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Preparation of fluorinated biaryls through direct palladium-catalyzed coupling of polyfluoroarenes with aryltrifluoroborates

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ABSTRACT

The direct palladium-catalyzed coupling of polyfluoroarenes with aryltrifluoroborates gave the desired products of fluorinated biaryls in good to excellent yields. A diverse set of important functional groups including methoxy, aldehyde, ester, nitro and halide can be well tolerated in the protocol.

1. Introduction

Fluorinated biaryl compounds have recently received considerable attention from both academic and industrial researchers owing to their importance in pharmaceuticals and functional materials [1–4]. As a consequence, strategies for the formation of such bonds have been the focus of intensive research [5–11].

The traditional routes for creation of such compounds involved using perfluoroaryl metal, halide, and aldehyde reagents [12–14]. However, these procedures suffer from a disadvantage as the necessity to prepare functionalized starting materials. The direct coupling of electron-deficient polyfluoroarenes with arylating reagents through C–H bonds activation represents a more atom-efficient method for the construction of polyfluorobiphenyls. For example, Fagnou [15–17] and Daugulis' [18,19] groups developed palladium and copper-catalyzed direct arylation of perfluorobenzenes with aryl halides, respectively; Su and co-workers reported a palladium-catalyzed method for the direct arylation of polyfluorobenzenes with arylboronic acids [20]; More recently, the Su [21] and the Shi [22] groups independently reported palladium-catalyzed oxidative cross-coupling of polyfluoroarenes with simple arenes. However, these approaches usually require the use of excessive external bases or acids for maximum reaction efficiency. Therefore, these promising protocols could still benefit from the development of milder conditions for the coupling reactions.

The use of organotrifluoroborates as nucleophiles provides an attractive method for carbon–carbon bond formation as they are easily accessible and handled, and they show high stability toward moisture and air, and produce relatively benign byproducts [23–26]. Moreover, organotrifluoroborates are insensitive to various functional groups and do not undergo undesirable side reactions even under harsh reaction conditions. To the best of our knowledge, metal-assisted coupling of polyfluoroarenes with organotrifluoroborates has not been reported in the literature.

Inspired by our experiences in the research of copper-catalyzed trifluoromethylation with organotrifluoroborates [27–30] and the recent advancements in the field of catalytic C–H activation [31–37], we explored the possibility of developing an alternative strategy for the synthesis of fluorinated biaryls by employing aryltrifluoroborates as synthetic reagents. Herein we report an efficient palladium-catalyzed coupling of polyfluoroarenes with aryltrifluoroborates for synthesis of fluorinated biaryls under mild conditions.

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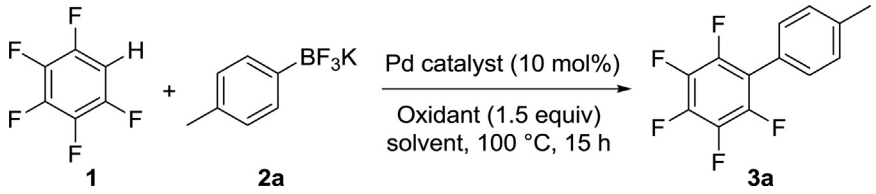
Table 1
Optimization of direct Pd-catalyzed coupling of pentafluorobenzene with aryltrifluoroborates[a]



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Entry	Pd catalyst	Oxidant	Solvent	Yield (%)[b]
1	$PdCl_2$	Ag_2O	NMP	43
2	$Pd(OAc)_2$	Ag_2O	NMP	83
3	$Pd(PPh_3)_4$	Ag_2O	NMP	13
4	$Pd(dba)_2$	Ag_2O	NMP	Trace
5	$Pd(OAc)_2$	Ag_2CO_3	NMP	24
6	$Pd(OAc)_2$	AgOAc	NMP	60
7	$Pd(OAc)_2$	AgF	NMP	26
8	$Pd(OAc)_2$	$AgNO_3$	NMP	15
9	$Pd(OAc)_2$	Ag_2O	DMF	68
10	$Pd(OAc)_2$	Ag_2O	$PhCH_3$	<5
11	$Pd(OAc)_2$	Ag_2O	MeCN	38
12	–	–	NMP	0
13	$Pd(OAc)_2$	–	NMP	0
14	–	Ag_2O	NMP	0

[a] Reaction conditions: pentafluorobenzene **1** (0.10 mmol), **2a** (0.10 mmol), Pd catalyst (0.010 mmol), oxidant (0.15 mmol), solvents (1.0 mL), 100 °C, 15 h.
[b] Isolated yield.

2. Results and discussion

We began by examining the coupling of pentafluorobenzene (**1**) with potassium 4-tolyltrifluoroborates (**2a**) as a model reaction (Table 1). To investigate the activity of palladium as a catalyst, we first screened four different Pd sources. As shown in Table 1, the combination of $Pd(OAc)_2$ and Ag_2O in NMP (N-Methyl-2-pyrrolidone) at 100 °C after 15 h gave the best result (entry 2). Under these reaction conditions, a 83% yield of 1,2,4,5-tetrafluoro-3-(p-tolyloxy)benzene (**3a**) was obtained. The use of other palladium catalysts, such as a simple catalyst system of $PdCl_2$ or $Pd(PPh_3)_4$ and $Pd(dba)_2$, caused the yield to decrease dramatically (entries 1, 3 and 4). As the oxidant, Ag_2O gave the highest yield for the coupling. The replacement of Ag_2O with other oxidants such as Ag_2CO_3, AgOAc, AgF and $AgNO_3$ resulted in much lower reaction efficiency (entries 5–8).

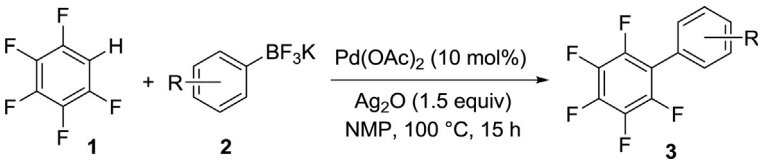
Further investigations into the solvent effect revealed that other solvents such as N,N-dimethylformamide (DMF) and MeCN resulted in lower yields (entries 9 and 11), whereas the use of less polar aromatic solvent, *i.e.* toluene, was detrimental to the reaction (entry 10). Importantly, control experiments revealed that no reaction was observed in the absence of either of $Pd(OAc)_2$, Ag_2O or both (entries 12–14), which suggests that the presence of palladium and oxidants is essential for an efficient catalytic system. This result is consistent with those previously reported of metal-catalyzed oxidative C–C formation [38–42]. Notably, in contrast to the reactions of polyfluoroarenes with arylboronic acids, which required additional base and/or acid to promote the coupling reactions smoothly [20], the present reaction proceeded efficiently in good yields without the use of other bases, as Ag_2O could also fulfill the role as a base.

