Supporting Information

One-Pot Synthesis of Trifluoromethyl Amines and Perfluoroalkyl Amines with CF_3SO_2Na and R_fSO_2Na

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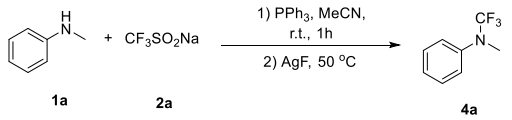
1. General information

Perfluoroalkanesulfinates (R_fSO2Na) were prepared according to the literature procedure.[1] Other chemical reagents are obtained from commercial suppliers and used without further purification. All reactions were carried out with dry solvents under anhydrous conditions, unless otherwise noted. All known compounds are identified by appropriate technique such as ^1H NMR, ^{13}C NMR, ^{19}F NMR and compared with previously reported data. All unknown compounds are characterized by ^1H NMR, ^{13}C NMR, ^{19}F NMR and HRMS. Analytical thin-layer chromatography is performed on glass plates precoated with silica gel impregnated with a fluorescent indicator (254 nm), and the plates are visualized by exposure to ultraviolet light. ^1H, ^{13}C and ^{19}F NMR spectra were recorded on a 500 MHz Bruker DRX 500 and tetramethylsilane (TMS) was used as a reference. Chemical shifts were reported in parts per million (ppm), and the residual solvent peak was used as an internal reference: proton (chloroform δ 7.26, acetonitrile δ 1.94), carbon (chloroform δ 77.0, acetonitrile δ 118.26, 1.39). and chemical shifts are reported in ppm. GC-MS data was recorded on a ISQ LT Single Quadrupole Mass Spectrometer, coupled with a Trace 1300 Gas Chromatograph (Thermo Fisher Scientific). Melting points were measured on a melting point apparatus and were uncorrected. High resolution mass spectral data were acquired on Waters Micromass GCT Premier spectrometer (electrospray ionization: EI).

2. Screening of reaction conditions

Table S1. Substrate Ratio and reaction temperature and time.[a]



1a 2a 4a

Entry	**1a**:**2a**:PPh_3:AgF	Tem (°C)	Time (h)	Yield (%)[b]
1	1:1.5:3:3	50	5	51
2	1:1.5:3:4	50	5	73
3	1:1.5:3:4.5	50	5	85
4	1:1.5:3:4.5	30	5	67
5	1:1.5:3:4.5	80	5	82
6	1:1.5:3:4.5	50	2	46
7	1:1.5:3:4.5	50	8	87

[a] Reaction conditions: *N*-methylaniline (0.5 mmol), CF_3SO_2Na (0.75 mmol), PPh_3 (1.5 mmol) in MeCN (2.5 mL) at room temperature for 1 h. AgF was then added. [b] Yield determined by ^{19}F NMR using benzotrifluoride as an internal standard on crude products.

3. Control Experiments

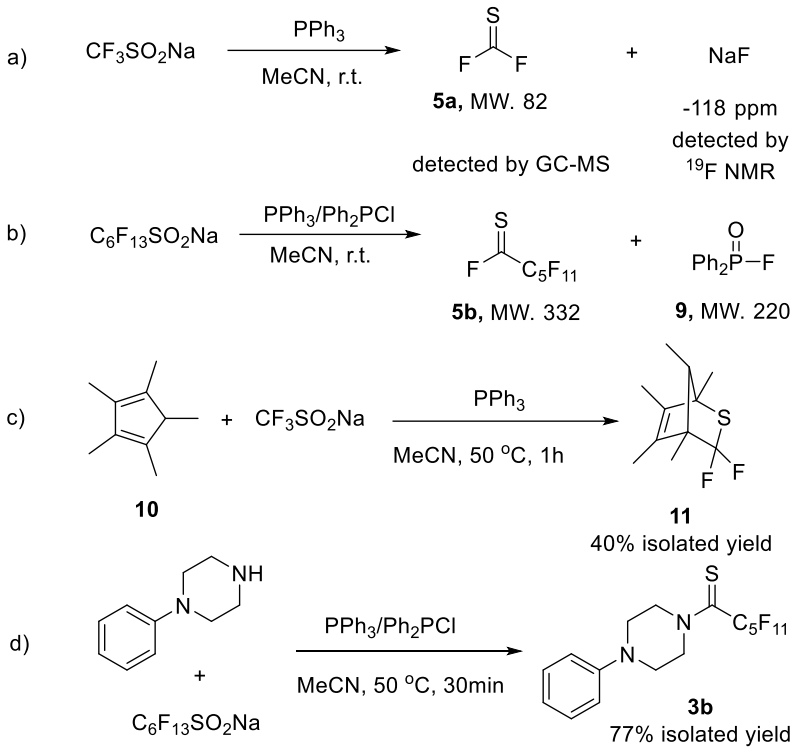
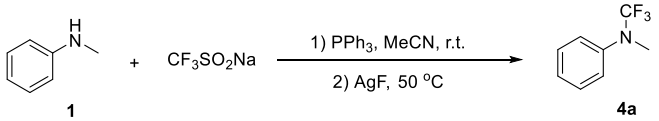


Figure S1. Control Experiments

4. General procedures

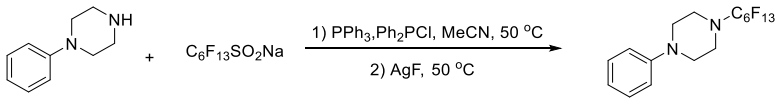
A typical procedure for preparation of trifluoromethyl amines



1 4a

In a nitrogen-filled glovebox, a 10 mL oven-dried reaction vessel was charged with CF_3SO_2Na (0.75 mmol, 117 mg, 1.5 equiv.) and PPh_3 (1.5 mmol, 393 mg, 3 equiv.), *N*-Methylaniline (0.5 mmol, 54 mg, 1.0 equiv.) was dissolved in MeCN (2.5 mL) and the solution was added to the vessel. The resulting solution was stirred at room temperature for 1h. After that, AgF (2.25 mmol, 286 mg, 4.5 equiv) was added. The resulting mixture was further stirred at 50 °C for 5 h. After cooling to room temperature the volatiles were removed under vacuum and the residue was purified by column chromatography to give the corresponding products.

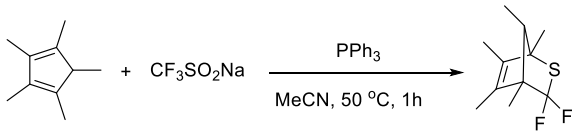
A typical procedure for preparation of perfluoroalkyl amines



1 2 4

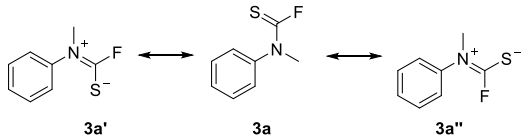
In a nitrogen-filled glovebox, a 10 mL oven-dried reaction vessel was charged with $C_6F_{13}SO_2Na$ (0.75 mmol, 305 mg, 1.5 equiv.), PPh_3 (0.75 mmol, 197 mg, 1.5 equiv.), and Ph_2PCl (0.75 mmol, 165 mg, 1.5 equiv.), 1-phenylpiperazine (0.5 mmol, 81 mg, 1.0 equiv.) was dissolved in MeCN (3 mL) and the solution was added to the vessel. The resulting solution was stirred at 50 °C for 30min. After that, AgF (2.25 mmol, 286 mg, 4.5 equiv) was added. The resulting mixture was further stirred at 50 °C for 5 h. After cooling to room temperature the volatiles were removed under vacuum and the residue was purified by column chromatography to give the corresponding products.

The synthesis of **11**



10 2a 11

In a nitrogen-filled glovebox, a 10 mL oven-dried reaction vessel was charged with CF_3SO_2Na (0.75 mmol, 117 mg, 1.5 equiv.) and PPh_3 (1.5 mmol, 393 mg, 3 equiv.), 1,2,3,4,5-pentamethylcyclopenta-1,3-diene (0.5 mmol, 68 mg, 1 equiv.) was dissolved in MeCN (2.5 mL) and the solution was added to the vessel. The resulting solution was stirred at 50 °C for 1h. After cooling to room temperature the volatiles were removed under vacuum and the residue was purified by column chromatography to give the corresponding products.



3a' **3a** **3a''**

***N*-methyl-*N*-phenylthiocarbamoyl fluoride 3a.**[2] Yellow oil, yield 93%. Eluent: ethyl acetate/petroleum ether (10:90). Due to a resonance effect, two configurations (3a' and 3a'') of thiocarbamoyl fluoride 2a could be observed with a ratio **3a**':**3a**'' = 6:1. ^{1}H NMR (500 MHz, Chloroform-*d*) δ 7.51 – 7.33 (m, 3H + 5H, **3a'** + **3a''**), 7.21 (dt, *J* = 8.0, 1.2 Hz, 2H, **3a'**), 3.66 (s, 3H, **3a'**), 3.50 (s, 3H, **3a''**); ^{19}F NMR (470 MHz, Chloroform-*d*) δ 22.55 (1F) (**3a**'), 21.01 (1F) (**3a**''); ^{13}C NMR (126 MHz, Chloroform-*d*) δ 142.19 , 130.70 , 129.58 , 125.94 , 45.92 (d, *J* = 7.2 Hz). Only signals of the most abundant **3a'** are observable in ^{13}C NMR.

***N*-methyl-*N*-(trifluoromethyl)aniline 4a.**[2] Eluent: ethyl acetate/petroleum ether (1:99). ^{1}H NMR (500 MHz, Acetone-d_6) δ 7.45 (dd, *J* = 8.6, 7.3 Hz, 2H), 7.36 – 7.32 (m, 2H), 7.27 (d, *J* = 7.2 Hz, 1H), 3.27 (t, *J* = 1.7 Hz, 3H); ^{19}F NMR (470 MHz, Acetone-d_6) δ -59.64 (3F).

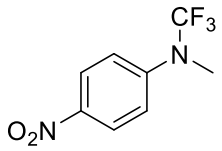
N,2-dimethyl-N-(trifluoromethyl)aniline 4b.[3] Colorless oil, yield 82% (154.3 mg). Eluent: ethyl acetate/petroleum ether (1:99). ^{1}H NMR (500 MHz, Chloroform-*d*) δ 7.38 – 7.33 (m, 1H), 7.29 – 7.21 (m, 3H), 2.94 (q, *J* = 1.1 Hz, 3H), 2.35 (s, 3H); ^{19}F NMR (470 MHz, Chloroform-*d*) δ -59.97 (3F); ^{13}C NMR (126 MHz, Chloroform-*d*) δ 142.33 , 138.64 , 132.10 , 128.80 , 127.87 , 127.62 , 124.86 (q, *J* = 254.3 Hz), 37.41 (d, *J* = 2.0 Hz), 18.75.

N,3-dimethyl-N-(trifluoromethyl)aniline 4c.[3] Colorless oil, yield 75% (141.4 mg). Eluent: ethyl acetate/petroleum ether (1:99). ^{1}H NMR (500 MHz, Chloroform-*d*) δ 7.25 (t, *J* = 7.6 Hz, 1H), 7.20 – 7.02 (m, 3H), 3.04 (q, *J* = 1.3 Hz, 3H), 2.38 (s, 3H); ^{19}F NMR (470 MHz, Chloroform-*d*) δ -59.95 (3F); ^{13}C NMR (126 MHz, Chloroform-*d*) δ 143.83 , 140.12 , 129.96 , 128.08 , 126.79 (d, *J* = 1.7 Hz), 124.61 (q, *J* = 255.2 Hz), 123.06 (d, *J* = 1.7 Hz), 37.41 (d, *J* = 2.2 Hz), 22.44.

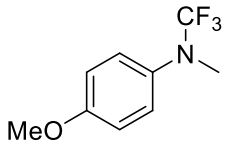
N,4-dimethyl-N-(trifluoromethyl)aniline 4d.[3] Colorless oil, yield 87% (164.7 mg). Eluent: ethyl acetate/petroleum ether (1:99). ^{1}H NMR (500 MHz, Chloroform-*d*) δ 7.17 (s, 4H), 3.02 (q, *J* = 1.3 Hz, 3H), 2.36 (s, 3H); ^{19}F NMR (470 MHz, Chloroform-*d*) δ -59.50 (3F); ^{13}C NMR (126 MHz, Chloroform-*d*) δ 141.34 , 137.32 , 130.79 , 126.34 , 124.68 (q, *J* = 255.4 Hz), 37.53 (d, *J* = 2.5 Hz), 21.97.

methyl 4-(methyl(trifluoromethyl)amino)benzoate 4e.[2] Yellow oil, yield 90% (104.8 mg). Eluent: ethyl acetate/petroleum ether (4:96). ^{1}H NMR (500 MHz, Chloroform-*d*) δ 8.01 (d, *J* = 8.9 Hz, 2H), 7.25 – 7.19 (m, 2H), 3.90 (s, 3H), 3.11 (q, *J* = 1.6 Hz, 3H); ^{19}F NMR (470 MHz, Chloroform-*d*) δ -58.23 (3F); ^{13}C NMR (126 MHz, Chloroform-*d*) δ 166.14 , 146.34 , 130.35 , 126.10 , 122.56 (q, *J* = 256.6 Hz), 121.54 , 51.75 , 35.08 (d, *J* = 2.2 Hz).

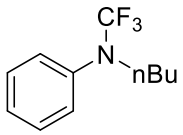
***N*-methyl-4-nitro-*N*-(trifluoromethyl)aniline 4f.**[2] Yellow oil, yield 87% (95.7 mg). Eluent: ethyl acetate/petroleum ether (5:95). ^{1}H NMR (500 MHz, Chloroform-*d*) δ 8.28 – 8.19 (m, 2H), 7.28 (dd, *J* = 8.6, 1.5 Hz, 2H), 3.20 (q, *J* = 1.7 Hz, 3H); ^{19}F NMR (470 MHz, Chloroform-*d*) δ -58.29 (3F); ^{13}C NMR (126 MHz, Chloroform-*d*) δ 149.08 , 144.83 , 125.94 , 123.44 (q, *J* = 257.7 Hz), 121.95 (q, *J* = 2.7 Hz), 36.26 (q, *J* = 2.3 Hz).



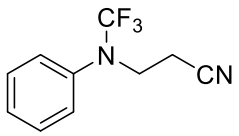
4-methoxy-N-methyl-N-(trifluoromethyl)aniline 4g.[3] Colorless oil, yield 77% (157.9 mg). Eluent: ethyl acetate/petroleum ether (2:98). ^{1}H NMR (500 MHz, Acetone-d6) δ 7.27 – 7.22 (m, 2H), 6.93 (d, J = 9.0 Hz, 2H), 3.78 (s, 3H), 2.97 (d, J = 1.3 Hz, 3H); ^{19}F NMR (470 MHz, Acetone-d6) δ -60.49 (3F); ^{13}C NMR (126 MHz, Acetone-d6) δ 159.70 , 136.37 , 128.48 , 124.98 (q, *J* = 253.3 Hz), 115.38 , 55.91 , 37.22 (q, *J* = 2.2 Hz).



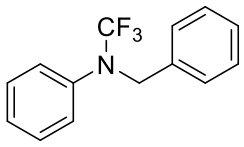
***N*-butyl-*N*-(trifluoromethyl)aniline 4h.** Colorless oil, yield 82% (88.9 mg). Eluent: ethyl acetate/petroleum ether (3:97). ^{1}H NMR (500 MHz, Chloroform-*d*) δ 7.38 (dd, *J* = 8.6, 7.0 Hz, 2H), 7.34 – 7.23 (m, 3H), 3.42 – 3.29 (m, 2H), 1.45 (ddd, *J* = 11.9, 8.7, 6.2 Hz, 2H), 1.40 – 1.31 (m, 2H), 0.90 (t, *J* = 7.3 Hz, 3H); ^{19}F NMR (470 MHz, Chloroform-*d*) δ -57.81 (3F); ^{13}C NMR (126 MHz, Acetone-d_6) δ 141.72 , 130.30 , 128.27 , 128.15 , 124.75 (q, *J* = 253.3 Hz), 49.37 , 31.04 , 20.45 , 14.04. HR-MS (EI) Calcd. For 217.1078, $C_{11}H_{14}F_3N$, found 217.1082.



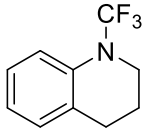
3-(phenyl(trifluoromethyl)amino)propanenitrile 4i.[2] Colorless oil, yield 81% (86.6 mg). Eluent: ethyl acetate/petroleum ether (5:95). ^{1}H NMR (500 MHz, Chloroform-*d*) δ 7.42 (dd, *J* = 8.3, 6.7 Hz, 2H), 7.38 – 7.29 (m, 3H), 3.65 (t, *J* = 6.9 Hz, 2H), 2.51 (t, *J* = 7.0 Hz, 2H); ^{19}F NMR (470 MHz, Chloroform-*d*) δ -58.62 (3F); ^{13}C NMR (126 MHz, Chloroform-*d*) δ 140.37 , 130.83 , 129.33 , 128.67 , 124.07 (q, *J* = 256.5 Hz), 118.15 , 46.26 , 18.76 .



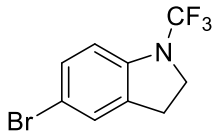
***N*-benzyl-*N*-(trifluoromethyl)aniline 4j.**[3] Colorless oil, yield 79% (99.1 mg). Eluent: ethyl acetate/petroleum ether (2:98). ^{1}H NMR (500 MHz, Chloroform-*d*) δ 7.40 – 7.28 (m, 7H), 7.28 – 7.22 (m, 3H), 4.63 (s, 2H); ^{19}F NMR (470 MHz, Chloroform-*d*) δ -57.38 (3F); ^{13}C NMR (126 MHz, Chloroform-*d*) δ 140.93 , 136.83 , 128.83 , 128.19 , 127.59 , 127.20 , 126.13 , 125.55 , 123.24 (q, *J* = 255.8 Hz), 52.98.



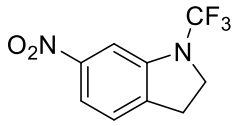
1-(trifluoromethyl)-1,2,3,4-tetrahydroquinoline 4k.[3] Yellow oil, yield 83% (83.4 mg). Eluent: ethyl acetate/petroleum ether (1:99). ^{1}H NMR (500 MHz, Chloroform-*d*) δ 7.20 – 7.04 (m, 3H), 6.96 (td, *J* = 7.3, 1.4 Hz, 1H), 3.46 (td, *J* = 5.7, 1.7 Hz, 2H), 2.78 (q, *J* = 5.4, 4.1 Hz, 2H), 1.97 (p, *J* = 6.4 Hz, 2H); ^{19}F NMR (470 MHz, Chloroform-*d*) δ -55.85 (3F); ^{13}C NMR (126 MHz, Chloroform-*d*) δ 138.67 , 130.46 , 129.31 , 127.70 , 124.13 (q, *J* = 256.8 Hz), 123.82 , 120.82 (q, *J* = 4.0 Hz), 44.81 (q, *J* = 2.4 Hz), 28.22 , 23.09.



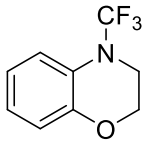
5-bromo-1-(trifluoromethyl)indoline 4l. Yellow oil, yield 80% (106.1 mg). Eluent: ethyl acetate/petroleum ether (1:99). ^{1}H NMR (500 MHz, Acetone-d_6) δ 7.42 (q, J = 1.4 Hz, 1H), 7.34 (dd, J = 8.5, 2.0 Hz, 1H), 6.94 (dq, J = 8.6, 1.7 Hz, 1H), 3.80 (td, J = 8.4, 1.2 Hz, 2H), 3.18 (t, J = 8.4 Hz, 2H); ^{19}F NMR (470 MHz, Acetone-d_6) δ -60.66 (3F); ^{13}C NMR (126 MHz, Acetone-d_6) δ 143.49 , 135.40 , 131.31 , 129.39 , 123.89 (q, J = 255.9 Hz), 115.68 , 114.53 (d, J = 3.2 Hz), 49.24 (d, J = 2.3 Hz), 28.66. HR-MS (EI) Calcd. For 264.9714, $C_9H_7BrF_3N$, found 264.9711.



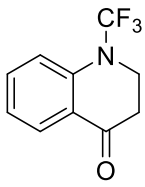
6-nitro-1-(trifluoromethyl)indoline 4m.[2] Yellow oil, yield 75% (86.8 mg). Eluent: ethyl acetate/petroleum ether (5:95). ^{1}H NMR (500 MHz, Chloroform-d) δ 7.98 – 7.72 (m, 2H), 7.31 (d, J = 8.1 Hz, 1H), 3.87 (t, J = 8.5 Hz, 2H), 3.22 (t, J = 8.5 Hz, 2H); ^{19}F NMR (470 MHz, Chloroform-d) δ -61.38 (3F); ^{13}C NMR (126 MHz, Chloroform-d) δ 149.37 , 145.38 , 139.28 , 126.23 , 123.22 (q, J = 258.0 Hz), 119.33 , 108.00 (q, J = 3.5 Hz), 49.52 (q, J = 1.9 Hz), 29.12 .



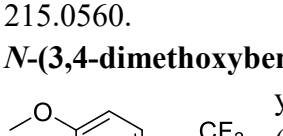
4-(trifluoromethyl)-3,4-dihydro-2H-benzo[*b*][1,4]oxazine 4n.[3] Yellow oil, yield 71% (72.1 mg). Eluent: ethyl acetate/petroleum ether (3:97). ^{1}H NMR (500 MHz, Methanol-d_4) δ 7.13 (dq, J = 8.2, 2.1 Hz, 1H), 6.99 (ddd, J = 8.4, 7.2, 1.5 Hz, 1H), 6.88 – 6.81 (m, 2H), 4.25 – 4.19 (m, 2H), 3.56 – 3.49 (m, 2H); ^{19}F NMR (470 MHz, Methanol-d_4) δ -57.03 (3F); ^{13}C NMR (126 MHz, Methanol-d_4) δ 146.64 , 124.40 , 124.22 , 122.30 (q, J = 256.2 Hz), 121.18 (d, J = 3.4 Hz), 120.11 , 116.98 , 63.47 , 41.44 (d, J = 2.3 Hz).



1-(trifluoromethyl)-2,3-dihydroquinolin-4(1H)-one 4o. Colorless oil, yield 82% (88.2 mg). Eluent: ethyl acetate/petroleum ether (3:97). ^{1}H NMR (500 MHz, Chloroform-d) δ 8.04 (dd, J = 7.9, 1.8 Hz, 1H), 7.51 (ddd, J = 8.8, 7.2, 1.8 Hz, 1H), 7.27 (dd, J = 8.4, 2.7 Hz, 1H), 7.19 – 7.13 (m, 1H), 3.83 (t, J = 6.5 Hz, 2H), 2.89 – 2.81 (m, 2H); ^{19}F NMR (470 MHz, Chloroform-d) δ -58.47 (3F); ^{13}C NMR (126 MHz, Chloroform-d) δ 192.48 , 143.19 , 134.61 , 127.95 , 123.63 , 123.08 , 121.94 (q, J = 258.8 Hz), 118.59 (d, J = 4.1 Hz), 43.32 (d, J = 2.7 Hz), 37.73. HR-MS (EI) Calcd. For 215.0558, $C_{10}H_8F_3NO$, found 215.0560.



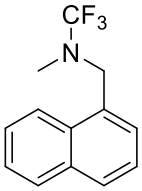
***N*-(3,4-dimethoxybenzyl)-1,1,1-trifluoro-*N*-methylmethanamine 4p.** Colorless oil, yield 81% (100.8 mg). Eluent: ethyl acetate/petroleum ether (5:95). ^{1}H NMR (500 MHz, Acetone-d_6) δ 6.95 – 6.89 (m, 2H), 6.86 (dd, J = 8.1, 1.9 Hz, 1H), 3.91 (s, 2H), 3.79 (d, J = 3.8 Hz, 6H); ^{19}F NMR (470 MHz, Acetone-d_6) δ -63.60 (3F); ^{13}C NMR (126 MHz, Acetone-d_6) δ 150.68 , 150.22 , 129.80 , 126.57 (q, J = 253.8 Hz), 121.81 , 113.17 , 112.76 , 56.23 (d, J = 3.4 Hz), 53.05 (q, J = 2.7 Hz), 33.36 (q, J = 2.9 Hz). HR-MS (EI) Calcd. For 249.0977, $C_{11}H_{14}F_3NO_2$, found 249.0984.



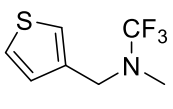
***N*,*N*-dibenzyl-1,1,1-trifluoromethanamine 4q.**[3] Yellow oil, yield 79% (104.6 mg). Eluent: ethyl acetate/petroleum ether (1:99). ^{1}H NMR (500 MHz, Chloroform-d) δ 7.37 – 7.20 (m, 10H), 4.03 (s, 4H); ^{19}F NMR (470 MHz, Chloroform-d) δ -59.12 (3F); ^{13}C NMR (126 MHz, Chloroform-d) δ 137.61 , 129.68 , 129.52 , 128.67 , 126.20 (q, J = 255.3 Hz),

50.71 (q, *J* = 2.0 Hz).

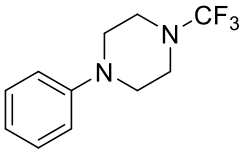
1,1,1-trifluoro-*N*-methyl-*N*-(naphthalen-1-ylmethyl)methanamine 4r.[3] ^{1}H NMR (500 MHz, Chloroform-*d*) δ 8.17 (dd, *J* = 8.6, 1.2 Hz, 1H), 7.89 (dd, *J* = 7.9, 1.6 Hz, 1H), 7.85 (dd, *J* = 7.6, 1.9 Hz, 1H), 7.55 (dddd, *J* = 18.5, 8.1, 6.8, 1.4 Hz, 2H), 7.52 – 7.43 (m, 2H), 4.41 (s, 2H), 2.45 (d, *J* = 1.2 Hz, 3H); ^{19}F NMR (470 MHz, Chloroform-*d*) δ -66.40 (3F).



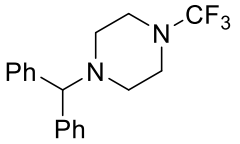
1,1,1-trifluoro-*N*-methyl-*N*-(thiophen-3-ylmethyl)methanamine 4s. Eluent: ethyl acetate/petroleum ether (1:99). ^{1}H NMR (500 MHz, Chloroform-*d*) δ 7.30 (dd, *J* = 4.8, 1.6 Hz, 1H), 7.03 – 6.97 (m, 2H), 4.17 (s, 2H), 2.54 (d, *J* = 1.4 Hz, 3H); ^{19}F NMR (470 MHz, Chloroform-*d*) δ -64.66 (3F); ^{13}C NMR (126 MHz, Chloroform-*d*) δ 140.54 , 127.82 , 127.80 , 126.79 , 126.00 (q, *J* = 256.5 Hz), 48.70 (d, *J* = 3.1 Hz), 34.13 (d, *J* = 2.8 Hz). HR-MS (EI) Calcd. For 195.0330, $C_7H_8F_3NS$, found 195.0332.



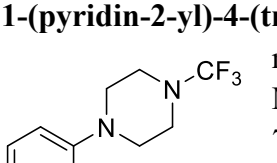
1-phenyl-4-(trifluoromethyl)piperazine 4t.[3] Colorless oil, yield 84% (96.5 mg). Eluent: ethyl acetate/petroleum ether (1:99). ^{1}H NMR (500 MHz, Chloroform-*d*) δ 7.29 (dd, *J* = 8.8, 7.2 Hz, 2H), 7.00 – 6.88 (m, 3H), 3.30 – 3.20 (m, 4H), 3.09 (dd, *J* = 6.1, 3.9 Hz, 4H); ^{19}F NMR (470 MHz, Chloroform-*d*) δ -68.15 (3F); ^{13}C NMR (126 MHz, Chloroform-*d*) δ 150.68 , 129.06 , 124.23 (q, *J* = 256.8 Hz) , 120.39 , 116.44 , 48.35 , 44.12 (d, *J* = 2.9 Hz).



1-benzhydryl-4-(trifluoromethyl)piperazine 4u. Colorless oil, yield 77% (123.1 mg). Eluent: ethyl acetate/petroleum ether (3:97). ^{1}H NMR (500 MHz, Chloroform-*d*) δ 7.42 (d, *J* = 7.3 Hz, 4H), 7.29 (t, *J* = 7.6 Hz, 4H), 7.20 (t, *J* = 7.3 Hz, 2H), 4.27 (s, 1H), 2.95 (t, *J* = 4.9 Hz, 4H), 2.46 (t, *J* = 4.9 Hz, 4H); ^{19}F NMR (470 MHz, Chloroform-*d*) δ -68.20 (3F); ^{13}C NMR (126 MHz, Chloroform-*d*) δ 142.06 , 128.42 , 127.66 , 126.96 , 124.36 (q, *J* = 256.1 Hz), 75.69 , 50.41 , 44.26 (d, *J* = 3.0 Hz). HR-MS (EI) Calcd. For 320.1500, $C_{18}H_{19}F_3N_2$, found 320.1505.



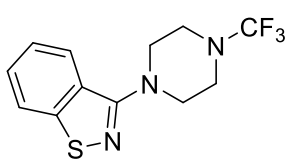
1-(pyridin-2-yl)-4-(trifluoromethyl)piperazine 4v. Colorless oil, yield 75% (86.6 mg). Eluent: ethyl acetate/petroleum ether (5:95). ^{1}H NMR (500 MHz, Chloroform-*d*) δ 8.32 – 8.15 (m, 1H), 7.52 (ddd, *J* = 9.1, 7.4, 2.0 Hz, 1H), 6.69 (dd, *J* = 7.6, 5.1 Hz, 2H), 3.70 – 3.59 (m, 4H), 3.16 – 3.00 (m, 4H); ^{19}F NMR (470 MHz, Chloroform-*d*) δ -68.13 (3F); ^{13}C NMR (126 MHz, Chloroform-*d*) δ 158.71 , 147.62 , 137.48 , 124.12 (q, *J* = 256.2 Hz), 113.71 , 107.05 , 44.07 , 43.81 (d, *J* = 3.0 Hz). HR-MS (EI) Calcd. For 231.0983, $C_{10}H_{12}F_3N_3$, found 231.0974.



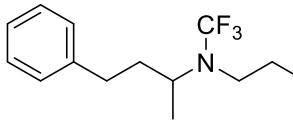
furan-2-yl(4-(trifluoromethyl)piperazin-1-yl)methanone 4w. White solid, M.p. 79.3-82.5 ºC, yield 80% (99.3 mg). Eluent: ethyl acetate/petroleum ether (5:95). ^{1}H NMR (500 MHz, Chloroform-*d*) δ 7.50 (d, *J* = 1.7 Hz, 1H), 7.05 (d, *J* = 3.5 Hz, 1H), 6.50 (dd, *J* = 3.5, 1.8 Hz, 1H), 3.88 (s, 4H), 3.10 – 2.97 (m, 4H); ^{19}F NMR (470 MHz, Chloroform-*d*) δ -67.27 (3F); ^{13}C NMR (126 MHz,

Chloroform-*d*) δ 158.78 , 147.31 , 143.65 , 123.76 (q, *J* = 256.5 Hz), 116.86 , 111.21 , 44.18 . HR-MS (EI) Calcd. For 248.0773, $C_{10}H_{11}F_3N_2O_2$, found 248.0771.

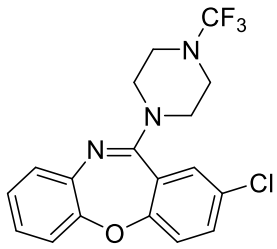
3-(4-(trifluoromethyl)piperazin-1-yl)benzo[*d*]isothiazole 4x. Colorless oil, yield 72% (103.3 mg). Eluent: ethyl acetate/petroleum ether (5:95). ^{1}H NMR (500 MHz, Chloroform-*d*) δ 7.90 (d, *J* = 8.2 Hz, 1H), 7.85 (d, *J* = 8.1 Hz, 1H), 7.51 (t, *J* = 7.5 Hz, 1H), 7.40 (t, *J* = 7.6 Hz, 1H), 3.68 – 3.56 (m, 4H), 3.25 – 3.14 (m, 4H); ^{19}F NMR (470 MHz, Chloroform-*d*) δ -68.07 (3F); ^{13}C NMR (126 MHz, Chloroform-*d*) δ 163.01 , 152.55 , 127.52 , 127.49 , 124.05 (q, *J* = 256.8 Hz) , 123.90 , 123.34 , 120.42 , 48.80 , 43.82 (d, *J* = 3.0 Hz). HR-MS (EI) Calcd. For 287.0704, $C_{12}H_{12}F_3N_3S$, found 287.0705.



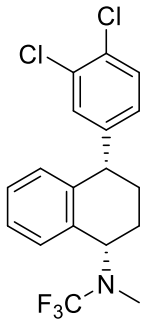
3-((4-phenylbutan-2-yl)(trifluoromethyl)amino)propanenitrile 4y. Yellow oil, yield 79% (106.5 mg). Eluent: ethyl acetate/petroleum ether (5:95). ^{1}H NMR (500 MHz, Acetone-d_6) δ 7.31 – 7.24 (m, 4H), 7.20 – 7.16 (m, 1H), 3.48 – 3.37 (m, 1H), 3.30 (ddddd, *J* = 23.2, 15.0, 13.4, 6.1, 1.5 Hz, 2H), 2.79 (ddd, *J* = 13.7, 10.1, 5.8 Hz, 1H), 2.74 – 2.64 (m, 3H), 2.01 – 1.91 (m, 1H), 1.79 (ddt, *J* = 13.2, 10.1, 6.2 Hz, 1H), 1.26 (d, *J* = 6.8 Hz, 3H); ^{19}F NMR (470 MHz, Acetone-d_6) δ -56.60 (3F); ^{13}C NMR (126 MHz, Acetone-d_6) δ 142.86 , 129.39 , 129.35 , 126.84 , 126.46 (q, *J* = 255.8 Hz) , 119.04 , 53.92 , 39.85 , 37.84 , 33.79 , 20.05 , 18.55.

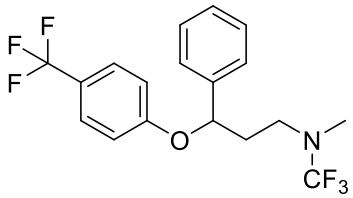


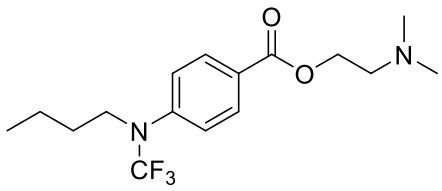
***tert*-butyl 4-(trifluoromethyl)piperazine-1-carboxylate 4z.**[2] Yellow oil, yield 72% (91.4 mg). Eluent: ethyl acetate/petroleum ether (3:97). ^{1}H NMR (500 MHz, Chloroform-*d*) δ 3.59 – 3.39 (m, 4H), 2.87 (t, *J* = 5.1 Hz, 4H), 1.47 (s, 9H); ^{19}F NMR (470 MHz, Chloroform-*d*) δ -68.09 (3F); ^{13}C NMR (126 MHz, Chloroform-*d*) δ 155.45 , 125.28 (q, *J* = 256.1 Hz), 81.26 , 45.16 (q, *J* = 2.8 Hz), 29.37 .

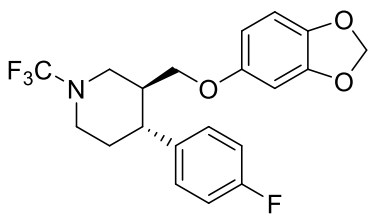


2-chloro-11-(4-(trifluoromethyl)piperazin-1-yl)dibenzo[*b*,*f*][1,4]oxazepine 4ee. Yellow oil, yield 82% (156.2 mg). Eluent: ethyl acetate/petroleum ether (5:95). ^{1}H NMR (500 MHz, Chloroform-*d*) δ 7.42 (dd, *J* = 8.6, 2.7 Hz, 1H), 7.33 (d, *J* = 2.6 Hz, 1H), 7.25 – 7.17 (m, 2H), 7.17 – 7.10 (m, 2H), 7.05 (td, *J* = 7.6, 1.7 Hz, 1H), 3.78 – 3.53 (m, 4H), 3.08 (s, 4H); ^{19}F NMR (470 MHz, Chloroform-*d*) δ -67.99 (3F); ^{13}C NMR (126 MHz, Chloroform-*d*) δ 159.13 , 158.46 , 151.54 , 139.47 , 132.59 , 130.19 , 128.60 , 126.90 , 125.62 , 124.79 , 124.48 , 124.00 (q, *J* = 257.0 Hz), 122.60 , 119.94 , 46.18 , 43.81 (d, *J* = 3.2 Hz). HR-MS (EI) Calcd. For 381.0856, $C_{18}H_{15}ClF_3N_3O$, found 381.0860.

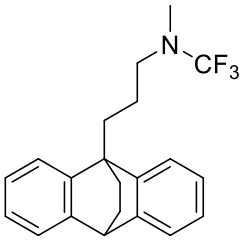
(1S,4S)-4-(3,4-dichlorophenyl)-*N*-methyl-*N*-(trifluoromethyl)-1,2,3,4-tetrahydronaphthalen-1-amine 4ff. 
Colorless oil, yield 61% (113.7 mg). Eluent: ethyl acetate/petroleum ether (3:97). ^{1}H NMR (500 MHz, Chloroform-*d*) δ 7.65 (d, *J* = 7.9 Hz, 1H), 7.39 – 7.32 (m, 2H), 7.24 (t, *J* = 7.4 Hz, 1H), 7.11 (d, *J* = 2.1 Hz, 1H), 7.01 – 6.96 (m, 1H), 6.84 (dd, *J* = 8.3, 2.1 Hz, 1H), 4.63 (dd, *J* = 10.6, 6.2 Hz, 1H), 4.21 (dd, *J* = 5.8, 2.8 Hz, 1H), 2.46 (d, *J* = 1.7 Hz, 3H), 2.27 (tdd, *J* = 12.8, 5.7, 3.4 Hz, 1H), 2.10 – 2.01 (m, 1H), 1.85 (tdd, *J* = 14.5, 10.3, 4.0 Hz, 2H); ^{19}F NMR (470 MHz, Chloroform-*d*) δ -59.28 (3F); ^{13}C NMR (126 MHz, Chloroform-*d*) δ 146.70 , 137.97 , 135.84 , 132.05 , 130.41 , 130.39 , 129.87 , 129.83 , 127.78 , 127.57 , 127.35 , 127.25 , 125.07 (q, *J* = 254.4 Hz), 54.93 , 42.71 , 29.66 , 27.96 (d, *J* = 2.3 Hz), 20.07 . HR-MS (EI) Calcd. For 373.0612, $C_{18}H_{16}Cl_2F_3N$, found 373.0619.

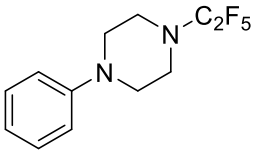
***N*-methyl-3-phenyl-*N*-(trifluoromethyl)-3-(4-(trifluoromethyl)phenoxy)propan-1-amine 4gg.** 
Colorless oil, yield 71% (133.8 mg). Eluent: ethyl acetate/petroleum ether (3:97). ^{1}H NMR (500 MHz, Acetone-d_6) δ 7.53 (d, *J* = 8.6 Hz, 2H), 7.50 – 7.44 (m, 2H), 7.37 (dd, *J* = 8.4, 6.9 Hz, 2H), 7.32 – 7.25 (m, 1H), 7.09 (d, *J* = 8.5 Hz, 2H), 5.52 (dd, *J* = 8.8, 4.2 Hz, 1H), 3.14 (dt, *J* = 14.8, 7.7 Hz, 1H), 3.01 (ddd, *J* = 13.3, 8.1, 4.8 Hz, 1H), 2.60 (d, *J* = 1.3 Hz, 3H), 2.23 (dtd, *J* = 13.5, 8.3, 4.7 Hz, 1H), 2.18 – 2.08 (m, 1H); ^{19}F NMR (470 MHz, Acetone-d_6) δ -60.91 (d, *J* = 8.6 Hz, 3F), -64.37 (d, *J* = 8.7 Hz, 3F); ^{13}C NMR (126 MHz, Acetone-d_6) δ 161.91 , 141.94 , 129.78 , 128.95 , 127.76 (d, *J* = 3.9 Hz), 127.08 , 126.49 (q, *J* = 260.8 Hz) , 125.71 (q, *J* = 230.4 Hz) , 117.16 , 78.27 , 46.22 (d, *J* = 2.4 Hz), 37.32 , 33.99 (d, *J* = 3.1 Hz). HR-MS (EI) Calcd. For 377.1214, $C_{18}H_{17}F_6NO$, found 377.1222.

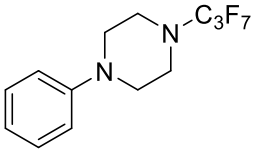
2-(dimethylamino)ethyl 4-(butyl(trifluoromethyl)amino)benzoate (*E*)-4hh.[2] 
Yellow oil, yield 74% (122.8 mg). Eluent: ethyl acetate/petroleum ether (5:95). ^{1}H NMR (500 MHz, Acetone-d_6) δ 8.04 (d, *J* = 8.3 Hz, 2H), 7.41 (d, *J* = 8.3 Hz, 2H), 4.39 (t, *J* = 5.8 Hz, 2H), 3.54 (t, *J* = 7.5 Hz, 2H), 2.66 (t, *J* = 5.8 Hz, 2H), 2.26 (s, 6H), 1.49 (t, *J* = 7.6 Hz, 2H), 1.34 (q, *J* = 7.5 Hz, 2H), 0.87 (t, *J* = 7.3 Hz, 3H); ^{19}F NMR (470 MHz, Acetone-d_6) δ -54.83 (3F); ^{13}C NMR (126 MHz, Acetone-d_6) δ 166.23 , 146.04 , 131.57 , 128.73 , 125.43 , 124.25 (q, *J* = 254.7 Hz), 63.77 , 58.68 , 49.03 , 46.11 , 31.20 , 20.47 , 14.01 .

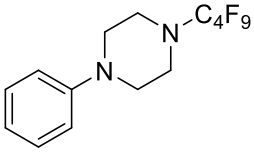
(3S,4R)-3-((benzo[*d*][1,3]dioxol-5-yloxy)methyl)-4-(4-fluorophenyl)-1-(trifluoromethyl)piperidine 4ii. 
Colorless oil, yield 69% (136.9 mg). Eluent: ethyl acetate/petroleum ether (3:97). ^{1}H NMR (500 MHz, Chloroform-*d*) δ 7.18 (dd, *J* = 8.6, 5.4 Hz, 2H), 7.02 (t, *J* = 8.6 Hz, 2H), 6.66 (d, *J* = 8.5 Hz, 1H), 6.38 (d, *J* = 2.5 Hz, 1H), 6.16 (dd, *J* = 8.5, 2.5 Hz, 1H), 5.91 (s, 2H), 3.73 – 3.58 (m, 2H), 3.56 – 3.41 (m, 2H), 2.78 – 2.54 (m, 3H), 2.22 (dtd, *J* = 14.9, 7.5, 3.5 Hz, 1H), 1.90 (dt, *J* = 7.5, 4.2 Hz,

2H);^{19}F NMR (470 MHz, Acetone-d_6) δ -67.24 (3F), -115.93 (t, J = 6.0 Hz, 1F); ^{13}C NMR (126 MHz, Acetone-d_6) δ 161.31 (d, J = 242.8 Hz), 154.05 , 148.02 , 141.49 , 139.15 (d, J = 3.2 Hz), 128.94 (d, J = 7.8 Hz), 124.50 (q, J = 254.3 Hz), 114.93 (d, J = 21.1 Hz), 107.44 , 105.25 , 100.87 , 97.44 , 68.53 , 47.50 (d, J = 2.8 Hz), 44.49 (d, J = 3.0 Hz), 43.00 , 40.76 , 32.60 . HR-MS (EI) Calcd. For 397.1301, $C_{20}H_{19}F_4NO_3$, found 397.1302.

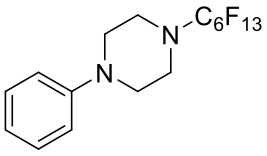
3-(9,10-ethanoanthracen-9(10H)-yl)-*N*-methyl-*N*-(trifluoromethyl)propan-1-amine 4jj. 
White solid, M.p. 95.8-97.7 ºC yield 78% (134.5 mg). Eluent: ethyl acetate/petroleum ether (2:98). ^{1}H NMR (500 MHz, Acetone-d_6) δ 7.28 (ddd, J = 6.9, 3.8, 1.3 Hz, 4H), 7.08 (dtd, J = 22.9, 7.5, 1.3 Hz, 4H), 4.32 (t, J = 2.8 Hz, 1H), 3.16 (t, J = 7.2 Hz, 2H), 2.69 (d, J = 1.3 Hz, 3H), 2.55 – 2.46 (m, 2H), 2.04 – 1.96 (m, 2H), 1.77 (ddd, J = 10.5, 4.4, 2.8 Hz, 2H), 1.59 – 1.52 (m, 2H); ^{19}F NMR (470 MHz, Acetone-d_6) δ -63.31 (3F); ^{13}C NMR (126 MHz, Acetone-d_6) δ 145.15 , 144.86 , 125.45 (q, J = 253.5 Hz) , 124.93 , 124.86 , 123.00 , 120.81 , 49.22 (d, J = 2.2 Hz), 44.22 , 44.01 , 32.76 (d, J = 3.0 Hz), 29.26 , 27.67 , 27.23 , 22.44 . HR-MS (EI) Calcd. For 345.1704, $C_{21}H_{22}F_3N$, found 345.1698.

1-(perfluoroethyl)-4-phenylpiperazine 4kk. 
Colorless oil, yield 81% (113.5 mg). Eluent: ethyl acetate/petroleum ether (5:95). ^{1}H NMR (500 MHz, Acetone-d_6) δ 7.30 – 7.21 (m, 2H), 7.00 (d, J = 8.2 Hz, 2H), 6.85 (t, J = 7.3 Hz, 1H), 3.26 (dd, J = 6.4, 3.6 Hz, 4H), 3.17 (t, J = 4.8 Hz, 4H); ^{19}F NMR (470 MHz, Acetone-d_6) δ -60.91 (d, J = 8.6 Hz, 3F), -64.37 (d, J = 8.4 Hz, 2F); ^{13}C NMR (126 MHz, Acetone-d_6) δ 150.86 , 128.70 , 119.67 , 116.02 , 48.32 , 43.75. HR-MS (EI) Calcd. For 280.0999, $C_{12}H_{13}F_5N_2$, found 280.0994.

