Synthesis of Functionalized Benzophenones and Terphenyls based on Site-Selective Suzuki-Miyaura Reactions of Bis(triflates) of various Hydroxylated Benzophenones and Benzoates

DISSERTATION

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Anyone who has never made a mistake
has never tried anything new.

Albert Einstein

Dedication

I dedicate this humble effort and fruit of my study to my dearest elder Brother

Malik Muhammad Mushtaq

Who always supported my morally and financially, prayed continuously for my success and sacrificed his precious today for my better tomorrow.

Acknowledgement

By the grace of **Allah**, the Almighty, the creator of universe, who granted Hidayah to the mankind and peace and blessings be upon his **prophet, Hazrat Muhammad** (Peace be upon Him), who exhorted his followers to seek knowledge from cradle to grave, I've been able to complete this academic enterprise.

The last day of a journey is always very close to the first day. So many people have helped and supported me during the last two years of my stay here at Rostock. I will try to thank all of them here, but it is almost inevitable that I will forget someone, so if you are that someone, please remember that it was not intentional and I truly appreciate everything what you did for me.

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Last, but not least I’d like to thank technical & non-technical staff of the Institute of Chemistry, especially Anna Hallmann and Claudia Vinke for their tremendous support during my stay.

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Muhammad Nawaz
University of Rostock
October, 2010

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Abbreviations

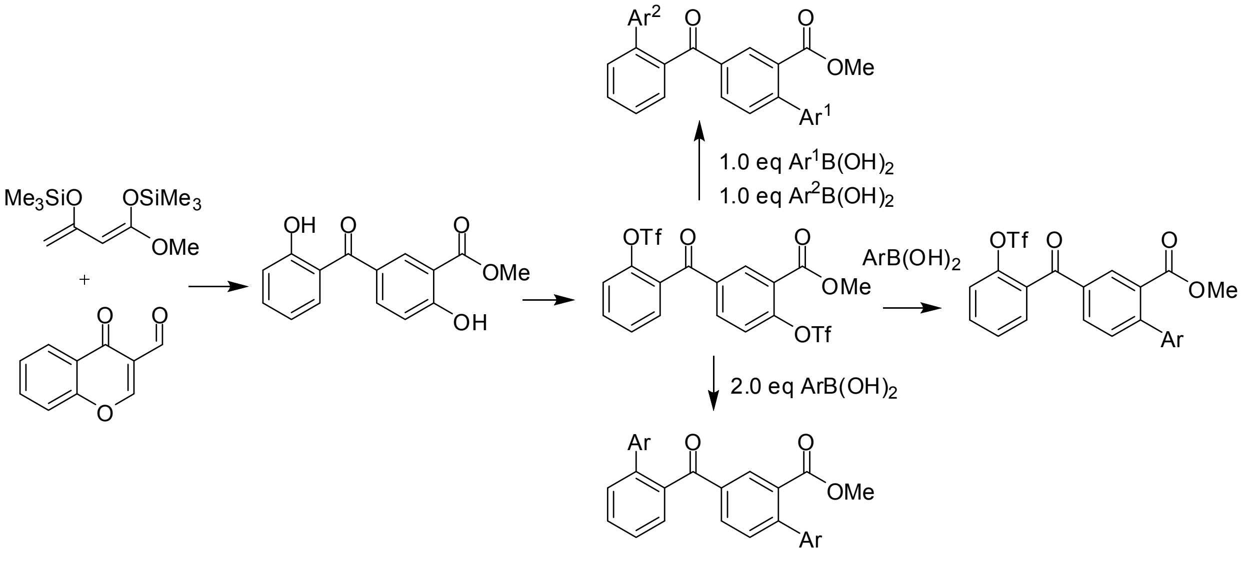
Ar	Aromatic
APT	Attached Proton Test
ATCC	American Type Culture Collection
*n*BuLi	*n*-Butylithium
DEPT	Distortionless Enhancement by Polarisation Transfer
EI	Electronic Impact
ESI	Electrospray Ionization
EtOAc	Ethylacetate
HRMS	High Resolution Mass Spectroscopy
IR	Infrared Spectroscopy
LDA	Lithium Diisopropylamide
MS	Mass Spectrometry
Ph	Phenyl
NEt_3	Triethylamine
NMR	Nuclear Magnetic Resonance
HMQC	Heteronuclear Multiple Quantum Coherence
HMBC	Heteronuclear Multiple Bond Correlation
COSY	Correlated Spectroscopy
NOESY	Nuclear Overhauser and Exchange Spectroscopy
Me_3SiOTf	Trimethylsilyl-trifluoromethanesulfonate
Me_3SiCl	Trimethylsilylchloride
RCM	Ring Closing Metathesis
TBAI	Tetrabutyl Amonium Iodide
TBAF	Tetrabutyl Amonium Fluoride
TFA	Trifluoroacetic Acid
Tf_2O	Trifluoromethanesulfonic Anhydride
THF	Tetrahydrofurane
TLC	Thin Layer Chromatography
TMS	Trimethylsilane
UV	Ultraviolet Spectroscopy

“Summary and Task of the Thesis”

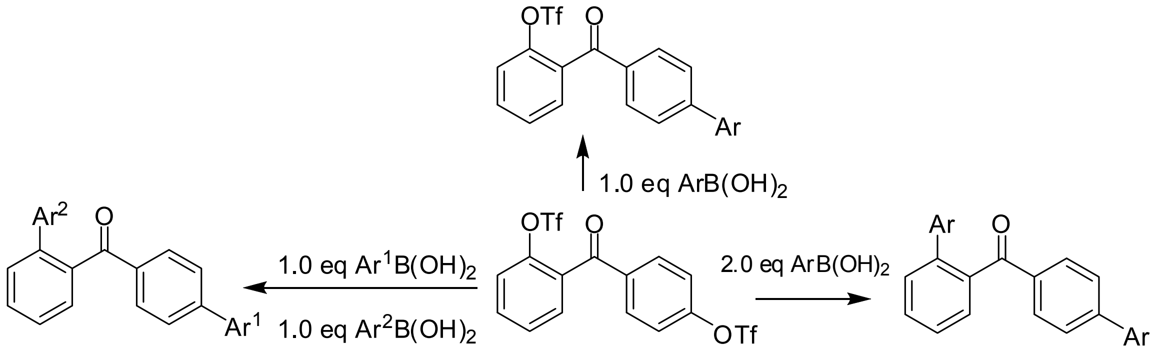
Most of the work mentioned here has already been published in reputed journals. This thesis can be summarized as follows:

The task of my thesis was to study palladium(0)-catalyzed Suzuki cross-coupling reactions of various types of bis(triflates) of benzophenones and benzoates. The triflates are readily available from the corresponding hydroxy compounds. The issue of site-selectivity plays an important role in my thesis. In this context, steric and electronic parameters have been investigated.

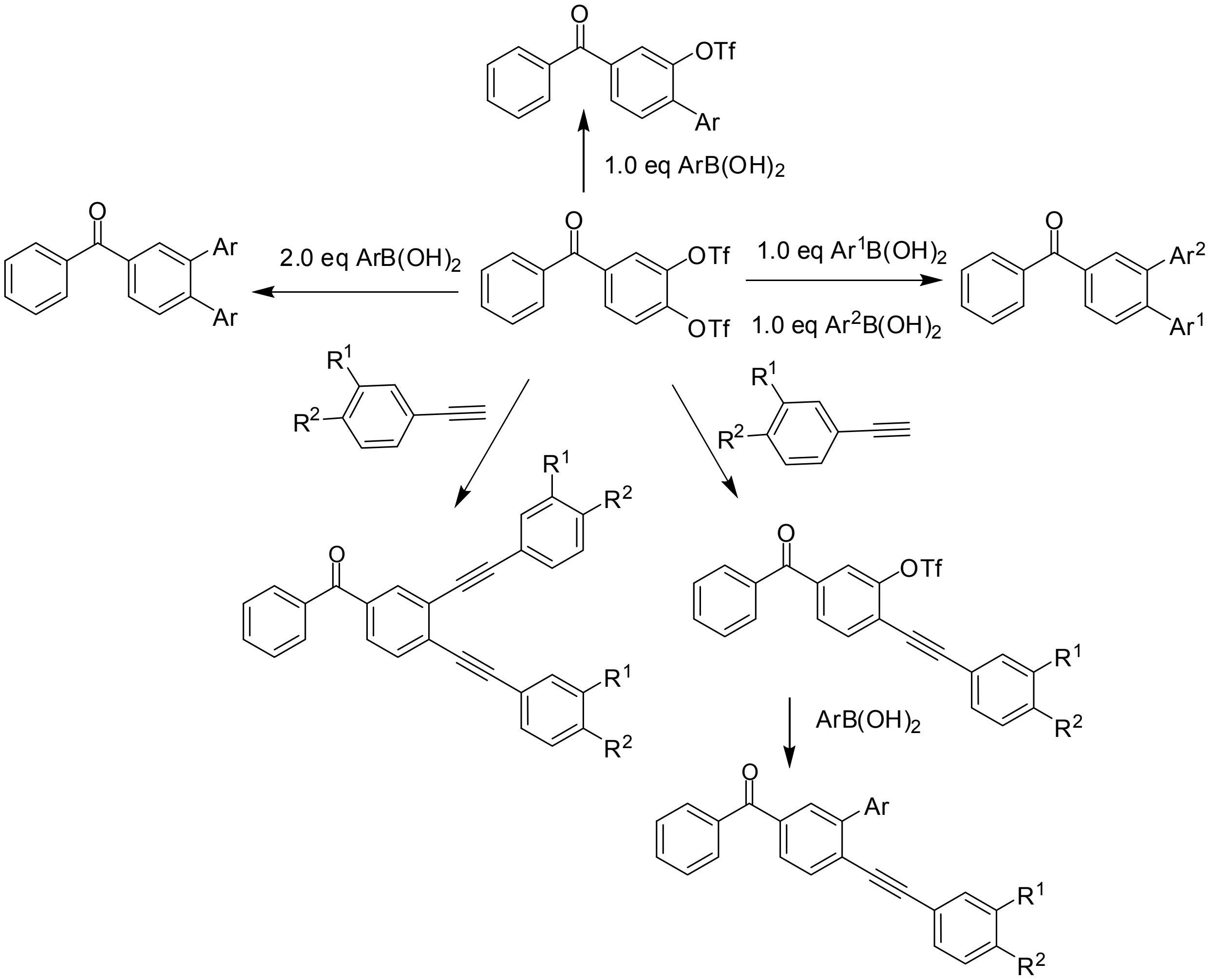
The palladium(0)-catalyzed Suzuki cross-coupling reaction of the bis(triflates) of 2′,4-dihydroxybenzophenones afforded 2′,4-diarylbenzophenones. The reactions proceeded with very good site-selectivity. The first attack takes place at carbon atom C-4. The site-selectivity of palladium(0)-catalyzed reactions of bis(triflates) is controlled by electronic and steric parameters. The oxidative addition of palladium usually occurs first at the most electron deficient and sterically less hindered carbon atom. Therefore, the site-selective formation of mono-adducts can be explained by the fact that carbon atom C-4 is more electrons deficient and less sterically hindered than C-2′. One electron-withdrawing benzoyl group is located *ortho* to C-2′. In contrast, both an electron-withdrawing benzoyl group and an electron-withdrawing ester group are located *para* and *ortho* to C-4, respectively.



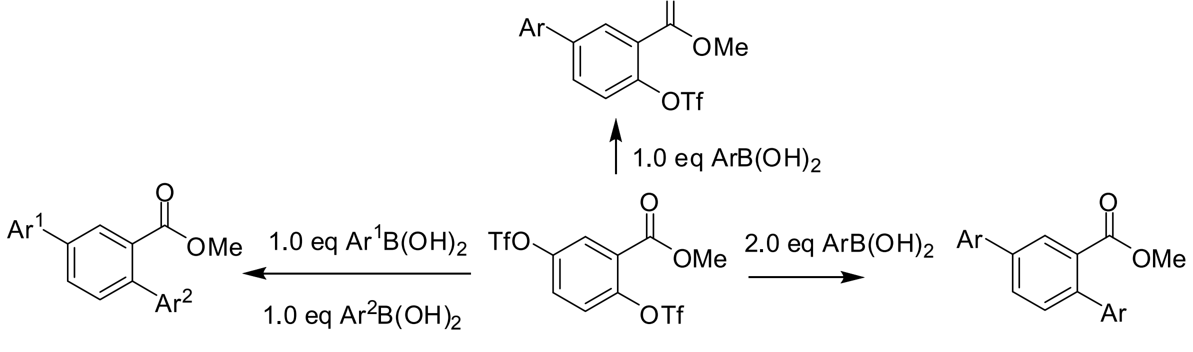
The Suzuki-Miyaura cross-coupling reaction of the bis(triflate) of 2,4′-dihydroxy benzophenone afforded 2,4′-diarylbenzophenones. The reactions again proceeded with very good site-selectivity in favour of carbon atom C-4′ which is less sterically hindered than C-2.



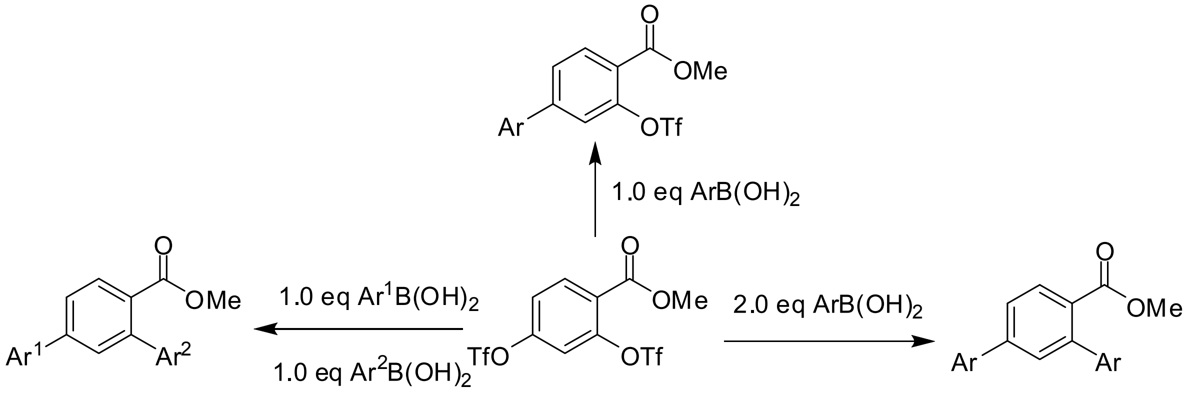
The Suzuki-Miyaura reaction of the bis(triflate) of 3,4-dihydroxybenzophenone with two equivalents of boronic acids gave 3,4-diarylbenzophenones. When one equivalent of boronic acid was used, the reaction proceeded with site-selective attack at carbon atom C-4. 3,4-diarylbenzophenones containing two different aryl groups were prepared by sequential addition of two different boronic acids. The site-selective formation of the mono-adducts can be explained by the fact that carbon atom C-4 (located *para* to the keto group) is more electron-deficient than C-3 (located *meta* to the keto group). Steric parameters have no role to play, due to the similar steric environment of carbon atoms C-3 and C-4. The Sonogashira cross-coupling reactions of the bis(triflate) of 3,4-dihydroxybenzophenone with terminal alkynes display remarkable compatibility with regard to the formation of symmetrical and unsymmetrical alkyne-substitution and the reaction proceeded with the same site-selectivity as was observed in case of Suzuki-Miyaura reaction of the same substrate.



The palladium(0)-catalyzed Suzuki cross-coupling reaction of the bis(triflate) of methyl 2,5-dihydroxybenzoate afforded *p*-terphenyls. The reaction takes place with very good site-selectivity. The first attack takes place at carbon atom C-5. Carbon atom C-2 of the bis(triflate) is expected to be more electron deficient than C-5. On the other hand, carbon atom C-5 is less sterically hindered than C-2. Therefore, the site-selective formation of mono-adducts is mainly influenced by steric parameters.



The palladium(0)-catalyzed Suzuki cross-coupling reaction of the bis(triflate) of methyl 2,4-dihydroxybenzoate resulted in the formation of *m*-terphenyls. The mono-adducts are formed as a result of site selective attack at carbon atom C-4. The steric factors have an important role to play in this regard. The site-selective formation of mono-adducts can be explained by the fact that carbon atom C-4 is less sterically hindered as compared to carbon atom C-2 of the bis(triflate) moiety.



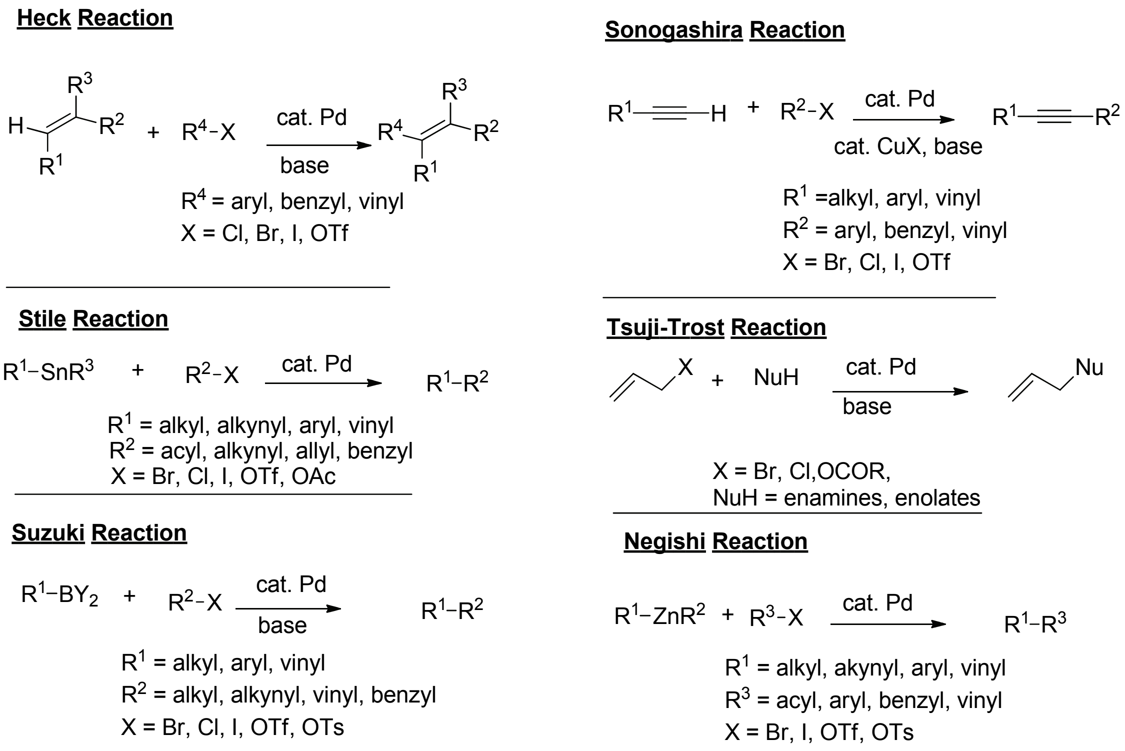
1. Introduction:

1.1 General Introduction:

The development of environmentally friendly and economical reactions for the formation of carbon-carbon and carbon-heteratom bonds is of great interest for the chemist. This methodology provides a simple route for the formation of different bulky molecules from simple starting material. Until now, different methodologies have been used by the chemist for making carbon-carbon bonds. Since the discovery of metal-catalyzed cross-coupling reactions, a variety of metals have proven to be productive in organic synthesis. For instance, different types of organometallics which are used by synthetic chemist are boron (Suzuki reaction), zinc (Negishi reaction), tin (Stille reaction) and copper (Sonogashira reaction). Recently, Perez *et al*, has found organoindium compounds as useful reagents in metal-catalyzed cross-coupling reactions.[1,2]

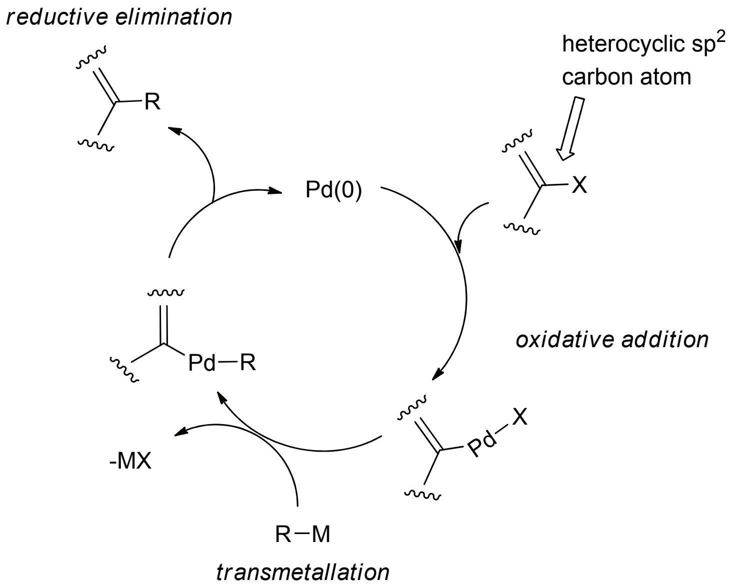
1.2 Pd-catalyzed Reactions:

Since the discovery and continuing evolution of metal-catalyzed cross coupling reactions, palladium(0)-catalyzed carbon-carbon bond forming reactions provide a useful methodology, which has not only facilitated the synthesis of complex molecules but also served as an efficient route for the formation of carbon-carbon bonds used by synthetic chemists.[3] Palladium-catalyzed cross-coupling is used in research worldwide, as well as in commercial production of, for example, pharmaceuticals and molecules used in the electronic industry. The tool allows scientists to build complex chemicals such as the carbon-based ones that are the basis of life. This technique is applied in every field of chemistry, such as, total synthesis, nanotechnology, synthesis of advanced materials, medicinal and pharmacological chemistry. Various types of palladium-catalyzed cross-coupling reactions[4,5] are known in organic synthesis, such as, Heck, Stille, Suzuki, Sonogashira, Tsuji-Trost and Negishi reactions (Scheme 1). Since last few decades, palladium-catalyzed cross-coupling reactions have evolved as the best tool for making carbon-carbon bonds between unsaturated organic moieties. The historical development and a variety of applications have put these reactions at the top list in synthetic organic chemistry. In short, it represents a well-established methodology in organic synthesis.



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

In the last decades, many research articles dealing with the reaction mechanism and synthetic applications of Pd catalysis appeared in the literature. If we closely observe the mechanism of a typical cross-coupling reaction, we can have an idea that the reaction proceeds to accomplish in three steps (Scheme 2). In the first step of the reaction, the addition of corresponding organic triflate or halide to the Pd(0) complex takes place. This addition results in the formation of organopalladium triflates or halides. The next step is the transmetallation with nucleophilic compounds to give a diorganopalladium complex. In the last step of the reaction, this complex undergoes a reductive elimination to create a carbon-carbon bond and the palladium catalyst is regenerated.



Scheme 2. General mechanism for palladium-catalyzed cross-coupling reaction (picture was taken from *Tetrahedron*, **2005**, *61*, 2245).

For many years, interesting and pharmacologically active compounds have been synthesized by using Pd-catalyzed cross-coupling reactions.[6] In particular, the ring forming reactions catalyzed by Pd(0) always remained a matter of interest for the synthetic organic chemist.[7] For instance, Lautens and Mark[8] have developed new Pd-catalyzed cyclization methods for the synthesis of highly functionalized carbocyclic, heterocyclic and arene compounds. Catellani and his co-workers discovered remarkable norbornene-mediated Pd-catalyzed reactions, inwhich three carbon-carbon bonds are formed in one pot.[9] In this reaction, they used an aryl iodide to react with an alkyl halide and a Heck acceptor in the presence of norbornene, a Pd catalyst and a base to form *ortho*, *ortho′*-disubstituted vinylarenes.

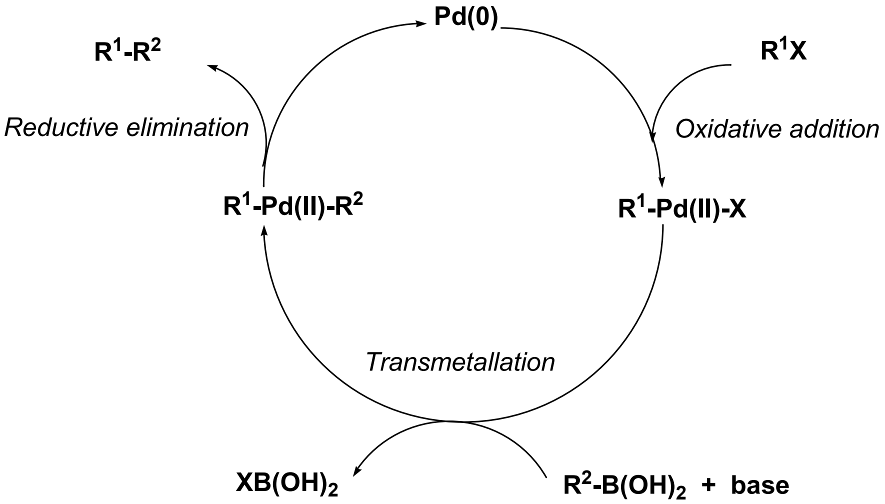
Pd-catalyzed Heck reactions[10] and cross coupling reactions[11] of aryl triflates and halides are powerful synthetic methodologies for new carbon-carbon bond formation in synthetic organic chemistry. In the last few decades, different methods have been applied by the chemist, which have greatly improved the synthetic utilization of these reactions, as a result of which they are now finding almost routine use in complex organic synthesis.[12]

A large number of reactions involve the generation and transformation in *situ* of σ-vinyl and σ-aryl palladium complexes. These complexes provide the precursors which can be used as substructures for the sythesis of many types of pharmacologically active compounds. Switching from vinyl and aryl mercury compounds to vinyl and aryl halides widened considerably the scope and utility of this methodology. More recently, the discovery of Cacchi and Sandro, that vinyl triflates (trifluoromethanesulfonates) can be used as precursors of σ-vinylpalladium complexes in the reaction with olefinic system[13] and the development of a procedure by Scott and Stille to allow the cross-coupling of vinyl triflates with organostannanes[14] marked a further significant step forward in homogeneous catalysis.

1.3 Palladium-catalyzed Suzuki-Miyaura Reaction:

In palladium-catalyzed catalytic tansformations, Suzuki-Miyaura cross-coupling has especially attracted the attention of chemists and has been used extensively in organic synthesis. Suzuki and Miyaura have invented this reaction in 1981. Since its inception, it has found multi-prong use in synthetic organic chemistry. This reaction refers to the cross-coupling of organoboron compounds and carbon electrophiles.[15] No one can deny from the importance of Suzuki-Miyaura cross-coupling reaction in academic and industrial chemistry as well as in production of a variety of fine chemicals.[16] The Pd-catalyzed Suzuki-Miyaura cross-coupling reaction has attained a great importance for the synthetic organic chemist to prepare different types of molecules which can be used as a backbone for different types of substructures, used in pharmaceutical chemistry. The Suzuki-Miyaura cross-coupling reaction has a number of advantages over the other available traditional methods for the synthesis of these types of moieties. For instance, this reaction requires mild reaction conditions to proceed, high level of tolerance to almost all types of functional groups and the commercial availability and stability of the reagents (to heat, oxygen and water) used in such reactions. The synthetic chemist can handle and separate the byproducts produced from the reaction mixture in a very easy way, which further enhances the importance of this reaction. These interesting advantages make the Suzuki-Miyaura cross-coupling reaction an important tool in medicinal chemistry and also in the preparation of fine chemicals as well as in large scale pharmaceutical industry.[17]

A general mechanism for the Suzuki-Miyaura cross coupling reaction of organic halides and triflates with organoboron reagents is elaborated in Scheme 3. This mechanism usually involves three steps. In the first step of the reaction, the oxidative addition of organic halides or triflates to the Pd(0) complex to form a organopalladium halide (R^1-Pd(II)-X) takes place. This step is then followed by transmetallation with a boronic acid derivative to give a diorganopalladium complex (R^1-Pd-R^2). In the final step of the reaction, this complex undergoes a reductive elimination resulting in the formation of a carbon-carbon bond and regeneration of the catalyst.



Scheme 3. Catalytic cycle of the Suzuki reaction

The rate of the Suzuki reaction is influenced by various factors, but mainly it depends upon the oxidative addition and transmetallation steps. In the oxidative addition step of the Suzuki reaction, the reactivity of the reacting substrates has a vital role to play. Generally, the reactivity of various substrates is observed in the following order, Ar-I > Ar-Br > Ar-OTf > Ar-Cl. The base supports the transmetallation step of the Suzuki reaction. The presence of a base usually enhances the nucleophilicity of the organoborane compound by formation of an organoborate containing a tetravalent boron atom. The rate of Suzuki reaction is also affected by the solvent to be used in the reaction. In my research work, the use of THF was most productive.

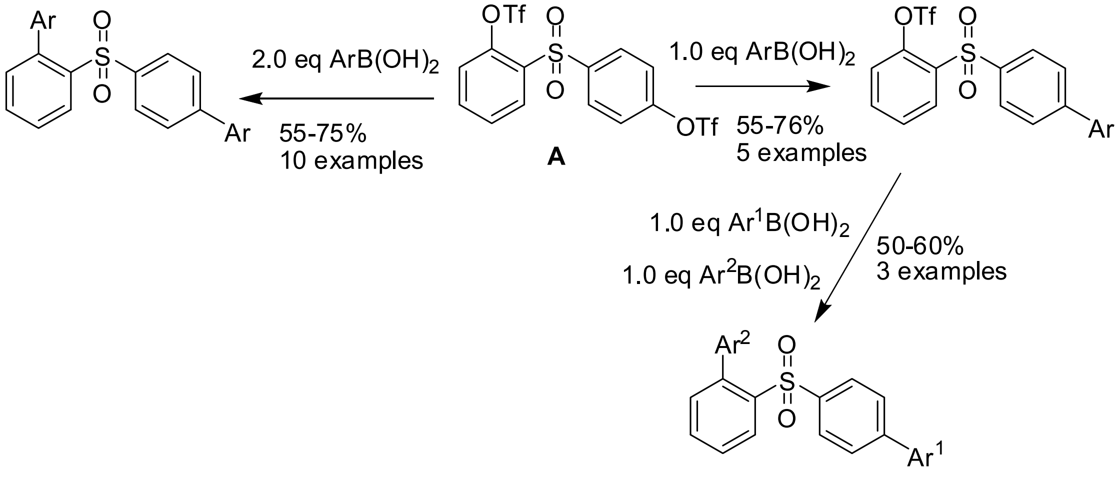
The rate of success of the Suzuki-Miyaura reaction also depends upon the selection of catalyst to be used in the reaction. To achieve this target, a variety of catalysts are used by the chemist. Until 1998, triarylphosphine ligands were used for most of the catalysts which were applied for Suzuki-Miyaura cross-coupling reactions. New bulky and electron-rich phosphine ligands have been introduced and it is experimentally proved that these ligands can improve the efficiency and selectivity in such type of reactions. It was believed that the use of such type of electron-rich and bulky phosphine ligands enhances the rate of both oxidative addition and reductive elimination processes. A new family of ligands, dialkybiarylphosphines L1-L12, has been designed by Rubert Martin and his co-workers. They applied these ligands in a wide variety of reactions which can be used for the synthesis of carbon-carbon, carbon-nitrogen, and carbon-oxygen bond forming processes. With the use of these types of bulky electron-rich ligands, it became possible to carry out the Suzuki-Miyaura reaction with a number of unactivated substrates, such as, aryl chlorides, aryl tosylates, heteroaryl, and extremely hindered substrates. The most common catalysts, which had found their utilization in palladium-catalyzed synthetic chemistry, includes, $Pd(OAc)_2$, $PdCl_2$, $Pd(PPh_3)_2Cl_2$ and $Pd(PPh_3)_4$.

As these catalysts serve as a source of electron in the reaction, the electron-rich ligands are often the key for a successful reaction. Sterically hindered and electron-rich phosphines serve the purpose in a best way. The reaction with ferrocenylphosphane[18], N-heterocyclic carbenes[19], $P(t\text{-}Bu)_3$[20], $P(Cy)_3$ often give good results. Jiwu Ruan and co-workers recently reported the synthesis of an electron-rich and bulky monophosine ligands based on [2.2] paracyclophane.[21] Prof. Matthias Beller at Universität Rostock has worked on the invention of some innovative ligands which had found tremendous use in palladium-catalyzed organic synthesis. His group has developed a methodology for the synthesis of some very useful catalysts, which are also commercially available, for instance, dibutyl-1-adamatylphosphine[22], and phosphino substituted *N*-aryl pyrroles.[23] Many chemists all over the globe are trying to synthesize most useful ligands which can be employed to achieve extraordinary results in the field of palladium-catalyzed chemistry. Prof. Buchwald and co-workers[24] have developed electron-rich, bulky biphenylphosphine ligands, such as S-Phos, X-Phos, Dave-Phos, and others. The organic chemists have successfully applied such ligands for different synthetic routes, including industrially relevant processes. I had also tried many types of catalyst in my projects. In my research, the best results were often achieved by using tetrakis(triphenylphosphine) palladium(0) for most of the Suzuki-Miyaura cross-coupling reactions.

1.4 Pd-catalyzed Reactions of Bis(triflates):

The palladium-catalyzed reactions had also been carried out with aryl bis(triflates). The palladium(0) catalyzed cross-coupling reaction of aryl triflates[25] with aryl boronic acids in the presence of a base is a versatile method for preparing unsymmetrically substituted biaryls. The use of aryl triflates instead of aryl halides is particularly important in organic synthesis because it can provide a way of forming a carbon-carbon bond at a phenolic site, which is often useful when appropriate halides are unavailable.[26] Since aryl triflates are easily available from the corresponding hydroxy compounds, the scope and applications of these compounds in transition metal catalyzed reactions has therefore, attracted the interest of chemists. This coupling reaction offers the advantage of high yields, clean products with less side reactions, tolerance of a variety of functional groups on either coupling partner, and no necessity for anhydrous conditions.

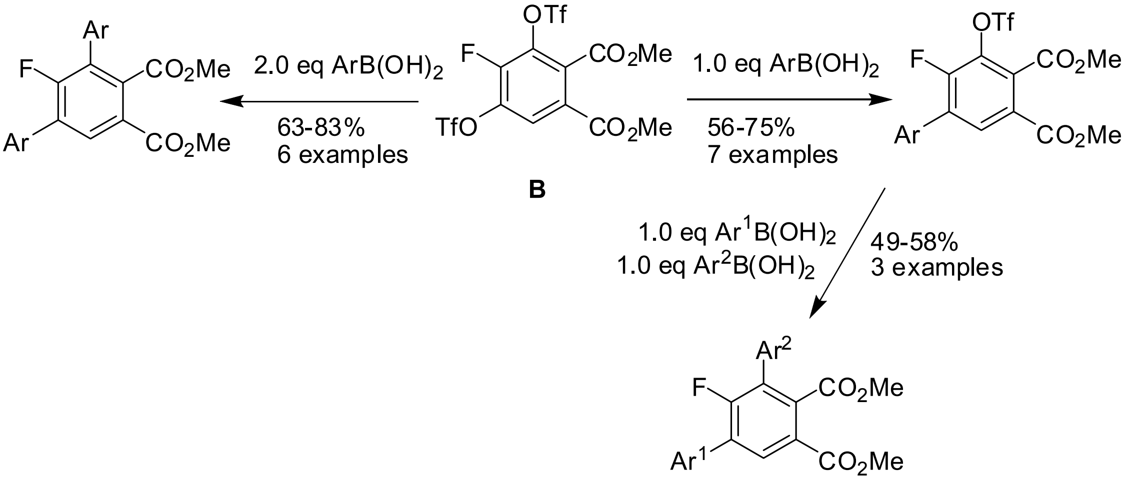
Recently, the group of Prof. Langer has thoroughly studied the Pd-catalyzed chemistry of bis(triflates). Langer *et al.* have reported the synthesis of bis(diaryl)sufones by site-selective Suzuki reactions of 2,4′-bis(trifluoromethylsulfonyloxy)diphenylsulfone **A** (Scheme 4).[27] These compounds are of considerable pharmacological relevance.[28] The reaction with two equivalents of boronic acids took place at both carbon atom of the triflate moiety, but when one equivalent of boronic acid was used, the site selective attack at carbon atom C-4′ takes place. This can be explained by the fact that carbon atom C-4′ is less sterically hindered as compared to carbon atom C-2.



Scheme 4. Site-selective reactions of bis(triflates) **A**

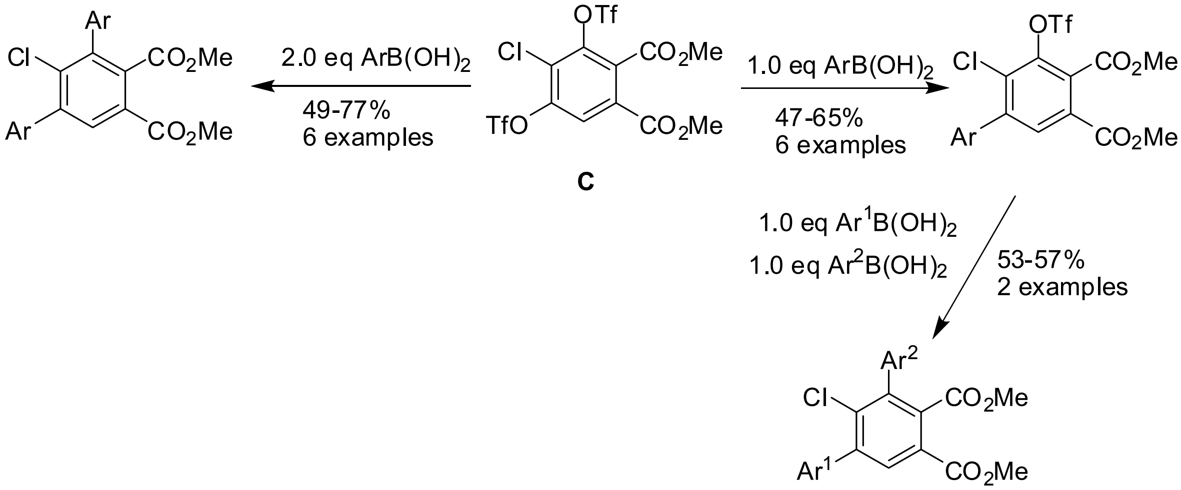
In the last decade, a dramatic increase in the interest of organofluorine compounds has been observed. The carbon-fluorine bond is chemically stable; therefore, undesired metabolic transformations are rather rare. Schlosser *et al.* reported the synthesis of fluorinated arenes by Diels-Alder reactions of alkenes or alkynes with fluorinated 1,3-butadienes.[29] Langer *et al.* have recently reported the synthesis of arenes and hetarenes based on formal [3+3] and [3+2] cyclizations of 1,3-bis(silyloxy)-1,3-butadienes.[30-32] They also reported the synthesis of dimethyl 4-fluoro-3,5-dihydroxyphthalate by [4+2] cycloaddition of 1-ethoxy-2-fluoro-1,3-

bis(trimethylsilyloxy)-1,3-diene with dimethyl acetylenedicarboxylate (DMAD). Pd-catalyzed Suzuki reactions of the bis(triflate) **B** proceeded with good site selectivity and resulted in the formation of novel 3,5-diaryl-4-fluorophthalates (Scheme 5).[33]



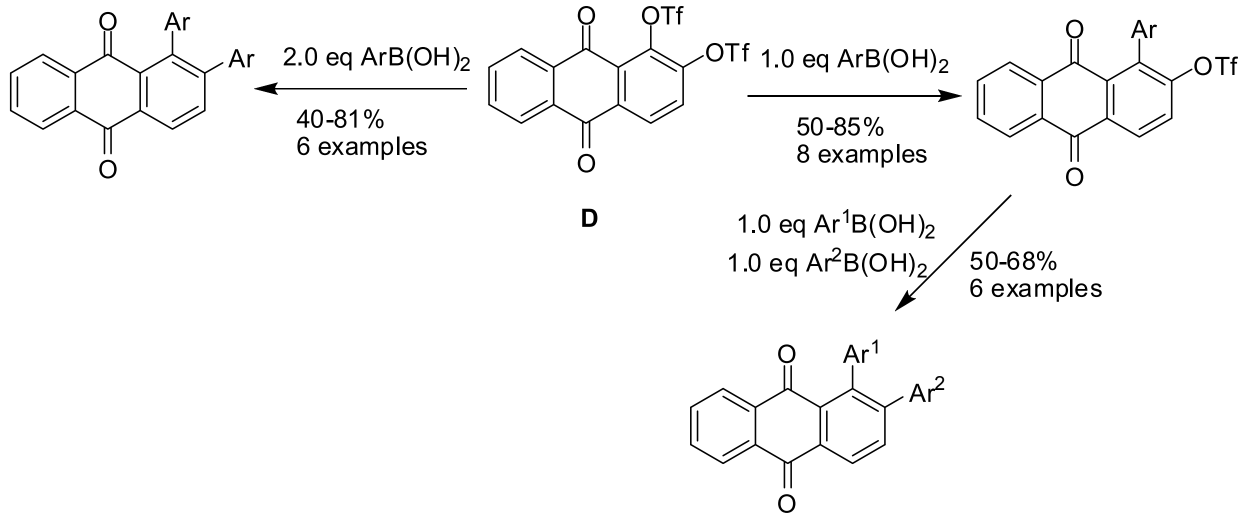
Scheme 5. Site-selective reactions of bis(triflates) **B**

Aryl chlorides possess interesting biological properties and they have also been isolated as natural products.[34] Corral and co-workers reported the synthesis of of 4-chloro phenol by [4+2] cycloaddition of a chlorinated thiophene with dimethyl acetylene dicarboxylate.[35] Langer and his co-workers has recently reported the synthesis of dimethyl 4-chloro-3,5-dihydroxyphthalate by [4+2] cycloaddition of 1-ethoxy-2-chloro-1,3-bis(trimethylsilyloxy)-1,3-diene with dimethyl acetylendicarboxylate (DMAD). Suzuki-Miyaura reactions of the bis(triflate) **C** afforded the formation of 3,5-diaryl-4-chlorophthalates (Scheme 6).[36] The site-selective formation of the products can be explained by steric reasons.



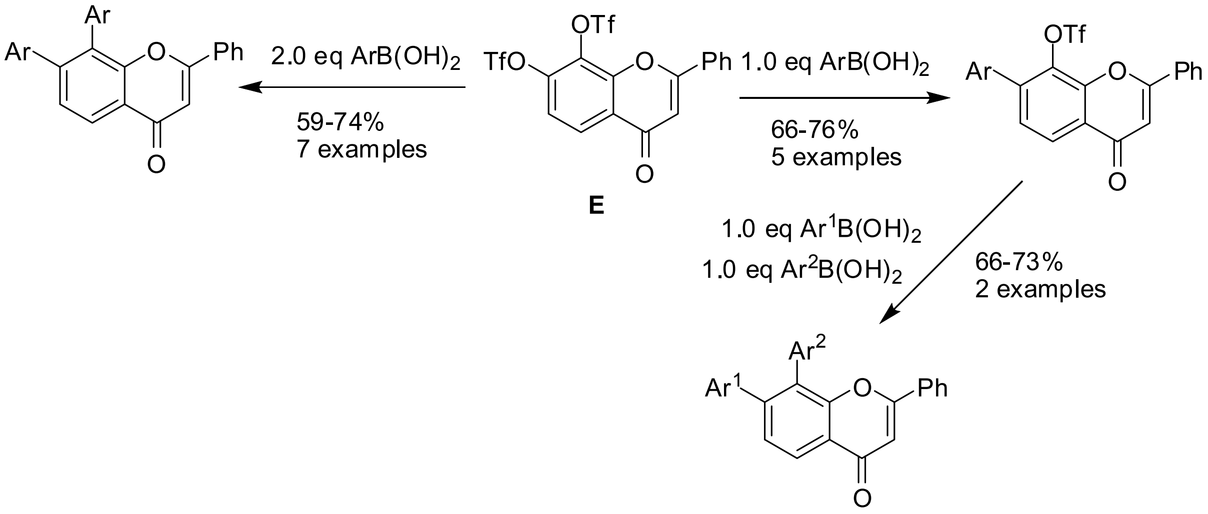
Scheme 6. Site-selective reactions of bis(triflates) **C**

Anthraquinones also show interesting pharmacological properties and occur in various natural products.[37] For instance, anthracyclines are important as antitumor agents and antibiotics. In the group of Prof. Langer, Pd-mediated study of bis(triflates) is always a matter of interest. Recently, they have reported the synthesis of 1,2-diarylanthraquinones (Scheme 7) by Pd-catalyzed Suzuki-Miyaura reaction of the bis(triflate) **D** of 1,2-dihydroxyanthraquinone.[38]



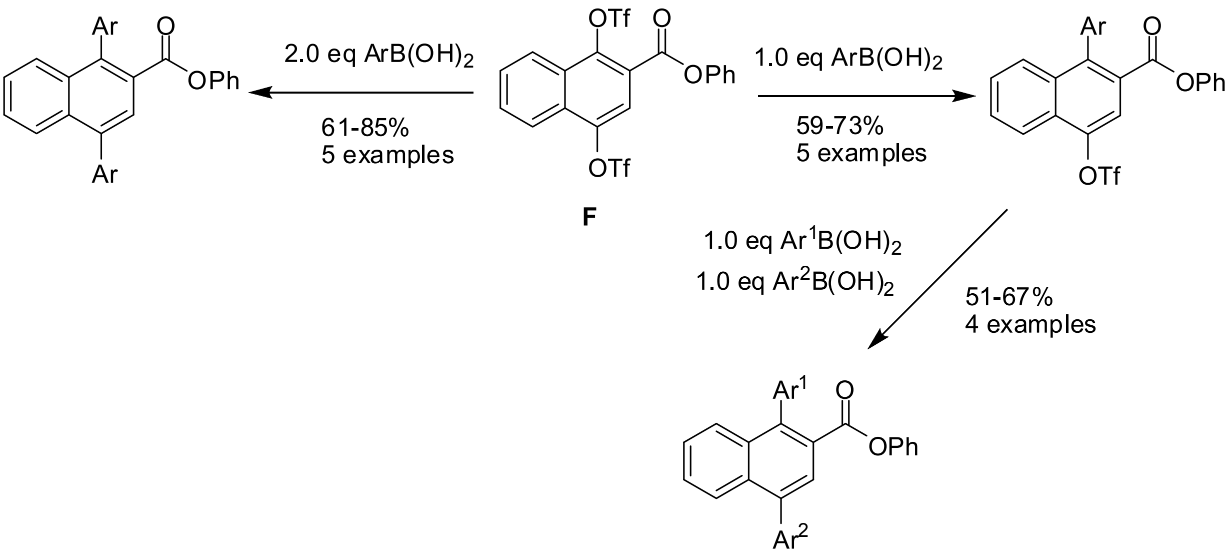
Scheme 7. Site-selective reactions of bis(triflates) **D**

The group of Prof. Langer, in continuation of their studies on bis(triflate) chemistry, studied the synthesis of 7,8-diaryl-flavones by site-selective Suzuki-Miyaura reactions of the bis(triflate) of 7,8-dihydroxyflavone.[39] Commercially available 7,8-dihydroxyflavone was transformed to its bis(triflate). When the Suzuki reaction of this bis(triflate) **E** was carried out, it resulted in the formation of interesting products (Scheme 8). When two equivalent of boronic acid was used, there was no issue of selectivity, but when one equivalent of boronic acid was employed, it afforded site-selective formation of products. Steric and electronic factors play a vital role in the formation of site-selective products. The first attack takes place at the most electron deficient and less sterially hindered carbon atom.



Scheme 8. Site-selective reactions of bis(triflates) **E**

Langer *et al.* also reported the formation of 1,4-diaryl-2-naphthoates (Scheme 9),[40] starting from bis(triflate) **F** of phenyl 1,4-dihydroxynaphthoate, which is an inexpensive, commercially available starting material. The Suzuki reaction with two equivalents of boronic acids proceeded without any problem. When one equivalent of boronic acid was used, a site selective formation of mono-adducts took place. This site-selective formation of products is controlled by electronic effects. Carbon atom C-1 of the naphthoate is more electron deficient, therefore, the addition of electron rich palladium species first takes place at this carbon atom, resulting in the site-selective formation of products.



Scheme 9. Site-selective reactions of bis(triflates) **F**

2. Synthesis of Functionalized 2′,4-diarylbenzophenones, 2′,4′-diarylbenzophenones, 3,4-diarylbenzophenones based on site-selective Suzuki-Miyaura cross-coupling reactions of bis(triflates) of various Hydroxylated Benzophenones.

2.1 General Introduction to Benzophenones:

In this project, my target was the synthesis of functionalized benzophenones based on site-selective Suzuki-Miyaura cross-coupling reactions. In the literature, it has been reported that these benzophenones show a variety of properties. For instance, 4-arylbenzophenones exhibit interesting pharmacological properties, such as cytotoxic and antibacterial activity,[41] and the inhibition of various enzymes.[42] In the group of Prof. Langer it has already been reported that 4-(2-hydroxybenzoyl)salicylic acids show a good *in vitro* activity in a selectin bioassay.[43] Similarly, structurally related benzoylfluorenones show interesting biological activities.[44] The 4-arylbenzophenones are are usually found in polycyclic frameworks, in anthraquinone and tetracycline natural products.[45] 2-Hydroxy- and 2-aminobenzophenones are of valuable importance in anticancer therapy, since they act as antitubulin agents.[46] Functionalized benzophenones are also widely used as photosensitizers and UV-filters (suncremes).[47]

Selectin antagonist activity of various aryl-substituted benzophenones have also been reported in the literature.[48] Substituted benzophenones under appropriate reaction conditions react to form strong fluorescent species. The 2,2′-dihydroxy-4,4′-dimethoxy-benzophenone is used as a new and sensitive fluorometric reagent for the determination of nitrate. The procedure to eliminate possible interferences from high concentrations of chloride, sulphides and humic acid substances is also incorporated in the automated method. This method has been applied to the analysis of a variety of natural waters and sediments.[49]

It is generally accepted that the majority of substituted benzophenones tend to produce phosphorescence instead of fluorescence.[50-52] The main reason for this is that the majority of these compounds possess the lowest excited singlet state character; therefore, intersystem crossing to triplet manifold is usually very efficient. It is also well established that certain environmental factors, such as substitution, solute-solvent interaction, and nature of the catalyst, can alter these compounds and the nature of the transition energies and the intensity of luminescence.[53]

Acetophenone and related compounds are known to react in concentrated sulphuric acid to produce polymeric species. Therefore, it is possible to alter the transition probabilities of these molecules by changing the reaction conditions, suitable substitution pattern, or solvent to produce species which may result in fluorescence instead of phosphorescence.

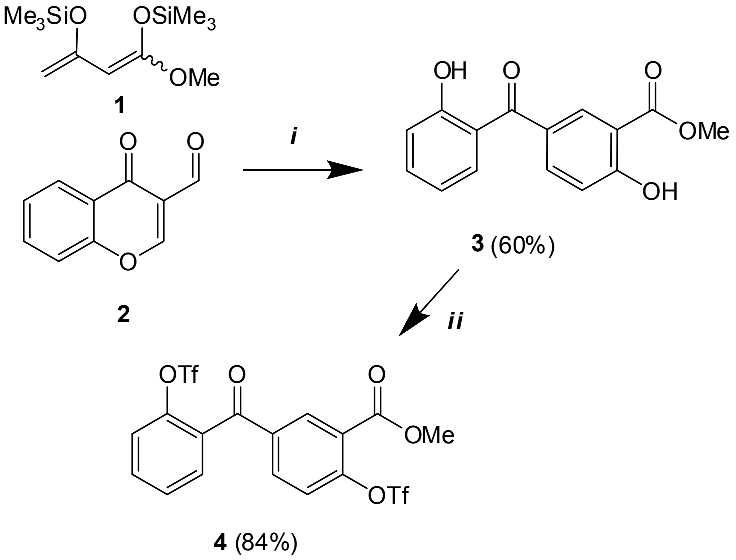
Some naturally available benzophenones, for instance, polyisoprenylated benzophenones, act as a therapeutic drug for the treatment of various diseases. Some novel therapeutic properties of naturally occurring benzophenones include 1) anti-microbial activity towards acne-causing bacteria; 2) strong anti-matrix metalloproteinase activity; and 3) anti-cyclooxygenase activity. Naturally occurring polyisoprenylated benzophenones have also been extensively studied as "cosmetics", the definition of which, would just classify them as cleansers, beautifiers, attraction promoters and agents that alter physical appearance. So, there is an enormous potential in these natural molecules to be used as a drug.

Classic syntheses of benzophenones rely on reactions of aryllithium or magnesium reagents with aldehydes and subsequent oxidation and on Friedel-Crafts acylations.[54,55] For the synthesis of functionalized benzophenones (e.g. containing a hydroxy, halide or ester group), these methods often give unsatisfactory results, due to competing side-reactions. Friedel-Crafts acylations of highly substituted derivatives not always proceed with good regioselectivity. An alternative strategy relies on the SmI_2 mediated reaction of benzaldehydes with benzylhalides and subsequent oxidation.[56] The group of Prof. Langer has studied domino reactions of silyl enol ethers with chromones. In this context, a new approach to 4-(2-hydroxybenzoyl)salicylates by cyclization of 1,3-bis(silyloxy)-1,3-butadienes with 3-formylchromones has been developed.

2.2 Synthesis of Functionalized 2′,4-Diarylbenzophenones:

The backbone of many types of polymers, ligands, natural products and pharmaceuticals contain biaryls or substituted aromatic structures and it is important for synthetic organic chemists to study reactions which can be applied for the synthesis of these types of moieties. To serve this purpose, Suzuki –Miyaura cross-coupling reactions have adopted extreme importance for the chemist. The TMSOTf-mediated domino′addition / retro-Michael / Mukaiyama-aldol′ reaction of 3-formylchromone (**2**) with 1,3-bis(trimethylsilyloxy)buta-1,3-diene (**1**) afforded the 2′,4-dihydroxybenzophenone[57] **3** which was transformed into its bis(triflate) **4** (Scheme 10).

The Suzuki reaction of **4** with boronic acids **5a-r** afforded the novel 2′,4-diarylbenzophenones **6a-r** in good yields (Scheme 11, Table 1). The best yields were obtained when $Pd(PPh_3)_4$ (3 mol-%) was used as the catalyst, when 2.6 equiv. of the boronic acid was employed, and when the reaction was carried out in 1,4-dioxane (reflux, 4 h) using K_3PO_4 as the base. Benzophenones **6g** and **6r** were prepared from 4- and 3-bromophenylboronic acid in good yields, respectively. These experiments show that the bromine atom is compatible with the reaction conditions. The structures of all products were confirmed by spectroscopic methods. The structure of **4** and **6a** were independently confirmed by X-ray crystallography (Figure 1 and 2).



Scheme 10. Synthesis of **3** and **4**. *Reagents and conditions: i*, 1) **2** (1.0 equiv), Me_3SiOTf (0.3 equiv), CH_2Cl_2, 0 °C, 2) **1** (1.1 equiv), 0 → 20 °C, 12 h, 3) HCl (10%); *ii*, 1) **3** (1.0 equiv), pyridine (4.0 equiv), CH_2Cl_2, -78 °C, 10 min, 2) Tf_2O (2.4 equiv), -78 → 0 °C, 4 h

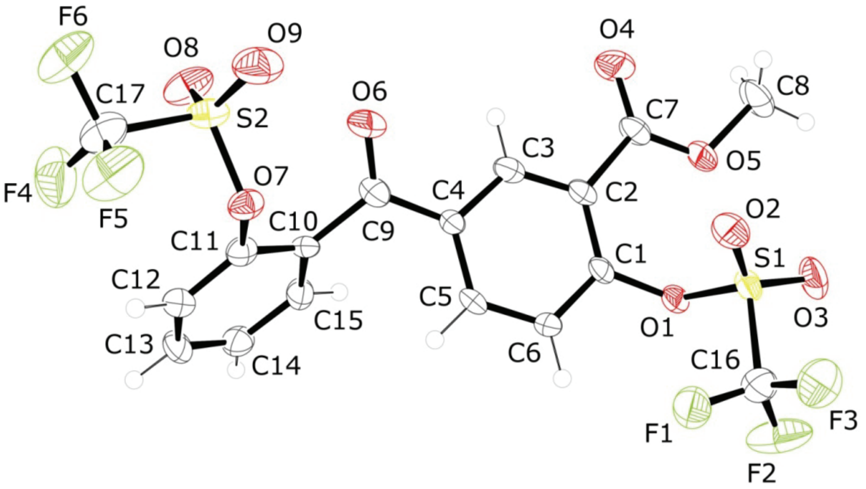
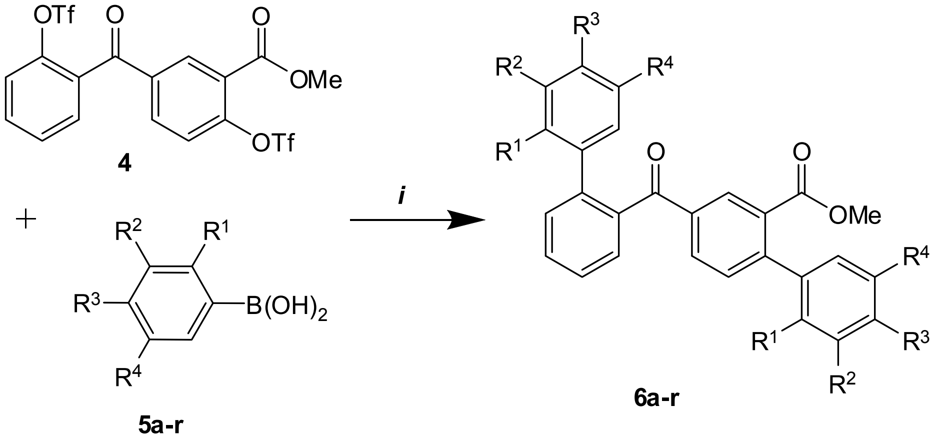


Figure 1. Ortep plot of **4**



Scheme 11. Synthesis of **6a-r**. *Reagents and conditions:* (*i*) 1,4-Dioxane (5mL/mmol of Triflate), **4** (1.0 equiv), **5a-r** (2.6 equiv), K_3PO_4 (3.0 equiv), $Pd(PPh_3)_4$ (6 mol %), 110 °C, 4h.

Table 1. Synthesis of **6a-r**

5,6	R[1]	R[2]	R[3]	R[4]	% (**6a-r**) [a]
a	H	H	Me	H	84
b	H	H	H	H	75
c	H	H	C_2H_5	H	62
d	H	Cl	H	H	77
e	H	H	Vinyl	H	72
f	H	H	Cl	H	64
g	H	H	Br	H	74
h	H	OMe	OMe	H	62
i	H	H	OH	H	67
j	H	OMe	OMe	OMe	58
k	H	H	F	H	62
l	H	OH	H	H	65
m	H	H	CF_3	H	76
n	OMe	H	H	OMe	67
o	OMe	H	H	H	69
p	H	H	*t*Bu	H	72
q	H	Me	H	Me	78
r	H	Br	H	H	64

[a] Yields of isolated products

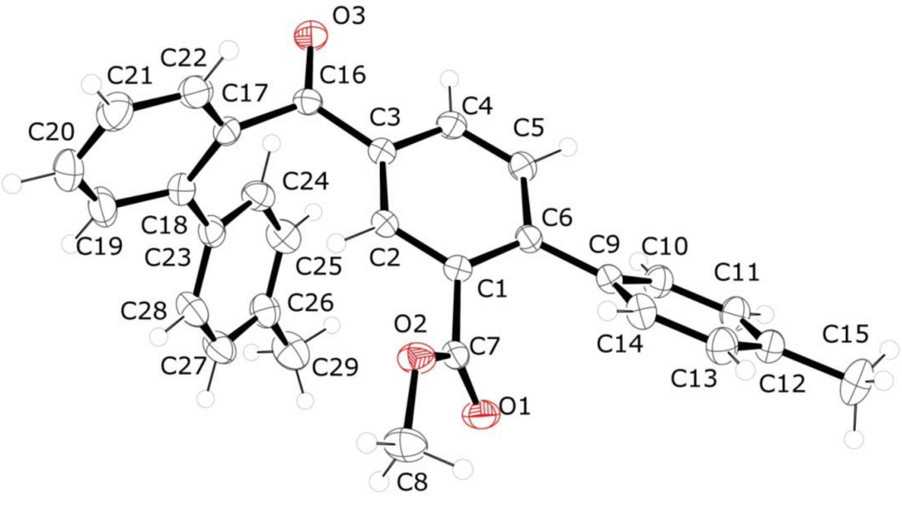
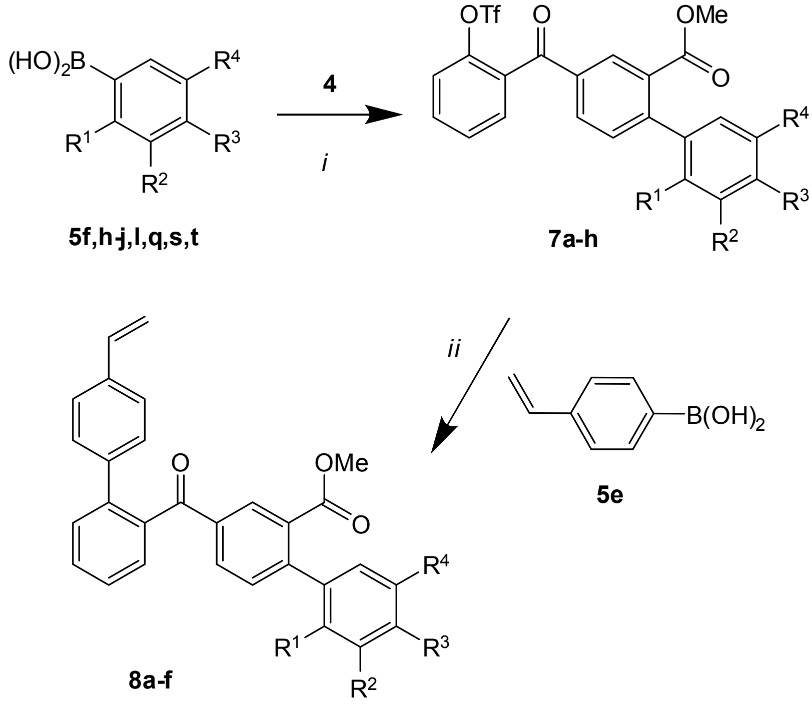


Figure 2. Ortep plot of **6a**

The Suzuki reaction of **4** with one equivalent of boronic acids **5f,h-j,l,q,s,t** resulted in the formation of the 4-arylbenzophenones **7a-h** with very good site-selectivity (Scheme 12, Table 2). The Suzuki-Miyaura reaction of **7a,c,e-h** with boronic acid **5e** gave 2′,4-diarylbenzophenones **8a-f** containing two different aryl groups (Scheme 12, Table 3). The structures of all the products were confirmed by spectroscopic methods. The structure of **7g** was independently confirmed by X-ray crystallography (Figure 3).



