SUPPORTING INFORMATION

Direct *C*-Arylation of Polyfluoroarenes with Diaryliodonium Salts *via* $Pd(OAc)_2$-Catalysis

Fenglou Guo[a], Jianwei Han[b]*, Song Mao[a], Juan Li[a], Xu Geng[a], Jianjun Yu[a] and Limin Wang[a]*

Key Laboratory for Advanced Materials and Institute of Fine Chemicals, East China University of Science and Technology, 130 Meilong Road, Shanghai 200237, P. R. China
[Tel./fax: (+86)-21-64253881; e-mail address: wanglimin@ecust.edu.cn.]
Shanghai-Hong Kong Joint Laboratory in Chemical Synthesis, Shanghai Institute of Organic Chemistry, The Chinese Academy of Sciences, 345 Ling Ling Road, Shanghai 200032, P. R. China
[Fax: (+86)-21-54925383; e-mail address: jianweihan@sioc.ac.cn]

Table of Contents

Part 1. General Information

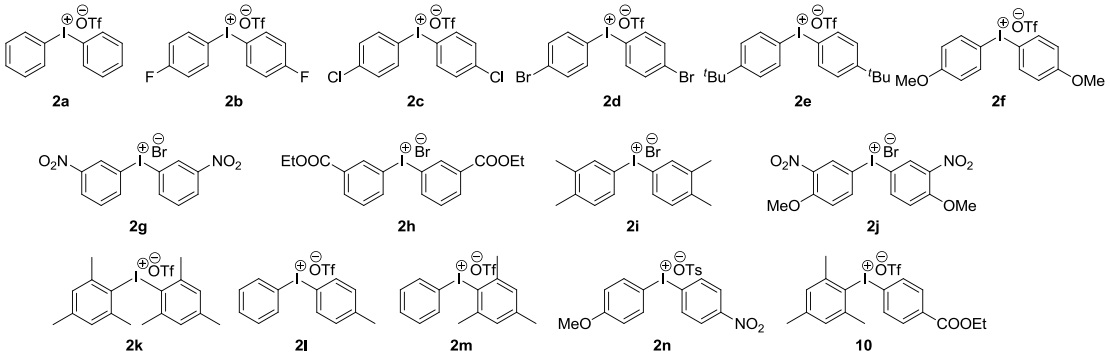
a. Methods:

NMR spectrum: ^{1}H and ^{13}C, ^{19}F NMR spectra were recorded on a Bruker AVANCE 400 spectrometer, operating at 400 MHz for ^{1}H NMR, 100 MHz for ^{13}C NMR, 377 MHz for ^{19}F NMR. Chemical shifts (δ) are reported in ppm, and coupling constants (J) are in Hertz (Hz). The following abbreviations were used to explain the multiplicities: s = singlet, d = doublet, t = triplet, q = quartet, m = multiplet, br = broad.

Mass spectroscopy: Mass spectra were in general recorded on an AMD 402/3 or a HP 5989A mass selective detector.

Chromatography: Column chromatography was performed with silica gel (300-400 mesh ASTM).

b. Materials: All solvents were dried and/or distilled by standard methods. All reagents were purchased from commercial sources and used without further purification. All the diaryliodonium salts were synthesized according to the literature procedures. Salts **2a, 2b, 2c, 2d, 2e, 2k, 2l,** and **2m** were prepared from iodine and the corresponding arene in the presence of *m*CPBA and TfOH described by Olofsson and co-workers.[1] Salt **2f** was synthesized by situ anion exchange described by Olofsson and co-workers.[2] Salt **2g**, **2h**, **2i** and **2j** were prepared from the corresponding arene with sodium metaperiodate as the coupling reagent in acidic media described by Skulski and co-workers.[3] **2n** was prepared from 1-iodo-4-nitrobenzene and anisole.[4] **10** was prepared from ethyl 4-iodobenzoate and mesitylene in the presence of *m*CPBA and TfOH.[5] Substrates **4a** and 2,2,2-trifluoroethyl 4-hydroxybenzoate were prepared according to the literatures.[6, 7]



Part 2. Experimental Section

a. Arylation of Pentafluorobenzene 1 with Diphenyliodonium Salts (Table 1)

$Pd(OAc)_2$ (0.05 mmol, 11.2 mg), base (1.0 mmol, 2 equiv.) and diphenyliodonium salt (0.65 mmol, 1.3

equiv.) were added into a dried Schlenk tube. The tube was stopped and degassed with Argon for three times. Then additives (0.5 mmol, 1 equiv.), pentafluorobenzene **1a** (0.5 mmol, 84 mg) and DMSO (100 μL) were added by syringe, followed by DMF (2.0 mL). The mixture was stirred under at 130 ^{o}C for 10 h, and then cooled down to room temperature. The resultant mixture was filtered through a short plug of gel to remove the deposition. The organic layers were washed with water (20 mL x 3), and then with brine, dried over Na_2SO_4, and filtered, the solvents were removed via rotary vapour. The residue was purified with silica gel chromatography (Petroleum ether (100%)) to provide pure product.

b. General Procedures for Arylation of Pentafluorobenzene 1 Diaryliodonium Salts (Table 2)

$Pd(OAc)_2$ (0.05 mmol, 11.2 mg), Ag_2CO_3 (1.0 mmol, 2 equiv., 276 mg) and diaryliodonium salt (0.65 mmol, 1.3 equiv.) were added into a dried Schlenk tube. The tube was degassed with Ar for three times. Then PivOH (0.5 mmol, 1 equiv. 51mg), pentafluorobenzene **1a** (0.5 mmol, 84 mg, 1.0 equiv.) and DMSO (100 μL) were added by syringe, followed by DMF (2.0 mL). The mixture was stirred under at 130 ^{o}C for 10 h, and then cooled down to room temperature. The resultant mixture was filtered through a short plug of gel to remove the deposition. The organic layers were washed with water (20 mL x 3), and then with brine, dried over Na_2SO_4, and filtered, the solvents were removed via rotary vapour. The residue was purified with silica gel chromatography (Petroleum ether (100%)) to provide pure product.

