UNIVERSITÄT ROSTOCK

Synthesis of 1-Alkenylpyrenes and of Fluorinated Arenes by Palladium(0)-Catalyzed Cross-Coupling Reactions and Photophysical Properties of the Products

Dissertation

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Dedicated
To
My loving Parents
M. Akbar Ali and Rashida Akbar
And
endearing "Minahel"

I would have been lost without them.

Acknowledgement

In the name of Allah, most gracious; most merciful.

"And say: Work (righteousness): Soon will Allah observe your work, and His messenger and believers"

All praise and glory to Allah Almighty who alone made this small objective to be accomplished I feel honored and privileged to glorify His name in the sincerest way through this small accomplishment and ask Him to accept my efforts. Peace be upon the Prophet, his companions and all who followed him until the Day of judgment.

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Lastly, and most importantly, I wish to thank my parents, M. Akbar Ali and Rashida Akbar. They bore me, raised me, supported me, taught me, and loved me. To them I dedicate this thesis.

Muhammad Sharif Akbar

March 2011

Rostock, Germany

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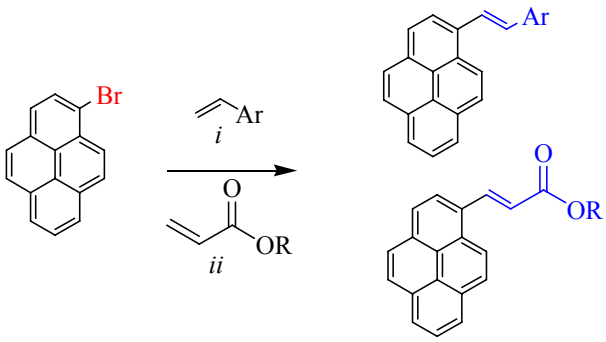
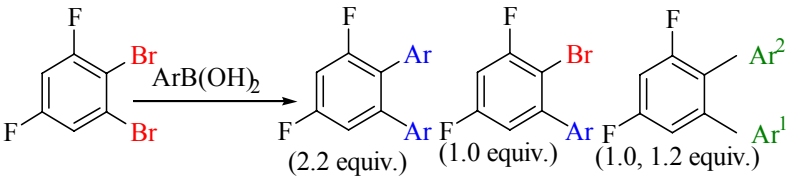
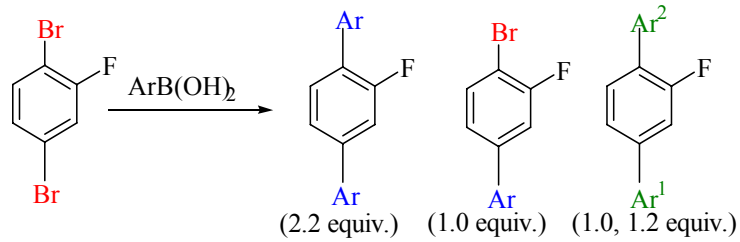


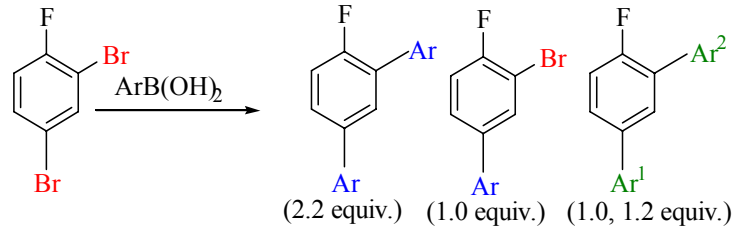
The palladium(0)-catalyzed Heck cross-coupling reactions of 1-bromopyrene with acrylates and styrenes provided 1-alkenylpyrenes. The absorption and emission spectroscopic properties and the electrochemical characteristics of the products were studied. The electrochemical band gaps are correlated with the HOMO-LUMO energy gaps derived from photophysical measurements and from theoretical calculations performed by density functional theory (DFT) calculations.

CHAPTER 2

One-pot Synthesis of Fluorinated Terphenyls by Site-Selective Suzuki-Miyaura Cross Coupling Reactions of 1,2-Dibromo-3,5-difluorobenes, 1,4-Dibromo-2-fluorobenzenes, 1,3-Dibromo-4-fluorobenzenes







Suzuki-Miyaura reactions of fluorinated benzenes proceeded with excellent yields and site-selectivity. The reactions with one equivalent of arylboronic acids resulted in site-selective attack onto less sterically hindered and more electron deficient carbon atoms. The Suzuki–Miyaura reaction with 2.2 equivalents of arylboronic acids gave fluorinated terphenyls. The one-pot reaction of fluorinated benzenes with two different aryl groups were prepared by sequential addition of two different aryl boronic acids.

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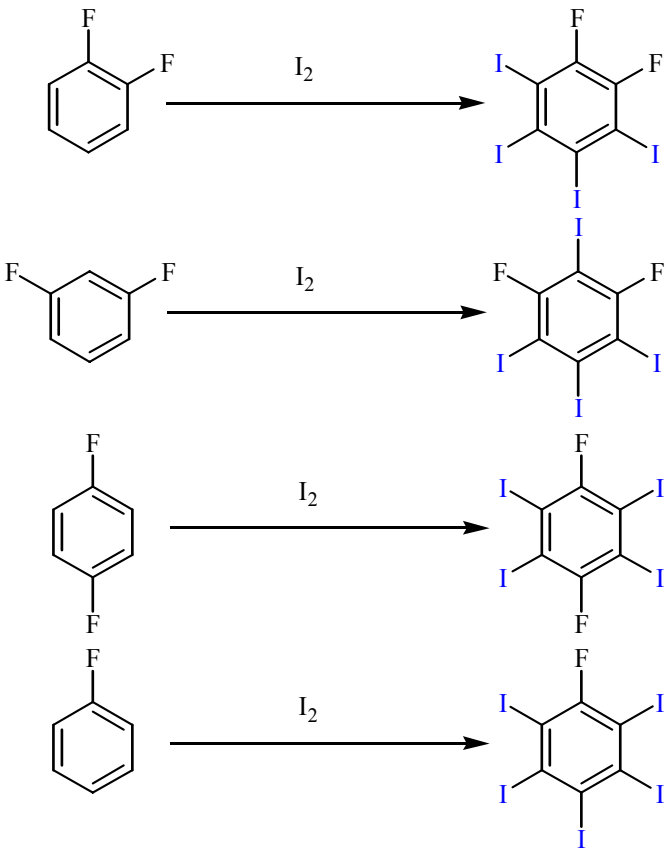
CHAPTER 3

A Novel and Convenient Synthesis of Mono- and Difluorinated Periodobenzenes



The periodination of 1,2-difluorobene, 1,3-difluorobenzene, 1,4-difluorobenzene and fluorobenzene afforded periodinated fluorinated benzene derivatives. Molecular iodine thoroughly iodinates aromatic hydrocarbons in the presence of potassium peroxodisulfate, concentrated sulfuric acid, and trifluoroacetic acid to give the periodinated aromatic compounds.

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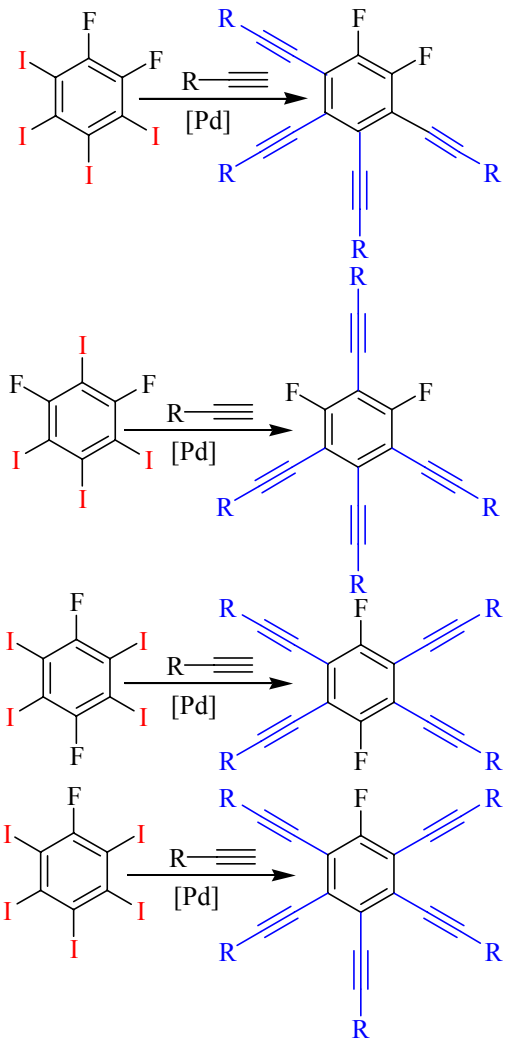
CHAPTER 4

Synthesis of Fluorinated Polyethynylbenzenes by Sonogashira Coupling Reactions of 1,2-, 1,3-, and 1,4-Difluorobenzenes and 1-Fluorobenzenes and their Absorption and Fluorescence Properties



Sonogashira coupling reactions of 1,2-, 1,3-, and 1,4-difluorobenzenes and 1-fluorobenzenes have been carried out in good to very good yields. Most products showed excellent fluorescence properties. The pruducts prepared have not been reported to date.

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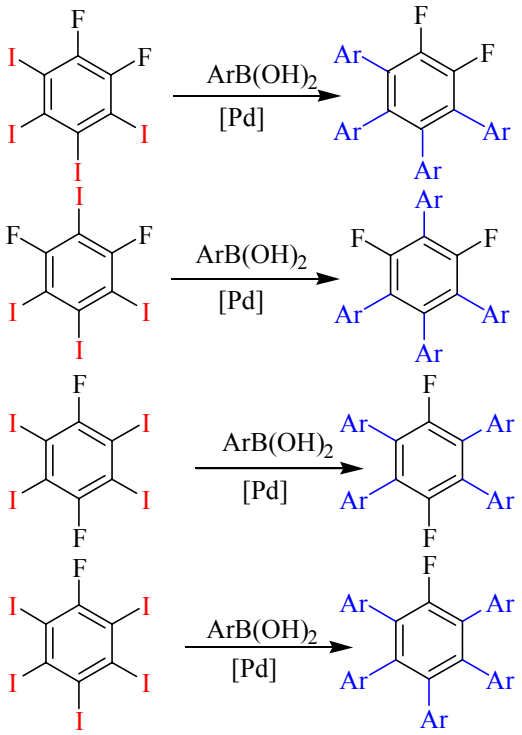
CHAPTER 5

Synthesis of Fluorinated Aryl-Substituted Benzenes by Suzuki-Miyaura Coupling Reactions of 1,2-, 1,3-, and 1,4-Difluorobenzenes and 1-Fluorobenzenes and their Absorption and Fluorescence Properties

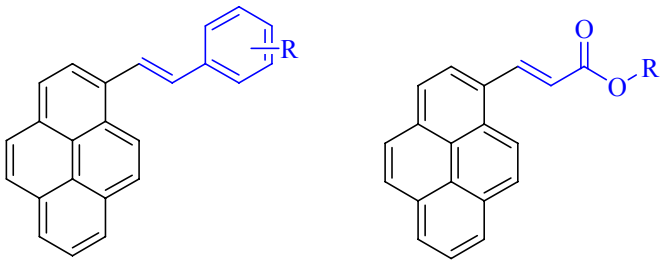


Suzuki-Miyaura reactions of 1,2-, 1,3-, and 1,4-difluorobenzenes and 1-fluorobenzenes allowed a convenient synthesis of fluoro-substituted aryl benzenes, such as symmetrical and unsymmetrical arenes by using the corresponding equivalents of aryl boronic acids. Fluoro-substituted aryl benzenes are prepared which are not readily available by other methods. All reactions proceeded with good to high yields.

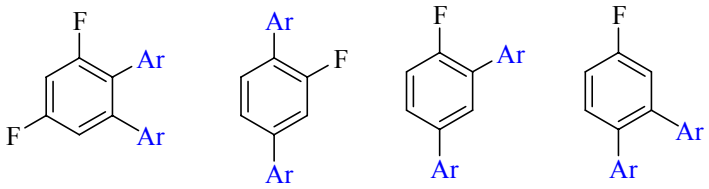
Detailed contents

Introduction and Tasks of the Thesis

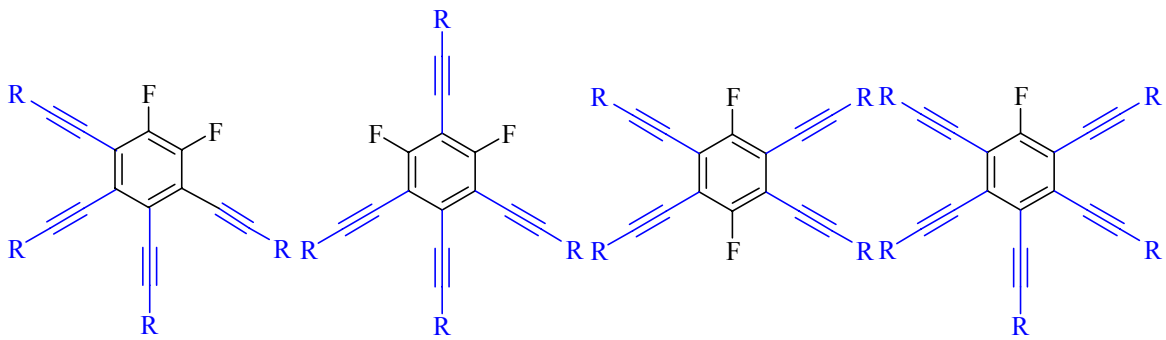
Palladium catalyzed transformations have gained remarkable importance for C-C bond formation; these reactions are being used for the synthesis of a number of natural products, pharmaceutical drugs and advanced materials. The aim of this work is to enhance the scope of palladium catalyzed reactions. In recent years, site-selective palladium(0)-catalyzed cross-coupling reactions of di- and trihalogenated molecules or the corresponding triflates have been studied. The Langer group has also greatly contributed to this. This paragraph outlines the tasks of this thesis. A more detailed introduction is given at the beginning of each individual chapter. Heck cross coupling reactions using substituted acrylates and styrenes on 1-bromopyrene was the primary task in the research work.



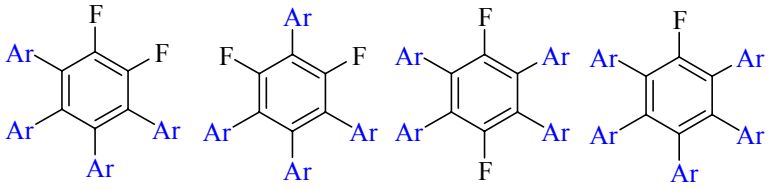
I have also studied the site-selectivity of palladium catalyzed transformations of a number of mono- and difluoro-substituted dibromo benzenes. Site-selective reactions of the substrates discussed in the thesis have not been previously studied by other research groups.



Although a diverse set of substrates were studied, the general topic of this thesis was to develop new polyiodinated benzene derivatives and their application as substrates in Sonogashira reactions for the synthesis of polyethynylbenzenes.



In continuation of the task, the synthesis of polyarylbenzenes was also performed by the application of the Suzuki-Miyaura cross coupling protocol.



Based on this, an important goal was to study the absorption and fluorescence properties of all products.

1 Synthesis and Properties of 1-Alkenylpyrenes

1.1 Introduction

1.1.1 Photochemical Properties of Pyrene

A critical photoactive component in supramolecular complexes and organic light emitting diodes is pyrene which has been selected for the present work, since it is by far the most frequently used dye in fluorescence studies of labeled polymers. Also, polycyclic aromatic hydrocarbons (PAH) and π-conjugated systems are interesting as fluorescent dyes,[1] optical sensors, molecular electronics,[2] nonlinear optical materials, light emitting diodes, photovoltaic cells and field-effect transistors.[3]

Pyrene has a reasonable excited state life time (650 ns) and shows a strong emission at 372 nm. Pyrene fluorescence has led to its use in various sensor applications where fluorescence quenching is a useful reported characteristic. Pyrene readily forms excimers. Moreover, it acts as an energy acceptor via nonradiative energy transfer from several dyes and the vibronic band structure of its emission is sensitive to the environment.[4] Our interest to make pyrene a part of our research interest is due to the high symmetry and interesting electronic structure of this polynuclear aromatic compound. The pyrene nucleus has three C_2 axes which allow some symmetry to be retained in various mono- and disubstituted derivatives. Also the pyrene nucleus is electroactive, having an oxidation potential of +1.28 V and a reduction potential of -2.09 V.[5] Pyrene has a strong chromophore that extends over the whole molecule.

The pyrene absorption spectrum has three prominent monomer absorption peaks at 314 nm, 328 nm and 344 nm. Absorption of a photon by the ground state of pyrene leads to the formation of excited states (^{1}Py* and ^{3}Py), which can either fluoresce with its natural lifetime (τ_M, usually in the 200-300 ns range) in the blue region of the visible light spectrum or encounter another ground-state pyrene.[6] The emission spectrum of pyrene in the blue region has also three prominent monomer emission peaks at 370 nm, 380-381 nm, and 390-391 nm. When the local concentration of pyrene is high, the excited pyrene molecule may bind to a ground-state pyrene molecule to form an excimer. The broad excimer fluorescence emission peak is observed at 470 nm (I_e). The ratio of two monomer peaks I_1/I_3 is sensitive to the micro

environmental polarity around the pyrene molecule,[7] and the excimer to monomer fluorescence intensity ratio. I_e/I_{mon}, for solubilized pyrene has been used to evaluate its distribution among micelles. Because excimer fluorescence requires dimerization during an excited-state lifetime, a minimum of two pyrenes per micelle is required for solubilized pyrene to produce excimer emission.[8]

A problem related to these systems is based on the fact that their emission in the solid state is suppressed by the formation of excimers by π-π-stacking.[9] The fluorescence properties of parent pyrene are well known and characterized by long excited state life times and distinct solvatochromic shifts. Furthermore, pyrene exhibits a characteristic excimer formation in concentrated solutions and in the solid state, due to self association by π-π-stacking.[10] These effects are disadvantageous because they lead to a dramatic decrease of the fluorescence and to less defined, broadened fluorescence spectra. Therefore, excimer formation of pyrene can be used to study the phenomenon of aggregation. In addition, the sensitive solvatochromic shifts of pyrene have been used to explore the inner structure and polarity of dendrimers by introducing pyrene in the outer and inner area of the dendritic structure.[11] Intramolecular charge transfer (ICT) in organic systems has been widely investigated in order to understand the factors controlling the charge separation and charge recombination.[12] Substituted pyrenes show interesting fluorescence properties and good quantum yields along with efficient excimer emission.[13] In fact, pyrene derivatives, containing appropriate substituents, have been applied as fluorescent biological probes,[14] as components of photoelectric devices, and as liquid crystalline materials.[15] The synthesis and photophysical properties of substituted pyrenes have been previously studied. For example, 1-arylpyrenes have been prepared by Suzuki-Miyaura reactions of monohalogenated pyrenes.[16] In my thesis, I have synthesized, 1-alkenylpyrenes by what are, to the best of my knowledge, the first Heck cross-coupling reactions of 1-bromopyrenes. The products contain a pyrene moiety linked to donor and acceptor substituents through an alkenyl bridge. The absorption and fluorescence properties and the electrochemical characteristics of the products have been studied. The electrochemical band gaps are correlated with the HOMO-LUMO energy gaps derived from photophysical measurements and from theoretical calculations performed by density functional theory (DFT) calculations.

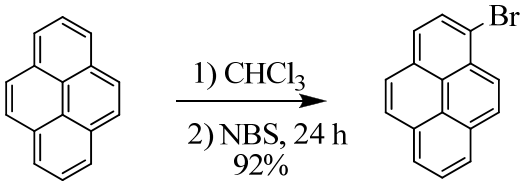
In the present studies, the Heck type reaction of 1-bromopyre with electron withdrawing and electron donating substituted styrenes and acrylates has been reported. This type of reaction gives rise to the products in an excellent yield.

1.2 Results and Discussion

1.2.1 Synthesis of styrene sunbtituted ethenylpyrenes

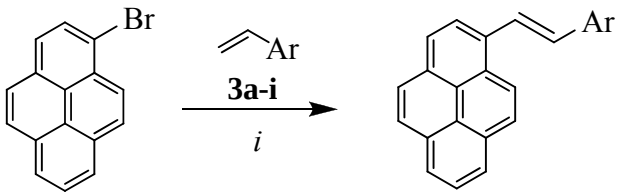
The parent pyrene **1** was used as a starting point of our synthetic strategy for the synthesis of different styrenes. To realize the syntheses of **4a-i,** pyrene **1** was treated first with NBS to afford 1-bromopyrene **2** (Scheme 1) according to a known procedure.[17] The Heck reaction of 2-bromopyrene **2** with styrenes **3a-i** (1.2 equiv.) afforded the 2-alkenylpyrenes **4a-i** and in 72-94% yields (Scheme 2 Table 1). The best yields were obtained when the reactions were carried out using $Pd(OAc)_2$ (5 mol%) and the biarylmonophosphine ligand XPhos (10 mol%). The use of $Pd(PPh_3)_4$ as the catalyst proved to be unsuccessful. The reaction was carried out in DMF at 60-70 °C for 5-6 hours. The yields significantly decreased when the temperature was increased. The use of potassium carbonate as the base proved to be very important. The employment of triethylamine resulted in the formation of an unseparable mixture of products, partly due to hydrogenation of the double bond.

The structures of all products were established by spectroscopic techniques. The structures of **4a**, and **4i** have been independently confirmed by X-ray crystal structure analyses (Figures 1-2). In the crystal structure **4e** and **4i** the aryl moiety seems to be twisted out of plan.



1 **2**

Scheme 1. Synthesis of 1-bromopyrene



2 **4a-i**

Scheme 2. Synthesis of **4a–i**. Conditions: (i) **1** (1.0 equiv), **3a–i** (1.2 equiv), K_2CO_3 (2.0 equiv), $Pd(OAc)_2$ (5 mol %), X-Phos (10 mol-%), DMF, 80 °C, 6 h.

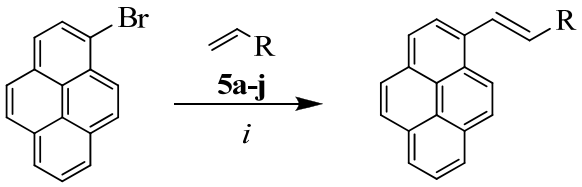
Table 1. Synthesis of **4a-i**

3,4	Ar	**4** (%)[a]
a	4-MeC_6H_4	92
b	4-$(MeO)C_6H_4$	89
c	C_6H_5	79
d	4-(*t*BuO)C_6H_4	86
e	4-ClC_6H_4	72
f	C_6F_5	76
g	4-*t*BuC_6H_4	94
h	2-pyridine	88
i	4-$(AcO)C_6H_4$	77

[a] Yields of isolated products

1.2.2 Synthesis of acrylate substituted pyrenes

Using the same protocol as above, the Heck reaction of 1-bromopyrene **2** with acrylates **5a-i** (1.2 equiv.) gave 1-alkenylpyrenes **6a-j** in 74-93% yield, (Schemes 3, Table 2). The structures of all products were also proved by spectroscopic techniques. The structure of **6a**, has been independently confirmed by X-ray crystal structure analysis (Figures 3). The crystal sructure shows that aromatic group is in plane with the pyrene moiety.



2 **6a-j**

Scheme 3. Synthesis of **6a–j**. Conditions: (i) **1** (1.0 equiv), **5a–j** (1.2 equiv), K_2CO_3 (2.0 equiv), $Pd(OAc)_2$ (5 mol %), X-Phos (10 mol %),DMF, 80 °C, 6 h.

Table 2. Synthesis of **6a-j**

5,6	R	**6** (%)[a]
a	CO_2nBu	84
b	CO_2Et	87
c	CO_2iOct	79
d	CO_2nHex	80
e	CO_2iBu	86
f	CO_2tBu	93
g	CO_2Me	90
h	CO_2R [b]	88
i	$CO_2(CH_2)CF_3$	83
j	$CO_2(CH_2)_2OH$	74

[a] Yields of isolated products; [b] R = 2-ethylhexyl

Table 3. Optimization of the synthesis of **4b**

Entry	Catalyst	Ligand	T (°C)	Base	t (h)	Yield (%)[a]
1	10%$Pd(OAc)_2$	10%XPhos	120	Triethanolamine	12	0
2	10%$Pd(PPh_3)_4$	-	120	K_2CO_3	12	0
3	5% $Pd(OAc)_2$	10%XPhos	110	NEt_3	10	mixture
4	5% $Pd(OAc)_2$	10%XPhos	100	K_2CO_3	10	60
5	5% $Pd(OAc)_2$	10%XPhos	80	K_2CO_3	8	70
6	5% $Pd(OAc)_2$	10%XPhos	60-70	K_2CO_3	6-7	94

[a] Isolated yields

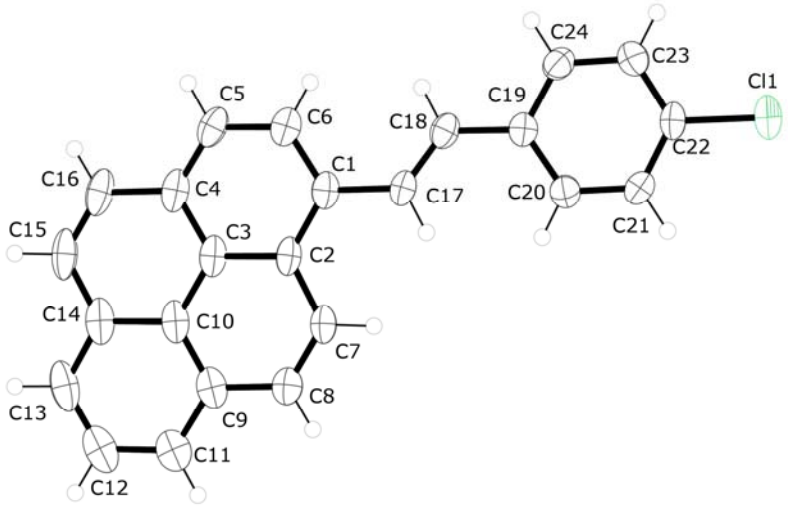


Figure 1. Crystal structure of **4e**

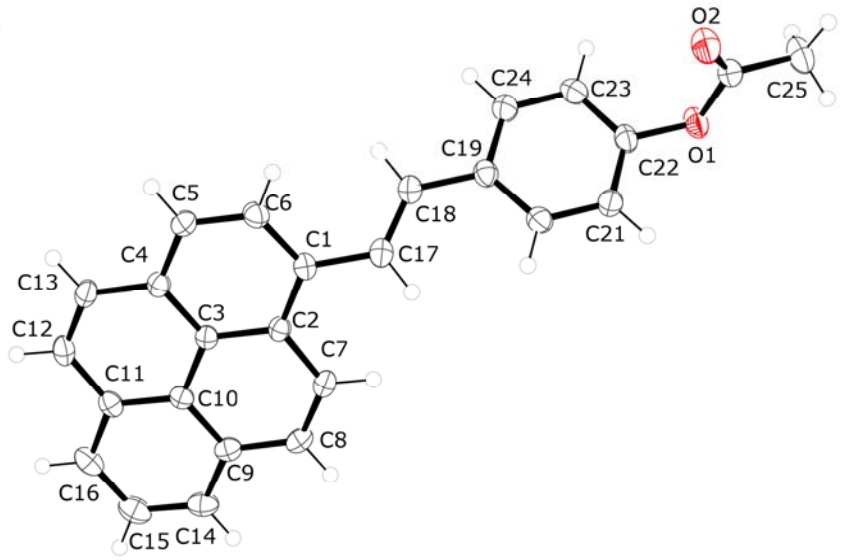


Figure 2. Crystal structure of **4i**

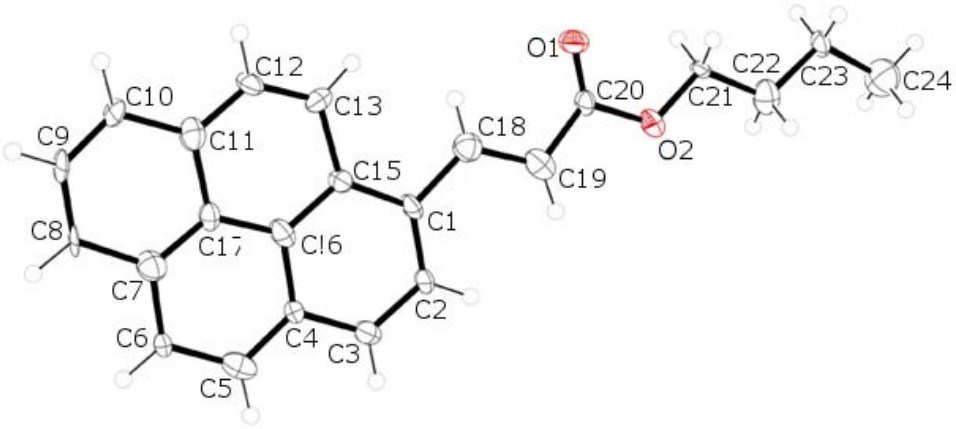


Figure 3. Crystal structure of **6a**

1.2.3 Absorption and fluorescence properties of pyrene compounds

The UV-Vis absorption spectra of compounds **4i,b,d,e** and **6e** (Table 4) recorded in acetonitrile, are shown in Figure 4. Compounds **4i** and **4e** (bearing electron acceptor groups) show a slight red shift with absorption maxima at about 375 nm and a shoulder at 390 nm. Compounds **4b** and **4d** (bearing electron donating groups) and acrylate **6e** show two absorptions at about 275 nm and 350 nm. Parent pyrene exhibits absorption at about 275 nm.

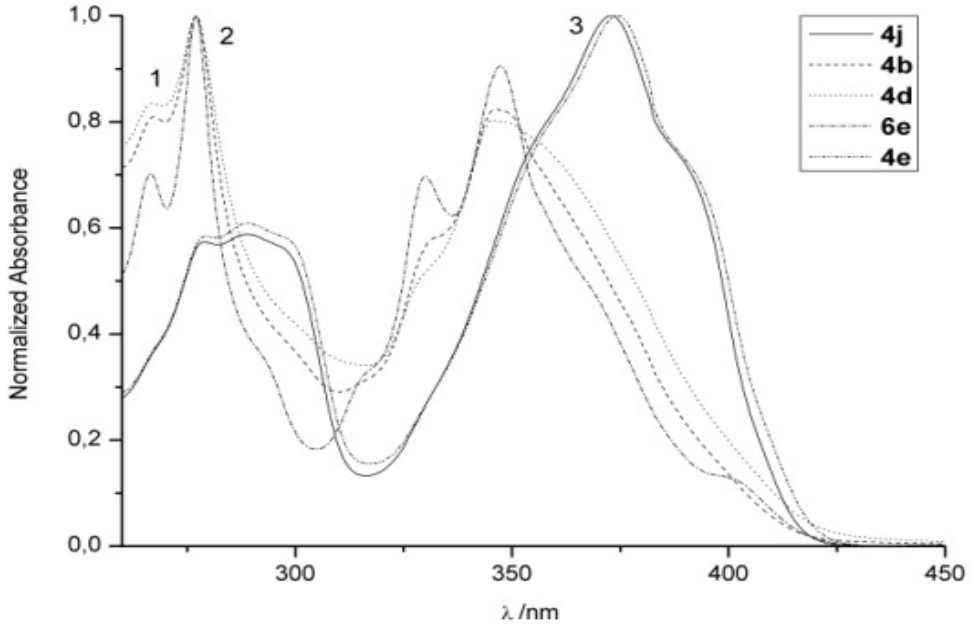


Figure 4. UV-Vis spectra of **4i,b,d,e** and **6e** (DCM, c = 10^{-5} M)

Table 4. Assigned transitions of **4i,b,d,e** and **6e**

	$\lambda 1_{abs}$ [nm]	$\lambda 2_{abs}$ [nm]	$\lambda 3_{abs}$ [nm]
4j	280	293	373
4b	268	280	347
4d	267	279	347
6e	266	280	347
4e	280	293	374

(DCM, c = 10^{-5} M)

The fluorescence emission spectra of **4i,b,d,e** (Table 5) (excitation wavelength λ_{ex} = 373 nm), again recorded in CH_3CN, show two bands at approx. 420 nm and 440 nm (Figure 5). The emissions of **4b** and **4d** (bearing electron donating groups) are shifted to higher wavelenghths compared to **4i,e**. The spectrum of acrylate **6e** exhibits one emission at 455 nm.

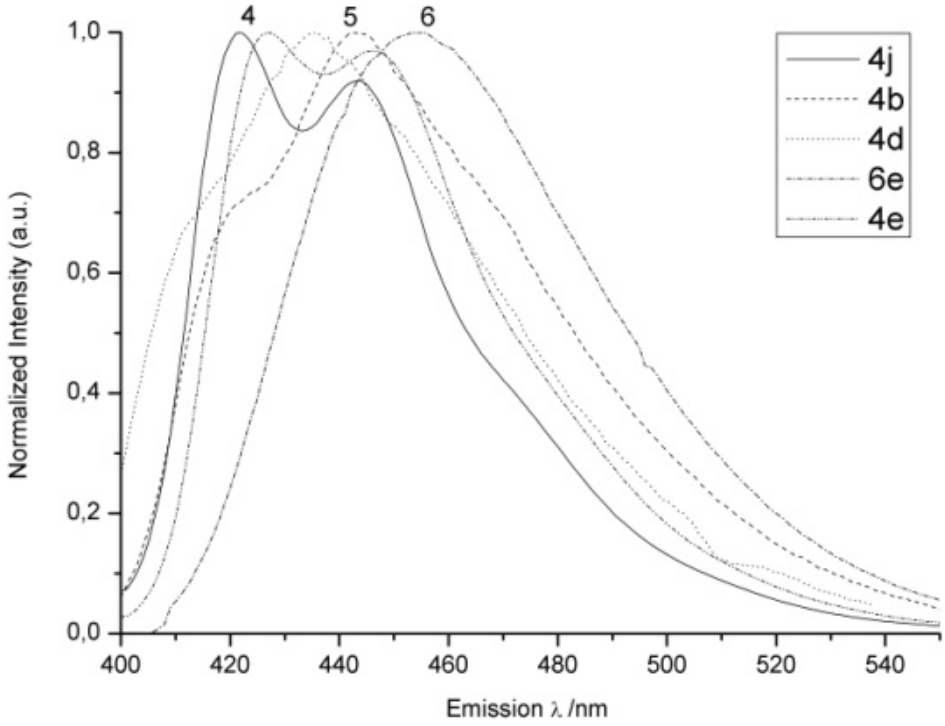


Figure 5. Fluorescence spectra of **4i,b,d,e** and **6e** (DCM, c = 10^{-6} M)

Table 5. Assigned transitions of **4i,b,d,e** and **6e**

	$\lambda 4_{em}$ [nm]	$\lambda 5_{em}$ [nm]	$\lambda 6_{em}$ [nm]
4j	420	443	-
4b	422	443	-
4d	417	434	-
6e	-	-	455
4e	426	446	-

Emissions of **4i,b,d,e** and **6e** measured in (DCM, c = 10^{-6} M)

Furthermore I have carried out solvatochromic studies for the UV-Vis absorption and fluorescence (Figures 6-10). In the UV-Vis spectra of **4e, j**, containing electron-withdrawing substituents, a red shift is observed for DMSO (15 nm) and DMF (10 nm) compared to acetonitrile. For unpolar solvents, like hexane, a slight blue shift (5 nm) is observed. On the other hand, a different effect is observed for pyrenes **4b** and **4d** containing electron-donating substituents. The use of hexane causes a significant red shift (20 nm). For compound **4b**, a

new absorption band is observed at about 375 nm. For acrylate **6e,** a slight red shift (10 nm) is observed for DMSO and a blue shift (10 nm) is observed for hexane.

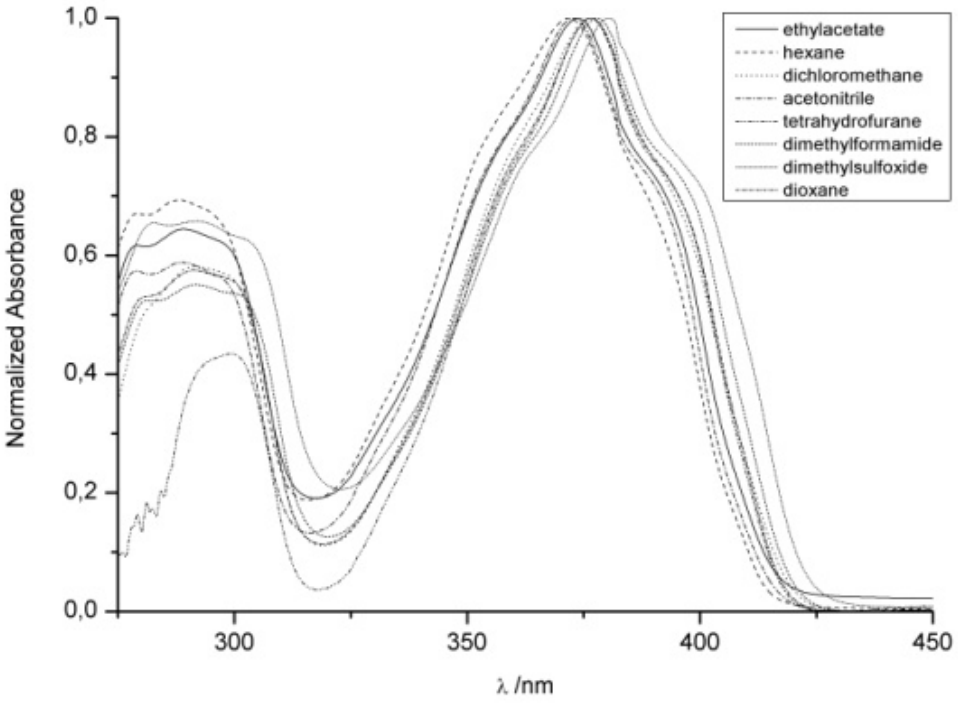


Figure 6. Solvatochromic effects (absorption) for **4i** ($c = 10^{-6}$ M)

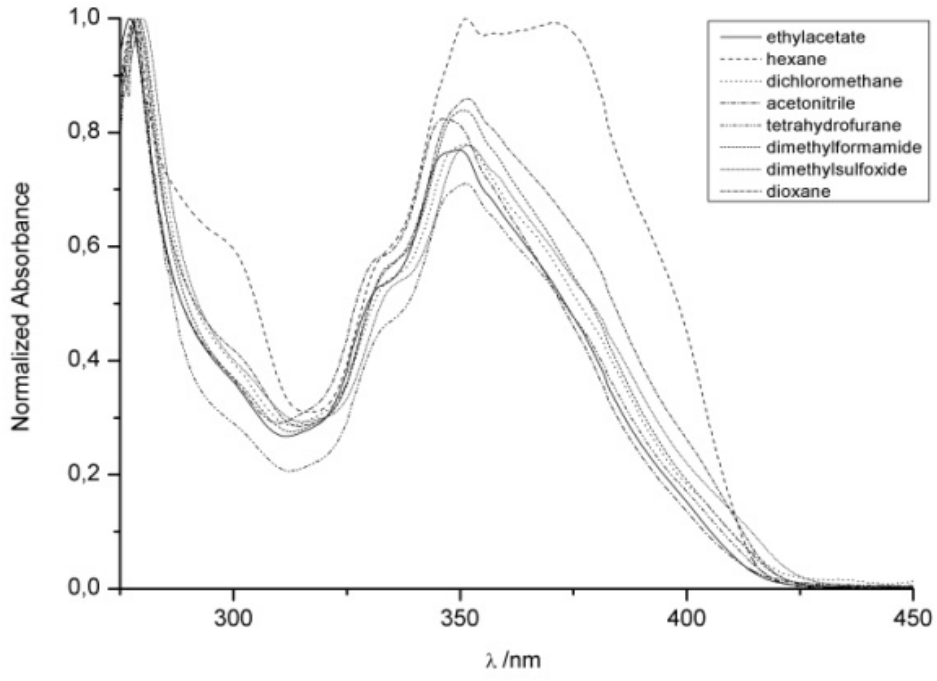


Figure 7. Solvatochromic effects (absorption) for **4b** ($c = 10^{-6}$ M)

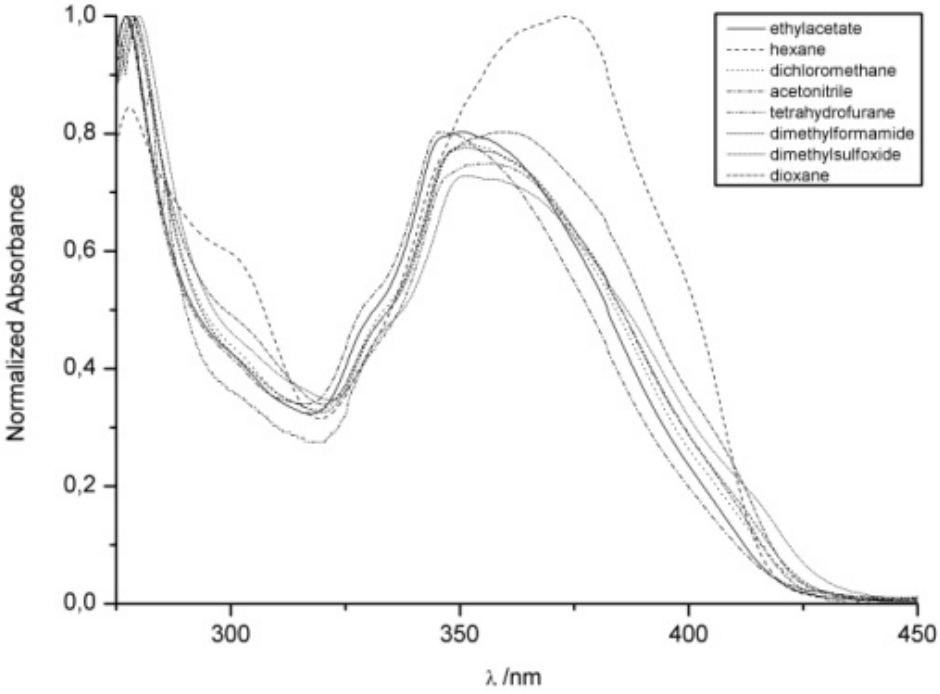


Figure 8. Solvatochromic effects (absorption) for **4d** ($c = 10^{-6}$ M)

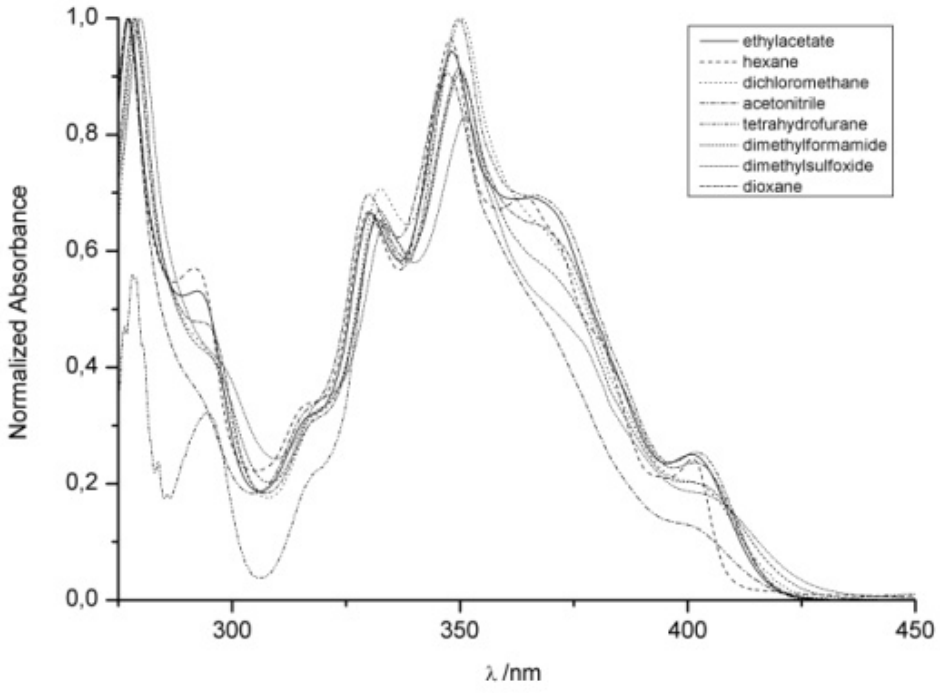


Figure 9. Solvatochromic effects (absorption) for **6e** ($c = 10^{-6}$ M)

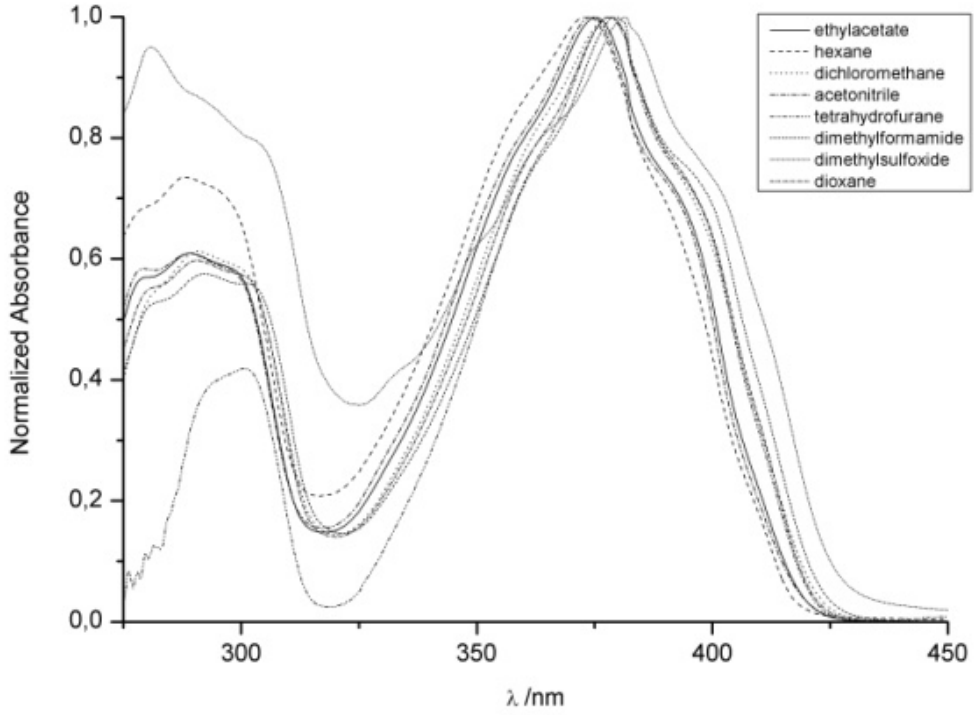


Figure 10. Solvatochromic effects (absorption) for **4e** ($c = 10^{-6}$ M)

The fluorescence emission spectra also show an influence of the solvent (Figures 11-15). Pyrenes **4e,i** containming electron-withdrawing substituents, show a slight red shift (5-10 nm) compared to acetonitrile. For pyrenes **4b,d**, containing electron-donating substituents, a red shift is observed for DMSO (20 nm) and for DMF (10 nm). For acyrlate **6e** a slight blue shift (10 nm) is observed for dichloromethane, DMSO and DMF. The strongest blue shift (approx. 30 nm) was observed for hexane, EtOAc, THF, and dioxane. Furthermore, in dioxane and EtOAc a new emission band appears at about 445 nm.

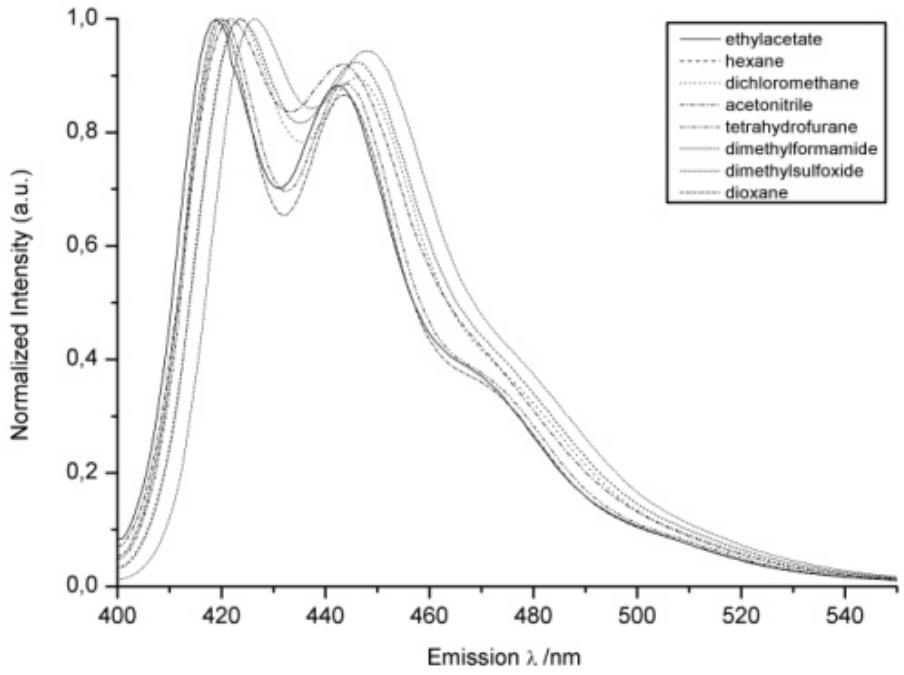


Figure 11. Solvatochromic effects (fluorescence) for **4i** ($c = 10^{-6}$ M)

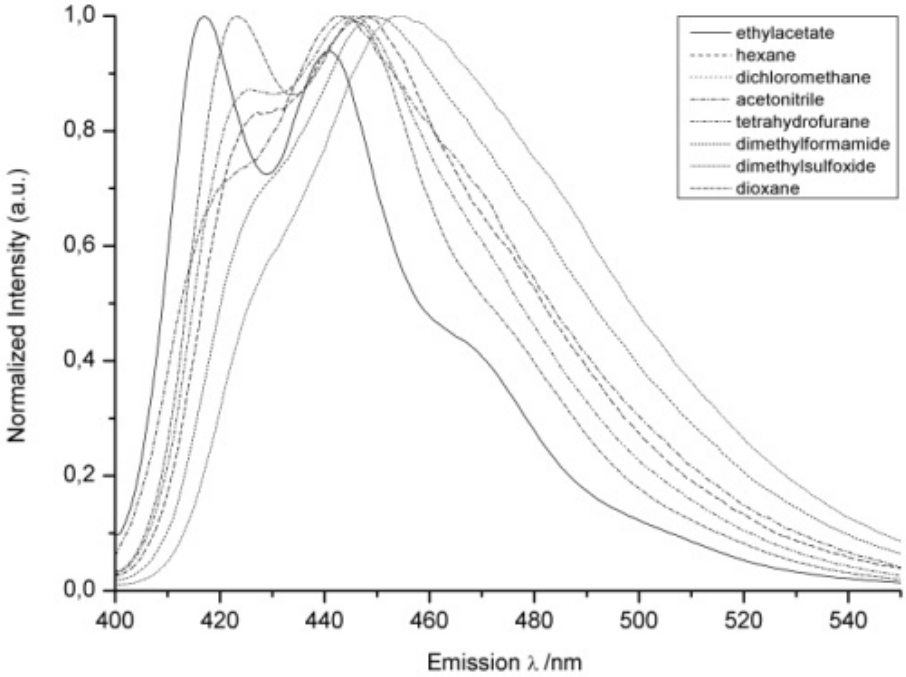


Figure 12. Solvatochromic effects (fluorescence) for **4b** ($c = 10^{-6}$ M)

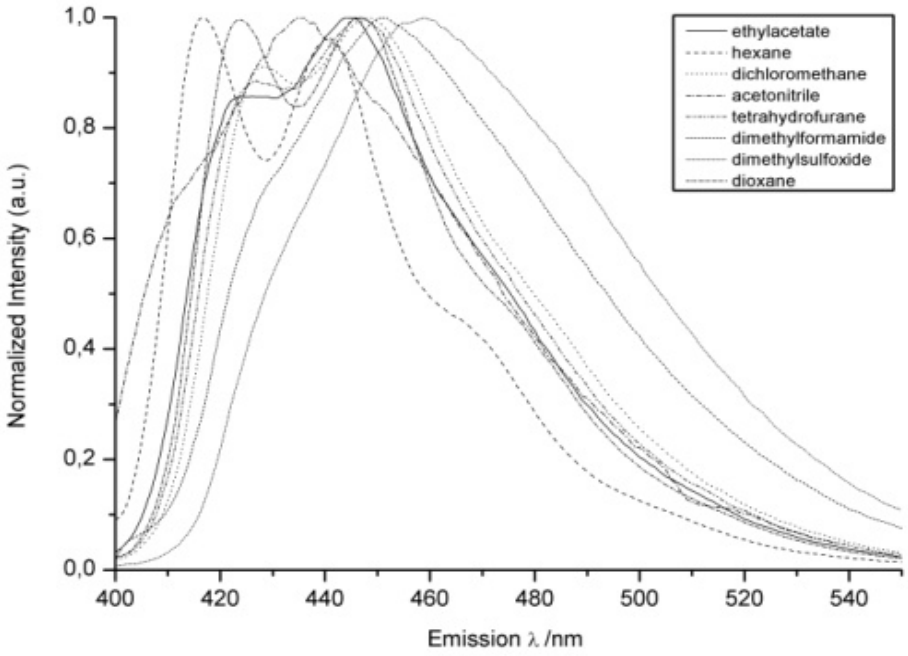


Figure 13. Solvatochromic effects (fluorescence) for **4d** ($c = 10^{-6}$ M)

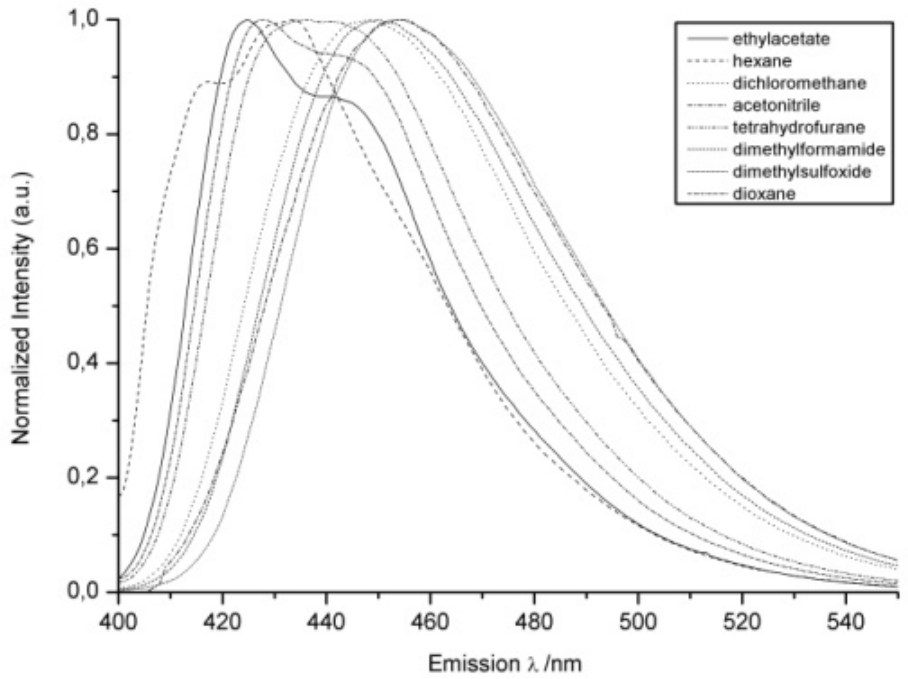


Figure 14. Solvatochromic effects (fluorescence) for **6e** ($c = 10^{-6}$ M)

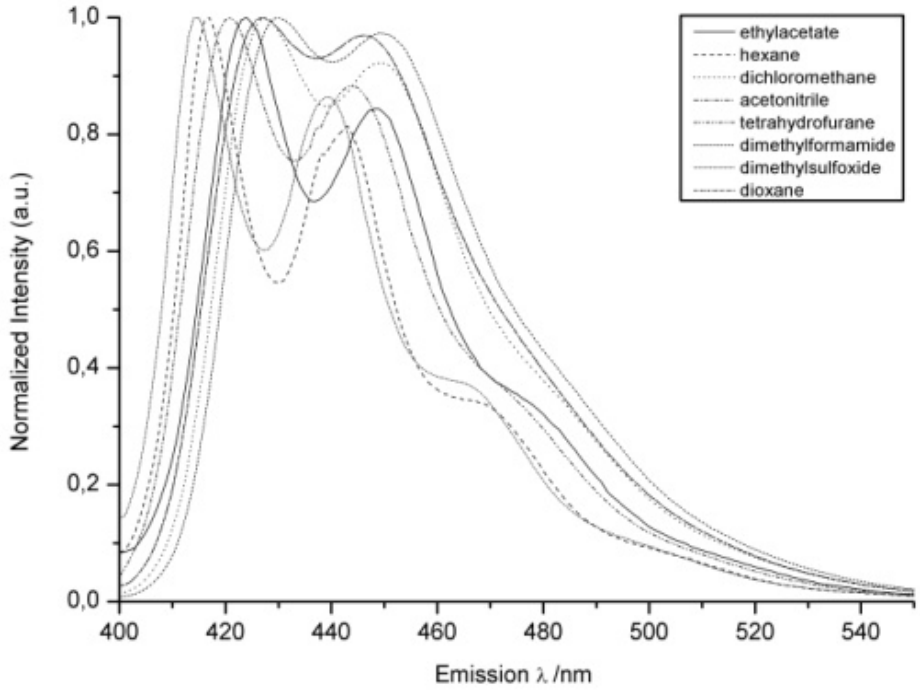


Figure 15. Solvatochromic effects (fluorescence) for **4e** ($c = 10^{-6}$ M)

1.2.4 Measurements of electrochemical properties pyrene compounds

Cyclo-voltammetric measurements were carried out to determine the electrochemical activity and to derive the potential values of the 1-alkenylpyrenes. Figure 16 shows the influence of different substituents on the oxidation potential. Most of the substrates exhibit two oxidation peaks. One of them is always located at 1.4 V, this peak is only weakly developed and it can also be found in the DPV of the starting material. The second oxidation peak is mostly well developed and is located between 1.0 and 1.2 V. The exact position of this peak depends on the type of substituent. For pyrenes containing electron-withdrawing substituents (**4e,i**) a slight shift to negative potential (1,05 V) is observed. For pyrenes **4b,d**, containing electron-donating substituents, a slight shift to positive potential (1,15 V) is observed.