Scheme 12. Synthesis of **7a-h** and **8a-f**. *Reagents and conditions: i*, **4** (1.0 equiv), **5f,h-j,l,q,s,t** (1.3 equiv), K_3PO_4 (3.0 equiv), $Pd(PPh_3)_4$ (3 mol %),1,4-dioxane, 110 °C, 4 h; *ii*, **7a,c,e-h** (1.0 equiv), **5e** (1.3 equiv), K_3PO_4 (3.0 equiv), $Pd(PPh_3)_4$ (3 mol %), 1,4-dioxane, 110 °C, 4 h

Table 2. Synthesis of **7a-h**

5	**7**	R^1	R^2	R^3	R^4	% (**7a-h**)[a]
q	**a**	H	Me	H	Me	78
f	**b**	H	H	Cl	H	45
s	**c**	OEt	H	H	H	89
t	**d**	Br	H	H	H	78
h	**e**	H	OMe	OMe	H	44
i	**f**	H	H	OH	H	63
j	**g**	H	OMe	OMe	OMe	43
l	**h**	H	OH	H	H	72

[a] Yields of isolated products

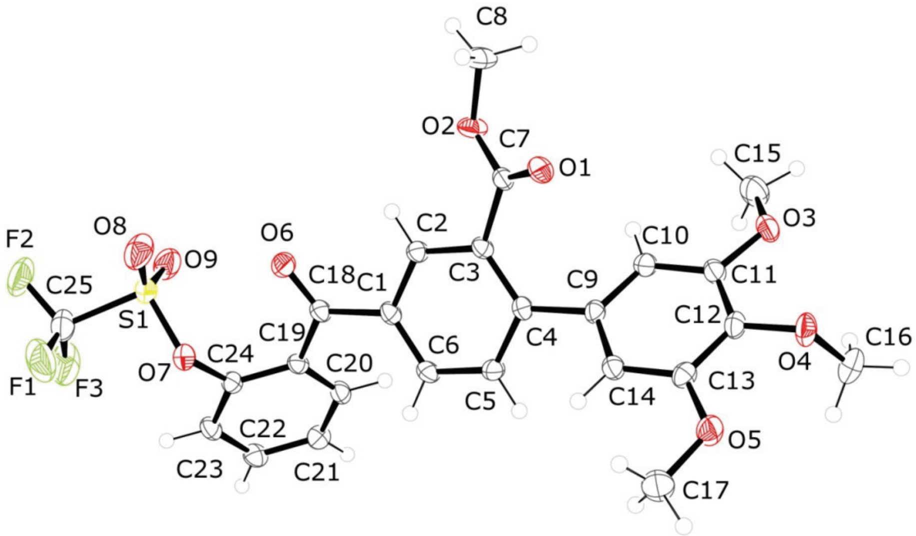


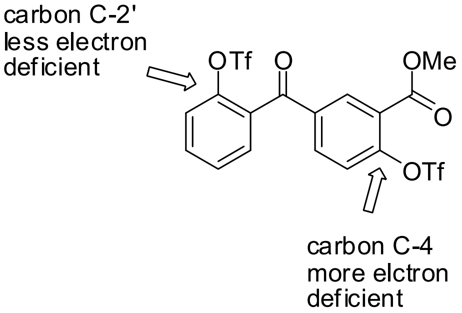
Figure 3. Ortep plot of **7g**

Table 3. Synthesis of **8a-f**

7	**8**	R^1	R^2	R^3	R^4	% (**8a-f**)[a]
a	**a**	H	Me	H	Me	60
f	**b**	H	H	OH	H	74
e	**c**	H	OMe	OMe	H	65
g	**d**	H	OMe	OMe	OMe	72
h	**e**	H	OH	H	H	64
c	**f**	OEt	H	H	H	68

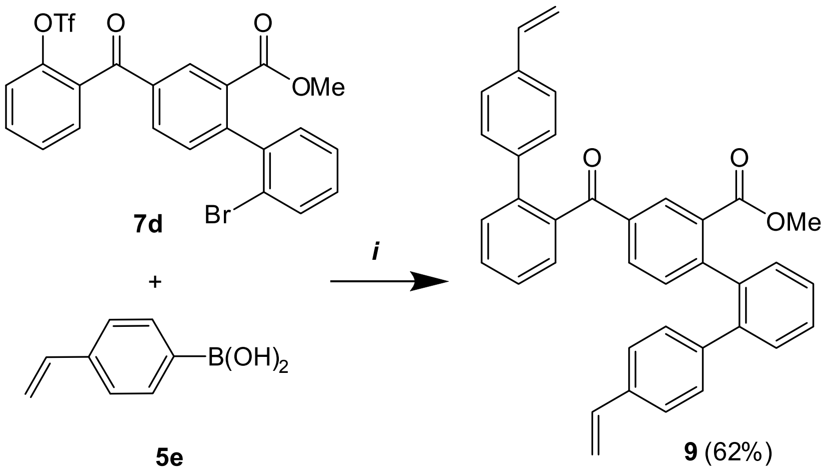
[a] Yields of isolated products

The site-selectivity of palladium(0)-catalyzed reactions of dihalides and bis(triflates) is controlled by electronic and steric parameters. The oxidative addition of palladium usually occurs first at the most electron deficient and sterically less hindered carbon atom. The site-selective formation of products **7a-h** can be explained by the fact that carbon atom C-4 is more electron deficient and less sterically hindered than C-2′. One electron-withdrawing benzoyl group is located *ortho* to C-2′. In contrast, both an electron-withdrawing benzoyl group and an electron-withdrawing ester group are located *para* and *ortho* to C-4, respectively.



Scheme 13. Possible explanation for the site-selective formation of products **7a-h**

The Suzuki-Miyaura reaction of **7d**, containing a bromide and a triflate group in *ortho* position, with **5e** (2.6 equiv.) afforded the bis-diphenyl-ketone **9** in good yield (Scheme 14).



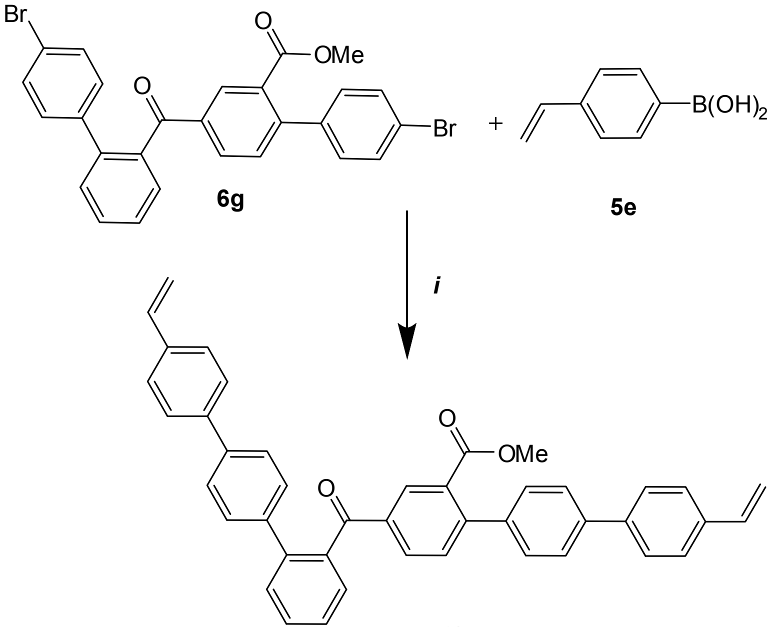
7d

5e

9 (62%)

Scheme 14. Synthesis of **9**. *Reagents and conditions: i*, **7d** (1.0 equiv), **5e** (2.6 equiv), K_3PO_4 (3.0 equiv), $Pd(PPh_3)_4$ (3 mol %), 1,4-dioxane, 110 °C, 4 h

The Suzuki-Miyaura reaction of **5e** (2.6 equiv.) with **6g**, containing two *para*-bromophenyl moieties, afforded the diphenyl-triphenyl-ketone **10** (Scheme 15).



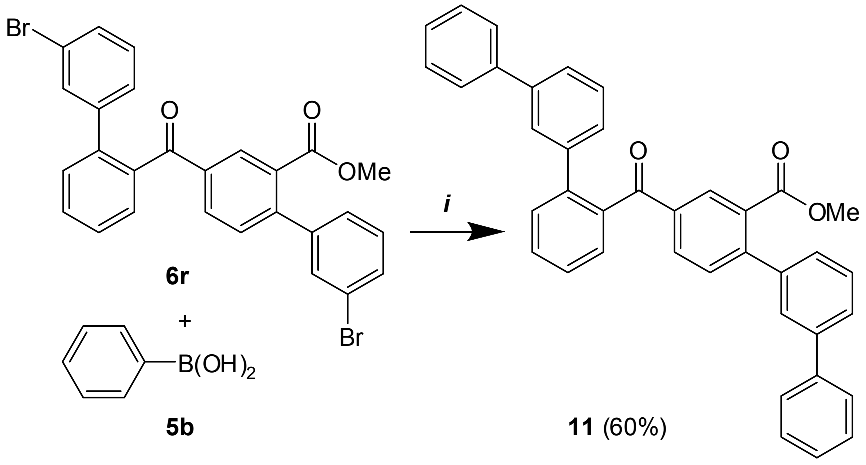
6g

5e

10 (72%)

Scheme 15. Synthesis of **10**. *Reagents and conditions: i*, **6g** (1.0 equiv), **5e** (2.6 equiv), K_3PO_4 (3.0 equiv), $Pd(PPh_3)_4$ (3 mol %), 1,4-dioxane, 110 °C, 4 h

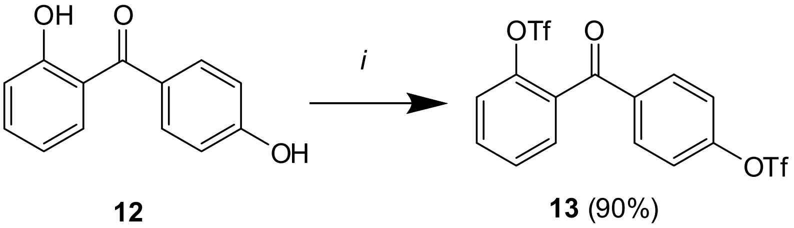
The Suzuki-Miyaura reaction of **5b** (2.6 equiv.) with **6r**, containing two *meta*-bromophenyl moieties, afforded the diphenyl-triphenyl-ketone **11** (Scheme 16).



Scheme 16. Synthesis of **11**. *Reagents and conditions: i*, **6r** (1.0 equiv), **5b** (2.6 equiv), K_3PO_4 (3.0 equiv), $Pd(PPh_3)_4$ (3 mol %), 1,4-dioxane, 110 °C, 4 h.

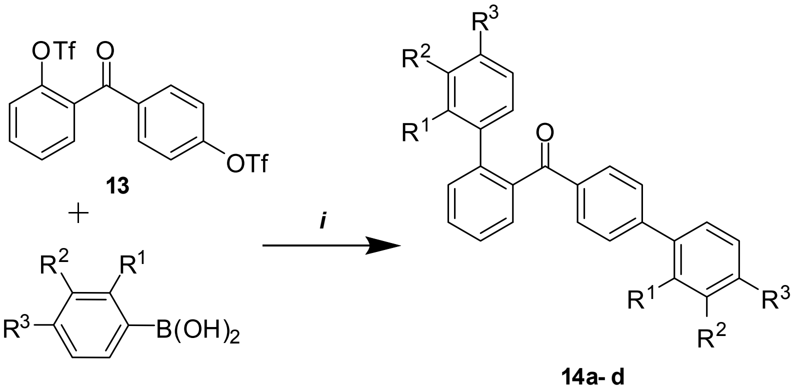
2.3 Synthesis of Functionalized 2′,4′-Diarylbenzophenones:

2,4′-dihydroxybenzophenone represents a commercially available and inexpensive substrate. 2,4′-dihydroxybenzophenone (**12**) was transformed into its bis(triflate) **13** in 90% yield (Scheme 17).



Scheme 17. Synthesis of **13**. *Reagents and conditions: i*, CH_2Cl_2, **12** (1.0 equiv), -78 °C, pyridine (4.0 equiv), Tf_2O (2.4 equiv), -78 → 0 °C, 4 h.

The Suzuki reaction of **13** with different boronic acids (2.6 equiv.) afforded the novel 2,4′-diarylbenzophenones **14a-d** in good yields (Scheme 18, Table 4). The best yields were obtained when $Pd(PPh_3)_4$ (6 mol-%) was used as the catalyst, when 2.6 equiv. of the boronic acid was employed, and when the reaction was carried out in 1,4-dioxane (reflux, 4 h) using K_3PO_4 as the base. The structures of all products were established by spectroscopic methods. The structure of **14b** was independently confirmed by X-ray crystallographic analysis (Figure 11).



Scheme 18. Synthesis of **14a-d**. *Reagents and conditions:* (*i*) 1,4-Dioxane (5mL/mmol of Triflate), 13 (1.0 equiv), a (2.6 equiv), K_3PO_4 (3.0 equiv), $Pd(PPh_3)_4$ (6 mol %), 110 °C, 4h.

Table 4. Synthesis of **14a-d**

14	R^1	R^2	R^3	% (**14a-d**)[a]
a	H	OCH_3	H	78
b	F	H	H	70
c	H	H	OCH_3	68
d	H	H	Vinyl	66

[a] Yields of isolated products.

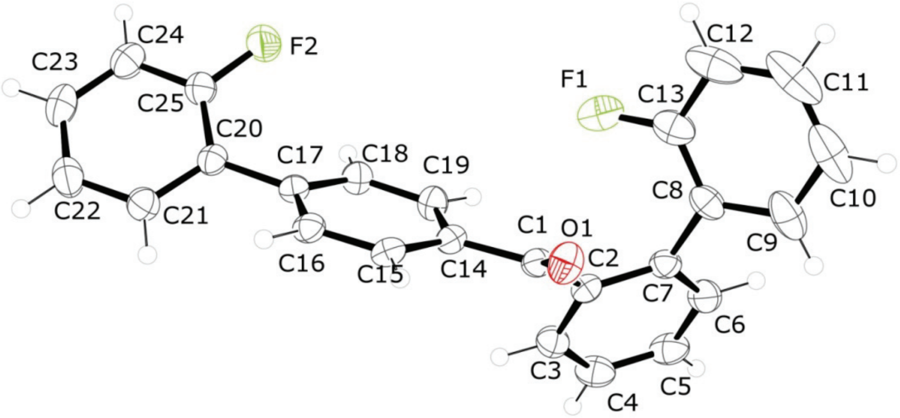
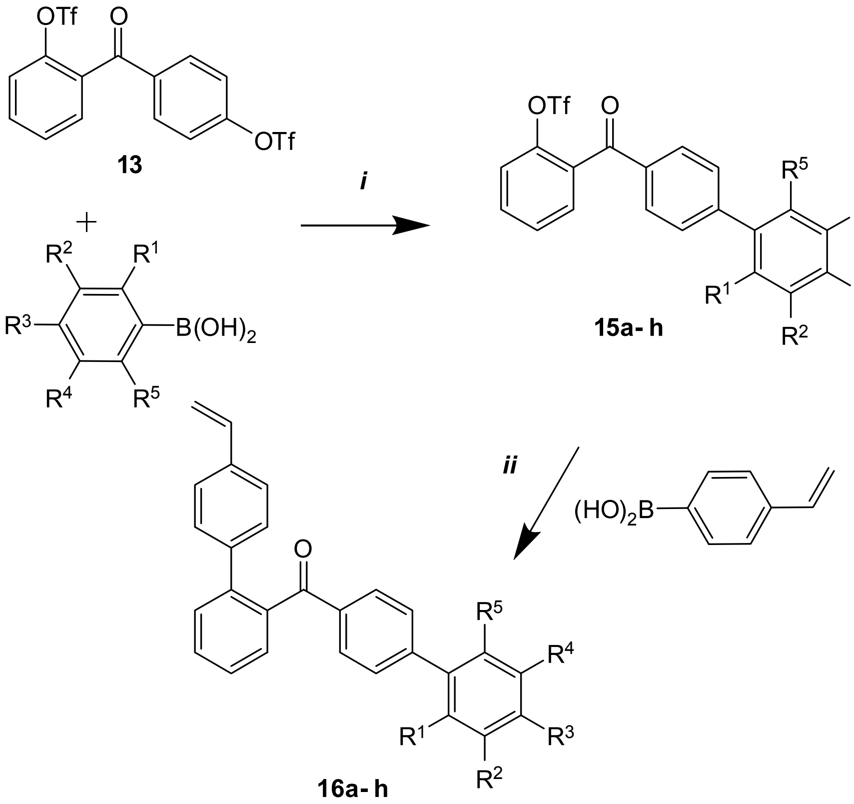


Figure 4. Ortep plot of **14b**

The Suzuki reaction of **13** with different boronic acids (1.3 equiv.), in the presence of $Pd(PPh_3)_4$ (3 mol-%), proceeded with very good site-selectivity (attack at carbon atom C-4′) to give the benzophenones **15a-h** (Scheme 19, Table 5). The pure mono-coupled product was obtained after chromatographic purification. The reaction of **15a-h** with (4-vinylphenyl) boronic acid (1.3 equiv.) gave 2,4-diarylbenzoates **16a-h** containing two different aryl groups. The structures of all the products were proved by spectroscopic methods. The structure of **15f** and **15h** were independently confirmed by X-ray crystallography (Figure 5 and 6), which further give a strong clue about the first regioselective attack at carbon atom C-4′.



Scheme 19. Synthesis of **15a-h** and **16a-h**. *Reagents and conditions: i*, **13** (1.0 equiv), boronic acids (1.3 equiv), K_3PO_4 (1.5 equiv), $Pd(PPh_3)_4$ (3 mol %), 1,4-dioxane, 110 °C, 4 h; *ii*, **15a-h** (1.0 equiv), 4-vinylphenyl boronic acid (1.3 equiv), K_3PO_4 (1.5 equiv), $Pd(PPh_3)_4$ (3 mol%), 1,4-dioxane, 110 °C, 4 h.

Table 5. Synthesis of **15a-h** and **16a-h**

15,16	R^1	R^2	R^3	R^4	R^5	% (**15a-h**)[a]	% (**16a-h**)[a]
a	H	OCH_3	H	H	H	68	70
b	OCH_3	H	H	OCH_3	H	72	72
c	OCH_3	H	H	H	OCH_3	64	68
d	OEt	H	H	H	H	76	62
e	H	Vinyl	H	H	H	70	66
f	H	H	*t*Bu	H	H	66	64
g	H	CH_3	H	CH_3	H	78	76
h	H	H	Et	H	H	74	74

[a] Yields of isolated products

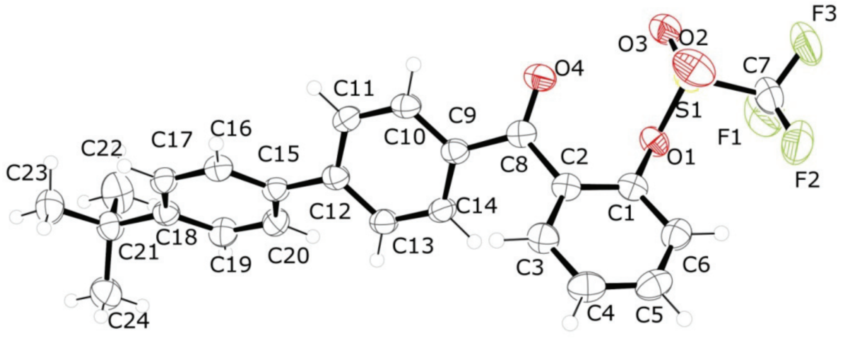


Figure 5. Ortep plot of **15f**

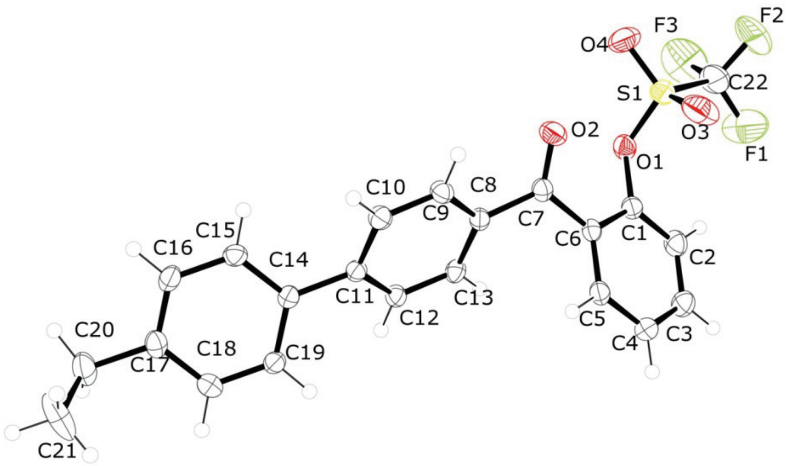
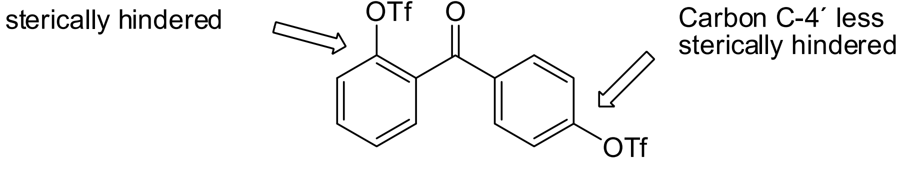


Figure 6. Ortep plot of **15h**

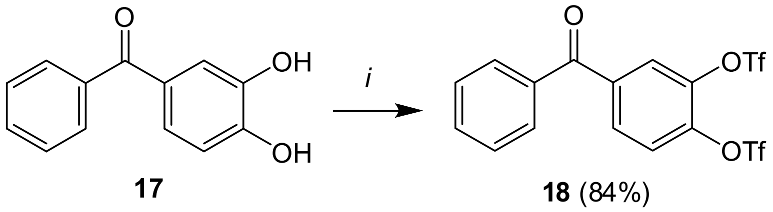
The site-selective formation of **15a-h** can be explained by the fact that carbon atom C-4´ (located *para* to the keto group) is less sterically hindered than C-2´ (located *ortho* to the keto group).



Scheme 20. Possible explanation for the site-selective formation of products **15a-h**

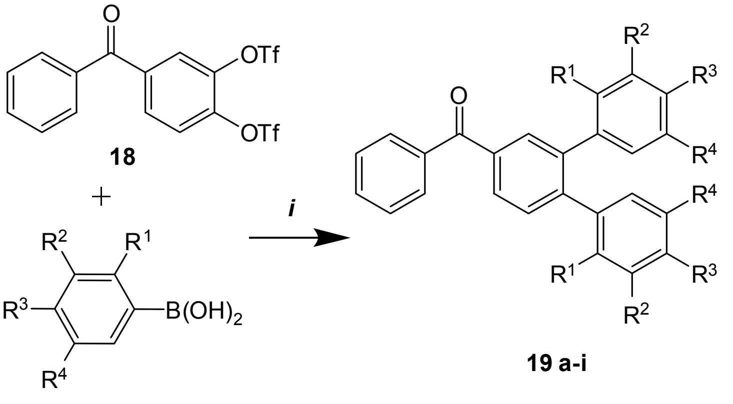
2.4 Synthesis of 3,4-Diarylbenzophenones:

In this chapter, I report what are, to the best of my knowledge, the first site-selective palladium(0)-catalyzed cross-coupling reactions of the bis(triflate) of 3,4-dihydroxy benzophenone which represents a commercially available and inexpensive substrate. The site-selectivity can be explained by electronic reasons. The products reported herein are not readily available by other methods. 3,4-Dihydroxybenzophenone (**17**) was transformed into its bis(triflate) **18** in 84% yield (Scheme 21).



Scheme 21. Synthesis of **18**. *Reagents and conditions: i*, CH_2Cl_2, **17** (1.0 equiv), -78 °C, pyridine (4.0 equiv), Tf_2O (2.4 equiv), -78 → 0 °C, 4 h.

The Suzuki reaction of **18** with different boronic acids (2.6 equiv.) afforded the novel 3,4-diarylbenzophenones **19a-i** in good yields (Scheme 22, Table 6). The best yields were obtained when $Pd(PPh_3)_4$ (6 mol-%) was used as the catalyst, when 2.6 equiv. of the boronic acid was employed, and when the reaction was carried out in 1,4-dioxane (reflux, 4 h) using K_3PO_4 as the base. The structures of all products were established by spectroscopic methods. The structure of **19c** was independently confirmed by X-ray crystal structure analysis (Figure 7).



Scheme 22. Synthesis of **19a-i**. *Reagents and conditions: i*, **18** (1.0 equiv.), boronic acids (2.6 equiv.), K_3PO_4 (3.0 equiv.), $Pd(PPh_3)_4$ (6 mol-%), 1,4-dioxane (5 mL per 1 mmol of **18**), 110 °C, 4 h

Table 6. Synthesis of **19a-i**

19	R^1	R^2	R^3	R^4	% (**19a-i**)[a]
a	H	H	H	H	78
b	H	H	F	H	69
c	H	Me	H	Me	75
d	OMe	H	OMe	H	74
e	OMe	H	H	H	67
f	H	H	OMe	H	54
g	OEt	H	H	H	76
h	H	Me	Me	H	58
i	H	H	Et	H	78

[a] Yields of isolated products

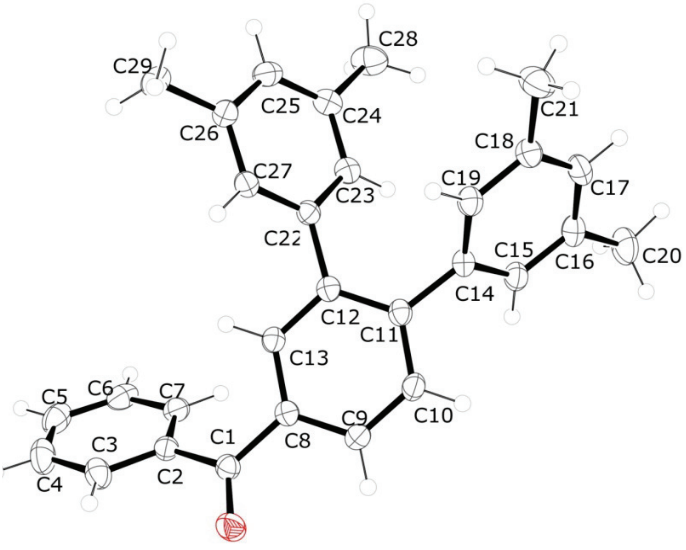
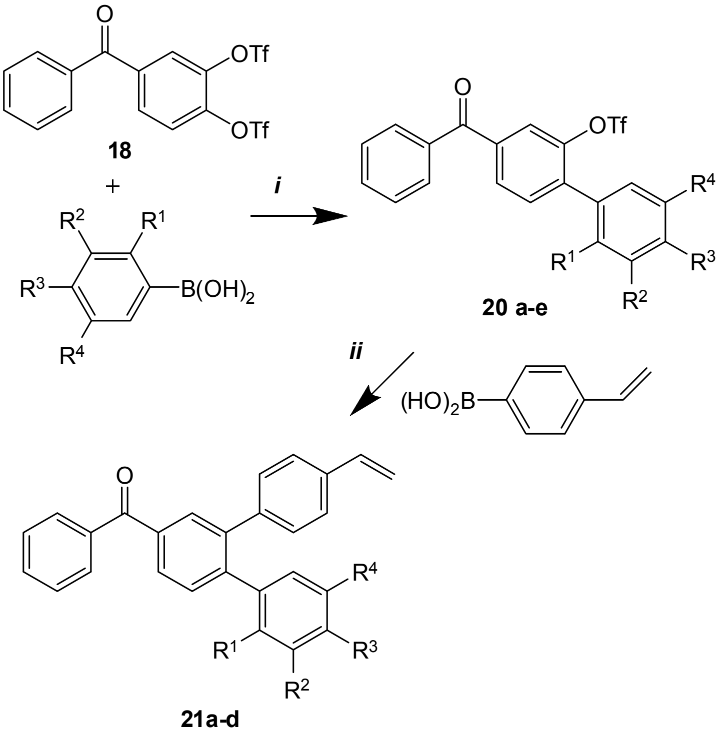


Figure 7. Ortep plot of **19c**

The Suzuki reaction of **18** with different boronic acids (1.3 equiv.), in the presence of $Pd(PPh_3)_4$ (3 mol-%), proceeded with very good site-selectivity (attack at carbon atom C-4) to give the benzophenones **20a-e** (Scheme 23, Table 7). In some cases, a small amount of the bis-coupled product could be detected in the crude product (by ^{1}H-NMR and GC-MS). The pure mono-coupled product was obtained after chromatographic purification. The reaction of **20a-d** with (4-vinylphenyl) boronic acid (1.3 equiv.) gave 2,4-diarylbenzoates **21a-d** containing two different aryl groups. The structures of the products were elucidated by spectroscopic methods.



Scheme 23. Synthesis of **20a-e** and **21a-d**. *Reagents and conditions: i*, **18** (1.0 equiv), boronic acids (1.3 equiv), K_3PO_4 (1.5 equiv), $Pd(PPh_3)_4$ (3 mol %), 1,4-dioxane, 110 °C, 4 h; *ii*, **20a-e** (1.0 equiv), 4-vinylphenyl boronic acid (1.3 equiv), K_3PO_4 (1.5 equiv), $Pd(PPh_3)_4$ (3 mol%), 1,4-dioxane, 110 °C, 4 h

Table 7. Synthesis of **20a-e** and **21a-d**

20	**21**	R^1	R^2	R^3	R^4	% (**20a-e**)[a]	% (**21a-d**)[a]
a	**a**	H	OMe	H	H	68	68
b	**-**	OMe	H	H	OMe	72	*b*
c	**b**	H	H	Me	H	64	78
d	**c**	H	OMe	OMe	OMe	76	64
e	**d**	H	H	*t*Bu	H	70	62

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

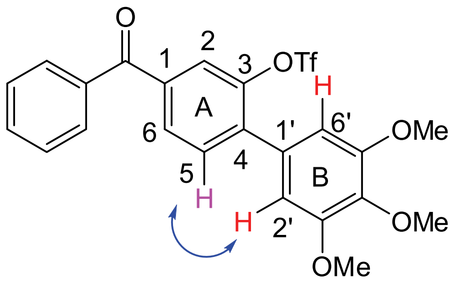
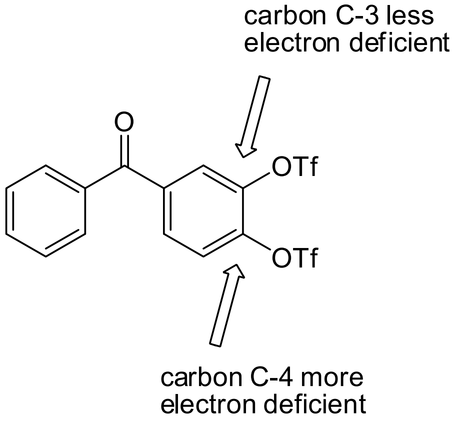


Figure 8. Relevant NOESY-correlation for Compound **20d**

The structure of compound (**20d**) was unambiguously confirmed by 2D-NMR techniques. In the NOESY spectrum, an interaction was observed between the aromatic proton attached to the carbon atom C-5 of the ring A, to that of the aromatic protons of ring B attached to the carbons atoms C-2□ and C-6□. This confirmed that the first attack of boronic acid takes place at carbon C-4 of the bis(triflate). These correlations are not observed, if the boronic acid is attached to the carbon atom C-3 of the bis(triflate).

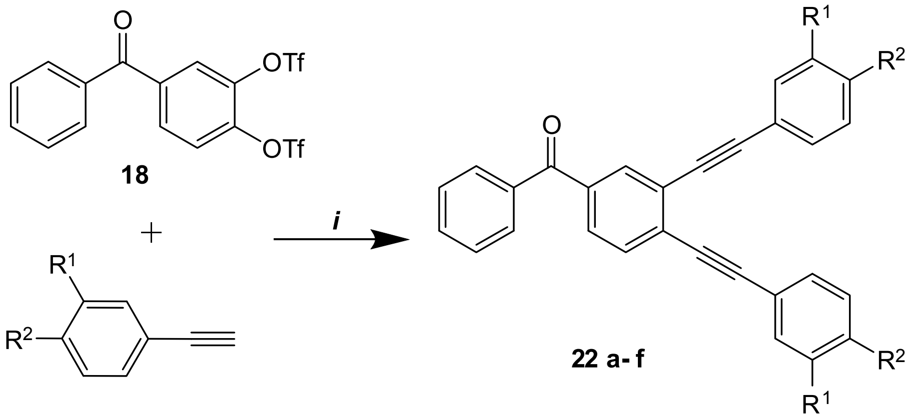
The site-selective formation of **20a-e** can be explained by the fact that carbon atom C-4 (located *para* to the keto group) is more electron-deficient than C-3 (located *meta* to the keto group). Steric parameters have presumably no effect, due to the similar steric environment of carbon atoms C-3 and C-4 (Scheme 24).



Scheme 24. Possible explanation for the site-selective formation of products **20a-e**

2.5 Sonogashira reaction of the bis(triflate) of 3,4-dihydroxybenzophenone:

The Sonogashira reaction of **18** with different alkynes (2.6 equiv.) afforded the novel 3,4-dialkynylbenzophenones **22a-f** in good yields (Scheme 25, Table 8). The best yields were obtained when $Pd(PPh_3)_2Cl_2$ (6 mol-%) was used as the catalyst, when 2.6 equiv. of the alkyne was employed, and when the reaction was carried out in DMF (reflux, 4 h) using Et_3N as the base. The structures of all products were established by spectroscopic methods.



Scheme 25. Synthesis of **22a-f.** *Reagents and conditions: i*, **18** (1.0 equiv), alkynes (2.0 equiv), Dry CuI (10%), $Pd(PPh_3)_2Cl_2$ (5 mol %), Et_3N (1.25 equiv), DMF, 110 °C, 4 h.

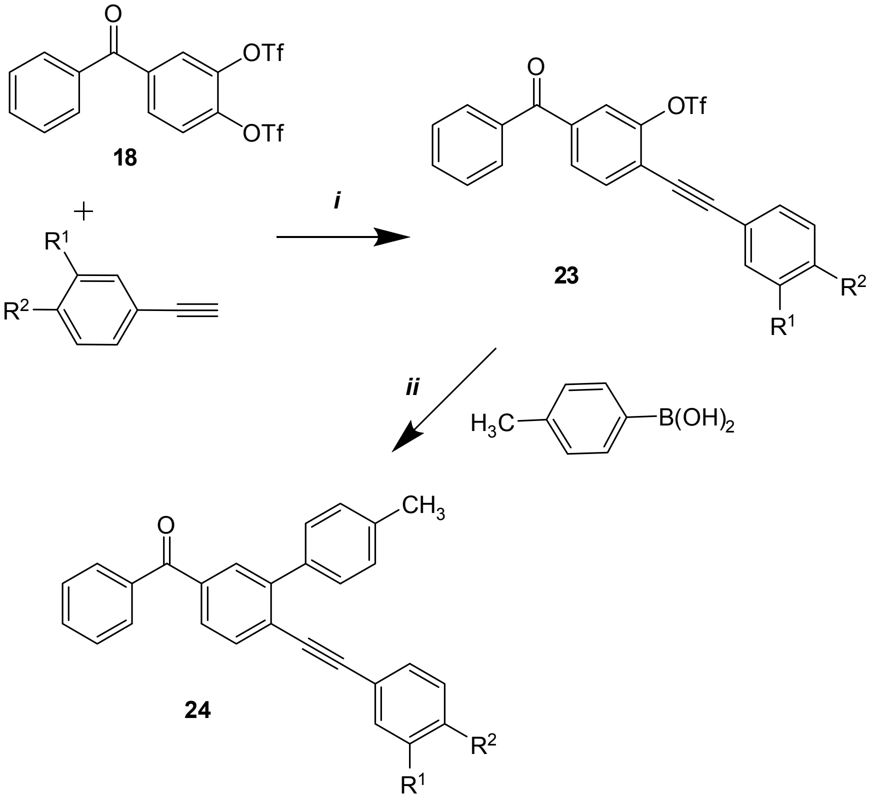
Table 8. Synthesis of **22a-f**

22	R^1	R^2	% (**22a-f**) [a]
a	H	*t*Bu	78
b	H	H	54
c	OMe	H	64
d	H	Me	66
e	H	F	60
f	Me	H	58

[a] Yields of isolated products

The Sonogashira reaction of 3,4-bis(trifluoromethylsulfonyloxy)benzophenone **(18)** with different alkynes (1.3 equiv.), in the presence of $Pd(PPh_3)_2Cl_2$ (3 mol-%) as a catalyst, proceeded with very good site-selectivity (attack at carbon atom C-4) to give the product **23** (Scheme 26).

The mono-Sonogashira product **23** was treated with 4-methylphenylboronic acid (1.2 equiv), in the presence of K_3PO_4 (1.5 equiv) and $Pd(PPh_3)_4$ (3 mol%) in 1,4-dioxane at 90 °C, to give **24** in good yield (64%). The structures of all products were established by spectroscopic methods. The structure of **24** was independently confirmed by X-ray crystal structure analysis (Figure 9). The crystal structure of **24** further proves that the first regioselective attack of the alkyne takes place at carbon atom C-4.



Scheme 26. Synthesis of **23** and **24.** *Reagents and conditions: i)* **18** (1.0 equiv), alkynes (1.1 equiv), dry CuI (10%), $Pd(PPh_3)_2Cl_2$ (5%), Et_3N (1.25 equiv), DMF, 90 °C, 8 h. *ii)* **23** (1.0 equiv), 4-methyl phenylboronic acid (1.3 equiv), K_3PO_4 (1.5 equiv), $Pd(PPh_3)_2Cl_2$ (3 mol%), DMF, 90°C, 4 h.

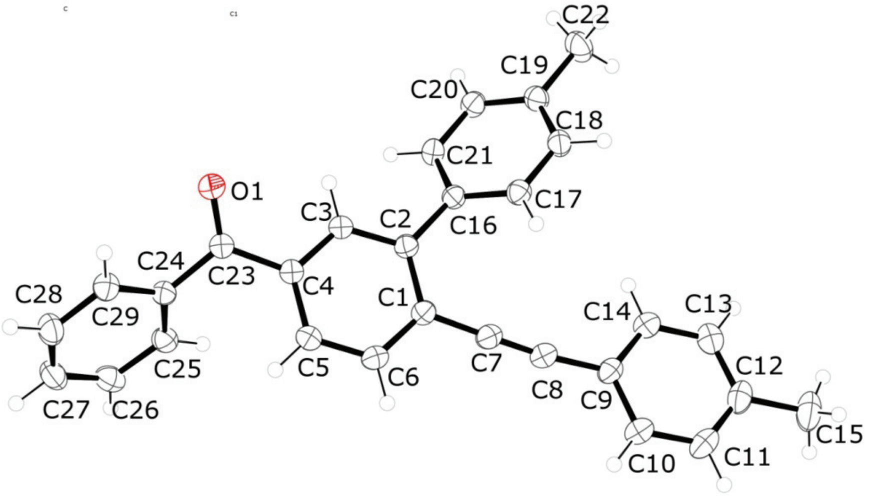


Figure 9. Ortep plot of **24**

2.6 Conclusion:

In conclusion, I have reported the synthesis of 2,4′-diarylbenzophenones based on what are, to the best of my knowledge, the first palladium(0)-catalyzed Suzuki cross-coupling reactions of bis(triflates) of 2,4′-dihydroxybenzophenones. These reactions proceed with very good site-selectivity. In addition, it has been shown that brominated 2,4′-diarylbenzophenones can be prepared which can be transformed into more complex bis-diphenyl-ketones and diphenyl-triphenyl-ketones. The products reported herein were prepared by a building block strategy. I have also reported the synthesis of 3,4-diarylbenzophenones. The products reported herein are prepared by palladium(0)-catalyzed Suzuki cross-coupling reactions of the bis(triflate) of 3,4-dihydroxybenzophenone. The Sonogashira cross-coupling reactions of the same substrate with terminal alkynes allow the formation of symmetrical and unsymmetrical alkynal-substituted benzophenones. All the products reported herein are not readily available by other methods.

3. Synthesis of Functionalized *p*-terphenyls and *m*-terphenyls based on site-selective Suzuki cross-coupling reactions of bis(triflates) of 2,5- and 2,4-dihydroxybenzoate

3.1 Introduction:

3.1.1 Introduction of *p*-terphenyls:

Functionalized *p*-terphenyls occur in a great variety of pharmacologically relevant natural products. Examples include terphenyllin,[58] terprenin,[59] curtisian A,[60] leucomentin-6,[61] thelephorin A,[62] ganbajunin D,[63] and thelephantin A.[64] Symmetrical and unsymmetrical terphenyls, functionalized with electron donor or acceptor groups, are the main constituents of a large number of mushrooms belonging to the *Thelephoraceae* family.[65] Recently, numerous natural products having a terphenyl architecture, such as thelephorin,[66] terphenyllin,[67] terferol[68] and terprenin,[69] have been reported to possess interesting biological properties. Several synthetic terphenyl derivatives have been designed as selective inhibitors for dihydroortate dehydrogenase[70] and cyclooxygenase[71] enzymes.

Terphenyl containing acidic groups have recently been found to be potent insulin sensitizers.[72] Recently, Yamazoe and Nozaki[73] have identified a terphenyl-based novel auxin signaling inhibitor, terfestatin A, from *Streptomyces* sp. F40. Owing to their interesting optical[74] and electrical[75] properties, terphenyls find several industrial applications as liquid crystals, conducting polymers, heat storage and heat transfer agents, as textile dye carriers and as laser dyes.

Transition metal-catalyzed aryl-aryl cross coupling reactions are commonly employed for constructing biaryls. Palladium-catalyzed aryl-aryl cross-coupling between electrophilic aromatic dihalides $Ar(X)_2$ (X being generally Br, I and OTf) and two equivalents of organometallic species Ar-M (M being Mg, Ni, Zn, Sn and B) constitute a versatile synthetic method for the preparation of symmetrical and unsymmetrical terphenyls.[76] Suzuki couplings[77] of a diverse array of haloarenes with aryl boronic acids gained wide popularity, due to the commercial availability of several aryl boronic acid and innocuous nature of the latter, easy work-up and tolerance of the reactions to aqueous media. Symmetrical terphenyls have been prepared by double coupling reactions of aryl boronic acids[78] with aryl halides and aryl distannanes.[79] The classical approach to unsymmetrical terphenyls requires either the reactions of biaryl boronic acids with aromatic halides[80] or the stepwise chemoselective cross-coupling of aryl compounds containing two dissimilar halides or triflates.[81]

A recent report by Wu & Luo[82] demonstrated the potential applications of *para*-terphenyl derivatives containing cyano groups in organic light emitting diode (OLED) fabrication. It has been well documented that the introduction of alkoxy substituents in conjugated materials enhances the solubility of the polymer. The presence of the cyano group influences photophysical and electroluminescent properties by lowering the energy of the LUMO, thus exhibiting a relatively low threshold voltage and high quantum efficiency in LED devices.[83]

Polychlorinated terphenyls (PCTs) are yellow resins that have a number of qualities which make them useful for industrial purposes. These qualities are similar to polychlorinated biphenyls (PCBs), and PCTs have also been used as PCB substitutes. Technical PCT products contain small amounts of PCBs, generally 0.5%, sometimes up to 10%.[84] Characteristics of PCTs include: very low electrical conductivity and extremely high resistance to thermal breakdown; insolubility in water, but solubility in various organic solvents and oils; resistance to attack by corrosive chemicals such as alkali and strong acids; heat stability and non-flammability. PCTs have been used in both closed systems, such as electric transformers, and open-ended applications, such as lubricating and cutting oils.

The main uses of PCTs have been as[85] plasticizers in synthetic resins, adhesives, lubricants, paper coatings, investment casting waxes, printing inks, carbonless copying paper, sealants (e.g., for concrete stave silos and caulking compounds), fire-retardants, vapour suppressants to extend the kill-life of insecticides, coatings to render fabric flame-proof, rot-proof and water-repellent, and in the manufacture of brake linings, abrasives for grinding wheels, lacquers, varnishes and paints; impregnants for braided cotton and asbestos insulation, in electrical wire and cable coatings, and as dielectric sealants, PCT-containing waxes used in making dental casts, costume jewelry and precision-cast aircraft parts.

Natural occurrence of products with a *p*-terphenyl core is essentially restricted to fungi and lichens. In particular, *p*-terphenylquinones were known as fungal pigments for a long time. Indeed, the colouring principles in mushrooms and toadstools attracted the interest of the scientists since the late 19th century and the pioneering work in this field has been reviewed in the older literature.

Fully aromatic polyhydroxy *p*-terphenyls have generally been reported later than the related terphenylquinones. An array of biological activity has been reported for these polyhydroxy-*p*-terphenyls, including cytotoxic activity against tumoral cells and other anti-proliferative properties, antibacterial activity, antioxidant or radical scavenging activity, anti-inflammatory activity and other properties of biomedical or agronomical interest. Recently, an increasing number of *p*-terphenyl metabolites showing interesting biological properties and unusual structures have been reported.[86]

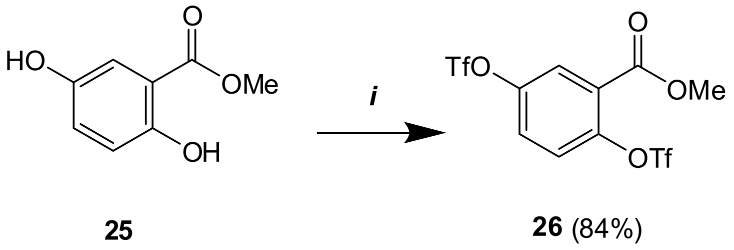
3.1.2 Introduction of *m*-terphenyls:

The chemical core structure of *meta*-terphenyls also occurs in a great variety of pharmacologically relevant natural products. Examples include various simple hydroxylated and alkylated *meta*-terphenyls, such as trifucolnonaacetate, dunnianol, or mulberrofuran R.[87] Other derivatives, such pusilatin A, are incorporated in cyclophanes.[88] The *meta*-terphenyl unit of various other natural products is incorporated in a bis(anthracene)[89] or bis(carbazol)[90] framework. The *meta*-terphenyl substructure is also found in complex macrocyclic natural products, such as acutissimins B, castalagin, or roburin A.[91-93] In addition; *meta*-terphenyls are ideal precursors in the design of cyclophanes and are useful as tectones in crystal engineering.[94]

3.2 Synthesis of Functionalized *p*-terphenyls:

Tschierske and coworkers reported the synthesis of *p*-terphenyls by double Suzuki reactions of methyl 2,5-dibromobenzoate. The employment of two equivalents of the same boronic acid in this study gave no rise to the issue of site-selectivity. Mioskowski *et al.* reported site-selective Sonogashira reactions of 2,5-diiodobenzoic acid. The scope of this approach is limited by the fact that polyhalogenated benzene derivatives are often not readily available. In this chapter I have studied palladium-catalyzed cross-coupling reactions of the bis(triflate) of methyl 2,5-dihydroxybenzoate, which represents a commercially available and inexpensive substrate. Reactions of this or related bis(triflates) have, to the best of my knowledge, not been reported to date. The reactions provide a facile synthesis of *p*-terphenyls.

Methyl 2,5-dihydroxybenzoate **(25)** was transformed into the bis(triflate) **26** in 84% yield (Scheme 27). The Suzuki reaction of **26** with different boronic acids (2.6 equiv.) afforded the novel *p*-terphenyls **27a-f** in good yields (Scheme 28, Table 9). The best yields were obtained when $Pd(PPh_3)_4$ (6 mol-%) was used as the catalyst, when 2.6 equiv. of the boronic acid was employed, and when the reaction was carried out in 1,4-dioxane (reflux, 4 h) using K_3PO_4 as the base. The structures of all products were established by spectroscopic methods. The structure of **25, 26, 27b** and **27d** was independently confirmed by X-ray crystal structure analysis (Figure 10, 11, 12, 13).



Scheme 27. Synthesis of 26. *Reagents and conditions:* (*i*) CH_2Cl_2, **25** (1.0 equiv), -78 °C, pyridine (4.0 equiv), -78°C, Tf_2O (2.4 equiv), 4h.

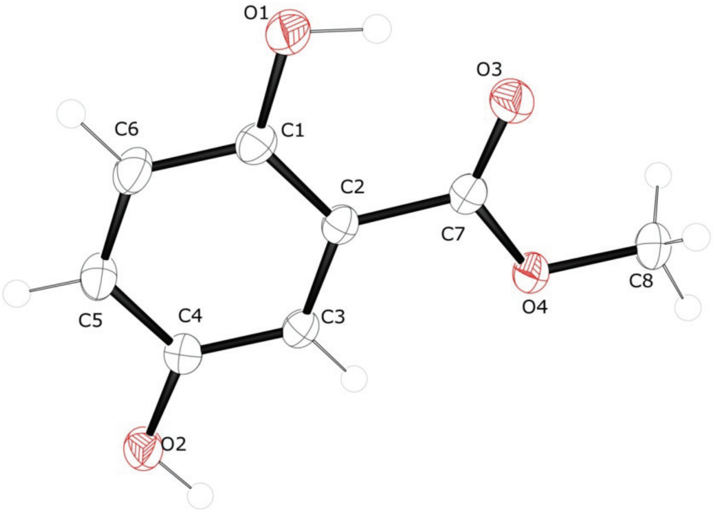


Figure 10. Ortep plot of **25**

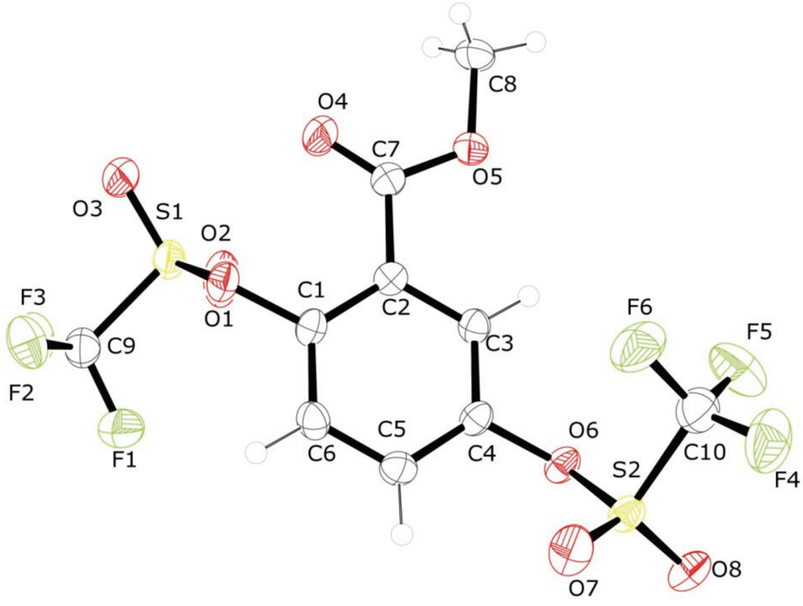
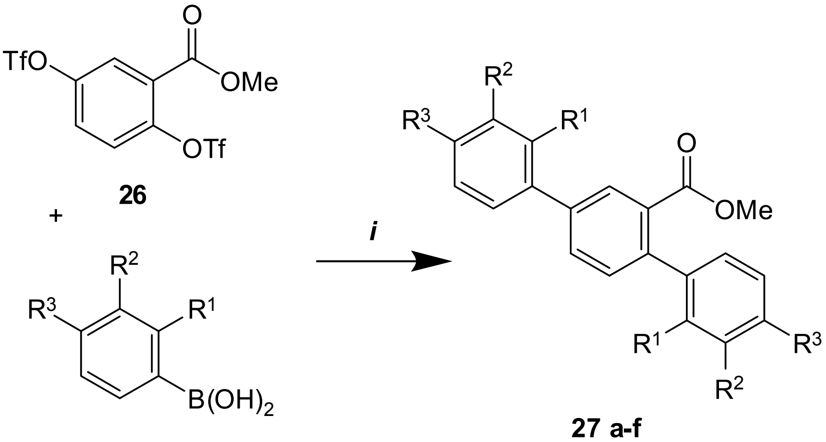


Figure 11. Ortep plot of **26**



Scheme 28. Synthesis of **27a-f**. *Reagents and conditions: i*, **26** (1.0 equiv.), boronic acids (2.6 equiv.), K_3PO_4 (3.0 equiv.), $Pd(PPh_3)_4$ (6 mol-%), 1,4-dioxane (5 mL per 1 mmol of **26**), 110 °C, 4 h

Table 9. Synthesis of **27a-f**

27	R^1	R^2	R^3	% (**27a-f**)^a
a	OMe	H	H	78
b	H	H	*t*Bu	75
c	H	OMe	OMe	56
d	H	H	*Vinyl*	77
e	H	Cl	H	67
f	H	H	H	54

^{a} Yields of isolated products

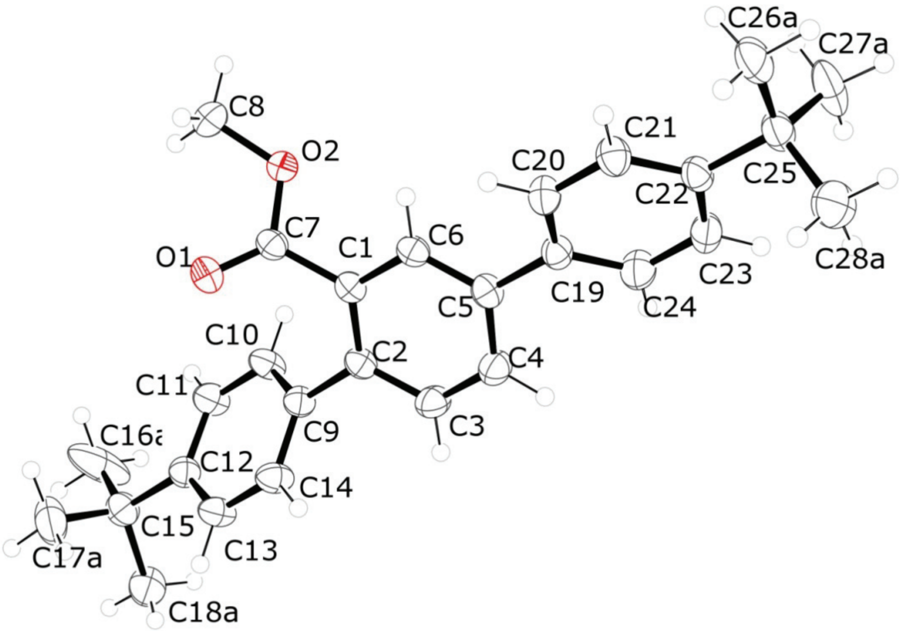


Figure 12. Ortep plot of **27b**

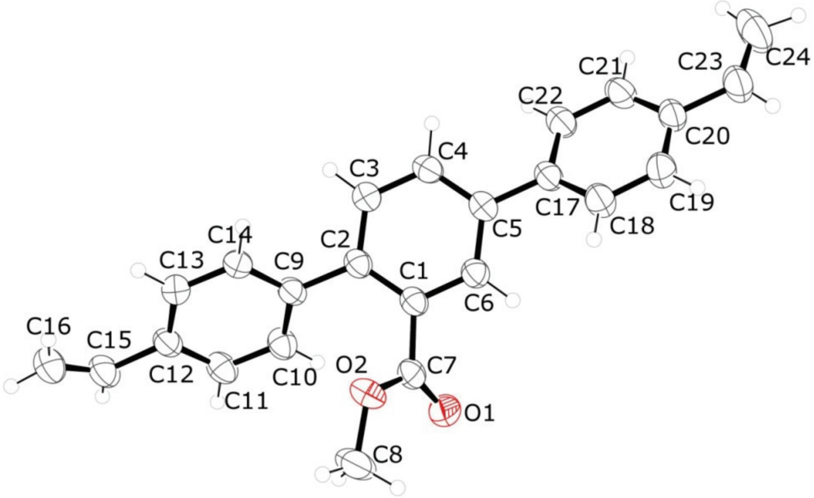
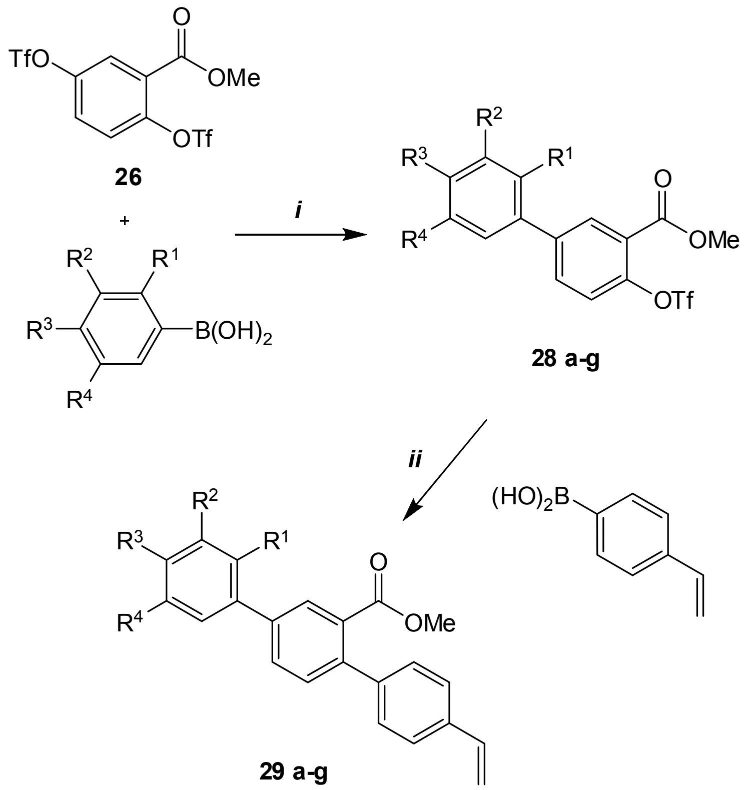


Figure 13. Ortep plot of **27d**

The Suzuki reaction of **26** with different boronic acids (1.3 equiv.), in the presence of $Pd(PPh_3)_4$ (3 mol-%), occurred site-selectively at carbon atom C-5, **28a-g** (Scheme 29, Table 10). The reaction of **28a-g** with 4-vinylphenyl boronic acid (1.3 equiv.) gave mixed *p*-terphenyls **29a-g** containing two different boronic acids. The structures of all the products were determined by NMR-spectroscopic methods. The structures of the mono-products were proved by 2D-NMR experiments (NOESY, HMBC).



Scheme 29. Synthesis of **28a-g** and **29a-g**. *Reagents and conditions: i*, **26** (1.0 equiv), boronic acids (1.3 equiv), K_3PO_4 (1.5 equiv), $Pd(PPh_3)_4$ (3 mol-%), 1,4-dioxane (5mL per 1 mmol of **26**), 110 °C, 4 h; *ii*, **28a-g** (1.0 equiv), 4-vinylphenyl boronic acid (1.3 equiv), K_3PO_4 (1.5 equiv), $Pd(PPh_3)_4$ (3 mol-%), 1,4-dioxane (5mL per 1 mmol of **28**), 110 °C, 4 h.

Table 10. Synthesis of **28a-g** and **29a-g**

28,29	R^1	R^2	R^3	R^4	% (**28a-g**)[a]	% (**29a-g**)[a]
a	H	Me	H	Me	83	72
b	OMe	H	H	OMe	72	78
c	H	H	Me	H	64	68
d	H	OMe	OMe	H	67	64
e	H	H	Br	H	63	62
f	OMe	H	OMe	H	73	67
g	H	H	Cl	H	59	59

[a] Yields of isolated products

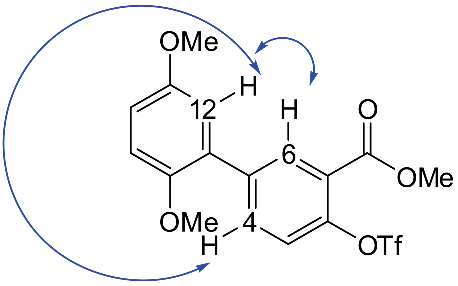
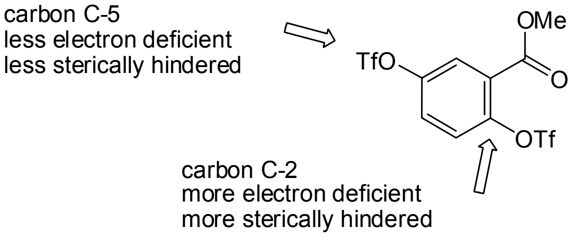


Figure 14. Relevant NOESY-correlation for Compound **28b**

The regioselectivity of compound **28b** was established unambiguously by 2D NMR using NOESY (H-H) correlations. The phenyl proton attached with carbon C-12 showed clear correlation through space with the benzoate protons attached with carbons C-4 and C-6. This confirmed that the first attack of the boronic acid takes place at carbon C-5 of the benzoate. These careful and clear correlations proved unambiguously the connectivity of the aryl group to carbon C-5 of the benzoate.

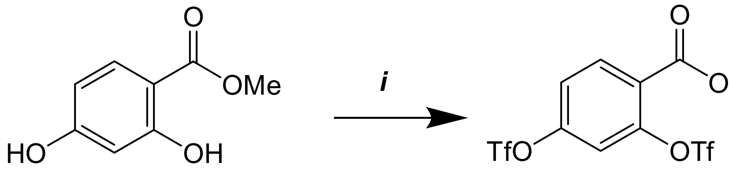
In some cases, a small amount of the bis-coupled product and of the other regioisomer could be detected in the crude product (by ^{1}H NMR and GC-MS). For example, 10% of the bis-coupled product was detected by ^{1}H NMR in the crude product of **28a**. The pure mono-coupled products were obtained after chromatographic purification. The oxidative addition of palladium usually occurs first at the most electron deficient carbon atom. Carbon atom C-2 of bis(triflate) **26** is expected to be more electron deficient than C-5. On the other hand, carbon C-5 is less sterically hindered than C-2. Therefore, the site-selective formation of **28a-g** seems to be mainly influenced by steric parameters (Scheme 30).



