Supporting Information

Direct Isoperfluoropropylation of Arenediazonium Salts with Hexafluoropropylene

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General information

Unless noted otherwise, the reactions were performed in oven-dried glassware containing a Teflon-coated stirrer bar and dry septum under a nitrogen atmosphere. Acetonitrile was dried by refluxing over CaH_2 and subsequent distillation.Room temperature (rt) was range from 17 °C to 24 °C. ^{1}H NMR spectra were recorded on a Agilent 400 spectrometer (400 MHz) spectrometer with residual solvent peak as internal reference. ^{19}F NMR spectra were taken on a Agilent 400 spectrometer (376 MHz). ^{13}C NMR spectra were taken a Bruker AM-400 spectrometer (101MHz) or Agilent 400 spectrometer (101MHz) with residual solvent peak as internal reference. $CDCl_3$ was referenced to 7.26 ppm in ^{1}H NMR and 77.00 ppm in ^{13}C spectra. DMSO-d_6 was referenced to 3.33 and 2.50 ppm in ^{1}H NMR and 39.52 ppm in ^{13}C spectra. ^{19}F NMR chemical shifts were determined relative to $CFCl_3$ as inter standard. Chemical shifts (δ) are reported in ppm, and coupling constants (*J*) are in Hertz (Hz). The following abbreviations were used to designate chemical shift multiplicities: s = singlet, d = doublet, t = triplet, q = quartet, h = heptet, m = multiplet, br = broad. Column chromatography over silica gel (mesh 300-400) and hexane/ethyl acetate or pentane/ dichloromethane were used as the eluent.

Aniline and cuprous iodide were freshly purified according to the purification handbook *Purification of Laboratory Chemicals* before using. Unless otherwise noted, all other reagents were purchased from commercial suppliers and used as received.

Synthesis of 4-(ethoxycarbonyl)benzenediazonium tetrafluoroborate[1]

In a 50 mL round-bottom flask, the ethyl 4-aminobenzoate (5 mmol) was dissolved in a mixture of absolute ethanol (2 mL) and an aqueous solution of HBF_4 (40%, 1.6 mL, 10 mmol) and tert-butyl nitrite (1.2 mL, 10 mmol) was added dropwise to the solution at 0 °C. The reaction was stirred at room temperature for 1 h and diethyl ether (10 mL) was added to precipitate the 4-(ethoxycarbonyl)benzenediazonium tetrafluoroborate that was filtered off and washed with diethyl ether (3 × 10 mL). The 4-(ethoxycarbonyl)benzenediazonium tetrafluoroborate was dried in vacuo and was then directly used without further purification.

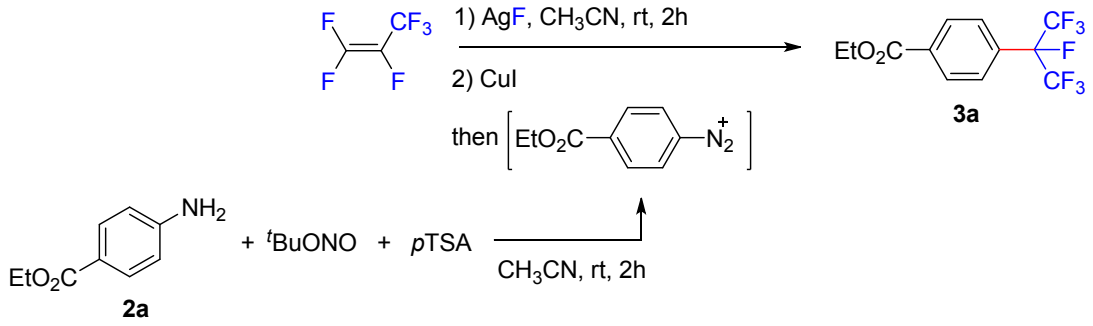
General procedure for the synthesis of isoperfluoropropylarenes from the 4-(ethoxycarbonyl)benzenediazonium tetrafluoroborate.

In a nitrogen-filled glove box, an oven-dried 20 mL crimp cap vessel with Teflon-coated stirrer bar was charged with silver fluoride (25.4 mg, 0.20 mmol) and was brought under an atmosphere of dry nitrogen. To this vessel were added 1.5 mL of anhydrous acetonitrile and hexafluoropropylene (balloon, excess) and the mixture was stirred at room temperature and

ordinary pressure in the dark until silver fluoride precipitate is disappeared. This process takes about two hours and the the isoperfluoropropyl silver is generate.[2] Then this solution was added to another oven-dried 20 mL crimp cap vessel with corresponding copper/cuprous salt/ copper salt (0.16 mmol) and additive in it. 4-(ethoxycarbonyl)benzenediazonium tetrafluoroborate (0.1 mmol)was dissolved in 1 mL acetonitrile and was added via syringe under nitrogen subsequently. The reaction mixture was stirred at ambient temperature for overnight. The resulting crud product was quantified by $PhCF_3$ as an internal standard.

General procedure for the synthesis of isoperfluoropropylarenes from the aromatic amines (one-pot protocol)

Table S1. Details of screening equivalents, temperature and reaction time.



Entry	equivivalent				Temperature(℃)	Time	Yield [%] [a]
	^{t}BuONO	*p*TSA	CuI	AgF			
1	1.00	1.5	1.6	2.0	rt	overnight	57
2	1.20	1.5	1.6	2.0	rt	overnight	75
3	1.35	1.5	1.6	2.0	rt	overnight	66
4	1.20	1.1	1.6	2.0	rt	overnight	53
5	1.20	2.0	1.6	2.0	rt	overnight	57
6	1.20	1.5	1.2	2.0	rt	overnight	32
7	1.20	1.5	1.8	2.0	rt	overnight	70
8	1.20	1.5	1.6	1.6	rt	overnight	73
9	1.20	1.5	1.6	2.4	rt	overnight	59
10	1.20	1.5	1.6	2.0	0 ℃	overnight	42

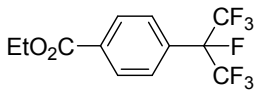
11	1.20	1.5	1.6	2.0	40 ℃	overnight	58
12	1.20	1.5	1.6	2.0	rt	20 min	70
13	1.20	1.5	1.6	2.0	rt	200 min	72

Reaction conditions: HFP (excessive), **2a** (0.1 mmol), CH_3CN (1.5 mL+1.5 mL), under N_2 atmosphere. a: Yield determined by ^{19}F NMR analysis versus $PhCF_3$ as an internal standard.

In a nitrogen-filled glove box, an oven-dried 20 mL crimp cap vessel (**1**) with Teflon-coated stirrer bar was charged with silver fluoride (76.2 mg, 0.60 mmol) and was brought under an atmosphere of dry nitrogen. To this vessel, 3 mL of anhydrous acetonitrile and hexafluoropropylene (balloon, excess) were added, and the mixture was stirred at room temperature under ordinary pressure in the dark until silver fluoride precipitate is disappeared. This process takes about two hours and the isoperfluoropropyl silver is generated. In the process of this reaction, in a nitrogen-filled glove box, an oven-dried 20 mL crimp cap vessel (**2**) with Teflon-coated stirrer bar was charged with p-toluenesulfonic acid (77.4 mg, 0.45 mmol) and was brought under an atmosphere of dry nitrogen. To this vessel, **2a** (49.5mg, 0.3 mmol), 3 mL of anhydrous acetonitrile and tert-butyl nitrite (37.1 mg, 0.36 mmol) were added. The reaction mixture was stirred at ambient temperature for 2 h to generate the corresponding diazonium salt. After these procedures, the reaction mixtures in crimp cap vessels (**1**) and (**2**) was added in sequence *via* syringe into an third oven-dried 20 mL crimp cap vessel with Teflon-coated stirrer bar charging with cuprous iodide (91.4 mg, 0.48 mmol) under nitrogen. The new reaction mixture was stirred at ambient temperature for overnight. The resulting mixture was diluted with Et_2O (10 mL), then filtered through a short pad of celite and rinsed with diethyl ether. The resulting organic solution was add into water (10 mL) and extracted by ethyl Et_2O (3×10 mL). The organic layer was dried over $MgSO_4$, filtered and concentrated. The residue was further purified by flash chromatography on silica gel to give the desired product.

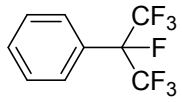
Spectral data of the products

3a, ethyl 4-(perfluoropropan-2-yl)benzoate



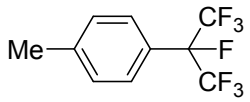
Yellow liquid; ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.17 (d, *J* = 8.3 Hz, 2H), 7.70 (d, *J* = 8.4 Hz, 2H), 4.41 (q, *J* = 7.1 Hz, 2H), 1.41 (t, *J* = 7.1 Hz, 3H); ^{19}F NMR (376 MHz, $CDCl_3$) δ -75.56 (d, *J* = 7.2 Hz, 6F), -182.59 (hept, *J* = 7.2 Hz, 1F); ^{13}C NMR (100 MHz, $CDCl_3$) δ 165.53, 133.28, 131.07 (d, *J* = 20.5 Hz), 130.10 (d, *J* = 2.2 Hz), 125.97 (d, *J* = 10.6 Hz), 120.78 (qd, *J* =285.3, 27.6 H), 93.191 – 89.85 (m), 61.67, 14.41; IR (film, cm^{-1}): ν 2986, 1729, 1615，1307, 1213, 985, 953, 723; MS (EI) m/z (relative intensity) 318 (15) [M^+], 273 (100); HRMS (EI) calcd. For $C_{12}H_9O_2F_7$: 318.0491, Found: 318.0488.

3b, (perfluoropropan-2-yl)benzene



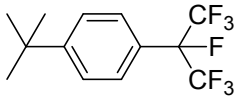
MS (EI) m/z (relative intensity) 246 [M^+], 127 (100);

3c, 1-methyl-4-(perfluoropropan-2-yl)benzene



MS (EI) m/z (relative intensity) 260 [M^+];

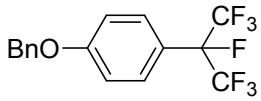
3d, 1-(tert-butyl)-4-(perfluoropropan-2-yl)benzene



Colorless liquid; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.57 – 7.47 (m, 4H), 1.35 (s, 9H); ^{19}F NMR (376 MHz, $CDCl_3$) δ -75.83 (d, *J* = 7.3 Hz, 6F), -182.68 (hept, *J* = 7.3 Hz, 1F); ^{13}C NMR (100 MHz, $CDCl_3$) δ 154.44, 125.98, 125.57 (d, *J* = 10.3 Hz), 123.91 (d, *J* = 20.6 Hz), 120.88 (qd, *J* = 286.8, 28.5 Hz), 93.40 – 90.09 (m), 34.95, 31.25; IR (film, cm^{-1}): ν 2968, 1611, 1308, 1218, 1100, 982, 832, 711; MS (EI) m/z (relative intensity) 302 [M^+], 287 (100); HRMS (EI) calcd. For $C_{13}H_{13}F_7$:

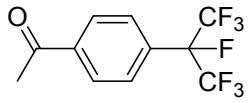
302.0905, Found: 302.0907.

3e, 1-(benzyloxy)-4-(perfluoropropan-2-yl)benzene



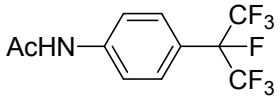
White solid, mp: 78-80 ^{o}C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.55 (d, *J* = 8.6 Hz, 2H), 7.50 – 7.32 (m, 4H), 7.09 (d, *J* = 8.9 Hz, 2H), 5.12 (s, 1H); ^{19}F NMR (376 MHz, $CDCl_3$) δ -75.96 (d, *J* = 7.3 Hz, 6F), -181.75 (hept, *J* = 7.3 Hz, 1F); ^{13}C NMR (100 MHz, $CDCl_3$) δ 160.84, 136.38, 128.87, 128.42, 127.67, 127.41 (d, *J* = 10.6 Hz), 120.84 (qd, *J* = 284.4, 27.6 Hz), 115.25 (d, *J* = 2.0 Hz), 93.30 – 89.99 (m), 70.32; IR (KBr, cm^{-1}): ν 2938, 1614, 1517, 1214, 1102, 980, 853, 738, 698; MS (EI) m/z (relative intensity) 352 [M^+], 91 (100); HRMS (EI) calcd. For $C_{16}H_{11}OF_7$: 352.0698, Found: 322.0700.

3f, 1-(4-(perfluoropropan-2-yl)phenyl)ethanone



Yellow liquid; ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.08 (d, *J* = 8.3 Hz, 2H), 7.73 (d, *J* = 8.6 Hz, 2H), 2.65 (s, 3H); ^{19}F NMR (376 MHz, $CDCl_3$) δ -75.52 (d, *J* = 7.2 Hz, 6F), -182.63 (hept, *J* = 7.1 Hz, 1F); ^{13}C NMR (100 MHz, $CDCl_3$) δ 197.09, 139.19, 131.22 (d, *J* = 20.5 Hz), 128.78 (d, *J* = 2.2 Hz), 126.29 (d, *J* = 10.6 Hz), 120.50 (qd, *J* = 285.8, 28.1 Hz), 93.16 – 89.82 (m), 26.86; IR (film, cm^{-1}): ν 3372, 3008, 1696, 1613, 1414, 1362, 1273, 1214, 1103, 985, 830, 708; MS (EI) m/z (relative intensity) 288 [M^+], 273 (100); HRMS (EI) calcd. For $C_{11}H_7OF_7$: 288.0385, Found: 288.0389.

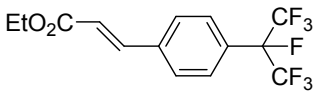
3g, N-(4-(perfluoropropan-2-yl)phenyl)acetamide



Light yellow solid; mp: 132-134 ^{o}C; ^{1}H NMR (400 MHz, DMSO-d6) δ 10.30 (s, 1H), 7.81 (d, *J* = 8.7 Hz, 2H), 7.59 (d, *J* = 8.7 Hz, 2H), 2.08 (s, 3H); ^{19}F NMR (376 MHz, $CDCl_3$) δ -75.88 (d, *J* = 7.2 Hz, 6F), -182.31 (hept, *J* = 7.2 Hz, 1F); ^{13}C NMR (100 MHz, $CDCl_3$) δ 168.94, 140.50, 126.77 (d, *J* = 10.6 Hz), 122.05, 120.69 (qd, *J* = 284.6, 27.3 Hz), 119.81, 93.13 – 89.81 (m), 24.74; IR

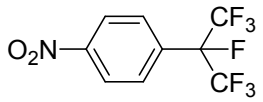
(KBr, cm^{-1}): ν 3301, 1674, 1604, 1306, 1266, 983, 739, 707; MS (EI) m/z (relative intensity) 303 (26) [M^+], 192 (100); HRMS (EI) calcd. For $C_{11}H_8NOF_7$: 303.0494, Found: 303.0490.

3h, (E)-ethyl 3-(4-(perfluoropropan-2-yl)phenyl)acrylate



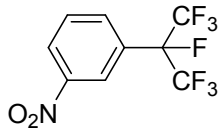
Yellow liquid; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.69 (d, *J* = 16.0 Hz, 1H), 7.63 (s, 4H), 6.51 (d, *J* = 16.0 Hz, 1H), 4.28 (q, *J* = 7.1 Hz, 2H), 1.34 (t, *J* = 7.1 Hz, 3H); ^{19}F NMR (376 MHz, $CDCl_3$) δ -75.66 (d, *J* = 7.3 Hz, 6F), -182.65 (hept, *J* = 7.3 Hz, 1F); ^{13}C NMR (100 MHz, $CDCl_3$) δ 166.54, 142.71, 137.37, 128.39, 128.16, 126.43 (d, *J* = 10.6 Hz), 121.01, 120.63 (qd, *J* =284.6, 28.0 H), 92.88 – 89.88 (m), 60.92, 14.36; IR (film, cm^{-1}): ν 2985, 1717, 1643, 1516, 1280, 1211, 1104, 984, 953, 827, 719; MS (EI) m/z (relative intensity) 344 (25) [M^+], 299 (100); HRMS (EI) calcd. For $C_{14}H_{11}O_2F_7$: 344.0647, Found: 344.0652.

3i, 1-nitro-4-(perfluoropropan-2-yl)benzene



Light yellow liquid; ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.38 (d, *J* = 8.7 Hz, 2H), 7.85 (d, *J* = 8.8 Hz, 2H); ^{19}F NMR (376 MHz, $CDCl_3$) δ -75.39 (d, *J* = 7.2 Hz, 6F), -181.99 (hept, *J* = 7.3 Hz, 1F); ^{13}C NMR (100 MHz, $CDCl_3$) δ 149.78, 133.09 (d, *J* = 20.7 Hz), 127.41 (d, *J* = 10.8 Hz), 124.21 (d, *J* = 2.1 Hz), 120.30 (qd, *J* = 285.7, 27.6 Hz), 93.01 – 89.64 (m); IR (film, cm^{-1}): ν 3118, 1611, 1536, 1276, 1217, 1106, 986, 854, 760; MS (EI) m/z (relative intensity) 291 [M^+], 145 (100); HRMS (EI) calcd. For $C_9H_4NO_2F_7$: 291.0130, Found: 291.0123.

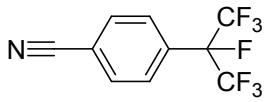
3j, 1-nitro-3-(perfluoropropan-2-yl)benzene



Light yellow liquid; ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.52 (s, 1H), 8.44 (d, *J* = 8.2 Hz, 1H), 7.96 (d, *J* = 7.7 Hz, 1H), 7.76 (t, *J* = 8.1 Hz, 1H); ^{19}F NMR (376 MHz, $CDCl_3$) δ -75.54 (d, *J* = 7.3 Hz, 6F), -181.94 (hept, *J* = 7.3 Hz, 1F); ^{13}C NMR (100 MHz, $CDCl_3$) δ 148.72, 131.68 (d, *J* = 9.9 Hz),

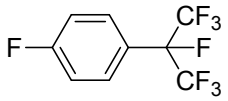
130.56 (d, J = 1.9 Hz), 128.95 (d, J = 21.3 Hz), 126.28, 121.52 (d, J = 12.4 Hz), 120.34 (qd, J = 285.4, 27.3 Hz), 92.71 – 89.34 (m); IR (film, cm^{-1}): ν 2927, 1543, 1284, 1216, 1106, 983, 906, 720; MS (EI) m/z (relative intensity) 291 [M^+], 145 (100); HRMS (EI) calcd. For $C_9H_4NO_2F_7$: 291.0130, Found: 291.0126.

3k, 4-(perfluoropropan-2-yl)benzonitrile



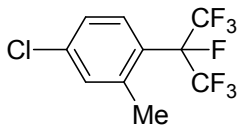
Colorless liquid; ^1H NMR (400 MHz, $CDCl_3$) δ 7.83 (d, J = 8.5 Hz, 2H), 7.76 (d, J = 8.4 Hz, 2H); ^{19}F NMR (376 MHz, $CDCl_3$) δ -75.40 (d, J = 7.3 Hz, 6F), -182.73(hept, J = 7.3 Hz, 1F); ^{13}C NMR (100 MHz, $CDCl_3$) δ 132.82 (d, J = 2.1 Hz), 131.53 (d, J = 20.8 Hz), 126.86 (d, J = 10.8 Hz), 120.35 (qd, J = 285.1, 27.6 Hz), 117.51, 115.76, 92.93 – 89.45 (m); IR (film, cm^{-1}): ν 2911, 1611, 1510, 1497, 1453, 1307, 1277, 1095, 1044, 979, 755; MS (EI) m/z (relative intensity) 271 (34) [M^+], 152 (100); HRMS (EI) calcd. For $C_{10}H_4NF_7$: 271.0232, Found: 271.0234.

3l, 1-fluoro-4-(perfluoropropan-2-yl)benzene



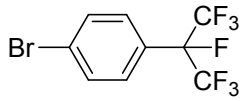
MS (EI) m/z (relative intensity) 264 [M^+];

3m, 4-chloro-2-methyl-1-(perfluoropropan-2-yl)benzene



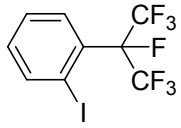
Yellow liquid; ^1H NMR (400 MHz, $CDCl_3$) δ 7.41 (d, J = 8.0 Hz, 1H), 7.32 – 7.24 (m, 2H), 2.51 (d, J = 9.0 Hz, 3H); ^{19}F NMR (376 MHz, $CDCl_3$) δ -74.93 (d, J = 5.9 Hz, 6F), -178.90(s, 1F); ^{13}C NMR (100 MHz, $CDCl_3$) δ 141.01, 137.05, 133.73, 128.07, 126.40, 121.02 (qd, J = 288.1, 28.3 Hz), 96.09 – 92.74 (m), 21.90 (d, J = 15.8 Hz); IR (film, cm^{-1}): ν 2925, 1599, 1492, 1306, 1209, 1101, 977, 950, 818, 737; MS (EI) m/z (relative intensity) 294 (42)[M^+], 225(100); HRMS (EI) calcd. For $C_{10}H_6F_7Cl$: 294.0046, Found: 294.0042.

3n, 1-bromo-4-(perfluoropropan-2-yl)benzene



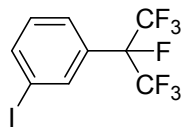
Yellow liquid; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.65 (d, *J* = 8.3 Hz, 2H), 7.48 (d, *J* = 8.5 Hz, 2H); ^{19}F NMR (376 MHz, $CDCl_3$) δ -75.81 (d, *J* = 7.3 Hz, 6F), -182.63 (hept, *J* = 7.3 Hz, 1F); ^{13}C NMR (100 MHz, $CDCl_3$) δ 132.42 (d, *J* = 2.1 Hz), 127.50 (d, *J* = 10.6 Hz), 126.10, 125.94 (d, *J* = 20.8 Hz), 120.51 (qd, *J* = 286.9, 27.8 Hz), 93.12 – 89.78 (m); IR (film, cm^{-1}): ν 2925, 1599, 1462, 1305, 1222, 986, 954, 822, 734; MS (EI) m/z (relative intensity) 324[M^+], 255(100); HRMS (EI) calcd. For $C_9H_4F_7Br$: 323.9385, Found: 323.9383.

3o, 1-iodo-2-(perfluoropropan-2-yl)benzene



Yellow liquid; ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.17 (d, *J* = 8.0 Hz, 2H), 7.51 – 7.43 (m, 2H), 7.15 (t, *J* = 7.6 Hz, 1H); ^{19}F NMR (376 MHz, $CDCl_3$) δ -73.94 (d, *J* = 7.8 Hz, 6F), -176.32 (hept, *J* = 7.7 Hz, 1F); ^{13}C NMR (100 MHz, $CDCl_3$) δ 144.98 (d, *J* = 2.5 Hz), 139.63, 137.65, 132.18, 130.39, 129.32, 128.72, 128.08, 127.94 (d, *J* = 2.1 Hz), 127.61, 120.75 (qd, *J* = 286.5, 27.8 Hz), 108.01, 93.11 – 90.03 (m), 89.42 (d, *J* = 3.3 Hz); IR (film, cm^{-1}): ν 2925, 1587, 1475, 1304, 1208, 976, 948, 758, 731; MS (EI) m/z (relative intensity) 372 (100) [M^+]; HRMS (EI) calcd. For $C_9H_4F_7I$: 371.9246, Found: 371.9243.

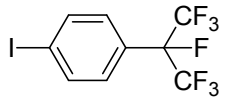
3p, 1-iodo-3-(perfluoropropan-2-yl)benzene



Yellow liquid; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.94 (s, 1H), 7.89 (d, *J* = 8.4 Hz, 1H), 7.58 (d, *J* = 7.9 Hz, 1H), 7.24 (t, *J* = 8.0 Hz, 1H); ^{19}F NMR (376 MHz, $CDCl_3$) δ -75.63 (d, *J* = 7.2 Hz, 6F), -182.57 (hept, *J* = 7.2 Hz, 1F); ^{13}C NMR (100 MHz, $CDCl_3$) δ 140.43, 134.68 (d, *J* = 11.8 Hz), 130.58 (d, *J* = 2.2 Hz), 128.87 (d, *J* = 20.6 Hz), 125.05 (d, *J* = 10.0 Hz), 120.53 (qd, *J* = 285.3, 27.6 Hz), 94.44 (d, *J* = 2.4 Hz), 92.53 – 89.18 (m); IR (film, cm^{-1}): ν 2926, 1593, 1477, 1305, 1212, 984, 764, 725; MS (EI) m/z (relative intensity) 372 (100) [M^+]; HRMS (EI) calcd. For

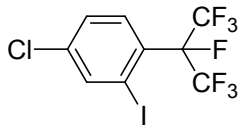
$C_9H_4F_7I$: 371.9246, Found: 371.9250.

3q, 1-iodo-4-(perfluoropropan-2-yl)benzene



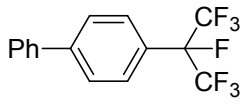
Colorless liquid; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.86 (d, *J* = 8.2 Hz, 2H), 7.34 (d, *J* = 8.2 Hz, 2H); ^{19}F NMR (376 MHz, $CDCl_3$) δ -75.77 (d, *J* = 7.3 Hz, 6F), -182.91 (hept, *J* = 7.3 Hz, 1F); ^{13}C NMR (100 MHz, $CDCl_3$) δ 138.35 (d, *J* = 1.8 Hz), 127.47 (d, *J* = 10.5 Hz), 126.65 (d, *J* = 20.8 Hz), 120.50 (qd, *J* = 287.5, 29.6 Hz), 98.07, 92.85 – 90.18 (m); IR (film, cm^{-1}): ν 2926, 1591, 1491, 1301, 1213, 984, 950, 816, 748; MS (EI) m/z (relative intensity) 372 (100) [M$^+$]; HRMS (EI) calcd. For $C_9H_4F_7I$: 371.9246, Found: 371.9251.