c. General Procedures for Arylation of Polyfluoroarenes 4 Diaryliodonium Salts (Table 3)

$Pd(OAc)_2$ (0.05 mmol, 11.2 mg), Ag_2CO_3 (1.0 mmol, 2 equiv., 276 mg) and diaryliodonium salt (0.65 mmol, 1.3 equiv.) were added into a dried Schlenk tube. The tube was degassed with Argon for three times. Then PivOH (0.5 mmol, 1 equiv. 51mg), polyfluoroarene **4** (0.5 mmol, 1.0 equiv.) and DMSO (100 μL) were added by syringe, followed by DMF (2.0 mL). The mixture was stirred under at 130 ^{o}C for 10 h, and then cooled down to room temperature. The resulted mixture was filtered through a short plug of gel to remove the deposition. The organic layers were washed with water (20 mL x 3), and then with brine, dried over Na_2SO_4, and filtered, the solvents were removed via rotary vapour. The residue was purified with silica gel chromatography (Petroleum ether (100%)) to provide pure product.

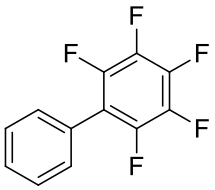
d. Synthesis of Liquid Crystal 12

$Pd(OAc)_2$ (0.1 mmol, 22.4 mg), Ag_2CO_3 (2.0 mmol, 2 equiv., 552 mg) and iodonium salt **10** (1.3 mmol, 1.3 equiv., 707 mg) were added into a dried Schlenk tube. The tube degassed with Argon for three times. Then PivOH (1.0 mmol, 1.0 equiv. 102 mg), polyfluoroarene **9** (1.0 mmol, 1.0 equiv., 222 mg) and DMSO (200 μL) were added by syringe, followed by DMF (4.0 mL). The mixture was stirred under at 130 ^{o}C for 10 h, and then cooled down to room temperature. The resulted mixture was filtered through a short plug of gel to remove the deposition. The organic layers were washed with water (20

mL x 3), and then with brine, dried over Na_2SO_4, and filtered, the solvents were removed via rotary vapour. The residue was purified with silica gel chromatography (Petroleum ether/Ethyl ether = 20:1) to provide pure product **11** in a yield of 68% (white solid, 0.67 mmol, 251 mg). Then **11** was added into a round-bottomed flask with EtOH (15 mL), KOH (76 mg), H_2O (2.7 mL) and stirred at 75 ^oC for 0.5 h. The pH of the system was adjusted to 2-3 using dilute aqueous hydrochloric acid (1M). The white precipitate was filtered off and the filtrate was washed with water for three times, then dried under vacuum conditions to give a white powder (95% yield, 215 mg, 0.63 mmol). Under dry argon, a mixture of 4'-butoxy-2',3',5',6'-tetrafluoro-[1,1'-biphenyl]-4-carboxylic acid (0.63 mmol, 215 mg), 2,2,2-trifluoroethyl 4-hydroxybenzoate (152 mg, 0.69 mmol, 1.1 equiv.), DCC (130 mg, 0.63 mmol, 1.0 equiv.) and DMAP (7.7 mg, 10 mol%) was added into anhydrous THF (8 mL). The resulted mixture was stirred at room temperature for 48 h. The precipitate was filtered and washed with ether. The filtrate was washed with water, then dried over Na_2SO_4. The solvent was removed in vacuo and the residue purified by column chromatography on silica gel using petroleum ether as the eluent to give a white solid (92% yield, 315 mg, 0.58 mmol).

Part 3. Characterization of the Products

2,3,4,5,6-pentafluoro-1,1'-biphenyl (3a)



The product (95 mg, 78% yield) as a white solid was purified with silica gel chromatography (petroleum ether). The analytical data is corresponding to those described in the literature.[8]

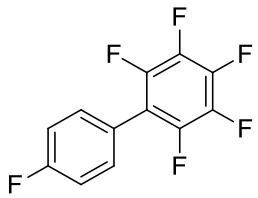
^{1}H NMR (400 MHz, $CDCl_3$) δ 7.57-7.48 (m, 3H), 7.48-7.44 (m, 2H).

^{13}C NMR (100 MHz, $CDCl_3$) δ 145.5-145.3 (m), 143.1-142.8 (m), 141.8-141.5 (m), 139.3-138.9 (m), 136.8-136.4 (m), 130.2, 129.3, 128.7, 126.4, 116.2-115.8 (m).

^{19}F NMR (377 MHz, $CDCl_3$) δ -143.3 (dd, J_F = 22.9, 8.1 Hz, 2F), -155.6 (t, J_F = 21.0 Hz, 1F), -162.3 (ddd, J_F = 23.0, 21.3, 8.3 Hz, 2F)

MS-EI (*m/z*): $[M]^+$ calcd for $C_{12}H_5F_5$, 244.03; found, 244.0.

2,3,4,4',5,6-hexafluoro-1,1'-biphenyl (3b)



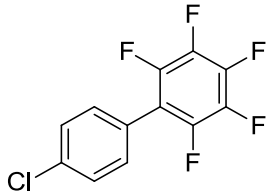
The product (84 mg, 64% yield) as a white solid was purified with silica gel chromatography (petroleum ether). The analytical data is corresponding to those described in the literature.[8]

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.45-7.41 (m, 2H), 7.24-7.19 (m, 2H).

