6H , $2OCH_3$), 6.34 (d, *J* = 8.7 Hz, 4H, ArH), 6.50 (d, *J* = 8.7 Hz, 4H, ArH), 6.60 (d, *J* = 8.7 Hz, 4H, ArH), 6.85 (d, *J* = 8.7 Hz, ArH). ^{13}C-NMR (74.4 MHz, $CDCl_3$): δ = 52.2, 54.9, 55.0 (OCH_3), 112.5, 112.9, 130.8 (CH), 131.3, 131.3 (C), 131.9 (CH), 132.1, 138.9, 143.3, 157.3, 158.1 (C), 168.9 (CO). IR (KBr, cm^{-1}): ν = 3039, 3003,

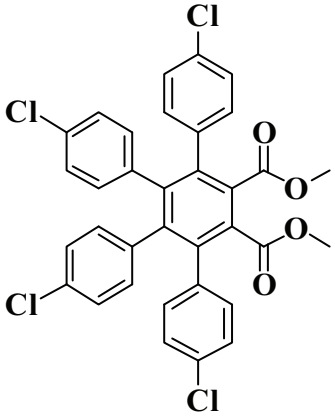


2952, 2932, 2909, 2835 (w), 1742, 1721, 1609 (s), 1575 (m), 1515 (s), 1461, 1435, 1417, 1343 (m), 1306 (w), 1286 (s), 1237 (s), 1194 (m), 1174 (s), 1151, 1109 (m), 1064, 1029 (s), 968 (m), 910, 890, 881, 858, 815 (w), 794 (s), 773, 758, 732, 708, 671, 638, 614, 575 (w), 546 (m). GC-MS (EI, 70 eV): *m/z* (%) = 619 ($[M+H]^+$, 35), 618 ($[M]^+$, 100), 512 (8), 262 (14). HRMS (EI, 70 eV): calcd for $C_{38}H_{34}O_8$ $[M]^+$: 618.22482, found 618.224059.

Dimethyl 3,4,5,6-tetra(4-fluorophenyl)phthalate (39g): Starting with **38** (75 mg, 0.147 mmol), **3g** (92 mg, 0.661 mmol), $Pd(PPh_3)_4$ (20 mg, 12 mol%, 0.0207 mmol), K_2CO_3 (2M, 1.0 mL), and 1,4-dioxane (4 mL), **39g** was isolated as a white solid (66 mg, 80%); mp 198-200 °C. ^{1}H NMR (300 MHz, $CDCl_3$*):* δ = 3.45 (s, 6H, OCH_3), 6.55 (d*,* J = 7.0 Hz, 8H, ArH), 6.75-6.80 (m, 4H, ArH), 6.88-6.93 (m, 4H, ArH). ^{13}C-NMR (74.4 MHz, $CDCl_3$): δ = 52.4 (OCH_3), 113.7 (d, J = 21.4 Hz), 114.1 (d, J = 21.4 Hz), 130.6 (d, J = 8 .0 Hz), 131.6 (d, J = 8 .0 Hz) (CH), 131.9, 133.5 (d, J = 3.6 Hz), 133.6 (d, J = 3.6 Hz), 138.0, 142.0, 160.4 (d, J_{CF} = 245.5 Hz, (CF)), 161.1 (d, J_{CF} = 245.5 Hz, (CF)), 167.6 (CO). IR (KBr, cm^{-1}): ν = 3065, 3052, 3005, 2956, 2846 (w), 1740, 1727, 1604 (s), 1545 (w), 1512, 1439 (s), 1421, 1395 (m), 1340 (s), 1272 (w), 1256, 1218, 1197 (s), 1177 (m), 1162, 1154, 1095, 1056 (s), 1013 (m), 967 (s), 927, 892, 979 (w), 860, 845 (m), 829, 803 (s), 788, 765, 736, 731, 693, 676, 637, 631, 611, 566, 557 (w), 545, 530 (s). GC-MS (EI, 70 eV): *m/z* (%) = 571 ($[M+H]^+$, 31), 570 ($[M]^+$, 100), 540 (15), 539 (47), 507 (22). HRMS (EI, 70 eV): calcd for $C_{34}H_{22}O_4F_4$ $[M]^+$: 570.14487, found 570.144951.