To explore the substrate scope, we examined a range of aryltrifluoroborates derivatives in the coupling reaction with pentafluorobenzene under the optimized reaction conditions (Table 2). The phenyltrifluoroborate and alkyl-substituted phenyltrifluoroborates gave the desired coupling products **3a**–**3d** in yields ranging from 72% to 85%. The *para*- and *meta*-phenyl-substituted phenyltrifluoroborates and 2-naphthyltrifluoroborate also smoothly underwent coupling reaction to give product **3e**, **3f** and **3 g** in 89%, 92% and 90% yields, respectively. Reactions of *para*- and *meta*-substituted phenyltrifluoroborates with electron-donating groups and 6-methoxy-2-naphthyltrifluoroborate also proceeded efficiently, and afforded the corresponding coupling products **3h**–**3k** in good to excellent yields of 79–91%.

To demonstrate the advantage of the mild reaction conditions of our method, we then tested substrates bearing sensitive functional groups. Encouragingly, *para*-aldehyde-substituted phenyltrifluoroborate could be employed as suitable substrate, albeit in a modest yield (46%) of product **3l**. Gratifyingly, phenyltrifluoroborates bearing sensitive ester groups provided the desired products **3m**–**3o** in 82–87% yields. Likewise, a reaction of 3-nitro-phenyltrifluoroborate with pentafluorobenzene afforded the product **3p** in an acceptable yield (53%) under the same reaction conditions. It should be mentioned that the aryl–Cl moiety of the aryltrifluoroborate did not interfere with the coupling reaction. Thereby, 4-chloro-phenyltrifluoroborate was readily employed in the coupling reaction to give **3q** as the exclusive product in a good yield of 71%. These functional groups present opportunities to further functionalize the fluorinated biaryl products.

To further probe substrate scope with respect to fluoroarenes, couplings of tetrafluoroarenes **4** with various aryltrifluoroborates were also tested and representative results are summarized in Table 3. 1,2,4,5-Tetrafluorobenzene bearing two reaction sites, reacted with aryltrifluoroborates to afford mixtures of mono- and diarylation products (**5a** + **5a′** and **5b** + **5b′**) in 75–80% overall yields. It was observed that electron-rich or electron-deficient substituents at the 3-position of tetrafluoroarenes did not significantly affect the reaction efficiency. In fact, the reaction of 1,2,4,5-tetrafluoro-3-methoxybenzene and 1,2,4,5-tetrafluoro-3-nitrobenzene with aryltrifluoroborates provided the corresponding products (**5c**–**5g** and **5h**–**5j**, respectively) in moderate to good yields. It is worth noting that the methoxy, chloro, nitro groups could be tolerated quite well again under the reaction conditions providing opportunities for further functionalization. In contrast, the 1,3,5-trifluorobenzene underwent a slow reaction with

Table 2
Pd-catalyzed direct cross-coupling of pentafluorobenzene with various aryltrifluoroborates[a,b]



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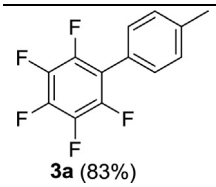
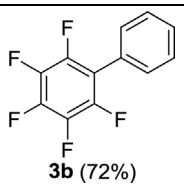
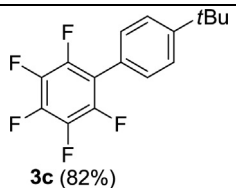
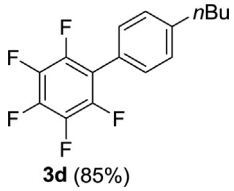

3a (83%)

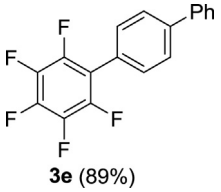

3b (72%)



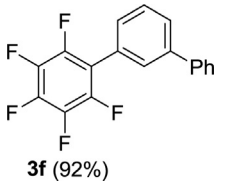
3c (82%)



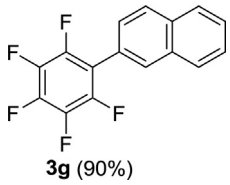
3d (85%)

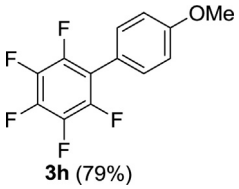


3e (89%)

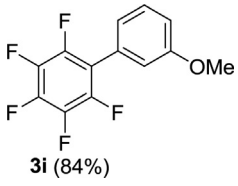


3f (92%)

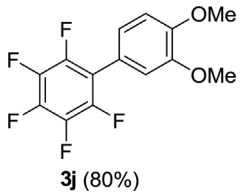

3g (90%)



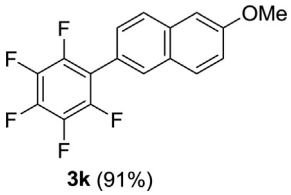
3h (79%)



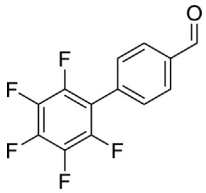
3i (84%)



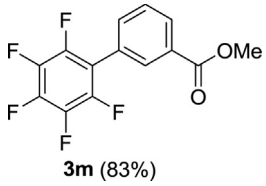
3j (80%)



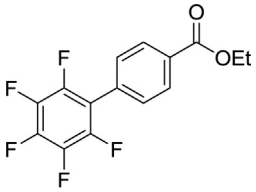
3k (91%)



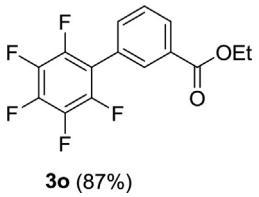
3l (46%)



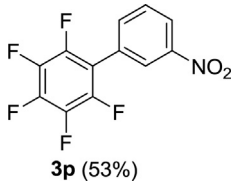
3m (83%)



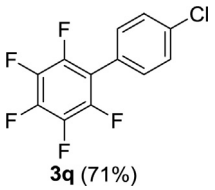
3n (82%)



3o (87%)



3p (53%)



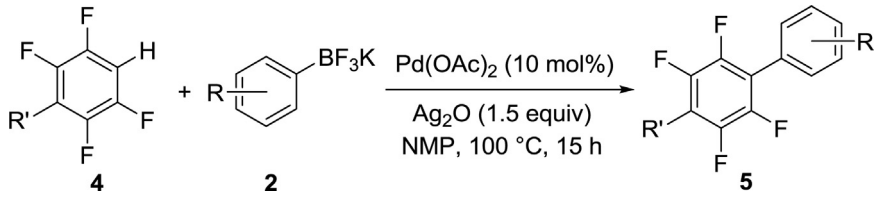
3q (71%)

[a] Reaction conditions: **1** (0.40 mmol), aryltrifluoroborates **2** (0.40 mmol), $Pd(OAc)_2$ (0.040 mmol), Ag_2O (0.60 mmol), NMP (3.0 mL), 100 °C, 15 h.
[b] Isolated yield.

aryltrifluoroborates under the chosen reaction conditions, which finally gave the product **5k** in 18% yield.

