

Supporting Information for

N-Heterocyclic Carbene-Catalysed Pentafluorophenylation of Aldehydes

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General Methods

Unless otherwise indicated, all reactions were conducted under nitrogen atmosphere in an oven-dried glassware with magnetic stirring bar. Column chromatography was performed with silica gel (200~300 mesh) and analytical TLC on silica gel 60-F254. ^1H NMR (400 MHz, CDCl_3), ^{13}C NMR (100 MHz, CDCl_3) and ^{19}F NMR (376 MHz, CDCl_3) spectra were recorded on a Bruker-DMX 400 spectrometer in CDCl_3 , with tetramethylsilane as an internal standard and reported in ppm (δ). N-heterocyclic carbenes **4-6** were prepared according to literature.¹ **1a** and **1b** were purchased from J&K Chemical Co., Ltd. All other chemicals were obtained from commercial supplies and used as received. Anhydrous THF and toluene were distilled from sodium and benzophenone. DMF, CH_2Cl_2 and CH_3CN were distilled from calcium hydride.

General procedure for N-heterocyclic carbene-catalysed pentafluorophenylation reaction of aldehydes

Aldehyde (0.3 mmol) was dissolved in 1 mL dry CH_3CN , cooled to 0 °C and TMSC_6F_5 **1a** (0.45 mmol, 80 μL) was added via a syringe under N_2 , then IPr (6 mg, 5 mol%) was added subsequently. The reaction mixture was stirred at room temperature for 1-3 h until full consume of the starting aldehyde indicated by TLC. Then HCl (1.0 mL, 1.0 mol/L) was added to the mixture and stirred for 30 mins at room temperature. The

mixture was extrated with EtOAc (10 mL×3) and the combined organic phase was washed subsequently by water and sat. aq. NaHCO₃ and dried over anhyd. Na₂SO₄, filtered, and concentrated. The crude product was purified by flash column chromatography on silica gel (PE-EtOAc, 10:1) to give the desired product.

General procedure for N-heterocyclic carbene-catalysed dual tetrafluorophenylation of aldehyde

Aldehyde (0.6 mmol) and 1,4-bis(trimethylsilyl)tetrafluorobenzene **1b** (0.2 mmol, 60 mg) were dissolved in 1 mL dry CH₃CN. The solution was cooled to 0 °C and IPr (6 mg, 5 mol%) was added subsequently. The reaction mixture was stirred at room temperature for 2-3 h until full consume of the starting aldehyde indicated by TLC. Then HCl (1.0 mL, 1.0 mol/L) was added to the mixture and stirred for 30 mins at room temperature. The mixture was extrated with EtOAc (10 mL×3) and the combined organic phase was washed subsequently by water and sat. aq. NaHCO₃ and dried over anhyd. Na₂SO₄, filtered, and concentrated. The crude product was purified by flash column chromatography on silica gel (PE-EtOAc, 3:1) to give the desired product.

Experimental Data:

(4-chlorophenyl)(perfluorophenyl)methanol (3a)^[2]

¹H NMR (400 MHz, CDCl₃) δ 7.36-7.17 (m, 4H), 6.11 (s, 1H), 2.86 (br s, 1H); ¹³C NMR (100 MHz, CDCl₃) δ 143.6 (dm, *J* = 248.0 Hz), 139.9 (dm, *J* = 248.0 Hz), 137.9, 136.6 (dm, *J* = 252.0 Hz), 133.0, 130.4, 127.8, 125.7 (t, *J* = 1.0 Hz), 65.8; ¹⁹F NMR (376 MHz, CDCl₃) δ -142.98 (dd, *J* = 21.7, 8.0 Hz, 2F), -153.97 (t, *J* = 20.6 Hz, 1F), -161.13 (ddd, *J* = 28.3, 21.02, 7.2 Hz, 2F).

(4-fluorophenyl)(perfluorophenyl)methanol (3b)

¹H NMR (400 MHz, CDCl₃) δ 7.40-7.37 (m, 2H), 7.10-7.04 (m, 2H), 6.23 (s, 1H), 3.02 (br s, 1H); ¹³C NMR (100 MHz, CDCl₃) δ 163.7, 161.2, 144.5 (dm, *J* = 248.0 Hz), 140.9 (dm, *J* = 249.0 Hz), 137.7 (dm, *J* = 253.0 Hz), 136.4 (m), 127.2 (dt, *J* = 8.0, 1.0 Hz), 115.7 (d, *J* = 21.0 Hz), 66.9; ¹⁹F NMR (376 MHz, CDCl₃) δ -113.79 (s, 1F), 143.16 (ddd, *J* = 22.5, 7.3, 0.83 Hz, 2F), -154.29 (t, *J* = 2.0 Hz, 1F), -161.32 (ddd, *J* = 27.9, 21.1, 7.4, 2F). HRMS (EI) calcd for C₁₃H₆OF₅ (M⁺) 292.0323, found 292.0322.

(4-bromophenyl)(perfluorophenyl)methanol (3c)^[2]

¹H NMR (400 MHz, CDCl₃) δ 7.53-7.45 (m, 1H), 7.30-7.28 (m, 2H), 6.20 (s, 1H), 2.87 (br s, 1H); ¹³C NMR (100MHz, CDCl₃) δ 144.6 (dm, *J* = 25.0 Hz), 141.0 (dm, *J* = 254.0 Hz), 139.5, 137.7 (dm, *J* = 245.0 Hz), 131.8, 127.0, 122.2, 116.4 (tm, *J* = 31.0 Hz), 66.8; ¹⁹F NMR (376 MHz,

CDCl₃) δ -142.94 (dd, J = 22.0, 8.1 Hz, 2F), -153.89 (t, J = 20.7 Hz, 1F), -160.73 - -161.43 (ddd, J = 26.1, 14.0, 504 Hz, 2F).

4-(hydroxy(perfluorophenyl)methyl)benzonitrile (3d)

¹H NMR (400 MHz, CDCl₃) δ 7.68-7.66 (m, 2H), 7.57-7.55 (m, 2H), 6.31 (s, 1H), 3.19 (br s, 1H); ¹³C NMR (100 MHz, CDCl₃) δ 145.9, 143.6 (dm, J = 246.0 Hz), 141.2 (dm, J = 254.0 Hz), 1347.7 (dm, J = 243.0 Hz), 132.4, 126.1 (t, J = 1.0 Hz), 118.4, 116.1 (tm, J = 18.0 Hz), 111.7, 66.1; ¹⁹F NMR (376 MHz, CDCl₃) δ -142.52- -142.63 (m, 2F), -153.15 (t, J = 23.0 Hz, 1F), -160.68- -160.83 (m, 2F); HRMS (EI) calcd for C₁₄H₆ONF₅ (M⁺) 299.0370, found 299.0373.

(4-nitrophenyl)(perfluorophenyl)methanol (3e)

¹H NMR (400 MHz, DMSO-d₆) δ 8.21 (d, J = 8.7 Hz, 2H), 7.67 (d, J = 8.5 Hz, 2H), 6.88 (d, J = 4.9 Hz, 1H), 6.24 (d, J = 4.9 Hz, 1H); ¹³C NMR (100 MHz, DMSO-d₆) δ 149.8, 147.1, 144.7 (dm, J = 245.0 Hz), 140.7 (dm, J = 250.0 Hz), 137.5 (dm, J = 250.0 Hz), 127.1, 123.8, 117.8 (m), 64.6; ¹⁹F NMR (376 MHz, DMSO-d₆) δ -142.6 (ddd, J = 23.3, 9.4, 2.1 Hz, 2F), -152.7 (tt, J = 20.7, 2.0 Hz, 1F), -160.77 (ddd, J = 27.7, 20.8, 6.9 Hz, 2F); HRMS (EI) calcd for C₁₆H₆O₃NF₅ (M⁺) 319.0268, found 319.0264.

(perfluorophenyl)(phenyl)methanol (3f)^[3]

¹H NMR (400 MHz, CDCl₃) δ 7.24-7.10 (m, 5H), 6.07 (s, 1H), 2.78 (br s, 1H); ¹³C NMR (100 MHz, CDCl₃) δ 144.7 (dm, J = 245.0 Hz), 140

.8 (dm, $J = 254.0$ Hz), 140.5, 137.7 (dm, $J = 262.0$ Hz), 128.7, 128.2, 125.3 (t, $J = 1.0$ Hz), 116.9, 67.5; ^{19}F NMR (376 MHz, CDCl_3) δ -142.54 (dd, $J = 22.1, 7.9$ Hz, 2F), -154.69 (t, $J = 21.1$ Hz, 1F), -161.6 (ddd, $J = 28.5, 21.7, 7.7$ Hz, 2F).

naphthalen-1-yl(perfluorophenyl)methanol (3g)^[3]

^1H NMR (400 MHz, CDCl_3) δ 8.08-8.05 (m, 1H), 7.93-7.86 (m, 2H), 7.65-7.48 (m, 4H), 6.87 (s, 1H), 3.07 (br s, 1H); ^{13}C NMR (100 MHz, CDCl_3) δ 144.9 (dm, $J = 256.0$ Hz), 140.9 (dm, $J = 253.0$ Hz), 137.7 (dm, $J = 252.0$ Hz), 134.8, 133.8, 130.3, 129.4, 129.0, 126.8, 125.9, 125.0, 123.9 (t, $J = 2.0$ Hz), 122.7 (t, $J = 2.0$ Hz), 116.0 (dm, $J = 15.0$ Hz), 65.1; ^{19}F NMR (376 MHz, CDCl_3) δ -12.3 (ddd, $J = 23.1, 8.9, 1.9$ Hz, 2F), -154.20 (t, $J = 21.1$ Hz, 1F), -161.4 (ddd, $J = 27.4, 20.6, 6.4$ Hz, 2F).

naphthalen-2-yl(perfluorophenyl)methanol (3h)

^1H NMR (400 MHz, CDCl_3) δ 7.86-7.82 (m, 4H), 7.54-7.45 (m, 3H), 6.39 (s, 1H), 2.99 (br s, 1H); ^{13}C NMR (100 MHz, CDCl_3) δ 144.7 (dm, $J = 245.0$ Hz), 140.5 (dm, $J = 245.0$ Hz), 137.8, 137.7 (dm, $J = 245.0$ Hz), 133.1, 133.0, 128.7, 128.1, 127.7, 126.6, 126.4, 124.1 (t, $J = 2.0$ Hz), 123.7 (t, $J = 2.0$ Hz), 116.8, 67.7; ^{19}F NMR (376 MHz, CDCl_3) δ -142.86 (ddd, $J = 25.0, 8.8, 2.0$ Hz, 2F), -154.38 (tt, $J = 21.2, 2.0$ Hz, 1F), -161.27-161.42 (m, 2F); HRMS (EI) calcd for $\text{C}_{17}\text{H}_9\text{OF}_5$ (M^+) 324.0574, found 324.0574.

(perfluorophenyl)(p-tolyl)methanol (3i)

^1H NMR (400 MHz, CDCl_3) δ 7.25 (m, 4H), 6.21 (s, 1H), 3.03 (br s, 1H), 2.39 (s, 3H); ^{13}C NMR (100 MHz, CDCl_3) δ 144.6 (dm, $J = 250.0$ Hz), 140.7 (dm, $J = 253.0$ Hz), 137.6 (dm, $J = 249.0$ Hz), 138.2, 137.6, 129.4, 125.3, 117.1, 67.5, 21.0; ^{19}F NMR (376 MHz, CDCl_3) δ -143.13 (dd, $J = 22.1, 7.9$ Hz, 2F), -154.91 (dd, $J = 40.9, 20.5$ Hz, 1F), -161.62- -161.76 (m, 2F); HRMS (EI) calcd for $\text{C}_{14}\text{H}_9\text{OF}_5$ (M^+) 288.0574, found 288.0578.

(4-methoxyphenyl)(perfluorophenyl)methanol (3j)^[4]

^1H NMR (400 MHz, CDCl_3) δ 7.29-7.27 (m, 2H), 6.87 – 6.85 (m, 2H), 6.14 (s, 1H), 3.78 (s, 3H), 2.89 (br s, 1H); ^{13}C NMR (100MHz, CDCl_3) δ 159.4, 144.6 (dm, $J = 250.0$ Hz), 140.6 (dm, $J = 252.0$ Hz), 137.7 (dm, $J = 234.0$ Hz), 132.7, 126.8 (t, $J = 2.0$ Hz), 117.1, 114.0, 67.4, 55.2; ^{19}F NMR (376 MHz, CDCl_3) δ -143.22 (dd, $J = 10.0, 2.5$ Hz, 2F), -155.08 (t, $J = 20.7$ Hz, 1F), -161.7(ddd, $J = 28.7, 21.8, 7.7$ Hz, 2F).

(2-methoxyphenyl)(perfluorophenyl)methanol (3k)^[5]

^1H NMR (400 MHz, CDCl_3) δ 7.53-7.49 (m, 1H), 7.35-7.28 (m, 1H), 7.05-7.01 (m, 1H), 6.90-6.88 (m, 1H), 6.37 (s, 1H), 3.83 (s, 1H), 3.33 (br s, 1H); ^{13}C NMR (100 MHz, CDCl_3) δ 156.1, 145.0 (dm, $J = 239.0$ Hz), 140.5 (dm, $J = 249.0$ Hz), 137.4 (dm, $J = 246.0$ Hz), 129.3, 128.2, 126.6 (t, $J = 2.0$ Hz), 120.6, 116.3, 110.4, 64.3, 55.2; ^{19}F NMR (376 MHz, CDCl_3) δ -142.25 (ddd, $J = 25.1, 10.8, 2.5$ Hz, 2F), -155.89(tm, $J = 20.9$ Hz, 1F), -162.7 (ddd, $J = 29.2, 22.4, 8.2$ Hz, 2F)

(3-methoxyphenyl)(perfluorophenyl)methanol (3l)^[3]

^1H NMR (400 MHz, CDCl_3) δ 7.15-7.10 (m, 1H), 6.85-6.68 (m, 3H), 6.04 (s, 1H), 3.66 (s, 3H), 2.92 (br s, 1H); ^{13}C NMR (100 MHz, CDCl_3) δ 159.8, 144.8 (dm, $J = 251.0$ Hz), 142.2, 140.8 (dm, $J = 253.0$ Hz), 137.6 (dm, $J = 260.0$ Hz), 129.8, 117.5 (t, $J = 2.0$ Hz), 116.8, 113.3, 111.3 (t, $J = 2.0$ Hz), 67.3, 55.2; ^{19}F NMR (376 MHz, CDCl_3) δ -142.70 – -143.42 (m, 2F), -154.73 (tt, $J = 21.3, 1.5$ Hz), -161.50 – -162.66 (m, 2F).

(perfluorophenyl)(o-tolyl)methanol (3m)

^1H NMR (400 MHz, CDCl_3) δ 7.57-7.53 (m, 1H), 7.29-7.26 (m, 2H), 7.23-7.19 (m, 1H), 6.33 (s, 1H), 2.34 (br s, 3H); ^{13}C NMR (100 MHz, CDCl_3) δ 144.8 (dm, $J = 247.0$ Hz), 140.8 (dm, $J = 264.0$ Hz), 138.3 (dm, $J = 248.0$ Hz), 137.8, 135.3, 130.8, 128.4, 126.1, 125.6 (t, $J = 3.0$ Hz), 115.8, 65.48, 18.93; ^{19}F NMR (376 MHz, CDCl_3) δ -142.09- -142.18 (m, 2F), -154.52 (ddd, $J = 21.2, 11.3, 2.1$ Hz), -161.62 (ddd, $J = 26.8, 20.1, 6.1$ Hz, 2F); HRMS (EI) calcd for $\text{C}_{14}\text{H}_9\text{OF}_5$ (M^+) 288.0574, found 288.0577.

(2-chlorophenyl)(perfluorophenyl)methanol (3n)

^1H NMR (400 MHz, CDCl_3) δ 7.83-7.79 (m, 1H), 7.40-7.28 (m, 3H), 6.40 (s, 1H), 3.20 (br s, 1H); ^{13}C NMR (100 MHz, CDCl_3) δ 145.1 (dm, $J = 245.0$ Hz), 141.1 (dm, $J = 258.0$ Hz), 137.6 (dm, $J = 250.0$ Hz), 137.4, 131.6, 129.5, 129.4, 127.6 (t, $J = 3.0$ Hz), 126.8, 114.9, 64.4; ^{19}F NMR (376 MHz, CDCl_3) δ -141.55 (ddd, $J = 23.1, 8.9, 3.2$ Hz, 2F), -154.01 (t, $J = 20.0$ Hz, 1F), -161.83 (ddd, $J = 27.7, 20.8, 6.7$ Hz, 2F); HRMS (EI) calcd for $\text{C}_{13}\text{H}_6\text{OCIF}_5$ (M^+) 308.0027, found 308.0024.

(3-bromophenyl)(perfluorophenyl)methanol (3o)

^1H NMR (400 MHz, CDCl_3) δ 7.58-7.56 (m, 1H), 7.47-7.45 (m, 1H), 7.33-7.24 (m, 2H), 6.22 (s, 1H), 2.94 (br s, 1H); ^{13}C NMR (100 MHz, CDCl_3) δ 144.7 (dm, $J = 248.0$ Hz), 142.7, 141.1 (dm, $J = 251.0$ Hz), 137.7 (dm, $J = 253.0$ Hz), 131.3, 130.2, 128.4 (t, $J = 1.0$ Hz), 123.9 (t, $J = 1.0$ Hz), 122.8, 116.3, 66.6; ^{19}F NMR (376 MHz, CDCl_3) δ -142.76- -142.81 (ddd, $J = 21.2, 7.3, 6.2$ Hz, 2F), -153.73 (tt, $J = 21.1, 2.1$ Hz), -160.92- -161.06 (m, 2F); HRMS (EI) calcd for $\text{C}_{13}\text{H}_6\text{BrF}_5\text{O}$ (M^+) 351.9522, found 351.9522.

(2,4-dichlorophenyl)(perfluorophenyl)methanol (3p)^[2]

^1H NMR (400 MHz, CDCl_3) δ 7.80 (d, $J = 8.8$ Hz, 1H), 7.38-7.33 (m, 2H), 6.34 (s, 1H), 2.87-2.77 (m, 1H); ^{13}C NMR (100 MHz, CDCl_3) δ 145.1 (dm, $J = 250$ Hz), 141.3 (dm, $J = 253$ Hz), 137.5 (dm, $J = 249$ Hz), 136.11 (m), 134.6, 132.2, 129.2, 128.7 (m), 127.1, 114.8 (m), 64.0; ^{19}F NMR (376 MHz, CDCl_3) δ -141.55- -141.67 (m, 2F), -153.44 (tt, $J = 20.3, 2.1$ Hz, 1F), -161.53 (ddd, $J = 26.7, 19.8, 5.9$ Hz, 2F).

benzo[d][1,3]dioxol-5-yl(perfluorophenyl)methanol (3q)

^1H NMR (400 MHz, CDCl_3) δ 6.87 (s, 1H), 6.82-6.70 (m, 2H), 6.10 (s, 1H), 5.93 (s, 2H), 2.94 (br s, 1H); ^{13}C NMR (100 MHz, CDCl_3) δ 148.1, 147.5, 144.5 (dm, $J = 251$ Hz), 140.4 (dm, $J = 252$ Hz), 137.6 (dm, $J = 252$ Hz), 134.5, 118.9, 116.9 (tm, $J = 19$ Hz), 108.3, 106.1, 101.3, 67.5; ^{19}F NMR (376 MHz, CDCl_3) δ -143.17 (dd, $J = 22.5, 8.3$ Hz, 2F), -154.80

(t, $J = 253.8$ Hz, 1F), -161.49 (tm, $J = 22.9$ Hz, 2F); HRMS (EI) calcd for $C_{14}H_7O_3F_5$ (M^+) 318.0315, found 318.0315.

furan-2-yl(perfluorophenyl)methanol (3r)^[6]

1H NMR (400 MHz, $CDCl_3$) δ 7.41 (dd, $J = 1.9$ Hz, 0.88 Hz, 1H), 6.38 (dd, $J = 3.3$, 1.8 Hz, 2H), 6.17 (s, 1H), 3.05 (br s, 1H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 152.1, 143.3 (dm, $J = 244.0$ Hz), 143.0, 141.0 (dm, $J = 254.0$ Hz), 137.65 (dm, $J = 246.0$ Hz), 114.4, 110.6, 107.6 (t, $J = 1.0$ Hz), 61.9; ^{19}F NMR (376 MHz, $CDCl_3$) δ -142.04 (ddd, $J = 21.1$, 7.2, 1.0 Hz, 2F), -154.1 (tm, $J = 20.7$ Hz, 1F), -161.57 (ddd, $J = 27.9$, 21.2, 7.2 Hz, 2F).

(perfluorophenyl)(thiophen-2-yl)methanol (3s)^[3]

1H NMR (400 MHz, $CDCl_3$) δ 7.34 (dd, $J = 5.1$, 1.2, 1H), 6.99 (dd, $J = 5.1$, 3.5 Hz, 1H), 6.93 (d, $J = 4.7$ Hz, 1H), 6.41 (s, 1H), 2.94 (br s, 1H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 144.6 (dm, $J = 252.0$ Hz), 144.1, 141.0 (dm, $J = 253.0$ Hz), 137.6 (dm, $J = 252.0$ Hz), 127.0, 126.1, 124.9, 116.3, 64.3; ^{19}F NMR (376 MHz, $CDCl_3$) δ -142.96 (ddd, $J = 21.5$, 7.3, 1.1 Hz, 2F), -153.93-154.13 (m, 1F), -161.19 (ddd, $J = 41.5$, 20.8, 6.7 Hz, 2F).

(E)-1-(perfluorophenyl)-3-phenylprop-2-en-1-ol (3t)^[3]

1H NMR (400 MHz, $CDCl_3$) δ 7.43-7.28 (m, 5H), 6.70 (d, $J = 15.8$ Hz, 1H), 6.54 (ddt, $J = 15.8$, 6.9, 1.5 Hz, 1H), 5.76 (d, $J = 6.92$ Hz, 1H), 2.64 (s, 1H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 144.7 (dm, $J = 222.0$ Hz), 140.8 (dm, $J = 253.0$ Hz), 137.6 (dm, $J = 251.0$ Hz), 135.58, 132.91, 128.7,

128.4, 127.2, 126.7, 115.9, 66.9; ^{19}F NMR (376 MHz, CDCl_3) δ -143.38 (ddd, $J = 20.9, 7.3, 0.9$ Hz, 2F), -154.7 (tm, $J = 19.1$ Hz, 1F), -162.04 (ddd, $J = 28.7, 21.8, 7.9$ Hz, 2F).

1-(perfluorophenyl)-3-phenylpropan-1-ol (3u)^[3]

^1H NMR (400 MHz, CDCl_3) δ 7.36-7.28 (m, 1H), 7.26-7.19 (m, 3H), 5.09 (dd, $J = 8.2, 6.2$, 1H), 2.90-2.82 (m, 1H), 2.72-2.64 (m, 1H), 2.40-2.14 (m, 3H); ^{13}C NMR (100 MHz, CDCl_3) δ 144.6 (dm, $J = 247.0$ Hz), 141.1 (dm, $J = 245.0$ Hz), 140.4, 137.6 (dm, $J = 240.0$ Hz), 128.5, 128.2, 126.2, 116.8, 65.8, 38.1, 32.0; ^{19}F NMR (376 MHz, CDCl_3) δ -143.72 (ddd, $J = 22.9, 8.7, 1.8$ Hz, 2F), -155.11 (t, $J = 20.5$, 1F), -161.75 (ddd, $J = 28.9, 22.4, 8.3$ Hz, 2F).

2-methyl-1-(perfluorophenyl)propan-1-ol (3v)^[3]

^1H NMR (400 MHz, CDCl_3) δ 4.63 (d, $J = 9.2$ Hz, 1H), 2.46 (br s, 1H), 2.19-2.14 (m, 1H), 1.15 (d, $J = 6.6$ Hz, 3H), 0.80 (d, $J = 6.6$ Hz, 3H); ^{13}C NMR (100 MHz, CDCl_3) δ 144.6 (dm, $J = 257.0$ Hz), 140.39 (dm, $J = 260.0$ Hz), 137.5 (dm, $J = 256.0$ Hz), 116.6, 72.4, 34.2, 19.1, 18.6; ^{19}F NMR (376 MHz, CDCl_3) δ -143.05 (dd, $J = 21.3, 7.1$ Hz, 2F), -155.6 (tm, $J = 20.1$ Hz, 1F), -162.20 (ddd, $J = 28.9, 22.5, 8.3$ Hz, 2F).

2,2-dimethyl-1-(perfluorophenyl)propan-1-ol (3w)^[3]

^1H NMR (400 MHz, CDCl_3) δ 4.80 (s, 1H), 2.44 (br s, 1H), 1.61-1.00 (m, 9H); ^{13}C NMR (100 MHz, CDCl_3) δ 145.0 (dm, $J = 278.0$ Hz), 140.1 (dm, $J = 257.0$ Hz), 137.1 (dm, $J = 259.0$ Hz), 115.3 (tm, $J = 14.0$ Hz), 75.6 (dd, $J =$

3.0, 2.0 Hz), 37.1, 25.5 (t, $J = 2.0$ Hz); ^{19}F NMR (376 MHz, CDCl_3) δ -139.34 (dd, $J = 22.6, 7.8$ Hz, 2F), -155.42 (tt, $J = 20.9, 1.8$ Hz), -162.23 (s, 2F).

(perfluoro-1,4-phenylene)bis(phenylmethanol) (9a)

^1H NMR (400 MHz, CDCl_3) δ 7.42-7.30 (m, 10H), 6.25 (s, 2H), 2.56 (br s, 2H); ^{13}C NMR (100 MHz, CDCl_3) δ 144.5 (dm, $J = 240.0$ Hz), 140.6, 128.7, 128.2, 125.5, 121.4, 67.9 (t, $J = 2.0$ Hz); ^{19}F NMR (376 MHz, CDCl_3) δ -143.3 (d, $J = 7.5$ Hz, 4F); HRMS (EI) calcd for $\text{C}_{20}\text{H}_{14}\text{O}_2\text{F}_4$ (M^+) 362.0930, found 362.0926.

(perfluoro-1,4-phenylene)bis((4-chlorophenyl)methanol) (9b)

^1H NMR (400 MHz, $\text{DMSO}-d_6$) δ 7.42-7.40 (m, 8H), 6.56 (s, 2H), 6.12 (br s, 2H); ^{13}C NMR (100 MHz, $\text{DMSO}-d_6$) δ 144.2 (dm, $J = 246.0$ Hz), 141.34, 132.2, 128.6, 127.7, 122.6, 64.9; ^{19}F NMR (376 MHz, $\text{DMSO}-d_6$) δ -144.01 (d, $J = 10.8$ Hz, 4F); HRMS (EI) calcd for $\text{C}_{20}\text{H}_{12}\text{O}_4\text{F}_4\text{Cl}_2$ (M^+) 430.0150, found 430.0154.

(perfluoro-1,4-phenylene)bis((4-methoxyphenyl)methanol) (9c)

^1H NMR (400 MHz, $\text{DMSO}-d_6$) δ 7.30 (d, $J = 8.7$ Hz, 4H), 6.90 (d, $J = 8.7$ Hz, 4H), 6.30 (d, $J = 4.5$ Hz, 2H), 6.05 (d, $J = 5.1$ Hz, 2H), 3.75-3.72 (d, $J = 1.0$ Hz, 6H); ^{13}C NMR (100 MHz, $\text{DMSO}-d_6$) δ 158.8, 144.0 (dm, $J = 245.0$ Hz), 134.4, 127.0, 123.0, 114.0, 65.4, 55.5; ^{19}F NMR (376 MHz, $\text{DMSO}-d_6$) δ -142.0 (d, $J = 10.8$ Hz, 4F); HRMS (EI) calcd for $\text{C}_{22}\text{H}_{18}\text{O}_4\text{F}_4$ (M^+) 422.1141, found 422.1143.

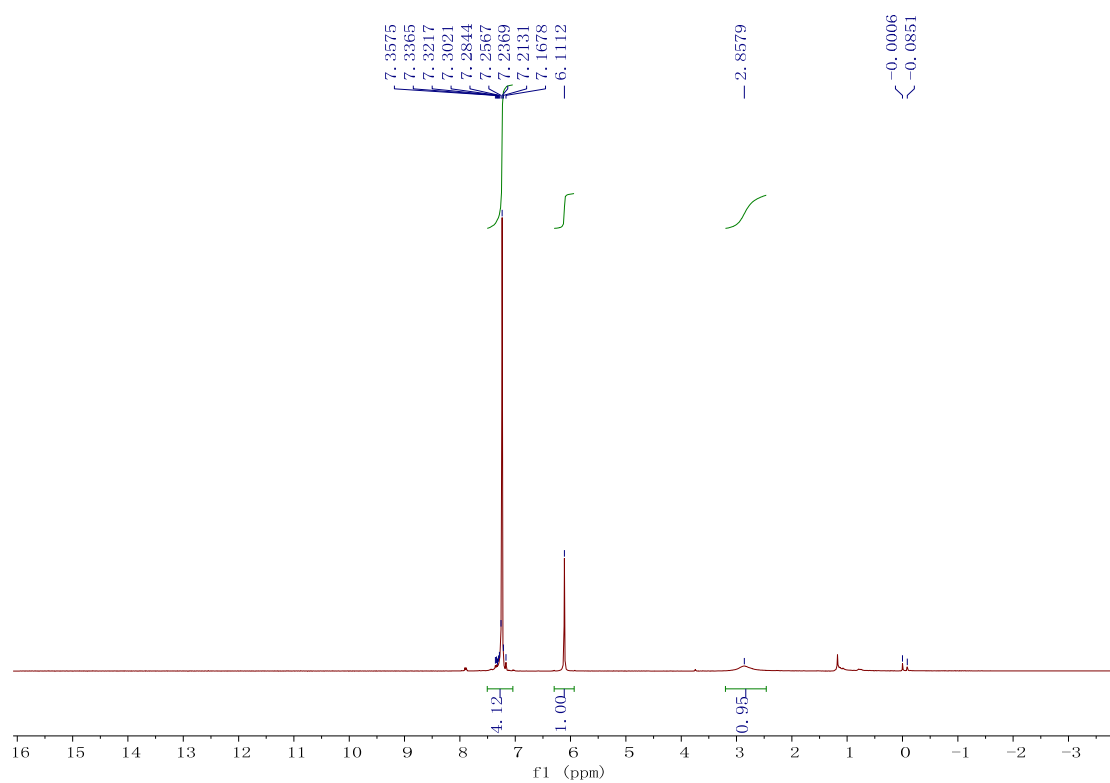
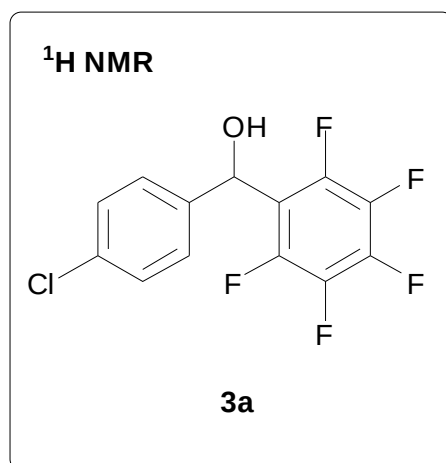
(perfluoro-1,4-phenylene)bis(furan-2-ylmethanol) (9d)

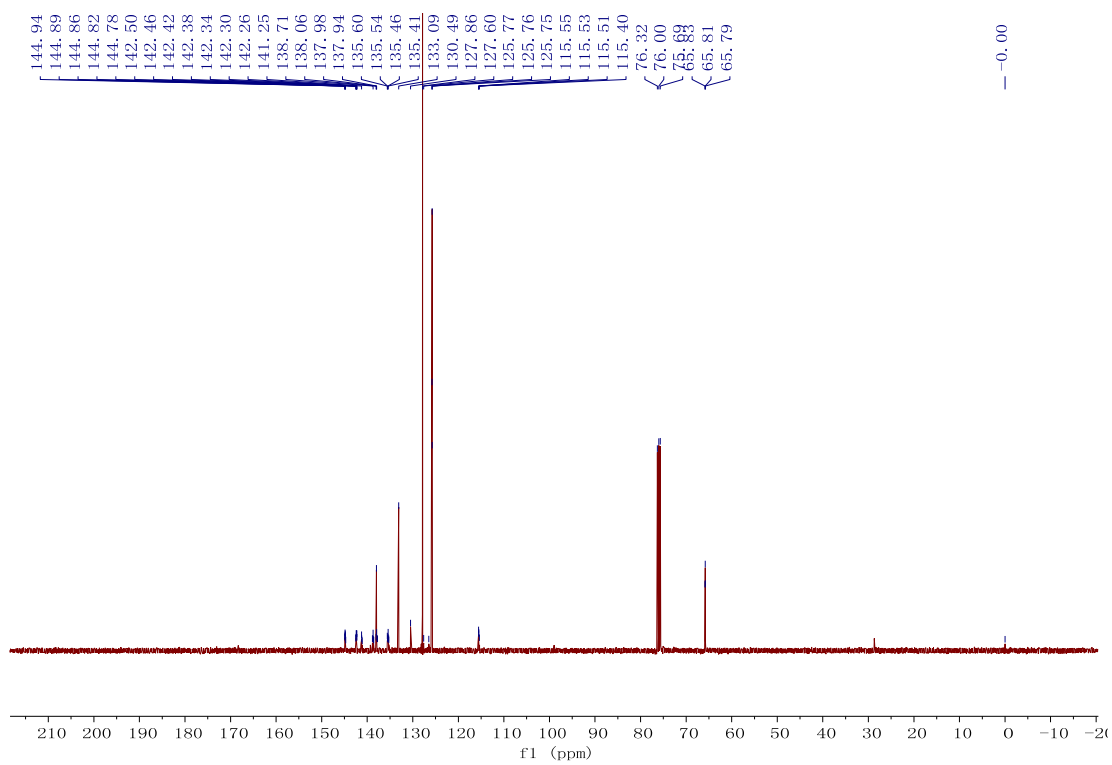
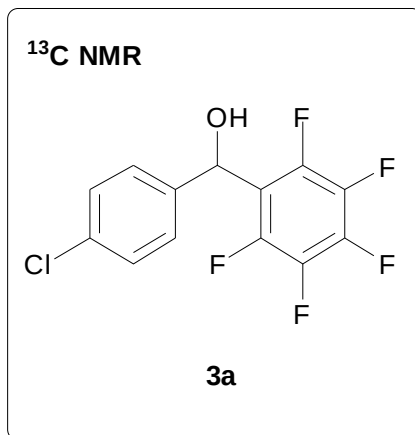
^1H NMR (400 MHz, DMSO- d_6) δ 7.60 (s, 2H), 6.53 (d, J = 5.16 Hz, 2H), 6.44-6.43 (m, 2H), 6.39-6.38 (m, 2H), 6.10-6.08 (m, 2H); ^{13}C NMR (100 MHz, DMSO- d_6) δ 153.9, 144.3 (dm, J = 246.0 Hz), 143.1, 120.5, 111.0, 107.3, 60.8 (t, J = 2.0 Hz); ^{19}F NMR (376 MHz, DMSO- d_6) δ -143.53 (d, J = 5.8 Hz, 4F); HRMS (EI) calcd for $\text{C}_{16}\text{H}_{10}\text{O}_4\text{F}_4$ (M^+) 342.0515, found 342.0511.