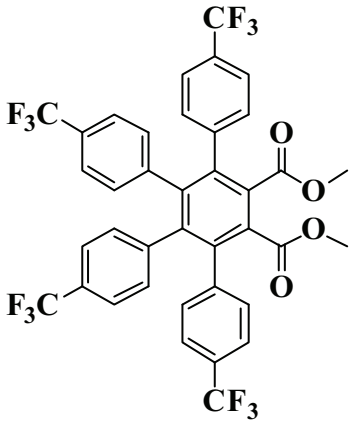


Dimethyl 3,4,5,6-tetra(4-chlorophenyl)phthalate (39h): Starting with **38** (75 mg, 0.147 mmol), **3h** (103 mg, 0.661 mmol), $Pd(PPh_3)_4$ (20 mg, 12 mol%, 0.0207 mmol), K_2CO_3 (2M, 1.0 mL), and 1,4-dioxane (4 mL), **39h** was isolated as a yellow solid (72 mg, 77%); mp 284-286 °C. ^{1}H NMR (300 MHz, $CDCl_3$): δ = 3.45 (s, 6H, $2OCH_3$), 6.53 (d, J = 8.5 Hz, 4H, ArH), 6.82-6.88 (m, 8H, ArH), 7.06 (d, J = 8.5 Hz, ArH). ^{13}C-NMR (62.9 MHz, $CDCl_3$): δ = 51.5 (OCH_3), 126.7, 127.0, 129.8, 130.8 (CH), 131.6, 132.4, 135.3, 135.5, 137.4, 141.0 (C), 166.9 (CO). IR (KBr, cm^{-1}): ν = 3032, 2993, 2949, 2288, 2255,



1903 (w), 1744, 1718 (s), 1595, 1573, 1547 (w), 1492, 1437 (s), 1416 (w), 1393 (m), 1340, 1332 (s), 1302 (w), 1244, 1223, 1195, 1171 (s), 1152 (m), 1089, 1059, 1013 (s), 966, 914 (m), 889, 879 (w), 862, 834, 813, 782 (s), 766 (w), 752, 743, 732 (s), 698, 644, 623, 604, 539 (w). GC-MS (EI, 70 eV): *m/z* (%) = 640 ($[M]^+$, [^{35}Cl] [^{37}Cl] [^{37}Cl] [^{37}Cl], 10), 638 ($[M]^+$, [^{35}Cl] [^{35}Cl] [^{37}Cl] [^{37}Cl],46), 636 ($[M]^+$, [^{35}Cl] [^{35}Cl] [^{35}Cl] [^{37}Cl], 100), 634 ($[M]^+$, [^{35}Cl] [^{35}Cl] [^{35}Cl] [^{35}Cl], 68), 607 (11), 605 (22), 603 (17). HRMS (EI, 70 eV): calcd for $C_{34}H_{22}O_4Cl_4$ ($[M]^+$, [^{35}Cl] [^{35}Cl] [^{37}Cl] [^{37}Cl]): 638.02077, found 638.020486, calcd for $C_{34}H_{22}O_4Cl_4$ ($[M]^+$, [^{37}Cl] [^{37}Cl] [^{35}Cl] [^{37}Cl]): 636.02372, found 636.021757, calcd for $C_{34}H_{22}O_4Cl_4$ ($[M]^+$, [^{35}Cl] [^{35}Cl] [^{35}Cl] [^{37}Cl]): 634.0266, found 634.025016.