Scheme 30. Possible explanation for the site-selective formation of products **28a-g**

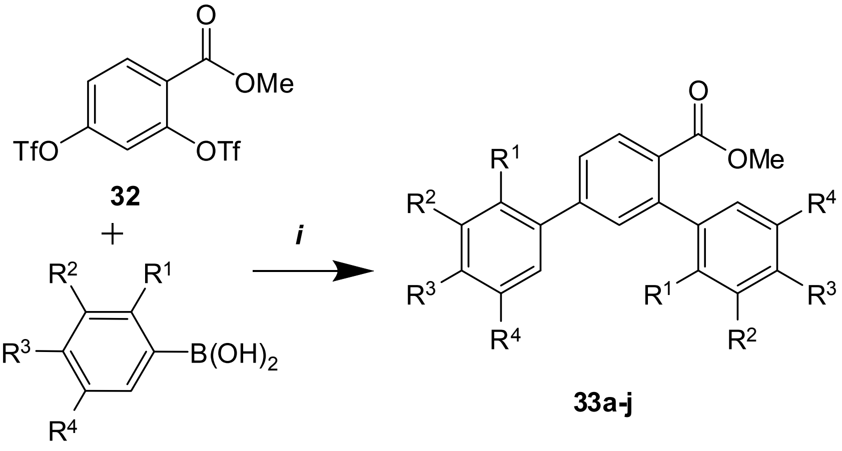
3.3 Synthesis of Functionalized *meta*-terphenyls:

To develop a new strategy for the synthesis of *meta*-terphenyls, I also studied palladium-catalyzed cross-coupling reactions of the bis(triflate) of methyl 2,4-dihydroxybenzoate which represents a commercially available and inexpensive substrate. Such reactions have, to the best of my knowledge, not been reported yet. Likewise, palladium-catalyzed cross-coupling reactions of 2,4-dibromo- or 2,4-diiodobenzoates are unknown to date. Methyl 2,4-dihydroxybenzoate **31** was transformed into its bis(triflate) **32** in 88% yield (Scheme 31). The Suzuki reaction of **32** with different boronic acids (2.6 equiv.) afforded the novel *m*-terphenyls **33a-j** in good yields (Scheme 32, Table 11). The best yields were obtained when $Pd(PPh_3)_4$ (6 mol-%) was used as the catalyst, when 2.6 equiv. of the boronic acid was employed, and when the reaction was carried out in 1,4-dioxane (reflux, 4 h) using K_3PO_4 as the base. The structures of all products were established by spectroscopic methods.



31 **32** (88%)

Scheme 31. Synthesis of **32**. *Reagents and conditions:* (*i*) CH_2Cl_2, **31** (1.0 equiv), -78 °C, pyridine (4.0 equiv), -78°C, Tf_2O (2.4 equiv), 4h.



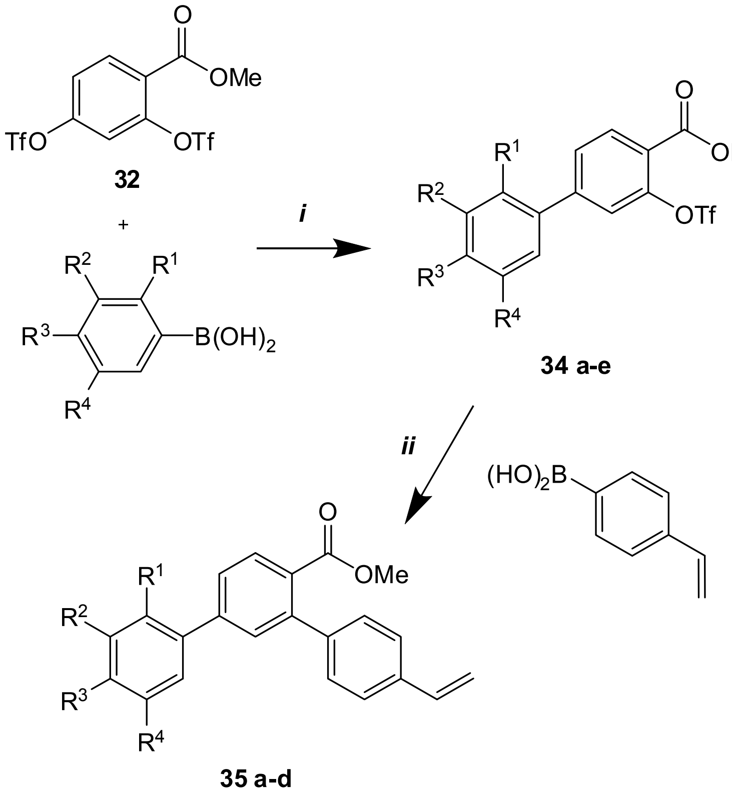
Scheme 32. Synthesis of **33a-j**. *Reagents and conditions: i*, **32** (1.0 equiv.), boronic acids (2.6 equiv.), K_3PO_4 (3.0 equiv.), $Pd(PPh_3)_4$ (6 mol-%), 1,4-dioxane (5 mL per 1 mmol of **32**), 110 °C, 4 h.

Table 11. Synthesis of **33a-j**

33	R^1	R^2	R^3	R^4	% (**33a-j**)[a]
a	H	H	Cl	H	72
b	OMe	H	H	OMe	78
c	H	H	H	H	65
d	H	H	*t*Bu	H	79
e	H	OH	H	H	62
f	Br	H	H	H	74
g	F	H	H	H	68
h	H	H	F	H	77
i	H	CF_3	H	H	63
j	H	H	CF_3	H	69

[a] Yields of isolated products

The Suzuki reaction of **32** with different boronic acids (1.3 equiv.), in the presence of $Pd(PPh_3)_4$ (3 mol-%), proceeded with very good site-selectivity at carbon atom C-4 to yield **34a-d** (Scheme 33, Table 12). In some cases, a small amount of the bis-coupled product could be detected in the crude product (by ^1H NMR and GC-MS). The pure mono-coupled products were obtained after chromatographic purification. The reaction of **34a-d** with 4-vinylphenyl boronic acid (1.3 equiv.) gave mixed *m*-terphenyls **35a-d** containing two different boronic acids. The structures of the products were proved by normal spectroscopic methods. The structure of **34c** was independently confirmed by X-ray crystal structure analysis (Figure 14).



Scheme 33. Synthesis of **34a-e** and **35a-g**. *Reagents and conditions: i*, **32** (1.0 equiv), boronic acids (1.3 equiv), K_3PO_4 (1.5 equiv), $Pd(PPh_3)_4$ (3 mol-%), 1,4-dioxane (5mL per 1 mmol of **32**), 110 °C, 4 h; *ii*, **34a-e** (1.0 equiv), 4-vinylpheny boronic acid (1.3 equiv), K_3PO_4 (1.5 equiv), $Pd(PPh_3)_4$ (3 mol-%), 1,4-dioxane (5mL per 1 mmol of **34**), 110 °C, 4 h.

Table 10. Synthesis of **34a-e** and **35a-d**

34,35	R^1	R^2	R^3	R^4	% (**34a-e**)[a]	% (**35a-d**) [a]
a	OMe	H	H	OMe	78	76
b	H	OMe	OMe	H	72	72
c	OMe	H	H	H	76	64
d	OMe	H	OMe	H	67	69
e	H	Me	H	Me	60	*b*

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

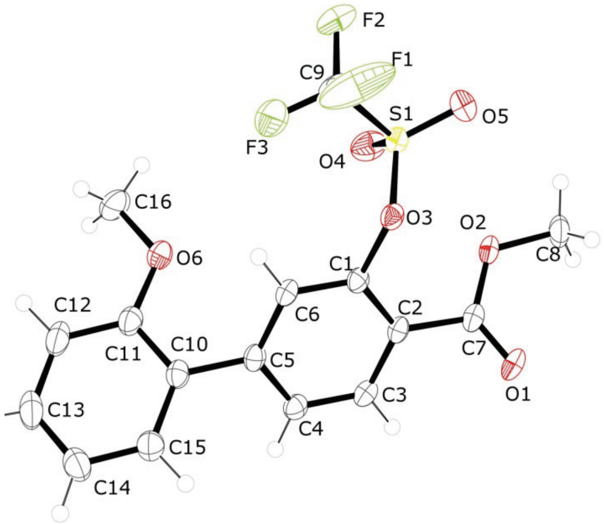
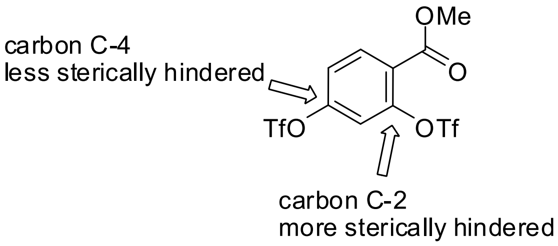


Figure 14. Ortep plot of **34c**

As discussed above, the oxidative addition of palladium usually occurs first at the most electron deficient carbon atom. Carbon atoms C-2 and C-4 of bis(triflate) **32** are expected to be equally electron deficient. The site-selective formation of **34 a-e** can be explained by the fact that carbon atom C-4 is less sterically hindered then C-2 (Scheme 34).



Scheme 34. Possible explanation for the site-selective formation of products **34 a-e**

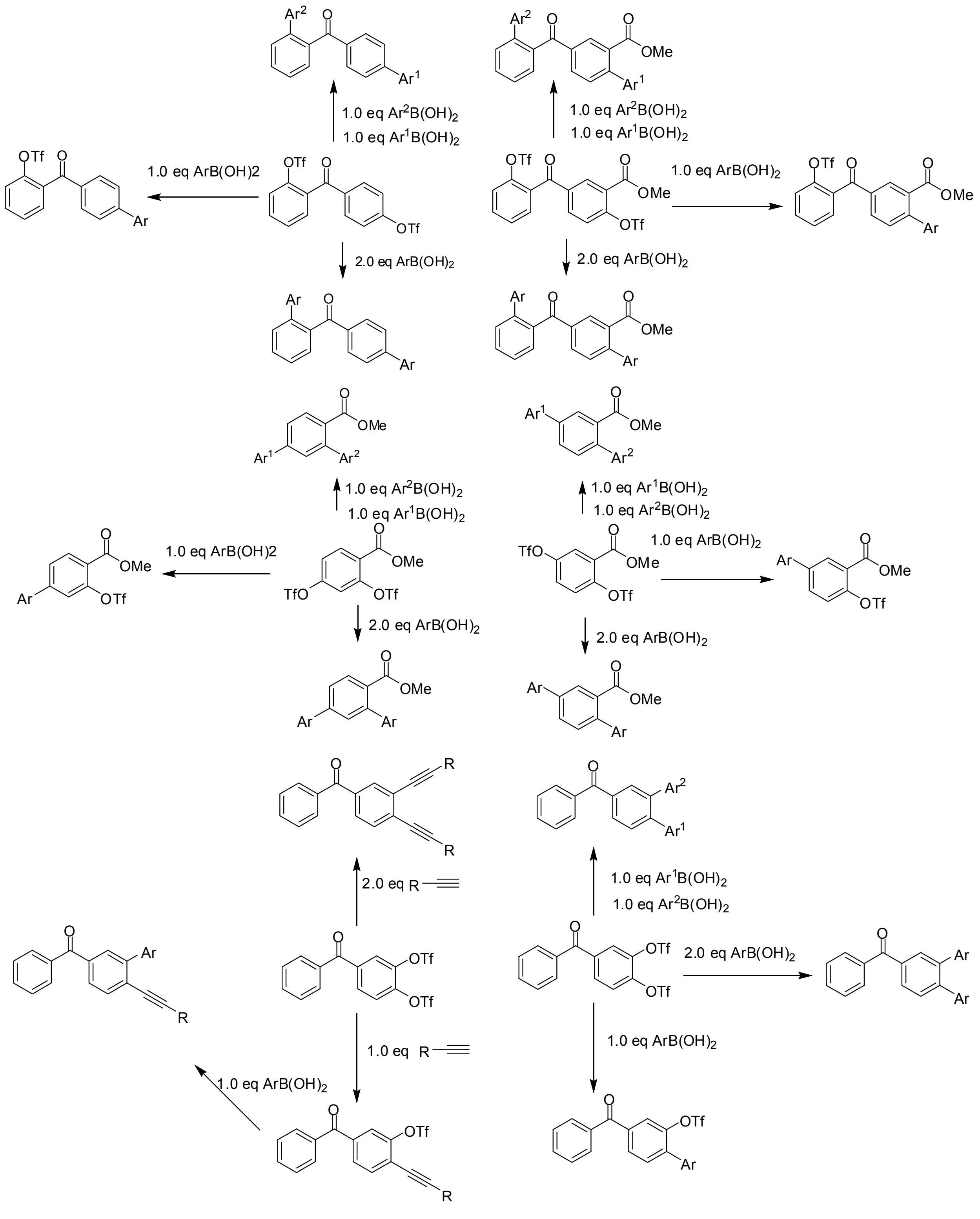
3.4 Conclusion:

In conclusion, I have reported the synthesis of *p*-terphenyls based on what are, to the best of my knowledge, the first palladium(0)-catalyzed Suzuki cross-coupling reactions of bis(triflates) of methyl 2,5-dihydroxybenzoate. These reactions proceed with very good site-selectivity. I have also reported the site-selective synthesis of *m*-terphenyls by Suzuki-Miyaura cross-coupling reactions of bis(triflates) of methyl 2,4-dihydroxybenzoate. All the products reported herein are not readily available by other methods.

4. Abstract:

This PhD thesis includes palladium(0)-catalyzed Suzuki cross-coupling reactions of various benzophenones and benzoates. The palladium(0)-catalyzed Suzuki cross-coupling reaction of the bis(triflates) of 2,4′-dihydroxybenzophenones afforded 2,4′-diarylbenzophenones. The reactions proceeded with very good site-selectivity. The Suzuki-Miyaura reaction of the bis(triflate) of 3,4-dihydroxybenzophenone with two equivalents of boronic acids gave 3,4-diarylbenzophenones. The reaction with one equivalent of arylboronic acids resulted in a site-selective attack. The Sonogashira cross-coupling reactions of the same substrate with terminal alkynes display remarkable compatibility with regard to the formation of symmetrical and unsymmetrical alkynylated products.The palladium(0)-catalyzed Suzuki cross-coupling reaction of the bis(triflates) of methyl 2,5-dihydroxybenzoate and methyl 2,4-dihydroxybenzoate afforded *p*-terphenyls and *m*-terphenyls respectively.

Diese Doktorarbeit umfasst neue Palladium(0)-katalysierte Suzuki-Kreuzkupplungsreaktionen von verschiedenen Benzophenonen und Benzoaten. Die Palladium(0)-katalysierten Suzuki-Kreuzkupplungsreaktionen der Bis(triflate) von 2,4′-Dihydroxybenzophenonen führten zur Bildung von 2,4′-Diarylbenzophenonen. Diese Reaktionen verliefen mit sehr guter Regioselektivität. Die Suzuki-Miyaura-Reaktion der Bis(triflate) von 3,4-Dihydroxybenzophenonen mit jeweils zwei Äquivalenten verschiedener Boronsäuren lieferte 3,4-Diarylbenzophenone. Die analoge Reaktion mit einem Äquivalent der Arylboronsäure ergab einen regioselektiven Angriff in 4-Position. Die Sonogashira-Kreuzkupplungsreaktion mit terminalen Alkinen, ausgehend vom gleichen Substrat, führte zur Bildung von symmetrischen und unsymmetrischen Alkinylderivaten. Die Palladium(0)-katalysierten Suzuki-Kreuzkupplungsreaktionen der Bis(triflate) von Methyl-2,5-dihydroxybenzoaten und Methyl-2,4-dihydroxybenzoaten führten zur Bildung von *p*- bzw. *m*-Terphenylen.



Scheme 35: Content of the present thesis

5. Experimental Section:

5.1 General: Equipment, Chemicals and Work Technique:

^{1}H NMR Spectroscopy:

Bruker: AM 250, Bruker ARX 300, Bruker ARX 500; δ = 0.00 ppm for Tetramethylsilane; δ = 2.04 ppm for Acetone-d_6; δ = 7.26 ppm for ($CDCl_3$); 2.50 ppm for DMSO-d_6; Characterization of the signal fragmentations: s = singlet, d = doublet, dd = double of doublet, ddd = doublet of a double doublet, t = triplet, q = quartet, quint = quintet; sext = Sextet, sept = Septet, m = multiplet, br = broadly. Spectra were evaluated according to first order rule. All coupling constants are indicated as (*J*).

^{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 for $(CD_3)_2CO$. δ = 128.00 ppm for benzene-d_6; δ = 77.00 ppm for $CDCl_3$. 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, AMD 402 (AMD Intectra), Varian MAT CH 7, MAT 731

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; Abbreviations for signal allocations: w = weak, m = medium, s = strong, br = broad.

Elementary analysis:

LECO CHNS-932, Thermoquest Flash EA 1112

X-ray crystal structure analysis:

Bruker X8Apex Diffractometer with CCD-Kamera (Mo-K_a und Graphit Monochromator, $\lambda = 0.71073$ Å).

Melting points:

Micro heating table HMK 67/1825 Kuestner (Büchi apparatus); Melting points are uncorrected.

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.

TLC:

Merck DC finished foils silica gel 60 F254 on aluminum foil and Macherey finished foils Alugram® Sil G/UV254. 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).

Chemicals and work technique:

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

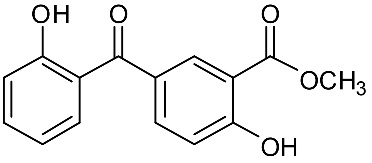
5.2 Procedures and Spectroscopic Data:

General Procedure for the Synthesis of Triflates:

To a soln of hydroxylated benzophenone or benzoate (1.0 equiv) in CH_2Cl_2 (10 mL/mmol), was added pyridine (4.0 equiv) at – 78 °C under an argon atmosphere. After 10 min, Tf_2O (2.4 equiv) was added at -78°C. The mixture was allowed to warm up to 0 °C and stirred for 4h. The reaction mixture was filtered and the filtrate was concentrated in vacuo. The products of the reaction mixture were isolated by rapid column chromatography (flash silica gel, heptanes/EtOAc).

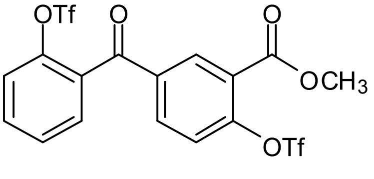
General Procedure for the Synthesis of Biaryls:

1,4-dioxane soln of the arylboronic acid, K_3PO_4, Pd $(PPh_3)_4$ and triflate of benzophenones was stirred at 110 °C for 4 h. After cooling to r.t., sat. aq NH_4Cl soln was added, the organic and aqueous layer were separated and the later was extracted with CH_2Cl_2. The combined organic layers were dried (Na_2SO_4), filtered and filtrate was concentrated in vacuo. The residue was purified by column chromatography.



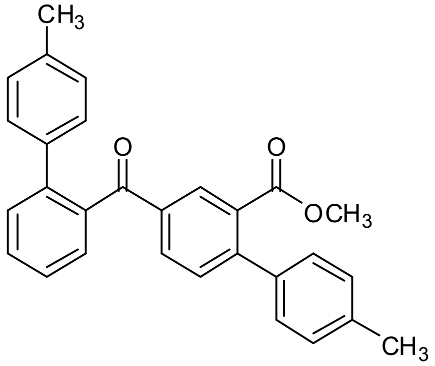
Methyl 2-hydroxy-5-(2-hydroxybenzoyl)benzoate (3): Starting with **2** (1740 mg, 10 mmol), 1,3-bis(silyloxy)-1,3-butadiene **(1)** (2860 mg, 11 mmol) and TMSOTf (0.54 ml, 3 mmol), **3** was isolated as yellowish oil (1650 mg, 60 %); ^{1}H NMR (300 MHz, $CDCl_3$): δ = 3.89 (s, 3H, OCH_3), 6.79-6.85 (m, 1H, ArH), 6.94-6.98 (m, 1H, ArH), 7.02 (s, 1H, ArH), 7.39-7.43 (m, 1H, ArH), 7.49 (dd, 1H, J = 1.6, 7.9 Hz, ArH), 7.77 (dd, 1H, J = 2.2, 8.7 Hz, ArH), 8.18 (d, 1H, J = 2.2 Hz, ArH), 11.1 (s, 1H, OH), 11.7 (s, 1H, OH). ^{13}C NMR (62.90 MHz, $CDCl_3$): δ = 52.7 (OCH_3), 117.8, 118.5, 118.7 (CH_{Ar}), 131.8 (C_{Ar}), 132.4, 132.9 (CH_{Ar}), 135.1, 135.6 (C_{Ar}), 136.1, 136.6 (CH_{Ar}), 161.9, 163.6 (C_{Ar}), 168.9 (COO), 197.9 (C=O). IR (KBr): $\tilde{\nu}$ = 3117, 3076, 3040 (w), 1671, 1624 (m), 1582 (s), 1438, 1341, 1291 (m), 1237, 1202 (s), 1164, 1087, 988, 933, 819, 779 (m), 725, 678 (s), 537 (m) cm^{-1}. GC-MS (EI, 70 eV): *m/z* (%): 272 (M^{+}, 92), 239 (25), 212 (06), 196 (02), 184 (11), 147 (38), 128 (04), 121 (96), 120 (100), 92 (20), 79 (07), 65 (13), 53 (05), 39 (06). HRMS (EI) calcd for $C_{15}H_{12}O_5$ [M^{+}H]: 272.07575, found 273.07625.

Methyl 2,5-(bis(trifluoromethylsulfonyloxy)benzoyl)-benzoate (4): Starting with **3** (120 mg, 0.44 mmol), pyridine (0.14 ml, 1.76 mmol) and Tf_2O (0.17 ml, 1.05 mmol), **4** was isolated as a colorless crystalline solid (200 mg,

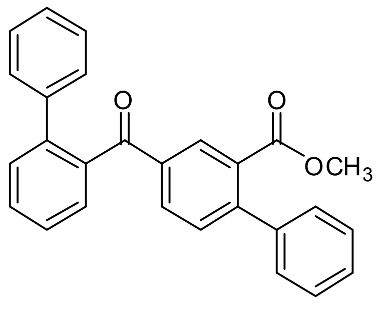


84 %), mp. = 124-126°C; ^{1}H NMR (300 MHz, CDCl$_3$): δ = 3.90 (s, 3H, OCH$_3$), 7.37 (dd, 2H, *J* = 2.2, 8.6 Hz, ArH), 7.48 (dd, 1H, *J* = 0.5, 7.1 Hz, ArH), 7.53 (dd, 1H, *J* = 2.1, 7.6 Hz, ArH), 7.60-7.66 (m, 1H, ArH), 8.00 (dd, 1H, *J* = 2.3, 8.5 Hz, ArH), 8.38 (d, 1H, *J* = 2.3 Hz, ArH); ^{13}C NMR (75.46 MHz, CDCl$_3$): δ = 53.0 (OCH$_3$), 120.5 (q, $J_{F,C}$= 320.0 Hz, CF$_3$), 120.7 (q, $J_{F,C}$= 320.2, CF$_3$), 122.8, 123.4 (CH$_{Ar}$), 124.9 (C$_{Ar}$), 128.5, 131.2, 133.7, 134.4, 135.3 (CH$_{Ar}$), 136.4, 146.7, 151.1 (C$_{Ar}$), 163.2 (COO), 190.1 (C=O); ^{19}F NMR (282 MHz, CDCl3): δ = -73.28 (CF); IR (KBr): $\tilde{\nu}$ = 3117, 3076, 3040 (w), 1671, 1624 (s), 1582 (m), 1479, 1341, 1237 (m), 1202 (s), 1164, 1087, 988 (m), 866, 793, 703 (s), 589, 537 (m) cm^{-1}; GC-MS (EI, 70 eV): *m/z* (%): 536 (M$^+$, 89), 505 (40), 467 (06), 403 (09), 375 (23), 311 (100), 247 (61), 211 (20), 183 (30), 155 (34), 120 (29), 92 (16), 69 (50); HRMS (EI) calcd for $C_{17}H_{10}F_6O_9S_2$ [M$^+$]: 535.96649, found 535.966638.

Methyl 4'-methyl-4-(4'-methylbiphenylcarbonyl)biphenyl-2-carboxylate (6a): Starting with **4** (220 mg, 0.41 mmol), K$_3$PO$_4$ (261 mg, 1.23 mmol), Pd (PPh$_3$)$_4$ (6 mol%), *p*-tolylboronic acid (144 mg, 1.06 mmol) and 1,4-dioxane (5ml/mmol of triflate), **6a** was isolated as a colorless crystalline solid, yield 145 mg, (84 %) mp. = 114-116°C; ^{1}H NMR (300 MHz, CDCl$_3$): δ = 2.17 (s, 3H, CH$_3$), 2.30 (s, 3H, CH$_3$), 3.56 (s, 3H, OCH$_3$), 6.95 (d, 2H, *J* = 8.0 Hz, ArH), 7.04-7.21 (m, 6H, ArH), 7.35-7.53 (m, 5H, ArH), 7.70 (dd, 1H, *J* = 2.9, 8.1 Hz, ArH), 7.98 (d, 1H, *J* = 1.9 Hz, ArH); ^{13}C NMR (62.89 MHz, CDCl$_3$): δ = 21.0 (CH$_3$), 21.2 (CH$_3$), 52.1 (OCH$_3$), 126.9, 127.9, 128.8, 128.9, 129.0 (CH$_{Ar}$), 129.9 (C$_{Ar}$), 130.2, 130.6, 131.4, 132.1 (CH$_{Ar}$), 135.8, 137.1, 137.2, 137.7, 138.3, 141.3, 146.3 (C$_{Ar}$), 168.4 (COO), 197.4 (C=O); IR (KBr): $\tilde{\nu}$ = 3080, 3057, 3025 (w), 1724, 1659 (s), 1613 (w), 1595 (m), 1574, 1518 (w), 1438, 1310, 1277 (m), 1231 (s), 1152, 1082, 972 (m), 819, 704 (s), 536 (m) cm^{-1}; MS (EI, 70 eV): *m/z* (%): 420 (M$^+$, 100), 405 (21), 373 (09), 359 (23), 332 (07), 253 (26), 210 (07), 195 (40), 165 (39) 152 (25); HRMS (EI) calcd for $C_{29}H_{24}O_3$ [M$^+$]: 420.17200, found 420.171525.

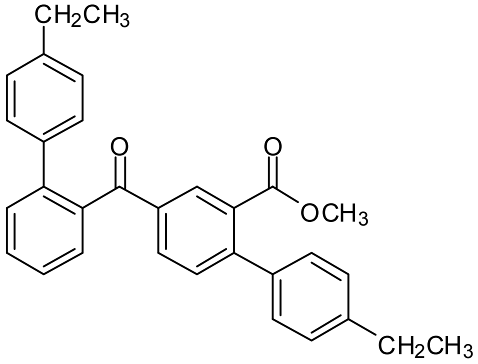


Methyl 4-(biphenylcarbonyl) biphenyl-2-carboxylate (6b): Starting with **4** (220 mg, 0.41 mmol), K$_3$PO$_4$ (261 mg, 1.23 mmol), Pd (PPh$_3$)$_4$ (6 mol%), phenylboronic acid (144 mg, 1.06 mmol) and 1,4-dioxane (5ml/mmol of triflate), **6b** was isolated as a colorless solid, yield 120 mg, (75 %), mp. = 124-126°C; ^{1}H NMR (300 MHz, CDCl$_3$): δ

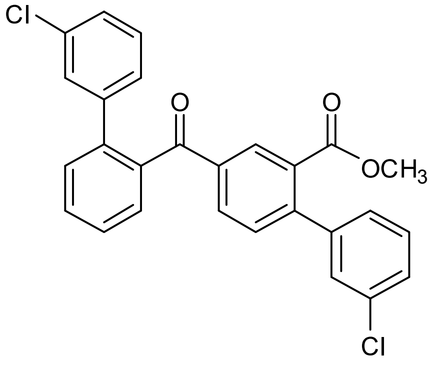


= 3.51 (s, 3H, OCH_3), 7.06-7.19 (m, 8H, ArH), 7.23(s, 1H, ArH), 7.37-7.54 (m, 6H, ArH), 7.69 (dd, 1H, J = 2.2, 8.4 Hz, ArH), 7.97 (d, 1H, J = 1.9 Hz, ArH); ^{13}C NMR (62.89 MHz, $CDCl_3$): δ = 52.0 (OCH_3), 115.3 (C_{Ar}), 127.3, 127.4, 127.8, 128.0, 128.1, 128.3, 128.9, 129.0, 130.2, 130.6, 130.8, 131.5, 132.1 (CH_{Ar}), 136.1, 138.3, 140.1, 140.2, 141.3, 146.3 (C_{Ar}), 168.2 (COO), 197.3 (C=O); IR (KBr): $\tilde{\nu}$ = 3056, 3024, 2849 (w), 1721, 1663 (s), 1596 (m), 1556 (w), 1433 (m), 1398 (w), 1303 (m), 1230 (s), 1151, 1086, 939, 967 (m), 742 (s), 539 (m) cm^{-1}; MS (EI, 70 eV): *m/z* (%): 392 (M^+, 100), 359 (11), 331 (41), 305 (11), 239 (39), 181 (54), 165 (06), 152 (51) 139 (04); HRMS (EI) calcd for $C_{27}H_{20}O_3$ [M^+]: 392.14070, found 392.140174.

Methyl 4'-ethyl-4-(4'-ethyl biphenyl carbonyl) biphenyl-2-carboxylate (6c): Starting with **4** (220 mg, 0.41 mmol), K_3PO_4 (261 mg, 1.23 mmol), Pd $(PPh_3)_4$ (6 mol%), 4-ethylphenyboronic acid (144 mg, 1.06 mmol) and 1,4-dioxane (5ml/mmol of triflate), **6c** was isolated as a yellow solid; yield 115 mg, (62 %) mp. = 93-94°C; ^{1}H NMR (300 MHz, $CDCl_3$): δ = 1.06 (t, 3H, J = 7.6 Hz, $CH_{3\textit{ethyl}}$), 1.18 (t, 3H, J = 7.6 Hz, $CH_{3\textit{ethyl}}$), 2.47 (q, 2H, J = 7.6 Hz, $CH_{2\textit{ethyl}}$), 2.62 (q, 2H, J = 7.5 Hz, $CH_{2\textit{ethyl}}$), 3.56 (s, 3H, OCH_3), 6.96 (d, 2H, J = 8.1 Hz, ArH), 7.02-712 (m, 4H, ArH), 7.14-7.18 (m, 2H, ArH), 7.21 (s, 1H, ArH), 7.37-7.44 (m, 2H, ArH), 7.48-7.54 (m, 2H, ArH), 7.68 (dd, 1H, J = 1.8, 7.7 Hz, ArH), 7.95 (d, 1H, J = 2.1 Hz, ArH); ^{13}C NMR (62.90 MHz, $CDCl_3$): δ = 15.3 (CH_3), 15.4 (CH_3), 28.4, 28.5 ($2CH_{2\textit{ethyl}}$), 52.0 (OCH_3), 127.0, 127.6, 127.8, 128.0, 128.9, 129.0, 130.1, 130.5, 130.6 (CH_{Ar}), 130.7 (C_{Ar}), 131.4, 132.0 (CH_{Ar}), 135.9, 137.4, 138.3, 141.4, 143.5, 143.9, 146.2, 147.2 (C_{Ar}), 168.4 (COO), 197.5 (C=O); IR (KBr): $\tilde{\nu}$ = 3055, 3021, 2962 (w), 1721, 1663 (s), 1597 (m), 1552, 1515 (w), 1434, 1303 (m), 1229 (s), 1150, 1085, 939 (m), 829, 760 (s), 584 (m) cm^{-1}; GC-MS (EI, 70 eV): *m/z* (%): 448 (M^+, 100), 419 (41), 387 (31), 359 (07), 267 (21), 209 (25), 165 (29), 152 (16); HRMS (EI) calcd for $C_{31}H_{28}O_3$ [M^+]: 448.20330, found 448.202658.

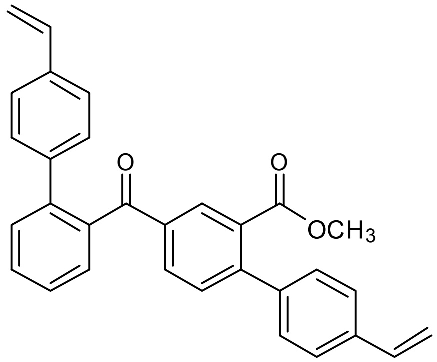


Methyl 3'-chloro-4-(3'-chlorobiphenylcarbonyl)biphenyl-2-carboxylate (6d): Starting with **4** (220 mg, 0.41 mmol), K_3PO_4 (261 mg, 1.23 mmol), Pd $(PPh_3)_4$ (6 mol%), 3-chlorophenylboronic acid (144 mg, 1.06 mmol) and 1,4-dioxane (5ml/mmol of triflate), **6d** was isolated as colorless oil; yield 146 mg, (77 %); ^{1}H NMR (300 MHz, $CDCl_3$): δ = 3.57 (s, 3H, OCH_3), 7.00-7.06 (m, 4H, ArH),

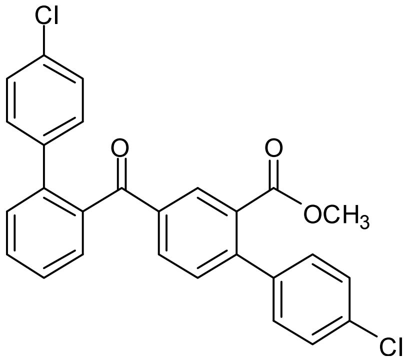


7.15-7.20 (m, 4H, ArH), 7.26 (s, 1H, ArH), 7.39-7.45 (m, 2H, ArH), 7.52-7.58 (m, 2H, ArH), 7.73 (dd, 1H, J = 1.9, 8.1 Hz, ArH), 7.94 (d, 1H, J = 1.9 Hz, ArH); ^{13}C NMR (75.46 MHz, $CDCl_3$): δ = 52.2 (OCH_3), 126.3, 127.4, 127.5, 127.9, 128.1, 129.1, 129.2, 129.3, 129.5, 130.1 (CH_{Ar}), 130.5 (C_{Ar}), 130.7, 131.1, 131.7, 132.0 (CH_{Ar}), 134.0, 134.2, 136.5, 138.1, 140.0, 141.8, 141.9, 145.0 (C_{Ar}), 167.5 (COO), 196.8 (C=O); IR (KBr): $\tilde{\nu}$ = 3059, 3024 (w), 1725, 1663, 1593 (s), 1557 (w), 1435 (m), 1303, 1231 (s), 1152, 1087 (m), 987 (w), 851 (m), 786 (s), 538 (m) cm^{-1}; GC-MS (EI, 70 eV): *m/z* (%): 461 (M^-, 47), 460 (97), 429 (18), 399 (70), 365 (12), 338 (10), 302 (09), 273 (74), 215 (88) 197 (36), 165 (28), 152 (100); HRMS (EI) calcd for $C_{27}H_{18}O_3Cl_2$ [M^+]: 460.06275, found 460.062304.

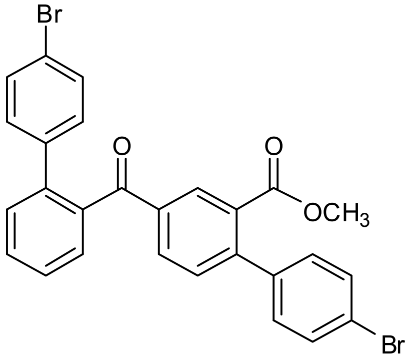
Methyl 4'-vinyl-4-(4'-vinylbiphenylcarbonyl)biphenyl-2-carboxylate (6e): Starting with **4** (220 mg, 0.41 mmol), K_3PO_4 (261 mg, 1.23 mmol), Pd $(PPh_3)_4$ (6 mol%), 4-vinylphenylboronic acid (144 mg, 1.06 mmol) and 1,4-dioxane (5ml/mmol of triflate), **6e** was isolated as a yellow solid; yield 132 mg, (72 %) mp. = 89-90°C; ^{1}H NMR (300 MHz, $CDCl_3$): δ = 3.55 (s, 3H, OCH_3), 5.16 (ddd, 2H, J = 0.8, 10.8, 24.2 Hz, CH_{2vinyl}), 5.65 (ddd, 2H, J = 0.8, 17.5, 33.0 Hz, CH_{2vinyl}), 6.59 (ddd, 2H, J = 10.9, 17.6, 28.5 Hz, $2CH_{vinyl}$), 7.00-7.12 (m, 4H, ArH), 7.14-7.18 (m, 2H, ArH), 7.21 (s, 1H, ArH), 7.34 (d, 2H, J = 8.1 Hz, ArH), 7.40-7.50 (m, 4H, ArH), 7.71 (dd, 1H, J = 1.8, 8.0 Hz, ArH), 7.99 (d, 1H, J = 1.6 Hz, ArH); ^{13}C NMR (75.46 MHz, $CDCl_3$): δ = 52.1 (OCH_3), 114.2, 114.4, ($2CH_{2vinyl}$), 126.0, 126.2, 127.3, 128.3, 128.9, 129.2, 130.1, 130.6, 130.8, 131.6, 132.2, 136.2, 136.3 (CH_{Ar}), 136.7, 137.1, 138.2, 139.5, 139.6, 141.0, 146.1 (C_{Ar}), 168.2 (COO), 197.3 (C=O); IR (KBr): $\tilde{\nu}$ = 3435, 3057, 3021, 2948 (w), 1721, 1663 (s), 1597 (m), 1548, 1514 (w), 1435, 1305 (m), 1230 (s), 1151, 1085, 939 (m), 838, 768 (s), 539 (m) cm^{-1}; GC-MS (EI, 70 eV): *m/z* (%): 444 (M^+, 100), 417 (05), 383 (08), 356 (04), 265 (19), 222 (11), 178 (30), 152 (07); HRMS (EI) calcd for $C_{31}H_{24}O_3$ [M^+]: 444.17200, found 444.171615.



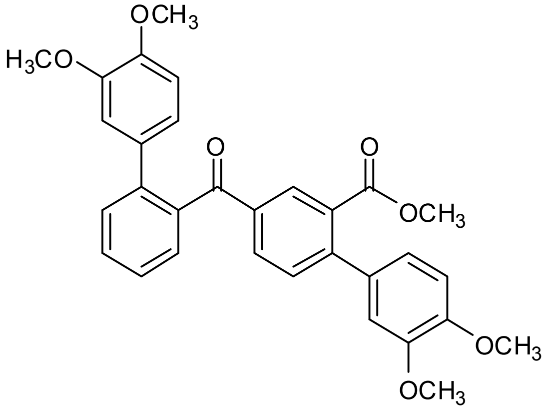
Methyl 4'-chloro-4-(4'-chlorobiphenylcarbonyl)biphenyl-2-carboxylate (6f): Starting with **4** (220 mg, 0.41 mmol), K_3PO_4 (261 mg, 1.23 mmol), Pd $(PPh_3)_4$ (6 mol%), 4-chlorophenylboronic acid (144 mg, 1.06 mmol) and 1,4-dioxane (5ml/mmol of triflate), **6f** was isolated as a colorless solid; yield 122 mg, (64 %) mp. = 49-50°C; ^{1}H NMR (300 MHz, $CDCl_3$): δ = 3.56 (s, 3H, OCH_3), 7.11 (s, 5H, ArH), 7.20 (d, 1H, *J* = 8.4 Hz, ArH), 7.30 (d, 2H, *J* = 8.6 Hz, ArH), 7.38-7.50 (m, 5H, ArH), 7.72 (dd, 1H, *J* = 1.8, 8.0 Hz, ArH), 7.98 (d, 1H, *J* = 1.8 Hz, ArH); ^{13}C NMR (62.89 MHz, $CDCl_3$): δ = 52.2 (OCH_3), 127.6, 128.3, 128.5, 129.0, 129.4, 130.1, 130.3 (CH_{Ar}), 130.5 (C_{Ar}), 130.8, 130.9, 131.7, 132.2 (CH_{Ar}), 133.7, 134.1, 136.2, 138.1, 138.6, 140.1, 145.5 (C_{Ar}), 167.7 (COO), 196.9 (C=O); IR (KBr): $\tilde{\nu}$ = 3058, 3027, 2949 (w), 1724, 1663 (s), 1599 (m), 1573, 1554 (w), 1472 (m), 1394 (w), 1230 (s), 1190 (w), 1152 (m), 1087 (s), 939 (m), 826 (s), 778, 535 (m) cm^{-1}; GC-MS (70 eV): *m/z* (%): 460 (M^+), 461 (46), 460 (100), 429 (15), 401 (30), 372 (07), 273 (67), 215 (69), 197 (31), 180 (10) 165 (21), 152 (82); HRMS (EI) calcd for $C_{27}H_{18}O_3Cl_2$ [M^+]: 460.06275, found 460.062308.



Methyl 4'-bromo-4-(4'-bromobiphenylcarbonyl)biphenyl-2-carboxylate (6g): Starting with **4** (220 mg, 0.41 mmol), K_3PO_4 (261 mg, 1.23 mmol), Pd $(PPh_3)_4$ (6 mol%), 4.bromophenylboronic acid (144 mg, 1.06 mmol) and 1,4-dioxane (5ml/mmol of triflate), **6g** was isolated as a yellow solid; yield 168 mg, (74 %) mp. = 49-51°C; ^{1}H NMR (300 MHz, $CDCl_3$): δ = 3.6 (s, 3H, OCH_3), 7.12 (d, 4H, *J* = 5.9 Hz, ArH), 7.43 (d, 4H, *J* = 6.1 Hz, ArH), 7.40 (s, 1H, ArH), 7.50-7.80 (m, 4H, ArH), 7.91 (dd, 1H, *J* = 2.0, 5.9 Hz, ArH), 8.19 (d, 1H, *J* = 1.7 Hz, ArH); ^{13}C NMR (75.46 MHz, $CDCl_3$): δ = 52.3 (OCH_3), 122.7, 123.2, 126.7, 127.3, 128.2, 129.8, 130.2, 131.9, 132.5, 133.0, 133.7 (CH_{Ar}), 139.0, 139.3, 139.6, 146.3, 146.8, 147.0, 167.6 (C_{Ar}), 167.9, (COO), 191.3 (C=O); IR (KBr): $\tilde{\nu}$ = 3063, 3031, 2951 (w), 1727, 1669 (s), 1477 (m), 1422 (s), 1307 (m), 1205 (s), 1167 (w), 1134 (m), 1086 (s), 944 (m), 884 (s), 781, 569 (m) cm^{-1}; MS (70 eV): *m/z* (%): 550 (M^+, 100), 513 (16), 410 (07), 379 (16), 319 (37), 298 (25), 215 (13), 181 (09), 151 (28) 121 (21), 82 (21), 69 (51); HRMS (EI) calcd for $C_{27}H_{18}Br_2O_3$ [M^+]: 550.17200, found 550.171525.

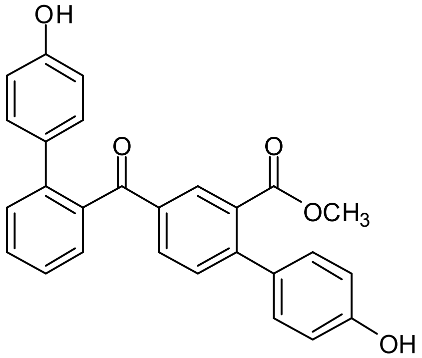


Methyl 4-(3',4'-dimethoxybiphenylcarbonyl)-3',4'-dimethoxybiphenyl-2-carboxylate (6h):

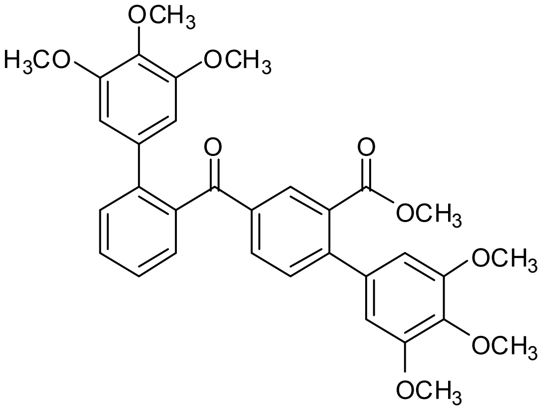


Starting with **4** (220 mg, 0.41 mmol), K_3PO_4 (261 mg, 1.23 mmol), Pd $(PPh_3)_4$ (6 mol%), 3,4-dimethoxyphenylboronic acid (144 mg, 1.06 mmol) and 1,4-dioxane (5ml/mmol of triflate), **6h** was isolated as a yellow solid; yield 132 mg, (62 %) mp. = 65-67°C; ^{1}H NMR (300 MHz, $CDCl_3$): δ = 3.54 (s, 3H, OCH_3), 3.70 (s, 6H, $2OCH_3$), 3.80 (s, 3H, OCH_3), 3.83 (s, 3H, OCH_3), 6.63 (d, 1H, *J* = 9.0 Hz, ArH), 6.69-6.72 (m, 2H, ArH), 6.73 (d, 2H, *J* = 2.7 Hz, ArH), 6.80 (d, 1H, *J* = 7.7 Hz, ArH), 7.19 (d, 2H, *J* = 2.2 Hz, ArH), 7.22 (s, 1H, ArH), 7.36-7.46 (m, 3H, ArH), 7.69 (dd, 1H, *J* = 2.2, 8.2 Hz, ArH), 7.86 (d, 1H, *J* = 1.8 Hz, ArH); ^{13}C NMR (62.89 MHz, $CDCl_3$): δ = 52.1, 55.7, 55.8, 55.8, 55.9 ($5OCH_3$), 110.8, 111.0, 111.4, 112.3, 120.6, 121.6, 127.1, 128.6, 129.8, 130.4, 130.6 (CH_{Ar}), 130.8 (C_{Ar}), 131.2, 131.6, (CH_{Ar}), 132.6, 132.8, 135.6, 138.4, 140.7, 145.7, 148.4, 148.6, 148.7, 148.9 (C_{Ar}), 168.7 (COO), 197.7 (C=O); IR (KBr): $\tilde{\nu}$ = 3057, 2998, 2950 (w), 1720 (m), 1662 (s), 1569 (w), 1518 (s), 1480 (m), 1437 (s), 1325 (m), 1243, 1214, 1171 (s), 1086, 941 (m), 881, 850, 756, 699 (s), 597 (m) cm^{-1}; MS (EI, 70 eV): *m/z* (%): 512 (M$^+$, 100), 496 (04), 465 (02), 299 (03), 241 (09), 210 (04), 167 (01), 126 (02) 91 (01), 43 (05); HRMS (EI) calcd for $C_{31}H_{28}O_7$ [M$^+$]: 512.18295, found 512.183285.

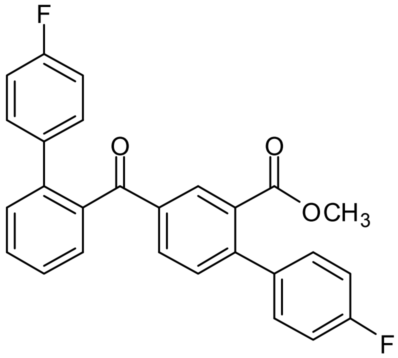
Methyl 4'-hydroxy-4-(4'-hydroxybiphenylcarbonyl)biphenyl-2-carboxylate (6i): Starting with



4 (220 mg, 0.41 mmol), K_3PO_4 (261 mg, 1.23 mmol), Pd $(PPh_3)_4$ (6 mol%), 4-hydroxyphenylboronic acid (144 mg, 1.06 mmol) and 1,4-dioxane (5ml/mmol of triflate), **6i** was isolated as a yellow solid; yield 114 mg, (65 %) mp. = 77-79°C; ^{1}H NMR (300 MHz, $CDCl_3$): δ = 3.64 (s, 3H, OCH_3), 6.52 (s, 1H, OH), 6.55 (s, 1H, OH), 6.66 (d, 2H, *J* = 7.9 Hz, ArH), 6.97-7.02 (m, 4H, ArH), 7.15 (s, 1H, ArH), 7.19 (d, 1H, *J* = 2.2 Hz, ArH), 7.39-7.41 (m, 3H, ArH), 7.48-7.51 (m, 2H, ArH), 7.66 (dd, 1H, *J* = 1.8, 8.0 Hz, ArH), 7.90 (d, 1H, *J* = 1.7 Hz, ArH); ^{13}C NMR (75.46 MHz, $CDCl_3$): δ = 52.5 (OCH_3), 115.4, 115.5, 126.8, 129.1, 129.5, 130.1, 130.4, 130.7, 131.0, 131.4 (CH_{Ar}), 131.7, 132.2 (C_{Ar}), 132.3 (CH_{Ar}), 135.5, 137.9, 141.3, 146.2, 155.6, 156.1 (C_{Ar}), 169.5 (COO), 198.4 (C=O); IR (KBr): $\tilde{\nu}$ = 3352, 3060, 2951 (w), 1708, 1649 (m), 1589 (s), 1553 (w), 1517 (s), 1476 (m), 1398 (w), 1232, 1172 (s), 1153 (m), 1087 (s), 941 (m), 832 (s), 761, 660, 539 (m) cm^{-1}; GC-MS (70 eV): *m/z* (%): 424 (M$^+$, 96), 392 (100), 372 (24), 255 (18), 223 (35), 212 (16), 197 (58), 168 (14), 139 (23) 115 (13), 89 (02); HRMS (EI) calcd for $C_{27}H_{20}O_5$ [M$^+$]: 424.13053, found 424.130645.



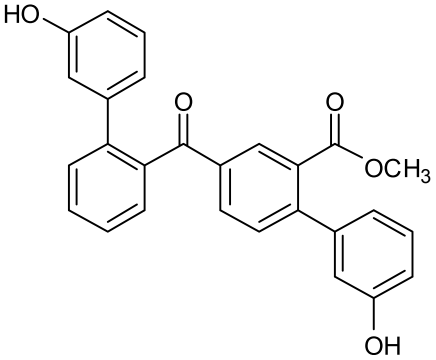
Methyl 3',4',5'-trimethoxy-4-(3',4',5'-trimethoxy biphenyl carbonyl) biphenyl-2-carboxylate (6j): Starting with **4** (220 mg, 0.41 mmol), K_3PO_4 (261 mg, 1.23 mmol), Pd $(PPh_3)_4$ (6 mol%), 4-hydroxyphenylboronic acid (144 mg, 1.06 mmol) and 1,4-dioxane (5ml/mmol of triflate), **6i** was isolated as a yellow solid; yield 136 mg, (58 %) mp. = 58-60°C; ^{1}H NMR (300 MHz, $CDCl_3$): δ = 3.52 (s, 3H, OCH_3), 3.62 (s, 3H, OCH_3), 3.69 (s, 6H, $2OCH_3$), 3.78 (s, 6H, $2OCH_3$), 3.81 (s, 3H, OCH_3), 6.35 (s, 2H, ArH), 6.39 (s, 2H, ArH), 7.21 (dd, 1H, *J* = 1.1, 7.4 Hz, ArH), 7.42-7.47 (m, 2H, ArH), 7.52-7.56 (m, 2H, ArH), 7.71 (d, 2H, *J* = 1.0 Hz, ArH); ^{13}C NMR (62.89 MHz, $CDCl_3$): δ = 52.1 (OCH_3), 55.9 ($2OCH_3$), 56.1 ($2OCH_3$), 60.6 (OCH_3), 60.9 (OCH_3), 105.2, 106.7, 127.6, 128.8, 129.4, 130.1, 130.8 (CH_{Ar}), 130.9 (C_{Ar}), 131.0, 131.1 (CH_{Ar}), 135.6, 135.8, 136.0, 137.3, 137.8, 138.4, 141.1, 145.6, 152.9, 153.0 (C_{Ar}), 168.7, (COO), 197.8 (C=O); IR (KBr): $\tilde{\nu}$ = 3057, 2921, 2851 (w), 1722 (m), 1661 (s), 1583 (w), 1563 (s), 1461 (m), 1432 (s), 1377 (m), 1343, 1292, 1236, 1171 (s), 1067, 942 (m), 884, 875, 765 , 679 (s), 532 (m) cm^{-1}; MS (EI, 70 eV): *m/z* (%): 572 (M$^+$, 100), 556 (08), 525 (03), 286 (07), 240 (02), 197 (01), 127 (01), 69 (03); HRMS (EI) calcd for $C_{33}H_{32}O_9$ [M$^+$]: 572.20408, found 572.204330.



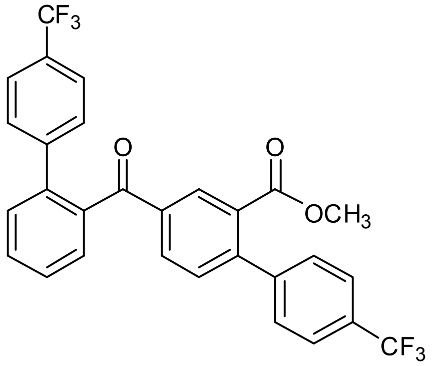
Methyl 4'-fluoro-4-(4'-fluorobiphenyl carbonyl)biphenyl-2-carboxylate (6k): Starting with **4** (220 mg, 0.41 mmol), K_3PO_4 (261 mg, 1.23 mmol), Pd $(PPh_3)_4$ (3 mol%), 4-flourophenylboronic acid (144 mg, 1.06 mmol) and 1,4-dioxane (5ml/mmol of triflate), **6k** was isolated as a yellow oil; yield 110 mg, (62 %); ^{1}H NMR (300 MHz, $CDCl_3$): δ = 3.55 (s, 3H, OCH_3), 6.82 (t, 2H, *J* = 8.7 Hz, ArH), 6.9 (t, 2H, *J* = 8.6 Hz, ArH), 7.10-7.17 (m, 4H, ArH), 7.20 (s, 1H, ArH), 7.38-7.50 (m, 4H, ArH), 7.70 (dd, 1H, *J* = 2.2, 8.3 Hz, ArH), 7.96 (d, 1H, *J* = 1.9 Hz, ArH); ^{13}C NMR (62.89 MHz, $CDCl_3$): δ = 52.1 (OCH_3), 115.0 (d, $^3J_{C,F}$ = 7.5 Hz, CH_{Ar}), 115.4 (d, $^3J_{C,F}$ = 7.1 Hz, CH_{Ar}), 127.4, 128.9, 129.7, 129.8, 130.1, 130.6 (CH_{Ar}), 130.8 (d, $^3J_{C,F}$ =

4.4 Hz, CH$_{Ar}$), 131.6, 132.0 (CH$_{Ar}$), 136.1 (d, $^4J_{C,F}$ = 3.7 Hz, CF), 136.2, 138.2, 140.1, 145.5, 160.4 (d, $J_{C,F}$ = 20.1 Hz, CF), 164.3 (d, $J_{C,F}$ = 21.1 Hz, CF), 167.9 (COO), 197.1 (C=O); ^{19}F NMR (282 MHz, CDCl3): δ = -73.34 (CF); IR (KBr): $\tilde{\nu}$ = 3062, 2950 (w), 1722, 1664 (s), 1557 (w), 1476, 1394, 1305, 1220 (m), 1154, 1085, 987 (m), 833, 760 (s), 657, 547 (m) cm^{-1}; GC-MS (EI, 70 eV): *m/z* (%): 428 (M$^+$, 100), 395 (09), 367 (30), 340 (10), 257 (51), 214 (10), 199 (59), 170 (47), 120 (02) 59 (02); HRMS (EI) calcd for $C_{27}H_{18}O_3F_2$ [M$^+$]: 428.12185, found 428.121344.

Methyl 3'-hydroxy-4-(3'-hydroxybiphenylcarbonyl)biphenyl-2-carboxylate (6l): Starting with **4** (220 mg, 0.41 mmol), K_3PO_4 (261 mg, 1.23 mmol), Pd $(PPh_3)_4$ (6 mol%), 3-hydroxyphenylboronic acid (144 mg, 1.06 mmol) and 1,4-dioxane (5ml/mmol of triflate), **6l** was isolated as a colorless solid; yield 114 mg, (65 %) mp. = 48-49°C; ^{1}H NMR (300 MHz, CDCl$_3$): δ = 3.63 (s, 3H, OCH$_3$), 6.75-6.88 (m, 5H, ArH), 7.02 (dd, 1H, *J* = 1.1, 8.5 Hz, ArH), 7.22 (d, 2H, *J* = 7.6 Hz, ArH), 7.42-7.48 (m, 3H, ArH), 7.54 (dd, 2H, *J* = 1.5, 8.0 Hz, ArH), 7.75 (dd, 1H, *J* = 2.1, 7.7 Hz, ArH), 8.02 (d, 1H, *J* = 1.8 Hz, ArH), 11.84 (s, 2H, OH); ^{13}C NMR (62.89 MHz, CDCl$_3$): δ = 52.4, (OCH$_3$), 115.0, 115.2, 116.2, 117.1, 118.5, 118.9, 119.2, 120.6, 129.5, 130.7, 131.1, 131.6, 132.2, 133.3, 136.7, (CH$_{Ar}$), 141.5, 142.2, 143.4, 144.2, 145.3, 147.2, 149.1, 155.6, 163.2 (C$_{Ar}$), 168.3 (COO), 197.5 (C=O). IR (KBr): $\tilde{\nu}$ = 3071, 3048, 2962, 2839, 2831 (w), 1721, 1662 (s), 1593, 1582 (m), 1478, 1452 (m), 1391, 1343, 1301 (m), 1281, 1235, 1168 (s), 1092, 941 (s), 892, 863, 774 , 694 (s), 591, 572, 530 (m) cm^{-1}; MS (EI, 70 eV): *m/z* (%): 424 (M$^+$, 50), 410 (20), 390 (36), 380 (45), 341 (17), 312 (38), 285 (23), 249 (80), 221 (11), 134 (13), 110 (100), 91 (13), 64 (19); HRMS (EI) calcd for $C_{27}H_{20}O_5$ [M$^+$]: 424.03841, found 424.045844.

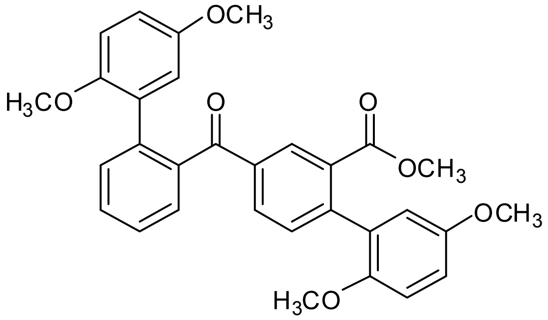


Methyl 4'-(trifluoromethyl)-4-(4'-(trifluoromethyl) biphenylcarbonyl) biphenyl-2-carboxylate (6m): Starting with **4** (220 mg, 0.41 mmol), K_3PO_4 (261 mg, 1.23 mmol), Pd $(PPh_3)_4$ (6 mol%), 4-(trifluoromethyl)phenylboronic acid (144 mg, 1.06 mmol) and 1,4-dioxane (5ml/mmol of triflate), **6m** was isolated as colorless oil; yield 165 mg, (76 %); ^{1}H NMR (300 MHz, CDCl$_3$): δ = 3.55 (s, 3H, OCH$_3$), 7.18-7-28 (m, 4H, ArH), 7.31 (s, 1H, ArH), 7.39-7.44 (m, 4H, ArH), 7.48-7.50 (m, 1H,



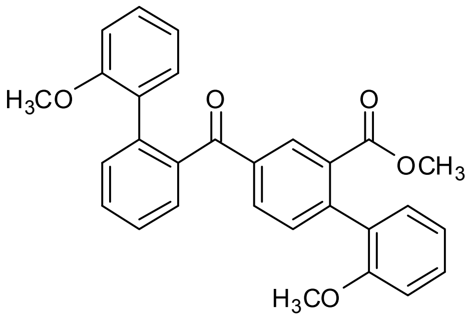
ArH), 7.54-7.58 (m, 3H, ArH), 7.74 (dd, 1H, *J* = 1.8, 8.0 Hz, ArH), 8.02 (d, 1H, *J* = 1.8 Hz, ArH); ^{13}C NMR (75.46 MHz, CDCl$_3$): δ = 52.2 (OCH$_3$), 125.0 (q, $^4J_{F,C}$= 3.6 Hz, CH$_{Ar}$), 125.2 (q, $^4J_{F,C}$= 3.9 Hz, CH$_{Ar}$), 128.1, 128.4, 129.3, 129.4 (CH$_{Ar}$), 129.8 (C$_{Ar}$), 130.2 (CH$_{Ar}$), 130.4 (C$_{Ar}$), 130.8, 131.2, 131.8, 132.2 (CH$_{Ar}$), 136.7, 138.1, 140.1, 143.7, 143.9, 145.4, 146.2 (C$_{Ar}$), 167.7 (COO), 196.6 (C=O); ^{19}F NMR (282 MHz, CDCl3): δ = -73.30 (CF); IR (KBr): $\tilde{\nu}$ = 3063, 2953, 2855 (w), 1727, 1666 (s), 1600 (w), 1437, 1321, 1233 (m), 1161, 1066, 940 (m), 838, 785, 705, (s), 671, 607, 539 (m) cm^{-1}; MS (EI, 70 eV): *m/z* (%): 528 (M$^+$, 10), 291 (17), 290 (100), 271 (23), 240 (12), 201 (16), 162 (14), 97 (12), 84 (73) 71 (16), 57 (29); HRMS (EI) calcd for C$_{29}$H$_{18}$O$_3$F$_6$ [M$^+$]: 528.11547, found 528.114737.