Reference

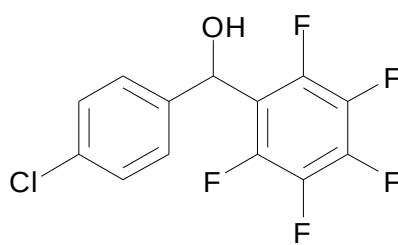
- [1] A. J. Arduengo III, R. Krafczyk and R. Schmutzler, *Tetrahedron* **1999**, 55, 14523.
- [2] N. V. Bogoslovskii, N. M. Kolbina, *Org. Khim.* **1976**, 39-43.
- [3] S. Brogan; N. B. Carter; H. W. Lam. *Synlett*, **2010**, 4, 615-617.
- [4] F. M. El-Torki, A. P. Zens, J. Jacobus, *J. Org. Chem.* **1985**, 50, 1314.
- [5] E. G. Lubenets, T. N. Gerasimova, Fokin, E. P. *Zh. Org. Khim* **1971**, 7, 805.
- [6] J. S. Reddy, V. G. Anand, *J. Am. Chem. Soc.* **2008**, 130, 3718.

Copies of ^1H NMR, ^{13}C NMR and ^{19}F NMR Spectra

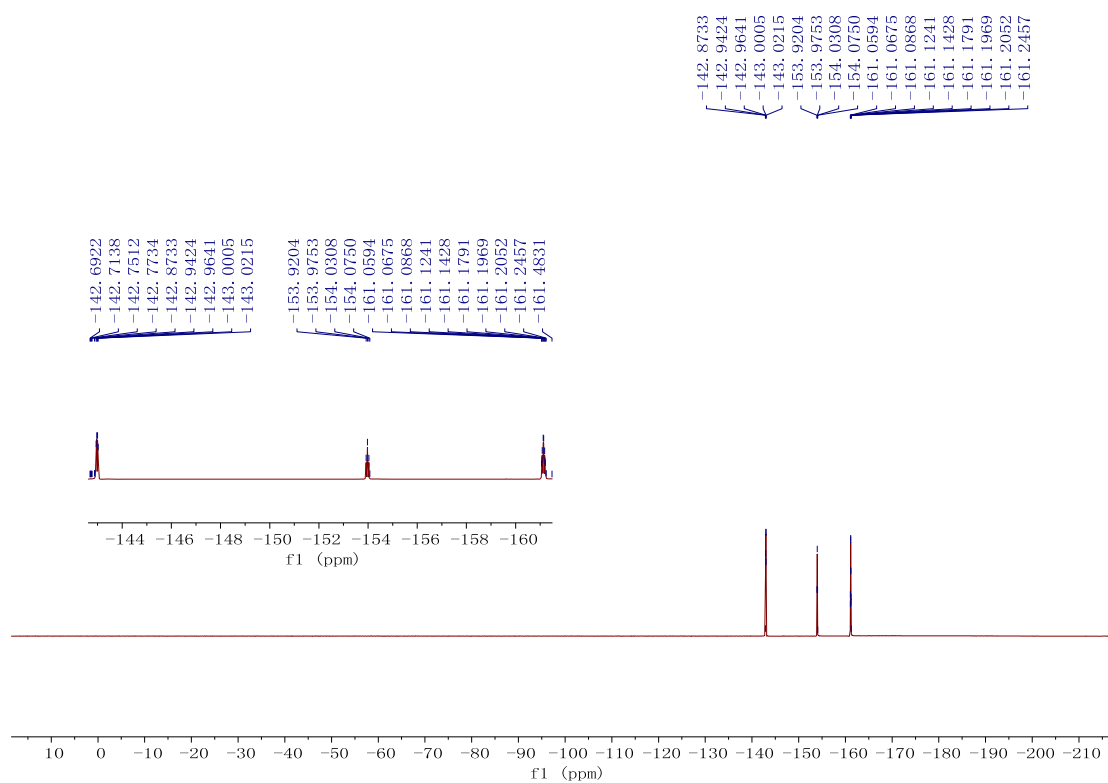


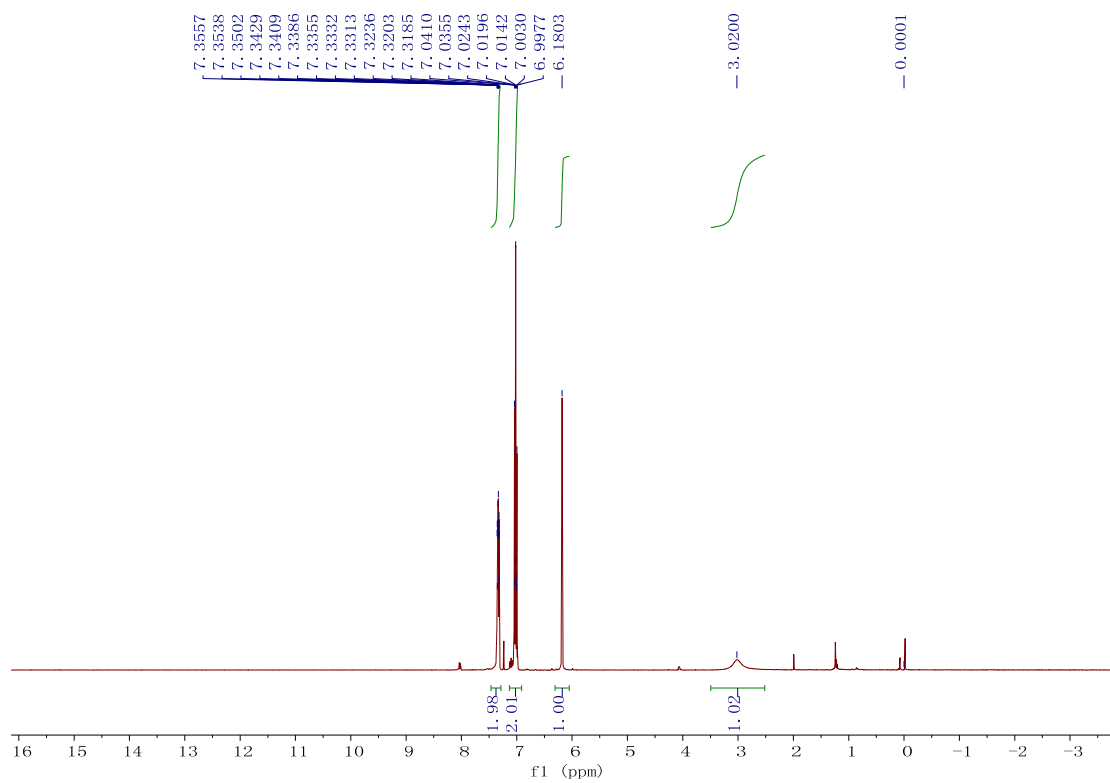
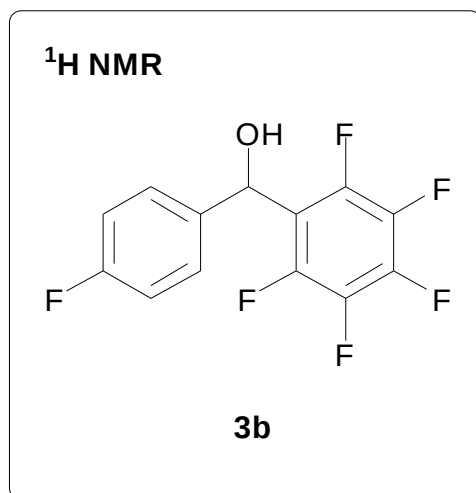


^{19}F NMR

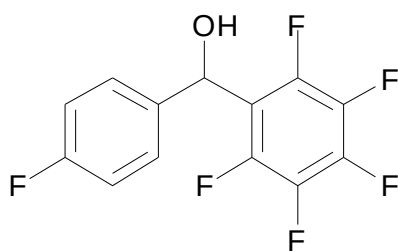


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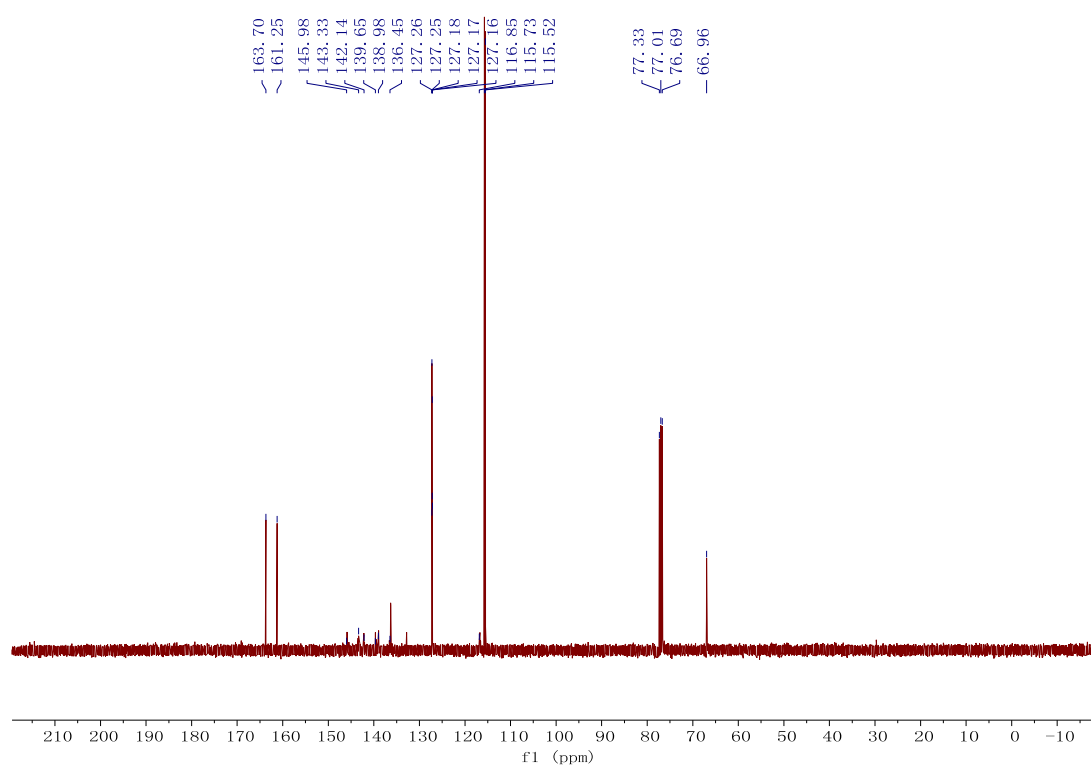




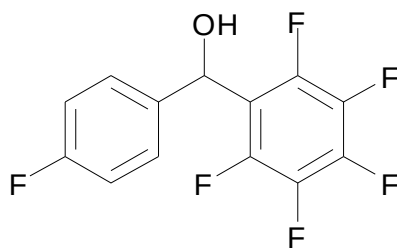
¹³C NMR



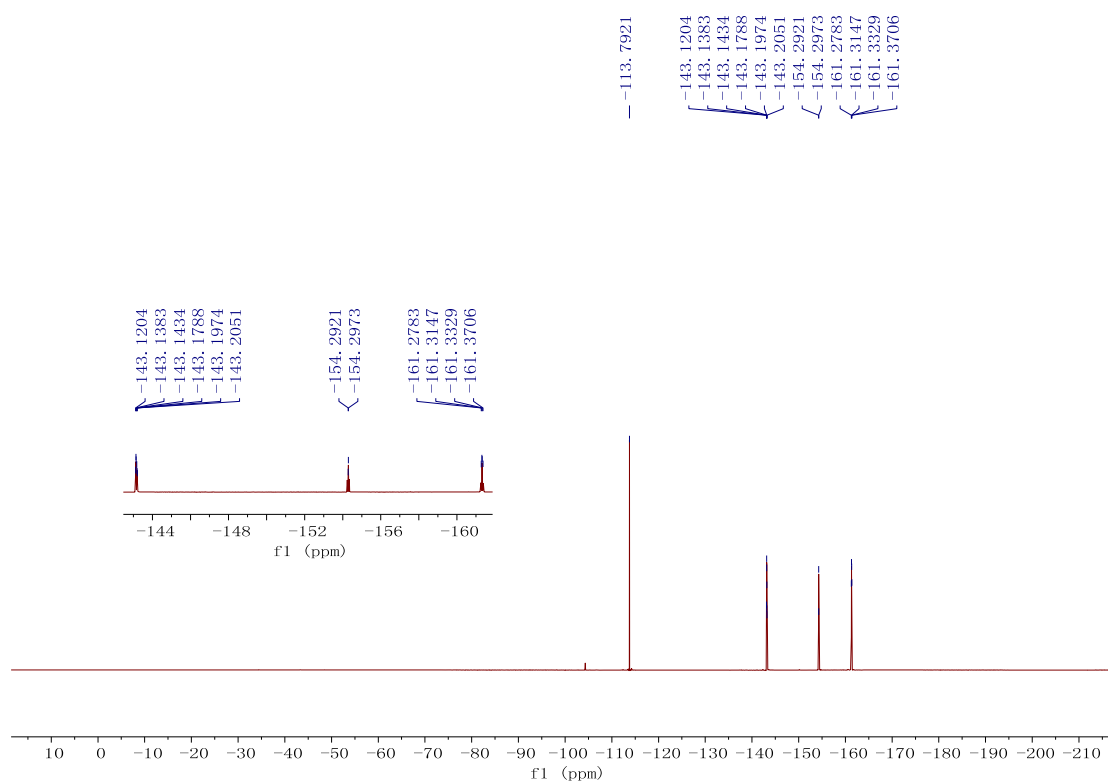
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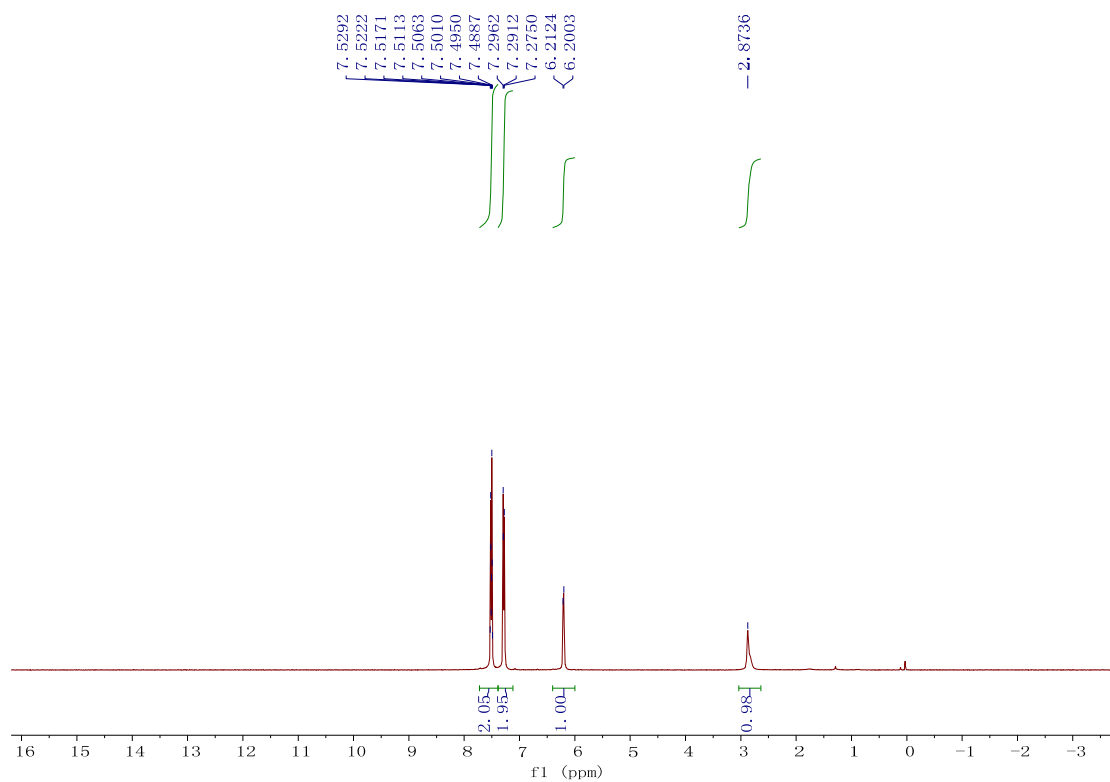
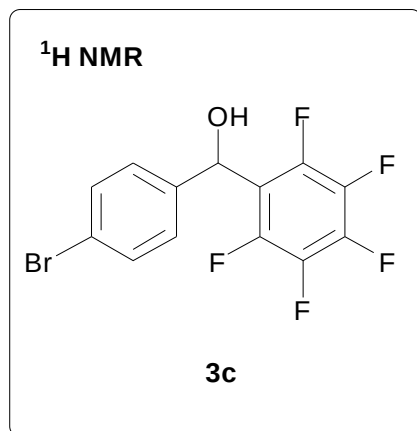


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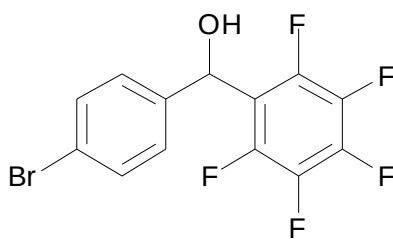


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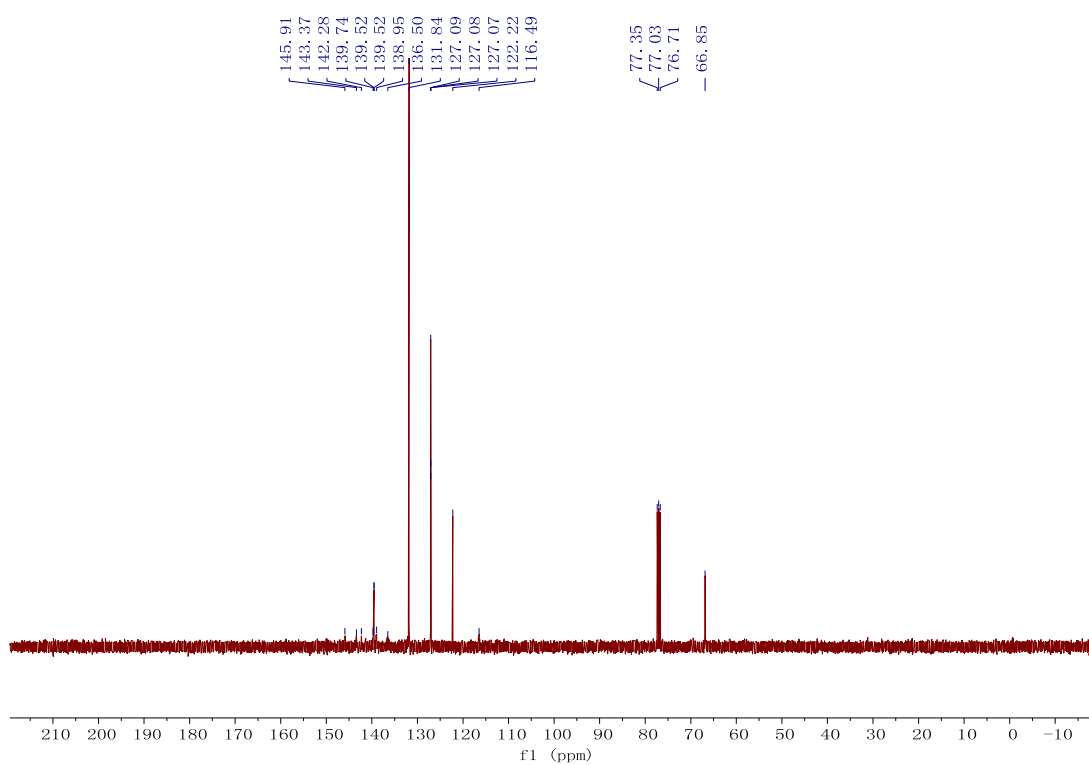




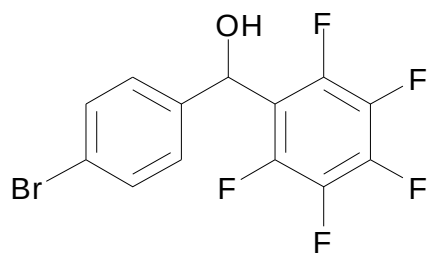
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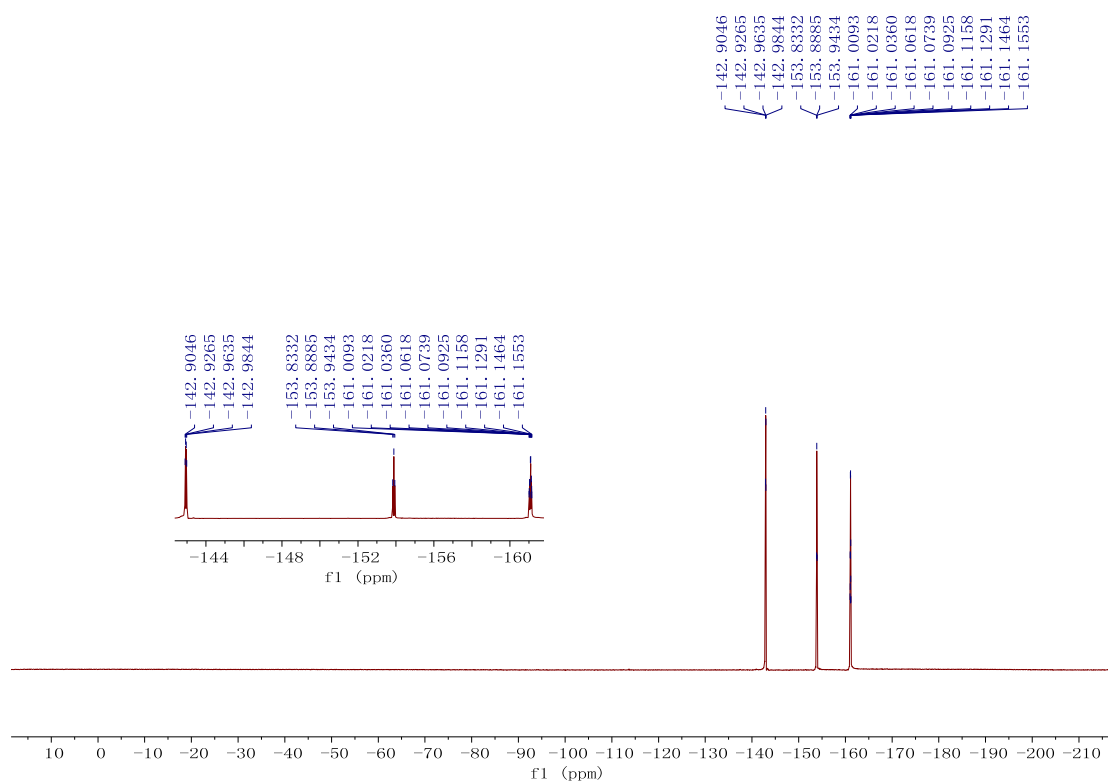
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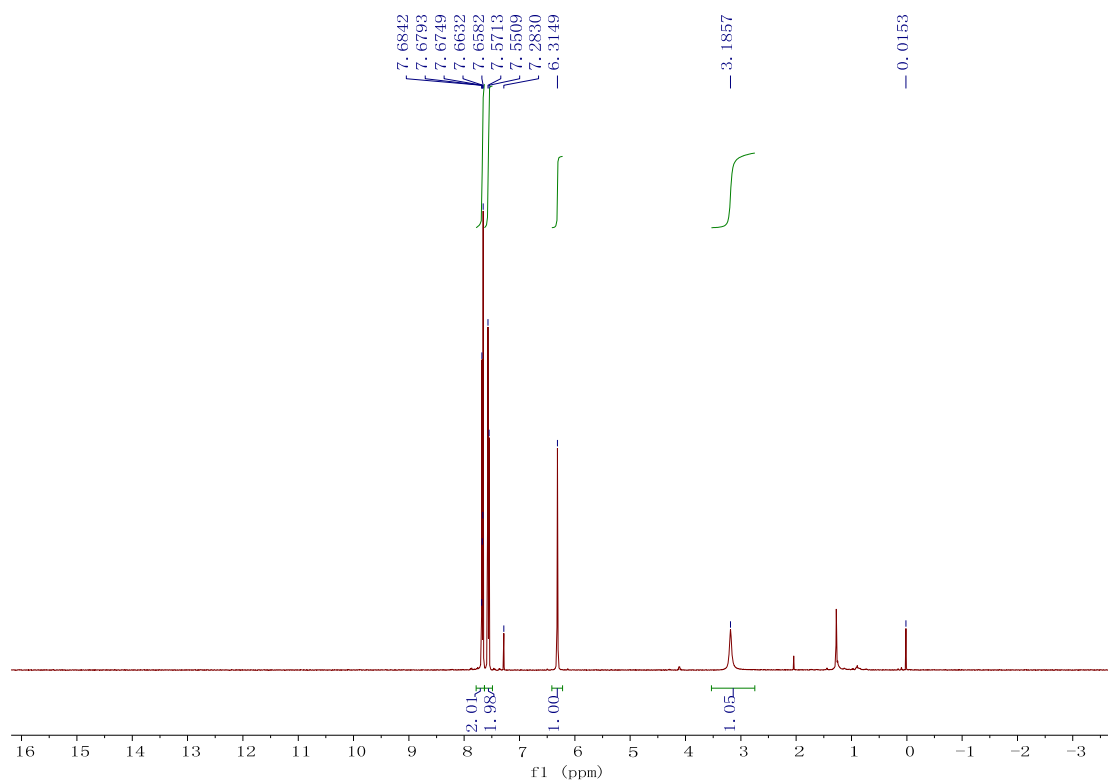
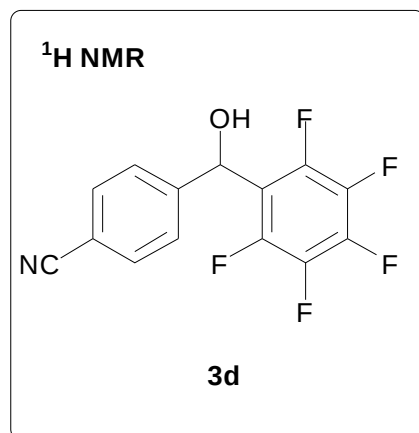


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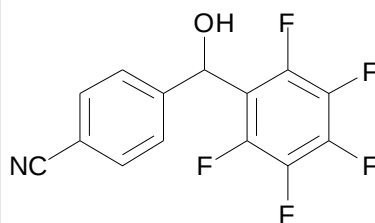


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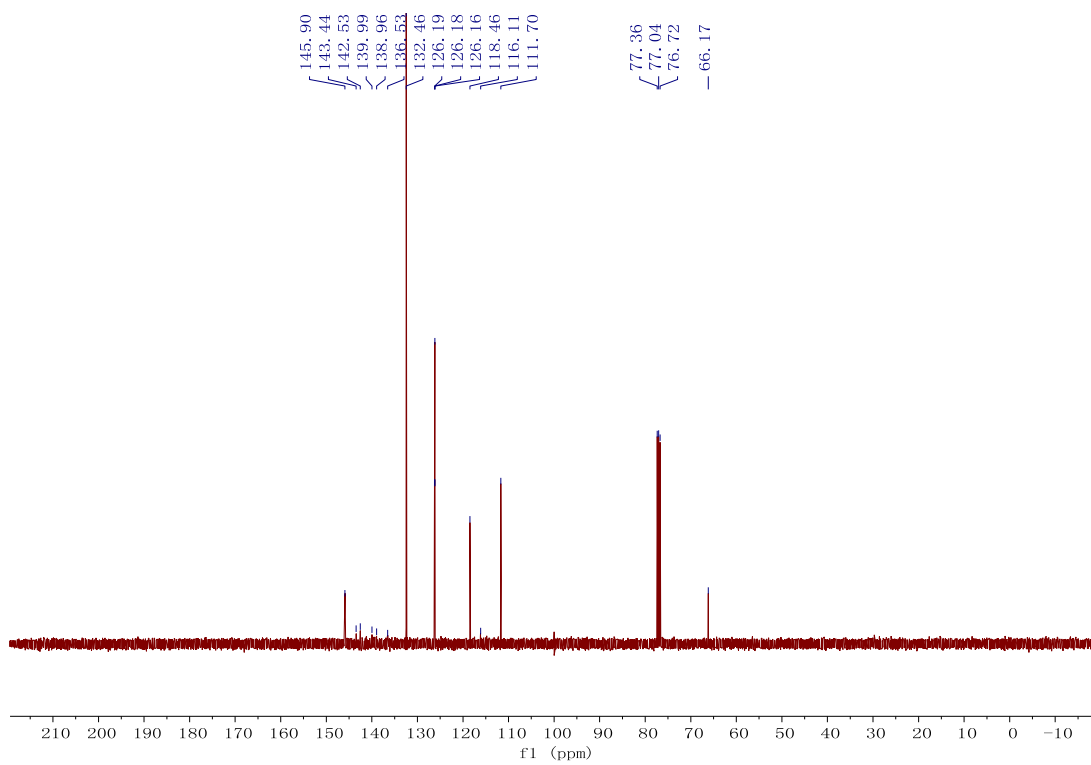




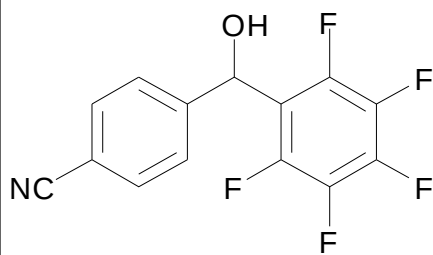
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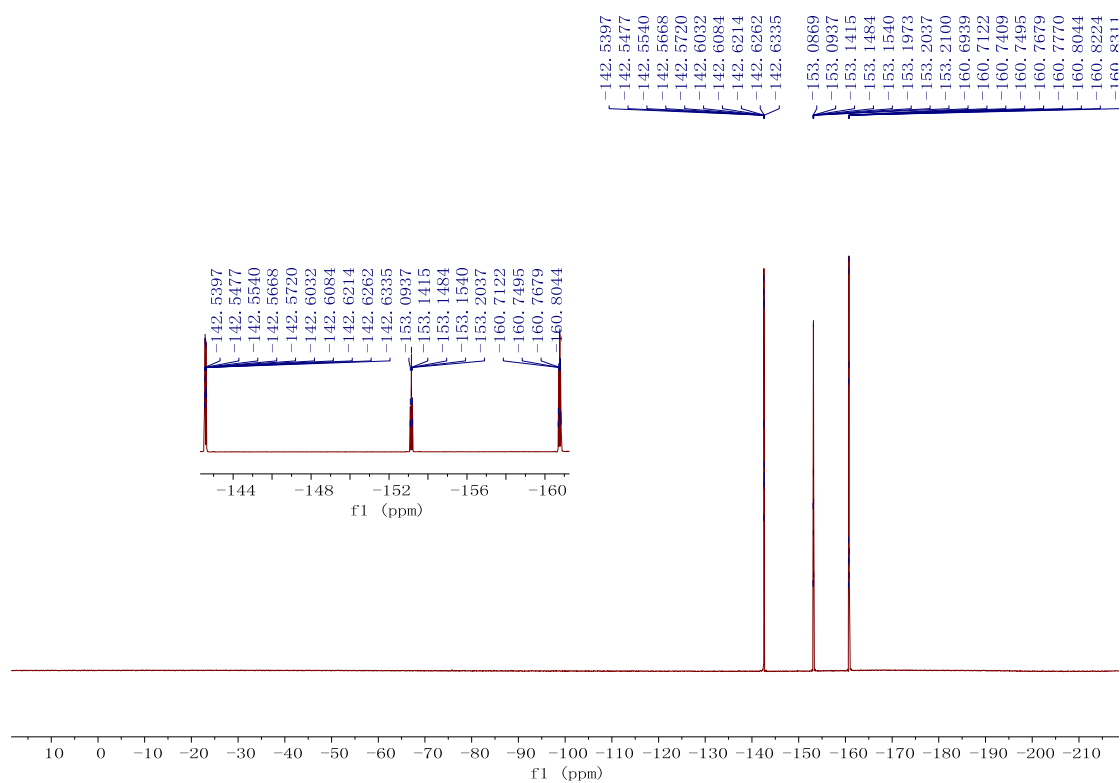
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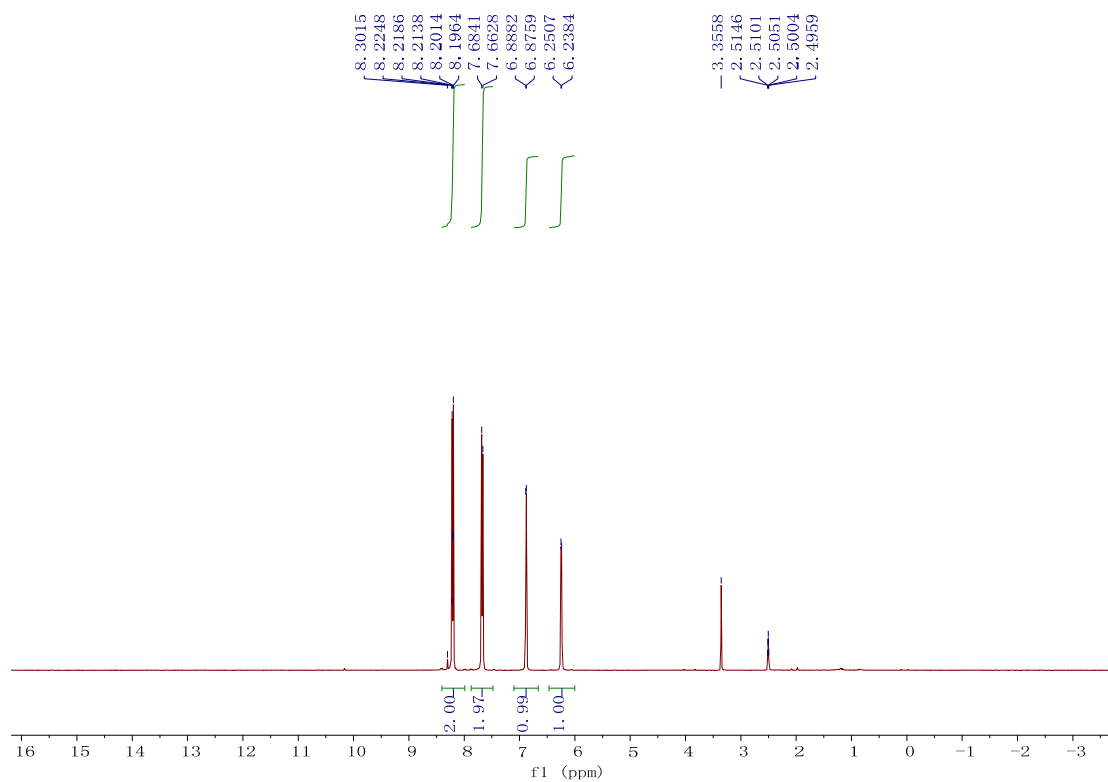
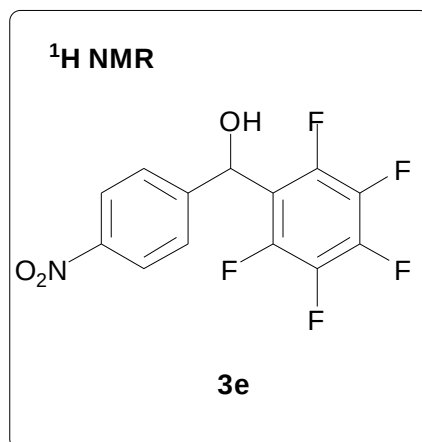


