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Supporting Information

Pd-Catalyzed Decarboxylative Coupling of Zinc Polyfluorobenzoate with Aryl Imidazolylsulfonate for Polyfluorinated Biaryl Synthesis

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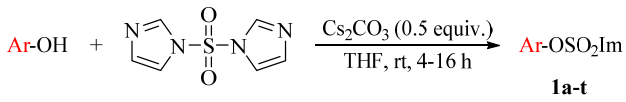
General information

Unless otherwise stated, all reagents (≥98% purity) were purchased from commercial suppliers and used without further purification. All the aryl imidazolylsulfonates were prepared according to previously reported methods.[1-5] Analytical thin layer chromatography (TLC) was performed using silica gel plate (0.2 mm thickness). Subsequent to elution, plates were visualized using UV radiation (254 nm). Flash chromatography was performed using Merck silica gel (200-300 mesh) for column chromatography with freshly distilled solvents. Columns were typically packed as slurry and equilibrated with the appropriate solvent system prior to use. IR spectra were recorded on a FT-IR spectrophotometer using KBr optics. ^{1}H, ^{19}F, and ^{13}C NMR spectra were recorded in $CDCl_3$ on Jeol 400 MHz spectrometers. Tetramethylsilane (TMS) served as internal standard for ^{1}H and ^{13}C NMR analysis. High resolution mass spectra (HRMS) were obtained on a Waters Q-TOF Premier Spectrometer (ESI or EI Source).

Experimental procedure

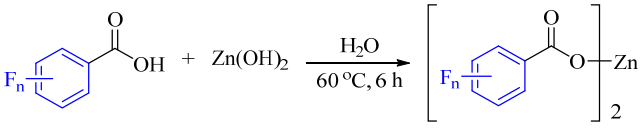
1. Typical procedure for the synthesis of aryl imidazolylsulfonates.[1-5]



1a-t

A round-bottom flask was charged with phenol (10 mmol, 1 equiv.), *N*,*N*-sulfonyldiimidazole (3.9640 g, 20 mmol, 2 equiv.), and cesium carbonate (1.6291 g, 5 mmol, 0.5 equiv.) in THF (20 mL). The reaction was stirred at room temperature for 4-16 h followed by quenching with saturated NH_4Cl solution (10 mL) and extracting with EtOAc (50 mL × 3). The organic layers were combined, washed with brine, and dried over anhydrous Na_2SO_4. The extracts were concentrated under reduced pressure to afford the crude product, which was further purified through silica gel column chromatography (using EtOAc/petroleum ether as eluents) to yield the product **1a-t**. Spectral data of the products are in accord with those previously reported.

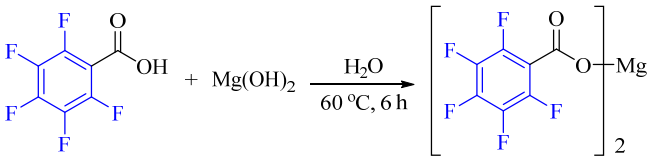
2. Typical procedure for the synthesis of zinc polyfluorobenzoates.[6]



2a-c

A round-bottom flask equipped with a magnetic stir bar was added polyfluorobenzoic acid (10 mmol, 1 equiv.) and deionized water (50 mL), and the reaction mixture was stirred at 60 °C for 0.5 h. Then $Zn(OH)_2$ (0.4969 g, 5 mmol, 0.5 equiv.) was added into the flask, and the reaction mixture was vigorously stirred at 60 °C for 6 h. Then the solvent was evaporated and the solid residue was dried under vacuum at 50 °C for 6 h to afford the zinc polyfluorobenzoates **2a-c**.

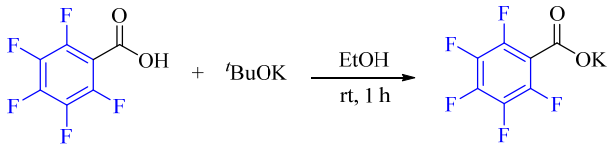
3. Typical produce for the synthesis of magnesium polyfluorobenzoate 5.



5

A round-bottom flask equipped with a magnetic stir bar was added 2,3,4,5,6-polyfluorobenzoic acid (2.1207 g, 10 mmol, 1 equiv.) and deionized water (50 mL), and the reaction mixture was stirred at 60 °C for 0.5 h. Then $Mg(OH)_2$ (0.2916 g, 5 mmol, 0.5 equiv.) was added into the flask, and the reaction mixture was vigorously stirred at 60 °C for 6 h. Then the solvent was evaporated and the solid residue was dried under vacuum at 50 °C for 6 h to afford the magnesium polyfluorobenzoate **5**.

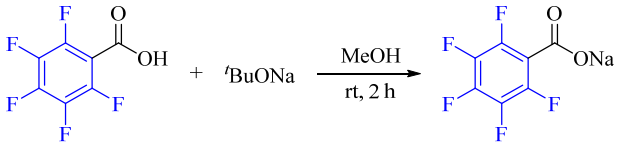
4. Typical produce for the synthesis of potassium polyfluorobenzoate 6.[7]



6

A round-bottom flask equipped with a magnetic stir bar was added 2,3,4,5,6-polyfluorobenzoic acid (2.1207 g, 10 mmol, 1 equiv.) and ethanol (10 mL), and the reaction mixture was stirred at room temperature for 0.5 h. Then ^{t}BuOK (1.1221 g, 10 mmol, 1 equiv.) in ethanol (10 mL) was added dropwise into the flask over 30 minutes. The reaction mixture was vigorously stirred at room temperature for 1 h. Then the solvent was evaporated and the solid residue was dried under vacuum at 30 °C for 6 h to afford the potassium polyfluorobenzoate **6**.

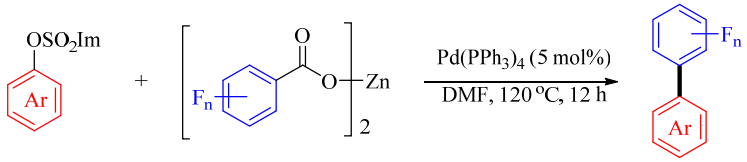
5. Typical produce for the synthesis of sodium polyfluorobenzoate 7.[8]



7

A round-bottom flask equipped with a magnetic stir bar was added 2,3,4,5,6-polyfluorobenzoic acid (2.1207 g, 10 mmol, 1 equiv.) and methanol (10 mL), and the reaction mixture was stirred at room temperature for 0.5 h. Then ^{t}BuONa (0.9610 g, 10 mmol, 1 equiv.) in methanol (10 mL) was added dropwise into the flask over 30 minutes. The reaction mixture was vigorously stirred at room temperature for 2 h. Then the solvent was evaporated and the solid residue was dried under vacuum at 40 °C for 48 h to afford the sodium polyfluorobenzoate **7**.

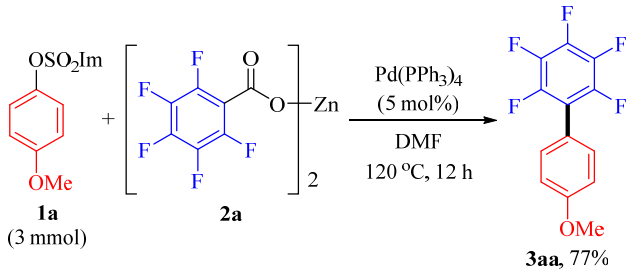
6. Typical procedure for the decarboxylative cross-couplings of aryl imidazolylsulfonates with zinc polyfluorobenzoates.



1 **2** **3** or **4**

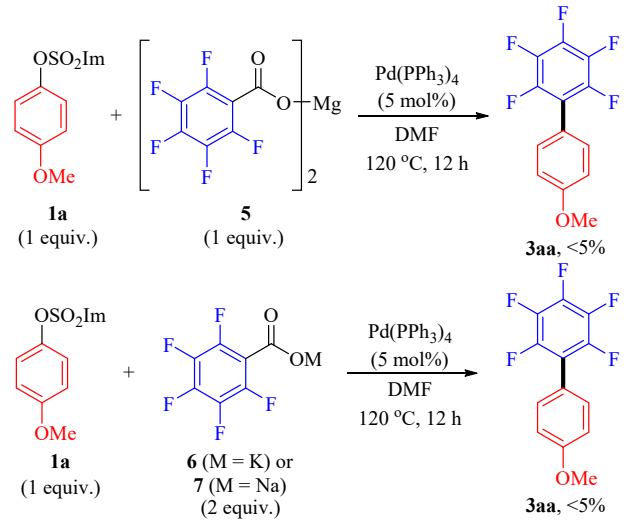
An oven-dried seal tube equipped with a magnetic stir bar was backfilled with nitrogen gas for three times. Then aryl imidazolylsulfonate **1** (0.5 mmol, 1 equiv.), zinc 2,3,4,5,6-pentafluorobenzoate **2** (0.5 mmol, 1 equiv.), and $Pd(PPh_3)_4$ (0.0289 g, 0.025 mmol, 5 mol%) were added into the tube. Then dry DMF (2 mL) was added, and the reaction mixture was stirred at 120 °C for 12 h followed by quenching with saturated NH_4Cl solution (10 mL) and extracting with EtOAc (20 mL × 3). The combined organic layers were washed with brine, dried over Na_2SO_4, and concentrated under reduced pressure to afford the crude product, which was further purified through silica gel column chromatography (using EtOAc/petroleum ether as eluents) to yield the product **3** or **4**

7. Typical procedure for the 3 mmol scale reaction of 1a with 2a.



An oven-dried flask equipped with a magnetic stir bar was backfilled with nitrogen gas for three times. Then aryl imidazolylsulfonate **1a** (0.7628 g, 3 mmol), zinc 2,3,4,5,6-pentafluorobenzoate **2a** (1.4625 g, 3 mmol), and $Pd(PPh_3)_4$ (0.1734 g, 0.15 mmol) were weighed into the tube. Then dry DMF (10 mL) was added, and the reaction mixture was stirred at 120 °C for 12 h followed by quenching with saturated NH_4Cl solution (30 mL) and extracting with EtOAc (60 mL × 3). The combined organic layers were washed with brine, dried over Na_2SO_4, and concentrated under reduced pressure to afford the crude product, which was further purified through silica gel column chromatography (using EtOAc/petroleum ether as eluents) to yield the product **3aa** in 77% yield (0.6304 g).

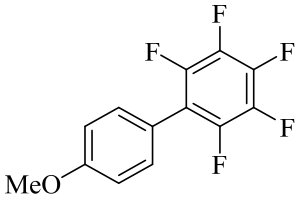
8. Decarboxylative cross-coupling using magnesium or potassium or sodium polyfluorobenzoates 5-7.



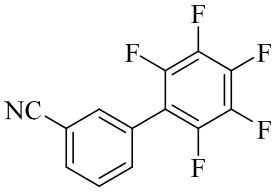
An oven-dried seal tube equipped with a magnetic stir bar was backfilled with nitrogen gas for three times. Then aryl imidazolylsulfonate **1a** (0.1271 g, 0.5 mmol, 1 equiv.), magnesium

polyfluorobenzoate **5** (0.2232 g, 0.5 mmol, 1 equiv.) or potassium polyfluorobenzoate **6** (0.2502 g, 1 mmol, 2 equiv.) or sodium polyfluorobenzoate **7** (0.2341 g, 1 mmol, 2 equiv.), and $Pd(PPh_3)_4$ (0.0289 g, 0.025 mmol, 5 mol%) were added into the tube. Then dry DMF (2 mL) was added, and the reaction mixture was stirred at 120 °C for 12 h followed by quenching with saturated NH_4Cl solution (10 mL) and extracting with EtOAc (20 mL × 3). The combined organic layers were washed with brine, dried over Na_2SO_4, and concentrated under reduced pressure. The residue obtained was purified through silica gel column chromatography (using EtOAc/petroleum ether as eluents), which showed that the NMR yield of the desired product **3aa** is <5% in these cases.

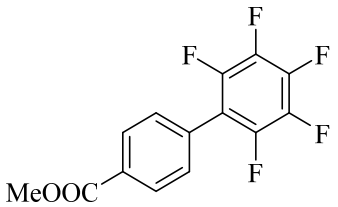
Characterization data of products



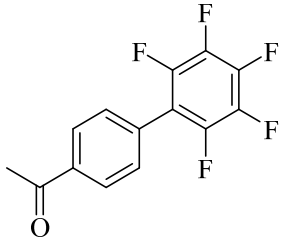
2,3,4,5,6-Pentafluoro-4'-methoxy-1,1'-biphenyl (3aa):[9] This product was purified by silica gel column chromatography using petroleum ether as eluant. 119.8 mg, 87% yield. White solid. M.p. 117.1–118.5 °C. **^{1}H NMR (400 MHz, $CDCl_3$):** δ 7.37 (d, J = 8.5 Hz, 2H), 7.05–6.99 (m, 2H), 3.87 (s, 3H) ppm. **^{13}C NMR (100 MHz, $CDCl_3$):** δ 160.4, 144.3 (dm, J = 248.2 Hz), 140.3 (dm, J = 219.1 Hz), 137.8 (dm, J = 217.3 Hz), 131.6, 118.5, 115.8 (td, J = 17.1, 3.8 Hz), 114.4, 55.5 ppm. **^{19}F NMR (376 MHz, $CDCl_3$):** δ -143.17 (dd, J = 22.9, 8.2 Hz, 2F), -155.50 (t, J = 21.0 Hz, 1F), -162.00 – -162.31 (m, 2F) ppm. **IR (KBr, neat):** ν = 2977, 1611, 1491, 1256, 1065, 982, 828, 777 cm^{-1}. **HRMS (ESI, m/z):** $[M+H]^+$ calcd for $C_{13}H_8F_5O^+$: 275.0490, found: 275.0488.



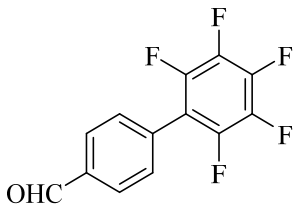
2',3',4',5',6'-Pentafluoro-[1,1'-biphenyl]-3-carbonitrile (3ba):[7] This product was purified by silica gel column chromatography using petroleum ether/ethyl acetate as eluant (petroleum ether/EtOAc = 100:1). 128.7 mg, 96% yield. White solid. M.p. 81.1–82.5 °C. **^{1}H NMR (400 MHz, $CDCl_3$):** δ 7.76 (dt, J = 7.5, 1.6 Hz, 1H), 7.73 (s, 1H), 7.71–7.65 (m, 1H), 7.63 (d, J = 8.1 Hz, 1H) ppm. **^{13}C NMR (100 MHz, $CDCl_3$):** δ 144.2 (dm, J = 249.2 Hz), 141.2 (dm, J = 255.8 Hz), 138.1 (dm, J = 253.6 Hz), 134.6, 133.7, 132.9, 129.9, 127.9, 118.0, 113.8 (td, J = 16.7, 3.7 Hz), 113.4 ppm. **^{19}F NMR (376 MHz, $CDCl_3$):** δ -142.79 – -143.14 (m, 2F), -153.09 (t, J = 20.9 Hz, 1F), -160.89 – -161.15 (m, 2F) ppm. **IR (KBr, neat):** ν = 2360, 2235, 1649, 1528, 1408, 1331, 1081, 901 cm^{-1}. **HRMS (ESI, m/z):** $[M+H]^+$ calcd for $C_{13}H_5F_5N^+$: 270.0337, found: 270.0342.



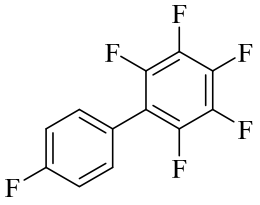
Methyl 2',3',4',5',6'-pentafluoro-[1,1'-biphenyl]-4-carboxylate (3ca):[6] This product was purified by silica gel column chromatography using petroleum ether/ethyl acetate as eluant (petroleum ether/EtOAc = 100:1). 137.3 mg, 91% yield. White solid. M.p. 118.3–118.7 °C. **^{1}H NMR (400 MHz, $CDCl_3$):** δ 8.17–8.09 (m, 2H), 7.50 (d, J = 8.4 Hz, 2H), 3.94 (s, 3H) ppm. **^{13}C NMR (100 MHz, $CDCl_3$):** δ 166.5, 144.2 (d, J = 248.9 Hz), 140.9 (d, J = 255.0 Hz), 138.0 (d, J = 253.3 Hz), 131.0, 130.4, 130.0, 115.1 (td, J = 17.0, 4.1 Hz), 52.4 ppm. **^{19}F NMR (376 MHz, $CDCl_3$):** δ -142.74 – -143.04 (m, 2F), -154.26 (t, J = 20.9 Hz, 1F), -161.61 – -161.90 (m, 2F) ppm. **IR (KBr, neat):** ν = 2963, 2360, 1730, 1532, 1489, 1281, 1118, 984 cm^{-1}. **HRMS (ESI, m/z):** $[M+H]^+$ calcd for $C_{14}H_8F_5O_2^+$: 303.0439, found: 303.0439.



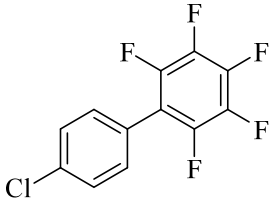
1-(2',3',4',5',6'-Pentafluoro-[1,1'-biphenyl]-4-yl)ethan-1-one (3da):[6] This product was purified by silica gel column chromatography using petroleum ether/ethyl acetate as eluant (petroleum ether/EtOAc = 100:1). 117.5 mg, 82% yield. White solid. M.p. 94.1–95.6 °C. **^{1}H NMR (400 MHz, $CDCl_3$):** δ 8.07–8.03 (m, 2H), 7.52 (d, J = 8.3 Hz, 2H), 2.63 (s, 3H) ppm. **^{13}C NMR (100 MHz, $CDCl_3$):** δ 197.4, 142.5 (dm, J = 244.8 Hz), 139.3 (d, J = 255.0 Hz), 137.5, 136.4 (d, J = 253.0 Hz), 131.1, 130.6, 128.6, 115.0 (td, J = 16.9, 3.9 Hz), 26.7 ppm. **^{19}F NMR (376 MHz, $CDCl_3$):** δ -142.64 (dd, J = 23.7, 9.3 Hz, 2F), -153.80 (t, J = 21.4 Hz, 1F), -160.52 – -162.19 (m, 2F) ppm. **IR (KBr, neat):** ν = 2832, 1609, 1529, 1362, 1269, 1027, 976, 855, 581 cm^{-1}. **HRMS (ESI, m/z):** $[M+H]^+$ calcd for $C_{14}H_8F_5O^+$: 287.0490, found: 287.0492.



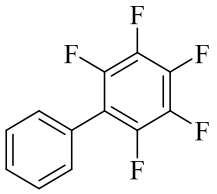
2',3',4',5',6'-Pentafluoro-[1,1'-biphenyl]-4-carbaldehyde (3ea):[6] This product was purified by silica gel column chromatography using petroleum ether/ethyl acetate as eluant (petroleum ether/EtOAc = 100:1). 92.4 mg, 68% yield. White solid. M.p. 78.9–79.5 °C. **^{1}H NMR (400 MHz, $CDCl_3$):** δ 10.09 (s, 1H), 8.01 (d, J = 8.3 Hz, 2H), 7.61 (d, J = 8.2 Hz, 2H) ppm. **^{13}C NMR (100 MHz, $CDCl_3$):** δ 191.6, 144.2 (dm, J = 249.3 Hz), 141.1 (dm, J = 255.5 Hz), 138.0 (dm, J = 253.3 Hz), 136.7, 132.5, 131.1, 130.0, 114.8 (td, J = 16.5, 3.6 Hz) ppm. **^{19}F NMR (376 MHz, $CDCl_3$):** δ -142.57 (dd, J = 22.6, 8.1 Hz, 2F), -153.42 (t, J = 21.0 Hz, 1F), -161.19 (td, J = 21.9, 7.8 Hz, 2F) ppm. **IR (KBr, neat):** ν = 2905, 1708, 1652, 1572, 1486, 1362, 1020, 835, 774 cm^{-1}. **HRMS (ESI, m/z):** $[M+H]^+$ calcd for $C_{13}H_6F_5O^+$: 273.0333, found: 273.0327.



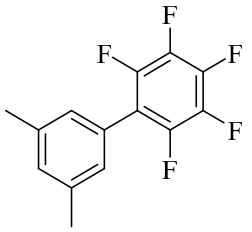
2,3,4,4',5,6-Hexafluoro-1,1'-biphenyl (3fa):[9] This product was purified by silica gel column chromatography using petroleum ether as eluant. 54.5 mg, 42% yield. White solid. M.p. 117.8–119.4 °C. **^{1}H NMR (400 MHz, $CDCl_3$):** δ 7.45–7.38 (m, 2H), 7.23–7.16 (m, 2H) ppm. **^{13}C NMR (100 MHz, $CDCl_3$):** δ 163.3 (d, J = 249.9 Hz), 144.3 (dm, J = 247.3 Hz), 140.6 (dm, J = 248.6 Hz), 138.0 (dm, J = 246.6 Hz), 132.2 (d, J = 8.1 Hz), 122.4–122.3 (m, 1C), 116.1 (d, J = 21.9 Hz), 115.5–114.6 (m, 1C) ppm. **^{19}F NMR (376 MHz, $CDCl_3$):** δ -111.17 – -111.27 (m, 1F), -143.25 (dd, J = 22.9, 8.2 Hz, 2F), -155.14 (t, J = 21.0 Hz, 1F), -161.93 (td, J = 22.6, 8.2 Hz, 2F) ppm. **IR (KBr, neat):** ν = 2359, 1656, 1493, 1403, 1226, 1162, 1066, 985 cm^{-1}. **HRMS (ESI, m/z):** $[M+H]^+$ calcd for $C_{12}H_5F_6^+$: 263.0290, found: 263.0292.



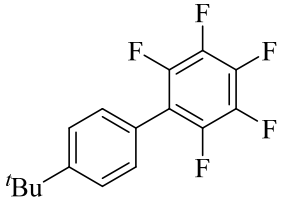
4'-Chloro-2,3,4,5,6-pentafluoro-1,1'-biphenyl (3ga):[10] This product was purified by silica gel column chromatography using petroleum ether as eluant. 103.9 mg, 75% yield. White solid. M.p. 82.9–84.7 °C. **^{1}H NMR (400 MHz, $CDCl_3$):** δ 7.50–7.45 (m, 2H), 7.37 (dt, J = 8.5, 1.2 Hz, 2H) ppm. **^{13}C NMR (100 MHz, $CDCl_3$):** δ 144.1 (dm, J = 248.0 Hz), 140.6 (dm, J = 259.8 Hz), 137.9 (dm, J = 253.2 Hz), 135.8, 131.6, 129.2, 124.9, 115.0 (td, J = 16.9, 4.0 Hz) ppm. **^{19}F NMR (376 MHz, $CDCl_3$):** δ -143.10 – -143.27 (m, 2F), -154.84 (t, J = 20.9 Hz, 1F), -161.74 – -162.01 (m, 2F) ppm. **IR (KBr, neat):** ν = 2925, 2340, 1915, 1656, 1529, 1398, 1016, 984 cm^{-1}. **HRMS (ESI, m/z):** $[M+H]^+$ calcd for $C_{12}H_5ClF_5^+$: 278.9994, found: 278.9985.



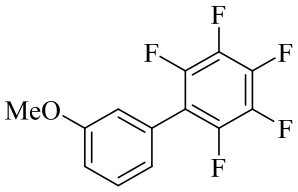
2,3,4,5,6-Pentafluoro-1,1'-biphenyl (3ha):[7] This product was purified by silica gel column chromatography using petroleum ether as eluant. 118.8 mg, 97% yield. White solid. M.p. 114.4–115.4 °C. **^{1}H NMR (400 MHz, $CDCl_3$):** δ 7.55–7.47 (m, 3H), 7.46–7.40 (m, 2H) ppm. **^{13}C NMR (100 MHz, $CDCl_3$):** δ 144.3 (dm, J = 247.6 Hz), 140.5 (dm, J = 239.9 Hz), 137.9 (dm, J = 240.2 Hz), 130.3, 129.4, 128.9, 126.5, 116.1 (td, J = 17.4, 4.0 Hz) ppm. **^{19}F NMR (376 MHz, $CDCl_3$):** δ -143.17 (dd, J = 22.9, 8.2 Hz, 2F), -155.50 (t, J = 21.0 Hz, 1F), -162.02 – -162.33 (m, 2F) ppm. **IR (KBr, neat):** ν = 2340, 1720, 1524, 1440, 1319, 983, 852, 751 cm^{-1}. **HRMS (ESI, m/z):** $[M+H]^+$ calcd for $C_{12}H_6F_5^+$: 245.0384, found: 245.0389.



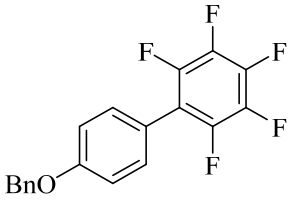
2,3,4,5,6-Pentafluoro-3',5'-dimethyl-1,1'-biphenyl (3ia):[11] This product was purified by silica gel column chromatography using petroleum ether as eluant. 98.5 mg, 72% yield. White solid. M.p. 82.1–82.8 °C. **^{1}H NMR (400 MHz, $CDCl_3$):** δ 7.14 (s, 1H), 7.06 (s, 2H), 2.41 (s, 6H) ppm. **^{13}C NMR (100 MHz, $CDCl_3$):** δ 144.2 (dm, J = 247.1 Hz), 140.3 (dm, J = 239.6 Hz), 138.5, 137.7 (dm, J = 238.7 Hz), 131.1, 127.9, 126.3, 116.5 (ddt, J = 21.6, 15.0, 3.3 Hz), 21.4 ppm. **^{19}F NMR (376 MHz, $CDCl_3$):** δ -140.75 – -145.12 (m, 2F), -156.11 (t, J = 22.3 Hz, 1F), -162.48 (t, J = 25.5 Hz, 2F) ppm. **IR (KBr, neat):** ν = 2973, 2352, 1716, 1602, 1521, 1272, 1049, 857 cm^{-1}. **HRMS (ESI, m/z):** $[M+H]^+$ calcd for $C_{14}H_{10}F_5^+$: 273.0697, found: 273.0702.



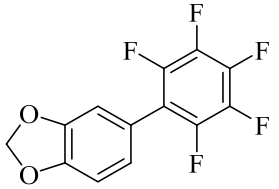
4'-(*tert*-Butyl)-2,3,4,5,6-pentafluoro-1,1'-biphenyl (3ja):[10] This product was purified by silica gel column chromatography using petroleum ether as eluant. 92.9 mg, 62% yield. White solid. M.p. 83.2–85.0 °C. **^{1}H NMR (400 MHz, $CDCl_3$):** δ 7.55–7.51 (m, 2H), 7.38 (dt, J = 8.6, 1.4 Hz, 2H), 1.38 (s, 9H) ppm. **^{13}C NMR (100 MHz, $CDCl_3$):** δ 152.6, 144.4 (dm, J = 247.5 Hz), 140.4 (dm, J = 234.5 Hz), 137.9 (dm, J = 234.0 Hz), 130.0, 125.9, 123.6, 116.4–115.9 (m, 1C), 34.9, 31.4 ppm. **^{19}F NMR (376 MHz, $CDCl_3$):** δ -143.25 (dd, J = 23.0, 8.1 Hz, 2F), -156.07 (t, J = 21.0 Hz, 1F), -162.19 – -162.50 (m, 2F) ppm. **IR (KBr, neat):** ν = 2967, 2360, 1649, 1492, 1314, 1267, 985, 863 cm^{-1}. **HRMS (ESI, m/z):** $[M+H]^+$ calcd for $C_{16}H_{14}F_5^+$: 301.1010, found: 301.1012.



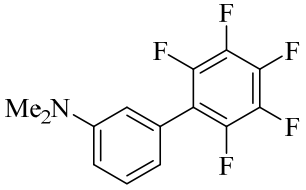
2,3,4,5,6-Pentafluoro-3'-methoxy-1,1'-biphenyl (3ka):[10] This product was purified by silica gel column chromatography using petroleum ether as eluant. 120.9 mg, 88% yield. White solid. M.p. 33.8–34.7 °C. **^{1}H NMR (400 MHz, $CDCl_3$):** δ 7.45–7.38 (m, 1H), 7.01 (dt, J = 7.6, 2.1 Hz, 2H), 6.98–6.94 (m, 1H), 3.85 (s, 3H) ppm. **^{13}C NMR (100 MHz, $CDCl_3$):** δ 159.8, 144.3 (dm, J = 247.8 Hz), 140.5 (dm, J = 260.5 Hz), 138.0 (dm, J = 251.0 Hz), 129.9, 127.6, 122.6, 116.0, 115.0, 55.5 ppm. **^{19}F NMR (376 MHz, $CDCl_3$):** δ -142.72 (dd, J = 22.9, 8.1 Hz, 2F), -155.51 (t, J = 21.0 Hz, 1F), -162.02 – -162.36 (m, 2F) ppm. **IR (KBr, neat):** ν = 2360, 1654, 1523, 1291, 1088, 990, 881, 782 cm^{-1}. **HRMS (ESI, m/z):** $[M+H]^+$ calcd for $C_{13}H_8F_5O^+$: 275.0490, found: 275.0496.



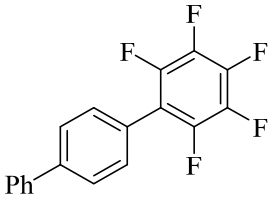
4'-(Benzyloxy)-2,3,4,5,6-pentafluoro-1,1'-biphenyl (3la):[12] This product was purified by silica gel column chromatography using petroleum ether as eluant. 96.3 mg, 55% yield. White solid. M.p. 148.8–149.4 °C. **^{1}H NMR (400 MHz, $CDCl_3$):** δ 7.49–7.45 (m, 2H), 7.45–7.40 (m, 2H), 7.40–7.34 (m, 3H), 7.13–7.08 (m, 2H), 5.13 (s, 2H) ppm. **^{13}C NMR (100 MHz, $CDCl_3$):** δ 159.6, 144.3 (dm, J = 242.7 Hz), 140.4 (dm, J = 208.3 Hz), 137.9 (dm, J = 205.5 Hz), 136.7, 131.6, 128.8, 128.3, 127.7, 118.8, 116.0–115.7 (m, 1C), 115.2, 70.2 ppm. **^{19}F NMR (376 MHz, $CDCl_3$):** δ -143.47 (dd, J = 23.2, 8.1 Hz, 2F), -156.28 (t, J = 21.1 Hz, 1F), -162.20 – -162.52 (m, 2F) ppm. **IR (KBr, neat):** ν = 2864, 2340, 1608, 1511, 1380, 1250, 1022, 869 cm^{-1}. **HRMS (ESI, m/z):** $[M+H]^+$ calcd for $C_{19}H_{12}F_5O^+$: 351.0803, found: 351.0806.



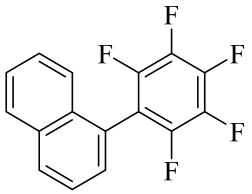
5-(Perfluorophenyl)benzo[*d*][1,3]dioxole (3ma):[6] This product was purified by silica gel column chromatography using petroleum ether as eluant. 81.6 mg, 57% yield. White solid. M.p. 86.9–87.4 °C. **^{1}H NMR (400 MHz, $CDCl_3$):** δ 6.95–6.86 (m, 3H), 6.04 (s, 2H) ppm. **^{13}C NMR (100 MHz, $CDCl_3$):** δ 148.6, 148.1, 144.5 (dm, J = 247.0 Hz), 140.7 (dm, J = 238.7 Hz), 138.1 (dm, J = 245.6 Hz), 124.4, 119.6, 115.8 (td, J = 17.0, 3.8 Hz), 110.5, 108.8, 101.7 ppm. **^{19}F NMR (376 MHz, $CDCl_3$):** δ -143.12 (dd, J = 23.1, 8.1 Hz, 2F), -155.92 (t, J = 21.0 Hz, 1F), -162.11 – -162.32 (m, 2F) ppm. **IR (KBr, neat):** ν = 2913, 2360, 1655, 1561, 1492, 1246, 1053, 986 cm^{-1}. **HRMS (ESI, m/z):** $[M+H]^+$ calcd for $C_{13}H_6F_5O_2^+$: 289.0282, found: 289.0290.



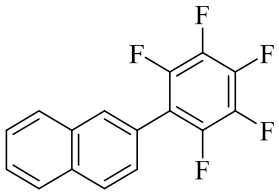
2',3',4',5',6'-Pentafluoro-*N*,*N*-dimethyl-[1,1'-biphenyl]-3-amine (3na):[10] This product was purified by silica gel column chromatography using petroleum ether as eluant. 111.4 mg, 78% yield. White solid. M.p. 91.4–92.4 °C. **^{1}H NMR (400 MHz, $CDCl_3$):** δ 7.39–7.33 (m, 1H), 6.84 (dd, J = 8.4, 2.6 Hz, 1H), 6.77–6.71 (m, 2H), 3.01 (s, 6H) ppm. **^{13}C NMR (100 MHz, $CDCl_3$):** δ 150.7, 144.4 (d, J = 247.0 Hz), 140.3 (dm, J = 243.4 Hz), 137.9 (d, J = 251.9 Hz), 129.5, 127.1, 118.1, 117.0 (td, J = 17.6, 3.7 Hz), 114.0, 113.3, 40.6 ppm. **^{19}F NMR (376 MHz, $CDCl_3$):** δ -142.46 (dd, J = 23.2, 8.1 Hz, 2F), -156.28 (t, J = 21.1 Hz, 1F), -162.33 – -162.67 (m, 2F) ppm. **IR (KBr, neat):** ν = 2925, 2359, 1603, 1492, 1235, 1069, 884, 748 cm^{-1}. **HRMS (ESI, m/z):** $[M+H]^+$ calcd for $C_{14}H_{11}F_5N^+$: 288.0806, found: 288.0810.



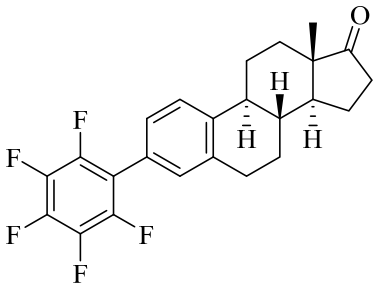
2,3,4,5,6-Pentafluoro-1,1':4',1''-terphenyl (3oa):[9] This product was purified by silica gel column chromatography using petroleum ether as eluant. 94.7 mg, 59% yield. White solid. M.p. 196.6–198.5 °C. **^{1}H NMR (400 MHz, $CDCl_3$):** δ 7.76–7.69 (m, 2H), 7.67–7.62 (m, 2H), 7.54–7.45 (m, 4H), 7.43–7.37 (m, 1H) ppm. **^{13}C NMR (100 MHz, $CDCl_3$):** δ 144.3 (dm, J = 244.7 Hz), 142.4, 141.0 (dm, J = 169.6 Hz), 140.3, 139.3 (d, J = 248.3 Hz), 130.7 (t, J = 2.2 Hz), 129.1, 128.0, 127.6, 127.3, 125.4, 115.8 (td, J = 18.0, 3.1 Hz) ppm. **^{19}F NMR (376 MHz, $CDCl_3$):** δ -144.76 (dd, J = 23.1, 7.5 Hz, 2F), -156.99 (t, J = 21.0 Hz, 1F), -163.62 (td, J = 22.6, 7.8 Hz, 2F) ppm. **IR (KBr, neat):** v = 1961, 1656, 1488, 1406, 1261, 1199, 1061, 979, 859 cm^{-1}. **HRMS (ESI, m/z):** $[M+H]^+$ calcd for $C_{18}H_{10}F_5^+$: 321.0697, found: 321.0706.



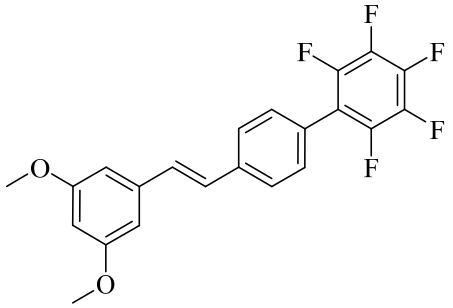
1-(Perfluorophenyl)naphthalene (3pa):[6] This product was purified by silica gel column chromatography using petroleum ether as eluant. 142.5 mg, 97% yield. White solid. M.p. 89.7–90.8 °C. **^{1}H NMR (400 MHz, $CDCl_3$):** δ 8.00 (dd, J = 20.0, 7.9 Hz, 2H), 7.63–7.50 (m, 4H), 7.48 (d, J = 6.7 Hz, 1H) ppm. **^{13}C NMR (100 MHz, $CDCl_3$):** δ 144.8 (dm, J = 247.5 Hz), 141.1 (dm, J = 253.9 Hz), 137.9 (dm, J = 253.3 Hz), 133.8, 131.6, 130.3, 129.1, 128.8, 127.2, 126.5, 125.4, 124.7, 123.9, 114.5 (td, J = 19.7, 3.9 Hz) ppm. **^{19}F NMR (376 MHz, $CDCl_3$):** δ -139.12 – -139.44 (m, 2F), -154.48 (t, J = 20.9 Hz, 1F), -161.54 – -161.90 (m, 2F) ppm. **IR (KBr, neat):** v = 2925, 2360, 1655, 1524, 1491, 1026, 985, 784 cm^{-1}. **HRMS (ESI, m/z):** $[M+H]^+$ calcd for $C_{16}H_8F_5^+$: 295.0541, found: 295.0539.



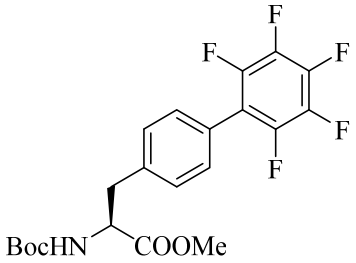
2-(Perfluorophenyl)naphthalene (3qa):[6] This product was purified by silica gel column chromatography using petroleum ether as eluant. 117.8 mg, 80% yield. White solid. M.p. 165.2–167.1 °C. **^{1}H NMR (400 MHz, $CDCl_3$):** δ 7.99–7.89 (m, 4H), 7.62–7.54 (m, 2H), 7.50 (dd, J = 8.7, 1.6 Hz, 1H) ppm. **^{13}C NMR (100 MHz, $CDCl_3$):** δ 144.5 (dm, J = 247.6 Hz), 140.7 (dm, J = 238.6 Hz), 138.0 (dm, J = 238.3 Hz), 133.4, 133.2, 130.2, 128.6, 128.4, 127.9, 127.3, 127.2, 126.8, 123.8, 116.4–115.9 (m, 1C) ppm. **^{19}F NMR (376 MHz, $CDCl_3$):** δ -142.89 (dd, J = 23.0, 8.2 Hz, 2F), -155.27 (t, J = 21.0 Hz, 1F), -161.82 – -162.22 (m, 2F) ppm. **IR (KBr, neat):** v = 2940, 1655, 1524, 1488, 1062, 984, 829, 781 cm^{-1}. **HRMS (ESI, m/z):** $[M+H]^+$ calcd for $C_{16}H_8F_5^+$: 295.0541, found: 295.0536.



