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Selective C4–F bond cleavage/C–O bond formation of polyfluoroarenes with phenols and benzyl alcohols

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ABSTRACT

A facile and efficient S_NAr method for the synthesis of unsymmetrical polyfluoroaryl ethers via selective C4–F bond cleavage of pentafluorobenzene is reported. The reaction could proceed smoothly without the requirement of additional metals or ligands, and afford a series of the corresponding products in good to high yields. A wide variety of substituted phenols and alcohols provided 1,2,4,5-tetrafluoropheny ether derivatives in regioselective manner.

1. Introduction

Aryl ethers and their derivatives are key intermediates in organic chemistry and their importance as structural motifs has been witnessed in a great number of natural products, polymer industries, pharmaceuticals, which provide a strong motivation for the developments of synthetic methodology [1]. Compounds with a polyfluorinated aromatic structure are useful moieties in medicinal chemistry and material science [2]. Hence, synthesis of polyfluorinated aromatic ethers is of high potential interest [3]. The Ullmann-type coupling reaction [4] and nucleophilic aromatic substitution (S_NAr) reaction [5] represent two classic methods for the preparation of the aryl ethers. As alternate methodologies, such as microwave and ultrasound assisted methods [6], use of metals and/or noble metal nanoparticles as catalysts [7] and directed C–H activation of aromatic compounds with alcohols [8] were also emerged for the preparation of the aryl ethers. Although these pioneering and intriguing works are very practical, yet, the methods presented above are mainly focused on the substrates of aryl chlorides, aryl bromides or aryl iodides reacting with phenols or alcohols.

It is well known that fluorocarbons are prone to be attacked by the electron-rich atoms or groups if the carbon atoms have a strong electron affinity, which is necessary for the carbon–fluorine bond breakage [9]. In other words, the fluorocarbons must be actived by the activating or directing atoms/groups. At present, there are reports on the C–O bond formation via C–F bond cleavage of aryl fluorides with phenols or alcohols [10], and usually the substrates are associated with the activating or directing atoms/groups on the aryl ring, such as nitro and cyano groups [11]. Pentafluoroarenes are known as electron-deficient compounds and important fluorine-containing compounds [12]. Because of the existence of several fluorine atoms on aryl ring and its high electronegativity of fluorine, we speculate that some of the carbon–fluorine bonds on the aryl ring of the polyfluoroarenes may be attacked by the electron-rich atoms or groups. To date, some strategies have revealed the synthesis of polyfluorinated aromatic ethers via the C–F cleavage of polyfluoroarenes, but they are suffering from some drawbacks, such as complex reaction system, limited substrate scope, lower yields, longer reaction time and so on [13]. Cao reported a catalytic strategy for C–F bond cleavage of octafluorotoluene with arylboronic acids in the presence of Ni catalyst to provide unsymmetrical biaryl ethers [14]. Additionally, Weng and co-workers demonstrated a Pd/Ag co-catalystic system for the access to polyfluorinated aromatic ethers [15]. Very recently, our group has reported the synthesis of *N*-tetrafluoroarylated heterocyclic compounds via selective C4–F bond cleavage of pentafluorobenzene with N–H containing heterocycles under mild conditions [16]. It will be of special interest to extend this facile approach to prepare polyfluorinated aromatic ethers. Although elegant work

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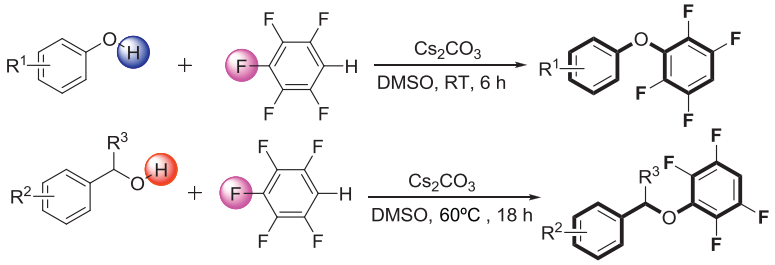
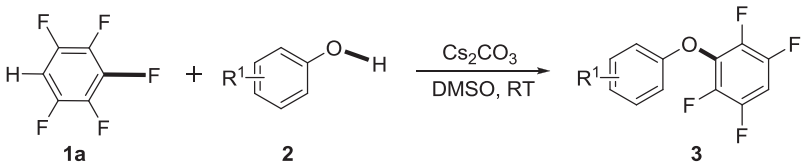
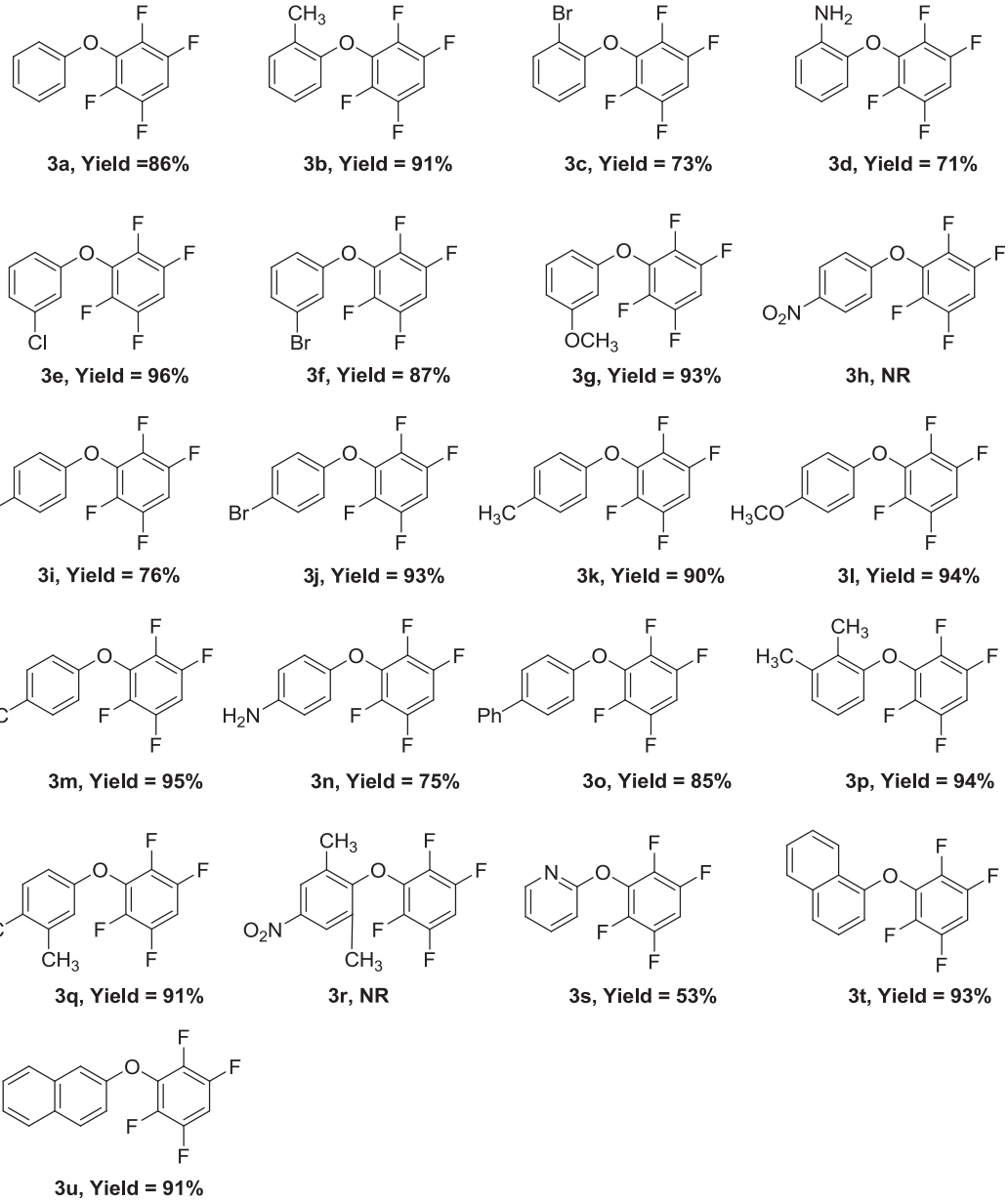


Scheme 1. Synthesis of polyfluorinated aromatic ethers.

Table 1
Synthesis of polyfluorinated diaromatic ethers derived from phenols with pentafluorobenzene.[a]



1a 2 3



3a, Yield =86% | 3b, Yield = 91% | 3c, Yield = 73% | 3d, Yield = 71%

3e, Yield = 96% | 3f, Yield = 87% | 3g, Yield = 93% | 3h, NR

3i, Yield = 76% | 3j, Yield = 93% | 3k, Yield = 90% | 3l, Yield = 94%

3m, Yield = 95% | 3n, Yield = 75% | 3o, Yield = 85% | 3p, Yield = 94%

3q, Yield = 91% | 3r, NR | 3s, Yield = 53% | 3t, Yield = 93%

3u, Yield = 91%

[a] Reaction conditions: **1a** (0.3 mmol), phenols (0.2 mmol) and Cs_2CO_3 (0.3 mmol) were added in DMSO (2.0 mL) with stirring at RT for 8 h. Yield: isolated yield.

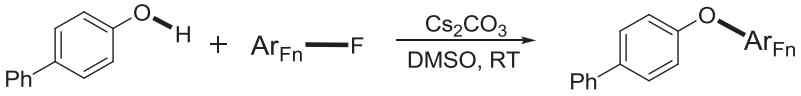
has been achieved, the development of a simple and efficient method for the polyfluorinated aromatic ethers with the strategy of C–F bond cleavage of polyfluoroarenes is highly desirable.