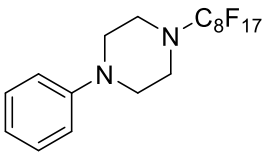
1-(perfluoropropyl)-4-phenylpiperazine 4ll. 
Colorless oil, yield 73% (120.5 mg). Eluent: ethyl acetate/petroleum ether (5:95). ^{1}H NMR (500 MHz, Acetone-d_6) δ 7.25 (dd, J = 8.8, 7.2 Hz, 2H), 6.99 (d, J = 8.1 Hz, 2H), 6.85 (t, J = 7.3 Hz, 1H), 3.25 (dd, J = 6.9, 3.4 Hz, 4H), 3.23 – 3.18 (m, 4H); ^{19}F NMR (470 MHz, Acetone-d_6) δ -79.77 (dh, J = 20.3, 8.4, 6.5 Hz, 3F)., -94.96 (dt, J = 23.7, 11.0 Hz, 2F), -121.32 (dd, J = 24.9, 13.3 Hz, 2F); ^{13}C NMR (126 MHz, Acetone-d_6) δ 152.19 , 130.05 , 121.02 , 117.34 , 49.66 , 45.23 (p, J = 3.8 Hz). HR-MS (EI) Calcd. For 330.0967, $C_{13}H_{13}F_7N_2$, found 330.0963.

1-(perfluorobutyl)-4-phenylpiperazine 4mm. 
Colorless oil, yield 74% (140.4 mg). Eluent: ethyl acetate/petroleum ether (5:95). ^{1}H NMR (500 MHz, Acetone-d_6) δ 7.25 (t, J = 7.8 Hz, 2H), 7.00 (d, J = 8.1 Hz, 2H), 6.85 (t, J = 7.3 Hz, 1H), 3.23 (q, J = 5.9 Hz, 8H); ^{19}F NMR (470 MHz, Acetone-d_6) δ -80.55 (t, J = 9.7 Hz, 3F), -95.42 (d, J = 12.7 Hz, 2F), -119.58 (d, J = 9.8 Hz, 2F), -126.09 (d, J = 11.1 Hz, 2F); ^{13}C NMR (126 MHz, Acetone-d_6) δ 150.85 , 128.70 , 119.67 , 116.01 , 48.39 , 43.98 (dt, J = 4.1, 1.9 Hz). HR-MS (EI) Calcd. For 380.0935, $C_{14}H_{13}F_9N_2$, found 380.0927.

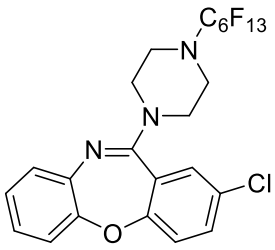
1-(perfluorohexyl)-4-phenylpiperazine 4nn. Colorless oil, yield 65% (156.1 mg). Eluent: ethyl acetate/petroleum ether (5:95). ^{1}H NMR (500 MHz, Acetonitrile-*d*3) δ 7.29 – 7.22 (m, 2H), 6.97 – 6.92 (m, 2H), 6.89 – 6.83 (m, 1H), 3.17 (s, 8H); ^{19}F NMR (470 MHz, Acetonitrile-*d*3) δ -80.71 (t, *J* = 10.0 Hz, 3F), -95.30 (t, *J* = 13.3 Hz, 2F), -119.03 (td, *J* = 15.5, 5.9 Hz, 2F), -121.97 – -122.26 (m, 2F), -122.27 – -122.59 (m, 2F), -125.75 (tq, *J* = 10.8, 5.6, 4.5 Hz, 2F); ^{13}C NMR (126 MHz, Acetonitrile-*d*3) δ 152.30 , 130.26 , 121.17 , 117.42 , 49.80 , 45.37 (t, *J* = 3.8 Hz). HR-MS (EI) Calcd. For 480.0871, $C_{16}H_{13}F_{13}N_2$, found 480.0865.



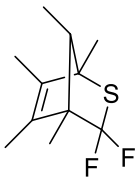
1-(perfluorooctyl)-4-phenylpiperazine 4oo. White solid, M.p. 65.7-68.3 ºC, yield 49% (141.7 mg). Eluent: ethyl acetate/petroleum ether (3:97). ^{1}H NMR (500 MHz, Acetone-d_6) δ 7.31 – 7.21 (m, 2H), 7.09 – 6.97 (m, 2H), 6.85 (t, *J* = 7.3 Hz, 1H), 3.26 (q, *J* = 6.3 Hz, 8H); ^{19}F NMR (470 MHz, Acetone-d_6) δ -80.39 (t, *J* = 10.2 Hz, 3F) , -95.03 (d, *J* = 13.0 Hz, 2F), -118.64 (t, *J* = 14.6 Hz, 2F), -120.76 – -121.29 (m, 4F), -121.41 – -121.76 (m, 2F), -122.02 (d, *J* = 11.8 Hz, 2F), -125.07 – -125.93 (m, 2F); ^{13}C NMR (126 MHz, Acetone-d_6) δ 152.22 , 130.04 , 121.00 , 117.35 , 49.79 , 45.38. HR-MS (EI) Calcd. For 580.0807, $C_{18}H_{13}F_{17}N_2$, found 580.0798.



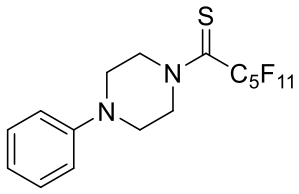
2-chloro-11-(4-(perfluorohexyl)piperazin-1-yl)dibenzo[*b*,*f*][1,4]oxazepine 4pp. Yellow oil, yield 61% (192.4 mg). Eluent: ethyl acetate/petroleum ether (5:95). ^{1}H NMR (500 MHz, Acetone-d_6) δ 7.55 (dd, *J* = 8.6, 2.6 Hz, 1H), 7.50 (d, *J* = 2.6 Hz, 1H), 7.35 (d, *J* = 8.6 Hz, 1H), 7.19 – 7.07 (m, 3H), 7.02 (td, *J* = 7.6, 2.0 Hz, 1H), 3.60 (s, 4H), 3.25 (s, 4H); ^{19}F NMR (470 MHz, Acetone-d_6) δ -80.44 (t, *J* = 10.3 Hz, 3F), -94.80 (t, *J* = 13.7 Hz, 2F), -118.76 (t, *J* = 15.6 Hz, 2F), -121.23 – -121.97 (m, 2F), -122.13 (d, *J* = 15.8 Hz, 2F), -125.50 (td, *J* = 14.8, 6.5 Hz, 2F); ^{13}C NMR (126 MHz, Acetone-d_6) δ 160.53 , 159.66 , 152.86 , 141.16 , 134.00 , 131.18 , 130.00 , 128.03 , 126.76 , 125.93 , 125.79 , 124.01 , 121.22 , 47.94 , 44.99 . HR-MS (EI) Calcd. For 631.0696, $C_{23}H_{15}ClF_{13}N_3O$, found 631.0693.



(1R,4R,7S)-3,3-difluoro-1,4,5,6,7-pentamethyl-2-thiabicyclo[2.2.1]hept-5-ene 11.[3] Yellow oil, yield 40% (43.7 mg). Eluent: ethyl acetate/petroleum ether (1:99). ^{1}H NMR (500 MHz, Chloroform-*d*) δ 2.47 (q, *J* = 6.5 Hz, 1H), 1.66 (d, *J* = 14.6 Hz, 6H), 1.43 (d, *J* = 1.4 Hz, 3H), 1.23 (d, *J* = 1.4 Hz, 3H), 0.72 (dd, *J* = 6.6, 1.6 Hz, 3H); ^{19}F NMR (470 MHz, Chloroform-*d*) δ -80.06 (d, *J* = 200.3 Hz, 1F), -87.13 (d, *J* = 200.3 Hz, 1F); ^{13}C NMR (126 MHz, Chloroform-*d*) δ 149.11 (t, *J* = 280.5 Hz) , 142.95 (d, *J* = 4.6 Hz), 134.25 (d, *J* = 3.2 Hz), 71.35 , 65.24 (t, *J* = 19.0 Hz), 63.13 (t, *J* = 1.9 Hz), 16.06 (d, *J* = 2.0 Hz), 12.64 , 11.11 , 10.74 , 9.86 (d, *J* = 5.3 Hz).



2,2,3,3,4,4,5,5,6,6,6-undecafluoro-1-(4-phenylpiperazin-1-yl)hexane-1-thione 3b.

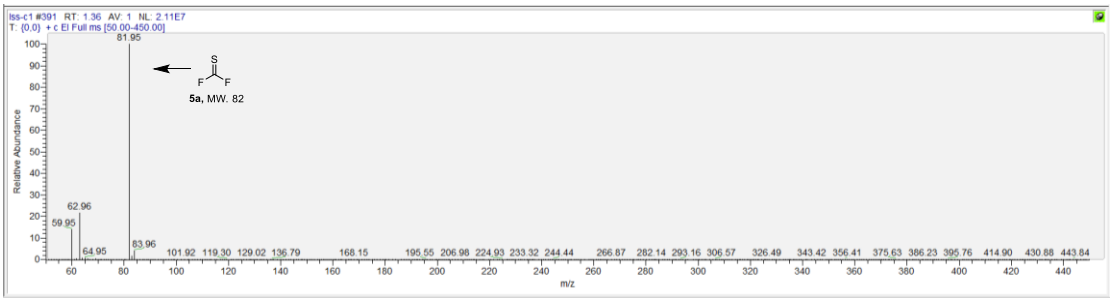


Yellow oil, yield 77% (182.4 mg). Eluent: ethyl acetate/petroleum ether (5:95). ^{1}H NMR (500 MHz, Acetone-d_6) δ 7.28 (dd, J = 8.6, 7.0 Hz, 2H), 7.02 (d, J = 8.1 Hz, 2H), 6.87 (t, J = 7.3 Hz, 1H), 4.52 (t, J = 5.3 Hz, 2H), 4.23 (t, J = 5.0 Hz, 2H), 3.45 (dt, J = 19.8, 5.1 Hz, 4H); ^{19}F NMR (470 MHz, Acetone-d_6) δ -80.83 (t, J = 10.1 Hz, 3F), -96.30 (t, J = 15.5 Hz, 2F), -118.08 (t, J = 10.9 Hz, 2F), -121.63 – -121.89 (m, 2F), -125.84 (td, J = 12.6, 11.8, 6.3 Hz, 2F); ^{13}C NMR (126 MHz, Acetone-d_6) δ 151.33 , 130.14 , 120.94 , 116.91 , 53.52 , 53.38 , 50.22 , 48.75 . HR-MS (EI) Calcd. For 474.0624, $C_{16}H_{13}F_{11}N_2S$, found 474.0617.

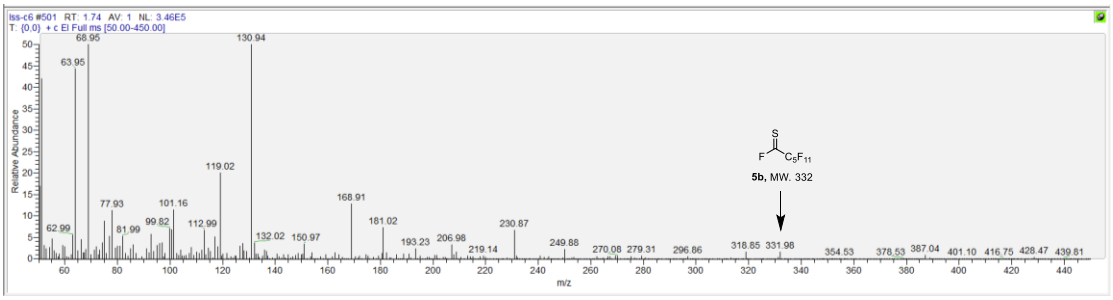
5. MS-EI study

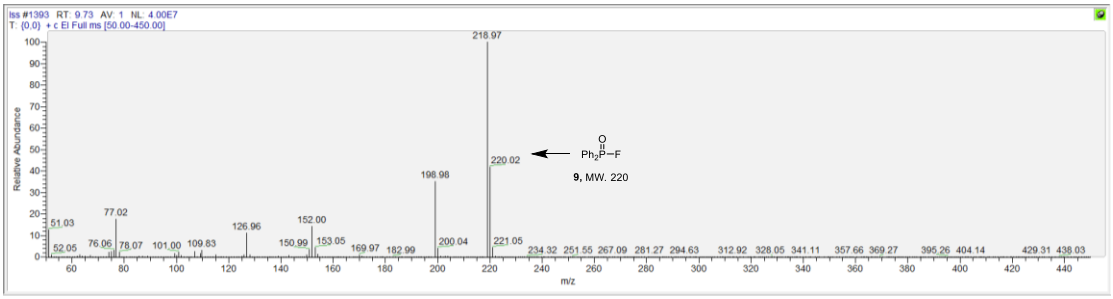
The following reactions do not require glove box.

To a miture of CF_3SO_2Na (0.5 mmol, 78 mg.) and PPh_3 (1 mmol, 262 mg.) was added MeCN (2 mL), the resulting solution was stirred at room temperature for few minutes, then the mixture was used for MS-EI test. The result was shown in the following spectra.

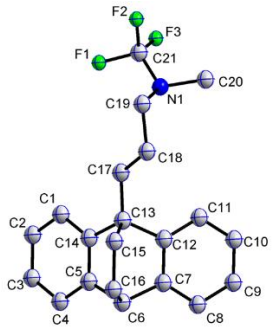


To a miture of $C_6F_{13}SO_2Na$ (0.5 mmol, 203 mg.) and PPh_3 (0.5 mmol, 131 mg.), Ph_2PCl (0.5 mmol, 110 mg.) dissolved in MeCN (3 mL) was added, the resulting solution was stirred at room temperature for few minutes, then the mixture was used for MS-EI test. The result was shown in the following spectra.





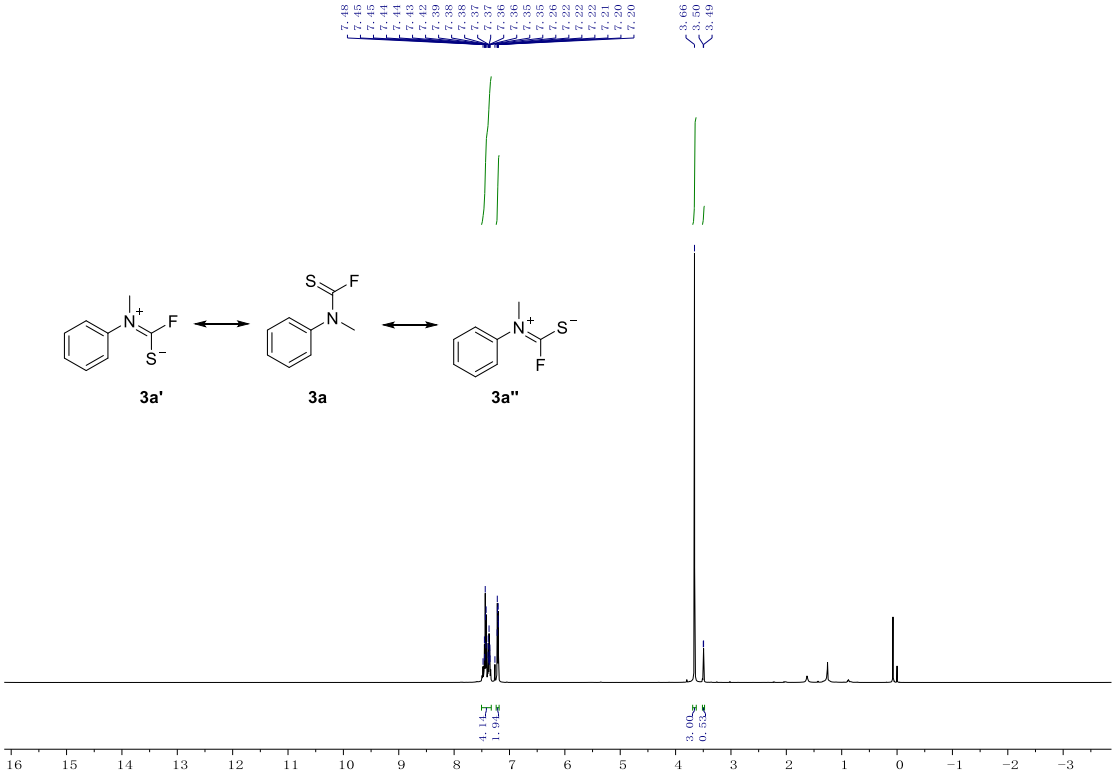
6. Crystallographic data for 4jj

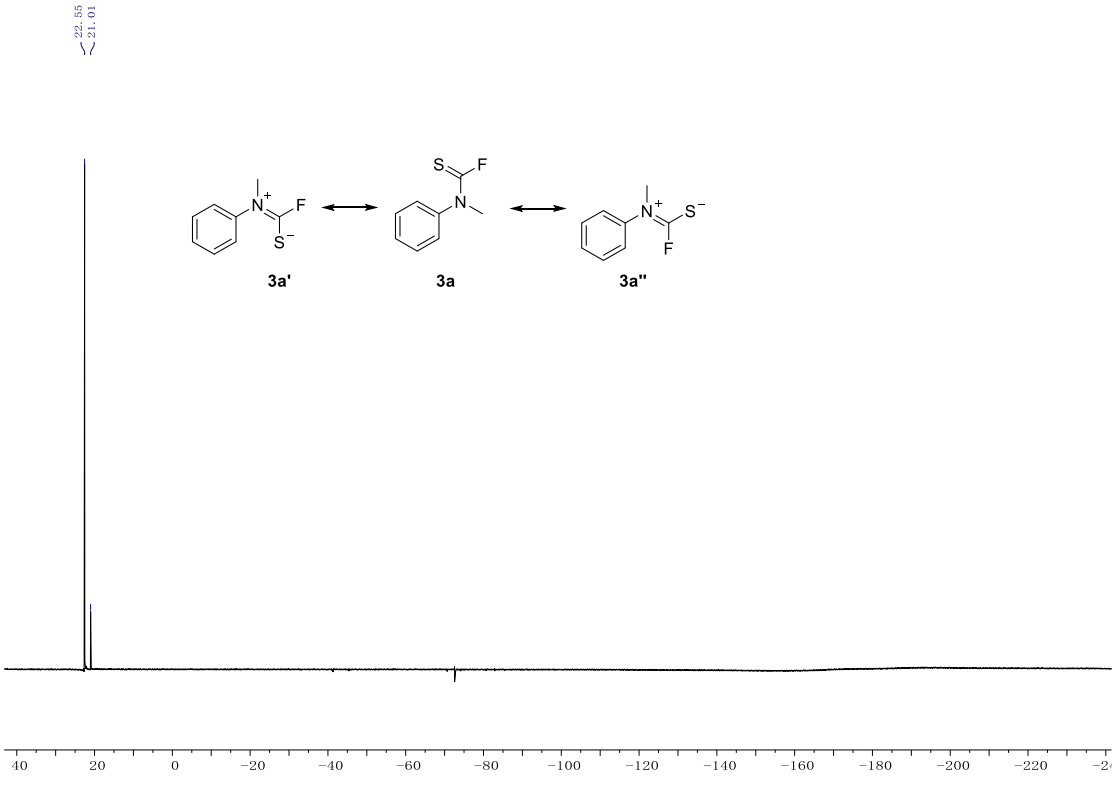


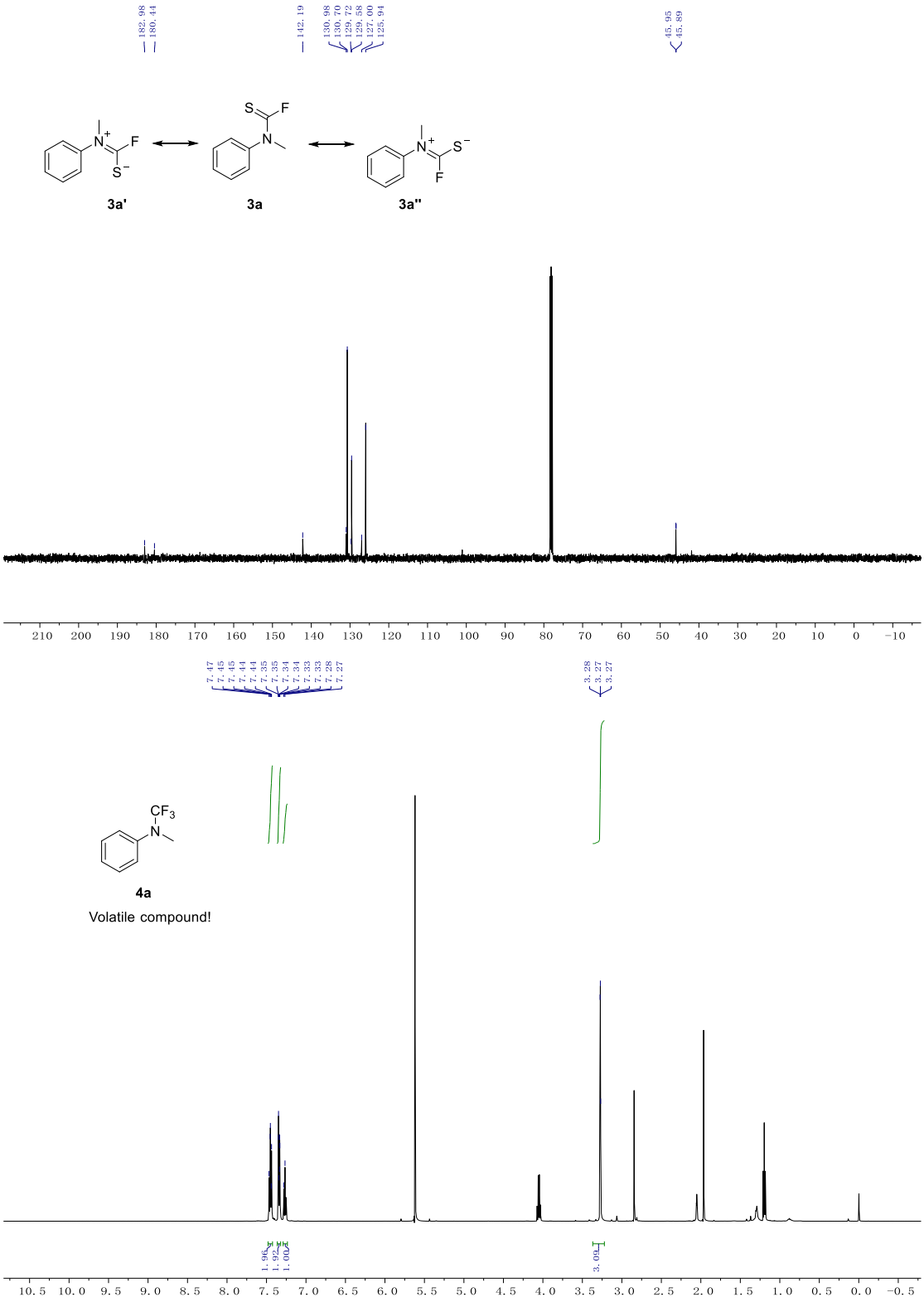
complex	**4jj**
Formula	$C_{21}H_{22}F_3N$
Formula weight	345.39
Crystal system	Monoclinic
space group	*P21/n*
a (Å)	8.815(4)
b (Å)	22.040(10)
c (Å)	9.233(4)
α (º)	90
β (º)	105.538(9)
γ (º)	90
Volume(Å^3)	1728.3(13)
Z	4
T (K)	173(2)
D_{calcd} (g/m^3)	1.327
F(000)	728
Reflections collected	4010
Unique reflections	2377
Goof	1.067
R_1[I> 2σ(I)]	0.0928
wR_2[I>2σ(I)]	0.2180[a]
CCDC NO.	1892271

[a] $w = 1/[\sigma^2(F_0)^2+(0.1030P)^2 +1.5674P]$, where P = $(F_0^2 + 2F_c^2)/3$;

7. NMR spectra



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130.98
130.70
129.72
129.58
127.00
125.94
45.95
45.89
3a'
3a
3a''
7.47
7.45
7.45
7.44
7.44
7.35
7.35
7.34
7.34
7.33
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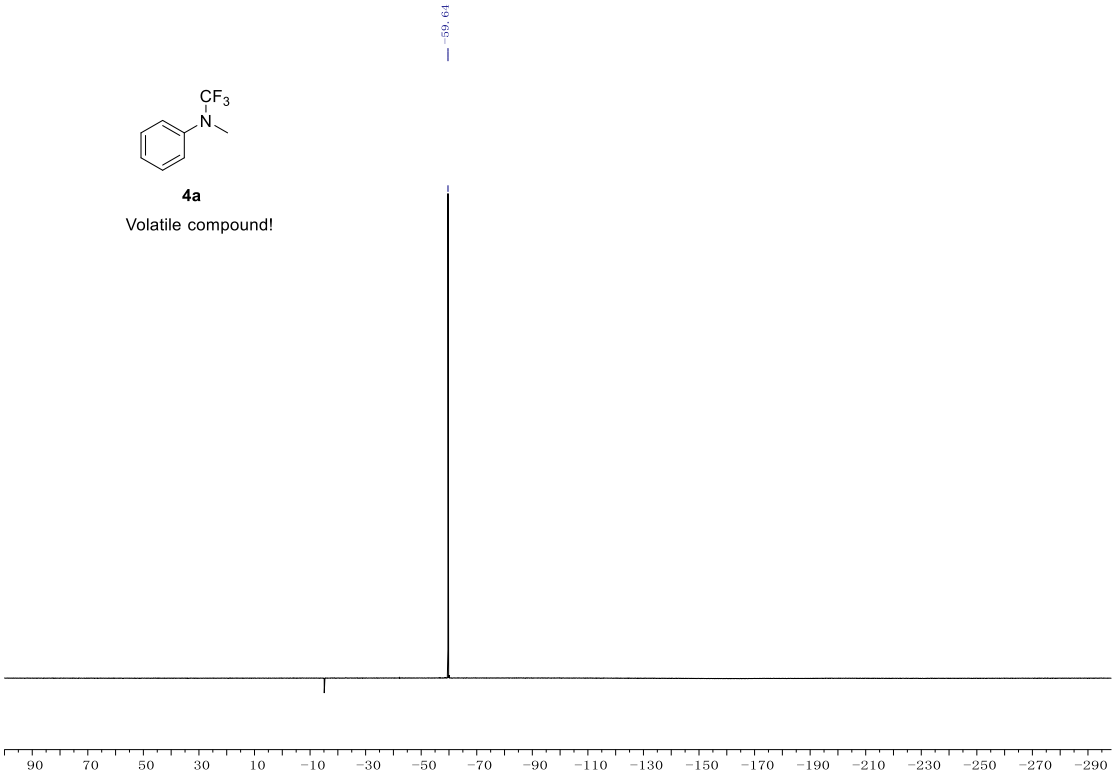
4a
Volatile compound!
1.96
1.92
1.00
3.09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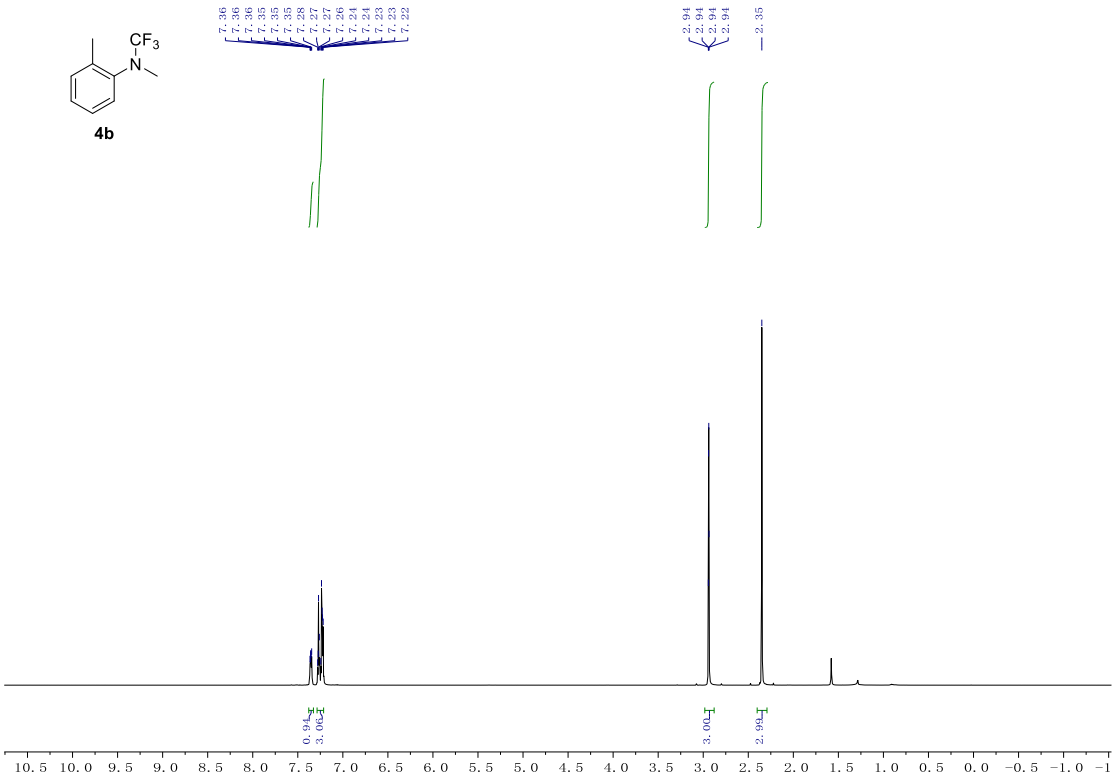
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7.24
7.23
7.23
7.22
2.94
2.94
2.94
2.94
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2.35
0.94
3.06
3.00
2.99
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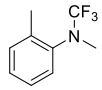
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4b

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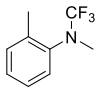
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4b

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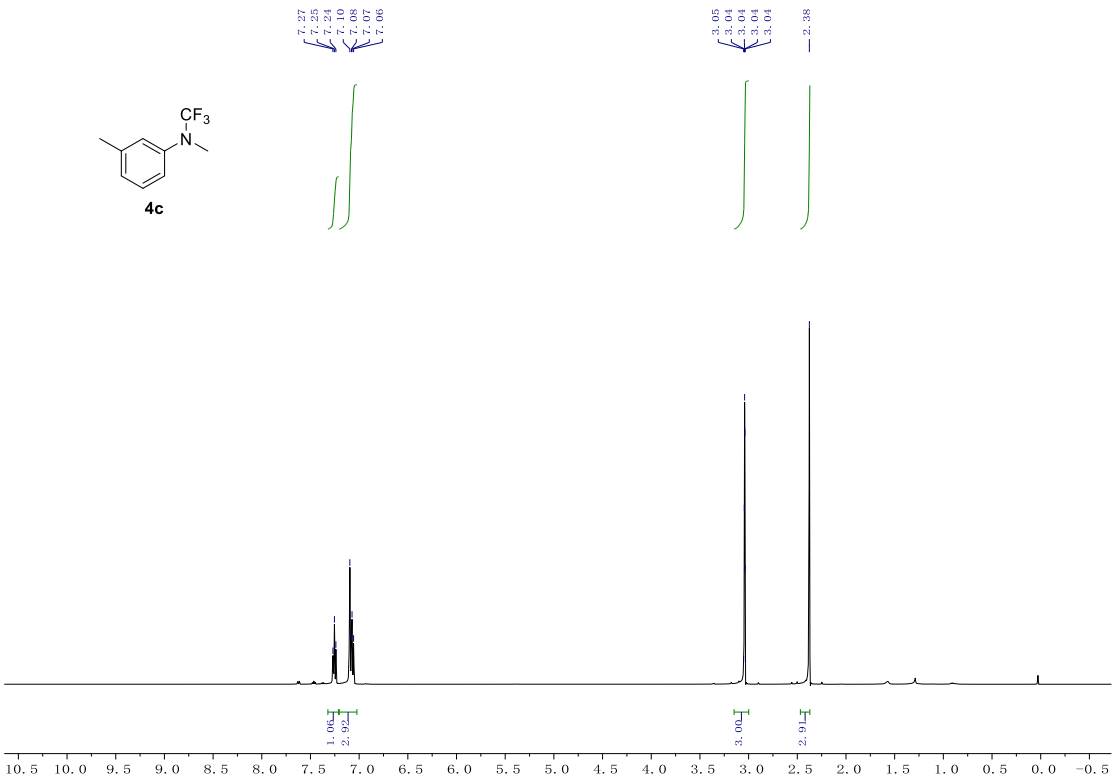
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4c
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2.92
3.00
2.91
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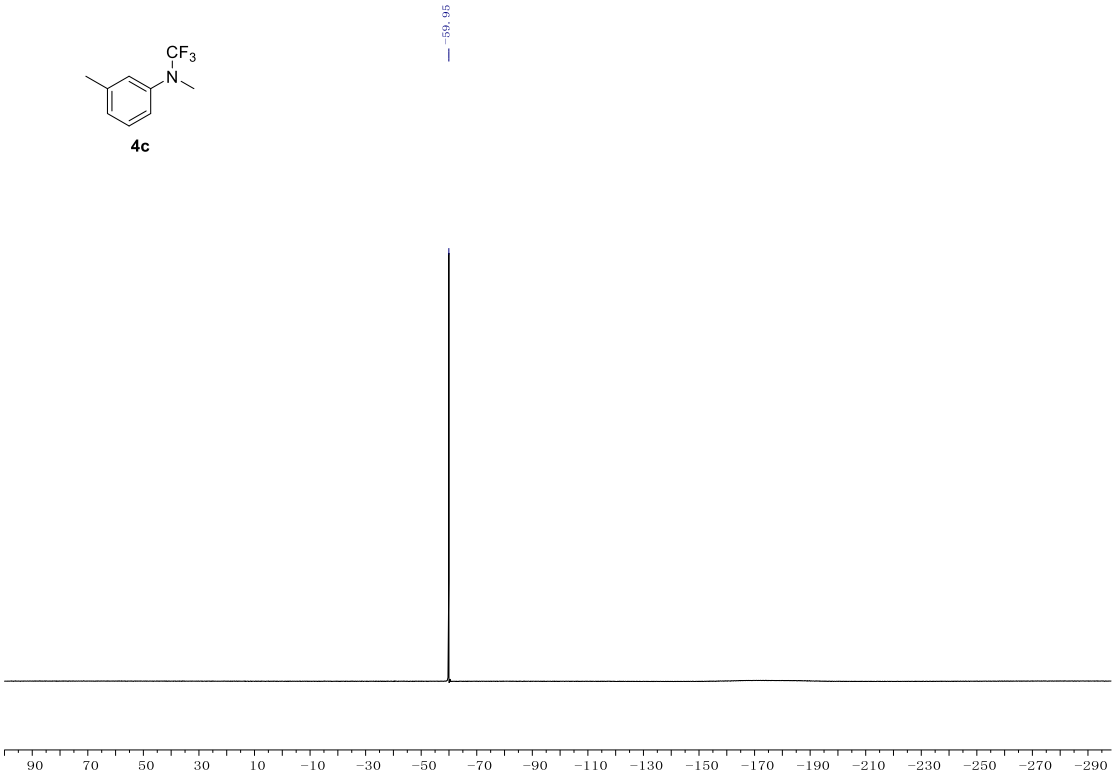
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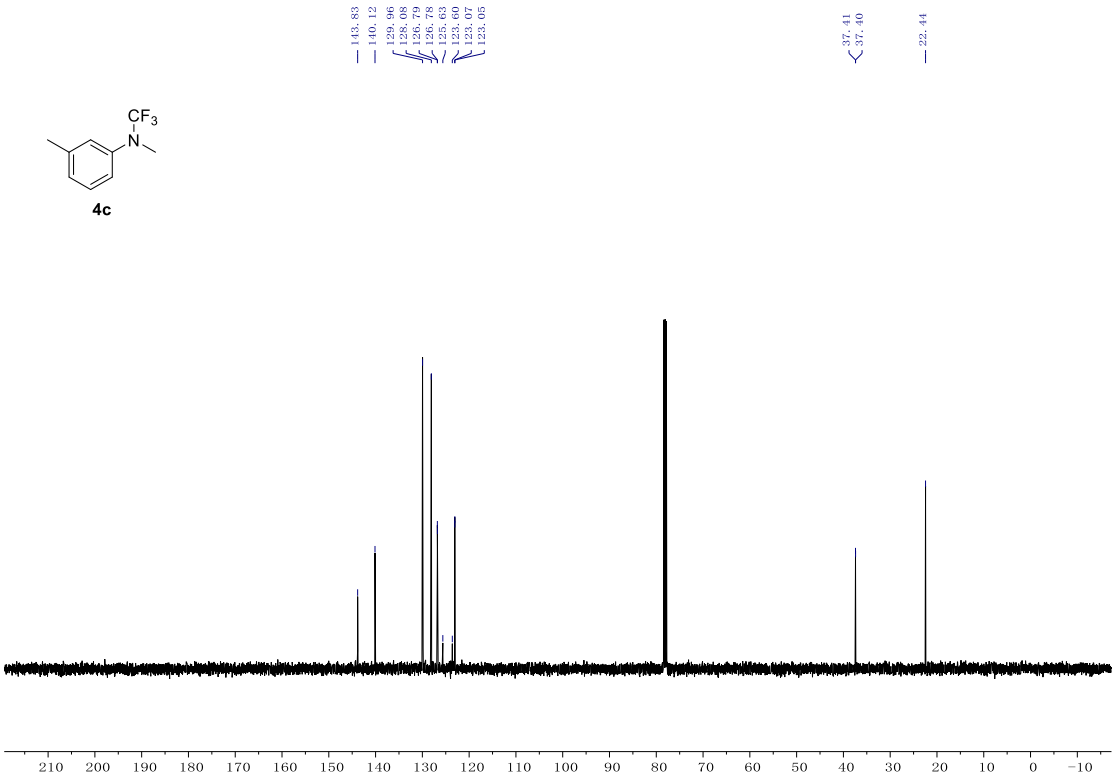
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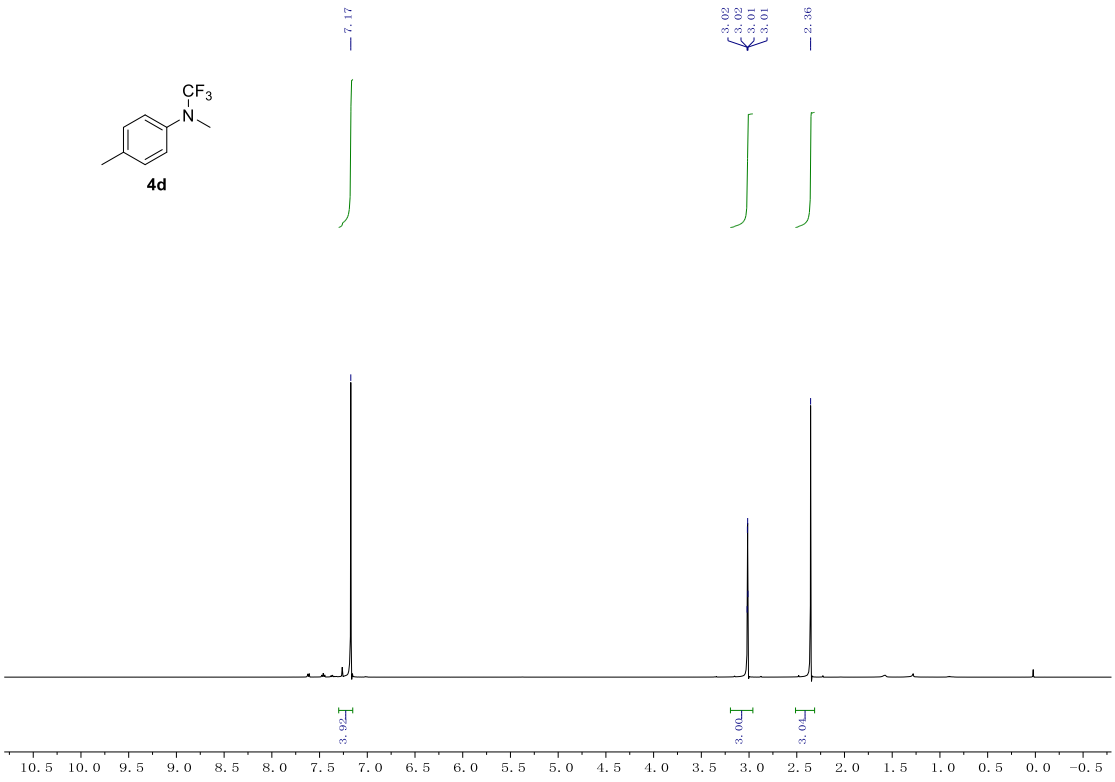
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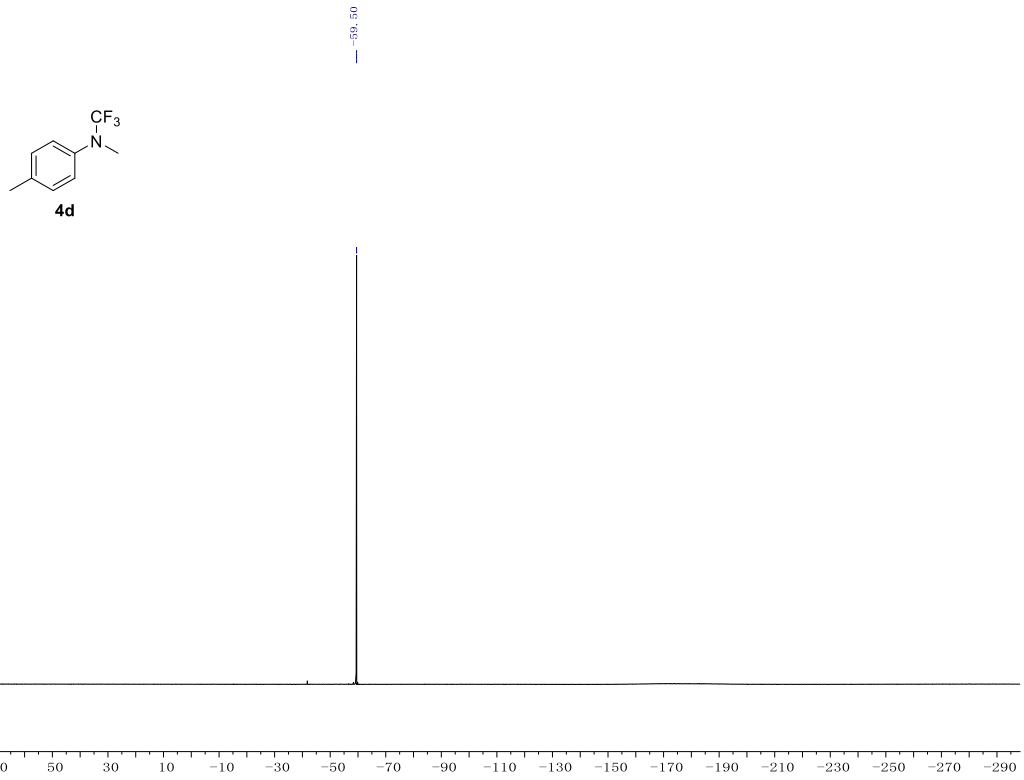
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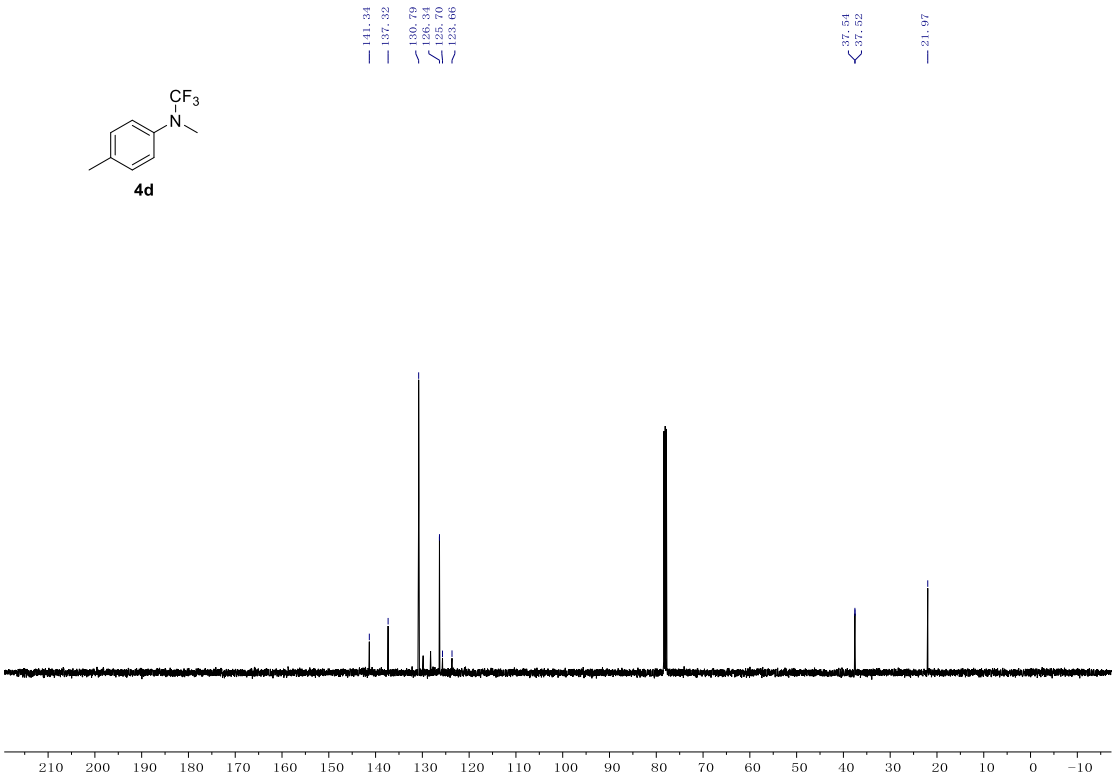
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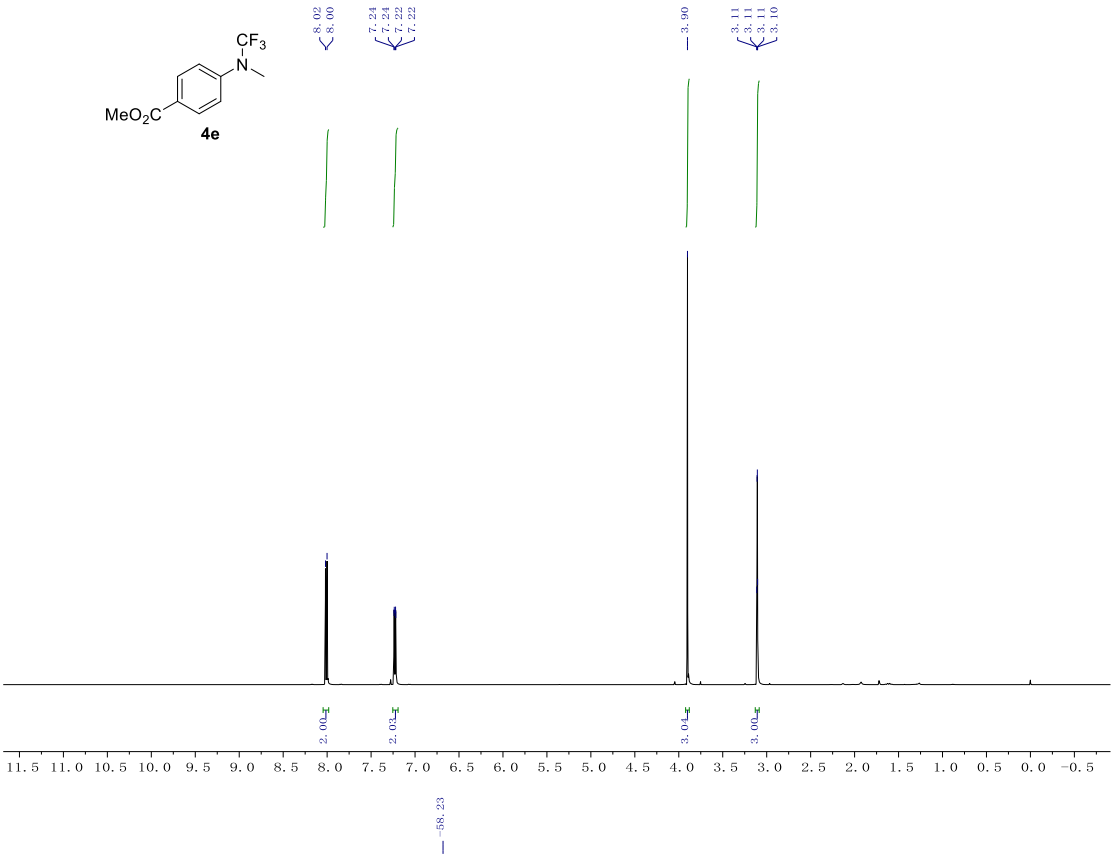
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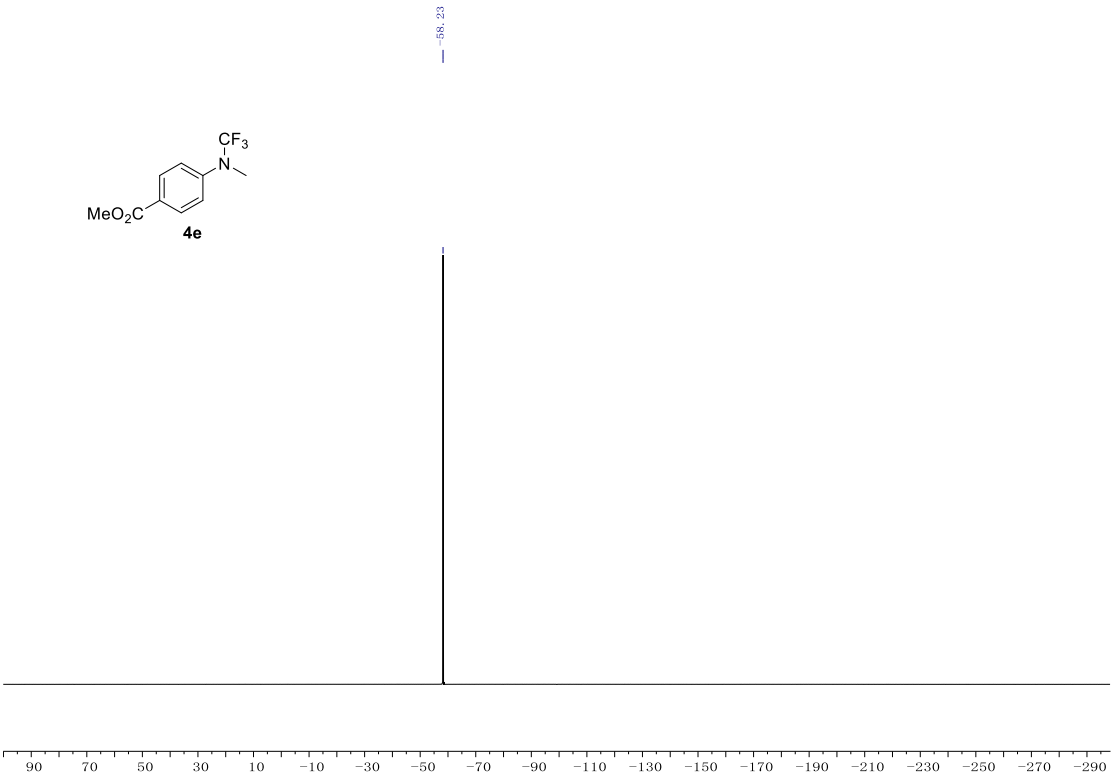
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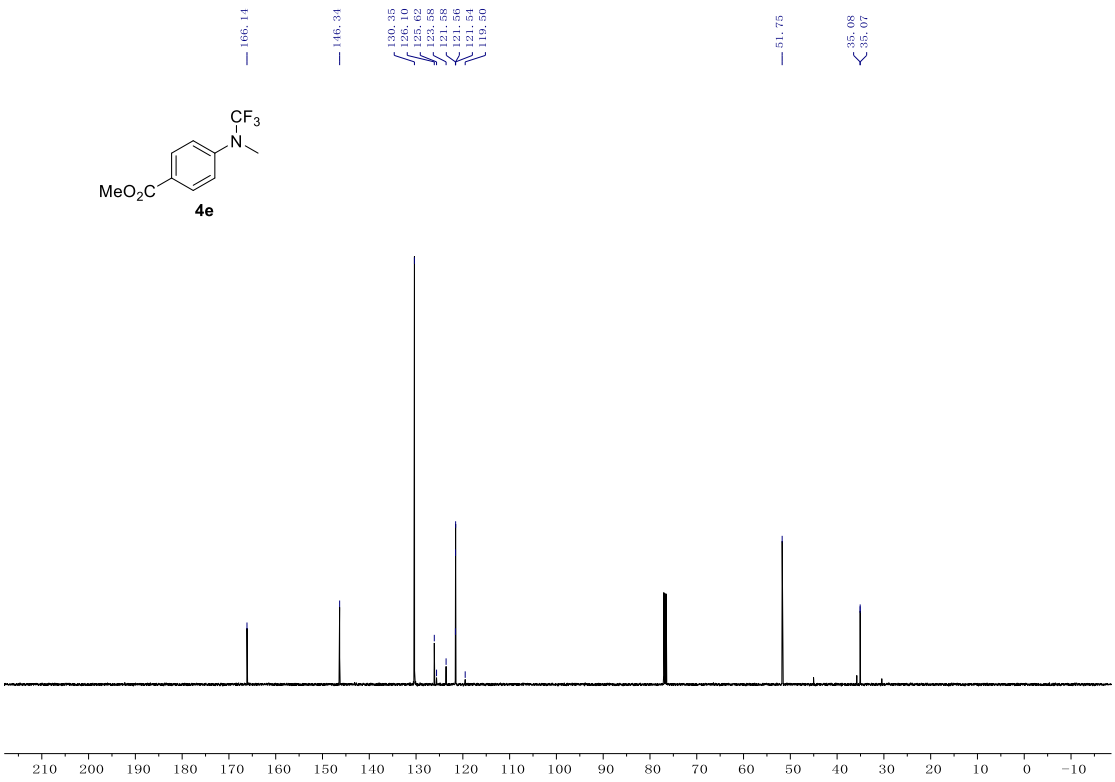
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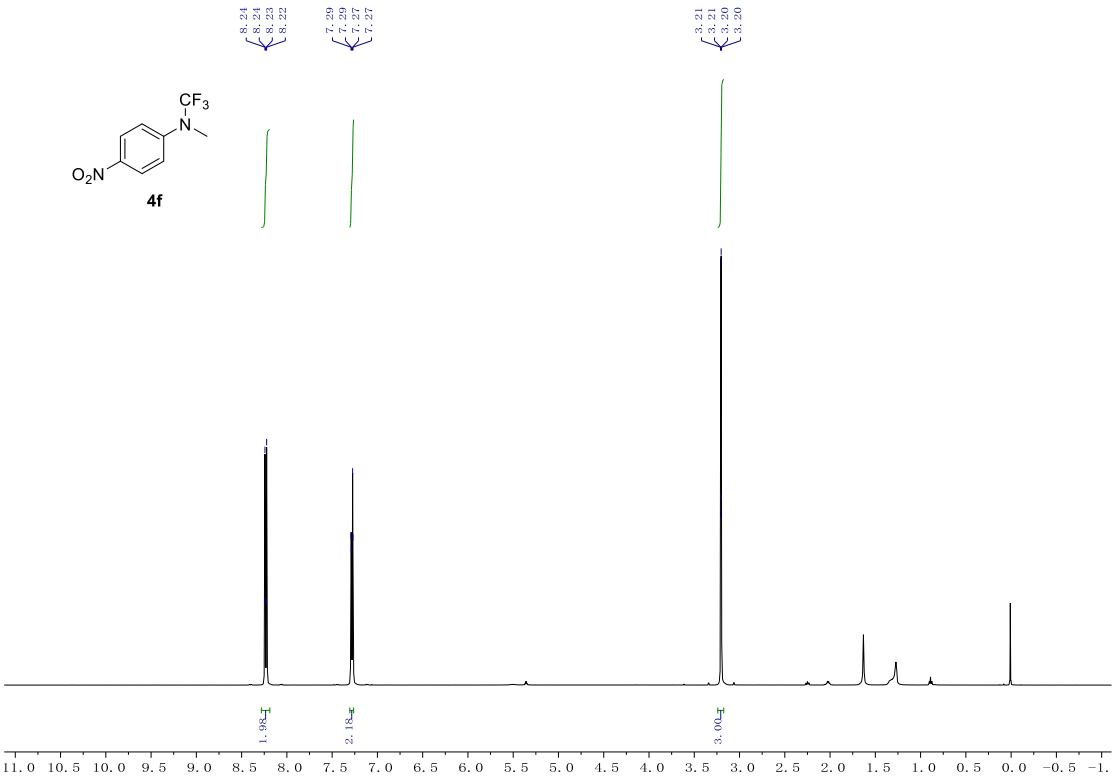
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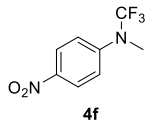
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O2N