A plausible catalytic cycle, as adapted from the mechanistic studies performed on the palladium-catalyzed direct arylation of polyfluoroarenes with arylboronic acids [20], is showed in Scheme 1. The initial transmetalation of $Pd^{II}(OAc)_2$ (**A**) with an aryltrifluoroborate would generate the arylpalladium intermediate **B**. The palladation of fluoroarene then occurs *via* a concerted metalation-deprotonation [15,43,44] to furnish the intermediate **C**, which would subsequently provides fluorinated biaryl product along with the Pd^0 complex through reductive elimination. Finally, the released Pd^0 is re-oxidized by Ag_2O to regenerate **A**, which would continue the catalytic cycle.

Table 3
Pd-catalyzed direct cross-coupling of tetrafluoroarenes with various aryltrifluoroborates[a,b]



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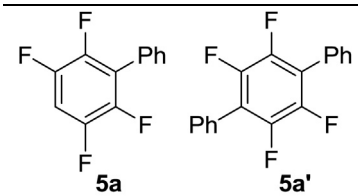
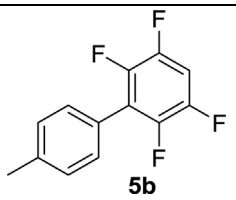
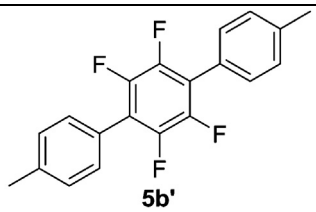
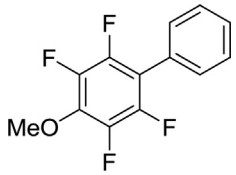


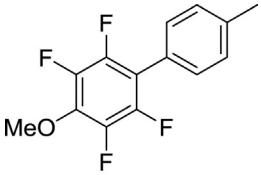
75% (**5a:5a'**=4.7:1)

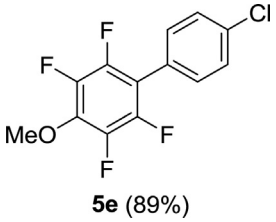


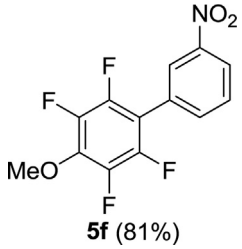


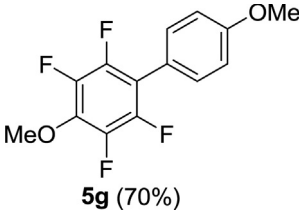
80% (**5b:5b'**=5.2:1)

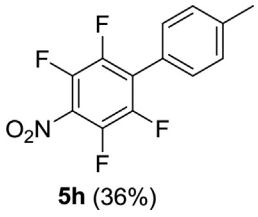


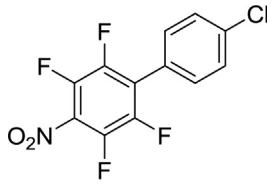


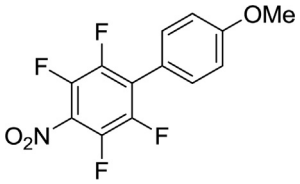


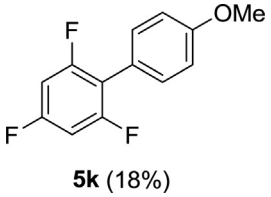




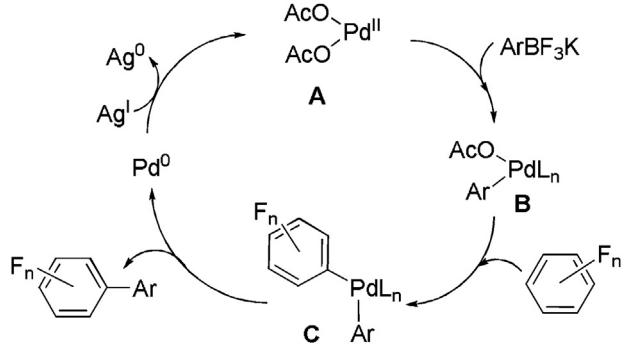








[a] Reaction conditions: tetrafluoroarenes **4** (0.40 mmol), aryltrifluoroborates **2** (0.40 mmol), $Pd(OAc)_2$ (0.040 mmol), Ag_2O (0.60 mmol), NMP (3.0 mL), 100 °C, 15 h.
[b] Isolated yield.



Scheme 1. Proposed mechanism of Pd-catalyzed direct cross-coupling of polyfluoroarenes with various aryltrifluoroborates.

3. Conclusions

In summary, we have reported an efficient palladium catalysis system for the direct cross-coupling of polyfluoroarenes with aryltrifluoroborates through C–H bond cleavage under mild conditions. The catalysis accommodates a diverse set of functional groups including methoxy, aldehyde, ester, nitro and chloride and affords the desired coupling products in good to excellent yields.

4. Experimental

4.1. General description of materials and methods

^{1}H NMR, ^{19}F NMR and ^{13}C NMR spectra were recorded using a Bruker AVIII 400 spectrometer. ^{1}H NMR and ^{13}C NMR chemical

shifts were reported in parts per million (ppm) downfield from tetramethylsilane and ^{19}F NMR chemical shifts were determined relative to $CFCl_3$ as the external standard and low field is positive. Coupling constants (J) are reported in Hertz (Hz). The residual solvent peaks were used as an internal reference: ^1H NMR (chloroform δ 7.26) and ^{13}C NMR (chloroform δ 77.0). The following abbreviations were used to explain the multiplicities: s = singlet, d = doublet, t = triplet, q = quartet, m = multiplet, br = broad. Potassium organotrifluoroborates were prepared according to literature procedures [45]. Other reagents were received from commercial sources. Solvents were freshly dried and degassed according to the purification handbook "*Purification of Laboratory Chemicals*" prior to use. Column chromatography purifications were performed by flash chromatography using Merck silica gel 60.