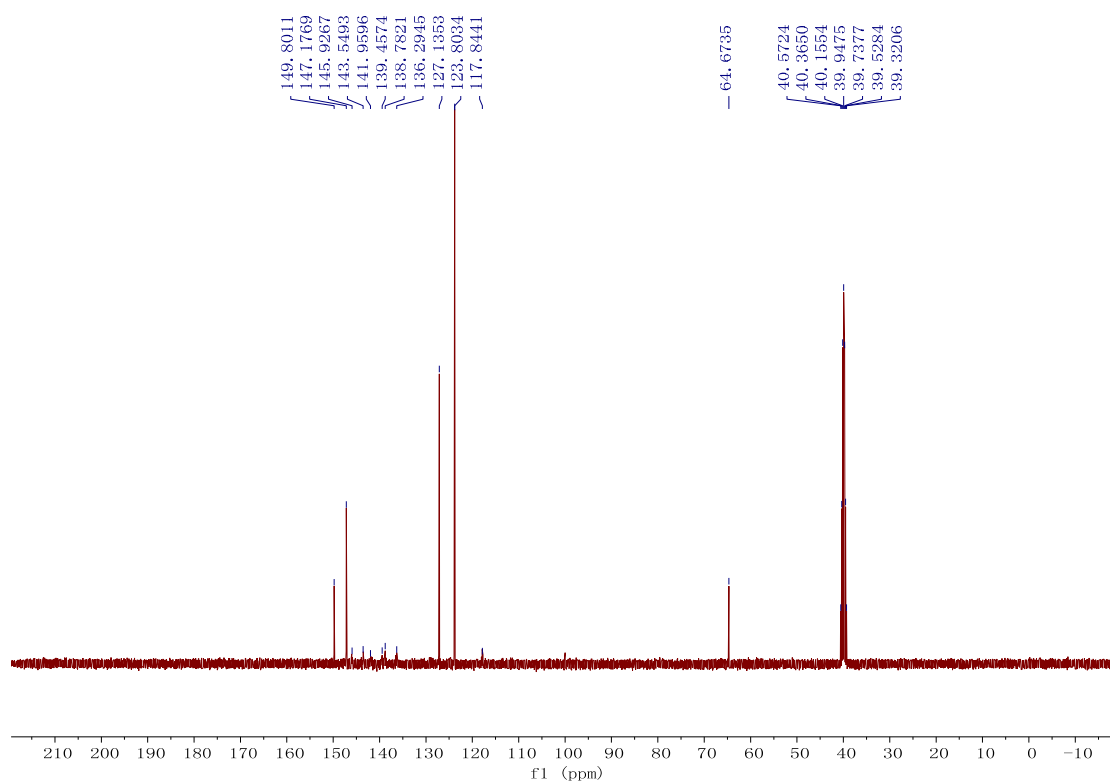
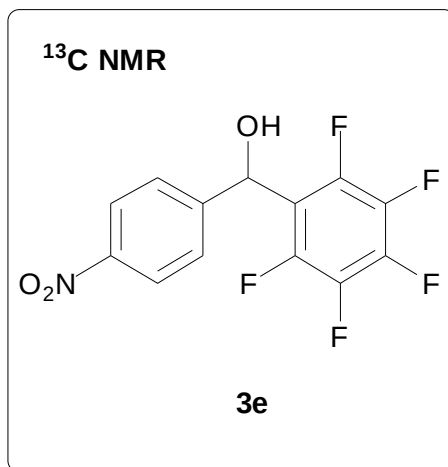
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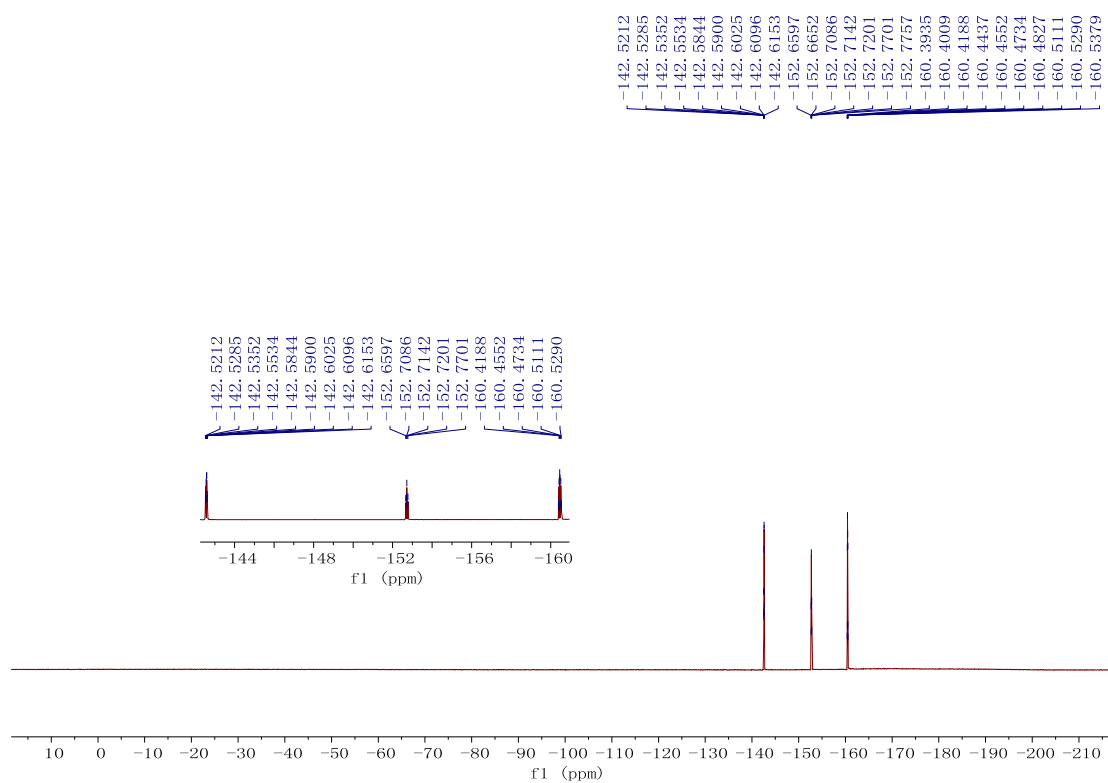
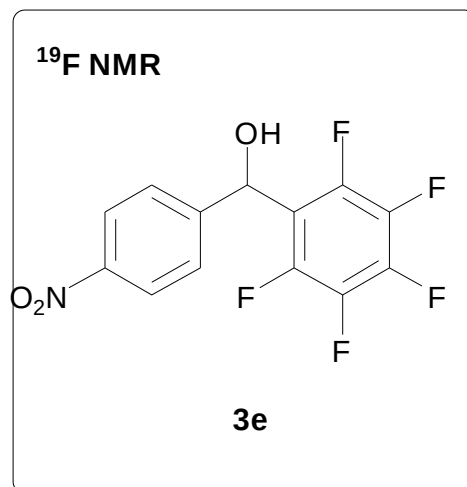


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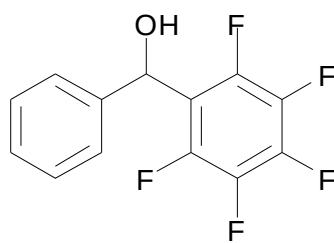




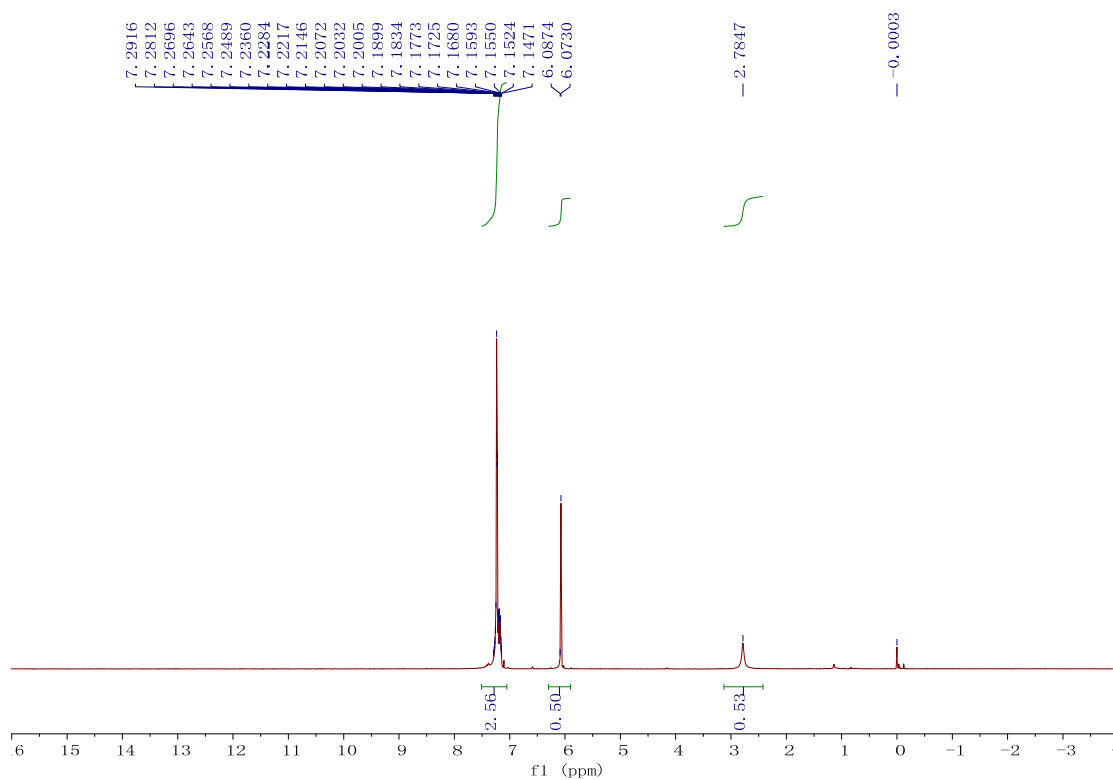




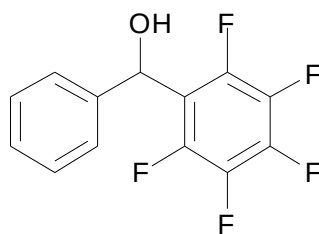
¹H NMR



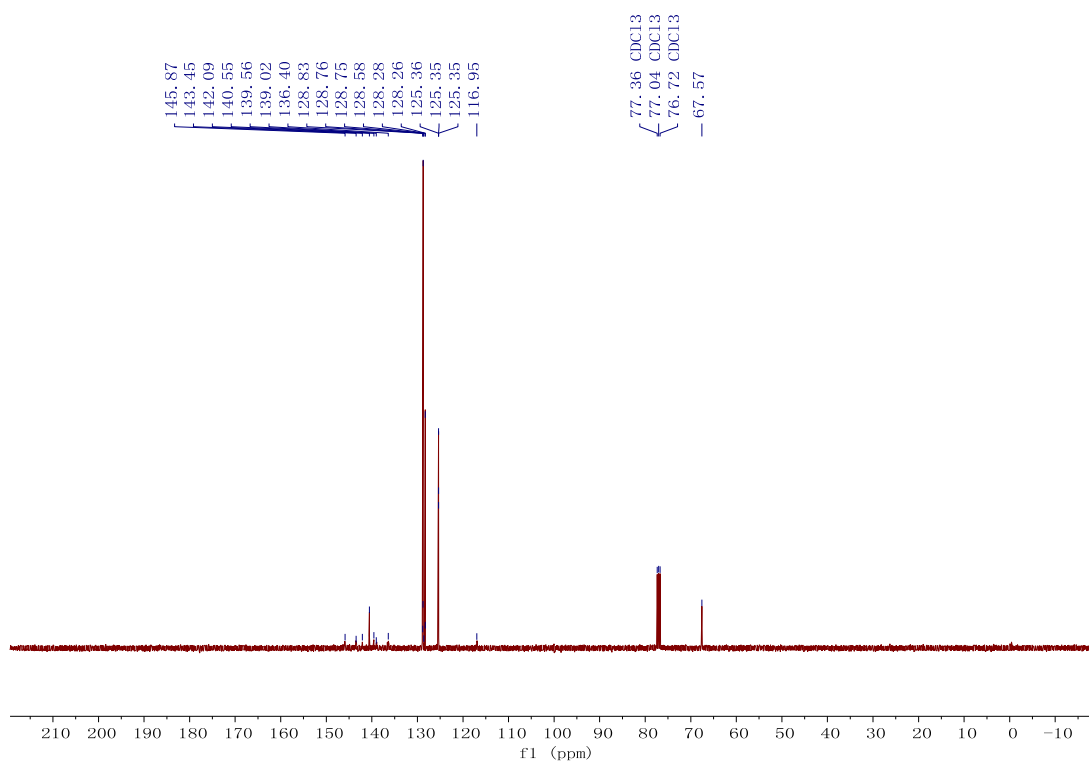
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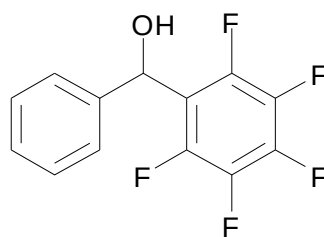
¹³C NMR



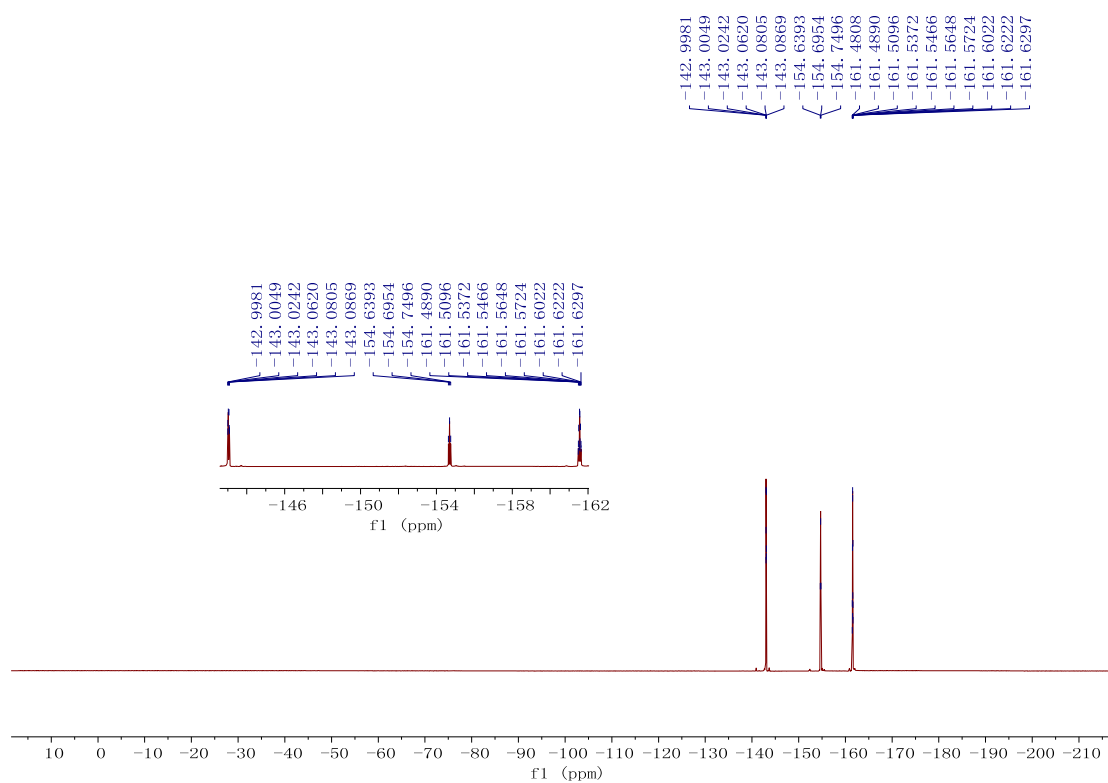
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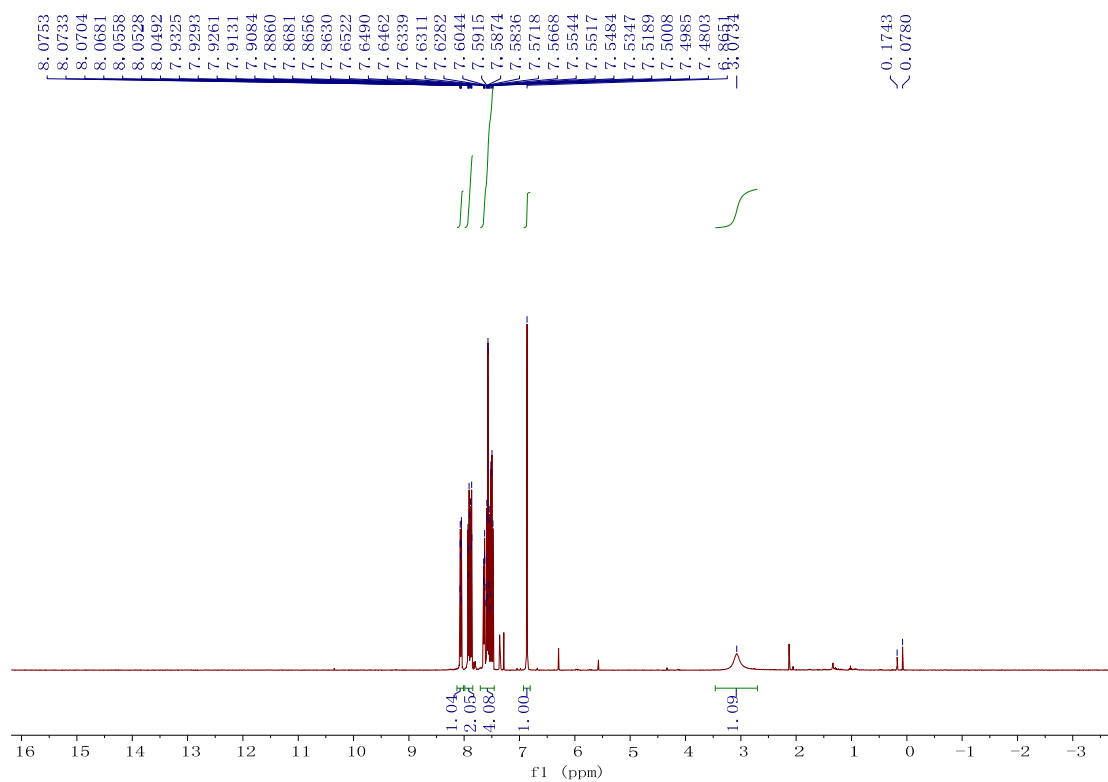
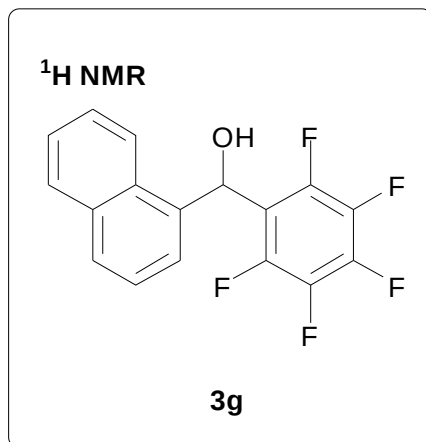


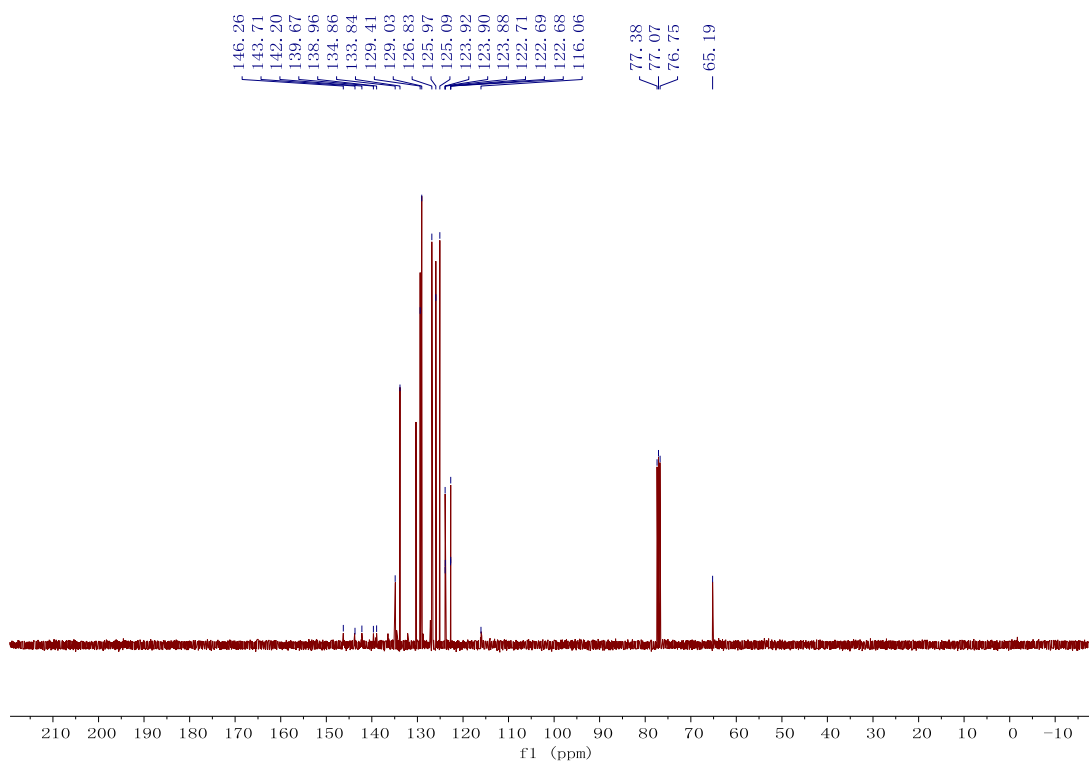
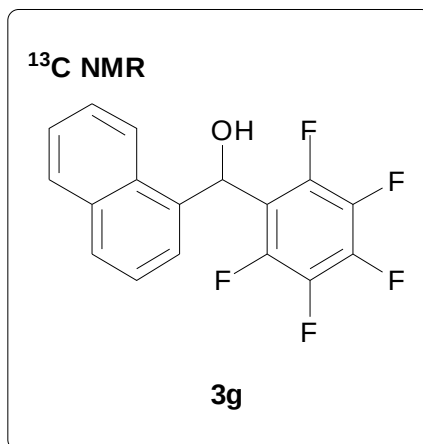
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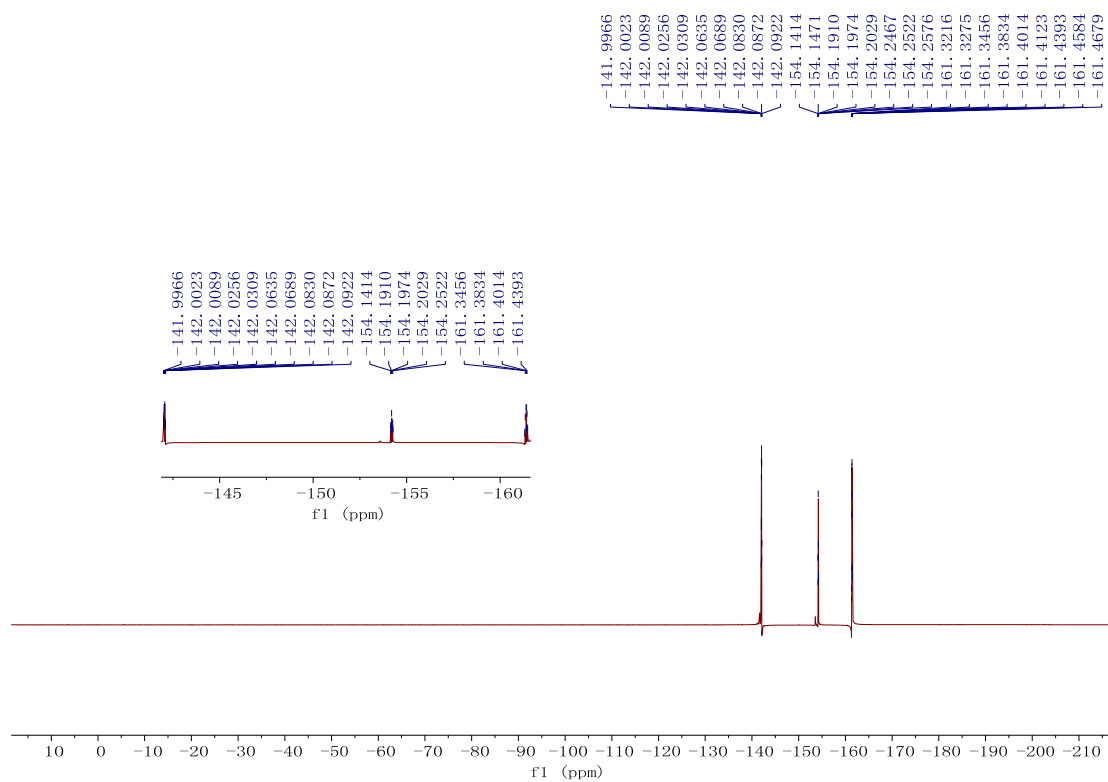
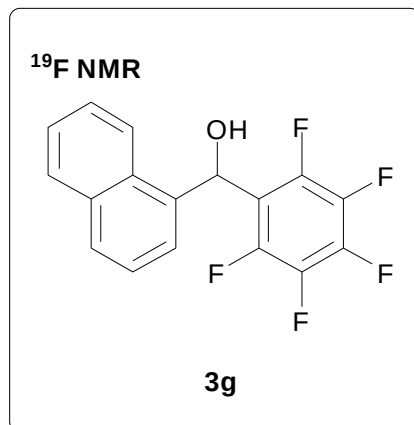


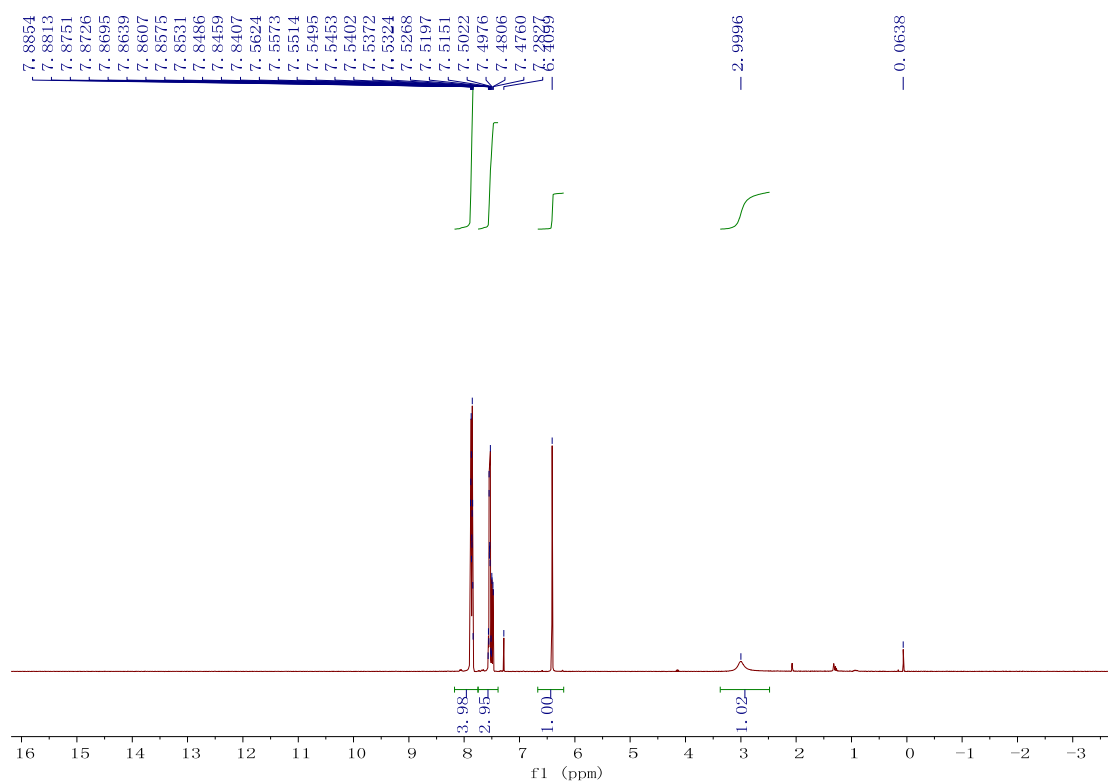
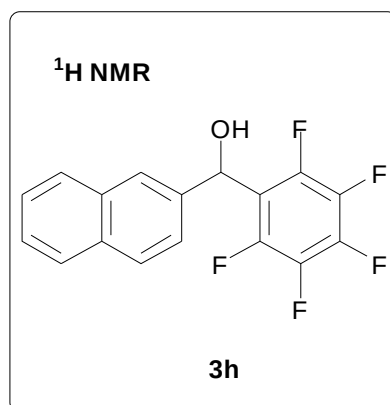
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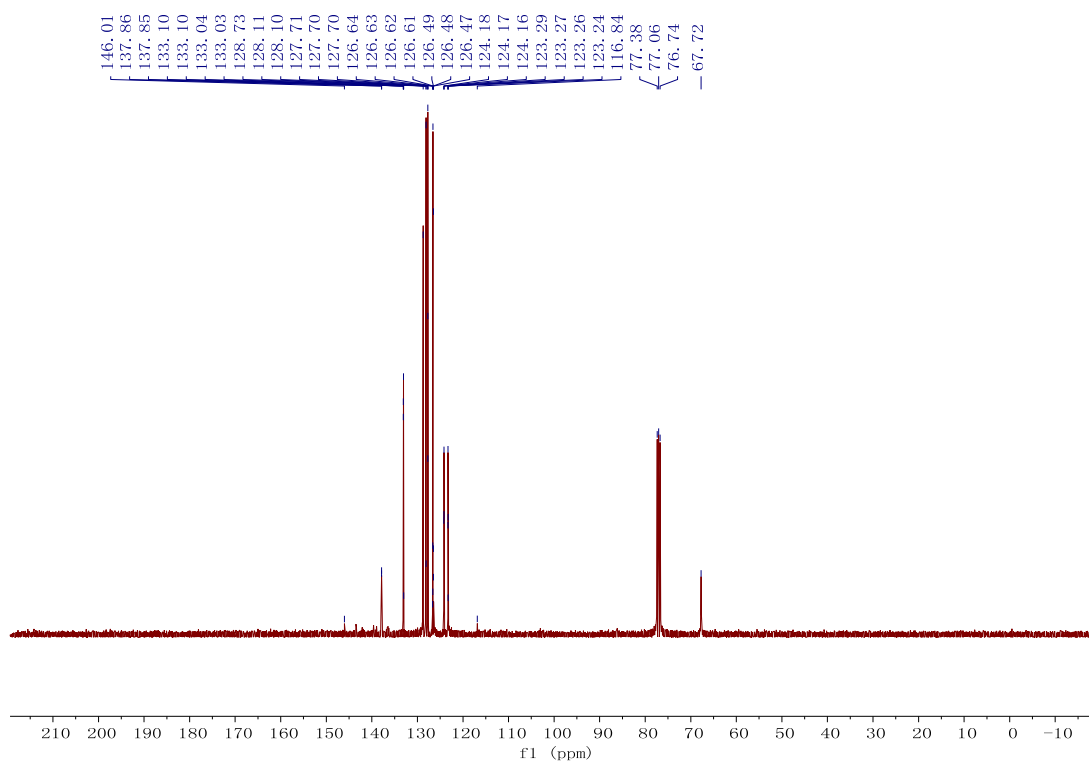
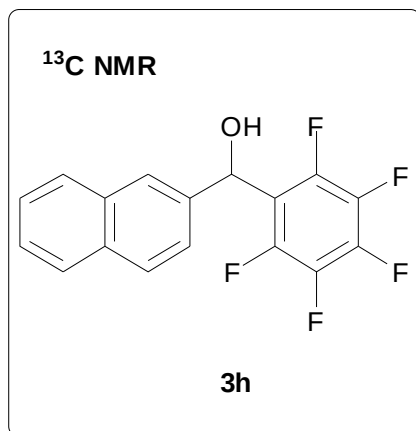