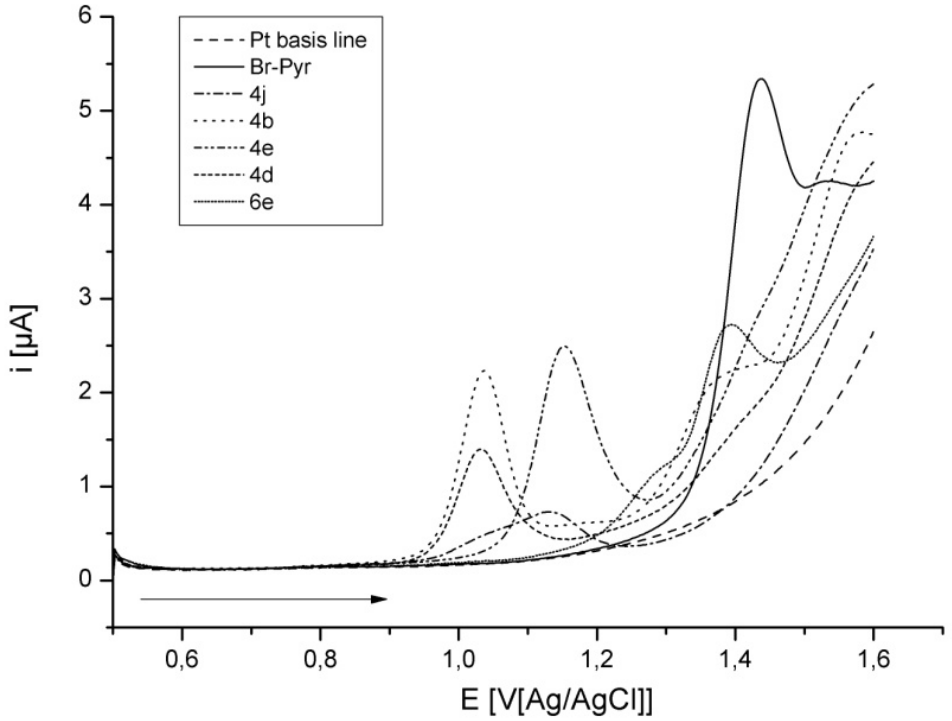


Figure 16. Oxidative DPVs of different substituted pyrenes in DMF (0.1 M $TBABF_4$); working electrode: platinum

1.2.5 Computational studies of pyrene compounds

In order to get a better understanding of the geometric and electronic structure of the molecules, Sebastian Reimann (Group of Prof. Langer) carried out density functional theory (DFT) calculations, using Becke's three parameter set with Lee-Yang-Parr modification (B3LYP) using a 6-31G* basis set of theory. The calculated HOMO and LUMO surfaces of the molecules along with their electrostatic potential maps in the ground states, the dipole moments and the calculated HOMO-LUMO energy gap are given in Figure 17. The calculations suggest that the 1-alkenylpyrenes are slightly twisted out of plane. The slight twisting might be a result of steric interactions and will not significantly disturb the conjugation. However, the X-ray crystal structures show that the pyrene moiety, the double bond and the phenyl ring (for products **4**) are in plane in the solid state. This result suggests that the planar structures in the solid state might be a result of the crystal packing. In case of pyrene **6e**, the HOMO and the LUMO are nearly fully localized on the pyrene moiety. In case

of **4e,i,b,d**, the HOMO and the LUMO are spread all over the molecule. The localization of HOMO and LUMO on either side of the alkenyl linkage (with contribution from the alkene to both HOMO and LUMO) suggests that the alkene acts as a conjugation bridge in all the molecules.

The electrostatic potential maps are supposed to indicate the drifting of charges in the molecules dependent on the type of substituents. In case of **4d** the strong donor group leads to an increase of the charge on the alkenyl moiety. This effect is also obvious in case of **4b** containing a weaker electron-donating group. In case of **4e**, the electron-withdrawing group leads to a decrease of the charge on the alkenyl moiety. In case of acrylate **6e**, the charge is mainly located on the pyrene and the carboxylate moiety which also slightly increases the charge on the alkenyl moiety.

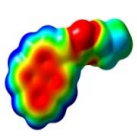
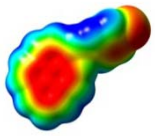
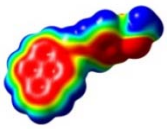
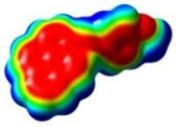
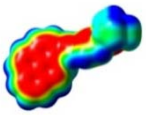
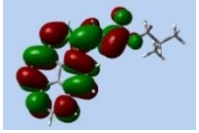
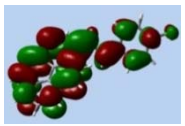
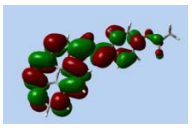
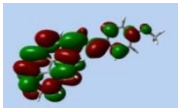
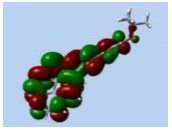
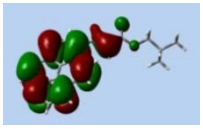
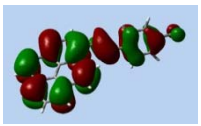
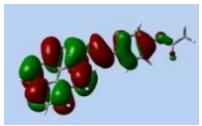
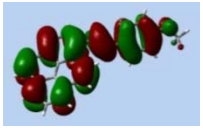
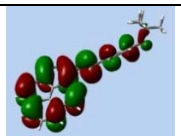
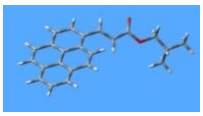
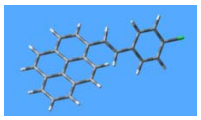
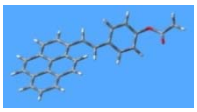
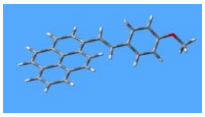
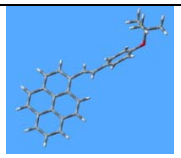
Compound	**6e**	**4e**	**4j**	**4b**	**4d**
Potential					
LUMO					
HOMO					
Geometry					
μcalc(D)	2.535	2.218	1.694	1.951	1.563
ΔEcalc HOMO-LUMO	3.338	3.278	3.287	3.2681	3.2912

Figure 17. DFT calculated ground-state geometries (with dipole vectors), HOMO, LUMO, and potential energy surfaces of 1-alkenylpyrenes

Inspection of the energy levels of the HOMO and LUMO of the 1-alkenylpyrenes show that electron donating groups (**4b,d**) cause a slight increase of both energy levels, while electron-withdrawing groups (**4e,j**) effect a decrease of the energy levels (Figure 18).

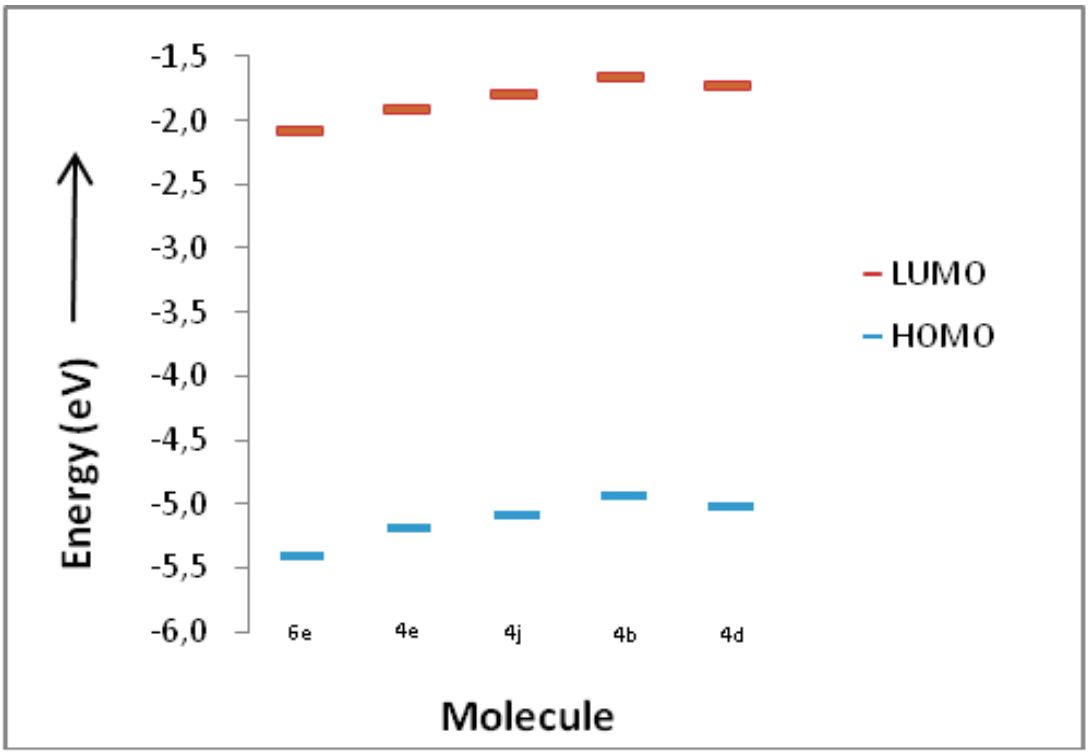


Figure 18. HOMO-LUMO energy levels (this energy level diagram shows the influence of the donor substituents on the HOMO and LUMO energies)

1.3 Conclusions

In conclusion, 1-alkenylpyrenes were prepared by Heck reaction of 1-bromopyrene with styrenes and acrylates. The absorption and emission spectroscopic properties of the products were studied. The electrochemical characteristics were also studied. The electrochemical band gaps are correlated with the HOMO-LUMO energy gaps derived from photophysical measurements and from theoretical calculations performed by density functional theory (DFT) calculations. The results suggest that the alkene act as a conjugation bridge in all the molecules.

2 Synthesis of Terphenyls from Mono- and Difluorinated Bromobenzenes by Site-Selective Suzuki-Miyaura Reactions

2.1 General Introduction

Chemists have always been interested in finiding new methods for the formation of carbon-carbon bonds. These reactions very much smooth the progress of the construction of complex molecules from simple precursors. The Grignard, Diels–Alder, and Wittig reaction have been of great use in this regard in the last century. But for the last three decades transition metal-catalyzed reactions, particularly palladium(0)-catalyzed transformations, have gained significant value for carbon-carbon bond formation and many new ideas have been tested and realized.[18] Currently, these reactions are being used for the synthesis of a number of natural products, pharmaceuticals and advanced materials.[19-21] The most commonly applied palladium-catalyzed carbon–carbon bond forming reactions in total synthesis are, namely, the Heck,[22] Stille,[23] Suzuki,[24] Sonogashira,[25] Tsuji–Trost,[26] and the Negishi[27] reaction. The mechanisms of these reactions are similar. The first step is usually the oxidative addition of organic halides or triflates to the Pd(0) complex to form organopalladium halides. The following step is, in case of the Suzuki, Sonogashira and Stille reaction, often a transmetallation with nucleophilic compounds to give a diorganopalladium complex. This complex undergoes a reductive elimination to create carbon-carbon bond and regeneration of the catalyst.

The Suzuki-Miyaura reaction is the reaction that gained much significance for its effectiveness for the cross-coupling between halides and organoboronic acids.[28] Advances made in this field include the improvement of new catalysts and modern methods have greatly increased the scope of this reaction and is now considered to be a quite general procedure for a wide range of selective carbon-carbon bond formations.[29] The scope of the reaction partners is not only restricted to arenes, but includes also alkyl, alkenyl and alkynyl compounds.

The mechanism of the Suzuki reaction involves the oxidative addition of organic halides or triflates to the Pd(0) complex to form a organopalladium halide (R^1-Pd(II)-X). This step is followed by transmetallation with a boronic acid derivative or a borane to give a diorganopalladium complex (R^1-Pd-R^2). This complex undergoes a reductive elimination with carbon-carbon bond formation and regeneration of the catalyst.[30-33] The reactivity order of

aryl halides and aryl triflates which act as electrophiles, is Ar-I > Ar-Br > Ar-OTf > Ar-Cl. The use of base accelerates the transmetalation. This is due to the increase of the carbanion character of the organoborane moiety by formation of an organoborate containing a tetravalent boron atom. The selection of a proper catalyst plays an important role in the success of the desired reaction. The common palladium sources employed include, for example, $Pd(OAc)_2$, $PdCl_2$, $Ph(PPh_3)_2Cl_2$, and $Pd(dba)_2$. The use of bulky electron-rich ligands is often the key for a successful transformation. The ferrocenylphosphine,[34] *N*-heterocyclic carbenes,[35] $P(t\text{Bu})_3$,[36] $P(Cy)_3$ often give a good yields.

Suzuki-Miyaura reactions[37] in particular are very attractive, due to the stability of the precursors, boronic acids, and facility of work up. In this reaction even an alkyl group (i.e. sp^3-hybridized C atom), as opposed to the more traditionally used vinyl or aryl groups, can be transferred from the organoborane component during the palladium-catalyzed coupling process with vinyl or aryl halides or triflates. Compared to Stille reactions,[38] Suzuki–Miyaura couplings have a much broader scope in a potentially vast range of alkyl boranes (typically prepared through the regio- and chemoselective hydroboration of readily available alkene precursors) can be employed in the reaction.[38] The interest of the chemist in this field is evident from the continuous developments in the use of new reaction conditions, catalysts and ligands.[40-42]

2.1.1 Introduction

Fluorinated arenes are often biologically active and thus interesting compounds which find many uses as pharmacologically active substances, agrochemicals, or as building blocks for their synthesis.[43] Fluorinated molecules are increasingly used in the pharma and crop protection industry. This is due to the fact that strategically placed fluorine atoms often have a positive influence on the biological properties of active compounds.[44] For this reason synthetic methods for the selective preparation of specifically fluorinated intermediates and building blocks are of high importance.

The fluorine compounds are the least abundant natural organohalides.[45] Until 1957, no fluorine containing drug had been developed. Since then, over 150 fluorinated drugs have come to market and now make about 20% of all pharmaceuticals[46], with even higher figures for agrochemicals up to 30%.[47]

A large number of known pharmaceutical and agrochemical products contain fluorinated arenes which enhance solubility, bioavailability and metabolic stability compared with non-

Fluorinated analogues.[48] Fast progress in this area has been fuelled by the development of new fluorination processes increasing the range of synthetic fluorinated building blocks acquiescent to functional group manipulation. The strategic use of fluorine substitution in drug design has culminated with the production of some of the key drugs available in the market.[49]

The site-selectivity of these reactions is generally influenced by electronic and steric parameters.[50] Our research group has already reported site-selective Suzuki-Miyaura (S-M) reactions of tetrabrominated thiophene, *N*-methylpyrrole, selenophene, and of other polyhalogenated heterocycles.[51] Site-selective S-M reactions of the bis(triflate) of methyl 2,5-dihydroxybenzoate have also been studied.[52] Site-selective palladium(0)-catalyzed cross-coupling reactions of dibromides, diiodides or bis(triflates) of fluorinated arenes have, to the best of our knowledge, not been reported to date.

2.2 Results and discussion

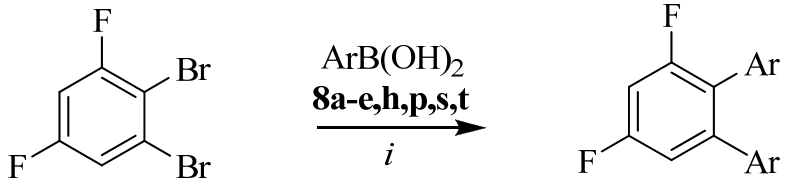
2.2.1 One pot synthesis of difluorinated ortho-terphenyls by site-selective Suzuki reactions of 1,2-dibromo-3,5-difluorobenzene

In the following section, first results of my study related to S–M reactions of 1,2-dibromo-3,5-difluorobenzene are reported. The products, difluorinated *ortho*-terphenyls, are not readily available by other methods. The S–M reaction of commercially available 1,2-dibromo-3,5-difluorobenzene **7** with two equivalents of arylboronic acids **8a**–**e,h,p,s,t** (Table 6) afforded the difluorinated *ortho*-terphenyls **9a**–**i** in moderate to good yields (Scheme 4, Table 7). The best yields were obtained using 2.2 equivalents of the arylboronic acid, $Pd(PPh_3)_4$ (0.03 equiv) as the catalyst, and Cs_2CO_3 (2.2 equiv) as the base (1,4-dioxane, 90 °C, 8 h)

Table 6. Aryl boronic acids

	Ar-$B(OH)_2$		Ar-$B(OH)_2$
8	Ar	**8**	Ar
a	C_6H_5	**l**	4-(Acetyl)C_6H_4
b	4-MeC_6H_4	**m**	3,5-$(Me)_2C_6H_3$
c	2-$(MeO)C_6H_4$	**n**	3-ClC_6H_4
d	4-$(MeO)C_6H_4$	**o**	4-ClC_6H_4
e	4-$(EtO)C_6H_4$	**p**	4-FC_6H_4
f	3,4-$(MeO)_2C_6H_3$	**q**	4-$CF_3C_6H_4$

g	2,6-$(MeO)_2C_6H_3$	**r**	2-$(MeO)C_6H_4$
h	2,4-$(MeO)_2C_6H_3$	**s**	3-$(MeO)C_6H_4$
i	4-$(Vinyl)C_6H_4$	**t**	3-MeC_6H_4
j	4-(tBu)C_6H_4	**u**	2-Thienyl
k	4-(tBuO)C_6H_4	**v**	2,3-$(MeO)_2C_6H_3$



7 **9a-i**

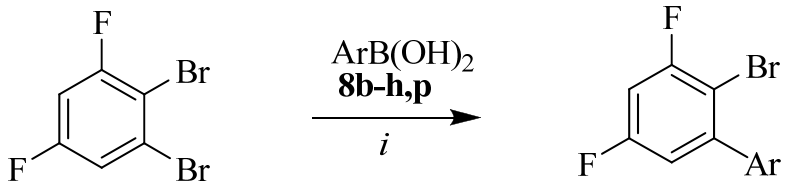
Scheme 4. Synthesis of **9a–i**. *Reagents and conditions*: *i*, **7** (1.0 equiv), **8a–e,h,p,s,t** (2.2 equiv), Cs_2CO_3 (2.2 equiv), $Pd(PPh_3)_4$ (3 mol%), 1,4-dioxane, 90 °C, 8 h.

Table 7. Synthesis of **9a-i**

8	**9**	Ar	Yields of **9** (%)[a]
a	**a**	C_6H_5	65
b	**b**	4-MeC_6H_4	45
c	**c**	2-$(MeO)C_6H_4$	60
d	**d**	4-$(MeO)C_6H_4$	70
e	**e**	4-$(EtO)C_6H_4$	68
h	**f**	2,4-$(MeO)_2C_6H_3$	58
p	**g**	4-FC_6H_4	45
s	**h**	3-$(MeO)C_6H_4$	70
t	**i**	3-MeC_6H_4	48

[a]Yields of isolated products

The S–M reaction of **7** with arylboronic acids **8b-h,p** (1.0 equiv) afforded the 2-bromo-3,5-difluoro-biphenyls **10a**–**h** in good yields and with very good site selectivity (Scheme 5, Table 8). The formation of the opposite regioisomer was not observed.



7 **10a-h**

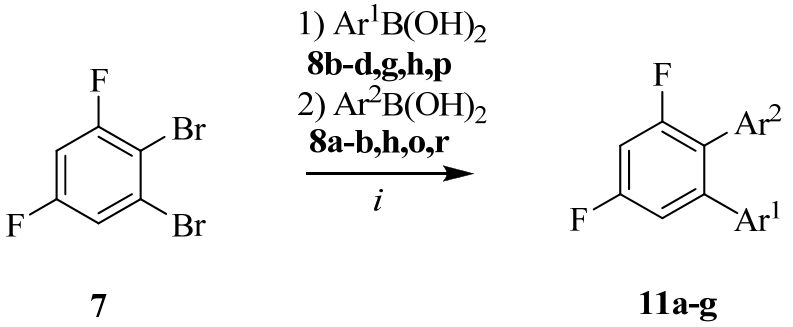
Scheme 5. Synthesis of **10a**–**h**. *Reagents and conditions*: *i*, **7** (1.0 equiv), **8b-h,p** (1.0 equiv), Cs_2CO_3 (1.5 equiv), $Pd(PPh_3)_4$ (3 mol%), 1,4-dioxane, 90 °C, 9 h.

Table 8. Synthesis of **10a-h**

8	**10**	Ar	Yields of **10 (%)**[a]
b	**a**	4-MeC_6H_4	45
c	**b**	2-$(MeO)C_6H_4$	60
d	**c**	4-$(MeO)C_6H_4$	60
e	**d**	4-$(EtO)C_6H_4$	65
f	**e**	3,4-$(MeO)_2C_6H_3$	60
g	**f**	2,6-$(MeO)_2C_6H_3$	68
h	**g**	2,4-$(MeO)_2C_6H_3$	67
p	**h**	4-FC_6H_4	63

[a]Yields of isolated products

The one-pot reaction of 1,2-dibromo-3,5-difluorobenzene with two different arylboronic acids afforded the unsymmetrical difluorinated *ortho*-terphenyls **11a**–**g** containing two different terminal aryl groups (Scheme 6, Table 9)



7 **11a-g**

Scheme 6. One-pot synthesis of **11a**–**g**. *Reagents and conditions: i*, **1** (1.0 equiv), **8b-d,g,h,p** (1.0 equiv), Cs_2CO_3 (1.5 equiv), $Pd(PPh_3)_4$ (3 mol%), 1,4-dioxane, 90 °C, 8 h; 2) **8a-b**,**h,o,r** (1.2 equiv), Cs_2CO_3 (1.5 equiv), 90 °C, 8 h.

Table 9. Synthesis of **11a-g**

8	**11**	Ar^1	Ar^2	Yield of **11**(%)[a]
b,h	**a**	4-MeC_6H_4	2,4-$(MeO)_2C_6H_3$	56
d,r	**b**	4-$(MeO)C_6H_4$	2-MeC_6H_4	68
d,a	**c**	4-$(MeO)C_6H_4$	C_6H_5	70
c,b	**d**	2-$(MeO)C_6H_4$	4-MeC_6H_4	62
g,b	**e**	2,6-$(MeO)_2C_6H_3$	4-MeC_6H_4	60
h,b	**f**	2,4-$(MeO)_2C_6H_3$	4-MeC_6H_4	48
p,o	**g**	4-FC_6H_4	4-ClC_6H_4	45

[a]Yields of isolated products

The structures of all products were established by spectroscopic methods. The structures of **9b** and **10f** were independently confirmed by X-ray crystal structure analyses (Figure 19 and Figure 20). The aryl group at positon 1 of structure **9b** is twisted out of plane whereas the aryl group at position 2 is in plane. In case of stucture **10f** the aryl groups are slightly out of plane.

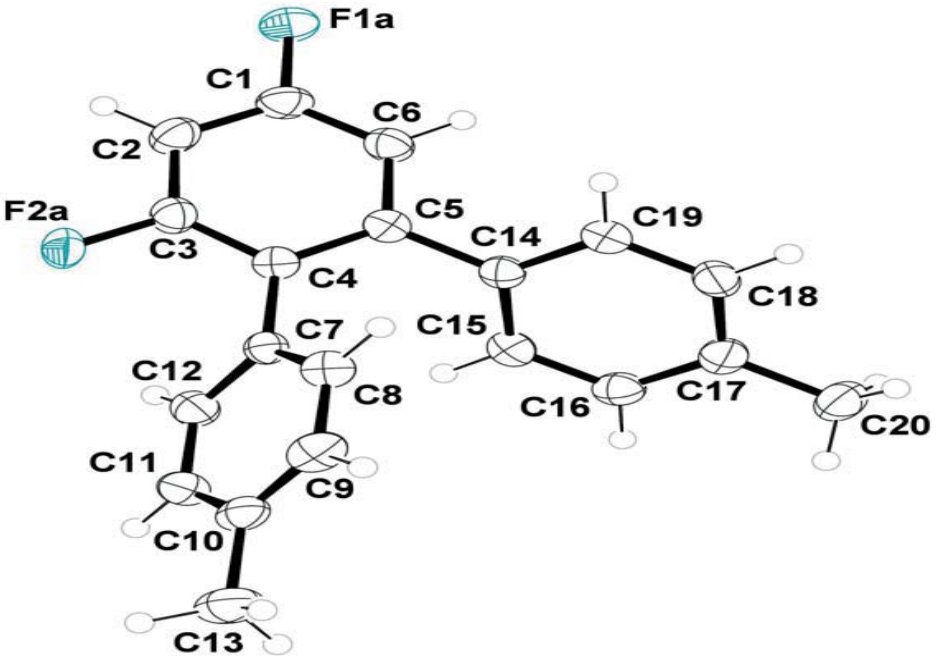


Figure 19. Ortep plot of **9b**

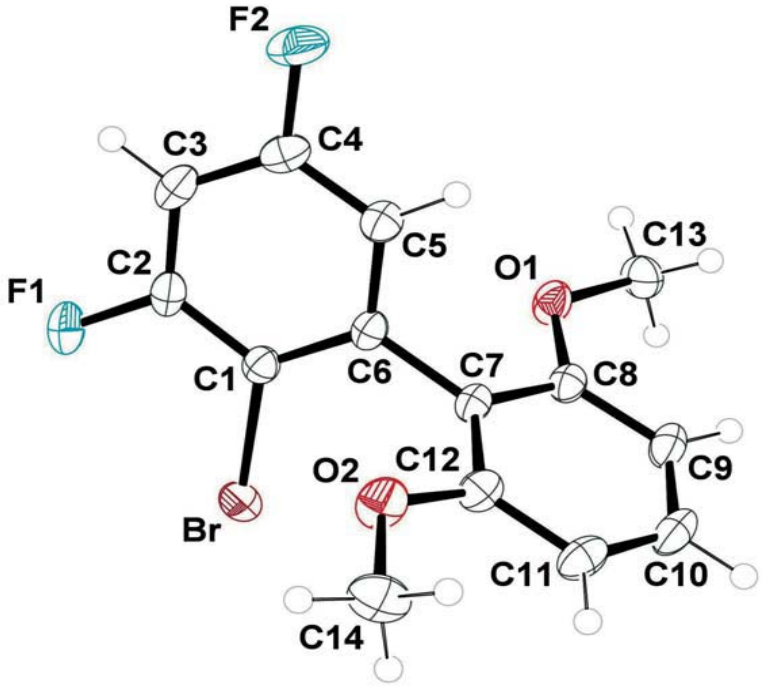


Figure 20. Ortep plot of **10f**

The structure of compound **10g** has also been confirmed by 2D NMR (NOESY; HMBC) (Figure 21). H-6 of the ring B resonating at δ = 7.08 ppm showed a clear and important NOESY correlation with the H-6 of ring A resonating at δ = 6.89 ppm. This proved the connectivtity of aryl group at C-1 of ring A. HMBC correlation of H-6 with carbon C-1 of ring A again confirmed that the aryl group is attached at the carbon C-1 of ring A.

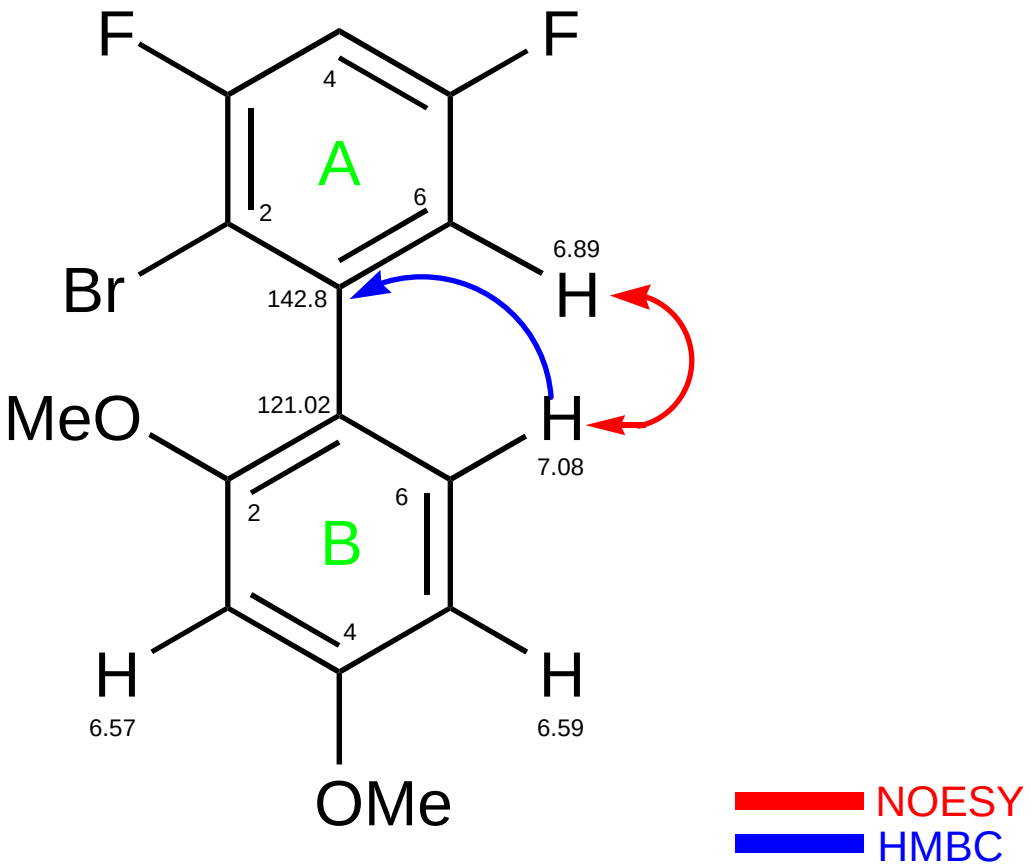
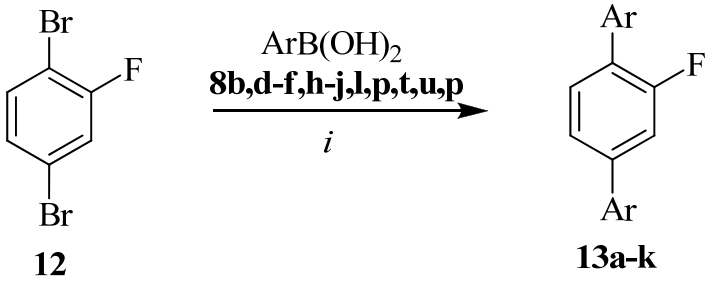


Figure 21.

2.2.2 One pot synthesis of fluorinated terphenyls by site-selective Suzuki-Miyaura reactions of 1,4-dibromo-2-flourobenzene

The S–M reaction of commercially available 1,4-dibromo-2-fluorobenzene **12** with 2 equiv. of arylboronic acids **8b,d,f,h-j,l,p,t,u** afforded the fluorinated para-terphenyls **13a–k** in moderate to good yields (Scheme 7, Table 10). The best yields were obtained using 2.2 equiv. of the arylboronic acid, $Pd(PPh_3)_4$ (0.03 equiv) as the catalyst and Cs_2CO_3 (2.2 equiv) as the base (1,4-dioxane, 90 °C, 8 h). The S–M reaction of **12** with arylboronic acids **8b,d,f,i,j,n,o** (1.0 equiv) afforded the biaryls **14a–h** in good yields and with very good site selectivity (Scheme 8, Table 11). The formation of the opposite regioisomers was not observed.



12 **13a-k**

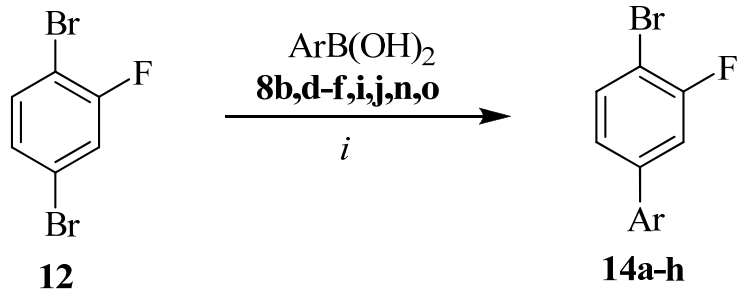
Scheme 7. Synthesis of **13a–k**. *Conditions*: (*i*) 1 (1.0 equiv), **8b,d,f,h-j,l,p,t,u** (2.2 equiv), Cs_2CO_3 (2.2 equiv), $Pd(PPh_3)_4$ (3 mol %), 1,4-dioxane, 90 °C, 6–8 h.

Table 10. Synthesis of **13a-k**

8	**13**	Ar	Yields of **13** (%)[a]
b	**a**	4-MeC_6H_4	60
d	**b**	4-$(MeO)C_6H_4$	52
e	**c**	4-$(EtO)C_6H_4$	65
f	**d**	3,4-$(MeO)_2C_6H_3$	58
h	**e**	2,4-$(MeO)_2C_6H_3$	63
i	**f**	4-$(Vinyl)C_6H_4$	45
j	**g**	4-*t*BuC_6H_4	63
l	**h**	4-$(Acetyl)C_6H_4$	52
p	**i**	4-FC_6H_4	48
t	**j**	3-MeC_6H_4	60
u	**k**	2-Thienyl	50

[a]Yields of isolated products

Interestingly, the yields of products **15a–c** are in the same range as the yields of **14a–h**. This might be explained by the assumption that the selectivity and the yields are mainly determined by the first attack of the boronic acid to **12**. The second attack during the synthesis of **15a–c** only has a small influence on the yield because no problem of site-selectivity exists. On the other hand, the yield of products **13a–k** (where no problem of site-selectivity exists) is in a similar range. Therefore, we believe that the chromatographic purification also has a great influence on the yield, due to some loss of material. For all reactions, only one chromatographic purification has to be carried out. Inspection of the NMR of the crude products **15a–c** (before purification) shows that a small amount of mono-coupling and double-coupling product (containing two Ar^1 groups) is present in most cases. In case of the synthesis of **14a–h**, a small amount of double-coupling product is present in the crude product mixture.



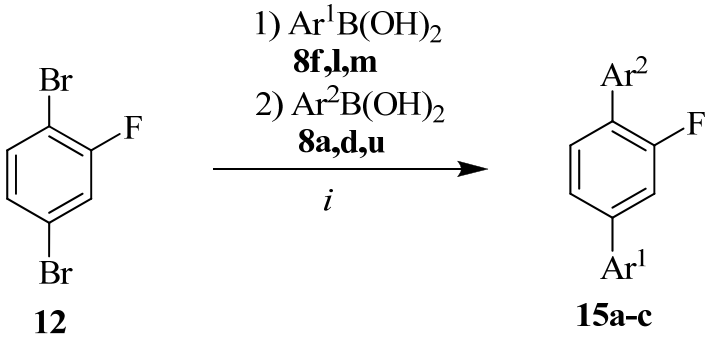
Scheme 8. Synthesis of **14a–h**. *Conditions*: (*i*) **12** (1.0 equiv), **8b,d-f,i,j,n,o** (1.0 equiv), Cs_2CO_3 (1.5 equiv), $Pd(PPh_3)_4$ (3 mol %), 1,4-dioxane, 90 °C, 6–8 h.

Table 11. Synthesis of **14a-h**

8	**14**	Ar	Yields of **14** (%)[a]
b	**a**	4-MeC_6H_4	60
d	**b**	4-$MeOC_6H_4$	60
e	**c**	4-$EtO(C_6H_4)$	68
f	**d**	3,4- $(MeO)_2C_6H_3$	67
i	**e**	4-(Vinyl)C_6H_4	45
j	**f**	4-(*t*Bu)C_6H_4	58
n	**g**	3-ClC_6H_4	57
o	**h**	4-ClC_6H_4	60

[a]Yields of isolated products

The one-pot reaction of 1,4-dibromo-2-fluorobenzene **12** with two different arylboronic acids afforded the unsymmetrical fluorinated *para*-terphenyls **15a–c** containing two different terminal aryl groups (Scheme 9, Table 12).



12 **15a-c**

Scheme 9. One-pot synthesis of **15a-c**. *Conditions:*1) **12** (1.0 equiv.), **8f,l,m** (1.0 equiv.), Cs_2CO_3 (1.5 equiv.), $Pd(PPh_3)_4$ (3 mol-%), 1,4-dioxane, 90 °C, 8 h, 2) **8a,d,u** (1.2 equiv.), Cs_2CO_3 (1. 5 equiv.), 90 °C, 8 h.

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

8	**15**	Ar^1	Ar^2	Yields of **15** (%)[a]
f,u	**a**	3,4-$(MeO)_2C_6H_3$	2-Thienyl	53
l,d	**b**	4-(Acetyl)C_6H_4	4-$MeOC_6H4$	60
m,a	**c**	3,5-$(Me)_2C_6H_3$	C_6H_5	65

[a]Yields of isolated products

The structures of all products were established by spectroscopic methods. The structures of **14e** and **13b** were independently confirmed by X-ray crystal structure analyses (Figure 22 and Figure 23). The aryl groups of structure **14f** are twisted out of plane whereas the aryl groups of **13c** are only slightly twisted.

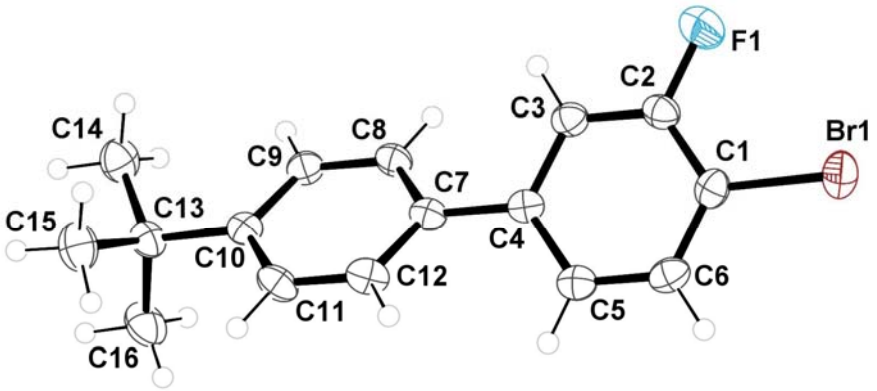


Figure 22. Ortep plot of **14f**

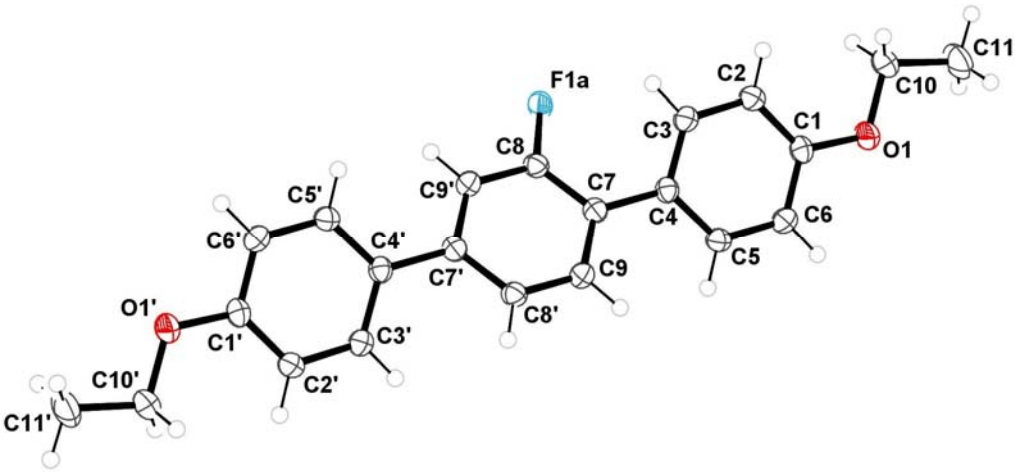
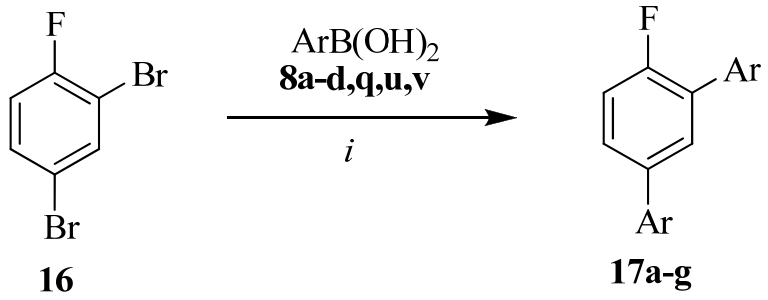


Figure 23. Ortep plot of **13c**

2.2.3. One pot synthesis of flourinated Terphenyls by site selective Suzuki- Miyura reactions of 1,3-dibromo-5-flourobenzene

The S–M reaction of commercially available 1,3-dibromo-5-fluorobenzene **16** with two equivalents of arylboronic acids **8a**–**d,q,u,v** afforded the difluorinated *ortho-para* terphenyls **17a**–**g** in moderate to good yields (Scheme 10, Table 13). The best yields were obtained using 2.2 equivalents of the arylboronic acid, $Pd(PPh_3)_4$ (0.03 equiv) as the catalyst, and Cs_2CO_3 (2.2 equiv) as the base (1,4-dioxane, 90 °C, 8 h).



16 **17a-g**

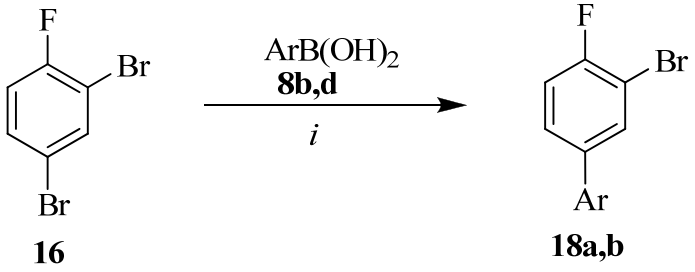
Scheme 10. Synthesis of **17a–g**. *Conditions*: (*i*) **16** (1.0 equiv), **8a-d,q,u,v** (2.2 equiv), Cs_2CO_3 (2.2 equiv), $Pd(PPh_3)_4$ (3 mol %), 1,4-dioxane, 90 °C, 6–8 h

Table 13. Synthesis of **17a-g**

8	**17**	Ar	Yields of **17**(%)[a]
a	**a**	C_6H_5	55
b	**b**	4-MeC_6H_4	62
c	**c**	2-$(MeO)C_6H_4$	60
d	**d**	4-$(MeO)C_6H_4$	70
q	**e**	4-$CF_3C_6H_4$	45
u	**f**	2-Thienyl	48
v	**g**	2,3-$(MeO)_2C_6H_3$	58

[a]Yields of isolated products

The S–M reaction of **16** with arylboronic acids **8b,d,** (1.0 equiv) afforded the 3-bromo-4-fluoro-biphenyls **18a**,**b** in good yields and with very good site selectivity (Scheme 11, Table 14). The formation of the opposite regioisomers was not observed.



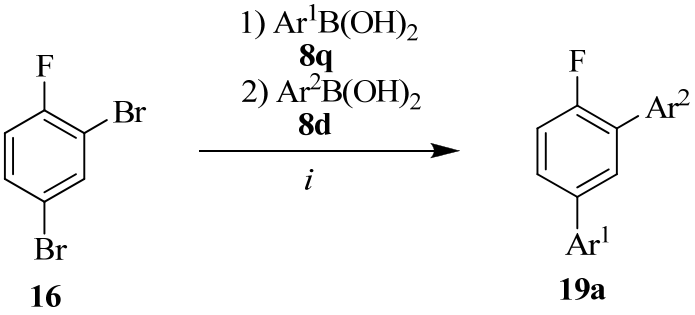
Scheme 11. Synthesis of **18a,b**. *Conditions*: (*i*) **16** (1.0 equiv), **8b,d** (1.0 equiv), Cs_2CO_3 (1.5 equiv), $Pd(PPh_3)_4$ (3 mol %), 1,4-dioxane, 90 °C, 6–8 h.

Table 14. Synthesis of **18a,b**

8	**18**	Ar	Yields of **18** (%)[a]
b	**a**	4-MeC_6H_4	63
d	**b**	4-$MeOC_6H_4$	70

[a]Yields of isolated products

The one-pot reaction of 1,3-dibromo-4-fluorobenzene **16** with two different arylboronic acids afforded the unsymmetrical fluorinated para-terphenyls **19a** containing two different terminal aryl groups (Scheme 12, Table 15).



Scheme 12. One-pot synthesis of 1**9a**. *Conditions* :*1*) **16** (1.0 equiv.), **8q** (1.0 equiv.), Cs_2CO_3 (1.5 equiv.), $Pd(PPh_3)_4$ (3 mol-%), 1,4-dioxane, 90 °C, 8 h, 2) **8d** (1.2 equiv.), Cs_2CO_3 (1. 5 equiv.), 90 °C, 8 h.

Table 15. Synthesis of **19a**

8	**19**	Ar^1	Ar^2	Yield of **19a** (%)[a]
q,d	**a**	4-$CF_3C_6H_4$	4-(MeO)C_6H_4	58

[a]Yields of isolated products

The structures of all products were established by spectroscopic methods. The site selectivity of **18b** was confirmed by 2D NMR (Fig. 21) the structure of **17b** was independently confirmed by x-ray crystal structure (Fig. 24). The aryl groups are twisted out of plane.

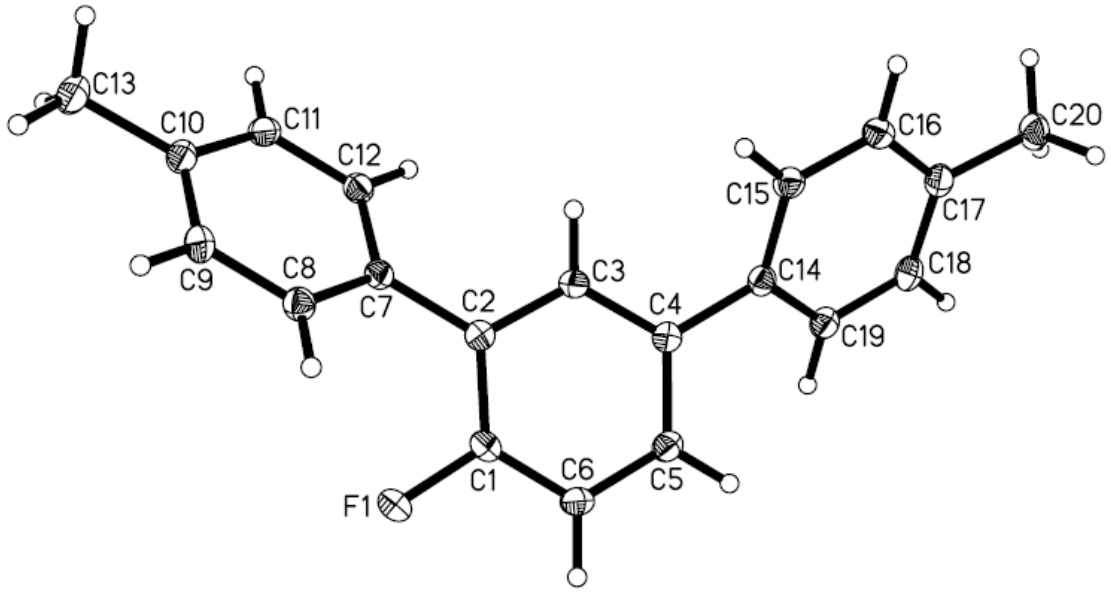


Figure 24. Ortep plot of **17b**

2.3 Conclusions

The site-selective formation of **10a–f** and **11a–d** can be explained by steric and electronic reasons. The first attack of palladium(0)-catalyzed cross-coupling reactions generally occurs at the more electron-deficient and sterically less hindered position.[53,54] Position 1 of 1,2-dibromo-3,5-difluorobenzene (**7**) is sterically less hindered because it is located next to a bromine and to a hydrogen atom while position 2 is located next to a bromine and to a fluorine atom (Figure 25). In addition, position 1 (located *meta* to the fluorine atoms) is

considerably more electron deficient than position 2 (located *ortho* and *para* to the fluorine atoms), due to the p-donating effect of the fluorine atom.

In fact, the ^{1}H NMR signals of aromatic protons located *ortho* or *para* to a fluorine atom are generally shifted to higher field compared to the proton located in *meta* position.[54]

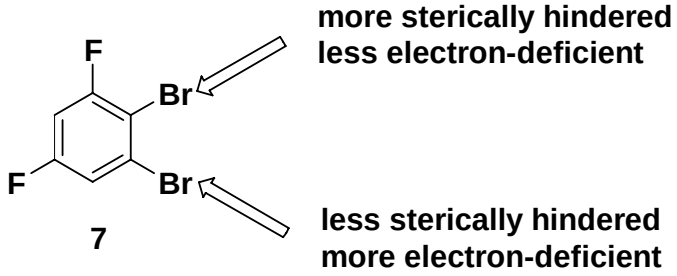


Figure 25. Possible explanation for the site-selectivity of cross-coupling reactions of **7**

So this way, we have reported site-selective Suzuki–Miyaura reactions of 1,2-dibromo-3,5-difluorobenzene which provide a convenient approach to difluorinated *ortho*-terphenyls and 2-bromo-3,5-difluoro-biphenyls.

Similarly, the site-selective formation of **14a–g** and **15a–b** can be explained by steric and electronic reasons. The first attack of palladium(0)-catalyzed cross-coupling reactions generally occurs at the more electronic deficient and sterically less hindered position.[53,54] Position 4 of 1,4-dibromo-2-fluorobenzene (**12**) is sterically less hindered because it is located next to two hydrogen atoms while position 1 is located next to a fluorine atom (Figure 26). In addition, position 4 (located meta to the fluorine atom) is more electron deficient than position 1 (located ortho to the fluorine atoms), due to the p-donating effect of the fluorine atom. In fact, the ^{1}H NMR signals of aromatic protons located ortho to a fluorine atom are generally shifted to higher field compared to the proton located in meta position.

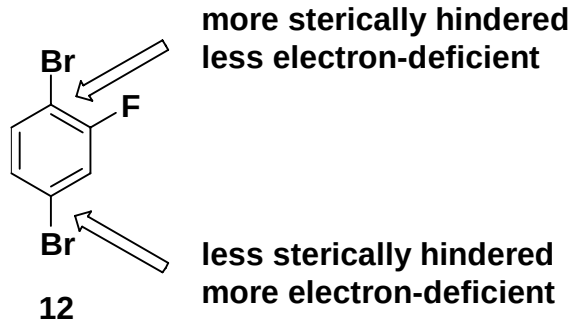


Figure 26. possible explanations for the site selectivity of cross coupling reactions of **12**

Furthermore, we have reported site-selective Suzuki–Miyaura reactions of 1,4-dibromo-2-fluorobenzene which provide a convenient approach to fluorinated terphenyls and biaryls.[55]

Thirdly, the site-selective formation of **18a**–**b** and **19a** can be explained by steric and by electronic reasons. The first attack of palladium(0)-catalyzed cross-coupling reactions generally occurs at the less electron-deficient position.[53] As per our previous knowledge we were expecting the attack on position 1 of 1,3-dibromo-4-fluorobenzene **16** but in this case the result was not according to our expectation rather it was opposite to that, in this case we observed the first attack on position 2 of 1,3-dibromo-4-fluorobenzene (**16**), which has been explained by NOESY correlation fig. 27A. In fact, the ^{1}H NMR signals of aromatic protons located *ortho* or *para* to a fluorine atom are generally shifted to higher field.[54]

So, we have also prepared site-selective Suzuki–Miyaura reactions of 1,3-dibromo-4-fluorobenzene which provide a convenient approach to fluorinated *ortho-para*-terphenyls and 3-bromo-4-fluoro-biphenyls.

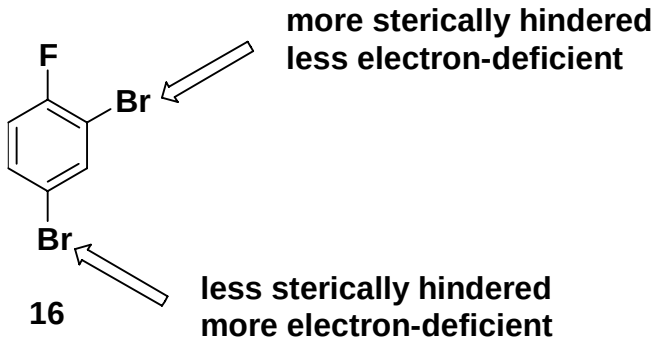


Figure 27. Possible explanations for the site selectivity of cross coupling reactions of **16**

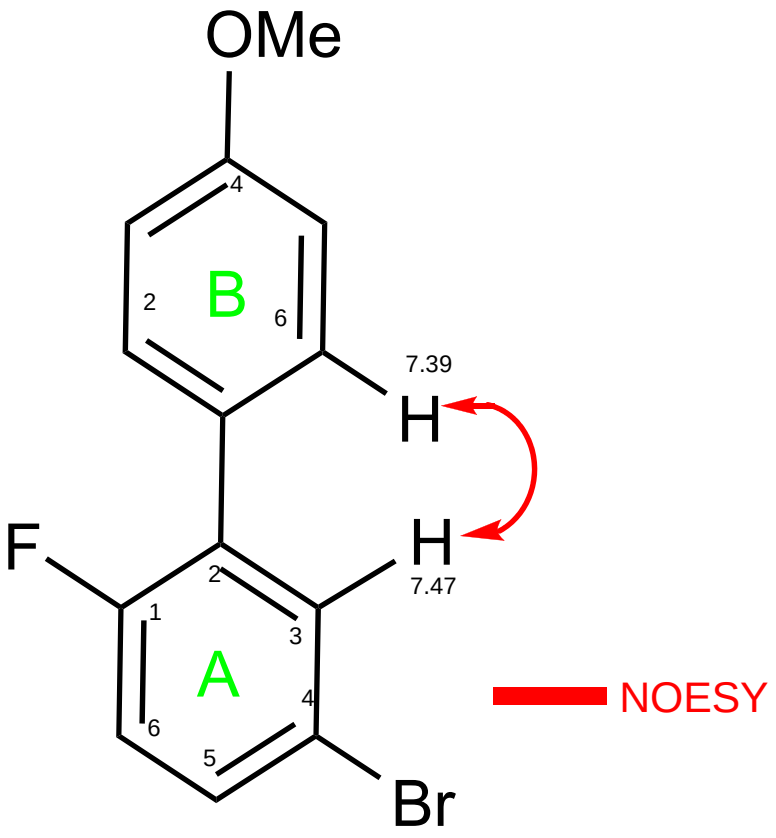


Figure 27A.

H-6 of the ring B resonating at δ = 7.39 ppm showed a clear and important NOESY correlation with the H-3 of ring A resonating at δ = 7.47 ppm. This proved the connectivtity of aryl group at C-1 of ring A.

3. A Novel and Convenient Synthesis of Mono- and Difluorinated Periodobenzenes

3.1 Introduction

Poly- and periodinated aromatic compounds are conventionally prepared by multi-step procedures from the corresponding amines involving acetylation, nitration, diazotization, and reduction,[56] which is time-consuming. The preparation of periodinated aromatic compounds through mercuration followed by iododemercuration with potassium triiodide has been reported.[57]

Molecular iodine is not commonly used for iodination of aromatic compounds due to its low electrophilic property. To carry out the direct iodination reaction using molecular iodine requires an appropriate oxidizing agent to convert molecular iodine into a powerful electrophile.[58] Preparation of periodinated aromatic compounds using molecular iodine in the presence of fuming sulfuric acid as an oxidizing agent has been reported. Mattern[59] reported the preparation of periodinated aromatic compounds using molecular iodine in the presence of H_5IO_6 in sulfuric acid. Although such reported methods for the preparation of periodinated aromatic compounds are excellent and powerful in most cases, these methods have drawbacks such as the need for longer reaction time and strong acidic or severe reaction conditions to carry out the reaction.

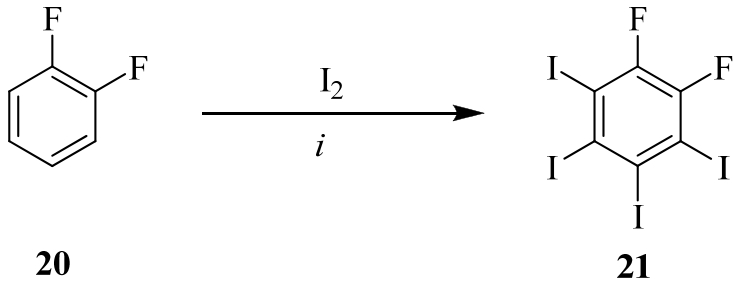
Recently, M. A. Rahman et al.[60] have found that the reaction of arenes with molecular iodine occurs very easily in the presence of $K_2S_2O_8$ as an oxidant and give iodoarenes in good yields. This reagent system is convenient and powerful even in the case of deactivated arenes. The reported periodination method is effective for the arenes bearing moderately deactivating groups as well as moderately activating groups.

We have extended our studies to the direct periodination reactions of difluorinated (Table 18) shows the results of direct periodination of different difluorinated benzenes using the molecular iodine in the presence of $K_2S_2O_8$ and sulfuric acid in trifluoroacetic acid (TFA) and 1,2-dichloroethane (DCE). The outline of the periodination is illustrated in Schemes 13-16.

3.2 Results and Discussions

3.2.1 Synthesis of 1,2-difluoro-3,4,5,6-tetraiodobenzene

The reaction of commercially available 1,2-difluorobenzene **20** with five equivalents of molecular Iodine afforded the 1,2-difluoro-3,4,5,6-tetraiodobenzene **21** in excellent yield (Scheme 13, Table 16). The excellent yields were obtained using molecular Iodine in excess, $K_2S_2O_8$ (5 equiv) as an oxidant, and H_2SO_4 (1.0 equiv) as an oxidizing agent (1,2-dichloroethane(DCE) as a solvent at 80 °C for 90 h.



20 **21**

Scheme 13. Synthesis of **21** *Conditions*: *i,* **20** (1 equiv.), I_2 (5 equiv.), $K_2S_2O_8$ (5 equiv.), TFA (5 equiv.), DCE, 80 °C, 90h.

The product was characterized by spectroscopic methods. The signal of the carbon atom located *ortho* to the fluorine atom is strongly shifted upfield (97.3 ppm) in the ^{13}C NMR spectrum, due to the anisotropic effect of iodine atom and due to the π-donating effect of the fluorine atom. The structure of **21** was independently confirmed by X-ray crystal structure analysis (Figure 28).

