Supporting Information

Trifluoromethylthiolation-Based Bifunctionalization of Diazocarbonyl Compounds by Rhodium Catalysis

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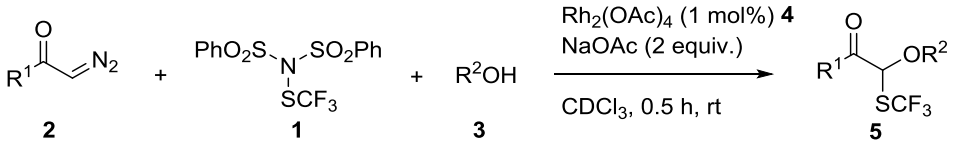
General Information

Diazo compounds **2** were prepared according to literature procedures.[1-3] Trifluoromethylthiolating reagent **1** was synthesized according to a procedure by Shen and co-workers.[4] Reagents were used as obtained from commercial suppliers without further purification. Dry $CDCl_3$ was used as obtained from a commercial supplier (Sigma-Aldrich). Dry CH_2Cl_2 was obtained from a solvent drying system (VAC Solvent Purifier from Vacuum Atmospheres). Flash chromatography was carried out on 60 Å (35-70 μm) silica gel (Davisil by Grace Discovery Sciences)) using petroleum ether / Et_2O or petroleum ether / CH_2Cl_2 mixtures as eluent. Analytical TLC was carried out on aluminum-backed plates (1.5 Å, ~ 5 cm) pre-coated (0.25 mm) with silica gel (Merck, Silica Gel 60 F254). Compounds were visualized by exposure to UV light or by dipping the plates in a solution of 0.75% $KMnO_4$ (w/v) in a aqueous solution of K_2CO_3 0.36 M. Melting points were recorded in a metal block and are uncorrected. ^1H NMR spectra were recorded at 400 MHz; ^{13}C NMR spectra were recorded at 100 MHz, ^{19}F NMR spectra were recorded at 377 MHz with a Bruker Advance spectrometer. ^1H and ^{13}C NMR chemical shifts (δ) are reported in ppm from tetramethylsilane, using the residual solvent resonance ($CHCl_3$: δ_H 7.26 and $CDCl_3$: δ_C 77.0) as an internal reference. Coupling constants (*J*) are given in Hz. High-resolution mass spectra (HRMS) were recorded with a Bruker microTOF ESI-TOF mass spectrometer.

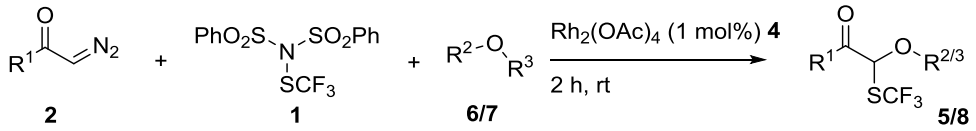
Experimental procedures and spctroscopic data

General procedure A for the multicomponent reaction of diazo compounds 2 with alcohols 3 and trifluoromethylthio reagent 1.



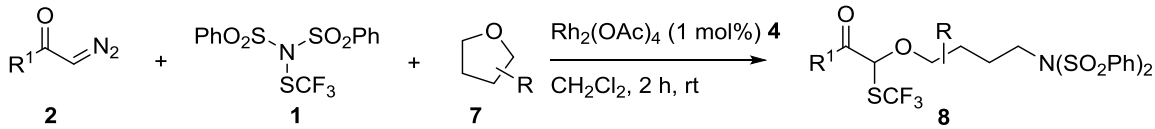
$(PhSO_2)_2NSCF_3$ (**1**) (40 mg, 0.1 mmol, 1.0 equiv.), $Rh_2(OAc)_4$ (**4**) (0.5 mg, 0.001 mmol, 0.01 equiv.) and anhydrous NaOAc (16 mg, 0.2 mmol, 2.0 equiv.) were placed to a vial under ambient conditions. Then, diazo compound **2** (0.12 mmol, 1.2 equiv.) and the corresponding alcohol **3** (0.4 mmol, 4.0 equiv.) in 1.5 mL of dry $CDCl_3$ were added under Ar. The reaction mixture was stirred for 30 minutes in the sealed vial, then the reaction mixture was purified by silica gel chromatography to obtain products **5**.

General procedure B for the multicomponent reaction of diazo compounds 2 with ethers 6, 7c and reagent 1.



$(PhSO_2)_2NSCF_3$ (**1**) (40 mg, 0.1 mmol, 1.0 equiv.) and $Rh_2(OAc)_4$ (**4**) (0.5 mg, 0.001 mmol, 0.01 equiv.) were placed to a vial under ambient conditions. Then, diazo compound **2** (0.12 mmol, 1.2 equiv.) in 1 mL of the appropriate ether **6** or **7c** were added under Ar. The reaction mixture was stirred for 2 h in the sealed vial, then the reaction mixture was purified by silica gel chromatography.

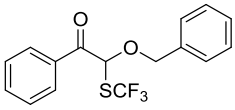
General procedure C for the multicomponent reaction of diazo compounds 2 with THF 7a-b and reagent 1.



$(PhSO_2)_2NSCF_3$ (**1**) (40 mg, 0.1 mmol, 1.0 equiv.) and $Rh_2(OAc)_4$ (**4**) (0.5 mg, 0.001 mmol,

0.01 equiv.) were placed to a vial under ambient conditions. Then, diazo compound **2** (0.12 mmol, 1.2 equiv.) and THF **7** (0.6 mmol, 6 equiv.) in 1 mL of dry CH_2Cl_2 were added under Ar. The reaction mixture was stirred for 2 h in the sealed vial, then the reaction mixture was purified by silica gel chromatography.

2-(benzyloxy)-1-phenyl-2-((trifluoromethyl)thio)ethan-1-one (5a)

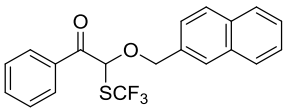


Title compound **5a** was prepared according to general procedure A and purified by column chromatography (SiO_2; petroleum ether / Et_2O, 16:1) affording **5a** as a colorless oil (23 mg, 71%). ^{1}H NMR (400 MHz, $CDCl_3$): δ = 8.07-8.03 (m, 2H), 7.67-7.62 (m, 1H), 7.53-7.47 (m, 2H), 7.34-7.29 (m, 3H), 7.26-7.22 (m, 2H), 6.59 (s, 1H), 4.86 (d, *J* = 11.0 Hz, 1H), 4.56 (d, *J* = 11.0 Hz, 1H); ^{13}C NMR (100 MHz, $CDCl_3$): δ = 191.4, 135.7, 134.8, 133.1, 130.3 (q, *J*(C,F) = 308.2 Hz), 129.6, 129.1, 128.7, 128.6, 128.5, 87.1 (q, *J*(C,F) = 1.6 Hz), 69.2; ^{19}F NMR (377 MHz, $CDCl_3$): δ = -38.47; HRMS (ESI): m/z calcd. for $C_{16}H_{13}O_2F_3S$+Na^+: 349.0481 [*M*+Na]$^+$; found: 349.0463.

2-(benzyloxy)-1-phenyl-2-((trifluoromethyl)thio)ethan-1-one (5a) at 1.0 mmol scale

The above preparation of **5a** was repeated at 1.0 mmol scale: $(PhSO_2)_2NSCF_3$ (**1**) (413 mg, 1.0 mmol, 1.0 equiv.), $Rh_2(OAc)_4$ (**4**) (4.9 mg, 0.01 mmol, 0.01 equiv.) and anhydrous NaOAc (169 mg, 2.0 mmol, 2.0 equiv.) were placed in a 25 mL Schlenk tube under ambient conditions. Then, diazo compound **2a** (189 mg, 1.2 mmol, 1.2 equiv.) and benzyl alcohol **3a** (433 mg, 4.0 mmol, 4.0 equiv.) dissolved together in 15 mL dry $CDCl_3$ were added under Ar. This reaction mixture was stirred for 30 minutes at 25 ºC, then the solvent was removed under reduced pressure. The crude mixture was purified by silica gel chromatography (SiO_2; petroleum ether / Et_2O, 16:1) to obtain product **5a** (229 mg, 67% yield).

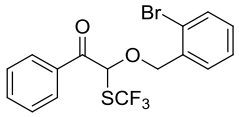
2-(naphthalen-2-ylmethoxy)-1-phenyl-2-((trifluoromethyl)thio)ethan-1-one (5b)



Title compound **5b** was prepared according to general procedure A and purified by column chromatography (SiO_2; petroleum ether / Et_2O, 16:1) affording **5b** as a colorless oil (25 mg, 67%). ^{1}H NMR (400 MHz, $CDCl_3$): δ = 8.07-8.03 (m, 2H), 7.83-7.76 (m, 3H), 7.72-7.69 (m, 1H), 7.66-7.61 (m, 1H), 7.51-7.45 (m, 4H), 7.34 (dd, *J* = 8.4 Hz, 1.7 Hz, 1H), 6.63 (s, 1H), 5.02 (d, *J* = 11.1 Hz, 1H), 4.74 (d, *J* = 11.1 Hz, 1H); ^{13}C NMR (100 MHz, $CDCl_3$): δ = 191.4, 134.7, 133.3, 133.3, 133.1, 133.1, 130.4 (q, *J*(C,F) = 308.2 Hz), 129.6, 129.1, 128.6, 128.1, 127.8, 127.7, 126.5, 126.4, 125.8, 87.0 (q, *J*(C,F) = 1.6 Hz), 69.3; ^{19}F NMR (377 MHz, $CDCl_3$): δ = -38.39; HRMS

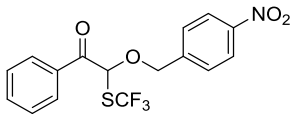
(ESI): m/z calcd. for $C_{20}H_{15}O_2F_3S+Na^+$: 399.0637 [*M*+Na]$^+$; found: 399.0653.

2-((2-bromobenzyl)oxy)-1-phenyl-2-((trifluoromethyl)thio)ethan-1-one (5c)



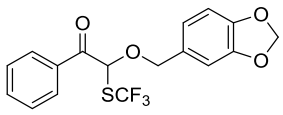
Title compound **5c** was prepared according to general procedure A and purified by column chromatography (SiO_2; petroleum ether / Et_2O, 16:1) affording **5c** as a colorless oil (20 mg, 50%). ^{1}H NMR (400 MHz, $CDCl_3$): δ = 8.10-8.06 (m, 2H), 7.67-7.61 (m, 1H), 7.54-7.47 (m, 3H), 7.40-7.36 (m, 1H), 7.31-7.25 (m, 1H), 7.18-7.13 (m, 1H), 6.62 (s, 1H), 4.89 (d, *J* = 11.8 Hz, 1H), 4.72 (d, *J* = 11.8 Hz, 1H); ^{13}C NMR (100 MHz, $CDCl_3$): δ = 191.1, 135.3, 134.8, 133.0, 132.8, 130.3 (q, *J*(C,F) = 308.3 Hz), 130.1, 129.9, 129.7, 129.1, 128.7, 127.7, 87.4 (q, *J*(C,F) = 1.6 Hz), 68.8; ^{19}F NMR (377 MHz, $CDCl_3$): δ = -38.52; HRMS (ESI): m/z calcd. for $C_{16}H_{12}O_2F_3S^{79}Br+Na^+$: 426.9586 [*M*+Na]$^+$; found: 426.9573.

2-((4-nitrobenzyl)oxy)-1-phenyl-2-((trifluoromethyl)thio)ethan-1-one (5d)



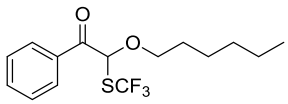
Title compound **5d** was prepared according to general procedure A and purified by column chromatography (SiO_2; petroleum ether / Et_2O, 16:1) affording **5d** as a yellowish oil (13 mg, 33%). ^{1}H NMR (400 MHz, $CDCl_3$): δ = 8.19-8.14 (m, 2H), 8.09-8.04 (m, 2H), 7.70-7.65 (m, 1H), 7.56-7.50 (m, 2H), 7.44-7.39 (m, 2H), 6.73 (s, 1H), 4.97 (d, *J* = 12.2 Hz, 1H), 4.63 (d, *J* = 12.2 Hz, 1H); ^{13}C NMR (100 MHz, $CDCl_3$): δ = 191.1, 147.9, 143.2, 135.1, 132.8, 130.2 (q, *J*(C,F) = 308.3 Hz), 129.5, 129.3, 128.4, 123.8, 87.1 (q, *J*(C,F) = 1.5 Hz), 67.4; ^{19}F NMR (377 MHz, $CDCl_3$): δ = -38.66; HRMS (ESI): m/z calcd. for $C_{16}H_{12}O_4NF_3S+Na^+$: 394.0331 [*M*+Na]$^+$; found: 394.0324.

2-(benzo[*d*][1,3]dioxol-5-ylmethoxy)-1-phenyl-2-((trifluoromethyl)thio)ethan-1-one (5e)



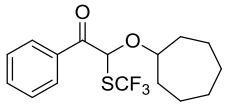
Title compound **5e** was prepared according to general procedure A and purified by column chromatography (SiO_2; petroleum ether / Et_2O, 16:1) affording **5e** as a colorless oil (24 mg, 58%). ^{1}H NMR (400 MHz, $CDCl_3$): δ = 8.07-8.01 (m, 2H), 7.68-7.62 (m, 1H), 7.54-7.47 (m, 2H), 6.75-6.67 (m, 3H), 6.56 (s, 1H), 5.95-5.92 (m, 2H), 4.75 (d, *J* = 10.8 Hz, 1H), 4.46 (d, *J* = 10.8 Hz, 1H); ^{13}C NMR (100 MHz, $CDCl_3$): δ = 191.5, 148.0, 147.9, 134.7, 133.1, 130.3 (q, *J*(C,F) = 308.2 Hz), 129.6, 129.3, 129.1, 122.6, 109.2, 108.3, 101.3, 86.8 (q, *J*(C,F) = 1.5 Hz), 69.1; ^{19}F NMR (377 MHz, $CDCl_3$): δ = -38.45; HRMS (ESI): m/z calcd. for $C_{17}H_{13}O_4F_3S+Na^+$: 393.0379 [*M*+Na]$^+$; found: 393.0387.

2-(hexyloxy)-1-phenyl-2-((trifluoromethyl)thio)ethan-1-one (5f)



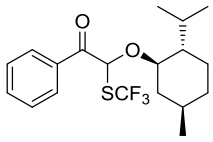
Title compound **5f** was prepared according to general procedure A and purified by column chromatography (SiO_2; petroleum ether / Et_2O, 16:1) affording **5f** as a colorless oil (22 mg, 68%). ^{1}H NMR (400 MHz, $CDCl_3$): δ = 8.10-8.06 (m, 2H), 7.67-7.62 (m, 1H), 7.54-7.48 (m, 2H), 6.50 (s, 1H), 3.76 (dt, *J* = 9.0 Hz, 6.4 Hz, 1H), 3.49 (dt, *J* = 9.0 Hz, 6.4 Hz, 1H), 1.61-1.53 (m, 2H), 1.34-1.15 (m, 6H), 0.84 (t, *J* = 6.9 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$): δ = 191.7, 134.7, 133.1, 130.5 (q, *J*(C,F) = 307.9 Hz), 129.6, 128.9, 88.2 (q, *J*(C,F) = 1.5 Hz), 67.4, 31.5, 29.2, 25.6, 22.6, 14.1; ^{19}F NMR (377 MHz, $CDCl_3$): δ = -38.68; HRMS (ESI): m/z calcd. for $C_{15}H_{19}O_2F_3S+Na^+$: 343.0950 [*M*+Na]$^+$; found: 343.0955.

2-(cycloheptyloxy)-1-phenyl-2-((trifluoromethyl)thio)ethan-1-one (5g)



Title compound **5g** was prepared according to general procedure A and purified by column chromatography (SiO_2; petroleum ether / Et_2O, 16:1) affording **5g** as a colorless oil (20 mg, 54%). ^{1}H NMR (400 MHz, $CDCl_3$): δ = 8.09-8.04 (m, 2H), 7.65-7.59 (m, 1H), 7.53-7.46 (m, 2H), 6.13 (s, 1H), 4.03 (tt, *J* = 8.1 Hz, 4.4 Hz, 1H), 1.94-1.84 (m, 2H), 1.75-1.57 (m, 4H), 1.56-1.47 (m, 4H), 1.42-1.32 (m, 2H); ^{13}C NMR (100 MHz, $CDCl_3$): δ = 191.2, 134.1, 133.2, 130.3 (q, *J*(C,F) = 308.3 Hz), 129.8, 128.8, 85.8 (q, *J*(C,F) = 1.4 Hz), 80.1, 34.7, 33.2, 28.4, 28.4, 22.9, 22.6; ^{19}F NMR (377 MHz, $CDCl_3$): δ = -38.51; HRMS (ESI): m/z calcd. for $C_{16}H_{19}O_2F_3S+Na^+$: 355.0950 [*M*+Na]$^+$; found: 355.0953.

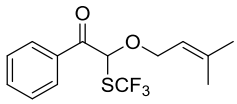
2-(((1*R*,2*S*,5*R*)-2-isopropyl-5-methylcyclohexyl)oxy)-1-phenyl-2-((trifluoromethyl)thio)ethan-1-one (5h)



Title compound **5h** was prepared according to general procedure A and purified by column chromatography (SiO_2; petroleum ether / Et_2O, 16:1) affording **5h** as a colorless oil (17 mg, 46%, dr = 1:1.4). As a mixture of two diastereoisomers: ^{1}H NMR (400 MHz, $CDCl_3$): δ = 8.08-8.00 (m, 2H), 7.65-7.59 (m, 1H), 7.52-7.46 (m, 2H), 6.06 & 6.00 (s, 1H), 3.71 & 3.51 (td, *J* = 10.6 Hz, 4.3 Hz, 1H), 2.31-1.95 (m, 2H), 1.73-1.60 (m, 2H), 1.45-1.27 (m, 2H), 1.15-0.97 (m, 1H), 0.96-0.90 (m, 5H), 0.88-0.80 (m, 4H), 0.64-0.60 (m, 1H); ^{13}C NMR (100 MHz, $CDCl_3$): δ = 190.5 (major) & 190.9 (minor), 134.2 (major) & 134.3 (minor), 132.9 (major) & 133.0 (minor), 130.2 (q, *J*(C,F) = 308.3 Hz, major), 130.1 (q, *J*(C,F) = 308.7 Hz, minor), 129.8 (major) & 129.8 (minor), 128.9 (major) & 128.9 (minor), 84.7 (q, *J*(C,F) = 1.3 Hz, major) & 86.2 (q, *J*(C,F) = 1.5 Hz, minor),

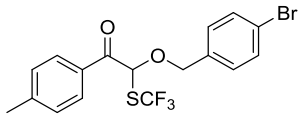
78.8 (major) & 82.0 (minor), 47.9 (major) & 48.7 (minor), 39.3 (major) & 41.3 (minor), 34.3 (major) & 34.2 (minor), 31.6 (major) & 31.8 (minor), 25.5 (major) & 25.3 (minor), 23.0 (major) & 23.0 (minor), 22.3 (major) & 22.3 (minor), 21.2 (major) & 21.2 (minor), 15.9 (major) & 15.8 (minor); ^{19}F NMR (377 MHz, $CDCl_3$): δ = -38.27 (major), -38.62 (minor); HRMS (ESI): m/z calcd. for $C_{19}H_{25}O_2F_3S+Na^+$: 397.1420 [*M*+Na]$^+$; found: 397.1427.

2-((3-methylbut-2-en-1-yl)oxy)-1-phenyl-2-((trifluoromethyl)thio)ethan-1-one (5i)



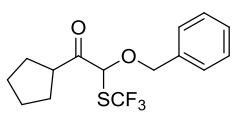
Title compound **5i** was prepared according to general procedure A and purified by column chromatography (SiO_2; petroleum ether / Et_2O, 16:1) affording **5i** as a colorless oil (21 mg, 66%). ^{1}H NMR (400 MHz, $CDCl_3$): δ = 8.09-8.05 (m, 2H), 7.66-7.61 (m, 1H), 7.53-7.47 (m, 2H), 6.50 (s, 1H), 5.25 (tdt, *J* = 7.2 Hz, 2.9 Hz, 1.5 Hz, 1H), 4.30 (dd, *J* = 11.2 Hz, 7.2 Hz, 1H), 4.08 (dd, *J* = 11.2 Hz, 7.2 Hz, 1H), 1.70 (s, 3H), 1.58 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$): δ = 191.8, 140.5, 134.6, 133.2, 130.4 (q, *J*(C,F) = 308.0 Hz), 129.6, 129.0, 118.8, 87.2 (q, *J*(C,F) = 1.6 Hz), 63.8, 25.9, 18.1; ^{19}F NMR (377 MHz, $CDCl_3$): δ = -38.62; HRMS (ESI): m/z calcd. for $C_{14}H_{15}O_2F_3S+Na^+$: 327.0637 [*M*+Na]$^+$; found: 327.0650.

2-((4-bromobenzyl)oxy)-1-(*p*-tolyl)-2-((trifluoromethyl)thio)ethan-1-one (5j)



Title compound **5j** was prepared according to general procedure A and purified by column chromatography (SiO_2; petroleum ether / Et_2O, 20:1) affording **5j** as a colorless oil (21 mg, 49%). ^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.97-7.92 (m, 2H), 7.45-7.41 (m, 2H), 7.32-7.28 (m, 2H), 7.13-7.09 (m, 2H), 6.62 (s, 1H), 4.80 (d, *J* = 11.2 Hz, 1H), 4.46 (d, *J* = 11.2 Hz, 1H), 2.44 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$): δ = 190.9, 146.2, 134.9, 131.8, 130.5, 130.4 (q, *J*(C,F) = 308.2 Hz), 130.0, 129.9, 129.7, 122.5, 87.2 (q, *J*(C,F) = 1.5 Hz), 68.0, 22.0; ^{19}F NMR (377 MHz, $CDCl_3$): δ = -38.60; HRMS (ESI): m/z calcd. for $C_{17}H_{14}O_2F_3S^{79}Br+Na^+$: 440.9748 [*M*+Na]$^+$; found: 440.9749.

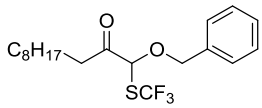
2-(benzyloxy)-1-cyclopentyl-2-((trifluoromethyl)thio)ethan-1-one (5k)



Title compound **5k** was prepared according to general procedure A and purified by column chromatography (SiO_2; petroleum ether / Et_2O, 16:1) affording **5k** as a colorless oil (21 mg, 63%). ^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.42-7.32 (m, 5H), 5.49 (s, 1H), 4.86 (d, *J* = 11.6 Hz, 1H), 4.70 (d, *J* = 11.8 Hz, 1H), 1.93-1.52 (m, 8H); ^{13}C NMR (100 MHz, $CDCl_3$): δ = 205.0, 135.6, 130.1 (q, *J*(C,F) =

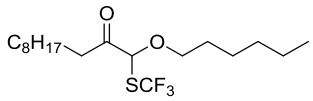
308.4 Hz), 128.8, 128.7, 128.4, 86.6 (q, *J*(C,F) = 1.2 Hz), 70.6, 47.1, 30.1, 29.7, 26.3, 26.2; ^{19}F NMR (377 MHz, $CDCl_3$): δ = -37.56; HRMS (ESI): m/z calcd. for $C_{15}H_{17}O_2F_3S+Na^+$: 341.0799 [*M*+Na]$^+$; found: 341.0793.

1-(benzyloxy)-1-((trifluoromethyl)thio)undecan-2-one (5l)



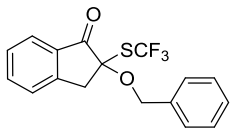
Title compound **5l** was prepared according to general procedure A and purified by column chromatography (SiO_2; petroleum ether / Et_2O, 16:1) affording **5l** as a colorless oil (21 mg, 51%). ^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.41-7.32 (m, 5H), 5.35 (s, 1H), 4.88 (d, *J* = 11.6 Hz, 1H), 4.67 (d, *J* = 11.8 Hz, 1H), 2.71-2.56 (m, 2H), 1.64-1.56 (m, 2H), 1.32-1.21 (m, 12H), 0.88 (t, *J* = 6.7 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$): δ = 202.5, 135.5, 130.0 (q, *J*(C,F) = 308.6 Hz), 128.9, 128.7, 128.5, 86.8 (q, *J*(C,F) = 1.2 Hz), 70.7, 38.4, 32.0, 29.5, 29.5, 29.4, 29.1, 23.5, 22.8, 14.2; ^{19}F NMR (377 MHz, $CDCl_3$): δ = -37.35; HRMS (ESI): m/z calcd. for $C_{19}H_{27}O_2F_3S+Na^+$: 399.1582 [*M*+Na]$^+$; found: 399.1587.

1-(hexyloxy)-1-((trifluoromethyl)thio)undecan-2-one (5m)



Title compound **5m** was prepared according to general procedure A and purified by column chromatography (SiO_2; petroleum ether / Et_2O, 16:1) affording **5m** as a colorless oil (25 mg, 62%). ^{1}H NMR (400 MHz, $CDCl_3$): δ = 5.32 (s, 1H), 3.79 (dt, *J* = 9.2 Hz, 6.6 Hz, 1H), 3.54 (dt, *J* = 9.2 Hz, 6.6 Hz, 1H), 2.71-2.55 (m, 2H), 1.69-1.57 (m, 4H), 1.40-1.21 (m, 18H), 0.92-0.85 (m, 6H); ^{13}C NMR (100 MHz, $CDCl_3$): δ = 202.9, 130.2 (q, *J*(C,F) = 308.1 Hz), 88.4 (q, *J*(C,F) = 1.1 Hz), 69.6, 38.2, 32.0, 31.6, 29.5, 29.5, 29.4, 29.2, 29.1, 25.8, 23.5, 22.8, 22.7, 14.2, 14.1; ^{19}F NMR (377 MHz, $CDCl_3$): δ = -37.64; HRMS (ESI): m/z calcd. for $C_{18}H_{33}O_2F_3S+Na^+$: 393.2051 [*M*+Na]$^+$; found: 393.2057.

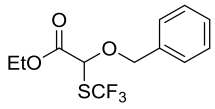
2-(benzyloxy)-2-((trifluoromethyl)thio)-2,3-dihydro-1*H*-inden-1-one (5n)



Title compound **5n** was prepared according to general procedure A and purified by column chromatography (SiO_2; petroleum ether / Et_2O, 16:1) affording **5n** as a colorless oil (29 mg, 75%). ^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.86-7.82 (m, 1H), 7.71-7.66 (m, 1H), 7.48-7.41 (m, 2H), 7.34-7.26 (m, 5H), 5.03 (d, *J* = 11.3 Hz, 1H), 4.84 (d, *J* = 11.3 Hz, 1H), 3.88 (d, *J* = 17.4 Hz, 1H), 3.67 (d, *J* = 17.4 Hz, 1H); ^{13}C NMR (100 MHz, $CDCl_3$): δ = 195.5, 149.6, 136.7, 136.7, 132.3, 130.1 (q, *J*(C,F) = 309.8 Hz), 128.7, 128.5, 128.2, 128.1, 126.5, 125.9, 93.9, 68.0, 43.6 (q, *J*(C,F) = 1.6 Hz);

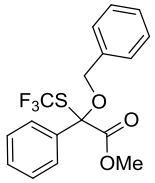
^{19}F NMR (377 MHz, $CDCl_3$): δ = -35.33; HRMS (ESI): m/z calcd. for $C_{17}H_{13}O_2F_3S+Na^+$: 361.0486 [*M*+Na]$^+$; found: 361.0470.

ethyl 2-(benzyloxy)-2-((trifluoromethyl)thio)acetate (5o)



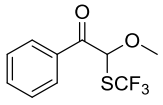
Title compound **5o** was prepared according to general procedure A and purified by column chromatography (SiO_2; petroleum ether / Et_2O, 16:1) affording **5o** as a colorless oil (8.0 mg, 27%). ^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.39-7.32 (m, 5H), 5.49 (s, 1H), 4.85 (d, *J* = 11.6 Hz, 1H), 4.74 (d, *J* = 11.6 Hz, 1H), 4.28 (qd, *J* = 7.1 Hz, 1.5 Hz, 2H), 1.31 (t, *J* = 7.1 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$): δ = 166.5, 135.5, 129.9 (q, *J*(C,F) = 308.5 Hz), 128.8, 128.7, 128.6, 80.9 (q, *J*(C,F) = 2.0 Hz), 70.5, 62.8, 14.1; ^{19}F NMR (377 MHz, $CDCl_3$): δ = -38.32; HRMS (ESI): m/z calcd. for $C_{12}H_{13}O_3F_3S+Na^+$: 317.0435 [*M*+Na]$^+$; found: 317.0429.

methyl 2-(benzyloxy)-2-phenyl-2-((trifluoromethyl)thio)acetate (5p)



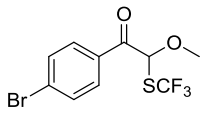
Title compound **5p** was prepared according to general procedure A and purified by column chromatography (SiO_2; petroleum ether / Et_2O, 16:1) affording **5p** as a white solid (8.0 mg, 20%). ^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.72-7.68 (m, 2H), 7.48-7.44 (m, 2H), 7.43-7.33 (m, 6H), 5.05 (d, *J* = 10.7 Hz, 1H), 4.56 (d, *J* = 10.7 Hz, 1H), 3.75 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$): δ = 168.9 (q, *J*(C,F) = 1.8 Hz), 138.0, 136.4, 129.4 (q, *J*(C,F) = 309.4 Hz), 129.3, 128.6, 128.6, 128.2, 128.2, 126.4, 97.0 (q, *J*(C,F) = 1.4 Hz), 68.8, 53.9; ^{19}F NMR (377 MHz, $CDCl_3$): δ = -37.47; HRMS (ESI): m/z calcd. for $C_{17}H_{15}O_3F_3S+Na^+$: 379.0592 [*M*+Na]$^+$; found: 379.0600; Mp: 78.5-79.5 ºC.

2-methoxy-1-phenyl-2-((trifluoromethyl)thio)ethan-1-one (5q)



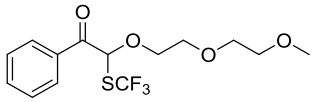
Title compound **5q** was prepared according to general procedure B from dimethoxymethane and trimethyl orthoformate and purified by column chromatography (SiO_2; petroleum ether / Et_2O, 16:1) affording **5q** as a colorless oil (11 mg, 41% from dimethoxymethane; 15 mg, 55% from trimethyl orthoformate). ^{1}H NMR (400 MHz, $CDCl_3$): δ = 8.08-8.03 (m, 2H), 7.68-7.62 (m, 1H), 7.55-7.48 (m, 2H), 6.47 (s, 1H), 3.48 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$): δ = 191.4, 134.8, 133.0, 130.3 (q, *J*(C,F) = 308.0 Hz), 129.6, 129.1, 88.8 (q, *J*(C,F) = 1.6 Hz), 54.6; ^{19}F NMR (377 MHz, $CDCl_3$): δ = -38.70; HRMS (ESI): m/z calcd. for $C_{10}H_9O_2F_3S+Na^+$: 273.0168 [*M*+Na]$^+$; found: 273.0175.

1-(4-bromophenyl)-2-methoxy-2-((trifluoromethyl)thio)ethan-1-one (5r)



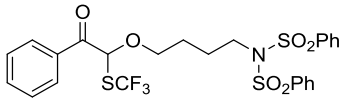
Title compound **5r** was prepared according to general procedure B and purified by column chromatography (SiO_2; petroleum ether / Et_2O, 16:1) affording **5r** as a colorless oil (12 mg, 34%). ^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.95-7.90 (m, 2H), 7.69-7.63 (m, 2H), 6.36 (s, 1H), 3.48 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$): δ = 190.5, 132.5, 131.7, 131.0, 130.3, 130.2 (q, *J*(C,F) = 308.1 Hz), 88.8 (q, *J*(C,F) = 1.5 Hz), 54.8; ^{19}F NMR (377 MHz, $CDCl_3$): δ = -38.65; HRMS (ESI): m/z calcd. for $C_{10}H_8O_2F_3S^{79}Br+Na^+$: 350.9278 [*M*+Na]$^+$; found: 350.9279.

2-(2-(2-methoxyethoxy)ethoxy)-1-phenyl-2-((trifluoromethyl)thio)ethan-1-one (5s)



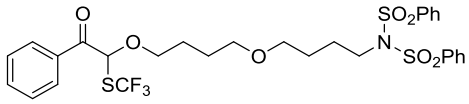
Title compound **5s** was prepared according to general procedure B and purified by column chromatography (SiO_2; petroleum ether / CH_2Cl_2, 1:1) affording **5s** as a colorless oil (24 mg, 72%). ^{1}H NMR (400 MHz, $CDCl_3$): δ = 8.10-8.04 (m, 2H), 7.66-7.60 (m, 1H), 7.53-7.46 (m, 2H), 6.61 (s, 1H), 4.00-3.92 (m, 1H), 3.79-3.72 (m, 1H), 3.68-3.64 (m, 2H), 3.58-3.48 (m, 2H), 3.44-3.40 (m, 2H); ^{13}C NMR (100 MHz, $CDCl_3$): δ = 191.3, 134.6, 133.2, 130.3 (q, *J*(C,F) = 308.2 Hz), 129.6, 129.0, 87.4 (q, *J*(C,F) = 1.5 Hz), 71.9, 70.6, 70.1, 66.9, 59.1; ^{19}F NMR (377 MHz, $CDCl_3$): δ = -38.55; HRMS (ESI): m/z calcd. for $C_{14}H_{17}O_4F_3S+Na^+$: 361.0692 [*M*+Na]$^+$; found: 361.0702.

***N*-(4-(2-oxo-2-phenyl-1-((trifluoromethyl)thio)ethoxy)butyl)-*N*-(phenylsulfonyl)benzenesulfonamide (8a)**



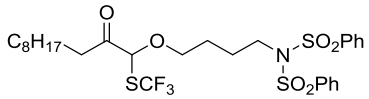
Title compound **8a** was prepared according to general procedure C and purified by column chromatography (SiO_2; petroleum ether / Et_2O, 3:1) affording **8a** as a colorless oil (40 mg, 66%). ^{1}H NMR (400 MHz, $CDCl_3$): δ = 8.08-8.03 (m, 2H), 8.02-7.96 (m, 4H), 7.68-7.61 (m, 3H), 7.56-7.48 (m, 6H), 6.52 (s, 1H), 3.71 (dt, *J* = 9.0 Hz, 6.1 Hz, 1H), 3.69-3.63 (m, 2H), 3.42 (dt, *J* = 9.0 Hz, 6.1 Hz, 1H), 1.77-1.67 (m, 2H), 1.58-1.48 (m, 2H); ^{13}C NMR (100 MHz, $CDCl_3$): δ = 191.4, 139.9, 134.9, 134.0, 132.8, 130.4 (q, *J*(C,F) = 308.0 Hz), 129.5, 129.2, 129.1, 128.2, 87.9 (q, *J*(C,F) = 1.3 Hz), 66.3, 49.1, 26.6, 26.2; ^{19}F NMR (377 MHz, $CDCl_3$): δ = -38.54; HRMS (ESI): m/z calcd. for $C_{25}H_{24}O_6F_3S_3+Na^+$: 610.0610 [*M*+Na]$^+$; found: 610.0619.

***N*-(4-(4-(2-oxo-2-phenyl-1-((trifluoromethyl)thio)ethoxy)butoxy)butyl)-*N*-(phenylsulfonyl)benzenesulfonamide (8b)**



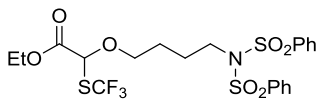
Title compound **8b** was prepared according to general procedure C using 60 equiv. of THF (**7a**) and purified by column chromatography (SiO_2; petroleum ether / Et_2O, 3:1) affording **8b** as a colorless oil (27 mg, 42%). ^{1}H NMR (400 MHz, $CDCl_3$): δ = 8.12-8.02 (m, 6H), 7.71-7.63 (m, 3H), 7.61-7.48 (m, 6H), 6.56 (s, 1H), 3.81 (dt, *J* = 9.0 Hz, 6.1 Hz, 1H), 3.76-3.69 (m, 2H), 3.52 (dt, *J* = 9.0 Hz, 6.1 Hz, 1H), 3.36-3.29 (m, 4H), 1.81-1.71 (m, 2H), 1.70-1.46 (m, 6H); ^{13}C NMR (100 MHz, $CDCl_3$): δ = 191.6, 140.0, 134.8, 133.9, 132.9, 130.4 (q, *J*(C,F) = 307.9 Hz), 129.5, 129.2, 129.1, 128.2, 88.0 (q, *J*(C,F) = 1.6 Hz), 70.3, 70.1, 67.0, 49.5, 27.1, 26.8, 26.2, 26.1; ^{19}F NMR (377 MHz, $CDCl_3$): δ = -38.55; HRMS (ESI): m/z calcd. for $C_{29}H_{32}O_7F_3S_3$+Na^+: 682.1185 [*M*+Na]$^+$; found: 682.1187.

_N_-(4-((2-oxo-1-((trifluoromethyl)thio)undecyl)oxy)butyl)-_N_-(phenylsulfonyl)benzenesulfonamide (8c)



Title compound **8c** was prepared according to general procedure C and purified by column chromatography (SiO_2; petroleum ether / Et_2O, 3:1) affording **8c** as a colorless oil (34 mg, 50%). ^{1}H NMR (400 MHz, $CDCl_3$): δ = 8.05-8.00 (m, 4H), 7.69-7.64 (m, 2H), 7.59-7.53 (m, 4H), 5.31 (s, 1H), 3.78-3.70 (m, 3H), 3.50 (dt, *J* = 9.2 Hz, 6.1 Hz, 1H), 2.69-2.52 (m, 2H), 1.85-1.77 (m, 2H), 1.66-1.56 (m, 4H), 1.33-1.21 (m, 12H), 0.87 (t, *J* = 6.8 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$): δ = 202.3, 140.0, 134.1, 130.1 (q, *J*(C,F) = 308.3 Hz), 129.3, 128.3, 88.1 (q, *J*(C,F) = 1.1 Hz), 68.6, 49.1, 38.3, 32.0, 29.5, 29.5, 29.4, 29.2, 26.7, 26.2, 23.4, 22.8, 14.2; ^{19}F NMR (377 MHz, $CDCl_3$): δ = -37.61; HRMS (ESI): m/z calcd. for $C_{28}H_{38}O_6F_3S_3$+Na^+: 660.1711 [*M*+Na]$^+$; found: 660.1724.

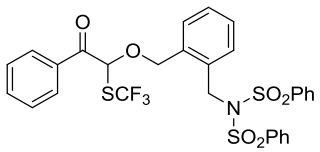
ethyl 2-(4-(_N_-(phenylsulfonyl)phenylsulfonamido)butoxy)-2-((trifluoromethyl)thio)acetate (8d)



Title compound **8d** was prepared according to general procedure C and purified by column chromatography (SiO_2; petroleum ether / Et_2O, 3:1) affording **8d** as a colorless oil (21 mg, 38%). ^{1}H NMR (400 MHz, $CDCl_3$): δ = 8.06-8.01 (m, 4H), 7.68-7.63 (m, 2H), 7.59-7.53 (m, 4H), 5.46 (s, 1H), 4.29 (q, *J* = 7.6 Hz, 2H), 3.78-3.68 (m, 3H), 3.58 (dt, *J* = 9.1 Hz, 6.1 Hz, 1H), 1.87-1.76 (m, 2H), 1.67-1.57 (m, 2H), 1.31 (t, *J* = 7.1 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$): δ = 166.4, 140.1, 134.0, 129.9 (q, *J*(C,F) = 308.2 Hz), 129.2, 128.3, 82.2 (q, *J*(C,F) = 2.0 Hz), 68.4, 62.8, 49.2, 26.7, 26.2, 14.1; ^{19}F NMR (377 MHz, $CDCl_3$): δ = -38.57; HRMS (ESI): m/z calcd. for

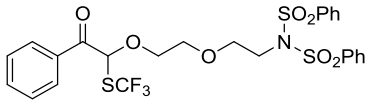
$C_{21}H_{24}NO_7F_3S+Na^+$: 578.0565 [*M*+Na]$^+$; found: 578.0575.

_N_-(2-((2-oxo-2-phenyl-1-((trifluoromethyl)thio)ethoxy)methyl)benzyl)-_N_-(phenylsulfonyl)benzenesulfonamide (8e)



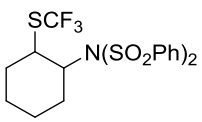
Title compound **8e** was prepared according to general procedure C using 60 equiv. of phthalane (**7b**) in 0.5 mL dry CH_2Cl_2. The title compound **8e** was purified by column chromatography (SiO_2; petroleum ether / Et_2O, 3:1) affording **8e** as a colorless oil (38 mg, 58%). ^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.98-7.93 (m, 2H), 7.75-7.69 (m, 4H), 7.61-7.54 (m, 3H), 7.45-7.38 (m, 6H), 7.29-7.25 (m, 1H), 7.20-7.15 (m, 2H), 7.09-7.03 (m, 1H), 6.53 (s, 1H), 4.93 (d, *J* = 11.3 Hz, 1H), 4.92 (d, *J* = 16.4 Hz, 1H), 4.82 (d, *J* = 16.4 Hz, 1H), 4.75 (d, *J* = 11.3 Hz, 1H); ^{13}C NMR (100 MHz, $CDCl_3$): δ = 191.1, 139.9, 134.7, 134.1, 133.8, 133.6, 133.0, 130.2 (q, *J*(C,F) = 308.4 Hz), 130.2, 129.6, 129.4, 129.1, 129.0, 128.9, 128.2, 128.0, 86.5 (q, *J*(C,F) = 1.5 Hz), 67.5, 48.8; ^{19}F NMR (377 MHz, $CDCl_3$): δ = -38.34; HRMS (ESI): m/z calcd. for $C_{29}H_{24}NO_6F_3S_3+Na^+$: 658.0616 [*M*+Na]$^+$; found: 658.0621.

_N_-(2-(2-(2-oxo-2-phenyl-1-((trifluoromethyl)thio)ethoxy)ethoxy)ethyl)-_N_-(phenylsulfonyl)benzenesulfonamide (8f)



Title compound **8f** was prepared according to general procedure B and purified by column chromatography (SiO_2; petroleum ether / Et_2O, 3:1) affording **8f** as a colorless oil (31 mg, 52%). ^{1}H NMR (400 MHz, $CDCl_3$): δ = 8.08-8.04 (m, 2H), 8.04-8.00 (m, 4H), 7.67-7.60 (m, 3H), 7.56-7.47 (m, 6H), 6.62 (s, 1H), 3.88-3.72 (m, 3H), 3.64-3.54 (m, 3H), 3.52-3.47 (m, 2H); ^{13}C NMR (100 MHz, $CDCl_3$): δ = 191.3, 139.7, 134.8, 134.0, 132.9, 130.3 (q, *J*(C,F) = 308.1 Hz), 129.6, 129.1, 129.1, 128.4, 87.6 (q, *J*(C,F) = 1.6 Hz), 69.8, 69.7, 66.3, 47.8; ^{19}F NMR (377 MHz, $CDCl_3$): δ = -38.53; HRMS (ESI): m/z calcd. for $C_{25}H_{24}NO_7F_3S_3+Na^+$: 626.0559 [*M*+Na]$^+$; found: 626.0572.

_N_-(phenylsulfonyl)-_N_-(2-((trifluoromethyl)thio)cyclohexyl)benzenesulfonamide (13)



Title compound **13** was prepared by the following procedure: In a 2 mL pressurizable reaction tube were meassured $(PhSO_2)_2NSCF_3$ (**1**) (40 mg, 0.1 mmol, 1.0 equiv.) and $Rh_2(OAc)_4$ (**4**) (0.5 mg, 0.001 mmol, 0.01 equiv.) under ambient conditions. In a dry argon filled glovebox was added a solution of diazo compound **2** (0.12 mmol, 1.2 equiv.) and cyclohexene oxide (**9**) (1.0 mmol, 10 equiv.) in 0.5

mL dry CH_2Cl_2 to the reaction vial. The mixture in the closed reaction vial was stirred for 24 h before being transferred directly on a chromatography column and purified on silica gel (SiO_2; petroleum ether / Et_2O, 3:1) affording **13** as a yellowish solid (12 mg, 24%). ^{1}H NMR (400 MHz, $CDCl_3$): δ = 8.26-7.82 (m, broad, 4H), 7.71-7.64 (m, 2H), 7.61-7.53 (m, 4H), 4.24 (td, *J* = 11.5 Hz, 4.1 Hz, 1H), 3.76 (td, *J* = 11.8 Hz, 3.7 Hz, 1H), 2.47-2.39 (m, 1H), 4.93 (qd, *J* = 12.5 Hz, 3.5 Hz 1H), 1.79-1.68 (m, 2H), 1.68-1.60 (m, 1H), 1.60-1.48 (m, 1H), 1.39-1.10 (m, 2H); ^{13}C NMR (100 MHz, $CDCl_3$): δ = 144.3 (broad), 141.5 (broad), 138.4 (broad), 134.0 (broad), 130.9 (q, *J*(C,F) = 307.1 Hz), 129.1 (broad), 65.7 (q, *J*(C,F) = 1.0 Hz), 41.7 (q, *J*(C,F) = 1.7 Hz), 37.0 (q, *J*(C,F) = 0.9 Hz), 32.8, 26.4, 25.5; ^{19}F NMR (377 MHz, $CDCl_3$): δ = -37.81; HRMS (ESI): m/z calcd. for $C_{19}H_{20}NO_4F_3S_3$+Na^+: 502.0399 [*M*+Na]$^+$; found: 502.0403, Mp: 156-157 ºC.