3r, 4-chloro-2-iodo-1-(perfluoropropan-2-yl)benzene



Yellow liquid; ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.18 (s, 1H), 7.50 – 7.36 (m, 2H); ^{19}F NMR (376 MHz, $CDCl_3$) δ -74.00 (d, *J* = 7.7 Hz, 6F), -176.27 (hept, *J* = 7.7 Hz, 1F); ^{13}C NMR (100 MHz, $CDCl_3$) δ 144.29 (d, *J* = 2.4 Hz), 137.92, 129.29, 128.30, 126.51 (d, *J* = 18.9 Hz), 120.59 (qd, *J* = 288.8, 28.7 Hz), 93.35 – 89.92 (m), 89.84 (d, *J* = 2.9 Hz); IR (film, cm^{-1}): ν 2926, 1581, 1476, 1302, 1208, 1108, 977, 948, 819, 735; MS (EI) m/z (relative intensity) 406 (100) [M$^+$]; HRMS (EI) calcd. For $C_9H_3F_7ClI$: 405.8856, Found: 405.8857.

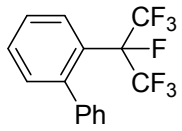
3s, 4-(perfluoropropan-2-yl)-1,1'-biphenyl



White solid, mp: 89-91 ^{o}C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.71 (q, *J* = 8.5 Hz, 4H), 7.62 (d, *J* = 7.1 Hz, 2H), 7.49 (t, *J* = 7.4 Hz, 2H), 7.45 – 7.36 (m, 1H); ^{19}F NMR (376 MHz, $CDCl_3$) δ -75.68 (d, *J* = 7.3 Hz, 6F), -182.52 (hept, *J* = 7.2 Hz, 1F); ^{13}C NMR (100 MHz, $CDCl_3$) δ 144.12, 139.75, 129.14, 128.33, 127.68 (d, *J* = 2.1 Hz), 127.38, 126.29 (d, *J* = 10.5 Hz), 125.66 (d, *J* = 20.7 Hz), 120.81 (qd, *J* = 286.6, 28.3 Hz), 93.36 – 90.04 (m); IR (KBr, cm^{-1}): ν 3078, 1446, 1280, 1218,

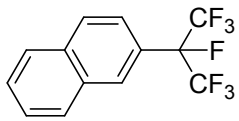
1101, 981, 835, 736, 697; MS (EI) m/z (relative intensity) 322 [M^+], 253 (100); HRMS (EI) calcd. For $C_{15}H_9F_7$: 322.0592, Found: 322.0587.

3t, 2-(perfluoropropan-2-yl)-1,1'-biphenyl



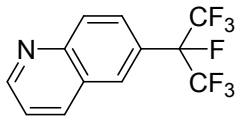
Colorless liquid; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.62 (d, *J* = 7.6 Hz, 1H), 7.54 – 7.44 (m, 2H), 7.38 – 7.33 (m, 3H), 7.28 (d, *J* = 1.5 Hz, 1H), 7.22 (dd, *J* = 6.4, 2.8 Hz, 2H); ^{19}F NMR (376 MHz, $CDCl_3$) δ -75.07 (d, *J* = 5.6 Hz, 6F), -175.95(s, 1F); ^{13}C NMR (100 MHz, $CDCl_3$) δ 142.99 (d, *J* = 2.8 Hz), 141.95 (d, *J* = 5.2 Hz), 133.78 (d, *J* = 1.8 Hz), 130.09, 128.90, 128.34 (d, *J* = 4.7 Hz), 127.60 (d, *J* = 2.4 Hz), 127.43, 127.32, 127.06, 126.23 (dt, *J* = 8.6, 2.8 Hz), 123.94 (d, *J* = 17.8 Hz), 120.88 (qd, *J* = 286.1, 28.1 Hz), 95.11 – 91.74 (m); IR (KBr, cm^{-1}): ν 3065, 1598, 1484, 1441, 1271, 1205, 1113, 977, 948, 739, 701; MS (EI) m/z (relative intensity) 322 [M^+], 183 (100); HRMS (EI) calcd. For $C_{15}H_9F_7$: 322.0592, Found: 322.0586.

3u, 2-(perfluoropropan-2-yl)naphthalene



White solid, mp: 65-66 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.16 (s, 1H), 8.00 – 7.87 (m, 3H), 7.69 – 7.55 (m, 3H); ^{19}F NMR (376 MHz, $CDCl_3$) δ -75.44 (d, *J* = 7.2 Hz, 6F), -181.96 (hept, *J* = 7.2 Hz, 1F); ^{13}C NMR (100 MHz, $CDCl_3$) δ 134.19, 132.64 (d, *J* = 2.1 Hz), 129.05 (d, *J* = 2.3 Hz), 128.91, 128.16, 127.86, 127.33, 126.64 (d, *J* = 11.9 Hz), 124.16 (d, *J* = 20.3 Hz), 121.76 (d, *J* = 9.4 Hz), 120.90 (qd, *J* = 285.6, 28.1 Hz), 93.54 – 90.18 (m); IR (KBr, cm^{-1}): ν 3060, 1276, 1220, 981, 907, 751; MS (EI) m/z (relative intensity) 296 (76) [M^+], 177 (100); HRMS (EI) calcd. For $C_{13}H_7F_7$: 296.0436, Found: 296.0433.

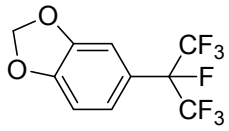
3v, 6-(perfluoropropan-2-yl)quinoline



Yellow solid, mp: 46-48 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 9.04 (dd, *J* = 4.1, 1.5 Hz, 1H), 8.32 –

8.20 (m, 2H), 8.14 (d, J = 1.2 Hz, 1H), 7.89 (d, J = 8.9 Hz, 1H), 7.51 (dd, J = 8.4, 4.2 Hz, 1H); ^{19}F NMR (376 MHz, $CDCl_3$) δ -75.42 (d, J = 7.2 Hz, 6F), -181.67 (hept, J = 7.2 Hz, 1F); ^{13}C NMR (100 MHz, $CDCl_3$) δ 152.61, 148.77, 1367.02, 130.74 (d, J = 1.7 Hz), 127.66 (d, J = 1.7 Hz), 126.81 (d, J = 11.9 Hz), 125.48 (d, J = 9.2 Hz), 125.06 (d, J = 20.5 Hz), 122.44, 120.74 (qd, J = 284.8, 27.6 Hz), 93.38 – 90.04 (m); IR (KBr, cm^{-1}): ν 2929, 1596, 1504, 1297, 1214, 1102, 982, 894, 838, 752; MS (EI) m/z (relative intensity) 297 (66) [M^+], 178 (100); HRMS (EI) calcd. For $C_{12}H_6NF_7$: 297.0388, Found: 297.0384.

3w, 5-(perfluoropropan-2-yl)benzo[d][1,3]dioxole



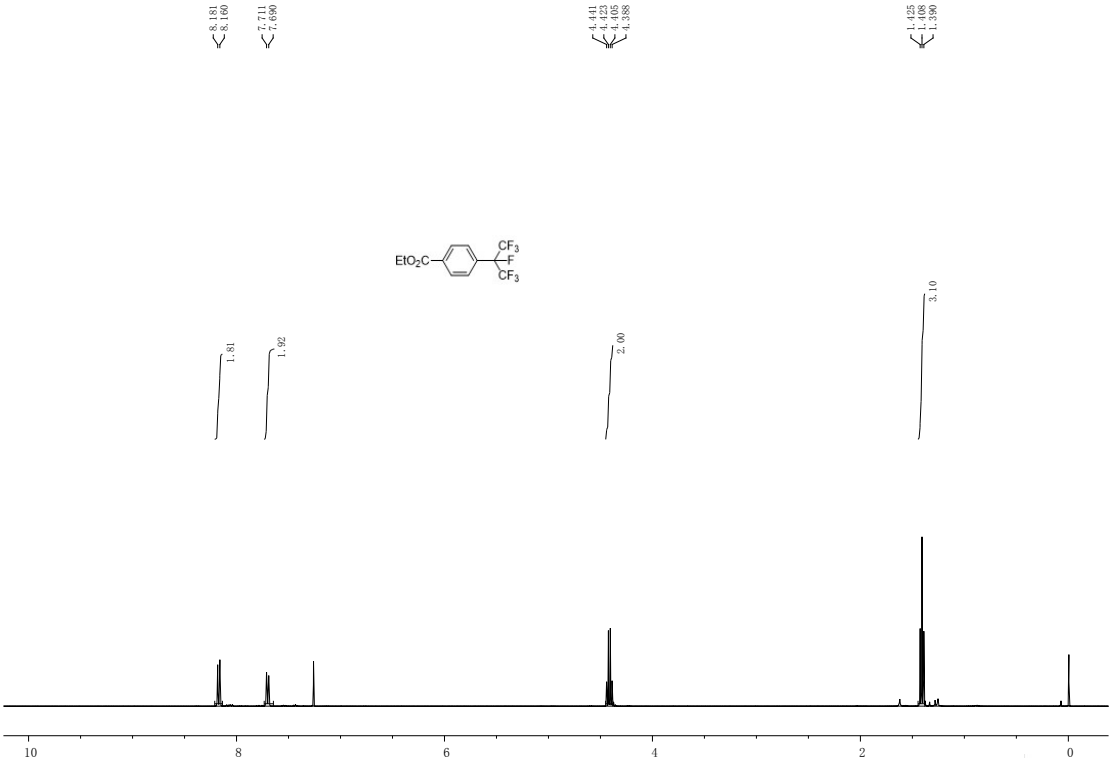
Colorless liquid; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.11 (d, J = 8.2 Hz, 1H), 7.05 (s, 1H), 6.90 (d, J = 8.3 Hz, 1H), 6.05 (s, 2H); ^{19}F NMR (376 MHz, $CDCl_3$) δ -75.97 (d, J = 7.2 Hz, 6F), -180.58 (hept, J = 7.3 Hz, 1F); ^{13}C NMR (100 MHz, $CDCl_3$) δ 149.99, 148.48 (d, J = 2.8 Hz), 120.74 (qd, J = 284.9, 27.5 Hz), 120.29 (d, J = 11.6 Hz), 120.07 (d, J = 20.8 Hz), 108.70 (d, J = 2.0 Hz), 106.41 (d, J = 11.6 Hz), 102.06, 93.20 – 89.88 (m); IR (film, cm^{-1}): ν 2934, 2237, 1508, 1310, 1277, 1212, 986, 836, 749, 705; MS (EI) m/z (relative intensity) 290 (46) [M^+], 221 (100); HRMS (EI) calcd. For $C_{10}H_5O_2F_7$: 290.0178, Found: 290.0173.

References

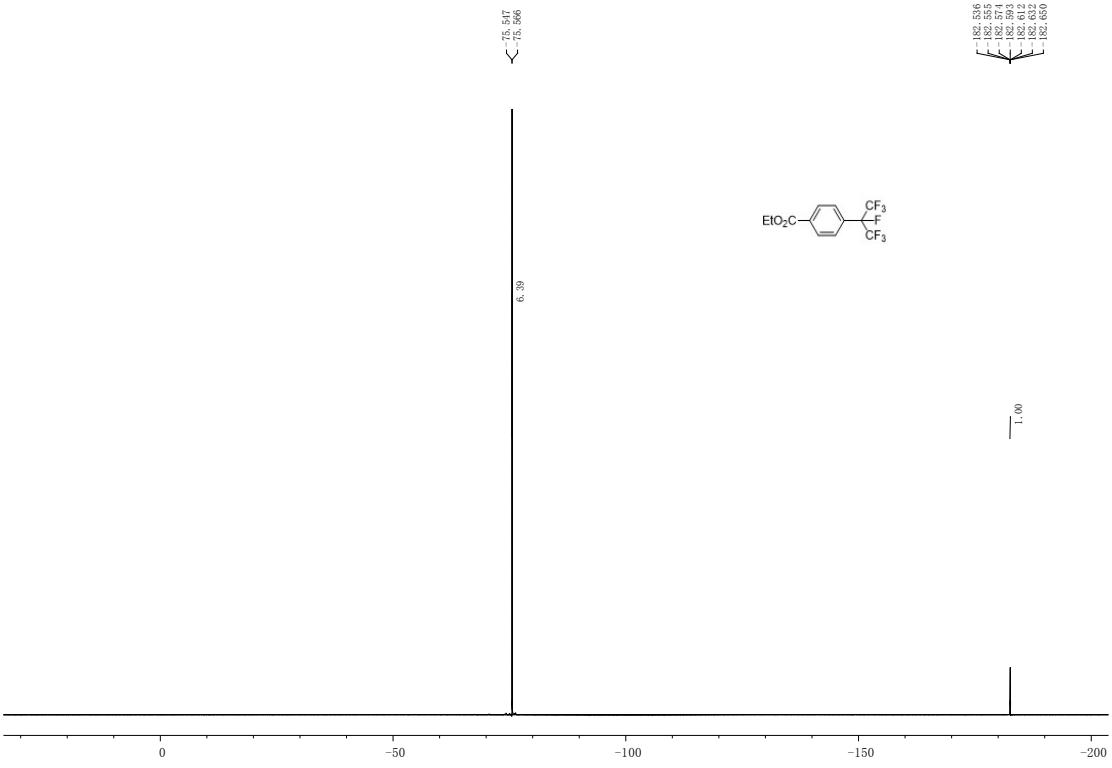
1. G. Danoun, B. Bayarmagnai, and M. F. Grünberg, L. J. Gooßen, *Angew. Chem. Int. Ed.*, 2013, **52**, 7972.
2. W. T. Miller, and Jr., R. J. Burnard, *J. Am. Chem. Soc.*, 1968, **90**, 7367.

Spectrum of the Products

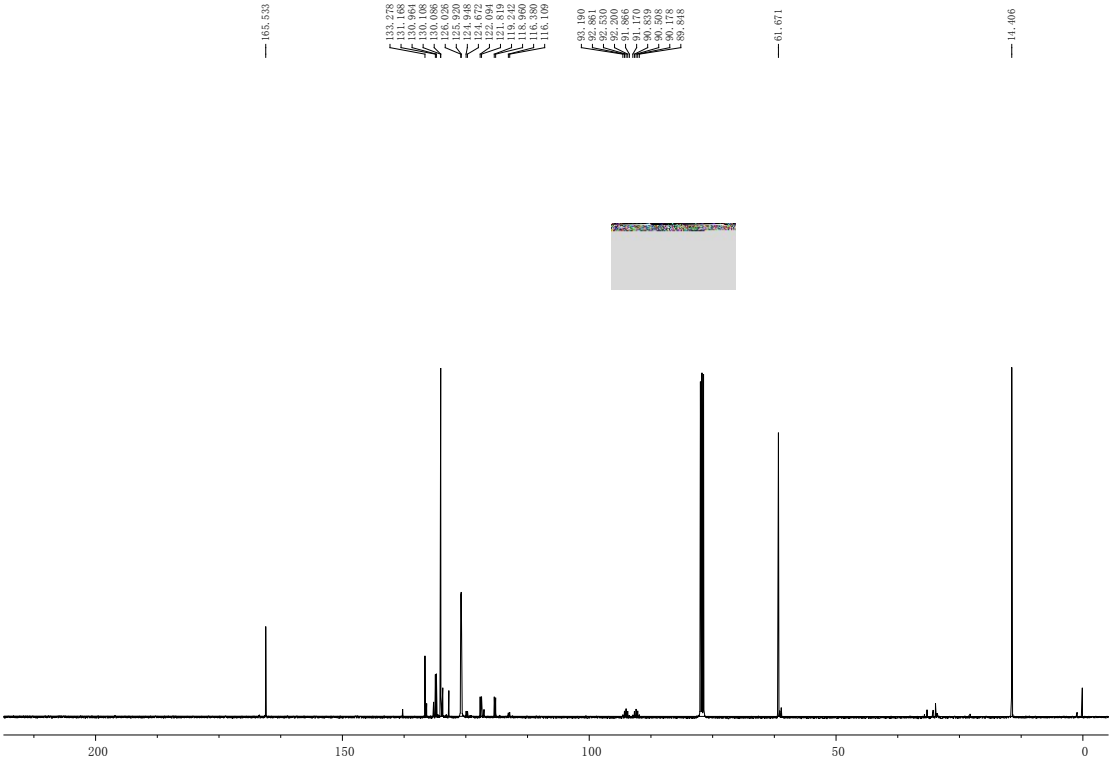
^{1}H NMR (400 MHz, $CDCl_3$) spectrum of ethyl 4-(perfluoropropan-2-yl)benzoate 3a



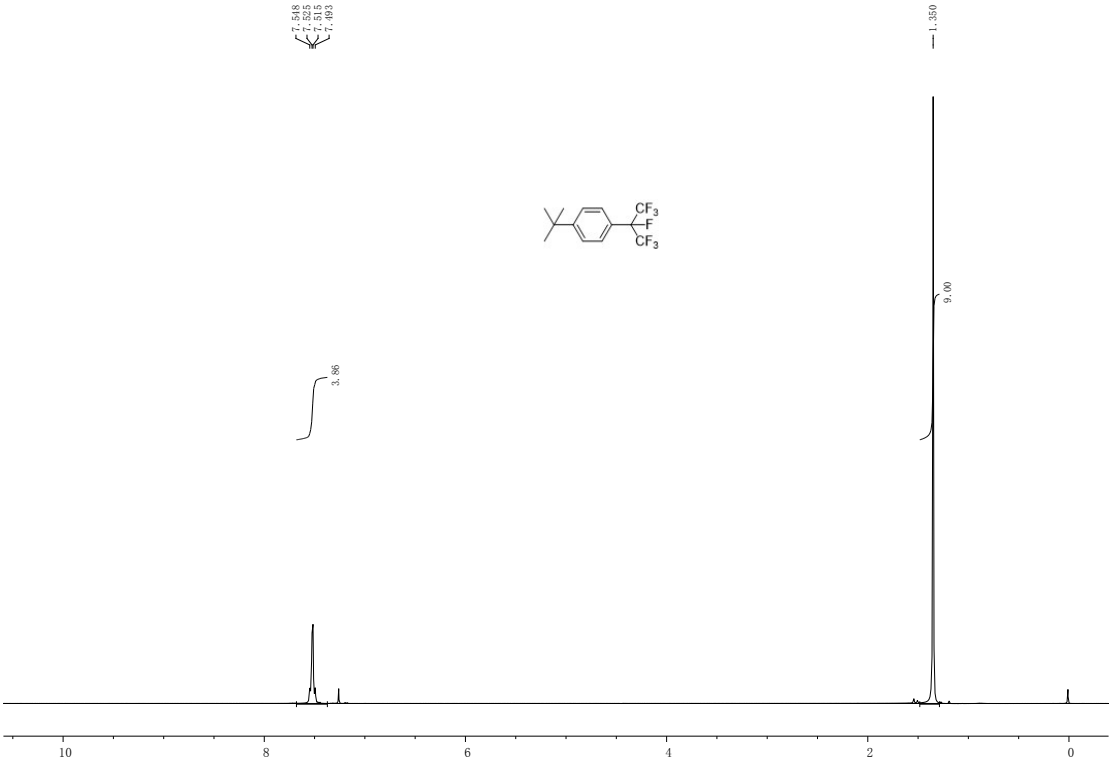
^{19}F NMR (376 MHz, $CDCl_3$) spectrum of ethyl 4-(perfluoropropan-2-yl)benzoate 3a



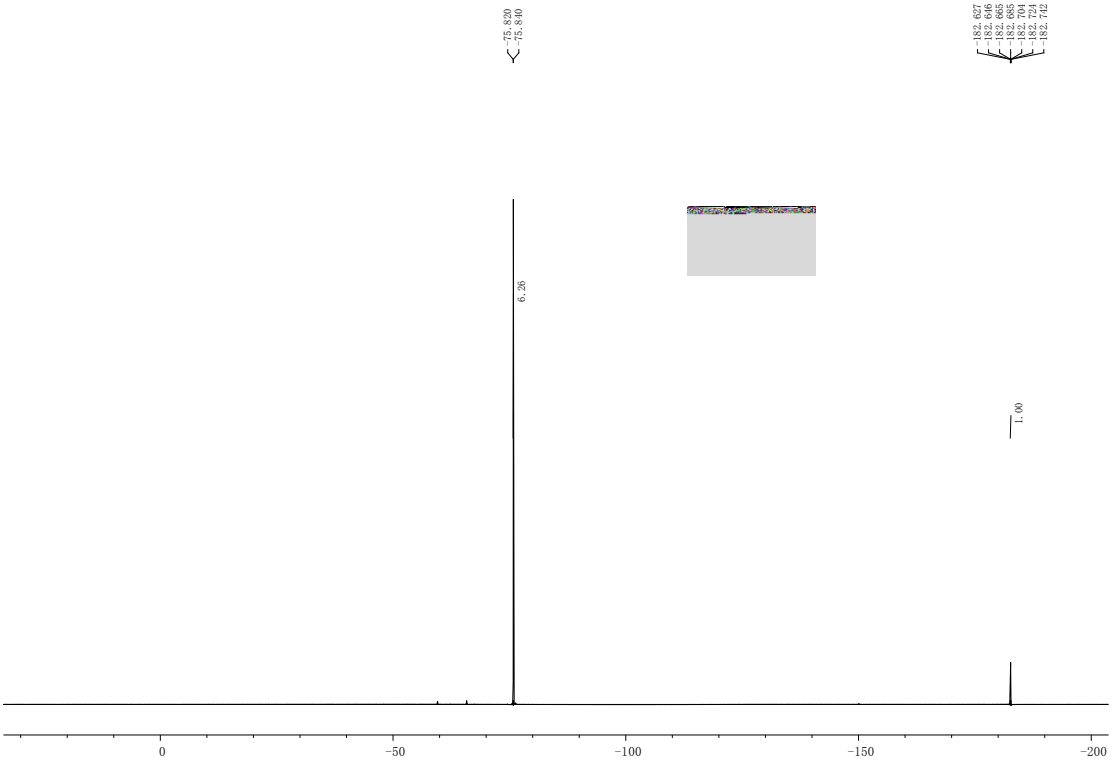
^{13}C NMR (101 MHz, $CDCl_3$) spectrum of ethyl 4-(perfluoropropan-2-yl)benzoate 3a



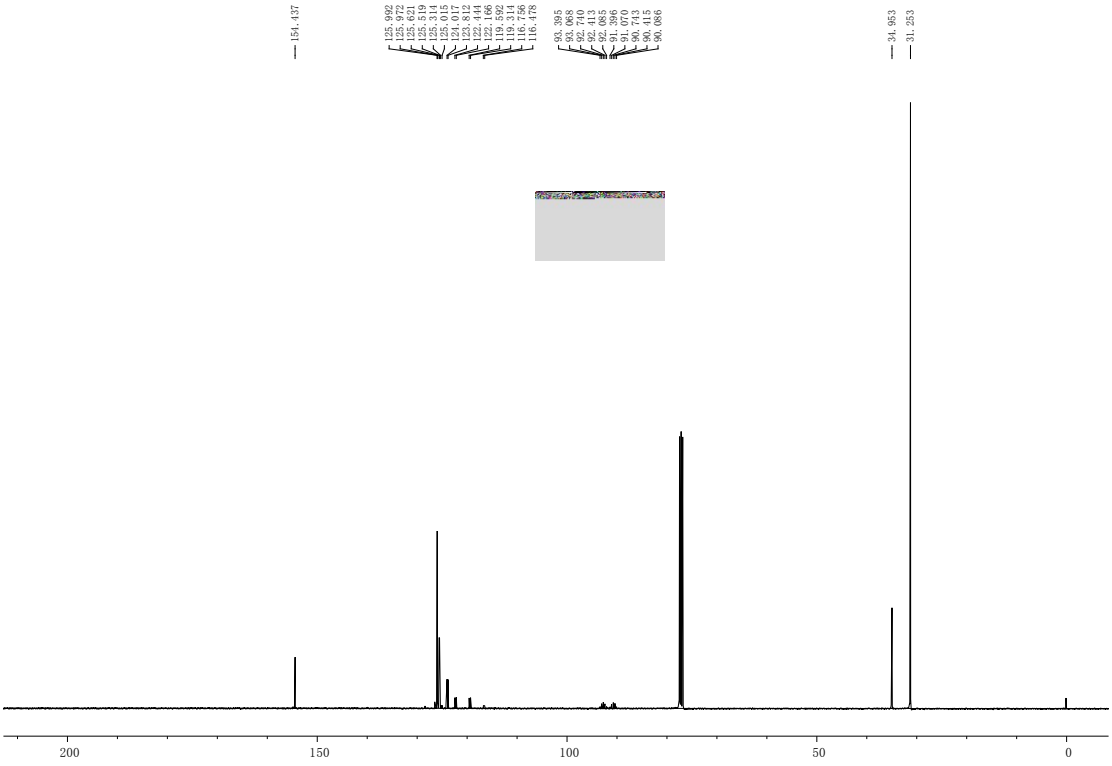
^{1}H NMR (400 MHz, $CDCl_3$) spectrum of 1-(tert-butyl)-4-(perfluoropropan-2-yl)benzene 3d