Methyl 4-(2',5'-dimethoxy biphenylcarbonyl)-2',5'-dimethoxy biphenyl-2-carboxylate (6n):

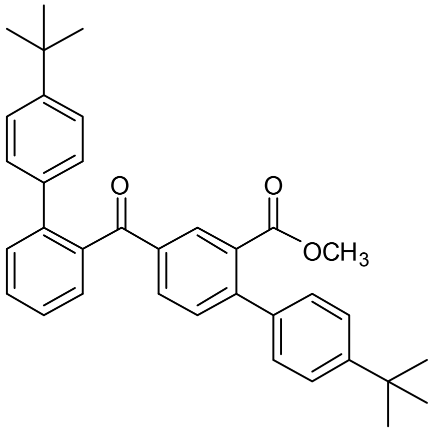


Starting with **4** (220 mg, 0.41 mmol), K$_3$PO$_4$ (261 mg, 1.23 mmol), Pd(PPh$_3$)$_4$ (6 mol%), 2,5-dimethoxyphenylboronic acid (144 mg, 1.06 mmol) and 1,4-dioxane (5ml/mmol of triflate), **6n** was isolated as a colorless solid; yield 140 mg, (67 %) mp. = 50-52°C; ^{1}H NMR (300 MHz, CDCl$_3$): *δ* = 3.27 (s, 3H, OCH$_3$), 3.55 (s, 3H, OCH$_3$), 3.57 (s, 3H, OCH$_3$), 3.67 (s, 3H, OCH$_3$), 3.72 (s, 3H, OCH$_3$), 6.50 (d, 1H, *J* = 8.9 Hz, ArH), 6.63 (dd, 1H, *J* = 3.6, 8.8 Hz, ArH), 6.71-6.74 (m, 2H, ArH), 6.78 (dd, 2H, *J* = 2.6, 7.7 Hz, ArH), 7.23 (d, 1H, *J* = 7.9 Hz, ArH), 7.37 (dd, 2H, *J* = 3.1, 7.3 Hz, ArH), 7.46-7.52 (m, 2H, ArH), 7.83 (dd, 1H, *J* = 1.8, 7.9 Hz, ArH), 8.08 (d, 1H, *J* = 1.7 Hz, ArH); ^{13}C NMR (75.47 MHz, CDCl$_3$): *δ* = 51.8 (OCH$_3$), 54.8 (OCH$_3$), 55.7 (2OCH$_3$), 55.8 (OCH$_3$), 111.1, 111.5, 113.5, 113.8, 116.0, 116.8, 127.0, 128.7, 130.9, 131.0, 131.1, 131.2, 132.5, (CH$_{Ar}$), 136.1, 137.8, 138.5, 142.3, 149.5, 150.2, 153.6, 153.7, 153.8, 156.0, 158.8 (C$_{Ar}$), 167.8 (COO), 195.7 (C=O). IR (KBr): $\tilde{\nu}$ = 3070, 3050, 2970, 2842, 2832 (w), 1721, 1662 (s), 1594, 1582 (m), 1475, 1452 (m), 1391, 1341, 1301 (m), 1281, 1233, 1164 (s), 1091, 940 (s), 891, 862, 773 , 691 (s), 592, 574, 530 (m) cm^{-1}; MS (EI, 70 eV): *m/z* (%): 512 (M$^+$, 40), 448 (19), 409 (31), 385 (04), 340 (15), 323 (33), 288 (20), 250 (81), 195 (01), 182 (38), 167 (40), 151 (10), 138 (25), 123 (36), 94 (68), 84 (100), 65 (10), 47 (21), 43 (44); HRMS (EI) calcd for C$_{31}$H$_{29}$O$_7$ [M+H] $^+$: 513.19078, found 513.18980.

Methyl 2'-methoxy-4-(2'-methoxybiphenylcarbonyl)biphenyl-2-carboxylate (6o): Starting with **4** (220 mg, 0.41 mmol), K_3PO_4 (261 mg, 1.23 mmol), Pd $(PPh_3)_4$ (6 mol%), 2-methoxyphenylboronic acid (144 mg, 1.06 mmol) and 1,4-dioxane (5ml/mmol of triflate), **6o** was isolated as a colorless solid; yield 128 mg, (69 %) mp. = 139-140°C; ^1H NMR (300 MHz, $CDCl_3$): δ = 3.32 (s, 3H, OCH_3), 3.56 (s, 3H, OCH_3), 3.61 (s, 3H, OCH_3), 6.58 (d, 1H, J = 7.2 Hz, ArH), 6.80-6.89 (m, 3H, ArH), 6.92-6.98 (m, 2H, ArH), 7.08-7.14 (m, 2H, ArH), 7.16 (s, 1H, ArH), 7.20-7.30 (m, 2H, ArH), 7.37 (dd, 1H, J = 3.0, 7.7 Hz, ArH), 7.46-7.52 (m, 1H, ArH), 7.82 (dd, 1H, J = 2.0, 8.4 Hz, ArH), 8.10 (d, 1H, J = 1.86 Hz, ArH); ^{13}C NMR (62.90 MHz, $CDCl_3$): δ = 51.8 (OCH_3), 54.4 (OCH_3), 55.2, (OCH_3), 109.9, 110.1, 110.3, 126.8, 128.6, 129.1, 129.4, 129.7, 130.8, 131.0, 131.1, 131.2, 132.5, 132.8 (CH_{Ar}), 135.1 (C_{Ar}), 136.8 (CH_{Ar}), 138.0, 138.5, 142.6, 144.2, 146.8, 155.2, 155.9, 164.5 (C_{Ar}), 167.9 (COO), 195.8 (C=O). IR (KBr): $\tilde{\nu}$ = 3072, 3049, 2968, 2842, 2832 (w), 1719, 1664 (s), 1593, 1581 (m), 1475, 1452 (m), 1389, 1341, 1301 (m), 1281, 1231, 1164 (s), 1092, 941 (s), 891, 864, 779 , 693 (s), 591, 573, 538 (m) cm^{-1}; MS (EI, 70 eV): *m/z* (%): 452 (M^+, 12), 421 (100), 405 (01), 375 (01), 347 (08), 269 (03), 195 (09), 168 (05), 139 (05); HRMS (EI) calcd for $C_{29}H_{24}O_5$ [M^+]: 452.16183, found 452.161882.

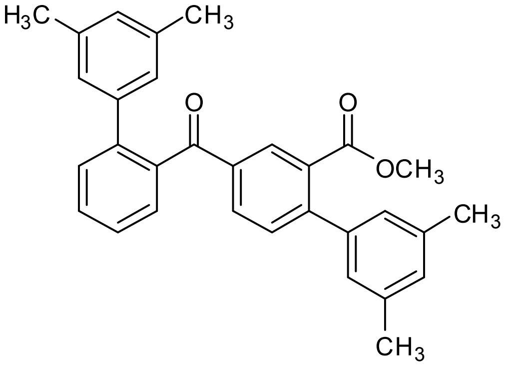


Methyl 2'-methoxy-4-(2'-methoxybiphenylcarbonyl)biphenyl-2-carboxylate (6p): Starting with **4** (220 mg, 0.41 mmol), K_3PO_4 (261 mg, 1.23 mmol), Pd $(PPh_3)_4$ (6 mol%), 4-tert-butylphenylboronic acid (144 mg, 1.06 mmol) and 1,4-dioxane (5ml/mmol of triflate), **6p** was isolated as a colorless solid; yield 150 mg, (72 %) mp. = 131-133°C; ^1H NMR (300 MHz, $CDCl_3$): δ = 1.13 (s, 9H, $3CH_3$), 1.26 (s, 9H, $3CH_3$), 3.53 (s, 3H, OCH_3), 7.06 (d, 2H, J = 8.6 Hz, ArH), 7.10 (d, 2H, J = 4.2 Hz, ArH), 7.14 (s, 1H, ArH), 7.16 (d, 1H, J = 2.0 Hz, ArH), 7.30 (d, 2H, J = 8.8 Hz, ArH), 7.38-7.44 (m, 3H, ArH), 7.48-7.53 (m, 2H, ArH), 7.63 (dd, 1H, J = 1.9, 8.1 Hz, ArH), 7.89 (d, 1H, J = 1.8 Hz, ArH); ^{13}C NMR (75.47 MHz, $CDCl_3$): δ = 31.3 ($6CH_3$), 34.6 ($2C_{tBu}$), 52.0 (OCH_3), 125.1, 125.2 (CH_{Ar}), 126.3 (C_{Ar}), 127.0, 127.8, 128.9, 129.0, 130.0, 130.4 (CH_{Ar}), 130.6 (C_{Ar}), 130.8, 131.3, 131.9 (CH_{Ar}), 136.1, 137.2, 138.4, 141.4, 145.9, 150.4, 150.8 (C_{Ar}), 168.5 (COO), 197.7 (C=O). IR (KBr): $\tilde{\nu}$ = 3068, 3049, 2969, 2842, 2829 (w), 1721, 1663 (s), 1592, 1581 (m), 1472, 1452 (m), 1390, 1339, 1301 (m), 1279, 1235, 1162 (s), 1090, 941 (s), 891, 862, 771 , 692 (s),



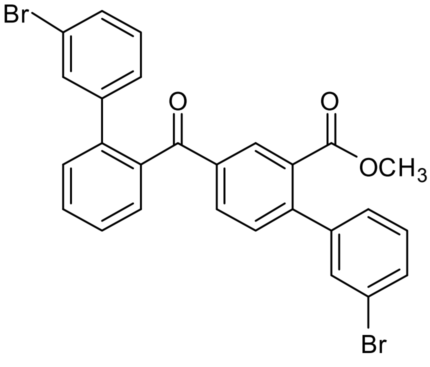
590, 572, 533 (m) cm^{-1}; MS (EI, 70 eV): *m/z* (%): 504 (M$^+$, 100), 490 (32), 489 (89), 457 (42), 447 (14), 401 (12), 359 (01), 295 (03), 252 (02), 237 (39), 181 (24), 152 (09), 126 (03), 57 (24), 41 (10); HRMS (EI) calcd for $C_{35}H_{36}O_3$ [M$^+$]: 504.26590, found 504.265979.

Methyl 4-(3',5'-dimethylbiphenylcarbonyl)-3',5'-dimethylbiphenyl-2-carboxylate (6q):



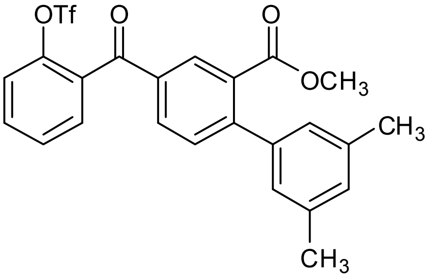
Starting with **4** (220 mg, 0.41 mmol), K_3PO_4 (261 mg, 1.23 mmol), $Pd(PPh_3)_4$ (6 mol%), 3,5-dimethylphenylboronic acid (144 mg, 1.06 mmol) and 1,4-dioxane (5ml/mmol of triflate), **6q** was isolated as a colorless solid; yield 144 mg, (78 %) mp. = 109-111°C; ^{1}H NMR (300 MHz, $CDCl_3$): $\delta = 2.11$ (s, 6H, 2CH_3), 2.26 (s, 6H, 2CH_3), 3.55 (s, 3H, OCH_3), 6.69 (s, 1H, ArH), 6.77 (d, 2H, $J = 3.0$ Hz, ArH), 6.92 (s, 1H, ArH), 7.16 (s, 1H, ArH), 7.19 (d, 1H, $J = 2.8$ Hz, ArH), 7.40 (d, 1H, $J = 1.9$ Hz, ArH), 7.42 (s, 2H, ArH), 7.49-7.54 (m, 2H, ArH), 7.66 (dd, 1H, $J = 1.9, 7.8$ Hz, ArH), 7.84 (d, 1H, $J = 2.7$ Hz, ArH); ^{13}C NMR (62.90 MHz, $CDCl_3$): $\delta = 21.0$ (2CH_3), 21.2 (2CH_3), 52.0 (OCH_3), 125.8, 127.1, 128.9, 129.0, 129.5, 129.9, 130.3, 130.7, 131.1, 131.5 (CH_{Ar}), 136.1, 137.6, 137.7, 138.3, 139.9, 140.1, 141.7, 146.1 (C_{Ar}), 168.5 (COO), 197.6 (C=O). IR (KBr): $\tilde{\nu} = 3068, 3048, 2969, 2837, 2821$ (w), 1721, 1659 (s), 1593, 1579 (m), 1481, 1461 (m), 1389, 1331, 1301 (m), 1282, 1239, 1164 (s), 1090, 941 (s), 893, 863, 776 , 691 (s), 593, 575, 530 (m) cm^{-1}; MS (EI, 70 eV): *m/z* (%): 448 (M$^+$, 87), 433 (100), 401 (32), 387 (17), 267 (12), 209 (37), 179 (19), 165 (36), 115 (01), 77 (01); HRMS (EI) calcd for $C_{31}H_{28}O_3$ [M$^+$]: 448.20330, found 448.202841.

Methyl 3'-bromo-4-(3'-bromobiphenylcarbonyl)biphenyl-2-carboxylate (6r): Starting with **4**

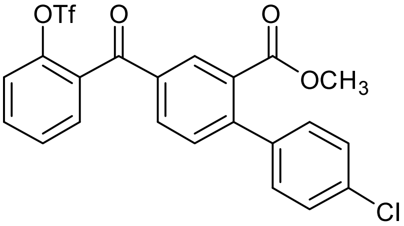


(220 mg, 0.41 mmol), K_3PO_4 (261 mg, 1.23 mmol), Pd $(PPh_3)_4$ (6 mol%), 3-bromophenylboronic acid (144 mg, 1.06 mmol) and 1,4-dioxane (5ml/mmol of triflate), **6r** was isolated as colorless oil; yield 144 mg, (64 %); ^{1}H NMR (300 MHz, $CDCl_3$): δ = 3.57 (s, 3H, OCH_3), 6.80 (d, 2H, $J = 7.1$ Hz, ArH), 6.90 (t, 2H, $J = 6.2$ Hz, ArH), 7.06 (d, 2H, $J = 5.1$ Hz, ArH), 7.26 (s, 1H, ArH), 7.39-7.58 (m, 6H, ArH), 7.73 (dd, 1H, $J = 2.5, 8.3$ Hz, ArH), 7.94 (d, 1H, $J = 1.9$ Hz, ArH); ^{13}C NMR (75.46 MHz, $CDCl_3$): δ = 52.2 (OCH_3), 126.3, 127.9, 128.1, 128.7, 129.1, 129.3, 129.5, 130.1, 130.7, 131.1, 131.6. 131.7, 132.0

(CH$_{Ar}$), 134.0, 135.2, 136.5, 137.1, 138.1, 139.9, 141.8, 141.9, 145.0 (C$_{Ar}$), 167.5 (COO), 196.8 (C=O); IR (KBr): $\tilde{\nu}$ = 3059, 3024 (w), 1725, 1663, 1593 (s), 1557 (w), 1435 (m), 1303, 1231 (s), 1152, 1087 (m), 987 (w), 851 (m), 786 (s), 538 (m) cm^{-1}; GC-MS (EI, 70 eV): *m/z* (%): 550 (M$^+$, 47), 510 (46), 489 (48), 456 (21), 461 (92), 427 (16), 398 (72), 362 (10), 336 (12), 302 (09), 271 (72), 212 (86) 195 (32), 162 (26), 150 (100), 120 (45), 102 (36), 89 (42), 62 (46), 48 (28); HRMS (EI) calcd for $C_{27}H_{18}O_3Br_2$ [M$^+$]: 550.24062, found 550.230120.

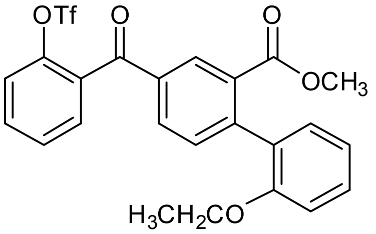


Methyl 3',5'-dimethyl-4-(2-(trifluoromethyl sulfonyloxy) benzoyl) biphenyl-2-carboxylate (7a): Starting with **4** (150 mg, 0.27 mmol), K_3PO_4 (171 mg, 0.81 mmol), Pd (PPh$_3$)$_4$ (3 mol%), 3,5-dimethylphenylboronic acid (140 mg, 0.70 mmol) and 1,4-dioxane (5ml/mmol of triflate), **7**$^{\mathbf{a}}$ was isolated as colorless oil; yield 120 mg, (78 %); ^{1}H NMR (300 MHz, CDCl$_3$): δ = 2.28 (s, 6H, 2CH$_3$), 3.58 (s, 3H, OCH$_3$), 6.88 (s, 2H, ArH), 6.96 (s, 1H, ArH), 7.36 (s, 1H, ArH), 7.47-7.61 (m, 4H, ArH), 7.89 (dd, 1H, *J* = 2.1, 8.3 Hz, ArH), 8.11 (d, 1H, *J* = 2.4 Hz, ArH); ^{13}C NMR (62.90 MHz, CDCl$_3$): δ = 21.2 (2CH$_3$), 52.2 (OCH$_3$), 110.8 (C), 121.0 (q, $J_{F,C}$= 320.7 Hz, CF$_3$), 122.6, 125.9, 128.1, 129.8, 131.0, 131.1, 131.3 (CH$_{Ar}$), 131.5, 132.0 (C$_{Ar}$), 132.2, 132.9 (CH$_{Ar}$), 135.0, 137.1, 139.8, 146.8, 147.6 (C$_{Ar}$), 168.4 (COO), 191.4 (C=O) ^{19}F NMR (282 MHz, CDCl3): δ = -73.34 (CF); IR (KBr): $\tilde{\nu}$ = 3065, 3004, 2950 (w), 1724 (m), 1669 (s), 1560 (w), 1422 (s), 1308 (m), 1245, 1205, 1135 (s), 1092, 944 (m), 886, 855, 593 (s) cm^{-1}; MS (EI, 70 eV): *m/z* (%): 492 (M$^+$, 100), 461 (19), 359 (03), 327 (31), 300 (14), 267 (19), 255 (07), 209 (03) 165 (09); HRMS (EI) calcd for $C_{24}H_{19}O_6F_3S$ [M$^+$]: 492.08490, found 492.084987.



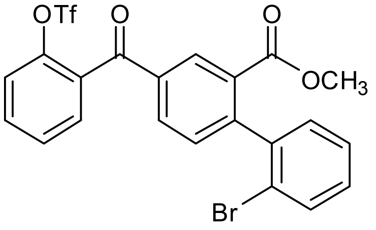
Methyl 4'-chloro-4-(2-(trifluoromethylsulfonyloxy)benzoyl)biphenyl-2-carboxylate (7b): Starting with **4** (150 mg, 0.27 mmol), K_3PO_4 (171 mg, 0.81 mmol), Pd(PPh$_3$)$_4$ (3 mol%), 4-chlorophenylboronic acid (140 mg, 0.70 mmol) and 1,4-dioxane (5ml/mmol of triflate), **7b** was isolated as a yellow solid; yield 90 mg, (64 %) mp. = 99-100°C; ^{1}H NMR (300 MHz, CDCl$_3$): δ = 3.61 (s, 3H, OCH$_3$), 7.21 (d, 2H, *J* = 8.5 Hz, ArH), 7.32 (s, 1H, ArH), 7.35-7.42 (m, 3H, ArH), 7.48 (dd, 1H, *J* = 1.0, 7.3 Hz, ArH), 7.53-7.63 (m, 2H, ArH), 7.90 (dd, 1H, *J* = 1.9, 8.0 Hz, ArH), 8.20 (d, 1H, *J* = 1.8 Hz, ArH); ^{13}C NMR (75.46 MHz, CDCl$_3$): δ = 52.3 (OCH$_3$), 116.3 (C$_{Ar}$), 120.5 (q, $J_{F,C}$= 321.1, CF$_3$), 122.7, 123.0, 128.2, 128.5, 129.5, 131.1, 131.8 (CH$_{Ar}$), 131.9 (C$_{Ar}$), 132.5, 133.1, (CH$_{Ar}$), 134.3, 135.5, 138.5, 146.3, 146.8 (C_{Ar}), 167.6 (COO), 191.3 (C=O). ^{19}F NMR (282 MHz, CDCl3): δ = -73.29 (CF); IR (KBr): $\tilde{\nu}$ = 3066, 3033, 2952 (w), 1727, 1670 (s), 1603 (m), 1573, 1554 (w), 1475, 1308 (m), 1245, 1134, 1084 (s), 1040 (w), 944 (m), 827, 767, 592 (s) cm^{-1}; GC-MS (70 eV): *m/z* (%): 498 (M$^+$, 100), 467 (30), 333 (26), 306 (14), 273 (32), 253 (07), 215 (06), 151 (07), 69 (06); HRMS (EI) calcd for $C_{22}H_{14}O_6ClF_3S$ [M$^+$]: 498.01462, found 498.014917.

Methyl 2'-ethoxy-4-(2-(trifluoromethylsulfonyloxy)benzoyl)biphenyl-2-carboxylate (7c):



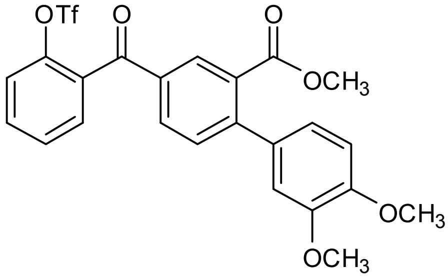
Starting with **4** (150 mg, 0.27 mmol), K_3PO_4 (171 mg, 0.81 mmol), $Pd(PPh_3)_4$ (3 mol%), 2-methoxyphenylboronic acid (140 mg, 0.70 mmol) and 1,4-dioxane (5ml/mmol of triflate), **7c** was isolated as yellow oil; yield 117 mg (82 %); ^{1}H NMR (300 MHz, $CDCl_3$): δ = 1.32 (t, 3H, *J* = 3.1 Hz, CH_3), 3.89 (s, 1H, OCH_3), 4.05 (q, 2H, *J* = 4.1 Hz, OCH_2), 6.82 (s, 1H, ArH), 6.90-7.76 (m, 8H, ArH), 7.91 (dd, 1H, *J* = 1.8, 8.1 Hz, ArH), 8.21 (d, 1H, *J* = 1.8 Hz, ArH); ^{13}C NMR (75.46 MHz, $CDCl_3$): δ = 14.8 (CH_3), 51.8 (OCH_3), 63.9 (OCH_2), 111.2 (CH), 120.8 (q, $J_{F,C}$= 320.1, CF_3), 122.6, 128.2, 129.6, 129.7, 131.1, 131.3, 131.8, 132.6, 132.9, 133.0 (CH_{Ar}), 135.0, 136.8, 137.5, 144.5, 146.8, 155.3, 163.9 (C_{Ar}), 167.6 (COO), 191.6 (C=O); ^{19}F NMR (282 MHz, CDCl3): δ = -73.34 (CF); IR (KBr): $\tilde{\nu}$ = 3497, 3067, 3032 (w), 1725, 1669 (s), 1599 (m), 1575, 1500 (w), 1445, 1309, 1282 (m), 1245, 1206 (s), 1083, 945 (m), 884, 751 (s), 569 (m) cm^{-1}; MS (EI, 70 eV): *m/z* (%): 508 (M$^+$ 100), 477 (04), 463 (38), 448 (64), 415 (38), 315 (78), 287 (18), 271 (42), 253 (18) 223 (46), 139 (28), 121 (14), 69 (10); HRMS (EI) calcd for $C_{24}H_{19}F_3O_7S$ [M$^+$]: 508.07981, found 508.079693.

Methyl 2'-bromo-4-(2-(trifluoromethylsulfonyloxy)benzoyl)biphenyl-2-carboxylate (7d):

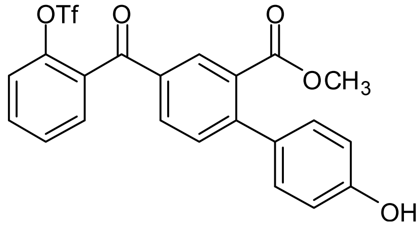


Starting with **4** (150 mg, 0.27 mmol), K_3PO_4 (171 mg, 0.81 mmol), Pd $(PPh_3)_4$ (3 mol%), 2-bromophenylboronic acid (140 mg, 0.70 mmol) and 1,4-dioxane (5ml/mmol of triflate), **7d** was isolated as a colorless solid; yield 118 mg, (78 %) mp. = 124-126°C; ^{1}H NMR (300 MHz, $CDCl_3$): δ = 3.58 (s, 3H, OCH_3), 7.13 (s, 1H, ArH), 7.28-7.40 (m, 4H, ArH), 7.48-7.62 (m, 4H, ArH), 7.94 (dd, 1H, *J* = 2.1, 8.1 Hz, ArH), 8.36 (d, 1H, *J* = 2.1 Hz, ArH); ^{13}C NMR (75.46 MHz, $CDCl_3$): δ = 52.3 (OCH_3), 122.7 (q, $J_{F,C}$= 321.4, CF_3), 127.1, 128.3, 129.2, 129.7, 129.8, 130.2, 131.3, 131.8, 132.3, 132.9, 133.2, (CH_{Ar}), 134.9, 135.0, 136.0, 141.5, 146.7, 146.8, 147.2 (C_{Ar}), 166.2 (COO), 191.4 (C=O). ^{19}F NMR (282 MHz, CDCl3): δ = -73.29 (CF); IR (KBr): $\tilde{\nu}$ = 3053, 2953, 2923 (w), 1728, 1672 (s), 1567 (m), 1482 (w), 1309, 1294 (m), 1241, 1203 (s), 1168 (m), 1087 (s), 948 (m), 887, 769, 592 (s) cm^{-1}; MS (EI, 70 eV): *m/z* (%): 543 (M$^+$, 100), 489 (19), 462 (21), 402 (13), 389 (29), 347 (31), 331 (12), 301 (48), 271 (24), 242 (75), 215 (7), 183 (5), 151 (11), 69 (15); HRMS (EI) calcd for $C_{22}H_{14}BrF_3O_6S$ [M$^+$]: 543.9647, found 543.171525.

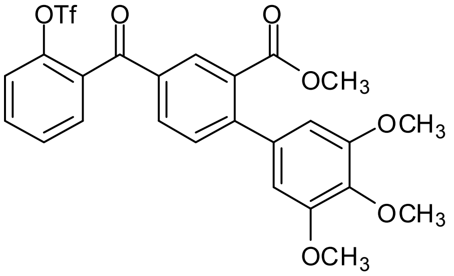
Methyl 3',4'-dimethoxy-4-(2-(trifluoromethyl sulfonyloxy) benzoyl) biphenyl-2-carboxylate (7e): Starting with **4** (150 mg, 0.27 mmol), K_3PO_4 (171 mg, 0.81 mmol), $Pd(PPh_3)_4$ (3 mol%), 3,4-dimethoxyphenylboronic acid (140 mg, 0.70 mmol) and 1,4-dioxane (5ml/mmol of triflate), **7e** was isolated as a yellow solid; yield 97 mg, (68 %) mp. = 48-49°C; ^{1}H NMR (300 MHz, $CDCl_3$): δ = 3.61 (s, 3H, OCH_3), 3.83 (s, 3H, OCH_3), 3.86 (s, 3H, OCH_3), 6.81 (s, 1H, ArH), 6.86 (d, 1H, *J* = 6.2 Hz, ArH), 7.19 (s, 1H, ArH), 7.37 (d, 1H, *J* = 6.9 Hz, ArH), 7.45-7.85 (m, 4H, ArH), 7.91 (dd, 1H, *J* = 3.9, 7.2 Hz, ArH), 8.1 (d, 1H, *J* = 1.9 Hz, ArH); ^{13}C NMR (62.89 MHz, $CDCl_3$): δ = 52.3, 55.8, 55.9, (3OCH_3), 110.9, 111.4 (CH_{Ar}), 120.7 (q, $J_{F,C}$= 320.1, CF_3), 122.6, 123.0, 128.1, 130.9, 131.1, 131.4, 132.2, 132.9, (CH_{Ar}), 133.9, 134.3, 134.8, 144.8, 146.8, 146.9, 148.7, 149.1 (C_{Ar}), 168.6 (COO), 191.3 (C=O). ^{19}F NMR (282 MHz, CDCl3): δ = -73.30 (CF); IR (KBr): $\tilde{\nu}$ = 3064, 2994, 2924 (w), 1726 (s), 1668, 1520, 1482 (m), 1421 (s), 1308 (m), 1243, 1206, 1170, 1086 (s), 944 (m), 891 (s), 830 (m), 763 (s), 732, 655(m), 602 (s), 592 (m) cm^{-1}; MS (EI, 70 eV): *m/z* (%): 524 (M$^+$, 100), 493 (03), 392 (11), 359 (29), 332 (07), 289 (04), 218 (02), 189 (02) 121 (04), 69 (05); HRMS (EI) calcd for $C_{24}H_{19}O_8F_3S$ [M$^+$]: 524.07472, found 524.075184.



Methyl 4'-hydroxy-4-(2-(trifluoromethylsulfonyloxy)benzoyl)biphenyl-2-carboxylate (7f): Starting with **4** (150 mg, 0.27 mmol), K_3PO_4 (171 mg, 0.81 mmol), $Pd(PPh_3)_4$ (3 mol%), 4-hydroxyphenylboronic acid (140 mg, 0.70 mmol) and 1,4-dioxane (5ml/mmol of triflate), **7f** was isolated as a colorless solid; yield 89 mg, (66 %) mp. = 47-48°C; ^{1}H NMR (300 MHz, $CDCl_3$): δ = 3.60 (s, 3H, OCH_3), 6.78 (d, 2H, *J* = 6.9 Hz, ArH), 7.13 (d, 2H, *J* = 6.2 Hz, ArH), 7.18 (s, 1H, OH), 7.37 (s, 1H, ArH), 7.40-7.62 (m, 4H, ArH), 7.89 (dd, 1H, *J* = 4.6, 6.9 Hz, ArH), 8.13 (d, 1H, *J* = 5.8 Hz, ArH); ^{13}C NMR (62.89 MHz, $CDCl_3$): δ = 52.3 (OCH_3), 115.3 (CH_{Ar}), 122.7 (q, $J_{F,C}$= 321.2, CF_3), 128.1, 129.6, 131.0, 131.1, 131.6, 132.4, 132.9, 133.0 (CH_{Ar}), 133.8, 134.2, 134.8, 145.1, 146.8, 147.1,

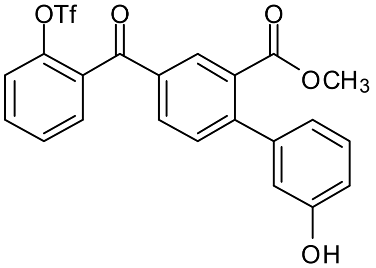


155.9 (C_{Ar}), 168.5 (COO), 191.4 (C=O). ^{19}F NMR (282 MHz, CDCl3): δ = -73.71 (CF); IR (KBr): $\tilde{\nu}$ = 3377, 3060, 2952 (w), 1715, 1667 (s), 1599 (m), 1555, 1520 (w), 1480, 1310 (m), 1245, 1134, 1086 (s), 1040 (w), 944 (m), 884, 767, 656, 592 (s) cm^{-1}; GC-MS (70 eV): *m/z* (%): 480 (M^+, 22), 449 (05), 348 (100), 315 (45), 289 (87), 272 (22), 255 (57), 228 (24), 197 (16), 139 (22), 121 (88), 93 (18), 65 (13); HRMS (EI) calcd for $C_{22}H_{15}O_7F_3S$ [M^+]: 480.04851, found 480.048783.



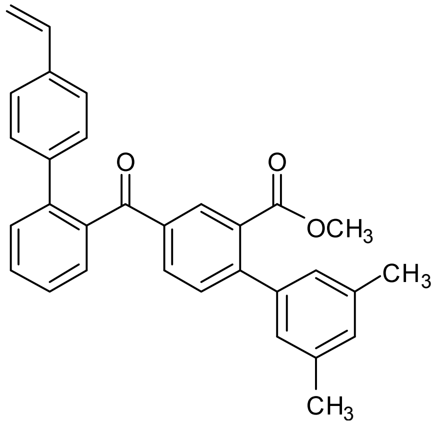
Methyl 3',4',5'-trimethoxy-4-(2-(trifluoromethyl sulfonyloxy) benzoyl) biphenyl-2-carboxylate (7g): Starting with **4** (150 mg, 0.27 mmol), K_3PO_4 (171 mg, 0.81 mmol), $Pd(PPh_3)_4$ (3 mol%), 3,4,5-trimethoxyphenylboronic acid (140 mg, 0.70 mmol) and 1,4-dioxane (5ml/mmol of triflate), **7g** was isolated as crystalline yellow solid; yield 116 mg, (74 %) mp. = 103-104°C; ^{1}H NMR (300 MHz, $CDCl_3$): δ= 3.61 (s, 9H, 3OCH_3), 3.83 (s, 3H, OCH_3), 6.49 (s, 2H, ArH), 7.40 (s, 1H, ArH), 7.45-7.63 (m, 4H, ArH), 7.91 (dd, 1H, *J* = 4.2, 6.4 Hz, ArH), 8.08 (d, 1H, *J* = 6.2 Hz, ArH); ^{13}C NMR (75.46 MHz, $CDCl_3$): δ= 52.4 (OCH_3), 56.2 (2OCH_3), 60.9 (OCH_3), 105.5 (CH_{Ar}), 122.7 (q, $J_{F,C}$= 320.1, CF_3), 128.2, 129.0, 130.8, 131.1, 131.2, 132.2, 133.0 (CH_{Ar}), 134.1, 135.1, 135.9, 136.8, 137.6, 138.0, 146.8, 153.1 (C_{Ar}), 168.5 (COO), 191.3 (C=O). ^{19}F NMR (282.40 MHz, CDCl3): δ = -73.27 (CF); IR (KBr): $\tilde{\nu}$ = 3074, 3052, 2972, 2846, 2835 (w), 1723, 1667 (s), 1597, 1586 (m), 1479, 1454 (m), 1394, 1344, 1300 (m), 1287, 1237, 1169 (s), 1093, 942 (s), 890, 865, 776 , 696 (s), 593, 579, 532 (m) cm^{-1}; MS (EI, 70 eV): *m/z* (%): 554 (M^+, 100), 539 (08), 422 (04), 389 (17), 347 (09), 319 (04), 203 (03), 69 (07); HRMS (EI) calcd for $C_{25}H_{21}O_9F_3S$ [M^+]: 554.08529, found 554.085710.

Methyl 3'-hydroxy-4-(2-(trifluoromethylsulfonyloxy)benzoyl)biphenyl-2-carboxylate (7h):



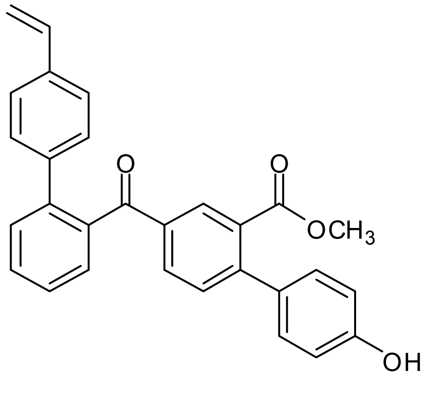
Starting with **4** (150 mg, 0.27 mmol), K_3PO_4 (171 mg, 0.81 mmol), $Pd(PPh_3)_4$ (3 mol%), 3-hydroxyphenylboronic acid (140 mg, 0.70 mmol) and 1,4-dioxane (5ml/mmol of triflate), **7h** was isolated as yellow oil; yield 100 mg, (74 %); ^{1}H NMR (300 MHz, $CDCl_3$): δ= 3.62 (s, 3H, OCH_3), 6.91 (s, 1H, ArH), 7.11 (s, 1H, ArH), 7.32 (d, 1H, *J* = 6.2 Hz, ArH), 7.34 (t, 1H, *J* = 2.2 Hz, ArH), 7.53 (d, 1H, *J* = 7.0 Hz, ArH), 7.54 (m, 4H, ArH), 7.81 (dd, 1H, *J* = 6.4, 2.1 Hz, ArH), 8.15 (d, 1H, *J* = 6.2 Hz, ArH), 11.80 (s, 1H, OH); ^{13}C NMR (62.90 MHz, $CDCl_3$): δ= 52.4, (OCH_3), 118.8, (C_{Ar}), 118.6, 119.0 (CH_{Ar}), 120.6 (q, $J_{F,C}$= 320.1, CF_3), 121.3, 128.2, 130.0, 130.9, 131.0, 131.8, 132.0, 133.2, 136.8, (CH_{Ar}), 137.6 141.1, 142.9, 143.6, 144.2, 149.2 (C_{Ar}), 168.5 (COO), 199.8 (C=O). ^{19}F NMR (282.40 MHz, CDCl3): δ = -73.27 (CF); IR (KBr): $\tilde{\nu}$ = 3071, 3049, 2965, 2832, 2826 (w), 1716, 1654 (s), 1582, 1578 (m), 1462, 1448 (m), 1389, 1339, 1301 (m), 1282, 1234, 1164 (s), 1091, 940 (s), 897, 862, 771 , 692 (s), 591, 575, 531 (m) cm^{-1}; MS (EI, 70 eV): *m/z* (%): 480 (M^+, 40), 448 (19), 421 (31), 387 (04), 347 (15), 315 (33), 287 (20), 255 (81), 226 (15), 139 (14), 121 (100), 93 (18), 69 (19), 44 (04); HRMS (EI) calcd for $C_{22}H_{15}O_7F_3S$ [M^+]: 480.04851, found 480.048846.

Methyl 3',5'-dimethyl-4-(2-(trifluoromethyl sulfonyloxy)benzoyl)biphenyl-2-carboxylate (8a):



Starting with **4** (150 mg, 0.27 mmol), K_3PO_4 (171 mg, 0.81 mmol), $Pd(PPh_3)_4$ (3 mol%), 4-vinylphenylboronic acid (140 mg, 0.70 mmol) and 1,4-dioxane (5ml/mmol of triflate), **10a** was isolated as colorless crystalline solid; yield 82 mg, (60 %), mp. = 49-50°C; ^{1}H NMR (300 MHz, $CDCl_3$): δ = 2.24 (s, 6H, $2CH_3$), 3.54 (s, 3H, OCH_3), 5.14 (dd, 1H, *J* = 2.3, 6.8 Hz, CH_{2vinyl}), 5.63 (dd, 1H, *J* = 1.5, 8.1 Hz, CH_{vinyl}), 6.59 (dd, 1H, *J* = 1.2, 6.8 Hz, CH_{2vinyl}), 6.76 (s, 2H, ArH), 6.91 (s, 1H, ArH), 7.13 (s, 1H, ArH), 7.21 (d, 2H, *J* = 7.2 Hz, ArH), 7.37 (d, 2H, *J* = 6.2 Hz, ArH), 7.54-7.65 (m, 4H, ArH), 7.71 (dd, 1H, *J* = 1.9, 8.0 Hz, ArH), 7.95 (d, 1H, *J* = 1.8 Hz, ArH); ^{13}C NMR (75.47 MHz, $CDCl_3$): δ = 21.3 ($2CH_3$), 52.0 (OCH_3), 113.1, 124.8, 125.0, (C_{Ar}), 125.9, 126.2, 127.2, 128.9, 129.6, 130.6, 131.3, 132.2, 133.4, 134.3, 136.3, (CH_{Ar}), 137.1, 137.3, 138.5, 139.0, 139.9, 145.6 (C_{Ar}), 167.4 (COO), 196.3 (C=O); IR (KBr): $\tilde{\nu}$ = 3057, 3019, 2948 (w), 1720, 1663 (s), 1596 (m), 1556, 1513 (w), 1435, 1306 (m), 1231 (s), 1151, 1099, 940 (m), 864, 786 (s), 694, 647, 575, 540 (m) cm^{-1}; GC-MS (EI, 70 eV): *m/z* (%): 446 (M^+, 100), 414 (16), 385 (16), 358 (08), 267 (29), 207 (20), 194 (08), 178 (49), 152 (14), 77 (01); HRMS (EI) calcd for $C_{31}H_{26}O_3$ [M^+]: 446.18765, found 446.187064.

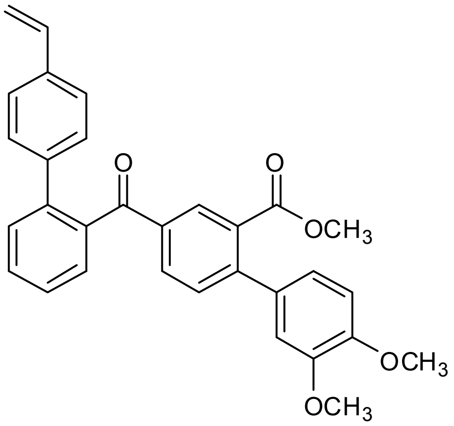
Methyl 4'-hydroxy-4-(4'-vinylbiphenylcarbonyl)biphenyl-2 carboxylate (8b): Starting with **7f**



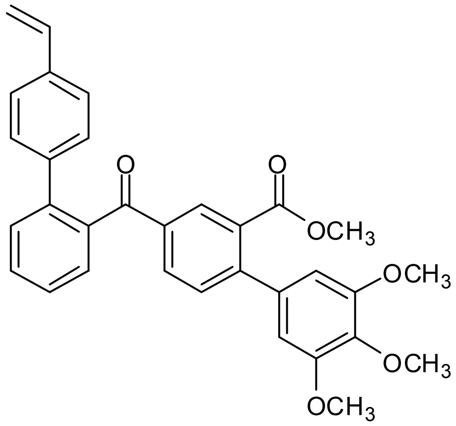
(150 mg, 0.27 mmol), K_3PO_4 (171 mg, 0.81 mmol), $Pd(PPh_3)_4$ (3 mol%), 4-vinylphenylboronic acid (140 mg, 0.70 mmol) and 1,4-dioxane (5ml/mmol of triflate), **8b** was isolated as a colorless oil; yield 100 mg, (74 %); ^{1}H NMR (300 MHz, $CDCl_3$): δ = 3.59 (s, 3H, OCH_3), 5.15 (dd, 1H, *J* = 3.9, 7.2 Hz, CH_{2vinyl}), 5.63 (dd, 1H, *J* = 2.2, 8.2 Hz, CH_{2vinyl}), 6.60 (dd, 1H,

J = 1.6, 6.8 Hz, CH$_{vinyl}$), 6.72 (d, 2H, J = 6.2 Hz, ArH), 6.90 (d, 2H, J = 6.8 Hz, ArH), 7.01 (d, 2H, J = 6.4 Hz, ArH), 7.14 (d, 2H, J = 6.7 Hz, ArH), 7.31-7.56 (m, 4H, ArH). 6.73 (dd, 2H, J = 1.4, 8.2 Hz, ArH), 7.97 (d, 1H, J = 1.9 Hz, ArH), 9.43 (s, 1H, OH); ^{13}C NMR (62.89 MHz, CDCl$_3$): δ = 52.1 (OCH$_3$), 114.1 (CH$_{2vinyl}$), 115.2, 126.2, 127.2 (CH$_{Ar}$), 127.9, 128.0, 128.1 (C$_{Ar}$), 128.8, 129.2, 130.1, 130.6, 130.7, 131.5, 132.1, 135.2, 136.2 (CH$_{Ar}$), 136.7, 138.2, 139.5, 140.9, 146.1, 155.7 (C$_{Ar}$), 168.6 (COO), 197.4 (C=O); IR (KBr): $\tilde{\nu}$ = 3417, 3060, 3022, 2946 (w), 1715, 1692 (s), 1597 (m), 1555, 1519 (w), 1434, 1306 (m), 1233 (s), 1153, 1087, 987, 939 (m), 831, 769 (s), 699, 607, 571, 539 (m) cm^{-1}; GC-MS (EI, 70 eV): *m/z* (%): 434 (M$^+$, 100), 401 (07), 373 (09), 347 (04), 255 (20), 212 (09), 178 (30), 152 (07), 91 (03); HRMS (EI) calcd for $C_{29}H_{22}O_4$ [M$^+$]: 434.15126, found 434.150613.

Methyl 3',4'-dimethoxy-4-(4'-vinylbiphenylcarbonyl)biphenyl-2-carboxylate (8c): Starting with **7e** (150 mg, 0.27 mmol), K_3PO_4 (171 mg, 0.81 mmol), Pd(PPh$_3$)$_4$ (3 mol%), 4-vinylphenylboronic acid (140 mg, 0.70 mmol) and 1,4-dioxane (5ml/mmol of triflate), **8c** was isolated as a colorless crystalline solid; yield 89 mg, (65 %), mp. = 75-76°C; ^{1}H NMR (300 MHz, CDCl$_3$): δ = 3.57 (s, 3H, OCH$_3$), 3.79 (s, 3H, OCH$_3$), 3.84 (s, 3H, OCH$_3$), 5.15 (dd, 1H, J = 1.6, 7.2 Hz, CH$_{2vinyl}$), 5.64 (dd, 1H, J = 3.2, 6.2 Hz, CH$_{vinyl}$), 6.60 (dd, 1H, J = 7.2, 6.4 Hz, CH$_{2vinyl}$), 6.69 (d, 1H, J = 6.4 Hz, ArH), 6.83 (d, 1H, J = 7.2 Hz, ArH), 6.90 (d, 2H, J = 6.4 Hz, ArH), 7.00 (s, 1H, ArH), 7.12, (d, 2H, J = 6.1 Hz, ArH), 7.21 (s, 1H, ArH), 7.38-7.56 (m, 4H, ArH), 7.73 (dd, 1H, J = 1.8, 8.0 Hz, ArH), 7.94 (d, 1H, J = 1.6 Hz, ArH); ^{13}C NMR (75.47 MHz, CDCl$_3$): δ = 52.2, 55.9, 55.9 (3OCH$_3$), 111.4 (CH$_{vinyl}$), 114.1 (CH$_{2vinyl}$), 120.7, 126.2, 127.2, 128.8, 129.2, 130.1, 130.5, 130.7, 131.3, 132.0, 135.2, 136.2 (CH$_{Ar}$), 136.7, 138.3, 139.5, 140.9, 141.1, 142.3, 143.6, 145.9, 148.6, 149.0 (C$_{Ar}$), 168.7 (COO), 197.2 (C=O); IR (KBr): $\tilde{\nu}$ = 3056, 2999 (w), 1720, 1663 (s), 1596 (m), 1554, 1519 (w), 1436, 1306 (m), 1232 (s), 1140, 1086, 940 (m), 843, 765 (s), 699, 606, 539 (m) cm^{-1}; GC-MS (EI, 70 eV): *m/z* (%): 478 (M$^+$, 100), 418 (02), 387 (03), 300 (05), 225 (12), 178 (20), 145 (06), 96 (03), 74 (02); HRMS (ESI$^+$) calcd for $C_{31}H_{26}O_5$ [M$^+$]: 478.1853, found 478.18582.

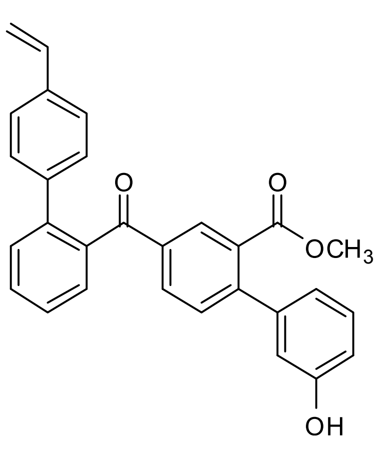


Methyl 3',4',5'-trimethoxy-4-(4'-vinylbiphenylcarbonyl) biphenyl-2-carboxylate (8d): Starting



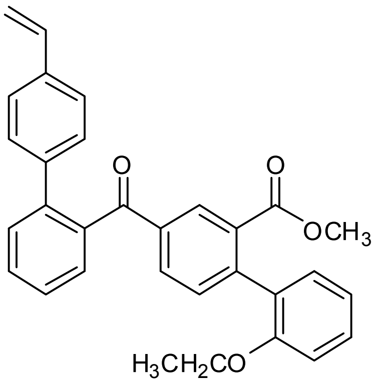
with **7g** (150 mg, 0.27 mmol), K_3PO_4 (171 mg, 0.81 mmol), $Pd(PPh_3)_4$ (3 mol%), 4-vinylphenylboronic acid (140 mg, 0.70 mmol) and 1,4-dioxane (5ml/mmol of triflate), **8d** was isolated as a colorless oil; yield 100 mg, (72 %); ^{1}H NMR (300 MHz, $CDCl_3$): δ = 3.57 (s, 3H, OCH_3), 3.77 (s, 6H, $2OCH_3$), 3.81 (s, 3H, OCH_3), 5.15 (dd, 1H, *J* = 5.9, 6.2 Hz, CH_{2vinyl}), 5.64 (dd, 1H, *J* = 4.6, 7.5 Hz, CH_{2vinyl}), 6.37 (s, 2H, ArH), 6.60 (dd, 1H, *J* = 7.1, 6.7 Hz, CH_{vinyl}), 7.14 (d, 2H, *J* = 7.5 Hz, ArH), 7.30 (d, 2H, *J* = 6.2 Hz, ArH), 7.41-7.61 (m, 4H, ArH), 7.73 (dd, 2H, *J* = 4.2, 7.2 Hz, ArH), 7.93 (d, 1H, *J* = 6.2 Hz, ArH); ^{13}C NMR (75.46 MHz, $CDCl_3$): δ = 52.2, 56.1, 60.9 ($3OCH_3$), 114.1 (CH_{2vinyl}), 127.2 (CH), 127.9, 128.5 (C_{Ar}), 128.9, 129.2, 130.1, 130.4, 130.8, 131.2, 131.9, 134.9, 135.0, 136.2 (CH_{Ar}), 136.1, 136.7, 138.2, 139.5, 140.9, 141.7, 145.9, 153.0 (C_{Ar}), 168.6 (COO), 197.2 (C=O); IR (KBr): $\tilde{\nu}$ = 3055, 2925, 2850 (w), 1722, 1663 (s), 1583 (m), 1556, 1512 (w), 1433, 1397, 1342 (m), 1296, 1233 (s), 1151, 1122, 1094, 1028, 940 (m), 880, 831, 769 721, (s), 693, 644, 539 (m) cm^{-1}; GC-MS (EI, 70 eV): *m/z* (%): 508 (M^+, 100), 493 (35), 277 (09), 262 (21), 219 (35), 201 (11), 183 (31), 152 (13), 108 (19), 57 (18), 44 (29); HRMS (EI) calcd for $C_{32}H_{28}O_6$ [M^+]: 508.18804, found 508.187819.

Methyl 3'-hydroxy-4-(4'-vinylbiphenylcarbonyl)biphenyl-2-carboxylate (8e): Starting with **7h**

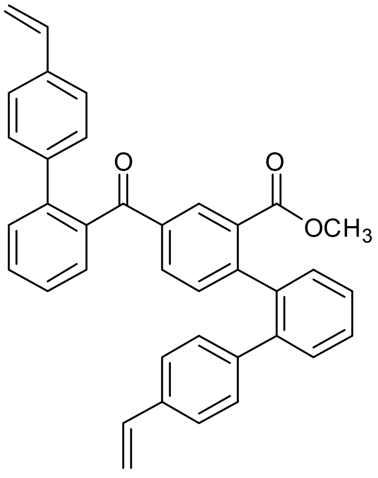


(150 mg, 0.27 mmol), K_3PO_4 (171 mg, 0.81 mmol), $Pd(PPh_3)_4$ (3 mol%), 4-vinylphenylboronic acid (140 mg, 0.70 mmol) and 1,4-dioxane (5ml/mmol of triflate), **8e** was isolated as yellow oil; yield 87 mg, (64 %); ^{1}H NMR (300 MHz, $CDCl_3$): δ = 3.61 (s, 3H, OCH_3), 4.12 (dd, 1H, *J* = 2.6, 8.1 Hz, CH_{2vinyl}), 5.19 (dd, 1H, *J* = 2.8, 8.6 Hz, CH_{2vinyl}), 5.77 (dd, 1H, *J* = 2.4, 8.2 Hz, CH_{vinyl}), 6.72 (d, 1H, *J* = 6.2 Hz, ArH), 6.90 (d, 1H, *J* = 6.8 Hz, ArH), 7.11 (s, 1H, ArH), 7.20 (t, 1H, *J* = 6.7 Hz, ArH), 7.30 (s, 1H, ArH). 7.35-7.45 (m, 4H, ArH), 7.54-7.65 (m, 4H, ArH), 7.73 (dd, 1H, *J* = 5.4, 6.2 Hz, ArH), 7.97 (d, 1H, *J* = 2.9 Hz, ArH); ^{13}C NMR (62.89 MHz, $CDCl_3$): δ = 51.5 (OCH_3), 114.3 (CH_{2vinyl}), 115.2, 117.2, 118.3, 126.2, 127.2 (CH_{Ar}), 127.9, 128.0, 128.1 (C_{Ar}), 128.8, 129.2, 130.1, 130.6, 130.7, 131.5, 132.1, 136.2 (CH_{Ar}), 136.5, 138.1, 139.2, 140.4, 146.0, 155.2 (C_{Ar}), 168.2 (COO), 197.2 (C=O); IR (KBr): $\tilde{\nu}$ = 3415, 3029, 3021, 2943 (w), 1719, 1691 (s), 1596 (m),

1553, 1517 (w), 1431, 1303 (m), 1231 (s), 1159, 1083, 981, 938 (m), 833, 767 (s), 691, 605, 573, 534 (m) cm^{-1}; GC-MS (EI, 70 eV): *m/z* (%): 434 (M$^+$, 100), 401 (16), 375 (40), 341 (07), 314 (09), 281 (33), 255 (33), 207 (87), 191 (09), 133 (06), 121 (46), 93 (10), 65 (09), 44 (15); HRMS (EI) calcd for $C_{29}H_{22}O_4$ [M$^+$]: 434.15180, found 434.48260.

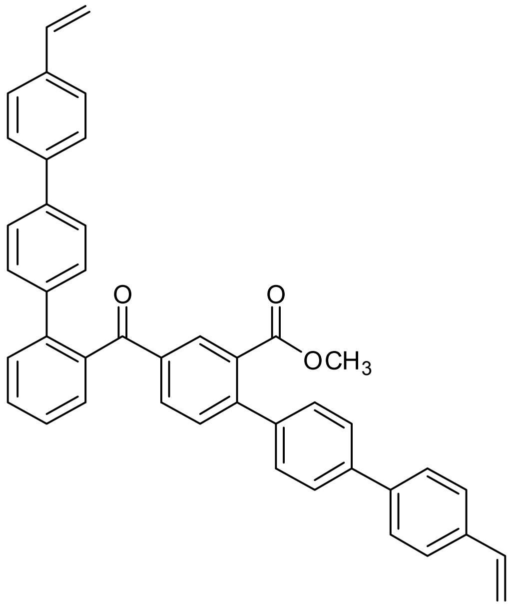


Methyl 2'-ethoxy-4-(4'-vinylbiphenylcarbonyl)biphenyl-2-carboxylate (8f): Starting with **7c** (150 mg, 0.27 mmol), K_3PO_4 (171 mg, 0.81 mmol), $Pd(PPh_3)_4$ (3 mol%), 4-vinylphenlboronic acid (140 mg, 0.70 mmol) and 1,4-dioxane (5ml/mmol of triflate), **8f** was isolated as a colorless crystalline solid; yield 93 mg (68 %), mp. = 53-55°C; ^{1}H NMR (300 MHz, $CDCl_3$): δ = 1.32 (t, 3H, *J* = 3.1 Hz, CH_3), 3.54 (s, 1H, OCH_3), 3.82 (q, 2H, *J* = 4.1 Hz, OCH_2), 6.82 (s, 1H, ArH), 6.907.12 (m, 4H, ArH), 7.20-7.30 (m, 4H, ArH), 7.42 (d, 2H, *J* = 2.4, 8.2 Hz, ArH), 7.52-7.62 (m, 2H, ArH), 7.91 (dd, 1H, *J* = 2.8, 7.2 Hz, ArH), 8.21 (d, 1H, *J* = 6.8 Hz, ArH); ^{13}C NMR (75.46 MHz, $CDCl_3$): δ = 14.4 (CH_3), 51.7 (OCH_3), 63.8 (OCH_2), 111.3 (CH_{vinyl}), 114.0 ($CH_{2\mathit{vinyl}}$), 120.7, 126.2, 127.2 (CH_{Ar}), 128.0 (C_{Ar}), 128.9, 129.2, 129.7, 130.1, 131.0, 131.4, 132.3, 133.2, 134.6, 136.2 (CH_{Ar}), 136.6, 137.2, 138.4, 139.5, 140.9, 141.1, 143.4, 144.2, 155.2 (C_{Ar}), 167.7 (COO), 197.5 (C=O); ^{19}F NMR (282 MHz, CDCl3): δ = -73.34 (CF); IR (KBr): $\tilde{\nu}$ = 3491, 3062, 3029 (w), 1723, 1661 (s), 1592 (m), 1571, 1504 (w), 1442, 1307, 1281 (m), 1241, 1202 (s), 1081, 942 (m), 883, 750 (s), 567 (m) cm^{-1}; MS (EI, 70 eV): *m/z* (%): 462 (M$^+$ 100), 430 (07), 417 (21), 401 (46), 373 (30), 357 (04), 313 (04), 283 (06), 223 (21) 201 (27), 178 (67), 139 (19); HRMS (EI) calcd for $C_{31}H_{26}O_4$ [M$^+$]: 462.18256, found 462.183193.

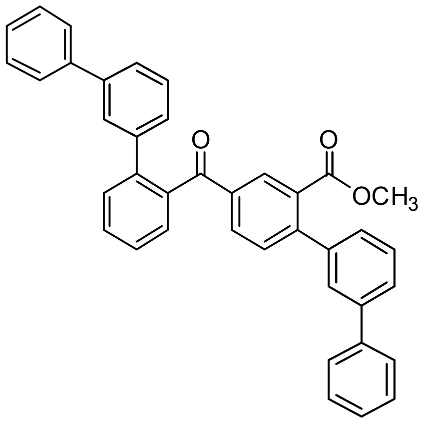


4''-Vinyl-4-(4'-vinyl-biphenyl-2-carbonyl)-[1,1';2',1'']terphenyl-2-carboxylic acid methyl ester (9). Starting with **7d** (150 mg, 0.27 mmol), K_3PO_4 (171 mg, 0.81 mmol), $Pd(PPh_3)_4$ (3 mol%), 4-vinylphenylboronic acid (140 mg, 0.70 mmol) and 1,4-dioxane (5ml/mmol of triflate), **9** was isolated as yellow oil; yield 90 mg, (62 %); ^{1}H NMR (300 MHz, $CDCl_3$): δ = 3.45 (s, 3H, OCH_3), 5.15 (ddd, 2H, *J* = 0.8, 5.7, 10.9 Hz, $CH_{2\mathit{vinyl}}$), 5.62 (ddd, 2H, *J* = 0.8, 5.0, 17.6 Hz, $CH_{2\mathit{vinyl}}$), 6.57 (ddd, 2H, *J* = 1.9, 10.9, 17.6 Hz, $2CH_{\mathit{vinyl}}$), 6.86 (d, 4H, *J* = 6.4 Hz, ArH), 6.95 (d, 4H, *J* =6.9 Hz, ArH), 7.12 (d, 2H, *J* = 5.7 Hz, ArH), 7.20 (t, 2H, J = 4.9 Hz, ArH), 7.31 (s, 1H, ArH). 7.40 (dd, 1H, J = 4.5, 6.7 Hz, ArH), 7.43-7.52 (m, 4H, ArH), 7.94 (d, 1H, J = 6.8 Hz, ArH); ^{13}C NMR (62.89 MHz, $CDCl_3$): δ = 52.0 (OCH_3), 113.8, 114.3 ($2CH_{2vinyl}$), 115.4 (C_{Ar}), 125.7, 126.1, 127.3, 128.9, 129.2, 129.8, 130.0, 130.7, 131.3, 131.9, 132.0, 133.2, 134.6, 136.2, 136.4 (CH_{Ar}), 136.6, 138.2, 138.9, 139.5, 139.8, 140.0, 140.7, 141.2, 143.4, 146.9 (C_{Ar}), 167.2 (COO), 197.4 (C=O); IR (KBr): $\tilde{\nu}$ = 3056, 3019, 2948 (w), 1724, 1662 (s), 1596 (m), 1555, 1514 (w), 1435, 1399, 1305 (m), 1258, 1230 (s), 1152, 1085, 988, 941 (m), 843, 765 (s), 694, 633, 596, 540 (m) cm^{-1}; GC-MS (EI, 70 eV): *m/z* (%): 520 (M^+, 16), 488 (100), 417 (14), 386 (32), 357 (07), 309 (20), 262 (48), 207 (50), 179 (77), 152 (20), 108 (13); HRMS (EI) calcd for $C_{37}H_{28}O_3$ [M^+]: 520.20330, found 520.202889.

4''-Vinyl-4-(4''-vinyl-[1,1';4',1'']terphenyl-2-carbonyl)-[1,1';4',1'']terphenyl-2-carboxylic acid methyl ester (10). Starting with **6g** (150 mg, 0.27 mmol), K_3PO_4 (171 mg, 0.81 mmol), $Pd(PPh_3)_4$ (3 mol%), 4-vinylphenylboronic acid (140 mg, 0.70 mmol) and 1,4-dioxane (5ml/mmol of triflate), **10** was isolated as a colorless crystalline solid; yield 100 mg, (72 %), mp. = 169-171°C; ^{1}H NMR (300 MHz, $CDCl_3$): δ = 3.58 (s, 3H, OCH_3), 5.05 (dd, 2H, J = 6.2, 5.4 Hz, CH_{2vinyl}), 5.16 (dd, 2H, J = 5.2, 6.4 Hz, CH_{2vinyl}), 5.23 (d, 2H, J = 6.4, 5.8 Hz, CH_{vinyl}), 5.48 (d, 8H, J = 6.4 Hz, ArH), 7.44 (d, 4H, J = 6.4 Hz, ArH), 7.59 (d, 4H, J = 6.2 Hz, ArH), 7.65-8.00 (m, 7H, ArH); ^{13}C NMR (62.89 MHz, $CDCl_3$): δ = 52.1 (OCH_3), 114.1 (CH_{2vinyl}), 126.2, 127.0, 127.9, 128.0, 128.9, 129.2, 130.1, 130.7, 131.1, 131.8, 132.2, 133.0 (CH_{Ar}), 134.9, 135.0, 136.1, 136.8, 138.2, 139.7, 140.1, 141.0, 146.0 (C_{Ar}), 168.2 (COO), 197.3 (C=O); IR (KBr): $\tilde{\nu}$ = 3427, 2948 (w), 1722, 1666 (s), 1596 (m), 1556, 1514 (w), 1434, 1305 (m), 1231 (s), 1152, 1093, 999, 939 (m), 843, 818, 768 (s), 726, 691, 649, 540 (m) cm^{-1}; GC-MS (EI, 70 eV): *m/z* (%): 596 (M^+, 10), 540 (30), 502 (12), 480 (21), 439 (15), 414 (16), 385 (16), 358 (08), 267 (29), 207 (20), 194 (08), 178 (49), 152 (14), 77 (10); HRMS (EI) calcd for $C_{43}H_{32}O_3$ [M^+]: 596.23510, found 596.71240.

