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PAPER

Scope of direct arylation of fluorinated aromatics with aryl sulfonates†

Joyce Wei Wei Chang,[a] Eugene Yurong Chia,[a] Christina Li Lin Chai[a,b] and Jayasree Seayad*[a]

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The scope and limitations of direct arylation of fluorinated aromatics with aryl sulfonates was examined. $Pd(OAc)_2$, in the presence of MePhos and KOAc in THF, efficiently catalyzed the direct arylation of fluoro aromatics with aryl triflates under ambient conditions. Sterically hindered triflates and heteroaryl triflates gave good to excellent yields of the cross coupled products using a modified catalyst system which involves $Pd(OAc)_2$–RuPhos at 100 °C. The direct arylation of electron deficient arenes with aryl mesylates is also established using $Pd(OAc)_2$–SPhos as the catalyst in toluene–^{t}BuOH at 120 °C.

Introduction

The prevalence of biaryl scaffolds[1] in natural products, biologically active compounds and functional materials has led to the development of numerous methodologies toward the construction of this important motif. Conventional approaches for the construction of biaryls by cross coupling reactions are reliant on a range of organometallics such as those of Mg, B, Zn, Sn, Si, with electrophiles like organic halides using transition metal catalysts.[2] While these methods have been generally versatile and used extensively, there exists some serious disadvantages with regard to atom economy and waste generation. The pre-functionalization of coupling partners is essentially uneconomical, as it entails fixing and successive removal of stoichiometric activating agents, in addition to the usual regioselectivity problems and waste generation involved in the multi step synthetic process. Moreover, halides and some of the organometallic reagents are environmentally harmful. Consequently, cross coupling reactions avoiding the synthesis and use of halo aromatics and organometallics are highly sought by the pharmaceutical and fine chemical industries.[3] Tremendous advances have been made in recent years to develop new methodologies based on direct C–H activation to form C–C and C–heteroatom bonds.[4] Direct arylation is one of such approaches in which only one of the coupling partners needs to be preactivated, while the other reacts by C–H bond activation.[5]

Fluorinated biaryls have important applications in medicinal chemistry as well as in materials chemistry.[6] The introduction of fluorine into small molecules has significant advantages in drug discovery such as increasing their binding affinity and selectivity to the target proteins,[7] fine tuning lipophilicity,[8] averting metabolism[9] *etc.* In materials chemistry, fluorinated polyaryl compounds have applications as high mobility n-type semiconductors, liquid crystals, optoelectronics, *etc.*[10–12]

Apart from the traditional C–C coupling methods,[13] modern C–C coupling methodologies such as palladium[14–16] or copper[17] catalyzed direct arylation of perfluoroarenes with aryl halides or boronic acids[18] and very recently oxidative arylation with simple arenes[19,20] were reported for the synthesis of fluorobiaryls. However, general methodologies for the direct coupling of fluorinated aromatics with aryl sulfonates are scarce. Fagnou and co-workers[15] have reported a single example of the coupling of pentafluorobenzene with phenyltriflate. Ackermann's group[21] has shown an example of the coupling of tetrafluorobenzene with electron rich aryl tosylates. Very recently, while we were preparing this manuscript, a report on the direct arylation of perfluoroarenes with heteroaromatic tosylates was published.[22] We report herein a general palladium catalyzed direct arylation of fluorinated aromatics with aryl triflates under mild conditions. The possibility of using more atom economic and cheap mesylates[23,24] as coupling partners is also demonstrated. Aryl sulfonates are complementary coupling partners to aryl halides and are easily accessible from hydroxylated arenes, which are commonly found in pharmaceutical and agrochemical intermediates, natural products as well as polymers.

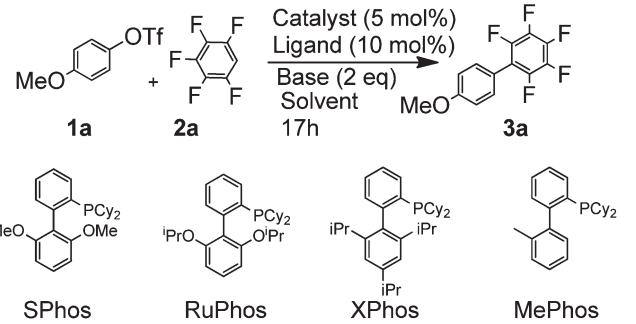
Results and discussion

The optimization studies were carried out using pentafluorobenzene and 4-methoxyphenyl triflate as coupling partners. Initial experiments showed that in the presence of $Pd(OAc)_2$ and SPhos in DMF using KOAc as the base at 80 °C, a high yield of the cross coupled product 2,3,4,5,6-pentafluoro-4′-methoxy-1,1′-biphenyl (**3a**) could be obtained (entry 1, Table 1). When the

[a]*Institute of Chemical and Engineering Sciences, 8 Biomedical Grove, Neuros, #07-01, Singapore 138665, Singapore. E-mail: jayasree_seayad@ices.a-star.edu.sg; Fax: +(65) 6464 2102; Tel: +(65) 6799 8515*
[b]*Department of Pharmacy, National University of Singapore, 18 Science Drive 4, Singapore 117543, Singapore*

†Electronic supplementary information (ESI) available: Experimental details and compound characterization data are available as supporting information. See DOI: 10.1039/c2ob06840k

Table 1 Optimization experiments for the direct arylation of pentafluorobenzene



Entry	Catalyst	Ligand	*T*, °C	Solvent	Base	Yield,[a] %
1	$Pd(OAc)_2$	SPhos	80	DMF	KOAc	91
2	$Pd(OAc)_2$	SPhos	60	DMF	KOAc	58
3	$Pd(OAc)_2$	SPhos	60	THF	KOAc	92
4	$Pd(OAc)_2$	SPhos	60	EtOAc	KOAc	91
5	$Pd(OAc)_2$	SPhos	40	THF	KOAc	87
6	$Pd(OAc)_2$	SPhos	40	EtOAc	KOAc	45
7	$Pd(TFA)_2$	SPhos	40	THF	KOAc	9
8	$PdCl_2$	SPhos	40	THF	KOAc	51
9	$Pd_2(dba)_3$	SPhos	40	THF	KOAc	5
10	$Pd(OAc)_2$	MePhos	40	THF	KOAc	99
11	$Pd(OAc)_2$	MePhos	25	THF	KOAc	99
12	$Pd(OAc)_2$	XPhos	40	THF	KOAc	79
13	$Pd(OAc)_2$	RuPhos	40	THF	KOAc	5
14	$Pd(OAc)_2$	MePhos	40	THF	K_2CO_3	34
15	$Pd(OAc)_2$	MePhos	40	THF	CsF	46

[a] NMR yield, determined using CH_2Br_2 as an internal standard.

reaction temperature was decreased to 60 °C, under these conditions, the yield decreased to 58% with the rest of the substrate remaining unreacted after 17 h (entry 2, Table 1). However, high yields of the desired product were obtained when the reactions were carried out in either EtOAc or THF as solvent at 60 °C (entries 3 and 4, Table 1). To our delight, further optimization studies by lowering the reaction temperature, screening of ligands, catalyst precursors and bases revealed that $Pd(OAc)_2$ with MePhos as ligand in the presence of KOAc in THF provides quantitative yields of the desired product even at rt after 17 h (entry 11). Recently, Fagnou's group[16] has reported similar direct arylation of fluoroarenes under ambient conditions in the presence of $Pd(OAc)_2$–MePhos under biphasic conditions (2.5 : 1 EtOAc : H_2O). However, only iodoarenes were used as coupling partners and the addition of Ag_2CO_3 was necessary to circumvent inhibition effect of iodide salts.

It is notable that the cross coupling reaction of aryl triflates and fluoroarenes has a narrow ligand scope and works efficiently, so far, only in the presence of Buchwald phosphines, the most efficient being MePhos. Reactions in the absence of any ligands or by using ligands such as simple monophosphines *e.g.* PPh_3, PCy_3, or diphosphines with small or wide bite angles *e.g.* dppp, dppf, XantPhos as well as *N*-ligands 1,10-phenanthroline, 4,4′ dimethyl 2,2′-bipyridine, lutidine *etc.* (see Table S1 in ESI†), gave no or traces of the product under these conditions. Other than the ligand, the counter anion of the base as well the catalyst precursor was found to have an important role on the catalytic activity. Thus, among various bases and catalyst precursors

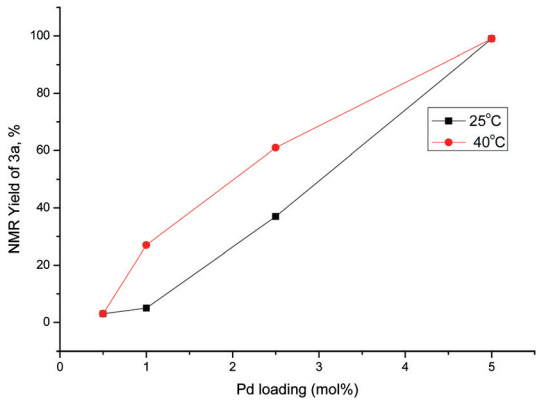


Fig. 1 Effect of Pd loading on the direct arylation of pentafluorobenzene with 4-methoxyphenyl triflate.