Attempted cleavage of epoxides

When epoxide **9** was reacted with diazoketone **2a** and **1** in the presence of Rh-catalyst we did not observe formation of the expected oxy-trifluoromethylthiolation product **10** (Figure S1a). Instead we isolated amino-trifluoromethylthiol derivative **13**. A possible explanation is a Rh-catalyzed deoxygenation[5] of **9** by diazoketone **2a** to give **11** and cyclohexene **12** (Figure S1b). Subsequently, cyclohexene **12** reacted with **1** to give **13**.[4]

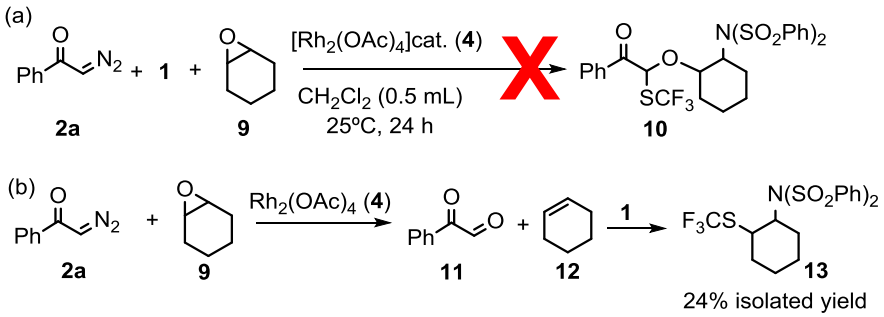


Figure S1: Attempted oxy-trifluoromethylthiolation with epoxide **9**.

Mechanistical aspects: competitive fluorination vs. trifluoromethylthiolation and proposed catalytic cycle

When a reaction was carried out in the absence of alcohol **3**, amino-trifluoromethylthiolation product **14** did not form (Figure S2a). This clearly shows that the $N(SO_2Ph)_2$ group cannot serve as nucleophile in place of the alkoxy groups. This control reaction shows a clear difference between the reactivity of NFSI and **1**. Using NFSI in place of **1** allows aminofluorination of diazocarbonyl compounds to be performed under similar conditions.[6, 7] We also have performed a competitive experiment between **1** and NFSI (Figure S2b). This experiment shows that under exactly the same reaction conditions oxy-trifluoromethylthiolation and –fluorination of diazoketones can be performed giving the analogous products **5a** and **15** in a ratio of 1:2.4. This suggests that the mechanisms of the two reactions are very similar and that the fluorine atom transfer is faster than transfer of the SCF_3 group from the same dibenzenesulfonimide carrier.

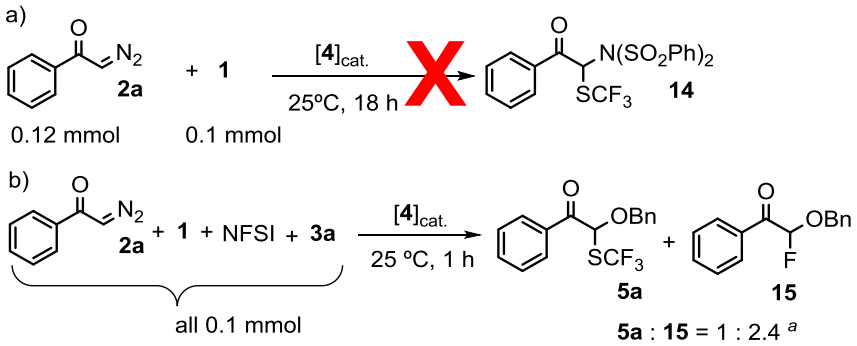


Figure S2: Control experiment without alcohol **3**, competitive fluorination/ trifluoromethylthiolation under limiting conditions. [a] Determined by ^{1}H-NMR-spectroscopy.

A plausible catalytic cycle for the Rh-catalyzed oxy-triflurомethylthiolation is given in Figure S3. The reactions with both dibenzenesulfonimide reagents (**1** and NFSI) or fluoro/trifluoromethyl-benziodoxols start with formation of Rh-carbenoid[8] **16** from **2a** and the catalyst **4**, which subsequently reacts with an alcohol, such as **3a** to give onium ylide **17**.[9-14] The subsequent step is trapping onium ylide **17** by the SCF_3 electrophile. Although the trapping of onium ylids with electrophiles is a well studied and documented process,[14] using F,[15] CF_3 [15] and SCF_3 (the above study) as electrophiles is a very new direction for this process. A possible oxidative addition of **1** with ylide **17** may result in **18**, which undergoes reductive elimination to give product **5a** and the regenerated catalyst **4**. In the case of using ethers **6-7** instead of alcohols **3** as substrates a similar mechanism can be suggested. It is well known[14] that ethers are also able to form onium ylids (such as **17**), which can be trapped by electrophiles. The main difference is that in the onium ylide formed from ethers has an oxygen atom with *two* alkyl groups (instead of an alkyl group and a proton, as in **17**).

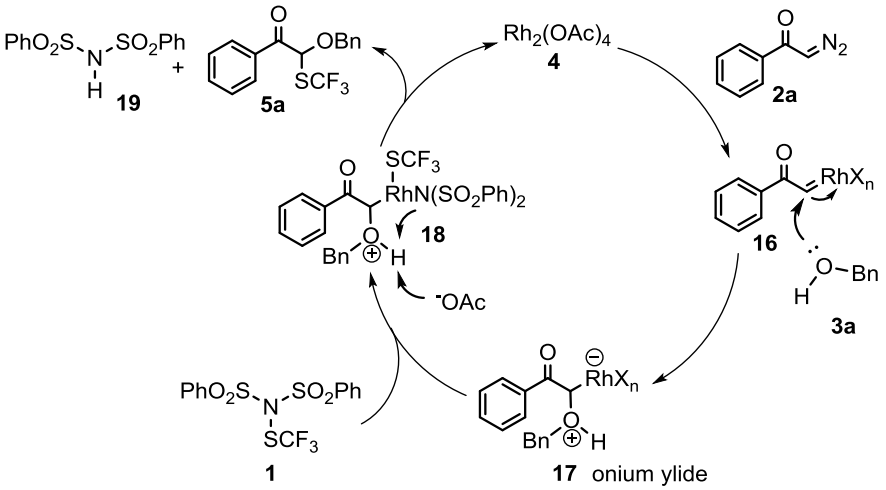
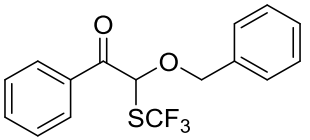
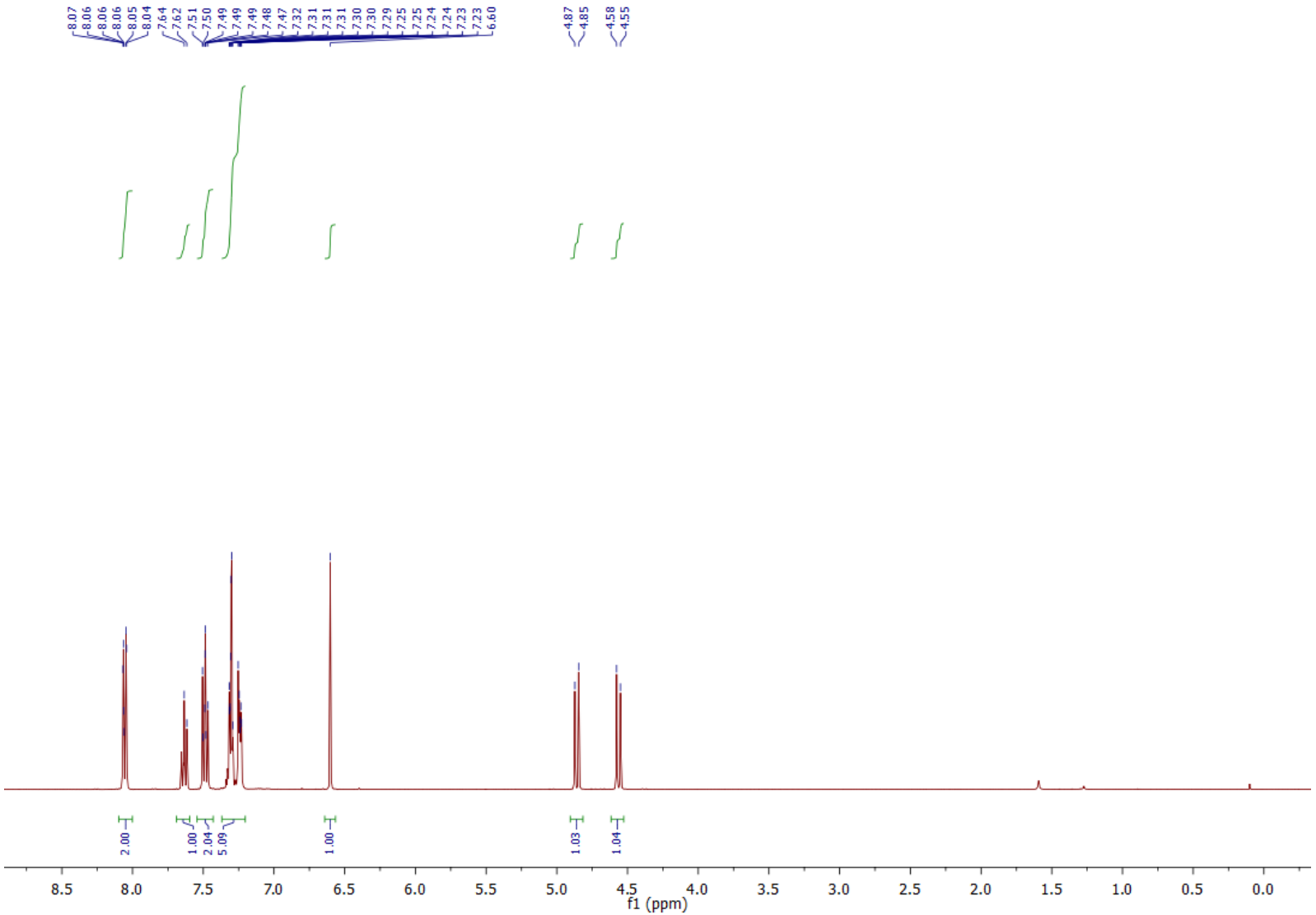


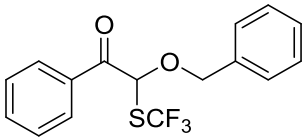
Figure S3: Plausible mechanism for the rhodium-catalyzed trifluoromethylthiolation reaction of diazo compounds together with alcohols.

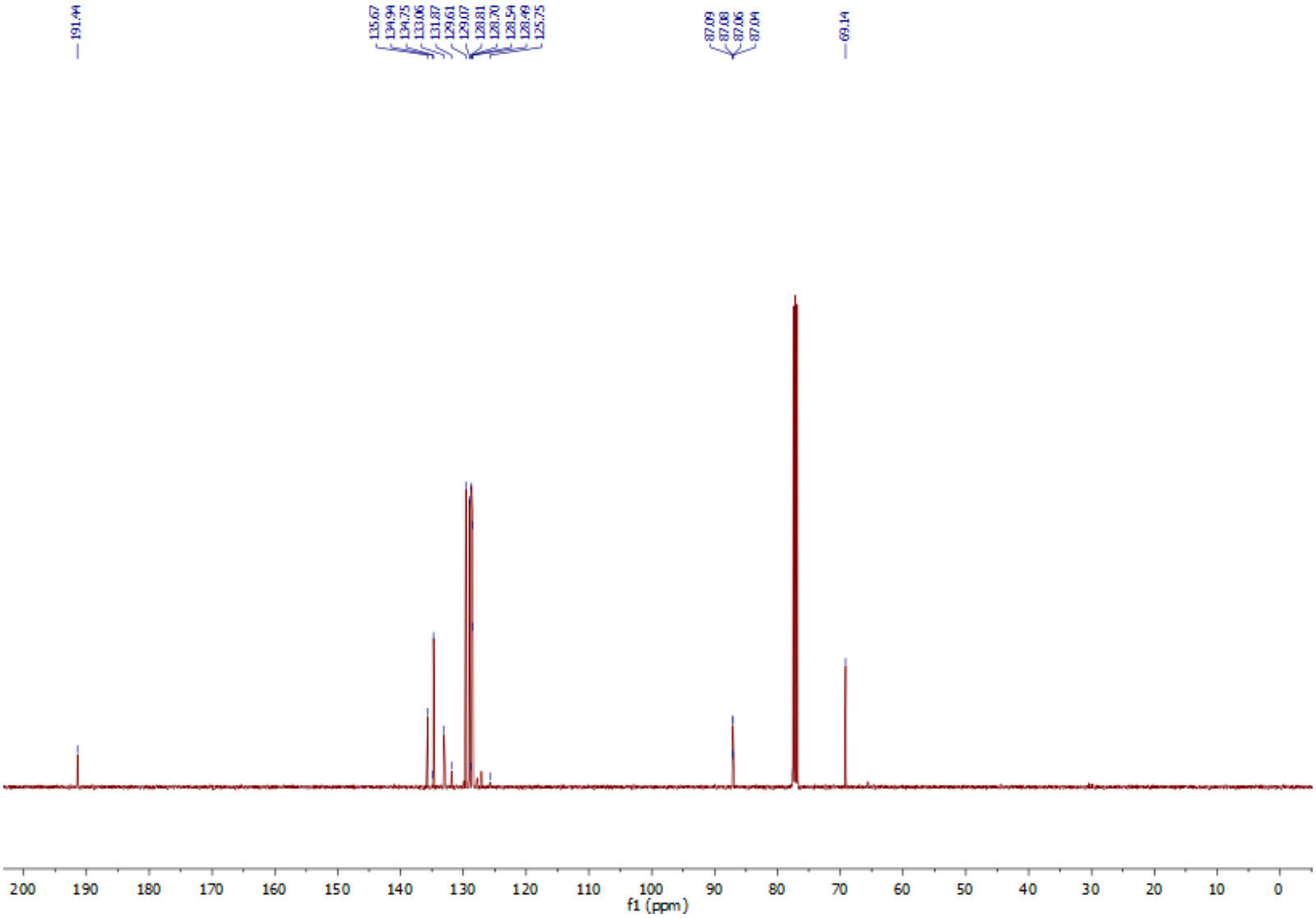
^{1}H NMR ($CDCl_3$, 400 MHz). 2-(Benzyloxy)-1-phenyl-2-((trifluoromethyl)thio)ethan-1-one (**5a**)



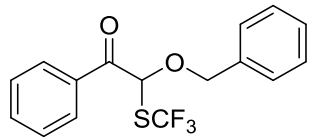


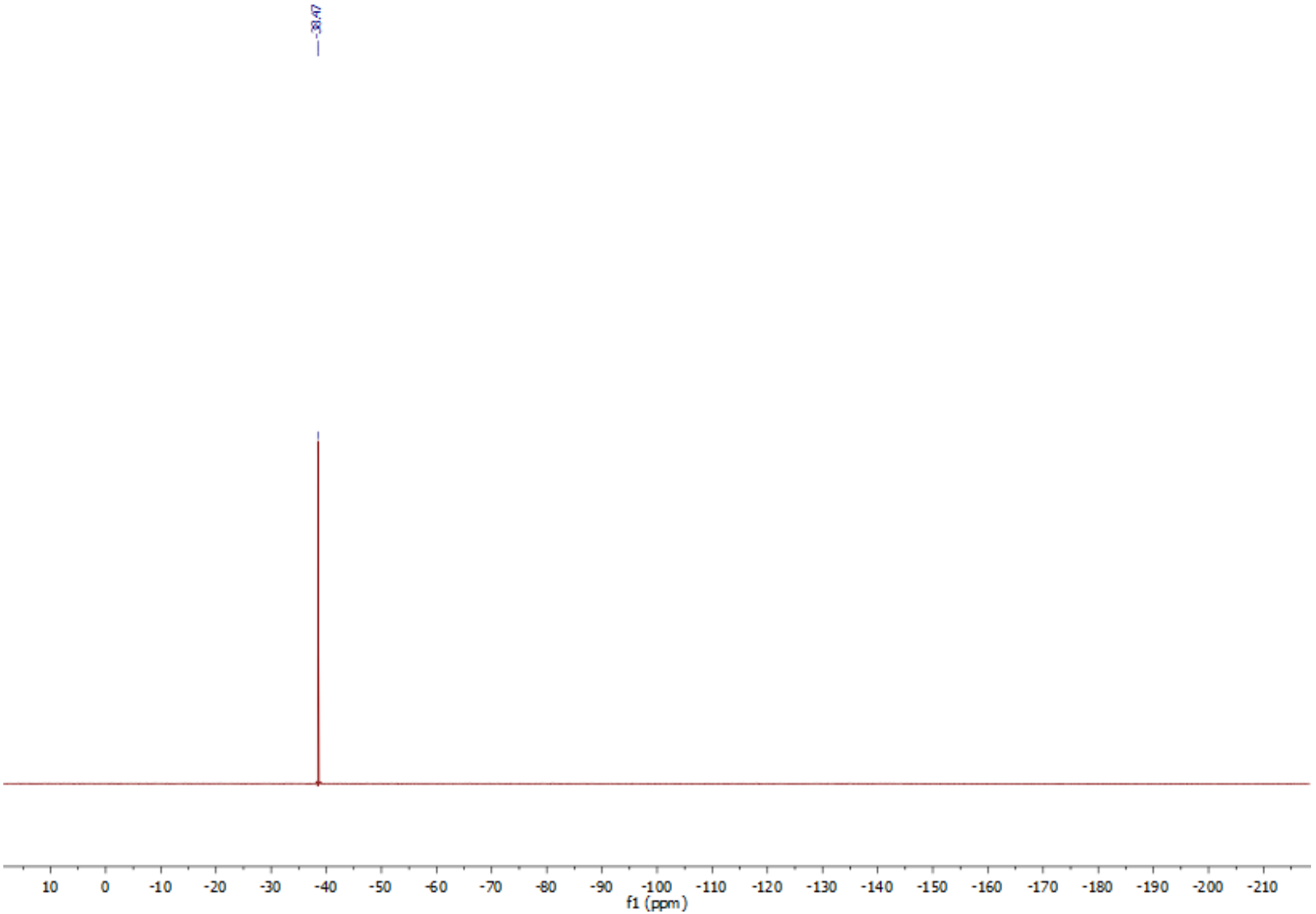
^{13}C NMR ($CDCl_3$, 100 MHz). 2-(Benzyloxy)-1-phenyl-2-((trifluoromethyl)thio)ethan-1-one (**5a**)



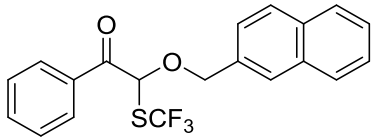


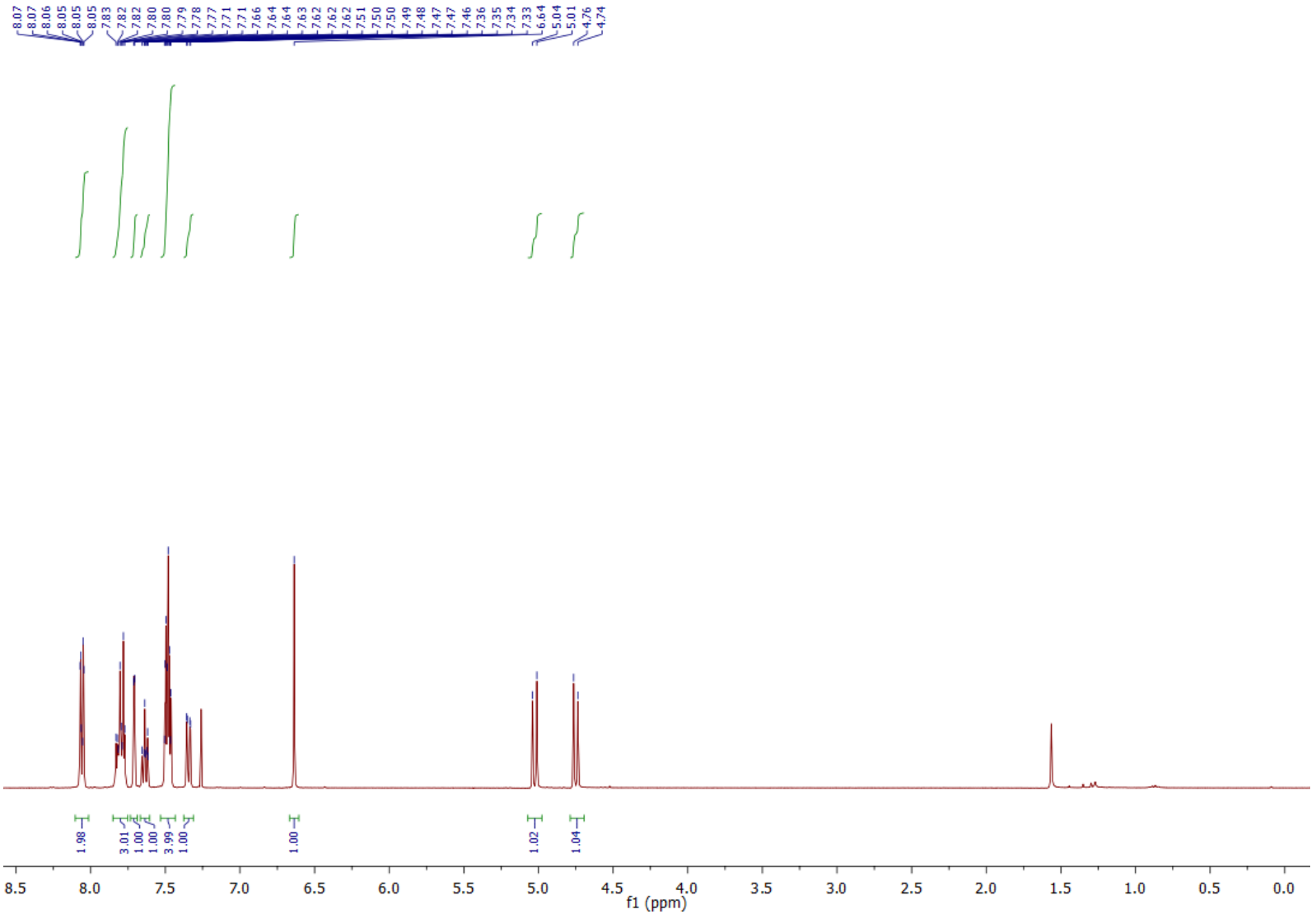
^{19}F NMR ($CDCl_3$, 377 MHz). 2-(Benzyloxy)-1-phenyl-2-((trifluoromethyl)thio)ethan-1-one (**5a**)



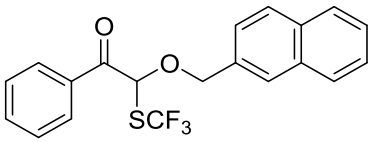


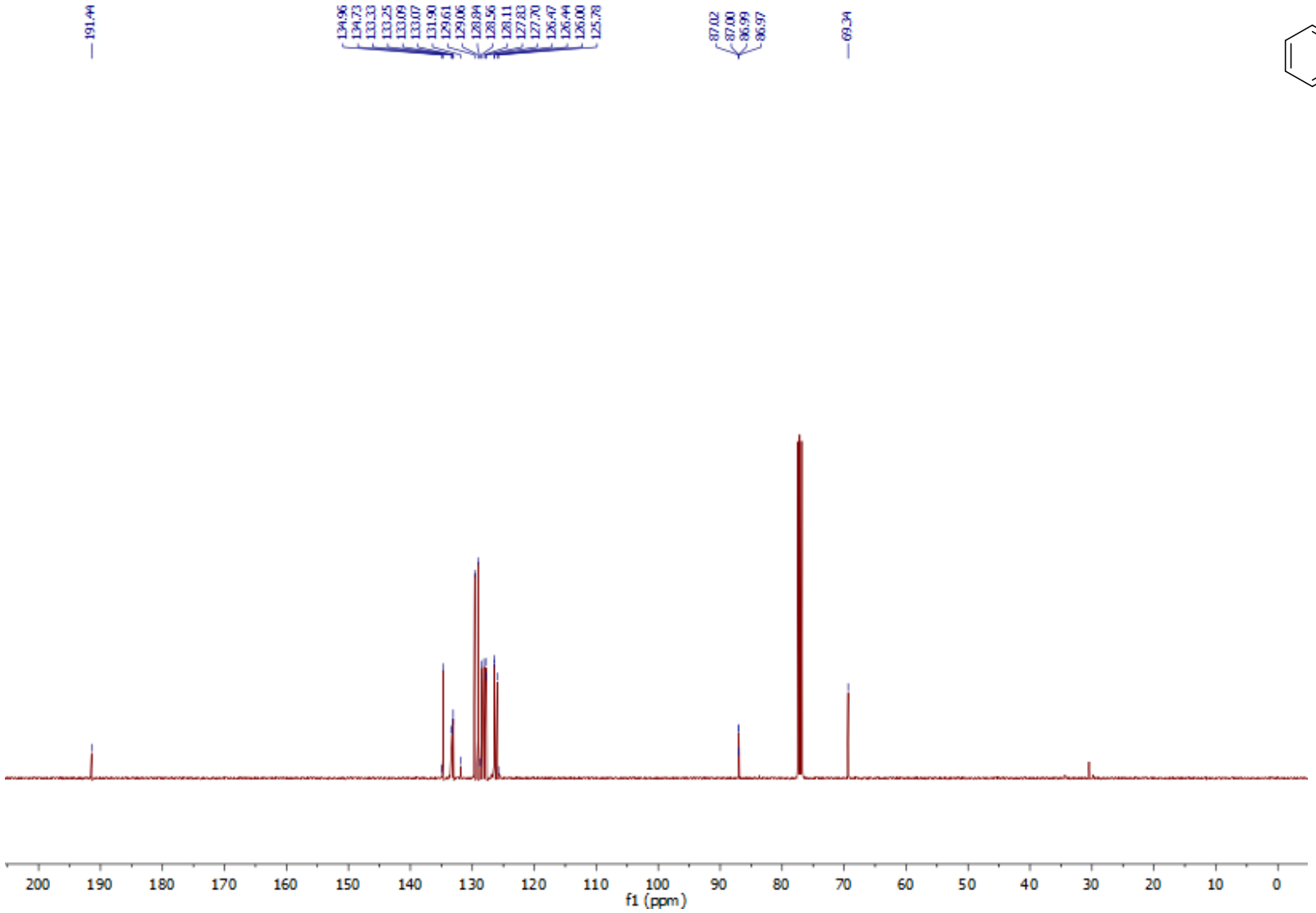
^{1}H NMR ($CDCl_3$, 400 MHz). 2-(Naphthalen-2-ylmethoxy)-1-phenyl-2-((trifluoromethyl)thio)ethan-1-one (**5b**)



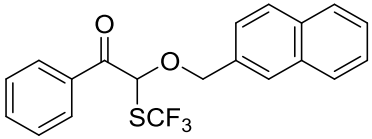


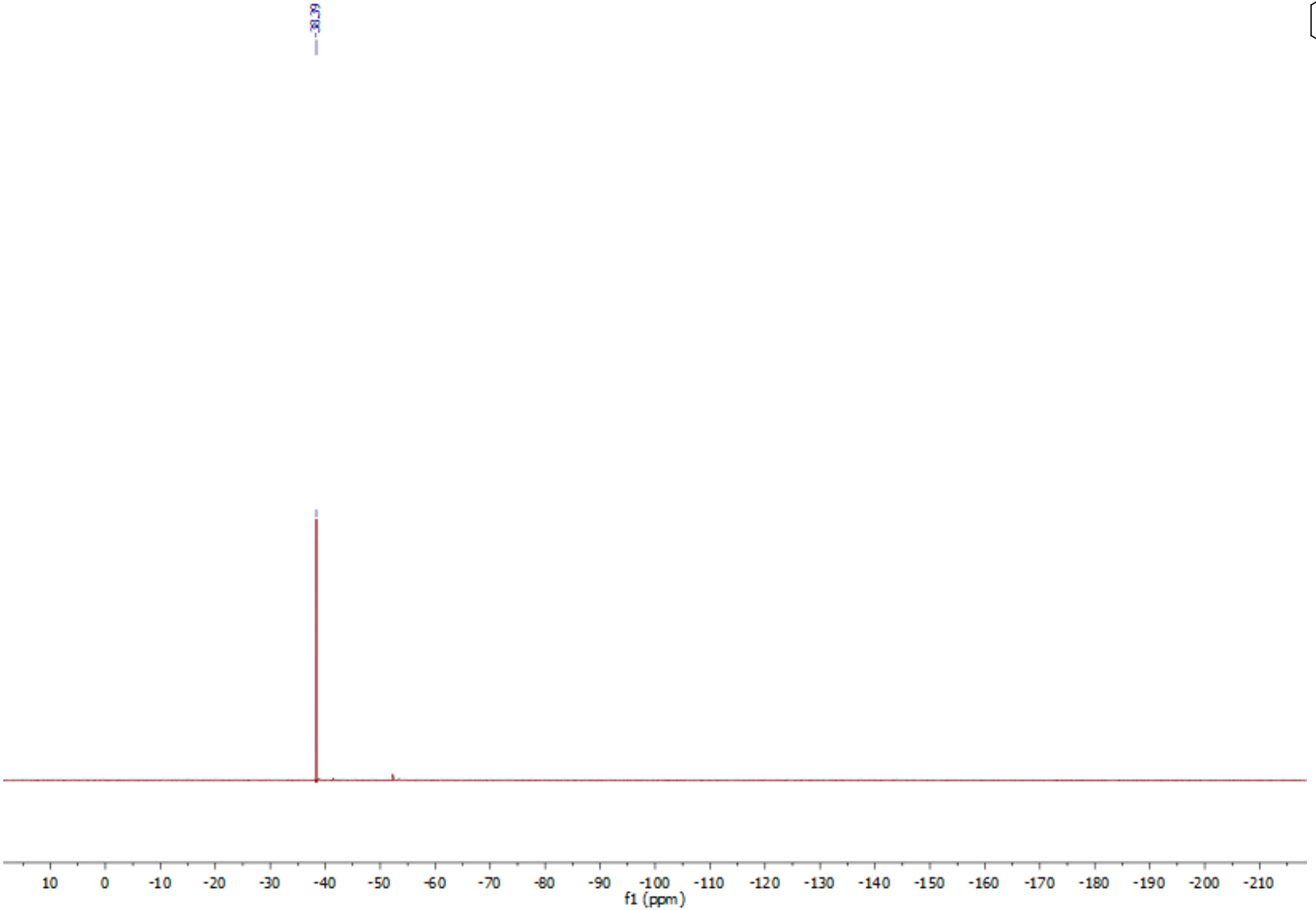
^{13}C NMR ($CDCl_3$, 100 MHz). 2-(Naphthalen-2-ylmethoxy)-1-phenyl-2-((trifluoromethyl)thio)ethan-1-one (**5b**)



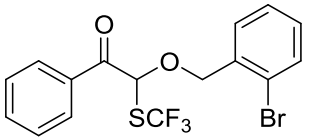


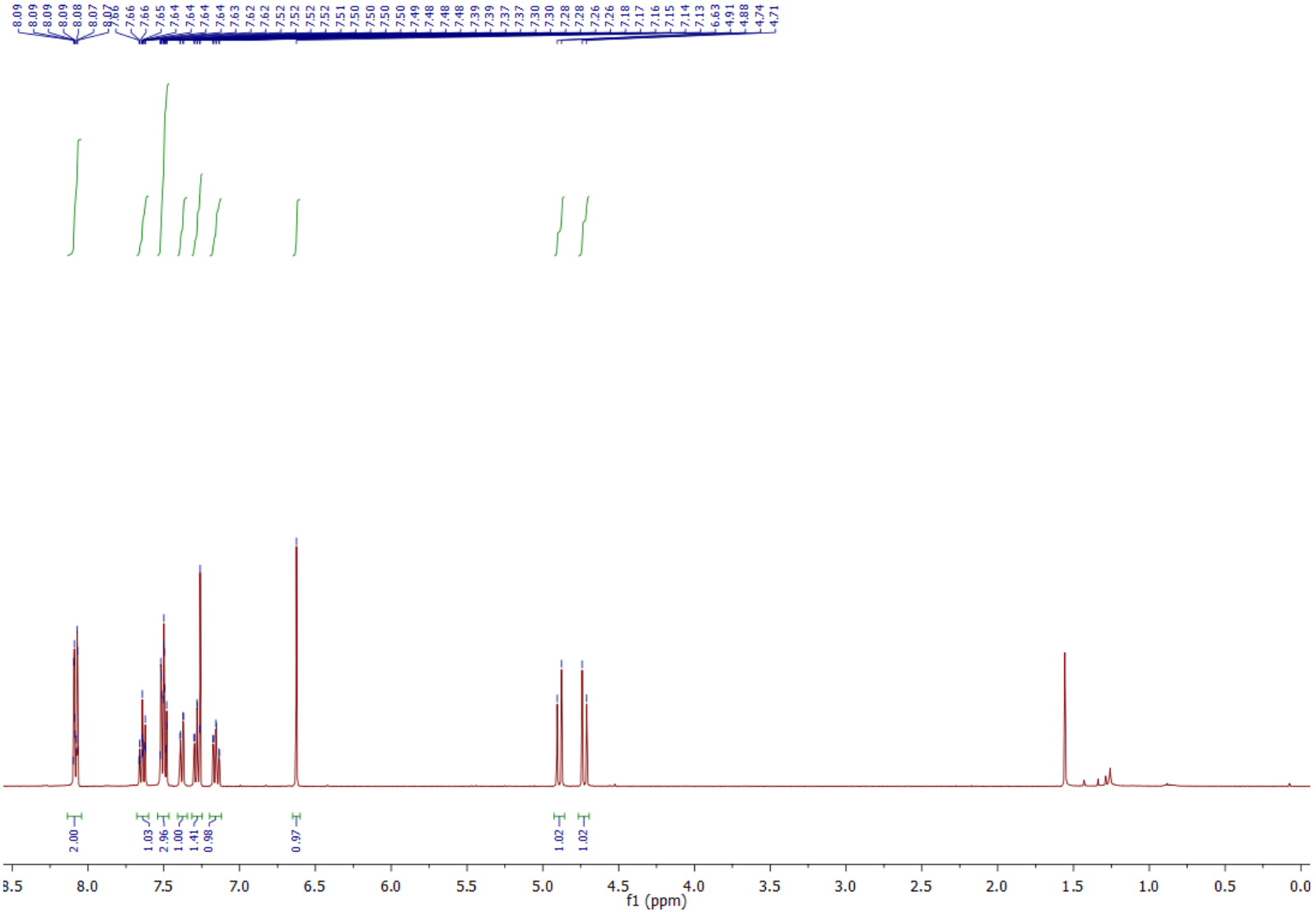
^{19}F NMR ($CDCl_3$, 377 MHz). 2-(Naphthalen-2-ylmethoxy)-1-phenyl-2-((trifluoromethyl)thio)ethan-1-one (**5b**)



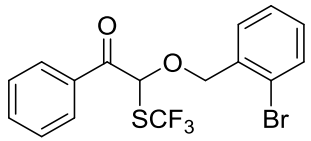


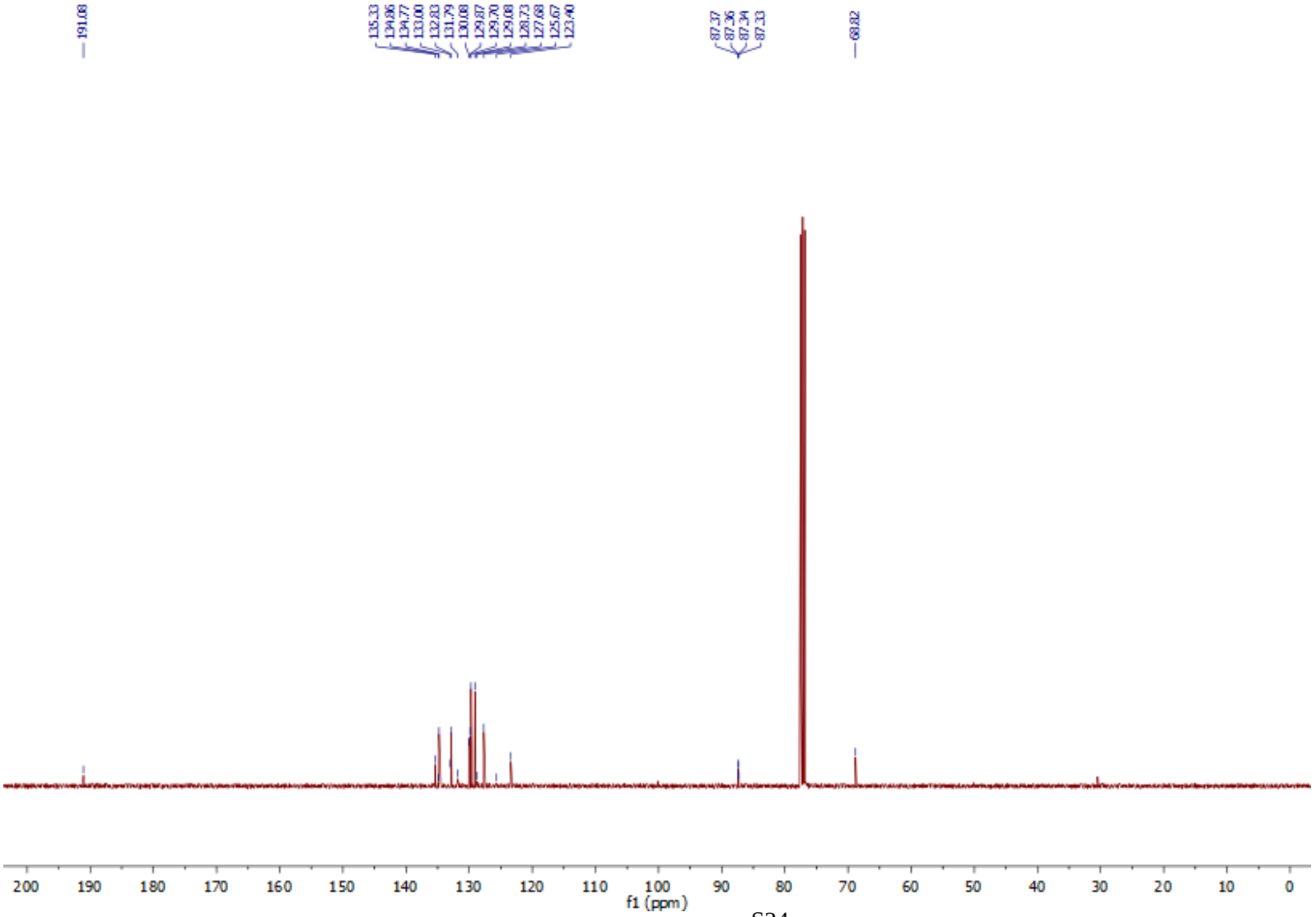
^{1}H NMR ($CDCl_3$, 400 MHz). 2-((2-Bromobenzyl)oxy)-1-phenyl-2-((trifluoromethyl)thio)ethan-1-one (**5c**)



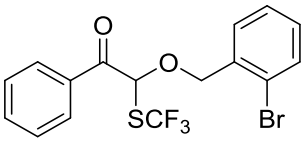


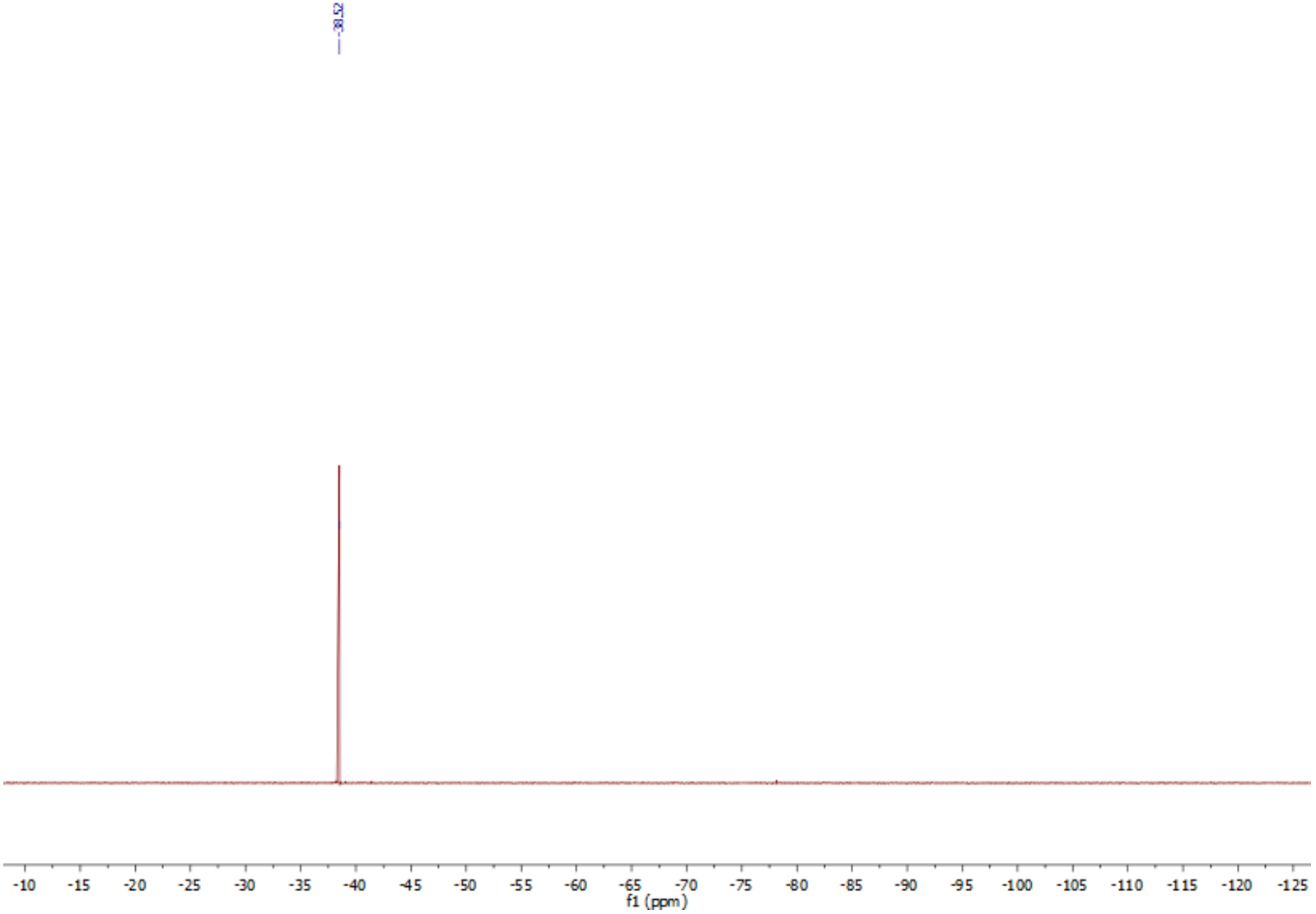
^{13}C NMR ($CDCl_3$, 100 MHz). 2-((2-Bromobenzyl)oxy)-1-phenyl-2-((trifluoromethyl)thio)ethan-1-one (**5c**)



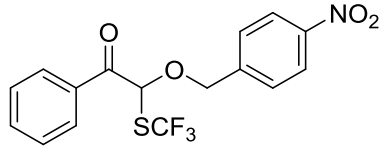


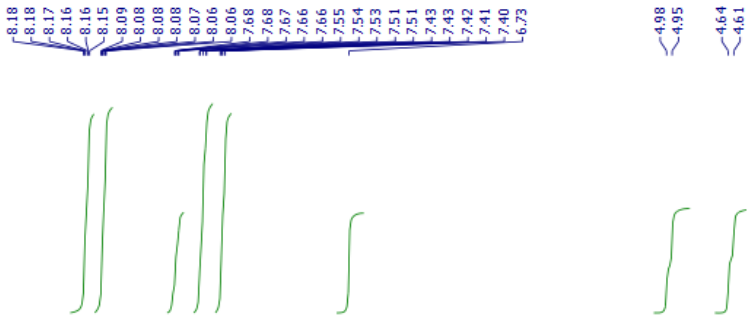
^{19}F NMR ($CDCl_3$, 377 MHz). 2-((2-Bromobenzyl)oxy)-1-phenyl-2-((trifluoromethyl)thio)ethan-1-one (**5c**)

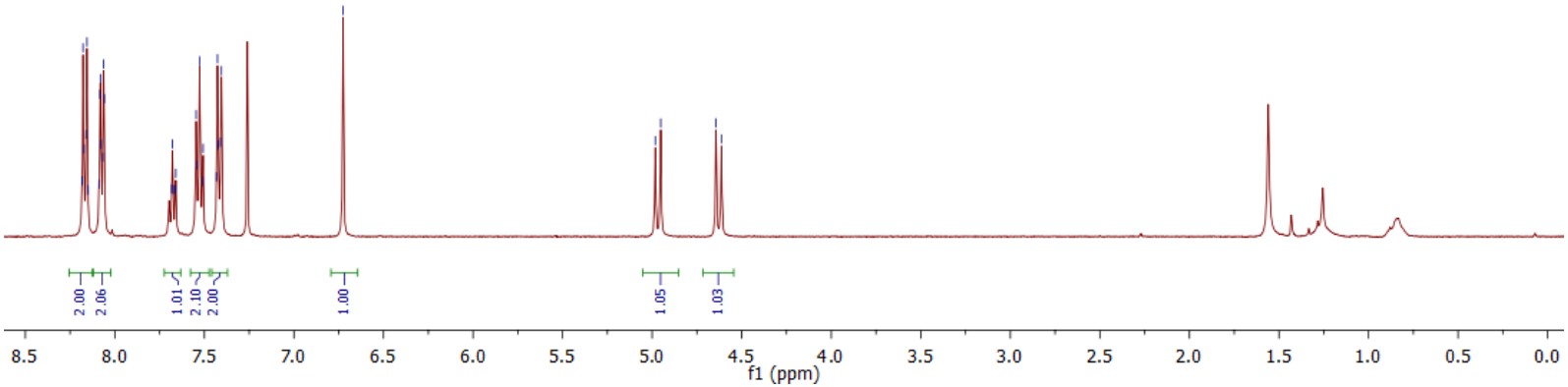




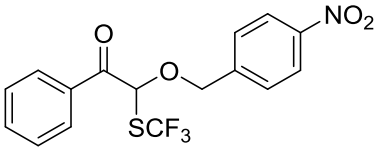
^{1}H NMR ($CDCl_3$, 400 MHz). 2-((4-Nitrobenzyl)oxy)-1-phenyl-2-((trifluoromethyl)thio)ethan-1-one (**5d**)

