Supporting information

Silver-mediated oxidative trifluoromethylthiolation of cycloalkanols by C-C bond cleavage: regioselective approach to distally trifluoromethylthiolated ketones

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General

All manipulations were conducted with a standard *Schlenk* tube under N_2. All solvents and chemicals were used as received from the suppliers (*Alfa*, *Aldrich*, *Acros*, *TCI*).

Flash column chromatography was carried out on silica gel (200-300 mesh). Thin layer chromatography (TLC) was performed using silica gel 60 F_{254} plates.

^{1}H NMR spectra were recorded on a *Bruker AV-300* spectrometer or a *Bruker AV-500* spectrometer at room temperature. Chemical shifts (in ppm) were referenced to tetramethylsilane (δ = 0 ppm) in $CDCl_3$ as an internal standard. ^{13}C NMR spectra were obtained by the same NMR spectrometer and were calibrated with $CDCl_3$ (δ = 77.00 ppm). ^{19}F-NMR spectra were recorded on a *Bruker AV-300* spectrometer and using $CFCl_3$ as external standard. Data for ^{1}H NMR are reported as follows: chemical shifts (δ ppm), multiplicity (s = singlet, d = doublet, t = triplet, q = quartet, m = multiplet or unresolved, br s = broad singlet), coupling constant (Hz) and integration. Data for ^{13}C NMR are reported in terms of chemical shift and multiplicity where appropriate. Mass spectra were performed on an *Aglient 6530 Q-TOF* for HRMS. The yields were determined on a *METTLER TOLEDO ME 104* balance (accuracy: 0.1 mg).

Tertiary cyclopropanols **3a-3d** were prepared by the addition of Grignard reagent to the corresponding esters according to the reported method.[1] Tertiary cyclobutanols **1a-1n**, cyclopentanols **3e-3i**, and cyclohexanol **3j** were prepared by the addition of Grignard reagent to the corresponding ketones according to the reported method.[2]

General procedure for silver-mediated oxidative trifluoromethylthiolation of cycloalkanols：

Method A:

Cycloalkanol (0.25 mmol, 1.0 equiv), $AgSCF_3$ (0.625 mmol, 2.5 equiv), $K_2S_2O_8$ (0.75 mmol, 3.0 equiv), and pyridine (0.5 mmol, 2.0 equiv) were placed in a dry *Schlenk* tube under N_2. Acetonitrile (2.5 mL) was added and the reaction mixture was stirred at 60 ^oC for 12 h. The reaction was monitored with TLC. The solvent was removed under reduced pressure and the residue was purified by silica gel column chromatography.

Method B:

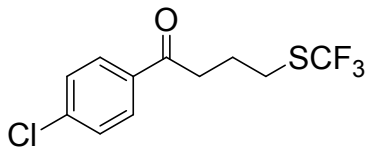
Cycloalkanol (0.25 mmol, 1.0 equiv), $AgSCF_3$ (0.625 mmol, 2.5 equiv), and $K_2S_2O_8$ (0.75 mmol, 3.0 equiv) were placed in a dry *Schlenk* tube under N_2. Acetonitrile (2.5 mL) was added and the reaction mixture was stirred at 60 ^oC for 12 h. The reaction was monitored with TLC. The solvent was removed under reduced pressure and the residue was purified by silica gel column chromatography.

Method C:

Cycloalkanol (0.25 mmol, 1.0 equiv), $AgSCF_3$ (0.625 mmol, 2.5 equiv), and $K_2S_2O_8$ (0.75 mmol, 3.0 equiv) were placed in a dry *Schlenk* tube under N_2. Acetonitrile (2.5 mL) was added and the reaction mixture was stirred at 80 ^oC for 6 h. The reaction was monitored with TLC. The solvent was removed under reduced pressure and the residue was purified by silica gel column chromatography.

Physical data of the compounds

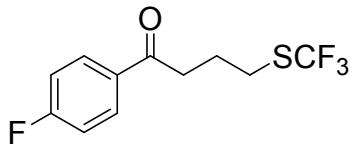
1-(4-Chlorophenyl)-4-((trifluoromethyl)thio)butan-1-one (2a)



According to **Method A** with 1-(4-chlorophenyl)cyclobutanol **1a** (45.5 mg, 0.25 mmol, 1.0 equiv), $AgSCF_3$ (130.6 mg, 0.625 mmol, 2.5 equiv), $K_2S_2O_8$ (202.7 mg,

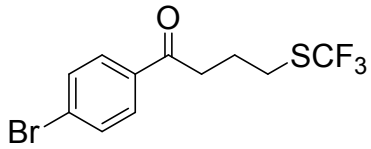
0.75 mmol, 3.0 equiv), and pyridine (40 μL, 0.5 mmol, 2.0 equiv). Flash column chromatography (petroleum ether/Et_2O = 50/1, v/v) gave the desired product **2a** as colourless oil (49.5 mg, 70%). **^{1}H NMR** (500 MHz, $CDCl_3$) δ 7.92-7.87 (m, 2H), 7.47-7.41 (m, 2H), 3.11 (t, *J* = 6.8 Hz, 2H), 3.02 (t, *J* = 7.0 Hz, 2H), 2.18-2.13 (m, 2H); **^{13}C NMR** (125 MHz, $CDCl_3$) δ 197.3, 139.8, 135.0, 131.0 (q, J_{C-F} = 304.1 Hz), 129.4, 129.0, 36.3, 29.3 (q, J_{C-F} = 2.0 Hz), 23.6; **^{19}F NMR** (282 MHz, $CDCl_3$) δ -39.87; **HRMS** (ESI) calculated for $C_{11}H_{11}ClF_3OS$ $[M+H]^+$ m/z 283.0166, found 283.0159.

1-(4-Fluorophenyl)-4-((trifluoromethyl)thio)butan-1-one (2b)



According to **Method A** with 1-(4-fluorophenyl)cyclobutanol **1b** (41.5 mg, 0.25 mmol, 1.0 equiv), $AgSCF_3$ (130.6 mg, 0.625 mmol, 2.5 equiv), $K_2S_2O_8$ (202.7 mg, 0.75 mmol, 3.0 equiv), and pyridine (40 μL, 0.5 mmol, 2.0 equiv). Flash column chromatography (petroleum ether/Et_2O = 50/1, v/v) gave the desired product **2b** as colourless oil (41.2 mg, 62%). **^{1}H NMR** (500 MHz, $CDCl_3$) δ 8.02-7.95 (m, 2H), 7.17-7.10 (m, 2H), 3.11 (t, *J* = 7.0 Hz, 2H), 3.02 (t, *J* = 7.0 Hz, 2H), 2.19-2.13 (m, 2H); **^{13}C NMR** (75 MHz, $CDCl_3$) δ 197.0, 165.9 (d, *J* = 253.3 Hz), 133.1 (d, *J* = 3.3 Hz), 131.0 (q, *J* = 304.1 Hz), 130.6 (d, *J* = 9.4 Hz), 115.8 (d, *J* = 22.0 Hz), 36.2, 29.4 (q, *J* = 2.0 Hz), 23.7; **^{19}F NMR** (282 MHz, $CDCl_3$) δ -39.89, -103.83; **HRMS** (ESI) calculated for $C_{11}H_{11}F_4OS$ $[M+H]^+$ m/z 267.0461, found 267.0464.

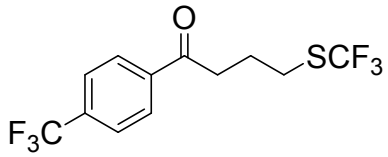
1-(4-Bromophenyl)-4-((trifluoromethyl)thio)butan-1-one (2c)



According to **Method A** with 1-(4-bromophenyl)cyclobutanol **1c** (56.5 mg, 0.25 mmol, 1.0 equiv), $AgSCF_3$ (130.6 mg, 0.625 mmol, 2.5 equiv), $K_2S_2O_8$ (202.7 mg, 0.75 mmol, 3.0 equiv), and pyridine (40 μL, 0.5 mmol, 2.0 equiv). Flash column chromatography (petroleum ether/Et_2O = 100/1, v/v) gave the desired product **2c** as colourless oil (50.3 mg, 62%). **^{1}H NMR** (300 MHz, $CDCl_3$) δ 7.87-7.79 (m, 2H), 7.67-7.59 (m, 2H), 3.10 (t, *J* = 6.8 Hz, 2H), 3.02 (t, *J* = 7.1 Hz, 2H), 2.20-2.11 (m, 2H); **^{13}C NMR** (75 MHz, $CDCl_3$) δ 197.5, 135.4, 132.0, 131.0 (q, *J* = 304.2 Hz),

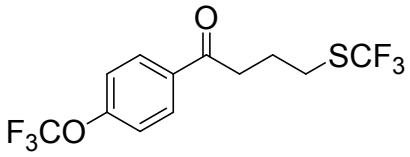
129.5,128.5, 36.3, 29.3 (q, J = 2.3 Hz), 23.6; **^{19}F NMR** (282 MHz, $CDCl_3$) δ -39.77; **HRMS** (ESI) calculated for $C_{11}H_{11}BrF_3OS$ $[M+H]^+$ m/z 326.9661, found 326.9656.

1-(4-(Trifluoromethyl)phenyl)-4-((trifluoromethyl)thio)butan-1-one (2d)



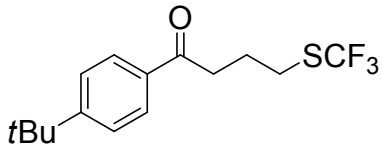
According to **Method A** with 1-(4-(trifluoromethyl)phenyl)cyclobutanol **1d** (54.0 mg, 0.25 mmol, 1.0 equiv), $AgSCF_3$ (130.6 mg, 0.625 mmol, 2.5 equiv), $K_2S_2O_8$ (202.7 mg, 0.75 mmol, 3.0 equiv), and pyridine (40 μL, 0.5 mmol, 2.0 equiv). Flash column chromatography (petroleum ether/Et_2O = 100/1, v/v) gave the desired product **2d** as colourless oil (52.1 mg, 66%). **^{1}H NMR** (300 MHz, $CDCl_3$) δ 8.07 (d, J = 8.1 Hz, 2H), 7.74 (d, J = 8.1 Hz, 2H), 3.17 (t, J = 6.9 Hz, 2H), 3.04 (t, J = 7.2 Hz, 2H), 2.23-2.14 (m, 2H); **^{13}C NMR** (75 MHz, $CDCl_3$) δ 197.6, 139.3, 134.7 (q, J = 32.6 Hz), 131.0 (q, J = 304.1 Hz), 128.3, 125.8 (q, J = 3.7 Hz), 123.3 (q, J = 271.2 Hz), 36.6, 29.3 (q, J = 2.2 Hz), 23.5; **^{19}F NMR** (282 MHz, $CDCl_3$) δ -39.87, -62.12; **HRMS** (ESI) calculated for $C_{12}H_{11}F_6OS$ $[M+H]^+$ m/z 317.0429, found 317.0428.

1-(4-(Trifluoromethoxy)phenyl)-4-((trifluoromethyl)thio)butan-1-one (2e)



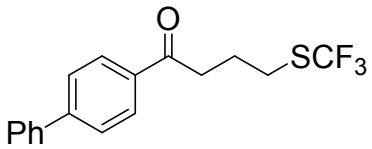
According to **Method A** with 1-(4-(trifluoromethoxy)phenyl)cyclobutanol **1e** (58.0 mg, 0.25 mmol, 1.0 equiv), $AgSCF_3$ (130.6 mg, 0.625 mmol, 2.5 equiv), $K_2S_2O_8$ (202.7 mg, 0.75 mmol, 3.0 equiv), and pyridine (40 μL, 0.5 mmol, 2.0 equiv). Flash column chromatography (petroleum ether/Et_2O = 100/1, v/v) gave the desired product **2e** as colourless oil (57.2 mg, 69%). **^{1}H NMR** (500 MHz, $CDCl_3$) δ 8.04-7.98 (m, 2H), 7.30 (d, J = 8.0 Hz, 2H), 3.13 (t, J = 6.8 Hz, 2H), 3.03 (t, J = 7.3 Hz, 2H), 2.19-2.14 (m, 2H); **^{13}C NMR** (75 MHz, $CDCl_3$) δ 197.0, 152.8 (q, J = 1.9 Hz), 134.9, 131.0 (q, J = 304.2 Hz), 130.0, 120.5, 120.3 (q, J = 257.4 Hz), 36.3, 29.3 (q, J = 1.7 Hz), 23.6; **^{19}F NMR** (282 MHz, $CDCl_3$) δ -39.91, -56.60; **HRMS** (ESI) calculated for $C_{12}H_{11}F_6O_2S$ $[M+H]^+$ m/z 333.0378, found 333.0380.

1-(4-(*tert*-Butyl)phenyl)-4-((trifluoromethyl)thio)butan-1-one (2f)



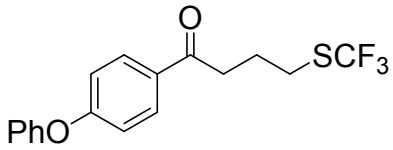
According to **Method A** with 1-(4-(*tert*-butyl)phenyl)cyclobutanol **1f** (51.0 mg, 0.25 mmol, 1.0 equiv), $AgSCF_3$ (130.6 mg, 0.625 mmol, 2.5 equiv), $K_2S_2O_8$ (202.7 mg, 0.75 mmol, 3.0 equiv), and pyridine (40 μL, 0.5 mmol, 2.0 equiv). Flash column chromatography (petroleum ether/Et_2O = 100/1, v/v) gave the desired product **2f** as colourless oil (58.2 mg, 76%). **^{1}H NMR** (300 MHz, $CDCl_3$) δ 7.95-7.86 (m, 2H), 7.54-7.45 (m, 2H), 3.12 (t, *J* = 6.9 Hz, 2H), 3.02 (t, *J* = 7.1 Hz, 2H), 2.20-2.11(m, 2H), 1.35 (s, 9H); **^{13}C NMR** (75 MHz, $CDCl_3$) δ 198.3, 157.1, 134.1, 131.1 (q, *J* = 304.2 Hz), 128.0, 125.6, 36.3, 35.1, 31.0, 29.5 (q, *J* = 2.3 Hz), 23.8; **^{19}F NMR** (282 MHz, $CDCl_3$) δ -39.87; **HRMS** (ESI) calculated for $C_{15}H_{20}F_3OS$ $[M+H]^+$ m/z 305.1181, found 305.1190.

1-([1,1'-Biphenyl]-4-yl)-4-((trifluoromethyl)thio)butan-1-one (2g)



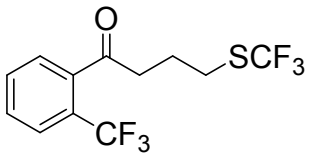
According to **Method A** with 1-([1,1'-biphenyl]-4-yl)cyclobutanol **1g** (56.0 mg, 0.25 mmol, 1.0 equiv), $AgSCF_3$ (130.6 mg, 0.625 mmol, 2.5 equiv), $K_2S_2O_8$ (202.7 mg, 0.75 mmol, 3.0 equiv), and pyridine (40 μL, 0.5 mmol, 2.0 equiv). Flash column chromatography (petroleum ether/Et_2O = 100/1, v/v) gave the desired product **2g** as white solid (55.1 mg, 68%). **^{1}H NMR** (500 MHz, $CDCl_3$) δ 8.05-7.99 (m, 2H), 7.71-7.65 (m, 2H), 7.64-7.59 (m, 2H)，7.49-7.43 (m, 2H), 7.42-7.37 (m, 1H), 3.16 (t, *J* = 7.0 Hz, 2H), 3.04 (t, *J* = 7.0 Hz, 2H), 2.21-2.15 (m, 2H); **^{13}C NMR** (75 MHz, $CDCl_3$) δ 198.1, 146.0, 139.8, 135.4, 131.0 (q, *J* = 305.5 Hz), 129.0, 128.6, 128.3, 127.3，127.2，36.4，29.4 (q, *J* = 2.3 Hz), 23.8; **^{19}F NMR** (282 MHz, $CDCl_3$) δ -39.82; **HRMS** (ESI) calculated for $C_{17}H_{16}F_3OS$ $[M+H]^+$ m/z 325.0868, found 325.0870.

1-(4-Phenoxyphenyl)-4-((trifluoromethyl)thio)butan-1-one (2h)



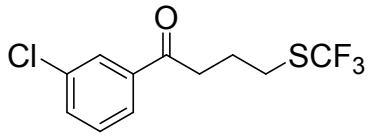
According to **Method A** with 1-(4-phenoxyphenyl)cyclobutanol **1h** (60.0 mg, 0.25 mmol, 1.0 equiv), $AgSCF_3$ (130.6 mg, 0.625 mmol, 2.5 equiv), $K_2S_2O_8$ (202.7 mg, 0.75 mmol, 3.0 equiv), and pyridine (40 μL, 0.5 mmol, 2.0 equiv). Flash column chromatography (petroleum ether/Et_2O = 100/1, v/v) gave the desired product **2h** as colourless oil (49.7 mg, 58%). **^{1}H NMR** (300 MHz, $CDCl_3$) δ 7.97-7.89 (m, 2H), 7.43-7.34 (m, 2H), 7.23-7.16 (m, 1H), 7.10-7.04 (m, 2H), 7.03-6.97 (m, 2H)，3.09（t，*J* = 6.9 Hz, 2H)，3.01 (t, *J* = 7.2 Hz, 2H), 2.19-2.10 (m, 2H); **^{13}C NMR** (125 MHz, $CDCl_3$) δ 197.1, 162.2, 155.5, 131.4, 131.0 (q, *J* = 304.4 Hz), 130.2, 130.1, 124.7, 120.2, 117.4, 36.1, 29.4, 23.8; **^{19}F NMR** (282 MHz, $CDCl_3$) δ -39.85; **HRMS** (ESI) calculated for $C_{17}H_{16}F_3O_2S$ $[M+H]^+$ m/z 341.0818, found 341.0827.

1-(2-(Trifluoromethyl)phenyl)-4-((trifluoromethyl)thio)butan-1-one (2i)



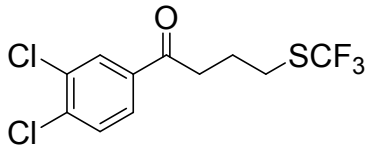
According to **Method A** with 1-(2-(trifluoromethyl)phenyl)cyclobutanol **1i** (54.0 mg, 0.25 mmol, 1.0 equiv), $AgSCF_3$ (130.6 mg, 0.625 mmol, 2.5 equiv), $K_2S_2O_8$ (202.7 mg, 0.75 mmol, 3.0 equiv), and pyridine (40 μL, 0.5 mmol, 2.0 equiv). Flash column chromatography (petroleum ether/Et_2O = 50/1, v/v) gave the desired product **2i** as white solid (49.0 mg, 62%). **^{1}H NMR** (300 MHz, $CDCl_3$) δ 7.72 (d, *J* = 7.2 Hz, 1H), 7.65-7.54 (m, 2H), 7.42 (d, *J* = 7.2 Hz, 1H), 3.04-2.99 (m, 4H), 2.19-2.12 (m, 2H); **^{13}C NMR** (75 MHz, $CDCl_3$) δ 202.8, 140.0 (q, *J* = 2.2 Hz), 131.9, 131.0 (q, *J* = 303.8 Hz), 130.2, 126.9-126.7 (m), 123.6 (q, *J* = 272.0 Hz), 40.9, 29.0 (q, *J* = 2.2 Hz), 23.4; **^{19}F NMR** (282 MHz, $CDCl_3$) δ -39.88, -57.00; **HRMS** (ESI) calculated for $C_{12}H_{11}F_6OS$ $[M+H]^+$ m/z 317.0429, found 317.0434.

1-(3-Chlorophenyl)-4-((trifluoromethyl)thio)butan-1-one (2j)



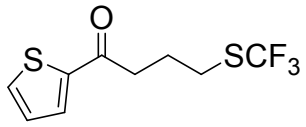
According to **Method A** with 1-(3-chlorophenyl)cyclobutanol **1j** (45.5 mg, 0.25 mmol, 1.0 equiv), $AgSCF_3$ (130.6 mg, 0.625 mmol, 2.5 equiv), $K_2S_2O_8$ (202.7 mg, 0.75 mmol, 3.0 equiv), and pyridine (40 μL, 0.5 mmol, 2.0 equiv). Flash column chromatography (petroleum ether/Et_2O = 100/1, v/v) gave the desired product **2j** as colourless oil (50.1 mg, 71%). **^{1}H NMR** (500 MHz, $CDCl_3$) δ 7.92 (s, 1H), 7.83 (d, *J* = 7.5 Hz, 1H), 7.55 (d, *J* = 8.0 Hz, 1H), 7.45-7.38 (m, 1H), 3.12 (t, *J* = 6.8 Hz, 2H), 3.02 (t, *J* = 7.0 Hz, 2H), 2.19-2.13 (m, 2H); **^{13}C NMR** (125 MHz, $CDCl_3$) δ 197.3, 138.2, 135.1, 133.2, 131.0 (q, *J* = 304.4 Hz), 130.0, 128.1, 126.0, 36.5, 29.3, 23.6; **^{19}F NMR** (282 MHz, $CDCl_3$) δ -39.86; **HRMS** (ESI) calculated for $C_{11}H_{11}ClF_3OS$ $[M+H]^+$ m/z 283.0166, found 283.0168.

1-(3,4-Dichlorophenyl)-4-((trifluoromethyl)thio)butan-1-one (2k)



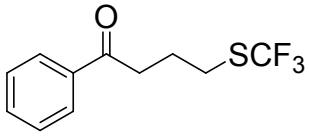
According to **Method A** with 1-(3,4-dichlorophenyl)cyclobutanol **1k** (54.0 mg, 0.25 mmol, 1.0 equiv), $AgSCF_3$ (130.6 mg, 0.625 mmol, 2.5 equiv), $K_2S_2O_8$ (202.7 mg, 0.75 mmol, 3.0 equiv), and pyridine (40 μL, 0.5 mmol, 2.0 equiv). Flash column chromatography (petroleum ether/Et_2O = 100/1, v/v) gave the desired product **2k** as colourless oil (51.2 mg, 65%). **^{1}H NMR** (300 MHz, $CDCl_3$) δ 8.03 (d, *J* = 1.8 Hz, 1H), 7.78 (dd, *J* = 8.4, 2.1 Hz, 1H), 7.56 (d, *J* = 8.4 Hz, 1H), 3.10 (t, *J* = 6.9 Hz, 2H), 3.02 (t, *J* = 7.1 Hz, 2H), 2.20-2.11 (m, 2H); **^{13}C NMR** (75 MHz, $CDCl_3$) δ 196.3, 137.9, 136.2, 133.5, 131.0 (q, *J* = 304.4 Hz), 130.8, 130.0, 127.0, 36.4, 29.3 (q, *J* = 2.2 Hz), 23.5; **^{19}F NMR** (282 MHz, $CDCl_3$) δ -39.84; **HRMS** (ESI) calculated for $C_{11}H_{10}Cl_2F_3OS$ $[M+H]^+$ m/z 316.9776, found 316.9778.

1-(Thiophen-2-yl)-4-((trifluoromethyl)thio)butan-1-one (2l)



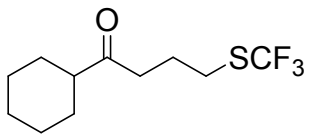
According to **Method A** with 1-(thiophen-2-yl)cyclobutanol **1l** (38.5 mg, 0.25 mmol, 1.0 equiv), $AgSCF_3$ (130.6 mg, 0.625 mmol, 2.5 equiv), $K_2S_2O_8$ (202.7 mg, 0.75 mmol, 3.0 equiv), and pyridine (40 μL, 0.5 mmol, 2.0 equiv). Flash column chromatography (petroleum ether/Et_2O = 50/1, v/v) gave the desired product **2l** as colourless oil (38.4 mg, 60%). **^{1}H NMR** (300 MHz, $CDCl_3$) δ 7.73 (d, *J* = 3.9 Hz, 1H), 7.65 (d, *J* = 4.8 Hz, 1H), 7.16-7.13 (m, 1H), 3.08 (t, *J* = 6.9 Hz, 2H), 3.02 (t, *J* = 7.2 Hz, 2H), 2.21-2.11 (m, 2H); **^{13}C NMR** (125 MHz, $CDCl_3$) δ 191.5, 143.9, 133.8, 131.9, 131.0 (q, *J* = 304.1 Hz), 128.2, 37.1, 29.3, 24.0; **^{19}F NMR** (282 MHz, $CDCl_3$) δ -39.85; **HRMS** (ESI) calculated for $C_9H_{10}F_3OS_2$ $[M+H]^+$ m/z 255.0120, found 255.0123.

1-Phenyl-4-((trifluoromethyl)thio)butan-1-one (2m)



According to **Method A** with 1-phenylcyclobutanol **1m** (37.0 mg, 0.25 mmol, 1.0 equiv), $AgSCF_3$ (130.6 mg, 0.625 mmol, 2.5 equiv), $K_2S_2O_8$ (202.7 mg, 0.75 mmol, 3.0 equiv), and pyridine (40 μL, 0.5 mmol, 2.0 equiv). Flash column chromatography (petroleum ether/Et_2O = 50/1, v/v) gave the desired product **2m** as colourless oil (40.2 mg, 65%). **^{1}H NMR** (300 MHz, $CDCl_3$) δ 7.96 (d, *J* = 7.2 Hz, 2H), 7.62-7.55 (m, 1H), 7.52-7.42 (m, 2H), 3.14 (t, *J* = 6.9 Hz, 2H), 3.03 (t, *J* = 7.1 Hz, 2H), 2.21-2.12 (m, 2H); **^{13}C NMR** (125 MHz, $CDCl_3$) δ 198.6, 136.7, 133.3, 131.1 (q, *J* = 304.4 Hz), 128.7, 128.0, 36.4, 29.4, 23.7; **^{19}F NMR** (282 MHz, $CDCl_3$) δ -39.87; **HRMS** (ESI) calculated for $C_{11}H_{12}F_3OS$ $[M+H]^+$ m/z 249.0555, found 249.0563.

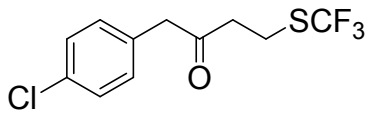
1-Cyclohexyl-4-((trifluoromethyl)thio)butan-1-one (2n)



According to **Method A** with 1-cyclohexylcyclobutanol **1n** (38.5 mg, 0.25 mmol, 1.0 equiv), $AgSCF_3$ (130.6 mg, 0.625 mmol, 2.5 equiv), $K_2S_2O_8$ (202.7 mg, 0.75 mmol, 3.0 equiv), and pyridine (40 μL, 0.5 mmol, 2.0 equiv). Flash column chromatography (petroleum ether/Et_2O = 100/1, v/v) gave the desired product **2n** as colourless oil (25.3 mg, 40%). **^{1}H NMR** (500 MHz, $CDCl_3$) δ 2.91 (d, *J* = 7.3 Hz, 2H), 2.59 (d, *J* = 6.8 Hz, 2H), 2.36-2.30 (m, 1H), 1.99-1.93 (m, 2H), 1.84-1.77 (m, 4H), 1.69-1.66 (m,

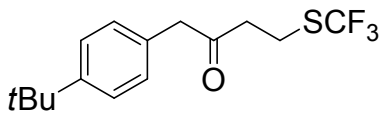
1H), 1.38-1.19 (m, 5H); **^{13}C NMR** (125 MHz, $CDCl_3$) δ 212.5, 131.0 (q, *J* = 304.4 Hz), 50.9, 38.2, 29.3, 28.5, 25.8, 25.6, 23.2; **^{19}F NMR** (282 MHz, $CDCl_3$) δ -41.06; **HRMS** (ESI) calculated for $C_{11}H_{18}F_3OS$ $[M+H]^+$ m/z 255.1030, found 255.1026.

1-(4-Chlorophenyl)-4-((trifluoromethyl)thio)butan-2-one (4a)



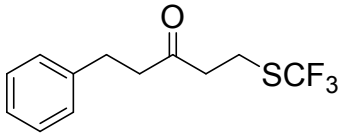
According to **Method B** with 1-(4-chlorobenzyl)cyclopropanol **3a** (45.5 mg, 0.25 mmol, 1.0 equiv), $AgSCF_3$ (130.6 mg, 0.625 mmol, 2.5 equiv), and $K_2S_2O_8$ (202.7 mg, 0.75 mmol, 3.0 equiv). Flash column chromatography (petroleum ether/Et_2O = 50/1, v/v) gave the desired product **4a** as colourless oil (31.5 mg, 45%). **^{1}H NMR** (500 MHz, $CDCl_3$) δ 7.34-7.29 (m, 2H), 7.15-7.10 (m, 2H), 3.69 (s, 2H), 3.04 (t, *J* = 6.8 Hz, 2H), 2.89 (t, *J* = 7.0 Hz, 2H); **^{13}C NMR** (125 MHz, $CDCl_3$) δ 204.5, 133.4, 131.8, 131.1 (q, *J* = 304.7 Hz), 130.7, 129.0, 49.2, 42.0, 23.4; **^{19}F NMR** (282 MHz, $CDCl_3$) δ -40.43; **HRMS** (ESI) calculated for $C_{11}H_{10}ClF_3NaOS$ $[M+Na]^+$ m/z 304.9991, found 304.9995.

1-(4-(*tert*-Butyl)phenyl)-4-((trifluoromethyl)thio)butan-2-one (4b)



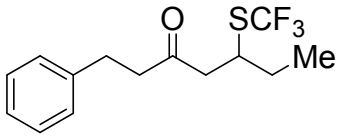
According to **Method B** with 1-(4-(*tert*-butyl)benzyl)cyclopropanol **3b** (51.0 mg, 0.25 mmol, 1.0 equiv), $AgSCF_3$ (130.6 mg, 0.625 mmol, 2.5 equiv), and $K_2S_2O_8$ (202.7 mg, 0.75 mmol, 3.0 equiv). Flash column chromatography (petroleum ether/Et_2O = 100/1, v/v) gave the desired product **4b** as colourless oil (33.4 mg, 44%). **^{1}H NMR** (500 MHz, $CDCl_3$) δ 7.38-7.33 (m, 2H), 7.15-7.10 (m, 2H), 3.68 (s, 2H), 3.03 (t, *J* = 6.8 Hz, 2H), 2.87 (t, *J* = 6.8 Hz, 2H),1.31 (s, 9H); **^{13}C NMR** (125 MHz, $CDCl_3$) δ 205.5, 150.3, 130.3, 131.1 (q, *J* = 304.4 Hz), 129.0, 125.8, 49.7, 41.7, 34.5, 31.3, 23.5; **^{19}F NMR** (282 MHz, $CDCl_3$) δ -40.48; **HRMS** (ESI) calculated for $C_{15}H_{19}F_3NaOS$ $[M+Na]^+$ m/z 327.1006, found 327.1006.

1-Phenyl-5-((trifluoromethyl)thio)pentan-3-one (4c)[3]



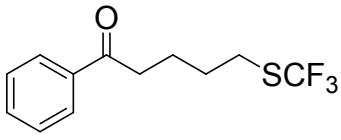
According to **Method B** with 1-phenethylcyclopropanol **3c** (40.5 mg, 0.25 mmol, 1.0 equiv), $AgSCF_3$ (130.6 mg, 0.625 mmol, 2.5 equiv), and $K_2S_2O_8$ (202.7 mg, 0.75 mmol, 3.0 equiv). Flash column chromatography (petroleum ether/Et_2O = 80/1, v/v) gave the desired product **4c** as colourless oil (23.2 mg, 35%). **^{1}H NMR** (500 MHz, $CDCl_3$) δ 7.32-7.24 (m, 2H), 7.21-7.16 (m, 3H), 3.05 (t, *J* = 6.8 Hz, 2H), 2.92 (t, *J* = 7.5 Hz, 2H), 2.81 (t, *J* = 6.5 Hz, 2H), 2.76 (t, *J* = 7.5 Hz, 2H); **^{13}C NMR** (125 MHz, $CDCl_3$) δ 206.7, 140.5, 131.1 (q, *J* = 304.4 Hz), 128.6, 128.3, 126.3, 44.3, 42.8, 29.6, 23.3 (q, *J* = 1.9 Hz); **^{19}F NMR** (282 MHz, $CDCl_3$) δ -40.43; **HRMS** (ESI) calculated for $C_{12}H_{13}F_3NaOS$ $[M+Na]^+$ m/z 285.0537, found 285.0537.

1-Phenyl-5-((trifluoromethyl)thio)heptan-3-one (4d)



According to **Method C** with 2-ethyl-1-phenethylcyclopropanol **3d** (47.5 mg, 0.25 mmol, 1.0 equiv), $AgSCF_3$ (130.6 mg, 0.625 mmol, 2.5 equiv), and $K_2S_2O_8$ (202.7 mg, 0.75 mmol, 3.0 equiv). Flash column chromatography (petroleum ether/Et_2O = 100/1, v/v) gave the desired product **4d** as colourless oil (25.2mg, 35%). **^{1}H NMR** (500 MHz, $CDCl_3$) δ 7.32-7.27 (m, 2H), 7.24-7.17 (m, 3H), 3.56-3.51 (m, 1H), 2.94-2.85 (m, 3H), 2.80-2.74 (m, 3H), 1.77-1.64 (m, 2H), 1.01 (t, *J* = 7.3Hz, 3H); **^{13}C NMR** (125 MHz, $CDCl_3$) δ 206.4, 140.6, 131.1 (q, *J* = 304.7 Hz), 128.5, 128.3, 126.2, 48.2, 44.7, 42.4, 29.6, 27.9, 11.1; **^{19}F NMR** (282 MHz, $CDCl_3$) δ -38.22; **HRMS** (ESI) calculated for $C_{14}H_{18}F_3OS$ $[M+H]^+$ m/z 291.1031, found 291.1024.

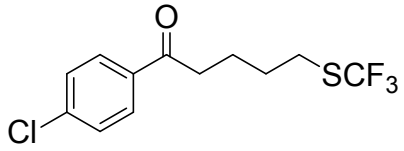
1-Phenyl-5-((trifluoromethyl)thio)pentan-1-one (4e)



According to **Method A** with 1-phenylcyclopentanol **3e** (40.5 mg, 0.25 mmol, 1.0 equiv), $AgSCF_3$ (130.6 mg, 0.625 mmol, 2.5 equiv), $K_2S_2O_8$ (202.7 mg, 0.75 mmol, 3.0 equiv), and pyridine (40 μL, 0.5 mmol, 2.0 equiv). Flash column chromatography (petroleum ether/Et_2O = 80/1, v/v) gave the desired product **4e** as colourless oil (33.4 mg, 51%). **^{1}H NMR** (500 MHz, $CDCl_3$) δ 7.97-7.93 (m, 2H), 7.59-7.54 (m, 1H), 7.49-7.44 (m, 2H), 3.01 (t, *J* = 7.0 Hz, 2H), 2.93 (t, *J* = 7.3 Hz, 2H), 1.90-1.84 (m, 2H), 1.83-1.78 (m, 2H); **^{13}C NMR** (125 MHz, $CDCl_3$) δ 199.4, 136.9, 133.1, 131.1 (q,

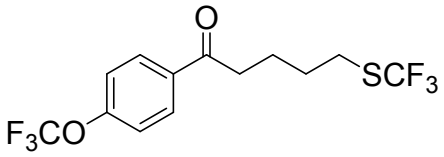
J = 304.1 Hz), 128.6, 128.0, 37.6, 29.7, 29.1, 22.9; **^{19}F NMR** (282 MHz, $CDCl_3$) δ -40.07; **HRMS** (ESI) calculated for $C_{12}H_{13}F_3NaOS$ $[M+Na]^+$ m/z 285.0537, found 285.0538.

1-(4-Chlorophenyl)-5-((trifluoromethyl)thio)pentan-1-one (4f)



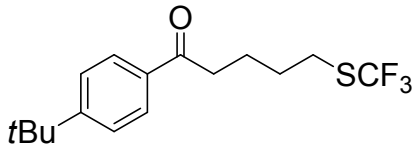
According to **Method A** with 1-phenylcyclopentanol **3f** (49.0 mg, 0.25 mmol, 1.0 equiv), $AgSCF_3$ (130.6 mg, 0.625 mmol, 2.5 equiv), $K_2S_2O_8$ (202.7 mg, 0.75 mmol, 3.0 equiv), and pyridine (40 μL, 0.5 mmol, 2.0 equiv). Flash column chromatography (petroleum ether/Et_2O = 100/1, v/v) gave the desired product **4f** as colourless oil (31.2 mg, 42%). **^{1}H NMR** (500 MHz, $CDCl_3$) δ 7.93-7.86 (m, 2H), 7.48-7.41 (m, 2H), 2.98 (t, *J* = 7.0 Hz, 2H), 2.93 (t, *J* = 7.0 Hz, 2H), 1.89-1.84 (m, 2H); 1.82-1.78 (m, 2H); **^{13}C NMR** (125 MHz, $CDCl_3$) δ 198.0, 139.6, 135.1, 131.1 (q, *J* = 304.1 Hz), 129.4, 128.9, 37.6, 29.7, 29.0, 22.8; **^{19}F NMR** (282 MHz, $CDCl_3$) δ -40.06; **HRMS** (ESI) calculated for $C_{12}H_{13}ClF_3OS$ $[M+H]^+$ m/z 297.0328, found 297.0327.

