Functionalized olefin cross-coupling as a powerful C–C bond construction

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SUPPLEMENTARY INFORMATION

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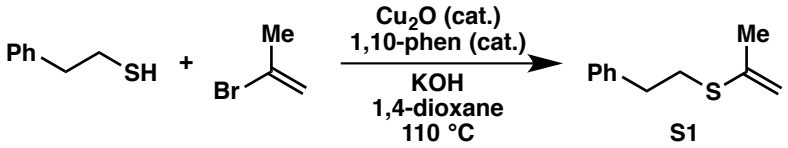
General Experimental

Dry tetrahydrofuran (THF) and dichloromethane (DCM) was obtained by passing the previously degassed solvent through an activated alumina column. Reagents were purchased at the highest commercial quality and used without further purification, unless otherwise stated. Yields refer to chromatographically and spectroscopically (^{1}H NMR) homogeneous material, unless otherwise stated. Reactions were monitored by thin layer chromatography (TLC) carried out on 0.25 mm E. Merck silica plates (60F-254), using shortwave UV light as the visualizing agent and a solution of vanillin and heat, *p*-anisaldehyde and heat, bromocresol green and heat, or $KMnO_4$ and heat as developing agents. Flash column chromatography was performed using E. Merck silica gel (60, particle size 0.043–0.063 mm). NMR spectra were recorded on Bruker AVIII-600, DRX-500, AV-400, and DPX-400 instruments and were calibrated using residual undeuterated solvent as an internal reference ($CHCl_3$: 7.26 ppm ^{1}H NMR, 77.16 ppm ^{13}C NMR; C_6D_6: 7.16 ppm ^{1}H NMR, 128.06 ppm ^{13}C NMR; acetone-d_6: 2.05 ppm ^{1}H NMR, 29.84 ppm ^{13}C NMR). The following abbreviations were used to explain NMR peak multiplicities: s = singlet, d = doublet, t = triplet, q = quartet, m = multiplet, br = broad. High–resolution mass spectra (HRMS) were recorded on an Agilent LC/MS TOF mass spectrometer using electrospray ionization time-of-flight (ESI-TOF) reflectron experiments. GC/MS experiments were recorded on an Agilent quadrupolar mass spectrometer using electron ionization (70 eV). IR experiments were recorded on a Perkin-Elmer Spectrum 100 FT-IR spectrometer.

Experimental Procedures and Characterization Data for Substrates



Phenethyl(prop-1-en-2-yl)sulfide (S1). Following the method of Kao and Lee,[1] 2-phenylethanethiol (670 µL, 5.00 mmol, 1.0 equiv) was added to a solution of KOH (560 mg, 10.0 mmol, 2.0 equiv), Cu_2O (35.8 mg, 250 µmol, 5 mol %), 1,10-phenanthroline (90.1 mg, 500 µmol, 10 mol %) and 2-bromopropene (533 µL, 6.00 mmol, 1.2 equiv) in 1,4-dioxane (2.5 mL). The reaction mixture was then heated at 110 °C with stirring for 12 h, cooled to rt, the reaction diluted with ethyl acetate, and filtered directly through a pad of Celite®. Concentration under reduced pressure and purification by flash column chromatography (SiO_2, 100:1 hexanes:EtOAc) furnished thioether **S1** as a colorless oil (445 mg, 2.50 mmol, 50%).

Physical State: colorless oil.

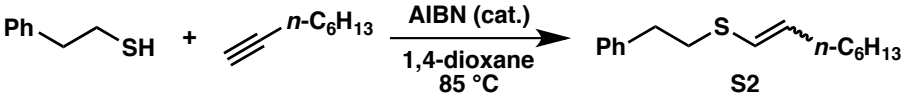
^{1}H NMR (600 MHz, $CDCl_3$): δ 7.33 – 7.30 (m, 2 H), 7.25 – 7.22 (m, 3 H), 5.04 (q, J = 1.4 Hz, 1 H), 4.77 (q, J = 0.7 Hz, 1 H), 2.98 – 2.92 (m, 4 H), and 1.99 (dd, J = 1.4, 0.7 Hz, 3 H).

^{13}C NMR (151 MHz, $CDCl_3$): δ 140.7, 140.5, 128.7, 128.6, 126.6, 106.8, 35.0, 32.9, and 23.7.

HRMS (*m*/*z*): calcd for $C_{11}H_{15}S$ $[M+H]^+$: 179.0889, found: 179.0893.

IR (film) ν_{max}: 2919, 1495, 1452, 1192, 840, and 695 cm^{-1}.

TLC: R_f = 0.75 (10:1 hexanes:EtOAc).



Oct-1-en-1-yl(phenethyl)sulfide (S2). Following the method of Lee, Baggiolini, and Uskoković,[2] a solution of 2-phenylethanethiol (402 µL, 3.00 mmol, 1.0 equiv), oct-1-yne (664 µL, 4.50 mmol, 1.5 equiv), and 2,2'-azobis(2-methylpropionitrile) (24.6 mg, 150 µmol, 5 mol %) in 1,4-dioxane (3.0 mL) was heated at 85 °C with stirring for 11 h. The reaction mixture was cooled to rt, concentrated under reduced pressure, and purified by flash column chromatography (SiO_2, 100:1 hexanes:EtOAc) to furnish thioether **S2** as 1:1.4 mixture of *E*:*Z* olefin isomers (574 mg, 2.31 mmol, 77%). Data is reported for the mixture of olefin isomers.

Physical State: colorless oil.

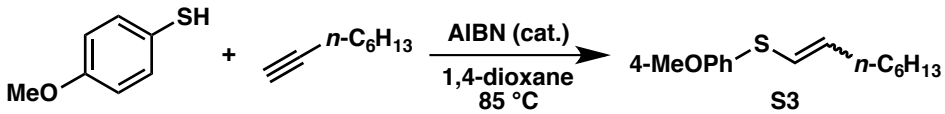
^{1}H NMR (600 MHz, $CDCl_3$): δ 7.32 – 7.29 (m, 2 H), 7.24 – 7.20 (m, 3 H), 5.93 – 5.90 (m, 1 H), 5.69 (dt, *J* = 15.0, 7.2 Hz, 0.58 H), 5.60 (dt, *J* = 9.0, 7.2 Hz, 0.42 H), 2.94 – 2.87 (m, 4 H), 2.13 (dtd, *J* = 7.2, 7.2, 1.2 Hz, 0.84 H), 2.09 (dtd, *J* = 7.2, 7.2, 1.3 Hz, 1.16 H), 1.42 – 1.35 (m, 2 H), 1.33 – 1.26 (m, 6 H), and 0.90 – 0.88 (m, 3 H).

^{13}C NMR (151 MHz, $CDCl_3$): δ 140.5, 140.4, 132.1, 130.6, 128.7, 128.7, 128.6, 126.5, 124.5, 122.2, 37.0, 36.2, 35.4, 34.4, 33.4, 31.9, 31.8, 29.4, 29.3, 29.1, 29.1, 28.9, 22.8, 22.8, and 14.2. 3 carbons were not observed due to incidental equivalence.

HRMS (*m*/*z*): calcd for $C_{16}H_{25}S$ $[M+H]^+$: 249.1671, found: 249.1672.

IR (film) ν_{max}: 2922, 2852, 1453, 1272, 1029, 938, and 694 cm^{-1}.

TLC: R_f = 0.55 (10:1 hexanes:EtOAc).



(4-Methoxyphenyl)(oct-1-en-1-yl)sulfide (S3). Following the method of Lee, Baggiolini, and Uskoković,[2] a solution of 4-methoxybenzenethiol (369 µL, 3.00 mmol, 1.0 equiv), oct-1-yne (664 mL, 4.50 mmol, 1.5 equiv), and 2,2'-azobis(2-methylpropionitrile) (24.6 mg, 150 µmol, 5 mol %) in 1,4-dioxane (3.0 mL) was heated at 85 °C with stirring for 11 h. The reaction mixture was cooled to rt, concentrated under reduced pressure, and purified by flash column chromatography (SiO_2, 100:1 hexanes:EtOAc) to furnish thioether **S3** as a 1:1 mixture of *E*:*Z* olefin isomers (480 mg, 1.92 mmol, 64%). Data is reported for the mixture of olefin isomers.

Physical State: colorless oil.

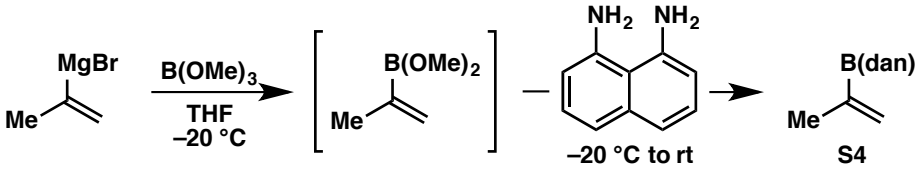
^{1}H NMR (600 MHz, $CDCl_3$): δ 7.32 – 7.29 (m, 2 H), 6.87 – 6.85 (m, 2 H), 6.10 – 6.01 (m, 1 H), 5.80 (dt, *J* = 15.0, 7.2 Hz, 0.5 H), 5.68 (dt, *J* = 9.6, 7.2 Hz, 0.5 H), 3.80 (s, 3 H), 2.22 (dt, *J* = 7.2, 7.2 Hz, 1 H), 2.11 (dt, *J* = 7.2, 7.2 Hz, 1 H), 1.46 – 1.26 (m, 8H), and 0.91 – 0.87 (m, 3 H).

^{13}C NMR (151 MHz, $CDCl_3$): δ 159.0, 158.9, 134.7, 132.1, 131.9, 131.6, 127.0, 126.4, 125.0, 122.9, 114.8, 114.8, 55.5, 33.1, 31.8, 31.8, 29.2, 29.2, 29.1, 28.9, 22.8, 22.8, 14.3, and 14.2. 2 carbons were not observed due to incidental equivalence.

HRMS (*m*/*z*): calcd for $C_{15}H_{23}OS$ $[M+H]^+$: 251.1464, found: 251.1469.

IR (film) ν_{max}: 2924, 2854, 1492, 1243, 1031, 823, and 721 cm^{-1}.

TLC: R_f = 0.55 (10:1 hexanes:EtOAc).



Isopropenyl 1,8-diaminonaphthyl boronamide (S4). To a solution of trimethyl borate (500 µL, 4.48 mmol, 1.0 equiv) in THF (4.5 mL) under an Ar atmosphere was added a solution of freshly prepared isopropenylmagnesium bromide[3] (0.68 M in THF, 398 µL, 4.48 mmol, 1.0 equiv) at –20 °C with stirring. The reaction mixture turned milky white upon stirring at –20 °C for 30 min, at which point 1,8-diaminonaphthalene (710 mg, 4.48 mmol, 1.0 equiv) was added in one portion. After stirring for 70 min at –20 °C, the reaction mixture was warmed to room temperature and then quenched with a saturated aqueous solution of NH_4Cl. The organic layer was separated and the aqueous layer was extracted with EtOAc. The organic layers were combined, washed with brine, dried over $MgSO_4$, filtered, and concentrated under reduced pressure. Purification by flash column chromatography (SiO_2, 9:1 hexanes:EtOAc) furnished boronamide **S4** as a white solid (555 mg, 2.67 mmol, 59%).

Physical State: white solid.

Melting Point: 91.4–91.6 °C.

^{1}H NMR (600 MHz, $CDCl_3$): δ 7.11 (dd, J = 8.0, 8.0 Hz, 2 H), 7.02 (d, J = 8.2 Hz, 2 H), 6.35 (d, J = 7.3 Hz, 2 H), 5.76 (br s, 2 H), 5.57 (br s, 1 H), 5.51 (br s, 1 H), and 1.92 (s, 3 H).

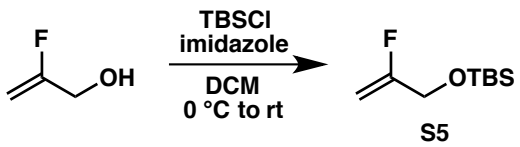
^{13}C NMR (151 MHz, $CDCl_3$): δ 141.2, 136.5, 127.7, 124.6, 119.9, 117.7, 105.9, and 21.6. The boron–bound carbon was not observed due to quadrupolar relaxation.

^{11}B NMR (128 MHz, $CDCl_3$): δ 8.7.

HRMS (*m*/*z*): calcd for $C_{13}H_{14}BN_2$ $[M+H]^+$: 209.1245, found: 209.1252.

IR (film) ν_{max}: 3413, 3050, 2959, 1624, 1596, 1505, 1411, 1327, 1118, and 928 cm^{-1}.

TLC: R_f = 0.48 (9:1 hexanes:EtOAc).



***tert*-Butyl((2-fluoroallyl)oxy)dimethylsilane (S5).** To a solution of 2-fluoro-2-propen-1-ol[4] (439 mg, 5.77 mmol, 1.0 equiv) and imidazole (786 mg, 11.5 mmol, 2.0 equiv) in DCM (19 mL) was added TBSCl (1.30 g, 8.66 mmol, 1.5 equiv) at 0 °C with stirring. The reaction mixture was

warmed to room temperature over 2 h and was quenched with a saturated aqueous solution of NH_4Cl. The organic layer was separated and the aqueous layer was extracted with Et_2O. The organic layers were combined, washed with brine, dried over $MgSO_4$, filtered, and concentrated under reduced pressure. Purification by flash column chromatography (SiO_2, pentane) furnished fluoride **S5** as a colorless oil (1.05 g, 5.49 mmol, 95%).

Physical State: colorless oil.

^{1}H NMR (600 MHz, $CDCl_3$): δ 4.65 (ddt, *J* = 17.2, 2.8, 0.7 Hz, 1 H), 4.54 (ddt, *J* = 49.3, 2.9, 1.2 Hz, 1 H), 4.14 (dd, *J* = 0.9, 0.9 Hz, 1 H), 4.13 (dd, *J* = 0.9, 0.9 Hz, 1 H), 0.92 (s, 9 H), and 0.10 (s, 6 H).

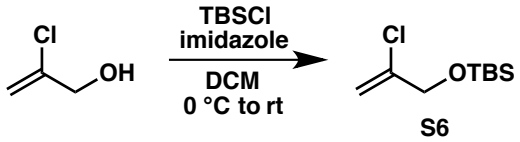
^{13}C NMR (151 MHz, $CDCl_3$): δ 165.1 (d, *J* = 257.4 Hz), 90.0 (d, *J* = 17.4 Hz), 60.9 (d, *J* = 38.3 Hz), 25.9, 18.5, and –5.3.

^{19}F NMR (376 MHz, $CDCl_3$): δ –108.4.

GC/MS (*m*/*z*): $[M–t\text{-Bu}]^+$: 133.

IR (film) ν_{max}: 2955, 2931, 2888, 2859, 1680, 1465, 1393, 1255, 1222, 1126, 937, and 824 cm^{-1}.

TLC: R_f = 0.74 (9:1 hexanes:EtOAc).



S6

***tert*-Butyl((2-chloroallyl)oxy)dimethylsilane (S6).** To a solution of 2-chloro-2-propen-1-ol (200 mg, 2.16 mmol, 1.0 equiv) and imidazole (294 mg, 4.32 mmol, 2.0 equiv) in DCM (7.0 mL) was added TBSCl (489 mg, 3.24 mmol, 1.5 equiv) at 0 °C with stirring. The reaction mixture was warmed to room temperature over 75 min and was quenched with a saturated aqueous solution of NH_4Cl. The organic layer was separated and the aqueous layer was extracted with Et_2O. The organic layers were combined, washed with brine, dried over $MgSO_4$, filtered, and concentrated under reduced pressure. Purification by flash column chromatography (SiO_2, hexanes) furnished chloride **S6** as a colorless oil (311 mg, 1.50 mmol, 69%).

Physical State: colorless oil.

^{1}H NMR (600 MHz, $CDCl_3$): δ 5.50 (dd, *J* = 3.1, 1.6 Hz, 1 H), 5.29 (dd, *J* = 2.9, 1.4 Hz, 1 H), 4.16 (dd, *J* = 1.6, 1.6 Hz, 2 H), 0.92 (s, 9 H), and 0.10 (s, 6 H).

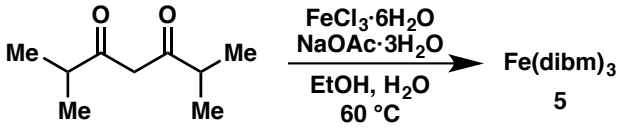
^{13}C NMR (151 MHz, $CDCl_3$): δ 140.6, 110.7, 65.9, 25.9, 18.5, and –5.3.

GC/MS (*m*/*z*): $[M–t\text{-Bu}]^+$: 149.

IR (film) ν_{max}: 2955, 2930, 2888, 2858, 1460, 1255, 1157, 1091, 1007, 884, and 835 cm^{-1}.

TLC: R_f = 0.45 (9:1 hexanes:EtOAc).

Preparation of $Fe(dibm)_3$



Iron(III) diisobutyrylmethane (5). To a biphasic mixture of 2,6-dimethylheptane-3,5-dione (2.60 g, 16.6 mmol, 3.0 equiv) and NaOAc•$3H_2O$ (2.27 g, 16.6 mmol, 3.0 equiv) in an aqueous solution of EtOH (1:1 EtOH:H_2O, 42 mL) was added ground $FeCl_3$•$6H_2O$ (1.50 g, 5.55 mmol, 1.0 equiv). A red slurry formed and the reaction mixture was heated at 60 °C with stirring for 1 h. The slurry was cooled at room temperature over 10 min, cooled at 0 °C for 15 min, and then filtered to give an orange powder. The orange powder was rinsed with H_2O, collected, placed in an Erlenmeyer flask, and heated with an aqueous solution of EtOH (9:1 EtOH:H_2O, 30 mL) using a heat gun until fully dissolved to give a red, homogenous solution. The solution was cooled to room temperature and then to 0 °C to give red crystals, which were filtered and rinsed with a –78 °C aqueous solution of EtOH (9:1 EtOH:H_2O, 10 mL) to furnish $Fe(dibm)_3$ (**5**) as a red crystalline solid (1.91 g, 3.67 mmol, 66%). A small amount was recrystallized from MeOH to provide crystals suitable for X-ray analysis.

Physical State: red crystalline solid.

Melting Point: 99.2–99.5 °C.

Elemental Analysis: calcd for $C_{27}H_{45}FeO_6$: C, 62.19; H, 8.70; N, 0.00 found: C, 62.16; H, 8.64; N, 0.00.

IR (film) ν_{max}: 2964, 2930, 2870, 1563, 1531, 1500, 1403, 1295, 1158, 1091, 922, and 789 cm^{-1}.

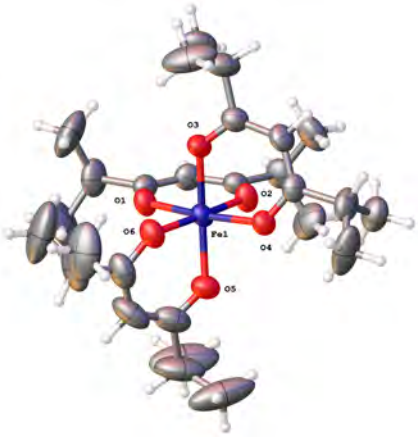


Figure S1. X-ray crystallographic structure of $Fe(dibm)_3$ (**5**).

The single crystal X-ray diffraction studies were carried out on a Bruker Kappa APEX-II CCD diffractometer equipped with Mo K_a radiation (l = 0.71073 Å). A 0.115 x 0.053 x 0.044 mm red block was mounted on a Cryoloop with Paratone oil. Data were collected in a nitrogen gas stream at 175(2) K using f and v scans. Crystal-to-detector distance was 40 mm using variable exposure time (30s or 60s) depending on q with a scan width of 1.0°. Data collection was 100% complete to 25.00° in *q*. A total of 75632 reflections were collected covering the indices, -14<=h<=13, -23<=k<=23, -18<=l<=18. 6312 reflections were found to be symmetry independent, with a R_{int} of 0.0793. Indexing and unit cell refinement indicated a primitive, monoclinic lattice. The space group was found to be $P2_1/c$. The data were integrated using the Bruker SAINT software program and scaled using the SADABS software program. Solution by direct methods (SHELXT) produced a complete phasing model consistent with the proposed structure.

All nonhydrogen atoms were refined anisotropically by full-matrix least-squares (SHELXL-2013). All hydrogen atoms were placed using a riding model. Their positions were constrained relative to their parent atom using the appropriate HFIX command in SHELXL-2014. Crystallographic data are summarized in Table S1.

Table S1. Crystal data and structure refinement for $Fe(dibm)_3$ (**5**).

Identification code	CCDC 1022625	
Empirical formula	C27 H45 Fe O6	
Molecular formula	C27 H45 Fe O6	
Formula weight	521.48	
Temperature	175 K	
Wavelength	0.71073 Å	
Crystal system	Monoclinic	
Space group	P 1 21/n 1	
Unit cell dimensions	a = 11.3761(2) Å	a= 90°.
	b = 18.9915(5) Å	b= 105.0130(14)°.
	c = 14.7639(4) Å	g = 90°.
Volume	3080.85(13) $Å^3$	
Z	4	
Density (calculated)	1.124 Mg/m^3	
Absorption coefficient	0.522 mm^{-1}	
F(000)	1124	
Crystal size	0.115 x 0.053 x 0.044 mm^3	

Crystal color, habit	Red Block
Theta range for data collection	1.786 to 26.423°.
Index ranges	-14<=h<=13, -23<=k<=23, -18<=l<=18
Reflections collected	75632
Independent reflections	6312 [R(int) = 0.0793]
Completeness to theta = 25.000°	100.0 %
Absorption correction	Semi-empirical from equivalents
Max. and min. transmission	0.7454 and 0.7010
Refinement method	Full-matrix least-squares on F^2
Data / restraints / parameters	6312 / 0 / 319
Goodness-of-fit on F^2	1.053
Final R indices [I>2sigma(I)]	R1 = 0.0579, wR2 = 0.1332
R indices (all data)	R1 = 0.1076, wR2 = 0.1599
Extinction coefficient	n/a
Largest diff. peak and hole	0.447 and -0.395 e.$Å^{-3}$

Photographic Guide for the Preparation of $Fe(dibm)_3$

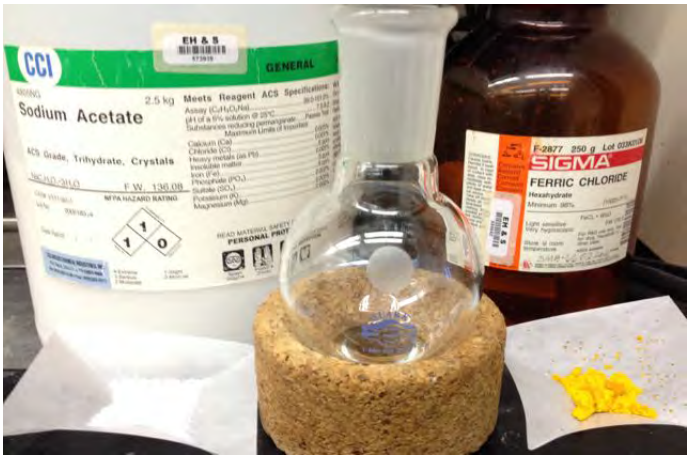


Figure S2. Reagents used in the synthesis of $Fe(dibm)_3$. From left to right: $NaOAc•3H_2O$, 2,6-dimethylheptane-3,5-dione, $FeCl_3•6H_2O$.