^{19}F NMR (377 MHz, $CDCl_3$) δ -111.3 (s, 1F), -143.3 (dd, J_F = 22.2, 14.3 Hz, 2F), -155.2 (t, J_F = 21.1 Hz, 1F), -162.0 (m, 2F).

MS-EI (*m/z*): $[M]^+$ calcd for $C_{12}H_4F_6$, 262.02; found, 262.0.

4'-chloro-2,3,4,5,6-pentafluoro-1,1'-biphenyl (3c)



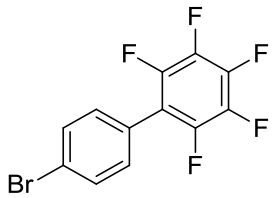
The product (104 mg, 75% yield) as a white solid was purified with silica gel chromatography (petroleum ether). The analytical data is corresponding to those described in the literature.[8]

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.54-7.45 (m, 2H), 7.40-7.37 (m, 2H).

^{19}F NMR (377 MHz, $CDCl_3$) δ -143.2 (dd, J_F = 23.0, 8.3 Hz, 2F), -154.8 (t, J_F = 20.7 Hz, 1F), -161.8 (m, 2F).

MS-EI (*m/z*): $[M]^+$ calcd for $C_{12}H_4ClF_5$, 277.99; found, 278.0.

4'-bromo-2,3,4,5,6-pentafluoro-1,1'-biphenyl (3d)



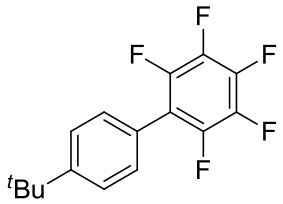
The product (121 mg, 78% yield) as a white solid was purified with silica gel chromatography (petroleum ether). The analytical data is corresponding to those described in the literature.[9]

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.67-7.64 (m, 2H), 7.33-7.28 (m, 2H).

^{19}F NMR (377 MHz, $CDCl_3$) δ -143.4 (dd, J_F = 22.2, 14.3 Hz, 2F), -155.0 (t, J_F = 21.1 Hz, 1F), -162.1 (m, 2F).

MS-EI (*m/z*): $[M]^+$ calcd for $C_{12}H_4BrF_5$, 321.94; found, 321.9.

4'-(tert-butyl)-2,3,4,5,6-pentafluoro-1,1'-biphenyl (3e)



The product (113 mg, 75% yield) as a white solid was purified with silica gel chromatography (petroleum ether).

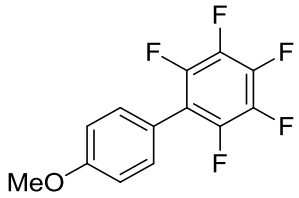
^{1}H NMR (400 MHz, $CDCl_3$) δ 7.59-7.51 (m, 2H), 7.44-7.36 (m, 2H), 1.41 (s, 9H).

^{13}C NMR (100 MHz, $CDCl_3$) δ 152.51, 145.6-145.4 (m), 143.2-142.9 (m), 141.6-141.2 (m), 139.3-138.7 (m), 136.8-136.4 (m), 129.8, 125.7, 123.4, 116.1-115.8 (m), 34.8, 31.2.

^{19}F NMR (377 MHz, $CDCl_3$) δ -143.36 (dd, J_F = 23.1, 8.1 Hz, 2F), -156.15 (t, J_F = 21.0 Hz, 1F), -162.44 (td, J_F = 22.9, 8.2 Hz, 2F).

HRMS-EI (*m/z*): $[M]^+$ calcd for $C_{16}H_{13}F_5$, 300.0937; found, 300.0936.

2,3,4,5,6-pentafluoro-4'-methoxy-1,1'-biphenyl (3f)



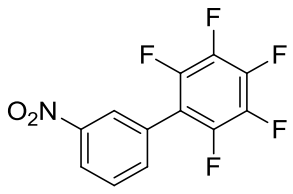
The product (110 mg, 80% yield) as a white solid was purified with silica gel chromatography (petroleum ether). The analytical data is corresponding to those described in the literature.[8]

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.40-7.37 (m, 2H), 7.05-7.02 (m, 2H), 3.89 (s, 3H).

^{19}F NMR (377 MHz, $CDCl_3$) δ-143.6 (dd, J_F = 23.4, 8.3 Hz, 2F), -156.5 (t, J_F = 21.1 Hz, 1F), -162.6 (m, 2F).

MS-EI (*m/z*): $[M]^+$ calcd for $C_{13}H_7F_5O$, 274.04; found, 274.0.

2,3,4,5,6-pentafluoro-3'-nitro-1,1'-biphenyl (3g)



The product (88 mg, 61% yield) as a white solid was purified with silica gel chromatography (petroleum ether). The analytical data is corresponding to those described in the literature.[8]

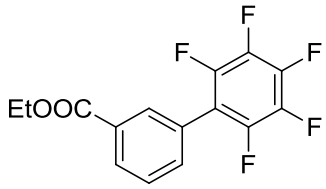
^{1}H NMR (400 MHz, $CDCl_3$) δ 8.38-8.36 (m, 2H), 7.81-7.78 (m, 1H), 7.75-7.71 (m, 1H).

^{19}F NMR (377 MHz, $CDCl_3$) δ -142.8 (dd, J_F = 22.5, 8.0 Hz, 2F), -152.7 (t, J_F = 20.9 Hz, 1F), -160.8 (qd,

J_F = 9.4, 2.1 Hz, 2F).