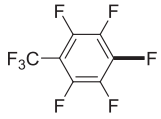
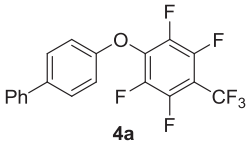
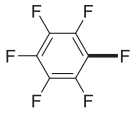
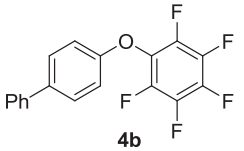
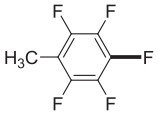
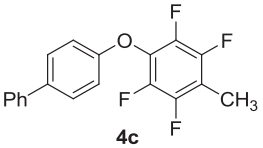
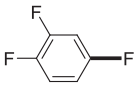
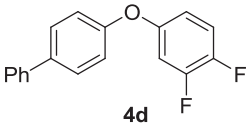
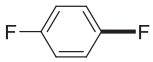
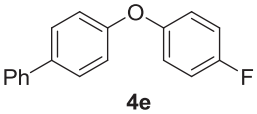
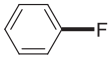
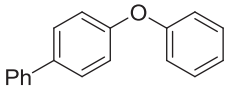
Herein, we report an operationally simple, effective and transition metal-free S_NAr reaction for the synthesis of unsymmetrical polyfluoroaryl ethers via selective C–F bond cleavage of pentafluorobenzene with a variety of phenols and benzyl alcohols (Scheme 1). In the absence of additional metals or ligands, the reaction could be carried out under mild conditions to afford a series of *O*-polyfluoroarylated products in good to high yields. In addition, our protocol was also applied to other polyfluoroarenes and some long-chain aliphatic alcohols.

2. Results and discussion

Initially, pentafluorobenzene **1a** was treated with 4-phenylphenol 2 in the presence of 1.5 equiv Cs_2CO_3 in DMSO at room temperature for 8 h. It was found that the corresponding polyfluoroaryl ether was obtained in 85% yield (Table S1, entry 3). This result suggested that C4–F bond cleavage/C–O bond formation occured under the ambient conditions, and showed that our speculation on the attack of the electron-rich atoms or groups to the carbon–fluorine bonds on the aryl ring of **1a** was reasonable. Note that no detectable amount of products via the other C–F bonds cleavage of **1a** was observed under our conditions, and thus implying that our method gave highly selective products through C4–F bond cleavage/C–O bond formation of pentafluorobenzene. But, in the absence of Cs_2CO_3 while remaining other conditions unchanged, no products were obtained even after 24 h at room temperature. These results suggested that the base played an important role in this S_NAr reaction. Next, a survey of reaction parameters including bases and solvents was carried out (Table S1 in the supporting information). After the screen of several bases, it was found that Cs_2CO_3 gave the best yield in this interesting reaction (Table S1, entries1, 2, 4–7). Subsequently, a broader investigation of solvents suggested that DMF was less favorable than DMSO and others were ineffective or useless for the synthesis of polyfluoroaryl ethers (Table S1, entries 9–15). We also tested the

Table 2
O-Polyfluoroarylation of 4-phenylphenol with polyfluoroarenes.[a]



Entry	Polyfluoroarenes	Products	Yields (%)
1		 **4a**	81
2		 **4b**	51
3		 **4c**	83
4		 **4d**	71[b]
5		 **4e**	-
6		 **4f**	-

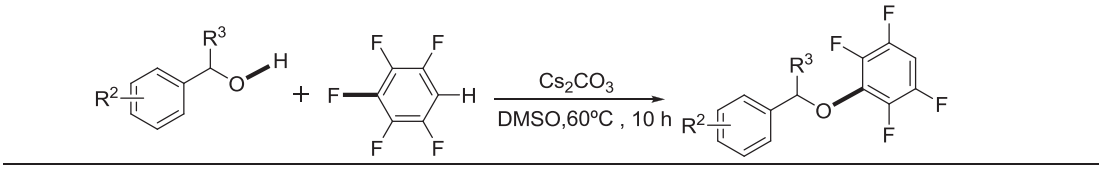
[a] Reaction conditions: polyfluoroarenes (0.3 mmol), 4-phenylphenol (0.2 mmol) and Cs_2CO_3 (0.3 mmol) were added in DMSO (2.0 mL) with stirring at RT for 8 h. Yield: isolated yield.
[b] The reaction was conducted at 150 °C for 2 h.

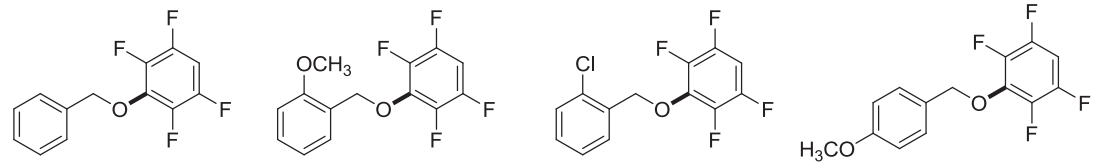
effect of temperature and found that a lower reaction temperature resulted in a longer reaction time and lead to a lower conversion. Elevation of the temperature did not show an obvious improvement. Hence, the optical conditions for this reaction are that DMSO as a solvent in combination with Cs_2CO_3 as a base at room temperature works well for this *O*-polyfluoroarylation protocol.

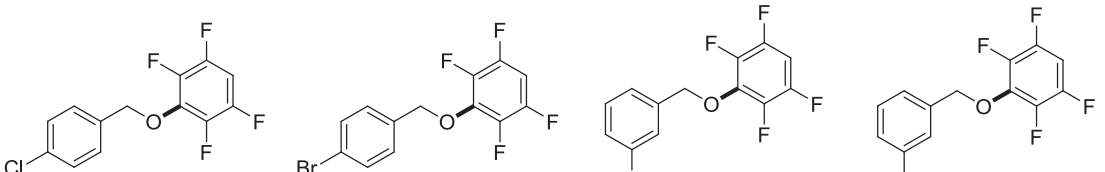
Encouraged by the efficiency of the protocol described above, the substrate scope was investigated. A variety of substituted phenols were tested under the optimized conditions using **1a** as the polyfluoroarylating agent (Table 1). Gratifyingly, several electron-rich phenols were suitable in this reaction to afford the corresponding ethers in excellent yields (entries **3b**, **3d**, **3g**, **3k**–**3p**). Phenols with electron withdrawing groups such as chlorine, bromine at the different positions successfully reacted with **1a** to give the desired products in good yields (entries **3c**, **3e**, **3f**, **3j**). Additionally, when cyano groups at the para-position of phenol led to a slightly decreased yield (entry **3i**). However, in the cases of the substrate having nitro group (**3h** and **3r**), the S_NAr reaction did not occur. This may be due to the strong electron-withdrawing property of nitro group. The presence of a heteroatom in the aromatic nucleus also provided the product in acceptable yield (entry **3s**). Either 1-naphthol or 2-naphthol was the suitable partner in this *O*-polyfluoroarylation reaction (entries **3t**, **3u**). Moreover, the di-substituted phenols did not hamper the reaction and afforded the corresponding products in high yields (**3p** and **3q**). These results further showed that our strategy gave highly selective products through C4–F bond cleavage/C–O bond formation of polyfluorobenzene with phenols.

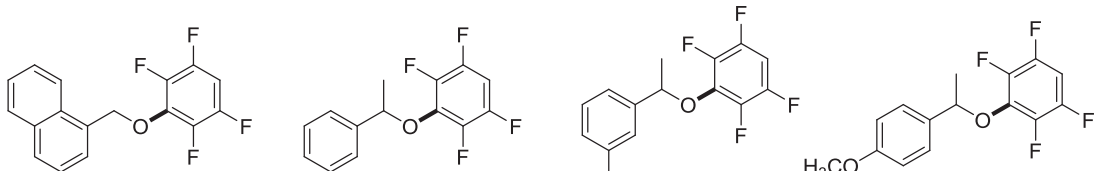
As an extension of this work, various polyfluoroarenes were treated. The results are consistent with the above when reacted octafluorotoluene, 2,3,4,5,6-pentafluorotoluene and hexafluorobenzene with 4-phenylphenol **2** and they all gave the desired products (Table 2, entries 1–3), despite a moderate yield for hexafluorobenzene (Table 2, entry 2). 1,2,4-Trifluorobenzene was

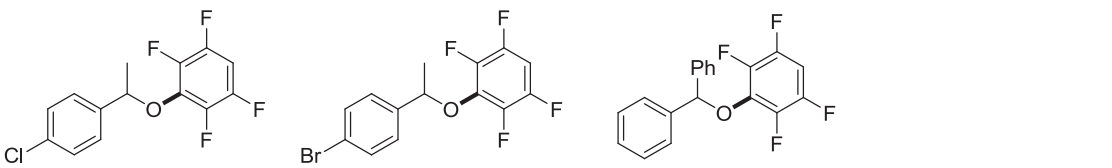
Table 3
Synthesize of polyfluorinated aromatic ethers derived from alcohols with pentafluorobenzene.[a]