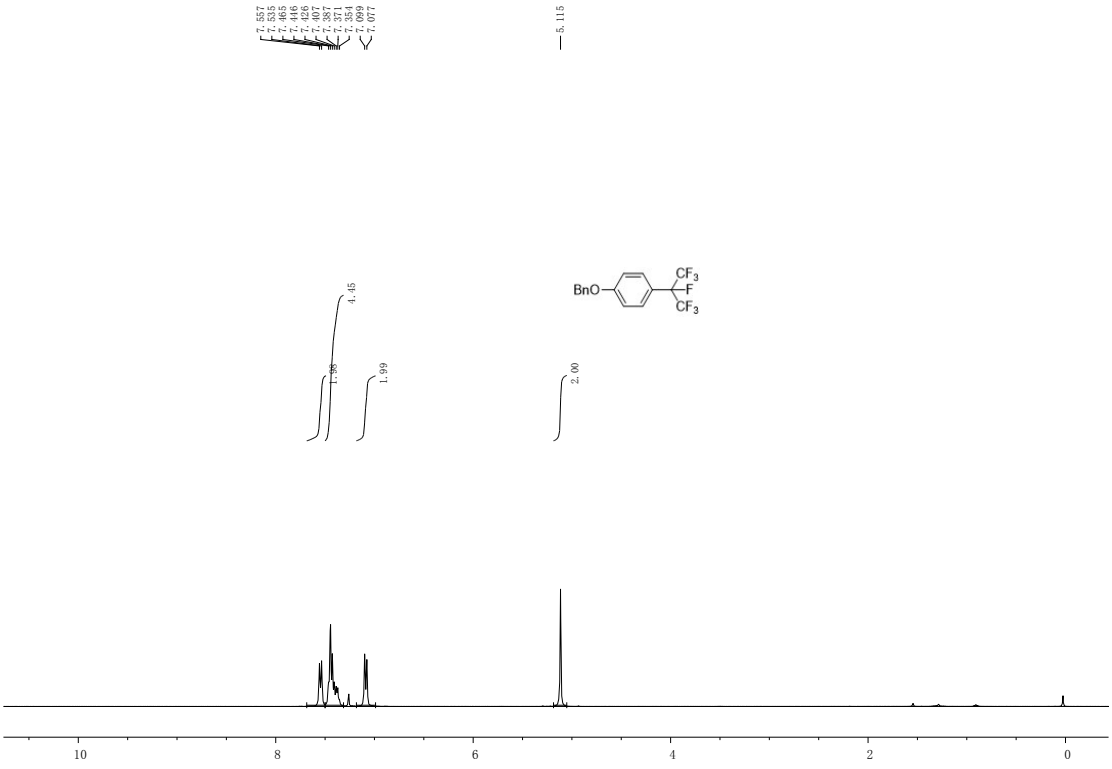
^{19}F NMR (376 MHz, $CDCl_3$) spectrum of 1-(tert-butyl)-4-(perfluoropropan-2-yl)benzene 3d



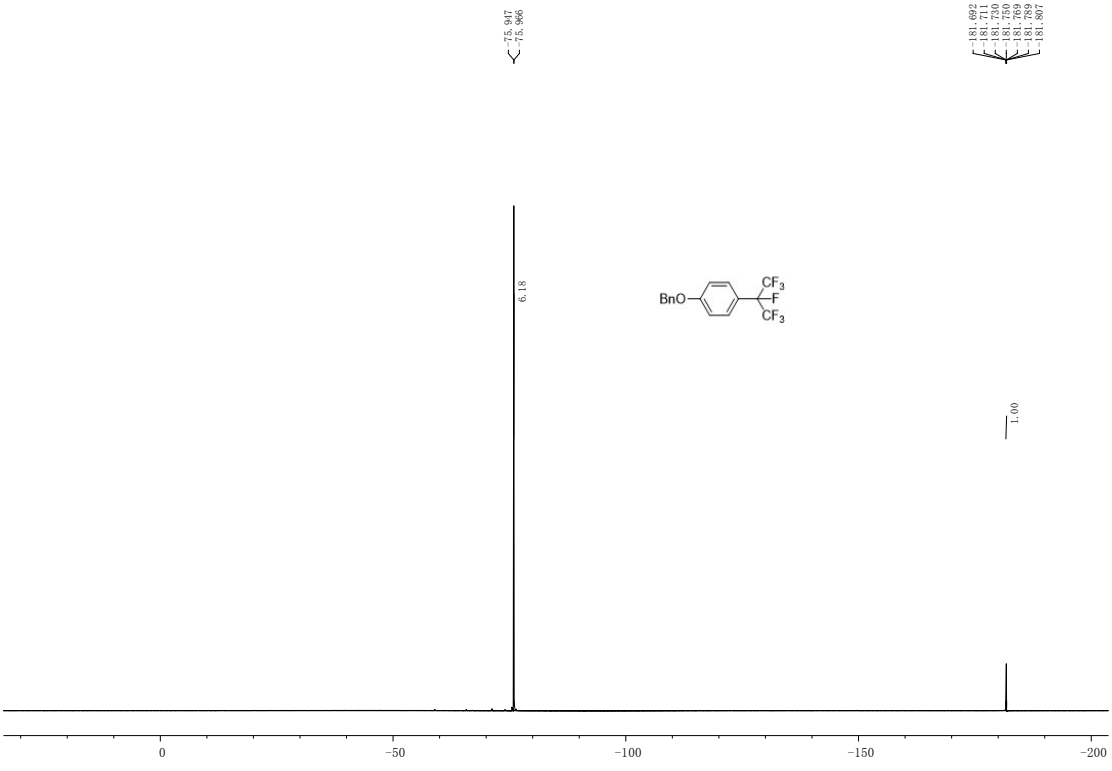
^{13}C NMR (101 MHz, $CDCl_3$) spectrum of 1-(tert-butyl)-4-(perfluoropropan-2-yl)benzene 3d



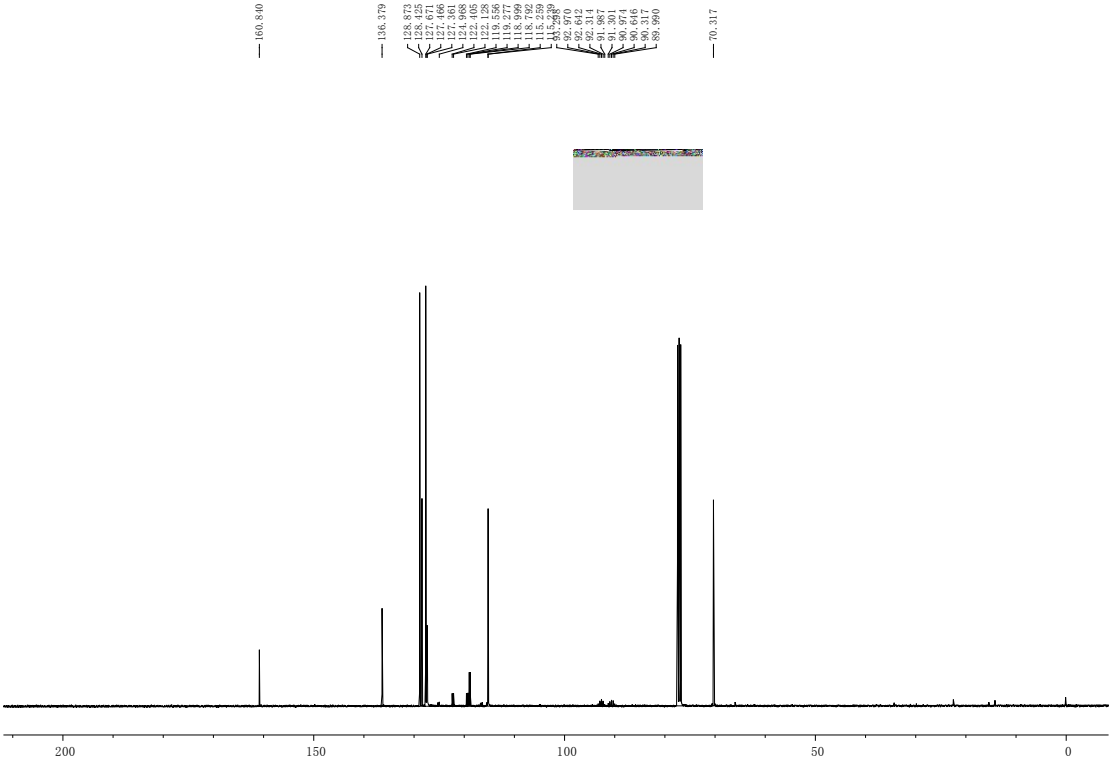
^{1}H NMR (400 MHz, $CDCl_3$) spectrum of 1-(benzyloxy)-4-(perfluoropropan-2-yl)benzene 3e



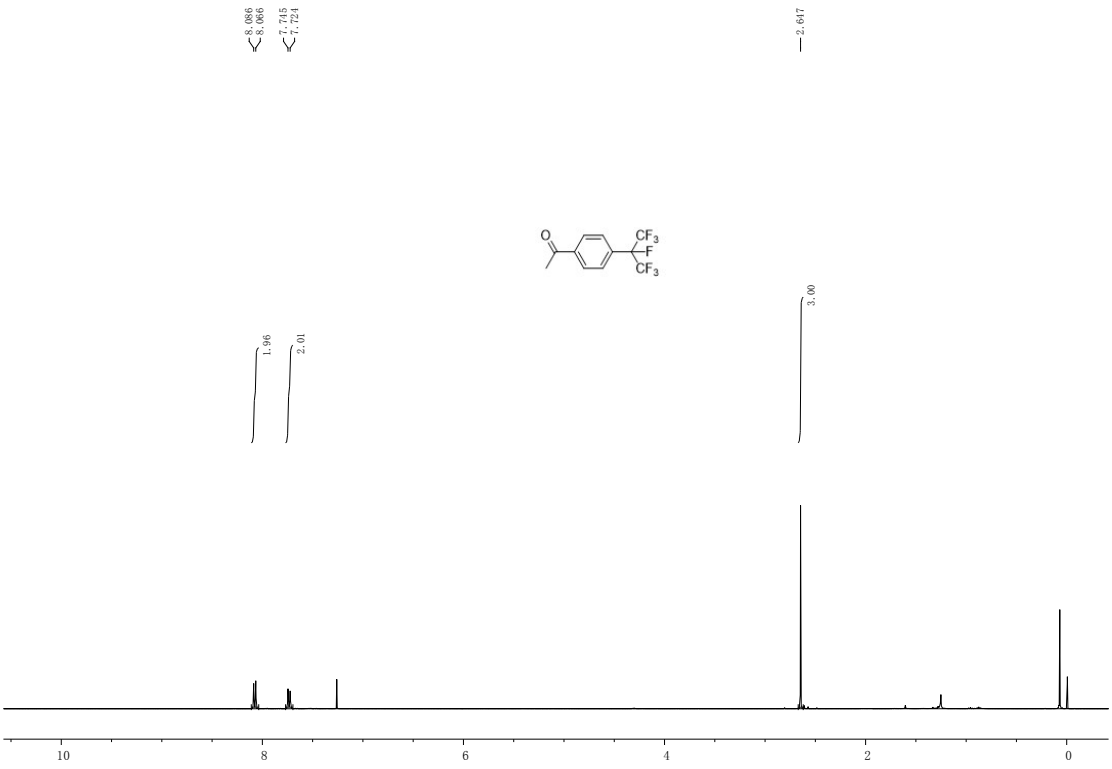
^{19}F NMR (376 MHz, $CDCl_3$) spectrum of 1-(benzyloxy)-4-(perfluoropropan-2-yl)benzene 3e



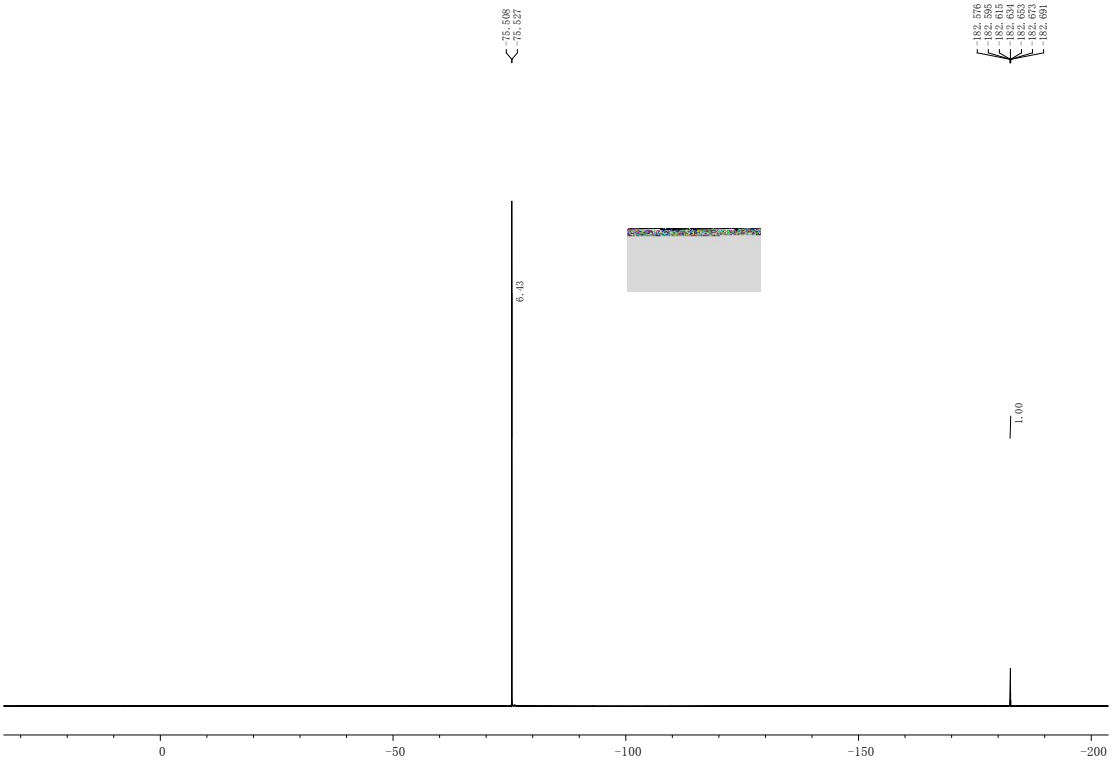
^{13}C NMR (101 MHz, $CDCl_3$) spectrum of 1-(benzyloxy)-4-(perfluoropropan-2-yl)benzene 3e



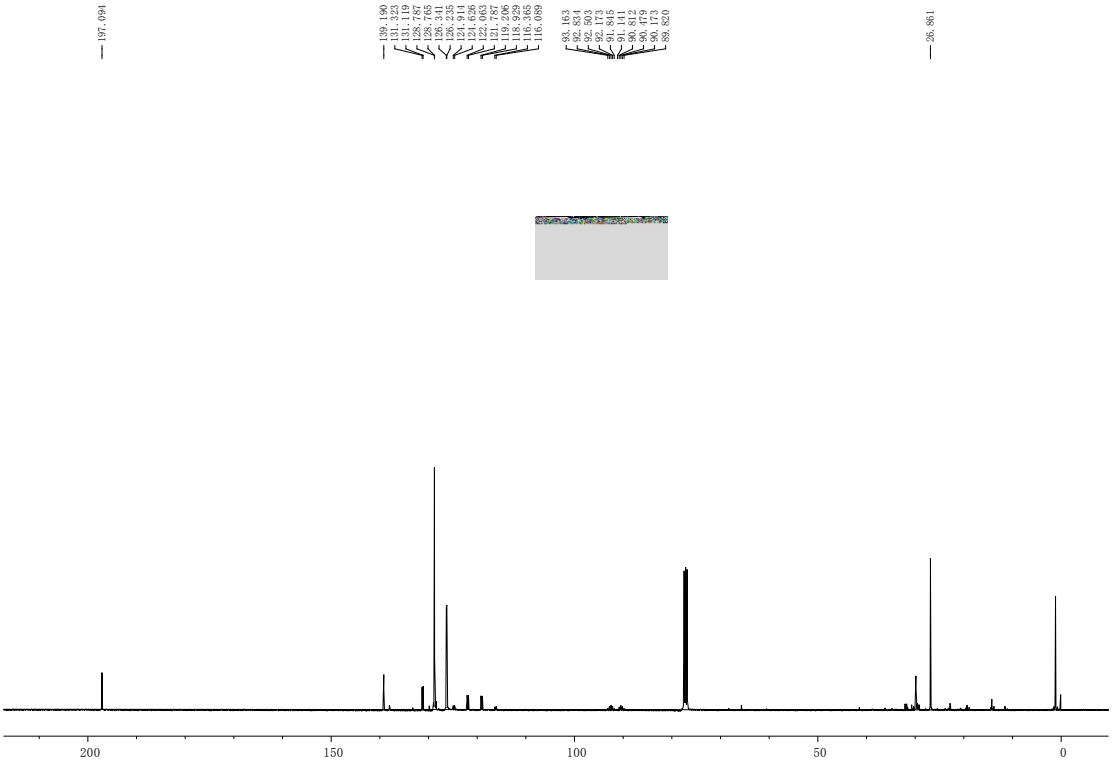
^{1}H NMR (400 MHz, $CDCl_3$) spectrum of 1-(4-(perfluoropropan-2-yl)phenyl)ethanone 3f



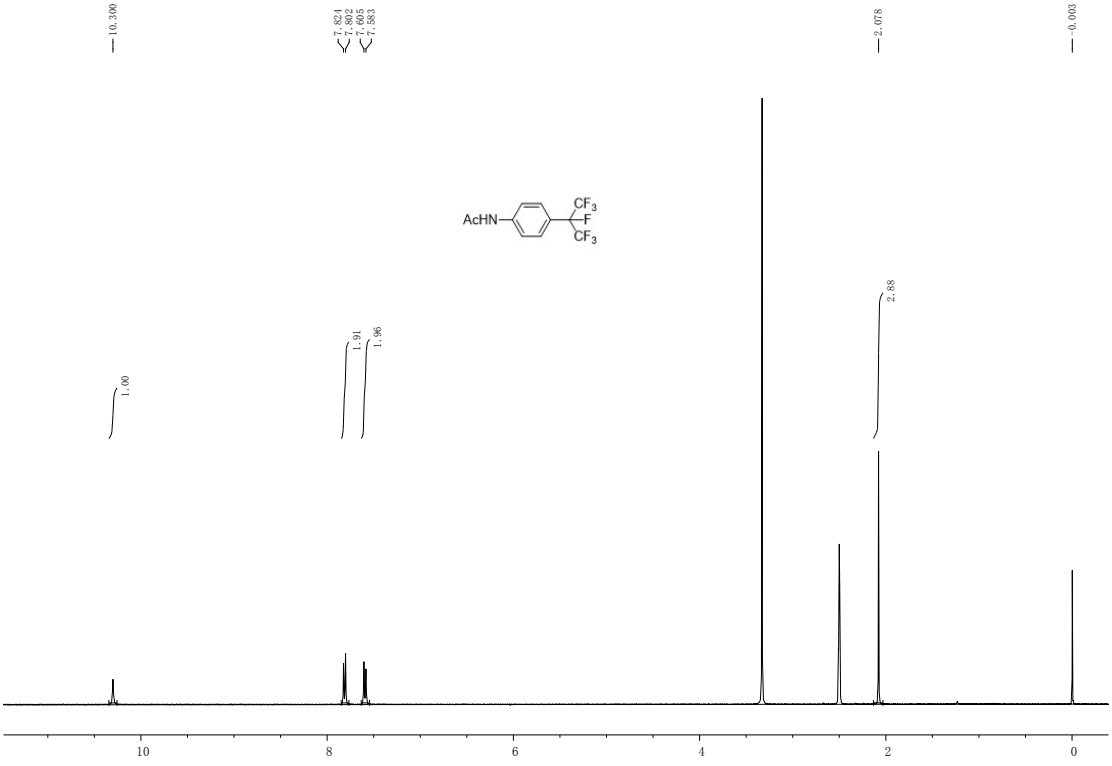
^{19}F NMR (376 MHz, $CDCl_3$) spectrum of 1-(4-(perfluoropropan-2-yl)phenyl)ethanone 3f



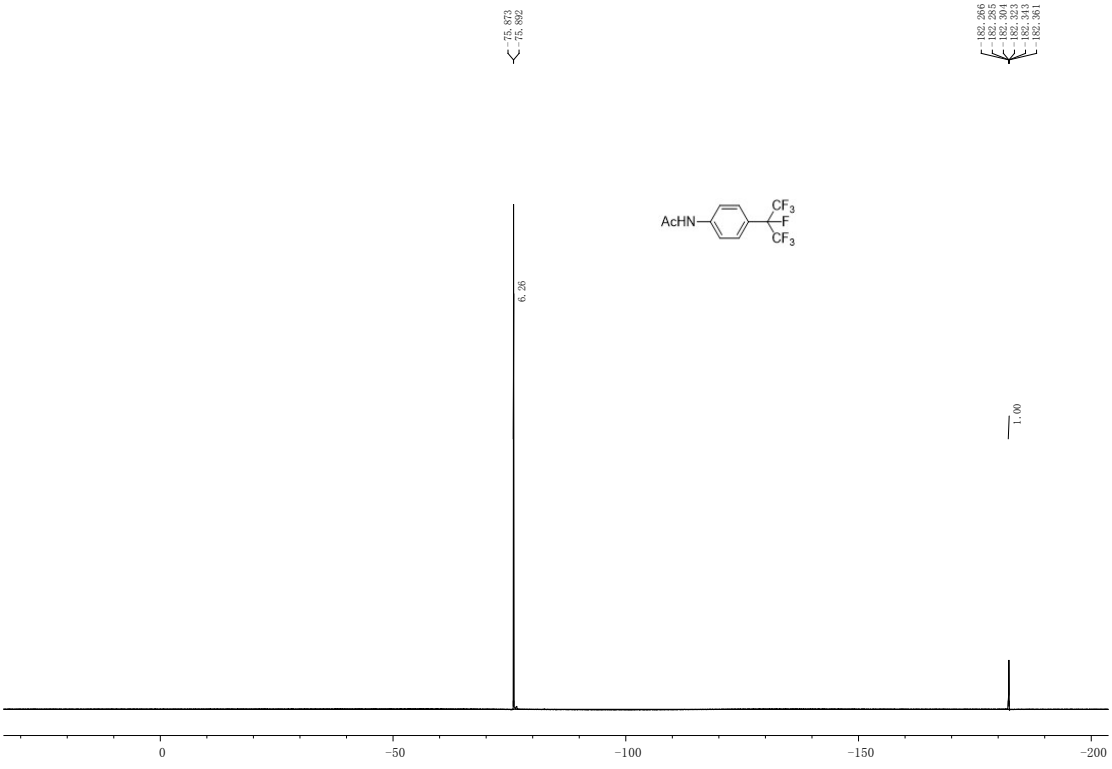
^{13}C NMR (101 MHz, $CDCl_3$) spectrum of 1-(4-(perfluoropropan-2-yl)phenyl)ethanone 3f



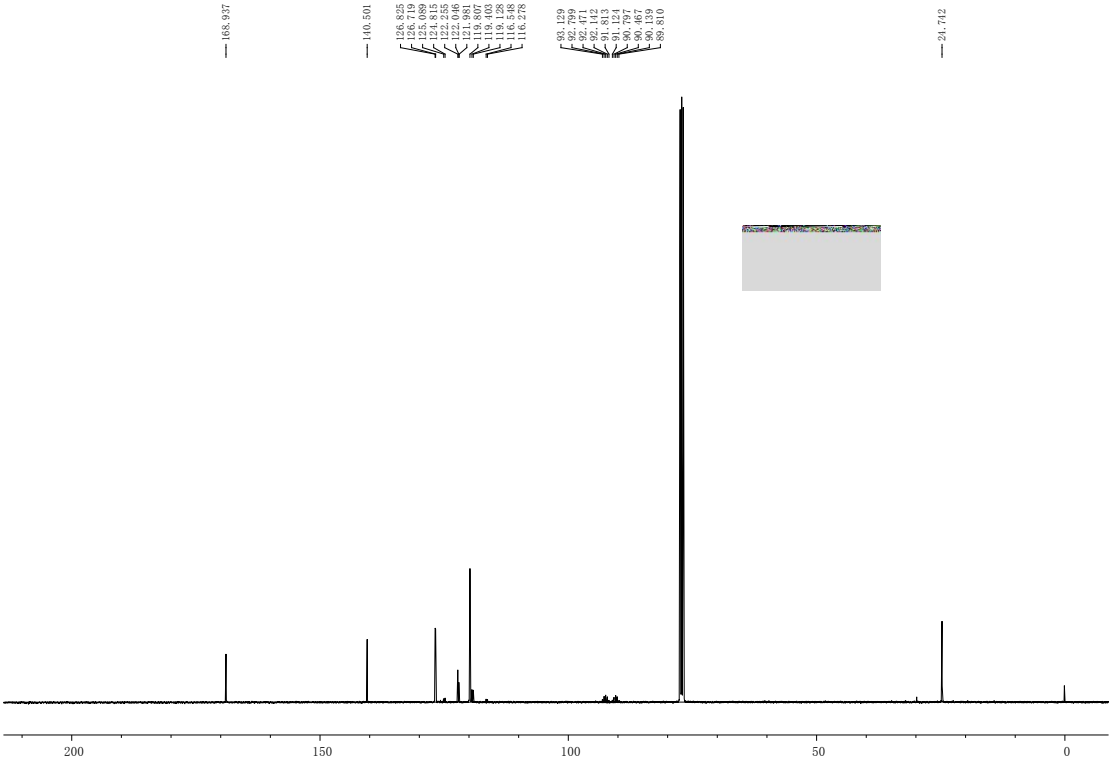
^{1}H NMR (400 MHz, DMSO-d6) spectrum of N-(4-(perfluoropropan-2-yl)phenyl)acetamide 3g