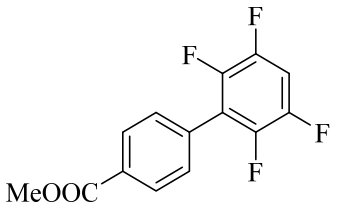
(8*R*,9*S*,13*S*,14*S*)-13-Methyl-3-(perfluorophenyl)-6,7,8,9,11,12,13,14,15,16-decahydro-17*H*-cyclopenta[*a*]phenanthren-17-one (3ra):[6] This product was purified by silica gel column chromatography using petroleum ether/ethyl acetate as eluant (petroleum ether/EtOAc = 50:1). 111.1 mg, 53% yield. White solid. M.p. 153.2–155.1 °C. **^{1}H NMR (400 MHz, $CDCl_3$):** δ 7.42 (d, J = 8.1 Hz, 1H), 7.21 (d, J = 8.1 Hz, 1H), 7.16 (s, 1H), 2.98 (dd, J = 8.5, 4.0 Hz, 2H), 2.57–2.43 (m, 2H), 2.37 (td, J = 10.7, 3.8 Hz, 1H), 2.20–1.96 (m, 4H), 1.73–1.50 (m, 6H), 0.94 (s, 3H) ppm. **^{13}C NMR (100 MHz, $CDCl_3$):** δ 220.8, 144.3 (dm, J = 247.2 Hz), 141.3, 140.5 (dm, J = 226.2 Hz), 137.7 (dm, J = 250.5 Hz), 137.2, 130.7, 127.5, 125.9, 123.9, 116.3–115.6 (m, 1C), 50.6, 48.1, 44.5, 38.0, 35.9, 31.7, 29.4, 26.5, 25.7, 21.7, 13.9 ppm. **^{19}F NMR (376 MHz, $CDCl_3$):** δ -143.08 (dd, J = 23.2, 8.2 Hz, 2F), -155.92 (t, J = 21.1 Hz, 1F), -162.28 (td, J = 22.5, 8.1 Hz, 2F) ppm. **IR (KBr, neat):** v = 2932, 2560, 1737, 1525, 1494, 1260, 1006, 983 cm^{-1}. **HRMS (ESI, m/z):** $[M+H]^+$ calcd for $C_{24}H_{22}F_5O^+$: 421.1585, found: 421.1584.



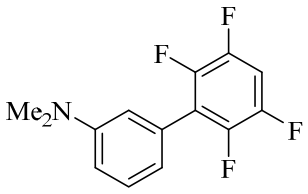
(*E*)-4'-(3,5-Dimethoxystyryl)-2,3,4,5,6-pentafluoro-1,1'-biphenyl (3sa): This product was purified by silica gel column chromatography using petroleum ether/ethyl acetate as eluant (petroleum ether/EtOAc = 100:1). 157.0 mg, 77% yield. White solid. M.p. 138.5–139.0 °C. **^{1}H NMR (400 MHz, $CDCl_3$):** δ 7.61 (d, J = 8.4 Hz, 2H), 7.43 (d, J = 8.3 Hz, 2H), 7.11 (s, 2H), 6.70 (d, J = 2.2 Hz, 2H), 6.43 (t, J = 2.2 Hz, 1H), 3.85 (s, 6H) ppm. **^{13}C NMR (100 MHz, $CDCl_3$):** δ 161.1, 144.3 (dm, J = 247.5 Hz), 140.5 (dm, J = 227.8 Hz), 139.0, 138.3, 137.9 (dm, J = 245.1 Hz), 130.6, 130.3, 128.2, 126.9, 125.5, 115.7 (td, J = 17.0, 4.1 Hz), 104.9, 100.4, 55.5 ppm. **^{19}F NMR (376 MHz, $CDCl_3$):** δ -143.08 (dd, J = 23.1, 8.1 Hz, 2F), -155.46 (t, J = 21.1 Hz, 1F), -161.90 – -162.17 (m, 2F) ppm. **IR (KBr, neat):** v = 2340, 1594, 1511, 1208, 1154, 964, 809, 716 cm^{-1}. **HRMS (ESI, m/z):** $[M+H]^+$ calcd for $C_{22}H_{16}F_5O_2^+$: 407.1065, found: 407.1065.



Methyl (*S*)-2-((*tert*-butoxycarbonyl)amino)-3-(2',3',4',5',6'-pentafluoro-[1,1'-biphenyl]-4-yl)propanoate (3ta): This product was purified by silica gel column chromatography using petroleum ether/ethyl acetate as eluant (petroleum ether/EtOAc = 20:1). 71.1 mg, 32% yield. White solid. M.p. 121.9–122.9 °C. **^{1}H NMR (400 MHz, $CDCl_3$):** δ 7.35 (d, J = 8.0 Hz, 2H), 7.27 (d, J = 8.0 Hz, 2H), 5.08 (d, J = 8.0 Hz, 1H), 4.64 (q, J = 6.4 Hz, 1H), 3.73 (s, 3H), 3.20 (dd, J = 13.7, 5.6 Hz, 1H), 3.08 (dd, J = 13.8, 6.6 Hz, 1H), 1.41 (s, 9H) ppm. **^{13}C NMR (100 MHz, $CDCl_3$):** δ 172.3, 155.2, 145.3 (dm, J = 247.6 Hz), 141.5 (dm, J = 239.7 Hz), 139.0 (dm, J = 242.6 Hz), 137.8, 130.4, 129.8, 125.2, 115.8 (td, J = 15.7, 14.6 Hz), 80.2, 54.4, 52.4, 38.4, 28.4 ppm. **^{19}F NMR (376 MHz, $CDCl_3$):** δ -143.94 (d, J = 26.3 Hz, 2F), -156.39 (t, J = 22.7 Hz, 1F), -161.52 – -164.80 (m, 2F) ppm. **IR (KBr, neat):** ν = 2934, 1737, 1509, 1439, 1368, 1295, 1175, 990 cm^{-1}. **HRMS (ESI, m/z):** $[M+H]^+$ calcd for $C_{21}H_{21}F_5NO_4^+$: 446.1385, found: 446.1386.

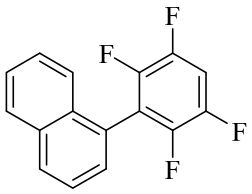


Methyl 2',3',5',6'-tetrafluoro-[1,1'-biphenyl]-4-carboxylate (4cb):[6] This product was purified by silica gel column chromatography using petroleum ether/ethyl acetate as eluant (petroleum ether/EtOAc = 100:1). 59.0 mg, 42% yield. White solid. M.p. 152.5–153.8 °C. **^{1}H NMR (400 MHz, $CDCl_3$):** δ 8.19–8.13 (m, 2H), 7.54 (dt, J = 8.3, 1.4 Hz, 2H), 7.11 (tt, J = 9.6, 7.3 Hz, 1H), 3.95 (s, 3H) ppm. **^{13}C NMR (100 MHz, $CDCl_3$):** δ 166.6, 146.3 (dm, J = 248.4 Hz), 143.6 (dm, J = 248.1 Hz), 132.1, 130.9, 130.4, 129.9, 120.6 (t, J = 16.2 Hz), 105.7 (t, J = 22.6 Hz), 52.5 ppm. **^{19}F NMR (376 MHz, $CDCl_3$):** δ -138.4 – -138.5 (m, 2F), -143.3 – -143.4 (m, 2F) ppm. **IR (KBr, neat):** ν = 2360, 1718, 1604, 1493, 1271, 1120, 935, 853 cm^{-1}. **HRMS (ESI, m/z):** $[M+H]^+$ calcd for $C_{14}H_9F_4O_2^+$: 285.0533, found: 285.0535.

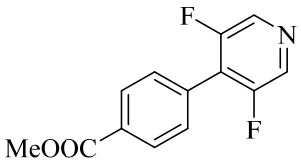


2',3',5',6'-Tetrafluoro-*N*,*N*-dimethyl-[1,1'-biphenyl]-3-amine (4nb): This product was purified by silica gel column chromatography using petroleum ether as eluant. 44.8 mg, 33% yield. Yellow oil. **^{1}H NMR (400 MHz, $CDCl_3$):** δ 7.39–7.33 (m, 1H), 7.05 (tt, J = 9.7, 7.3 Hz, 1H), 6.84–6.81 (m, 1H), 6.80–6.75 (m, 2H), 3.00 (s, 6H) ppm. **^{13}C NMR (100 MHz, $CDCl_3$):** δ 150.6, 146.3 (dm, J = 236.3 Hz), 143.8 (dm, J = 228.2 Hz), 129.3, 128.2, 123.0–122.2 (m, 1C), 118.2, 114.0, 113.3, 104.6 (t, J = 22.8 Hz), 40.6 ppm. **^{19}F NMR (376 MHz, $CDCl_3$):** δ -139.49 (dd, J = 22.6, 12.8 Hz,

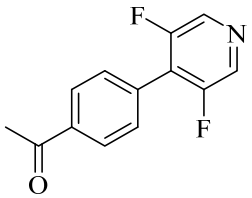
2F), -143.21 (dd, J = 22.6, 12.7 Hz, 2F) ppm. **IR (KBr, neat):** v = 2360, 1603, 1493, 1445, 1354, 1261, 1173, 936 cm^{-1}. **HRMS (ESI, m/z):** $[M+H]^+$ calcd for $C_{14}H_{12}F_4N^+$: 270.0900, found: 270.0904.



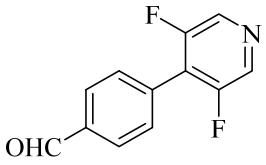
1-(2,3,5,6-Tetrafluorophenyl)naphthalene (4pb):[13] This product was purified by silica gel column chromatography using petroleum ether as eluant. 99.7 mg, 72% yield. White solid. M.p. 77.9–79.7 °C. **^{1}H NMR (400 MHz, $CDCl_3$):** δ 8.01 (d, J = 8.2 Hz, 1H), 7.99–7.94 (m, 1H), 7.64–7.47 (m, 5H), 7.21 (tt, J = 9.7, 7.3 Hz, 1H) ppm. **^{13}C NMR (100 MHz, $CDCl_3$):** δ 146.2 (dm, J = 248.2 Hz), 144.4 (dm, J = 246.4 Hz), 133.8, 131.6, 130.1, 128.8, 128.7, 127.1, 126.5, 125.3, 125.0, 124.9, 120.3 (t, J = 19.0 Hz), 105.7 (t, J = 22.6 Hz) ppm. **^{19}F NMR (376 MHz, $CDCl_3$):** δ -138.6 – -138.8 (m, 2F), -139.9 – -140.0 (m, 2F) ppm. **IR (KBr, neat):** v = 2360, 1607, 1489, 1398, 1174, 1036, 892, 776 cm^{-1}. **HRMS (ESI, m/z):** $[M+H]^+$ calcd for $C_{16}H_9F_4^+$: 277.0635, found: 277.0636.



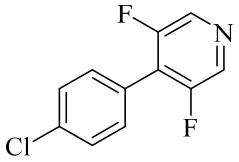
Methyl 4-(3,5-difluoropyridin-4-yl)benzoate (4cc): This product was purified by silica gel column chromatography using petroleum ether/ethyl acetate as eluant (petroleum ether/EtOAc = 20:1). 75.7 mg, 61% yield. White solid. M.p. 103.3–104.7 °C. **^{1}H NMR (400 MHz, $CDCl_3$):** δ 8.45 (s, 2H), 8.15 (d, J = 8.6 Hz, 2H), 7.59 (d, J = 8.5 Hz, 2H), 3.94 (s, 3H) ppm. **^{13}C NMR (100 MHz, $CDCl_3$):** δ 166.5, 156.0 (dd, J = 261.9, 1.9 Hz), 135.3–134.5 (m, 1C), 131.9, 131.2 (d, J = 8.8 Hz), 130.2 (t, J = 2.2 Hz), 129.8, 124.6 (t, J = 15.0 Hz), 52.5 ppm. **^{19}F NMR (376 MHz, $CDCl_3$):** δ -129.78 (s, 2F) ppm. **IR (KBr, neat):** v = 2360, 1729, 1544, 1423, 1283, 1114, 1021, 855 cm^{-1}. **HRMS (ESI, m/z):** $[M+H]^+$ calcd for $C_{13}H_{10}F_2NO_2^+$: 250.0674, found: 250.0672.



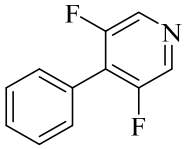
1-(4-(3,5-Difluoropyridin-4-yl)phenyl)ethan-1-one (4dc): This product was purified by silica gel column chromatography using petroleum ether/ethyl acetate as eluant (petroleum ether/EtOAc = 20:1). 80.9 mg, 69% yield. White solid. M.p. 107.3–109.0 °C. **^{1}H NMR (400 MHz, $CDCl_3$):** δ 8.47 (s, 2H), 8.09 (d, J = 8.4 Hz, 2H), 7.64 (d, J = 8.3 Hz, 2H), 2.66 (s, 3H) ppm. **^{13}C NMR (100 MHz, $CDCl_3$):** δ 197.6, 156.1 (d, J = 260.3 Hz), 137.8, 135.7–134.4 (m, 1C), 131.3, 130.5, 128.6, 125.2–123.8 (m, 1C), 26.9 ppm. **^{19}F NMR (376 MHz, $CDCl_3$):** δ -129.61 (s, 2F) ppm. **IR (KBr, neat):** v = 3416, 2926, 2832, 1679, 1421, 1362, 1145, 962, 835, 552 cm^{-1}. **HRMS (ESI, m/z):** $[M+H]^+$ calcd for $C_{13}H_{10}F_2NO^+$: 234.0725, found: 234.0729.



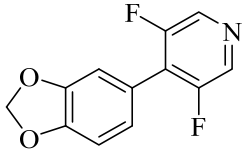
4-(3,5-Difluoropyridin-4-yl)benzaldehyde (4ec): This product was purified by silica gel column chromatography using petroleum ether/ethyl acetate as eluant (petroleum ether/EtOAc = 20:1). 67.7 mg, 62% yield. White solid. M.p. 103.3–104.7 °C. **^{1}H NMR (400 MHz, $CDCl_3$):** δ 10.08 (s, 1H), 8.47 (s, 2H), 8.03–7.98 (m, 2H), 7.69 (d, J = 8.2 Hz, 2H) ppm. **^{13}C NMR (100 MHz, $CDCl_3$):** δ 191.7, 155.9 (d, J = 261.0 Hz), 136.8, 135.1 (d, J = 28.5 Hz), 132.6, 130.9, 129.8, 124.4 (td, J = 15.7, 3.3 Hz) ppm. **^{19}F NMR (376 MHz, $CDCl_3$):** δ -129.54 (s, 2F) ppm. **IR (KBr, neat):** ν = 3037, 2831, 1708, 1428, 1365, 1291, 1151, 1022, 830, 768 cm^{-1}. **HRMS (ESI, m/z):** $[M+H]^+$ calcd for $C_{12}H_8F_2NO^+$: 220.0568, found: 220.0566.



4-(4-Chlorophenyl)-3,5-difluoropyridine (4gc): This product was purified by silica gel column chromatography using petroleum ether/ethyl acetate as eluant (petroleum ether/EtOAc = 50:1). 70.5 mg, 62% yield. White solid. M.p. 84.9–86.3 °C. **^{1}H NMR (400 MHz, $CDCl_3$):** δ 8.44 (s, 2H), 7.50–7.45 (m, 4H) ppm. **^{13}C NMR (100 MHz, $CDCl_3$):** δ 156.1 (d, J = 262.8 Hz), 136.0, 135.0 (d, J = 29.3 Hz), 131.5, 129.1, 125.0, 124.5 (t, J = 14.9 Hz) ppm. **^{19}F NMR (376 MHz, $CDCl_3$):** δ -130.04 (s, 2F) ppm. **IR (KBr, neat):** ν = 2360, 1594, 1478, 1397, 1274, 1150, 1021, 828 cm^{-1}. **HRMS (ESI, m/z):** $[M+H]^+$ calcd for $C_{11}H_7ClF_2N^+$: 226.0230, found: 226.0231.

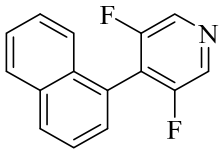


3,5-Difluoro-4-phenylpyridine (4hc):[14] This product was purified by silica gel column chromatography using petroleum ether/ethyl acetate as eluant (petroleum ether/EtOAc = 50:1). 60.6 mg, 63% yield. Yellow solid. M.p. 89.5–91.3 °C. **^{1}H NMR (400 MHz, $CDCl_3$):** δ 8.44 (s, 2H), 7.56–7.44 (m, 5H) ppm. **^{13}C NMR (100 MHz, $CDCl_3$):** δ 156.3 (d, J = 260.8 Hz), 134.9 (d, J = 29.4 Hz), 130.1, 129.7, 128.7, 126.6, 125.7 (t, J = 15.2 Hz) ppm. **^{19}F NMR (376 MHz, $CDCl_3$):** δ -130.24 (s, 2F) ppm. **IR (KBr, neat):** ν = 2360, 1550, 1418, 1291, 1143, 1019, 883, 770 cm^{-1}. **HRMS (ESI, m/z):** $[M+H]^+$ calcd for $C_{11}H_8F_2N^+$: 192.0619, found: 192.0614.



4-(Benzo[*d*][1,3]dioxol-5-yl)-3,5-difluoropyridine (4mc): This product was purified by silica gel column chromatography using petroleum ether/ethyl acetate as eluant (petroleum ether/EtOAc = 20:1). 76.1 mg, 64% yield. White solid. M.p. 124.1–125.2 °C. **^{1}H NMR (400 MHz, $CDCl_3$):** δ 8.40 (s, 2H), 7.03 (dq, J = 8.1, 1.5 Hz, 1H), 7.00 (q, J = 1.4 Hz, 1H), 6.93 (d, J = 8.1 Hz, 1H), 6.04

(s, 2H) ppm. **^{13}C NMR (100 MHz, $CDCl_3$):** δ 156.3 (dd, J = 260.2, 2.1 Hz), 148.8, 148.0, 135.5–133.8 (m, 1C), 125.4 (t, J = 14.8 Hz), 124.6 (t, J = 2.6 Hz), 119.8, 110.4 (t, J = 2.5 Hz), 108.7, 101.7 ppm. **^{19}F NMR (376 MHz, $CDCl_3$):** δ -130.23 (s, 2F) ppm. **IR (KBr, neat):** ν = 2360, 1604, 1510, 1421, 1342, 1248, 1041, 933 cm^{-1}. **HRMS (ESI, m/z):** $[M+H]^+$ calcd for $C_{12}H_8F_2NO_2^+$: 236.0518, found: 236.0519.



3,5-Difluoro-4-(naphthalen-1-yl)pyridine (4pc): This product was purified by silica gel column chromatography using petroleum ether/ethyl acetate as eluant (petroleum ether/EtOAc = 50:1). 81.1 mg, 67% yield. White solid. M.p. 96.3–97.6 °C. **^{1}H NMR (400 MHz, $CDCl_3$):** δ 8.55 (d, J = 6.7 Hz, 2H), 8.01–7.94 (m, 2H), 7.63–7.47 (m, 5H) ppm. **^{13}C NMR (100 MHz, $CDCl_3$):** δ 157.0 (dd, J = 260.9, 1.9 Hz), 156.0 (d, J = 267.0 Hz), 135.1–134.3 (m, 1C), 133.7, 131.1, 130.3, 128.7, 128.5, 127.1, 126.5, 125.3, 124.8, 124.2 ppm. **^{19}F NMR (376 MHz, $CDCl_3$):** δ -138.46 (s, 2F) ppm. **IR (KBr, neat):** ν = 2360, 1592, 1508, 1421, 1284, 1031, 874, 776 cm^{-1}. **HRMS (ESI, m/z):** $[M+H]^+$ calcd for $C_{15}H_{10}F_2N^+$: 242.0776, found: 242.0776.

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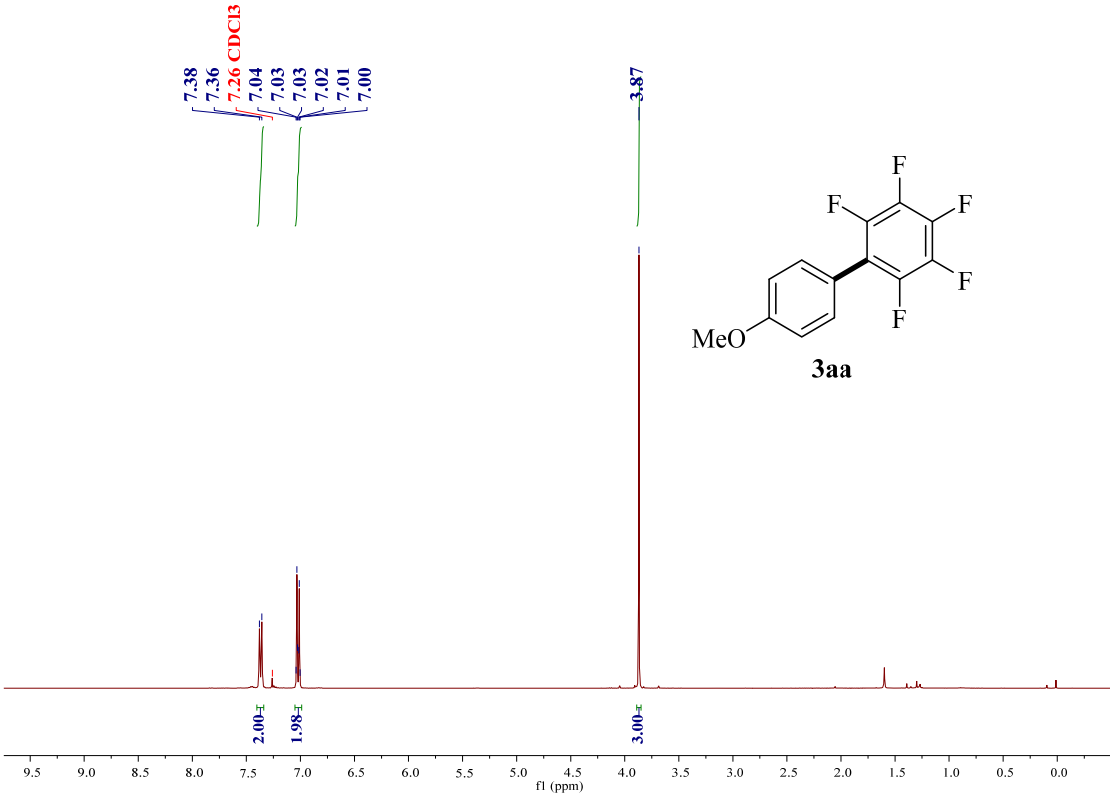
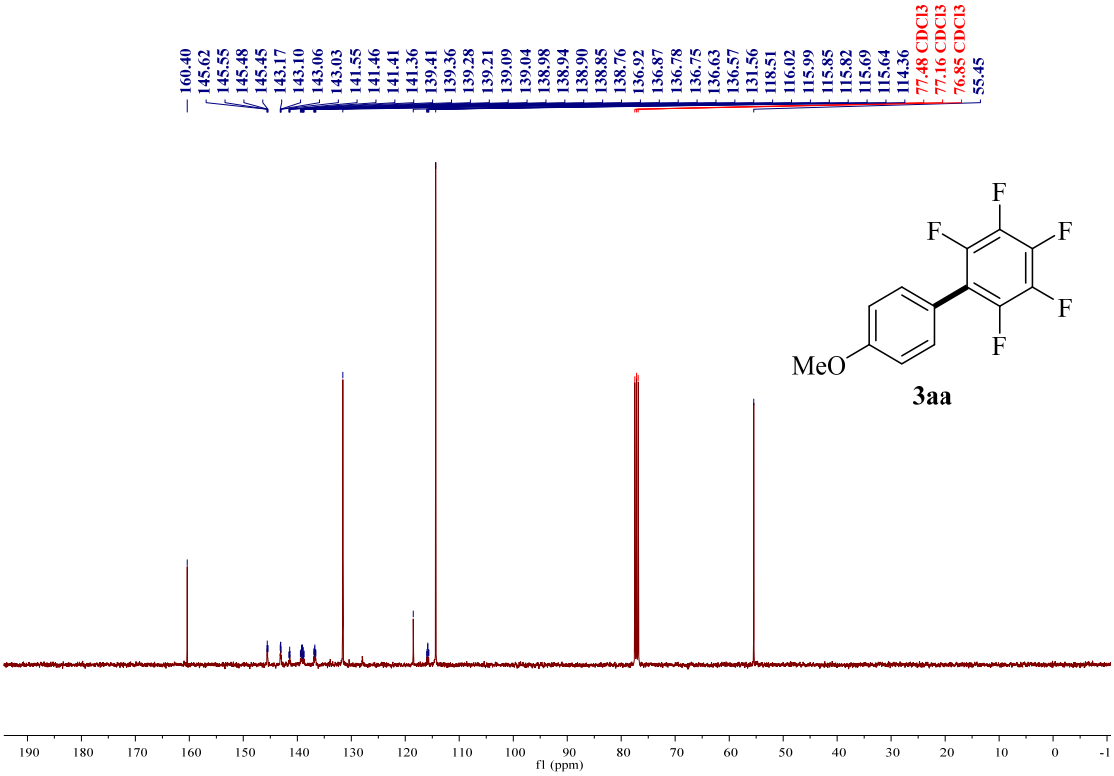
^{1}H, ^{13}C, and ^{19}F NMR spectra of products

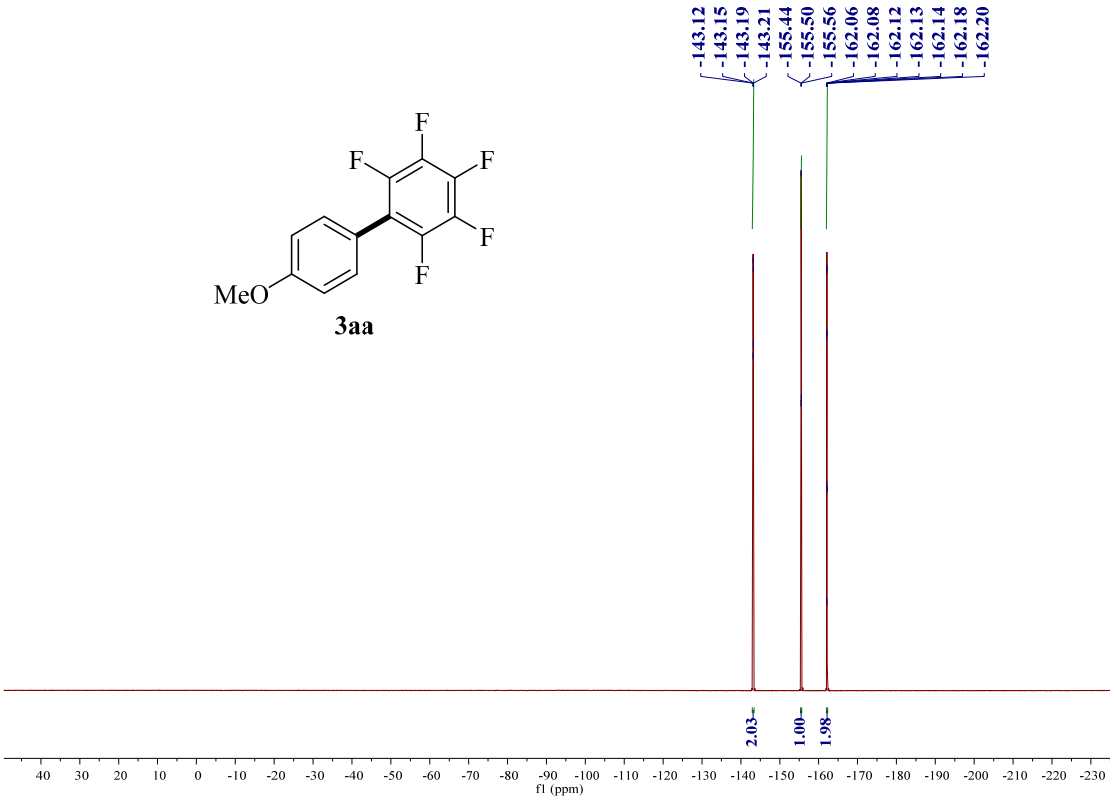
^{1}H NMR spectrum of 3aa (400 MHz, $CDCl_3$)



^{13}C NMR spectrum of 3aa (100 MHz, $CDCl_3$)

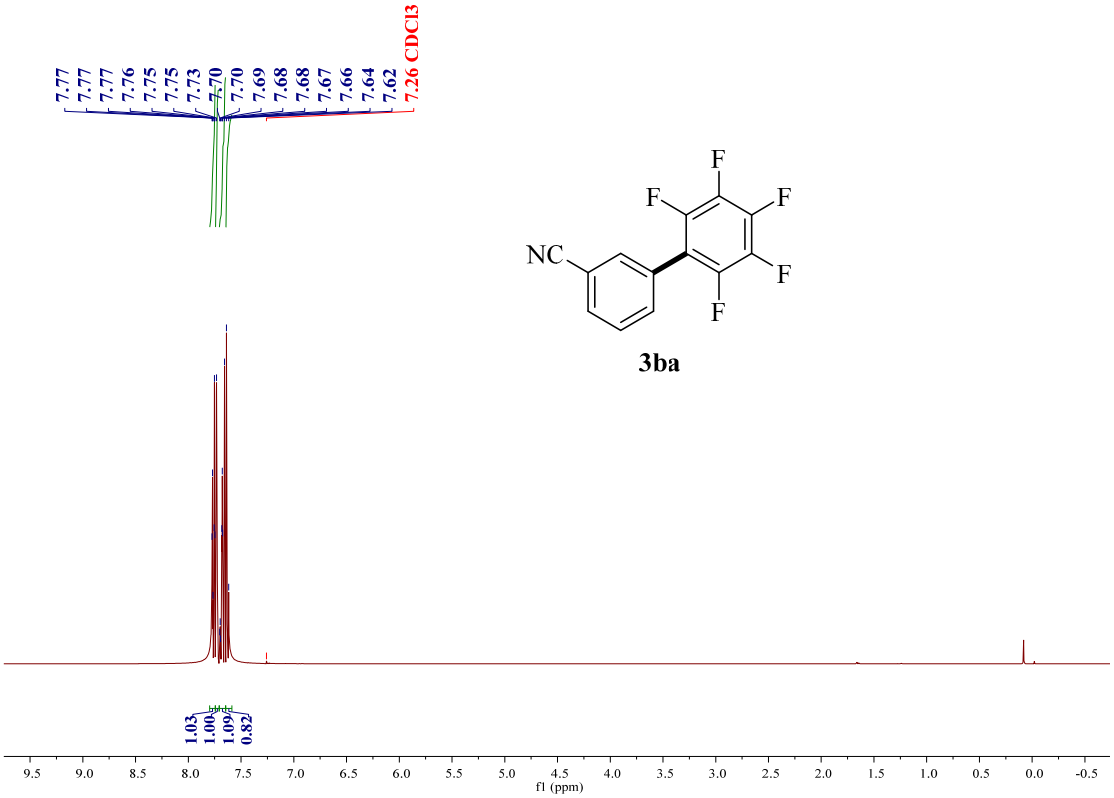


^{19}F NMR spectrum of 3aa (376 MHz, $CDCl_3$)



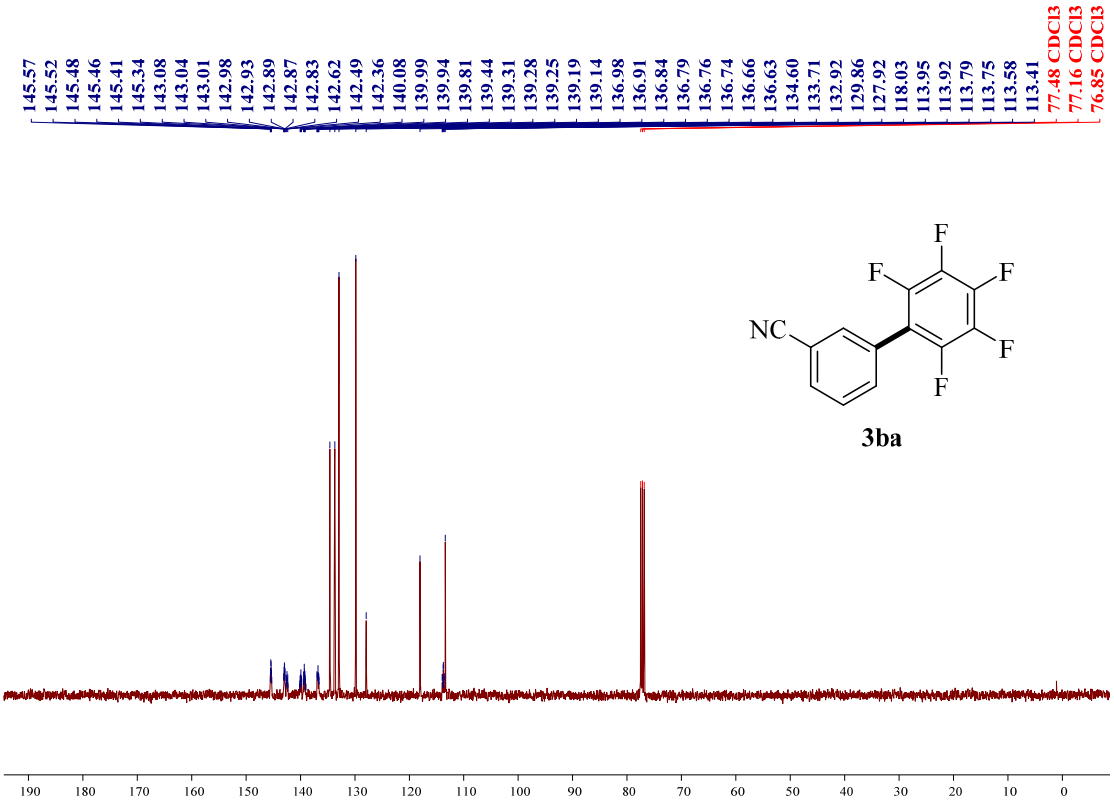
3aa

^{1}H NMR spectrum of 3ba (400 MHz, $CDCl_3$)



3ba

^{13}C NMR spectrum of 3ba (100 MHz, $CDCl_3$)



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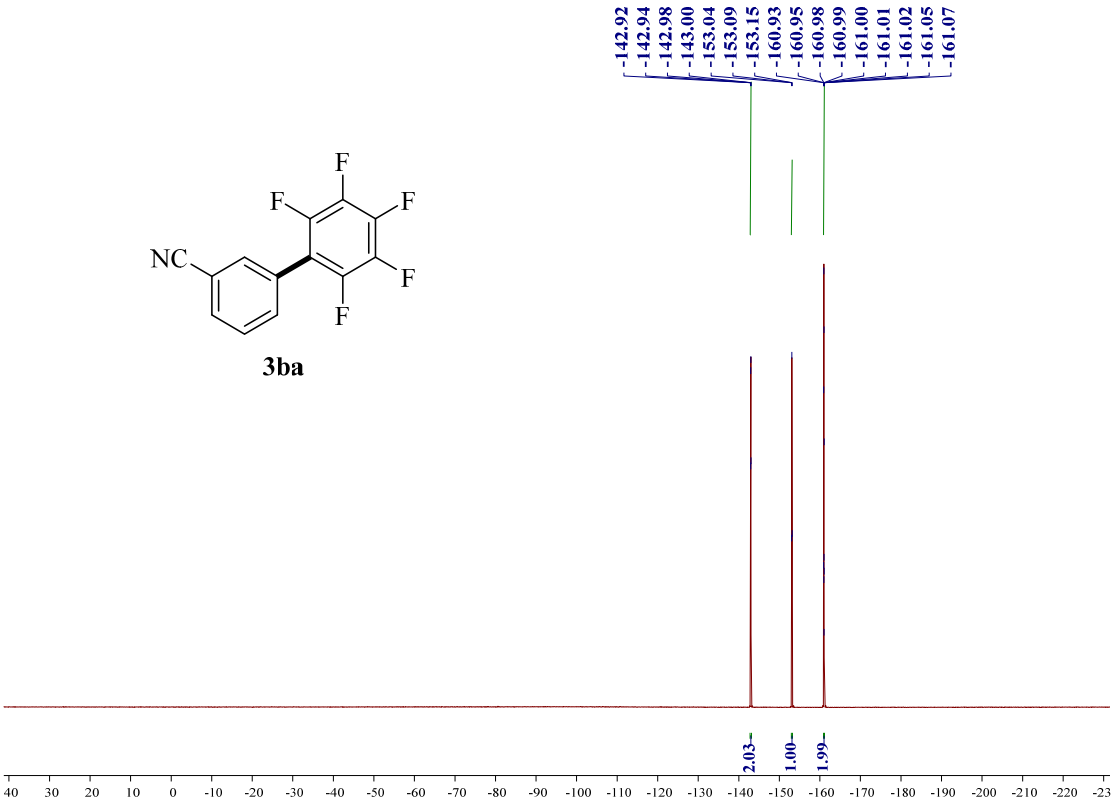
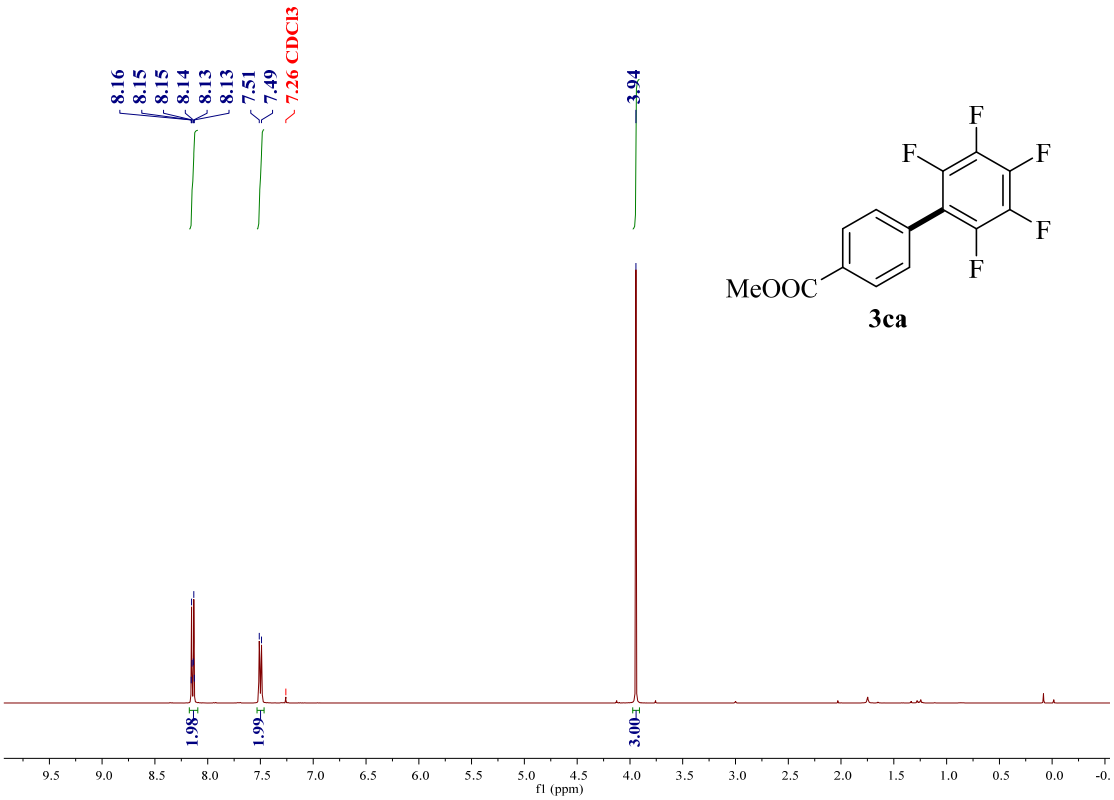
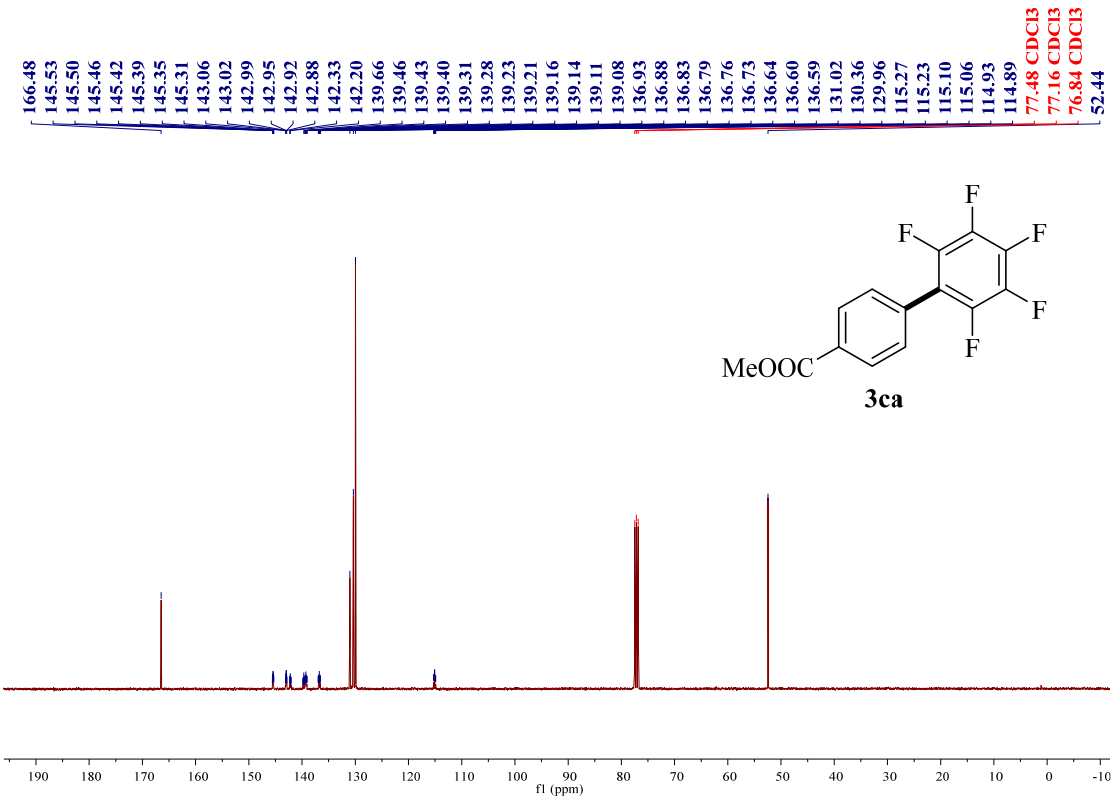