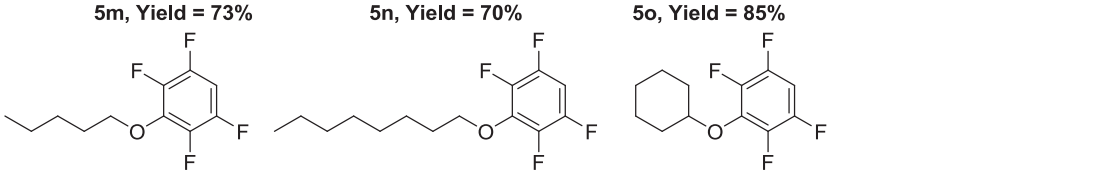




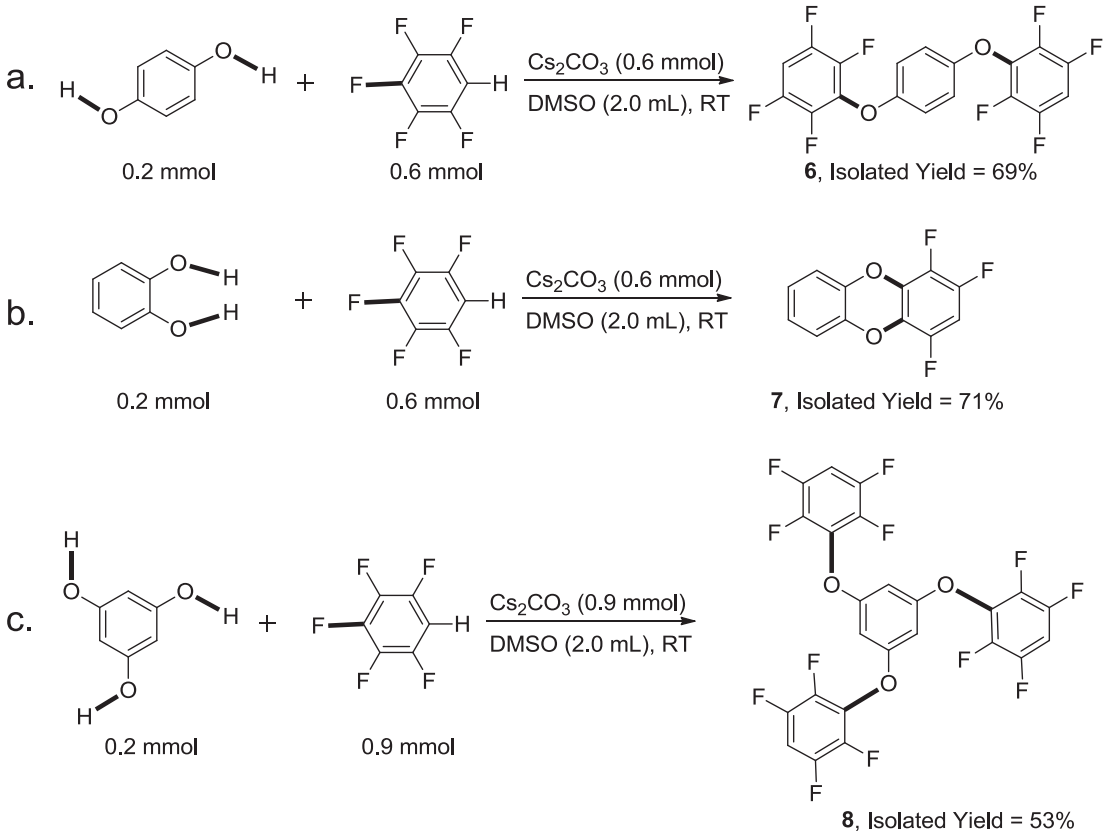








[a] Reaction conditions: **1a** (0.3 mmol), alcohols (0.2 mmol) and Cs_2CO_3 (0.3 mmol) were added in DMSO (2.0 mL) with stirring at 60 °C for 18 h. Yield: isolated yield.



Scheme 2. S_NAr reaction of diphenols and triphenol with pentafluorobenzene.

also chosen as the investigated target for this reaction. Yet, the result was obtained at elevated reaction temperature (150 °C) rather than at room temperature (Table 2, entry 4). However, mono-fluorobenzene and 1,4-difluorobenzene were not reactive under the selected conditions (Table 2, entries 5, 6).

After investigation of phenols with polyfluoroarenes, we further applied this system to the *O*-polyfluoroarylation of benzyl alcohols. Unfortunately, the standard conditions were less suitable for benzyl alcohol substrates. We found that the reaction temperature of 60 °C and the reaction time for 18 h were determined to be optimal. As revealed in Table 3, the reaction conditions were compatible with a number of benzyl alcohols, including substrates bearing electron-donating and electron-withdrawing groups and most of the reactants afforded the polyfluoroaryl benzyl ethers in good to high yields (entries **5a**–**5o**). To our delight, when the reaction of long-chain aliphatic alcohols such as pentanol and octanol with **1a** was carried out under the given conditions, the reaction could also proceed, albeit lower yields were observed (entries **5p**–**5r**). These results again confirm that this strategy gives highly selective products via C4–F bond cleavage/C–O bond formation of polyfluorobenzene with alcohols.

To test the versatility of this methodology, we carried out several comparative experiments. Reactions of hydroquinone and benzene-1,3,5-triol with an excess amount of pentafluorobenzene smoothly proceeded at all of the hydroxyl groups to give the corresponding tetrafluoropheny ether compounds **6** and **8**, respectively as shown in Scheme 2. Very interestingly, when hydroquinone was replaced by pyrocatechol, the main product was cyclic compound **7** rather than di-tetrafluoroaryl substituted S_NAr product. This further proved that our strategy might be broadened to create polyfluoroary heterocyclic compounds via selective C–F bond cleavage/C–O bond formation of pentafluorobenzene with pyrocatechol and its derivates (Scheme 2, b).

3. Conclusions

In summary, we have developed a facile, efficient and transition metal-free S_NAr method for the synthesis of unsymmetrical polyfluoroaryl ethers via selective C4–F bond cleavage of pentafluorobenzene with a wide variety of substituted phenols and benzyl alcohols. The reaction proceeded smoothly to generate a series of products in good to excellent yields. Our method is of high versatility, which is also applicable to other polyfluoroarenes and long-chain aliphatic alcohols. In addition, this strategy might be broadened to create polyfluoroary heterocyclic compounds via the reaction of polyfluorobenzene with pyrocatechol and its derivates.

4. Experimental

^1H, ^{13}C, ^{19}F NMR were recorded on Varian Mercury Plus 400 instruments at 400 MHz (^1H NMR), 100 MHz (^{13}C NMR), as well as 376 MHz (^{19}F NMR). Chemical shifts were reported in ppm down field from internal Me_4Si and external CCl_3F, respectively. Multiplicity was indicated as follows: s (singlet), d (doublet), t (triplet), q (quartet), m (multiplet), dd (doublet of doublet), br (broad). Coupling constants were reported in Hertz (Hz). Tetrahydrofuran (THF) and toluene were distilled from sodium/benzophenone; CH_3CN was distilled from P_2O_5. All purchased reagents were used without further purification. Analytical thin layer chromatography was performed on 0.20 mm Qingdao Haiyang silica gel plates. Silica gel (200–300 mesh) (from Qingdao Haiyang Chem. Company, Ltd.)

was used for flash column chromatography. Standard reagents and solvents were purified according to known procedures.

4.1. General procedure for the synthesis of the products (4-phenylphenol with pentafluorobenzene as the example)

4-Phenylphenol **2** (34.0 mg, 0.2 mmol) and cesium carbonate (97.7 mg, 0.3 mmol) were weighed to a sealed Schlenk (25 mL) under Ar atmosphere. Pentafluorobenzene **1a** (50.4 mg, 0.3 mmol) and DMSO (2.0 mL) were added to the sealed Schlenk via syringe at room temperature respectively. The mixture was stirred at room temperature until the completion of the reaction (by TLC). Water (5 mL) was added and the mixture was extracted with ethyl acetate (3 × 10 mL). The organic extracts were combined, dried with anhydrous magnesium sulfate and then concentrated in vacuo. The residue was purified on silica gel to afford the product **3o** (54.1 mg, 85% yield).

*4.1.1. 1,2,4,5-Tetrafluoro-3-phenoxybenzene (**3a**)*

41.7 mg, **Yield**: 86%; **Yellow oil**; **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.37 (*t*, *J* = 8.0 Hz, 2H), 7.15 (*t*, *J* = 7.4 Hz, 1H), 7.05–6.94 (*m*, 3H); **^{19}F NMR** (376 MHz, $CDCl_3$) [ppm] δ −138.72–−138.73 (*m*, 2F), −154.00–−154.10 (*m*, 2F); **^{13}C NMR** (100 MHz, $CDCl_3$) [ppm] δ 157.2, 146.5 (dm, J_{C-F} = 246 Hz), 141.6 (dm, J_{C-F} = 250 Hz), 134.3 (*m*), 129.8, 123.8, 115.6, 101.9 (*t*, J_{C-F} = 13 Hz); **IR** (KBr) ν (cm^{-1}): **IR** (KBr) ν (cm^{-1}): 2957, 2922, 2852, 1710, 1591, 1486, 1466, 1261, 1205, 1079, 965, 913, 799, 746; MS (EI): *m*/*z* 242.2.

*4.1.2. 1,2,4,5-Tetrafluoro-3-(o-tolyloxy)benzene (**3b**)*

48.2 mg, **Yield**: 94%; **Yellow oil**; **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.29 (d, *J* = 7.5 Hz, 1H), 7.15 (*t*, *J* = 7.5 Hz, 1H), 7.07 (*t*, *J* = 7.1 Hz, 1H), 7.03–6.93 (*m*, 1H), 6.67 (d, *J* = 8.0 Hz, 1H), 2.47 (s, 3H); **^{19}F NMR** (376 MHz, $CDCl_3$) [ppm] δ −138.94–−139.06 (*m*, 2F), −154.75–−154.85 (*m*, 2F); **^{13}C NMR** (100 MHz, $CDCl_3$) [ppm] δ 155.6, 146.5 (dm, J_{C-F} = 246 Hz), 141.2 (dm, J_{C-F} = 249 Hz), 134.9 (*m*), 131.5, 127.3, 126.9, 123.7, 113.5, 101.5 (*t*, J_{C-F} = 13 Hz), 15.9; **IR** (KBr) ν (cm^{-1}): 3083, 2928, 1641, 1588, 1520, 1487, 1274, 1177, 1118, 1066, 945, 833, 712, 642; MS (EI): *m*/*z* 256.2.

*4.1.3. 3-(2-Bromophenoxy)-1,2,4,5-tetrafluorobenzene (**3c**)*

46.9 mg, **Yield**: 73%; **Yellow solid**; **Mp**: 54–56 °C; **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.66 (dd, *J* = 7.9, 1.2 Hz, 1H), 7.28–7.23 (*m*, 1H), 7.06–6.97 (*m*, 2H), 6.78 (d, *J* = 8.2 Hz, 1H); **^{19}F NMR** (376 MHz, $CDCl_3$) [ppm] δ −138.36–−138.47 (*m*, 2F), −153.98–−154.09 (*m*, 2F); **^{13}C NMR** (100 MHz, $CDCl_3$) [ppm] δ 153.6, 146.5 (dm, J_{C-F} = 247 Hz), 141.1 (dm, J_{C-F} = 250 Hz), 134.2 (*m*), 134.1, 128.6, 125.1, 115.5, 112.0, 102.2 (*t*, J_{C-F} = 22 Hz); **IR** (KBr) ν (cm^{-1}): 3084, 2927, 2855, 1642, 1578, 1522, 1473, 1443, 1406, 1266, 1219, 1176, 1127, 1071, 1032, 948, 840, 746, 715, 600, 591, 438.