1-(4-(Trifluoromethoxy)phenyl)-5-((trifluoromethyl)thio)pentan-1-one (4g)



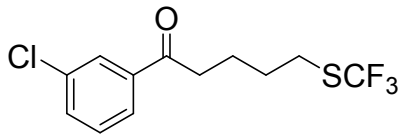
According to **Method A** with 1-(4-(trifluoromethoxy)phenyl)cyclopentanol **3g** (61.5 mg, 0.25 mmol, 1.0 equiv), $AgSCF_3$ (130.6 mg, 0.625 mmol, 2.5 equiv), $K_2S_2O_8$ (202.7 mg, 0.75 mmol, 3.0 equiv), and pyridine (40 μL, 0.5 mmol, 2.0 equiv). Flash column chromatography (petroleum ether/Et_2O = 100/1, v/v) gave the desired product **4g** as colourless oil (49.4 mg, 57%). **^{1}H NMR** (500 MHz, $CDCl_3$) δ 8.03-7.97 (m, 2H), 7.29 (d, *J* = 8.5 Hz, 2H), 3.00 (t, *J* = 7.0 Hz, 2H), 2.94 (t, *J* = 7.0 Hz, 2H), 1.89-1.85 (m, 2H), 1.83-1.78 (m, 2H); **^{13}C NMR** (125 MHz, $CDCl_3$) δ 197.7, 152.7, 135.1, 131.1 (q, *J* = 303.8 Hz), 130.0, 120.5, 120.3 (q, *J* = 257.1 Hz), 37.7, 29.7, 29.1, 22.8; **^{19}F NMR** (282 MHz, $CDCl_3$) δ -40.08, -56.56; **HRMS** (ESI) calculated for $C_{13}H_{13}F_6O_2S$ $[M+H]^+$ m/z 347.0540, found 347.0546.

1-(4-(*tert*-Butyl)phenyl)-5-((trifluoromethyl)thio)pentan-1-one (4h)



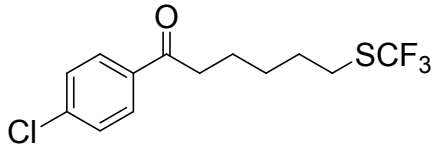
According to **Method A** with 1-(4-(*tert*-butyl)phenyl)cyclopentanol **3h** (54.5 mg, 0.25 mmol, 1.0 equiv), $AgSCF_3$ (130.6 mg, 0.625 mmol, 2.5 equiv), $K_2S_2O_8$ (202.7 mg, 0.75 mmol, 3.0 equiv), and pyridine (40 μL, 0.5 mmol, 2.0 equiv). Flash column chromatography (petroleum ether/Et_2O =100/1, v/v) gave the desired product **4h** as colourless oil (35.3 mg, 44%). **^{1}H NMR** (500 MHz, $CDCl_3$) δ 7.91-7.86 (m, 2H), 7.50-7.45 (m, 2H), 2.99 (t, *J* = 6.8 Hz, 2H), 2.93 (t, *J* = 7.0 Hz, 2H), 1.89-1.84 (m, 2H), 1.82-1.77 (m, 2H), 1.34 (s, 9H); **^{13}C NMR** (125 MHz, $CDCl_3$) δ 199.0, 156.9, 134.3, 131.1 (q, *J* = 304.1 Hz), 128.0, 125.5, 37.5, 35.1, 31.0, 29.7, 29.1, 23.0; **^{19}F NMR** (282 MHz, $CDCl_3$) δ -40.07; **HRMS** (ESI) calculated for $C_{16}H_{22}F_3OS$ $[M+H]^+$ m/z 319.1344, found 319.1338.

1-(3-Chlorophenyl)-5-((trifluoromethyl)thio)pentan-1-one (4i)



According to **Method A** with 1-(3-chlorophenyl)cyclopentanol **3i** (49.0 mg, 0.25 mmol, 1.0 equiv), $AgSCF_3$ (130.6 mg, 0.625 mmol, 2.5 equiv), $K_2S_2O_8$ (202.7 mg, 0.75 mmol, 3.0 equiv), and pyridine (40 μL, 0.5 mmol, 2.0 equiv). Flash column chromatography (petroleum ether/Et_2O = 100/1, v/v) gave the desired product **4i** as colourless oil (46.7 mg, 63%). **^{1}H NMR** (500 MHz, $CDCl_3$) δ 7.91 (s, 1H), 7.82 (d, *J* = 7.5 Hz, 1H), 7.53 (d, *J* = 7.5 Hz, 1H), 7.44-7.38 (m, 1H), 2.99 (t, *J* =6.8 Hz, 2H), 2.93 (t, *J* =7.3 Hz, 2H), 1.89-1.84 (m, 2H), 1.82-1.76 (m, 2H); **^{13}C NMR** (125 MHz, $CDCl_3$) δ 198.0, 138.4, 135.0, 133.0, 131.1 (q, *J* = 304.1 Hz), 130.0, 128.1, 126.0, 37.8, 29.7, 29.0, 22.7; **^{19}F NMR** (282 MHz, $CDCl_3$) δ -40.05; **HRMS** (ESI) calculated for $C_{12}H_{13}ClF_3OS$ $[M+H]^+$ m/z 297.0328, found 297.0334.

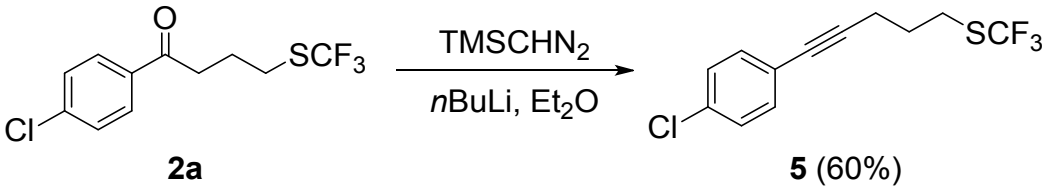
1-(4-Chlorophenyl)-6-((trifluoromethyl)thio)hexan-1-one (4j)



According to **Method A** with 1-(4-chlorophenyl)cyclohexanol **3j** (52.5 mg, 0.25 mmol, 1.0 equiv), $AgSCF_3$ (130.6 mg, 0.625 mmol, 2.5 equiv), $K_2S_2O_8$ (202.7 mg, 0.75 mmol, 3.0 equiv), and pyridine (40 μL, 0.5 mmol, 2.0 equiv). Flash column chromatography (petroleum ether/Et_2O = 100/1, v/v) gave the desired product **4j** as colourless oil (24.1 mg, 31%). **^{1}H NMR** (500 MHz, $CDCl_3$) δ 7.93-7.86 (m, 2H), 7.50-7.40 (m, 2H), 2.95 (t, *J* = 7.0 Hz, 2H), 2.90 (t, *J* = 7.5 Hz, 2H), 1.80-1.72 (m, 4H), 1.53-1.48 (m, 2H); **^{13}C NMR** (125 MHz, $CDCl_3$) δ 198.6, 139.5, 135.3, 131.2 (q, *J* = 303.8 Hz), 129.4, 128.9, 38.1, 29.6 (q, *J* = 2.0 Hz), 29.3, 28.0, 23.4; **^{19}F NMR** (282 MHz, $CDCl_3$) δ -40.07; **HRMS** (ESI) calculated for $C_{13}H_{14}ClF_3NaOS$ $[M+Na]^+$ m/z 333.0304, found 333.0300.

Transformations of 2a

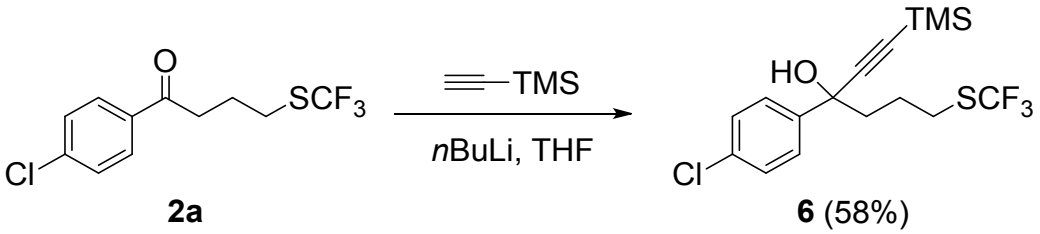
(5-(4-Chlorophenyl)pent-4-yn-1-yl)(trifluoromethyl)sulfane (5)



2a **5** (60%)

To a solution of (trimethylsilyl)diazomethane (0.30 mL, 0.6 mmol, 2 M in hexanes) in Et_2O (4 mL), *n*BuLi (0.38 mL, 0.6 mmol, 1.6 M in hexane) was added dropwise at -78 °C. After the mixture was stirred for 1 h at -78 °C, a solution of **2a** (84.6 mg, 0.3 mmol) in THF (2 mL) was added dropwise at 0 °C. The reaction mixture was stirred for another 5 h. After it was quenched with saturated aqueous ammonium chloride (5 mL), the aqueous phase was extracted with EtOAc (3×10 mL). The combined organic extracts were dried over $MgSO_4$ and concentrated in vacuo. The residue was purified by flash column chromatography (petroleum ether/Et_2O = 100/1, v/v) on silica gel to give product **5** (50.1 mg, 60%) as colorless oil. **^{1}H NMR** (500 MHz, $CDCl_3$) δ 7.31-7.30 (m, 2H), 7.27-7.25 (m, 2H), 3.05 (t, *J* = 7.0 Hz, 2H), 2.56 (t, *J* = 6.5 Hz, 2H), 2.02-1.98 (m, 2H); **^{13}C NMR** (125 MHz, $CDCl_3$) δ 133.9, 132.8, 131.1 (q, *J* = 304.1 Hz), 128.6, 122.0, 88.8, 80.9, 28.8 (q, *J* = 2.0 Hz), 28.4, 18.2; **^{19}F NMR** (282 MHz, $CDCl_3$) δ -39.91; **HRMS** (ESI) calculated for $C_{12}H_{11}ClF_3S$ $[M+H]^+$ m/z 279.0222, found 279.0224.

3-(4-Chlorophenyl)-6-((trifluoromethyl)thio)-1-(trimethylsilyl)hex-1-yn-3-ol (6)

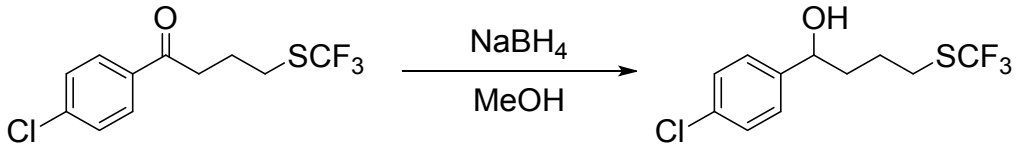


2a **6** (58%)

To a solution of trimethylsilylacetylene (58.9 mg, 0.6 mmol) in THF (1 mL), *n*BuLi (0.38 mL, 0.6 mmol, 1.6 M in hexane) was added dropwise at -78 °C. After the mixture was stirred for 1 h at room temperature, a solution of **2a** (84.6 mg, 0.3 mmol) in THF (2 mL) was added dropwise at -78 °C. The reaction mixture was warmed up to room temperature gradually and further stirred for overnight. The reaction mixture was quenched with saturated aqueous ammonium chloride (5 mL). The aqueous phase was extracted with EtOAc (2×10 mL). The combined organic extracts were dried over

$MgSO_4$ and concentrated in vacuo. The residue was purified by flash column chromatography (petroleum ether/Et_2O = 100/1, v/v) on silica gel to give product **6** (65.6 mg, 58%) as colorless oil. **^{1}H NMR** (500 MHz, $CDCl_3$) δ 7.55-7.51 (m, 2H), 7.35-7.30 (m, 2H), 2.94-2.84 (m, 2H), 2.37 (br s, 1H), 2.01-1.75 (m, 4H), 0.22 (s, 9H); **^{13}C NMR** (125 MHz, $CDCl_3$) δ 142.8, 133.8, 131.1 (q, J = 304.4 Hz), 128.4, 126.9, 106.6, 91.9, 72.7, 43.7, 29.7, 25.0, 0.3; **^{19}F NMR** (282 MHz, $CDCl_3$) δ -39.99; **HRMS** (ESI) calculated for $C_{16}H_{21}ClF_3OSSi$ $[M+H]^+$ m/z 381.0723, found 381.0724.

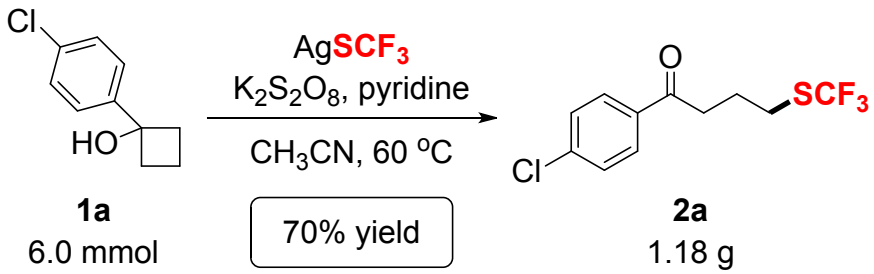
1-(4-Chlorophenyl)-4-((trifluoromethyl)thio)butan-1-ol (7)



2a **7** (77%)

To a stirred solution of **2a** (84.6 mg, 0.3 mmol) in MeOH (2 mL), $NaBH_4$ (22.7 mg, 0.6 mmol) was added in one portion at 0 °C. The reaction mixture was stirred for 30 min. After it was quenched by saturated aqueous ammonium chloride (3 mL), the mixture was extracted with EtOAc (5 mL× 3). The combined organic layer was dried over $MgSO_4$ and concentrated in vacuo. The crude residue was purified by flash column chromatography (petroleum ether/Et_2O = 10/1, v/v) on silica gel to afford product **7** (65.5 mg,77%) as colorless oil. **^{1}H NMR** (500 MHz, $CDCl_3$) δ 7.34-7.28 (m, 2H), 7.28-7.22 (m, 2H), 4.69-4.62 (m, 1H), 2.89-2.87 (m, 2H), 2.02 (br s, 1H), 1.87-1.68 (m, 4H); **^{13}C NMR** (125 MHz, $CDCl_3$) δ 142.7, 133.5, 131.1 (q, J = 304.1 Hz), 128.7, 127.1, 73.2, 37.5, 29.7, 25.7; **^{19}F NMR** (282 MHz, $CDCl_3$) δ -40.03; **HRMS** (ESI) calculated for $C_{11}H_{13}ClF_3OS$ $[M+H]^+$ m/z 285.0328, found 285.0332.

Lager scale experiment



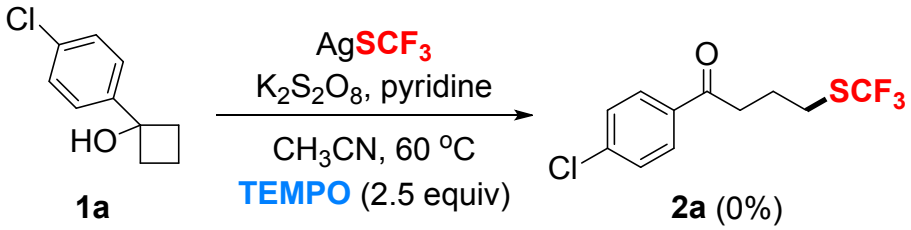
1a
6.0 mmol

2a
1.18 g

1-(4-Chlorophenyl)cyclobutanol **1a** (1.09 g, 6.0 mmol, 1.0 equiv), $AgSCF_3$ (3.13 g, 15.0 mmol, 2.5 equiv), $K_2S_2O_8$ (4.87 g, 18.0 mmol, 3.0 equiv), and pyridine (950 mg, 12.0 mmol, 2.0 equiv) were placed in a dry *Schlenk* tube under N_2. Acetonitrile (60 mL) was added and the reaction mixture was stirred at 60 °C for 12 h. The reaction was monitored with TLC. The solvent was removed under reduced pressure and the residue was purified by silica gel column chromatography. Flash column chromatography (petroleum ether/Et_2O = 50/1, v/v) gave the desired product **2a** as colourless oil (1.18 g, 70%).

Mechanistic studies

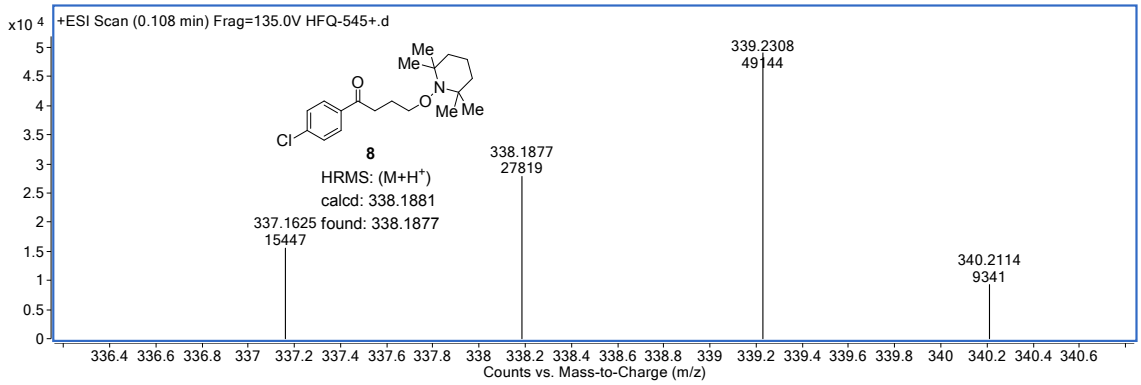
(1) Radical inhibition and capturing experiments:

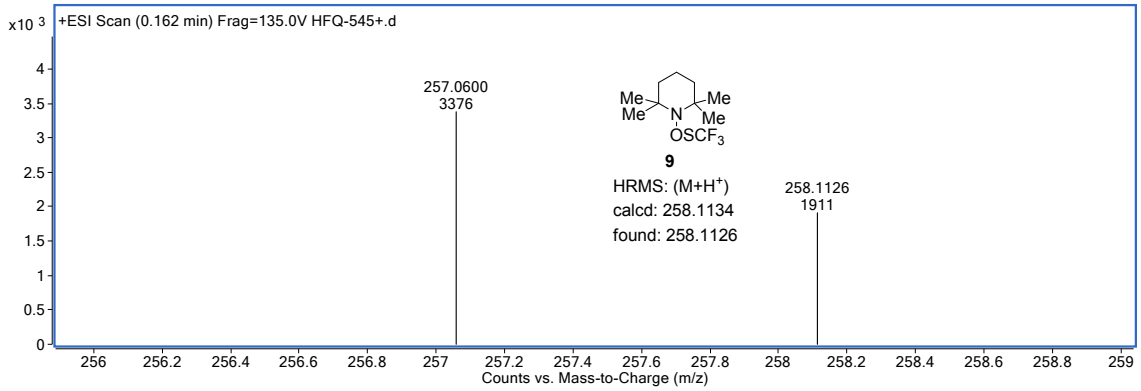


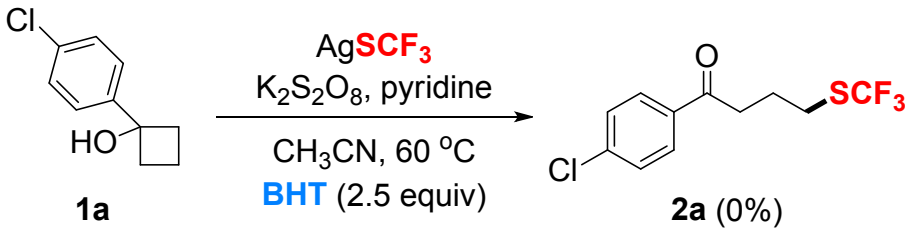
1a

2a (0%)

1-(4-Chlorophenyl)cyclobutanol **1a** (45.5 mg, 0.25 mmol, 1.0 equiv), $AgSCF_3$ (130.6 mg, 0.625 mmol, 2.5 equiv), $K_2S_2O_8$ (202.7 mg, 0.75 mmol, 3.0 equiv), pyridine (40 ul, 0.5 mmol, 2.0 equiv), and 2,2,6,6-tetramethyl-1-piperidinyloxy (TEMPO) (97.7 mg, 0.625 mmol, 2.5 equiv) were placed in a dry *Schlenk* tube under N_2. Acetonitrile (2.5 mL) was added and the reaction mixture was stirred at 60 °C for 12 h. The formation of **2a** was completely suppressed. High-resolution mass spectra analysis of the reaction mixture showed that TEMPO-trapped products **8** and **9** were formed.

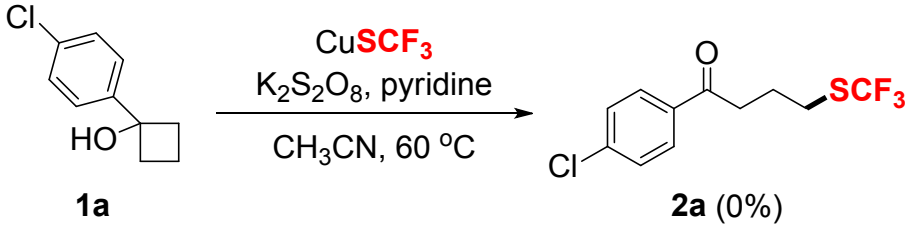






1-(4-Chlorophenyl)cyclobutanol **1a** (45.5 mg, 0.25 mmol, 1.0 equiv), $AgSCF_3$ (130.6 mg, 0.625 mmol, 2.5 equiv), $K_2S_2O_8$ (202.7 mg, 0.75 mmol, 3.0 equiv), pyridine (40 ul, 0.5 mmol, 2.0 equiv), and 2,6-di-*tert*-butyl-4-methylphenol (BHT) (137.7 mg, 0.625 mmol, 2.5 equiv) were placed in a dry *Schlenk* tube under N_2. Acetonitrile (2.5 mL) was added and the reaction mixture was stirred at 60 °C for 12 h. The formation of **2a** was completely suppressed.

(2) Control experiment:



1-(4-Chlorophenyl)cyclobutanol **1a** (45.5 mg, 0.25 mmol, 1.0 equiv), $CuSCF_3$ (102.4 mg, 0.625 mmol, 2.5 equiv), $K_2S_2O_8$ (202.7 mg, 0.75 mmol, 3.0 equiv), and pyridine (40 ul, 0.5 mmol, 2.0 equiv) were placed in a dry *Schlenk* tube under N_2. Acetonitrile (2.5 mL) was added and the reaction mixture was stirred at 60 ^oC for 12 h. The reaction did not afford the desired product **2a**.

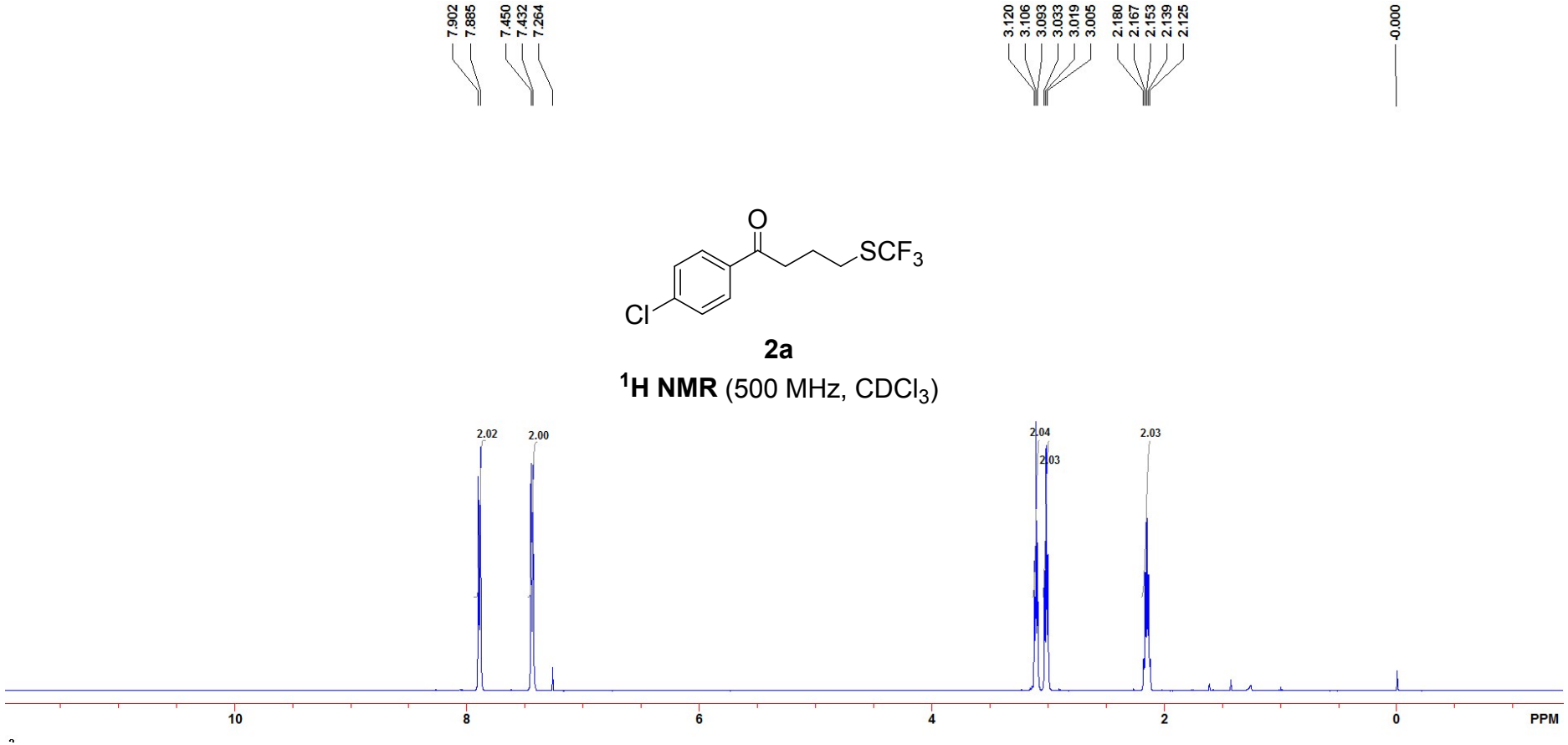
References:

[1] (a) Ilangovan, A.; Saravanakumar, S.; Malayappasamy, S. *Org. Lett.* **2013**, *15*, 4968. (b) Rosa, D.; Orellana, A. *Chem. Commun.* **2013**, *49*, 5420. (c) Jiao, J.; Nguyen, L. X.; Patterson, D. R.; Flowers, R. A. II. *Org. Lett.* **2007**, *9*, 1323. (d) Wang, Y.-F.; Chiba, S. *J. Am. Chem. Soc.* **2009**, *131*, 12570.

[2] (a) Casey, B. M.; Eakin, C. A.; Flowers, R. A. II. *Tetrahedron Lett.* **2009**, *50*, 1264. (b) Rosa, D.; Chtchemelinine, A.; Orellana, A. *Synthesis* **2012**, 1885. (c) Xu, H.-J.; Zhu, F.-F.; Shen, Y.-Y.; Wan, X.; Feng, Y.-S. *Tetrahedron* **2012**, *68*, 4145.

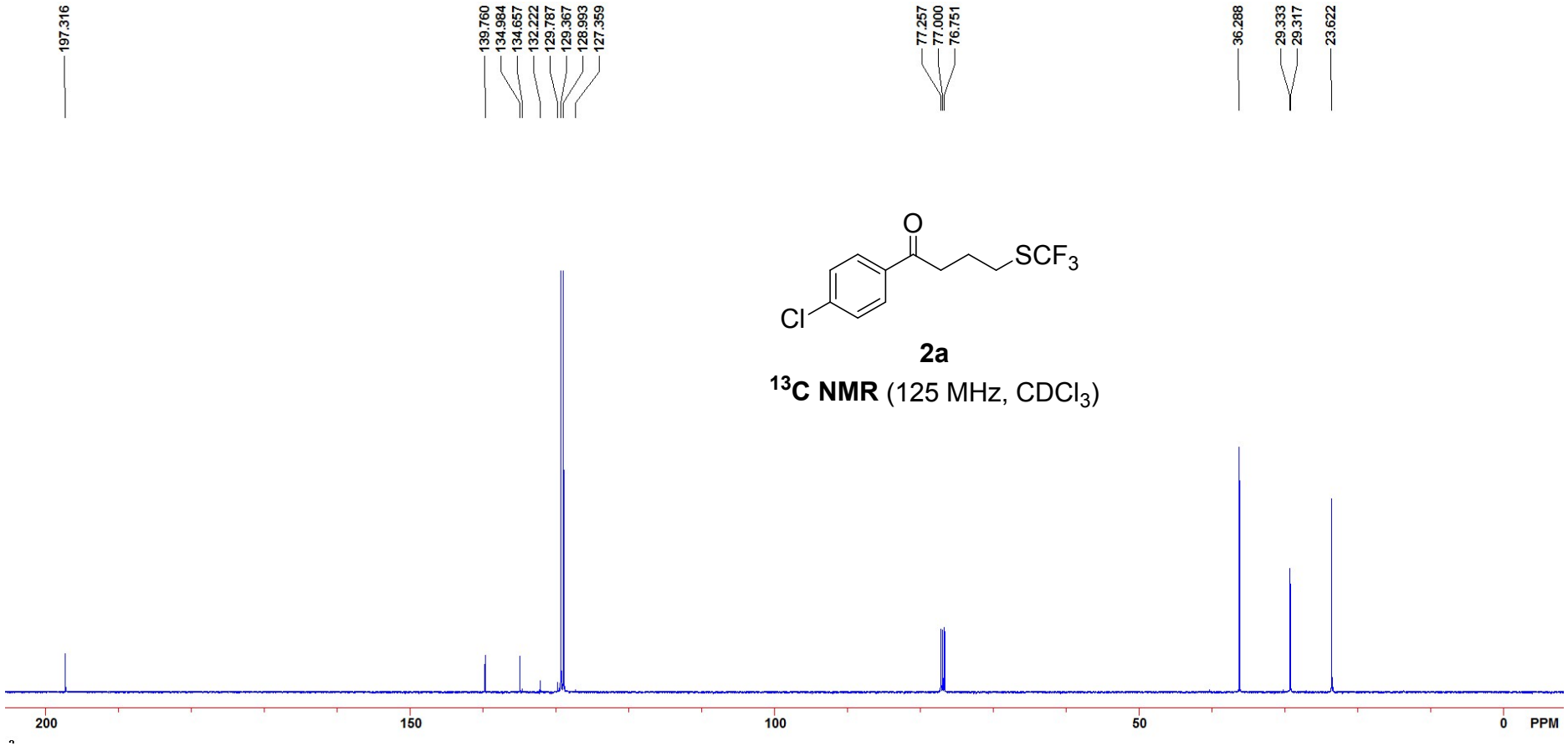
(d) Zhao, H.; Fan, X.; Yu, J.; Zhu, C. *J. Am. Chem. Soc.* **2015**, *137*, 3490.

[3] Li, Y.; Ye, Z.-S.; Bellman, T.-M.; Chi, T.; Dai, M.-J. *Org. Lett.* **2015**, *17*, 2186.



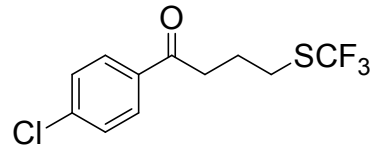
2a

^{1}H NMR (500 MHz, $CDCl_3$)



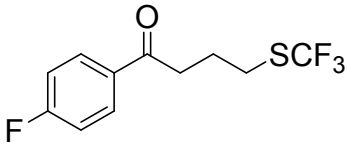
2a

^{13}C NMR (125 MHz, $CDCl_3$)



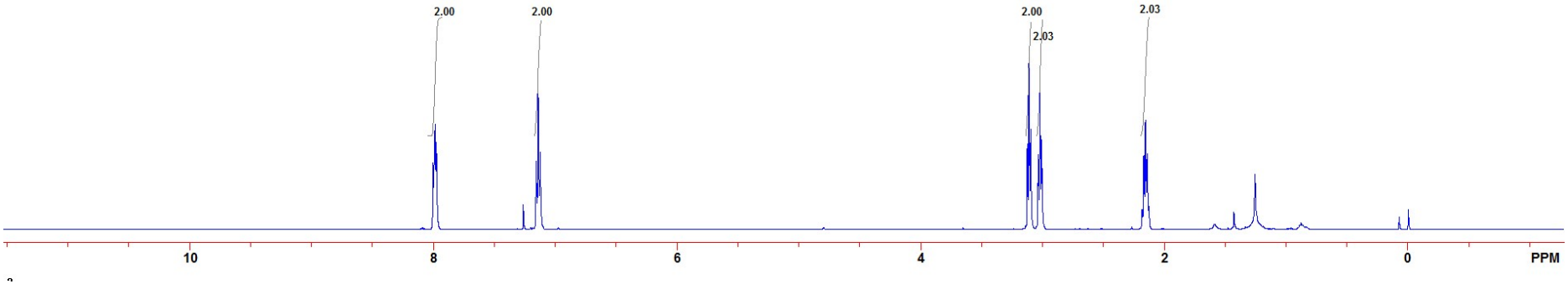
2a

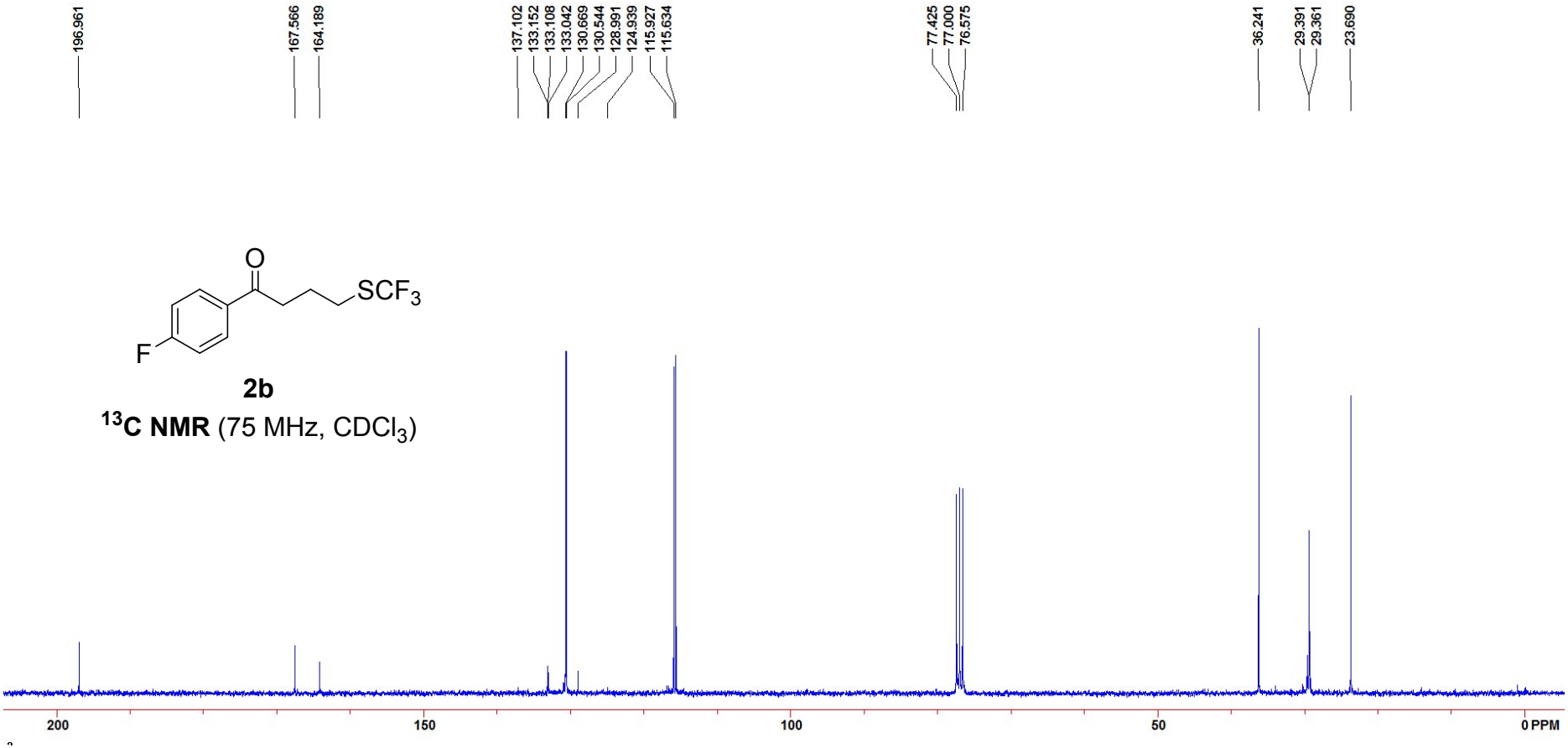
^{19}F NMR (282 MHz, $CDCl_3$)