MS-EI (*m/z*): $[M]^+$ calcd for $C_{12}H_4F_5NO_2$, 289.02; found, 289.0.

ethyl 2',3',4',5',6'-pentafluoro-[1,1'-biphenyl]-3-carboxylate (3h)

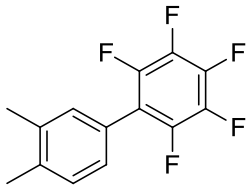


The product (117 mg, 74% yield) as a white solid was purified with silica gel chromatography (petroleum ether). The analytical data is corresponding to those described in the literature.[10]

^{1}H NMR (400 MHz, $CDCl_3$) δ 8.18-8.15 (m, 1H), 8.13 (s, 1H), 7.61-7.59 (m, 2H), 4.43 (q, *J* = 7.2 Hz, 2H), 1.43 (t = 7.2 Hz, 3H).

^{19}F NMR (377 MHz, $CDCl_3$) δ -142.56 (dd, J_F = 22.7, 8.1 Hz, 2F), -154.16 (t, J_F = 21.0 Hz,1F), -161.32 (dt, J_F = 22.7, 8.3 Hz, 2F).

2,3,4,5,6-pentafluoro-3',4'-dimethyl-1,1'-biphenyl (3i)

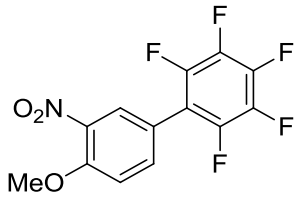


The product (90 mg, 66% yield) as a white solid was purified with silica gel chromatography (petroleum ether). The analytical data is corresponding to those described in the literature.[11]

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.30-7.27 (m, 1H), 7.24-7.13 (m, 2H), 2.35 (s, 6H).

^{19}F NMR (377 MHz, $CDCl_3$) δ -143.24 (dd, J_F = 23.2, 8.2 Hz, 2F), -156.33 (t, J_F = 21.0 Hz, 1F), -162.55 (dt, J_F = 23.0, 8.2 Hz, 2F).

2,3,4,5,6-pentafluoro-4'-methoxy-3'-nitro-1,1'-biphenyl (3j)



The product (96 mg, 66% yield) as a white solid was purified with silica gel chromatography (petroleum ether).

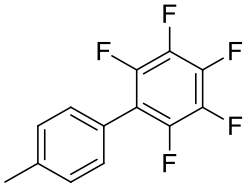
^{1}H NMR (400 MHz, $CDCl_3$) δ 7.99 (d, *J* = 0.9 Hz, 1H), 7.64 (dd, *J* = 8.7, 1.0 Hz, 1H), 7.24 (d, *J* = 8.8 Hz, 1H), 4.06 (s, 3H).

^{19}F NMR (377 MHz, $CDCl_3$) δ -143.22 (dd, J_F = 22.7, 8.1 Hz, 2F), -153.84 (t, J_F = 21.0 Hz, 1F), -161.25 (dt, J_F = 22.7, 8.2 Hz, 2F).

^{13}C NMR (100 MHz, $CDCl_3$) δ 153.5, 145.5-145.3 (m), 143.0-142.8 (m), 142.1-142.0 (m), 139.6, 139.3-139.0 (m), 136.8-136.5 (m), 135.8, 127.5, 118.5, 113.9, 113.4-113.1 (m), 56.7.

HRMS-EI (*m/z*): $[M]^+$ calcd for $C_{13}H_6F_5NO_3$, 319.0268; found, 319.0265.

2,3,4,5,6-pentafluoro-4'-methyl-1,1'-biphenyl (3l)



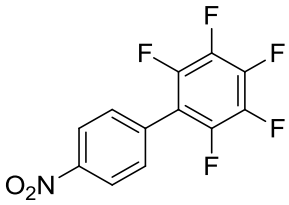
Following the general procedure, but using petroleum ether as the eluant afforded an inseperable mixture of 2,3,4,5,6-pentafluoro-4'-methyl-1,1'-biphenyl and 2,3,4,5,6-pentafluoro-1,1'-biphenyl, according to the ^{1}H NMR spectra and ^{19}F NMR the ratio of **3l**: **3a** is 1.1 : 1 and the overall yield is 70%.

For **3l**: The analytical data is corresponding to those described in the literature.[8]

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.33 (s, 4H), 2.45 (s, 3H).

^{19}F NMR (377 MHz, $CDCl_3$) δ -143.32 (dd, J_F = 23.0, 8.3 Hz, 2F), -155.17 (t, J_F = 21.1 Hz, 1F), -162.44--162.56 (m, 2F)

2,3,4,5,6-pentafluoro-4'-nitro-1,1'-biphenyl (3n)

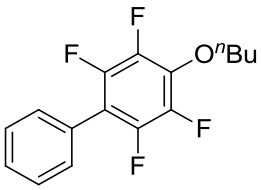


The product (29 mg, 20% yield) as a white solid was purified with silica gel chromatography (petroleum ether). The analytical data is corresponding to those described in the literature.[8]

^{1}H NMR (400 MHz, $CDCl_3$) δ 8.38 (d, *J* = 8.9 Hz, 2H), 7.66 (d, *J* = 8.7 Hz, 2H).

^{19}F NMR (377 MHz, $CDCl_3$) δ -142.53 (dd, J_F = 22.7, 8.2 Hz, 2F), -152.51 (t, J_F = 20.9 Hz, 1F), -160.82 (td, J_F = 21.3, 7.2 Hz, 2F).

4-butoxy-2,3,5,6-tetrafluoro-1,1'-biphenyl (6a)



The product (136 mg, 91% yield) as a white solid was purified with silica gel chromatography (petroleum ether).

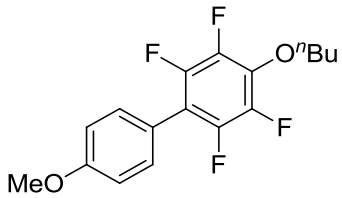
^{1}H NMR (400 MHz, $CDCl_3$) δ 7.52-7.45 (m, 5H), 4.30 (t, *J* = 6.5 Hz, 2H), 1.86-1.78 (m, 2H), 1.56-1.50 (m, 2H), 1.02 (t, *J* = 7.4 Hz, 3H).