^{1}H NMR spectrum of 3ca (400 MHz, $CDCl_3$)



^{13}C NMR spectrum of 3ca (100 MHz, $CDCl_3$)



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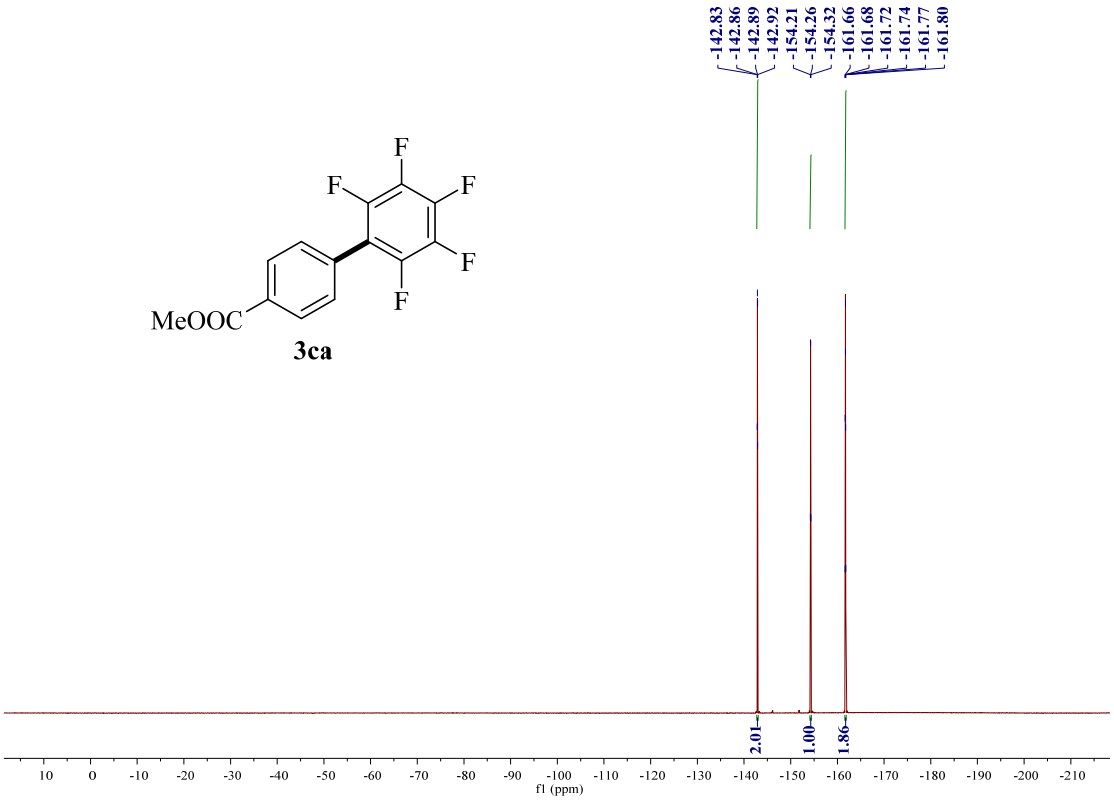
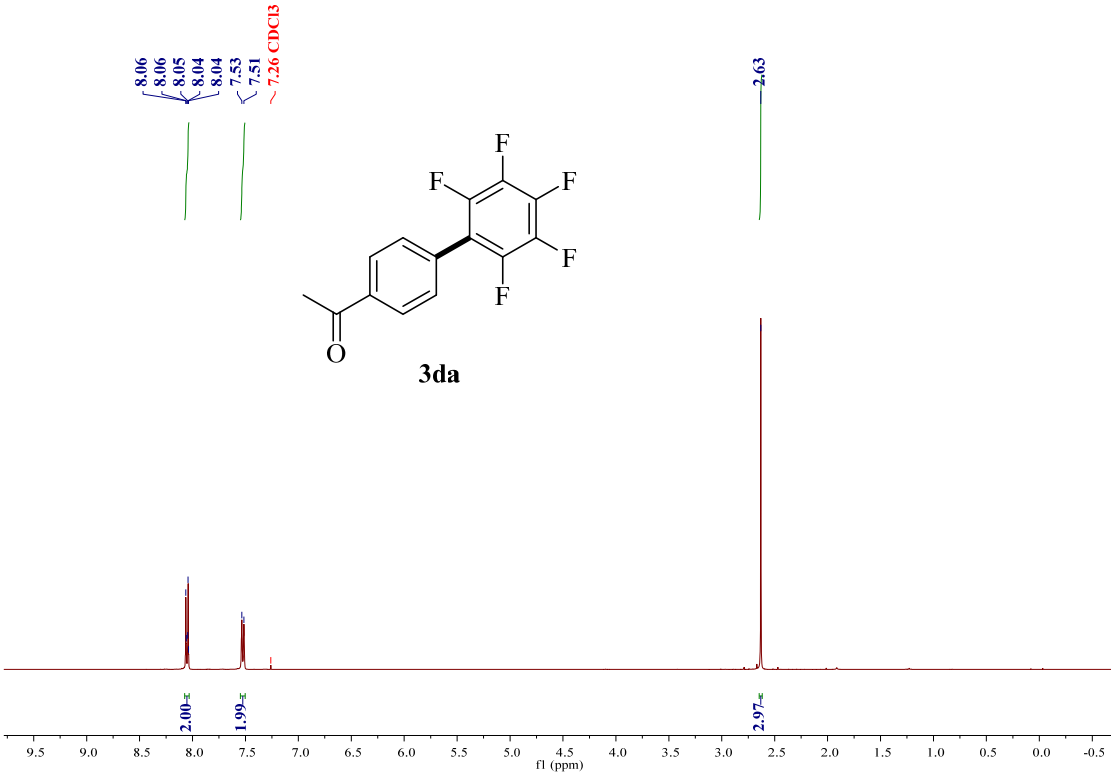


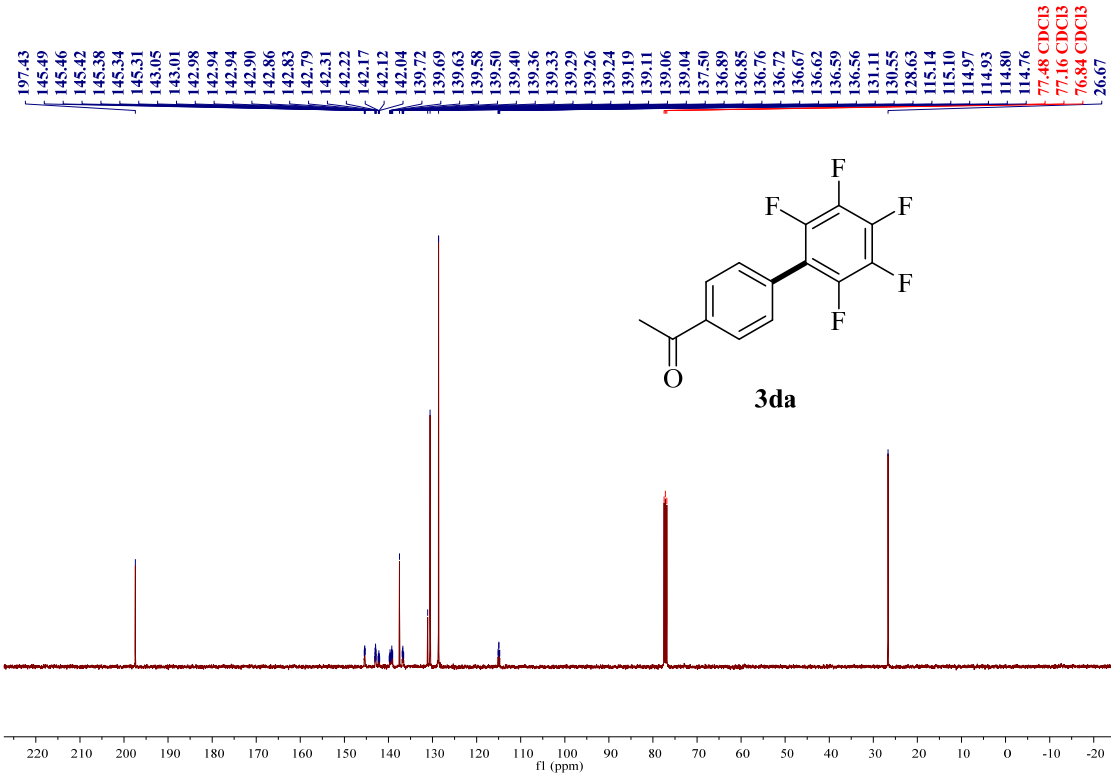
3ca

^{1}H NMR spectrum of 3da (400 MHz, $CDCl_3$)

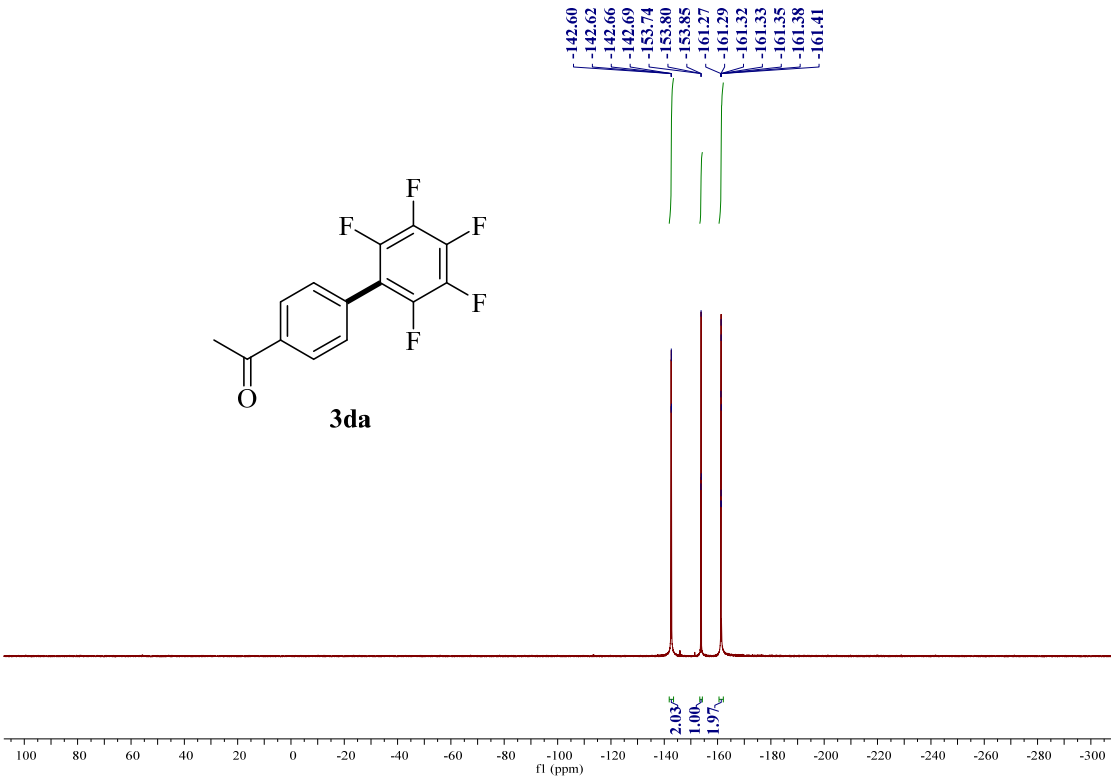


3da

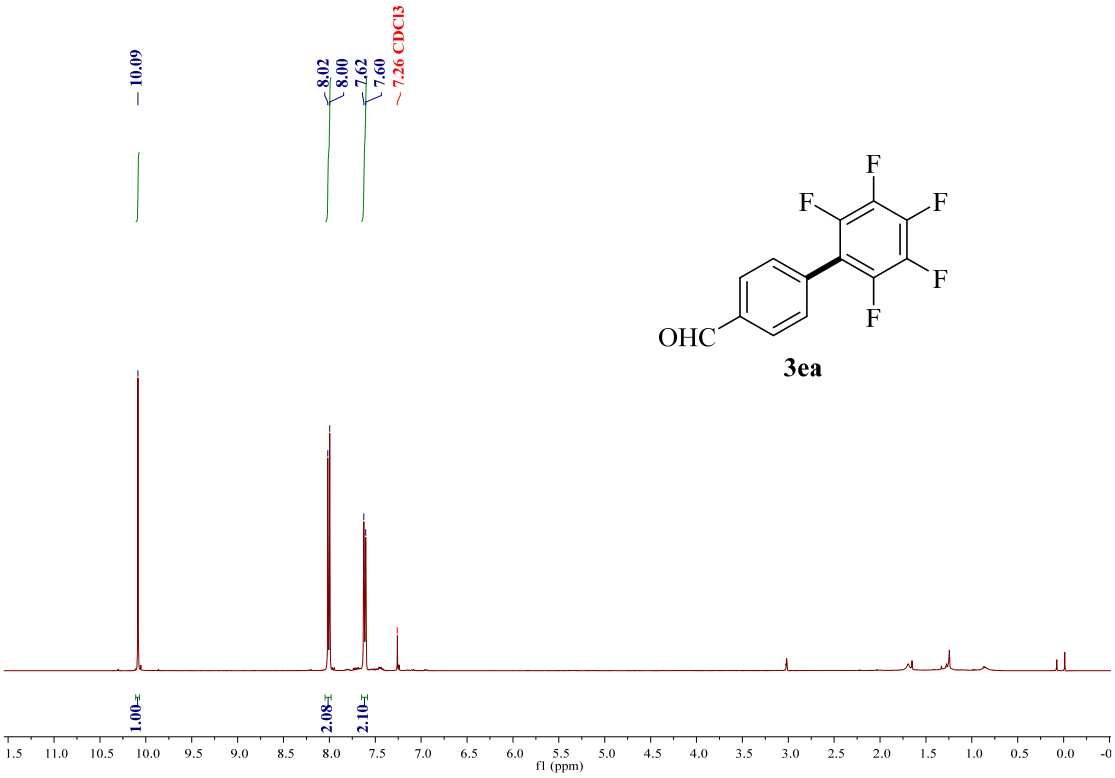
^{13}C NMR spectrum of 3da (100 MHz, $CDCl_3$)



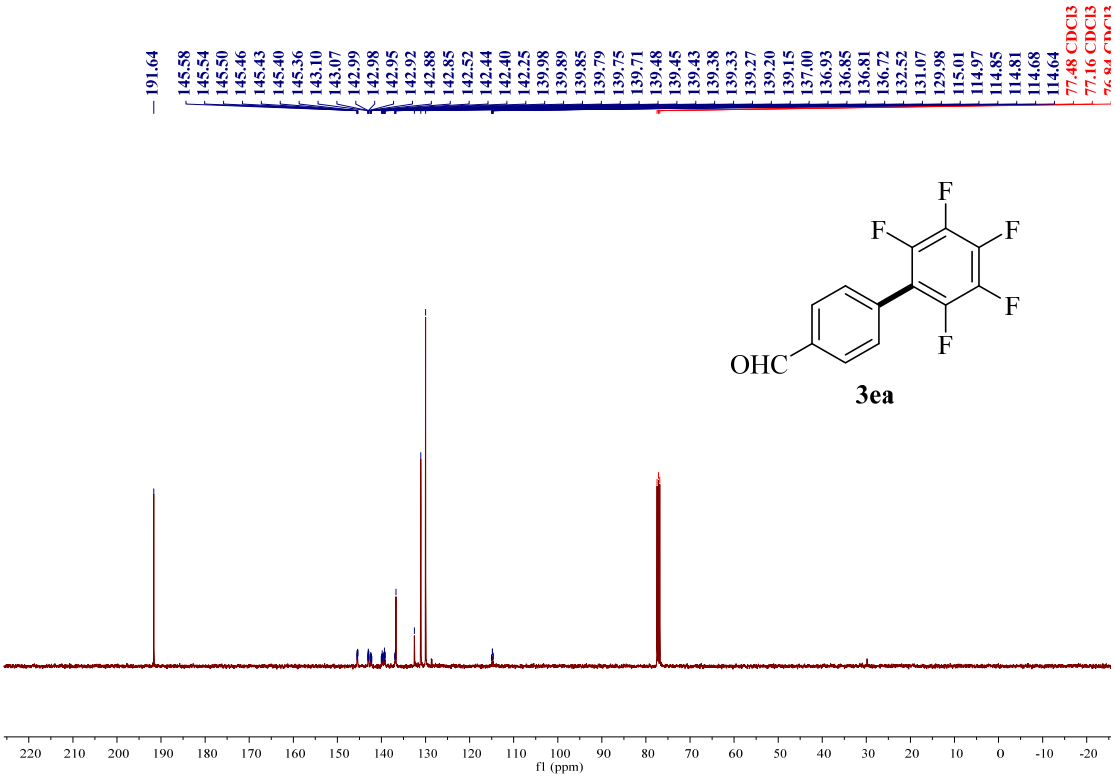
^{19}F NMR spectrum of 3da (376 MHz, $CDCl_3$)



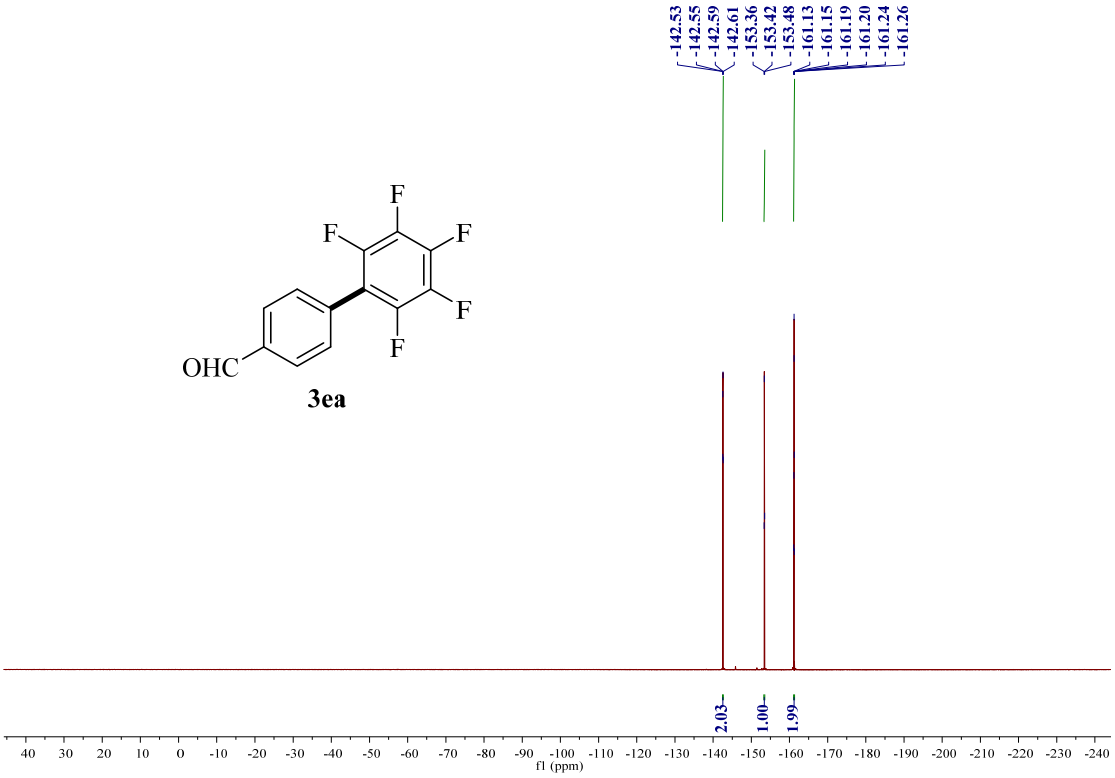
^{1}H NMR spectrum of 3ea (400 MHz, $CDCl_3$)



^{13}C NMR spectrum of 3ea (100 MHz, $CDCl_3$)

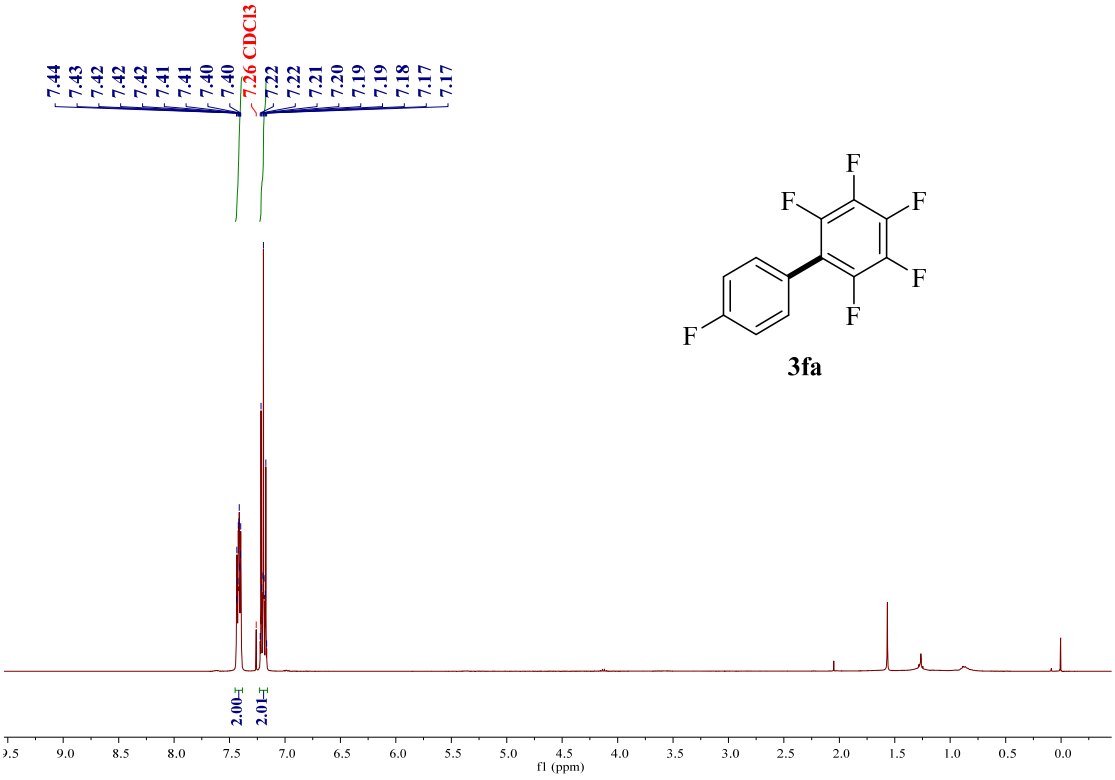


^{19}F NMR spectrum of 3ea (376 MHz, $CDCl_3$)



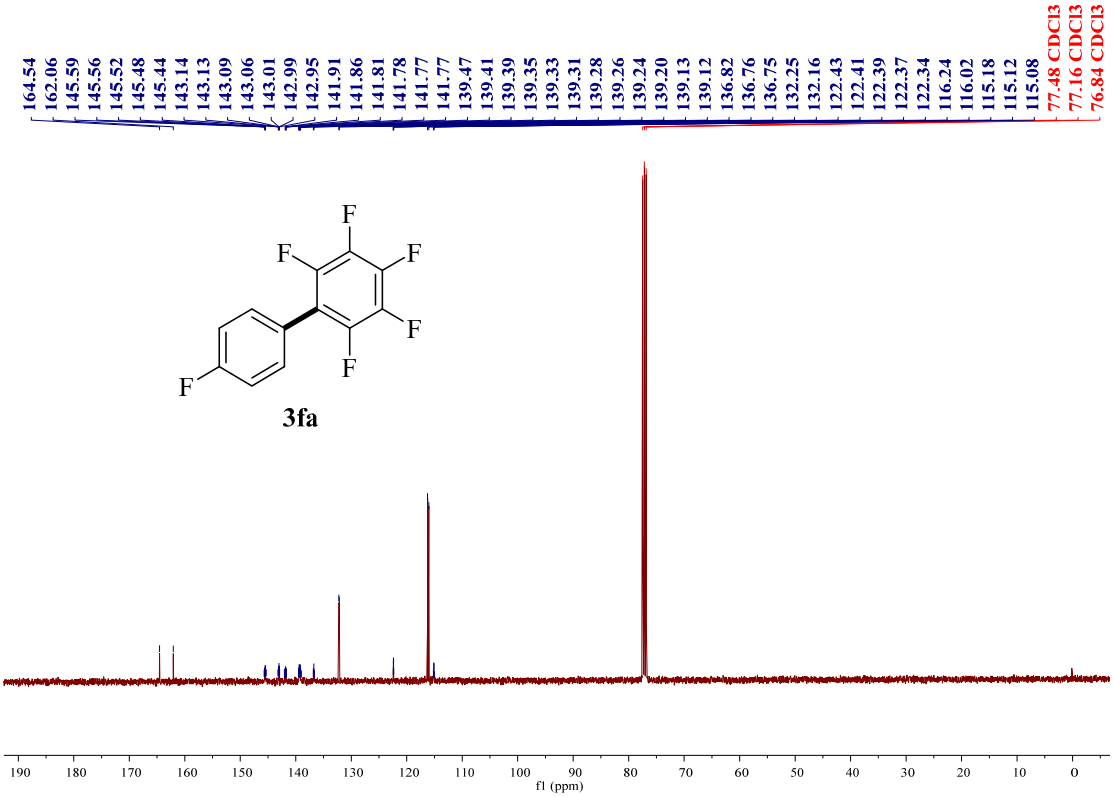
3ea

^{1}H NMR spectrum of 3fa (400 MHz, $CDCl_3$)

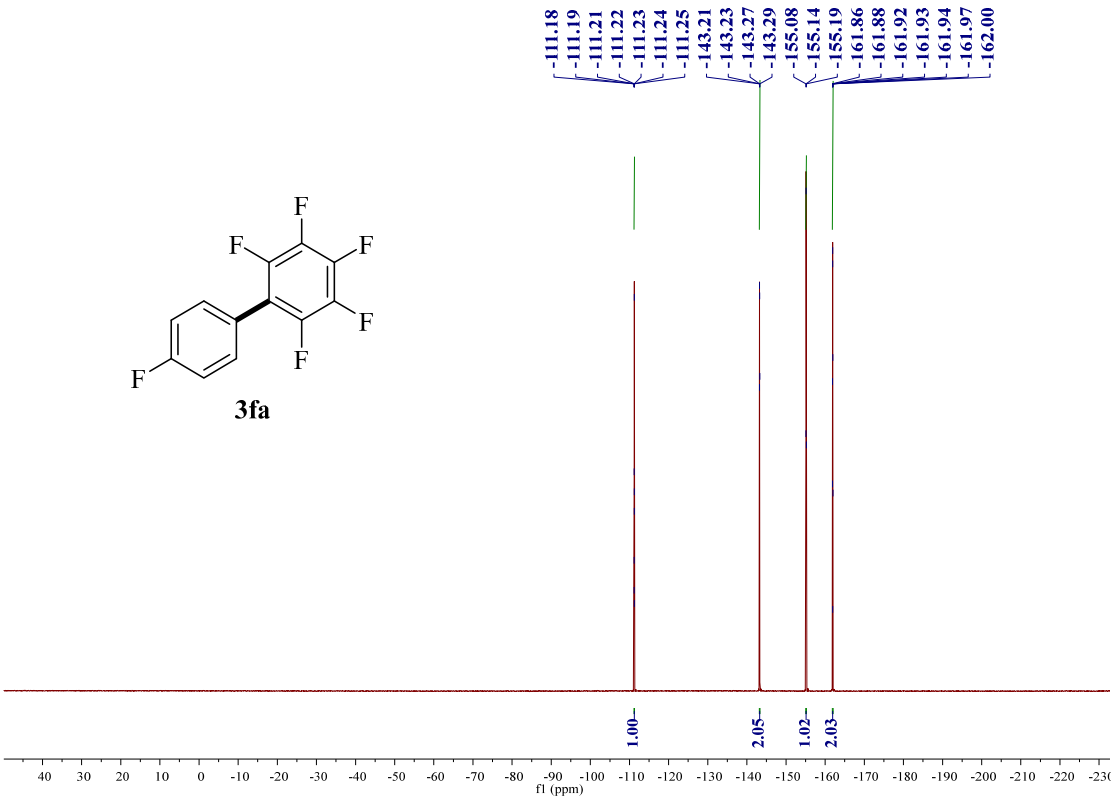


3fa

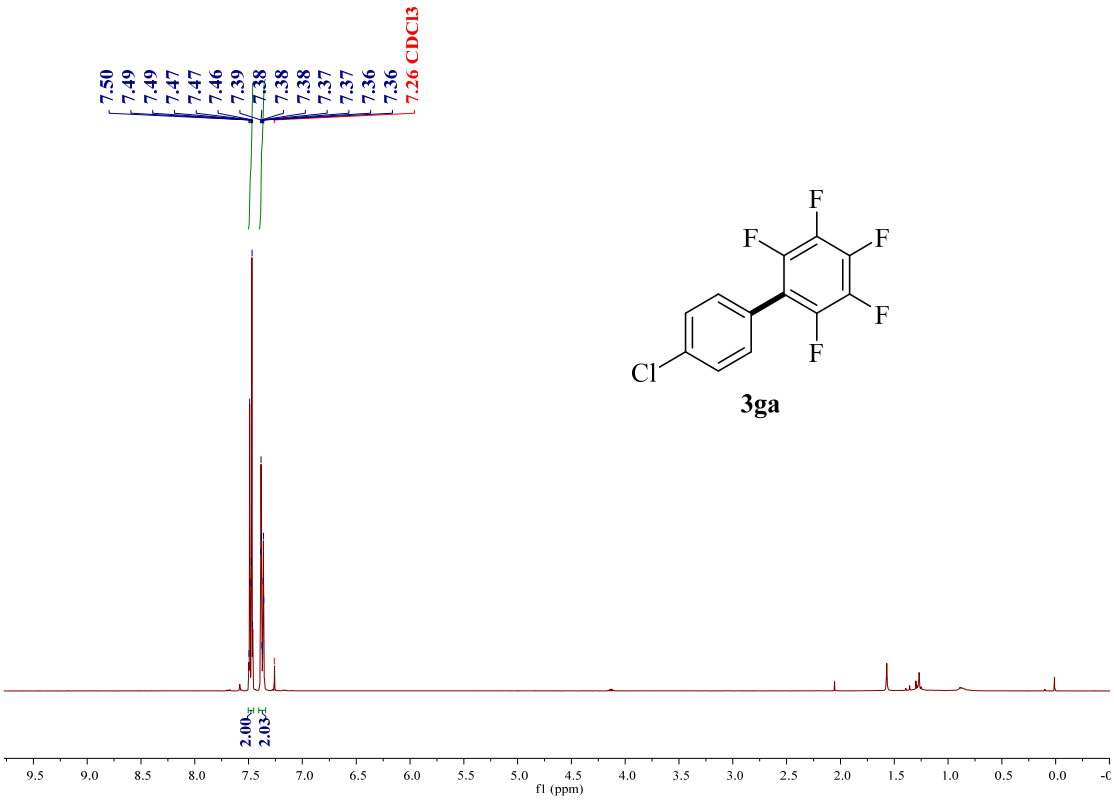
^{13}C NMR spectrum of 3fa (100 MHz, $CDCl_3$)



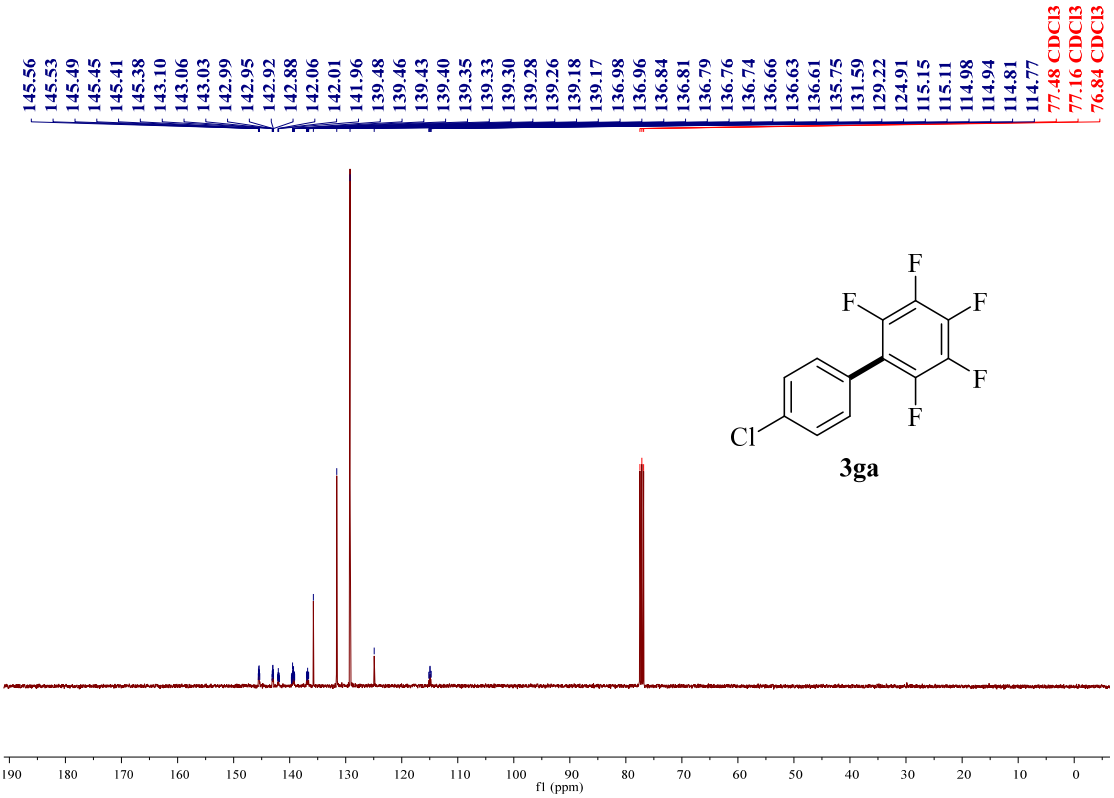
^{19}F NMR spectrum of 3fa (376 MHz, $CDCl_3$)