*4.1.4. 2-(2,3,5,6-Tetrafluorophenoxy)aniline (**3d**)*

36.5 mg, **Yield**: 71%; **Yellow solid**; **Mp**: 40–42 °C; **^{1}H NMR** (400 MHz, $CDCl_3$) δ 6.98 (dd, *J* = 8.5, 4.3 Hz, 2H), 6.85 (d, *J* = 7.6 Hz, 1H), 6.66 (q, *J* = 7.9 Hz, 2H), 4.01 (s, 2H); **^{19}F NMR** (376 MHz, $CDCl_3$) [ppm] δ −138.72–−138.83 (*m*, 2F), −154.57–−154.68 (*m*, 2F); **^{13}C NMR** (100 MHz, $CDCl_3$) δ 146.4 (dm, J_{C-F} = 247 Hz), 141.5 (dm, J_{C-F} = 249 Hz), 145.0, 136.5, 134.8 (*m*), 124.6, 118.4, 116.6, 114.3, 101.7 (*t*, J_{C-F} = 22 Hz); **IR** (KBr) ν (cm^{-1}): 3477, 3390, 3076, 2924, 2854, 1623, 1520, 1305, 1277, 1181, 1073, 945, 839, 743, 714; MS (EI): *m*/*z* 257.2.

*4.1.5. 3-(3-Chlorophenoxy)-1,2,4,5-tetrafluorobenzene (**3e**)*

39.3 mg, **Yield**: 71%; **Yellow oil**; **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.29 (*t*, *J* = 8.2 Hz, 1H), 7.14 (d, *J* = 8.0 Hz, 1H), 7.08–6.97 (*m*, 2H), 6.90 (d, *J* = 9.6 Hz, 1H); **^{19}F NMR** (376 MHz, $CDCl_3$) [ppm] δ −138.19–−138.30 (*m*, 2F), −153.83–−153.94 (*m*, 2F); **^{13}C NMR** (100 MHz, $CDCl_3$) δ 157.6, 146.5 (dm, J_{C-F} = 247 Hz), 141.4 (dm, J_{C-F} = 251 Hz), 133.7 (*m*), 135.3, 130.6, 124.5, 116.2, 113.8, 102.4 (*t*, J_{C-F} = 23 Hz); **IR** (KBr) ν (cm^{-1}): 3085, 2927, 2855, 2404, 2353, 2078, 1642, 1591, 1521, 1432, 1407, 1301, 1273, 1209, 1180, 1129, 1100, 1072, 948, 872, 840, 777, 717, 677.15, 638, 443; MS (EI): *m*/*z* 276.2.

*4.1.6. 3-(3-Bromophenoxy)-1,2,4,5-tetrafluorobenzene (**3f**)*

55.9 mg, **Yield**: 87%; **Yellow oil**; **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.29 (d, *J* = 8.2 Hz, 1H), 7.23 (*t*, *J* = 8.1 Hz, 1H), 7.17 (s, 1H), 7.08–6.98 (*m*, 1H), 6.95 (d, *J* = 6.8 Hz, 1H); **^{19}F NMR** (376 MHz, $CDCl_3$) [ppm] δ −138.13–−138.24 (*m*, 2F), −153.77–−153.88 (*m*, 2F); **^{13}C NMR** (100 MHz, $CDCl_3$) δ 157.6, 146.5 (dm, J_{C-F} = 247 Hz), 141.4 (dm, J_{C-F} = 250 Hz), 133.7 (*m*), 130.9, 127.0, 123.0, 119.1, 114.3, 102.4 (*t*, J_{C-F} = 22 Hz); **IR** (KBr) ν (cm^{-1}): 3084, 2927, 2855, 1642, 1585, 1521, 1487, 1428, 1406, 1274, 1203, 1180, 1069, 947, 851, 840, 717, 676, 635, 596, 438.

*4.1.7. 1,2,4,5-Tetrafluoro-3-(3-methoxyphenoxy)benzene (**3g**)*

52.8 mg, **Yield**: 97%; **Yellow oil**; **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.25 (*t*, *J* = 8.3 Hz, 1H), 7.05–6.94 (*m*, 1H), 6.70 (d, *J* = 8.3 Hz, 1H), 6.64–6.52 (*m*, 2H), 3.83 (s, 3H); **^{19}F NMR** (376 MHz, $CDCl_3$) [ppm] δ −138.74–−138.85 (*m*, 2F), −154.09–−154.20 (*m*, 2F); **^{13}C NMR** (100 MHz, $CDCl_3$) δ 161.0, 158.3, 146.5 (dm, J_{C-F} = 247 Hz), 141.6 (dm, J_{C-F} = 251 Hz), 134.1 (*m*), 130.2, 109.1, 107.4, 102.3, 102.0 (*t*, J_{C-F} = 23 Hz), 55.4; **IR** (KBr) ν (cm^{-1}): 3081, 2947, 2841, 1606, 1521, 1487, 1263, 1184, 1143, 1068, 947, 838, 762, 712, 647; MS (EI): *m*/*z* 272.2.

*4.1.8. 4-(2,3,5,6-Tetrafluorophenoxy)benzonitrile (**3i**)*

40.6 mg, **Yield**: 76%; **Yellow solid**; **Mp**: 98–100 °C; **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.67 (d, *J* = 8.7 Hz, 2H), 7.14–7.01 (*m*, 3H); **^{19}F NMR** (376 MHz, $CDCl_3$) [ppm] δ −137.54–−137.65 (*m*, 2F), −153.46–−153.57 (*m*, 2F); **^{13}C NMR** (100 MHz, $CDCl_3$) δ 159.8, 146.5 (dm, J_{C-F} = 248 Hz), 141.1 (dm, J_{C-F} = 252 Hz), 134.4, 132.8 (*m*), 118.2, 116.2, 107.2, 103.1 (*t*, J_{C-F} = 23 Hz); **IR** (KBr) ν (cm^{-1}): 3062, 2925, 2854, 2230, 1602, 1512, 1488, 1222, 1190, 1067, 946, 868, 836, 544; MS (EI): *m*/*z* 267.2.

*4.1.9. 3-(4-Bromophenoxy)-1,2,4,5-tetrafluorobenzene (**3j**)*

59.7 mg, **Yield**: 97%; **White solid**; **Mp**: 44–46 °C; **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.46 (d, *J* = 8.9 Hz, 2H), 7.07–6.94 (*m*, 1H), 6.90 (d, *J* = 8.8 Hz, 2H); **^{19}F NMR** (376 MHz, $CDCl_3$) [ppm] δ −138.26–−138.37 (*m*, 2F), −153.90–−154.01 (*m*, 2F); **^{13}C NMR** (100 MHz, $CDCl_3$) δ 156.2, 146.5 (dm, J_{C-F} = 247 Hz), 141.1 (dm, J_{C-F} = 251 Hz), 133.9 (*m*), 132.8, 117.4, 116.4, 103.1 (*t*, J_{C-F} = 23 Hz); **IR** (KBr) ν (cm^{-1}): 3075, 2922, 1888, 1636, 1587, 1516, 1403, 1275, 1216, 1173, 1067, 941, 832, 715, 629, 498.

*4.1.10. 1,2,4,5-Tetrafluoro-3-(p-tolyloxy)benzene (**3k**)*

46.1 mg, **Yield**: 90%; **Yellow oil**; **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.16 (d, *J* = 8.1 Hz, 2H), 6.98 (td, *J* = 9.9, 5.0 Hz, 1H), 6.92 (d, *J* = 8.4 Hz, 2H), 2.36 (s, 3H); **^{19}F NMR** (376 MHz, $CDCl_3$) [ppm] δ −138.90–−139.02 (*m*, 2F), −154.21–−154.32 (*m*, 2F); **^{13}C NMR** (100 MHz, $CDCl_3$) δ 155.2, 146.5 (dm, J_{C-F} = 247 Hz), 141.6 (dm, J_{C-F} = 249 Hz), 134.7 (*m*), 133.3, 130.2, 115.5, 101.6 (*t*, J_{C-F} = 22 Hz), 20.5; **IR** (KBr) ν (cm^{-1}): 3084, 2928, 2866, 1641, 1608, 1521, 1485, 1203, 1173, 1067, 943, 834, 766, 749, 692, 473; MS (EI): *m*/*z* 256.2.

*4.1.11. 1,2,4,5-Tetrafluoro-3-(4-methoxyphenoxy)benzene (**3l**)*

52.3 mg, **Yield**: 96%; **White solid**; **Mp**: 45–47 °C; **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.01–6.90 (*m*, 3H), 6.87 (d, *J* = 9.1 Hz, 2H), 3.81 (s, 3H); **^{19}F NMR** (376 MHz, $CDCl_3$) [ppm] δ −138.95–−139.05 (*m*, 2F), −154.47–−154.58 (*m*, 2F); **^{13}C NMR** (100 MHz, $CDCl_3$) δ 156.0, 151.3, 146.5 (dm, J_{C-F} = 247 Hz), 141.6 (dm, J_{C-F} = 249 Hz), 135.2

(*m*), 116.9, 114.8, 101.5 (*t*, J_{C-F} = 23 Hz), 55.6; **IR** (KBr) ν (cm^{-1}): 3090, 2963, 2842, 1896, 1865, 1834, 1642, 1518, 1485, 1460, 1274, 1248, 1179, 1102, 1066, 1030, 941, 833, 768, 729, 711, 567, 521, 507; MS (EI): *m/z* 272.2.