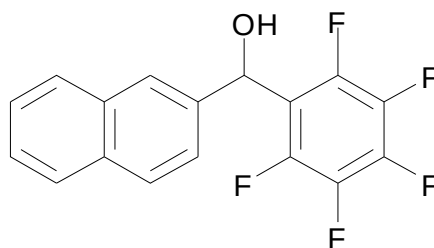




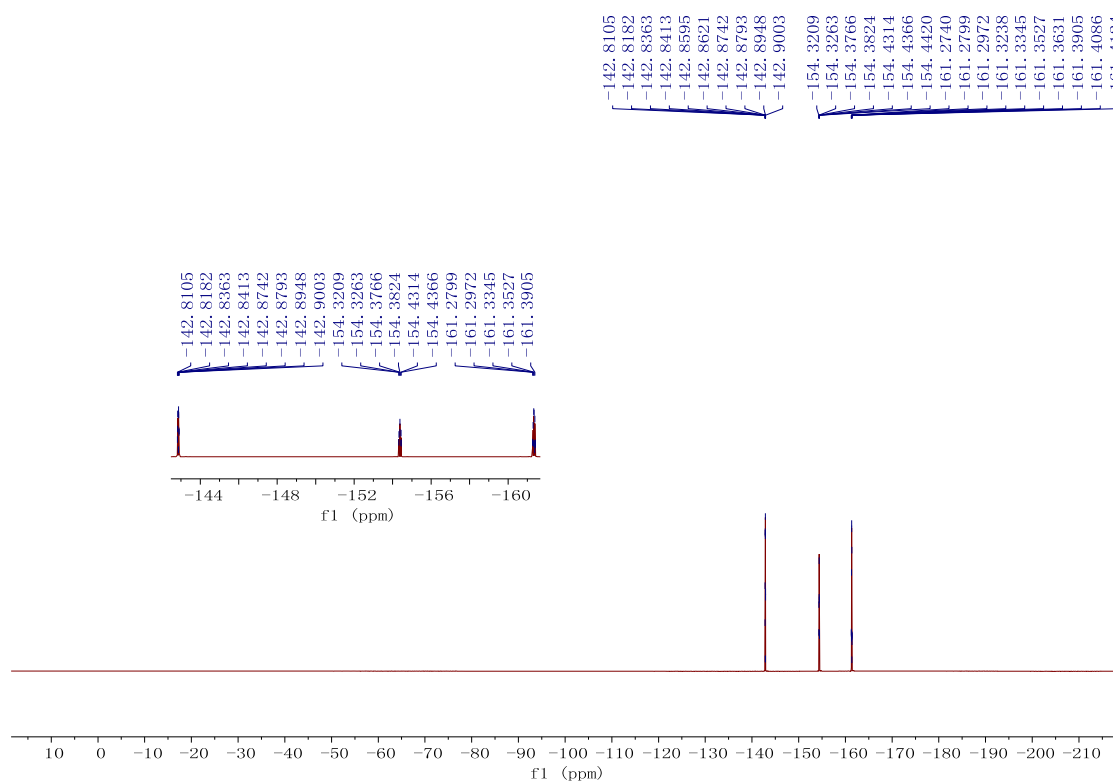


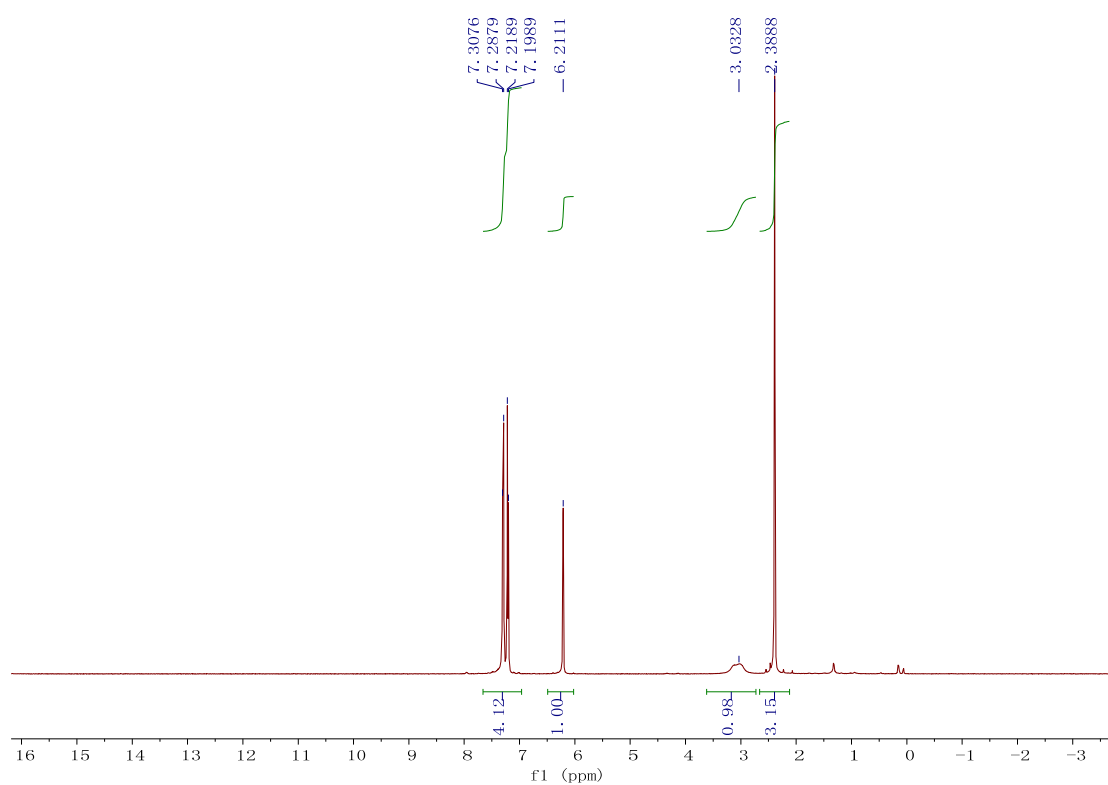
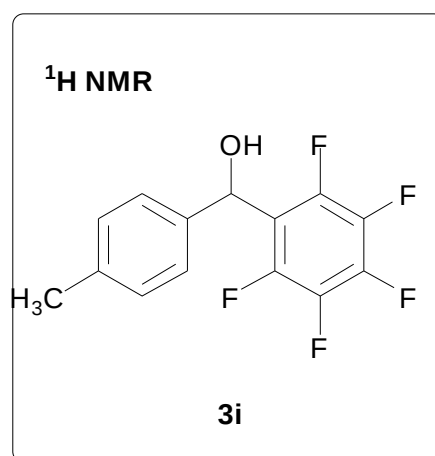


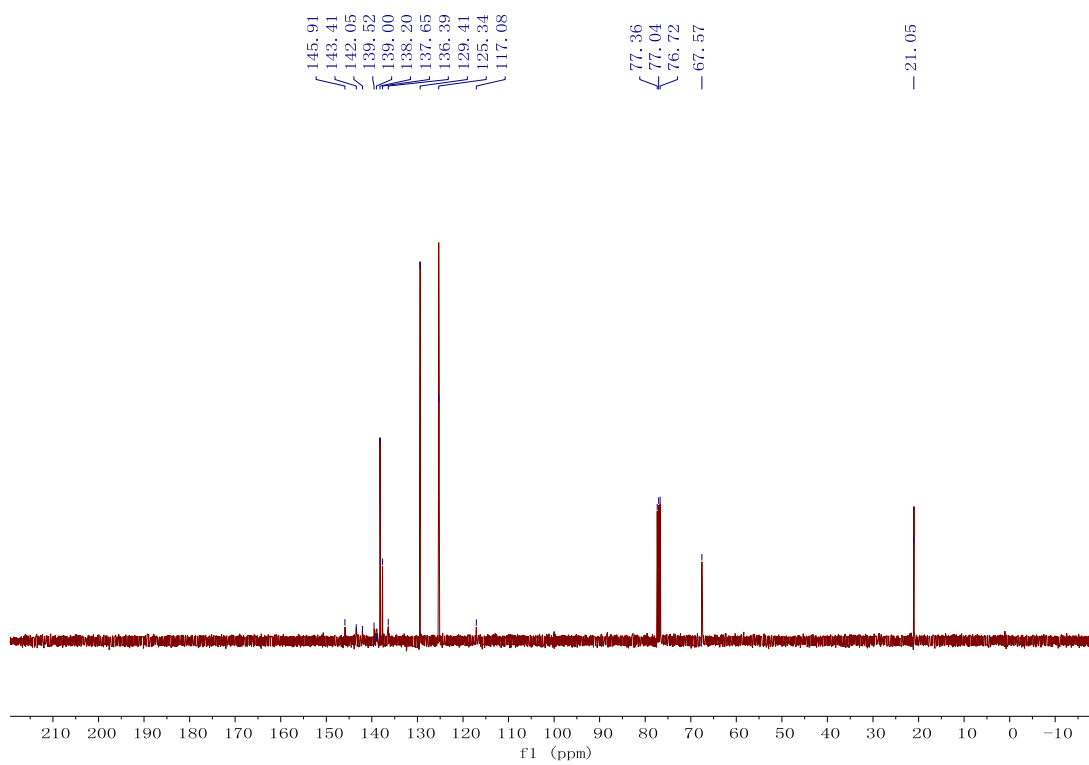
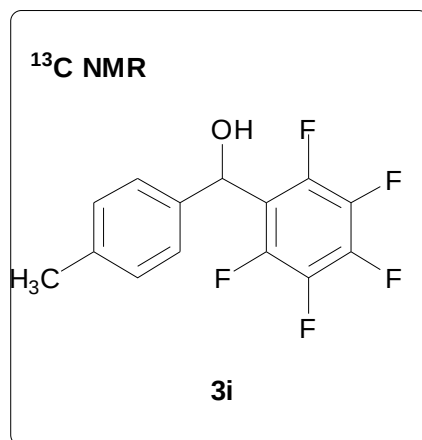
^{19}F NMR

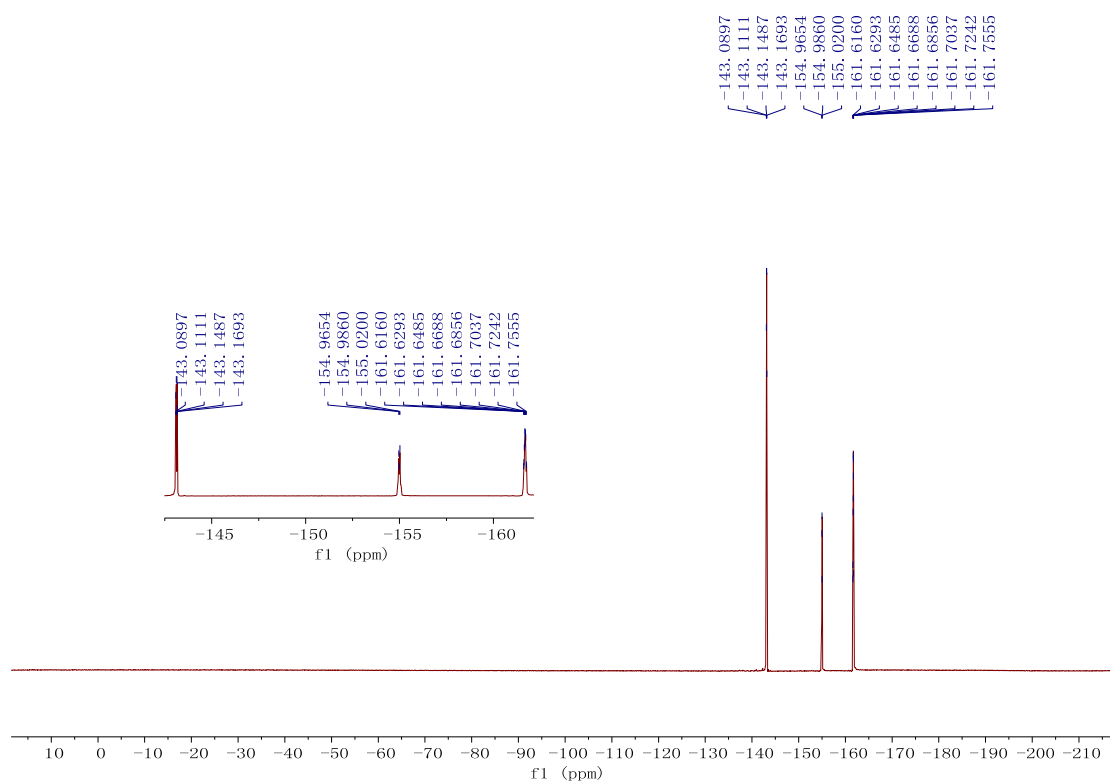
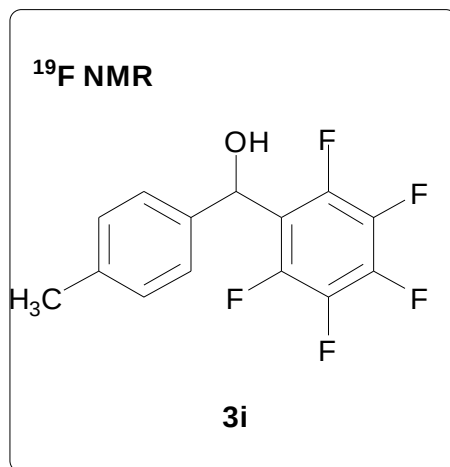


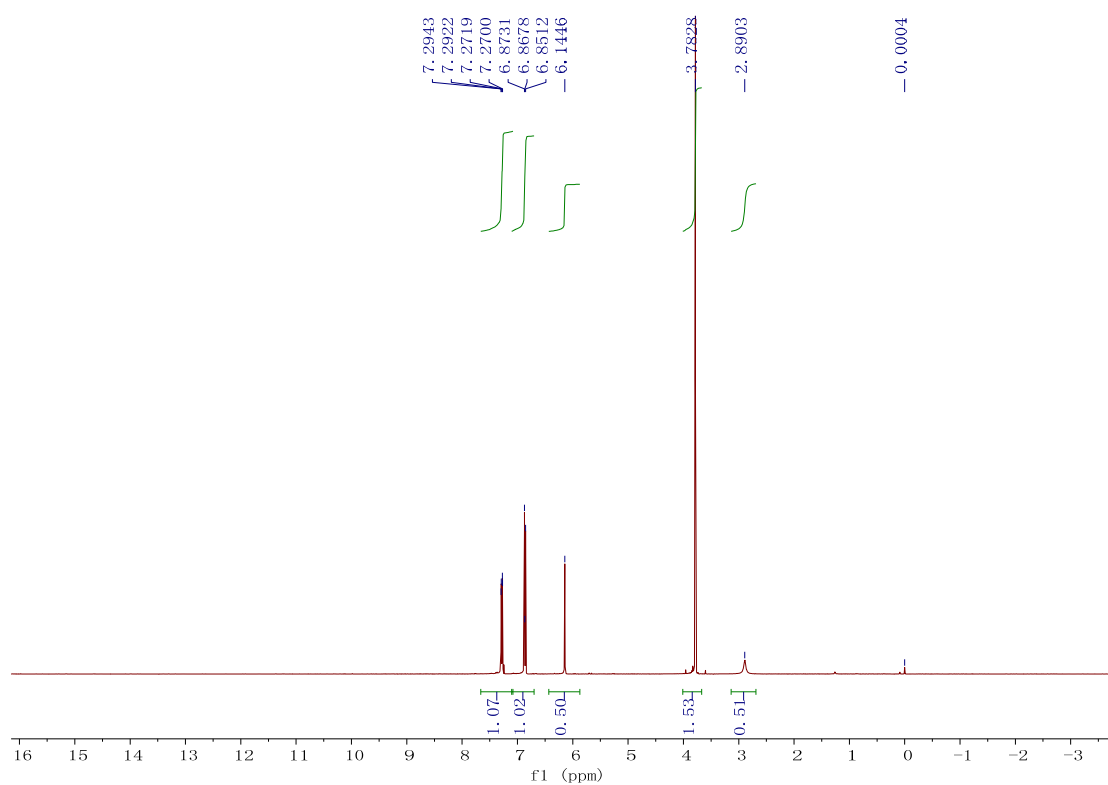
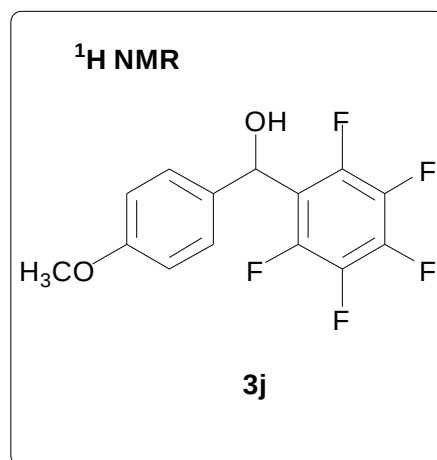
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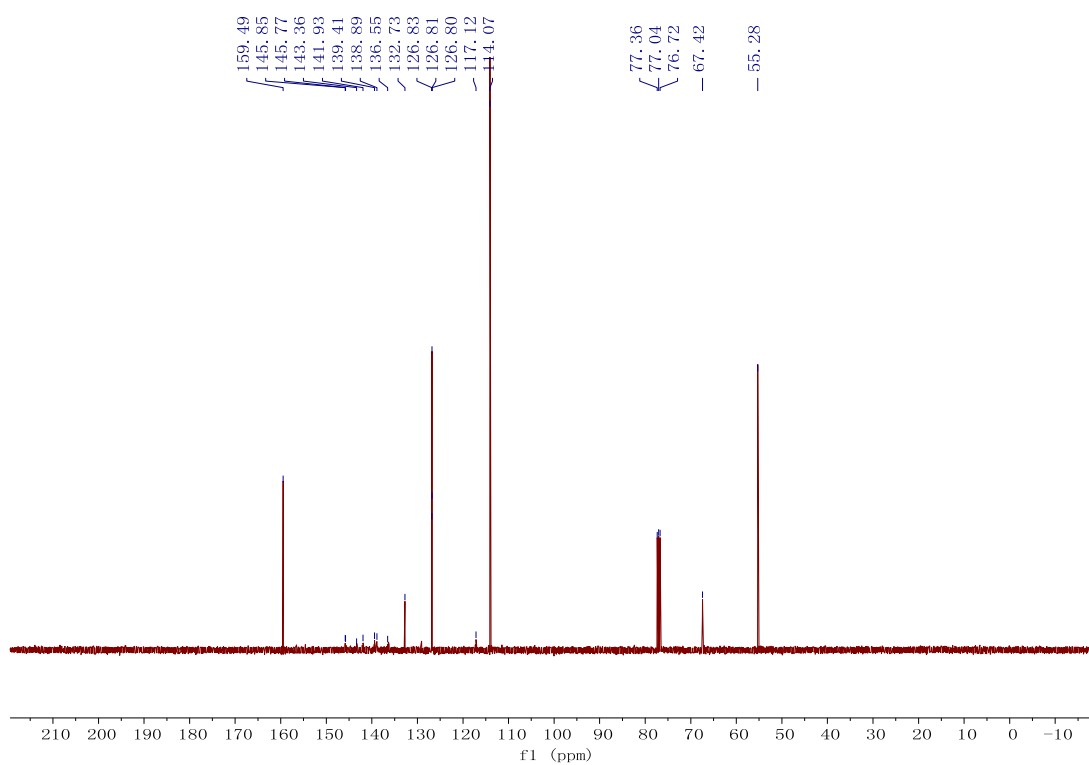
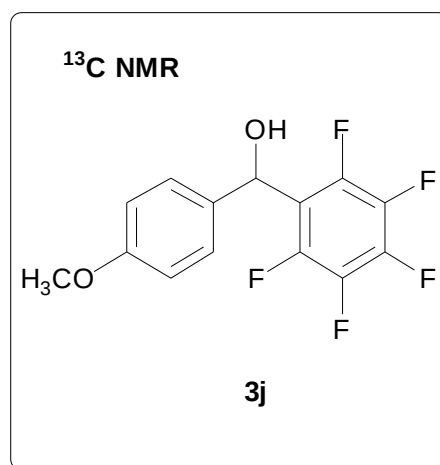


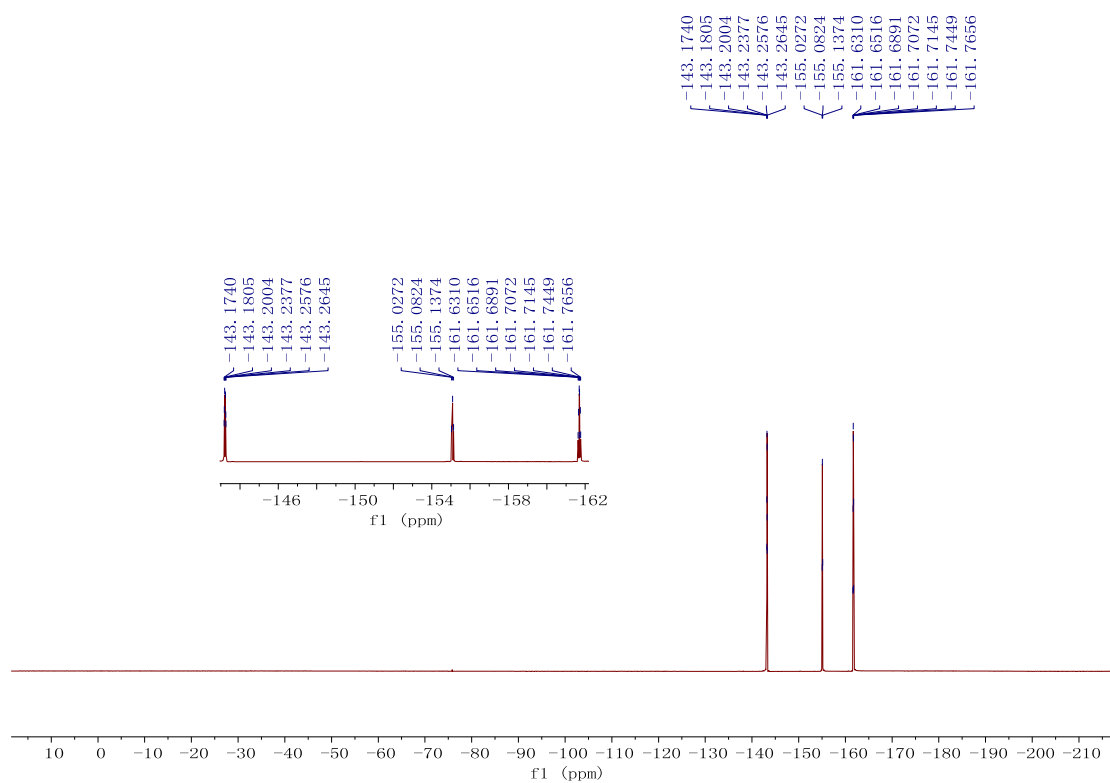
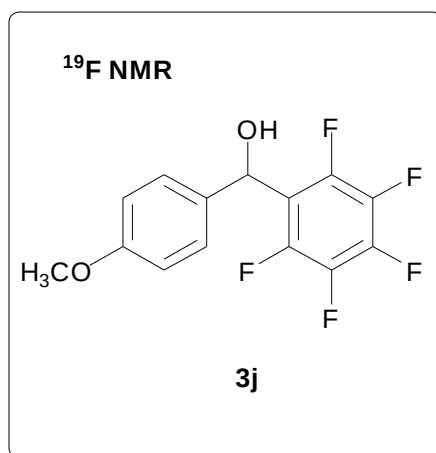




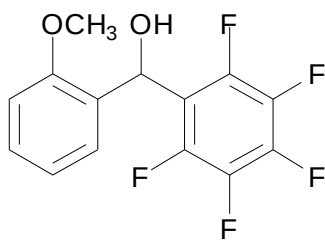




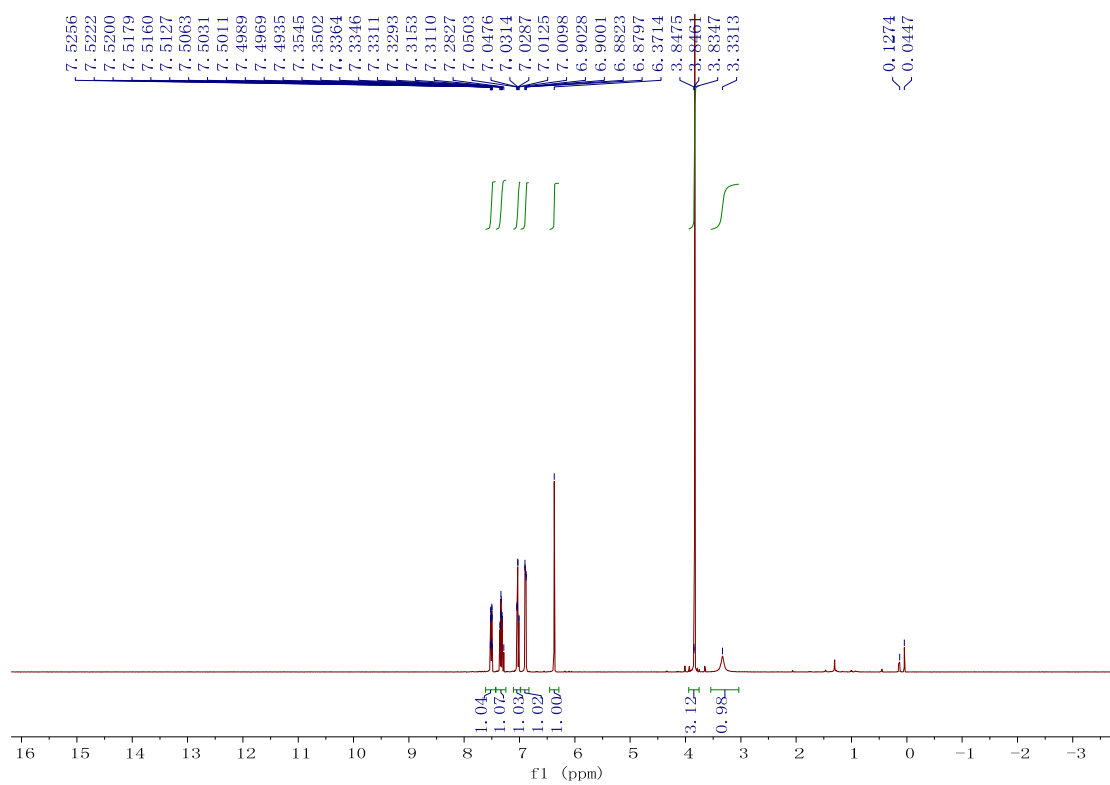




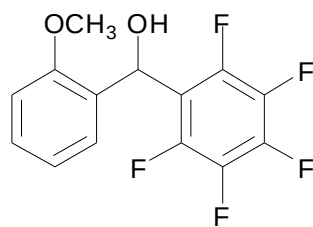
¹H NMR



3k



¹³C NMR

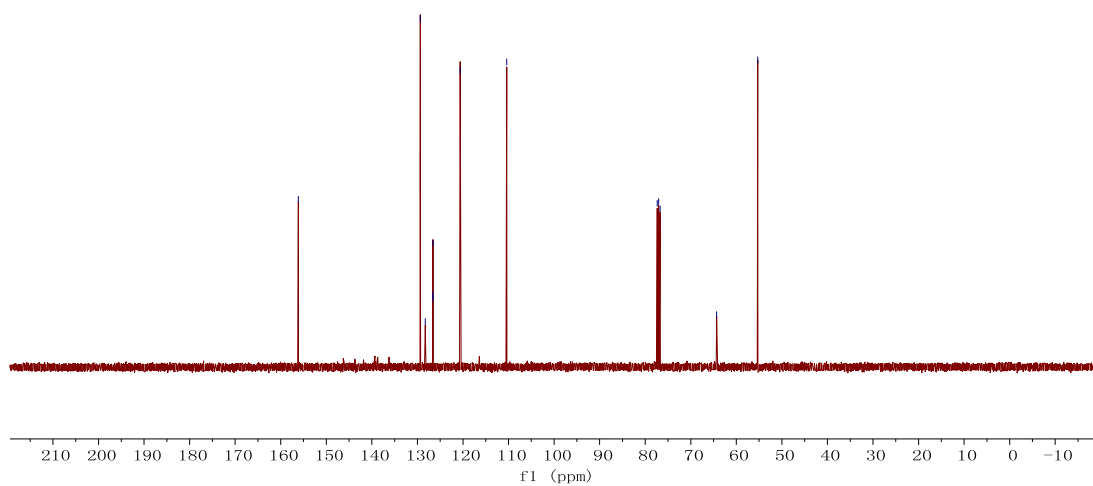


3k

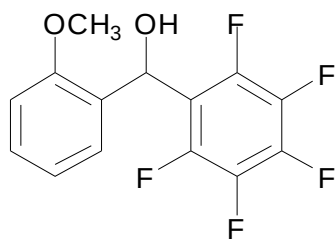
— 156.14

129.36
128.28
126.62
126.60
126.58
120.62
— 110.41

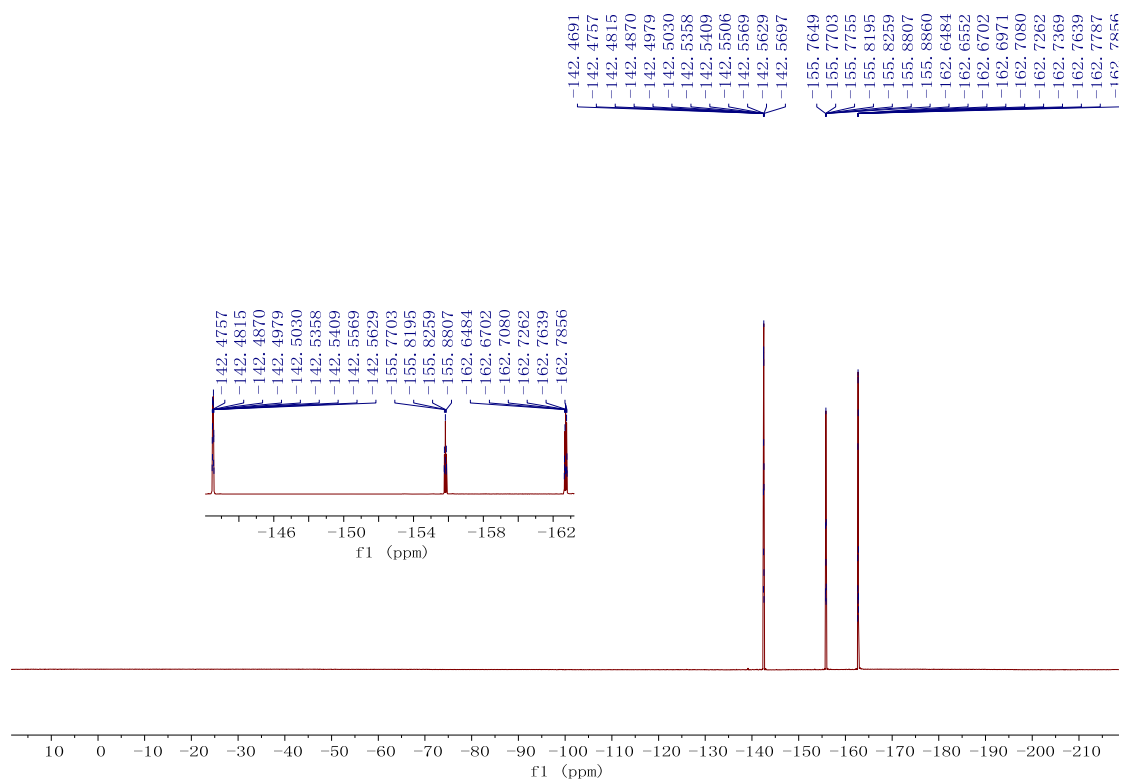
77.36
77.04
76.72
— 64.31
— 55.29

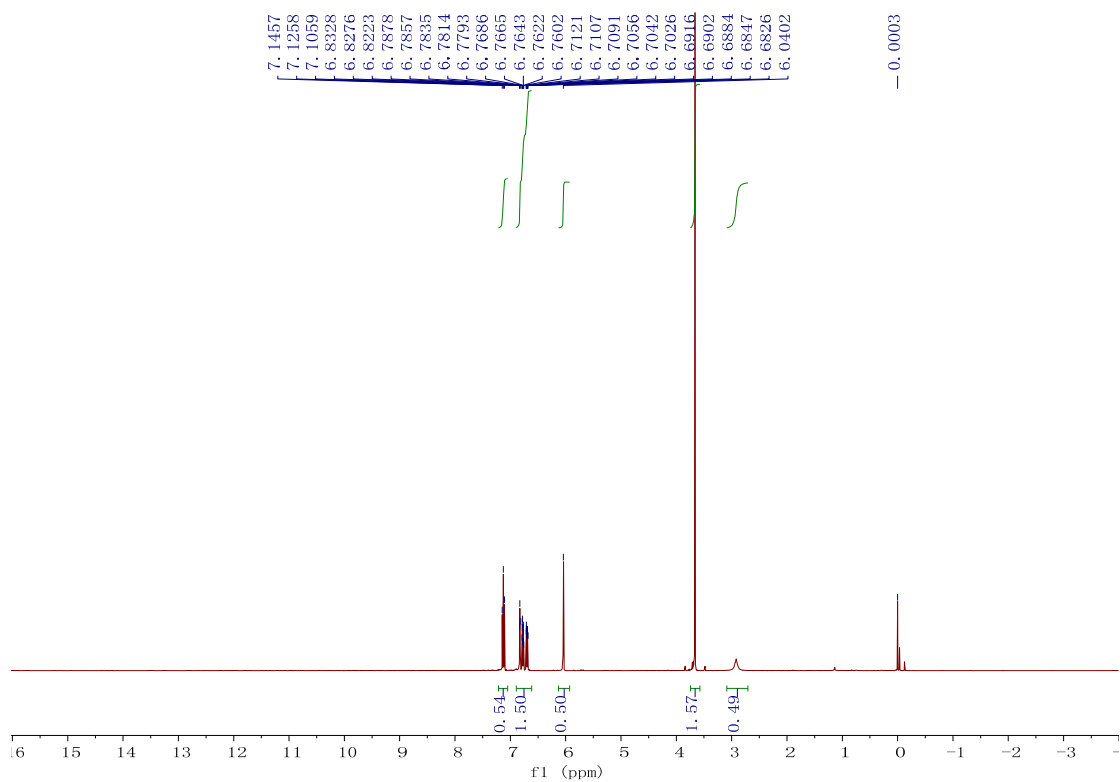
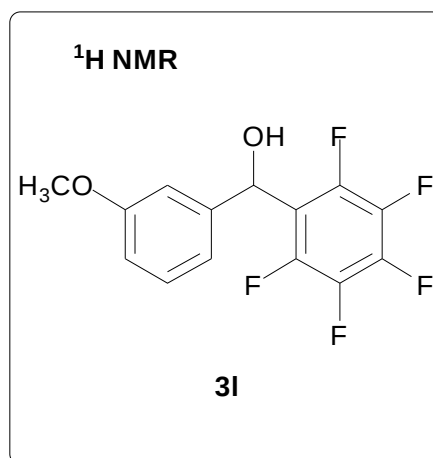


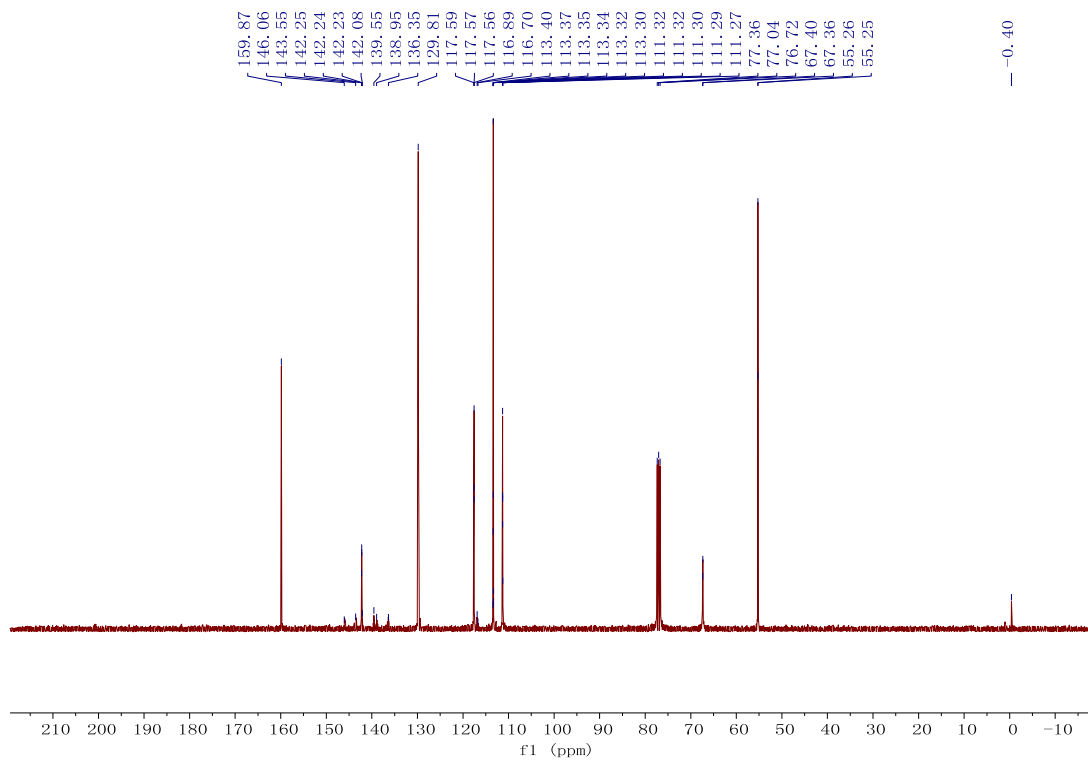
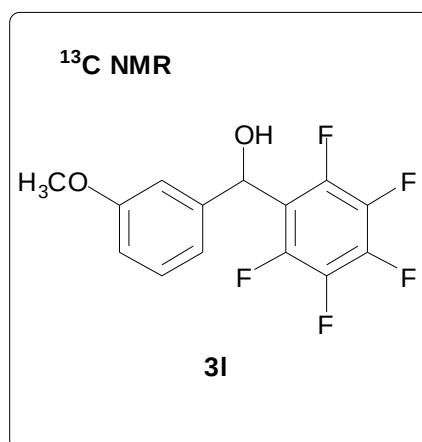
^{19}F NMR