4.2. General procedure for Pd-catalyzed direct cross-coupling of polyfluoroarenes with aryltrifluoroborates

In a glovebox, $Pd(OAc)_2$ (9.0 mg, 0.040 mmol), Ag_2O (138.0 mg, 0.60 mmol) and aryltrifluoroborates (0.40 mmol) were added to a Schlenk tube that was equipped with a stirring bar. Freshly distilled solvent NMP (3.0 mL) was added into this tube, polyfluoroarene (0.40 mmol) were added in turn to the Schlenk tube through the rubber septum *via* syringe. The tube was capped with a septum and taken out. The reaction mixture was stirred at 100 °C for 15 h. After cooling down, the reaction mixture was diluted with 10 mL of ethyl ether, filtered through a pad of silica gel, followed by washing the pad of the silica gel with the same solvent (10 mL). The filtrate was washed with water (3 × 10 mL). The organic phase was dried over $MgSO_4$, filtered, concentrated *in vacuo*. The residue was then purified by flash chromatography on silica gel to provide the corresponding product.

4.2.1. 2,3,4,5,6-Pentafluoro-4′-methylbiphenyl (**3a**) [6,15]

Following the general procedure, using petroleum ether as the eluent afforded a white solid (83% yield). mp: 116–118 °C. ^1H NMR (400 MHz, $CDCl_3$) δ 7.34 (s, 4H), 2.45 (s, 3H). ^{19}F NMR (376 MHz, $CDCl_3$) δ −143.4 (dd, J = 23.2, 7.9 Hz, 2F), −156.2 (t, J = 20.9 Hz, 1F), −162.5 (m, 2F). ^{13}C NMR (101 MHz, $CDCl_3$) δ 145.7–145.2 (m), 143.2–142.4 (m), 141.7–141.3 (m), 139.4 (s), 139.3–138.7 (m), 136.8–136.3 (m), 130.0 (s), 129.5 (s), 123.4 (s), 116.5–115.6 (m), 21.3 (s). GC–MS m/z 258 (M^+).

4.2.2. 2,3,4,5,6-Pentafluorobiphenyl (**3b**) [6]

Following the general procedure, using petroleum ether as the eluent afforded a white solid (72% yield). mp: 104–106 °C. ^1H NMR (400 MHz, $CDCl_3$) δ 7.56–7.49 (m, 3H), 7.49–7.43 (m, 2H). ^{19}F NMR (376 MHz, $CDCl_3$) δ −143.3 (dd, J = 22.9, 8.3 Hz, 2F), −155.7 (t, J = 21.0 Hz, 1F), −162.3 (m, 2F). ^{13}C NMR (101 MHz, $CDCl_3$) δ 145.5–145.3 (m), 143.0–142.8 (m), 142.1–141.1 (m), 139.3–138.9 (m), 137.0–136.0 (m), 130.1 (s), 129.3 (s), 128.7 (s), 126.4 (s), 115.9 (td, J = 17.2, 3.9 Hz). GC–MS m/z 244 (M^+).

4.2.3. 4′-tert-Butyl-2,3,4,5,6-pentafluorobiphenyl (**3c**) [46]

Following the general procedure, using petroleum ether as the eluent afforded a white solid (82% yield). mp: 78–80 °C. ^1H NMR (400 MHz, $CDCl_3$) δ 7.55 (d, J = 7.5 Hz, 2H), 7.40 (d, J = 7.5 Hz, 2H), 1.40 (s, 9H). ^{19}F NMR (376 MHz, $CDCl_3$) δ −143.4 (dd, J = 23.0, 8.2 Hz, 2F), −156.2 (t, J = 21.0 Hz, 1F), −162.5 (m, 2F). ^{13}C NMR (101 MHz, $CDCl_3$) δ 152.5 (s), 145.7–145.3 (m), 143.3–142.6 (m), 139.2–138.6 (m), 136.9–136.2 (m), 129.8 (s), 125.7 (s), 123.4 (s), 116.3–115.5 (m), 34.8 (s), 31.2 (s). GC–MS m/z 300 (M^+).

4.2.4. 4′-Butyl-2,3,4,5,6-pentafluorobiphenyl (**3d**) [47]

Following the general procedure, using petroleum ether as the eluent afforded a white solid (85% yield). mp: 58–60 °C. ^1H NMR (400 MHz, $CDCl_3$) δ 7.36 (d, J = 8.2 Hz, 2H), 7.33 (d, J = 8.2 Hz, 2H), 2.70 (t, J = 7.8 Hz, 2H), 1.73–1.63 (m, 2H), 1.48–1.36 (m, 2H), 0.98 (t, J = 7.3 Hz, 3H). ^{19}F NMR (376 MHz, $CDCl_3$) δ −143.4 (dd, J = 22.9, 7.8 Hz, 2F), −156.3 (t, J = 21.0 Hz, 1F), −162.5 (m, 2F). ^{13}C NMR (101 MHz, $CDCl_3$) δ 145.7–145.1 (m), 144.4 (s), 143.2–142.7 (m), 141.6–141.2 (m), 139.3–138.8 (m), 136.9–136.4 (m), 130.0 (s), 128.8 (s), 123.6 (s), 116.3–115.7 (m), 35.5 (s), 33.4 (s), 22.4 (s), 13.9 (s). GC–MS m/z 300 (M^+).

4.2.5. 4-Perfluorophenylbiphenyl (**3e**) [48]

Following the general procedure, using petroleum ether as the eluent afforded a white solid (89% yield). mp: 193–195 °C. ^1H NMR (400 MHz, $CDCl_3$) δ 7.75 (d, J = 8.0 Hz, 2H), 7.67 (d, J = 8.0 Hz, 2H), 7.52 (dd, J = 15.7, 7.9 Hz, 4H), 7.42 (t, J = 7.3 Hz, 1H). ^{19}F NMR (376 MHz, $CDCl_3$) δ −143.1 (dd, J = 22.9, 7.9 Hz, 2F), −155.5 (t, J = 21.0 Hz, 1F), −162.1 (m, 2F). ^{13}C NMR (101 MHz, $CDCl_3$) δ 142.2 (s), 140.2 (s), 130.6 (s), 128.9 (s), 127.8 (s), 127.4 (s), 127.2 (s), 125.3 (s). GC–MS m/z 320 (M^+).

4.2.6. 3-Perfluorophenylbiphenyl (**3f**) [49]

Following the general procedure, using petroleum ether as the eluent afforded a white solid (92% yield). mp: 148–150 °C. ^1H NMR (400 MHz, $CDCl_3$) δ 7.75–7.55 (m, 5H), 7.54–7.38 (m, 4H). ^{19}F NMR (376 MHz, $CDCl_3$) δ −142.9 (dd, J = 23.1, 7.7 Hz, 2F), −155.4 (t, J = 20.9 Hz, 1F), −162.1 (m, 2F). ^{13}C NMR (101 MHz, $CDCl_3$) δ 145.6–145.4 (m), 143.4–142.5 (m), 141.8–141.6 (m), 139.5–138.6 (m), 136.9–136.2 (m), 141.9 (s), 140.3 (s), 129.2 (s), 129.0 (s), 128.9 (s), 128.1 (s), 127.7 (s), 127.2 (s), 126.9 (s), 116.2–115.4 (m). GC–MS m/z 320 (M^+).

