Supporting Information

Palladium catalysed deaminative/decarboxylative corsscoupling of organoammonium salts with carboxylic acids

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1. General Information

The reactions were carried out in Schlenk tubes of 25 mL under N₂ atmosphere. For reactions that require heating, heating mantle was used as the heat source. Organoammonium salts 1 were prepared according to the reported literatures.¹ All solvents were purified according to standard operation procedures. All solvents and reagents were purchased from Tansoole, Meryer, Heowns, Energy Chemical, Alfa Aesar, and Aladdin. Column chromatography was performed using Silica Gel 60 (300-400 mesh). The reactions were monitored by GC and GC-MS, GC-MS results were recorded on GC-MS QP2010, and GC analysis was performed on GC 2014. The ¹H, ¹³C NMR spectra were recorded on a Bruker ADVANCE III spectrometer at 400 MHz, 100 MHz respectively, and chemical shifts were reported in parts per million (ppm). The electron ionization (EI) method was used as the ionization method for the HRMS measurement, and the mass analyzer type is TOF for EI.

2. Experimental Procedure

2.1 Experimental Procedure I: Reaction of Benzylic Ammonium Salts with Polyfluoroaromatic Carboxylic Acids.

In an oven dried 25 mL Schlenk tube charged with 1 (0.2 mmol), 2a (0.3-0.5 mmol), Pd(OAc)₂ (5 mol%), dppb (5 mol%), 'BuOK (2.0 equiv) after charging N₂ for three times, DME (0.5 mL) were added. The reaction mixture was reacted at 130 °C for 3 h. The experiment was conducted in two sets, and the reaction mixtures of two sets were combined and concentrated after completion of the reaction, The desired product was isolated by column chromatography over silica gel (300-400 mesh) using petroleum ether/ethyl acetate (PE/EA) as eluent.

2.2 Experimental Procedure II: Reaction of Heterocyclic Fused Ammonium Salts with Polyfluoroaromatic Carboxylic Acids.

In an oven dried 25 mL Schlenk tube charged with 1 (0.2 mmol), 2a (0.3 mmol), Pd(OAc)₂ (5 mol%), xantphos (5 mol%), 'BuOK (1.5 equiv) after charging N₂ for three times, DME (0.5 mL) were added. The reaction mixture was reacted at 130 °C for 3 h. The experiment was conducted in two sets, and the reaction mixtures of two sets were combined and concentrated after completion of the reaction, The desired product was isolated by column chromatography over silica gel (300-400 mesh) using petroleum ether/ethyl acetate (PE/EA) as eluent.

2.3 Experimental Procedure III: Reaction of Benzylic Ammonium Salts 1k with Phenylpropiolic Acids.

In an oven dried 25 mL Schlenk tube charged with **1k** (0.2 mmol), **2** (0.5 mmol), Pd(OAc)₂ (5 mol%), dppb (5 mol%), 'BuOK (2.0 equiv) after charging N₂ for three times, THF (0.5 mL) were added. The reaction mixture was reacted at 80 °C for 12 h. The experiment was conducted in two sets, and the reaction mixtures of two sets were combined and concentrated after completion of the reaction, The desired product was isolated by column chromatography over silica gel (300-400 mesh) using petroleum ether/ethyl acetate (PE/EA) as eluent.

2.4 Experimental Procedure IV: Reaction of Benzylic Ammonium Salts 1k with Benzyl Carboxylic Acids 2k.

In an oven dried 25 mL Schlenk tube charged with **1k** (0.2 mmol), **2k** (0.5 mmol), Pd(OAc)₂ (5 mol%), dppb (5 mol%), 'BuOK (2.0 equiv) after charging N₂ for three times, DME (0.5 mL) were added. The reaction mixture was reacted at 130 °C for 12 h. The experiment was conducted in two sets, and the reaction mixtures of two sets were combined and concentrated after completion of the reaction, The desired product **3zb** was isolated by column chromatography over silica gel (300-400 mesh) using petroleum ether/ethyl acetate (PE/EA) as eluent.

2.5 Gram-Scale Synthesis.

In an oven dried 100 mL Schlenk tube charged with **1a** (5.0 mmol, 1.495 g), **2a** (6.0 mmol, 1.5 equiv, 1.59 g), Pd(OAc)₂ (5 mol%, 0.055 g), dppb (5 mol%, 0.1075 g), 'BuOK (2.0 equiv, 1.1225 g), after charging N₂ for three times, DME (12.5 mL) were added. The reaction mixture

was reacted at 130° C for 3 h. The reaction mixtures were concentrated after completion of the reaction. The desired product was isolated by column chromatography over silica gel (300-400 mesh) using petroleum ether/ethyl acetate (PE/EA) as eluent to give the analytically pure product **3a** in 82% isolated yield (1.0573 g).

3. Characterization Data for the Products

1-benzyl-2,3,4,5,6-pentafluorobenzene (3a)

The title compound was prepared according to the Experimental Procedure I, and purified by column chromatography on silica gel with PE to afford a white solid in 86% yield (88.4 mg). 1 H NMR (400 MHz, CDCl₃) δ 7.31 - 7.28 (m, 2H), 7.23 (d, J = 8.0 Hz, 3H), 4.02 (s, 2H). 13 C { 1 H} NMR (100 MHz, CDCl₃) δ 145.0 (dm, J_{C-F} = 245 Hz), 139.9 (dm, J_{C-F} = 251 Hz), 137.6 (dm, J_{C-F} = 250 Hz), 137.4, 128.8, 128.3, 127.0, 114.5 (td, J_{C-F} = 19.0, 4.0 Hz), 28.1. 19 F NMR (376 MHz, CDCl₃) δ -143.21 - -143.30 (m, 2F), -157.06 (t, J = 21.0 Hz, 1F), -162.24 - -162.41 (m, 2F). This compound is known.²

1-(4-(tert-butyl)benzyl)-2,3,4,5,6-pentafluorobenzene (3b)

The title compound was prepared according to the Experimental Procedure I, and purified by column chromatography on silica gel with PE to afford colorless oil in 91% yield (113.9 mg). 1 H NMR (400 MHz, CDCl₃) δ 7.31 (d, J = 8.0 Hz, 2H), 7.17 (d, J = 8.0 Hz, 2H), 3.98 (s, 2H), 1.28 (s, 9H). 13 C { 1 H} NMR (100 MHz, CDCl₃) δ 149.9, 145.0 (dm, J_{C-F} = 245 Hz), 139.9 (dm, J_{C-F} = 250 Hz), 137.6 (dm, J_{C-F} = 250 Hz), 134.4, 128.0, 125.7, 114.7 (td, J_{C-F} = 19.0, 4.0 Hz), 34.4, 31.3, 27.6. 19 F NMR (376 MHz, CDCl₃) δ -143.34 (dd, J = 23.0, 9.0 Hz, 2F), -157.37 – -157.50 (m, 1F), -162.43 – -162.57 (m, 2F). HRMS (APCI) m/z: [M-H]⁻ calcd. for $C_{17}H_{15}F_5$: 313.1021; found: 313.1021.

1,2,3,4,5-pentafluoro-6-(4-methoxybenzyl)benzene (3c)

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The title compound was prepared according to the Experimental Procedure I, and purified by column chromatography on silica gel with PE to afford colorless oil in 90% yield (103.5 mg). 1 H NMR (400 MHz, CDCl₃) δ 7.15 (d, J = 8.0 Hz, 2H), 6.81 (d, J = 8.0 Hz, 2H), 3.94 (s, 2H), 3.75 (s, 3H). 13 C { 1 H} NMR (100 MHz, CDCl₃) δ 158.6, 144.9 (dm, J_{C-F} = 244 Hz), 139.8 (dm, J_{C-F} = 245 Hz), 137.5 (dm, J_{C-F} = 250 Hz), 129.5, 129.4, 115.1 – 114.7 (m), 114.1, 55.1, 27.2. 19 F NMR (376 MHz, CDCl₃) δ -143.67 – 143.77 (m, 2F), -157.45 – -157.60 (m, 1F), -162.46 – -162.63 (m, 2F). This compound is known.²

1,2,3,4,5-pentafluoro-6-(4-methylbenzyl)benzene (3d)

The title compound was prepared according to the Experimental Procedure I, and purified by column chromatography on silica gel with PE to afford colorless oil in 78% yield (84.7 mg). 1 H NMR (400 MHz, CDCl₃) δ 7.10 (q, J = 8.0 Hz, 4H), 3.96 (s, 2H), 2.30 (s, 3H). 13 C { 1 H} NMR (100 MHz, CDCl₃) δ 144.9 (dm, J_{C-F} = 245 Hz), 139.8 (dm, J_{C-F} = 250 Hz), 137.5 (dm, J_{C-F} = 250 Hz), 136.7, 134.4, 129.5, 128.2, 114.7 (td, J_{C-F} = 19.0, 4.0 Hz), 27.7, 20.9. 19 F NMR (376 MHz, CDCl₃) δ -143.45 (dd, J = 23.0, 9.0 Hz, 2F), -157.41 (t, J = 21.0 Hz, 1F), -162.44 - -162.58 (m, 2F). This compound is known.²

1,2,3,4,5-pentafluoro-6-(3-methylbenzyl)benzene (3e)

The title compound was prepared according to the Experimental Procedure I, and purified by column chromatography on silica gel with PE to afford colorless oil in 82% yield (92.1 mg). ¹H

NMR (400 MHz, CDCl3) δ 7.16 (t, J = 8.0 Hz, 1H), 7.03 (d, J = 8.0 Hz, 3H), 3.97 (s, 2H), 2.31 (s, 3H). ¹³C {¹H} NMR (100 MHz, CDCl₃) δ 145.0 (dm, J_{C-F} = 244 Hz), 139.9 (dm, J_{C-F} = 250 Hz), 137.6 (dm, J_{C-F} = 250 Hz), 138.5, 137.4, 129.1, 128.7, 127.7, 125.3, 114.6 (td, J_{C-F} = 19.0, 4.0 Hz), 28.0, 21.3.¹⁹F NMR (376 MHz, CDCl₃) δ -143.28 (dd, J = 24.0, 10.0 Hz, 2F), -157.24 - -157.38 (m, 1F), -162.40 - -162.56 (m, 2F). This compound is known.³

1,2,3,4,5-pentafluoro-6-(2-methylbenzyl)benzene (3f)

The title compound was prepared according to the Experimental Procedure I, and purified by column chromatography on silica gel with PE to afford colorless oil in 76% yield (82.9 mg). 1 H NMR (400 MHz, CDCl₃) δ 7.18 – 7.08 (m, 3H), 6.94 (d, J = 8.0 Hz, 1H), 4.00 (s, 2H), 2.38 (s, 3H). 13 C { 1 H} NMR (100 MHz, CDCl₃) δ 145.3 (dm, J_{C-F} = 245 Hz), 140.0 (dm, J_{C-F} = 251 Hz), 137.6 (dm, J_{C-F} = 251 Hz), 136.0, 135.2, 130.4, 128.1, 127.0, 126.2, 113.7 (td, J_{C-F} = 19.0, 4.0 Hz), 25.5, 19.5. 19 F NMR (376 MHz, CDCl₃) δ -142.29 (dd, J = 23.0, 9.0 Hz, 2F), -156.89 (t, J = 21.0 Hz, 1F), -162.44 (td, J = 23.0, 9.0 Hz, 2F). This compound is known.