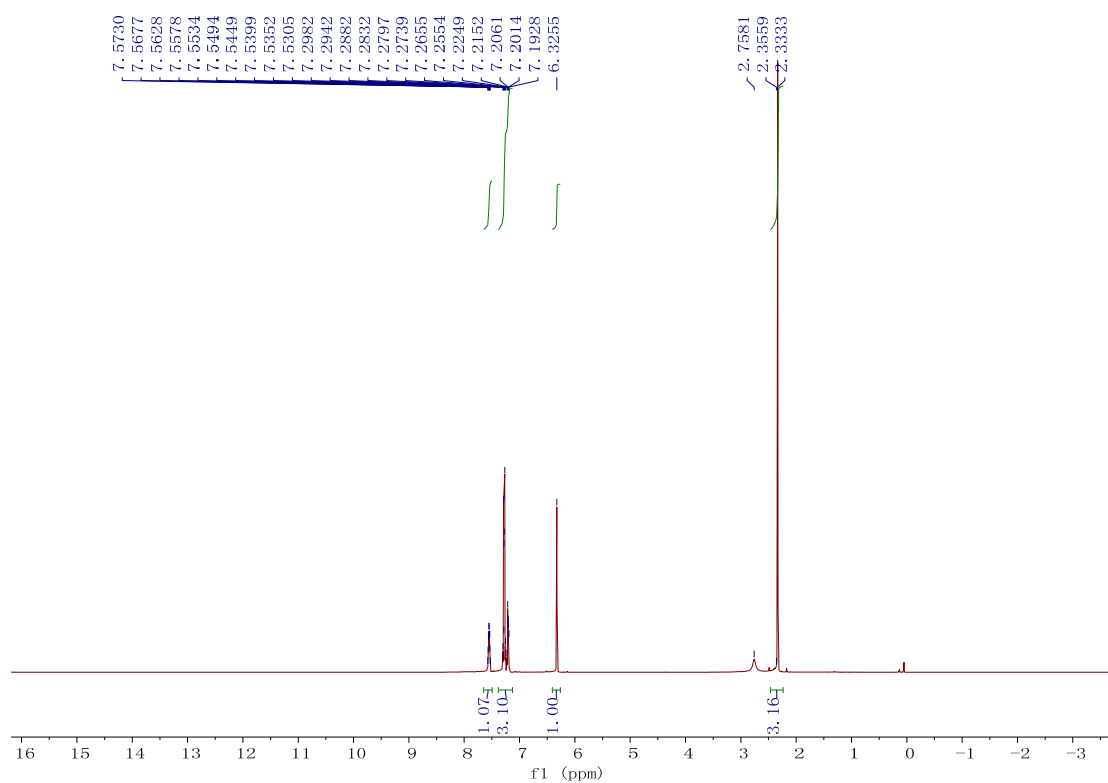
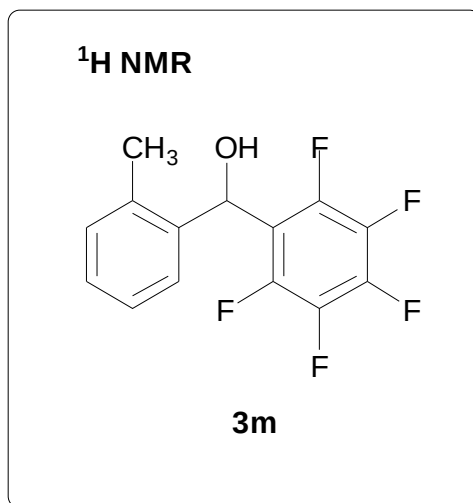
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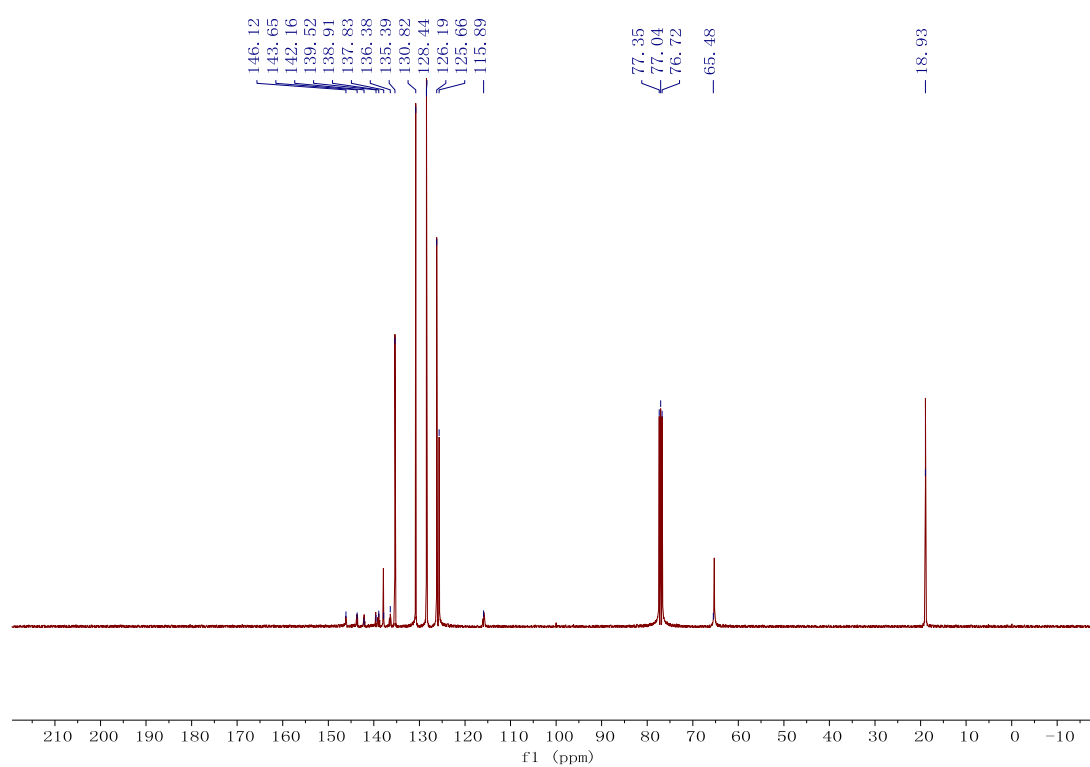
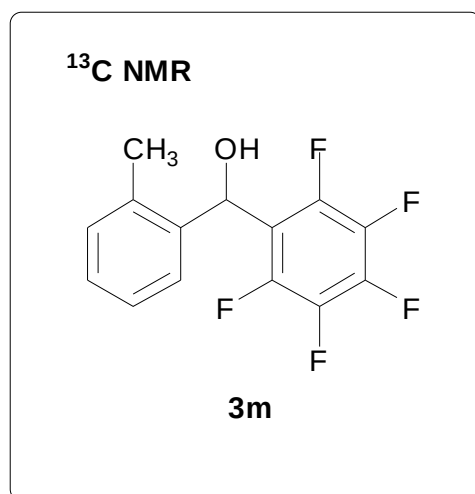




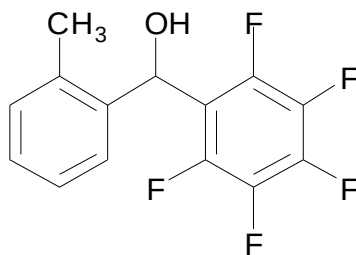




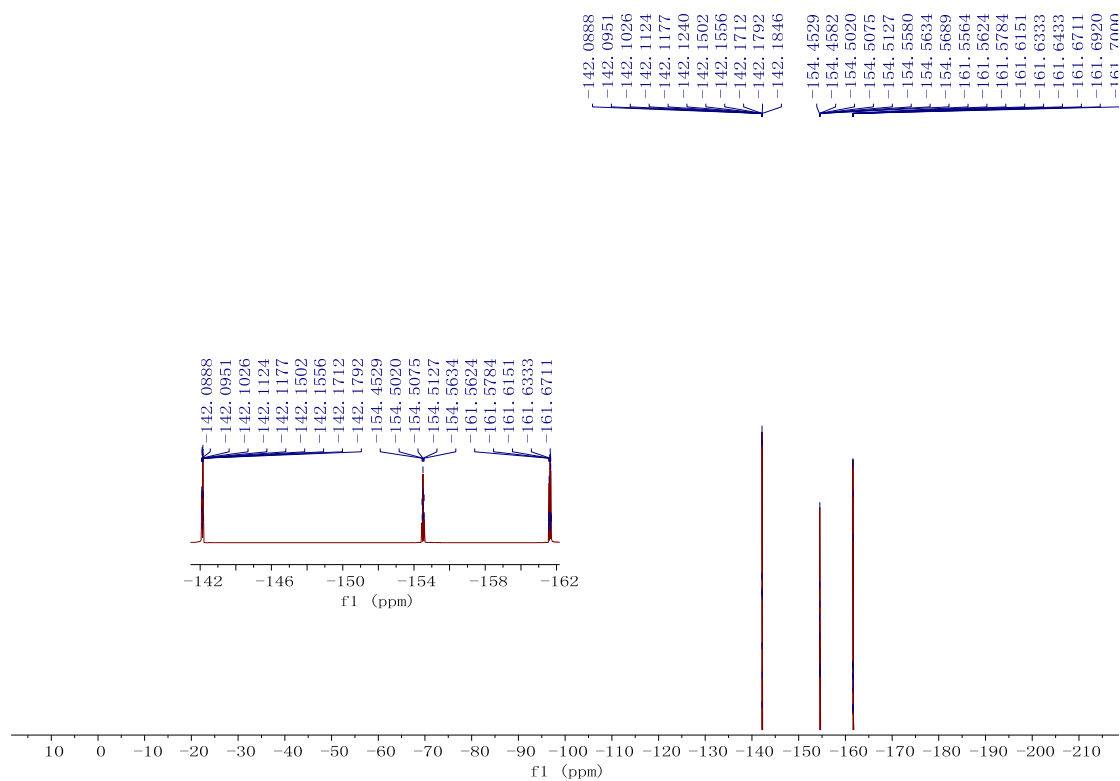




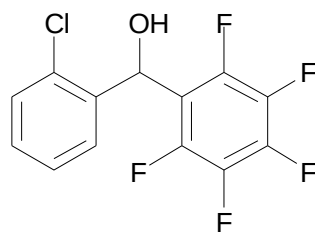
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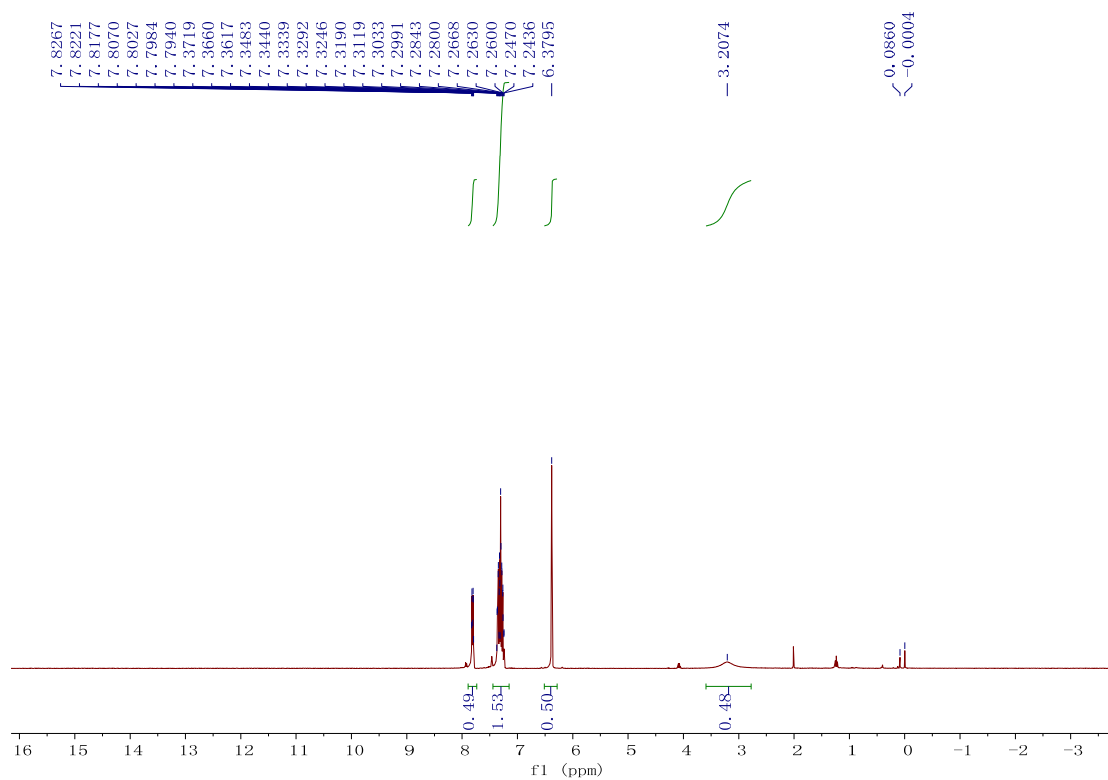
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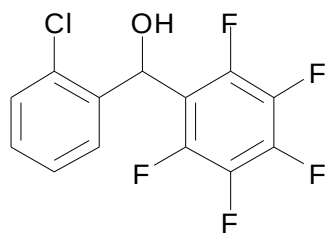
¹H NMR



3n



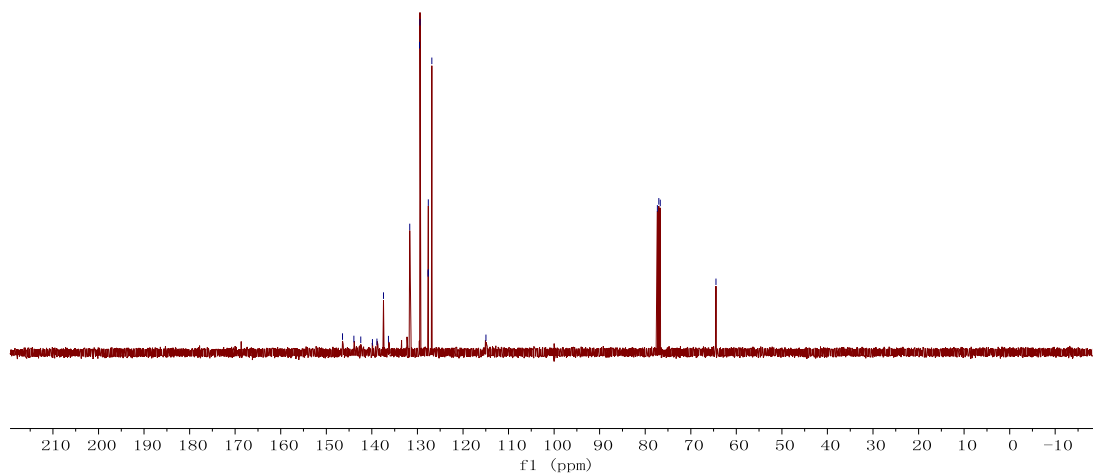
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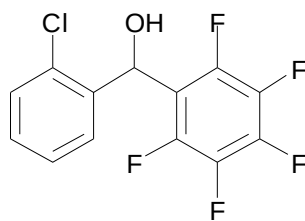
3n

146.44
143.94
142.44
139.86
138.87
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129.43
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114.97

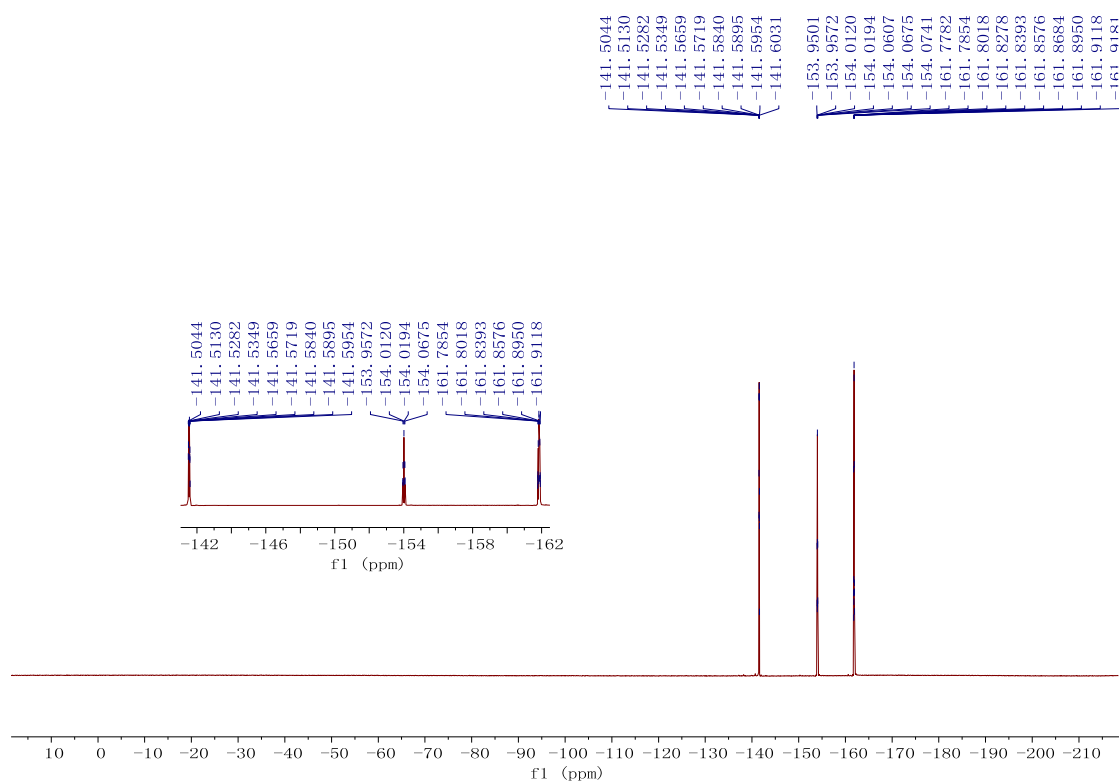
77.34
77.03
76.71
64.46

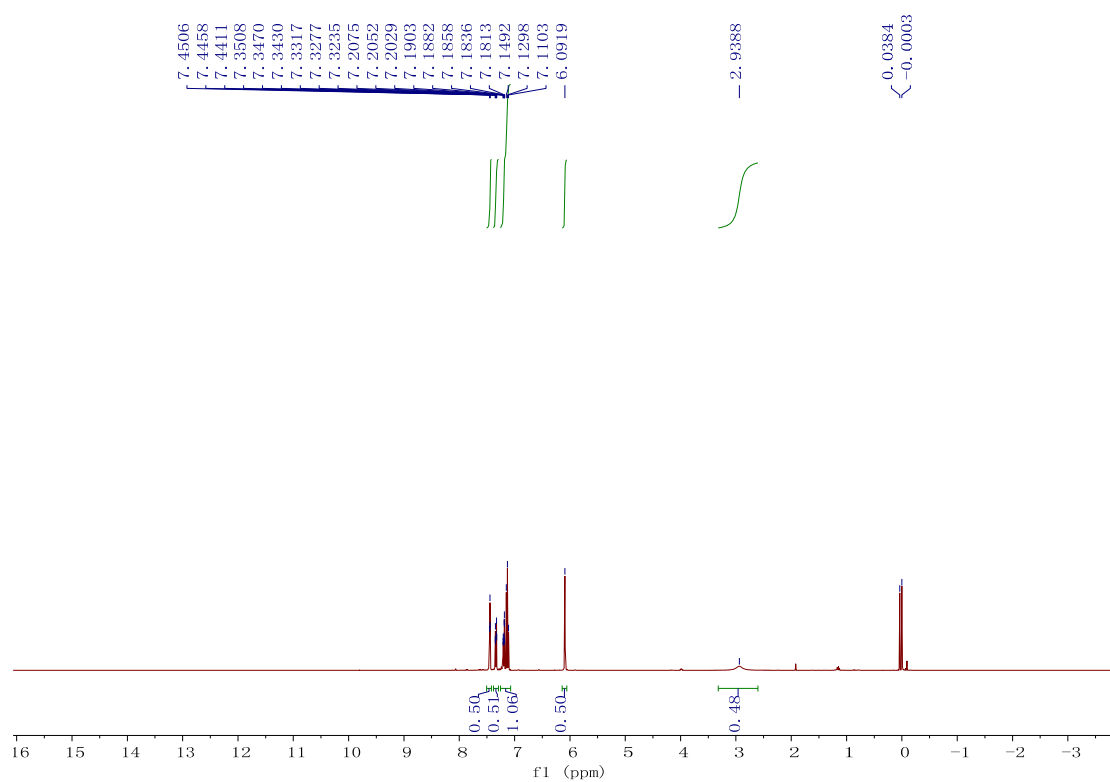
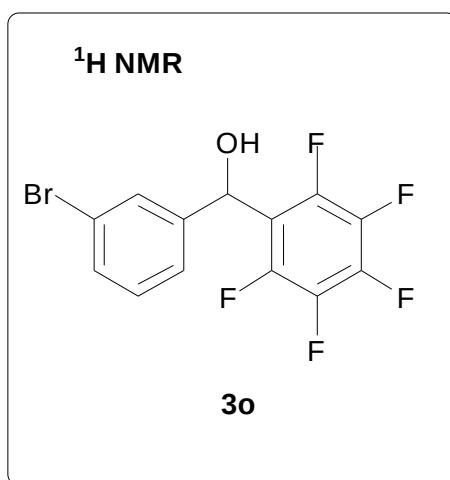


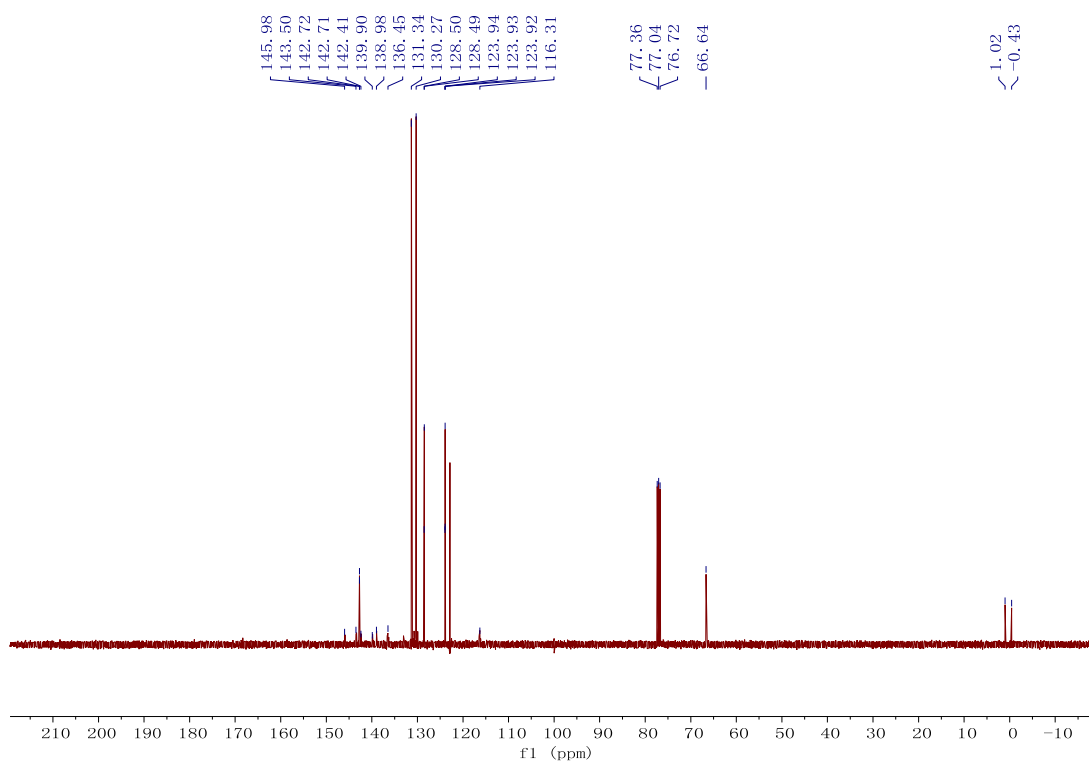
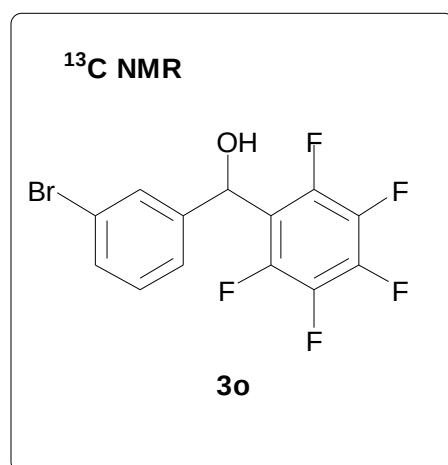
¹⁹F NMR



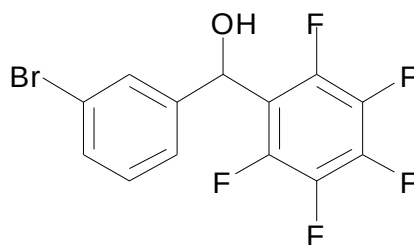
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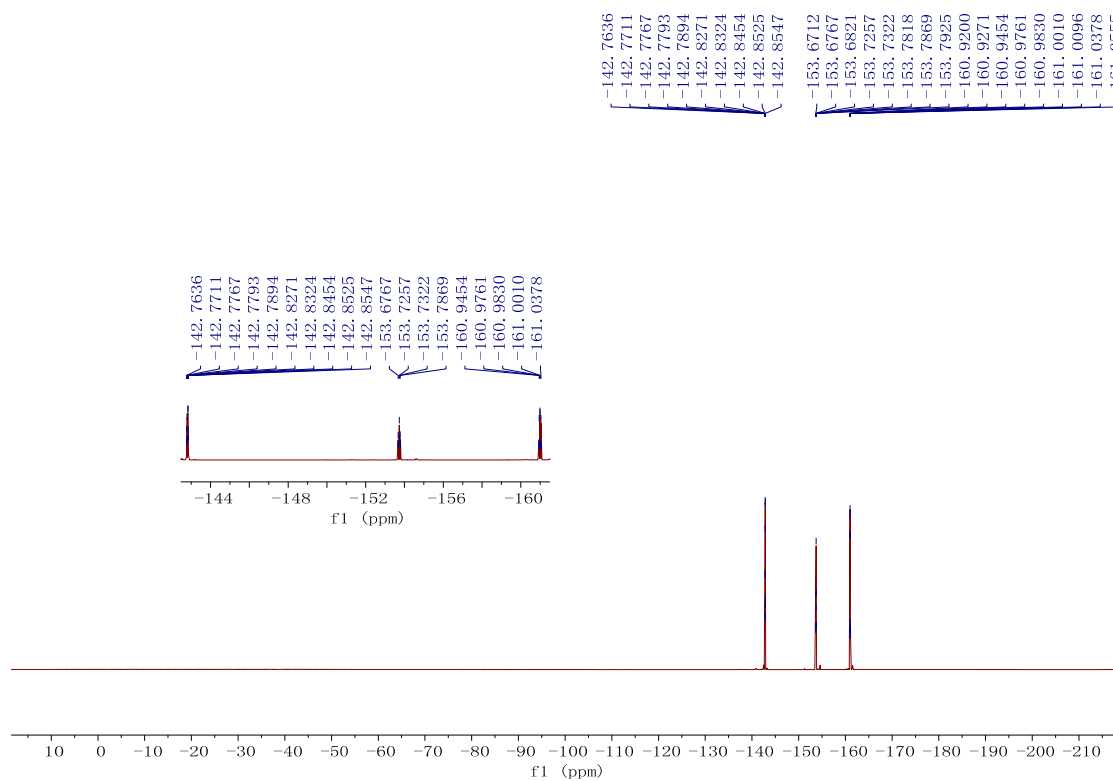


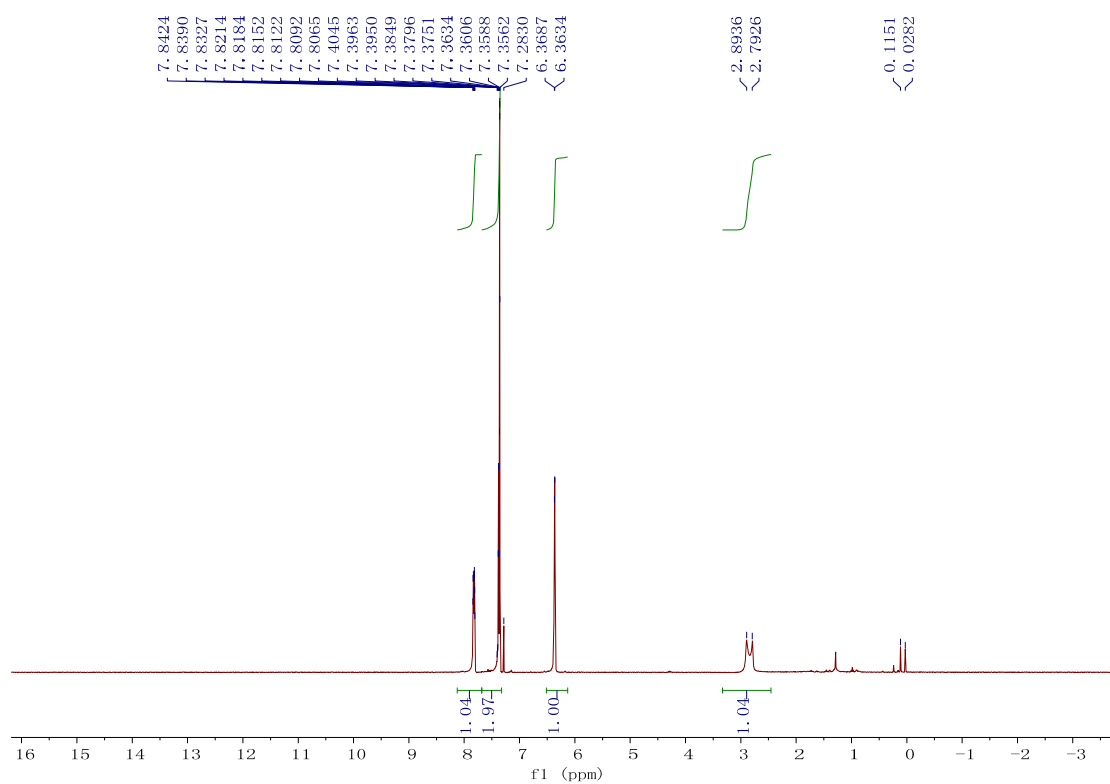
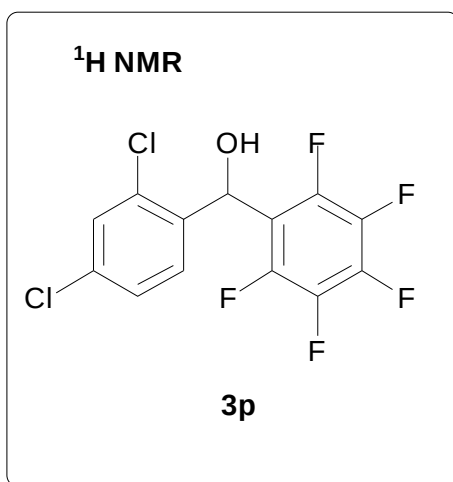


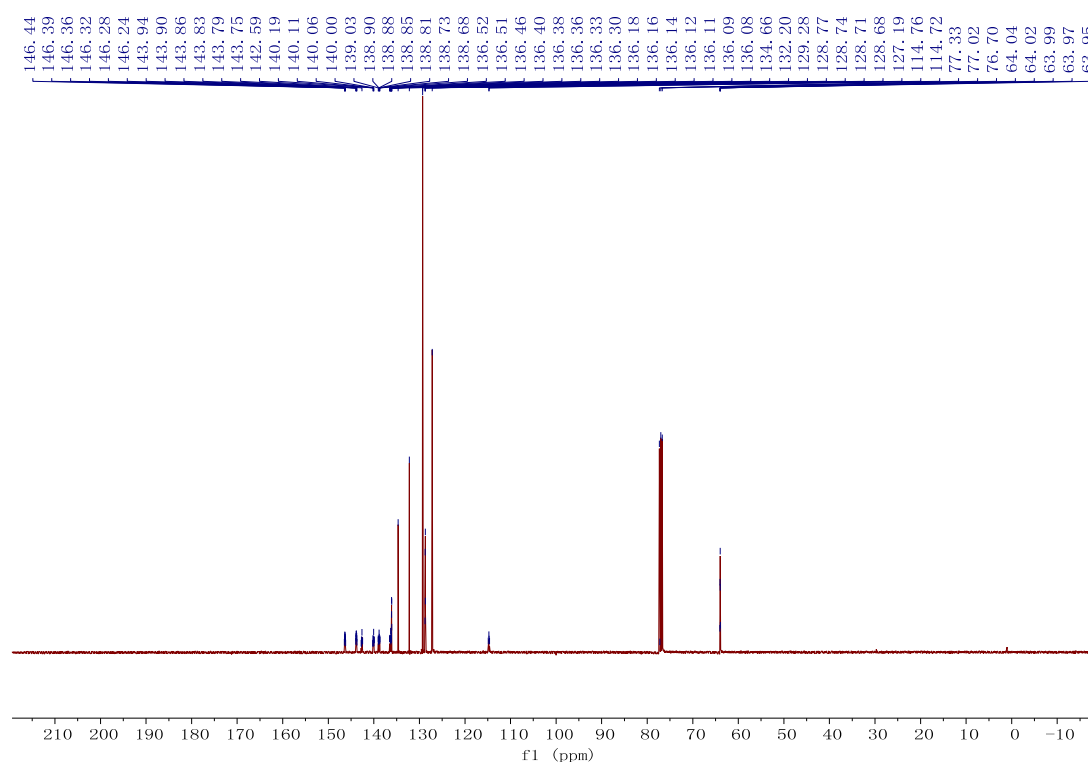
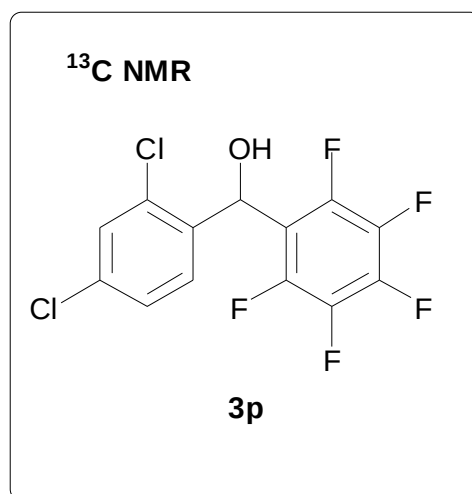
^{19}F NMR