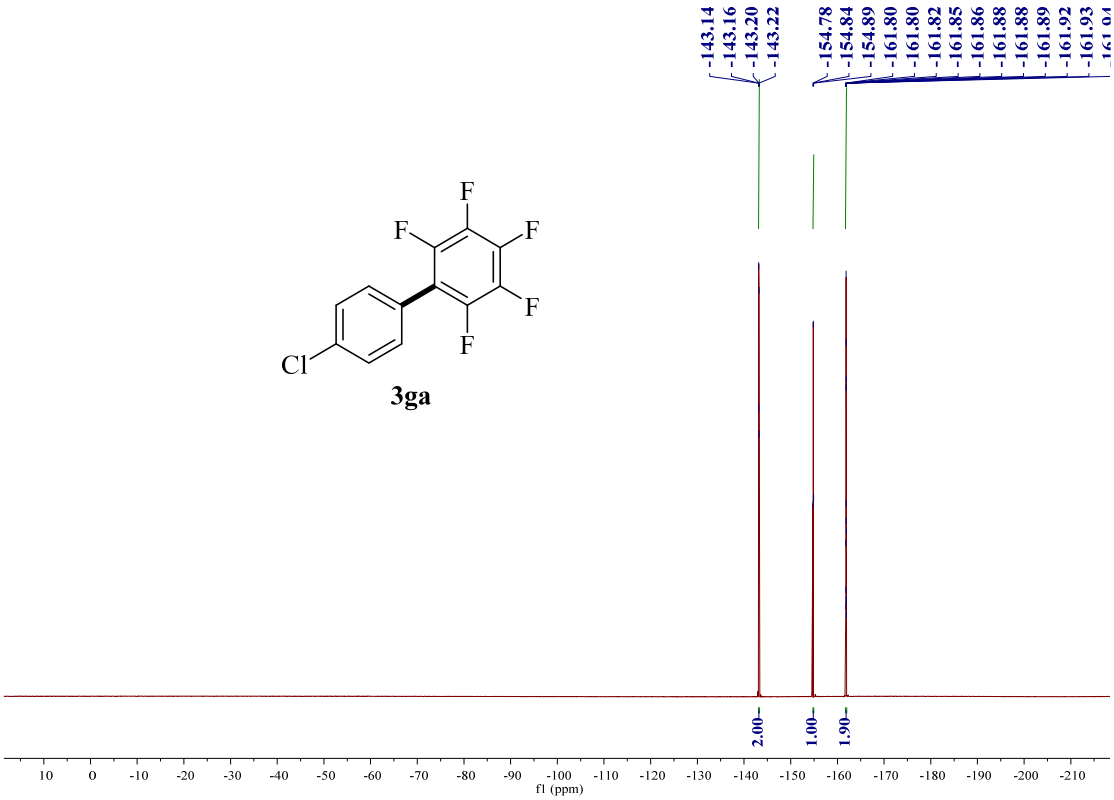
^{1}H NMR spectrum of 3ga (400 MHz, $CDCl_3$)



^{13}C NMR spectrum of 3ga (100 MHz, $CDCl_3$)

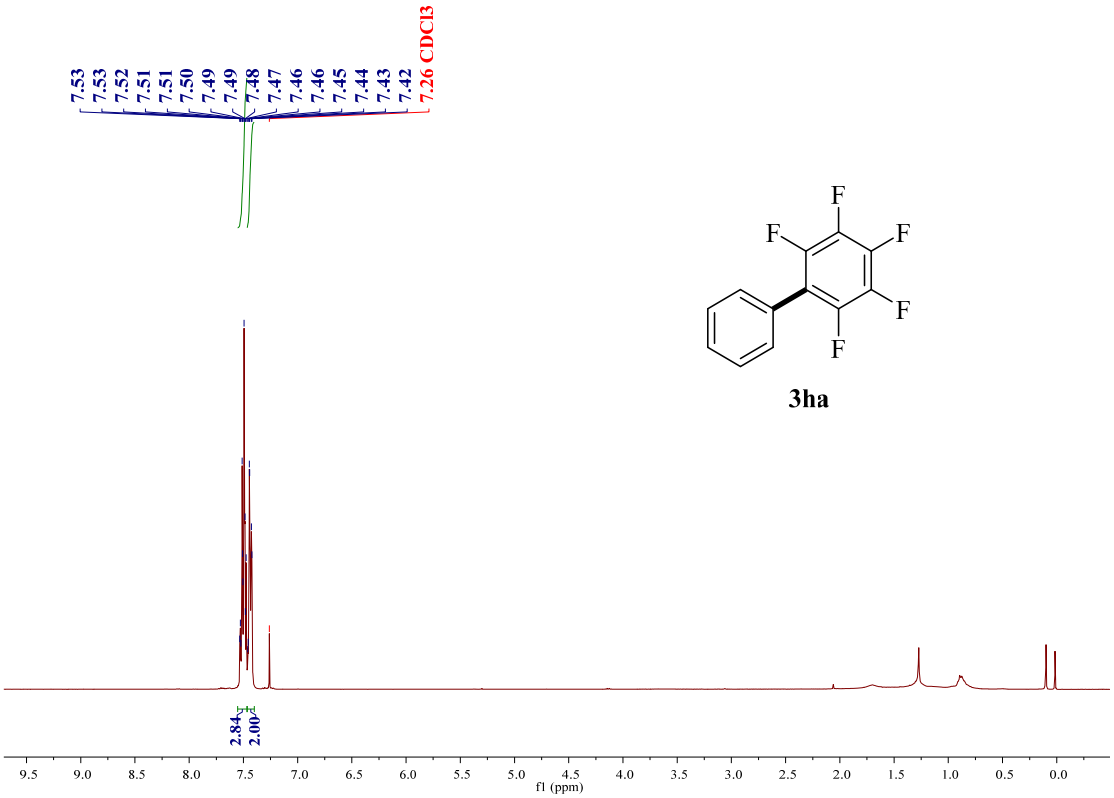


^{19}F NMR spectrum of 3ga (376 MHz, $CDCl_3$)



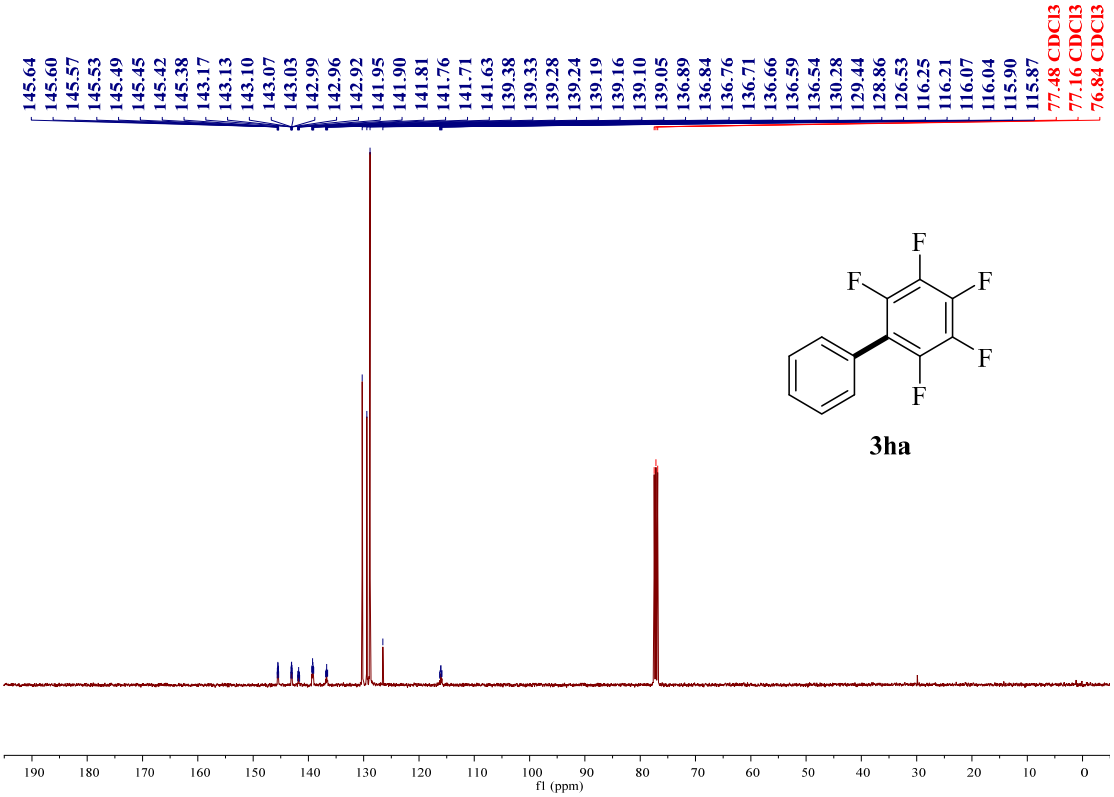
3ga

^{1}H NMR spectrum of 3ha (400 MHz, $CDCl_3$)

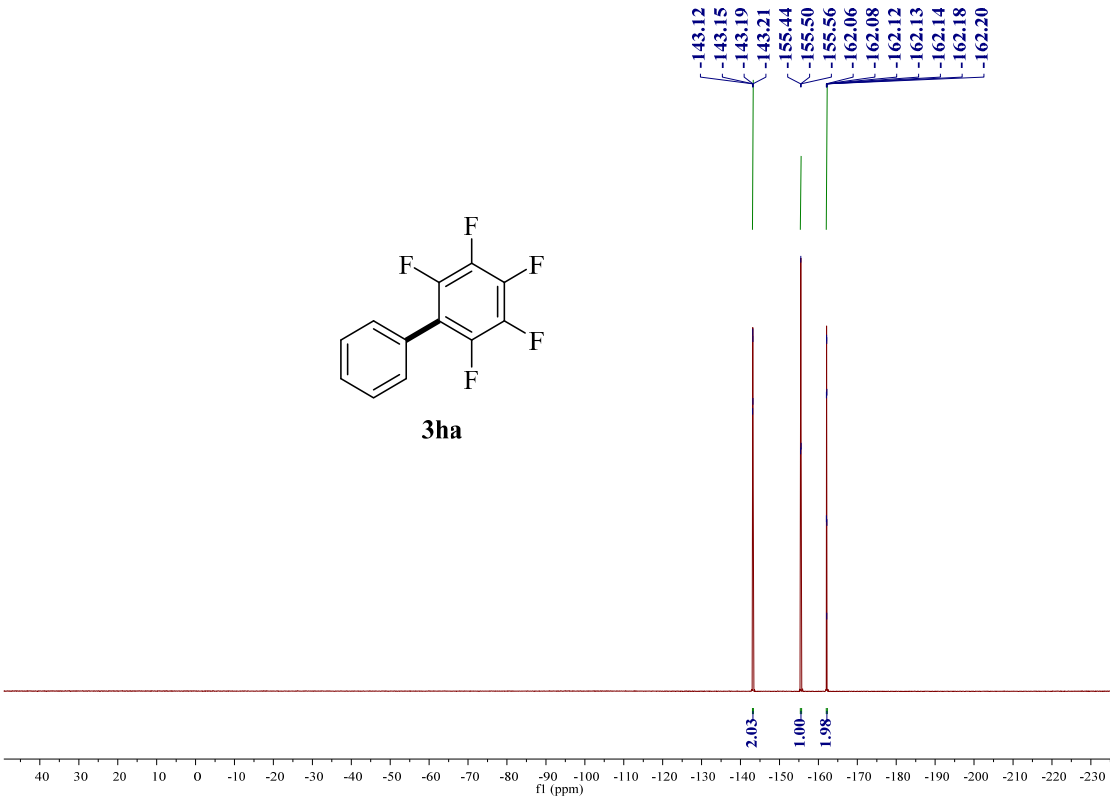


3ha

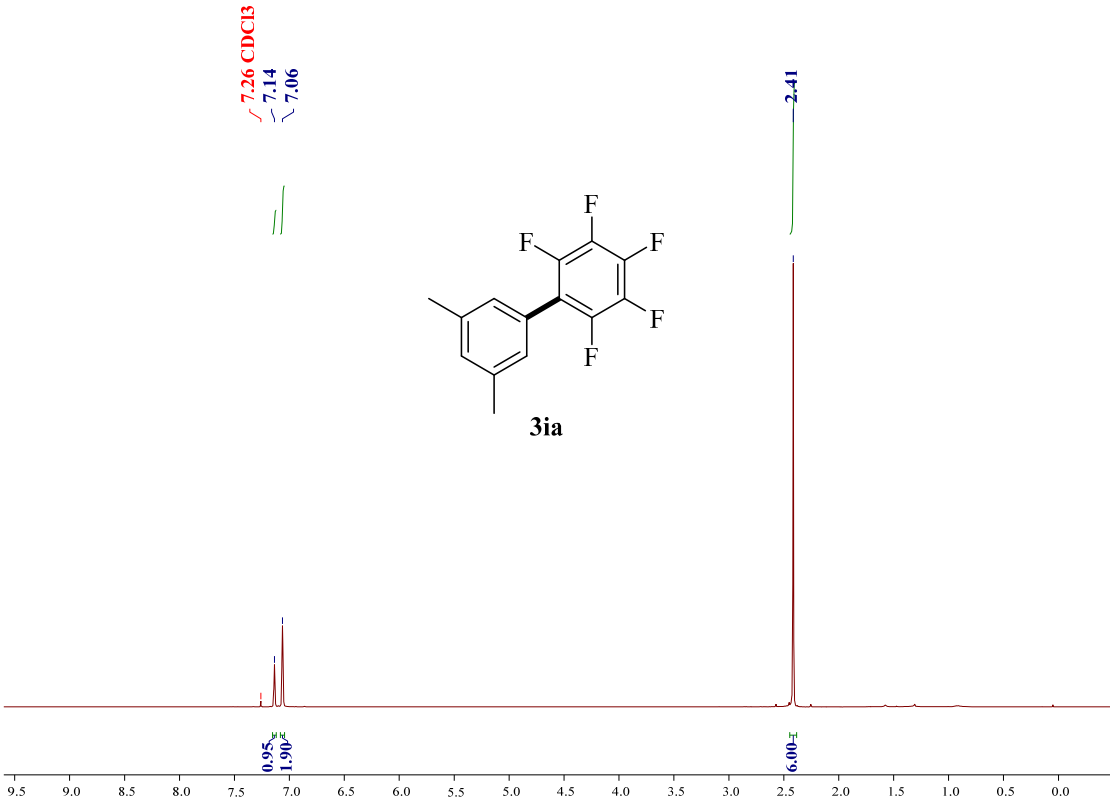
^{13}C NMR spectrum of 3ha (100 MHz, $CDCl_3$)



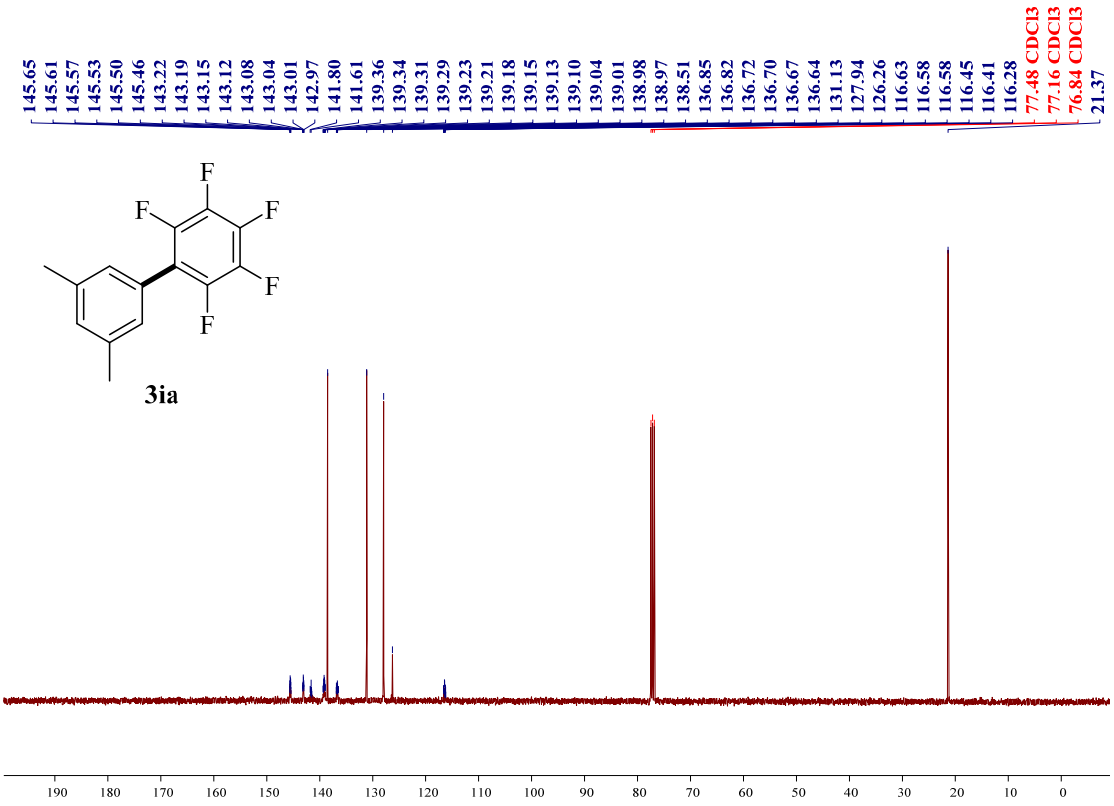
^{19}F NMR spectrum of 3ha (376 MHz, $CDCl_3$)



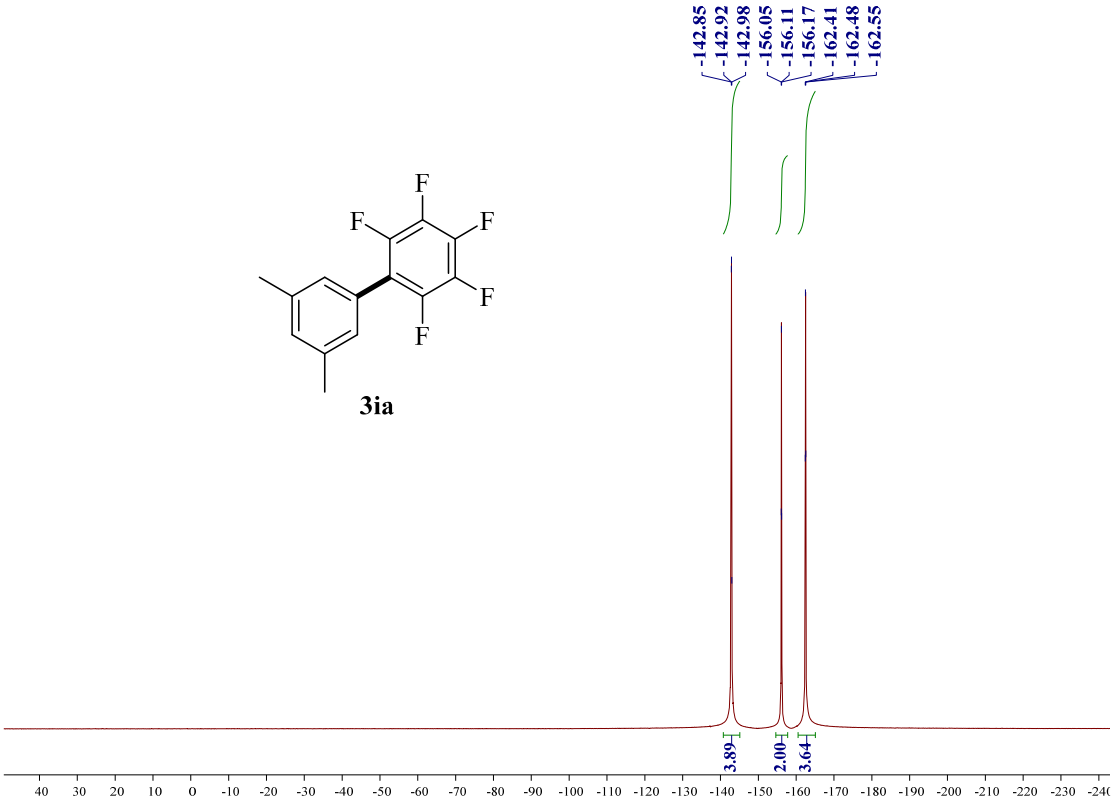
^{1}H NMR spectrum of 3ia (400 MHz, $CDCl_3$)



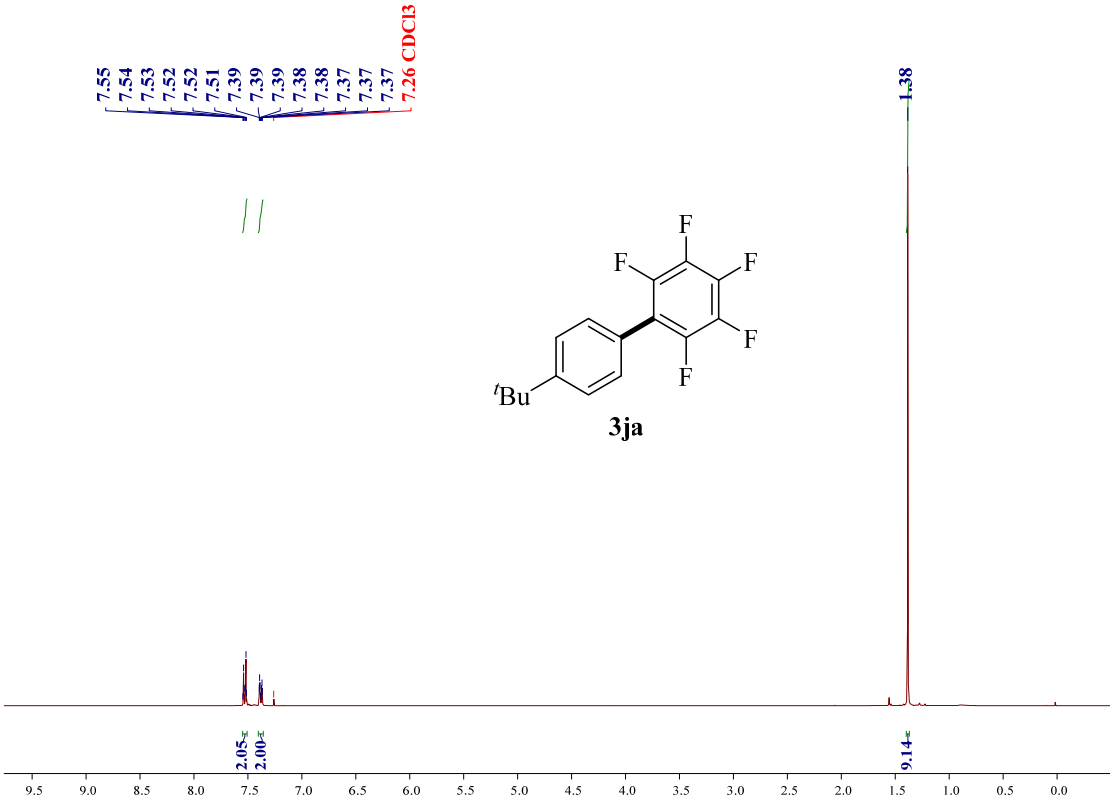
^{13}C NMR spectrum of 3ia (100 MHz, $CDCl_3$)



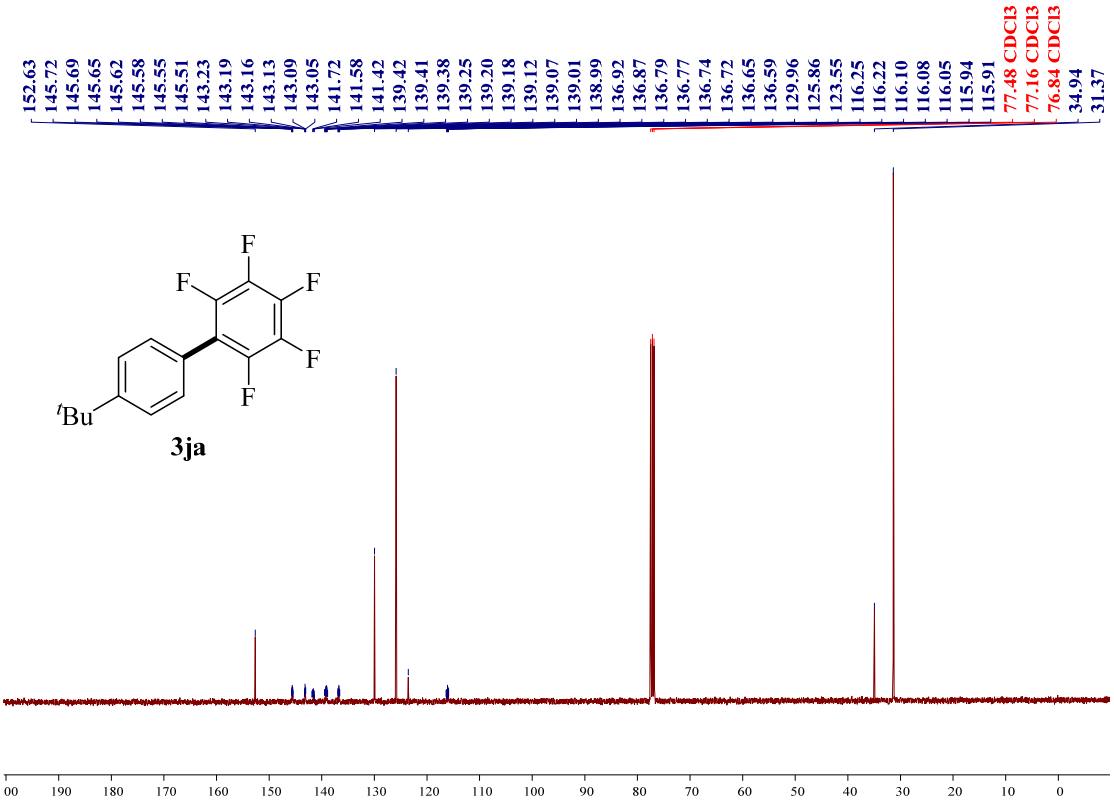
^{19}F NMR spectrum of 3ia (376 MHz, $CDCl_3$)



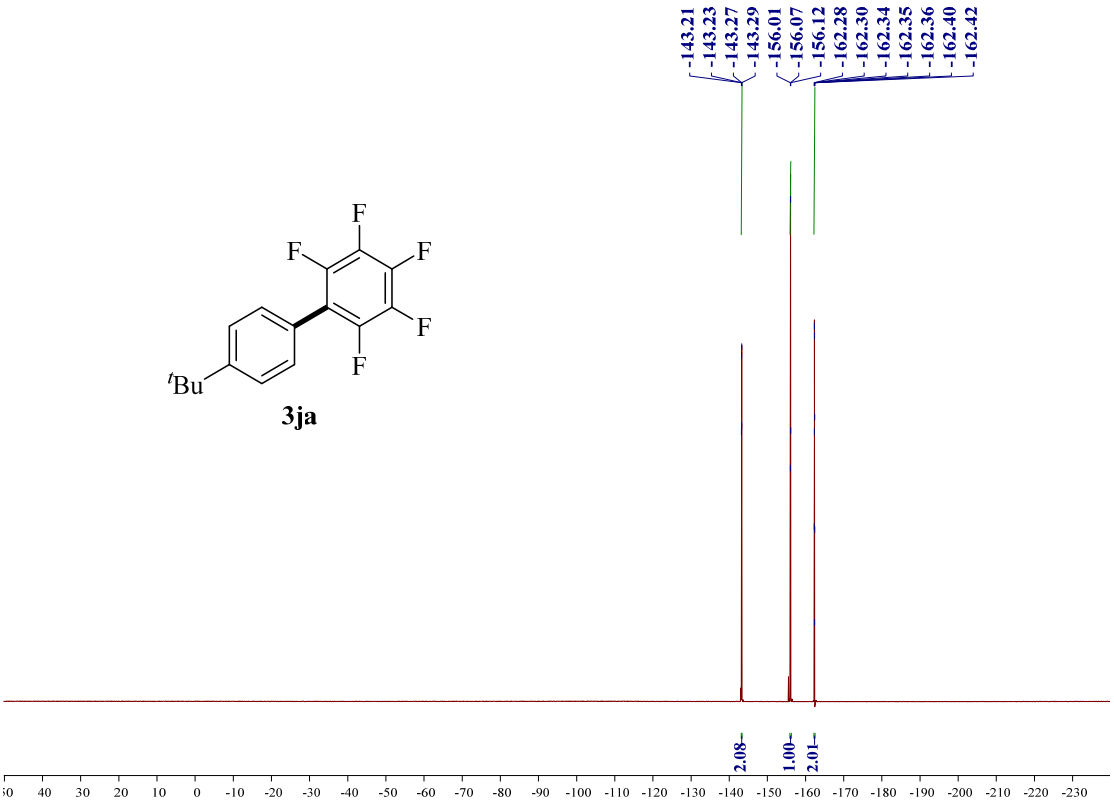
^{1}H NMR spectrum of 3ja (400 MHz, $CDCl_3$)



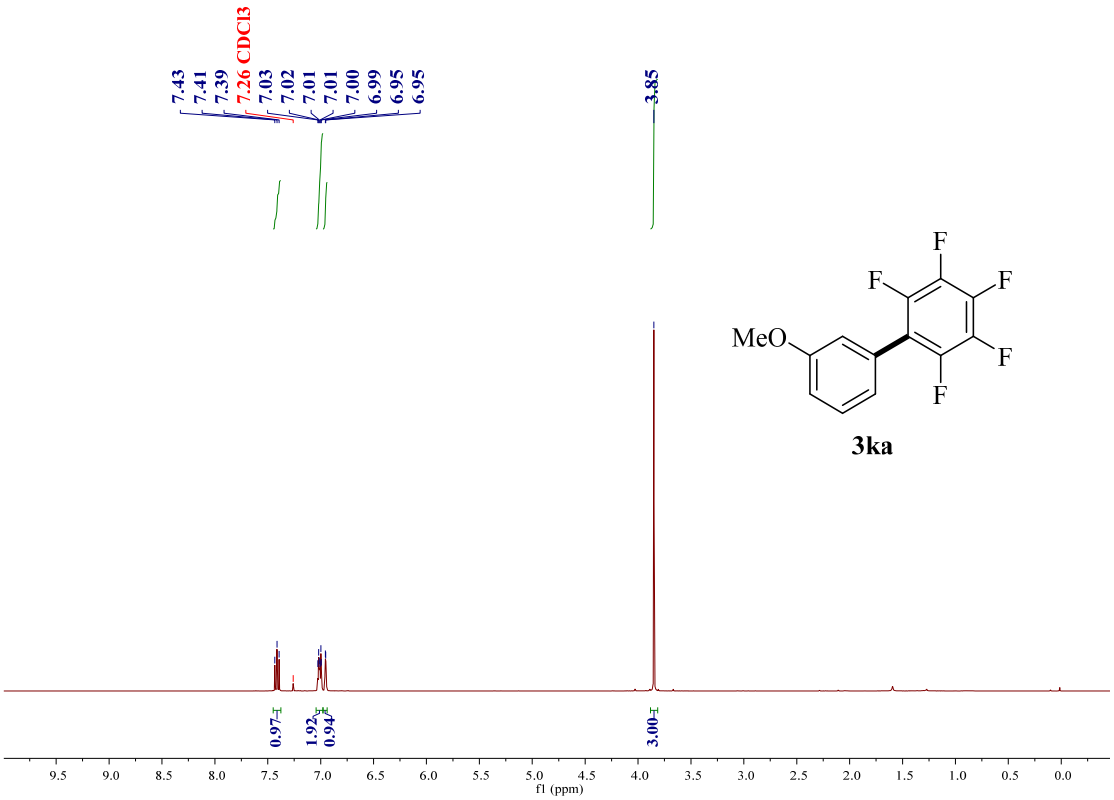
^{13}C NMR spectrum of 3ja (100 MHz, $CDCl_3$)



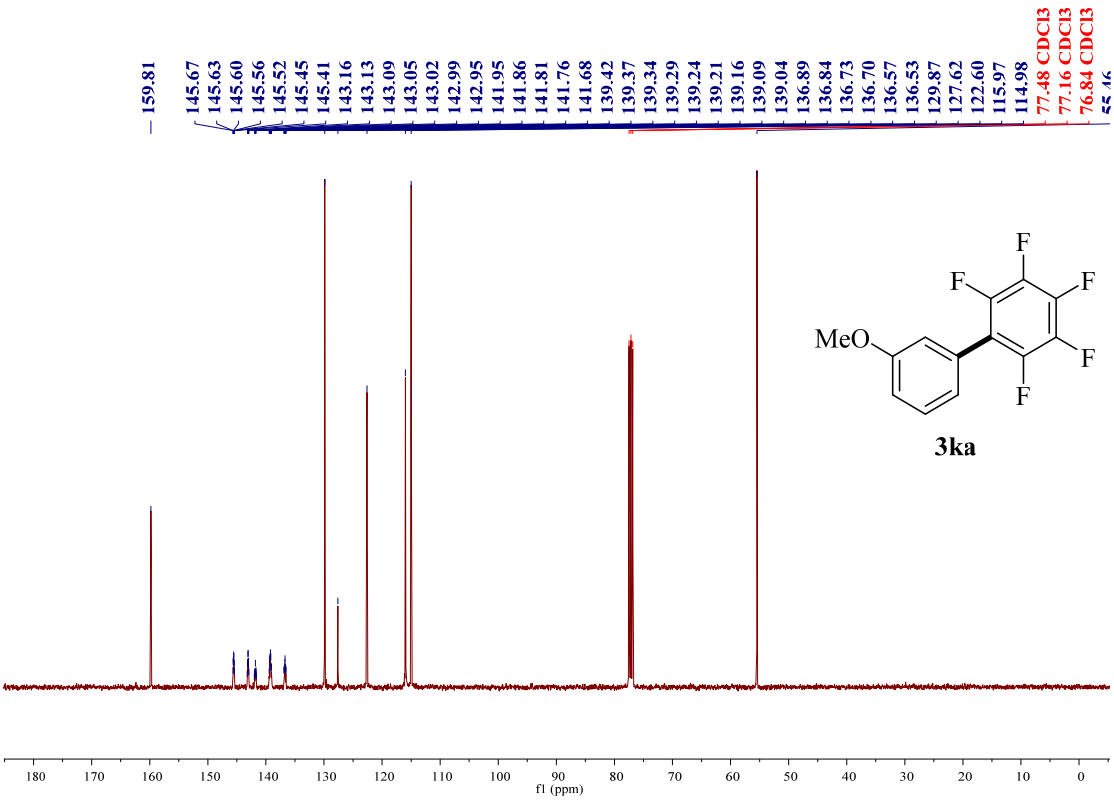
^{19}F NMR spectrum of 3ja (376 MHz, $CDCl_3$)



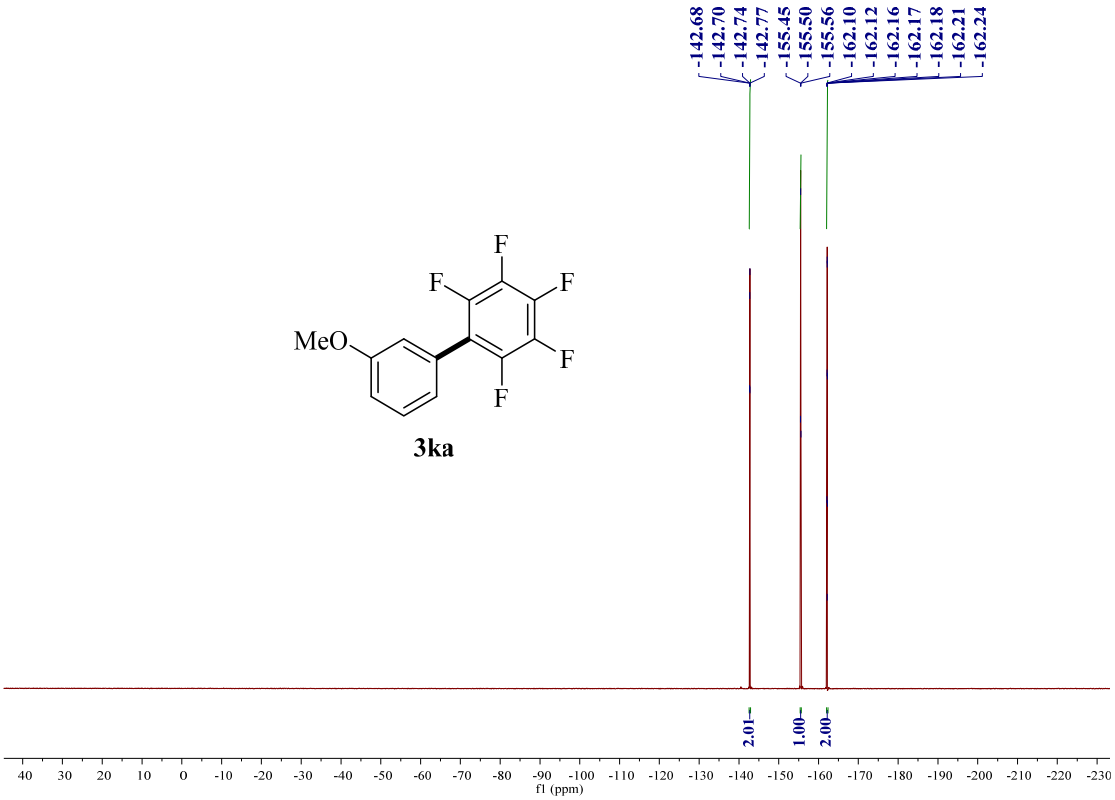
^{1}H NMR spectrum of 3ka (400 MHz, $CDCl_3$)



^{13}C NMR spectrum of 3ka (100 MHz, $CDCl_3$)

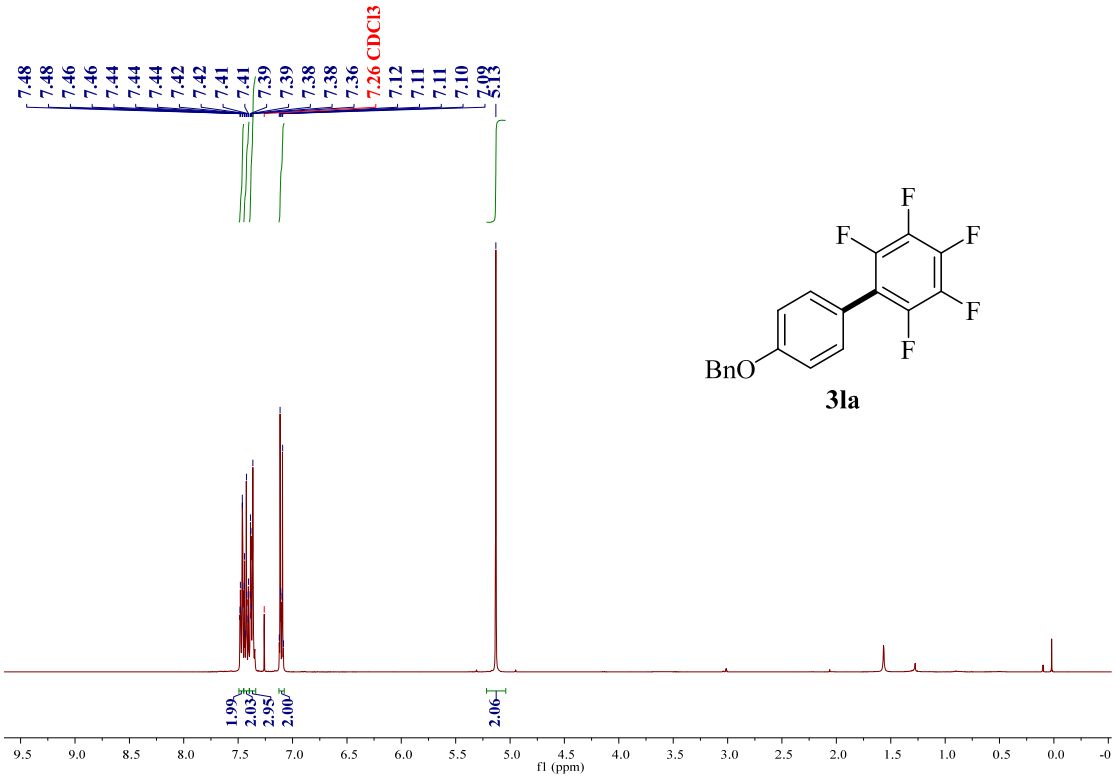


^{19}F NMR spectrum of 3ka (376 MHz, $CDCl_3$)