5-((perfluorophenyl)methyl)benzo[d][1,3]dioxole (3g)

The title compound was prepared according to the Experimental Procedure I, and purified by column chromatography on silica gel with PE to afford colorless oil in 93% yield (112.3 mg). 1 H NMR (400 MHz, CDCl₃) δ 6.71 (t, J = 8.0 Hz, 3H), 5.92 (s, 2H), 3.92 (s, 2H). 13 C { 1 H} NMR (100 MHz, CDCl₃) δ 147.9, 146.5, 144.9 (dm, J_{C-F} = 245 Hz), 139.9 (dm, J_{C-F} = 251 Hz), 137.5 (dm, J_{C-F} = 250 Hz), 131.1, 121.4, 114.6 (td, J = 19.0, 4.0 Hz), 108.8, 108.4, 101.1, 27.7. 19 F NMR (376 MHz, CDCl₃) δ -143.59 - -144.70 (m, 2F), -157.15 - -157.33 (m, 1F), -162.34 - -162.46 (m, 2F). This compound is known.⁴

4-((perfluorophenyl)methyl)-1,1'-biphenyl (3h)

The title compound was prepared according to the Experimental Procedure I, and purified by column chromatography on silica gel with PE to afford a white solid in 61% yield (81.8 mg). 1 H NMR (400 MHz, CDCl₃) 7.54 – 7.49 (m, 4H), 7.40 (t, J = 8.0 Hz, 2H), 7.33 – 7.28 (m, 3H), 4.03 (s, 2H). 13 C { 1 H} NMR (100 MHz, CDCl₃) 145.0 (dm, $J_{C-F} = 245$ Hz), 140.0 (dm, $J_{C-F} = 250$ Hz), 140.6, 140.0, 137.6 (dm, $J_{C-F} = 251$ Hz), 136.4, 128.8, 127.5, 127.3, 127.0, 114.3 (td, $J_{C-F} = 19.0$, 4.0 Hz), 27.8. 19 F NMR (376 MHz, CDCl₃) δ -143.21 (dd, J = 23.0, 9.0 Hz, 2F), -156.93 (t, J = 21.0 Hz, 1F), -162.19 (td, J = 23.0, 9.0 Hz, 2F). This compound is known.

methyl 4'-((perfluorophenyl)methyl)-[1,1'-biphenyl]-2-carboxylate (3i)

The title compound was prepared according to the Experimental Procedure I, and purified by column chromatography on silica gel with PE/EA = 20:1(v/v) to afford colorless oil in 72% yield (113.1 mg). 1 H NMR (400 MHz, CDCl₃) δ 7.81 (dd, J = 8.0, 1.0 Hz, 1H), 7.49 (td, J = 8.0, 1.0 Hz, 1H), 7.38 (td, J = 8.0, 1.0 Hz, 1H), 7.31 (dd, J = 8.0, 1.0 Hz, 1H), 7.28 – 7.23 (m, 4H), 4.06 (s, 2H), 3.64 (s, 3H). 13 C { 1 H} NMR (100 MHz, CDCl₃) δ 168.8, 145.0 (dm, J_{C-F} = 244 Hz), 142.0, 139.9 (dm, J_{C-F} = 251 Hz), 140.0, 137.5 (dm, J_{C-F} = 249 Hz), 136.3, 131.3, 130.7, 130.6, 129.8, 128.7, 128.0, 127.2, 114.3 (td, J_{C-F} = 19.0, 3.0 Hz), 51.9, 27.8. 19 F NMR (376 MHz, CDCl₃) δ - 143.17 (dd, J = 23.0, 9.0 Hz, 2F), -156.92 – -157.04 (m, 1F), -162.22 – -162.37 (m, 2F). HRMS (EI) m/z: [M+H] $^{+}$ calcd. for C₂₁H₁₃F₅O₂: 393.0908 ; found: 393.0905.

1-((perfluorophenyl)methyl)naphthalene (3j)

The title compound was prepared according to the Experimental Procedure I, and purified by column chromatography on silica gel with PE to afford a white solid in 78% yield (95.5 mg). 1 H NMR (400 MHz, CDCl₃) δ 8.09 (d, J = 8.0 Hz, 1H), 7.85 (d, J = 8.0 Hz, 1H), 7.74 (d, J = 8.0 Hz, 1H), 7.58 – 7.53 (m, 1H), 7.51 – 7.47 (m, 1H), 7.35 (t, J = 8.0 Hz, 1H), 7.11 (d, J = 8.0 Hz, 1H), 4.45 (s, 2H). 13 C { 1 H} NMR (100 MHz, CDCl₃) δ 145.4 (dm, J_{C-F} = 245 Hz), 140.1 (dm, J_{C-F} = 251 Hz), 137.6 (dm, J_{C-F} = 251 Hz), 133.8, 132.7, 131.5, 128.9, 127.8, 126.4, 125.8, 125.7, 125.4, 122.9, 113.4 (td, J_{C-F} = 18.0, 3.0 Hz), 25.3. 19 F NMR (376 MHz, CDCl₃) δ -141.85 – -141.94 (m, 2F), -156.50 (t, J = 21.0 Hz, 1F), -162.13 – -162.29 (m, 2F). This compound is known.²

methyl(4-((perfluorophenyl)methyl)phenyl)sulfane (3k)

The title compound was prepared according to the Experimental Procedure II, and purified by column chromatography on silica gel with PE to afford a white solid in 59% yield (72.2 mg). mp 44-45 °C. 1 H NMR (400 MHz, CDCl₃) δ 7.19 - 7.14 (m, 4H), 3.97 (s, 2H), 2.45 (s, 3H). 13 C { 1 H} NMR (100 MHz, CDCl₃) δ 144.9 (dm, J_{C-F} = 244 Hz), 139.9 (dm, J_{C-F} = 251 Hz), 137.5 (dm, J_{C-F} = 251 Hz), 137.2, 134.3, 128.8, 127.1, 114.3 (td, J_{C-F} = 19.0, 4.0 Hz), 27.6, 15.9. 19 F NMR (376 MHz, CDCl₃) δ -143.33 - -143.42 (m, 2F), -156.97 (t, J = 21.0 Hz, 1F), -162.17 - -162.32 (m, 2F). HRMS (APCI) m/z: [M-H]⁻ calcd. for $C_{14}H_9F_5S$: 303.0272; found: 303.0272.

1,2,3,4,5-pentafluoro-6-(4-fluorobenzyl)benzene (3l)

The title compound was prepared according to the Experimental Procedure I, and purified by column chromatography on silica gel with PE to afford colorless oil in 75% yield (83.1 mg). 1 H NMR (400 MHz, CDCl₃) δ 7.22 - 7.18 (m, 2H), 6.97 (t, J = 8.0 Hz, 2H), 3.99 (s, 2H). 13 C { 1 H} NMR (100 MHz, CDCl₃) δ 161.8 (d, J_{C-F} = 244 Hz), 144.9 (dm, J_{C-F} = 244 Hz), 140.0 (dm, J_{C-F} = 251 Hz), 137.6 (dm, J_{C-F} = 251 Hz), 133.1 (d, J_{C-F} = 1.0 Hz), 129.9 (d, J_{C-F} = 8.0 Hz), 115.6 (d, J_{C-F} = 21.0 Hz), 114.3 (td, J_{C-F} = 19.0, 3.0 Hz), 27.3. 19 F NMR (376 MHz, CDCl₃) δ -115.71 (t, J = 3.0 Hz, 1F), -143.53 - -143.61 (m, 2F), -156.75 - -156.89 (m, 1F), -161.13 - -162.28 (m, 2F). This compound is known.⁴

1-(4-chlorobenzyl)-2,3,4,5,6-pentafluorobenzene (3m)

The title compound was prepared according to the Experimental Procedure I, and purified by column chromatography on silica gel with PE to afford colorless oil in 62% yield (72.5 mg). 1 H NMR (400 MHz, CDCl₃) δ 7.26 (d, J = 8.0 Hz, 2H), 7.17 (d, J = 8.0 Hz, 2H), 3.98 (s, 2H). 13 C { 1 H} NMR (100 MHz, CDCl₃) δ 144.9 (dm, J_{C-F} = 244 Hz), 140.1 (dm, J_{C-F} = 251 Hz), 137.6 (dm, J_{C-F} = 250 Hz), 135.8, 132.9, 129.7, 128.9, 113.9 (td, J_{C-F} = 19.0, 4.0 Hz), 27.5. 19 F NMR (376 MHz, CDCl₃) δ -143.28 - -143.36 (m, 2F), -156.48 (t, J = 21.0 Hz, 1F), -161.92 - -162.07 (m, 2F). This compound is known.⁴

1-(2-chlorobenzyl)-2,3,4,5,6-pentafluorobenzene (3n)

The title compound was prepared according to the Experimental Procedure I, and purified by

column chromatography on silica gel with PE to afford colorless oil in 66% yield (76.7 mg). 1 H NMR (400 MHz, CDCl₃) δ 7.39 – 7.36 (m, 1H), 7.22 – 7.15 (m, 2H), 7.05 – 7.03 (m, 1H), 4.15 (s, 2H). 13 C { 1 H} NMR (100 MHz, CDCl₃) δ 145.4 (dm, J_{C-F} = 246 Hz), 140.2 (dm, J_{C-F} = 251 Hz), 137.6 (dm, J_{C-F} = 250 Hz), 134.7, 133.9, 129.7, 128.4, 127.0, 112.6 (td, J_{C-F} = 18.0, 4.0 Hz), 26.0. 19 F NMR (376 MHz, CDCl₃) δ -141.67 (dd, J = 23.0, 9.0 Hz, 2F), -156.17 – -156.29 (m, 1F), -162.23 – -162.38 (m, 2F). This compound is known.²

methyl 4-((perfluorophenyl)methyl)benzoate (30)

The title compound was prepared according to the Experimental Procedure I, and purified by column chromatography on silica gel with PE to afford a white solid in 39% yield (48.8 mg). 1 H NMR (400 MHz, CDCl₃) δ 7.97 (d, J = 8.0 Hz, 2H), 7.30 (d, J = 8.0 Hz, 2H), 4.07 (s, 2H), 3.90 (s, 3H). 13 C { 1 H} NMR (100 MHz, CDCl₃) δ 166.7, 145.0 (dm, J_{C-F} = 245 Hz), 142.5, 140.1 (dm, J_{C-F} = 251 Hz), 137.6 (dm, J_{C-F} = 251 Hz), 130.1, 129.0, 128.3, 113.5 (td, J_{C-F} = 19.0, 4.0 Hz), 52.1, 28.1. 19 F NMR (376 MHz, CDCl₃) δ -143.05 (dd, J = 23.0, 9.0 Hz, 2F), -156.20 (t, J = 21.0 Hz, 1F), -161.91 (td, J = 23.0, 9.0 Hz, 2F). This compound is known.

1,2,3,4,5-pentafluoro-6-(4-(trifluoromethyl)benzyl)benzene (3p)

The title compound was prepared according to the Experimental Procedure I, and purified by column chromatography on silica gel with PE to afford a white solid in 43% yield (55.9 mg). 1 H NMR (400 MHz, CDCl₃) δ 7.56 (d, J = 8.0 Hz, 2H), 7.35 (d, J = 8.0 Hz, 2H), 4.08 (s, 2H). 13 C { 1 H} NMR (100 MHz, CDCl₃) δ 145.0 (dm, J_{C-F} = 245 Hz), 140.2 (dm, J_{C-F} = 252 Hz), 141.4, 137.6 (dm, J_{C-F} = 251 Hz), 129.5 (d, J_{C-F} = 33 Hz), 128.7, 125.8 (q, J_{C-F} = 4.0 Hz), 124.0 (d, J_{C-F} = 270 Hz), 113.4 (td, J_{C-F} = 19.0, 4.0 Hz), 28.0. 19 F NMR (376 MHz, CDCl₃) δ -62.62 (s, 3F), -143.12 (dd, J = 23.0, 9.0 Hz, 2F), -156.00 (t, J = 21.0 Hz, 1F), -161.77 (td, J = 22.0, 9.0 Hz, 2F).

This compound is known.4

2-((perfluorophenyl)methyl)benzo[b]thiophene (3q)

The title compound was prepared according to the Experimental Procedure II, and purified by column chromatography on silica gel with PE to afford a white solid in 55% yield (69.4 mg). mp 87 –88 °C. ¹H NMR (400 MHz, CDCl₃) δ 7.73 (d, J = 8.0 Hz, 1H), 7.66 (d, J = 8.0 Hz, 1H), 7.33 – 7.24 (m, 2H), 7.06 (s, 1H), 4.27 (s, 2H). ¹³C {¹H} NMR (100 MHz, CDCl₃) δ 145.0 (dm, $J_{\text{C-F}}$ = 246 Hz), 140.4 (dm, $J_{\text{C-F}}$ = 252 Hz), 140.1, 139.7, 139.6, 137.6 (dm, $J_{\text{C-F}}$ = 251 Hz), 124.5, 124.2, 123.2, 122.4, 122.2, 113.1 (td, $J_{\text{C-F}}$ = 19.0, 4.0 Hz), 23.3. ¹°F NMR (376 MHz, CDCl₃) δ -143.19 (dd, J = 23.0, 9.0 Hz, 2F), -155.84 (t, J = 21.0 Hz, 1F), -161.67 – -161.82 (m, 2F). HRMS (APCI) m/z: [M-H] calcd. for C₁₅H₇F₅S: 313.0116; found: 313.0116.

2-((perfluorophenyl)methyl)benzofuran (3r)

The title compound was prepared according to the Experimental Procedure II, and purified by column chromatography on silica gel with PE to afford a white solid in 49% yield (58.3 mg). mp 109 - 110 °C. ¹H NMR (400 MHz, CDCl₃) δ Unknown NMR (400 MHz,) δ 7.47 (d, J = 8.0 Hz, 1H), 7.39 (d, J = 8.0 Hz, 1H), 7.24 – 7.16 (m, 2H), 6.45 (s, 1H), 4.17 (s, 2H). ¹³C {¹H} NMR (100 MHz, CDCl₃) δ 154.9, 153.1, 145.3 (dm, $J_{C-F} = 246$ Hz), 140.5 (dm, $J_{C-F} = 252$ Hz), 137.6 (dm, $J_{C-F} = 251$ Hz), 128.3, 124.0, 122.8, 120.6, 111.0, 110.8 (td, $J_{C-F} = 19.0$, 4.0 Hz), 103.7, 21.6. ¹°F NMR (376 MHz, CDCl₃) δ -142.92 (dd, J = 23.0, 10.0 Hz, 2F), -155.69 – -155.81 (m, 1F), -161.93 – -162.08 (m, 2F). HRMS (APCI) m/z: [M-H]- calcd. for C₁₅H₇F₅O: 297.0344; found: 297.0344.