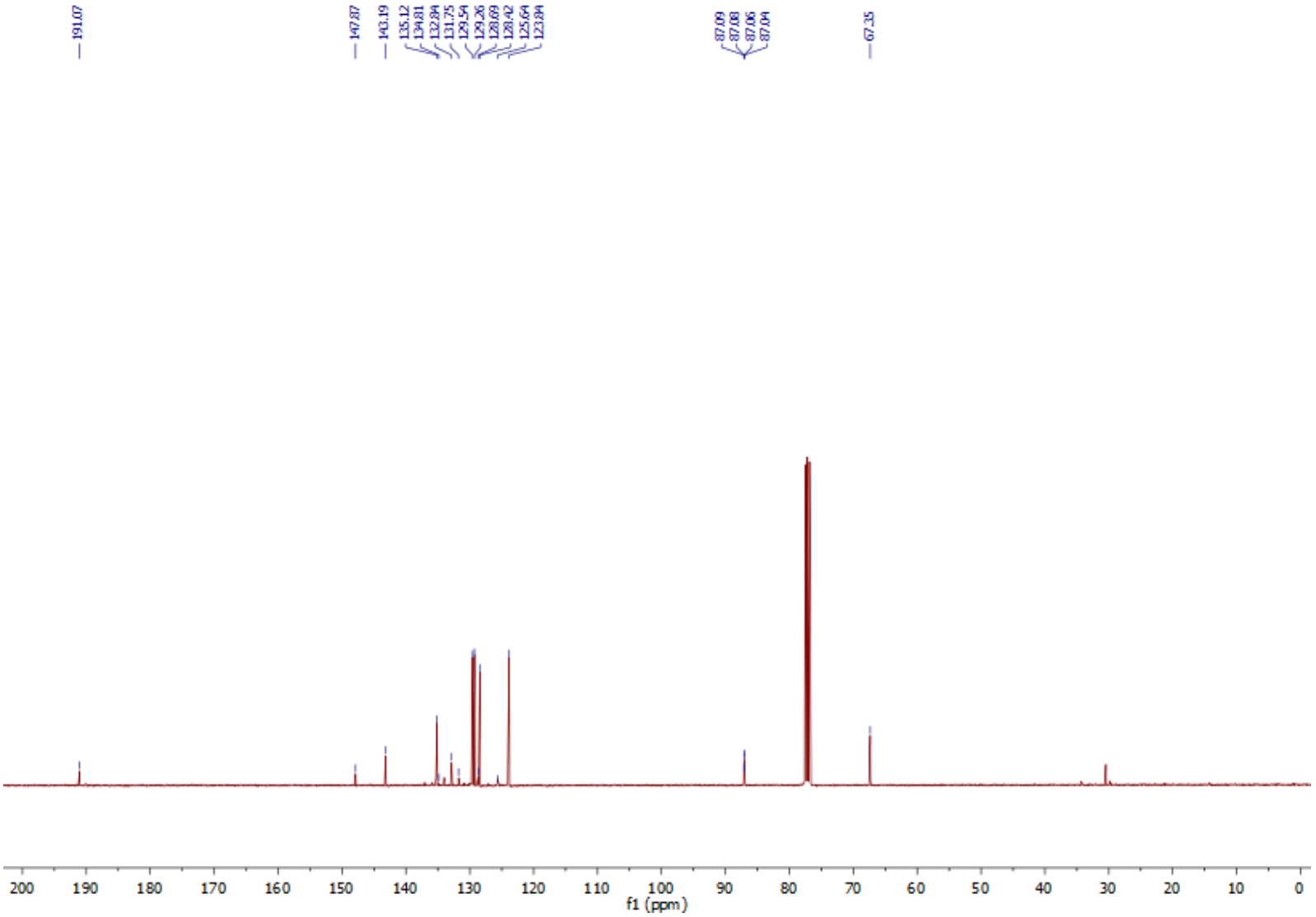




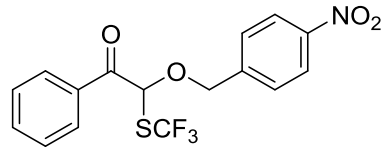


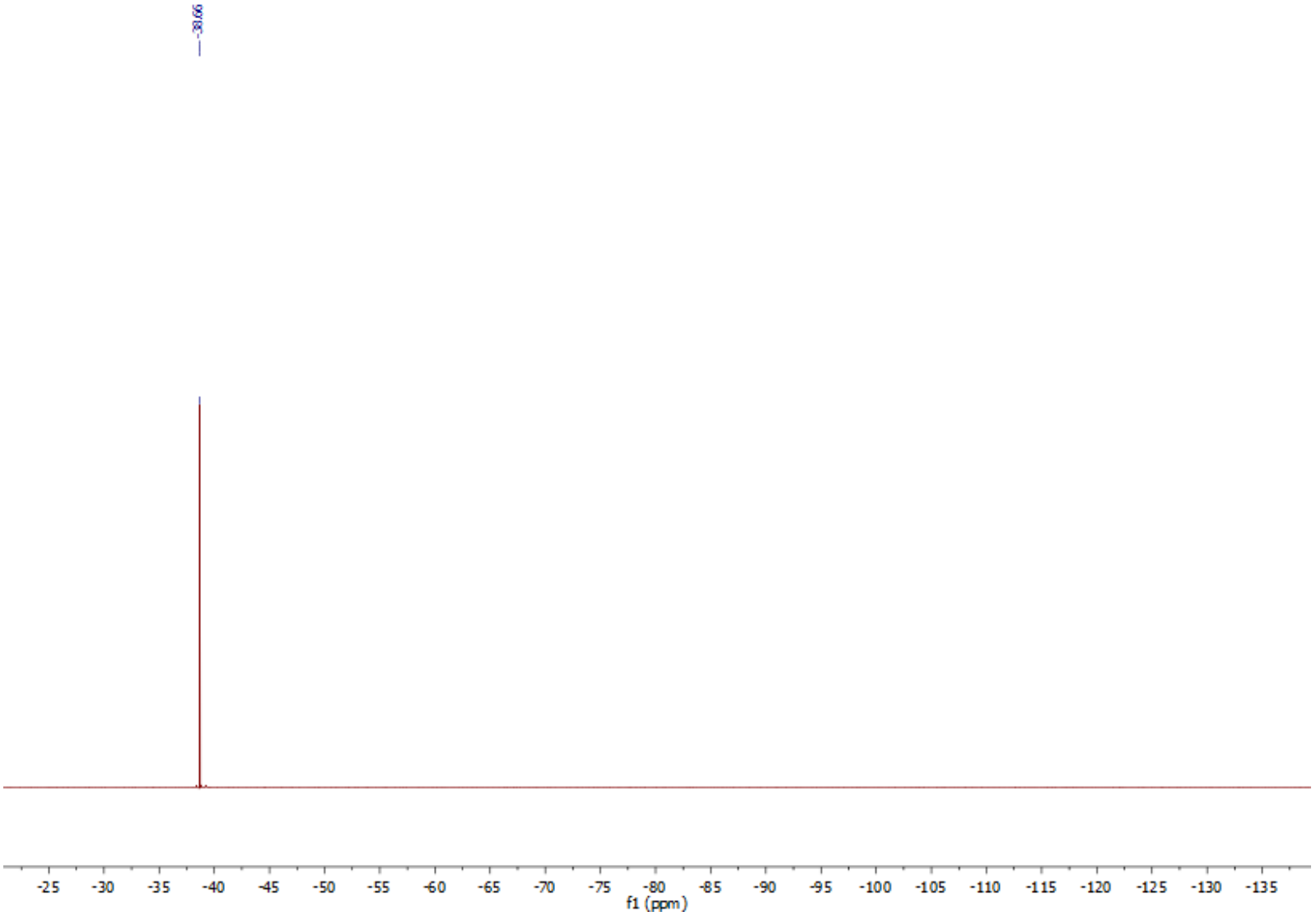
^{13}C NMR ($CDCl_3$, 100 MHz). 2-((4-Nitrobenzyl)oxy)-1-phenyl-2-((trifluoromethyl)thio)ethan-1-one (**5d**)



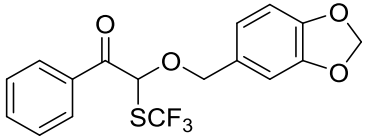


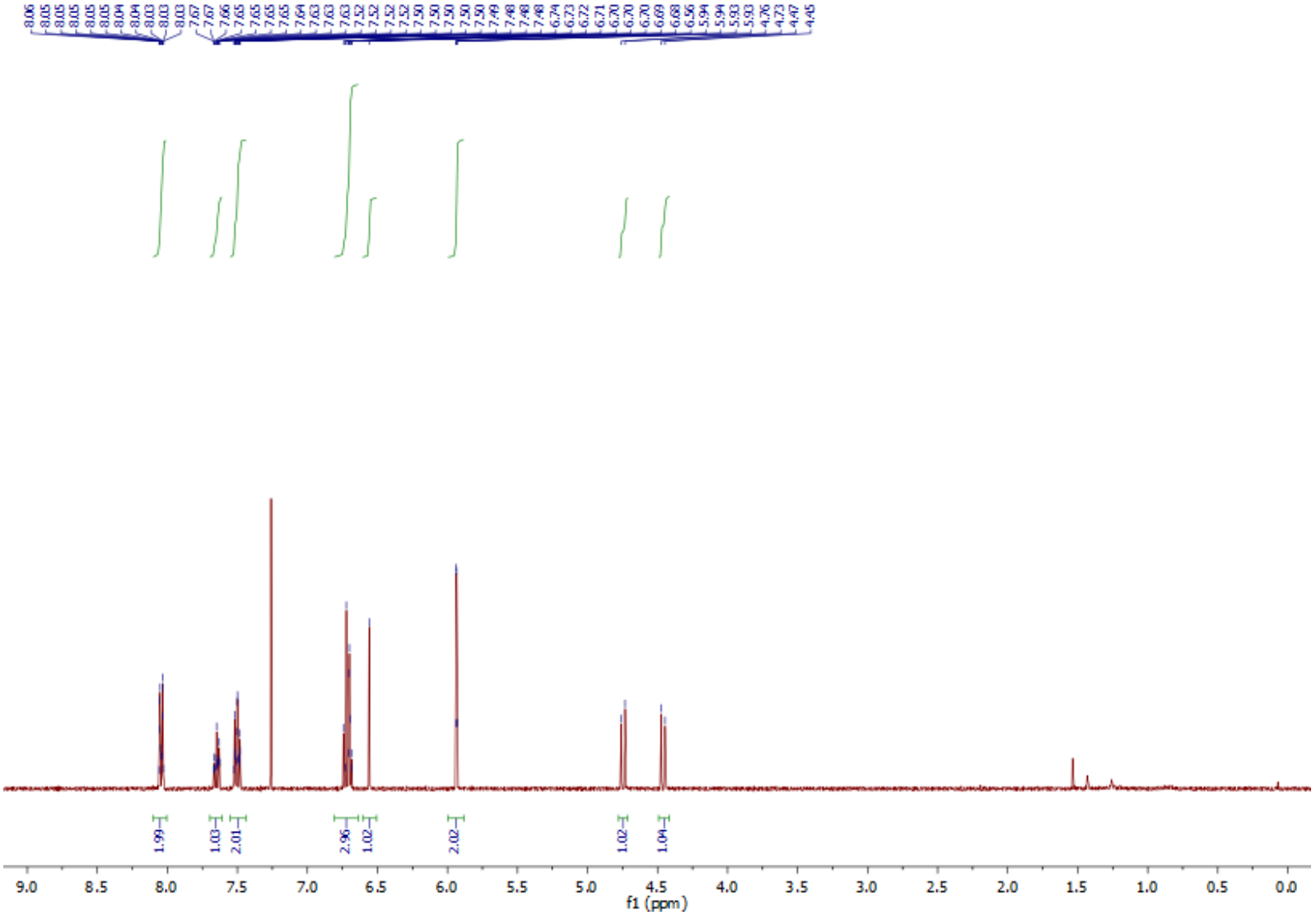
^{19}F NMR ($CDCl_3$, 377 MHz). 2-((4-Nitrobenzyl)oxy)-1-phenyl-2-((trifluoromethyl)thio)ethan-1-one (**5d**)



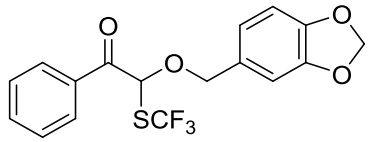


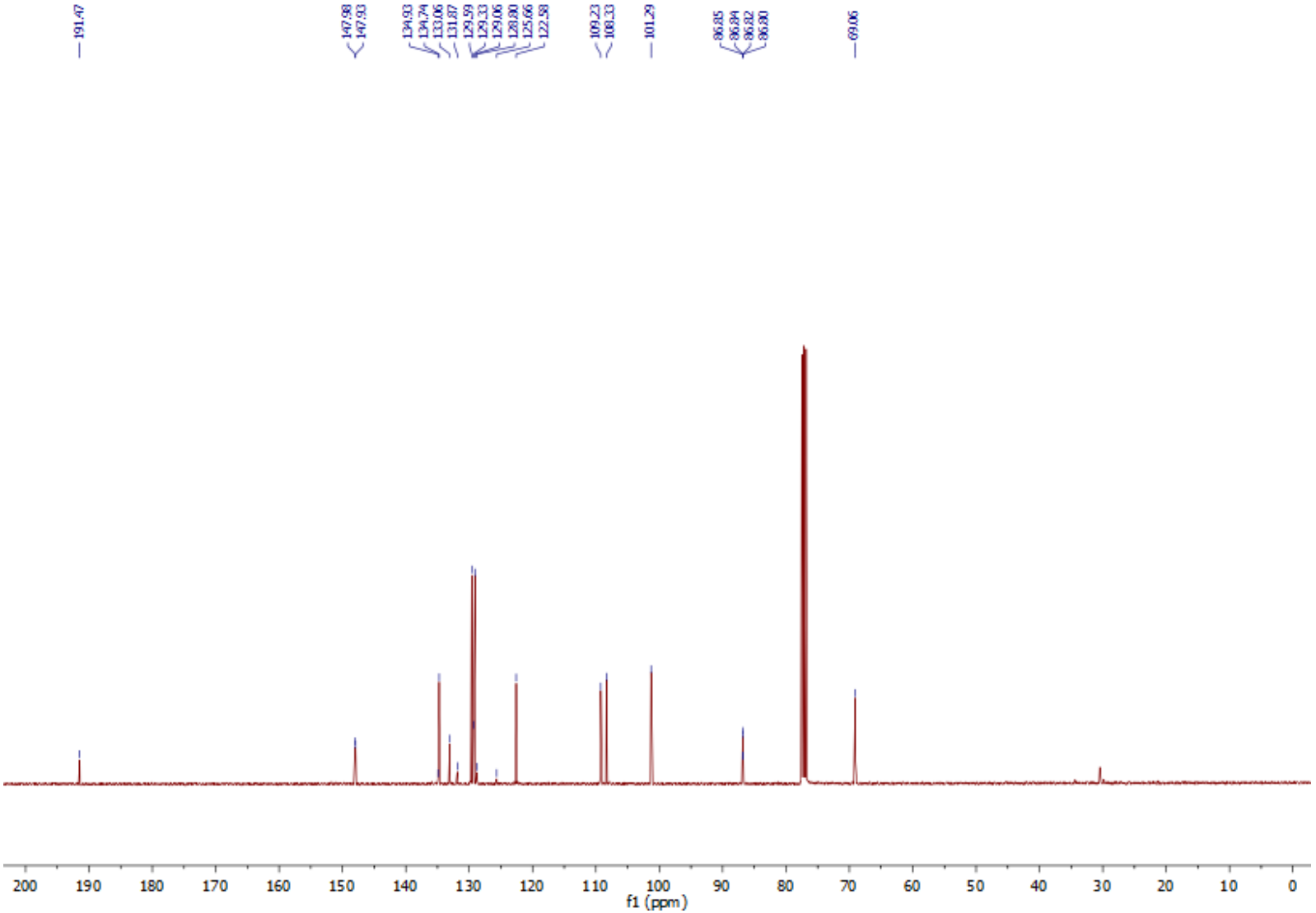
^{1}H NMR ($CDCl_3$, 400 MHz). 2-(Benzo[*d*][1,3]dioxol-5-ylmethoxy)-1-phenyl-2-((trifluoromethyl)thio)ethan-1-one (**5e**)



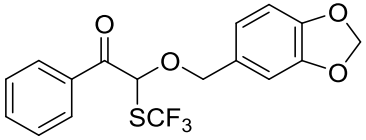


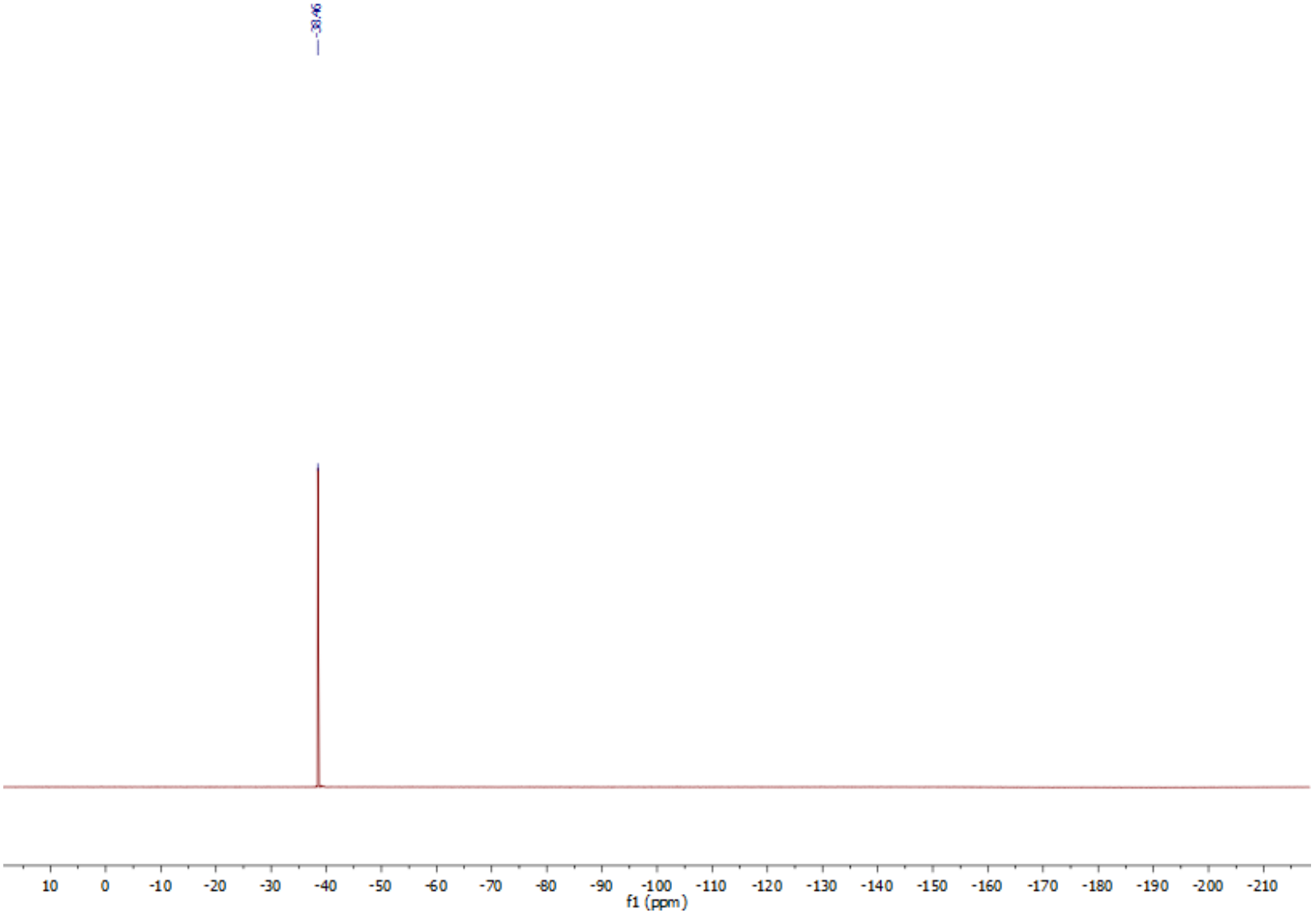
^{13}C NMR ($CDCl_3$, 100 MHz). 2-(Benzo[*d*][1,3]dioxol-5-ylmethoxy)-1-phenyl-2-((trifluoromethyl)thio)ethan-1-one (**5e**)



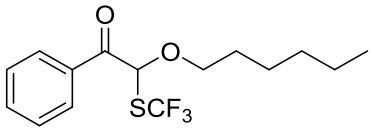


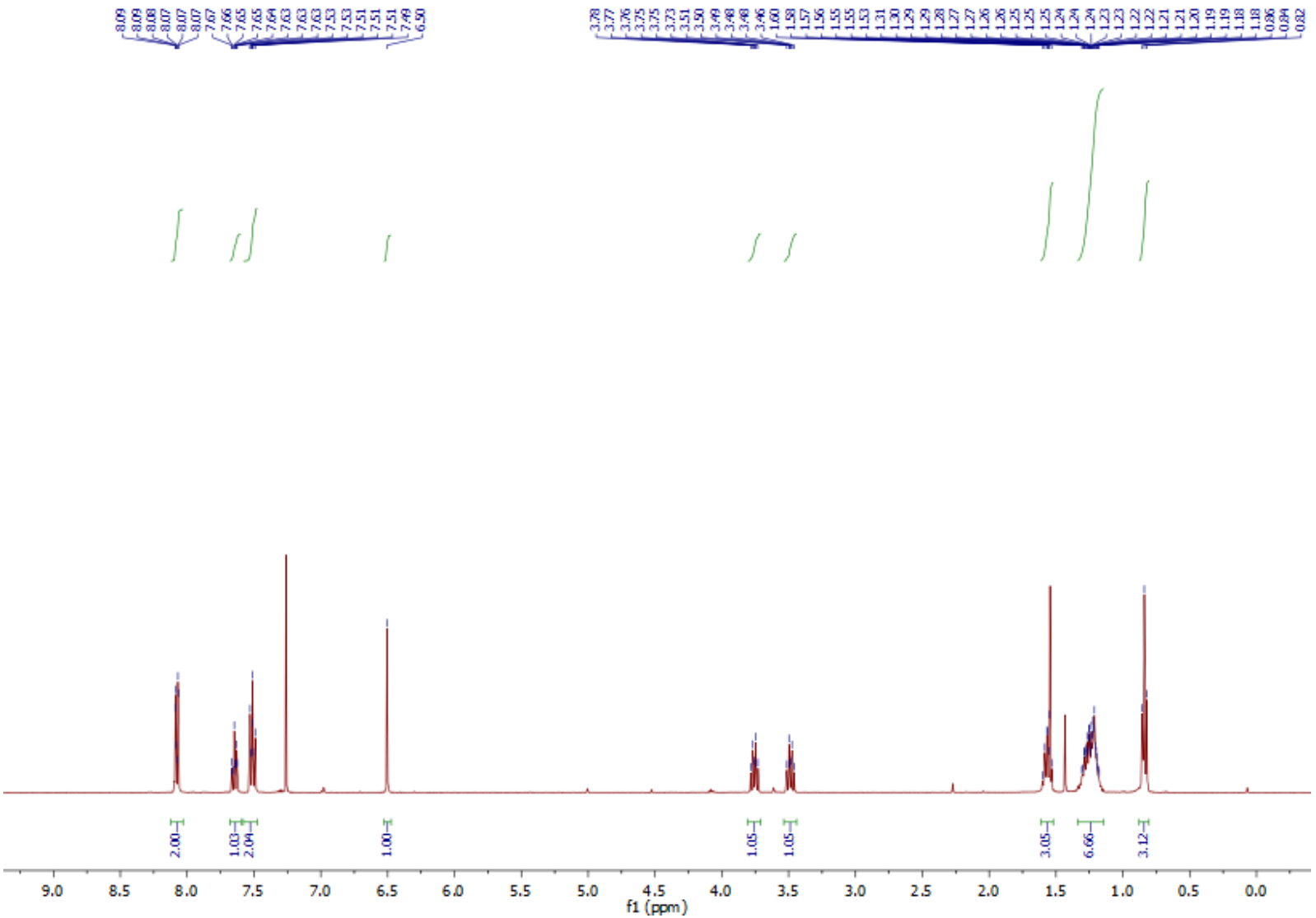
^{19}F NMR ($CDCl_3$, 377 MHz). 2-(Benzo[*d*][1,3]dioxol-5-ylmethoxy)-1-phenyl-2-((trifluoromethyl)thio)ethan-1-one (**5e**)



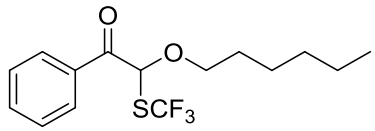


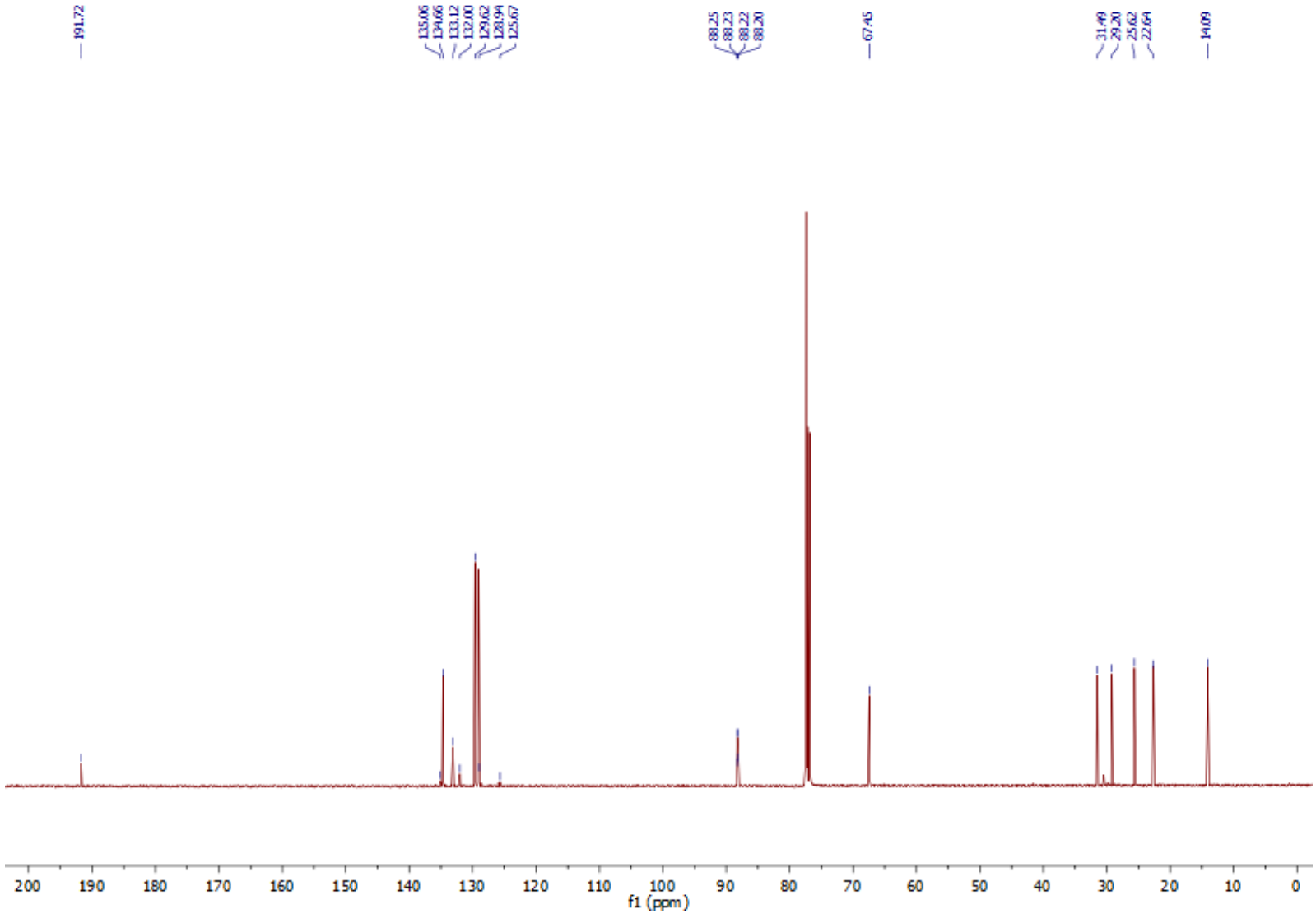
^{1}H NMR ($CDCl_3$, 400 MHz). 2-(Hexyloxy)-1-phenyl-2-((trifluoromethyl)thio)ethan-1-one (**5f**)



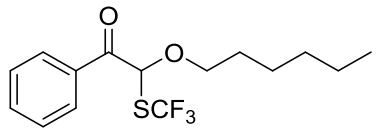


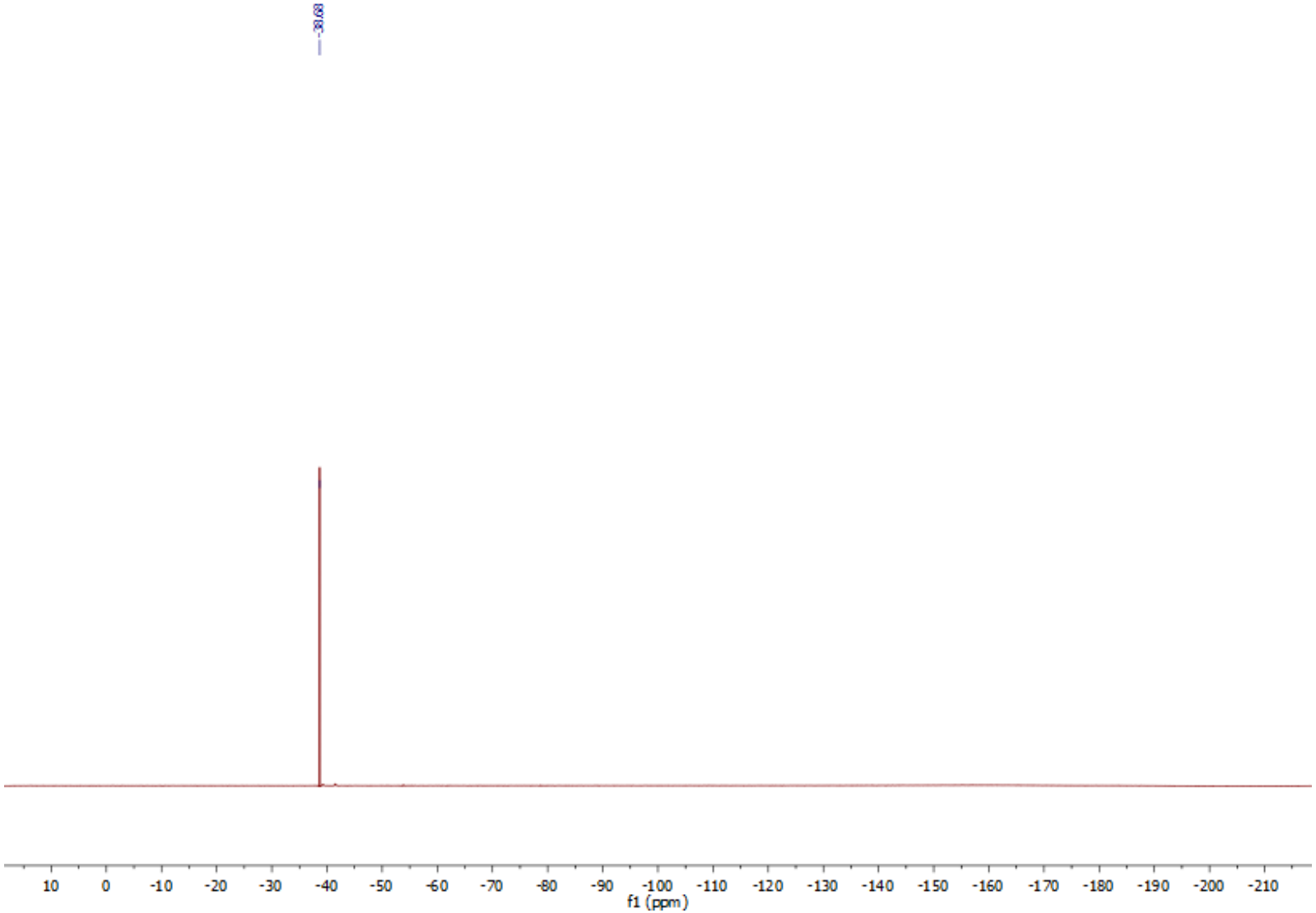
^{13}C NMR ($CDCl_3$, 100 MHz). 2-(Hexyloxy)-1-phenyl-2-((trifluoromethyl)thio)ethan-1-one (**5f**)



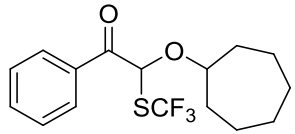


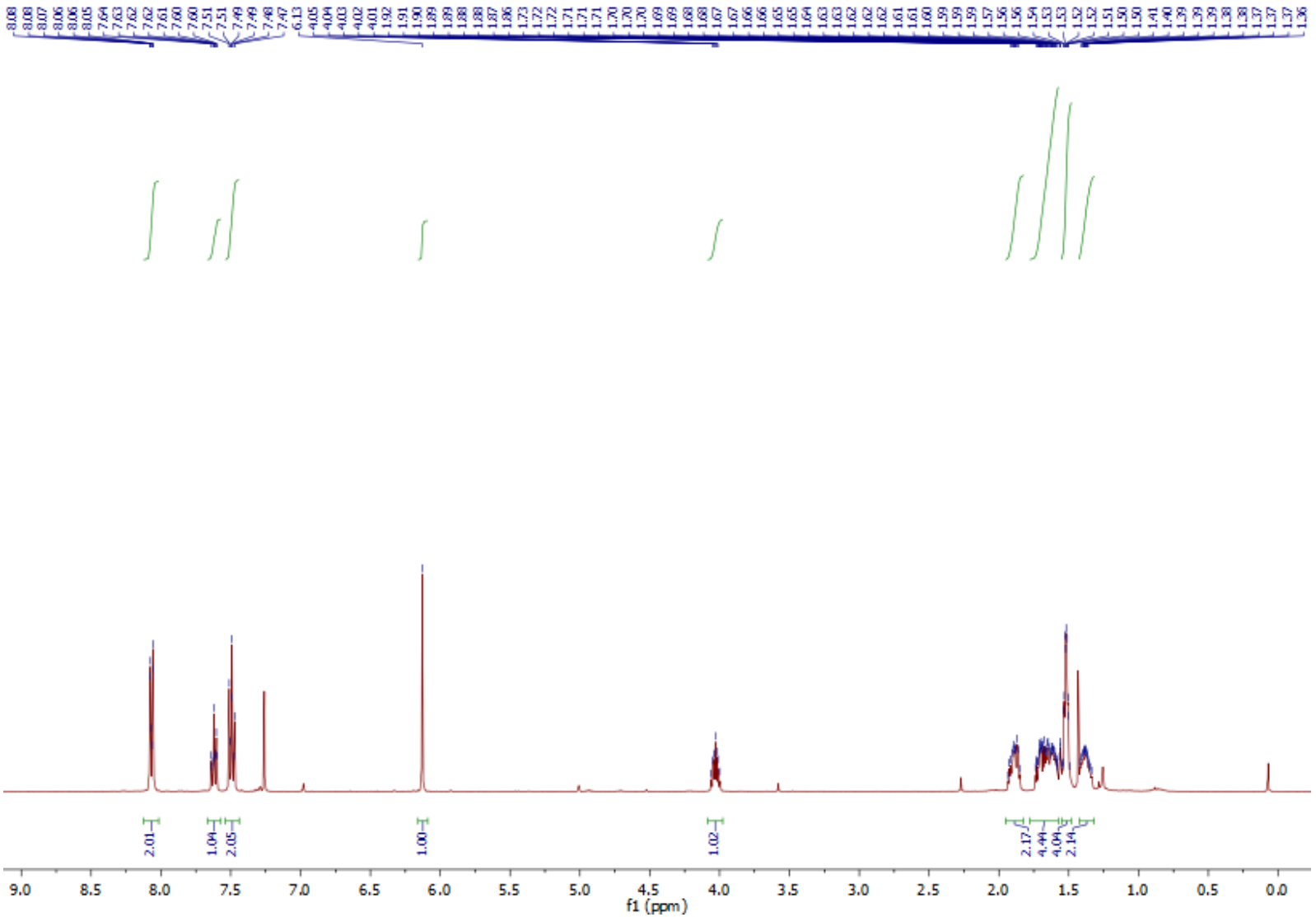
^{19}F NMR ($CDCl_3$, 377 MHz). 2-(Hexyloxy)-1-phenyl-2-((trifluoromethyl)thio)ethan-1-one (**5f**)



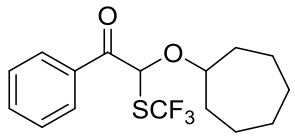


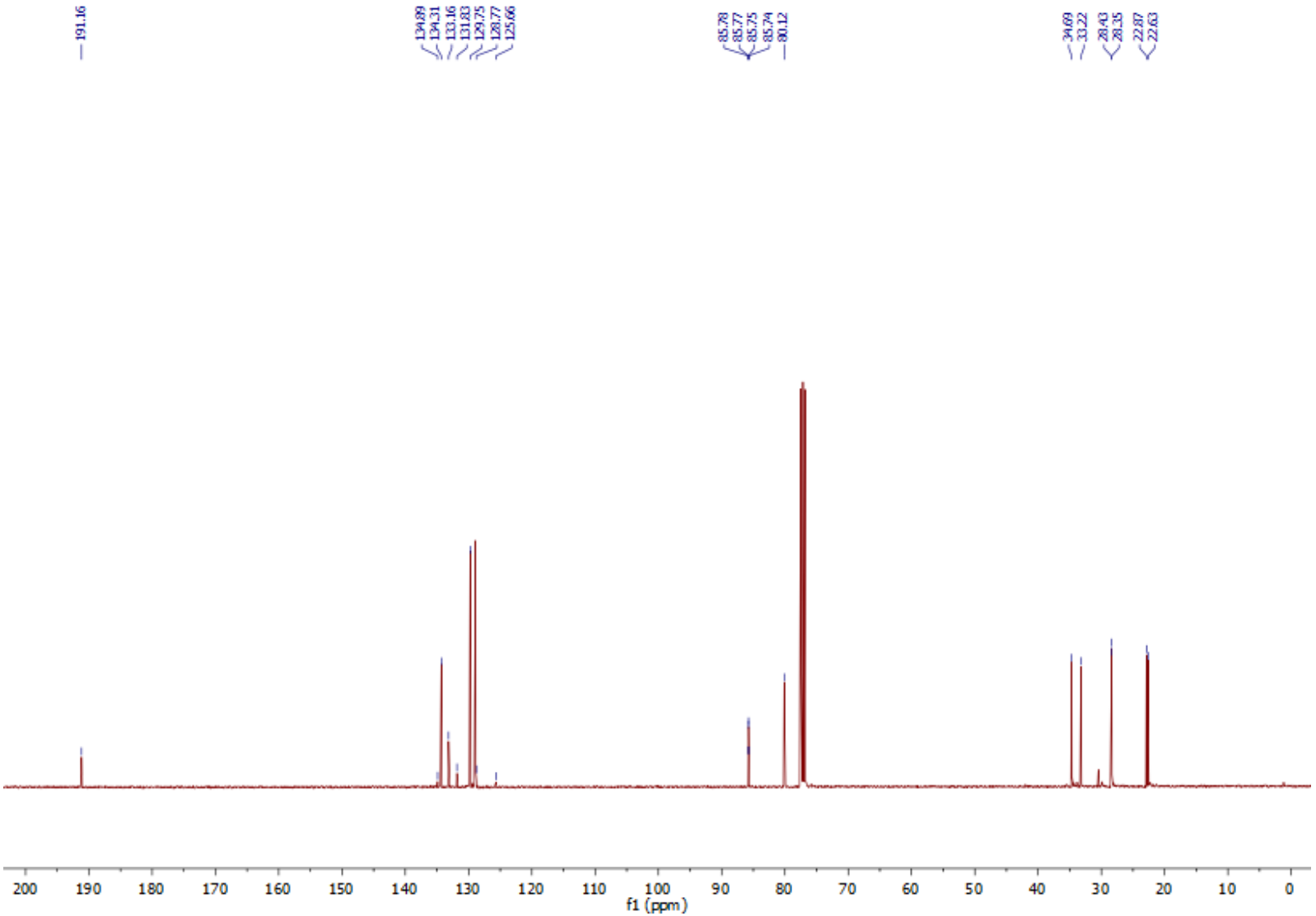
^{1}H NMR ($CDCl_3$, 400 MHz). 2-(Cycloheptyloxy)-1-phenyl-2-((trifluoromethyl)thio)ethan-1-one (**5g**)



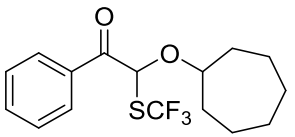


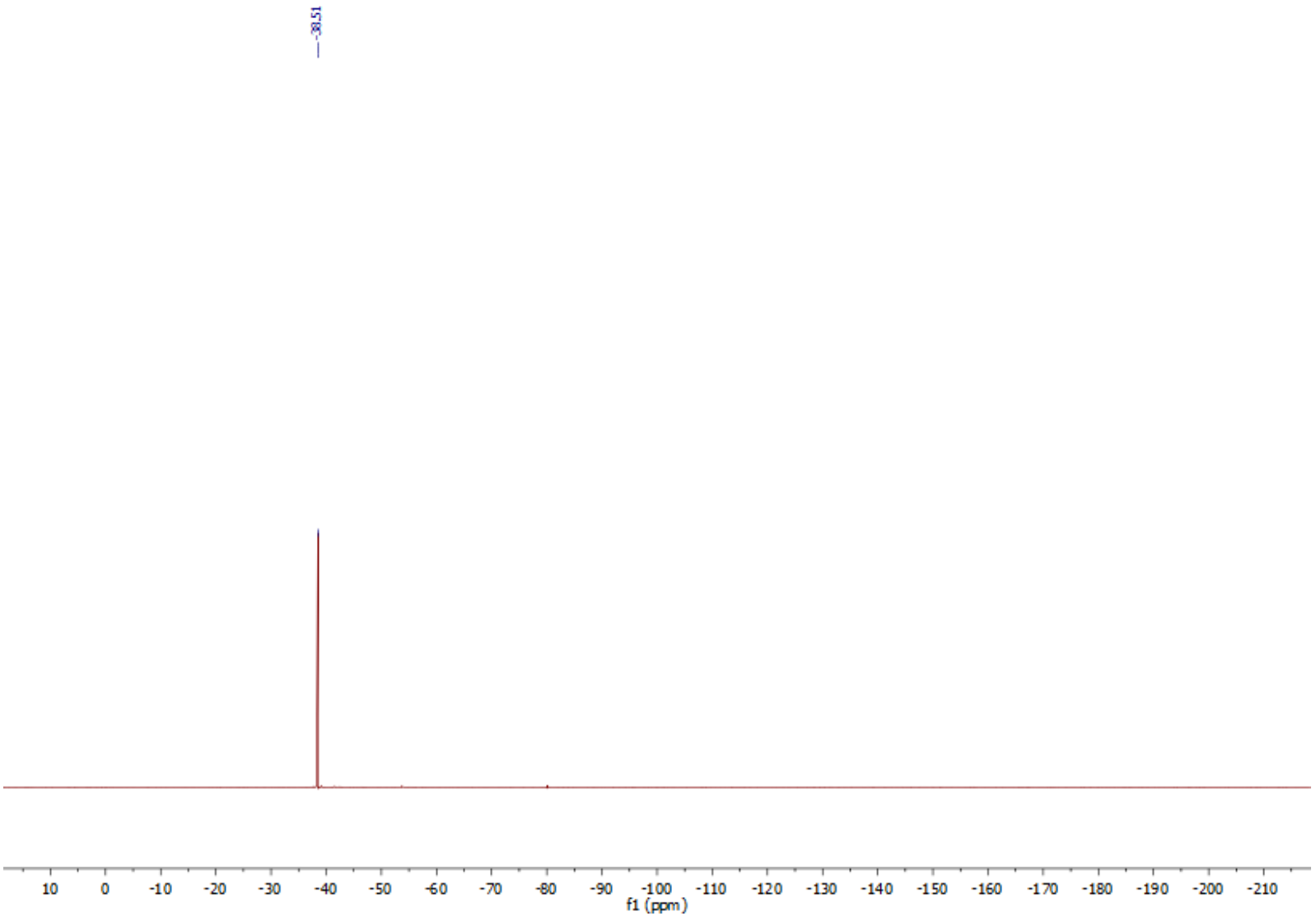
^{13}C NMR ($CDCl_3$, 100 MHz). 2-(Cycloheptyloxy)-1-phenyl-2-((trifluoromethyl)thio)ethan-1-one (**5g**)