^{13}C NMR (100 MHz, $CDCl_3$) δ 145.6-145.4 (m), 143.2-142.6 (m), 140.4-140.2 (m), 137.0-136.7 (m), 130.3-130.2 (m), 128.8, 128.6, 127.4, 114.2 (t, J_F = 17.2 Hz), 75.1, 32.0, 18.8, 13.7.

^{19}F NMR (377 MHz, $CDCl_3$) δ -145.41 (dd, J_F = 22.2, 8.8 Hz, 2F), -157.54 (dd, J_F = 22.1, 8.8 Hz, 2F).

HRMS-EI (*m/z*): $[M]^+$ calcd for $C_{16}H_{14}F_4O$, 298.0981; found, 2298.0979.

4-butoxy-2,3,5,6-tetrafluoro-4'-methoxy-1,1'-biphenyl (6b)



The product (148 mg, 90% yield) as a white solid was purified with silica gel chromatography (petroleum ether).

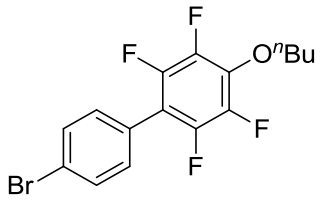
^{1}H NMR (400 MHz, $CDCl_3$) δ 7.41-7.38 (m, 2H), 7.04-7.00 (m, 2H), 4.27 (t, *J* = 6.5 Hz, 2H), 3.88 (s, 3H), 1.8-1.77 (m, 2H), 1.57-1.49 (dt, *J* = 14.7, 7.5 Hz, 2H), 1.01 (t, *J* = 7.4 Hz, 3H).

^{13}C NMR (100 MHz, $CDCl_3$) δ 160.0, 145.6-145.4 (m), 143.2-142.6 (m), 140.5-140.2 (m), 136.6-136.2 (m), 131.4, 119.4, 114.0, 75.1 (t, J_F = 11.7 Hz), 55.2, 32.0, 18.8, 13.7.

^{19}F NMR (377 MHz, $CDCl_3$) δ -145.71 (dd, J_F = 22.3, 8.7 Hz, 2F), -157.73 (dd, J_F = 22.4, 8.8 Hz, 2F).

HRMS-EI (*m/z*): $[M]^+$ calcd for $C_{17}H_{16}F_4O_2$, 328.1086; found, 328.1084.

4'-bromo-4-butoxy-2,3,5,6-tetrafluoro-1,1'-biphenyl (6c)



The product (158 mg, 84% yield) as a white solid was purified with silica gel chromatography (petroleum ether).

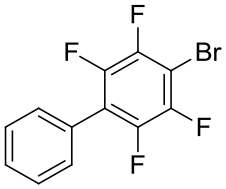
^{1}H NMR (400 MHz, $CDCl_3$) δ 7.64-7.61 (m, 2H), 7.34-7.32 (m, 2H), 4.29 (t, *J* = 6.5 Hz, 2H), 1.85-1.77 (m, 2H), 1.58-1.50 (m, 2H), 1.01 (t, *J* = 7.4 Hz, 3H).

^{13}C NMR (100 MHz, $CDCl_3$) δ 145.5-145.2 (m), 143.0-142.6 (m), 140.6-140.2 (m), 137.3-137.0 (m), 131.9, 131.8-131.7 (m), 126.3, 123.2, 112.9 (t, J_F = 16.9 Hz), 75.1, 31.9, 18.8, 13.7.

^{19}F NMR (377 MHz, $CDCl_3$) δ -145.30 (dd, J_F = 22.2, 8.8 Hz, 2F), -157.16 (dd, J_F = 22.0, 8.7 Hz, 2F).

HRMS-EI (*m/z*): $[M]^+$ calcd for $C_{16}H_{13}BrF_4O$, 376.0086; found, 376.0087.

4-bromo-2,3,5,6-tetrafluoro-1,1'-biphenyl (6d)

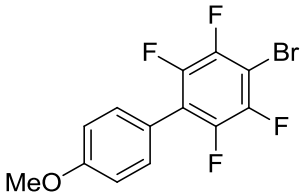


The product (127 mg, 83% yield) as a white solid was purified with silica gel chromatography (petroleum ether). The analytical data is corresponding to those described in the literature.[12]

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.58-7.44 (m, 5H).

^{19}F NMR (377 MHz, $CDCl_3$) δ -133.56 (td, J_F = 12.5, 4.2 Hz, 2F), -142.09 (td, J_F = 12.5, 4.0 Hz, 2F).

4-bromo-2,3,5,6-tetrafluoro-4'-methoxy-1,1'-biphenyl (6e)

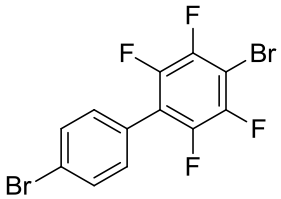


The product (126 mg, 75% yield) as a white solid was purified with silica gel chromatography (petroleum ether). The analytical data is corresponding to those described in the literature.[10]

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.42 (d, J = 8.8 Hz, 2H), 7.04 (dd, J = 6.9, 2.0 Hz, 2H), 3.89 (s, 3H).

^{19}F NMR (377 MHz, $CDCl_3$) δ -133.90 (td, J_F = 12.5, 4.2 Hz, 2F), -142.37 - -142.54 (m, 2F).

4,4'-dibromo-2,3,5,6-tetrafluoro-1,1'-biphenyl (6f)



The product (167 mg, 88% yield) as a white solid was purified with silica gel chromatography (petroleum ether).