*4.1.12. 3-(4-*Tert*-butylphenoxy)-1,2,4,5-tetrafluorobenzene (**3m**)*

56.7 mg, **Yield**: 97%; **Yellow oil**; **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.39 (d, *J* = 8.8 Hz, 2H), 7.04–6.91 (*m*, 3H), 1.36 (s, 9H); **^{19}F NMR** (376 MHz, $CDCl_3$) [ppm] δ −138.88––139.00 (*m*, 2F), −154.02––154.13 (*m*, 2F); **^{13}C NMR** (100 MHz, $CDCl_3$) δ 155.0, 146.7, 146.5 (dm, J_{C-F} = 247 Hz), 141.7 (dm, J_{C-F} = 245 Hz), 134.6 (*m*), 126.6, 115.0, 101.7 (*t*, J_{C-F} = 23 Hz), 34.3, 31.4; **IR** (KBr) ν (cm^{-1}): 3083, 2965, 2872, 1640, 1606, 1521, 1409, 1366, 1271, 1212, 1176, 1067, 945, 833, 718, 547; MS (EI): *m/z* 298.9.

*4.1.13. 4-(2,3,5,6-Tetrafluorophenoxy)aniline (**3n**)*

38.6 mg, **Yield**: 75%; **Yellow solid**; **Mp**: 48–50 °C; **^{1}H NMR** (400 MHz, $CDCl_3$) δ 6.93 (ddd, *J* = 19.9, 10.0, 7.1 Hz, 1H), 6.86 (d, *J* = 8.7 Hz, 2H), 6.64 (d, *J* = 8.8 Hz, 2H), 3.53 (s, 2H); **^{19}F NMR** (376 MHz, $CDCl_3$) [ppm] δ −139.15––139.27 (*m*, 2F), −154.63–−154.74 (*m*, 2F); **^{13}C NMR** (100 MHz, $CDCl_3$) δ 150.2, 146.3 (dm, J_{C-F} = 246 Hz), 142.8, 141.6 (dm, J_{C-F} = 249 Hz), 135.5 (*m*), 117.1, 116.0, 101.2 (*t*, J_{C-F} = 23 Hz); **IR** (KBr) ν (cm^{-1}): 3455, 3375, 3222, 3081, 2924, 1640, 1518, 1485, 1271, 1198, 1125, 1067, 945, 830, 714, 515; MS (EI): *m/z* 257.2.

*4.1.14. 4-(2,3,5,6-Tetrafluorophenoxy)biphenyl (**3o**)*

54.1 mg, **Yield**: 85%; **White solid**; **Mp**: 129–133 °C; **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.61 (d, *J* = 8.4 Hz, 4H), 7.49 (*t*, *J* = 7.5 Hz, 2H), 7.40 (*t*, *J* = 7.3 Hz, 1H), 7.11 (d, *J* = 8.5 Hz, 2H), 7.03 (ddd, *J* = 16.9, 9.8, 7.1 Hz, 1H); **^{19}F NMR** (376 MHz, $CDCl_3$) [ppm] δ −138.50–−138.62 (*m*, 2F), −153.84––153.95 (*m*, 2F); **^{13}C NMR** (100 MHz, $CDCl_3$) δ 156.7, 146.5 (dm, J_{C-F} = 247 Hz), 141.6 (dm, J_{C-F} = 251 Hz), 140.2, 137.1, 135.5 (*m*), 128.8, 128.6, 127.3, 127.0, 115.9, 102.0 (*t*, J_{C-F} = 22 Hz); **IR** (KBr) ν (cm^{-1}): 3091, 2923, 2853, 1641, 1598, 1517, 1490, 1405, 1225, 1176, 1119, 1067, 943, 834, 766, 749, 692, 473.

*4.1.15. 3-(2,3-Dimethylphenoxy)-1,2,4,5-tetrafluorobenzene (**3p**)*

50.8 mg, **Yield**: 94%; **Yellow solid**; **Mp**: 89–91 °C; **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.04 (*t*, *J* = 7.8 Hz, 1H), 7.01–6.91 (*m*, 2H), 6.54 (d, *J* = 8.0 Hz, 1H), 2.39 (s, 6H); **^{19}F NMR** (376 MHz, $CDCl_3$) [ppm] δ −138.50––138.62 (*m*, 2F), −139.05––139.16 (*m*, 2F); **^{13}C NMR** (100 MHz, $CDCl_3$) δ 155.5, 146.0 (dm, J_{C-F} = 246 Hz), 141.5 (dm, J_{C-F} = 248 Hz), 139.0, 135.2 (*m*), 126.0, 125.8, 125.3, 111.2, 101.3 (*t*, J_{C-F} = 22 Hz), 20.0, 11.8; **IR** (KBr) ν (cm^{-1}): 3093, 2923, 2527, 1643, 1609, 1581, 1516, 1492, 1234, 1177, 1163, 1126, 1110, 939, 846, 763, 641; MS (EI): *m/z* 270.3.

*4.1.16. 3-(3,4-Dimethylphenoxy)-1,2,4,5-tetrafluorobenzene (**3q**)*

49.2 mg, **Yield**: 91%; **Yellow oil**; **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.12 (d, *J* = 8.2 Hz, 1H), 7.05–6.92 (*m*, 1H), 6.85 (s, 1H), 6.75 (d, *J* = 6.9 Hz, 1H), 2.29 (d, *J* = 7.7 Hz, 6H); **^{19}F NMR** (376 MHz, $CDCl_3$) [ppm] δ −138.98––139.09 (*m*, 2F), −139.05––139.16 (*m*, 2F); **^{13}C NMR** (100 MHz, $CDCl_3$) δ 155.4, 146.5 (dm, J_{C-F} = 246 Hz), 141.7 (dm, J_{C-F} = 247 Hz), 138.4, 134.8 (*m*), 132.0, 130.6, 116.9, 112.6, 101.6 (*t*, J_{C-F} = 22 Hz), 19.9, 18.9; **IR** (KBr) ν (cm^{-1}): 3084, 3028, 2926, 1641, 1612, 1520, 1485, 1275, 1242, 1196, 1177, 1155, 1116, 1069, 947, 808, 713, 638, 443; MS (EI): *m/z* 270.3.

*4.1.17. 2-(2,3,5,6-Tetrafluorophenoxy)pyridine (**3s**)*

25.8 mg, **Yield**: 53%; **Yellow solid**; **Mp**: 154–158 °C; **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.47 (*t*, *J* = 8.0 Hz, 1H), 7.30–7.20 (*m*, 1H), 7.18 (d, *J* = 7.0 Hz, 1H), 6.71 (d, *J* = 9.4 Hz, 1H), 6.33 (*t*, *J* = 6.7 Hz, 1H); **^{19}F NMR** (376 MHz, $CDCl_3$) [ppm] δ −137.45––137.57 (*m*, 2F), −145.01––145.14 (*m*, 2F); **^{13}C NMR** (100 MHz, $CDCl_3$) δ 160.8, 146.2 (dm, J_{C-F} = 249 Hz), 142.9 (dm, J_{C-F} = 249 Hz), 141.0, 137.3, 122.0, 120.1 (*m*), 106.9 (*t*, J_{C-F} = 22 Hz), 106.8; **IR** (KBr) ν (cm^{-1}): 3415, 3053, 2920, 2852, 1674, 1590, 1515, 1275, 1148, 1074, 945, 844, 757, 732, 516; MS (EI): *m/z* 243.2.

*4.1.18. 1-(2,3,5,6-Tetrafluorophenoxy)naphthalene (**3t**)*

54.4 mg, **Yield**: 93%; **White solid**; **Mp**: 63–66 °C; **^{1}H NMR** (400 MHz, $CDCl_3$) δ 8.49 (d, *J* = 8.2 Hz, 1H), 7.94 (d, *J* = 8.6 Hz, 1H), 7.71–7.58 (*m*, 3H), 7.37 (*t*, *J* = 8.0 Hz, 1H), 7.12–6.98 (*m*, 1H), 6.75 (d, *J* = 7.5 Hz, 1H); **^{19}F NMR** (376 MHz, $CDCl_3$) [ppm] δ −138.48–−138.59 (*m*, 2F), −153.87––153.98 (*m*, 2F); **^{13}C NMR** (100 MHz, $CDCl_3$) δ 153.2, 147.1 (dm, J_{C-F} = 247 Hz), 141.6 (dm, J_{C-F} = 248 Hz), 134.9, 134.5 (*m*), 127.7, 127.0, 126.3, 125.2, 124.9, 123.6, 121.7, 107.7, 102.1 (*t*, J_{C-F} = 23 Hz); **IR** (KBr) ν (cm^{-1}): 3092, 2923, 1627, 1599, 1518, 1463, 1245, 1210, 1163, 1119, 1060, 942, 817, 750, 725, 475; MS (EI): *m/z* 292.3.

*4.1.19. 2-(2,3,5,6-Tetrafluorophenoxy)naphthalene (**3u**)*

53.2 mg, **Yield**: 91%; **White solid**; **Mp**: 89–93 °C; **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.89 (*t*, *J* = 8.5 Hz, 2H), 7.76 (d, *J* = 8.0 Hz, 1H), 7.51 (dt, *J* = 14.8, 7.0 Hz, 2H), 7.39 (d, *J* = 8.9 Hz, 1H), 7.26 (s, 1H), 7.11–6.96 (*m*, 1H); **^{19}F NMR** (376 MHz, $CDCl_3$) [ppm] δ −138.48–−138.59 (*m*, 2F), −153.87––153.98 (*m*, 2F); **^{13}C NMR** (100 MHz, $CDCl_3$) δ 155.1, 146.6 (dm, J_{C-F} = 247 Hz), 141.7 (dm, J_{C-F} = 251 Hz), 134.3 (*m*), 134.0, 130.4, 130.3, 127.9, 127.2, 127.0, 125.1, 117.2, 110.3, 102.1 (*t*, J_{C-F} = 23 Hz); **IR** (KBr) ν (cm^{-1}): 3077, 2925, 2854, 1641, 1599, 1577, 1520, 1445, 1392, 1259, 1228, 1176, 1128, 1099, 1068, 945, 838, 770, 719, 650, 562; MS (EI): *m/z* 292.3.