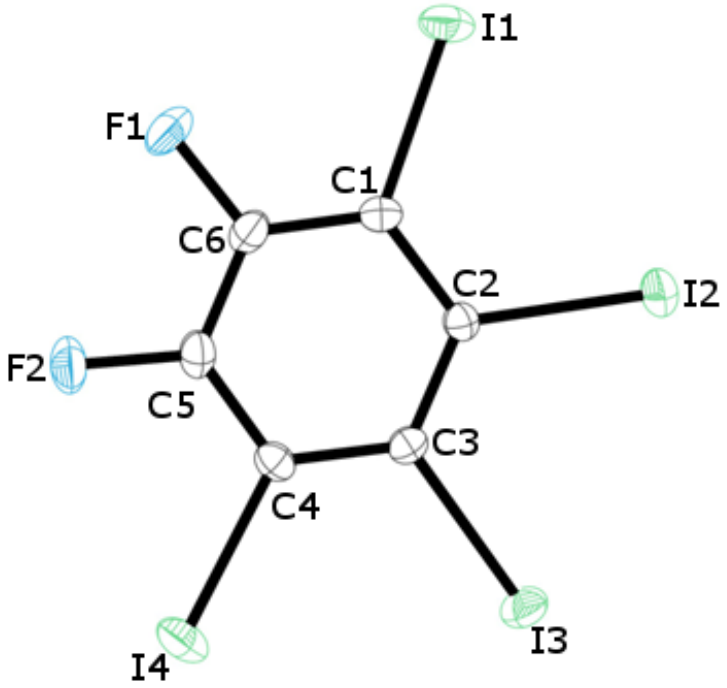
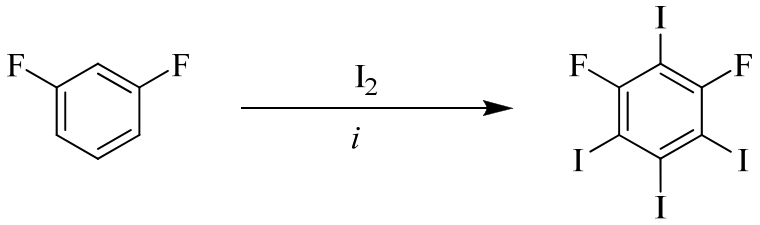


Figure 28. Ortep plot of **21**

3.2.2 Synthesis of 1,3-difluoro-2,4,5,6-tetraiodobenzene

The reaction of commercially available 1,3-difluorobenzene **22** with seven equivalents of molecular iodine afforded the 1,3-difluoro-2,4,5,6-tetraiodobenzene **23** in good to excellent yield (Scheme 14, Table 16). The excellent yields were obtained using molecular Iodine in excess, $K_2S_2O_8$ (5 equiv) as an oxidant, and H_2SO_4 (1.0 equiv) as an oxidizing agent (1,2-dichloroethane (DCE) as a solvent at 70 °C for 120 h.



22 **23**

Scheme 14. Synthesis of **23**. *Conditions*: *i,* **22** (1 equiv.), I_2 (7 equiv.), $K_2S_2O_8$ (5 equiv.), TFA (5 equiv.), DCE, 70 °C, 120 h.

The product was characterized by spectroscopic methods. The structure of **23** was also independently confirmed by X-ray crystal structure analysis (Figure 29).

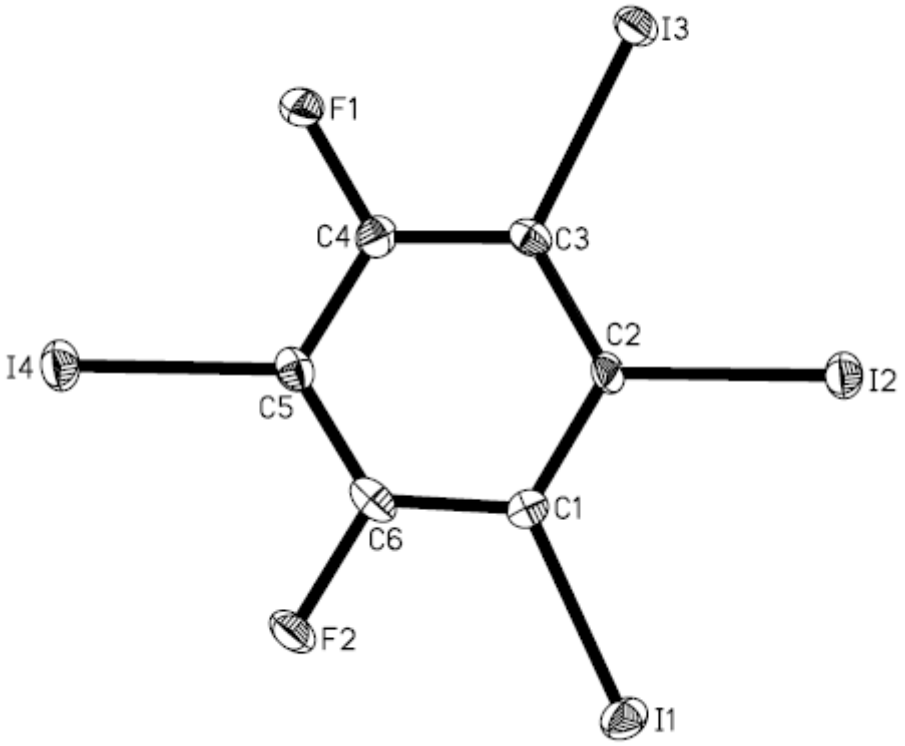
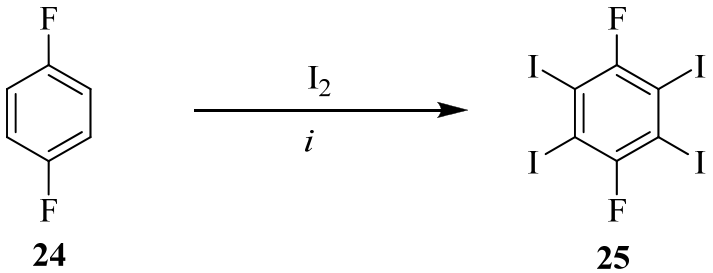


Figure 29. Ortep plot of **23**

3.2.3 Synthesis of 1,4-difluoro-2,3,5,6-tetraiodobenzene

The reaction of commercially available 1,4-difluorobenzene **24** with six equivalents of molecular iodine afforded the 1,4-difluoro-2,3,5,6-tetraiodobenzene **25** in good to excellent yield (Scheme 17, Table 18). The excellent yields were obtained using molecular iodine in excess, $K_2S_2O_8$ (5 equiv) as an oxidant, H_2SO_4 (1.0 equiv) and 1,2-dichloroethane (DCE) as a solvent at 70 °C for 80 h.



24 **25**

Scheme 15. Synthesis of **25** *Conditions*: *i,* 24 (1 equiv.), I_2 (5 equiv.), $K_2S_2O_8$ (5 equiv.), TFA (5 equiv.), DCE, 70 °C, 80h.

The product was characterized by spectroscopic methods. The structure of **25** was independently confirmed by X-ray crystal structure analysis (Figure 30). Due to the anisotropic effect of iodine and due to the π-donating effect of the fluorine atom, the signal of the carbon atom attached to the iodine atom is strongly shifted upfield (98.0 ppm) in the ^{13}C NMR spectrum.

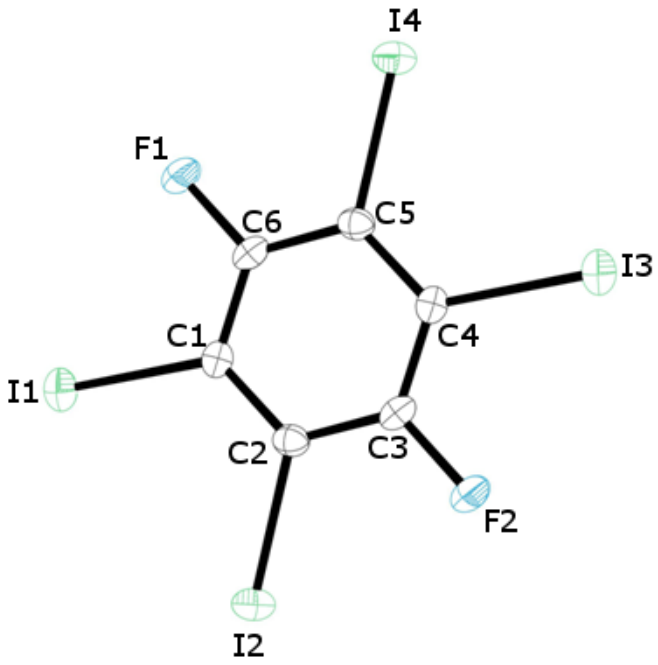
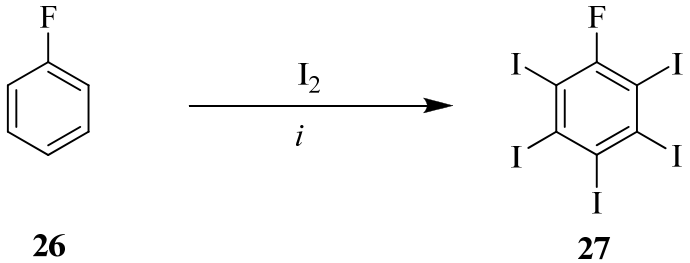


Figure 30. Ortep plot of **25**

3.2.4 Synthesis of 1-fluoro-2,3,4,5,6-pentaiodobenzene[61]

The reaction of commercially available fluorobenzene **26** with eight equivalents of molecular iodine afforded the 1-fluoro-2,3,4,5,6-pentaiodobenzene **27** in good yield (Scheme 18, Table 18). The excellent yields were obtained using molecular iodine in excess, $K_2S_2O_8$ (5 equiv) as an oxidant, and H_2SO_4 (1.0 equiv) and 1,2-dichloroethane (DCE) as a solvent at 70 °C for 80 h.



Scheme 16. Synthesis of **27** *Conditions*: *i,* 26 (1 equiv.), I_2 (6 equiv.), $K_2S_2O_8$ (6 equiv.), TFA (5 equiv.), DCE, 70 °C, 60h.

Similar to compound **25**, the signal of the carbon atom located *ortho* to the fluorine atom is strongly shifted upfield (96.6 ppm) in the ^{13}C NMR spectrum, due to the anisotropic effect of iodine atom and due to the π-donating effect of the fluorine atom. The structure of **27** was also independently confirmed by X-ray crystal structure analysis (Figure 31).

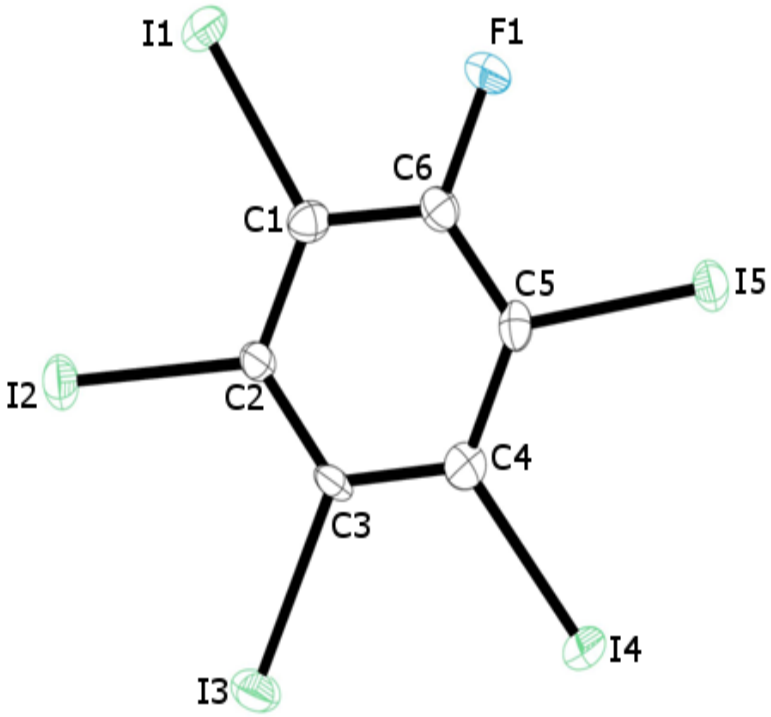


Figure 31. Ortep plot of **27**

Table 16. Synthesis of polyiodoarenes **21-27**

Entry	Arene	Temp (°C)	Time (h)	Products	Yields (%)[a]
1	**20**	80	90	**21**	90
2	**22**	70	120	**23**	88
3	**24**	70	80	**25**	92
4	**26**	70	60	**27**	76

[a]Yields of isolated products

3.3 Conclusion

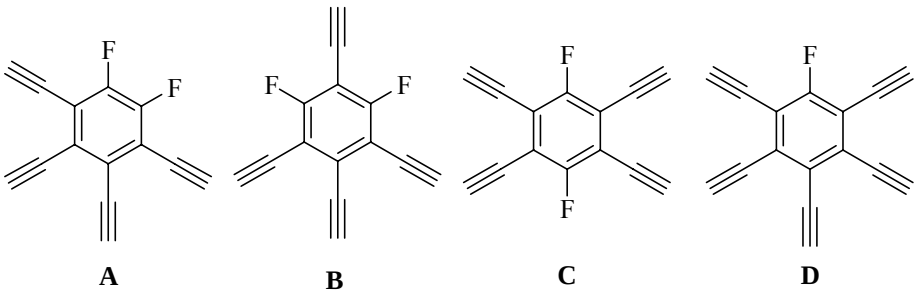
In short, I have demonstrated a direct and very convenient method for the preparation of fluorinated polyiodobenzenes using the molecular iodine. The present periodination method is suitable for the synthesis of polyfunctionalized products.

4 Synthesis of fluorinated polyethynylbenzenes by Sonogashira reactions

4.1 Introduction

In current years much attention has been dedicated to polyethynylated carbon rich molecules, because of their potential as liquid crystals,[62] non linear optical materials,[63] light-harvesting materials,[64] and building blocks for two-dimensional carbon net works.[65] Star-shaped molecules with C_6 and C_3 symmetries have also attracted considerable attention in the field of materials science because of their divergence and extended π-conjugation.[66] In particular, D_{6h}-symmetric hexaethynylbenzenes and related compounds have been used as core structures for dendritic materials,[67] and functional dyes.[68] Recently, hexaethynylbenzene derivatives have also been employed for constructing supramolecular architectures[69] and reported as potential nonlinear optical materials for two-photon absorption (TPA) and third-order optical nonlinearity.[70] Various functionalized hexa(arylethynyl)benzenes have been synthesized by different groups to date.[71] The independent approaches to the differentially substituted hexaethynylbenzenes of C_{2v} symmetry based on the Diels−Alder reaction of tetraethynylcyclopentadienones have already been reported.[72] A method for the synthesis of hexaethynylbenzenes of D_{3h} symmetry was also developed by Rubin.[73] Recently, Anthony reported the synthesis of a D_{2h} symmetric hexaethynylbenzene from tetrabromobenzoquinone.[74]

Hydrocarbons bearing the multiple alkenyl groups have received considerable attention, due to their interesting physicochemical properties, as synthetic building blocks of new and interesting arenes, and because, of their aesthetic attraction. For example, Vollhardt and coworkers reported the synthesis and characterizations of hexaethynylenzenes and its applications to the first synthesis of the so-called archemedanes benzenes and cyclobutane moieties.[75] In contrast to the general hydrocarbons counterparts, fluorinated multiple alkynylated arenes have not been yet known. Fluorinated compounds constitute an important class of natural products and various synthetic drugs which have come to the market and constitute approx. 20% all pharmaceuticals,[76] with even higher figures for agrochemicals (up to 30%).[77] The strategic use of fluorine substitution in drug design has culminated with the production of some of the key drugs available on the market. The synthesis of difluorotetraalkynylbenzenes **A, B, C** and fluoropentaalkynylbenzenes **D** has, to the best our knowledge, not been reprted to date (Scheme A).



Scheme A. Molecules with multiple alkynyl groups

Light emitting materials are applied in biological and material sciences. Conjugated organic systems have significant applications in various fields, such as LC (liquid crystals), FET (field effect transistors), OLED (organic light emitting devices), photovoltaic cells, and 3D-optical memory devices.[79] The extended π-systems often brings extraordinary electronic and optical changes to the compounds. These changes may result in liquid crystalline and fluorescence properties.[78] In this chapter, I have synthesized and optimized the reaction conditions to achieve convenient synthesis of Sonogashira products of monofluoro pentakis(arylethynyl)benzenes and 1,2-, 1,3-, 1,4-difluorotetrakis(aryl)benzenes and studied their UV-Vis and fluorescence properties.

4.2 Results and Discussions

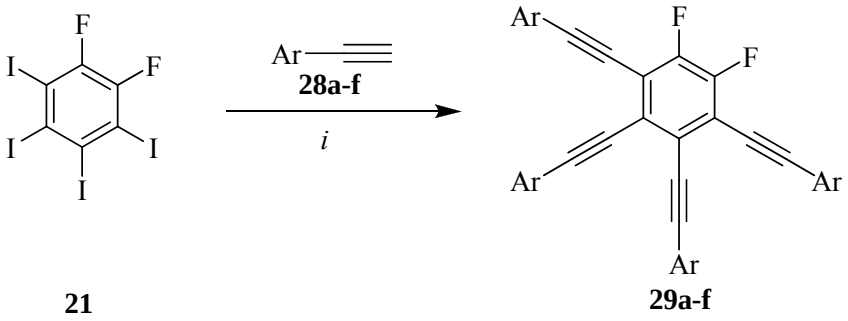
As a part of our research project on the construction of extended π-electronic systems, we designed to develop an efficient synthesis of fluoropentakis(arylethynyl)benzene and difluorotetrakis(arylethynyl)benzene derivatives from polyhalogenated benzenes using the Sonogashira coupling reaction as a essential step. In this context, we report herein the efficient synthesis of polyethynyl-substituted aromatic compounds, **32a-d** and the same protocol was appllied to the differentially substituted tetraarylethynylbenzenes, **29a-f, 30a,** and **31a** from difluoroiodobenzenes by ingenious combination with **28a-f.**

The Sonogashira reaction of **21, 23, 25, 27** with different substituted aryl acetylenes **28a-f** (6 equiv) afforded the 1,2-difluoro-3,4,5,6-tetrakis(arylethynyl)benzen **29a-f** (Scheme 17, Table 17), 1,3-difluoro-3,4,5,6-tetra(arylethynyl)benzene **30a** (Scheme 18, Table 18), 1,4-difluoro-2,3,5,6-tetra(arylethynyl)benzene **31a** (Scheme 19, Table 19), 1-fluoro-2,3,4,5-pentakis(arylethynyl)benzenes **32a-d** (Scheme 20, Table 20), in 55-78% yields. During optimization $Pd(PPh_3)_4$ (10mol-%), $Pd(OAc)_2$ (5 mol-%) in the presence of PCy_3 (10 mol-%) were initially employed, but no satisfactory results were obtained. The progress of reactions

were monitored at temperature (80-100 °C), as higher temperature increases the chances of removal of Iodine. X-Phos (10 mol%) was found to be the best catalyst. Several solvents were tried, but several of them did not work well, while good yields were obtained when DMF was used. Almost all pentakis and tetrakis-Sonogashira products were obtained in good to excellent yields. All structures were confirmed by spectroscopic analysis.

4.2.1 Synthesis of 1,2-difluoro-3,4,5,6-tetrakis(arylethynyl)benzenes

The Sonogashira reaction of 1,2-difluoro-3,4,5,6-tetraiodobenzene (**21**) with different substituted alkynes (**28a-f**) (6.0 equiv) afforded 1,2-difluoro-3,4,5,6 tetrakis(arylethynyl)benzenes **29a-f** (Scheme 17, Table 17) in 60-78% yield.



21 **29a-f**

Scheme 17. Synthesis of **29a–f**: (*i*) conditions and reagents: **21**(1.0 eq), **28a-f** (6.0 eq), CuI (5 mol %), X-Phos (10 mol %), $Pd(OAc)_2$ (5 mol %), DMF (5mL), 100 °C, 72 h.

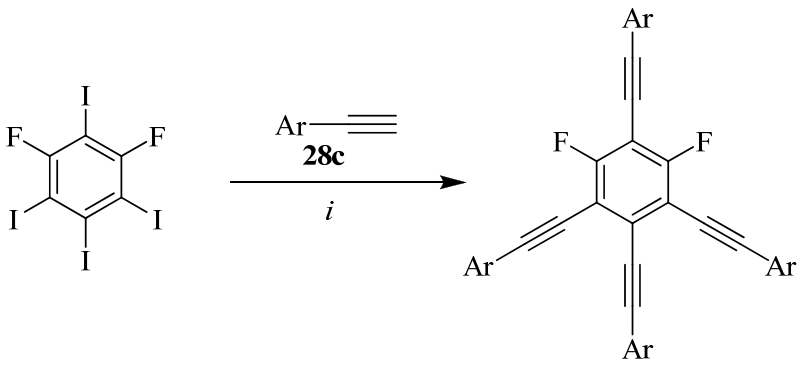
Table 17. Synthesis of **29a-f**

28	**29**	Ar	Yields (%)[a]
a	**a**	C_6H_5	78
b	**b**	4-MeC_6H_4	65
c	**c**	4-$(MeO)C_6H_4$	70
d	**d**	4-*t*BuC_6H_4	62
e	**e**	4-Propyl(C_6H_4)	67
f	**f**	*n*-Butyl	64

[a] isolated yields

4.2.2 Synthesis of 1,3-difluoro-2,4,5,6-tetrakis(arylethynyl)benzenes

The Sonogashira reaction of **23** with the substituted acetylenes **28c** (6.0 equiv.) afforded the 1,3-difluoro-2,4,5,6-tetrakis(arylethynyl)benzen **30a** (Scheme 18, Table 18) in 68 % yield.



23 **30a**

Scheme 18. Synthesis of **30a**: (*i*) conditions and reagents: **23**(1.0 eq), **28c** (6.0 eq), CuI (5 mol %), X-Phos (10 mol %), $Pd(OAc)_2$ (5 mol %), DMF (5mL) , 80°C, 72 h.

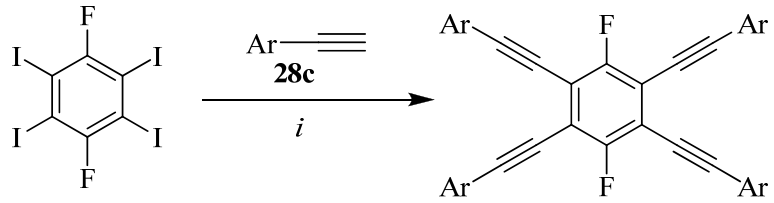
Table 18. Synthesis of **30a**

28	**30**	Ar	Yields (%)[a]
c	**a**	4-(MeO)C_6H_4	68

[a]isolated yields

4.2.3 Synthesis of 1,4-Difluoro-3,4,5,6-tetrakis(arylethynyl)benzenes

The Sonogashira reaction of **25** with the substituted acetylenes **28c** (6.0 equiv.) afforded the 1,4-difluoro-2,3,5,6-tetrakis(arylethynyl)benzen **31a** (Scheme 19, Table 19) in 78 % yield.



25 **31a**

Scheme 19. Synthesis of **31a**: (*i*) conditions and reagents: **25** (1.0 eq), 28c (6.0 eq), CuI (5 mol %), X-Phos (10 mol %), $Pd(OAc)_2$ (5 mol %), DMF (5mL) , 80°C, 72 h.

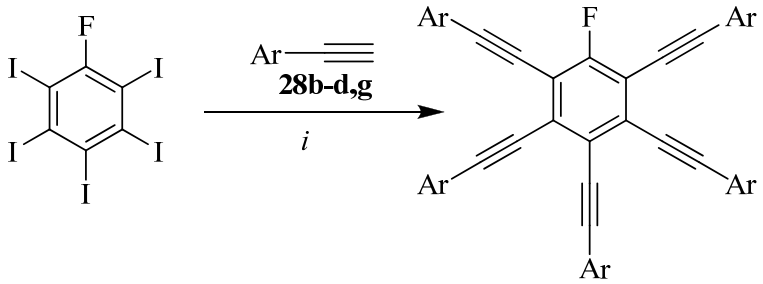
Table 19. Synthesis of **31a**

28	**31**	Ar	Yields (%)[a]
c	**a**	4-(MeO)C_6H_4	78

[a]isolated yields

4.2.3 Synthesis of 1-fluoro-2,3,4,5,6-pentakis(arylethynyl)benzenes

The Sonogashira reaction of **27** with the substituted acetylenes **28b-d,g** (6.0 equiv.) afforded the 1-fluoro-2,3,4,5,6-tetrakis(arylethynyl)benzene **32a-d** (Scheme 20, Table 20) in 55-78 % yields.



27 **32a-d**

Scheme 20. Synthesis of **32a-d**: (*i*) conditions and reagents: **27**(1.0 eq), **28b-d,g** (6.0 eq), CuI (5 mol %), X-Phos (10 mol %), $Pd(OAc)_2$ (5 mol %), DMF (5mL) , 80°C, 100 h.

Table 20. Synthesis of **32a-d**

28	**32**	Ar	Yields (%)
b	**a**	4-MeC_6H_4	69
c	**b**	4-(MeO)C_6H_4	78
d	**c**	4-*t*BuC_6H_4	68
g	**d**	2-MeC_6H_4	55

[a] isolated yields

The electronic absorption and fluorescence-emission data for compounds **29a-d** (Fig. 32, 33, 34, 35) **30a, 31a** (Fig. 36) and **34b-c** are listed in Table 21. The spectra were recorded in DCM, typically in the concentration range of 10^{-4}-10^{-6} M. Typically, three absorption bands were observed in the region 227-333 nm for **29a-c**, and a single band at 229 nm for **29d**. The compounds **31a**, **32b** (Fig. 37) and **32c** (Fig. 38) show well-resolved absorption bands in

range of 227-381. All compounds except **29d** show the excellent absorption properties. The compounds **29a-d** shows the absorptions at 309, 309, 333 and 229 nm respectively. The same compounds **29a-d** showed the emissions at 390, 424, 396, and 352 nm respectively. The compound **29a** and **29b** both showed the absorption at same wavelength 309 nm which is bit unusual and it is supposed to be investigated. The compound **30a** showed very good absorption at 317 nm and the emission at 428 nm with stock's shift 111. The compounds **31a** showed the absorption maxima 323 nm and the emission maxima at 440 nm with stock's shift 117. The compounds **32b-c** showed absorptions at 346 and 336 nm, respectively, while the emissions were recorded at 454 and 432 nm, respectively.

Table 21. Electronic absorption and fluorescence-emission properties

Products	λ_{abs}[nm]	λ_{em}[nm]	Stokes Shift[nm]
29a	309	390	81
29b	309	424	115
29c	333	396	63
29d	229	352	123
30a	317	428	111
31a	323	440	117
32b	346	454	108
32c	336	432	96

Absorpion- fluorescence measured in DCM ($c = 10^{-5}$-10^{-6} M)

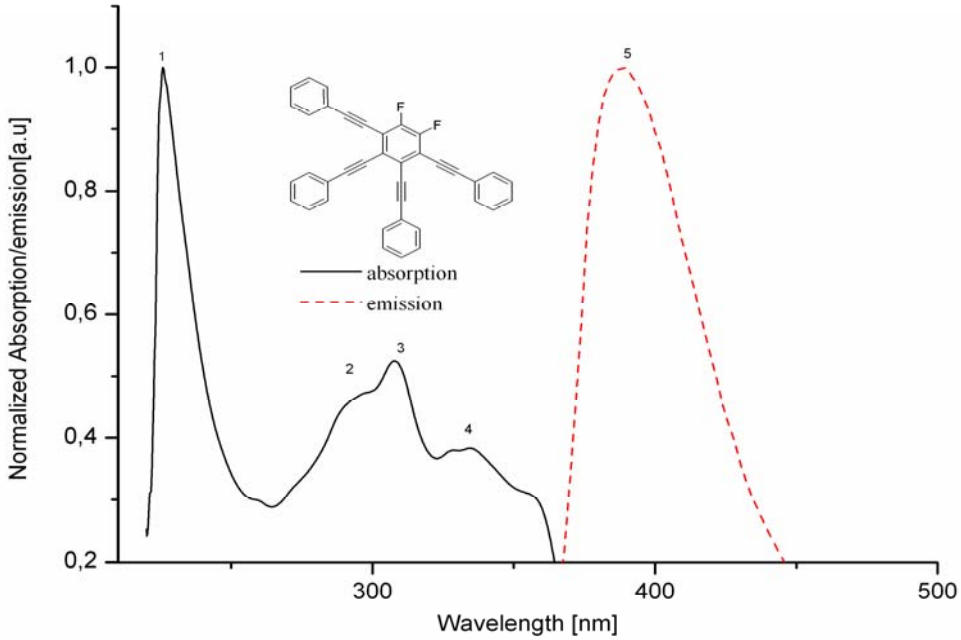


Figure 32. Absorption and emission spectra of compound **29a**

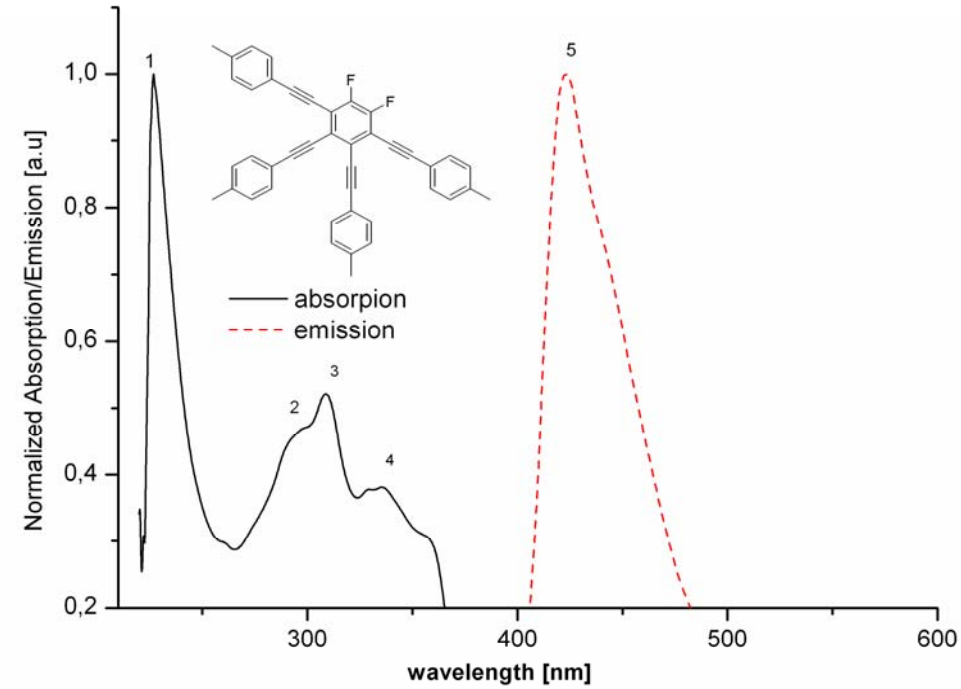


Figure 33. Absorption and emission spectra of compound **29b**

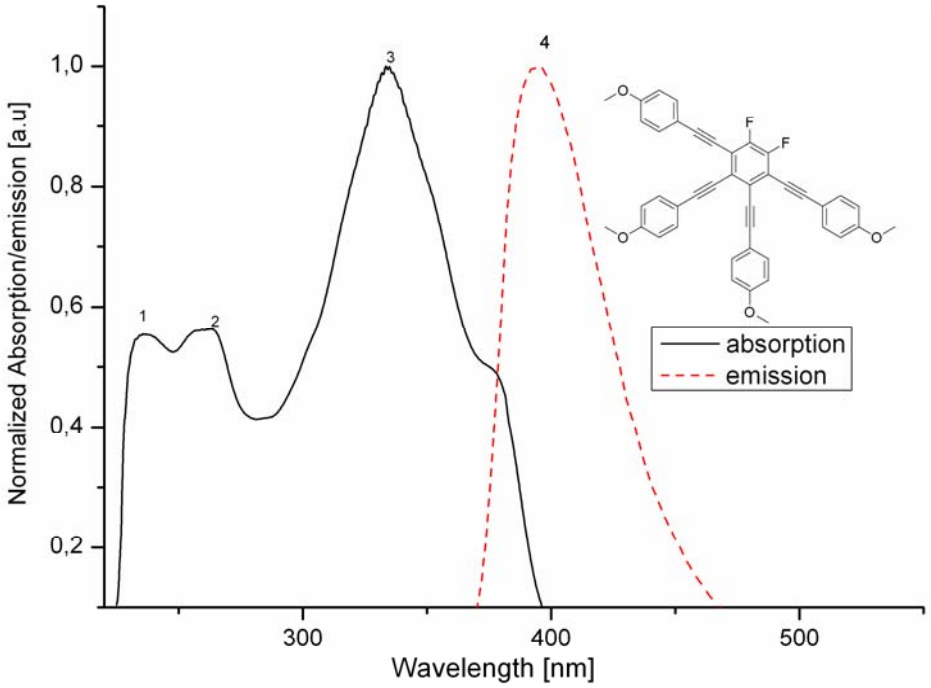


Figure 34. Absorption and emission spectra of compound **29c**

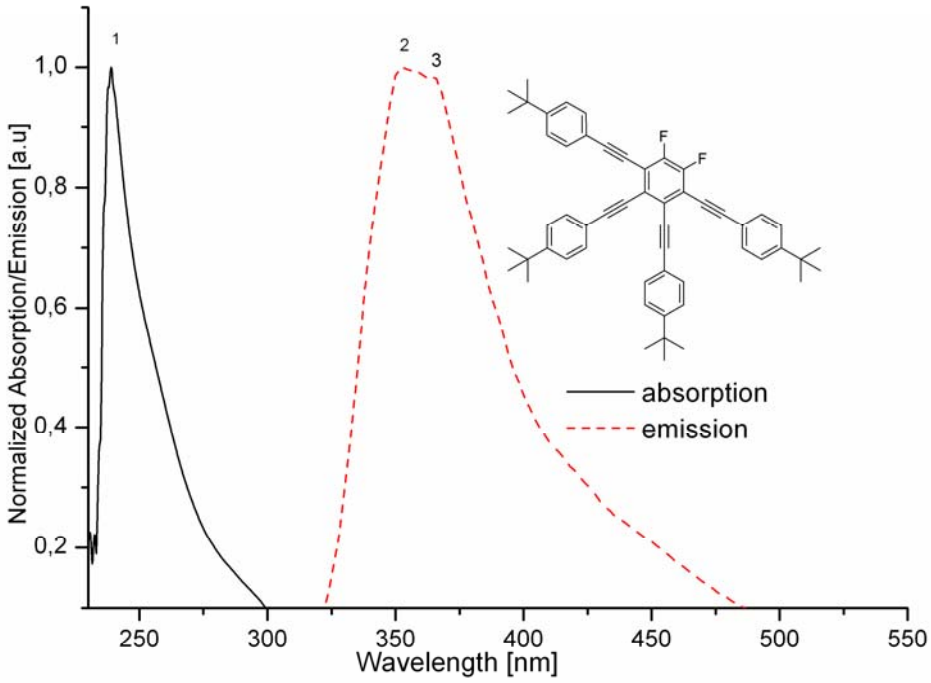


Figure 35. Absorption and emission spectra of compound **29d**

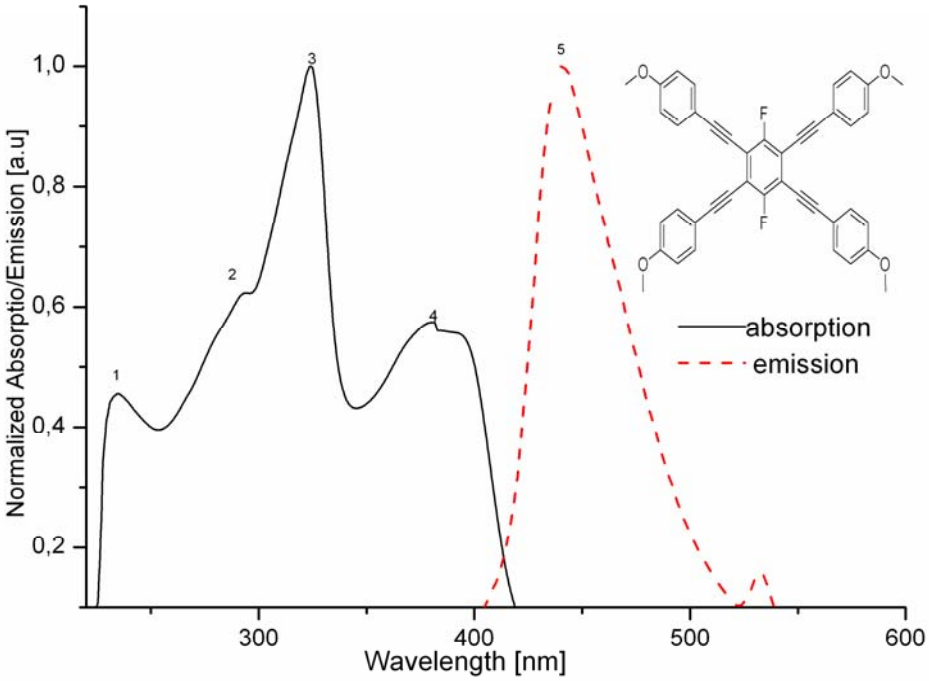


Figure 36. Absorption and emission spectra of compound **31a**

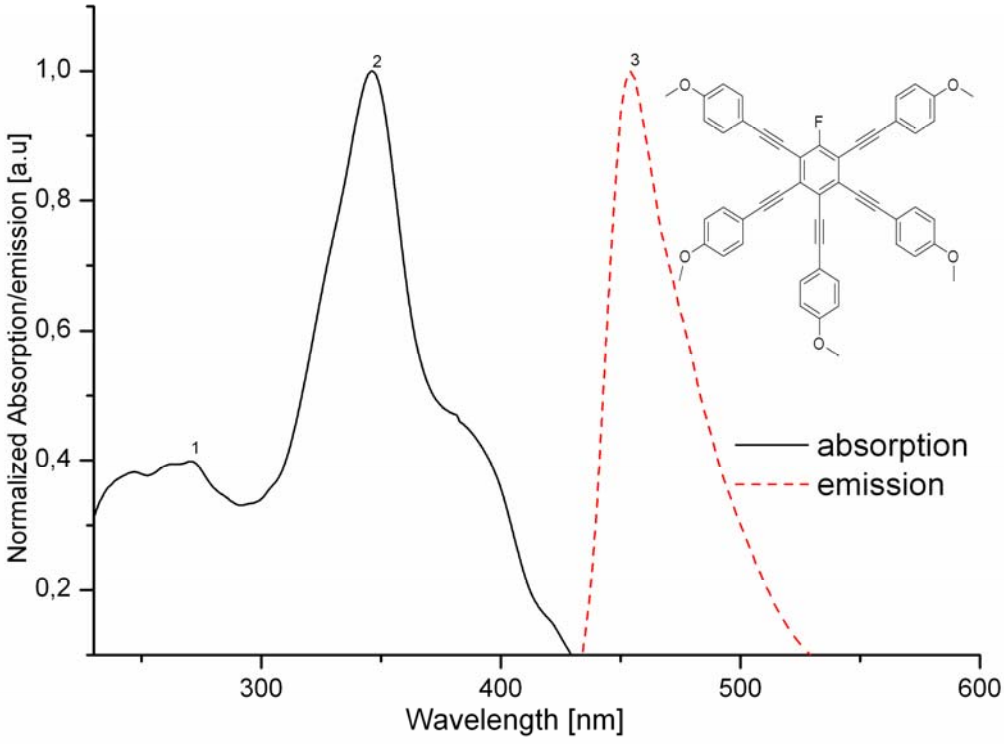


Figure 37. Absorption and emission spectra of compound **32b**

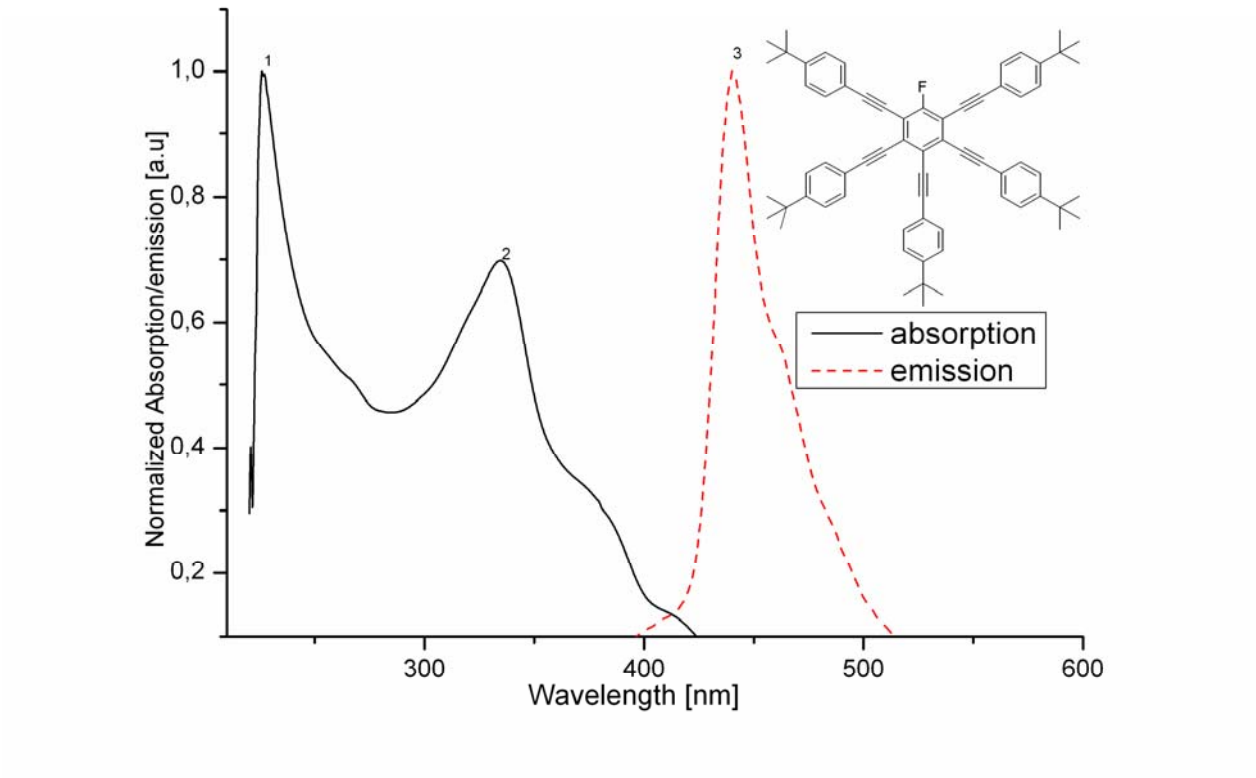


Figure 38. Absorption and emission spectra of compound **32c**

4.3 Conclusion

In conclusion, I have synthesized difluorotetrakis(arylethynyl)benzenes and monofluoropentaakis(arylethynyl)benzenes by Sonogashira coupling reactions in good to excellent yields. Sonogashira coupling reactions of tetraiodobenzenes and pentaiodobenzenes provided the corresponding products. All products showed excellent fluorescence properties.

5 Synthesis of fluorinated polyarenes by Suzuki-Miyaura cross coupling reaction

5.1 Introduction

Electroluminescent materials containing differently substituted mono- and difluorine-atome were synthesized and characterized by IR, NMR, UV-Vis and emission spectroscopic studies. The electronic absorption and emission characteristics of the new functional materials were affected by the nature of the chromophore present.

The chemistry of fluorine containing compounds and its derivatives has been intensively studied, due to their pharmacological and physical properties. Fluorine containing compounds are fundamental materials for the synthesis of medicines that are encountered in our daily lives. The detailed introduction has been been given in the chapter 2. Hydrocarbons bearing the multiple phenyl groups have received considerable attention, due to their interesting physicochemical properties, as synthetic building blocks of new and interesting arenes and because of their aesthetic attraction.

The fluorinated penta and tetrafold Suzuki-Miyaura reaction have not been reported to date. Here I report first time the fluorinated penta and tetrafold Suzuki-Miyaura results.

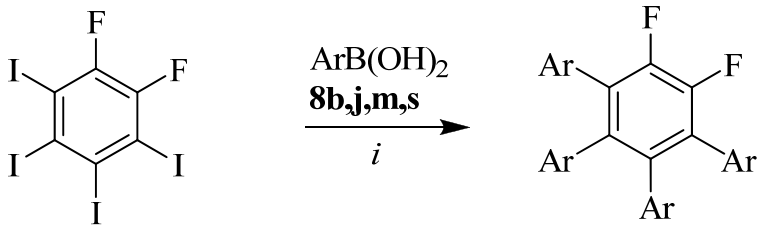
5.2 Results and Discussions

Approaching to the end of our another important research project about the preparation of fluorinated penta and hexaphenyls, we designed to develop an efficient synthesis of fluoropentakis(aryl)benzenes and difluorotetrakis(aryl)benzene derivatives from polyhalogenated benzenes using the Suzuki-Miyaura protocol as an essential step. In this context, we report herein the efficient synthesis of polyephenyl-substituted aromatic compounds **33a-d** and the same protocol was appllied to the differentially substituted tetra(aryl)benzenes, **34a-c, 35a-b,** and **36a-b** from difluorotetraiodobenzenes and monofluoropentaiodobenzenes by ingenious combination with (**8a,b,d,j,m,s**).

The Suzuki-Miyaura reaction of **21, 23, 25, 27** with different substituted arylboronic acids (**8a,b,d,j,m,s**) (6 equiv) afforded the 1,2-difluoro-3,4,5,6-tetrakis(aryl)benzenes **33a-d** (Scheme 21, Table 22), 1,3-difluoro-3,4,5,6-tetra(aryl)benzene **34a-c** (Scheme 22, Table 23), 1,4-difluoro-2,3,5,6-tetra(aryl)benzenes **35a-b** (Scheme 23, Table 24), 1-fluoro-2,3,4,5-pentakis(aryl)benzenes **36a-b** (Scheme 24, Table 25), in 70-85% yields.

5.2.1 Synthesis of 1,2-difluoro-3,4,5,6-tetrakis(aryl)benzenes

The Suzuki-Miyaura reaction of 1,2-difluoro-3,4,5,6-tetraiodobenzen **21** with substituted phenylboronic acids (**8b,j,m,s**) resulted in the formation of **33a-d** (Scheme 21, Table 22) in good to excellent yields (70-85%).



21 **33a-d**

Scheme 21. Synthesis of **33a-d**: conditions and reagents: *i)* **21** (1.0 equiv), **8b,j,m,s** (6.0 equiv), $Pd(PPh_3)_4$ (10 mol-%), Cs_2CO_3 (5equiv), DMF (5 mL), 110°C, 60 h.

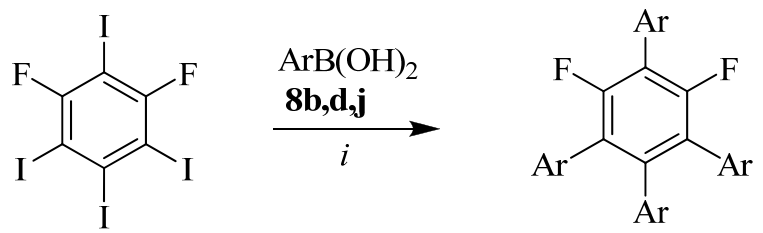
Table 22. Synthesis of **33a-d**

8	**33**	Ar	Yields (%)[a]
b	**a**	4-MeC_6H_4	80
j	**b**	4-*t*BuC_6H_4	85
m	**c**	3,5-$(Me)_2C_6H_3$	78
s	**d**	3-$(MeO)C_6H_4$	72

[a]isolated yields

5.2.2 Synthesis of 1,3-Difluoro-2,4,5,6-tetrakis(aryl)benzenes

The Suzuki-Miyaura reaction of 1,3-difluoro-2,4,5,6-tetraiodobenzen **23** with substituted phenylboronic acids (**8b,d,j**) resulted in the formation of **34a-c** (Scheme 22, Table 23) in good to excellent yields (70-80%).



23 **34a-c**

Scheme 22. Synthesis of **34a-c**: conditions and reagents: *i)* **23** (1.0 equiv), **8b,d,j** (6.0 equiv), $Pd(PPh_3)_4$ (10 mol-%), Cs_2CO_3 (5equiv), DMF (5 mL), 110°C, 80 h

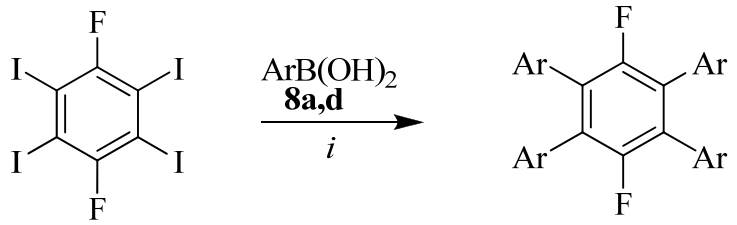
Table 25. Synthesis of **34a-c**

8	**34**	Ar	Yields(%)[a]
b	**a**	4-MeC_6H_4	78
d	**b**	4-$(MeO)C_6H_4$	80
j	**c**	4-*t*BuC_6H_4	73

[a]isolated yields

5.2.3 Synthesis of 1,4-Difluoro-2,3,5,6-tetrakis(aryl)benzenes

The Suzuki-Miyaura reaction of 1,4-difluoro-2,3,5,6-tetraiodobenzen **25** with substituted phenylboronic acids (**8a,d**) resulted in the formation of **35a-b** (Scheme 23, Table 24) in good to excellent yields (70-80%).



25 **35a-b**

Scheme 23. Synthesis of **35a-b**: conditions and reagents: *i)* **25** (1.0 equiv), **8a,d** (6.0 equiv), $Pd(PPh_3)_4$ (10 mol-%), Cs_2CO_3 (5equiv), DMF (5 mL), 100°C, 60 h.

Tabe 24. Synthesis of **35a-b**

8	**35**	Ar	Yields (%)[a]
a	**a**	C_6H_5	76
d	**b**	4-$(MeO)C_6H_4$	80

[a]isolated yields

The X-ray measuments for the compound **35a** (Fig. 39) have also been performed which confirmed the structure independebtly. The aryl substitutents in the crystal structure **35b** were twisted out of plan.

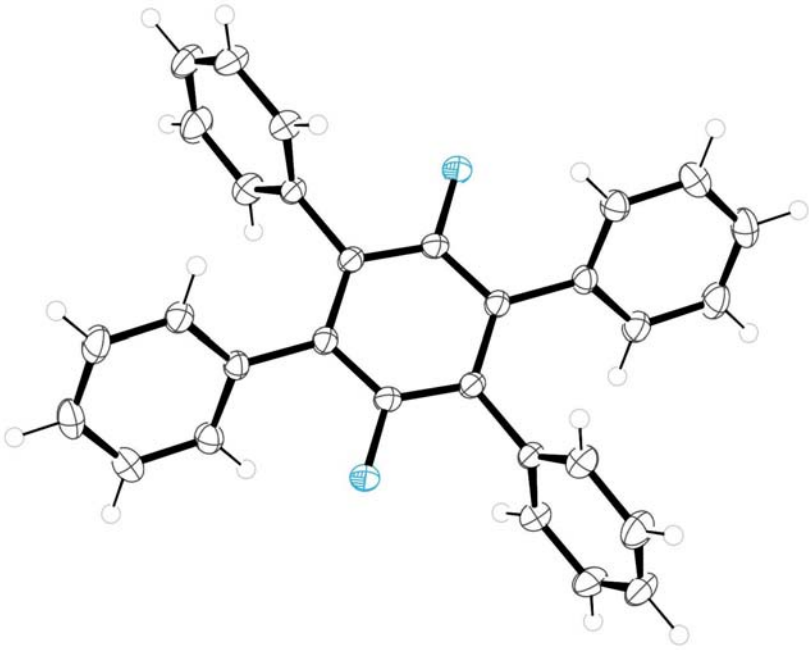
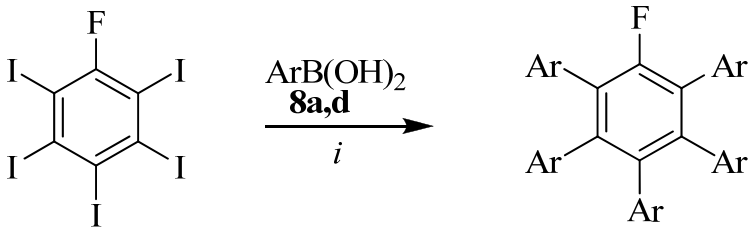


Figure 39. Ortep plot of **35a**

5.2.4 Synthesis of 1-fluoro-2,3,4,5,6-pentakis(aryl)benzenes

The Suzuki-Miyaura reaction of 1-fluoro-2,3,4,5,6-pentaiodobenzen **27** with substituted phenylboronic acids (**8b,d**) resulted in the formation of **36a-b** (Scheme 24, Table 25) in good to excellent yields (70-80%).



27 **36a-b**

Scheme 24. Synthesis of **36a-b**: conditions and reagents: *i)* **27** (1.0 equiv), **8b,d** (6.0 equiv), $Pd(PPh_3)_4$ (10 mol-%), Cs_2CO_3 (5equiv), DMF (5 mL), 100°C, 100 h.

Table 25. Synthesis of **36a-b**

8	**36**	Ar	Yields (%)[a]
b	**a**	4-MeC_6H_4	72
d	**b**	4-$(MeO)C_6H_4$	78

[a]isolated yields

The X-ray measuments for the compound **36a** have also been performed which confirmed the structure independently (Figure 40). The aryl groups are twisted out of plane.

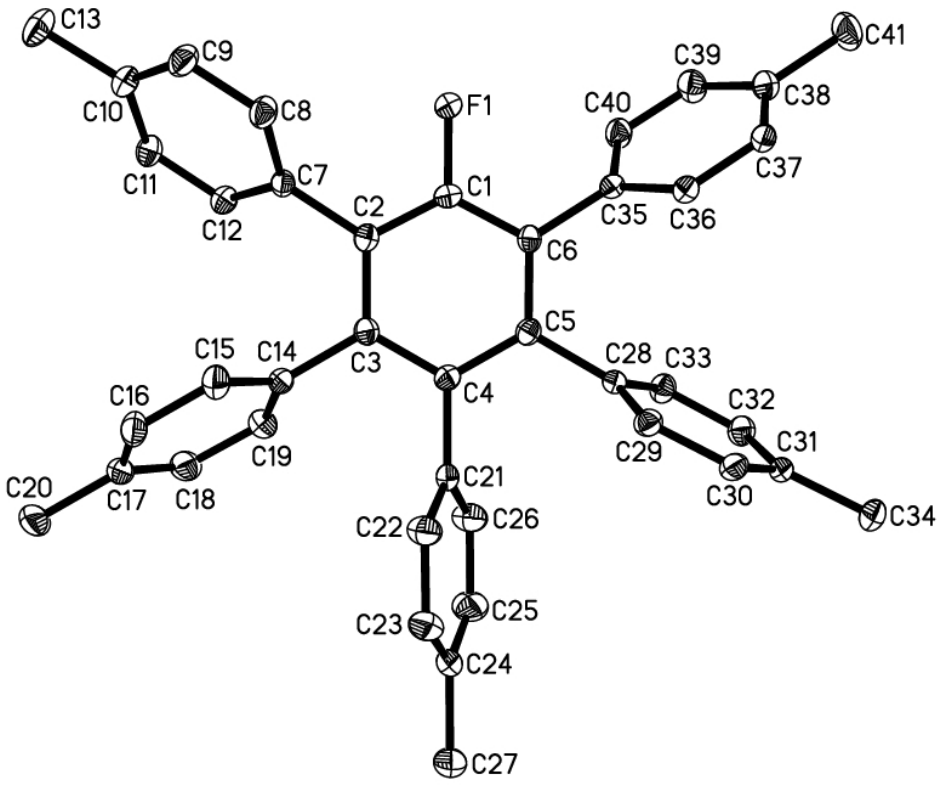


Figure 40. Ortep plot of **36a**

The electronic absorption and fluorescence-emission data for compounds **33d, 34b** and **35b** are listed in Table 26. The spectra were recorded in DCM, typically in the concentration range of 10^{-4}-10^{-6} M. Typically, three absorption bands were observed in the region 227-330 nm for **33d** (Fig. 41) and the absorption maxima was observed at 227 nm whereas a broad shoulder at 260 nm was also observed. The compound **33d** showed emission at 390nm. It showed a broader spectrum at 350-459 nm. The compounds **34b** (Fig. 42) and **35b** (Fig. 43) showed well-resolved absorption bands in range of 227-320. The compounds **34b and 35b** showed

the absorptions at 256 and 258 nm respectively. The same compounds **34b** showed the emission at 374 nm the spectrum showed also a broader emission at 350-450 nm. The compound **35b** showed the emissions at 375 and 380 nm respectively, which is unusual and supposed to be investigated.