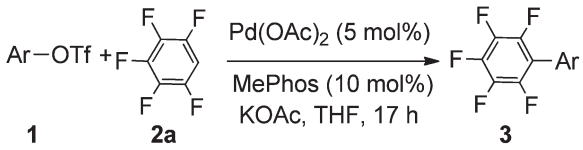
studied, KOAc and $Pd(OAc)_2$ were found to be the best. The effect of catalyst loading for the direct arylation was studied at 40 °C and 25 °C (Fig. 1) and a nearly linear effect of Pd loading was observed at both temperatures, with an optimum of 5 mol% of Pd to obtain quantitative yield of the product after 17 h.

This effect is analogous to most of the arylation reactions by C–H activation in which a catalyst loading between 5–20 mol% is found to be essential in general.

After attaining the optimized conditions, we examined the scope of the reaction with regard to the aryl triflates. As shown in Table 2, the reaction of pentafluorobenzene with various 3-,4- or 5-functionalized aryl triflates (**1a–1l**) gave good to excellent yields of the corresponding cross coupled products (**3a–3l**) under nearly ambient conditions (25–40 °C). Functional groups such as nitro, acetyl and nitrile were well tolerated. A noteworthy example is the 4-chlorophenyl triflate in which only monoarylated product was formed due to the lower reactivity of the chloro group compared to the triflate group under these conditions. Such a difference in reactivity could be useful in organic synthesis for further derivatization of the chloro group by other types of coupling reactions. No significant electronic effects on the activity for the triflate counter partners were observed. For instance, the electron rich 4-methoxy (**1a**) and 4-methyl (**1f**) phenyl triflates, performed well at 25 °C with 89–90% yield. Similarly, in the case the electron poor 4-chloro (**1c**), 4-fluoro (**1d**) and 4-nitrile (**1h**) phenyl triflates the isolated yields of the corresponding biaryls were 86%, 85% and 98% respectively. 4-Nitro (**1e**), 4-acetyl (**1g**) (entries 5 and 7, Table 2) as well as 3,5-difluoro (**1j**), 3,5-dimethoxy (**1k**) and 3,5-bistrifluoromethyl (**1l**) phenyl triflates performed more efficiently at 40 °C (entries 10–12, Table 2).

Table 3 demonstrates the coupling of various di-, tri- and tetrafluoroarenes with phenyl triflate. In general, the activity of the C–H arylation was found to be related to its acidity, as also shown by Fagnou *et al.* for the direct arylation of perfluorobenzenes with aryl bromides.[14] Thus C–H bonds, *ortho* to the C–F bonds that are more acidic, react preferentially. Besides, higher the number of the electron withdrawing fluorine on the arene, *i.e.* more electron deficient the arene, the lower the temperature required for its activation. Accordingly, 1,2,4,5-tetrafluoro-3-methoxybenzene, 1,2,4,5-tetrafluoro-3-methyl benzene and 2,3,5,6-tetrafluoropyridine formed the coupling products (**3m**,

Table 2 Direct arylation of pentafluorobenzene with aryl triflates



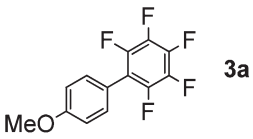
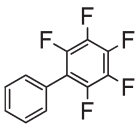
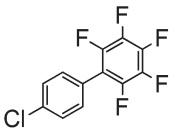
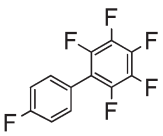
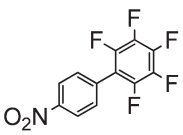
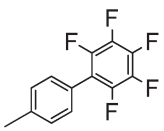
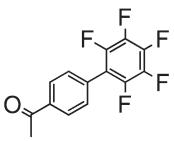
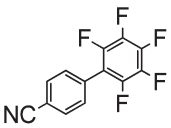
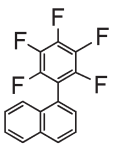
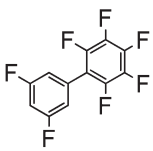
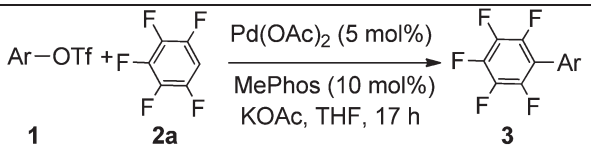
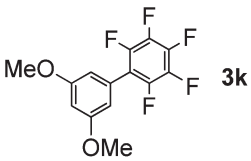
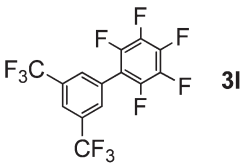
Entry	Product	*T*, °C	Yield, %[a]
1	 **3a**	25	90
2	 **3b**	25	97
3	 **3c**	25	86
4	 **3d**	25	85
5	 **3e**	40	77
6	 **3f**	25	89
7	 **3g**	40	89
8	 **3h**	25	98
9	 **3i**	40	86
10	 **3j**	40	81

Table 2 *(Contd.)*



Entry	Product	*T*, °C	Yield, %[a]
11	 **3k**	40	75
12	 **3l**	40	75

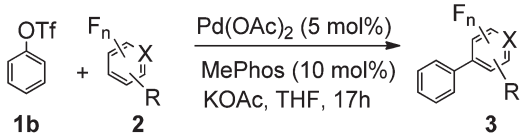
[a] Isolated yield.

3n and **3o**) in good to excellent yields at 40 °C. In the case of 1,2,3,5-tetrafluorobenzene and 1-(2,5,6-trifluoro-[1,1′-biphenyl]-3-yl)ethanone having two potential C–H bonds to react, the mono arylated products **3p** and **3r** were formed along with small amounts of the corresponding diarylated products (entries 5 and 7, Table 3). However, the arylation of 2,4,5-trifluorobenzaldehyde resulted in exclusive formation of the monoarylated product 2,5,6-trifluoro-[1,1′-biphenyl]-3-carbaldehyde (**3q**) in 83% yield by the selective activation of the C–H bond in between the two fluorine substituents. 1,2,4-trifluorobenzene required slightly higher temperature (60 °C) for activation and the corresponding monoarylated product was formed in moderate yields (47%). No diarylation was observed in this case. Similarly, the difluoroderivative, 1-(2,4-difluorophenyl)ethanone formed the monoarylated product **3t** exclusively, in 70% yield by the selective activation of C–H bond in between the two fluorine atoms.

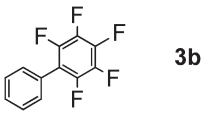
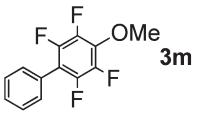
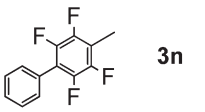
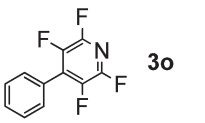
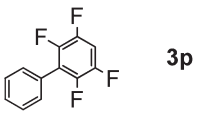
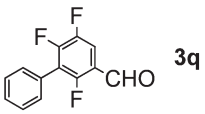
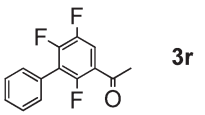
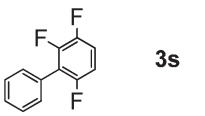
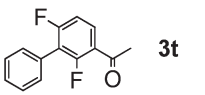
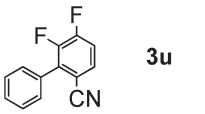
It is noteworthy that 2,5-difluorobenzonitrile could also be arylated by the selective activation of C–H bond in between the fluorine and nitrile substituents to form 3,6-difluoro-[1,1′-biphenyl]-2-carbonitrile (**3u**), although in moderate yields.

In the case of arylation using sterically hindered and heteroaryl triflates, this catalyst system was not suitable. Consequently, after additional optimization studies on the cross coupling of mesityl triflate with pentafluorobenzene (see Table S2 in ESI†) we found that a catalyst system consisting of $Pd(OAc)_2$ with RuPhos in the presence of K_2CO_3 in dioxane at 100 °C could form the cross coupled product 2,3,4,5,6-pentafluoro-2′,4′,6′-trimethyl-1,1′-biphenyl (**3v**) in excellent yields (entry 1, Table 4). SPhos was also effective although the yield was slightly lower compared to that in the case of RuPhos, but other Buchwald ligands MePhos, XPhos and ^{t}BuXPhos were ineffective. This might be due to the enhanced ability of RuPhos to facilitate oxidative addition and reductive elimination of the sterically bulkier aryl groups, due to its relatively higher nucleophilicity and steric bulk. Accordingly, various functionalized

Table 3 Direct arylation of fluorinated arenes with phenyl triflate

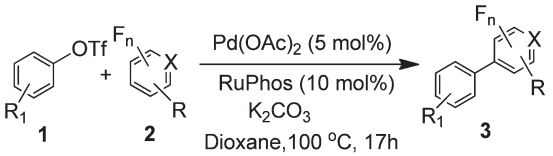


1b **2** **3**

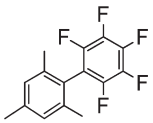
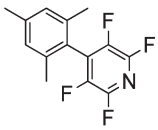
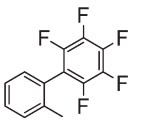
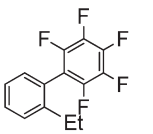
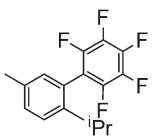
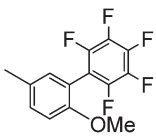
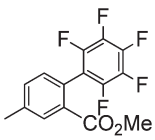
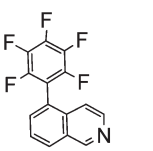
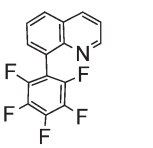
Entry	Product	*T*, °C	Yield, %[a]
1	 **3b**	25	97
2	 **3m**	40	93
3	 **3n**	40	78
4	 **3o**	40	79
5	 **3p**	40	52 (17)[b]
6	 **3q**	40	83
7	 **3r**	40	50[c]
8	 **3s**	60	47
9	 **3t**	80	70
10	 **3u**	100	30

[a] Isolated yield of the fluorobiaryl product. [b] Isolated yield of the diarylated product (**3p′** in ESI†) in parenthesis. [c] Diarylated product was formed with mono:di arylated product ratio of 7 : 1 (determined by NMR).