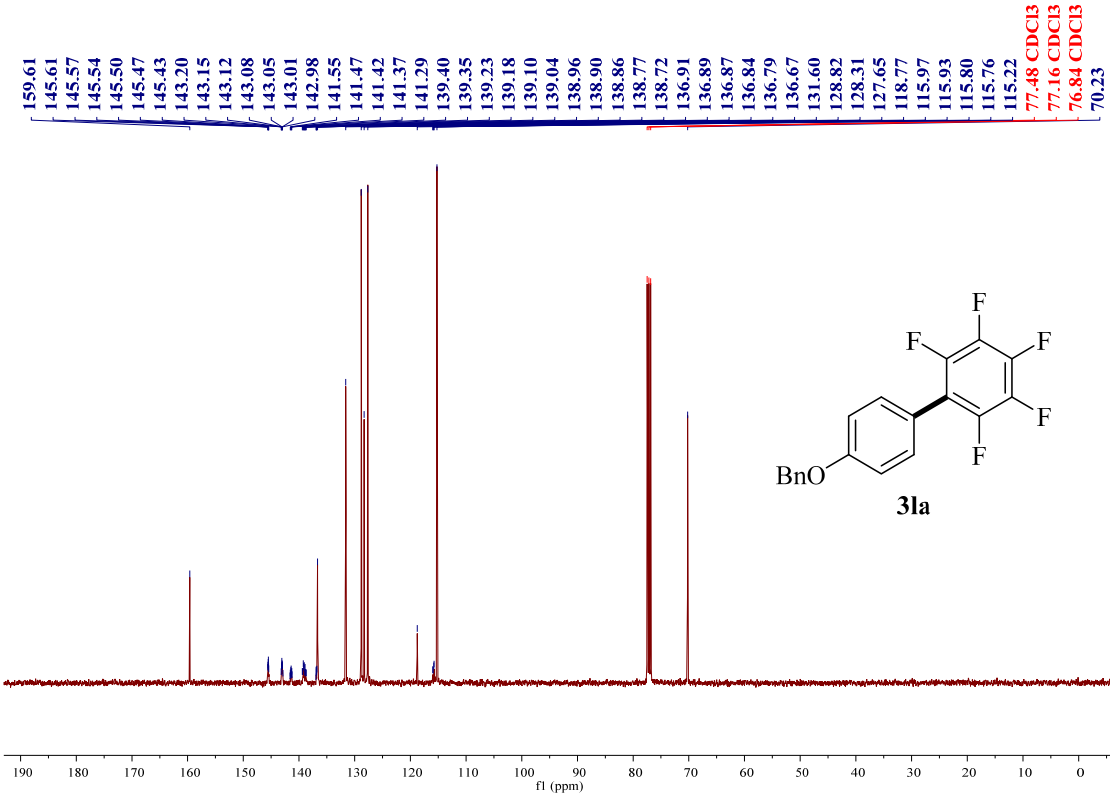
3ka

^{1}H NMR spectrum of 3la (400 MHz, $CDCl_3$)

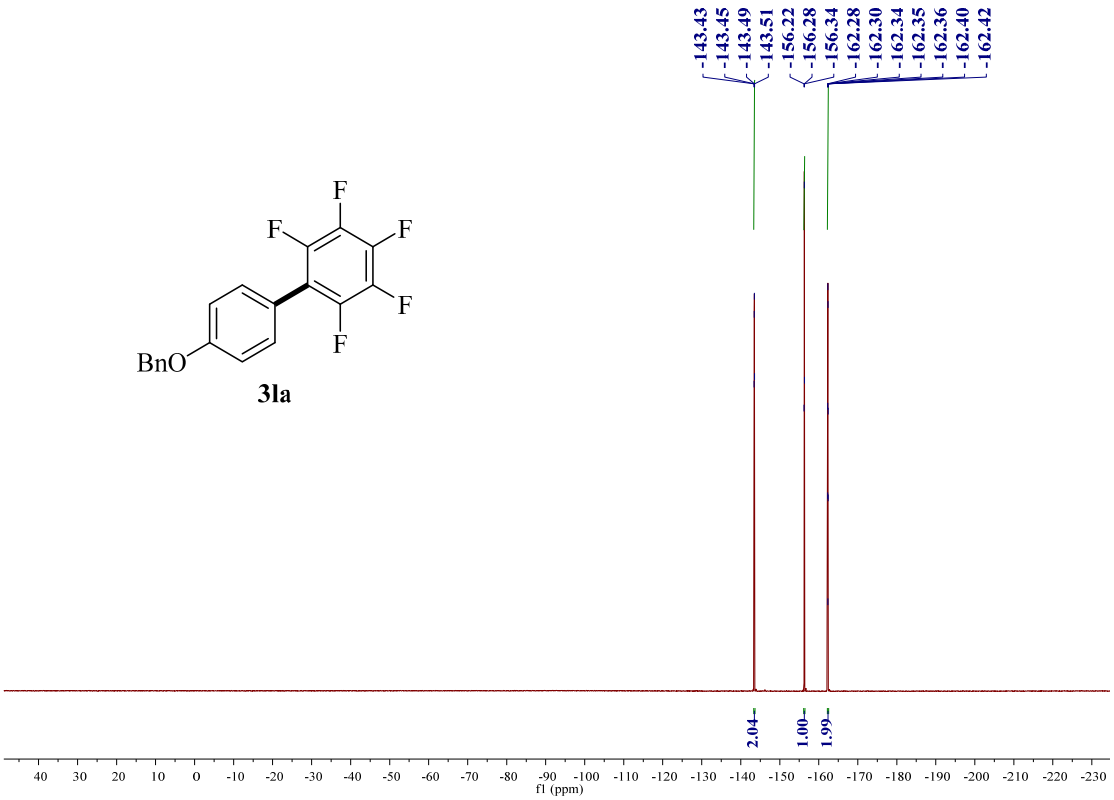


3la

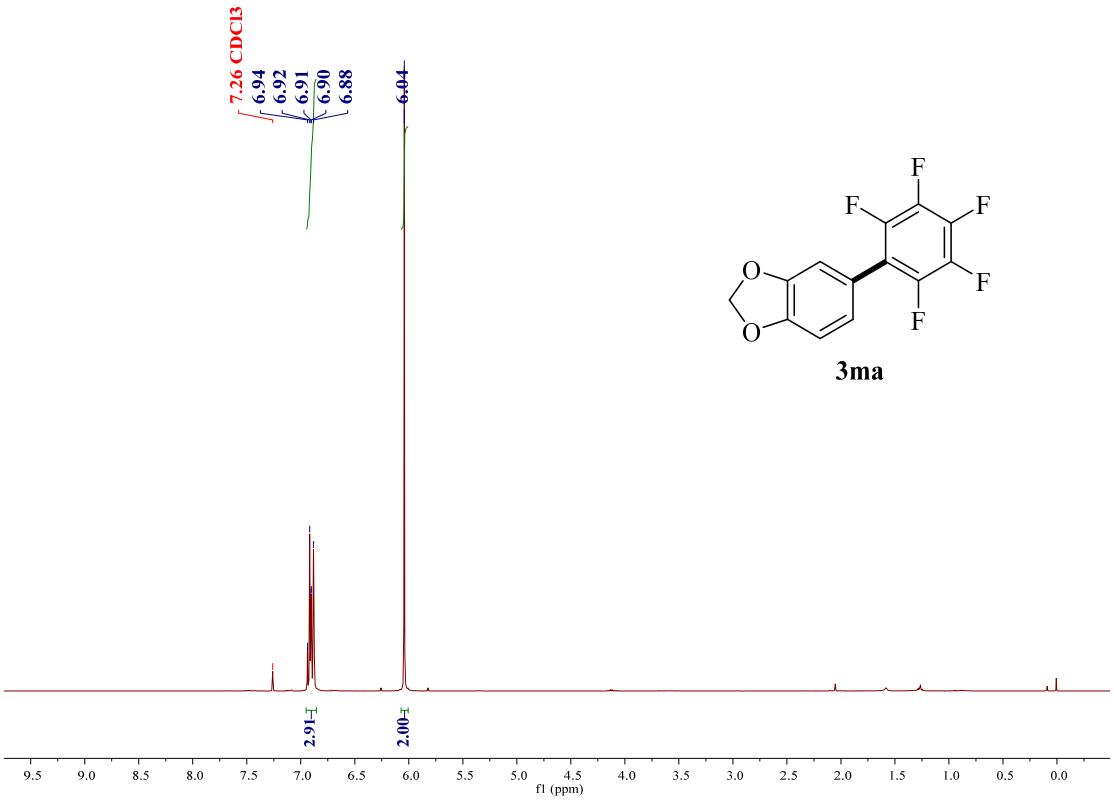
^{13}C NMR spectrum of 3la (100 MHz, $CDCl_3$)



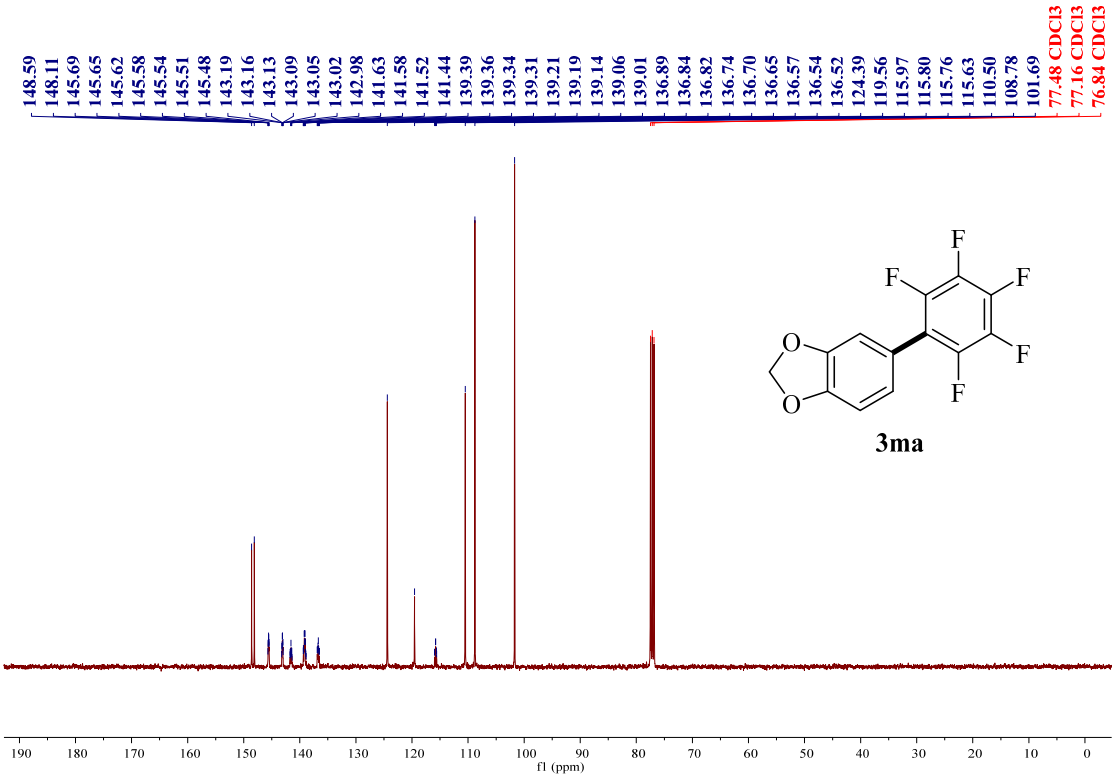
^{19}F NMR spectrum of 3la (376 MHz, $CDCl_3$)



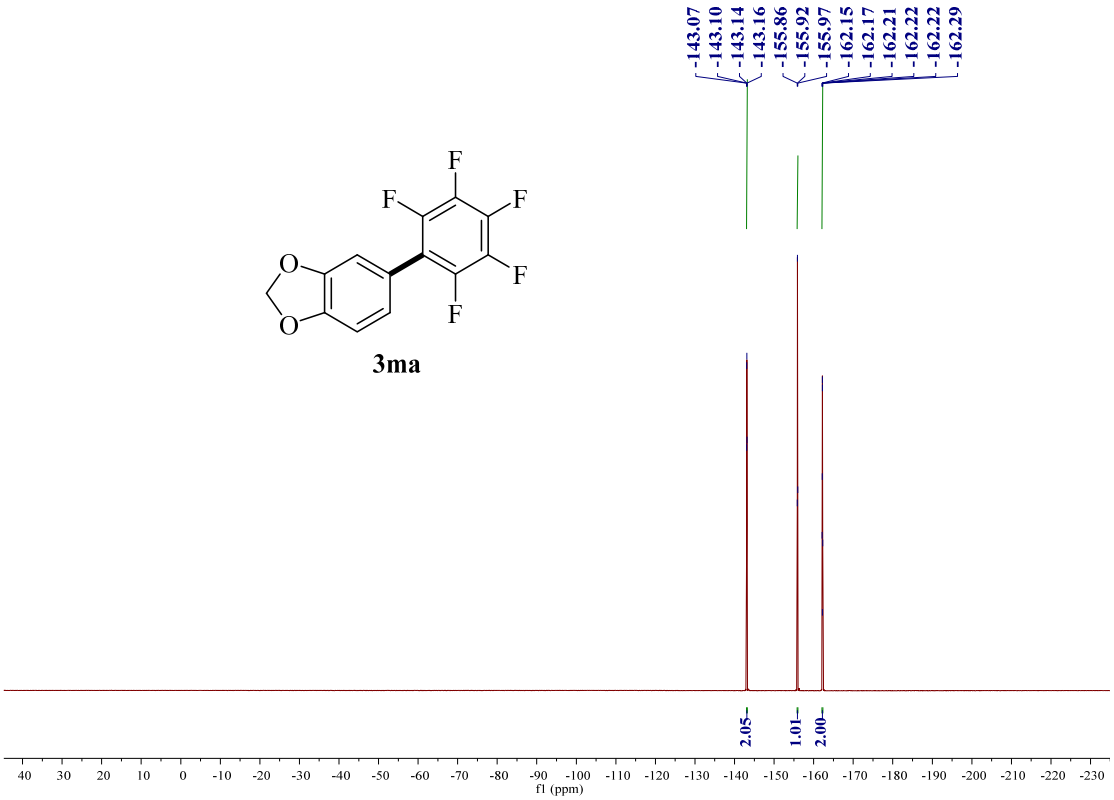
^{1}H NMR spectrum of 3ma (400 MHz, $CDCl_3$)



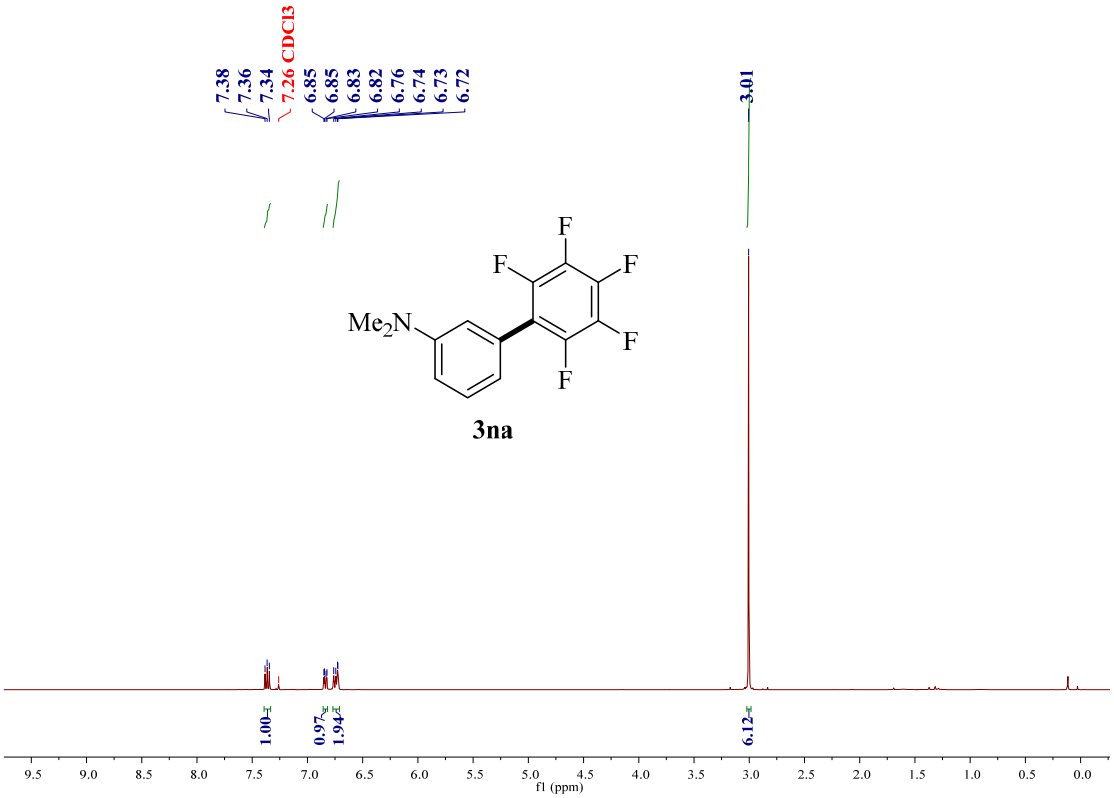
^{13}C NMR spectrum of 3ma (100 MHz, $CDCl_3$)



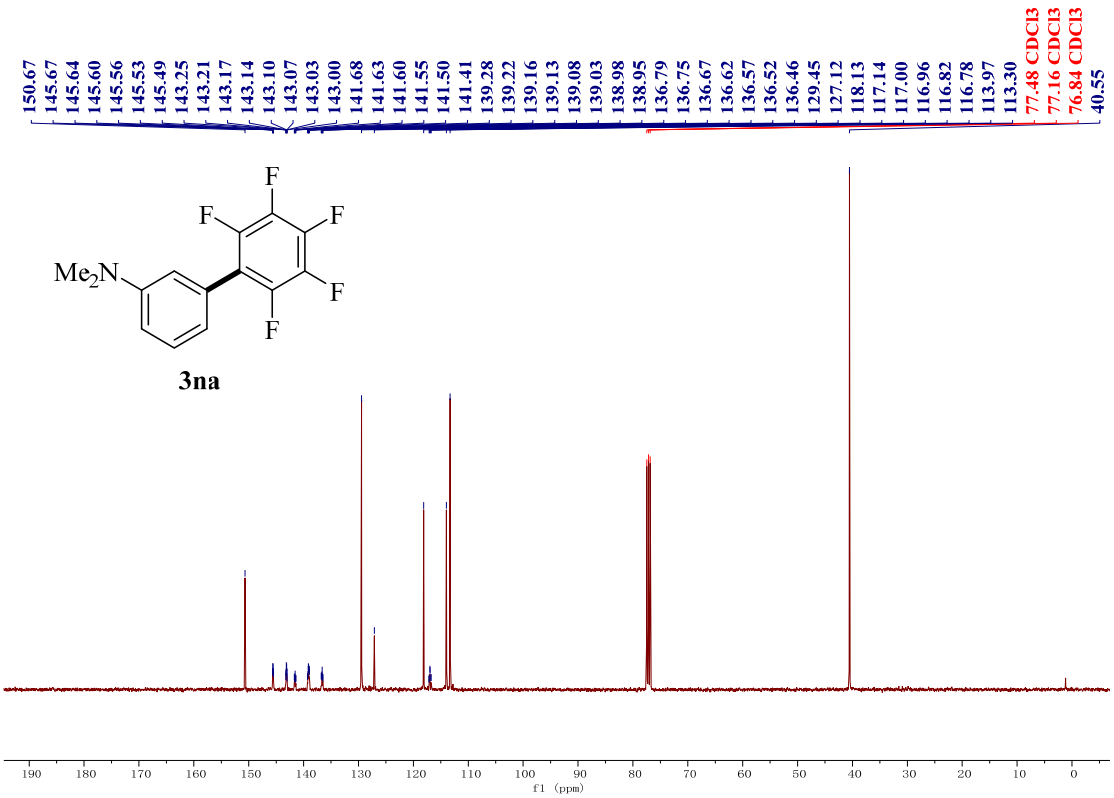
^{19}F NMR spectrum of 3ma (376 MHz, $CDCl_3$)



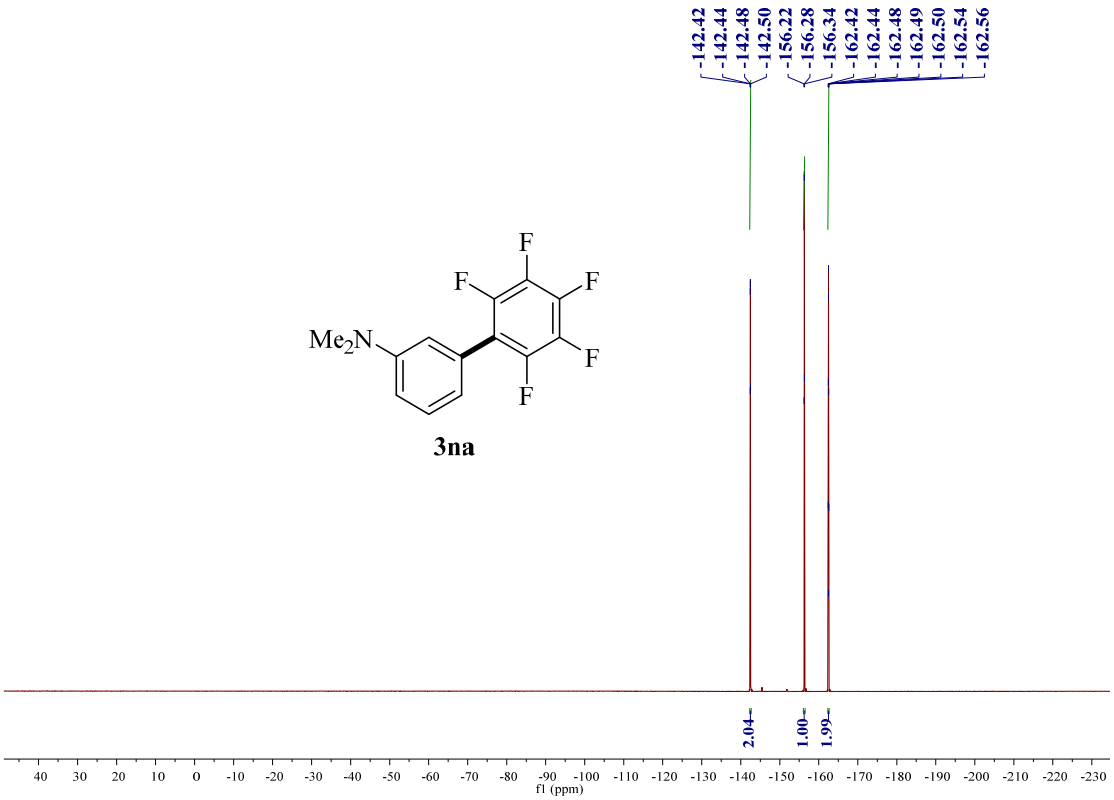
^{1}H NMR spectrum of 3na (400 MHz, $CDCl_3$)



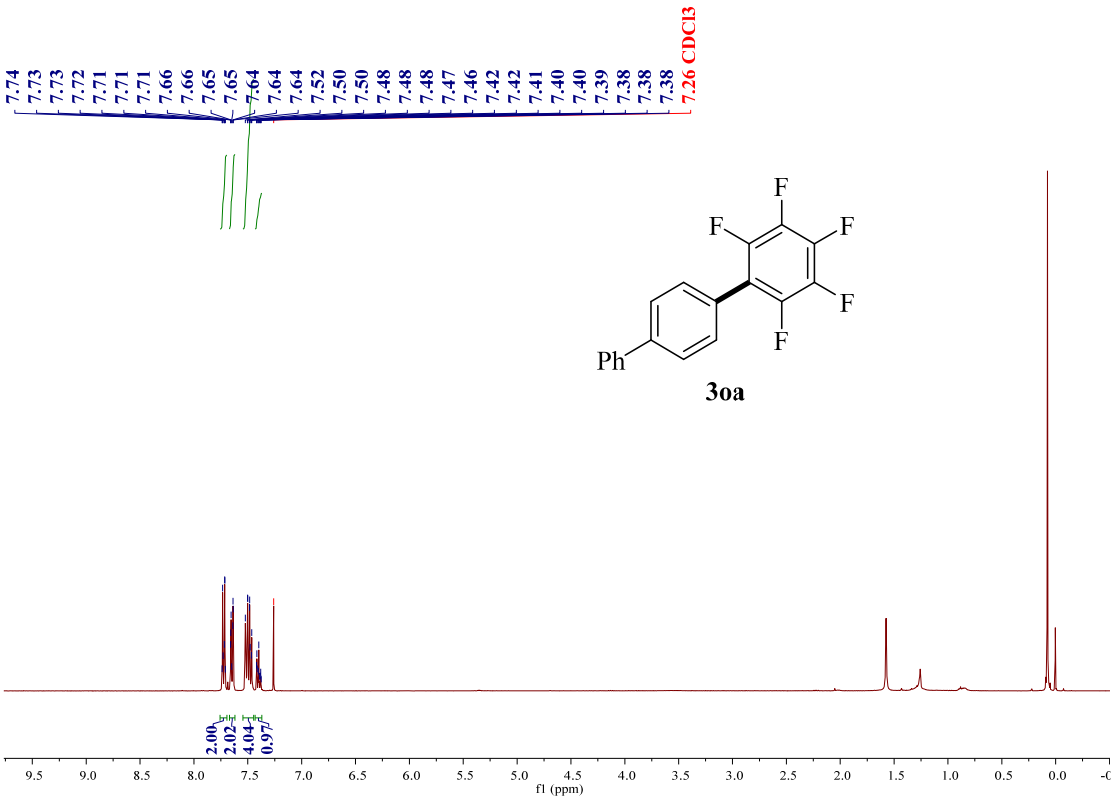
^{13}C NMR spectrum of 3na (100 MHz, $CDCl_3$)



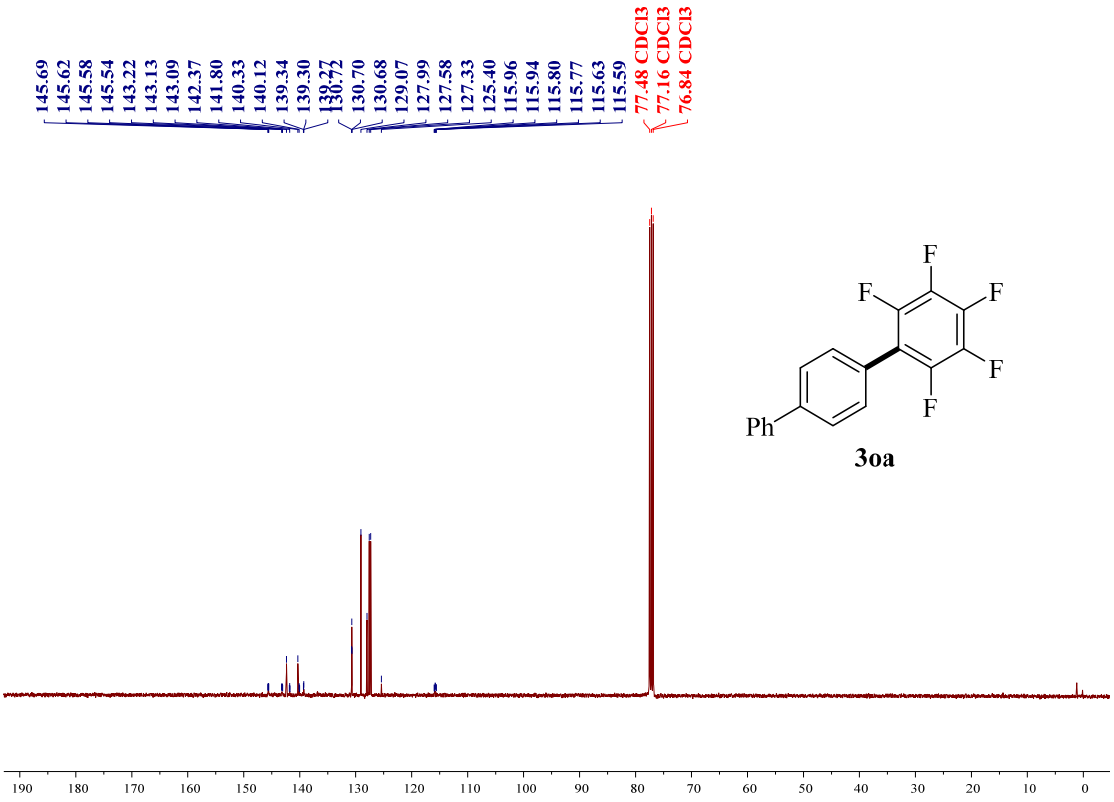
^{19}F NMR spectrum of 3na (376 MHz, $CDCl_3$)



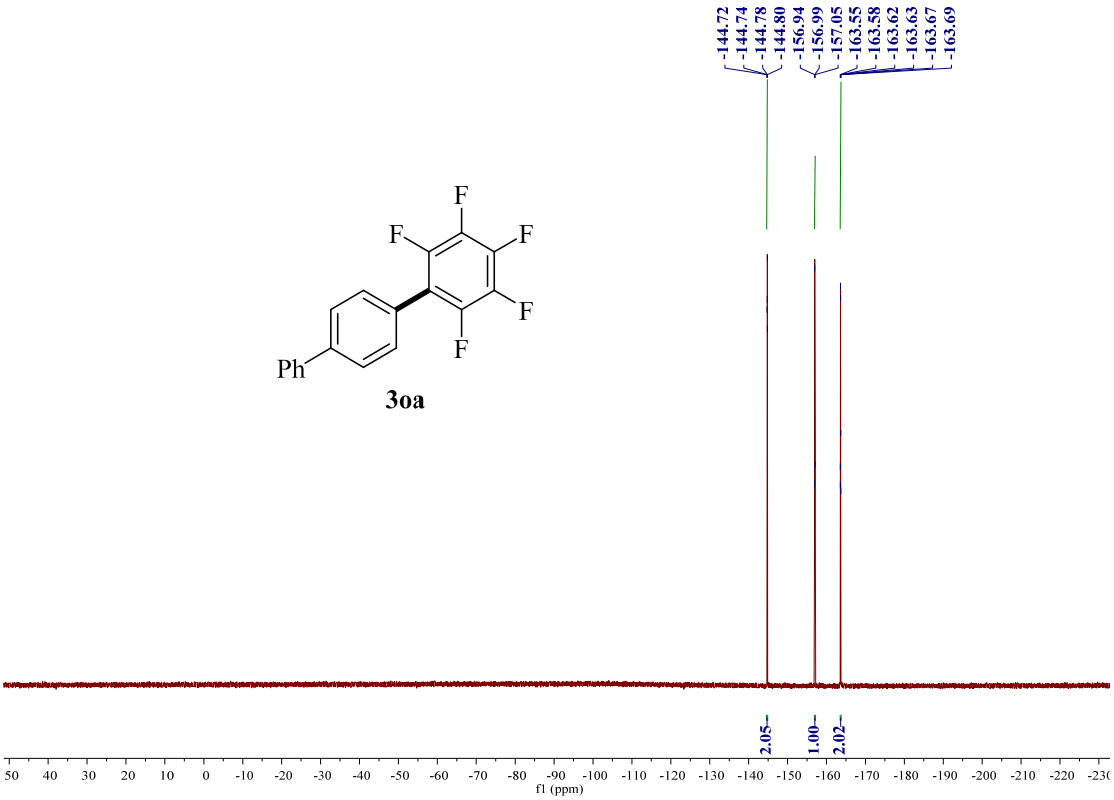
^{1}H NMR spectrum of 3oa (400 MHz, $CDCl_3$)



^{13}C NMR spectrum of 3oa (100 MHz, $CDCl_3$)

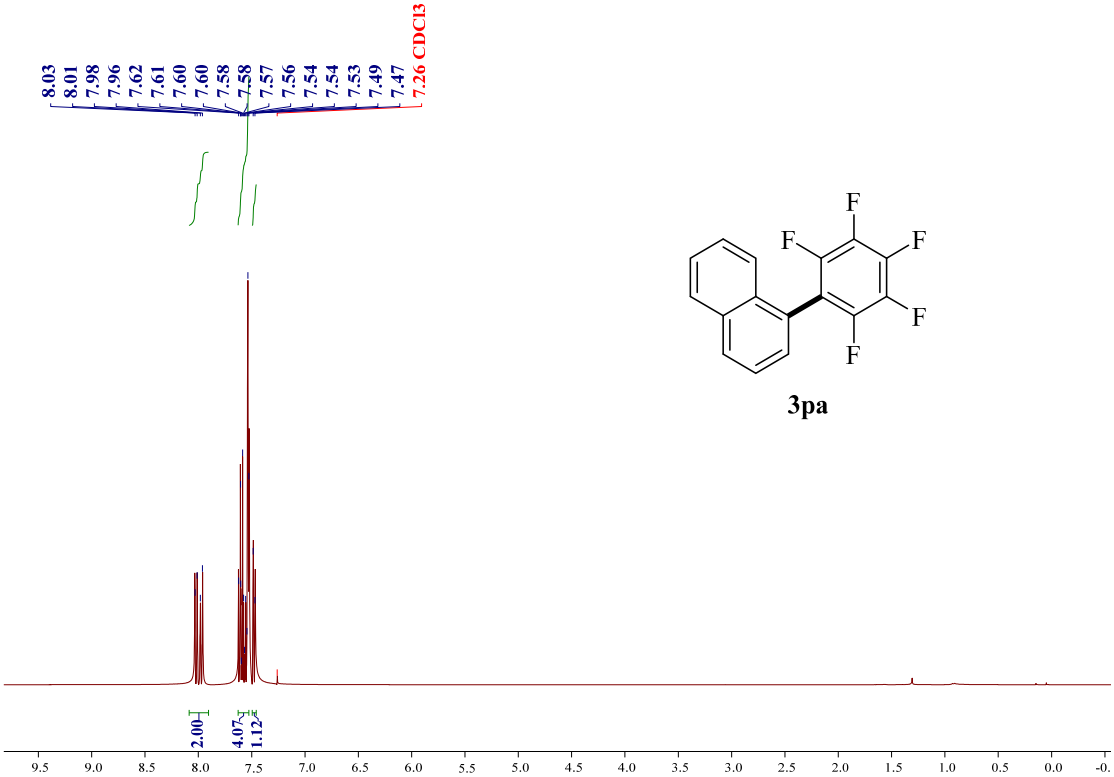


^{19}F NMR spectrum of 3oa (376 MHz, $CDCl_3$)



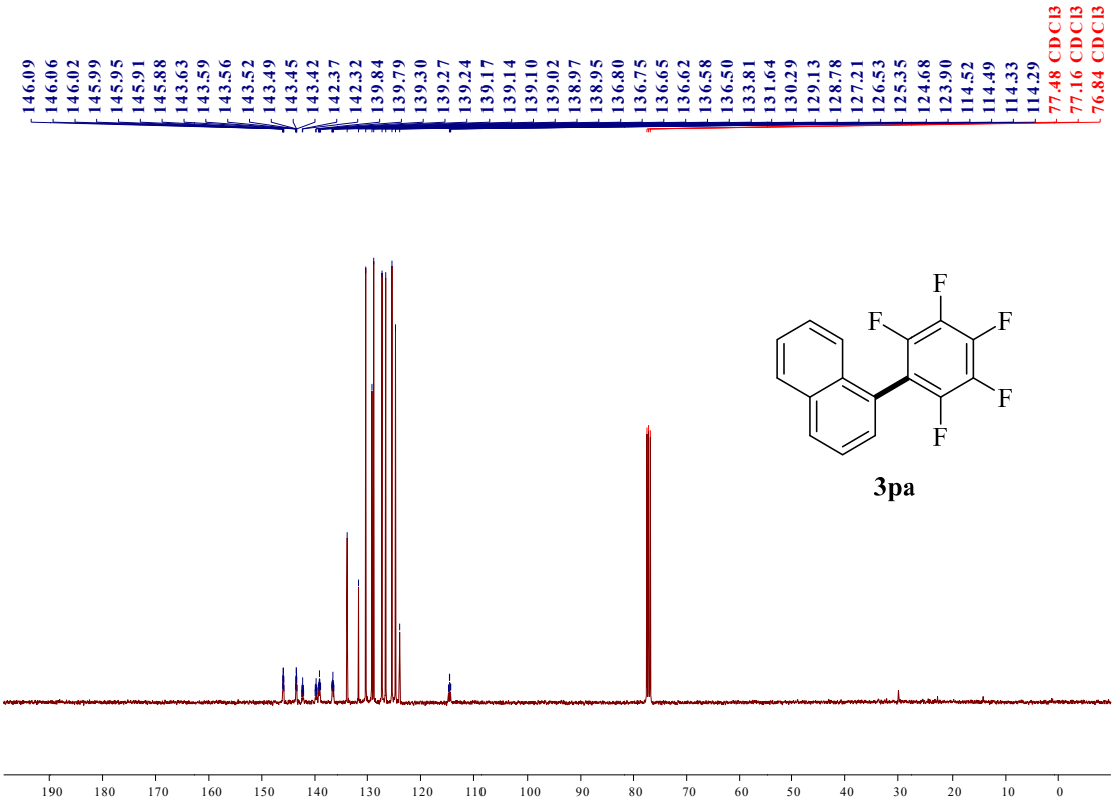
3oa

^{1}H NMR spectrum of 3pa (400 MHz, $CDCl_3$)