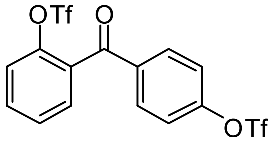


4-([1,1';3',1'']Terphenyl-2-carbonyl)-[1,3';1',1'']terphenyl-2-carboxylic acid methyl ester (11).



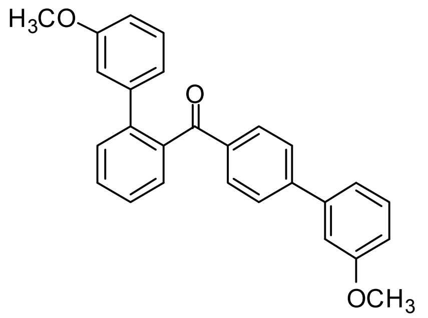
Starting with **6r** (150 mg, 0.27 mmol), K_3PO_4 (171 mg, 0.81 mmol), $Pd(PPh_3)_4$ (3 mol%), phenylboronic acid (140 mg, 0.70 mmol) and 1,4-dioxane (5ml/mmol of triflate), **11** was isolated as yellow oil; yield 90 mg, (60 %); ^{1}H NMR (300 MHz, $CDCl_3$): δ = 3.46 (s, 3H, OCH_3), 7.10 (s, 1H, ArH), 7.23 (s, 2H, ArH), 7.25-7.50 (m, 17H, ArH), 7.57 (t, 1H, *J* = 5.9 Hz, ArH), 7.65 (d, 2H, *J* = 6.2 Hz, ArH), 7.73 (dd, 1H, *J* = 6.2, 4.6 Hz, ArH), 7.94 (d, 1H, *J* = 6.8 Hz, ArH); ^{13}C NMR (62.89 MHz, $CDCl_3$): δ = 52.0 (OCH_3), 126.2, 127.0, 127.5, 127.9, 128.1, 128.7, 129.0, 130.9, 131.5, 131.8, 134.9, 135.0, 135.8 (CH_{Ar}), 136.3, 138.5, 140.6, 141.1, 142.0, 143.0, 146.2, 166.3 (C_{Ar}), 168.1 (COO), 197.5 (C=O); IR (KBr): $\tilde{\nu}$ = 3055, 3028, 2947 (w), 1720, 1662 (s), 1595 (m), 1572, 1487, (w), 1434, 1303 (m), 1210 (s), 1151, 1086, 1031, 940 (m), 896, 783 (s), 696, 628, 539 (m) cm^{-1}; GC-MS (EI, 70 eV): *m/z* (%): 544 (M^+, 20), 520 (20), 490 (10), 465 (12), 430 (19), 414 (16), 385 (16), 358 (08), 267 (29), 207 (20), 194 (08), 178 (49), 152 (14), 77 (01); HRMS (EI) calcd for $C_{39}H_{28}O_3$ [M^+]: 544.20380, found 544.63780.

2-(4-(Trifluoromethylsulfonyloxy)benzoyl)phenyl trifluoromethanesulfonate (13):

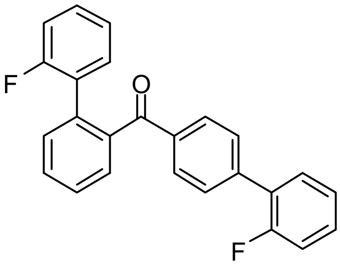


Starting with **12** (168 mg, 1.0 mmol), pyridine (0.32 ml, 4.0 mmol) and Tf_2O (0.39 ml, 2.4 mmol), **13** was isolated as a yellow oil, yield, (330 mg, 88 %); ^{1}H NMR (300 MHz, $CDCl_3$): *δ* = 7.31-7.38 (m, 3H, ArH), 7.43-7.53 (m, 2H, ArH), 7.58-7.64 (m, 1H, ArH), 7.83 (d, 2H, *J* = 8.91 Hz, ArH); ^{13}C NMR (62.90 MHz, $CDCl_3$): δ = 115.8 (q, $J_{F,C}$ = 320.0 Hz, CF_3), 120.9 (q, $J_{F,C}$ = 321.3 Hz, CF_3), 121.6, 122.7, 128.3, 131.1, 132.2, 133.3 (CH_{Ar}), 133.3, 136.3, 146.6, 152.7 (C_{Ar}), 190.8 (C=O). ^{19}F NMR (282 MHz, CDC13): δ = -73.3, 72.6 (2CF). IR (KBr): $\tilde{\nu}$= 1598, 1589, 1580, (m), 1496, 1431, 1414, 1319, 1291 (m), 1265 (s), 1165, 1077, 1028, 989, 976, 932 (m), 887, 787, 757 (s), 680, 595, 572 (m) cm^{-1}; GC-MS (EI, 70 eV): *m/z* (%): 478 (M^+, 58), 345 (06), 317 (13), 281 (09), 253 (100), 212 (12), 184 (28), 155 (07), 128 (12), 92 (10), 69 (17), 63 (06); HRMS (EI) calcd for $C_{15}H_8F_6O_7S_2$ [M^+]: 477.96101 found 477.960813.

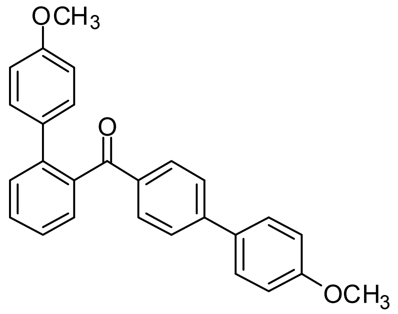
(3'-Methoxybiphenyl-2-yl)(3'-methoxybiphenyl-4-yl)methanone (14a): Starting with **13** (200 mg, 0.41 mmol), K_3PO_4 (292 mg, 1.38 mmol), $Pd(PPh_3)_4$ (6 mol%), 3-methoxyphenylboronic acid (162 mg, 1.06 mmol) and 1,4-dioxane (5ml/mmol of triflate), **14a** was isolated as a colorless solid, yield 128 mg, (78 %) mp. = 152-154°C; ^{1}H NMR (300 MHz, $CDCl_3$): δ = 3.61, 3.78 (s, 6H, $2OCH_3$), 6.61-6.64 (m, 2H, ArH), 6.75-6.86 (m, 3H, ArH), 6.99-7.07 (m, 2H, ArH), 7.26 (t, 1H, J = 7.95 Hz, ArH), 7.39-7.51 (m, 6H, ArH), 7.63-7.66 (m, 2H, ArH). ^{13}C NMR (75.47 MHz, $CDCl_3$): δ = 55.1, 55.3 ($2OCH_3$), 113.0, 113.2, 113.4, 114.4, 119.7, 121.5, 126.8, 127.1, 128.5, 129.3, 129.9, 130.2, 130.4, 131.0 (CH_{Ar}), 136.2, 139.0, 140.8, 141.3, 141.5, 145.2, 159.3, 160.0 (C_{Ar}), 198.2 (C=O). IR (KBr): $\tilde{\nu}$ = 3058, 2998, 2834 (w), 1725 (w), 1661, 1581, 1477, 1435, 1398, 1307 (m), 1278, 1210 (s), 1170, 1150, 1049, 1027, 1019 (m), 929 (s), 844, 775 (m), 757, 689 (s), 672, 617, 565, 531 (m) cm^{-1}; GC-MS (EI, 70 eV): *m/z* (%): 394 (M^+, 100), 363 (15), 281 (04), 211 (47), 168 (23), 139 (19), 44 (05); HRMS (EI) calcd for $C_{27}H_{22}O_3$ [M^+]: 394.15689, found 394.46178.



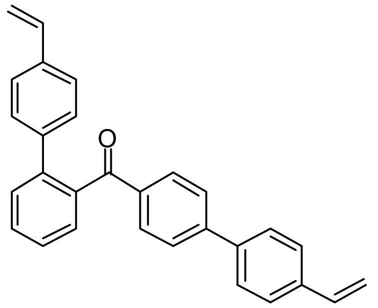
(2'-Fluorobiphenyl-2-yl)(2'-fluorobiphenyl-4-yl)methanone (14b): Starting with **13** (200 mg, 0.41 mmol), K_3PO_4 (292 mg, 1.38 mmol), $Pd(PPh_3)_4$ (6 mol%), 2-fluorophenylboronic acid (149 mg, 1.06 mmol) and 1,4-dioxane (5ml/mmol of triflate), **14b** was isolated as colorless crystalline solid, yield 108 mg, (70 %) mp. = 146-148°C; ^{1}H NMR (300 MHz, $CDCl_3$): δ = 6.80 (t, 1H, J = 8.67 Hz, ArH), 6.93-7.00 (m, 2H, ArH), 7.04-7.12 (m, 3H, ArH), 7.17-7.23 (m, 3H, ArH), 7.34-7.42 (m, 3H, ArH), 7.46-7.50 (m, 2H, ArH), 7.67 (d, 2H, J = 8.25 Hz, ArH). ^{13}C NMR (75.47 MHz, $CDCl_3$): δ = 115.5 (d, $^2J_{C,F}$ = 22.3 Hz, CH_{Ar}), 116.3 (d, $^2J_{C,F}$ = 22.6 Hz, CH_{Ar}), 124.2 (d, $^4J_{C,F}$ = 3.6 Hz, CH_{Ar}), 124.5 (d, $^4J_{C,F}$ = 3.6 Hz, CH_{Ar}), 127.5 (CH_{Ar}), 128.7 (d, $^4J_{C,F}$ = 3.1 Hz, CH_{Ar}), 129.2 (CH_{Ar}), 129.5 (d, $^3J_{C,F}$ = 8.1 Hz, CH_{Ar}), 129.7 (d, $^3J_{C,F}$ = 8.3 Hz, CH_{Ar}), 130.1, 130.6, 131.2 (CH_{Ar}), 131.4 (d, $^4J_{C,F}$ = 3.2 Hz, CH_{Ar}), 135.3, 136.3, 139.1, 140.1, 157.4, 158.1, 160.7, 161.4 (C_{Ar}), 197.0 (C=O). ^{19}F NMR (282 MHz, CDCl3): δ = -117.3, -115.6 (2CF). IR (KBr): $\tilde{\nu}$ = 3310, 3039, 2954, 2852, 1728 (w), 1665 (s), 1606, 1593, 1567, 1447, 1404, 1313, 1280, 1260, 1201, 1187, 1156, 1103, 1079, 1036, 975, 963, 945, 883, 844, 790 (m), 728, 719 (s), 694, 638, 614, 559 (w) cm^{-1}; GC-MS (EI, 70 eV): *m/z* (%): 370 (M^+, 100), 351 (26), 199 (72), 170 (48), 151 (10); HRMS (EI) calcd for $C_{25}H_{16}OF_2$ [M^+]: 370.11637, found 370.115915.



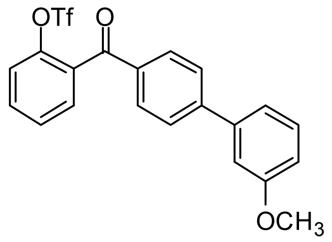
(4'-Methoxybiphenyl-2-yl)(3'-methoxybiphenyl-4-yl)methanone (14c): Starting with **13** (200 mg, 0.41 mmol), K_3PO_4 (292 mg, 1.38 mmol), $Pd(PPh_3)_4$ (6 mol%), 4-methoxyphenylboronic acid (162 mg, 1.06 mmol) and 1,4-dioxane (5ml/mmol of triflate), **14c** was isolated as a yellow solid, yield 112 mg, (68 %) mp. = 138-140°C; ^{1}H NMR (300 MHz, $CDCl_3$): δ = 3.61, 3.78 (s, 6H, $2OCH_3$), 6.61-6.64 (m, 2H, ArH), 6.75-6.86 (m, 3H, ArH), 6.99-7.07 (m, 2H, ArH), 7.26 (t, 1H, J = 7.95 Hz, ArH), 7.39-7.51 (m, 6H, ArH), 7.63-7.66 (m, 2H, ArH). ^{13}C NMR (75.47 MHz, $CDCl_3$): δ = 55.1, 55.3 ($2OCH_3$), 113.0, 113.4, 114.4, 119.7, 121.5, 126.8, 127.1, 128.5, 129.9, 130.4 (CH_{Ar}), 136.1, 139.2, 140.6, 141.4, 141.8, 145.6, 159.8, 160.3 (C_{Ar}), 198.3 (C=O). IR (KBr): $\tilde{\nu}$ = 3033, 2965, 2839 (w), 1671, 1594, 1526, 1480, 1442, 1399, 1297, 1267 (m), 1248, 1226, 1189, 1133, 1090, 1030 (m), 1010, 936, 876, 824, 768 (s), 743, 717, 690, 627, 616, 542 (m) cm^{-1}; GC-MS (EI, 70 eV): *m/z* (%): 394 (M^+, 100), 363 (15), 281 (04), 211 (47), 168 (23), 139 (19), 44 (05); HRMS (EI) calcd for $C_{27}H_{22}O_3$ [M^+]: 394.15689, found 394.46178.



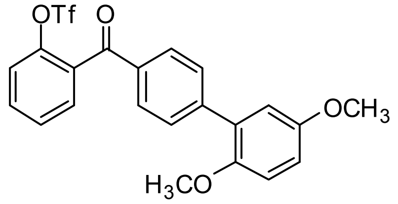
(4'-Vinylbiphenyl-2-yl)(4'-vinylbiphenyl-4-yl)methanone (14d): Starting with **13** (200 mg, 0.41 mmol), K_3PO_4 (292 mg, 1.38 mmol), $Pd(PPh_3)_4$ (6 mol%), 4-vinylphenylboronic acid (157 mg, 1.06 mmol) and 1,4-dioxane (5ml/mmol of triflate), **14d** was isolated as a colorless oil, yield 107 mg, (66 %); ^{1}H NMR (300 MHz, $CDCl_3$): δ = 5.01-5.11 (dd, 1H, J = 1.7, 10.8 Hz, CH_{2vinyl}), 5.19-5.24 (dd, 1H, J = 1.7, 11.2 Hz, CH_{2vinyl}), 5.54-5.61 (dd, 1H, J = 1.7, 17.5 Hz, CH_{2vinyl}), 5.68-5.74 (dd, 1H, J = 1.6, 17.5 Hz, CH_{2vinyl}), 6.47-6.57 (dd, 1H, J = 10.8, 17.5 Hz, CH_{vinyl}), 6.62-6.72 (dd, 1H, J = 10.8, 17.5 Hz, CH_{vinyl}), 7.18 (m, 4H, ArH), 7.31-7.38 (m, 4H, ArH), 7.40-7.48 (m, 4H, ArH), 7.54 (s, 1H, ArH), 7.66 (d, 2H, J = 8.5 Hz, ArH); ^{13}C NMR (75.47 MHz, $CDCl_3$): δ = 114.2, 114.8 ($2CH_{2vinyl}$), 125.3, 125.7, 126.3, 126.6, 126.9, 127.2, 128.6, 129.2, 129.7, 130.0, 130.3, 130.7 (CH_{Ar}), 136.1 (C_{Ar}), 136.3, 136.5 (CH_{Ar}), 136.8, 138.3, 138.9, 139.7, 140.2, 140.7, 146.4 (C_{Ar}), 198.2 (C=O). IR (KBr): $\tilde{\nu}$ = 3043, 3029, 2952, 2847, 1721 (w), 1657, 1597 (s), 1579, 1513, 1475, 1447, 1403, 1317 (m), 1266, 1253, 1235 (s), 1187, 1153, 1041, 987 (m), 925 (s), 861, 803, 783, 708, 665, 627, 543 (m) cm^{-1}; GC-MS (EI, 70 eV): *m/z* (%): 386 (M^+, 100), 369 (8), 281 (07), 253 (04), 207 (56), 193 (08), 178 (51), 152 (16); HRMS (EI) calcd for $C_{29}H_{22}O$ [M^+]: 386.16652, found 386.166535.

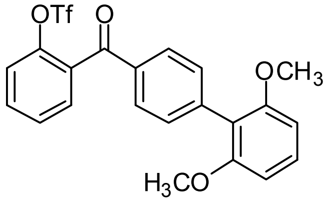


2-(3'-Methoxybiphenylcarbonyl)phenyl trifluoromethanesulfonate (15a): Starting with **13** (200 mg, 0.41 mmol), K_3PO_4 (146 mg, 0.69 mmol), Pd $(PPh_3)_4$ (3 mol%), 3-methoxyphenylboronic acid (80 mg, 0.53 mmol) and 1,4-dioxane (5ml/mmol of triflate), **15a** was isolated as a colorless oil, yield 124 mg, (68 %); ^{1}H NMR (300 MHz, $CDCl_3$): δ = 3.77 (s, 3H, OCH_3), 6.86 (dd, 1H, J = 1.8, 8.10 Hz, ArH), 7.07-7.14 (m, 2H, ArH), 7.27-7.38 (m, 2H, ArH), 7.43 (d, 1H, J = 7.11 Hz, ArH), 7.50-7.54 (m, 3H, ArH), 7.61 (d, 1H, J = 8.31 Hz, ArH), 7.80 (d, 2H, J = 8.28 Hz, ArH). ^{13}C NMR (62.90 MHz, $CDCl_3$): δ = 55.3 (OCH_3), 113.1, 113.7, 119.8 (CH_{Ar}), 121.0 (q, $J_{F,C}$ = 320 Hz, CF_3), 122.5, 127.2, 128.0, 130.0, 130.7, 131.1, 132.6 (CH_{Ar}), 135.2, 141.1, 146.3, 146.7, 147.2, 160.0 (C_{Ar}), 198.2 (C=O). ^{19}F NMR (282 MHz, CDCl3): δ = -73.3 (CF_3). IR (KBr): $\tilde{\nu}$ = 3066, 2921, 1727 (w), 1665 (m), 1599 (s), 1479 (m), 1421 (s), 1400, 1309, 1293, 1274, 1247 (m), 1205, 1135 (s), 1086, 1051, 1028, 1013 (m), 936, 879, 845, 765 (s), 748, 691, 618, 568 (m) cm^{-1}; GC-MS (EI, 70 eV): *m/z* (%): 436 (M^+, 100), 303 (40), 287 (08), 260 (18), 231 (07), 211 (22), 168 (06), 139 (13), 69 (04); HRMS (EI) calcd for $C_{21}H_{15}O_5F_3S$ [M^+]: 436.05868 found 436.058091.

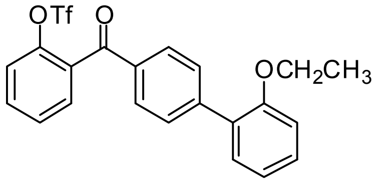


2-(2',5'-Dimethoxybiphenylcarbonyl)phenyl trifluoromethanesulfonate (15b): Starting with **13** (200 mg, 0.41 mmol), K_3PO_4 (146 mg, 0.69 mmol), Pd $(PPh_3)_4$ (3 mol%), 2,5-dimethoxyphenylboronic acid (96 mg, 0.53 mmol) and 1,4-dioxane (5ml/mmol of triflate), **15b** was isolated as a reddish solid, yield 140 mg, (72 %) mp. = 138-140°C; ^{1}H NMR (300 MHz, $CDCl_3$): δ = 3.66 (s, 6H, $2OCH_3$), 6.60 (d, 2H, J = 8.4 Hz, ArH), 7.17-7.26 (m, 2H, ArH), 7.35-7.43 (m, 3H, ArH), 7.52-7.58 (m, 2H, ArH), 7.77 (d, 2H, J = 8.37 Hz, ArH). ^{13}C NMR (75.47 MHz, $CDCl_3$): δ = 55.9 ($2OCH_3$), 104.2 (CH_{Ar}), 118.2 (C_{Ar}), 120.6 (q, $J_{F,C}$ = 320 Hz, CF_3), 122.4, 127.8, 129.5, 129.6, 130.0, 131.3, 131.4, 132.3 (CH_{Ar}), 132.7, 133.0, 134.5, 140.6, 146.9, 157.5 (C_{Ar}), 192.3 (C=O). ^{19}F NMR (282 MHz, CDCl3): δ = -74.6 (CF_3). IR (KBr): $\tilde{\nu}$ = 3068, 3002, 2839, 1726 (w), 1665, 1603, 1588 (m), 1471 (s), 1402, 1294, 1272 (m), 1204, 1135, 1103, 1087 (s), 1036, 935 (m), 878, 782, 725 (s), 693, 620, 569 (m) cm^{-1}; GC-MS (EI, 70 eV): *m/z* (%): 466 (M^+, 100), 317 (25), 287 (15), 241 (12), 198 (05), 155 (04), 69 (04); HRMS (EI) calcd for $C_{22}H_{17}O_6F_3S$ [M^+]: 466.06925 found 466.068723.

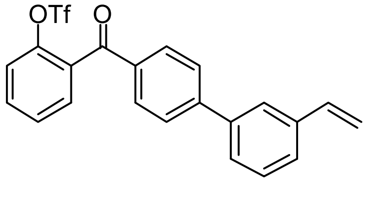




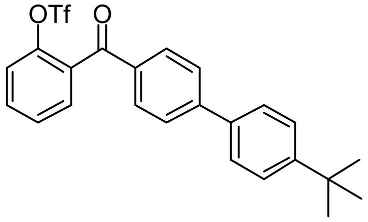
2-(2',6'-Dimethoxybiphenylcarbonyl)phenyl trifluoromethanesulfonate (15c): Starting with **13** (200 mg, 0.41 mmol), K_3PO_4 (146 mg, 0.69 mmol), Pd $(PPh_3)_4$ (3 mol%), 2,6-dimethoxyphenylboronic acid (96 mg, 0.53 mmol) and 1,4-dioxane (5ml/mmol of triflate), **15c** was isolated as a clolorless solid, yield 124 mg, (64 %) mp. = 162-164°C; ^{1}H NMR (300 MHz, $CDCl_3$): δ = 3.65 (s, 6H, $2OCH_3$), 6.57 (d, 2H, J = 8.4 Hz, ArH), 7.21 (t, 1H, J = 8.37 Hz, ArH), 7.33-7.41 (m, 4H, ArH), 7.50-7.56 (m, 2H, ArH), 7.75 (d, 2H, J = 8.37 Hz, ArH). ^{13}C NMR (62.90 MHz, $CDCl_3$): δ = 55.8 ($2OCH_3$), 104.2 (CH_{Ar}), 118.2 (C_{Ar}), 120.6 (q, $J_{F,C}$ = 320 Hz, CF_3), 122.4, 127.8, 129.5, 129.6, 131.3, 131.4, 132.3 (CH_{Ar}), 132.6, 134.5, 140.6, 146.9, 157.4 (C_{Ar}), 192.2 (C=O). ^{19}F NMR (282 MHz, CDCl3): δ = -73.5 (CF_3). IR (KBr): $\tilde{\nu}$= 3065, 3004, 2841, 1721 (w), 1667, 1605, 1587 (m), 1473 (s), 1403, 1295, 1273 (m), 1205, 1137, 1105, 1081 (s), 1033, 931 (m), 877, 781, 722 (s), 693, 620, 569 (m) cm^{-1}; GC-MS (EI, 70 eV): *m/z* (%): 466 (M^+, 100), 317 (23), 287 (14), 241 (11), 198 (05), 155 (04), 69 (04); HRMS (EI) calcd for $C_{22}H_{17}O_6F_3S$ [M^+]: 466.06925 found 466.069423.



2-(2'-Ethoxybiphenylcarbonyl)phenyl trifluoromethanesulfonate (15d): Starting with **13** (200 mg, 0.41 mmol), K_3PO_4 (146 mg, 0.69 mmol), Pd $(PPh_3)_4$ (3 mol%), 2-ethoxyphenylboronic acid (88 mg, 0.53 mmol) and 1,4-dioxane (5ml/mmol of triflate), **15d** was isolated as a colorless solid, yield 144 mg, (76 %) mp. = 150-152°C; ^{1}H NMR (300 MHz, $CDCl_3$): δ = 1.25 (t, 3H, J = 6.99 Hz, CH_3), 3.97 (q, 2H, J = 6.9 Hz, OCH_2), 6.89-6.98 (m, 2H, ArH), 7.23-7.28 (m, 2H, ArH), 7.34-7.44 (m, 2H, ArH), 7.51-7.61 (m, 4H, ArH), 7.76 (d, 2H, J = 8.52 Hz, ArH). ^{13}C NMR (75.47 MHz, $CDCl_3$): δ = 14.7 (CH_3), 64.1 (OCH_2), 112.6 (CH_{Ar}), 120.6 (q, $J_{F,C}$ = 321.0 Hz, CF_3), 120.9, 122.4, 128.0 (CH_{Ar}), 129.3 (C_{Ar}), 129.6, 129.7, 129.8, 130.7, 131.2, 132.4 (CH_{Ar}), 132.7, 134.6, 144.5, 146.8, 155.9 (C_{Ar}), 192.3 (C=O). ^{19}F NMR (282 MHz, CDCl3): δ = -73.4 (CF_3). IR (KBr): $\tilde{\nu}$= 3068, 3034, 2925, 1722 (w), 1665, 1602 (m), 1581, 1511, 1446 (w), 1422 (s), 1312, 1264 (m), 1204, 1135 (s), 1086, 1039, 935 (m), 879, 750 (s), 693, 668, 646, 590 (m) cm^{-1}; GC-MS (EI, 70 eV): *m/z* (%): 450 (M^+, 100), 422 (28), 289 (30), 215 (08), 197 (21), 168 (13), 121 (17), 92 (04), 69 (05); HRMS (EI) calcd for $C_{22}H_{17}O_5F_3S$ [M^+]: 450.07433 found 450.074381.

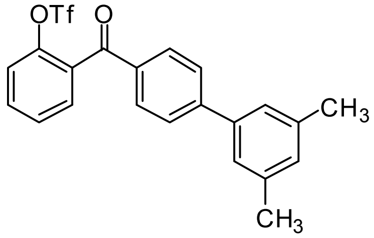


2-(3'-Vinylbiphenylcarbonyl)phenyl trifluoromethanesulfonate (15e): Starting with **13** (200 mg, 0.41 mmol), K_3PO_4 (114 mg, 0.54 mmol), Pd $(PPh_3)_4$ (3 mol%), 3-vinylphenylboronic acid (78 mg, 0.53 mmol) and 1,4-dioxane (5ml/mmol of triflate), **15e** was isolated as yellow oil, yield 127 mg, (70 %); ^{1}H NMR (300 MHz, $CDCl_3$): δ = 5.23 (d, 1H, J = 10.95 Hz, CH_{2vinyl}), 5.74 (d, 1H, J = 17.55 Hz, CH_{2vinyl}), 6.65-6.74 (dd, 1H, J = 10.8, 17.5 Hz, CH_{vinyl}), 7.33-7.38 (m, 3H, ArH), 7.40-7.43 (m, 2H, ArH), 7.50-7.55 (m, 3H, ArH), 7.61 (d, 2H, J = 8.43 Hz, ArH), 7.80 (d, 2H, J = 8.40 Hz, ArH); ^{13}C NMR (75.47 MHz, $CDCl_3$): δ = 114.7 (CH_{2vinyl}), 120.6 (q, $J_{C,F}$ = 322.20 Hz, CF_3), 122.5, 125.3, 126.1, 126.8, 127.2, 128.1, 129.2, 130.8, 131.2, 132.6 (CH_{Ar}), 135.2 (C_{Ar}), 136.5 (CH_{Ar}), 138.3, 139.4, 140.0, 146.4, 146.8 (C_{Ar}), 192.1 (C=O). ^{19}F NMR (282 MHz, CDCl3): δ = -73.3 (CF_3). IR (KBr): $\tilde{\nu}$ = 3085, 3060, 2957, 2854 (w), 1665, 1601 (m), 1579, 1559, 1480 (w), 1421 (s), 1294, 1274, 1246 (w), 1204, 1134 (s), 1087 (m), 1039, 1014, 955 (w), 878, 866, 778, 766 (s), 747, 710, 670, 617, 568, 545 (m) cm^{-1}; GC-MS (EI, 70 eV): *m/z* (%): 432 (M^+, 100), 299 (35), 284 (14), 255 (09), 207 (42), 178 (23), 152 (09), 69 (05); HRMS (EI) calcd for $C_{22}H_{15}O_4F_3S$ [M^+]: 432.06377, found 432.062617.

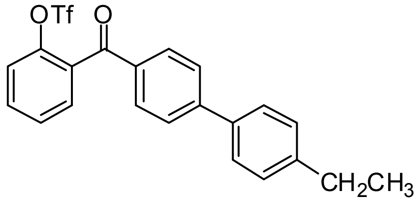


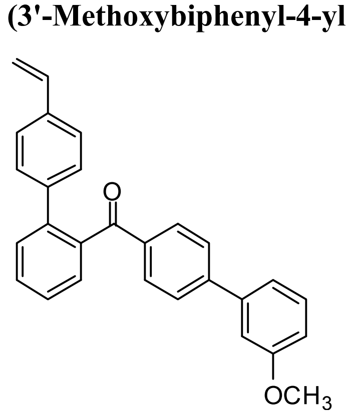
2-(4'-Tert-butylbiphenylcarbonyl)phenyl trifluoromethanesulfonate (15f): Starting with **13** (200 mg, 0.41 mmol), K_3PO_4 (146 mg, 0.69 mmol), Pd $(PPh_3)_4$ (3 mol%), 4-*tert*-butylphenylboronic acid (94 mg, 0.53 mmol) and 1,4-dioxane (5ml/mmol of triflate), **15f** was isolated as a colorless crystalline solid, yield 128 mg, (66 %), mp = 140-142°C; ^{1}H NMR (300 MHz, $CDCl_3$): δ = 1.27 (s, 9H, $3CH_3$), 7.32-7.42 (m, 4H, ArH), 7.48-7.52 (m, 4H, ArH), 7.60 (d, 2H, J = 8.28 Hz, ArH), 7.78 (d, 2H, J = 8.25 Hz, ArH). ^{13}C NMR (75.47 MHz, $CDCl_3$): δ = 31.3 ($3CH_3$), 34.6 (C_{tBu}), 120.0 (q, $J_{F,C}$ = 320 Hz, CF_3), 122.5, 126.0, 127.0, 127.1, 128.0, 130.8, 131.2, 132.5 (CH_{Ar}), 132.6, 134.9, 136.7, 146.4, 146.8, 151.7 (C_{Ar}), 192.1 (C=O). ^{19}F NMR (282 MHz, CDCl3): δ = -73.4 (CF_3). IR (KBr): $\tilde{\nu}$ = 3070, 3030, 2929 (w), 1660, 1600 (m), 1550, 1521, 1495, 1443 (w), 1425 (s), 1393, 1366, 1300 (w), 1278,1269 (m), 1197, 1142 (s), 1112, 1040, 1003, 937, 882, 864 (m), 831, 767, 735 (s), 700, 645, 596, 567 (w) cm^{-1}; GC-MS (EI, 70 eV): *m/z* (%): 462 (M^+, 43), 447 (100), 313 (43), 299 (09), 273 (04), 178 (04), 69 (04); HRMS (EI) calcd for $C_{24}H_{21}F_3O_4S$ [M^+]: 462.11072 found 462.111365.

2-(3',5'-Dimethylbiphenylcarbonyl)phenyl trifluoromethanesulfonate (15g): Starting with **13** (200 mg, 0.41 mmol), K$_3$PO$_4$ (146 mg, 0.69 mmol), Pd (PPh$_3$)$_4$ (3 mol%), 3,5-dimethylphenylboronic acid (79 mg, 0.53 mmol) and 1,4-dioxane (5ml/mmol of triflate), **15g** was isolated as a colorless oil, yield 142 mg, (78 %); ^{1}H NMR (300 MHz, CDCl$_3$): δ= 2.28 (s, 6H, 2CH$_3$), 6.94 (s, 1H, ArH), 7.14 (s, 2H, ArH), 7.35 (dd, 2H, J = 8.25, 19.6 Hz, ArH), 7.47-7.51 (m, 2H, ArH), 7.56 (d, 2H, J = 8.3 Hz, ArH), 7.75 (d, 2H, J = 8.3 Hz, ArH). ^{13}C NMR (75.47 MHz, CDCl$_3$): δ = 21.3 (2CH$_3$), 120.6 (q, $J_{\mathrm{F,C}}$ = 321.0 Hz, CF$_3$), 122.5, 125.2, 127.2, 128.0, 130.1, 130.7, 131.2, 132.6 (CH$_{\mathrm{Ar}}$), 133.0, 135.0, 138.5, 139.6, 146.8, 146.9, (C$_{\mathrm{Ar}}$), 192.2 (C=O). ^{19}F NMR (282 MHz, CDCl3): δ = -73.4 (CF$_3$). IR (KBr): $\tilde{\nu}$= 3032, 2850, 2850, 1725 (w), 1665, 1600 (m), 1560, 1480 (w), 1422 (s), 1294, 1246 (m), 1203, 1135 (s), 1084, 1038, 1016 (m), 936 (m), 879, 850, 779 (s), 742, 639, 618, 568 (w) cm^{-1}; GC-MS (EI, 70 eV): *m/z* (%): 434 (M$^+$, 100), 301 (57), 285 (06), 258 (07), 209 (30), 165 (19), 69 (05); HRMS (EI) calcd for C$_{22}$H$_{17}$O$_4$F$_3$S [M$^+$]: 434.07942 found 434.079488.

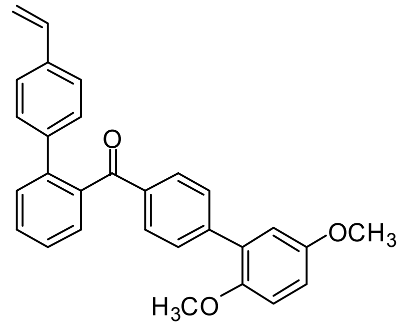


2-(4'-Ethylbiphenylcarbonyl)phenyl trifluoromethanesulfonate (15h): Starting with **13** (200 mg, 0.41 mmol), K$_3$PO$_4$ (146 mg, 0.69 mmol), Pd (PPh$_3$)$_4$ (3 mol%), 4-ethylphenylboronic acid (79 mg, 0.53 mmol) and 1,4-dioxane (5ml/mmol of triflate), **15h** was isolated as a colorless crystalline solid, yield 134 mg, (74 %) mp. = 170-172°C; ^{1}H NMR (300 MHz, CDCl$_3$): δ= 1.17 (t, 3H, J = 7.5 Hz, CH$_{3\,ethyl}$), 2.59 (q, 2H, J = 7.5 Hz, CH$_{2\,ethyl}$), 7.19 (d, 2H, J = 8.1 Hz, ArH), 7.35 (dd, 2H, J = 8.2, 18.5 Hz, ArH), 7.44-7.51 (m, 4H, ArH), 7.57 (d, 2H, J = 8.4 Hz, ArH), 7.77 (d, 2H, J = 8.4 Hz, ArH). ^{13}C NMR (75.47 MHz, CDCl$_3$): δ = 14.4 (CH$_3$), 28.6 (CH$_2$), 120.6 (q, $J_{\mathrm{F,C}}$ = 321.0 Hz, CF$_3$), 122.5, 127.0, 127.2, 128.0, 128.5, 130.8, 131.2, 132.6 (CH$_{\mathrm{Ar}}$), 133.0, 134.8, 137.0, 144.8, 146.5, 146.8 (C$_{\mathrm{Ar}}$), 192.1 (C=O). ^{19}F NMR (282 MHz, CDCl3): δ = -73.4 (CF$_3$). IR (KBr): $\tilde{\nu}$= 3065, 3031, 2923, 1721 (w), 1663, 1605 (m), 1583, 1511, 1443 (w), 1421 (s), 1312, 1264 (m), 1203, 1137 (s), 1083, 1037, 931 (m), 877, 751 (s), 691, 667, 645, 591 (m) cm^{-1}; GC-MS (EI, 70 eV): *m/z* (%): 434 (M$^+$, 100), 419 (08), 301 (41), 273 (17), 209 (21), 165 (13), 69 (05); HRMS (EI) calcd for C$_{22}$H$_{17}$O$_4$F$_3$S [M$^+$]: 434.07942 found 434.079081.



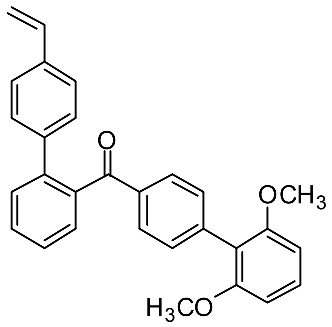


(3'-Methoxybiphenyl-4-yl)(4'-vinylbiphenyl-2-yl)methanone (16a): Starting with **15a** (100 mg, 0.23 mmol), K_3PO_4 (63 mg, 0.30 mmol), Pd $(PPh_3)_4$ (3 mol%), 4-vinylphenylboronic acid (44 mg, 0.30 mmol) and 1,4-dioxane (5ml/mmol of triflate), **16a** was isolated as yellow oil; yield 63 mg, (70 %); ^{1}H NMR (300 MHz, $CDCl_3$): δ = 3.76 (s, 3H, OCH_3), 5.08-5.12 (dd, 1H, *J* = 1.7, 10.8 Hz, CH_2), 5.55-5.61 (dd, 1H, *J* = 1.2, 17.6 Hz, CH_2), 6.48-6.57 (dd, 1H, *J* = 10.8, 17.6 Hz, CH), 6.81-6.85 (m, 1H, ArH), 6.99 (t, 1H, *J* = 1.7 Hz, ArH), 7.03-7.07 (m, 1H, ArH), 7.18 (s, 4H, ArH), 7.24 (t, 1H, *J* = 7.9 Hz, ArH), 7.40-7.47 (m, 6H, ArH), 7.66 (d, 2H, *J* = 8.4 Hz, ArH); ^{13}C NMR (75.47 MHz, $CDCl_3$): δ = 55.3 (OCH_3), 113.0, 113.5 (CH_{Ar}), 114.0 (CH_2), 119.7, 126.2, 126.9, 127.0, 128.7, 129.1, 129.9, 130.0, 130.3, 130.5 (CH_{Ar}), 136.2 (C_{Ar}), 136.3 (CH_{Ar}), 136.6, 138.9, 139.6, 140.7, 141.3, 145.4, 160.0 (C_{Ar}), 198.1 (C=O). IR (KBr): $\tilde{\nu}$ = 3054, 3001, 2953, 2851, 1725 (w), 1660, 1582, 1512, 1477, 1464, 1398, 1308 (m), 1212, 1170, 1116, 1050, 1012, 1003, 992 (m), 927, 842, 767, 743, 690 (s), 667, 641, 568 (m) cm^{-1}; GC-MS (EI, 70 eV): *m/z* (%): 390 (M^+, 100), 373 (09), 283 (04), 211 (42), 178 (24), 152 (13), 101 (05); HRMS (EI) calcd for $C_{28}H_{22}O_2$ [M^+]: 390.16143, found 390.161279.

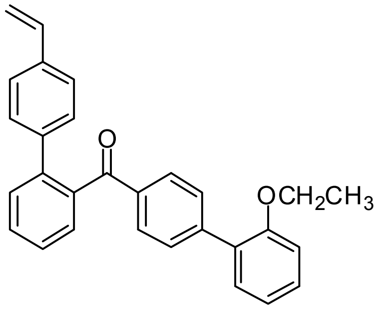


(2',5'-Dimethoxybiphenyl-4-yl)(4'-vinylbiphenyl-2-yl)methanone (16b): Starting with **15b** (100 mg, 0.21 mmol), K_3PO_4 (57 mg, 0.27 mmol), Pd $(PPh_3)_4$ (3 mol%), 4-vinylphenylboronic acid (40 mg, 0.27 mmol) and 1,4-dioxane (5ml/mmol of triflate), **16b** was isolated as colorless oil; yield 65 mg, (72 %); ^{1}H NMR (300 MHz, $CDCl_3$): δ = 3.61 (s, 6H, $2OCH_3$), 5.12 (d, 1H, *J* = 11.3 Hz, CH_2), 5.58-5.64 (dd, 1H, *J* = 1.4, 17.6 Hz, CH_2), 6.56 (d, 1H, *J* = 8.4 Hz, CH), 7.17 (s, 1H, ArH), 7.22 (s, 4H, ArH), 7.24-7.27 (m, 3H, ArH), 7.34-7.48 (m, 5H, ArH), 7.68 (d, 2H, *J* = 8.3 Hz, ArH); ^{13}C NMR (75.47 MHz, $CDCl_3$): δ = 55.9 ($2OCH_3$), 104.2, 104.4 (CH_{Ar}), 113.8 (CH_2), 118.5 (C_{Ar}), 126.1, 126.8, 128.8, 128.9, 129.2, 129.3, 129.4, 130.1, 130.6, 130.9 (CH_{Ar}), 135.5 (C_{Ar}), 136.4 (CH_{Ar}), 136.6, 139.0, 139.5, 139.8, 141.0, 157.5 (C_{Ar}), 198.1 (C=O). IR (KBr): $\tilde{\nu}$ = 3056, 3002, 2954, 2851, 1724 (w), 1661, 1601, 1587, 1514, 1441, 1432, 1401, 1330, 1277 (m), 1244 (s), 1183, 1171, 1033, 1001, 953, 879, 798, 768, 755, 693, 638, 611, 572 (m) cm^{-1}; GC-MS (EI, 70 eV): *m/z* (%): 420 (M^+, 100), 403 (07), 241 (40), 198 (10), 178 (23), 152 (07), 127 (05); HRMS (EI) calcd for $C_{29}H_{24}O_3$ [M^+]: 420.17200, found 420.171846.

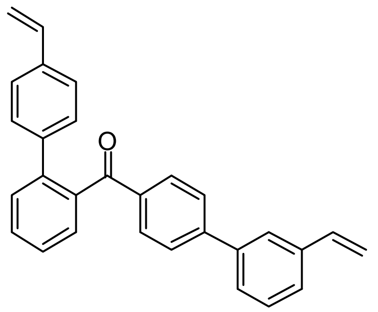
(2',6'-Dimethoxybiphenyl-4-yl)(4'-vinylbiphenyl-2-yl)methanone (16c): Starting with **15c** (100 mg, 0.21 mmol), K_3PO_4 (57 mg, 0.27 mmol), Pd $(PPh_3)_4$ (3 mol%), 4-vinylphenylboronic acid (40 mg, 0.27 mmol) and 1,4-dioxane (5ml/mmol of triflate), **16c** was isolated as yellow oil; yield 62 mg, (68 %); ^{1}H NMR (300 MHz, $CDCl_3$): δ = 3.59 (s, 6H, $2OCH_3$), 5.08-5.12 (dd, 1H, J = 1.7, 10.8 Hz, CH_2), 5.57-5.63 (dd, 1H, J = 1.8, 17.6 Hz, CH_2), 6.54 (d, 1H, J = 8.4 Hz, CH), 7.14-7.21 (m, 6H, ArH), 7.24 (d, 2H, J = 8.4 Hz, ArH), 7.33-7.36 (m, 1H, ArH), 7.41-7.46 (m, 4H, ArH), 7.66 (d, 2H, J = 8.4 Hz, ArH); ^{13}C NMR (62.90 MHz, $CDCl_3$): δ = 55.9 ($2OCH_3$), 104.4 (CH_{Ar}), 113.8 (CH_2), 118.5 (C_{Ar}), 126.1, 126.7, 128.9, 129.2, 129.3, 129.4, 130.1, 130.6, 130.9 (CH_{Ar}), 135.5 (C_{Ar}), 136.4 (CH_{Ar}), 136.5, 139.0, 139.5, 139.8, 141.0, 157.5 (C_{Ar}), 198.1 (C=O). IR (KBr): $\tilde{\nu}$ = 3054, 3029, 2951, 2857, 1726 (w), 1667, 1623, 1593, 1517, 1443, 1435, 1403, 1332, 1279 (m), 1245 (s), 1187, 1173, 1035, 1003, 957, 881, 783, 761, 757, 689, 632, 609, 571 (m) cm^{-1}; GC-MS (EI, 70 eV): *m/z* (%): 420 (M^+, 100), 403 (08), 241 (35), 198 (09), 178 (23), 152 (07), 127 (05); HRMS (EI) calcd for $C_{29}H_{24}O_3$ [M^+]: 420.17200, found 420.171372.



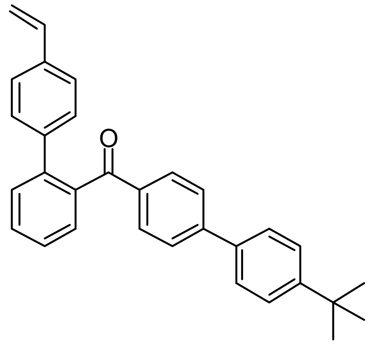
(2'-Ethoxybiphenyl-4-yl)(4'-vinylbiphenyl-2-yl)methanone (16d): Starting with **15d** (100 mg, 0.22 mmol), K_3PO_4 (61 mg, 0.29 mmol), Pd $(PPh_3)_4$ (3 mol%), 4-vinylphenylboronic acid (42 mg, 0.29 mmol) and 1,4-dioxane (5ml/mmol of triflate), **16d** was isolated as pink oil; yield 56 mg, (62 %); ^{1}H NMR (300 MHz, $CDCl_3$): δ = 1.21 (t, 3H, J = 6.9 Hz, CH_3), 3.92 (q, 2H, J = 6.9 Hz, OCH_2), 5.09-5.13 (dd, 1H, J = 1.7, 10.8 Hz, CH_2), 5.56-5.62 (dd, 1H, J = 1.8, 17.6 Hz, CH_2), 6.49-6.59 (dd, 1H, J = 10.8, 17.6 Hz, CH), 6.86-6.59 (m, 2H, ArH), 7.15-7.21 (m, 6H, ArH), 7.40-7.46 (m, 6H, ArH), 7.65 (d, 2H, J = 8.5 Hz, ArH); ^{13}C NMR (75.47 MHz, $CDCl_3$): δ = 14.7 (CH_3), 64.1 (OCH_2), 112.8 (CH_{Ar}), 113.9 (CH_2), 118.5 (C_{Ar}), 120.9, 126.1, 126.9, 128.8, 129.1, 129.3, 129.4, 129.7, 130.0, 130.2, 130.7 (CH_{Ar}), 135.5 (C_{Ar}), 136.3 (CH_{Ar}), 136.5, 139.1, 139.7, 140.8, 143.5, 155.8 (C_{Ar}), 198.3 (C=O). IR (KBr): $\tilde{\nu}$ = 3056, 3031, 2954, 2850, 1724 (w), 1661, 1599 (s), 1580, 1511, 1473, 1446, 1401, 1311 (m), 1277, 1260, 1237 (s), 1185, 1150, 1039, 988 (m), 927 (s), 860, 803, 785, 708, 666, 628, 541 (m) cm^{-1}; GC-MS (EI, 70 eV): *m/z* (%): 404 (M^+, 100), 375 (18), 357 (10), 225 (23), 197 (14), 178 (44), 168 (13), 139 (12), 115 (06); HRMS (EI) calcd for $C_{29}H_{24}O_2$ [M^+]: 404.17708, found 404.176499.



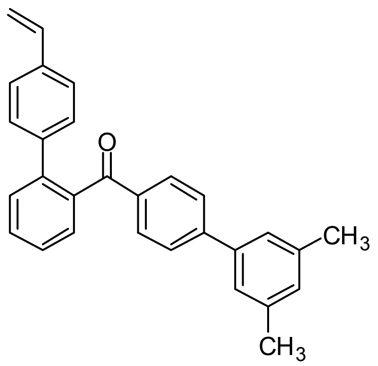
(4'-Vinylbiphenyl-2-yl)(3'-vinylbiphenyl-4-yl)methanone (16e): Starting with **15e** (100 mg, 0.23 mmol), K_3PO_4 (61 mg, 0.30 mmol), Pd $(PPh_3)_4$ (3 mol%), 4-vinylphenylboronic acid (44 mg, 0.30 mmol) and 1,4-dioxane (5ml/mmol of triflate), **16e** was isolated as colorless oil; yield 59 mg, (66 %); ^{1}H NMR (300 MHz, $CDCl_3$): δ = 5.01-5.11 (dd, 1H, J = 1.7, 10.8 Hz, $CH_{2\mathit{vinyl}}$), 5.19-5.24 (dd, 1H, J = 1.7, 11.2 Hz, $CH_{2\mathit{vinyl}}$), 5.54-5.61 (dd, 1H, J = 1.7, 17.5 Hz, $CH_{2\mathit{vinyl}}$), 5.68-5.74 (dd, 1H, J = 1.6, 17.5 Hz, $CH_{2\mathit{vinyl}}$), 6.47-6.57 (dd, 1H, J = 10.8, 17.5 Hz, CH_{vinyl}), 6.62-6.72 (dd, 1H, J = 10.8, 17.5 Hz, CH_{vinyl}), 7.18 (s, 4H, ArH), 7.31-7.38 (m, 4H, ArH), 7.40-7.48 (m, 5H, ArH), 7.66 (d, 2H, J = 8.5 Hz, ArH); ^{13}C NMR (75.47 MHz, $CDCl_3$): δ = 114.0, 114.6 ($2CH_{2\mathit{vinyl}}$), 125.2, 125.9, 126.2, 126.7, 126.9, 127.0, 128.7, 129.0, 129.1, 130.0, 130.3, 130.5 (CH_{Ar}), 136.1 (C_{Ar}), 136.3, 136.5 (CH_{Ar}), 136.6, 138.2, 138.9, 139.6, 140.2, 140.7, 145.4 (C_{Ar}), 198.2 (C=O). IR (KBr): $\tilde{\nu}$ = 3043, 3029, 2952, 2847, 1721 (w), 1657, 1597 (s), 1579, 1513, 1475, 1447, 1403, 1317 (m), 1266, 1253, 1235 (s), 1187, 1153, 1041, 987 (m), 925 (s), 861, 803, 783, 708, 665, 627, 543 (m) cm^{-1}; GC-MS (EI, 70 eV): *m/z* (%): 386 (M$^+$, 100), 359 (10), 281 (04), 207 (50), 193 (07), 178 (53), 152 (16); HRMS (EI) calcd for $C_{29}H_{22}O$ [M$^+$]: 386.16652, found 386.165803.



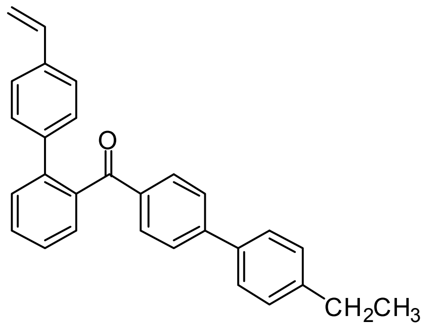
(4'-Tert-butylbiphenyl-4-yl)(4'-vinylbiphenyl-2-yl)methanone (16f): Starting with **15f** (100 mg, 0.21 mmol), K_3PO_4 (59 mg, 0.28 mmol), Pd $(PPh_3)_4$ (3 mol%), 4-vinylphenylboronic acid (41 mg, 0.28 mmol) and 1,4-dioxane (5ml/mmol of triflate), **16f** was isolated as yellow oil; yield 58 mg, (64 %); ^{1}H NMR (300 MHz, $CDCl_3$): δ = 1.26 (s, 9H, $3CH_3$), 5.07-5.11 (dd, 1H, J = 1.8, 10.8 Hz, CH_2), 5.54-5.60 (dd, 1H, J = 1.8, 17.5 Hz, CH_2), 6.47-6.57 (dd, 1H, J = 10.8, 17.6 Hz, CH), 7.17 (s, 4H, ArH), 7.35-7.39 (m, 4H, ArH), 7.42-7.49 (m, 6H, ArH), 7.66 (d, 2H, J = 10.2 Hz, ArH). ^{13}C NMR (62.90 MHz, $CDCl_3$): δ = 31.2 ($3CH_3$), 34.6 (C), 125.8, 126.2, 126.6, 126.9, 127.0, 128.6, 129.1, 130.0, 130.2, 130.5 (CH_{Ar}), 135.8 (C_{Ar}), 136.3 (CH_{Ar}), 136.5, 136.9, 139.0, 139.6, 140.7, 145.3, 151.4 (C_{Ar}), 198.2 (C=O). IR (KBr): $\tilde{\nu}$ = 3055, 3030, 2956 (w), 1724, 1661, 1600 (m), 1573, 1514, 1476, 1440, 1392, 1311 (w), 1276 (s), 1242, 1183, 1150, 1112, 1070, 1018, 987, 951 (w), 927 (s), 907, 861, 842, 781 (m), 756, 722 (s), 696, 649, 570 (w) cm^{-1}; GC-MS (EI, 70 eV): *m/z* (%): 416 (M$^+$, 100), 401 (92), 383 (05), 281 (05), 237 (10), 207 (20), 178 (37), 152 (09), 41 (05); HRMS (EI) calcd for $C_{31}H_{28}O$ [M$^+$]: 416.21347, found 416.212861.



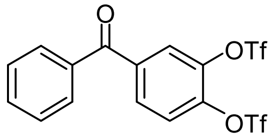
(3',5'-Dimethylbiphenyl-4-yl)(4'-vinylbiphenyl-2-yl)methanone (16g): Starting with **15g** (100 mg, 0.23 mmol), K_3PO_4 (63 mg, 0.30 mmol), Pd $(PPh_3)_4$ (3 mol%), 4-vinylphenylboronic acid (44 mg, 0.30 mmol) and 1,4-dioxane (5ml/mmol of triflate), **16g** was isolated as colorless viscous oil; yield 68 mg, (76 %); ^{1}H NMR (250 MHz, $CDCl_3$): δ = 2.28 (s, 6H, $2CH_3$), 5.10 (d, 1H, J = 11.5 Hz, CH_2), 5.54-5.62 (dd, 1H, J = 1.6, 17.6 Hz, CH_2), 6.47-6.58 (dd, 1H, J = 10.8, 17.6 Hz, CH), 6.93 (s, 1H, ArH), 7.08 (s, 2H, ArH), 7.18 (s, 4H, ArH), 7.36-7.48 (m, 6H, ArH), 7.64 (d, 2H, J = 8.4 Hz, ArH). ^{13}C NMR (62.90 MHz, $CDCl_3$): δ = 21.3 ($2CH_3$), 113.9 (CH_{2vinyl}), 125.1, 126.2, 126.8, 127.0, 128.6, 129.1, 129.8, 130.0, 130.2, 130.4 (CH_{Ar}), 135.8 (C_{Ar}), 136.3 (CH_{Ar}), 136.5, 138.4, 139.0, 139.6, 139.8, 140.7, 145.8 (C_{Ar}), 198.2 (C=O). IR (KBr): $\tilde{\nu}$ = 3019, 2916, 1724 (w), 1661 (m), 1598 (s), 1556, 1475, 1440, 1397, 1313 (m), 1277 (s), 1209, 1184, 1150, 1117, 1071, 1033, 1002, 987 (m), 928 (s), 907, 781, 768, 695, 646, 581 (m) cm^{-1}; GC-MS (EI, 70 eV): *m/z* (%): 388 (M^+, 100), 371 (10), 209 (28), 194 (05), 178 (21), 165 (22), 152 (06); HRMS (EI) calcd for $C_{29}H_{24}O$ [M^+]: 388.18217, found 388.182014.



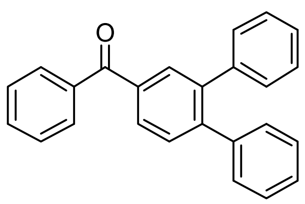
(4'-Ethylbiphenyl-4-yl)(4'-vinylbiphenyl-2-yl)methanone (16h): Starting with **15h** (100 mg, 0.23 mmol), K_3PO_4 (63 mg, 0.30 mmol), Pd $(PPh_3)_4$ (3 mol%), 4-vinylphenylboronic acid (44 mg, 0.30 mmol) and 1,4-dioxane (5ml/mmol of triflate), **16h** was isolated as colorless oil; yield 66 mg, (74 %); ^{1}H NMR (250 MHz, $CDCl_3$): δ = 1.16 (t, 3H, J = 7.6 Hz, CH_3), 2.58 (q, 2H, J = 7.6 Hz, CH_2CH_3), 5.06 (d, 1H, J = 11.5 Hz, CH_2), 5.52-5.60 (dd, 1H, J = 1.7, 17.6 Hz, CH_2), 6.45-6.56 (dd, 1H, J = 10.8, 17.5 Hz, CH), 7.17 (s, 4H, ArH), 7.32 (d, 2H, J = 6.2 Hz, ArH), 7.37 (d, 2H, J = 6.8 Hz, ArH), 7.39-7.49 (m, 6H, ArH), 7.64 (d, 2H, J = 8.4 Hz, ArH). ^{13}C NMR (62.90 MHz, $CDCl_3$): δ = 15.5 (CH_3), 28.5 (CH_{2Ethyl}), 114.0 (CH_{2vinyl}), 126.2, 126.6, 127.0, 127.1, 128.4, 128.6, 129.1, 130.0, 130.2, 130.5 (CH_{Ar}), 135.8 (C_{Ar}), 136.3 (CH_{Ar}), 136.5, 137.1, 139.0, 139.6, 140.7, 144.5, 145.5 (C_{Ar}), 198.1 (C=O). IR (KBr): $\tilde{\nu}$ = 3053, 2926, 1725 (w), 1660, 1598 (s), 1574, 1523, 1514, 1476, 1440, 1399, 1310 (m), 1277 (s), 1189, 1118, 1060, 1032, 1003, 987 (m), 928 (s), 908, 842, 780 (m), 735 (s), 700, 654, 539 (m) cm^{-1}; GC-MS (EI, 70 eV): *m/z* (%): 388 (M^+, 100), 371 (09), 209 (28), 178 (20), 152 (17); HRMS (EI) calcd for $C_{29}H_{24}O$ [M^+]: 388.18217, found 388.182058.



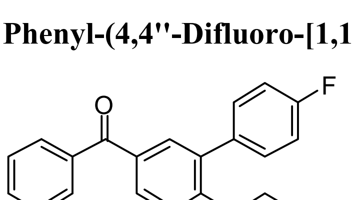
4-Benzoyl-1,2-phenylene bis(trifluoromethanesulfonate) (18): Starting with **17** (168 mg, 1.0 mmol), pyridine (0.32 ml, 4.0 mmol) and Tf_2O (0.39 ml, 2.4 mmol), **18** was isolated as a colorless oil, yield, (318 mg, 84 %); ^{1}H NMR (300 MHz, $CDCl_3$): δ = 7.44-7.60 (m, 5H, ArH), 7.68-7.72 (m, 2H, ArH), 7.86 (s, 1H, ArH); ^{13}C NMR (62.89 MHz, $CDCl_3$): δ = 115.9 (q, $J_{F,C}$ = 320.0 Hz, CF_3), 121.1 (q, $J_{F,C}$ = 321.3 Hz, CF_3), 123.6, 125.2, 128.7, 129.9, 130.9, 133.6 (CH_{Ar}), 135.7, 138.7, 140.2, 142.9 (C_{Ar}), 192.6 (C=O). ^{19}F NMR (282 MHz, CDCl3): δ = -73.3, 72.0 (2CF). IR (KBr): $\tilde{\nu}$ = 3061, (w), 1598, 1589, 1580, (m), 1496, 1431, 1414, 1319, 1291 (m), 1265 (s), 1165, 1077, 1028, 989, 976, 932 (m), 887, 787, 757 (s), 680, 595, 572 (m) cm^{-1}; GC-MS (EI, 70 eV): *m/z* (%): 478 (M^+, 74), 401 (05), 345 (08), 253 (26), 225 (32), 204 (04), 167 (22), 156 (06), 128 (27), 105 (100), 77 (43), 69 (30), 51 (14); HRMS (EI) calcd for $C_{15}H_8F_6O_7S_2$ [M^+]: 477.96101 found 477.960958.



Phenyl-([1,1';2',1'']terphenyl-4'-yl)-methanone (19a): Starting with **18** (200 mg, 0.46 mmol), K_3PO_4 (292 mg, 1.38 mmol), $Pd(PPh_3)_4$ (6 mol%), phenylboronic acid (64 mg, 0.53 mmol) and 1,4-dioxane (5ml/mmol of triflate), **19a** was isolated as a colorless solid, yield 108 mg, (78 %) mp. = 138-140°C; ^{1}H NMR (300 MHz, $CDCl_3$): δ = 7.00-7.12 (m, 10H, ArH), 7.38-7.47 (m, 4H, ArH), 7.72 (d, 1H, J = 6.5 Hz, ArH), 7.74-7.80 (m, 3H, ArH). ^{13}C NMR (75.47 MHz, $CDCl_3$): δ = 126.9, 127.2, 128.0, 128.1, 128.4, 129.1, 129.7, 129.8, 130.0, 130.6, 132.2, 132.5 (CH_{Ar}), 136.5, 137.7, 138.3, 140.6, 140.7, 144.7 (C_{Ar}), 196.3 (C=O). IR (KBr): $\tilde{\nu}$ = 3286, 3010, 2912, 2854, 2728 (w), 1728, (s), 1574, 1502 (m), 1492, 1452, 1436, 1386, 1328, 1294 (m), 1250 (s), 1198, 1116, 1064, 1036, 959, 902 (m), 882, 840, 793, 738 (s), 695, 648, 594, 563 (m) cm^{-1}; GC-MS (EI, 70 eV): *m/z* (%): 334 (M^+, 100), 257 (52), 228 (31), 202 (07), 128 (06), 105 (24), 77 (20); HRMS (EI) calcd for $C_{25}H_{18}O$ [M^+]: 334.13522, found 334.134837.