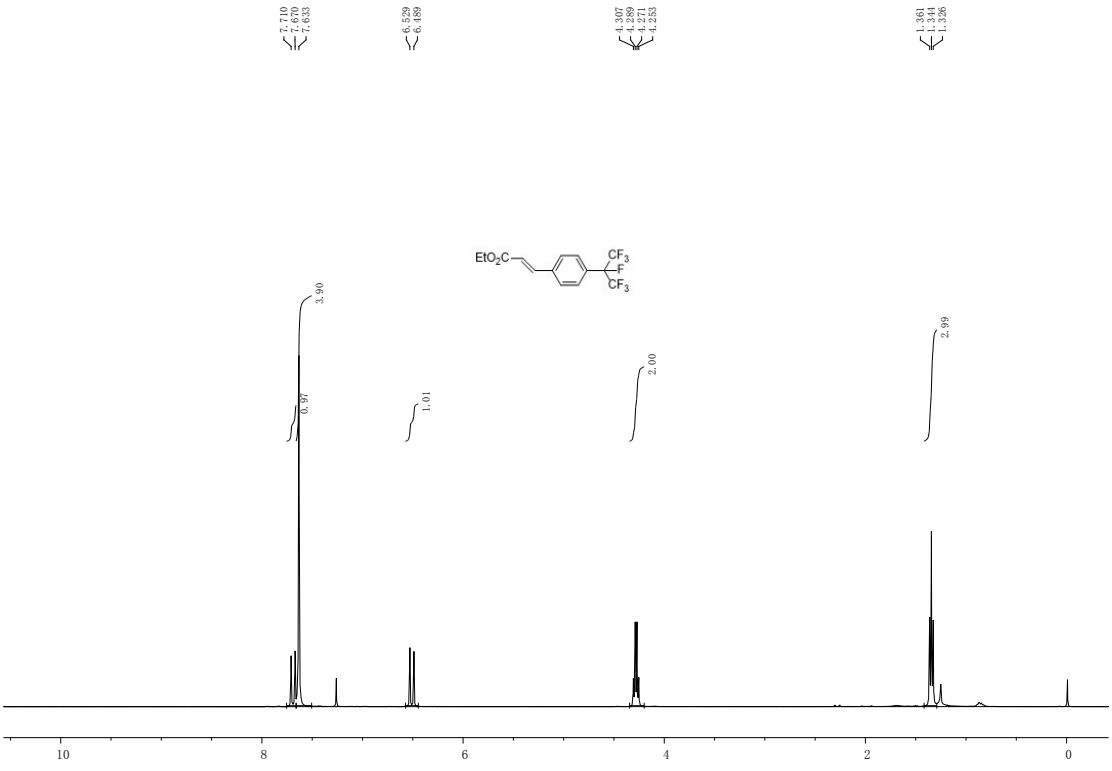
^{19}F NMR (376 MHz, $CDCl_3$) spectrum of N-(4-(perfluoropropan-2-yl)phenyl)acetamide 3g



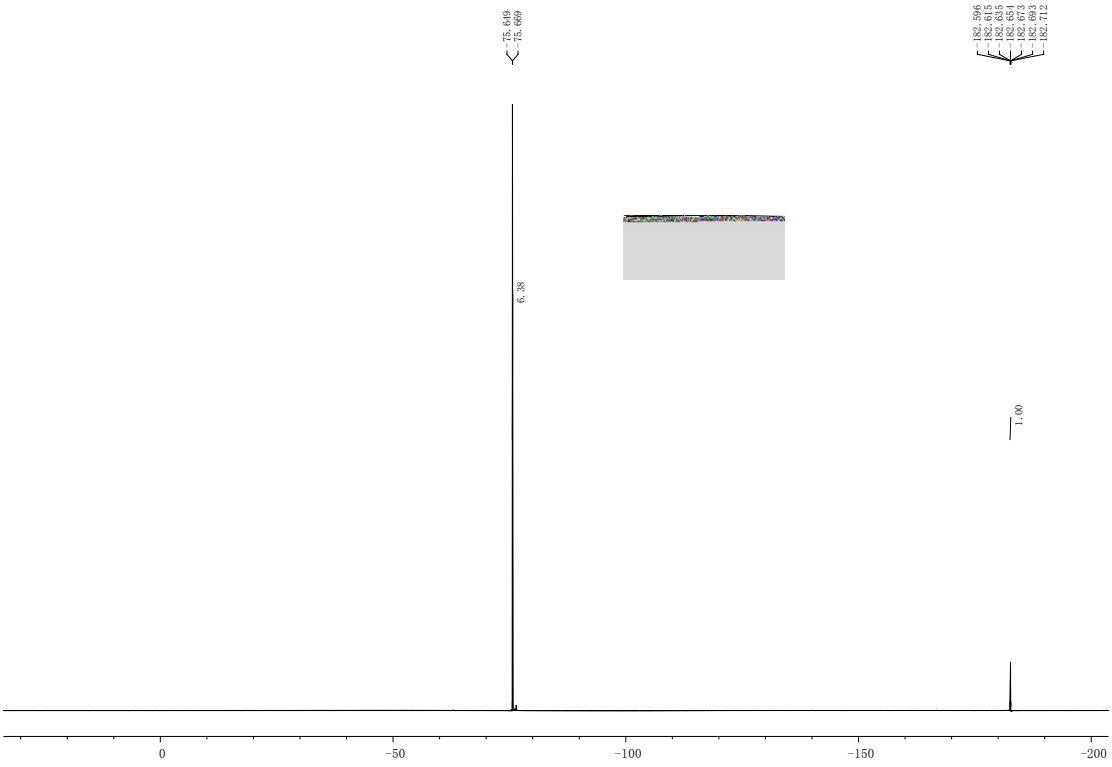
^{13}C NMR (101 MHz, $CDCl_3$) spectrum of N-(4-(perfluoropropan-2-yl)phenyl)acetamide 3g



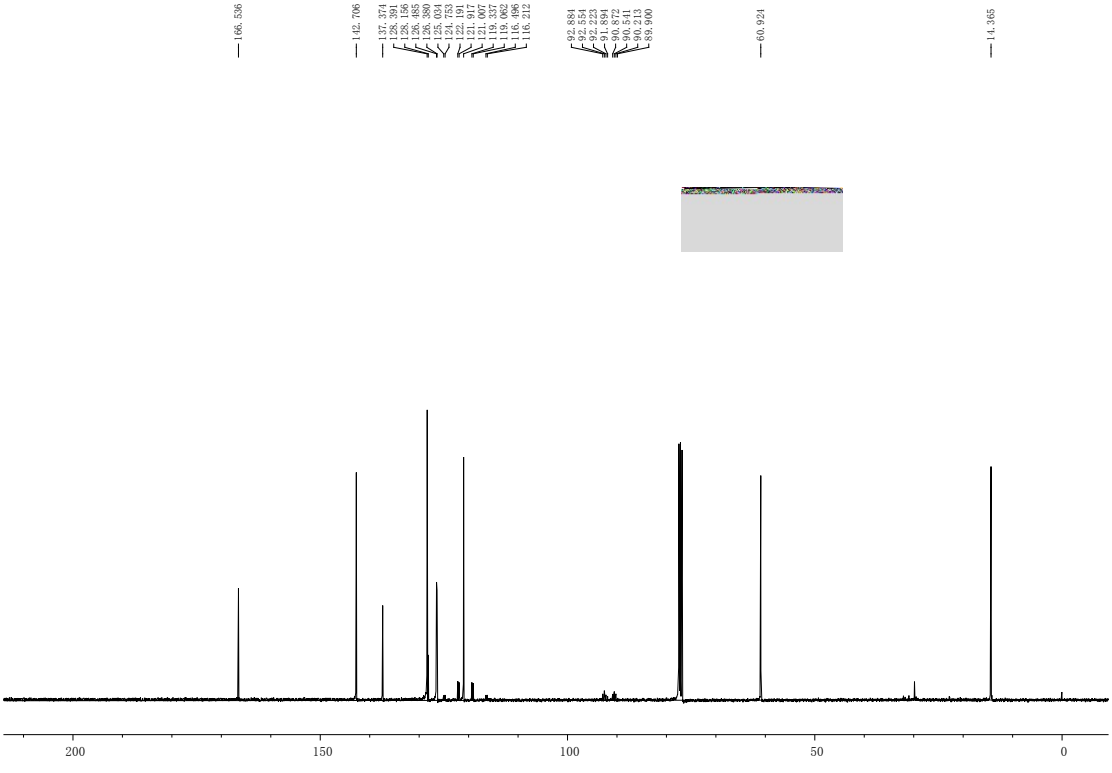
^{1}H NMR (400 MHz, $CDCl_3$) spectrum of (E)-ethyl 3-(4-(perfluoropropan-2-yl)phenyl)acrylate 3h



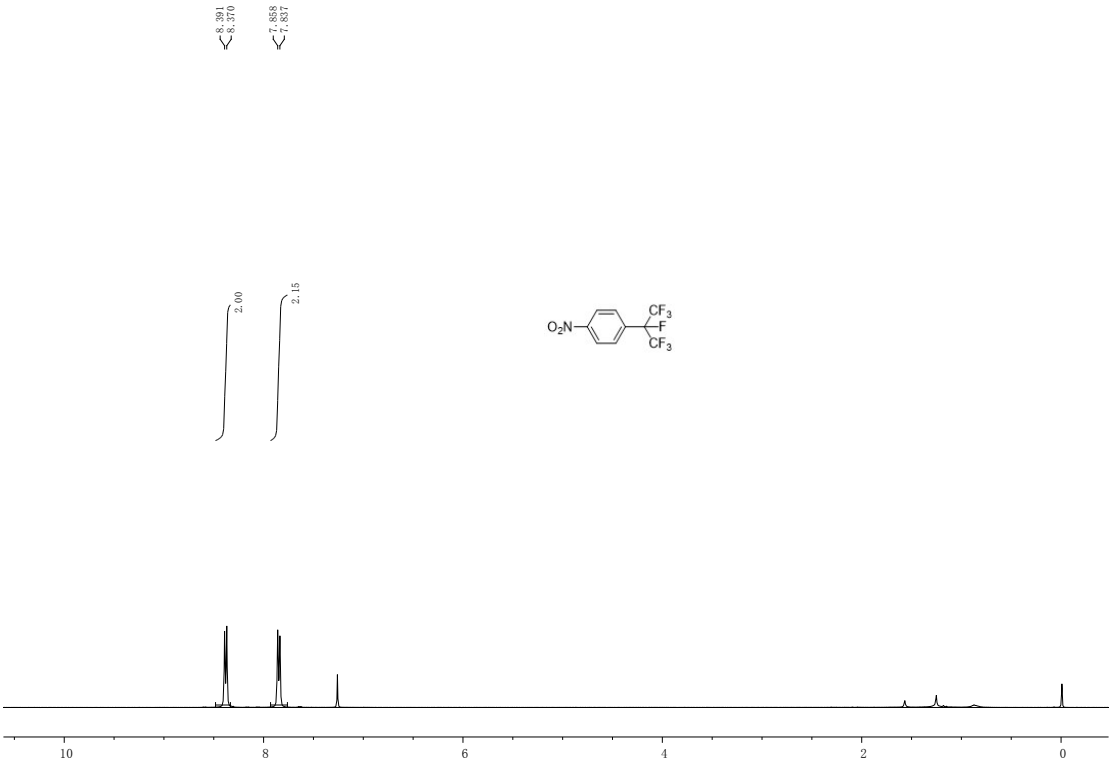
^{19}F NMR (376 MHz, $CDCl_3$) spectrum of (E)-ethyl 3-(4-(perfluoropropan-2-yl)phenyl)acrylate 3h



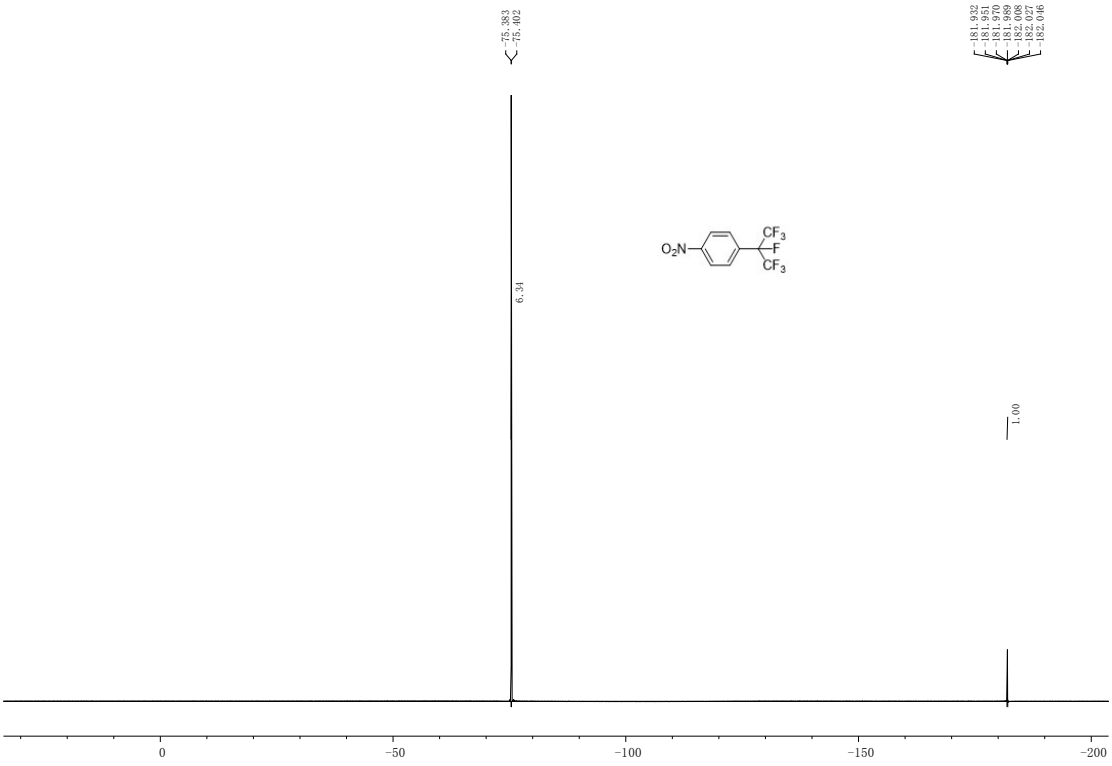
^{13}C NMR (101 MHz, $CDCl_3$) spectrum of 3-(4-(perfluoropropan-2-yl)phenyl)acrylate 3h



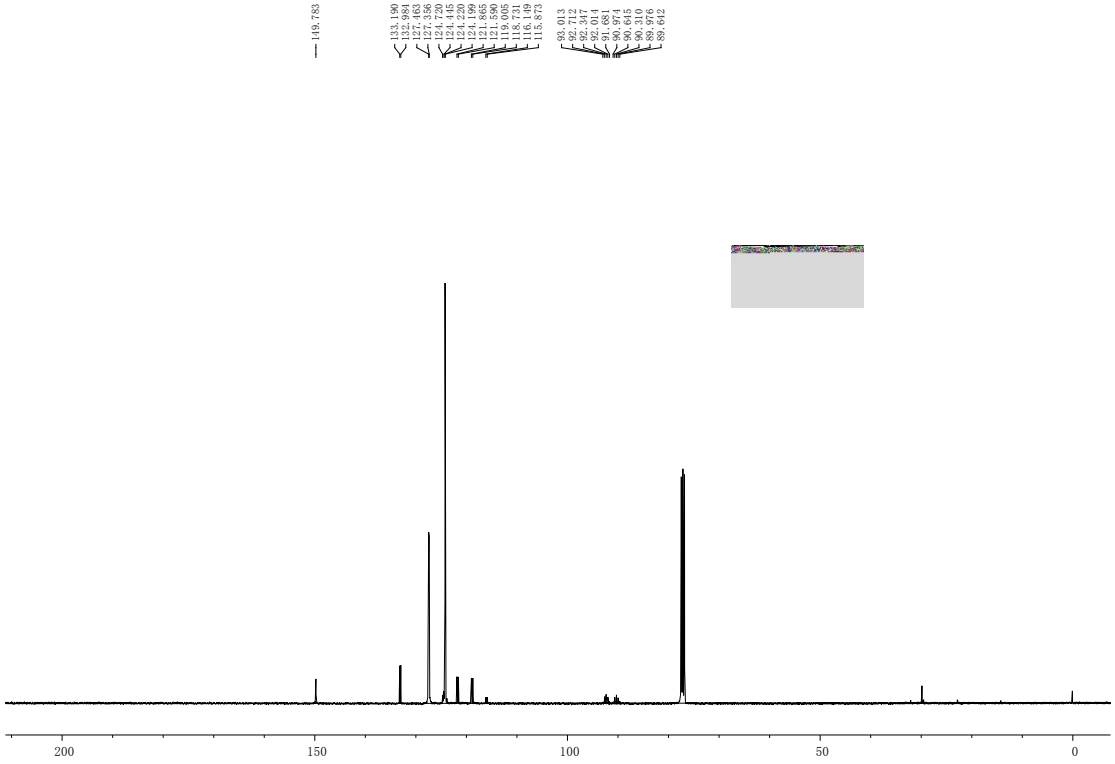
^{1}H NMR (400 MHz, $CDCl_3$) spectrum of 1-nitro-4-(perfluoropropan-2-yl)benzene 3i



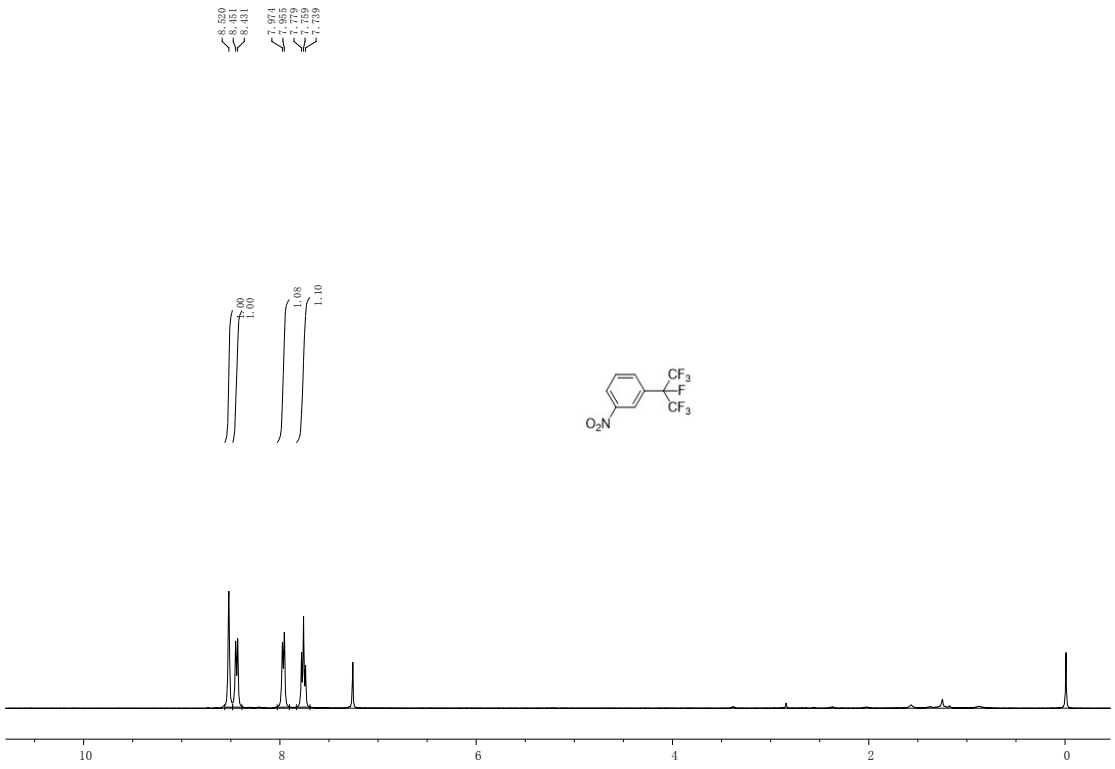
^{19}F NMR (376 MHz, $CDCl_3$) spectrum of 1-nitro-4-(perfluoropropan-2-yl)benzene 3i



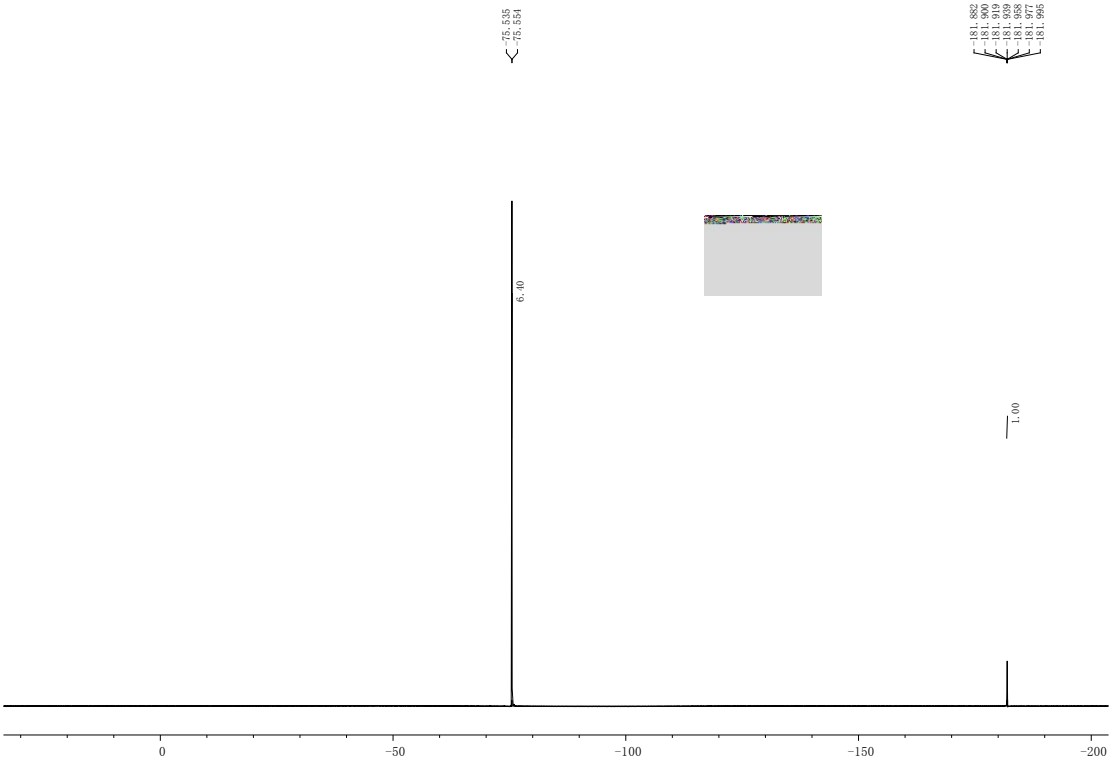
^{13}C NMR (101 MHz, $CDCl_3$) spectrum of 1-nitro-4-(perfluoropropan-2-yl)benzene 3i



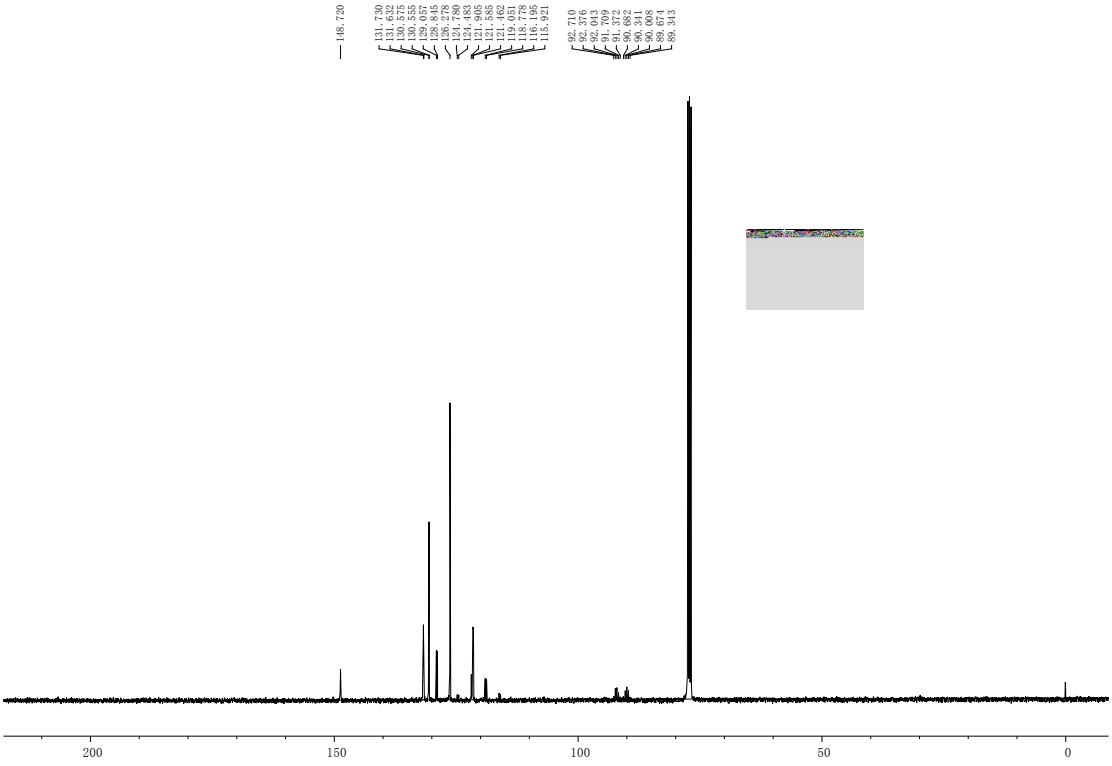
^{1}H NMR (400 MHz, $CDCl_3$) spectrum of 1-nitro-3-(perfluoropropan-2-yl)benzene 3j