Table 4 Direct arylation of fluoroarenes with sterically hindered aryl and heteroaryl triflates



1 **2** **3**

Entry	Product	Yield, %[a]
1	 **3v**	92
2	 **3w**	85
3	 **3x**	97
4	 **3y**	53
5	 **3z**	72
6	 **3a1**	76
7	 **3b1**	99
8	 **3c1**	79
9	 **3d1**	54

[a] Isolated yield.

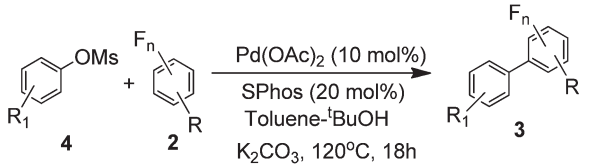
sterically hindered aryl triflates as well as heteroaryl triflates gave the corresponding cross coupled products in good to excellent yields using this catalyst system (Table 4). For instance, the reaction of mesityl triflate with pentafluorobenzene and 2,3,5,6-tetrafluoropyridine formed the coupling products **3v** and **3w** in 92% and 85% respectively. Similarly, in the case of the direct arylation of pentafluorobenzene with 2-methyl, 2-ethyl, 2-isopropyl-5-methyl, 2-methoxy-5-methyl and 2-carbomethoxy-4-methyl phenyl triflates, good to excellent yields (53–99%) of the corresponding fluorobiaryls (**3x–3b1**) were obtained. The heteroaryl sulfonates quinolin-8-yl and isoquinolin-5-yl triflates also reacted well under these conditions forming the coupling products **3c1** and **3d1** in good yields.

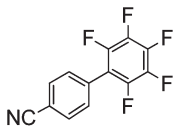
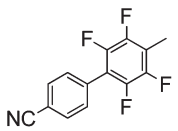
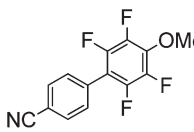
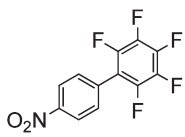
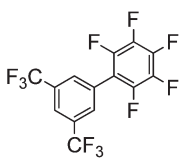
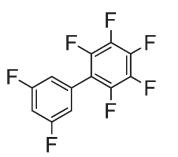
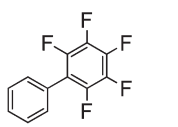
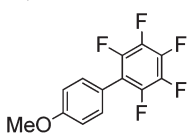
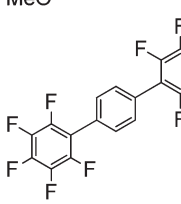
Our next goal was to use aryl mesylates, that are more attractive than triflates with regard to cost, stability and atom economy,[23] as the coupling partners. Generally, mesylates are poorer leaving groups, due to the higher pK_a of the conjugate acid–methane sulfonic acid (pK_a = −1.6)[25] and hence significantly less reactive towards C–O bond activation. Our preliminary reactions of 4-methoxyphenyl mesylate or 4-cyanophenyl mesylate with pentafluorobenzene using the aforementioned reaction conditions used for the triflates, formed only traces of the arylation products. Further optimization studies using 4-cyanophenyl mesylate (see Table S3 in the ESI†) revealed that 5 mol% $Pd(OAc)_2$ in the presence of SPhos and K_2CO_3 in toluene–^{t}BuOH (2 : 1) was the catalyst system of choice for this reaction giving up to 70% yield of the coupled product at 120 °C after 18 h. CMPhos, BrettPhos or XPhos which are known to be efficient ligands for other cross coupling reactions of aryl mesylates[23] were less effective in the present case. Inferior yields were obtained when either toluene or ^{t}BuOH was used by itself as the solvent. Other solvents such as DMF and dioxane were also not suitable. A small improvement in yield (73%) was achieved by increasing catalyst loading to 10 mol% and further study on the scope and limitations of this methodology with regard to other substrates was carried out using 10 mol% of Pd.

Among the various aryl mesylates studied, those with electron withdrawing substituents generally gave better yields. Thus, the direct arylation of the tetrafluorobenzenes 4-methyltetrafluorobenzene and 4-methoxytetrafluorobenzene with 4-cyanophenyl mesylate gave the coupled products **3e1** and **3f1** in 80% and 60% respectively (entries 2–3, Table 5). 4-Nitrophenyl mesylate and 3,5-ditrifluoromethylphenyl mesylate furnished 60–63% yield of the corresponding fluorobiaryls, while in the case of 3,5-difluorophenyl mesylate, phenyl mesylate and 4-methoxy mesylate the yield ranged between 20 and 40%. 4-Chlorophenyl mesylate produced only the corresponding diarylated product (**5**, 74% yield) under these conditions. Although the yields are modest in these cases, it has to be noted that this is the first demonstrated example of the direct arylation of simple arenes with aryl mesylates and further studies are ongoing in our laboratory to improve the efficiency and to broaden the scope of this methodology.

The mechanism of this reaction would be similar to that of the aryl bromides as proposed by Fagnou and co-workers.[14] Thus, initial oxidative addition of aryl sulfonate to the *in situ* generated Pd(0) complex **i** leads to Pd(II)(aryl)sulfonate intermediate **ii** followed by exchange of the sulfonate with acetate or carbonate. The Pd(II) species **iii** activates the fluorinated arene by the cyclometallation deprotonation (CMD) pathway assisted by OAc^- or CO_3^{2-}. The reductive elimination of the product from the Pd(II) diaryl intermediate **v** regenerates the Pd(0) species for further cycles. The positive effect of the counter anions OAc^- or CO_3^{2-} on the catalytic activity and the connection of the reactivity of fluorobenzenes to the acidity of its C–H bonds support this mechanism (Scheme 1).

Table 5 Direct arylation of fluoroarenes with aryl mesylates

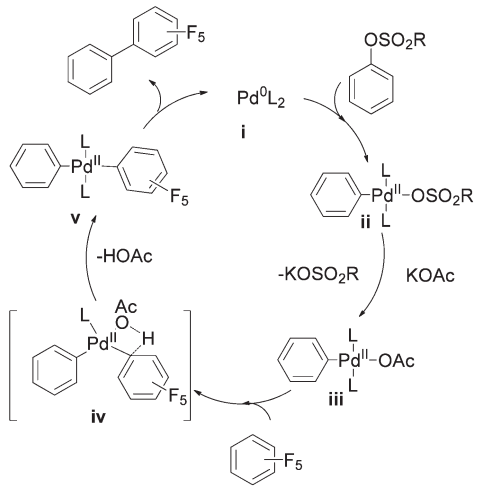


Entry	Product	Yield, %[a]
1	 **3h**	73
2	 **3e1**	80
3	 **3f1**	60
4	 **3e**	60
5	 **3l**	63
6	 **3j**	35
7	 **3b**	40
8	 **3a**	20
9[b]	 **5**	74

[a] Isolated yield. [b] 4-Chlorophenyl mesylate was used as the substrate.

Conclusions

In conclusion, we have established an efficient and general method for the direct arylation of fluorinated aromatics, having two or more fluorine substituents, with aryl triflates under ambient conditions using a catalyst system consisting of Pd $(OAc)_2$, MePhos and KOAc in THF. A modified catalyst system



Scheme 1 Proposed catalytic cycle for the direct arylation of fluorinated arenes with aryl sulfonates.

which involves $Pd(OAc)_2$, RuPhos and K_2CO_3 in dioxane at 100 °C was necessary in the case of sterically hindered aryl and heteroaryl triflates. The possibility of using more atom economic and cheap aryl mesylates as coupling partners for the coupling of these electron deficient arenes is also demonstrated. This method avoids the synthesis and use of haloaromatics and organometallic reagents for the C–C cross coupling and is applicable for the synthesis of a wide range of functionalized electron deficient fluorobiaryls. Further studies directed towards the extension of the scope of this reaction for the direct arylation of simple arenes with aryl mesylates towards a general atom economic and green synthesis of biaryls are underway.