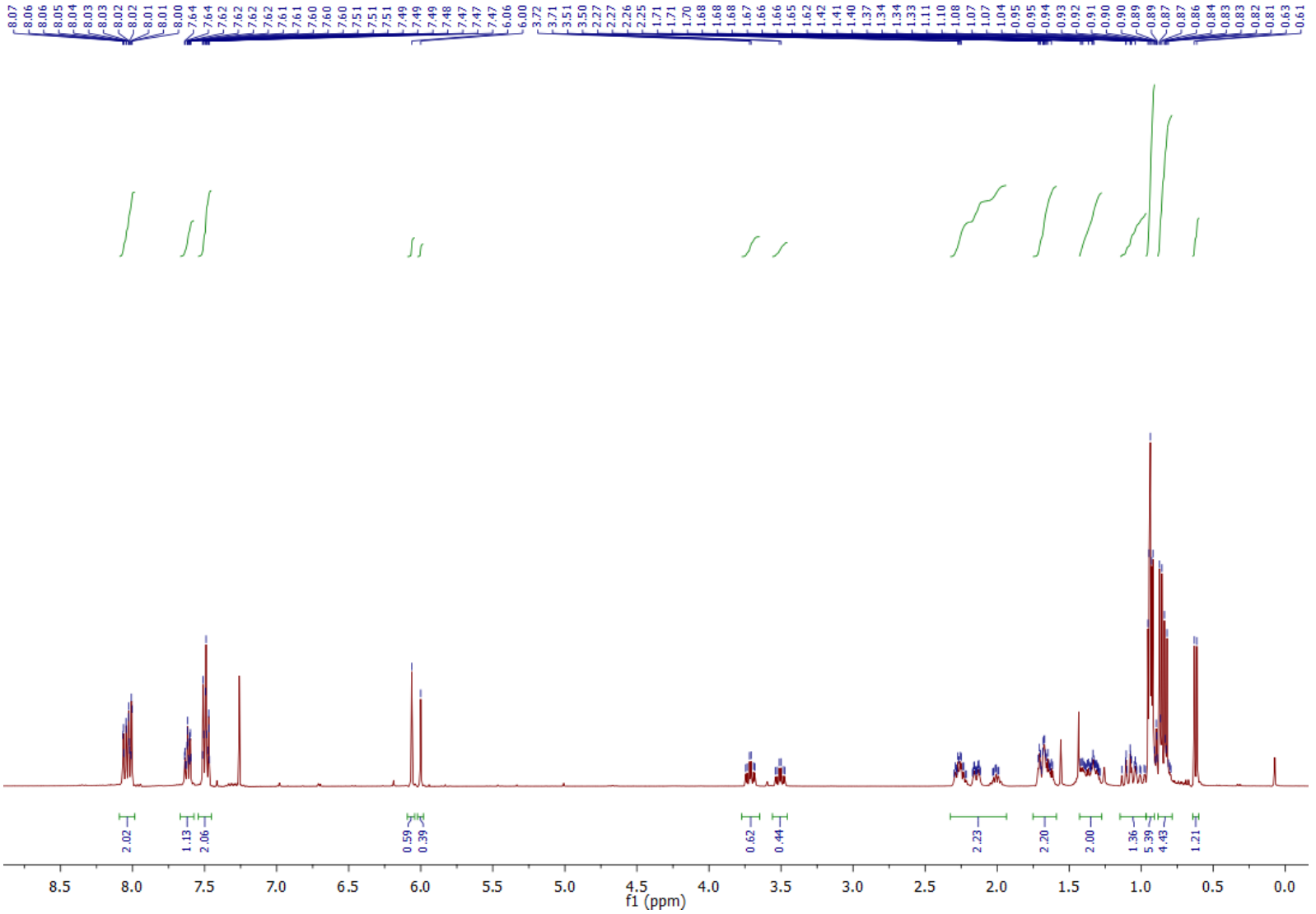


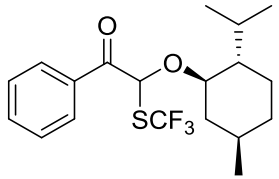
^{19}F NMR ($CDCl_3$, 377 MHz). 2-(Cycloheptyloxy)-1-phenyl-2-((trifluoromethyl)thio)ethan-1-one (**5g**)



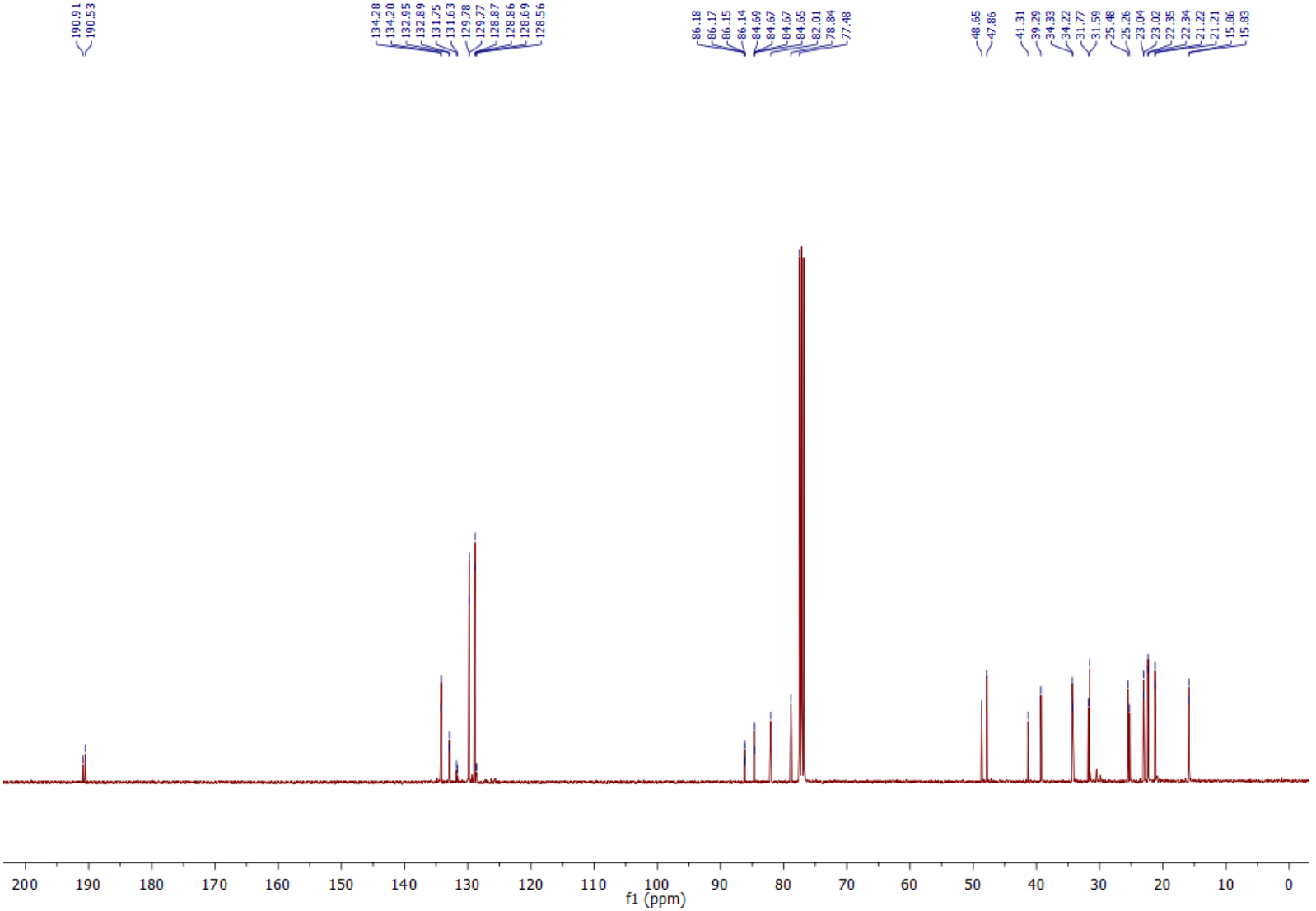


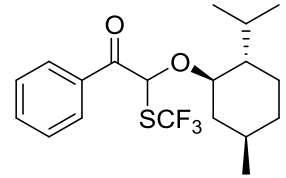
^{1}H NMR ($CDCl_3$, 400 MHz). 2-(((1*R*,2*S*,5*R*)-2-Isopropyl-5-methylcyclohexyl)oxy)-1-phenyl-2-((trifluoromethyl)thio)ethan-1-one (**5h**)



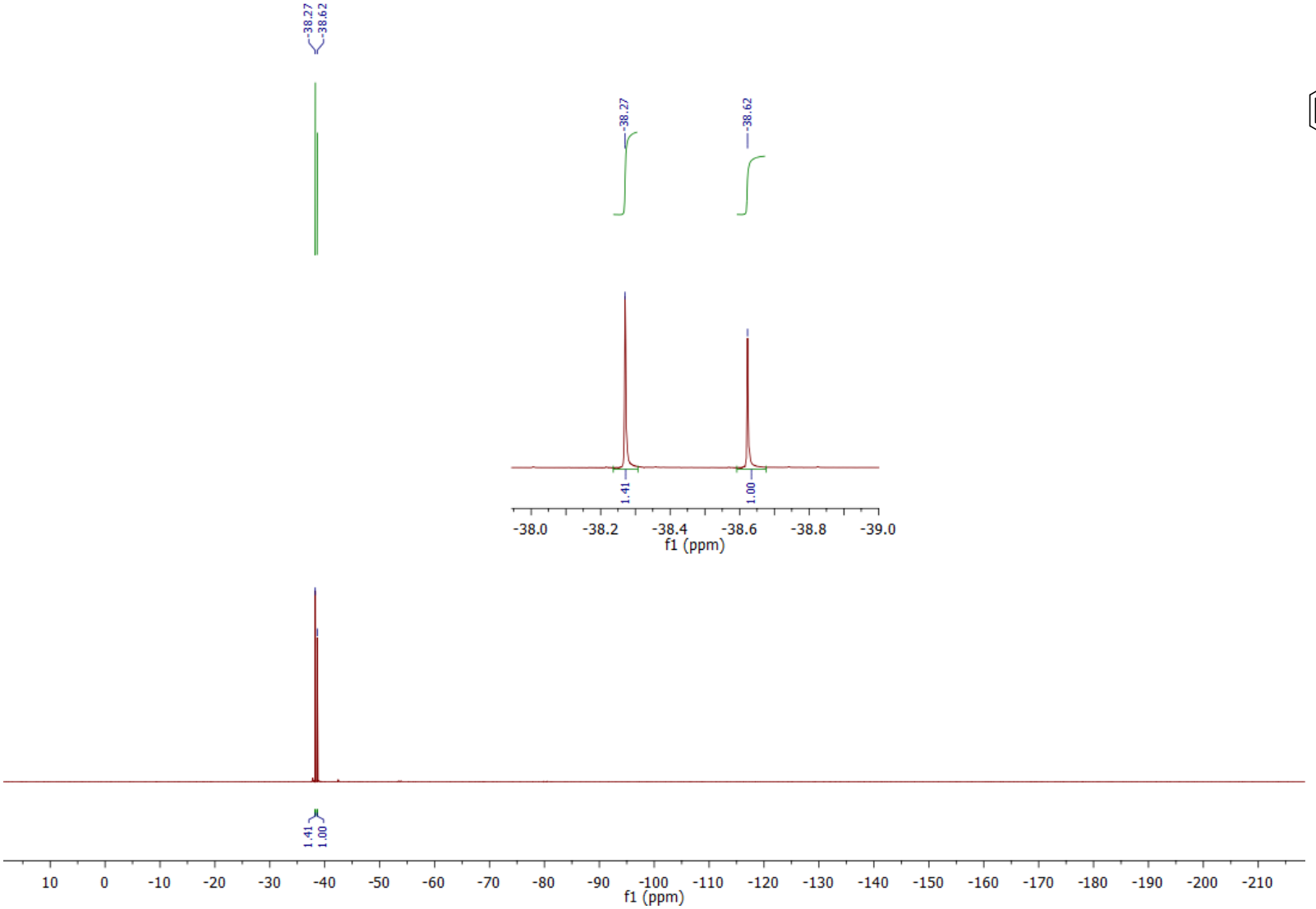


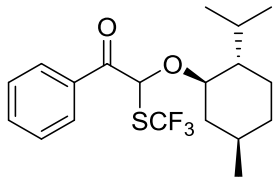
^{13}C NMR ($CDCl_3$, 100 MHz). 2-(((1*R*,2*S*,5*R*)-2-Isopropyl-5-methylcyclohexyl)oxy)-1-phenyl-2-((trifluoromethyl)thio)ethan-1-one (**5h**)



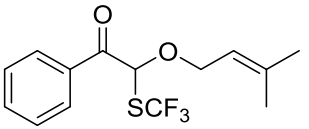


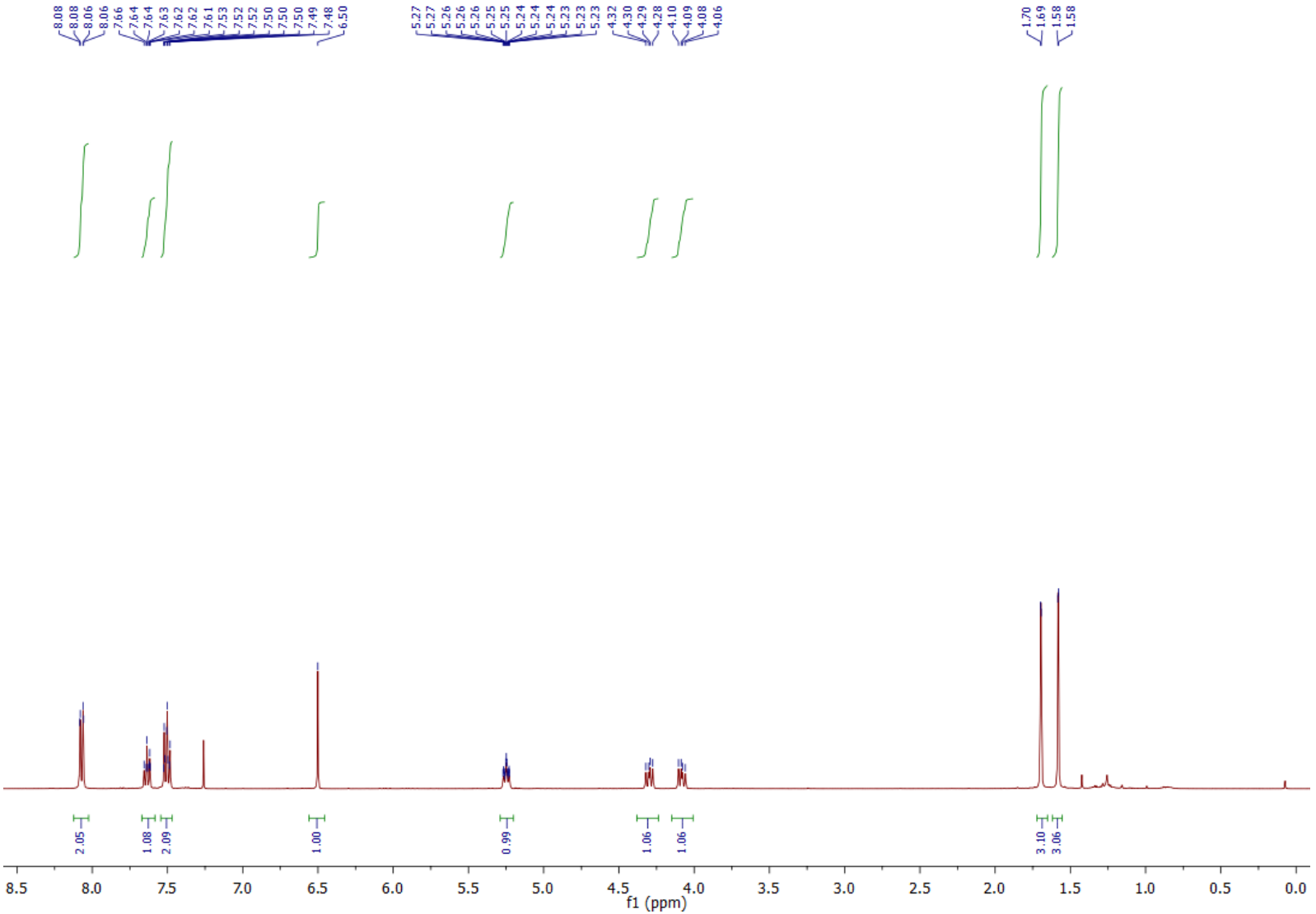
^{19}F NMR ($CDCl_3$, 377 MHz). 2-(((1*R*,2*S*,5*R*)-2-Isopropyl-5-methylcyclohexyl)oxy)-1-phenyl-2-((trifluoromethyl)thio)ethan-1-one (**5h**)



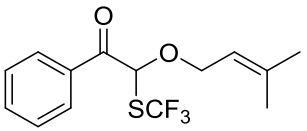


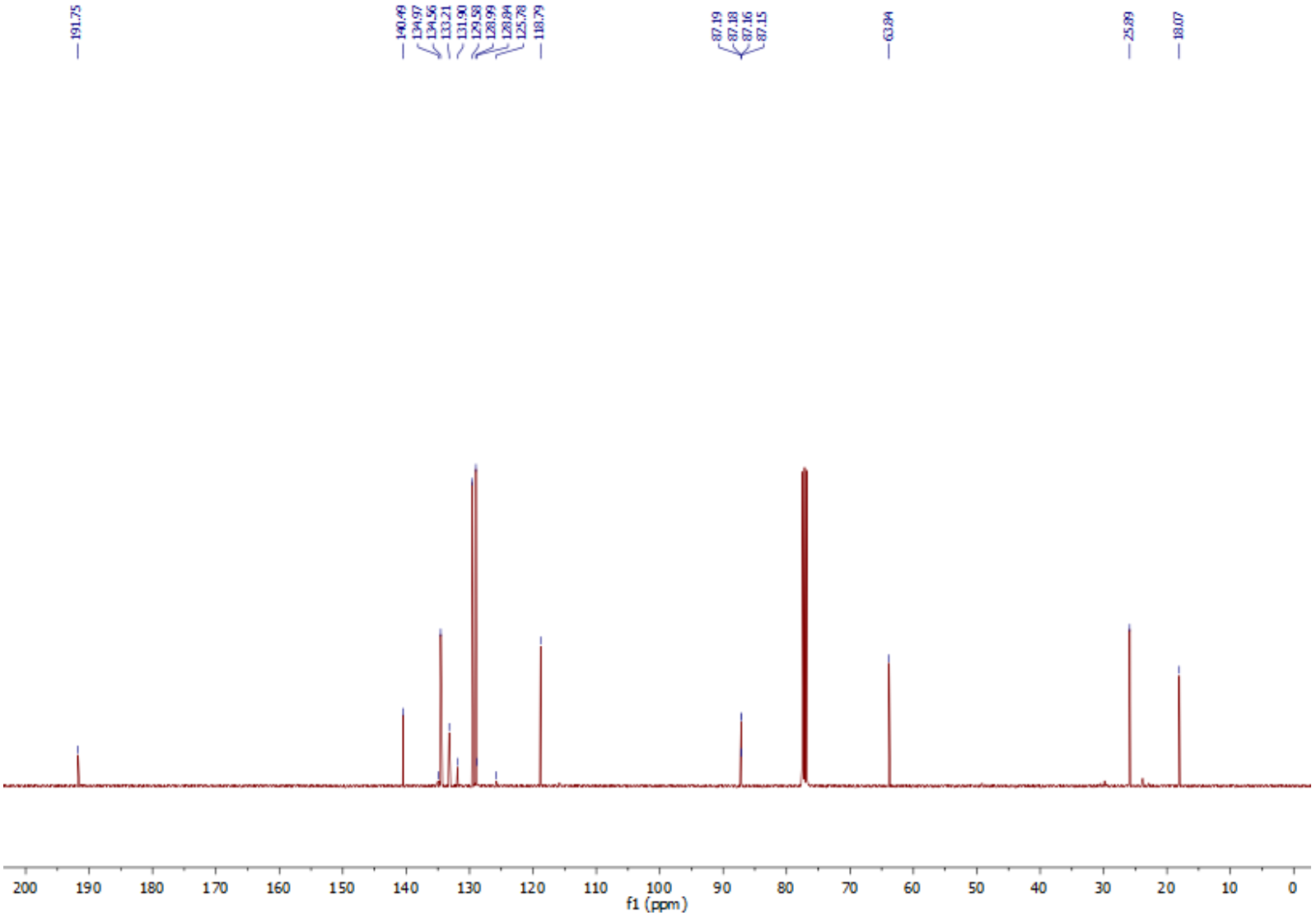
^{1}H NMR ($CDCl_3$, 400 MHz). 2-((3-Methylbut-2-en-1-yl)oxy)-1-phenyl-2-((trifluoromethyl)thio)ethan-1-one (**5i**)



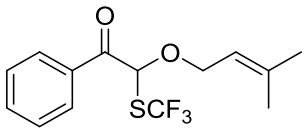


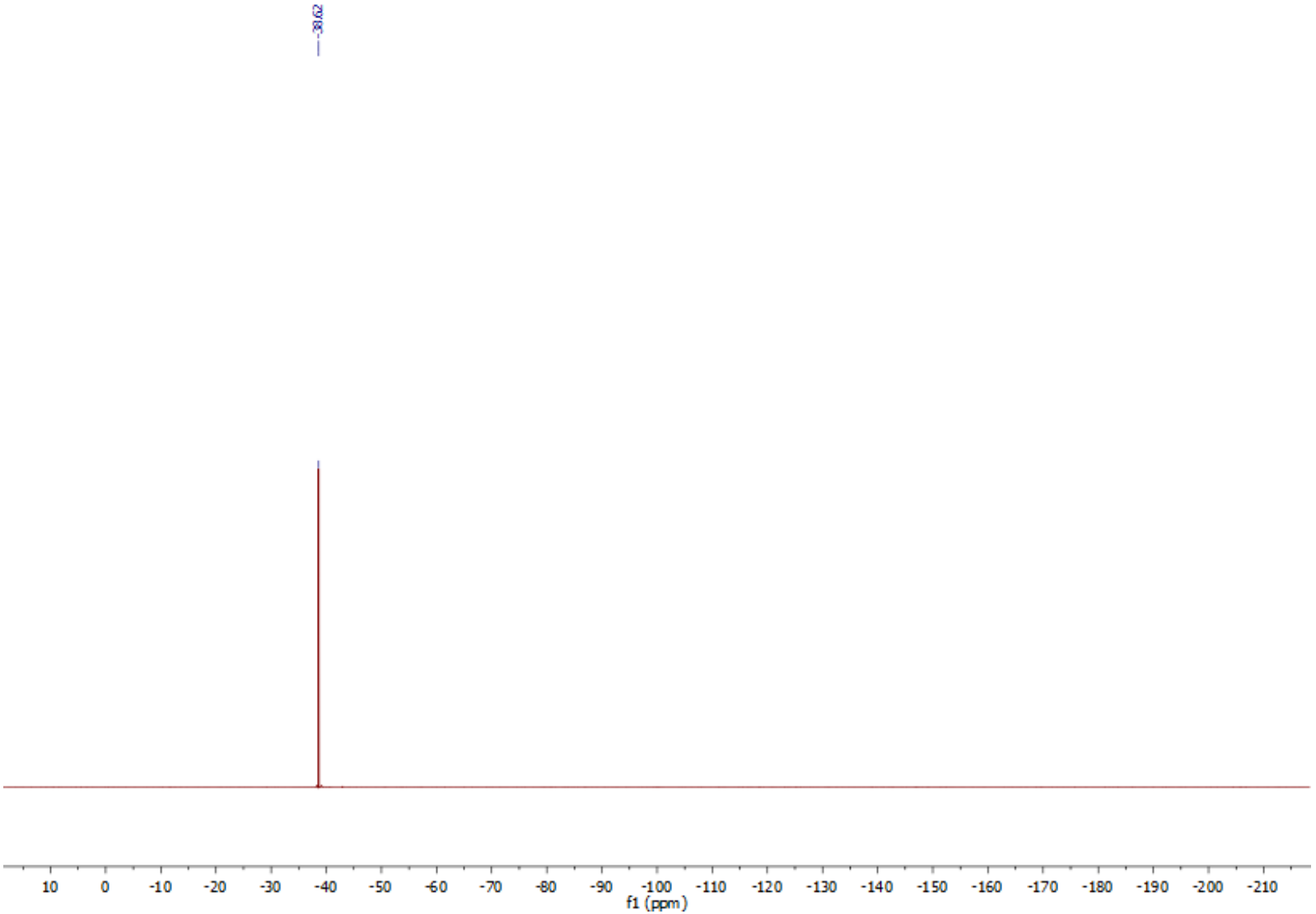
^{13}C NMR ($CDCl_3$, 100 MHz). 2-((3-Methylbut-2-en-1-yl)oxy)-1-phenyl-2-((trifluoromethyl)thio)ethan-1-one (**5i**)



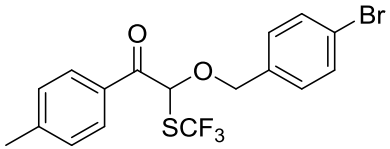


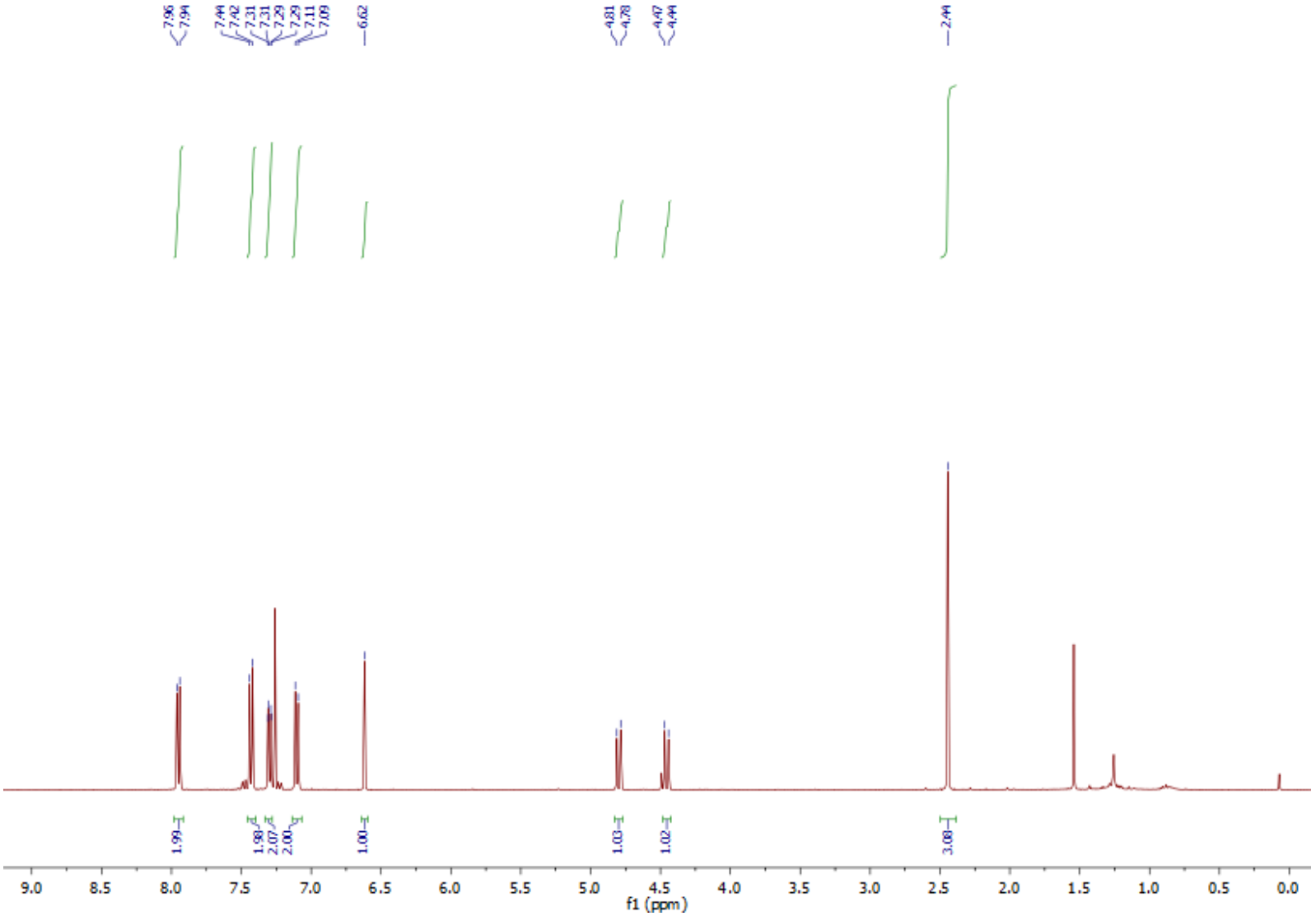
^{19}F NMR ($CDCl_3$, 377 MHz). 2-((3-Methylbut-2-en-1-yl)oxy)-1-phenyl-2-((trifluoromethyl)thio)ethan-1-one (**5i**)



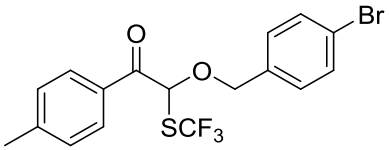


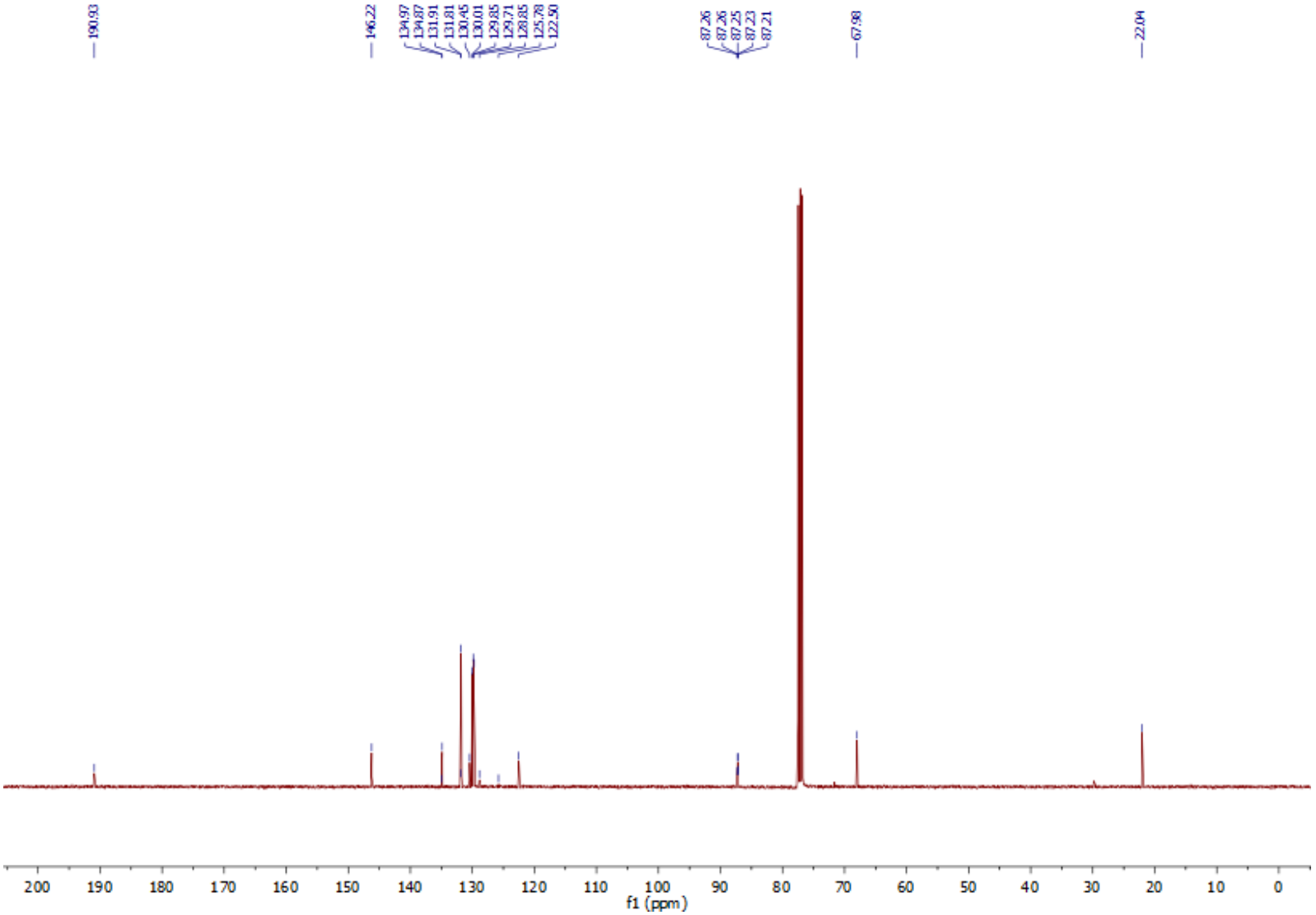
^{1}H NMR ($CDCl_3$, 400 MHz). 2-((4-Bromobenzyl)oxy)-1-(*p*-tolyl)-2-((trifluoromethyl)thio)ethan-1-one (**5j**)



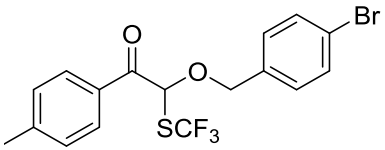


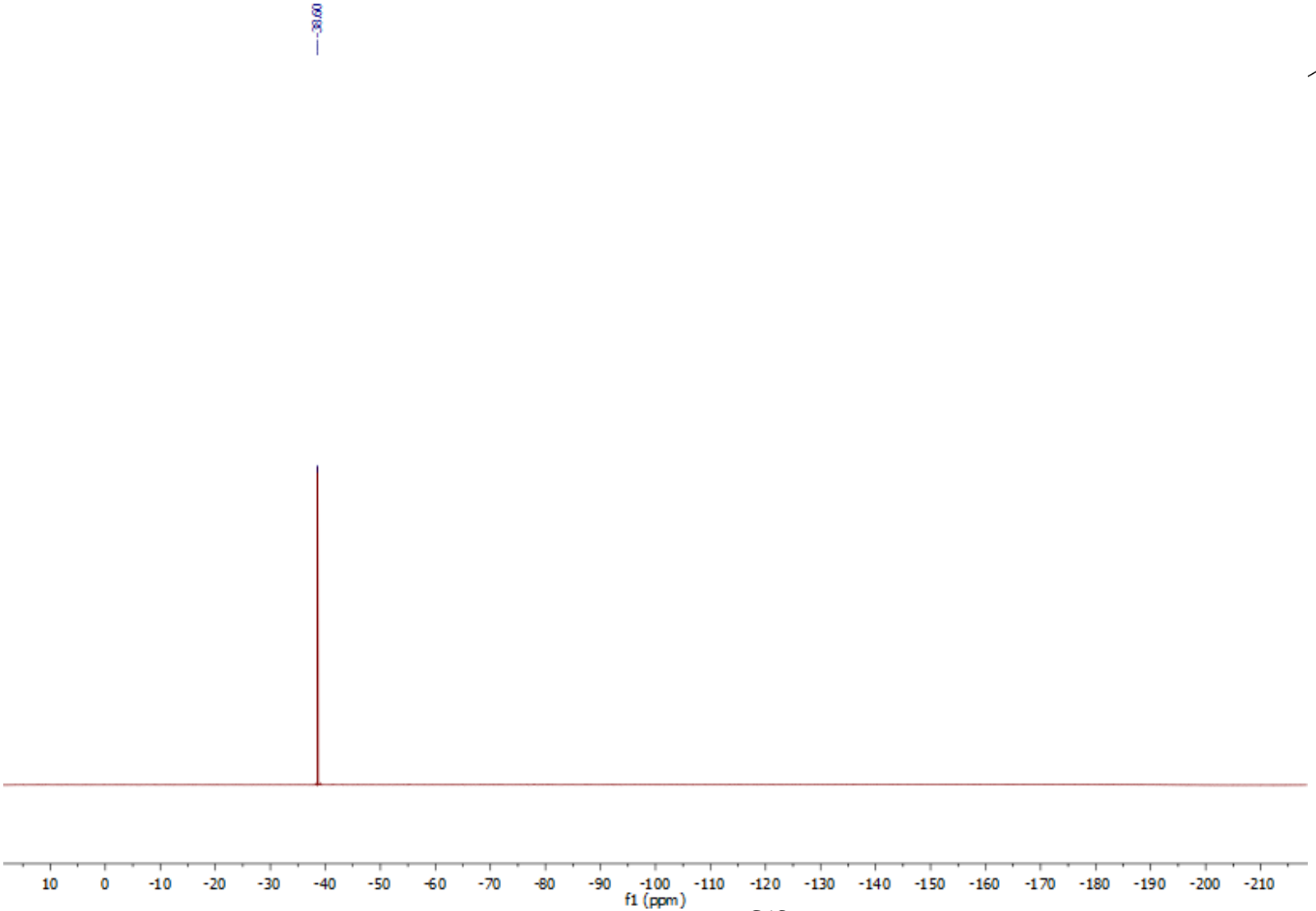
^{13}C NMR ($CDCl_3$, 100 MHz). 2-((4-Bromobenzyl)oxy)-1-(*p*-tolyl)-2-((trifluoromethyl)thio)ethan-1-one (**5j**)



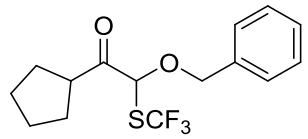


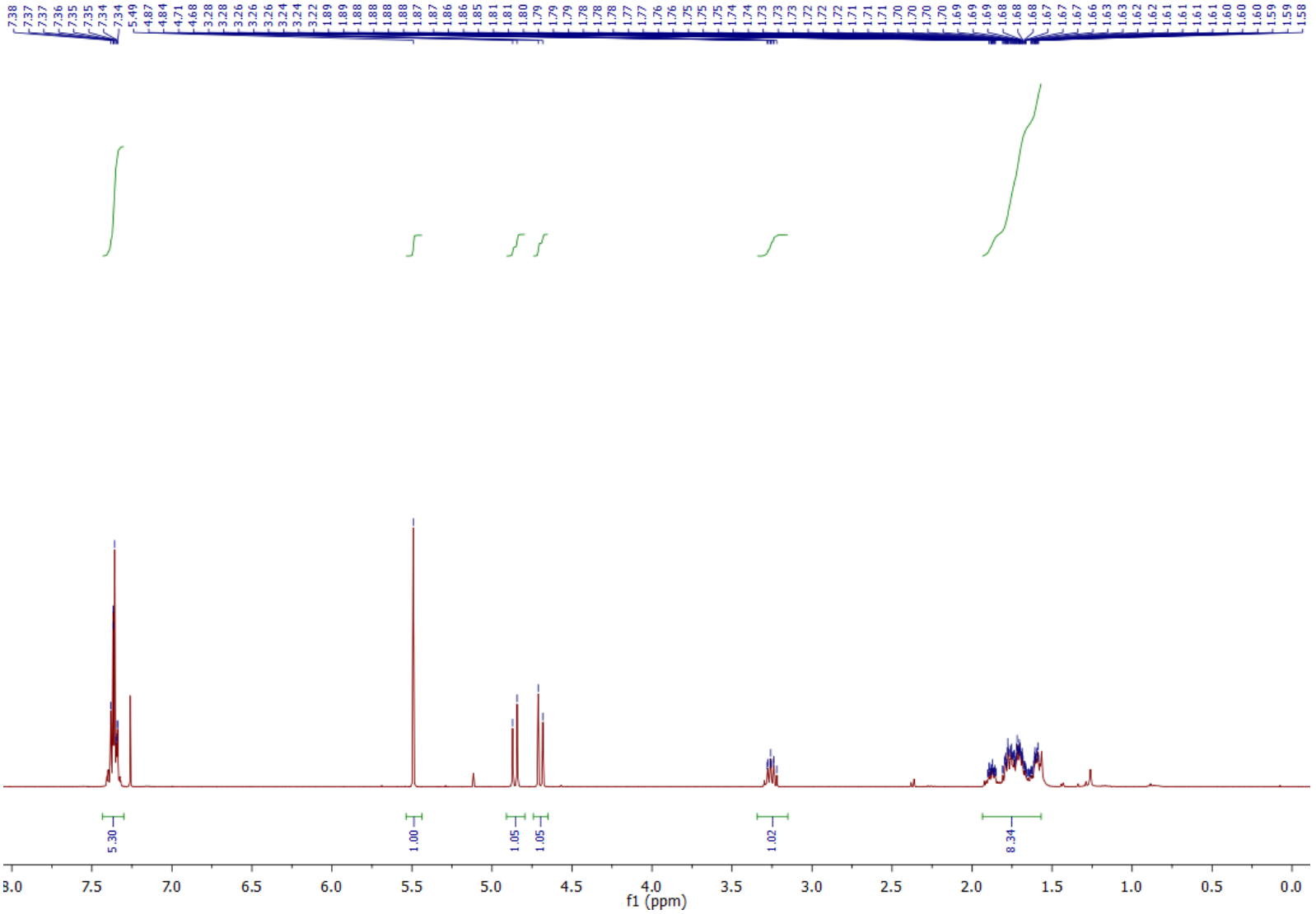
^{19}F NMR ($CDCl_3$, 377 MHz). 2-((4-Bromobenzyl)oxy)-1-(*p*-tolyl)-2-((trifluoromethyl)thio)ethan-1-one (**5j**)



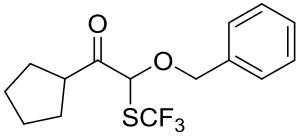


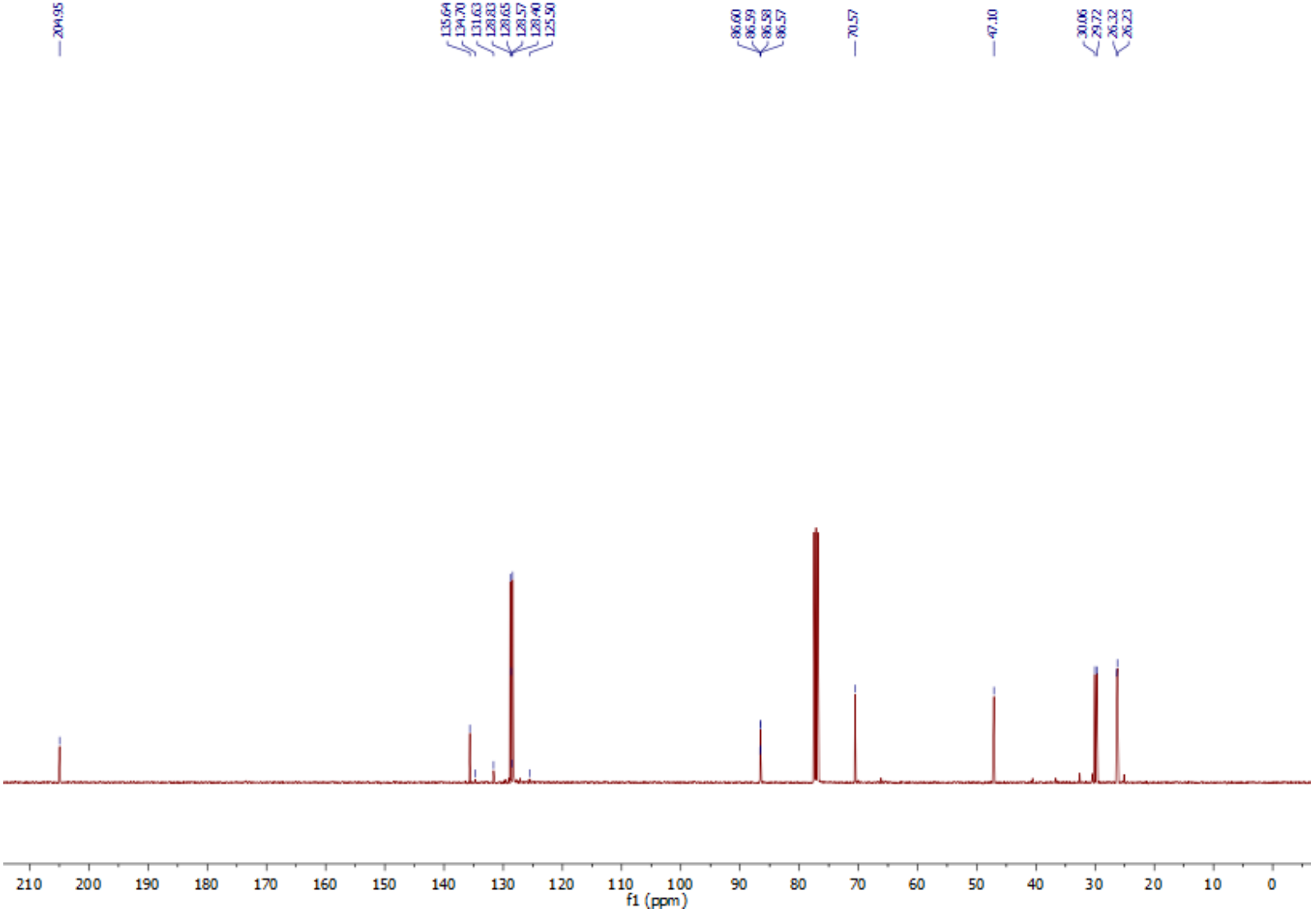
^{1}H NMR ($CDCl_3$, 400 MHz). 2-(Benzyloxy)-1-cyclopentyl-2-((trifluoromethyl)thio)ethan-1-one (**5k**)