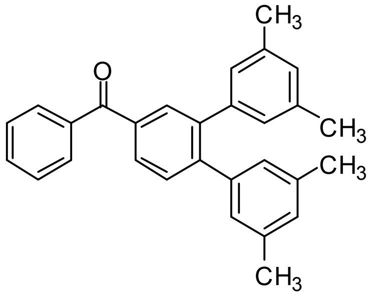


Phenyl-(4,4''-Difluoro-[1,1';2',1'']terphenyl-4'-yl)-methanone (19b): Starting with **18** (200 mg, 0.41 mmol), K_3PO_4 (292 mg, 1.38 mmol), $Pd(PPh_3)_4$ (6 mol%), 4-fluorophenylboronic acid (74 mg, 0.53 mmol) and 1,4-dioxane (5ml/mmol of triflate), **19b** was isolated as a yellow oil, yield 107 mg, (69 %); ^{1}H NMR (300 MHz, $CDCl_3$): δ = 6.82-6.90 (m, 3H, ArH), 6.99-7.10 (m, 4H, ArH), 7.40-7.55 (m, 5H, ArH), 7.73-7.80 (m, 4H, ArH). ^{13}C NMR (75.47 MHz, $CDCl_3$): δ = 115.0, 115.3, 128.4, 129.3, 130.0, 130.5, 131.1, 131.4, 132.1, 132.5 (CH_{Ar}), 136.3, 136.8, 137.5, 138.2, 139.7, 143.5, 160.5, 163.7, (C_{Ar}), 196.1 (C=O). IR (KBr): $\tilde{\nu}$ = 3052, 3020,

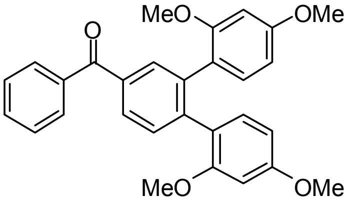


2996, 2830, (w), 1716, (s), 1656, 1596 (m), 1490, 1456, 1432, 1398, 1317, 1273 (m), 1178, 1118, 1072, 1054, 945, 936 (m), 843, 827, 796, 746 (s), 695, 642, 581, 532 (m) cm^{-1}; GC-MS (EI, 70 eV): *m/z* (%): 370 (M$^+$, 100), 293 (58), 264 (17), 244 (19), 105 (22), 77 (16); HRMS (EI) calcd for $C_{25}H_{16}OF_2$ [M$^+$]: 370.11637, found 370.116373.

Phenyl-(3,5,3'',5''-tetramethyl-[1,1';2',1'']terphenyl-4'-yl)-methanone (19c): Starting with **18** (200 mg, 0.41 mmol), K_3PO_4 (292 mg, 1.38 mmol), $Pd(PPh_3)_4$ (6 mol%), 3,5-dimethylphenylboronic acid (79 mg, 0.53 mmol) and 1,4-dioxane (5ml/mmol of triflate), **19c** was isolated as a colorless crystalline solid, yield 123 mg, (75 %) mp. = 140-142°C; ^{1}H NMR (250 MHz, $CDCl_3$): δ = 2.09 (s, 6H, $2CH_3$), 2.11 (s, 6H, $2CH_3$), 6.68 (d, 3H, *J* = 4.45 Hz, ArH), 6.75 (d, 2H, *J* = 6.55 Hz, ArH), 7.38-7.48 (m, 5H, ArH), 7.68, 7.72 (dd, 1H, *J* = 1.85, 9.8 Hz, ArH), 7.75 (m, 3H, ArH). ^{13}C NMR (75.46 MHz, $CDCl_3$): δ = 21.2 ($2CH_3$), 21.3 ($2CH_3$), 125.1, 127.5, 127.7, 128.3, 128.6, 128.8, 130.0, 130.4, 132.1, 132.3 (CH_{Ar}), 136.3, 137.1, 137.8, 138.1, 140.4, 140.9, 144.9 (C_{Ar}), 196.4 (C=O). IR (KBr): $\tilde{\nu}$ = 3289, 3013, 2916, 2857, 2732 (w), 1732, (s), 1574 1505 (m), 1495, 1455, 1436, 1386, 1328, 1296 (m), 1250 (s), 1199, 1118, 1067, 1036, 959, 902 (m), 882, 842, 793, 738 (s), 695, 648, 596, 567 (m) cm^{-1}; GC-MS (EI, 70 eV): *m/z* (%): 390 (M$^+$, 100), 313 (29), 270 (13), 239 (07), 148 (04), 105 (22), 77 (11); HRMS (EI) calcd for $C_{29}H_{26}O$ [M$^+$]: 390.19782, found 390.197629.

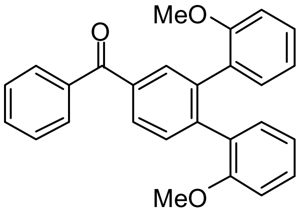


Phenyl-(2,4,2'',4''-tetramethoxy-[1,1';2',1'']terphenyl-4'-yl)-methanone (19d): Starting with **18** (200 mg, 0.41 mmol), K_3PO_4 (292 mg, 1.38 mmol), $Pd(PPh_3)_4$ (6 mol%), 2,4-dimethoxyphenylboronic acid (96 mg, 0.53 mmol) and 1,4-dioxane (5ml/mmol of triflate), **19d** was isolated as a colorless oil, yield 140 mg, (74 %) mp. = 136-138°C; ^{1}H NMR (250 MHz, $CDCl_3$): δ = 3.53, 3.55, 3.77, 3.78 (s, 12H, $4OCH_3$), 6.35-6.41 (m, 3H, ArH), 6.93 (t, 1H, *J* = 8.9 Hz, ArH), 7.48-7.57 (m, 5H, ArH), 7.81-7.92 (m, 5H, ArH). ^{13}C NMR (75.46 MHz, $CDCl_3$): δ = 55.1, 55.3 ($4OCH_3$), 98.2, 103.9 (CH_{ArH}), 123.0 (C_{ArH}), 128.1, 128.4, 130.0, 131.0, 131.5, 132.0, 133.1 (CH_{Ar}), 135.6, 138.0, 142.9, 157.1, 160.0 (C_{Ar}), 196.3 (C=O). IR (KBr): $\tilde{\nu}$ = 3288, 3012, 2914, 2856, 2730 (w), 1731, (s), 1572, 1505 (m), 1495, 1455, 1436, 1386, 1328, 1296 (m), 1250 (s), 1199, 1118, 1067, 1036, 959, 902 (m), 882, 842, 793, 738 (s), 695, 648, 596, 567 (m) cm^{-1};

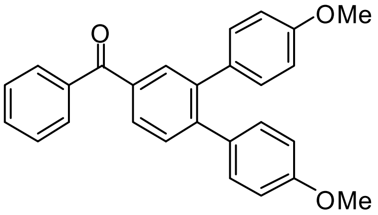


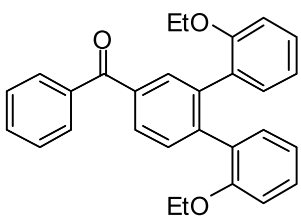
GC-MS (EI, 70 eV): *m/z* (%): 454 (M^+, 100), 377 (03), 227 (05), 105 (37); HRMS (EI) calcd for $C_{29}H_{26}O_5$ [M^+]: 45417748, found 454.177776.

Phenyl-(2,2''-Dimethoxy-[1,1';2',1'']terphenyl-4'-yl)-methanone (19e): Starting with **18** (200 mg, 0.41 mmol), K_3PO_4 (292 mg, 1.38 mmol), $Pd(PPh_3)_4$ (6 mol%), 2-methoxyphenylboronic acid (80 mg, 0.53 mmol) and 1,4-dioxane (5ml/mmol of triflate), **19e** was isolated as a colorless solid, yield 110 mg, (67 %) mp. = 152-154°C; ^{1}H NMR (250 MHz, $CDCl_3$): δ = 3.39, 3.41 (s, 6H, $2OCH_3$), 6.61-6.77 (m, 2H, ArH), 6.94-7.09 (m, 5H, ArH), 7.35-7.46 (m, 4H, ArH), 7.75-7.82 (m, 5H, ArH). ^{13}C NMR (62.90 MHz, $CDCl_3$): δ = 54.9 ($2OCH_3$), 110.4, 120.0, 128.2, 128.5, 128.7, 130.0, 130.7, 131.2, 132.1, 132.7 (CH_{Ar}), 135.9, 137.9, 138.4, 143.0, 156.0, 156.8 (C_{Ar}), 196.3 (C=O). IR (KBr): $\tilde{\nu}$ = 3055, 3024, 2998, 2832, (w), 1712, (s), 1654, 1597 (m), 1493, 1459, 1434, 1396, 1317, 1273 (m), 1178, 1118, 1074, 1051, 946, 932 (m), 843, 827, 796, 748 (s), 695, 642, 581, 531 (m) cm^{-1}; GC-MS (EI, 70 eV): *m/z* (%): 394 (M^+, 100), 363 (21), 317 (80), 289 (20), 274 (46), 259 (11), 202 (18), 158 (15), 105 (83), 77 (68); HRMS (EI) calcd for $C_{27}H_{22}O_3$ [M^+]: 394.15689, found 394.46178.

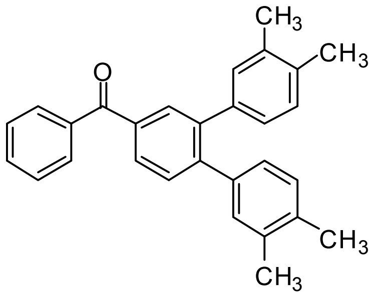


Phenyl-(4,4'-Dimethoxy-[1,1';2',1'']terphenyl-4'-yl)-methanone (19f): Starting with **18** (200 mg, 0.41 mmol), K_3PO_4 (292 mg, 1.38 mmol), $Pd(PPh_3)_4$ (6 mol%), 4-methoxyphenylboronic acid (80 mg, 0.53 mmol) and 1,4-dioxane (5ml/mmol of triflate), **19f** was isolated as a yellow oil, yield 90 mg, (54 %); ^{1}H NMR (300 MHz, $CDCl_3$): δ = 3.68, 3.69 (s, 6H, $2OCH_3$), 6.66-6.71 (m, 4H, ArH), 6.96-7.04 (m, 4H, ArH), 7.37-7.46 (m, 3H, ArH), 7.68, 7.71 (d, 1H, *J* = 1.80, 9.75 Hz, ArH), 7.74-7.79 (m, 4H, ArH). ^{13}C NMR (62.90 MHz, $CDCl_3$): δ = 55.1 ($2OCH_3$), 113.5, 128.3, 128.8, 130.0, 130.5, 130.8, 131.0, 132.3, 132.4, 132.9 (CH_{Ar}), 133.0, 136.2, 137.8, 140.1, 144.2, 158.8 (C_{Ar}), 196.3 (C=O). IR (KBr): $\tilde{\nu}$ = 3052, 3022, 2996, 2830, (w), 1716, (s), 1652, 1596 (m), 1492, 1456, 1432, 1394, 1316, 1272 (m), 1176, 1116, 1072, 1050, 945, 932 (m), 843, 827, 796, 748 (s), 692, 642, 579, 529 (m) cm^{-1}; GC-MS (EI, 70 eV): *m/z* (%): 394 (M^+, 100), 317 (11), 289 (04), 258 (03), 202 (07), 105 (24); HRMS (EI) calcd for $C_{27}H_{22}O_3$ [M^+]: 394.15635, found 394.156091.



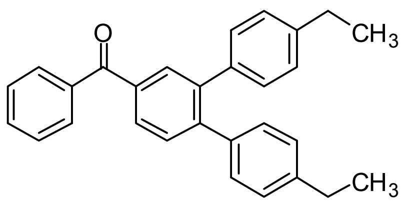


Phenyl-(2,2'-diethoxy-[1,1';2',1'']terphenyl-4'-yl)-methanone (19g): Starting with **18** (200 mg, 0.41 mmol), K_3PO_4 (292 mg, 1.38 mmol), $Pd(PPh_3)_4$ (6 mol%), 2-ethoxyphenylboronic acid (88 mg, 0.53 mmol) and 1,4-dioxane (5ml/mmol of triflate), **19g** was isolated as a colorless solid, yield 135 mg, (76 %) mp. = 168-170°C; ^{1}H NMR (300 MHz, $CDCl_3$): δ = 1.09-1.15 (m, 6H, $2CH_3$), 3.64 (q, 4H, J = 6.8 Hz, $2CH_2$), 6.59-6.70 (m, 4H, ArH), 6.90-6.96 (m, 2H, ArH), 7.00-7.10 (m, 2H, ArH), 7.32-7.44 (m, 4H, ArH), 7.72, 7.75 (dd, 1H, J = 1.86, 7.89 Hz, ArH), 7.77-7.81 (m, 3H, ArH). ^{13}C NMR (62.90 MHz, $CDCl_3$): δ = 14.5, 14.7 ($2CH_3$), 63.1, 63.3 ($2CH_2$), 111.3, 119.6, 128.2, 128.6, 130.0, 131.0, 131.5, 131.7, 132.1, 132.9 (CH_{Ar}), 135.6, 138.0, 138.5, 143.1, 155.5, 155.6 (C_{Ar}), 196.5 (C=O). IR (KBr): $\tilde{\nu}$ = 3048, 3024, 2994, 2832, (w), 1718, (s), 1654, 1598 (m), 1494, 1452, 1430, 1396, 1318, 1274 (m), 1178, 1116, 1074, 1052, 947, 932 (m), 843, 823, 798, 748 (s), 690, 644, 577, 527 (m) cm^{-1}; GC-MS (EI, 70 eV): *m/z* (%): 422 (M$^+$, 100), 407 (07), 365 (06), 347 (04), 289 (08), 261 (11), 202 (08), 144 (05), 105 (89), 77 (33); HRMS (EI) calcd for $C_{29}H_{26}O_3$ [M$^+$]: 422.18765, found 422.187400.

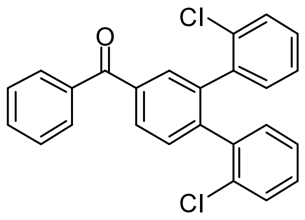


Phenyl-(3,4,3'',4''-tetramethyl-[1,1';2',1'']terphenyl-4'-yl)-methanone (19h): Starting with **18** (200 mg, 0.41 mmol), K_3PO_4 (292 mg, 1.38 mmol), $Pd(PPh_3)_4$ (6 mol%), 3,4-dimethylphenylboronic acid (79 mg, 0.53 mmol) and 1,4-dioxane (5ml/mmol of triflate), **19h** was isolated as a colorless oil, yield 96 mg, (58 %); ^{1}H NMR (300 MHz, $CDCl_3$): δ = 2.03, 2.05, 2.06, 2.08 (s, 12H, $4CH_3$), 6.71-6.83 (m, 4H, ArH), 6.90 (d, 2H, J = 6.8 Hz, ArH), 7.30-7.41 (m, 5H, ArH), 7.64, 7.66 (dd, 1H, J = 1.8, 7.9 Hz, ArH), 7.72, 7.74 (dd, 2H, J = 1.9, 4.5 Hz, ArH). ^{13}C NMR (62.90 MHz, $CDCl_3$): δ = 19.4, 19.5, 19.7, 19.8 ($4CH_3$), 126.7, 127.3, 128.3, 128.8, 129.2, 130.0, 130.6, 130.8, 130.9, 132.3 (CH_{Ar}), 135.0, 135.4, 136.1, 137.8, 138.2, 140.7, 144.7 (C_{Ar}), 196.4 (C=O). IR (KBr): $\tilde{\nu}$ = 3044, 3020, 2990, 2838, (w), 1716, (s), 1656, 1594 (m), 1492, 1450, 1432, 1396, 1318, 1270 (m), 1172, 1118, 1072, 1050, 945, 930 (m), 841, 821, 796, 746 (s), 692, 644, 575, 525 (m) cm^{-1}; GC-MS (EI, 70 eV): *m/z* (%): 390 (M$^+$, 100), 375 (04), 313 (15), 285 (04), 270 (18), 239 (08), 148 (05), 105 (42), 77 (13); HRMS (EI) calcd for $C_{29}H_{26}O$ [M$^+$]: 390.19782 found 390.197714.

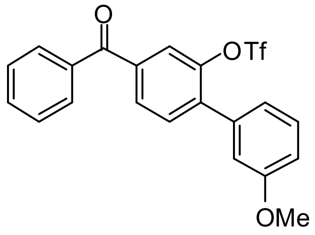
Phenyl-(4,4'-diethyl-[1,1';2',1'']terphenyl-4'-yl)-methanone (19i): Starting with **18** (200 mg, 0.41 mmol), K_3PO_4 (292 mg, 1.38 mmol), $Pd(PPh_3)_4$ (6 mol%), 4-ethylphenylboronic acid (79 mg, 0.53 mmol) and 1,4-dioxane (5ml/mmol of triflate), **19i** was isolated as a colorless solid, yield 128 mg, (78 %) mp. = 138-140°C; ^{1}H NMR (300 MHz, $CDCl_3$): δ = 1.06-1.13 (m, 6H, $2CH_3$), 2.45-2.54 (m, 4H, $2CH_2$), 6.95-7.02 (m, 8H, ArH), 7.32-7.45 (m, 4H, ArH), 7.69, 7.71 (dd, 1H, J = 1.8, 7.9 Hz, ArH), 7.72-7.77 (m, 3H, ArH). ^{13}C NMR (62.90 MHz, $CDCl_3$): δ = 15.3 ($2CH_3$), 28.4, 28.5 ($2CH_2$), 127.5, 127.6, 128.3, 128.9, 129.6, 129.7, 130.0, 130.7, 132.3, 132.4 (CH_{Ar}), 133.0, 136.6, 137.4, 138.6, 138.7, 142.7 (C_{Ar}), 196.3 (C=O). IR (KBr): $\tilde{\nu}$ = 3046, 3026, 2992, 2834, (w), 1716, (s), 1652, 1596 (m), 1492, 1454, 1432, 1394, 1316, 1276 (m), 1176, 1114, 1072, 1054, 945, 934 (m), 841, 825, 796, 746 (s), 692, 642, 574, 524 (m) cm^{-1}; GC-MS (EI, 70 eV): *m/z* (%): 390 (M^+, 100), 375 (06), 313 (16), 241 (12), 105 (58), 77 (17); HRMS (EI) calcd for $C_{29}H_{26}O$ [M^+]: 390.19782, found 390.197822.



Phenyl-(2,2'-dichloro-[1,1';2',1'']terphenyl-4'-yl)-methanone (19j): Starting with **18** (200 mg, 0.41 mmol), K_3PO_4 (146 mg, 0.69 mmol), Pd $(PPh_3)_4$ (3 mol%), 2-chlorophenylboronic acid (82 mg, 0.53 mmol) and 1,4-dioxane (5ml/mmol of triflate), **19j** was isolated as a colorless oil, yield 144 mg, (68 %); ^{1}H NMR (300 MHz, $CDCl_3$): δ = 6.96-7.06 (m, 5H, ArH), 7.20-7.26 (m, 2H, ArH), 7.39-7.50 (m, 5H, ArH), 7.80-7.86 (m, 4H, ArH). ^{13}C NMR (62.90 MHz, $CDCl_3$): δ = 126.2, 127.2, 128.3, 128.9, 129.1, 129.7, 130.0, 130.1, 130.9, 131.2, 132.5, 132.8 (CH_{Ar}), 133.0, 136.6, 137.4, 138.6, 138.7, 142.7 (C_{Ar}), 196.0 (C=O). ^{19}F NMR (282 MHz, CDCl3): δ = -73.4 (CF_3). IR (KBr): $\tilde{\nu}$ = 3054, 2958, 2842 (w), 1662, 1594 (s), 1558, 1486 (m), 1442, 1428, 1396, 1312, 1276, 1242 (m), 1211 (s), 1160, 1132, 1096, 1024, 983 (m), 873, 816, 792, 761 (s), 692, 672, 571 (m) cm^{-1}; GC-MS (EI, 70 eV): *m/z* (%): 402 (M^+, 100), 367 (09), 325 (81), 291 (07), 262 (61), 226 (80), 200 (07), 150 (05), 113 (06), 105 (64), 77 (36), 51 (06); HRMS (EI) calcd for $C_{25}H_{16}Cl_2O$ [M^+]: 402.05782 found 402.29994.

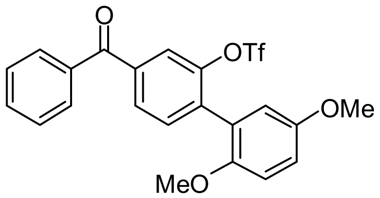


4-Benzoyl-3'-methoxybiphenyl-2-yl trifluoromethanesulfonate (20a): Starting with **18** (200 mg, 0.41 mmol), K_3PO_4 (146 mg, 0.69 mmol), Pd $(PPh_3)_4$ (3 mol%), 3-methoxyphenyl boronic acid (80 mg, 0.53 mmol) and 1,4-dioxane (5ml/mmol of triflate), **20a** was isolated as a colorless viscous oil, yield

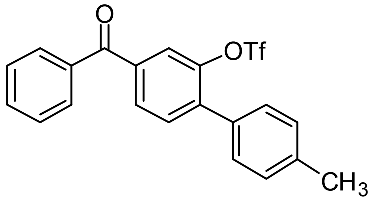


124 mg, (68 %); ^{1}H NMR (250 MHz, $CDCl_3$): δ = 3.76 (s, 3H, OCH_3), 6.89-7.01 (m, 3H, ArH), 7.28 (d, 1H, J = 7.8 Hz, ArH), 7.40-7.54 (m, 3H, ArH), 7.73-7.81 (m, 2H, ArH). ^{13}C NMR (75.47 MHz, $CDCl_3$): δ = 55.3 (OCH_3), 114.7, 114.8, 11.7 (q, $J_{F,C}$ = 320 Hz, CF_3), 123.8, 128.6, 129.8, 129.9, 130.0, 131.9, 133.1 (CH_{Ar}), 135.9, 136.5, 138.2, 139.2, 146.4, 159.7 (C_{Ar}), 194.0 (C=O). ^{19}F NMR (282 MHz, CDCl3): δ = -73.8 (CF_3). IR (KBr): $\tilde{\nu}$ = 3063, 3003, 2940 (w), 1660, 1598 (s), 1580, 1552, 1479 (m), 1447, 1421, 1396, 1317, 1278, 1244 (m), 1204 (s), 1179, 1167, 1047, 1020, 990 (m), 883, 841, 788, 762 (s), 695, 629, 597, 568 (m) cm^{-1}; GC-MS (EI, 70 eV): *m/z* (%): 436 (M^+, 80), 303 (07), 225 (03), 202 (05), 183 (04), 155 (06), 127 (05), 105 (100), 77 (32); HRMS (EI) calcd for $C_{21}H_{15}O_5F_3S$ [M^+]: 436.05868 found 436.058307.

4-Benzoyl-2',5'-dimethoxybiphenyl-2-yl trifluoromethanesulfonate (20b): Starting with **18** (200 mg, 0.41 mmol), K_3PO_4 (146 mg, 0.69 mmol), Pd $(PPh_3)_4$ (3 mol%), 2,5-dimethoxyphenylboronic acid (96 mg, 0.53 mmol) and 1,4-dioxane (5ml/mmol of triflate), **20b** was isolated as a colorless solid, yield 140 mg, (72 %) mp. = 138-140°C; ^{1}H NMR (250 MHz, $CDCl_3$): δ = 3.69 (s, 6H, $2OCH_3$), 6.61 (d, 1H, J = 8.4 Hz, ArH), 7.18 (s, 1H, ArH), 7.28-7.38 (m, 2H, ArH), 7.42-7.56 (m, 3H, ArH), 7.70-7.84 (m, 4H, ArH). ^{13}C NMR (75.47 MHz, $CDCl_3$): δ = 55.8 ($2OCH_3$), 103.8, 104.0, 121.1 (q, $J_{F,C}$ = 320 Hz, CF_3), 122.7, 128.3, 128.4, 129.0, 130.0, 130.1, 131.0, 132.8, 133.8 (CH_{Ar}), 136.1, 136.8, 137.1, 137.9, 148.0, 157.7 (C_{Ar}), 194.3 (C=O). ^{19}F NMR (282 MHz, CDCl3): δ = -74.6 (CF_3). IR (KBr): $\tilde{\nu}$ = 3061, 3005, 2929 (w), 1661, 1590 (s), 1554, 1472 (m), 1446, 1418, 1399, 1317, 1280, 1244 (m), 1204 (s), 1169, 1137, 1087, 1033, 985 (m), 880, 844, 794, 766 (s), 699, 671, 587 (m) cm^{-1}; GC-MS (EI, 70 eV): *m/z* (%): 466 (M^+, 100), 333 (28), 302 (24), 225 (32), 197 (04), 105 (84), 77 (28); HRMS (EI) calcd for $C_{22}H_{17}O_6F_3S$ [M^+]: 466.06925 found 466.068859.

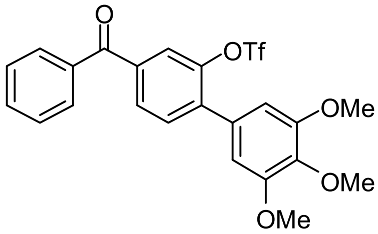


4-Benzoyl-4'-methylbiphenyl-2-yl trifluoromethanesulfonate (20c): Starting with **18** (200 mg, 0.41 mmol), K_3PO_4 (146 mg, 0.69 mmol), Pd $(PPh_3)_4$ (3 mol%), 4-methoxyphenylboronic acid (72 mg, 0.53 mmol) and 1,4-dioxane (5ml/mmol of triflate), **20c** was isolated as a colorless viscous oil, yield 112 mg, (64 %); ^{1}H NMR (250 MHz, $CDCl_3$): δ = 2.33 (s, 3H, OCH_3), 7.19 (d, 3H, J = 7.8 Hz, ArH), 7.34 (d, 1H, J = 8.2 Hz, ArH), 7.40-7.55 (m, 5H, ArH), 7.72-7.77 (m, 3H, ArH). ^{13}C NMR (75.47 MHz, $CDCl_3$): δ = 21.3 (CH_3), 121.1 (q, $J_{F,C}$ = 321 Hz, CF_3), 123.8, 128.5, 129.1, 129.4, 129.9, 130.0, 131.9, 133.0 (CH_{Ar}), 137.6, 138.7, 139.1, 139.5,

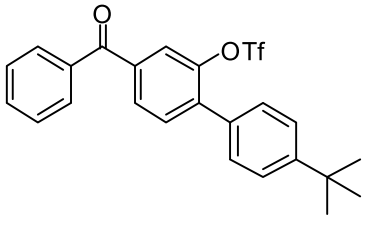


146.5, 149.2 (C_{Ar}), 194.1 (C=O). ^{19}F NMR (282 MHz, CDCl3): δ = -73.8 (CF_3). IR (KBr): $\tilde{\nu}$ = 3060, 3027, 2922 (w), 1660, 1597 (s), 1549, 1484 (m), 1446, 1421, 1317, 1277, 1244 (m), 1204 (s), 1167, 1135, 1098, 1037, 985 (m), 876, 814, 788, 762 (s), 697, 669, 573 (m) cm^{-1}; GC-MS (EI, 70 eV): *m/z* (%): 420 (M^+, 59), 209 (04), 181 (04), 139 (06), 105 (100), 77 (29); HRMS (EI) calcd for $C_{21}H_{15}O_4F_3S$ [M^+]: 420.06377 found 420.063160.

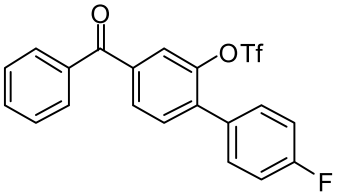
4-Benzoyl-3',4',5'-trimethoxybiphenyl-2-yl trifluoromethanesulfonate (20d): Starting with **18** (200 mg, 0.41 mmol), K_3PO_4 (146 mg, 0.69 mmol), Pd $(PPh_3)_4$ (3 mol%), 3,4,5-trimethoxyphenylboronic acid (112 mg, 0.53 mmol) and 1,4-dioxane (5ml/mmol of triflate), **20d** was isolated as a yellow solid, yield 159 mg, (76 %) mp. = 139-140°C; ^{1}H NMR (300 MHz, $CDCl_3$): δ = 3.82 (s, 6H, 2OCH_3), 3.83 (s, 3H, OCH_3), 6.62 (s, 2H, ArH), 7.39-7.47 (m, 3H, ArH), 7.56 (s, 1H, ArH), 7.68-7.78 (m, 3H, ArH), 7.88 (d, 1H, *J* = 6.4 Hz, ArH). ^{13}C NMR (75.47 MHz, $CDCl_3$): δ = 56.2 (2OCH_3), 61.0 (OCH_3), 106.8 (CH_{Ar}), 120 (q, $J_{F,C}$ = 320 Hz, CF_3), 122.0, 128.5, 130.0, 130.4, 133.1, 133.3 (CH_{Ar}), 135.8, 136.7, 137.7, 138.6, 149.0, 153.3 (C_{Ar}), 194.8 (C=O). ^{19}F NMR (282 MHz, CDCl3): δ = -73.8 (CF_3). IR (KBr): $\tilde{\nu}$ = 3065, 2999, 2936 (w), 1660, 1609 (s),1584, 1514, 1488 (m), 1463, 1418, 1393, 1317, 1291, 1278 (m), 1241 (s), 1170, 1104, 1063, 1001, 978 (m), 889, 831, 790, 745 (s), 675, 630, 598, 569 (m) cm^{-1}; GC-MS (EI, 70 eV): *m/z* (%): 496 (M^+, 92), 363 (26), 332 (100), 317 (17), 255 (12), 227 (07), 185 (05), 105 (57), 77 (19); HRMS (EI) calcd for $C_{23}H_{19}F_3O_7S$ [M^+]: 496.07981 found 496.079887.



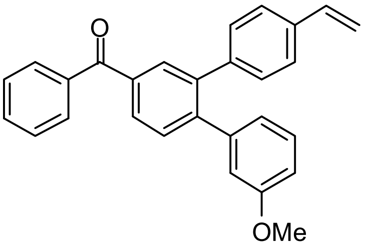
4-Benzoyl-4'-tert-butylbiphenyl-2-yl trifluoromethanesulfonate (20e): Starting with **18** (200 mg, 0.41 mmol), K_3PO_4 (146 mg, 0.69 mmol), Pd $(PPh_3)_4$ (3 mol%), 4-tert-butylphenylboronic acid (94 mg, 0.53 mmol) and 1,4-dioxane (5ml/mmol of triflate), **20e** was isolated as a colorless viscous oil, yield 145 mg, (70 %); ^{1}H NMR (300 MHz, $CDCl_3$): δ = 1.19, 1.21 (s, 6H, 2CH_3), 1.28 (s, 3H, CH_3), 6.97, 7.00 (dd, 1H, *J* = 1.80, 8.90 Hz, ArH), 7.12, 7.15 (dd, 1H, J = 2.1, 8.4 Hz, ArH), 7.34, 7.45 (m, 3H, ArH), 7.48-7.54 (m, 4H, ArH), 7.72-7.80 (m, 4H, ArH). ^{13}C NMR (75.47 MHz, $CDCl_3$): δ = 31.2 (2CH_3), 31.3 (CH_3), 34.7 (C), 120 (q, $J_{F,C}$ = 320 Hz, CF_3), 123.9, 124.8, 125.6, 128.3, 129.0, 129.4, 130.0, 131.9, 132.3,133.0 (CH_{Ar}), 136.6, 137.9, 138.0, 139.4, 141.0, 146.6, 152.3 (C_{Ar}), 194.8 (C=O). ^{19}F NMR (282 MHz, CDCl3): δ = -73.8 (CF_3). IR (KBr): $\tilde{\nu}$ = 3060, 2904, 2868 (w), 1713, 1610, 1579, 1518,



1462, 1446 (w), 1392, 1317, 1278,1268, 1178, 1117, 1027, 1016, 1001, 973, 954, 854, 765, (m), 734, 698, 605 (w), 565 (m) cm^{-1}; GC-MS (EI, 70 eV): *m/z* (%): 462 (M^+, 39), 447 (100), 299 (35), 273 (07), 209 (05), 165 (06), 105 (30), 77 (15), 57 (09); HRMS (EI) calcd for $C_{24}H_{21}F_3O_4S$ [M^+]: 462.11072 found 462.111104.

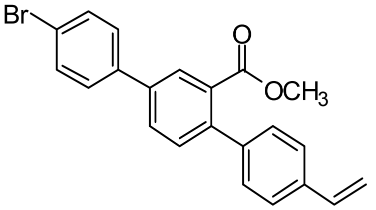


4-Benzoyl-4'-fluorobiphenyl-2-yl trifluoromethanesulfonate (20f): Starting with **18** (200 mg, 0.41 mmol), K_3PO_4 (146 mg, 0.69 mmol), Pd $(PPh_3)_4$ (3 mol%), 4-fluorophenylboronic acid (74 mg, 0.53 mmol) and 1,4-dioxane (5ml/mmol of triflate), **20f** was isolated as a colorless solid, yield 88 mg, (66 %) mp. = 158-160°C; ^{1}H NMR (300 MHz, $CDCl_3$): δ = 7.00-7.17 (m, 2H, ArH), 7.39-7.48 (m, 5H, ArH), 7.50-7.56 (m, 2H, ArH), 7.74-7.82 (m, 3H, ArH). ^{13}C NMR (75.47 MHz, $CDCl_3$): δ = 115.7, 116.0 (CH), 120.0 (q, $J_{F,C}$ = 321 Hz, CF_3), 123.8, 128.5, 129.1, 129.4, 129.9, 130.0, 131.9, 133.1 (CH_{Ar}), 136.5, 138.3, 138.4, 146.4, 161.5, 164.8 (C_{Ar}), 193.9 (C=O). ^{19}F NMR (282 MHz, CDCl3): δ = -73.8 (CF_3). IR (KBr): $\tilde{\nu}$ = 3066, 2957, 2849 (w), 1661, 1598 (s), 1552, 1486 (m), 1447, 1421, 1394, 1318, 1279, 1242 (m), 1205 (s), 1160, 1134, 1096, 1028, 987 (m), 875, 818, 790, 763 (s), 694, 670, 572 (m) cm^{-1}; GC-MS (EI, 70 eV): *m/z* (%): 424 (M^+, 53), 233 (04), 213 (08), 186 (04), 157 (14), 105 (100), 77 (33), 51 (04); HRMS (EI) calcd for $C_{20}H_{12}O_4F_4S$ [M^+]: 424.04376 found 424.37142.

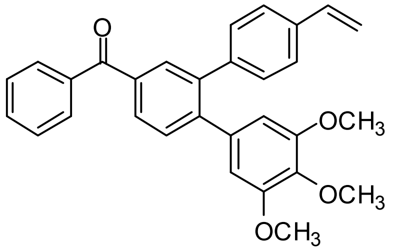


(3-Methoxy-4''-vinyl-[1,1';2',1'']terphenyl-4'-yl)-phenyl-methanone (21a): Starting with **20a** (70 mg, 0.18 mmol), K_3PO_4 (114 mg, 0.54 mmol), Pd $(PPh_3)_4$ (3 mol%), 4-vinylphenylboronic acid (89 mg, 1.60 mmol) and 1,4-dioxane (5ml/mmol of triflate), **21a** was isolated as colorless viscous oil; yield 42 mg, (68 %); ^{1}H NMR (300 MHz, $CDCl_3$): δ = 3.53 (s, 3H, OCH_3), 5.10 (dd, 1H, J = 1.4, 9.8 Hz, CH_2), 5.58 (dd, 1H, J = 1.2, 8.1 Hz, CH_2), 6.52 (dd, 1H, J = 1.3, 8.2 Hz, CH), 6.52-6.72 (m, 3H, ArH), 7.00-7.20 (m, 5H, ArH), 7.37-7.50 (m, 4H, ArH), 7.72-7.79 (m, 4H, ArH); ^{13}C NMR (62.89 MHz, $CDCl_3$): δ = 55.1 (OCH_3), 113.2 (CH_{vinyl}), 113.9 (CH_2), 115.1, 122.1, 125.9, 128.3, 129.1, 129.2, 129.9, 130.0, 132.1, 132.4, 136.3 (CH_{Ar}), 136.7, 137.6, 140.0, 140.1, 140.3, 141.8, 144.4, 159.2, (C_{Ar}), 196.2 (C=O). IR (KBr): $\tilde{\nu}$ = 3055, 3003, 2953, 2833 (w), 1655 (s), 1628 (w), 1595 (s), 1513 (w), 1494, 1464, 1427, 1389, 1294 (m), 1248 (s), 1177, 1114, 1074, 1018, 989, 947 (m), 869, 842, 783, 765 (s), 696, 638, 564, 540 (m) cm^{-1}; GC-MS (EI, 70 eV): *m/z* (%): 390 (M^+, 100), 349 (03), 313

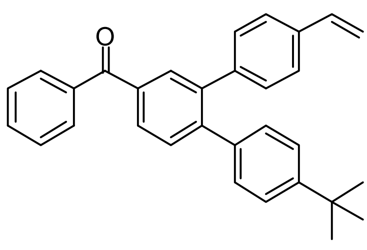
(15), 285 (04), 239 (09), 105 (33), 77 (16); HRMS (EI) calcd for $C_{28}H_{22}O_2$ [M^+]: 390.16143, found 390.161704.



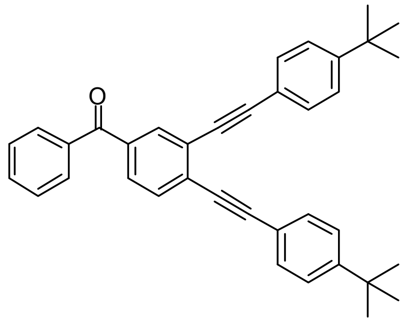
(4-Methyl-4''-vinyl-[1,1';2',1'']terphenyl-4'-yl)-phenyl-methanone (21b): Starting with **20c** (70 mg, 0.18 mmol), K_3PO_4 (114 mg, 0.54 mmol), Pd $(PPh_3)_4$ (3 mol%), 4-vinylphenylboronic acid (89 mg, 1.60 mmol) and 1,4-dioxane (5ml/mmol of triflate), **21b** was isolated as colorless solid, mp= 148-150°C; yield 48 mg, (78 %); ^{1}H NMR (300 MHz, $CDCl_3$): δ = 2.24 (s, 3H, CH_3), 5.15 (d, 1H, J = 10.8 Hz, CH_2), 5.66 (d, 1H, J = 9.6 Hz, CH_2), 6.63 (dd, 1H, J = 1.3, 8.2 Hz, CH), 6.96-7.00 (m, 2H, ArH), 7.16-7.21 (m, 3H, ArH), 7.41-7.51 (m, 6H, ArH), 7.72-7.80 (m, 5H, ArH); ^{13}C NMR (62.90 MHz, $CDCl_3$): δ = 21.1 (CH_3), 113.8 (CH_2), 125.9, 128.3, 128.8, 129.1, 129.5, 130.0, 130.6, 132.2, 132.4, 136.4 (CH_{Ar}), 136.9, 137.5, 137.8, 140.1, 140.3, 144.6, 144.4, 159.2 (C_{Ar}), 196.2 (C=O). IR (KBr): $\tilde{\nu}$ = 3052, 3002, 2952, 2830 (w), 1654 (s), 1630 (w), 1596 (s), 1512 (w), 1496, 1462, 1428, 1390, 1296 (m), 1246 (s), 1178, 1116, 1072, 1016, 987, 945 (m), 869, 842, 781, 765 (s), 696, 634, 564, 542 (m) cm^{-1}; GC-MS (EI, 70 eV): *m/z* (%): 374 (M^+, 100), 359 (04), 297 (19), 253 (10), 148 (04), 105 (24), 77 (12); HRMS (EI) calcd for $C_{28}H_{22}O_1$ [M^+]: 374.16652, found 374.166329.



Phenyl-(3,4,5-trimethoxy-4''-vinyl-[1,1';2',1'']terphenyl-4'-yl)-methanone (21c): Starting with **20d** (70 mg, 0.18 mmol), K_3PO_4 (114 mg, 0.54 mmol), Pd $(PPh_3)_4$ (3 mol%), 4-vinylphenylboronic acid (89 mg, 1.60 mmol) and 1,4-dioxane (5ml/mmol of triflate), **21c** was isolated as colorless viscous oil; yield 40 mg, (64 %); ^{1}H NMR (300 MHz, $CDCl_3$): δ = 3.54 (s, 6H, $2OCH_3$), 3.75 (s, 3H, OCH_3), 5.19 (dd, 1H, J = 1.3, 10.8 Hz, CH_2), 5.69 (dd, 1H, J = 2.1, 9.6 Hz, CH_2), 6.63 (dd, 1H, J = 1.3, 8.2 Hz, CH), 7.09 (d, 1H, J = 8.2 Hz, ArH), 7.24-7.36 (m, 4H, ArH), 7.40-7.48 (m, 3H, ArH), 7.50-7.65 (m, 3H, ArH), 7.71 (dd, 1H, J = 1.8, 7.9 Hz, ArH), 7.80-7.86 (m, 3H, ArH); ^{13}C NMR (62.90 MHz, $CDCl_3$): δ = 55.9 ($2OCH_3$), 60.9 (OCH_3), 107.3 (CH_{vinyl}), 114.2 (CH_2), 125.9, 128.0, 128.3, 129.6, 130.0, 131.6, 135.0, 135.8, 136.4 (CH_{Ar}), 136.9, 137.5, 137.8, 140.1, 140.3, 144.6, 144.4, 152.7 (C_{Ar}), 196.2 (C=O). IR (KBr): $\tilde{\nu}$ = 3054, 3002, 2952, 2830 (w), 1654 (s), 1630 (w), 1596 (s), 1512 (w), 1496, 1462, 1428, 1390, 1296 (m), 1246 (s), 1178, 1116, 1072, 1016, 987, 945 (m), 869, 842, 781, 765 (s), 696, 634, 564, 542 (m) cm^{-1}; GC-MS (EI, 70 eV): *m/z* (%): 450 (M^+, 100), 435 (20), 332 (05), 207 (07), 105 (33), 77 (20); HRMS (EI) calcd for $C_{30}H_{26}O_4$ [M^+]: 450.18256, found 450.182820.

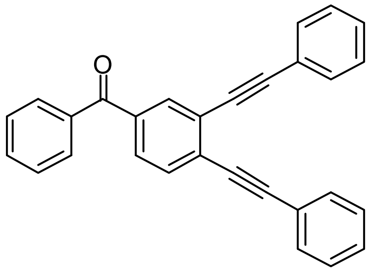


(4-*tert*-Butyl-4''-vinyl-[1,1';2',1'']terphenyl-4'-yl)-phenyl-methanone (21d): Starting with **20e** (70 mg, 0.18 mmol), K_3PO_4 (114 mg, 0.54 mmol), Pd $(PPh_3)_4$ (3 mol%), 4-vinylphenylboronic acid (89 mg, 1.60 mmol) and 1,4-dioxane (5ml/mmol of triflate), **21d** was isolated as colorless Solid, mp= 138-140°C; yield 39 mg, (62 %); ^{1}H NMR (300 MHz, $CDCl_3$): δ = 1.21 (s, 3H, CH_3), 1.22 (s, 6H, $2CH_3$), 5.13 (dd, 1H, J = 1.2, 10.6 Hz, CH_2), 5.61 (dd, 1H, J = 2.4, 9.5 Hz, CH_2), 6.55 (dd, 1H, J = 1.3, 8.2 Hz, CH), 7.00-7.10 (m, 4H, ArH), 7.15-7.23 (m, 4H, ArH), 7.40-7.54 (m, 4H, ArH), 7.72-7.81 (m, 4H, ArH); ^{13}C NMR (62.90 MHz, $CDCl_3$): δ = 31.3 ($2CH_3$), 34.5 (CH_3), 113.8 (CH_2), 125.0, 125.8, 128.3, 129.1, 129.3, 129.6, 130.0, 130.7, 132.2, 132.3, 136.4 (CH_{Ar}), 136.9, 137.1, 137.3, 137.7, 140.1, 140.2, 144.5, 150.2 (C_{Ar}), 196.2 (C=O). IR (KBr): $\tilde{\nu}$ = 3052, 3006, 2956, 2832 (w), 1656 (s), 1632 (w), 1598 (s), 1516 (w), 1496, 1464, 1432, 1392, 1298 (m), 1246 (s), 1178, 1118, 1072, 1014, 985, 943 (m), 869, 842, 785, 765 (s), 694, 634, 562, 541 (m) cm^{-1}; GC-MS (EI, 70 eV): *m/z* (%): 416 (M^+, 87), 401 (100), 252 (06), 105 (53), 77 (23); HRMS (EI) calcd for $C_{31}H_{28}O$ [M^+]: 416.21347, found 416.213534.

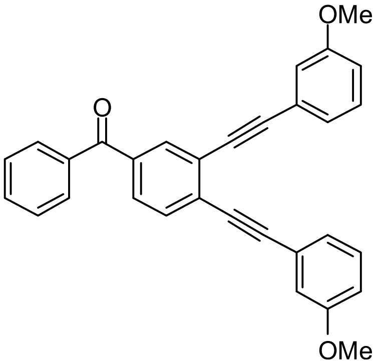


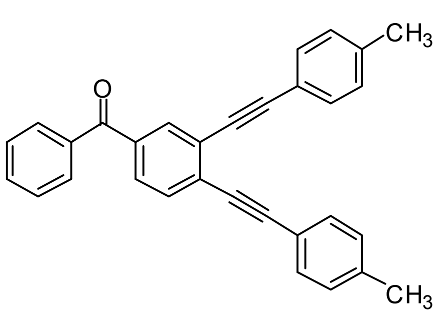
(3,4-bis((4-tert-butylphenyl)ethynyl) phenyl)(phenyl) methanone (22a): Starting with **18** (238mg, 0.50 mmol), Pd $(PPh_3)_4$ (5 mol%), dry CuI (10 mol%), triethylamine (126 mg, 1.25 mmol), *p*-terbutylphenylacetylene (51mg, 0.55 mmol) was added in DMF (5mL per 1 mmol of 2a), **22a** was isolated after chromatography (silica gel, *n*-heptane/EtOAc) as a colourless oil (41mg, 78%). ^{1}H NMR (250 MHz, $CDCl_3$): δ = 1.26, 1.27 (s, 18H, 2 *t*Bu), 7.16 (s, 1H, ArH), 7.28-7.33 (m, 3H, ArH), 7.41-7.48 (m, 3H, ArH), 7.51-7.59 (m, 3H, ArH), 7.64-7.75 (m, 5H, ArH), 7.88 (d, 1H, J = 1.65 Hz, ArH). ^{13}C NMR (62.90 MHz, $CDCl_3$): δ = 30.9, 31.1 (6 CH_3), 87.0, 87.4, 94.6, 96.8, 119.8, 119.9 (C), 125.4, 125.5 (CH_{Ar}), 126.0 (C_{Ar}), 128.4, 128.9 (CH_{Ar}), 129.7 (C_{Ar}), 129.9, 131.4, 131.6, 131.7, 132.6, 133.3 (CH_{Ar}), 136.4, 137.2, 152.0, 152.2 (C_{Ar}), 195.3 (C=O). IR (KBr): $\tilde{\nu}$ = 3083, 3060, 2959, 2866, 2211 (w), 1714 (s), 1659 (s), 1591, 1506, 1462, 1406, 1363, 1322 (m), 1268 (s), 1201, 1163, 1104, 1084, 982, 968, 882, 872, 792, 742, 651, 615, 528 (w) cm^{-1}; GC-MS (EI, 70 eV): *m/z* (%): 494 (M^+, 100), 479 (50), 262 (04), 232 (19), 204 (05), 105 (18), 77 (04); HRMS (EI) calcd for $C_{37}H_{34}O$ [M^+]: 494.26042, found 494.260148.

(3,4-Bis(phenylethynyl)phenyl)(phenyl)methanone (22b): Starting with **18** (238mg, 0.50 mmol), Pd $(PPh_3)_4$ (5 mol%), dry CuI (10 mol%), triethylamine (126 mg, 1.25 mmol), phenylacetylene (56mg, 0.59 mmol) was added in DMF (5mL per 1 mmol of 2a), **22b** was isolated after chromatography (silica gel, *n*-heptane/EtOAc) as a colourless oil (24 mg, 54%). ^{1}H NMR (250 MHz, $CDCl_3$): δ = 7.23-7.27 (m, 4H, ArH), 7.37 (s, 1H, ArH), 7.40-7.54 (m, 6H, ArH), 7.57 (s, 1H, ArH), 7.62 (d, 1H, J = 1.72 Hz, ArH), 7.66 (d, 1H, J = 1.72 Hz, ArH), 7.69-7.73 (m, 3H, ArH), 7.88 (d, 1H, J = 1.62 Hz, ArH)). ^{13}C NMR (62.90 MHz, $CDCl_3$): δ = 87.5, 87.9, 94.5, 96.6 (C), 120.4, 122.8 (C_{Ar}), 125.3, 128.2, 128.4, 128.5, 128.7, 128.9, 129.1, 129.9, 131.7, 131.8, 132.7, 133.3 (CH_{Ar}), 133.5, 136.7, 137.1 (C_{Ar}), 195.2 (C=O). IR (KBr): $\tilde{\nu}$ = 3081, 3062, 2958, 2864, 2210 (w), 1716 (s), 1658 (s), 1592, 1508, 1464, 1408, 1362, 1320 (m), 1266 (s), 1203, 1161, 1106, 1082, 981, 967, 881, 873, 792, 741, 653, 613, 523 (w) cm^{-1}; GC-MS (EI, 70 eV): *m/z* (%): 382 (M^+, 100), 352 (18), 305 (06), 276 (28), 250 (04), 176 (08), 77 (11); HRMS (EI) calcd for $C_{29}H_{18}O$ [M^+]: 382.13522, found 382.134497.

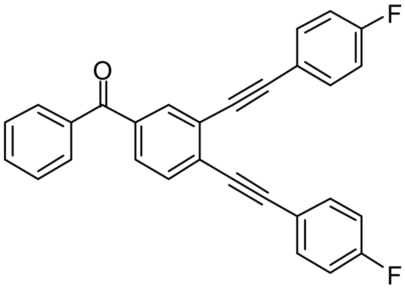


(3,4-Bis((3-methoxyphenyl)ethynyl)phenyl)(phenyl) methanone (22c): Starting with **18** (238mg, 0.50 mmol), Pd $(PPh_3)_4$ (5 mol%), dry CuI (10 mol%), triethylamine (126 mg, 1.25 mmol), 3-methoxyphenylacetylene (48mg, 0.52 mmol) was added in DMF (5mL per 1 mmol of 2a), **22c** was isolated after chromatography (silica gel, *n*-heptane/EtOAc) as a colorless viscous oil (28mg, 64%). ^{1}H NMR (300 MHz, $CDCl_3$): δ = 3.68, 3.69 (s, 6H, $2OCH_3$), 6.81-6.87 (m, 2H, ArH), 7.00-7.06 (m, 2H, ArH), 7.08-7.20 (m, 4H, ArH), 7.41-7.46 (m, 2H, ArH), 7.52-7.60 (m, 2H, ArH), 7.66, 7.69 (dd, 1H, J = 1.74, 8.07 Hz, ArH), 7.72-7.75 (m, 2H, ArH), 7.90 (d, 1H, J = 1.71 Hz, ArH). ^{13}C NMR (62.90 MHz, $CDCl_3$): δ = 55.2 ($2OCH_3$), 87.3, 87.6, 94.4, 96.5 (4 C), 115.6, 115.8, 116.2, 116.3 (CH_{Ar}), 123.7, 123.8 (C_{Ar}), 124.2, 124.3 (CH_{Ar}), 126.0 (C_{Ar}), 128.4, 129.2, 129.4, 129.5, 129.9, 131.6, 132.7, 133.2 (CH_{Ar}), 136.7, 137.1, 159.4 (C_{Ar}), 195.2 (C=O). IR (KBr): $\tilde{\nu}$ = 3061 (w), 2998, 2832 (m), 2203 (w), 1656 (m), 1591 (s), 1540, 1488, 1446, 1402, 1317 (m), 1279, 1219 (s), 1179, 1127, 1091, 985, 972, 869, 848 (m), 777, 710, 681 (s), 603, 562 (w) cm^{-1}; GC-MS (EI, 70 eV): *m/z* (%): 442 (M^+, 100), 427 (05), 399 (12), 365 (18), 337 (07), 250 (12), 105 (37), 77 (15), 57 (05), 44 (41); HRMS (EI) calcd for $C_{31}H_{22}O_3$ [M^+]: 442.15689, found 442.50458.



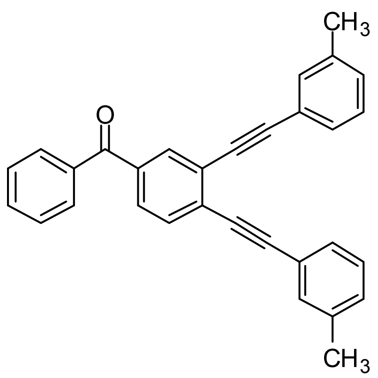


(3,4-Bis(p-tolylethynyl)phenyl)(phenyl) methanone (22d): Starting with **18** (238mg, 0.50 mmol), Pd $(PPh_3)_4$ (5 mol%), dry CuI (10 mol%), triethylamine (126 mg, 1.25 mmol), *p*-methylphenylacetylene (56 mg, 0.61 mmol) was added in DMF (5mL per 1 mmol of 2a), **22d** was isolated after chromatography (silica gel, *n*-heptane/EtOAc) as a reddish oil (32 mg, 66%). ^{1}H NMR (300 MHz, $CDCl_3$): δ = 2.28, 2.29 (s, 6H, $2CH_3$), 7.00-7.10 (m, 4H, ArH), 7.36-7.44 (m, 6H, ArH), 7.50-7.57 (m, 2H, ArH), 7.63 (dd, 1H, J = 1.77 8.10 Hz, ArH), 7.70-7.74 (m, 2H, ArH), 7.87 (d, 1H, J = 1.71Hz, ArH). ^{13}C NMR (62.90 MHz, $CDCl_3$): δ = 21.2, 21.5 ($2CH_3$), 87.0, 87.4, 94.7, 96.9 (C_{Ar}), 123.8, 125.2, 126.0, 126.6 (C_{Ar}), 128.4, 128.9, 129.2, 129.3, 129.5, 129.9, 131.6, 131.7, 132.6, 133.2 (CH_{Ar}), 136.4, 137.2, 138.9, 139.2 (C_{Ar}), 195.3 (C=O). IR (KBr): $\tilde{\nu}$ = 3058, 3025, 2916, 2858, 2204 (w), 1651, 1587, 1514, 1444, 1404, 1317 (m), 1267, 1246 (m), 1177, 1104, 1040 (w), 981, 913, 871, 834, 787, 664 (m), 612, 586, 560 (w) cm^{-1}; GC-MS (EI, 70 eV): *m/z* (%):410 (M^+, 100), 409 (33), 408 (15), 395 (29), 393 (12), 289 (16), 181 (10), 77 (10). HRMS (EI) calcd for $C_{31}H_{22}O$ [M^+]: 410.16652, found 410.166081.

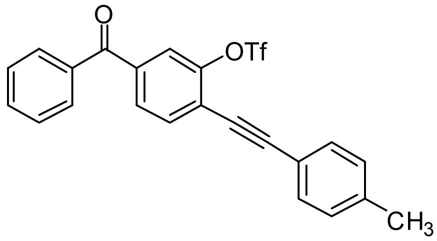


(3,4-Bis((4-fluorophenyl)ethynyl)phenyl)(phenyl)methanone (22e): Starting with **18** (238mg, 0.50 mmol), Pd $(PPh_3)_4$ (5 mol%), dry CuI (10 mol%), triethylamine (126 mg, 1.25 mmol), *p*-flourophenylacetylene (58 mg, 0.59 mmol) was added in DMF (5mL per 1 mmol of 2a), **22e** was isolated after chromatography (silica gel, *n*-heptane/EtOAc) as a colorless viscous oil (30 mg, 60%). ^{1}H NMR (250 MHz, $CDCl_3$): δ= 6.99-7.04 (m, 2H, ArH), 7.14-7.23 (m, 4H, ArH), 7.25-7.30 (m, 3H, ArH), 7.42-7.47 (m, 2H, ArH), 7.53-7.61 (m, 2H, ArH), 7.66 (d, 1H, J = 1.47 Hz, ArH), 7.70-7.75 (m, 2H, ArH), 7.90 (d, 1H, J = 1.12 Hz, ArH)). ^{13}C NMR (62.90 MHz, $CDCl_3$): δ = 86.1, 86.9, 92.5, 96.9 (C), 120.4, 122.8 (C_{Ar}), 125.1, 127.2, 127.9, 128.2, 128.7, 129.1, 129.9, 131.7, 132.7, 133.3 (CH_{Ar}), 134.0, 135.0, 136.7, 137.1 (C_{Ar}), 195.2 (C=O). IR (KBr): $\tilde{\nu}$ = 3066, 2918, 2859, 2207, 1681 (w), 1648 (s), 1589, 1547, 1486, 1434, 1405, 1278, 1210, 1138, 1114, 1089, 1073, 937, 918, 867, 777, 695 (m), 605, 596, 546 (w) cm^{-1}; GC-MS (EI, 70 eV): *m/z* (%): 418 (M^+ 100), 389 (05), 341 (34), 312 (40), 293 (07), 216 (05), 187 (05), 147 (06), 105 (30), 77 (12); HRMS (EI) calcd for $C_{29}H_{16}OF_2$ [M^+]: 418.11637, found 418.115424.

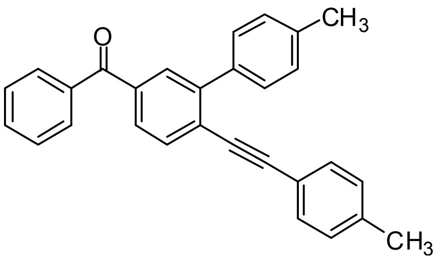
(3,4-Bis(m-tolylethynyl)phenyl)(phenyl)methanone (22f): Starting with **18** (238mg, 0.50 mmol), Pd (PPh$_3$)$_4$ (5 mol%), dry CuI (10 mol%), triethylamine (126 mg, 1.25 mmol), 3-methylphenylacetylene (48mg, 0.52 mmol) was added in DMF (5mL per 1 mmol of 2a), **22f** was isolated after chromatography (silica gel, *n*-heptane/EtOAc) as a colourless oil (24mg, 58%). ^{1}H NMR (300 MHz, CDCl$_3$): δ = 2.17, 2.18 (s, 6H, 2CH$_3$), 7.02-7.10 (m, 4H, ArH), 7.35-7.45 (m, 6H, ArH), 7.52-7.59 (m, 2H, ArH), 7.62 (dd, 1H, J = 1.77 8.10 Hz, ArH), 7.68-7.72 (m, 2H, ArH), 7.85 (d, 1H, J = 1.71Hz, ArH). ^{13}C NMR (62.90 MHz, CDCl$_3$): δ = 21.2, 21.5 (2CH$_3$), 87.1, 87.9, 94.8, 96.7 (C_{Ar}), 123.6, 125.3, 126.0, 126.8 (C_{Ar}), 128.3, 128.4, 128.8, 128.9, 129.1, 129.7, 129.9, 131.5, 132.4, 132.5, 132.7, 133.1, 133.5 (CH_{Ar}), 136.2, 137.6, 138.5, 139.6 (C_{Ar}), 195.1 (C=O). IR (KBr): $\tilde{\nu}$ = 3056, 3021, 2914, 2857, 2206 (w), 1653, 1585, 1513, 1441, 1402, 1315 (m), 1265, 1245 (m), 1177, 1104, 1040 (w), 981, 913, 871, 834, 787, 664 (m), 612, 586, 560 (w) cm^{-1}; GC-MS (EI, 70 eV): *m/z* (%): 410 (M$^+$, 100), 333 (23), 305 (08), 289 (34), 207 (07), 105 (15), 77 (15); HRMS (EI) calcd for $C_{31}H_{22}O$ [M$^+$]: 410.16652, found 410.166081.



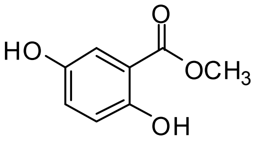
3-Trifourosulphonolyxy-4-methylphenylaceylene-benzophenone (23): Starting with **18** (238mg, 0.50 mmol), Pd (PPh$_3$)$_4$ (5 mol%), dry CuI (10 mol%), triethylamine (126 mg, 1.25 mmol), *p*-methylphenylacetylene (45mg, 0.50 mmol) was added in DMF (5mL per 1 mmol of 2a), **23** was isolated after chromatography (silica gel, *n*-heptane/EtOAc) as a yellow oil (41mg, 51%). ^{1}H NMR (300 MHz, CDCl$_3$): δ = 2.31 (s, 3H, CH$_3$), 7.12 (d, 2H, J = 7.92 Hz, ArH), 7.42-7.47 (m, 4H, ArH), 7.55 (d, 1H, J = 7.13 Hz, ArH), 7.63-7.67 (m, 2H, ArH), 7.70-7.74 (m, 3H, ArH). ^{13}C NMR (75.47 MHz, CDCl$_3$): δ = 21.6 (CH$_3$), 81.7, 99.9 (C), 118.6 (C_{Ar}), 122.6 (q, $J_{C,F}$ = 320.0 Hz, CF$_3$), 123.1 (C_{Ar}), 128.6, 129.3, 129.4, 129.9, 131.9, 133.1, 133.3 (C_{Ar}), 136.4, 138.0, 140.0, 149.3 (C_{Ar}), 193.7 (C=O). IR (KBr): $\tilde{\nu}$ = 3305, 3062, 2922, 2867, 1909 (w), 1659, 1599 (m), 1515, 1446 (w), 1423 (s), 1319 (m), 1290, 1244 (m), 1171, 1076, 976 (m), 883, 844, 815 (s), 754, 733, 639, 532 (m) cm^{-1}; GC-MS (EI, 70 eV): *m/z* (%): 444 (M$^+$, 100), 311 (46), 255 (22), 176 (08), 115 (05), 105 (39), 77 (28), 51 (05); HRMS (EI) calcd for $C_{23}H_{15}O_4F_3S$ [M$^+$]: 444.06377, found 444.063860.



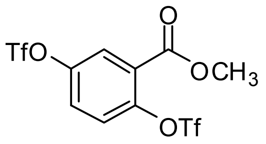
(4'-Methyl-6-(p-tolylethynyl)biphenyl-3-yl)(phenyl)methanone (24): Starting with **(23)** (70 mg, 0.18 mmol), K_3PO_4 (114 mg, 0.54 mmol), Pd $(PPh_3)_4$ (3 mol%), 4-methylphenylboronic acid (89 mg, 1.60 mmol) and 1,4-Dioxane (5ml/mmol of triflate), **24** was isolated as colorless crystalline solid; yield 40 mg, (64 %); ^{1}H NMR (300 MHz, $CDCl_3$): δ = 2.26, 2.33 (s, 6H, $2CH_3$), 7.05 (d, 2H, J = 7.89 Hz, ArH), 7.16-7.20 (m, 4H, ArH), 7.40-7.52 (m, 5H, ArH), 7.60-7.64 (m, 2H, ArH), 7.73 (d, 1H, J = 1.53 Hz, ArH), 7.76-7.80 (m, 2H, ArH). ^{13}C NMR (62.90 MHz, $CDCl_3$): δ = 21.2, 21.5 ($2CH_3$), 88.4, 95.4 (2C), 125.9 (C_{Ar}), 128.2, 128.3, 128.7, 129.1, 129.2, 129.9, 130.9, 131.3, 131.4, 132.4, 132.4 (CH_{Ar}), 132.7, 136.7, 136.8, 137.5, 137.6,138.8, 143.5 (C_{Ar}), 195.9 (C=O). IR (KBr): $\tilde{\nu}$ = 3078, 3057, 3028, 2916, 2858, 2209 (w), 1651, 1591 (s), 1512, 1442, 1412, 1394 (w), 1267, 1245 (m), 1182, 1143, 1075, 1040, 1016, 999 (w), 951 (m), 909, 857, 838 (w), 748, 697 (m), 610, 586 cm^{-1}; GC-MS (EI, 70 eV): *m/z* (%): 386 (M^+, 100), 371 (05), 309 (27), 281 (12), 266 (36), 239 (05), 132 (05), 105 (39), 77 (22); HRMS (EI) calcd for $C_{29}H_{22}O$ [M^+]: 386.16652, found 386.166115.