Table 41. Electronic absorption and fluorescence-emission properties

Products	λ_{abs}[nm]	λ_{em}[nm]	Stokes Shift[nm]
33d	227	390	163
34b	256	374	118
35b	258	375, 380	117, 122

Absorpion- fluorescence measured in DCM ($c = 10^{-5}$-10^{-6} M)

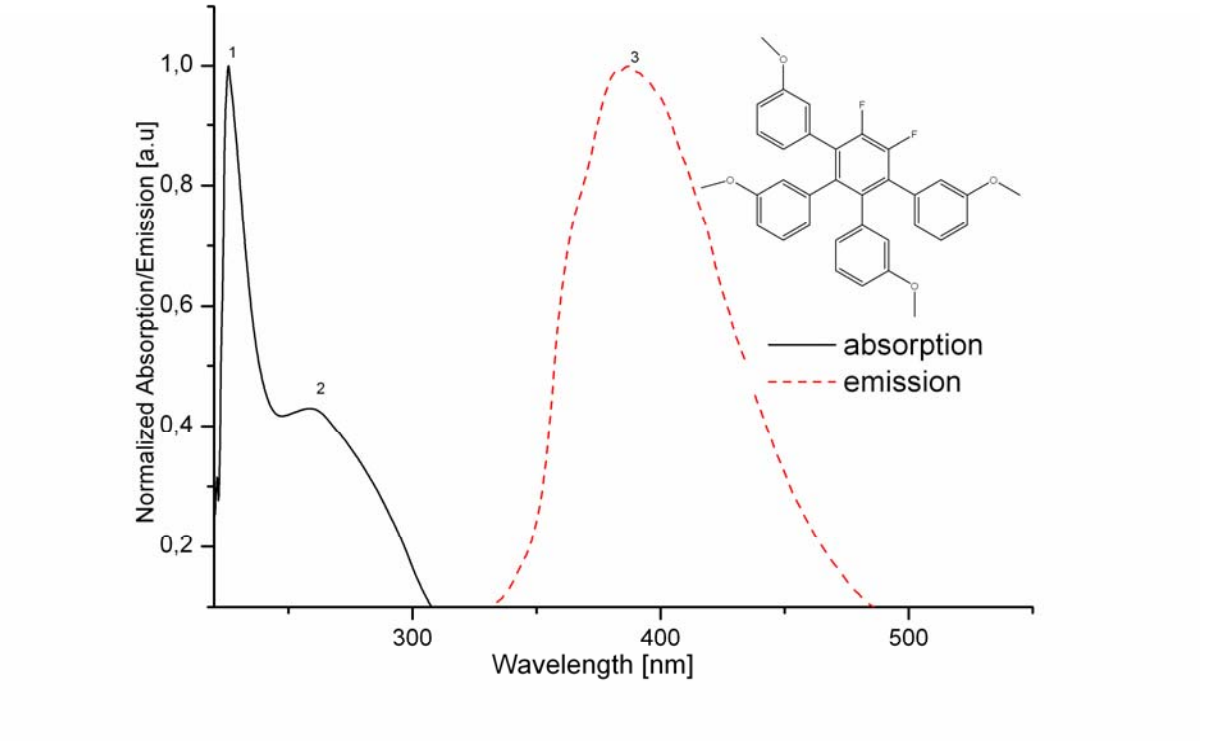


Figure 41. Absorption and emission spectra of compound **33d**

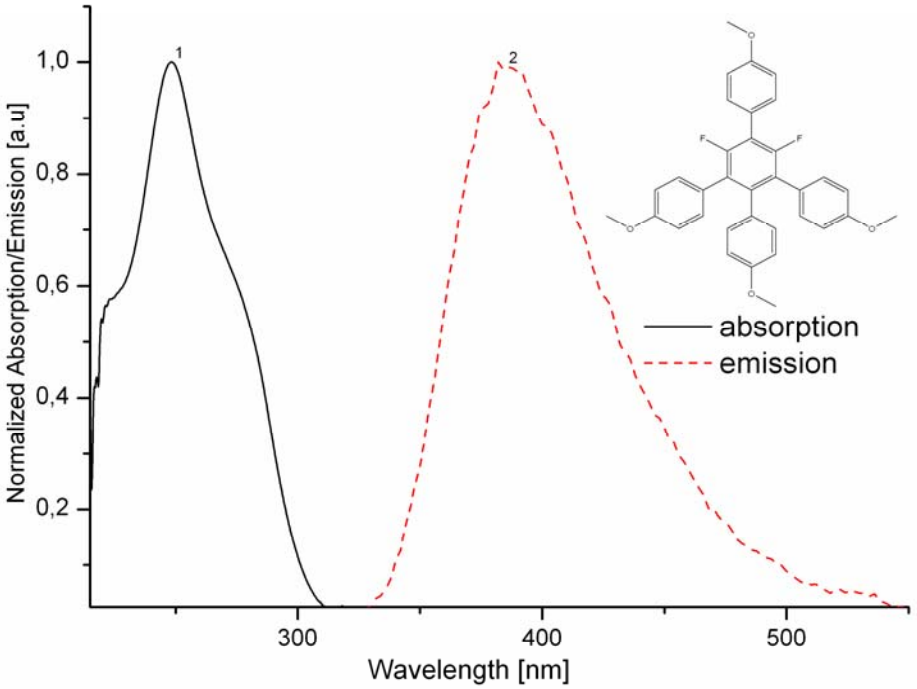


Figure 42. Absorption and emission spectra of compound **34b**

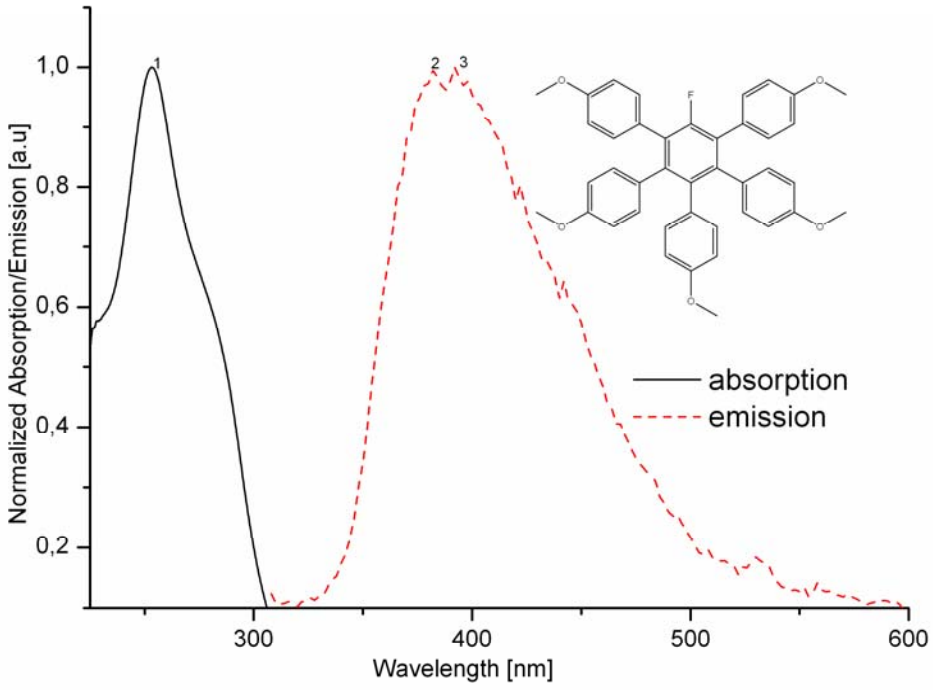


Figure 43. Absorption and emission spectra of compound **35b**

5.3 Conclusion

In conclusion, I have synthesized difluorotetrakis(aryl)benzenes and monofluoropentaakis(aryl)benzenes by Suzuki–Miyaura (S–M) reactions in good to high yields. Suzuki–Miyaura (S–M) reactionsof tetraiodobenzenes and pentaiodobenzenes provided the corresponding products. All products showed good absorption and fluorescence properties.

6 *Abstract*

The palladium(0)-catalyzed Heck cross-coupling reactions of 1-bromopyrene with styrenes and acrylates provided functionalized alkenylpyrenes. The effect of the temperature on the product distribution was studied. Suzuki-Miyaura cross coupling reactions of different substituted di- and mono-fluorobenzenes with different arylboronic acids afforded fluoro-substituted terphenyls with excellent site-selectivity. The first attack occurred at the more electronically deficient and sterically less hindered positions. Sonogashira and Suzuki-Miyaura coupling reactions of 1,2-difluoro-, 1,3-difluoro-, and 1,4-difluoro-tetraiodobenzenes and of fluoro-pentaiodobenzene afforded tetra- and penta-alkynylated and arylated benzene derivatives. The fluorescence properties of various pyrene and benzene derivatives was studied.

Die Palladium(0) katalysierte Heck-Reaktion von 1-Brompyren mit Styrolen bzw. Acrylaten lieferte funktionalisierte Alkenylpyrene. Der Temperatureinfluss bei der Produktbildung wurde untersucht. Suzuki-Miyaura Kreuzkupplungen von unterschiedlich substituierten di- und mono-Fluorobenzenen mit verschiedenen Boronsäuren lieferte fluorsubstituierte Terphenyle mit hervorragender Seitenselektivität. Der erste Angriff fand an der elektronenärmeren und sterisch weniger gehinderten Position statt. Sonogashira und Suzuki-Miyaura Kupplungsreaktionen von 1,2-Difluoro-, 1,3-Difluoro- und 1,4-Difluoro-tetraiodobenzen sowie 1-Fluoro-pentaiodobenzen ergaben die entsprechenden 4-fach bzw. 5-fach alkinylierten bzw. arylierten Produkte. Die Fluoreszenzeigenschaften der Pyrene und vieler Benzenderivate wurden untersucht.

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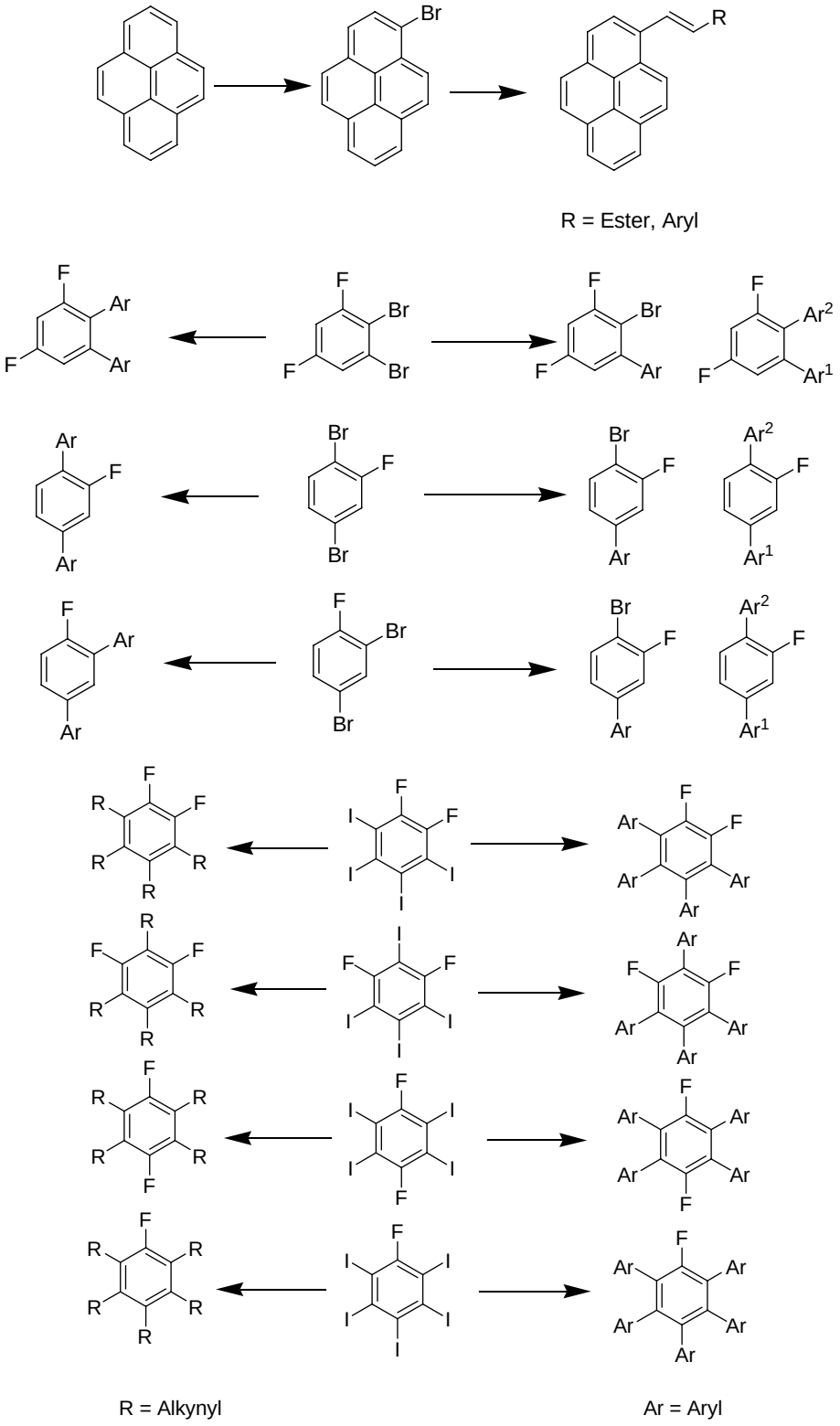


General Scheme. Palladium(0)-catalyzed reactions developed in this thesis.

7 *Experimental Section*

7.1 General: Equipment, Chemicals and Work techniques

^{1}H NMR Spectroscopy:

Bruker: AM 250, Bruker ARX 300, Bruker ARX 500; δ = 0.00 ppm for Tetramethylsilane; δ = 7.26 ppm for (CDCl3); Characterization of the signal fragmen- tations: s = singlet, d = doublet, dd = double of doublet, t = triplet, q = quartet, m = multiplet, br = broadly. All coupling constants are indicated as (*J*). 2D NMR techniques (NOESY, COSY, HMQC, and HMBC) were used for the confirmation of structure.

^{13}C NMR Spectroscopy:

Bruker: AM 250, (62.9 MHz); Bruker: ARX 300, (75 MHz), Bruker: ARX 500, (125 MHz) Ref: 29.84 ± 0.01 ppm and 206.26 ± 0.13 ppm δ = 77.00 ppm for CDCl3. The multiplicity of the carbon atoms was determined by the DEPT 135 and APT technique (APT = Attached Proton Test) and quoted as CH_3, CH_2, CH and C for primary, secondary, tertiary and quaternary carbon atoms. Characterization of the signal fragmentations: quart = quartet the multiplicity of the signals was determined by the DEPT recording technology and/or the APT recording technology.

Mass Spectroscopy:

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 spectroscopy:

Finnigan MAT 95 or Varian MAT 311; Bruker FT
CIR, AMD 402 (AMD Intectra).

Infrared spectroscopy (IR):

Bruker IFS 66 (FT IR), Nicolet 205 FT IR; Nicolet Protege 460, Nicolet 360 Smart Orbit (ATR); KBr, KAP, Nujol, and ATR; Peaks are given following assignments: w = weak, m = medium, s = strong, br = broad.

Elemental Analysis

LECO CHNS-932, Thermoquest Flash EA 1112.

X-ray crystal structure analysis:

Crystallographic data were collected on a Bruker X8Apex, Diffractometer with CCD-Kamera (MoKa und Graphit Monochromator, = 0.71073 Å). The structures were solved by direct methods using SHELXS-97 and refined against *F*2 on all data by full matrix least-squares with SHELXL-97.

Melting points:

Micro heating table HMK 67/1825 Kuestner (Büchi apparatus).

Column chromatography:

Chromatography was performed over Merck silica gel 60 (0,063 -0,200 mm, 70 - 230 mesh) as normal and/or over mesh silica gel 60 (0,040 - 0,063 mm, 200 -400 mesh) as Flash Chromatography. All solvent were distilled before use.

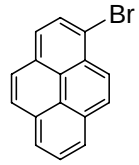
Thin Layer Chromatography (TLC):

Merck DC finished foils silica gel 60 F_{254} on aluminum foil and Macherey finished foils Alugram® Sil G/UV_{254}. Detection under UV light with 254 nm and/or 366 nm without dipping reagent, as well as with anisaldehyde sulfuric acid reagent (1 mL anisaldehyde consisting in 100 mL stock solution of 85% methanol, 14% acetic acid and 1% sulfuric acid).

7.2 Synthesis of 1-Alkenylpyrenes by Heck Coupling Reaction

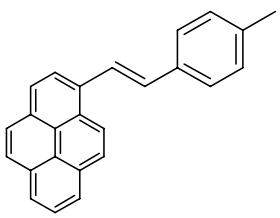
General procedure for synthesis of (*E*)-pyren-3-yl-acrylates: Palladium (II) acetate (5 mol %) and XPhos (10 mol %) were placed under Argon atmosphere in a pressure tube and 5 mL of DMF was added. After stirring for 15 min, 1-bromopyrene **2**, the acrylate **5** and triehtylamine were added. Subsequently, the mixture was heated at 90 °C for 6 h. To the mixture were added water and CH_2Cl_2 (20 mL each) and the organic and the aqueous layer were separated. The latter was extracted with CH_2Cl_2 (2 × 20 mL). The combined organic layers were dried (Na_2SO_4), filtered and the filtrate was concentrated in vacuo. The residue was purified by a column chromatography (hexane/ethylacetate).

7.3 Synthesis of 1-bromopyrene[17] **(2):** To a stirred solution of pyrene (2.02 g, 10.0 mmol) in chloroform (100 mL), NBS (2.40 g, 12.0 mmol) was added slowly. The reaction mixture was stirred at room temperature for 24 h while its progress was monitored by TLC. After the completion of monobromination, the solvent was removed under reduced pressure and the crude product was taken in DCM (2*200 mL) and washed with water and dried over anhydrous sodium sulfate. The pure product was isolated by careful column chromatography on silica gel using n-hexane as eluent to get pure 1-bromopyrene as a light brown solid.

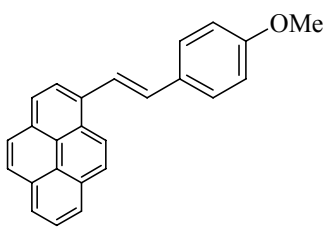


7.4 Synthesis of ethenylpyrenes. To a stirred solution of $Pd(OAc)_2$ (5 mol%) and XPhos (10 mol%) in DMF was added a solution of styrenes (0.53 mmol) and 1-bromopyrene (100 mg, 0.35 mmol). Then K_2CO_3 (98 mg, 0.71 mmol) was added and kept stirring at 70 °C for 6 h. after the completion of reaction, the solvent was removed under the reduced pressure on rotary evaporator and the crude product was taken in DCM and washed with water and dries over anhydrous sodium sulphate. The pure product was isolated by careful column chromatography on silica gel as yellow solids.

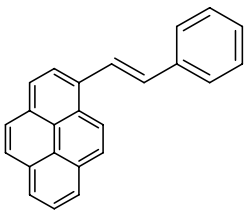
(*E*)-1-(4-Methylstyryl)pyrene (4a): Starting with **1** (100 mg, 0.35 mmol), **3a** (62.8 mg, 0.53 mmol), $Pd(OAc)_2$ (5 mol%, 4.3 mg, 0.017 mmol), X-Phos (10 mol%, 16.0 mg, 0.035 mmol), K_2CO_3 (98 mg, 0.71 mmol) in DMF (5 ml), **5a** was isolated as a yellow solid (104 mg, 92%). Mp 138-140 °C. ^{1}H NMR (300 MHz, $CDCl_3$): δ = 2.33 (s, 3H, CH_3), 7.17 (d, *J* = 8.00 Hz, 2H, Ph), 7.25 (d, *J* = 16.12 Hz, 1H, CH), 7.51 (d, *J* = 8.00 Hz, 2H, Ph), 7.89-8.10 (m, 8H, Py), 8.23 (d, *J* = 8.00 Hz, 1H, CH), 8.41 (d, *J* = 9.28 Hz, 1H**).** ^{13}C NMR (62.89 MHz, $CDCl_3$): δ = 20.3 (CH_3), 122.1 (C), 122.6 (C), 123.6 (CH), 123.9 (CH), 124.1 (C), 124.2 (C), 124.9 (CH), 125.6 (2CH), 126.1 (CH), 126.4 (C), 126.5 (C), 127.3 (CH), 127.7 (CH), 128.5 (2CH), 129.7 (CH), 129.9 (C), 130.5 (C), 130.8 (CH), 131.1 (CH), 133.9 (CH), 136.7 (CH). IR (ATR, cm^{-1})**:** $\tilde{\nu}$ = 3043 (w), 2962 (w), 2914 (w), 2854 (w), 2732 (w), 1908 (w), 1778 (w), 1600 (w), 1567 (w), 1512 (w), 1462 (w), 1434 (w), 1378 (w), 1316 (w), 1260 (w), 1205 (w), 1159 (w), 1108 (w), 1048 (w), 1019 (w), 963 (m), 907 (w), 863 (w), 837 (m), 807 (m), 751 (w), 715 (w), 679 (w), 604 (w), 543 (w). MS (EI, 70 eV): *m/z* (%) = 318 (100) $[M]^+$, 317 (67), 304 (10), 302 (38), 300 (16), 226 (21), 151 (20), 150 (12), 69 (11). HRMS (EI) calcd for $C_{25}H_{18}$ $[M+H]^+$: 318.14030 found 318.139964.



***(E)*-1-(4-Methoxystyryl)pyrene (4b):** Starting with **1** (100 mg, 0.35 mmol), **3b** (71.3 mg, 0.53 mmol), $Pd(OAc)_2$ (5 mol%, 4.3 mg, 0.017 mmol), X-Phos (10 mol%, 16.0 mg, 0.035 mmol), K_2CO_3 (98 mg, 0.71 mmol) in DMF (5 ml), **4b** was isolated as a yellow solid (105 mg, 89%). Mp 147-149 °C. ^{1}H NMR (300 MHz, $CDCl_3$): δ = 3.81 (s, 3H, OCH_3), 6.90 (d, *J* = 8.80 Hz, 2H, Ph), 7.24 (d, *J* = 15.97 Hz, 1H, CH), 7.56 (d, *J* = 8.80 Hz, 2H, Ph), 7.89-8.11 (m, 8H, Py), 8.24 (d, *J* = 8.15 Hz, 1H), 8.43 (d, *J* = 9.18 Hz). ^{13}C NMR (62.89 MHz, $CDCl_3$) :δ = 55.4 (OCH_3), 114.2 (2CH), 123.2 (CH), 123.5 (CH), 123.6 (CH), 124.9 (CH), 125.1 (CH), 125.2 (CH), 126.0 (CH), 127.1 (CH), 127.4 (CH), 127.5 (CH), 128.0 (2CH), 128.2 (C), 128.8 (C), 130.6 (C), 130.9 (C), 131.0 (C), 131.4 (CH), 131.6 (C), 132.3 (C), 132.5 (C), 159.5 (C). IR (ATR, cm^{-1})**:** $\tilde{\nu}$ =3042 (w), 2999 (w), 2965 (w), 2932 (w), 2837 (w), 1598 (m), 1537 (m), 1510 (m), 1455 (m), 1415 (m), 1325 (m), 1301 (m), 1263 (m), 1203 (m), 1174 (m), 1108 (m), 1072 (m), 1025 (s), 964 (s), 947 (m), 893 (w), 843 (s), 815 (s), 765 (m), 722 (m), 707 (s), 638 (m), 605 (m), 566 (m), 544 (m). MS (EI, 70 eV): *m/z* (%) = 334 (100) $[M]^+$, 333 (28), 318 (18), 303 (17), 291 (17), 290 (14), 289 (36), 226 (14), 145 (10), 111 (11), 97 (18), 95 (13), 85 (15), 83 (20), 81 (24), 71 (25), 57 (38), 55 (25), 43 (22), 41 (21). HRMS (EI) calcd. for $C_{25}H_{18}O_1$ $[M+H]^+$: 334.13522; found 334.134251.



(*E*)-1-Styrylpyrene (4c): Starting with **1** (100 mg, 0.35 mmol), **3c** (55.6 mg, 0.53 mmol), $Pd(OAc)_2$ (5 mol%, 4.3 mg, 0.017 mmol), X-Phos (10 mol%, 16 mg, 0.035 mmol), K_2CO_3 (98 mg, 0.71 mmol) in DMF (5 ml), **4c** was isolated as a yellow oil. (85 mg, 79%). ^{1}H NMR (300 MHz, $CDCl_3$)**:** δ = 7.22-7.39 (M, 5H, Ph), 7.60-7.63 (m, 2H, Py), 7.89-8.15 (m, 7H, Py), 8.25 (d, *J* = 8.40 Hz, 1H, CH), 8.42 (d, *J* = 9.20 Hz, 1H, CH). ^{13}C NMR (62.89 MHz, $CDCl_3$): δ = 123.5 (CH), 123.7 (CH), 124.3 (C), 124.9 (CH), 125.0 (CH), 125.3 (CH), 125.7 (CH), 126.3 (CH), 126.4 (CH), 126.5 (C), 126.6 (CH), 126.7 (CH), 126.8 (C), 127.1 (CH), 127.2 (CH), 127.3 (CH), 127.4 (CH), 127.8 (CH), 129.9 (CH), 130.0 (C), 130.5 (C), 130.8 (CH), 130.9 (C). IR (ATR, cm^{-1})**:** $\tilde{\nu}$ = 3080 (w), 2998 (w), 2956 (w), 2836 (w), 1736 (w), 1609 (s), 1586 (s), 1508 (s), 1454 (s), 1425 (m), 1401 (m), 1372 (w), 1303 (s), 1255 (m), 1184 (w), 1158 (s), 1145 (s), 1092 (s), 1032 (s), 996 (s), 925 (m), 861 (w), 834 (m), 818 (s) 796 (m), 736 (w), 718 (w), 663 (w), 607 (w), 587 (m). MS (EI, 70 eV): *m/z* (%) = 304 (100) $[M]^+$, 303 (80), 302 (29), 300 (14), 226 (15), 151 (17). HRMS (EI) calcd. for $C_{24}H_{16}$ $[M+H]^+$: 304.12465; found 304.124431.



(*E*)-1-(4-*tert*-Butoxystyryl)pyrene (4d): Starting with **1** (100 mg, 0.35 mmol), **3d** (93.8 mg, 0.53 mmol), $Pd(OAc)_2$ (5 mol%, 4.3 mg, 0.017 mmol), X-Phos (10 mol%, 16 mg, 0.035 mmol), K_2CO_3 (98 mg, 0.71 mmol) in DMF (5 ml), **4d** was isolated as a yellow solid (115 mg, 86%). Mp 122-124 °C. ^{1}H NMR (300 MHz, $CDCl_3$): δ = 1.34 (s, 9H, *t*-BuO), 7.05 (*d*, *J* = 8.59 Hz, 2H, Ph), 7.28 (*d*, *J* = 16.05 Hz, 1H, CH), 7.57 (*d*, *J* = 8.59 Hz, 2H, Ph), 7.95-8.15 (*m*, 8H, Py), 8.25 (*d*, *J* = 8.22 Hz, 1H, CH), 8.45 (*d*, *J* = 9.41 Hz, 1H, CH). ^{13}C NMR (62.89 MHz, $CDCl_3$): δ = 28.9 (OCH_3), 123.1 (CH), 123.6 (CH), 123.4 (2CH), 124.5 (CH), 12 4.9 (2CH), 125.0 (C), 125 (C), 125.2 (CH), 125.9 (CH), 127.1 (CH), 127.5 (2CH), 127.4 (2CH), 128.2 (C), 130.7 (C), 130.9 (C), 131.4 (2CH), 131.5 (C) 132.1 (C), 132.9 (C), 155.4 (CO). IR (ATR, cm^{-1}): $\tilde{\nu}$ = 3038 (w), 2974 (m), 2929 (w), 2870 (w), 1712 (w), 1680 (w), 1598 (m), 1504 (s), 1458 (w), 1415 (w), 1364 (m), 1296 (w), 1238 (s), 1157 (s), 1101 (w), 1012 (w), 958 (m), 894 (m), 840 (s), 756 (w), 713 (m), 641 (w), 608 (w), 552 (w), 539 (m). MS (EI, 70 eV): *m/z* (%) = 376 (16) $[M]^+$, 2360 (14), 321 (32), 320 (100), 319 (62), 303 (13), 289 (29), 1226 (33). HRMS (EI) calcd. for $C_{28}H_{24}O_1$ $[M+H]^+$: 376.18217; found 376.181427.

***(E)*-1-(4-Chlorostyryl)pyrene (4e):** Starting with **1** (100 mg, 0.35 mmol), **3e** (73.7 mg, 0.53 mmol), $Pd(OAc)_2$ (5 mol%, 4.3 mg, 0.017 mmol), X-Phos (10 mol%, 16 mg, 0.035 mmol), K_2CO_3 (98 mg, 0.71 mmol) in DMF (5 ml), **4e** was isolated as a yellow solid (86 mg, 72%). Mp 149-151 °C. ^{1}H NMR (300 MHz, $CDCl_3$): δ = 7.30 (d, *J* = 16.21 Hz, 1H, CH), 7.40 (d, *J* = 8.40 Hz, 2H, Py), 7.61 (d, *J* = 8.40 Hz, 2H, Py), 7.99-8.21 (m, 8H, Py), 8.30 (d, *J* = 7.99 Hz, 1H, Py), 8.48 (d, *J* = 9.28 Hz, 1H). ^{13}C NMR (62.89 MHz, $CDCl_3$): δ = 122.8 (CH), 123.0 (CH), 125.1 (2CH), 125.4 (CH), 125.9 (CH), 126.2 (CH), 127.3 (CH), 127.4 (CH), 127.6 (CH), 127.7 (2CH), 128.4 (C),128.7 (C) 128.9 (2CH), 130.3 (C), 130.8 (CH), 130.9 (C), 130.4 (C), 130.5 (C), 132.4 (C), 133.3 (C), 136.2 (C). IR (ATR, cm^{-1}): $\tilde{\nu}$ = 3044 (w), 3013 (w), 2958 (w), 2857 (w), 1923 (w), 1859 (w), 1796 (w), 1724 (w), 1681 (w), 1620 (w), 1584 (w), 1504 (w), 1488 (m), 1414 (w), 1317 (w), 1240 (w), 1185 (w), 1112 (w), 1089 (m), 1009 (m), 956 (s), 939 (s), 862 (w), 837 (s), 800 (s), 753 (m), 713 (s), 676 (m), 605 (s), 553 (m), 536 (s). MS (EI, 70 eV): *m/z* (%) = 338 (100) $[M]^+$, 337 (31), 303 (22), 302 (22), 301 (13, 300 (13), 299 (16), 227 (12), 226 (17), 225 (12), 207 (15), 151 (27),

150 (20), 149 (24), 136 (12). HRMS (EI) calcd for $C_{24}H_{15}Cl$ $[M+H]^+$: 338.08568; found 338.085035.

(*E*)-1-(Perfluorostyryl)pyrene (4f): Starting with **1** (100 mg, 0.35 mmol), **3f** (103 mg, 0.53 mmol), $Pd(OAc)_2$ (5 mol%, 4.3 mg, 0.017 mmol), X-Phos (10 mol%, 16 mg, 0.035 mmol), K_2CO_3 (98 mg, 0.71 mmol) in DMF (5 ml), **4f** was isolated as a yellow solid (106 mg, 76%). Mp 208-210 °C. ^{1}H NMR (300 MHz, $CDCl_3$): δ = 7.21 (d, *J* = 16.47 Hz, 1H, CH), 8.04-8.24 (m, 7H, Py), 8.32 (d, *J* = 8.10 Hz, 1H Py), 8.41 (d, *J* = 9.47 Hz, 1H), 8.54 (d, *J* = 16.47 Hz, 1H, CH). ^{13}C NMR (62.89 MHz, $CDCl_3$): δ = 12.6 (C), 123.4 (CH), 124.9 (C), 125.0 (2C), 125.5 (CH), 125.7 (CH), 126.1 (CH), 127.3 (CH), 127.4 (2C), 127.7 (C), 127.9 (CH), 128.3 (CH), 128.8 (2CH), 130.8 (2CH), 130.9 (2C), 131.4 (C), 132.4 (2C), 167.0 (C). ^{19}F: δ = -142.22 (2CF), -155.8 (2CF), -162.4 (CF**).**). IR (ATR, cm^{-1})**:** $\tilde{\nu}$ = 3024 (w), 2961 (w), 2920 (w), 2875 (w), 1698 (m), 1617 (m), 1599 (m), 1435 (w), 1361 (w), 1276 (m), 1088 (s), 1036 (w), 979 (w), 838 (s). MS (EI, 70 eV): *m/z* (%) = 394 (100) $[M]^+$, 393 (58), 392 (17), 374 (13), 226 (12). HRMS (EI) calcd for $C_{24}H_{11}F_5$ $[M+H]^+$: 394.07754; found 394.076693.

(E)-1-(4-*tert*-Butylstyryl)pyrene (4g): Starting with **1** (100 mg, 0.35 mmol), **3g** (85.2 mg, 0.53 mmol), $Pd(OAc)_2$ (5 mol%, 4.3 mg, 0.017 mmol), X-Phos (10 mol%, 16 mg, 0.035 mmol), K_2CO_3 (98 mg, 0.71 mmol) in DMF (5 ml), **4g** was isolated as a yellow solid (120 mg, 94%). Mp 125-127 °C**.** ^{1}H NMR (300 MHz, $CDCl_3$): δ = 1.29 (s, 9H, CH_3) 7.24 (d, *J* = 16.14 Hz, 1H, CH), 7.37 (d, *J* = 8.36, 2H, Ph), 7.53 (d, *J* = 8.36 Hz, 2H, Ph), 7.87-8.08 (m, 8H, Py), 8.20 (d, *J* = 8.10 Hz, 1H, CH), 8.38 (d, *J* = 9.33 Hz, 1H, CH). ^{13}C NMR (75 MHz, $CDCl_3$): δ = 31.4 ($3CH_3$), 34.8 (C), 123.15 (CH), 123.71 (CH), 125.03 (CH), 125.06 (CH), 125.13 (C), 125.19 (CH), 125.28 (CH), 125.82 (CH), 126.02 (2CH), 126.54 (2CH), 127.22 (CH), 127.54 (CH), 127.56 (CH), 128.38 (C), 130.78 (C), 131.02, (CH), 131.60, 131.77, 132.23 (C), 135.07 (C), 151.12 (C). IR (ATR, cm^{-1})**:** $\tilde{\nu}$ = 3040 (w), 2952 (w), 2900 (w), 2864 (w), 1598 (w), 1513 (w), 1461 (w), 1413 (w), 1361 (w), 1267 (w), 1201 (w), 1137 (w), 1090 (w), 1022 (w), 962 (w), 904 (w), 863 (w), 836 (m), 773 (w), 710 (m), 611 (w), 556 (m). GC-MS (EI, 70 eV): m/z (%): 360 (100) $[M]^+$, 346 (14), 345 (56), 329 (10), 304 (16), 303(68), 302 (24), 228 (16), 227 (90), 226 (40), 215 (18), 151 (46), 150 (22). HRMS (EI) calcd for $C_{28}H_{24}$ $[M]^+$: 360.18725; found 360.186333.

(*E*)-2-(2-(Pyren-1-yl)vinyl)pyridine (4h): Starting with **1** (100 mg, 0.35 mmol), **3h** (55.9 mg, 0.53 mmol), $Pd(OAc)_2$ (5 mol%, 4.3 mg, 0.017 mmol), X-Phos (10 mol%, 16 mg, 0.035 mmol), K_2CO_3 (98 mg, 0.71 mmol) in DMF (5 ml), **4h** was isolated as a yellow solid (95 mg, 88%). Mp 107-109 °C. ^{1}H NMR (300 MHz, $CDCl_3$): δ = 7.13 (*dd*, *J* = 4.82, 7.70 Hz, 1H, CH), 7.34 (*d*, *J* = 15.85 Hz, 1H, CH), 7.43 (*d*, *J* = 7.85 Hz, 1H, CH), 7**.** 7.65 (*t*, *J* = 7.70 Hz, 1H, CH), 7.92 (*t*, *J* = 7.70 Hz, 1H, CH), 7.99-8.12 (m, 6H, CH), 8.30 (*d*, *J* = 8.30 Hz, 1H, CH), 8.53 (*d*, *J* = 9.21 Hz, 1H, CH), 8.63 (*d*, *J* = 4.53 Hz, 1H, CH), 8.72 (*d*, *J* = 15.85 Hz, 1H, CH). ^{13}C NMR (62.89 MHz, $CDCl_3$) :δ = 122.3 (CH), 122.6 (CH), 123.3 (CH), 123.8 (CH), 124.3 (C), 124.8 (C), 125.1 (C), 125.2 (CH), 125.3 (CH), 125.5 (CH), 126.1 (CH), 127.4 (C), 127.4 (CH), 127.5 (C), 127.6 (CH), 127.8 (CH), 129.5 (C), 129.8 (CH), 130.5 (CH), 131.1 (C), 131.5 (C), 136.8 (CH), 149.7 (CH). IR (ATR, cm^{-1})**:** $\tilde{\nu}$ = 3044 (w), 2923 (m), 2551 (w), 1730 (w), 1678 (w), 1622 (w), 1581 (s), 1506 (w), 1467 (s), 1360 (w), 1300 (w), 1243 (w), 1186 (w), 1108 (w), 1049 (w), 991 (w), 965 (w), 894 (w), 841 (s), 793 (w), 740 (w), 679 (w), 607 (w), 539 (w). MS (EI, 70 eV): *m/z* (%) = 305 (68) $[M]^+$, 304 (100), 230 (14), 226 (26), 152 (29), 97 (10). HRMs (EI) calcd. for $C_{23}H_{15}N_1$ $[M+H]^+$: 305.11990; found 305.24472

(*E*)-4-(Pyren-1-yl)vinylphenyl acetate (4i): Starting with **1** (100 mg, 0.35 mmol), **3i** (86.3 mg, 0.53 mmol), $Pd(OAc)_2$ (5 mol%, 4.3 mg, 0.017 mmol), X-Phos (10 mol%, 16 mg, 0.035 mmol), K_2CO_3 (98 mg, 0.71 mmol) in DMF (5 ml), **4i** was isolated as a yellow solid (99 mg, 77%). Mp 150-152 °C. ^{1}H NMR (300 MHz, $CDCl_3$): δ = 2.33 (s, 3H, CH_3), 7.14 (d, *J* = 8.71Hz, 2H, Ar), 7.28 (d, *J* = 16.19 Hz, 1H, Ar), 7.65 (d, *J* = 8.71 Hz, 2H, Ar), 7.94-8.03 (m, 3H, Ar), 8.06-8.17 (m, 5H, Ar), 8.25 (d, *J* = 8.12 Hz, 1H, Ar), 8.42 (d, *J* = 9.25 Hz, 1H, Ar)**.** ^{13}C NMR (62.89 MHz, $CDCl_3$): δ = 21.2 (CH_3), 121.9 (2CH), 122.9 (CH), 123.6 (CH), 124.9 (C), 125.0 (2CH), 125.1 (2CH), 125.3 (C), 125.9 (2CH), 127.2 (CH), 127.4 (CH), 127.6 (3CH), 128.3 (C), 130.7 (CH), 130.9 (C), 131.5 (C), 131.7 (C), 135.6 (C), 150.2 (C), 169.5 (CO)**.** IR (ATR, cm^{-1})**:** $\tilde{\nu}$ = 3473 (w), 3042 (w), 2992 (w), 2849 (w), 1742 (s), 1714 (s), 1661 (m), 1597 (m), 1538 (w), 1505 (m), 1463 (w), 1415 (m), 1368 (m), 1322 (w), 1262 (w), 1221 (s), 1188 (s), 1137 (s), 1092 (m), 1041 (m), 968 (w), 914 (s), 863 (m), 810 (s), 761 (s), 710 (s), 657 (s), 612 (s), 562 (m), 534 (m). MS (EI, 70 eV): *m/z* (%) = 362 (38) $[M]^+$, 321 (16), 320 (81), 319 (37), 289 (19), 226 (15), 43 (100). HRMS (EI) calcd.for $C_{26}H_{18}O_2$ $[M+H]^+$: 362.13013; found 362.129652.

7.5 Synthesis of acrylate substituted pyrenes.

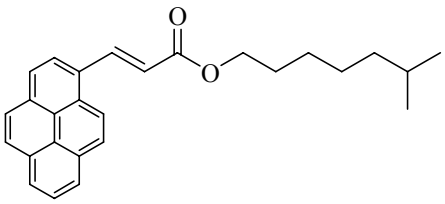
Starting with **2** (100 mg, 0.35 mmol), **5a-e** (0.53 mmol), $Pd(OAc)_2$ (5 mol%, 4.3 mg, 0.017 mmol), X-Phos (10 mol%, 16 mg, 0.035 mmol), K_2CO_3 (98 mg, 0.71 mmol) in DMF (5 ml), was stirred at 80 °C for 6-7 h. The reaction mixture was diluted with dichloromethane and washed with water. The combined organic layers were evaporated and column chromatography was performed with *n*-hexane:ethyle acetate(4:1). The products were isolated as yellow solids.

(*E*)-Butyl-3-(pyren-1-yl)acrylate (6a): Starting with **1** (100 mg, 0.35 mmol), **5a** (68 mg, 0.53 mmol), $Pd(OAc)_2$ (5 mol%, 4.3 mg, 0.017 mmol), X-Phos (10 mol%, 16 mg, 0.035 mmol), K_2CO_3 (98 mg, 0.71 mmol) in DMF (5 ml), **6a** was isolated as a luminous yellow oil (98 mg, 84%). ^{1}H NMR (300 MHz, $CDCl_3$): δ = 1.01 (t, *J* = 7.4 Hz, 3H, CH_3), 1.50 (sext, *J* = 7.2 Hz 2H, CH_2), 1.77 (p, *J* = 6.8 Hz, 2H, CH_2), 4.31 (t, *J* = 6.7 Hz, 2H, OCH_2), 7.83 (d, *J* = 7.84 Hz, 3H, CH), 7.89-8.00 (m, 4H, Py), 8.03-8.12 (m, 4H, Py), 8.13-8.23 (m, 2H, Ar). ^{13}C NMR (62.89 MHz, $CDCl_3$): δ=13.2 (CH_3), 27.6 (CH_2), 35.1 (CH_2), 59.6 (OCH_2), 121.9 (CH), 123.8 (CH), 123.9 (2CH), 124.8 (CH), 125.8 (CH), 126.0 (CH), 126.4 (CH), 126.5 (CH), 127.5 (C), 127.7 (CH), 129.1 (C), 129.8 (CH), 130.3 (C), 133.5 (C), 135.9 (C), 140.3 (C), 171.9 (CO). IR (ATR, cm^{-1})**:** $\tilde{\nu}$ = 3433 (w), 3039 (w), 2955 (w), 2869 (w), 2135 (w), 1920 (w), 1796 (w), 1720 (s), 1619 (m), 1594 (m), 1537 (w), 1487 (w), 1434 (w), 1381 (w), 1312 (m), 1274 (m), 1200 (m), 1162 (s), 1061 (m), 973 (m), 900 (w), 838 (s), 795 (m), 731 (m), 680 (m), 635 (m), 594 (m), 538 (m). MS (EI, 70 eV): *m/z* (%) = 328 (61) $[M]^+$, 255 (19), 227 (100), 226 (85), 225 (12), 224 (12), 113 (18). HRMS (EI) calcd.for $C_{23}H_{20}O_2$ $[M+H]^+$: 328.14578; found 328.145349.

(*E*)-Ethyl-3-(pyren-1-yl)acrylate (6b): Starting with **1)** (100.0 mg, 0.355 mmol), **(5b)** (53.2 mg, 0.532 mmol), $Pd(OAc)_2$ (5mol%, 4.33 mg, 0.017 mmol), X-Phos Ligand (10mol%, 16.0 mg, 0.035 mmol), K_2CO_3 (98.0 mg, 0.71 mmol) in DMF (5 ml), **(6b)** was isolated as a yellow solid (92.0 mg, 87%)**.** Mp 94-96 °C**.** ^{1}H NMR (300 MHz, $CDCl_3$): δ = 1.34 (*t, J* = 6.98 Hz*,* 3H, CH_3), 4.29 (*q*, *J* = 14.3 Hz, 2H, CH_2), 6.26 (*d*, *J* = 15.74 Hz, 1H, CH), 7.92-8.12 (*m*, 8H, Py), 8.34 (*d*, *J* = 9.23 Hz, 1H, Py), 8.75 (*d*, *J* = 15.74 Hz, 1H, CH**).** ^{13}C NMR (62.89 MHz, $CDCl_3$): δ = 30.9 (CH_3), 61.2 ($0CH_2$), 120.3 (CH), 122.5 (CH), 122.9 (C), 124.1 (CH), 124.6 (C), 124.8 (CH), 125.0 (CH), 125.7 (CH), 125.8 (C), 125.9 (CH), 126.2 (CH), 127.3

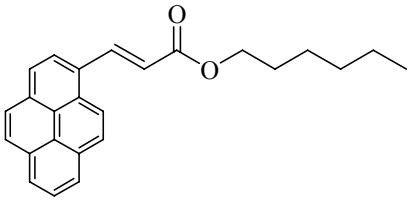
(CH), 127.4 (C), 128.3 (C), 128.4 (CH), 128.5 (C), 129.7 (C), 130.7 (C), 131.3 (C), 132.6 (C), 141.3 (CH), 167.1 (CO). IR (ATR, cm^{-1})**:** $\tilde{\nu}$ = 3041 (w), 2977 (w), 2925 (w), 2904 (w), 2852 (w), 1731 (w), 1705 (m), 1619 (m), 1538 (w), 1479 (w), 1442 (m), 1391 (w), 1340 (w), 1277 (m), 1210 (m), 1156 (s), 1107 (m), 1053 (m), 971 (m), 897 (m), 837 (s), 788 (m), 748 (m), 700 (m), 616 (m), 593 (m). MS (EI, 70 eV): *m/z* (%) = 300(64) $[M]^+$, 255 (16), 227 (100), 226 (86), 224 (13), 113 (27) HRMs (EI) calcd. for $C_{21}H_{16}O_2$ $[M+H]^+$: 300.114633; found 300.11448

(*E*)-6-Methylheptyl-3-(pyrene-1-yl)acrylate (6c): Starting with **1** (100 mg, 0.35 mmol), **5c**



(98 mg, 0.53 mmol), $Pd(OAc)_2$ (5 mol%, 4.3 mg, 0.017 mmol), X-Phos (10 mol%, 16 mg, 0.035 mmol), K_2CO_3 (98 mg, 0.71 mmol) in DMF (5 ml), **6c** was isolated as a yellow oil (107 mg, 79%)**.** ^{1}H NMR (300 MHz, $CDCl_3$): δ = 0.76-0.90 (m, 8H), 1.19-1.37 (m, 7H, CH_2), 4.13-4.16 (m, 2H, OCH_3), 7.91-8.22 (m, 9H, Py), 8.39 (d, *J* = 9.15 Hz, 1H, CH), 9.75 (d, *J* = 15.63 Hz, 1H, CH). ^{13}C NMR (75 MHz, $CDCl_3$): δ = 10.1 (CH_3), 14.1 (CH_3), 23.0 (CH_2), 23.8 (CH_2), 28.9 (CH_2), 30.4 (CH_2), 38.7 (CH), 68.2 (OCH_2), 120.4 (CH), 122.5(CH), 124.2 (CH), 125.1 (CH), 125.8 (CH), 126.0 (CH), 126.3 (CH), 127.3 (CH), 128.3 (C), 128.5 (CH), 128.8 (CH), 129.7 (C), 130.7 (C), 130.9 (CH), 131.3 (C), 132.5, (C), 132.7 (C), 141.3 (C), 167.8 (CO). IR (ATR, cm^{-1})**:** $\tilde{\nu}$ = 3435 (w), 3041 (w), 2955 (w), 2870 (w), 2731 (m), 1722 (s), 1621 (m), 1584 (w), 1510 (w), 1460 (m), 1416 (w), 1312 (m), 1270 (s), 1209 (m), 1163 (m), 1120 (m), 1070 (m), 1039 (m), 975 (m), 866 (m), 841 (s), 741 (m), 705 (m), 651 (w), 609 (w), 538 (w). HRMS (EI) calcd. for $C_{27}H_{28}O_2$ $[M]^+$: 384.20838; found 384.207745.

(*E*)-Hexyl-3-(pyren-1-yl)acrylate (6d): Starting with **1** (100 mg, 0.35 mmol), **5d** (82.9 mg,



0.53 mmol), $Pd(OAc)_2$ (5 mol%, 4.3 mg, 0.017 mmol), X-Phos (10 mol%, 16.0 mg, 0.035 mmol), K_2CO_3 (98 mg, 0.71 mmol) in DMF (5 ml), **6d** was isolated as a yellow oil (101 mg, 80%). ^{1}H NMR (300 MHz, $CDCl_3$): δ = 0.86 (t, *J* = 7.1 Hz 3H, CH_3), 1.26-1.41 (m, 6H, CH_2), 1.70 (p, *J* = 6.7 Hz 2H, CH_2), 4.22 (t, *J* = 6.76, 2H, OCH2), 6.62 (d, *J* = 15.73, 1H, CH), 7.90-8.19 (m, 8H, py), 8.38 (d, ^3J = 9.41 Hz, 1H, CH), 8.73 (d, *J* = 15.73 Hz, 1H, CH). ^{13}C NMR (75 MHz, $CDCl_3$): δ = 14.1 (CH_3), 22.6 (CH_2), 25.8 (CH_2), 28.8 (CH_2), 31.6 (CH_2), 64.9 (OCH_2), 120.4 (CH), 122.5 (CH), 124.2 (CH), 124.6 (C), 124.9 (CH), 125.0 (CH), 125.8 (CH), 126.0 (CH), 126.3 (CH), 127.2 (C),

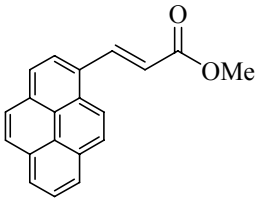
127.3 (CH), 128.3 (C), 128.5 (CH), 129.7 (C), 130.7 (C), 131.3 (C), 132.7,(C), 141.3 (CH), 167.3 (CO). IR (ATR, cm^{-1}): $\tilde{\nu}$ = 3040 (w), 2952 (m), 2926 (m), 2855 (w), 1918 (w), 1707 (s), 1620 (m), 1478 (w), 1416 (w), 1368 (w), 1313 (m), 1241 (m), 1162 (s), 1053 (m), 975 (m), 840 (s), 794 (w), 716 (w), 680 (w), 609 (w), 536 (w). GC-MS (EI, 70 eV): m/z (%) = 356 (44) $[M]^+$, 167 (36), 149 (100), 228 (19), 227 (100). HRMS (EI) calcd. for $C_{25}H_{24}O_2$ $[M]^+$: 356.17708; found 356.176071.

(*E*)-*iso*-Butyl 3-(pyren-3-yl)acrylate (6e): Starting with **1** (100 mg, 0.35 mmol), **5e** (76 mg, 0.53 mmol), $Pd(OAc)_2$ (5 mol %,4.3 mg, 0.017 mmol), X-Phos (10 mol%, 16 mg, 0.035 mmol), K_2CO_3 (98 mg, 0.71 mmol) in DMF (5 ml), **6e** was isolated as a luminous yellow oil (100 mg, 86%). ^1H NMR (300 MHz, $CDCl_3$): δ = 0.97 (d, *J* = 6.6 Hz, 6H, CH_3), 2.05-1.99 (m, 1H, CH), 4.00 (d, *J* = 6.6 Hz, 2H, CH_2), 6.61 (d, *J* = 15.6 Hz, 1H, CH), 7.89 (d, *J* = 15.5 Hz, 1H, CH), 7.91-8.15 (m, 7H, CH), 8.31 (d, *J* = 8.4 Hz, 1H, CH), 8.70 (d, *J* = 15.8 Hz, 1H, CH). ^{13}C NMR (75 MHz, $CDCl_3$): δ = 19.3 (CH_3), 19.3 (CH_3), 28.0 (CH), 70.9 (CH_2), 120.3 (CH), 122.4 (CH), 124.2 (CH), 124.6 (C), 124.9 (C), 125.0 (CH), 125.8 (CH), 125.9 (CH), 126.3 (CH), 127.3 (CH), 128.3 (C), 128.5 (CH), 128.6 (CH), 129.7, 130.7, 131.3, 132.7 (C), 141.3 (CH), 167.3 (CO). IR (ATR, cm^{-1}): $\tilde{\nu}$ = 3040 (w), 2958 (w), 2872 (w), 1703 (m), 1619 (m), 1595 (m), 1466 (w), 1374 (w), 1240 (m), 1153 (s), 1013 (m), 971 (m), 839 (s), 755 (m), 704 (m), 679 (w), 488 (w).GC-MS (EI, 70 eV): m/z (%) = 328 $[M]^+$, 255 (31), 249 (30), 228 (23), 227 (100), 226 (96), 225 (12), 224 (16), 113 (15). Anal. calcd. for C_{23} $H_{20}O_2$ (328.40): C, 84.12; H, 6.14. Found: C, 83.67; H, 6.241. HRMS (EI) calcd. for C_{23} $H_{20}O_2$ $[M]^+$: 328.14578; found 328.145716.

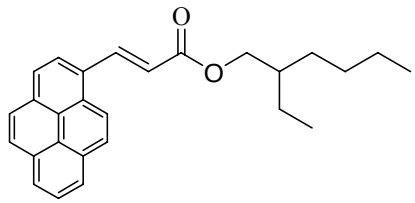
(*E*)-*tert*-Butyl 3-(pyren-3-yl)acrylate (6f): Starting with **1** (100 mg, 0.35 mmol), **5f** (76. mg, 0.53 mmol), $Pd(OAc)_2$ (5 mol %, 4.3 mg, 0.017 mmol), X-Phos (10 mol %, 16 mg, 0.035 mmol), K_2CO_3 (98 mg, 0.71 mmol) in DMF (5 ml), **6f** was isolated as a luminous yellow oil (108 g, 93%). ^1H NMR (300 MHz, $CDCl_3$): δ = 0.97 (s, 9H, CH_3), 6.55 (d, *J* = 15.9 Hz, 1H, CH), 7.96 (d, *J* = 15.6 Hz, 1H, CH), 7.97-8.18 (m, 7H, CH), 8.37 (d, *J* = 9.0 Hz, 1H, CH), 8.69 (d, *J* = 15.8 Hz, 1H, CH). ^{13}C NMR (75 MHz, $CDCl_3$): δ = 28.4 (CH_3, *t*-Bu), 80.7 (C, *t*-Bu), 122.3 (CH), 124.2 (CH), 124.8 (C), 124.9 (C), 125.0 (CH), 125.7 (CH), 125.9 (CH), 126.3 (CH), 127.4 (CH), 128.4 (C), 128.5 (CH), 128.8 (CH), 128.9 (CH), 129.6, 130.8, 131.4, 132.5 (C), 140.3 (CH), 166.5 (CO). IR (ATR, cm^{-1}): $\tilde{\nu}$ = 3042 (w), 2959 (w), 2928 (w), 2859

(w), 1705 (m), 1621 (m), 1596 (m), 1458 (w), 1390 (w), 1276 (s), 1143 (s), 1070 (m), 1039 (w), 976 (m), 840 (s), 743 (w), 706 (m), 680 (w). GC-MS (EI, 70 eV): m/z (%) = 328 $[M]^+$, (44), 255 (26), 248 (30), 228 (19), 227 (100), 226 (88), 225 (17), 224 (22). HRMS (EI): calcd. for $C_{23}H_{20}O_2$ $[M]^+$: 328.14578; found 328.145734.

(*E*)-Methyl-3-(pyren-3-yl)acrylate (6g): Starting with **1** (100 mg, 0.35 mmol), **5g** (46 mg, 0.53 mmol), $Pd(OAc)_2$ (5 mol%, 4.3 mg, 0.017 mmol), X-Phos Ligand (10 mol%, 16 mg, 0.035 mmol), K_2CO_3 (98 mg, 0.71 mmol) in DMF (5 ml), **6g** was isolated as a yellow solid (91.mg, 90%). Mp 135-137 °C. ^{1}H NMR (300 MHz, $CDCl_3$): δ = 3.82 (s, 3H, OCH_3), 6.62 (d, *J* = 15.6 Hz, 1H, CH), 7.92-8.19 (m, 8H, CH), 8.39 (d, *J* = 9.3 Hz, 1H, CH), 8.75 (d, *J* = 15.9 Hz, 1H, CH). ^{13}C NMR (75 MHz, $CDCl_3$): δ = 51.9 (OCH_3), 119.8 (CH), 122.5 (CH), 124.2 (CH), 124.7 (C), 124.9 (C), 125.1 (CH), 125.9 (CH), 126.0 (CH), 126.3 (CH), 127.4 (CH), 128.2 (C), 128.6 (CH), 128.9 (CH), 129.8 (C), 130.7 (C), 131.3 (C), 132.8 (C), 141.6 (CH), 167.6 (CO). IR (ATR, cm^{-1})**:** $\tilde{\nu}$ = 3072 (w), 3043 (w), 2956 (w), 2927 (w), 2859 (w), 1700 (s), 1611 (m), 1592 (w), 1433 (m), 1368 (m), 1273 (m), 1121 (m), 1071 (m), 982 (m), 838 (s), 760 (m), 707 (m), 677 (w). GC-MS (EI, 70 eV): m/z (%) = 286 (58) $[M]^+$, 255 (14), 228 (18), 227 (100), 226 (93), 225 (15), 224 (18), 200 (8), 113 (26), 112 (12). HRMS (EI) calcd. for $C_{20}H_{14}O_2$ $[M]^+$: 286.09883; found 286.098350.



(*E*)-2-Ethylhexyl-3-(pyren-3-yl)acrylate (6h): Starting with **1** (100 mg, 0.35 mmol), **5h** (111 mg, 0.53 mmol), $Pd(OAc)_2$ (5 mol%, 4.3 mg, 0.017 mmol), X-Phos (10 mol%, 16 mg, 0.03 mmol), K_2CO_3 (98 mg, 0.71 mmol) in DMF (5 ml), **6h** was isolated as a yellow oil (120 mg, 88%). ^{1}H NMR (300 MHz, $CDCl_3$): δ = 0.81-0.90 (m, 6H, CH_3), 1.23-1.46 (m, 8H, CH_2), 1.65-1.71 (m, 1H, CH), 4.15 (d, *J* = 6.3 Hz, 2H, OCH_2), 6.66 (d, *J* = 15.6 Hz, 1H, CH), 7.85-8.07 (m, 8H, CH), 8.24 (d, *J* = 8.7 Hz, 1H, CH), 8.75 (d, *J* = 15.8 Hz, 1H, CH). ^{13}C NMR (75 MHz, $CDCl_3$): δ = 11.2 (CH_3), 14.2 (CH_3), 23.0, 23.8, 29.1, 30.6 (CH_2), 39.0 (CH-chain), 67.2 (OCH_2), 120.4 (CH), 122.5 (CH), 124.2 (CH), 124.7 (C), 124.9 (C), 125.1 (CH), 125.8 (CH), 126.0 (CH), 126.3 (CH), 127.4 (CH), 128.3 (C), 128.6 (CH), 128.6 (CH), 129.7, 130.7, 131.4, 132.7 (C), 141.3 (CH), 167.4 (CO). IR (ATR, cm^{-1})**:** $\tilde{\nu}$ = 3041 (w), 2956 (w), 2925 (w), 2857 (w), 1709 (m), 1620 (m), 1595 (m), 1459 (w), 1379 (w), 1275 (m), 1162 (s), 1030 (w), 975 (w), 840 (s), 756 (w), 705 (m), 680 (w). GC-MS (EI, 70 eV): m/z (%) = 384 (100)



$[M]^+$, 272 (17), 255 (36), 248 (30), 228 (24), 227 (88), 226 (78), 225 (10), 224 (10). Anal. calcd. for $C_{27}H_{28}O_2$: C, 84.34. H, 7.34. Found: C, 83.89. H, 7.652. HRMS (EI) calcd. for $C_{27}H_{28}O_2[M]^+$: 384.20838; found 384.208096.