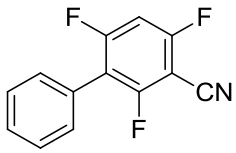
^{1}H NMR (400 MHz, $CDCl_3$) δ 7.66 (dd, J = 6.7, 1.8 Hz, 2H), 7.35 (d, J = 8.4 Hz, 2H).

^{13}C NMR (100 MHz, $CDCl_3$) δ 146.6-146.3 (m), 145.2-145.0 (m), 144.1-143.9 (m), 142.7-142.5 (m), 138.8, 132.0, 131.6-131.5 (m), 128.5, 125.8, 124.0, 122.0, 119.1 (t, J_F = 16.6 Hz), 99.4-99.0 (m).

^{19}F NMR (377 MHz, $CDCl_3$) δ -133.04 (td, J_F = 12.5, 3.8 Hz, 2F), -141.99 (td, J_F = 11.9, 3.2 Hz, 2F).

HRMS-EI (*m/z*): $[M]^+$ calcd for $C_{12}H_4Br_2F_4$, 381.8616; found, 381.8611.

2,4,6-trifluoro-[1,1'-biphenyl]-3-carbonitrile (6g)



The product (52 mg, 45% yield) as a white solid was purified with silica gel chromatography (petroleum ether).

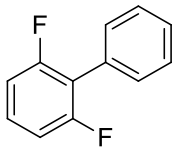
^{1}H NMR (400 MHz, $CDCl_3$) δ 7.52 (q, *J* = 5.7 Hz, 3H), 7.42 (d, *J* = 6.7 Hz, 2H), 6.97 (td, *J* = 9.0, 1.9 Hz, 1H).

^{13}C NMR (100 MHz, $CDCl_3$) δ 164.5-164.3 (m), 163.8-163.6 (m), 162.5-162.3 (m), 161.9-161.7 (m), 161.2-161.0 (m), 159.9-159.7 (m), 139.3, 130.0, 129.4, 128.8, 126.0, 116.9-116.5 (m), 114.1, 108.7 (d, J_F = 9.2 Hz), 102.1-101.5 (m), 90.0-89.5 (m).

^{19}F NMR (377 MHz, $CDCl_3$) δ -98.91 (d, J_F = 10.3 Hz, 1F), -102.60 (t, J_F = 9.2 Hz, 1F), -103.78 (d, J_F = 10.9 Hz, 1F).

HRMS-EI (*m/z*): $[M]^+$ calcd for $C_{13}H_6F_3N$, 233.0452; found, 233.0450.

2,6-difluoro-1,1'-biphenyl (6h)



Following the general procedure, but using petroleum ether as the eluant afforded an inseperable mixture of 2,6-difluoro-1,1'-biphenyl and 1,1'-biphenyl, according to the GC-MS and ^{1}H NMR spectra, the ratio of **6h** : **1,1'-biphenyl** is 1 : 2 and the overall yield is 33%.

For **6h**: The analytical data is corresponding to those described in the literature.[11]

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.52-7.50 (m, 5H), 7.34-7.29 (m, 1H), 7.05-7.00 (m, 2H).

^{19}F NMR (377 MHz, $CDCl_3$) δ -114.53 (t, J_F = 6.6 Hz, 2F).

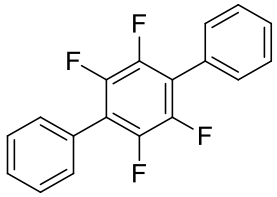
GC-MS (*m/z*): 190.

For **1,1'-biphenyl**: The analytical data is corresponding to those described in the literature.[13]

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.66-7.64 (m, 8H), 7.50-7.46 (m, 8H), 7.41-7.37 (m, 4H).

GC-MS (*m/z*): 154.

2',3',5',6'-tetrafluoro-1,1':4',1''-terphenyl (6i)



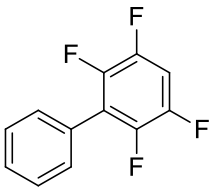
The product (27 mg, 18% yield) as a white solid was purified with silica gel chromatography (petroleum ether). The analytical data is corresponding to those described in the literature.[11]

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.56-7.47 (m, 10H).

^{19}F NMR (377 MHz, $CDCl_3$) δ -144.4 (s, 4F).

MS-EI (*m/z*): $[M]^+$ calcd for $C_{18}H_{10}F_4$, 302.07; found, 302.1.

2,3,5,6-tetrafluoro-1,1'-biphenyl (6j)

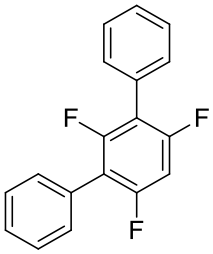


The product (33 mg, 29% yield) as a white solid was purified with silica gel chromatography (petroleum ether). The analytical data is corresponding to those described in the literature.[11]

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.54-7.45 (m, 5H), 7.13-7.05 (m, 1H).

^{19}F NMR (377 MHz, $CDCl_3$) δ -139.1--139.2 (m, 2F), -143.9--140.0 (m, 2F).

2',4',6'-trifluoro-1,1':3',1''-terphenyl (6k)

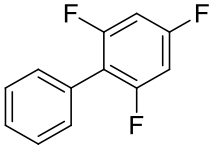


The product (24 mg, 17% yield) as a white solid was purified with silica gel chromatography (petroleum ether). The analytical data is corresponding to those described in the literature.[11]

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.51-7.43 (m, 10H), 6.94-6.88 (m, 1H).

^{19}F NMR (377 MHz, $CDCl_3$) δ -112.9--113.0 (m, 2F), -115.0 (t, J_F = 6.4 Hz, 2F).