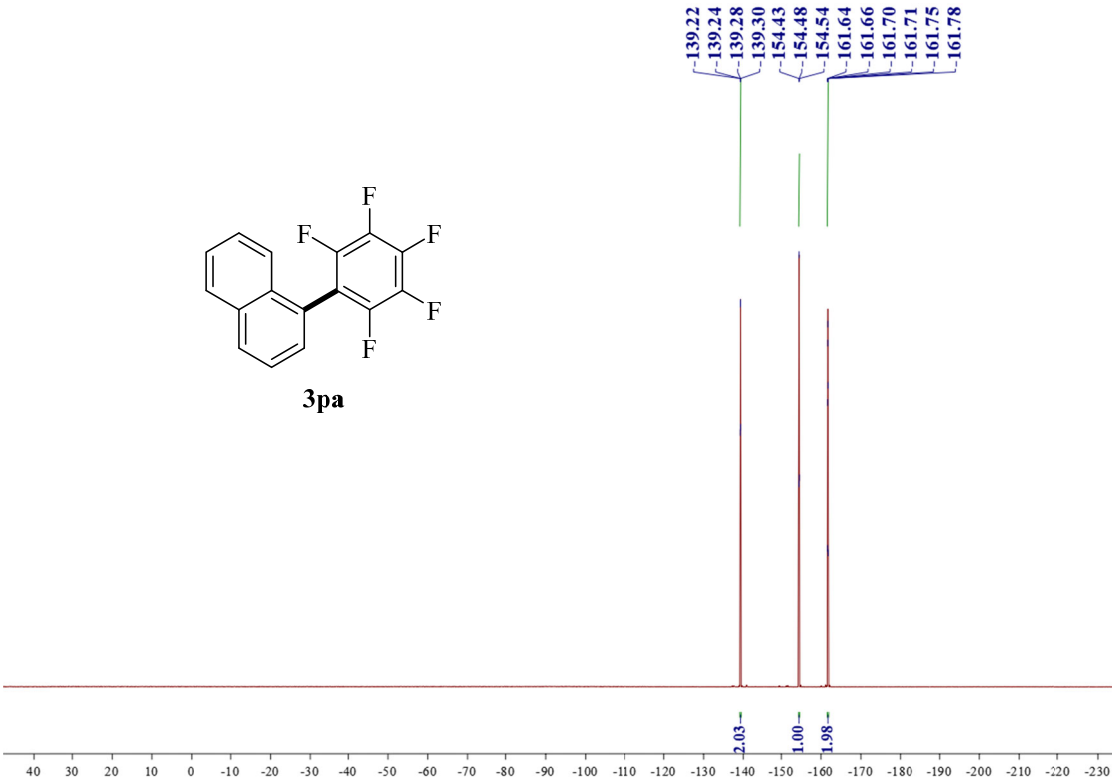


3pa

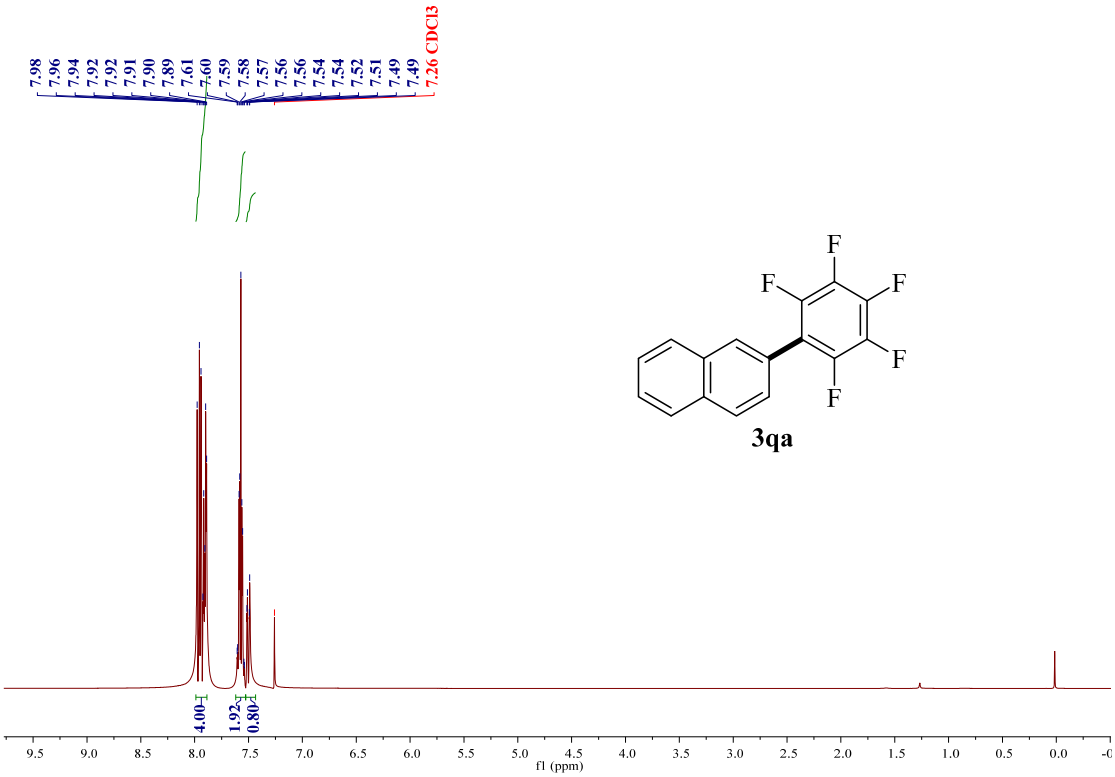
^{13}C NMR spectrum of 3pa (100 MHz, $CDCl_3$)



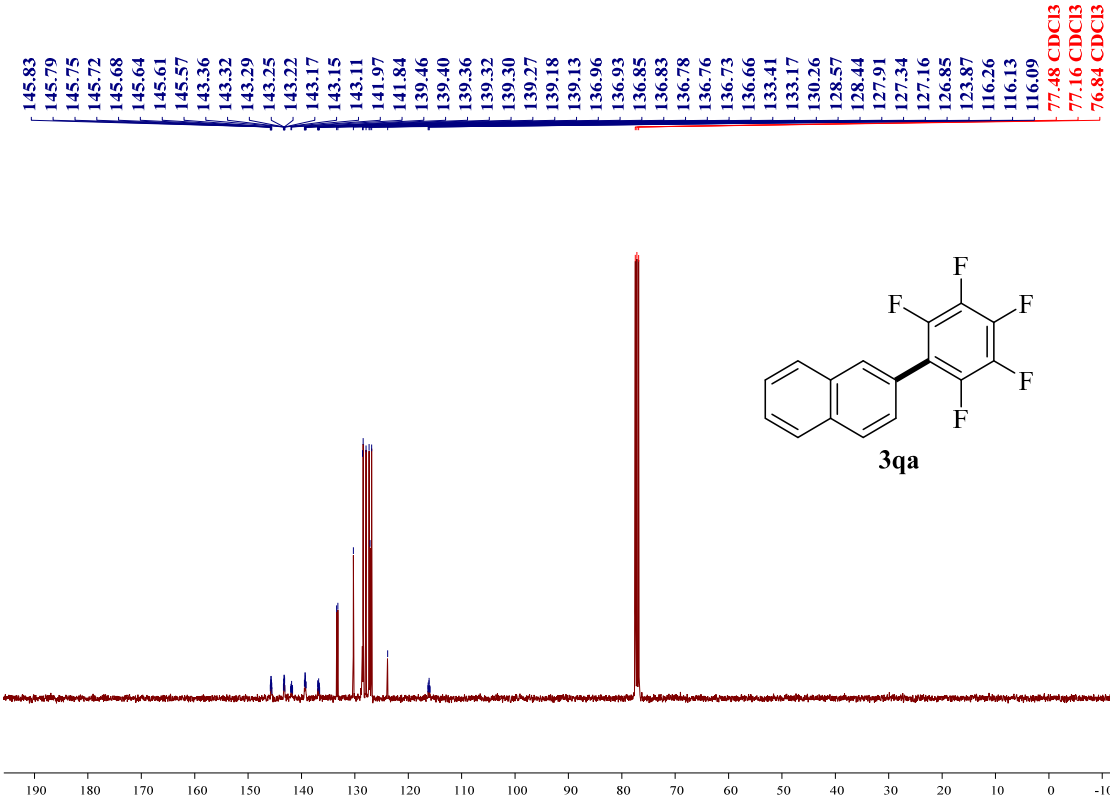
^{19}F NMR spectrum of 3pa (376 MHz, $CDCl_3$)



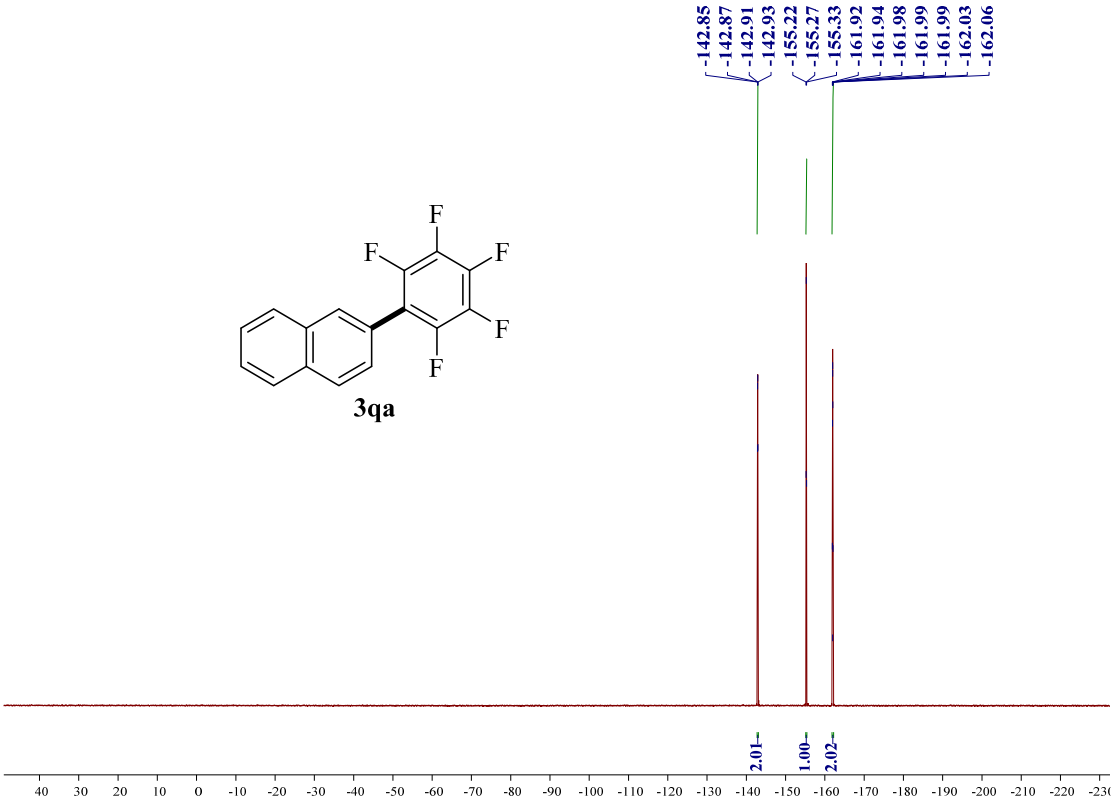
^{1}H NMR spectrum of 3qa (400 MHz, $CDCl_3$)



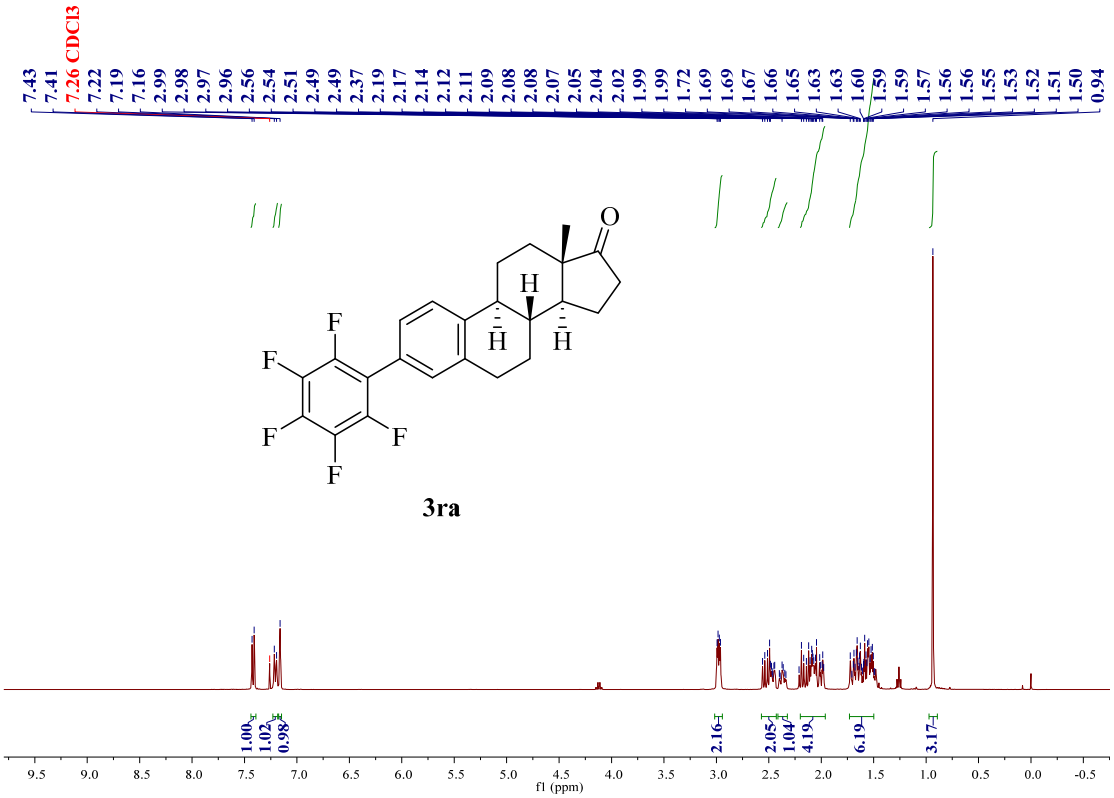
^{13}C NMR spectrum of 3qa (100 MHz, $CDCl_3$)



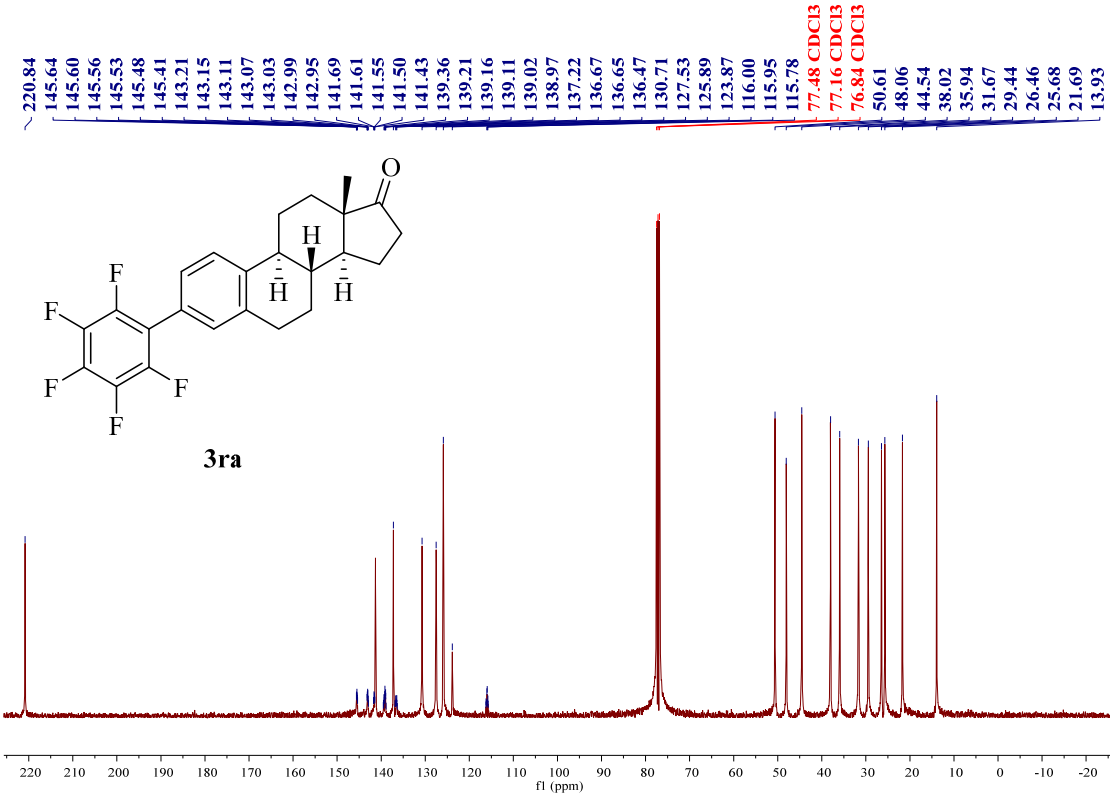
^{19}F NMR spectrum of 3qa (376 MHz, $CDCl_3$)



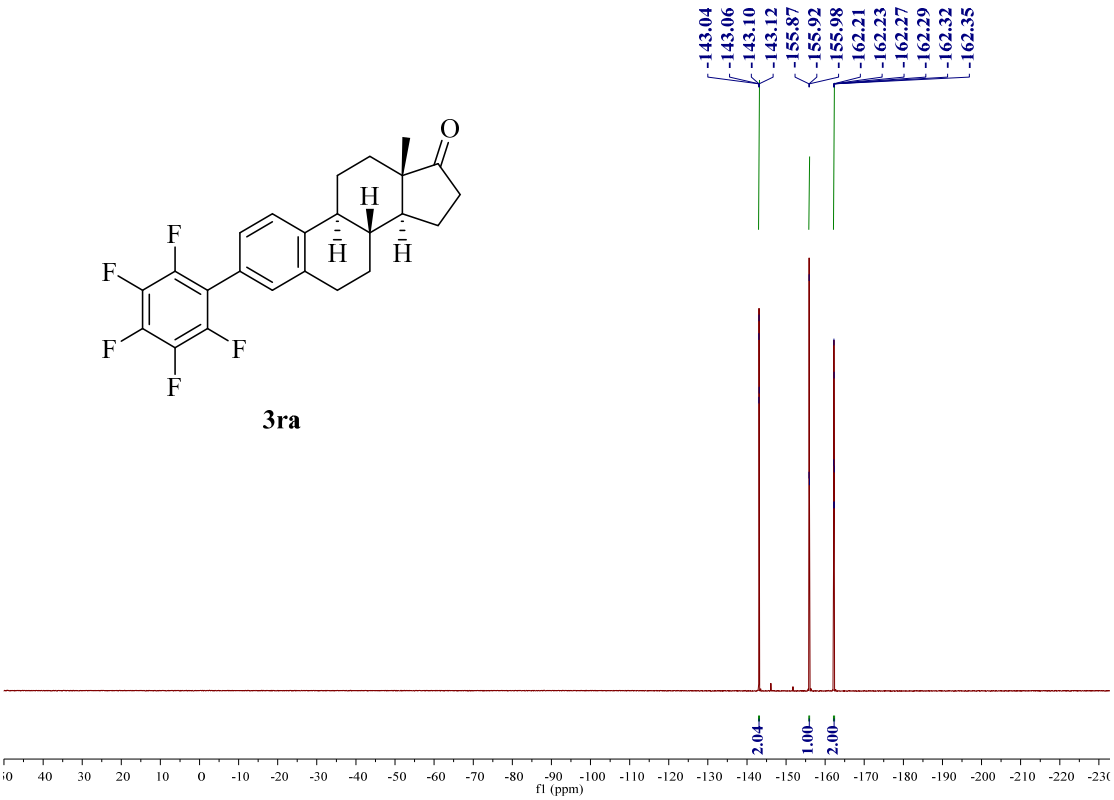
^{1}H NMR spectrum of 3ra (400 MHz, $CDCl_3$)



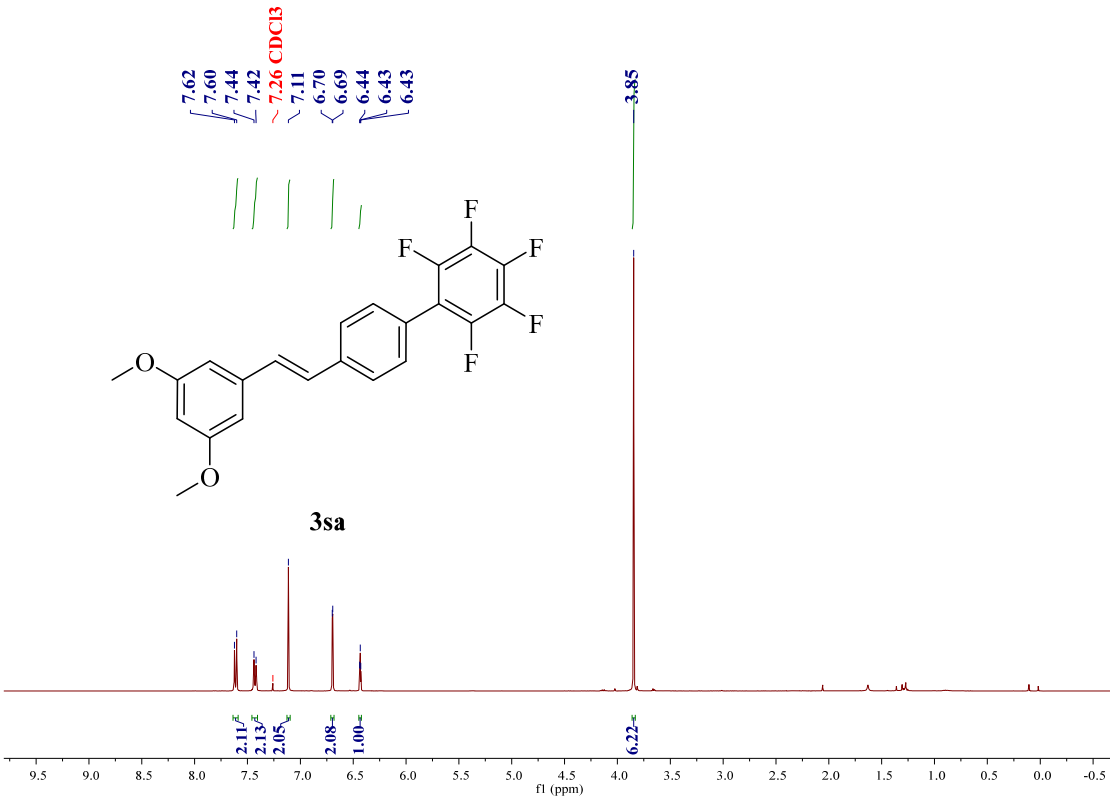
^{13}C NMR spectrum of 3ra (100 MHz, $CDCl_3$)



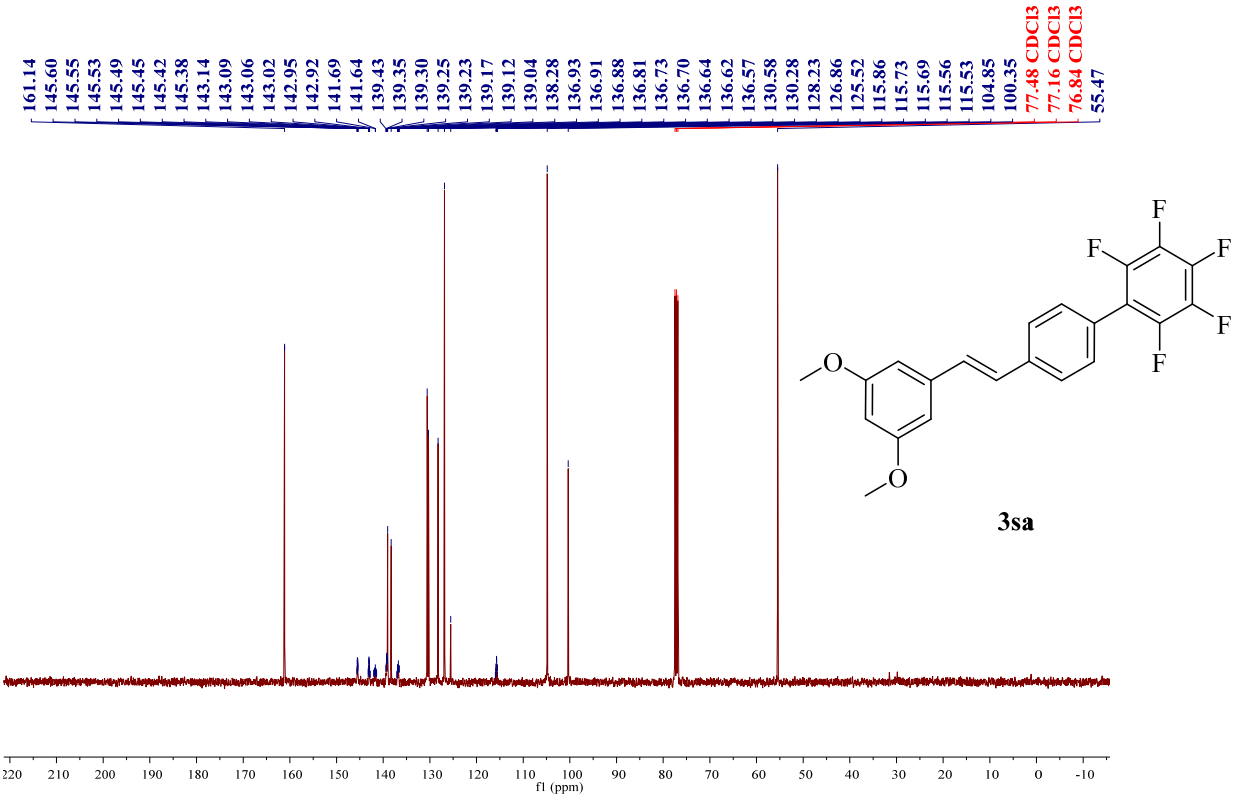
^{19}F NMR spectrum of 3ra (376 MHz, $CDCl_3$)



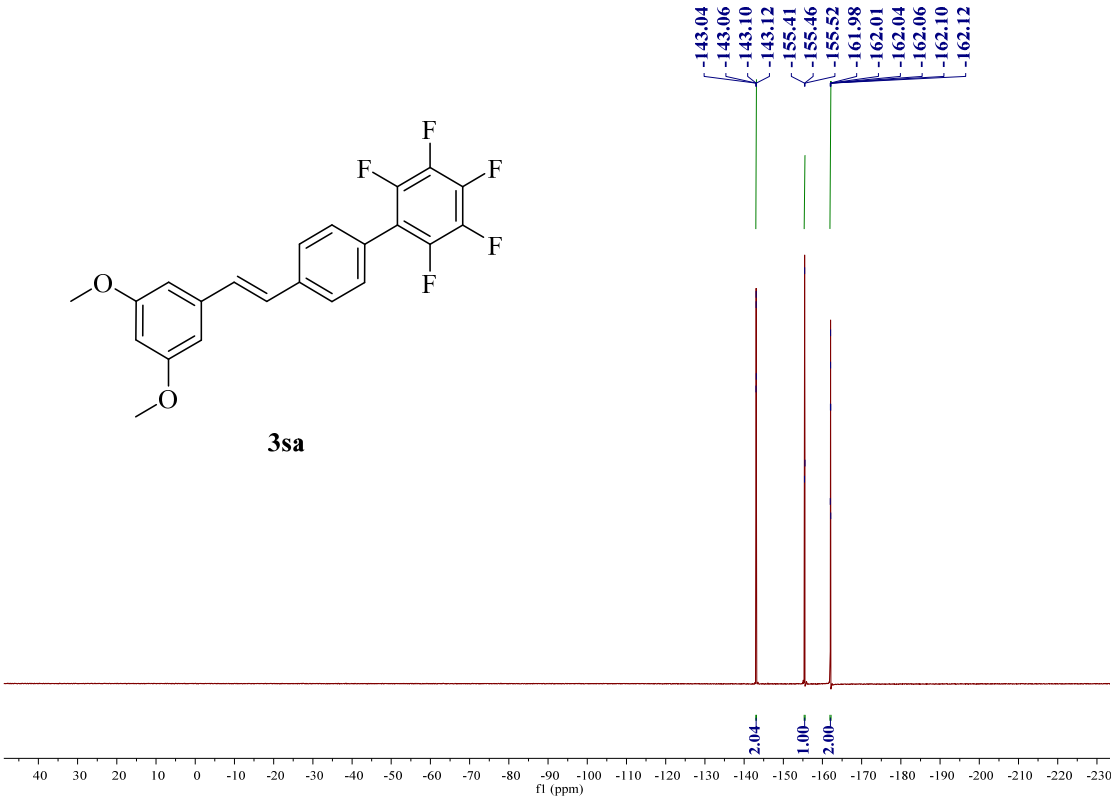
^{1}H NMR spectrum of 3sa (400 MHz, $CDCl_3$)



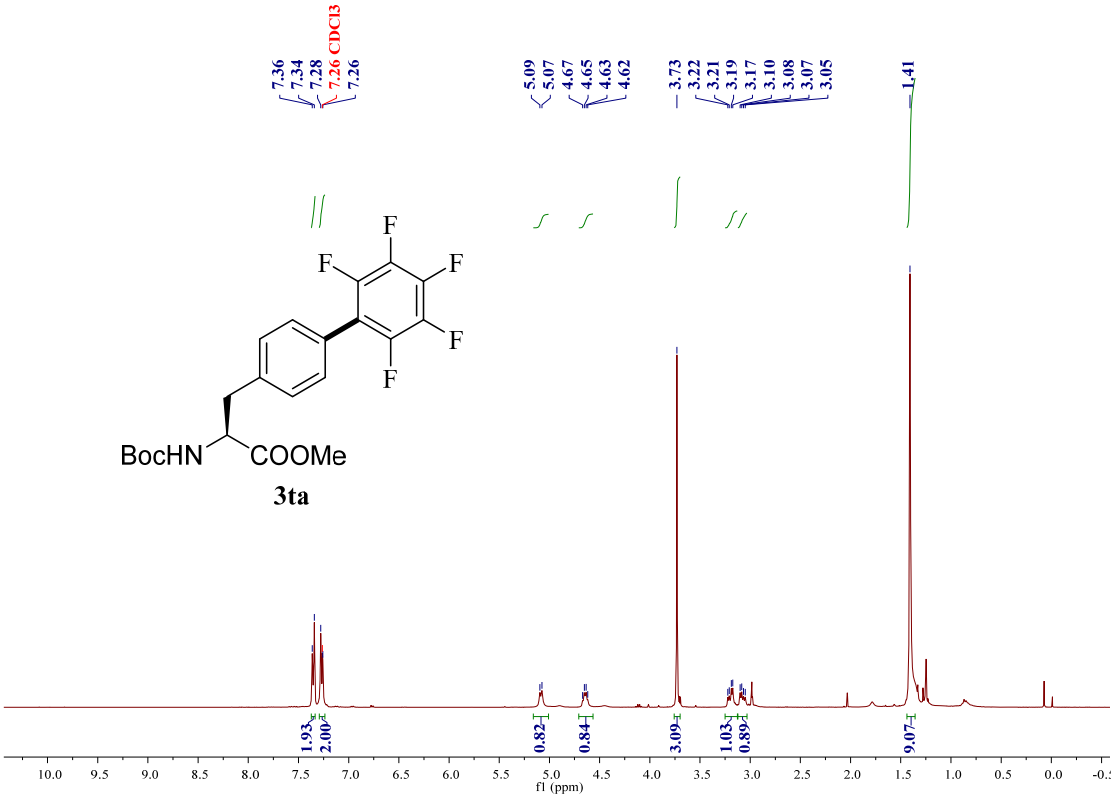
^{13}C NMR spectrum of 3sa (100 MHz, $CDCl_3$)



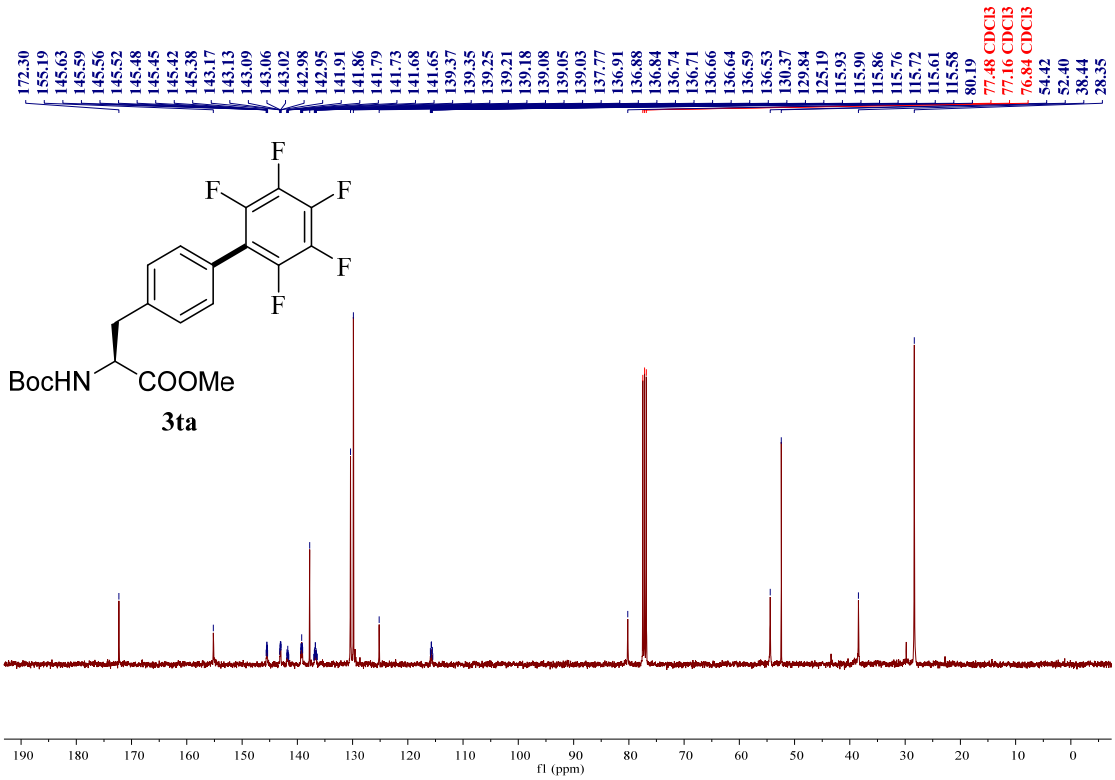
^{19}F NMR spectrum of 3sa (376 MHz, $CDCl_3$)



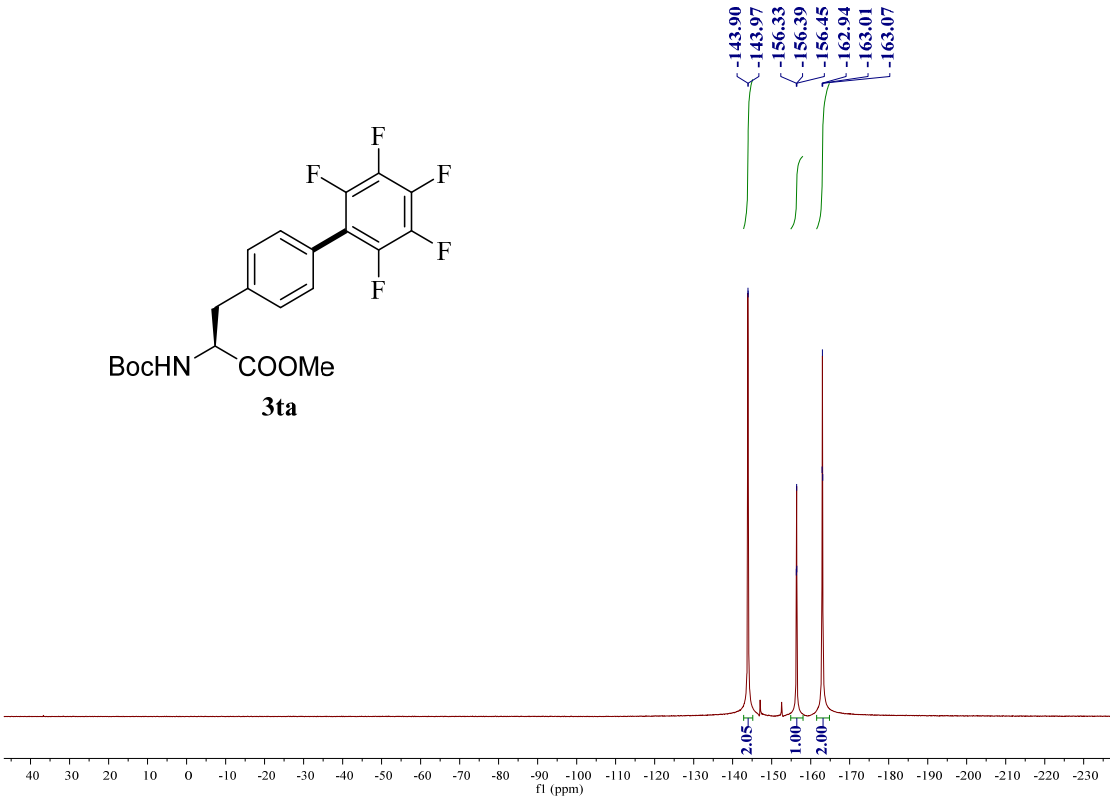
^{1}H NMR spectrum of 3ta (400 MHz, $CDCl_3$)



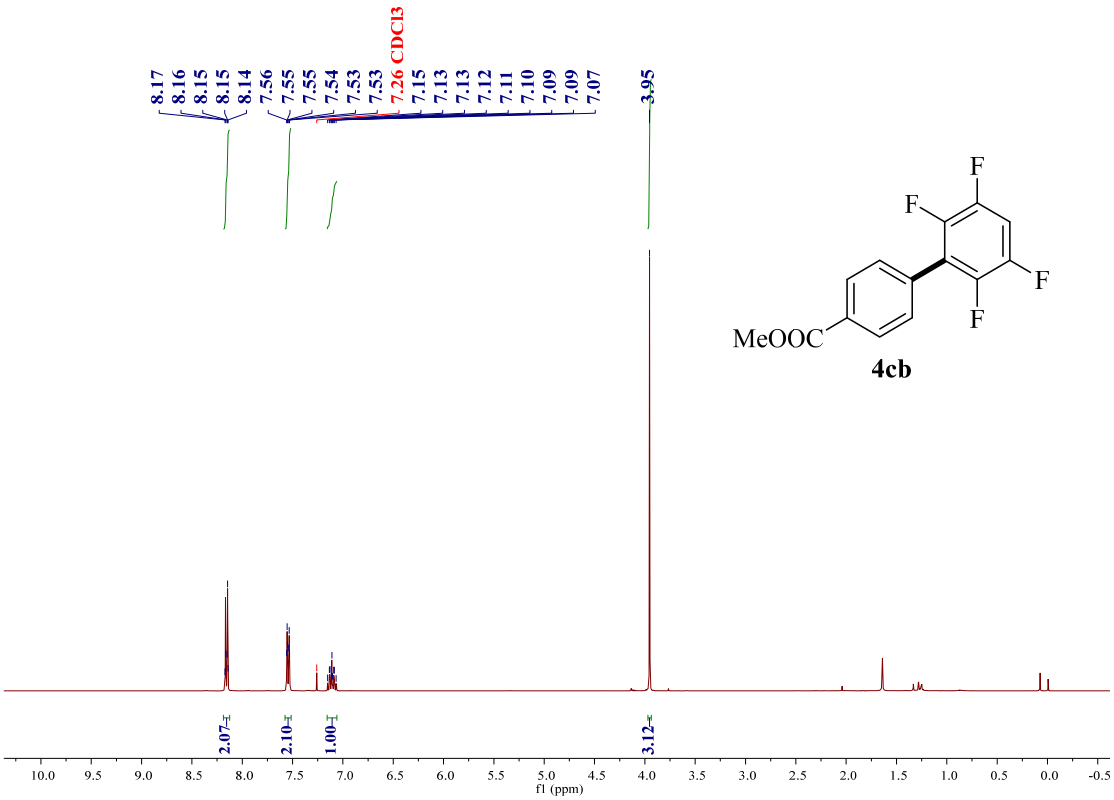
^{13}C NMR spectrum of 3ta (100 MHz, $CDCl_3$)