Dimethyl 3,4,5,6-tetra(4-trifluoromethylphenyl)phthalate (39i): Starting with **38** (75 mg, 0.147 mmol), **3j** (125 mg, 0.661 mmol), $Pd(PPh_3)_4$ (20 mg, 12 mol%, 0.0207 mmol), K_2CO_3 (2M, 1.0 mL), and 1,4-dioxane (4 mL), **39i** was isolated as a white solid (82 mg, 73%); mp 234-235 °C. ^{1}H NMR (300 MHz, $CDCl_3$): δ = 3.43 (s, 6H, 2OCH_3), 6.74 (d, J = 8.0 Hz, 4H, ArH), 7.10 (t, J = 8.1, 16.5 Hz, 8H, ArH), 7.36 (d, J = 8.1 Hz, 4H, ArH). ^{13}C-NMR (74.4 MHz, $CDCl_3$): δ = 52.6 (OCH_3), 123.5 (q, J_{CF} = 270.5 Hz, CF_3), 123.7 (q, J_{CF} = 270.5 Hz, CF_3), 124.4 (d, J_{CF} = 3.7 Hz, CH), 124.8 (d, J_{CF} = 3.7 Hz, CH), 129.2 (q, J_{CF} = 32.4 Hz, C), 129.7 (q, J_{CF} = 32.4 Hz, C), 129.9, 130.8 (CH), 138.6, 141.1, 141.4, 141.4, 141.7 (C), 167.5 (CO). ^{19}F NMR (282.40 MHz, $CDCl_3$): δ = -62.96, -62.81 (CF_3). IR (KBr, cm^{-1}): ν = 2959 (w), 1737 (s), 1693 (w), 1617 (m), 1574, 1549 (w), 1441, 1405 (m), 1321 (s), 1243, 1231 (m), 1191 (w), 1158, 1106 (s), 1076 (w), 1064, 1052, 1018 (s), 971 (m), 890, 883 (w), 869, 847, 825, 814, 797 (m), 777, 760, 749 (w), 711, 703 (m), 670, 663, 648, 637, 627 (w), 613 (s), 582, 531 (w). GC-MS (EI, 70 eV): *m/z* (%) = 771 ($[M+H]^+$, 34), 770 ($[M]^+$, 94), 751 (11), 740 (35), 739 (100), 707 (12). HRMS (EI, 70 eV): calcd for $C_{38}H_{22}O_4F_{12}$ $[M]^+$: 770.13210, found 770.130669.



Dimethyl 3,4,5,6-tetra(phenyl)phthalate (39j): Starting with **38** (75 mg, 0.147 mmol), **3l** (80 mg, 0.661 mmol), $Pd(PPh_3)_4$ (20 mg, 12 mol%, 0.0207 mmol), K_2CO_3 (2M, 1.0 mL), and 1,4-dioxane (4 mL), **39j** was isolated as a white solid (57 mg, 80%); mp 215-217 °C. ^{1}H NMR (300 MHz, $CDCl_3$): δ = 3.40 (s, 6H, $2OCH_3$), 6.60-6.64 (m, 4H, ArH), 6.76-6.78 (m, 6H, ArH), 6.94-6.98 (m, 4H, ArH), 7.01-7.04 (m, 6H, ArH). ^{13}C-NMR (74.4 MHz, $CDCl_3$): δ = 52.2 (OCH_3), 125.9, 126.8, 126.9, 127.4, 129.7, 130.8 (CH), 132.2, 138.6, 138.7, 139.3, 143.2 (C), 168.7 (CO). IR (KBr, cm^{-1}): ν = 3080, 3052, 3026, 3004, 2950, 2847, 1746 (w), 1720 (s), 1600, 1576, 1548 (w), 1496, 1440, 1434, 1410, 1335 (m), 1276 (w), 1241, 1225 (s), 1196, 1171, 1158, 1153 (m), 1065 (s), 1030, 999, 963, 912, 886, 841, 820, 799 (m), 772 (w), 761, 716, 708, 697 (s), 649, 642, 614 (w), 567 (s). GC-MS (EI, 70 eV): *m/z* (%) = 499 ($[M+H]^+$, 37), 498 ($[M]^+$, 100), 467 (16), 436 (13), 435 (38), 377 (11), 376 (11), 363 (8). HRMS (EI, 70 eV): calcd for $C_{34}H_{26}O_4$ $[M]^+$: 498.18256, found 498.182831.