1,2,4,5-tetrafluoro-3-(4-methoxybenzyl)benzene (3s)

The title compound was prepared according to the Experimental Procedure I, and purified by column chromatography on silica gel with PE to afford a white solid in 69% yield (74.6 mg). 1 H NMR (400 MHz, CDCl₃) δ 7.18 (d, J = 8.0 Hz, 2H), 6.94 – 6.85 (m, 1H), 6.84 – 6.80 (m, 2H), 3.98 (s, 2H), 3.76 (s, 3H). 13 C { 1 H} NMR (100 MHz, CDCl₃) δ 158.5, 145.9 (dm, J_{C-F} = 246 Hz), 144.6 (dm, J_{C-F} = 243 Hz), 129.7, 129.5, 120.8 (t, J_{C-F} = 18.0 Hz), 114.1, 103.9 (t, J_{C-F} = 22.0 Hz), 55.2, 27.9. 19 F NMR (376 MHz, CDCl₃) δ -139.45 – -139.54 (m, 2F), -144.08 – -144.17 (m, 2F). This compound is known.⁴

methyl 2,3,5,6-tetrafluoro-4-(4-methoxybenzyl)benzoate (3t)

The title compound was prepared according to the Experimental Procedure I, and purified by column chromatography on silica gel with PE/EA = 20:1(v/v) to afford a white solid in 84% yield (110.2 mg). mp 73 –74 °C. ¹H NMR (400 MHz, CDCl₃) δ 7.17 (d, J = 8.0 Hz, 2H), 6.84 – 6.80 (m, 2H), 4.00 (s, 2H), 3.95 (s, 3H), 3.76 (s, 3H). 13 C {¹H} NMR (100 MHz, CDCl₃) δ 160.3, 158.6, 144.7 (dm, J_{C-F} = 251 Hz), 144.5 (dm, J_{C-F} = 255 Hz), 129.5, 128.9, 123.6 (t, J_{C-F} = 18.0 Hz), 114.1, 110.4 (t, J_{C-F} = 16.0 Hz), 55.1, 53.1, 27.9. 19 F NMR (376 MHz, CDCl₃) δ -139.75 – -139.85 (m, 2F), -142.75 – -142.83 (m, 2F). HRMS (APCI) m/z: [M-H] calcd. for $C_{16}H_{12}F_4O_3$: 327.0650; found: 327.0650.

2,3,5,6-tetrafluoro-4-(4-methoxybenzyl)-1,1'-biphenyl (3u)

The title compound was prepared according to the Experimental Procedure I, and purified by column chromatography on silica gel with PE/EA = 20:1(v/v) to afford a white solid in 56% yield (78.2 mg). mp 87 –88 °C. ¹H NMR (400 MHz, CDCl₃) δ 7.49 – 7.41 (m, 5H), 7.26 – 7.23 (m, 2H), 6.87 – 6.83 (m, 2H), 4.04 (s, 2H), 3.78 (s, 3H). ¹³C {¹H} NMR (100 MHz, CDCl₃) δ 158.5, 144.9 (dm, J_{C-F} = 246 Hz), 143.7 (dm, J_{C-F} = 251 Hz), 130.1, 129.9, 129.6, 128.9, 128.5, 127.6, 119.2 – 118.8 (m), 118.7 (d, J_{C-F} = 16.0 Hz), 114.1, 55.2, 27.8. ¹°F NMR (376 MHz, CDCl₃) δ -144.39 – 144.49 (m, 2F), -144.52 – -144.62 (m, 2F). HRMS (APCI) m/z: [M-H] calcd. for C₂₀H₁₄F₄O: 345.0908; found: 345.0908.

1,2,4,5-tetrafluoro-3-(4-methoxybenzyl)-6-methylbenzene (3v)

The title compound was prepared according to the Experimental Procedure I, and purified by column chromatography on silica gel with PE to afford a white solid in 71% yield (80.5 mg). 1 H NMR (400 MHz, CDCl₃) δ 7.18 (d, J = 8.0 Hz, 2H), 6.83 – 6.79 (m, 2H), 3.96 (s, 2H), 3.76 (s, 3H), 2.22 (t, J = 2.0 Hz, 3H). 13 C { 1 H} NMR (100 MHz, CDCl₃) δ 158.4, 144.9 (dm, J_{C-F} = 243 Hz), 144.4 (dm, J_{C-F} = 243 Hz), 130.2, 129.4, 117.0 (t, J_{C-F} = 19.0 Hz), 114.1, 113.9 (t, J_{C-F} = 20.0 Hz), 55.2, 27.6, 7.4. 19 F NMR (376 MHz, CDCl₃) δ -144.36 – -144.46 (m, 2F), -145.77 – -145.86 (m, 2F). This compound is known.⁴

1-methoxy-4-(3-phenylprop-2-yn-1-yl)benzene (3x)

The title compound was prepared according to the Experimental Procedure IV, and purified by column chromatography on silica gel with PE/EA = 20:1(v/v) to afford a yellow oil in 95% yield (84.8 mg). ¹H NMR (400 MHz, CDCl₃) δ 7.45 – 7.43 (m, 2H), 7.33 – 7.28 (m, 5H), 6.90 – 6.86 (m, 2H), 3.80 (s, 3H), 3.77 (s, 2H). ¹³C {¹H} NMR (100 MHz, CDCl₃) δ 158.4, 131.6, 128.9, 128.8, 128.2, 127.7, 123.7, 113.9, 88.0, 82.4, 55.3, 24.9. This compound is known.⁶

4,4'-(prop-1-yne-1,3-diyl)bis(methoxybenzene) (3y)

The title compound was prepared according to the Experimental Procedure IV, and purified by column chromatography on silica gel with PE/EA = 20:1(v/v) to afford a yellow oil in 96% yield (96.7 mg). ¹H NMR (400 MHz, CDCl₃) δ 7.39 – 7.36 (m, 2H), 7.34 – 7.31 (m, 2H), 6.90 – 6.86 (m, 2H), 6.84 – 6.81 (m, 2H), 3.81 (s, 6H), 3.76 (s, 2H). ¹³C {¹H} NMR (100 MHz, CDCl₃) δ 159.2, 158.3, 134.0, 132.9, 128.9, 115.9, 113.9, 113.8, 86.4, 82.1, 55.3, 24.9. This compound is known.⁶

1-fluoro-4-(3-(4-methoxyphenyl)prop-1-yn-1-yl)benzene (3z)

The title compound was prepared according to the Experimental Procedure IV, and purified by column chromatography on silica gel with PE/EA = 20:1(v/v) to afford a yellow oil in 94% yield (90.8 mg). ¹H NMR (400 MHz, CDCl₃) δ 7.42 – 7.39 (m, 2H), 7.31 (d, J = 8.0 Hz, 2H), 7.00 – 6.96 (m, 2H), 6.89 – 6.87 (m, 2H), 3.80 (s, 3H), 3.75 (s, 2H). ¹³C {¹H} NMR (100 MHz, CDCl₃) δ 162.2 (d, J_{C-F} = 247 Hz), 158.4, 133.4 (d, J_{C-F} = 9.0 Hz), 128.9, 128.7, 119.8 (d, J_{C-F} = 4.0 Hz), 115.4 (d, J_{C-F} = 22.0 Hz), 114.0, 87.6, 81.3, 55.3, 24.8. ¹⁹F NMR (376 MHz, CDCl₃) δ -111.9. This compound is known.⁶

(S)-3-(4-methoxyphenyl)-2-phenylpropanenitrile (3zb)

The title compound was prepared according to the Experimental Procedure III, and purified by column chromatography on silica gel with PE/EA = 20:1(v/v) to afford a yellow oil in 78% yield (74.0 mg). ¹H NMR (400 MHz, CDCl₃) δ 7.36 – 7.30 (m, 3H), 7.25 – 7.22 (m, 2H), 7.05 – 7.01 (m, 2H), 6.83 – 6.79 (m, 2H), 3.96 – 3.93 (m, 1H), 3.76 (s, 3H), 3.14 – 3.03 (m, 2H). ¹³C { ¹H} NMR (100 MHz, CDCl₃) δ 158.9, 135.3, 130.4, 129.1, 128.4, 128.2, 127.6, 120.6, 114.0, 55.3,

41.4, 40.1. This compound is known.⁷

1-(perfluorophenyl)naphthalene (3zc)

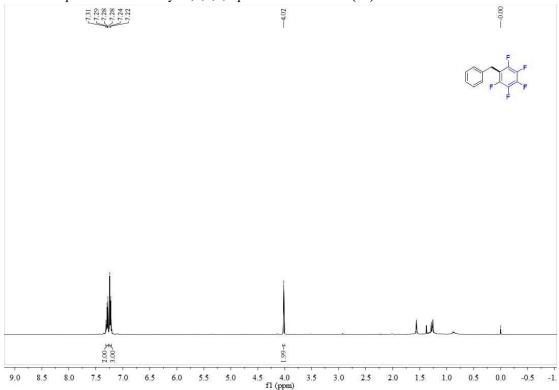
The title compound was prepared according to the Scheme 2c, and purified by column chromatography on silica gel with PE to afford a white solid in 41% yield (48.6 mg). ¹H NMR (400 MHz, CDCl₃) δ 7.99 (d, J = 8.0 Hz, 1H), 7.94 (d, J = 8.0 Hz, 1H), 7.59 – 7.43 (m, 5H). ¹³C { ¹H} NMR (100 MHz, CDCl₃) δ 144.6 (dm, J_{C-F} = 246 Hz), 140.9 (dm, J_{C-F} = 252 Hz), 137.7 (dm, J_{C-F} = 251 Hz), 133.7, 131.5, 130.1, 129.0, 128.6, 127.1, 126.4, 125.2, 124.5, 123.8, 114.4 (td, J_{C-F} = 20.0, 4.0 Hz). ¹⁹F NMR (376 MHz, CDCl₃) δ -139.39 (dd, J = 25.0, 10.0 Hz, 2F), -154.63 (t, J = 21.0 Hz, 1F), -161.85 (dt, J = 24.0, 10.0 Hz, 2F). This compound is known.⁸

4. References

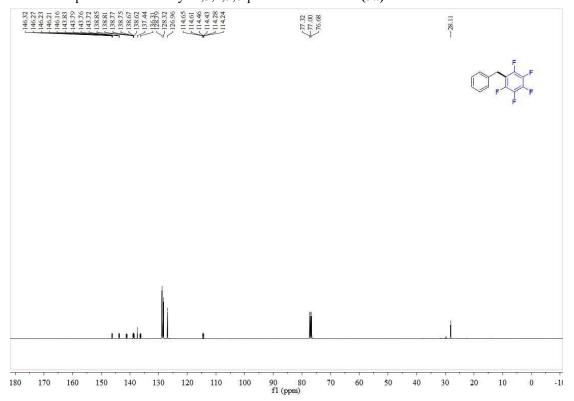
- (1) Maity, P.; Shacklady-McAtee, D. M.; Yap, G. P. A.; Sirianni, E. R.; Watson, M. P. J. Am. Chem. Soc. 2013, 135, 280-285.
- (2) Yang, G.; Jiang, X.; Liu, Y.; Li, N.; Yin, G.; Yu, C. Asian J. Org. Chem. 2016, 5, 882-885.
- (3) Qin, Q.; Xie, Y.; Floreancig, P.E. Chem. Sci. 2018, 9, 8528-8534.
- (4) Fan, S.; H, C.-Y.; Zhang, X. Chem. Commun. 2010, 46, 4926-4928.
- (5) Zhu, Z.; Liu, J.; Dong, S.; Chen, B.; Wang, Z.; Tang, R.-Y.; Li, Z. Asian J. Org. Chem. 2020, 9, 631-636.
- (6) Ueda, M.; Nishimura, K.; Ryu, I. Synlett. 2013, 24, 1683-1686.
- (7) Paudel, K.; Xu, S.; Ding, K. J. Org. Chem. 2020, 85, 14980-14988.
- (8) Shang, R.; Xu, Q.; Jiang, Y.-Y.; Wang, Y.; Liu, L. Org. Lett. 2010, 12, 1000-1003.