4f

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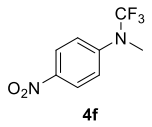
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N
O2N

4f

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121.94
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36.25
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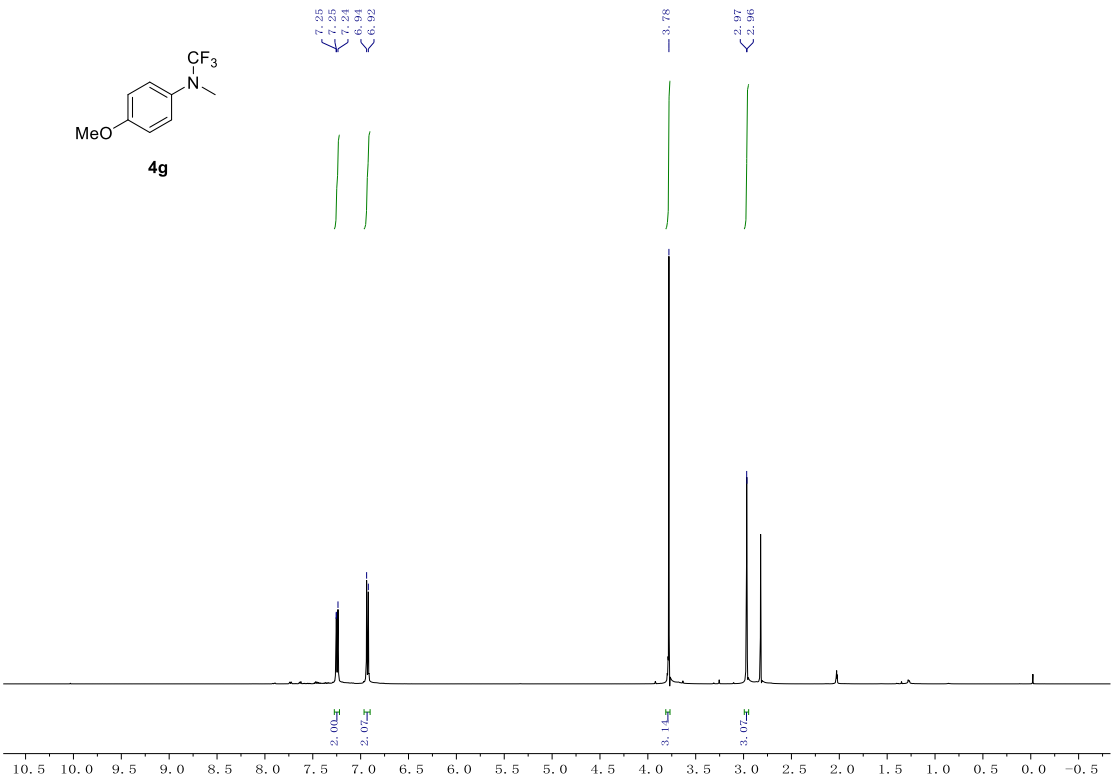
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2.96
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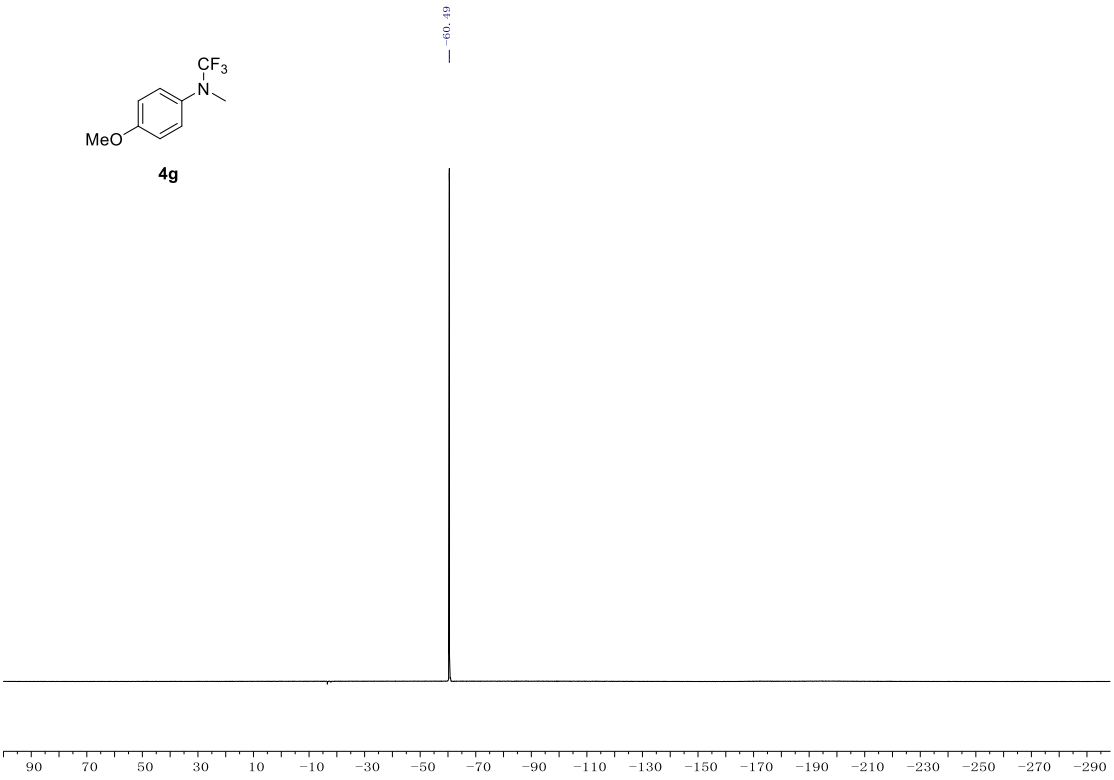
2.07
3.14
3.07
10.5 10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0 -0.5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4g
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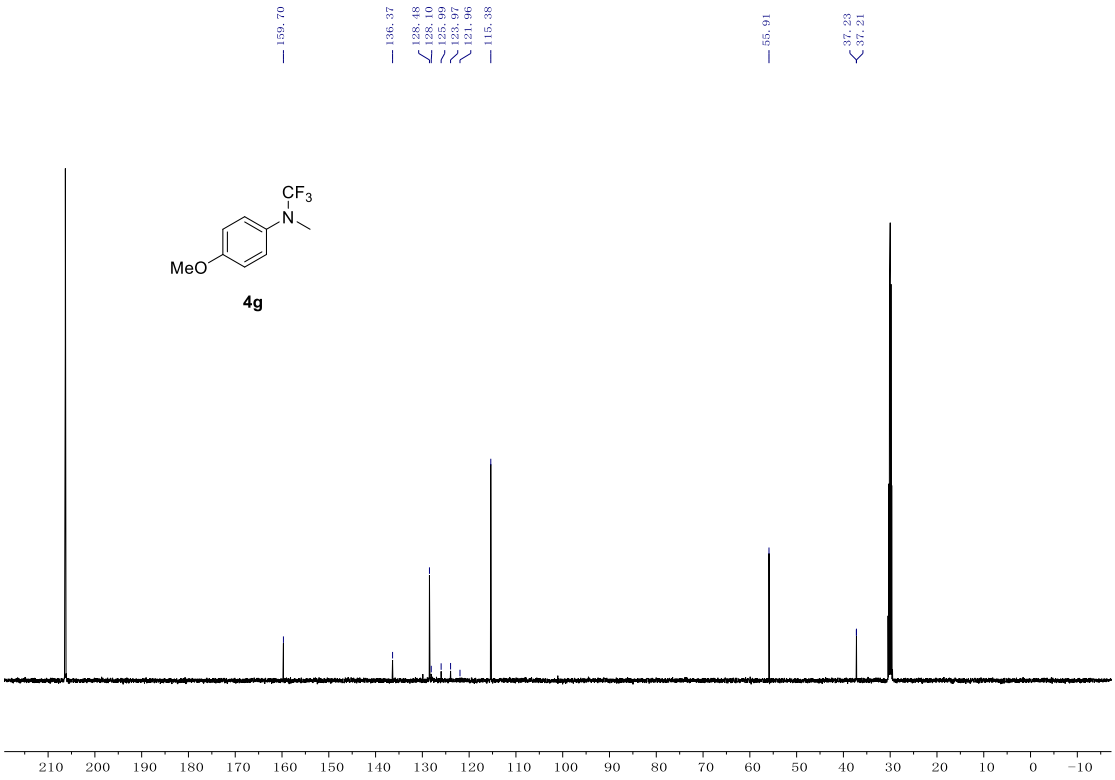
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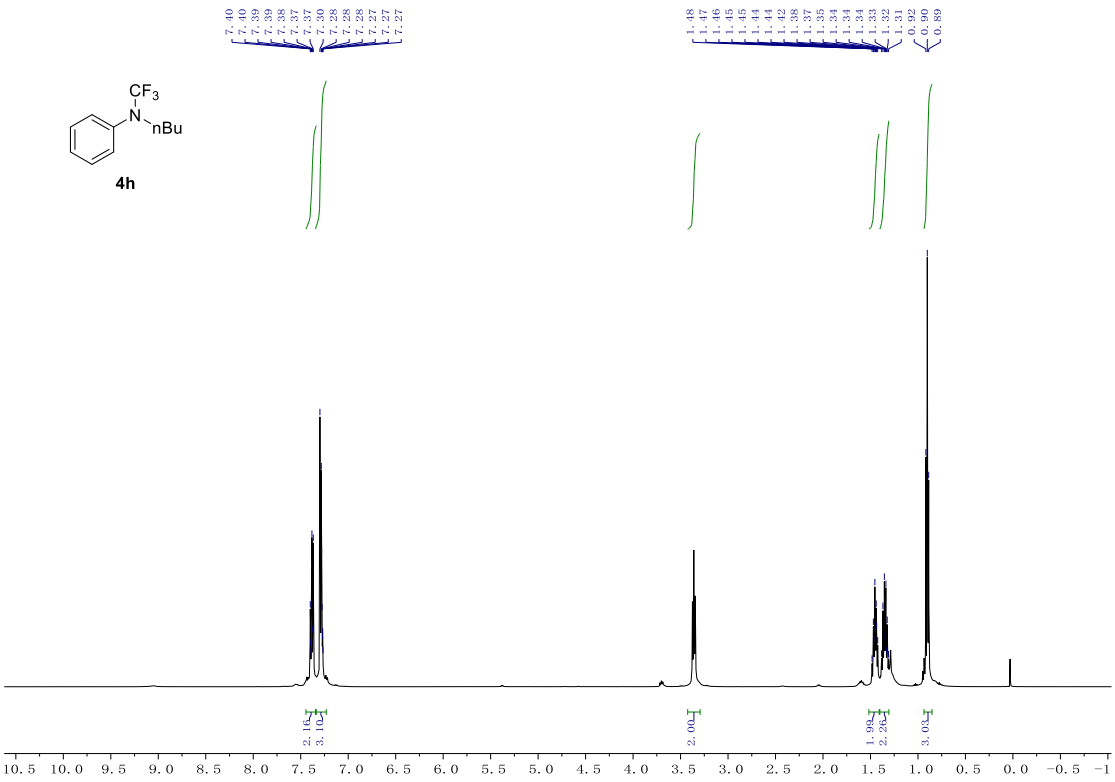
MeO
4g
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 −10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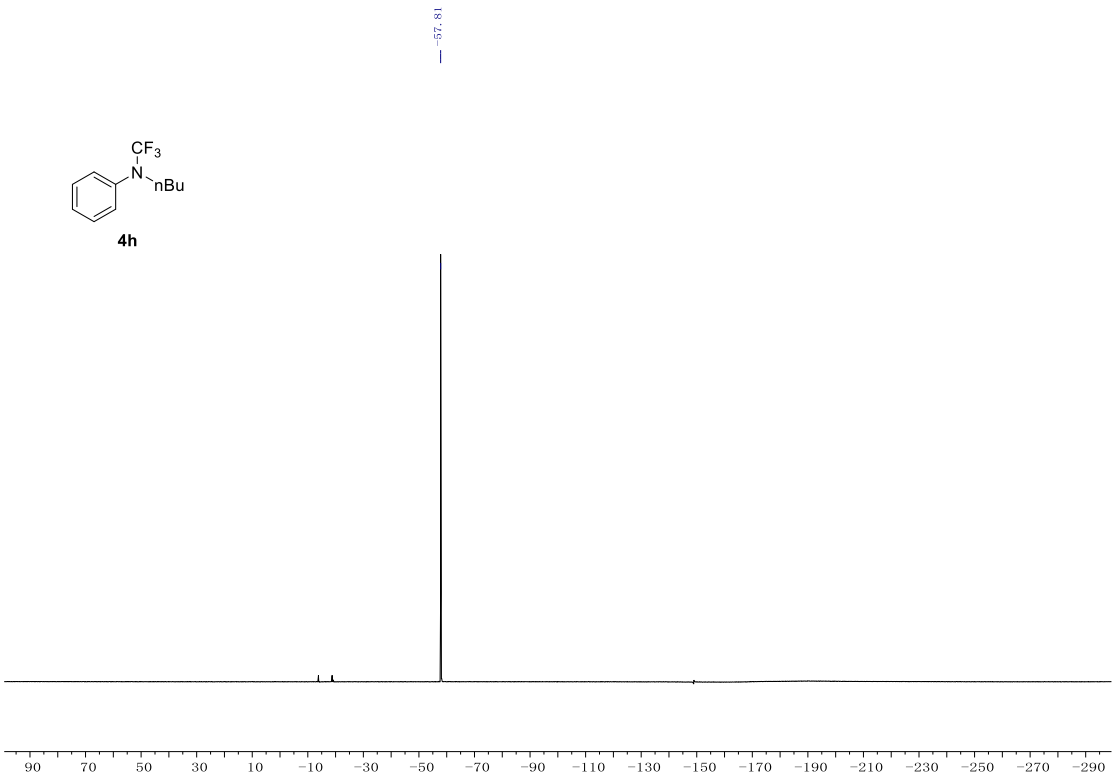
7.27
7.27
1.48
1.47
1.46
1.45
1.45
1.44
1.44
1.42
1.38
1.37
1.35
1.34
1.34
1.34
1.33
1.32
1.31
0.92
0.90
0.89
CF3
N
nBu
4h
2.16
3.10
2.00
1.99
2.26
3.03
10.5 10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0 −0.5 −1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nBu
4h
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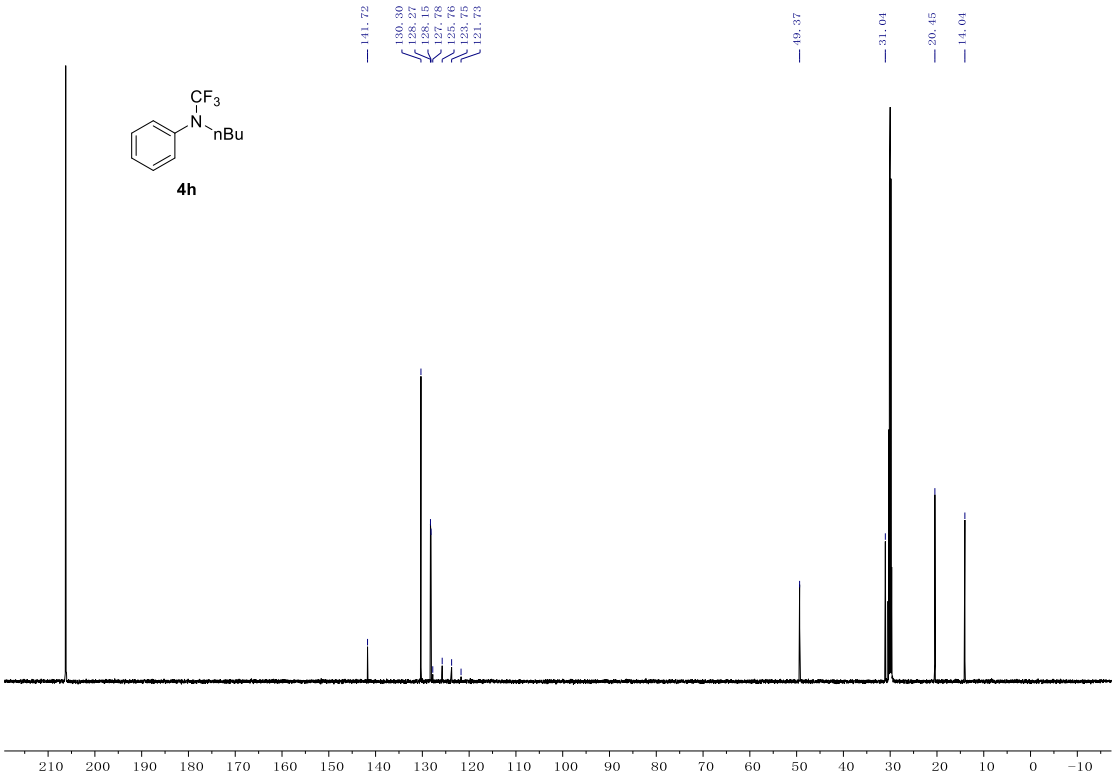
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N
nBu
4h
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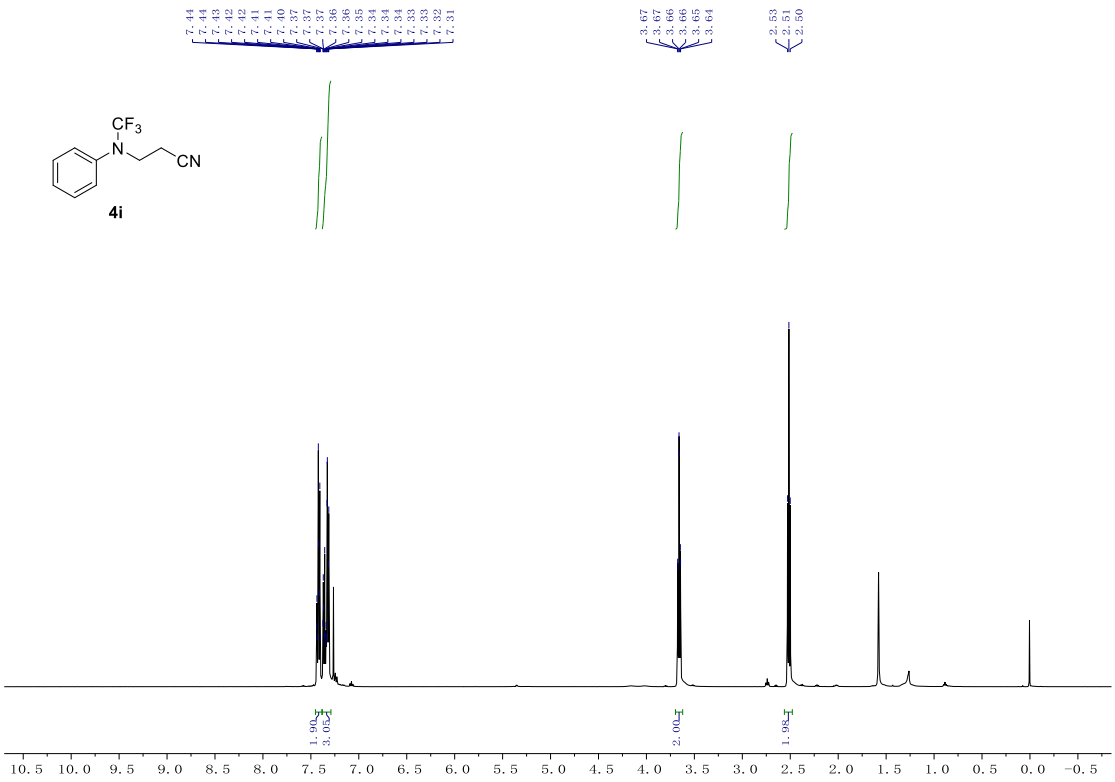
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7.31
3.67
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3.66
3.66
3.65
3.64
2.53
2.51
2.50
CF3
N
CN
4i
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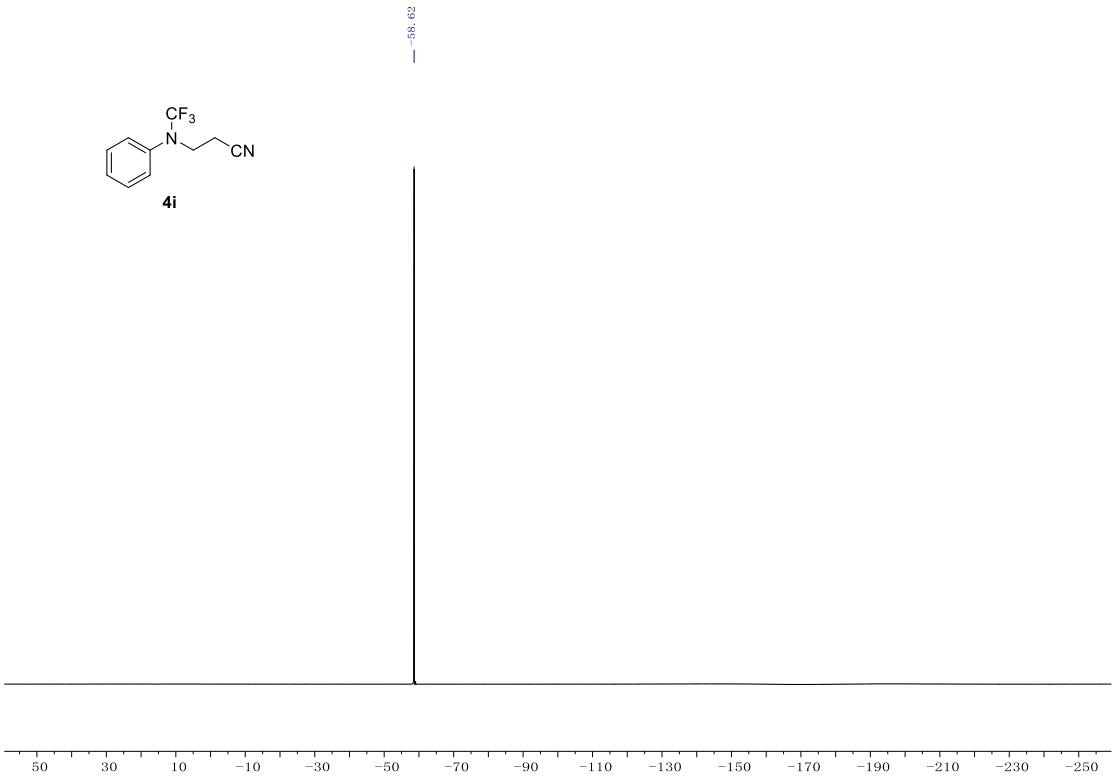
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CN
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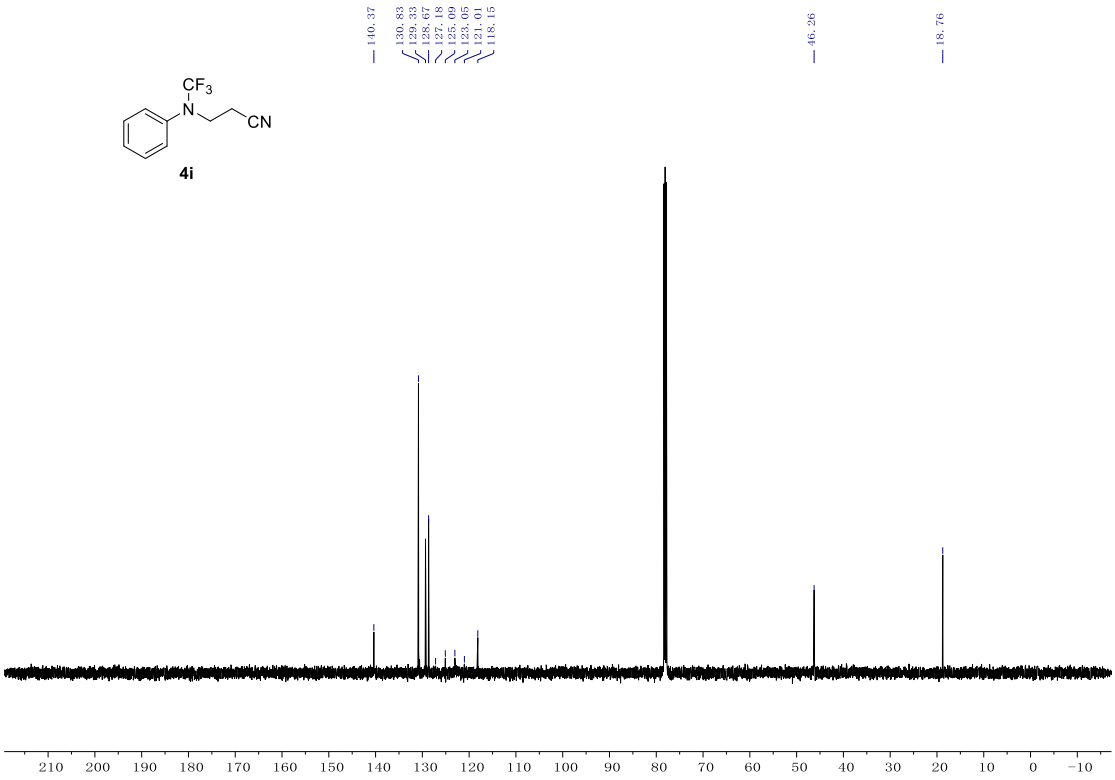
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121.01
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46.26
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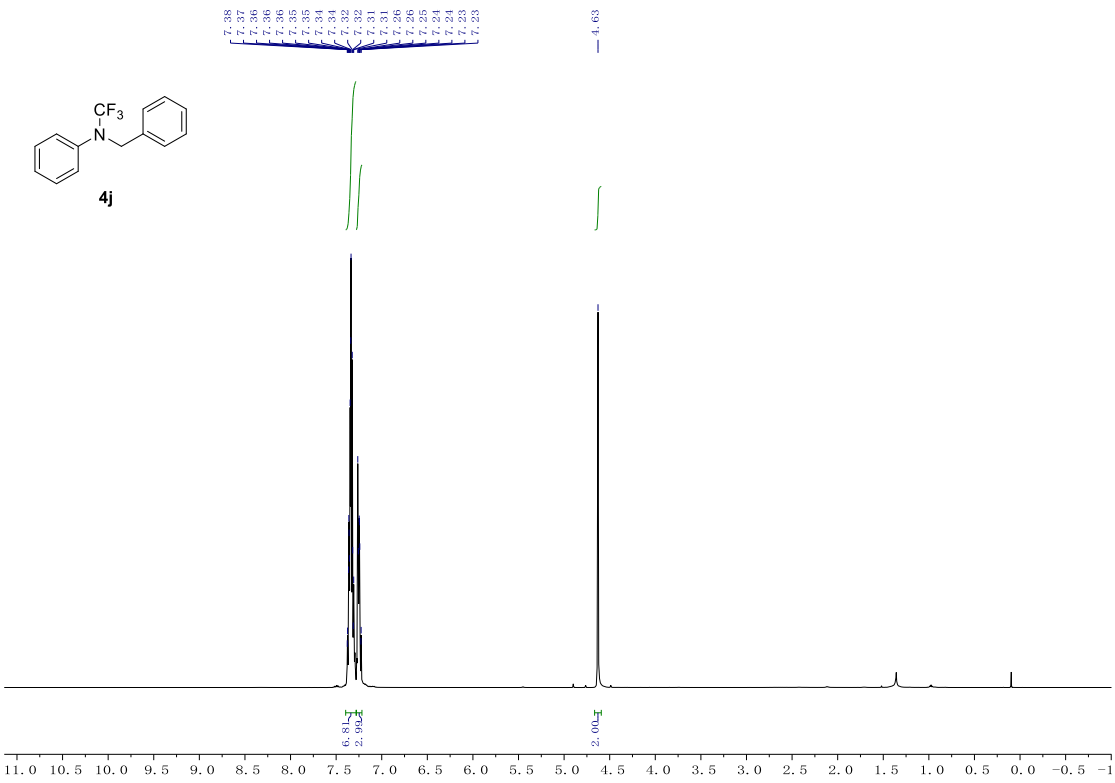
CF3
N
CN
4i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7.24
7.23
7.23
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CF3
N
4j
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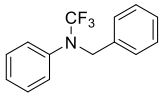
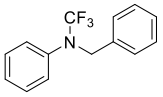
2.99
2.00



4j

-57.38
90 70 50 30 10 -10 -30 -50 -70 -90 -110 -130 -150 -170 -190 -210 -230 -250 -270 -290