Experimental

General

Unless otherwise specified, all reagents and starting materials were purchased from commercial sources and used as received. The solvents were purified prior to use by passing through a Glass Contour Solvent Purification System Model-AOCSOLCOL and degassed with argon. All glassware used in these reactions was oven dried at 60 °C. Unless otherwise stated, all reagents were measured in a glove box. All reactions were conducted under an atmosphere of anhydrous argon. Reactions were monitored by analytical thin layer chromatography using Merck 60 F254 pre-coated silica gel plate. Visualization was achieved by UV-vis light (254 nm). Crude reaction mixtures were analyzed *via* GCMS Agilent 7890A GC System connected to an Agilent 5975C Triple-Axis Mass Detector. Flash chromatography was performed manually using Merck silica gel 60 or by using Biotage SP1™ purification system by gradient with ethyl acetate/petroleum ether as eluant. Unless otherwise stated, ^1H, ^{13}C and ^{19}F NMR spectra were measured on a Bruker Avance 400 MHz spectrometer. Unless otherwise stated, chemical shifts (δ) were recorded in $CDCl_3$ solution with tetramethylsilane (TMS) as the internal reference standard. Trifluorotoluene was used as an external standard for ^{19}F NMR spectroscopy. Coupling constants (J values) are reported in hertz (Hz), and spin multiplicities are indicated by the following symbols: s (singlet), d (doublet), t (triplet), q (quartet) and m (multiplet). NMR yields of crude reaction mixtures were determined by ^1H NMR spectroscopy using dibromomethane as the internal standard. High resolution mass spectra (HRMS) were obtained using HRMS were run by electron ionization or electro spray ionization-time-of-flight mode on Agilent 6210 Series 1969A.

Optimization studies of direct arylation of 4-methoxyphenyl triflate with pentafluorobenzene (Table 1)

A Radleys carousel reaction tube was charged with the Pd catalyst (0.025 mmol, 5 mol%), ligand (0.05 mmol, 10 mol%), base (1.0 mmol, 2 equiv), pentafluorobenzene (1.5 mmol, 3 equiv), 4-methoxyphenyl triflate (0.5 mmol, 1 equiv) and the solvent (1.5 mL) in a glove box. The reaction tube was brought out of the glove box and stirred at the specified temperature under argon for 17 h, after which it was cooled to room temperature and the solvent evaporated. The reaction mixture was then resuspended in CH_2Cl_2, and washed successively with deionized water and brine. The combined organic layer was dried over Na_2SO_4 and evaporated under reduced pressure. The crude reaction yield was then determined by ^1H NMR spectroscopy by the addition of dibromomethane (20 μL, 0.285 mmol) as the internal standard.

Pd-catalyzed direct arylation of aryl triflates with fluoroaromatics

Method A (Tables 2 and 3). A Radleys carousel reaction tube was charged with $Pd(OAc)_2$ (5.6 mg, 0.025 mmol, 5 mol%), MePhos (18.2 mg, 0.05 mmol, 10 mol%), KOAc (98.1 mg, 1.0 mmol, 2 equiv) fluoroarene (1.5 mmol, 3 equiv), and degassed anhydrous THF (1.5 mL) followed by aryl triflate (0.5 mmol, 1 equiv) in a glove box. The reaction tube was brought out of the glove box and stirred at the specified temperature under argon for 17 h. Upon completion, the reaction was cooled to room temperature and the solvent evaporated. The reaction mixture was then resuspended in dichloromethane, and washed successively with deionized water and brine. The combined organic layer was dried over Na_2SO_4 and evaporated under reduced pressure. The reaction yield was then determined by ^1H NMR spectroscopy by the addition of dibromomethane (20 μL, 0.285 mmol) as the internal standard and the residue purified by flash silica gel column chromatography.

Method B (Table 4). A microwave reaction tube was charged with $Pd(OAc)_2$ (5.6 mg, 0.025 mmol, 5 mol%) RuPhos (23.3 mg, 0.05 mmol, 10 mol%), K_2CO_3 (138.2 mg, 1 mmol, 2 equiv), 1,4-dioxane (1.5 mL), aryl triflate (0.5 mmol, 1 equiv), and fluoroarene (1.5 mmol, 3 equiv) in a glove box. The tube was sealed and stirred at 100 °C for 17 h, after which the reaction was cooled to room temperature. The reaction mixture was filtered through celite, the solvent removed under vacuum and the reaction yield was determined by ^1H NMR spectroscopy by the addition of dibromomethane (35 μL, 0.5 mmol). The residue was then purified by flash silica gel column chromatography.

Method C (Table 5). A microwave reaction tube was charged with $Pd(OAc)_2$ (11.2 mg, 0.05 mmol, 10 mol%) SPhos (41.05 mg, 0.1 mmol, 20 mol%), K_2CO_3 (138.2 mg, 1 mmol, 2 equiv), toluene (1.0 mL), *tert*-butanol (0.5 mL), aryl mesylate (0.5 mmol, 1 equiv), and fluoroarene (1.5 mmol, 1.5 equiv) in a glove box. The tube was sealed and stirred at 120 °C for 17 h, after which the reaction was cooled to room temperature. The reaction mixture was filtered through celite and washed with CH_2Cl_2. The solvent was removed under vacuum and the reaction yield was determined by ^{1}H NMR spectroscopy by the addition of dibromomethane (35 μL, 0.5 mmol). The residue was then purified by flash silica gel column chromatography.

2,3,4,5,6-Pentafluoro-4′-methoxy-1,1′-biphenyl (3a)[16]

Prepared according to Method A using 4-methoxyphenyl triflate and pentafluorobenzene at 25 °C. White solid; Yield: 82%; ^{1}H NMR δ 7.36 (dt, J = 8.9, 1.4 Hz, 2H), 7.02 (dt, J = 8.9, 2.5 Hz, 2H), 3.87 (s, 3H); ^{13}C NMR δ 160.3, 144.2 (m, incl. app. d, J_{C-F} = 246.6 Hz), 140.0 (m, incl. app. d, J_{C-F} = 253.1 Hz), 137.9 (m, incl. app. d, J_{C-F} = 252.6 Hz), 131.4, 118.4, 115.7 (td, J_{C-F} = 17.2, 4.1 Hz), 114.2, 55.3; ^{19}F NMR δ −143.8 (dd, J_{F-F} = 23.1, 8.1 Hz, 2F), −156.7 (t, J_{F-F} = 21.0 Hz, 1F), −162.7 (td, J_{F-F} = 23.1, 8.1 Hz, 2F); EI-MS [M^+] m/z 274.

2,3,4,5,6-Pentafluoro-1,1′-biphenyl (3b)[20]

Prepared according to Method A using phenyl triflate and pentafluorobenzene at 25 °C. White solid; Yield: 97%; ^{1}H NMR δ 7.54–7.48 (m, 3H), 7.46–7.44 (m, 2H); ^{13}C NMR δ 144.2 (m, incl. app. d, J_{C-F} = 247.6 Hz), 140.4 (m, incl. app. d, J_{C-F} = 253.6 Hz), 137.9 (m, incl. app. d, J_{C-F} = 252.9 Hz), 130.1, 129.3, 128.7, 126.4, 116.0 (td, J_{C-F} = 17.2, 4.0 Hz); ^{19}F NMR δ −143.4 (dd, J_{F-F} = 22.9, 8.2 Hz, 2F), −155.8 (t, J_{F-F} = 21.0 Hz, 1F), −162.4 (td, J_{F-F} = 21.8, 7.8 Hz, 2F); EI-MS [M^+] m/z 244.

4′-Chloro-2,3,4,5,6-pentafluoro-1,1′-biphenyl (3c)[18]

Prepared according to Method A using 4-chlorophenyl triflate and pentafluorobenzene at 25 °C. White solid; Yield = 86%; ^{1}H NMR δ 7.48 (dt, J = 8.6, 2.2 Hz, 2H), 7.37 (dt, J = 8.5, 2.2 Hz, 2H); ^{13}C NMR δ 144.1 (m, incl. app. d, J_{C-F} = 252.0 Hz), 140.6 (m, incl. app. d, J_{C-F} = 254.7 Hz), 137.9 (m, incl. app. d, J_{C-F} = 253.3 Hz), 135.6, 131.4, 129.1, 124.8, 114.8 (td, J_{C-F} = 17.1, 4.1 Hz); ^{19}F NMR δ −143.3 (dd, J_{F-F} = 22.7, 8.1 Hz, 2F), −155.0 (t, J_{F-F} = 21.0 Hz, 1F), −162.0 (dt, J_{F-F} = 22.8, 8.3 Hz, 2F); EI-MS [M^+] m/z 278.