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X-Ray Crystals Data:
Crystal data and structure refinement for 5,7,8-Tris(4-*tert*-butylphenyl)quinoline (4e)

Identification code	av-nhn11	
Empirical formula	$C_{30}H_{25}N$	
Formula weight	399.51	
Temperature	173 (2) K	
Wavelength	0.71073 Å	
Crystal system	triclinic	
Space group (H-M)	P - 1	
Space group (Hall)	-P 1	
Unit cell dimensions	*a* = 9.9811 (6) Å	α = 76.095. (3)°
	b = 10.4272 (8) Å	β = 78.038 (3)°
	c = 12.2032 (8) Å	γ = 65.899 (3)°
Volume	1116.86 (12) $Å^3$	
Z	2	
Density (calculated)	1.188 Mg/ m^3	
Absorption coefficient	0.222 mm^{-1}	
F(000)	424	
Crystal size	0.63 × 0.21× 0.05 mm^3	
Θ range for data collection	4.9 – 59.5 °	
Reflections collected	21369	
Independent reflections	5872	
Absorption correction	multi-scan	
Max. and Min. transmission	0.958 and 0.997	
Refinement method	full-matrix	
Goodness-of-fit F2	1.093	
Final R indices [I>2b%σ (I)]	R1 = 0.0488, wR2 = 0.1279	
R indices (all data)	R1 = 0.0789, wR2 = 0.1388	

Crystal data and structure refinement for 5,7-Bis(3,5-dimethylphenyl)-8-(trifluoromethanesulfonyloxy)quinoline (5c):

Identification code	ch-nhn3	
Empirical formula	$C_{26}H_{22}F_3NO_3S$	
Formula weight	485.51	
Temperature	173 (2) K	
Wavelength	0.71073 Å	
Crystal system	triclinic	
Space group (H-M)	P - 1	
Space group (Hall)	-P 1	
Unit cell dimensions	*a* = 7.9947 (2) Å	α = 102.726 (1)°
	b = 12.4621 (5) Å	β = 105.867 (1)°
	c = 13.1276 (8) Å	γ = 104.093 (1)°
Volume	1116.10 (5) $Å^3$	
Z	2	
Density (calculated)	1.389 Mg/ m^3	
Absorption coefficient	0.19 mm^{-1}	
F(000)	504	
Crystal size	0.53 × 0.38× 0.013 mm^3	
Θ range for data collection	5.5 – 59.9 °	
Reflections collected	24316	
Independent reflections	6648	
Absorption correction	multi-scan	
Max. and Min. transmission	0.905 and 0.975	
Refinement method	full-matrix	
Goodness-of-fit F2	1.071	
Final R indices [I>2b%σ (I)]	R1 = 0.0387, wR2 = 0.11975	
R indices (all data)	R1 = 0.0479, wR2 = 0.1160	

Crystal data and structure refinement for 5-(4-Ethylphenyl)-7-bromo-8-(trifluoromethanesulfonyloxy)quinoline (6a):

Identification code	is_nhn2	
Empirical formula	$C_{18}H_{13}BrF_3NO_3S$	
Formula weight	460.26	
Temperature	173 (2) K	
Wavelength	0.71073 Å	
Crystal system	Monclinic	
Space group (H-M)	C2/C	
Space group (Hall)	-C 2yc	
Unit cell dimensions	*a* = 28.1762 (5) Å	α = 90.00. (0)°
	b = 8.2666 (2) Å	β = 122.2180 (10)°
	c = 18.3492 (3) Å	γ = 90.00 (0)°
Volume	3615.84 (12) $Å^3$	
Z	8	
Density (calculated)	1.691 Mg/ m^3	
Absorption coefficient	0.244 mm^{-1}	
F(000)	1840	
Crystal size	0.40 × 0.19× 0.18 mm^3	
Θ range for data collection	5.4 – 62.6 °	
Reflections collected	26864	
Independent reflections	5734	
Absorption correction	multi-scan	
Max. and Min. transmission	0.442 and 0.668	
Refinement method	full-matrix	
Goodness-of-fit F2	1.054	
Final R indices [I>2b%σ (I)]	R1 = 0.0303, wR2 = 0.0768	
R indices (all data)	R1 = 0.0452, wR2 = 0.0808	

Crystal data and structure refinement for 5,7-Bis(4-*tert*-butylphenyl)-8-(4-methoxyphenyl)quinoline (7b):