5. Copies of ¹H, ¹³C NMR Spectra of the Products

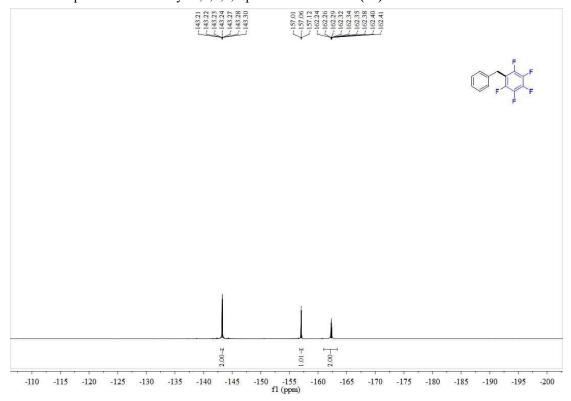
¹H NMR Spectrum of 1-benzyl-2,3,4,5,6-pentafluorobenzene (3a)

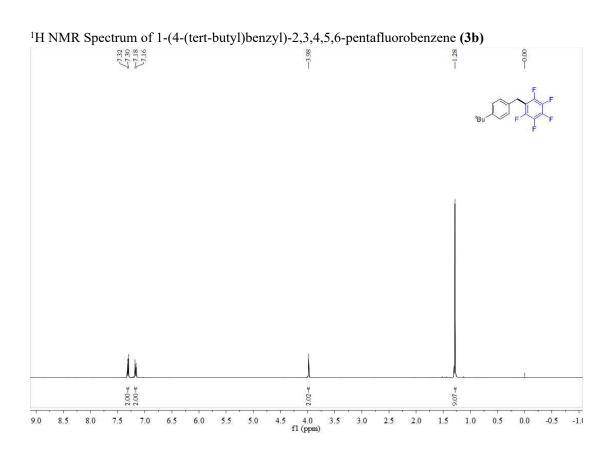


¹³C NMR Spectrum of 1-benzyl-2,3,4,5,6-pentafluorobenzene (3a)

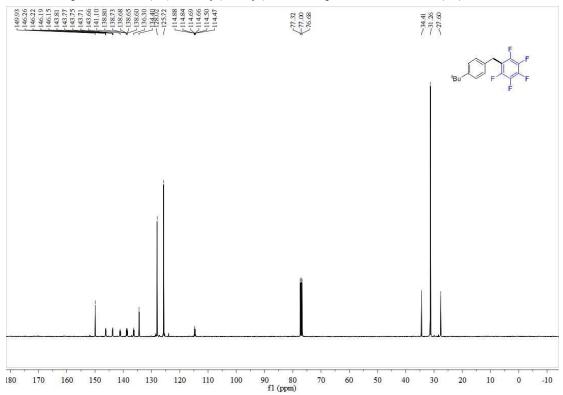


¹⁹F NMR Spectrum of 1-benzyl-2,3,4,5,6-pentafluorobenzene (3a)

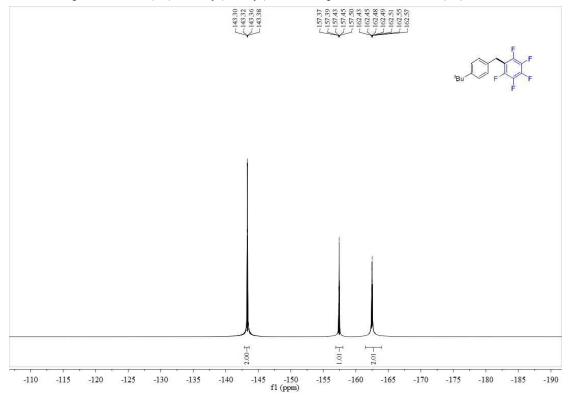


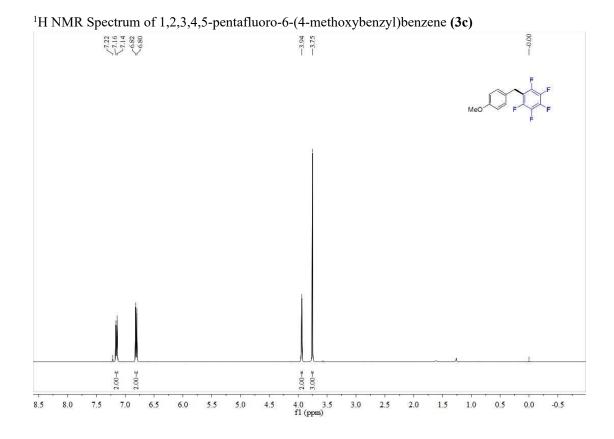


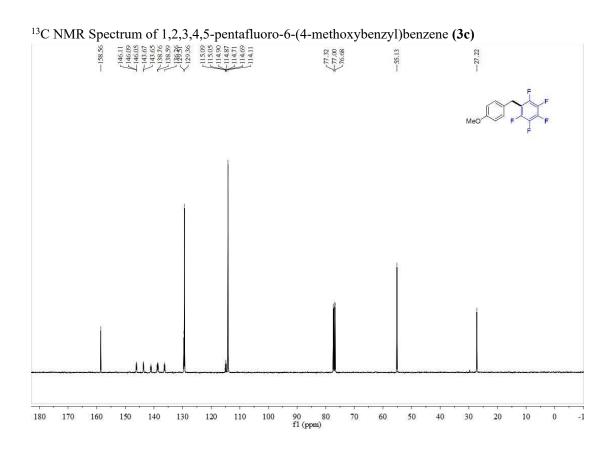
¹³C NMR Spectrum of 1-(4-(tert-butyl)benzyl)-2,3,4,5,6-pentafluorobenzene (3b)



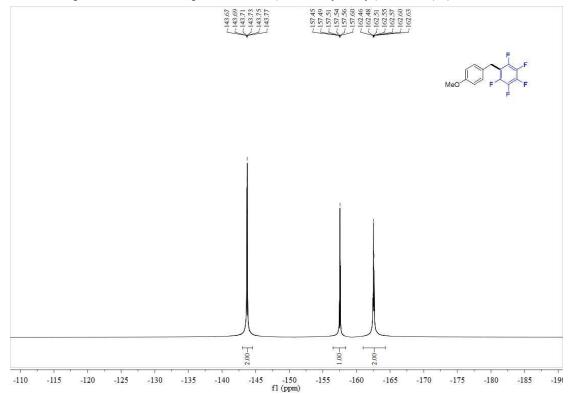
¹⁹F NMR Spectrum of 1-(4-(tert-butyl)benzyl)-2,3,4,5,6-pentafluorobenzene (**3b**)

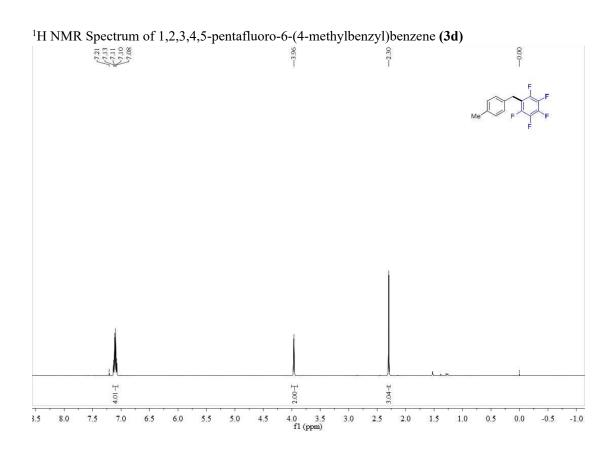




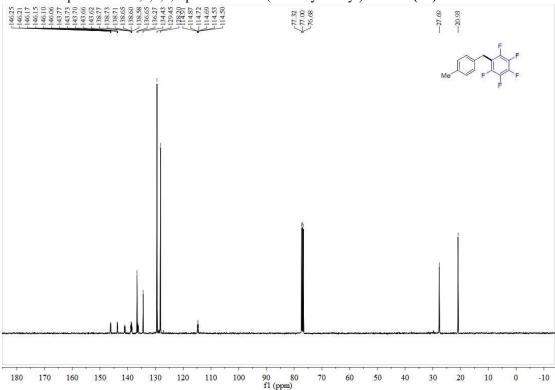


¹⁹F NMR Spectrum of 1,2,3,4,5-pentafluoro-6-(4-methoxybenzyl)benzene (3c)

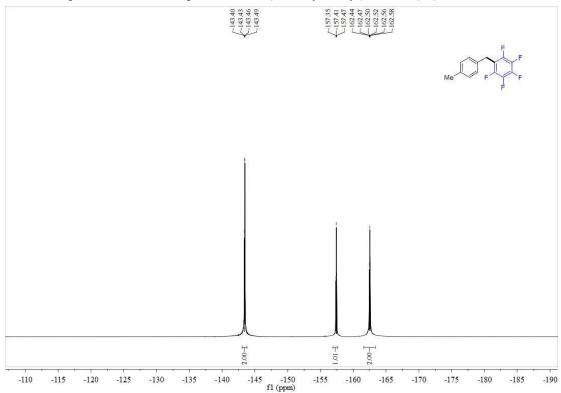


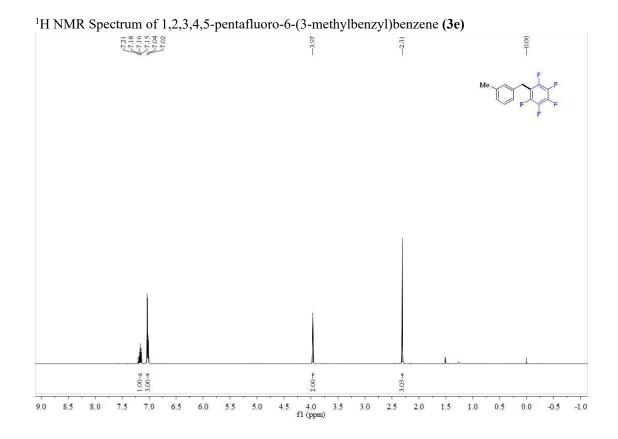


¹³C NMR Spectrum of 1,2,3,4,5-pentafluoro-6-(4-methylbenzyl)benzene (3d)

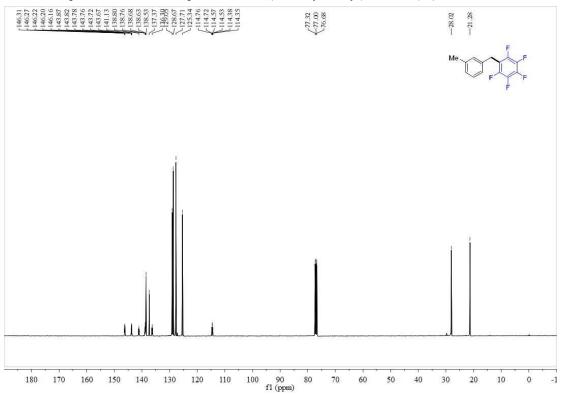


¹⁹F NMR Spectrum of 1,2,3,4,5-pentafluoro-6-(4-methylbenzyl)benzene (3d)

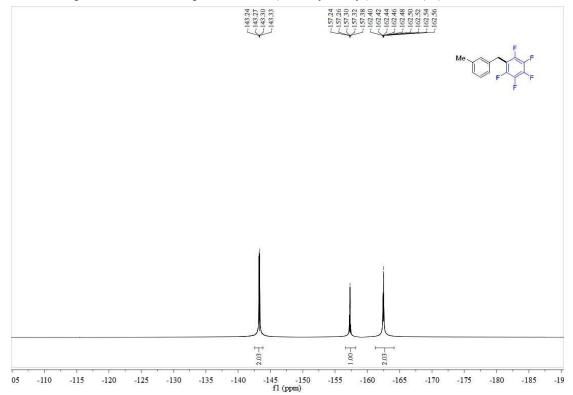


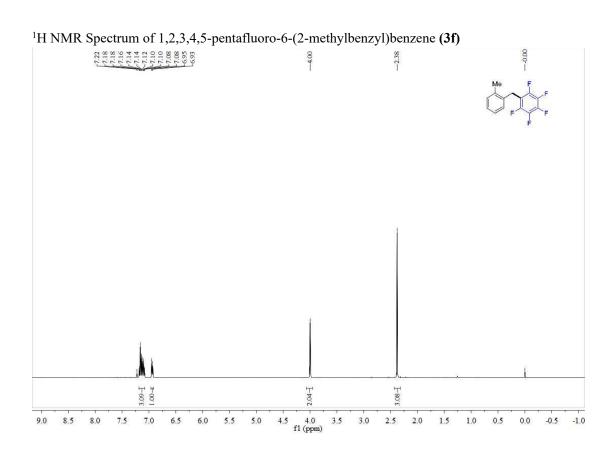


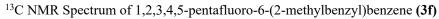
¹³C NMR Spectrum of 1,2,3,4,5-pentafluoro-6-(3-methylbenzyl)benzene (3e)

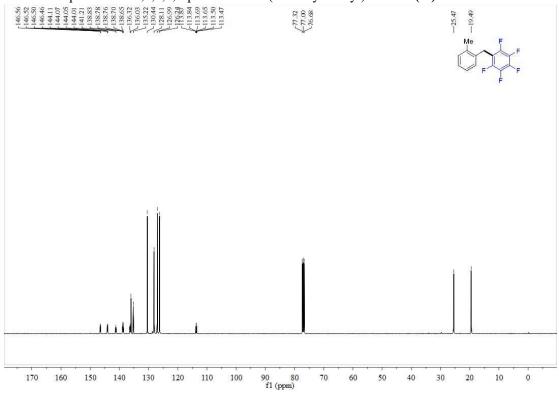


¹⁹F NMR Spectrum of 1,2,3,4,5-pentafluoro-6-(3-methylbenzyl)benzene (3e)