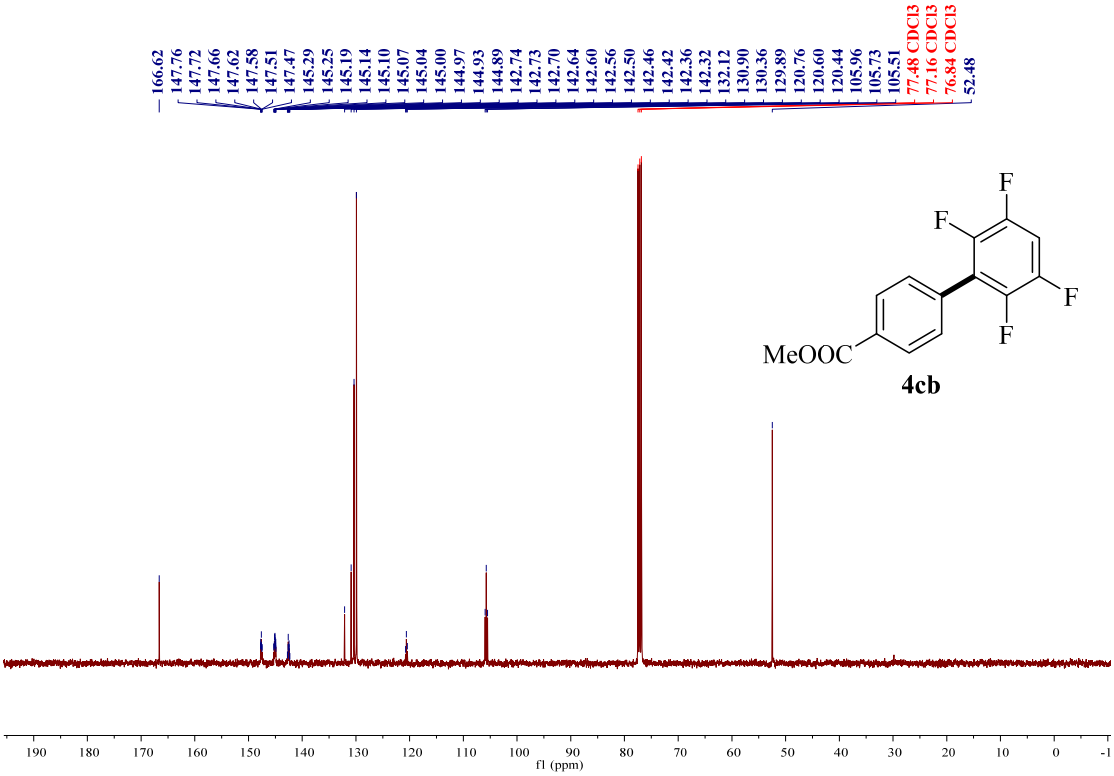
^{19}F NMR spectrum of 3ta (376 MHz, $CDCl_3$)



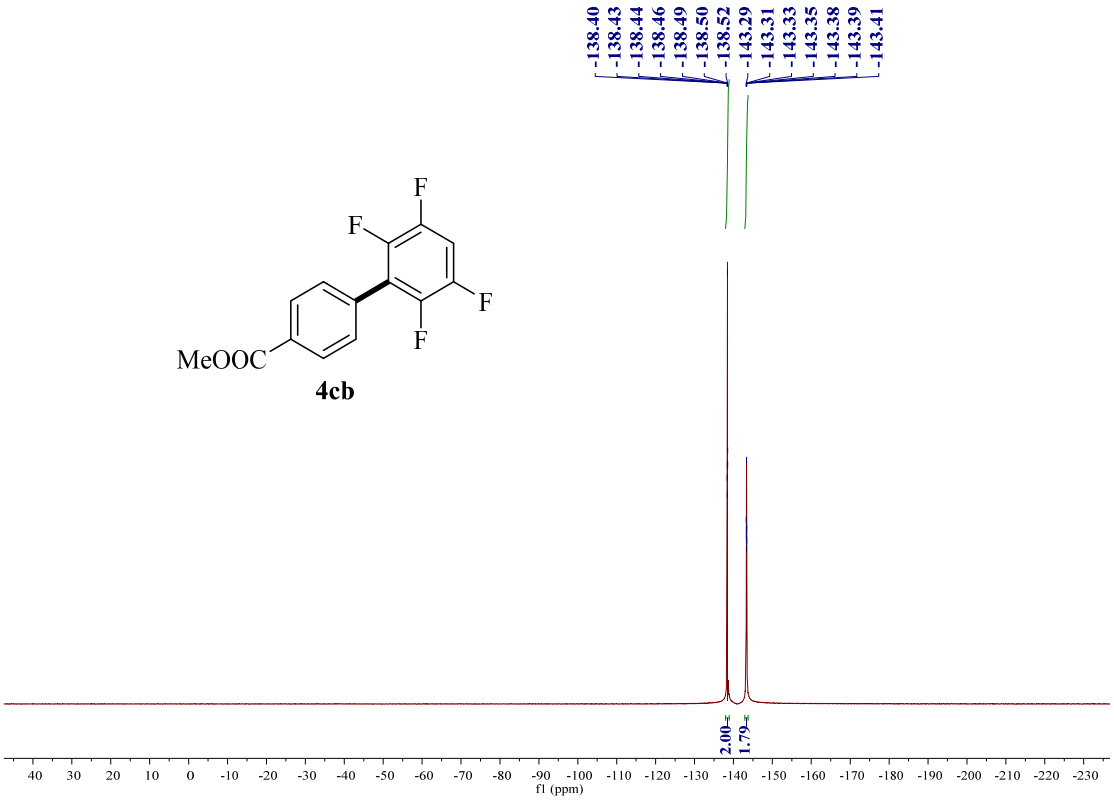
^{1}H NMR spectrum of 4cb (400 MHz, $CDCl_3$)



^{13}C NMR spectrum of 4cb (100 MHz, $CDCl_3$)

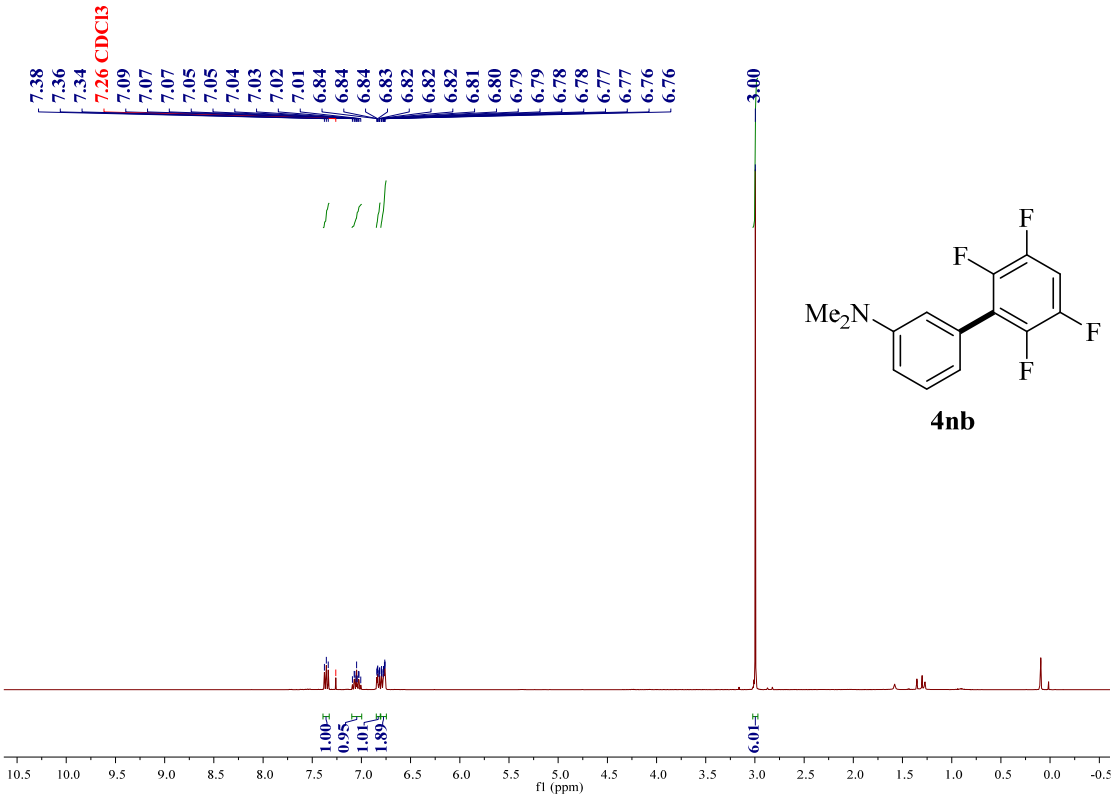


^{19}F NMR spectrum of 4cb (376 MHz, $CDCl_3$)



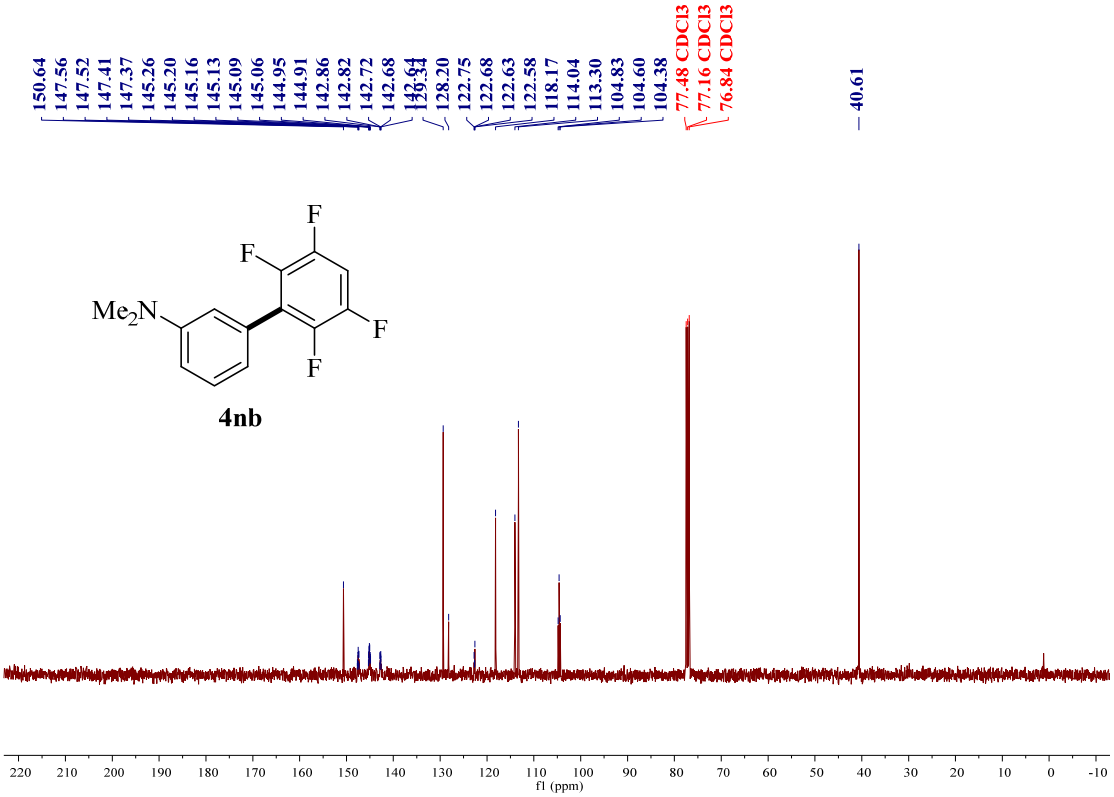
4cb

^{1}H NMR spectrum of 4nb (400 MHz, $CDCl_3$)

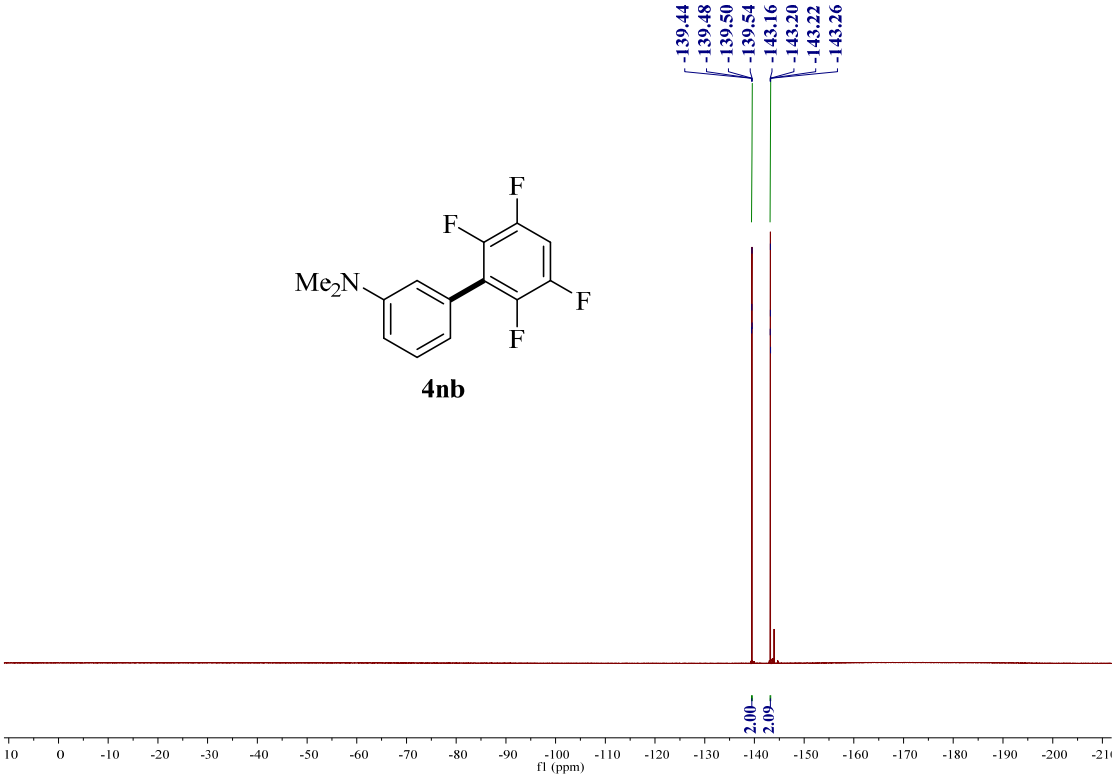


4nb

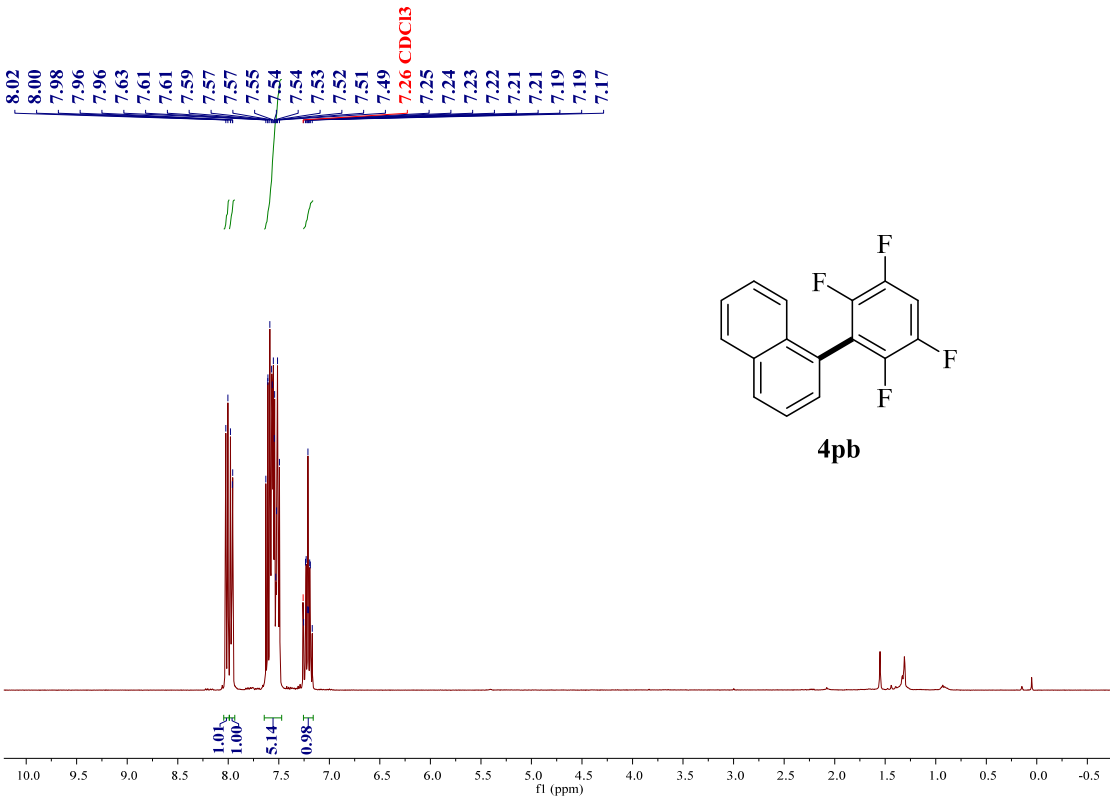
^{13}C NMR spectrum of 4nb (100 MHz, $CDCl_3$)



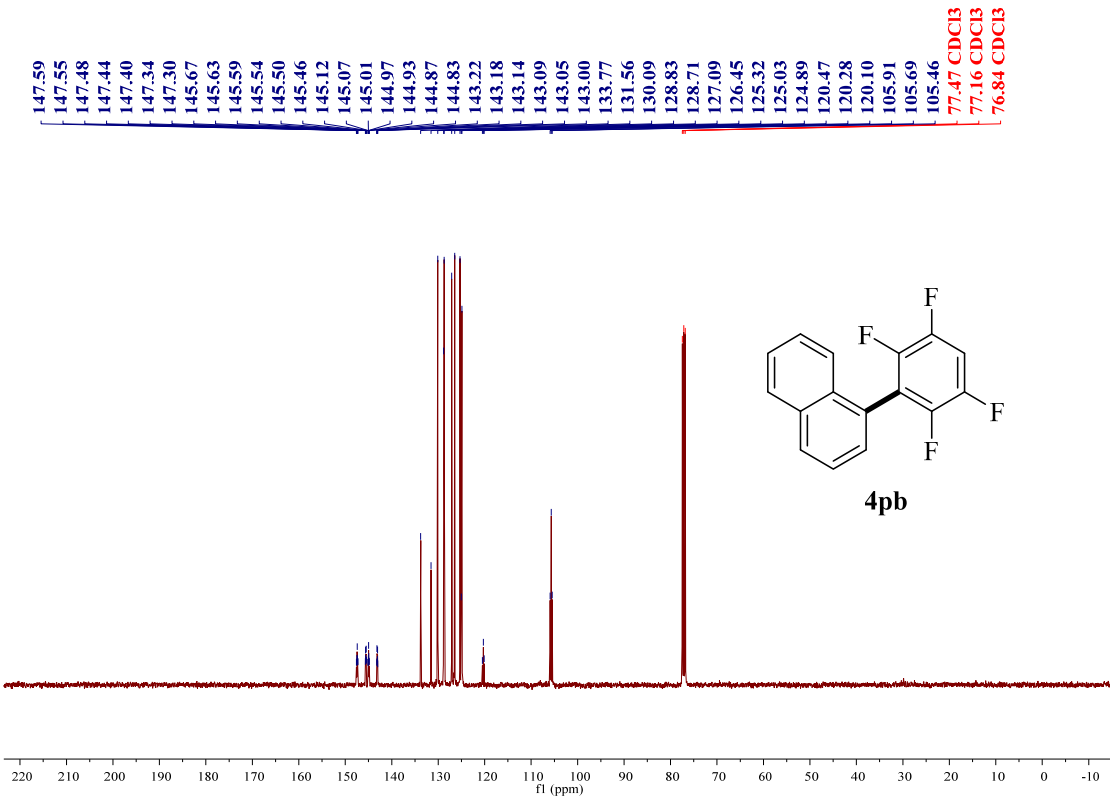
^{19}F NMR spectrum of 4nb (376 MHz, $CDCl_3$)



^{1}H NMR spectrum of 4pb (400 MHz, $CDCl_3$)



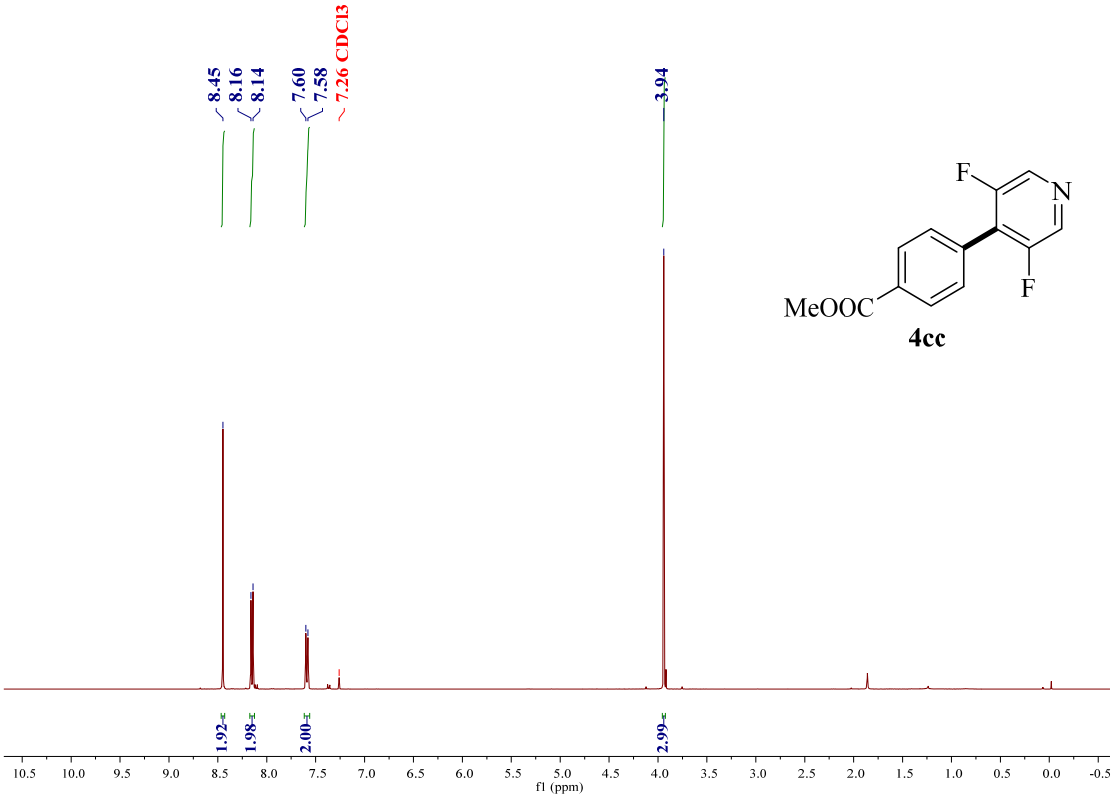
^{13}C NMR spectrum of 4pb (100 MHz, $CDCl_3$)



^{19}F NMR spectrum of 4pb (376 MHz, $CDCl_3$)

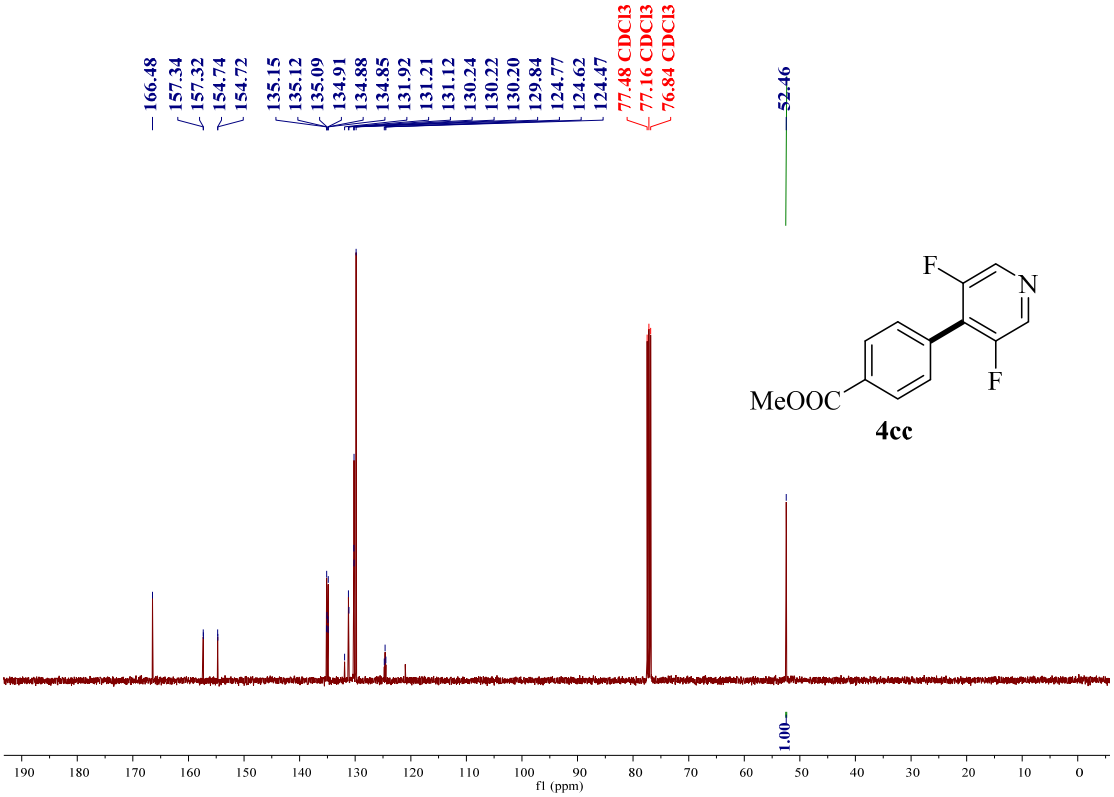
4pb

^{1}H NMR spectrum of 4cc (400 MHz, $CDCl_3$)

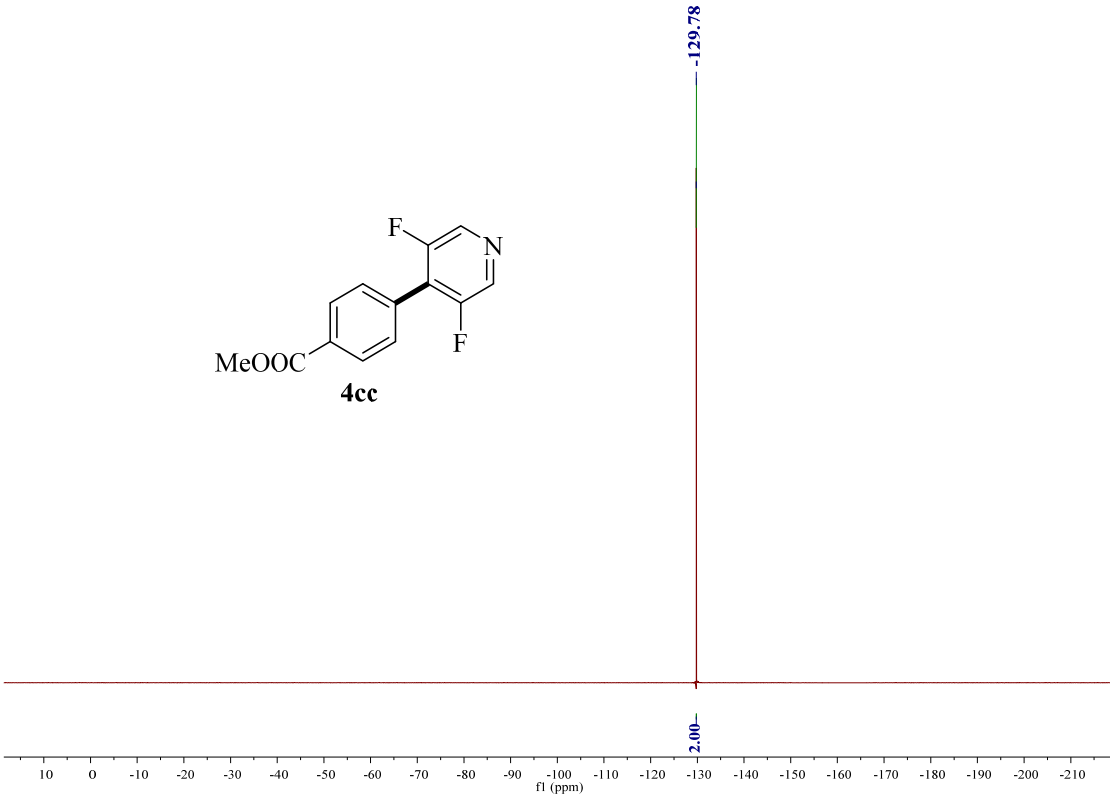


4cc

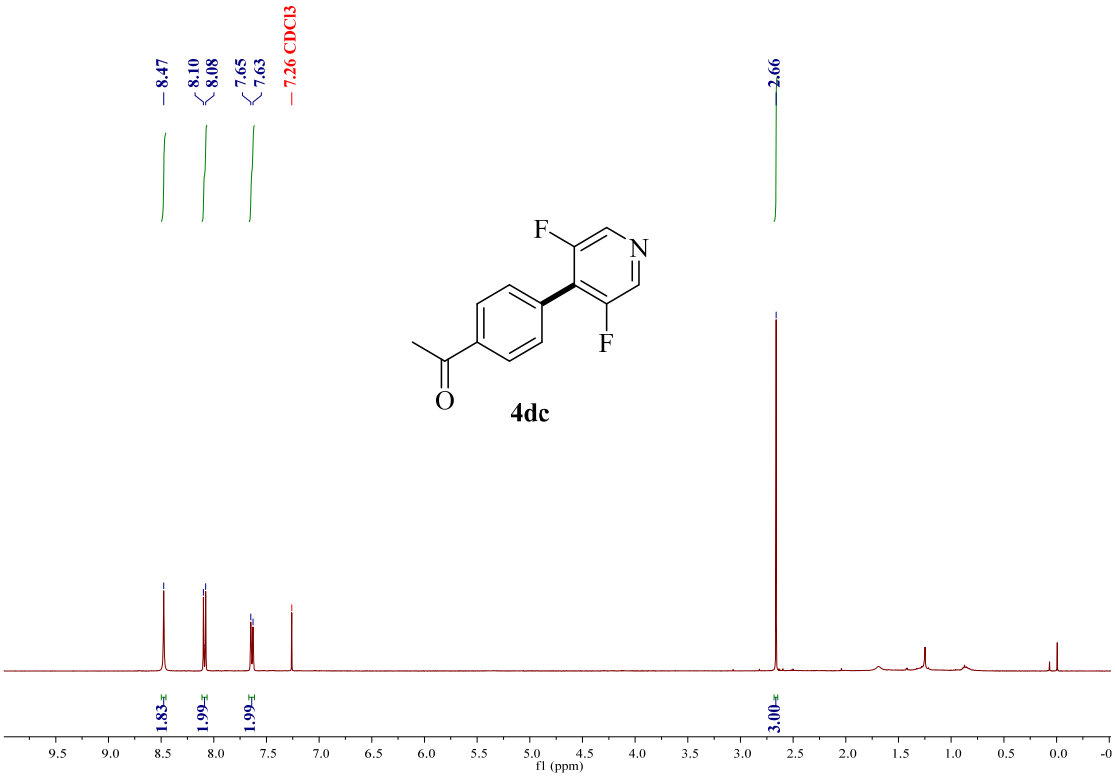
^{13}C NMR spectrum of 4cc (100 MHz, $CDCl_3$)



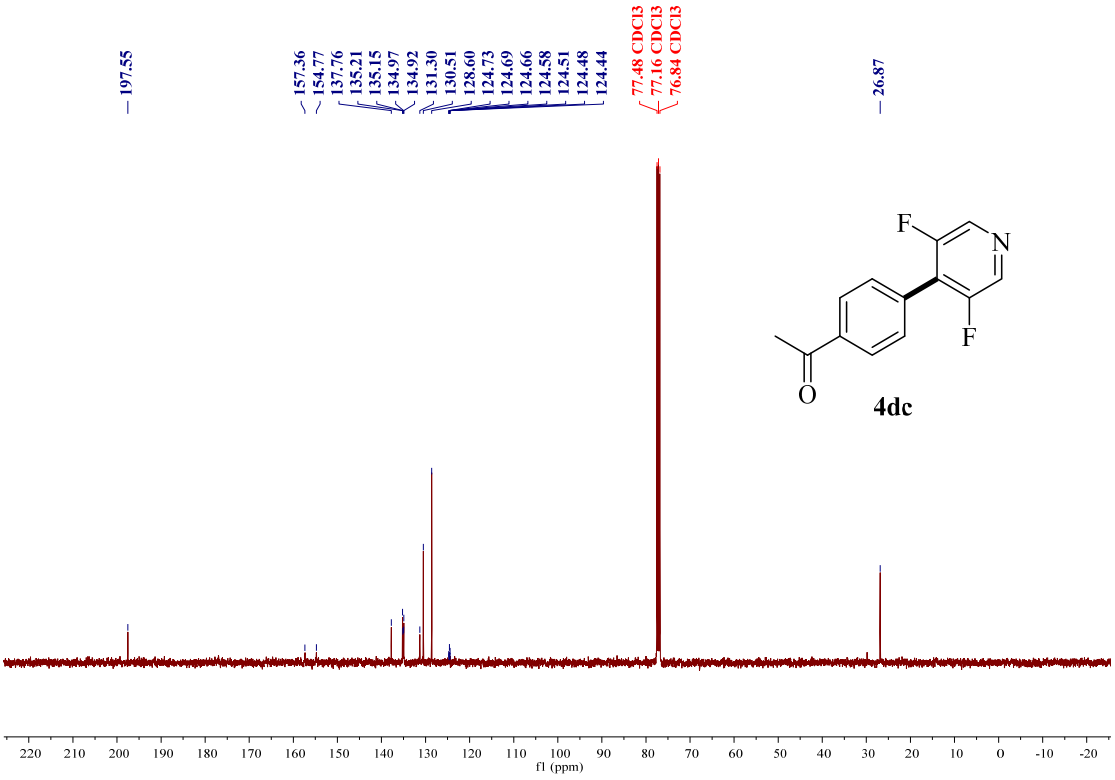
^{19}F NMR spectrum of 4cc (376 MHz, $CDCl_3$)



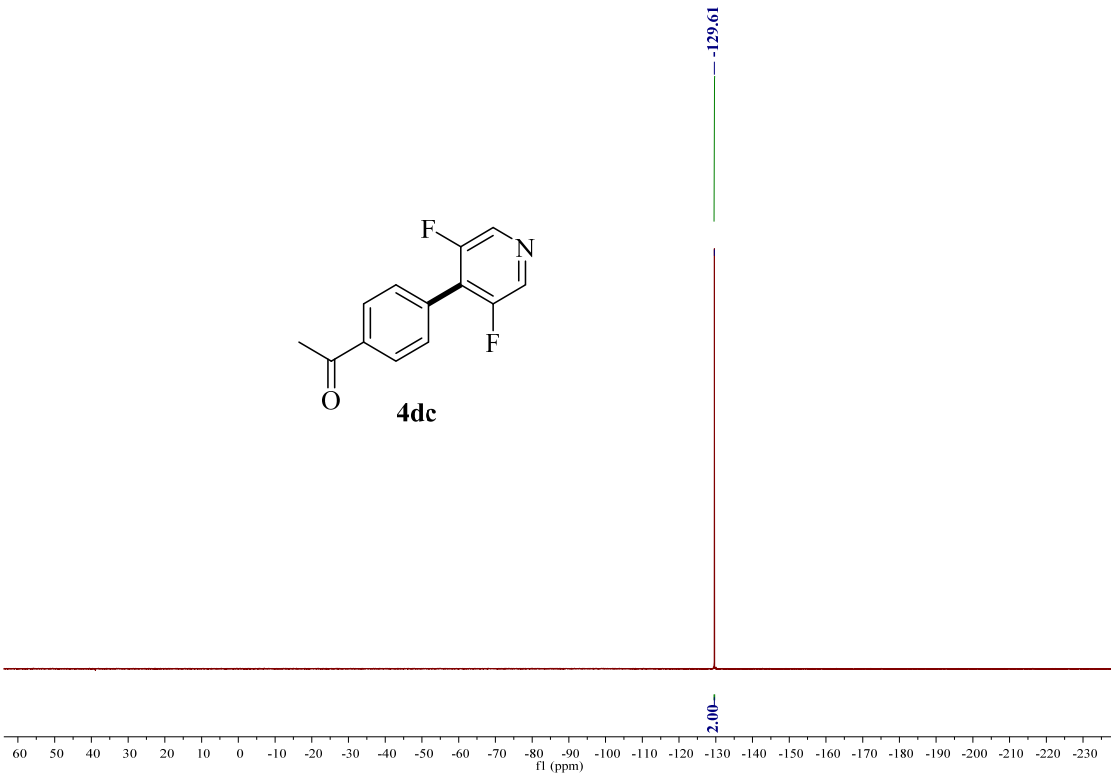
^{1}H NMR spectrum of 4dc(400 MHz, $CDCl_3$)



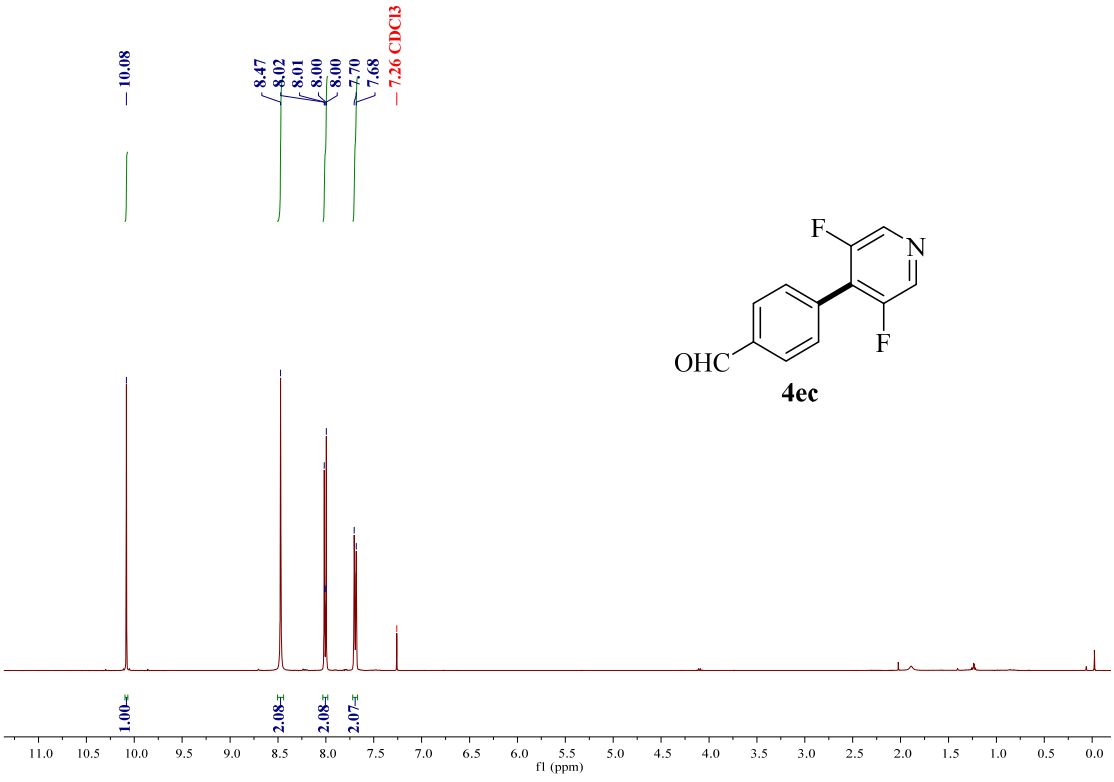
^{13}C NMR spectrum of 4dc (100 MHz, $CDCl_3$)