Identification code	is-nhn26	
Empirical formula	$C_{36}H_{37}NO$	
Formula weight	499.67	
Temperature	173 (2) K	
Wavelength	0.71073 Å	
Crystal system	triclinic	
Space group (H-M)	P -1	
Space group (Hall)	-P 1	
Unit cell dimensions	*a* = 10.5822 (3) Å	α = 112.647 (1)°
	b = 12.2222 (4) Å	β = 108.831 (1)°
	c = 12.6439 (4) Å	γ = 90.557 (2)°
Volume	1411.55 (8) $Å^3$	
Z	2	
Density (calculated)	1.176Mg/ m^3	
Absorption coefficient	0.07 mm^{-1}	
F(000)	536	
Crystal size	0.63 × 0.18× 0.10 mm^3	
Θ range for data collection	5.2 – 64.4 °	
Reflections collected	32159	
Independent reflections	7493	
Absorption correction	multi-scan	
Max. and Min. transmission	0.958 and 0.993	
Refinement method	full-matrix	
Goodness-of-fit F2	1.068	
Final R indices [I>2b%σ (I)]	R1 = 0.0461, wR2 = 0.1166	
R indices (all data)	R1 = 0.0789, wR2 = 0.1272	

Crystal data and structure refinement for7-(2-Methoxyphenyl)-4-oxo-2-phenyl-4*H*-chromen-5-yl trifluoromethanesulfonate (14a)

Identification code	av-fle	
Empirical formula	$C_{23}H_{15}F_3O_6S$	
Formula weight	476.41	
Temperature	173 (2) K	
Wavelength	0.71073 Å	
Crystal system	Monoclinic	
Space group (H-M)	P 21/ n^1	
Space group (Hall)	-P 2 yn	
Unit cell dimensions	*a* = 15.77301 (8) Å	α = 90.00 (0)°
	b = 13.2613 (7) Å	β =98.461 (2)°
	c = 19.9804 (10)Å	γ =90.00 (0)°
Volume	4133.8 (4) $Å^3$	
Z	8	
Density (calculated)	1.531 Mg/ m^3	
Absorption coefficient	0.22 mm^{-1}	
F(000)	1952	
Crystal size	0.40 × 0.22× 0.05 mm^3	
Θ range for data collection	2.6 – 28.3 °	
Reflections collected	6380	
Independent reflections	10254	
Absorption correction	multi-scan	
Max. and Min. transmission	0.9159 and 0.9889	
Refinement method	full-matrix	
Goodness-of-fit F2	1.022	
Final R indices [I>2b%σ (I)]	R1 = 0.0497, wR2 = 0.1028	
R indices (all data)	R1 = 0.0996, wR2 = 0.1238	

Crystal data and structure refinement for 5,7-Bis(3,5-dimethylphenyl)-4-methyl-2*H*-chromen-2-one (20b):

Identification code	av_a35me	
Empirical formula	$C_{26}H_{14}O_2$	
Formula weight	368.45	
Temperature	173 (2) K	
Wavelength	0.71073 Å	
Crystal system	monoclinic	
Space group (H-M)	P 21/c	
Space group (Hall)	-P 2ybc	
Unit cell dimensions	*a* = 10.7876 (5) Å	α = 90.00 (0)°
	b = 14.3492 (7) Å	β = 105.438 (2)°
	c = 13.0705 (6) Å	γ = 90.00 (0)°
Volume	1950.23 (16) $Å^3$	
Z	4	
Density (calculated)	1.255 Mg/ m^3	
Absorption coefficient	0.08 mm^{-1}	
F(000)	784	
Crystal size	0.79 × 0.39× 0.04 mm^3	
Θ range for data collection	5.2 – 59.9 °	
Reflections collected	20600	
Independent reflections	5165	
Absorption correction	multi-scan	
Max. and Min. transmission	0.941 and 0.997	
Refinement method	phi and omega scan	
Goodness-of-fit F2	1.049	
Final R indices [I>2b%σ (I)]	R1 = 0.0500, wR2 = 0.1285	
R indices (all data)	R1 = 0.0660, wR2 = 0.13954	

Crystal data and structure refinement for 7-(3,5-dimethylphenyl)-5-(4-fluorophenyl)-4-methyl-2*H*-chromen-2-one (22b):