4.2.7. 2-(Perfluorophenyl) naphthalene (**3g**) [18]

Following the general procedure, using petroleum ether as the eluent afforded a white solid (90% yield). mp: 172–174 °C. ^1H NMR (400 MHz, $CDCl_3$) δ 8.02–7.89 (m, 4H), 7.64–7.50 (m, 3H). ^{19}F NMR (376 MHz, $CDCl_3$) δ −143.0 (dd, J = 23.2, 7.7 Hz, 2F), −155.4 (t, J = 20.9 Hz, 1F), −162.0 to −162.2 (m, 2F). ^{13}C NMR (101 MHz, $CDCl_3$) δ 145.9–145.3 (m), 143.4–142.9 (m), 141.8–141.6 (m), 139.5–138.9 (m), 137.1–136.3 (m), 133.3 (s), 133.0 (s), 130.1 (s), 128.4 (s), 128.3 (s), 127.8 (s), 127.2 (s), 127.0 (s), 126.7 (s), 123.7 (s), 116.3–115.6 (m). GC–MS m/z 294 (M^+).

4.2.8. 2,3,4,5,6-Pentafluoro-4′-methoxy-1,1′-biphenyl (**3h**) [15]

Following the general procedure, using petroleum ether as the eluent afforded a white solid (79% yield). mp: 117–119 °C. ^1H NMR (400 MHz, $CDCl_3$) δ 7.28 (d, J = 8.4 Hz, 2H), 6.94 (d, J = 8.4 Hz, 2H), 3.79 (s, 3H). ^{19}F NMR (376 MHz, $CDCl_3$) δ −143.6 (dd, J = 23.1, 8.0 Hz, 2F), −156.5 (t, J = 21.0 Hz, 1F), −162.6 (m, 2F). ^{13}C NMR (101 MHz, $CDCl_3$) δ 160.3 (s), 146.1–144.7 (m), 143.8–142.1 (m), 141.6–141.0 (m), 139.4–138.3 (m), 136.8–136.2 (m), 131.4 (s), 118.4 (s), 116.5–115.3 (m), 114.3 (s), 55.3 (s). GC–MS m/z 274 (M^+).

4.2.9. 2,3,4,5,6-Pentafluoro-3′-methoxy-1,1′-biphenyl (**3i**) [15]

Following the general procedure, using petroleum ether as the eluent afforded a colorless oil (84% yield). ^1H NMR (400 MHz, $CDCl_3$) δ 7.44 (t, J = 8.0 Hz, 1H), 7.07–6.99 (m, 2H), 6.97 (s, 1H), 3.87 (s, 3H). ^{19}F NMR (376 MHz, $CDCl_3$) δ −142.8 (dd, J = 22.9, 8.1 Hz, 2F), −155.6 (t, J = 21.0 Hz, 1F), −162.3 (m, 2F). ^{13}C NMR (101 MHz, $CDCl_3$) δ 159.7 (s), 145.8–145.0 (m), 143.2–142.6 (m), 142.1–141.3 (m), 139.5–138.8 (m), 136.9–136.3 (m), 129.7 (s), 127.5 (s), 122.5 (s), 115.9 (s), 116.1–115.6 (m), 114.9 (s), 55.3 (s). GC–MS m/z 274 (M^+).

4.2.10. 2,3,4,5,6-Pentafluoro-3′,4′-dimethoxy-1,1′-biphenyl (**3j**) [50]

Following the general procedure, using petroleum ether as the eluent afforded a white solid (80% yield). mp: 105–108 °C. ^1H NMR (400 MHz, $CDCl_3$) δ 7.05–6.98 (m, 2H), 6.94 (s, 1H), 3.96 (s, 3H), 3.93 (s, 3H). ^{19}F NMR (376 MHz, $CDCl_3$) δ −143.2 (dd, J = 23.3,

8.2 Hz, 2F), −156.3 (t, *J* = 21.0 Hz, 1F), −162.5 (m, 2F). ^{13}C NMR (101 MHz, $CDCl_3$) δ 149.9 (s), 149.0 (s), 145.7–145.2 (m), 143.1–142.9 (m), 141.7–140.9 (m), 139.5–138.5 (m), 137.2–136.2 (m), 123.1 (s), 118.6 (s), 116.4–115.1 (m), 113.2 (s), 111.2 (s), 56.0 (s), 55.9 (s). GC–MS *m*/*z* 304 (M^+).

4.2.11. 2-Methoxy-6-(perfluorophenyl)naphthalene (**3k**)

Following the general procedure, using petroleum ether as the eluent afforded a white solid (91% yield). mp: 148–150 °C. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.87 (d, *J* = 8.7 Hz, 2H), 7.81 (d, *J* = 8.7 Hz, 1H), 7.48 (ddd, *J* = 8.6, 3.2, 1.6 Hz, 1H), 7.26–7.20 (m, 2H), 3.98 (s, 3H). ^{19}F NMR (376 MHz, $CDCl_3$) δ −143.2 (dd, *J* = 23.2, 7.6 Hz, 2F), −155.9 (t, *J* = 21.0 Hz, 1F), −162.3 (m, 2F). ^{13}C NMR (101 MHz, $CDCl_3$) δ 158.7 (s), 145.7–145.4 (m), 143.3–143.0 (m), 141.7–141.3 (m), 139.4–138.9 (m), 136.9–136.5 (m), 134.7 (s), 129.8 (s), 128.6 (s), 127.5 (s), 127.2 (s), 125.1 (s), 121.4 (s), 119.6 (s), 116.3–115.9 (m), 105.7 (s), 55.4 (s). IR (KBr) ν 2923, 1483, 1265, 1224, 983, 853 cm^{-1}. GC–MS *m*/*z* 324 (M^+). HRMS (EI): calcd. for $C_{17}H_9F_5O$ $[M]^+$ 324.0574; found 324.0567.