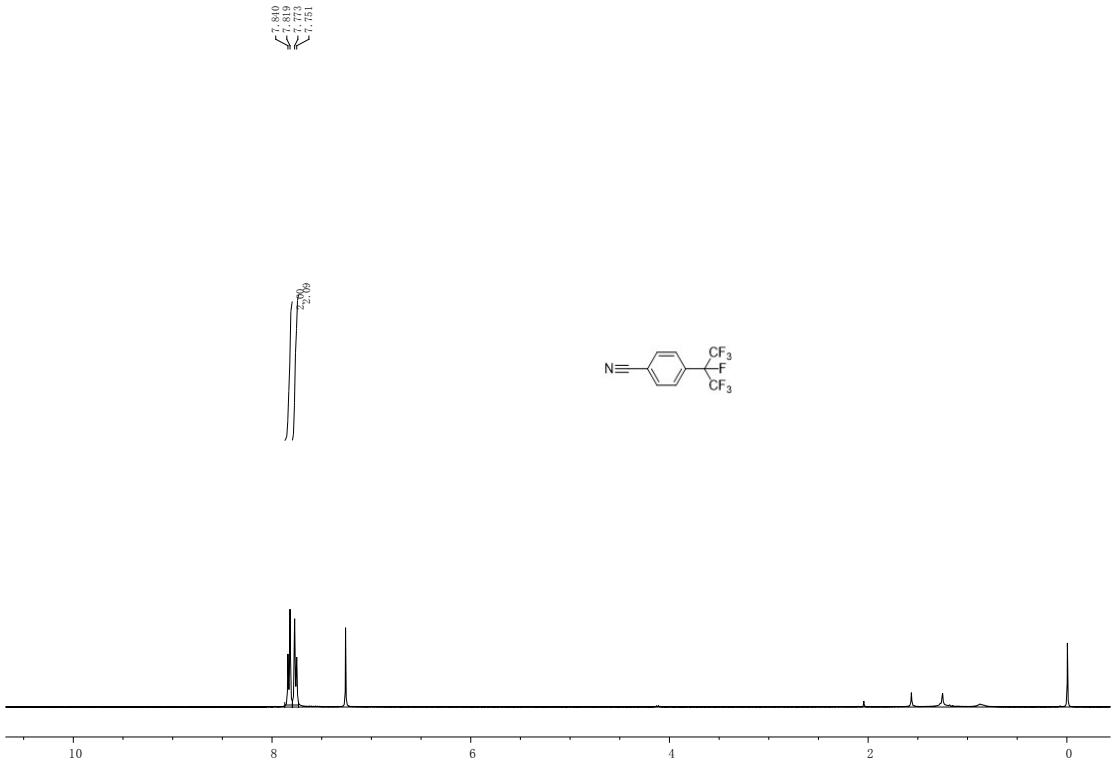
^{19}F NMR (376 MHz, $CDCl_3$) spectrum of 1-nitro-3-(perfluoropropan-2-yl)benzene 3j



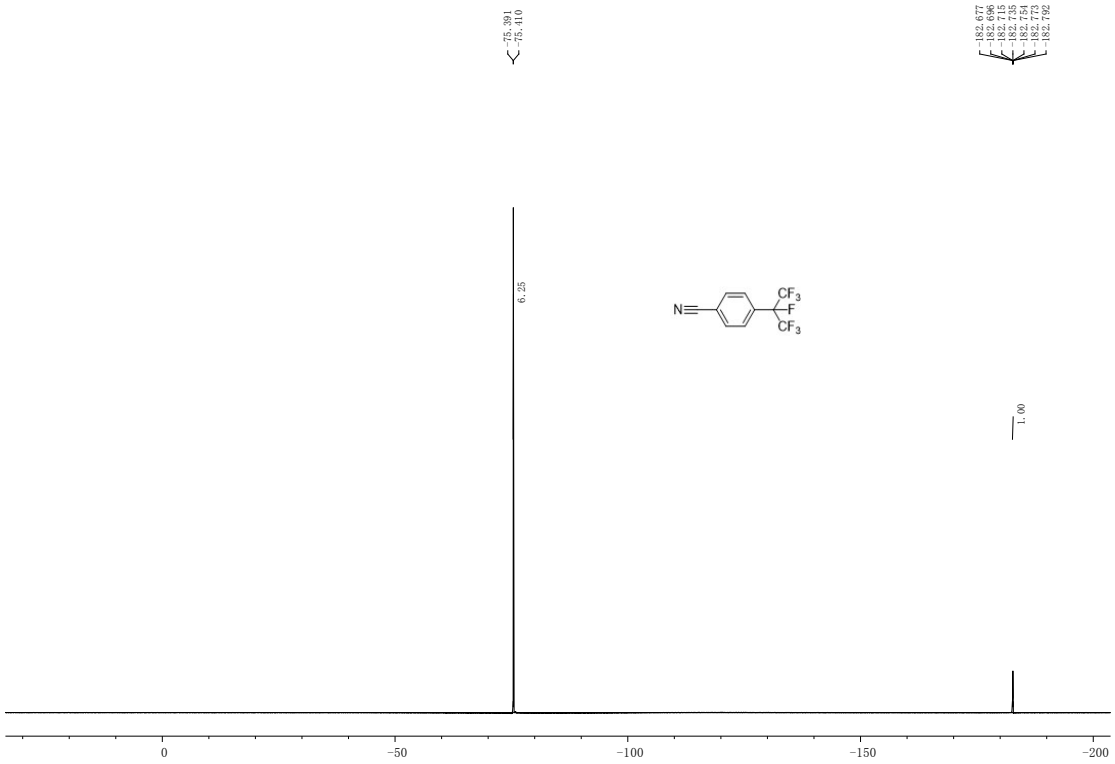
^{13}C NMR (101 MHz, $CDCl_3$) spectrum of 1-nitro-3-(perfluoropropan-2-yl)benzene 3j



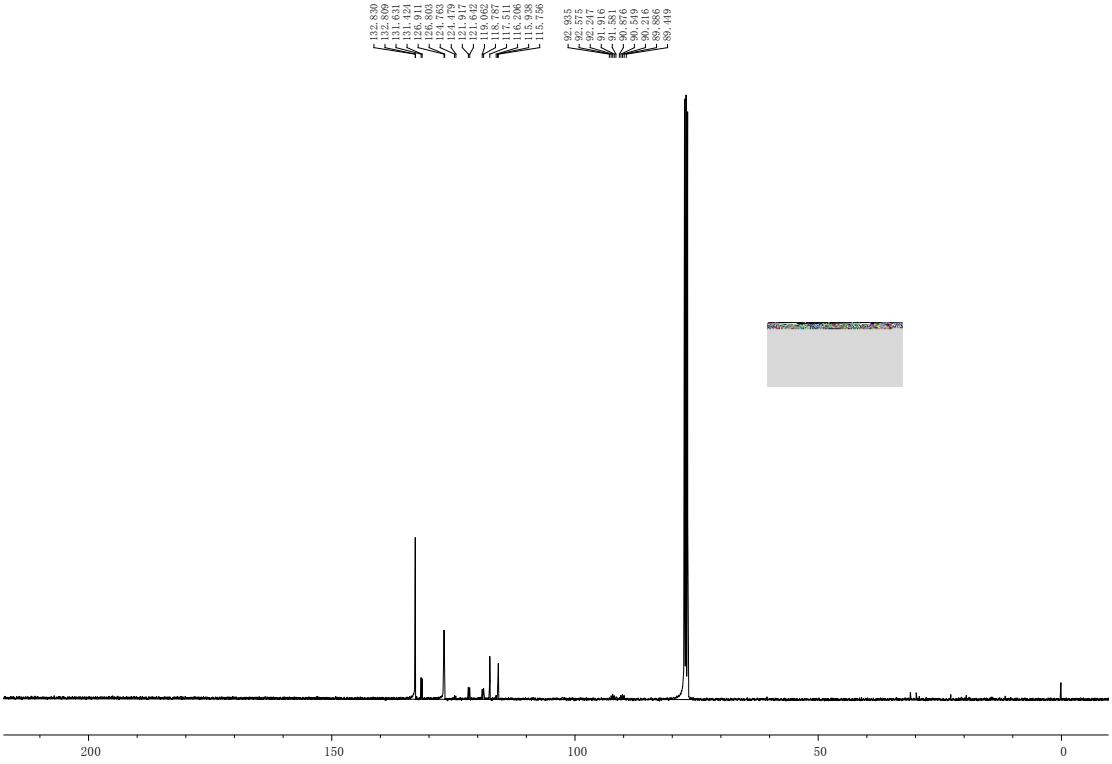
^{1}H NMR (400 MHz, $CDCl_3$) spectrum of 4-(perfluoropropan-2-yl)benzonitrile 3k



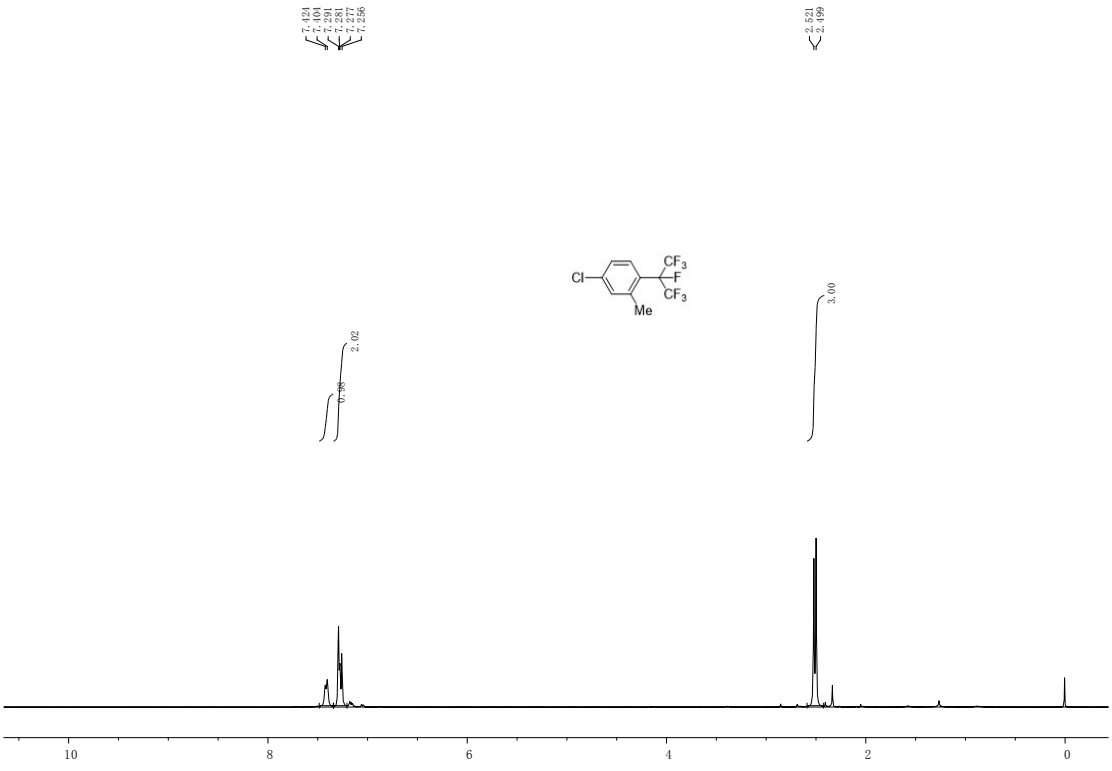
^{19}F NMR (376 MHz, $CDCl_3$) spectrum of 4-(perfluoropropan-2-yl)benzonitrile 3k



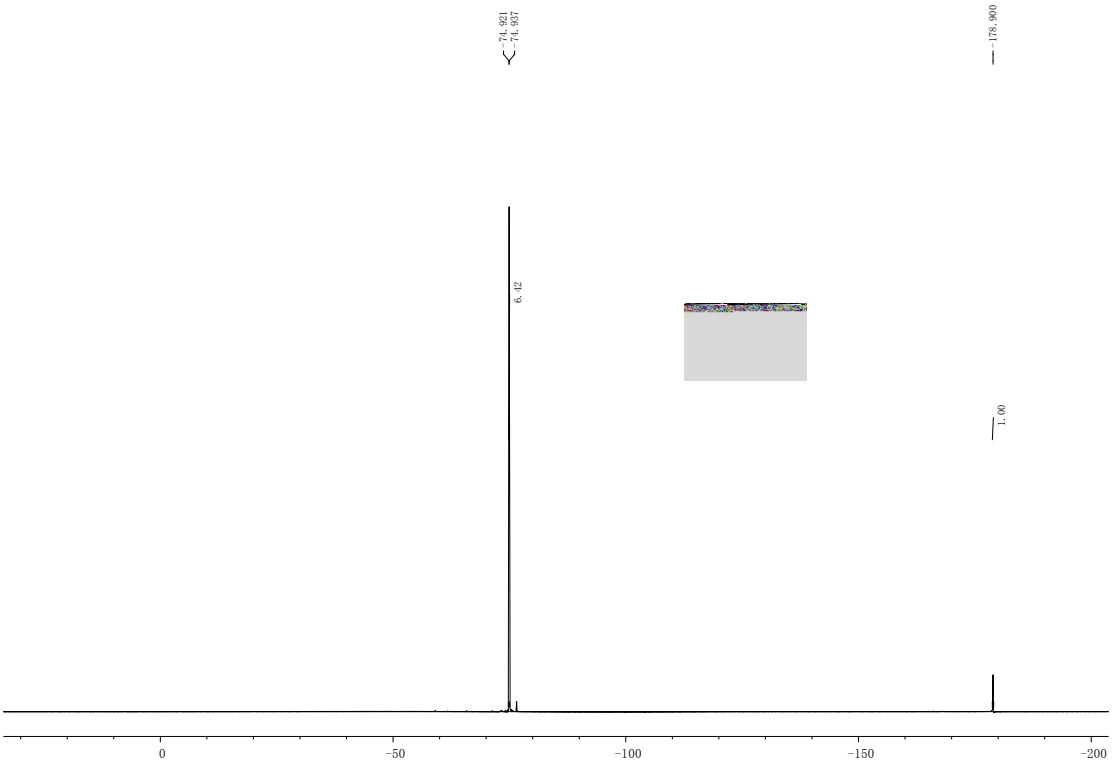
^{13}C NMR (101 MHz, $CDCl_3$) spectrum of 4-(perfluoropropan-2-yl)benzonitrile 3k



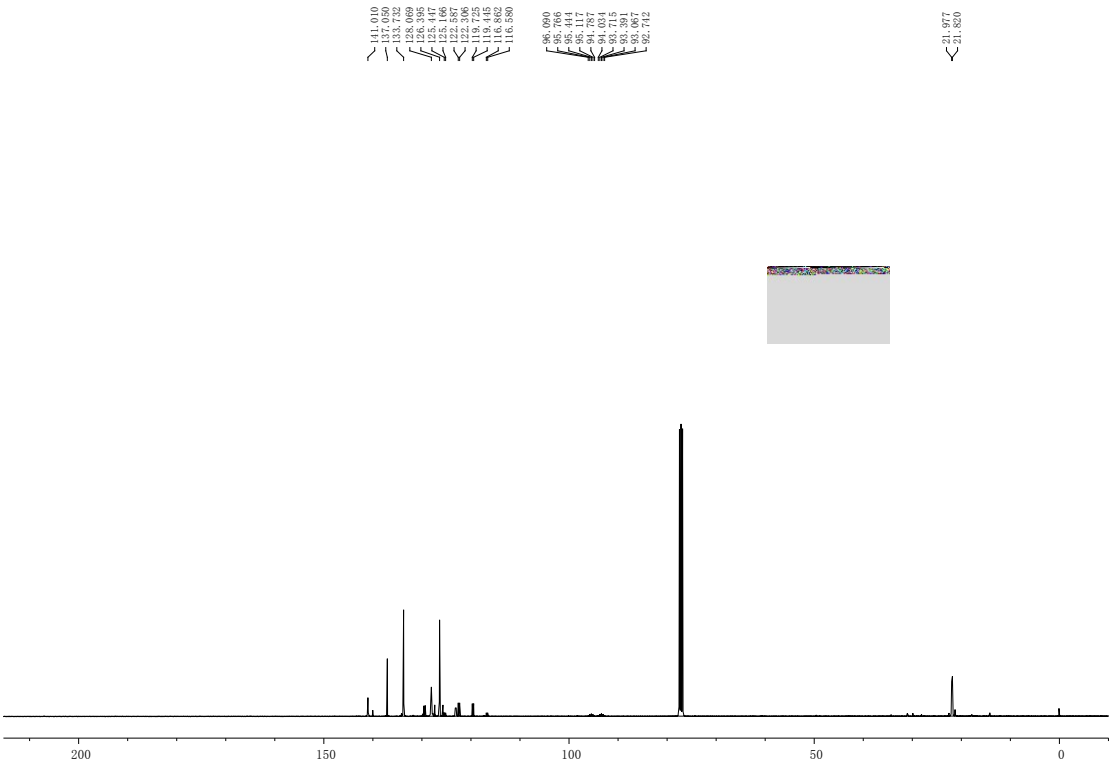
^{1}H NMR (400 MHz, $CDCl_3$) spectrum of 4-chloro-2-methyl-1-(perfluoropropan-2-yl)benzene 3m



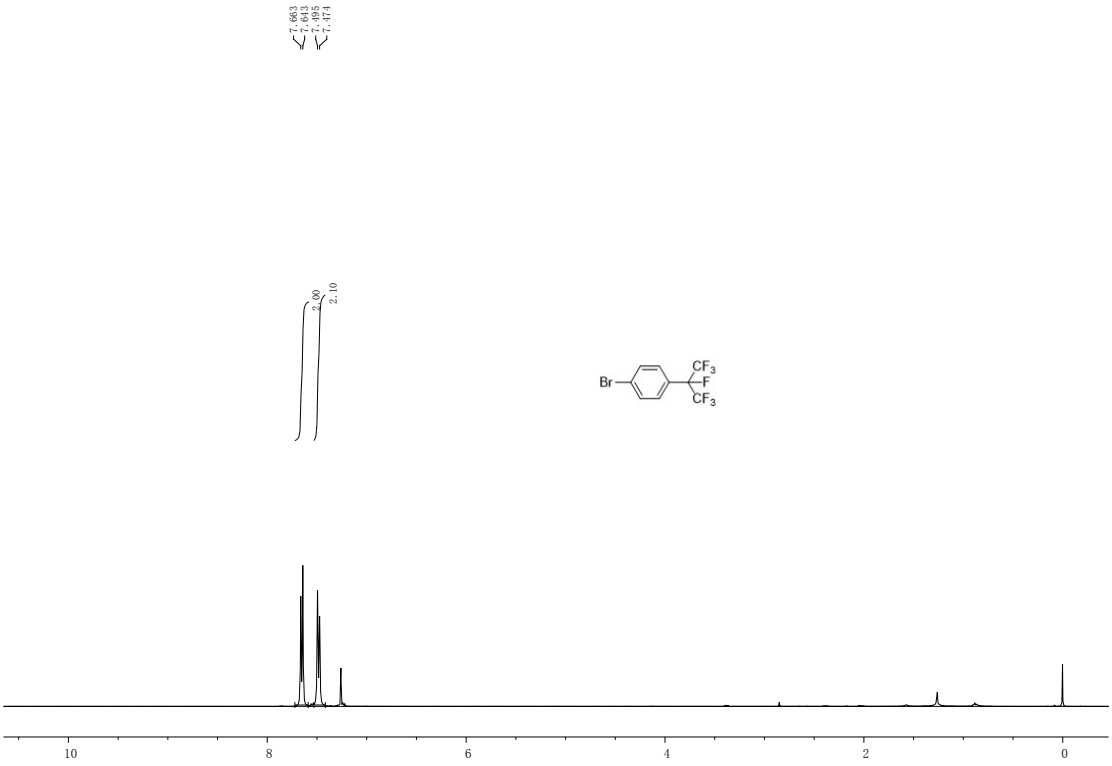
^{19}F NMR (376 MHz, $CDCl_3$) spectrum of 4-chloro-2-methyl-1-(perfluoropropan-2-yl)benzene 3m



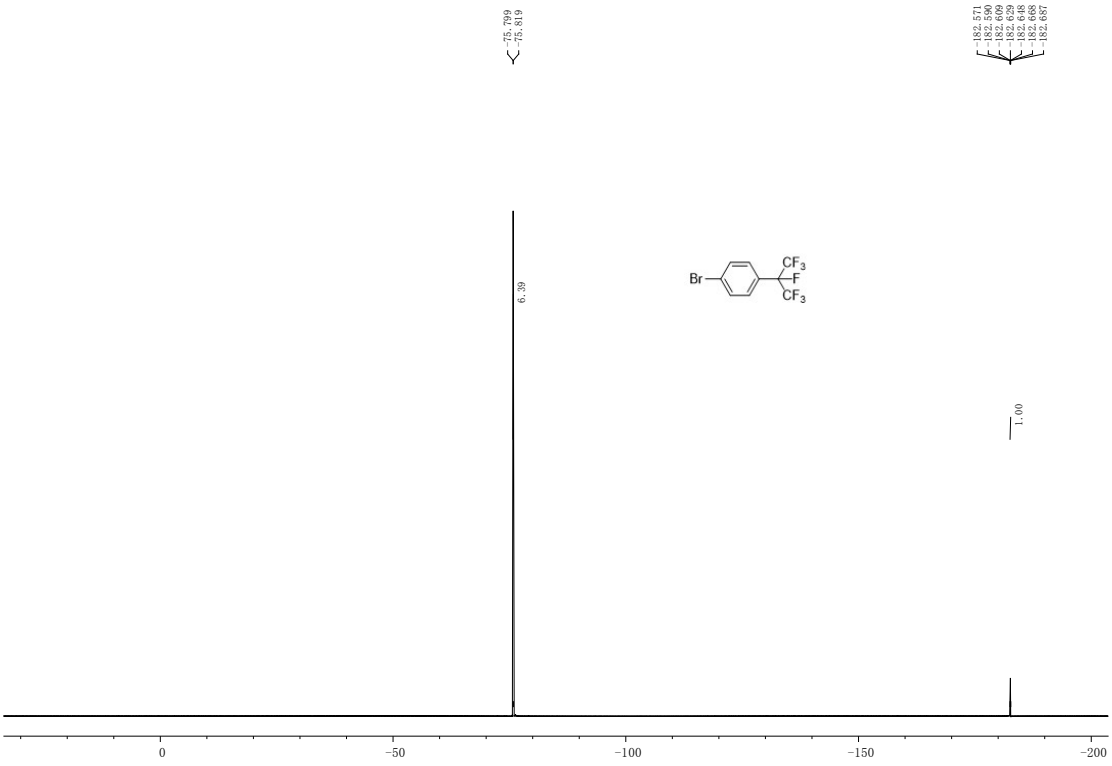
^{13}C NMR (101 MHz, $CDCl_3$) spectrum of 4-chloro-2-methyl-1-(perfluoropropan-2-yl)benzene 3m



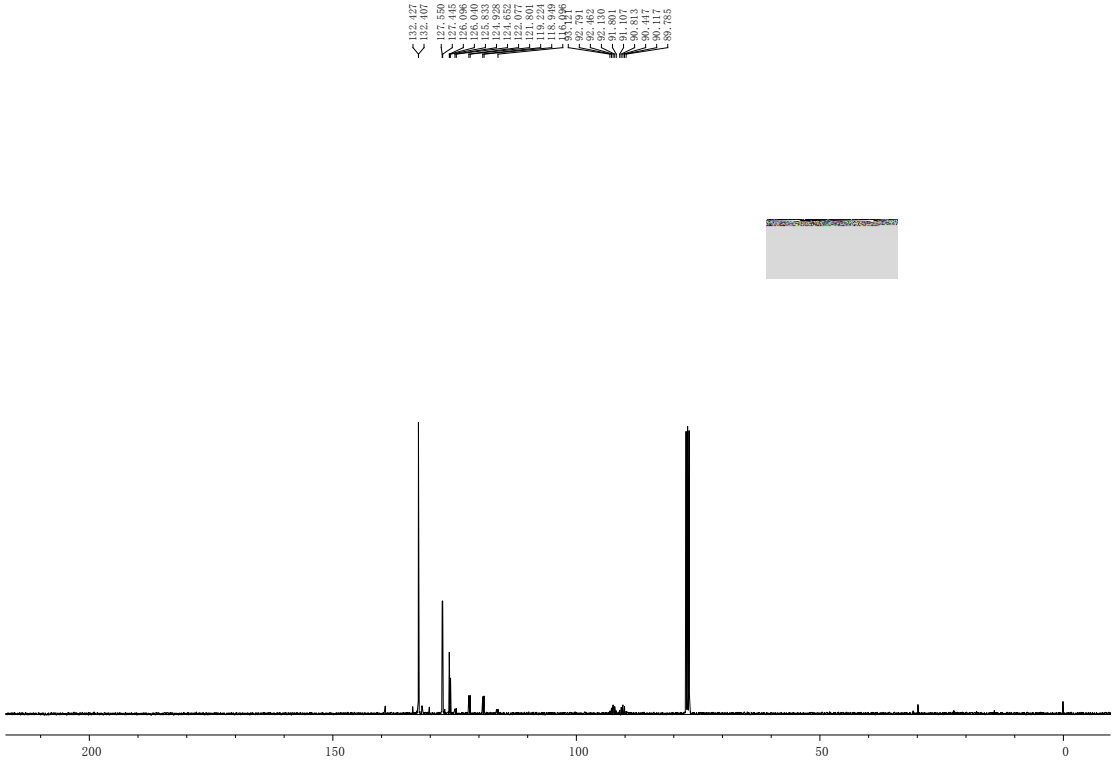
^{1}H NMR (400 MHz, $CDCl_3$) spectrum of 1-bromo-4-(perfluoropropan-2-yl)benzene 3n