2,3,4,4′,5,6-Hexafluoro-1,1′-biphenyl (3d)[16]

Prepared according to Method A using 4-fluorophenyl triflate and pentafluorobenzene at 25 °C. White solid; Yield: 85%; ^{1}H NMR δ 7.44–7.40 (m, 2H), 7.19 (t, J = 8.6 Hz, 2H); ^{13}C NMR δ 163.2 (d, J = 249.9 Hz), 144.2 (m, incl. app. d, J_{C-F} = 251.6 Hz), 140.5 (m, incl. app. d, J_{C-F} = 254.2 Hz), 137.9 (m, incl. app. d, J_{C-F} = 253.0 Hz), 132.0 (d, J_{C-F} = 8.5 Hz), 122.3, 115.9 (d, J_{C-F} = 22.0 Hz), 115.0 (td, J_{C-F} = 17.1, 4.0 Hz);^{19}F NMR δ −111.5 (s, 1F), −143.5 (dd, J_{F-F} = 22.8, 8.2 Hz, 2F), −155.4 (t, J_{F-F} = 21.0 Hz, 1F), −162.2 (td, J_{F-F} = 22.7, 8.2 Hz, 2F); EI-MS [M^+] m/z 262.

2,3,4,5,6-Pentafluoro-4′-nitro-1,1′-biphenyl (3e)[27]

Prepared according to Method A using 4-nitrophenyl triflate and pentafluorobenzene at 40 °C. White solid; Yield: 77%; ^{1}H NMR δ 8.35 (d, J = 8.4 Hz, 2H), 7.65 (d, J = 7.9 Hz, 2H); ^{13}C NMR δ 148.3, 144.1 (m, incl. app. d, J_{C-F} = 253.9 Hz), 141.3 (m, incl. app. d, J_{C-F} = 256.4 Hz), 138.0 (m, incl. app. d, J_{C-F} = 254.0 Hz), 133.0, 131.3, 123.9, 113.8 (td, J_{C-F} = 16.8, 4.0 Hz);^{19}F NMR δ −142.7 (dd, J_{F-F} = 22.6, 8.3 Hz, 2F), −152.6 (t, J_{F-F} = 21.0 Hz, 1F), −161.0 (td, J_{F-F} = 21.4, 7.2 Hz, 2F); EI-MS [M^+] m/z 289.

2,3,4,5,6-Pentafluoro-4′-methyl-1,1′-biphenyl (3f)[16]

Prepared according to Method A using *p*-tolyl triflate and pentafluorobenzene at 25 °C. White solid; Yield: 89%; ^{1}H NMR δ 7.33 (s, 4H), 2.45 (s, 3H); ^{13}C NMR δ 144.2 (m, incl. app. d, J_{C-F} = 250.9 Hz), 140.2 (m, incl. app. d, J_{C-F} = 253.2 Hz), 139.5, 137.8 (m, incl. app. d, J_{C-F} = 250.3 Hz), 130.0, 129.5, 123.4, 116.0 (td, J_{C-F} = 17.3, 4.0 Hz), 21.3; ^{19}F NMR δ −143.5 (dd, J_{F-F} = 23.0, 8.2 Hz, 2F), −156.3 (t, J_{F-F} = 21.0 Hz, 1F), −162.6 (td, J_{F-F} = 22.9, 8.2 Hz, 2F); EI-MS [M^+] m/z 258.

1-(2′,3′,4′,5′,6′-Pentafluoro-[1,1′-biphenyl]-4-yl)ethanone (3g)[14]

Prepared according to Method A using 4-acetylphenyl triflate and pentafluorobenzene at 40 °C. White solid; Yield: 89%; ^{1}H NMR δ 8.06 (d, J = 8.4 Hz, 2H), 7.53 (d, J = 8.2 Hz, 2H), 2.64 (s, 3H); ^{13}C NMR δ 197.2, 144.1 (m, incl. app. d, J_{C-F} = 252.7 Hz), 140.9 (m, incl. app. d, J_{C-F} = 255.2 Hz), 137.9 (m, incl. app. d, J_{C-F} = 253.3 Hz), 137.5, 131.0, 130.5, 128.5, 114.9 (td, J_{C-F} = 16.9, 3.9 Hz), 26.5; ^{19}F NMR δ −142.9 (dd, J_{F-F} = 22.6, 8.1 Hz, 2F), −154.1 (t, J_{F-F} = 21.0 Hz, 1F), −161.7 (td, J_{F-F} = 22.5, 8.1 Hz, 2F); EI-MS [M^+] m/z 286.

2′,3′,4′,5′,6′-Pentafluoro-[1,1′-biphenyl]-4-carbonitrile (3h)[16]

Prepared according to Method A using 4-cyanophenyl triflate and pentafluorobenzene at 25 °C. White solid; Yield: 98%; ^{1}H NMR δ 7.79 (d, J = 8.6 Hz, 2H), 7.57 (d, J = 8.2 Hz, 2H); ^{13}C NMR δ 144.0 (m, incl. app. d, J_{C-F} = 249.5 Hz), 141.2 (m, incl. app. d, J_{C-F} = 256.1 Hz), 138.0 (m, incl. app. d, J_{C-F} = 253.8 Hz), 132.4, 131.1, 131.0, 118.1, 114.1 (td, J_{C-F} = 16.7, 4.1 Hz), 113.4; ^{19}F NMR δ −142.9 (dd, J_{F-F} = 22.5, 8.1 Hz, 2F), −153.0 (t, J_{F-F} = 21.0 Hz, 1F), −161.1 (td, J_{F-F} = 21.5, 7.3 Hz, 2F); EI-MS [M^+] m/z 269.

1-(Perfluorophenyl)naphthalene (3i)[16]

Prepared according to Method A using 1-naphthyl triflate and pentafluorobenzene at 40 °C. White solid; Yield: 86%; ^{1}H NMR δ 8.00 (dd, J = 19.7, 8.0 Hz, 2H), 7.63–7.52 (m, 4H), 7.48 (d, J = 6.9 Hz, 1H); ^{13}C NMR δ 144.7 (m, incl. app. d, J_{C-F} = 251.3 Hz), 141.0 (m, incl. app. d, J_{C-F} = 254.0 Hz), 137.8 (m, incl. app. d, J_{C-F} = 253.5 Hz), 133.7, 131.6, 130.2, 129.0,

128.7, 127.1, 126.4, 125.2, 124.6, 123.8, 114.5 (td, J_{F-F} = 19.6, 3.9 Hz); ^{19}F NMR δ −139.6 (dd, J_{F-F} = 23.1, 8.1 Hz, 2F), −154.8 (t, J_{F-F} = 20.9 Hz, 1F), −162.0 (td, J_{F-F} = 22.9, 8.2 Hz, 2F); EI-MS [M^+] *m/z* 294.

2,3,3′,4,5,5′,6-Heptafluoro-1,1′-biphenyl (3j)

Prepared according to Method A using 3,5-difluorophenyl triflate and pentafluorobenzene at 40 °C. White solid; Yield: 81%; ^{1}H NMR δ 6.98 (d, J = 6.4 Hz, 2H), 6.92 (dt, J = 8.8, 2.1 Hz, 1H); ^{13}C NMR δ 162.9 (dd, J_{C-F} = 249.8, 12.9 Hz), 144.1 (d, J_{C-F} = 249.3 Hz), 141.1 (d, J_{C-F} = 255.9 Hz), 137.9 (d, J_{C-F} = 253.7 Hz), 129.1 (t, J_{C-F} = 10.4 Hz), 113.4 (d, J_{C-F} = 26.9 Hz), 105.0 (t, J_{C-F} = 25.1 Hz); ^{19}F NMR δ −108.8 (s, 2F), −142.75 (dd, J_{F-F} = 21.9, 7.5 Hz, 2F), −153.6 (t, J_{F-F} = 21.0 Hz, 1F), −161.39 (td, J_{F-F} = 21.5, 7.2 Hz, 2F); EI-MS [M^+] *m/z* 280; HRMS (EI) *m/z* for $C_{12}H_3F_7$ calcd 280.0123, found 280.0122.

2,3,4,5,6-Pentafluoro-3′,5′-dimethoxy-1,1′-biphenyl (3k)[26]

Prepared according to Method A using 3,5-methoxyphenyl triflate and pentafluorobenzene at 40 °C. White solid; Yield: 75%; ^{1}H NMR δ 6.55 (s, 3H), 3.82 (s, 6H); ^{13}C NMR δ 160.9, 144.2 m, incl. app. d, J_{C-F} = 247.9 Hz), 140.4 (m, incl. app. d, J_{C-F} = 253.7 Hz), 137.8 (m, incl. app. d, J_{C-F} = 252.5 Hz), 127.9, 115.9 (td, J_{C-F} = 17.4, 3.9 Hz), 108.3, 101.3, 55.4; ^{19}F NMR δ −142.5 (dd, J_{F-F} = 23.0, 8.1 Hz, 2F), −155.7 (t, J_{F-F} = 21.0 Hz, 1F), −162.4 (td, J_{F-F} = 23.0, 8.2 Hz, 2F); EI-MS [M^+] *m/z* 304.