*4.1.20. 4-(2,3,5,6-Tetrafluoro-4-(trifluoromethyl)phenoxy)biphenyl (**4a**)*

62.6 mg, **Yield**: 81%; **White solid**; **Mp**: 130–134 °C; **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.61 (*t*, *J* = 8.7 Hz, 4H), 7.48 (*t*, *J* = 7.3 Hz, 2H), 7.40 (*t*, *J* = 6.9 Hz, 1H), 7.12 (d, *J* = 8.2 Hz, 2H); **^{19}F NMR** (376 MHz, $CDCl_3$) [ppm] δ −55.8––56.1 (*m*, 3F), −140.28––140.48 (*m*, 2F), −151.82––152.04 (*m*, 2F); **^{13}C NMR** (100 MHz, $CDCl_3$) δ 156.1, 145.0 (dm, J_{C-F} = 256 Hz), 141.8 (dm, J_{C-F} = 252 Hz), 140.0, 137.9, 137.5 (*m*), 128.9, 128.6, 127.4, 127.0, 120.9 (q, $^1J_{C-F}$ = 252 Hz), 116.3, 105.8 (*m*); **IR** (KBr) ν (cm^{-1}): 3077, 2924, 2854, 1620, 1599, 1453, 1429, 1303, 1246, 1224, 1138, 1097, 871, 833, 758, 689.

*4.1.21. 4-(Perfluorophenoxy)biphenyl (**4b**)*

34.3 mg, **Yield**: 51%; **White solid**; **Mp**: 130–132 °C; **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.60 (d, *J* = 7.7 Hz, 4H), 7.49 (*t*, *J* = 7.4 Hz, 2H), 7.40 (*t*, *J* = 7.2 Hz, 1H), 7.08 (d, *J* = 8.3 Hz, 2H); **^{19}F NMR** (376 MHz, $CDCl_3$) [ppm] δ −153.82––153.86 (*m*, F), −159.73––159.85 (*m*, 2F), −161.91––162.04 (*m*, 2F); **^{13}C NMR** (100 MHz, $CDCl_3$) δ 156.7, 142.2 (dm, J_{C-F} = 247 Hz), 140.2, 138.3 (dm, J_{C-F} = 257 Hz), 137.7 (*m*), 137.3, 129.8 (*m*), 128.8, 128.7, 127.3, 127.0, 115.8, 112.3 (*t*, J_{C-F} = 20 Hz); **IR** (KBr) ν (cm^{-1}): 1517, 1225, 1172, 1115, 998, 835, 765, 693.

*4.1.22. 4-(2,3,5,6-Tetrafluoro-4-methylphenoxy)biphenyl (**4c**)*

55.2 mg, **Yield**: 83%; **White solid**; **Mp**: 131–134 °C; **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.59 (d, *J* = 7.8 Hz, 4H), 7.48 (*t*, *J* = 7.5 Hz, 2H), 7.38 (*t*, *J* = 7.3 Hz, 1H), 7.09 (d, *J* = 8.4 Hz, 2H), 2.33 (d, *J* = 16.8 Hz, 3H); **^{19}F NMR** (376 MHz, $CDCl_3$) [ppm] δ −143.43––143.52 (*m*, 2F), −155.65––155.74 (*m*, 2F); **^{13}C NMR** (100 MHz, $CDCl_3$) δ 156.9, 145.5 (dm, J_{C-F} = 245 Hz), 141.5 (dm, J_{C-F} = 250 Hz), 140.3, 131.2 (*m*), 136.8, 128.8, 128.5, 127.2, 127.0, 115.8, 112.3 (*t*, J_{C-F} = 20 Hz), 7.2; **IR** (KBr) ν (cm^{-1}): 1654, 1598, 1493, 1229, 1198, 1115, 1065, 962, 929, 835, 759, 691, 478.

*4.1.23. 4-(3,4-Difluorophenoxy)biphenyl (**4d**)*

40.1 mg, **Yield**: 71%; **White solid**; **Mp**: 63–65 °C; **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.67–7.58 (*m*, 4H), 7.49 (*t*, *J* = 7.6 Hz, 2H), 7.40 (*t*, *J* = 7.3 Hz, 1H), 7.24–7.09 (*m*, 3H), 6.90–6.80 (*m*, 2H); **^{19}F NMR** (376 MHz, $CDCl_3$) [ppm] δ −115.91––116.00 (*m*, F), −136.74––136.83 (*m*, F); **^{13}C NMR** (100 MHz, $CDCl_3$) δ 156.0, 140.4, 137.2, 128.9, 128.6, 127.3, 127.0, 118.3; **IR** (KBr) ν (cm^{-1}): 3431, 3076, 2924, 2854, 1620, 1599, 1503, 1429, 1303, 1246, 1194, 1097, 967, 871, 833, 758, 689, 482; MS (EI): *m*/*z* 282.4.

*4.1.24. 3-(Benzyloxy)-1,2,4,5-tetrafluorobenzene (**5a**)*

40.0 mg, **Yield**: 78%; **Yellow oil**; **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.47 (d, *J* = 6.8 Hz, 2H), 7.45–7.38 (*m*, 3H), 6.85–6.72 (*m*, 1H), 5.29 (s, 2H); **^{19}F NMR** (376 MHz, $CDCl_3$) [ppm] δ −139.98––140.09 (*m*, 2F), −155.98––156.09 (*m*, 2F); **^{13}C NMR** (100 MHz, $CDCl_3$) δ 146.3 (dm, J_{C-F} = 246 Hz), 141.4 (dm, J_{C-F} = 246 Hz), 137.6 (*m*), 135.6, 128.8, 128.6, 128.3, 99.8 (*t*, J_{C-F} = 23 Hz), 76.4 (*t*, J_{C-F} = 3 Hz); **IR** (KBr) ν (cm^{-1}): 3082, 3036, 2958, 1641, 1516, 1486, 1377, 1174, 1089, 941, 697, 647; MS (EI): *m*/*z* 256.2.

*4.1.25. 1,2,4,5-Tetrafluoro-3-(2-methoxybenzyloxy)benzene (**5b**)*

51.0 mg, **Yield**: 89%; **White solid**; **Mp**: 36–38 °C; **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.45 (d, *J* = 7.3 Hz, 1H), 7.37 (*t*, *J* = 7.6 Hz, 1H), 7.00 (*t*, *J* = 7.4 Hz, 1H), 6.93 (d, *J* = 8.2 Hz, 1H), 6.84–6.72 (*m*, 1H), 5.35 (s, 2H), 3.86 (s, 3H); **^{19}F NMR** (376 MHz, $CDCl_3$) [ppm] δ −140.42––140.54 (*m*, 2F), −156.06––156.17 (*m*, 2F); **^{13}C NMR** (100 MHz, $CDCl_3$) δ 157.7, 146.3 (dm, J_{C-F} = 245 Hz), 142.5 (dm, J_{C-F} = 246 Hz), 138.2 (*m*), 130.2, 130.1, 124.2, 120.5, 110.5, 99.5 (*t*, J_{C-F} = 23 Hz), 72.0 (*t*, J_{C-F} = 3 Hz), 55.3; **IR** (KBr) ν (cm^{-1}): 3083, 2945, 2841, 1640, 1602, 1515, 1463, 1376, 1289, 1246, 1172, 1090, 1027, 934, 823, 751, 731; MS (EI): *m*/*z* 286.4.

*4.1.26. 3-(2-Chlorobenzyloxy)-1,2,4,5-tetrafluorobenzene (**5c**)*

45.9 mg, **Yield**: 79%; **Yellow oil**; **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.66–7.57 (*m*, 1H), 7.47–7.39 (*m*, 1H), 7.38–7.29 (*m*, 2H), 6.89–6.75 (*m*, 1H), 5.40 (s, 2H); **^{19}F NMR** (376 MHz, $CDCl_3$) [ppm] δ −139.76––139.88 (*m*, 2F), −156.00––156.11 (*m*, 2F); **^{13}C NMR** (100 MHz, $CDCl_3$) δ 146.4 (dm, J_{C-F} = 246 Hz), 141.3 (dm, J_{C-F} = 248 Hz), 137.7 (*m*), 133.5, 133.6, 129.9, 129.8, 129.6, 127.0, 100.0 (*t*, J_{C-F} = 23 Hz), 73.5 (*t*, J_{C-F} = 4 Hz), 55.3; **IR** (KBr) ν (cm^{-1}): 3084, 2959, 2928, 1641, 1521, 1448, 1377, 1274, 1213, 1174, 1089, 1055, 941, 831, 755, 714, 568, 438; MS (EI): *m*/*z* 290.6.

*4.1.27. 1,2,4,5-Tetrafluoro-3-(4-methoxybenzyloxy)benzene (**5d**)*

48.7 mg, **Yield**: 85%; **Yellow oil**; **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.38 (d, *J* = 8.5 Hz, 2H), 6.92 (d, *J* = 8.6 Hz, 2H), 6.83–6.70 (*m*, 1H), 5.21 (s, 2H), 3.83 (s, 3H); **^{19}F NMR** (376 MHz, $CDCl_3$) [ppm] δ −140.14––140.22 (*m*, 2F), −155.87––155.98 (*m*, 2F); **^{13}C NMR** (100 MHz, $CDCl_3$) δ 160.1, 146.3 (dm, J_{C-F} = 246 Hz), 141.5 (dm, J_{C-F} = 246 Hz), 137.5 (*m*), 130.2, 127.7, 114.0, 99.7 (*t*, J_{C-F} = 23 Hz), 76.1 (*t*, J_{C-F} = 3 Hz), 55.2; **IR** (KBr) ν (cm^{-1}): 3079, 2964, 2841, 1641, 1587, 1486, 1432, 1402, 1375, 1303, 1253, 1175, 1085, 1035, 944, 824, 688; MS (EI): *m*/*z* 286.4.