4j

140.93
136.83
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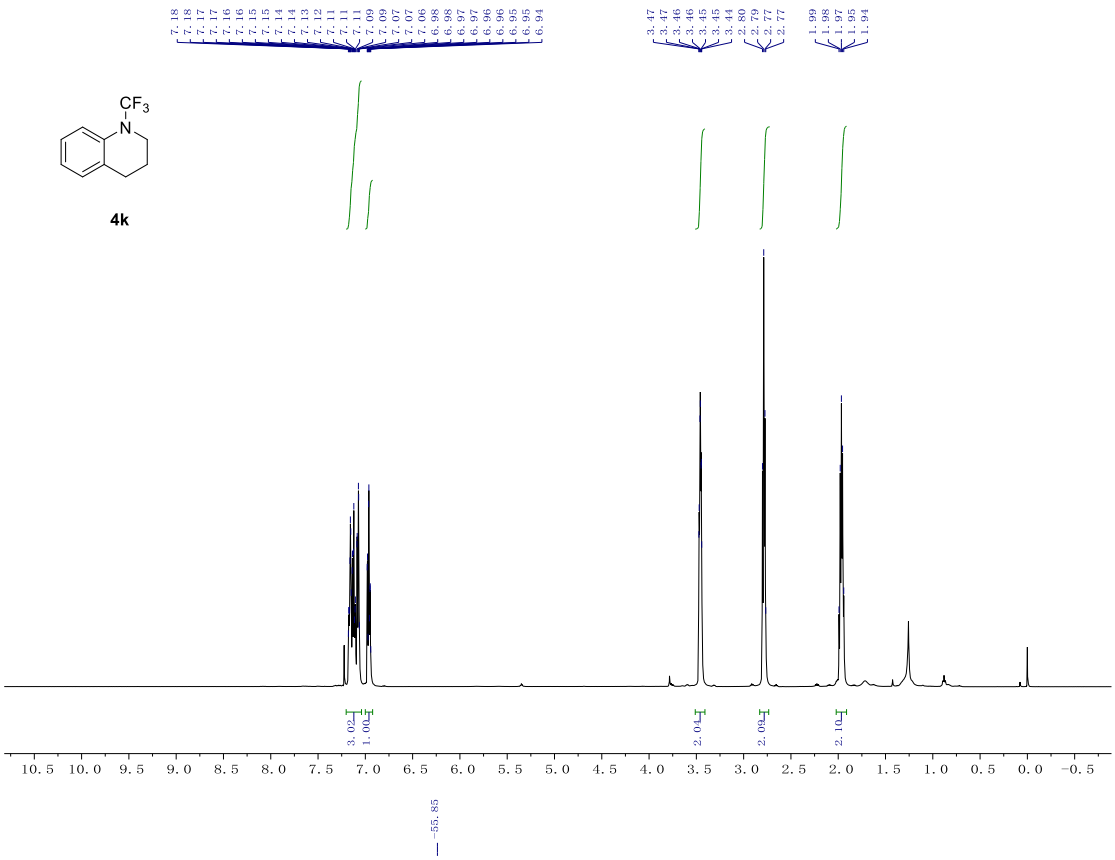
124.25
122.22
120.19
52.98
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10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2.77
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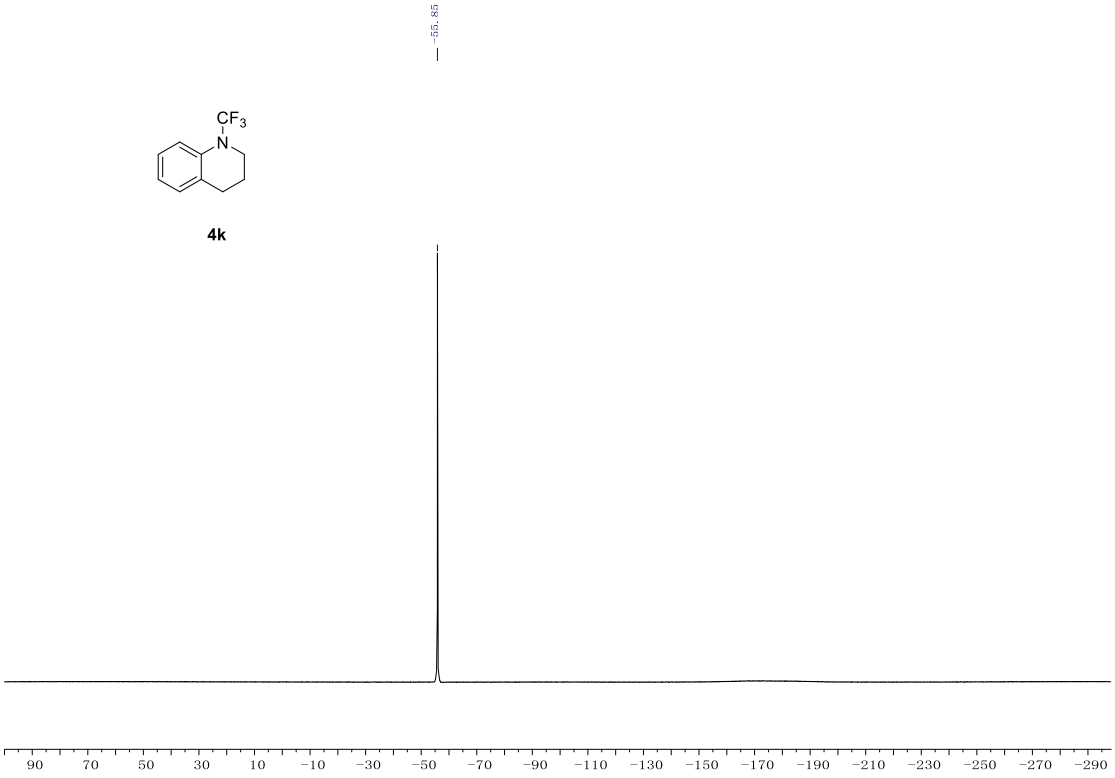
1.98
1.97
1.95
1.94
CF3
N
4k
3.02
1.00
2.04
2.09
2.10
10.5 10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0 −0.5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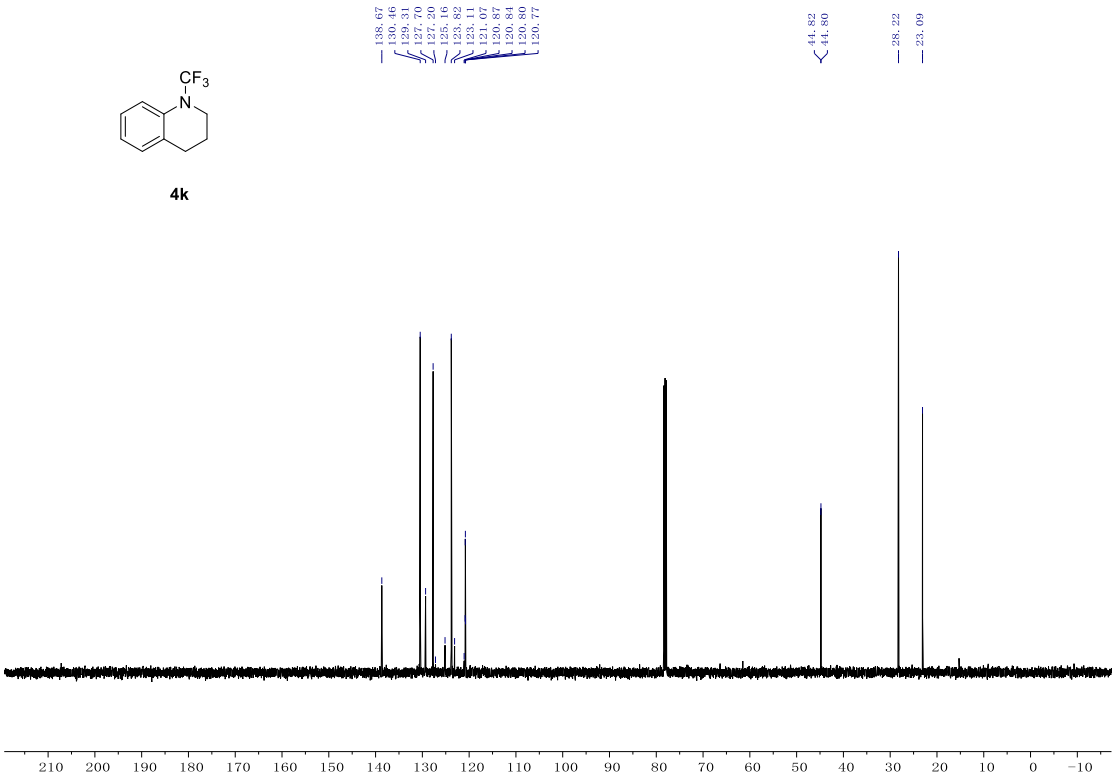
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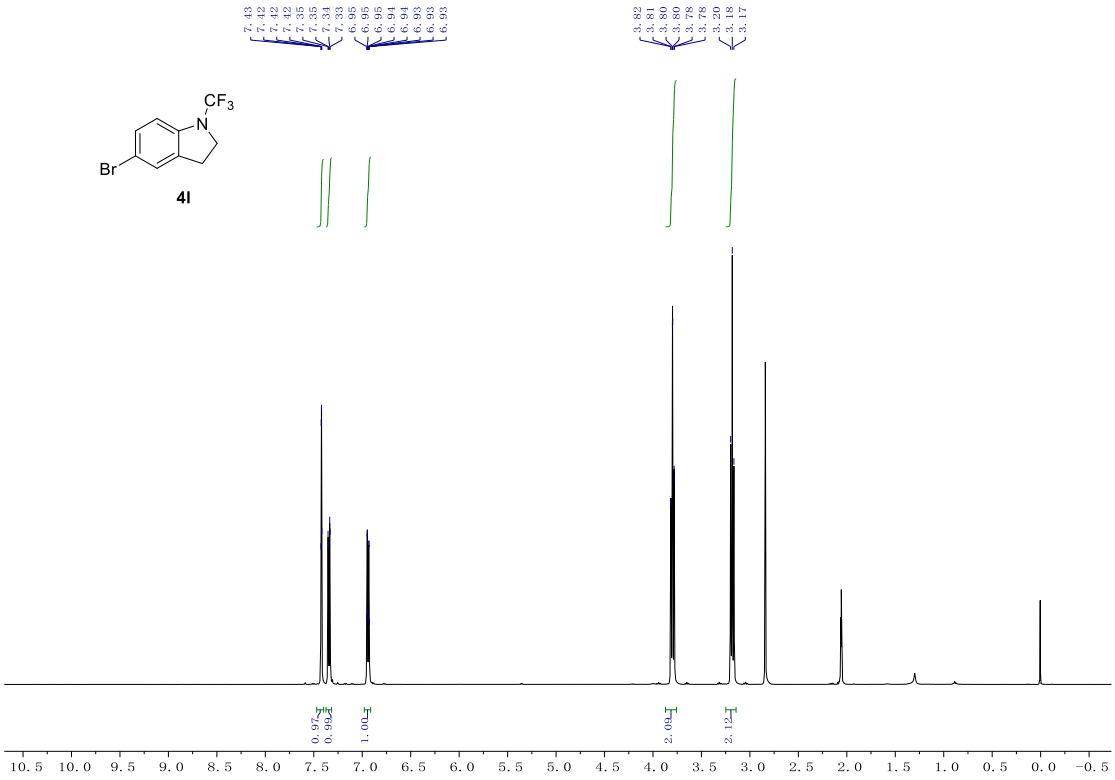
123.11
121.07
120.87
120.84
120.80
120.77
44.82
44.80
28.22
23.09
CF3
N
4k
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 −10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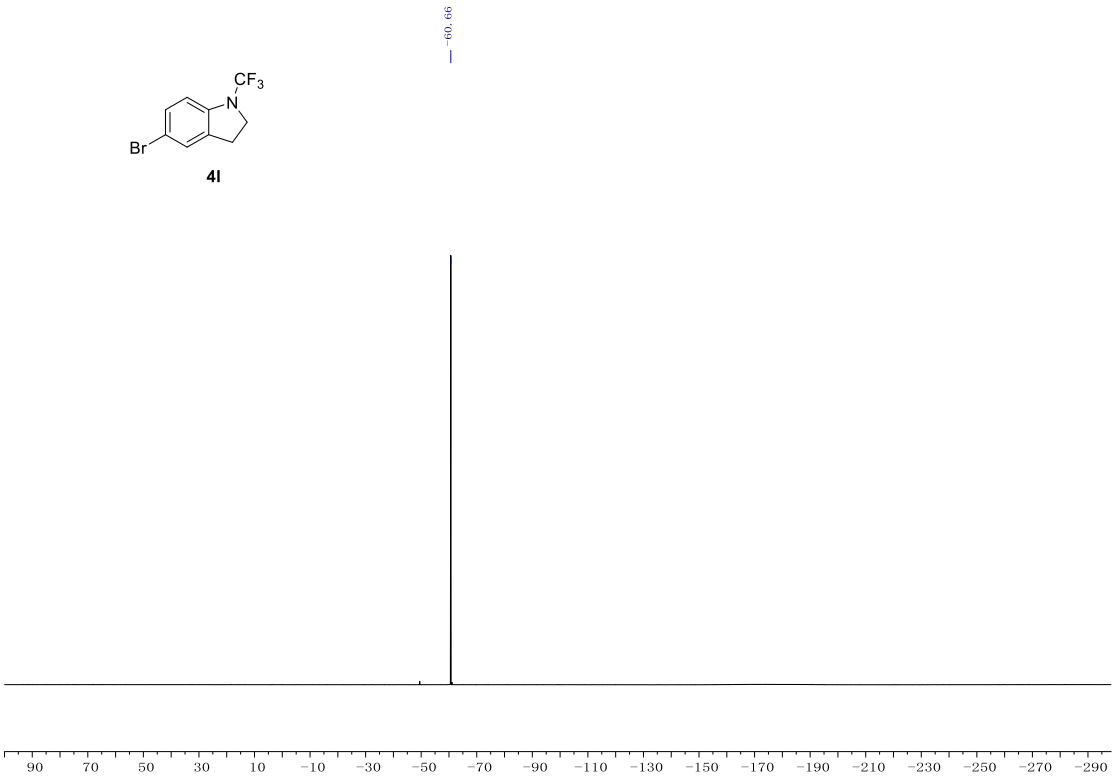
3.81
3.80
3.80
3.78
3.78
3.20
3.18
3.17
CF3
N
Br
4l
0.97
0.99
1.00
2.09
2.12
10.5 10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0 −0.5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Br
4l
-60.66
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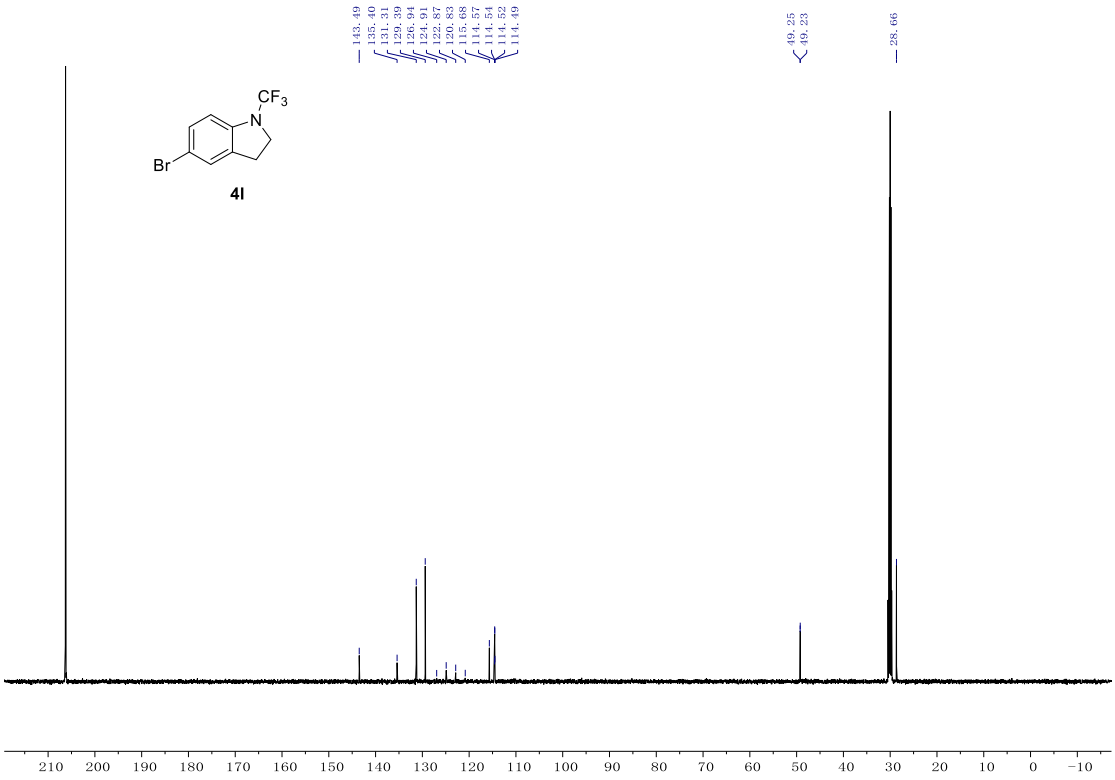
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114.54
114.52
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Br
4l
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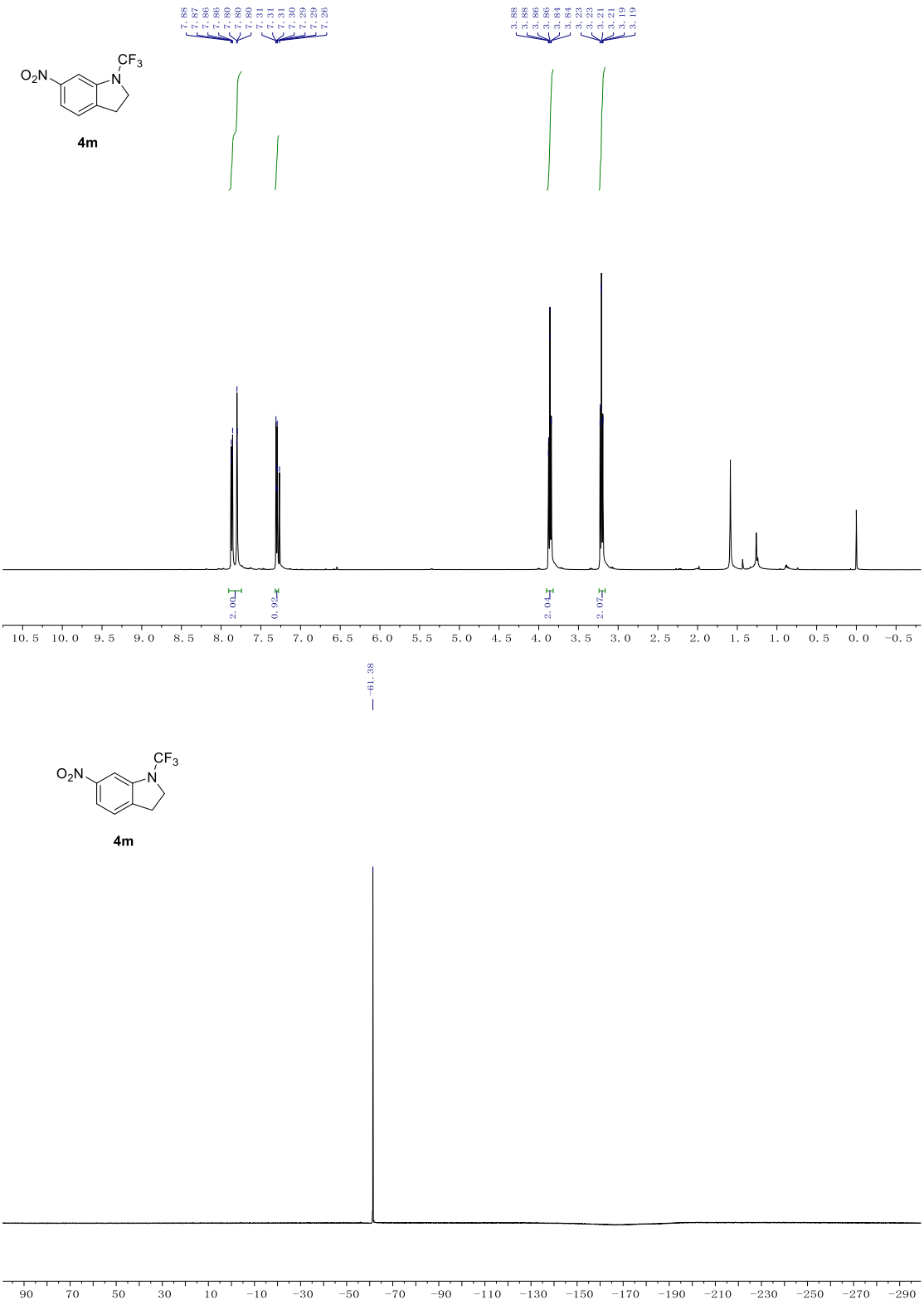
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3.88
3.86
3.86
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3.84
3.23
3.21
3.21
3.19
3.19
O2N
CF3
N
4m
2.00
0.92
2.04
2.07
10.5 10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0 −0.5
−61.38
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CF3
N
4m
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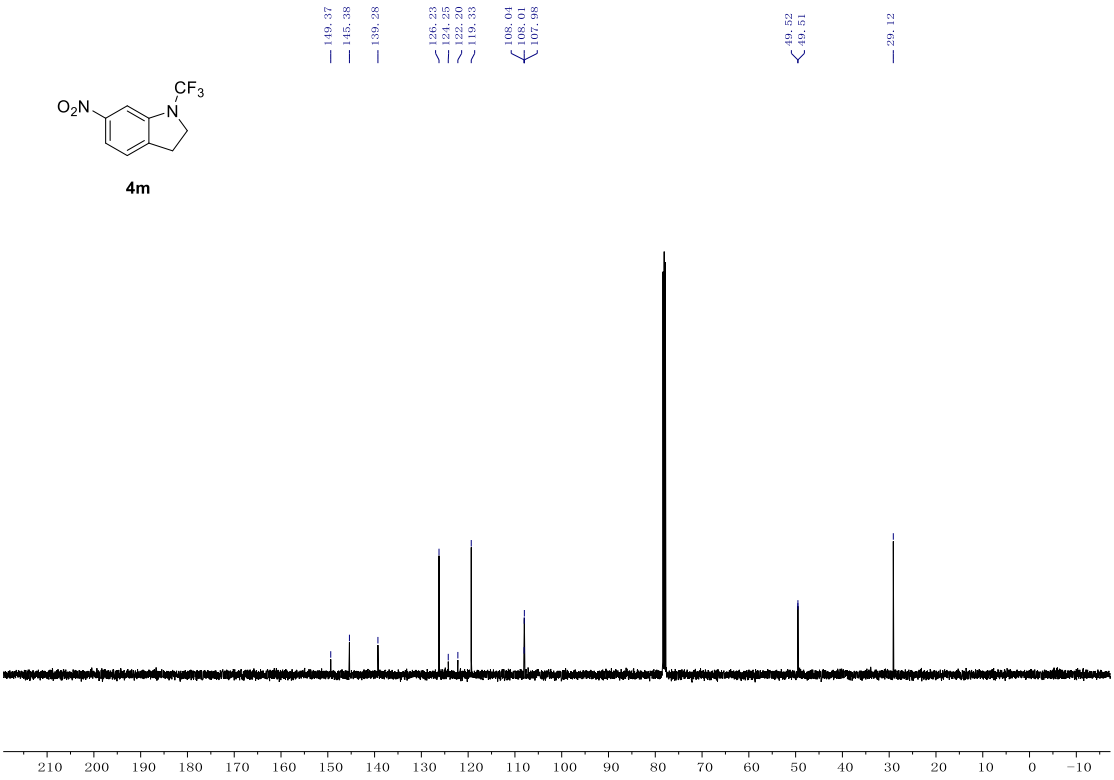
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122.20
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108.04
108.01
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29.12
O2N
CF3
N
4m
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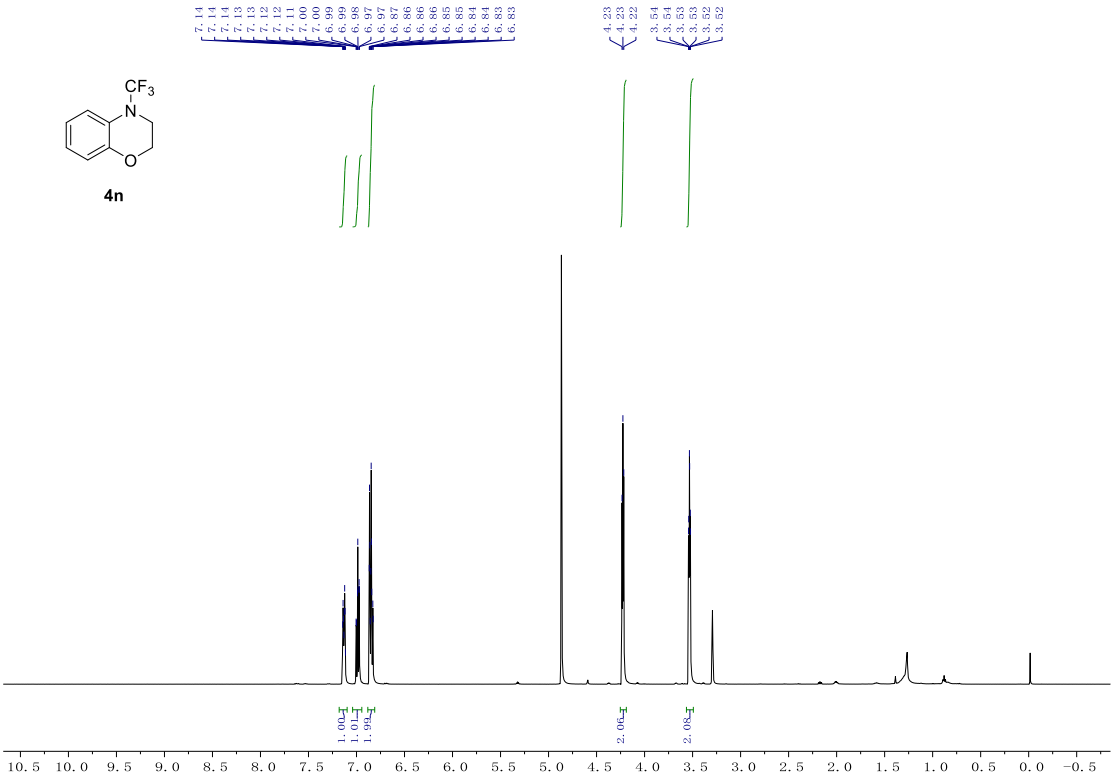
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6.98
6.97
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3.54
3.53
3.53
3.52
3.52
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N
O
4n
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1.01
1.99
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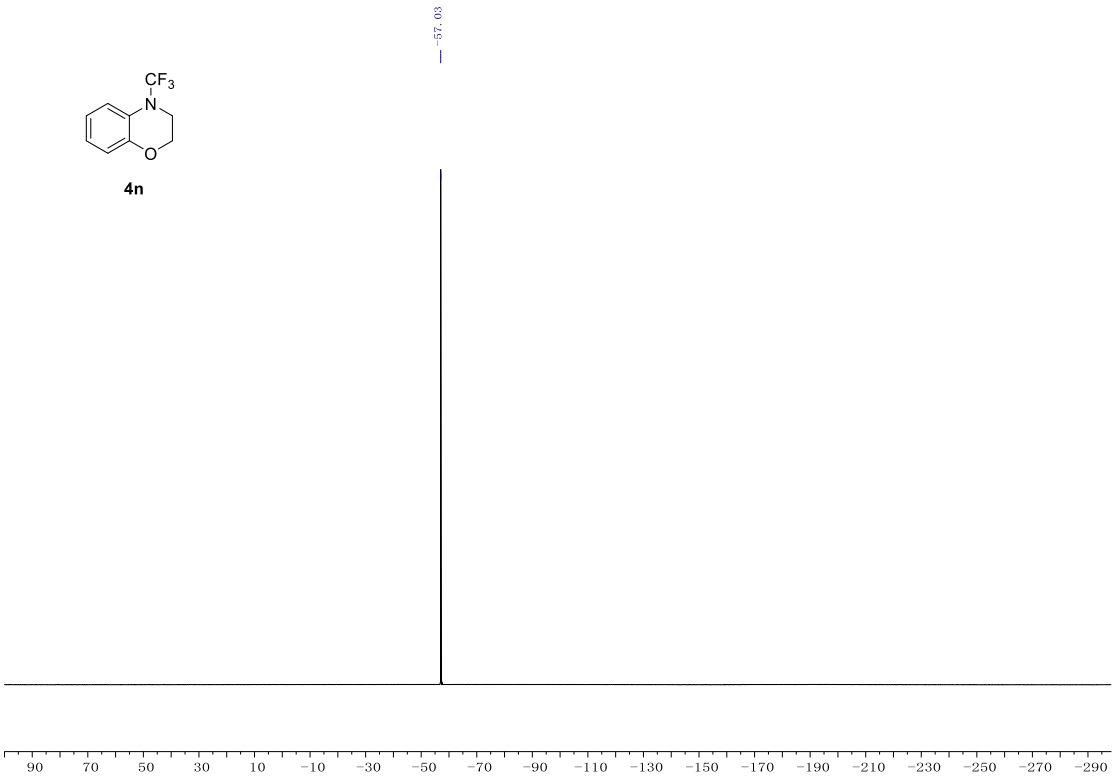
2.08
10.5 10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0 −0.5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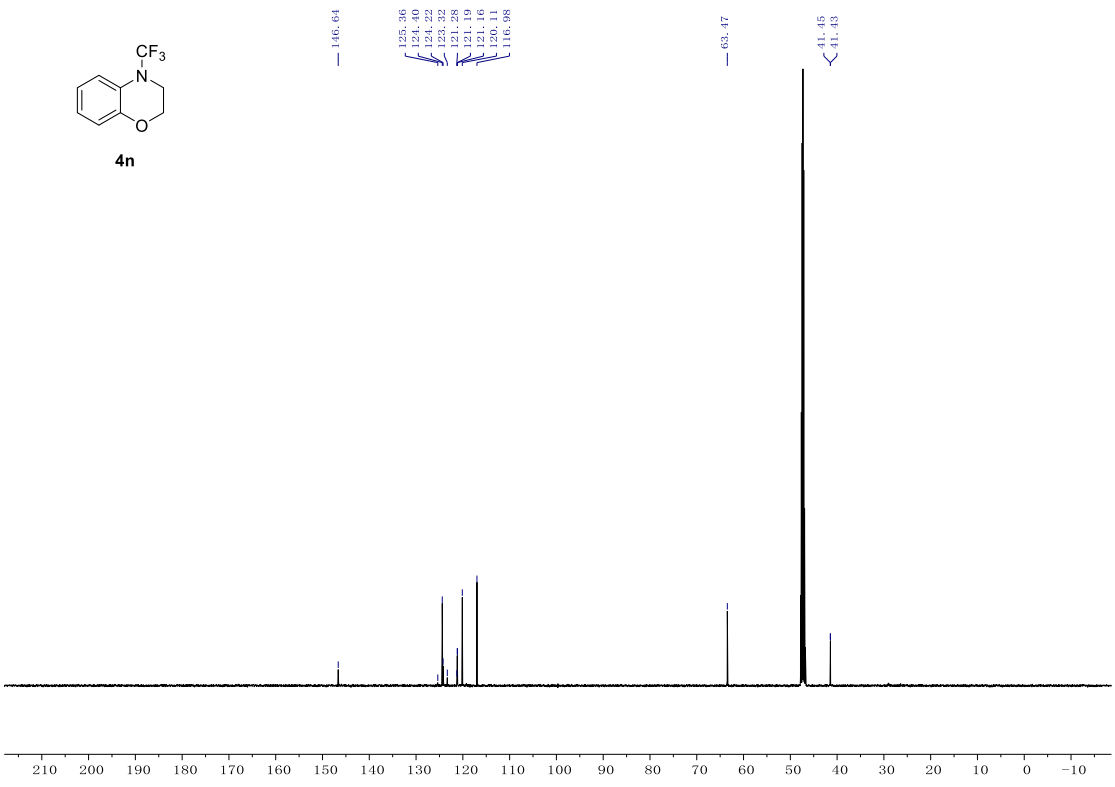
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41.45
41.43
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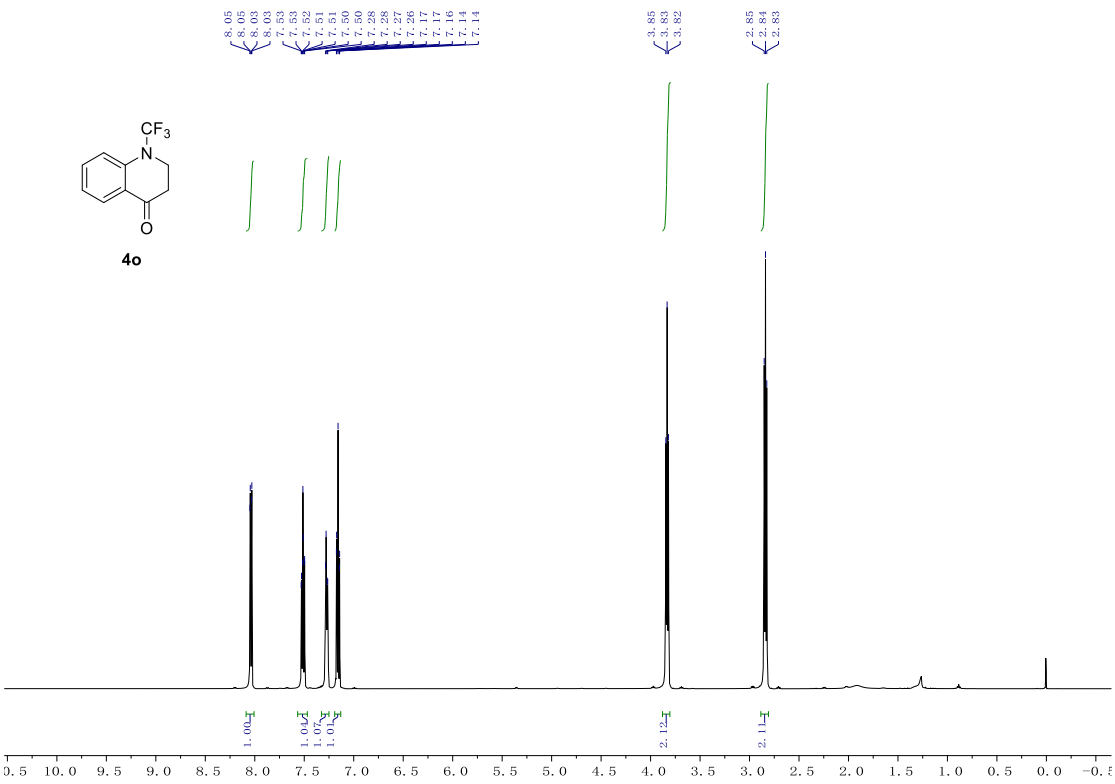
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7.14
7.14
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3.82
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2.84
2.83
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O
4o
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1.04
1.07
1.01
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2.11
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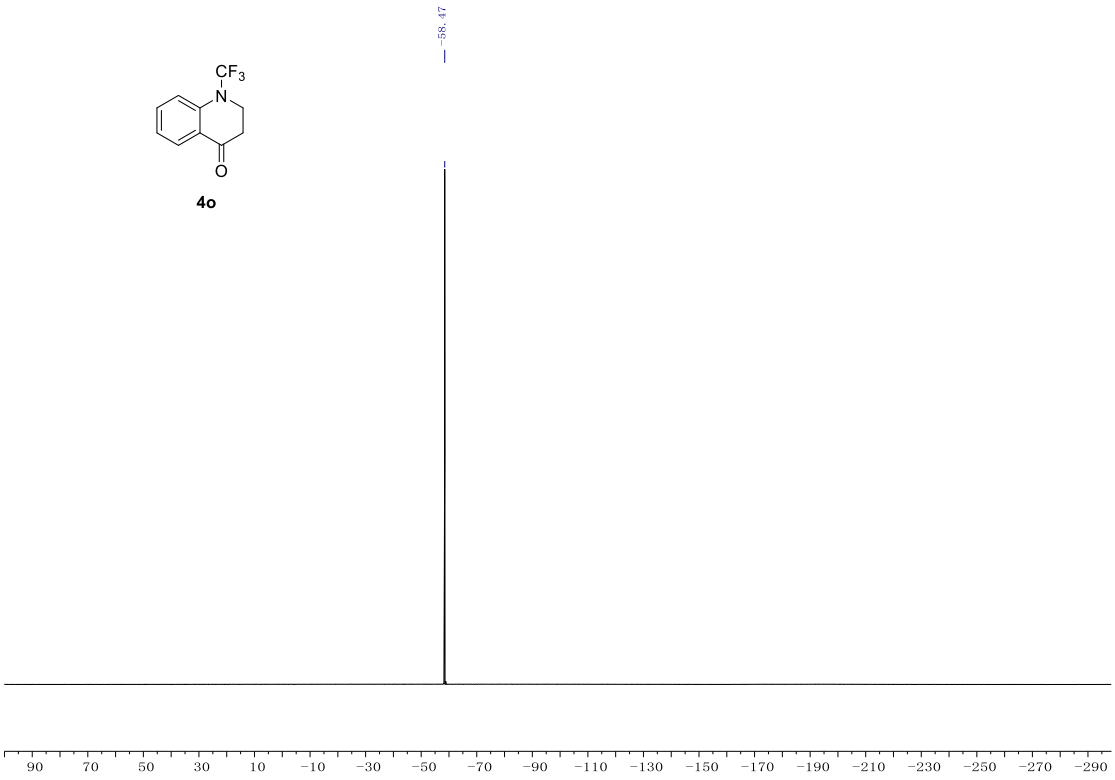
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-70
-90
-110
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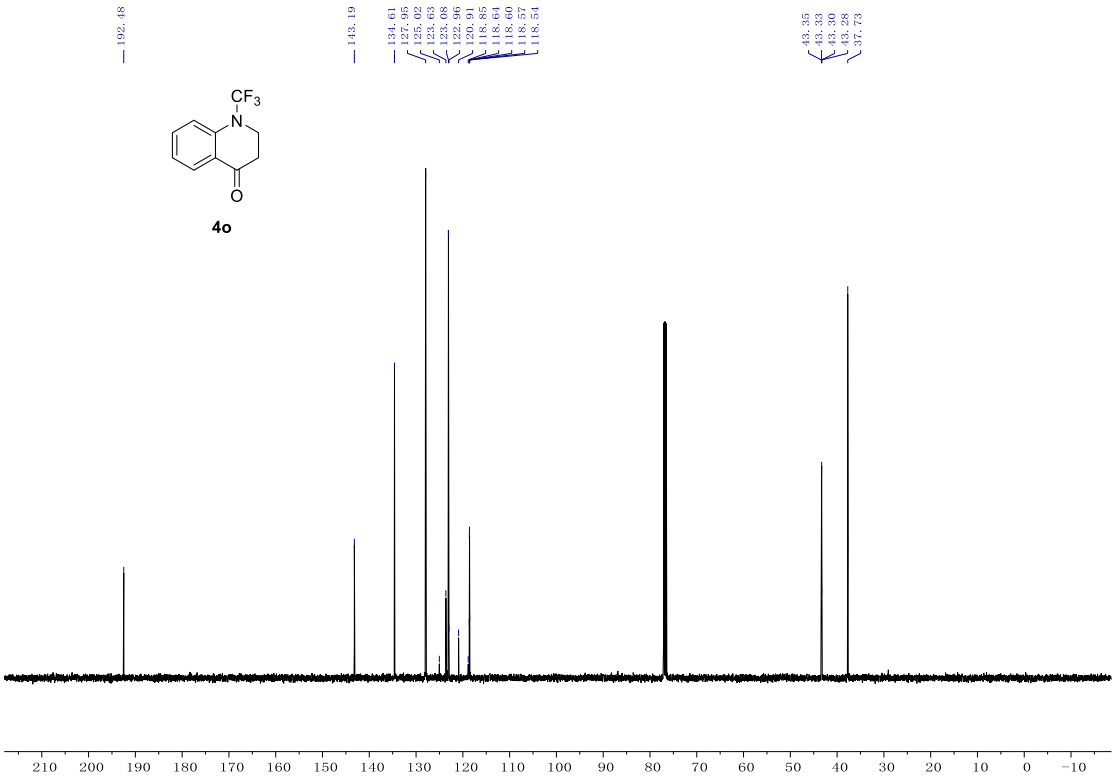
-150
-170
-190
-210
-230
-250
-270
-290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118.57
118.54
43.35
43.33
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43.28
37.73
CF3
N
O
4o
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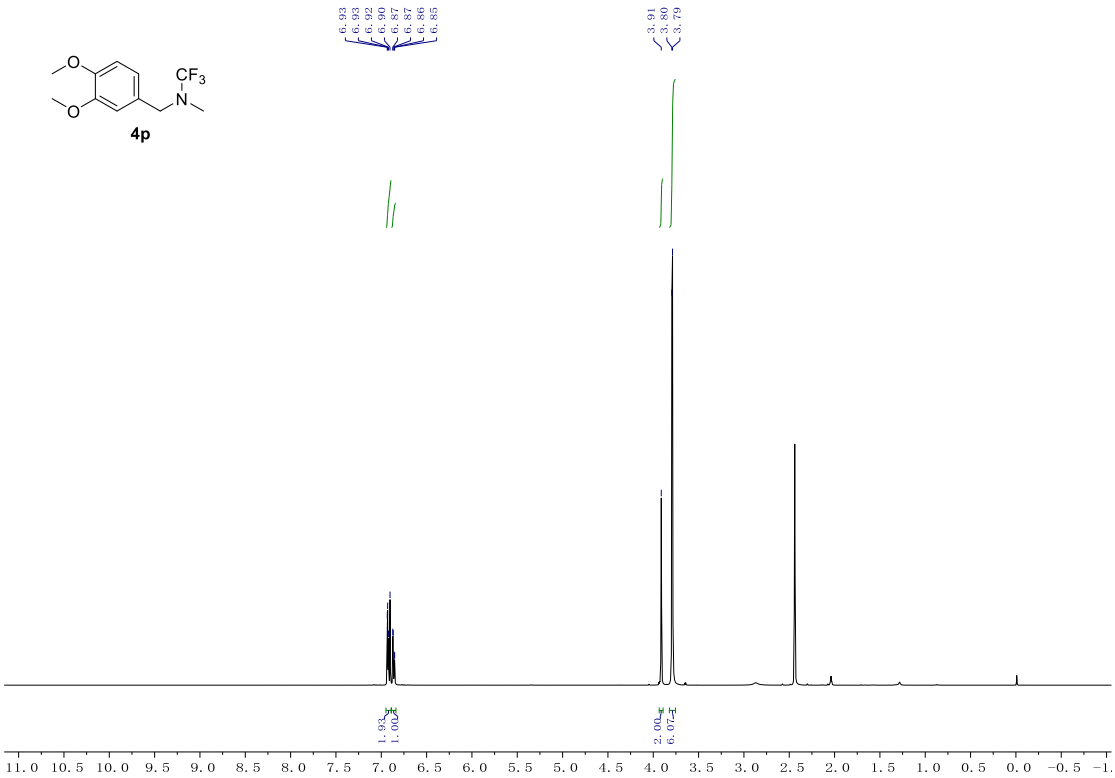
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6.85
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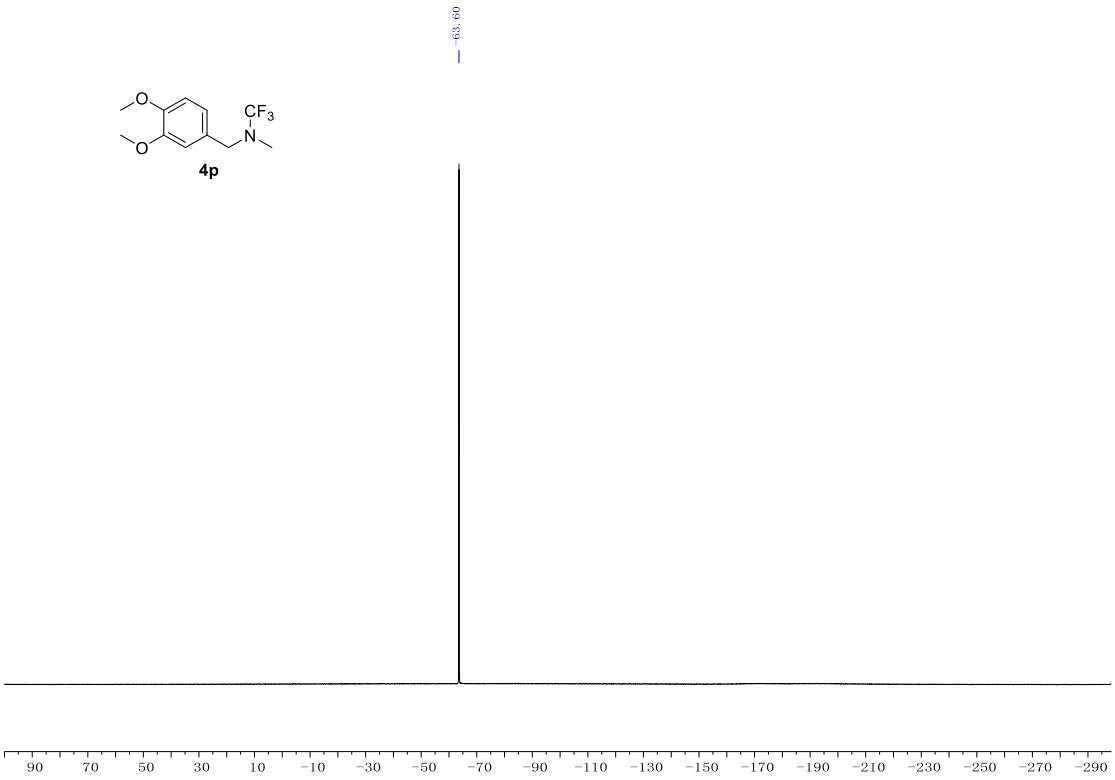
3.80
3.79
O
O
CF3
N
4p
1.93
1.00
2.00
6.07
11.0 10.5 10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0 -0.5 -1.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O
O
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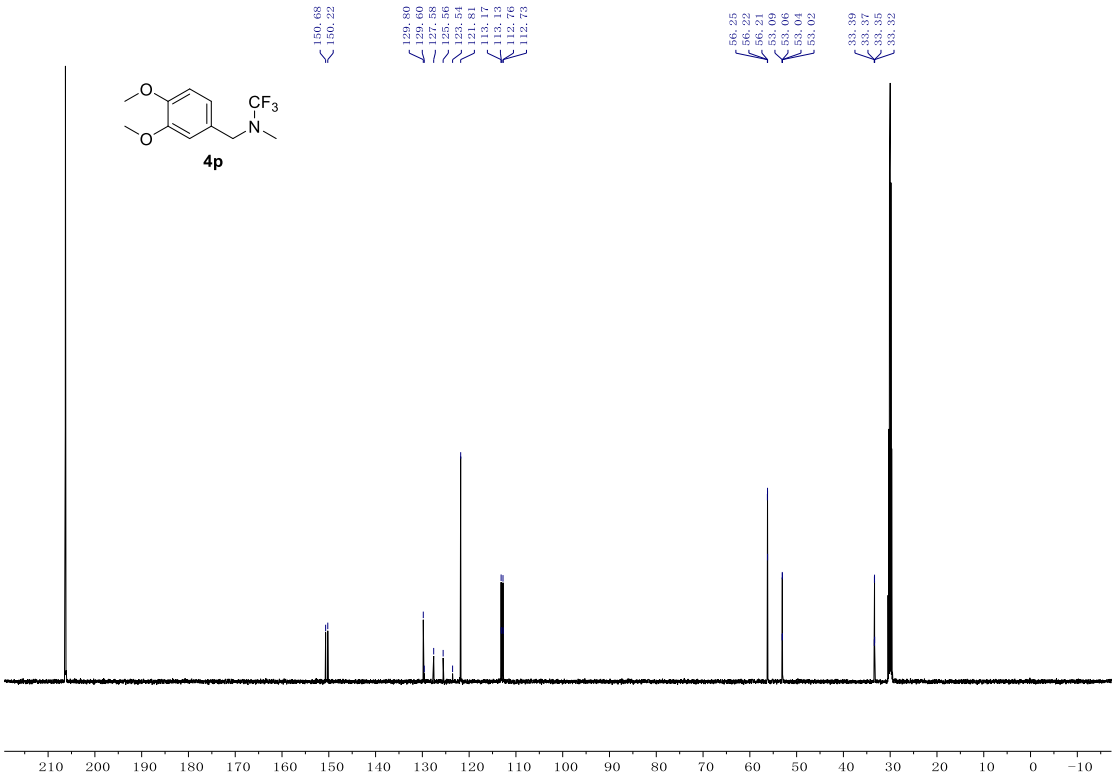
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CF3
N
O
O
4p
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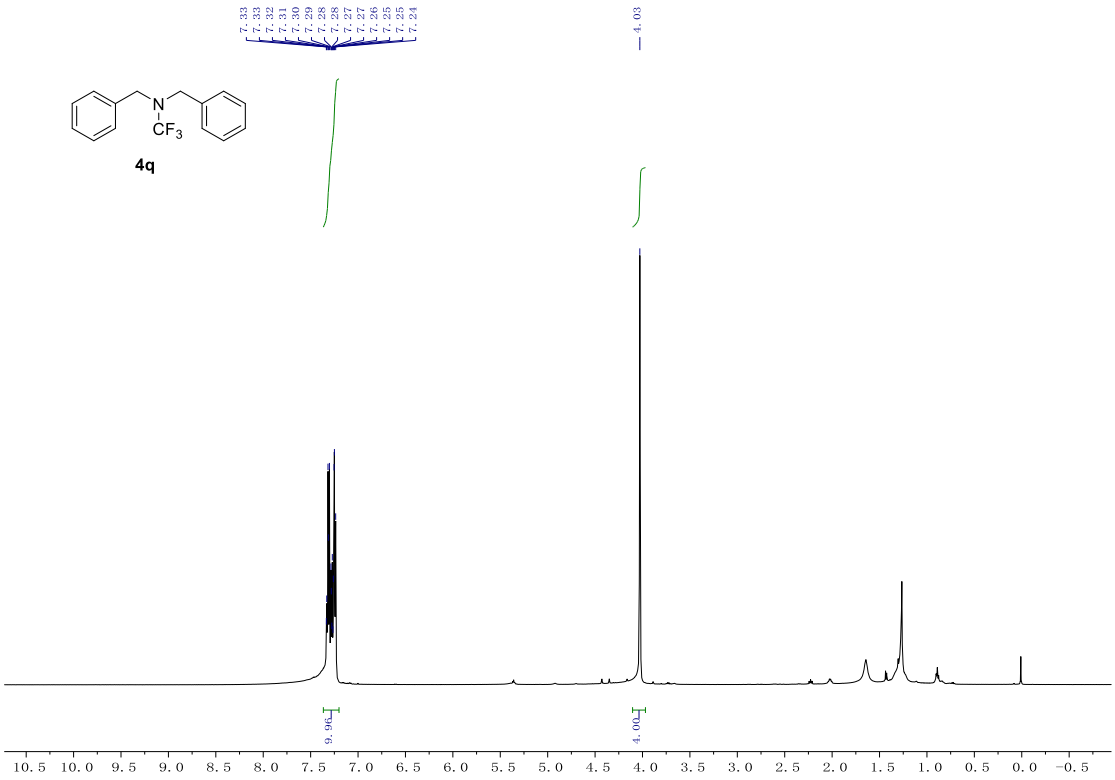
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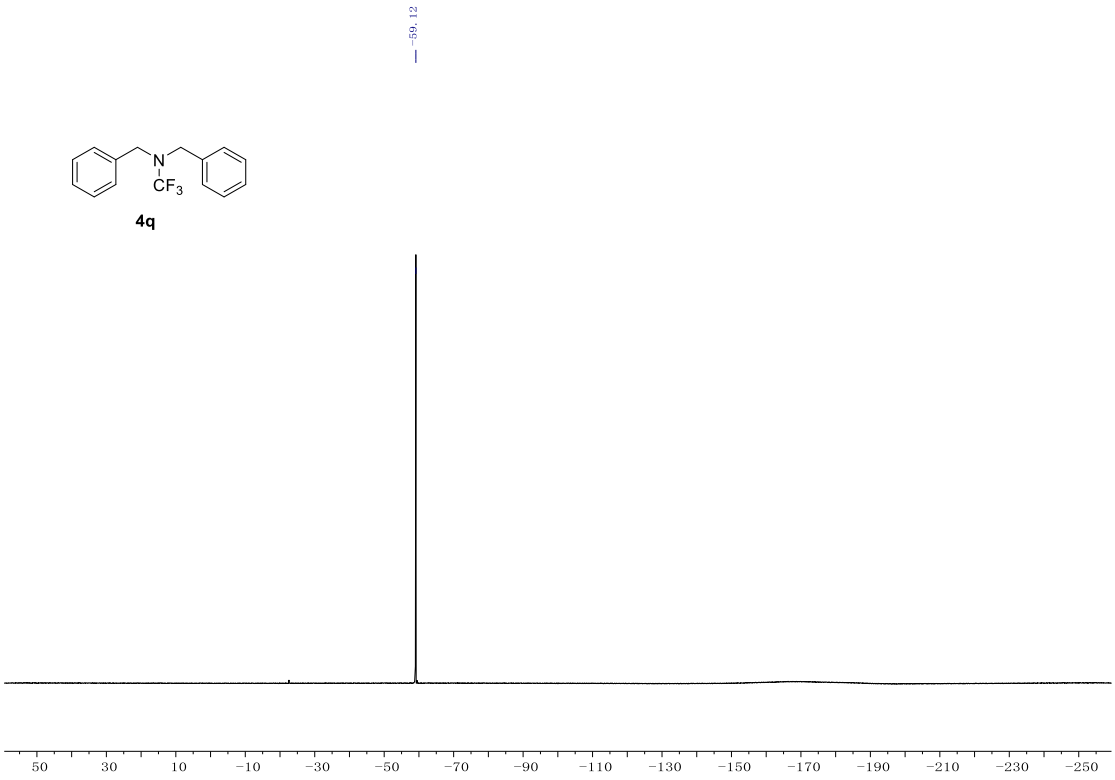
7.25
7.24
4.03
N
CF3
4q
9.96
4.00
10.5 10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0 -0.5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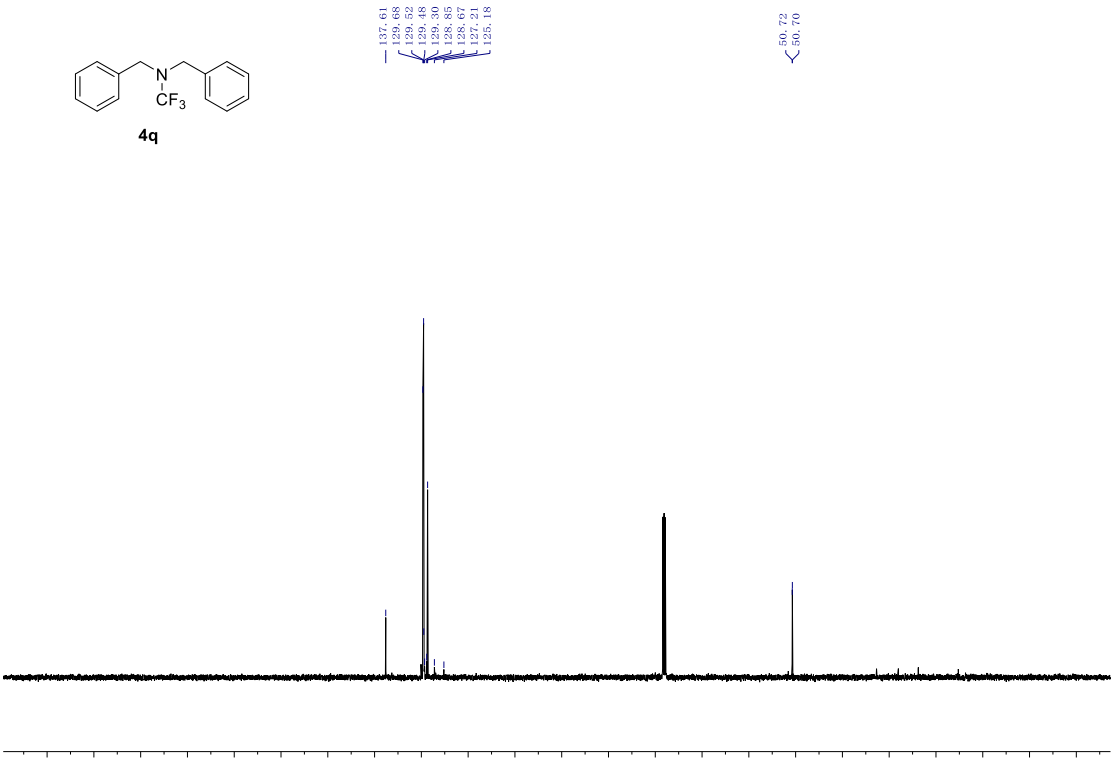
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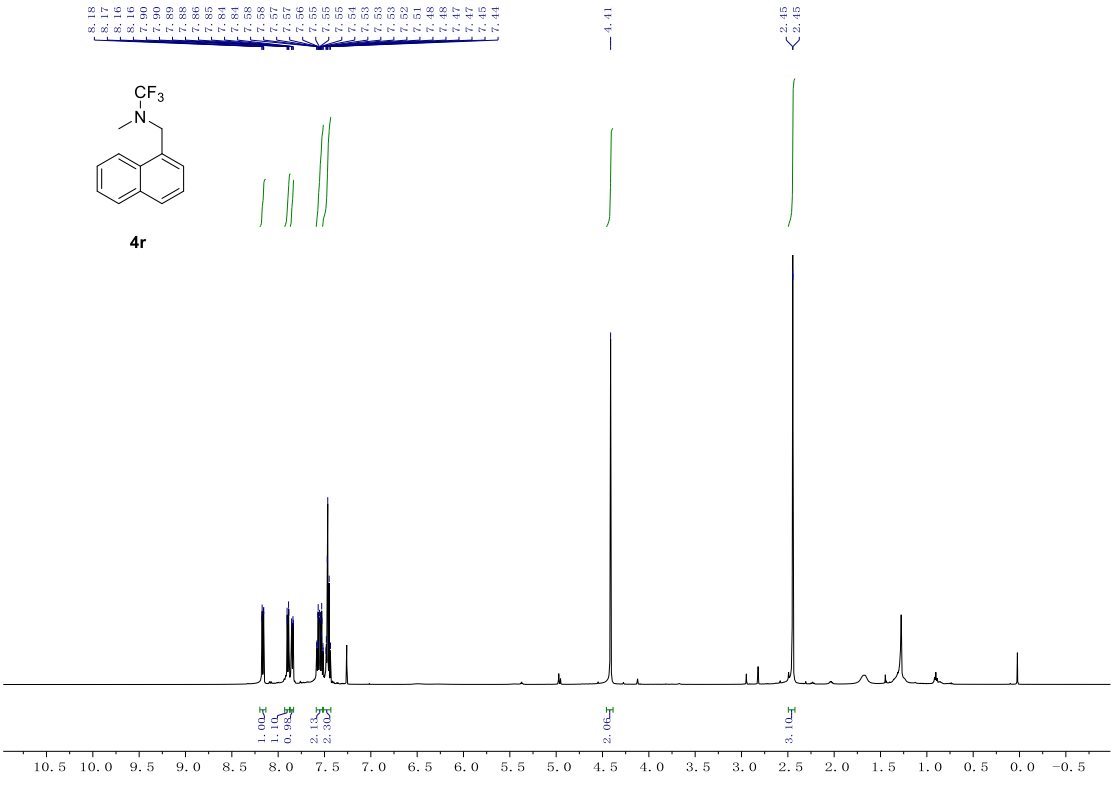
CF3
4q
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 −10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7.57
7.57
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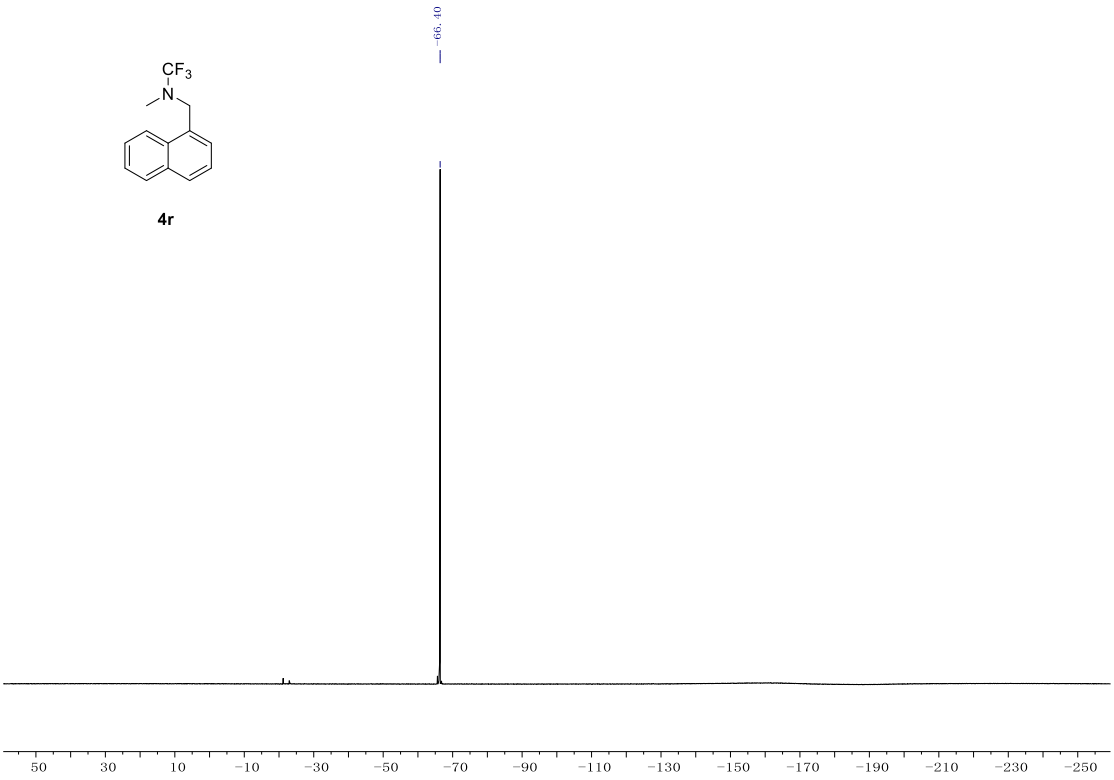
7.51
7.48
7.48
7.47
7.47
7.45
7.44
4.41
2.45
2.45
CF3
N
4r
1.00
1.10
0.99
2.13
2.30
2.06
3.10
10.5 10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0 −0.5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4r
-66.40
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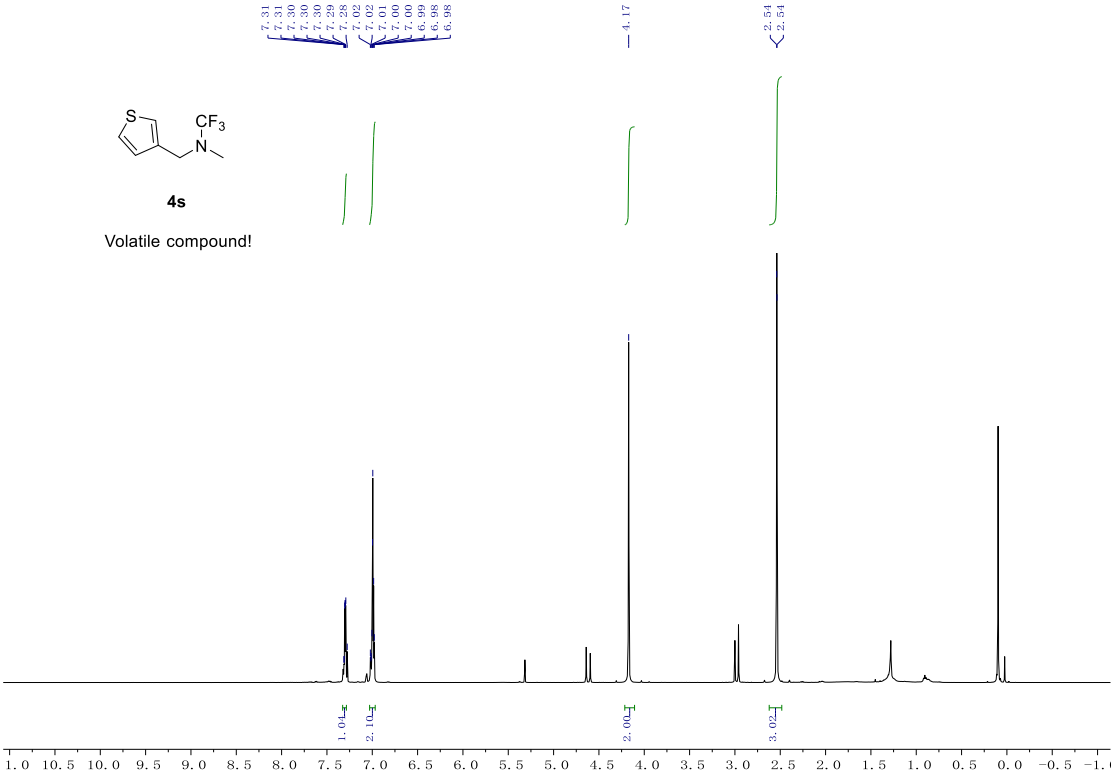
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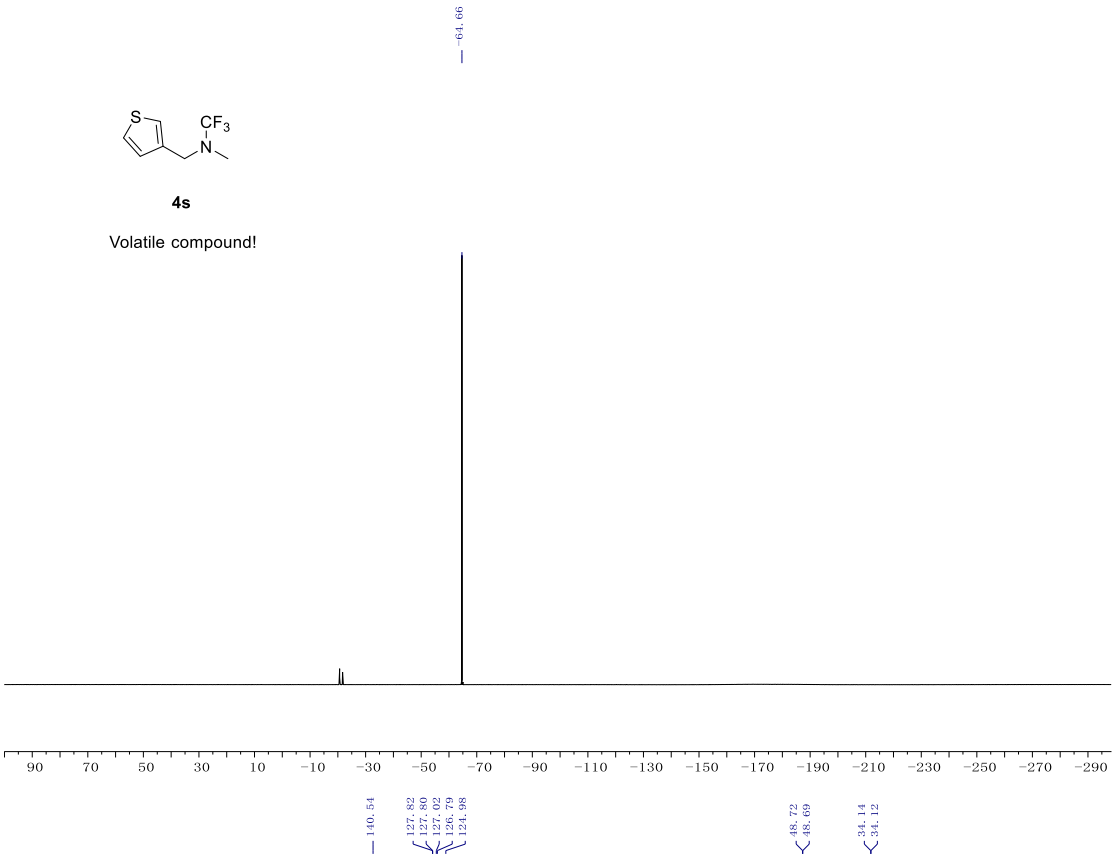
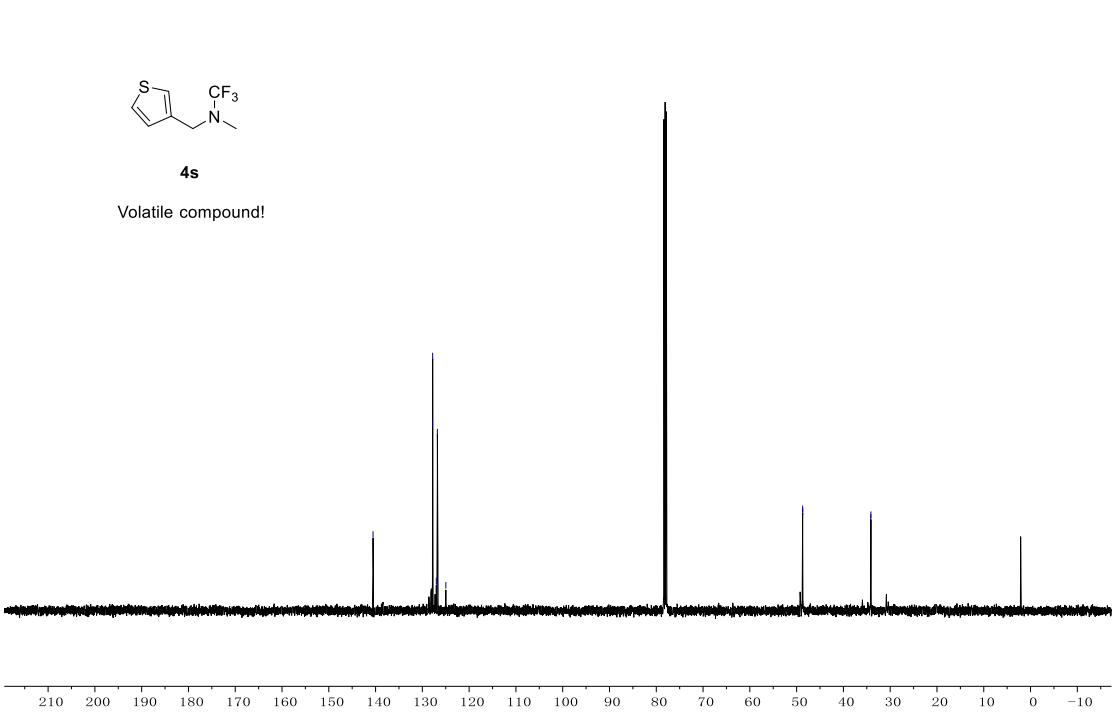
7.29
7.28
7.02
7.02
7.01
7.00
7.00
6.99
6.98
6.98
4.17
2.54
2.54
S
CF3
N
4s
Volatile compound!
1.04
2.10
2.00
3.02
1.0 10.5 10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0 -0.5