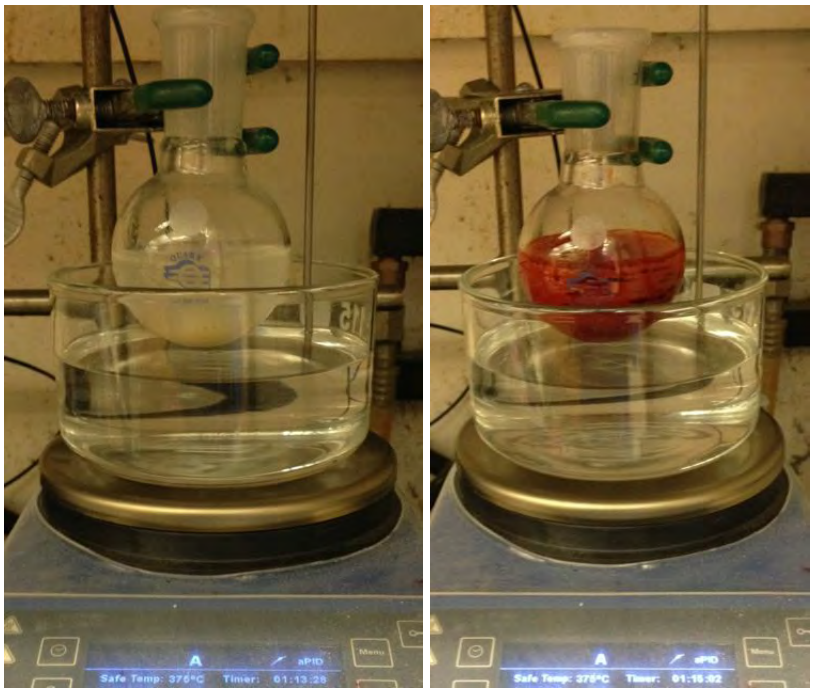


Figure S3. Setting up the synthesis of $Fe(dibm)_3$. From left to right: biphasic mixture of $NaOAc•3H_2O$ and 2,6-dimethylheptane-3,5-dione in aqueous EtOH, after addition of $FeCl_3•6H_2O$.

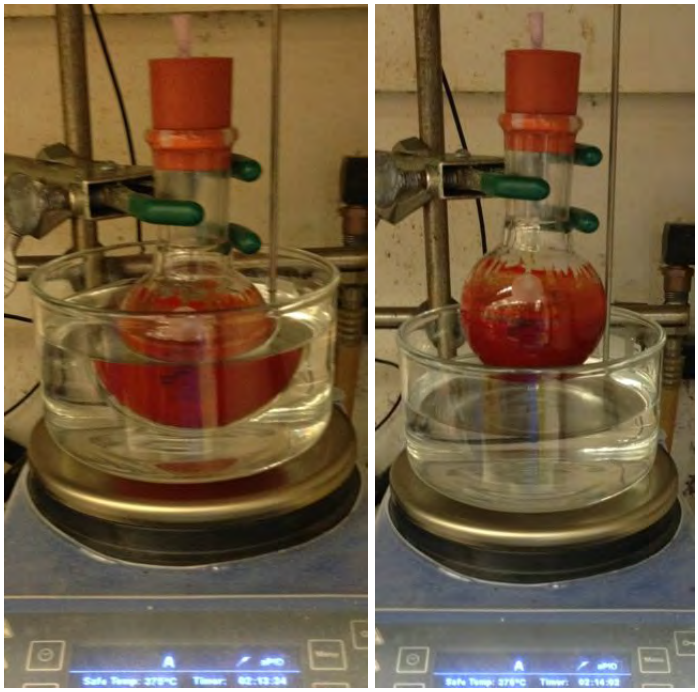


Figure S4. Synthesis of $Fe(dibm)_3$. From left to right: heating the reaction mixture at 60 °C, cooling the reaction mixture to room temperature after heating at 60 °C for 1 h.

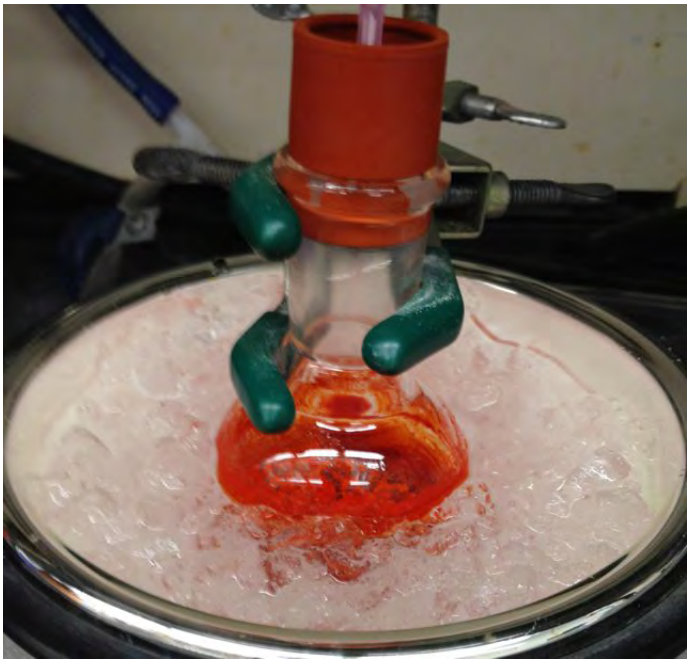


Figure S5. Cooling the slurry at 0 °C.

Figure S6. Filtering the slurry through a Büchner funnel.

Figure S7. Crude $Fe(dibm)_3$.

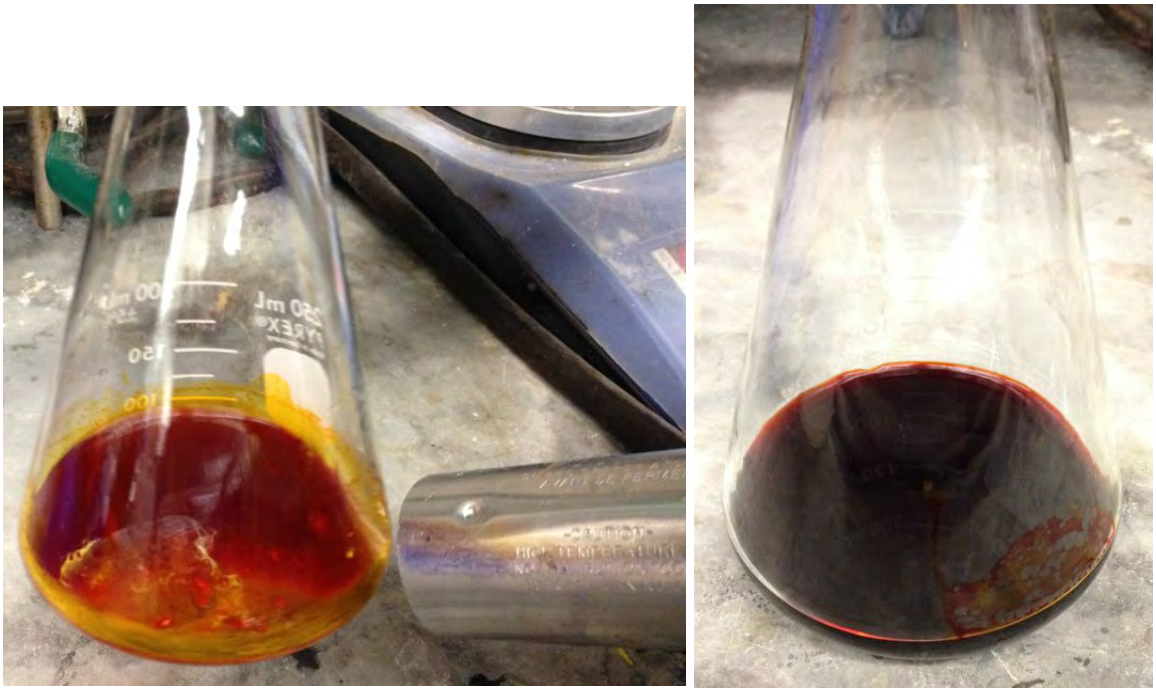


Figure S8. Recrystallization of $Fe(dibm)_3$ in an Erlenmeyer flask. From left to right: heating with a heat gun, dark red solution of fully dissolved $Fe(dibm)_3$.

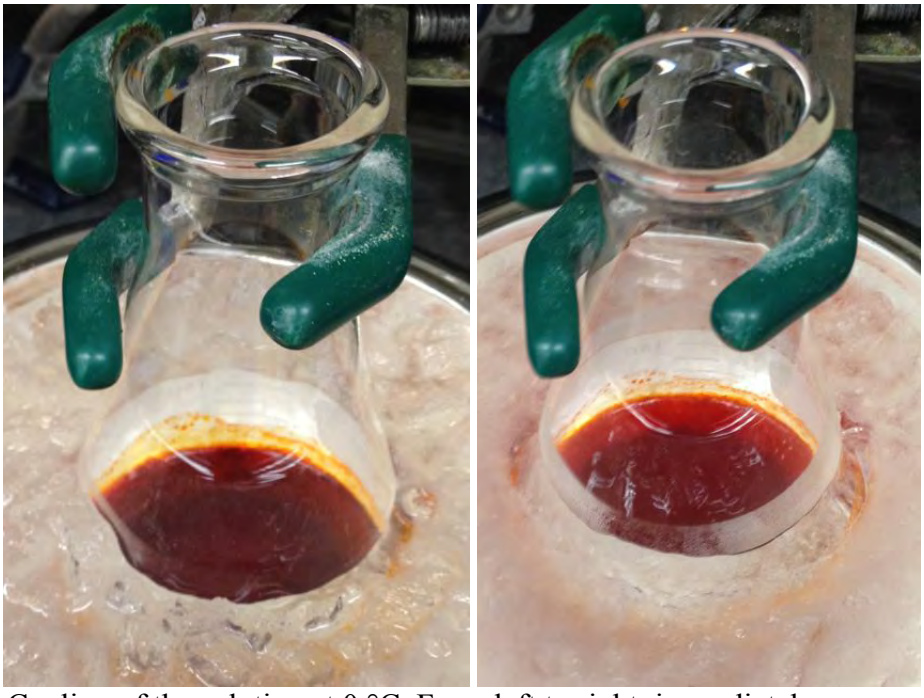


Figure S9. Cooling of the solution at 0 °C. From left to right: immediately upon cooling, after cooling ca. 1 h.

Figure S10. Collecting the recrystallized $Fe(dibm)_3$. From left to right: filtering through a Büchner funnel, rinsing with aqueous EtOH precooled to –78 °C.

Figure S11. Recrystallized $Fe(dibm)_3$.

General Procedure for the Olefin Cross–Coupling

To a solution of donor olefin in EtOH or *n*-PrOH was added anhydrous Na_2HPO_4, $Fe(dibm)_3$ or $Fe(acac)_3$, acceptor olefin, and $PhSiH_3$ [CAUTION: gas evolution (presumably H_2) is occasionally observed upon addition of $PhSiH_3$]. The resulting mixture was stirred at room temperature or heated in an oil bath preheated to 60 °C or 80 °C with stirring for the indicated time (typically until TLC analysis indicated the consumption of starting material). The reaction mixture was then cooled to room temperature and diluted with brine and EtOAc. The organic layer was separated and the aqueous layer was extracted with EtOAc. The organic layers were combined, washed with brine, dried over Na_2SO_4, filtered, and concentrated under reduced pressure. The resulting crude product was then purified on SiO_2 (preparative TLC or flash column chromatography) to furnish the coupled product.

Photographic Guide for the Olefin Cross–Coupling

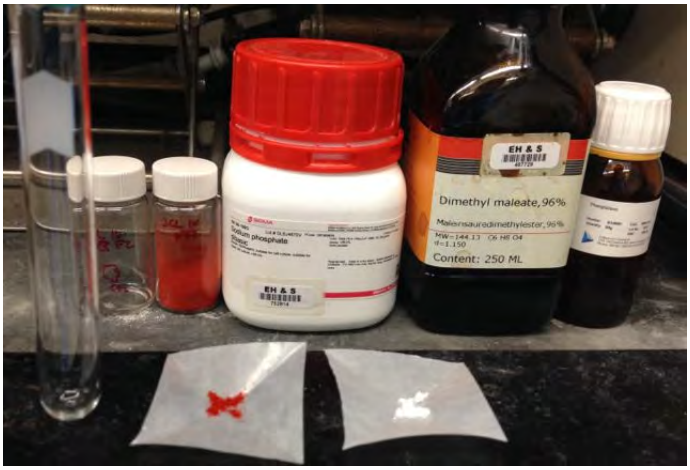


Figure S12. Reagents used in the olefin cross–coupling. From left to right: donor olefin, $Fe(dibm)_3$, Na_2HPO_4, acceptor olefin, $PhSiH_3$.

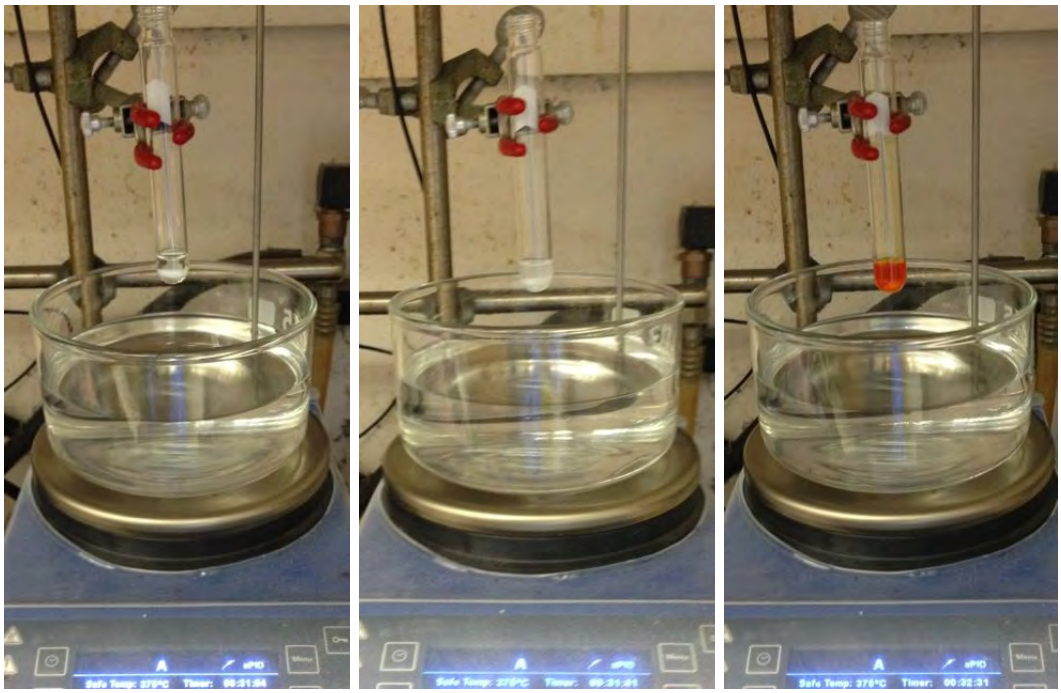


Figure S13. Addition of reagents. From left to right: donor olefin in EtOH, after addition of Na_2HPO_4, after addition of $Fe(dibm)_3$.

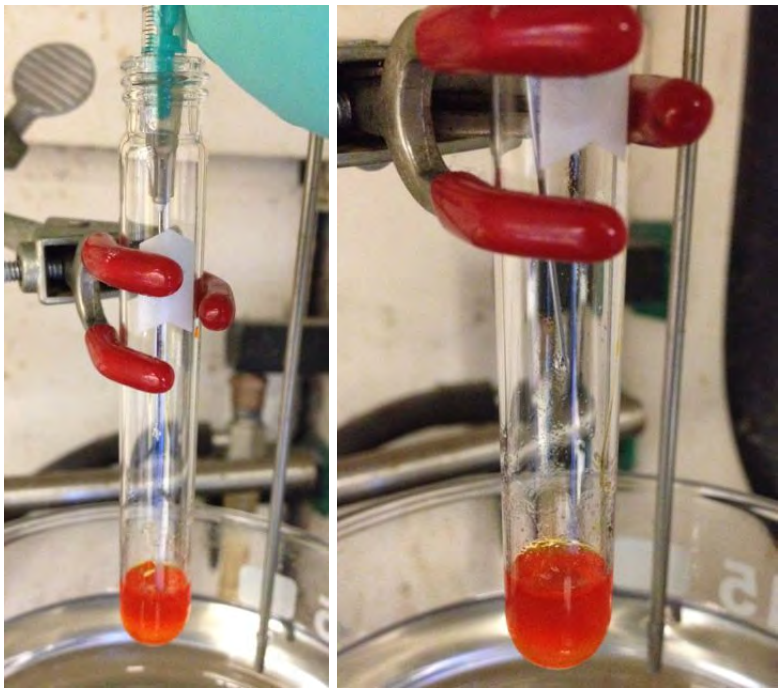


Figure S14. Addition of reagents, continued. From left to right: addition of acceptor olefin, addition of $PhSiH_3$.

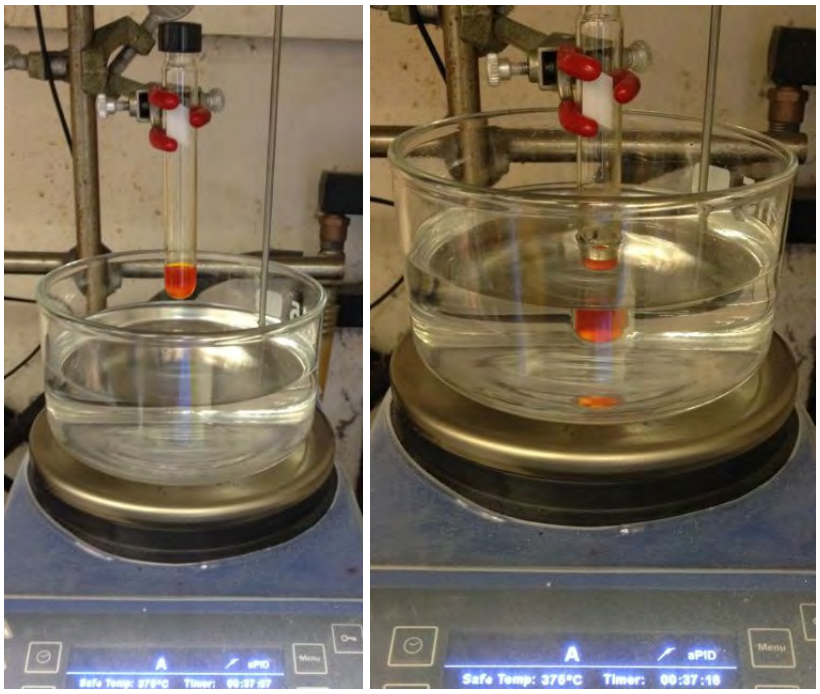


Figure S15. Setting up the olefin cross–coupling. From left to right: prior to heating at 60 °C, heating at 60 °C.

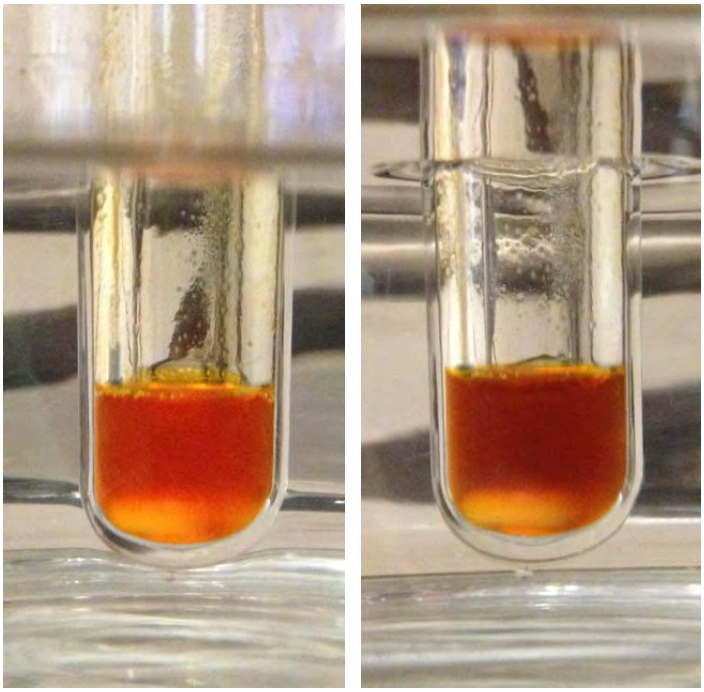


Figure S16. Close ups of reaction mixture while heating. From left to right: immediately upon heating at 60 °C, ca. 5 min after heating at 60 °C (note color change).

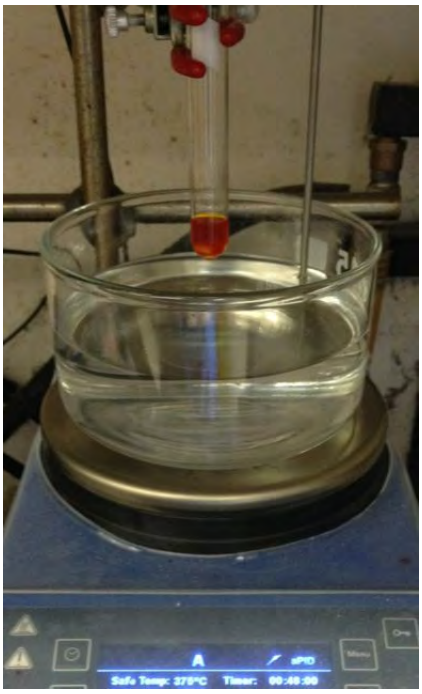


Figure S17. Cooling reaction mixture at rt.

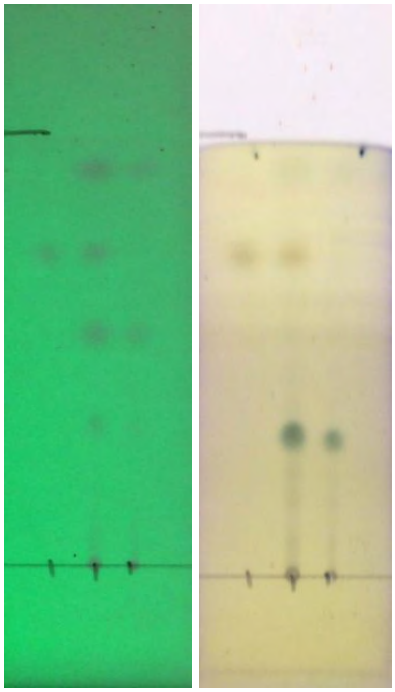


Figure S18. TLC of reaction mixture (7:3 hexanes:EtOAc). From left to right: visualized with shortwave UV light, visualized with vanillin.

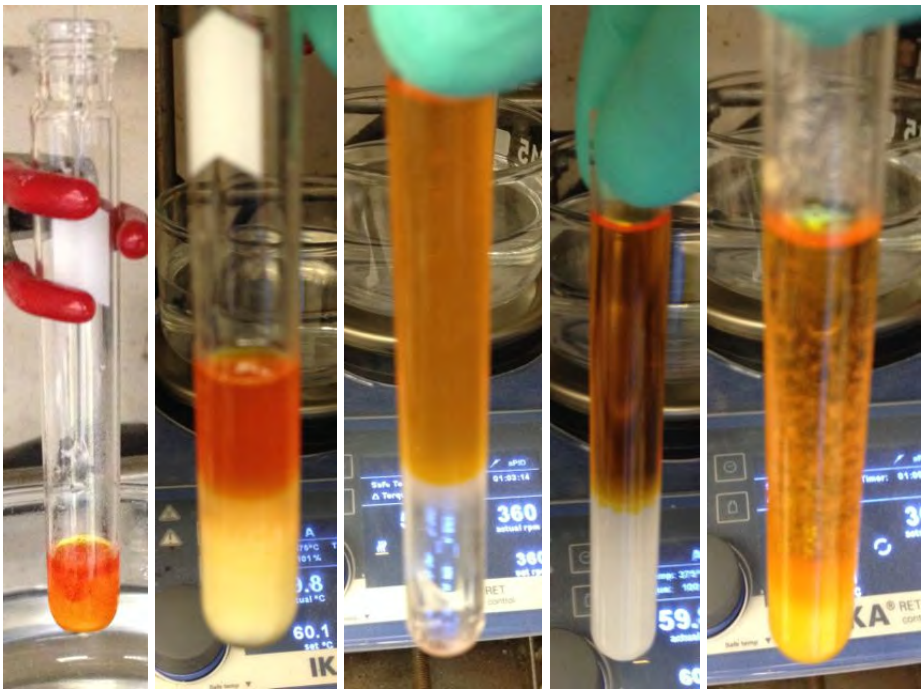


Figure S19. Work up of olefin cross–coupling. From left to right: addition of brine to reaction mixture, extraction with EtOAc, addition of brine to combined organic layers, phase separation after brine wash, drying over Na_2SO_4.