Methyl 2,5-dihydroxybenzoate (25): ^{1}H NMR (250 MHz, $CDCl_3$): δ = 3.86 (s, 3H, OCH_3), 6.82 (s, 1H, ArH), 6.92 (d, J = 2.9 Hz, 1H, ArH), 7.21 (d, 1H, J = 3.2 Hz, ArH), 10.25 (s, 2H, 2OH); ^{13}C NMR (62.89 MHz, $CDCl_3$): δ = 52.3 (OCH_3), 112.1 (C_{Ar}), 114.7, 118.5, 124.0 (CH_{Ar}), 147.7, 155.7 (2COH), 170.1 (C=O); IR (KBr): $\tilde{\nu}$ = 3332, 3029, 2958 (w), 1682, 1615 (s), 1504, 1435, 1367, 1261 (m), 1211 (s), 1185, 1076, 976 (m), 871, 779, 677 (s), 557 (m), cm^{-1}; GC-MS (EI, 70 eV): *m/z* (%): 168 (M^+, 38), 136 (100), 108 (24), 80 (16), 69 (03), 63 (02), 53 (13), 44 (01), 39 (02). HRMS (EI) calcd for $C_8H_8O_4$ [M^+]: 168.04231, found 168.14670.

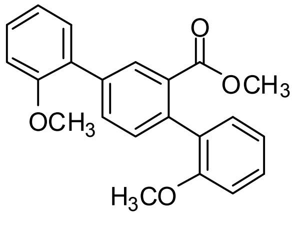


Methyl 2,5-bis(trifluoromethylsulfonyloxy)benzoate (26): Starting with **25** (168 mg, 1.0 mmol), pyridine (0.32 ml, 4.0 mmol) and Tf_2O (0.39 ml, 2.4 mmol), **26** was isolated as a colorless crystalline solid, (364 mg, 84 %), mp. = 152-154°C; ^{1}H NMR (300 MHz, $CDCl_3$): δ = 3.92 (s, 3H, OCH_3), 7.36 (s, 1H, ArH), 7.47 (d, 1H, J = 3.0 Hz, ArH), 7.92 (d, 1H, J = 3.2 Hz, ArH); ^{13}C NMR (75.46 MHz, $CDCl_3$): δ = 53.2 (OCH_3), 116.5 (q, $J_{C,F}$ = 320.0 Hz, CF_3), 120.2 (q, $J_{C,F}$ = 318.0 Hz, CF_3), 125.0, 125.6, 127.0 (CH_{Ar}), 147.1, 147.9, 148.0 (C_{Ar}), 162.3 (C=O). ^{19}F NMR (282 MHz, CDCl3): δ = -73.3 (CF). IR (KBr): $\tilde{\nu}$ = 3121, 3088, 2961 (w), 1736, 1618 (s), 1586, 1485, 1300, 1279 (m), 1244 (s), 1124,

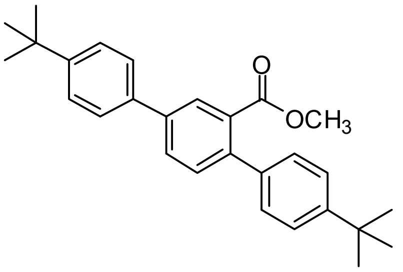


1075, 977 (m), 875, 781, 759 (s), 698, 581, 543 (m) cm^{-1}; GC-MS (EI, 70 eV): *m/z* (%): 432 (M^+, 70), 401 (40), 363 (06), 337 (02), 299 (32), 273 (13), 235 (98), 205 (27), 179 (24), 135 (62), 107 (33), 79 (26), 69 (100), 53 (28); HRMS (EI) calcd for $C_{10}H_6F_6O_8S_2$ [M^+]: 431.94028 found 431.940891.

2,2''-Dimethoxy-[1,1';4',1'']terphenyl-2'-carboxylic acid methyl ester (27a): Starting with **26** (200 mg, 0.46 mmol), K_3PO_4 (292 mg, 1.38 mmol), Pd(PPh_3)$_4$ (6 mol%), 2-methoxyphenylboronic acid (180 mg, 1.19 mmol) and 1,4-dioxane (5ml/mmol of triflate), **27a** was isolated as colorless viscous oil; yield 126 mg, (78 %); ^{1}H NMR (300 MHz, CDCl$_3$): δ = 3.57 (s, 3H, OCH$_3$), 3.65 (s, 3H, OCH$_3$), 3.74 (s, 3H, OCH$_3$), 6.82 (d, 2H, *J* = 8.2 Hz, ArH), 6.90-6.99 (m, 3H, ArH), 7.20-7.29 (m, 3H, ArH), 7.32 (d, 1H, *J* = 6.9 Hz, ArH), 7.64 (dd, 1H, *J* = 1.9, 7.9 Hz, ArH), 7.95 (d, 1H, *J* = 1.7 Hz, ArH); ^{13}C NMR (62.90 MHz, CDCl$_3$): δ = 51.6 (OCH$_3$), 55.2 (OCH$_3$), 55.5 (OCH$_3$), 110.0, 111.2, 120.7, 120.9, 128.7, 129.0 (CH$_{\text{Ar}}$), 129.4 (C$_{\text{Ar}}$), 130.0, 130.4 (CH$_{\text{Ar}}$), 130.5 (C$_{\text{Ar}}$), 130.8, 130.9 (CH$_{\text{Ar}}$), 131.3 (C$_{\text{Ar}}$), 132.6 (CH$_{\text{Ar}}$), 137.1, 137.4, 156.1, 156.5 (C$_{\text{Ar}}$), 168.7 (C=O). IR (KBr): $\tilde{\nu}$ = 3055, 3024, 2945, 2834 (w), 1720 (m), 1597, 1508 (w), 1492, 1479, 1433, 1311 (m), 1242 (s), 1179, 1120, 1086, 1053, 1003, 969, 910, 857, 789 (m), 748 (s), 686, 672, 576 (m) cm^{-1}; GC-MS (EI, 70 eV): *m/z* (%): 348 (M^+, 72), 317 (100), 302 (16), 255 (27), 231 (06), 215 (07), 166 (08), 101 (05); HRMS (EI) calcd for $C_{22}H_{20}O_4$ [M^+]: 348.13561, found 348.135865.

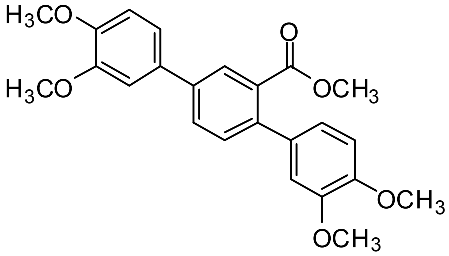


4,4''-Di-*tert*-butyl-[1,1';4',1'']terphenyl-2'-carboxylic acid methyl ester (27b): Starting with **26** (200 mg, 0.46 mmol), K_3PO_4 (292 mg, 1.38 mmol), Pd(PPh_3)$_4$ (6 mol%), 4-*tert*-butylphenylboronic acid (211 mg, 1.19 mmol) and 1,4-dioxane (5ml/mmol of triflate), **27b** was isolated as a colorless crystalline solid; yield 140 mg, (75 %), mp. = 148-150°C; ^{1}H NMR (300 MHz, CDCl$_3$): δ = 1.28 (s, 18H, 6CH$_3$), 3.58 (s, 3H, OCH$_3$), 7.15-7.25 (m, 4H, ArH), 7.28-7.42 (m, 4H, ArH), 7.49 (s, 1H, ArH), 7.63 (d, 1H, *J* = 5.0 Hz, ArH), 7.94 (d, 1H, *J* = 6.9 Hz, ArH); ^{13}C NMR (75.46 MHz, CDCl$_3$): δ = 31.3 (6CH$_3$), 34.5 (2C$_{t\text{Bu}}$), 51.9 (OCH$_3$), 125.0, 125.8, 126.7, 127.0, 128.2, 129.2, 131.2 (CH$_{\text{Ar}}$), 131.7, 132.0, 135.3, 136.8, 137.9, 140.8, 150.8 (C$_{\text{Ar}}$), 168.9 (C=O). IR (KBr): $\tilde{\nu}$ = 3031, 2951, 2902 (w), 1727, 1605, (s), 1483 (m), 1461, 1362, 1267 (m), 1234 (s), 1180, 1085, 959 (m), 895, 788, 765 (s), 698, 572, 554 (m) cm^{-1}; GC-MS (EI, 70 eV): *m/z* (%): 400 (M^+, 58), 385 (100), 357 (02), 297 (03),

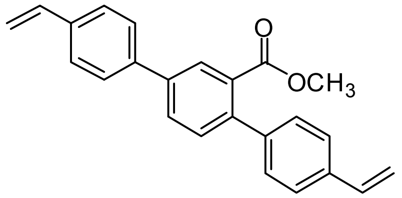


252 (02), 185 (14), 157 (09), 141 (04), 57 (06), 41 (03); HRMS (EI) calcd for $C_{28}H_{32}O_2$ [M$^+$]: 400.23968, found 400.239581.

3,4,3'',4''-Tetramethoxy-[1,1';4',1'']terphenyl-2'-carboxylic acid methyl ester (27c): Starting with **26** (200 mg, 0.46 mmol), K_3PO_4 (292 mg, 1.38 mmol), Pd(PPh_3)$_4$ (6 mol%), 3,4-dimethoxyphenylboronic acid (216 mg, 1.19 mmol) and 1,4-dioxane (5ml/mmol of triflate), **27c** was isolated as a reddish solid; yield 114 mg, (60 %), mp. = 140-142°C; ^{1}H NMR (300 MHz, $CDCl_3$): δ = 3.62 (s, 3H, OCH_3), 3.82 (s, 3H, OCH_3), 3.86 (s, 3H, OCH_3), 3.87 (s, 3H, OCH_3), 3.90 (s, 3H, OCH_3), 6.81 (s, 1H, ArH), 6.85 (s, 2H, ArH), 6.90 (d, 1H, J = 8.3 Hz, ArH), 7.07 (d, 1H, J = 6.2 Hz, ArH), 7.12 (dd, 1H, J = 2.4, 8.6 Hz, ArH), 7.37 (d, 1H, J = 8.0 Hz, ArH), 7.63 (dd, 1H, J = 2.0, 8.0 Hz, ArH), 7.87 (d, 1H, J = 1.9 Hz, ArH); ^{13}C NMR (62.90 MHz, $CDCl_3$): δ = 52.1 (OCH_3), 55.8 (OCH_3), 56.0 (OCH_3), 110.2, 111.9, 111.5, 111.7, 119.4, 120.6, 127.7, 129.2, 130.9 (CH_{Ar}), 131.5, 132.6, 133.5, 139.7, 140.1, 148.4, 148.6, 149.0, 149.6 (C_{Ar}), 169.7 (C=O). IR (KBr): $\tilde{\nu}$ = 2922, 2848 (w), 1724 (s), 1598, 1524, 1488, 1461, 1430, 1321, 1297 (m), 1240, 1215, 1174, 1137, 1090, 1020 (s), 960, 901, 864, 855, 807, 746, 671, 630, 578 (m) cm^{-1}; GC-MS (EI, 70 eV): m/z (%): 408 (M$^+$, 100), 393 (05), 333 (04), 204 (06), 145 (05); HRMS (EI) calcd for $C_{24}H_{24}O_6$ [M$^+$]: 408.15674, found 408.157243.

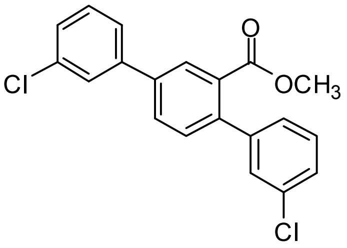


4,4''-Divinyl-[1,1';4',1'']terphenyl-2'-carboxylic acid methyl ester (27d): Starting with **26** (200 mg, 0.46 mmol), K_3PO_4 (292 mg, 1.38 mmol), Pd(PPh_3)$_4$ (6 mol%), 4-vinylphenylboronic acid (176 mg, 1.19 mmol) and 1,4-dioxane (5ml/mmol of triflate), **27d** was isolated as a yellow solid; yield 121 mg, (77 %), mp. = 156-158°C; ^{1}H NMR (300 MHz, $CDCl_3$): δ= 3.61 (s, 3H, OCH_3), 5.9 (dd, 1H, J= 1.8, 6.2 Hz, CH_{2vinyl}), 5.23 (dd, 1H, J= 1.6, 6.9 Hz, CH_{2vinyl}), 5.70 (dd, 1H, J = 1.9, 7.6 Hz, CH_{2vinyl}), 5.76 (dd, 1H, J = 1.8, 6.9 Hz, CH_{2vinyl}), 6.66 (d, 1H, J = 10.8 Hz, CH_{vinyl}), 6.72 (d, 1H, J = 10.2 Hz, CH_{vinyl}), 7.17 (s, 1H, ArH), 7.35-7.47 (m, 4H, ArH), 7.54 (d, 1H, J = 8.3 Hz, ArH), 7.66-7.72 (m, 4H, ArH), 7.98 (d, 1H, J = 1.8 Hz, ArH); ^{13}C NMR (62.90 MHz, $CDCl_3$): δ = 52.0 (OCH_3), 114.4, 114.6 (2CH_{2vinyl}), 126.0, 126.7, 127.1, 128.2, 128.5, 129.5, 131.1, 136.2, 136.4 (CH_{Ar}), 136.6, 137.1, 138.9, 139.6, 140.3, 140.8, 141.3 (C_{Ar}), 169.2 (C=O). IR (KBr): $\tilde{\nu}$ = 3085, 3032, 2947, 2923 (w), 1719 (s), 1626, 1481, 1426, 1309, 1298 (m), 1237, 1139 (s), 1088, 1049, 991, 972, 898 (m), 823 (s), 783, 700, 672, 568 (m) cm^{-}

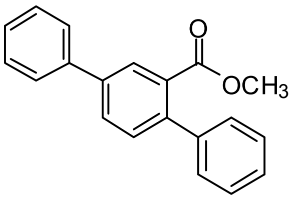


^{1}; GC-MS (EI, 70 eV): *m/z* (%): 340 (M^+, 100), 309 (09), 281 (04), 265 (12), 162 (08), 133 (05); HRMS (EI) calcd for $C_{24}H_{20}O_2$ [M^+]: 340.14578, found 340.146235.

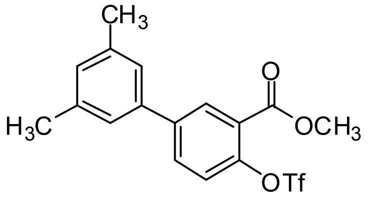
3,3''-Dichloro-[1,1';4',1'']terphenyl-2'-carboxylic acid methyl ester (27e): Starting with **26** (200 mg, 0.46 mmol), K_3PO_4 (292 mg, 1.38 mmol), $Pd(PPh_3)_4$ (6 mol%), 3-chlorophenylboronic acid (185 mg, 1.19 mmol) and 1,4-dioxane (5ml/mmol of triflate), **27e** was isolated as a colorless viscous oil; yield 110 mg, (67 %); ^1H NMR (300 MHz, $CDCl_3$): δ = 3.61 (s, 3H, OCH_3), 7.10-7.14 (m, 1H, ArH), 7.18-7.24 (m, 2H, ArH), 7.26 (s, 1H, ArH), 7.27-7.29 (m, 1H, ArH), 7.31 (d, 1H, *J* = 6.9 Hz, ArH), 7.42 (t, 1H, *J* = 1.8 Hz, ArH), 7.44 (t, 1H, *J* = 1.6 Hz, ArH), 7.52-7.55 (m, 1H, ArH), 7.63 (dd, 1H, *J* = 2.0, 8.0 Hz, ArH), 7.96 (d, 1H, *J* = 1.95 Hz, ArH); ^{13}C NMR (62.90 MHz, $CDCl_3$): δ = 52.0 (OCH_3), 125.2, 126.6, 127.2, 127.5, 128.4, 128.4, 129.2, 130.2, 131.2, 133.5, 133.8 (CH_{Ar}), 134.9, 135.2, 136.0 139.2, 140.5, 141.3, 142.5 (C_{Ar}), 168.3 (C=O). IR (KBr): $\tilde{\nu}$ = 3057, 2947, 2848 (w), 1719 (s), 1594, 1566, 1463, 1435, 1311, 1294 (m), 1235 (s), 1192, 1146, 1092, 1054, 1022, 997, 970, 873 (m), 779, 691 (s), 673, 618, 559 (m) cm^{-1}; GC-MS (EI, 70 eV): *m/z* (%): 356 (M^+, 100), 325 (71), 290 (20), 262 (40), 200 (04), 160 (19), 131 (05), 113 (21), 75 (03); HRMS (EI) calcd for $C_{20}H_{14}O_2Cl_2$ [M^+]: 356.03654, found 356.036229.



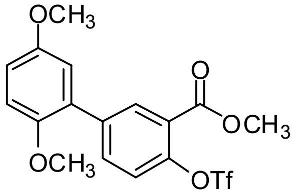
[1,1';4',1'']Terphenyl-2'-carboxylic acid methyl ester (27f): Starting with **26** (200 mg, 0.46 mmol), K_3PO_4 (292 mg, 1.38 mmol), $Pd(PPh_3)_4$ (6 mol%), phenylboronic acid (145 mg, 1.19 mmol) and 1,4-dioxane (5ml/mmol of triflate), **27f** was isolated as a colorless viscous oil; yield 66 mg, (62 %); ^1H NMR (300 MHz, $CDCl_3$): δ = 3.51 (s, 3H, OCH_3), 7.22-7.25 (m, 4H, ArH), 7.26 (s, 1H, ArH), 7.27-7.30 (m, 3H, ArH), 7.46-7.50 (m, 4H, ArH), 7.79 (dd, 1H, *J* = 1.7, 7.7 Hz, ArH); ^{13}C NMR (62.89 MHz, $CDCl_3$): δ = 51.9 (OCH_3), 125.7, 127.3, 127.4, 128.0, 128.1, 128.4, 128.9 (CH_{Ar}), 129.3 (C_{Ar}), 129.6, 130.6 (CH_{Ar}), 139.8, 141.5, 143.3, 144.1 (C_{Ar}), 168.8 (C=O). IR (KBr): $\tilde{\nu}$ = 3052, 2927, 2842 (w), 1716 (s), 1591, 1567, 1467, 1439, 1313, 1295 (m), 1231 (s), 1191, 1143, 1091, 1051, 1027, 993, 970, 873 (m), 779, 691 (s), 673, 618, 559 (m) cm^{-1}; GC-MS (EI, 70 eV): *m/z* (%): 288 (M^+, 75), 257 (100), 228 (34), 202 (08), 152 (05), 128 (04), 113 (08); HRMS (EI) calcd for $C_{20}H_{16}O_2$ [M^+]: 288.11448, found 288.114296.



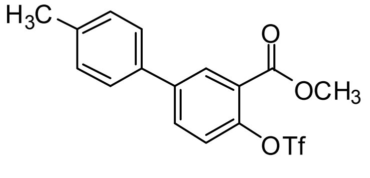
Methyl 3',5'-dimethyl-4-(trifluoromethylsulfonyloxy)biphenyl-3-carboxylate (28a): Starting with **26** (200 mg, 0.46 mmol), K_3PO_4 (146 mg, 0.69 mmol), Pd $(PPh_3)_4$ (3 mol%), 3,5-dimethylphenylboronic acid (88 mg, 0.59 mmol) and 1,4-dioxane (5ml/mmol of triflate), **28a** was isolated as a colorless solid; yield 150 mg, (83 %), mp. = 160-162°C; ^{1}H NMR (300 MHz, $CDCl_3$): δ = 2.27 (s, 6H, $2CH_3$), 3.61 (s, 3H, OCH_3), 6.82 (s, 1H, ArH), 6.95 (s, 1H, ArH), 7.17 (s, 1H, ArH), 7.35 (d, 1H, J = 3.4 Hz, ArH), 7.36 (s, 1H, ArH), 7.63 (d, 1H, J = 3.4 Hz, ArH); ^{13}C NMR (62.89 MHz, $CDCl_3$): δ = 21.2 ($2CH_3$), 52.3 (OCH_3), 120.0 (q, $J_{F,C}$ = 320 Hz, CF_3), 122.4, 123.8, 126.1, 129.6, 132.6 (CH_{Ar}), 137.7, 139.2, 141.1, 143.0, 148.0 (C_{Ar}), 167.1 (C=O). ^{19}F NMR (282 MHz, CDCl3): δ = -73.4 (CF). IR (KBr): $\tilde{\nu}$ = 3018, 2951, 2920 (w), 1723, 1601 (s), 1489 (m), 1467, 1328, 1271 (m), 1243 (s), 1137, 1099, 978 (m), 863, 785, 751 (s), 699, 577, 540 (m) cm^{-1}; GC-MS (EI, 70 eV): *m/z* (%): 388 (M^+, 66), 357 (07), 255 (100), 227 (12), 152 (15), 115 (03), 69 (08); HRMS (EI) calcd for $C_{17}H_{15}F_3O_5S$ [M^+]: 388.05868 found 388.05879.



Methyl 2',5'-dimethoxy-4-(trifluoromethyl sulfonyloxy) biphenyl-3-carboxylate (28b): Starting with **26** (200 mg, 0.46 mmol), K_3PO_4 (146 mg, 0.69 mmol), Pd $(PPh_3)_4$ (3 mol%), 2,5-dimethoxyphenylboronic acid (107 mg, 0.59 mmol) and 1,4-dioxane (5ml/mmol of triflate), **28b** was isolated as a yellow solid; yield 140 mg, (72 %), mp. = 148-150°C; ^{1}H NMR (300 MHz, $CDCl_3$): δ = 3.69 (s, 3H, OCH_3), 3.74 (s, 3H, OCH_3), 3.90 (s, 3H, OCH_3), 6.81 (s, 1H, ArH), 6.83-6.86 (m, 2H, ArH), 7.24 (d, 1H, J = 8.5 Hz, ArH), 7.71 (dd, 1H, J = 2.4, 8.5 Hz, ArH), 8.14 (d, 1H, J = 2.3 Hz, ArH); ^{13}C NMR (62.90 MHz, $CDCl_3$): δ = 52.6 (OCH_3), 55.8 (OCH_3), 56.1 (OCH_3), 112.6, 114.3, 116.4 (CH_{Ar}), 120.0 (q, $J_{F,C}$ = 320.0 Hz, CF_3), 122.2 (CH_{Ar}), 123.8, 128.3 (C_{Ar}), 133.5, 135.1 (CH_{Ar}), 138.9, 147.0, 150.5, 153.8 (C_{Ar}), 164.2 (C=O). ^{19}F NMR (282 MHz, CDCl3): δ = -73.5 (CF). IR (KBr): $\tilde{\nu}$ = 3001, 2953, 2837 (w), 1728 (m), 1681, 1606, 1582 (w), 1504, 1464 (m), 1422 (s), 1307, 1248, 1171, 1074, 1051, 973, 905, 839, 804, 760, 693, 647, 572 (m) cm^{-1}; GC-MS (EI, 70 eV): *m/z* (%): 420 (M^+, 100), 389 (08), 287 (46), 257 (19), 227 (14), 185 (12), 162 (06), 113 (06), 69 (08); HRMS (EI) calcd for $C_{17}H_{15}F_3O_7S$ [M^+]: 420.04851 found 420.049146.

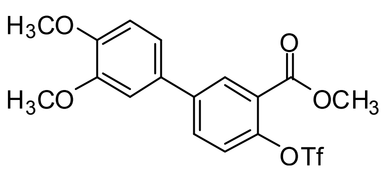


Methyl 4'-methyl-4-(trifluoromethylsulfonyloxy)biphenyl-3-carboxylate (28c): Starting with **26** (200 mg, 0.46 mmol), K_3PO_4 (146 mg, 0.69 mmol), Pd $(PPh_3)_4$ (3 mol%), 4-methylphenylboronic acid (80 mg, 0.59 mmol) and 1,4-



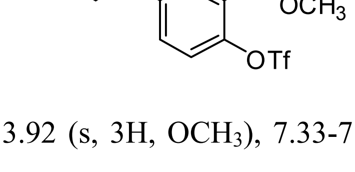
dioxane (5ml/mmol of triflate), **28c** was isolated as a colorless solid; yield 108 mg, (62 %), mp. = 152-154°C; ^{1}H NMR (300 MHz, $CDCl_3$): δ = 2.26 (s, 3H, CH_3), 3.61 (s, 3H, OMe), 6.45 (dd, 2H, J = 8.3, 18.5 Hz, ArH), 7.24 (d, 1H, J = 7.5 Hz, ArH), 7.27-7.31 (m, 1H, ArH), 7.47 (s, 1H, ArH), 7.52 (dd, 1H, J = 1.4, 8.1 Hz, ArH), 8.00 (d, 1H, J = 8.1 Hz, ArH); ^{13}C NMR (62.89 MHz, $CDCl_3$): δ = 21.2 (CH_3), 52.3 (OCH_3), 111.7 (CH_{Ar}), 120.0 (q, $J_{F,C}$ = 320.0 Hz, CF_3), 123.0 (C_{Ar}), 124.1, 129.3, 130.7 (CH_{Ar}), 131.0 (C_{Ar}), 132.5 (CH_{Ar}), 145.2, 147.9, 156.3 (C_{Ar}), 167.1 (C=O). ^{19}F NMR (282 MHz, CDCl3): δ = -73.4 (CF). IR (KBr): $\tilde{\nu}$ = 3012, 2952, 2926 (w), 1714, 1602 (s), 1493 (m), 1469, 1328, 1271 (m), 1243 (s), 1137, 1099, 978 (m), 863, 785, 751 (s), 699, 577, 540 (m) cm^{-1}; GC-MS (EI, 70 eV): *m/z* (%): 374 (M^+, 66), 361 (07), 257 (100), 223 (12), 148 (15), 113 (03), 69 (08); HRMS (EI) calcd for $C_{16}H_{13}F_3O_5S$ [M^+]: 374.04358 found 374.33163.

Methyl 3',4'-dimethoxy-4-(trifluoromethylsulfonyloxy)biphenyl-3-carboxylate (28d): Starting



with **26** (200 mg, 0.46 mmol), K_3PO_4 (146 mg, 0.69 mmol), Pd $(PPh_3)_4$ (3 mol%), 3,4-dimethoxyphenylboronic acid (107 mg, 0.59 mmol) and 1,4-dioxane (5ml/mmol of triflate), **28d** was isolated as a reddish solid; yield 125 mg, (64 %), mp. = 166-168°C; ^{1}H NMR (300 MHz, $CDCl_3$): δ = 3.59 (s, 3H, OCH_3), 3.64 (s, 3H, OCH_3), 3.80 (s, 3H, OCH_3), 6.79 (s, 1H, ArH), 6.84-6.87 (m, 2H, ArH), 7.26 (d, 1H, J = 8.2 Hz, ArH), 7.671 (dd, 1H, J = 2.6, 8.2 Hz, ArH), 8.16 (d, 1H, J = 2.3 Hz, ArH); ^{13}C NMR (62.90 MHz, $CDCl_3$): δ = 52.4 (OCH_3), 55.2 (OCH_3), 56.4 (OCH_3), 112.3, 114.6, 116.8 (CH_{Ar}), 121.0 (q, $J_{F,C}$ = 320.2 Hz, CF_3), 122.4 (CH_{Ar}), 123.4, 127.2 (C_{Ar}), 133.4, 136.1 (CH_{Ar}), 137.9, 146.0, 150.1, 152.4 (C_{Ar}), 168.2 (C=O). ^{19}F NMR (282 MHz, CDCl3): δ = -73.2 (CF). IR (KBr): $\tilde{\nu}$ = 2999, 2952, 2849 (w), 1726 (m), 1603, 1588 (w), 1520, 1463 (m), 1421 (s), 1325, 1289, 1171, 1080, 1052, 974, 905, 883, 827, 806, 755, 684, 664, 573 (m) cm^{-1}; GC-MS (EI, 70 eV): *m/z* (%): 420 (M^+, 51), 389 (04), 287 (100), 257 (15), 229 (17), 213 (04), 185 (05), 157 (04), 114 (05), 69 (06); HRMS (EI) calcd for $C_{17}H_{15}F_3O_7S$ [M^+]: 420.04731 found 420.037247.

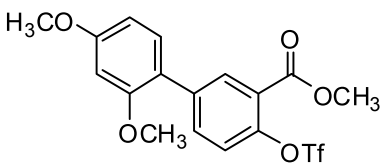
Methyl 4'-bromo-4-(trifluoromethylsulfonyloxy)biphenyl-3-carboxylate (28e): Starting with **26**



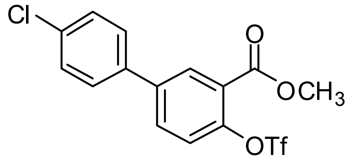
(200 mg, 0.46 mmol), K_3PO_4 (292 mg, 1.38 mmol), $Pd(PPh_3)_4$ (6 mol%), 4-bromophenylboronic acid (118 mg, 0.59 mmol) and 1,4-dioxane (5ml/mmol of triflate), **28e** was isolated as a colorless viscous oil; yield 136 mg, (67 %); ^{1}H NMR (300 MHz, $CDCl_3$): δ = 3.92 (s, 3H, OCH_3), 7.33-7.41 (m, 2H, ArH), 7.44 (d, 1H, J = 6.2 Hz, ArH), 7.48-7.52 (m, 2H, ArH), 7.59 (s, 1H, ArH), 7.93 (d, 1H, J = 6.2 Hz, ArH); ^{13}C NMR (62.90 MHz, $CDCl_3$): δ = 52.7

(OCH_3), 120.0 (q, $J_{F,C}$ = 320.0 Hz, CF_3), 125.0, 125.6, 127.5, 128.6, 132.0 (CH_{Ar}), 133.0, 134.9, 136.0, 147.1, 147.8 (C_{Ar}), 168.3 (C=O). IR (KBr): $\tilde{\nu}$ = 3119, 2959, 2872 (w), 1725 (s), 1613, 1586, 1479, 1461 (m), 1426 (s), 1300, 1278, 1244 (m), 1127 (s), 1076, 1001, 975, 921, 842, 782, 697, 665, 542 (m) cm^{-1}; GC-MS (EI, 70 eV): *m/z* (%): 439 (M^+, 60), 383 (71), 353 (20), 307 (100), 215 (43), 170 (08), 139 (16), 69 (05); HRMS (EI) calcd for $C_{15}H_{10}BrF_3O_5S$ [M^+]: 438.02642, found 439.014672.

Methyl 2',4'-dimethoxy-4-(trifluoromethyl sulfonyloxy) biphenyl-3-carboxylate (28f): Starting with **26** (200 mg, 0.46 mmol), K_3PO_4 (146 mg, 0.69 mmol), Pd (PPh_3)$_4$ (3 mol%), 2,4-dimethoxyphenylboronic acid (107 mg, 0.59 mmol) and 1,4-dioxane (5ml/mmol of triflate), **28f** was isolated as a colorless solid; yield 123 mg, (63 %), mp. = 168-170°C; ^{1}H NMR (300 MHz, $CDCl_3$): δ = 3.73 (s, 3H, OCH_3), 3.78 (s, 3H, OCH_3), 3.89 (s, 3H, OCH_3), 6.48-6.52 (m, 2H, ArH), 7.15-7.22 (m, 2H, ArH), 7.67 (dd, 1H, *J* = 2.4, 8.5 Hz, ArH), 8.1 (d, 1H, *J* = 2.3 Hz, ArH); ^{13}C NMR (62.90 MHz, $CDCl_3$): δ = 52.5 (OCH_3), 55.4 (OCH_3), 55.5 (OCH_3), 99.0, 104.9 (CH_{Ar}), 120.0 (q, $J_{F,C}$ = 320.0 Hz, CF_3), 122.1 (CH_{Ar}), 123.7 (C_{Ar}), 131.1, 133.4 (CH_{Ar}), 134.9 (C_{Ar}), 135.0 (CH_{Ar}), 139.0, 146.6, 157.4, 161.2 (C_{Ar}), 168.4 (C=O). ^{19}F NMR (282 MHz, CDCl3): δ = -73.5 (CF). IR (KBr): $\tilde{\nu}$ = 2921, 2871 (w), 1727 (m), 1677, 1609, 1578 (w), 1512, 1463 (m), 1422 (s), 1305, 1281, 1160, 1074, 1053, 967, 905, 890, 835, 797, 761, 686, 638, 571 (m) cm^{-1}; GC-MS (EI, 70 eV): *m/z* (%): 420 (M^+, 38), 389 (05), 287 (100), 257 (11), 229 (04), 185 (10), 128 (06), 69 (08); HRMS (EI) calcd for $C_{17}H_{15}F_3O_7S$ [M^+]: 420.04851 found 420.049176.

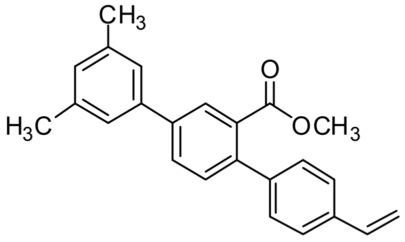


Methyl 4'-chloro-4-(trifluoromethylsulfonyloxy)biphenyl-3-carboxylate (28g): Starting with **26** (200 mg, 0.46 mmol), K_3PO_4 (292 mg, 1.38 mmol), Pd(PPh_3)$_4$ (6 mol%), 4-chlorophenylboronic acid (92 mg, 0.59 mmol) and 1,4-dioxane (5ml/mmol of triflate), **28g** was isolated as a yellow solid; yield 134 mg, (73 %), mp. = 140-142°C; ^{1}H NMR (300 MHz, $CDCl_3$): δ = 3.91 (s, 3H, OCH_3), 7.12-7.15 (m, 1H, ArH), 7.27-7.33 (m, 1H, ArH), 7.36 (s, 1H, ArH), 7.47 (dd, 1H, *J* = 3.1, 9.0 Hz, ArH), 7.61-7.71 (m, 1H, ArH), 7.92 (d, 1H, *J* = 3.0 Hz, ArH), 8.16 (d, 1H, *J* = 2.4 Hz, ArH); ^{13}C NMR (62.90 MHz, $CDCl_3$): δ = 53.1 (OCH_3), 120.0 (q, $J_{F,C}$ = 320.0 Hz, CF_3), 124.1, 125.6, 127.0, 128.3, 129.2 (CH_{Ar}), 133.0, 134.9, 136.0, 147.1, 147.8 (C_{Ar}), 168.4 (C=O). IR (KBr): $\tilde{\nu}$ = 3119, 2959, 2872 (w), 1725 (s), 1613, 1586, 1479, 1461 (m), 1426 (s), 1300, 1278, 1244 (m), 1127 (s), 1076, 1001, 975, 921, 842, 782, 697, 665, 542 (m) cm^{-1}; GC-MS (EI, 70 eV): *m/z* (%): 394 (M^+,

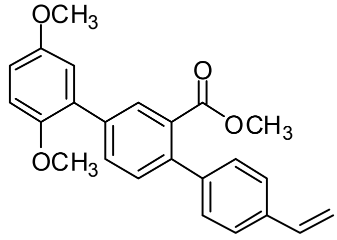


66), 363 (11), 261 (100), 233 (20), 198 (13), 175 (06), 155 (05), 139 (35), 113 (05), 69 (16), 63 (05); HRMS (EI) calcd for $C_{15}H_{10}ClF_3O_5S$ [M^+]: 393.98841, found 393.987890.

3'',5''-Dimethoxy-4-vinyl-(1,1';4',1'')terphenyl-2'-carboxylic acid methyl ester (29a): Starting with **28a** (100 mg, 0.25 mmol), K_3PO_4 (114 mg, 0.54 mmol), Pd $(PPh_3)_4$ (3 mol%), 4-vinylphenylboronic acid (47 mg, 0.32 mmol) and 1,4-dioxane (5ml/mmol of triflate), **29a** was isolated as colorless solid; yield 64 mg, (72 %), mp. = 144-146°C; ^{1}H NMR (300 MHz, $CDCl_3$): δ = 2.28 (s, 6H, $2CH_3$), 3.60 (s, 3H, OCH_3), 5.20 (dd, 1H, *J* = 7.5, 3.2 Hz, CH_{2vinyl}), 5.24 (dd, 1H, *J* = 7.3, 4.2 Hz, CH_{2vinyl}), 5.71 (dd, 1H, *J* = 6.48, 3.2 Hz, CH_{vinyl}), 6.65 (d, 2H, *J* = 4.0 Hz, ArH) 6.90 (s, 1H, ArH), 7.18 (s, 1H, ArH), 7.45 (s, 2H, ArH), 7.65 (d, 2H, *J* = 2.4 Hz, ArH), 7.68 (d, 1H, *J* = 2.4 Hz, ArH), 7.94 (d, 1H, *J* = 2.4 Hz, ArH); ^{13}C NMR (75.46 MHz, $CDCl_3$): δ = 21.3 ($2CH_3$), 52.0 (OCH_3), 113.9 (CH_{2vinyl}), 126.1, 126.7, 127.1, 127.9, 128.4, 129.3, 131.2, 130.1 (CH_{Ar}), 132.1, 133.6, 136.4, 137.0, 138.4, 139.4, 140.7 (C_{Ar}), 169.4 (C=O). IR (KBr): $\tilde{\nu}$ = 3029, 2947, 2900 (w), 1723, 1604, (s), 1479 (m), 1459, 1361, 1264 (m), 1231 (s), 1179, 1081, 957 (m), 893, 785, 762 (s), 693, 571, 551 (m) cm^{-1}; GC-MS (EI, 70 eV): *m/z* (%): 342 (M^+, 100), 326 (01), 311 (22), 296 (06), 267 (08), 253 (07), 202 (01), 163 (10), 133 (05); HRMS (EI) calcd for $C_{24}H_{22}O_2$ [M^+]: 342.16208, found 342.43081.

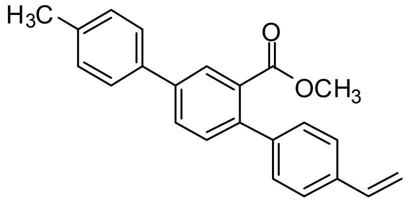


2'',5''-Dimethoxy-4-vinyl-(1,1';4',1'')terphenyl-2'-carboxylic acid methyl ester (29b): Starting with **28b** (100 mg, 0.23 mmol), K_3PO_4 (114 mg, 0.54 mmol), Pd $(PPh_3)_4$ (3 mol%), 4-vinylphenylboronic acid (42 mg, 0.29 mmol) and 1,4-dioxane (5ml/mmol of triflate), **29b** was isolated as colorless solid; yield 70 mg, (78 %), mp. = 156-158°C; ^{1}H NMR (300 MHz, $CDCl_3$): δ = 3.59 (s, 3H, OCH_3), 3.71 (s, 3H, OCH_3), 3.74 (s, 3H, OCH_3), 5.52 (dd, 1H, *J* = 1.5, 7.2 Hz, CH_{2vinyl}), 5.62 (dd, 1H, *J* = 2.3, 6.2 Hz, CH_{2vinyl}), 5.72 (dd, 1H, *J* = 1.8, 6.2 Hz, CH_{vinyl}), 6.82-6.88 (m, 2H, ArH), 7.24 (d, 1H, *J* = 8.2 Hz, ArH), 7.30-7.40 (m, 4H, ArH), 7.60-7.66 (m, 2H, ArH), 7.92 (d, 1H, *J* = 1.8 Hz, ArH); ^{13}C NMR (62.90 MHz, $CDCl_3$): δ = 51.9 (OCH_3), 55.8 (OCH_3), 56.3 (OCH_3), 113.7 (CH), 113.8 (CH_{2vinyl}), 116.5, 125.9, 128.0, 128.5, 130.4, 132.3, 133.0, 134.9 (CH_{Ar}), 135.0, 135.1, 136.4, 136.5, 137.4, 140.6, 150.8, 153.8 (C_{Ar}), 169.1 (C=O). IR (KBr): $\tilde{\nu}$ = 2922, 2850 (w), 1715, 1604, 1462, 1391, 1275 (m), 1227 (s), 1176, 1118, 1041, 1024, 998, 907, 877, 800, 788, 722, 639, 540 (m) cm^{-1}; GC-MS (EI, 70 eV): *m/z* (%):



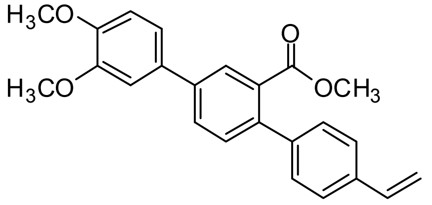
374 (M$^+$, 100), 327 (07), 300 (19), 285 (07), 257 (07), 228 (04), 202 (06), 150 (06), 101 (04), 59 (06); HRMS (EI) calcd for $C_{24}H_{22}O_4$ [M$^+$]: 374.15126, found 374.150994.

4''-Methyl-4-vinyl-(1,1';4',1'')terphenyl-2'-carboxylic acid methyl ester (29c): Starting with



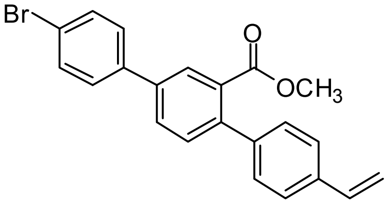
28c (100 mg, 0.26 mmol), K_3PO_4 (114 mg, 0.54 mmol), Pd $(PPh_3)_4$ (3 mol%), 4-vinylphenylboronic acid (50 mg, 0.33 mmol) and 1,4-dioxane (5ml/mmol of triflate), **29e** was isolated as colorless solid; yield 60 mg, (68 %), mp. = 132-134°C; ^{1}H NMR (300 MHz, $CDCl_3$): δ = 2.31 (s, 3H, CH_3), 3.60 (s, 3H, OCH_3), 5.19 (dd, 1H, *J* = 2.4, 9.4 Hz, CH_{2vinyl}), 5.71 (dd, 1H, *J* = 3.8, 8.6 Hz, CH_{2vinyl}), 6.67 (dd, 1H, *J* = 10.8, 17.6 Hz, CH_{vinyl}), 7.15 (d, 2H, *J* = 6.2 Hz, ArH), 7.24 (s, 1H, ArH), 7.35-7.40 (m, 3H, ArH), 7.54-7.66 (m, 4H, ArH), 7.95 (d, 1H, *J* = 1.9 Hz, ArH); ^{13}C NMR (75.47 MHz, $CDCl_3$): δ = 21.2 (CH_3), 52.0 (OCH_3), 113.9 (CH_{2Vinyl}), 126.0, 126.8, 127.1, 128.1, 128.5, 129.5, 131.1, 136.2 (CH_{Ar}), 136.3, 136.5, 137.1, 137.9, 139.0, 139.4, 140.8 (C_{Ar}), 169.3 (C=O). IR (KBr): $\tilde{\nu}$ = 3052, 2946, 2920 (w), 1722, 1604, (s), 1482 (m), 1434, 1308, 1254 (m), 1234 (s), 1164, 1072, 971 (m), 854, 783, 750 (s), 694, 567 (m) cm^{-1}; GC-MS (EI, 70 eV): *m/z* (%): 328 (M$^+$, 100), 297 (24), 282 (05), 253 (11), 157 (11), 126 (06); HRMS (EI) calcd for $C_{23}H_{20}O_2$ [M$^+$]: 328.14578, found 328.146151.

3'',4''-Dimethoxy-4-vinyl-(1,1';4',1'')terphenyl-2'-carboxylic acid methyl ester (29d): Starting

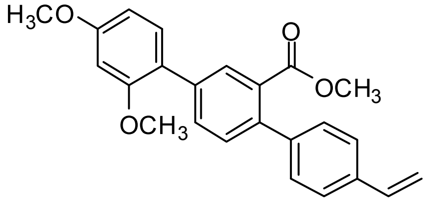


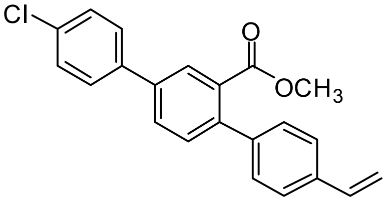
with **28d** (100 mg, 0.23 mmol), K_3PO_4 (114 mg, 0.54 mmol), Pd $(PPh_3)_4$ (3 mol%), 4-vinylphenylboronic acid (42 mg, 0.29 mmol) and 1,4-dioxane (5ml/mmol of triflate), **29d** was isolated as yellow solid; yield 57 mg, (64 %), mp. = 138-140°C; ^{1}H NMR (250 MHz, $CDCl_3$): δ = 3.58 (s, 3H, OCH_3), 3.69 (s, 3H, OCH_3), 3.72 (s, 3H, OCH_3), 5.50 (dd, 1H, *J* = 2.6, 6.4 Hz, CH_{2vinyl}), 5.60 (dd, 1H, *J* = 2.4, 7.2 Hz, CH_{2vinyl}), 5.70 (dd, 1H, *J* = 1.4, 7.8 Hz, CH_{vinyl}), 6.80-6.86 (m, 2H, ArH), 7.22 (d, 1H, *J* = 6.2 Hz, ArH), 7.28-7.38 (m, 4H, ArH), 7.58-7.64 (m, 2H, ArH), 7.88 (d, 1H, *J* = 4.6 Hz, ArH); ^{13}C NMR (62.90 MHz, $CDCl_3$): δ = 52.1 (OCH_3), 53.3 (OCH_3), 55.8 (OCH_3), 111.6, 113.4 (CH_{Ar}), 114.6 (CH_{2vinyl}), 126.7, 127.1, 128.0, 130.5, 134.6, 135.0, 135.1 (CH_{Ar}), 136.0, 136.1, 137.4, 138.5, 139.4, 140.6, 149.1, 151.4 (C_{Ar}), 168.1 (C=O). IR (KBr): $\tilde{\nu}$ = 3050, 2922, 2851 (w), 1721, 1602 (s), 1461, 1433, 1390, 1240, 1215, 1171, 1093, 967, 888, 788, 722 (s), 665, 539 (m) cm^{-1}; GC-MS (EI, 70 eV): *m/z* (%): 374 (M$^+$, 100), 325 (03), 301 (16), 281 (05), 253 (04), 226 (06), 207 (05), 153 (08), 121 (05), 57 (10); HRMS (EI) calcd for $C_{24}H_{22}O_4$ [M$^+$]: 374.12536, found 374.046421.

4''-Bromo-4-vinyl-(1,1';4',1'')terphenyl-2'-carboxylic acid methyl ester (29e): Starting with **28e** (100 mg, 0.22 mmol), K_3PO_4 (114 mg, 0.54 mmol), Pd $(PPh_3)_4$ (3 mol%), 4-vinylphenylboronic acid (42 mg, 0.29 mmol) and 1,4-dioxane (5ml/mmol of triflate), **29e** was isolated as a colorless viscous oil; yield 56 mg, (62 %); ^{1}H NMR (250 MHz, $CDCl_3$): δ = 3.61 (s, 3H, OCH_3), 5.22 (dd, 1H, J = 2.4, 8.4 Hz, CH_{2vinyl}), 5.70 (dd, 1H, J = 2.8, 7.6 Hz, CH_{2vinyl}), 5.77 (dd, 1H, J = 2.4, 8.6 Hz, CH_{vinyl}), 7.24 (d, 2H, J = 6.2 Hz, ArH), 7.36-7.42 (m, 4H, ArH), 7.45 (s, 1H, ArH), 7.56 (d, 2H, J = 6.8 Hz, ArH), 7.66-7.70 (dd, 1H, J = 2.4, 9.6 Hz, ArH), 7.98 (d, 1H, J = 2.3 Hz, ArH); ^{13}C NMR (62.90 MHz, $CDCl_3$): δ = 52.0 (OCH_3), 113.9 (CH_{2vinyl}), 126.0, 126.7, 127.1, 128.2, 128.5, 129.5, 131.1, 136.2 (CH_{Ar}), 136.4, 136.6, 137.1, 138.9, 139.6, 140.3, 140.8 (C_{Ar}), 169.1 (C=O). IR (KBr): $\tilde{\nu}$ = 3084, 2946, 2921 (w), 1716 (s), 1604 (m), 1481 (m), 1455, 1389, 1256 (m), 1235 (s), 1185, 1090, 973 (m), 857, 781, 743 (s), 694, 653, 539 (m) cm^{-1}; GC-MS (EI, 70 eV): *m/z* (%): 392 (M^+, 100), 319 (03), 279 (10), 231 (05), 201 (04), 173 (06), 126 (11), 107 (08), 77 (05), 57 (10); HRMS (EI) calcd for $C_{22}H_{17}BrO_2$ [M^+]: 392.04119, found 393.27318.

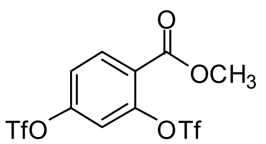


2'',4''-Dimethoxy-4-vinyl-(1,1';4',1'')terphenyl-2'-carboxylic acid methyl ester (29f): Starting with **28f** (100 mg, 0.23 mmol), K_3PO_4 (114 mg, 0.54 mmol), Pd $(PPh_3)_4$ (3 mol%), 4-vinylphenylboronic acid (42 mg, 0.29 mmol) and 1,4-dioxane (5ml/mmol of triflate), **29f** was isolated as a colorless viscous oil; yield 67 mg, (67 %); ^{1}H NMR (300 MHz, $CDCl_3$): δ = 3.59 (s, 3H, OCH_3), 3.75 (s, 3H, OCH_3), 3.79 (s, 3H, OCH_3), 5.20 (dd, 1H, J = 2.4, 10.8 Hz, CH_{2vinyl}), 5.72 (dd, 1H, J = 2.4, 9.6 Hz, CH_{2vinyl}), 6.69 (dd, 1H, J = 2.4, 10.6 Hz, CH_{vinyl}), 7.21-7.24 (m, 3H, ArH), 7.26 (s, 1H, ArH), 7.30-7.39 (m, 4H, ArH), 7.60 (dd, 1H, J = 1.9, 7.9 Hz, ArH), 7.88 (d, 1H, J = 1.6 Hz, ArH); ^{13}C NMR (75.47 MHz, $CDCl_3$): δ = 51.9 (OCH_3), 55.4 (OCH_3), 55.6 (OCH_3), 99.0, 104.8 (CH_{Ar}), 113.8 (CH_{2vinyl}), 125.9, 128.6, 130.3 (CH_{Ar}), 130.4 (C_{Ar}), 130.7, 131.2, 132.0, 136.5 (CH_{Ar}), 136.6, 137.5, 138.9, 139.6, 140.0, 141.6, 142.0 (C_{Ar}), 169.1 (C=O). IR (KBr): $\tilde{\nu}$ = 3052, 2921, 2848 (w), 1716, 1608 (s), 1463, 1435, 1391 (m), 1242, 1217 (s), 1173, 1095, 965, 887, 783, 721, 663, 537(m) cm^{-1}; GC-MS (EI, 70 eV): *m/z* (%): 374 (M^+, 100), 343 (04), 285 (06), 257 (05), 179 (06), 120 (04); HRMS (EI) calcd for $C_{24}H_{22}O_4$ [M^+]: 374.15126, found 374.151040.

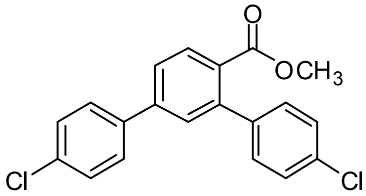




4''-Chloro-4-vinyl-(1,1';4',1'')terphenyl-2'-carboxylic acid methyl ester (29g): Starting with **28g** (100 mg, 0.25 mmol), K_3PO_4 (114 mg, 0.54 mmol), Pd $(PPh_3)_4$ (3 mol%), 4-vinylphenylboronic acid (47 mg, 0.32 mmol) and 1,4-dioxane (5ml/mmol of triflate), **29g** was isolated as reddish solid; yield 65 mg, (74 %), mp. = 152-154°C; ^{1}H NMR (300 MHz, $CDCl_3$): δ = 3.61 (s, 3H, OCH_3), 5.22 (dd, 1H, J = 4.6, 10.8 Hz, CH_{2vinyl}), 5.72 (dd, 1H, J = 4.3, 17.6 Hz, CH_{2vinyl}), 6.69 (dd, 1H, J = 10.8, 17.5 Hz, CH_{vinyl}), 7.21-7.25 (m, 2H, ArH), 7.35-7.41 (m, 2H, ArH), 7.44 (s, 1H, ArH), 7.54 (d, 2H, J = 8.2 Hz, ArH), 7.58-7.62 (m, 2H, ArH), 7.68 (dd, 1H, J = 1.9, 8.6 Hz, ArH), 7.98 (d, 1H, J = 1.9 Hz, ArH); ^{13}C NMR (75.47 MHz, $CDCl_3$): δ = 52.1 (OCH_3), 114.0 (CH_{2vinyl}), 126.0, 126.8, 127.1, 128.2, 129.5, 130.0, 131.1, 136.2 (CH_{Ar}), 136.5, 137.1, 138.9, 139.7, 140.3, 140.8, 141.0 (C_{Ar}), 169.1 (C=O). IR (KBr): $\tilde{\nu}$ = 3054, 2922, 2852 (w), 1715, 1604 (m), 1501, 1462, 1391, 1306, 1275, 1241 (m), 1227 (s), 1176, 11181092, 1024, 998, 907, 877, 800, 788, 722, 639, 540 (m) cm^{-1}; GC-MS (EI, 70 eV): *m/z* (%): 348 (M^+, 100), 317 (13), 282 (31), 254 (18), 226 (07), 156 (16), 126 (10); HRMS (EI) calcd for $C_{22}H_{17}O_2Cl$ [M^+]: 348.09116, found 348.091376.

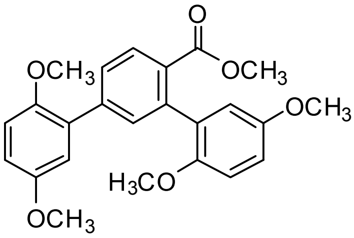


Methyl 2,4-bis(trifluoromethylsulfonyloxy)benzoate (32): Starting with **31** (168 mg, 1.0 mmol), pyridine (0.32 ml, 4.0 mmol) and Tf_2O (0.39 ml, 2.4 mmol), **32** was isolated as colorless oil (382 mg, 88 %); ^{1}H NMR (300 MHz, $CDCl_3$): δ = 3.92 (s, 3H, OCH_3), 7.19 (s, 1H, ArH), 7.35 (d, 1H, J = 8.2 Hz, ArH), 8.17 (d, 1H, J = 8.6 Hz, ArH); ^{13}C NMR (75.46 MHz, $CDCl_3$): δ = 53.1 (OCH_3), 116.1 (CH_{Ar}), 116.8 (q, $J_{F,C}$ = 320.2 Hz, CF_3), 120.8 (CH_{Ar}), 121.4 (q, $J_{F,C}$ = 321.2 Hz, CF_3), 124.7 (C_{Ar}), 133.8 (CH_{Ar}), 148.6, 151.8, (C_{Ar}), 162.7 (C=O). ^{19}F NMR (282 MHz, CDCl3): δ = -72.4, -73.1 ($2CF_3$). IR (KBr): $\tilde{\nu}$ = 3117, 3085, 2960 (w), 1733, 1617 (s), 1583 (m), 1481, 1302, 1277 (m), 1241 (s), 1123, 1073, 975 (m), 873, 780, 758 (s), 697, 580, 541 (m) cm^{-1}; GC-MS (EI, 70 eV): *m/z* (%): 432 (M^+, 61), 401 (61), 363 (06), 337 (52), 273 (77), 207 (53), 179 (15), 138 (10), 107 (34), 95 (06), 79 (22), 69 (100), 51 (16), 39 (03); HRMS (EI) calcd for $C_{10}H_6F_6O_8S_2$ [M^+]: 431.94028 found 431.941432.

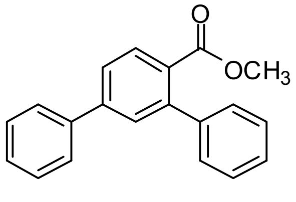


4,4''-Dichloro-[1,1';3',1'']terphenyl-4'-carboxylic acid methyl ester (33a): Starting with **32** (300 mg, 0.69 mmol), K_3PO_4 (440 mg, 2.07 mmol), $Pd(PPh_3)_4$ (6 mol%), 4-chlorophenylboronic acid (280 mg, 1.80 mmol) and 1,4-dioxane (5ml/mmol of triflate), **33a** was isolated as a yellow oil; yield 240 mg, (76 %); ^{1}H NMR (300 MHz, $CDCl_3$): δ = 3.56 (s, 3H, OCH_3), 7.06-7.09 (m, 1H, ArH), 7.19-7.23 (m, 4H, ArH), 7.32-7.34 (m, 2H, ArH), 7.37 (d, 1H, J = 3.2 Hz, ArH), 7.44 (d, 1H, J = 1.9 Hz, ArH), 7.45-7.47 (m, 1H, ArH), 7.82 (d, 1H, J = 8.1 Hz, ArH); ^{13}C NMR (62.90 MHz, $CDCl_3$): δ = 52.2 (OCH_3), 125.4, 126.7, 127.5, 128.2, 129.3 (CH_{Ar}), 129.6 (C_{Ar}), 130.2, 130.9 (CH_{Ar}), 133.9, 134.9, 141.3, 142.0, 142.8, 143.0 (C_{Ar}), 168.0 (C=O). IR (KBr): $\tilde{\nu}$ = 3053, 2945, 2847 (w), 1716 (s), 1593, 1567, 1461, 1432, 1317, 1291 (m), 1231 (s), 1193, 1147, 1091, 1053, 1021, 996, 971, 875 (m), 773, 693 (s), 671, 617, 541 (m) cm^{-1}; GC-MS (EI, 70 eV): *m/z* (%): 356 (M^+, 73), 325 (100), 290 (11), 262 (38), 226 (36), 200 (04), 161 (22), 131 (05), 113 (19); HRMS (EI) calcd for $C_{20}H_{14}O_2Cl_2$ [M^+]: 356.03654, found 356.036629.

2,5,2'',5''-Tetramethoxy-[1,1';3',1'']terphenyl-4'-carboxylic acid methyl ester (33b): Starting with **32** (300 mg, 0.69 mmol), K_3PO_4 (440 mg, 2.07 mmol), $Pd(PPh_3)_4$ (6 mol%), 2,5-dimethoxyphenylboronic acid (327 mg, 1.80 mmol) and 1,4-dioxane (5ml/mmol of triflate), **33b** was isolated as colorless solid; yield 234 mg, (82 %), mp. = 148-150°C; ^{1}H NMR (300 MHz, $CDCl_3$): δ = 3.59 (s, 6H, $2OCH_3$), 3.66 (s, 3H, OCH_3), 3.70 (s, 3H, OCH_3), 3.71 (s, 3H, OCH_3), 6.74 (d, 1H, J = 2.3 Hz, ArH), 6.76 (s, 1H, ArH), 6.78 (d, 1H, J = 2.9 Hz, ArH), 6.82-6.83 (m, 2H, ArH), 6.85 (d, 1H, J = 2.8 Hz, ArH), 7.43 (d, 1H, J = 1.6 Hz, ArH), 7.50 (dd, 1H, J = 1.8, 8.0 Hz, ArH), 7.82 (d, 1H, J = 7.9 Hz, ArH); ^{13}C NMR (62.90 MHz, $CDCl_3$): δ = 51.6 (OCH_3), 55.7 (OCH_3), 55.8 (OCH_3), 56.3 (OCH_3), 111.1, 112.7, 113.0, 113.8, 116.1, 116.5, 128.3, 129.1 (CH_{Ar}), 130.0, 130.3, 131.5 (C_{Ar}), 132.2 (CH_{Ar}), 138.2, 141.7, 150.4, 150.8, 153.6, 153.8 (C_{Ar}), 168.4 (C=O). IR (KBr): $\tilde{\nu}$ = 2928, 2831 (w), 1721, 1601, 1585, 1498, 1461, 1378,1250 (m), 1213 (s), 1175, 1092, 1040, 964, 904, 860, 821, 789 (m), 723 (s), 694, 605, 539 (m) cm^{-1}; GC-MS (EI, 70 eV): *m/z* (%): 408 (M^+, 100), 393 (05), 377 (71), 346 (20), 204 (08); HRMS (EI) calcd for $C_{24}H_{24}O_6$ [M^+]: 408.15674, found 408.156969.

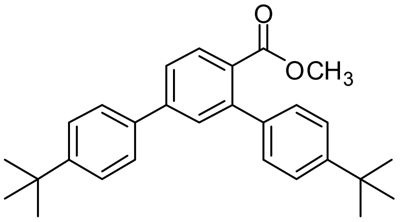


[1,1';3',1'']Terphenyl-4'-carboxylic acid methyl ester (33c): Starting with **32** (300 mg, 0.69 mmol), K_3PO_4 (440 mg, 2.07 mmol), $Pd(PPh_3)_4$ (6 mol%), phenylboronic acid (219 mg, 1.80 mmol) and 1,4-dioxane (5ml/mmol of triflate), **33c** was isolated as a reddish solid; yield 148 mg, (74 %), mp. = 150-152°C; ^{1}H NMR (300 MHz, $CDCl_3$): δ = 3.51 (s, 3H, OCH_3), 7.22-7.25 (m, 4H, ArH), 7.26 (s, 1H, ArH), 7.27-7.30 (m, 3H, ArH), 7.46-7.50 (m, 4H, ArH), 7.79 (dd, 1H, J = 1.7, 7.7 Hz, ArH); ^{13}C NMR (62.89 MHz, $CDCl_3$): δ = 51.9 (OCH_3), 125.7, 127.3, 127.4, 128.0, 128.1,

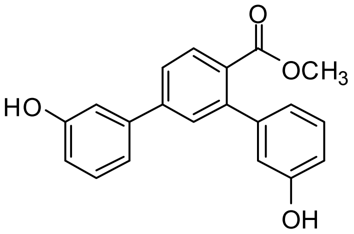


128.4, 128.9 (CH_{Ar}), 129.3 (C_{Ar}), 129.6, 130.6 (CH_{Ar}), 139.8, 141.5, 143.3, 144.1 (C_{Ar}), 168.8 (C=O). IR (KBr): $\tilde{\nu}$= 3052, 2927, 2842 (w), 1716 (s), 1591, 1567, 1467, 1439, 1313, 1295 (m), 1231 (s), 1191, 1143, 1091, 1051, 1027, 993, 970, 873 (m), 779, 691 (s), 673, 618, 559 (m) cm^{-1}; GC-MS (EI, 70 eV): *m/z* (%): 288 (M^+, 75), 257 (100), 228 (34), 202 (08), 152 (05), 128 (04), 113 (08); HRMS (EI) calcd for $C_{20}H_{16}O_2$ [M^+]: 228.11448, found 228.114296.