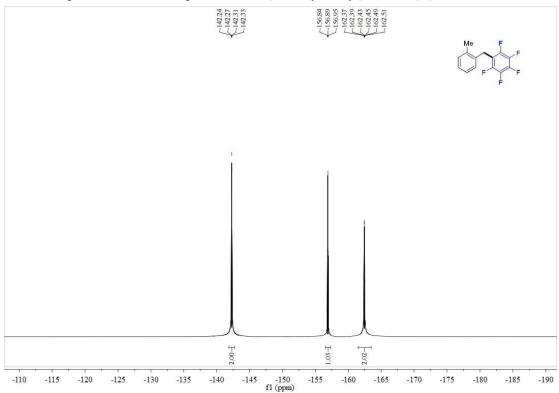


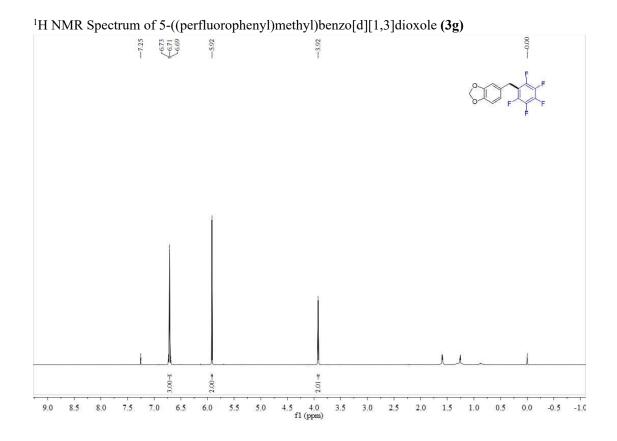




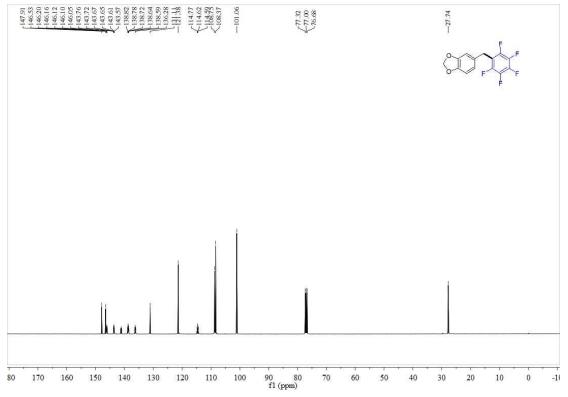


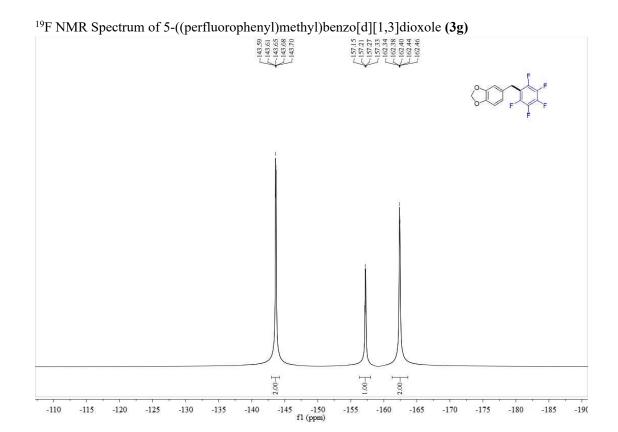
¹⁹F NMR Spectrum of 1,2,3,4,5-pentafluoro-6-(2-methylbenzyl)benzene (3f)

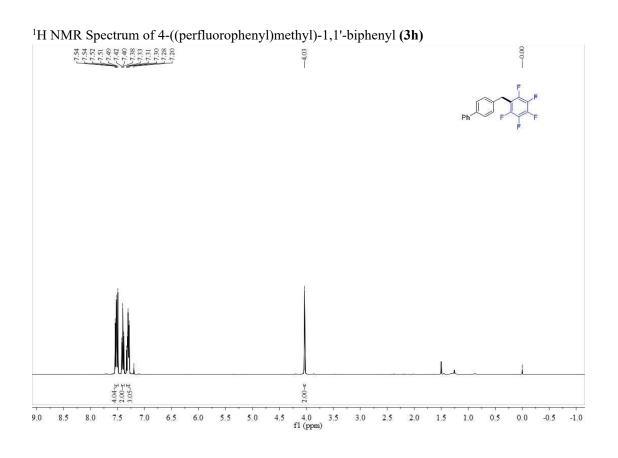




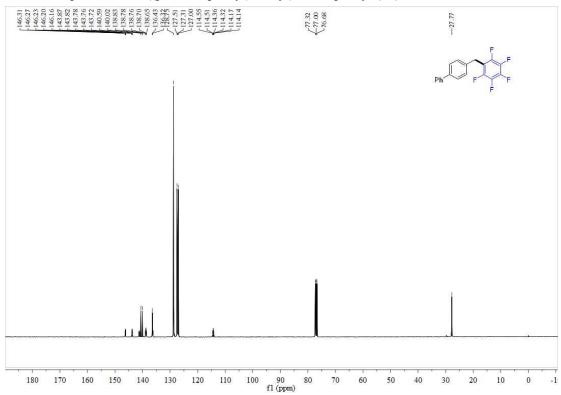
¹³C NMR Spectrum of 5-((perfluorophenyl)methyl)benzo[d][1,3]dioxole (3g)



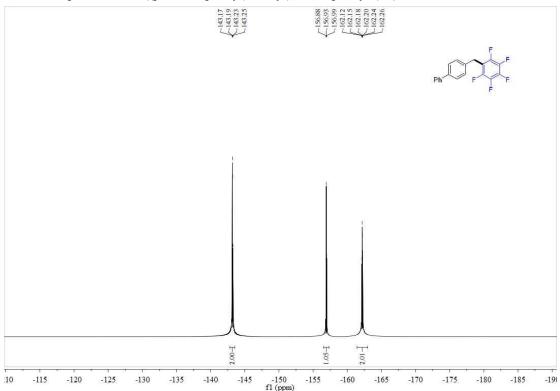




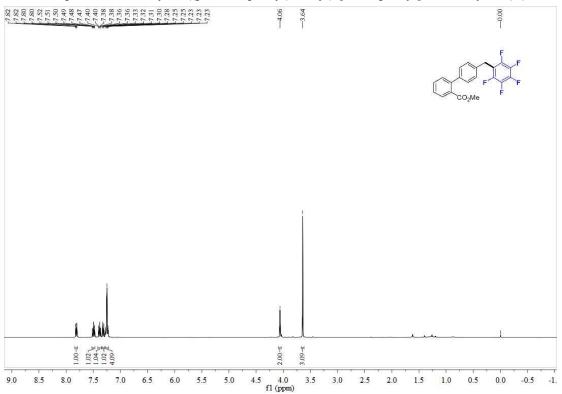
¹³C NMR Spectrum of 4-((perfluorophenyl)methyl)-1,1'-biphenyl (3h)



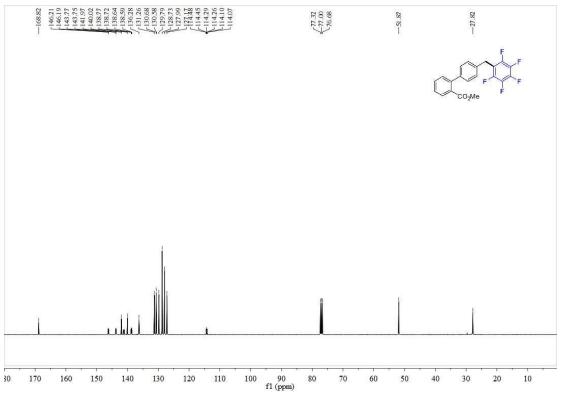
¹⁹F NMR Spectrum of 4-((perfluorophenyl)methyl)-1,1'-biphenyl (3h)



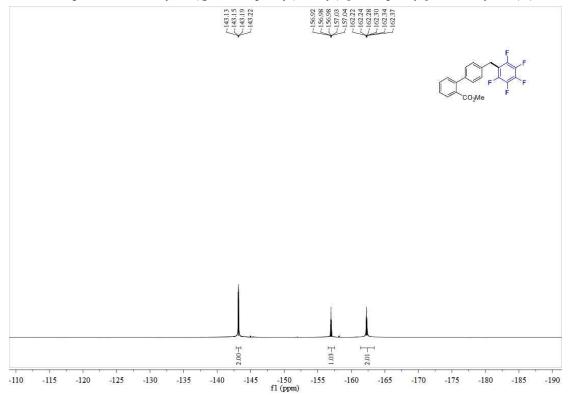
¹H NMR Spectrum of methyl 4'-((perfluorophenyl)methyl)-[1,1'-biphenyl]-2-carboxylate (3i)



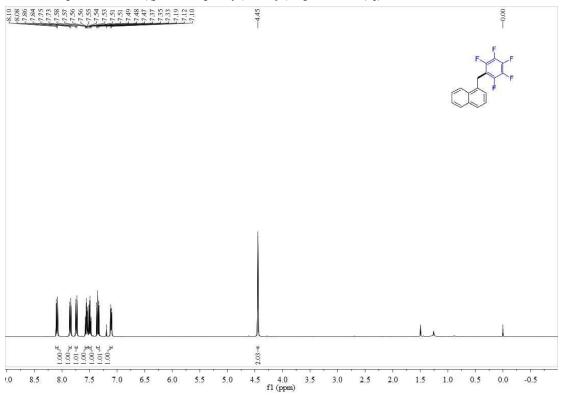
¹³C NMR Spectrum of methyl 4'-((perfluorophenyl)methyl)-[1,1'-biphenyl]-2-carboxylate (3i)



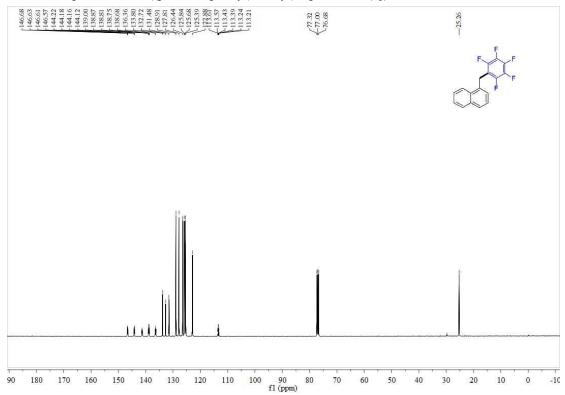
³¹P NMR Spectrum of methyl 4'-((perfluorophenyl)methyl)-[1,1'-biphenyl]-2-carboxylate (3i)



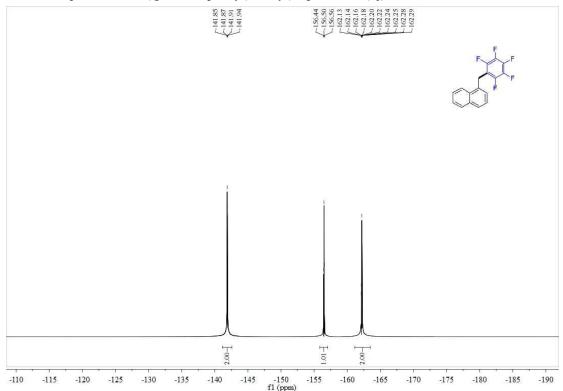
¹H NMR Spectrum of 1-((perfluorophenyl)methyl)naphthalene (3j)



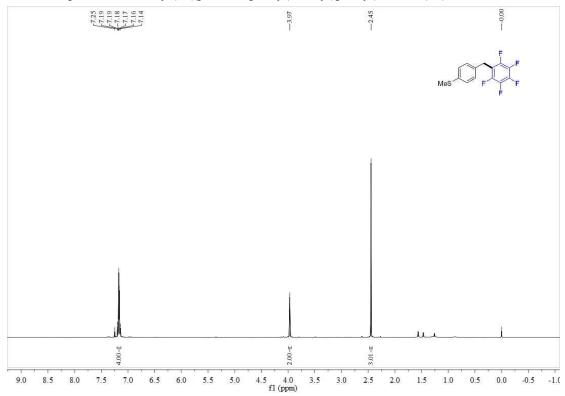
¹³C NMR Spectrum of 1-((perfluorophenyl)methyl)naphthalene (3j)



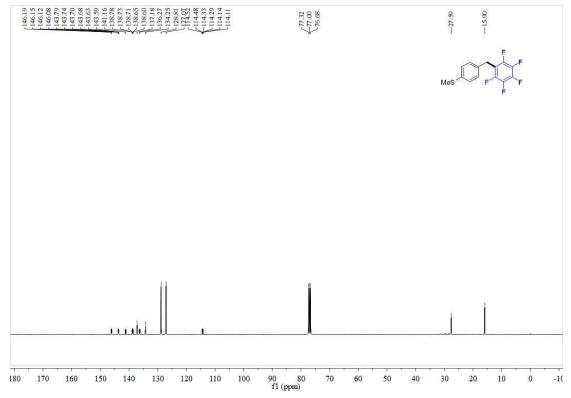
¹⁹F NMR Spectrum of 1-((perfluorophenyl)methyl)naphthalene (3j)