Figure S20. Filtering off the Na_2SO_4.

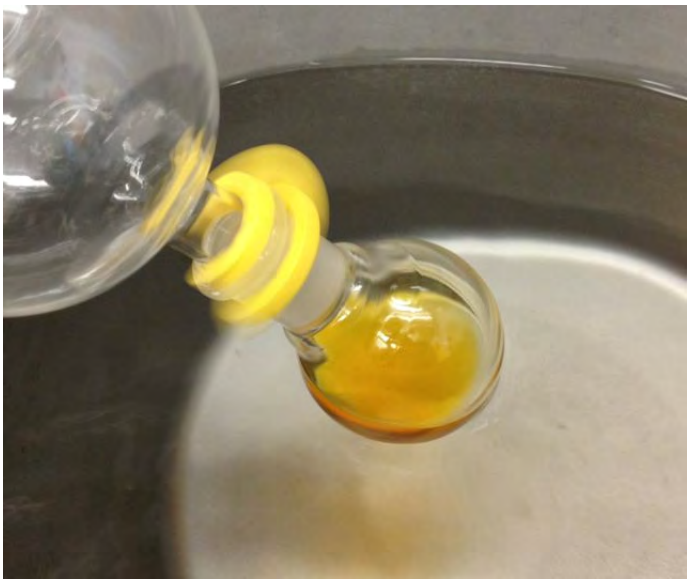
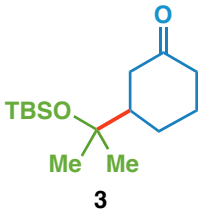


Figure S21. Concentrating under reduced pressure.

Figure S22. Crude coupled product.

Experimental Procedures and Characterization Data for Products



3

3-(2-((*tert*-Butyldimethylsilyl)oxy)propan-2-yl)cyclohexan-1-one (3). Following the general procedure, a mixture of *tert*-butyldimethyl(prop-1-en-2-yloxy)silane[5] (51.7 mg, 300 µmol, 3.0 equiv), cyclohex-2-enone (9.6 mg, 100 µmol, 1.0 equiv), Na_2HPO_4 (14.2 mg, 100 µmol, 1.0 equiv), $Fe(dibm)_3$ (2.6 mg, 5.0 µmol, 5 mol %), and $PhSiH_3$ (25.0 µL, 200 µmol, 2.0 equiv) in EtOH (0.50 mL) was heated at 60 °C with stirring for 1 h. Purification by flash column chromatography (SiO_2, 10:1 hexanes:EtOAc) furnished silyl ether **3** as a pale yellow oil (21.9 mg, 78.1 µmol, 78%).

Physical State: pale yellow oil.

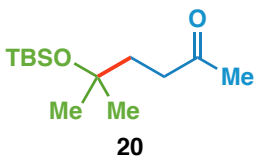
^{1}H NMR (600 MHz, $CDCl_3$): δ 2.48 (dddd, *J* = 13.9, 4.1, 2.1, 2.1 Hz, 1 H), 2.34 (ddddd, *J* = 14.3, 4.2, 2.2, 2.2, 2.2 Hz, 1 H), 2.25 – 2.19 (m, 2 H), 2.09 (ddddd, *J* = 3.2, 3.2, 3.2, 6.1, 12.6 Hz, 1 H), 1.97 (dddddd, *J* = 13.0, 3.5, 3.5, 3.5, 1.8, 1.8, 1 H), 1.64 (dddd, *J* = 12.4, 12.4, 3.6, 3.6 Hz, 1 H), 1.56 (ddddd, *J* = 13.4, 13.4, 13.4, 3.9, 3.9, 1 H), 1.46 (dddd, *J* = 13.0, 13.0, 11.7, 3.3 Hz, 1 H), 1.22 (s, 3 H), 1.18 (s, 3 H), 0.86 (s, 9 H), 0.08 (s, 3 H), and 0.07 (s, 3 H).

^{13}C NMR (151 MHz, $CDCl_3$): δ 213.4, 74.6, 50.8, 43.3, 41.5, 28.1, 26.0, 25.3, 19.3, 18.4, and –2.0.

HRMS (*m*/*z*): calcd for $C_{15}H_{31}O_2Si$ $[M+H]^+$: 271.2088, found: 271.2087.

IR (film) ν_{max}: 2930, 2587, 2516, 1713, 1462, 1365, 1254, 1223, 1155, 1153, 1099, 1036, 1006, 939, 834, 772, and 671 cm^{-1}.

TLC: R_f = 0.55 (10:1 hexanes:EtOAc).



20

5-((*tert*-Butyldimethylsilyl)oxy)-5-methylhexan-2-one (20). Following the general procedure, a mixture of *tert*-butyldimethyl(prop-1-en-2-yloxy)silane[5] (17.3 mg, 100 µmol, 1.0 equiv), methyl vinyl ketone (24.9 µL, 300 µmol, 3.0 equiv), Na_2HPO_4 (14.2 mg, 100 µmol, 1.0 equiv), $Fe(dibm)_3$ (2.6 mg, 5.0 µmol, 5 mol %), and $PhSiH_3$ (24.6 µL, 200 µmol, 2.0 equiv) in EtOH (0.50 mL) was heated at 60 °C with stirring for 1 h. Purification by flash column chromatography (SiO_2, 97:3 hexanes:EtOAc) furnished silyl ether **20** as a colorless oil (16.8 mg, 68.8 µmol, 69%).

Physical State: colorless oil

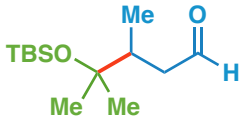
^{1}H NMR (600 MHz, $CDCl_3$): δ 2.54 (t, *J* = 7.8 Hz, 2 H), 2.16 (s, 3 H), 1.69 (t, *J* = 7.8 Hz, 2 H), 1.20 (s, 6 H), 0.85 (s, 9 H), and 0.07 (s, 6 H).

^{13}C NMR (151 MHz, $CDCl_3$): δ 209.8, 72.8, 39.1, 38.5, 30.1, 29.9, 26.0, 18.2, and –1.9.

HRMS (*m*/*z*) calcd for $C_{13}H_{29}O_2Si$ $[M+H]^+$: 245.1931, found: 245.1928.

IR (film) ν_{max}: 2955, 2929, 2856, 1717, 1253, 1049, 834, 772, and 670 cm^{-1}.

TLC: R_f = 0.33 (97:3 hexanes:EtOAc)



21

4-((*tert*-Butyldimethylsilyl)oxy)-3,4-dimethylpentanal (21). Following the general procedure, a mixture of *tert*-butyldimethyl(prop-1-en-2-yloxy)silane[5] (17.2 mg, 100 µmol, 1.0 equiv), (*E*)-but-2-enal (25.0 µL, 300 µmol, 3.0 equiv), Na_2HPO_4 (14.2 mg, 100 µmol, 1.0 equiv), $Fe(dibm)_3$ (2.6 mg, 5 µmol, 5 mol %), and $PhSiH_3$ (25.0 µL, 200 µmol, 2.0 equiv) in EtOH (0.50 mL) was heated at 60 °C with stirring for 1 h. Purification by flash column chromatography (SiO_2, 20:1 hexanes:EtOAc) furnished silyl ether **21** as a pale yellow oil (9.7 mg, 39.6 µmol, 40%).

Physical State: pale yellow oil.

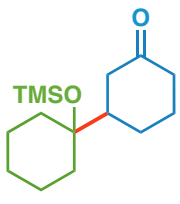
^{1}H NMR (600 MHz, $CDCl_3$): δ 9.76 (dd, *J* = 3.0, 1.8 Hz, 1 H), 2.74 (dd, *J* = 16.2, 3.0 Hz, 1 H), 2.16 (ddd, *J* = 16.2, 9.2, 3.0 Hz, 1 H), 2.08 (dqd, *J* = 10.2, 6.5, 3.5, 1 H), 1.23 (s, 3 H), 1.14 (s, 3 H), 0.92 (d, *J* = 7.2 Hz, 3 H), 0.85 (s, 9 H), 0.09 (s, 3 H) and 0.08 (s, 3 H).

^{13}C NMR (151 MHz, $CDCl_3$): δ 203.5, 75.4, 47.1, 40.0, 28.7, 26.0, 25.9, 18.3, 15.9, –1.9, and –2.0.

GC/MS (*m*/*z*): $[M–Me]^+$: 229, $[M–t\text{-}Bu]^+$: 187, $[M–CH(CH_3)CH_2CHO]^+$: 173.

IR (film) ν_{max}: 2956, 2931, 2885, 2857, 1724, 1463, 1366, 1255, 1161, 1034, 910, and 834 cm^{-1}.

TLC: R_f = 0.45 (20:1 hexanes:EtOAc).



22

1'-((Trimethylsilyl)oxy)-[1,1'-bi(cyclohexan)]-3-one (22). A solution of $PhSiH_3$ (4.0 M in EtOH, 78.0 µL, 312 µmol, 2.0 equiv) was added slowly via syringe pump to a mixture of (cyclohex-1-en-1-yloxy)trimethylsilane[6] (79.2 mg, 468 µmol, 3.0 equiv), cyclohex-2-enone (15.0 mg, 156 µmol, 1.0 equiv), Na_2HPO_4 (22.1 mg, 156 µmol, 1.0 equiv), and $Fe(dibm)_3$ (4.1 mg, 7.8 µmol, 5

mol %) in EtOH (0.78 mL) while heating at 60 °C with stirring for 1 h. After work up following the general procedure, purification by flash column chromatography (SiO_2, 96:4 hexanes:EtOAc) furnished silyl ether **22** as a colorless oil (19.1 mg, 71.1 µmol, 46%).

Physical State: colorless oil.

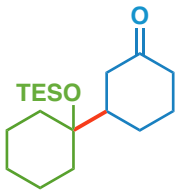
^{1}H NMR (600 MHz, $CDCl_3$): δ 2.38 (dddd, J = 14.0, 4.1, 2.1, 2.1 Hz, 1 H), 2.36 – 2.32 (m, 1 H), 2.26 – 2.20 (m, 2 H), 2.10 (dddd, J = 16.4, 6.4, 3.4, 3.4 Hz, 1 H), 1.94 (dddd, J = 11.8, 11.8, 3.8, 3.8 Hz, 1 H), 1.90 – 1.84 (m, 1 H), 1.71 – 1.67 (m, 1 H), 1.62 – 1.52 (m, 4 H), 1.51 – 1.31 (m, 7 H), and 0.12 (s, 9 H).

^{13}C NMR (151 MHz, C_6D_6): δ 209.8, 77.4, 42.6, 41.4, 36.0, 35.8, 30.2, 26.1, 25.3, 25.2, 22.9, 22.8, and 2.9.

HRMS (*m*/*z*) calcd for $C_{15}H_{29}O_2Si$ $[M+H]^+$: 269.1931, found: 269.1933.

IR (film) ν_{max}: 2933, 2862, 1711, 1450, 1249, 1059, 1005, 899, 833, and 751 cm^{-1}.

TLC: R_f = 0.41 (9:1 hexanes:EtOAc)



23

1'-((Triethylsilyl)oxy)-[1,1'-bi(cyclohexan)]-3-one (23). A solution of $PhSiH_3$ (4.0 M in EtOH, 78.0 µL, 312 µmol, 2.0 equiv) was added slowly via syringe pump to a mixture of (cyclohex-1-en-1-yloxy)triethylsilane[7] (99.4 mg, 468 µmol, 3.0 equiv), cyclohex-2-enone (15.0 mg, 156 µmol, 1.0 equiv), Na_2HPO_4 (22.1 mg, 156 µmol, 1.0 equiv), and $Fe(dibm)_3$ (4.1 mg, 7.8 µmol, 5 mol %) in EtOH (0.78 mL) while heating at 60 °C with stirring for 1 h. After work up following the general procedure, purification by flash column chromatography (SiO_2, 95:5 hexanes:EtOAc) furnished silyl ether **23** as a colorless oil (15.9 mg, 51.2 µmol, 33%).

Physical State: colorless oil.

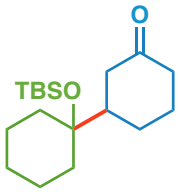
^{1}H NMR (600 MHz, $CDCl_3$): δ 2.35 – 2.30 (m, 3 H), 2.25 – 2.20 (m, 1 H), 2.12 – 2.10 (m, 1 H), 2.05 – 2.01 (m, 1 H), 1.88 – 1.83 (m, 2 H), 1.73 – 1.68 (m, 1 H), 1.59 – 1.50 (m, 5 H), 1.41 – 1.20 (m, 5 H), 0.96 (t, J = 7.8 Hz, 9 H), and 0.60 (q, J = 7.8 Hz, 6 H).

^{13}C NMR (151 MHz, $CDCl_3$): δ 214.0, 76.4, 42.9, 42.2, 41.5, 37.0, 36.5, 25.8, 25.4, 24.6, 23.2, 23.1, 7.5, and 7.2.

HRMS (*m*/*z*): calcd for $C_{18}H_{35}O_2Si$ $[M+H]^+$: 311.2401, found: 311.2402.

IR (film) ν_{max}: 2936, 2872, 1712, 1114, 721, and 671 cm^{-1}.

TLC: R_f = 0.44 (9:1 hexanes:EtOAc)



19

1'-((*tert*-Butyldimethylsilyl)oxy)-[1,1'-bi(cyclohexan)]-3-one (19). A solution of $PhSiH_3$ (4.0 M in EtOH, 78.0 µL, 312 µmol, 2.0 equiv) was added slowly via syringe pump to a mixture of *tert*-butyl(cyclohex-1-en-1-yloxy)dimethylsilane[8] (99.4 mg, 468 µmol, 3.0 equiv), cyclohex-2-enone (15.0 mg, 156 µmol, 1.0 equiv), Na_2HPO_4 (22.1 mg, 156 µmol, 1.0 equiv), and $Fe(dibm)_3$ (4.1 mg, 7.8 µmol, 5 mol %) in EtOH (0.78 mL) while heating at 60 °C with stirring for 1 h. After work up following the general procedure, purification by flash column chromatography (SiO_2, 96:4 hexanes:EtOAc) furnished silyl ether **19** as a white solid (17.8 mg, 57.3 µmol, 37%).

Physical State: white solid.

Melting Point: 59.0–60.0 °C.

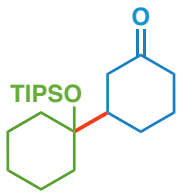
^{1}H NMR (600 MHz, $CDCl_3$): δ 2.38 – 2.30 (m, 3 H), 2.21 (ddd, *J* = 13.6, 6.8, 6.8 Hz, 1 H), 2.12 – 2.03 (m, 2 H), 1.89 – 1.85 (m, 2 H), 1.74 – 1.72 (m, 1 H), 1.65 – 1.50 (m, 5 H), 1.39 (ddd, *J* = 12.4, 12.4, 3.5 Hz, 1 H), 1.36 – 1.20 (m, 4 H), 0.87 (s, 9 H), 0.10 (s, 3 H), and 0.08 (s, 3H).

^{13}C NMR (151 MHz, $CDCl_3$): δ 213.9, 76.6, 42.7, 42.1, 41.5, 36.8, 36.2, 26.1, 25.7, 25.4, 24.5, 23.1, 23.0, 18.7, –1.6, and –1.6.

HRMS (*m*/*z*) calcd for $C_{18}H_{35}O_2Si$ $[M+H]^+$: 311.2401, found: 311.2402.

IR (film) ν_{max}: 2929, 2856, 1711, 1460, 1252, 1113, 1091, 1002, 831, 770, and 668 cm^{-1}.

TLC: R_f = 0.44 (9:1 hexanes:EtOAc)



24

1'-((Triisopropylsilyl)oxy)-[1,1'-bi(cyclohexan)]-3-one (24). A solution of $PhSiH_3$ (4.0 M in EtOH, 78.0 µL, 312 µmol, 2.0 equiv) was added slowly via syringe pump to a mixture of (cyclohex-1-en-1-yloxy)triisopropylsilane[9] (119.1 mg, 468 µmol, 3.0 equiv), cyclohex-2-enone (15.0 mg, 156 µmol, 1.0 equiv), Na_2HPO_4 (22.1 mg, 156 µmol, 1.0 equiv), and $Fe(dibm)_3$ (4.1 mg, 7.8 µmol, 5 mol %) in EtOH (0.78 mL) while heating at 60 °C with stirring for 1 h. After work up following the general procedure, purification by flash column chromatography (SiO_2, 95:5 hexanes:EtOAc) followed by preparative TLC (SiO_2, 95:5 hexanes:EtOAc) furnished silyl ether **24** as a colorless oil (4.3 mg, 13.3 µmol, 9%).

Physical State: colorless oil.

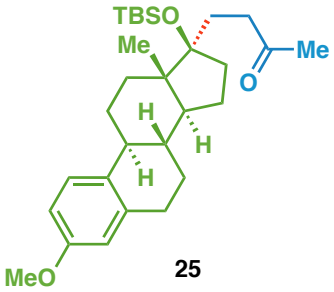
^{1}H NMR (600 MHz, $CDCl_3$): δ 2.47 (dd, *J* = 13.7, 13.7 Hz, 1 H), 2.38 – 2.33 (m, 2 H), 2.23 (ddd, *J* = 13.7, 13.7, 6.0 Hz, 1 H), 2.16 (dddd, *J* = 12.1, 12.1, 3.8, 3.8 Hz, 1 H), 2.13 – 2.10 (m, 1 H), 2.06 – 2.02 (m, 1 H), 1.87 – 1.84 (m, 2 H), 1.59 – 1.57 (m, 4 H), 1.41 (ddd, *J* = 13.1, 13.1, 3.7 Hz, 1 H), 1.33 (ddd, *J* = 12.8, 12.8, 3.2 Hz, 1 H), 1.29 – 1.22 (m, 3 H), 1.21 – 1.13 (m, 1 H), and 1.10 – 1.04 (m, 21 H).

^{13}C NMR (151 MHz, $CDCl_3$): δ 214.2, 76.4, 42.1, 41.6, 41.5, 37.5, 37.0, 25.6, 25.6, 24.4, 23.5, 23.5, 18.7, and 13.9.

HRMS (*m*/*z*) calcd for $C_{21}H_{41}O_2Si$ $[M+H]^+$: 353.2870, found: 353.2868.

IR (film) ν_{max}: 2939, 2865, 1713, 1459, 1115, 1095, 1067, 1007, 883, and 672 cm^{-1}.

TLC: R_f = 0.44 (9:1 hexanes:EtOAc).



25

4-((8*R*,9*S*,13*S*,14*S*,17*R*)-17-((*tert*-Butyldimethylsilyl)oxy)-3-methoxy-13-methyl-7,8,9,11,12,13,14,15,16,17-decahydro-6H-cyclopenta[a]phenanthren-17-yl)butan-2-one (25). Following the general procedure using THF as a cosolvent, a mixture of *tert*-butyl(((8*R*,9*S*,13*S*,14*S*)-3-methoxy-13-methyl-7,8,9,11,12,13,14,15-octahydro-6*H*-cyclopenta[*a*]phenanthren-17-yl)oxy)dimethylsilane[10] (19.9 mg, 50.0 µmol, 1.0 equiv), methyl vinyl ketone (24.8 µL, 300 µmol, 6.0 equiv), Na_2HPO_4 (7.1 mg, 50.0 µmol, 1.0 equiv), $Fe(dibm)_3$ (1.3 mg, 2.5 µmol, 5 mol %), and $PhSiH_3$ (36.9 µL, 300 µmol, 6.0 equiv) in EtOH (0.12 mL) and THF (0.12 mL) was heated at 60 °C with stirring for 1 h. Purification by flash column chromatography (SiO_2, 50:1→30:1 hexanes:EtOAc) furnished estrone derivative **25** as a white solid (10.0 mg, 21.3 µmol, 43%).

Physical State: white solid.

Melting Point: 72.2–74.9 °C.

^{1}H NMR (600 MHz, $CDCl_3$): δ 7.20 (d, *J* = 8.4 Hz, 1 H), 6.71 (dd, *J* = 8.4, 3.0 Hz, 1 H), 6.62 (d, *J* = 3.0 Hz, 1 H), 3.78 (s, 3 H), 2.86 – 2.83 (m, 2 H), 2.64 – 2.59 (m, 2 H), 2.30 – 2.28 (m, 1 H), 2.17 (s, 3 H), 0.90 (s, 9 H), 0.83 (s, 3 H), 0.11 (s, 3 H), and 0.10 (s, 3 H).

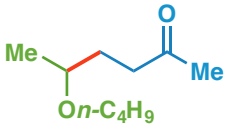
^{13}C NMR (151 MHz, $CDCl_3$): δ 209.6, 157.6, 138.2, 132.9, 126.4, 113.9, 111.6, 86.1, 55.4, 48.6, 48.2, 43.9, 40.0, 39.9, 35.5, 32.5, 32.2, 30.3, 30.0, 27.7, 26.6, 26.3, 23.5, 18.9, 15.5, –1.3, and –1.7.

HRMS (*m*/*z*): calcd for $C_{29}H_{47}O_3Si$ $[M+Na]^+$: 493.3108, found: 493.3109.

IR (film) ν_{max}: 2929, 2855, 1714, 1500, 1252, 1059, 833 and 735 cm^{-1}.

$[\alpha]_{20}^{D}$: +22.0 (c = 0.50, $CHCl_3$).

TLC: R_f = 0.48 (10:1 hexanes:EtOAc).



26

5-Butoxyhexan-2-one (26). Following the general procedure, a mixture of butyl vinyl ether (54.6 µL, 600 µmol, 3.0 equiv), methyl vinyl ketone (16.5 µL, 200 µmol, 1.0 equiv), Na_2HPO_4 (28.4 mg, 200 µmol, 1.0 equiv), $Fe(dibm)_3$ (5.2 mg, 10 µmol, 5 mol %), and $PhSiH_3$ (49.2 µL, 400 µmol, 2.0 equiv) in EtOH (1.0 mL) was heated at 60 °C with stirring for 1 h. Purification by flash column chromatography (SiO_2, 50:1→20:1 hexanes:EtOAc) furnished ether **26** as a colorless oil (17.6 mg, 102 µmol, 51%).

Physical State: colorless oil.

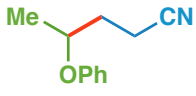
^{1}H NMR (600 MHz, $CDCl_3$): δ 3.46 (ddd, *J* = 9.0, 6.0, 6.0 Hz, 1 H), 3.37 – 3.34 (m, 1 H), 3.26 (ddd, *J* = 9.6, 6.6, 6.6 Hz, 1 H), 2.54 – 2.46 (m, 2 H), 2.13 (s, 3 H), 1.75 – 1.73 (m, 1 H), 1.71 – 1.64 (m, 1 H), 1.53 – 1.46 (m, 2 H), 1.37 – 1.32 (m, 2 H), 1.11 (d, *J* = 6.0 Hz, 3 H), and 0.90 (t, *J* = 7.2 Hz, 3 H).

^{13}C NMR (151 MHz, $CDCl_3$): δ 209.2, 74.3, 68.3, 39.8, 32.3, 30.7, 30.1, 19.8, 19.5, and 14.0.

HRMS (*m*/*z*): calcd for $C_{10}H_{21}O_2$ $[M+H]^+$: 173.1536, found: 173.1546.

IR (film) ν_{max}: 2960, 2931, 2869, 1716, 1357, 1134, and 1094 cm^{-1}.

TLC: R_f = 0.21 (10:1 hexanes:EtOAc).