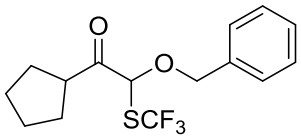


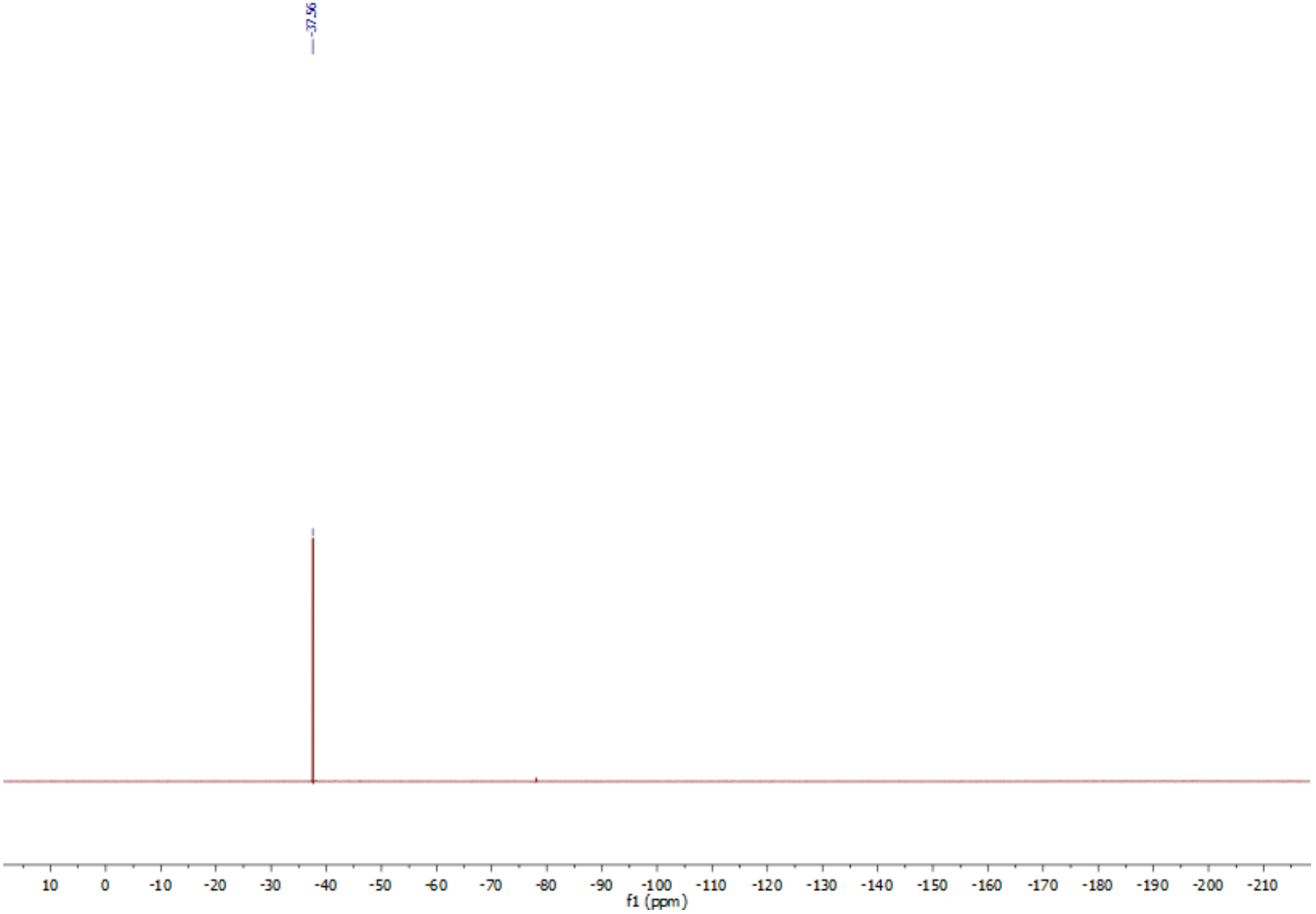
^{13}C NMR ($CDCl_3$, 100 MHz). 2-(Benzyloxy)-1-cyclopentyl-2-((trifluoromethyl)thio)ethan-1-one (**5k**)



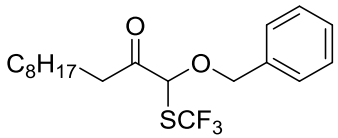


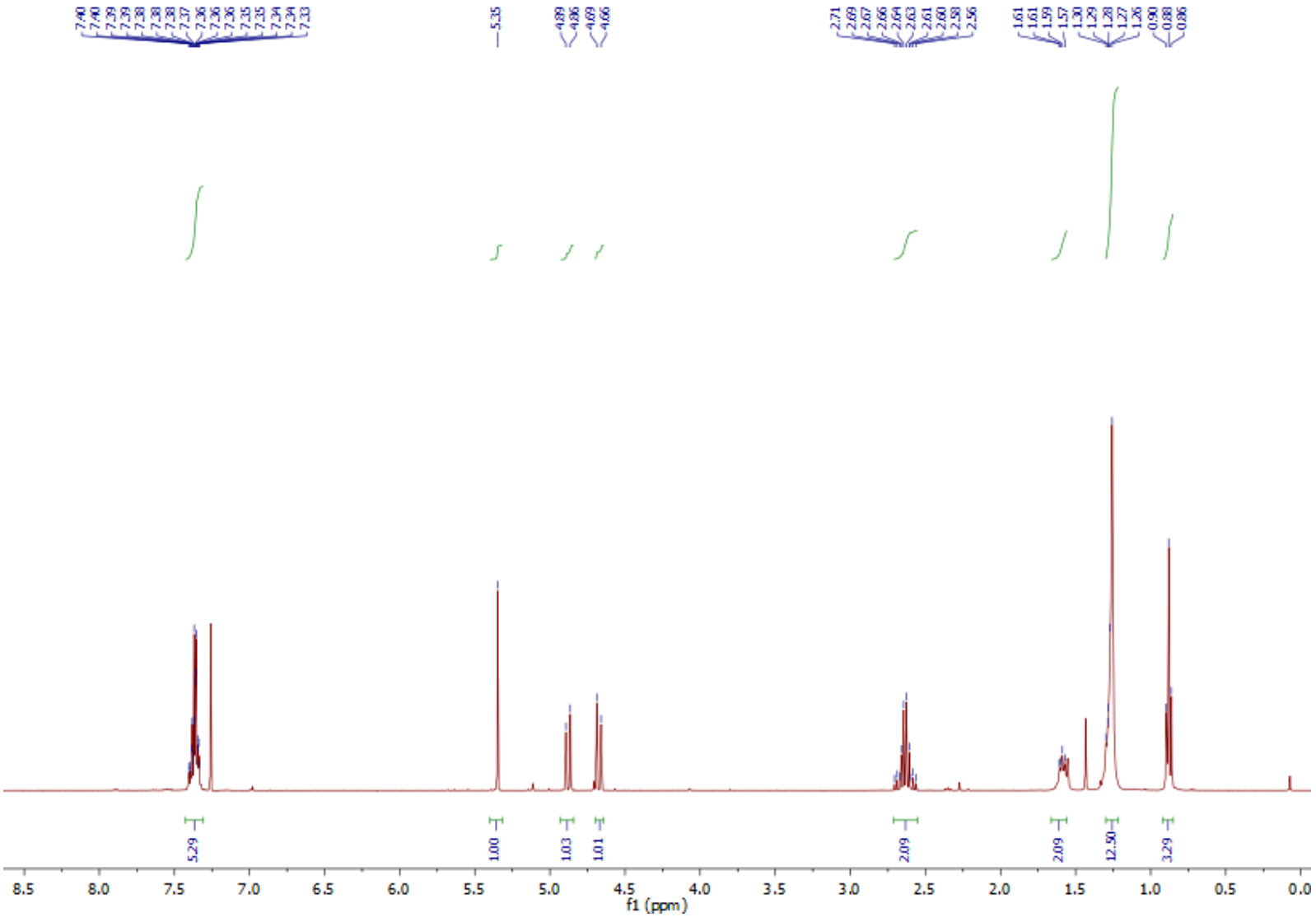
^{19}F NMR ($CDCl_3$, 377 MHz). 2-(Benzyloxy)-1-cyclopentyl-2-((trifluoromethyl)thio)ethan-1-one (**5k**)



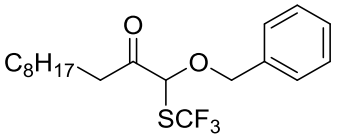


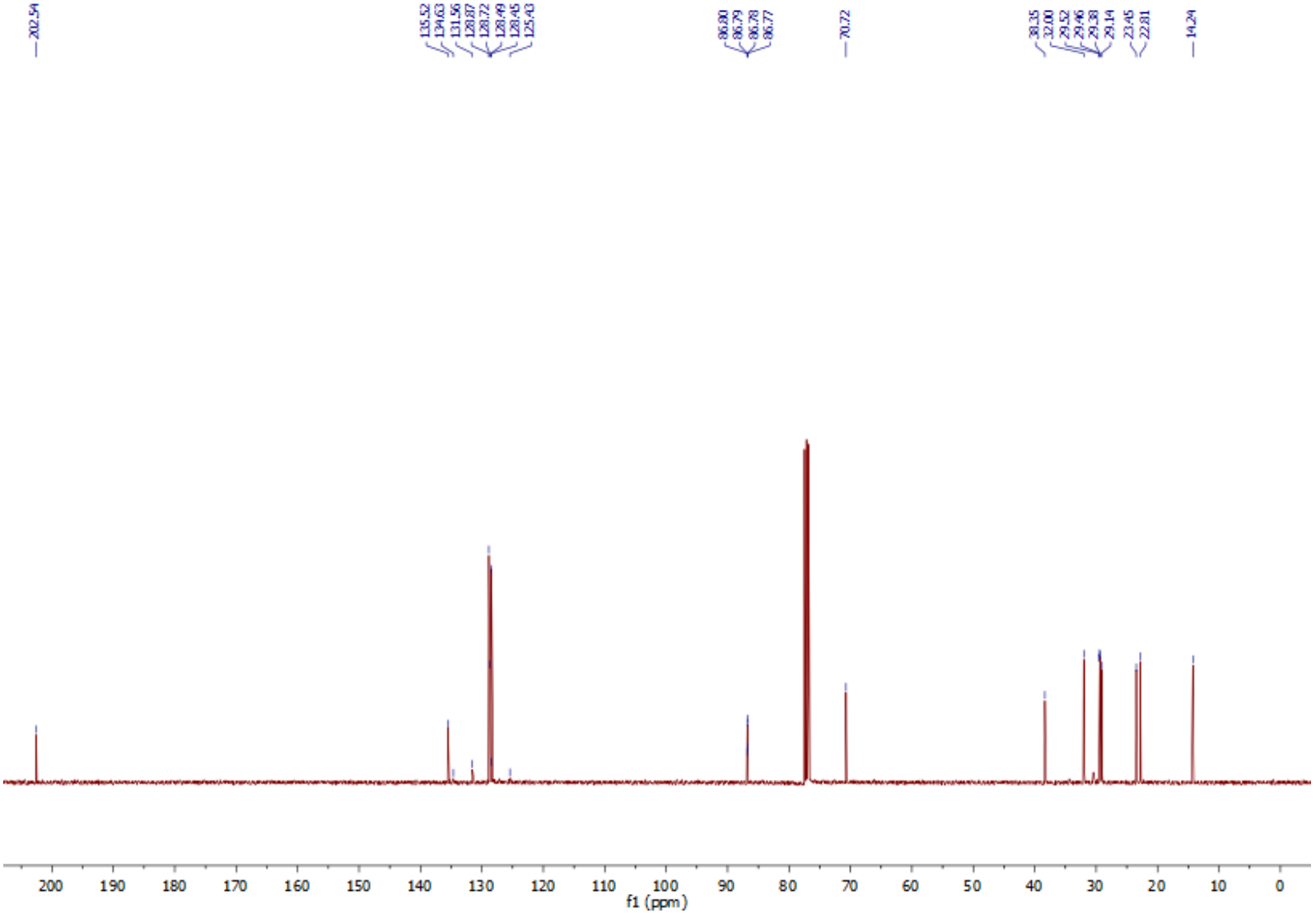
^{1}H NMR ($CDCl_3$, 400 MHz). 1-(Benzyloxy)-1-((trifluoromethyl)thio)undecan-2-one (**5l**)



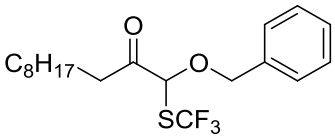


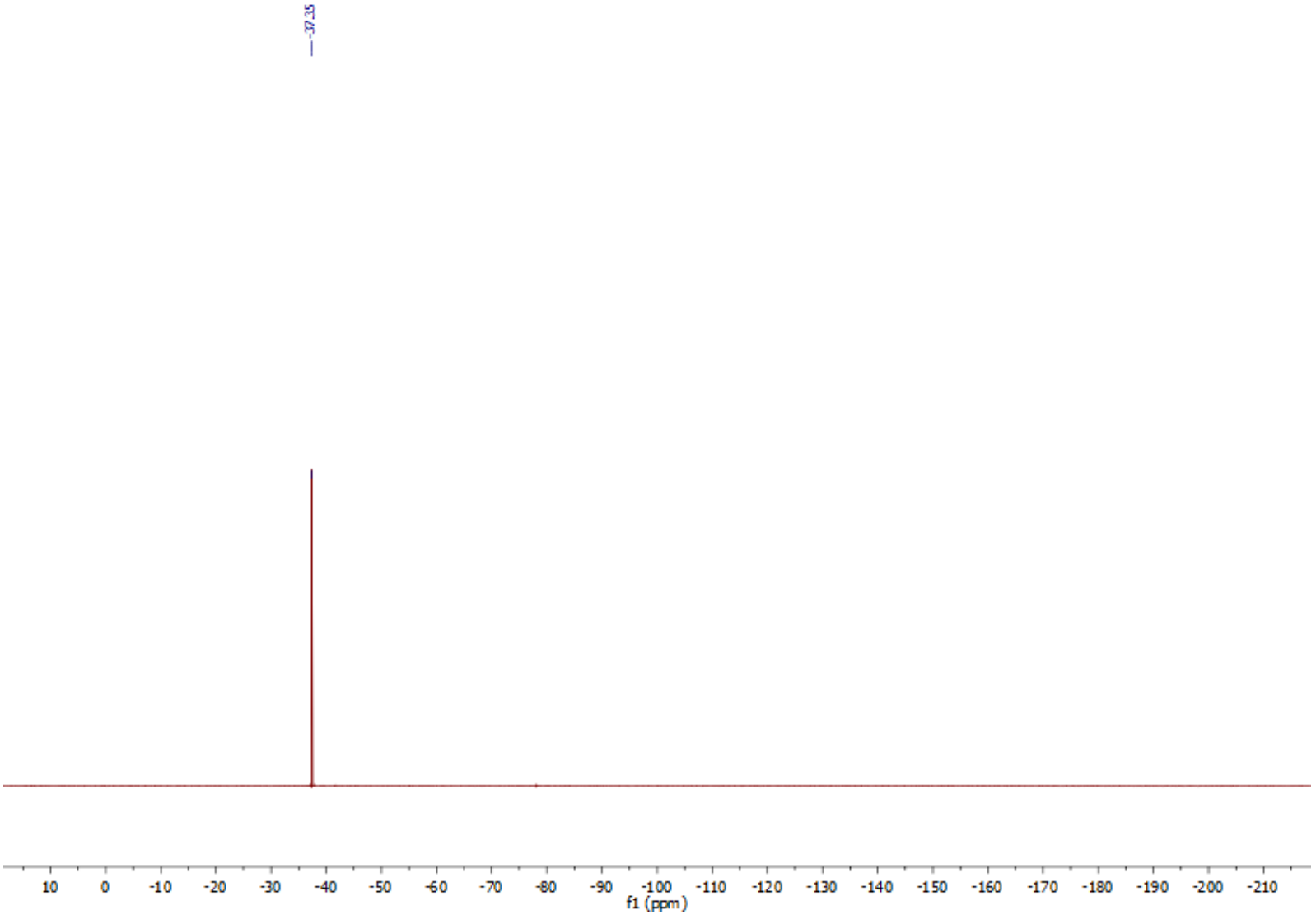
^{13}C NMR ($CDCl_3$, 100 MHz). 1-(Benzyloxy)-1-((trifluoromethyl)thio)undecan-2-one (**5l**)



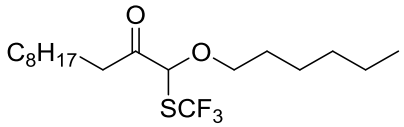


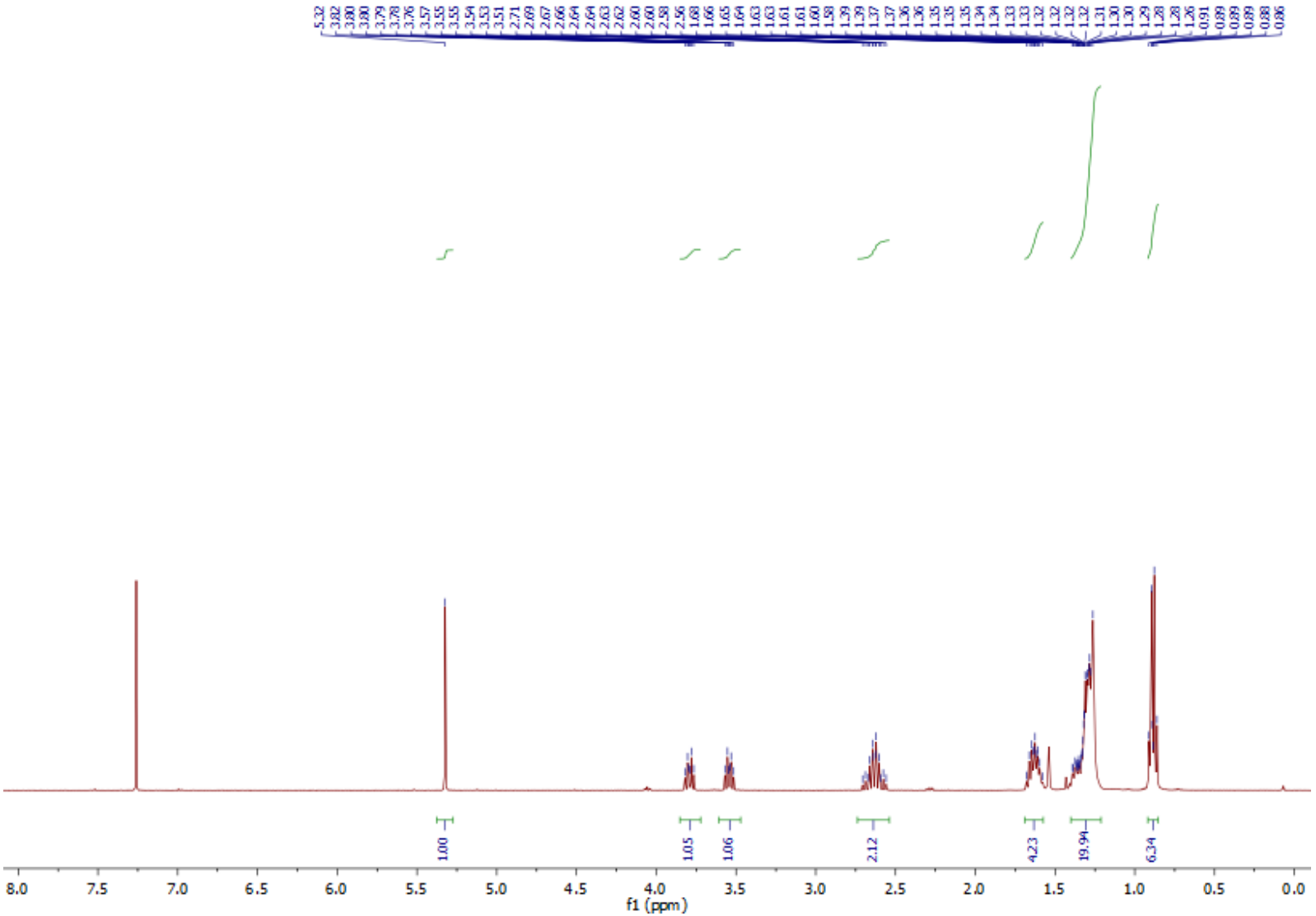
^{19}F NMR ($CDCl_3$, 377 MHz). 1-(Benzyloxy)-1-((trifluoromethyl)thio)undecan-2-one (**5l**)



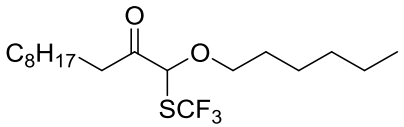


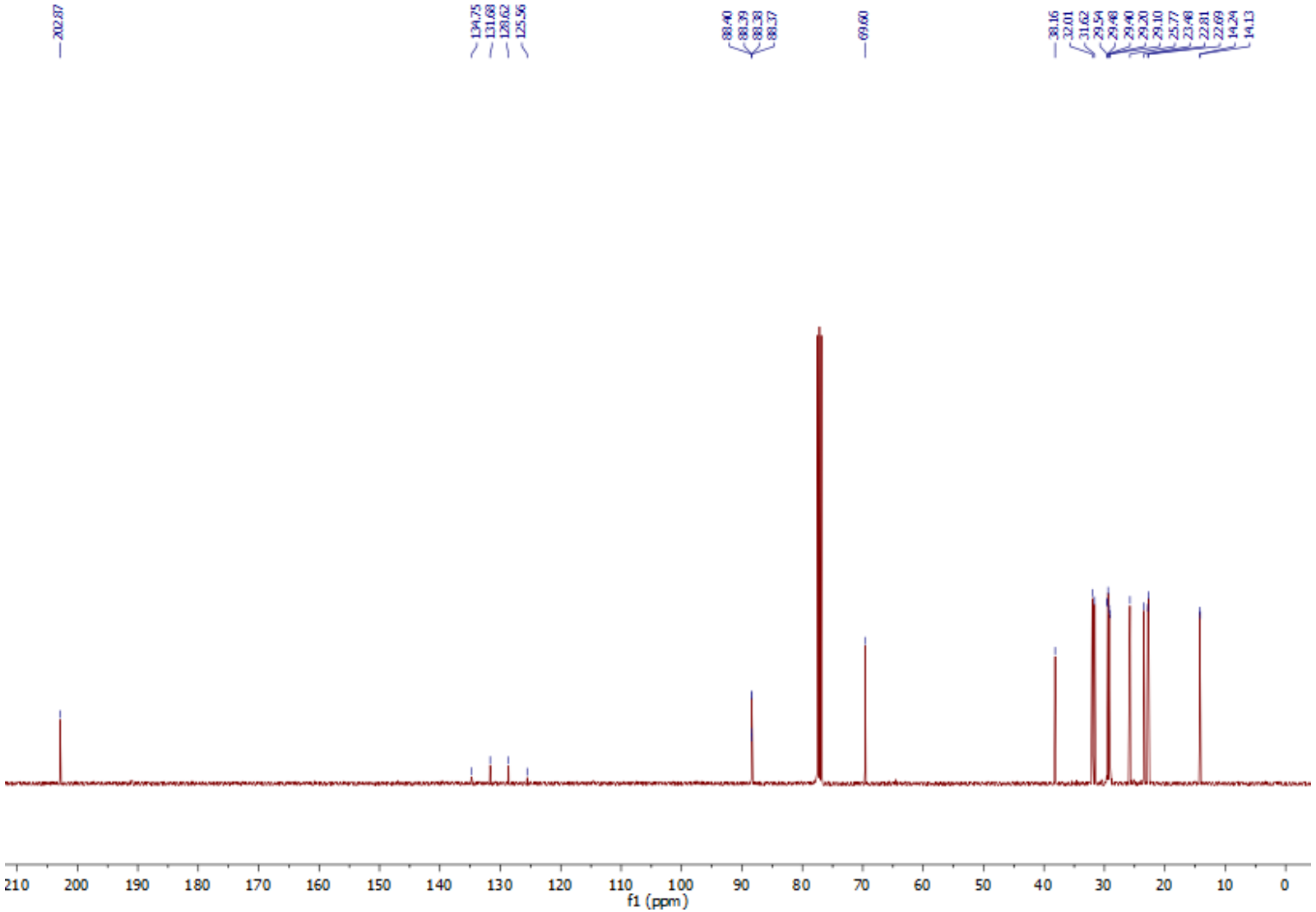
^{1}H NMR ($CDCl_3$, 400 MHz). 1-(Hexyloxy)-1-((trifluoromethyl)thio)undecan-2-one (**5m**)



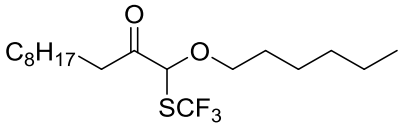


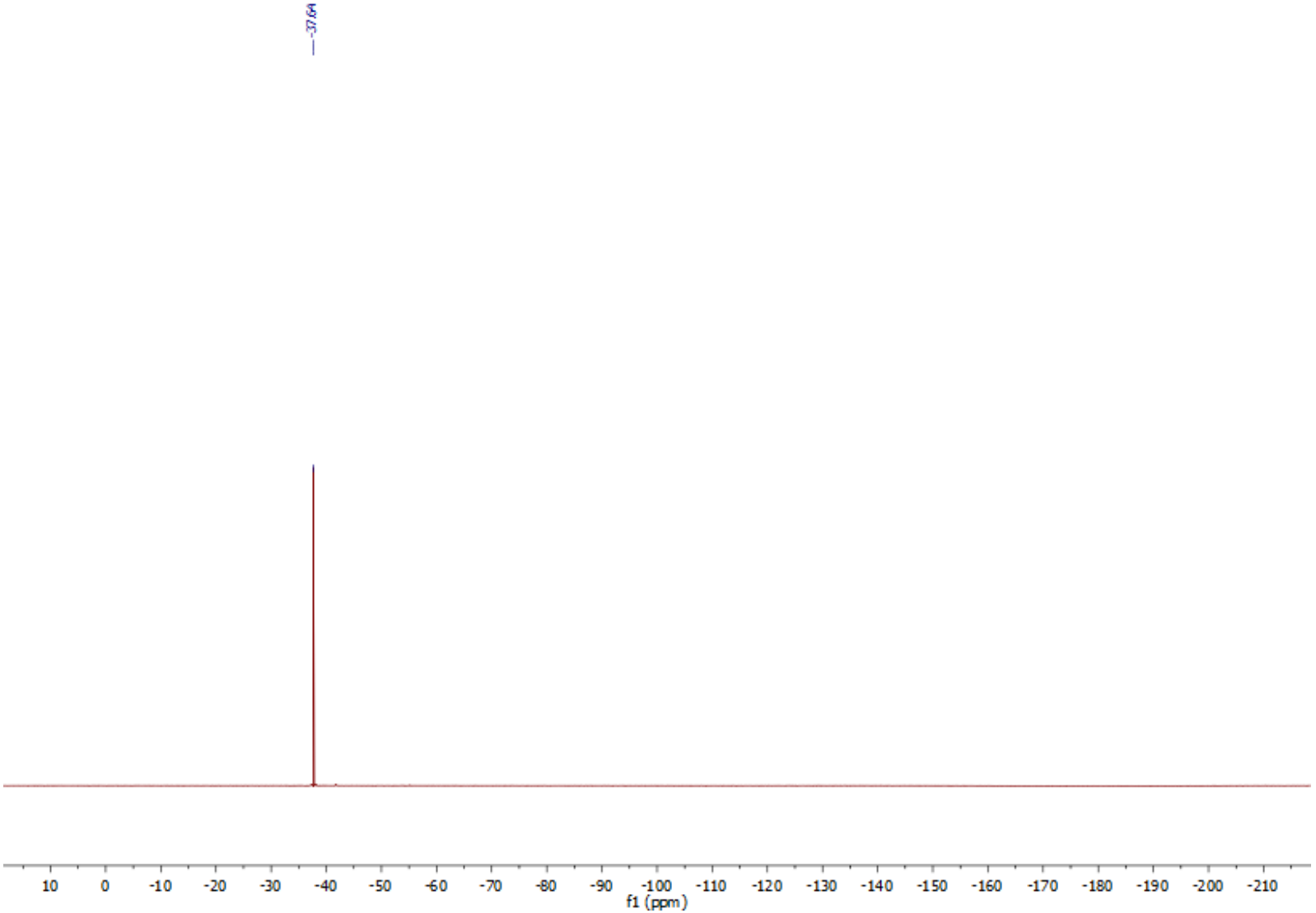
^{13}C NMR ($CDCl_3$, 100 MHz). 1-(Hexyloxy)-1-((trifluoromethyl)thio)undecan-2-one (**5m**)



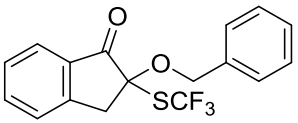


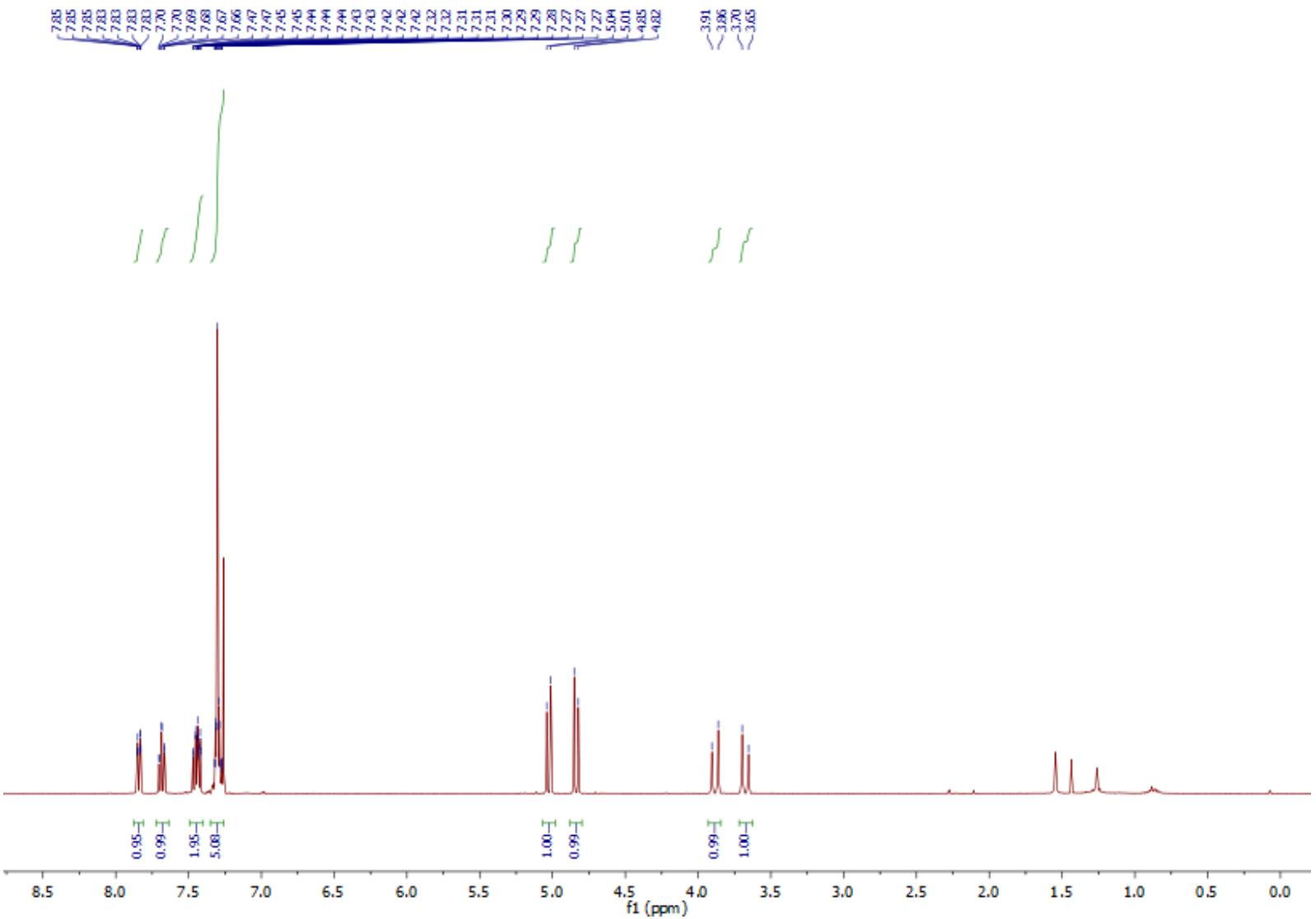
^{19}F NMR ($CDCl_3$, 377 MHz). 1-(Hexyloxy)-1-((trifluoromethyl)thio)undecan-2-one (**5m**)



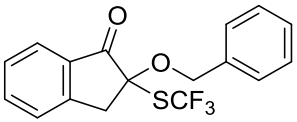


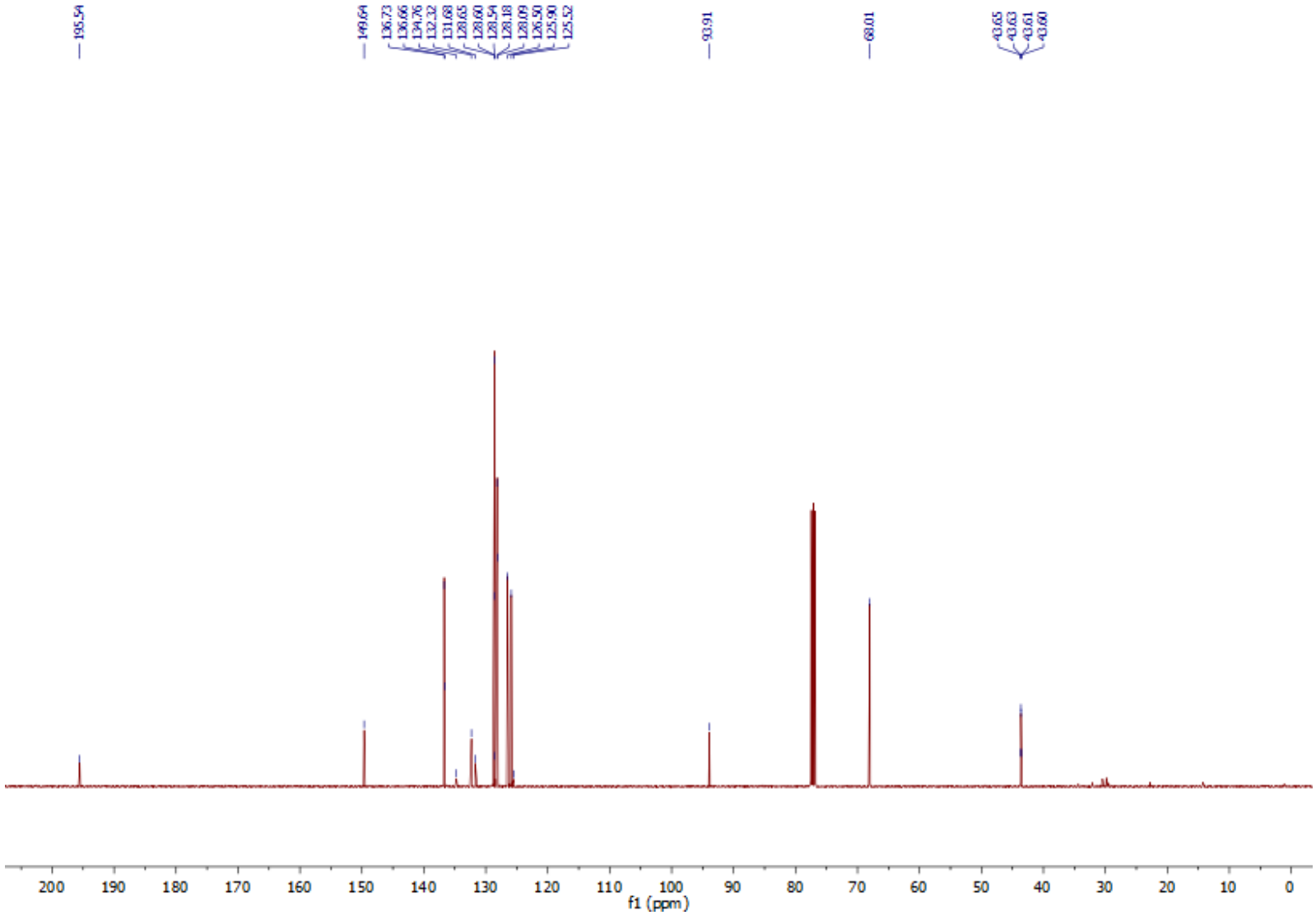
^{1}H NMR ($CDCl_3$, 400 MHz). 2-(Benzyloxy)-2-((trifluoromethyl)thio)-2,3-dihydro-1*H*-inden-1-one (**5n**)



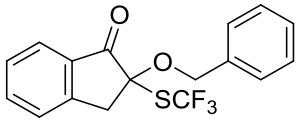


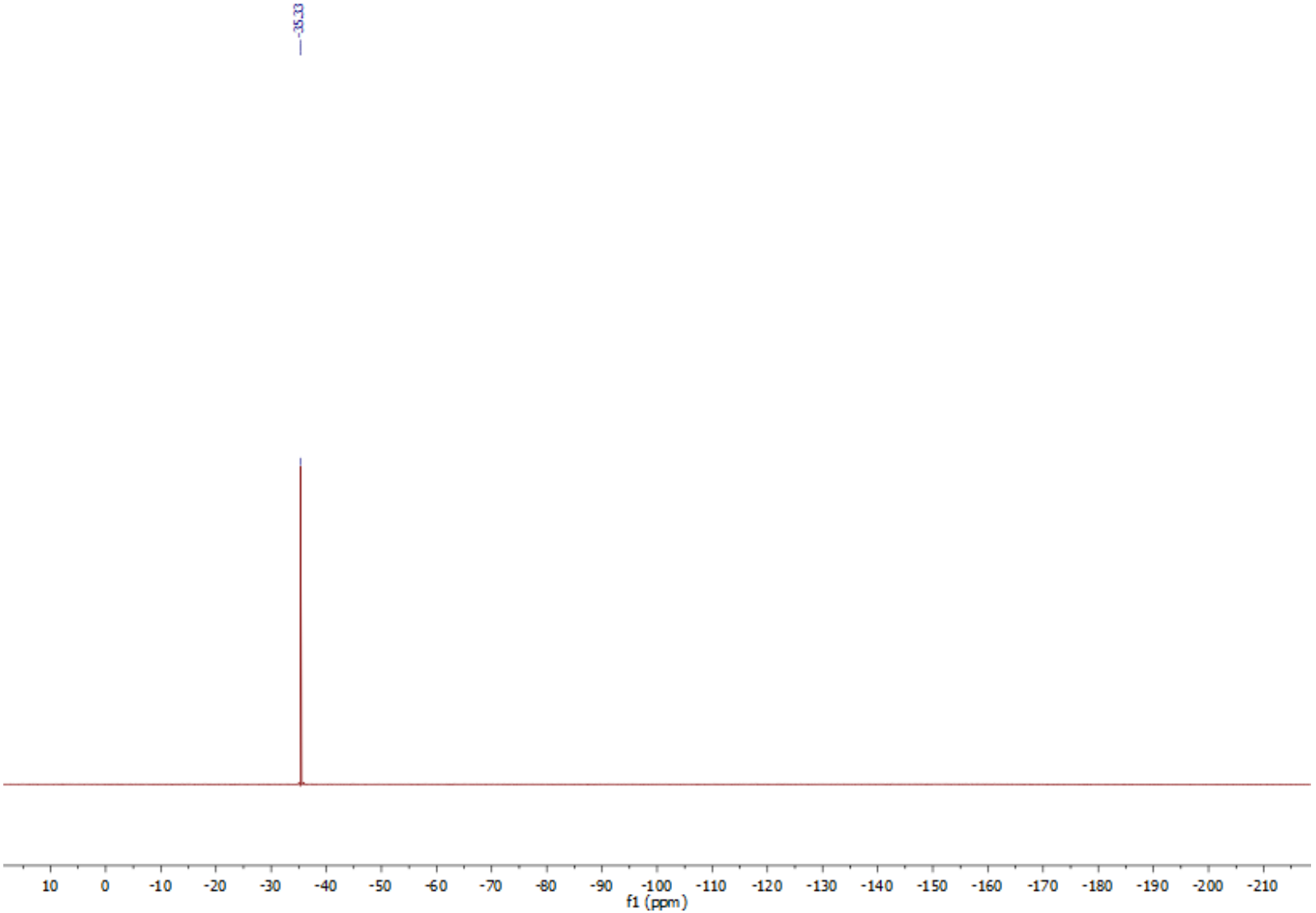
^{13}C NMR ($CDCl_3$, 100 MHz). 2-(Benzyloxy)-2-((trifluoromethyl)thio)-2,3-dihydro-1*H*-inden-1-one (**5n**)



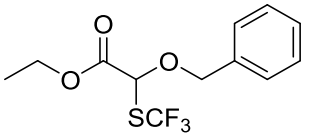


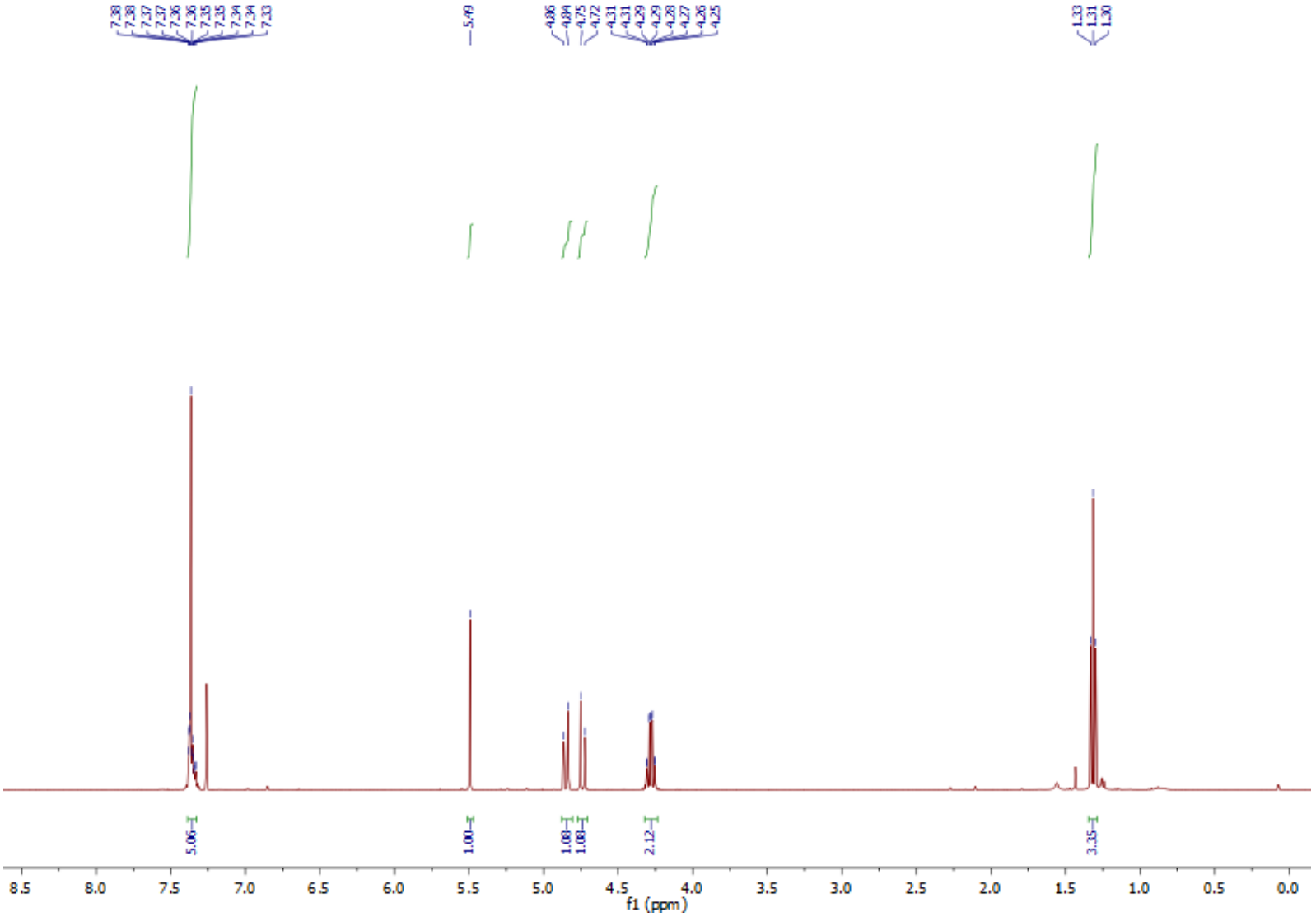
^{19}F NMR ($CDCl_3$, 377 MHz). 2-(Benzyloxy)-2-((trifluoromethyl)thio)-2,3-dihydro-1*H*-inden-1-one (**5n**)