2,4,6-trifluoro-1,1'-biphenyl (6l)

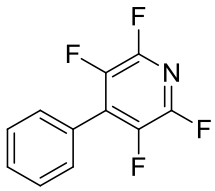


The product (27 mg, 26% yield) as a white solid was purified with silica gel chromatography (petroleum ether). The analytical data is corresponding to those described in the literature.[11]

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.50-7.40 (m, 5H), 6.82-6.77 (m, 2H).

^{19}F NMR (377 MHz, $CDCl_3$) δ -109.0--109.1 (m, 1F), -111.3 (t, J_F = 6.4 Hz, 2F).

2,3,5,6-tetrafluoro-4-phenylpyridine (6m)

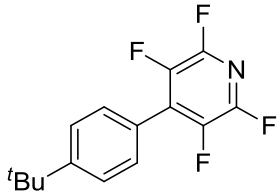


The product (91 mg, 80% yield) as a white solid was purified with silica gel chromatography (petroleum ether). The analytical data is corresponding to those described in the literature.[11]

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.56 (s, 5H).

^{19}F NMR (377 MHz, $CDCl_3$) δ -90.74 (td, J_F = 29.3, 13.8 Hz, 2F), -145.13 (td, J_F = 29.2, 13.8 Hz, 2F).

4-(4-(tert-butyl)phenyl)-2,3,5,6-tetrafluoropyridine (6n)



The product (88 mg, 62% yield) as a white solid was purified with silica gel chromatography (petroleum ether).

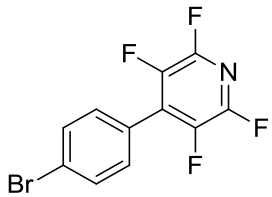
^{1}H NMR (400 MHz, $CDCl_3$) δ 7.62-7.55 (m, 2H), 7.54-7.47 (m, 2H), 1.40 (s, 9H).

^{13}C NMR (100 MHz, $CDCl_3$) δ 154.0, 145.4-145.1 (m), 143.0-142.6 (m), 140.7-140.4 (m), 138.2-137.8 (m), 133.6-133.2 (m), 129.6-129.5 (m), 125.9, 123.0, 35.0, 31.1.

^{19}F NMR (377 MHz, $CDCl_3$) δ -91.07 (td, J_F = 29.3, 13.8 Hz, 2F), -145.31 (qd, J_F = 14.5, 1.2 Hz, 2F).

HRMS-EI (*m/z*): $[M]^+$ calcd for $C_{15}H_{13}F_4N$, 283.0984; found, 283.0992.

4-(4-bromophenyl)-2,3,5,6-tetrafluoropyridine (6o)



The product (107 mg, 70% yield) as a white solid was purified with silica gel chromatography (petroleum ether).

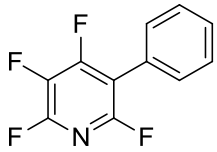
^{1}H NMR (400 MHz, $CDCl_3$) δ 7.75-7.67 (m, 2H), 7.43 (dd, J = 7.1, 1.4 Hz, 2H).

^{13}C NMR (100 MHz, $CDCl_3$) δ 145.4-145.0 (m), 143.0-142.6 (m), 140.5-140.1 (m), 138.0-137.6 (m), 132.3, 131.3 (t, J = 2.5 Hz), 125.3, 124.7.

^{19}F NMR (377 MHz, $CDCl_3$) δ -90.14 (td, J_F = 29.1, 13.7 Hz, 2F), -144.91 (td, J_F = 29.2, 13.7 Hz, 2F).

HRMS-EI (*m/z*): $[M]^+$ calcd for $C_{11}H_4BrF_4N$, 304.9463; found, 304.9461.

2,3,4,6-tetrafluoro-5-phenylpyridine (6p)



The product (92 mg, 82% yield) as a white solid was purified with silica gel chromatography (petroleum ether).

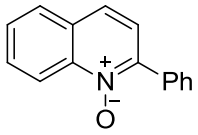
^{1}H NMR (300 MHz, $CDCl_3$) δ 7.54-7.50 (m, 5H).

^{13}C NMR (75 MHz, $CDCl_3$) δ 159.1-158.8 (m), 155.5-155.3 (m), 153.-153.4 (m), 150.3-149.7 (m), 146.8-146.3 (m), 135.1-134.5(m), 131.1-131.1 (m), 129.8, 129.5, 128.8, 125.7 (d, J_F = 4.1 Hz).

^{19}F NMR (282 MHz, $CDCl_3$) δ -72.11 - -72.57 (m, 1F), -86.01 (dd, *J* = 36.7, 17.8 Hz, 1F), -117.45 (dd, *J* = 34.3, 18.8 Hz,1F), -166.79 (dd, *J* = 44.5, 21.9 Hz, 1F).

HRMS-EI (*m/z*): $[M]^+$ calcd for $C_{11}H_5F_4N$, 227.0358; found, 227.0361.

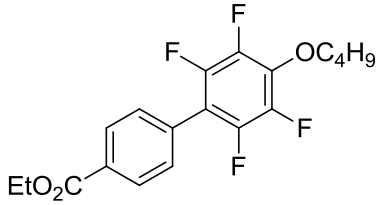
2-phenylquinoline 1-oxide (6q)



The product (50 mg, 45% yield) as a white solid was purified with silica gel chromatography (Petroleum ether /Ethyl ether = 20:1). The analytical data is corresponding to those described in the literature.[14]

^{1}H NMR (400 MHz, $CDCl_3$) δ 8.88 (d, *J* = 8.9 Hz, 1H), 7.99 (dd, *J* = 8.2, 1.3 Hz, 2H), 7.89 (d, *J* = 8.1 Hz, 1H), 7.81 (ddd, *J* = 9.1, 5.4, 1.9 Hz, 2H), 7.70-7.64 (m, 1H), 7.58-7.47 (m, 4H).

ethyl 4'-butoxy-2',3',5',6'-tetrafluoro-[1,1'-biphenyl]-4-carboxylate (11)



The product (251 mg, 68% yield) as a white solid was purified with silica gel chromatography (Petroleum ether /Ethyl ether = 20:1).