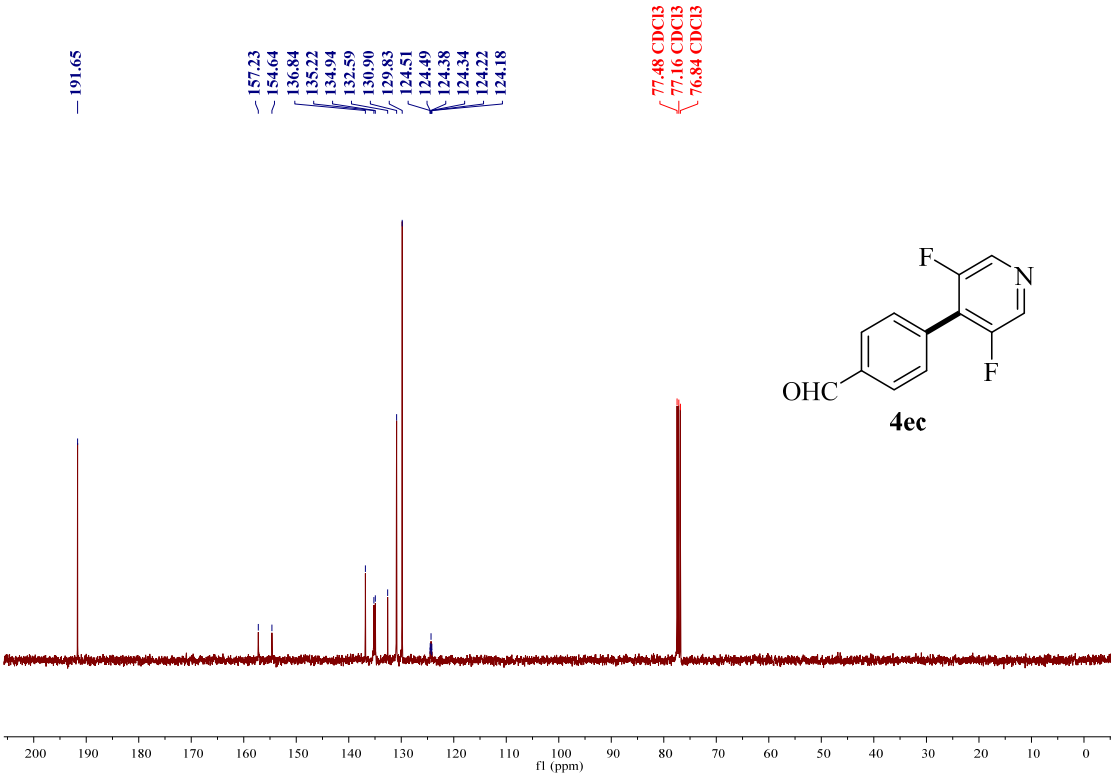
^{19}F NMR spectrum of 4dc (376 MHz, $CDCl_3$)



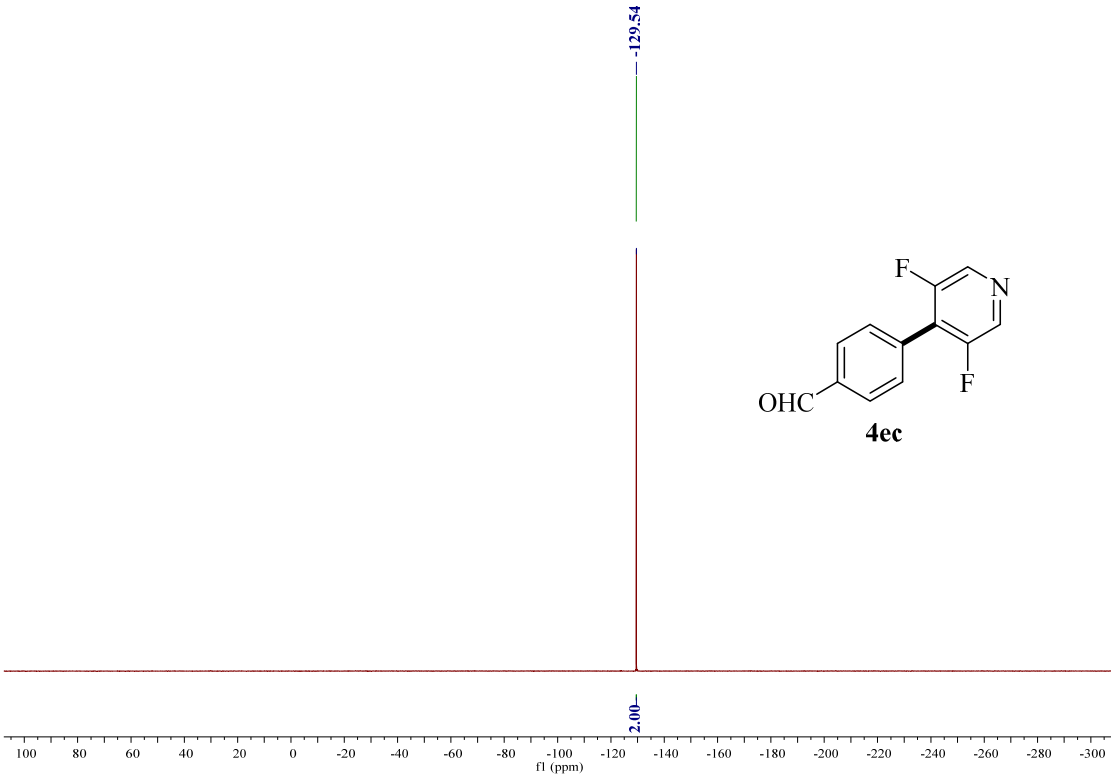
^{1}H NMR spectrum of 4ec (400 MHz, $CDCl_3$)



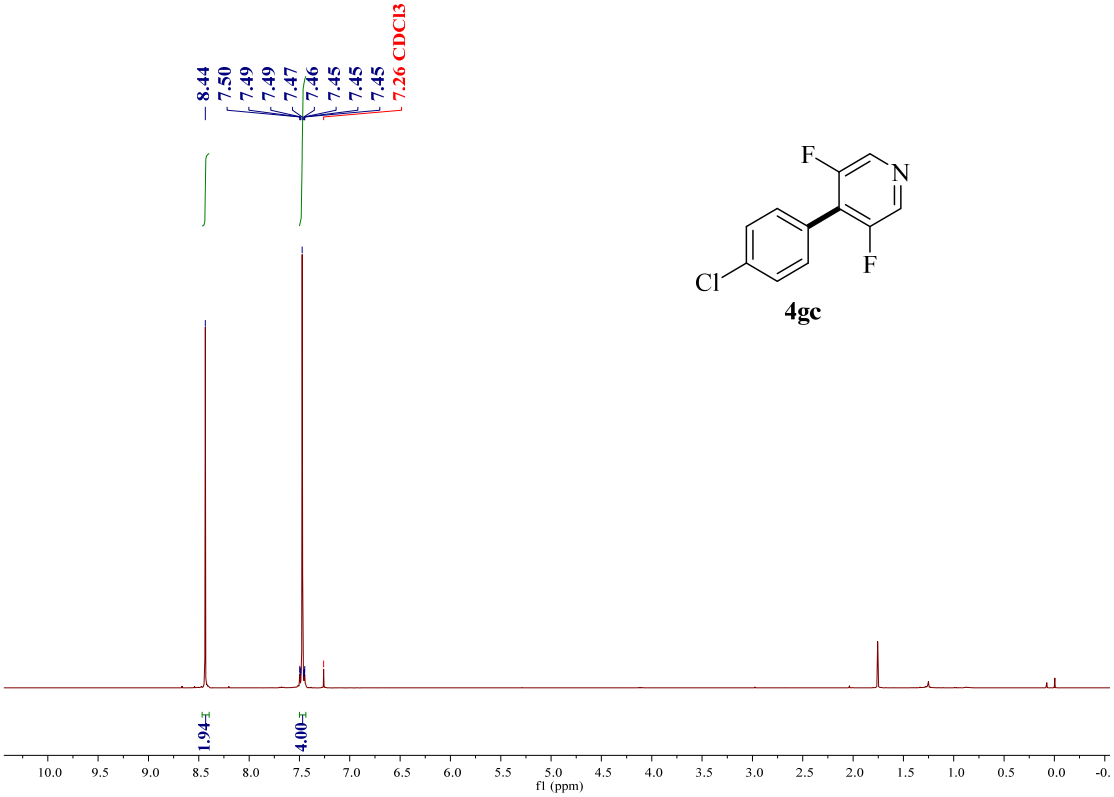
^{13}C NMR spectrum of 4ec (100 MHz, $CDCl_3$)



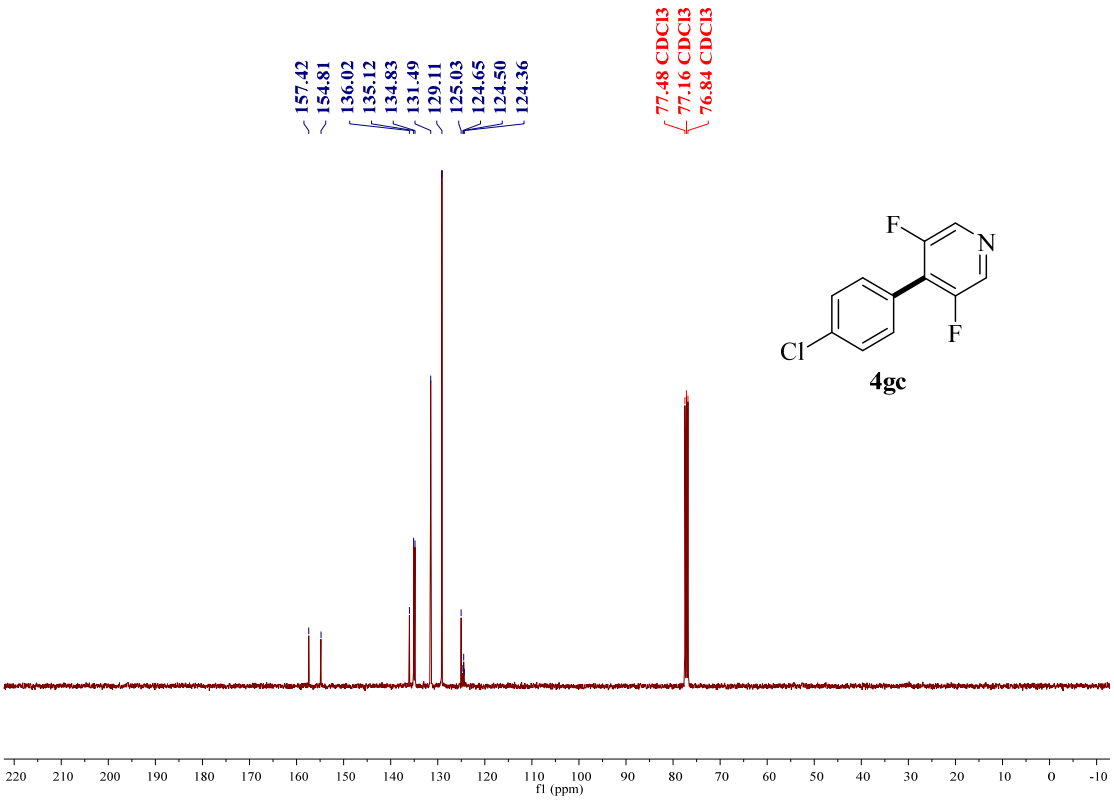
^{19}F NMR spectrum of 4ec (376 MHz, $CDCl_3$)



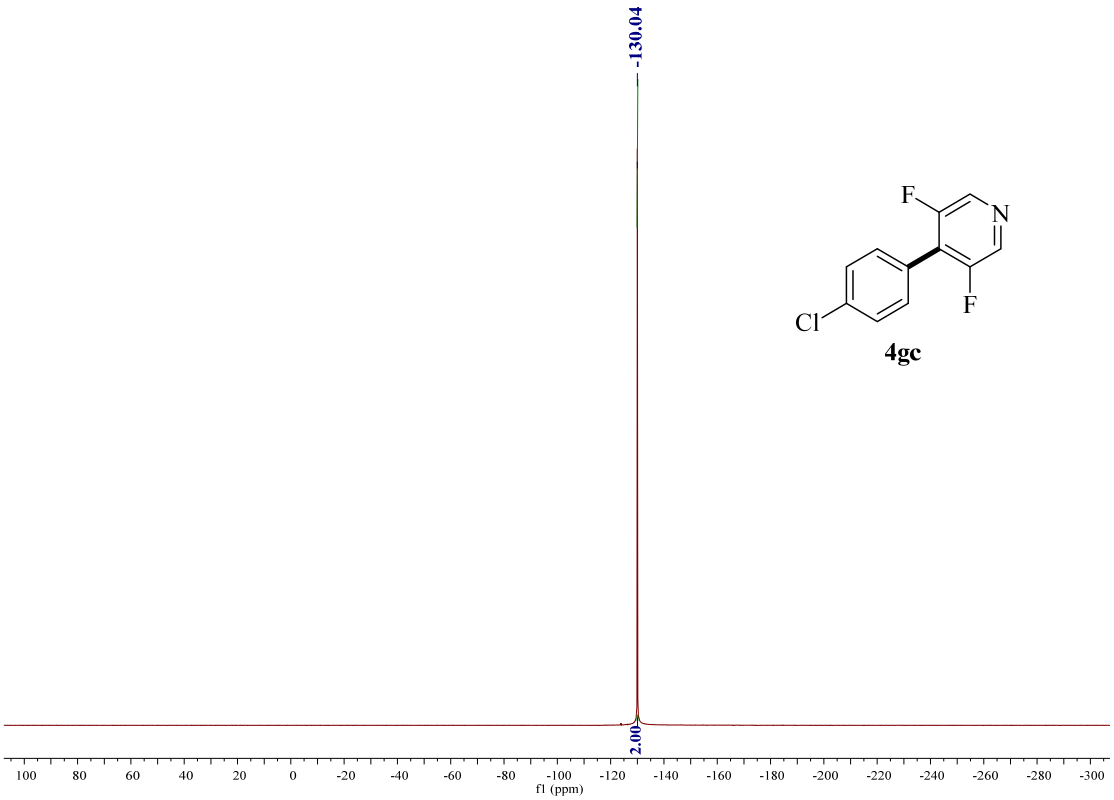
^{1}H NMR spectrum of 4gc (400 MHz, $CDCl_3$)



^{13}C NMR spectrum of 4gc (100 MHz, $CDCl_3$)

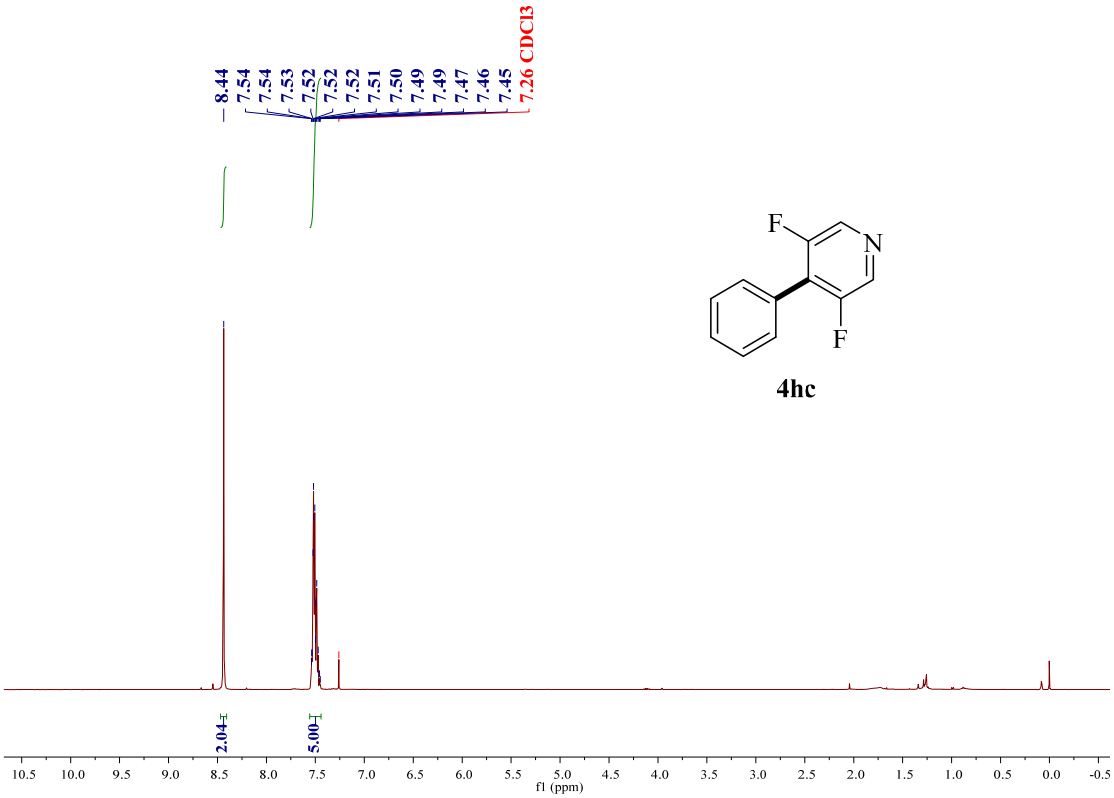


^{19}F NMR spectrum of 4gc (376 MHz, $CDCl_3$)



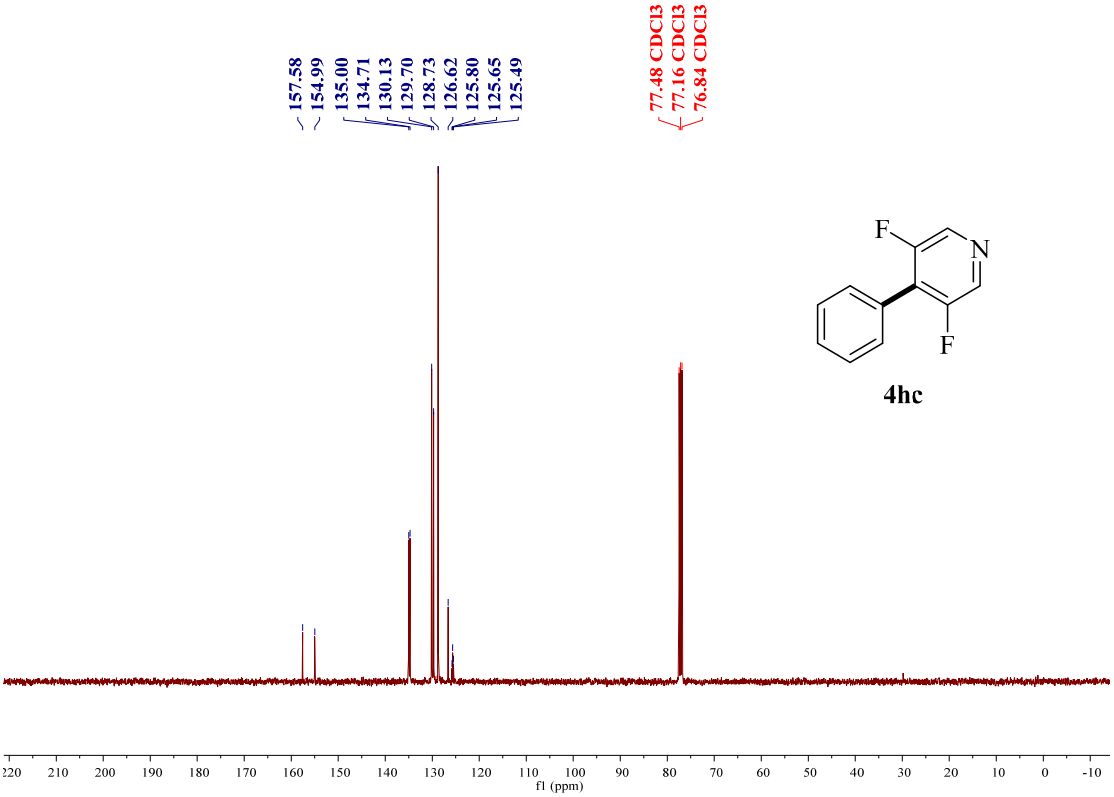
4gc

^{1}H NMR spectrum of 4hc (400 MHz, $CDCl_3$)

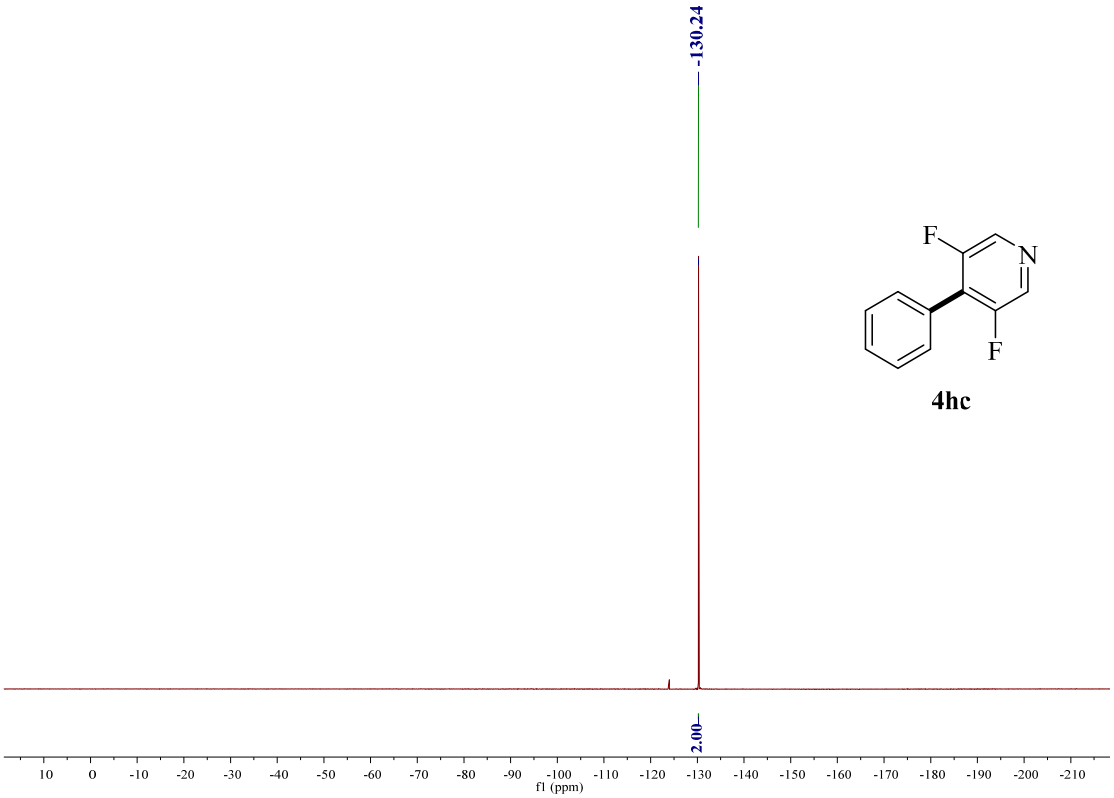


4hc

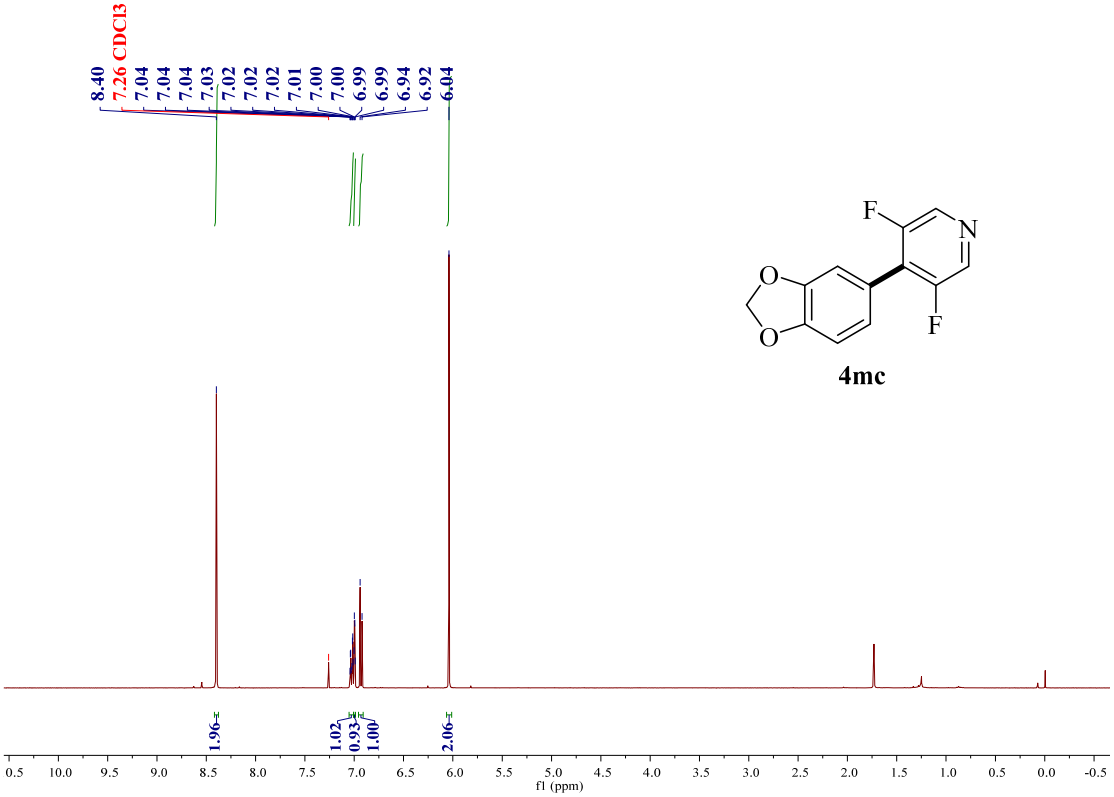
^{13}C NMR spectrum of 4hc (100 MHz, $CDCl_3$)



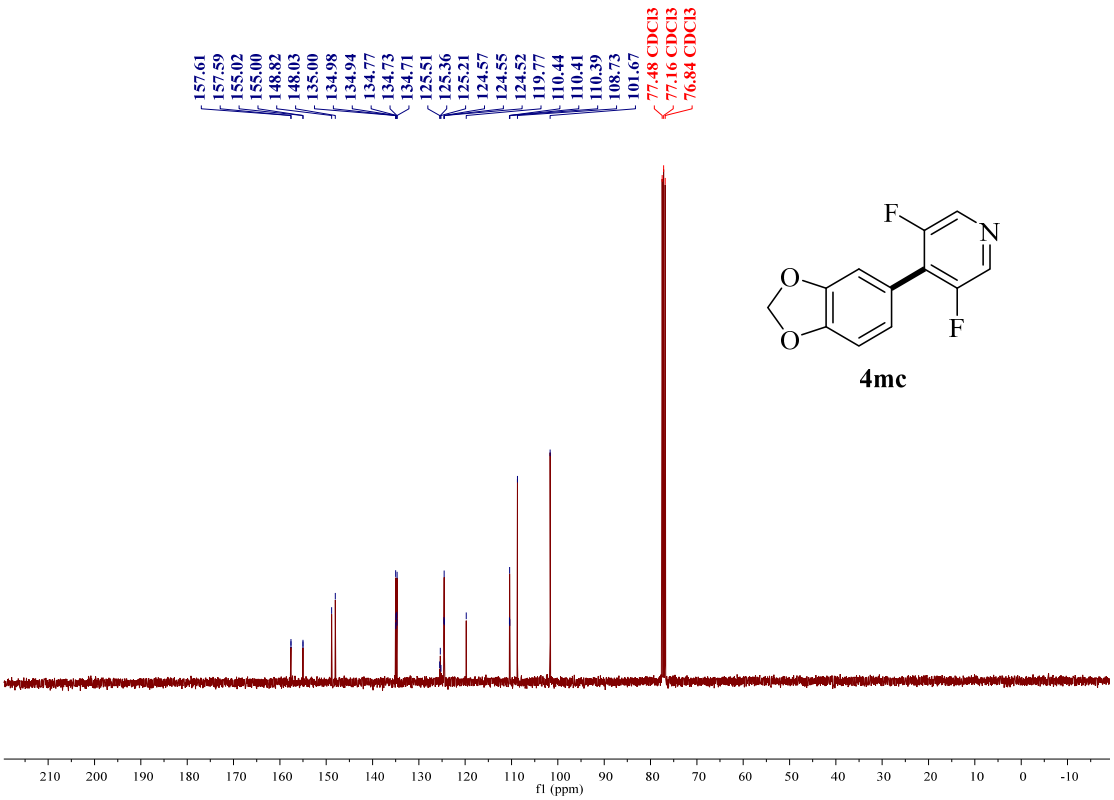
^{19}F NMR spectrum of 4hc (376 MHz, $CDCl_3$)



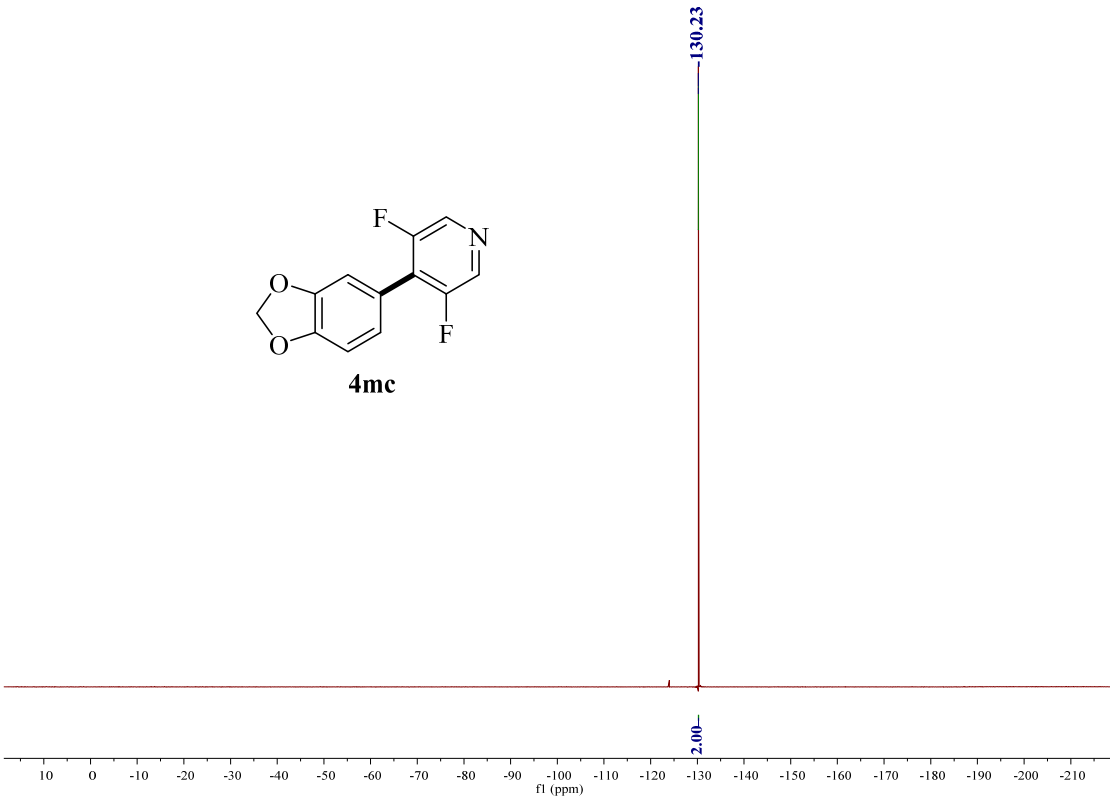
^{1}H NMR spectrum of 4mc (400 MHz, $CDCl_3$)



^{13}C NMR spectrum of 4mc (100 MHz, $CDCl_3$)

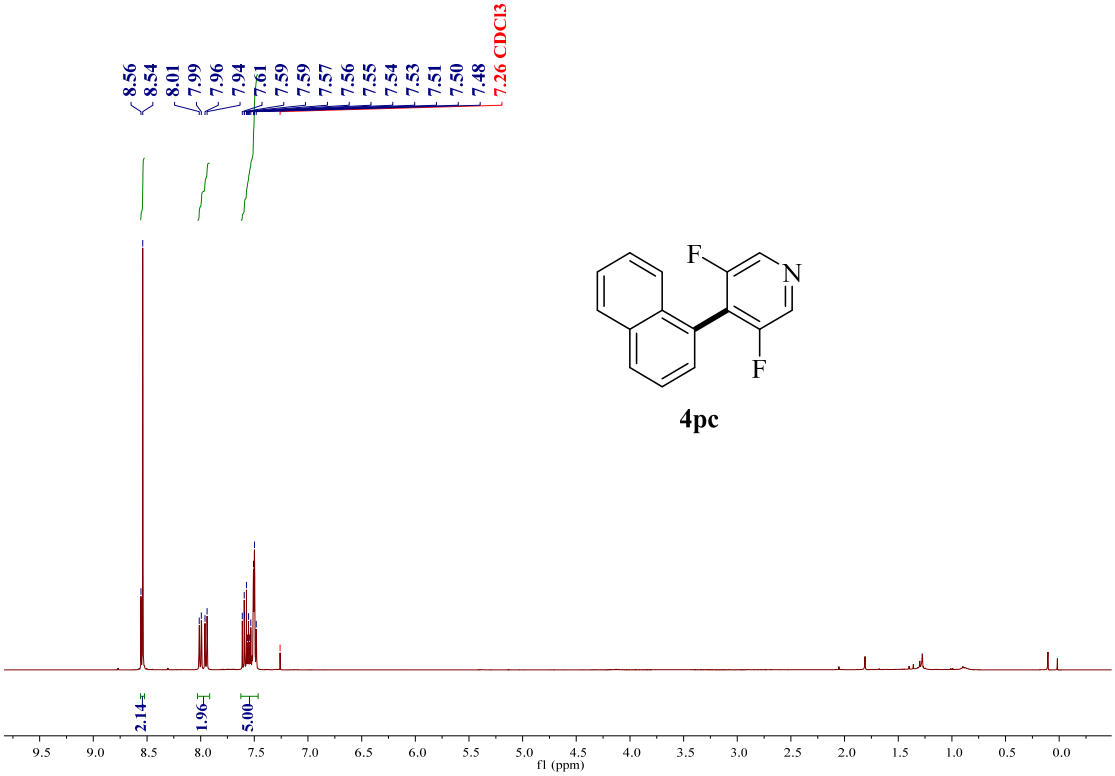


^{19}F NMR spectrum of 4mc (376 MHz, $CDCl_3$)



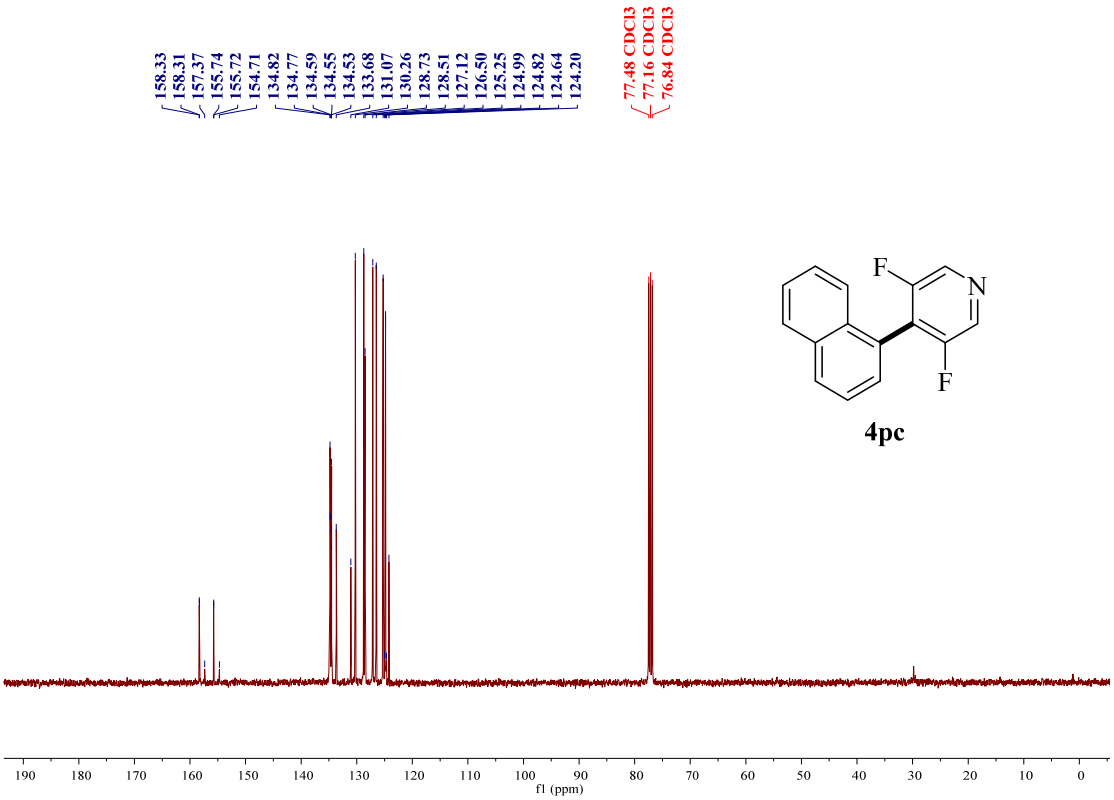
4mc

^{1}H NMR spectrum of 4pc (400 MHz, $CDCl_3$)



4pc

^{13}C NMR spectrum of 4pc (100 MHz, $CDCl_3$)



^{19}F NMR spectrum of 4pc (376 MHz, $CDCl_3$)