4.2.12. 2′,3′,4′,5′,6′-Pentafluorobiphenyl-4-carbaldehyde (**3l**) [20]

Following the general procedure, using 1% ether in petroleum ether as the eluent afforded a white solid (46% yield). mp: 73–75 °C. ^{1}H NMR (400 MHz, $CDCl_3$) δ 10.12 (s, 1H), 8.04 (d, *J* = 8.2 Hz, 2H), 7.64 (d, *J* = 8.2 Hz, 2H). ^{19}F NMR (376 MHz, $CDCl_3$) δ −142.6 (dd, *J* = 22.9, 7.3 Hz, 2F), −153.5 (t, *J* = 20.9 Hz, 1F), −161.3 (m, 2F). ^{13}C NMR (101 MHz, $CDCl_3$) δ 191.4 (s), 145.5–145.2 (m), 143.0–142.3 (m), 139.9–139.5 (m), 136.7 (s), 132.4 (s), 130.9 (s), 129.8 (s), 115.0–114.6 (m). GC–MS *m*/*z* 272 (M^+).

4.2.13. Methyl 2′,3′,4′,5′,6′-pentafluorobiphenyl-3-carboxylate (**3m**) [5]

Following the general procedure, using petroleum ether/EtOAc = 40:1 as the eluent afforded a pale yellow solid (85% yield), mp: 102–104 °C. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.44 (t, *J* = 8.0 Hz, 1H), 7.03 (dd, *J* = 6.6, 2.4 Hz, 2H), 6.97 (s, 1H), 3.87 (s, 3H). ^{19}F NMR (376 MHz, $CDCl_3$) δ −143.1 (dd, *J* = 22.9, 7.8 Hz, 2F), −154.6 (t, *J* = 20.9 Hz, 1F), −161.8 (m, 2F). ^{13}C NMR (101 MHz, $CDCl_3$) δ 166.3 (s), 145.6–145.2 (m), 143.1–142.8 (m), 139.5–138.9 (m), 136.9–136.4 (m), 134.4 (s), 131.3 (s), 130.9 (s), 130.4 (s), 128.9 (s), 126.8 (s), 115.4–114.7 (m), 52.3 (s). GC–MS *m*/*z* 302 (M^+).

4.2.14. Ethyl 2′, 3′, 4′, 5′, 6′-pentafluorobiphenyl-4-carboxylate (**3n**) [15]

Following the general procedure, using petroleum ether/EtOAc = 50:1 as the eluent afforded a white solid (82% yield). mp: 149–151 °C. ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.17 (d, *J* = 7.8 Hz, 2H), 7.52 (d, *J* = 7.8 Hz, 2H), 4.42 (q, *J* = 7.1 Hz, 2H), 1.43 (t, *J* = 7.1 Hz, 3H). ^{19}F NMR (376 MHz, $CDCl_3$) δ −142.8 (dd, *J* = 22.9, 7.9 Hz, 2F), −154.2 (t, *J* = 21.0 Hz, 1F), −161.6 (m, 2F). ^{13}C NMR (101 MHz, $CDCl_3$) δ 165.9 (s), 145.6–145.0 (m), 143.2–142.5 (m), 142.2–141.7 (m), 139.8–138.9 (m), 137.0–136.3 (m), 131.3 (s), 130.8 (s), 130.2 (s), 129.8 (s), 116.1–112.9 (m), 61.3 (s), 14.3 (s). GC–MS *m*/*z* 316 (M^+).

4.2.15. Ethyl 2′,3′,4′,5′,6′-pentafluoro-[1,1′-biphenyl]-3-carboxylate (**3o**) [48]

Following the general procedure, using petroleum ether as the eluent afforded a pale yellow solid (87% yield). mp: 57–59 °C. ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.19–8.12 (m, 2H), 7.65–7.57 (m, 2H), 4.43 (q, *J* = 7.1 Hz, 2H), 1.43 (t, *J* = 7.1 Hz, 3H). ^{19}F NMR (376 MHz, $CDCl_3$) δ −143.1 (dd, *J* = 22.7, 8.0 Hz, 2F), −154.7 (t, *J* = 20.9 Hz, 1F), −161.9 (m, 2F). ^{13}C NMR (101 MHz, $CDCl_3$) δ 165.7 (s), 145.5–145.3 (m), 143.0–142.8 (m), 142.2–141.6 (m), 139.6–138.9 (m), 137.1–135.8 (m), 134.3 (s), 131.3 (s), 130.3 (s), 128.8 (s), 126.7 (s), 115.0 (td, *J* = 17.2, 4.1 Hz), 61.3 (s), 14.2 (s). GC–MS *m*/*z* 316 (M^+).

4.2.16. 2,3,4,5,6-Pentafluoro-3′-nitrobiphenyl (**3p**) [51]

Following the general procedure, using petroleum ether as the eluent afforded a pale yellow solid (53% yield). mp: 106–108 °C. ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.26 (d, *J* = 7.3 Hz, 2H), 7.73–7.60 (m, 2H). ^{19}F NMR (376 MHz, $CDCl_3$) δ −142.8 (dd, *J* = 22.8, 7.5 Hz, 2F), −152.7 (t, *J* = 20.9 Hz, 1F), −160.8 (m, 2F). ^{13}C NMR (101 MHz, $CDCl_3$) δ 148.5 (s), 145.6–145.2 (m), 143.2–142.4 (m), 140.2–139.8 (m), 139.5–139.0 (m), 137.0–136.4 (m), 136.1 (s), 129.9 (s), 128.1 (s), 125.3 (s), 124.2 (s), 114.2–112.9 (m). GC–MS *m*/*z* 289 (M^+).

4.2.17. 4′-Chloro-2,3,4,5,6-pentafluorobiphenyl (**3q**) [52]

Following the general procedure, using petroleum ether as the eluent afforded a white solid (71% yield). mp: 77–79 °C. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.50 (d, *J* = 8.2 Hz, 2H), 7.39 (d, *J* = 8.2 Hz, 2H). ^{19}F NMR (376 MHz, $CDCl_3$) δ −143.2 (dd, *J* = 22.8, 8.2 Hz, 2F), −154.8 (t, *J* = 20.9 Hz, 1F), −161.8 (m, 2F). ^{13}C NMR (101 MHz, $CDCl_3$) δ 145.5–145.2 (m), 143.0–142.7 (m), 142.1–141.6 (m), 139.5–138.9 (m), 135.6 (s), 131.4 (t, *J* = 1.8 Hz), 129.1 (s), 124.8 (q, *J* = 1.9 Hz), 115.0–114.6 (m). GC–MS *m*/*z* 278 (M^+).