^{1}H NMR (400 MHz, $CDCl_3$) δ 8.16 (d, *J* = 8.6 Hz, 2H), 7.54 (dd, *J* = 7.2, 1.3 Hz, 2H), 4.43 (q, *J* = 7.1 Hz, 2H), 4.31 (t, *J* = 6.5 Hz, 2H), 1.82 (dt, *J* = 14.6, 6.6 Hz, 2H), 1.60 – 1.50 (m, 2H), 1.43 (t, *J* = 7.1 Hz, 3H), 1.01 (t, *J* = 7.4 Hz, 3H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 165.9, 145.5-145.2 (m), 143.0-142.6 (m), 140.3-140.1 (m), 137.4-137.2

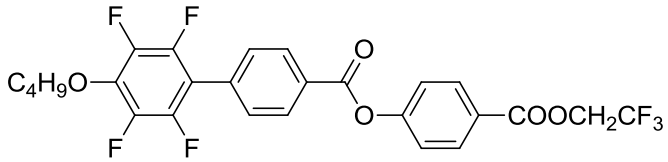
(m), 131.8, 130.7, 130.2, 129.6, 113.0 (t, J = 16.9 Hz), 75.0, 61.1, 31.9, 18.7, 14.2, 13.6.

^{19}F NMR (376 MHz, $CDCl_3$) δ -145.01 (td, J_F = 8.7, 1.1 Hz, 2F), -157.10 (td, J = 8.7, 1.1 Hz, 2F).

HRMS-EI (*m/z*): $[M]^+$ calcd for $C_{19}H_{18}F_4O_3$, 370.1192; found, 370.1190.

4-((2,2,2-trifluoroethoxy)carbonyl)phenyl

4'-butoxy-2',3',5',6'-tetrafluoro-[1,1'-biphenyl]-4-carboxylate (12)



^{1}H NMR (400 MHz, $CDCl_3$) δ 8.34-8.31 (m, 2H), 8.22-8.19 (m, 2H), 7.64 (d, J = 8.4 Hz, 2H), 7.41-7.37 (m, 2H), 4.74 (q, J = 8.4 Hz, 2H), 4.33 (t, J = 6.5 Hz, 2H), 1.83 (dt, J = 14.5, 6.6 Hz, 2H), 1.55 (dt, J = 16.7, 7.5 Hz, 2H), 1.02 (t, J = 7.4 Hz, 3H).

^{13}C NMR (100 MHz, $CDCl_3$) δ 164.1, 164.0, 155.3, 145.6-145.3 (m), 143.0-142.7 (m), 140.4-140.2 (m), 137.8-137.7 (m), 133.2, 131.8, 130.6, 130.4, 129.1, 128.7, 126.1, 124.5, 122.1, 121.7, 112.86-112.52 (m), 75.2-75.1 (m), 61.43, 61.4-60.3 (m), 31.9, 18.8, 13.7.

^{19}F NMR (377 MHz, $CDCl_3$) δ -73.63 (s, 3F), -144.92 (dd, J_F = 22.3, 8.9 Hz, 2F), -156.86 (dd, J_F = 21.3, 8.1 Hz, 2F).

HRMS-EI (*m/z*): $[M]^+$ calcd for $C_{26}H_{19}F_7O_5$, 544.1121; found, 544.1117.

Part 4. References

1. M. Bielawski, Z. Zhu and B. Olofsson, *Adv. Synth. Catal.* **2007**, *349*, 2610.
2. M. Zhu, N. Jalalian and B. Olofsson, *Synlett* **2008**, *4*, 592.
3. L. Kraszkiewicz, and L. Skulski, *Synthesis* **2008**, *15*, 2373.
4. T. B. Petersen, R. Khan and B. Olofsson, *Org. Lett.* **2011**, *12*, 3462.
5. R. J. Phipps,and M. J. Gaunt, *Science* **2009**, *323*, 1593.
6. D. W. Bruce, P. Metrangogo, F. Meyer, T. Pilati, C. Prasang, G. Resnati, G. Terraneo, S. G. Wainwright and A. C. Whitwood, *Chem. Eur. J.* **2010**, *16*, 9511.
7. S. Ahmed, K. James and C. P. Owen, *Bioorg. Med. Chem. Lett.* **2002**, *12*, 2391.
8. R. Shang, Y. Fu, Y. Wang, Q. Xu, H. Z. Yu and L. Liu, *Angew. Chem. Int. Ed.* **2009**, *48*, 9350.
9. R. Shang, Q. Xu, Y. -Y. Jiang, Y. Wang and L. Liu, *Org. Lett.* **2010**, *12*, 1000.
10. F. Chen, Q. -Q. Min and X. Zhang, *J. Org. Chem.* **2012**, *77*, 2992.
11. H. Li, J. Liu, C. -L. Sun, B. -J. Li and Z. -J. Shi, *Org. Lett.* **2011**, *13*, 276.
12. Y. Wei, J. Kan, M. Wang, W. Su and M. Hong, *Org. Lett.* **2009**, *11*, 3346.
13. Z. Du, W. Zhou, F. Wang and J. -X. Wang, *Tetrahedron*, **2011**, *67*, 4914
14. S. C. Cho, S. J. Hwang and S. Chang, *J. Am. Chem. Soc.* **2008**, *130*, 9254.

Part 5. Copies of ^{1}H-NMR, ^{13}C-NMR and ^{19}F-NMR Spectra