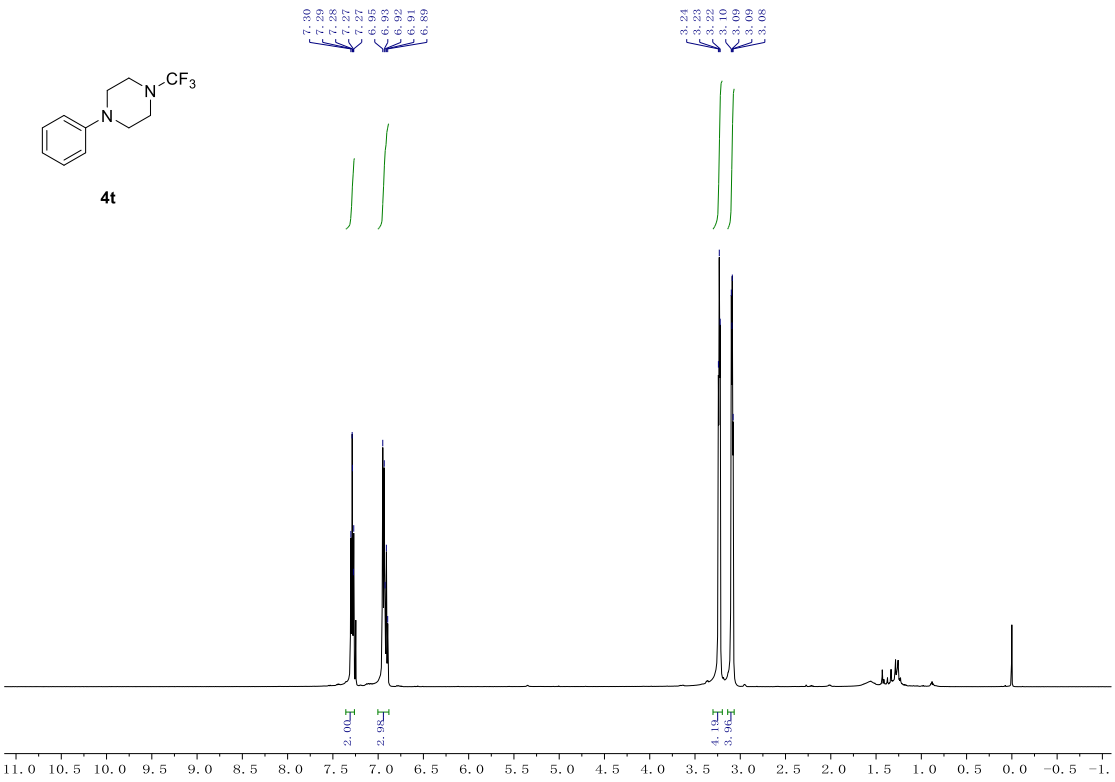
4s

Volatile compound!



4s

Volatile compound!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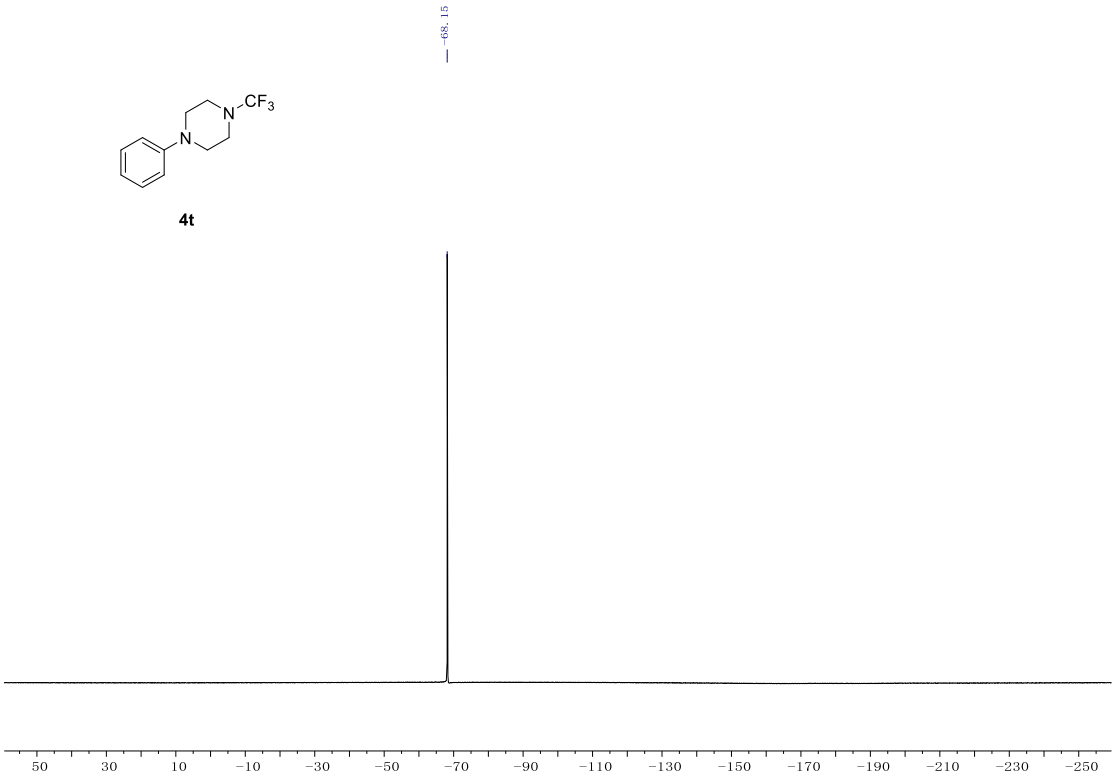
6.93
6.92
6.91
6.89
3.24
3.23
3.22
3.10
3.09
3.09
3.08
CF3
N
N
4t
2.00
2.98
4.19
3.96
11.0 10.5 10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0 -0.5 -1.


-68.15
CF3
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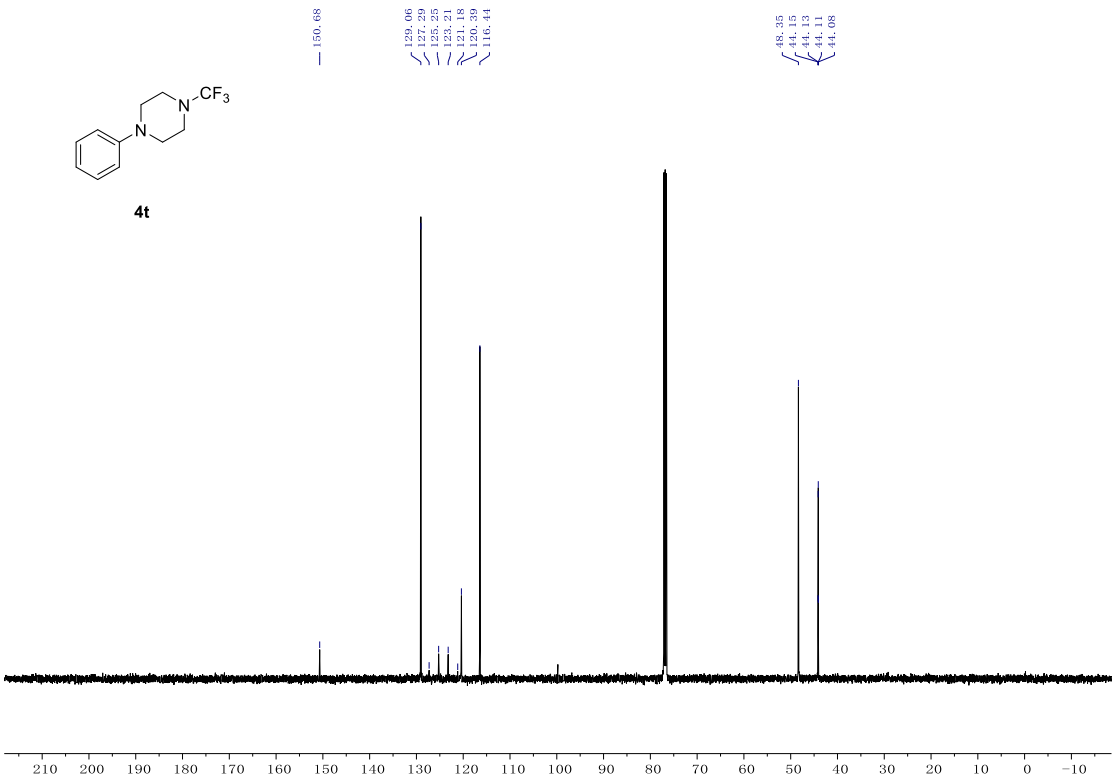
N
4t
50 30 10 -10 -30 -50 -70 -90 -110 -130 -150 -170 -190 -210 -230 -250


150.68
139.06
129.29
125.25
123.21
121.18
120.39
116.44
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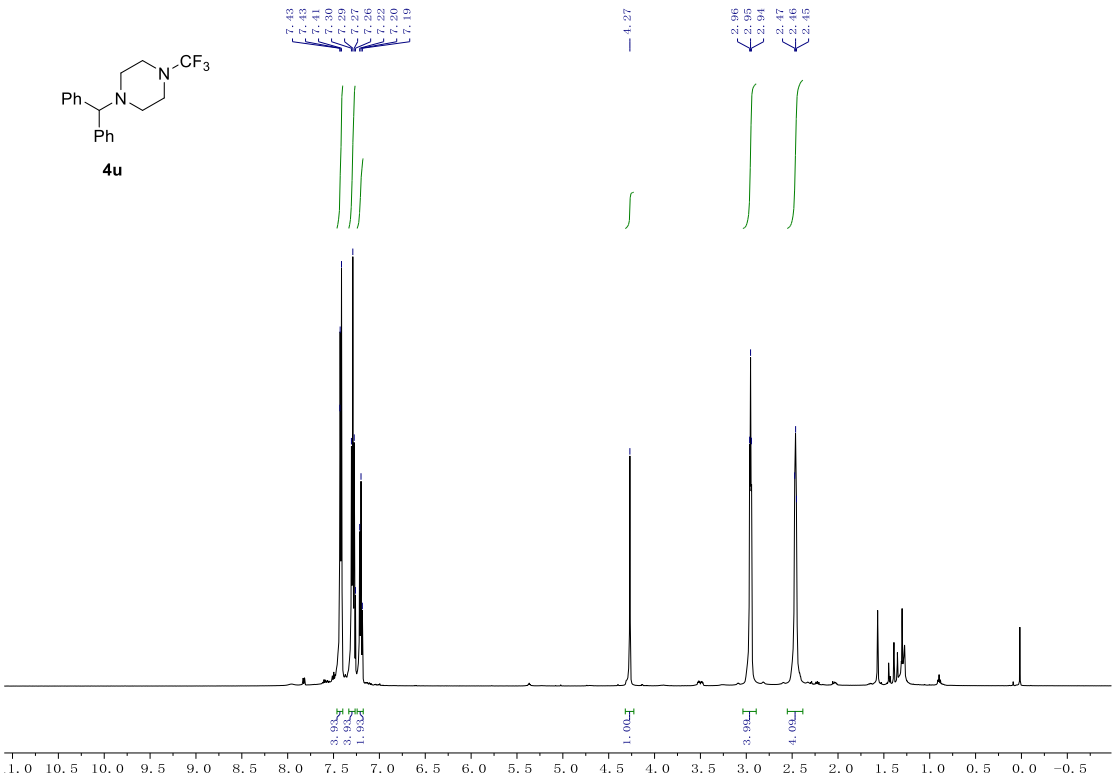
44.13
44.11
44.08
N
CF3
4t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7.22
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7.19
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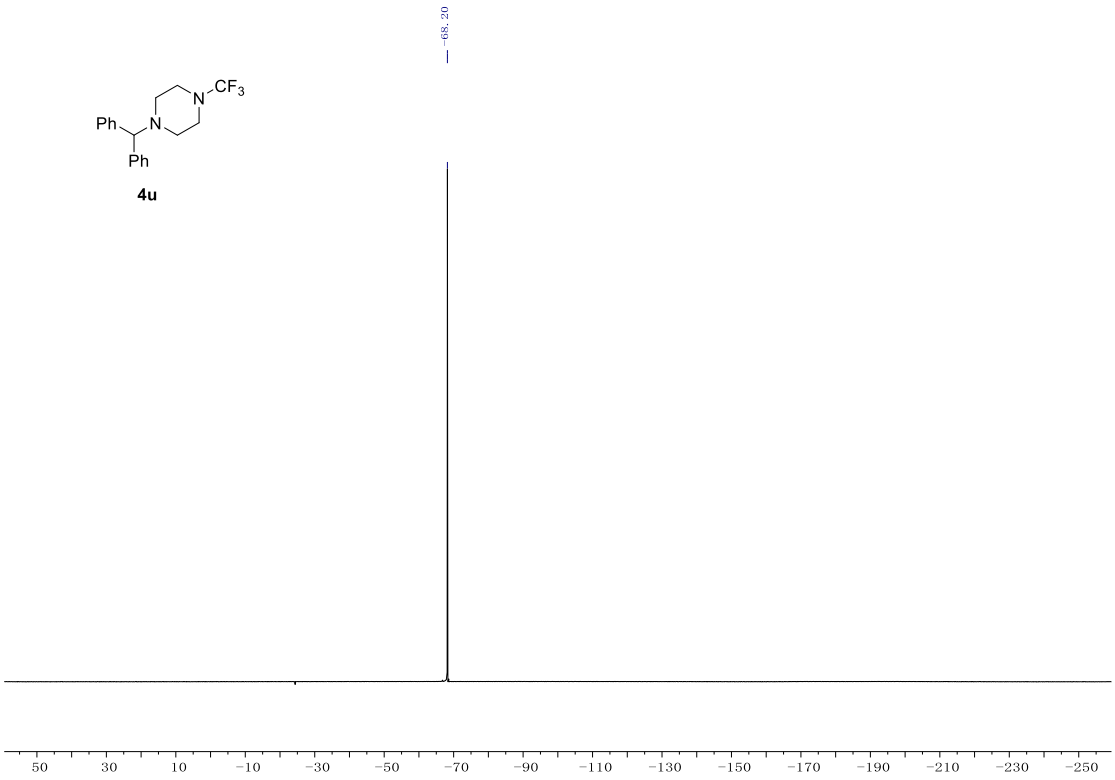
2.95
2.94
2.47
2.46
2.45
N
CF3
Ph
Ph
4u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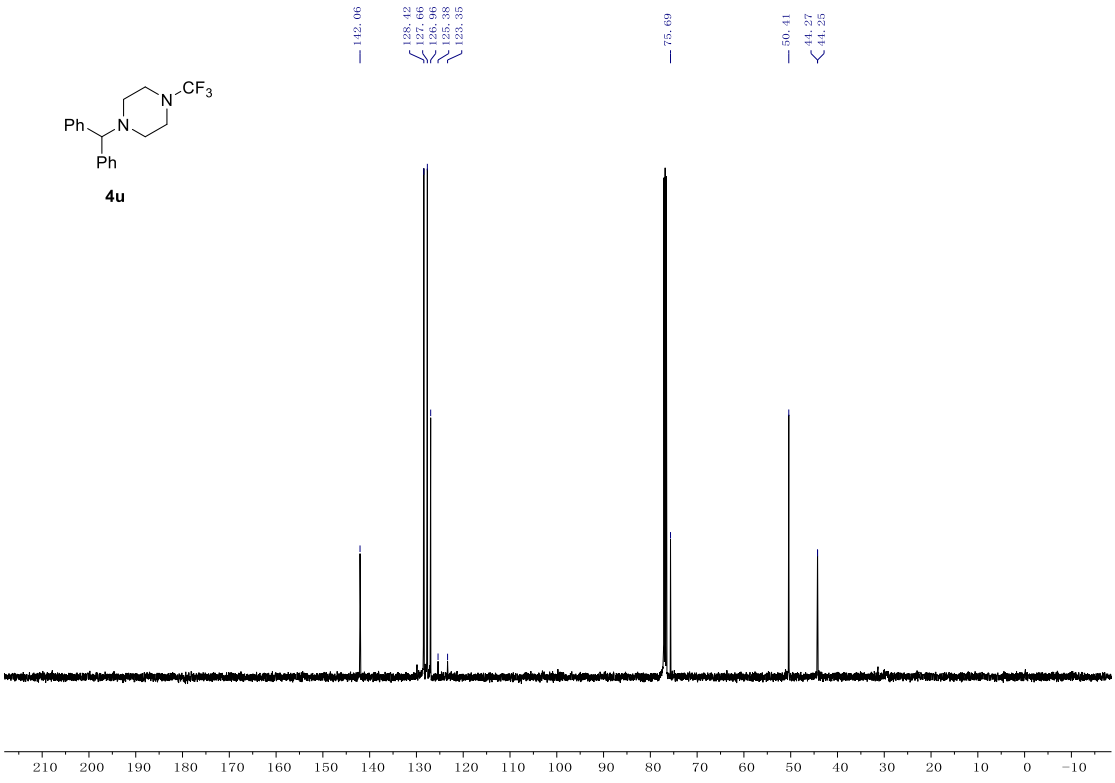
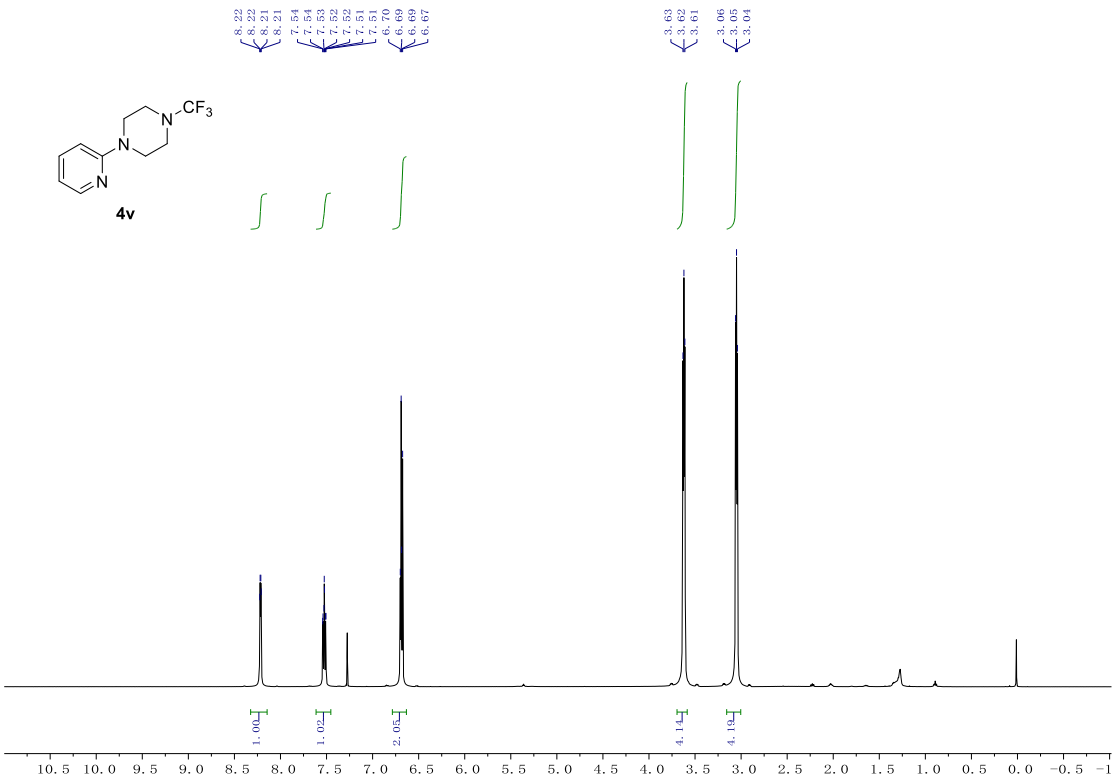
N
Ph
N
Ph
4u
50 30 10 -10 -30 -50 -70 -90 -110 -130 -150 -170 -190 -210 -230 -250


142.06
128.42
127.66
126.96
125.38
123.35
75.69
50.41
44.27
44.25
CF3
N
Ph
N
Ph
4u
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10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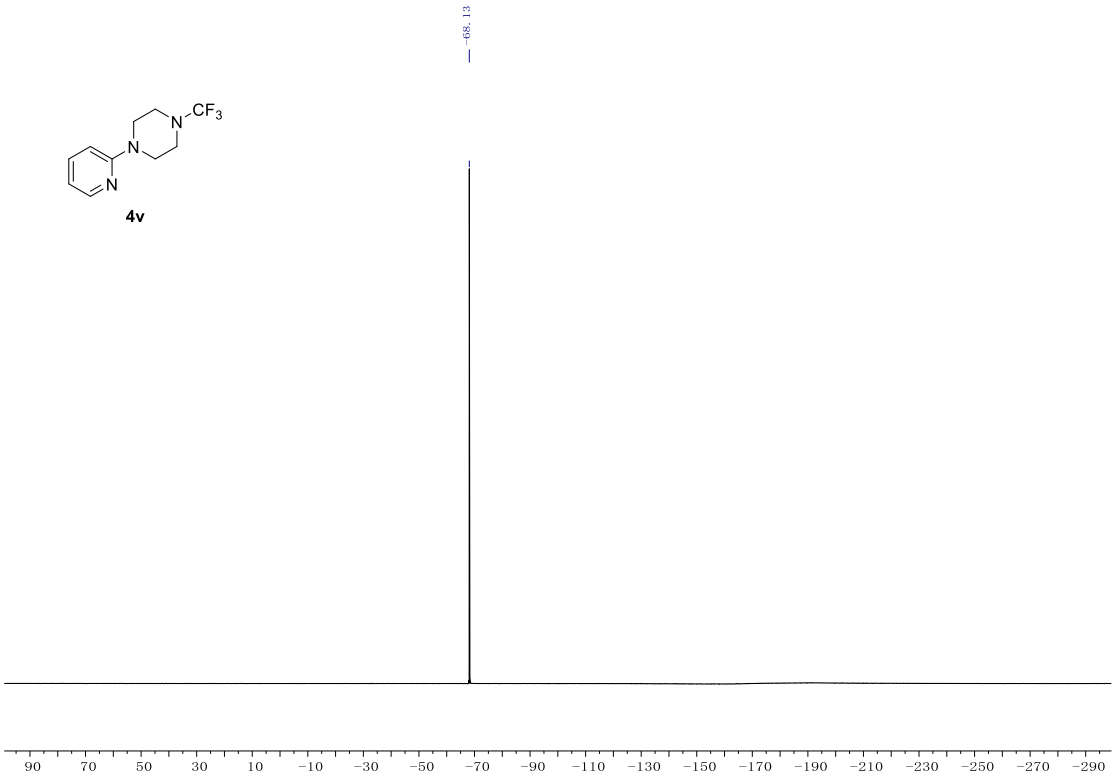
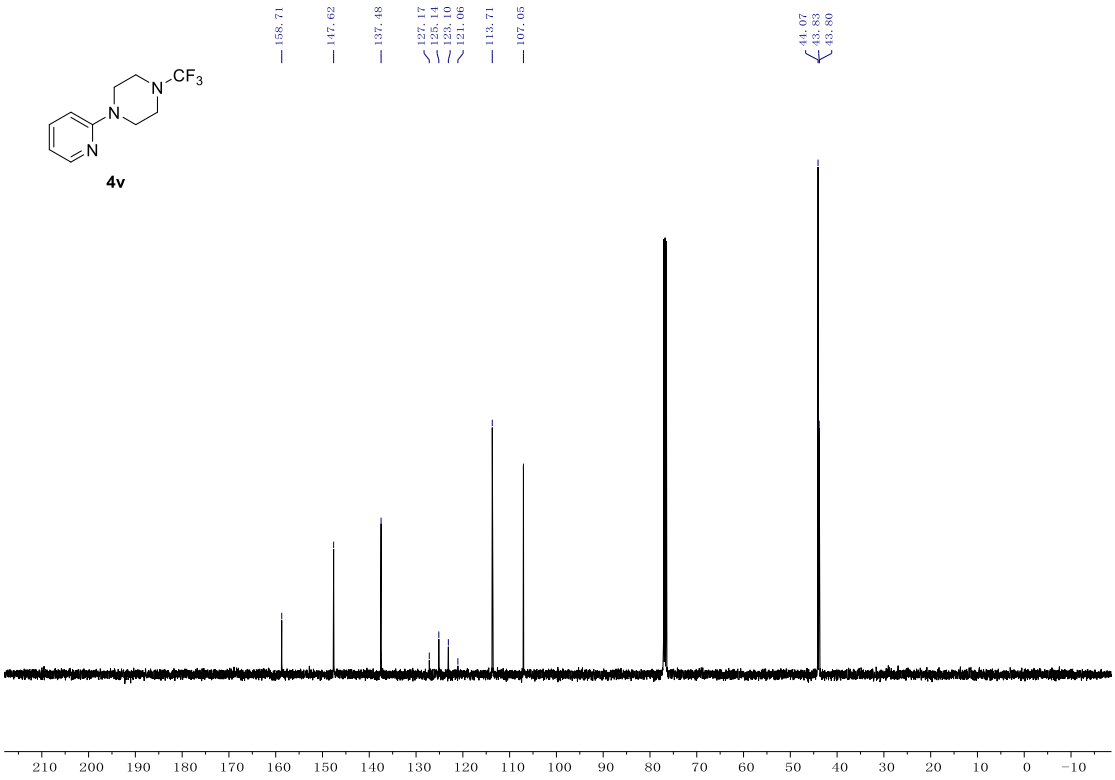
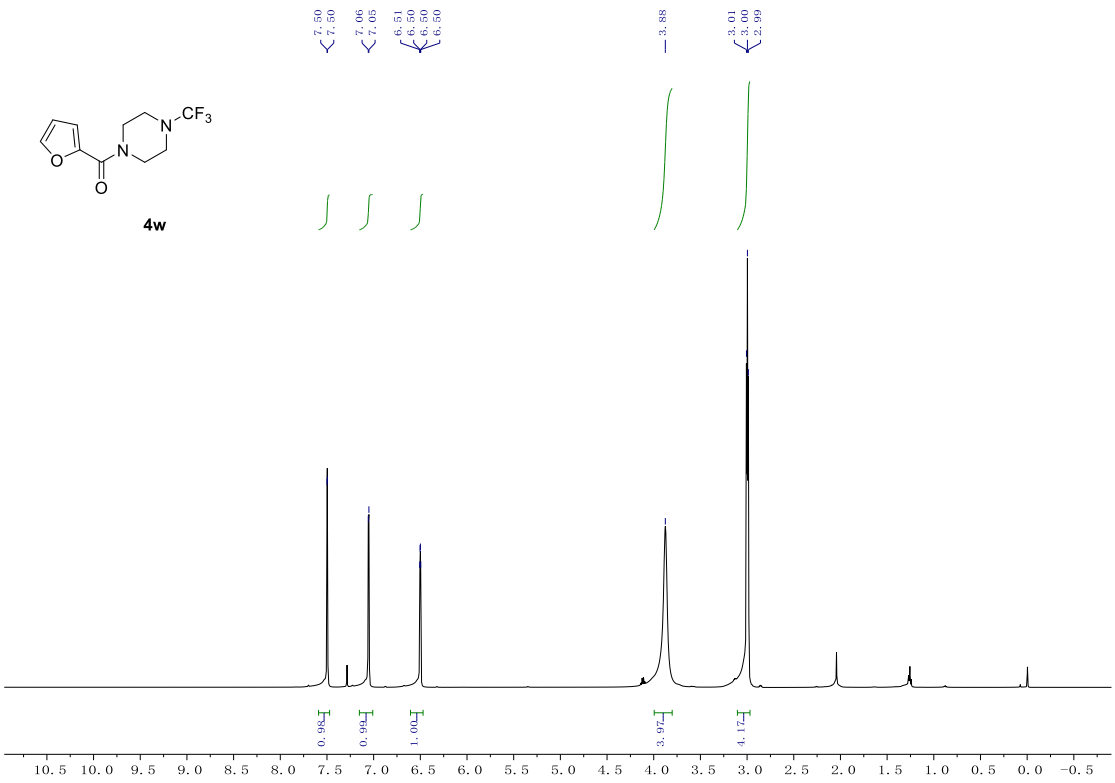
6.70
6.69
6.69
6.67
3.63
3.62
3.61
3.06
3.05
3.04
CF3
N
N
4v
1.00
1.02
2.05
4.14
4.19
10.5 10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0 −0.5 −1


−68.13
CF3
N
N
4v
90 70 50 30 10 −10 −30 −50 −70 −90 −110 −130 −150 −170 −190 −210 −230 −250 −270 −290