27

4-Phenoxy-1-pentanitrile (27). Following the general procedure, a mixture of phenyl vinyl ether (36.0 mg, 300 µmol, 3.0 equiv), acrylonitrile (6.58 µL, 100 µmol, 1.0 equiv), Na_2HPO_4 (14.2 mg, 100 µmol, 1.0 equiv), $Fe(dibm)_3$ (2.6 mg, 5.0 µmol, 5 mol %), and $PhSiH_3$ (25.0 µL, 200 µmol, 2.0 equiv) in EtOH (0.50 mL) was heated at 60 °C with stirring for 1 h. Purification by flash column chromatography (SiO_2, 10:1 hexanes:EtOAc) furnished ether **27** as a pale yellow oil (10.4 mg, 59.3 µmol, 59%).

Physical State: pale yellow oil.

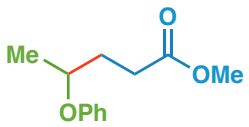
^{1}H NMR (600 MHz, $CDCl_3$): δ 7.31 – 7.27 (m, 2 H), 6.97 (dddd, *J* = 7.3, 7.3, 1.0, 1.0 Hz, 1 H), 6.91 – 6.90 (m, 2 H), 4.49 (dqd, *J* = 4.4, 6.1, 7.9 Hz, 1 H), 2.54 (dd, *J* = 7.2, 7.2 Hz, 2 H), 2.06 – 1.97 (m, 2 H), and 1.33 (d, *J* = 6.1 Hz, 3 H).

^{13}C NMR (151 MHz, $CDCl_3$): δ 157.5, 129.8, 121.5, 119.7, 116.2, 71.8, 32.5, 19.5, and 13.8.

HRMS (*m*/*z*): calcd for $C_{11}H_{14}NO$ $[M+H]^+$: 176.1070, found: 176.1074.

IR (film) ν_{max}: 3017, 2977, 2935, 2249, 2021, 1944, 1596, 1491, 1380, 1292, 1237, 1173, 1136, 1083, 1026, 958, 911, and 753 cm^{-1}.

TLC: R_f = 0.20 (10:1 hexanes:EtOAc).



28

Methyl 4-phenoxypentanoate (28). Following the general procedure, a mixture of phenyl vinyl ether (36.0 mg, 300 µmol, 3.0 equiv), methyl acrylate (9.00 µL, 100 µmol, 1.0 equiv), Na_2HPO_4 (14.2 mg, 100 µmol, 1.0 equiv), $Fe(dibm)_3$ (2.6 mg, 5.0 µmol, 5 mol %), and $PhSiH_3$ (25.0 µL, 200 µmol, 2.0 equiv) in EtOH (0.50 mL) was heated at 60 °C with stirring for 1 h. Purification by flash column chromatography (SiO_2, 10:1 hexanes:EtOAc) furnished ether **28** as a pale yellow oil (12.1 mg, 58.1 µmol, 58%).

Physical State: pale yellow oil.

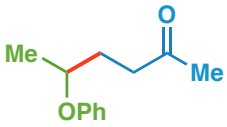
^{1}H NMR (600 MHz, $CDCl_3$): δ 7.27 – 7.25 (m, 2 H), 6.92 (dddd, *J* = 7.4, 7.4, 1.0, 1.0 Hz, 1 H), 6.88 – 6.66 (m, 2 H), 4.41 (dqd, *J* = 4.7, 6.0, 7.5 Hz, 1 H), 3.65 (s, 3 H), 2.53 – 2.42 (m, 2 H), 2.04 – 1.93 (m, 2 H), and 1.30 (d, *J* = 6.1 Hz, 3 H).

^{13}C NMR (151 MHz, $CDCl_3$): δ 174.1, 158.0, 129.6, 120.9, 116.0, 72.7, 51.7, 31.7, 30.2, and 19.7.

HRMS (*m*/*z*): calcd for $C_{12}H_{17}O_3$ $[M+H]^+$: 209.1172, found: 209.1169.

IR (film) ν_{max}: 2796, 1735, 1598, 1493, 1438, 1240, 1172, 1133, 1084, 753 and 693 cm^{-1}.

TLC: R_f = 0.35 (10:1 hexanes:EtOAc).



29

5-Phenoxy-2-hexanone (29). Following the general procedure, a mixture of phenyl vinyl ether (36.0 mg, 300 µmol, 3.0 equiv), methyl vinyl ketone (8.11 µL, 100 µmol, 1.0 equiv), Na_2HPO_4 (14.2 mg, 100 µmol, 1.0 equiv), $Fe(dibm)_3$ (2.6 mg, 5.0 µmol, 5 mol %), and $PhSiH_3$ (25.0 µL, 200 µmol, 2.0 equiv) in EtOH (0.50 mL) was heated at 60 °C with stirring for 1 h. Purification by flash column chromatography (SiO_2, 5:1 hexanes:EtOAc) furnished ether **29** as a pale yellow oil (5.9 mg, 30.6 µmol, 31%).

Physical State: pale yellow oil.

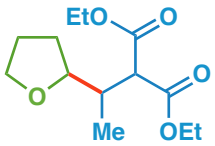
^{1}H NMR (600 MHz, $CDCl_3$): δ 7.28 – 7.25 (m, 2 H), 6.92 (dd, *J* = 7.3, 7.3 Hz, 1 H), 6.87 (d, *J* = 8.0 Hz, 2 H), 4.40 (dqd, *J* = 6.1, 6.1, 6.1 Hz, 1 H), 2.66 – 2.55 (m, 2 H), 2.13 (s, 3 H), 1.98 – 1.89 (m, 2 H), and 1.29 (d, *J* = 6.1 Hz, 3 H).

^{13}C NMR (151 MHz, $CDCl_3$): δ 208.7, 158.1, 134.3, 129.7, 127.8, 120.8, 115.9, 72.8, 39.6, 30.6, 30.2, and 19.9.

HRMS (*m*/*z*): calcd for $C_{12}H_{17}O_2$ $[M+H]^+$: 193.1223, found: 193.1226.

IR (film) ν_{max}: 2930, 1716, 1493, 1240, 1132, 911, 751, 670, and 490 cm^{-1}.

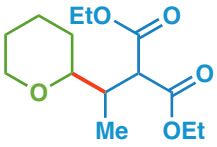
TLC: R_f = 0.40 (10:1 hexanes:EtOAc).



30

Diethyl 2-(1-(tetrahydrofuran-2-yl)ethyl)malonate (30). Following the general procedure, a mixture of 2,3-dihydrofuran (14.0 mg, 200 µmol, 1.0 equiv), diethyl ethylidenemalonate (109.6 µL, 600 µmol, 3.0 equiv), Na_2HPO_4 (28.4 mg, 200 µmol, 1.0 equiv), $Fe(dibm)_3$ (5.2 mg, 10 µmol, 5 mol %), and $PhSiH_3$ (49.2 µL, 400 µmol, 2.0 equiv) in EtOH (1.0 mL) was heated at 60 °C with stirring for 1 h. Purification by flash column chromatography (SiO_2, 20:1→10:1 hexanes:EtOAc) furnished a 1:1.2 diastereomeric mixture of ethers **30** as a colorless oil (27.9 mg, 108.1 µmol, 54%).

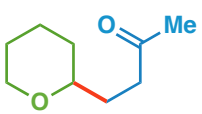
Spectroscopic data was identical to that reported in the literature.[11]



31

Diethyl 2-(1-(tetrahydro-2H-pyran-2-yl)ethyl)malonate (31). Following the general procedure, a mixture of 3,4-dihydro-2*H*-pyran (16.8 mg, 200 µmol, 1.0 equiv), diethyl ethylidenemalonate (110 µL, 600 µmol, 3.0 equiv), Na_2HPO_4 (28.4 mg, 200 µmol, 1.0 equiv), $Fe(dibm)_3$ (5.2 mg, 10 µmol, 5 mol %), and $PhSiH_3$ (49.2 µL, 400 µmol, 2.0 equiv) in EtOH (1.0 mL) was heated at 60 °C with stirring for 1 h. Purification by flash column chromatography (SiO_2, 50:1→20:1 hexanes:EtOAc) furnished a 1:1.8 diastereomeric mixture of ethers **31** as a colorless oil (41.1 mg, 15.1 µmol, 76%).

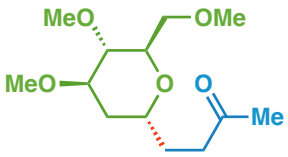
Spectroscopic data was identical to that reported in the literature.[11]



32

4-(Tetrahydro-2H-pyran-2-yl)butan-2-one (32). Following the general procedure, a mixture of 3,4-dihydro-2*H*-pyran (54.6 µL, 600 µmol, 3.0 equiv), methyl vinyl ketone (16.5 µL, 200 µmol, 1.0 equiv), Na_2HPO_4 (28.4 mg, 200 µmol, 1.0 equiv), $Fe(dibm)_3$ (5.2 mg, 10 µmol, 5 mol %), and $PhSiH_3$ (49.2 µL, 400 µmol, 2.0 equiv) in EtOH (1.0 mL) was stirred at room temperature for 1 h. Purification by flash column chromatography (SiO_2, 6:1→5:1 pentanes:Et_2O) furnished ether **32** as a colorless oil (13.5 mg, 86.5 µmol, 43%).

Spectroscopic data was identical to that reported in the literature.[12]



33

4-((2*R*,4*R*,5*S*,6*R*)-4,5-Dimethoxy-6-(methoxymethyl)tetrahydro-2H-pyran-2-yl)butan-2-one (33). A solution of methyl vinyl ketone (49.6 µL, 600 µmol, 6.0 equiv) and $PhSiH_3$ (73.8 µL, 600 µmol, 6.0 equiv) in EtOH (0.50 mL) was added slowly via syringe pump to a mixture of 3,4,6-tri-O-methyl-D-glucal[13] (18.8 mg, 100 µmol, 1.0 equiv), Na_2HPO_4 (14.2 mg, 100 µmol, 1.0 equiv), $Fe(dibm)_3$ (2.6 mg, 5.00 µmol, 5 mol %) in EtOH (0.50 mL) while heating at 60 °C with stirring for 1 h. The reaction mixture was then heated at 60 °C with stirring for another 1 h. After workup following the general procedure, purification by flash column chromatography (SiO_2, 2:1→1:2 hexanes:EtOAc) furnished glucal derivative **33** as a colorless oil (16.5 mg, 63.5 µmol, 64%).

Physical State: colorless oil.

$[\alpha]_{20}^{D}$ = +34.2 (c = 1.00, $CHCl_3$)

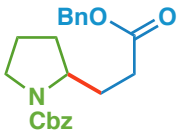
^{1}H NMR (600 MHz, $CDCl_3$): δ 3.89 (ddd, *J* = 6.0, 4.5, 4.5 Hz, 1 H), 3.60 (dd, *J* = 9.6, 5.4 Hz, 1 H), 3.56 (ddd, *J* = 7.2, 2.4, 2.4 Hz, 1 H), 3.51 (dd, *J* = 9.6, 3.0 Hz, 1 H), 3.49 – 3.46 (m, 4 H), 3.40 (s, 3 H), 3.38 (s, 3 H), 3.09 (dd, *J* = 7.2, 7.2 Hz, 1 H), 2.56 – 2.50 (m, 2 H), 2.15 (s, 3 H), 1.98 – 1.92 (m, 1 H), 1.87 (ddd, *J* = 13.8, 4.8, 4.2 Hz, 1 H), and 1.70 – 1.62 (m, 2 H).

^{13}C NMR (151 MHz, $CDCl_3$): δ 208.6, 78.8, 78.0, 72.3, 71.6, 70.0, 59.7, 59.3, 57.1, 39.9, 33.0, 30.3, and 26.0.

HRMS (*m*/*z*): calcd for $C_{13}H_{25}O_5$ $[M+H]^+$: 261.1697, found: 261.1706.

IR (film) ν_{max}: 2927, 1714, 1453, 1359, 1095, and 730 cm^{-1}.

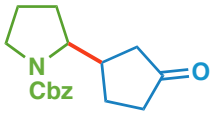
TLC: R_f = 0.12 (1:1 hexanes:EtOAc).



34

Benzyl 2-(3-(benzyloxy)-3-oxopropyl)pyrrolidine-1-carboxylate (34). Following the general procedure, a mixture of benzyl 2,3-dihydro-1*H*-pyrrole-1-carboxylate[14] (30.0 mg, 148 µmol, 1.0 equiv), benzyl acrylate (67.8 µL, 443 µmol, 3.0 equiv), Na_2HPO_4 (21.0 mg, 148 µmol, 1.0 equiv), $Fe(dibm)_3$ (3.8 mg, 7.4 µmol, 5 mol %), and $PhSiH_3$ (109 µL, 886 µmol, 6.0 equiv) in EtOH (0.74 mL) was heated at 60 °C with stirring for 10 min. Purification by flash column chromatography (SiO_2, 8:2 hexanes:EtOAc) furnished carbamate **34** as a pale yellow oil (35.4 mg, 96.3 µmol, 65%).

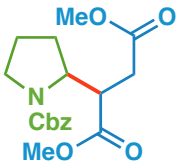
Spectroscopic data was identical to that reported in the literature.[11]



35

Benzyl 2-(3-oxocyclopentyl)pyrrolidine-1-carboxylate (35). Following the general procedure, a mixture of benzyl 2,3-dihydro-1*H*-pyrrole-1-carboxylate[14] (30.0 mg, 148 µmol, 1.0 equiv), cyclopent-2-enone (37.5 µL, 443 µmol, 3.0 equiv), Na_2HPO_4 (21.0 mg, 148 µmol, 1.0 equiv), $Fe(dibm)_3$ (3.8 mg, 7.4 µmol, 5 mol %), and $PhSiH_3$ (109 µL, 886 µmol, 6.0 equiv) in EtOH (0.74 mL) was heated at 60 °C with stirring for 10 min. Purification by flash column chromatography (SiO_2, 6:4 hexanes:EtOAc) furnished a diastereomeric mixture of carbamates **35** as a pale yellow oil (31.6 mg, 110 µmol, 75%).

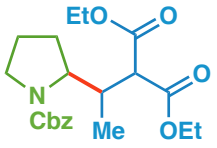
Spectroscopic data was identical to that reported in the literature.[11]



36

Dimethyl 2-(1-((benzyloxy)carbonyl)pyrrolidin-2-yl)succinate (36). Following the general procedure, a mixture of benzyl 2,3-dihydro-1*H*-pyrrole-1-carboxylate[14] (30.0 mg, 148 µmol, 1.0 equiv), dimethyl maleate (55.4 µL, 443 µmol, 3.0 equiv), Na_2HPO_4 (21.0 mg, 148 µmol, 1.0 equiv), $Fe(dibm)_3$ (3.8 mg, 7.4 µmol, 5 mol %), and $PhSiH_3$ (36.4 µL, 296 µmol, 2.0 equiv) in EtOH (0.74 mL) was heated at 60 °C with stirring for 10 min. Purification by flash column chromatography (SiO_2, 7:3 hexanes:EtOAc) furnished a diastereomeric mixture of carbamates **36** as a pale yellow oil (38.7 mg, 111 µmol, 75%).

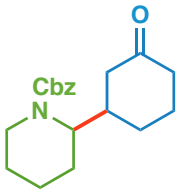
Spectroscopic data was identical to that reported in the literature.[11]



37

Diethyl 2-(1-(1-((benzyloxy)carbonyl)pyrrolidin-2-yl)ethyl)malonate (37) Following the general procedure, a mixture of benzyl 2,3-dihydro-1*H*-pyrrole-1-carboxylate[14] (20.3 mg, 100 µmol, 1.0 equiv), diethyl 2-ethylidenemalonate (54.8 µL, 300 µmol, 3.0 equiv), Na_2HPO_4 (14.2 mg, 100 µmol, 1.0 equiv), $Fe(dibm)_3$ (2.6 mg, 5.0 µmol, 5 mol %), and $PhSiH_3$ (24.6 µL, 200 µmol, 2.0 equiv) in EtOH (0.50 mL) was heated at 60 °C with stirring for 1 h. Purification by flash column chromatography (SiO_2, 10:1→5:1 hexanes:EtOAc) furnished a diastereomeric mixture of carbamates **37** as a colorless oil (34.3 mg, 87.7 µmol, 88%).

Spectroscopic data was identical to that reported in the literature.[11]



38

Benzyl 2-(3-oxocyclohexyl)piperidine-1-carboxylate (38). Following the general procedure, a mixture of benzyl 3,4-dihydropyridine-1(2*H*)-carboxylate[15] (21.7 mg, 100 µmol, 1.0 equiv), cyclohex-2-enone (58.0 µL, 600 µmol, 6.0 equiv), Na_2HPO_4 (14.2 mg, 100 µmol, 1.0 equiv), $Fe(dibm)_3$ (7.9 mg, 15.0 µmol, 15 mol %), and $PhSiH_3$ (73.8 µL, 600 µmol, 6.0 equiv) in EtOH (0.50 mL) was heated at 60 °C with stirring for 1 h. Purification by flash column chromatography (SiO_2, 5:1→3:1 hexanes:EtOAc) furnished a 1:1.5 diastereomeric mixture of carbamates **38** as a colorless oil (17.3 mg, 54.6 µmol, 55%). Data is reported for the mixture of diastereomers.

Physical State: colorless oil.

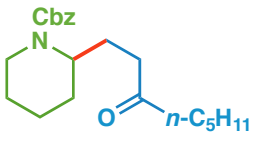
^{1}H NMR (500 MHz, $CDCl_3$, 50 °C): δ 7.36 – 7.34 (m, 5 H), 5.18 – 5.09 (m, 2 H), 4.13 – 4.08 (m, 2 H), 2.76 – 2.70 (m, 1 H), 2.44 – 2.20 (m, 4 H), 2.13 – 2.01 (m, 2 H), 1.95 – 1.71 (m, 2 H), 1.68 – 1.42 (m, 6 H), and 1.39 – 1.30 (m, 1 H).

^{13}C NMR (126 MHz, acetone-d_6, 45 °C): δ 210.1, 210.0, 156.5, 139.0, 129.6, 129.0, 128.9, 67.7, 67.7, 57.1, 56.8, 46.1, 45.4, 42.0, 41.9, 40.7, 37.9, 28.8, 27.2, 26.6, 26.2, 25.8, 20.1, and 20.0.

HRMS (*m*/*z*): calcd for $C_{19}H_{26}NO_3$ $[M+H]^+$: 316.1907, found: 316.1925.

IR (film) ν_{max}: 2937, 2863, 1685, 1422, 1258, 1087, 736, and 696 cm^{-1}.

TLC: R_f = 0.27 (3:1 hexanes:EtOAc).



39

Benzyl 2-(3-oxooctyl)piperidine-1-carboxylate (39). Following the general procedure, a mixture of benzyl 3,4-dihydropyridine-1(2*H*)-carboxylate[15] (21.7 mg, 100 µmol, 1.0 equiv), oct-1-en-3-one (44.9 µL,

300 µmol, 3.0 equiv), Na_2HPO_4 (14.2 mg, 100 µmol, 1.0 equiv), $Fe(dibm)_3$ (2.6 mg, 5.0 µmol, 5 mol %), and $PhSiH_3$ (24.6 µL, 200 µmol, 2.0 equiv) in EtOH (0.50 mL) was heated at 60 °C with stirring for 1 h. Purification by flash column chromatography (SiO_2, 20:1→10:1 hexanes:EtOAc) furnished carbamate **39** as a colorless oil (21.1 mg, 61.1 µmol, 61%).

Physical State: colorless oil.

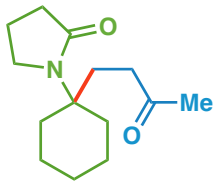
^{1}H NMR (600 MHz, $CDCl_3$): δ 7.36 – 7.35 (m, 5 H), 5.13 – 5.08 (m, 2 H), 4.29 – 4.27 (m, 1 H), 4.07 – 3.97 (m, 1 H), 2.83 – 2.75 (m, 1 H), 2.34 – 2.21 (m, 4 H), 2.08 – 1.99 (m, 1 H), 1.62 – 1.19 (m, 13 H), and 0.87 (t, J = 7.2 Hz, 3 H).

^{13}C NMR (151 MHz, $CDCl_3$): δ 210.9, 155.7, 137.1, 128.6, 128.1, 128.0, 67.1, 50.6, 43.1, 39.4, 39.2, 31.5, 29.2, 25.7, 23.7, 23.6, 22.6, 19.1, and 14.1.

HRMS (*m*/*z*): calcd for $C_{21}H_{31}NO_3$ $[M+H]^+$: 346.2377, found: 346.2377.

IR (film) ν_{max}: 2930, 2860, 1691, 1421, 1257, 1071, 737 and 698 cm^{-1}.

TLC: R_f = 0.21 (5:1 hexanes:EtOAc).



40

1-(1-(3-Oxobutyl)cyclohexyl)pyrrolidin-2-one (40). Following the general procedure, a mixture of 1-(cyclohex-1-en-1-yl)pyrrolidin-2-one[16] (16.5 mg, 100 µmol, 1.0 equiv), methyl vinyl ketone (24.9 µL, 300 µmol, 3.0 equiv), Na_2HPO_4 (14.2 mg, 100 µmol, 1.0 equiv), $Fe(dibm)_3$ (7.9 mg, 15 µmol, 15 mol %), and $PhSiH_3$ (73.8 µL, 600 µmol, 6.0 equiv) in EtOH (0.50 mL) was heated at 60 °C with stirring for 1 h. The reaction mixture was then cooled to room temperature and a second portion of methyl vinyl ketone (24.8 µL, 300 µmol, 3.0 equiv), $Fe(dibm)_3$ (7.9 mg, 15.0 µmol, 15 mol %), and $PhSiH_3$ (73.8 µL, 600 µmol, 6.0 equiv) was added. After heating the reaction mixture at 60 °C with stirring for 1 h and work up following the general procedure, purification by flash column chromatography (SiO_2, 1:1→1:2 hexanes:EtOAc→EtOAc) furnished amide **40** as a colorless oil (16.6 mg, 70.0 µmol, 70%).

Physical State: colorless oil.

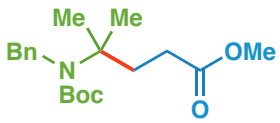
^{1}H NMR (600 MHz, $CDCl_3$): δ 3.39 (dd, J = 7.2, 6.6 Hz, 2 H), 2.50 (dd, J = 7.8, 7.2 Hz, 2 H), 2.35 – 2.32 (m, 4 H), 2.14 (s, 3 H), 1.94 – 1.90 (m, 4 H), 1.55 – 1.54 (m, 3 H), and 1.39 – 1.34 (m, 5 H).

^{13}C NMR (151 MHz, $CDCl_3$): δ 209.2, 176.5, 59.4, 45.5, 38.3, 34.7, 33.6, 31.4, 30.2, 25.8, 22.6, and 18.3.

HRMS (*m*/*z*): calcd for $C_{14}H_{24}NO_2$ $[M+H]^+$: 238.1802, found: 238.1806.

IR (film) ν_{max}: 2929, 2857, 1712, 1671, 1404, 1269, 1166, and 670 cm^{-1}.

TLC: R_f = 0.18 (1:2 hexanes:EtOAc).



41

Methyl 4-(benzyl(*tert*-butoxycarbonyl)amino)-4-methylpentanoate (41). Following the general procedure, a mixture of *tert*-butyl benzyl(prop-1-en-2-yl)carbamate[17] (74.2 mg, 300 µmol, 3.0 equiv), methyl acrylate (9.00 µL, 100 µmol, 1.0 equiv), Na_2HPO_4 (14.2 mg, 100 µmol, 1.0 equiv), $Fe(dibm)_3$ (2.6 mg, 5.0 µmol, 5 mol %), and $PhSiH_3$ (25.0 µL, 200 µmol, 2.0 equiv) in EtOH (0.50 mL) was heated at 60 °C with stirring for 1 h. Purification by flash column chromatography (SiO_2, 5:1 hexanes:EtOAc) furnished carbamate **41** as a pale yellow oil (23.6 mg, 70.3 µmol, 70%).