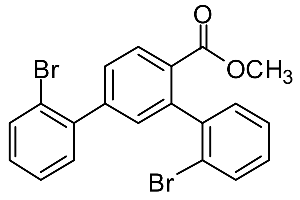
4,4''-Di-*tert*-butyl-[1,1';3',1'']terphenyl-4'-carboxylic acid methyl ester (33d): Starting with **32** (300 mg, 0.69 mmol), K_3PO_4 (440 mg, 2.07 mmol), $Pd(PPh_3)_4$ (6 mol%), 4-*ter*-butylphenylboronic acid (320 mg, 1.80 mmol) and 1,4-dioxane (5ml/mmol of triflate), **33d** was isolated as a colorless solid; yield 86 mg, (72 %), mp. = 168-170°C; ^{1}H NMR (300 MHz, $CDCl_3$): δ= 1.48 (s, 9H, $3CH_3$), 1.50 (s, 9H, $3CH_3$), 3.78 (s, 3H, OCH_3), 7.44 (d, 1H, *J* = 8.3 Hz, ArH), 7.55-7.60 (m, 4H, ArH), 7.68 (s, 1H, ArH), 7.70-7.75 (m, 4H, ArH), 8.00 (d, 1H, *J* = 8.1 Hz, ArH); ^{13}C NMR (75.46 MHz, $CDCl_3$): δ = 31.4 ($3CH_3$), 31.5 ($3CH_3$), 34.5 ($2C_{tBu}$), 51.9 (OCH_3), 125.0, 125.4, 125.9, 127.0, 128.2, 129.5, 130.6 (CH_{Ar}), 133.9, 137.0, 138.5, 143.2, 143.9, 150.1, 151.2 (C_{Ar}), 169.0 (C=O). IR (KBr): $\tilde{\nu}$= 3031, 2951, 2902 (w), 1727, 1605, (s), 1483 (m), 1461, 1362, 1267 (m), 1234 (s), 1180, 1085, 959 (m), 895, 788, 765 (s), 698, 572, 554 (m) cm^{-1}; GC-MS (EI, 70 eV): *m/z* (%): 400 (M^+, 36), 385 (100), 357 (05), 313 (03), 252 (04), 185 (11), 157 (07), 141 (04), 57 (04); HRMS (EI) calcd for $C_{28}H_{32}O_2$ [M^+]: 400.23968, found 400.2399954.



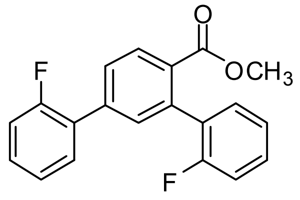
3,3''-Dihydroxy-[1,1';3',1'']terphenyl-4'-carboxylic acid methyl ester (33e): Starting with **32** (300 mg, 0.69 mmol), K_3PO_4 (440 mg, 2.07 mmol), $Pd(PPh_3)_4$ (6 mol%), 3-hydroxyphenylboronic acid (248 mg, 1.80 mmol) and 1,4-dioxane (5ml/mmol of triflate), **33e** was isolated as a colorless viscous oil; yield 138 mg, (62 %); ^{1}H NMR (300 MHz, $CDCl_3$): δ= 3.56 (s, 3H, OCH_3), 6.02 (s, 2H, 2OH), 6.68 (s, 1H, ArH), 6.70.6.75 (m, 3H, ArH), 6.90 (t, 1H, *J* = 1.8 Hz, ArH), 6.98 (d, 1H, *J* = 7.9 Hz, ArH), 7.08 (d, 1H, *J* = 7.5 Hz, ArH), 7.11 (m, 1H, ArH), 7.34 (s, 1H, ArH), 7.37 (d, 1H, *J* = 1.7 Hz, ArH), 7.68 (d, 1H, *J* = 7.9 Hz, ArH); ^{13}C NMR (75.47 MHz, $CDCl_3$): δ = 52.3 (OCH_3), 114.2, 114.5, 115.2, 115.4, 119.6, 120.8, 125.7, 129.2, 129.3, 130.1, 130.3 (CH_{Ar}), 139.0, 141.2, 142.5, 142.6, 143.7, 155.4, 156.0 (C_{Ar}), 169.9 (C=O). IR (KBr): $\tilde{\nu}$= 3058, 2941, 2927 (w), 1721, 1607, (s), 1481 (m), 1462, 1357, 1243 (m), 1221 (s), 1179, 1081, 957 (m), 891, 787, 761 (s), 697, 571, 541 (m) cm^{-1}; GC-MS (EI,



70 eV): *m/z* (%): 320 (M^+, 100), 289 (75), 260 (13), 231 (08), 215 (09), 202 (08), 189 (05), 152 (06), 101 (05); HRMS (EI) calcd for $C_{20}H_{16}O_4$ [M^+]: 320.10431, found 320.104231.

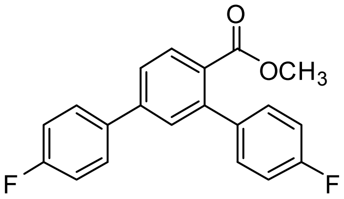


2,2''-Dibromo-[1,1';3',1'']terphenyl-4'-carboxylic acid methyl ester (33f): Starting with **32** (300 mg, 0.69 mmol), K_3PO_4 (440 mg, 2.07 mmol), $Pd(PPh_3)_4$ (6 mol%), 2-bromophenylboronic acid (360 mg, 1.80 mmol) and 1,4-dioxane (5ml/mmol of triflate), **33f** was isolated as a yellow solid; yield 219 mg, (70 %), mp. = 138-140°C; ^{1}H NMR (300 MHz, $CDCl_3$): δ = 3.60 (s, 3H, OCH_3), 7.10-7.15 (m, 2H, ArH), 7.22 (d, 1H, J = 1.9 Hz, ArH), 7.24 (d, 1H, J = 1.5 Hz, ArH), 7.26-7.30 (m, 2H, ArH), 7.43 (dd, 1H, J = 1.8, 8.1 Hz, ArH), 7.52-7.59 (m, 3H, ArH), 8.00 (d, 1H, J = 8.0 Hz, ArH); ^{13}C NMR (62.90 MHz, $CDCl_3$): δ = 52.0 (OCH_3), 122.3, 122.9 (C_{Ar}), 127.0, 127.5, 128.7, 128.8 (CH_{Ar}), 129.0 (C_{Ar}), 129.3, 130.0, 130.1, 131.1, 132.1, 132.6, 133.3 (CH_{Ar}), 141.1, 141.9, 142.4, 144.4 (C_{Ar}), 167.0 (C=O). IR (KBr): $\tilde{\nu}$ = 3052, 2946, 2839 (w), 1716 (s), 1605, 1562, 1474, 1430, 1387 (m), 1286 (s), 1189, 1118, 1060, 1004, 962, 904, 827, 788 (m), 749 (s), 697, 660, 587 (m) cm^{-1}; GC-MS (EI, 70 eV): *m/z* (%): 446 (M^+, 69), 370 (12), 289 (10), 257 (100), 231 (30), 202 (08), 148 (05), 128 (04), 113 (08); HRMS (EI) calcd for $C_{20}H_{14}Br_2O_2$ [M^+]: 446.93605, found 446.13196.

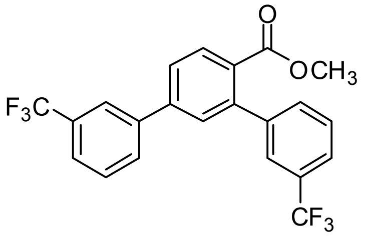


2,2''-Diflouro-[1,1';3',1'']terphenyl-4'-carboxylic acid methyl ester (33g): Starting with **32** (300 mg, 0.69 mmol), K_3PO_4 (440 mg, 2.07 mmol), $Pd(PPh_3)_4$ (6 mol%), 1-flourophenylboronic acid (252 mg, 1.80 mmol) and 1,4-dioxane (5ml/mmol of triflate), **33g** was isolated as a reddish solid; yield 150 mg, (66 %), mp. = 144-146°C; ^{1}H NMR (300 MHz, $CDCl_3$): δ = 3.60 (s, 3H, OCH_3), 6.95-7.10 (m, 4H, ArH), 7.18-7.26 (m, 3H, ArH), 7.35 (dt, 1H, J = 1.8, 7.7 Hz, ArH), 7.43 (t, 1H, J = 1.5 Hz, ArH), 7.53 (dt, 1H, J = 1.7, 8.1 Hz, ArH), 7.95 (d, 1H, J = 8.1 Hz, ArH); ^{13}C NMR (62.90 MHz, $CDCl_3$): δ = 52.0 (OCH_3), 115.0 (d, $^2J_{C,F}$ = 22.2 Hz, CH_{Ar}), 116.2 (d, $^2J_{C,F}$ = 22.5 Hz, CH_{Ar}), 124.0 (d, $^4J_{C,F}$ = 3.5 Hz, CH_{Ar}), 124.5 (d, $^4J_{C,F}$ = 3.7 Hz, CH_{Ar}), 127.5 (d, $^2J_{C,F}$ = 13.0 Hz, CF), 128.4 (d, $^4J_{C,F}$ = 3.3 Hz, CH_{Ar}), 128.9 (C_{Ar}), 129.1 (C_{Ar}), 129.3 (d, $^3J_{C,F}$ = 8.1 Hz, CH_{Ar}), 129.9 (d, $^3J_{C,F}$ = 8.3 Hz, CH_{Ar}), 130.4 (CH_{Ar}), 130.5 (d, $^4J_{C,F}$ = 3.3 Hz, CH_{Ar}), 130.6 (d, $^4J_{C,F}$ = 3.1 Hz, CH_{Ar}), 132.0 (d, $^4J_{C,F}$ = 2.9 Hz, CH_{Ar}), 136.3 (C_{Ar}), 139.4 (d, $^4J_{C,F}$ = 1.0 Hz, CF), 157.7 (d, $^2J_{C,F}$ = 11.5 Hz, CF), 161.6 (d, $^2J_{C,F}$ = 14.3 Hz, CF), 167.5 (C=O). IR (KBr): $\tilde{\nu}$ = 3030, 2950, 2850 (w), 1722 (s), 1614, 1604, 1579, 1494, 1433, 1392, 1284, 1220, 1190, 1109, 1049, 1011, 960, 915, 842 (m), 817, 758 (s), 692, 638, 541 (m) cm^{-1}; GC-MS (EI, 70 eV): *m/z* (%): 324 (M^+, 81), 293 (100), 264 (17), 244 (35), 170 (04), 146 (05), 122 (12); HRMS (EI) calcd for $C_{20}H_{14}O_2F_2$ [M$^+$]: 324.09564, found 324.095647.

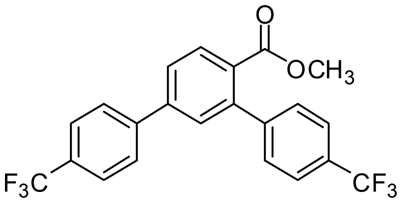
4,4''-Diflouro-[1,1';3',1'']terphenyl-4'-carboxylic acid methyl ester (33h): Starting with **32** (300 mg, 0.69 mmol), K_3PO_4 (440 mg, 2.07 mmol), Pd(PPh_3)$_4$ (6 mol%), 4-flourophenylboronic acid (252 mg, 1.80 mmol) and 1,4-dioxane (5ml/mmol of triflate), **33h** was isolated as a colorless solid; yield 168 mg, (74 %), mp. = 156-158°C; ^{1}H NMR (300 MHz, $CDCl_3$): δ = 3.58 (s, 3H, OCH_3), 6.97-7.06 (m, 4H, ArH), 7.19-7.23 (m, 2H, ArH), 7.40 (d, 1H, J = 1.8 Hz, ArH), 7.46-7.51 (m, 3H, ArH), 7.84 (d, 1H, J = 8.1 Hz, ArH); ^{13}C NMR (62.90 MHz, $CDCl_3$): δ = 51.9 (OCH_3), 114.9 (d, $^2J_{C,F}$ = 21.5 Hz, CH_{Ar}), 115.8 (d, $^2J_{C,F}$ = 21.5 Hz, CH_{Ar}), 125.7 (CH_{Ar}), 128.9 (d, $^3J_{C,F}$ = 8.2 Hz, CH_{Ar}), 129.1 (C_{Ar}), 129.4 (CH_{Ar}), 129.9 (d, $^3J_{C,F}$ = 8.1 Hz, CH_{Ar}), 130.8 (CH_{Ar}), 135.7 (d, $^4J_{C,F}$ = 3.2 Hz, CF), 137.2 (d, $^4J_{C,F}$ = 3.3 Hz, CF), 142.4 (C_{Ar}), 143.1 (C_{Ar}), 162.3 (d, $^1J_{C,F}$ = 246.4 Hz, CF), 162.9 (d, $^1J_{C,F}$ = 247.9 Hz, CF), 168.3 (C=O). IR (KBr): $\tilde{\nu}$ = 3043, 2927, 2843 (w), 1721 (s), 1617, 1603, 1573, 1497, 1431, 1389, 1277, 1221, 1189, 1117, 1051, 1011, 957, 923, 839 (m), 817, 757 (s), 689, 638, 543 (m) cm^{-1}; GC-MS (EI, 70 eV): *m/z* (%): 324 (M$^+$, 81), 293 (100), 264 (20), 244 (25), 170 (04), 122 (08); HRMS (EI) calcd for $C_{20}H_{14}O_2F_2$ [M$^+$]: 324.09564, found 324.09544.



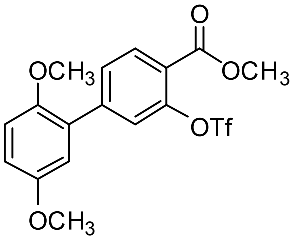
3,3''-Bis-trifluoromethyl-[1,1';3',1'']terphenyl-4'-carboxylic acid methyl ester (33i): Starting with **32** (300 mg, 0.69 mmol), K_3PO_4 (440 mg, 2.07 mmol), Pd(PPh_3)$_4$ (6 mol%), 3-triflouromethylphenylboronic acid (342 mg, 1.80 mmol) and 1,4-dioxane (5ml/mmol of triflate), **33i** was isolated as a colorless viscous oil; yield 203 mg, (69 %); ^{1}H NMR (300 MHz, $CDCl_3$): δ = 3.59 (s, 3H, OCH_3), 7.44-7.48 (m, 4H, ArH), 7.54 (d, 2H, J = 7.6 Hz, ArH), 7.59 (dd, 2H, J = 1.8, 8.1 Hz, ArH), 7.72 (d, 1H, J = 7.6 Hz, ArH), 7.77 (s, 1H, ArH), 7.94 (d, 1H, J = 8.1 Hz, ArH); ^{13}C NMR (62.90 MHz, $CDCl_3$): δ = 52.0 (OCH_3), 121.9 (q, $J_{F,C}$ = 320.0 Hz, CF_3), 122.0 (q, $J_{F,C}$ = 321.0 Hz, CF_3), 124.0 (dq, $J_{C,F}$ = 3.8 Hz, CH_{Ar}), 124.2 (dq, $J_{F,C}$ = 3.9 Hz, CH_{Ar}), 124.9 (q, $J_{C,F}$ = 3.7 Hz, CH_{Ar}), 125.3 (q, $J_{C,F}$ = 3.7 Hz, CH_{Ar}), 126.5, 128.4, 129.5 (CH_{Ar}), 129.8, 130.2 (C_{Ar}), 130.6 (CH_{Ar}), 130.7 (C_{Ar}), 131.2, 131.7, 132.0 (CH_{Ar}), 140.3, 141.9, 142.1, 142.9 (C_{Ar}), 167.8 (C=O). IR (KBr): $\tilde{\nu}$ = 3075, 2952, 2843 (w), 1725 (s), 1606, 1564, 1583, 1428, 1341, 1298 (m), 1244 (s), 1157 (m), 1125, 1071, 1035 (s), 965, 903, 844 (m), 803, 700 (s), 661, 612 (m) cm^{-1}; GC-MS (EI, 70 eV): *m/z* (%): 424 (M$^+$, 57), 405 (09),



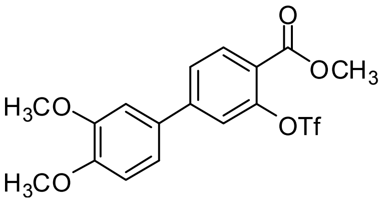
393 (100), 373 (10), 345 (13), 325 (07), 296 (13), 275 (05), 226 (05); HRMS (EI) calcd for $C_{22}H_{14}O_2F_6$ [M$^+$]: 424.08925, found 424.088866.



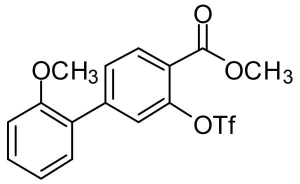
4,4''-Bis-trifluoromethyl-[1,1';3',1'']terphenyl-4'-carboxylic acid methyl ester (33j): Starting with **32** (300 mg, 0.69 mmol), K_3PO_4 (440 mg, 2.07 mmol), $Pd(PPh_3)_4$ (6 mol%), 4-triflouromethylphenylboronic acid (342 mg, 1.80 mmol) and 1,4-dioxane (5ml/mmol of triflate), **33j** was isolated as a yellow solid; yield 172 mg, (76 %), mp. = 142-144°C; ^{1}H NMR (300 MHz, $CDCl_3$): δ = 3.61 (s, 3H, OCH_3), 7.38 (d, 2H, J = 7.9 Hz, ArH), 7.46 (d, 1H, J = 1.7 Hz, ArH), 7.58 (d, 1H, J = 1.7 Hz, ArH), 7.62 (d, 2H, J = 1.8 Hz, ArH), 7.64 (m, 4H, ArH), 7.95 (d, 1H, J = 8.1 Hz, ArH); ^{13}C NMR (62.90 MHz, $CDCl_3$): δ = 52.0 (OCH_3), 121.9 (q, $J_{F,C}$ = 320.0 Hz, CF_3), 122.0 (q, $J_{F,C}$ = 321.0 Hz, CF_3), 124.0 (q, $J_{C,F}$ = 250.2 Hz, CF_3), 124.9 (q, $J_{C,F}$ = 3.8 Hz, CH_{Ar}), 125.9 (q, $J_{F,C}$ = 3.8 Hz, CH_{Ar}), 126.6, 127.6, 128.7, 129.6 (CH_{Ar}), 129.7, 129.8, 130.6 (C_{Ar}), 131.1 (CH_{Ar}), 142.3, 142.9, 143.0, 144.8 (C_{Ar}), 167.8 (C=O). IR (KBr): $\tilde{\nu}$= 3071, 2947, 2841 (w), 1717 (s), 1607, 1563, 1579, 1421, 1343, 1293 (m), 1241 (s), 1161 (m), 1131, 1077, 1031 (s), 967, 907, 844 (m), 805, 703 (s), 661, 613 (m) cm^{-1}; GC-MS (EI, 70 eV): *m/z* (%): 424 (M$^+$, 56), 405 (10), 393 (100), 373 (07), 345 (11), 325 (07), 296 (20), 275 (05), 226 (05); HRMS (EI) calcd for $C_{22}H_{14}O_2F_6$ [M$^+$]: 424.08925, found 424.089297.



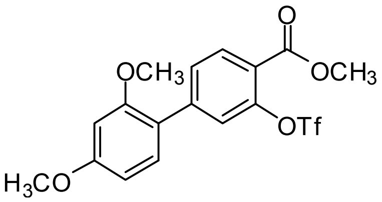
2',5'-Dimethoxy-3-trifluoromethanesulfonyloxy-biphenyl-4-carboxylic acid methyl ester (34a): Starting with **32** (300 mg, 0.69 mmol), K_3PO_4 (219 mg, 1.03 mmol), $Pd(PPh_3)_4$ (6 mol%), 2,5-dimethoxyphenylboronic acid (163 mg, 0.90 mmol) and 1,4-dioxane (5ml/mmol of triflate), **34a** was isolated as a colorless viscous oil; yield 199 mg, (68 %); ^{1}H NMR (300 MHz, $CDCl_3$): δ = 3.67 (s, 3H, OCH_3), 3.71 (s, 3H, OCH_3), 3.88 (s, 3H, OCH_3), 6.80-6.84 (m, 3H, ArH), 7.47 (s, 1H, ArH), 7.52 (dd, 1H, J = 1.6, 8.3 Hz, ArH), 8.00 (d, 1H, J = 8.1 Hz, ArH); ^{13}C NMR (62.90 MHz, $CDCl_3$): δ = 52.5 (OCH_3), 55.8 (OCH_3), 56.0 (OCH_3), 112.8, 114.8, 116.3 (CH_{Ar}), 121.3 (q, $J_{F,C}$ = 320.0 Hz, CF_3), 122.2 (C_{Ar}), 123.8 (CH_{Ar}), 127.9 (C_{Ar}), 129.0, 132.2 (CH_{Ar}), 145.0, 147.9, 150.6, 153.8 (C_{Ar}), 164.1 (C=O). ^{19}F NMR (282 MHz, CDCl3): δ = -73.4 (CF). IR (KBr): $\tilde{\nu}$= 3001, 2953, 2837 (w), 1725, 1614, 1553, 1510, 1464 (m), 1421 (s), 1387, 1270, 1246 (m), 1202, 1135, 1072 (s), 1022, 893, 824, 778, 730, 664, 571 (m) cm^{-1}; GC-MS (EI, 70 eV): *m/z* (%): 420 (M$^+$, 100), 389 (06), 255 (11), 240 (15), 187 (17), 162 (05), 114 (04), 69 (05); HRMS (EI) calcd for $C_{17}H_{15}F_3O_7S$ [M$^+$]: 420.04851 found 420.048583.



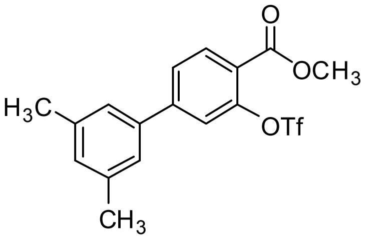
3',4'-Dimethoxy-3-trifluoromethanesulfonyloxy-biphenyl-4-carboxylic acid methyl ester (34b): Starting with **32** (300 mg, 0.69 mmol), K_3PO_4 (219 mg, 1.03 mmol), $Pd(PPh_3)_4$ (6 mol%), 3,4-dimethoxyphenylboronic acid (163 mg, 0.90 mmol) and 1,4-dioxane (5ml/mmol of triflate), **34b** was isolated as a colorless solid; yield 210 mg, (72 %); mp. = 148-150°C; ^{1}H NMR (300 MHz, $CDCl_3$): δ = 3.82 (s, 3H, OCH_3), 3.85 (s, 3H, OCH_3), 3.86 (s, 3H, OCH_3), 6.97 (d, 1H, J = 2.1 Hz, ArH), 7.05 (dd, 1H, J = 2.1, 8.3 Hz, ArH), 7.20 (s, 1H, ArH), 7.33 (d, 1H, J = 1.3 Hz, ArH), 7.52 (d, 1H, J = 1.7, 8.1 Hz, ArH), 8.00 (d, 1H, J = 8.2 Hz, ArH); ^{13}C NMR (62.90 MHz, $CDCl_3$): δ = 52.4 (OCH_3), 55.2 (OCH_3), 56.4 (OCH_3), 110.1, 111.6, 119.9 (CH_{Ar}), 120.2 (q, $J_{F,C}$ = 320.2 Hz, CF_3), 120.6, 126.1 (CH_{Ar}), 127.7, 131.6 (C_{Ar}), 133.0 (CH_{Ar}), 147.5, 148.6, 149.5, 150.2 (C_{Ar}), 168.2 (C=O). ^{19}F NMR (282 MHz, CDCl3): δ = -73.2 (CF). IR (KBr): $\tilde{\nu}$ = 2999, 2952, 2849 (w), 1726 (m), 1603, 1588 (w), 1520, 1463 (m), 1421 (s), 1325, 1289, 1171, 1080, 1052, 974, 905, 883, 827, 806, 755, 684, 664, 573 (m) cm^{-1}; GC-MS (EI, 70 eV): *m/z* (%): 420 (M^+, 100), 389 (07), 259 (62), 228 (09), 185 (05), 157 (04), 114 (06), 69 (06); HRMS (EI) calcd for $C_{17}H_{15}F_3O_7S$ [M^+]: 420.04731 found 420.037247.



2'-Methoxy-3-trifluoromethanesulfonyloxy-biphenyl-4-carboxylic acid methyl ester (34c): Starting with **32** (300 mg, 0.69 mmol), K_3PO_4 (219 mg, 1.03 mmol), $Pd(PPh_3)_4$ (6 mol%), 2-methoxyphenylboronic acid (136 mg, 0.90 mmol) and 1,4-dioxane (5ml/mmol of triflate), **34c** was isolated as a colorless crystalline solid; yield 190 mg, (70 %); mp. = 150-152°C; ^{1}H NMR (300 MHz, $CDCl_3$): δ = 3.74 (s, 3H, OCH_3), 3.89 (s, 3H, OCH_3), 6.91-7.00 (m, 2H, ArH), 7.22-7.32 (m, 2H, ArH), 7.47 (s, 1H, ArH), 7.53 (dd, 1H, J = 1.6, 8.7 Hz, ArH), 8.03 (d, 1H, J = 8.1 Hz, ArH); ^{13}C NMR (62.89 MHz, $CDCl_3$): δ = 52.5 (OCH_3), 55.4 (OCH_3), 111.4, 121.1 (CH_{Ar}), 122.0 (q, $J_{F,C}$ = 321.0 Hz, CF_3), 123.8, 129.0 (CH_{Ar}), 127.1 (C_{Ar}), 130.4, 130.6, 132.2 (CH_{Ar}), 145.2, 146.1, 147.9, 156.3 (C_{Ar}), 164.2 (C=O). ^{19}F NMR (282 MHz, CDCl3): δ = -73.5 (CF_3). IR (KBr): $\tilde{\nu}$ = 3072, 2954, 2918 (w), 1726 (s), 1687 (w), 1615 (m), 1582 (w), 1483 (m), 1422 (s), 1397, 1292 (m), 1245 (s), 1136, 1073 (s), 969 (w), 914 (s), 858 (w), 826 (s), 783 (m), 752 (s), 695, 568 (m) cm^{-1}; GC-MS (EI, 70 eV): *m/z* (%): 390 (M^+, 100), 359 (19), 225 (27), 197 (11), 169 (21), 155 (10), 69 (07); HRMS (EI) calcd for $C_{16}H_{13}F_3O_6S$ [M^+]: 390.03794 found 390.037761.

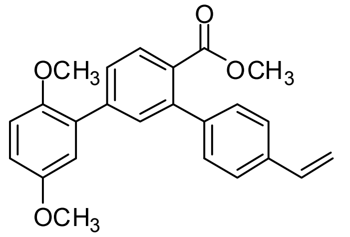


2',4'-Dimethoxy-3-trifluoromethanesulfonyloxy-biphenyl-4-carboxylic acid methyl ester (34d): Starting with **32** (300 mg, 0.69 mmol), K_3PO_4 (219 mg, 1.03 mmol), $Pd(PPh_3)_4$ (6 mol%), 2,4-dmethoxyphenylboronic acid (136 mg, 0.90 mmol) and 1,4-dioxane (5ml/mmol of triflate), **34d** was isolated as a colorless crystalline solid; yield 190 mg, (70 %); mp. = 150-152°C; ^{1}H NMR (300 MHz, $CDCl_3$): δ = 3.73 (s, 3H, OCH_3), 3.78 (s, 3H, OCH_3), 3.89 (s, 3H, OCH_3), 6.48-6.52 (m, 2H, ArH), 7.15-7.22 (m, 2H, ArH), 7.67 (dd, 1H, J = 2.4, 8.5 Hz, ArH), 8.1 (d, 1H, J = 2.3 Hz, ArH); ^{13}C NMR (62.90 MHz, $CDCl_3$): δ = 52.5 (OCH_3), 55.4 (OCH_3), 55.5 (OCH_3), 99.0, 104.9 (CH_{Ar}), 120.0 (q, $J_{F,C}$ = 320.0 Hz, CF_3), 122.1 (CH_{Ar}), 123.7 (C_{Ar}), 131.1, 133.4 (CH_{Ar}), 134.9 (C_{Ar}), 135.0 (CH_{Ar}), 139.0, 146.6, 157.4, 161.2 (C_{Ar}), 168.4 (C=O). ^{19}F NMR (282 MHz, CDCl3): δ = -73.5 (CF). IR (KBr): $\tilde{\nu}$ = 2921, 2871 (w), 1727 (m), 1677, 1609, 1578 (w), 1512, 1463 (m), 1422 (s), 1305, 1281, 1160, 1074, 1053, 967, 905, 890, 835, 797, 761, 686, 638, 571 (m) cm^{-1}; GC-MS (EI, 70 eV): *m/z* (%): 420 (M^+, 38), 389 (05), 287 (100), 257 (11), 229 (04), 185 (10), 128 (06), 69 (08); HRMS (EI) calcd for $C_{17}H_{15}F_3O_7S$ [M^+]: 420.04851 found 420.049176.



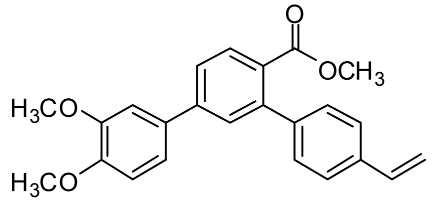
Methyl 3',5'-dimethyl-3-(trifluoromethylsulfonyloxy)biphenyl-4-carboxylate (34e): Starting with **32** (200 mg, 0.46 mmol), K_3PO_4 (146 mg, 0.69 mmol), Pd $(PPh_3)_4$ (3 mol%), 3,5-dimethylphenylboronic acid (88 mg, 0.59 mmol) and 1,4-dioxane (5ml/mmol of triflate), **34e** was isolated as colorless oil; yield 150 mg, (83 %); ^{1}H NMR (300 MHz, $CDCl_3$): δ = 2.25 (s, 6H, $2CH_3$), 3.59 (s, 3H, OCH_3), 6.81 (s, 1H, ArH), 6.92 (s, 1H, ArH), 7.15 (s, 1H, ArH), 7.34 (d, 1H, J = 3.4 Hz, ArH), 7.36 (s, 1H, ArH), 7.61 (d, 1H, J = 3.4 Hz, ArH); ^{13}C NMR (62.89 MHz, $CDCl_3$): δ = 21.1 ($2CH_3$), 52.4 (OCH_3), 120.0 (q, $J_{F,C}$ = 320 Hz, CF_3), 122.6, 123.4, 126.0, 129.3, 132.4 (CH_{Ar}), 137.7, 139.2, 141.1, 143.0, 148.0 (C_{Ar}), 167.1 (C=O). ^{19}F NMR (282 MHz, CDCl3): δ = -73.4 (CF). IR (KBr): $\tilde{\nu}$ = 3016, 2948, 2920 (w), 1723, 1600 (s), 1485 (m), 1462, 1324, 1268 (m), 1241 (s), 1136, 1099, 975 (m), 861, 785, 753 (s), 699, 577, 540 (m) cm^{-1}; GC-MS (EI, 70 eV): *m/z* (%): 388 (M^+, 66), 357 (07), 255 (100), 227 (12), 152 (15), 115 (03), 69 (08); HRMS (EI) calcd for $C_{17}H_{15}F_3O_5S$ [M^+]: 388.05868 found 388.05878.

2,5-Dimethoxy-4''-vinyl-[1,1';3',1'']terphenyl-4'-carboxylic acid methyl ester (35a): Starting



with **34a** (150 mg, 0.36 mmol), K_3PO_4 (114 mg, 0.54 mmol), Pd $(PPh_3)_4$ (3 mol%), 4-vinylphenylboronic acid (69 mg, 0.47 mmol) and 1,4-dioxane (5ml/mmol of triflate), **35a** was isolated as yellow solid; yield 83 mg, (62 %), mp. = 156-158°C; ^{1}H NMR (300 MHz, $CDCl_3$): δ= 3.59 (s, 3H, OCH_3), 3.71 (s, 3H, OCH_3), 3.74 (s, 3H, OCH_3), 5.19 (d, 1H, J = 10.8 Hz, CH_{2vinyl}), 5.71 (d, 1H, J = 17.5 Hz, CH_{2vinyl}), 6.67 (d, 1H, J = 6.3 Hz, CH_{vinyl}), 6.82 (d, 3H, J = 6.4 Hz, ArH), 7.24 (d, 2H, J = 7.3 Hz, ArH), 7.36 (d, 2H, J = 7.3 Hz, ArH), 7.46 (s, 1H, ArH), 7.50 (d, 1H, J = 7.8 Hz, ArH), 7.80 (d, 1H, J = 7.7 Hz, ArH); ^{13}C NMR (62.90 MHz, $CDCl_3$): δ = 51.9 (OCH_3), 55.8 (OCH_3), 56.3 (OCH_3), 112.7 (CH), 113.8 (CH_{2vinyl}), 113.9, 116.5, 125.8, 128.3, 128.6, 129.7 (CH_{Ar}), 130.2 (C_{Ar}), 131.7 (CH_{Ar}), 136.4 (C_{Ar}), 136.5 (CH_{Ar}), 135.0, 140.9, 141.6, 142.0, 150.7, 153.8 (C_{Ar}), 168.9 (C=O). IR (KBr): $\tilde{\nu}$= 2996, 2832 (w), 1716 (s), 1600, 1553, 1483, 1431, 1379 (m), 1266, 1211 (s), 1138 (m), 1095, 1021, 1012 (s), 989, 906, 877 (m), 843 (s), 827, 752, 688, 631, 542 (m) cm^{-1}; GC-MS (EI, 70 eV): *m/z* (%): 374 (M^+, 100), 343 (04), 327 (06), 300 (15), 285 (10), 257 (06), 227 (04), 202 (07), 180 (04), 150 (06), 101 (04), 59 (06); HRMS (EI) calcd for $C_{24}H_{22}O_4$ [M^+]: 374.15126, found 374.151271.

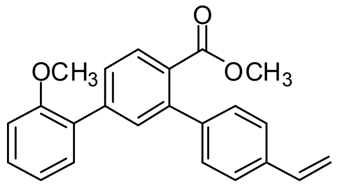
3,4-Dimethoxy-4''-vinyl-[1,1';3',1'']terphenyl-4'-carboxylic acid methyl ester (35b): Starting



with **34b** (150 mg, 0.36 mmol), K_3PO_4 (114 mg, 0.54 mmol), Pd $(PPh_3)_4$ (3 mol%), 4-vinylphenylboronic acid (69 mg, 0.47 mmol) and 1,4-dioxane (5ml/mmol of triflate), **35b** was isolated as yellow solid; yield 88 mg, (66 %), mp. = 142-144°C; ^{1}H NMR (300 MHz, $CDCl_3$): δ= 3.57 (s, 3H, OCH_3), 3.81 (s, 3H, OCH_3), 3.83 (s, 3H, OCH_3), 5.17 (d, 1H, J = 11.1 Hz, CH_{2vinyl}), 5.69 (d, 1H, J = 17.5 Hz, CH_{2vinyl}), 6.66 (dd, 1H, J = 10.9, 17.6 Hz, CH_{vinyl}), 6.84 (d, 1H, J = 8.3 Hz, ArH), 7.03 (d, 1H, J = 1.8 Hz, ArH), 7.10 (dd, 1H, J = 2.0, 8.3 Hz, ArH), 7.22 (d, 2H, J = 8.1 Hz, ArH), 7.36 (d, 1H, J = 8.1 Hz, ArH), 7.44 (d, 2H, J = 1.5 Hz, ArH), 7.48 (dd, 1H, J = 1.7, 8.0 Hz, ArH), 7.82 (d, 1H, J = 8.0 Hz, ArH); ^{13}C NMR (62.90 MHz, $CDCl_3$): δ = 52.1 (OCH_3), 55.9 (OCH_3), 56.0 (OCH_3), 111.3, 111.5 (CH_{Ar}), 113.9 (CH_{2vinyl}), 119.7, 125.4, 125.9, 128.6, 129.0, 130.7 (CH_{Ar}), 132.6 (C_{Ar}), 136.4 (CH_{Ar}), 136.6, 137.0, 138.2, 141.0, 142.9, 143.9, 149.3 (C_{Ar}), 168.6 (C=O). IR (KBr): $\tilde{\nu}$= 2998, 2835 (w), 1715 (s), 1600, 1518, 1485, 1462, 1432, 1379, 1283 (m), 1246 (s), 1212, 1170, 1097, 1041, 990, 905, 843, 808, 784, 732, 682, 620, 541 (m) cm^{-1}; GC-MS (EI, 70 eV): *m/z* (%): 374 (M^+, 100), 359 (04), 331

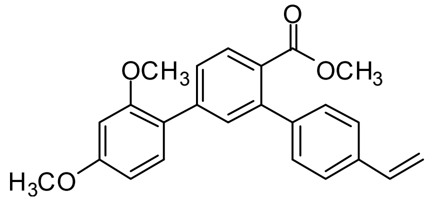
(07), 301 (12), 281 (06), 253 (08), 226 (06), 207 (05), 153 (08), 121 (05), 57 (10); HRMS (EI) calcd for $C_{24}H_{22}O_4$ [M^+]: 374.15126, found 374.151281.

2-Methoxy-4''-vinyl-[1,1';3',1'']terphenyl-4'-carboxylic acid methyl ester (35c): Starting with



34c (150 mg, 0.36 mmol), K_3PO_4 (114 mg, 0.54 mmol), Pd $(PPh_3)_4$ (3 mol%), 4-vinylphenylboronic acid (69 mg, 0.47 mmol) and 1,4-dioxane (5ml/mmol of triflate), **35c** was isolated as white solid; yield 85 mg, (64 %), mp. = 160-162°C. ^{1}H NMR (250 MHz, $CDCl_3$): δ = 3.58 (s, 3H, OCH_3), 3.72 (s, 3H, OCH_3), 5.17 (d, 1H, *J* = 10.9 Hz, CH_{2vinyl}), 5.68 (d, 1H, *J* = 17.6 Hz, CH_{2vinyl}), 6.67 (dd, 1H, *J* = 10.9, 17.6 Hz, CH_{vinyl}), 6.94 (dd, 2H, *J* = 7.9, 14.0 Hz, ArH), 7.22-7.29 (m, 4H, ArH), 7.36 (d, 1H, *J* = 8.1 Hz, ArH), 7.46 (d, 1H, *J* = 1.2 Hz, ArH), 7.50 (dd, 1H, *J* = 1.6, 8.0 Hz, ArH), 7.42 (s, 1H, ArH), 7.80 (d, 1H, *J* = 8.0 Hz, ArH); ^{13}C NMR (62.90 MHz, $CDCl_3$): δ = 51.9 (OCH_3), 55.5 (OCH_3), 111.3 (CH_{Ar}), 113.8 (CH_{2vinyl}), 120.9, 125.8, 128.3, 128.6 (CH_{Ar}), 128.8 (C_{Ar}), 129.4, 129.7, 130.7, 131.8 (CH_{Ar}), 136.4 (C_{Ar}), 136.5 (CH_{Ar}), 141.0, 141.8, 141.9, 142.6, 156.4 (C_{Ar}), 168.9 (C=O). IR (KBr): $\tilde{\nu}$ = 3002, 2947, 2835 (w), 1716 (s), 1627, 1580, 1513, 1498, 1461, 1386 (m), 1243 (s), 1180, 1137, 1120, 1055, 1024, 1005, 904, 786 (m), 750 (s), 715, 637, 574, 541 (m) cm^{-1}; GC-MS (EI, 70 eV): *m/z* (%): 344 (M^+, 100), 313 (24), 285 (06), 270 (10), 239 (10), 164 (06), 119 (04); HRMS (EI) calcd for $C_{23}H_{20}O_3$ [M^+]: 344.14070, found 344.140881.

2,4-Dimethoxy-4''-vinyl-[1,1';3',1'']terphenyl-4'-carboxylic acid methyl ester (35d): Starting



with **34d** (150 mg, 0.36 mmol), K_3PO_4 (114 mg, 0.54 mmol), Pd $(PPh_3)_4$ (3 mol%), 4-vinylphenylboronic acid (69 mg, 0.47 mmol) and 1,4-dioxane (5ml/mmol of triflate), **35d** was isolated as a colorless solid; yield 80 mg, (60 %), mp. = 160-162°C. ^{1}H NMR (300 MHz, $CDCl_3$): δ = 3.59 (s, 3H, OCH_3), 3.75 (s, 3H, OCH_3), 3.79 (s, 3H, OCH_3), 5.20 (dd, 1H, *J* = 2.4, 10.8 Hz, CH_{2vinyl}), 5.72 (dd, 1H, *J* = 2.4, 9.6 Hz, CH_{2vinyl}), 6.69 (dd, 1H, *J* = 2.4, 10.6 Hz, CH_{vinyl}), 7.21-7.24 (m, 3H, ArH), 7.26 (s, 1H, ArH), 7.30-7.39 (m, 4H, ArH), 7.60 (dd, 1H, *J* = 1.9, 7.9 Hz, ArH), 7.88 (d, 1H, *J* = 1.6 Hz, ArH); ^{13}C NMR (75.47 MHz, $CDCl_3$): δ = 51.9 (OCH_3), 55.4 (OCH_3), 55.6 (OCH_3), 99.0, 104.8 (CH_{Ar}), 113.8 (CH_{2vinyl}), 125.9, 128.6, 130.3 (CH_{Ar}), 130.4 (C_{Ar}), 130.7, 131.2, 132.0, 136.5 (CH_{Ar}), 136.6, 137.5, 138.9, 139.6, 140.0, 141.6, 142.0 (C_{Ar}), 169.1 (C=O). IR (KBr): $\tilde{\nu}$ = 3052, 2921, 2848 (w), 1716, 1608 (s), 1463, 1435, 1391 (m), 1242, 1217 (s), 1173, 1095, 965, 887, 783, 721, 663, 537(m) cm^{-1}; GC-MS (EI, 70 eV):

m/z (%): 374 (M^+, 100), 343 (04), 285 (06), 257 (05), 179 (06), 120 (04); HRMS (EI) calcd for $C_{24}H_{22}O_4$ [M^+]: 374.15126, found 374.151040.

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X-Ray Crystals Data

Data for Compound 4 Chapter 2:

Identification code	av_mn41	
Empirical formula	$C_{17}H_{10}F_6O_9S_2$	
Formula weight	$M_r = 536.37$	
Temperature	$T = 173$ K	
Wavelength	0.71073 Å	
Crystal system	Orthorhombic	
Space group (H.-M.)	'P 21 21 21'	
Space group (Hall)	'P 2ac 2ab'	
Unit cell dimensions	$a = 7.3168$ (5) Å	$\alpha = 90.00°$
	$b = 11.9492$ (5) Å	$\beta = 90.00°$
	$c = 23.5888$ (14) Å	$\gamma = 90.00°$
Volume	2062.4 (2) $Å^3$	
Z	4	
Crystal Density (Calculated)	1.727 Mg m^{-3}	
Absorption coefficient	0.36 mm^{-1}	
F(000)	1080	
Crystal size	0.40 × 0.19 × 0.06 mm	
Θ range for data collection	4.4°–27.5°	
Reflections collected	10600	
Independent reflections	4696 [R(int) = 0.035]	
Completeness to $\Theta = 29.00°$	98.7%	
Absorption correction	multi-scan	
Max. and min. transmission	0.869 and 0.979	
Refinement method	phi and psi scans	
Data / restraints / parameters	3761 / 0 / 309	
Goodness-of-fit on F^2	1.07	
Final R indices [$I>2\sigma(I)$]	R1 = 0.0798, wR2 = 0.1533	
R indices (all data)	R1 = 0.0617, wR2 = 0.1455	
Largest diff. peak and hole	0.782 and -0.317 e.$Å^{-3}$	

Data for Compound 6a Chapter 2:

Identification code	av_mn42	
Empirical formula	$C_{29}H_{24}O_3$	
Formula weight	420.48	
Temperature	173(2) K	
Wavelength	0.71073 Å	
Crystal system	Monoclinic	
Space group (H.-M.)	$P2_1/c$	
Space group (Hall)	-P 2ybc	
Unit cell dimensions	a = 13.7757 (10) Å	α= 90.00°
	b = 14.2815 (9) Å	β= 116.716 (2)°
	c = 12.4993 (9) Å	γ= 90.00°
Volume	2196.6 (3) Å^3	
Z	4	
Density (calculated)	1.271 Mg m^{-3}	
Absorption coefficient	0.08 mm^{-1}	
F(000)	888	
Crystal size	0.70 × 0.47 × 0.29 mm	
Θ range for data collection	1.7° to 29.0°.	
Reflections collected	22988	
Independent reflections	5817 [R(int) = 0.027]	
Completeness to Θ = 29.00°	99.6%	
Absorption correction	multi-scan	
Max. and min. transmission	0.9453 and 0.9768	
Refinement method	phi and psi scans	
Data / restraints / parameters	4737 / 0 / 292	
Goodness-of-fit on F2	1.10	
Final R indices [$I>2\sigma(I)$]	R1 = 0.0567, wR2 = 0.1388	
R indices (all data)	R1 = 0.0459, wR2 = 0.1317	
Largest diff. peak and hole	0.376 and -0.290 e.Å-3	

Data for Compound 7g Chapter 2:

Identification code	av_mn70b	
Empirical formula	$C_{25}H_{21}F_3O_9S$	
Formula weight	554.49	
Temperature	173(2) K	
Wavelength	0.71073 Å	
Crystal system	Monoclinic	
Space group (H.-M.)	$P2_1/c$	
Space group (Hall)	-P 2ybc	
Unit cell dimensions	a = 13.8684 (11) Å	α= 90.00°
	b = 15.6453 (12) Å	β= 98.288 (2)°
	c = 12.9560 (8) Å	γ= 90.00°
Volume	2781.8 (4) $Å^3$	
Z	4	
Density (calculated)	1.527 Mg m^{-3}	
Absorption coefficient	0.381 mm^{-1}	
F(000)	1312	
Crystal size	0.47 × 0.22 × 0.10 mm	
Θ range for data collection	3.4° to 27.8°.	
Reflections collected	24192	
Independent reflections	6561 [R(int) = 0.027]	
Completeness to Θ = 29.00°	99.4%	
Absorption correction	multi-scan	
Max. and min. transmission	0.8413 and 0.9629	
Refinement method	phi and psi scans	
Data / restraints / parameters	5043 / 0 / 374	
Goodness-of-fit on F^2	1.090	
Final R indices [I>2σ(I)]	R1 = 0.0615, wR2 = 0.1279	
R indices (all data)	R1 = 0.0441, wR2 = 0.1205	
Largest diff. peak and hole	0.491 and -0.667 e.$Å^{-3}$	

Data for Compound 14b Chapter 2:

Identification code	av_mn214	
Empirical formula	$C_{25}H_{16}F_2O$	
Formula weight	370.38	
Temperature	173(2) K	
Wavelength	0.71073 Å	
Crystal system	Monoclinic	
Space group (H.-M.)	*C*2/*c*	
Space group (Hall)	-C 2yc	
Unit cell dimensions	a = 25.4358 (6) Å	α= 90.0°
	b =11.8456 (3) Å	β= 126.439 (1)°
	c = 15.2452 (4) Å	γ= 90.0°
Volume	3695.35 (16) $Å^3$	
Z	8	
Density (calculated)	1.331 Mg m^{-3}	
Absorption coefficient	0.09 mm^{-1}	
Crystal size	0.50 × 0.28 × 0.24 mm	
Θ range for data collection	2.7° to 27.5°.	
Reflections collected	22802	
Independent reflections	4241 [R(int) = 0.025]	
Completeness to Θ = 29.00°	97.7 %	
Absorption correction	multi-scan	
Max. and min. transmission	0.955 and 0.978	
Refinement method	phi and psi scans	
Data / restraints / parameters	3323 / 0 / 253	
Goodness-of-fit on F^2	1.09	
Final R indices [I>2σ(I)]	R1 = 0.046, wR2 = 0.1421	
R indices (all data)	R1 = 0.062, wR2 = 0.1331	
Largest diff. peak and hole	0.808 and -0.319 e.$Å^{-3}$	

Data for Compound 15f Chapter 2:

Identification code	av_mn215b	
Empirical formula	$C_{24}H_{21}F_3O_4S$	
Formula weight	462.47	
Temperature	173(2) K	
Wavelength	0.71073 Å	
Crystal system	Monoclinic	
Space group (H.-M.)	$P2_1/c$	
Space group (Hall)	P 2ybc	
Unit cell dimensions	a = 18.5491 (11) Å	α= 90.0°
	b =10.8383 (5) Å	β= 100.602 (2)°
	c = 11.2417 (7) Å	γ= 90.0°
Volume	2221.5 (2) $Å^3$	
Z	4	
Density (calculated)	1.383 Mg m^{-3}	
Absorption coefficient	0.21 mm^{-1}	
Crystal size	0.80 × 0.14 × 0.06 mm	
Θ range for data collection	2.6° to 29.0°.	
Reflections collected	22333	
Independent reflections	5906 [R(int) = 0.042]	
Completeness to Θ = 29.00°	99.6 %	
Absorption correction	multi-scan	
Max. and min. transmission	0.857 and 0.988	
Refinement method	phi and psi scans	
Data / restraints / parameters	3674 / 0 / 292	
Goodness-of-fit on F^2	1.01	
Final R indices [I>2σ(I)]	R1 = 0.087, wR2 = 0.1096	
R indices (all data)	R1 = 0.043, wR2 = 0.0987	
Largest diff. peak and hole	0.232 and -0.360 e.$Å^{-3}$	

Data for Compound 15h Chapter 2:

Identification code	av_mn218	
Empirical formula	$C_{22}H_{17}F_3O_4S$	
Formula weight	434.42	
Temperature	173(2) K	
Wavelength	0.71073 Å	
Crystal system	Monoclinic	
Space group (H.-M.)	$P2_1/c$	
Space group (Hall)	-P 2ybc	
Unit cell dimensions	a = 17.7277 (7) Å	α= 90.0°
	b =8.9214 (5) Å	β= 97.313 (3)°
	c = 12.6395 (6) Å	γ= 90.0°
Volume	1982.75 (17) Å^3	
Z	4	
Density (calculated)	1.455 Mg m^{-3}	
Absorption coefficient	0.22 mm^{-1}	
Crystal size	0.93 × 0.73 × 0.07 mm	
Θ range for data collection	2.6° to 30.0°.	
Reflections collected	19639	
Independent reflections	5772 [R(int) = 0.043]	
Completeness to Θ = 29.00°	99.7 %	
Absorption correction	multi-scan	
Max. and min. transmission	0.823 and 0.985	
Refinement method	phi and psi scans	
Data / restraints / parameters	3587 / 0 / 272	
Goodness-of-fit on F^2	1.01	
Final R indices [$I>2\sigma(I)$]	R1 = 0.0931, wR2 = 0.1273	
R indices (all data)	R1 = 0.0464, wR2 = 0.1150	
Largest diff. peak and hole	0.405 and -0.464 e.Å^{-3}	

Data for Compound 19c Chapter 2:

Identification code	av_mn152	
Empirical formula	$C_{29}H_{26}O_2$	
Formula weight	390.50	
Temperature	173(2) K	
Wavelength	0.71073 Å	
Crystal system	Monoclinic	
Space group (H.-M.)	$P2_1/c$	
Space group (Hall)	-P 2ybc	
Unit cell dimensions	a = 18.055 (4) Å	α= 90.00°
	b =8.1746 (16) Å	β= 111.43 (3)°
	c = 16.069 (3) Å	γ= 90.00°
Volume	2207.7 (8) $Å^3$	
Z	4	
Density (calculated)	1.175 Mg m^{-3}	
Absorption coefficient	0.07 mm^{-1}	
F(000)	832	
Crystal size	1.21 × 0.29 × 0.13 mm	
Θ range for data collection	4.2° to 28.5°.	
Reflections collected	4435	
Independent reflections	5560 [R(int) = 0.045]	
Completeness to Θ = 29.00°	99.5%	
Absorption correction	multi-scan	
Max. and min. transmission	0.921 and 0.991	
Refinement method	phi and ω scans	
Data / restraints / parameters	4435 / 0 / 341	
Goodness-of-fit on F^2	1.08	
Final R indices [I>2σ(I)]	R1 = 0.064, wR2 = 0.1458	
R indices (all data)	R1 = 0.049, wR2 = 0.1370	
Largest diff. peak and hole	0.327 and -0.331 e.$Å^{-3}$	

Data for Compound 24 Chapter 2:

Identification code	av_rk231	
Empirical formula	$C_{29}H_{22}O$	
Formula weight	386.47	
Temperature	173(2) K	
Wavelength	0.71073 Å	
Crystal system	Triclinic	
Space group (H.-M.)	$P\bar{1}$	
Space group (Hall)	-P 1	
Unit cell dimensions	a = 8.612 (7) Å	α= 91.992 (16)°
	b =10.015 (6) Å	β= 107.669 (16)°
	c = 13.765 (8) Å	γ= 111.33 (3)°
Volume	1039.5 (12) Å^3	
Z	2	
Density (calculated)	1.235 Mg m^{-3}	
Absorption coefficient	0.07 mm^{-1}	
Crystal size	0.99 × 0.57 × 0.21 mm	
Θ range for data collection	1.6° to 27.5°.	
Reflections collected	13753	
Independent reflections	4732 [R(int) = 0.037]	
Completeness to Θ = 29.00°	99.2 %	
Absorption correction	multi-scan	
Max. and min. transmission	0.931 and 0.985	
Refinement method	phi and ω scans	
Data / restraints / parameters	4071 / 0 / 275	
Goodness-of-fit on F^2	1.12	
Final R indices [I>2σ(I)]	R1 = 0.0600, wR2 = 0.1520	
R indices (all data)	R1 = 0.0525, wR2 = 0.1435	
Largest diff. peak and hole	0.370 and -0.364 e.Å^{-3}	

Data for Compound 25 Chapter 3:

Identification code	av_mn100b	
Empirical formula	$C_8H_8O_4$	
Formula weight	168.14	
Temperature	173(2) K	
Wavelength	0.71073 Å	
Crystal system	Monoclinic	
Space group (H.-M.)	$P2_1/n$	
Space group (Hall)	-P 2yn	
Unit cell dimensions	a = 4.869 (5) Å	α= 90.00°
	b =12.833 (12) Å	β= 96.23 (4)°
	c = 12.255 (13) Å	γ= 90.00°
Volume	761.2 (13) $Å^3$	
Z	4	
Density (calculated)	1.467 Mg m^{-3}	
Absorption coefficient	0.12 mm^{-1}	
F(000)	352	
Crystal size	0.51 × 0.32 × 0.08 mm	
Θ range for data collection	4.4° to 30.0°.	
Reflections collected	8723	
Independent reflections	2201 [R(int) = 0.026]	
Completeness to Θ = 29.00°	99.4%	
Absorption correction	multi-scan	
Max. and min. transmission	0.942 and 0.991	
Refinement method	phi and psi scans	
Data / restraints / parameters	1824 / 0 / 118	
Goodness-of-fit on F^2	1.07	
Final R indices [$I>2\sigma(I)$]	R1 = 0.049, wR2 = 0.1231	
R indices (all data)	R1 = 0.041, wR2 = 0.1157	
Largest diff. peak and hole	0.451 and -0.235 e.$Å^{-3}$	

Data for Compound 26 Chapter 3:

Identification code	av_mn101	
Empirical formula	$C_{10}H_6F_6O_8S_2$	
Formula weight	432.27	
Temperature	173(2) K	
Wavelength	0.71073 Å	
Crystal system	Monoclinic	
Space group (H.-M.)	*C*2/*c*	
Space group (Hall)	-C 2yc	
Unit cell dimensions	a = 33.116 (2) Å	α= 90.00°
	b =5.5154 (3) Å	β= 118.757 (2)°
	c = 19.1402 (13) Å	γ= 90.00°
Volume	3064.8 (3) $Å^3$	
Z	8	
Density (calculated)	1.874 Mg m^{-3}	
Absorption coefficient	0.46 mm^{-1}	
F(000)	1728	
Crystal size	0.65 × 0.26 × 0.07 mm	
Θ range for data collection	4.2° to 28.0°.	
Reflections collected	2908	
Independent reflections	3693 [R(int) = 0.035]	
Completeness to Θ = 29.00°	99.5%	
Absorption correction	multi-scan	
Max. and min. transmission	0.755 and 0.969	
Refinement method	phi and ω scans	
Data / restraints / parameters	2908 / 0 / 236	
Goodness-of-fit on F^2	1.05	
Final R indices [I>2σ(I)]	R1 = 0.050, wR2 = 0.0916	
R indices (all data)	R1 = 0.035, wR2 = 1.050	
Largest diff. peak and hole	0.417 and -0.312 e.$Å^{-3}$	

Data for Compound 27b Chapter 3:

Identification code	av_mn104	
Empirical formula	$C_{28}H_{32}O_2$	
Formula weight	400.54	
Temperature	173(2) K	
Wavelength	0.71073 Å	
Crystal system	Monoclinic	
Space group (H.-M.)	$P2_1/c$	
Space group (Hall)	-P 2ybc	
Unit cell dimensions	a = 8.7751 (6) Å	α= 90.00°
	b =26.497 (2) Å	β= 101.856 (3)°
	c = 10.1463 (7) Å	γ = 90.00°
Volume	2308.9 (3) Å^3	
Z	4	
Density (calculated)	1.152 Mg m^{-3}	
Absorption coefficient	0.07 mm^{-1}	
F(000)	864	
Crystal size	0.65 × 0.25 × 0.14 mm	
Θ range for data collection	4.1° to 27.5°.	
Reflections collected	20313	
Independent reflections	5292 [R(int) = 0.040]	
Completeness to Θ = 29.00°	99.6%	
Absorption correction	multi-scan	
Max. and min. transmission	0.956 and 0.990	
Refinement method	phi and ω scans	
Data / restraints / parameters	3557 / 0 / 341	
Goodness-of-fit on F^2	1.05	
Final R indices [$I>2\sigma(I)$]	R1 = 0.0917, wR2 = 0.1575	
R indices (all data)	R1 = 0.0555, wR2 = 0.1433	
Largest diff. peak and hole	0.367 and -0.244 e.Å^{-3}	

Data for Compound 27d Chapter 3:

Identification code	av_mn108a	
Empirical formula	$C_{24}H_{20}O_2$	
Formula weight	340.40	
Temperature	173(2) K	
Wavelength	0.71073 Å	
Crystal system	Monoclinic	
Space group (H.-M.)	$P2_1/c$	
Space group (Hall)	-P 2ybc	
Unit cell dimensions	a = 12.712 (5) Å	α= 90.00°
	b =21.899 (7) Å	β= 105.43 (3)°
	c = 6.783 (2) Å	γ = 90.00°
Volume	1820.1 (11) $Å^3$	
Z	4	
Density (calculated)	1.242 Mg m^{-3}	
Absorption coefficient	0.08 mm^{-1}	
F(000)	720	
Crystal size	0.67 × 0.18 × 0.16 mm	
Θ range for data collection	3.3° to 28.0°.	
Reflections collected	18253	
Independent reflections	4351 [R(int) = 0.049]	
Completeness to Θ = 29.00°	99.3%	
Absorption correction	multi-scan	
Max. and min. transmission	0.950 and 0.988	
Refinement method	phi and ω scans	
Data / restraints / parameters	2595 / 0 / 237	
Goodness-of-fit on F^2	1.04	
Final R indices [I>2σ(I)]	R1 = 0.098, wR2 = 0.1387	
R indices (all data)	R1 = 0.047, wR2 = 0.1208	
Largest diff. peak and hole	0.261 and -0.232 e.$Å^{-3}$	

Data for Compound 34c Chapter 3:

Identification code	av_mn133	
Empirical formula	$C_{16}H_{13}F_3O_6S$	
Formula weight	390.32	
Temperature	173(2) K	
Wavelength	0.71073 Å	
Crystal system	Triclinic	
Space group (H.-M.)	$P\bar{1}$	
Space group (Hall)	-P 1	
Unit cell dimensions	a = 7.6106 (6) Å	α= 113.815 (4)°
	b =11.2409 (9) Å	β= 102.495 (4)°
	c = 11.9009 (10) Å	γ = 106.407 (3)°
Volume	827.76 (12) $Å^3$	
Z	2	
Density (calculated)	1.566 Mg m^{-3}	
Absorption coefficient	0.26 mm^{-1}	
Crystal size	0.88 × 0.24 × 0.13 mm	
Θ range for data collection	3.0° to 27.5°.	
Reflections collected	14195	
Independent reflections	3723 [R(int) = 0.033]	
Completeness to Θ = 29.00°	97.7 %	
Absorption correction	multi-scan	
Max. and min. transmission	0.804 and 0.967	
Refinement method	phi and psi scans	
Data / restraints / parameters	3341 / 0 / 237	
Goodness-of-fit on F^2	1.09	
Final R indices [$I>2\sigma(I)$]	R1 = 0.042, wR2 = 0.1176	
R indices (all data)	R1 = 0.038, wR2 = 0.1143	
Largest diff. peak and hole	0.447 and -0.517 e.$Å^{-3}$	

Declaration/Erklärung

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

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

Ferner erkläre ich, dass ich diese Arbeit selbständig verfasst und keine anderen als die darin angegebenen Hilfsmittel benutzt habe.

I hereby apply irrevocably to take oral examination in the form of a private viva voce and a public presentation.

Muhammad Nawaz