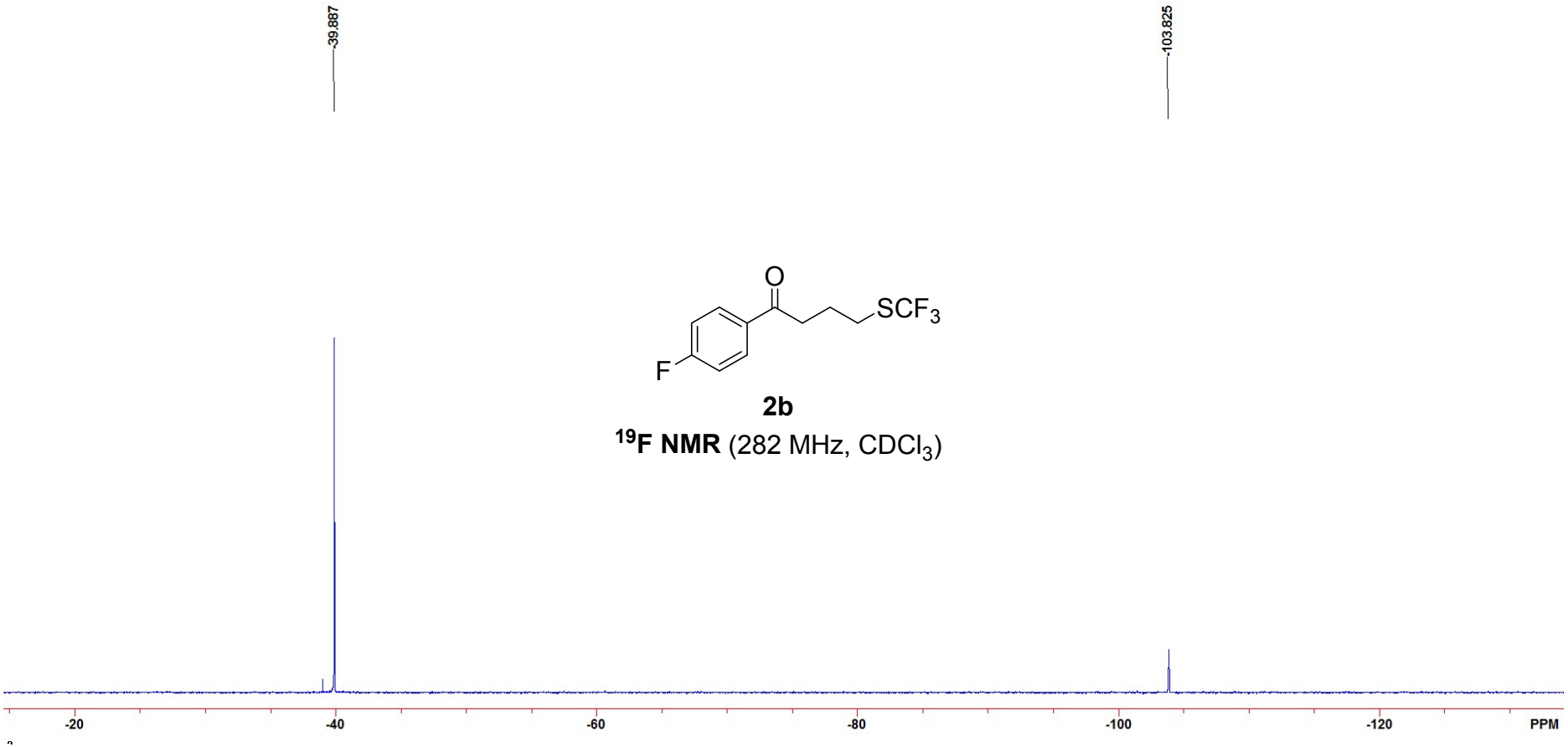


2b

^{1}H NMR (500 MHz, $CDCl_3$)

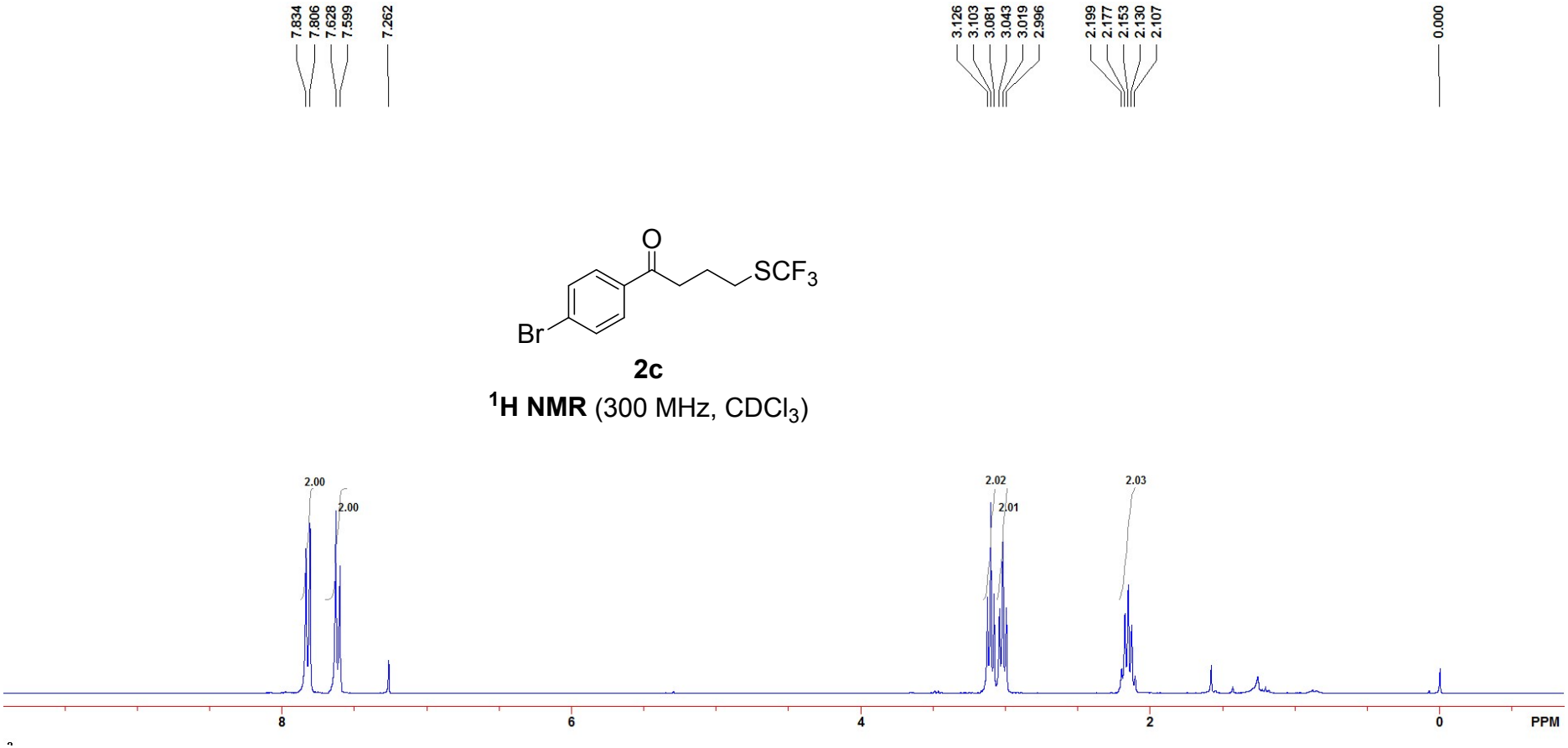


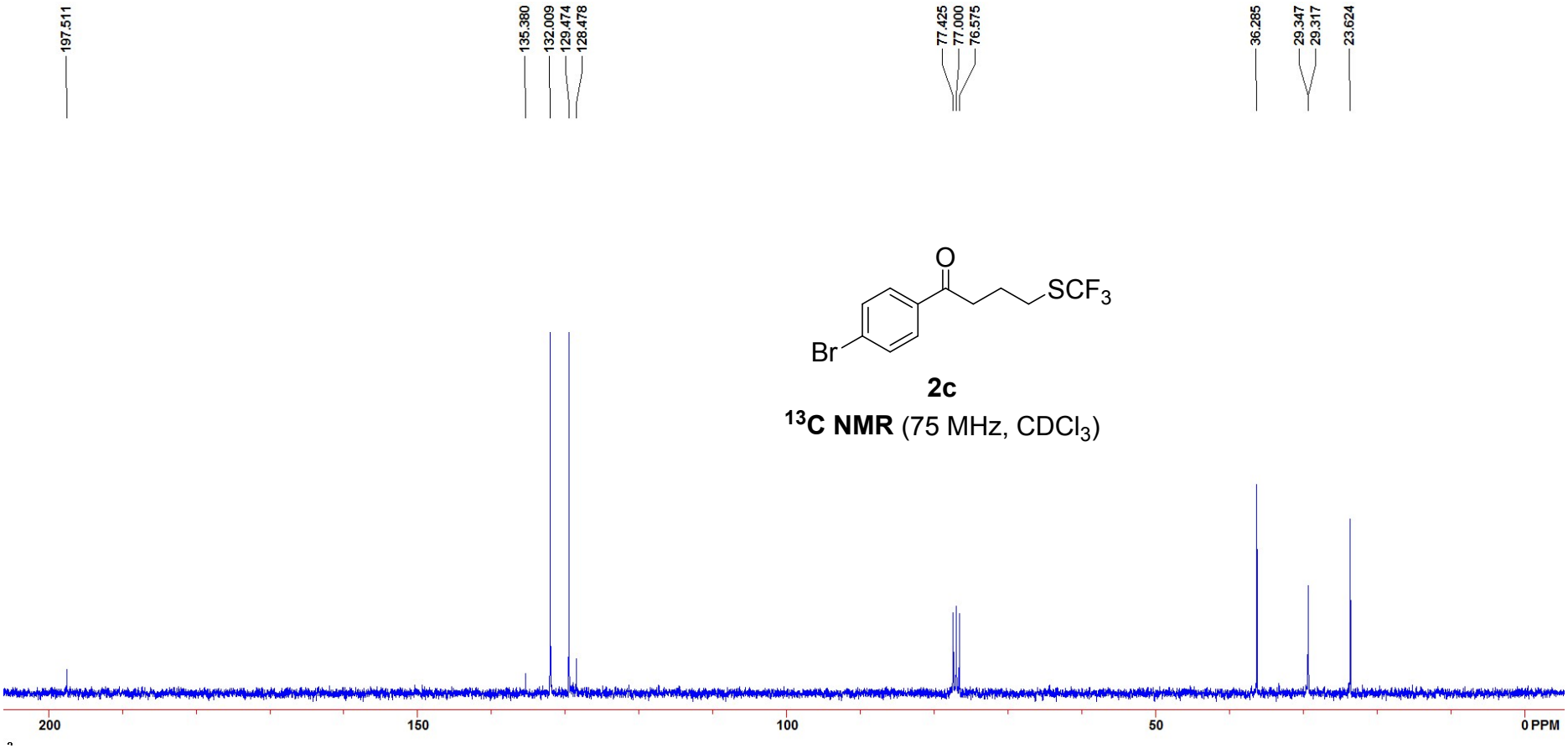

196.961
167.566
164.189
137.102
133.152
133.108
133.042
130.669
130.544
128.991
124.939
115.927
115.634
77.425
77.000
76.575
36.241
29.391
29.361
23.690
O
SCF3
F
2b
13C NMR (75 MHz, CDCl3)
200
150
100
50
0 PPM



2b

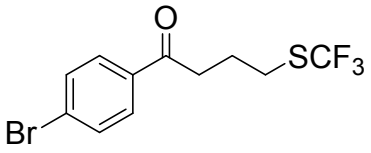
^{19}F NMR (282 MHz, $CDCl_3$)


7.834
7.806
7.628
7.599
7.262
3.126
3.103
3.081
3.043
3.019
2.996
2.199
2.177
2.153
2.130
2.107
0.000
O
SCF3
Br
2c
1H NMR (300 MHz, CDCl3)
2.00
2.00
2.02
2.01
2.03
8
6
4
2
0
PPM



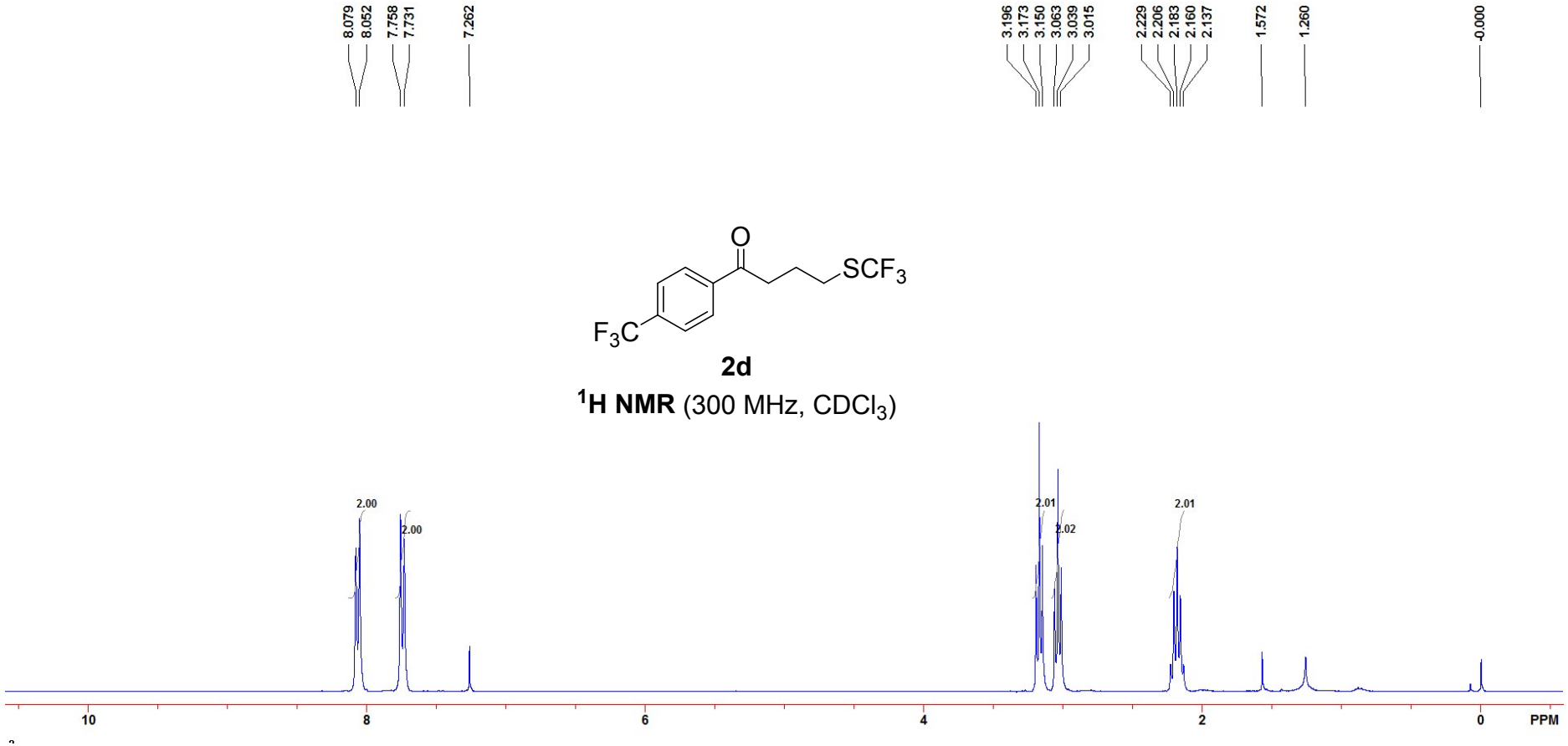
2c

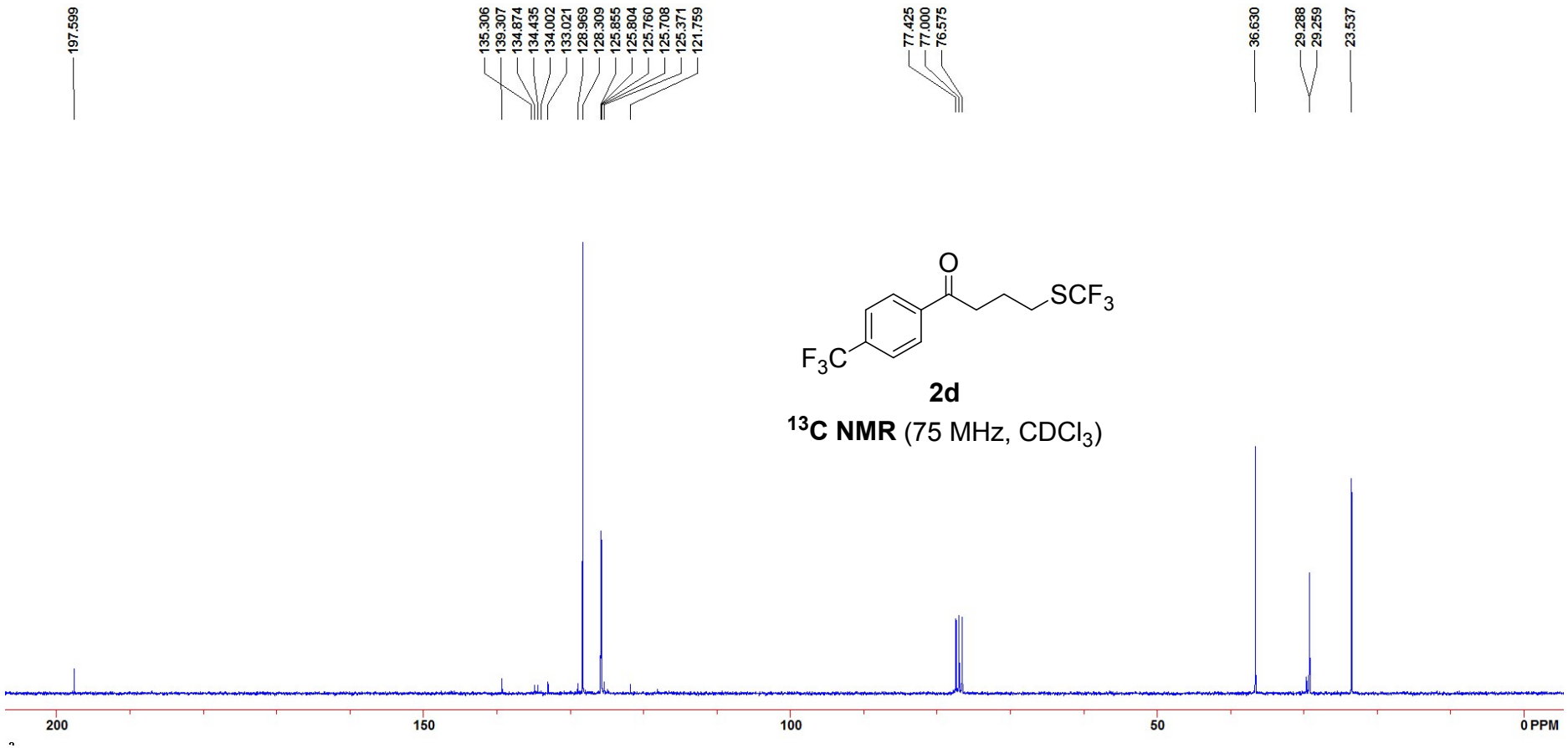
^{13}C NMR (75 MHz, $CDCl_3$)



2c

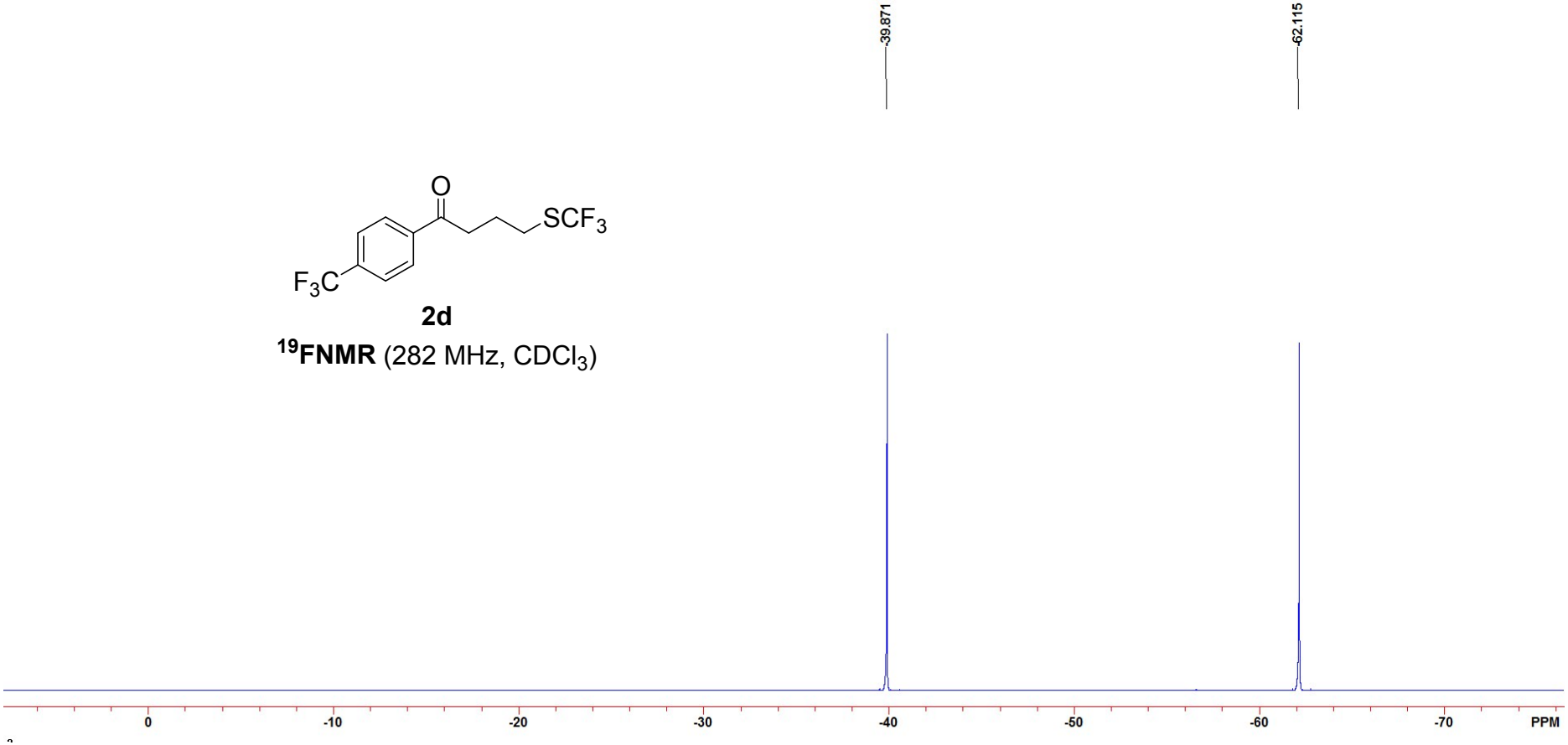
^{19}F NMR (282 MHz, $CDCl_3$)


8.079
8.052
7.758
7.731
7.262
3.196
3.173
3.150
3.063
3.039
3.015
2.229
2.206
2.183
2.160
2.137
1.572
1.260
0.000
O
SCF3
F3C
2d
1H NMR (300 MHz, CDCl3)
2.00
2.00
2.01
2.02
2.01
10
8
6
4
2
0
PPM



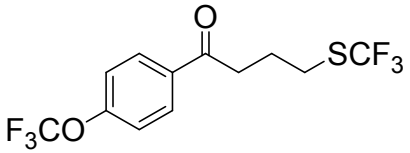
2d

^{13}C NMR (75 MHz, $CDCl_3$)



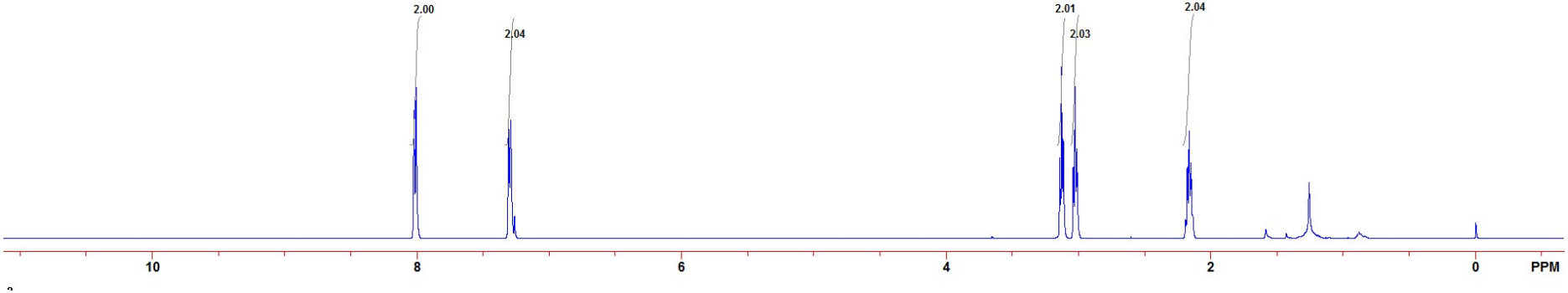
2d

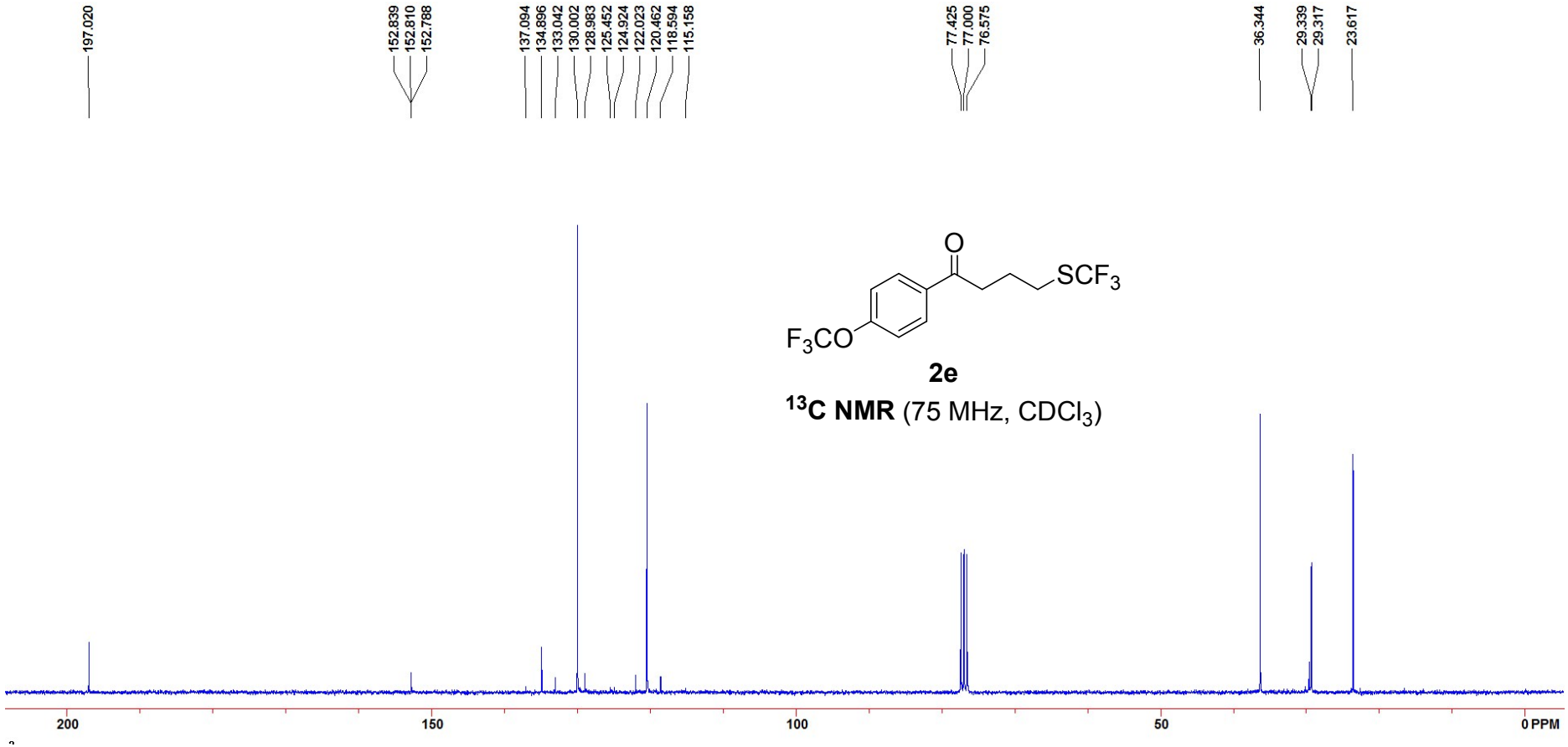
^{19}FNMR (282 MHz, $CDCl_3$)

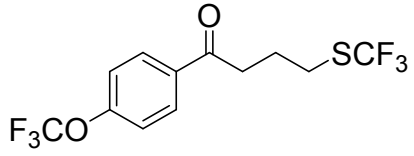


2e

^{1}H NMR (500 MHz, $CDCl_3$)

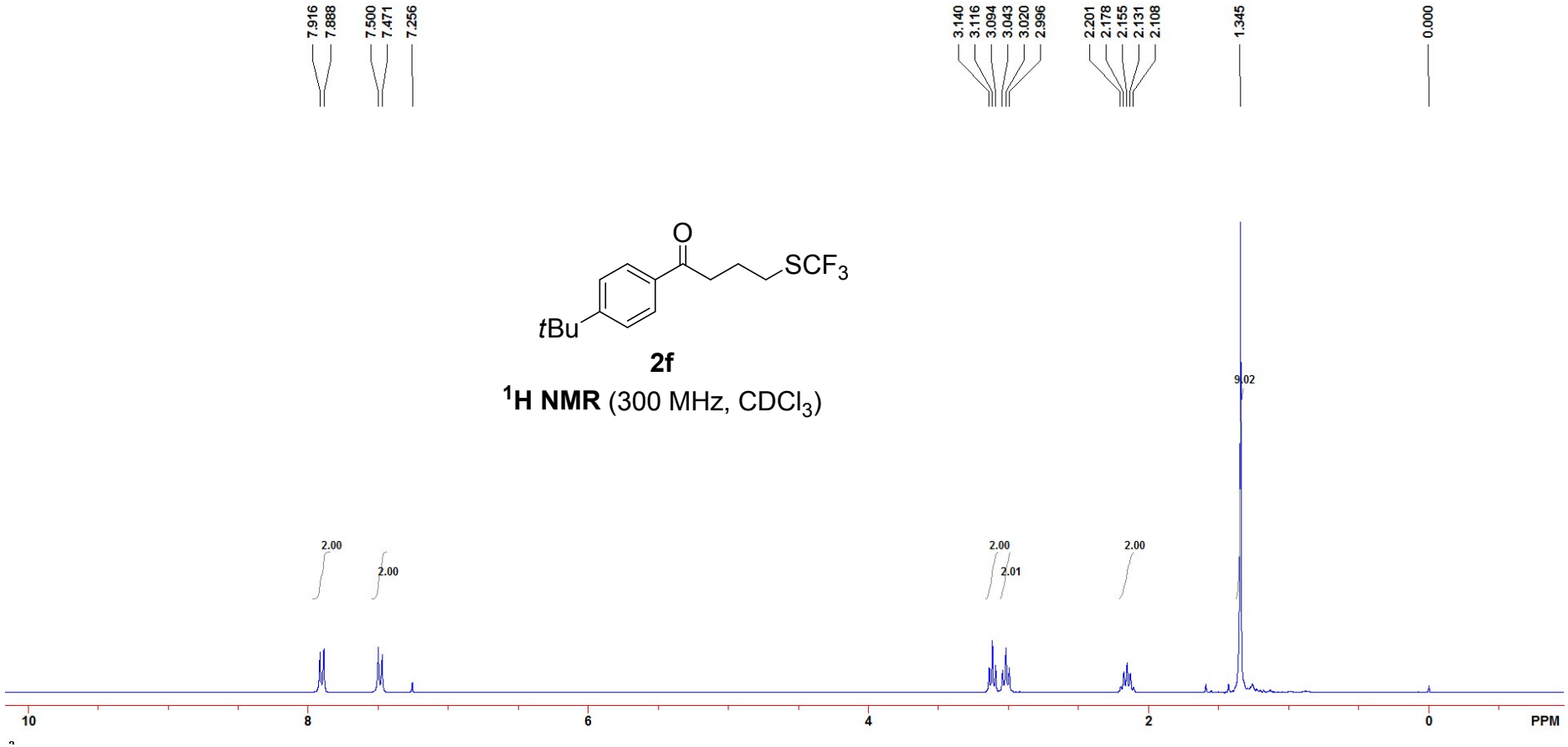


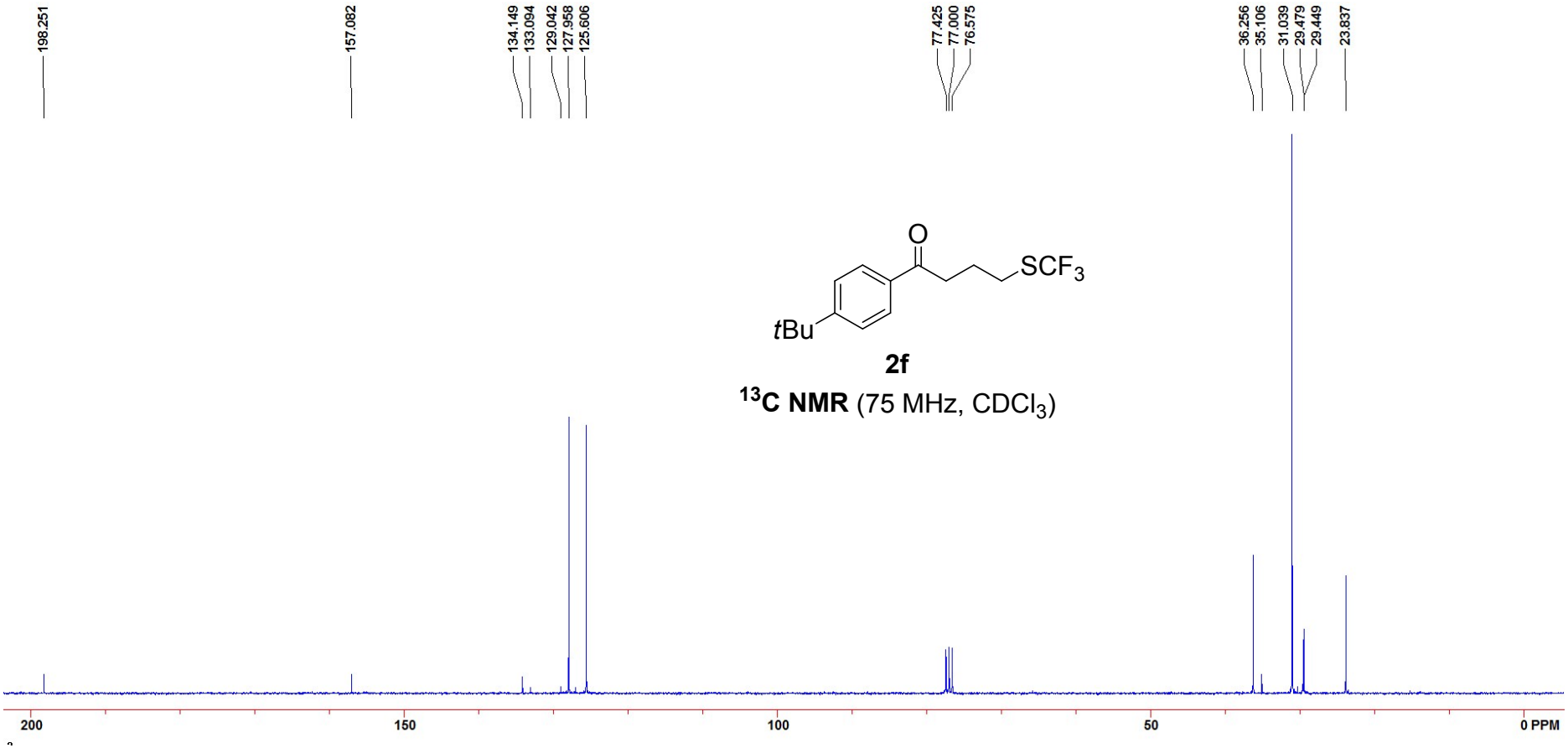

197.020
152.839
152.810
152.788
137.094
134.896
133.042
130.002
128.983
125.452
124.924
122.023
120.462
118.594
115.158
77.425
77.000
76.575
36.344
29.339
29.317
23.617
O
SCF3
F3CO
2e
13C NMR (75 MHz, CDCl3)
200
150
100
50
0 PPM



2e

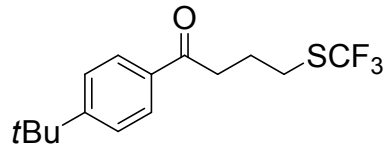
^{19}F NMR (282 MHz, $CDCl_3$)


7.916
7.888
7.500
7.471
7.256
3.140
3.116
3.094
3.043
3.020
2.996
2.201
2.178
2.155
2.131
2.108
1.345
0.000
O
SCF3
tBu
2f
1H NMR (300 MHz, CDCl3)
9.02
2.00
2.00
2.00
2.01
2.00
10
8
6
4
2
0
PPM



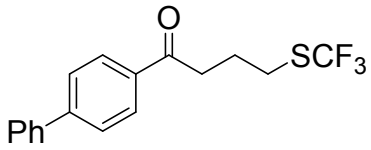
2f

^{13}C NMR (75 MHz, $CDCl_3$)