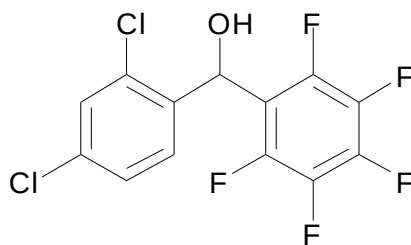
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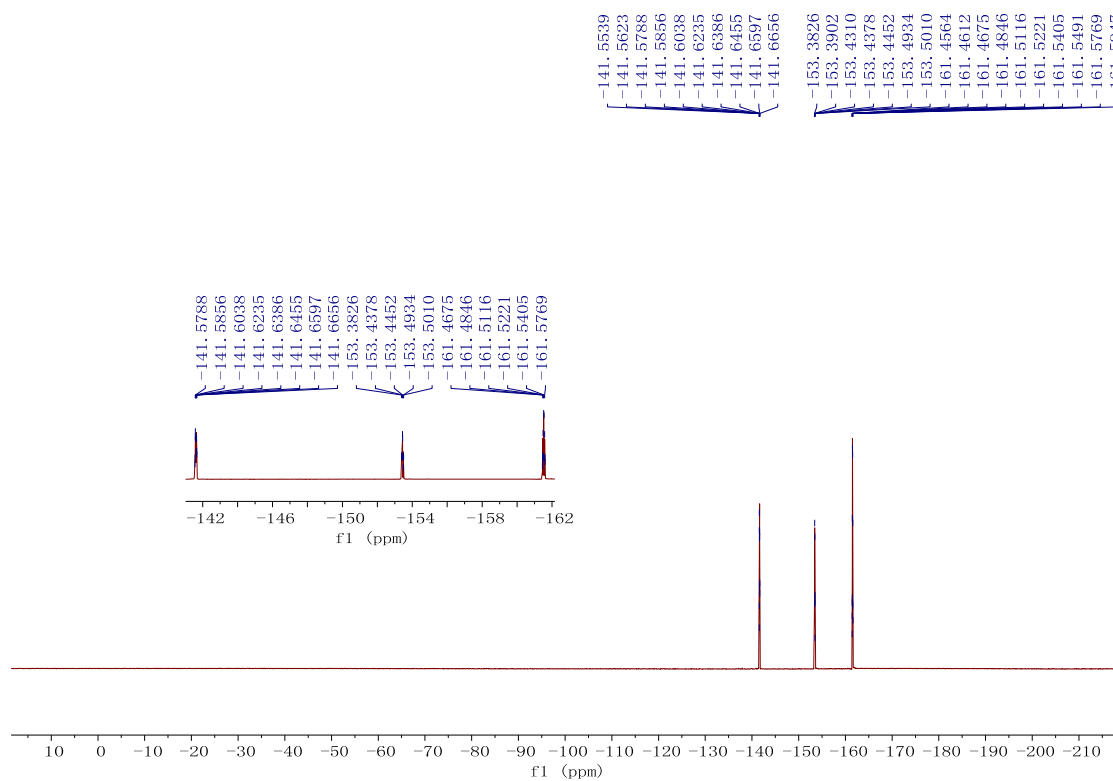


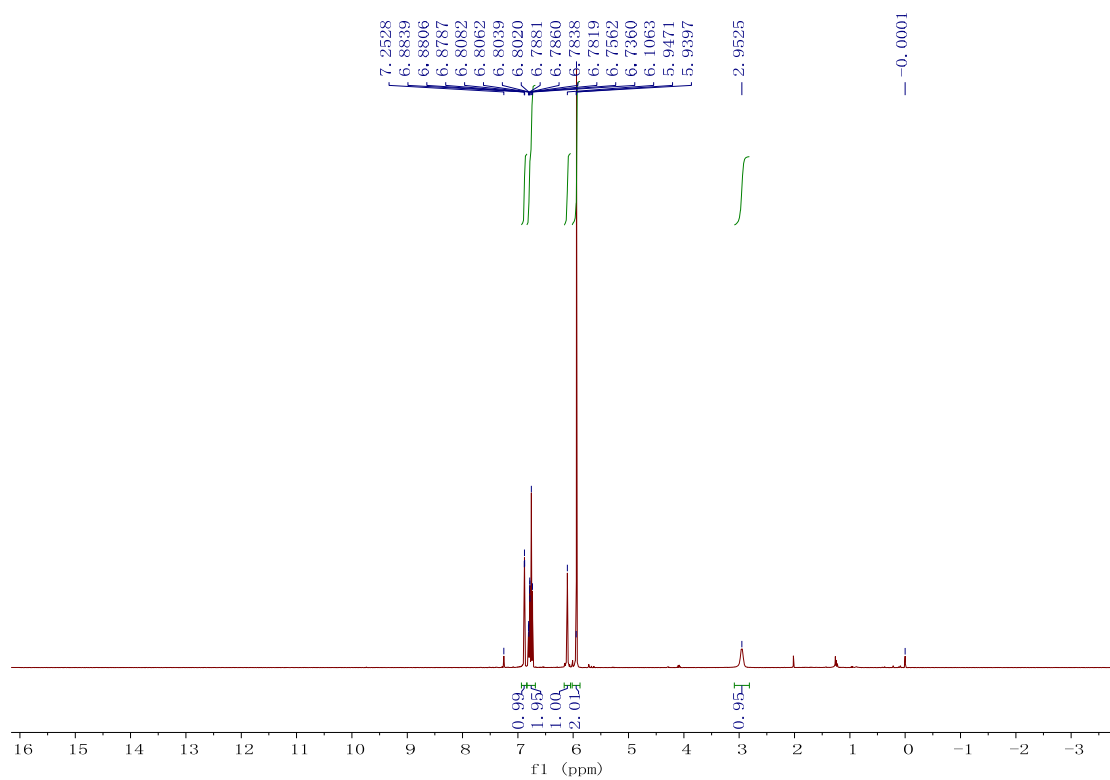
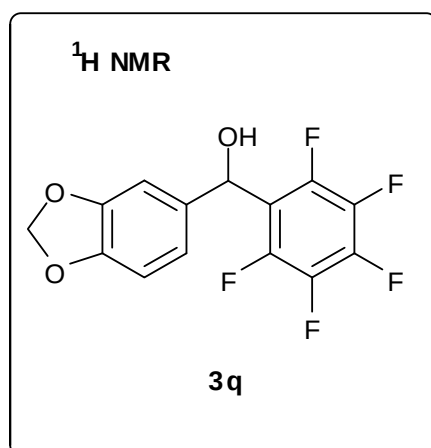


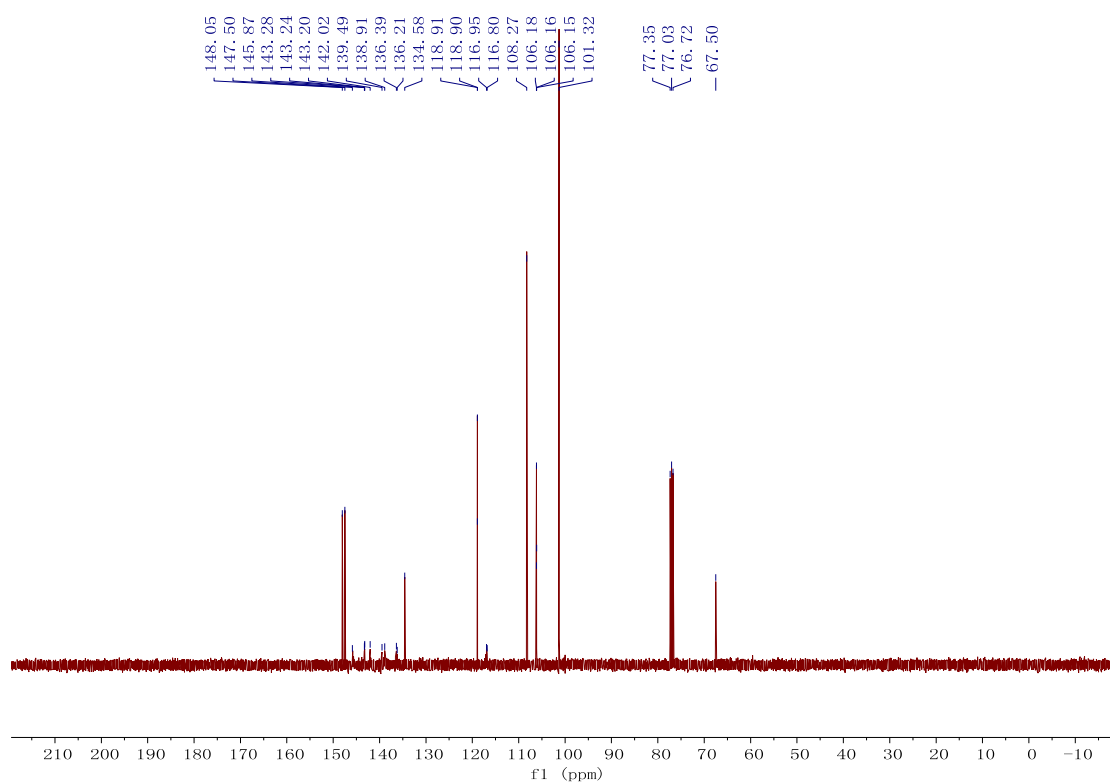
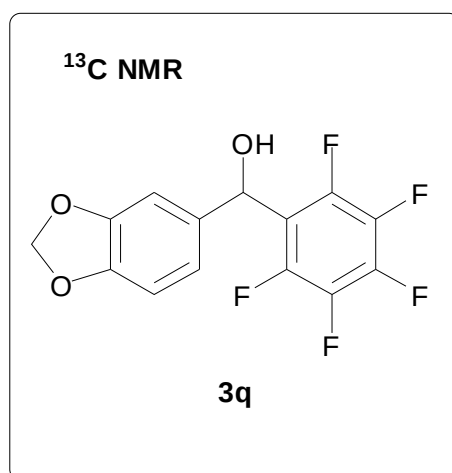
^{19}F NMR

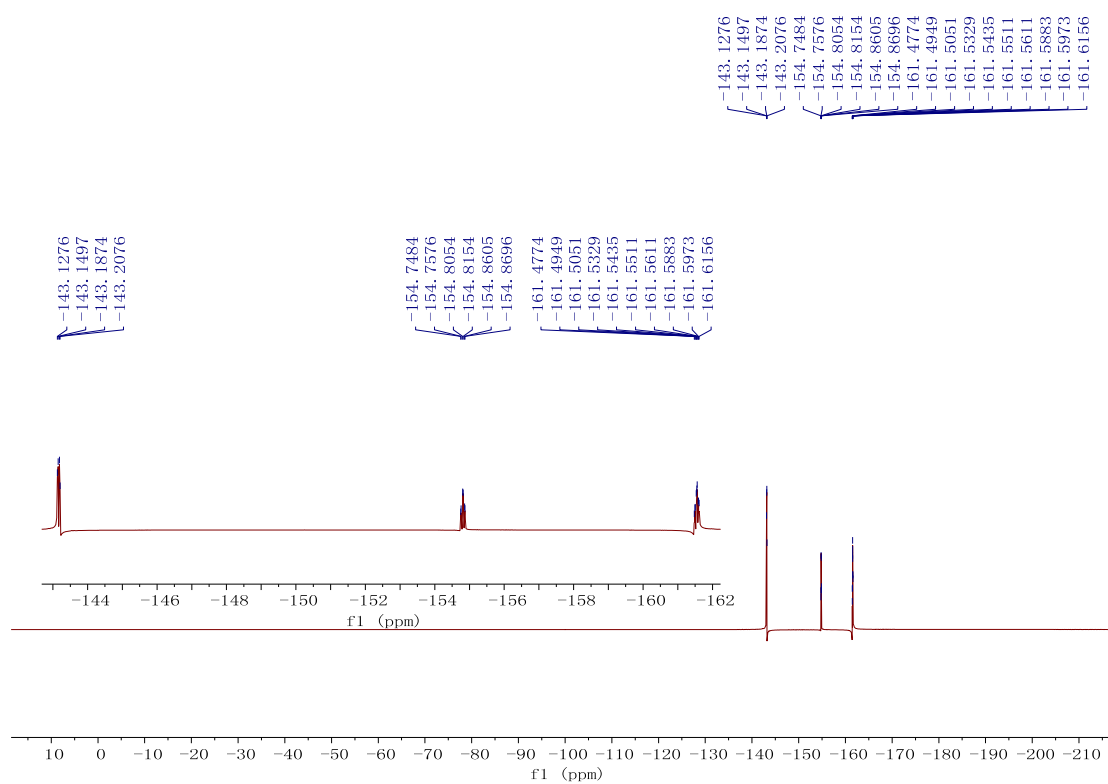
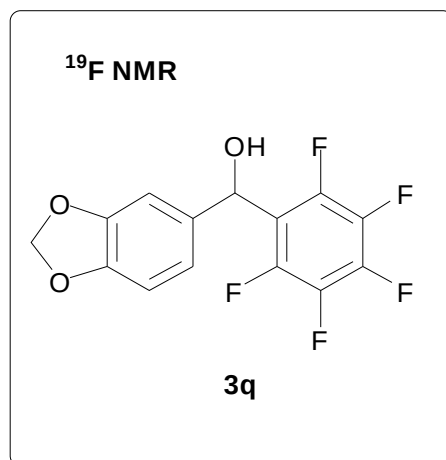


3p

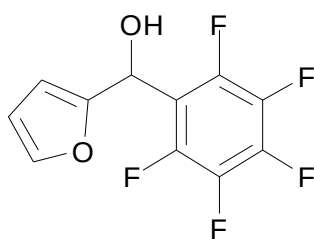




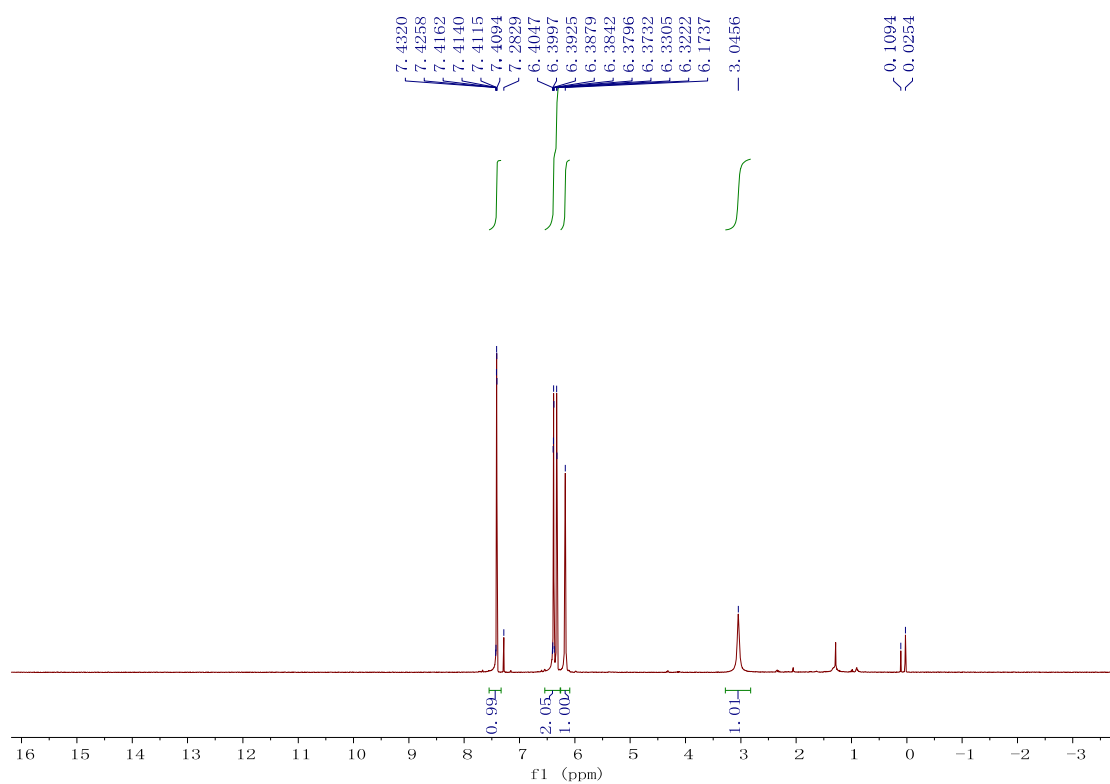




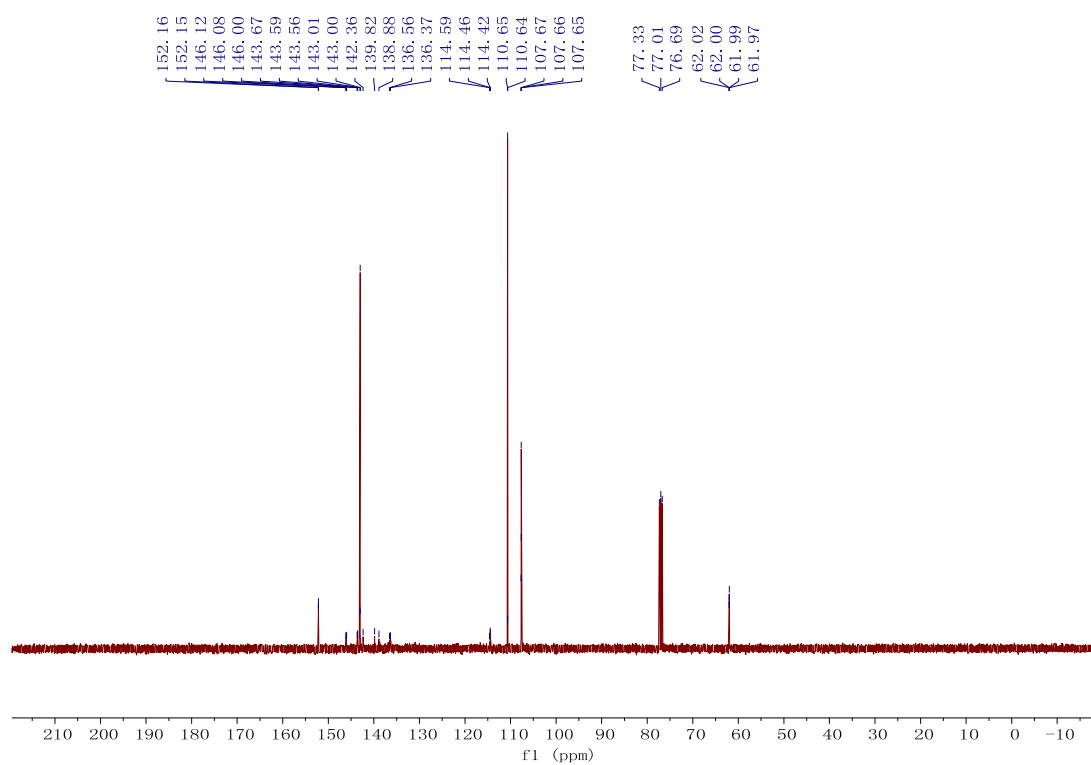
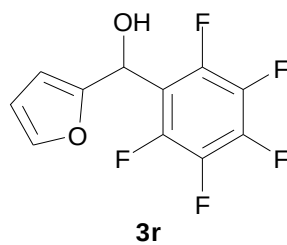
¹H NMR



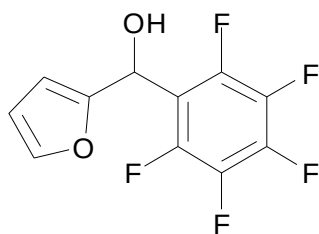
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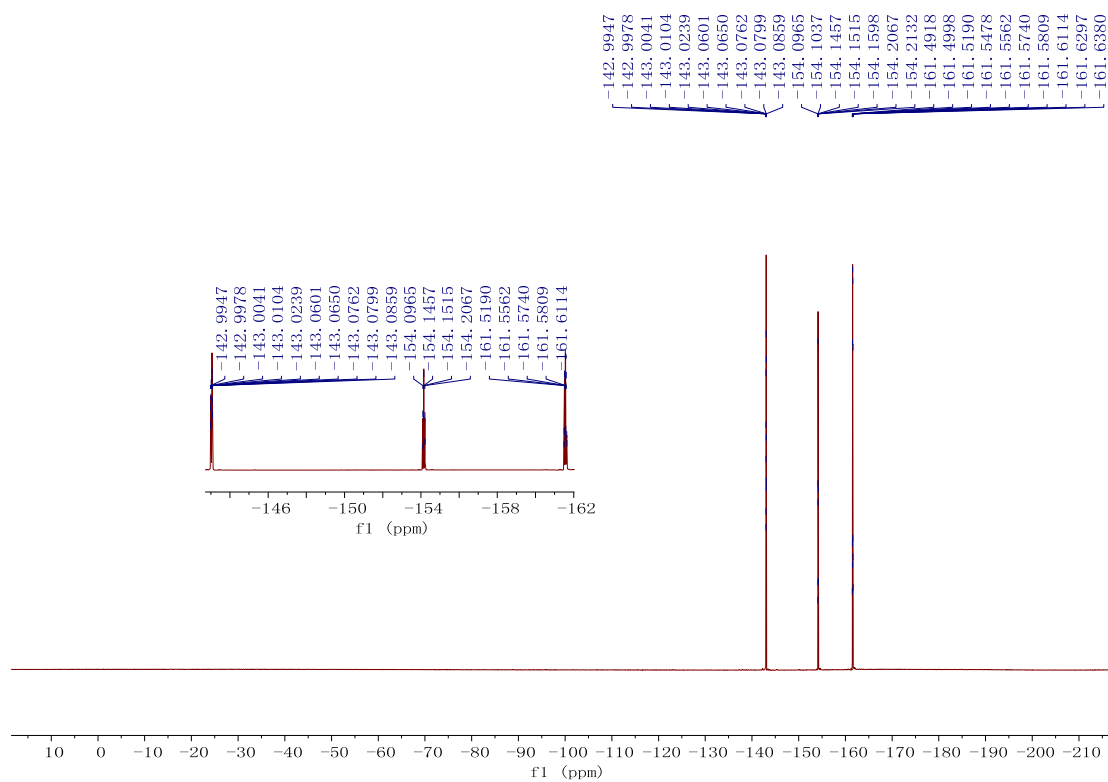
^{13}C NMR

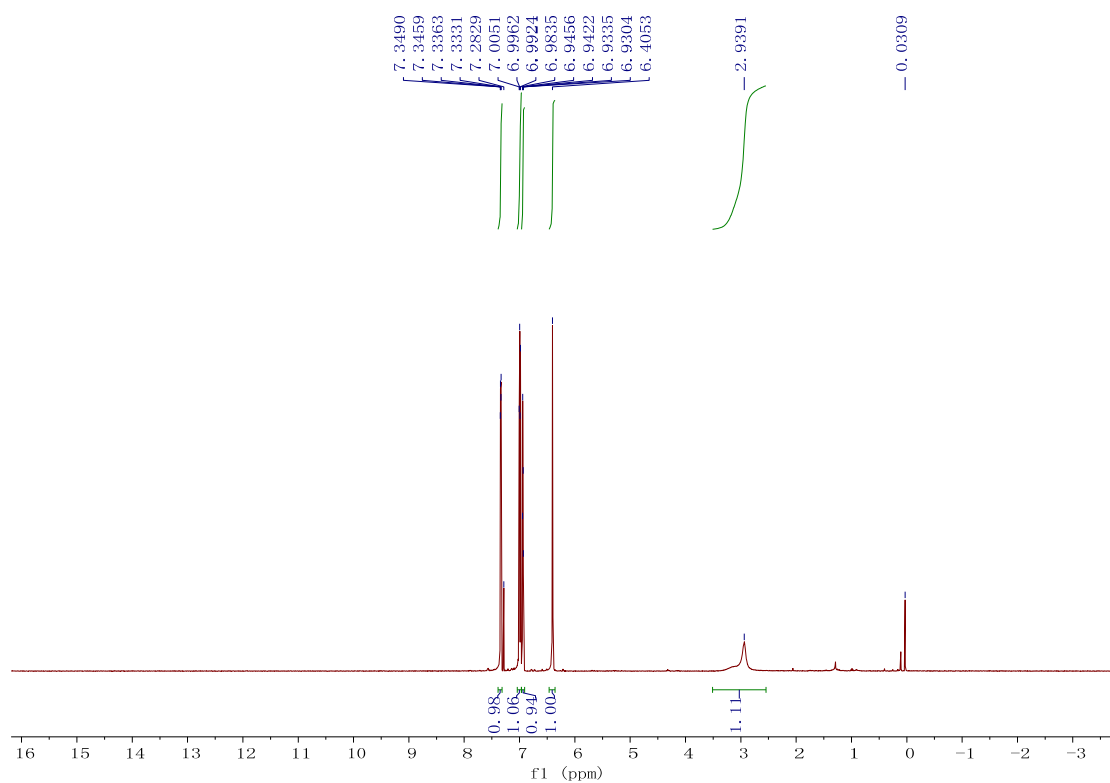
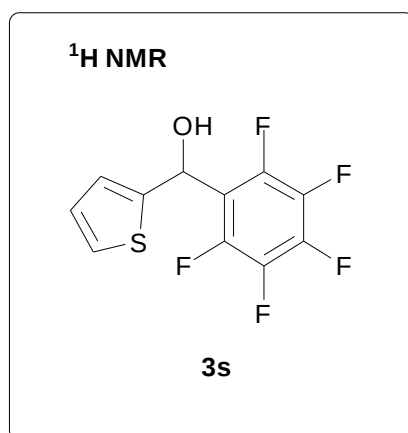


^{19}F NMR

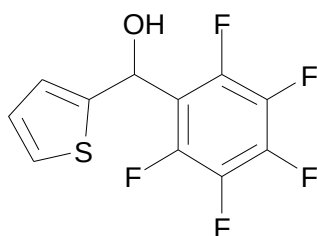


3r

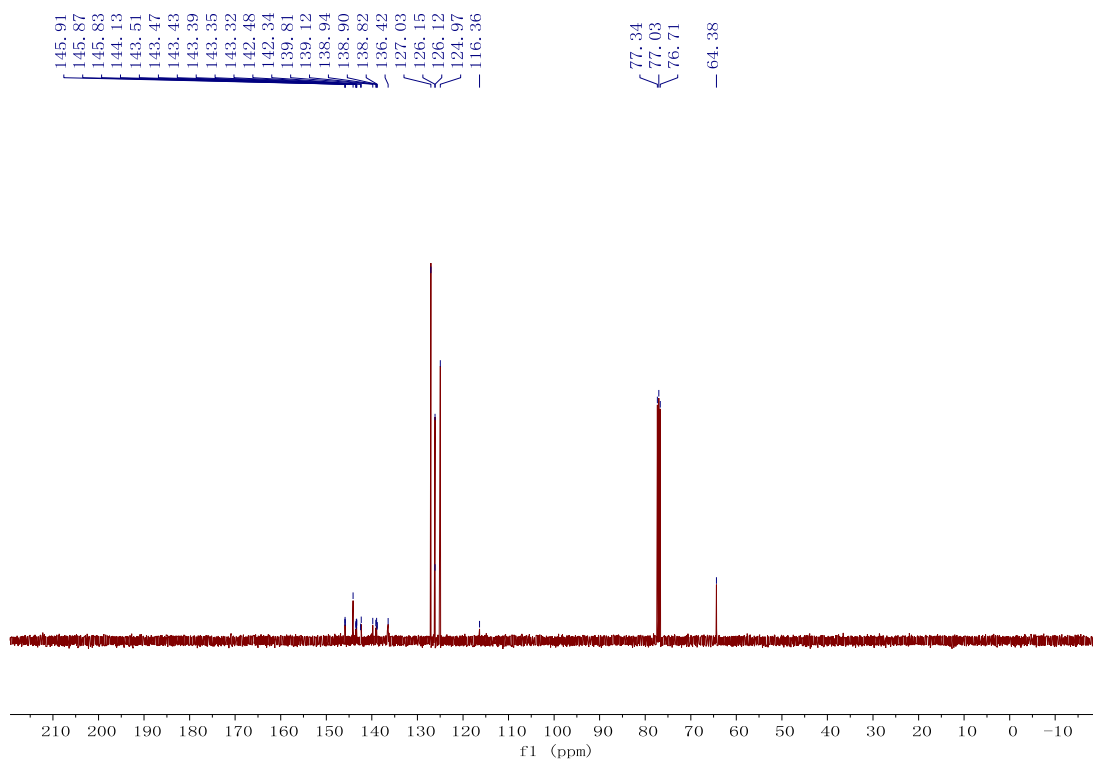




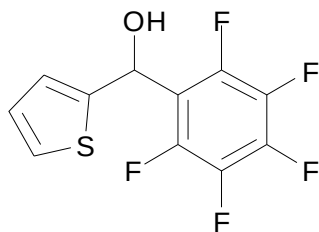
^{13}C NMR



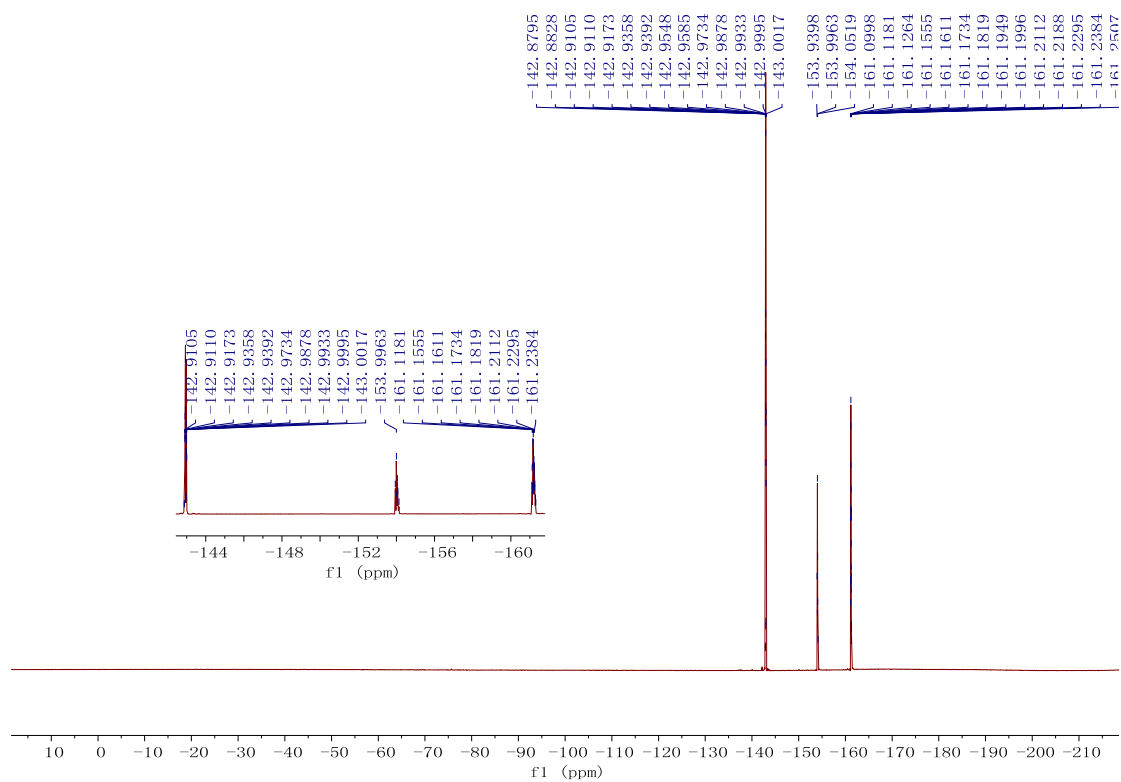
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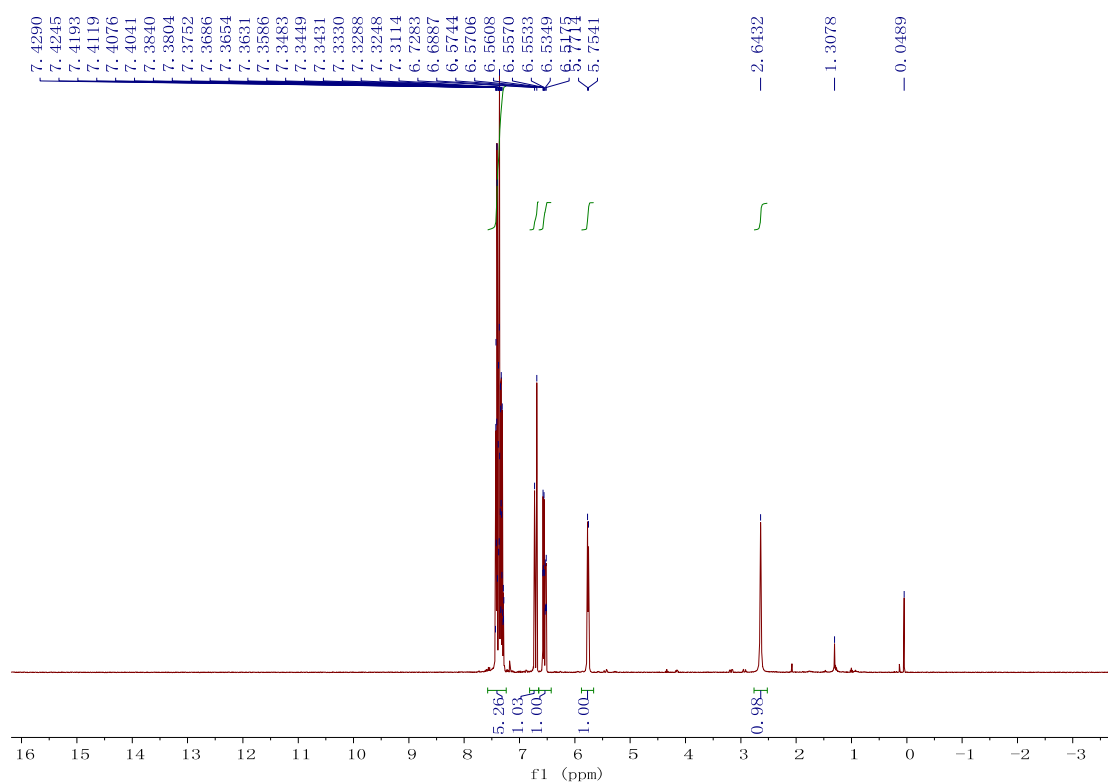
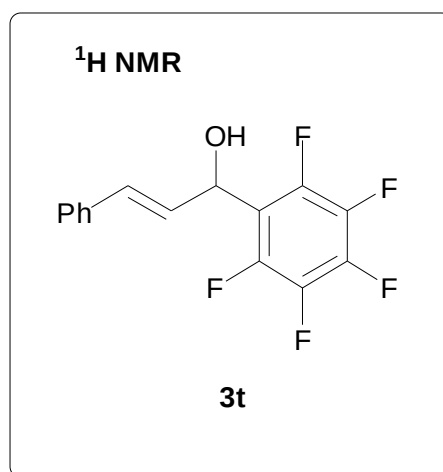