Identification code	is_a35mef	
Empirical formula	$C_{24}H_{19}FO_2$	
Formula weight	358.39	
Temperature	173 (2) K	
Wavelength	0.71073 Å	
Crystal system	Triclinic	
Space group (H-M)	P -1	
Space group (Hall)	-P 1	
Unit cell dimensions	*a* = 8.1628 (2) Å	α = 85.336 (2)°
	b = 11.9720 (3) Å	β = 82928 (2)°
	c = 13.1723 (4) Å	γ = 76.848 (4)°
Volume	930.83 (8) $Å^3$	
Z	4	
Density (calculated)	1.279 Mg/ m^3	
Absorption coefficient	0.09 mm^{-1}	
F(000)	376	
Crystal size	0.48 × 0.32× 0.08 mm^3	
Θ range for data collection	5.7 – 60.8 °	
Reflections collected	19684	
Independent reflections	5372	
Absorption correction	multi-scan	
Max. and Min. transmission	0.958 and 0.993	
Refinement method	phi and omega scan	
Goodness-of-fit F2	1.033	
Final R indices [I>2b%σ (I)]	R1 = 0.0474, wR2 = 0.1251	
R indices (all data)	R1 = 0.0620, wR2 = 0.1343	

Crystal data and structure refinement for 7-[4-(*tert*-butyl)phenyl]-4-methyl-2-oxo-2*H*-chromen-8-yl trifluoromethanesulfonate (25e):

Identification code	is_78coll	
Empirical formula	$C_{21}H_{19}F_3O_5S$	
Formula weight	440.42	
Temperature	173 (2) K	
Wavelength	0.71073 Å	
Crystal system	Monoclinic	
Space group (H-M)	P 21/C	
Space group (Hall)	-P 2 ybc	
Unit cell dimensions	*a* = 18.7358 (5) Å	α = 90.00 (0)°
	b = 8.8693 (3) Å	β = 107.312 (1)°
	c = 13.4210 (4) Å	γ = 90.00 (0)°
Volume	2129.18 (11) $Å^3$	
Z	4	
Density (calculated)	1.374 Mg/ m^3	
Absorption coefficient	0.21 mm^{-1}	
F(000)	912	
Crystal size	0.99 × 0.17× 0.08 mm^3	
Θ range for data collection	5.6 – 61.9 °	
Reflections collected	23248	
Independent reflections	6169	
Absorption correction	multi-scan	
Max. and Min. transmission	0.821 and 0.984	
Refinement method	full-matrix	
Goodness-of-fit F2	1.045	
Final R indices [I>2b%σ (I)]	R1 = 0.0484, wR2 = 0.1243	
R indices (all data)	R1 = 0.0667, wR2 = 0.1375	

Crystal data and structure refinement for Methyl 3,7-bis(4-fluorophenyl)-2-naphthoate (35e):

Identification code	is_zen6	
Empirical formula	$C_{24}H_{16}F_2O_2$	
Formula weight	374.37	
Temperature	173 (2) K	
Wavelength	0.71073 Å	
Crystal system	Monoclinic	
Space group (H-M)	C c	
Space group (Hall)	C -2yc	
Unit cell dimensions	*a* = 16.9602 (3) Å	α = 90.00 (0)°
	b = 25.6488 (5) Å	β = 99.497 (3)°
	c = 12.4814 (2) Å	γ = 90.00 (0)°
Volume	5381.42 (17) $Å^3$	
Z	12	
Density (calculated)	1.386 Mg/ m^3	
Absorption coefficient	0.10 mm^{-1}	
F(000)	2328	
Crystal size	0.84 × 0.24× 0.09 mm^3	
Θ range for data collection	4.9 – 60.3 °	
Reflections collected	57186	
Independent reflections	15084	
Absorption correction	multi-scan	
Max. and Min. transmission	0.920 and 0.991	
Refinement method	full-matrix	
Goodness-of-fit F2	1.024	
Final R indices [I>2b%σ (I)]	R1 = 0.0472, wR2 = 0.0885	
R indices (all data)	R1 = 0.0750, wR2 = 0.0966	

Dimethyl 3,4,5,6-tetra(3,5-dimethylphyenyl)phthalate (39c):