*4.1.28. 3-(4-Chlorobenzyloxy)-1,2,4,5-tetrafluorobenzene (**5e**)*

48.2 mg, **Yield**: 83%; **Yellow oil**; **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.45–7.32 (*m*, 4H), 6.86–6.73 (*m*, 1H), 5.24 (s, 2H); **^{19}F NMR** (376 MHz, $CDCl_3$) [ppm] δ −139.71––139.83 (*m*, 2F), −156.06––156.17 (*m*, 2F); **^{13}C NMR** (100 MHz, $CDCl_3$) δ 146.3 (dm, J_{C-F} = 246 Hz), 141.3 (dm, J_{C-F} = 250 Hz), 137.3 (*m*), 134.8, 134.1, 129.6, 128.9, 99.8 (*t*, J_{C-F} = 23 Hz), 75.4 (*t*, J_{C-F} = 4 Hz), 55.2; **IR** (KBr) ν (cm^{-1}): 3086, 2972, 2877, 1904, 1644, 1604, 1515, 1406, 1376, 1266, 1170, 1089, 983, 930, 811, 711; MS (EI): *m*/*z* 290.6.

*4.1.29. 3-(4-Bromobenzyloxy)-1,2,4,5-tetrafluorobenzene (**5f**)*

54.3 mg, **Yield**: 81%; **Yellow oil**; **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.53 (d, *J* = 8.3 Hz, 2H), 7.33 (d, *J* = 8.2 Hz, 2H), 6.86–6.73 (*m*, 1H), 5.22 (s, 2H); **^{19}F NMR** (376 MHz, $CDCl_3$) [ppm] δ −139.71––139.83 (*m*, 2F), −156.06––156.17 (*m*, 2F); **^{13}C NMR** (100 MHz, $CDCl_3$) δ 146.3 (dm, J_{C-F} = 246 Hz), 141.3 (dm, J_{C-F} = 250 Hz), 137.3 (*m*), 134.6, 131.8, 129.8, 123.0, 100.0 (*t*, J_{C-F} = 23 Hz), 75.5 (*t*, J_{C-F} = 3 Hz), 55.2; **IR** (KBr) ν (cm^{-1}): 3085, 2967, 2876, 1642, 1596, 1516, 1404, 1373, 1267, 1170, 1089, 984, 930, 806, 710, 482.

*4.1.30. 1,2,4,5-Tetrafluoro-3-(3-methoxybenzyloxy)benzene (**5g**)*

46.4 mg, **Yield**: 81%; **Yellow oil**; **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.30 (dd, *J* = 13.9, 5.8 Hz, 1H), 7.02 (d, *J* = 6.9 Hz, 2H), 6.92 (d, *J* = 7.4 Hz, 1H), 6.85–6.71 (*m*, 1H), 5.26 (s, 2H), 3.85 (s, 3H); **^{19}F NMR** (376 MHz, $CDCl_3$) [ppm] δ −139.94––140.06 (*m*, 2F), −155.96––156.07 (*m*, 2F); **^{13}C NMR** (100 MHz, $CDCl_3$) δ 159.8, 146.3 (dm, J_{C-F} = 245 Hz), 141.3 (dm, J_{C-F} = 246 Hz), 137.5 (*m*), 137.1, 129.7, 120.4, 114.6, 113.4, 99.8 (*t*, J_{C-F} = 23 Hz), 76.2 (*t*, J_{C-F} = 3 Hz), 55.2; **IR** (KBr) ν (cm^{-1}): 3079, 2959, 2840, 1641, 1604, 1516, 1483, 1374, 1269, 1173, 1088, 1051, 940, 766, 693; MS (EI): *m*/*z* 286.4.

*4.1.31. 1,2,4,5-Tetrafluoro-3-(3-phenoxybenzyloxy)benzene (**5h**)*

63.4 mg, **Yield**: 91%; **Yellow oil**; **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.47–7.32 (*m*, 3H), 7.27–7.11 (*m*, 3H), 7.06 (d, *J* = 7.9 Hz, 3H), 6.87–6.73 (*m*, 1H), 5.27 (s, 2H); **^{19}F NMR** (376 MHz, $CDCl_3$) [ppm] δ −139.78––139.89 (*m*, 2F), −155.83––155.94 (*m*, 2F); **^{13}C NMR** (100 MHz, $CDCl_3$) δ 157.7, 156.9, 146.3 (dm, J_{C-F} = 246 Hz), 140.3 (dm, J_{C-F} = 246 Hz), 137.5, 137.4 (*m*), 130.1, 123.6, 122.9, 119.2, 119.1, 118.4, 99.9 (*t*, J_{C-F} = 23 Hz), 75.9 (*t*, J_{C-F} = 3 Hz); **IR** (KBr) ν (cm^{-1}): 3079, 2958, 2926, 1641, 1587, 1516, 1487, 1444, 1374, 1253, 1215, 1172, 1089, 944, 829, 693.

*4.1.32. 1-((2,3,5,6-Tetrafluorophenoxy)methyl)naphthalene (**5i**)*

50.8 mg, **Yield**: 83%; **White solid**; **Mp**: 37–39 °C; **^{1}H NMR** (400 MHz, $CDCl_3$) δ 8.33 (d, *J* = 8.3 Hz, 1H), 7.94 (*t*, *J* = 7.6 Hz, 2H), 7.68 (*t*, *J* = 7.2 Hz, 1H), 7.61 (*t*, *J* = 7.0 Hz, 2H), 7.50 (*t*, *J* = 7.6 Hz, 1H), 6.87–6.69 (*m*, 1H), 5.75 (s, 2H); **^{19}F NMR** (376 MHz, $CDCl_3$) [ppm] δ −139.79––139.91 (*m*, 2F), −155.54––155.65 (*m*, 2F); **^{13}C NMR** (100 MHz, $CDCl_3$) δ 146.4 (dm, J_{C-F} = 245 Hz), 141.5 (dm, J_{C-F} = 245 Hz), 137.5 (*m*), 133.8, 131.8, 131.2, 130.0, 128.7, 127.8, 126.8, 126.2, 125.1, 123.8, 99.9 (*t*, J_{C-F} = 23 Hz), 74.8 (*t*, J_{C-F} = 3 Hz); **IR** (KBr) ν (cm^{-1}): 3616, 3122, 2925, 2853, 2314, 1642, 1515, 1486, 1401, 1386, 1261, 1173, 1083, 946, 798, 714.

*4.1.33. 1,2,4,5-Tetrafluoro-3-(1-phenylethoxy)benzene (**5j**)*

38.4 mg, **Yield**: 71%; **Yellow oil**; **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.43 (d, *J* = 7.1 Hz, 2H), 7.40–7.31 (*m*, 3H), 6.78–6.65 (*m*, 1H), 5.52 (q, *J* = 6.4 Hz, 1H), 1.74 (d, *J* = 6.4 Hz, 3H); **^{19}F NMR** (376 MHz, $CDCl_3$) [ppm] δ −140.25––140.37 (*m*, 2F), −155.17––155.28 (*m*, 2F); **^{13}C NMR** (100 MHz, $CDCl_3$) δ 144.7 (dm, J_{C-F} = 248 Hz), 141.6 (dm, J_{C-F} = 253 Hz), 140.9, 136.8 (*m*), 128.5, 126.3, 126.2, 99.6 (*t*, J_{C-F} = 23 Hz), 82.6 (*t*, J_{C-F} = 3 Hz), 23.1; **IR** (KBr) ν (cm^{-1}): 3080, 2985, 2932, 2858, 1640, 1515, 1482, 1173, 1085, 943, 829, 761, 700, 540; MS (EI): *m*/*z* 270.2.

*4.1.34. 1,2,4,5-Tetrafluoro-3-(1-(3-methoxyphenyl)ethoxy)benzene (**5k**)*

45.0 mg, **Yield**: 75%; **Yellow oil**; **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.27 (*t*, *J* = 7.8 Hz, 1H), 7.06–6.94 (*m*, 2H), 6.86 (dd, *J* = 8.2, 1.6 Hz, 1H), 6.79–6.64 (*m*, 1H), 5.51 (q, *J* = 6.3 Hz, 1H), 3.84 (s, 3H), 1.73 (d, *J* = 6.4 Hz, 3H); **^{19}F NMR** (376 MHz, $CDCl_3$) [ppm] δ −140.22––140.33 (*m*, 2F), −155.15––155.26 (*m*, 2F); **^{13}C NMR** (100 MHz, $CDCl_3$) δ 159.8, 146.2 (dm, J_{C-F} = 245 Hz), 142.5, 141.5 (dm, J_{C-F} = 245 Hz), 136.8 (*m*), 129.6, 118.6, 114.2, 111.5, 99.7 (*t*, J_{C-F} = 23 Hz), 82.4 (*t*, J_{C-F} = 3 Hz), 55.2, 23.2; **IR** (KBr) ν (cm^{-1}): 3078,

2985, 2840, 1640, 1605, 1515, 1484, 1376, 1263, 1173, 1122, 1085, 1047, 943, 831, 786, 699.

*4.1.35. 1,2,4,5-Tetrafluoro-3-(1-(4-methoxyphenyl)ethoxy)benzene (**5l**)*

41.4 mg, **Yield**: 69%; **Yellow oil**; **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.34 (d, J = 8.5 Hz, 2H), 6.87 (d, J = 8.6 Hz, 2H), 6.77–6.64 (m, 1H), 5.48 (q, J = 6.3 Hz, 1H), 3.81 (s, 3H), 1.72 (d, J = 6.4 Hz, 3H); **^{19}F NMR** (376 MHz, $CDCl_3$) [ppm] δ −140.39–−140.51 (m, 2F), −155.13–−155.24 (m, 2F); **^{13}C NMR** (100 MHz, $CDCl_3$) δ 159.8, 146.2 (dm, J_{C-F} = 246 Hz), 141.6 (dm, J_{C-F} = 250 Hz), 136.9 (m), 132.8, 127.9, 113.9, 99.6 (t, J_{C-F} = 23 Hz), 82.2 (t, J_{C-F} = 3 Hz), 55.2, 22.9; **IR** (KBr) ν (cm^{-1}): 3078, 2985, 2840, 1640, 1605, 1515, 1484, 1376, 1263, 1173, 1122, 1085, 1047, 943, 831,786, 699.