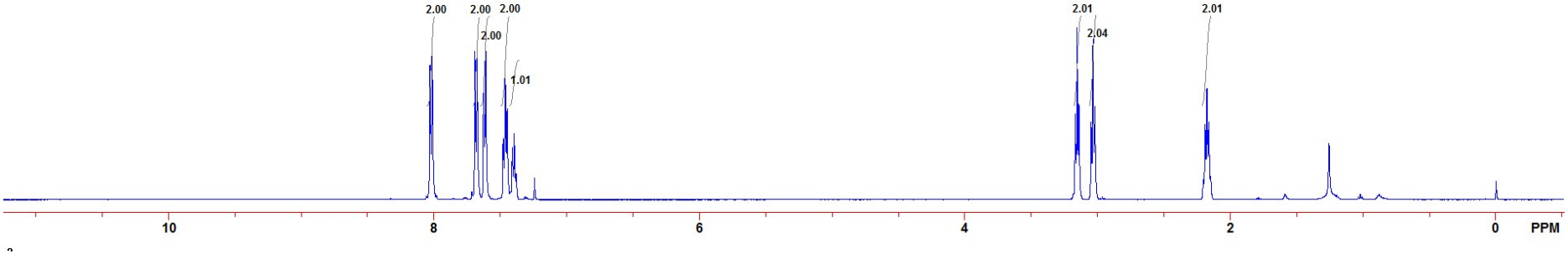
2f

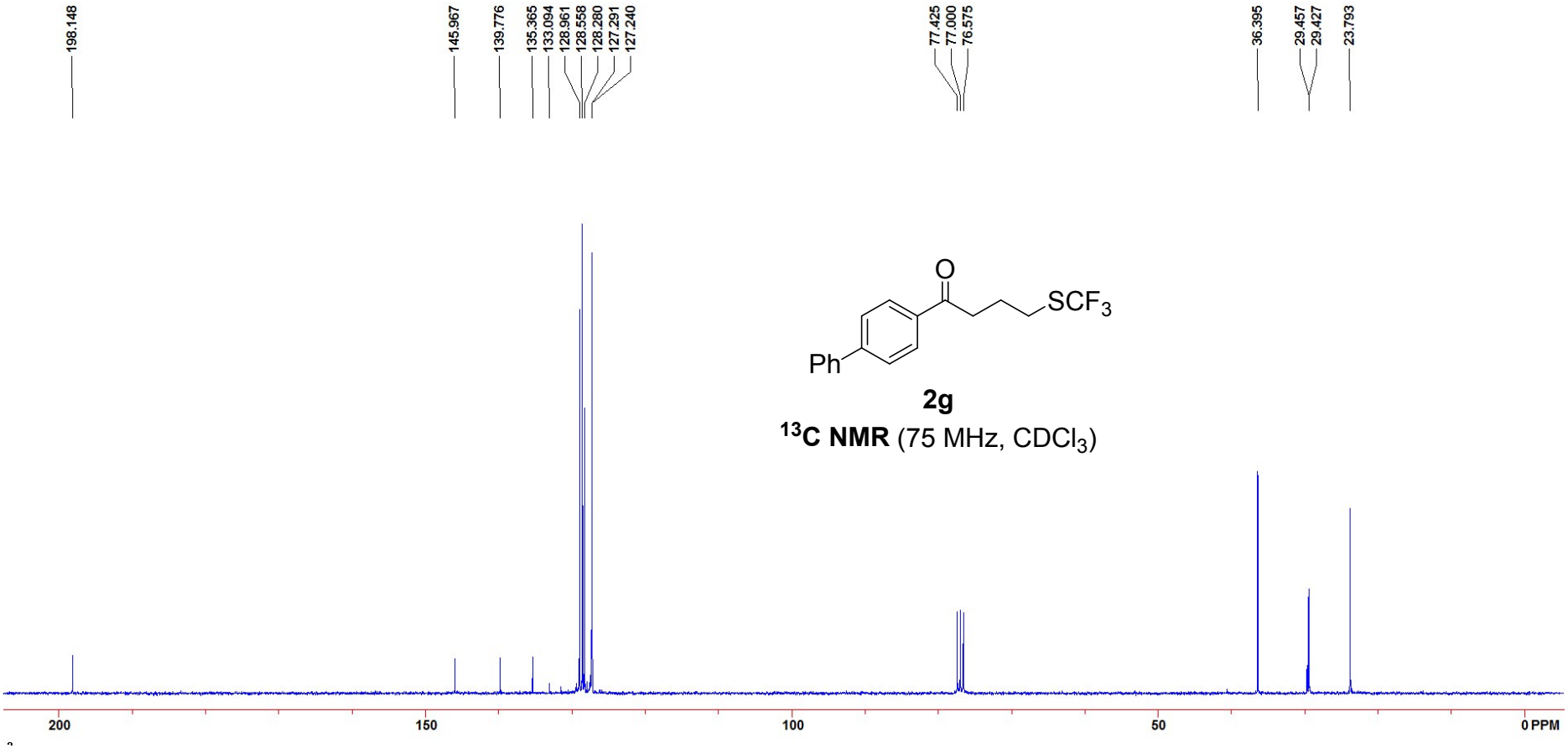
^{19}F NMR (282 MHz, $CDCl_3$)



2g

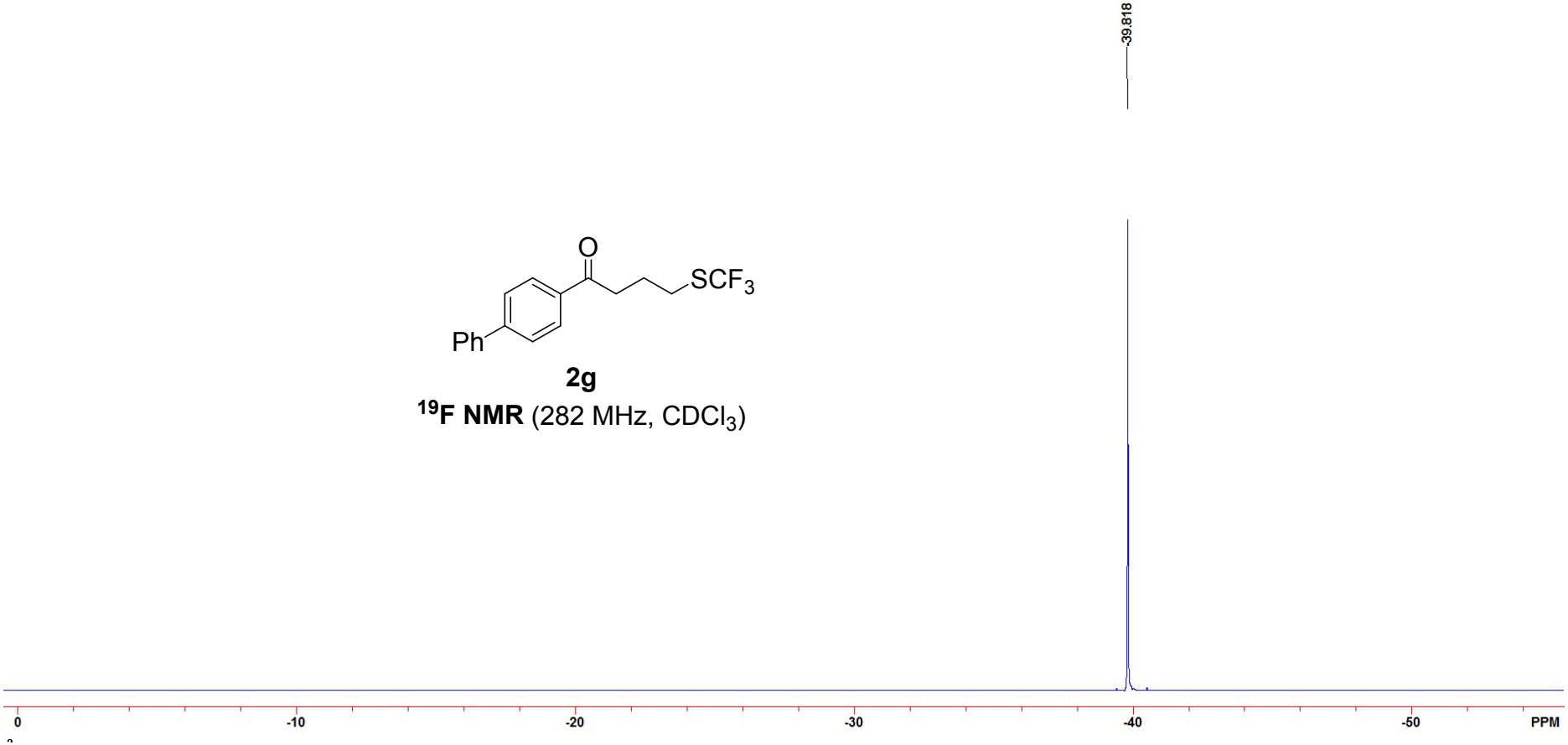
^{1}H NMR (500 MHz, $CDCl_3$)





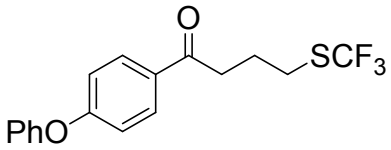
2g

^{13}C NMR (75 MHz, $CDCl_3$)



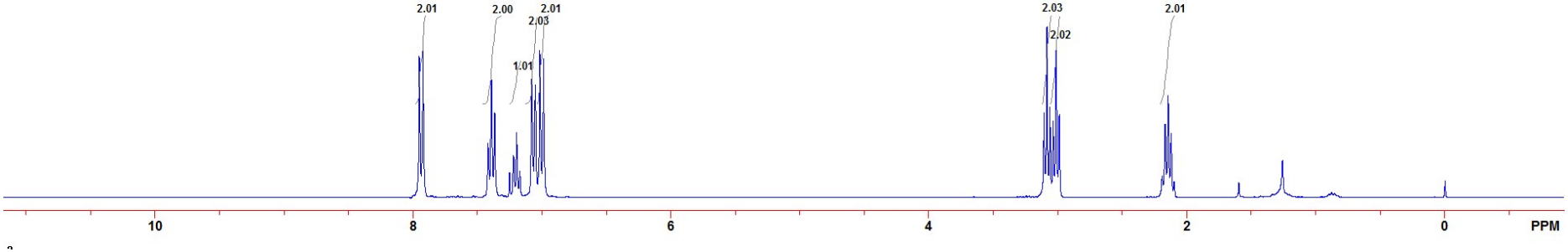
2g

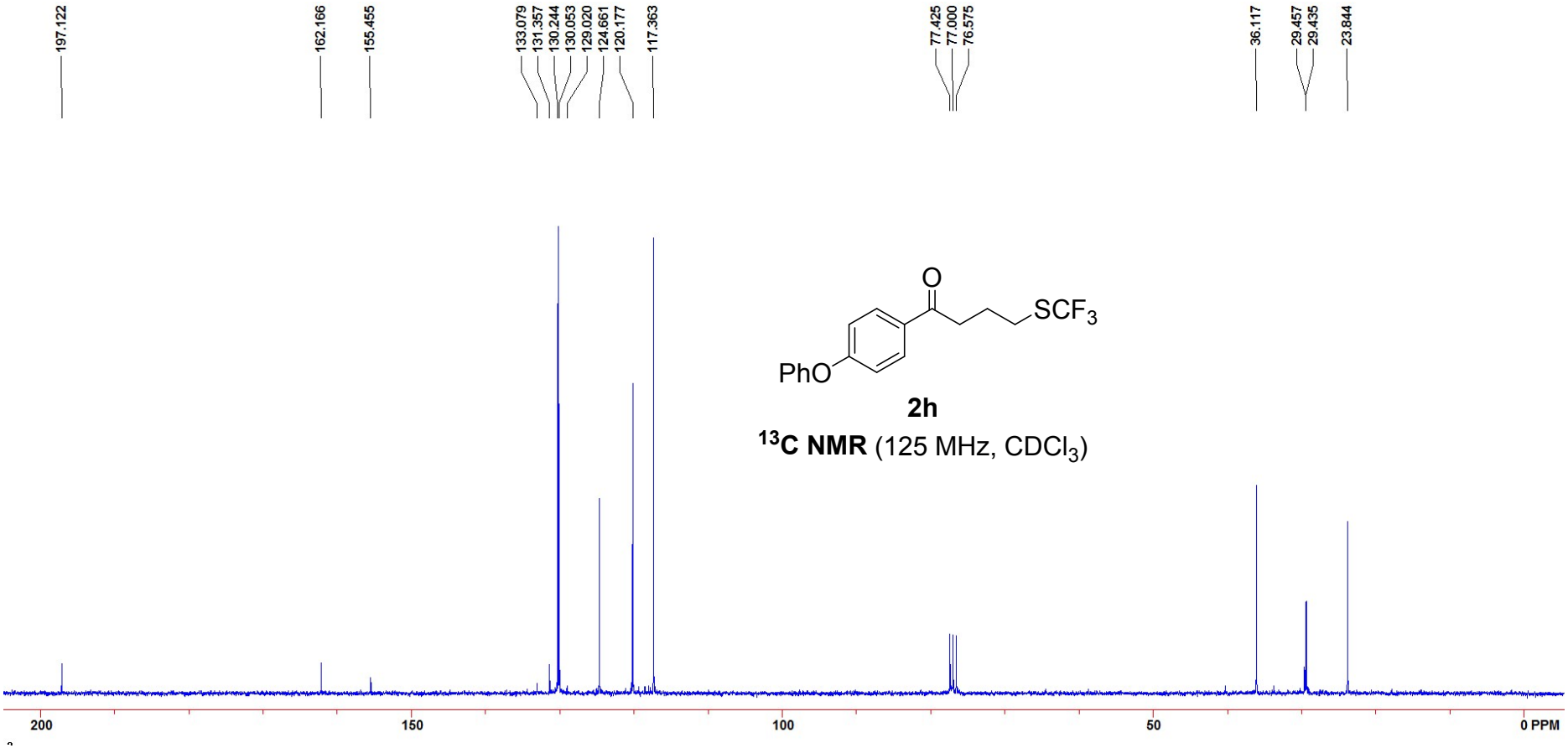
^{19}F NMR (282 MHz, $CDCl_3$)



2h

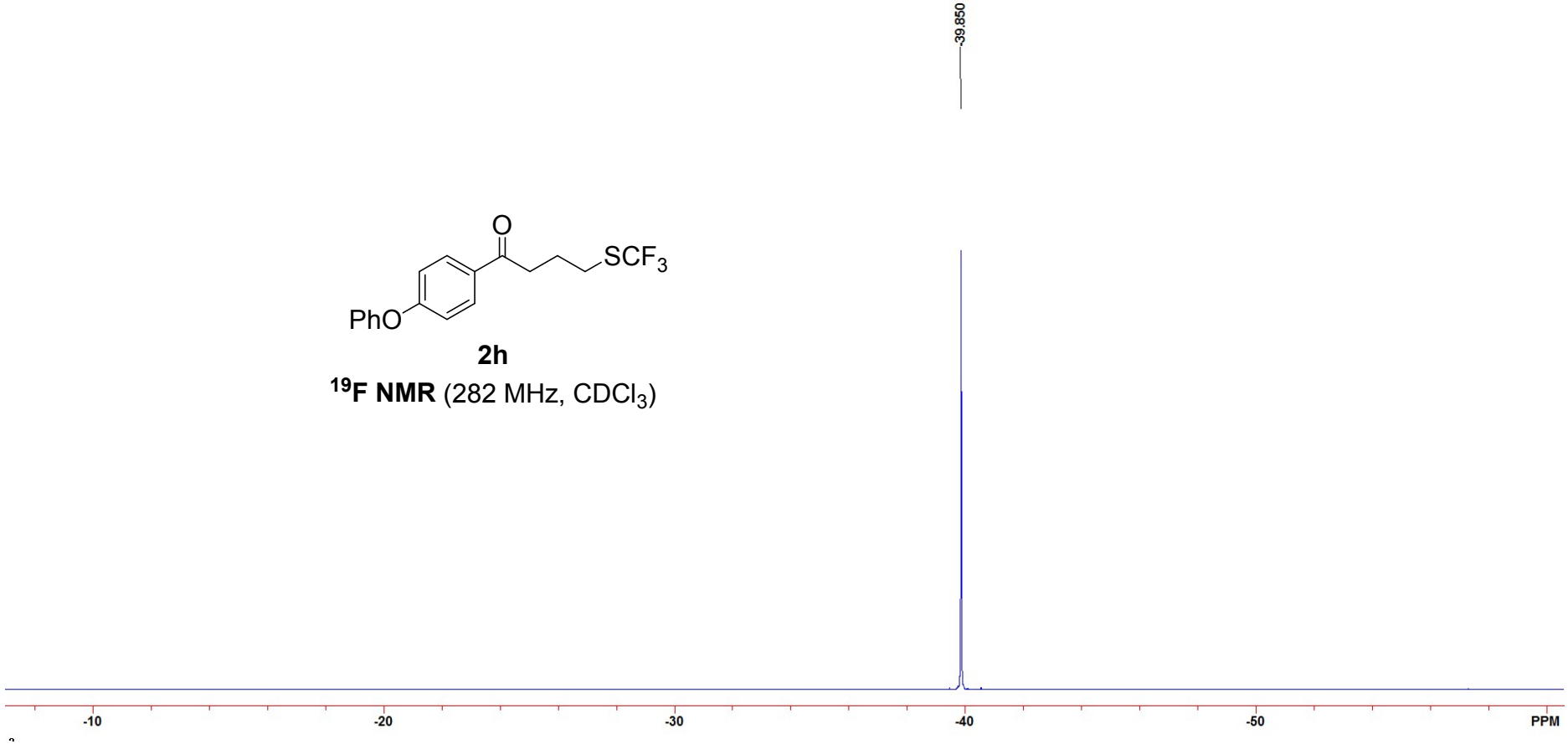
^{1}H NMR (300 MHz, $CDCl_3$)





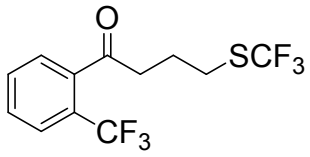
2h

^{13}C NMR (125 MHz, $CDCl_3$)



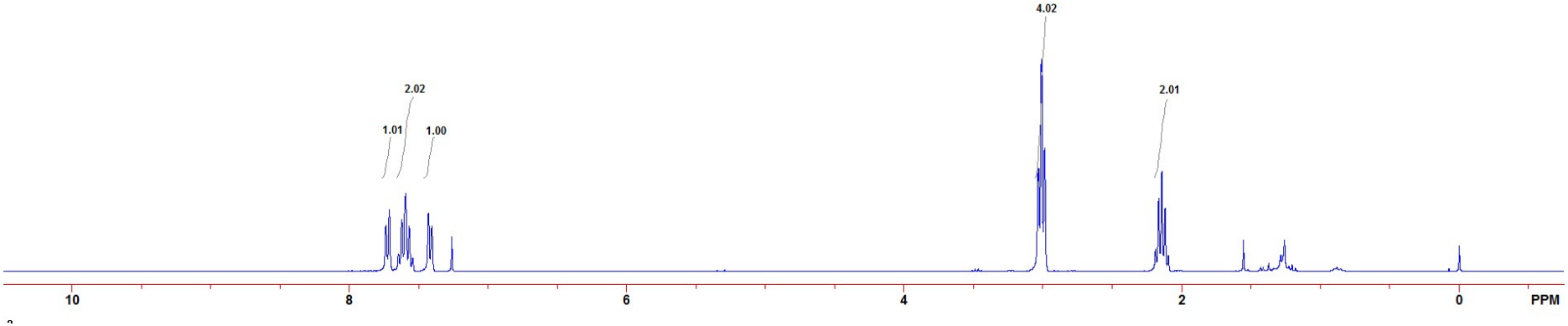
2h

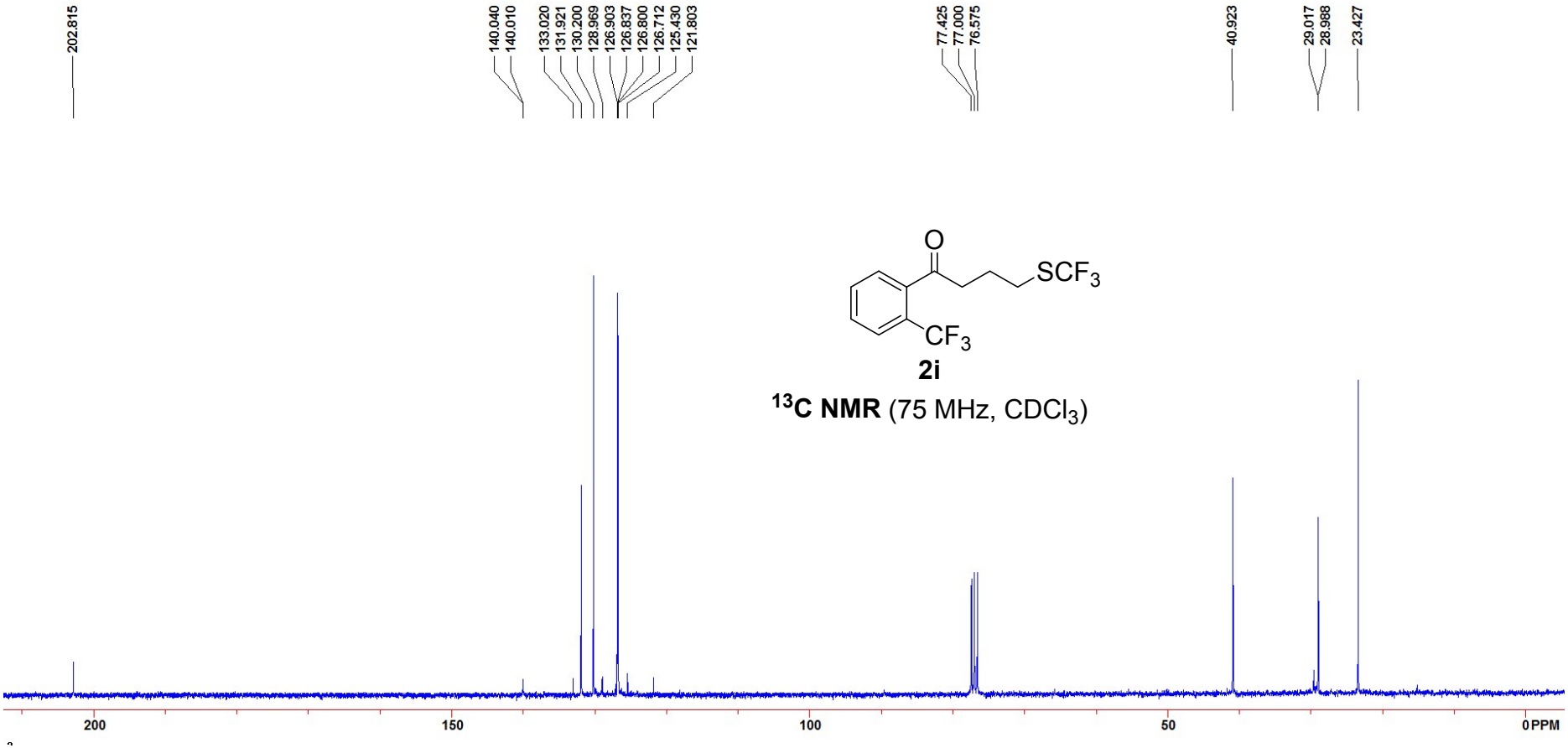
^{19}F NMR (282 MHz, $CDCl_3$)



2i

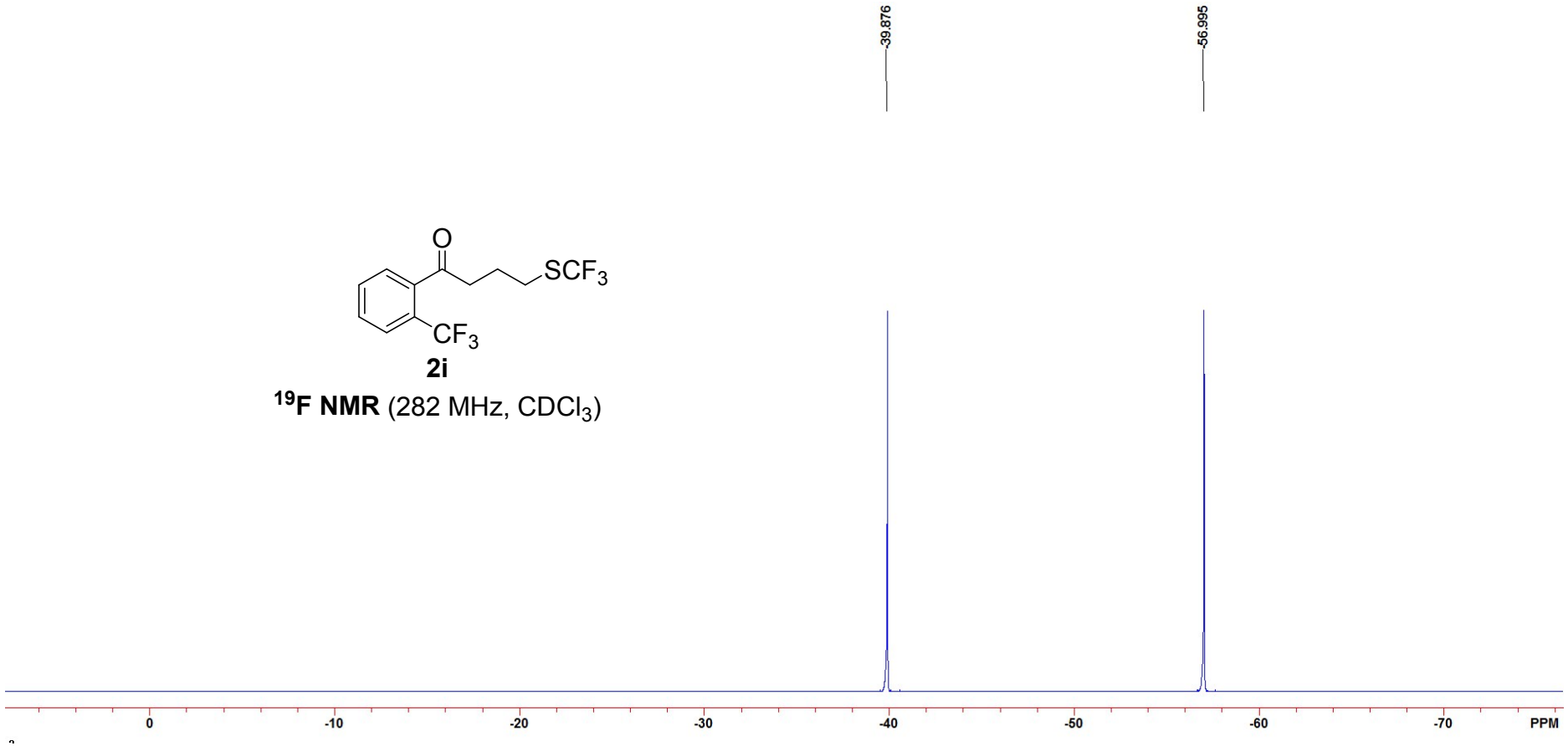
^{1}H NMR (300 MHz, $CDCl_3$)





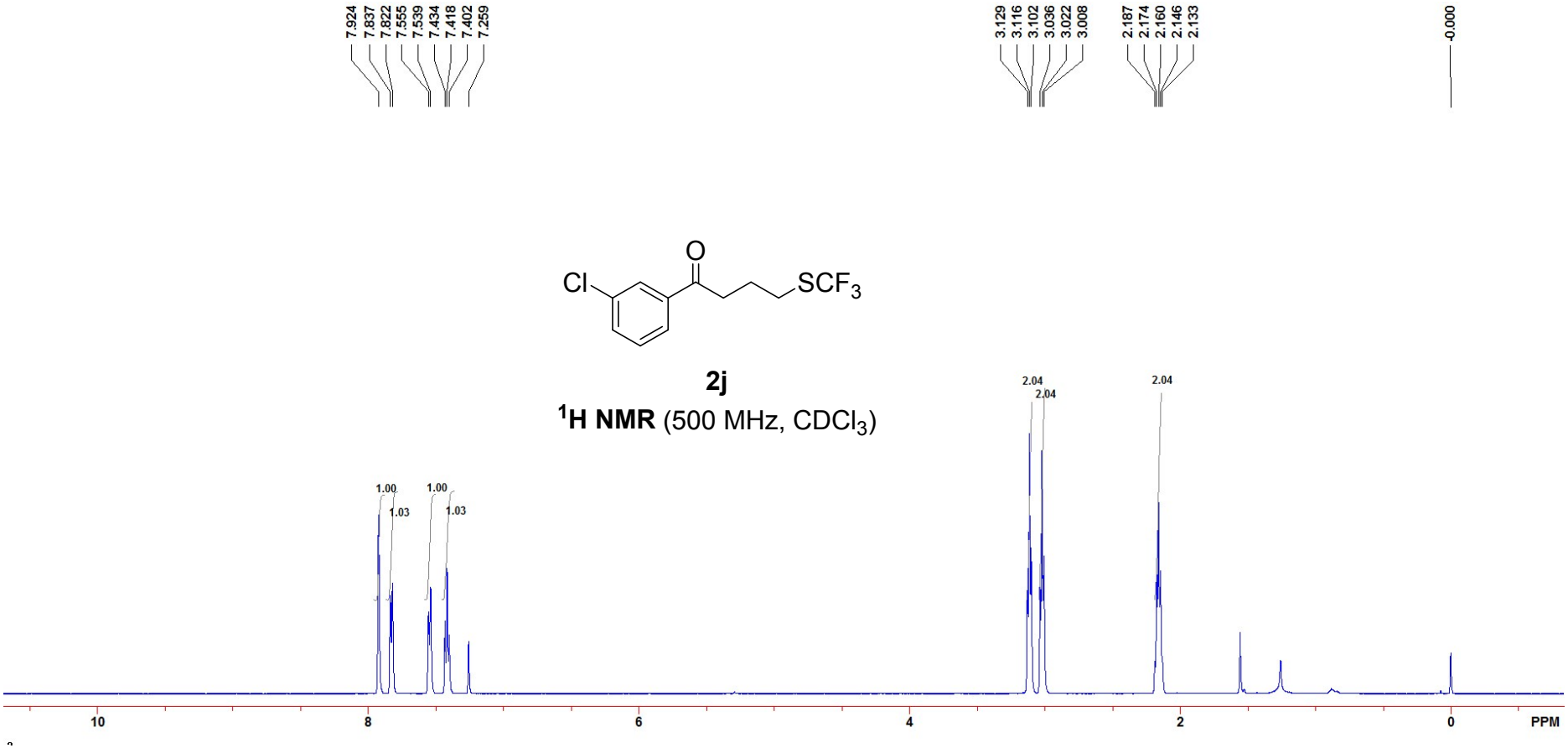
2i

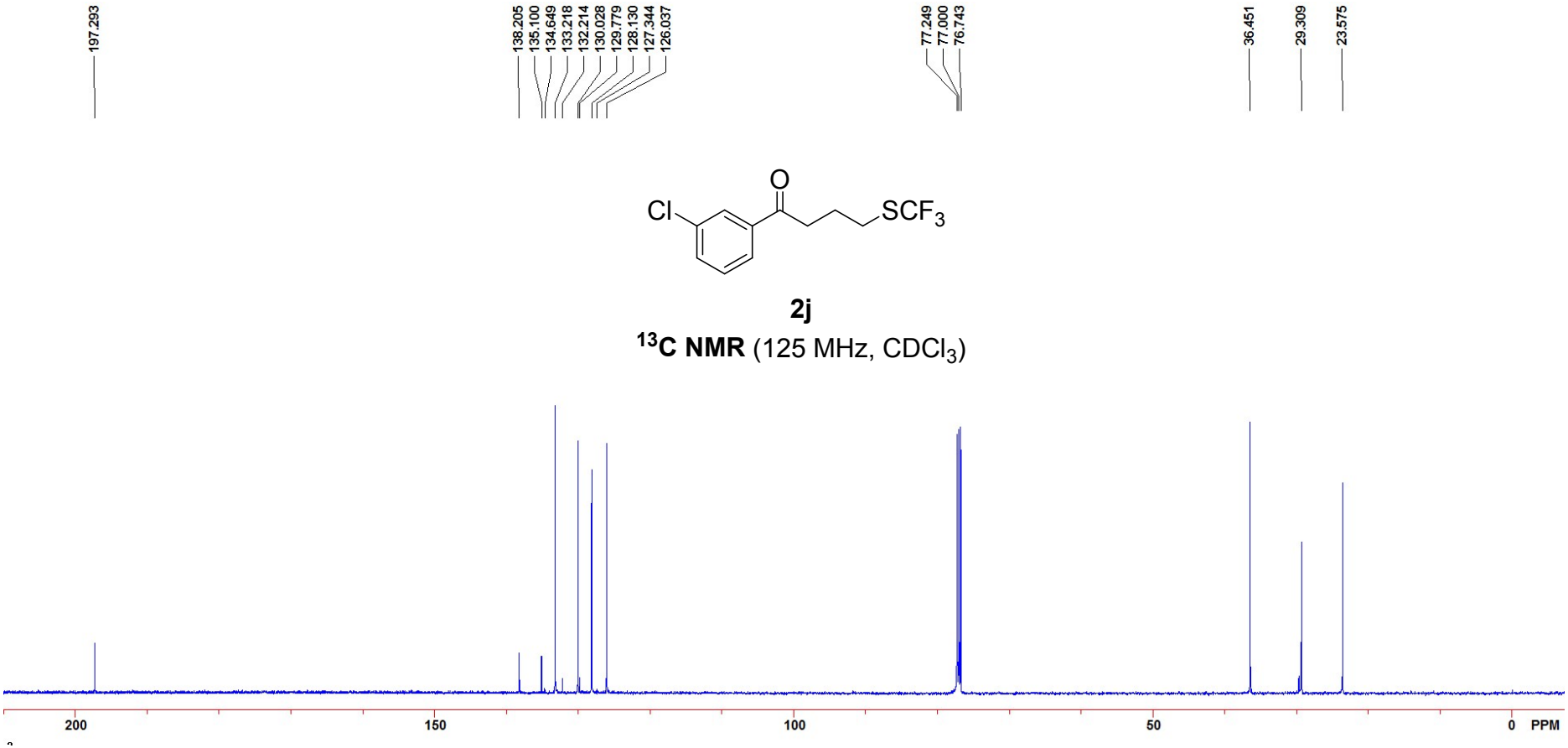
^{13}C NMR (75 MHz, $CDCl_3$)



2i

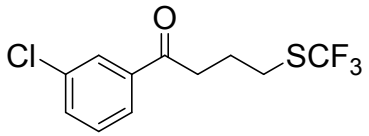
^{19}F NMR (282 MHz, $CDCl_3$)


7.924
7.837
7.822
7.555
7.539
7.434
7.418
7.402
7.259
3.129
3.116
3.102
3.036
3.022
3.008
2.187
2.174
2.160
2.146
2.133
0.000
Cl
O
SCF3
2j
1H NMR (500 MHz, CDCl3)
1.00
1.03
1.00
1.03
2.04
2.04
2.04
10
8
6
4
2
0
PPM



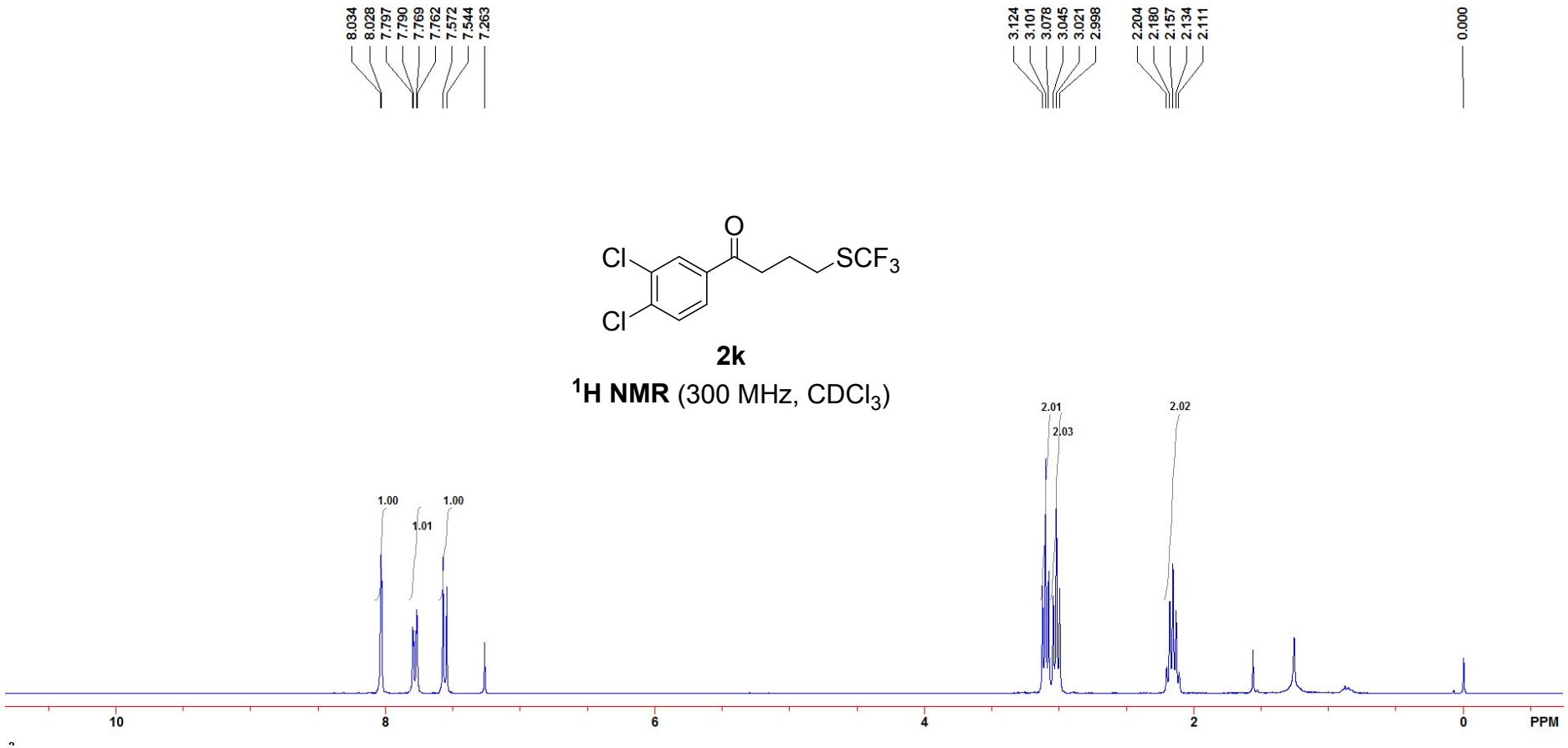
2j

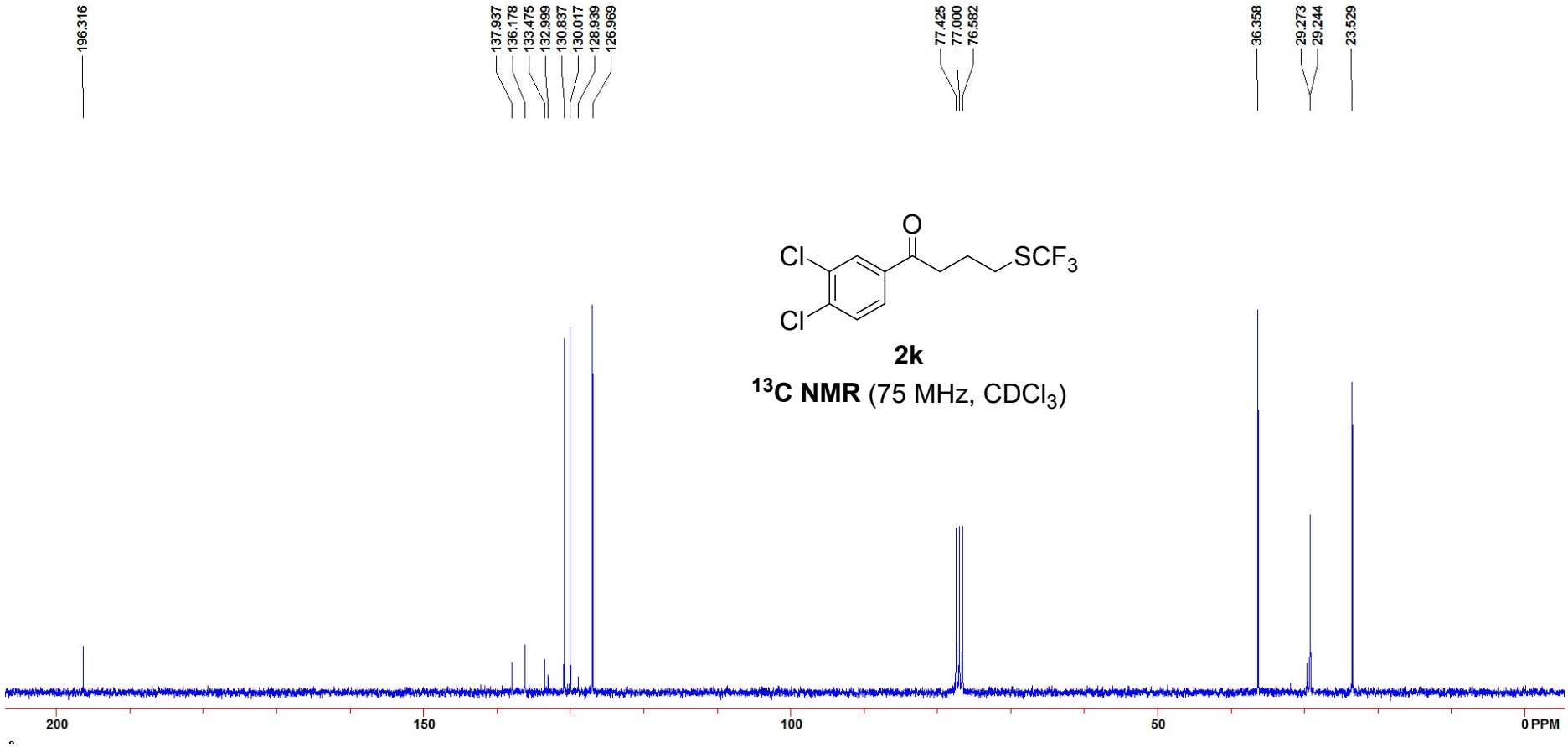
^{13}C NMR (125 MHz, $CDCl_3$)