4.2.18. 2,3,5,6-Tetrafluoro-1,1′-biphenyl (**5a**) and 1,4-di-phenyl-2,3,5,6-tetrafluorobenzene (**5a′**) [21]

Following the general procedure, using petroleum as the eluent afforded **5a** in 62% yield (mp: 97–99 °C) and **5a′** in 13% yield (mp: 220–222 °C), they were both white solids. **5a**: ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.57–7.46 (m, 5H), 7.14–7.05 (m, 1H). ^{19}F NMR (376 MHz, $CDCl_3$) δ −139.1 to −139.2 (m, 2F), −143.8 to −144.0 (m, 2F). ^{13}C NMR (101 MHz, $CDCl_3$) δ 147.6–147.4 (m), 145.6–144.0 (m), 142.6–142.4 (m), 130.1 (s), 129.2 (s), 128.6 (s), 121.7–121.3 (m), 104.8–104.6 (m). GC–MS: 226 (M^+). **5a′**: ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.58–7.47 (m). ^{19}F NMR (376 MHz, $CDCl_3$) δ −144.4 (s, 4F). ^{13}C NMR (101 MHz, $CDCl_3$, except for C–F carbons because of the low solubility of it in $CDCl_3$) δ 130.2 (s), 129.1 (s), 128.6 (s), 127.5 (s). GC–MS *m*/*z* 302 (M^+).

4.2.19. 2,3,5,6-Tetrafluoro-4′-methylbiphenyl (**5b**) and 1,4-di-methylbiphenyl-2,3,5,6-tetrafluorobenzene (**5b′**) [15]

Following the general procedure, using petroleum as the eluent afforded **5b** in 67% yield (mp: 88–90 °C) and **5b′** in 13% yield (mp: 210–212 °C), they were both white solids. **5b**: ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.38 (d, *J* = 7.9 Hz, 2H), 7.33 (d, *J* = 8.0 Hz, 2H), 7.13–7.01 (m, 1H), 2.45 (s, 3H). ^{19}F NMR (376 MHz, $CDCl_3$) δ −139.3 to −139.4 (m, 2F), −143.9 to −144.1 (m, 2F). ^{13}C NMR (101 MHz, $CDCl_3$) δ 147.7–144.7 (m), 145.3–142.3 (m), 139.3 (s), 129.9 (t, *J* = 2.1 Hz), 129.3 (s), 124.5 (t, *J* = 2.4 Hz), 121.8–121.3 (m), 104.5 (t, *J* = 22.7 Hz), 21.3 (s). GC–MS: 240 (M^+). **5b′**: ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.44 (d, *J* = 7.9 Hz, 4H), 7.35 (d, *J* = 7.9 Hz, 4H), 2.46 (s, 6H). ^{19}F NMR (376 MHz, $CDCl_3$) δ −144.7 (s, 4F). ^{13}C NMR (101 MHz, $CDCl_3$, except for C–F carbons because of the low solubility of it in $CDCl_3$) δ 139.1 (s), 130.0 (s), 129.3 (s), 124.6 (s), 21.4 (s). GC–MS *m*/*z* 330 (M^+).

4.2.20. 2,3,5,6-Tetrafluoro-4-methoxy-biphenyl (**5c**) [20]

Following the general procedure, using petroleum ether as the eluent afforded a colorless oil (52% yield). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.54–7.43 (m, 5H), 4.15 (s, 3H). ^{19}F NMR (376 MHz, $CDCl_3$) δ −145.2 (dd, *J* = 22.0, 8.8 Hz, 2F), −158.3 (dd, *J* = 22.0, 8.8 Hz, 2F). ^{13}C NMR (101 MHz, $CDCl_3$) δ 145.6–145.4 (m), 143.2–142.9 (m), 142.6–142.3 (m), 140.1–139.8 (m), 137.7–137.3 (m), 130.2 (t, *J* = 2.0 Hz), 128.9 (s), 128.6 (s), 127.3 (s), 114.4–114.1 (m), 62.2 (t, *J* = 3.7 Hz). GC–MS *m*/*z* 256 (M^+).

4.2.21. 2,3,5,6-Tetrafluoro-4-methoxy-4′-methylbiphenyl (**5d**) [17]

Following the general procedure, using petroleum ether as the eluent afforded a white solid (58% yield). mp: 49–51 °C. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.36 (d, *J* = 8.2 Hz, 2H), 7.32 (d, *J* = 8.2 Hz, 2H),

4.14 (t, J = 1.3 Hz, 3H), 2.45 (s, 3H). ^{19}F NMR (376 MHz, $CDCl_3$) δ −145.3 (dd, J = 22.1, 8.7 Hz, 2F), −158.4 (dd, J = 22.3, 8.7 Hz, 2F). ^{13}C NMR (101 MHz, $CDCl_3$) δ 145.8–142.9 (m), 142.4–139.9 (m), 138.9 (s), 137.4–137.1 (m), 130.0 (t, J = 2.0 Hz), 129.3 (s), 124.3 (t, J = 2.2 Hz), 114.3 (t, J = 17.3 Hz), 62.2 (t, J = 3.7 Hz), 21.3 (s). GC–MS m/z 270 (M^+).

*4.2.22. 4′-Chloro-2,3,5,6-tetrafluoro-4-methoxybiphenyl (**5e**) [21]*

Following the general procedure, using petroleum ether as the eluent afforded a white solid (89% yield). mp: 46–48 °C. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.48 (d, J = 8.4 Hz, 2H), 7.40 (d, J = 8.4 Hz, 2H), 4.15 (s, 3H). ^{19}F NMR (376 MHz, $CDCl_3$) δ −145.1 (dd, J = 21.9, 8.7 Hz, 2F), −157.9 (dd, J = 21.8, 8.3 Hz, 2F). ^{13}C NMR (101 MHz, $CDCl_3$) δ 145.6–145.3 (m), 143.1–142.9 (m), 142.5–142.3 (m), 140.0–139.8 (m), 137.9–137.6 (m), 135.1 (s), 131.5 (t, J = 2.2 Hz), 128.9 (s), 125.7 (s), 113.0 (t, J = 17.0 Hz), 62.1 (t, J = 3.8 Hz). GC–MS m/z 290 (M^+).

*4.2.23. 2,3,5,6-Tetrafluoro-4-methoxy-3′-nitro-1,1′-biphenyl (**5f**) [21]*

Following the general procedure, using petroleum ether as the eluent afforded a white solid (81% yield). mp: 138–140 °C. ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.41–8.29 (m, 2H), 7.80 (d, J = 6.6 Hz, 1H), 7.71 (t, J = 7.9 Hz, 1H), 4.19 (s, 3H). ^{19}F NMR (376 MHz, $CDCl_3$) δ −145.0 (dd, J = 21.4, 8.3 Hz, 2F), −157.2 (dd, J = 21.4, 8.3 Hz, 2F). ^{13}C NMR (101 MHz, $CDCl_3$) δ 148.4 (s), 145.8–145.3 (m), 143.3–142.8 (m), 142.7–142.1 (m), 140.1–139.7 (m), 138.9–138.4 (m), 136.2 (s), 129.7 (s), 129.0, 125.3 (s), 111.8–111.1 (m), 62.2 (t, J = 3.9 Hz). GC–MS m/z 301 (M^+).