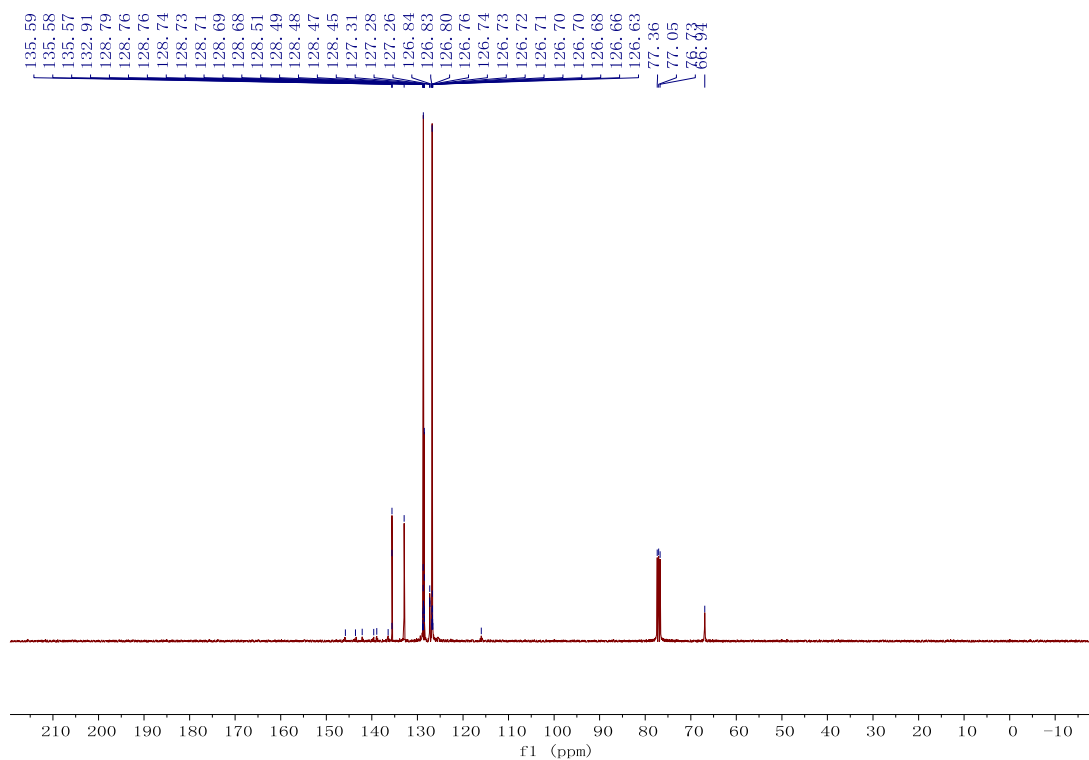
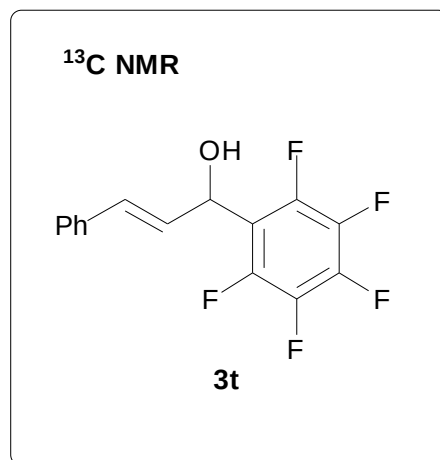
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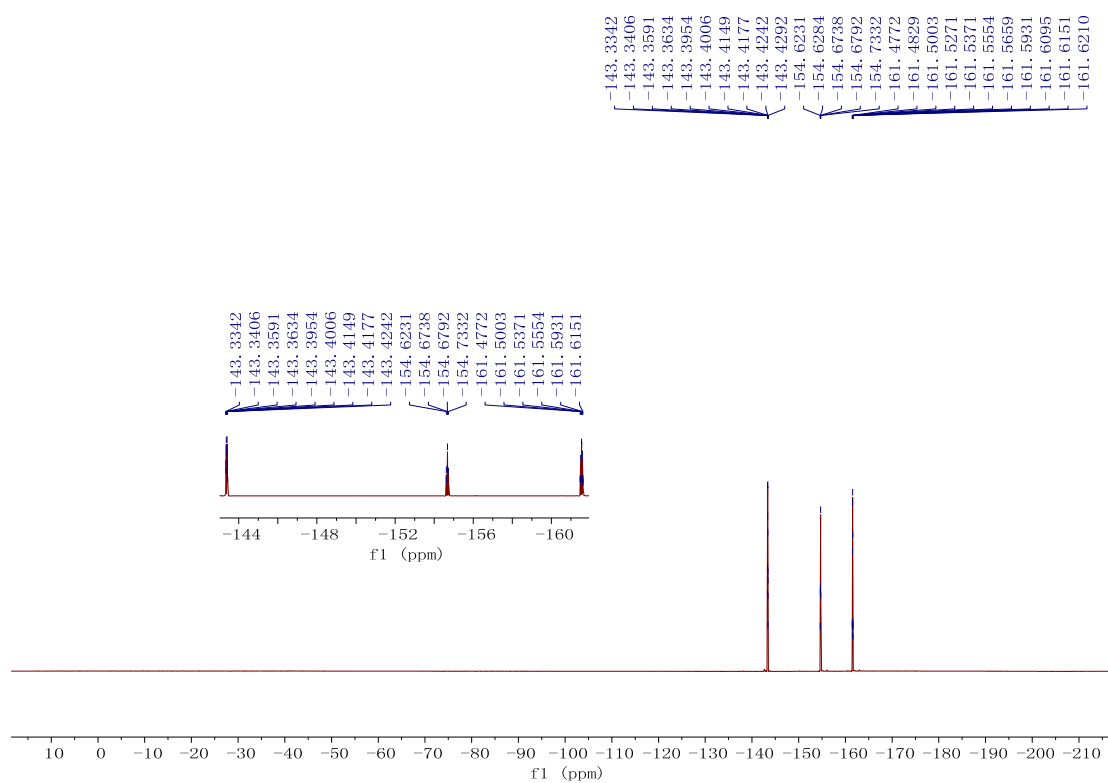
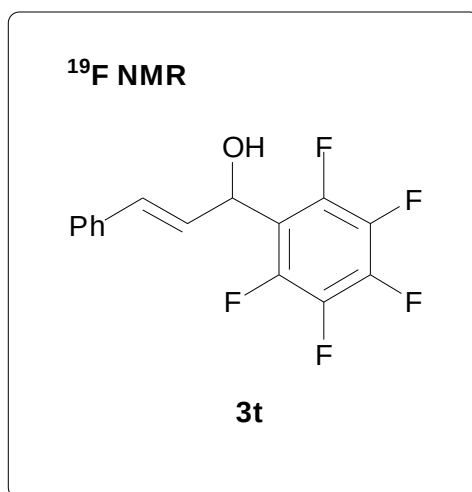


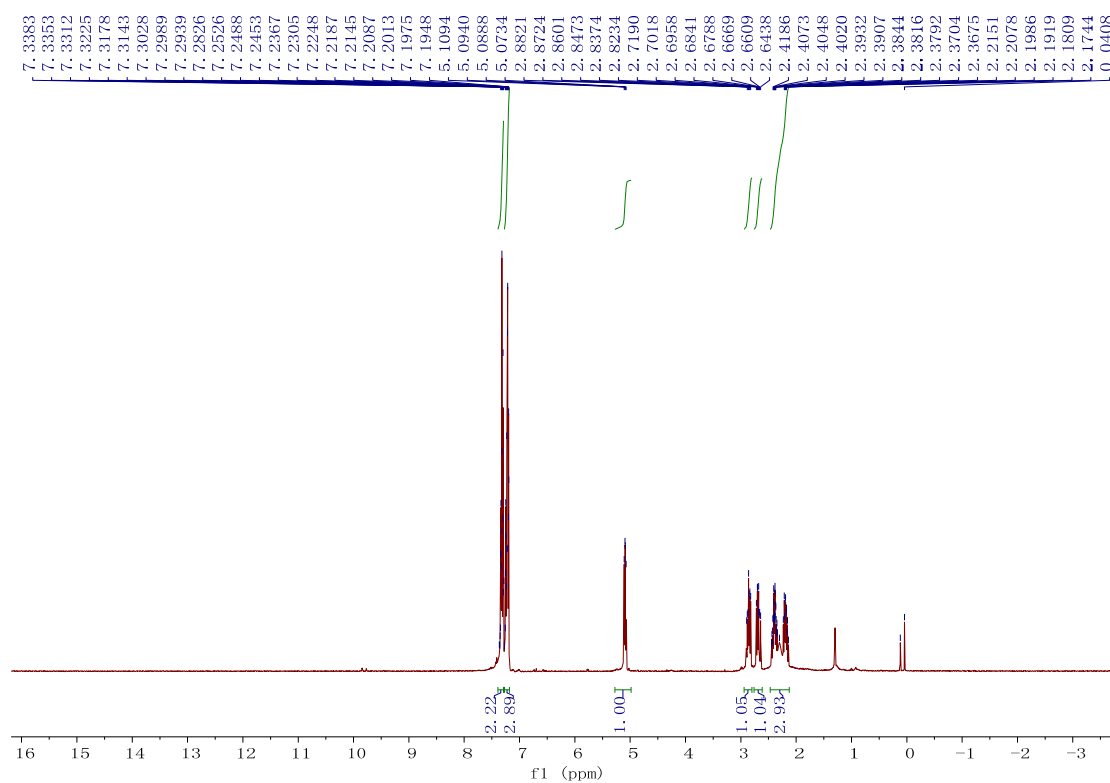
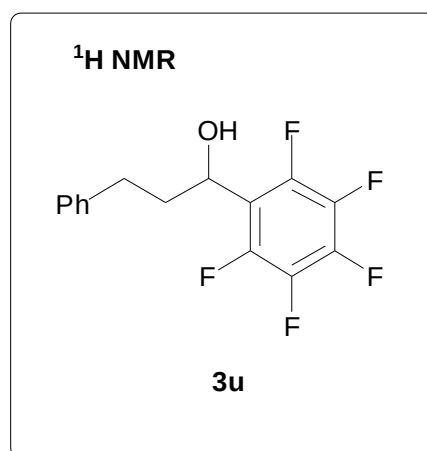
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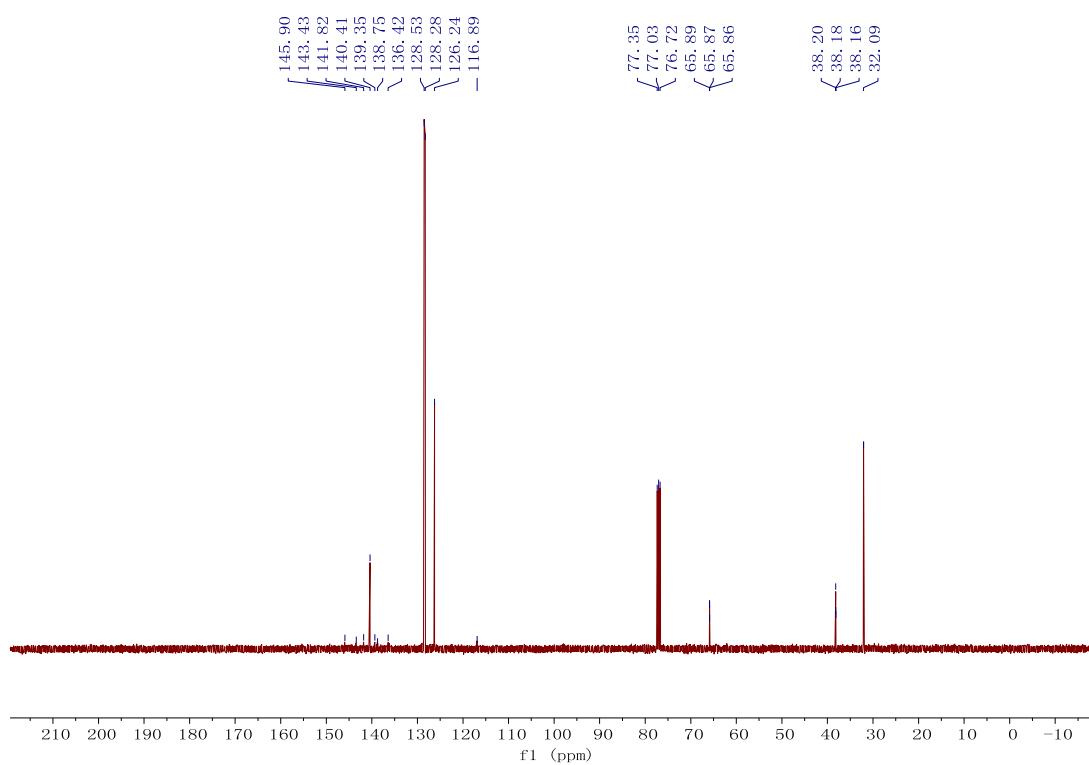
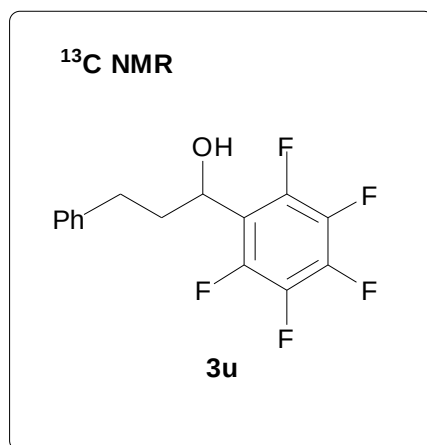




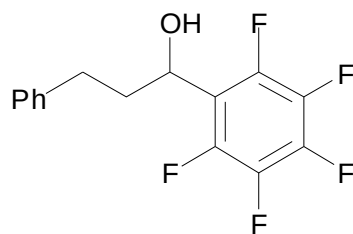




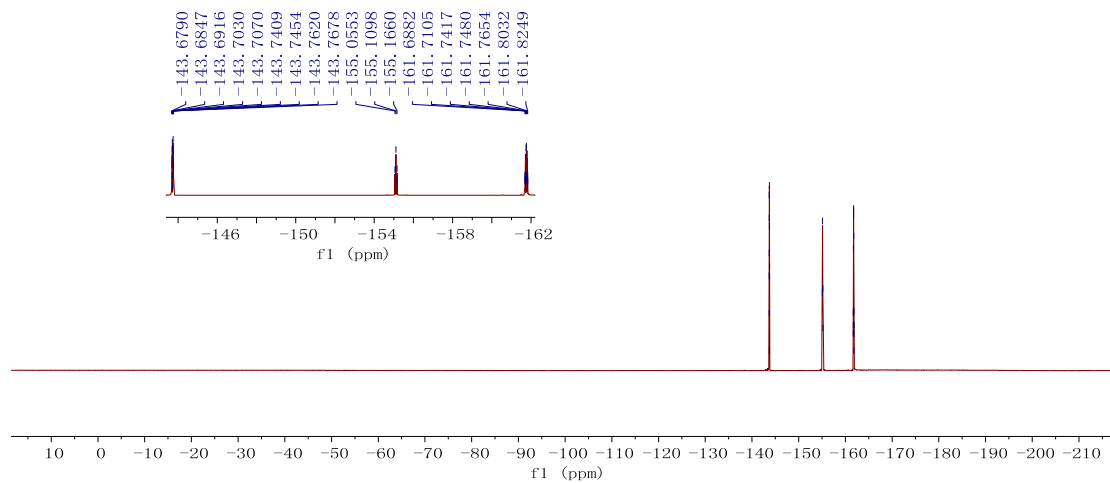
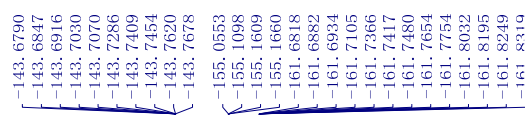


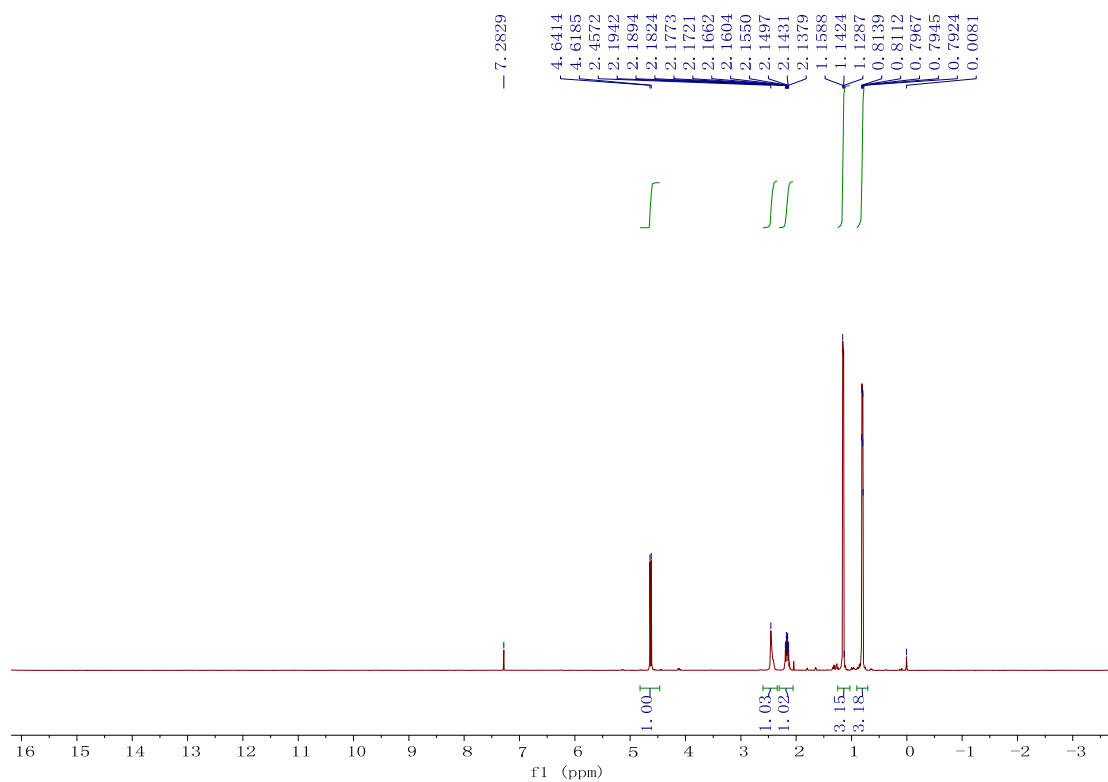
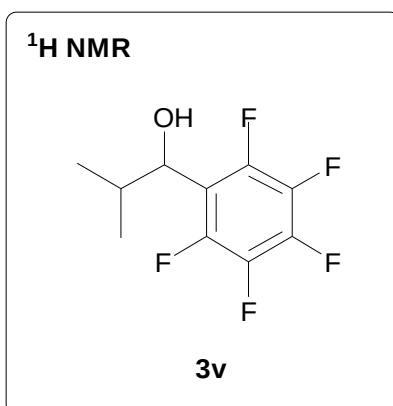


¹⁹F NMR

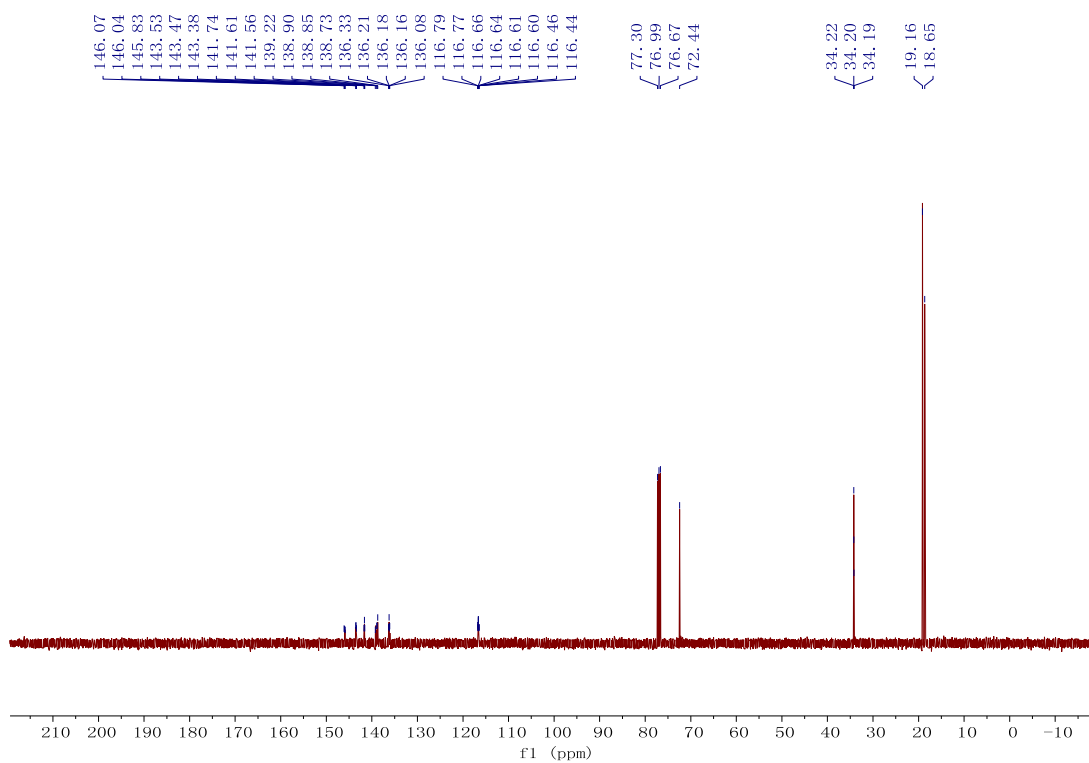
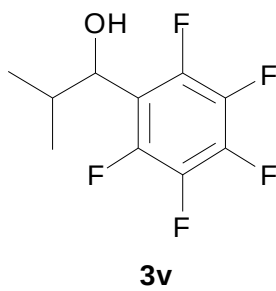


3u

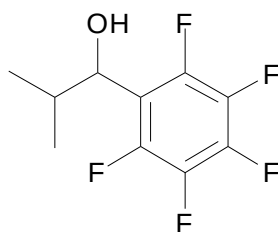




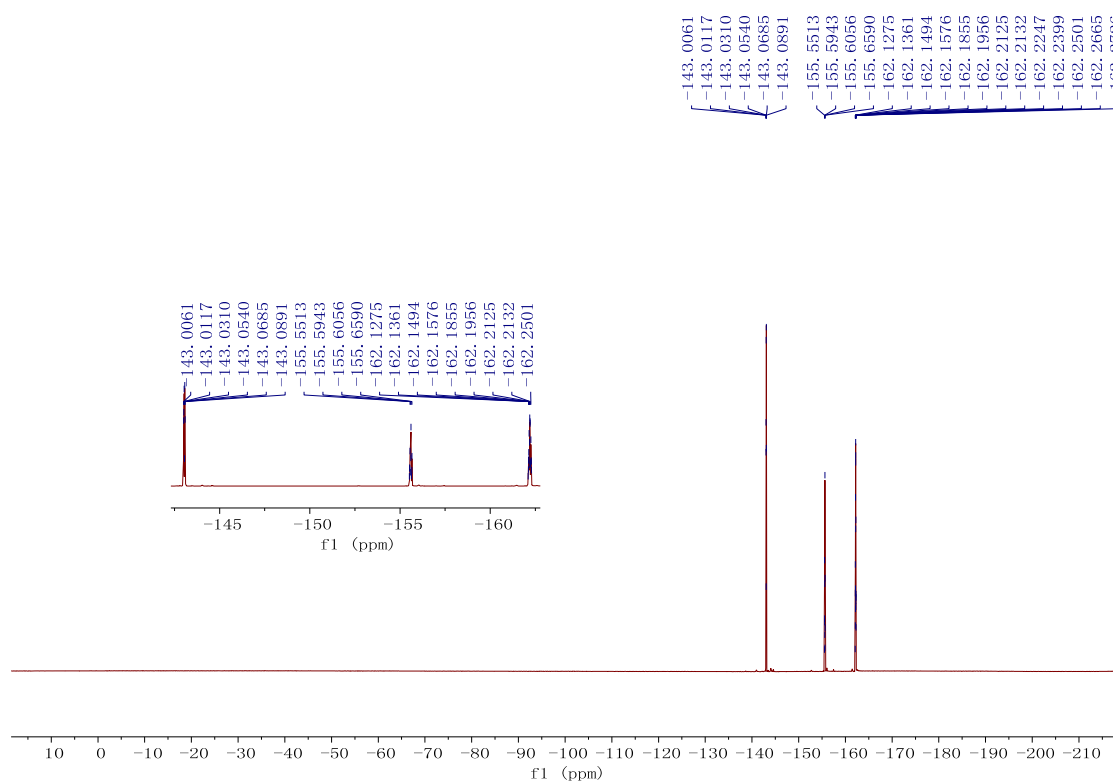
^{13}C NMR



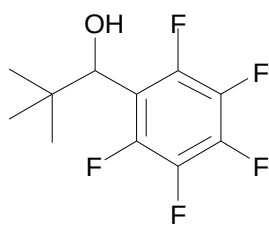
^{19}F NMR



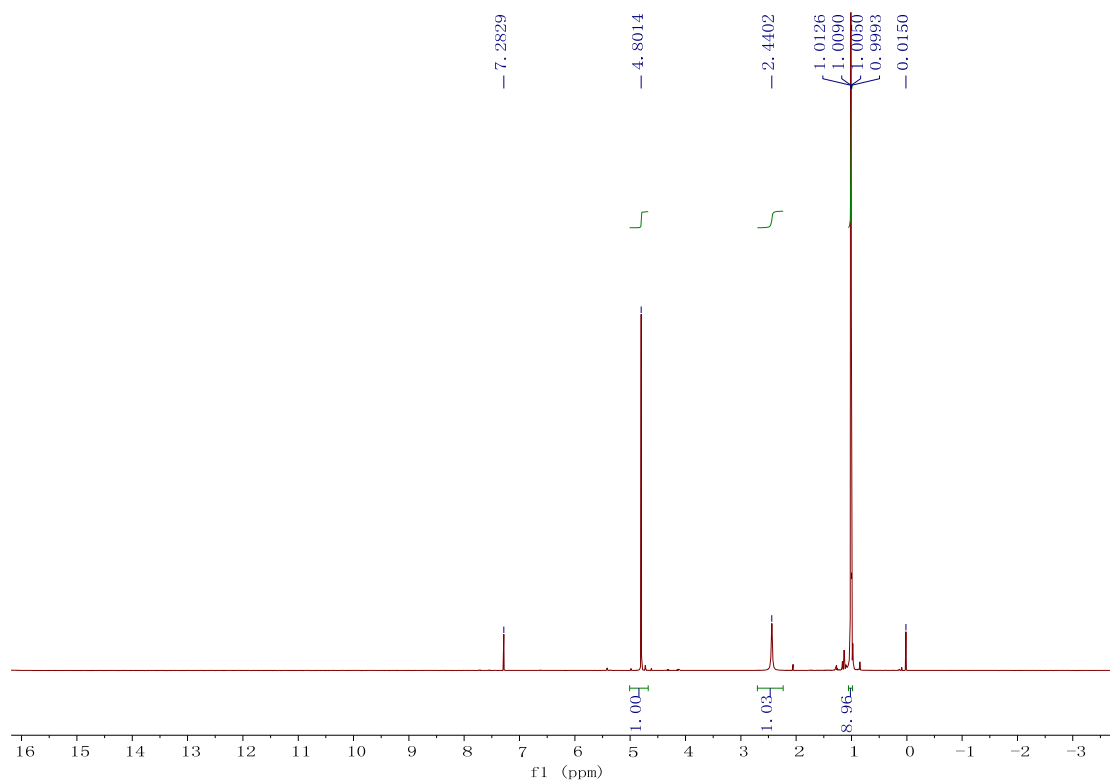
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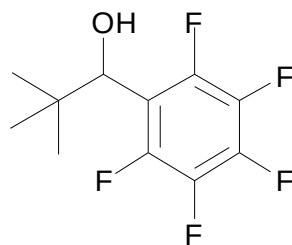
^1H NMR



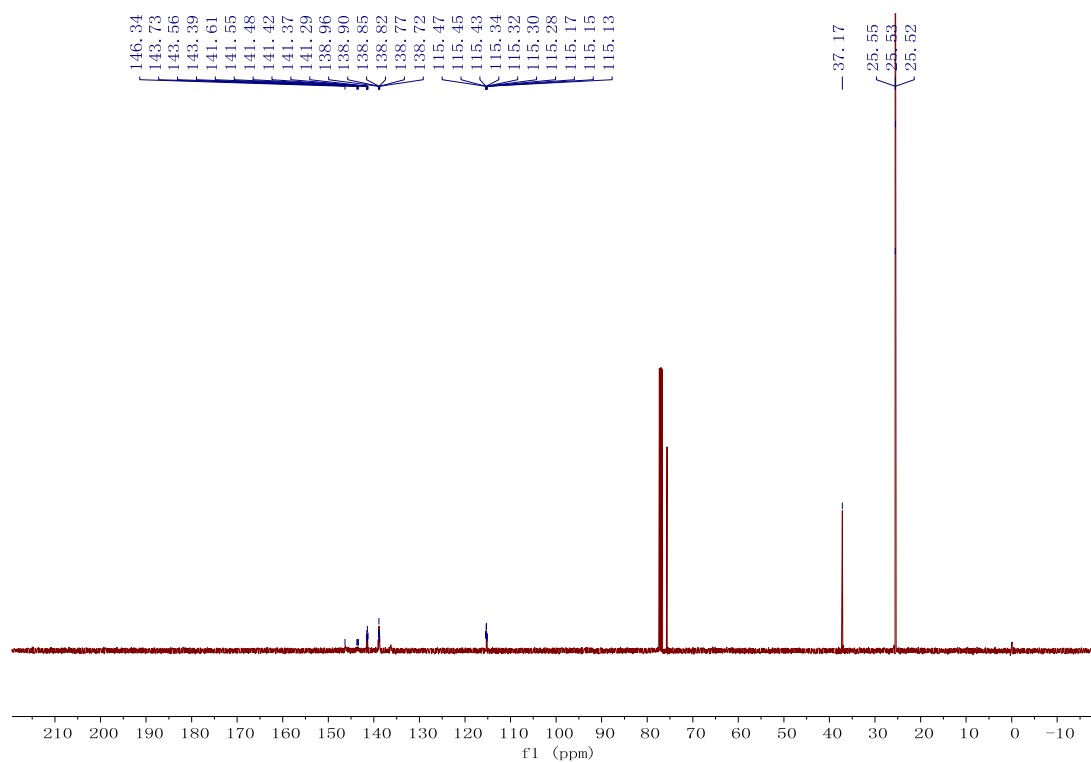
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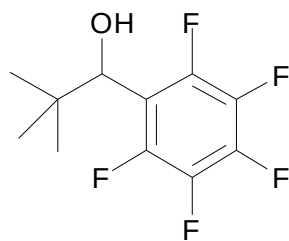
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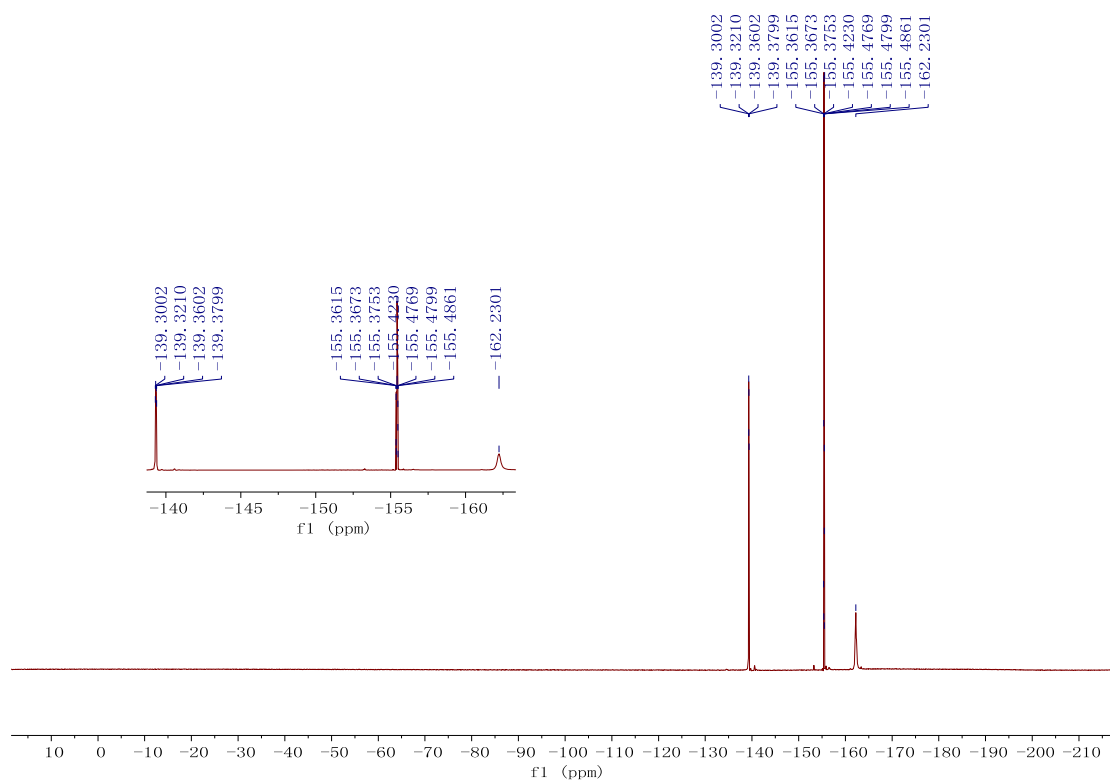
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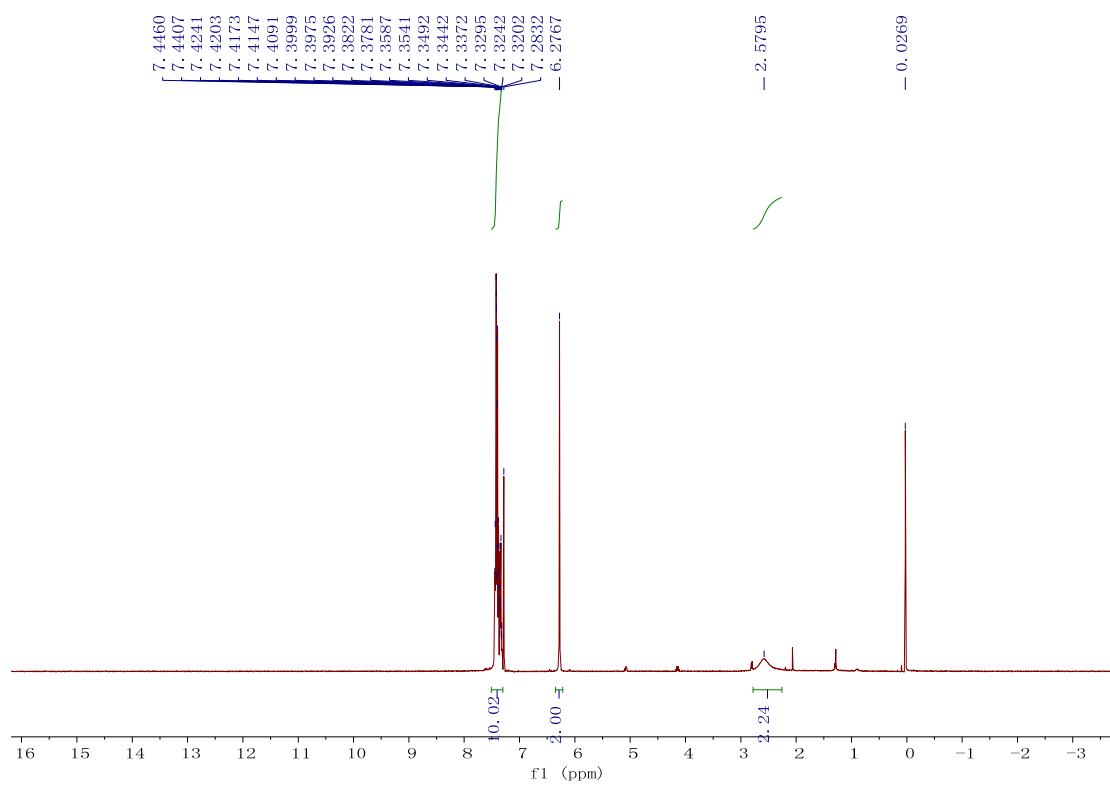
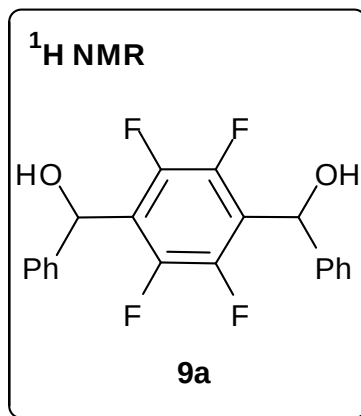