2j

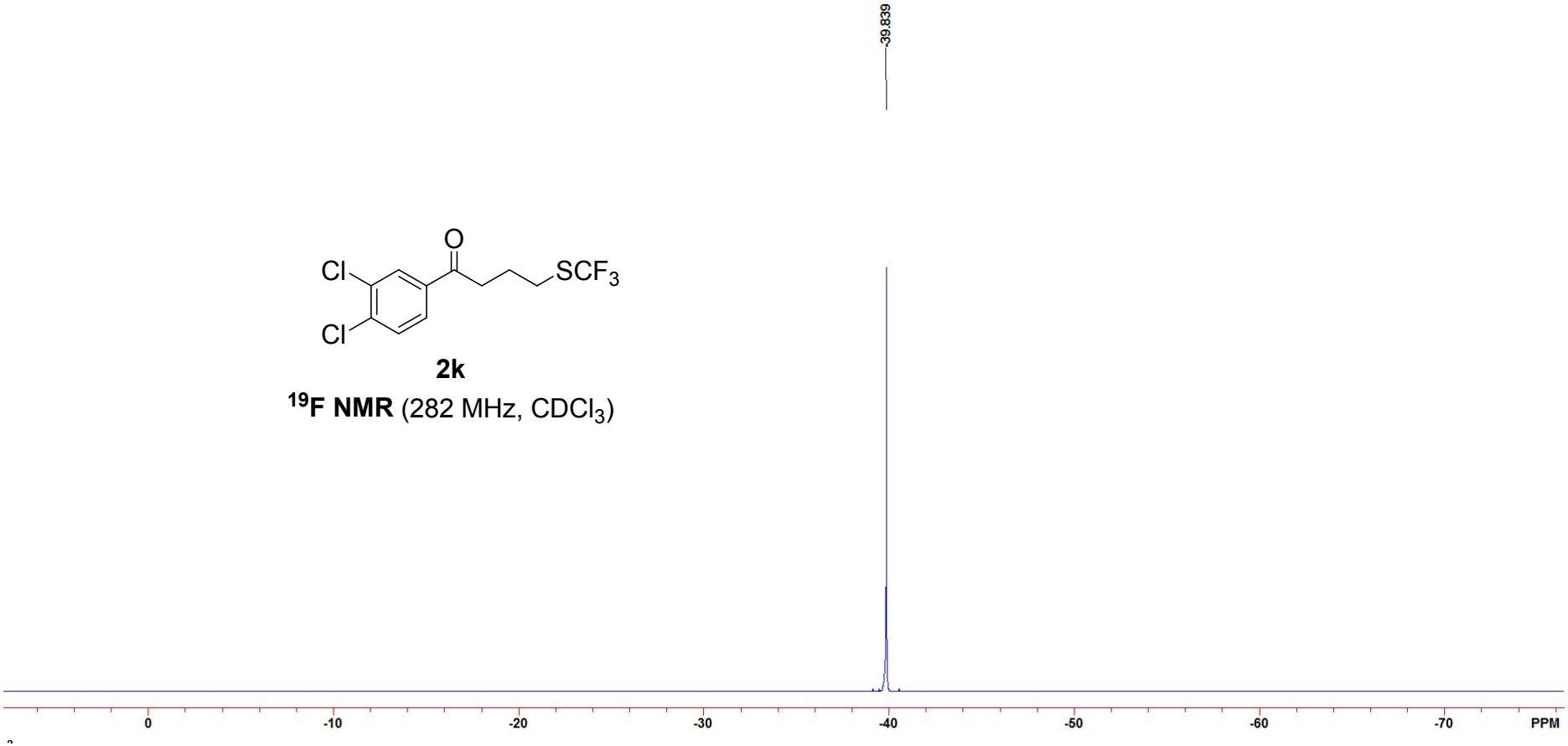
^{19}F NMR (282 MHz, $CDCl_3$)


8.034
8.028
7.797
7.790
7.769
7.762
7.572
7.544
7.263
3.124
3.101
3.078
3.045
3.021
2.998
2.204
2.180
2.157
2.134
2.111
0.000
O
Cl
Cl
SCF3
2k
1H NMR (300 MHz, CDCl3)
1.00
1.01
1.00
2.01
2.03
2.02
10
8
6
4
2
0
PPM



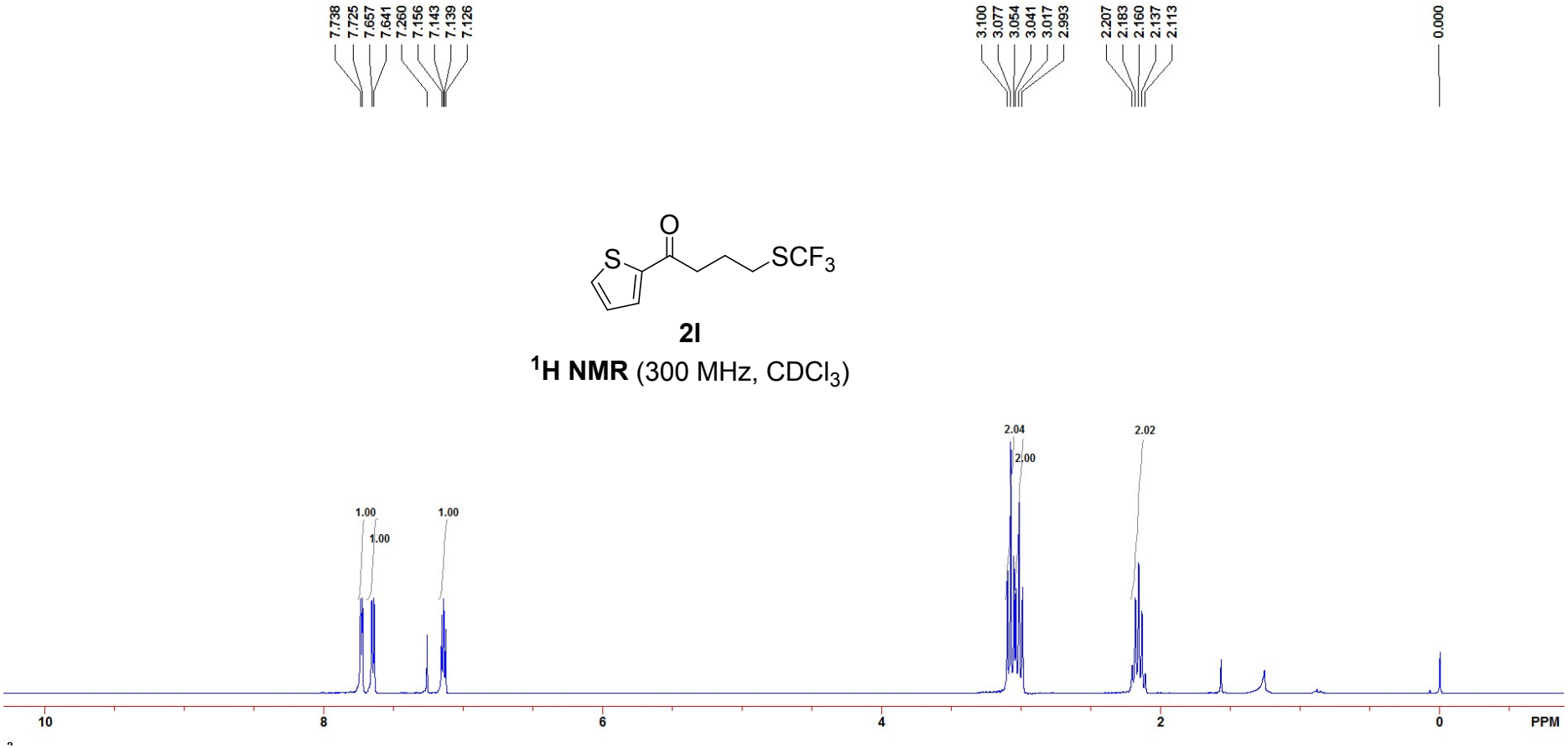
2k

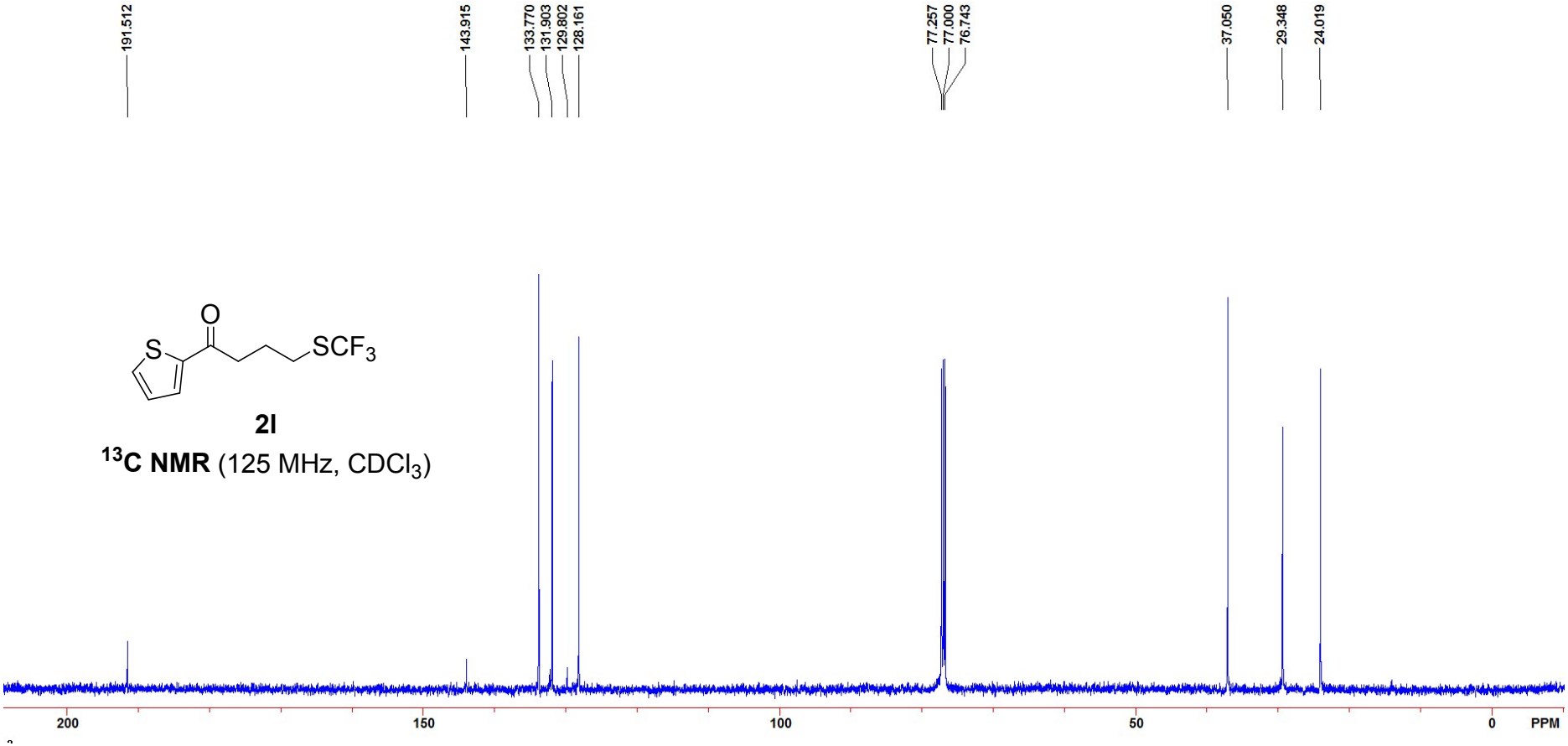
^{13}C NMR (75 MHz, $CDCl_3$)



2k

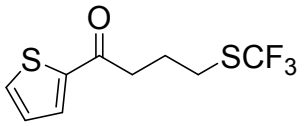
^{19}F NMR (282 MHz, $CDCl_3$)


7.738
7.725
7.657
7.641
7.260
7.156
7.143
7.139
7.126
3.100
3.077
3.054
3.041
3.017
2.993
2.207
2.183
2.160
2.137
2.113
0.000
O
S
SCF3
2l
1H NMR (300 MHz, CDCl3)
1.00
1.00
1.00
2.04
2.00
2.02
10
8
6
4
2
0
PPM



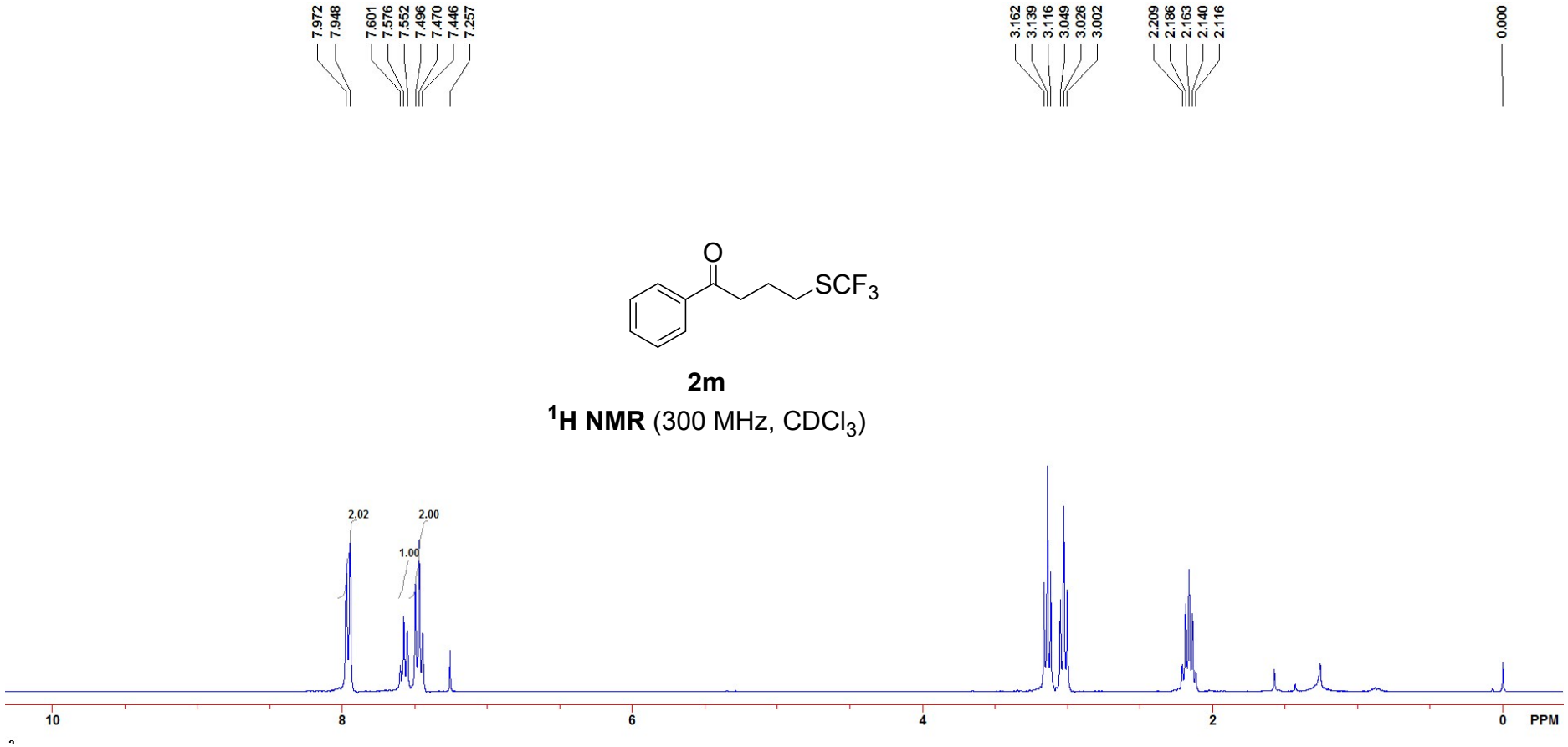
2l

^{13}C NMR (125 MHz, $CDCl_3$)



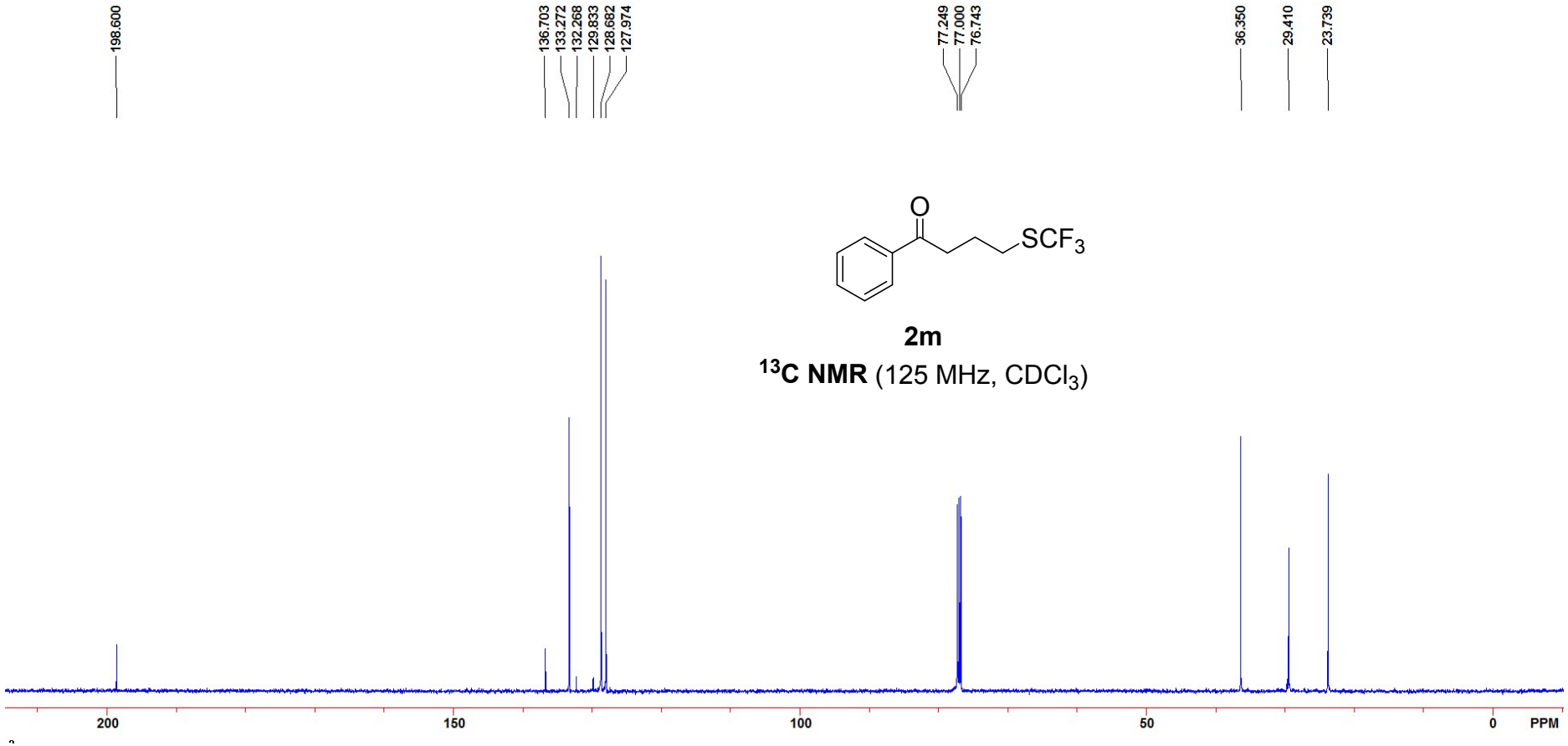
2l

^{19}F NMR (282 MHz, $CDCl_3$)



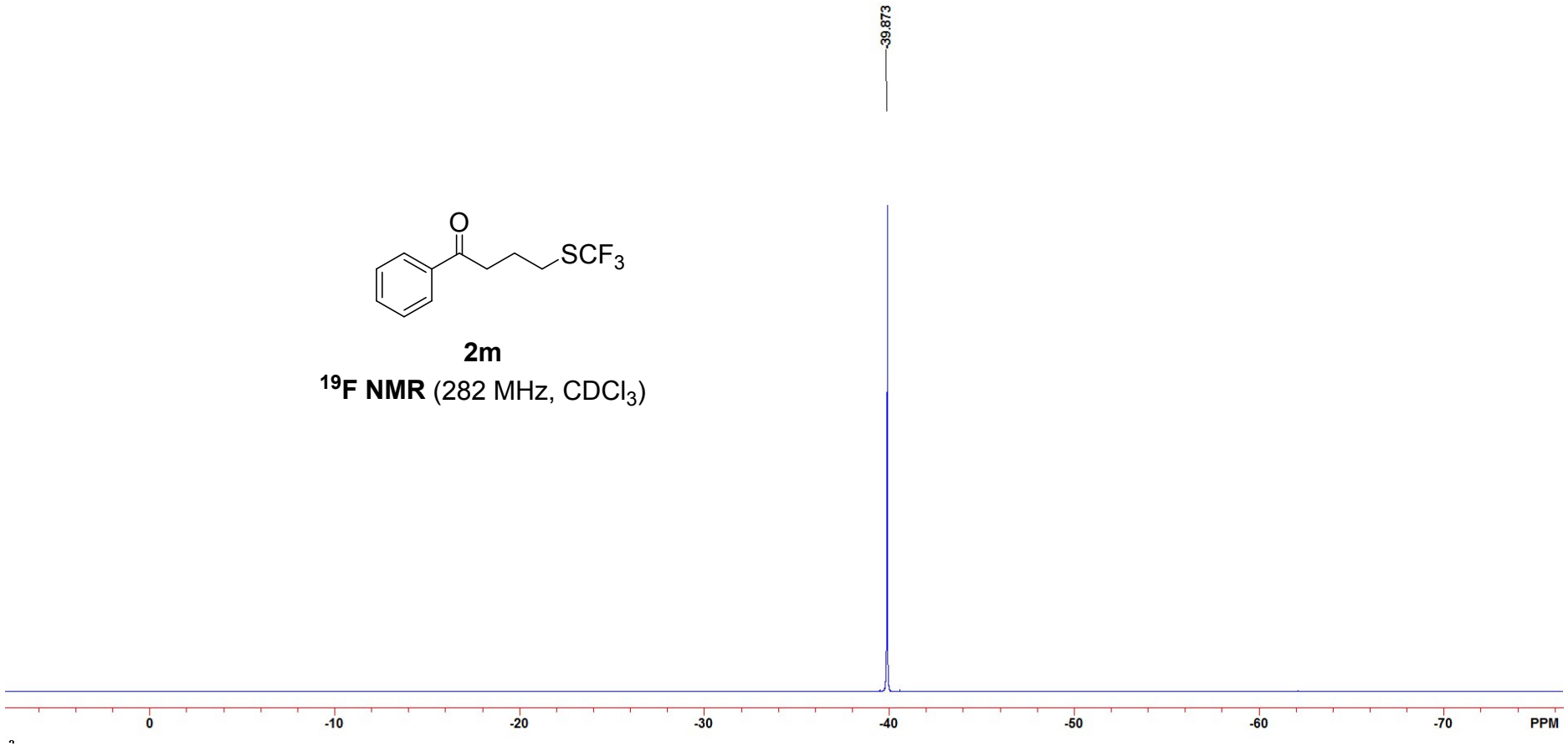
2m

^{1}H NMR (300 MHz, $CDCl_3$)



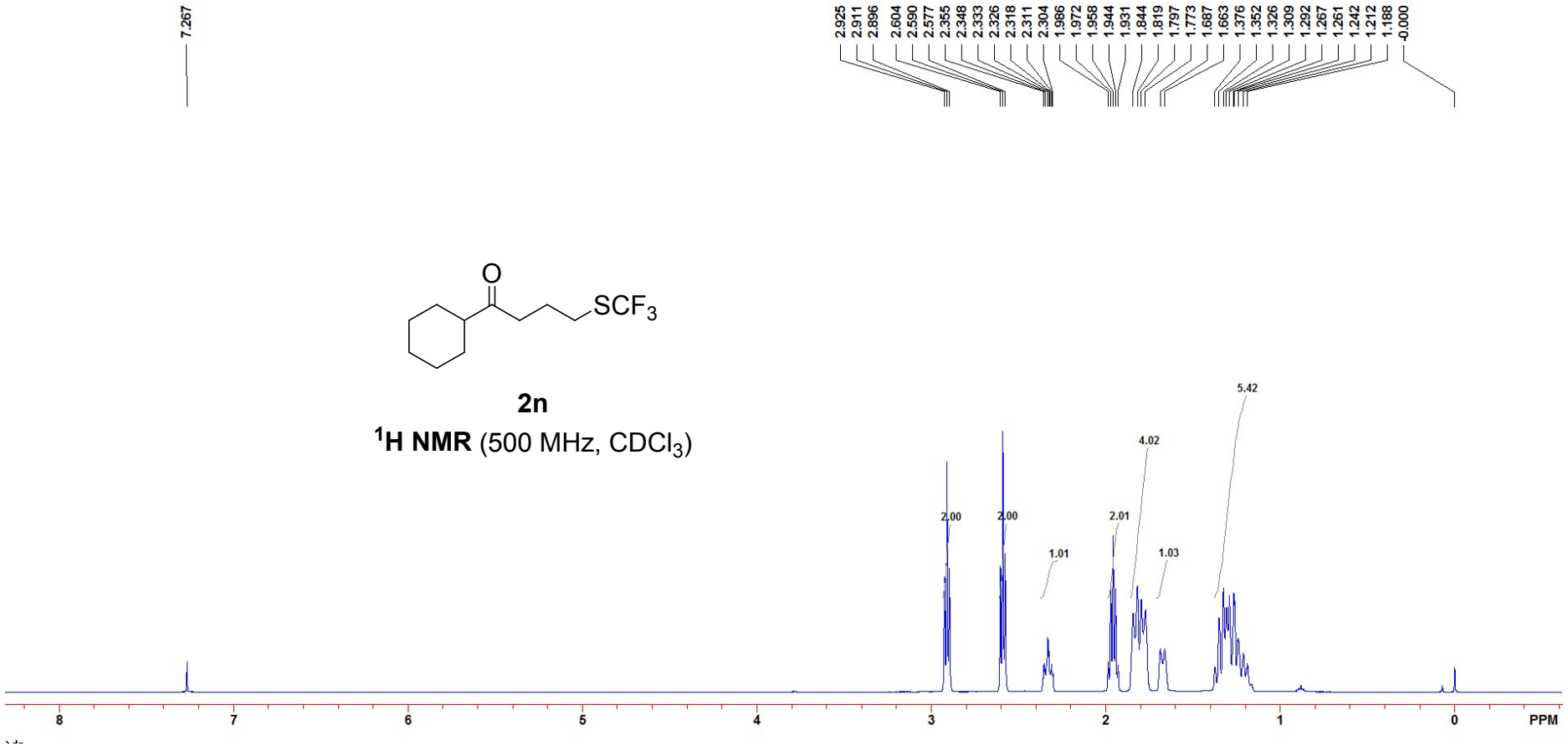
2m

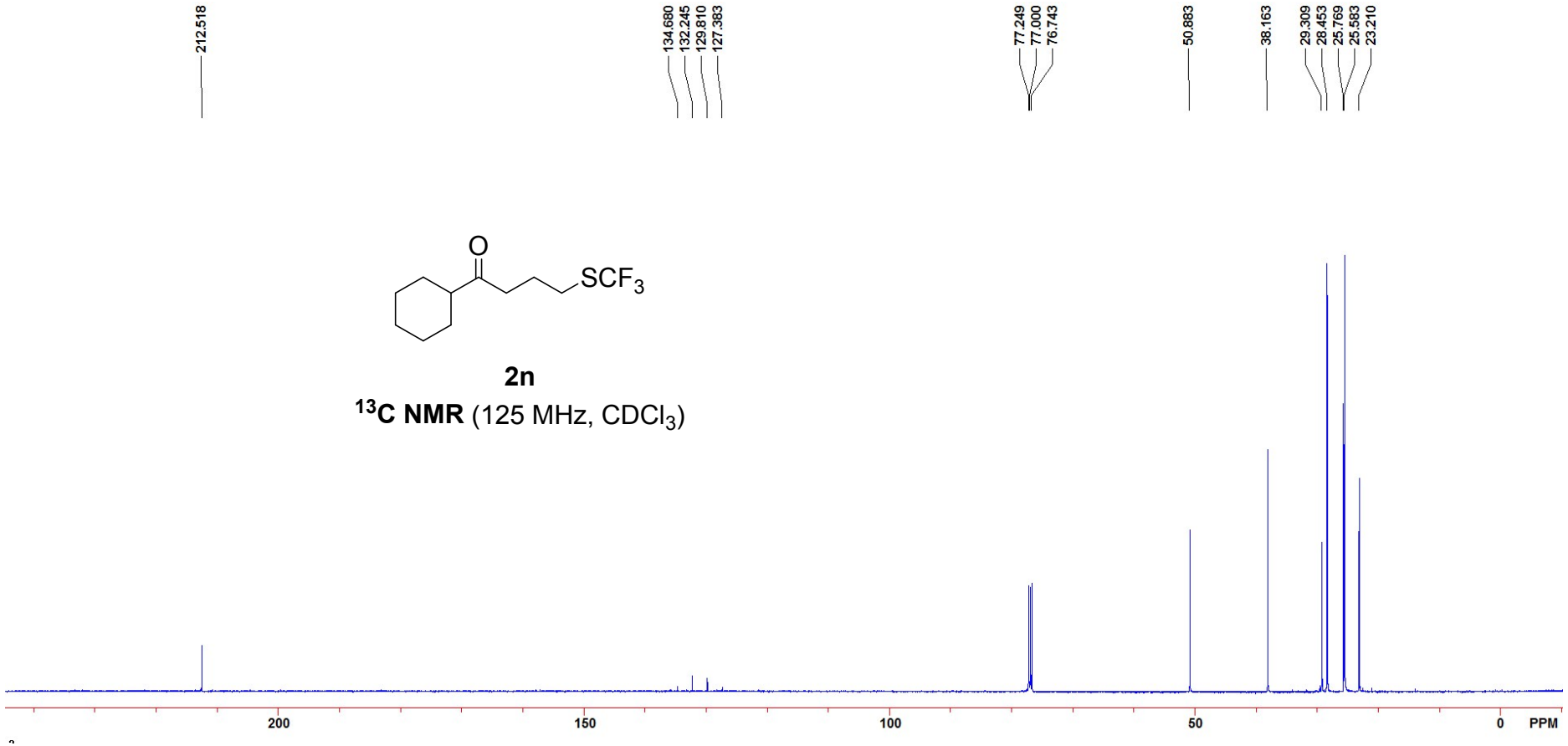
^{13}C NMR (125 MHz, $CDCl_3$)



2m

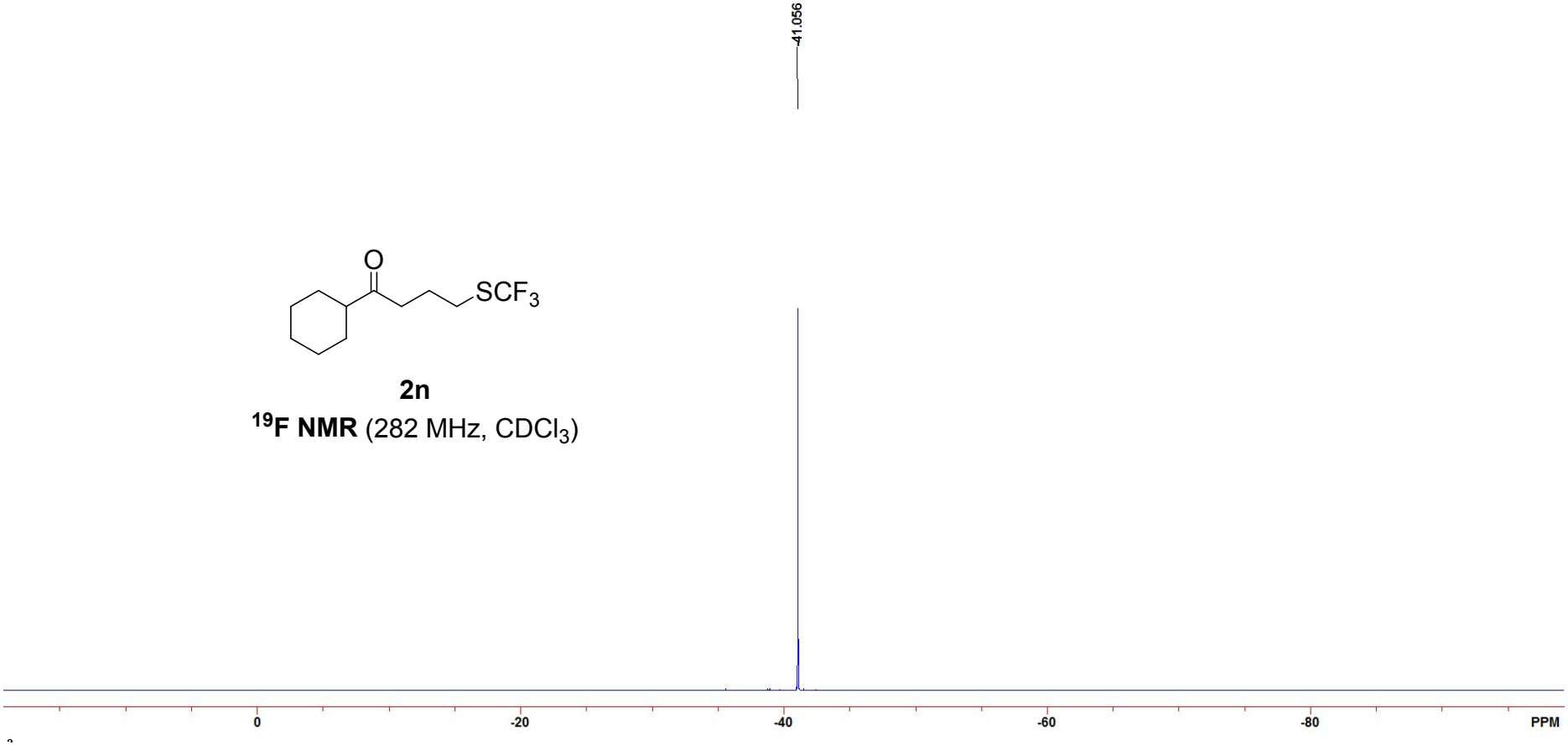
^{19}F NMR (282 MHz, $CDCl_3$)