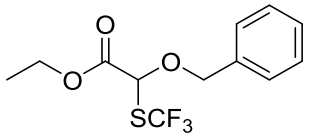


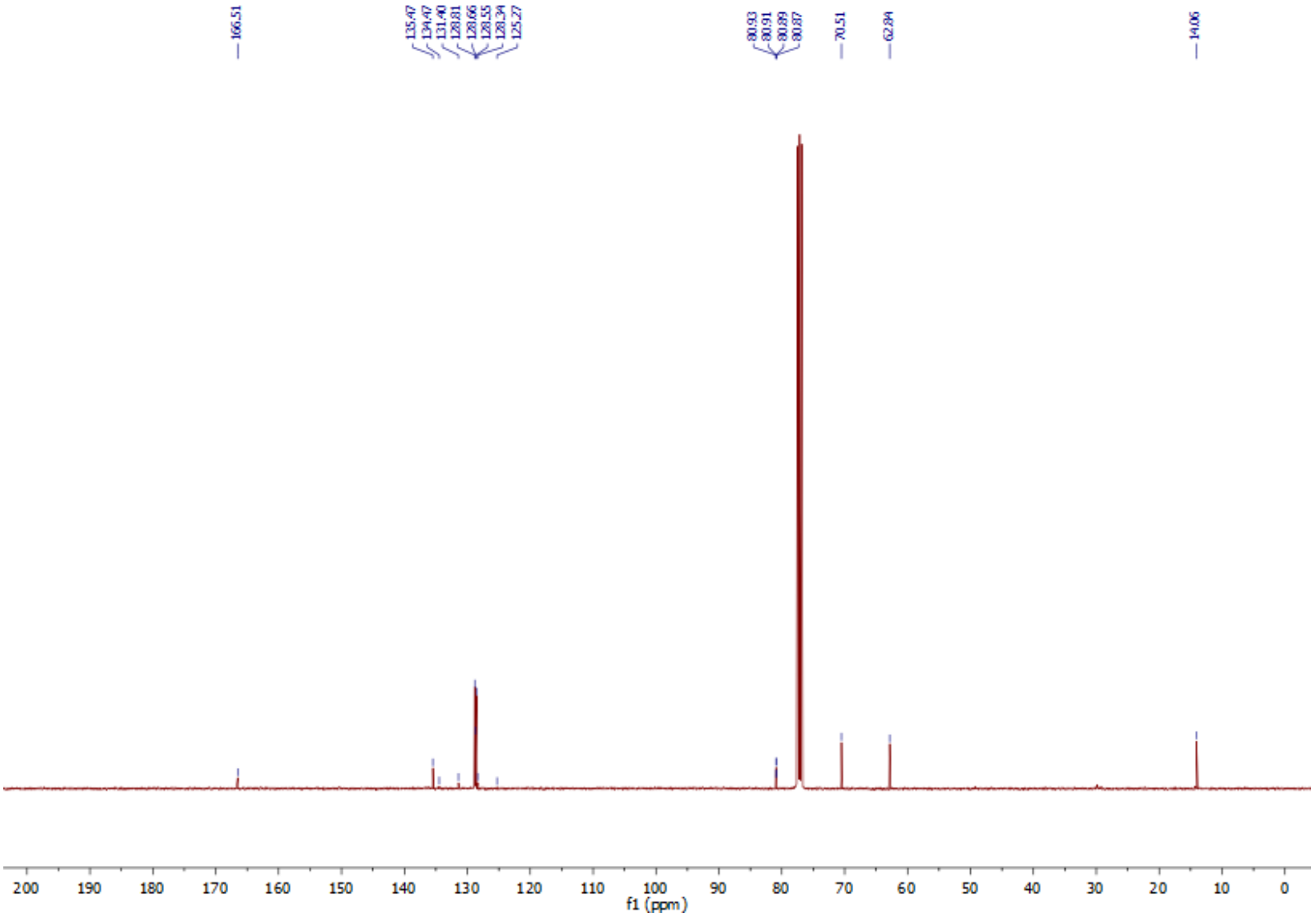
^{1}H NMR ($CDCl_3$, 400 MHz). Ethyl 2-(benzyloxy)-2-((trifluoromethyl)thio)acetate (**5o**)



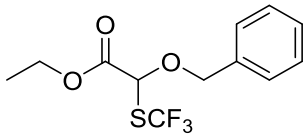


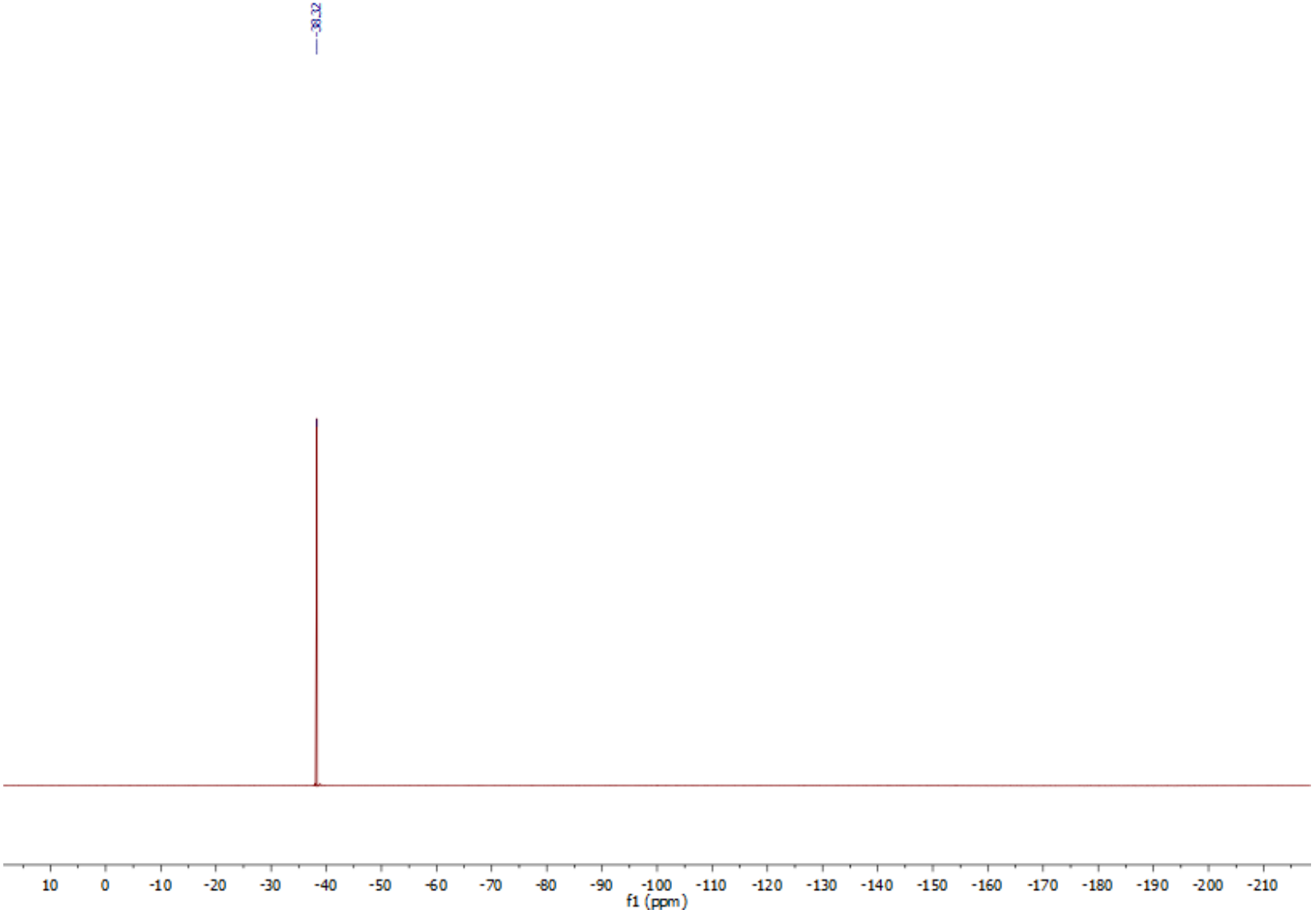
^{13}C NMR ($CDCl_3$, 100 MHz). Ethyl 2-(benzyloxy)-2-((trifluoromethyl)thio)acetate (**5o**)



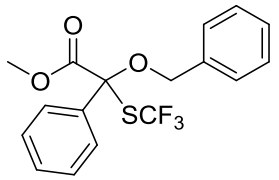


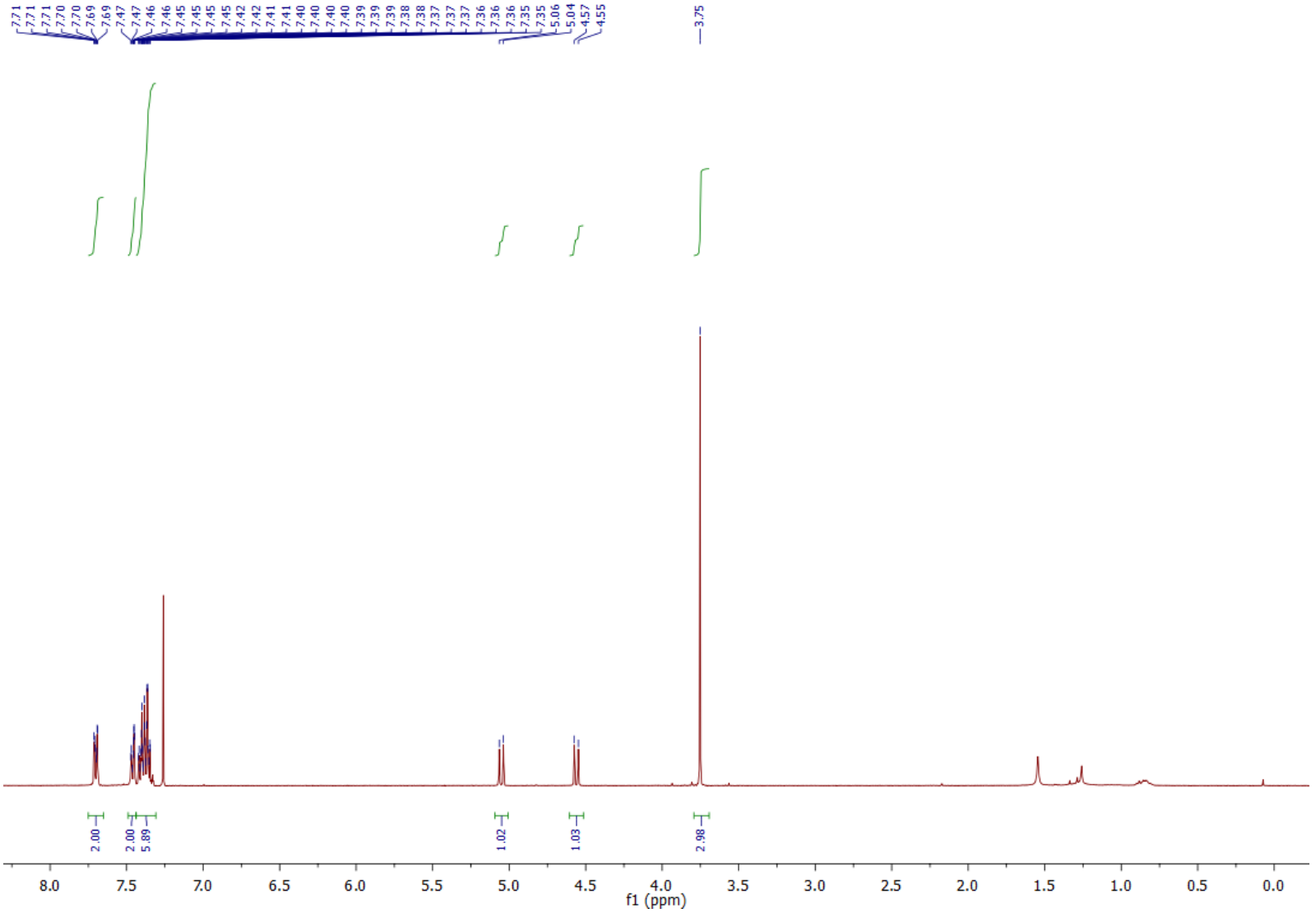
^{19}F NMR ($CDCl_3$, 377 MHz). Ethyl 2-(benzyloxy)-2-((trifluoromethyl)thio)acetate (**5o**)



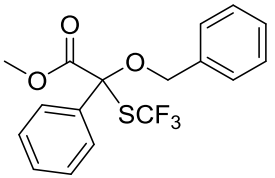


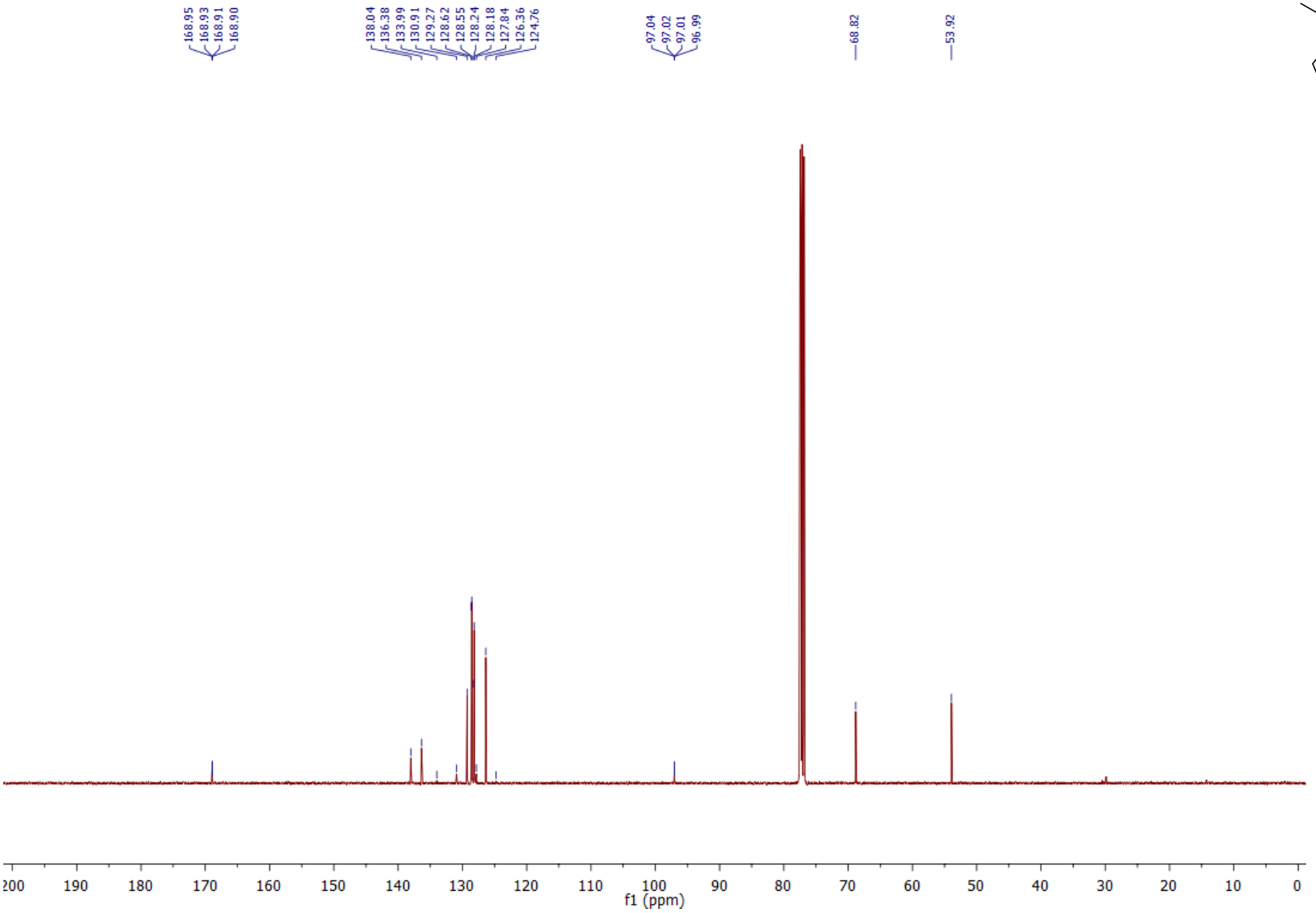
^{1}H NMR ($CDCl_3$, 400 MHz). Methyl 2-(benzyloxy)-2-phenyl-2-((trifluoromethyl)thio)acetate (**5p**)



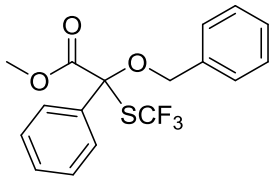


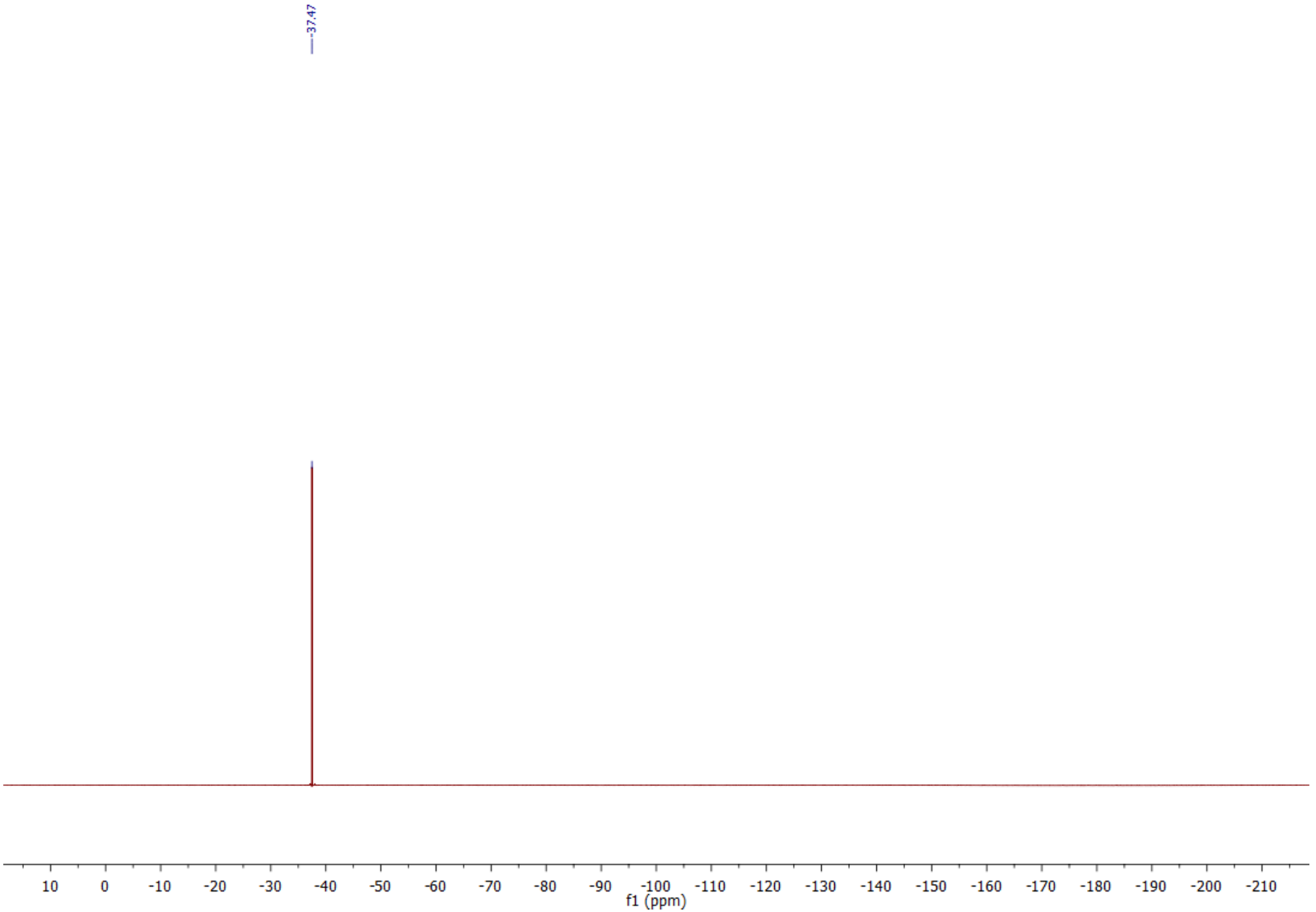
^{13}C NMR ($CDCl_3$, 100 MHz). Methyl 2-(benzyloxy)-2-phenyl-2-((trifluoromethyl)thio)acetate (**5p**)



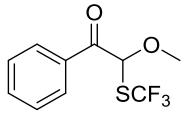


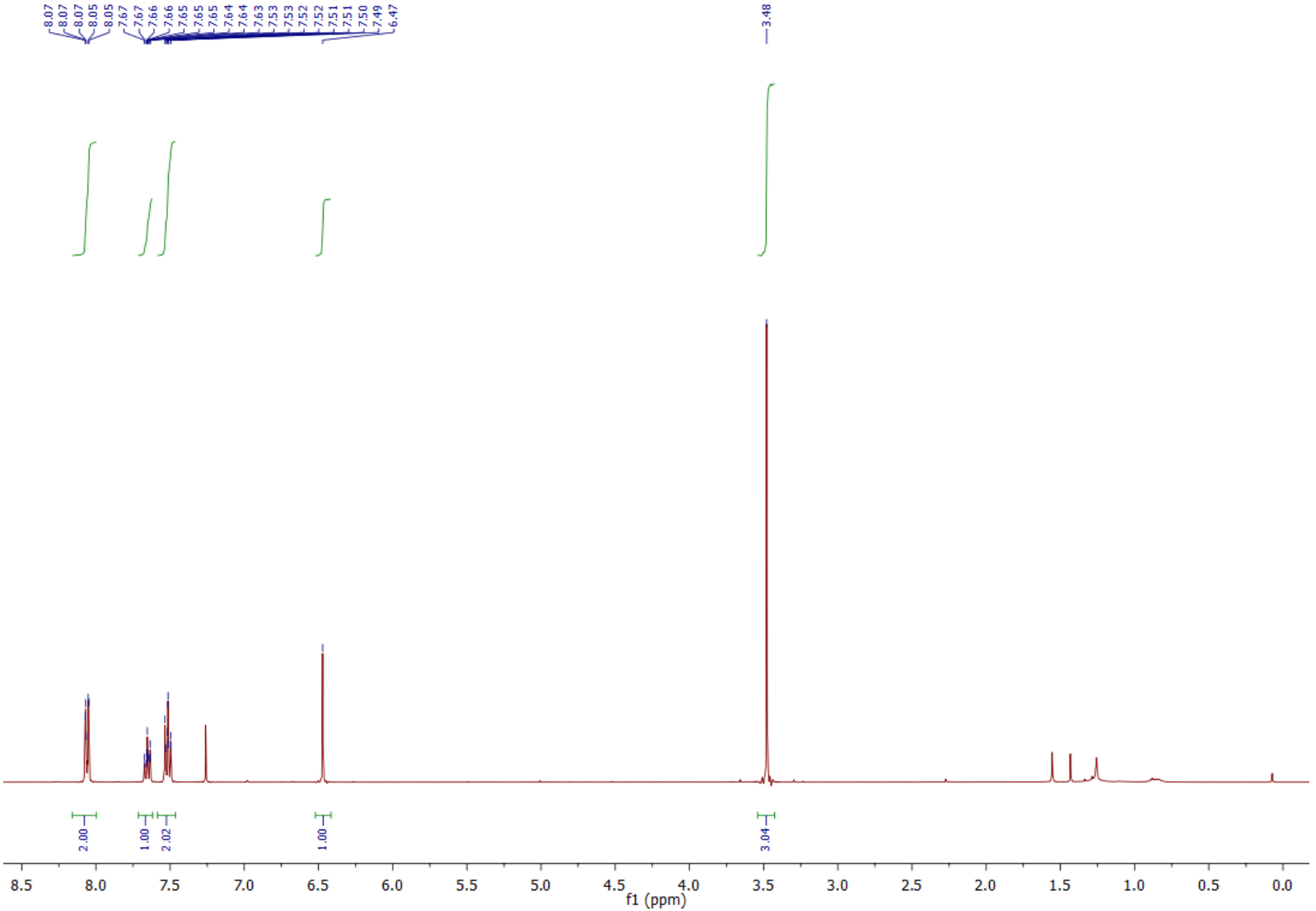
^{19}F NMR ($CDCl_3$, 377 MHz). Methyl 2-(benzyloxy)-2-phenyl-2-((trifluoromethyl)thio)acetate (**5p**)



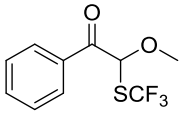


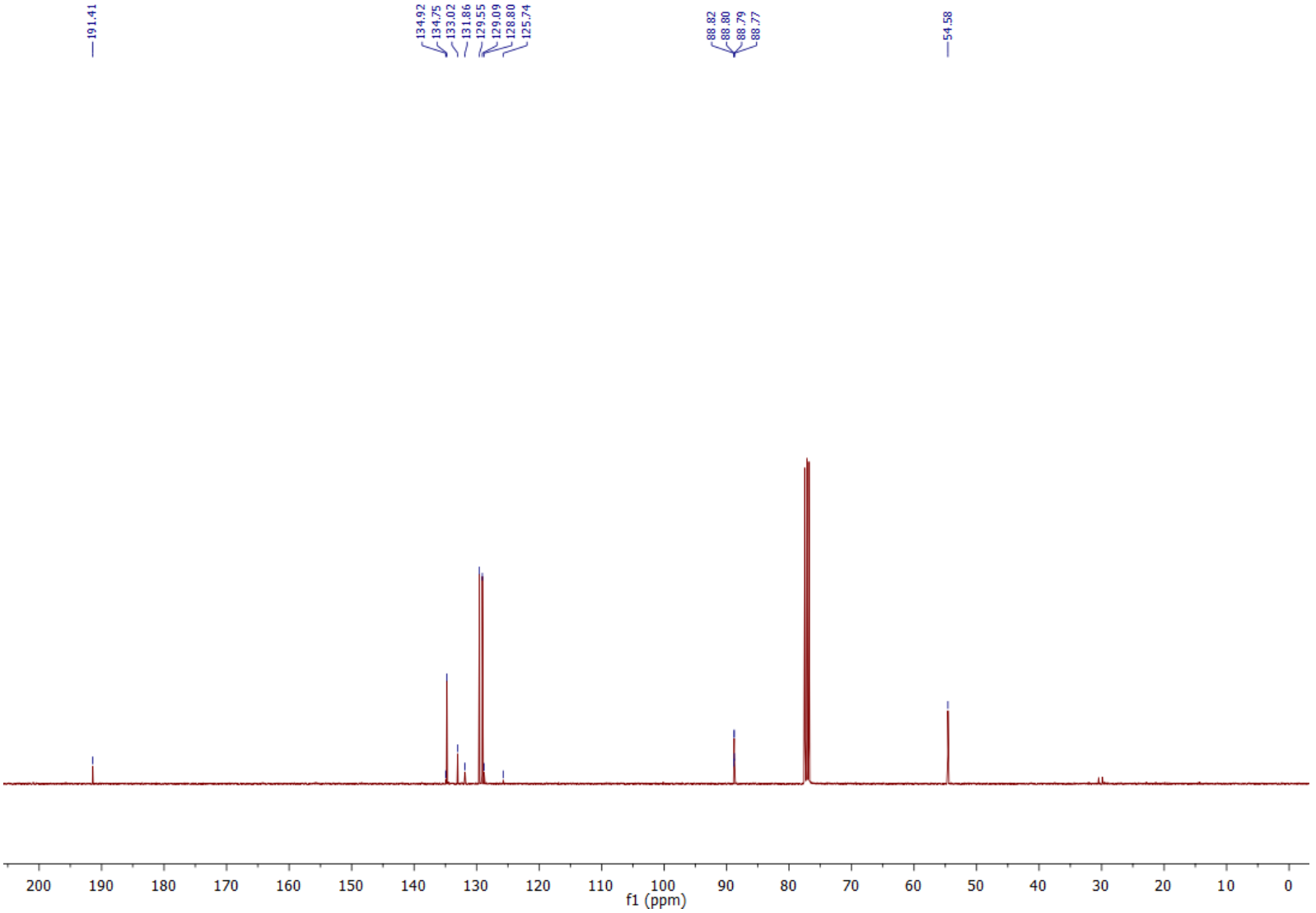
^{1}H NMR ($CDCl_3$, 400 MHz). 2-Methoxy-1-phenyl-2-((trifluoromethyl)thio)ethan-1-one (**5q**)



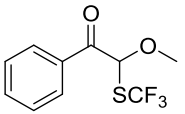


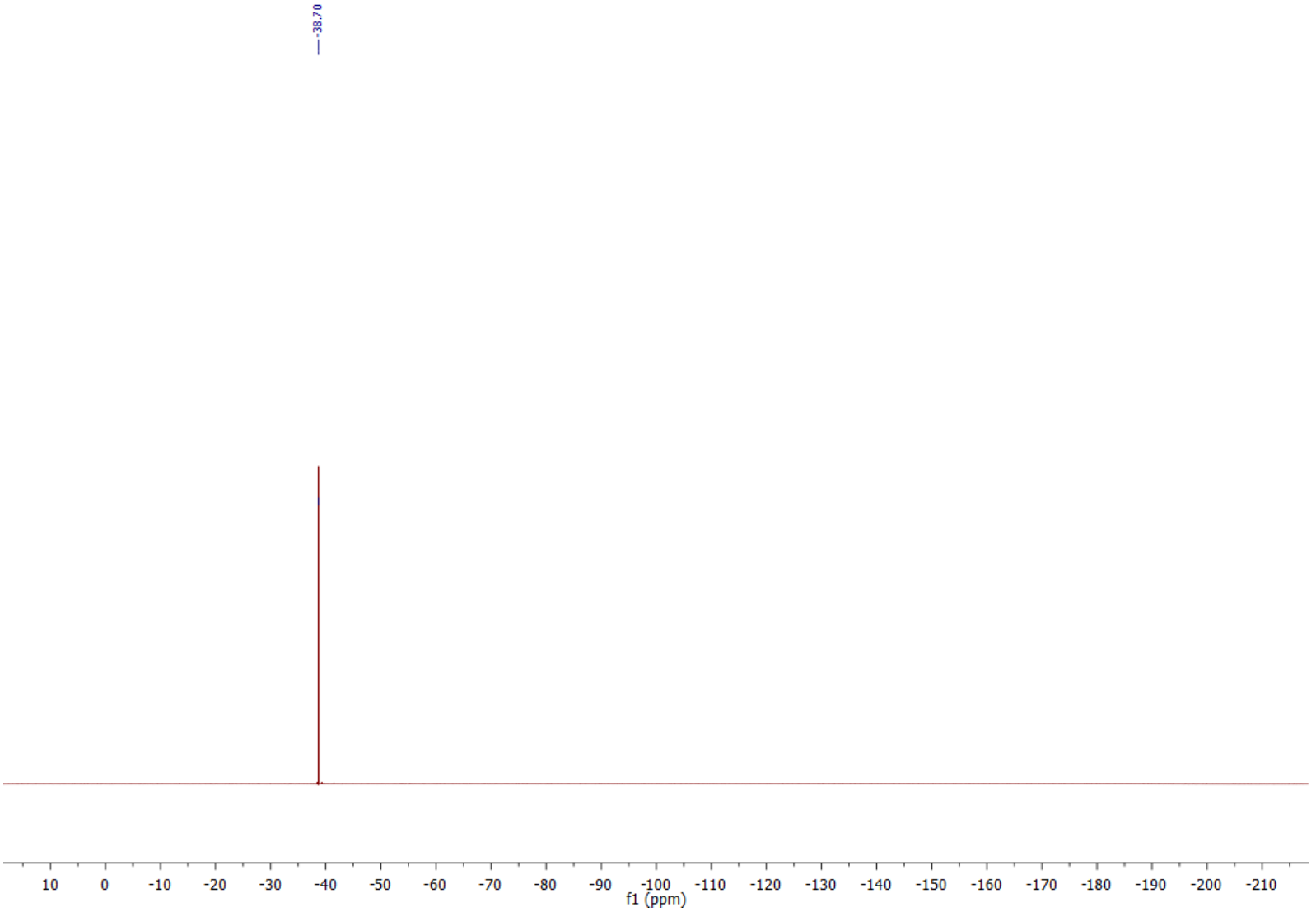
^{13}C NMR ($CDCl_3$, 100 MHz). 2-Methoxy-1-phenyl-2-((trifluoromethyl)thio)ethan-1-one (**5q**)



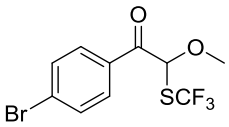


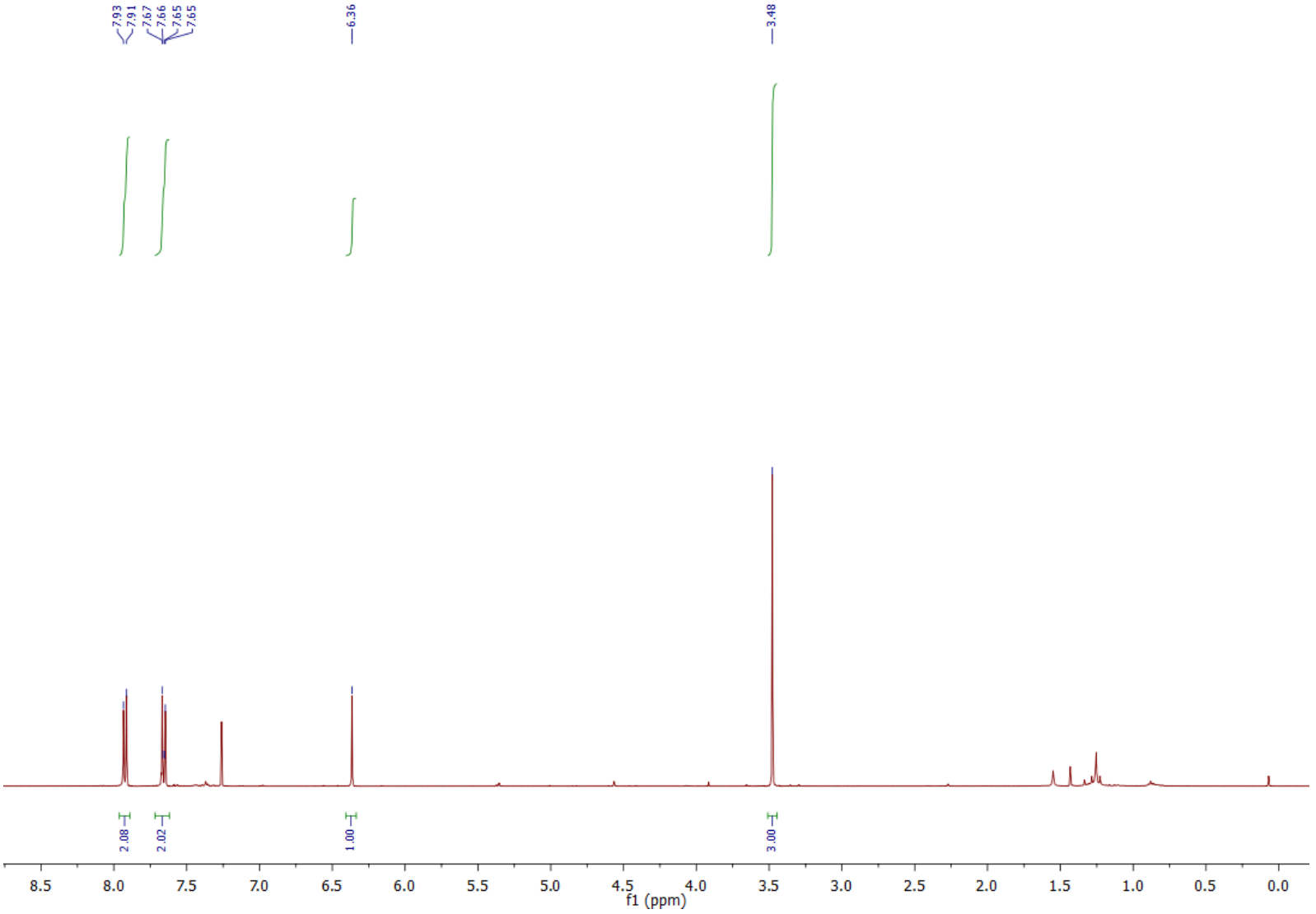
^{19}F NMR ($CDCl_3$, 377 MHz). 2-Methoxy-1-phenyl-2-((trifluoromethyl)thio)ethan-1-one (**5q**)



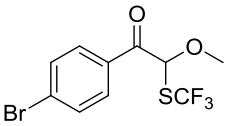


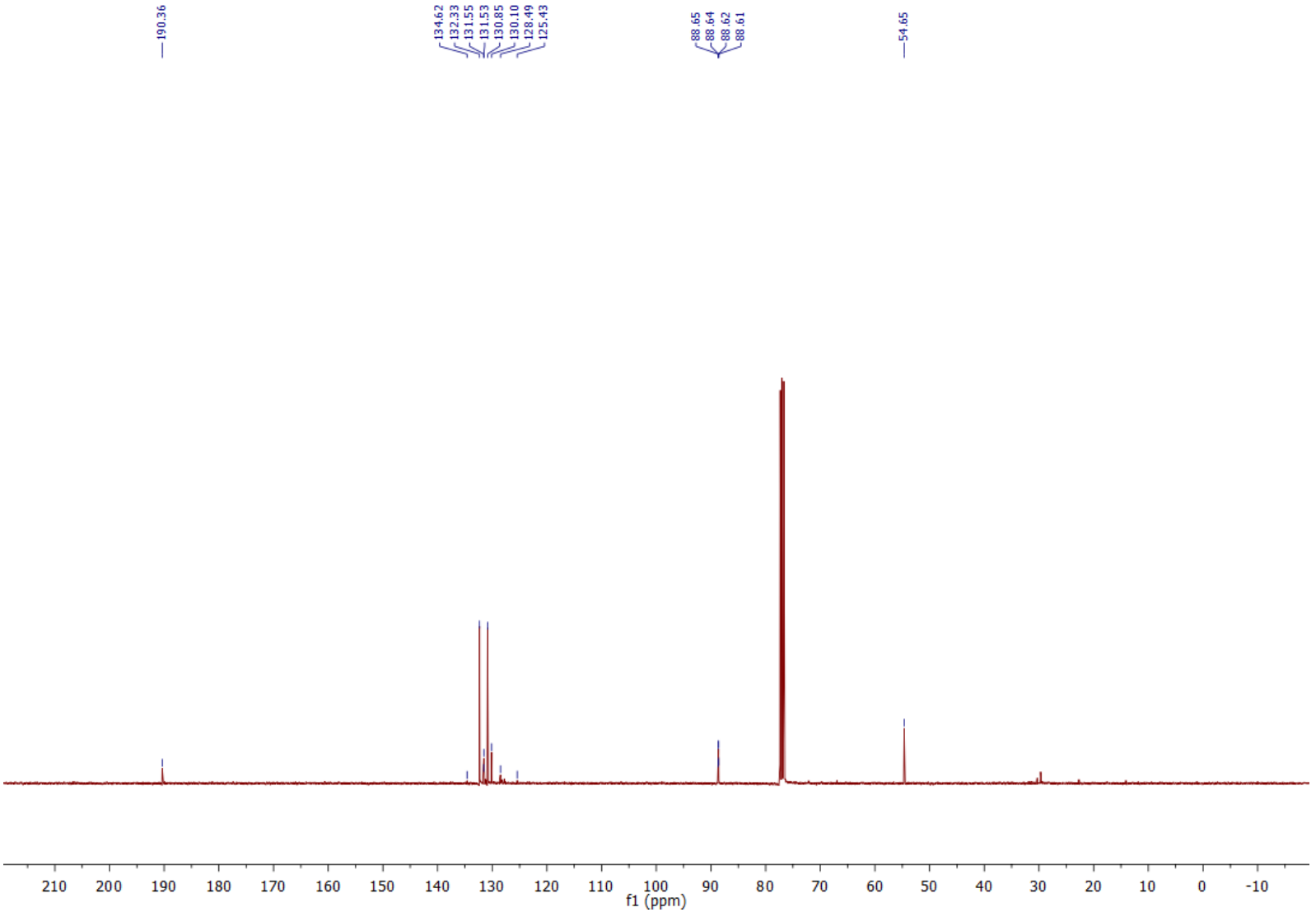
^{1}H NMR ($CDCl_3$, 400 MHz). 1-(4-Bromophenyl)-2-methoxy-2-((trifluoromethyl)thio)ethan-1-one (**5r**)



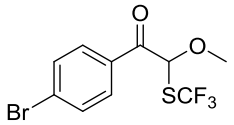


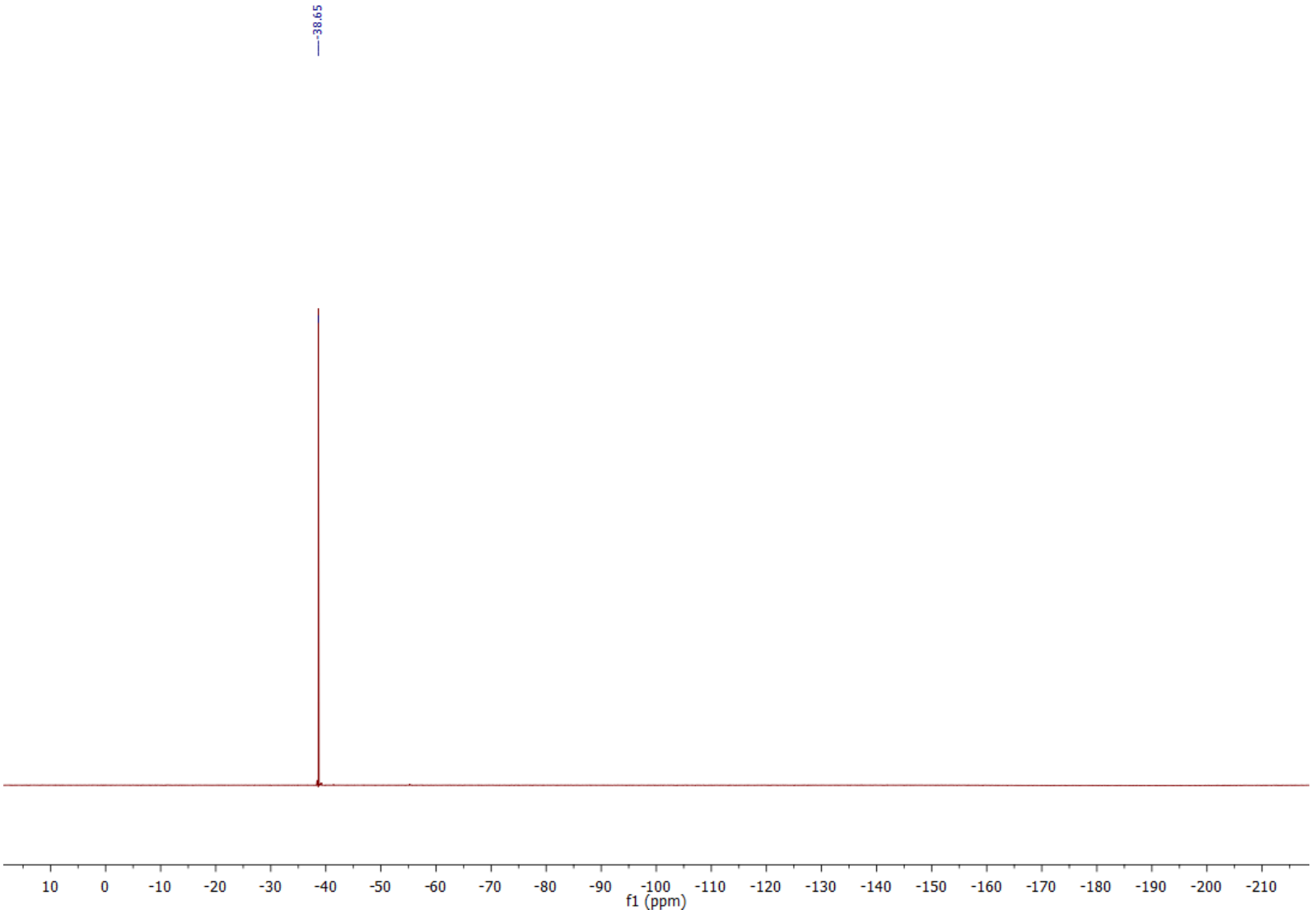
^{13}C NMR ($CDCl_3$, 100 MHz). 1-(4-Bromophenyl)-2-methoxy-2-((trifluoromethyl)thio)ethan-1-one (**5r**)



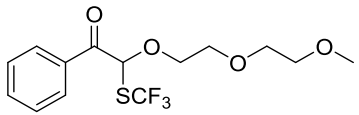


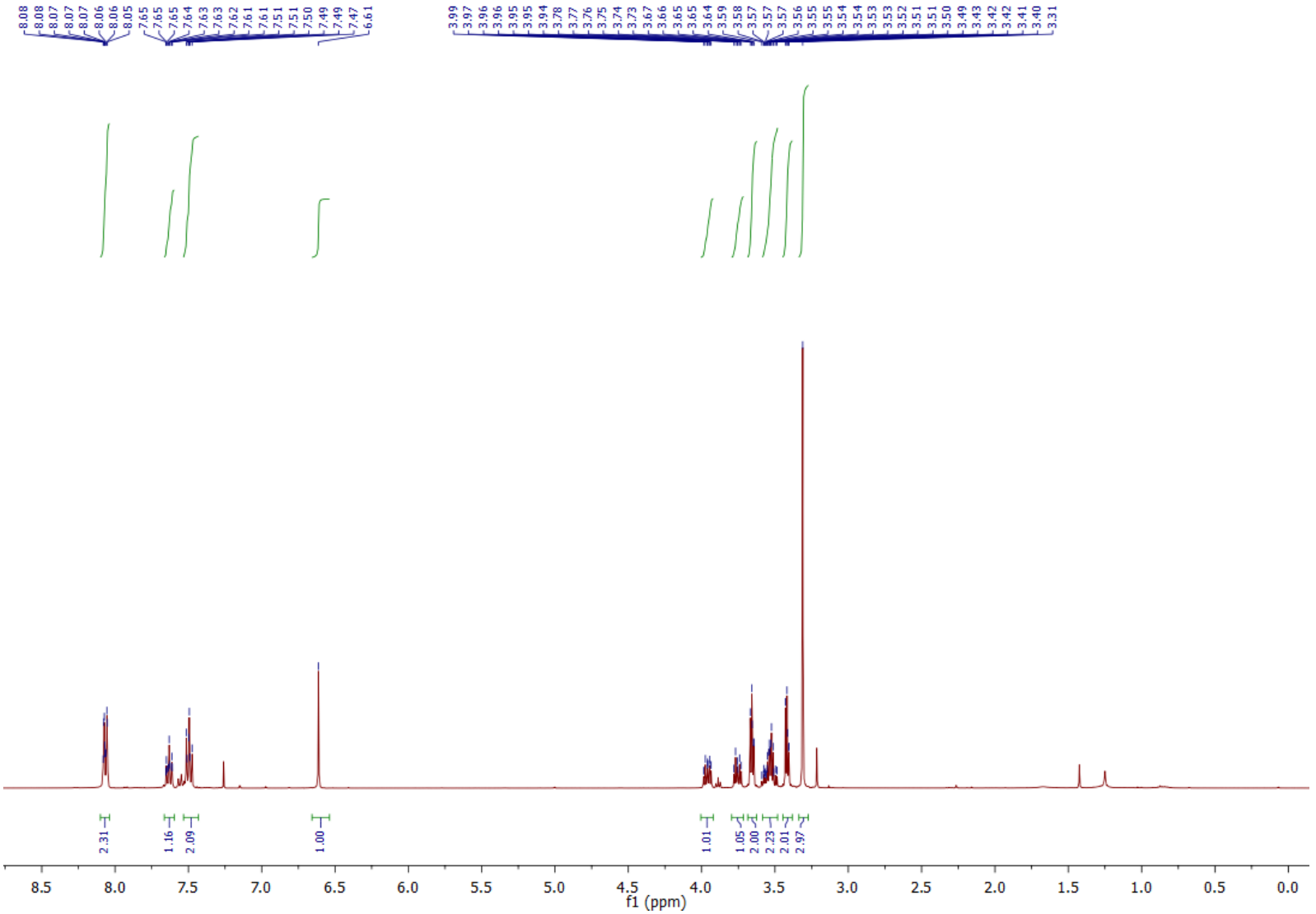
^{19}F NMR ($CDCl_3$, 377 MHz). 1-(4-Bromophenyl)-2-methoxy-2-((trifluoromethyl)thio)ethan-1-one (**5r**)