2,3,4,5,6-Pentafluoro-3′,5′-bis(trifluoromethyl)-1,1′-biphenyl (3l)

Prepared according to Method A using 3,5-bis(trifluoromethyl) phenyl triflate and pentafluorobenzene at 40 °C. Colorless oil; Yield: 78%; ^{1}H NMR δ 8.01 (s, 1H), 7.92 (s, 2H); ^{13}C NMR δ 144.2 (m, incl. app. d, J_{C-F} = 250.8 Hz), 141.5 (m, incl. app. d, J_{C-F} = 252.0 Hz), 138.1 (m, incl. app. d, J_{C-F} = 254.3 Hz), 132.5 (q, J_{C-F} = 33.9 Hz), 130.3, 128.67, 123.2 (dt, J_{C-F} = 7.5, 3.7 Hz), 122.9 (q, J_{C-F} = 272.8 Hz), 113.0 (td, J_{C-F} = 16.5, 4.1 Hz); ^{19}F NMR δ −63.2 (s, 6F), −142.9 (dd, J_{F-F} = 21.7, 7.5 Hz, 2F), −152.0 (t, J_{F-F} = 21.0 Hz, 1F), −160.6 (td, J_{F-F} = 21.1, 7.0 Hz, 2F); EI-MS [M^+] *m/z* 380; HRMS (EI) *m/z* for $C_{14}H_3F_{11}$ calcd 380.0059, found 380.0058.

2,3,5,6-Tetrafluoro-4-methoxy-1,1′-biphenyl (3m)[20]

Prepared according to Method A using phenyl triflate and 1,2,4,5-tetrafluoro-3-methoxybenzene at 40 °C. White solid; Yield: 93%; ^{1}H NMR δ 7.50–7.45 (m, 5H), 4.13 (s, 3H); ^{13}C NMR δ 143.3 (m, incl. app. d, J_{C-F} = 246.0 Hz), 140.1 (m, incl. app. d, J_{C-F} = 247.0 Hz), 136.5 (tt, J_{C-F} = 11.9, 3.5 Hz), 129.2, 127.8, 127.5, 126.3, 113.2 (t, J_{C-F} = 17.3 Hz), 61.1 (t, J_{C-F} = 3.7 Hz); ^{19}F NMR δ −145.4 (dd, J_{F-F} = 21.9, 8.7 Hz, 2F), −158.4 (dd, J_{F-F} = 22.0, 8.7 Hz, 2F); HRMS (EI) *m/z* for $C_{13}H_8F_4O$ calcd 256.0511, found 256.0521.

2,3,5,6-Tetrafluoro-4-methyl-1,1′-biphenyl (3n)[20]

Prepared according to Method A using phenyl triflate and 1,2,4,5-tetrafluoro-3-methybenzene at 40 °C. White solid; Yield: 78%; ^{1}H NMR δ 7.53–7.46 (m, 5H), 2.35 (s, 3H); ^{13}C NMR δ 145.5 (m, incl. app. d, J_{C-F} = 244.0 Hz), 143.7 (m, incl. app. d, J_{C-F} = 244.2 Hz), 130.3, 129.0, 128.7, 127.9, 118.1 (t, J_{C-F} = 16.8 Hz), 115.2 (t, J_{C-F} = 19.3 Hz), 7.6; ^{19}F NMR δ −144.3 (dd, J_{F-F} = 22.3, 12.7 Hz, 2F), −145.9 (dd, J_{F-F} = 22.3, 12.7 Hz, 2F); EI-MS [M^+] *m/z* 240.

2,3,5,6-Tetrafluoro-4-phenylpyridine (3o)[20]

Prepared according to Method A using phenyl triflate and 2,3,5,6-tetrafluoropyridine at 40 °C. White solid; Yield: 79%; ^{1}H NMR δ 7.54 (s, 5H); ^{13}C NMR δ 144.0 (m, incl. app. d, J_{C-F} = 245.4 Hz), 139.1 (m, incl. app. d, J_{C-F} = 258.7 Hz), 133.5 (tt, J_{C-F} = 14.7, 2.8 Hz), 130.5, 129.7, 128.9, 125.9; ^{19}F NMR δ −90.9 (td, J_{F-F} = 29.3, 13.8 Hz, 2F), −145.3 (td, J_{F-F} = 29.2, 13.8 Hz, 2F); HRMS (EI) *m/z* for $C_{11}H_5F_4N$ calcd 227.0358, found 227.0352.

2,3,5,6-Tetrafluoro-1,1′-biphenyl (3p)

Prepared according to Method A using phenyl triflate and 1,2,4,5-tetrafluorobenzene at 60 °C. White solid; Yield: 51%; ^{1}H NMR δ 7.52–7.44 (m, 5H), 7.11–7.03 (m, 1H); ^{13}C NMR δ 146.3 (m, incl. app. d, J_{C-F} = 243.3 Hz), 143.7 (m, incl. app. d, J_{C-F} = 247.1 Hz), 130.1, 129.2, 128.6, 127.4, 121.5 (t, J_{C-F} = 16.7 Hz), 104.8 (t, J_{C-F} = 22.7 Hz); ^{19}F NMR δ −139.4 (dd, J_{F-F} = 21.8, 13.3 Hz, 2F), −144.1 (dd, J_{F-F} = 22.2, 12.9 Hz, 2F); EI-MS [M^+] *m/z* 226.

2′,3′,5′,6′-Tetrafluoro-1,1′ : 4′,1″-terphenyl (3p′)[14]

Prepared according to general procedure using phenyl triflate (113 mg) and 1,2,4,5-tetrafluorobenzene (225 mg) at 60 °C. The title compound was obtained as a white solid (26 mg, 17%). ^{1}H NMR δ 7.56–7.44 (m, 10H). ^{13}C NMR δ 130.3, 129.3, 128.8, 127.7. ^{19}F NMR δ −144.6 (s, 4F), EI-MS [M^+] *m/z* 302.

2,5,6-Trifluoro-[1,1′-biphenyl]-3-carbaldehyde (3q)

Prepared according to general procedure using phenyl triflate and 2,4,5-trifluorobenzaldehyde at 40 °C. White solid; Yield: 83%; ^{1}H NMR δ 10.32 (s, 1H), 7.69 (td, J = 9.0, 6.2 Hz, 1H), 7.54–7.46 (m, 5H); ^{13}C NMR δ 185.0 (d, J_{C-F} = 7.2 Hz), 158.1 (ddd, J_{C-F} = 257.2, 5.6, 2.3 Hz), 152.2 (m, incl. app. d, J_{C-F} = 260.6 Hz), 147.9 (m, incl. app. d, J_{C-F} = 249.8 Hz), 130.1, 129.4, 128.7, 126.9 (d, J_{C-F} = 1.8 Hz), 121.5 (dd, J_{C-F} = 20.4, 16.0 Hz), 120.5 (dt, J_{C-F} = 11.2, 4.3 Hz), 114.1–113.8 (m); ^{19}F NMR δ −125.8 (dd, J_{F-F} = 21.8, 8.8 Hz, 1F), −127.8 (dd, J_{F-F} = 16.2, 8.8 Hz, 1F), −139.3 (dd, J_{F-F} = 21.7, 16.2 Hz, 1F); EI-MS [M^+] *m/z* 236; HRMS (EI) *m/z* for $C_{13}H_7F_3O$ calcd 236.0449, found 236.0435.

1-(2,5,6-Trifluoro-[1,1′-biphenyl]-2-yl)ethanone (3r)

Prepared according to general procedure using phenyl triflate and 2,4,5-trifluoroacetophenone at 40 °C. Colorless oil; Yield: 40%; ^{1}H NMR δ 7.51–7.37 (m, 5H), 6.83 (td, J = 9.7, 2.0 Hz, 1H), 2.61 (t, J = 1.8 Hz, 3H); ^{13}C NMR δ 193.7, 161.1 (ddd, J_{C-F} = 254.2, 15.2, 10.0 Hz), 159.4 (ddd, J_{C-F} = 255.3, 15.6, 10.4 Hz), 157.9 (dt, J_{C-F} = 254.9, 9.8 Hz), 130.2, 128.8, 128.5, 127.5, 116.2–115.6 (m), 115.2 (ddd, J_{C-F} = 20.5, 18.6, 4.6 Hz), 101.2 (td, J_{C-F} = 27.1, 4.1 Hz), 32.4 (t, J_{C-F} = 2.6 Hz); EI-MS [M^{+}] m/z 250; HRMS (EI) m/z for $C_{14}H_9F_3O$ calcd 250.2159, found 250.0592.

2,3,6-Trifluoro-1,1′-biphenyl (3s)[19]

Prepared according to general procedure using phenyl triflate and 1,2,4-trifluorobenzene at 60 °C. White solid; Yield: 47%; ^{1}H NMR δ 7.49–7.44 (m, 5H), 7.13 (ddd, J = 18.0, 9.3, 4.9 Hz, 1H), 6.93 (tdd, J = 9.1, 3.9, 2.2 Hz, 1H); ^{13}C NMR δ 155.3 (m, incl. app. d, J_{C-F} = 245.0 Hz), 147.9 (ddd, J_{C-F} = 250.2, 14.3, 7.4 Hz), 147.5 (ddd, J_{C-F} = 244.6, 13.7, 3.7 Hz), 130.2 (t, J_{C-F} = 1.9 Hz), 128.7, 128.4, 126.7 (d, J_{C-F} = 2.7 Hz), 115.6 (ddd, J_{C-F} = 19.5, 10.0, 1.4 Hz), 110.9 (ddd, J_{C-F} = 25.5, 6.7, 4.3 Hz); ^{19}F NMR δ −120.0 (dd, J_{F-F} = 15.0, 2.9 Hz, 1F), −138.1 (dd, J_{F-F} = 21.4, 3.0 Hz, 1F), −142.2 (dd, J_{F-F} = 21.4, 15.1 Hz, 1F); EI-MS [M^{+}] m/z 208.