(*E*)-2,2,2-Trifluoroethyl-3-(pyren-3-yl)acrylate (6i): Starting with **1** (100 mg, 0.35 mmol), **5i** (67 mg, 0.532 mmol), $Pd(OAc)_2$ (5 mol%, 4.3 mg, 0.017 mmol), X-Phos (10 mol%, 16 mg, 0.035 mmol), K_2CO_3 (98 mg, 0.71 mmol) in DMF (5 ml), **6i** was isolated as a luminous yellow solid (105 mg, 83%). Mp 118-120 °C. ^{1}H NMR (300 MHz, $CDCl_3$): δ = 4.75 (q, ^3J = 9.0 Hz, 2H, OCH_2CF_3), 6.66 (d, ^3J = 15.0 Hz, 1H, CH), 8.08-8.37 (m, 8H, CH), 8.24 (d, ^3J = 9.0 Hz, 1H, CH), 8.99 (d, ^3J = 15.0 Hz, 1H, CH). ^{13}C NMR (75 MHz, $CDCl_3$): δ = 68.1 (OCH_2), 117.6 (CH), 122.5 (CH), 124.3 (CH), 124.7 (C), 124.7 (C), 125.0 (CH), 125.2 (CH), 126.1 (CH), 126.3 (CH), 126.4 (CH), 127.4 (CH), 128.6 (C), 128.9 (CH), 129.9, 131.8, 133.5, 133.7 (C), 143.8 (CH), 166.9 (CO). IR (ATR, cm^{-1})**:** $\tilde{\nu}$ = 3045 (w), 2956 (w), 2922 (w), 2852 (w), 1718 (m), 1614 (m), 1538 (m), 1441 (w), 1371 (w), 1267 (m), 1138 (s), 1054 (w), 973 (w), 839 (s), 755 (w), 701 (m), 678 (w). GC-MS (EI, 70 eV): m/z (%) = 354 (90) $[M]^+$, 255 (23), 228 (19), 227 (100), 226 (92), 225 (15), 224 (17), 113 (34), 112 (13). HRMS (EI, 70 eV) calcd. for $C_{21}H_{13}F_3O_2$ $[M]^+$: 354.08622 found 354.086153.

(*E*)-2-Hydroxyethyl-3-(pyren-3-yl)acrylate (6j): Starting with **1** (100 mg, 0.35 mmol), **5j** (56 mg, 0.53 mmol), $Pd(OAc)_2$ (5 mol%, 4.3 mg, 0.017 mmol), X-Phos (10 mol%, 16 mg, 0.035 mmol), K_2CO_3 (98 mg, 0.71 mmol) in DMF (5 ml), **6j** was isolated as a yellow solid (84 mg, 74%). Mp 132-134 °C. ^{1}H NMR (300 MHz, $CDCl_3$): δ = 1.99 (s, 1H, OH), 3.86-3.89 (m, 2H, CH_2), 4.33-4.37 (m, 2H, CH_2), 6.63 (d, J = 15.9 Hz, 1H, CH), 7.89-8.01 (m, 8H, CH), 8.38 (d, J = 8.6 Hz, 1H, CH), 8.74 (d, J = 15.9 Hz, 1H, CH). ^{13}C NMR (75 MHz, $CDCl_3$): δ = 61.6, 66.4 (CH_2), 119.4 (CH), 122.4 (CH), 124.2 (CH), 124.3 (CH), 124.6 (C), 124.7 (C), 125.1 (CH), 125.9 (CH), 126.1 (CH), 126.3 (CH), 127.3 (CH), 128.7 (CH), 130.7, 130.9, 131.3, 132.6, 132.9 (C), 142.3 (CH), 167.5 (CO). IR (ATR, cm^{-1})**:** $\tilde{\nu}$ = 3024 (w), 2961 (w), 2920 (w), 2875 (w), 1698 (m), 1617 (m), 1599 (m), 1435 (w), 1361 (w), 1276 (m), 1088 (s), 1036 (w), 979 (w), 838 (s), 760 (w), 703 (m), 678 (w). GC-MS (EI, 70 eV): m/z (%) = 316 (63) $[M]^+$, 255 (28), 248 (30), 228 (20), 227 (98), 226 (100), 225 (13), 224 (15), 113 (24). Anal. calcd. for $C_{21}H_{16}O_3$; C, 79.73. H,

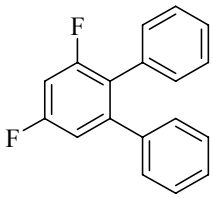
5.10. Found: C, 79.52. H, 5.334. HRMS (EI) calcd. for $C_{21}H_{16}O_3$ $[M]^+$: 316.10940; found 316.108872.

7.6 Synthesis of terphenyls from mono- and difluorinated bromobenzenes by site-selective Suzuki-Miyaura reactions

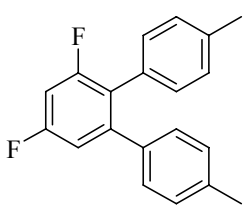
General Procedure for Suzuki Reactions (9a-I, 10a-h)

A 1,4-dioxane solution (4 mL per 0.3 mmol of **7**) of **7**, Cs_2CO_3, $Pd(PPh_3)_4$, and arylboronic acid **8** was stirred at 90 °C for 6 or 8 h. After cooling to r.t. the organic and the aqueous layer were separated and the latter was extracted with CH_2Cl_2. The combined organic layers were dried (Na_2SO_4), filtered, and the filtrate was concentrated in vacuo. The residue was purified by column chromatography.

1,2-Diphenyl-3,5-difluorobenzene (9a): Starting with **7** (100 mg, 0.37 mmol), Cs_2CO_3 (263 mg, 0.81 mmol), $Pd(PPh_3)_4$ (3 mol%), Phenylboronic acid (98 mg, 0.81 mmol), and 1,4-dioxane (4 mL), **9a** was isolated as a colorless solid (62 mg, 65%). Mp 70–72 °C. ^{1}H NMR (300 MHz, $CDCl_3$): δ = 6.87-6.94 (m, 1H, ArH), 6.96–7.00 (m, 1H, ArH), 7.04-7.10 (m, 4H, ArH), 7.16–7.24 (m, 6H, ArH). ^{13}C NMR (62.89 MHz, $CDCl_3$): ^{13}C NMR (62.89 MHz, $CDCl_3$): δ = 102.7 (d, *J* = 27.9 Hz, CH), 112.9 (d, *J* = 3.1 Hz, CH), 127.2 (2CH), 127.8 (2CH), 127.9 (2CH), 129.6 (2CH), 131.0 (2CH), 133.4 (C), 139.4 (t, *J* = 2.1 Hz, C), 144.4 (d, *J* = 9.18 Hz, C), 160.0 (dd, *J* = 247.2 12.3 Hz, CF), 161.3 (dd, *J* = 248.2, 12.6 Hz, CF). ^{19}F NMR (282.4 MHz, $CDCl_3$): δ = –110.61 (CF), –111.64 (CF). IR (ATR, cm^{-1}): $\tilde{\nu}$ = 3065 (w), 3027 (w), 2923 (w), 2852 (w), 1617 (m), 1589 (m), 1537 (w), 1498 (w), 1465 (m), 1438 (m), 1413 (m), 1328 (m), 1265 (w), 1204 (w), 1155 (w), 1139 (m), 1101 (m), 1038 (w), 997 (m), 918 (w), 874 (w), 866 (m), 840 (m), 780 (m), 766 (s), 716 (w), 697 (s), 632 (m), 597 (m), 557 (m). MS (EI, 70 eV): m/z (%) = 266 (100) $[M]^+$, 264 (14), 251 (36), 244 (26), 238(10). HRMS (EI) calcd. for $C_{18}H_{12}F_2$ $[M]^+$: 266.09016; found 266.090819.

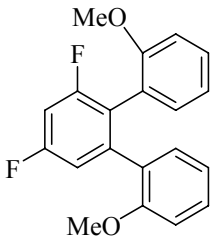


1,2-Di(4´-methylphenyl)-3,5-difluorobenzene (9b): Starting with **7** (100 mg, 0.37 mmol), Cs_2CO_3 (263 mg, 0.81 mmol), $Pd(PPh_3)_4$ (3 mol%), 4-methylphenylboronic acid (110 mg, 0.81 mmol) and 1,4-dioxane (4 mL), **9b** was isolated as a colorless solid (48 mg, 45%). Mp 68-70 °C. ^{1}H NMR (300 MHz, $CDCl_3$): δ = 2.38 (s, 3H, CH_3) 2.40 (s, 3H, CH_3), 6.92-6.96 (m, 2H, ArH), 7.02-7.06 (m, 4H, ArH), 7.08-7.10 (m, 4H, ArH). ^{13}C NMR (75 MHz,

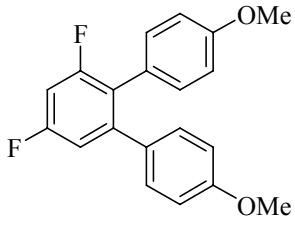


$CDCl_3$): δ = 21.1, (CH_3) 21.3 (CH_3), 102.6 (t, *J* = 24.8 Hz, CH), 112.9 (d, *J* = 18.5 Hz, CH), 124.4 (d, *J* = 12.5 Hz, CH), 128.8 (4CH), 129.8 (4CH), 130.8 (2C), 136.7 (2C), 144.4 (dd, *J* = 4.5, 4.5 Hz, C), 159.1 (dd, *J* = 246.1, 11.8 Hz, CF), 160.1 (dd, *J* = 247.2, 12.6 Hz, CF).^{19}F NMR (282 MHz, $CDCl_3$): δ = –110.24 (CF), –111.73 (CF). IR (ATR, cm^{-1}): $\tilde{\nu}$ = 3027 (w), 2973 (w), 2923 (w), 2865 (w), 1905 (w), 1611 (w), 1587 (w), 1514 (w), 1453 (w), 1399 (w), 1335 (w), 1267 (w), 1202 (w), 1141 (w), 1111 (w), 1098 (w), 997 (w), 945 (w), 844 (w), 815 (w), 756 (w), 716 (w), 665 (w), 623 (w), 599 (w), 520 (m). MS (EI, 70 eV): *m/z* (%) = 294 (100) $[M]^+$, 293 (13), 280 (18), 275 (12), 265(14). HRMS (EI) calcd. for $C_{20}H_{16}F_2$ $[M]^+$: 294.12146; found 294.121005.

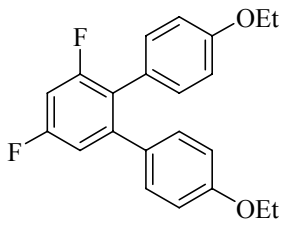
1,2-Di(2´-methoxyphenyl)-3,5-difluorobenzene (9c): Starting with **7** (100 mg, 0.37 mmol),



Cs_2CO_3 (263 mg, 0.81 mmol), $Pd(PPh_3)_4$ (3 mol%), 2-methoxyphenylboronic acid (123 mg, 0.81 mmol), and 1,4-dioxane (4 mL), **9c** was isolated as a colorless solid (71 mg, 60%). Mp 111–113 °C. ^{1}H NMR (300 MHz, $CDCl_3$): δ = 3.42 (s, 3H, OCH_3), 3.55 (s, 3H, OCH_3), 6.60 (dd, *J* = 8.3, 0.7 Hz, 1H, ArH), 6.67–6.88 (m, 6H, ArH), 6.94 (dd, *J* = 7.5, 1.7 Hz, 1H, ArH), 7.05–7.12 (m, 2H, ArH). ^{13}C NMR (62.89 MHz, $CDCl_3$): δ = 54.9 (OCH_3), 55.2 (OCH_3), 102.6 (t, *J* = 26.5 Hz, CH), 110.2 (CH), 110.3 (CH), 113.2 (dd, *J* = 21.2, 3.5 Hz, CH), 119.7 (CH), 119.9 (CH), 122.1 (dd, *J* = 17.1, 3.8 Hz, C), 123.1 (C), 128.6 (t, *J* = 2.1 Hz, C), 128.90 (CH), 128.92 (CH), 131.0 (CH), 131.7 (CH), 141.9 (t, *J* = 4.9 Hz, C), 156.0 (C), 157.0 (C), 160.1 (dd, *J* = 247.2, 12.8 Hz, CF), 161.6 (dd, Jc_F = 247.2, 13.3 Hz, CF). ^{19}F NMR (282.4 MHz, $CDCl_3$): δ = –112.82 (CF), –118.20 (CF). IR (ATR): $\tilde{\nu}$ = 3067 (w), 2956 (w), 2926 (w), 2835 (w), 1616 (w), 1596 (w), 1503 (w), 1494 (w), 1455 (w), 1421 (w), 1338 (w), 1287 (w), 1247 (m), 1201 (w), 1180 (w), 1120 (w), 1089 (w), 1024 (m), 928 (w), 877 (w), 865 (w), 800 (w), 755 (w), 744 (m), 701 (w), 635 (w), 586 (m), 537 (w) cm^{-1}. MS (EI, 70 eV): *m/z* (%) = 326 (100) $[M]^+$, 295 (12), 251 (21), 238 (10). HRMS (EI) calcd. for $C_{20}H_{16}O_2F_2$ $[M]^+$: 326.11129; found 326.11090.

1,2-Di(4-methoxyphenyl)-3,5-difluorobenzene (9d): Starting with **7** (100 mg, 0.37 mmol), 

Cs_2CO_3 (263 mg, 0.81 mmol), $Pd(PPh_3)_4$ (3 mol%), 2-methoxyphenylboronic acid (123 mg, 0.81 mmol), and 1,4-dioxane (4 mL), **9d** was isolated as a colorless oil (58 mg, 70%). ^{1}H NMR (300 MHz, $CDCl_3$): δ = 3.59 (s, 3H, OCH_3), 3.71 (s, 3H, OCH_3), 6.61-6.95 (m, 10H, ArH). ^{13}C NMR (62.89 MHz, $CDCl_3$): δ = 55.0 (OCH_3), 55.2 (OCH_3), 102.6 (dd, *J* = 29.3, 2.02 Hz, 2CH), 113.4 (d, *J* = 2.86 Hz, 2CH), 114.2 (2CH), 125.8 (C), 127.7 (CH), 130.7 (2CH), 131.9 (t, *J* = 2.91 Hz, CH), 132.0 (CH), 144.0 (dd, *J* = 9.57, 4.16 Hz, C), 158.7 (d, *J* = 10.8 Hz, C), 160.3 (dd, J_{CF} = 247.0, 12.9 Hz, CF), 161.6 (dd, J_{CF} = 248.1, 14.5 Hz, CF). ^{19}F NMR (282.4 MHz, $CDCl_3$): δ = –110.45 (CF), –111.95 (CF). IR (ATR): $\tilde{\nu}$ = 3076 (w), 3035 (w), 2955 (w), 2933 (w), 2836 (w), 2537 (w), 2047 (w), 1887 (w), 1726 (w), 1607 (s), 1587 (s), 1512 (s), 1461 (s), 1439 (s), 1402 (m), 1335 (w), 1289 (m), 1242 (s), 1204 (m), 1175 (s), 1139 (s), 1098 (s), 1034 (s), 997 (s), 874 (m), 827 (s), 799 (s), 760 (m), 732 (m), 665 (w), 585 (s), 543 (s) cm^{-1}. MS (EI, 70 eV): *m/z* (%) = 326 (100) $[M]^+$, 251 (21), 239 (11), 238 (11). HRMS (EI) calcd. for $C_{20}H_{16}O_2F_2$ $[M]^+$: 326.11129; found 326.111300

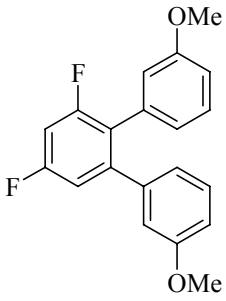
1,2-Di(4´-ethoxyphenyl)-3,5-difluorobenzene (9e): Starting with **7** (100 mg, 0.37 mmol), 

Cs_2CO_3 (263 mg, 0.81 mmol), $Pd(PPh_3)_4$ (3 mol%), 4-ethoxyphenylboronic acid (135 mg, 0.81 mmol), and 1,4-dioxane (4 mL) **9e** was isolated as a colorless solid (88 mg, 68%). Mp 69–71 °C. ^{1}H NMR (300 MHz, $CDCl_3$): δ = 1.36-1.43 (m, 4H, CH_2), 3.94-4.03 (m, 6H, OCH_3), 6.69-7.01 (m, 10H, ArH). ^{13}C NMR (62.89 MHz, $CDCl_3$): δ = 14.8 (CH_3), 14.9 (CH_3), 63.2 (OCH_2), 63.3 (OCH_2), 102.3 (t, *J* = 26.5 Hz, CH), 112. (dd, *J* = 21.8, 3.6 Hz, CH), 113.9 (2CH), 114.0 (2CH), 114.7 (2CH), 125.6 (C), 127.7 (C), 130.7 (2CH), 131.0 (C), 132.2 (C), 157.9 (C), 158.1 (C), 160.0 (dd, J_{CF} = 249.2, 12.6 Hz, CF), 161.1 (dd, J_{CF} = 249.2, 13.3 Hz, CF). ^{19}F NMR (282.4 MHz, $CDCl_3$): δ = –110.09 (CF), –112.02 (CF). IR (ATR, cm^{-1}): $\tilde{\nu}$ = 3062 (w), 3036 (w), 2975 (w), 2929 (w), 2873 (w), 1730 (w), 1605 (m), 1586 (m), 1511 (m), 1460 (m), 1432 (m), 1393 (m), 1335 (w), 1285 (m), 1239 (s), 1177 (m), 1110 (m), 1046 (m), 997 (m), 934 (w), 867 (m), 819 (s), 758 (m), 647 (w), 616 (m), 594 (w), 559 (m), 536 (m). MS (EI, 70 eV): *m/z* (%) = 354 (100) $[M]^+$, 326 (21), 298 (30), 297 (22), 251 (24). HRMS (EI) calcd. for $C_{22}H_{20}O_2F_2$ $[M]^+$: 354.14259; found 354.142299

1,2-Di(2´,4´-dimethoxyphenyl)-3,5-difluorobenzene (9f): Starting with **7** (100 mg, 0.37 mmol), Cs_2CO_3 (263 mg, 0.81 mmol), $Pd(PPh3)_4$ (3 mol%), 2,4-dimethoxyphenylboronic acid (148 mg, 0.81 mmol), and 1,4-dioxane (4 mL), **9f** was isolated as a colorless solid (81 mg, 58%). Mp 96–98 °C. ^{1}H NMR (300 MHz, $CDCl_3$): δ = 3.44 (s, 3H, OCH_3), 3.56 (s, 3H, OCH_3), 3.68 (s, 3H, OCH_3), 3.69 (s, 3H, OCH_3), 6.20-6.30 (m,3H, ArH), 6.72-6.85 (m,3H, ArH), 7.29-7.42 (m,1H, ArH), 761-766 (m,1H, ArH). ^{13}C NMR (62.89 MHz, $CDCl_3$): δ = 55.0 (OCH_3), 55.2 (OCH_3), 55.3 (OCH_3), 55.4 (OCH_3), 98.1 (d, *J* = 12.7 Hz, CH), 98.9 (C), 102.4 (d, *J* = 109.9 Hz, C), 103.8 (d, *J* = 16.3 Hz, CH), 113.2 (d, *J* = 14.5 Hz, C), 113.8 (d, *J* = 16.5 Hz, CH), 115.8 (C), 121.2 (t, *J* = 9.25 Hz, C), 127.9 (t, *J* = 21.7 Hz, H), 130.2 (C), 131.4 (CH), 131.9 (C), 134.7 (t, *J* = 25.5 Hz, CH), 157.5 (d, *J* = 245.5 Hz, CF), 160.0 (C), 160.3 (C). ^{19}F NMR (282.4 MHz, $CDCl_3$): δ = –110.09 (CF), –113.03 (CF). IR (ATR, cm^{-1}): $\tilde{\nu}$ = 3054 (w), 2997 (w), 2921 (w), 2851 (w), 1607 (w), 1579 (w), 1508 (w), 1461 (w), 1435 (w), 1410 (w), 1337 (w), 1280 (w), 1205 (m), 1156 (m), 1124 (w), 1092 (m), 1030 (m), 981 (w), 935 (w), 830 (w), 647 (w), 723 (w), 692 (w), 613 (w), 588 (w), 540 (w). MS (EI, 70 eV): m/z (%) = 386 (100) $[M]^+$, 355 (11). HRMS (EI) calcd. for $C_{22}H_{20}O_4F_2$ $[M]^+$: 386.13242; found 386.132496

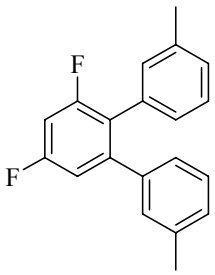
1,2-Di(4´-Fluorophenyl)-3,5-difluorobenzene (9g): Starting with **7** (100 mg, 0.37 mmol), Cs_2CO_3 (263 mg, 0.81 mmol), $Pd(PPh_3)_4$ (3 mol%), 4-fluorophenylboronic acid (114 mg, 0.81 mmol), and 1,4-dioxane (4 mL), **9g** was isolated as a colorless solid (49 mg, 45%). Mp 96–98 °C. ^{1}H NMR (300 MHz, $CDCl_3$): δ = 6.79-6.88 (m, 1H, ArH), 6.96–7.09 (m, 1H, ArH), 7.22-7.45 (m, 8H, ArH).^{13}C NMR (62.89 MHz, $CDCl_3$): δ = 103.9 (d, *J* = 3.09 Hz, C), 113.5 (t, *J* = 3.2 Hz, CH), 115.1 (CH), 115.6 (CH), 115.9 (CH), 128.2 (CH), 128.5 (CH), 128.6 (d, *J* = 2.7 Hz, CH), 128.9 (CH), 129.0 (CH), 130.5 (CH), 130.7 (C), 133.7 (CH), 136.1 (d, *J* = 216.5 Hz, CF), 136.6 (d, *J* = 255.4 Hz, CF), 138.4 (C), 153.5 (d, *J* = 234.7 Hz, CF), 157.6 (d, *J* = 245.8 Hz, CF). ^{19}F NMR (282.4 MHz, $CDCl_3$): δ = –98.84 (CF), –109.67 (CF), –111.15 (CF), –115.15 (CF). IR (ATR, cm^{-1}): $\tilde{\nu}$ = 3084 (w), 3050 (w), 2925 (w), 1903 (w), 1619 (w), 1587 (m), 1494 (m), 1474 (m), 1424 (m), 1348 (m), 1279 (w), 1222 (m), 1157 (m), 1113 (m), 1088 (s), 1029 (w), 1001 (s), 943 (w), 847 (m), 811 (s), 723 (m), 701 (m), 626 (m), 605 (s), 545 (m). MS (EI, 70 eV); m/z (%) = 302 (100) $[M]^+$, 282 (18). HRMS (EI) calcd. for $C_{18}H_{10}OF_4$ $[M]^+$: 302.07131; found 302.070651.

1,2-Di(3-methoxyphenyl)-3,5-difluorobenzene (9h): Starting with **7** (100 mg, 0.37 mmol),



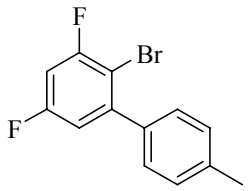
Cs_2CO_3 (263 mg, 0.81 mmol), $Pd(PPh_3)_4$ (3 mol%), 3-methoxyphenylboronic acid (123 mg, 0.81 mmol), and 1,4-dioxane (4 mL), **9h** was isolated as a colorless solid (58 mg, 70%). Mp 118–120 °C. ^{1}H NMR (300 MHz, $CDCl_3$): δ = 3.43 (s, 3H, OCH_3), 3.57 (s, 3H, OCH_3), 6.61 (d, *J* = 7.69 Hz, 1H, ArH), 6.66-6.97 (m, 7H, ArH), 7.06-713 (m, 2H, ArH). ^{13}C NMR (62.89 MHz, $CDCl_3$): δ = 55.4 (OCH_3), 55.9 (OCH_3), 102.6 (t,. *J* = 26.4 Hz, C), 110.4 (CH), 113.1 (d, *J* = 3.6 Hz, CH), 119.2 (d, J = 16.5 Hz, CH) 123.1 (C), 128.6 (t, *J* = 2.9 Hz, CH), 130.0 (C), 131.0 (2CH), 156.0 (C), 157.0 (C), 159.0 (dd, J_{CF} = 247.4, 14.31 Hz, CF), 161.7 (dd, J_{CF} = 247.4, 14.31 Hz, CF). ^{19}F NMR (282.4 MHz, $CDCl_3$): δ = –110.45 (CF), –111.95 (CF). IR (ATR): $\tilde{\nu}$ = 3055 (w), 2922 (w), 2851 (w), 1726 (w), 1618 (w), 1590 (w), 1580 (w), 1494 (w), 1436 (m), 1377 (w), 1336 (w), 1277 (w), 1245 (w), 1177 (m), 1117 (s), 1091 (m), 1026 (m), 996 (m), 877 (w), 838 (w), 798 (w), 747 (s), 720 (s), 692 (s), 637 (m), 587 (w), 538 (s) cm^{-1}. MS (EI, 70 eV); *m/z* (%) = 326 (100) $[M]^+$, 295 (13), 251 (22), 238 (11). HRMS (EI) calcd. for $C_{20}H_{16}O_2F_2$ $[M]^+$: 326.11129; found 326.110991.

1,2-Di(3-methylphenyl)-3,5-difluorobenzene (9i): Starting with **7** (100 mg, 0.37 mmol),

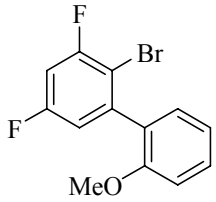


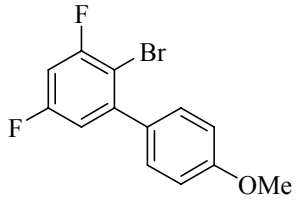
Cs_2CO_3 (263 mg, 0.81 mmol), $Pd(PPh_3)_4$ (3 mol%), 3-methylphenylboronic acid (110 mg, 0.81 mmol) and 1,4-dioxane (4 mL), **9i** was isolated as a colorless solid (51 mg, 48%). Mp 73-75 °C. ^{1}H NMR (300 MHz, $CDCl_3$): δ = 2.38 (s, 3H, CH_3) 2.40 (s, 3H, CH_3), 6.92-6.96 (m, 2H, ArH), 7.02-7.06 (m, 4H, ArH), 7.08-7.10 (m, 4H, ArH). ^{13}C NMR (75 MHz, $CDCl_3$): δ = 21.1, 21.3 ($ArCH_3$), 102.6 (t, *J* = 24.8 Hz, CH), 112.9 (d, *J* = 18.5 Hz, CH), 124.4 (d, *J* = 12.5 Hz, C), 128.8 (4CH), 129.8 (4CH), 130.8 (2C), 136.7 (2C), 144.4 (dd, *J* = 4.5, 4.5 Hz, C), 159.1 (dd, $^1J_{CF}$ = 246.1, 11.8 Hz, CF), 160.1 (dd, $^1J_{CF}$ = 247.2, 12.6 Hz, CF).^{19}F NMR (282 MHz, $CDCl_3$): δ = –110.69 (CF), –112.19 (CF). IR (ATR, cm^{-1}): $\tilde{\nu}$ = 3087 (w), 3052 (w), 2974 (w), 2923 (w), 2865 (w), 1905 (w), 1610 (w), 1587 (m), 1514 (w), 1453 (w), 1398 (w), 1335 (m), 1310 (w), 1277 (w), 1201 (w), 1141 (m), 1111 (w), 1097 (m), 997 (m), 968 (w), 870 (m), 844 (m), 815 (s), 756 (w), 726 (m), 664 (w), 623 (m), 598 (w), 530 (w). MS (EI, 70 eV): *m/z* (%) = 294 (100) $[M]^+$, 293 (12), 280 (18), 279 (87), 278 (22), 277 (11), 265(14), 264 (45), 259 (10), 257 (10). HRMS (EI) calcd. for $C_{20}H_{16}F_2$ $[M]^+$: 294.12146; found 294.121750.

2-Bromo-3,5-difluoro-4`-methylbiphenyl (10a): Starting with **7** (100 mg, 0.37 mmol), Cs_2CO_3 (119 mg, 0.37 mmol), $Pd(PPh_3)_4$ (3 mol%), 4-methylphenylboronic acid (50 mg, 0.37 mmol), and 1,4-dioxane (4 mL), **10a** was isolated as a colorless solid (46 mg, 45%). Mp 68–70 °C. ^{1}H NMR (300 MHz, $CDCl_3$): δ = 6.85–6.92 (m, 2H, Ar), 7.23–67.29 (m, 4H, Ar). ^{13}C NMR (75.46 MHz, $CDCl_3$): δ = 21.3 (CH_3), 103.5 (t, *J* = 26.6 Hz, CH), 104.9 (dd, *J* = 20.1, 4.3 Hz, CH), 113.8 (dd, *J* = 22.6, 3.7 Hz, C), 128.9 (CH), 129.0 (CH), 136.3 (t, *J* = 2.8 Hz, C), 138.4 (C), 159.6 (dd, J_{CF} = 248.1, 13.2 Hz, CF), 159.9 (CH), 161.6 (dd, J_{CF} = 249.4, 13.6 Hz, CF). ^{19}F NMR (282.4 MHz, $CDCl_3$): δ = –98.94 (CF), –111.30 (CF). IR (ATR): $\tilde{\nu}$ = 3086 (w), 3028 (w), 2989 (w), 2921 (w), 2856 (w), 1914 (w), 1747 (w), 1666 (w), 1604 (w), 1584 (m), 1514 (m), 1468 (w), 1421 (m), 1398 (m), 1350 (m), 1278 (w), 1205 (w), 1183 (w), 1139 (m), 1111 (m), 1042 (w), 998 (m), 949 (w), 870 (m), 818 (s), 782 (m), 710 (m), 641 (w), 606 (m), 597 (m), 579 (m). MS (EI, 70 eV): m/z (%) = 284 (97) $[M]^+$ (^{81}Br), 283 (22), 282 (100) (^{79}Br), 201 (67), 183(53). HRMS (EI) calcd. for $C_{13}H_9{}^{79}BrF_2$ $[M]^+$: 281.98502; found 281.170318.

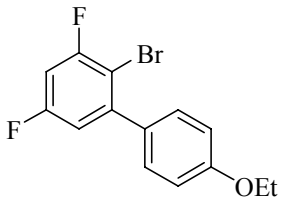


2-Bromo-3,5-difluoro-2`-methoxybiphenyl (10b): Starting with **7** (100 mg, 0.37 mmol), Cs_2CO_3 (119 mg, 0.37 mmol), $Pd(PPh_3)_4$ (3 mol%), 2-methoxyphenylboronic acid (56 mg, 0.37 mmol), and 1,4-dioxane (4 mL), **10b** was isolated as a colorless oil (65 mg, 60%). ^{1}H NMR (300 MHz, $CDCl_3$): δ = 3.68 (s, 3H, OCH_3), 6.75-6.81 (m, 1H, ArH), 6.86-6.95 (m, 2H, ArH), 7.03 (dd, *J* = 7.45, 2.00 Hz, 1H, ArH), 7.27-74 (m, 1H, ArH), 7.55-7.62 (m, 1H, ArH). ^{13}C NMR (62.89 MHz, $CDCl_3$): δ = 55.6 (OCH_3), 103.6 (t, *J* = 27.4 Hz, CH), 106.5 (q, *J* = 20.7 Hz, CH), 111.0 (C), 114.2 (dd, *J* = 3.71 Hz, C), 120.5 (CH), 128.5 (CH), 130.3 (d, *J* = 26.2 Hz, C), 132.2 (CH), 156.4 (C), 159.2 (dd, J_{CF} = 247.6, 13.4 Hz, CF), 161.3 (dd, J_{CF} = 248.3, 12.7 Hz, CF). ^{19}F NMR (282.4 MHz, $CDCl_3$): δ = –100.33 (CF), –111.80 (CF). IR (ATR): $\tilde{\nu}$ = 3090 (w), 3056 (w), 3016 (w), 2936 (w), 2835 (w), 1614 (m), 1580 (m), 1495 (m), 1434 (s), 1345 (m), 1296 (m), 1241 (s), 1196 (m), 1119 (s), 1071 (w), 1022 (s), 996 (s), 939 (w), 873 (s), 844 (s), 779 (w), 751 (s), 719 (s), 692 (s), 639 (m), 596 (s), 538 (s) cm^{-1}. MS (EI, 70 eV): *m/z* (%) = 300 (37) $[M]^+$, (^{81}Br), 298 (^{79}Br) (37), 219 (33), 205 (12), 204 (100), 188 (14), 175 (21). HRMS (EI) calcd. for $C_{13}H_9O^{79}BrF_2$ $[M]^+$: 297.97994; found 297.980349, $C_{13}H_9O^{81}BrF_2$ $[M]^+$: 299.97789; found 299.978435.



2-Bromo-3,5-difluoro-4`-methoxybiphenyl (10c): Starting with **7** (100 mg, 0.37 mmol), 

Cs_2CO_3 (263 mg, 0.81 mmol), $Pd(PPh_3)_4$ (3 mol%), 4-methoxyphenylboronic acid (56 mg, 0.37 mmol), and 1,4-dioxane (4 mL), **10c** was isolated as a colorless solid (65 mg, 60%). Mp 61–62 °C. ^{1}H NMR (300 MHz, $CDCl_3$): δ = 3.86 (s, 3H, OCH_3), 6.84-6.98 (m, 4H, ArH), 7.30-7.35 (m, 2H, ArH). ^{13}C NMR (62.89 MHz, $CDCl_3$): δ = 55.3 (OCH_3), 103.6 (t, *J* = 26.8 Hz, CH), 113.6 (2CH), 113.9 (d, *J* = 3.58 Hz, CH), 114.4 (C), 115.1 (C), 130.4 (2CH), 131.5 (t, *J* = 2.2 Hz, C), 145.3 (d, *J* = 8.3 Hz, C) 159.6 (C), 160.0 (dd, J_{CF} = 238.0, 13.4 Hz, CF), 161.4 (dd, J_{CF} = 248.3, 12.7 Hz, CF). ^{19}F NMR (282.4 MHz, $CDCl_3$): δ = –98.86 (CF), –111.35 (CF). IR (ATR): $\tilde{\nu}$ = 3094 (w), 3013 (w), 2964 (w), 2914 (w), 2836 (w), 1889 (w), 1604 (s), 1588 (s), 1514 (s), 1496 (m), 1445 (m), 1377 (m), 1292 (m), 1244 (s), 1205 (m), 1183 (s), 1140 (m), 1071 (w), 1029 (m), 998 (s), 937 (w), 870 (s), 833 (s), 799 (m), 753 (m), 708 (w), 679 (m), 641 (m), 600 (s), 569 (s) cm^{-1}. MS (EI, 70 eV): *m/z* (%) = 300 (100) $[M]^+$ (^{81}Br), 299 (14), 298 (98) (^{79}Br), 285 (12), 283 (12), 257 (18), 255 (18), 188 (11), 176 (32), 175 (39). HRMS (EI) calcd. for $C_{13}H_9O^{79}BrF_2$ $[M]^+$: 297.97994; found 297.979859 $C_{13}H_9O^{81}BrF_2$ $[M]^+$: 299.97789; found 299.977797.

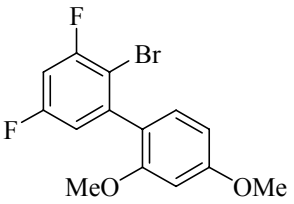
2-Bromo-3,5-difluoro-4`-ethoxybiphenyl (10d): Starting with **7** (100 mg, 0.37 mmol), 

Cs_2CO_3 (119 mg, 0.37 mmol), $Pd(PPh_3)_4$ (3 mol%), 4-ethoxyphenylboronic acid (61 mg, 0.37 mmol), and 1,4-dioxane (4 mL), **10d** was isolated as a colorless solid (74 mg, 65%). Mp 111–113 °C. ^{1}H NMR (300 MHz, $CDCl_3$): δ = 1.44 (t, *J* = 6.95 Hz, 3H, CH_3), 4.07 (q, *J* = 6.95, 3H, OCH_3), 3.55 (s, 3H, OCH_3), 6.83–6.97 (m, 3H, ArH), 7.28–7.34 (m, 3H, ArH). ^{13}C NMR (62.89 MHz, $CDCl_3$): δ = 14.8 (CH_3), 63.5 (OCH_2), 103.2 (t, *J* = 27.0 Hz, CH), 113.5 (d, *J* = 4.0 Hz, CH), 113.7 (dd, *J* = 22.2, 3.4 Hz, C), 114.1 (2CH), 128.4 (d, *J* = 6.9 Hz,CH), 128.7 (CH), 130.4 (CH), 133.7 (CH), 141.3 (d, *J* = 9.4 Hz, C), 159.0 (C), 159.3 (dd, J_{CF} = 247.9, 13.3 Hz, CF), 161.3 (dd, J_{CF} = 249.5, 13.3 Hz, CF). ^{19}F NMR (282.4 MHz, $CDCl_3$): δ = –101.8 (CF), –112.5 (CF). IR (ATR): $\tilde{\nu}$ = 3067 (w), 2956 (w), 2926 (w), 2835 (w), 1616 (w), 1596 (w), 1503 (w), 1494 (w), 1455 (w), 1421 (w), 1338 (w), 1287 (w), 1247 (m), 1201 (w), 1180 (w), 1120 (w), 1089 (w), 1024 (m), 928 (w), 877 (w), 865 (w), 800 (w), 755 (w), 744 (m), 701 (w), 635 (w), 586 (m), 537 (w) cm^{-1}. MS (EI, 70 eV): m/z (%) = 312 (61) (^{79}Br) $[M]^+$, 287 (12), 286 (98), 284 (100), 204(10). HRMS (EI) calcd. for $C_{14}H_{11}O^{81}BrF_2$ $[M]^+$: 313.99354; found 313.993486

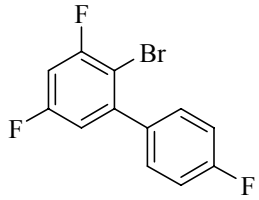
2-Bromo-3,5-difluoro-3`,4`-dimethoxybiphenyl (10e): Starting with **7** (100 mg, 0.37 mmol), Cs_2CO_3 (119 mg, 0.37 mmol), $Pd(PPh_3)_4$ (3 mol%), 3,4-dimethoxyphenylboronic acid (67 mg, 0.37 mmol), and 1,4-dioxane (4 mL), **10e** was isolated as a colorless solid (72 mg, 60%). Mp 110–112 °C. ^{1}H NMR (300 MHz, $CDCl_3$): δ = 3.84 (s, 3H, OCH_3), 3.87 (s, 3H, OCH_3), 6.78–6.88 (m, 5H, ArH). ^{13}C NMR (75.46 MHz, $CDCl_3$): δ = 55.9 (OCH_3), 56.0 (OCH_3), 103.4 (t, *J* = 27.2 Hz, CH), 110.7 (CH), 112.5 (CH), 113.8 (dd, *J* = 22.7, 3.41 Hz, CH), 121.7 (CH), 131.1 (C), 148.4 (C), 149.1 (C), 158.2 (C), 158.4 (C), 159.22 (dd, *J* = 248.0, 13.7 Hz, CF), 161.3 (dd, *J* = 248.6, 13.2 Hz, CF). ^{19}F NMR (282.4 MHz, $CDCl_3$): δ = –98.7 (CF), –111.6 (CF). IR (ATR): $\tilde{\nu}$ = 3062 (w), 3016 (w), 2961 (w), 2848 (w), 1607 (w), 1579 (w), 1518 (w), 1468 (w), 1437 (w), 1398 (w), 1323 (w), 1283 (w), 1235 (w), 1188 (w), 1137 (w), 1108 (w), 1044 (w), 999 (w), 911 (w), 865 (w), 828 (w), 790 (w), 730 (w), 666 (w), 628 (w), 597 (w), 556 (w). MS (EI, 70 eV): m/z (%) = 330 (^{81}Br) (97) $[M]^+$, 329 (15), 328 (^{79}Br) (100), 287 (16), 206(62), 191 (12), 188 (19). HRMS (EI) calcd. for $C_{14}H_{11}O_2{}^{81}BrF_2$ $[M]^+$: 329.98845; found 329.988725.

2-Bromo-3,5-difluoro-2',6'-dimethoxybiphenyl (10f): Starting with **7** (100 mg, 0.37 mmol), Cs_2CO_3 (263 mg, 0.81 mmol), $Pd(PPh_3)_4$ (3 mol%), 2,6-dimethoxyphenylboronic acid (67 mg, 0.37 mmol) and 1,4-dioxane (4 mL), **10f** was isolated as a colorless solid (82 mg, 68%). Mp 121-123 °C. ^{1}H NMR (300 MHz, $CDCl_3$): δ =3.76 (s, 6H, OCH_3), 6.66 (d, *J* = 8.4 Hz, 2H, CH), 6.81-6.89 (m, 2H, CH), 7.41 (t, *J* = 9.0, 1H, ArH). ^{13}C NMR (75 MHz, $CDCl_3$): δ = 55.9 ($2OCH_3$), 103.0 (C), 103.4 (t, *J* = 26.6 Hz, CH), 103.9 (2CH), 114.0 (C), 114.8 (d, *J* = 4.5 Hz, CH), 130.1 (CH), 138.2 (C), 157.2 (2C), 157.4 (dd, J_{CF} = 247.0 Hz, 12.9 Hz, CF), 160.3 (dd, J_{CF} = 247.6 Hz, 12.1 Hz, CF). ^{19}F NMR (282 MHz, $CDCl_3$): δ = –101.15 (CF), –112.73 (CF). IR (ATR, cm^{-1}): $\tilde{\nu}$ = 3086 (w), 3017 (w), 2959 (m), 2838 (w), 1590(s), 1472 (s), 1416 (m), 1110 (s), 867 (s), 778 (s), 724 (s), 599 (s). GC-MS (EI, 70 eV): *m/z* (%) = 328 $[M]^+$, (37), 249 (11), 234 (100), 219 (16), 191 (16), 175 (12), 163 (6). ESI-HRMS calcd. for $C_{14}H_{12}BrF_2O_2$ $[M+H]^+$: 328.9983; found 328.9983.

2-Bromo-3,5-difluoro-2`,4`-dimethoxybiphenyl (10g): Starting with **1** (100 mg, 0.37 mmol), Cs_2CO_3 (119 mg, 0.37 mmol), $Pd(PPh_3)_4$ (3 mol%), 2,4-dimethoxyphenylboronic acid (67 mg, 0.37 mmol), and 1,4-dioxane (4 mL), **10g** was isolated as a colorless solid (81 mg, 67%). Mp 64–66 °C. ^{1}H NMR (300 MHz, $CDCl_3$): δ = 3.75 (s, 3H, OCH_3), 3.89 (s, 3 H, OCH_3), 6.53–6.57 (m, 2H, Ar), 6.82–6.88 (m, 2H, Ar), 7.04 (d, *J* = 8.9 Hz, 1H, Ar). ^{13}C NMR (75.46 MHz, $CDCl_3$): δ = 55.4 (OCH_3), 55.6 (OCH_3), 98.7 (CH), 103.4 (t, *J* = 26.6 Hz, CH), 104 (CH), 106.9 (dd, *J* = 20.4, 4.0 Hz, C), 114.5 (dd, *J* = 22.3, 3.3 Hz, CH), 121.0 (t, *J* = 2.2, C), 131.1 (CH), 142.9 (d, *J* = 9.8 Hz, C), 157.4 (C), 159.22 (dd, J_{CF} = 248.0, 13.7 Hz, CF), 161.3 (dd, J_{CF} = 248.6, 13.2 Hz, CF) 161.4 (C). ^{19}F NMR (282.4 MHz, $CDCl_3$): δ = –100.5 (CF), –112.4 (CF). IR (ATR): $\tilde{\nu}$ = 3079 (w), 3002 (w), 2958 (w), 2937 (w), 2836 (w), 1692 (s), 1785 (s), 1509 (s), 1463 (m), 1447 (m), 1468 (w), 1435 (s), 1345 (w), 1304 (s), 1281 (m), 1256 (m), 1206 (s), 1146 (m), 1127 (s), 1101 (s), 1031 (s), 997 (s), 924 (m), 833 (s), 796 (m), 716 (w), 637 (w), 599 (s), 587 (m) cm^{-1}. MS (EI, 70 eV): *m/z* (%) = 330 (^{81}Br) (95) $[M]^+$, 328 (^{81}Br) (93), 329 (15), 331 (14), 235 (15), 234 (100), 219 (35), 204(12), 191 (20), 175 (26), 163 (13). ESI-HRMS calcd. for $C_{14}H_{12}{}^{79}BrF_2O_2$ $[M+H]^+$: 328.9983; found 328.9979.



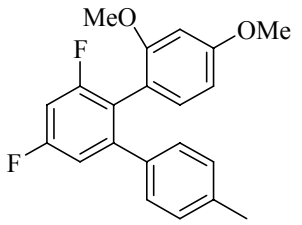
2-Bromo-3,5-difluoro-4-fluorobiphenyl (10h): Starting with **7** (100 mg, 0.37 mmol), Cs_2CO_3 (263 mg, 0.81 mmol), $Pd(PPh_3)_4$ (3 mol%), 4-fluorophenylboronic acid (52 mg, 0.37 mmol) and 1,4-dioxane (4 mL), **10h** was isolated as a colorless solid (66 mg, 63%). Mp 146-148 °C. ^{1}H NMR (300 MHz, $CDCl_3$): δ = 6.74-6.80 (m, 2H, CH), 6.96-7.12 (m, 2H, CH), 7.20-7.26 (m, 2H, CH). ^{13}C NMR (75 MHz, $CDCl_3$): δ = 103.8 (t, *J* = 27.0 Hz, CH), 104.9 (d, *J* = 25.0 Hz, CBr), 103.4 (CH), 113.6 (dd, *J* = 19.5 Hz, *J* = 3.0, CH), 115.2 (CH), 130.9 (CH), 131.04 (CH), 135.1 (C), 144.6 (C), 157.9 (dd, $^1J_{CF}$ = 248.0 Hz, $^3J_{CF}$ =12.9 Hz, CF), 161.3 (dd, $^1J_{CF}$ = 248.6 Hz, $^3J_{CF}$ = 12.8 Hz, CF), 161.1 (d, $^1J_{CF}$= 245.0 Hz, CF).^{19}F NMR (282 MHz, $CDCl_3$): δ = -98.53 (CF), -110.91 (CF), -112.80 (CF). IR (ATR, cm^{-1}): $\tilde{\nu}$ = 3340 (w), 2921 (w), 2852 (w), 1904 (w), 1711 (w), 1470 (w), 1455 (w), 1388 (w), 1087 (s), 1002 (s), 811 (s), 701 (m), 625 (w), 544 (m). GC-MS (EI, 70 eV): *m/z* (%) = 286 (100) (^{81}Br) $[M]^+$, 207 (23), 206 (77), 188 (11), 187 (20), 186 (13), 103 (11), 93 (5). HRMS (EI, 70 eV) calcd. for $C_{12}H_6BrF_3$ $[M]^+$: 285.95995; found 285.959530 and calcd for $C_{12}H_6{}^{81}BrF_3$ $[M]^+$: 287.95790; found 287.957528.



General Procedure for the Synthesis of 11a–g

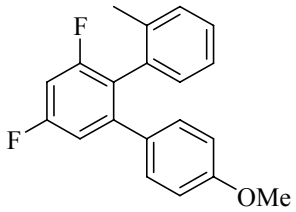
The reaction was carried out in a pressure tube. To a dioxane suspension (4 mL) of **7** (200 mg, 0.74 mmol), Pd(PPh3)4 (3 mol%), and $Ar^1B(OH)_2$ (0.74 mmol) was added Cs_2CO_3 (359 mg, 1.11 mmol), and the resultant solution was degassed by bubbling argon through the solution for 10 min. The mixture was heated at 90 °C under Argon atmosphere for 8 h. The mixture was cooled to 20 °C and $Ar^2B(OH)_2$ (0.89 mmol) and Cs_2CO_3 (359 mg, 1.11 mmol) was added. The reaction mixtures were heated under Argon atmosphere for 6 h at 100 °C. They were diluted with H_2O and extracted with CH_2Cl_2 (3 × 50 mL). The combined organic layers were dried (Na_2SO_4), filtered, and the filtrate was concentrated in vacuo. The residue was purified by flash chromatography (silica gel, EtOAc: hexane = 1:4).

1-(4´-Methylphenyl)-2-(2´´,4´´-dimethoyphenyl)-3,5-difluorobenzene (11a): Starting with

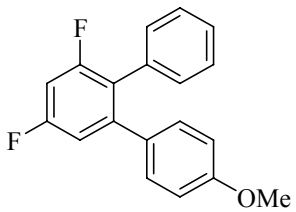


7 (200 mg, 0.74 mmol), Cs_2CO_3 (359 mg, 1.11 mmol), $Pd(PPh_3)_4$ (3 mol%), 4-methylboronic acid (100 mg, 0.74 mmol), 2,4-dimethoxyphenylboronic (161 mg, 0.88 mmol), 1,4-dioxane (4 mL), and **11a** was isolated as a colorless highly viscous oil (140 mg, 56%). ^{1}H NMR (300 MHz, $CDCl_3$): δ = 2.19 (s, 3H, CH_3), 3.32 (s, 3H, OCH_3), 3.69 (s, 3H, OCH_3), 6.17 (d, *J* = 2.3 Hz, 1H, Ar), 6.32 (dd, *J* = 8.3, 2.3 Hz, 1 H, Ar), 6.74–6.83 (m, 2H, Ar), 6.86–6.91 (m, 5H, Ar). ^{13}C NMR (62.89 MHz, $CDCl_3$): δ = 21.2 (CH_3), 55.0 (OCH_3), 55.3 (OCH_3), 98.4 (CH), 102.5 (t, *J* = 26.3 Hz, CH), 104.1 (CH), 113.6 (dd, *J* = 21.9, 3.6 Hz, CH), 121.5 (t, *J* = 2.8 Hz, C), 125.7 (dd, *J* = 15.3, 3.6 Hz, C), 128.1 (2CH), 130.0 (2CH), 131.1 (C), 131.6 (CH), 136.4 (C), 141.2 (dd, *J* = 9.6, 4.5 Hz, C), 157.0 (C), 159.8 (dd, J_{CF} = 246.8, 13.0 Hz, CF), 160.6 (C), 161.1 (dd, J_{CF} = 247.1, 13.4 Hz, C). ^{19}F NMR (282.4 MHz, $CDCl_3$): δ = –111.86 (CF), –112.9 (CF). IR (ATR): $\tilde{\nu}$ = 3080 (w), 2998 (w), 2956 (w), 2836 (w), 1736 (w), 1609 (s), 1586 (s), 1508 (s), 1454 (s), 1425 (m), 1401 (m), 1372 (w), 1303 (s), 1255 (m), 1184 (w), 1158 (s), 1145 (s), 1092 (s), 1032 (s), 996 (s), 925 (m), 861 (w), 834 (m), 818 (s)796 (m), 736 (w), 718 (w), 663 (w), 607 (w), 587 (m) cm^{-1}. MS (EI, 70 eV): *m/z* (%) = 340 (100) $[M]^+$, 294 (11), 265 (13), 238 (12). ESI-HRMS calcd. for $C_{21}H_{19}F_2O_2$ $[M+H]^+$: 341.1348; found 341.1348.

1-(4`-Methoxyphenyl)-2-(2´´-methylphenyl)-3,5-difluorobenzene (11b): Starting with **7** (200 mg, 0.74 mmol), Cs_2CO_3 (359 mg, 1.11 mmol), $Pd(PPh_3)_4$ (3 mol%), 4-methoxyphenylboronic (112 mg, 0.74 mmol), 1,4-dioxane (4 mL), and 2-methylphenylboronic acid (121 mg, 0.89 mmol), **11b** was isolated as a colorless oil (155 mg, 68%). ^{1}H NMR (300 MHz, $CDCl_3$): δ = 2.14 (s, 3H, CH_3), 3.32 (s, 3H, OCH_3), 6.72-6.88 (m, 6H, ArH), 6.93-6.97 (m, 1H, ArH), 7.06–7.23 (m, 2H, ArH), 7.23–7.37 (m, 1H, ArH). ^{13}C NMR (62.89 MHz, $CDCl_3$): δ = 21.2 (CH_3), 55.0 (OCH_3), 102.8 (CH), 110.7 (t, J = 26.3 Hz, CH), 115.0 (CH), 120.3 (CH), 128.0 (CH), 128.1 (CH), 129.2 (CH), 130.10 (CH), 131.2 (C), 133.6 (C), 156.0 (C), 157.7 (C), 159.2 (C), 159.6 (d, J = 13.8 Hz, C), 159.9 (dd, J_{CF} = 248.0, 13.0 Hz, CF), 161.1 (dd, J_{CF} = 247.0, 13.4 Hz, C). ^{19}F NMR (282.4 MHz, $CDCl_3$): δ = –111.86 (CF), –112.9 (CF). IR (ATR): $\tilde{\nu}$ = 3082 (w), 3053 (w), 3008 (w), 2978 (w), 2928 (w), 2835 (w), 1600 (m), 1558 (w), 1495 (m), 1445 (m), 1394 (m), 1333 (m), 1283 (m), 1241 (s), 1201 (m), 1159 (m), 1091 (m), 1025 (m), 995 (m), 937 (m), 893 (w), 837 (m), 803 (m), 782 (m), 742 (m), 700 (m), 640 (m), 573 (m), 541 (m), 530 (m). MS (EI, 70 eV): m/z (%) = 310 (100) $[M]^+$, 295 (24), 279 (29), 264 (27), 262(10). HRMS (EI) calcd. for $C_{20}H_{16}OF_2$ $[M]^+$: 310.11637; found 310.115566

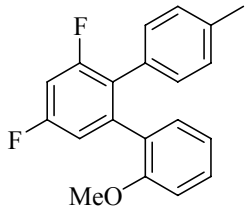


1-(4`-Methoxyphenyl)-2-phenyl-3,5-difluorobenzene (11c): Starting with **7** (200 mg, 0.74 mmol), Cs_2CO_3 (359 mg, 1.11 mmol), $Pd(PPh_3)_4$ (3 mol%), 4-methoxyphenylboronic (112 mg, 0.74 mmol), 1,4-dioxane (4 mL), and phenylboronic acid (107 mg, 0.89 mmol), **11c** was isolated as a colorless oil (152 mg, 70%). ^{1}H NMR (300 MHz, $CDCl_3$): δ = 3.68 (s, 3H, OCH_3), 6.64 (dt, J = 9.13 Hz, 2H, ArH), 6.76-6.83 (m, 1H, ArH), 6.88-6.94 (m, 3H, ArH), 6.97–7.04 (m, 2H, ArH), 7.11–7.18 (m, 3H, ArH). ^{13}C NMR (62.89 MHz, $CDCl_3$): δ = 55.2 (OCH_3), 102.4 (d, J = 27.5 Hz, CH), 112.7 (d, J = 3.72 Hz, C), 112.9 (d, J = 3.72 Hz, C), 113.4 (CH), 124.2 (d, J = 3.50 Hz, C), 124.4 (d, J = 3.50 Hz, CH), 125.6 (C), 127.2 (CH), 129.6 (CH), 130.7 (CH), 130.9 (CH), 131.7 (t, J = 2.74 Hz, C), 132.0 (C), 133.7 (C), 144.0 (d, J = 4.73 Hz, C), 144.1 (d, J = 4.73 Hz, C), 158.8 (C), 160.1 (dd, J_{CF} = 247.2, 12.6 Hz, CF), 161.6 (dd, J_{CF} = 248.4, 13.4 Hz, C). ^{19}F NMR (282.4 MHz, $CDCl_3$): δ = –110.40 (CF), –111.44 (CF). IR (ATR): $\tilde{\nu}$ = 3061 (w), 3032 (w), 3000 (w), 2956 (w), 2929 (w), 2836 (w), 2541 (w), 1885 (w),1725 (w), 1608 (s), 1588 (s), 1514 (s), 1461 (m), 1405 (m), 1335 (m), 1291 (m), 1245 (s), 1204 (m), 1176 (s), 1139 (s), 1100 (s), 1072 (m), 1034 (m), 998 (s), 915 (w), 873 (m), 829 (s), 773 (s), 746 (m), 711 (m), 698 (s), 647 (w), 610 (w), 586 (s),

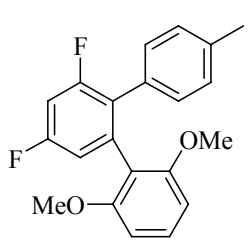


556 (s), 543 (m). MS (EI, 70 eV): m/z (%) = 296 (100) $[M]^+$, 295 (19), 265 (16), 264 (11), 263(10), 238 (15), 233 (16). HRMS (EI) calcd. for $C_{19}H_{14}OF_2$ $[M]^+$: 296.10072; found 296.099982.