158.71
147.62
137.48
127.17
125.14
123.10
121.06
113.71
107.05
44.07
43.83
43.80
N
CF3
N
N
4v
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10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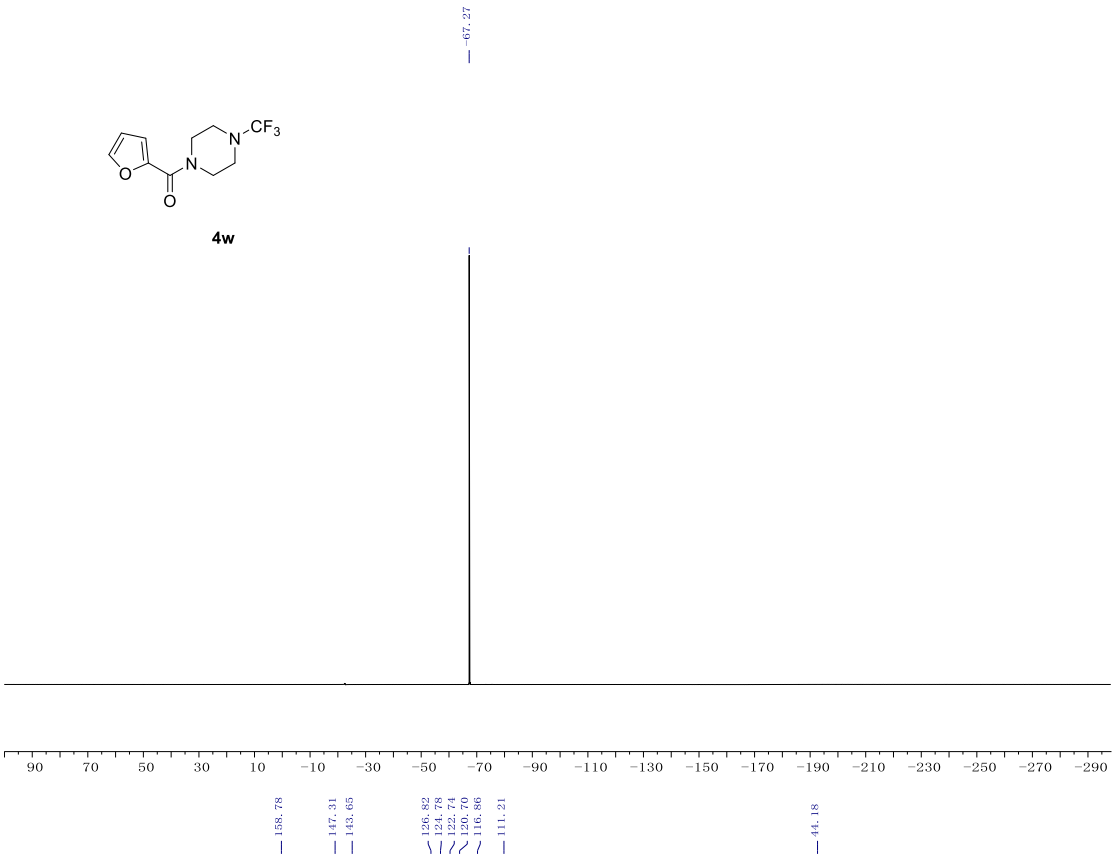
6.50
6.50
6.50
3.88
3.01
3.00
2.99
N
CF3
O
N
O
4w
0.98
0.99
1.00
3.97
4.17
10.5 10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0 -0.5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4w
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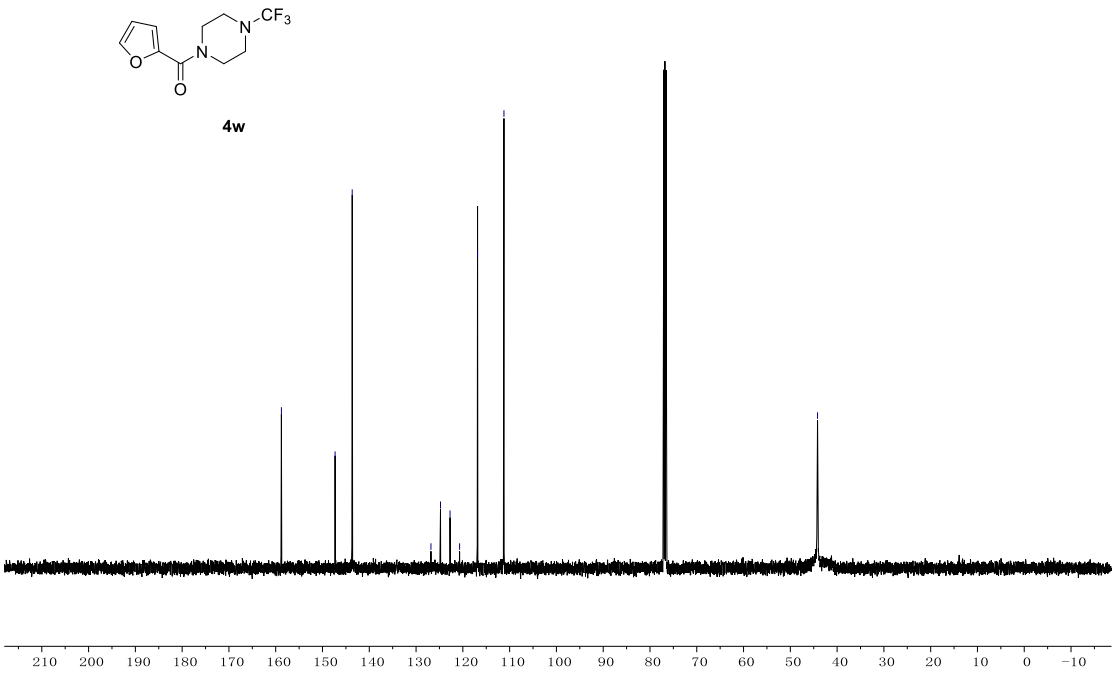
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124.78
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120.70
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44.18
4w
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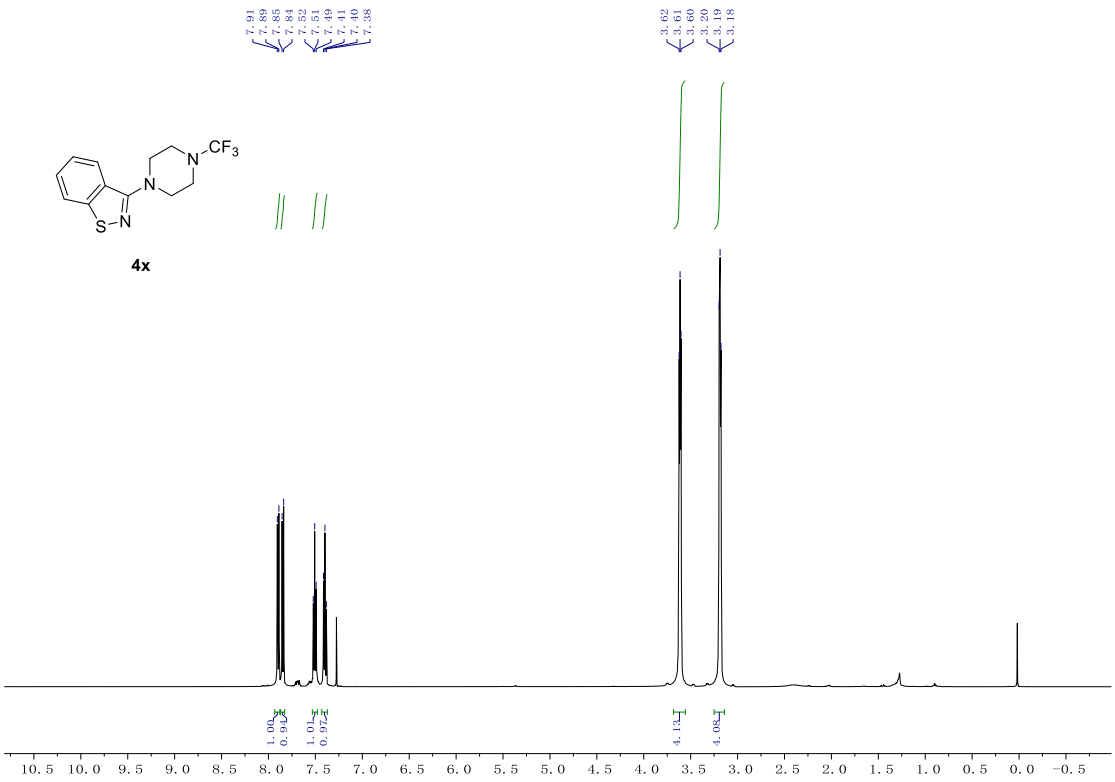
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7.38
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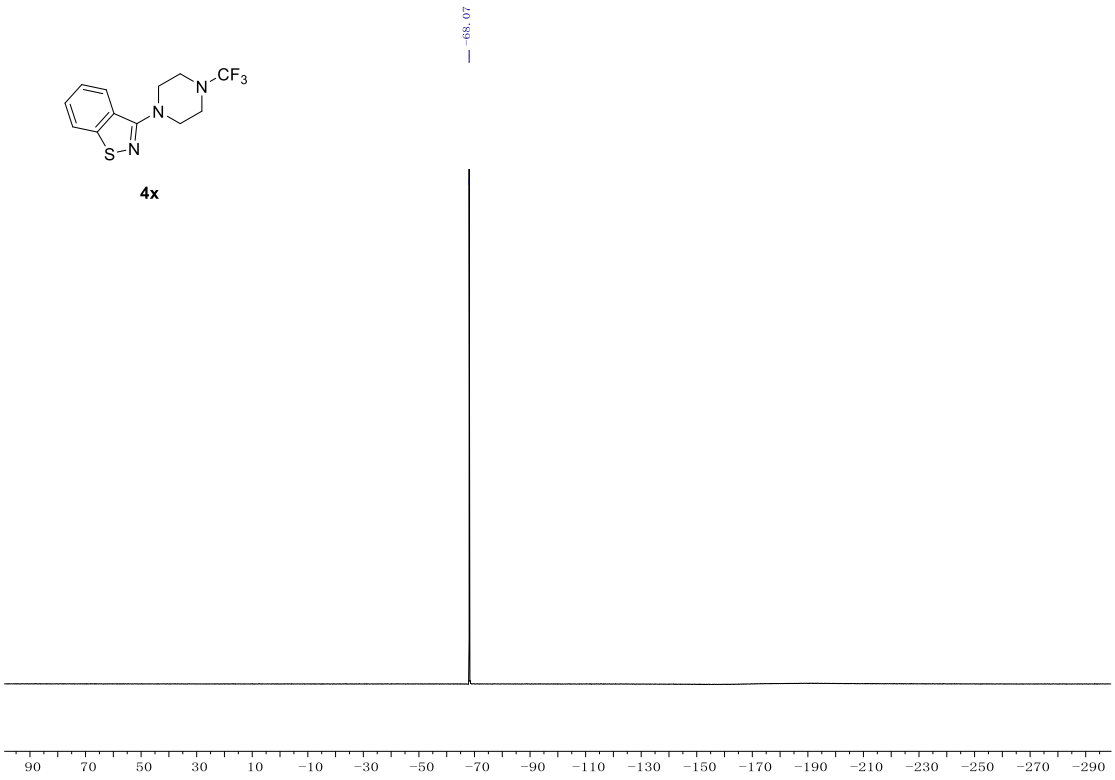
3.61
3.60
3.20
3.19
3.18
CF3
N
S
N
4x
1.00
0.94
1.01
0.97
4.13
4.08
10.5 10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0 −0.5


−68.07
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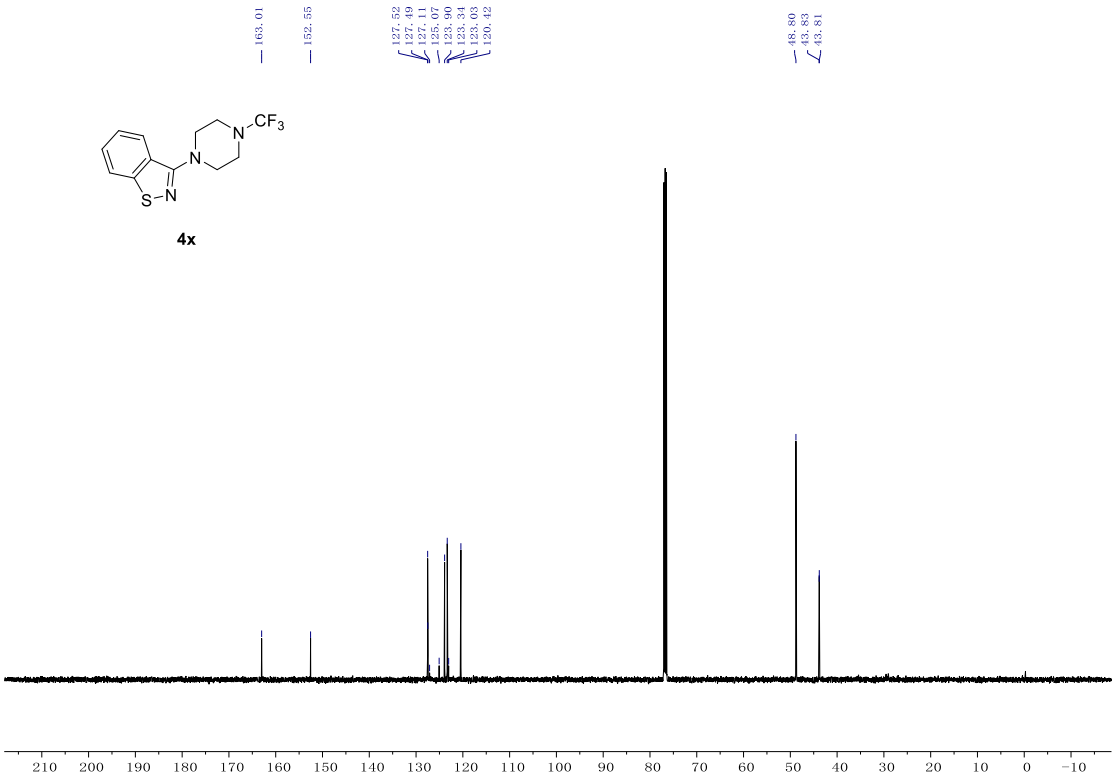
N
S
N
4x
90 70 50 30 10 −10 −30 −50 −70 −90 −110 −130 −150 −170 −190 −210 −230 −250 −270 −290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123.90
123.34
123.03
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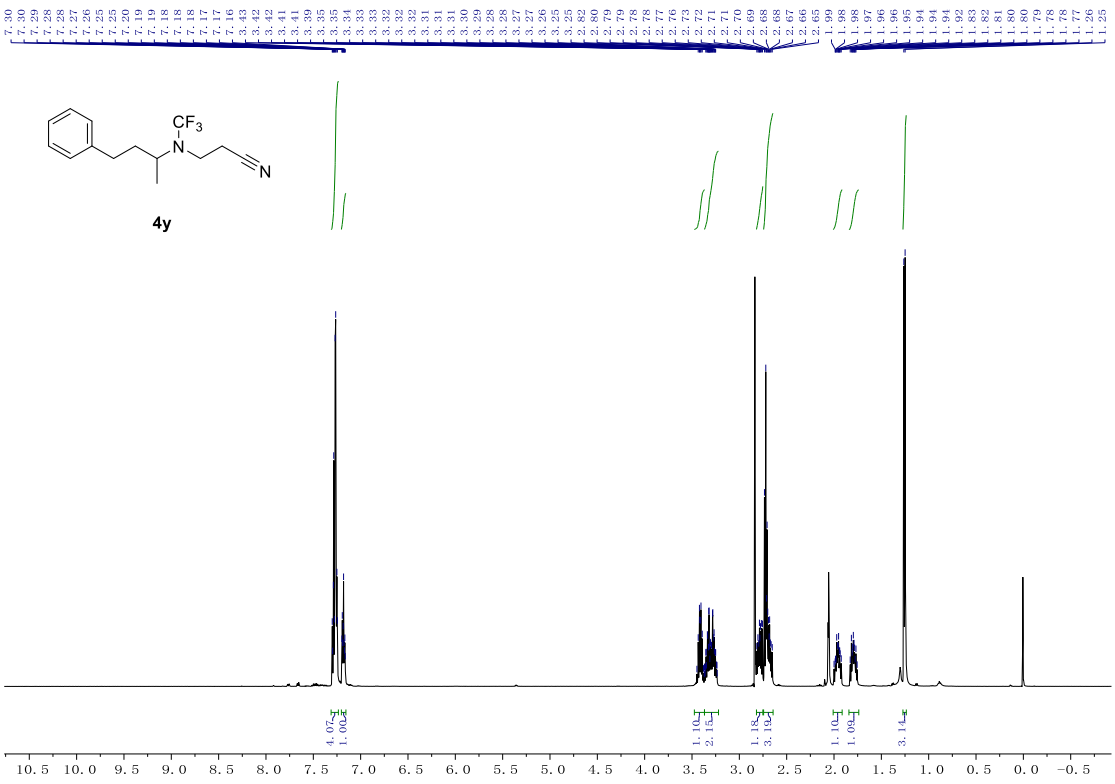
43.81
N
CF3
S
N
4x
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 −10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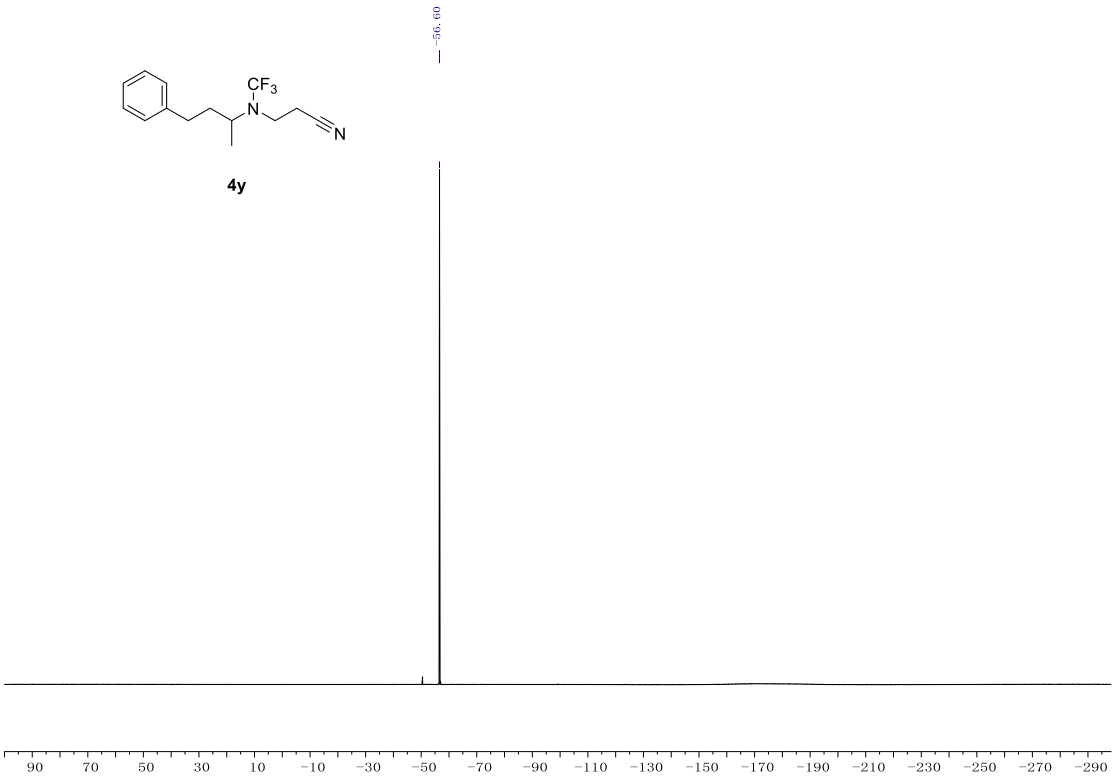
1.94
1.92
1.83
1.82
1.81
1.80
1.80
1.79
1.78
1.78
1.77
1.26
1.25
CF3
N
N
4y
4.07
1.00
1.10
2.15
1.18
3.19
1.10
1.09
3.14
10.5 10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0 −0.5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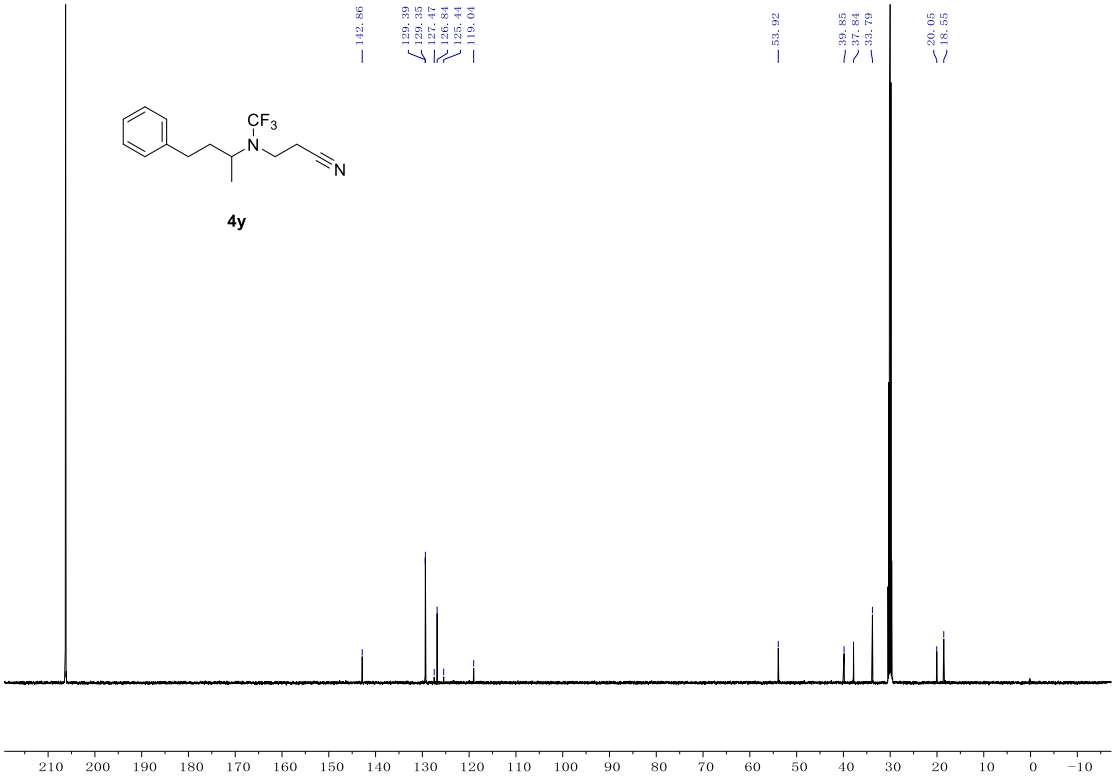
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129.39
129.35
127.47
126.84
125.44
119.04
53.92
39.85
37.84
33.79
20.05
18.55
CF3
N
N
4y
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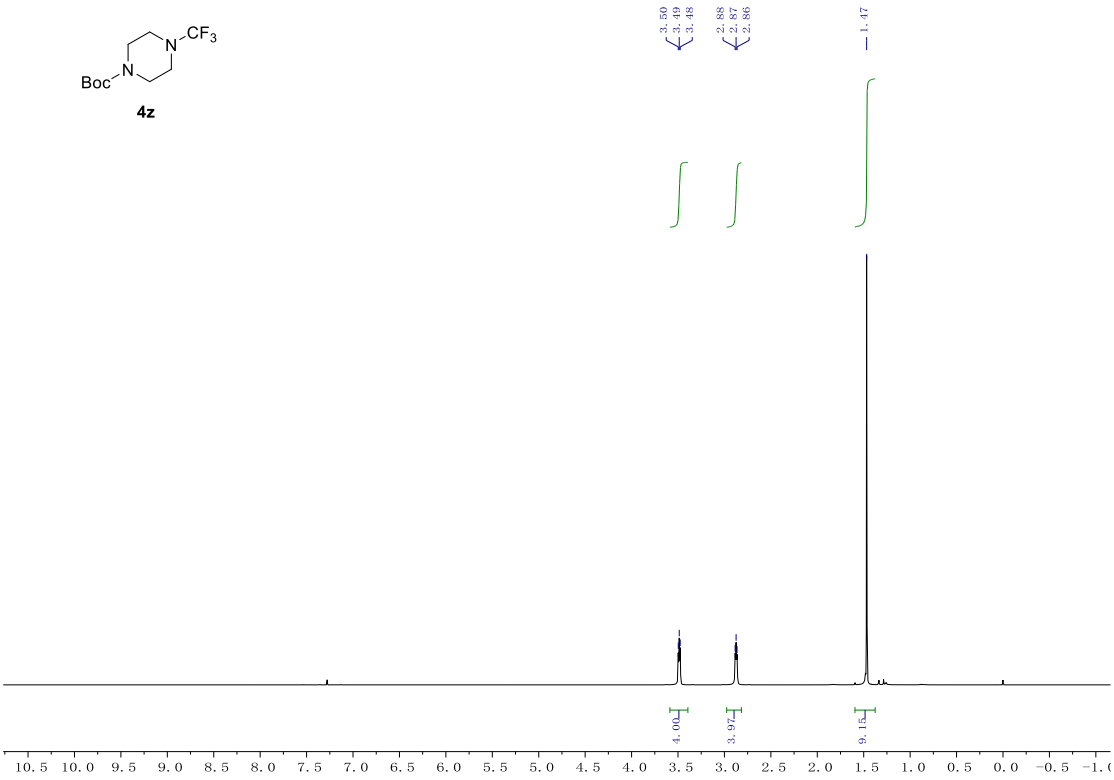
Boc
CF3
4z
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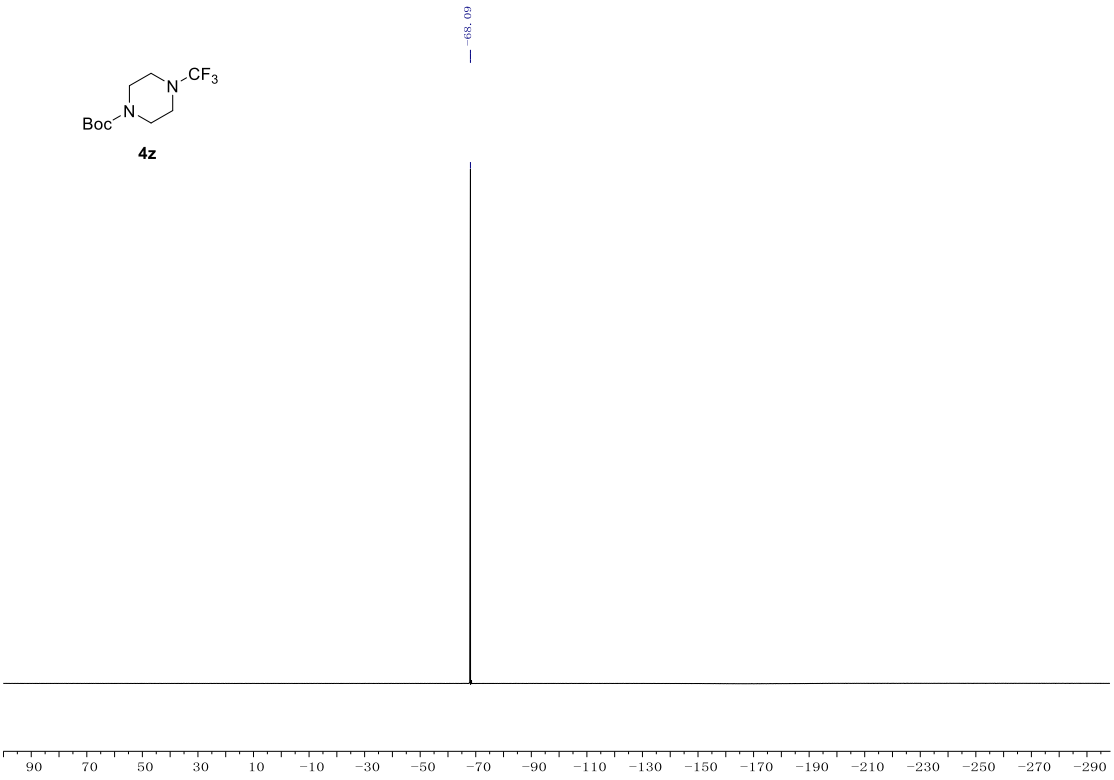
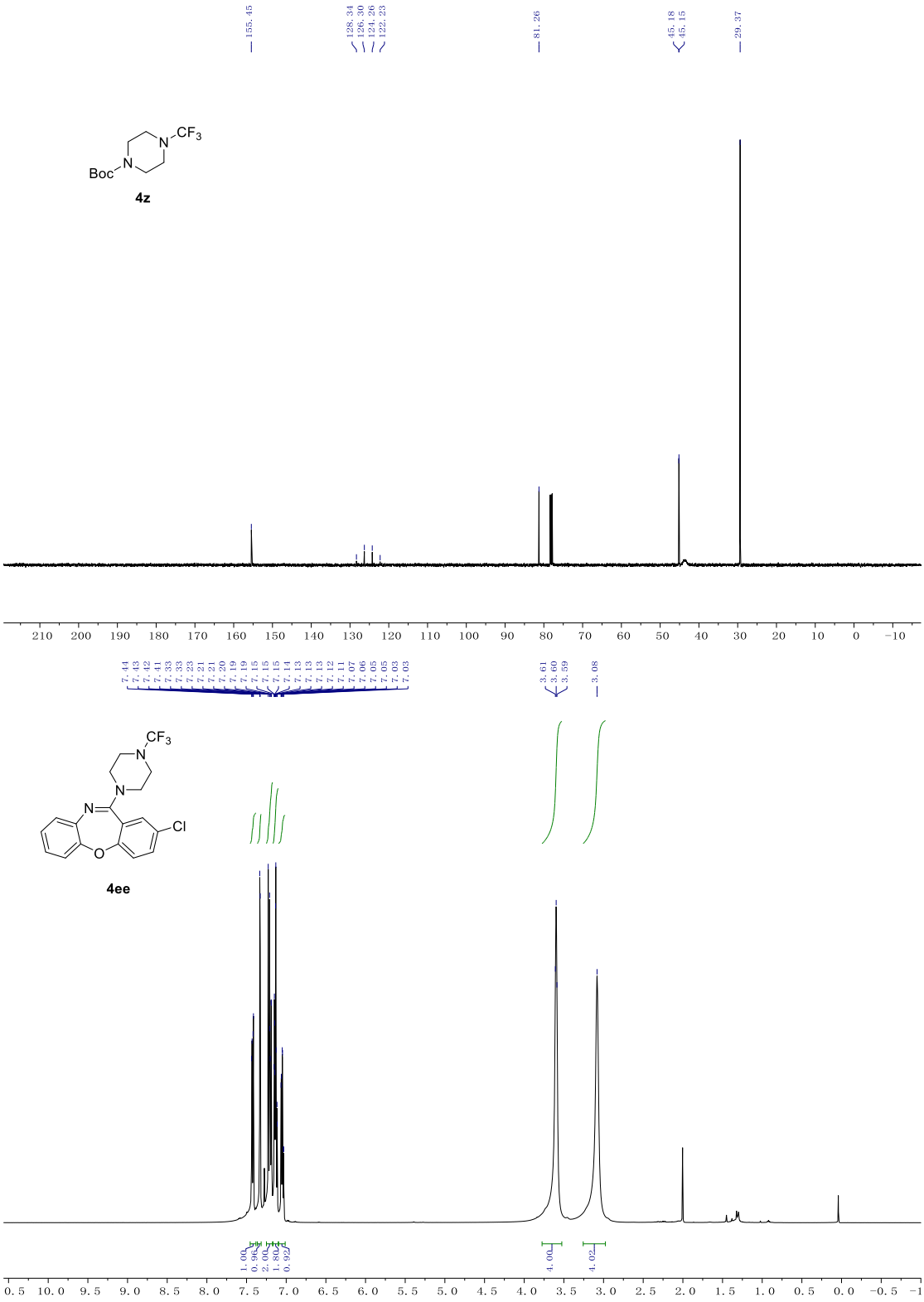
3.48
2.88
2.87
2.86
1.47
4.00
3.97
9.15
10.5 10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0 -0.5


Boc
CF3
4z
-68.09
90 70 50 30 10 -10 -30 -50 -70 -90 -110 -130 -150 -170 -190 -210 -230 -250 -270 -290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136.30
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122.23
81.26
45.18
45.15
29.37
Boc
CF3
4z
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7.43
7.42
7.41
7.33
7.33
7.23
7.21
7.21
7.20
7.19
7.15
7.15
7.15
7.14
7.13
7.13
7.12
7.11
7.07
7.06
7.05
7.05
7.03
7.03
3.61
3.60
3.59
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CF3
Cl
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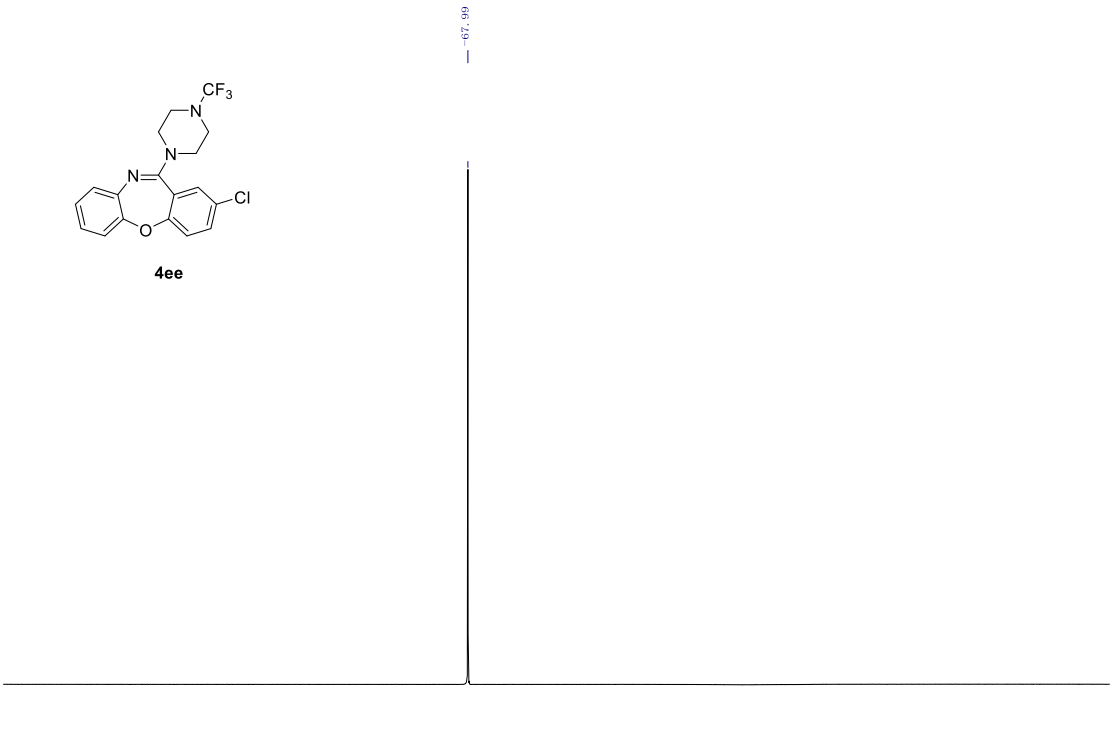
0.96
2.00
1.80
0.92
4.00
4.02


-67.99
CF3
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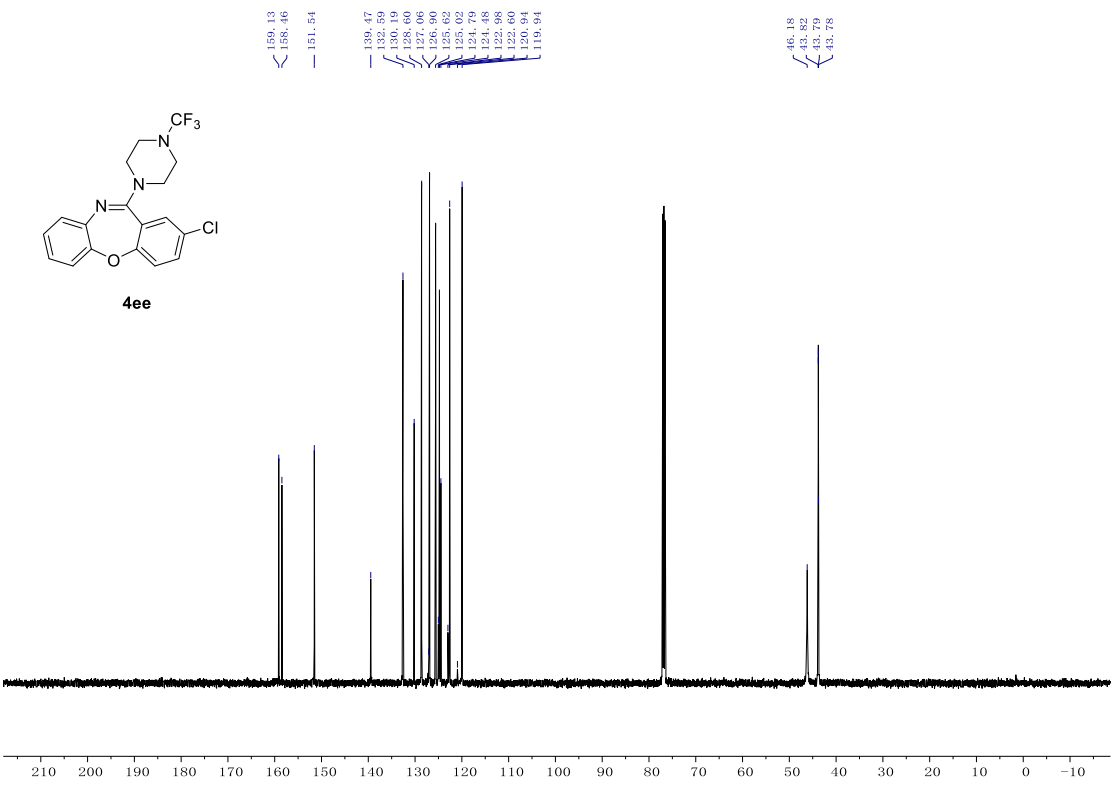
N
N
Cl
O
90 70 50 30 10 -10 -30 -50 -70 -90 -110 -130 -150 -170 -190 -210 -230 -250 -270 -290

4ee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125.02
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124.48
122.98
122.60
120.94
119.94
46.18
43.82
43.79
43.78
CF3
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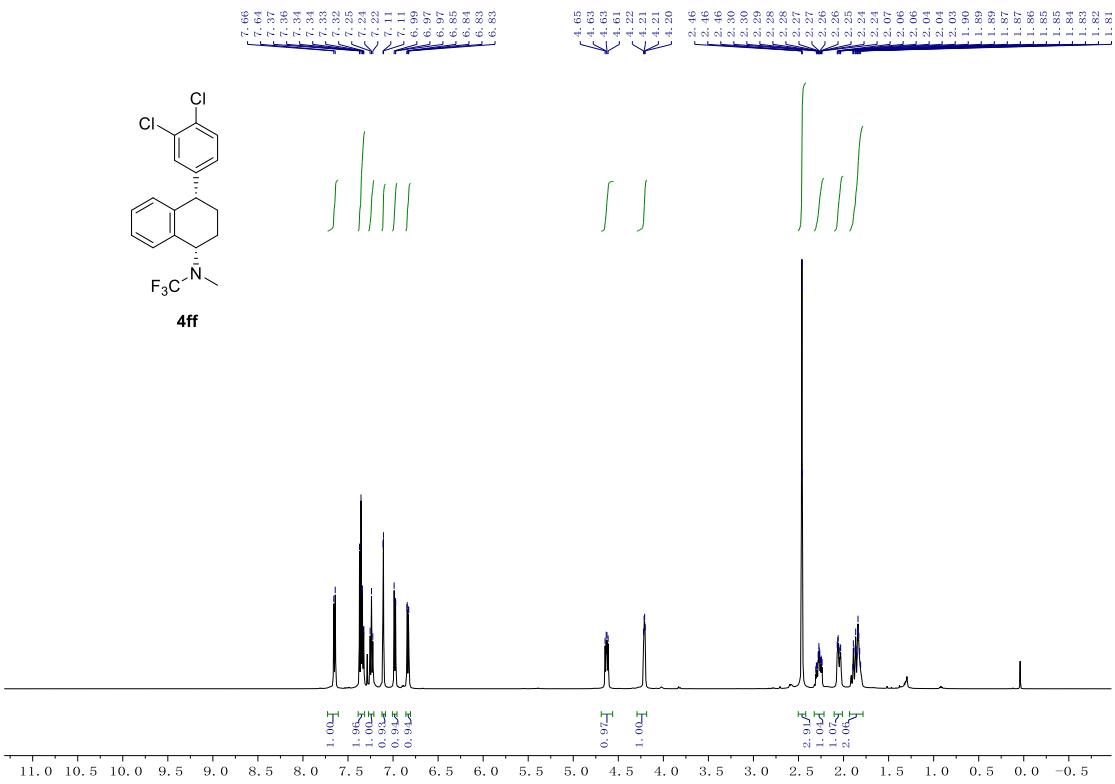
N
N
Cl
O
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10