7.267
2.925
2.911
2.896
2.604
2.590
2.577
2.355
2.348
2.333
2.326
2.318
2.311
2.304
1.986
1.972
1.958
1.944
1.931
1.844
1.819
1.797
1.773
1.687
1.663
1.376
1.352
1.326
1.309
1.292
1.267
1.261
1.242
1.212
1.188
0.000
O
SCF3
2n
1H NMR (500 MHz, CDCl3)
5.42
4.02
2.00
2.00
2.01
1.01
1.03
8
7
6
5
4
3
2
1
0
PPM



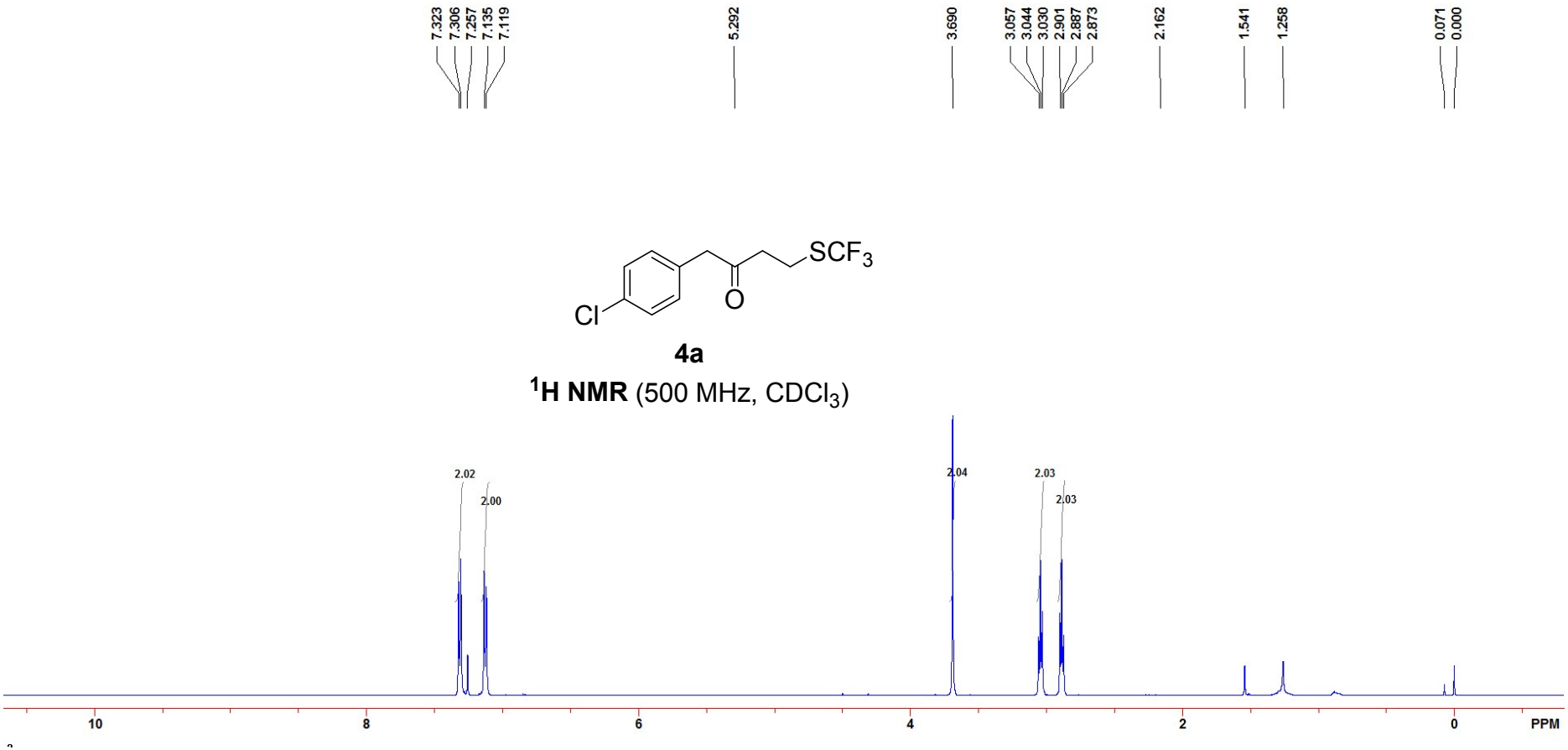
2n

^{13}C NMR (125 MHz, $CDCl_3$)



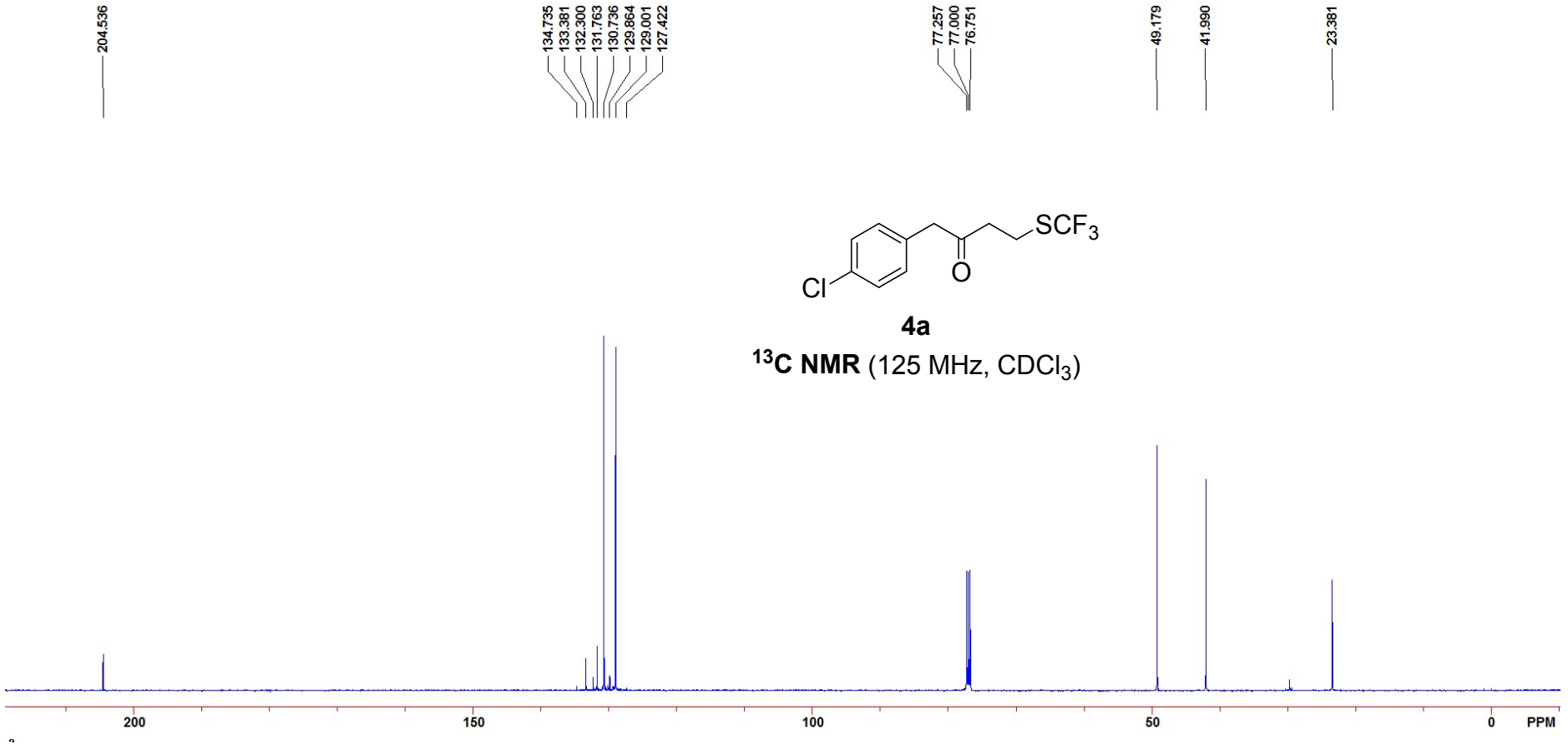
2n

^{19}F NMR (282 MHz, $CDCl_3$)



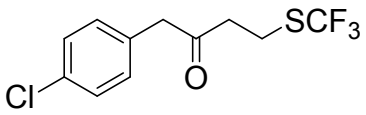
4a

^{1}H NMR (500 MHz, $CDCl_3$)



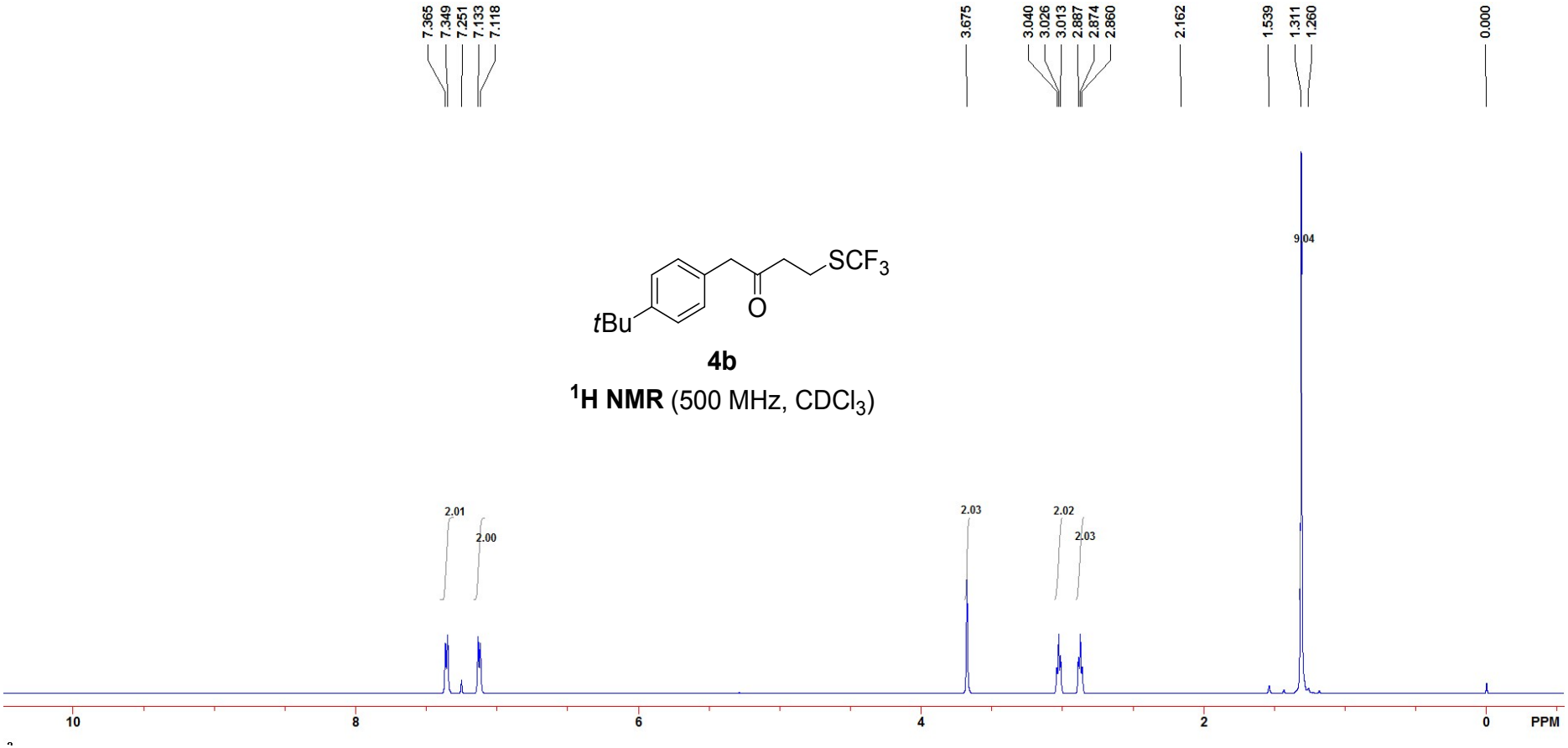
4a

^{13}C NMR (125 MHz, $CDCl_3$)



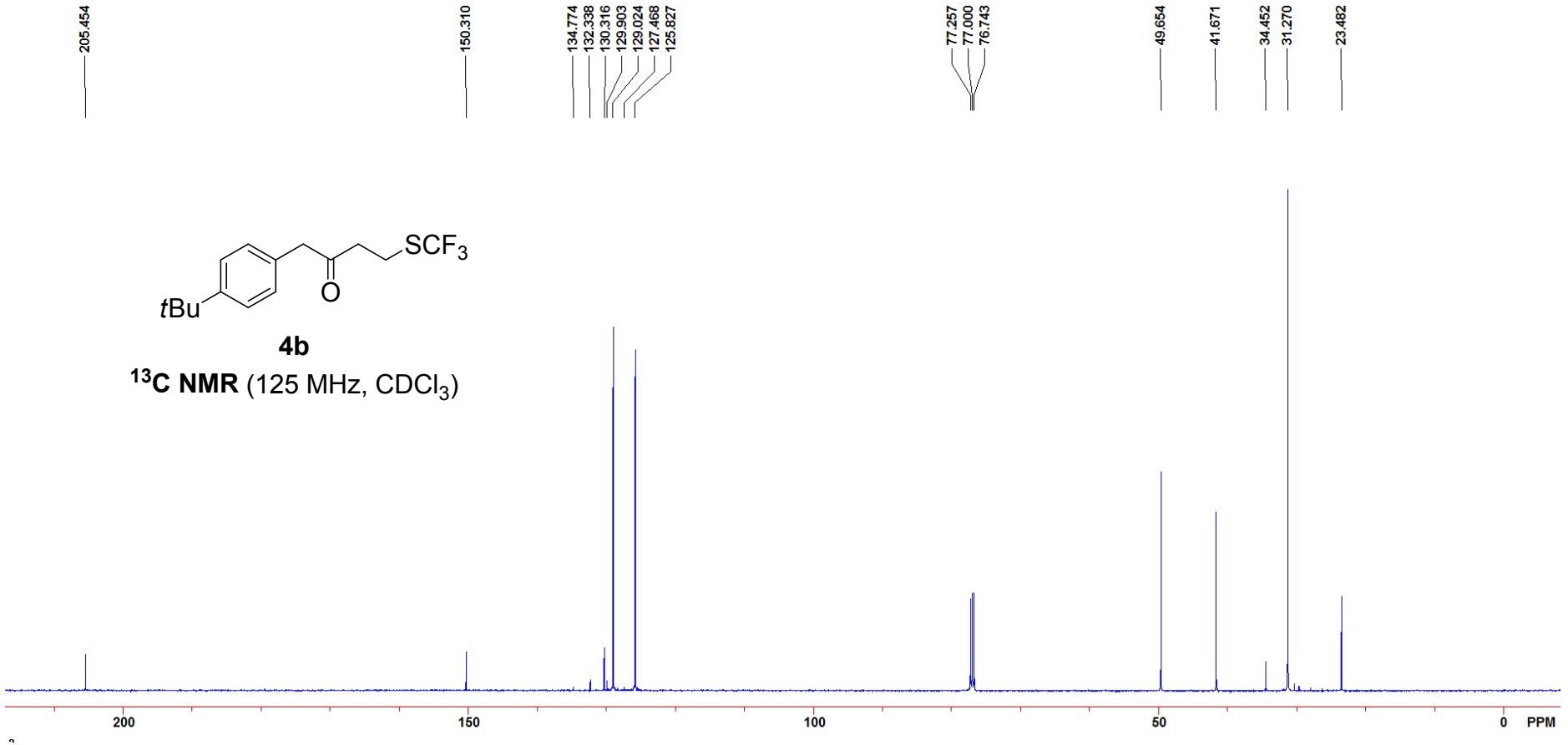
4a

^{19}F NMR (282 MHz, $CDCl_3$)



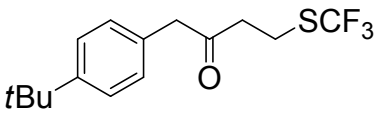
4b

^{1}H NMR (500 MHz, $CDCl_3$)



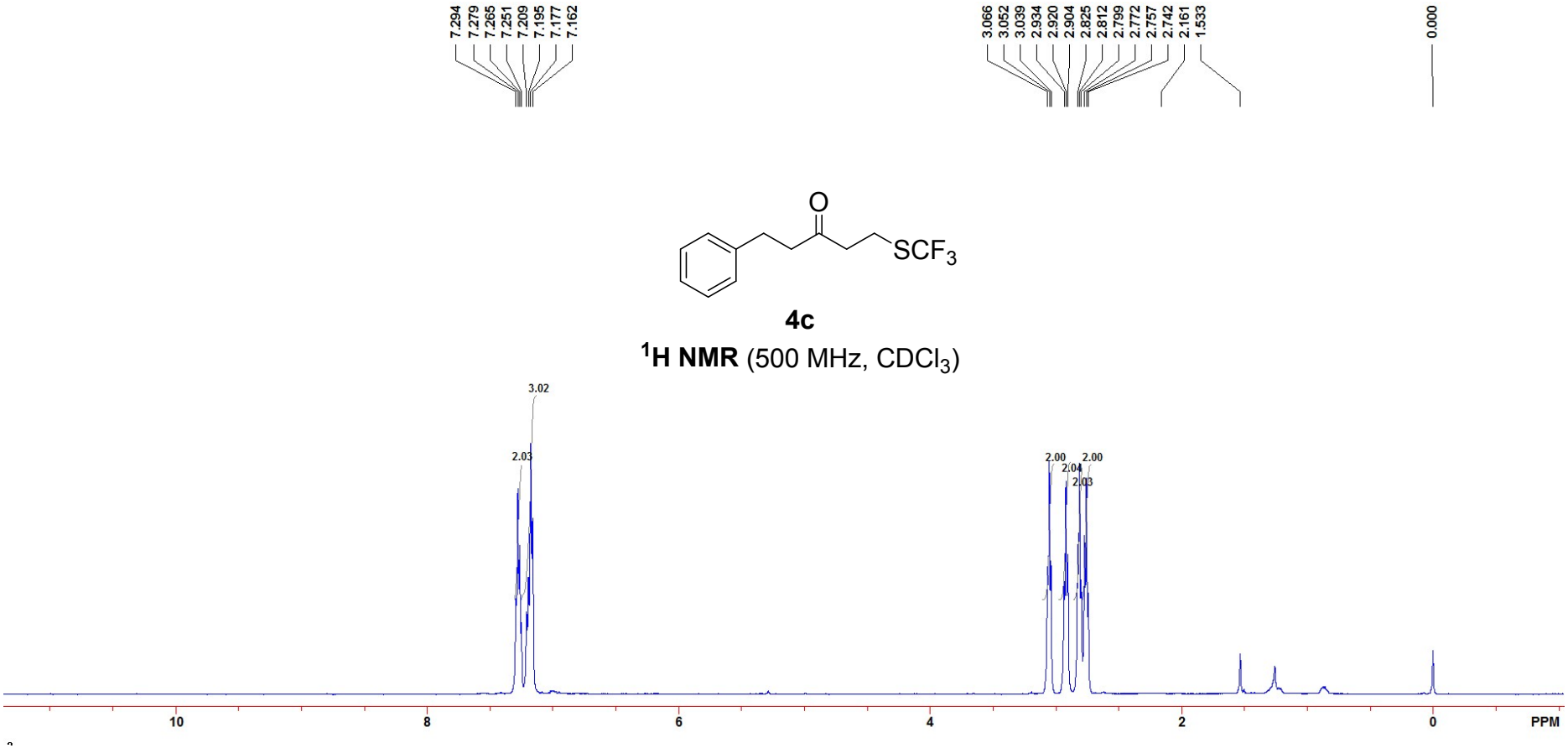
4b

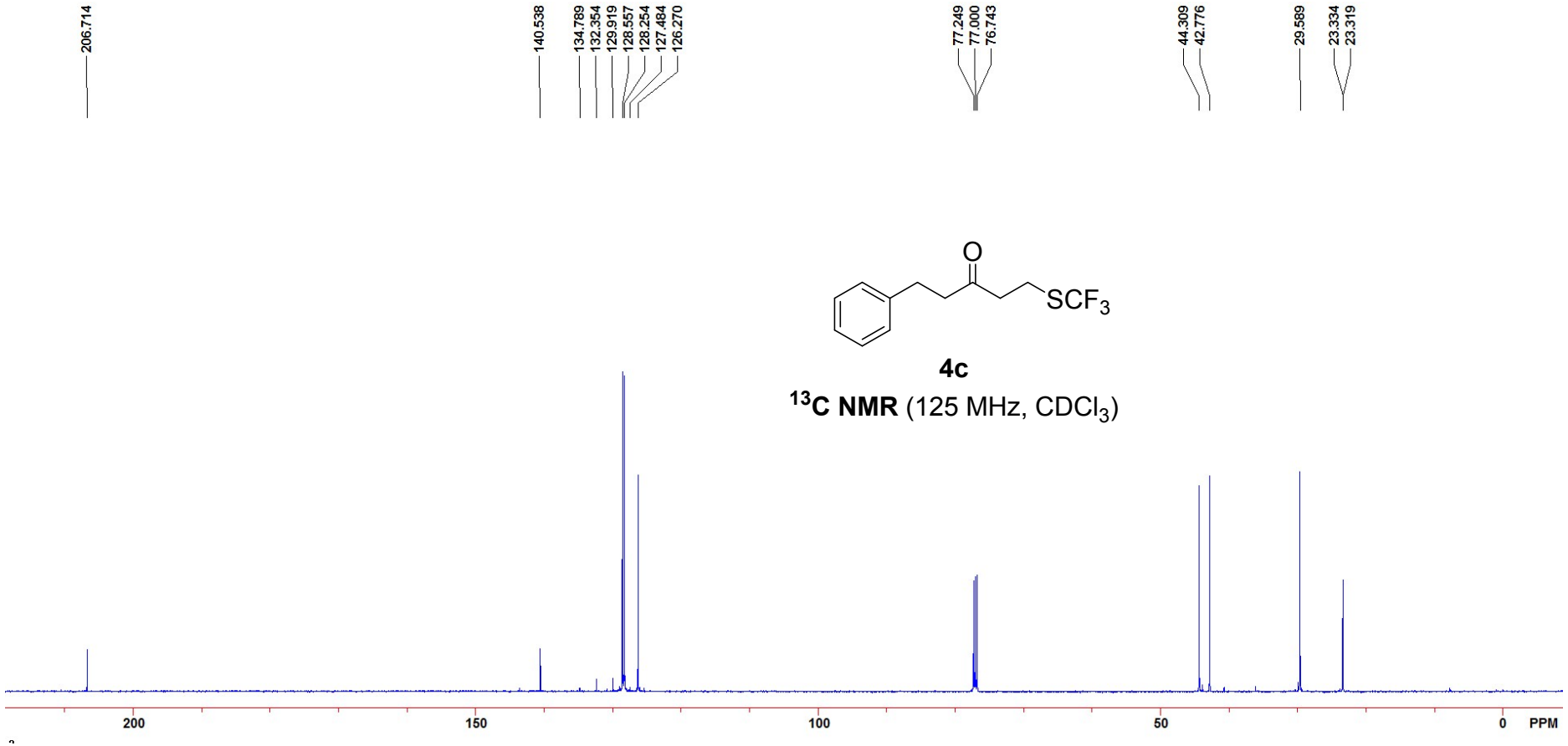
^{13}C NMR (125 MHz, $CDCl_3$)



4b

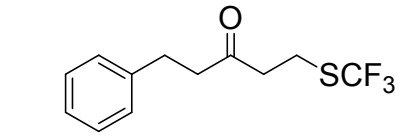
^{19}F NMR (282 MHz, $CDCl_3$)


7.294
7.279
7.265
7.251
7.209
7.195
7.177
7.162
3.066
3.052
3.039
2.934
2.920
2.904
2.825
2.812
2.799
2.772
2.757
2.742
2.161
1.533
0.000
O
SCF3
4c
1H NMR (500 MHz, CDCl3)
3.02
2.03
2.00
2.04
2.03
2.00
10
8
6
4
2
0
PPM



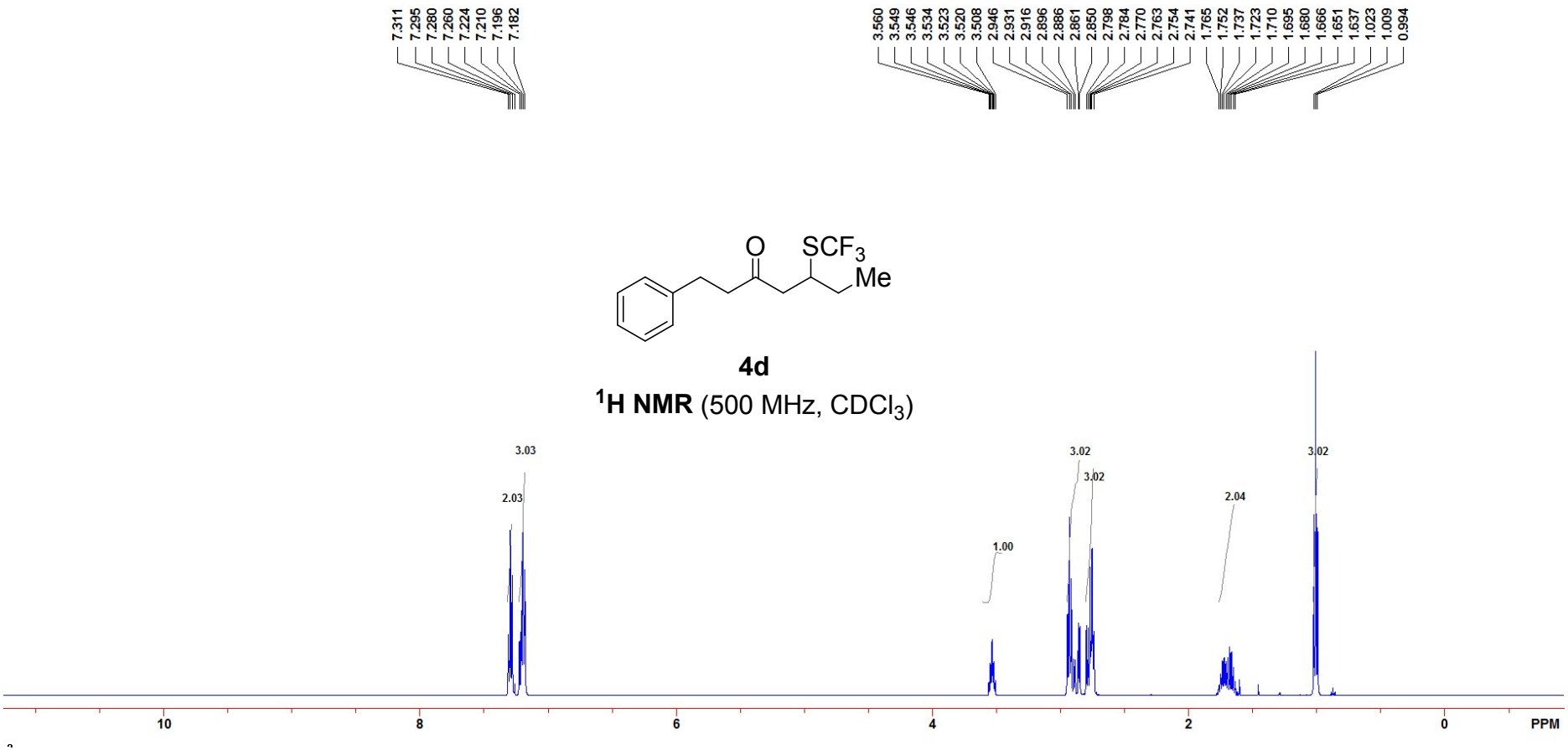
4c

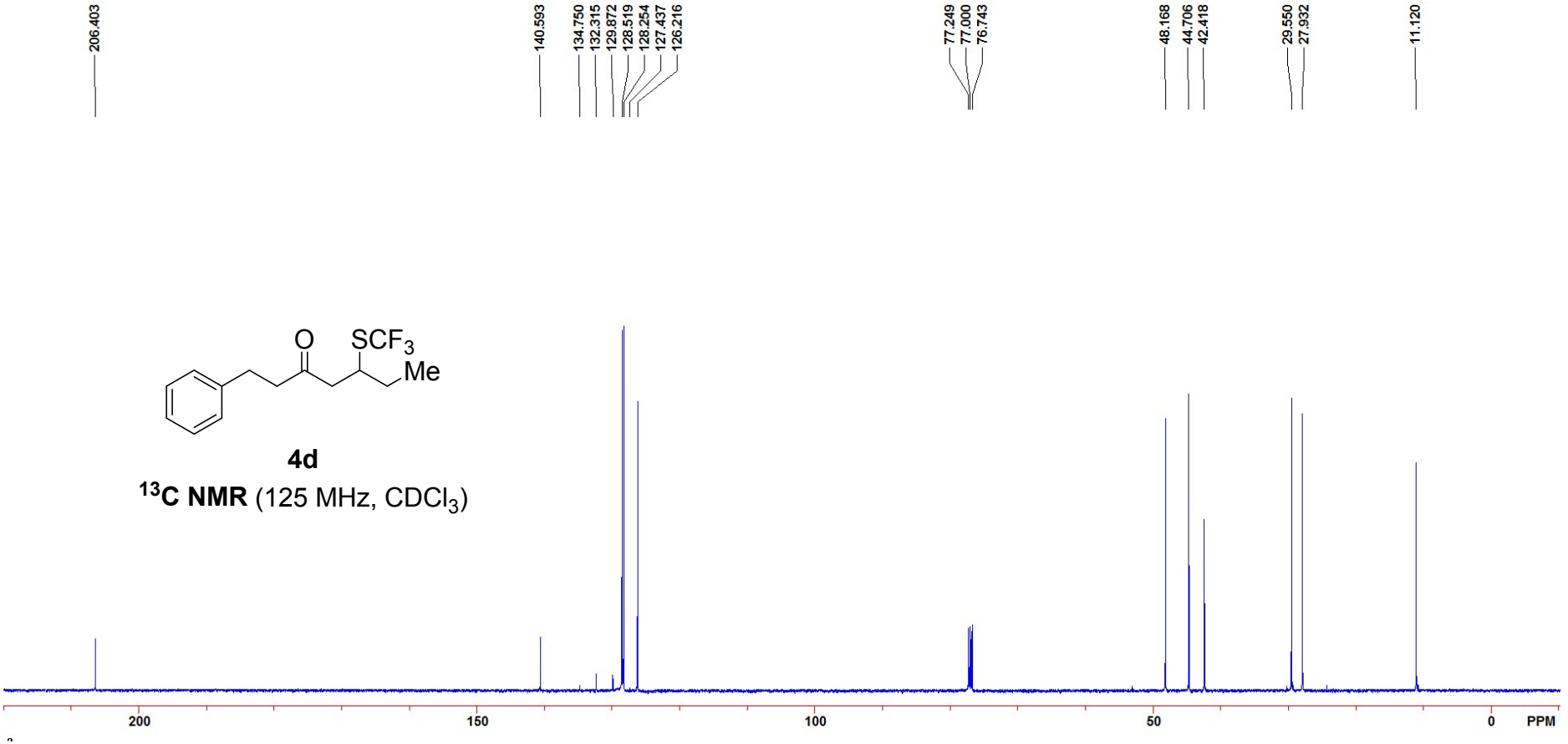
^{13}C NMR (125 MHz, $CDCl_3$)



4c

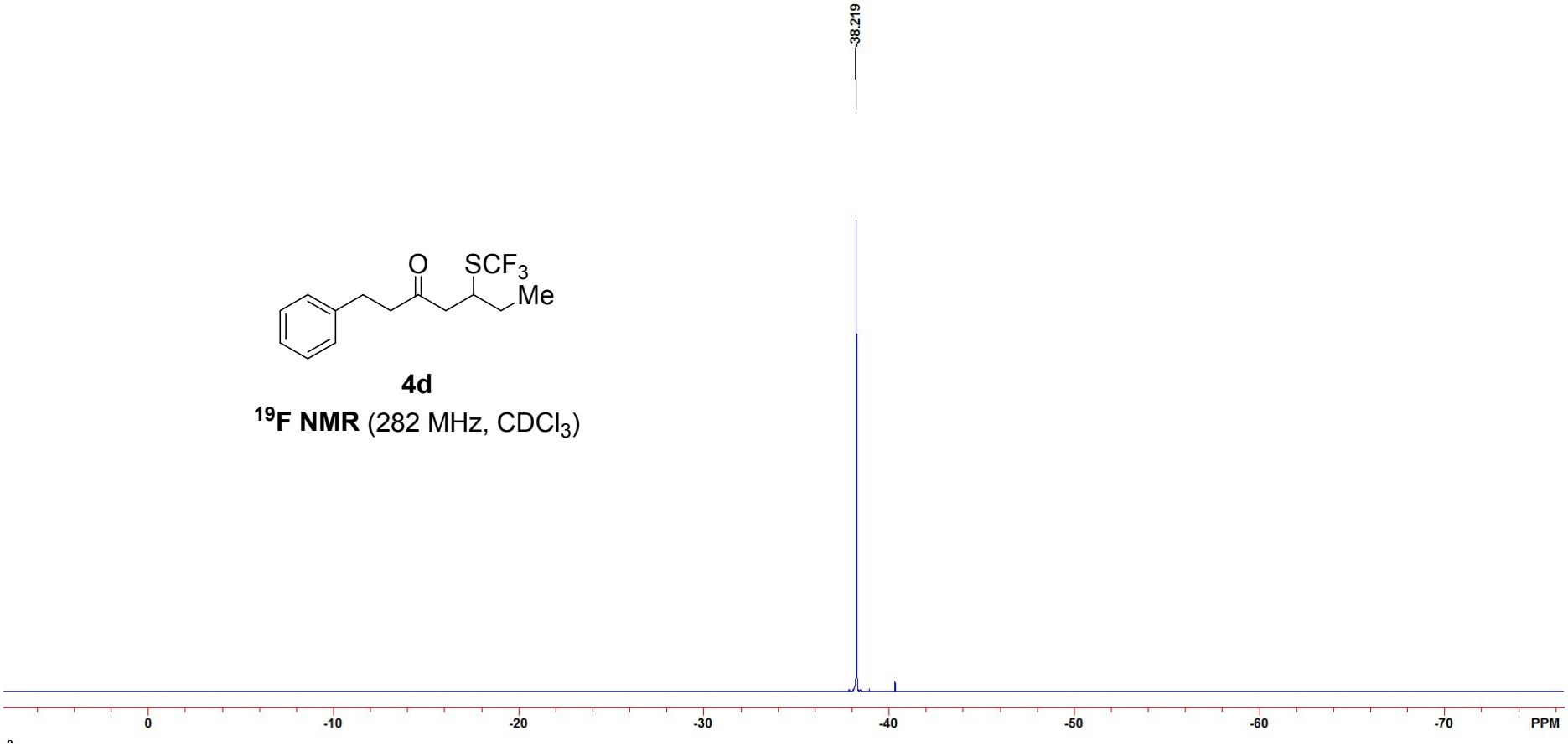
^{19}F NMR (282 MHz, $CDCl_3$)


7.311
7.295
7.280
7.260
7.224
7.210
7.196
7.182
3.560
3.549
3.546
3.534
3.523
3.520
3.508
2.946
2.931
2.916
2.896
2.886
2.861
2.850
2.798
2.784
2.770
2.763
2.754
2.741
1.765
1.752
1.737
1.723
1.710
1.695
1.680
1.666
1.651
1.637
1.023
1.009
0.994
O
SCF3
Me
4d
1H NMR (500 MHz, CDCl3)
3.03
2.03
1.00
3.02
3.02
2.04
3.02
10
8
6
4
2
0
PPM