*4.1.36. 3-(1-(4-Chlorophenyl)ethoxy)-1,2,4,5-tetrafluorobenzene (**5m**)*

44.5 mg, **Yield**: 73%; **Yellow oil**; **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.35 (q, J = 8.6 Hz, 4H), 6.80–6.67 (m, 1H), 5.48 (q, J = 6.4 Hz, 1H), 1.71 (d, J = 6.4 Hz, 3H); **^{19}F NMR** (376 MHz, $CDCl_3$) [ppm] δ −139.93–−140.04 (m, 2F), −155.23–−155.34 (m, 2F); **^{13}C NMR** (100 MHz, $CDCl_3$) δ 146.2 (dm, J_{C-F} = 246 Hz), 141.4 (dm, J_{C-F} = 246 Hz), 139.4, 136.6 (m), 134.4, 128.8, 127.7, 99.9 (t, J_{C-F} = 23 Hz), 81.8 (t, J_{C-F} = 3 Hz), 23.1; **IR** (KBr) ν (cm^{-1}): 3085, 2986, 2855, 1640, 1516, 1484, 1410, 1377, 1342, 1270, 1173, 1084, 996, 788, 714, 539.

*4.1.37. 3-(1-(4-Bromophenyl)ethoxy)-1,2,4,5-tetrafluorobenzene (**5n**)*

48.9 mg, **Yield**: 70%; **Yellow oil**; **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.49 (d, J = 8.4 Hz, 2H), 7.31 (d, J = 8.3 Hz, 2H), 6.80–6.66 (m, 1H), 5.47 (q, J = 6.4 Hz, 1H), 1.70 (d, J = 6.4 Hz, 3H); **^{19}F NMR** (376 MHz, $CDCl_3$) [ppm] δ −139.88–−140.00 (m, 2F), −155.22–−155.33 (m, 2F); **^{13}C NMR** (100 MHz, $CDCl_3$) δ 146.2 (dm, J_{C-F} = 246 Hz), 141.4 (dm, J_{C-F} = 246 Hz), 140.0, 136.6 (m), 131.8, 128.0 122.5, 99.9 (t, J_{C-F} = 23 Hz), 81.8 (t, J_{C-F} = 3 Hz), 23.1; **IR** (KBr) ν (cm^{-1}): 3084, 2986, 2932, 1641, 1516, 1484, 1407, 1377, 1341, 1298, 1209, 1123, 1083, 1010, 945, 780, 714, 536.

*4.1.38. (2,3,5,6-Tetrafluorophenoxy)methylene)dibenzene (**5o**)*

56.5 mg, **Yield**: 89%; **White solid**; **Mp**: 56–59 °C; **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.54 (d, J = 7.1 Hz, 4H), 7.45–7.35 (m, 6H), 6.79–6.66 (m, 1H), 6.57 (s, 1H); **^{19}F NMR** (376 MHz, $CDCl_3$) [ppm] δ −139.99–−140.11 (m, 2F), −155.35–−155.45 (m, 2F); **^{13}C NMR** (100 MHz, $CDCl_3$) δ 146.3 (dm, J_{C-F} = 245 Hz), 141.5 (dm, J_{C-F} = 245 Hz), 139.8, 136.6 (m), 128.7, 128.5, 127.2, 99.9 (t, J_{C-F} = 24 Hz), 86.8; **IR** (KBr) ν (cm^{-1}): 3077, 3034, 2959, 1955, 1640, 1515, 1481, 1454, 1399, 1349, 1226, 1172, 1118, 1108, 974, 935, 931, 700, 593.

*4.1.39. 1,2,4,5-Tetrafluoro-3-(pentyloxy)benzene (**5p**)*

29.8 mg, **Yield**: 63%; **Yellow oil**; **^{1}H NMR** (400 MHz, $CDCl_3$) δ 6.77 (tt, J = 10.0, 7.0 Hz, 1H), 4.24 (t, J = 6.6 Hz, 2H), 1.85–1.76 (m, 2H), 1.43 (ddd, J = 21.2, 13.5, 6.3 Hz, 4H), 0.95 (t, J = 7.1 Hz, 3H); **^{19}F NMR** (376 MHz, $CDCl_3$) [ppm] δ −140.26–−140.37 (m, 2F), −157.13–−157.23 (m, 2F); **^{13}C NMR** (100 MHz, $CDCl_3$) δ 145.4 (dm, J_{C-F} = 246 Hz), 141.2 (dm, J_{C-F} = 245 Hz), 138.4 (m), 99.1 (t, J_{C-F} = 23 Hz), 75.3 (t, J_{C-F} = 4 Hz), 29.6, 27.7, 22.3, 13.9; **IR** (KBr) ν (cm^{-1}): 3480, 3346, 3074, 2959, 2855, 1654, 1487, 1372, 1261, 1125, 1085, 997, 936, 800, 707; MS (EI): m/z 236.6.

*4.1.40. 1,2,4,5-Tetrafluoro-3-(octyloxy)benzene (**5q**)*

37.8 mg, **Yield**: 68%; **Yellow oil**; **^{1}H NMR** (400 MHz, $CDCl_3$) δ 6.85–6.69 (m, 1H), 4.24 (t, J = 6.5 Hz, 2H), 1.84–1.75 (m, 2H), 1.47 (dd, J = 14.1, 6.5 Hz, 2H), 1.37–1.29 (m, 8H), 0.91 (t, J = 6.2 Hz, 3H); **^{19}F NMR** (376 MHz, $CDCl_3$) [ppm] δ −140.29–−140.41 (m, 2F), −157.14–−157.24 (m, 2F); **^{13}C NMR** (100 MHz, $CDCl_3$) δ 146.3 (dm, J_{C-F} = 245 Hz), 141.2 (dm, J_{C-F} = 245 Hz), 138.3 (m), 99.1 (t, J_{C-F} = 23 Hz), 75.3 (t, J_{C-F} = 3 Hz), 31.7, 29.9, 29.2, 25.5, 22.6, 14.0; **IR** (KBr) ν (cm^{-1}): 3083, 2929, 2858, 1641, 1516, 1490, 1470, 1385, 1173, 1094, 941, 827, 742, 713; MS (EI): m/z 278.5.

*4.1.41. 3-(Cyclohexyloxy)-1,2,4,5-tetrafluorobenzene (**5r**)*

34.8 mg, **Yield**: 70%; **Yellow oil**; **^{1}H NMR** (400 MHz, $CDCl_3$) δ 6.87–6.67 (m, 1H), 4.34–4.22 (m, 1H), 2.02–1.95 (m, 2H), 1.84 (dd, J = 9.4, 5.3 Hz, 2H), 1.65–1.56 (m, 3H), 1.35 (t, J = 8.0 Hz, 3H); **^{19}F NMR** (376 MHz, $CDCl_3$) [ppm] δ −140.41–−140.52 (m, 2F), −155.90–−156.00 (m, 2F); **^{13}C NMR** (100 MHz, $CDCl_3$) δ 146.3 (dm, J_{C-F} = 252 Hz), 141.8 (dm, J_{C-F} = 245 Hz), 137.1 (m), 99.3 (t, J_{C-F} = 23 Hz), 83.1, 32.3, 25.3, 23.5; **IR** (KBr) ν (cm^{-1}): 2937, 2860, 1653, 1482, 1372, 1260, 1176, 1126, 992, 935, 708; MS (EI): m/z 248.2.

*4.1.42. 1,4-Bis(2,3,5,6-tetrafluorophenoxy)benzene (**6**)*

56.1 mg, **Yield**: 69%; **White solid**; **Mp**: 130–133 °C; **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.05–6.92 (m, 6H); **^{19}F NMR** (376 MHz, $CDCl_3$) [ppm] δ −138.50–−138.61 (m, 4F), −154.07–−154.18 (m, 4F); **^{13}C NMR** (100 MHz, $CDCl_3$) δ 153.3, 146.5 (dm, J_{C-F} = 247 Hz), 141.5 (dm, J_{C-F} = 249 Hz), 134.6 (m), 117.0, 102.0 (t, J_{C-F} = 22 Hz); **IR** (KBr) ν (cm^{-1}): 2921, 1622, 1519, 1276, 1175, 941, 834, 685, 630, 508.

*4.1.43. 1,2,4-Trifluorodibenzo[*b,e*][1,4]dioxine (**7**)*

33.8 mg, **Yield**: 71%; **White solid**; **Mp**: 137–140 °C; **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.03–6.95 (m, 4H), 6.65 (td, J = 10.1, 6.8 Hz, 1H); **^{19}F NMR** (376 MHz, $CDCl_3$) [ppm] δ −138.65–−138.81 (m, F), −140.50–−140.59 (m, F), −162.95–−163.06 (m, F); **^{13}C NMR** (100 MHz, $CDCl_3$) δ 140.6, 140.2, 125.2, 124.9, 124.7, 116.9; **IR** (KBr) ν (cm^{-1}): 3439, 3128, 2924, 2852, 2313, 1731, 1644, 1522, 1489, 1401, 1257, 1175, 1137, 1070, 946; MS (EI): m/z 238.3.

*4.1.44. 1,3,5-Tris(2,3,5,6-tetrafluorophenoxy)benzene (**8**)*

60.4 mg, **Yield**: 53%; **White solid**; **Mp**: 67–70 °C; **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.09–6.98 (m, 3H), 6.36 (s, 3H); **^{19}F NMR** (376 MHz, $CDCl_3$) [ppm] δ −137.81–−137.94 (m, 6F), −153.37–−153.48 (m, 6F); **^{13}C NMR** (100 MHz, $CDCl_3$) δ 158.8, 146.4 (dm, J_{C-F} = 248 Hz), 141.3 (dm, J_{C-F} = 252 Hz), 133.1 (m), 102.8 (t, J_{C-F} = 22 Hz), 98.9; **IR** (KBr) ν (cm^{-1}): 3091, 2962, 2855, 1611, 1524, 1486, 1464, 1274, 1179, 1139, 1073, 944, 840, 716.

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Appendix A. Supplementary data

Supplementary material related to this article can be found, in the online version, at http://dx.doi.org/10.1016/j.jfluchem.2013.08.013.

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