4ee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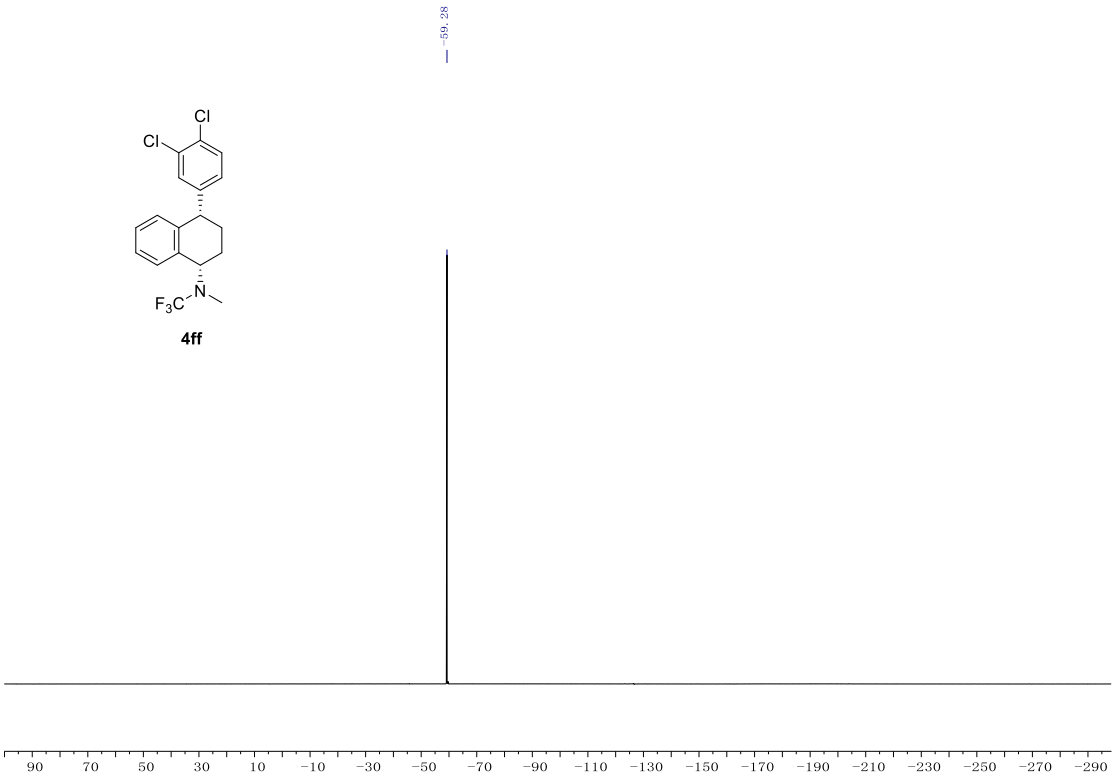
4.65 4.63 4.63 4.61 4.22 4.21 4.21 4.20
2.46 2.46 2.46 2.30 2.30 2.28 2.28 2.27 2.27 2.26 2.26 2.25 2.24 2.24 2.07 2.06 2.06 2.04 2.04 2.03 1.90 1.89 1.89 1.87 1.87 1.86 1.85 1.85 1.84 1.83 1.82 1.81
Cl
Cl
F3C
N
4ff
1.00 1.96 1.00 0.93 0.94 0.94 0.97 1.00 2.91 1.04 1.07 2.06
11.0 10.5 10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0 -0.5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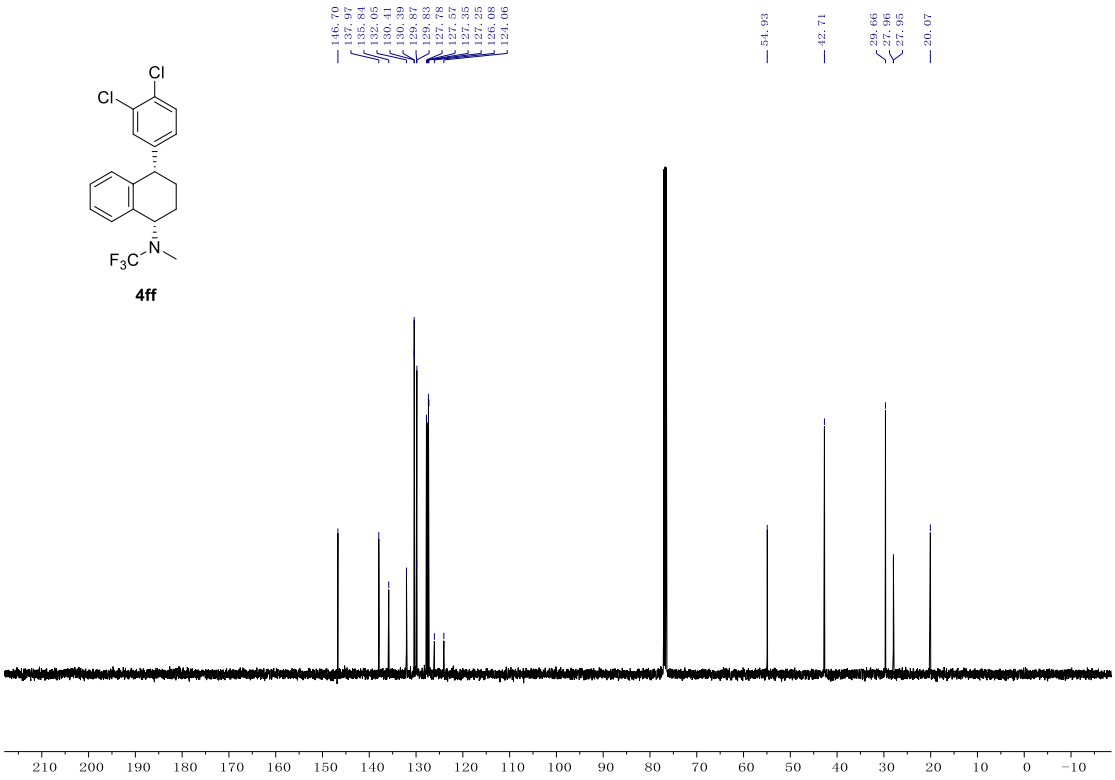
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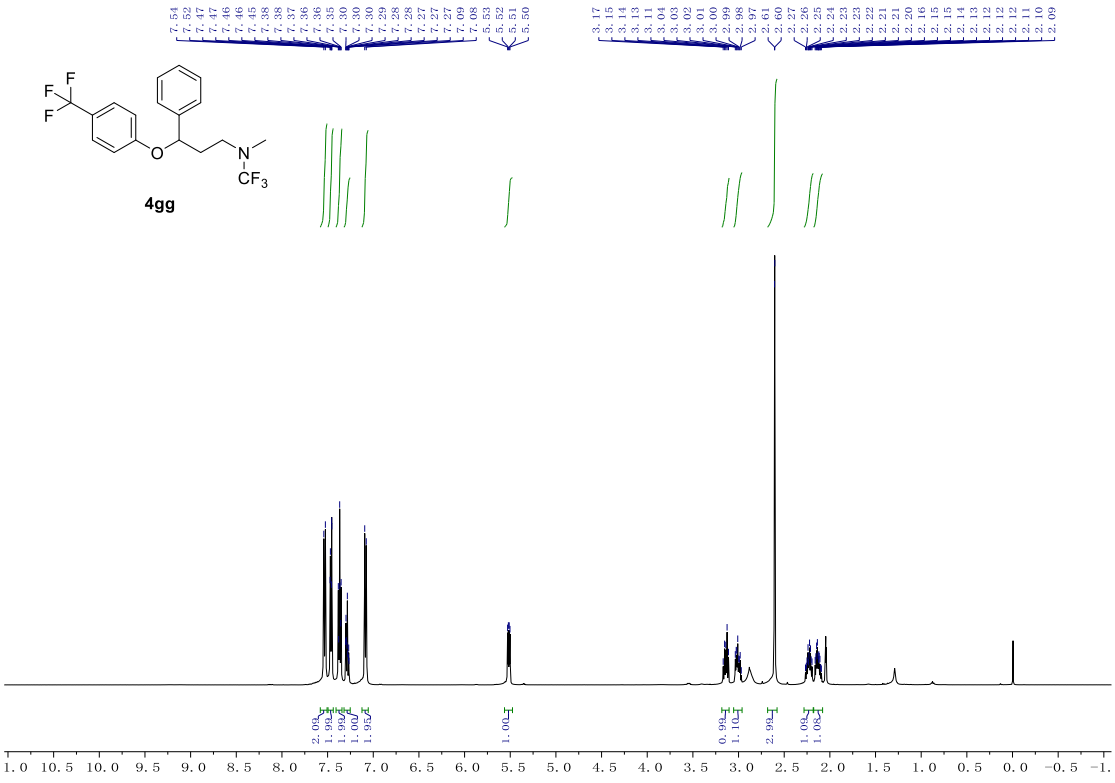
20.07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O
N
CF3
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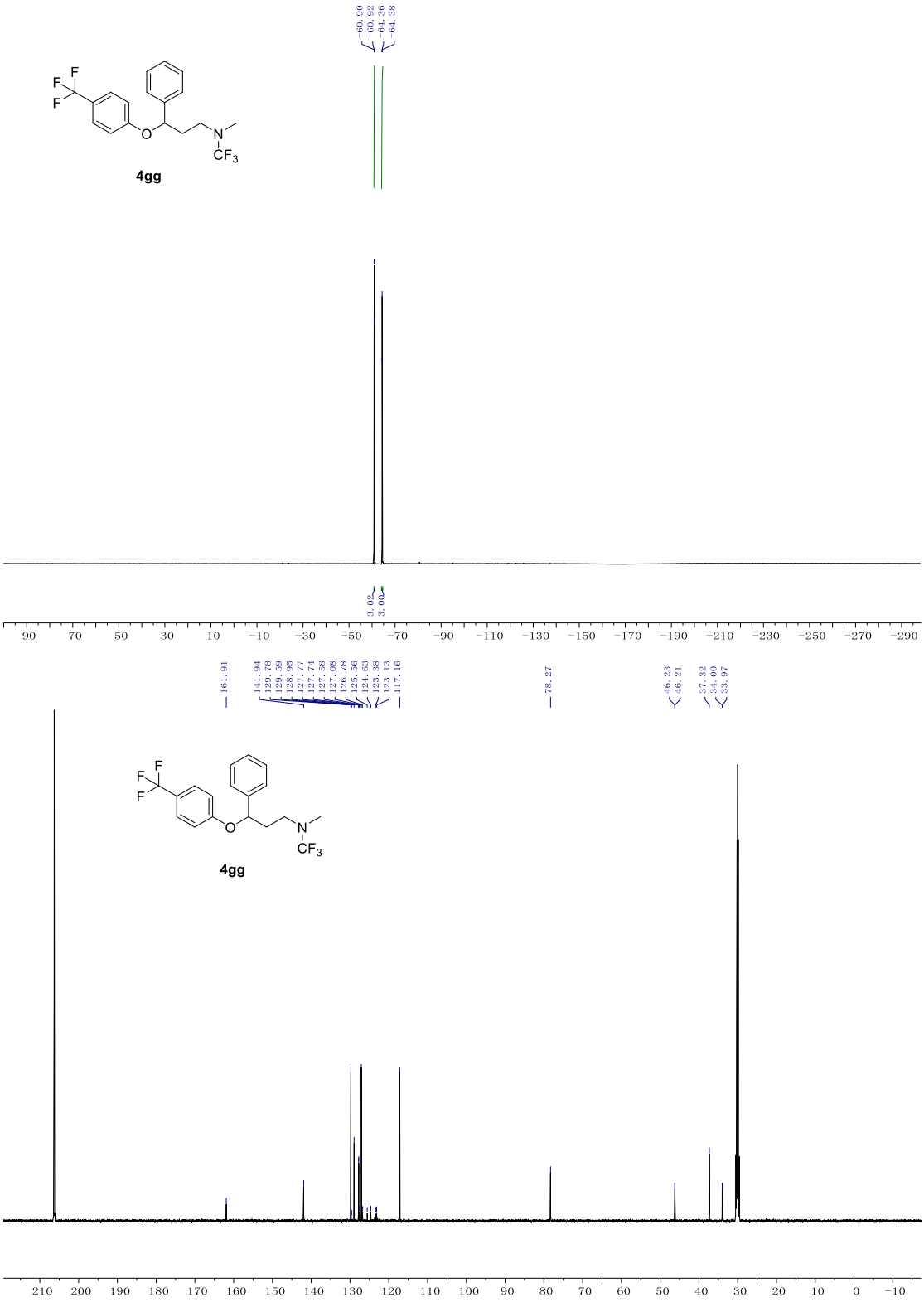
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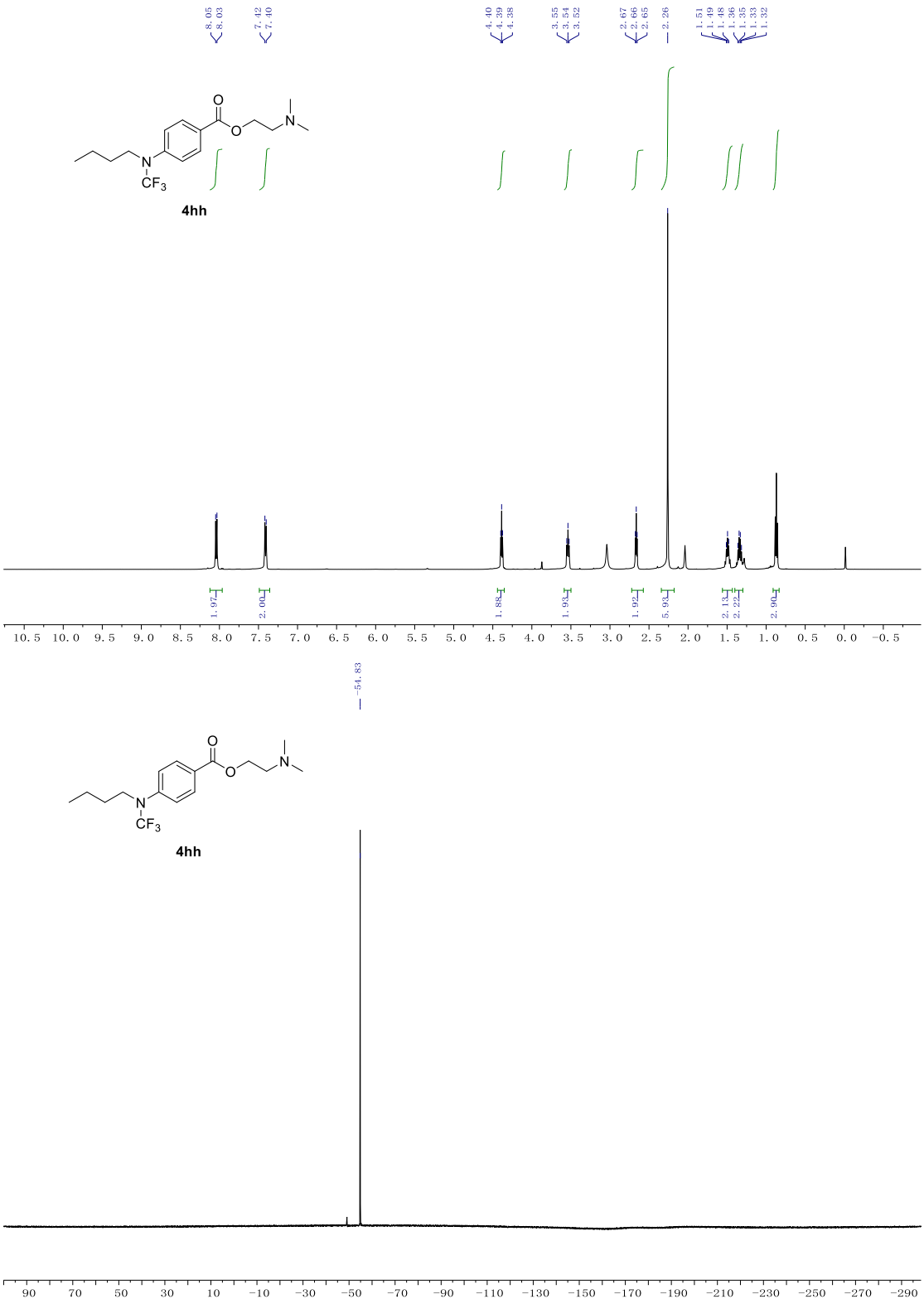
33.97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2.26
1.51
1.49
1.48
1.36
1.35
1.33
1.32
4hh
1.97
2.00
1.88
1.93
1.92
5.93
2.13
2.22
2.90
10.5 10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0 −0.5
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4hh
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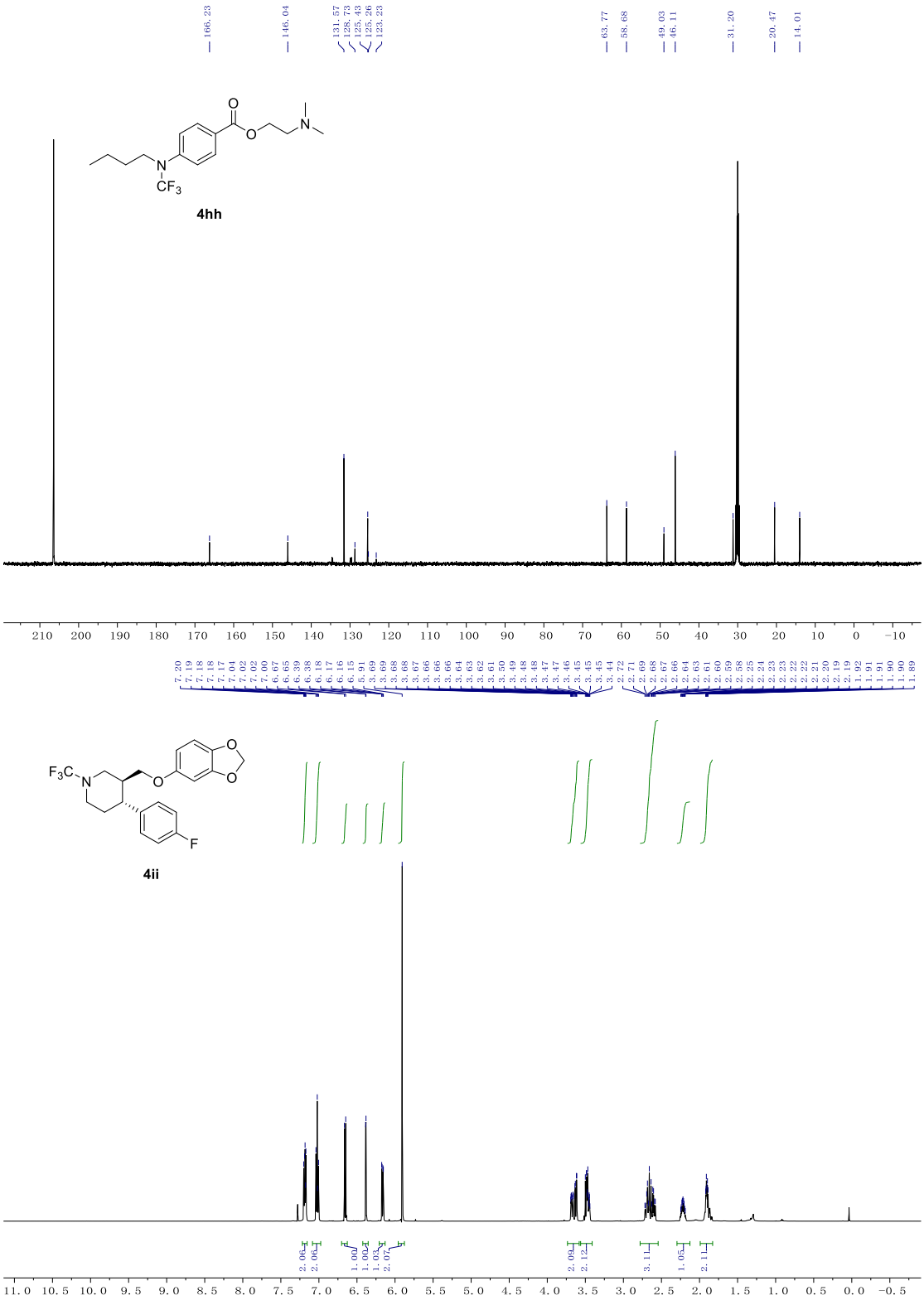
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63.77
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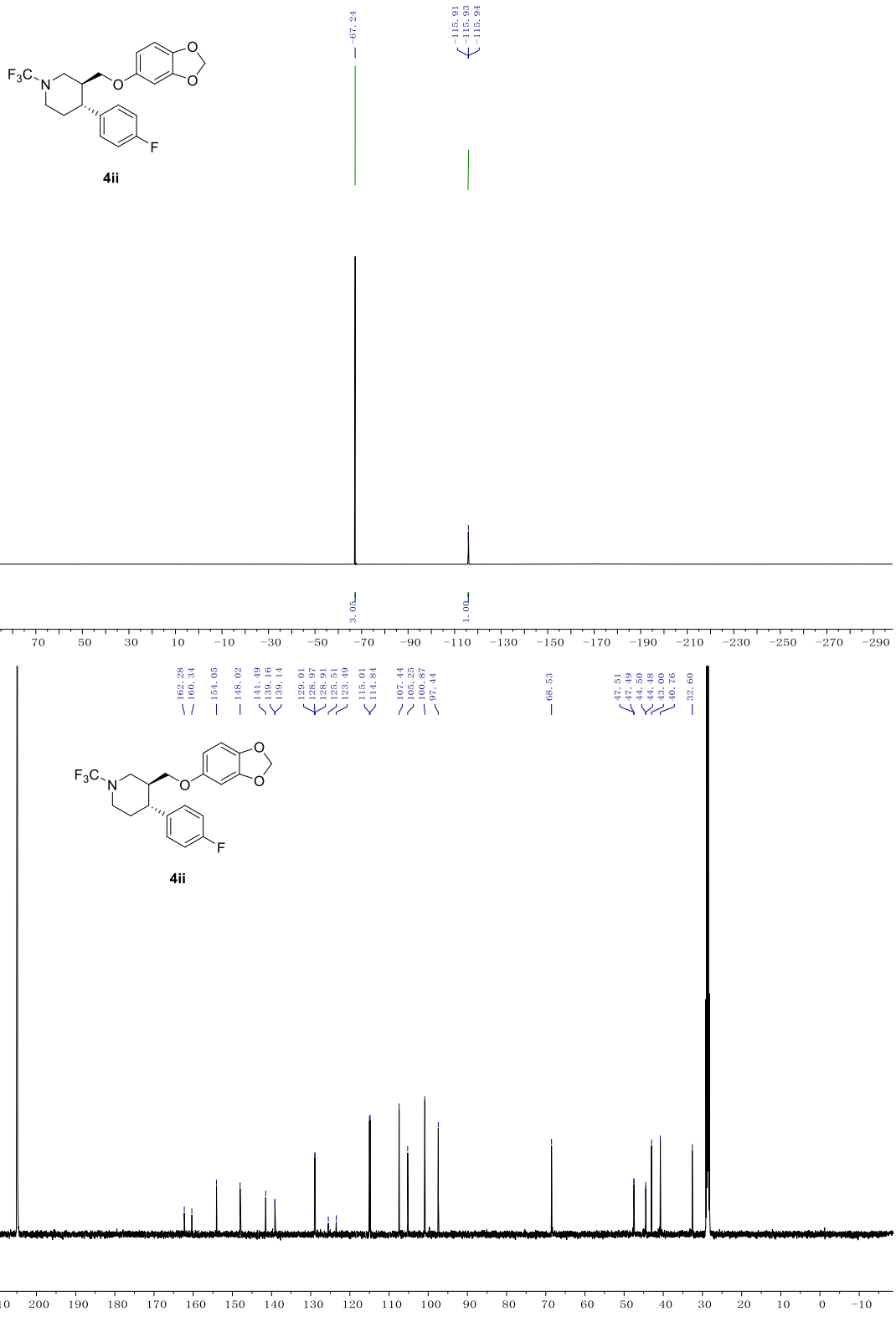
31.20
20.47
14.01
4hh
4ii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162.28
160.34
154.05
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139.14
129.01
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123.49
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97.44
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44.50
44.48
43.00
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O
F
4ii
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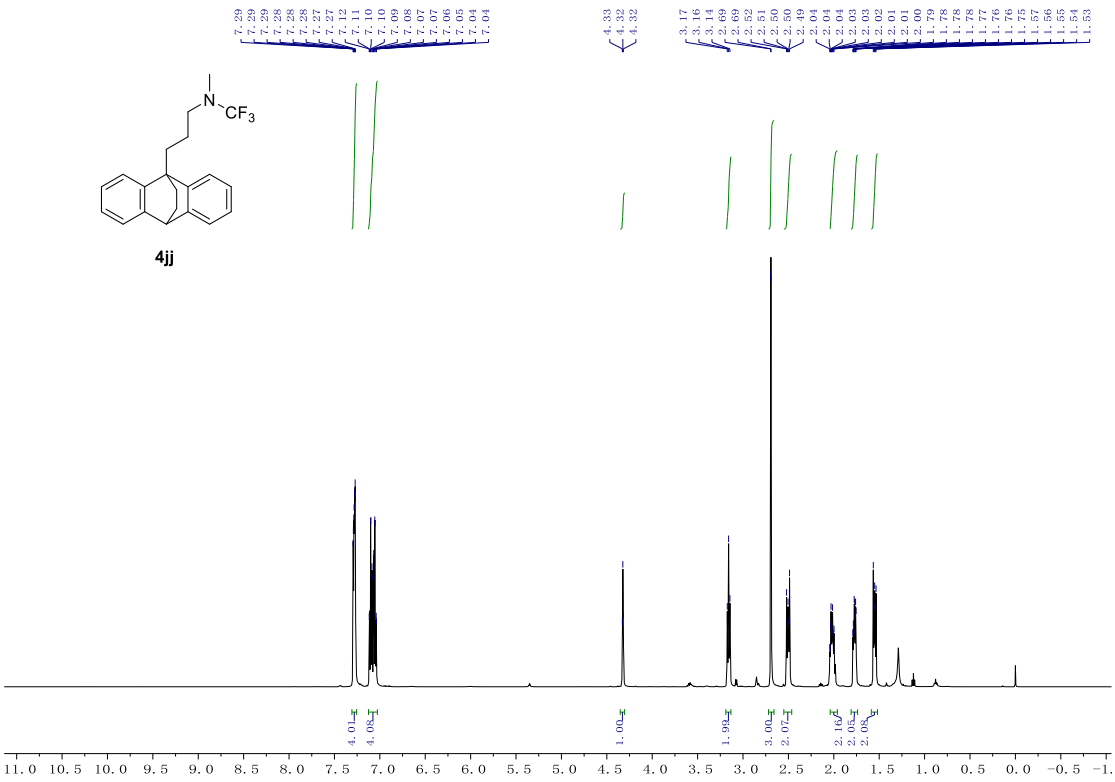
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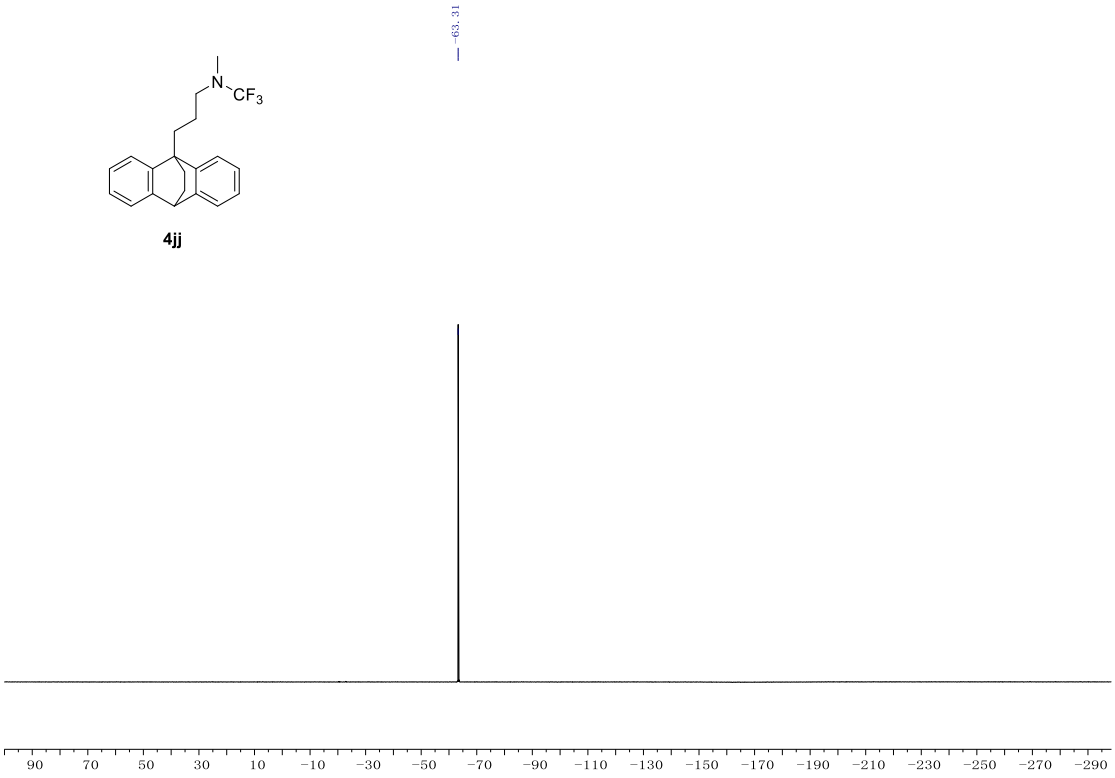
4.33 4.32 4.32
3.17 3.16 3.14 2.69 2.69 2.52 2.51 2.50 2.50 2.49 2.04 2.04 2.04 2.03 2.02 2.01 2.01 2.00 1.79 1.78 1.78 1.78 1.77 1.76 1.76 1.75 1.57 1.56 1.55 1.54 1.53
N
CF3
4jj
4.01 4.08 1.00 1.99 3.00 2.07 2.16 2.05 2.08
11.0 10.5 10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0 −0.5 −1.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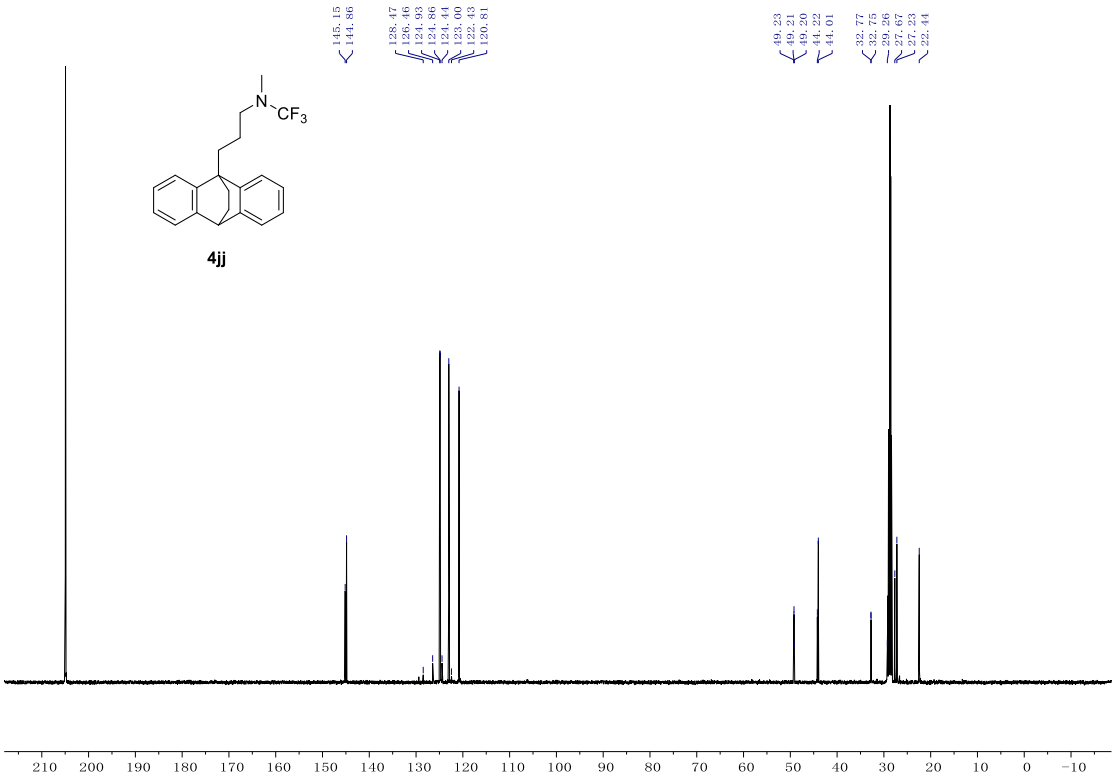
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49.20
44.22
44.01
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27.23
22.44
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CF3
4jj
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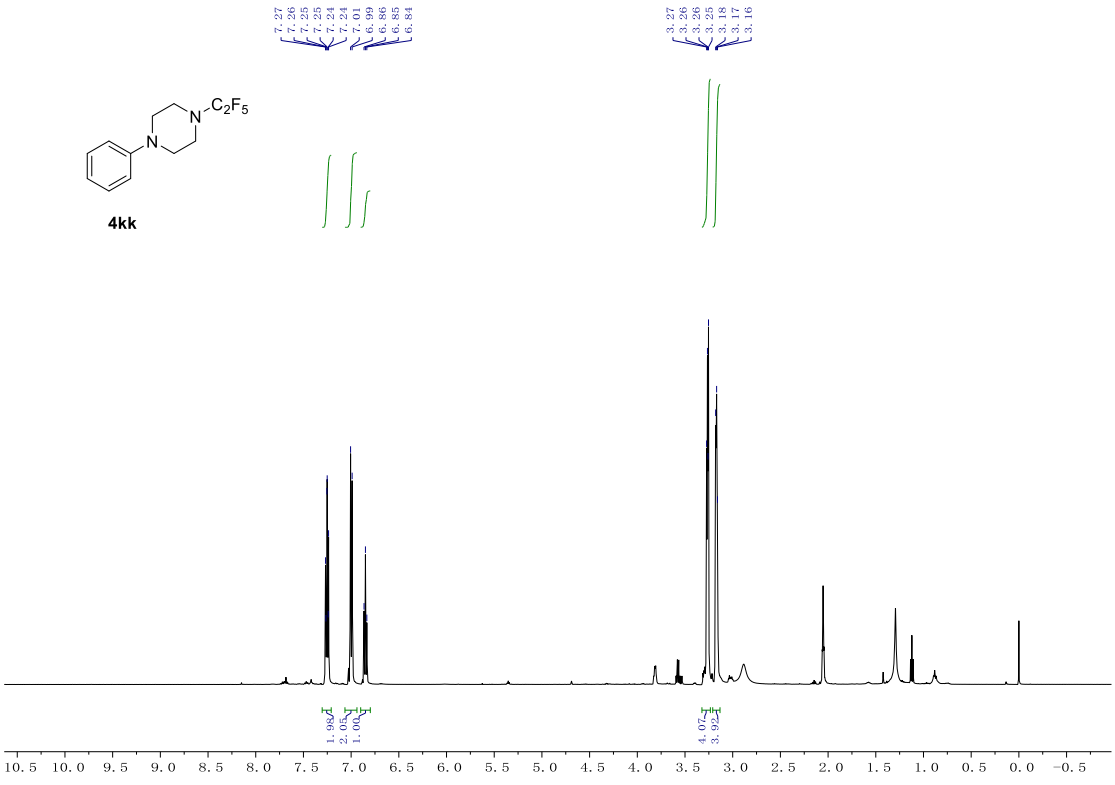
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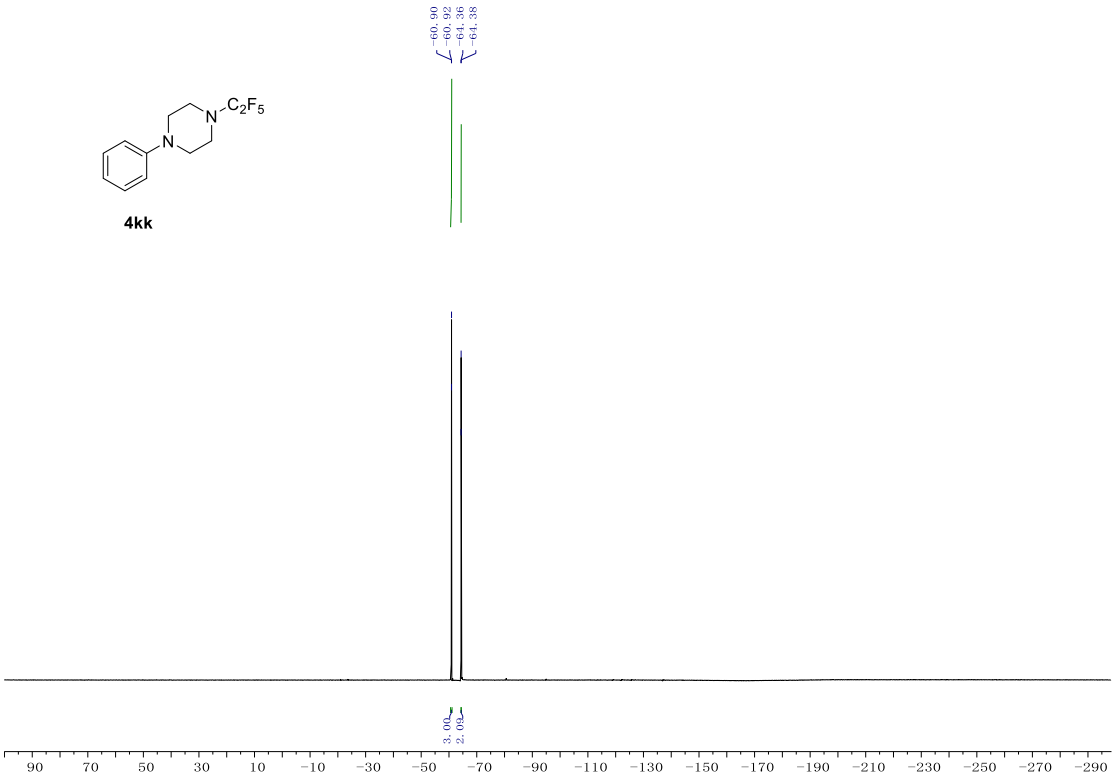
3.26
3.25
3.18
3.17
3.16
N
N
C2F5
4kk
1.98
2.05
1.00
4.07
3.92
10.5 10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0 -0.5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C_2F_5
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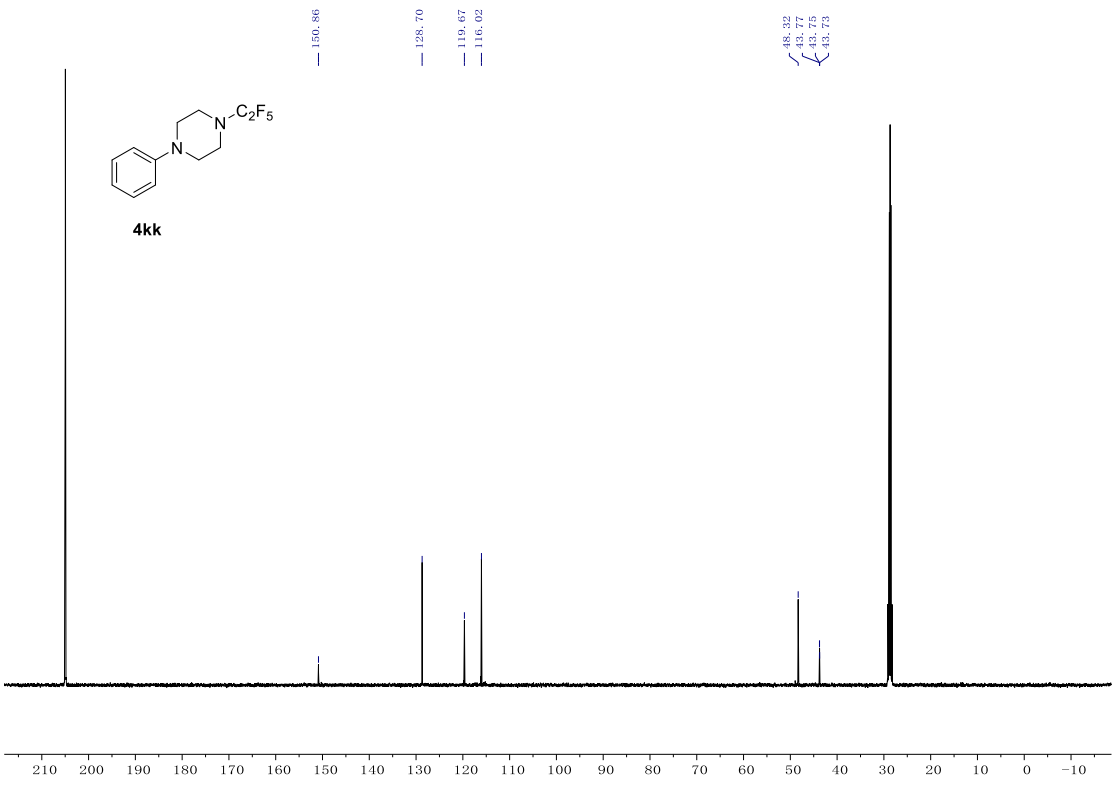
2.03
90 70 50 30 10 −10 −30 −50 −70 −90 −110 −130 −150 −170 −190 −210 −230 −250 −270 −290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43.73
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N
C_2F_5
4kk
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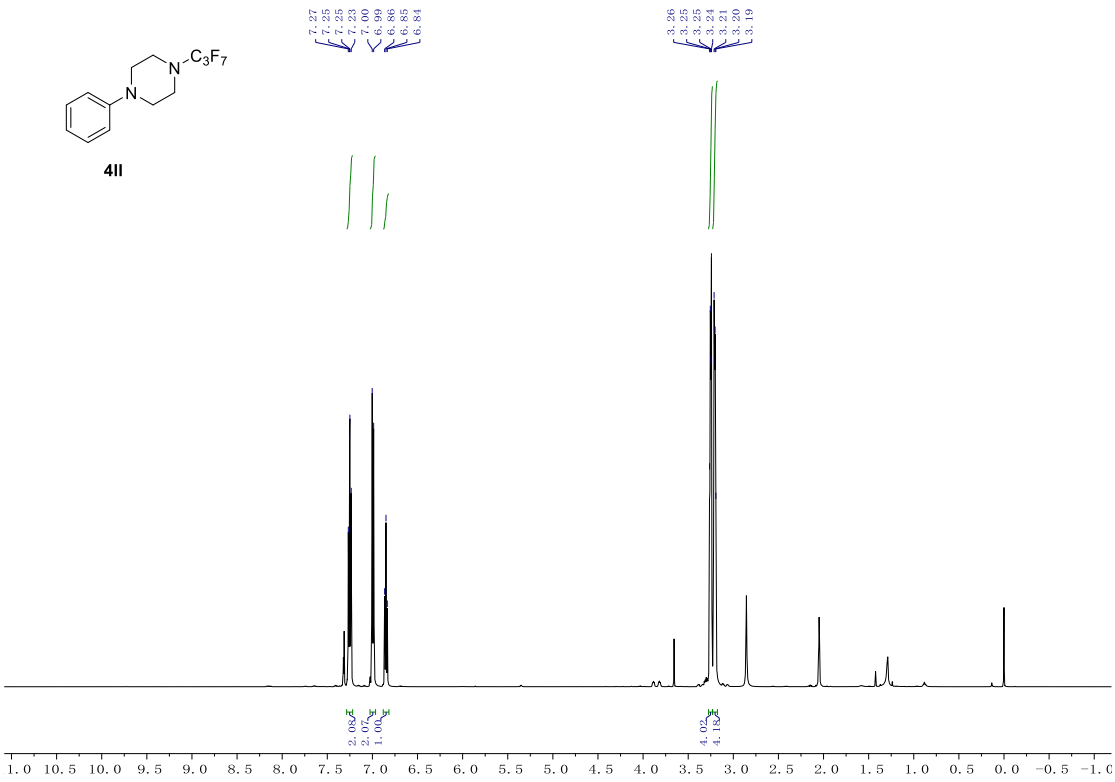
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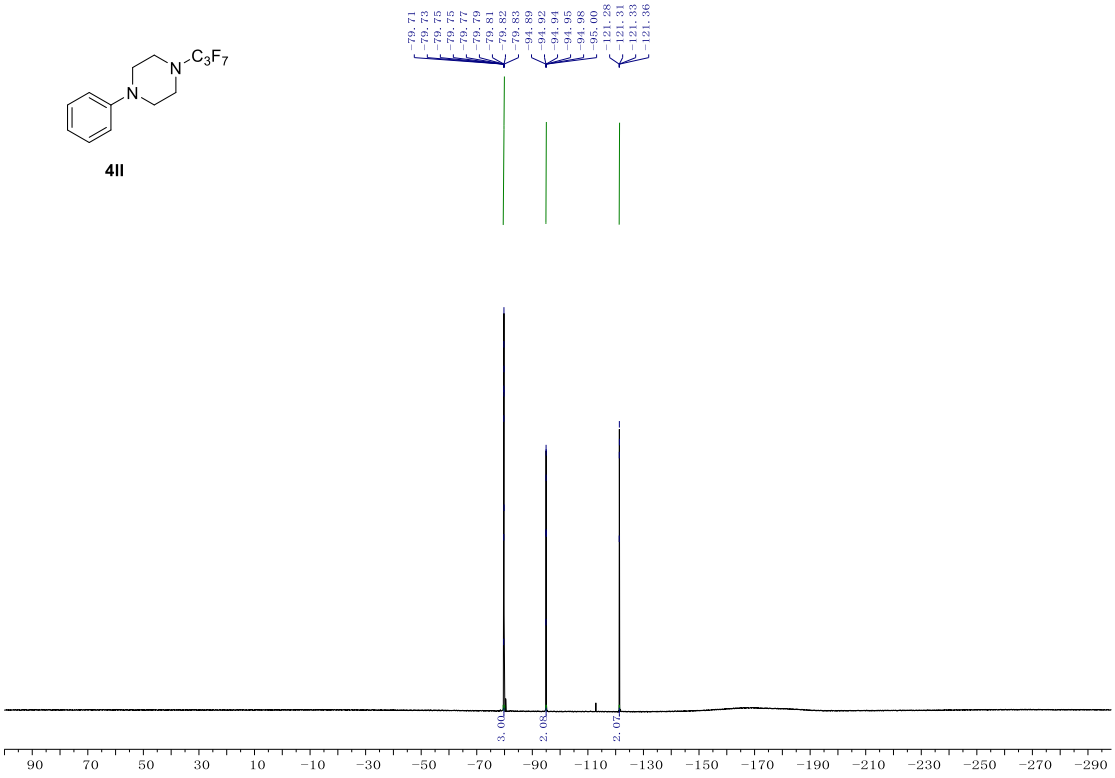
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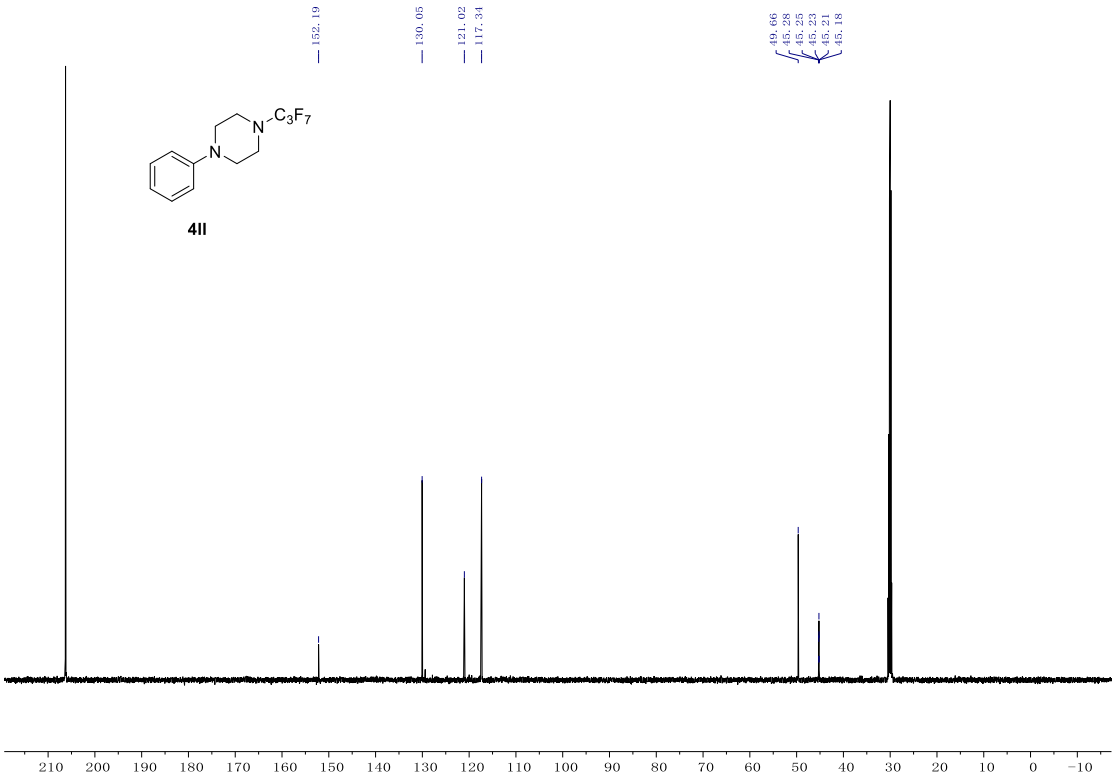
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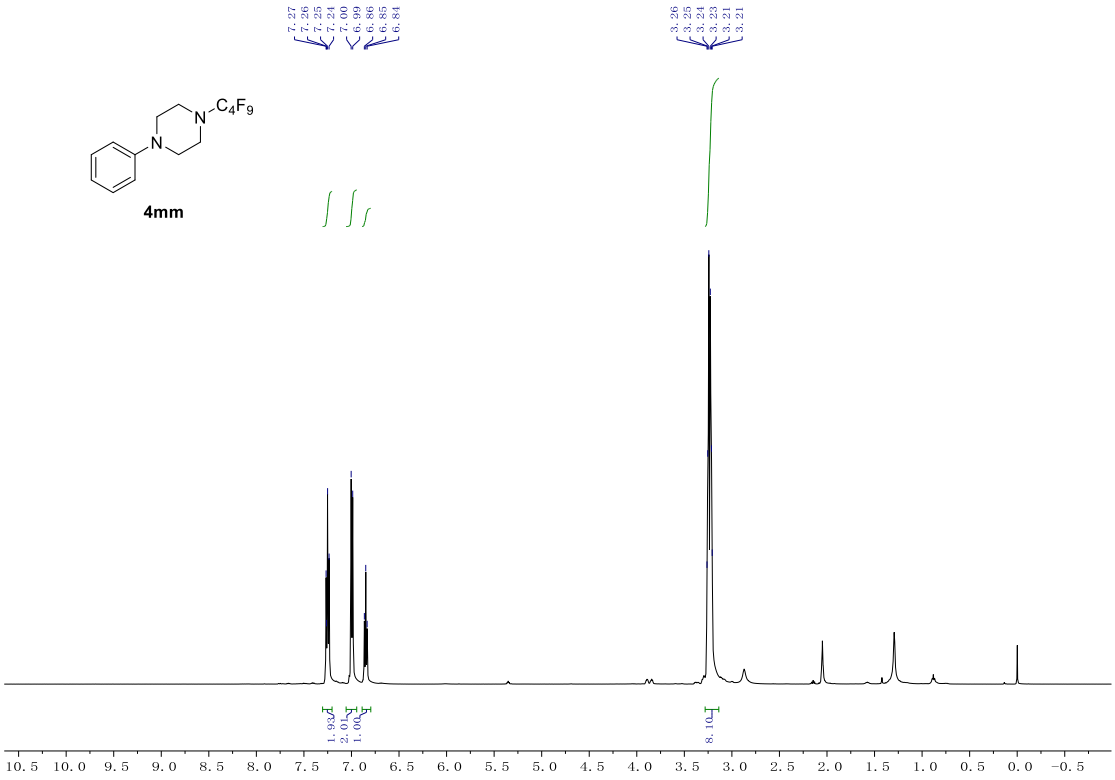
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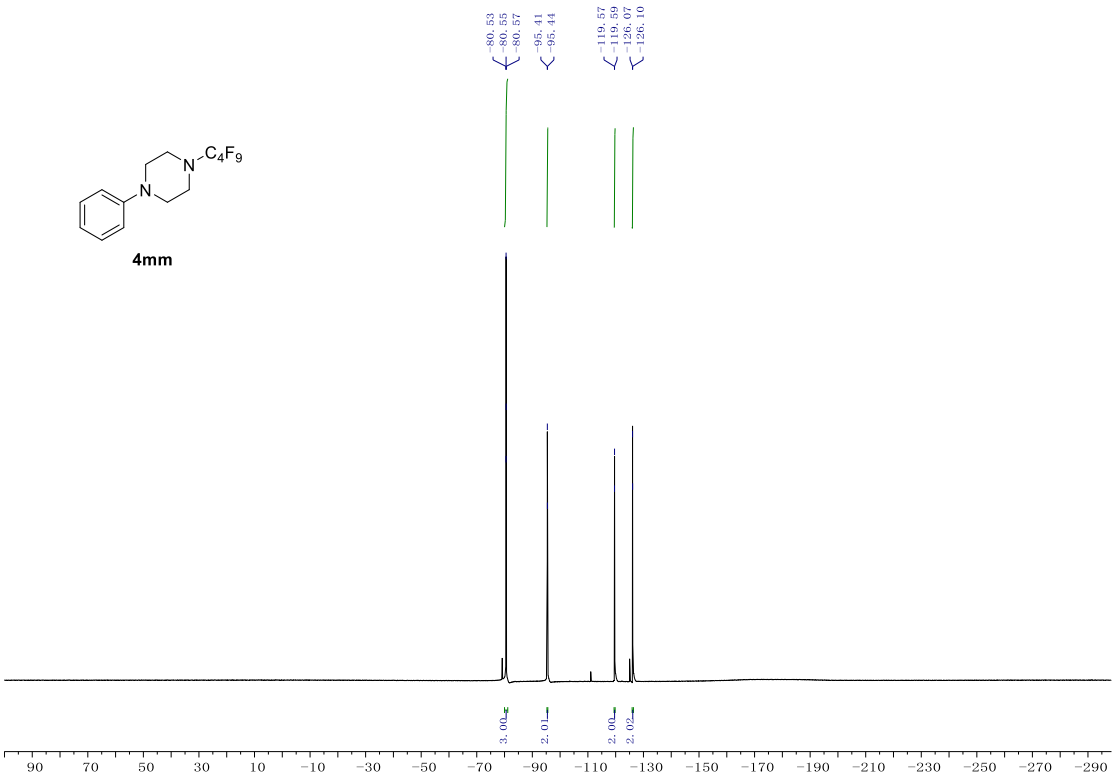
8.10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-126.10