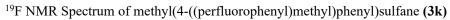


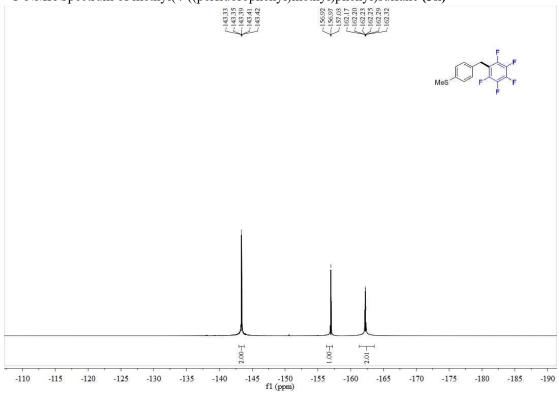
 $^1\mathrm{H}$ NMR Spectrum of methyl(4-((perfluorophenyl)methyl)phenyl)sulfane (3k)



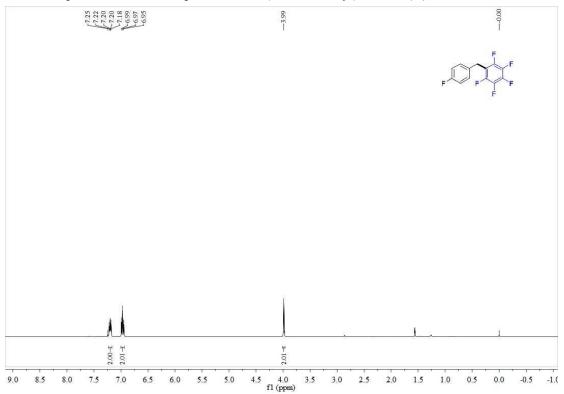
 $^{13}\mathrm{C}$ NMR Spectrum of methyl(4-((perfluorophenyl)methyl)phenyl)sulfane (3k)

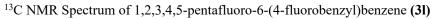


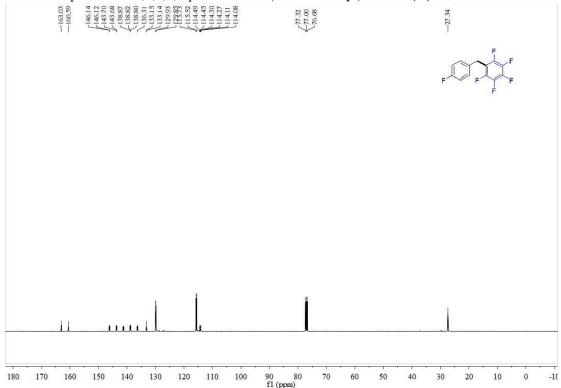


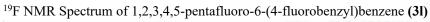


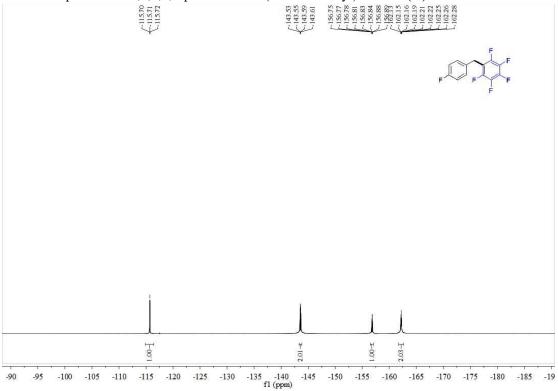
¹H NMR Spectrum of 1,2,3,4,5-pentafluoro-6-(4-fluorobenzyl)benzene (31)

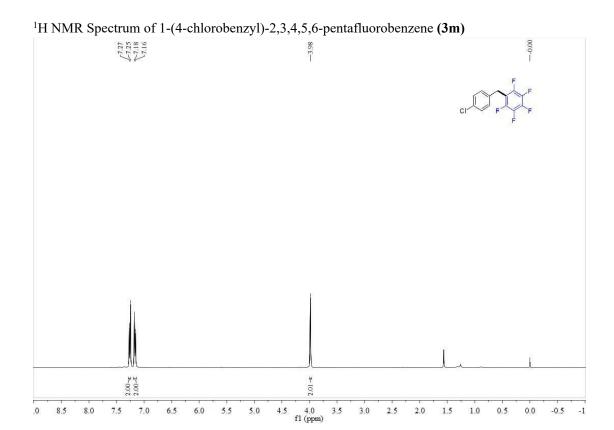


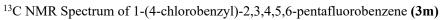


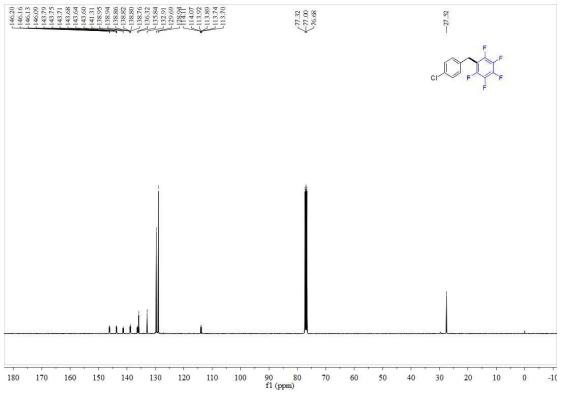




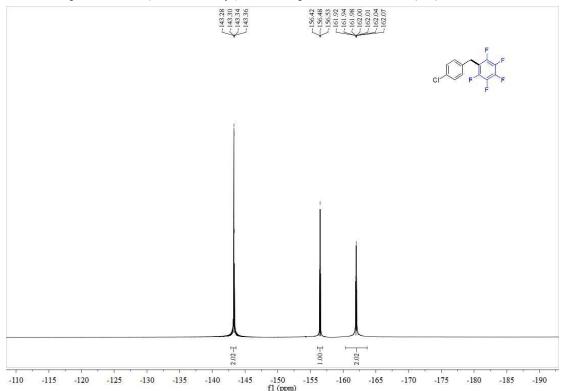


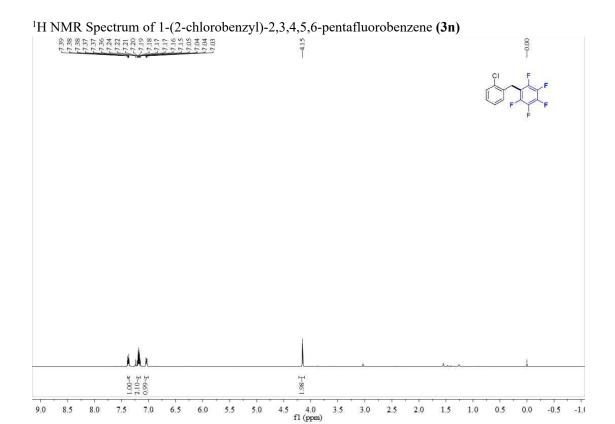




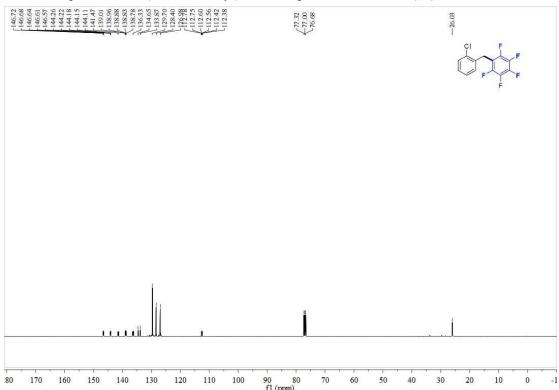


 $^{19}\mathrm{F}$ NMR Spectrum of 1-(4-chlorobenzyl)-2,3,4,5,6-pentafluorobenzene (3m)

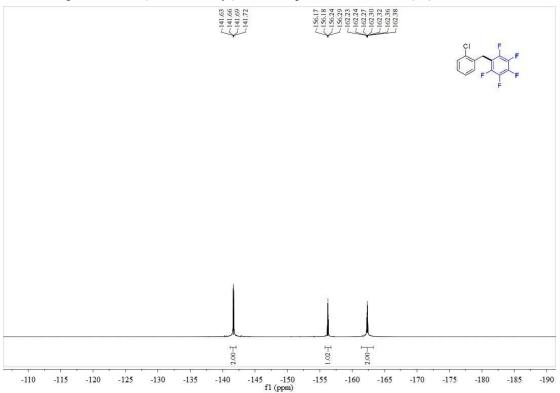




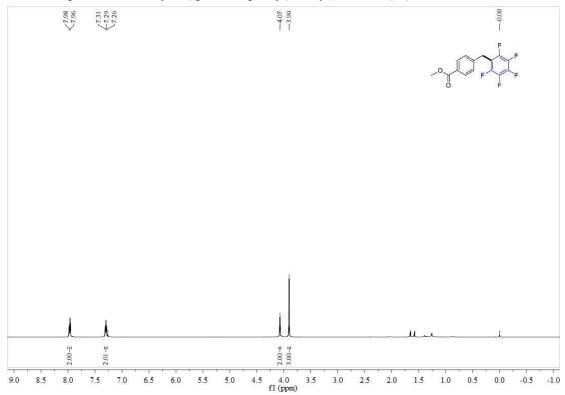
¹³C NMR Spectrum of 1-(2-chlorobenzyl)-2,3,4,5,6-pentafluorobenzene (3n)



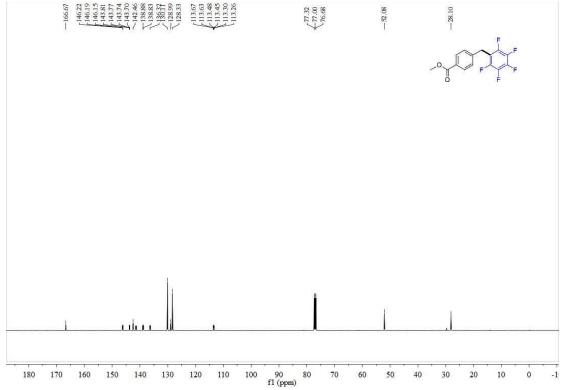
¹⁹F NMR Spectrum of 1-(2-chlorobenzyl)-2,3,4,5,6-pentafluorobenzene (3n)



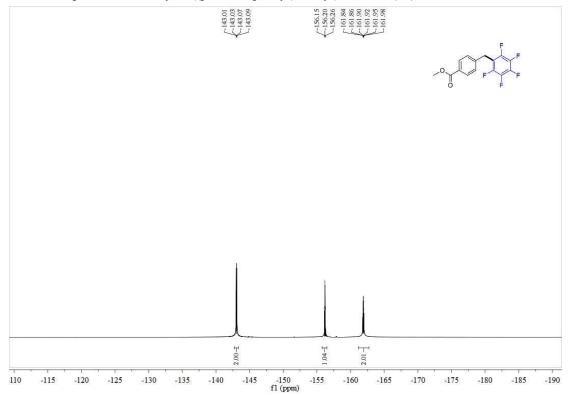
 1H NMR Spectrum of methyl 4-((perfluorophenyl)methyl)benzoate (30)



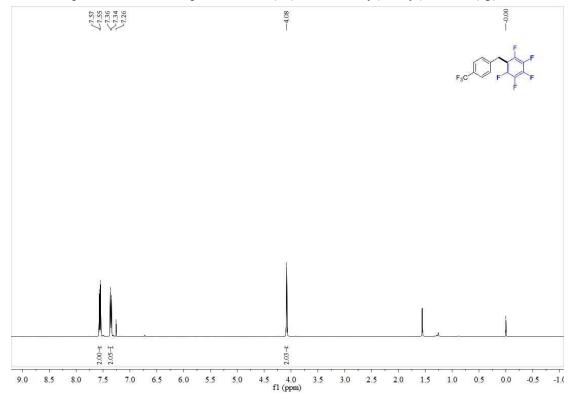




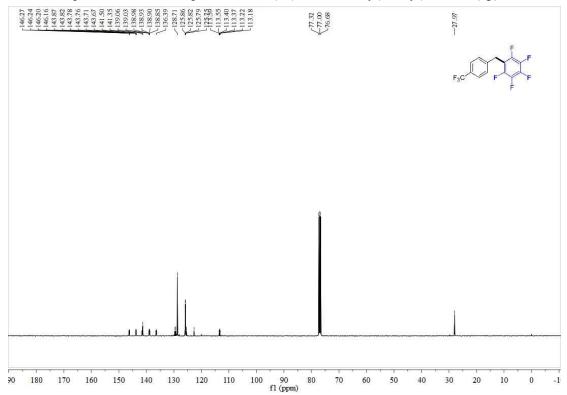
 $^{19}\mathrm{F}$ NMR Spectrum of methyl 4-((perfluorophenyl)methyl)benzoate (30)



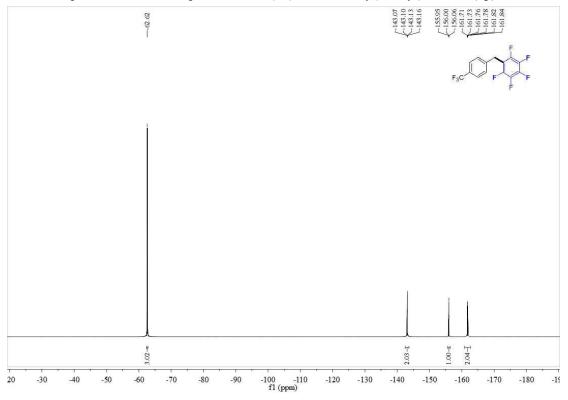
¹H NMR Spectrum of 1,2,3,4,5-pentafluoro-6-(4-(trifluoromethyl)benzyl)benzene (**3p**)