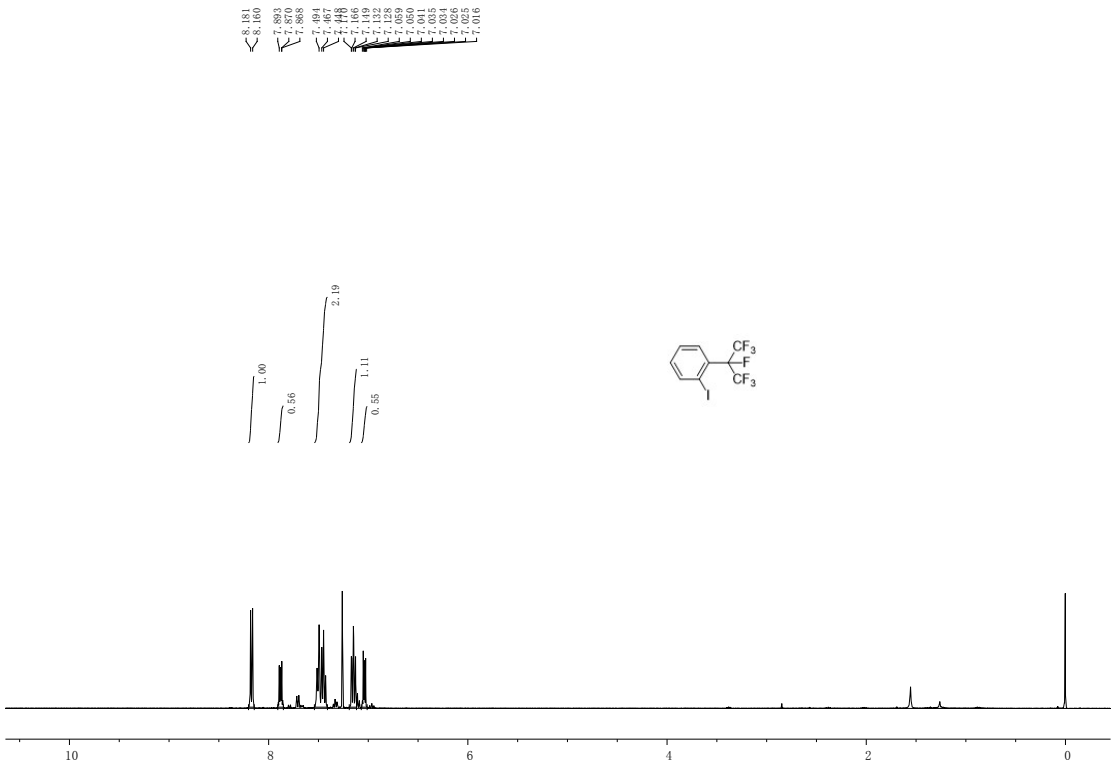
^{19}F NMR (376 MHz, $CDCl_3$) spectrum of 1-bromo-4-(perfluoropropan-2-yl)benzene 3n



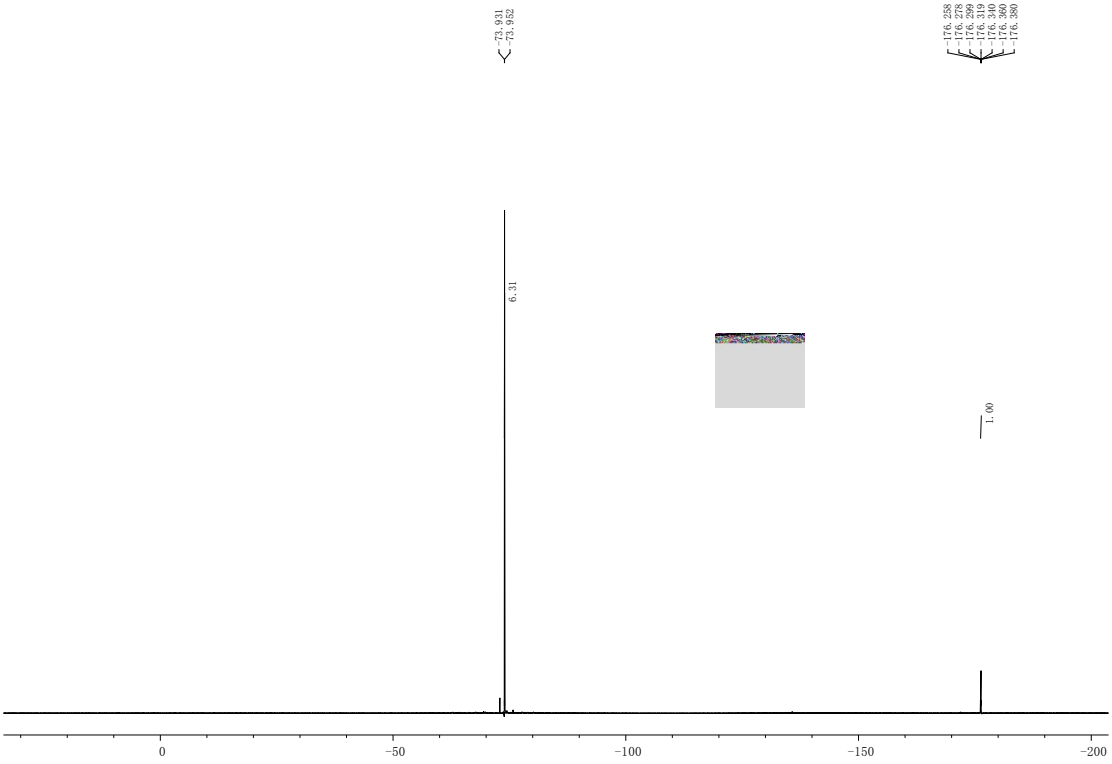
^{13}C NMR (101 MHz, $CDCl_3$) spectrum of 1-bromo-4-(perfluoropropan-2-yl)benzene 3n



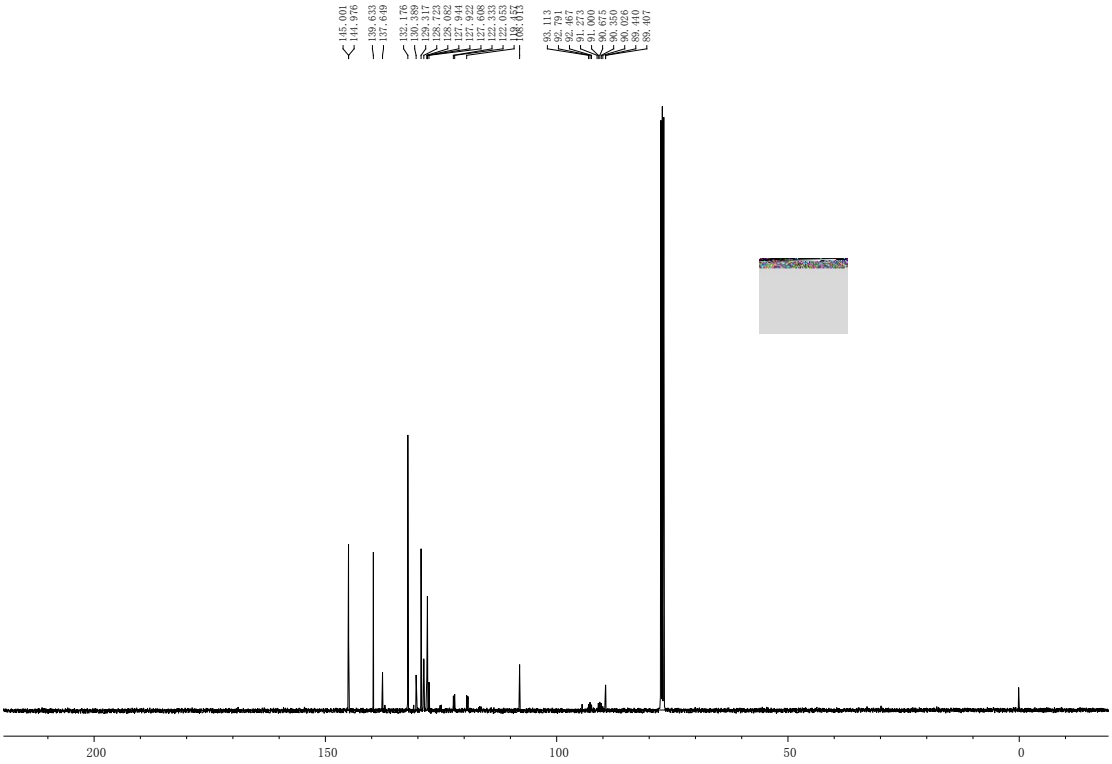
^{1}H NMR (400 MHz, $CDCl_3$) spectrum of 1-iodo-2-(perfluoropropan-2-yl)benzene 3o



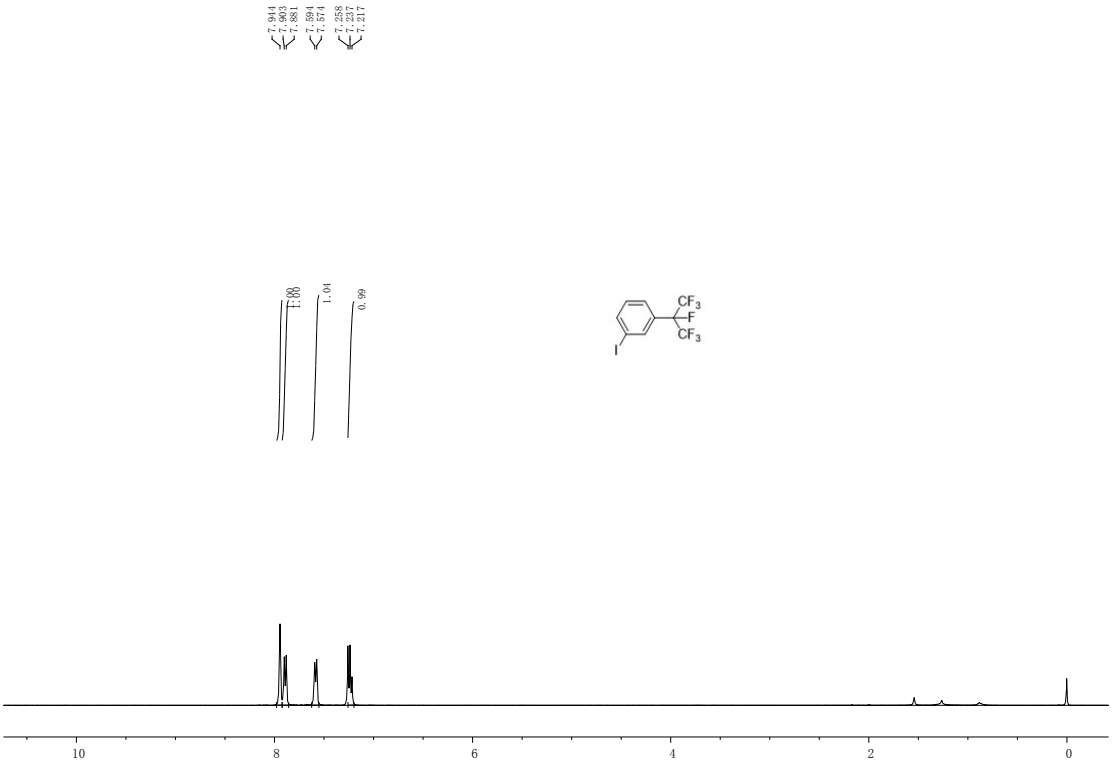
^{19}F NMR (376 MHz, $CDCl_3$) spectrum of 1-iodo-2-(perfluoropropan-2-yl)benzene 3o



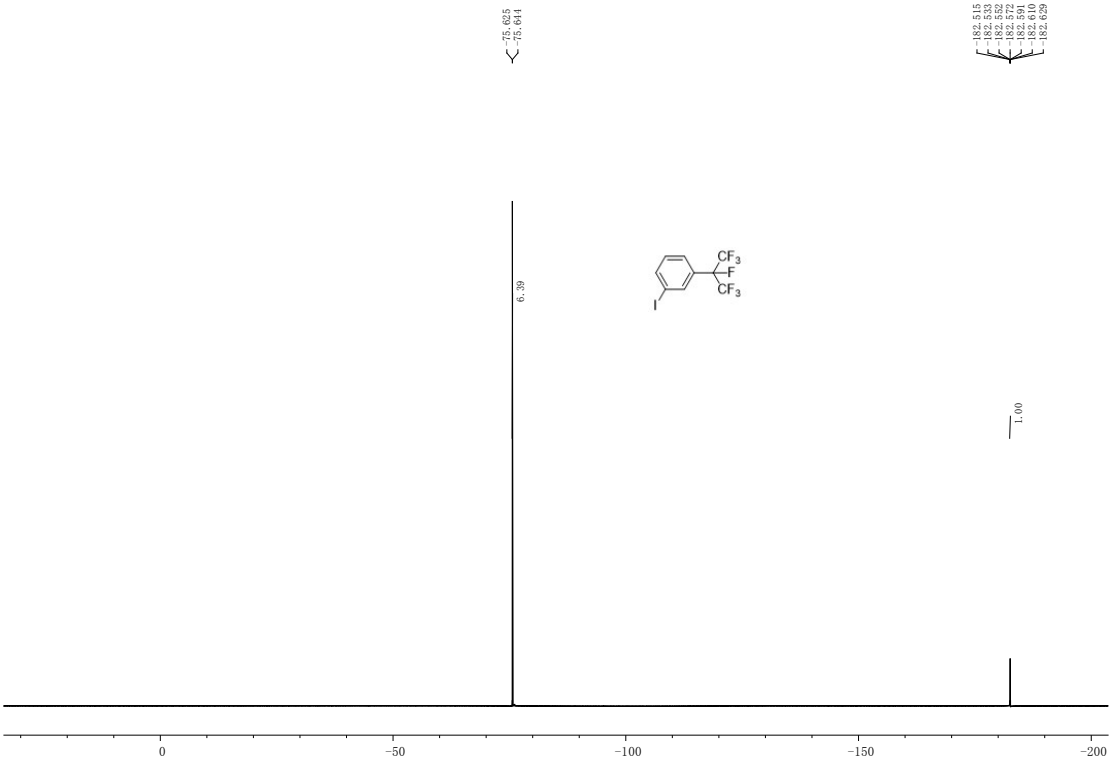
^{13}C NMR (101 MHz, $CDCl_3$) spectrum of 1-iodo-2-(perfluoropropan-2-yl)benzene 3o



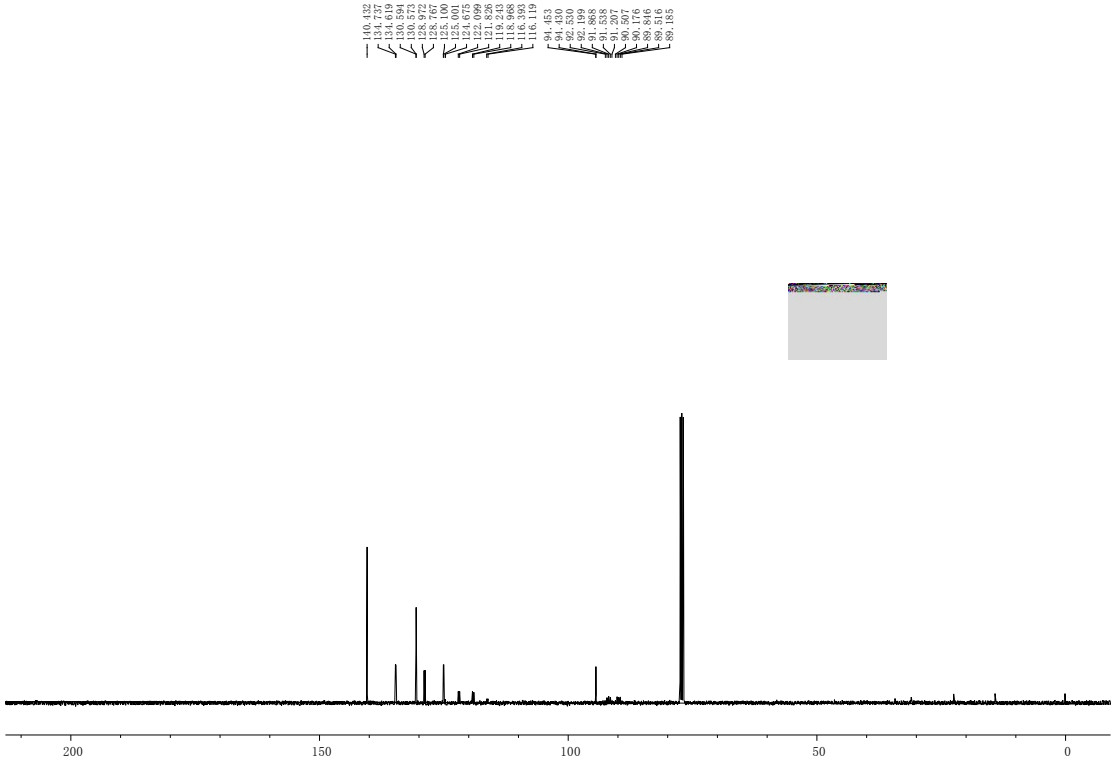
^{1}H NMR (400 MHz, $CDCl_3$) spectrum of 1-iodo-3-(perfluoropropan-2-yl)benzene 3p



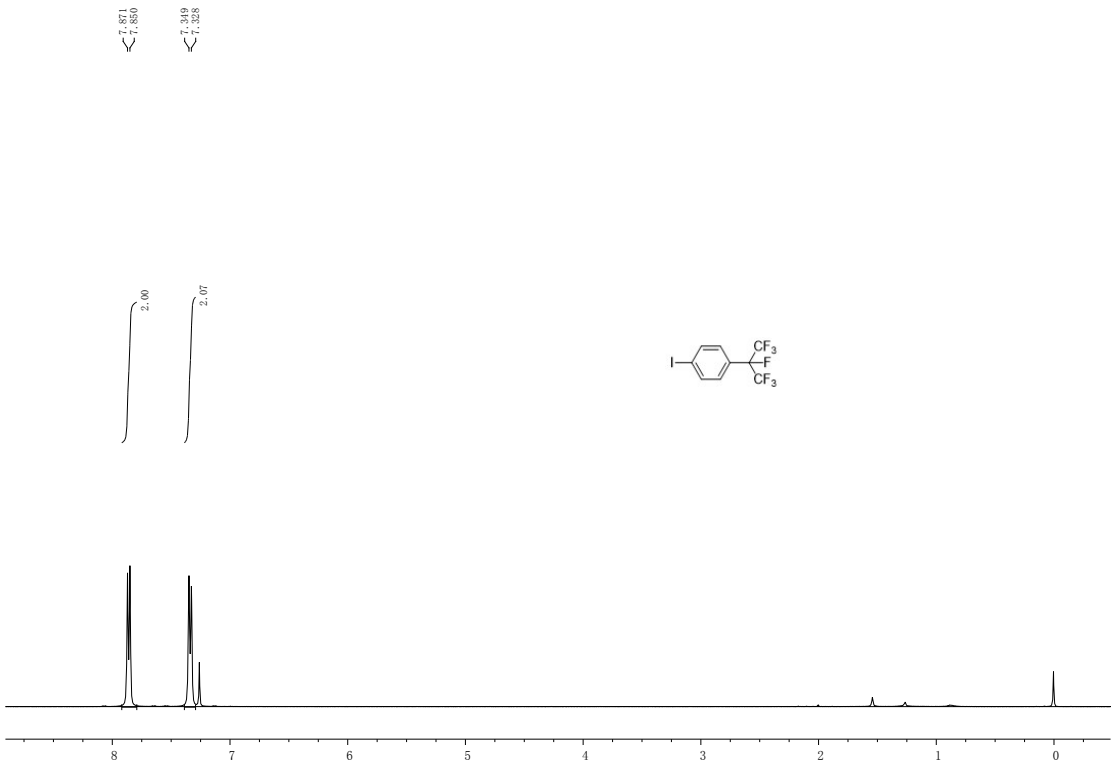
^{19}F NMR (376 MHz, $CDCl_3$) spectrum of 1-iodo-3-(perfluoropropan-2-yl)benzene 3p



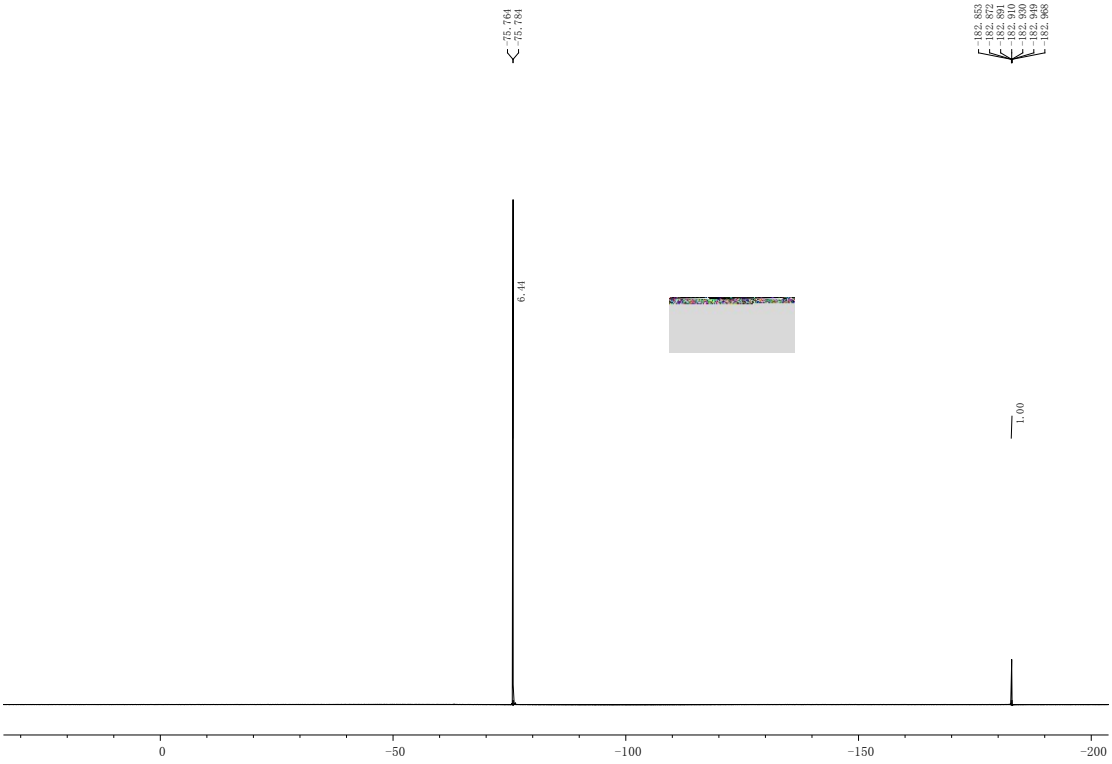
^{13}C NMR (101 MHz, $CDCl_3$) spectrum of 1-iodo-3-(perfluoropropan-2-yl)benzene 3p



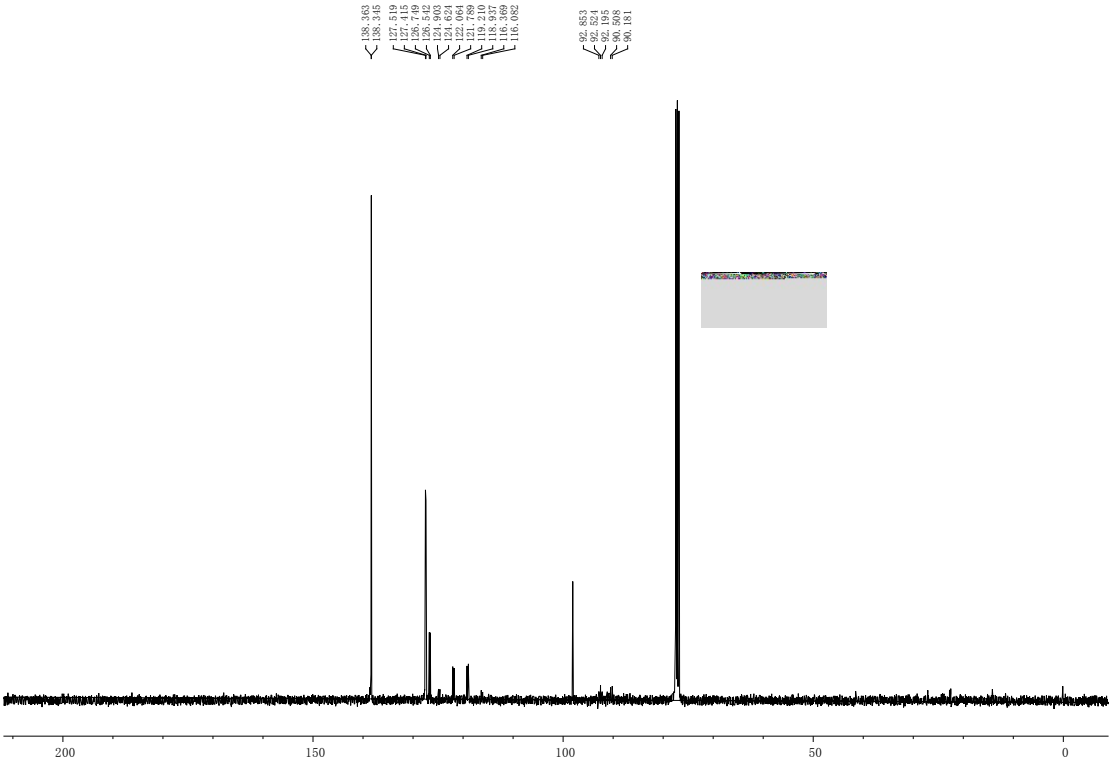
^{1}H NMR (400 MHz, $CDCl_3$) spectrum of 1-iodo-4-(perfluoropropan-2-yl)benzene 3q