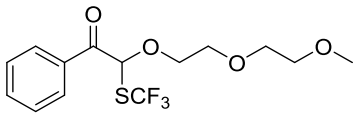


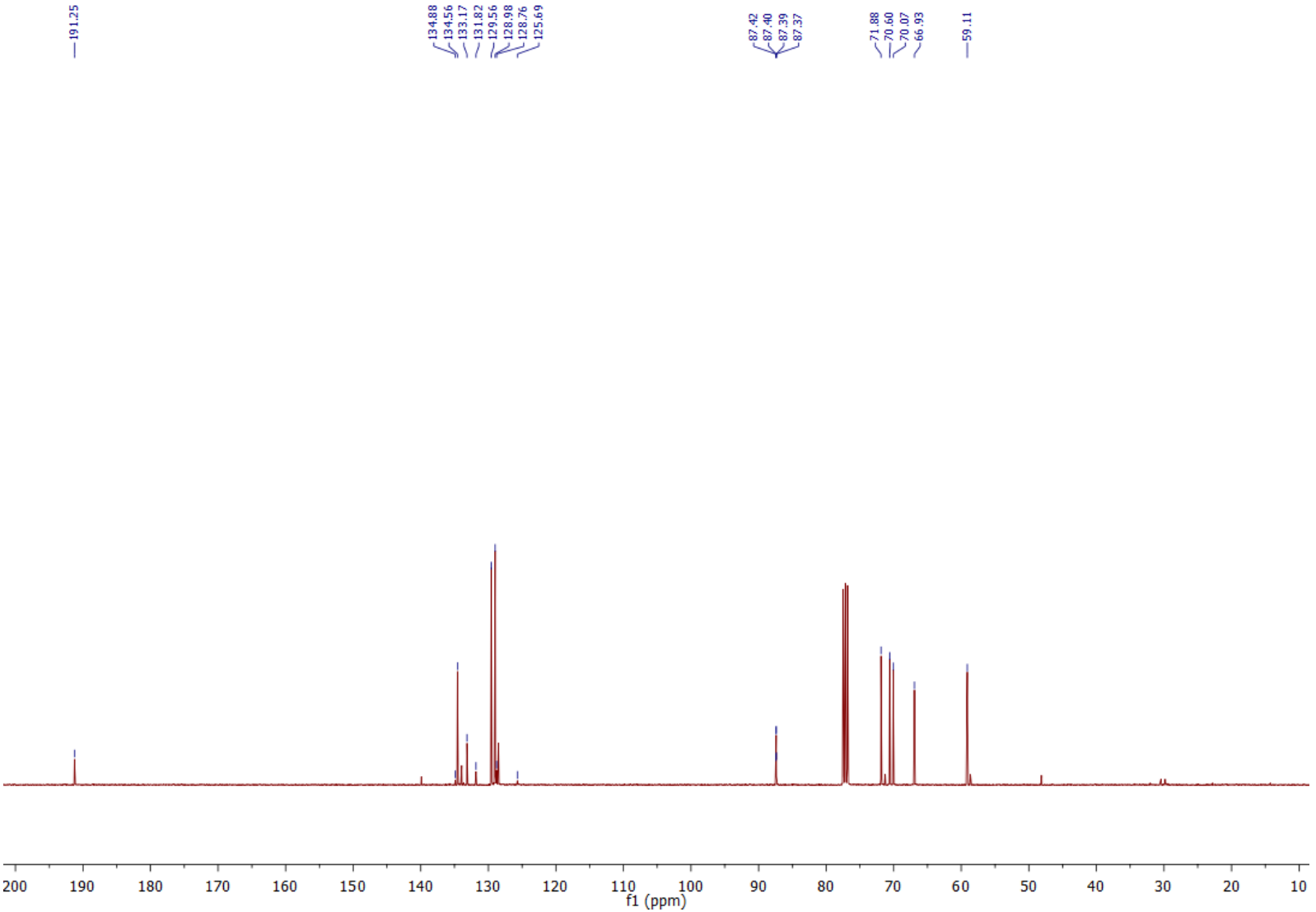
^{1}H NMR ($CDCl_3$, 400 MHz). 2-(2-(2-Methoxyethoxy)ethoxy)-1-phenyl-2-((trifluoromethyl)thio)ethan-1-one (**5s**)



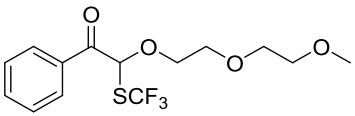


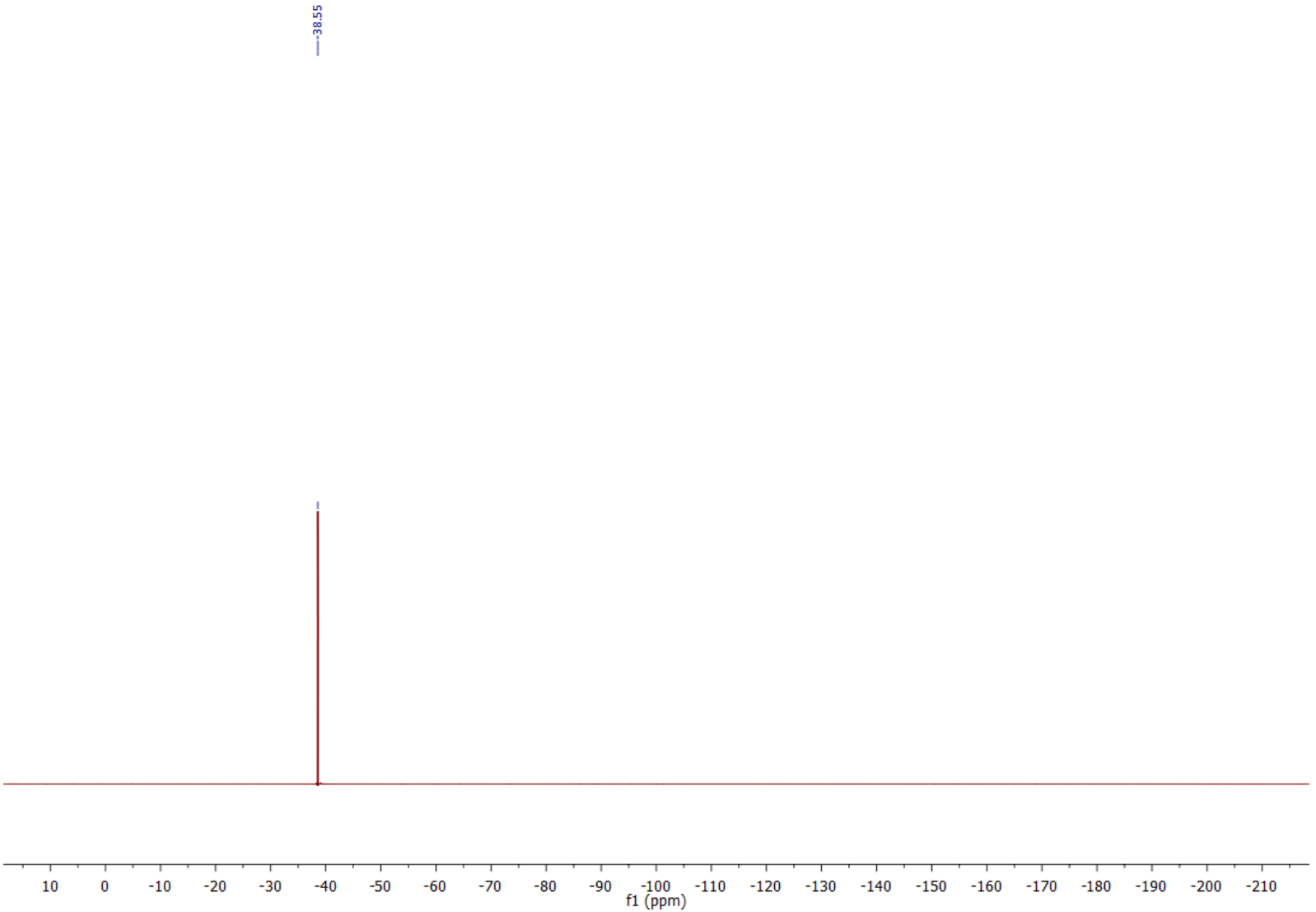
^{13}C NMR ($CDCl_3$, 100 MHz). 2-(2-(2-Methoxyethoxy)ethoxy)-1-phenyl-2-((trifluoromethyl)thio)ethan-1-one (**5s**)



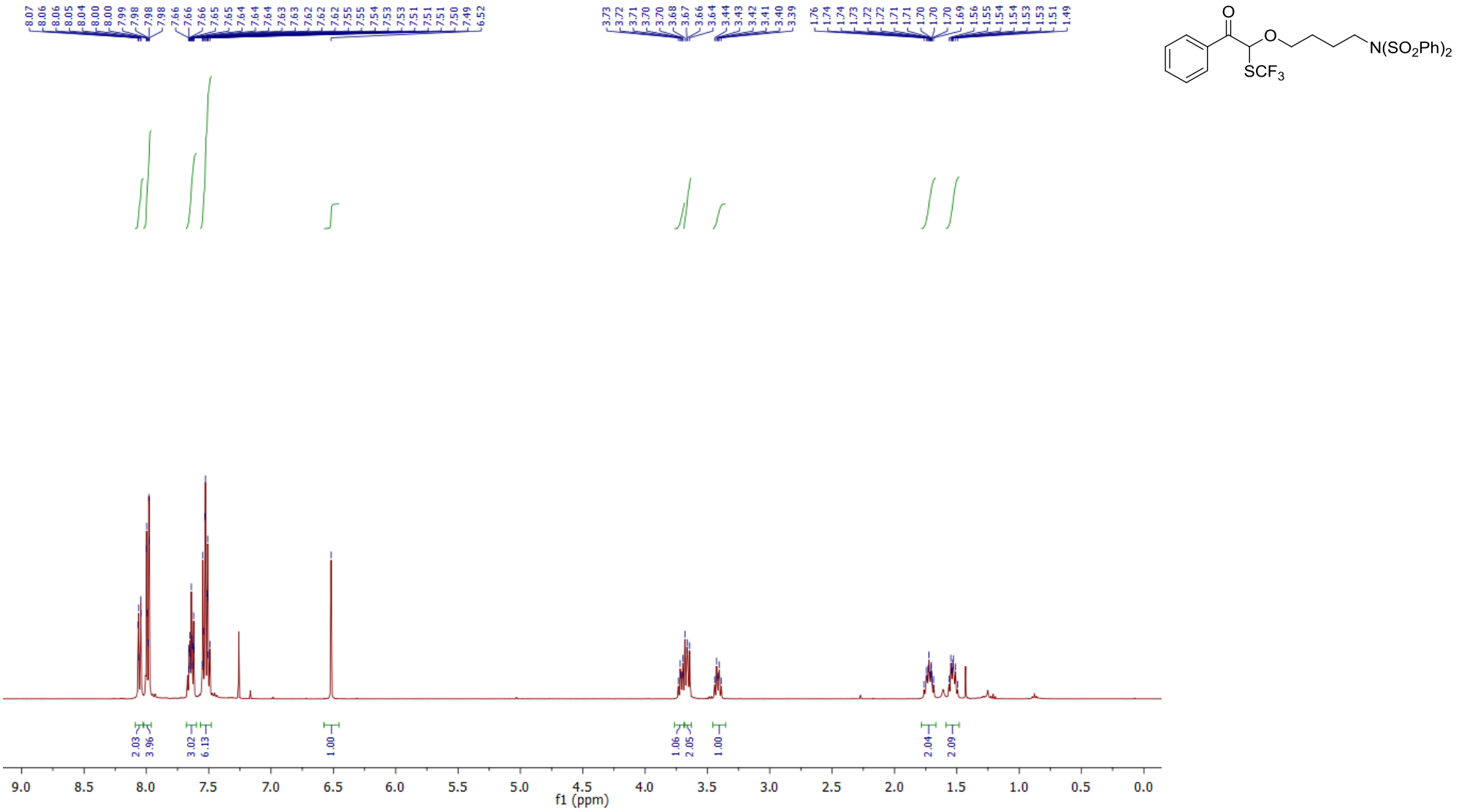


^{19}F NMR ($CDCl_3$, 377 MHz). 2-(2-(2-Methoxyethoxy)ethoxy)-1-phenyl-2-((trifluoromethyl)thio)ethan-1-one (**5s**)

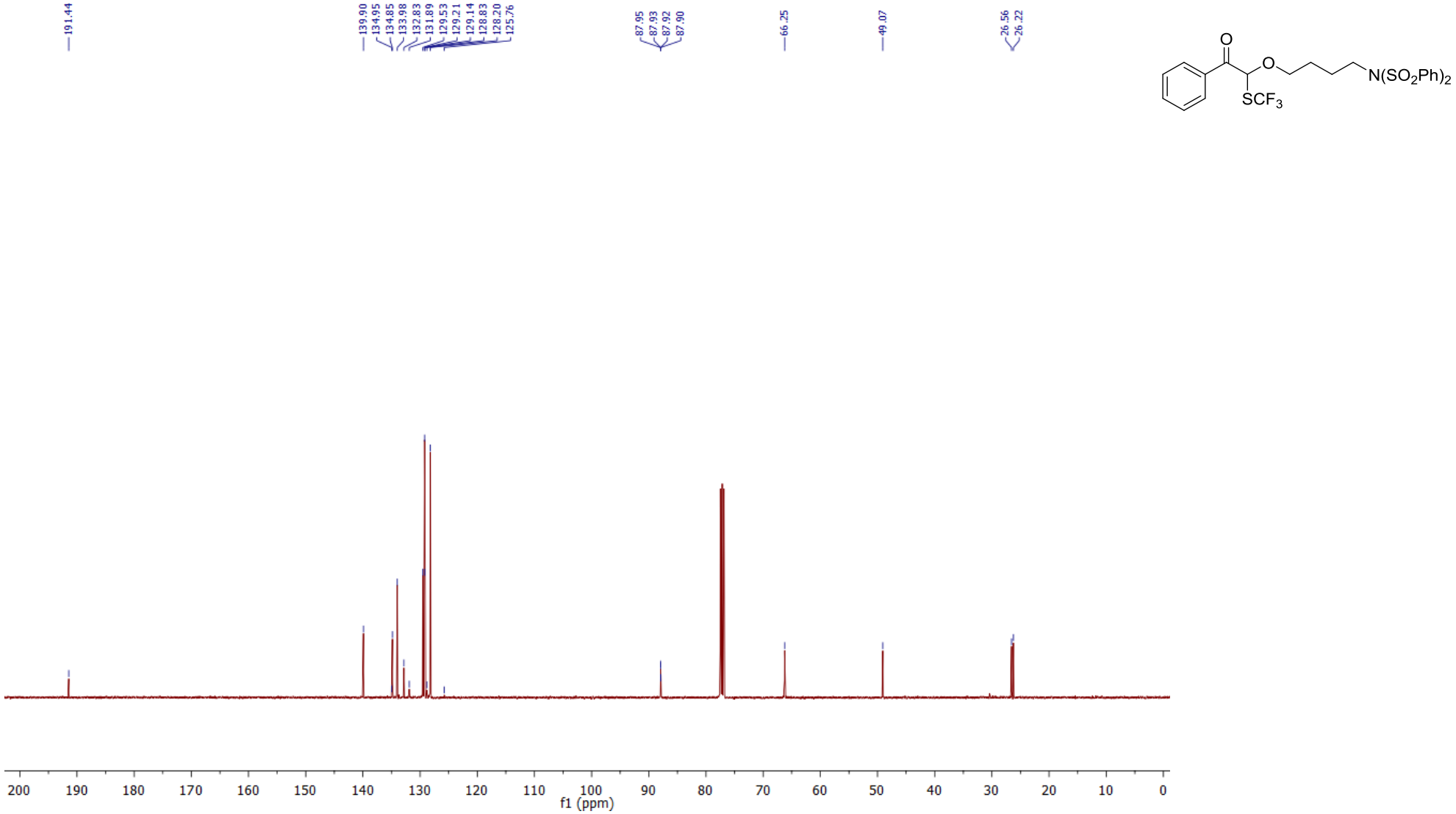




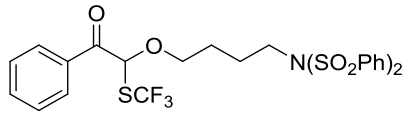
^{1}H NMR ($CDCl_3$, 400 MHz). *N*-(4-(2-oxo-2-phenyl-1-((trifluoromethyl)thio)ethoxy)butyl)-*N*-(phenylsulfonyl)benzenesulfonamide (**8a**)

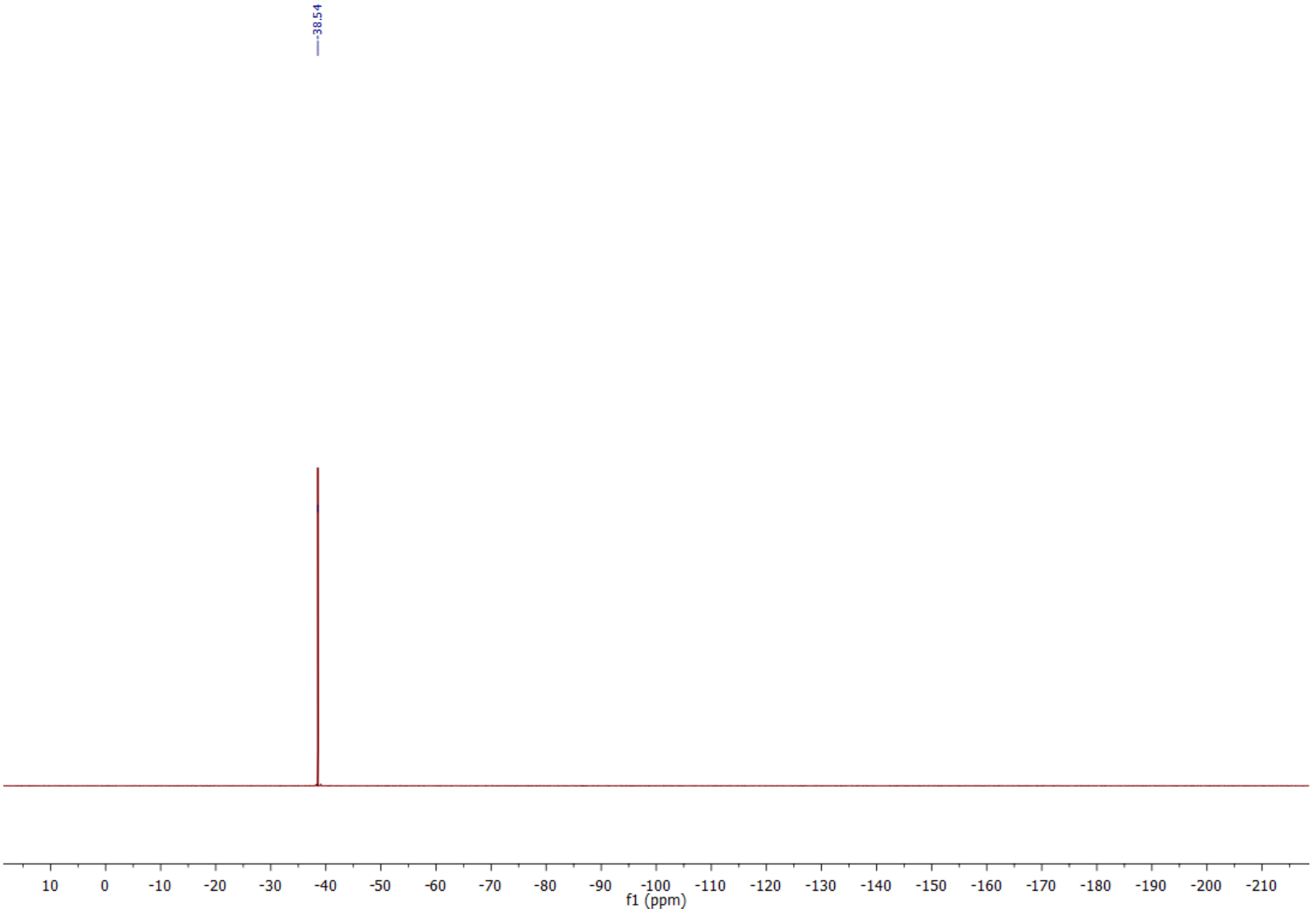


^{13}C NMR ($CDCl_3$, 100 MHz). *N*-(4-(2-oxo-2-phenyl-1-((trifluoromethyl)thio)ethoxy)butyl)-*N*-(phenylsulfonyl)benzenesulfonamide (**8a**)



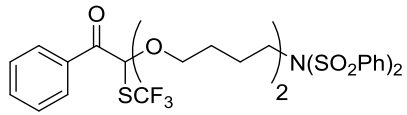
^{19}F NMR ($CDCl_3$, 377 MHz). *N*-(4-(2-oxo-2-phenyl-1-((trifluoromethyl)thio)ethoxy)butyl)-*N*-(phenylsulfonyl)benzenesulfonamide (**8a**)

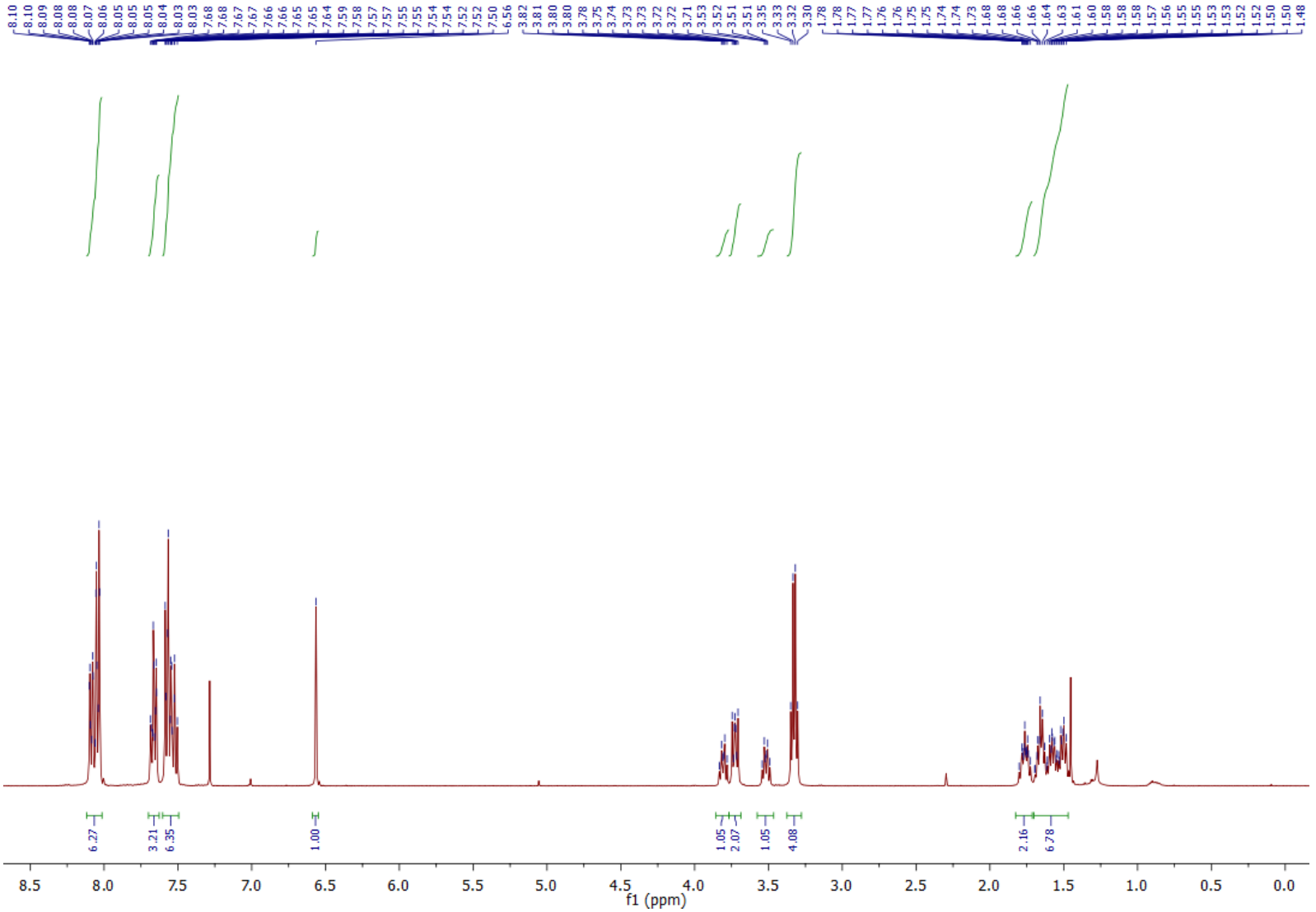




^{1}H NMR ($CDCl_3$, 400 MHz).

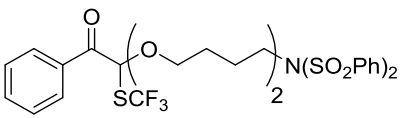
N-(4-(4-(2-oxo-2-phenyl-1-((trifluoromethyl)thio)ethoxy)butoxy)butyl)-*N*-(phenylsulfonyl)benzenesulfonamide (**8b**)

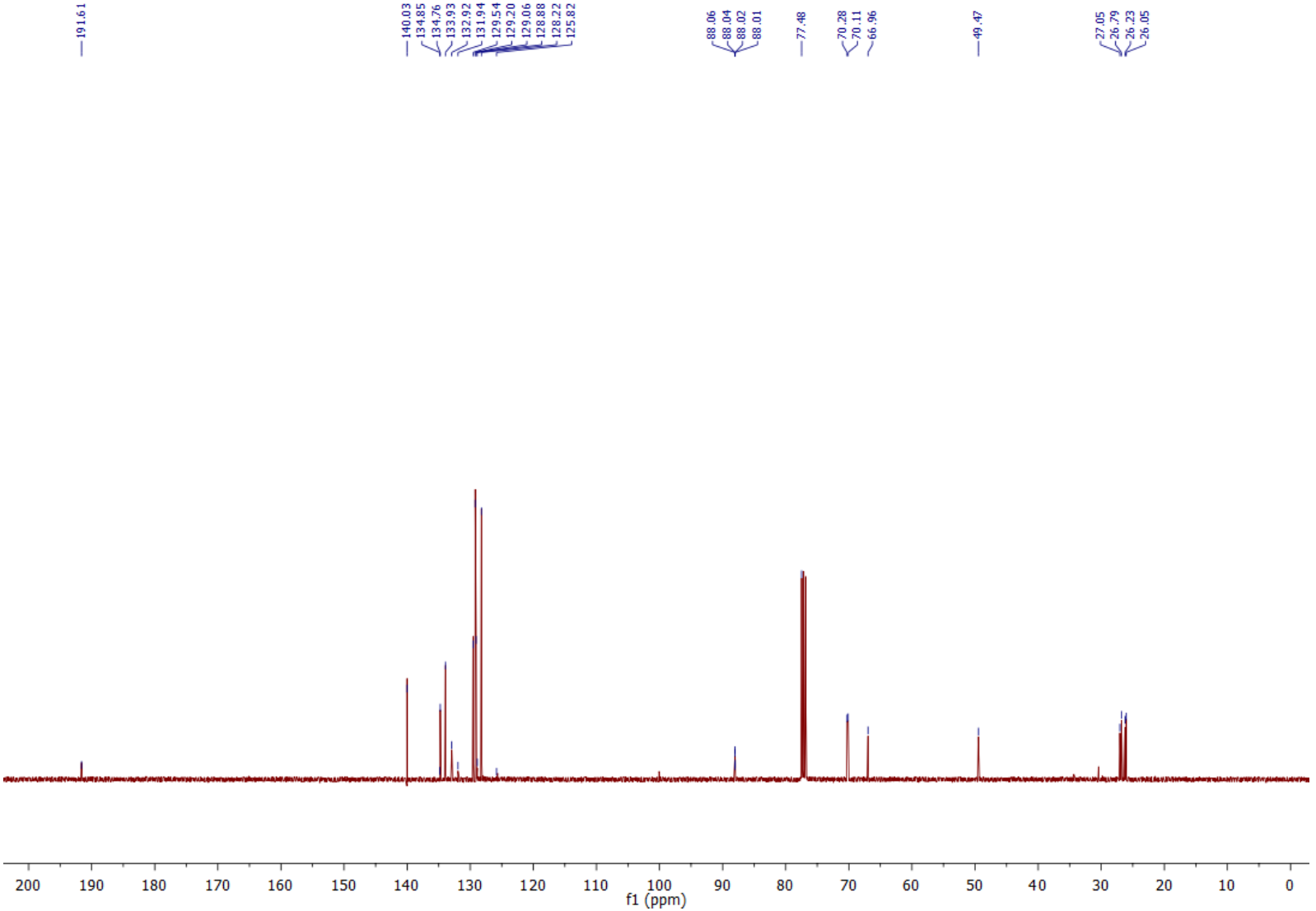




^{13}C NMR ($CDCl_3$, 100 MHz).

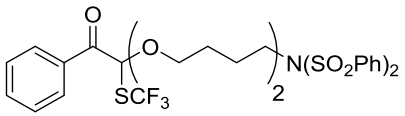
N-(4-(4-(2-oxo-2-phenyl-1-((trifluoromethyl)thio)ethoxy)butoxy)butyl)-*N*-(phenylsulfonyl)benzenesulfonamide (**8b**)

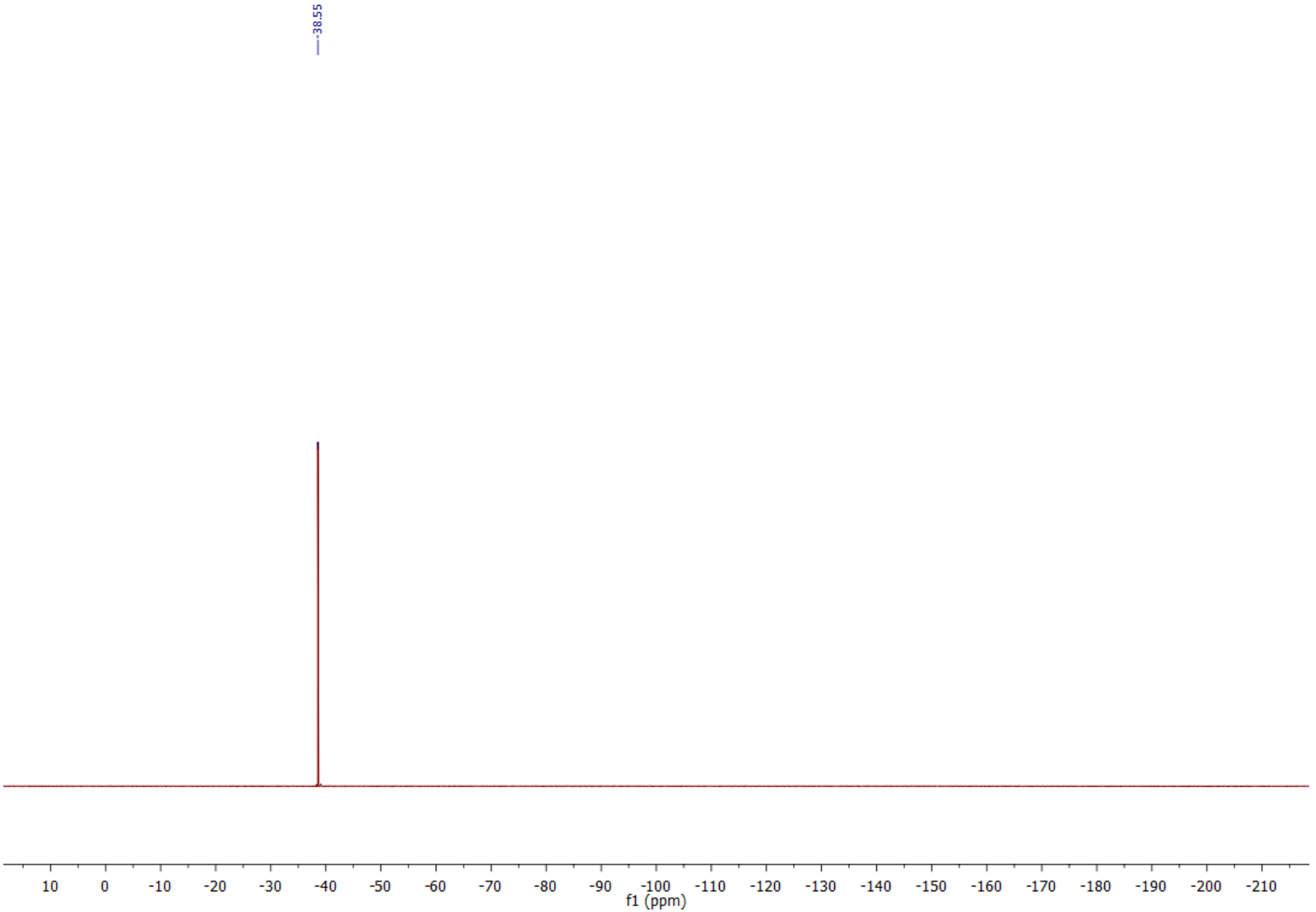




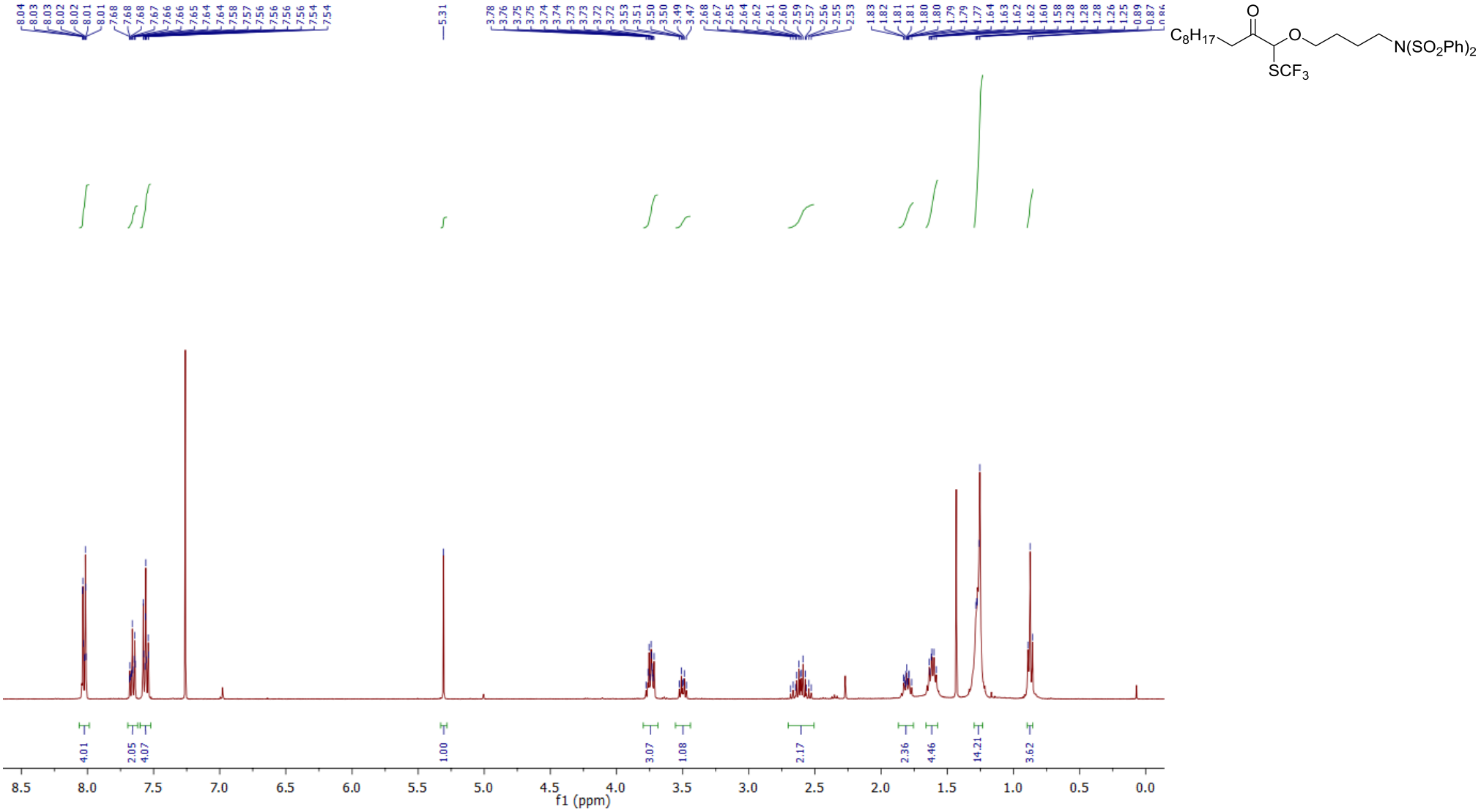
^{19}F NMR ($CDCl_3$, 377 MHz).

N-(4-(4-(2-oxo-2-phenyl-1-((trifluoromethyl)thio)ethoxy)butoxy)butyl)-*N*-(phenylsulfonyl)benzenesulfonamide (**8b**)

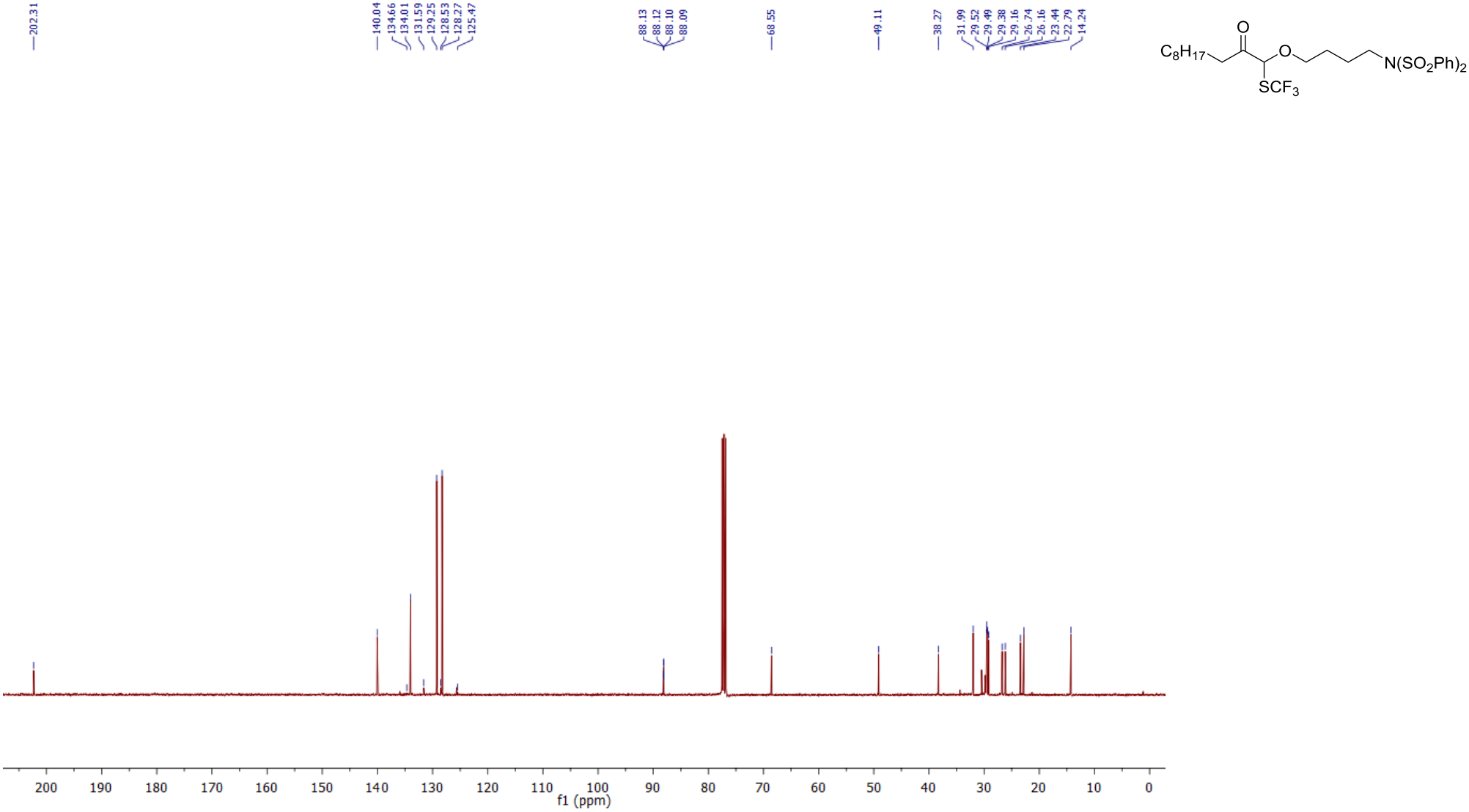




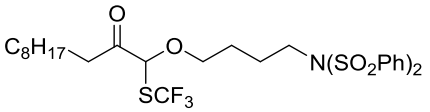
^{1}H NMR ($CDCl_3$, 400 MHz). *N*-(4-((2-oxo-1-((trifluoromethyl)thio)undecyl)oxy)butyl)-*N*-(phenylsulfonyl)benzenesulfonamide (**8c**)

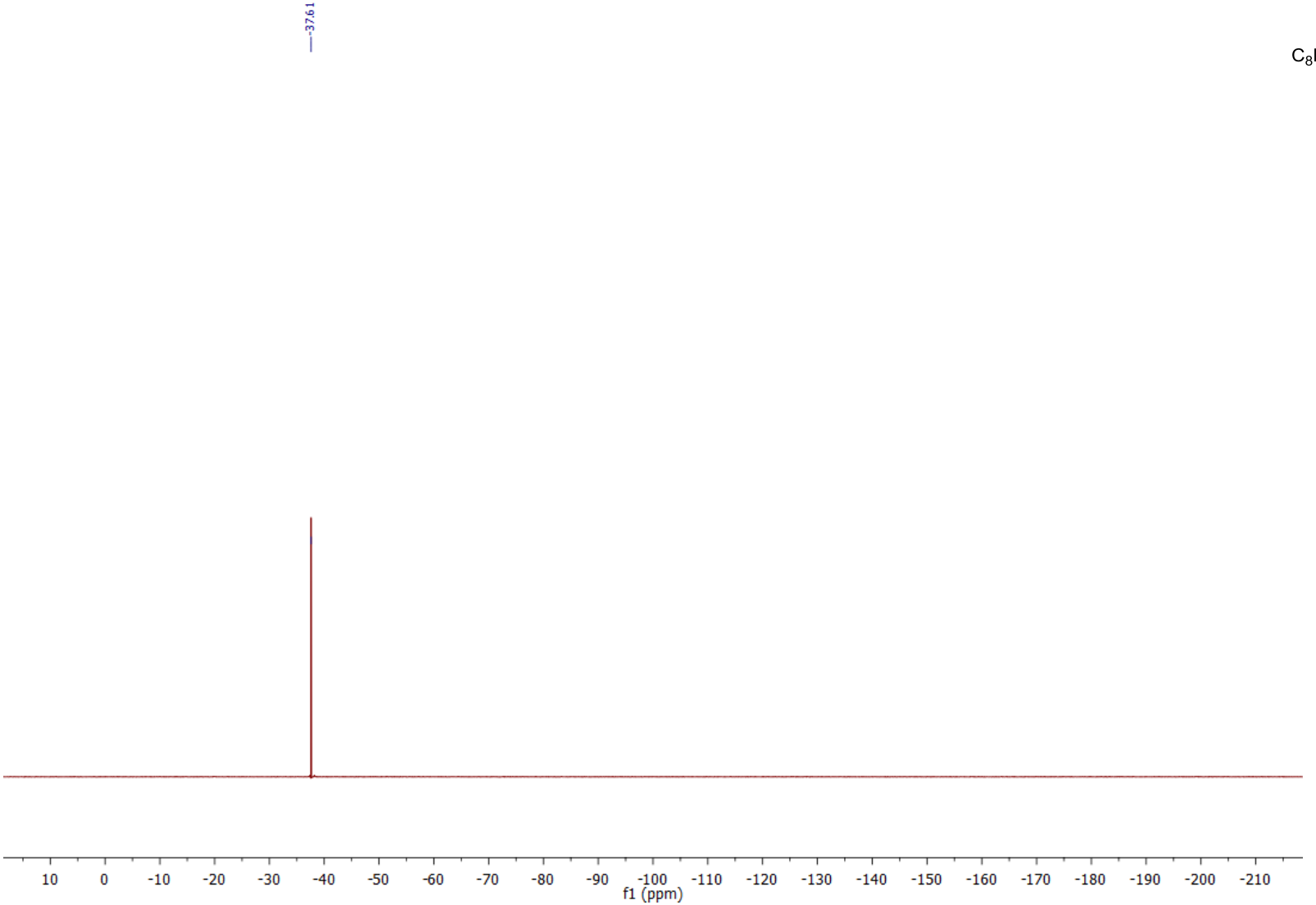


^{13}C NMR ($CDCl_3$, 100 MHz). *N*-(4-((2-oxo-1-((trifluoromethyl)thio)undecyl)oxy)butyl)-*N*-(phenylsulfonyl)benzenesulfonamide (**8c**)