1-(2`-Methoxyphenyl)-2-(4´´-methylphenyl)-3,5-difluorobenzene (11d): Starting with **7** (200 mg, 0.74 mmol), Cs_2CO_3 (359 mg, 1.11 mmol), $Pd(PPh_3)_4$ (3 mol%), 2-methylphenylboronic (100 mg, 0.74 mmol), 1,4-dioxane (4 mL), and 4-methylphenylboronic acid (123 mg, 0.89 mmol), **11d** was isolated as a colorless solid (142 mg, 62%). Mp 67-69 °C. ^{1}H NMR (300 MHz, $CDCl_3$): δ = 2.14 (s, 3H, CH_3), 3.32 (s, 3H, OCH_3), 6.72-6.88 (m, 6H, ArH), 6.93-6.97 (m, 1H, ArH), 7.06–7.23 (m, 2H, ArH), 7.23–7.37 (m, 1H, ArH). ^{13}C NMR (62.89 MHz, $CDCl_3$): δ = 21.2 (CH_3), 55.0 (OCH_3), 102.8 (CH), 110.7 (t, J = 26.3 Hz, CH), 115.0 (CH), 120.3 (CH), 128.0 (CH), 128.1 (CH), 129.2 (CH), 130.10 (CH), 131.2 (C), 133.6 (C), 156.0 (C), 157.7 (C), 159.2 (C), 159.6 (d, J = 13.8 Hz, C), 159.9 (dd, J_{CF} = 248.0, 13.0 Hz, CF), 161.1 (dd, J_{CF} = 247.0, 13.4 Hz, C). ^{19}F NMR (282.4 MHz, $CDCl_3$): δ = –111.86 (CF), –112.9 (CF). IR (ATR): $\tilde{\nu}$ = 3082 (w), 3053 (w), 3008 (w), 2978 (w), 2928 (w), 2835 (w), 1600 (m), 1558 (w), 1495 (m), 1445 (m), 1394 (m), 1333 (m), 1283 (m), 1241 (s), 1201 (m), 1159 (m), 1091 (m), 1025 (m), 995 (m), 937 (m), 893 (w), 837 (m), 803 (m), 782 (m), 742 (m), 700 (m), 640 (m), 573 (m), 541 (m), 530 (m). MS (EI, 70 eV): m/z (%) = 310 (100) $[M]^+$, 295 (24), 279 (29), 264 (27), 262(10). HRMS (EI) calcd. for $C_{20}H_{16}OF_2$ $[M]^+$: 310.11637; found 310.115566.

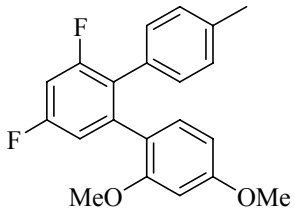


1-(2´,6´-Dimethoxyphenyl)-2-(4´´-methylphenyl)-3,5-difluorobenzene (11e): Starting with **7** (200 mg, 0.74 mmol), Cs_2CO_3 (359 mg, 1.11 mmol), $Pd(PPh_3)_4$ (3 mol%), 2,6-dimethoxyphenylboronic (134 mg, 0.74 mmol), 1,4-dioxane (4 mL), and 4-methylboronic acid (121 mg, 0.89 mmol), **11e** was isolated as a colorless highly viscous oil (150 mg, 60%). ^{1}H NMR (300 MHz, $CDCl_3$): δ = 2.19 (s, 3H, CH_3), 3.32 (s, 3H, OCH_3), 3.69 (s, 3H, OCH_3), 6.17 (d, J = 2.64 Hz, 1H, Ar), 6.34 (dd, J = 8.4, 2.9 Hz, 1 H, Ar), 6.74–6.93 (m, 7H, Ar). ^{13}C NMR (62.89 MHz, $CDCl_3$): δ = 21.2 (CH_3), 55.0 (OCH_3), 55.3 (OCH_3), 98.4 (CH), 102.6 (t, J = 27.3 Hz, CH), 104.1 (CH), 113.6 (dd, J = 20.8, 3.7 Hz, CH), 121.5 (q, J = 3.71 Hz, C), 125.7 (dd, J = 15.3, 4.0 Hz, C), 128.2 (2CH), 128.6 (d, J = 19.8 Hz C), 130.1 (CH), 131.1 (CH), 136.4 (C), 141.2 (dd, J = 9.6, 4.5 Hz, C), 157.0 (C), 159.8 (dd, J_{CF} = 248.3, 13.2 Hz, CF), 161.1 (dd, J_{CF} = 248.3, 13.2 Hz, CF). ^{19}F NMR (282.4 MHz, $CDCl_3$): δ = –111.52



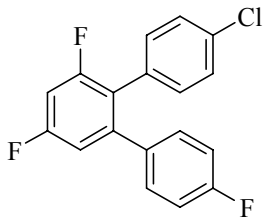
(CF), –112.49 (CF). IR (ATR): $\tilde{\nu}$ = 3081 (w), 3054 (w) 2999 (w), 2956 (w), 2835 (w), 1609 (s), 1586 (s), 1508 (s), 1454 (s), 1436 (m), 1425 (m), 1401 (m), 1335 (w), 1303 (s), 1265 (m), 1207 (s), 1184 (w), 1158 (s), 1145 (s), 1092 (s), 1031 (s), 996 (s), 936 (m), 861 (m), 834 (m), 818 (s), 796 (s), 733 (m), 663 (m), 608 (m), 587 (m), 530 (m) cm^{-1}. MS (EI, 70 eV): *m/z* (%) = 340 (100) $[M]^+$, 294 (11), 265 (14), 238 (11). HRMS(EI) calcd. for $C_{21}H_{19}F_2O_2$ $[M]^+$: 340.12694; found 340.126828.

1-(2´,4´-Dimethoxyphenyl)-2-(4´´-methylphenyl)-3,5-difluorobenzene (11f): Starting with



7 (200 mg, 0.74 mmol), Cs_2CO_3 (359 mg, 1.11 mmol), $Pd(PPh_3)_4$ (3 mol%), 2,4-dimethoxyphenylboronic (134 mg, 0.74 mmol), 1,4-dioxane (4 mL), and 4-methylboronic acid (121 mg, 0.89 mmol), **11f** was isolated as a colorless highly viscous oil (121 mg, 48%). ^{1}H NMR (300 MHz, $CDCl_3$): δ = 2.19 (s, 3H, CH_3), 3.32 (s, 3H, OCH_3), 3.69 (s, 3H, OCH_3), 6.17 (d, *J* = 2.3 Hz, 1H, Ar), 6.32 (dd, *J* = 8.3, 2.3 Hz, 1 H, Ar), 6.74–6.83 (m, 2H, Ar), 6.86–6.91 (m, 5H, Ar). ^{13}C NMR (62.89 MHz, $CDCl_3$): δ = 21.2 (CH_3), 55.0 (OCH_3), 55.3 (OCH_3), 98.4 (CH), 102.5 (t, *J* = 26.3 Hz, CH), 104.1 (CH), 113.6 (dd, *J* = 21.9, 3.6 Hz, CH), 121.5 (t, *J* = 2.8 Hz, C), 125.7 (dd, *J* = 15.3, 3.6 Hz, C), 128.1 (2CH), 130.0 (2CH), 131.1 (C), 131.6 (CH), 136.4 (C), 141.2 (dd, *J* = 9.6, 4.5 Hz, C), 157.0 (C), 159.8 (dd, J_{CF} = 246.8, 13.0 Hz, CF), 160.6 (C), 161.1 (dd, J_{CF} = 247.1, 13.4 Hz, C). ^{19}F NMR (282.4 MHz, $CDCl_3$): δ = –111.86 (CF), –112.9 (CF). IR (ATR): $\tilde{\nu}$ = 3080 (w), 2998 (w), 2956 (w), 2836 (w), 1736 (w), 1609 (s), 1586 (s), 1508 (s), 1454 (s), 1425 (m), 1401 (m), 1372 (w), 1303 (s), 1255 (m), 1184 (w), 1158 (s), 1145 (s), 1092 (s), 1032 (s), 996 (s), 925 (m), 861 (w), 834 (m), 818 (s), 796 (m), 736 (w), 718 (w), 663 (w), 607 (w), 587 (m) cm^{-1}. MS (EI, 70 eV): *m/z* (%) = 340 (100) $[M]^+$, 294 (11), 265 (13), 238 (12). ESI-HRMS calcd. for $C_{21}H_{19}F_2O_2$ $[M+H]^+$: 341.1348; found 341.1348

1-(4´-Fluorophenyl)-2-(4´´-chlorophenyl)-3,5-difluorobenzene (11g): Starting with **1** (200

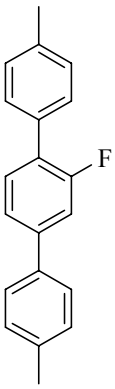


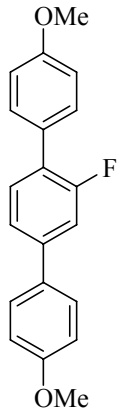
mg, 0.74 mmol), Cs_2CO_3 (359 mg, 1.11 mmol), $Pd(PPh_3)_4$ (3 mol%), 4-fluorophenylboronic (103 mg, 0.74 mmol), 1,4-dioxane (4 mL), and 4-chlorophenylboronic acid (138 mg, 0.89 mmol), **11g** was isolated as colorless highly viscous oil (106 mg, 45%) ^{1}H NMR (300 MHz, $CDCl_3$): δ = 6.93-7.13 (m, 8H, ArH), 7.23-7.32 (m, 2H, ArH). ^{13}C NMR (75 MHz, $CDCl_3$): δ = 102.8 (t, J_{CF} = 3.5 Hz, CH), 103.2 (t, J_{CF} = 3.5 Hz, CH), 103.6 (t, J_{CF} = 3.51 Hz, CH), 112.6 (dd, J_{CF} = 20.4, 4.2 Hz, CH), 115.3 (dd, J_{CF} = 20.7, 4.9 Hz, CH),

123.4 (t, J_{CF} = 2.8 Hz, CH), 128.5 (m, CH), 130.9 (CH), 131.2 (CH), 132.3 (C), 135.9 (dd, J_{CF}= 238.1, 14.6 Hz, CF), 143.4 (C), 160.1 (dd, $^{1}J_{CF}$ = 245.1, 14.6 Hz, CF), 161.9 (dd, $^{1}J_{CF}$ = 251.2, 13.6 Hz, CF).^{19}F NMR (282 MHz, $CDCl_3$): δ = –110.46 (CF), –110.99 (CF), –114.19 (CF). IR (ATR, cm^{-1}): $\tilde{\nu}$ = 3086 (w), 3052 (w), 1896 (w), 1606 (m), 1582 (s), 1511 (s), 1457 (s), 1392 (m), 1336 (m), 1298 (w), 1222 (s), 1159 (m), 1119 (m), 1091 (s), 1015 (m), 960 (w), 901 (w), 872 (m), 827 (s), 758 (m), 712 (w), 645 (w), 595 (m), 576 (s), 532 (m). MS (EI, 70 eV): *m/z* (%) = 318 (100) $[M]^+$, 284 (11), 283 (66), 282 (54), 280 (18), 264 (12), 263 (53). HRMS (EI) calcd for $C_{18}H_{10}ClF_3$ $[M]^+$: 318.04176; found 318.041545.

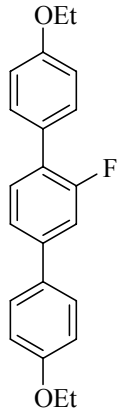
General procedure for Suzuki–Miyaura reactions(13a-k, 14a-h): A 1,4-dioxane solution (4 mL per 0.3 mmol of **12**) of **12**, Cs_2CO_3, $Pd(PPh_3)_4$ and arylboronic acid **8** were stirred at 90 °C for 6 or 8 h. After cooling to room temperature, the organic and the aqueous layers were separated and 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.

1,4-Di(4´-methylphenyl)-2-fluorobenzene (13a): Starting with **12** (100 mg, 0.39 mmol), Cs_2CO_3 (190 mg, 0.50 mmol), $Pd(PPh_3)_4$ (3 mol%), 4-methylphenylboronic acid (106 mg, 0.78 mmol) and 1,4-dioxane (4 mL), **13a** was isolated as a colorless solid (65 mg, 60%). Mp 178-180 °C. ^{1}H NMR (300 MHz, $CDCl_3$): δ = 2.33 (s, 6H, CH_3), 7.15-7.18 (m, 4H, CH), 7.20-7.31 (m, 3H, CH), 7.31-7.35 (m, 4H, CH). ^{13}C NMR (75 MHz, $CDCl_3$): δ = 21.2, 21.3 (CH_3), 114.4 (d, *J* = 24.0 Hz, CH), 122.7 (d, *J* = 12.0 Hz, CH), 126.8, 126.8 (CH), 127.4 (d, *J* = 13.5 Hz, C), 128.8, 128.9 (CH), 129.3 (CH), 129.7 (CH), 130.9 (d, *J* = 4.5 Hz, CH), 132.7 (C), 136.7 (C), 137.6, 137.6 (C), 137.8, 137.8 (C), 142.0 (d, *J* = 7.5 Hz, C), 160.1 (d, $^{1}J_{CF}$ = 246.0 Hz, CF). ^{19}F NMR (282 MHz, $CDCl_3$): δ = -115.21. IR (ATR, cm^{-1}): $\tilde{\nu}$ = 2916 (w), 1912 (w), 1614 (w), 1570 (w), 1545 (w), 1484 (w), 1392 (w), 1118 (M), 1133 (m), 1041 (m), 1005 (w), 948 (w), 890 (w), 844 (w), 807 (w), 731 (w), 646 (w), 557 (m), 496 (w), 455 (w). GC-MS (EI, 70 eV): *m/z* (%) = 276 (100) $[M]^+$, 275 (13), 239 (5), 183 (7), 137 (4). HRMS (EI, 70 eV) calcd. for $C_{20}H_{17}F$ $[M]^+$: 276.13008; found 276.130318.



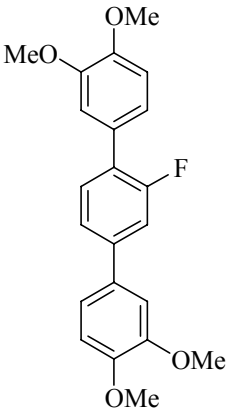
1,4-Di(4´-methoxyphenyl)-2-fluorobenzene (13b): Starting with **12** (100 mg, 0.39 mmol), 

Cs_2CO_3 (190 mg, 0.50 mmol), $Pd(PPh_3)_4$ (3 mol%), 4-methoxyphenylboronic acid (106 mg, 0.78 mmol) and 1,4-dioxane (4 mL), **13b** was isolated as a light yellow solid (42 mg, 52%). Mp 182-184 °C. ^{1}H NMR (300 MHz, $CDCl_3$): δ = 3.79 (s, 6H, OCH_3), 6.91-6.94 (m, 4H, CH), 7.19-7.29 (m, 3H, CH), 7.36-7.46 (m, 4H, CH). ^{13}C NMR (75 MHz, $CDCl_3$): δ = 55.4, 55.4 (OCH_3), 114.0, 114.0 (CH), 114.3, 114.3 (CH) 114.4 (d, J = 20.0 Hz, CH), 122.4 (d, J = 3.0 Hz, CH), 128.2, 128.2 (CH), 130.1 (d, J = 3.0, 2C, CH), 130.7 (d, J = 4.5 Hz, CH), 130.9, 130.9 (C), 132.1, 132.1 (C), 142.0 (d, J = 7.5 Hz, C), 158.6 (d, $^1J_{CF}$ = 248.0 Hz, CF), 159.2, 159.6 (C). ^{19}F NMR (282 MHz, $CDCl_3$): δ = -114.88. IR (ATR, cm^{-1}): $\tilde{\nu}$ = 3035 (w), 3016 (w), 2960 (w), 2933 (w), 2909 (w), 2836 (w),1605 (s), 1578 (m), 1476 (m), 1391 (m), 1292 (m), 1030 (m), 871 (m), 807 (s), 6963 (w), 578 (m), 522 (m), 456 (m). GC-MS (EI, 70 eV); *m/z* (%) = 308 (100) $[M]^+$, 293 (40), 265 (11), 222 (10), 154 (7), 133 (5). HRMS (EI) calcd. for $C_{20}H_{17}FO_2$ $[M]^+$: 308.12071; found 308.120220.

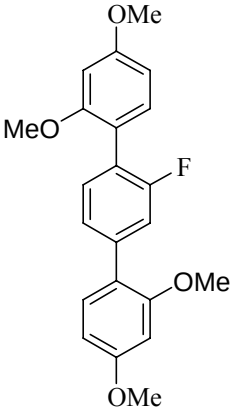
1,4-Di(4`-ethoxyphenyl)-2-fluorobenzene (13c): Starting with **12** (100 mg, 0.39 mmol), 

Cs_2CO_3 (190 mg, 0.50 mmol), $Pd(PPh_3)_4$ (3 mol%), 4-ethoxyphenylboronic acid (64 mg, 0.39 mmol) and 1,4-dioxane (4 mL), **13c** was isolated as a colorless solid (86 mg, 65%). Mp 96-98 °C. ^{1}H NMR (300 MHz, $CDCl_3$): δ = 1.39 (t, J = 7.2 Hz, 6H, CH_3), 3.99 (q, J = 6.89 Hz, 4H, OCH_2), 6.85-6.91 (m, 4H, CH), 7.21-7.28 (m, 3H, CH), 7.36-7.50 (m, 4H, CH). ^{13}C NMR (75 MHz, $CDCl_3$): δ = 14.9 ($2CH_3$), 63.6 ($2OCH_2$), 106.8 (d, J = 22.0 Hz, C), 114.5 (d, J = 16.5 Hz, CH), 114.7 (CH), 115.0 (CH), 123.4 (d, J = 3.8 Hz, CH), 127.7 (CH), 128.0 (CH), 131.3 (C), 133.6 (CH), 133.9 (C), 144.1 (C), 159.2 (d, $^1J_{CF}$ = 247.0 Hz, C). ^{19}F NMR (282 MHz, $CDCl_3$): δ = -114.92. IR (ATR, cm^{-1}): $\tilde{\nu}$ = 2958 (w), 2935 (w), 2838 (w), 1897 (w), 1597 (m), 1474 (s), 1243 (s), 1180(m), 1027 (s), 805 (s), 751 (m), 692 (m), 412 (w). GC-MS (EI, 70 eV): *m/z* (%) = 336 (100) $[M]^+$, 307 (22), 280 (32), 279 (15), 251 (14). HRMS (EI) calcd. for $C_{22}H_{21}FO_2$ $[M]^+$: 336.15201; found 336.151958.

1,4-Di(3`,4`-dimethoxyphenyl)-2-fluorobenzene (13d): Starting with **12** (100 mg, 0.39 mmol), Cs_2CO_3 (263 mg, 0.81 mmol), $Pd(PPh_3)_4$ (3 mol%), 3,4-dimethoxyphenylboronic acid (141 mg, 0.78 mmol) and 1,4-dioxane (4 mL), **13d** was isolated as a colourless oil (84 mg, 58%). ^{1}H NMR (300 MHz, $CDCl_3$): δ = 3.84 (s, 6H, OCH_3), 3.85 (s, 3H, OCH_3), 3.88 (s, 3H, OCH_3), 6.24-6.65 (m, 1H, ArH), 6.86-6.91 (m, 2H, ArH), 6.99 (m, 3H, ArH), 7.23–7.42 (m, 3H, ArH). ^{13}C NMR (75.46 MHz, CDCl3): δ = 55.8 (OCH_3), 55.9 ($2OCH_3$), 56.5 (OCH_3), 100.5 (CH), 100.7 (CH), 110.1 (CH), 111.3 (d, *J* = 19.9 Hz, CH), 112.3 (t, *J* = 3.5 Hz, CH), 114. (d, *J* = 23.9 Hz, CH), 119.3 (CH), 128.2 (C), 130.6 (d, *J* = 4.3 Hz, CH), 132.4 (d, *J* = 2.4 Hz, C), 134.7 (C), 141.7 (d, *J* = 8.1 Hz, C), 143.1 (C), 148.8 (d, *J* = 3.23 Hz, C), 149.1 (C), 149.3 (C), 159.9 (d, *J* = 247.1 Hz, CF). ^{19}F NMR (282.4 MHz, $CDCl_3$): δ = -117.7 (CF). IR (ATR, cm-1): $\tilde{\nu}$ = 3103 (w), 3072 (w), 2996 (w), 2931 (w), 2833 (w), 2732 (w), 2700 (w), 2583 (w), 2551 (w), 2457 (w), 2400 (w), 2353 (w), 2277 (w), 2052 (w), 1907 (w), 1797 (w), 1737 (w), 1621 (w), 1578 (m), 1536 (w), 1498 (w), 1467 (s), 1426 (s), 1404 (s), 1354 (w), 1318 (m), 1259 (s), 1226 (s), 1197 (m), 1137 (m), 1104 (s), 1084 (m), 1035 (m), 1001 (s), 966 (m), 920 (m), 879 (m), 850 (m), 820 (s), 787 (s), 744 (s), 692 (s), 657 (m), 606 (m), 570 (m), 536 (m). MS (EI, 70 eV): m/z (%) = 368 (100) $[M]^+$, 338 (35). HRMS (EI) calcd. for $C_{22}H_{21}O_4F$ $[M]^+$: 368.14184; found 368.14198.

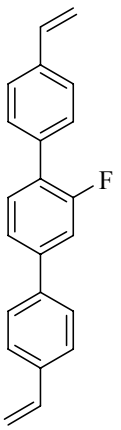


1,4-Di(2`,4`-dimethoxyphenyl)-2-fluorobenzene (13e): Starting with **12** (100 mg, 0.39 mmol), Cs_2CO_3 (263 mg, 0.81 mmol), $Pd(PPh_3)_4$ (3 mol%), 2,4-dimethoxyphenylboronic acid (141 mg, 0.78 mmol) and 1,4-dioxane (4 mL), **13e** was isolated as a colourless semi solid (91 mg, 63%). ^{1}H NMR (300 MHz, $CDCl_3$): δ = 3.60 (s, 3H, OCH_3), 3.63 (s, 3H, OCH_3), 3.85 (s, 3H, OCH_3), 3.86 (s, 3H, OCH_3), 6.86-6.95 (m, 4H, ArH), 7.03.-7.09 (m, 2H, ArH), 7.28–7.34 (m, 3H, ArH). ^{13}C NMR (75.46 MHz, CDCl3): δ = 55.9 (OCH_3), 56.0 (OCH_3), 60.7 (OCH_3), 60.8 (OCH_3), 112.0 (CH), 112.4 (CH), 122.5 (CH), 123.3 (d, *J* = 2.6 Hz, CH), 123.7 (CH), 124.2 (CH), 124.6 (d, *J* = 3.9 Hz, C), 130.1 (C), 131.4 (d, *J* = 3.7 Hz, CH), 134.5 (d, *J* = 2.0 Hz, C), 139.4 (d, *J* = 8.3 Hz, C), 146.9 (d, *J* = 52.3 Hz, C), 153.1 (d, *J* = 29.3 Hz, C), 159.4 (d, *J* = 247.2 Hz, CF). ^{19}F NMR (282.4 MHz, $CDCl_3$): δ = -114.8 (CF). IR (ATR, cm-1): $\tilde{\nu}$ = 3103 (w), 3058 (w), 3006 (w), 2962 (w), 2838 (w), 1621 (w), 1598 (w), 1579 (w), 1515 (w), 1402 (w), 1316 (w), 1264 (m), 1199 (w), 1133 (w), 1113 (m), 1085 (m), 1019 (w), 934 (w), 875 (w), 824 (w),

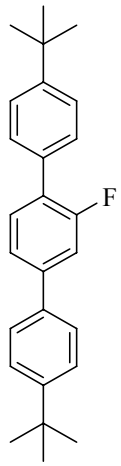


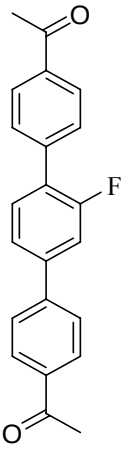
787 (m), 734 (m), 651 (w), 581 (w), 535 (m). MS (EI, 70 eV): m/z (%) = 368 (100) $[M]^+$, 338 (36). HRMS (EI) calcd. for $C_{22}H_{21}O_4F_1$ $[M]^+$: 368.14184; found 368.124183.

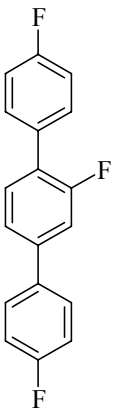
1,4-Di(4´-vinylebutylphenyl)-2-fluorobenzene (13f): Starting with **12** (100 mg, 0.39 mmol), Cs_2CO_3 (263 mg, 0.81 mmol), $Pd(PPh_3)_4$ (3 mol%), 4-vinylphenylboronic acid (115 mg, 0.78 mmol) and 1,4-dioxane (4 mL), **13f** was isolated as a colourless solid (53 mg, 45%). Mp stable upto 375 °C. ^{1}H NMR (300 MHz, $CDCl_3$): δ = 5.23 (dt, *J* = 10.87 Hz, 2H, CH_2), 5.75 (q, *J* = 17.7, 2H, CH_2), 6.70 (q, *J* = 17.6 Hz, 2H, CH), 7.30–7.54 (m, 11H, ArH). ^{13}C NMR (75.46 MHz, $CDCl_3$): δ = 29.6 (CH_3), 114.3 (CH), 126.3 (2CH), 126.8 (2CH), 127.0 (2CH), 129.0 (2CH), 129.7 (2CH), 130.8 (d, *J* = 3.89 Hz, C), 133.1 (C), 136.2 (C), 136.4 (C), 136.9 (C), 137.2 (t, *J* = 2.39 Hz, C), 153.1 (d, J_{CF} = 237.0 Hz, CF). ^{19}F NMR (282.4 MHz, $CDCl_3$): d -117.50 (CF). IR (ATR, cm-1): $\tilde{\nu}$ = 2922 (m), 2852 (m), 1740 (w), 1696 (w), 1604 (w), 1547 (w), 1486 (w), 1395 (w), 1242 (w), 1185 (w), 1134 (w), 1045 (w), 1006 (w), 893 (w), 878 (w), 814 (w), 771 (w), 700 (w), 580 (w), 548 (w). MS (EI, 70 eV): m/z (%) = 300 (100) $[M]^+$. HRMS (EI) calcd. for $C_{22}H_{17}F$ $[M]^+$: 300.13088; found 300.130205.

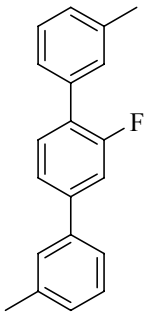


1,4-Di(4´-*tert*-butylphenyl)-2-fluorobenzene (13g): Starting with **12** (100 mg, 0.39 mmol), Cs_2CO_3 (263 mg, 0.81 mmol), $Pd(PPh_3)_4$ (3 mol%), 4-*tert*-butylphenylboronic acid (138 mg, 0.78 mmol) and 1,4-dioxane (4 mL), **13g** was isolated as a colourless solid (89 mg, 63%). Mp 184–186 °C. ^{1}H NMR (300 MHz, $CDCl_3$): δ = 1.29 (s, 18H, CH_3), 7.30 (dd, *J* = 12.1, 1.6 Hz, 1H, ArH), 7.36–7.42 (m, 6H, ArH), 7.45–7.50 (m, 4H, ArH). ^{13}C NMR (75.46 MHz, $CDCl_3$): δ = 31.3 (CH3), 34.6 (C), 111.3 (CH), 114.3 (d, J = 23.9 Hz, CH), 122.7 (d, *J* = 3.2 Hz, CH), 125.4 (2CH), 125.9 (2CH), 126.6 (2CH), 127.3 (d, *J* = 13.6 Hz, C), 128.6 (d, *J* = 3.2 Hz, CH), 130.8 (d, *J* = 4.3 Hz, C), 132.6 (d, *J* = 1.4 Hz, CH), 136.7 (d, *J* = 1.9 Hz, C), 141.8 (C), 141.9 (C), 150.8 (d, J_{CF} = 19.3 Hz, C), 160.1 (d, J_{CF} = 247 Hz, C). ^{19}F NMR (282.4 MHz, $CDCl_3$): δ = 117.97 (CF). IR (ATR, cm-1): $\tilde{\nu}$ = 3033 (w), 2950 (m), 2860 (w), 2705 (w), 2163 (w), 1977 (w), 1910 (w), 1741 (w), 1616 (w), 1543 (w), 1486 (m), 1428 (w), 1394 (m), 1305 (w), 1261 (m), 1200 (w), 1187 (m), 1122 (w), 1045 (w), 1004 (w), 948 (w), 894 (m), 816 (s), 829 (w), 750 (w), 675 (w), 586 (m), 548 (m). MS (EI, 70 eV): m/z (%) = 360 (54) $[M]^+$, 346 (26), 345 (100), 137 (12). HRMS (EI) calcd for $C_{26}H_{29}F[M]^+$: 360.22478; found 360.224193.

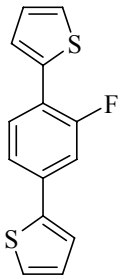


1,4-Di(4`-Acetylphenyl)-2-fluorobenzene (13h): Starting with **12** (100 mg, 0.39 mmol),  Cs_2CO_3 (263 mg, 0.81 mmol), $Pd(PPh_3)_4$ (3 mol%), 4-Acetylphenylboronic acid (127 mg, 0.78 mmol) and 1,4-dioxane (4 mL), **13h** was isolated as a colorless solid (68 mg, 52%). Mp 178-180 °C. ^{1}H NMR (300 MHz, $CDCl_3$): δ = 2.58 (s, 6H, CH_3), 7.37-7.53 (m, 3H, ArH), 7.61-7.66 (m, 4H, ArH), 7.97-8.00 (m, 4H, ArH). ^{13}C NMR (75.46 MHz, $CDCl_3$): δ = 26.7 (CH_3), 29.7 (CH_3), 114.8 (CH), 115. (d, *J* = 2.3 Hz, CH), 123.3 (d, *J* = 3.6 Hz, CH), 127.31 (2CH), 128.6 (2CH), 129.0 (CH), 129.2 (CH), 130.9 (CH), 131.9 (d, *J* = 4.3 Hz, CH), 136.3 (C), 136.5 (C), 139.9 (d, *J* = 1.3 Hz, C), 141.8 (d, *J* = 7.8 Hz, C), 143.6 (d, *J* = 1.8 Hz, C), 160.6 (d, *J* = 249.5 Hz, CF), 197.6 (CO), 197.8 (CO). ^{19}F NMR (282.4 MHz, CDCl3): δ = -116.6 (CF). IR (ATR, cm-1): $\tilde{\nu}$ = 3039 (w), 2921 (w), 2852 (w), 2387 (w), 2325 (w), 1731 (w), 1678 (m), 1602 (w), 1563 (w), 1520 (w), 1484 (w), 1423 (w), 1392 (w), 1357 (w), 1289 (w), 1264 (m), 1184 (m), 1112 (w), 1052 (w), 1005 (w), 961 (w), 877 (w), 811 (m), 754 (w), 691 (w), 623 (m), 592 (m) 531 (w). MS (EI, 70 eV): m/z (%) = 332 (51) $[M]^+$, 318 (22), 317 (100), 244 (11). HRMS (EI) calcd. for $C_{22}H_{17}FO_2$ $[M]^+$: 332.12126; found 332.12776.

1,3-Di(4`-fluorphenyl-5-fluorobenzene (13i): Starting with **12** (100 mg, 0.37 mmol),  Cs_2CO_3 (263 mg, 0.81 mmol), $Pd(PPh_3)_4$ (3 mol%), 4-fluoromethylphenylboronic acid (109 mg, 0.78 mmol) and 1,4-dioxane (4 mL), **13i** was isolated as a colorless solid (54 mg, 48%). Mp 145-149 °C. ^{1}H NMR (300 MHz, $CDCl_3$): δ = 7.03-7.09 (m, 2H, ArH), 7.24-7.29 (m, 1H, ArH), 7.32-7.36 (m, 4H, ArH), 7.41-7.50 (m, 4H, ArH). ^{13}C NMR (75 MHz, $CDCl_3$): δ = 114.5 (dd, *J* = 24.2, 3.8 Hz, CH), 115.5 (d, *J* = 21.5 Hz, CH), 115.9 (d, *J* = 21.4, Hz, CH), 122.8 (t, *J* = 3.2 Hz, CH), 128.2 (CH), 128.8 (CH), 129.2 (CH), 130.5 (d, *J* = 3.34 Hz, CH), 130.7 (dd, *J* = 8.2, 3.3 Hz, CH), 130.9 (d, *J* = 3.3 Hz, CH), 131.3 (CH), 133.7 (d, *J* = 1.1 Hz, C), 134.2 (d, *J* = 4.9 Hz, C), 137.8 (d, *J* = 1.7 Hz, C), 141.1 (d, *J* = 8.3 Hz, C), 159.9 (d, J_{CF} = 248.2 Hz, CF), 162.5 (d, J_{CF} = 247.6 Hz, CF), 168.8, (d, J_{CF}= 247.7 Hz, CF). ^{19}F NMR (282 MHz, $CDCl_3$): δ = -114.2.5, -117.3, -117.6 (CF). IR (ATR, cm^{-1}): $\tilde{\nu}$ = 3070 (w), 3041 (w), 2953 (w), 2917 (w), 2849 (w), 1907 (w), 1602 (w), 1595 (w), 1524 (w), 1480 (m), 1429 (w), 1387 (w), 1298 (w), 1224 (m), 1163 (m), 1094 (w), 1006 (w), 967 (w), 892 (m), 833 (m), 809 (s), 751 (w), 709 (w), 690 (w), 613 (w), 577 (m), 546 (w). MS (EI, 70 eV); *m/z* (%) = 284 (100) $[M]^+$. HRMS (EI) calcd. for $C_{18}H_{11}F_3$ $[M]^+$: 284.08074; found 284.1082698.

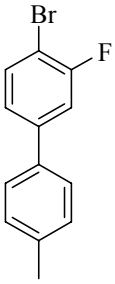
1,4-Di(3´-methylphenyl)-2-fluorobenzene (13j): Starting with **12** (100 mg, 0.39 mmol), 

Cs_2CO_3 (190 mg, 0.50 mmol), $Pd(PPh_3)_4$ (3 mol%), 3-methylphenylboronic acid (106 mg, 0.78 mmol) and 1,4-dioxane (4 mL), **13j** was isolated as a colorless solid (65 mg, 60%). Mp 180-182 °C. ^{1}H NMR (300 MHz, $CDCl_3$): δ = 2.33 (s, 6H, CH_3), 7.19 (d, *J* = 8.1 Hz, 4H, ArH), 7.26-7.37 (m, 2H, ArH), 7.42 (t, *J* = 7.2 Hz, 5H, ArH). ^{13}C NMR (75 MHz, $CDCl_3$): δ = 21.1, 21.2 (CH_3), 114.1 (d, *J*= 23.8 Hz, CH), 122.6 (d, *J* = 3.2 Hz, CH), 126.8, (2CH), 127.5 (d, *J* = 3.2 Hz, C), 128.7 (d, *J* = 3.2 Hz, 2CH), 129.2, (2CH), 129.6 (2CH), 130.7 (d, *J* = 4.0 Hz, CH), 132.6 (C), 136.7 (d, *J* = 18.0 Hz, C), 137.5 (d, *J* = 14.6 Hz, C), 147.9 (d, *J* = 8.2 Hz, C), 160.0, (d, *J* = 246.8 Hz, CF). ^{19}F NMR (282 MHz, $CDCl_3$): δ = -117.97. IR (ATR, cm^{-1}): $\tilde{\nu}$ = 3027 (w), 2917 (w), 2853 (w), 2735 (w), 1914 (w), 1614 (w), 1569 (w), 1547 (w), 1423 (w), 1392 (w), 1296 (w), 1215 (w), 1182 (w), 1133 (w), 1042 (w), 1005 (w), 947 (w), 890 (w), 869 (w), 807 (m), 731 (w), 647 (w), 557 (w), 556 (w). GC-MS (EI, 70 eV); *m/z* (%) = 276 (100) $[M]^+$, 275 (11). HRMS (EI) calcd. for $C_{20}H_{17}F$ $[M]^+$: 276.13008; found 276.131090.

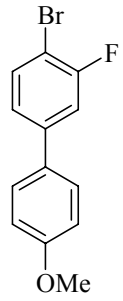
1,4-Di(2-thienyl)-2-fluorobenzene (13k): Starting with **12** (100 mg, 0.39 mmol), Cs_2CO_3 

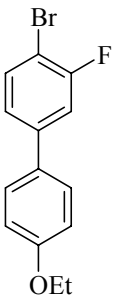
(190 mg, 0.50 mmol), $Pd(PPh_3)_4$ (3 mol%), 2-thienylboronic acid (49 mg, 0.39 mmol) and 1,4-dioxane (4 mL), **13k** was isolated as a colourless solid (51 mg, 50%). Mp 94-96 °C. ^{1}H NMR (300 MHz, $CDCl_3$): δ = 7.00-7.06 (m, 2H, ArH), 7.22-7.34 (m, 5H, ArH), 7.41–7.43 (m, 1H, ArH), 7.52–7.57 (m, 1H, ArH). ^{13}C NMR (75.46 MHz, $CDCl_3$): δ = 113.4 (d, *J* = 24.5 Hz, CH), 121.1 (d, *J* = 13.5 Hz, C), 121.8 (d, *J* = 3.1 Hz, CH), 123.8 (CH), 125.6 (CH), 125.8 (d, *J* = 4.5 Hz, CH), 126.3 (d, *J* = 7.1 Hz, CH), 127.8 (CH), 128.3 (CH), 129.0 (d, *J* = 4.2 Hz, CH), 134.9 (d, *J* = 9.4 Hz, C), 136.9 (d, *J* = 3.87 Hz, C), 142.6 (d, *J* = 2.9 Hz, C), 159.2 (d, J_{CF} = 250.2 Hz, CF). ^{19}F NMR (282.4 MHz, $CDCl_3$): δ = -107.4 (CF). IR (ATR, cm^{-1}): $\tilde{\nu}$ = 3100 (w), 3074 (w), 2961 (w), 2854 (w), 1799 (w), 1606 (w), 1553 (w), 1483 (m), 1419 (m), 1354 (w), 1289 (w), 1259 (m), 1207 (w), 1135 (w), 1058 (m), 1015 (m), 945 (w), 866 (m), 805 (s), 692 (s), 630 (m), 579 (w), 550 (m), 528 (m). GC-MS (EI, 70 eV): *m/z* (%) = 260 (100) $[M^+]$, 215 (12). HRMS (EI) calcd. for $C_{14}H_9FS_2$ $[M]^+$: 260.01242; found 260.012690.

1-Bromo-4(4´-methylphenyl)-2-fluorobenzene (14a): Starting with **12** (100 mg, 0.39 mmol), Cs_2CO_3 (190 mg, 0.50 mmol), $Pd(PPh_3)_4$ (3 mol%), 4-methylphenylboronic acid (53 mg, 0.39 mmol) and 1,4-dioxane (4 mL), **14a** was isolated as a colourless solid (63 mg, 60%). Mp 81-83 °C. ^{1}H NMR (300 MHz, $CDCl_3$): δ = 2.25 (s, 3H, CH_3), 7.05-7.09 (m, 3H, ArH), 7.14–7.18 (m, 1H, ArH), 7.26–7.29 (m, 2H, ArH), 7.40 (dd, *J* = 1.5 Hz, 1H, ArH). ^{13}C NMR (75.46 MHz, $CDCl_3$): δ = 21.1 (CH_3), 107.4 (d, *J* = 27.3 Hz, C), 114.8 (d, *J* = 22.5 Hz, CH), 123.3 (d, *J* = 3.3 Hz, CH), 126.7 (2CH), 129.7 (2CH), 133.6 (CH), 136.1 (d, *J* = 1.6 Hz, C), 138.2 (C), 142.6 (d, *J* = 7.1 Hz, C), 159.3 (d, J_{CF} = 246.2 Hz, CF). ^{19}F NMR (282.4 MHz, $CDCl_3$): δ = -107.4 (CF). IR (ATR, cm^{-1}): $\tilde{\nu}$ = 3027 (w), 2918 (w), 2852 (w), 2732 (w), 2602 (w), 2496 (w), 1907 (w), 1599 (w), 1556 (w), 1472 (w), 1417 (w), 1390 (w), 1301 (w), 1262 (w), 1197 (w), 1137 (w), 1055 (w), 1019 (w), 944 (w), 871 (w), 801 (m), 693 (w), 643 (w), 594 (w), 546 (w), 529 (w). MS (EI, 70 eV): m/z (%) = 266 (100) (^{81}Br) $[M]^+$, 265 (25), 264 (98) (^{79}Br), 263 (12), 185 (17), 184 (19), 183 (48), 170 (18), 165 (26). HRMS (EI) calcd. for $C_{13}H_{10}BrF$ $[M]^+$: 263.99444; found 263.994605. HRMS (EI); calcd. for $C_{13}H_{10}{}^{81}BrF$ $[M]^+$: 265.99240; found 265.992813.

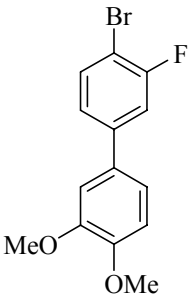


1-Bromo-4(4´-methoxyphenyl)-2-fluorobenzene (14b): Starting with **12** (100 mg, 0.39 mmol), Cs_2CO_3 (190 mg, 0.50 mmol), $Pd(PPh_3)_4$ (3 mol%), 4-methoxyphenylboronic acid (59.3 mg, 0.39 mmol) and 1,4-dioxane (4 mL), **14b** was isolated as a colorless oil (67 mg, 60%). ^{1}H NMR (300 MHz, $CDCl_3$): δ = 3.77 (s, 3H, OCH3), 6.90 (td, *J* = 8.85, 2.18 Hz, 2H, ArH), 7.20–7.27 (m, 3H, ArH), 7.34–7.39 (m, 2H, ArH). ^{13}C NMR (75.46 MHz, $CDCl_3$): δ = 55.3 (OCH_3), 114.1 (2CH), 119.6 (d, *J* = 25.9 Hz, CH), 120.5 (d, *J* = 9.5 Hz, C), 127.6 (d, *J* = 3.70 Hz, C), 128.5 (d, *J* = 12.4 Hz, CH), 129.9 (d, *J* = 2.8 Hz, CH), 131.4 (d, *J* = 4.07 Hz, CH), 131.9 (d, *J* = 2.77 Hz, C), 132.1 (d, *J* = 9.8 Hz, CH), 159.4 (C), 159.5 (d, J_{CF} = 251 Hz, C). ^{19}F NMR (282.4 MHz, $CDCl_3$): δ = -115.31 (CF). IR (ATR, cm^{-1}): $\tilde{\nu}$ = 3067 (w), 2999 (w), 2922 (w), 2835 (w), 2712 (w), 2550 (w), 2158 (w), 2048 (w), 1980 (w), 1891 (w), 1607 (m), 1518 (m), 1477 (s), 1390 (m), 1264 (m), 1247 (s), 1178 (s), 1112 (m), 1037 (m), 963 (w), 869 (s), 807 (s), 719 (m), 636 (w), 570 (m), 539 (s). MS (EI, 70 eV): m/z (%) = 281 (13) $[M]^+$, 280 (100), 267 (30), 265 (31), 239 (29), 158 (15), 157 (35). HRMS (EI) calcd. for $C_{13}H_{10}OBrF$ $[M]^+$: 281.98731; found 281.987694.

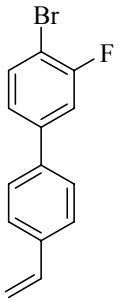


1-Bromo-4(4´-ethoxyphenyl)-2-fluorbenzene (**14c**): Starting with **12** (100 mg, 0.39 mmol), 

Cs_2CO_3 (190 mg, 0.50 mmol), $Pd(PPh_3)_4$ (3 mol%), 4-ethoxyphenylboronic acid (64.7 mg, 0.39 mmol) and 1,4-dioxane (4 mL), **14c** was isolated as a colorless solid (79 mg, 68%). Mp 76-78 °C. ^{1}H NMR (300 MHz, $CDCl_3$): δ = 1.37 (t, *J* = 7.2 Hz, 3H, CH_3), 3.99 (q, *J* = 6.9 Hz, 2H, OCH_2), 6.85-6.91 (m, 2H, CH), 7.21-7.28 (m, 3H, CH), 7.36-7.50 (m, 2H, CH). ^{13}C NMR (75 MHz, $CDCl_3$): δ = 14.9 (CH_3), 63.6 (OCH_2), 106.8 (d, *J* = 22.0 Hz, C), 114.5 (d, *J* = 16.5 Hz, CH), 114.7 (CH), 115.0 (CH), 123.4 (d, *J* = 3.8 Hz, CH), 127.7 (CH), 128.0 (CH), 131.3 (C), 133.6 (CH), 133.9 (C), 144.1 (C), 159.2 (d, $^1J_{CF}$ = 247.0 Hz, C). ^{19}F NMR (282 MHz, $CDCl_3$): δ = -114.92. IR (ATR, cm^{-1}): $\tilde{\nu}$ = 2958 (w), 2935 (w), 2838 (w), 1897 (w), 1597 (m), 1474 (s), 1243 (s), 1180(m), 1027 (s), 805 (s), 751 (m), 692 (m), 412 (w). GC-MS (EI, 70 eV): *m/z* (%) = 294 (78) $[M]^+$, 268 (100), 239 (22), 211 (20), 157 (32), 133 (12), 106 (10). HRMS (EI) calcd. for $C_{14}H_{12}BrFO$ $[M]^+$: 294.00556; found 294.005131.

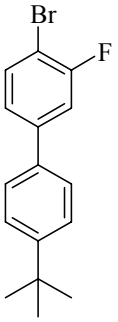
1-Bromo-4(3´,4´-di-methoxyphenyl)-2-fluorbenzene (**14d**): Starting with **12** (100 mg, 0.39 

mmol), Cs_2CO_3 (190 mg, 0.50 mmol), $Pd(PPh_3)_4$ (3 mol%), 3,4-dimethoxyphenylboronic acid (71.0 mg, 0.39 mmol) and 1,4-dioxane (4 mL), **14d** was isolated as a colorless oil (82 mg, 67%). ^{1}H NMR (300 MHz, $CDCl_3$): δ = 3.84 (s, 3H, OCH_3), 3.86 (s, 3H, OCH_3), 6.86-6.89 (m, 1H, CH), 6.96-6.99 (m, 3H, CH), 7.18-7.23 (m, 2H, CH). ^{13}C NMR (75 MHz, $CDCl_3$): δ = 55.9, 56.0 (OCH_3), 110.0 (C), 111.2, 112.1 (CH), 112.1 (CH), 119.7 (d, *J* = 3.7 Hz, CH), 121.3 (CH), 121.4 (d, *J* = 3.0 Hz, CH), 127.6 (CH), 131.5 (C), 131.6 (C), 149.8 ($COCH_3$), 149.9 ($COCH_3$), 158.9 (d, $^1J_{CF}$ = 247.0 Hz, CF). ^{19}F NMR (282 MHz, $CDCl_3$): δ = -115.11. IR (ATR, cm^{-1}): $\tilde{\nu}$ = 2960 (w), 2936 (w), 1599 (m), 1581 (m), 1475 (m), 1339 (m), 1243 (m), 1180 (m), 1028 (s), 891 (s), 871 (m), 834 (m), 752 (m), 693 (m), 640 (w), 597 (w), 542 (m), 412 (m). GC-MS (EI, 70 eV): *m/z* (%) = 310 (100) $[M]^+$, 295 (18), 269 (16), 267 (18), 188 (66), 173 (11), 157 (15), 145 (18), 106 (8). HRMS (EI) calcd. for $C_{14}H_{12}BrFO_2$ $[M]^+$: 310.00047; found 310.000984.

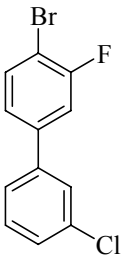
1-Bromo-4(4´-*vinyl*phenyl)-2-fluorobenzene (14e): Starting with **12** (100 mg, 0.39 mmol), 

Cs_2CO_3 (190 mg, 0.50 mmol), $Pd(PPh_3)_4$ (3 mol%), 4-vinylphenylboronic acid (57 mg, 0.39 mmol) and 1,4-dioxane (4 mL), **14e** was isolated as a colorless solid. (49 mg, 45%). Mp 338-340 °C. ^{1}H NMR (300 MHz, $CDCl_3$): δ = 5.03 (d, *J* = 2.3 Hz, 1H, CH), 5.58 (d, *J* = 4.3 Hz, 1H, CH), 6.52 (q, *J* = 3.7 Hz, 1H, CH), 7.00-7.13 (m, 3H, ArH), 7.23-7.35 (m, 4H, ArH). ^{13}C NMR (75.46 MHz, $CDCl_3$): δ = 114.5 (CH), 114.9 (CH), 123.5 (d, *J* = 4.3 Hz, CH), 126.4 (CH), 126.8 (CH), 126.9 (CH), 128.9 (d, *J* = 3.2 Hz, CH), 133.7 (CH), 136.1 (CH), 136.3 (d, *J* = 19.6 C), 137.5 (C), 137.6 (d, *J* = 2.4 Hz, C), 142.1 (d, *J* = 7.4 Hz, C), 159.4 (d, J_{CF} = 243.3 Hz, CF). ^{19}F NMR (282.4 MHz, $CDCl_3$): δ = -107.1 (CF). IR (ATR, cm^{-1}): $\tilde{\nu}$ = 2922 (w), 2852 (w), 2368 (w), 2165 (w), 2046 (w), 1977 (w), 1711 (m), 1605 (w), 1573 (w), 1521 (w), 1486 (w), 1432 (w), 1359 (m), 1301 (w), 1219 (m), 1186 (w), 1116 (w), 1090 (w), 1006 (w), 989 (w), 905 (w), 878 (w), 814 (m), 771 (w), 721 (w), 668 (w), 622 (w), 578 (w), 529 (w). MS (EI, 70 eV); m/z (%) = 278 (96) (^{81}Br) $[M]^+$, 276 (100), 277 (18), 196 (41), 170 (14), 158. HRMS (EI) calcd. for $C_{14}H_{10}{}^{81}BrF$ $[M]^+$: 277.99240; found 277.992413.

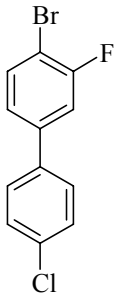
1-Bromo-4(4´-*tert*-butylphenyl)-2-fluorobenzene (14f): Starting with **12** (100 mg, 0.39 mmol), Cs_2CO_3 (190 mg, 0.50 mmol), $Pd(PPh_3)_4$ (3 mol%), 4-*tert*-butylphenylboronic acid (46 mg, 0.39 mmol) and 1,4-dioxane (4 mL), **14f** was isolated as a colorless solid. (70 mg, 58%). Mp 75-77 °C. ^{1}H NMR (300 MHz, $CDCl_3$): δ = 1.14 (s, 9H, CH_3), 7.02-7.38 (m, 7H, ArH). ^{13}C NMR (75.46 MHz, $CDCl_3$): δ = 31.2 (CH_3), 34.7 (C), 114.8 (d, *J* = 22.1 Hz, CH), 123.6 (d, *J* = 3.2 Hz, CH), 125.6 (CH), 125.9 (CH), 126.5 (CH), 128.5 (d, *J* = 3.51 Hz, CH), 131.6 (t, *J* = 3.7 Hz, C), 133.6 (CH), 136.1 (d, *J* = 2.3 Hz, C), 142.7 (d, *J* = 6.9 Hz, C), 151.4 (C), 159.3 (d, J_{CF} = 246.7 Hz, CF). ^{19}F NMR (282.4 MHz, $CDCl_3$): δ =-115.01 (CF). IR (ATR, cm^{-1}): $\tilde{\nu}$ = 3066 (w), 2960 (w), 2927 (w), 2866 (w), 2718 (w), 1915 (w), 1892 (w), 1599 (w), 1519 (w), 1477 (m), 1387 (m), 1266 (m), 1245 (m), 1196 (m), 1109 (m), 1053 (m), 967 (w), 873 (m), 810 (s), 716 (w), 643 (w), 575 (m), 545 (s). MS (EI, 70 eV): m/z (%) = 308 (33) (^{81}Br) $[M]^+$, 306 (32), 293 (100), 292 (16), 291 (99), 265 (17), 212 (15), 183 (18). HRMS (EI) calcd. for $C_{16}H_{16}{}^{81}BrF$ $[M]^+$: 308.03935; found 308.039487



1-Bromo-4(3´-chlorophenyl)-2-fluorobenzene (14g) : Starting with **12** (100 mg, 0.39 mmol), Cs_2CO_3 (190 mg, 0.50 mmol), $Pd(PPh_3)_4$ (3 mol%), 3-chlorophenylboronic acid (60 mg, 0.39 mmol) and 1,4-dioxane (4 mL), **14g** was isolated as a colourless solid (56 mg, 50%). Mp 94-95 °C. ^{1}H NMR (300 MHz, $CDCl_3$): δ = 7.21 (d, *J* = 8.7 Hz, 1H, ArH), 7.25-7.33 (m, 2H, ArH), 7.35-7.39 (m, 4H, ArH). ^{13}C NMR (75.46 MHz, $CDCl_3$): δ = 119.8 (d, *J* = 25.5 Hz, CH), 128.8 (CH), 129.1 (CH), 130.0 (CH), 131.1 (CH), 133.2 (C), 134.2 (C), 135.5 (C), 146.0 (C), 160.1 (d, *J* = 245.1 Hz, CF), 161.1 (C). ^{19}F NMR (282.4 MHz, $CDCl_3$): δ = -115.0 (CF). IR (ATR, cm^{-1}): $\tilde{\nu}$ = 2954 (w), 2919 (m), 2850 (m), 1737 (w), 1591 (w), 1555 (w), 1501 (w), 1473 (m), 1411 (w), 1302 (w), 1275 (w), 1213 (w), 1125 (w), 1088 (m), 1018 (m), 888 (m), 837 (m), 807 (s), 749 (m), 701 (w), 630 (m), 582 (m), 543 (w). MS (EI, 70 eV); m/z (%) = 286 (100) (^{81}Br) $[M]^+$, 285 (10), 284 (77) (^{79}Br), 170 (54), 169 (11). HRMS (EI) calcd. for $C_{12}H_7BrClF$ $[M]^+$: 283.93982; found 283.987663. HRMS (EI) calcd. for $C_{12}H_7{}^{81}BrClF$ $[M]^+$: 285.93687; found 285.937585.



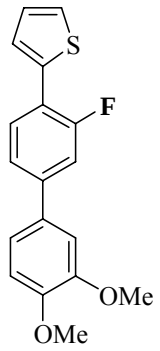
1-Bromo-4(4´-chlorophenyl)-2-fluorobenzene (14h): Starting with **12** (100 mg, 0.39 mmol), Cs_2CO_3 (190 mg, 0.50 mmol), $Pd(PPh_3)_4$ (3 mol%), 4-chlorophenylboronic acid (60 mg, 0.39 mmol) and 1,4-dioxane (4 mL), **14h** was isolated as a colourless solid (68 mg, 60%). Mp 94-95 °C. ^{1}H NMR (300 MHz, $CDCl_3$): δ = 7.19-7.24 (m, 1H, ArH), 7.31 (dd, *J* = 12.6, 1.8 Hz, 1H, ArH), -7.41-7.49 (m, 4H, ArH), 7.50 (dd, *J* = 8.1, 1.2 Hz, 1H, ArH). ^{13}C NMR (75.46 MHz, $CDCl_3$): δ = 108.3 (d, *J* = 20.9 Hz, C), 114.9 (d, *J* = 23.1 Hz, CH), 123.7 (d, *J* = 3.3 Hz, CH), 128.2 (2CH), 129.2 (2CH), 133.9 (CH), 134.4 (C), 137.4 (C), 141.4 (d, *J* = 7.1 Hz, C), 159.4 (d, J_{CF} = 247.7 Hz, CF). ^{19}F NMR (282.4 MHz, $CDCl_3$): δ = -106.8 (CF). IR (ATR, cm^{-1}): $\tilde{\nu}$ = 2954 (w), 2919 (m), 2850 (m), 1737 (w), 1591 (w), 1555 (w), 1501 (w), 1473 (m), 1411 (w), 1302 (w), 1275 (w), 1213 (w), 1125 (w), 1088 (m), 1018 (m), 888 (m), 837 (m), 807 (s), 749 (m), 701 (w), 630 (m), 582 (m), 543 (w). MS (EI, 70 eV): m/z (%) = 286 (100) (^{81}Br) $[M]^+$, 284 (77) (^{79}Br), 170 (54), 169 (11). HRMS (EI) calcd for $C_{12}H_7{}^{79}BrClF$ $[M]^+$: 283.93982; found 283.939663. HRMS (EI) calcd. for $C_{12}H_7{}^{81}BrClF$ $[M]^+$: 285.93687; found 285.987585.



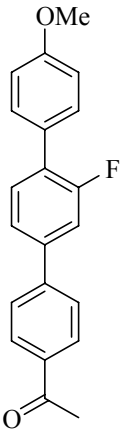
General procedure for the synthesis of 15a–c.

The reaction was carried out in a pressure tube. To a dioxane suspension (4 mL) of 12 (200 mg, 0.79 mmol), $Pd(PPh3)_4$ (3 mol%) and $Ar^1B(OH)_2$ (0.79 mmol) was added Cs_2CO_3 (385 mg, 1.18 mmol), 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 8 h. The mixture was cooled to 20 °C and $Ar_2B(OH)_2$ (0.95 mmol) and Cs_2CO_3 (385 mg, 1.18 mmol) was added. The reaction mixtures were heated under Argon atmosphere for 6 h at 100 °C. They were diluted with water and extracted with CH_2Cl_2 (3 * 50 mL). The combined organic layers were dried (Na_2SO_4), filtered and the filtrate was concentrated in vacuo. The residue was purified by flash chromatography (silica gel, EtOAc/ hexane = 1:4).