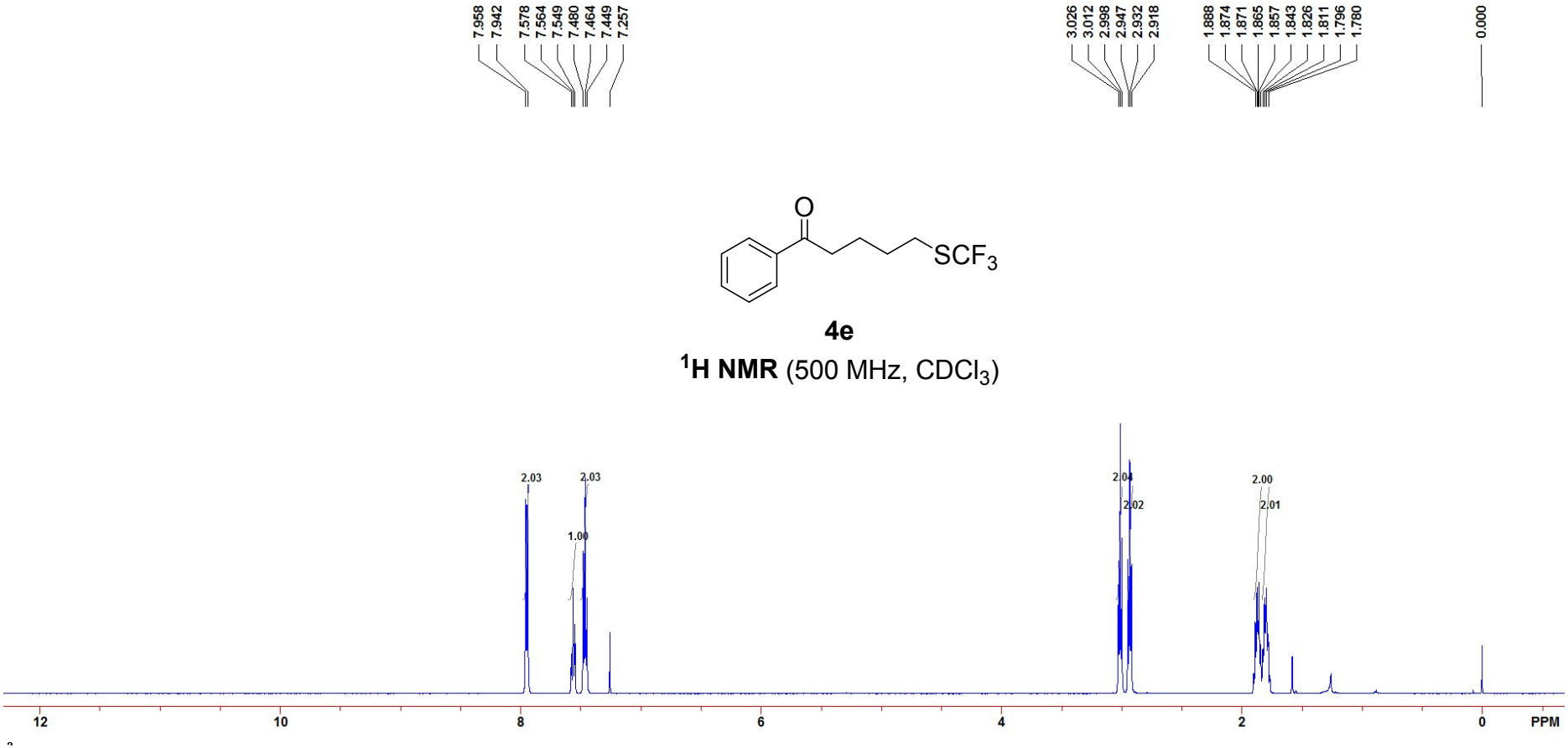
4d

^{13}C NMR (125 MHz, $CDCl_3$)



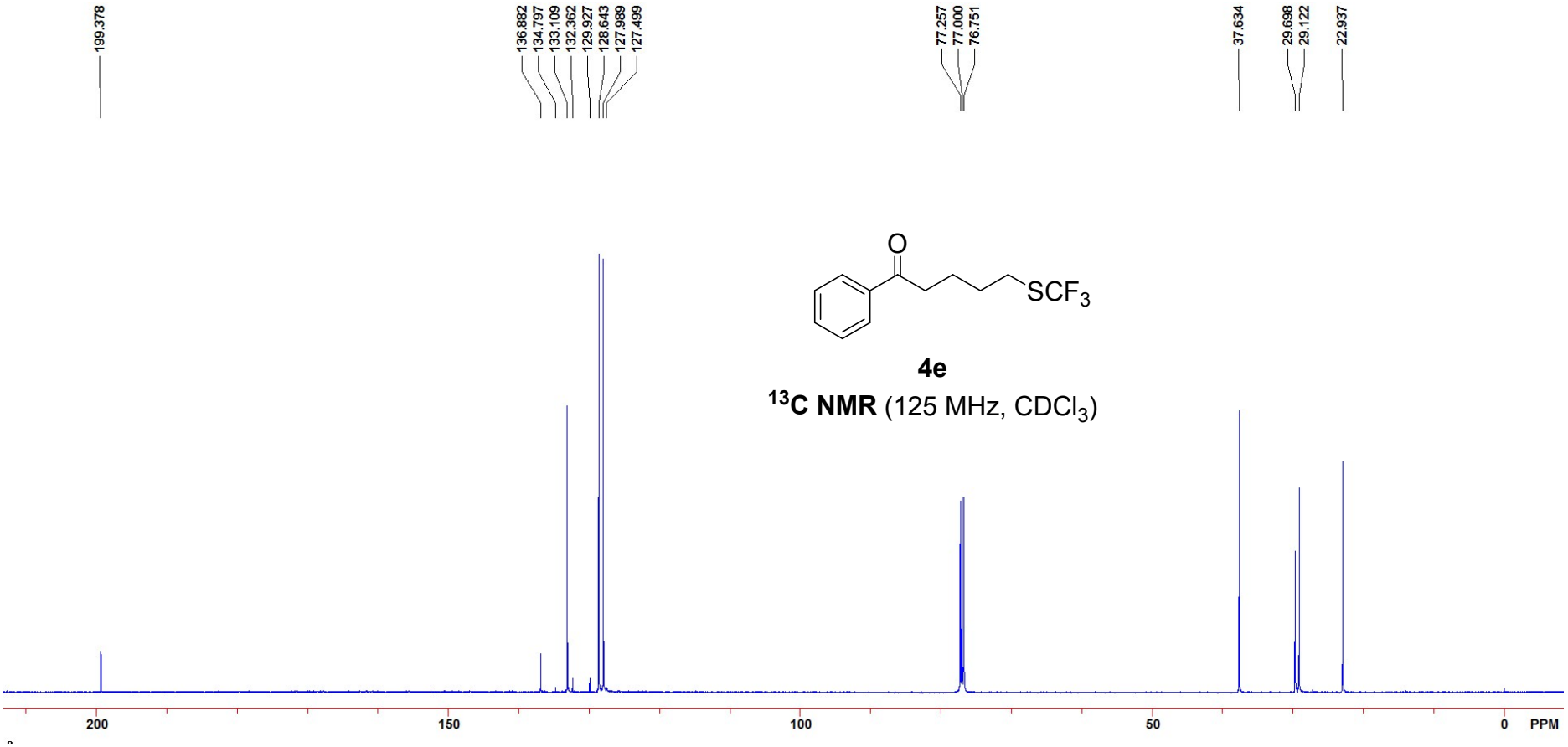
4d

^{19}F NMR (282 MHz, $CDCl_3$)



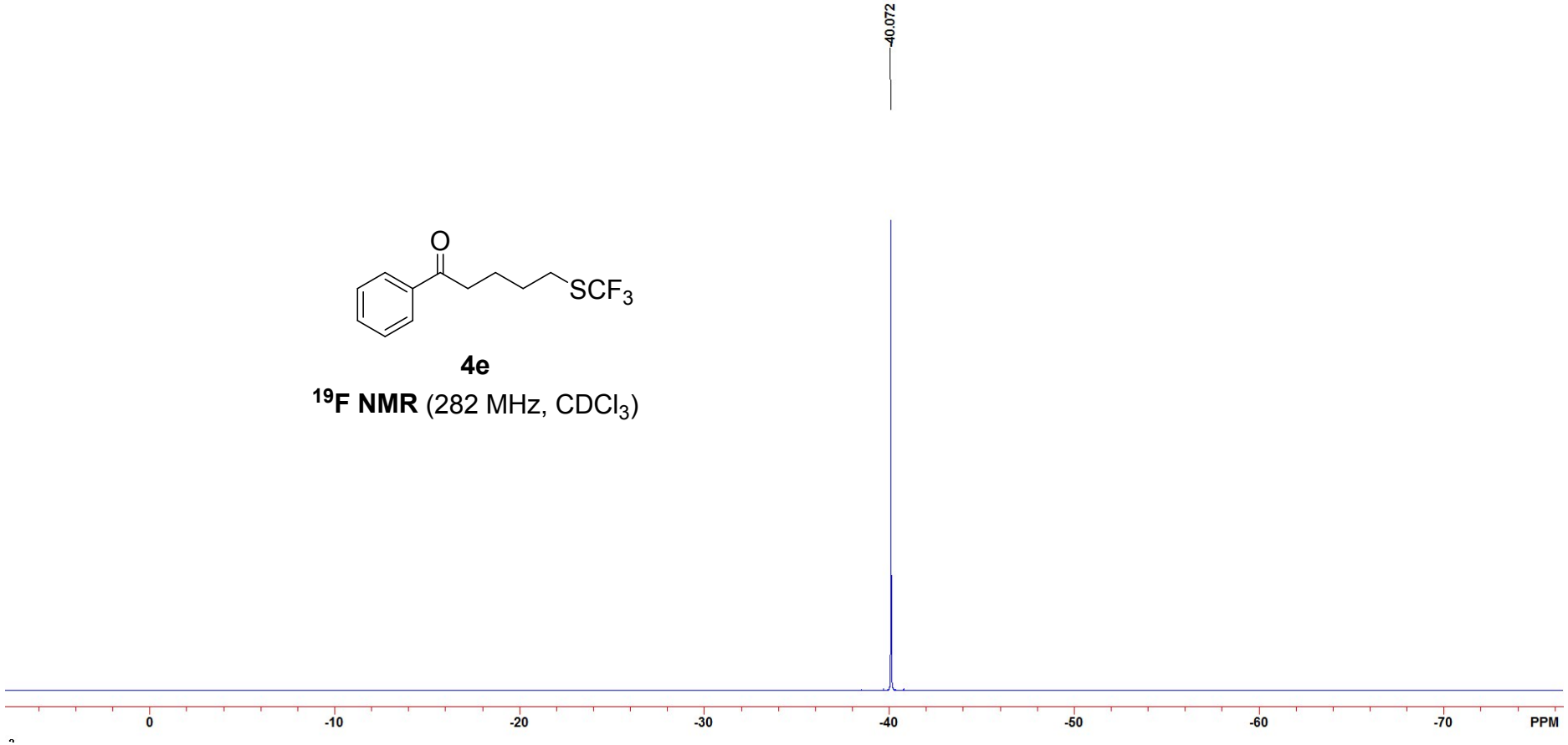
4e

^{1}H NMR (500 MHz, $CDCl_3$)



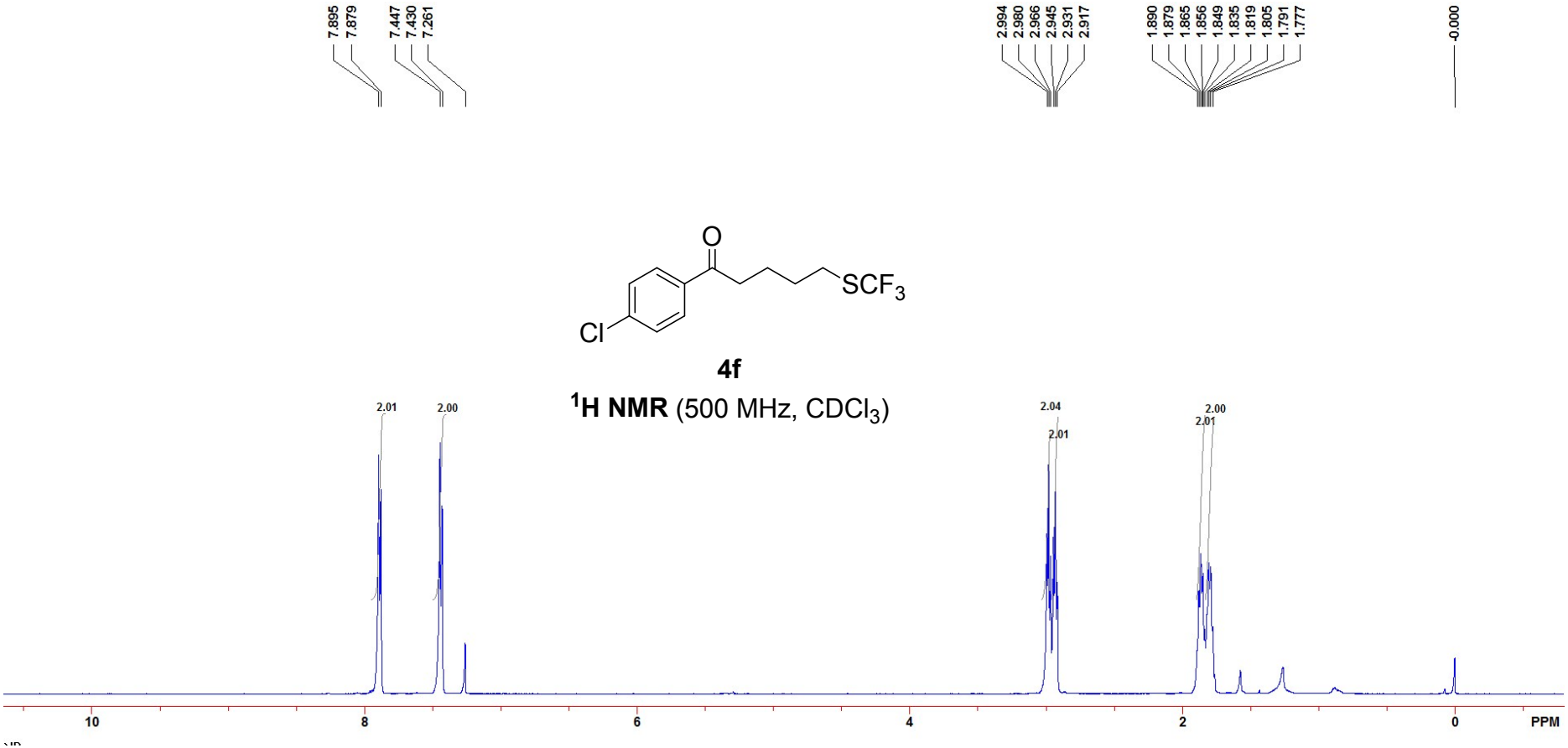
4e

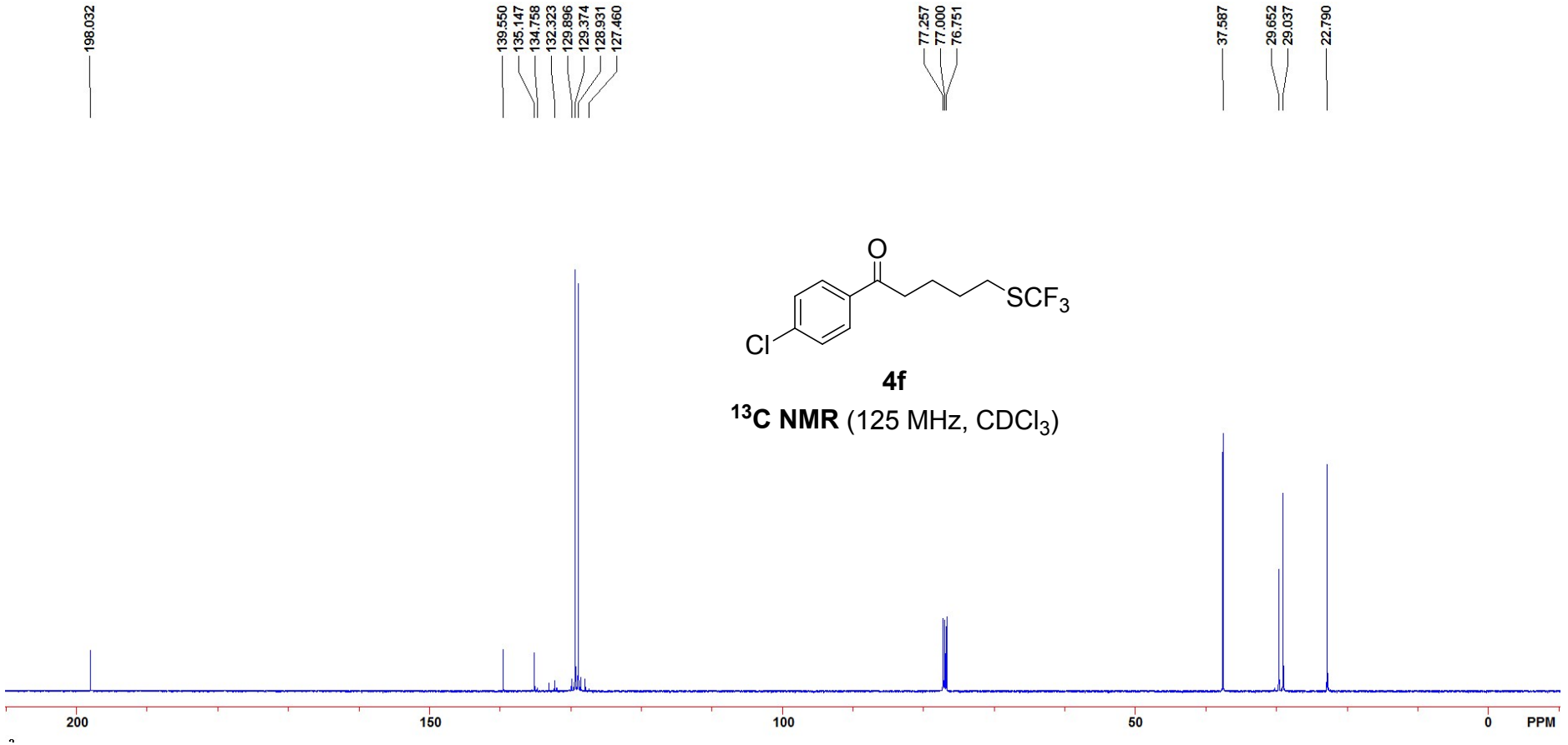
^{13}C NMR (125 MHz, $CDCl_3$)



4e

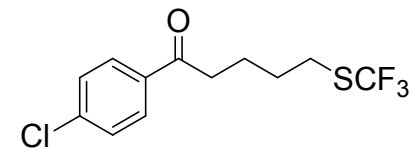
^{19}F NMR (282 MHz, $CDCl_3$)


7.895
7.879
7.447
7.430
7.261
2.994
2.980
2.966
2.945
2.931
2.917
1.890
1.879
1.865
1.856
1.849
1.835
1.819
1.805
1.791
1.777
0.000
O
SCF3
Cl
4f
1H NMR (500 MHz, CDCl3)
2.01
2.00
2.04
2.01
2.00
2.01
10
8
6
4
2
0
PPM



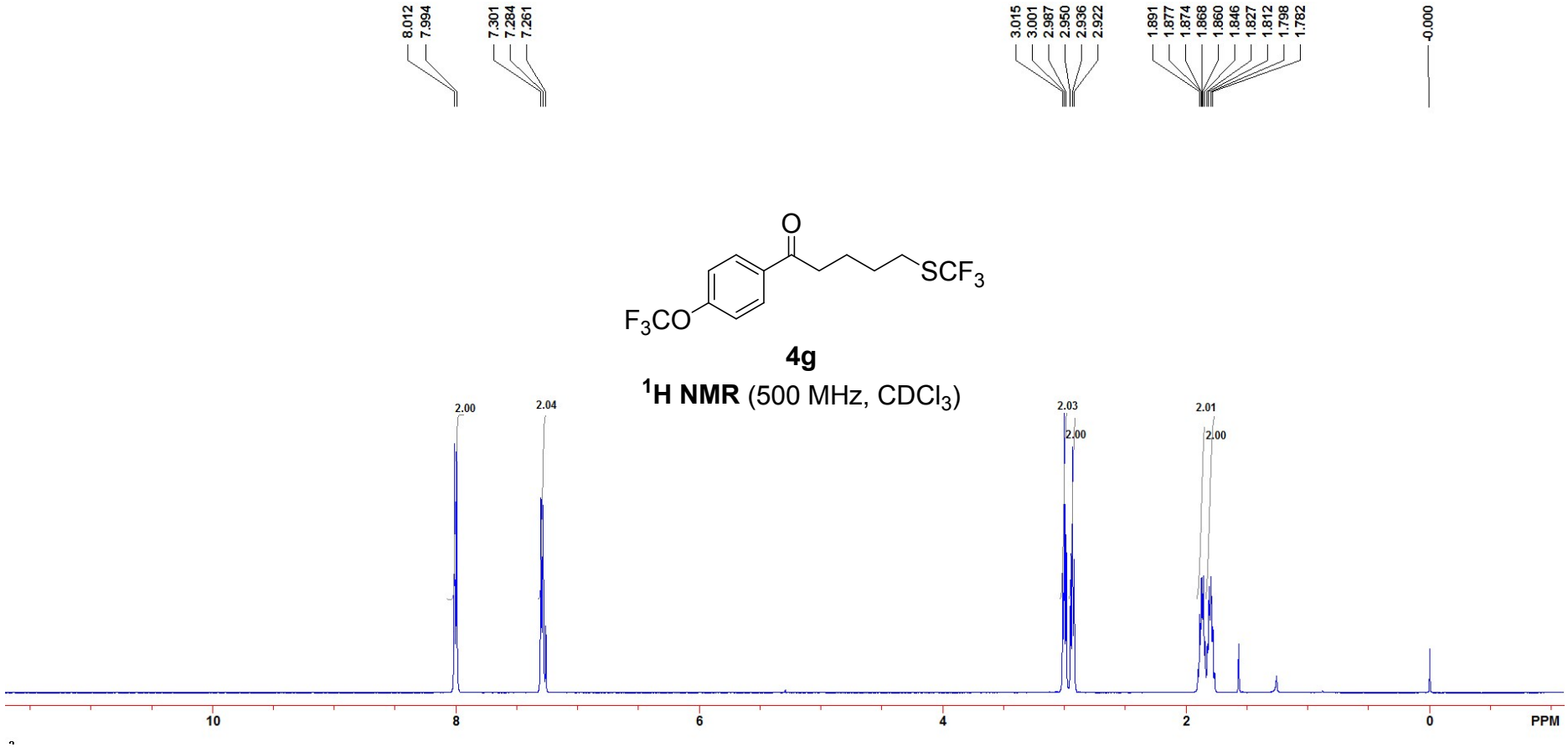
4f

^{13}C NMR (125 MHz, $CDCl_3$)



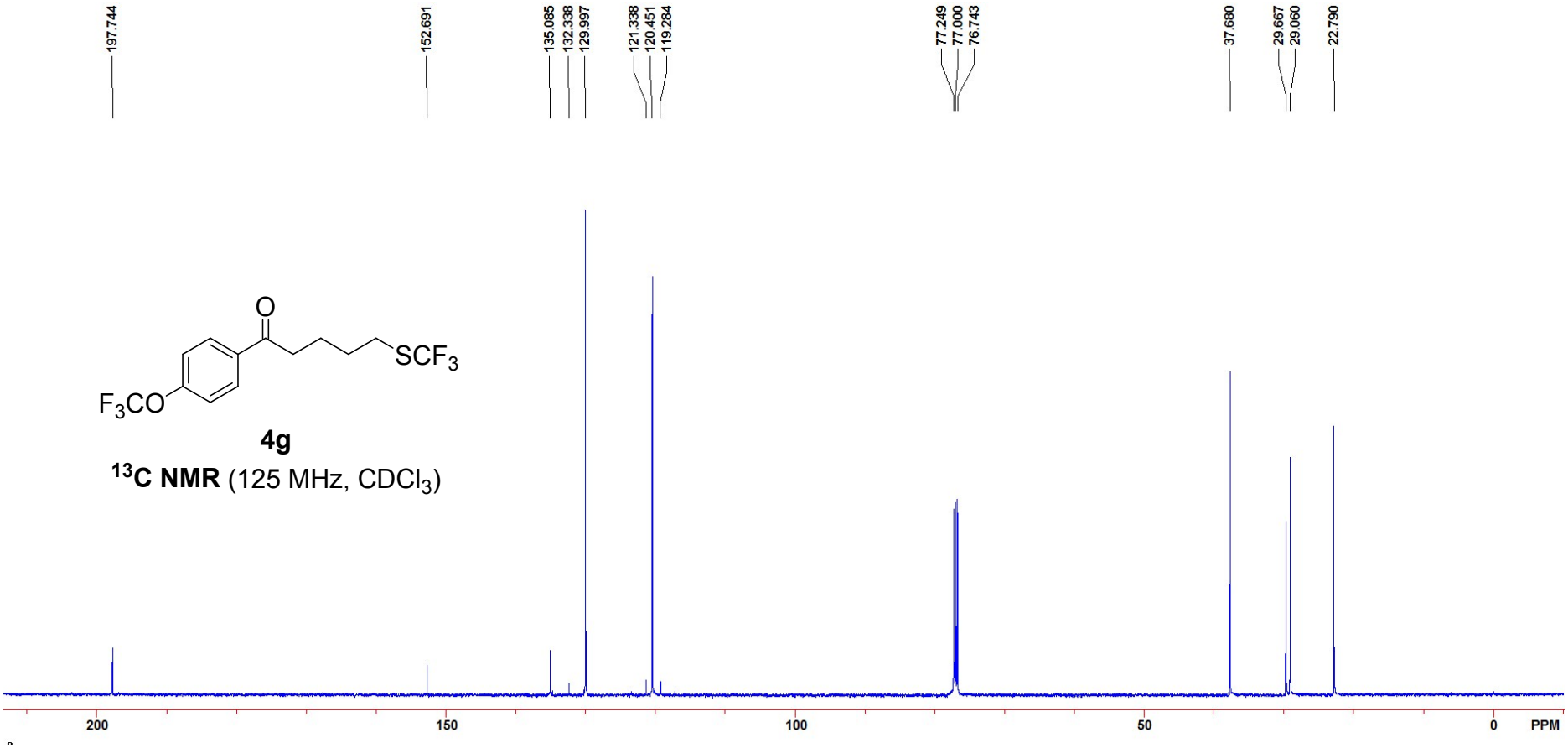
4f

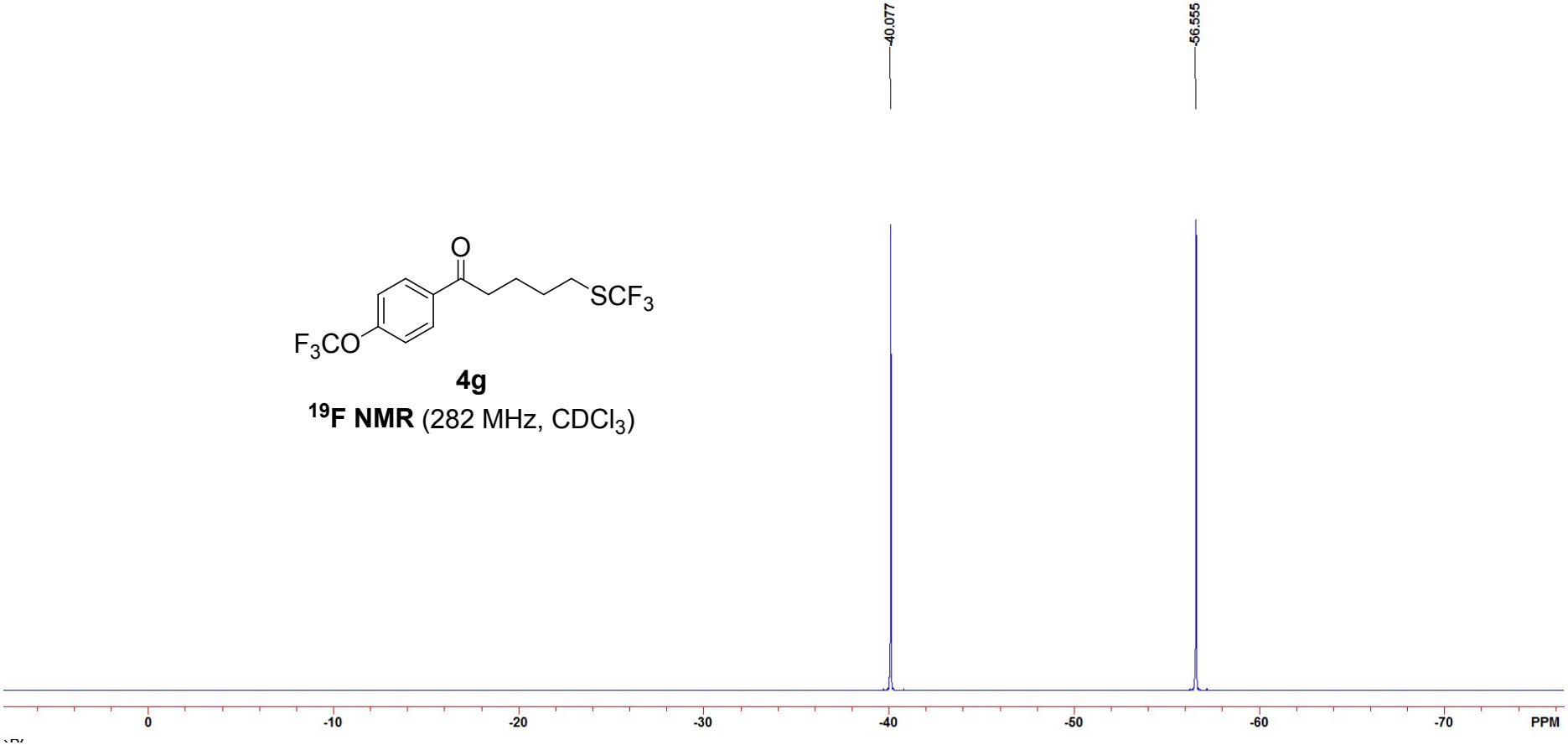
^{19}F NMR (282 MHz, $CDCl_3$)



4g

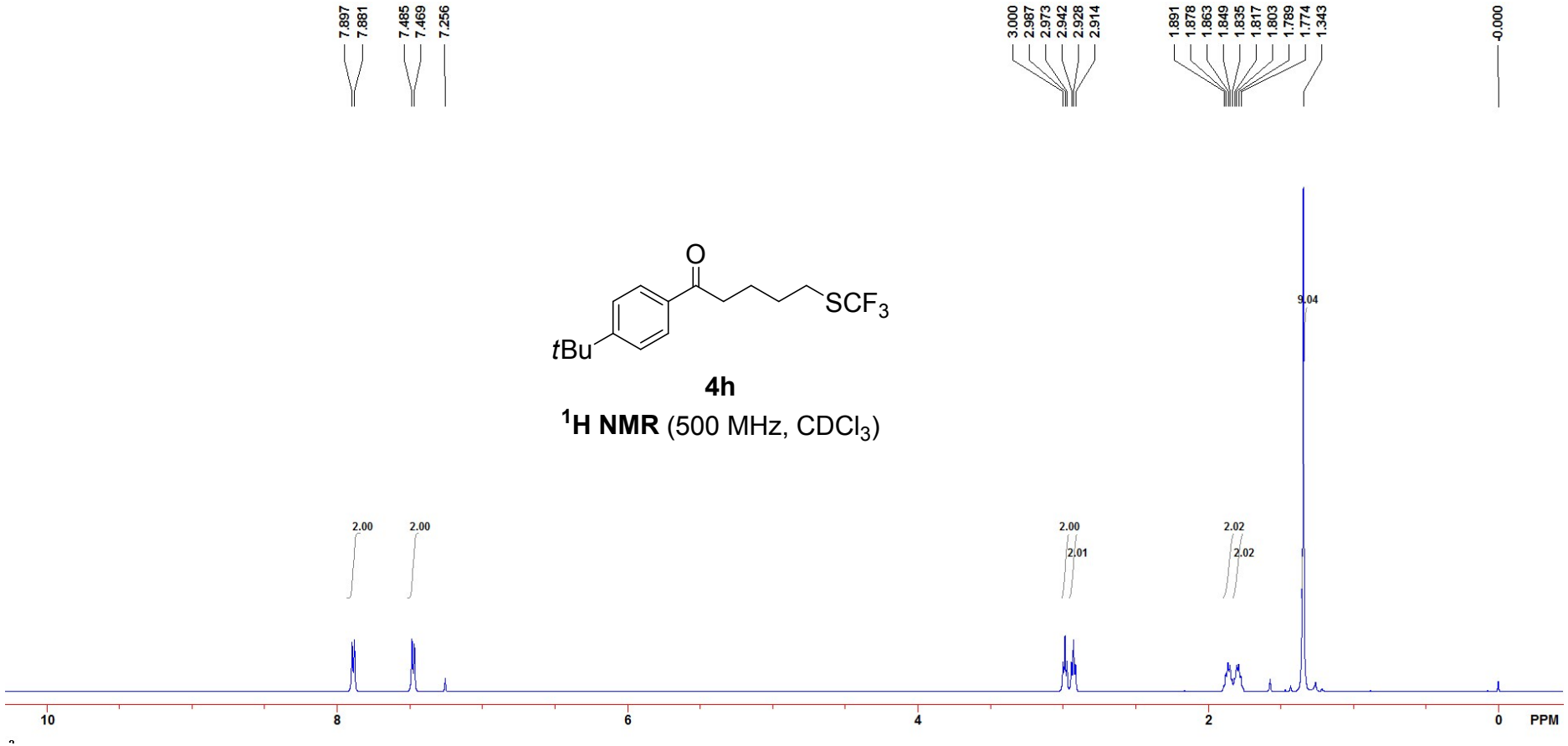
^{1}H NMR (500 MHz, $CDCl_3$)

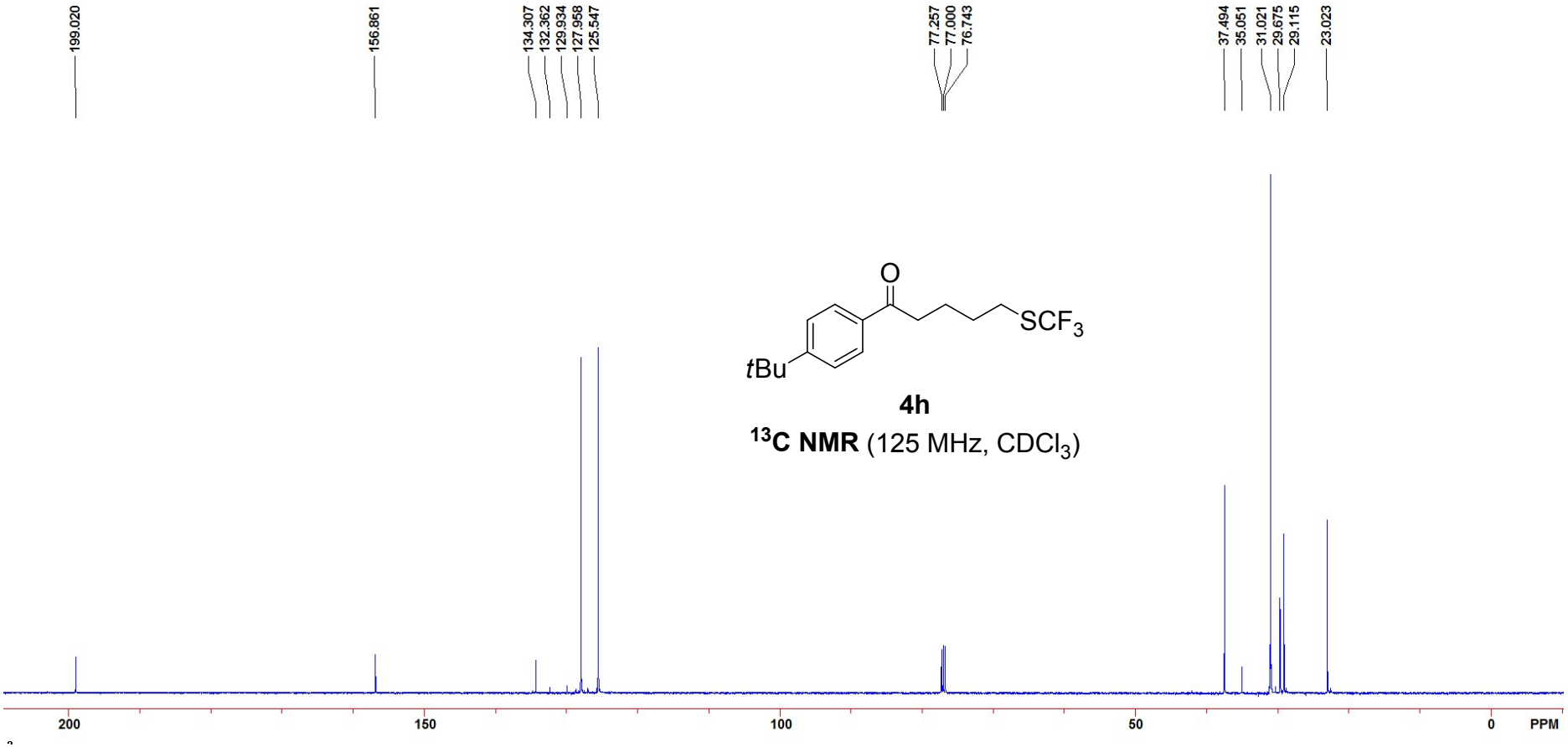

197.744
152.691
135.085
132.338
129.997
121.338
120.451
119.284
77.249
77.000
76.743
37.680
29.667
29.060
22.790
O
SCF3
F3CO
4g
13C NMR (125 MHz, CDCl3)
200
150
100
50
0
PPM



4g

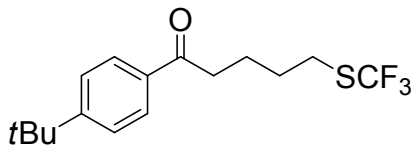
^{19}F NMR (282 MHz, $CDCl_3$)


7.897
7.881
7.485
7.469
7.256
3.000
2.987
2.973
2.942
2.928
2.914
1.891
1.878
1.863
1.849
1.835
1.817
1.803
1.789
1.774
1.343
-0.000
O
SCF3
tBu
4h
1H NMR (500 MHz, CDCl3)
9.04
2.00
2.00
2.00
2.01
2.02
2.02
10
8
6
4
2
0
PPM



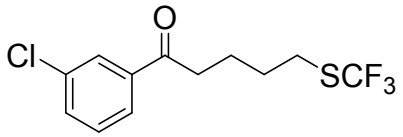
4h

^{13}C NMR (125 MHz, $CDCl_3$)