1-(2,6-Difluoro-[1,1′-biphenyl]-3-yl)ethanone (3t)

Prepared according to Method A using phenyl triflate and 2′,4′-difluoroacetophenone at 80 °C. Pale yellow oil; Yield: 70%; ^{1}H NMR δ 7.93–7.89 (m, 1H), 7.52–7.43 (m, 2H), 7.07 (td, J = 8.7, 1.3 Hz, 1H), 2.64 (d, J = 5.5 Hz, 1H); ^{13}C NMR δ 194.8 (d, J_{C-F} = 3.7 Hz), 162.8 (dd, J_{C-F} = 256.4, 7.0 Hz), 160.0 (dd, J_{C-F} = 256.7, 7.5 Hz), 130.6 (dd, J_{C-F} = 10.9, 4.5 Hz), 130.3 (t, J_{C-F} = 1.7 Hz), 128.7, 128.4, 128.3, 122.6 (dd, J_{C-F} = 14.7, 3.6 Hz), 119.2 (dd, J_{C-F} = 21.2, 19.3 Hz), 112.2 (dd, J_{C-F} = 23.3, 3.6 Hz), 31.4 (d, J_{C-F} = 7.9 Hz); 19F NMR δ −105.5 (d, J_{F-F} = 12.6 Hz, 1F), −109.2 (d, J_{F-F} = 12.7 Hz, 1F); EI-MS [M+] m/z 232; HRMS (ESI) m/z for $C_{14}H_{10}F_2ONa$ [M + Na]$^{+}$ calcd 255.0597 found 255.0599.

5,6-Difluoro-[1,1′-biphenyl]-2-carbonitrile (3u)

Prepared according to Method A using phenyl triflate and 3,4-difluorobenzonitrile at 100 °C. Pale yellow solid; Yield: 30%; ^{1}H NMR δ 7.60–7.44 (m, 1H), 7.31–7.23 (m, 1H); ^{13}C NMR δ 152.2 (dd, J_{C-F} = 569.6, 13.5 Hz), 149.6 (dd, J_{C-F} = 562.0, 13.5 Hz), 136.0 (d, J_{C-F} = 14.9 Hz), 130.4 (d, J_{C-F} = 2.3 Hz), 130.0 (dd, J_{C-F} = 8.0, 4.8 Hz), 129.8, 129.6, 128.8, 117.1 (d, J_{C-F} = 18.6 Hz), 116.8, 109.5 (t, J_{C-F} = 3.3 Hz); ^{19}F NMR δ −127.0 (d, J_{F-F} = 21.8 Hz, 1F), −137.5 (d, J_{F-F} = 21.8 Hz, 1F); EI-MS [M^{+}] m/z 215; HRMS (ESI) m/z for $C_{13}H_7F_2NNa$ [M + Na]$^{+}$ calcd 238.0444 found 238.0441.

2,3,4,5,6-Pentafluoro-2′,4′,6′-trimethyl-1,1′-biphenyl (3v)[17]

Prepared according to Method B using 2,4,6-trimethylphenyl triflate and pentafluorobenzene. White solid; Yield: 92%; ^{1}H NMR δ 6.99 (s, 1H), 2.34 (s, 1H), 2.05 (s, 1H); ^{13}C NMR δ 143.8 (m, incl. app. d, J_{C-F} = 246.8 Hz), 140.5 (m, incl. app. d, J_{C-F} = 264.7 Hz), 137.8 (m, incl. app. d, J_{C-F} = 254.4 Hz), 137.2, 128.6, 122.6 (d, J_{C-F} = 1.3 Hz), 114.5 (td, J_{C-F} = 21.0, 3.8 Hz), 21.1, 20.0;EI-MS [M^{+}] m/z 286.

2,3,5,6-Tetrafluoro-4-mesitylpyridine (3w)

Prepared according to Method B using 2,4,6-trimethylphenyl triflate and 2,3,5,6-tetrafluoropyridine. Colorless oil; Yield: 85%; ^{1}H NMR δ 7.04 (s, 2H), 2.37 (s, 3H), 2.10 (s, 6H); ^{13}C NMR δ 143.8 (m, incl. app. d, J_{C-F} = 246.4 Hz), 140.1, 139.3 (m, incl. app. d, J_{C-F} = 257.6 Hz), 136.2, 133.6 (tt, J_{C-F} = 19.0, 3.0 Hz,), 128.8, 127.0 (d, J_{C-F} = 295.0 Hz), 122.2, 21.1, 19.8; ^{19}F NMR δ −90.8 (dd, J_{F-F} = 23.3, 15.8 Hz, 2F), −141.5 (td, J_{F-F} = 29.5, 13.7 Hz, 2F); EI-MS [M^{+}] m/z 269; HRMS (EI) m/z for $C_{14}H_{11}F_4N$ calcd 269.0828 found 269.0822.

2,3,4,5,6-Pentafluoro-2′-methyl-1,1′-biphenyl (3x)[14]

Prepared according to Method B using 2-methylphenyl triflate and pentafluorobenzene. Colorless oil; Yield: 97%; ^{1}H NMR δ 7.43–7.36 (m, 2H), 7.31 (td, J = 7.3, 1.4 Hz, 1H), 7.21 (d, J = 7.6 Hz, 1H), 2.21 (2, 3H); ^{13}C NMR δ 144.08 (m, incl. app. d, J_{C-F} = 246.3 Hz), 140.6 (m, incl. app. d, J_{C-F} = 253.4 Hz), 137.7 (m, incl. app. d, J_{C-F} = 253.1 Hz), 137.4, 130.6, 130.5, 129.6, 126.0, 125.9 (d, J_{C-F} = 1.4 Hz), 115.5 (td, J_{C-F} = 19.9, 3.9 Hz), 19.6; ^{19}F NMR δ −140.7 (dd, J_{F-F} = 23.2, 8.3 Hz, 2F), −155.5 (t, J_{F-F} = 20.9 Hz, 1H), −162.39 (dt, J_{F-F} = 23.2, 8.5 Hz, 2F); EI-MS [M^{+}] m/z 258.

2′-Ethyl-2,3,4,5,6-pentafluoro-1,1′-biphenyl (3y)[15]

Prepared according to Method B using 2-ethylphenyl triflate and pentafluorobenzene. Colorless oil; Yield: 54%; ^{1}H NMR δ 7.43 (ddd, J = 13.4, 7.7, 3.8 Hz, 1H), 7.31 (td, J = 7.4, 1.6 Hz, 1H), 7.17 (d, J = 7.6 Hz, 1H), 2.47 (q, J = 7.6 Hz, 1H), 1.12 (t, J = 7.6 Hz, 2H); ^{13}C NMR δ 144.1 (m, incl. app. d, J_{C-F} = 242.1 Hz), 143.4, 140.6 (m, incl. app. d, J_{C-F} = 253.4 Hz), 137.6 (m, incl. app. d, J_{C-F} = 253.2 Hz), 130.7, 129.9, 128.8, 126.0, 125.2, 115.5 (td, J_{C-F} = 20.1, 3.8 Hz), 26.4, 14.8; ^{19}F NMR δ −140.3 (dd, J_{F-F} = 23.4, 8.4 Hz, 2F), −155.5 (t, J_{F-F} = 20.9 Hz, 1F), −162.4 (dt, J_{F-F} = 23.4, 8.5 Hz, 2F); EI-MS [M^{+}] m/z 272.

2,3,4,5,6-Pentafluoro-2′-isopropyl-5′-methyl-1,1′-biphenyl (3z)

Prepared according to Method B using 2-isopropyl-5-methyl-phenyl triflate and pentafluorobenzene. White solid; Yield: 72%; ^{1}H NMR δ 7.37 (d, J = 8.1 Hz, 1H), 7.30 (dd, J = 8.1, 1.2 Hz, 1H), 6.96 (s, 1H), 2.62 (ht, J = 6.8 Hz, 1H), 2.37 (s, 3H), 1.17 (d, J = 6.9 Hz, 6H); ^{13}C NMR δ ^{13}C NMR δ 145.1, 144.2 (m, incl. app. d, J_{C-F} = 245.3 Hz), 140.5 (m, incl. app. d, J_{C-F} = 253.2 Hz), 137.6 (m, incl. app. d, J_{C-F} = 253.2 Hz), 135.6, 130.9 (d, J_{C-F} = 1.9 Hz), 125.8, 124.2 (d, J_{C-F} = 1.3 Hz), 115.7

(td, J_{C-F} = 20.3, 3.8 Hz), 30.7, 23.9, 20.8; ^{19}F NMR δ −140.27 (dd, J_{F-F} = 23.6, 8.5 Hz, 2F), −155.81 (t, J_{F-F} = 20.9 Hz, 1F), −162.5 (td, J_{F-F} = 23.6, 8.6 Hz, 2F); EI-MS [M$^+$] *m/z* 300; HRMS (EI) *m/z* for $C_{16}H_{13}F_5$ calcd 300.0937 found 300.0928.