Physical State: pale yellow oil.

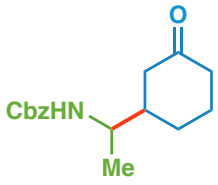
^{1}H NMR (600 MHz, $CDCl_3$): δ 7.34 – 7.27 (m, 3 H), 7.21 – 7.20 (m, 2 H), 4.54 (s, 2 H), 3.66 (s, 3 H), 2.27 – 2.24 (m, 2 H), 2.22 – 2.19 (m, 2 H), 1.46 (s, 9 H), and 1.31 (s, 6 H).

^{13}C NMR (151 MHz, $CDCl_3$): δ 174.4, 156.1, 141.1, 128.5, 126.6, 126.5, 80.1, 58.4, 51.7, 49.2, 36.0, 30.0, 28.6, and 27.9.

HRMS (*m*/*z*): calcd for $C_{19}H_{30}NO_4$ $[M+H]^+$: 336.2175, found: 336.2172.

IR (film) ν_{max}: 2977, 1732, 1682, 1543, 1380, 1366, 1241, 1216, 1159, 1076, 864, and 750 cm^{-1}.

TLC: R_f = 0.50 (5:1 hexanes:EtOAc).



42

Benzyl (1-(3-oxocyclohexyl)ethyl)carbamate (42). Following the general procedure, a mixture of benzyl vinylcarbamate[18] (17.7 mg, 100 µmol, 1.0 equiv), cyclohex-2-enone (29.0 µL, 300 µmol, 3.0 equiv), Na_2HPO_4 (14.2 mg, 100 µmol, 1.0 equiv), $Fe(dibm)_3$ (7.9 mg, 15 µmol, 15 mol %), and $PhSiH_3$ (73.8 µL, 600 µmol, 6.0 equiv) in EtOH (0.50 mL) was heated at 60 °C with stirring for 1 h. The reaction mixture was then cooled to room temperature and a second portion of cyclohex-2-enone (29.0 µL, 300 µmol, 3.0 equiv), $Fe(dibm)_3$ (7.9 mg, 15.0 µmol, 15 mol %), and $PhSiH_3$ (73.8 µL, 600 µmol, 6.0 equiv) was added. After heating the reaction mixture at 60 °C with stirring for 1 h and work up following the general procedure, purification by flash column chromatography (SiO_2, 5:1→3:1 hexanes:EtOAc) furnished a diastereomeric mixture of

carbamates **42** as a colorless oil (13.1 mg, 47.6 µmol, 48%). Data is reported for the mixture of diastereomers.

Physical State: colorless oil.

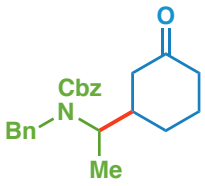
^{1}H NMR (500 MHz, $CDCl_3$, 50 °C): δ 7.37 – 7.30 (m, 5 H), 5.13 – 5.07 (m, 2 H), 4.54 (br s, 1 H), 3.77 – 3.72 (m, 1 H), 2.47 – 2.34 (m, 2 H), 2.27 – 2.20 (m, 1 H), 2.14 – 2.05 (m, 2 H), 1.95 – 1.79 (m, 2 H), 1.63 – 1.54 (m, 1 H), 1.44 – 1.33 (m, 1 H), and 1.16 – 1.14 (m, 3H).

^{13}C NMR (151 MHz, $CDCl_3$): δ 211.2, 211.2, 156.1, 156.0, 136.5, 128.7, 128.3, 128.3, 128.3, 67.0, 50.9, 50.7, 44.9, 44.6, 44.6, 44.0, 42.3, 41.5, 41.4, 35.1, 34.8, 28.2, 27.2, 25.8, 25.4, 25.2, 25.1, 24.9, 22.0, 22.0, 18.7, and 18.2.

HRMS (*m*/*z*): calcd for $C_{16}H_{22}NO_3$ $[M+H]^+$: 276.1594, found: 276.1598.

IR (film) ν_{max}: 3318, 2936, 1695, 1528, 1235, 1094, and 741 cm^{-1}.

TLC: R_f = 0.16 (3:1 hexanes:EtOAc).



43

Benzyl benzyl(1-(3-oxocyclohexyl)ethyl)carbamate (43). Following the general procedure, a mixture of benzyl benzyl(vinyl)carbamate[19](26.7 mg, 100 µmol, 1.0 equiv), cyclohex-2-enone (58.0 µL, 600 µmol, 6.0 equiv), Na_2HPO_4 (14.2 mg, 100 µmol, 1.0 equiv), $Fe(dibm)_3$ (7.9 mg, 15.0 µmol, 15 mol %), and $PhSiH_3$ (73.8 µL, 600 µmol, 6.0 equiv) in EtOH (0.50 mL) was heated at 60 °C with stirring for 1 h. Purification by flash column chromatography (SiO_2, 5:1→4:1 hexanes:EtOAc) furnished a 1:1.3 diastereomeric mixture of carbamates **43** as a colorless oil (29.0 mg, 79.4 µmol, 79%). Data is reported for the mixture of diastereomers.

Physical State: colorless oil.

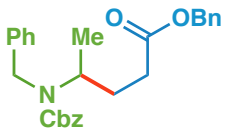
^{1}H NMR (500 MHz, $CDCl_3$, 50 °C): δ 7.29 – 7.21 (m, 10 H), 5.18 – 5.15 (m, 2 H), 4.53 – 4.27 (m, 2 H), 3.92 – 3.65 (m, 1 H), 2.42 – 2.32 (m, 2 H), 2.21 – 2.17 (m, 1 H), 2.07 – 1.78 (m, 4 H), 1.59 – 1.33 (m, 2 H), 1.16 (d, J = 6.5 Hz, 1.7 H), and 1.11 (d, J = 6.7 Hz, 1.3 H).

^{13}C NMR (151 MHz, C_6D_6, 55 °C): δ 207.9, 207.7, 156.6, 139.8, 139.7, 137.5, 137.5, 128.6, 128.6, 128.5, 128.3, 127.3, 67.4, 58.0, 57.8, 48.8, 45.4, 45.3, 42.9, 42.7, 41.0, 28.9, 28.7, 25.0, 24.8, 17.2, and 16.3. 11 carbons were not observed due to incidental equivalence.

HRMS (*m*/*z*): calcd for $C_{23}H_{28}NO_3$ $[M+H]^+$: 366.2064, found: 366.2064.

IR (film) ν_{max}: 2942, 1690, 1450, 1096, 733, and 697 cm^{-1}.

TLC: R_f = 0.33 (3:1 hexanes:EtOAc).



44

Benzyl 4-(benzyl((benzyloxy)carbonyl)amino)pentanoate (44). Following the general procedure, a mixture of benzyl benzyl(vinyl)carbamate[19] (26.7 mg, 100 µmol, 1.0 equiv), benzyl acrylate (45.9 µL, 300 µmol, 3.0 equiv), Na_2HPO_4 (14.2 mg, 100 µmol, 1.0 equiv), $Fe(dibm)_3$ (2.6 mg, 5.0 µmol, 5 mol %), and $PhSiH_3$ (24.6 µL, 200 µmol, 2.0 equiv) in EtOH (0.50 mL) was heated at 60 °C with stirring for 1 h. Purification by flash column chromatography (SiO_2, 5:1 hexanes:EtOAc) furnished carbamate **44** as a colorless oil (31.7 mg, 73.5 µmol, 73%).

Physical State: colorless oil.

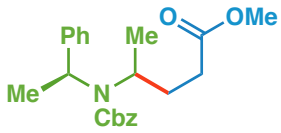
^{1}H NMR (500 MHz, $CDCl_3$, 50 °C): δ 7.40 – 7.26 (m, 15 H), 5.20 (s, 2 H), 5.12 (s, 2 H), 4.46 (s, 2 H), 5.20 (m, 1 H), 2.32 (m, 2 H), 2.00 (m, 1 H), 1.84 (m, 1 H), and 1.17 (d, J = 6.5 Hz, 3 H).

^{13}C NMR (126 MHz, $CDCl_3$, 50 °C): δ 183.0, 172.8, 139.1, 136.8, 136.1, 128.5, 128.4, 128.4, 128.2, 127.9, 127.9, 127.3, 127.0, 67.2, 66.2, 52.7, 47.7, 31.4, 29.9, and 19.0.

HRMS (*m*/*z*): calcd for $C_{27}H_{30}NO_4$ $[M+H]^+$: 432.2169, found: 432.2178.

IR (film) ν_{max}: 2937, 1731, 1689, 1452, 1160, 733, and 696 cm^{-1}.

TLC: R_f = 0.42 (3:1 hexanes:EtOAc).



45

Methyl 4-(((benzyloxy)carbonyl)((*S*)-1-phenylethyl)amino)pentanoate (45). Following the general procedure, a mixture of benzyl (*S*)-(1-phenylethyl)(vinyl)carbamate[20] (10.0 mg, 35.5 µmol, 1.0 equiv), methyl acrylate (19.3 µL, 213 µmol, 6.0 equiv), Na_2HPO_4 (5.0 mg, 35.5 µmol, 1.0 equiv), $Fe(dibm)_3$ (2.8 mg, 5.3 µmol, 15 mol %), and $PhSiH_3$ (26.3 µL, 213 µmol, 6.0 equiv) in EtOH (0.18 mL) was heated at 60 °C with stirring for 1h. Purification by preparative TLC (SiO_2, 8:2 hexanes:EtOAc) furnished a 1:1.5 diastereomeric mixture of carbamates **45** as a colorless oil (9.0 mg, 24.4 µmol, 69%). Data is reported for the mixture of diastereomers.

Physical State: colorless oil.

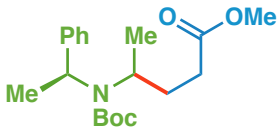
^{1}H NMR (500 MHz, $CDCl_3$, 50 °C): δ 7.34 – 7.22 (m, 10 H), 5.34 (m, 1 H), 5.21 – 5.14 (m, 2H), 3.67 (s, 1.8 H), 3.52 (s, 1.2 H), 3.40 – 3.32 (m, 1 H), 2.35 – 2.22 (m, 1 H), 2.09 – 1.98 (m, 1 H), 1.81 – 1.67 (m, 2 H), 1.57 (d, J = 7.1 Hz, 3 H), 1.49 (br s, 1 H), 1.31 (d, J = 6.8 Hz, 1.2 H), and 0.90 (d, J = 6.6 Hz, 1.8 H).

^{13}C NMR (151 MHz, $CDCl_3$): δ 173.9, 173.7, 141.4, 141.2, 136.9, 128.6, 128.4, 128.4, 128.1, 128.0, 127.6, 127.4, 67.1, 67.1, 51.8, 51.5, 31.6, 31.3, 29.9, and 14.3.

HRMS (*m*/*z*): calcd for $C_{22}H_{27}NNaO_4$ $[M+Na]^+$: 392.1832, found: 392.1833.

IR (film) ν_{max}: 3063, 3028, 2951, 1736, 1686, 1435, 1374, 1286, 1206, 1166, 11114, 1026, 744, and 698 cm^{-1}.

TLC: R_f = 0.45 (8:2 hexanes:EtOAc).



46

Methyl 4-((*tert*-butoxycarbonyl)((*S*)-1-phenylethyl)amino)pentanoate (46). Following the general procedure, a mixture of *tert*-butyl (*S*)-(1-phenylethyl)(vinyl)carbamate[20] (14.3 mg, 57.8 µmol, 1.0 equiv), methyl acrylate (31.4 µL, 347 µmol, 6.0 equiv), Na_2HPO_4 (8.2 mg, 57.8 µmol, 1.0 equiv), $Fe(dibm)_3$ (4.5 mg, 8.7 µmol, 15 mol %), and $PhSiH_3$ (42.8 µL, 347 µmol, 6.0 equiv) in EtOH (0.29 mL) was heated at 60 °C with stirring for 1h. Purification by preparative TLC (SiO_2, 9:1 hexanes:EtOAc) furnished a 1:1.4 diastereomeric mixture of carbamates **46** as a colorless oil (10.7 mg, 31.9 µmol, 55%). Data is reported for the mixture of diastereomers.

Physical State: colorless oil.

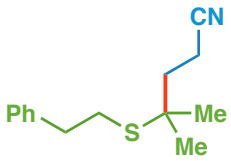
^{1}H NMR (500 MHz, $CDCl_3$, 50 °C): δ 7.35 – 7.21 (m, 5 H), 5.26 (m, 1 H), 3.69 (s, 1.75 H), 3.54 (s, 1.25 H), 3.39 – 3.26 (m, 1 H), 2.36 – 2.25 (m, 1 H), 2.06 – 1.93 (m, 1 H), 1.81 – 1.67 (m, 2 H), 1.56 – 1.54 (m, 3 H), 1.48 – 1.44 (m, 9 H), 1.30 (d, J = 6.7 Hz, 1.25 H), and 0.90 (d, J = 6.8 Hz, 1.75 H).

^{13}C NMR (151 MHz, $CDCl_3$): δ 173.5, 173.3, 127.7, 127.6, 126.8, 126.4, 79.3, 52.8, 52.0, 51.2, 51.0, 31.1, 30.9, 30.2, 30.2, 28.1, and 18.1. 13 carbons were not observed due to incidental equivalence.

HRMS (*m*/*z*): calcd for $C_{19}H_{29}NNaO_4$ $[M+Na]^+$: 358.1989, found: 358.1988.

IR (film) ν_{max}: 3028, 2974, 2934, 1737, 1679, 1433, 1365, 1299, 1251, 1159, 1120, 1023, 772, and 700 cm^{-1}.

TLC: R_f = 0.57 (8:2 hexanes:EtOAc).



47

4-Methyl-4-(phenethylthio)pentanenitrile (47). Following the general procedure, a mixture of **S1** (17.8 mg, 100 µmol, 1.0 equiv), acrylonitrile (19.8 µL, 300 µmol, 3.0 equiv), Na_2HPO_4 (14.2 mg, 100 µmol, 1.0 equiv), $Fe(dibm)_3$ (2.6 mg, 5.0 µmol, 5 mol %), and $PhSiH_3$ (24.6 µL, 200 µmol, 2.0 equiv) in EtOH (0.50 mL) was stirred at room temperature for 1 h. Purification by flash column chromatography (SiO_2, 50:1→20:1 hexanes:EtOAc) furnished thioether **47** as a colorless oil (15.2 mg, 65.2 µmol, 65%).

Physical State: colorless oil.

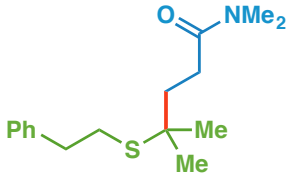
^{1}H NMR (600 MHz, $CDCl_3$): δ 7.31 (dd, *J* = 7.8, 7.2 Hz, 2 H), 7.25 – 7.20 (m, 3 H), 2.84 (dd, *J* = 8.4, 7.2 Hz, 2 H), 2.70 (dd, *J* = 8.4, 7.2 Hz, 2 H), 2.43 (dd, *J* = 8.4, 7.8 Hz, 2 H), 1.85 (dd, *J* = 8.4, 7.8 Hz, 2 H), and 1.29 (s, 6 H).

^{13}C NMR (151 MHz, $CDCl_3$): δ 140.5, 128.7, 128.6, 126.7, 120.3, 44.7, 37.4, 35.9, 29.6, 28.7, and 13.2.

HRMS (*m*/*z*): calcd for $C_{14}H_{20}NS$ $[M+H]^+$: 234.1311, found: 234.1312.

IR (film) ν_{max}: 2959, 2925, 1453, 1126, 732, and 696 cm^{-1}.

TLC: R_f = 0.41 (10:1 hexanes:EtOAc).



48

***N*,*N*,4-Trimethyl-4-(phenethylthio)pentanamide (48).** Following the general procedure, a mixture of **S1** (17.8 mg, 100 µmol, 1.0 equiv), *N*,*N*-dimethylacrylamide (31.0 µL, 300 µmol, 3.0 equiv), Na_2HPO_4 (14.2 mg, 100 µmol, 1.0 equiv), $Fe(dibm)_3$ (2.6 mg, 5.0 µmol, 5 mol %), and $PhSiH_3$ (24.6 µL, 200 µmol, 2.0 equiv) in EtOH (0.50 mL) was stirred at room temperature for 1 h. Purification by flash column chromatography (SiO_2, 3:1→2:1 hexanes:EtOAc) furnished thioether **48** as a colorless oil (18.7 mg, 67.0 µmol, 67%).

Physical State: colorless oil.

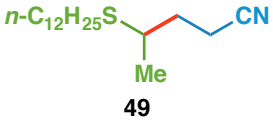
^{1}H NMR (600 MHz, $CDCl_3$): δ 7.30 – 7.27 (m, 2 H), 7.21 – 7.19 (m, 3 H), 2.99 (s, 3 H), 2.94 (s, 3 H), 2.83 (dd, *J* = 7.8, 7.8 Hz, 2 H), 2.73 (dd, *J* = 7.8, 7.8 Hz, 2 H), 2.43 – 2.40 (m, 2 H), 1.87 – 1.84 (m, 2 H), and 1.29 (s, 6 H).

^{13}C NMR (151 MHz, $CDCl_3$): δ 173.0, 140.9, 128.6, 128.5, 126.4, 45.3, 37.4, 36.8, 36.2, 35.6, 29.5, 29.2, and 29.1.

HRMS (*m*/*z*): calcd for $C_{16}H_{26}NOS$ $[M+H]^+$: 280.1730, found: 280.1734.

IR (film) ν_{max}: 2923, 2852, 1642, 1453, 1397, 1129, 736, and 698 cm^{-1}.

TLC: R_f = 0.58 (1:1 hexanes:EtOAc).



49

4-(Dodecylthio)pentanenitrile (49). Following the general procedure, a mixture of lauryl vinyl sulfide[21] (22.8 mg, 100 µmol, 1.0 equiv), acrylonitrile (19.8 µL, 300 µmol, 3.0 equiv), Na_2HPO_4 (14.2 mg, 100 µmol, 1.0 equiv), $Fe(dibm)_3$ (2.6 mg, 5.0 µmol, 5 mol %), and $PhSiH_3$ (24.6 µL, 200 µmol, 2.0 equiv) in EtOH (0.50 mL) was stirred at 60 °C for 1 h. A solution of TBAF (1 M in THF, 600 µL, 600 µmol, 6.0 equiv) was then added and the reaction mixture was heated at 60 °C with stirring for 1 h. Purification by flash column chromatography (SiO_2, 100:1→50:1 hexanes:EtOAc) furnished thioether **49** as a colorless oil (13.6 mg, 48.1 µmol, 48%).

Physical State: colorless oil.

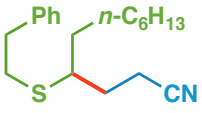
^{1}H NMR (600 MHz, $CDCl_3$): δ 2.86 – 2.82 (m, 1 H), 2.61 – 2.47 (m, 2 H), 2.51 (dd, *J* = 7.8, 7.2 Hz, 2 H), 1.92 – 1.86 (m, 1 H), 1.83 – 1.78 (m, 1 H), 1.59 – 1.55 (m, 2 H), 1.32 (d, *J* = 6.6 Hz, 3 H), 1.37 – 1.26 (m, 18 H), and 0.88 (dd, *J* = 7.2, 6.6 Hz, 3 H).

^{13}C NMR (151 MHz, $CDCl_3$): δ 119.7, 39.1, 32.4, 32.1, 30.5, 29.9, 29.8, 29.8, 29.7, 29.7, 29.5, 29.4, 29.1, 22.8, 21.7, 15.1, and 14.3.

HRMS (*m*/*z*): calcd for $C_{17}H_{34}NS$ $[M+H]^+$: 284.2407, found: 284.2409.

IR (film) ν_{max}: 2921, 2852, 1457, 1377, 721, and 671 cm^{-1}.

TLC: R_f = 0.33 (10:1 hexanes:EtOAc).



50

4-(Phenethylthio)undecanenitrile (50). Following the general procedure, a mixture of **S2** (24.8 mg, 100 µmol, 1.0 equiv), acrylonitrile (19.8 µL, 300 µmol, 3.0 equiv), Na_2HPO_4 (14.2 mg, 100 µmol, 1.0 equiv), $Fe(dibm)_3$ (7.9 mg, 15.0 µmol, 15 mol %), and $PhSiH_3$ (73.8 µL, 600 µmol, 6.0 equiv) in EtOH (0.50 mL) was stirred at room temperature for 1 h. A second portion of acrylonitrile (19.8 µL, 300 µmol, 3.0 equiv), $Fe(dibm)_3$ (7.9 mg, 15 µmol, 15 mol %), and $PhSiH_3$ (73.8 µL, 600 µmol, 6.0 equiv) was added. After stirring at room temperature for an additional 1 h, a solution of TBAF (1 M in THF, 1.20 mL, 1.20 mmol, 12.0 equiv) was added and the reaction mixture was heated at 60 °C with stirring for 1 h. Purification by flash column chromatography (SiO_2, 100:1→50:1 hexanes:EtOAc) furnished thioether **50** as a colorless oil (12.1 mg, 39.9 µmol, 40%).

Physical State: colorless oil.

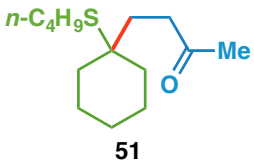
^{1}H NMR (600 MHz, $CDCl_3$): δ 7.31 (dd, *J* = 7.8, 7.2 Hz, 2 H), 7.24 – 7.20 (m, 3 H), 2.87 (dd, *J* = 8.4, 7.2 Hz, 2 H), 2.75 (dd, *J* = 8.4, 7.2 Hz, 2 H), 2.67 – 2.63 (m, 1 H), 2.57 – 2.52 (m, 1 H), 2.49 – 2.44 (m, 1 H), 1.97 – 1.91 (m, 1 H), 1.75 – 1.69 (m, 1 H), 1.57 – 1.21 (m, 12 H), and 0.89 (dd, *J* = 7.2, 6.6 Hz, 3 H).

^{13}C NMR (151 MHz, $CDCl_3$): δ 140.4, 128.7, 128.6, 126.6, 119.9, 45.3, 36.5, 35.3, 32.1, 31.9, 30.5, 29.6, 29.3, 27.0, 22.8, 14.9, and 14.2.

HRMS (*m*/*z*): calcd for $C_{19}H_{30}NS$ $[M+H]^+$: 304.2093, found: 304.2099.

IR (film) ν_{max}: 2924, 2853, 1453, 1131, 697 and 671 cm^{-1}.

TLC: R_f = 0.40 (10:1 hexanes:EtOAc).



51

4-(1-(Butylthio)cyclohexyl)butan-2-one (51). A solution of methyl vinyl ketone (49.6 µL, 600 µmol, 6.0 equiv) and $PhSiH_3$ (73.8 µL, 600 µmol, 6.0 equiv) in EtOH (0.50 mL) was added slowly via syringe pump to a mixture of butyl cyclohex-1-enyl sulfide[22] (17.0 mg, 100 µmol, 1.0 equiv), Na_2HPO_4 (14.2 mg, 100 µmol, 1.0 equiv), $Fe(dibm)_3$ (2.6 mg, 5.0 µmol, 5 mol %) in EtOH (0.5 mL) while stirring at room temperature for 1 h. After stirring at room temperature for an additional 1 h, a solution of TBAF (1 M in THF, 600 µL, 600 µmol, 6.0 equiv) was added and the reaction mixture was heated at 60 °C with stirring for 1 h. Purification by flash column chromatography (SiO_2, 100:1→50:1 hexanes:EtOAc) furnished thioether **51** as a colorless oil (11.8 mg, 48.8 µmol, 49%).

Physical State: colorless oil.