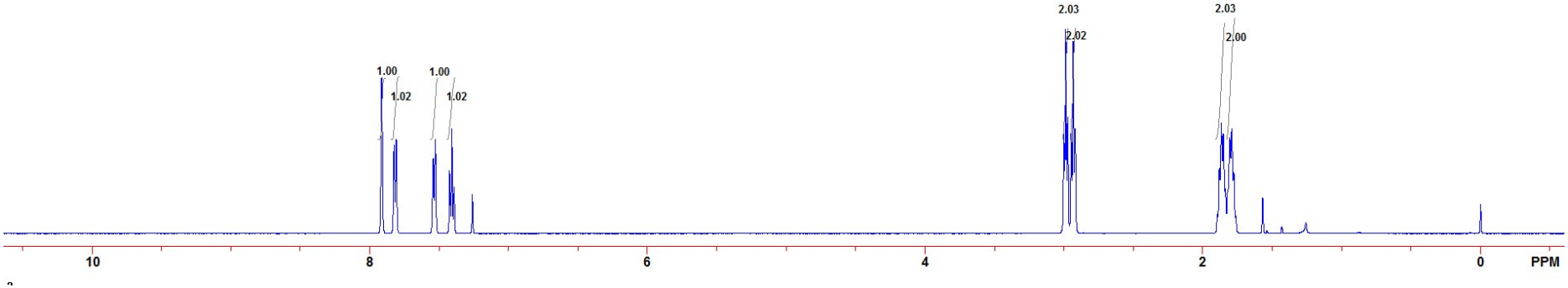
4h

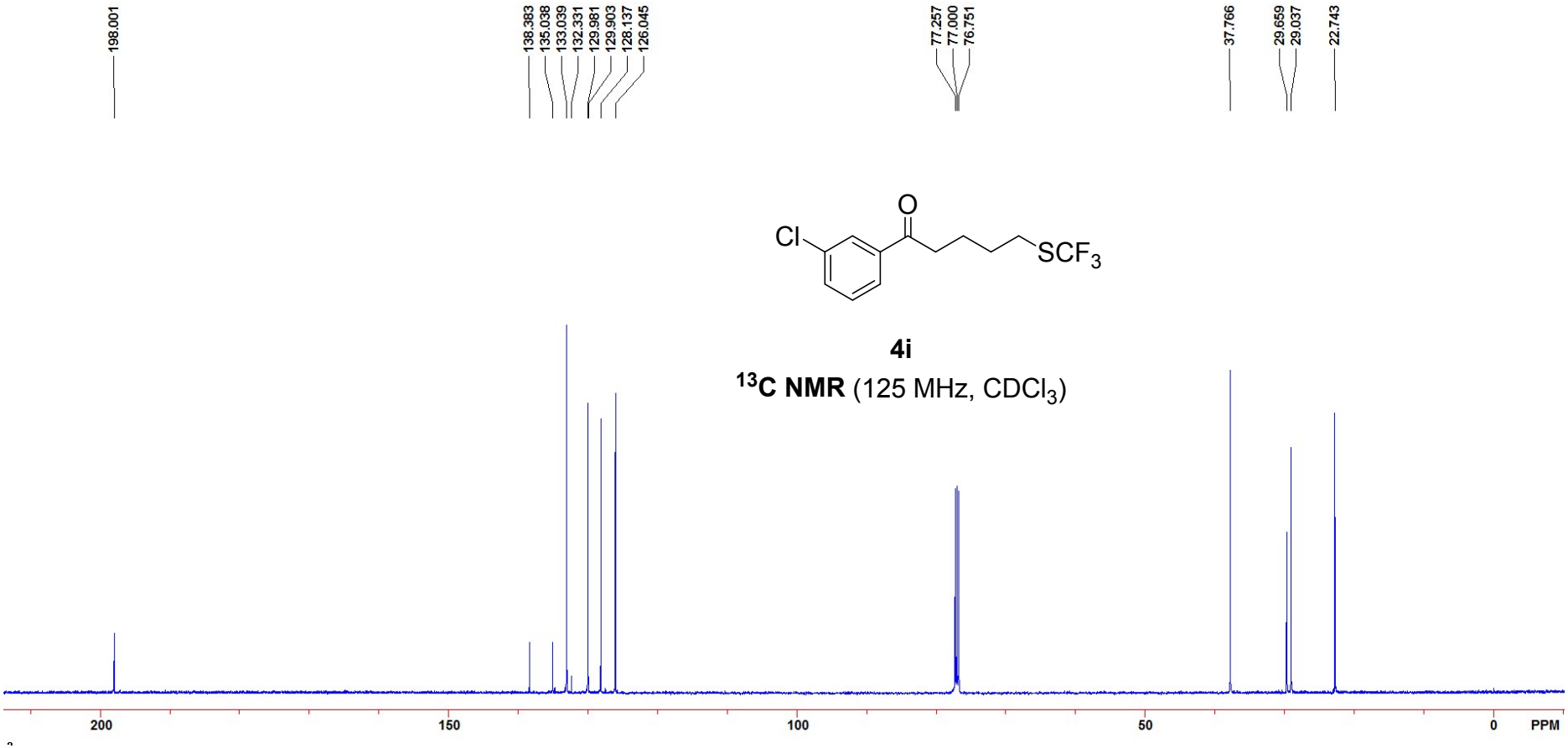
^{19}F NMR (282 MHz, $CDCl_3$)



4i

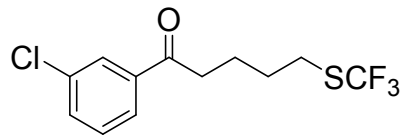
^{1}H NMR (500 MHz, $CDCl_3$)





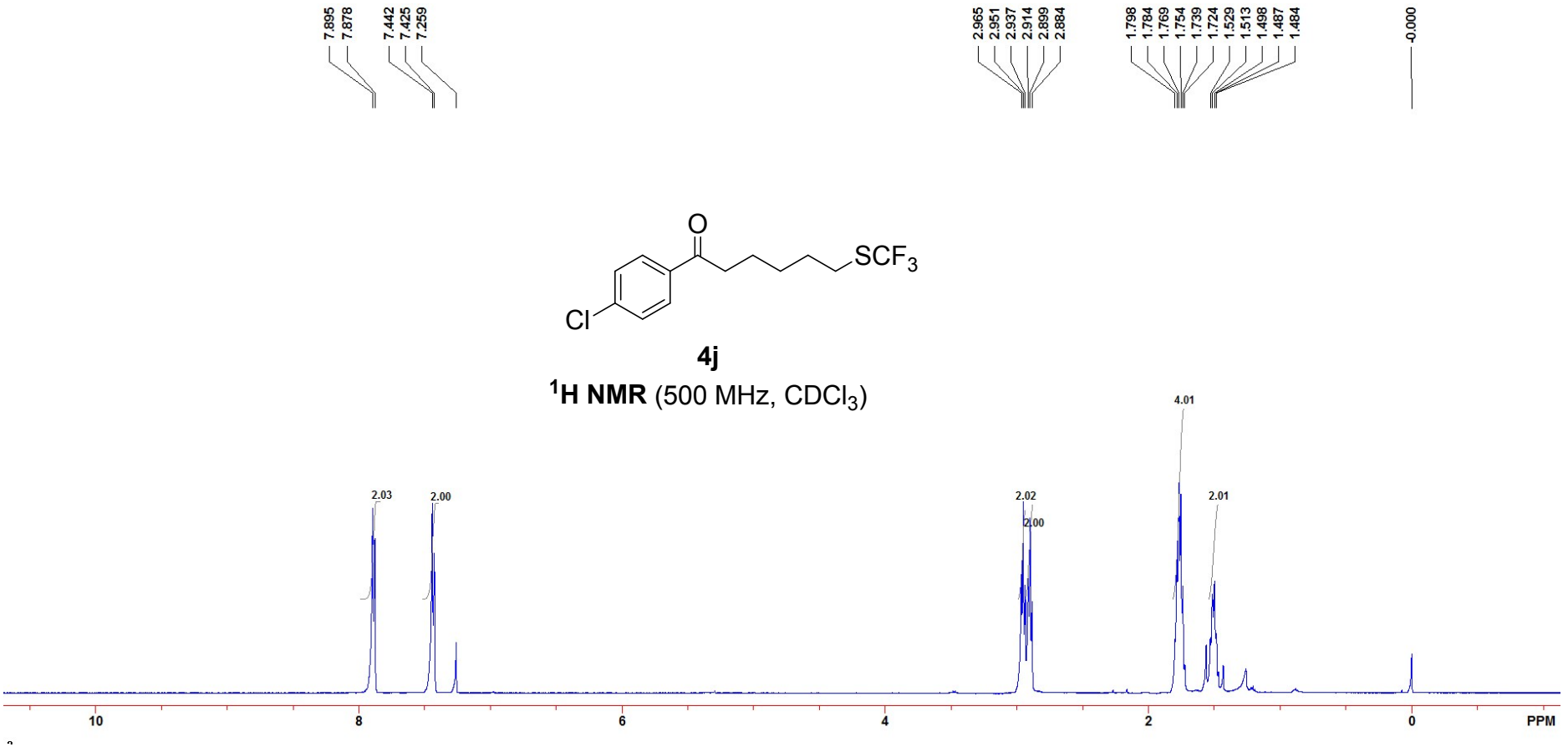
4i

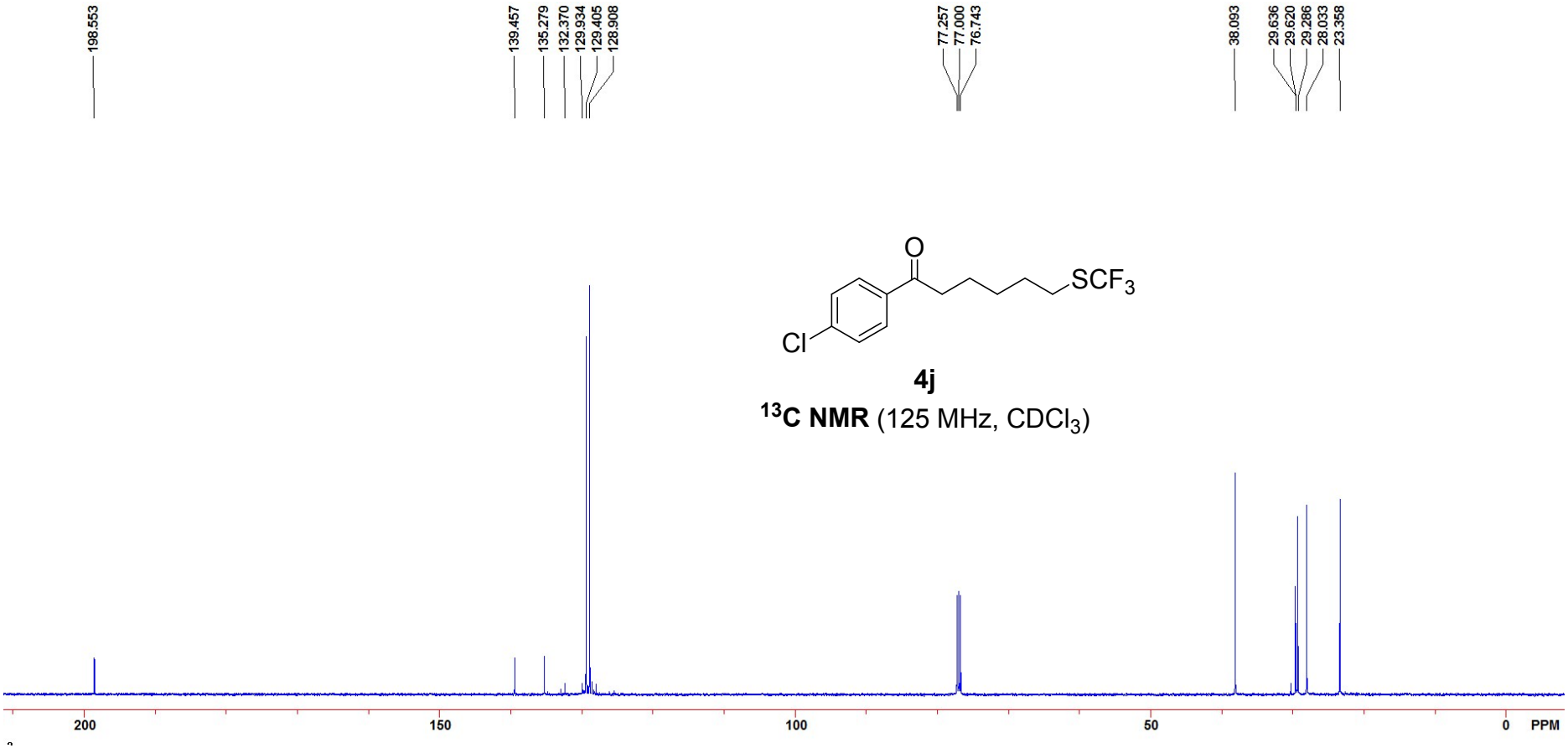
^{13}C NMR (125 MHz, $CDCl_3$)



4i

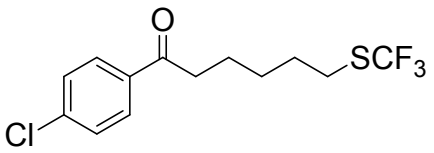
^{19}F NMR (282 MHz, $CDCl_3$)


7.895
7.878
7.442
7.425
7.259
2.965
2.951
2.937
2.914
2.899
2.884
1.798
1.784
1.769
1.754
1.739
1.724
1.529
1.513
1.498
1.487
1.484
0.000
O
SCF3
Cl
4j
1H NMR (500 MHz, CDCl3)
4.01
2.03
2.00
2.02
2.00
2.01
10
8
6
4
2
0
PPM



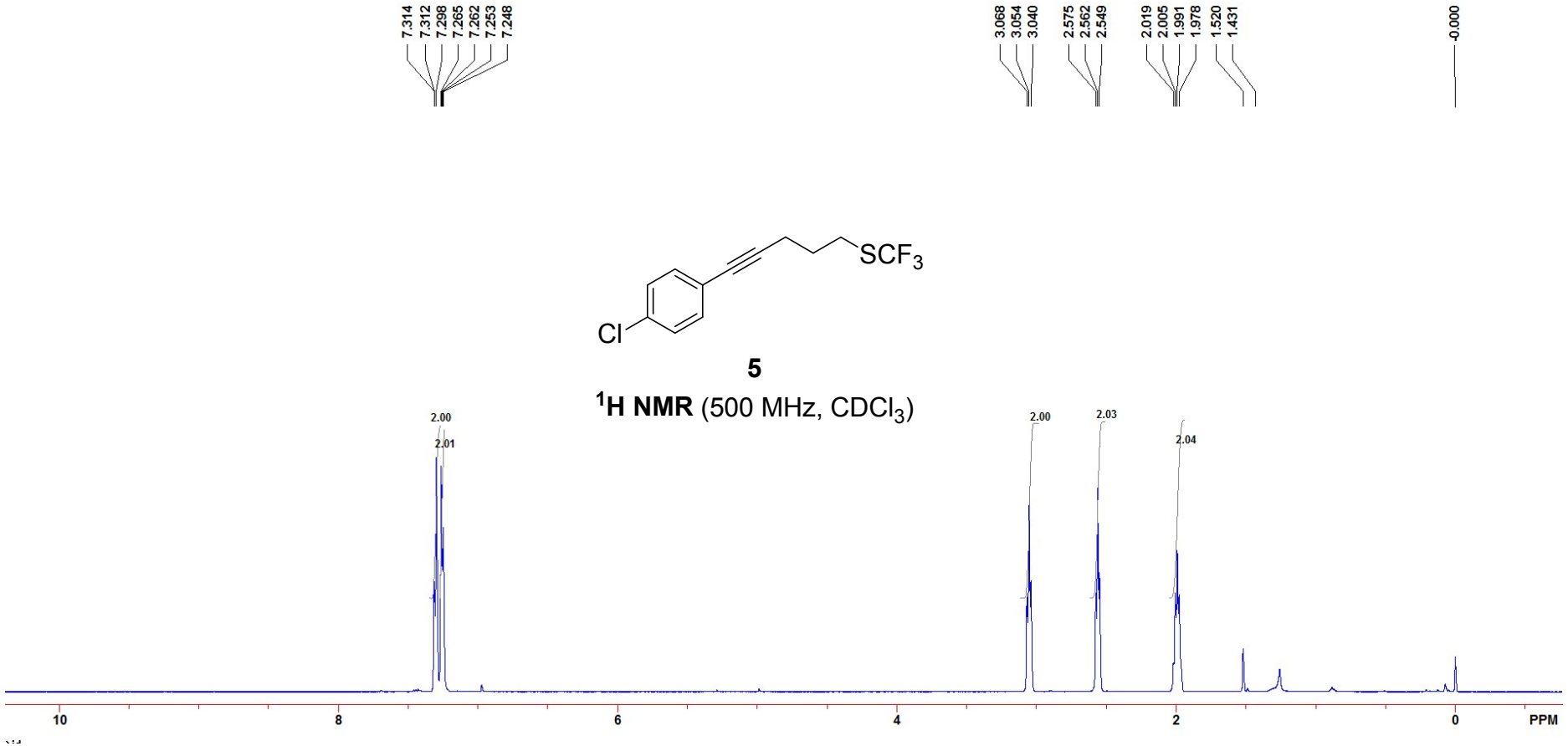
4j

^{13}C NMR (125 MHz, $CDCl_3$)



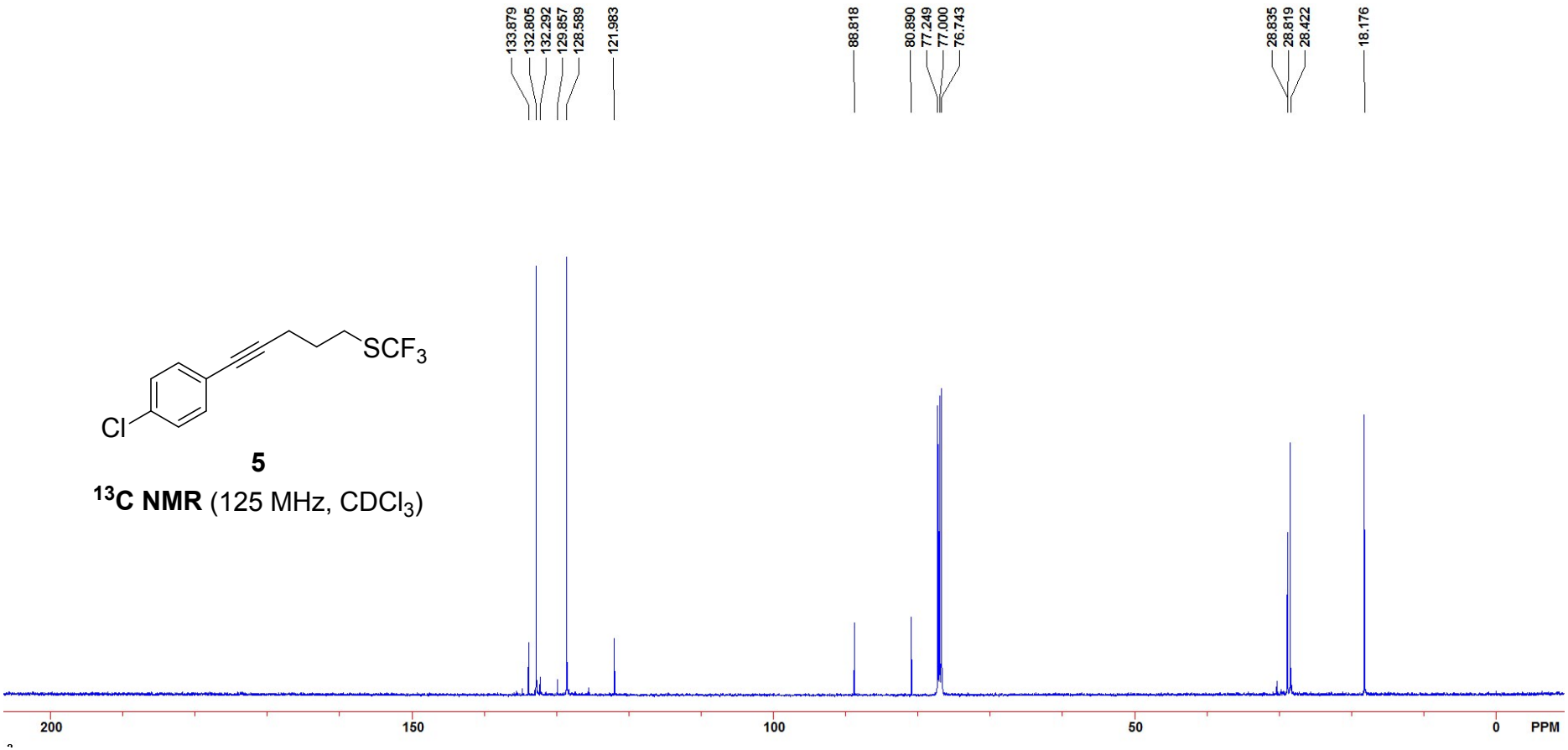
4j

^{19}F NMR (282 MHz, $CDCl_3$)



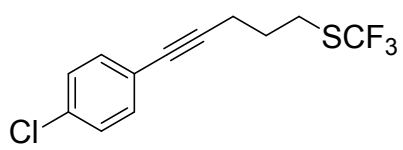
5

^{1}H NMR (500 MHz, $CDCl_3$)



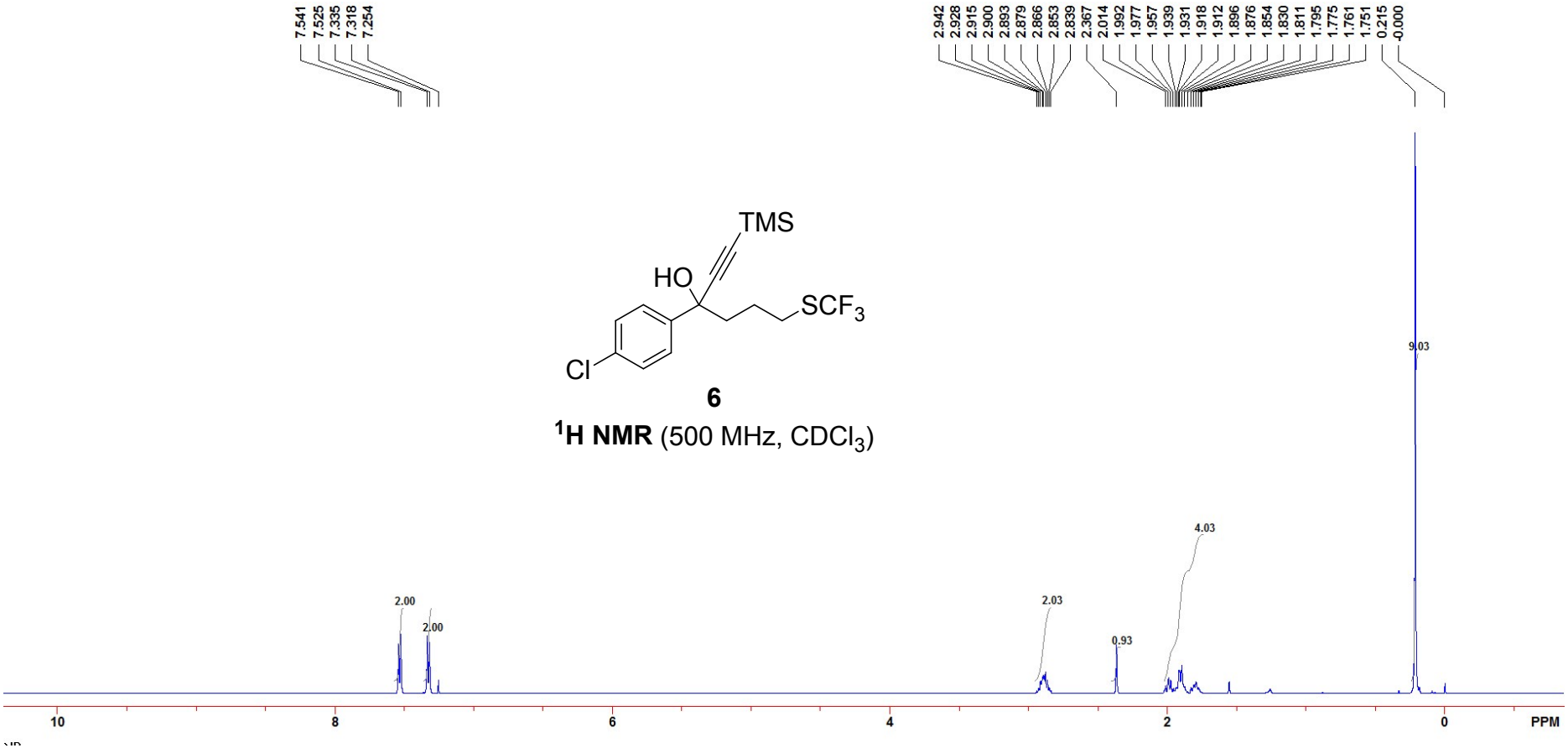
5

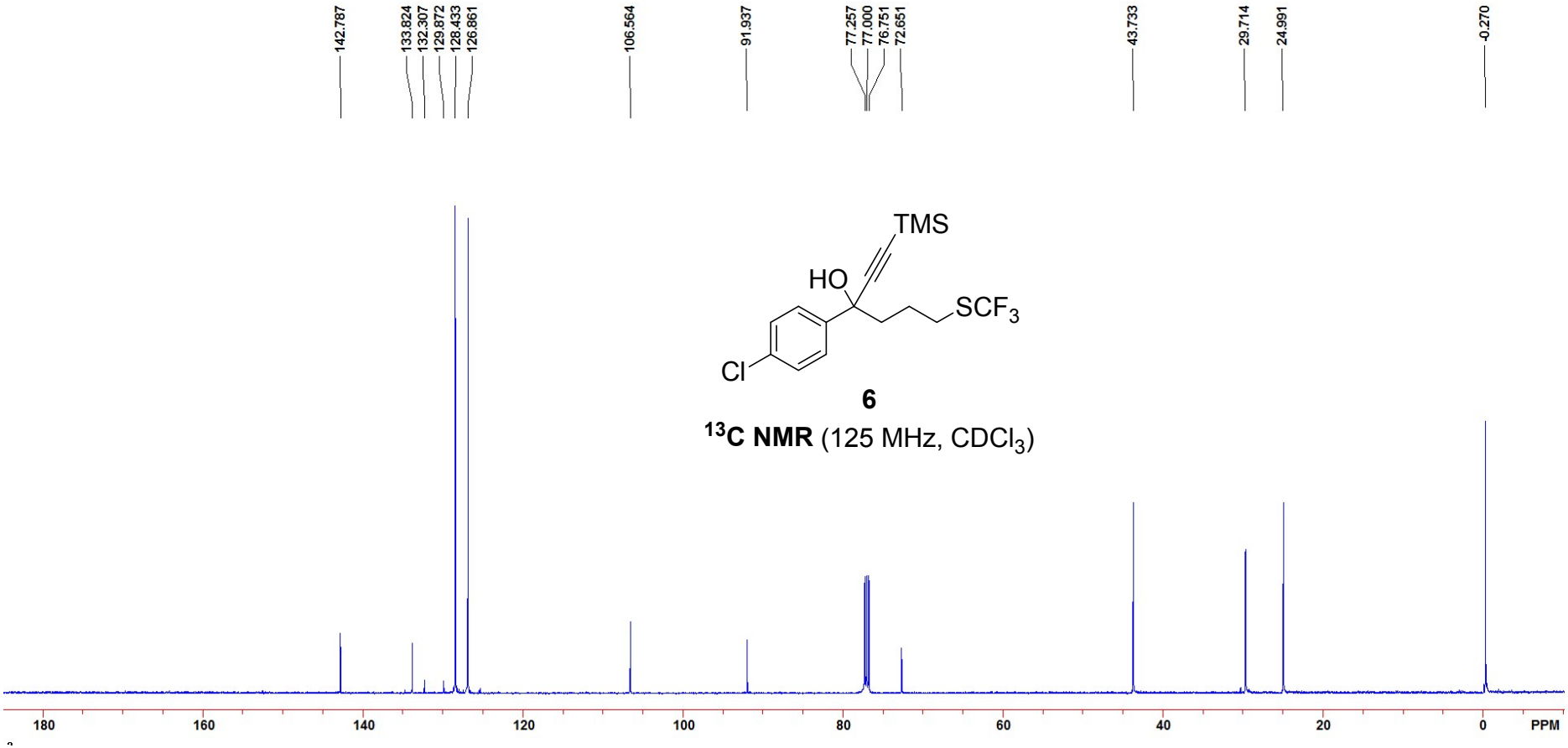
^{13}C NMR (125 MHz, $CDCl_3$)

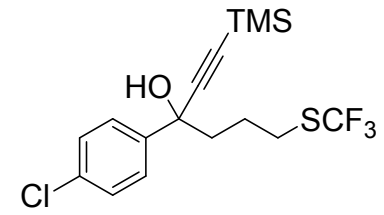


5

^{19}F NMR (282 MHz, $CDCl_3$)

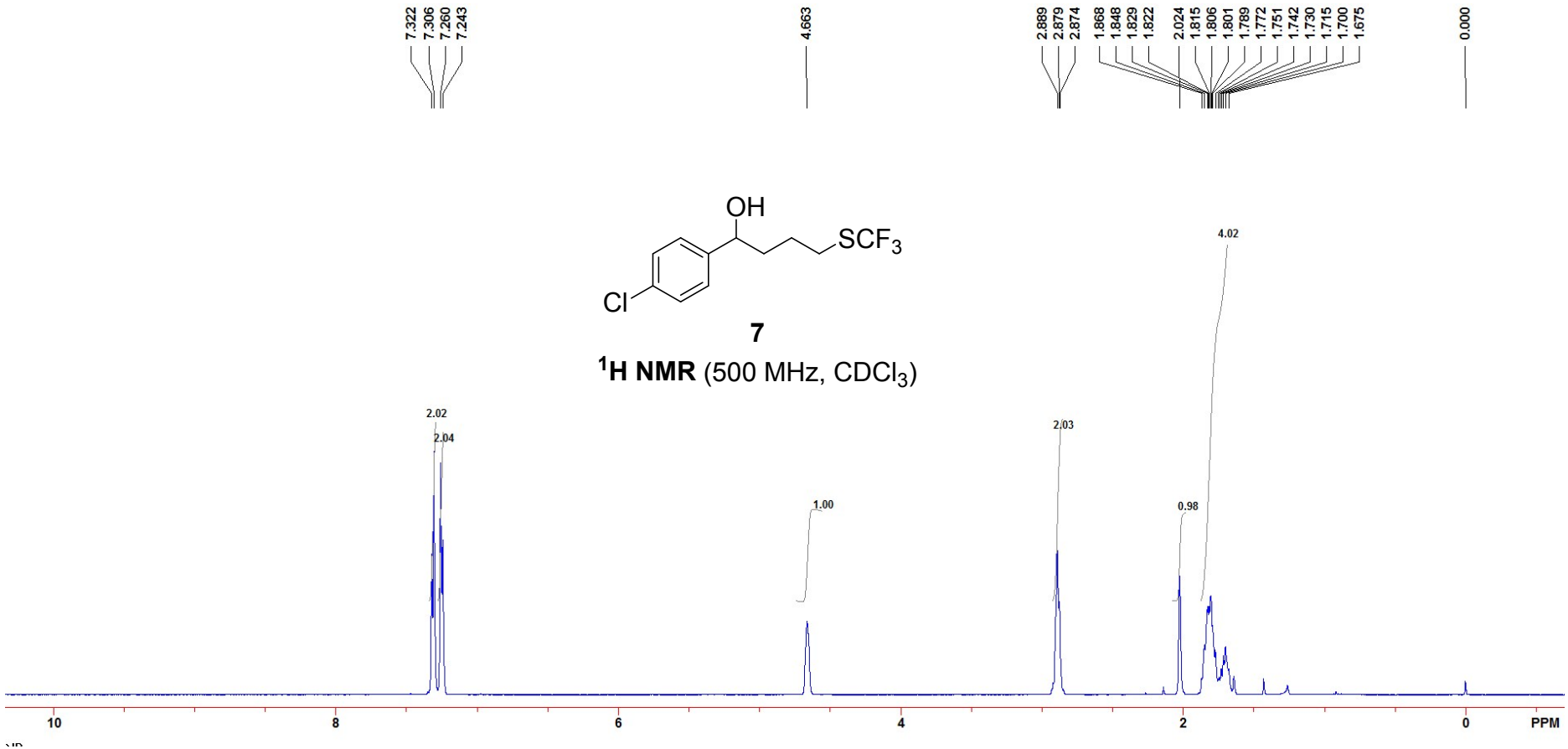

7.541
7.525
7.335
7.318
7.254
2.942
2.928
2.915
2.900
2.893
2.879
2.866
2.853
2.839
2.367
2.014
1.992
1.977
1.957
1.939
1.931
1.918
1.912
1.896
1.876
1.854
1.830
1.811
1.795
1.775
1.761
1.751
0.215
-0.000
TMS
HO
SCF3
Cl
6
1H NMR (500 MHz, CDCl3)
9.03
4.03
2.00
2.00
2.03
0.93
10
8
6
4
2
0
PPM

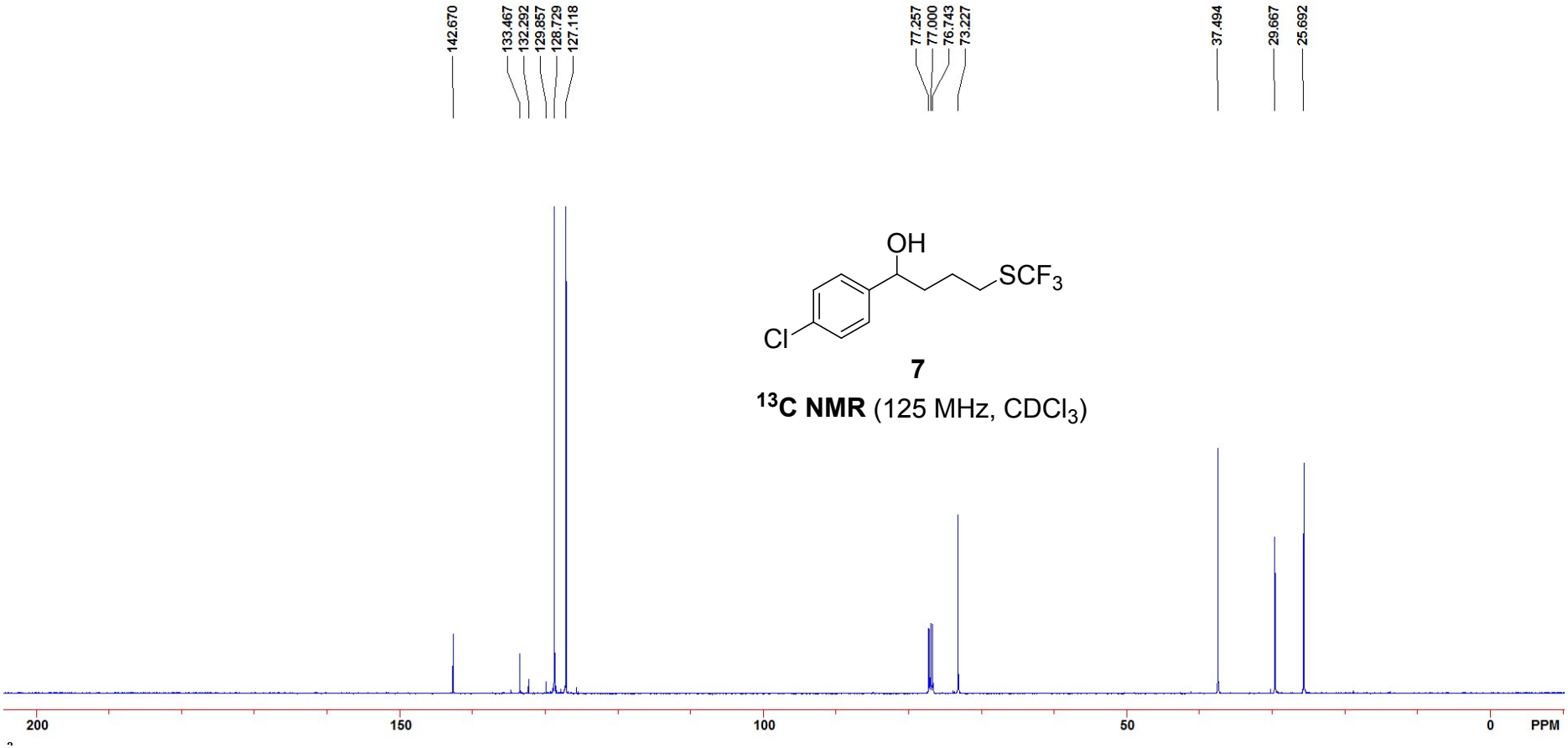

142.787
133.824
132.307
129.872
128.433
126.861
106.564
91.937
77.257
77.000
76.751
72.651
43.733
29.714
24.991
-0.270
TMS
HO
SCF3
Cl
6
13C NMR (125 MHz, CDCl3)
180
160
140
120
100
80
60
40
20
0
PPM



6

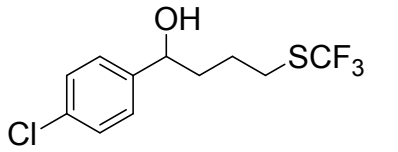
^{19}F NMR (282 MHz, $CDCl_3$)


7.322
7.306
7.260
7.243
4.663
2.889
2.879
2.874
1.868
1.848
1.829
1.822
2.024
1.815
1.806
1.801
1.789
1.772
1.751
1.742
1.730
1.715
1.700
1.675
0.000
OH
SCF3
Cl
7
1H NMR (500 MHz, CDCl3)
2.02
2.04
1.00
2.03
0.98
4.02
10
8
6
4
2
0
PPM



7

^{13}C NMR (125 MHz, $CDCl_3$)



7

^{19}F NMR (282 MHz, $CDCl_3$)