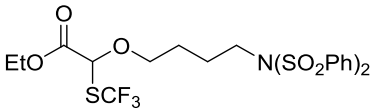


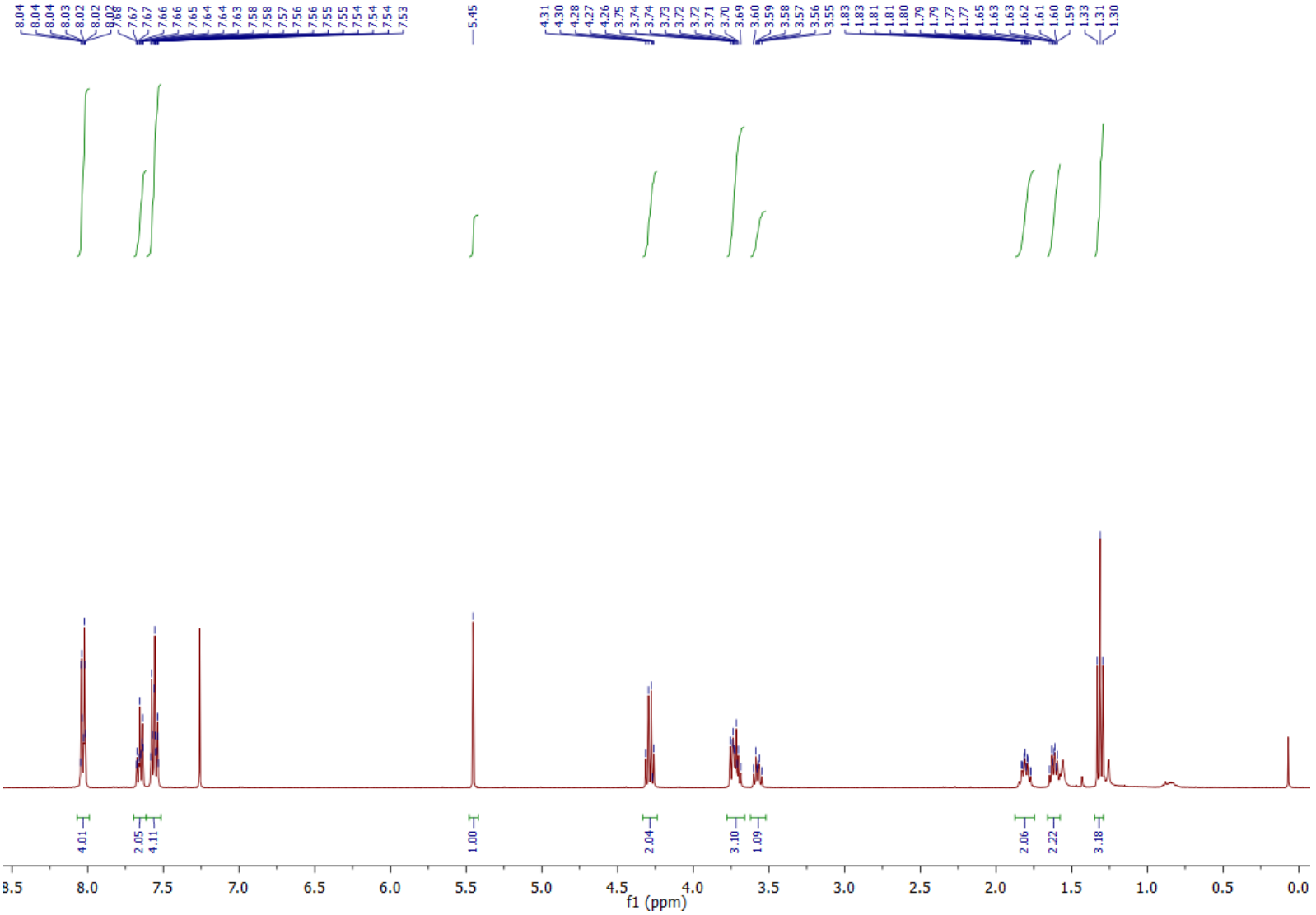
^{19}F NMR ($CDCl_3$, 377 MHz). *N*-(4-((2-oxo-1-((trifluoromethyl)thio)undecyl)oxy)butyl)-*N*-(phenylsulfonyl)benzenesulfonamide (**8c**)



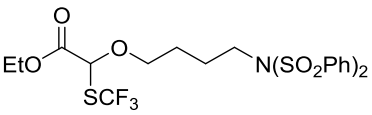


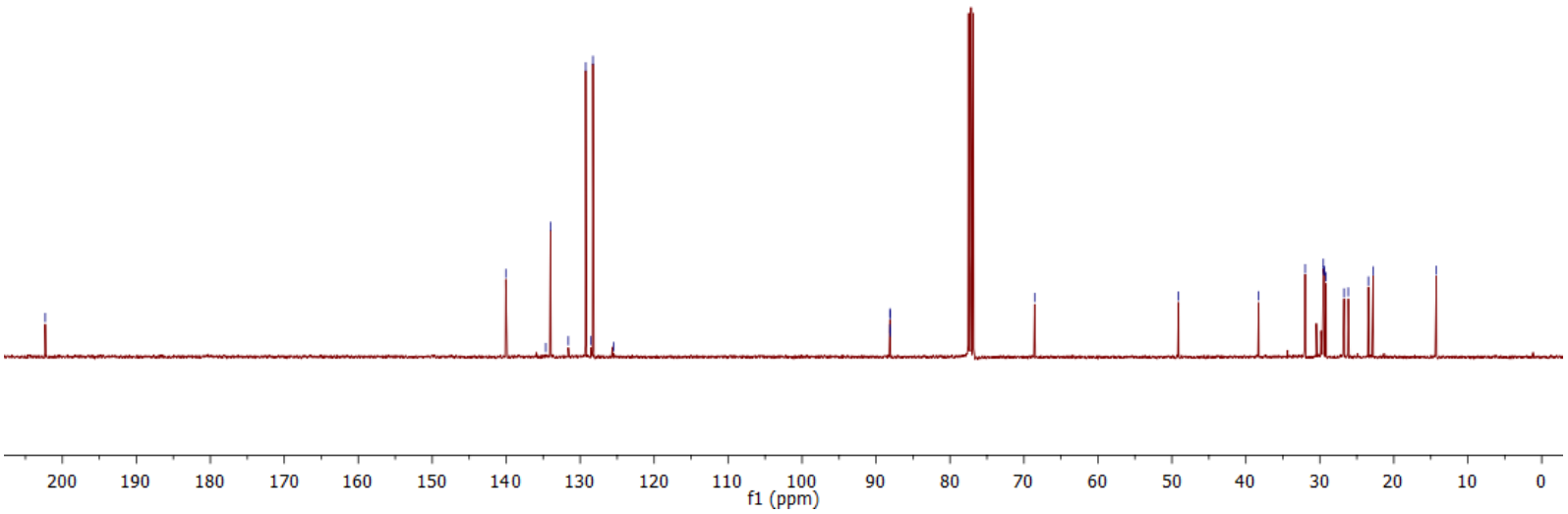
^{1}H NMR ($CDCl_3$, 400 MHz). Ethyl 2-(4-(*N*-(phenylsulfonyl)phenylsulfonamido)butoxy)-2-((trifluoromethyl)thio)acetate (**8d**)



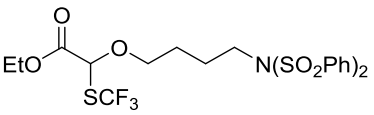


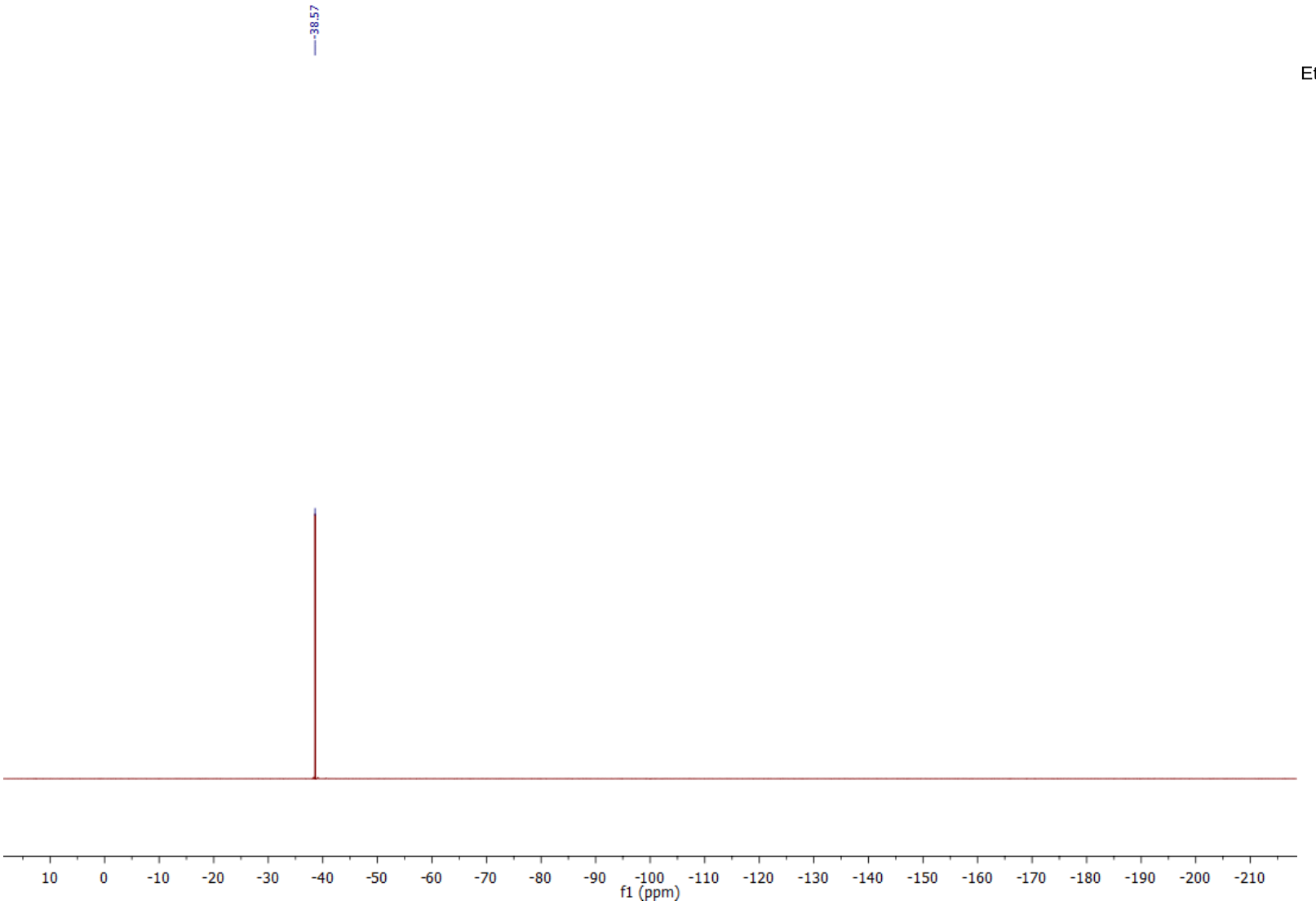
^{13}C NMR ($CDCl_3$, 100 MHz). Ethyl 2-(4-(*N*-(phenylsulfonyl)phenylsulfonamido)butoxy)-2-((trifluoromethyl)thio)acetate (**8d**)





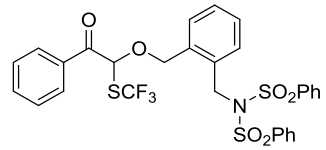
^{19}F NMR ($CDCl_3$, 377 MHz). Ethyl 2-(4-(*N*-(phenylsulfonyl)phenylsulfonamido)butoxy)-2-((trifluoromethyl)thio)acetate (**8d**)

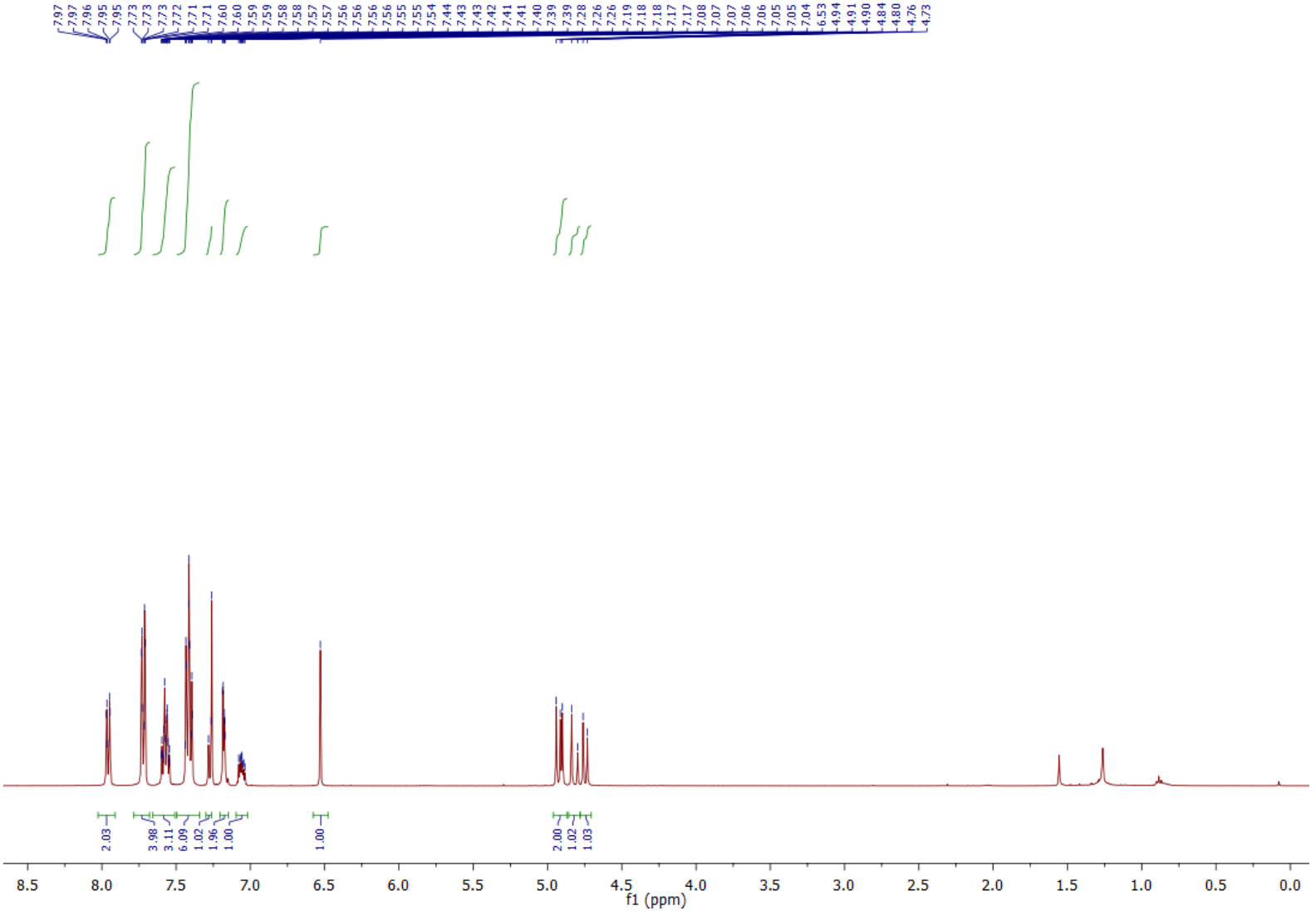




^{1}H NMR ($CDCl_3$, 400 MHz).

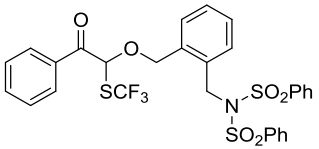
N-(2-((2-oxo-2-phenyl-1-((trifluoromethyl)thio)ethoxy)methyl)benzyl)-*N*-(phenylsulfonyl)benzenesulfonamide (**8e**)

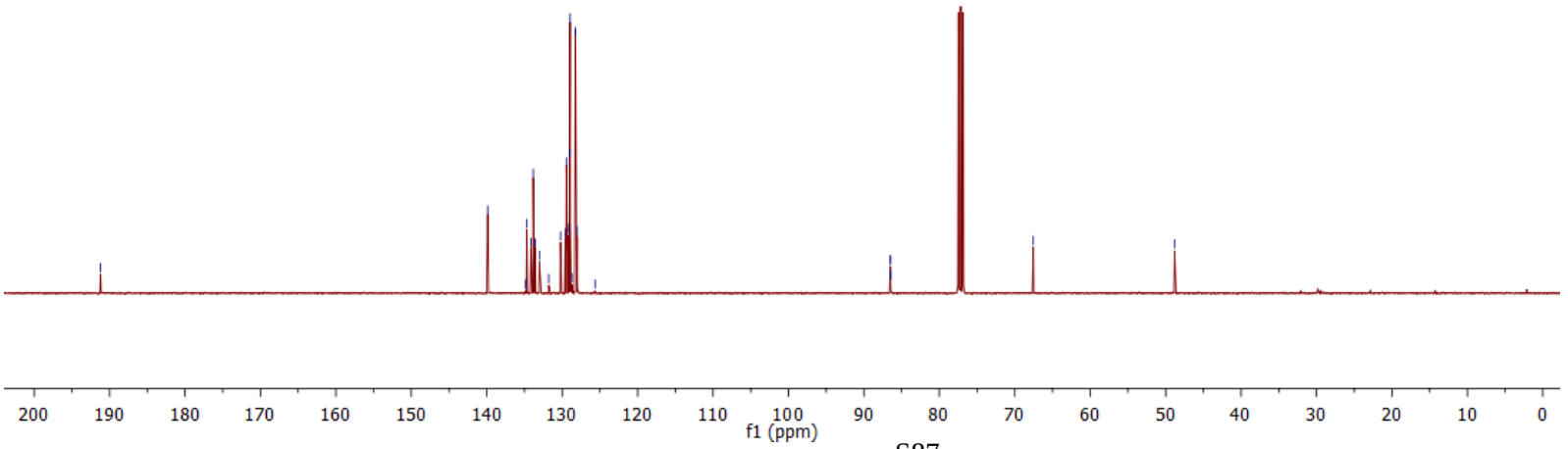




^{13}C NMR ($CDCl_3$, 100 MHz).

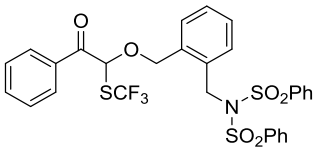
N-(2-((2-oxo-2-phenyl-1-((trifluoromethyl)thio)ethoxy)methyl)benzyl)-*N*-(phenylsulfonyl)benzenesulfonamide (**8e**)

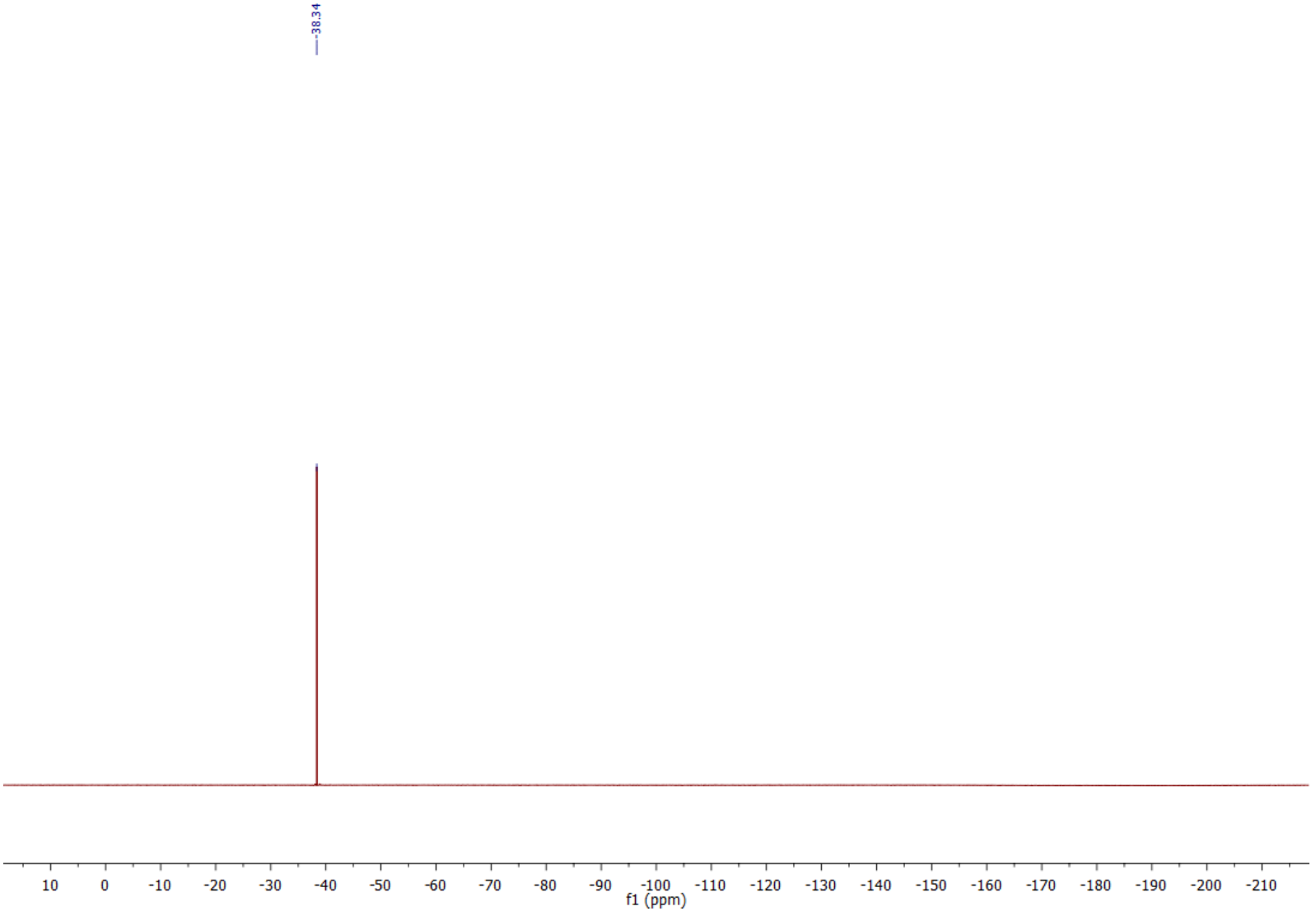




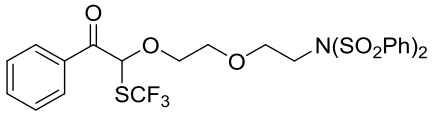
^{19}F NMR ($CDCl_3$, 377 MHz).

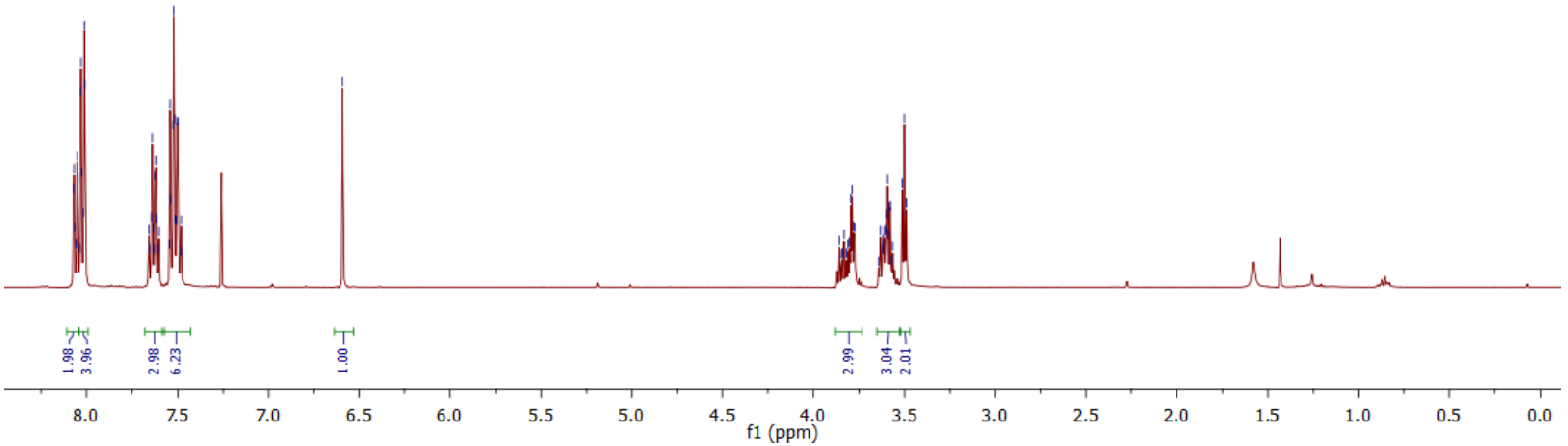
N-(2-((2-oxo-2-phenyl-1-((trifluoromethyl)thio)ethoxy)methyl)benzyl)-*N*-(phenylsulfonyl)benzenesulfonamide (**8e**)





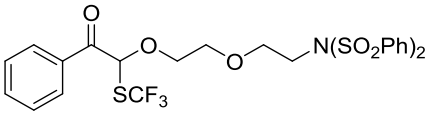
^{1}H NMR ($CDCl_3$, 400 MHz).
N-(2-(2-(2-oxo-2-phenyl-1-((trifluoromethyl)thio)ethoxy)ethoxy)ethyl)-*N*-(phenylsulfonyl)benzenesulfonamide (**8f**)

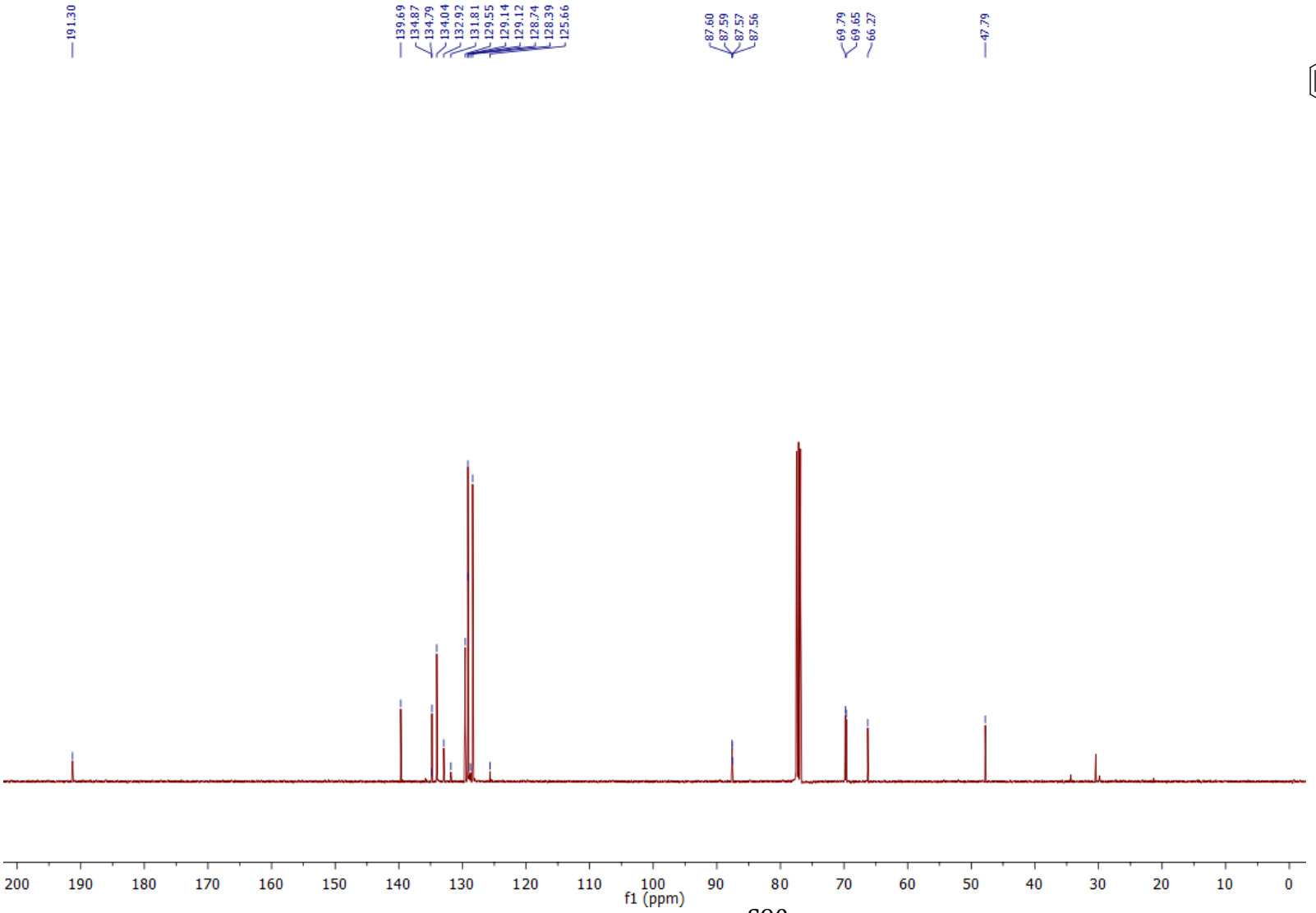




^{13}C NMR ($CDCl_3$, 100 MHz).

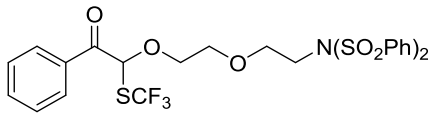
N-(2-(2-(2-oxo-2-phenyl-1-((trifluoromethyl)thio)ethoxy)ethoxy)ethyl)-*N*-(phenylsulfonyl)benzenesulfonamide (**8f**)

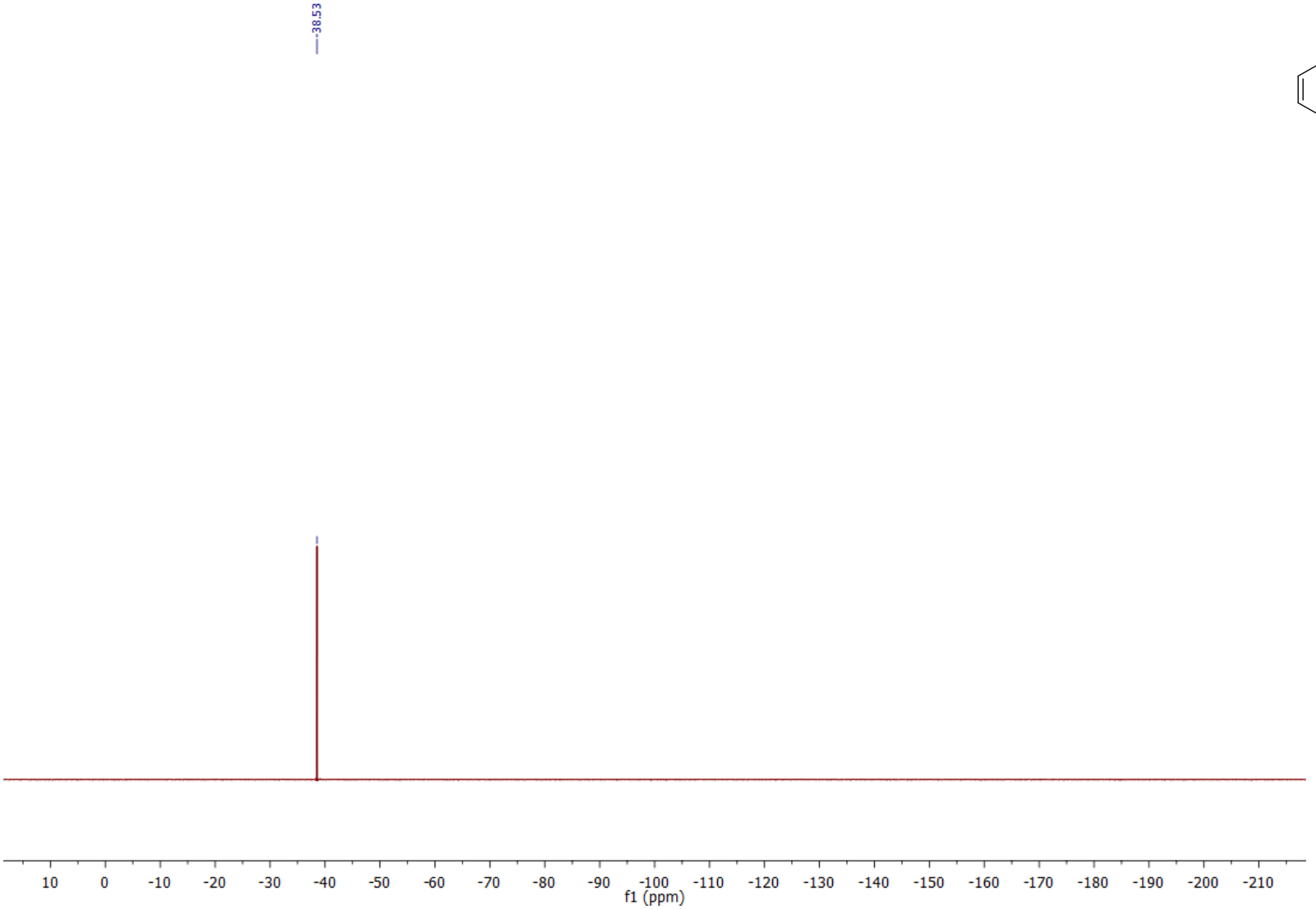




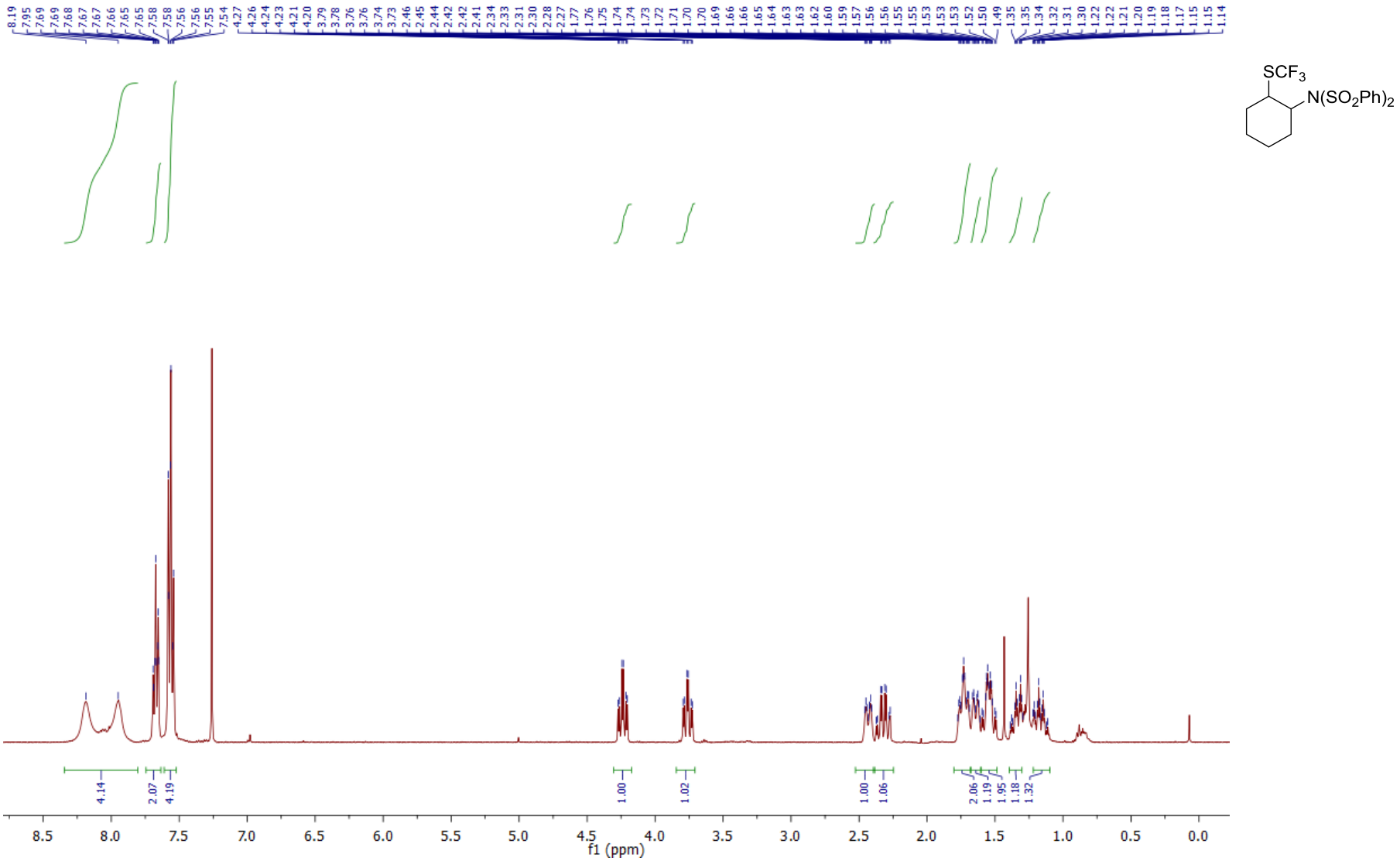
^{19}F NMR ($CDCl_3$, 377 MHz).

N-(2-(2-(2-oxo-2-phenyl-1-((trifluoromethyl)thio)ethoxy)ethoxy)ethyl)-*N*-(phenylsulfonyl)benzenesulfonamide (**8f**)

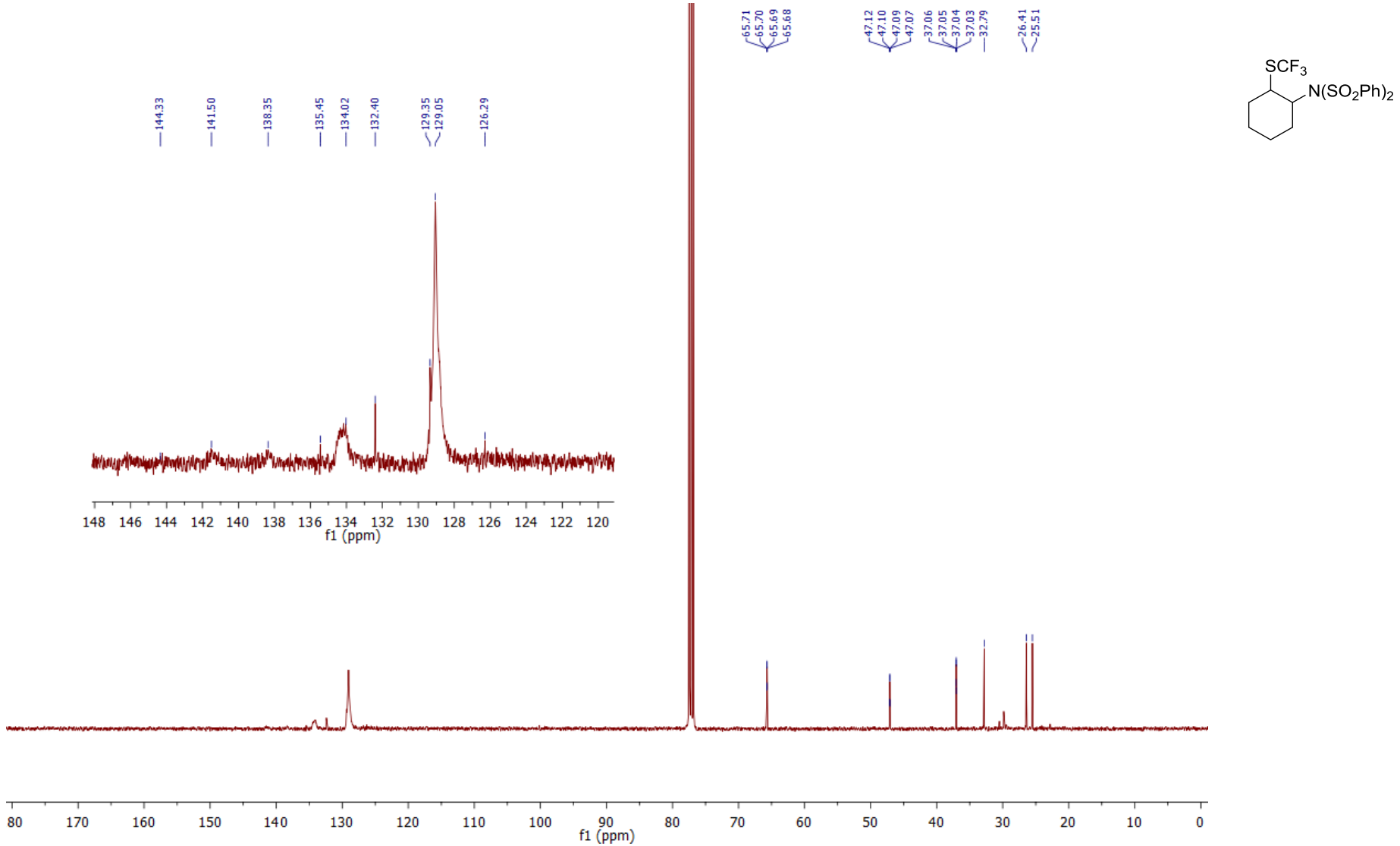




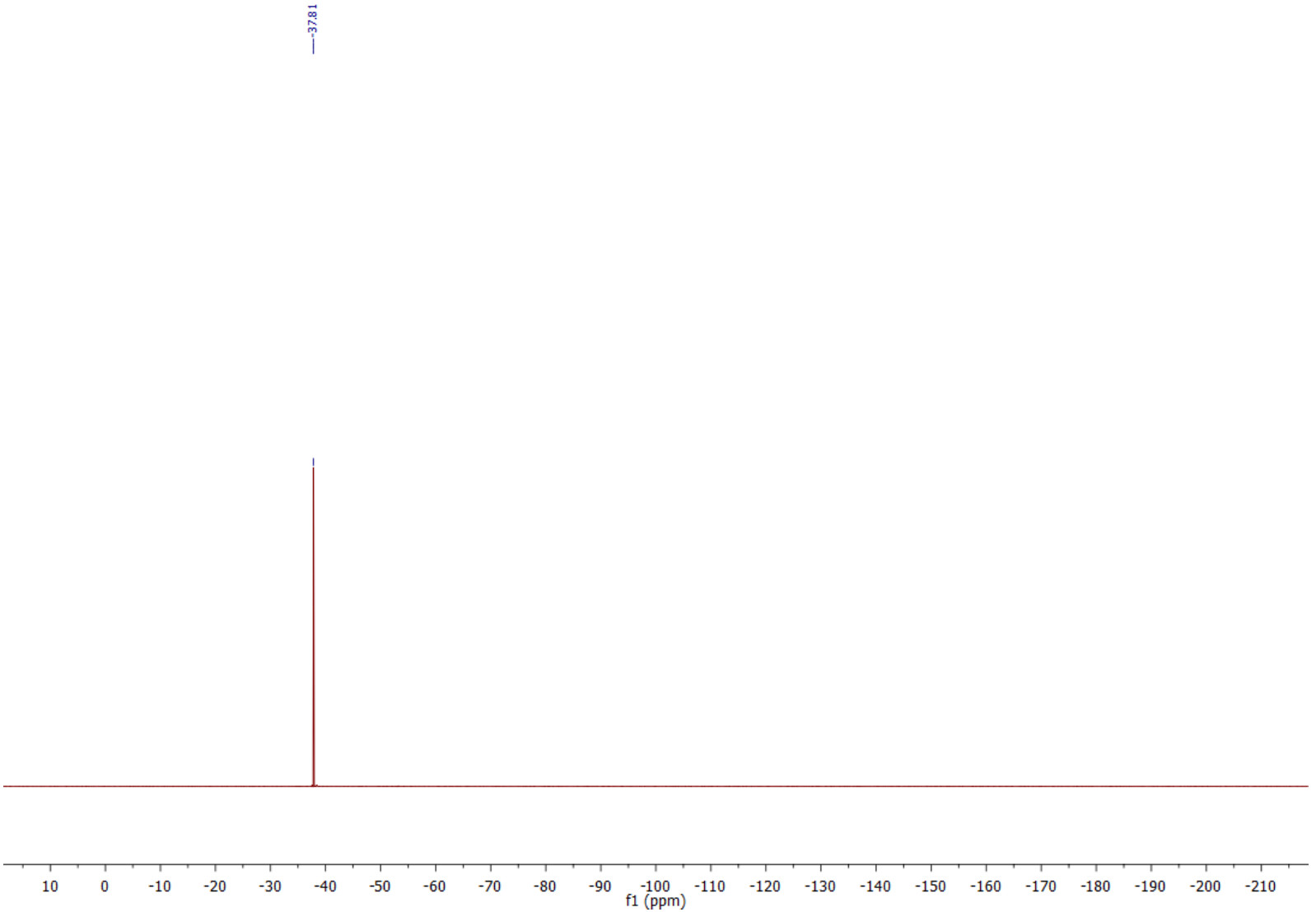
^{1}H NMR ($CDCl_3$, 400 MHz). *N*-(phenylsulfonyl)-*N*-(2-((trifluoromethyl)thio)cyclohexyl)benzenesulfonamide (**13**)



^{13}C NMR ($CDCl_3$, 100 MHz). *N*-(phenylsulfonyl)-*N*-(2-((trifluoromethyl)thio)cyclohexyl)benzenesulfonamide (**13**)



^{19}F NMR ($CDCl_3$, 377 MHz). *N*-(phenylsulfonyl)-*N*-(2-((trifluoromethyl)thio)cyclohexyl)benzenesulfonamide (**13**)



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