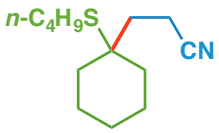
^{1}H NMR (600 MHz, $CDCl_3$): δ 2.64 (dd, *J* = 7.8, 7.8 Hz, 2 H), 2.31 (dd, *J* = 7.8, 7.8 Hz, 2 H), 2.17 (s, 3 H), 1.76 (dd, *J* = 7.8, 7.8 Hz, 2 H), 1.71 – 1.63 (m, 4 H), 1.54 – 1.36 (m, 9 H), 1.31 – 1.25 (m, 1 H), and 0.90 (t, *J* = 7.2 Hz, 3 H).

^{13}C NMR (151 MHz, $CDCl_3$): δ 209.3, 49.2, 38.6, 36.6, 33.1, 31.7, 30.4, 26.2, 26.2, 22.5, 22.1, and 13.9.

HRMS (*m*/*z*): calcd for $C_{14}H_{27}OS$ $[M+H]^+$: 243.1777, found: 243.1776.

IR (film) ν_{max}: 2925, 2854, 1714, 1447, 1355, and 1160 cm^{-1}.

TLC: R_f = 0.62 (10:1 hexanes:EtOAc).



52

3-(1-(Butylthio)cyclohexyl)propanenitrile (52). Following the general procedure, a mixture of butyl cyclohex-1-enyl sulfide[22] (17.0 mg, 100 µmol, 1.0 equiv), acrylonitrile (19.8 µL, 300 µmol, 3.0 equiv), Na_2HPO_4 (14.2 mg, 100 µmol, 1.0 equiv), $Fe(dibm)_3$ (2.6 mg, 5.0 µmol, 5 mol %), and $PhSiH_3$ (24.6 µL, 200 µmol, 2.0 equiv) in EtOH (0.50 mL) was stirred at room temperature for 1 h. A solution of TBAF (1 M in THF, 600 µL, 600 µmol, 6.0 equiv) was then added and the reaction mixture was heated at 60 °C with stirring for 1 h. Purification by flash column chromatography (SiO_2, 100:1→50:1 hexanes:EtOAc) furnished thioether **52** as a colorless oil (11.3 mg, 50.2 µmol, 50%).

Physical State: colorless oil.

^{1}H NMR (600 MHz, $CDCl_3$): δ 2.56 – 2.54 (m, 2 H), 2.31 (t, J = 7.2 Hz, 2 H), 1.86 – 1.83 (m, 2 H), 1.73 – 1.64 (m, 4 H), 1.60 – 1.34 (m, 9 H), 1.31 – 1.25 (m, 1 H), and 0.92 (t, J = 7.2 Hz, 3 H).

^{13}C NMR (151 MHz, $CDCl_3$): δ 120.7, 49.0, 36.0, 35.9, 31.6, 26.3, 26.0, 22.5, 21.9, 13.9, and 12.2.

HRMS (*m*/*z*): calcd for $C_{13}H_{24}NS$ $[M+H]^+$: 226.1624, found: 226.1621.

IR (film) ν_{max}: 2928, 2856, 2310, 1452, and 670 cm^{-1}.

TLC: R_f = 0.65 (10:1 hexanes:EtOAc).

53

4-(Phenylthio)pentanenitrile (53). Following the general procedure, a mixture of phenyl vinyl sulfide (13.6 mg, 100 µmol, 1.0 equiv), acrylonitrile (19.6 µL, 300 µmol, 3.0 equiv), Na_2HPO_4 (14.2 mg, 100 µmol, 1.0 equiv), $Fe(dibm)_3$ (2.6 mg, 5.0 µmol, 5 mol %), and $PhSiH_3$ (73.8 µL, 600 µmol, 6.0 equiv) in EtOH (0.50 mL) was stirred at room temperature for 1 h. Purification by flash column chromatography (SiO_2, 50:1→20:1 hexanes:EtOAc) furnished thioether **53** as a colorless oil (12.8 mg, 67.0 µmol, 67%).

Physical State: colorless oil.

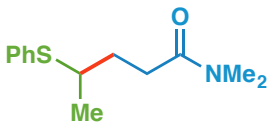
^{1}H NMR (600 MHz, $CDCl_3$): δ 7.43 – 7.41 (m, 2 H), 7.34 – 7.31 (m, 2 H), 7.30 – 7.28 (m, 1 H), 3.27 (dqd, J = 6.8, 6.8, 6.8 Hz, 1 H), 2.62 – 2.50 (m, 2 H), 1.92 – 1.83 (m, 2 H), and 1.32 (d, J = 7.2 Hz, 3 H).

^{13}C NMR (151 MHz, $CDCl_3$): δ 133.5, 133.1, 129.2, 127.8, 119.4, 42.6, 32.0, 21.1, and 15.0.

HRMS (*m*/*z*): calcd for $C_{11}H_{14}NS$ $[M+H]^+$: 192.0841, found: 192.0845.

IR (film) ν_{max}: 2962, 2925, 2866, 2247, 1582, 1475, 1439, 1023, 744, and 692 cm^{-1}.

TLC: R_f = 0.39 (10:1 hexanes:EtOAc).



54

***N,N*-Dimethyl-4-(phenylthio)pentanamide (54).** Following the general procedure, a mixture of phenyl vinyl sulfide (13.6 mg, 100 µmol, 1.0 equiv), *N,N*-dimethylacrylamide (31.0 µL, 300 µmol, 3.0 equiv), Na_2HPO_4 (14.2 mg, 100 µmol, 1.0 equiv), $Fe(dibm)_3$ (2.6 mg, 5.0 µmol, 5 mol %), and $PhSiH_3$ (73.8 µL, 600 µmol, 6.0 equiv) in EtOH (0.50 mL) was stirred at room temperature for 1 h. Purification by flash column chromatography (SiO_2, 2:1→1:1 hexanes:EtOAc) furnished thioether **54** as a colorless oil (11.4 mg, 48.1 µmol, 48%).

Physical State: colorless oil.

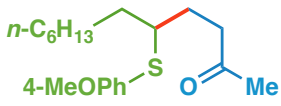
^{1}H NMR (600 MHz, $CDCl_3$): δ 7.38 (d, *J* = 7.8 Hz, 2 H), 7.25 (dd, *J* = 7.8, 7.2 Hz, 2 H), 7.21 (dd, *J* = 7.2, 7.2 Hz, 1 H), 3.32 (dqd, *J* = 6.7, 6.7, 6.7 Hz, 1 H), 2.96 (s, 3 H), 2.92 (s, 3 H), 2.55 – 2.49 (m, 2 H), 2.01 – 1.95 (m, 1 H), 1.87 – 1.81 (m, 1 H), and 1.32 (d, *J* = 6.6 Hz, 3 H).

^{13}C NMR (151 MHz, $CDCl_3$): δ 172.5, 135.2, 131.9, 129.0, 126.8, 43.2, 37.3, 35.5, 32.0, 30.7, and 21.7.

HRMS (*m*/*z*): calcd for $C_{13}H_{20}NOS$ $[M+H]^+$: 238.1260, found: 238.1267.

IR (film) ν_{max}: 2925, 1641, 1424, 1270, 991, 757, and 671 cm^{-1}.

TLC: R_f = 0.31 (1:1 hexanes:EtOAc).



55

5-((4-Methoxyphenyl)thio)dodecan-2-one (55). A solution of methyl vinyl ketone (49.6 µL, 600 µmol, 6.0 equiv) and $PhSiH_3$ (73.8 µL, 600 µmol, 6.0 equiv) in EtOH (0.5 mL) was added slowly via syringe pump to a mixture of **S3** (25.0 mg, 100 µmol, 1.0 equiv), Na_2HPO_4 (14.2 mg, 100 µmol, 1.0 equiv), $Fe(dibm)_3$ (2.6 mg, 5.0 µmol, 5 mol %) in EtOH (0.50 mL) while stirring at room temperature for 1 h. Purification by flash column chromatography (SiO_2, 50:1→20:1 hexanes:EtOAc) furnished thioether **55** as a colorless oil (11.2 mg, 34.8 µmol, 35%).

Physical State: colorless oil.

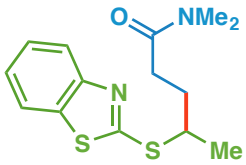
^{1}H NMR (600 MHz, $CDCl_3$): δ 7.34 (d, *J* = 7.8 Hz, 2 H), 6.83 (d, *J* = 7.8 Hz, 2 H), 3.80 (s, 3 H), 2.86 – 2.83 (m, 1 H), 2.66 – 2.69 (m, 2 H), 2.13 (s, 3 H), 1.89 – 1.83 (m, 1 H), 1.68 – 1.62 (m, 1 H), 1.51 – 1.42 (m, 4 H), 1.29 – 1.22 (m, 8 H), and 0.88 (dd, *J* = 7.2, 6.6 Hz, 3 H).

^{13}C NMR (151 MHz, $CDCl_3$): δ 208.8, 159.6, 135.8, 124.7, 114.6, 55.5, 50.0, 40.9, 34.9, 32.0, 30.2, 29.6, 29.3, 28.1, 27.0, 22.8, and 14.3.

HRMS (*m*/*z*): calcd for $C_{19}H_{31}O_2S$ $[M+H]^+$: 323.2039, found: 323.2047.

IR (film) ν_{max}: 2924, 2853, 1714, 1592, 1492, 1242, 826, and 670 cm^{-1}.

TLC: R_f = 0.31 (10:1 hexanes:EtOAc).



56

4-(Benzo[d]thiazol-2-ylthio)-*N*,*N*-dimethylpentanamide (56). Following the general procedure, a mixture of 2-(vinylthio)benzo[*d*]thiazole[23] (19.3 mg, 100 µmol, 1.0 equiv), *N*,*N*-dimethylacrylamide (31.0 µL, 300 µmol, 3.0 equiv), Na_2HPO_4 (14.2 mg, 100 µmol, 1.0 equiv), $Fe(dibm)_3$ (2.6 mg, 5.0 µmol, 5 mol %), and $PhSiH_3$ (24.6 µL, 200 µmol, 2.0 equiv) in EtOH (0.50 mL) was stirred at room temperature for 1 h. Purification by flash column chromatography (SiO_2, 2:1→1:1 hexanes:EtOAc) furnished thioether **56** as a colorless oil (16.0 mg, 54.4 µmol, 54%).

Physical State: colorless oil.

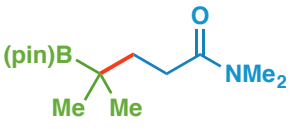
^{1}H NMR (600 MHz, $CDCl_3$): δ 7.85 (d, *J* = 8.4 Hz, 1 H), 7.75 (d, *J* = 7.8 Hz, 1 H), 7.41 (dd, *J* = 7.8, 7.2 Hz, 1 H), 7.29 (dd, *J* = 7.8, 7.8 Hz, 1 H), 4.06 (dqd, *J* = 6.8, 6.8, 6.8 Hz, 1 H), 2.94 (s, 3 H), 2.93 (s, 3 H), 2.58 – 2.49 (m, 2 H), 2.22 – 2.17 (m, 1 H), 2.07 – 2.00 (m, 1 H), and 1.55 (d, *J* = 6.6 Hz, 3 H).

^{13}C NMR (151 MHz, $CDCl_3$): δ 172.1, 166.3, 153.4, 135.5, 126.1, 124.4, 121.7, 121.1, 44.6, 37.3, 35.6, 32.2, 30.8, and 22.1.

HRMS (*m*/*z*): calcd for $C_{14}H_{19}N_2OS_2$ $[M+H]^+$: 295.0933, found: 295.0939.

IR (film) ν_{max}: 2925, 1642, 1424, 991, 757, and 671 cm^{-1}.

TLC: R_f = 0.24 (1:1 hexanes:EtOAc).



57

***N*,*N*,4-Trimethyl-4-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)pentanamide (57).** Following the general procedure, a mixture of isopropenylboronic acid pinacol ester (30.0 mg, 179 µmol, 1.0 equiv), *N*,*N*-dimethylacrylamide (55.2 µL, 536 µmol, 3.0 equiv), Na_2HPO_4

(25.3 mg, 179 µmol, 1.0 equiv), $Fe(acac)_3$ (3.2 mg, 8.9 µmol, 5 mol %), and $PhSiH_3$ (66.0 µL, 536 µmol, 3.0 equiv) in EtOH (0.89 mL) was heated at 60 °C with stirring for 1 h. Purification by flash column chromatography (SiO_2, 1:1 hexanes:EtOAc) furnished boronic ester **57** as a pale yellow oil (33.8 mg, 126 µmol, 70%).

Physical State: pale yellow oil.

^{1}H NMR (600 MHz, $CDCl_3$): δ 3.02 (s, 3 H), 2.92 (s, 3 H), 2.31 – 2.28 (m, 2 H), 1.60 – 1.57 (m, 2 H), 1.21 (s, 12 H), and 0.94 (s, 6 H).

^{13}C NMR (151 MHz, $CDCl_3$): δ 174.0, 83.1, 37.5, 36.3, 35.5, 31.0, 24.9, and 24.8. The boron–bound carbon was not observed due to quadrupolar relaxation.

^{11}B NMR (128 MHz, $CDCl_3$): δ 15.2.

HRMS (*m*/*z*): calcd for $C_{14}H_{29}BNO_3$ $[M+H]^+$: 270.2235, found: 270.2234.

IR (film) ν_{max}: 2974, 2934, 2862, 1645, 1474, 1391, 1366, 1307, 1270, 1212, 1132, 966, and 853 cm^{-1}.

TLC: R_f = 0.39 (1:1 hexanes:EtOAc).

58

***N*,*N*,4-Trimethyl-4-(6-methyl-4,8-dioxo-1,3,6,2-dioxazaborocan-2-yl)pentanamide (58).** Following the general procedure using THF as a cosolvent, a mixture of isopropenylboronic acid MIDA ester (30.0 mg, 152 µmol, 1.0 equiv), *N*,*N*-dimethylacrylamide (47.1 µL, 457 µmol, 3.0 equiv), Na_2HPO_4 (21.6 mg, 153 µmol, 1.0 equiv), $Fe(acac)_3$ (2.7 mg, 7.6 µmol, 5 mol %), and $PhSiH_3$ (56.3 µL, 457 µmol, 3.0 equiv) in EtOH (0.38 mL) and THF (0.38 mL) was heated at 60 °C with stirring for 30 min. Purification by flash column chromatography (SiO_2, 94:6→9:1 DCM:MeOH) furnished MIDA boronate **58** as a colorless amorphous solid (26.2 mg, 87.9 µmol, 58%).

Physical State: colorless amorphous solid.

^{1}H NMR (600 MHz, acetone-d_6): δ 4.18 (d, *J* = 16.9 Hz, 2 H), 4.03 (d, *J* = 16.8 Hz, 2 H), 3.28 (s, 3 H), 3.03 (s, 3 H), 2.84 (s, 3 H), 2.36 – 2.33 (m, 2 H), 1.66 – 1.64 (m, 2 H), and 0.95 (s, 6 H).

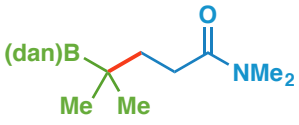
^{13}C NMR (151 MHz, acetone-d_6): δ 173.9, 168.9, 64.0, 47.3, 37.4, 35.3, 35.1, 28.6, and 23.9. The boron–bound carbon was not observed due to quadrupolar relaxation.

^{11}B NMR (128 MHz, acetone-d_6): δ –6.4.

HRMS (*m*/*z*): calcd for $C_{13}H_{24}BN_2O_5$ $[M+H]^+$: 299.1773, found: 299.1779.

IR (film) ν_{max}: 2999, 2949, 2872, 1739, 1604, 1472, 1404, 1343, 1302, 1251, 1044, 984, and 858 cm^{-1}.

TLC: R_f = 0.19 (95:5 DCM:MeOH).



59

***N*,*N*,4-Trimethyl-4-(1*H*-naphtho[1,8-*de*][1,3,2]diazaborinin-2(3*H*)-yl)pentanamide (59).** Following the general procedure, a mixture of **S4** (30.0 mg, 144 µmol, 1.0 equiv), *N*,*N*-dimethylacrylamide (44.6 µL, 433 µmol, 3.0 equiv), Na_2HPO_4 (20.5 mg, 144 µmol, 1.0 equiv), $Fe(acac)_3$ (2.6 mg, 7.2 µmol, 5 mol %), and $PhSiH_3$ (53.3 µL, 433 µmol, 3.0 equiv) in EtOH (0.72 mL) was heated at 60 °C with stirring for 50 min. Purification by flash column chromatography (SiO_2, 3:7→2:8 hexanes:EtOAc) furnished boronamide **59** as a colorless amorphous solid (31.6 mg, 102 µmol, 71%).

Physical State: colorless amorphous solid.

^{1}H NMR (600 MHz, $CDCl_3$): δ 7.10 (dd, *J* = 7.4, 8.2 Hz, 2 H), 7.00, (dd, *J* = 0.8, 8.3 Hz, 2 H), 6.34 (dd, *J* = 0.9, 7.3 Hz, 2 H), 5.77 (br s, 2 H), 2.96 (s, 3 H), 2.92 (s, 3 H), 2.31 – 2.28(m, 2 H), 1.71 – 1.69 (m, 2 H), and 1.04 (s, 6 H).

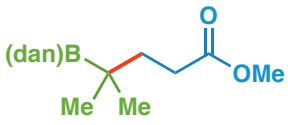
^{13}C NMR (151 MHz, $CDCl_3$): δ 173.5, 141.2, 136.4, 127.7, 119.6, 117.6, 105.9, 37.4, 36.5, 35.6, 30.2, and 25.7. The boron–bound carbon was not observed due to quadrupolar relaxation.

^{11}B NMR (128 MHz, $CDCl_3$): δ 14.2.

HRMS (*m*/*z*): calcd for $C_{18}H_{25}BN_3O$ $[M+H]^+$: 310.2085, found: 310.2086.

IR (film) ν_{max}: 2930, 2862, 1621, 1596, 1515, 1472, 1407, 1318, 1149, 1108, 909, and 821 cm^{-1}.

TLC: R_f = 0.21 (3:7 hexanes:EtOAc).



60

Methyl 4-methyl-4-(1*H*-naphtho[1,8-*de*][1,3,2]diazaborinin-2(3*H*)-yl)pentanoate (60). Following the general procedure, a mixture of **S4** (30.0 mg, 144 µmol, 1.0 equiv), methyl acrylate (39.2 µL, 433 µmol, 3.0 equiv), Na_2HPO_4 (20.5 mg, 144 µmol, 1.0 equiv), $Fe(acac)_3$ (2.6 mg, 7.2 µmol, 5 mol %), and $PhSiH_3$ (53.3 µL, 433 µmol, 3.0 equiv) in EtOH (0.72 mL) was heated at 60 °C with stirring for 70 min. Purification by flash column chromatography (SiO_2, 9:1 hexanes:EtOAc) furnished boronamide **60** as a colorless oil (36.5 mg, 123 µmol, 86%).

Physical State: colorless oil.

^{1}H NMR (600 MHz, $CDCl_3$): δ 7.11 (dd, J = 7.8 Hz, 2 H), 7.02 (d, J = 8.1 Hz, 2 H), 6.34 (d, J = 7.3 Hz, 2 H), 5.65 (br s, 2 H), 3.64 (s, 3 H), 2.34 – 2.31 (m, 2 H), 1.71 – 1.69 (m, 2 H), and 1.03 (s, 6 H).

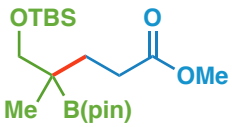
^{13}C NMR (151 MHz, $CDCl_3$): δ 174.7, 141.1, 136.4, 127.7, 119.6, 117.7, 105.9, 51.8, 36.4, 31.2, and 25.3. The boron–bound carbon was not observed due to quadrupolar relaxation.

^{11}B NMR (128 MHz, $CDCl_3$): δ 13.7.

HRMS (*m*/*z*): calcd for $C_{17}H_{22}BN_2O_2$ $[M+H]^+$: 297.1769, found: 297.1769.

IR (film) ν_{max}: 3052, 2946, 2859, 1721, 1506, 1409, 1371, 1319, 1164, 1105, 907, 818, and 762 cm^{-1}.

TLC: R_f = 0.32 (9:1 hexanes:EtOAc).



61

Methyl 5-((*tert*-butyldimethylsilyl)oxy)-4-methyl-4-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)pentanoate (61). Following the general procedure, a mixture of *tert*-butyldimethyl((2-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)allyl)oxy)silane[24] (30.0 mg, 101 µmol, 1.0 equiv), methyl acrylate (27.3 µL, 302 µmol, 3.0 equiv), Na_2HPO_4 (14.3 mg, 101 µmol, 1.0 equiv), $Fe(acac)_3$ (1.8 mg, 5.0 µmol, 5 mol %), and $PhSiH_3$ (37.2 µL, 302 µmol, 3.0 equiv) in EtOH (0.50 mL) was heated at 60 °C with stirring for 70 min. Purification by flash column chromatography (SiO_2, 9:1 hexanes:EtOAc) furnished boronic ester **61** as a colorless oil (18.3 mg, 47.4 µmol, 47%).

Physical State: colorless oil.

^{1}H NMR (600 MHz, $CDCl_3$): δ 3.65 (s, 3 H), 3.48 (d, J = 9.2 Hz, 1 H), 3.43 (d, J = 9.2 Hz, 1 H), 2.34 – 2.31 (m, 2 H), 1.78 (ddd, J = 7.2, 9.6, 13.3 Hz, 1 H), 1.58 – 1.52 (m, 1 H), 1.22 (s, 12 H), 0.91 (s, 3 H), 0.88 (s, 9 H), –0.02 (s, 3 H), and –0.02 (s, 3 H).

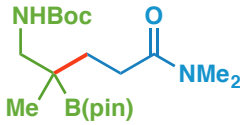
^{13}C NMR (151 MHz, $CDCl_3$): δ 174.9, 83.3, 69.9, 51.6, 30.8, 30.3, 26.1, 24.9, 18.8, 18.4, and –5.4. The boron–bound carbon was not observed due to quadrupolar relaxation.

^{11}B NMR (128 MHz, $CDCl_3$): δ 15.0.

HRMS (*m*/*z*): calcd for $C_{19}H_{40}BO_5Si$ $[M+H]^+$: 387.2733, found: 387.2235.

IR (film) ν_{max}: 2953, 2929, 2856, 1741, 1462, 1372, 1315, 1255, 1144, 1080, 837, and 775 cm^{-1}.

TLC: R_f = 0.47 (9:1 hexanes:EtOAc).



62

***tert*-Butyl (5-(dimethylamino)-2-methyl-5-oxo-2-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)pentyl)carbamate (62).**

Following the general procedure, a mixture of *tert*-butyl (2-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)allyl)carbamate[24] (15.0 mg, 53.0 µmol, 1.0 equiv), *N,N*-dimethylacrylamide (16.4 µL, 159 µmol, 3.0 equiv), Na_2HPO_4 (7.5 mg, 53.0 µmol, 1.0 equiv), $Fe(acac)_3$ (0.9 mg, 2.7 µmol, 5 mol %), and $PhSiH_3$ (19.6 µL, 159 µmol, 3.0 equiv) in EtOH (0.27 mL) was heated at 60 °C with stirring for 1 h. Purification by preparative TLC (SiO_2, 94:6 DCM:MeOH) furnished boronic ester **62** as a colorless oil (6.5 mg, 16.9 µmol, 32%).

Physical State: colorless oil.

^{1}H NMR (600 MHz, $CDCl_3$): δ 4.95 (br s, 1 H), 3.15 (dd, J = 12.8, 6.1 Hz, 1 H), 3.04 – 3.01 (m, 4 H), 2.93 (s, 3 H), 2.34 – 2.31 (m, 2 H), 1.75 – 1.70 (m, 2 H), 1.42 (s, 9 H), 1.23 (s, 12 H), and 0.94 (s, 3 H).

^{13}C NMR (151 MHz, $CDCl_3$): δ 173.6, 156.3, 83.5, 47.2, 37.5, 35.6, 31.2, 29.9, 29.5, 28.6, 25.0, 24.9, and 19.9. The boron–bound carbon was not observed due to quadrupolar relaxation.