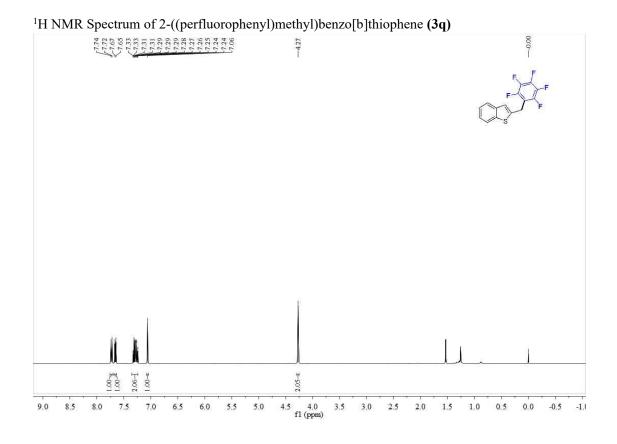


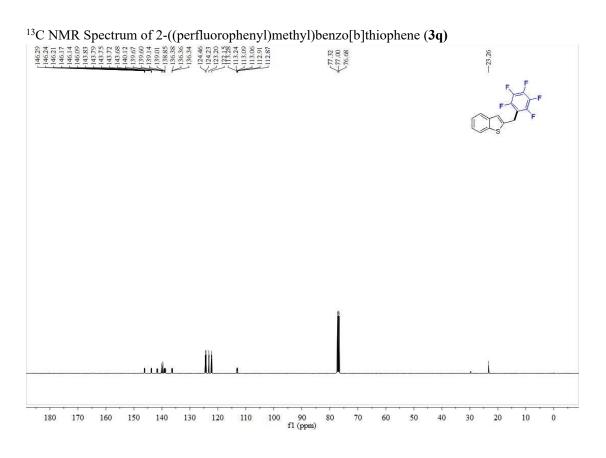
 $^{13}\mathrm{C}$ NMR Spectrum of 1,2,3,4,5-pentafluoro-6-(4-(trifluoromethyl)benzyl)benzene (3p)



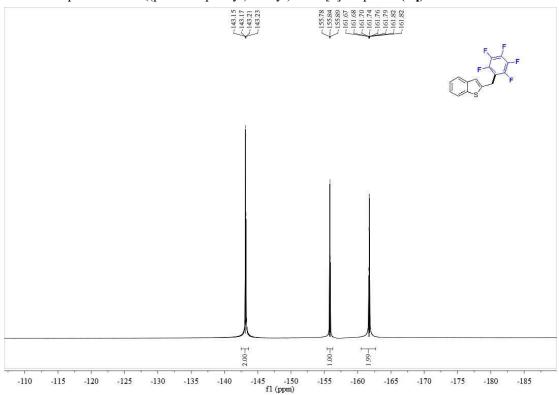
¹⁹F NMR Spectrum of 1,2,3,4,5-pentafluoro-6-(4-(trifluoromethyl)benzyl)benzene (**3p**)

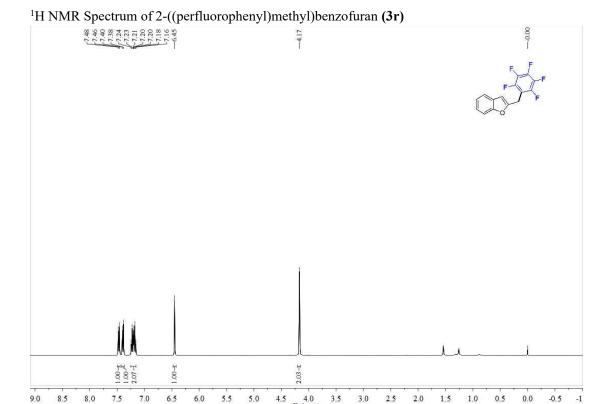




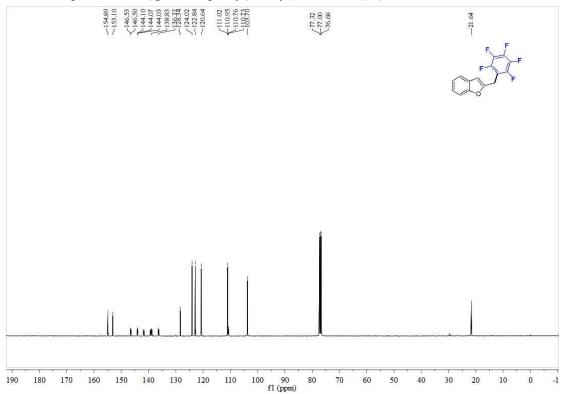


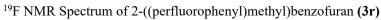
¹⁹F NMR Spectrum of 2-((perfluorophenyl)methyl)benzo[b]thiophene (3q)

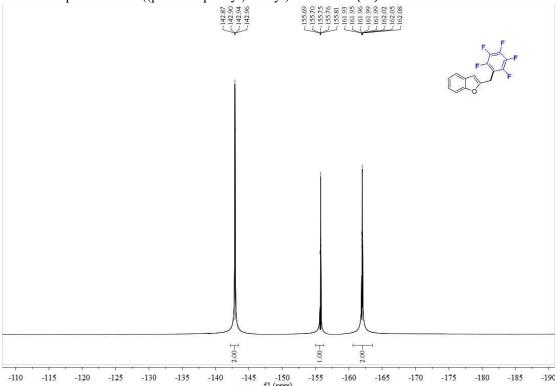




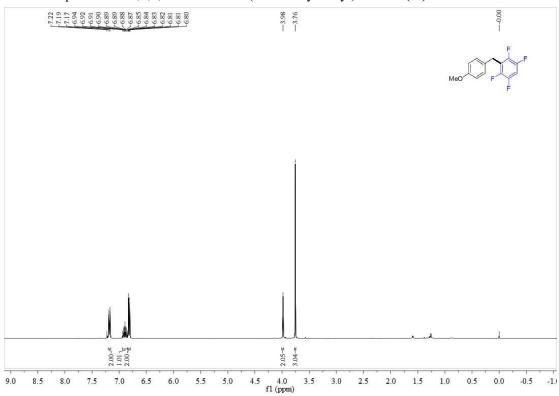
 $^{13}\mathrm{C}$ NMR Spectrum of 2-((perfluorophenyl)methyl)benzofuran (3r)



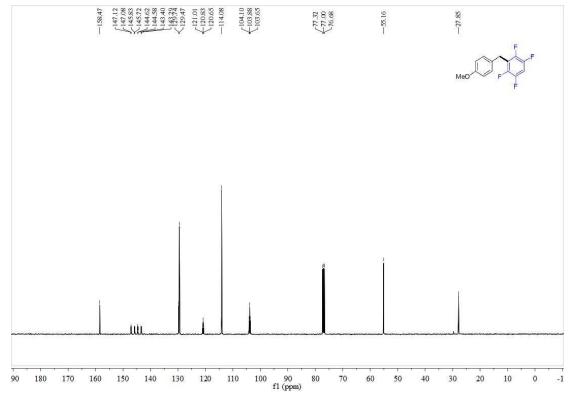




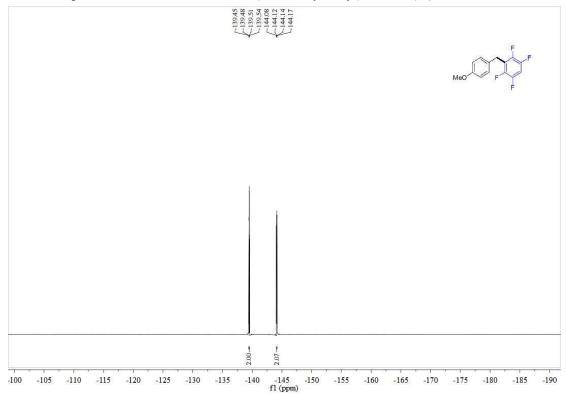
 $^1\mathrm{H}$ NMR Spectrum of 1,2,4,5-tetrafluoro-3-(4-methoxybenzyl)benzene (3s)



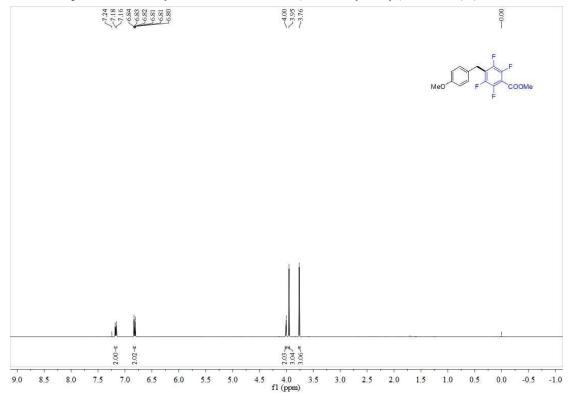
¹³C NMR Spectrum of 1,2,4,5-tetrafluoro-3-(4-methoxybenzyl)benzene (3s)



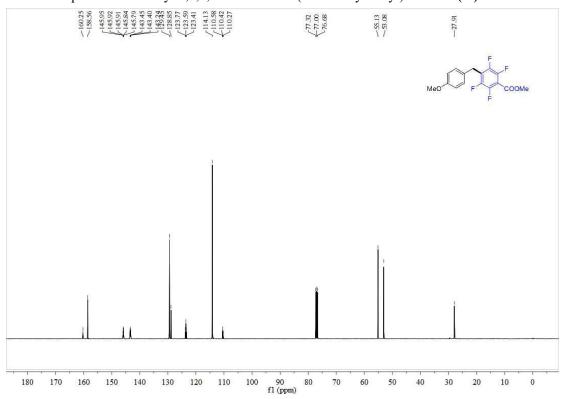
 $^{19}\mathrm{F}$ NMR Spectrum of 1,2,4,5-tetrafluoro-3-(4-methoxybenzyl)benzene (3s)



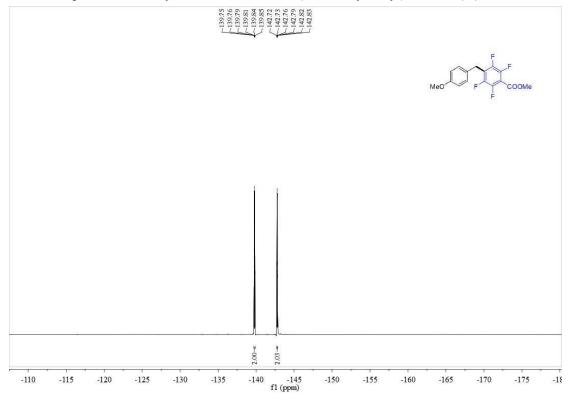
 $^1\mathrm{H}$ NMR Spectrum of methyl 2,3,5,6-tetrafluoro-4-(4-methoxybenzyl)benzoate (3t)



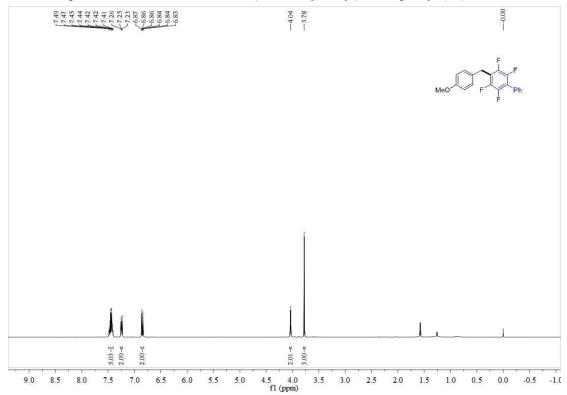
¹³C NMR Spectrum of methyl 2,3,5,6-tetrafluoro-4-(4-methoxybenzyl)benzoate (3t)



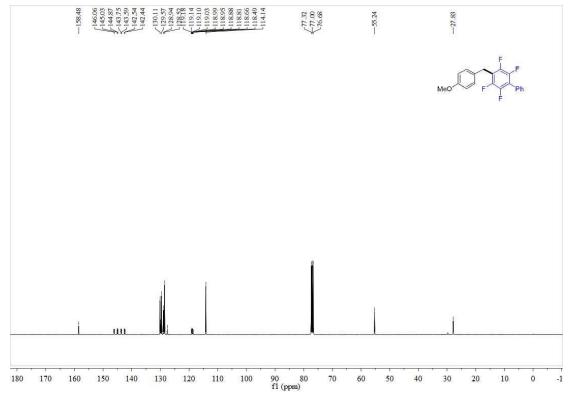
¹⁹F NMR Spectrum of methyl 2,3,5,6-tetrafluoro-4-(4-methoxybenzyl)benzoate (3t)