Identification code	is_tetra6	
Empirical formula	$C_{42}H_{142}O_4$	
Formula weight	610.76	
Temperature	173 (2) K	
Wavelength	0.71073 Å	
Crystal system	Monoclinic	
Space group (H-M)	p 21/n	
Space group (Hall)	-p 2yn	
Unit cell dimensions	*a* = 20.0785 (5) Å	α = 90.00 (0)°
	b = 9.3103 (2) Å	β = 113.301 (1)°
	c = 20.8028 (4) Å	γ = 90.00 (0)°
Volume	3571.64 (17) $Å^3$	
Z	4	
Density (calculated)	1.136 Mg/ m^3	
Absorption coefficient	0.07 mm^{-1}	
F(000)	1304	
Crystal size	0.41 × 0.33× 0.23 mm^3	
Θ range for data collection	4.9 – 60.7 °	
Reflections collected	37832	
Independent reflections	9483	
Absorption correction	multi-scan	
Max. and Min. transmission	0.971 and 0.984	
Refinement method	full-matrix	
Goodness-of-fit F2	1.074	
Final R indices [I>2b%σ (I)]	R1 = 0.0466, wR2 = 0.1251	
R indices (all data)	R1 = 0.0642, wR2 = 0.1329	

LIST OF PUBLICATIONS

Nadi Eleya, Ahmed Mahal, Alexander Villinger, Peter Langer*, *Adv. Synth. Catal.* **2011**, *353*, 2761–2774. "Synthesis of Arylated Quinolines by Chemo- and Site-selective Suzuki-Miyaura Reactions of 5,7-Dibromo-8-(trifluoromethylsulfonyloxy)quinoline".

Nadi Eleya, Imran Malik, Sebastian Reimann, Kai Wittler, Martin Hein, Tamás Patonay, Alexander Villinger, Ralf Ludwig, Peter Langer*, *Eur. J. Org. Chem.* **2012**, 1639-1652. "Efficient Synthesis of Arylated Flavones by Site-Selective Suzuki–Miyaura Cross-Coupling Reactions of the Bis(triflate) of 5,7- and 7,8-Dihydroxyflavone".

Nadi Eleya, Zein Khaddour, Tamás Patonay, Peter Langer*, *Synlett* **2012**, *23*, 223-226. "Efficient Synthesis of Arylated Coumarins by Site-Selective Suzuki–Miyaura Cross-Coupling Reactions of the Bis(triflate) of 4-Methyl-5,7-dihydroxycoumarin".

Muhammad Farooq Ibad, **Nadi Eleya**, Obaid-Ur-Rahman Abid, Ahmed Mahal, Munawar Hussain, Alexander Villinger, Peter Langer,* *Synthesis* **2011**, 2101-2116. "Site-Selective Suzuki-Miyaura Reactions of 1,4- and 3,5-Bis(trifluoromethyl-sulfonyloxy)-2-naphthoates".

Rasheed Ahmad Khera, Munawar Hussain, Nguyen Thai Hung, **Nadi Eleya**, Holger Feist, Alexander Villinger, Peter Langer*, *Helv. Chim. Acta* **2012,** *95*, 469-482. "Regioselective Arylation and Alkynylation of 2,3-Dibromoindenones by Suzuki-Miyaura and Sonogashira Cross-Coupling Reactions".

Nadi Eleya, Tamás Patonay, Alexander Villinger, Peter Langer*, *Helv. Chim. Acta* **2012**, accepted**.** "Synthesis of Tetraarylphthalates by Suzuki-Miyaura Reactions of Dimethyl Tetrabromophthalate".

Curriculum Vitae

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- Practical organic Chemistry (*Identification of organic compounds)* Laboratories 4th grade, Depart. of Chemistry - College of Science.

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Scholarship:

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Declaration/Erklärung

Here by I declare that this work has so far neither submitted to the Faculty of Mathematics and Natural Sciences at the University of Rostock nor to any other scientific Institution for the purpose of doctorate. Further more, I declare that I have written this work by myself and that I have not used any other sources, other than mentioned earlier in this work.

Hiermit erkläre ich, daß diese Arbeit bisher von mir weder an der Mathematisch-Naturwissenschaftlichen Fakultät der Universität Rostock noch einer anderen wissenschaftlichen Einrichtung zum Zwecke der Promotion eingereicht wurde.

Ferner erkläre ich, dass ich diese Arbeit selbständig verfasst und keine anderen als die darin angegebenen Hilfsmittel benutzt habe.
I hereby apply irrevocably to take oral examination in the form of a private viva voce and a public presentation.

_____

NADI ELEYA