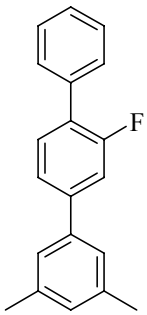
1-(3´,4´-Dimethoxyphenyl)-4-(2-thienyl)-2-fluorobenzene (15a): Starting with **12** (200 mg, 0.79 mmol), Cs_2CO_3 (385 g, 1.81 mmol), $Pd(PPh_3)_4$ (3 mol%), 3,4-dimethoxyyphenylboronic acid (143 mg, 0.79 mmol) and 1,4-dioxane (4 mL) and 2-thienylphenylboronic acid (121 mg, 0.95 mmol), **15a** was isolated as a colorless solid (131 mg, 53%). Mp 94-96 °C. ^{1}H NMR (300 MHz, $CDCl_3$): δ = 3.81 (s, 3H, OCH_3), 3.88 (s, 3H, OCH_3), 6.85-7.17 (m, 5H, ArCH), 7.21-7.52 (m, 4H, ArH). ^{13}C NMR (75 MHz, $CDCl_3$): δ = 56.0 (OCH_3), 56.1 (OCH_3), 107.2 (d, *J* = 20.0 CH), 110.0 (CH), 110.3 (CH), 111.5 (d, *J* = 4.5 Hz, CH), 113.6 (dd, *J* = 21.4, 7.1 Hz, *J* = 2.4 Hz, C), 114.7 (d, *J* = 22.6 Hz, CH), 119.4 (CH), 119.5 (C), 122.4 (t, *J* = 2.4 Hz, C), 123.5 (d, *J* = 3.4 Hz, C), 128.5 (d, *J* = 13.2 Hz, C), 130.2 (d, *J* = 9.5 Hz, C), 131.6 (t, *J* = 3.2 Hz, C), 131.9 (C), 132.3 (d, *J* = 11.1 Hz, C), 133.6 (CH), 142.5 (d, *J* = 7.4 Hz, CH), 149.3 (C), 159.3 (d, *J* = 247.0 Hz, CF). IR (ATR, cm^{-1}): $\tilde{\nu}$ = 3058 (w), 3014 (w), 2938 (w), 2838 (w), 1723 (w), 1595 (w), 1563 (w), 1481 (m), 1439 (w), 1315 (w), 1280 (w), 1250 (m), 1197 (w), 1160 (m), 1104 (w), 1023 (m), 935 (w), 870 (w), 801 (m), 718 (w), 640 (w), 594 (w), 539 (w). GC-MS (EI, 70 eV): *m/z* (%) = 314 (100) $[M]^+$, 311 (16), 310 (99), 297 (18), 295 (19), 269 (16), 267 (18), 188 (65), 173 (11), 170 (14), 157 (15) 145 (18). HRMS (EI) calcd. for $C_{18}H_{15}FO_2S$ $[M]^+$: 314.07768; found 314.06859.



1-(4´-Acetylphenyl)-4-(4´´-methoxyphenyl)-2-fluorobenzene (15b): Starting with **12** (200 mg, 0.79 mmol), Cs_2CO_3 (385 g, 1.81 mmol), $Pd(PPh_3)_4$ (3 mol%), 4-acetylyphenylboronic acid (129 mg, 0.79 mmol) and 1,4-dioxane (4 mL) and 4-methoxyphenylboronic acid (144 mg, 0.95 mmol), **15b** was isolated as a colorless solid (151 mg, 60%). Mp 89-90 °C. ^{1}H NMR (300 MHz, $CDCl_3$): δ = 2.57 (s, 3H, CH_3), 3.79 (s, 6H, OCH_3), 6.91-6.94 (m, 2H, CH), 7.28-7.50 (m, 5H, CH), 7.61-7.65 (m, 2H, CH), 7.96-8.00 (m, 2H,CH).^{13}C NMR (75 MHz, $CDCl_3$): δ = 26.7 (CH_3), 55.4 (OCH_3), 114.2, 114.2 (CH), 114.3(d, *J*=23.8 Hz, CH), 125.7(d, *J*=3.2 Hz, CH), 127.1(d, *J* =16.1 Hz, CH), 128.1 (2CH), 128.8(2CH), 129.1 (2CH), 130.1 (C), 130.3 (C), 136.2 (C), 140.4, 140.9 (C), 159.8 (C), 160.3(d, $^1J_{CF}$=249 Hz, C), 197.7(CO). ^{19}F NMR (282 MHz, $CDCl_3$): δ = -113.40 (CF). IR (ATR, cm^{-1}): $\tilde{\nu}$ = 2956 (w), 2837 (w), 1675 (m), 1602 (m), 1578 (m), 1545 (m), 1484 (m), 1464 (m), 1393 (m), 1357 (m), 1300 (m), 1249 (m), 1173 (m), 1127 (m), 1023 (m), 1045 (w), 1023 (m), 809 (s), 693 (m), 577 (m), 3053 (w), (w). GC-MS (EI, 70 eV): *m/z* (%) = 320 (100) $[M]^+$, 306 (16), 305 (72), 277 (6), 234 (10), 233 (23), 153 (11), 117 (3). HRMS (EI) calcd. for $C_{21}H_{17}FO_2$ $[M]^+$: 320.120627; found 320.12071.

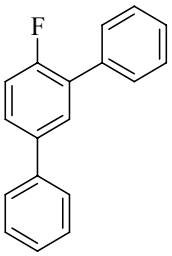


1-(3´,5´-Dimethylphenyl)-4-(phenyl)-2-fluorobenzene (15c): Starting with **12** (200 mg, 0.79 mmol), Cs_2CO_3 (385 mg, 1.18 mmol), $Pd(PPh_3)_4$ (3 mol%), 3,5-di-methylphenylboronic acid (118 mg, 0.79 mmol) and 1,4-dioxane (4 mL), and phenylboronic acid (114 mg, 0.95mmol) and **15c** was isolated as a colorless solid (141 mg, 65%). Mp 85-87 °C. ^{1}H NMR (300 MHz, $CDCl_3$): δ = 2.29 (s, 6H, CH_3), 6.93 (s, 1H, ArH), 7.12-7.14 (m, 2H, ArH), 7.25-7.42 (m, 6H, ArH), 7.49-7.54 (m, 2H, ArH). ^{13}C NMR (75 MHz, $CDCl_3$): δ = 21.4, 29.3 (CH_3), 114.6 (d, *J* = 23.8 Hz, CH), 126.3 (d, *J* = 2.8 Hz, CH), 126.9, (2CH), 127.7 (CH), 127.9 (CH), 128.5 (d, *J* = 1.4 Hz, CH), 128.9 (d, *J* = 3.48 Hz, CH), 129.4 (CH), 129.5 (d, *J* = 4.1 Hz, C), 130.8 (CH), 130.9 (d, *J* = 1.3 Hz, CH), 131.1 (C), 137.9, 138.5, 139.6 (C), 137.8, 142.4 (d, *J* = 16.9 Hz, C), 160.0 (d, $^1J_{CF}$ = 247.1 Hz, CF). ^{19}F NMR (282 MHz, $CDCl_3$): δ = -117.7. IR (ATR, cm^{-1}): $\tilde{\nu}$ = 3052 (w), 3034 (w), 2915 (w), 2857 (w), 2732 (w), 1953 (w), 1892 (w), 1771 (w), 1747 (w), 1620 (m), 1601 (m), 1555 (m), 1475 (m), 1395 (m), 1328 (w), 1258 (m), 1183 (m), 1133 (m), 1037 (w), 1009 (w), 937 (m), 873 (m), 850 (m), 826 (s), 787 (m), 755 (s), 695 (s), 644 (m), 589 (m), 538 (m). GC-MS (EI, 70 eV): *m/z* (%) = 276 (100) $[M]^+$. HRMS (EI) calcd. for $C_{20}H_{17}F$ $[M]^+$: 276.13088; found 276.130583

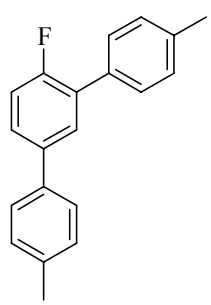


General procedure for Suzuki–Miyaura reactions(17a-g, 18a,b): A 1,4-dioxane solution (4 mL per 0.3 mmol of **17**) of **17**, Cs_2CO_3, $Pd(PPh_3)_4$ and arylboronic acid **8** were stirred at 90 °C for 6 or 8 h. After cooling to room temperature, the organic and the aqueous layers were separated and 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.

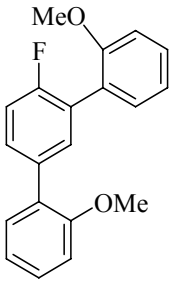
1,3-Diphenyl-4-fluorobenzene (17a): Starting with **16** (100 mg, 0.39 mmol), Cs_2CO_3 (253 mg, 0.78 mmol), $Pd(PPh_3)_4$ (3 mol%), phenylboronic acid (94 mg, 0.78 mmol) and 1,4-dioxane (4 mL), **17a** was isolated as a colorless oil (54 mg, 55%). ^{1}H NMR (300 MHz, $CDCl_3$): δ = 7.09-7.16 (m, 1H, ArH), 7.23-7.32 (m, 2H, ArH), 7.33-7.45 (m, 5H, ArH), 7.47-7.63 (m, 5H, ArH. ^{13}C NMR (75 MHz, $CDCl_3$): δ = 116.3 (d, *J* = 23.6 Hz, CH), 127.1 (2CH), 127.6 (d, *J* = 8.02 Hz, CH), 128.6 (2CH), 128.9 (2CH), 129.1 (CH), 129.6 (CH), 130.9 (CH), 132.5 (C), 135.8 (C), 137.7 (d, *J*= 3.57 Hz, C), 140.2 (C), 159.4, (d, J_{CF}= 249.0 Hz, CF).^{19}F NMR (282 MHz, $CDCl_3$): δ = -120.67 (CF). IR (ATR, cm^{-1}): $\tilde{\nu}$ = 3058 (w), 3029 (w), 2956 (w), 2927 (w), 2857 (w), 1948 (w), 1883 (w), 1806 (w), 1723 (m), 1600 (w), 1539 (w), 1478 (s), 1392 (w), 1332 (w), 1257 (m), 1183 (w), 1121 (m), 1073 (m), 1000 (w), 945 (w), 892 (m), 823 (s), 759 (s), 721 (m), 693 (s), 631 (s), 584 (s), 539 (m). MS (EI, 70 eV); m/z (%) = 248 (100) $[M]^+$. HRMS (EI) calcd. for $C_{18}H_{13}O$ F $[M]^+$: 248.09958; found 248.8935680.



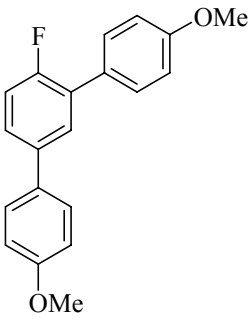
1,3-Di(4´-methylphenyl)-4-fluorobenzene (17b): Starting with **16** (100 mg, 0.39 mmol), Cs_2CO_3 (253 mg, 0.78 mmol), $Pd(PPh_3)_4$ (3 mol%), 4-methylphenylboronic acid (106 mg, .78 mmol) and 1,4-dioxane (4 mL), **17b** was isolated as a colorless solid (67 mg, 62%). Mp 96-98 °C. ^{1}H NMR (300 MHz, $CDCl_3$): δ = 2.32 (CH_3), 2.34 (CH_3), 7.08-7.21 (m, 5H, ArH), 7.38-7.42 (m, 5H, CH), 7.51-7.58 (m, 1h, ArH). ^{13}C NMR (75 MHz, $CDCl_3$): δ = 21.1, 21.3 (CH_3), 116.3 (d, *J* = 23.3 Hz, CH), 127.1 (2CH), 127.1 (2CH), 127.1 (d, *J* = 8.0 Hz, CH), 128.9 (d, *J* = 8.0 Hz, CH), 129.1 (C), 129.3 (C), 129.6 (2CH), 129.6 (2CH), 132.9 (2C), 137.7 (2C), 160.9 (d, J_{CF} = 248.0 Hz, CF). ^{19}F NMR (282 MHz, $CDCl_3$): δ = -120.72 (CF). $\tilde{\nu}$ = 3052 (w), 2975 (w), 2916 (w), 2848 (w), 2734 (w), 1899 (w), 1797 (w), 1731 (w), 1645 (w), 1590 (w), 1515 (w), 1483 (m), 1450 (w), 1381 (w), 1280 (w), 1249 (w), 1214 (w), 1126 (w), 1039 (w), 960 (w), 902 (w), 834 (w), 809



(s), 719 (m), 663 (w), 615 (w), 549 (m). IR (ATR, cm^{-1}): GC-MS (EI, 70 eV); *m/z* (%) = 276 (100) $[M]^+$. HRMS (EI) calcd. for $C_{20}H_{17}F$ $[M]^+$: 276.13088; found 276.130620

1,3-Di(2´-methoxyphenyl)-4-fluorobenzene (17c): Starting with **16** (100 mg, 0.39 mmol), 

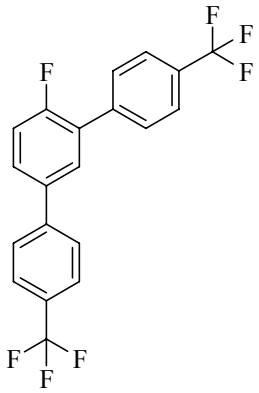
Cs_2CO_3 (253 mg, 0.78 mmol), $Pd(PPh_3)_4$ (3 mol%), 2-methoxyphenylboronic acid (94 mg, 78 mmol) and 1,4-dioxane (4 mL), **17c** was isolated as a colorless solid (73 mg, 60%). Mp 99-100 °C. ^{1}H NMR (300 MHz, $CDCl_3$): δ = 3.75, 3.75 (s, 3H, OCH_3), 6.89-6.98 (m, 4H, ArH), 7.04-7.11 (m, 1H, ArH), 7.17-7.25 (m, 3H, ArH), 7.39-7.48 (m, 2H, ArH). ^{13}C NMR (75 MHz, $CDCl_3$): δ = 55.6, 55.7 (OCH_3), 111.1 (CH), 111.2 (CH), 114.9 (d, *J* = 22.5 Hz, CH), 120.5 (CH), 120.9 (CH), 128.7 (2C), 125.7 (d, *J* = 15.8 Hz, C), 130.1 (d, *J* = 8.3 Hz, CH), 130.9 (2CH), 131.5 (2CH), 133.0 (d, *J* = 8.3 Hz, CH), 134.1 (d, *J* = 3.8 Hz, C), 157.1, 157.6 (C), 159.1 (d, *J* = 244.0 Hz, CF).^{19}F NMR (282 MHz, $CDCl_3$): δ = -116.36 (CF). IR (ATR, cm^{-1}): $\tilde{\nu}$ = 3053 (w), 2959 (m), 2924 (m), 2852 (m), 2836 (m), 1577 (m), 1494 (s), 1455 (s), 1434 (m), 1390 (m), 1256 (m), 1228 (m), 1109 (m), 1022 (s), 825 (m), 792 (m), 825 (s), 792 (s), 748 (s), 625 (m), 597 (m), 544 (m). GC-MS (EI, 70 eV); *m/z* (%) = 308 (100) $[M]^+$, 278 (13), 260 (6), 233 (10), 110 (3). HRMS (EI) calcd. for $C_{20}H_{17}O_2F[M]^+$: 308.12071; found 308.120178.

1,3-Di(4´-methoxyphenyl)-4-fluorobenzene (17d): Starting with **16** (100 mg, 0.39 mmol), 

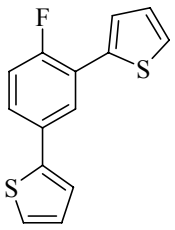
Cs_2CO_3 (253 mg, 0.78 mmol), $Pd(PPh_3)_4$ (3 mol%), 4-methoxyphenylboronic acid (85 mg, 70 mmol) and 1,4-dioxane (4 mL), **17d** was isolated as a colorless solid (94 mg, 70%). Mp 101-103 °C. ^{1}H NMR (300 MHz, $CDCl_3$): δ = 3.74, (s, 3H, OCH_3), 3.76 (s, 3H, OCH_3), 6.84-6.92 (m, 4H, ArH), 7.04-7.14 (m, 1H, ArH), 7.23-7.36 (m, 2H, ArH), 7.39-7.49 (m, 4H, ArH). ^{13}C NMR (75 MHz, $CDCl_3$): δ = 55.3, (OCH_3) 55.4 (OCH_3), 114.0 (2CH), 114.1 (2CH), 114.3 (d, *J* = 23.7 Hz, CH), 116.4 (d, *J* = 23.3 Hz, CH), 126.6 (d, *J* = 8.57 Hz, CH), 127.7 (C), 128.1 (2CH), 128.9 (C), 130.2 (2CH), 132.8 (C), 137.3 (d, *J* = 3.52 Hz, C) 159.1 (d, *J* = 247.0 Hz, CF), 159.1 (d, *J* = 10.9 Hz, C). ^{19}F NMR (282 MHz, $CDCl_3$): δ = -119.9 (CF). IR (ATR, cm^{-1}): $\tilde{\nu}$ = 3037 (w), 3000 (w), 2955 (w), 2907 (w), 2836 (w), 1605 (m), 1571 (w), 1500 (w), 1480 (s), 1439 (m), 1383 (w), 1310 (w), 1247 (s), 1179 (s), 1114 (m), 1076 (m), 1016 (s), 1000 (m), 962 (w), 886 (w), 832 (s), 808 (s), 791 (s), 765 (w), 717 (w), 656 (w), 589 (w), 550

(m), 529 (m). MS (EI, 70 eV): *m/z* (%) = 308 (100) $[M]^+$, 293 (26), 265 (14). ESI-HRMS calcd. for $C_{20}H_{17}FO_2$ $[M+H]^+$: 308.12071; found 308.120987.

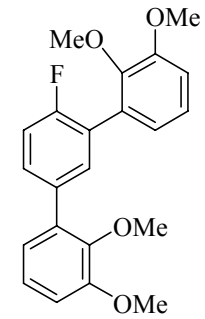
1,3-Di(4´-trifluoromethylphenyl-4-fluorobenzene (17e): Starting with **16** (100 mg, 0.37 mmol), Cs_2CO_3 (253 mg, 0.78 mmol), $Pd(PPh_3)_4$ (3 mol%), 4-trifluoromethylphenylboronic acid (148 mg, 0.78 mmol) and 1,4-dioxane (4 mL), **17e** was isolated as a colorless solid (68 mg, 45%). Mp 148-150 °C. ^{1}H NMR (300 MHz, $CDCl_3$): δ = 7.21 (dd, *J* = 18.6, 8.46 Hz, 1H, ArH), 7.49-7.68 (m, 10H, ArH). ^{13}C NMR (75 MHz, $CDCl_3$): δ = 117.0 (d, *J* = 22.9 Hz, CH), 125.5 (dd, *J* = 7.85, 3.92 Hz, CH), 125.9 (dd, *J* = 7.71, 3.49 Hz, CH), 127.4 (2CH), 128.7 (d, *J* = 9.1 Hz, CH), 129.4 (d, *J* = 3.34 Hz, CH), 129.6 (d, *J* = 3.49 Hz, CH), 136.5 (C), 139.0 (C), 143.3 (2C), 149.7 (C), 158.7 (d, J_{CF} = 244.0 Hz, CF_3), 159.2, (d, J_{CF} = 239.0 Hz, CF_3), 159.9, (d, J_{CF} = 252.0 Hz, CF). ^{19}F NMR (282 MHz, $CDCl_3$): δ = -62.5, -62.6 (CF_3), -118.8 (CF). IR (ATR, cm^{-1}): $\tilde{\nu}$ = 3052 (w), 3028 (w), 2959 (w), 2900 (w), 2864 (w), 1519 (w), 1484 (m), 1420 (w), 1380 (w), 1319 (w), 1269 (m), 1212 (m), 1045 (w), 1007 (w), 964 (w), 896 (w), 831 (m), 813 (m), 759 (w), 722 (w), 676 (w), 615 (w), 563 (m), 536 (w). MS (EI, 70 eV): *m/z* (%) = 384 (100) $[M]^+$. ESI-HRMS calcd. for $C_{20}H_{11}F_7$ $[M+H]^+$: 384.07435; found 384.074697.



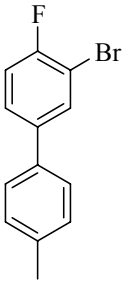
1,3-Di(2-thienyl)-4-fluorobenzene (17f): Starting with **16** (100 mg, 0.39 mmol), Cs_2CO_3 (190 mg, 0.50 mmol), $Pd(PPh_3)_4$ (3 mol%), 2-thienylboronic acid (49 mg, 0.39 mmol) and 1,4-dioxane (4 mL), **17f** was isolated as a colourless solid (49 mg, 48%). Mp 91-93 °C. ^{1}H NMR (300 MHz, $CDCl_3$): δ = 7.00-7.06 (m, 2H, ArH), 7.22-7.34 (m, 5H, ArH), 7.41–7.43 (m, 1H, ArH), 7.52–7.57 (m, 1H, ArH). ^{13}C NMR (75.46 MHz, $CDCl_3$): δ = 113.4 (d, *J* = 24.5 Hz, CH), 121.1 (d, *J* = 13.5 Hz, C), 121.8 (d, *J* = 3.1 Hz, CH), 123.8 (CH), 125.6 (CH), 125.8 (d, *J* = 4.5 Hz, CH), 126.3 (d, *J* = 7.1 Hz, CH), 127.8 (CH), 128.3 (CH), 129.0 (d, *J* = 4.2 Hz, CH), 134.9 (d, *J* = 9.4 Hz, C), 136.9 (d, *J* = 3.87 Hz, C), 142.6 (d, *J* = 2.9 Hz, C), 159.2 (d, J_{CF} = 250.2 Hz, CF). ^{19}F NMR (282.4 MHz, $CDCl_3$): δ = -107.4 (CF). IR (ATR, cm^{-1}): $\tilde{\nu}$ = 3102 (w), 3067 (w), 2956 (w), 2871 (w), 1886 (w), 1799 (w), 1724 (w), 1605 (w), 1555 (w), 1484 (w), 1421 (w), 1355 (w), 1289 (w), 1244 (w), 1177 (w), 1121 (w), 1071 (w), 999 (w), 960 (w), 866 (w), 841 (w), 808 (m), 746 (w), 696 (m), 613 (w), 561 (w), 529 (w). GC-MS (EI, 70 eV); *m/z* (%) = 260 (100) $[M]^+$, 215 (13). HRMS (EI) calcd. for $C_{14}H_9FS_2$ $[M]^+$: 260.01242; found 260.0135983.



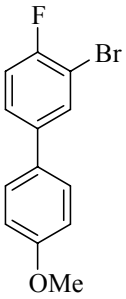
1,3-Di(2´,3´-dimethoxyphenyl)-4-fluorobenzene (17g): Starting with **16** (100 mg, 0.39 mmol), Cs_2CO_3 (263 mg, 0.81 mmol), $Pd(PPh_3)_4$ (3 mol%), 2,3-dimethoxyphenylboronic acid (141 mg, 0.78 mmol) and 1,4-dioxane (4 mL), **17g** was isolated as a colourless solid (84 mg, 58%). Mp 176-178 °C. ^{1}H NMR (300 MHz, $CDCl_3$): δ = 3.59 (s, 3H, OCH_3), 3.75 (s, 3H, OCH_3), 3.81 (s, 3H, OCH_3), 3.83 (s, 3H, OCH_3), 6.76-6.87 (m, 4H, ArH), 7.01.-7.07 (m, 2H, ArH), 7.28–7.32 (m, 3H, ArH). ^{13}C NMR (75.46 MHz, CDCl3): δ = 55.8 (OCH_3), 55.9 (OCH_3), 60.6 (OCH_3), 60.7 (OCH_3), 111.6 (CH), 112.1 (d, *J* = 32.6 Hz, CH), 116.3 (d, *J* = 25.2 Hz, CH), 122.4 (CH), 123.3 (d, *J* = 1.3 Hz, CH), 123.9 (d, *J* = 36.6 Hz, CH), 124.5 (CH), 124.6 (d, *J* = 3.6 Hz, C), 130.1 (CH), 131.4 (d, *J* = 3.8 Hz, C), 134.4 (d, *J* = 1.8 Hz, C), 139.4 (d, *J* = 8.2 Hz, C), 146.9 (d, *J* = 36.8 Hz, C), 152.8 (C), 153.1 (d, *J* = 21.2 Hz, C), 159.6 (d, *J* = 246.6 Hz, CF). ^{19}F NMR (282.4 MHz, $CDCl_3$): δ = -114.7 (CF). IR (ATR, cm-1): $\tilde{\nu}$ = 3103 (w), 3058 (w), 3006 (w), 2962 (w), 2930 (w), 2837 (w), 1621 (w), 1598 (w), 1579 (w), 1556 (w), 1515 (w), 1478 (w), 1441 (w), 1402 (m), 1316 (w), 1264 (m), 1208 (w), 1188 (w), 1113 (m), 1084 (w), 1032 (m), 998 (m), 934 (w), 875 (w), 831 (w), 787 (m), 751 (m), 651 (w), 600 (w), 535 (m). MS (MS, 70 eV): m/z (%) = 368 (100) $[M]^+$, 338 (38). HRMS (EI) calcd. for $C_{22}H_{21}O_4F[M]^+$: 368.14184; found 368.121183.



3-Bromo-4(4'-methyl)-4-fluorobiphenyl (18a): Starting with **16** (100 mg, 0.39 mmol), Cs_2CO_3 (126 mg, 0.39 mmol), $Pd(PPh_3)_4$ (3 mol%), 4-methylphenylboronic acid (53 mg, 0.39 mmol) and 1,4-dioxane (4 mL), **18a** was isolated as a colorless solid (65 mg, 63%). Mp 99-101 °C ^{1}H NMR (300 MHz, $CDCl_3$): δ = 2.33 (s, 3H, CH_3), 6.93-6.98 (m, 1H, ArH), 7.17-7.20 (m, 2H, ArH), 7.29-7.36 (m, 2H, ArH), 7.46-7.49 (dd, *J* = 6.87, 2.60 Hz, 1H, ArH), 7.38 (d, *J* = 1.5 Hz, 1H, CH).^{13}C NMR (75 MHz, $CDCl_3$): δ = 21.3 (OCH_3), 108.9 (d, *J* = 21.0 Hz, C), 114.1 (2CH), 117.8 (d, *J* = 18.0 Hz, CH), 130.1, 130.2 (CH), 131.0 (C), 131.1 (C), 132.2 (C), 136.1 (C), 159.7 (C), 165.8 (d, *J* = 248.0 Hz, CF).^{19}F NMR (282 MHz, $CDCl_3$): δ = -119.8 (CF). IR (ATR, cm^{-1}): $\tilde{\nu}$ = 3029 (w), 2918 (w), 2853 (w), 2733 (w), 1914 (w), 1755 (w), 1725 (w), 1596 (w), 1519 (w),1468 (w), 1378 (w), 1288 (w), 1265 (m), 1131 (w), 1074 (w), 1014 (s), 949 (w), 881 (w), 806 (s), 717 (w), 695 (m), 656 (w), 591 (w), 531 (w). GC-MS (EI, 70 eV): *m/z* (%) = 264(100) (^{79}Br $[M]^+$, 185 (15), 184 (19), 183 (52), 170 (21), 165 (42). HRMS (EI) calcd. for $C_{13}H_{10}BrF$ $[M]^+$: 263.99444; found 263.994477 and calcd for $C_{13}H_{10}{}^{81}BrF$ $[M]^+$: 265.99240; found 265.992517.



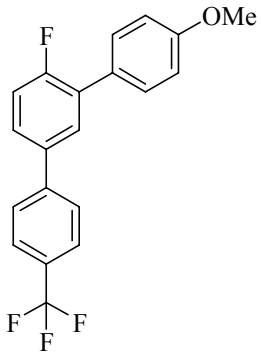
3-Bromo-1-(4'-methoxy)-4-fluorobiphenyl (18b): Starting with **16** (100 mg, 0.39 mmol), Cs_2CO_3 (126 mg, 0.78 mmol), $Pd(PPh_3)_4$ (3 mol%), 4-methoxyphenylboronic acid (59 mg, 0.39 mmol) and 1,4-dioxane (4 mL), **18b** was isolated as a colorless solid (78 mg, 70%). Mp 66-68 °C. ^{1}H NMR (300 MHz, $CDCl_3$): δ = 3.78 (s, 3H, OCH_3), 6.89-6.96 (m, 2H, ArH), 6.96 (d, *J* = 6.6 Hz, 1H, CH), 7.18-7.20 (m, 2H, CH), 7.34 (d, *J* = 1.5 Hz, 1H, CH), 7.38 (d, *J* = 1.5 Hz, 1H, CH). ^{13}C NMR (75 MHz, $CDCl_3$): δ = 55.4 (OCH_3), 108.9 (d, *J* = 21.0 Hz, C), 114.1 (2CH), 117.8 (d, *J* = 18.0 Hz, CH), 130.1, 130.2 (CH), 131.0 (CH), 131.1 (CH), 132.2 (C), 136.1 (C), 159.7 (C), 165.8 (d, *J* = 248.0 Hz, CF). ^{19}F NMR (282 MHz, $CDCl_3$): δ = -119.8 (CF). IR (ATR, cm^{-1}): $\tilde{\nu}$ = 3074 (m), 3015 (m), 2960 (m), 2837 (w), 1605 (m), 1514 (m), 1295 (m), 1255 (s), 1075 (s), 1016 (s), 875 (m), 792 (m), 696 (m), 624 (m), 576 (s). GC-MS (EI, 70 eV); *m/z* (%) = 280 (100) (^{79}Br) $[M]^+$, 267 (24), 265 (18), 239 (34), 237 (30), 213 (11), 170 (11), 158 (24), 157 (51), 138 (9), 44 (11). HRMS (EI) calcd. for $C_{13}H_{10}OBrF$ $[M]^+$: 279.98936; found 279.989522 and calcd. for $C_{13}H_{10}O^{81}BrF$ $[M]^+$: 281.98731; found 281.987381.



General procedure for the synthesis of 19a.

The reaction was carried out in a pressure tube. To a dioxane suspension (4 mL) of 16 (200 mg, 0.79 mmol), $Pd(PPh3)_4$ (3 mol %) and $Ar^1B(OH)_2$ (0.79 mmol) was added Cs_2CO_3 (385 mg, 1.18 mmol), 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 8 h. The mixture was cooled to 20 °C and $Ar_2B(OH)_2$ (0.95 mmol) and Cs_2CO_3 (385 mg, 1.18 mmol) was added. The reaction mixtures were heated under Argon atmosphere for 6 h at 100 °C. They were diluted with water and extracted with CH_2Cl_2 (3 * 50 mL). The combined organic layers were dried (Na_2SO_4), filtered and the filtrate was concentrated in vacuo. The residue was purified by flash chromatography (silica gel, EtOAc/ hexane = 1:4).

1-(4`-Trifluoromethylphenyl)-3-(4`-methylphenyl)-4-fluorobenzene (19a): Starting with

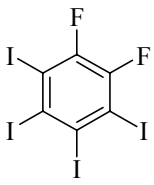


16 (200 mg, 0.78 mmol), Cs_2CO_3 (253 mg, 0.78 mmol), $Pd(PPh_3)_4$ (3 mol%), 4-trifluoromethylphenylboronic acid (148 mg, 0.78 mmol) and 4-methoxyphenylboronic acid(142 mg, 0.93 mmol) and 1,4-dioxane (4 mL), **19a** was isolated as a colorless solid (79 mg, 58%). Mp 149-151 °C. ^{1}H NMR (300 MHz, $CDCl_3$): δ = 3.73 (s, OCH_3), 6.86-6.95 (m, 4H, ArH), 7.05-7.16 (m, 1H, ArH), 7.26-7.45 (m, 2H, ArH), 7.60-7.65 (m, 4H, ArH). ^{13}C NMR (75 MHz, $CDCl_3$): δ = 55.4 (OCH_3), 110.3 (CH), 110.4 (CH), 111.3 (CH), 114.1 (CH), 114.4 (CH), 116.6 (d, J = 22.8 Hz, CH), 125.4 (d, J = 24.5, Hz, CH), 126.7 (C), 127.1 (CH), 127.4 (CH), 128.1 (t, J = 3.87 Hz, CH), 129.4 (CH), 130.2 (CH), 132.4 (C), 155.4 (C), 157.9 (d, J = 13.3 Hz, C), 158.2, (d, J_{CF}= 247.8 Hz, CF), 159.4, (d, J = 11.2.0 Hz, C), 160.0 (d, J = 9.6 Hz, C). ^{19}F NMR (282 MHz, $CDCl_3$): δ = -61.9, -(CF_3), -110.7 (CF). IR (ATR, cm^{-1}): $\tilde{\nu}$ = 3072 (w), 3037 (w), 2957 (w), 2912 (w), 2837 (w), 1605 (m), 1569 (m), 1517 (m), 1486 (s), 1439 (s), 1384 (m), 1323 (s), 1273 (s), 1234 (s), 1177 (s), 1124 (s), 1069 (s), 1012 (s), 962 (w), 891 (w), 835 (m), 809 (s), 794 (m), 765 (m), 714 (w), 656 (w), 598 (w), 550 (m), 530 (m). MS (EI, 70 eV): *m/z* (%) = 346 (100) $[M]^+$, 331 (11). HRMS (EI) calcd. for $C_{20}H_{14}OF_4$ $[M]^+$: 346.09753; found 346.096887.

7.7 Direct Periodination of Aromatic Compounds; General Procedure

Required molar amount of arene (1.0 mmol), molecular I_2 (1.27 g, 5.0 mmol), and $K_2S_2O_8$ (1.35 g, 5.0 mmol) were dissolved in DCE (10 mL). The reaction mixture was stirred in an ice bath for about 5 min, and then TFA (4 mL) and aq concd H_2SO_4 (0.18 mL, 1 mmol) were gradually added with constant stirring. The mixture was stirred for about 10 min in the ice bath and stirred further for 15 min at r.t. The temperature of the mixture was then gradually increased to the required temperature and stirred until the completion of the reaction. The mixture was cooled and poured into ice-cold H_2O (40-50 mL). The precipitated solid was collected by suction, washed with H_2O (30-40 mL), and CH_2Cl_2 (20-25 mL) or CH_2Cl_2-hexane to remove the unreacted I_2.

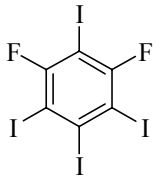
1,2-Difluoro-3,4,5,6-tetraiodobenzene (21): Starting with **20** (1 g, 0.008 mol), $K_2S_2O_8$ (11 g,



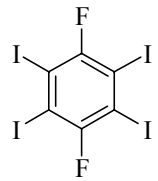
0.044 mol), TFA (11.8g, 0.044 mol) and **I_2** (12.1 g, 0.048 mmol) was refluxed in DCE, was isolated as a yellow crystalline solid (4.8 g, 90%). Mp 153-155 °C. ^{19}F NMR (282 MHz, $CDCl_3$): δ = -94.3. ^{13}C NMR (62.8 MHz, $CDCl_3$): δ = 97.3 (d, ^2J = 23.3 Hz, C), 115.3 (C), 150.3 (d, ^1J = 243.2 Hz, C). IR (KBr): $\tilde{\nu}$ =

2635, 2366, 2340, 2188, 2043, 1979 (w), 1537 (m), 1408, 1402 (s), 1316, 1224, 1172, 1046, 876, 702 (m), 678, 656, 557 (s) cm^{-1}. GC-MS (EI, 70 eV): *m/z* (%) = 617 ($[M]^+$, 100), 490 (24), 237 (22), 127 (10), 110 (22). HRMS (EI) calcd. for $C_6F_2I_4$ $[M]^+$: 617.61413 found 617.613808. Anal. Calcd for $C_6F_2I_4$: C, 11.67. Found: C, 11.68

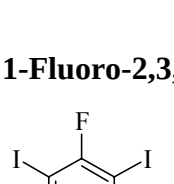
1,3-Difluoro-2,4,5,6-tetraiodobenzene (23): Starting with **22** (1 g, 0.008 mol), $K_2S_2O_8$ (11 g, 0.044 mol), TFA (11.8g, 0.044 mol) was refluxed in DCE, was isolated as a yellow crystalline solid (4.7g, 88%). Mp 176-177 °C. IR (KBr): $\tilde{\nu}$ = 2921 (w), 2764 (w), 2591 (w), 2412 (w), 2351 (w), 1667 (w), 1604 (w), 1474 (w), 1380 (w), 1355 (w), 1275 (w), 1238 (w), 1188 (w), 1079 (w), 1033 (w), 923 (w), 889 (w), 820 (w), 699 (w), 634 (w), 559 (w) cm^{-1}. M, 70 eV): *m/z* (%) = 617 (100) $[M]^+$, 490 (2), 237 (22), 127 (10), 110 (22). HRMS (EI) calcd. for $C_6F_2I_4$ $[M]^+$: 617.61413; found 617.61438. Anal. Calcd for $C_6F_2I_4$: C, 11.67. Found: C, 12.147



1,4-Difluoro-2,3,5,6-tetraiodobenzene (25): Starting with **24** (1 g, 0.008 mol), $K_2S_2O_8$ (11 g, 0.044 mol), TFA (11.8g, 0.044 mol) was refluxed in DCE, was isolated as a yellow crystalline solid (4.3g, 80%). Mp 253-255 °C. ^{19}F NMR (282 MHz, $CDCl_3$): δ = -54.40. ^{13}C NMR (62.8 MHz, DMSO-d_6): δ = 98.0 (dd, *J* = 38.6, 4.74 Hz, C), 156.9 (dd, *J* = 239.5, 4.5 Hz, C). IR (KBr): $\tilde{\nu}$ = 2773 (w), 2655 (w), 2515 (w), 1380 (w), 1311 (w), 1268 (w), 1222 (w), 1172 (w), 1099 (w), 1005 (w), 920 (w), 806 (w), 705 (w), 664 (w), 616 (w), 586 (w), 538 (w) cm^{-1}. MS (EI, 70 eV): *m/z* (%) = 617 (100) $[M]^+$, 491 (17), 490 (11), 363 (31), 237 (14), 128 (13), 110 (17), 43 (14). HRMS (EI): calcd for $C_6F_2I_4$ $[M]^+$: 617.61413; found 617.614004. Anal. Calcd for $C_6F_2I_4$: C, 11.67. Found: C, 11.94



1-Fluoro-2,3,4,5,6-pentaiodobenzene (27): Starting with **26** (1 g, 0.008 mol), $K_2S_2O_8$ (11 g, 0.044 mol), TFA (11.8g, 0.044 mol) was refluxed in DCE, was isolated as a yellow crystalline solid (4.1g, 76%). Mp 259-260 °C. ^{19}F NMR (282 MHz, $CDCl_3$): δ = -39.8. ^{13}C NMR (62.8 MHz, $CDCl_3$): δ = 96.6 (d, *J* = 31.7 Hz, C), 117.8 (d, *J* = 3.92 Hz, C), 124.1 (C), 158.8 (d, *J* = 241.6 Hz, C). IR (KBr): $\tilde{\nu}$ = 2924 (m), 2810 (m), 2778 (m), 2533 (m), 2477 (m), 2351 (m), 1693 (m), 1650 (m), 1587 (m), 1494 (m), 1471 (m), 1327 (s), 1274 (s), 1206 (m), 1150 (m), 1052 (m), 923 (m), 875 (s), 802 (m), 764 (m), 688 (m), 620 (s), 584 (s), 539 (m) cm^{-1}. MS (EI, 70 eV): *m/z* (%) = 726 (30)



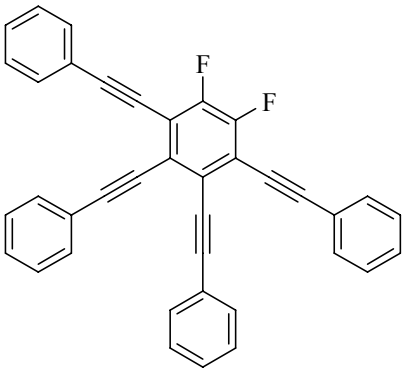
$[M]^+$, 600 (100), 473 (25), 346 (22), 219 (16), 92 (19). HRMS (EI) calcd. for $C_6F_1I_5$ $[M]^+$: 725.52319; found: 725.519725.

7.8 Synthesis of fluorinated polyethynylbenzenes by Sonogashira reactions

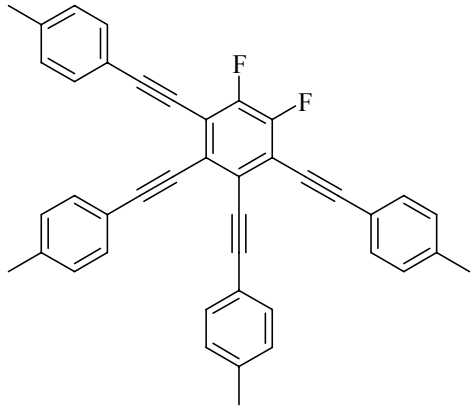
General Procedure for Sonogashira coupling Reactions

A suspension of tetraiodobenzenes (**21, 23, 25, 27**), X-phos (10 mol %), $Pd(OAc)_2$ (5 mol %), CuI (5 mol %), Cs_2CO_3 (5 eq) in DMF was degassed three time in ace pressure tube. Acetylene (1.2 eq per bromine atom) were added using a syringe. The mixture was heated at the indicated temperature (60–100 °C) for 60-100 h. The reaction mixture was filtered and residue washed with CH_2Cl_2 . The filtrate was washed with saturated solution of ammonium chloride (2 x 25ml), water (2 x 25ml) and dried over anhydrous Na_2SO_4. Solvent was removed in vacuo. The product was purified by column chromatography on silica gel.

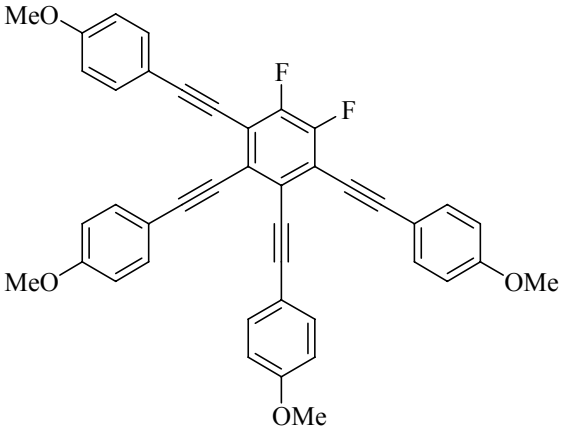
1,2-Difluoro-3,4,5,6-tetrakis(phenylethynyl)benzene (29a): starting with **21** (150 mg, 0.24 mmol), phenylacetylene **28a** (149 mg, 1.45 mmol), CuI (5 mol%), X-Phos (10 mol%), $Pd(OAc)_2$ (5 mol%), Cs_2CO_3 (5 eq) and DMF (5mL), **29a** was isolated as yellow solid (97 mg, 78%). Mp. 150–152 °C. ^{1}H NMR (300 MHz, $CDCl_3$): δ = 7.27-7.34 (m, 10H, ArH), 7.52-7.57 (m, 10H, ArH). ^{13}C NMR (75.4 MHz, $CDCl_3$): δ = 80.8 (C≡C), 85.9 (C≡C), 98.5 (C≡C), 101.4 (C≡C), 116.1 (t, J = 6.25 Hz,C), 122.6 (d, J = 58.7 Hz, C), 125.1 (C), 128.2 (CH), 128.5 (CH), 129.1 (d, J = 38.7 Hz, CH), 131.6 (CH), 131.7 (CH), 131.9 (CH), 150.1 (dd, J = 256.2, 16.3 Hz, CF). ^{19}F NMR (282 MHz, $CDCl_3$): δ = -131.12. IR (ATR, cm^{-1})**:** $\tilde{\nu}$ = 3078 (w), 3052 (w),3030 (w), 2928 (w), 2872 (w), 2714 (w), 2524 (w), 2435 (w), 2393 (w), 2207 (w), 1947 (w), 1872 (w), 1798 (w), 1744 (w), 1666 (w), 1584 (w), 1492 (m), 1453 (m), 1441 (m), 1409 (m), 1355 (w) 1327 (w), 1276 (w), 1235 (w), 1194 (w), 1174 (w), 1132 (w), 1093 (w), 1066 (m), 1023 (m), 998 (w),966 (w) 934 (m), 910 (w), 871 (w), 835 (w), 771 (w), 748 (s), 682 (s), 622 (w), 577 (m), 528 (m). MS (EI, 70 eV); *m/z* (%) = 514 (100) $[M]^+$, 513 (19), 512 (17), 492 (10), 436 (14), 385 (19), 384 (78), 369 (10).198 (11). HRMS (EI) calcd. for $C_{38}H_{20}F_2$ $[M]^+$: 514.15276; found 514.153109



1,2-Difluoro-3,4,5,6-tetrakis(4-methylphenylethynyl)benzene (29b): starting with **21** (150 mg, 0.24 mmol), 4-methylphenylacetylene (**28b**) (168 mg, 1.45 mmol), CuI (5 mol%), X-Phos (10 mol%), $Pd(OAc)_2$ (5 mol%), Cs_2CO_3 (5 eq) and DMF (5mL), **29b** was isolated as yellow solid (90 mg; 65%). Mp 171–173 °C. ^{1}H NMR (300 MHz, $CDCl_3$): δ = 2.33 (s, 12H, CH_3), 7.09-7.14 (m, 8H, ArH), 7.42-7.45 (m, 8H, ArH).). ^{13}C NMR (75.4 MHz, $CDCl_3$): δ =21.60, 21.63, 29.6 (CH_3), 80.5 (C≡C), 85.5 (C≡C), 98.5 (C≡C), 101.5 (C≡C), 115.9 (CH), 119.4 (C), 119.9 (C), 125.0 (C), 128.2 (CH), 129.5 (CH), 131.6 (CH), 139.1 (C), 139.6 (C), 159.8 (d, J_{CF} = 247.6 Hz, CF). ^{19}F NMR (282 MHz, $CDCl_3$): δ = -131.78. IR (ATR, cm^{-1})**:** $\tilde{\nu}$ = 3051 (w), 3028 (w), 2960 (w), 2917 (w), 2849 (w), 2733 (w), 2204 (w), 1895 (w), 1739 (w), 1603 (m), 1581 (w), 1509 (m), 1450 (m), 1412 (w), 1378 (w), 1316 (w), 1280 (w), 1260 (w), 1212 (w), 1195 (w), 1177 (w), 1101 (m), 1076 (w), 1037 (w), 1019 (m), 941 (m), 869 (w), 810 (s) 728 (w), 659 (w), 646 (w). MS (EI, 70 eV); *m/z* (%) = 6570 (41) $[M]^+$. HRMS (EI) calcd. for $C_{42}H_{28}F_2$ $[M]^+$: 570.21536; found 570.213690.

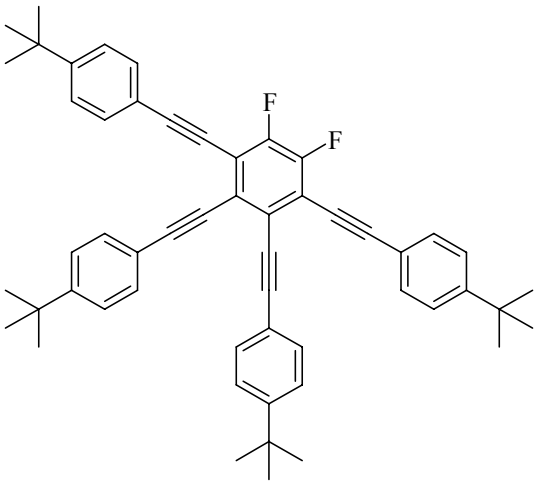


1,2-Difluoro-3,4,5,6-tetrakis(4-methoxylphenylethynyl)benzene (29c): starting with **21** (150 mg, 0.24 mmol), 4-methoxylphenylacetylene (**28c**) (191 mg, 1.45 mmol), CuI (5 mol%), X-Phos (10 mol%), $Pd(OAc)_2$ (5 mol%), Cs_2CO_3 (5 eq) and DMF (5mL), **29c** was isolated as yellow solid (107 mg; 70%). Mp 151–153 °C. ^{1}H NMR (300 MHz, $CDCl_3$): δ = 3.75 (s, 6H, OCH_3), 3.76 (s, 6H, OCH_3), 6.79-6.83 (m, 8H, ArH), 7.44-7.48 (m, 8H, ArH). ^{13}C NMR (75.4 MHz, $CDCl_3$): δ = 55.4 (2OCH_3), 80.1 (C≡C), 85.1 (C≡C), 98.3 (C≡C), 101.4 (C≡C), 114.2 (CH), 114.6 (CH), 115.2 (C), 122.2 (C), 124.8 (C), 128.8 (CH), 130.9 (CH), 133.3 (CH), 133.5 (CH), 152.2 (d, J = 258.0 Hz, CF), 160.1 (C), 167.8 (C). ^{19}F NMR (282 MHz, $CDCl_3$): δ = -132.35. IR (ATR, cm^{-1})**:** $\tilde{\nu}$ = 2957 (w), 2931 (w), 2838 (w), 2536 (w), 2206 (w), 2041 (w), 1907 (w), 1722 (w), 1660 (w), 1602 (m), 1565 (w), 1509 (s), 1455 (m), 1415 (w), 1389 (w), 1286 (m), 1244 (s), 1203 (w), 1177 (m), 1167 (s), 1103 (m), 1072 (w) 1022 (s), 939 (m), 832 (s), 795 (m) 743 (w), 705 (w), 651 (w), 642 (w), 636 (w),

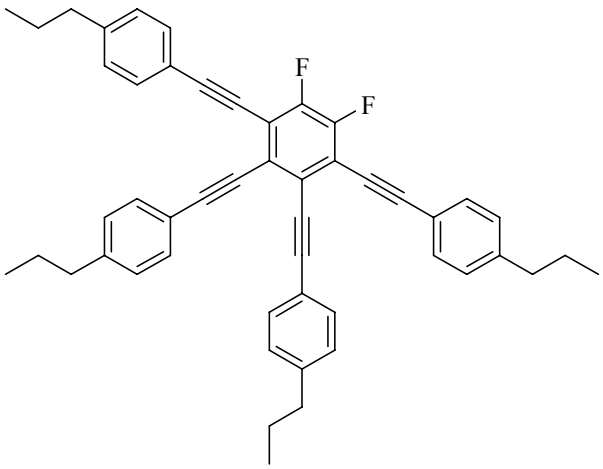


533 (m). MS (EI, 70 eV); *m/z* (%) = 634 (100) $[M]^+$. HRMS (EI) calcd. for $C_{42}H_{28}O_4F_2$ $[M]^+$: 634.19502; found 634.195842.

1,2-Difluoro-3,4,5,6-tetrakis(4-*tert*-butylphenylethynyl)benzene (29d): starting with **21** (100 mg, 0.16 mmol), 4-*tert*-butylphenylacetylene **28d** (153 mg, 0.97 mmol), CuI (5 mol%), X-Phos (10 mol%), $Pd(OAc)_2$ (5 mol%), Cs_2CO_3 (5 eq) and DMF (5mL), **29d** was isolated as yellow oil. (74 mg; 62%). ^{1}H NMR (300 MHz, $CDCl_3$): δ = 1.27 (s, 18H, CH_3), 1.28 (s, 18H, CH_3), 7.19-7.35 (m, 8H, ArH), 7.47-7.50 (m, 8H, ArH). ^{13}C NMR (75.4 MHz, $CDCl_3$): δ = 31.2 [$(CH_3)_3C$], 34.9 ($C(CH_3)$), 80.5 (C≡C), 85.5 (C≡C), 98.5 (C≡C), 101.5 (C≡C), 119.5 (C), 120.0 (C), 125.04 (C), 125.5 (CH), 131.6 (CH), 131.7 (CH), 152.3 (C), 152.6 (C), 158.1 (d, J = 242.2 Hz, CF). ^{19}F NMR (282 MHz, $CDCl_3$): δ = -131.77, -131.77. IR (ATR, cm^{-1})**:** $\tilde{\nu}$ = 3083 (w), 3035 (w), 2956 (m), 2901 (w), 2865 (w), 2710 (w), 2212 (w), 1912 (w), 1660 (w), 1607 (w), 1587 (w), 1552 (w), 1515 (w), 1455 (m), 1409 (w), 1391 (w), 1315 (w), 1267 (w), 1200 (w), 1182 (w), 1107 (m), 1079 (w), 1064 (w), 1015 (w), 943 (m), 830 (s), 784 (w), 735 (w), 697 (w), 656 (w), 620 (w), 559 (s), 528 (w). MS (EI, 70 eV); *m/z* (%) = 728 (36) $[M]^+$, 617 (73), 364 (15), 237 (10), 128 (27), 110 (20), 57 (17), 44 (100). HRMS (EI) calcd. for $C_{54}H_{52}F_2$ $[M]^+$: 738.40316; found 738.409188.

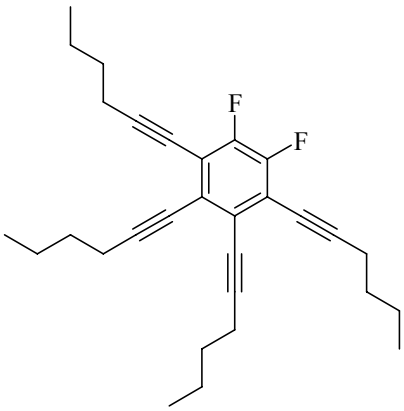


1,2-Difluoro-3,4,5,6-tetrakis(4-n-*propyl*-phenylethynyl)benzene (29e): starting with **21** (100 mg, 0.16 mmol), 4-*n*-*propyl*-butylphenylacetylene **28e** (139 mg, 0.97 mmol), CuI (5 mol%), X-Phos (10 mol%), $Pd(OAc)_2$ (5 mol%), Cs_2CO_3 (5 eq) and DMF (5mL), **29e** was isolated as yellow oil (74 mg; 67%). ^{1}H NMR (300 MHz, $CDCl_3$): δ = 0.89 (t, J = 7.11 Hz, 12H, CH*3*), 1.53-1.66 (sext, 8H, CH_2), 2.54 (t, J = 7.4, 8H, CH_2), 7.09-7.13 (m, 8H, ArH), 7.44-7.47 (m, 8H, ArH). ^{13}C NMR (75.4 MHz, $CDCl_3$): δ =13.8 ($2CH_3$), 24.3 ($2CH_2$), 38.0 ($2CH_2$), 80.5 (C≡C), 85.5 (C≡C), 98.6 (C≡C), 101.6 (C≡C), 119.7 (C), 120.2 (C), 125.0 (C),

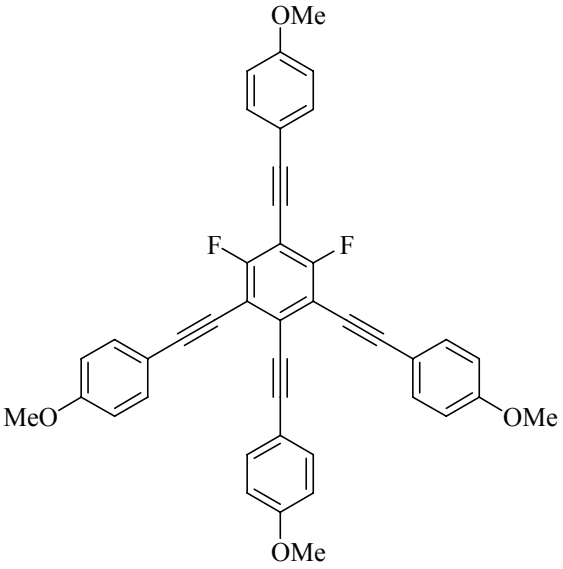


128.6 (C), 128.7 (CH), 131.5 (CH), 131.8 (CH), 143.9 (C), 144.3 (C), 160.2 (dd, J = 251.0, 13.6 Hz, CF) ^{19}F NMR (282 MHz, $CDCl_3$): δ = -131.76. IR (ATR, cm^{-1})**:** $\tilde{\nu}$ = 3400 (w), 3119 (w), 3078 (w), 2956 (m), 2927 (m), 2869 (m), 2732 (w), 2668 (w), 2206 (m), 1906 (w), 1787 (w), 1703 (w), 1666 (w), 1604 (w), 1553 (w), 1509 (m), 1454 (s), 1412 (m), 1338 (m), 1258 (m), 1178 (m), 1113 (m), 1079 (m), 1018 (m), 941 (m), 867 (m), 800 (s), 741 (m), 660 (m), 561 (m), 528 (m). MS (EI, 70 eV); *m/z* (%) = 682 (91) $[M]^+$, 653 (11), 397 (17), 396 (78), 394 (20), 329 (12), 153 (10), 44 (100). HRMS (EI) calcd. for $C_{50}H_{44}F_2$ $[M]^+$ 682.34056; found 682.339960.

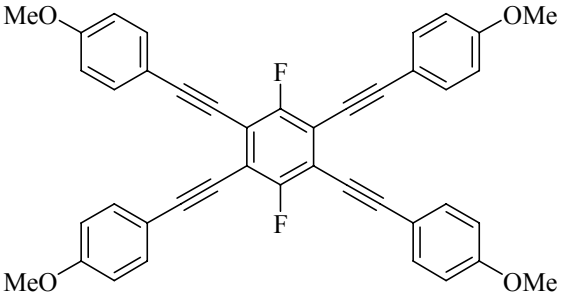
1,2-Difluoro-3,4,5,6-*tetra*kis(4-n-*butyl*-ethynyl)benzene (29f): starting with **21** (100 mg, 0.16 mmol), 4-*n*-*butyl*-acetylene (**28f**) (80 mg, 0.97 mmol), CuI (5 mol%), X-Phos (10 mol%), $Pd(OAc)_2$ (5 mol%), Cs_2CO_3 (5 eq) and DMF (5mL), **29f** was isolated as yellow oil (45 mg; 64%). ^{1}H NMR (300 MHz, $CDCl_3$): δ = 0.88 (t, J = 7.20, 12H, CH_3), 1.40-1.57 (m, 16H CH_2), 2.40-2.46 (sext, 8H, CH_2). ^{13}C NMR (75.4 MHz, $CDCl_3$): δ =13.6 ($2CH_3$), 19.6 ($2CH_3$), 21.9 ($2CH_2$), 22.6 ($2CH_2$), 29.6 ($2CH_2$), 30.6 ($2CH_2$), 31.5 ($2CH_2$), 38.1 ($2CH_2$), 59.5 (C≡C), 72.3 (C≡C), 98.5 (C≡C), 102.1 (C≡C), 125.9 (C), 135.5 (C), 137.0 (C), 148.3 (C), 150.9 (dd, J_{CF} = 246.8, 14.3 Hz, CF). ^{19}F NMR (282 MHz, $CDCl_3$): δ = -133.81. IR (ATR, cm^{-1})**:** $\tilde{\nu}$ = 3390 (w), 2956 (w), 2930 (w), 2871 (w), 2228 (w), 1714 (w), 1683 (w), 1608 (w), 1558 (w), 1509 (w), 1456 (m), 1378 (w), 1341 (w), 1246 (w), 1180 (w), 1119 (w), 1068 (w), 997 (w), 900 (w), 828 (w), 745 (w), 723 (w), 694 (w), 541 (m). MS (EI, 70 eV); *m/z* (%) = 434 (36) $[M]^+$, 397 (33), 396 (94), 394 (36), 331 (11), 329 (21), 277(15), 210 (15), 198 (11), 186 (16), 44 (100). HRMS (EI) calcd. for $C_{30}H_{36}F_2$ $[M]^+$: 434.27786; found 434.278396.