*4.2.24. 2,3,5,6-Tetrafluoro-4,4′-dimethoxybiphenyl (**5g**)*

Following the general procedure, using petroleum ether as the eluent afforded a white solid (70% yield). mp: 112–114 °C. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.40 (d, J = 8.9 Hz, 2H), 7.03 (d, J = 8.9 Hz, 2H), 4.13 (t, J = 1.3 Hz, 3H), 3.89 (s, 3H). ^{19}F NMR (376 MHz, $CDCl_3$) δ −145.5 (dd, J = 22.3, 8.7 Hz, 2F), −158.5 (dd, J = 22.3, 8.7 Hz, 2F). ^{13}C NMR (101 MHz, $CDCl_3$) δ 160.0 (s), 145.6–145.5 (m), 143.2–143.0 (m), 142.6–142.3 (m), 140.1–139.9 (m), 137.2–136.9 (m), 131.4 (t, J = 2.1 Hz), 127.7 (s), 119.3 (t, J = 2.3 Hz), 114.1 (s), 62.2 (t, J = 3.7 Hz), 55.3 (s). IR (KBr) ν 2961, 1501, 1486, 1251, 1083, 980, 827 cm^{-1}. GC–MS m/z 286 (M^+). HRMS (EI): calcd. for $C_{14}H_{10}F_4O_2$ [M] 286.0617; found 286.0616.

*4.2.25. 2,3,5,6-Tetrafluoro-4′-methyl-4-nitrobiphenyl (**5h**)*

Following the general procedure, using petroleum ether as the eluent afforded a pale yellow solid (36% yield). mp:53–56 °C. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.31 (d, J = 8.1 Hz, 2H), 7.23 (d, J = 8.1 Hz, 2H), 2.44 (s, 3H). ^{19}F NMR (376 MHz, $CDCl_3$) δ −137.8 to −137.9 (m, 1F), −147.5 to −147.6 (m, 1F), −149.6 to −149.7 (m, 1F), −152.8 to −152.9 (m, 1F). ^{13}C NMR (101 MHz, $CDCl_3$) 145.9–145.8 (m), 143.9–143.3 (m), 142.1–141.9 (m), 141.4–141.0 (m), 140.4 (s), 139.5–139.3 (m), 138.7–138.4 (m), 129.9 (s), 128.8 (s), 123.6 (s), 120.9–120.8 (m), 21.3 (s). IR (KBr) ν 2923, 1548, 1477, 1368, 1112, 1048, 756 cm^{-1}. GC–MS m/z 285 (M^+). HRMS (EI): calcd. for $C_{13}H_7F_4NO_2$ $[M]^+$ 285.0413; found 285.0409.

*4.2.26. 4′-Chloro-2,3,5,6-tetrafluoro-4-nitro-1,1′-biphenyl (**5i**)*

Following the general procedure, using petroleum ether as the eluent afforded a colorless oil (52% yield). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.49 (d, J = 8.4 Hz, 2H), 7.29 (d, J = 8.4 Hz, 2H). ^{19}F NMR (376 MHz, $CDCl_3$) δ −137.3 to −137.4 (m, 1F), −146.6 to −146.7 (m, 1F), −148.7 to −149.0 (m, 1F), −151.3 to −151.4 (m, 1F). ^{13}C NMR (101 MHz, $CDCl_3$) δ 145.9–145.8 (m), 144.2–143.3 (m), 142.2–142.1 (m), 141.8–141.3 (m), 139.2–138.6 (m), 136.7 (s), 130.4 (s), 129.6 (s), 125.0 (s), 120.4–118.6 (m). IR (KBr) ν 2929, 1551, 1495, 1477, 1363, 1045, 762 cm^{-1}. GC–MS m/z 305 (M^+). HRMS (EI): calcd. for $C_{12}H_4ClF_4NO_2$ $[M]^+$ 304.9867; found 304.9860.

*4.2.27. 2,3,5,6-Tetrafluoro-4′-methoxy-4-nitro-1,1′-biphenyl (**5j**)*

Following the general procedure, using petroleum ether as the eluent afforded a pale yellow solid (73% yield). mp: 85–87 °C. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.27 (d, J = 9.0 Hz, 2H), 7.01 (d, J = 9.0 Hz, 2H), 3.87 (s, 3H). ^{19}F NMR (376 MHz, $CDCl_3$) δ −137.9 to −138.0 (m, 1F), −147.6 to −147.7 (m, 1F), −149.6 to −150.0 (m, 1F), −152.9 to −153.5 (m, 1F). ^{13}C NMR (101 MHz, $CDCl_3$) δ 160.9 (s), 145.9–145.8 (m), 143.9–143.4 (m), 142.0–141.9 (m), 141.3–141.0 (m), 139.5–139.3 (m), 138.6–138.3 (m), 130.4 (s), 127.7 (s), 120.8–120.5 (m), 114.70 (s), 55.3 (s). IR (KBr) ν 2923, 1542, 1510, 1477, 1254, 1042, 756 cm^{-1}. GC–MS m/z 301 (M^+). HRMS (EI): calcd. for $C_{13}H_7F_4NO_3$ $[M]^+$ 301.0362; found 301.0363.

*4.2.28. 2,4,6-trifluoro-4′-methoxybiphenyl (**5k**) [48]*

Following the general procedure, using petroleum ether/diethyl ether = 100:1 as the eluent afforded a white solid (18% yield). mp: 93–94 °C. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.39 (d, J = 8.8 Hz, 2H), 7.02 (d, J = 8.8 Hz, 2H), 6.80–6.74 (m, 2H), 3.88 (s, 3H). ^{19}F NMR (376 MHz, $CDCl_3$) δ −109.9 (tt, J = 8.7, 5.7 Hz, 1F), −111.5 to −111.6 (m, 2F). ^{13}C NMR (101 MHz, $CDCl_3$) δ 161.4 (dt, J = 248.5, 15.7 Hz), 160.3 (ddd, J = 248.7, 14.7, 9.9 Hz), 159.6 (s), 131.4 (td, J = 1.9, 0.6 Hz), 120.4 (s), 114.7 (td, J = 19.2, 4.8 Hz), 113.9 (s), 100.7–100.1 (m), 55.3 (s). GC–MS m/z 238 (M^+).

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Appendix A. Supplementary data

Supplementary data associated with this article can be found, in the online version, at http://dx.doi.org/10.1016/j.jfluchem.2013.03.017.

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