2,3,4,5,6-Pentafluoro-2′-methoxy-5′-methyl-1,1′-biphenyl (3a1)

Prepared according to Method B using 2-methoxy-5-methylphenyl triflate and pentafluorobenzene. Colorless oil; Yield: 76%; ^{1}H NMR δ 7.31–7.19 (m, 2H), 7.03 (s, 1H), 6.92 (d, J = 8.4 Hz, 1H), 3.78 (s, 3H), 2.33 (s, 3H); ^{13}C NMR δ 155.1, 144.4 (m, incl. app. d, J_{C-F} = 243.1 Hz), 140.4 (m, incl. app. d, J_{C-F} = 252.5 Hz), 137.6 (m, incl. app. d, J_{C-F} = 251.9 Hz), 132.1, 131.5, 131.1, 130.0, 127.4, 115.0, 112.9 (t, J_{C-F} = 6.9 Hz), 111.3, 55.8, 20.4; ^{19}F NMR δ −140.47 (dd, J_{F-F} = 23.0, 7.8 Hz), −156.51 (t, J_{F-F} = 20.9 Hz), −160.66–−169.95 (m); EI-MS [M$^+$] *m/z* 288; HRMS (EI) *m/z* for $C_{14}H_9F_5O$ calcd 288.0574 found 288.0562.

Methyl 2′,3′,4′,5′,6′-pentafluoro-4-methyl-[1,1′-biphenyl]-2-carboxylate (3b1)

Prepared according to Method B using methyl 5-methyl-2-(((trifluoromethyl)sulfonyl)oxy)benzoate and pentafluorobenzene. Colorless oil; Yield: 99%; ^{1}H NMR δ 7.98 (d, J = 0.7 Hz, 1H), 7.45 (dd, J = 7.8, 1.1 Hz, 1H), 7.22 (d, J = 7.8 Hz, 1H), 3.78 (s, 3H), 2.47 (s, 3H); ^{13}C NMR δ 166.3, 144.0 (m, incl. app. d, J_{C-F} = 245.2 Hz), 140.5 (m, incl. app. d, J_{C-F} = 252.9 Hz), 139.9, 137.4 (m, incl. app. d, J_{C-F} = 252.0 Hz), 133.1, 131.9, 131.7, 130.0, 124.4 (d, J_{C-F} = 1.5 Hz), 115.8 (td, J_{C-F} = 19.1, 4.1 Hz), 52.1, 21.1; ^{19}F NMR δ −142.1 (dd, J_{F-F} = 23.2, 7.9 Hz, 2F), −156.2 (t, J_{F-F} = 20.9 Hz, 1F), −163.4 (dt, J_{F-F} = 23.2, 8.0 Hz, 2F); EI-MS [M$^+$] *m/z* 316; HRMS (ESI) *m/z* for $C_{15}H_9F_5O_2Na$ [M + Na]$^+$ calcd 339.0420 found 339.0419.

5-(Perfluorophenyl)isoquinoline (3c1)

Prepared according to Method B using isoquinolin-5-yl triflate and pentafluorobenzene. Pale yellow solid; Yield: 79%; ^{1}H NMR δ 9.37 (s, 1H), 8.57 (d, J = 6.0 Hz, 1H), 8.16 (d, J = 7.9 Hz, 1H), 7.73 (dt, J = 7.1, 6.5 Hz, 2H), 7.32 (d, J = 6.0 Hz, 1H); ^{13}C NMR δ 158.0, 144.5 (m, incl. app. d, J_{C-F} = 248.4 Hz), 144.0, 141.3 (m, incl. app. d, J_{C-F} = 255.4 Hz), 137.9 (m, incl. app. d, J_{C-F} = 254.3 Hz), 134.3, 133.4, 129.8, 128.8, 126.8, 123.1, 117.4, 112.6(t, J_{C-F} = 37.0 Hz); ^{19}F NMR δ −139.4 (dd, J_{F-F} = 22.3, 6.9 Hz), −153.1 (t, J_{F-F} = 20.9 Hz), −161.1 (dt, J_{F-F} = 21.7, 7.3 Hz); EI-MS [M$^+$] *m/z* 295; HRMS (ESI) *m/z* for $C_{15}H_7F_5N$ [M + H]$^+$ calcd 296.0499 found 296.0490.

8-(Perfluorophenyl)quinoline (3d1)

Prepared according to Method B using quinolin-8-yl triflate and pentafluorobenzene. Off-white solid; Yield: 54%; ^{1}H NMR δ 8.90 (dd, J = 4.1, 1.7 Hz, 1H), 8.24 (dd, J = 8.3, 1.6 Hz, 1H), 7.98 (dd, J = 8.1, 1.3 Hz, 1H), 7.77–7.61 (m, 2H), 7.47 (dd, J = 8.3, 4.2 Hz, 1H); ^{13}C NMR δ 150.85, 146.1, 144.6 (m, incl. app. d, J_{C-F} = 242.9 Hz), 136.31, 132.2, 129.9, 128.6, 126.3, 126.0, 121.7, 114.32–113.54 (m); ^{19}F NMR δ −139.6 (dd, J_{F-F} = 23.3, 7.9 Hz), −155.6 (t, J_{F-F} = 20.8 Hz), −163.1 (td, J_{F-F} = 23.0, 7.7 Hz); EI-MS [M$^+$] *m/z* 295; HRMS (ESI) *m/z* for $C_{15}H_7F_5N$ [M + H]$^+$ calcd 296.0499 found 296.0485.

2′,3′,5′,6′-Tetrafluoro-4′-methyl-[1,1′-biphenyl]-4-carbonitrile (3e1)

Prepared according to Method C using *p*-cyanophenyl mesylate and 1,2,4,5-tetrafluoro-3-methybenzene. White solid; Yield: 80%; ^{1}H NMR δ 7.77 (d, J = 8.7 Hz, 2H), 7.58 (dt, J = 8.7, 1.4 Hz, 2H), 2.34 (t, J = 2.1 Hz, 3H); ^{13}C NMR δ 145.4 (dddd, J_{C-F} = 245.3, 14.4, 7.3, 4.0 Hz), 143.4 (dt, J_{C-F} = 247.1, 14.2 Hz), 132.5, 132.2, 131.0 (t, J_{C-F} = 2.3 Hz), 118.3, 116.7 (t, J_{C-F} = 19.2 Hz), 116.0 (t, J_{C-F} = 16.2 Hz), 112.8, 7.7; ^{19}F NMR δ −143.1 (dd, J_{F-F} = 22.0, 12.6 Hz, 2F), −145.5 (dd, J_{F-F} = 22.0, 12.6 Hz, 2F); EI-MS [M$^+$] *m/z* 265; HRMS (ESI) *m/z* for $C_{16}H_{14}F_5$ [M + H]$^+$ calcd 266.0587 found 266.0592.

2′,3′,5′,6′-Tetrafluoro-4′-methoxy-[1,1′-biphenyl]-4-carbonitrile (3f1)

Prepared according to Method C using *p*-cyanophenyl mesylate and 1,2,4,5-tetrafluoro-3-methoxybenzene. White solid; Yield: 60%; ^{1}H NMR δ 7.77 (dt, J = 8.6, 1.6 Hz, 2H), 7.57 (dd, J = 5.7, 4.3 Hz, 2H), 4.15 (s, 3H); ^{13}C NMR δ 144.2 (m, incl. app. d, J_{C-F} = 246.1 Hz), 141.1 (m, incl. app. d, J_{C-F} = 246.6 Hz), 138.6, 132.3, 132.1, 131.0 (t, J_{C-F} = 2.1 Hz), 118.3, 112.8, 112.0 (t, J_{C-F} = 16.6 Hz), 62.1 (t, J_{C-F} = 3.8 Hz); ^{19}F NMR δ −145.0 (dd, J_{F-F} = 21.3, 8.2 Hz, 2F), −157.5 (dd, J_{F-F} = 21.4, 8.4 Hz, 2F); EI-MS [M$^+$] *m/z* 281; HRMS (ESI) *m/z* for $C_{16}H_{15}F_5$ [M + H]$^+$ calcd 282.0537 found 282.0543.

2,2″,3,3″,4,4″,5,5″,6,6″-Decafluoro-1,1′ : 4′,1″-terphenyl (5)[27]

Prepared according to Method C using *p*-chlorophenyl mesylate and pentafluorobenzene. White solid; Yield: 74%; ^{1}H NMR δ 7.42 (s, 4H); ^{13}C NMR δ 144.2 (m, incl. app. d, J_{C-F} = 248.5 Hz), 140.7 (m, incl. app. d, J_{C-F} = 254.8 Hz), 138.0 (m, incl. app. d, J_{C-F} = 253.3 Hz), 130.5, 127.5, 115.0 (td, J_{C-F} = 16.9, 4.1 Hz); ^{19}F NMR δ −143.0 (dd, J_{F-F} = 24.0, 8.4 Hz, 2F), −154.5 (t, J_{F-F} = 22.0 Hz, 1F), −161.7 (dt, J_{F-F} = 37.6, 8.8 Hz, 2F); EI-MS [M$^+$] *m/z* 410.

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