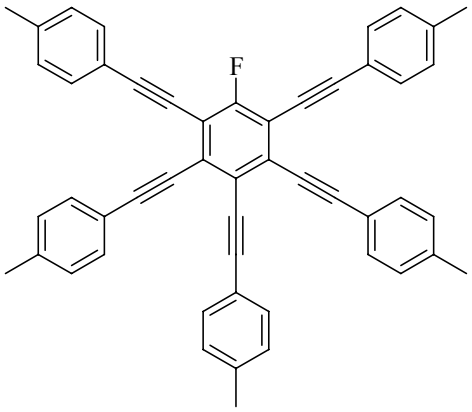
1,3-Difluoro-2,4,5,6-*tetra*kis(4-methoxylphenylethynyl)benzene (30a): starting with **23** (100 mg, 0.16 mmol), 4-methoxyphenylacetylene (**28c**) (128 mg, 0.97 mmol), CuI (5 mol%), X-Phos (10 mol%), $Pd(OAc)_2$ (5 mol%), Cs_2CO_3 (5 eq) and DMF (5mL), **30a** was isolated as yellow solid (69 mg; 68 %). Mp 124–126 °C. ^{1}H NMR (300 MHz, $CDCl_3$): δ = 3.88-3.94 (m, 12H, OCH_3), 6.90-6.97 (m, 9H, ArH), 7.07 (d, *J* = 8.5 Hz, 2H, ArH), 7.55-7.60 (m, 5H, ArH). ^{19}F NMR (282 MHz, $CDCl_3$): δ = -102.21. IR (ATR, cm^{-1})**:** $\tilde{\nu}$ = 2917 (w), 2542 (w), 2205 (w), 1644 (w), 1602 (w), 1567 (w), 1509 (w), 1447 (w), 1368 (w), 1289 (w), 1245 (w), 1169 (w), 1104 (w), 1028 (w), 955 (w), 913 (w), 868 (w), 828 (w), 766 (w), 708 (w), 679 (w), 615 (w), 532 (w). MS (EI, 70 eV); *m/z* (%) = 634 (17) $[M]^+$, 397 (23), 396 (100), 394 (25), 329 (13), 210 (10), 186 (10), 153 (10), 152 (10). HRMS (EI) calcd. for $C_{42}H_{28}O_4F_1$ $[M]^+$: 634.19502; found 634.197057.



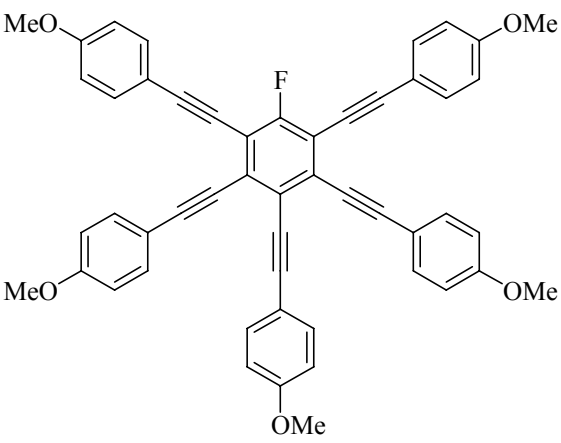
1,4-Difluoro-2,3,5,6-tetrakis(4-methoxylphenylethynyl)benzene (31a): starting with **25** (100 mg, 0.16 mmol), 4-methoxyphenylacetylene (**28c**) (128 mg, 0.97 mmol), CuI (5 mol%), X-Phos (10 mol%), $Pd(OAc)_2$ (5 mol%), Cs_2CO_3 (5 eq) and DMF (5mL), **31a** was isolated as yellow solid (80 mg, 78%). Mp 179–180 °C. ^{1}H NMR (300 MHz, $CDCl_3$): δ = 3.78 (s, 12H, OCH_3), 6.83 (dt, *J* = 9.00 Hz, 8H, ArH), 7.47 (dt, *J* = 9.00 Hz, 8H, ArH). ^{13}C NMR (75.4 MHz, $CDCl_3$): δ = 55.4 (OCH_3), 80.2 (C≡C), 101.1 (C≡C), 114.2 (CH), 114.7 (C), 132.2 (C), 133.5 (CH), 160.4 (C), 162.9 (d, J_{CF} = 257.2 Hz, CF) ^{19}F NMR (282 MHz, $CDCl_3$): δ = -103.13. IR (ATR, cm^{-1})**:** $\tilde{\nu}$ = 2914 (w), 2847 (w), 2206 (w), 1604 (w), 1566 (w), 1513 (w), 1467 (w), 1413 (w), 1376 (w), 1343 (w), 1292 (w), 1249 (w), 1170 (w), 1105 (w), 1025 (w), 944 (w), 821 (w), 792 (w), 718 (w), 660 (w), 643 (w), 628 (w), 594 (w), 531 (m). MS (EI, 70 eV); *m/z* (%) = 634 (70) $[M]^+$, 396 (15), 119 (25), 91 (25), 69 (10), 57 (14), 55 (11), 44 (100), 41 (15). HRMS (EI) calcd. for $C_{42}H_{28}F_2O_4$ $[M]^+$: 634.19502; found 634.197451.



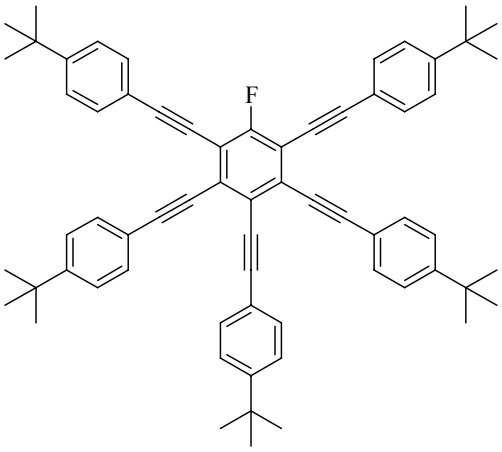
1-Fluoro-2,3,4,5,6-*penta*kis(4-methylphenylethynyl)benzene (32a): starting with **27** (100 mg, 0.14 mmol), 4-methylphenylacetylene **28b** (95 mg, 0.82 mmol), CuI (5 mol%), X-Phos (10 mol%), $Pd(OAc)_2$ (5 mol%), Cs_2CO_3 (5 eq) and DMF (5mL), **32a** was isolated as yellow solid (63 mg, 69%). Mp 102–104 °C. ^{1}H NMR (300 MHz, $CDCl_3$): δ = 2.32 (s, 15H, CH_3), 7.09-7.13 (m, 10H, ArH), 7.43-7.45 (m, 10H, ArH). ^{19}F NMR (282 MHz, $CDCl_3$): δ = -103.13. IR (ATR, cm^{-1})**:** $\tilde{\nu}$ = 3171 (w), 3077 (w), 3025 (w), 2952 (w), 2918(w), 2856 (w), 2729 (w), 2204 (w), 1903 (w), 1726 (w), 1604 (w), 1115 (w), 1069 (w), 1019 (w), 985 (w), 961 (w), 945 (w), 932 (w), 811 (s), 741 (w), 721 (w), 706 (w), 690 (w), 659 (w), 645 (w), 526 (w). MS (EI, 70 eV); *m/z* (%) = 666 (36) $[M]^+$, 397 (33), 396 (94), 394 (36), 331 (11), 329 (21), 277(15), 210 (15), 198 (11), 186 (16), 44 (100). HRMS (EI) calcd. for $C_{51}H_{35}F_1$ $[M]^+$: 666.27173; found 666.273441.



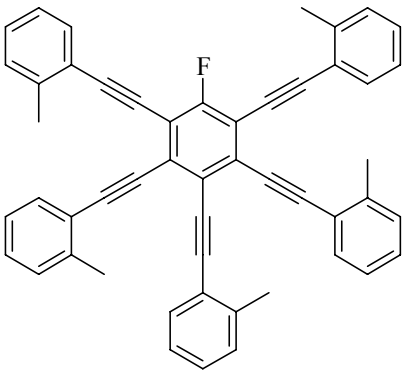
1-Fluoro-2,3,4,5,6-pentakis(4-methoyphenylethynyl)benzene (32b): starting with **27** (100 mg, 0.16 mmol), 4-methoxyphenylacetylene (**28c**) (108 mg, 0.82 mmol), CuI (5 mol%), X-Phos (10 mol %), $Pd(OAc)_2$ (5 mol %), Cs_2CO_3 (5 eq) and DMF (5mL), **32b** was isolated as yellow solid (94 mg, 78%). Mp 151–153 °C. ^{1}H NMR (300 MHz, $CDCl_3$): δ = 3.77 (s, 6H, OCH_3), 3.78 (s, 9H, OCH_3), 6.79-6.84 (m, 10H, ArH), 7.45-7.48 (m, 10H, ArH). ^{13}C NMR (75.4 MHz, $CDCl_3$): δ = 55.4 ($2OCH_3$), 55.5 ($2OCH_3$), 80.5 (C≡C), 100.1 (C≡C), 100.2 (C≡C), 114.1 (CH), 114.2 (CH), 115.0 (C), 115.5 (C), 116.6 (C), 133.2 (CH), 133.3 (CH), 160.0 (C), 160.2 (C), 160.9*. ^{19}F NMR (282 MHz, $CDCl_3$): δ = -103.84. IR (ATR, cm^{-1})**:** $\tilde{\nu}$ = 3045 (w), 2999 (w), 2954 (w), 2835 (w), 2536 (w), 2203 (w), 1715 (w), 1603 (m), 1565 (w), 1505 (s), 1455 (m), 1413 (w), 1361 (w), 1288 (m), 1243 (s), 1167 (s), 1104 (m), 1024 (m), 932 (m), 825 (s), 717 (w), 665 (w), 642 (w), 627 (w), 531 (m). MS (EI, 70 eV); *m/z* (%) = 746 (100) $[M]^+$, 135 (10), 57 (15). HRMS (EI) calcd. for $C_{51}H_{35}O_5F$ $[M]^+$: 746.24630; found 746.248188. *: CF-group not resolved in ^{13}C-NMR



1-Fluoro-2,3,4,5,6-pentakis(4-*tert*-butylphenylethynyl)benzene (32c): starting with **27** (100 mg, 0.16 mmol), 4-butylphenylacetylene **28d** (129 mg, 0.82 mmol), CuI (5 mol%), X-Phos (10 mol%), $Pd(OAc)_2$ (5 mol%), Cs_2CO_3 (5 eq) and DMF (5mL), **32c** was isolated as yellow solid (96 mg, 68%). Mp 161–163 °C. ^{1}H NMR (300 MHz, $CDCl_3$): δ = 1.28 (s, 27H, CH_3), 1.29 (s, 9H, CH_3), 1.48 (s, 9H, CH_3), 7.31-7.35 (m, 10H, ArH), 7.48-7.51 (m, 10H, ArH).). ^{13}C NMR (75.4 MHz, $CDCl_3$): δ = 31.2 ($(CH_3)_3C$), 34.9 ($C(CH_3)_3$) 80.3 (C≡C), 80.9 (C≡C), 83.3 (C≡C), 86.2 (C≡C), 89.8 (C≡C), 100.3 (C≡C), 100.5 (C≡C), 119.8 (C), 120.1 (C), 125.5 (CH), 125.6 (CH), 131.5 (C), 131.6 (C), 131.7 (C), 152.0 (C) 152.4 (C).* ^{19}F NMR (282 MHz, $CDCl_3$): δ = -103.10. IR (ATR, cm^{-1})**:** $\tilde{\nu}$ = 3082 (w), 3033 (w), 2958 (w), 2902 (w), 2866 (w), 2205 (w), 1605 (w), 1513 (w), 1504 (w), 1462 (w), 1406 (w), 1361 (w), 1267 (w), 1201 (w), 1107 (w), 1016 (w), 934 (w), 876 (w), 831 (m),736 (w), 665 (w), 614 (w), 559 (w). MS (EI, 70 eV); *m/z* (%) = 876 (17) $[M]^+$, 207 (11), 97 (10), 69 (23), 44 (100). HRMS (EI): calcd for $C_{66}H_{65}F$ $[M]^+$: 876.50648; found 876.513743. Anal. Calcd for $C_{66}H_{65}F_1$: C, 90.37. H, 7.47 Found: C, 90.35. H, 6.70 *: CF-group not resolved in ^{13}C-NMR



1-Fluoro-2,3,4,5,6-pentakis(2-methylphenylethynyl)benzene (32d): starting with **27** (100 mg, 0.16 mmol), 2-methylphenylacetylene **28g** (95 mg, 0.82 mmol), CuI (5 mol%), X-Phos (10 mol%), $Pd(OAc)_2$ (5 mol %), Cs_2CO_3 (5 eq) and DMF (5mL), **32d** was isolated as yellow solid (59 mg, 55%). Mp 128–130 °C. ^{1}H NMR (300 MHz, $CDCl_3$): δ = 2.37 (s, 3H, CH_3), 2.39 (s, 6H, CH_3), 2.46 (s, 6H, CH_3), 7.04-7.17 (m, 15H, ArH), 7.21-7.49 (m, 5H, ArH). ^{13}C NMR (75.4 MHz, $CDCl_3$): δ = 20.8, 20.9, 21.0, 29.7 (CH_3), 85.2 (C≡C), 85.3 (C≡C), 90.7 (C≡C), 99.1 (C≡C), 122.4 (CH), 122.6 (CH), 125.5 (CH), 1125.6 (CH), 129.1 (d, *J* = 3.85 Hz, C), 132.2 (C), 132.4 (C), 140.6 (C), 140.8 (C), 140.9 (C), 155.9 (C) 157.9 (d, *J* = 233 Hz, CF). ^{19}F NMR (282 MHz, $CDCl_3$): δ = -102.35. MS (EI, 70 eV): *m/z* (%) = 666 (100) $[M]^+$. HRMS (EI) calcd. for $C_{51}H_{35}F_1$ $[M]^+$: 666.271173; found 666.271113.

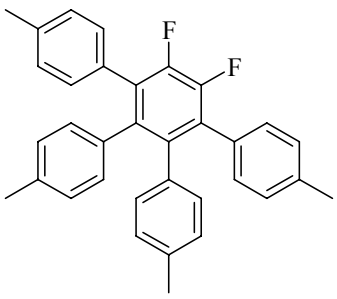


7.9 Synthesis of Fluorinated polyarenes by Suzuki-Miyaura cross coupling reaction

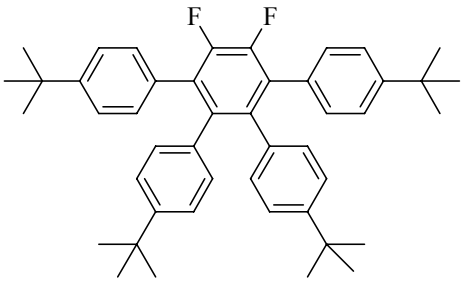
General Procedure for Poly Suzuki cross coupling Reaction

The reaction was carried out in a pressure tube. To a suspension **21, 23, 25, 27** (100 mg, 0.1 mmol), $Pd(PPh_3)_4$ (10 mol %), arylboronic acid (1.1 eq per bromine atom) and Cs_2CO_3 (5eq) in dioxin, was added. The mixture was heated at the indicated temperature (60-100 °C) for the indicated period of time (60-100h). The reaction mixture was diluted with water and extracted with CH_2Cl_2 (3 x 25ml). The combined organic layers were dried over Na_2SO_4, filtrated and the filtrate was concentrated in vacuo the residue was purified by flash chromatography (silica gel, ethyl acetate / heptanes)

1,2-Difluoro-3,4,5,6-*tetra*kis(4-methxphenyl)benzene (33a): Starting with **21** (100 mg, 0.16 mmol), $Pd(PPh_3)_4$ (10 mol%), Cs_2CO_3 (5eq) and *p*-tolylboronic acid (130 mg, 0.96 mmol), **33a** was isolated as a white solid (61 mg, 80%). Mp 164–166°C. ^{1}H NMR (300 MHz, $CDCl_3$): δ = 2.03 (s, 6H, $2CH_3$), 2.19 (s, 6H, $2CH_3$), 6.51-6.54 (m, 8H, ArH), 6.59-6.61 (m, 8H, ArH). ^{19}F NMR (282 MHz, $CDCl_3$): δ = -140.2. ^{13}C NMR (75.4 MHz, $CDCl_3$): δ = 20.0, 20.1 (CH_3), 126.6, 127.3 (CH), 128.8 (t, J = 6.1 Hz, C), 129.4 (CH), 129.9 (C), 130.1 (CH), 134.1 (CH), 134.5 (C), 135.6 (CH), 136.4 (t, J = 2.7 Hz, C), 146.3 (dd, J_{CF} = 247.9, 16.3 Hz, CF). IR (KBr): $\tilde{\nu}$ = 3023, 2921, 2856, 1605, 1558, 1518, 1460 (w), 1443, 1398 (m), 1348, 1260, 1202, 1185, 1176, 1109 (w), 1094, 1020, 913, 840 (m), 806, 754 (s), 726 (m), 684, 641, 576 (w), 539 (m), 528 (s) cm^{-1}. GC-MS (EI, 70 eV); *m/z* (%) = 474 (100) $[M]^+$, 459 (12), 419 (6), 367 (5), 207 (10), 44 (10). HRMS (EI) calcd. for $C_{34}H_{28}F_2$ $[M]^+$: 474.21536; found 474.215243.

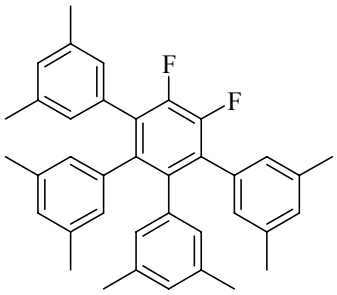


1,2-Difluoro-3,4,5,6-tetrakis(4-*tert*-butylphenyl)benzene (33b): Starting with **21** (100 mg, 0.16 mmol), $Pd(PPh_3)_4$ (10 mol%), Cs_2CO_3 (5eq) and 4-tert-phenylboronic acid (113 mg, 0.96 mmol), **33b** was isolated as a white solid (88 mg, 85%). Mp 203–205°C. ^{1}H NMR (300 MHz, $CDCl_3$): δ = 1.03 (s, 18H, $6CH_3$), 1.17 (s, 18H, $6CH_3$), 6.52 (d, 4H, J = 8.4Hz, ArH), 6.76 (d, 4H, J = 8.4Hz, ArH), 6.93 (d, 4H, J = 8.4Hz, ArH), 7.09 (d, 4H, J = 8.4Hz, ArH). ^{19}F NMR (282 MHz, $CDCl_3$): δ = -140.6. ^{13}C NMR (75.4 MHz, $CDCl_3$): δ = 31.14, 31.22 (CH_3), 34.12, 34.41 (C), 123.4, 124.3 (CH), 1298.8 (t, J = 6.6 Hz,

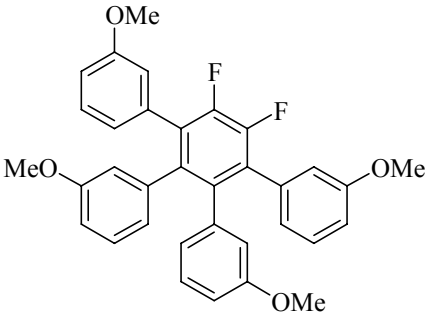


C), 130.3, 131.0 (CH), 135.6 (C), 137.5 (t, J = 2.6 Hz, C), 147.0 (dd, J = 248.4, 16.6 Hz, CF), 148.4, 149.7 (C). IR (KBr): $\tilde{\nu}$ = 3030, 2949, 2922, 2853 (m), 1731, 1610, 1513 (m), 1446 (s), 1392, 1362 (m), 1313 (w), 1268 (m), 1202, 1120, 1087, 1019, 853 (m), 834 (s), 779, 720, 677,568 (m) cm^{-1}. MS (EI, 70 eV); *m/z* (%) = 642 (100) $[M^+]$, 628 (22), 627 (51), 306 (22), 57 (82). HRMS (EI) calcd. for $C_{46}H_{52}F_2$ $[M]^+$: 642.40316; found 642.40384.

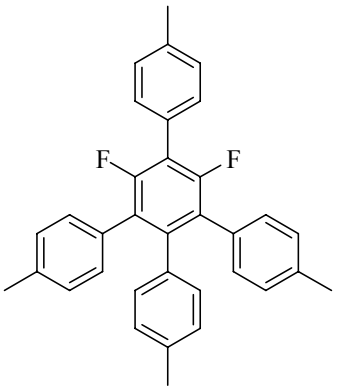
1,2-Difluoro-3,4,5,6-tetrakis(3,5-dimethylphenyl)benzene (33c): Starting with **21** (100 mg, 0.16 mmol), $Pd(PPh_3)_4$ (10 mol%), Cs_2CO_3 (5eq) and 3,5-dimethylphenylboronic acid (144 mg, 0.96 mmol), **33c** was isolated as a white solid (67 mg, 78%). Mp 163–165 °C. ^1H NMR (300 MHz, $CDCl_3$): δ = 1.89 (s, 12H, $4CH_3$), 2.10 (s, 12H, $4CH_3$), 6.30, 6.39, 6.66, 6.70 (s, 12H, ArH). ^{19}F NMR (282 MHz, $CDCl_3$): δ = -140.7. ^{13}C NMR (75.4 MHz, $CDCl_3$): δ = 20.9 (CH_3), 21.1 (CH_3), 127.0, 128.4, 128.6, 129.2 (CH), 129.8 (t, J = 8.7 Hz, C), 131.7 (C), 135.5, 136.6 (C), 137.7 (t, J = 2.8 Hz, C), 138.1 (C), 147.1 (dd, J = 247.3, 15.9 Hz, C). IR (KBr): $\tilde{\nu}$ = 3023, 2916, 2851, 2723 (w), 1601, 1435, 1375 (m), 1302, 1261, 1219, 1163 (w), 1125, 1034 (m), 962, 910 (w), 859 (m), 843 (s), 813, 763 (m), 699 (s), 676 (m), 616, 559 (m) cm^{-1}. GC-MS (EI, 70 eV); *m/z* (%) = 530 (100) $[M]^+$, 426 (4), 207 (8), 44 (10). HRMS (EI) calcd. for $C_{38}H_{36}F_2$ $[M^+]$: 530.27796; found 530.278685.



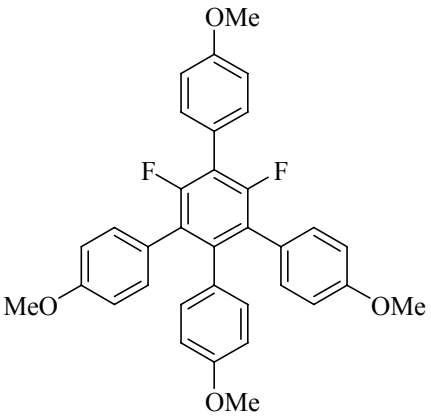
1,2-Difluoro-3,4,5,6-*tetr*akis(3-methoxyphenyl)benzene (33d) Starting with **21** (100 mg, 0.16 mmol), $Pd(PPh_3)_4$ (10 mol%), Cs_2CO_3 (5eq) and 3-methoxyphenylboronic acid (145 mg, 0.96 mmol), **33d** was isolated as a white solid (62 mg, 72%). Mp 136–138°C. ^1H NMR (300 MHz, $CDCl_3$): δ = 3.77 (s, 6H, OCH_3), 3.79 (s, 6H, OCH_3), 6.84-6.90 (m, 6H), 6.92-6.97 (m, 6H), 7.01-7.03 (m, 4H). ^{19}F NMR (282 MHz, $CDCl_3$): δ = -140.24. ^{13}C NMR (75.4 MHz, $CDCl_3$): δ = 55.3, 55.4 (OCH_3), 110.9, 114.2, 114.3, 120.5, 122.8 (CH), 123.7 (C), 126.4, 127.7 (CH), 128.0 (t, J = 2.7 Hz, C), 128.3 (C), 133.4 (C), 150.6 (dd, J = 244.7, 13.6 Hz, C),158.6, 159.9 (C). IR (KBr): $\tilde{\nu}$ = 3032, 2960, 2926, 2904, 2853 (m), 1601, 1519 (w), 1474, 1439, 1392, 1361 (m), 1260, 1096, 1017 (s), 946, 928, 879 (m), 831, 797 (s), 733, 720, 679,564 (m) cm^{-1}. GC-MS (EI, 70 eV); *m/z* (%) = 538 (100) $[M]^+$. HRMS (EI) calcd. for $C_{34}H_{28}O_4F_2$ $[M]^+$: 538.19557; found 538.19345.



1,3-Difluoro-2,4,5,6-tetrakis(4-methylphenyl)benzene (34a): Starting with **23** (100 mg, 0.16 mmol), $Pd(PPh_3)_4$ (10 mol%), Cs_2CO_3 (5eq) and *p*-tolylboronic acid (130 mg, 0.96 mmol), **34a** was isolated as a white solid (68 mg, 78%). Mp 166–168 °C. ^{1}H NMR (300 MHz, $CDCl_3$): δ = 2.08 (s, 3H, CH_3), 2.19 (s, 6H, CH_3), 2.33 (s, 3H, CH_3), 6.56-6.69 (m, 4H, ArH), 6.83-6.94 (m, 8H, ArH), 7.21-7.57 (m, 4H, ArH). ^{13}C NMR δ = 21.2 (CH_3), 21.3 (CH_3), 21.4 (CH_3), 112.(C), 116.9 (C), 124.4 (d, J = 4.8 Hz, C), 125.4 (d, J = 8.9 Hz, C), 126.7 (C), 127.9 (CH), 127.9 (CH), 128.4 (CH), 128.9 (CH), 130.4 (CH), 130.8 (CH), 130.9 (C), 131.0 (CH), 131.4 (C), 134.6 (d, J = 2.6 Hz, C), 135.6 (C), 136.4 (C), 137.9 (C), 142.0 (C), 156.1 (d, J_{CF} = 248.6 Hz, CF). IR (KBr): $\tilde{\nu}$ = 3084 (w), 3051 (w), 2958 (w), 2919 (w), 2867 (w), 2850 (w), 1899 (w), 1722 (w), 1657 (w), 1607 (w), 1579 (w), 1518 (w), 1430 (w), 1393 (w), 1360 (w), 1310 (w), 1262 (w), 1213 (w), 1195 (w), 1130 (w), 1111 (w), 1070 (w), 1030 (w), 960 (w), 926 (w), 891 (w), 841 (w), 834 (w), 784 (w), 744 (w), 685 (w), 664 (w), 587 (m), 566 (w), 536 (w) cm^{-1}. GC-MS (EI, 70 eV); *m/z* (%) = 474 (100) $[M]^+$. HRMS (EI) calcd. for $C_{34}H_{28}F_2$ $[M]^+$: 474.21591; found 474.20942.

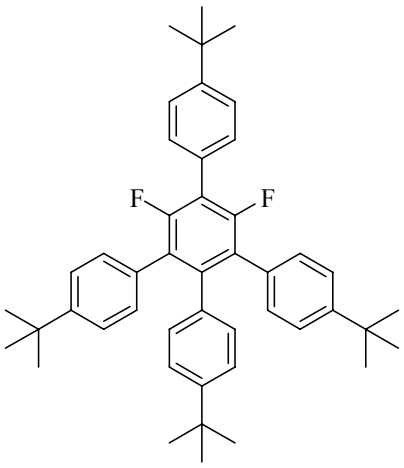


1,3-Difluoro-2,4,5,6-tetrakis(4-methoxyphenyl)benzene (34b): Starting with **23** (100 mg, 0.16 mmol), $Pd(PPh_3)_4$ (10 mol%), Cs_2CO_3 (5eq) and 4-methoxyphenylboronic acid (145 mg, 0.96 mmol), **34b** was isolated as a white solid (69 mg, 80%). Mp 236–238 °C . ^{1}H NMR (300 MHz, $CDCl_3$): δ = 3.60 (s, 3H, OCH_3), 3.68 (s, 6H, $2OCH_3$), 3.78 (s, 3H, OCH_3), 6.42-6.46 (m, 2H, ArH), 6.59-6.71 (m, 6H, ArH), 6.89-6.94 (m, 6H, ArH), 7.42-7.46 (m, 2H, ArH). ^{13}C NMR (75.4 MHz, $CDCl_3$): δ = 55.0 (OCH_3), 55.1 (OCH_3), 55.3 (OCH_3), 112.1, 112.7, 113.2, 113.7 (CH), 117.6 (d, ^3J = 3.89 Hz, C), 120.5 (d, ^3J = 8.3 Hz, C), 126.7 (C), 131.7 (CH), 132.0 (CH), 132.4 (CH), 140.4 (d, J = 2.8 Hz, C), 141.7 (C), 150.5 (d, J = 20.6 Hz, C), 154.3 (C), 154.6 (C), 156.1 (C), 158.3 (C),161.0 (d, J_{CF} = 241.9 Hz, CF). IR (KBr): $\tilde{\nu}$ = 3000, (w), 2959 (w), 2916 (w), 2838 (w), 1609 (w), 1575 (w), 1536 (w), 1462 (w), 1433 (w), 1398 (w), 1357 (w), 1303 (w), 1289 (w), 1241 (m), 1199 (w), 1174 (w), 1108, (w), 1031 (m), 959 (w), 894 (w), 829 (w), 790 (w), 747 (w), 696 (w), 664 (w), 595 (w) cm^{-1}.

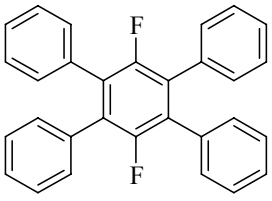


GC-MS (EI, 70 eV); *m/z* (%) = 538 (100) $[M]^+$, 536 (17), 131 (10), 71 (10), 69 (40), 57 (17), 55 (14), 44 (36), 43 (21), 41 (14). HRMS (EI) calcd for $C_{34}H_{28}F_2O_4$ $[M]^+$: 538.19502; found 538.195178.

1,3-Difluoro-2,4,5,6-tetrakis(4-*tert*-butylphenyl)benzene (34c): Starting with **23** (100 mg, 0.16 mmol), $Pd(PPh_3)_4$ (10 mol%), Cs_2CO_3 (5eq) and 4-*ter*t-phenylboronic acid (113 mg, 0.96 mmol), **34c** was isolated as a white solid (75 mg, 73%). Mp 166–168 °C. ^{1}H NMR (300 MHz, $CDCl_3$): δ = 1.06 (s, 9H, CH_3), 1.16 (s, 18H, CH_3), 6.55 (d, *J* = 8.39 Hz, 2H ArH)-6.81(d, *J* = 8.39 Hz, 2H, ArH), 6.91 (d, *J* = 8.39 Hz, 4H, ArH), 7.08 (d, *J* = 8.39 Hz, 4H, ArH), 7.38-7.47 (m, 4H, ArH). ^{19}F NMR (282 MHz, $CDCl_3$): δ = -115.8. ^{13}C NMR (75.4 MHz, $CDCl_3$): δ = 31.1 (CH_3), 31.2 (CH_3), 31.3 (CH_3), 34.2 (C), 34.4 (C), 34.6 (C) 116.3 (d, *J* = 22.6 Hz, C), 123.6 (CH), 124.3 (CH), 125.1 (CH), 125.5 (d, *J* = 22.6 Hz, C), 126.7 (C), 130.2 (CH), 130.6 (CH), 130.8 (CH), 131.4 (C), 134.8 (t, *J* = 2.7 Hz, C), 142.5 (t, *J* = 4.0 Hz, C), 148.9 (C), 149.5 (C), 150.9 (C), 156.0 (dd, J_{CF} = 246.9, 8.0 Hz, CF). IR (KBr): $\tilde{\nu}$ = 3089, (w), 3056 (w), 2960 (m), 2902 (w), 2866 (w), 1904 (w), 1786 (w), 1737 (w), 1661 (w), 1604 (w), 1573 (w), 1520 (w), 1460 (w), 1433 (w), 1392 (w), 1320 (w), 1267 (w), 1235 (w), 1203 (w), 1189 (w), 1120 (w), 1100, (w), 1031 (m), 1020 (w), 964 (w), 922 (w), 897 (w), 854 (w), 833 (m), 797 (m), 742 (w), 698 (w), 664 (w), 562 (m) cm^{-1}. GC-MS (EI, 70 eV); *m/z* (%) = 642 (100) $[M]^+$, 628 (20), 627 (43), 306 (18), 91 (82). HRMS (EI) calcd. for $C_{46}H_{52}F_2$ $[M]^+$: 642.403161; found 642.402961.

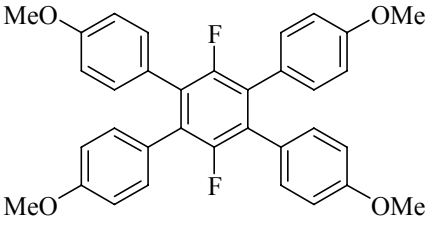


1,4-Difluoro-2,3,5,6-tetrakis(phenyl)benzene (35a): Starting with **25** (100 mg, 0.16 mmol), $Pd(PPh_3)_4$ (10 mol%), Cs_2CO_3 (5eq) and phenylboronic acid (116 mg, 0.96 mmol), **35a** was isolated as a white solid (51 mg, 76%). Mp 273–275 °C. ^{1}H NMR (300 MHz, $CDCl_3$): δ = 7.08-7.17 (m, 20H, ArH). ^{13}C NMR (75.4 MHz, $CDCl_3$): δ = 127.7 (CH), 127.8 (CH), 129.3 (dd, *J* = 13.4, 9.9 Hz, C), 130.9 (CH), 133.5 (C), 152.6 (d, J_{CF} = 243.0, CF) IR (KBr): $\tilde{\nu}$ = 3085 (w), 3059 (w), 3024 (w), 2918 (w), 2849 (w), 1953 (w), 1884 (w), 1810 (w), 1764 (w), 1599 (w), 1578 (w), 1502 (w), 1455 (w), 1438 (w), 401 (m), 1301 (w), 1183 (w), 1162 (w), 1117 (w), 1081 (w), 1068 (w), 1030 (w), 1000 (w), 966 (w), 924 (w), 907 (w), 870 (m), 854 (w), 776 (m), 755 (m), 740 (m), 693 (s), 672 (m), 660 (m), 612 (w), 540 (m) cm^{-1}. GC-MS (EI, 70

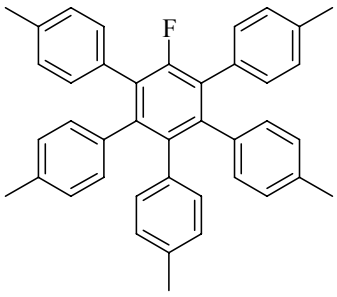


eV); *m/z* (%) = 418 $[M]^+$, (100), 403 (10). HRMS (EI, 70 eV) calcd. for $C_{30}H_{20}F_2$ $[M]^+$: 418.15276; found 418.274205.

1,4-Difluoro-2,3,5,6-*tetra*kis(4-methoxyphenyl)benzene (35b): Starting with **25** (100 mg, 0.16 mmol), $Pd(PPh_3)_4$ (10 mol%), Cs_2CO_3 (5eq) and 4-methoxyphenylboronic acid (145 mg, 0.96 mmol), **35b** was isolated as a white solid (69 mg, 80%). Mp 213–215 °C. ^{1}H NMR (300 MHz, $CDCl_3$): δ = 3.70 (s, 3H, OCH_3), 6.69 (td, J = 8.7 Hz, 8H, ArH), 7.00 (td, J = 8.7 Hz, 8H, ArH). ^{13}C NMR (75.4 MHz, $CDCl_3$): δ = 55.2 (OCH_3), 113.3 (CH), 126.0 (C), 128.5 (d, J = 21.9 Hz, C), 132.1 (CH), 153.3 (d, J_{CF} = 244.4 Hz, CF), 158.6 (C). IR (KBr): $\tilde{\nu}$ = 3007 (w), 2958 (w), 2930 (w), 2847 (w), 2836 (w), 1608 (w), 1579 (w), 1518 (w), 1461 (w), 1430 (w), 1391 (w), 1284 (w), 1246 (m), 1175 (w), 1150 (w), 1110 (w), 1071 (w), 1027 (m), 934 (w), 875 (w), 847 (w), 822 (m), 787 (w), 775 (w), 734 (w), 702 (w), 677 (w), 638 (w), 593 (w), 563 (w), 538 (w) cm^{-1}. GC-MS (EI, 70 eV); *m/z* (%) = 538 (100) $[M]^+$, 281 (10), 231 (12), 181 (26), 131 (30), 119 (25), 108 (22), 71 (17), 55 (27), 44 (43), 43 (28), 41 (31). HRMS (EI) calcd. for $C_{34}H_{28}F_2O_4$ $[M]^+$: 538.19502; found 538.194659.



1-Fluoro-2,3,4,5,6-*penta*kis(4-methylphenyl)benzene (36a): Starting with **27** (100 mg, 0.16 mmol), $Pd(PPh_3)_4$ (10 mol%), Cs_2CO_3 (5eq) and *p*-tolylboronic acid (130 mg, 0.96 mmol), **36a** was isolated as a white solid (54 mg, 72%). ^{1}H NMR (300 MHz, $CDCl_3$): δ = 2.03 (s, 3H, CH_3), 2.06 (s, 6H, CH_3), 2.19 (s, 6H, CH_3), 6.52-6.64 (m, 12H, ArH), 6.88-6.96 (m, 8H, ArH). ^{13}C NMR (75.4 MHz, $CDCl_3$): δ = 21.0 (CH_3), 21.1 (CH_3), 21.2 (CH_3) 127.5 (d, J = 15.0 Hz, CH), 127.9 (C), 128.2 (CH), 130.7 (CH), 131.1 (CH), 131.4 (CH), 132.1 (C), 134.4 (C), 134.9 (C), 136.1 (C), 136.3 (d, J = 2.8 Hz, C), 137.1 (d, J = 18.0 Hz, C), 137.3 (C), 141.7 (d, J = 3.2 Hz,C), 156.1 (d, J = 257.9 Hz, CF). ^{19}F NMR (282 MHz, $CDCl_3$): δ = -115.87. IR (ATR, cm^{-1})**:** $\tilde{\nu}$ = 3131 (w), 3047 (w), 2991 (w), 2919 (w), 2861 (w), 2730 (w), 1898 (w), 1789 (w), 1613 (w), 1585 (w), 1517 (w), 1446 (w), 1390 (w), 1319 (w), 1269 (w), 1212 (w), 1182 (w), 1144 (w), 1095 (w), 1021 (w), 940 (w), 848 (w), 800 (w), 740 (w), 704 (w), 669 (w), 630 (w), 578 (w), 532 (m). MS (EI, 70 eV); *m/z* (%) = 546 (74) $[M]^+$, 281 (10), 231 (14), 219 (11), 181 (24), 169 (21), 131 (31), 119 (28), 83 (12), 69 (100), 57 (22), 55 (20), 44 (72), 43 (31), 41 (23), 40 (40). HRMS (EI) calcd. for $C_{41}H_{35}F_1$ $[M]^+$: 546.27173; found 546.271731.



1-Fluoro-2,3,4,5,6-*penta*kis(4-methoxyphenyl)benzene (36b): Starting with **27** (100 mg, 0.16 mmol), $Pd(PPh_3)_4$ (10 mol%), Cs_2CO_3 (5eq) and 4-methoxyphenylboronic acid (145 mg, 0.96 mmol) **36b** was isolated as a white solid (67 mg, 78%). Mp 100–102 °C. ^{1}HNMR (300 MHz, $CDCl_3$): δ = 3.55 (s, 3H, OCH_3), 3.57 (s, 6H, OCH_3), 3.67 (s, 6H, OCH_3), 6.33-6.40 (m, 6H, ArH), 6.54-6.66 (m, 10H, ArH), 6.95-6.99 (m, 4H, ArH). ^{13}C NMR (75.4 MHz, $CDCl_3$): δ = 54.9 ($2OCH_3$), 55.1 (OCH_3), 112.3 (CH), 112.4 (CH), 113.0 (CH), 127.4 (C), 127.8 (d, J = 16.5 Hz, C), 131.8 (d, J = 2.8 Hz, C), 131.9 (CH), 132.5 (CH), 132.6 (C), 137.2 (d, J = 3.8 Hz, C), 141.4 (d, J = 3.2 Hz, C),155.0 (d, J = 256.0 Hz, CF) 156.9 (C), 157.3 (C), 157.9 (C), 158.1 (C), 162.5 (C). ^{19}F NMR (282 MHz, $CDCl_3$): δ = -115.84. IR (ATR, cm^{-1})**:** $\tilde{\nu}$ = 3034 (w), 2998 (w), 2954 (w), 2932 (w), 2835 (w), 1678 (w), 1608 (w), 1575 (w), 1514 (w), 1462 (w), 1424 (w), 1394 (w), 1322 (w), 1286 (w), 1241 (m), 1174 (m), 1108 (w), 1029 (w), 927 (w), 852 (w), 831 (w), 806 (m), 771 (w), 729 (w), 675 (w), 648 (w), 625 (w), 590 (w), 544 (m). MS (EI, 70 eV): *m/z* (%) = 626 (100) $[M]^+$, 231 (10), 181 (18), 169 (16), 131 (25), 119 (22), 69 (81), 44 (34). HRMS (EI) calcd. for $C_{41}H_{35}FO_5$ $[M]^+$: 626.24630; found 626.246476. Anal. Calcd for $C_{41}H_{35}F_1O_5$: C, 78.57. H, 5.63 Found: C, 78.59. H, 5.75.

Table 29. Crystal data and structure refinement for 4e

Identification code	4e
Empirical formula	$C_{24}H_{15}Cl$
Formula weight	338.81
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 = 24.956(14) Å α. = 90.00.
b = 4.293(2) Å	β = 98.943
c = 31.007(14) Å	γ = 90.00.
Volume	3282(3) $Å^3$
Z	8
Density (calculated)	1.371 Mg/m^3
Absorption coefficient	0.235mm^{-1}
F(000)	1408
Crystal size	0.46x 0.15x 0.14mm^3
Θ range for data collection	4.82 to 28.00°.
Index ranges	-31≤h≤32, -5≤k≤5, -40≤l≤40
Reflections collected	26598
Independent reflections	7784 [R(int) = 0.0453]
Completeness to Θ = 29.00°	99.6%
Absorption correction	0.89997-0.9679
Max. and min. transmission	0.900 and 0.968
Refinement method	Hydrogen site location: infrared from neighbouring sites
Data / restraints / parameters	5781 / 2 / 451
Goodness-of-fit on F^2	1.000
Final R indices [I>2σ(I)]	R1 = 0.0403, wR2 = 0.0892
R indices (all data)	R1 = 0.0673, wR2 = 0.0976
Largest diff. Peak and hole	0.207 and -0.221 e.$Å^{-3}$

Table 30. Crystal data and structure refinement for 4i

Identification code	4i
Empirical formula	$C_{26}H_{18}O_2$
Formula weight	362.40
Temperature	173 (2) K
Wavelength	0.71073 Å
Crystal system	Monoclinic
Space group (H.-M.)	´P 21´
Space group (Hall)	´P 2yb
Unit cell dimensions	a = 9.717(18) Å α = 90.00.
b = 6.861(14) Å	β = 95.15
c = 13.69(3) Å	γ = 90.00.
Volume	909 (4) $Å^3$
Z	2
Density (calculated)	1.324 Mg/m^3
Absorption coefficient	0.08mm^{-1}
F(000)	380
Crystal size	0.99x 0.21x 0.04mm^3
Θ range for data collection	4.21 to 30.00°.
Index ranges	-13≤h≤13, -9≤k≤4, -19≤l≤19
Reflections collected	10297
Independent reflections	3682 [R(int) = 0.0364]
Completeness to Θ = 29.00°	99.3%
Max. and min. transmission	0.9227 and 0.9967
Refinement method	Hydrogen site location: infrared from neighbouring sites
Data / restraints / parameters	3128 / 1 / 255
Goodness-of-fit on F^2	1.078
Final R indices [I>2σ(I)]	R1 = 0.0406, wR2 = 0.0989
R indices (all data)	R1 = 0.0522, wR2 = 0.10944
Largest diff. Peak and hole	0.300 and -0.221 e.$Å^{-3}$

Table 31. Crystal data and structure refinement for 10f

Identification code	10f
Empirical formula	$C_{14}H_{11}BrF_2O_2$
Formula weight	329.14
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 = 8.304 (5) Å α = 86.185
b = 8.382 (5) Å	β = 82.352
c = 9.533 (5) Å	γ = 80.395
Volume	647.7 (6) $Å^3$
Z	2
Density (calculated)	1.688 Mg/m^3
Absorption coefficient	3.19 mm^{-1}
F(000)	328
Crystal size	0.67x 0.37x 0.16 mm^3
Θ range for data collection	2.16 to 30.12°.
Index ranges	$-11\leq h\leq 11$, $-11\leq k\leq 9$, $-13\leq l\leq 13$
Reflections collected	13433
Independent reflections	3769 [R(int) = 0.0214]
Completeness to Θ = 29.00°	98.7%
Max. and min. transmission	0.224 and 0.629
Refinement method	Secondary atom site location: Difference Fourier map
Data / restraints / parameters	3446 / 0 / 174
Goodness-of-fit on F^2	1.047
Final R indices [I>2σ(I)]	R1 = 0.0254, wR2 = 0.0683
R indices (all data)	R1 = 0.0299, wR2 = 0.0701
Largest diff. Peak and hole	0.973 and -0.374 $e.Å^{-3}$

Table 32. Crystal data and structure refinement for 14f

Identification code	14f	
Empirical formula	$C_{16}H_{16}BrF$	
Formula weight	307.20	
Temperature	173(2) K	
Wavelength	0.71073 Å	
Crystal system	Orthorhombic	
Space group (H.-M.)	´ p b c a´	
Space group (Hall)	-P 2ac 2ab	
Unit cell dimensions	a = 18.472(5) Å	α = 90.000(5)°
	b = 6.058(5) Å	β = 90.00(5)°
	c = 24.298(5) Å	γ = 90.00(14)°.
Volume	2719(2) $Å^3$	
Z	8	
Density (calculated)	1.501 Mg/m^3	
Absorption coefficient	3.014 mm^{-1}	
F(000)	1248	
Crystal size	0.99 x 0.65 x 0.20 mm^3	
Θ range for data collection	2.20 to 28.00°.	
Index ranges	-24≤h≤24, -4≤k≤8, -32≤l≤32	
Reflections collected	24785	
Independent reflections	3270 [R(int) = 0.0522]	
Completeness to Θ = 29.00°	99.9%	
Absorption correction	*´multi-scan´*	
Max. and min. transmission	0.1543 and 0.5839	
Data / restraints / parameters	2573 / 0 / 166	
Goodness-of-fit on F^2	1.090	
Final R indices [I>2σ(I)]	R1 = 0.0548, wR2 = 0.1131	
R indices (all data)	R1 = 0.0782, wR2 = 0.1212	
Largest diff. peak and hole	0.935 and -0.507 $e.Å^{-3}$	

Table 33. Crystal data and structure refinement for 13c

Identification code	13c	
Empirical formula	$C_{22}H_{20}FO_2$	
Formula weight	335.38	
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 = 7.1559 (7) Å	α = 78.858
	b = 7.7609 (8) Å	β = 85.856
	c = 15.8149 (6) Å	γ = 82.055
Volume	852.54 (14) $Å^3$	
Z	2	
Density (calculated)	1.306 Mg/m^3	
Absorption coefficient	11.53mm^{-1}	
F(000)	354	
Crystal size	0.70x 0.22x 0.02 mm^3	
Θ range for data collection	3.22 to 28.99°.	
Index ranges	-9≤h≤9, -10≤k≤10, -21≤l≤21	
Reflections collected	16675	
Independent reflections	4501 [R(int) = 0.0496]	
Completeness to Θ = 29.00°	99.1%	
Absorption correction	*multi-scan*	
Max. and min. transmission	0.9399 and 0.9982	
Data / restraints / parameters	2836 / 0 / 255	
Goodness-of-fit on F^2	1.011	
Final R indices [I>2σ(I)]	R1 = 0.0495, wR2 = 0.1258	
R indices (all data)	R1 = 0.0906, wR2 = 0.1390	
Largest diff. Peak and hole	0.363 and -0.221 e.$Å^{-3}$	

Table 34. Crystal data and structure refinement for 17b

Identification code	17b
Empirical formula	$C_{20}H_{17}F$
Formula weight	276.34
Temperature	150 K
Wavelength	0.71073 Å
Crystal system	Monoclinic
Space group (H.-M.)	P2 (1)/C
Unit cell dimensions	a = 7.0936 (3) Å α = 90.00.
b = 11.7294 (3) Å	β = 96.539
c = 17.3372 (7) Å	γ = 90.00
Volume	1433.13 (9) $Å^3$
Z	4
Density (calculated)	1.281 Mg/m^3
Absorption coefficient	0.08 mm^{-1}
F(000)	584
Crystal size	0.48x 0.28x 0.26 mm^3
Θ range for data collection	2.1 to 29.7°.
Index ranges	-9≤h≤9, -16≤k≤16, -23≤l≤23
Reflections collected	27058
Independent reflections	3871 [R(int) = 0.034]
Completeness to Θ = 29.00°	99.7%
Refinement method	Hydrogen site location: infrared from neighbouring sites
Data / restraints / parameters	2795 / 0 / 192
Goodness-of-fit on F^2	0.963
Final R indices [I>2σ(I)]	R1 = 0.0363, wR2 = 0.0928
R indices (all data)	R1 = 0.0548, wR2 = 0.0968
Largest diff. Peak and hole	0.238 and -0.175 $e.Å^{-3}$

Table 35. Crystal data and structure refinement for 24

Identification code	24	
Empirical formula	$C_5I_4F_2$	
Formula weight	617.66	
Temperature	173(2) K	
Wavelength	0.71073 Å	
Crystal system	tetragonal	
Space group (H.-M.)	P -41/a	
Space group (Hall)	´ -1 4ad´	
Unit cell dimensions	a = 21.0421 (8) Å	α = 90.0000
	b = 21.0421 (8) Å	β = 90.0000
	c = 9.7438 (6) Å	γ = 90.0000
Volume	4314.3 (3) $Å^3$	
Z	16	
Density (calculated)	3.804 Mg/m^3	
Absorption coefficient	11.53 mm^{-1}	
F(000)	4256	
Crystal size	0.37x 0.25x 0.21 mm^3	
Θ range for data collection	5.476 to 65.284°.	
Index ranges	-30≤h≤31, -30≤k≤31, -14≤l≤12	
Reflections collected	18097	
Independent reflections	3864 [R(int) = 0.0266]	
Completeness to Θ = 29.00°	99.0%	
Absorption correction	*numerical*	
Max. and min. transmission	0.1000 and 0.1957	
Data / restraints / parameters	3583 / 0 / 110	
Goodness-of-fit on F^2	1.122	
Final R indices [I>2σ(I)]	R1 = 0.0213, wR2 = 0.0423	
R indices (all data)	R1 = 0.0247, wR2 = 0.0431	
Largest diff. Peak and hole	0.902 and -0.931 e.$Å^{-3}$	

Table 36. Crystal data and structure refinement for 26

Identification code	26
Empirical formula	$C_6I_4F_2$
Formula weight	617.66
Temperature	150 K
Wavelength	0.71073 Å
Crystal system	Monoclinic
Space group (H.-M.)	P2 (1)
Unit cell dimensions	a = 8.9948 (8) Å α = 90.00
b = 4.3318 (3) Å	β = 101.428
c = 13.7958 (12) Å	γ = 90.00.
Volume	526.88 (8) $Å^3$
Z	2
Density (calculated)	3.893 Mg/m^3
Absorption coefficient	11.80mm^{-1}
F(000)	532
Crystal size	0.40x 0.13x 0.06 mm^3
Θ range for data collection	1.5 to 27.2°.
Index ranges	-11≤h≤11, -5≤k≤5, -17≤l≤17
Reflections collected	8124
Independent reflections	2238 [R(int) = 0.0777]
Completeness to Θ = 29.00°	99.9%
Absorption correction	*k* = -5to 5
Max. and min. transmission	0.069 and 0.6407
Refinement method	Secondary atom site location: Difference Fourier map
Data / restraints / parameters	2147 / 1 / 109
Goodness-of-fit on F^2	1.062
Final R indices [I>2σ(I)]	R1 = 0.0395, wR2 = 0.1011
R indices (all data)	R1 = 0.0415, wR2 = 0.1029
Largest diff. Peak and hole	1.839 and -1.793 e.$Å^{-3}$

Table 37. Crystal data and structure refinement for 28

Identification code	28	
Empirical formula	$C_6I_4F_2$	
Formula weight	617.66	
Temperature	173(2) K	
Wavelength	0.71073 Å	
Crystal system	Monoclinic	
Space group (H.-M.)	P 21/n	
Space group (Hall)	´ -P 2yn	
Unit cell dimensions	a = 7.7983 (5) Å	α = 90.00
	b = 5.2394 (3) Å	β = 101.625
	c = 13.2812 (7) Å	γ = 90.00.
Volume	531.52 (6) $Å^3$	
Z	2	
Density (calculated)	3.859 Mg/m^3	
Absorption coefficient	11.699 mm^{-1}	
F(000)	532	
Crystal size	0.22x 0.20x 0.10 mm^3	
Θ range for data collection	3.13 to 29.00°.	
Index ranges	-10≤h≤10, -7≤k≤6, -18≤l≤16	
Reflections collected	4913	
Independent reflections	1388 [R(int) = 0.0212]	
Completeness to Θ = 29.00°	98.4%	
Absorption correction	*multi-scan*	
Max. and min. transmission	0.1828 and 0.3875	
Data / restraints / parameters	1286 / 0 / 55	
Goodness-of-fit on F^2	1.0099	
Final R indices [I>2σ(I)]	R1 = 0.0166, wR2 = 0.0358	
R indices (all data)	R1 = 0.0192, wR2 = 0.0363	
Largest diff. Peak and hole	0.534 and -0.775 $e.Å^{-3}$	

Table 38. Crystal data and structure refinement for 30

Identification code	30	
Empirical formula	C_5I_5F	
Formula weight	725.56	
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 = 8.5263 (3) Å	α = 96.8430
	b = 9.0042 (3) Å	β = 105.5000
	c = 15.9132 (6) Å	γ = 90.0580
Volume	1168.19 (7) $Å^3$	
Z	4	
Density (calculated)	4.125 Mg/m^3	
Absorption coefficient	13.275 mm^{-1}	
F(000)	1240	
Crystal size	0.28x 0.04x 0.04 mm^3	
Θ range for data collection	1.34 to 30.06°.	
Index ranges	-12≤h≤11, -12≤k≤12, -22≤l≤22	
Reflections collected	24078	
Independent reflections	6734 [R(int) = 0.0252]	
Completeness to Θ = 29.00°	98.5%	
Absorption correction	*multi-scan*	
Max. and min. transmission	0.1186 and 0.6188	
Data / restraints / parameters	5518 / 0 / 218	
Goodness-of-fit on F^2	1.011	
Final R indices [I>2σ(I)]	R1 = 0.0229, wR2 = 0.0382	
R indices (all data)	R1 = 0.0361, wR2 = 0.0404	
Largest diff. Peak and hole	1.075 and -0.977 $e.Å^{-3}$	

Table 39. Crystal data and structure refinement for 38a

Identification code	38a	
Empirical formula	$C_{41}H_{35}F_1$	
Formula weight	546.47	
Temperature	150(2) K	
Wavelength	0.71073 Å	
Crystal system	Triclinic	
Space group (H.-M.)	P-1	
Unit cell dimensions	a = 10.9740 (5) Å	α = 91.08
	b = 12.4164 (7) Å	β = 104.89
	c = 13.7056 (7) Å	γ = 105.28.
Volume	1733.43 (15) $Å^3$	
Z	2	
Density (calculated)	1.121 Mg/m^3	
Absorption coefficient	0.067mm^{-1}	
F(000)	623	
Crystal size	0.40x 0.32x 0.16 mm^3	
Θ range for data collection	2.0 to 27.50°.	
Index ranges	-14≤h≤14, -15≤k≤16, -17≤l≤17	
Reflections collected	28842	
Independent reflections	7979 [R(int) = 0.0607]	
Completeness to Θ = 29.00°	100.0%	
Absorption correction	*numerical*	
Max. and min. transmission	0.9407 and 0.9893	
Data / restraints / parameters	3937 / 14 / 416	
Goodness-of-fit on F^2	0.819	
Final R indices [I>2σ(I)]	R1 = 0.0532, wR2 = 0.1306	
R indices (all data)	R1 = 0.1133, wR2 = 0.1438	
Largest diff. Peak and hole	0.500 and -0.250 e.$Å^{-3}$	

Abbreviations

Ac	Acetyl
Anal	Elemental Analysis
bp	Boiling point
calcd	Calculated
CI	Chemical Ionization
COSY	Correlated Spectroscopy
DEPT	Distortionless Enhancement by Polarization Transfer
dr	Diastereomeric ratio
ee	Enantiomeric excess
EI	Electron Impact
Et_2O	Diethyl ether
EtOH	Ethanol
GC	Gas Chromatography
GP	General Procedure
HMBC	Heteronuclear Multiple Bond Correlation
HPLC	High Performance Liquid Chromatography
HRMS	High Resolution Mass Spectrometry
IR	Infrared Spectroscopy
MS	Mass Spectrometry
mp	Melting point
NaOEt	Sodium ethanolate
*n*BuLi	*n*-Butyllithium
NEt_3	Triethylamine
NMR	Nuclear Magnetic Resonance
NOESY	Nuclear Overhauser and Exchange Spectroscopy
ORTEP	Oak Ridge Thermal Ellipsoid Plot
OTf	Triflate
Ph	Phenyl
ppm	Parts per million
R_f	Retention factor
Tf_2O	Trifluoromethanesulfonic anhydride (triflic anhydride)
TFA	Trifluoroacetic acid
THF	Tetrahydrofuran

TLC	Thin Layer Chromatography
TMS	Tetramethylsilane
Tol	Tolyl (*p*-MeC_6H_4)
Tos	Tosyl (*p*-$MeC_6H_4SO_2$

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Erklärung/ Daclaration

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.

Here by I declare that this work has so for 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.

Muhammad Sharif Akbar