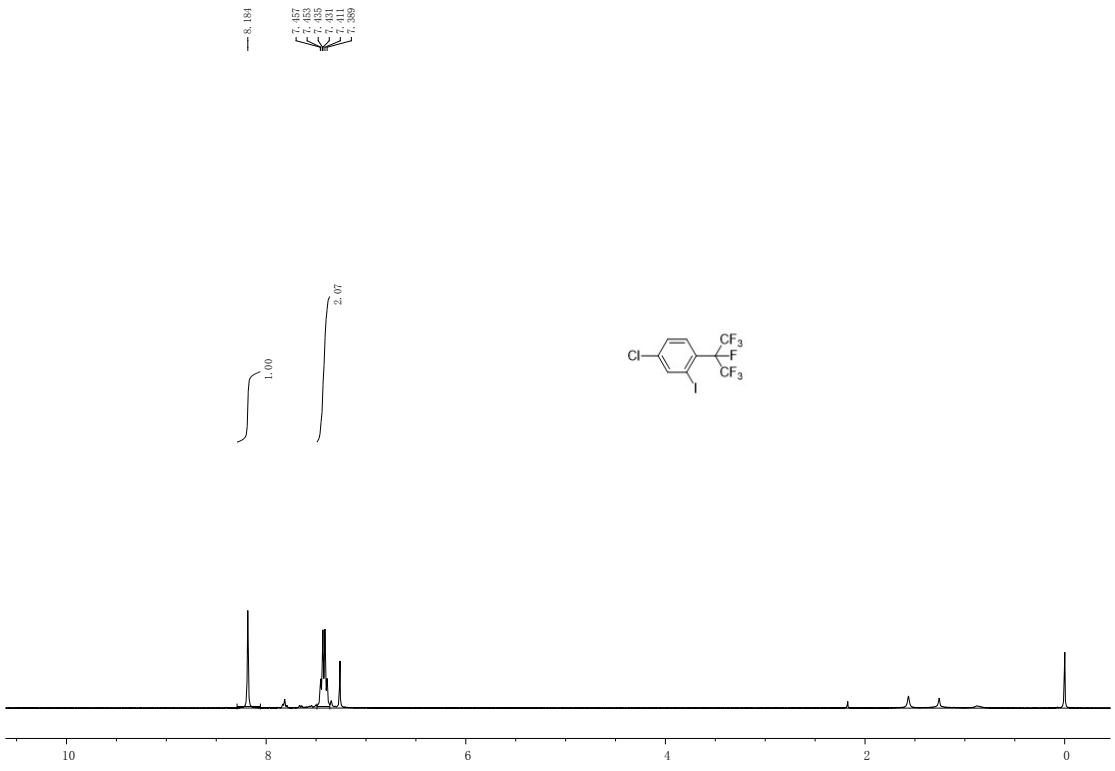
^{19}F NMR (376 MHz, $CDCl_3$) spectrum of 1-iodo-4-(perfluoropropan-2-yl)benzene 3q



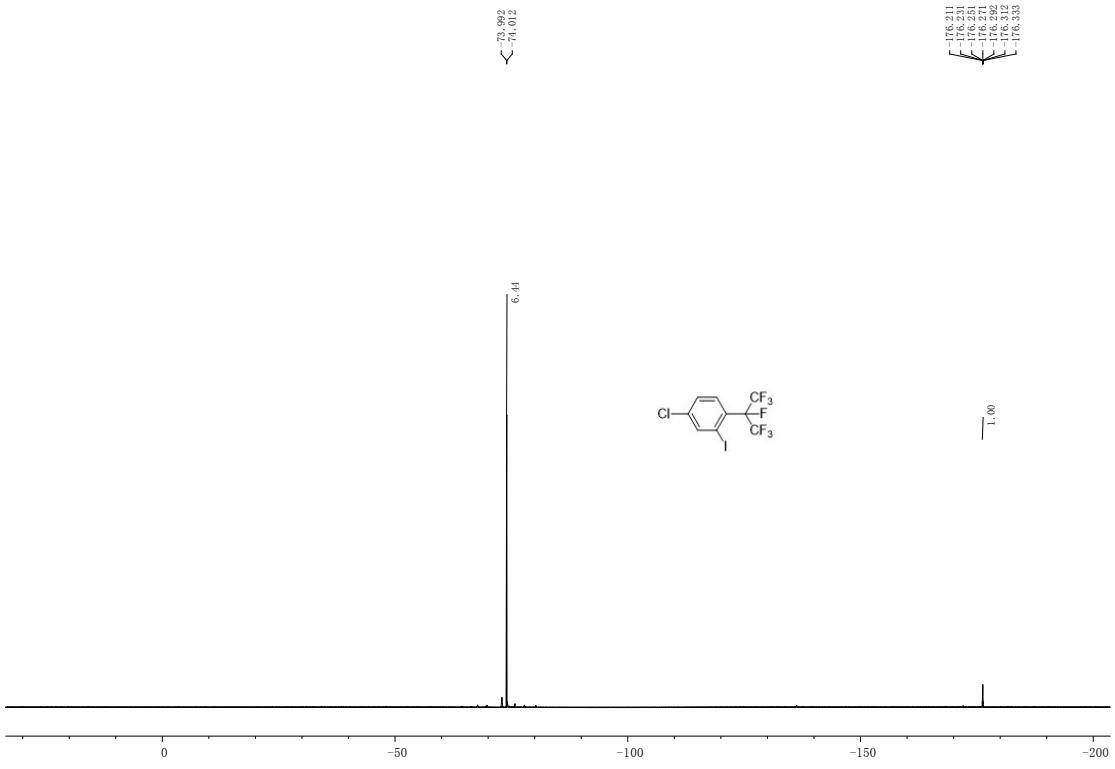
^{13}C NMR (101 MHz, $CDCl_3$) spectrum of 1-iodo-4-(perfluoropropan-2-yl)benzene 3q



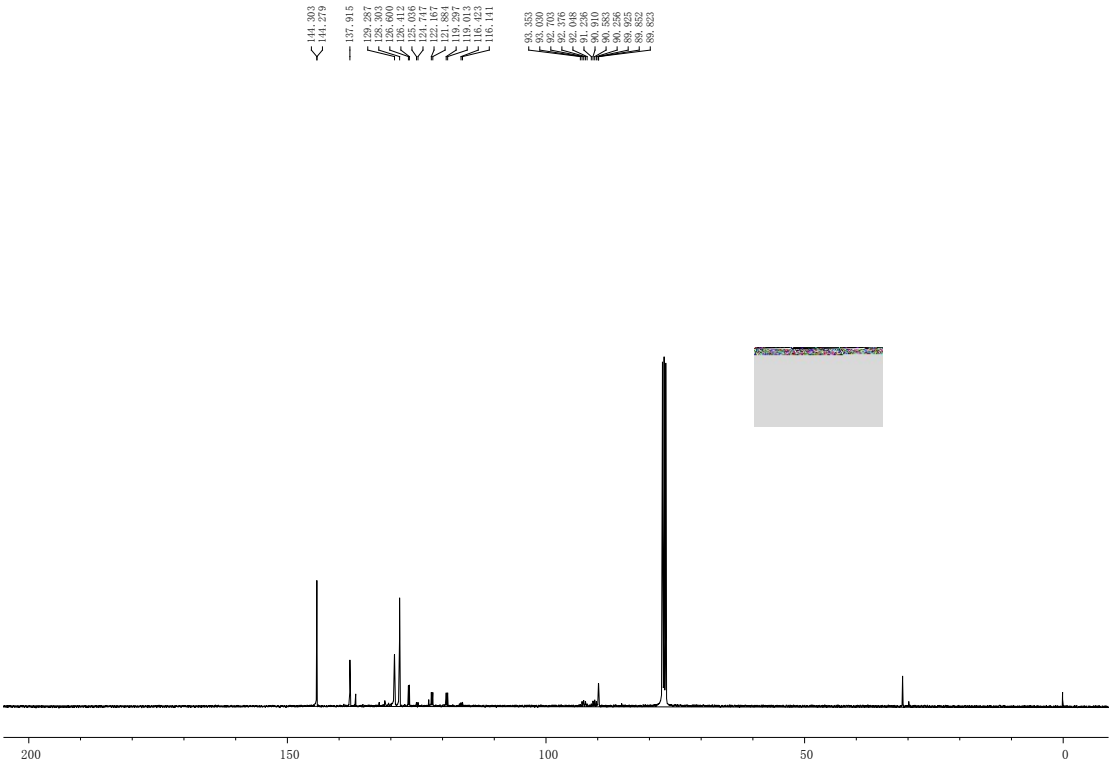
^{1}H NMR (400 MHz, $CDCl_3$) spectrum of 4-chloro-2-iodo-1-(perfluoropropan-2-yl)benzene 3r



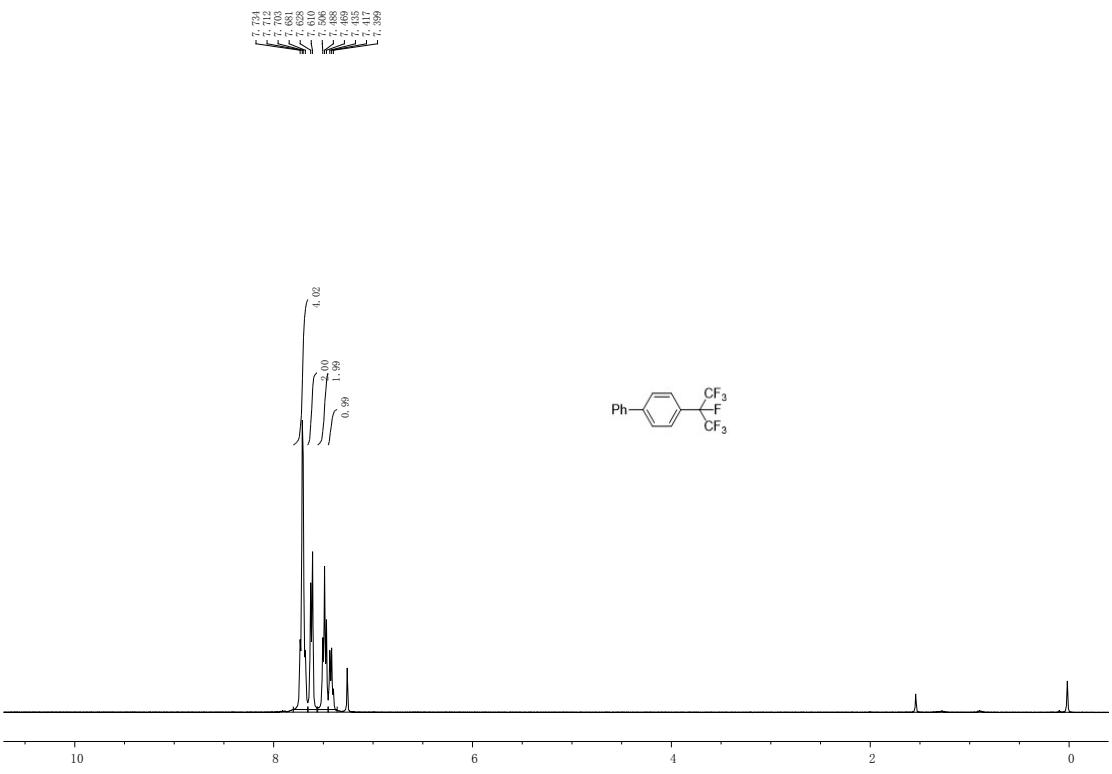
^{19}F NMR (376 MHz, $CDCl_3$) spectrum of 4-chloro-2-iodo-1-(perfluoropropan-2-yl)benzene 3r



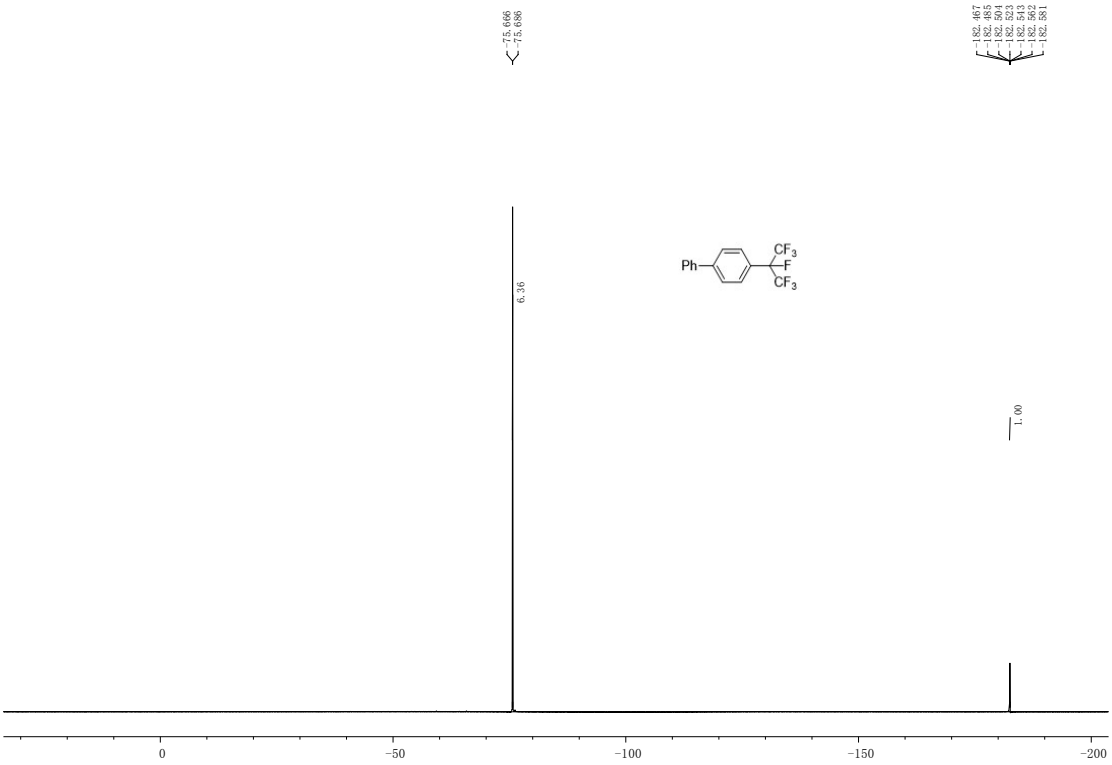
^{13}C NMR (101 MHz, $CDCl_3$) spectrum of 4-chloro-2-iodo-1-(perfluoropropan-2-yl)benzene 3r



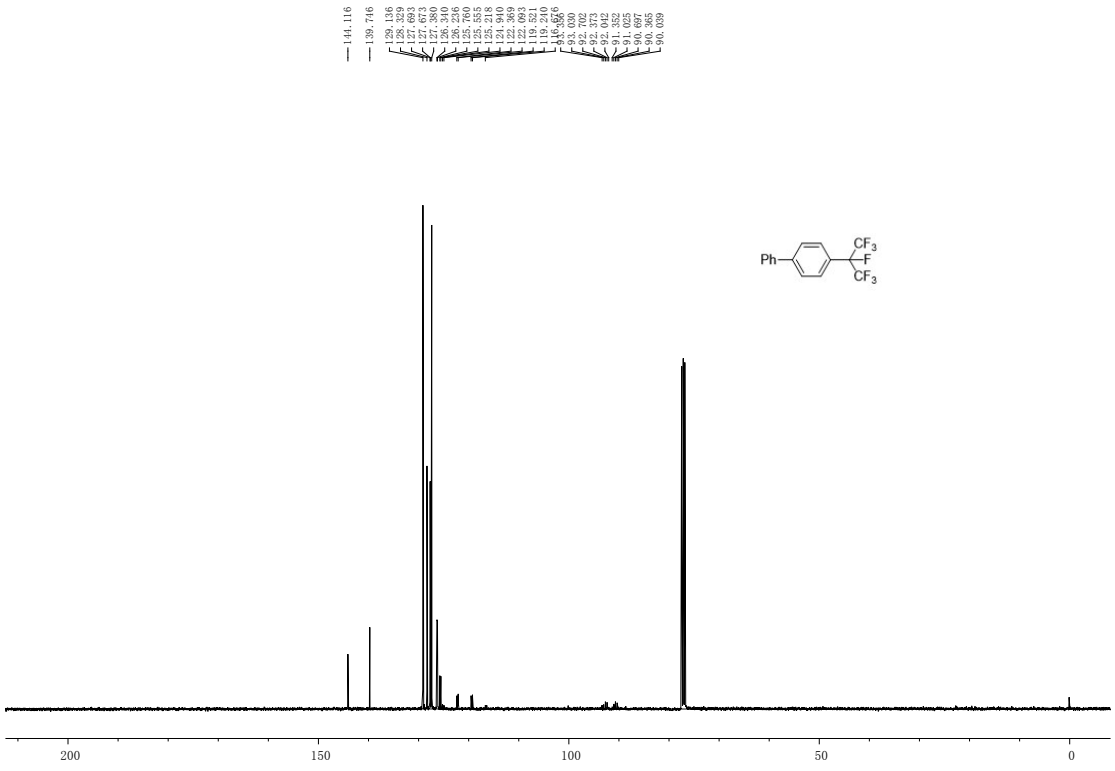
^{1}H NMR (400 MHz, $CDCl_3$) spectrum of 4-(perfluoropropan-2-yl)-1,1'-biphenyl 3s



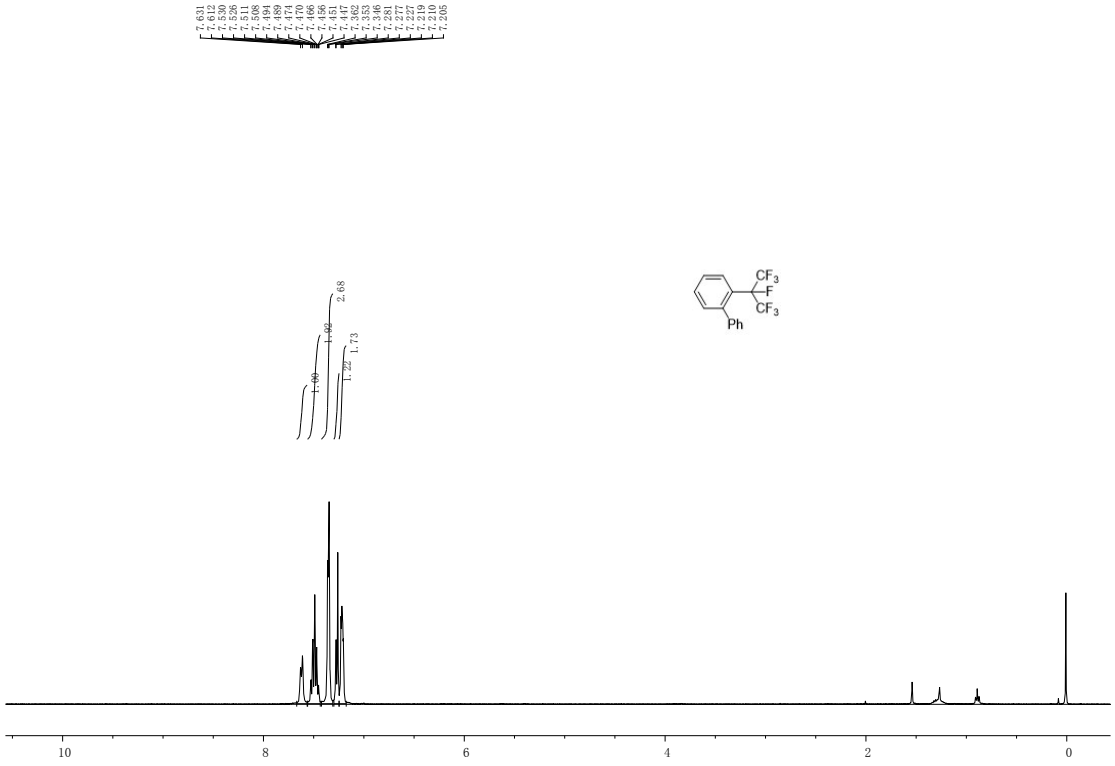
^{19}F NMR (376 MHz, $CDCl_3$) spectrum of 4-(perfluoropropan-2-yl)-1,1'-biphenyl 3s



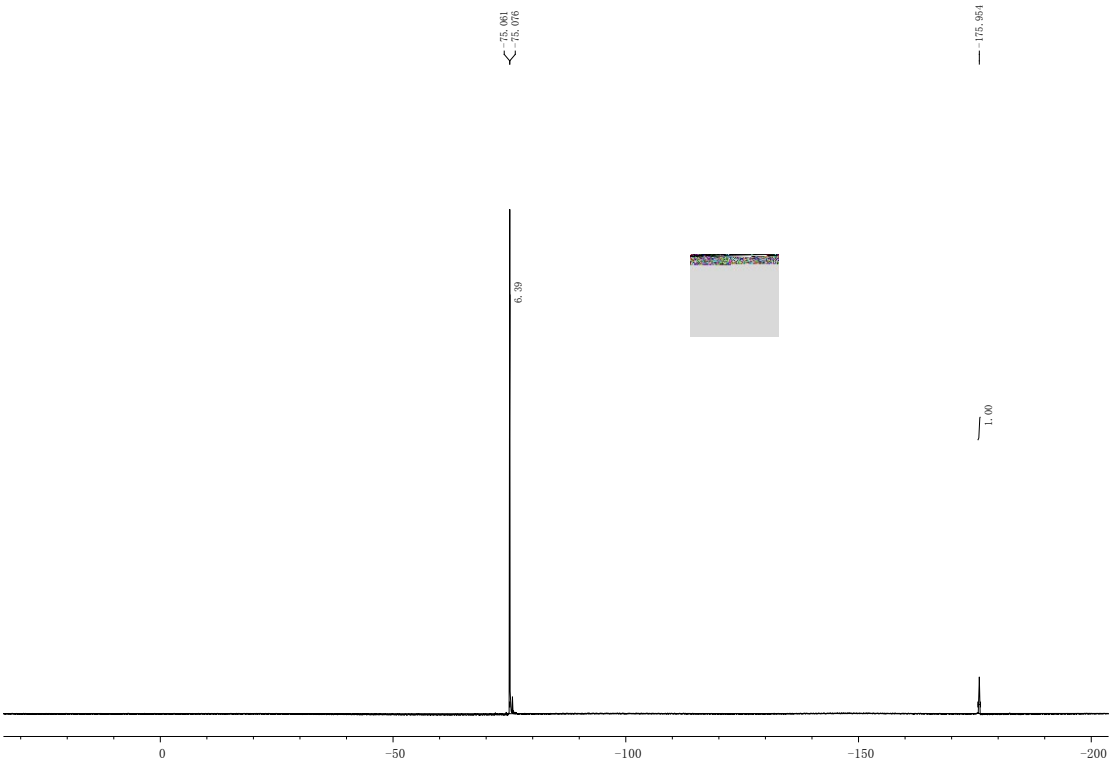
^{13}C NMR (101 MHz, $CDCl_3$) spectrum of 4-(perfluoropropan-2-yl)-1,1'-biphenyl 3s



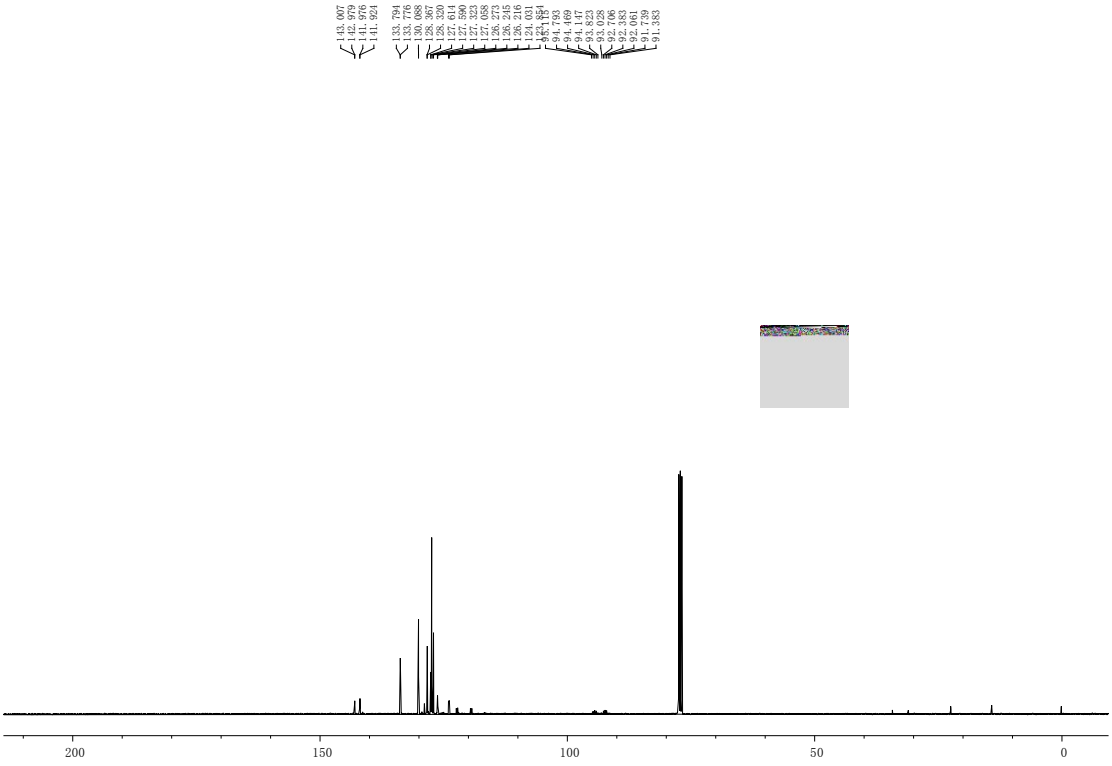
^{1}H NMR (400 MHz, $CDCl_3$) spectrum of 2-(perfluoropropan-2-yl)-1,1'-biphenyl 3t