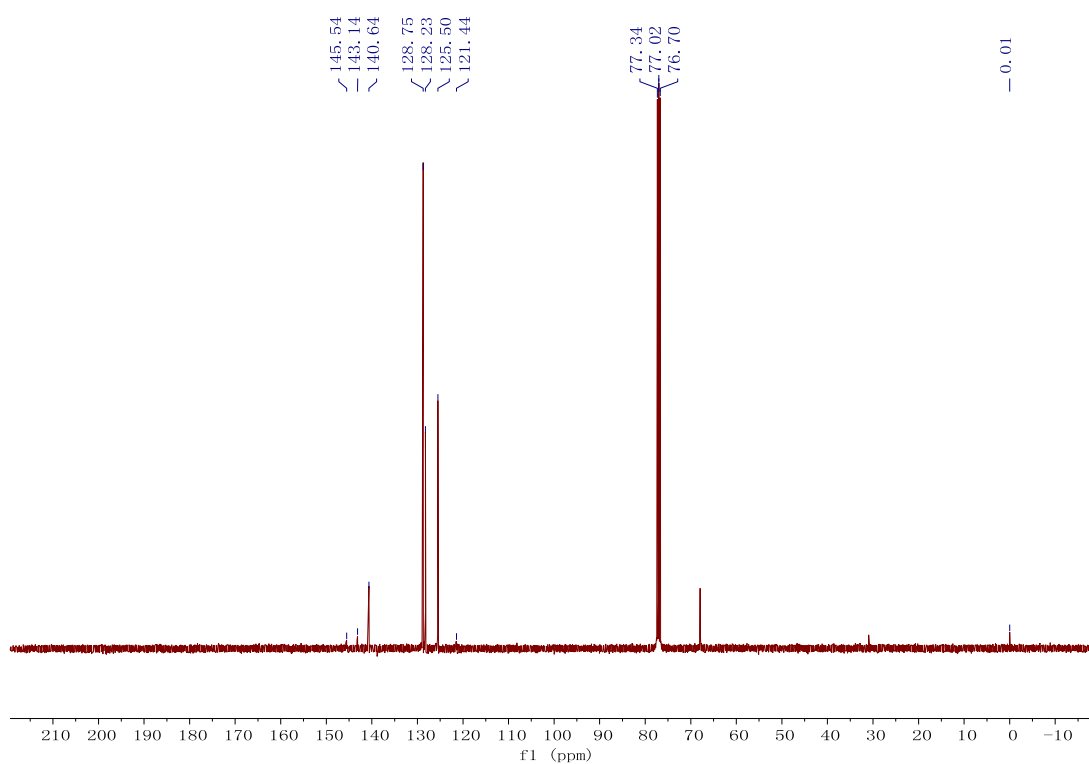
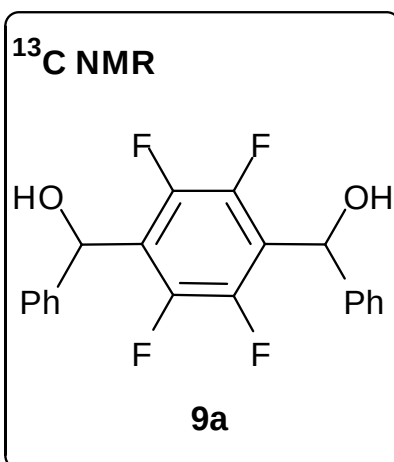
^{19}F NMR

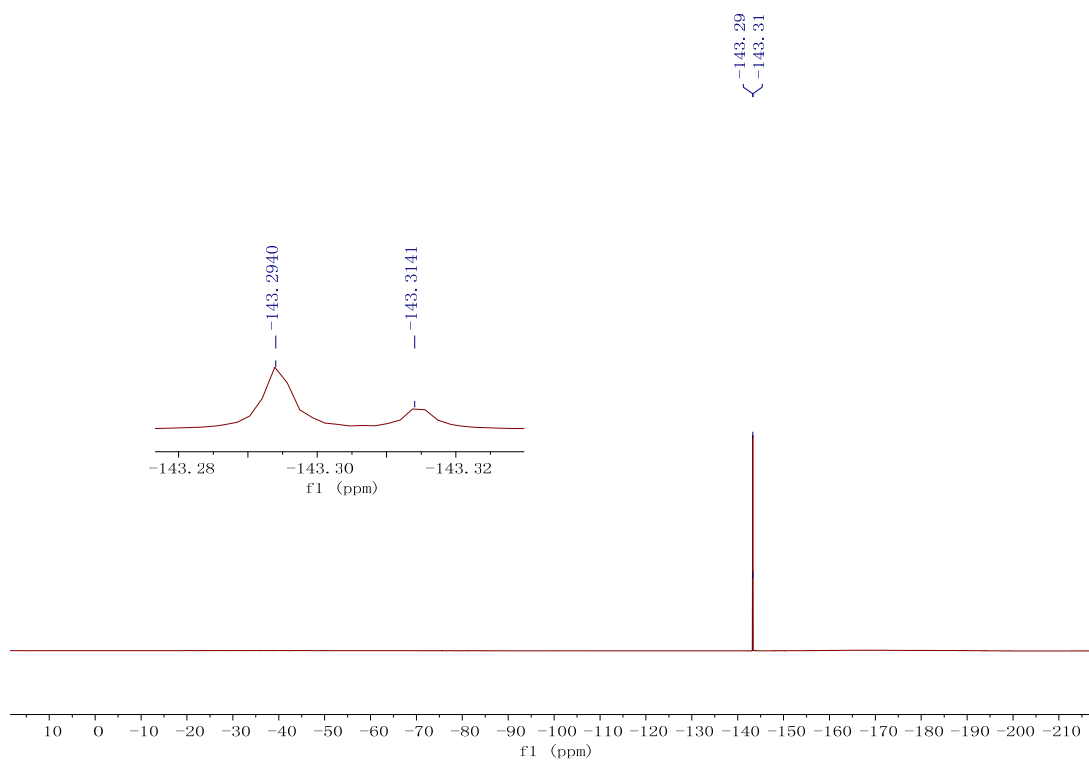
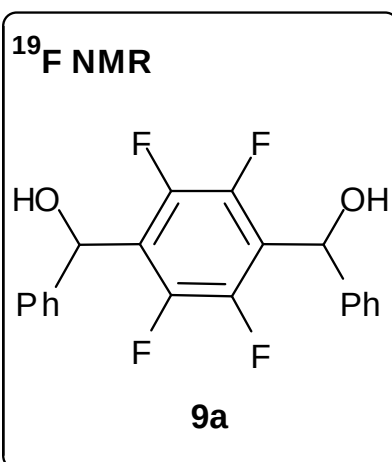


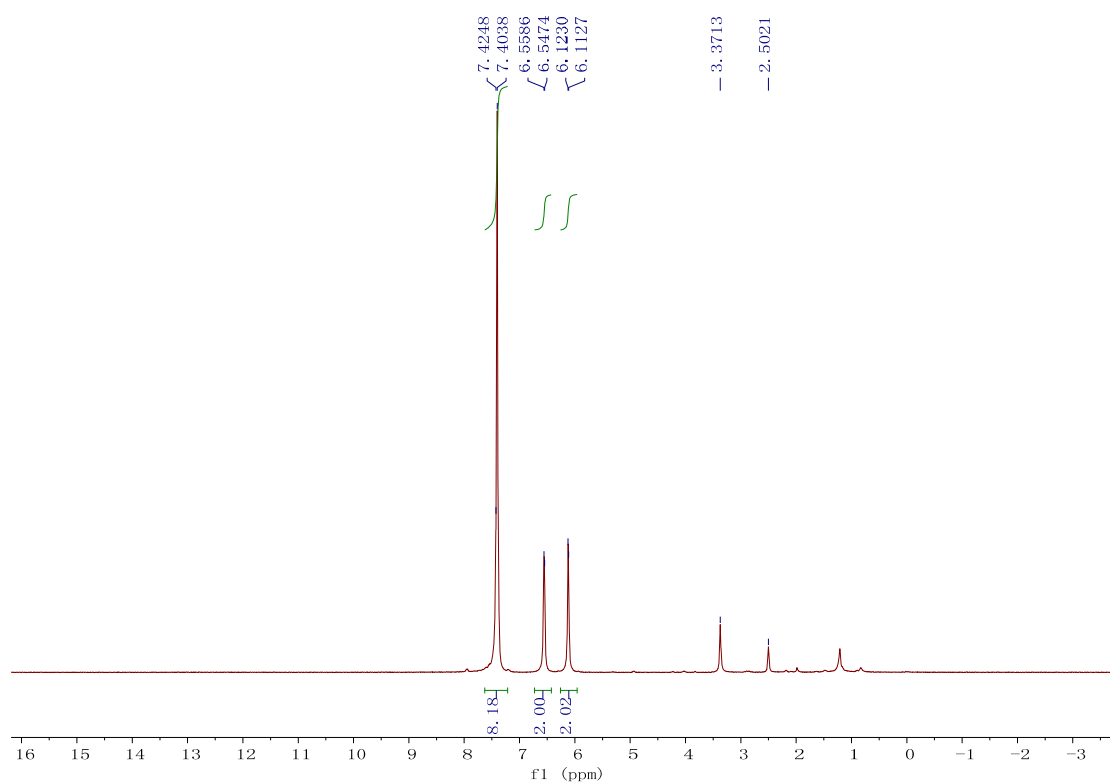
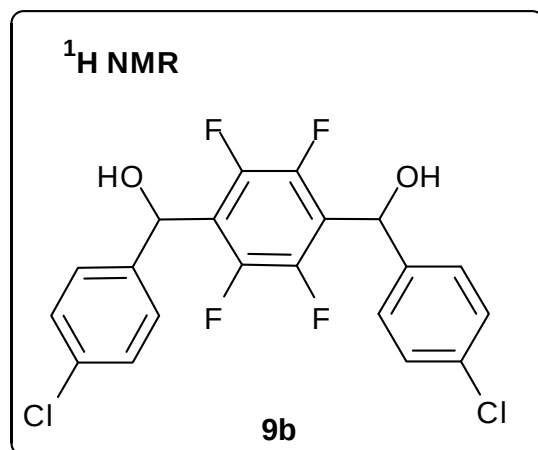
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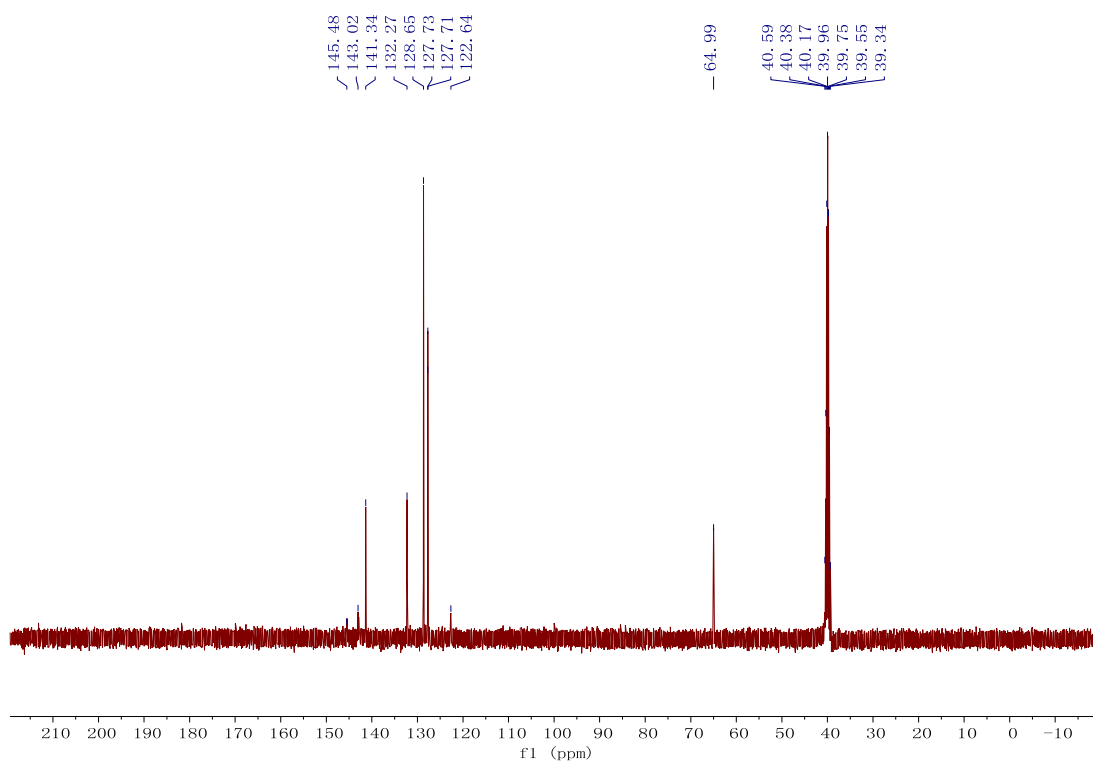
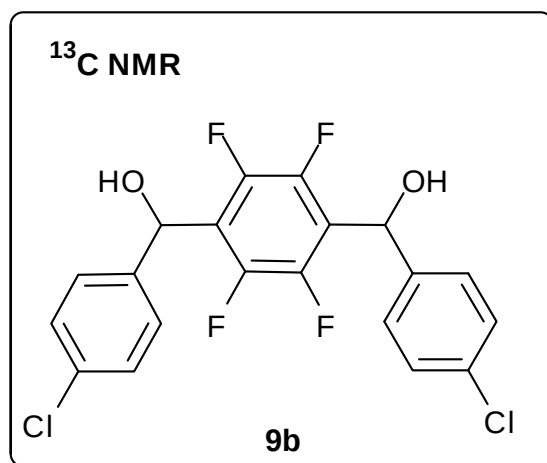


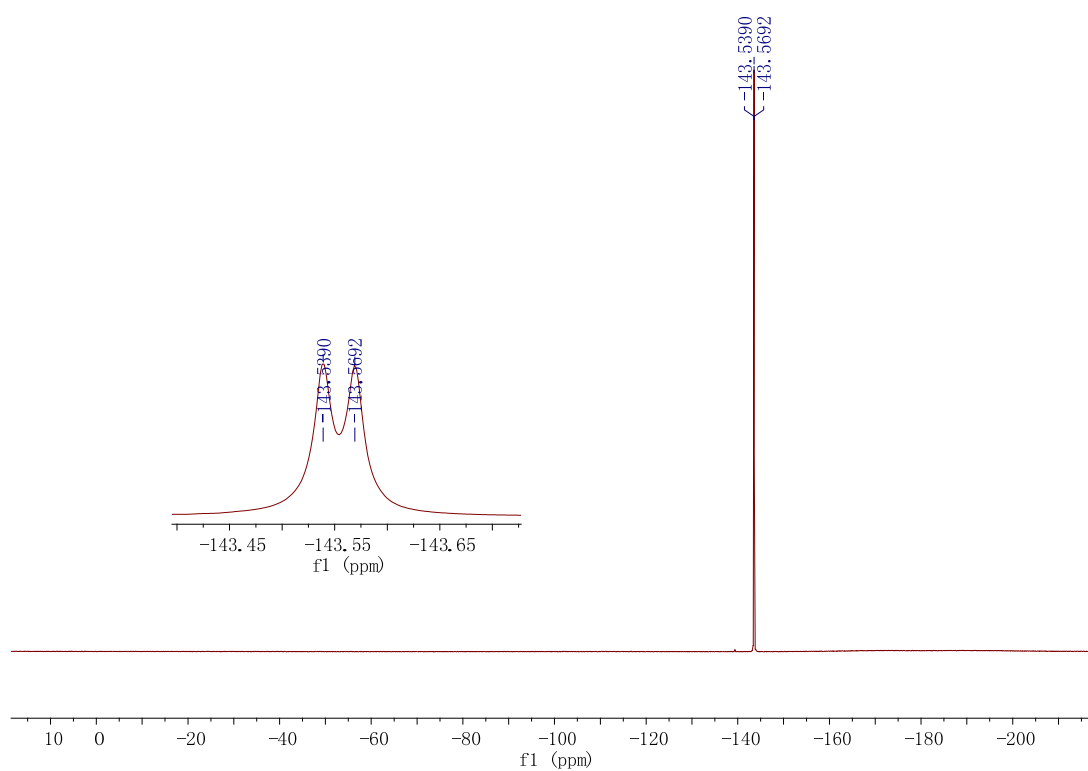
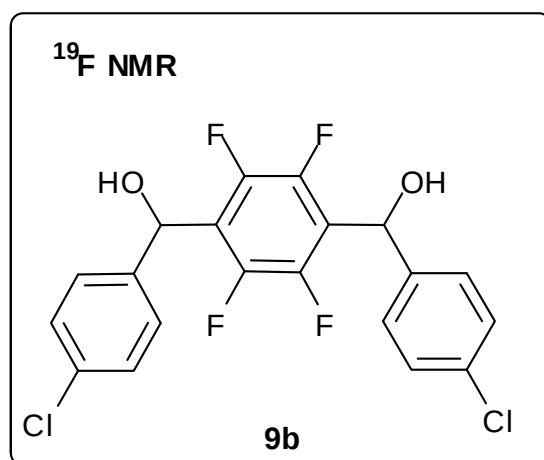


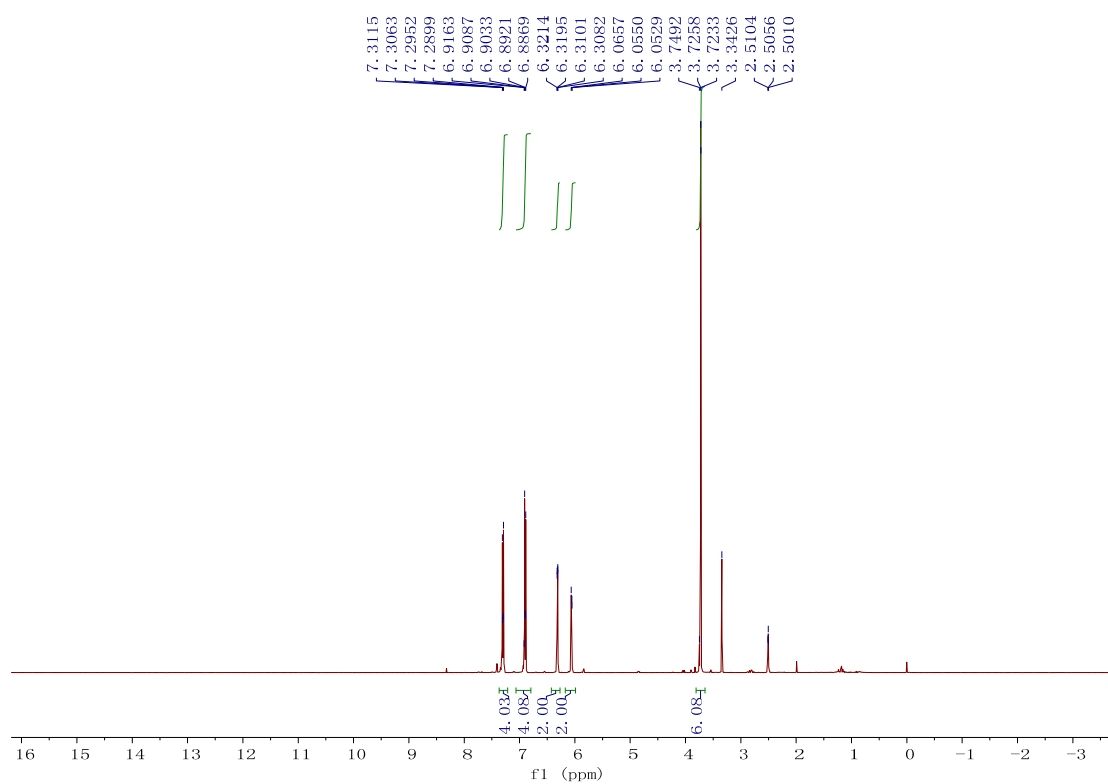
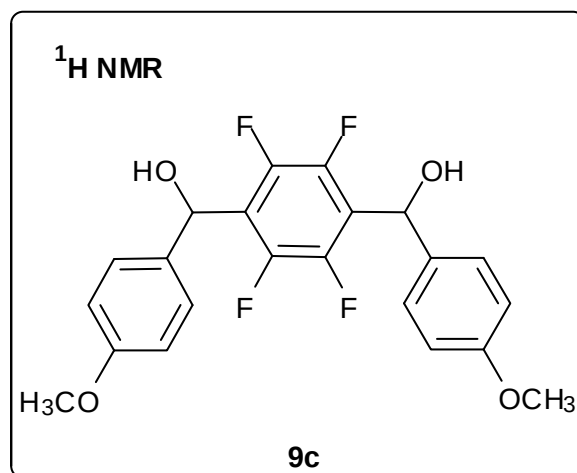


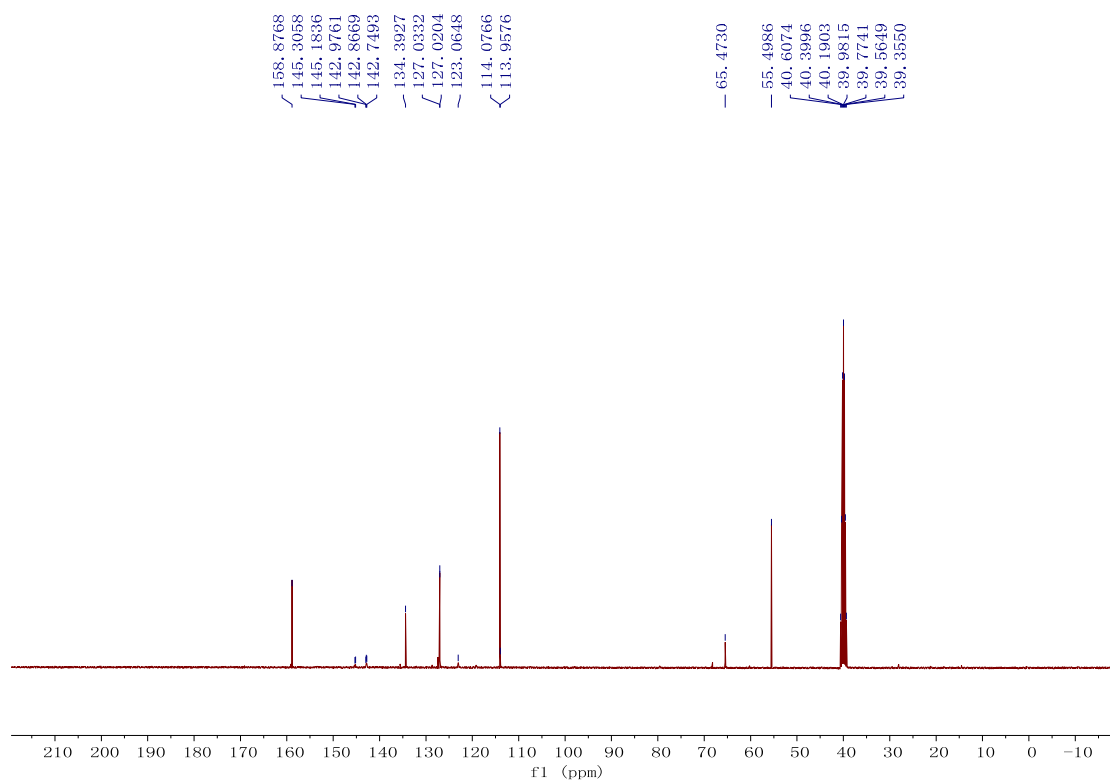
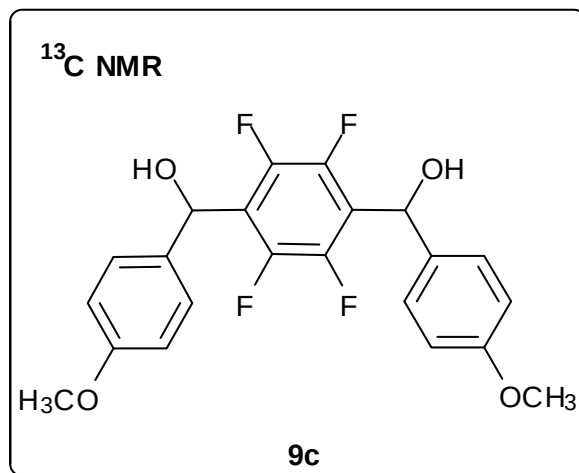


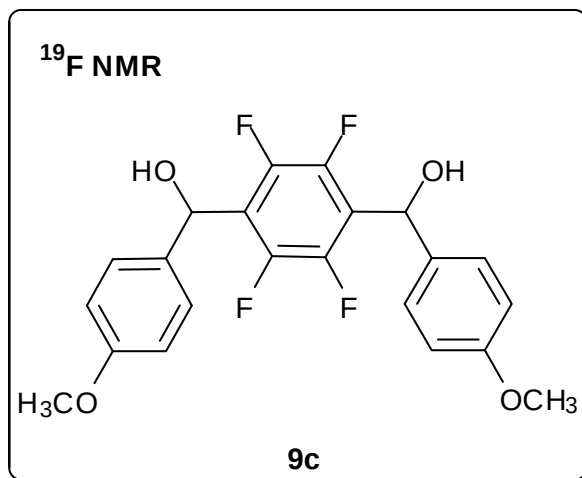




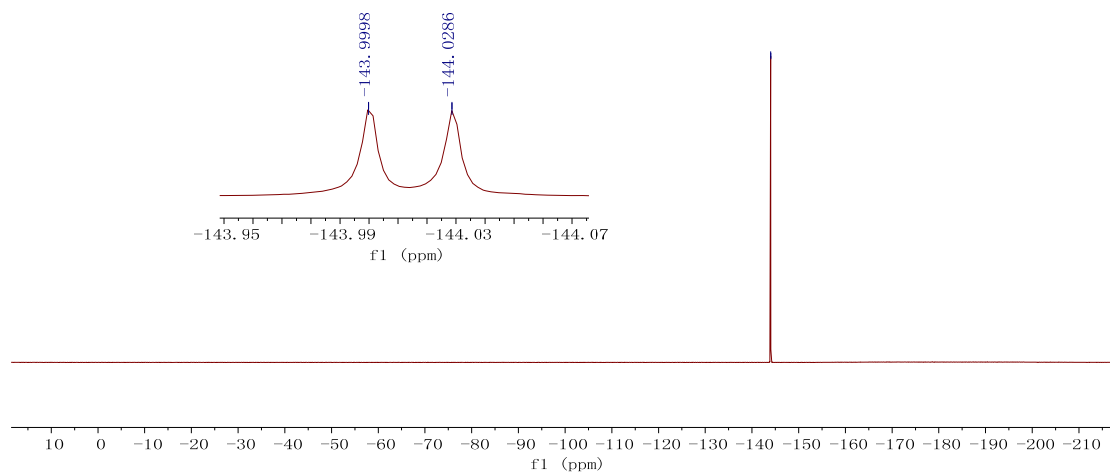


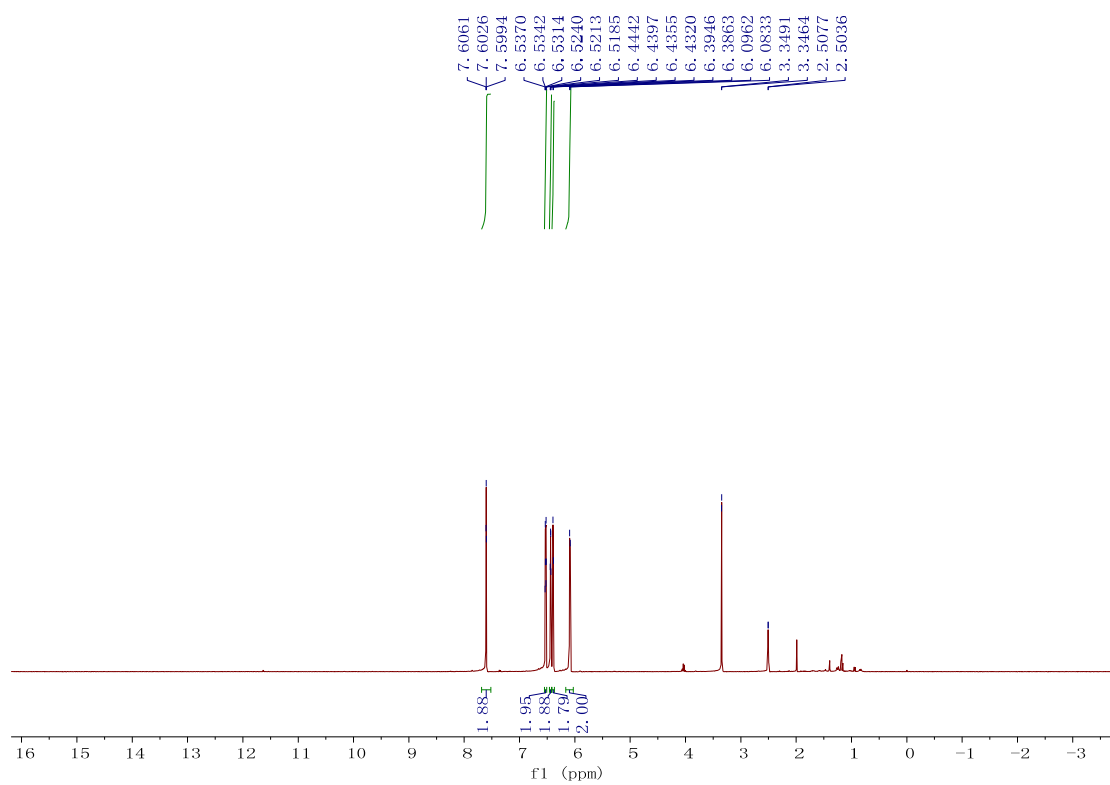
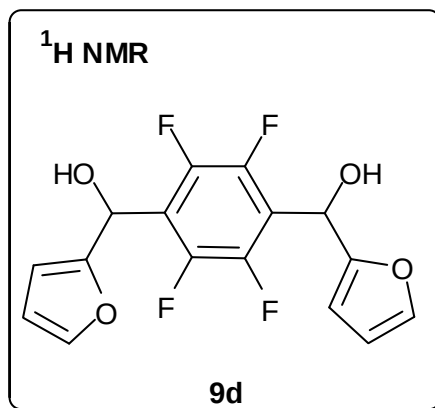


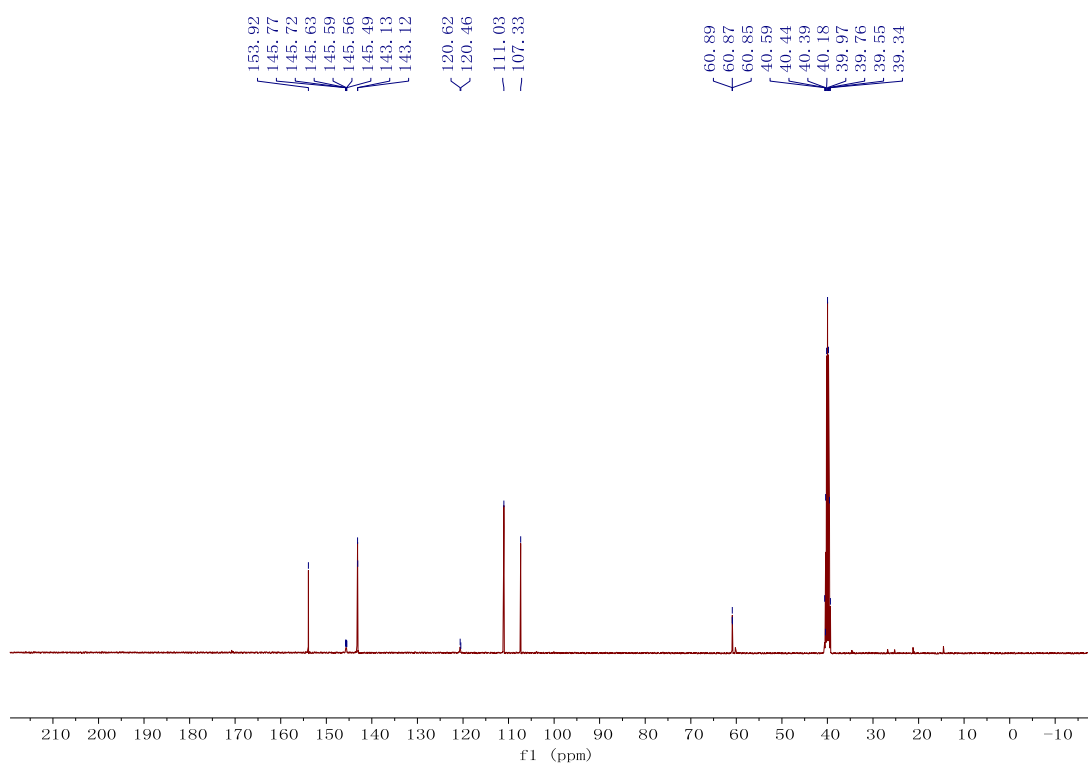
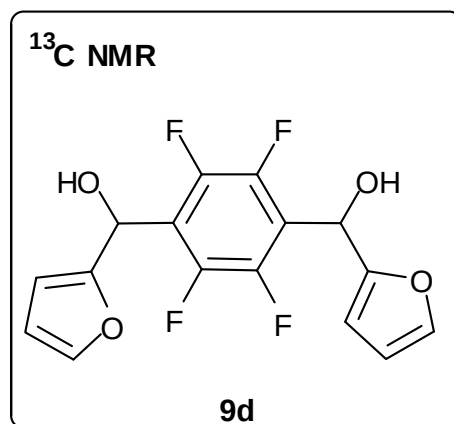


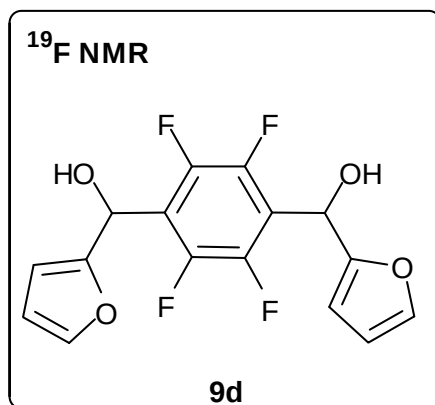


^{143.9998}
^{144.0286}









~ 143.5258
 ~ 143.5413