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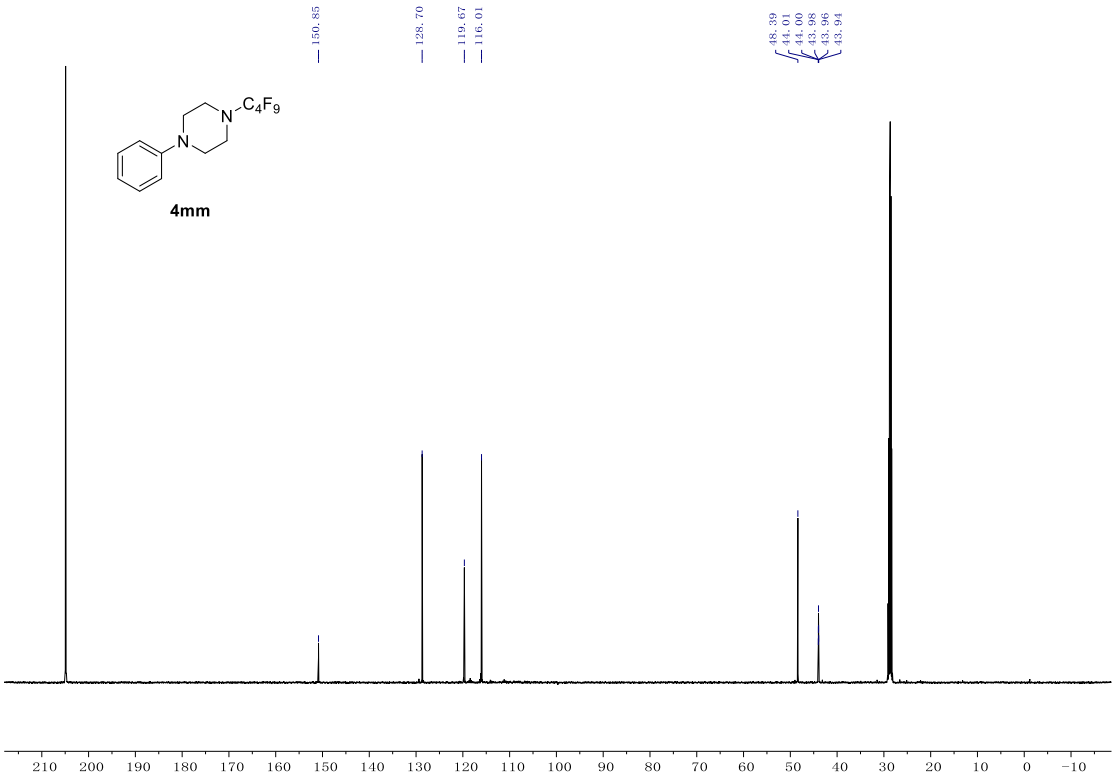
2.01
2.00
2.02
90 70 50 30 10 -10 -30 -50 -70 -90 -110 -130 -150 -170 -190 -210 -230 -250 -270 -290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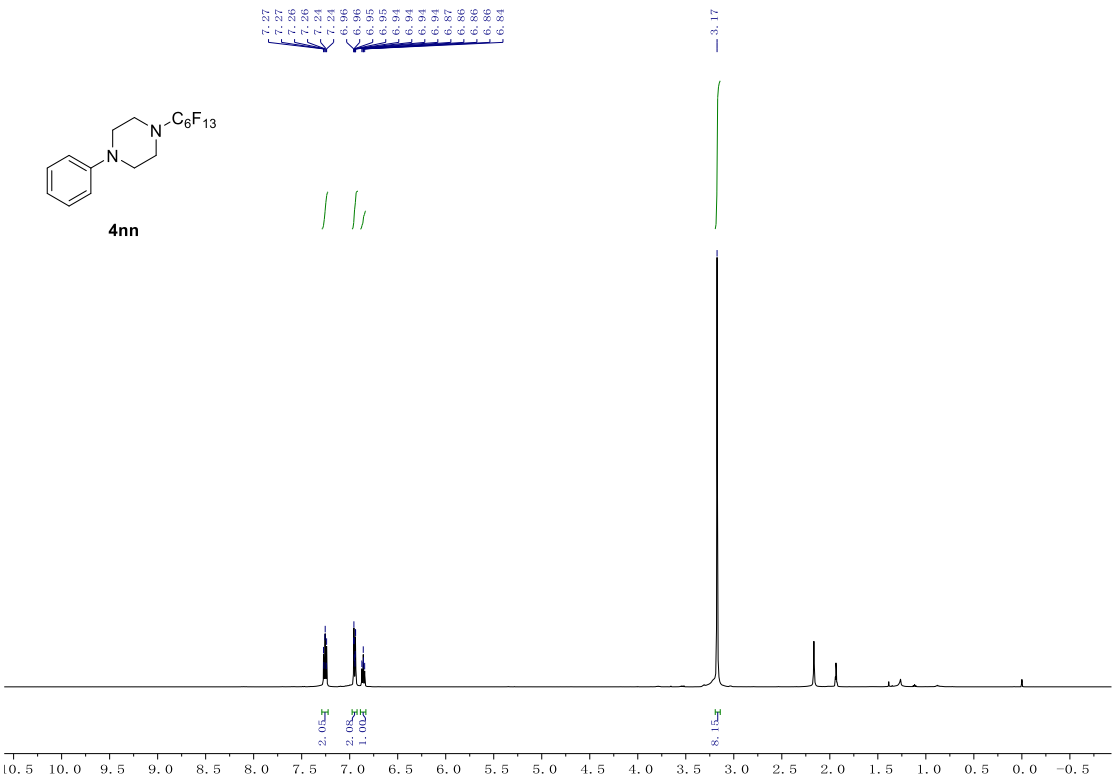
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6.87
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6.84
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C6F13
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4nn
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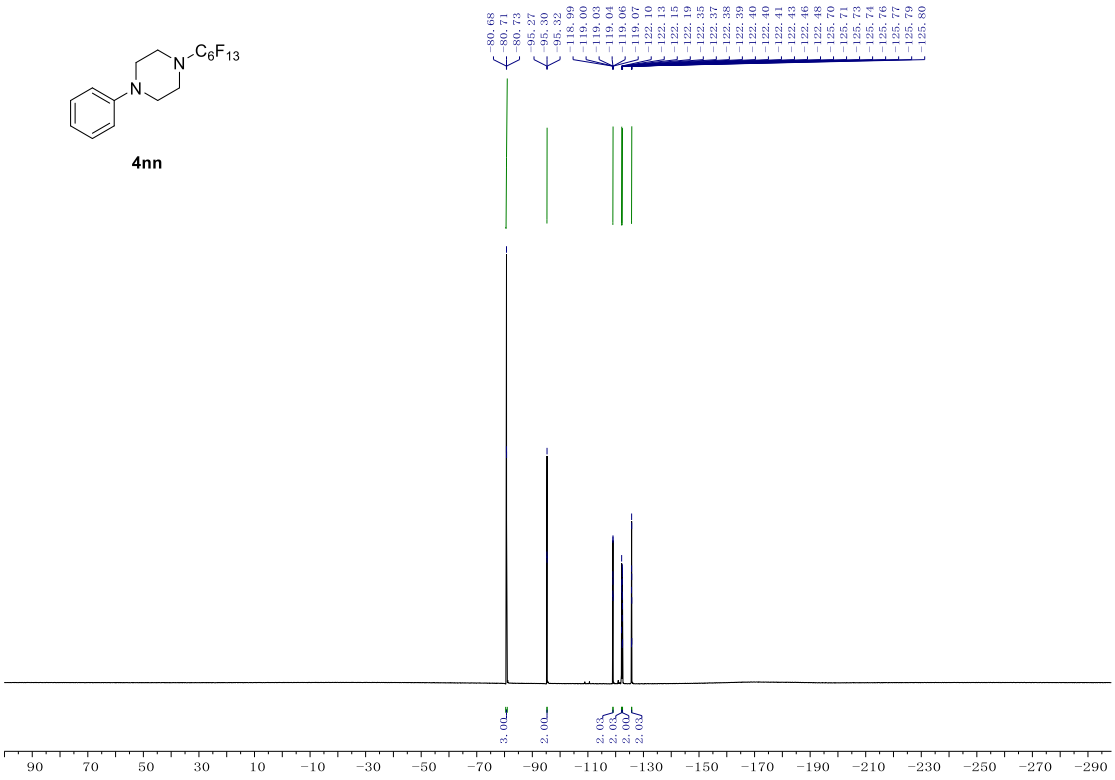
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−125.80
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C6F13
N
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2.00
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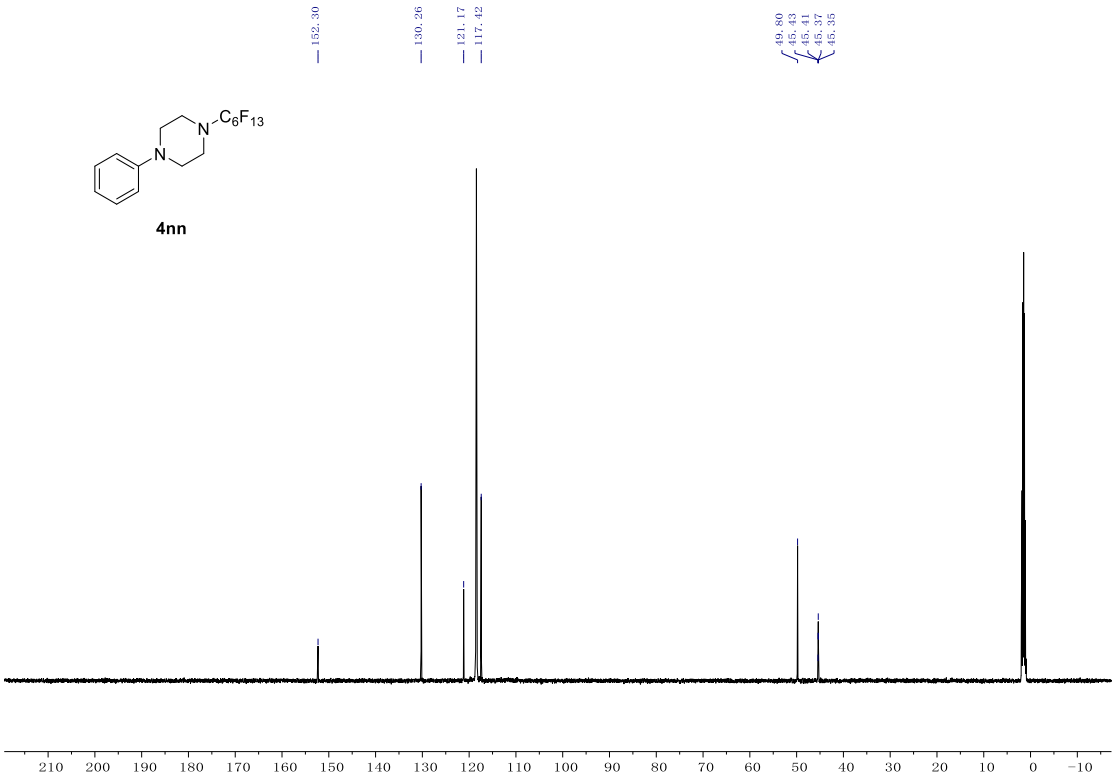
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N
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4nn
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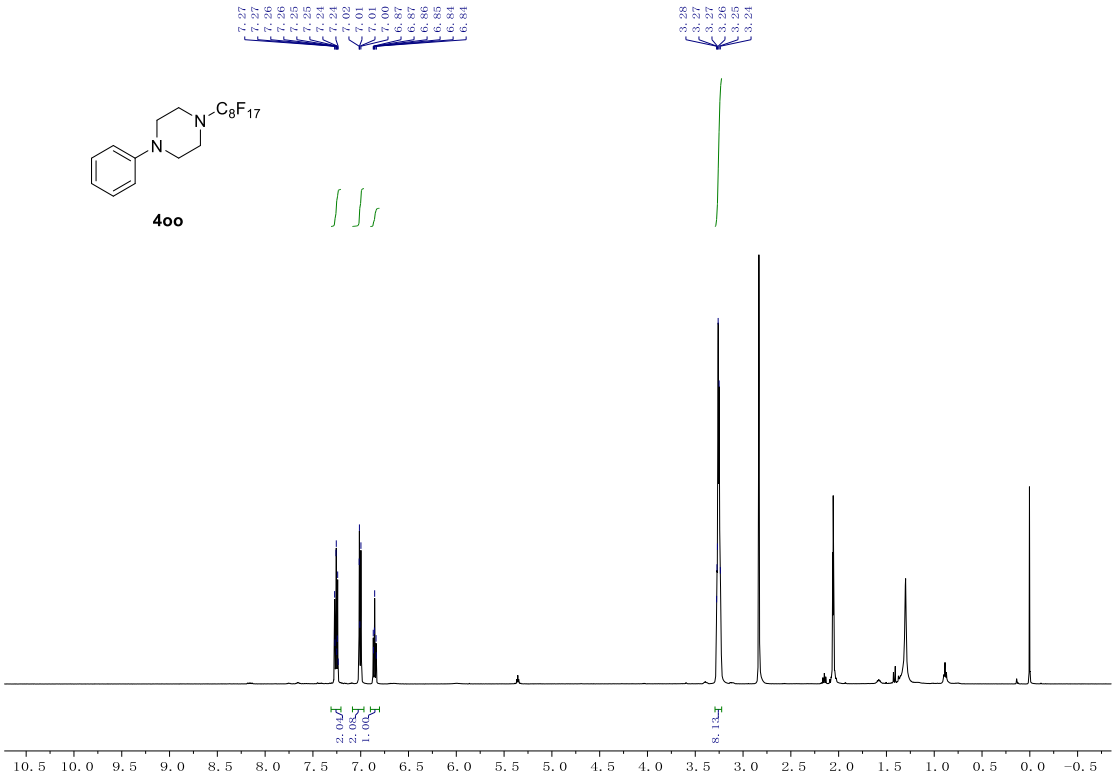
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3.24
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N
C8F17
4oo
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2.08
1.00
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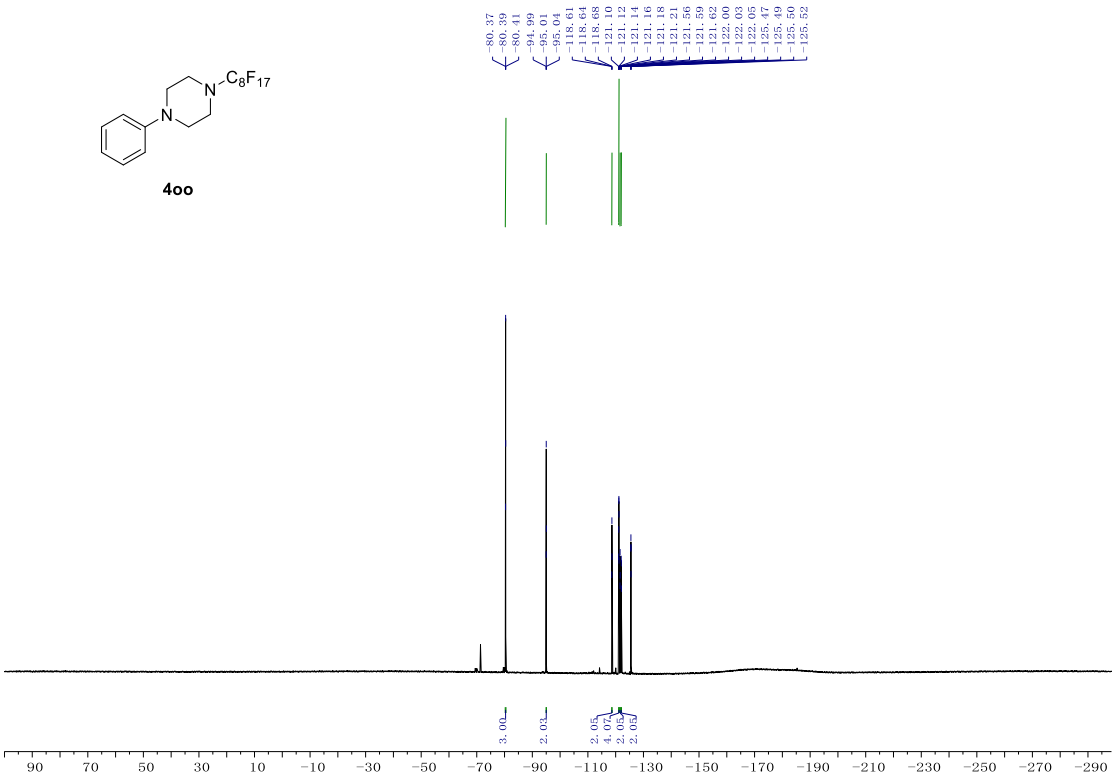
10.5 10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0 −0.5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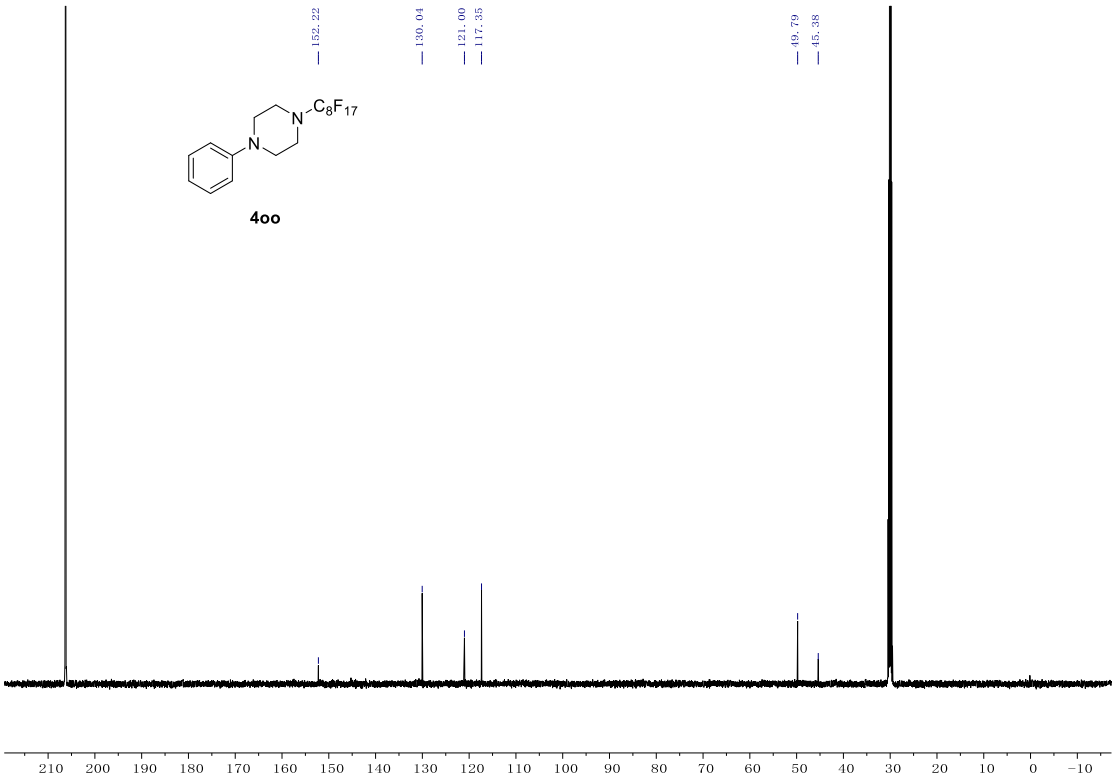
2.03
2.05
4.07
2.03
2.05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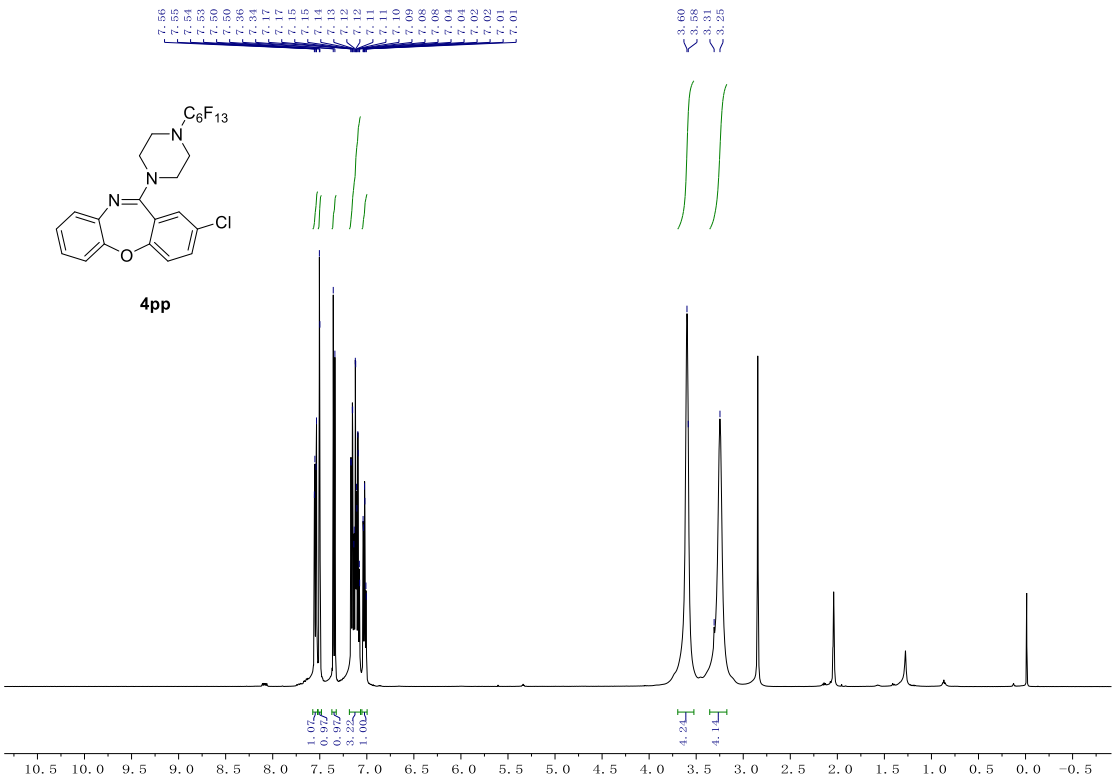
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7.10
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7.08
7.04
7.02
7.01
3.60
3.58
3.31
3.25
C6F13
N
N
N
Cl
O
4pp
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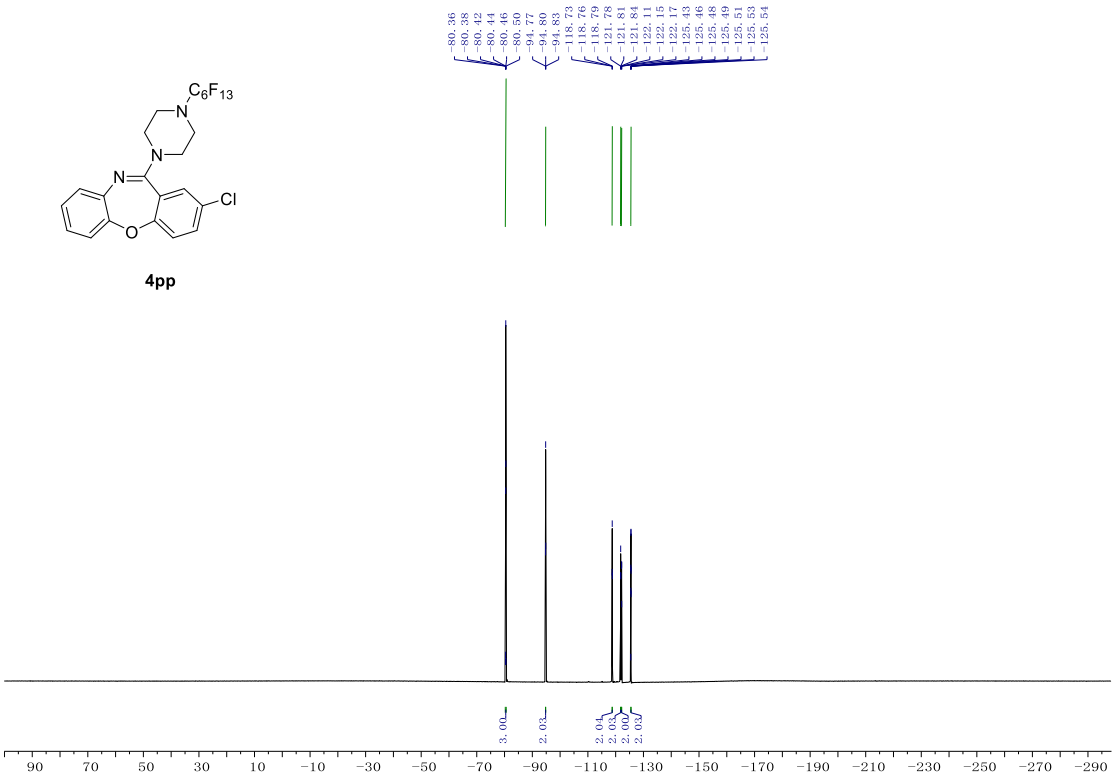
0.97
3.22
1.00
4.24
4.14
10.5 10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0 −0.5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C6F13
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N
N
Cl
O
4pp
3.00
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2.00
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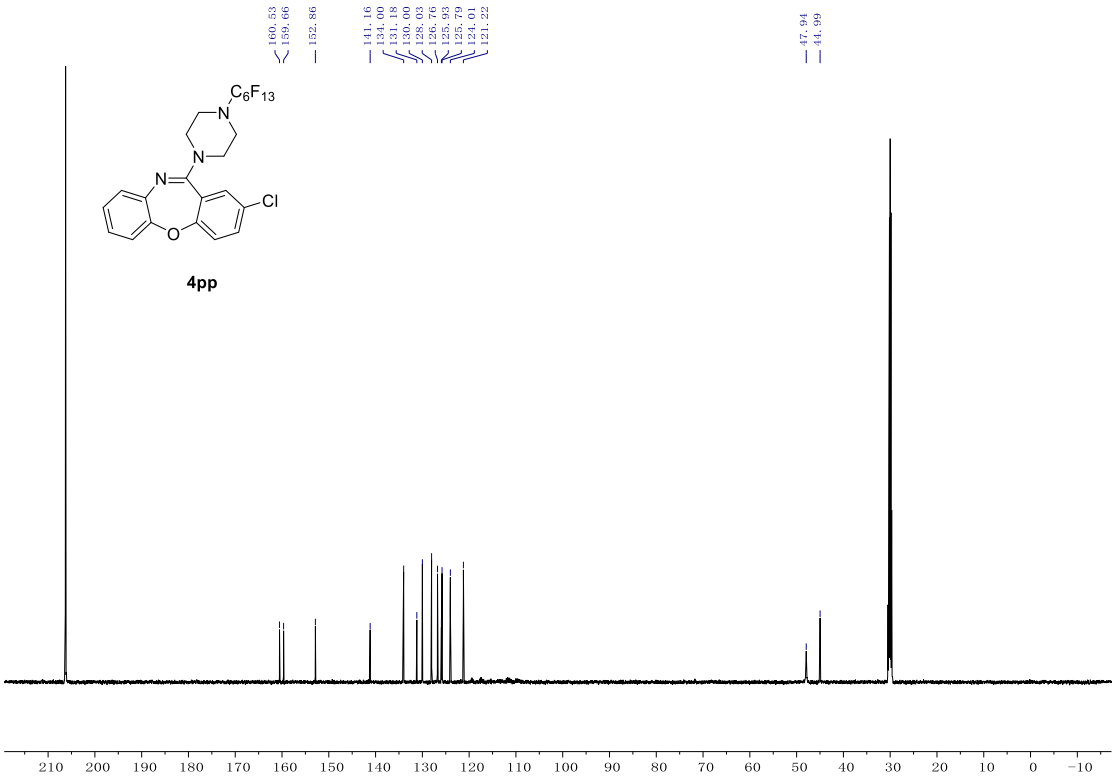
90 70 50 30 10 −10 −30 −50 −70 −90 −110 −130 −150 −170 −190 −210 −230 −250 −270 −290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134.00
131.18
130.00
128.03
126.76
125.93
125.79
124.01
121.22
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Cl
O
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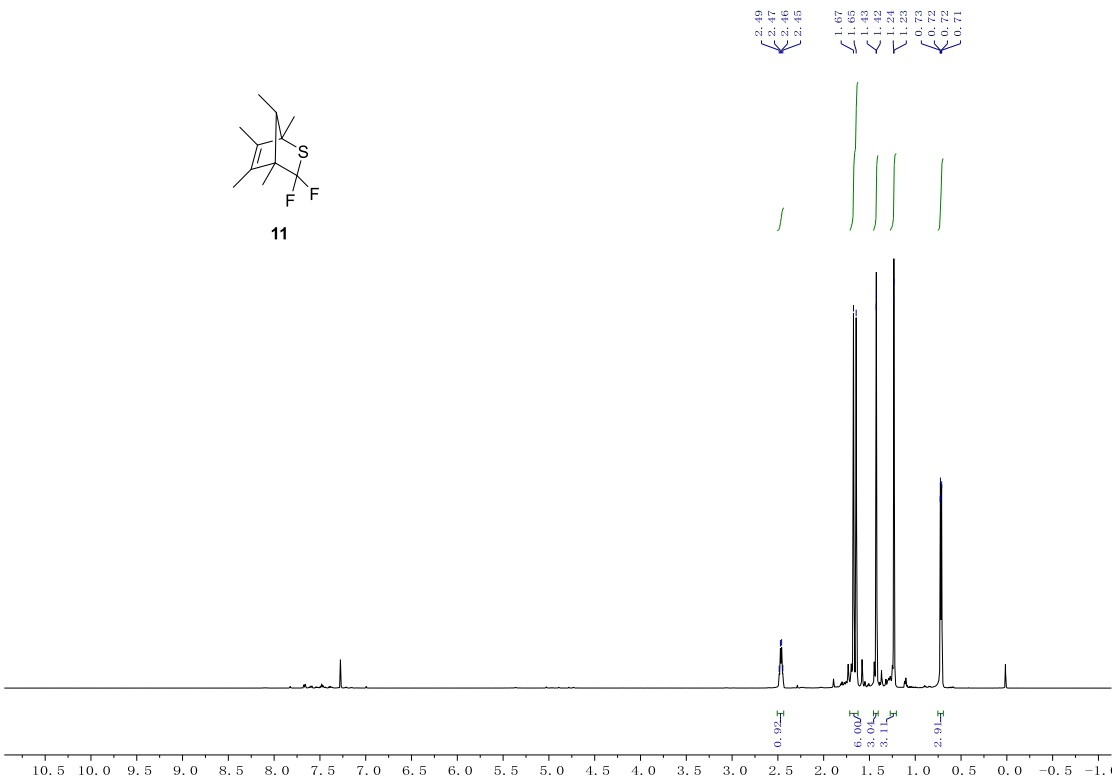
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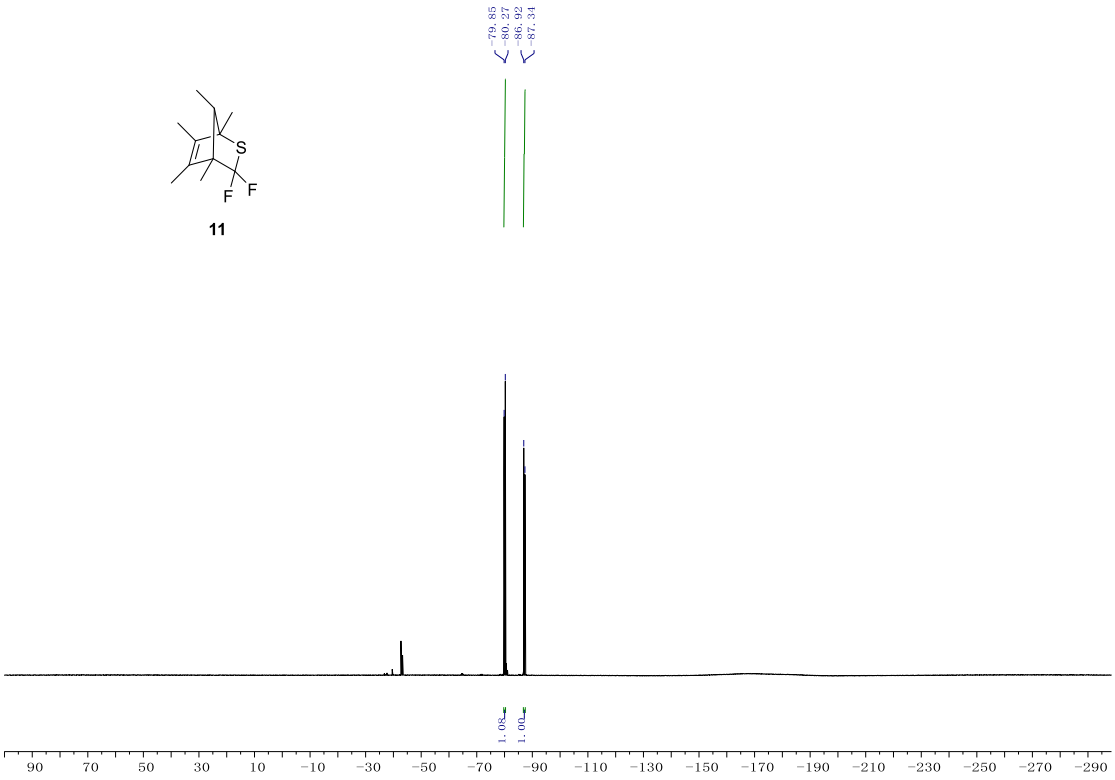
0.72
0.71
S
F
F
11
0.92
6.00
3.04
3.11
2.91
10.5 10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0 −0.5 −1.0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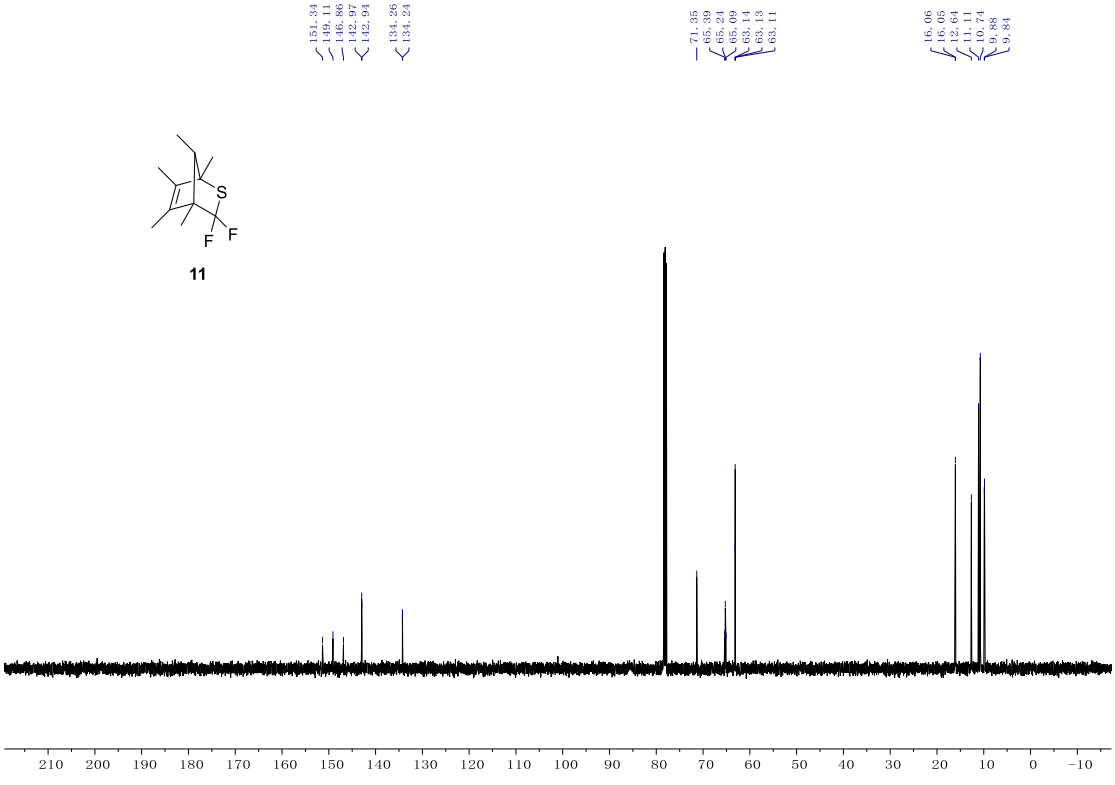
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63.13
63.11
16.06
16.05
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F
11
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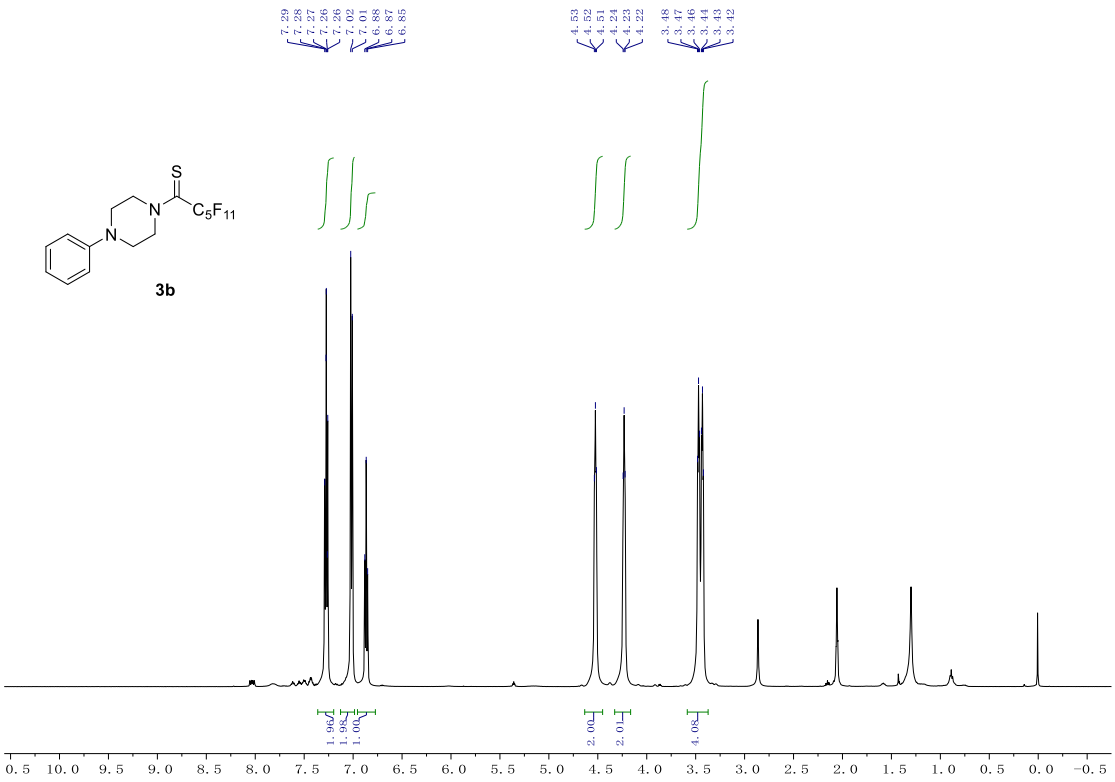
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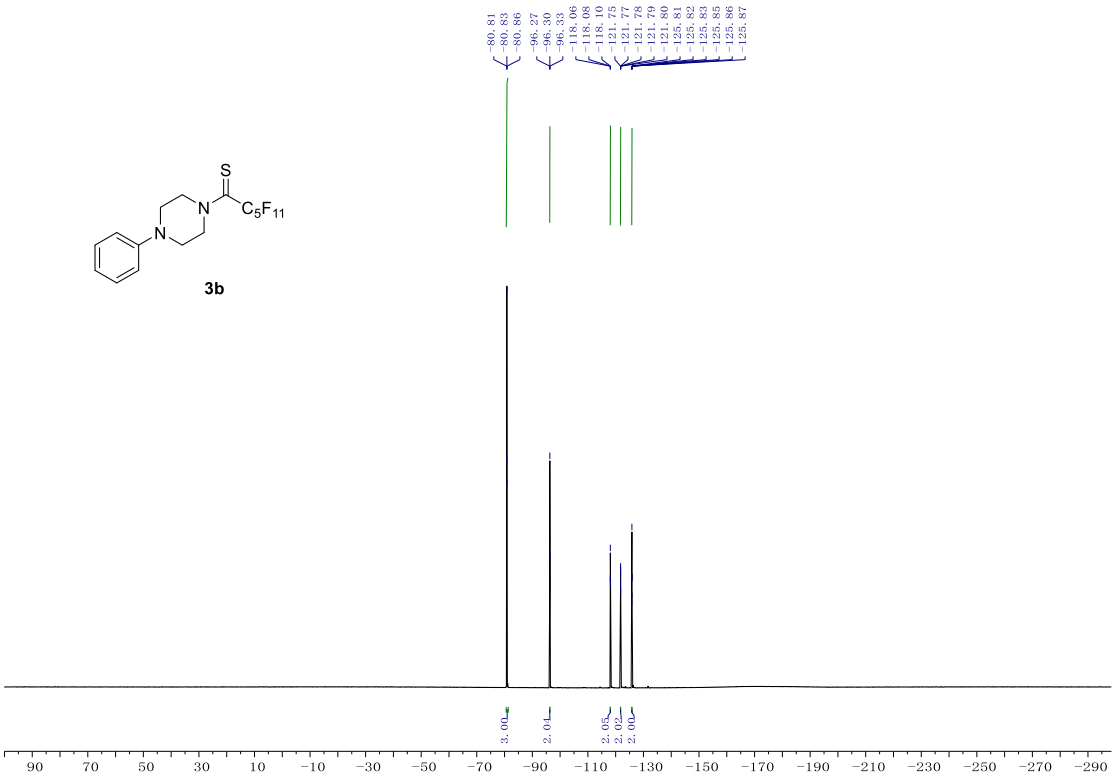
3.48
3.47
3.46
3.44
3.43
3.42
S
N
N
C5F11
3b
1.96
1.98
1.00
2.00
2.01
4.08
0.5 10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0 -0.5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S
N
N
C5F11
3b
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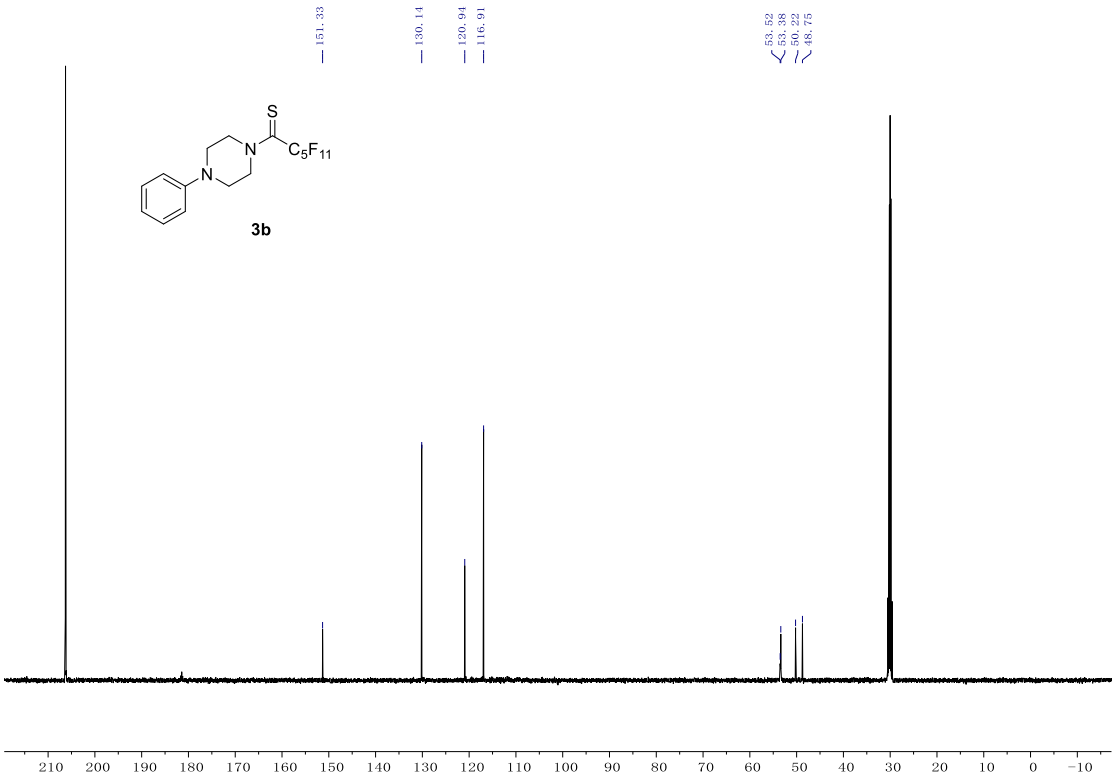
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N
N
C_5F_{11}
3b
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8. References

[1] (a) W. Y. Huang, B. N. Huang, G. -M. Hu. J. Fluorine Chem., **1983**, *23*, 193-204.
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