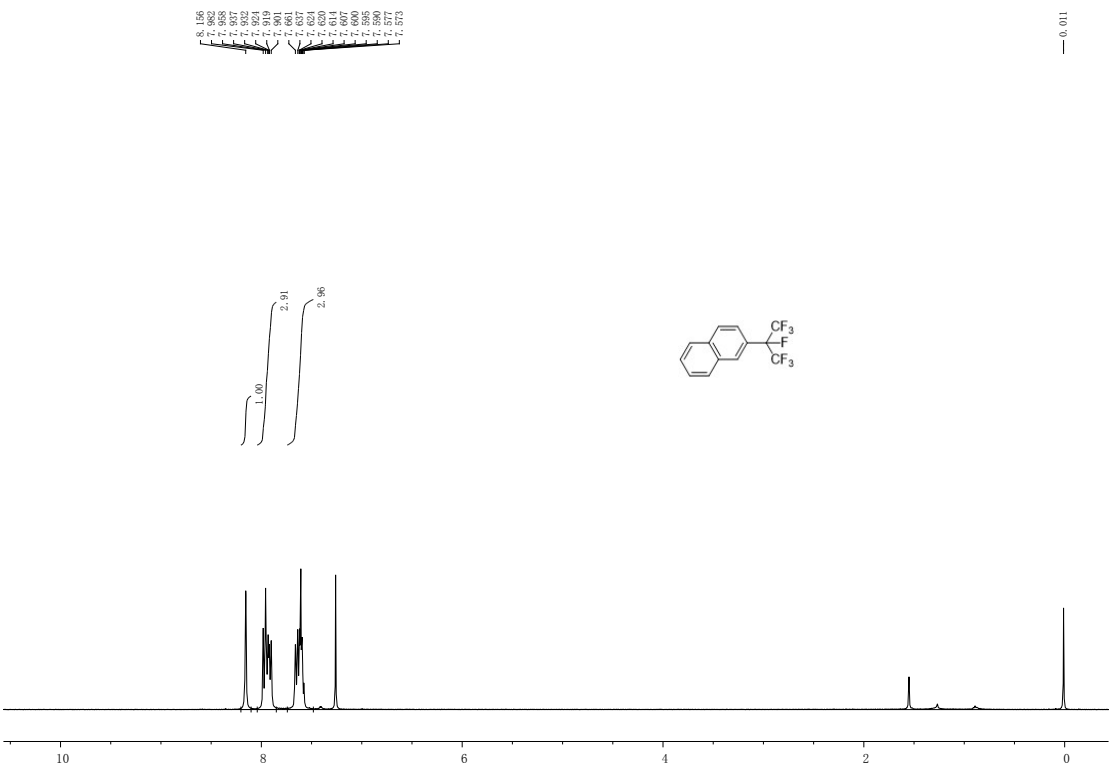
^{19}F NMR (376 MHz, $CDCl_3$) spectrum of 2-(perfluoropropan-2-yl)-1,1'-biphenyl 3t



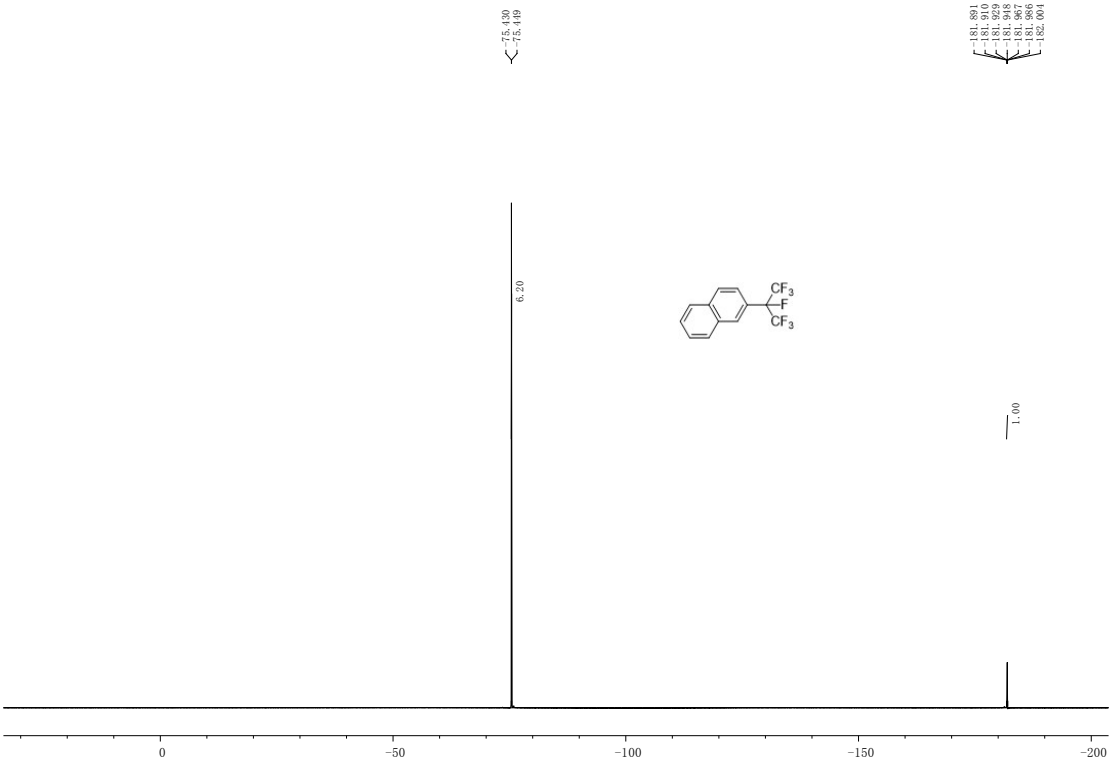
^{13}C NMR (101 MHz, $CDCl_3$) spectrum of 2-(perfluoropropan-2-yl)-1,1'-biphenyl 3t



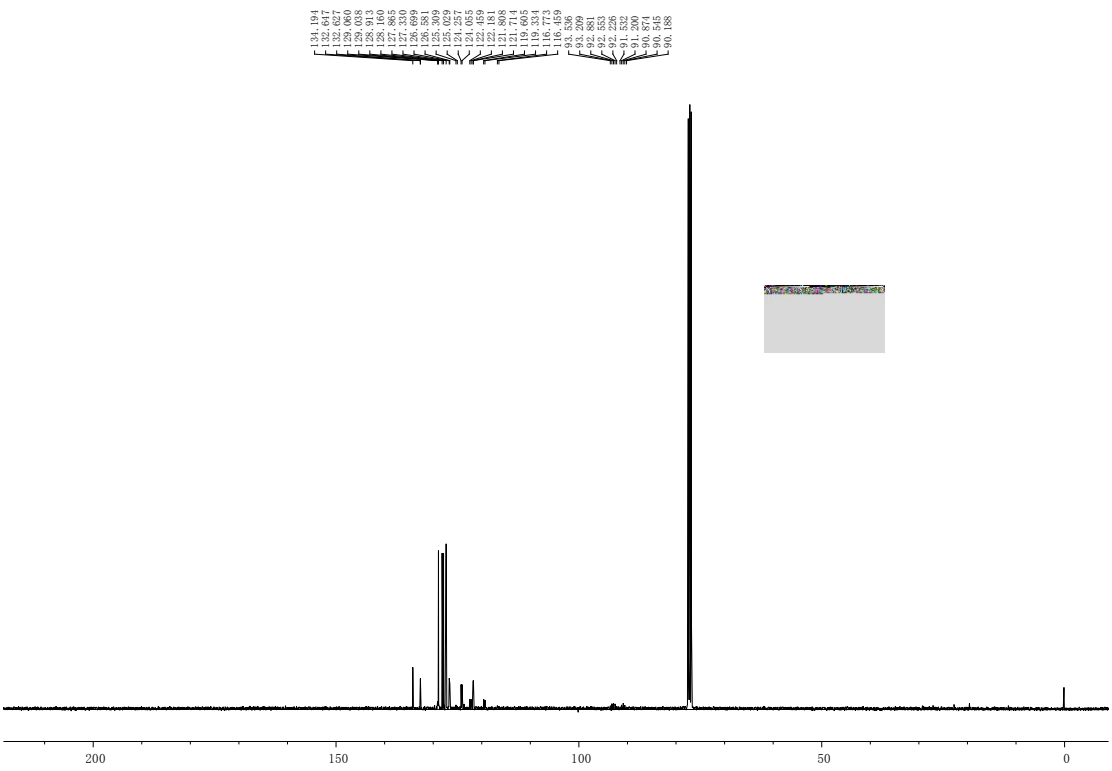
^{1}H NMR (400 MHz, $CDCl_3$) spectrum of 2-(perfluoropropan-2-yl)naphthalene 3u



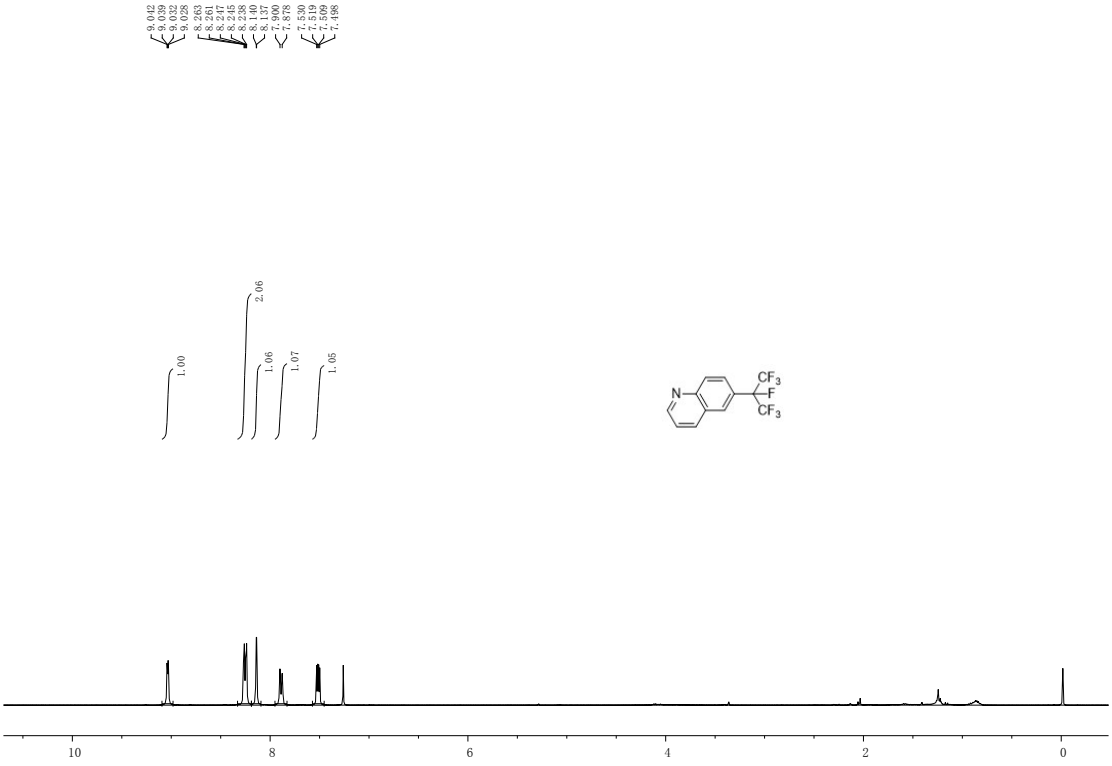
^{19}F NMR (376 MHz, $CDCl_3$) spectrum of 2-(perfluoropropan-2-yl)naphthalene 3u



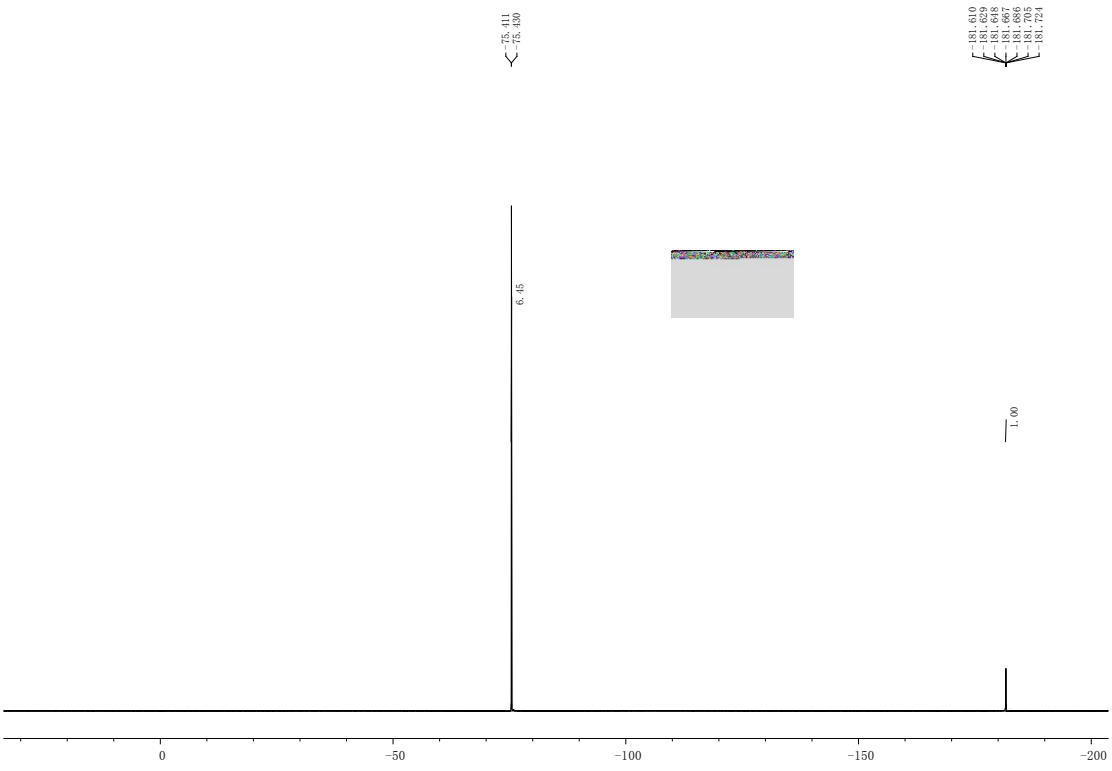
^{13}C NMR (101 MHz, $CDCl_3$) spectrum of 2-(perfluoropropan-2-yl)naphthalene 3u



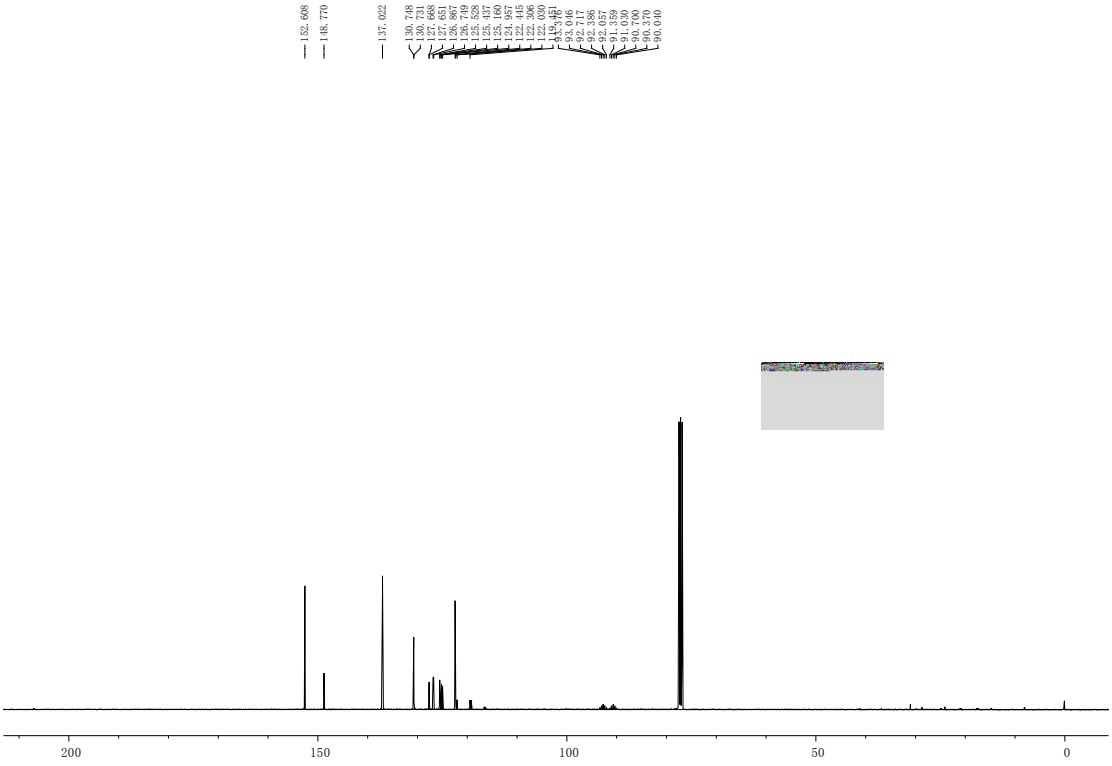
^{1}H NMR (400 MHz, $CDCl_3$) spectrum of 6-(perfluoropropan-2-yl)quinolone 3v



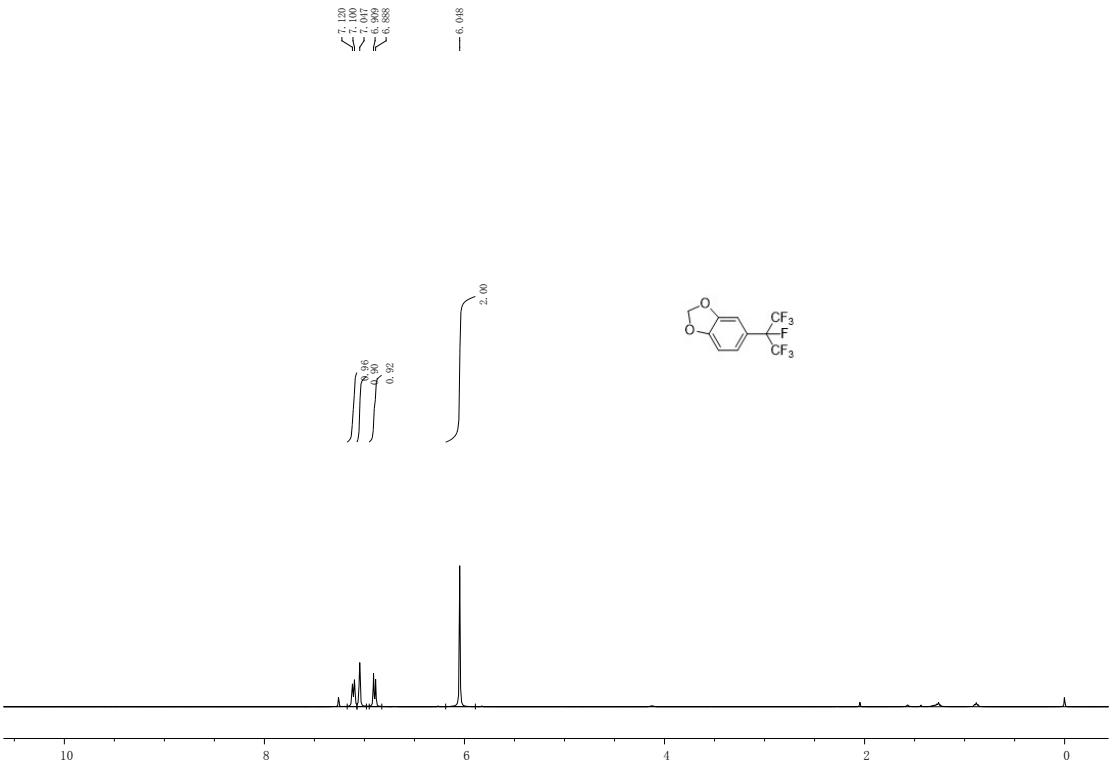
^{19}F NMR (376 MHz, $CDCl_3$) spectrum of 6-(perfluoropropan-2-yl)quinolone 3v



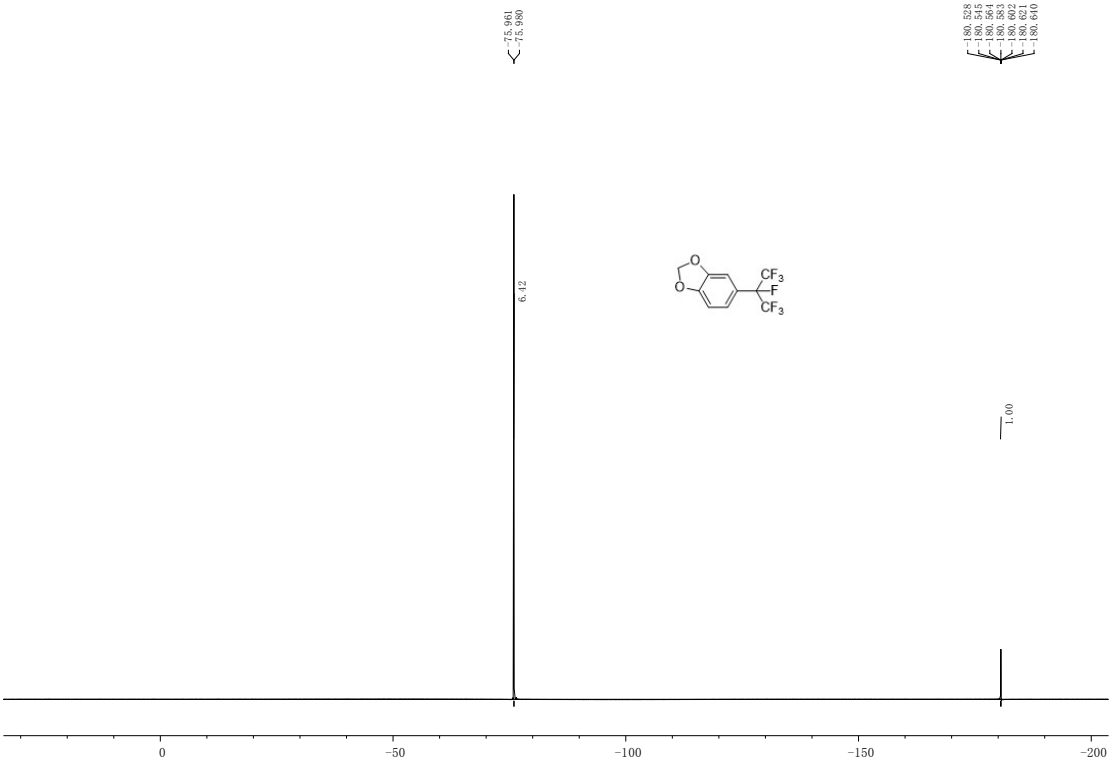
^{13}C NMR (101 MHz, $CDCl_3$) spectrum of 6-(perfluoropropan-2-yl)quinolone 3v



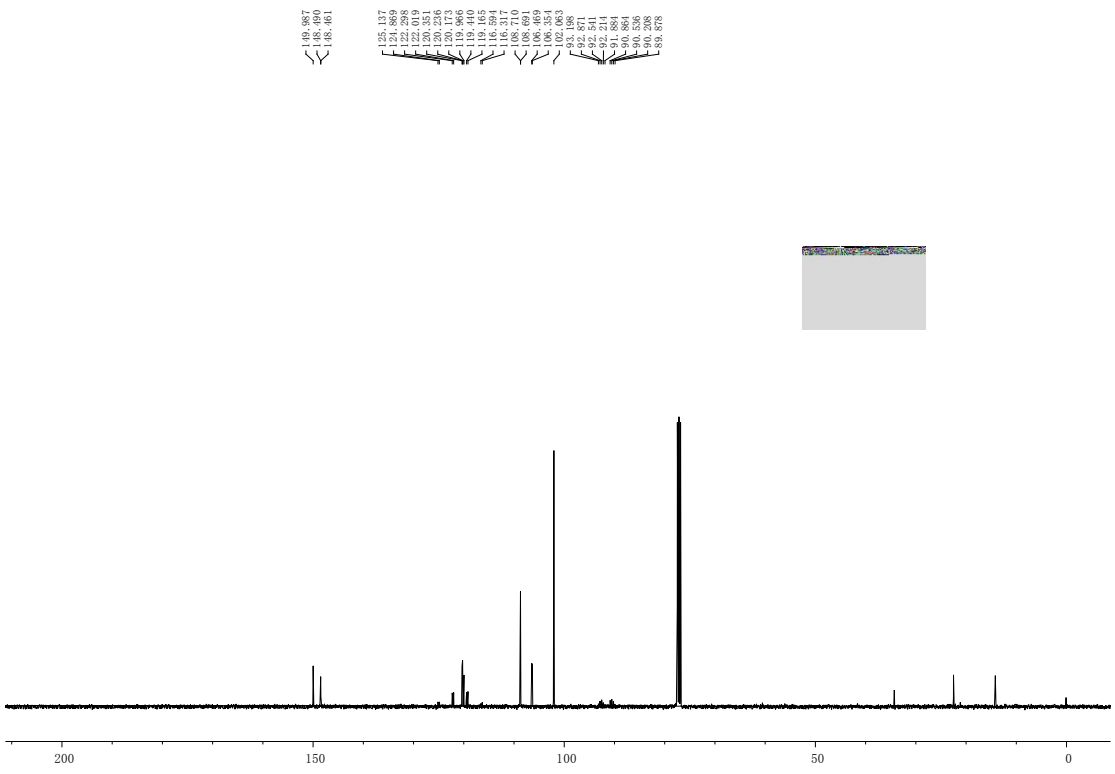
^{1}H NMR (400 MHz, $CDCl_3$) spectrum of 5-(perfluoropropan-2-yl)benzo[d][1,3]dioxole 3w



^{19}F NMR (376 MHz, $CDCl_3$) spectrum of 5-(perfluoropropan-2-yl)benzo[d][1,3]dioxole 3w



^{13}C NMR (101 MHz, $CDCl_3$) spectrum of 5-(perfluoropropan-2-yl)benzo[d][1,3]dioxole 3w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