^{11}B NMR (128 MHz, $CDCl_3$): δ 14.5.

HRMS (*m*/*z*): calcd for $C_{19}H_{38}BN_2O_5$ $[M+H]^+$: 385.2868, found: 385.2868.

IR (film) ν_{max}: 2926, 1712, 1640, 1508, 1458, 1367, 1316, 1261, 1168, 1142, 852, and 870 cm^{-1}.

TLC: R_f = 0.25 (94:6 DCM:MeOH).

63

Methyl 4-(dimethyl(phenyl)silyl)-4-methylpentanoate (63).

Following the general procedure, a mixture of dimethyl(phenyl)(prop-1-en-2-yl)silane[25] (17.6 mg, 100 µmol, 1.0 equiv), methyl acrylate (27.0 µL, 300 µmol, 3.0 equiv), Na_2HPO_4 (14.2 mg, 100 µmol, 1.0 equiv), $Fe(acac)_3$ (17.7 mg, 50.0 µmol, 50 mol %), and $PhSiH_3$ (25.0 µL, 200 µmol, 2.0 equiv) in *n*-PrOH (0.50 mL) was heated at 80 °C with stirring for 1 h. Purification by flash column chromatography (SiO_2, 10:1 hexanes:EtOAc) furnished silane **63** as a pale yellow oil (16.2 mg, 61.2 µmol, 61%).

Physical State: pale yellow oil.

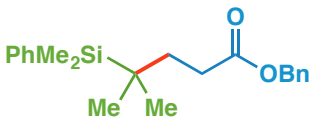
^{1}H NMR (600 MHz, $CDCl_3$): δ 7.52 – 7.50 (m, 2 H), 7.37 – 7.33 (m, 3 H), 3.64 (s, 3 H), 2.24 – 2.21 (m, 2 H), 1.65 – 1.62 (m, 2 H), 0.87 (s, 6 H), and 0.30 (s, 6 H).

^{13}C NMR (151 MHz, $CDCl_3$): δ 175.2, 137.4, 134.7, 129.1, 127.7, 51.7, 33.3, 28.6, 22.5, 19.4, and –5.7.

HRMS (*m*/*z*): calcd for $C_{15}H_{24}NaO_2Si$ $[M+Na]^+$: 287.1438, found: 287.1432.

IR (film) ν_{max}: 2955, 2861, 1738, 1464, 1429, 1365, 1253, 1194, 1111, 1018, 816, 770, 737, 668, and 475 cm^{-1}.

TLC: R_f = 0.60 (10:1 hexanes:EtOAc).



64

Benzyl 4-(dimethyl(phenyl)silyl)-4-methylpentanoate (64). Following the general procedure, a mixture of dimethyl(phenyl)(prop-1-en-2-yl)silane[25] (17.6 mg, 100 µmol, 1.0 equiv), acrylic acid (45.0 µL, 300 µmol, 3.0 equiv), $Fe(acac)_3$ (17.7 mg, 50.0 µmol, 50 mol %), and $PhSiH_3$ (25.0 µL, 200 µmol, 2.0 equiv) in *n*-PrOH (0.50 mL) was heated at 80 °C with stirring for 1 h. Purification by flash column chromatography (SiO_2, 10:1 hexanes:EtOAc) furnished silane **64** as a pale yellow oil (18.4 mg, 54.0 µmol, 54%).

Physical State: pale yellow oil.

^{1}H NMR (600 MHz, $CDCl_3$): δ 7.52 – 7.50 (m, 2 H), 7.38 – 7.31 (m, 8 H), 5.09 (s, 2 H), 2.29 – 2.26 (m, 2 H), 1.68 – 1.65 (m, 2 H), 0.87 (s, 6 H), and 0.30 (s, 6 H).

^{13}C NMR (151 MHz, $CDCl_3$): δ 174.6, 137.3, 136.2, 134.7, 129.1, 128.7, 128.7, 128.3, 127.7, 66.3, 33.2, 28.7, 22.5, 19.4, and –5.7.

HRMS (*m*/*z*): calcd for $C_{21}H_{28}NaO_2Si$ $[M+Na]^+$: 363.1751, found: 363.1753.

IR (film) ν_{max}: 3069, 2956, 2861, 1733, 1459, 1427, 1382, 1285, 1252, 1252, 1215, 1164, 1109, 1073, 1015, and 738 cm^{-1}.

TLC: R_f = 0.40 (20:1 hexanes:EtOAc).

65

4-(Dimethyl(phenyl)silyl)-4-methylpentanenitrile (65). Following the general procedure, a mixture of dimethyl(phenyl)(prop-1-en-2-yl)silane[25] (17.6 mg, 100 µmol, 1.0 equiv), acrylonitrile (19.7 µL, 300 µmol, 3.0 equiv), Na_2HPO_4 (14.2 mg, 100 µmol, 1.0 equiv), $Fe(acac)_3$ (17.7 mg, 50.0 µmol, 50 mol %), and $PhSiH_3$ (25.0 µL, 200 µmol, 3.0 equiv) in *n*-PrOH (0.50 mL) was heated at 80 °C with stirring for 1 h. Purification by flash column chromatography (SiO_2, 3:1 hexanes:EtOAc) furnished silane **65** as a pale yellow oil (19.5 mg, 84.2 µmol, 84%).

Physical State: pale yellow oil.

^{1}H NMR (600 MHz, $CDCl_3$): δ 7.51 – 7.49 (m, 2 H), 7.39 – 7.36 (m, 3 H), 2.20 – 2.17 (m, 2 H), 1.71 – 1.69 (m, 2 H), 0.91 (s, 6 H), and 0.31 (s, 6 H).

^{13}C NMR (151 MHz, $CDCl_3$): δ 136.5, 134.6, 129.4, 127.9, 121.0, 34.2, 22.0, 19.7, 11.4, and –6.0.

HRMS (*m*/*z*): calcd for $C_{14}H_{21}NNaSi$ $[M+Na]^+$: 254.1336, found: 254.1346.

IR (film) ν_{max}: 3070, 2957, 2863, 2245, 1464, 1427, 1252, 1109, 1081, 1015, and 737 cm^{-1}.

TLC: R_f = 0.60 (10:1 hexanes:EtOAc).

66

Dimethyl(2-methyl-4-(phenylsulfonyl)butan-2-yl)(phenyl)silane (66). Following the general procedure, a mixture of dimethyl(phenyl)(prop-1-en-2-yl)silane[25] (17.6 mg, 100 µmol, 1.0 equiv), phenyl vinyl sulfone (50.5 mg, 300 µmol, 3.0 equiv), $Fe(acac)_3$ (17.7 mg, 50.0 µmol, 100 mol %), and $PhSiH_3$ (25.0 µL, 200 µmol, 2.0 equiv) in *n*-PrOH (0.50 mL) was heated at 80 °C with stirring for 1 h. Purification by flash column chromatography (SiO_2, 5:1 hexanes:EtOAc) furnished silane **66** as a white solid (12.3 mg, 35.4 µmol, 35%).

Physical State: white solid.

Melting point: 112.0–114.0 °C

^{1}H NMR (600 MHz, $CDCl_3$): δ 7.84 – 7.82 (m, 2 H), 7.65 – 7.62 (m, 1 H), 7.55 – 7.52 (m, 2 H), 7.42 – 7.40 (m, 2 H), 7.37 – 7.34 (m, 1 H), 7.33 – 7.30 (m, 2 H), 2.95 – 2.93 (m, 2 H), 1.69 – 1.66 (m, 2 H), 0.82 (s, 6 H), and 0.25 (s, 6 H).

^{13}C NMR (151 MHz, $CDCl_3$): δ 139.3, 136.6, 134.5, 133.7, 129.3, 129.3, 128.1, 127.9, 51.7, 30.6, 22.7, 19.2, and –5.9.

HRMS (*m*/*z*): calcd for $C_{19}H_{26}NaO_2SSi$ $[M+Na]^+$: 369.1315, found: 369.1312.

IR (film) ν_{max}: 3278, 3268, 2927, 1300, 1256, 1147, 1087, 913, 817, 741, 689, 533, 438, and 419 cm^{-1}.

TLC: R_f = 0.40 (5:1 hexanes:EtOAc).

67

4-(Dimethyl(phenyl)silyl)-4-methylpentanoic acid (67). Omitting Na_2HPO_4 from the general procedure, a mixture of dimethyl(phenyl)(prop-1-en-2-yl)silane[25] (17.6 mg, 100 µmol, 1.0

equiv), acrylic acid (21.0 µL, 300 µmol, 3.0 equiv), $Fe(acac)_3$ (17.7 mg, 50.0 µmol, 50 mol %), and $PhSiH_3$ (25.0 µL, 200 µmol, 2.0 equiv) in *n*-PrOH (0.50 mL) was heated at 80 °C with stirring for 1 h. Purification by flash column chromatography (SiO_2, 3:1 DCM:MeOH) furnished silane **67** as a white solid (13.3 mg, 53.1 µmol, 53%).

Physical State: white solid.

^{1}H NMR (600 MHz, $CDCl_3$): δ 7.52 – 7.50 (m, 2 H), 7.37 – 7.33 (m, 3 H), 2.26 – 2.24 (m, 2 H), 1.66 – 1.63 (m, 2 H), 0.88 (s, 6 H), and 0.30 (s, 6 H).

^{13}C NMR (151 MHz, $CDCl_3$): δ 180.1, 137.3, 134.7, 129.1, 127.7, 33.1, 28.4, 22.5, 19.4, and –5.7.

HRMS (*m*/*z*): calcd for $C_{14}H_{22}NaOSi$ $[M+Na]^+$: 273.1821, found: 273.1290.

IR (film) ν_{max}: 3071, 2956, 2930, 2861, 1711, 1462, 1428, 1293, 1252, 1134, 1109, 909, and 817 cm^{-1}.

TLC: R_f = 0.25 (50:1 DCM:MeOH).

68

5-(Dimethyl(phenyl)silyl)-5-methylhexan-2-one (68). Following the general procedure, a mixture of dimethyl(phenyl)(prop-1-en-2-yl)silane[25] (17.6 mg, 100 µmol, 1.0 equiv), methyl vinyl ketone (49.0 µL, 600 µmol, 6.0 equiv), Na_2HPO_4 (14.2 mg, 100 µmol, 1.0 equiv), $Fe(acac)_3$ (17.7 mg, 50.0 µmol, 50 mol %), and $PhSiH_3$ (25.0 µL, 200 µmol, 2.0 equiv) in *n*-PrOH (0.50 mL) was heated at 80 °C with stirring for 1 h. Purification by flash column chromatography (SiO_2, 10:1 hexanes:EtOAc) furnished silane **68** as a pale yellow oil (14.8 mg, 59.5 µmol, 60%).

Physical State: pale yellow oil.

^{1}H NMR (600 MHz, $CDCl_3$): δ 7.52 – 7.50 (m, 2 H), 7.37 – 7.33 (m, 3 H), 2.32 – 2.29 (m, 2 H), 2.08 (s, 3 H), 1.57 – 1.55 (m, 2 H), 0.87 (s, 6 H), and 0.30 (s, 6 H).

^{13}C NMR (151 MHz, $CDCl_3$): δ 210.0, 137.5, 134.7, 129.1, 127.7, 38.1, 32.1, 30.1, 22.5, 19.3, and –5.7.

HRMS (*m*/*z*): calcd for $C_{15}H_{24}NaOSi$ $[M+Na]^+$: 271.1487, found: 271.1489.

IR (film) ν_{max}: 2956, 2860, 1714, 1466, 1427, 1361, 1251, 1134, 1111, 1069, 909, 818, and 770 cm^{-1}.

TLC: R_f = 0.45 (10:1 hexanes:EtOAc).

69

4-(Dimethyl(phenyl)silyl)-*N*,*N*,4-trimethylpentanamide (69). Following the general procedure, a mixture of dimethyl(phenyl)(prop-1-en-2-yl)silane[25] (17.6 mg, 100 µmol, 1.0 equiv), *N*,*N*-dimethylacrylamide (31.0 µL, 300 µmol, 3.0 equiv), Na_2HPO_4 (14.2 mg, 100 µmol, 1.0 equiv), $Fe(acac)_3$ (17.7 mg, 50.0 µmol, 50 mol %), and $PhSiH_3$ (25.0 µL, 200 µmol, 2.0 equiv) in *n*-PrOH (0.50 mL) was heated at 80 °C with stirring for 1 h. Purification by flash column chromatography (SiO_2, 3:1 hexanes:EtOAc) furnished silane **69** as pale yellow oil (19.4 mg, 69.9 µmol, 70%).

Physical State: pale yellow oil.

^{1}H NMR (600 MHz, $CDCl_3$): δ 7.52 – 7.51 (m, 2 H), 7.37 – 7.33 (m, 3 H), 2.90 (s, 3 H), 2.86 (s, 3 H) 2.19 – 2.16 (m, 2 H), 1.64 – 1.62 (m, 2 H), 0.91 (s, 6 H), and 0.30 (s, 6 H).

^{13}C NMR (151 MHz, $CDCl_3$): δ 174.0, 137.8, 134.7, 128.9, 127.7, 37.3, 33.6, 27.8, 22.9, 22.9, 19.6, and –5.7.

HRMS (*m*/*z*): calcd for $C_{16}H_{27}NNaOSi$ $[M+Na]^+$: 300.1754, found: 300.1754.

IR (film) ν_{max}: 2928, 2859, 1727, 1647, 1464, 1427, 1396, 1251, 1133, 1110, 830, and 815 cm^{-1}.

TLC: R_f = 0.20 (3:1 hexanes:EtOAc).

70

4-(Dimethyl(phenyl)silyl)-*N*,*N*-dimethylpentanamide (70). Following the general procedure, a mixture of dimethyl(phenyl)(vinyl)silane[26] (16.2 mg, 100 µmol, 1.0 equiv), *N*,*N*-dimethylacrylamide (62.0 µL, 600 µmol, 6.0 equiv), Na_2HPO_4 (14.2 mg, 100 µmol, 1.0 equiv), $Fe(acac)_3$ (17.7 mg, 50.0 µmol, 50 mol %), and $PhSiH_3$ (25.0 µL, 200 µmol, 2.0 equiv) in *n*-PrOH (0.50 mL) was heated at 80 °C with stirring for 1 h. Purification by flash column chromatography (SiO_2, 2:1 PhMe:EtOAc) furnished silane **70** as a pale yellow oil (13.3 mg, 50.5 µmol, 51%).

Physical State: pale yellow oil.

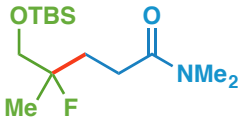
^{1}H NMR (600 MHz, $CDCl_3$): δ 7.51 – 7.49 (m, 2 H), 7.35 – 7.32 (m, 3 H), 2.90 (s, 3 H), 2.87 (s, 3 H), 2.42 – 2.37 (m, 1 H), 2.18 – 2.13 (m, 1 H), 1.86 – 1.82 (m, 1 H), 1.46 – 1.35 (m, 1 H), 0.96 (d, *J* = 7.2 Hz, 3 H), 0.92 – 0.87 (m, 1 H), 0.27 (s, 3 H), and 0.26 (s, 3 H).

^{13}C NMR (151 MHz, $CDCl_3$): δ 173.5, 134.1, 129.0, 128.9, 127.8, 37.3, 35.5, 32.8, 27.4, 19.4, 14.2, –4.6, and –5.0.

HRMS (*m*/*z*): calcd for $C_{15}H_{26}NOSi$ $[M+H]^+$: 264.1778, found: 264.1779.

IR (film) ν_{max}: 2928, 2013, 1979, 1368, 1398, 1251, 1112, 911, 816, 734, and 670 cm^{-1}.

TLC: R_f = 0.45 (2:1 PhMe:EtOAc).



71

5-((*tert*-Butyldimethylsilyl)oxy)-4-fluoro-*N*,*N*,4-trimethylpentanamide (71). Following the general procedure, a mixture of **S5** (30.0 mg, 158 µmol, 1.0 equiv), *N*,*N*-dimethylacrylamide (48.7 µL, 473 µmol, 3.0 equiv), Na_2HPO_4 (22.4 mg, 158 µmol, 1.0 equiv), $Fe(acac)_3$ (55.7 mg, 158 µmol, 100 mol %), and $PhSiH_3$ (58.3 µL, 473 µmol, 3.0 equiv) in EtOH (0.53 mL) was heated at 60 °C with stirring for 1 h. Purification by flash column chromatography (SiO_2, 7:3 hexanes:EtOAc) furnished fluoride **71** as a pale yellow oil (22.2 mg, 76.2 µmol, 48%).

Physical State: pale yellow oil.

^{1}H NMR (600 MHz, $CDCl_3$): δ 3.62 – 3.55 (m, 2 H), 3.02 (s, 3 H), 2.94 (s, 3 H), 2.48 – 2.40 (m, 2 H), 2.07 – 2.89 (m, 2 H), 1.30 (d, *J* = 21.8 Hz, 3 H), 0.89 (s, 9 H), 0.06 (s, 3 H), and 0.06 (s, 3 H).

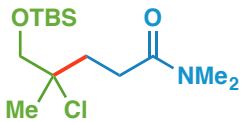
^{13}C NMR (151 MHz, $CDCl_3$): δ 172.7, 96.6 (d, *J* = 171.5 Hz), 68.5 (d, *J* = 28.6), 37.4, 35.6, 31.8 (d, *J* = 21.7 Hz), 27.4, 26.0, 21.5 (d, *J* = 24.1 Hz), 18.4, –5.29, and –5.34.

^{19}F NMR (376 MHz, $CDCl_3$): δ –156.6.

HRMS (*m*/*z*): calcd for $C_{14}H_{31}FNO_2Si$ $[M+H]^+$: 292.2103, found: 292.2105.

IR (film) ν_{max}: 2952, 2930, 2857, 1649, 1462, 1397, 1361, 1254, 1103, 837, 778, and 670 cm^{-1}.

TLC: R_f = 0.27 (7:3 hexanes:EtOAc).



72

5-((*tert*-Butyldimethylsilyl)oxy)-4-chloro-*N*,*N*,4-trimethylpentanamide (72). Following the general procedure, a mixture of **S6** (30.0 mg, 145 µmol, 1.0 equiv), *N*,*N*-dimethylacrylamide (44.9 µL, 435 µmol, 3.0 equiv), Na_2HPO_4 (20.6 mg, 145 µmol, 1.0 equiv), $Fe(acac)_3$ (51.2 mg, 145 µmol, 100 mol %), and $PhSiH_3$ (53.6 µL, 435 µmol, 3.0 equiv) in EtOH (0.73 mL) was heated at 60 °C with stirring for 1 h. Purification by flash column chromatography (SiO_2, 7:3 hexanes:EtOAc) furnished chloride **72** as a pale yellow oil (26.9 mg, 87.4 µmol, 60%).

Physical State: pale yellow oil.

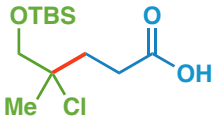
^{1}H NMR (600 MHz, $CDCl_3$): δ 3.67 (d, *J* = 10.1 Hz, 1 H), 3.61 (d, *J* = 10.1 Hz, 1 H), 3.03 (s, 3 H), 2.95 (s, 3 H), 2.52 (m, 2 H), 2.11 (m, 2 H), 1.51 (s, 3 H), 0.89 (s, 9 H), 0.07 (s, 3 H), and 0.07 (s, 3 H).

^{13}C NMR (151 MHz, $CDCl_3$): δ 172.6, 72.6, 71.2, 37.4, 35.6, 28.9, 27.1, 26.0, 18.4, –5.27, and –5.32.

HRMS (*m*/*z*): calcd for $C_{14}H_{31}ClNO_2Si$ $[M+H]^+$: 308.1807, found: 308.1807.

IR (film) ν_{max}: 2952, 2929, 2857, 1650, 1462, 1397, 1361, 1255, 1098, 1075, 837, 777, and 671 cm^{-1}.

TLC: R_f = 0.35 (7:3 hexanes:EtOAc).



73

5-((*tert*-Butyldimethylsilyl)oxy)-4-chloro-4-methylpentanoic acid (73). Omitting Na_2HPO_4 from the general procedure, a mixture of **S5** (30.0 mg, 145 µmol, 1.0 equiv), acrylic acid (29.8 µL, 435 µmol, 3.0 equiv), $Fe(acac)_3$ (51.2 mg, 145 µmol, 100 mol %), and $PhSiH_3$ (53.7 µL, 435 µmol, 3.0 equiv) in EtOH (0.73 mL) was heated at 60 °C with stirring for 1 h. Purification by flash column chromatography (SiO_2, 8:2 hexanes:EtOAc), followed by preparative TLC (SiO_2, 7:3 hexanes:EtOAc) furnished chloride **73** as a pale yellow oil (18.9 mg, 67.3 µmol, 46%).

Physical State: pale yellow oil.

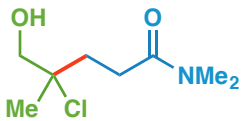
^{1}H NMR (600 MHz, $CDCl_3$): δ 3.66 (d, *J* = 10.1 Hz, 1 H), 3.60 (d, *J* = 10.0 Hz, 1 H), 2.58 – 2.46 (m, 2 H), 2.15 (ddd, *J* = 7.5, 8.6, 14.5 Hz, 1 H), 2.09 (ddd, *J* = 6.7, 9.6, 14.5 Hz, 1 H), 1.52 (s, 3 H), 0.90 (s, 9 H), 0.07 (s, 3 H), and 0.07 (s, 3 H).

^{13}C NMR (151 MHz, $CDCl_3$): δ 178.6, 71.4, 70.7, 34.9, 29.5, 27.2, 25.9, 18.4, –5.31, and –5.35.

HRMS (*m*/*z*): calcd for $C_{12}H_{26}ClO_3Si$ $[M+H]^+$: 281.1334, found: 281.1337.

IR (film) ν_{max}: 2953, 2930, 2857, 1710, 1459, 1418, 1254, 1099, 1080, 834, 776, and 671 cm^{-1}.

TLC: R_f = 0.31 (8:2 hexanes:EtOAc).



74

4-Chloro-5-hydroxy-*N*,*N*,4-trimethylpentanamide (74). Following the general procedure, a mixture of 2-chloro-2-propen-1-ol (30.0 mg, 324 µmol, 1.0 equiv), *N*,*N*-dimethylacrylamide (100 µL, 973 µmol, 3.0 equiv), Na_2HPO_4 (46.0 mg, 324 µmol, 1.0 equiv), $Fe(acac)_3$ (115 mg, 324 µmol, 100 mol %), and $PhSiH_3$ (120 µL, 973 µmol, 3.0 equiv) in EtOH (1.6 mL) was heated at 60 °C

with stirring for 1 h. Purification by flash column chromatography (SiO_2, EtOAc), followed by preparative TLC (SiO_2, 95:5 DCM:MeOH) furnished chloride **74** as a pale yellow oil (42.1 mg, 217 µmol, 67%).

Physical State: pale yellow oil.

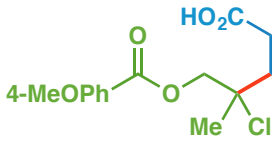
^{1}H NMR (600 MHz, $CDCl_3$): δ 4.29 (dd, *J* = 6.0, 9.1 Hz, 1 H), 3.48 – 3.42 (m, 2 H), 3.05 (s, 3 H), 2.98 (s, 3 H), 2.68 (ddd, *J* = 4.3, 8.9, 17.5 Hz, 1 H), 2.46 – 2.39 (m, 2 H), 1.91 (dddd, *J* = 0.8, 4.3, 7.5, 15.4 Hz, 1 H), and 1.63 (s, 3 H).

^{13}C NMR (151 MHz, $CDCl_3$): δ 173.3, 73.9, 68.6, 37.4, 36.0, 33.7, 28.6, and 28.5.

HRMS (*m*/*z*): calcd for $C_8H_{17}ClNO_2$ $[M+H]^+$: 194.0942, found: 194.0943.