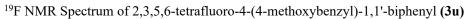


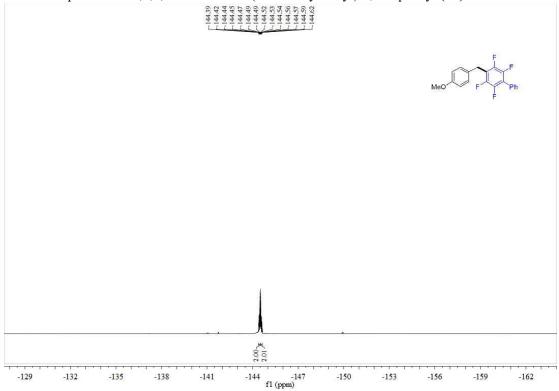
¹H NMR Spectrum of 2,3,5,6-tetrafluoro-4-(4-methoxybenzyl)-1,1'-biphenyl (3u)



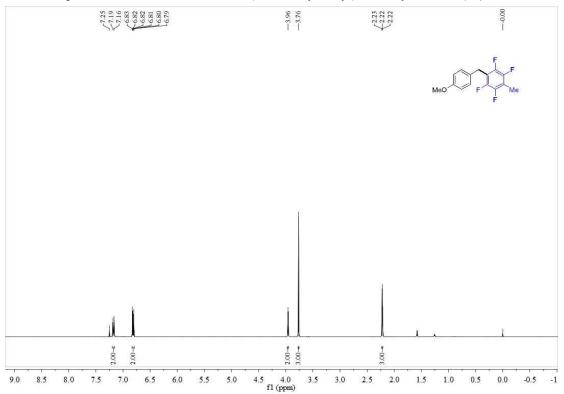
 $^{13}\mathrm{C}$ NMR Spectrum of 2,3,5,6-tetrafluoro-4-(4-methoxybenzyl)-1,1'-biphenyl (3u)



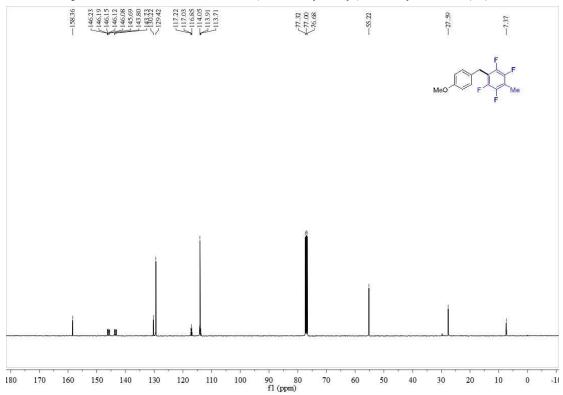




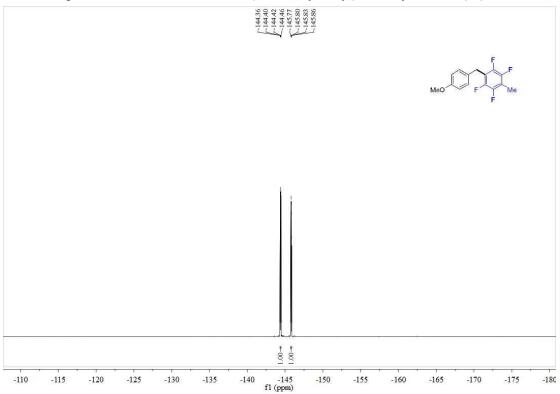
¹H NMR Spectrum of 1,2,4,5-tetrafluoro-3-(4-methoxybenzyl)-6-methylbenzene (3v)



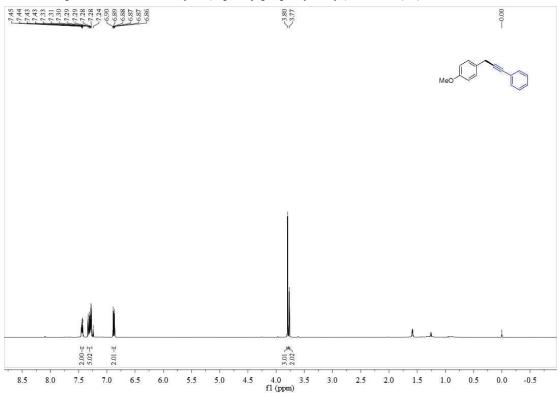
 $^{13}\mathrm{C}$ NMR Spectrum of 1,2,4,5-tetrafluoro-3-(4-methoxybenzyl)-6-methylbenzene (3v)



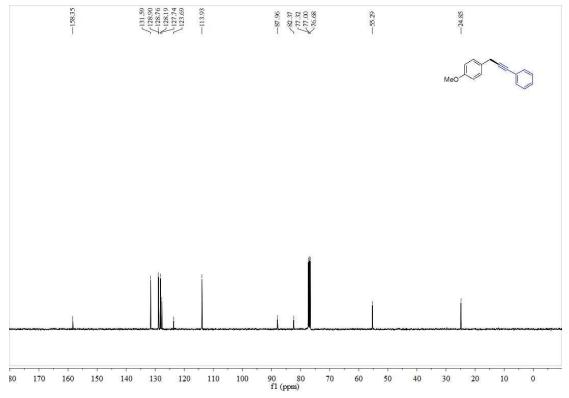
¹⁹F NMR Spectrum of 1,2,4,5-tetrafluoro-3-(4-methoxybenzyl)-6-methylbenzene (3v)



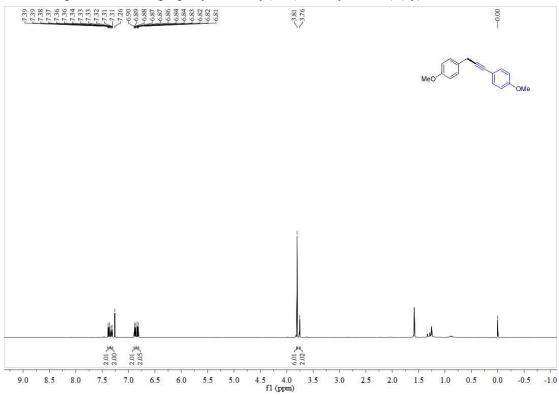
 ^{1}H NMR Spectrum of 1-methoxy-4-(3-phenylprop-2-yn-1-yl)benzene (3x)



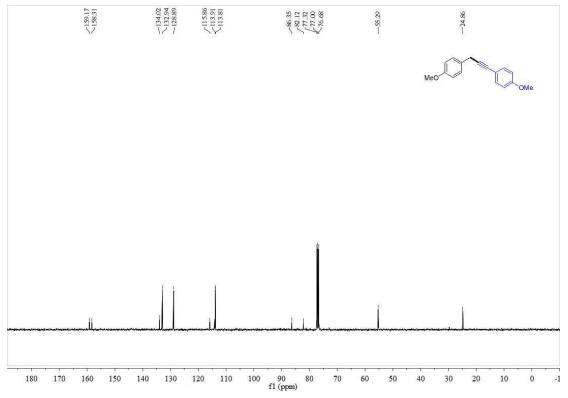
¹³C NMR Spectrum of 1-methoxy-4-(3-phenylprop-2-yn-1-yl)benzene (3x)



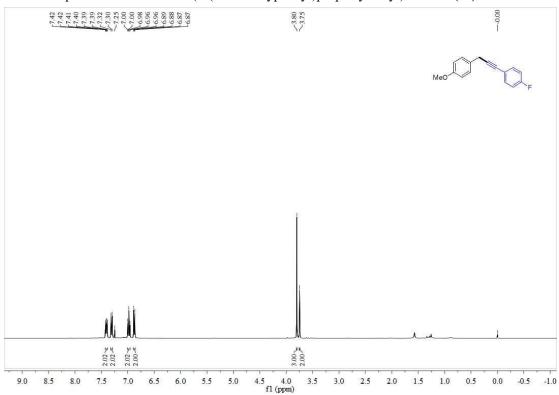
¹H NMR Spectrum of 4,4'-(prop-1-yne-1,3-diyl)bis(methoxybenzene) (3y)



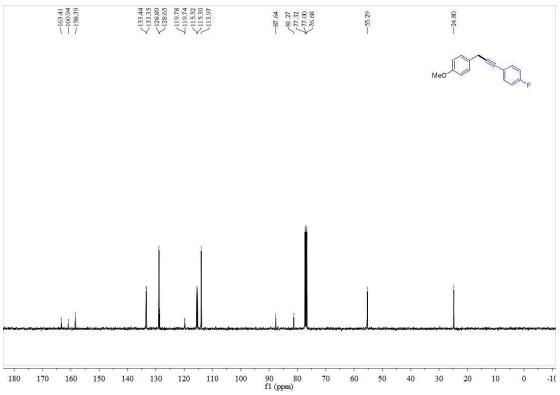
¹³C NMR Spectrum of 4,4'-(prop-1-yne-1,3-diyl)bis(methoxybenzene) (3y)



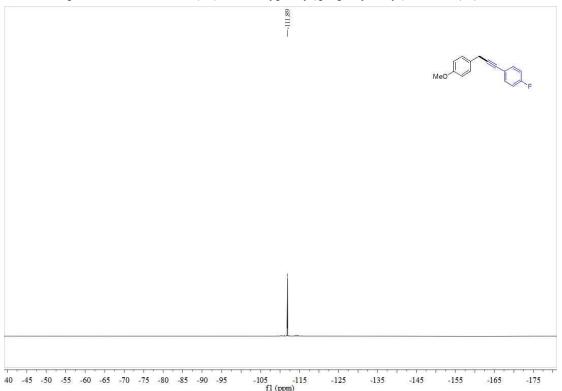
¹H NMR Spectrum of 1-fluoro-4-(3-(4-methoxyphenyl)prop-1-yn-1-yl)benzene (3z)



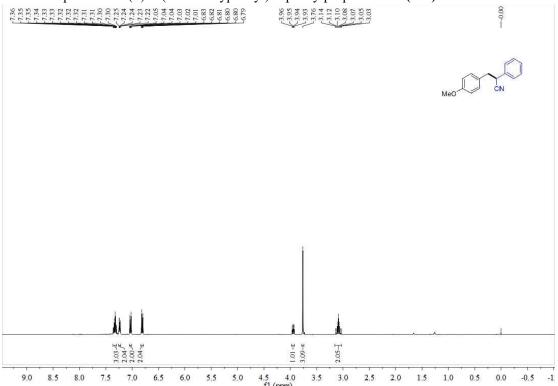
¹³C NMR Spectrum of 1-fluoro-4-(3-(4-methoxyphenyl)prop-1-yn-1-yl)benzene (3z)



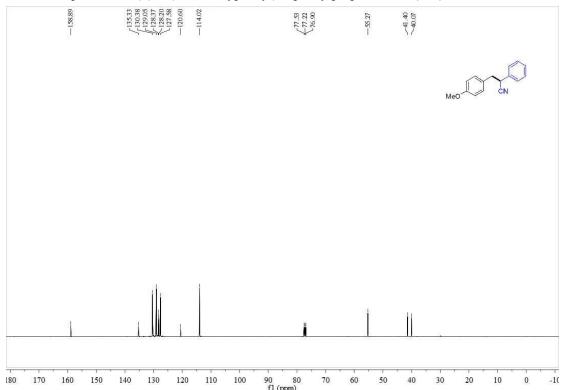
 $^{19}\mathrm{F}$ NMR Spectrum of 1-fluoro-4-(3-(4-methoxyphenyl)prop-1-yn-1-yl)benzene (3z)



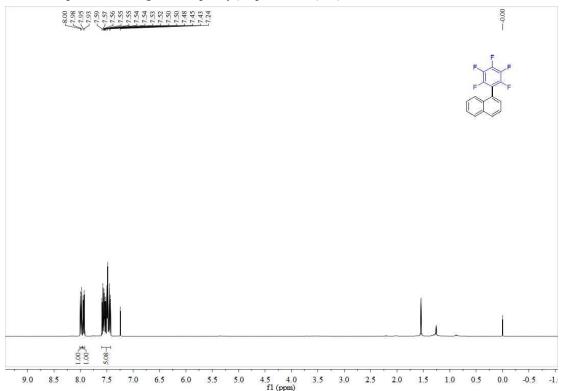




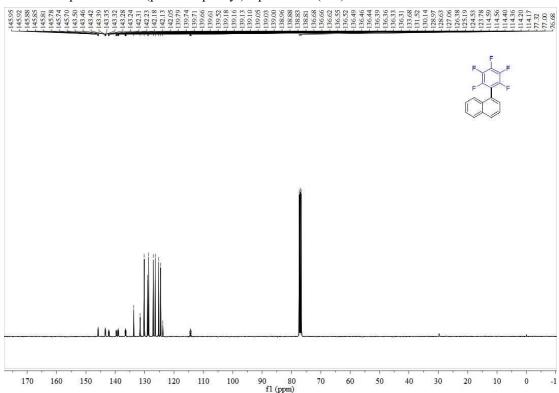
¹³C NMR Spectrum of (S)-3-(4-methoxyphenyl)-2-phenylpropanenitrile (3zb)



¹H NMR Spectrum of 1-(perfluorophenyl)naphthalene (**3zc**)



 $^{13}\mathrm{C}$ NMR Spectrum of 1-(perfluor ophenyl)naphthalene $(\boldsymbol{3zc})$



 $^{19}\mathrm{F}$ NMR Spectrum of 1-(perfluorophenyl)naphthalene (3zc)