IR (film) ν_{max}: 3375 (br), 2971, 2934, 1608, 1503, 1455, 1405, 1262, 1150, 1045, and 912 cm^{-1}.

TLC: R_f = 0.40 (EtOAc).



75

4-Chloro-5-((4-methoxybenzoyl)oxy)-4-methylpentanoic acid (75). Omitting Na_2HPO_4 from the general procedure, a mixture of 2-chloroallyl 4-methoxybenzoate[4] (22.6 mg, 100 µmol, 1.0 equiv), acrylic acid (20.6 µL, 300 µmol, 3.0 equiv), $Fe(acac)_3$ (35.3 mg, 100 µmol, 100 mol %), and $PhSiH_3$ (36.9 µL, 300 µmol, 3.0 equiv) in EtOH (0.50 mL) was heated to 60 °C with stirring for 1 h. Purification by flash column chromatography (SiO_2, 2:1→1:2 hexanes:EtOAc) furnished chloride **75** as a colorless oil (14.9 mg, 49.6 µmol, 50%).

Physical State: colorless oil.

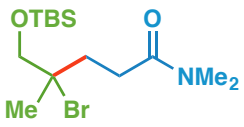
^{1}H NMR (600 MHz, $CDCl_3$): δ 8.00 (d, *J* = 9.0 Hz, 2 H), 6.94 (d, *J* = 9.0 Hz, 2 H), 4.39 (s, 2 H), 3.86 (s, 3H), 2.71 – 2.61 (m, 2 H), 2.29 – 2.24 (m, 1 H), 2.20 – 2.15 (m, 1 H), and 1.65 (s, 3 H).

^{13}C NMR (151 MHz, $CDCl_3$): δ 178.2, 165.7, 163.8, 131.9, 122.0, 113.9, 70.7, 68.9, 55.6, 35.5, 29.4, and 27.4.

HRMS (*m*/*z*): calcd for $C_{14}H_{18}ClO_5$ $[M+H]^+$: 301.0837, found: 301.0830.

IR (film) ν_{max}: 2934, 1706, 1604, 1252, 1165, 1097, and 729 cm^{-1}.

TLC: R_f = 0.50 (1:2 hexanes:EtOAc).



76

4-Bromo-5-((*tert*-butyldimethylsilyl)oxy)-*N*,*N*,4-trimethylpentanamide (76). A solution of *N*,*N*-dimethylacrylamide (62.0 µL, 600 µmol, 6.0 equiv), and $PhSiH_3$ (73.8 µL, 600 µmol, 6.0 equiv) in EtOH (0.50 mL) was added

slowly via syringe pump to a mixture of ((2-bromoallyl)oxy)(*tert*-butyl)dimethylsilane[27] (25.0 mg, 100 µmol, 1.0 equiv), Na_2HPO_4 (14.2 mg, 100 µmol, 1.0 equiv), and $Fe(acac)_3$ (35.3 mg, 100 µmol, 100 mol %) in EtOH (0.50 mL) while heating at 60 °C with stirring for 1 h. After work up following the general procedure, purification by flash column chromatography (SiO_2, 5:1→3:1 hexanes:EtOAc) furnished bromide **76** as a colorless oil (14.8 mg, 42.4 µmol, 42%).

Physical State: colorless oil.

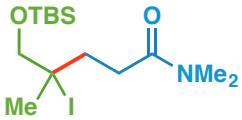
^{1}H NMR (600 MHz, $CDCl_3$): δ 3.77 (d, *J* = 10.2 Hz, 1 H), 3.71 (d, *J* = 10.2 Hz, 1 H), 3.05 (s, 3 H), 2.95 (s, 3 H), 2.61 – 2.56 (m, 1 H), 2.54 – 2.49 (m, 1 H), 2.20 – 2.11 (m, 2 H), 1.71 (s, 3 H), 0.89 (s, 9 H), 0.07 (s, 3 H), and 0.07 (s, 3 H).

^{13}C NMR (151 MHz, $CDCl_3$): δ 172.4, 71.8, 70.6, 37.4, 36.7, 35.6, 30.3, 28.5, 26.0, 18.4, and –5.3.

HRMS (*m*/*z*): calcd for $C_{14}H_{31}BrNO_2Si$ $[M+H]^+$: 352.1302, found: 352.1308.

IR (film) ν_{max}: 2929, 2856, 1650, 1463, 1091, 838, 777 and 671 cm^{-1}.

TLC: R_f = 0.45 (2:1 hexanes:EtOAc).



77

5-((*tert*-Butyldimethylsilyl)oxy)-4-iodo-*N*,*N*,4-trimethylpentanamide (77). A solution of *N*,*N*-dimethylacrylamide (62.0 µL, 600 µmol, 6.0 equiv), and $PhSiH_3$ (73.8 µL, 600 µmol, 6.0 equiv) in EtOH (0.50 mL) was added slowly via syringe pump to a mixture of *tert*-butyl((2-iodoallyl)oxy)dimethylsilane[28] (29.8 mg, 100 µmol, 1.0 equiv), Na_2HPO_4 (14.2 mg, 100 µmol, 1.0 equiv), and $Fe(acac)_3$ (35.3 mg, 100 µmol, 100 mol %) in EtOH (0.50 mL) while heating at 60 °C with stirring for 1 h. After work up following the general procedure, purification by flash column chromatography (SiO_2, 5:1→4:1 hexanes:EtOAc) furnished iodide **77** as a colorless oil (14.6 mg, 36.6 µmol, 37%).

Physical State: colorless oil.

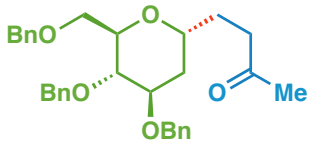
^{1}H NMR (600 MHz, $CDCl_3$): δ 3.76 (d, *J* = 10.2 Hz, 1 H), 3.71 (d, *J* = 10.2 Hz, 1 H), 3.06 (s, 3H), 2.95 (s, 3H), 2.61 – 2.56 (m, 1 H), 2.53 – 2.47 (m, 1 H), 2.10 – 2.04 (m, 1 H), 1.97 – 1.94 (m, 1 H), 1.90 (s, 3 H), 0.90 (s, 9 H), 0.07 (s, 3 H), and 0.07 (s, 3 H).

^{13}C NMR (151 MHz, $CDCl_3$): δ 172.3, 74.1, 57.3, 39.0, 37.4, 35.6, 32.7, 31.6, 26.0, 18.4, and –5.2.

HRMS (*m*/*z*): calcd for $C_{14}H_{31}INO_2Si$ $[M+H]^+$: 400.1163, found: 400.1171.

IR (film) ν_{max}: 2928, 2856, 1646, 1462, 1092, 834, 776 and 670 cm^{-1}.

TLC: R_f = 0.55 (2:1 hexanes:EtOAc).



79

4-((2*R*,4*R*,5*S*,6*R*)-4,5-Bis(benzyloxy)-6-((benzyloxy)methyl)tetrahydro-2H-pyran-2-yl)butan-2-one (79). A solution of methyl vinyl ketone (49.6 µL, 600 µmol, 12.0 equiv) and $PhSiH_3$ (73.8 µL, 600 µmol, 12.0 equiv) in EtOH (0.25 mL) was added slowly via syringe pump to a mixture of 3,4,6-tri-O-methyl-D-glucal (20.8 mg, 50.0 µmol, 1.0 equiv), Na_2HPO_4 (7.1 mg, 50.0 µmol, 1.0 equiv), $Fe(dibm)_3$ (7.9 mg, 15 µmol, 30 mol %) in EtOH (0.25 mL) while heating at 60 °C with stirring for 2 h. After work up following the general procedure, purification by preparative TLC (SiO_2, 3:1 hexanes:EtOAc) furnished glucal derivative **79** as a colorless oil (16.7 mg, 34.1 µmol, 68%) and recovered starting material (5.1 mg, 12.2 µmol, 24%).

Spectroscopic data was identical to that reported in the literature.[29]

Physical State: colorless oil.

$[\alpha]_{20}^{D}$: +28.2 (c = 0.50, $CHCl_3$).

^{1}H NMR (600 MHz, $CDCl_3$): δ 7.33 – 7.26 (m, 13 H), 7.21 – 7.20 (m, 2 H), 4.78 (d, *J* = 10.8 Hz, 1 H), 4.60 (d, *J* = 11.4 Hz, 1 H), 4.58 (d, *J* = 11.4 Hz, 1 H), 4.56 (d, *J* = 12.6 Hz, 1 H), 4.52 (d, *J* = 10.8 Hz, 1 H), 4.51 (d, *J* = 12.0 Hz, 1 H), 3.96 – 3.93 (m, 1 H), 3.82 – 3.78 (m, 1 H), 3.75 – 3.69 (m, 2 H), 3.66 – 3.63 (m, 1 H), 3.49 (dd, *J* = 7.2, 7.2 Hz, 1 H), 2.59 – 2.54 (m, 1 H), 2.51 – 2.45 (m, 1 H), 2.12 (s, 3 H), 1.99 – 1.94 (m, 2 H), 1.83 – 1.78 (m, 1 H), and 1.68 – 1.63 (m, 1 H).

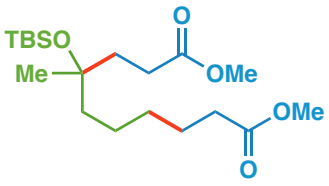
^{1}H NMR (600 MHz, C_6D_6): δ 7.30 – 7.10 (m, 15 H), 4.75 (d, *J* = 11.4 Hz, 1 H), 4.54 (d, *J* = 11.4 Hz, 1 H), 4.44 – 4.33 (m, 4 H), 3.91 – 3.72 (m, 5 H), 3.56 (dd, *J* = 6.6, 6.6 Hz, 1 H), 2.23 – 2.10 (m, 2 H), 1.88 – 1.83 (m, 1 H), 1.78 – 1.74 (m, 1 H), 1.68 (s, 3 H), 1.67 – 1.64 (m, 1 H), and 1.55 – 1.52 (m, 1 H).

^{13}C NMR (151 MHz, $CDCl_3$): δ 208.6, 138.6, 138.5, 138.4, 128.5, 128.5, 128.0, 127.9, 127.8, 127.7, 76.9, 76.7, 74.1, 73.5, 72.6, 71.6, 70.2, 69.2, 39.8, 33.7, 30.3, and 25.9.

HRMS (*m*/*z*): calcd for $C_{31}H_{37}O_5$ $[M+H]^+$: 489.2636, found: 489.2646.

IR (film) ν_{max}: 2924, 1711, 1452, 1360, 1092, 734 and 695 cm^{-1}.

TLC: R_f = 0.21 (3:1 hexanes:EtOAc).



89

Dimethyl 4-((*tert*-butyldimethylsilyl)oxy)-4-methyldecanedioate (89). Following the general procedure, a mixture of *tert*-butyl((1-cyclopropylvinyl)oxy)dimethylsilane[30] (65.0 mg, 331 µmol, 3.0 equiv), methyl acrylate (10.0 µL, 110 µmol, 1.0 equiv), Na_2HPO_4 (15.7 mg, 110 µmol, 1.0 equiv), $Fe(dibm)_3$ (2.9 mg, 5.5 µmol, 5 mol %), and $PhSiH_3$ (27.2 µL, 221 µmol, 2.0 equiv) in EtOH (0.55 mL) was heated at 60 °C with stirring for 1 h. Purification by preparative TLC (SiO_2, 95:5 hexanes:EtOAc) furnished silyl ether **89** as a pale yellow oil (2.5 mg, 6.71 µmol, 6%).

Physical State: pale yellow oil.

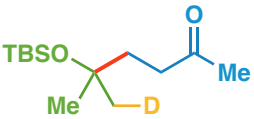
^{1}H NMR (600 MHz, $CDCl_3$): δ 3.68 (s, 3 H), 3.62 (s, 3 H), 2.78 (dd, *J* = 7.1, 7.1 Hz, 1 H), 2.43 (ddd, *J* = 16.0, 11.2, 5.1 Hz, 1 H), 2.35 (ddd, *J* = 15.7, 11.3, 5.5 Hz, 1 H), 2.08 (ddd, *J* = 13.4, 6.8, 6.8 Hz, 1 H), 2.03 – 1.83 (m, 6 H), 1.84 – 1.71 (m, 2 H), 1.69 – 1.59 (m, 2 H), 1.15 (s, 3 H), 0.86 (s, 9 H), 0.09 (s, 3 H), and 0.07 (s, 3 H).

^{13}C NMR (151 MHz, $CDCl_3$): δ 176.6, 174.6, 76.0, 55.4, 53.6, 51.8, 51.4, 44.6, 36.7, 30.3, 29.2, 26.1, 24.9, 24.5, 22.5, –1.68, and –1.72.

HRMS (*m*/*z*) calcd for $C_{19}H_{39}O_5Si$ $[M+H]^+$: 375.2561, found: 375.2569.

IR (film) ν_{max}: 2953, 2930, 2855, 1735, 1458, 1434, 1378, 1193, 1163, 1109, and 1015 cm^{-1}.

TLC: R_f = 0.60 (9:1 hexanes:EtOAc).



90

5-((*tert*-Butyldimethylsilyl)oxy)-5-methylhexan-2-one-6-d (90). Following the general procedure, a mixture of *tert*-butyldimethyl(prop-1-en-2-yloxy)silane[5] (17.3 mg, 100 µmol, 1.0 equiv), methyl vinyl ketone (24.9 µL, 300 µmol, 3.0 equiv), Na_2HPO_4 (14.2 mg, 100 µmol, 1.0 equiv), $Fe(dibm)_3$ (2.6 mg, 5.0 µmol, 5 mol %), and a solution of $PhSiD_3$[31] (7.4 M in Et_2O, 270 µL, 200 µmol, 2.0 equiv) in EtOH (0.23 mL) was heated at 60 °C with stirring for 1 h. Purification by flash column chromatography (SiO_2, 97:3 hexanes:EtOAc) furnished deuterated **90** as a colorless oil (15.8 mg, 66.1 µmol, 66%).

Physical State: colorless oil.

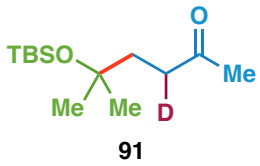
^{1}H NMR (600 MHz, $CDCl_3$): δ 2.56 – 2.52 (m, 2 H), 2.16 (s, 3 H), 1.71 – 1.67 (m, 2 H), 1.20 (s, 3 H), 1.19 – 1.18 (m, 2 H), 0.85 (s, 9 H), 0.07 (s, 3 H), and 0.07 (s, 3 H).

^{13}C NMR (151 MHz, $CDCl_3$): δ 209.7, 72.8, 39.1, 38.5, 30.5, 29.6 (t, J = 19.5 Hz), 25.9, 18.3, –1.9, and –1.9.

HRMS (*m*/*z*) calcd for $C_{13}H_{28}DO_2Si$ $[M+H]^+$: 246.1994, found: 246.1996.

IR (film) ν_{max}: 2955, 2929, 2856, 1717, 1253, 1049, 834, 772, and 670 cm^{-1}.

TLC: R_f = 0.33 (97:3 hexanes:EtOAc).



91

5-((*tert*-Butyldimethylsilyl)oxy)-5-methylhexan-2-one-3-d (91). Following the general procedure, a mixture of *tert*-butyldimethyl(prop-1-en-2-yloxy)silane[5] (17.3 mg, 100 µmol, 1.0 equiv), methyl vinyl ketone (24.9 µL, 300 µmol, 3.0 equiv), Na_2HPO_4 (14.2 mg, 0.1 mmol, 1.0 equiv), $Fe(dibm)_3$ (2.6 mg, 5.0 µmol, 5 mol %), and $PhSiH_3$ (24.6 µL, 200 µmol, 2.0 equiv) in ethanol-d_1 or ethanol-d_6 (0.50 mL) was heated at 60 °C with stirring for 1 h. Purification by flash column chromatography (SiO_2, 97:3 hexanes:EtOAc) furnished deuterated **91** as a colorless oil (16.5 mg, 68.1 µmol, 68%) when using ethanol-d_1 as the solvent and (16.6 mg, 67.7 µmol, 68%) when using ethanol-d_6 as the solvent.

Physical State: colorless oil.

^{1}H NMR (600 MHz, $CDCl_3$): δ 2.55 – 2.50 (m, 1 H), 2.16 (s, 3 H), 1.70 – 1.65 (m, 2 H), 1.20 (s, 3 H), 1.20 (s, 3H), 0.85 (s, 9 H), 0.07 (s, 3 H), and 0.07 (s, 3 H).

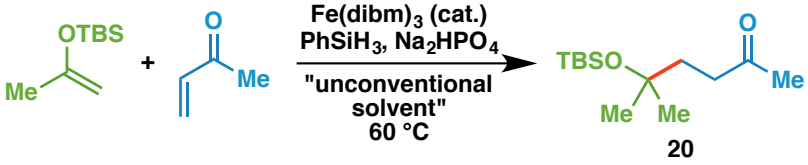
^{13}C NMR (151 MHz, $CDCl_3$): δ 209.8, 72.8, 38.8 (t, J = 18.8 Hz), 38.5, 30.1, 29.9, 26.0, 18.2, –1.9, and –1.9. 1 carbon was not observed due to incidental equivalence.

HRMS (*m*/*z*) calcd for $C_{13}H_{28}DO_2Si$ $[M+H]^+$: 246.1994, found: 246.1996.

IR (film) ν_{max}: 2955, 2929, 2856, 1717, 1253, 1049, 834, 772, and 670 cm^{-1}.

TLC: R_f = 0.33 (97:3 hexanes:EtOAc).

Use of Unconventional Solvents for Olefin Cross–Coupling



Following the general procedure, a mixture of *tert*-butyldimethyl(prop-1-en-2-yloxy)silane[5] (30.0 mg, 174 µmol, 1.0 equiv), methyl vinyl ketone (43.5 µL, 522 µmol, 3.0 equiv), Na_2HPO_4 (24.7 mg, 174 µmol, 1.0 equiv), $Fe(dibm)_3$ (4.5 mg, 8.71 µmol, 5 mol %), and $PhSiH_3$ (42.9 µL, 348 µmol, 2.0 equiv) in an unconventional solvent (0.87 mL) was heated at 60 °C with stirring for 1 h. The reaction mixture was then cooled to rt, diluted with EtOAc, and analyzed by TLC (95:5 hexanes:EtOAc) and GC/MS to confirm the formation of silyl ether **20**.

Table S2. Unconventional solvents used.

A. EtOH (control)	**E**. Jack Daniel's Whiskey
B. Smirnoff Vodka	**F**. Stone IPA
C. Jose Cuervo Tequila Gold	**G**. Turning Leaf Chardonnay
D. Seagram's Extra Dry Gin	**H**. Woodbridge Merlot, 2012 Vintage

Figure S23. Reaction mixtures using solvents **A**–**E** prior to heating at 60 °C.

Figure S24. Reaction mixtures using solvents **A**–**E** after heating at 60 °C.

Figure S25. TLC of reactions using solvents **A**–**E** (95:5 hexanes:EtOAc).

Figure S26. Reaction mixtures using solvents **F**–**H** prior to heating at 60 °C.

Figure S27. Reaction mixtures using solvents **F**–**H** after heating at 60 °C.

Figure S28. TLC of reactions using solvents **F**–**H** (95:5 hexanes:EtOAc).

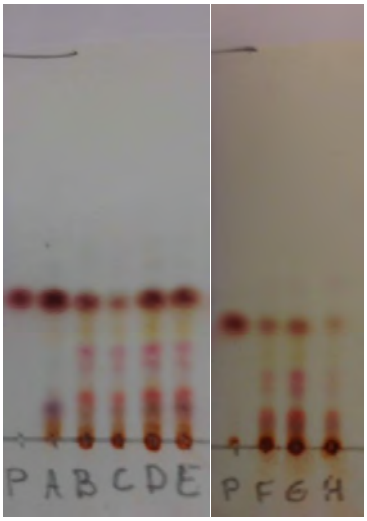


Figure S29. Close ups of TLCs of reactions using solvents **A**–**H** (95:5 hexanes:EtOAc, P is isolated product).

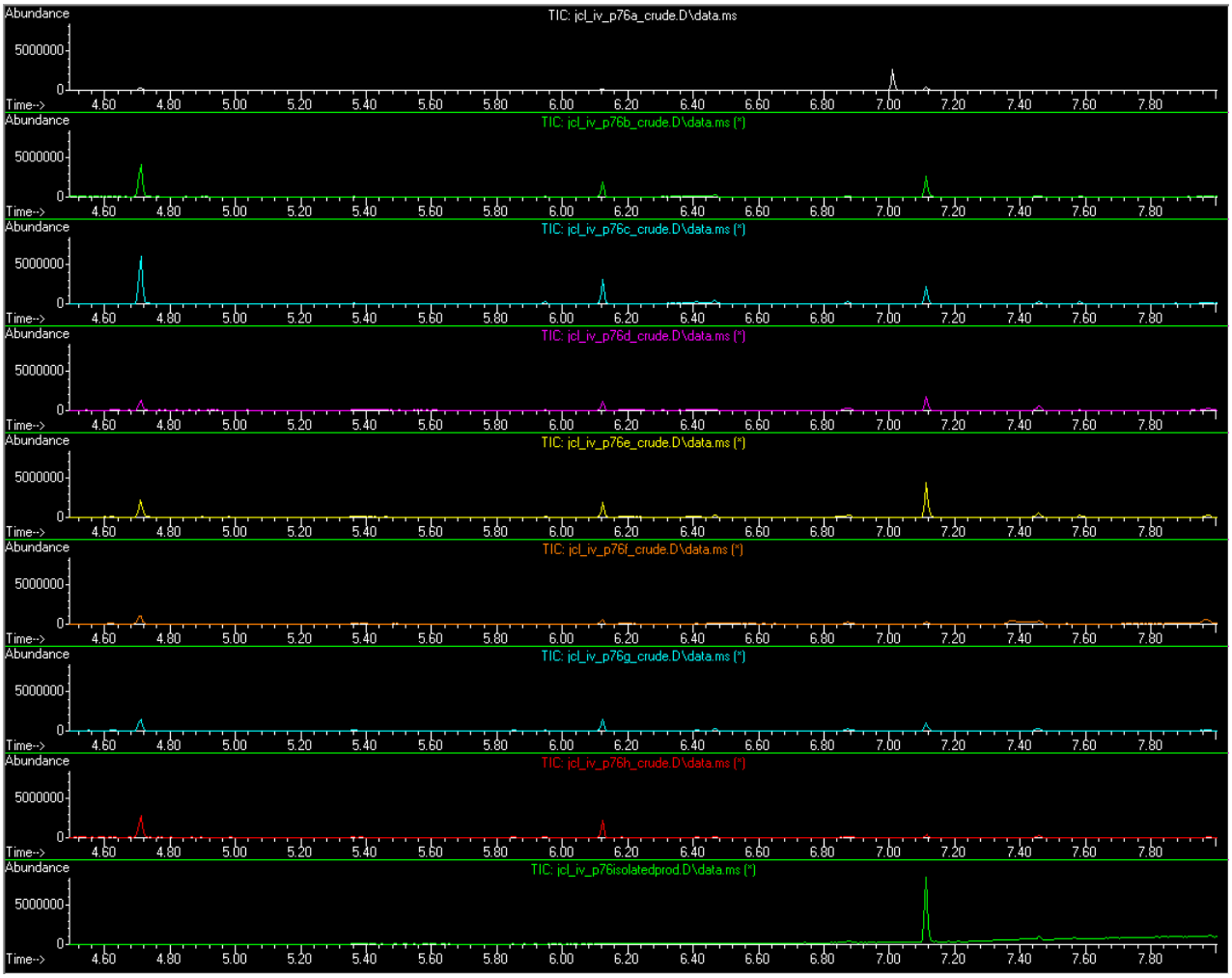


Figure S30. GC/MS analysis of reactions using solvents A–H. From top to bottom: **A**, **B**, **C**, **D**, **E**, **F**, **G**, **H**, isolated product.

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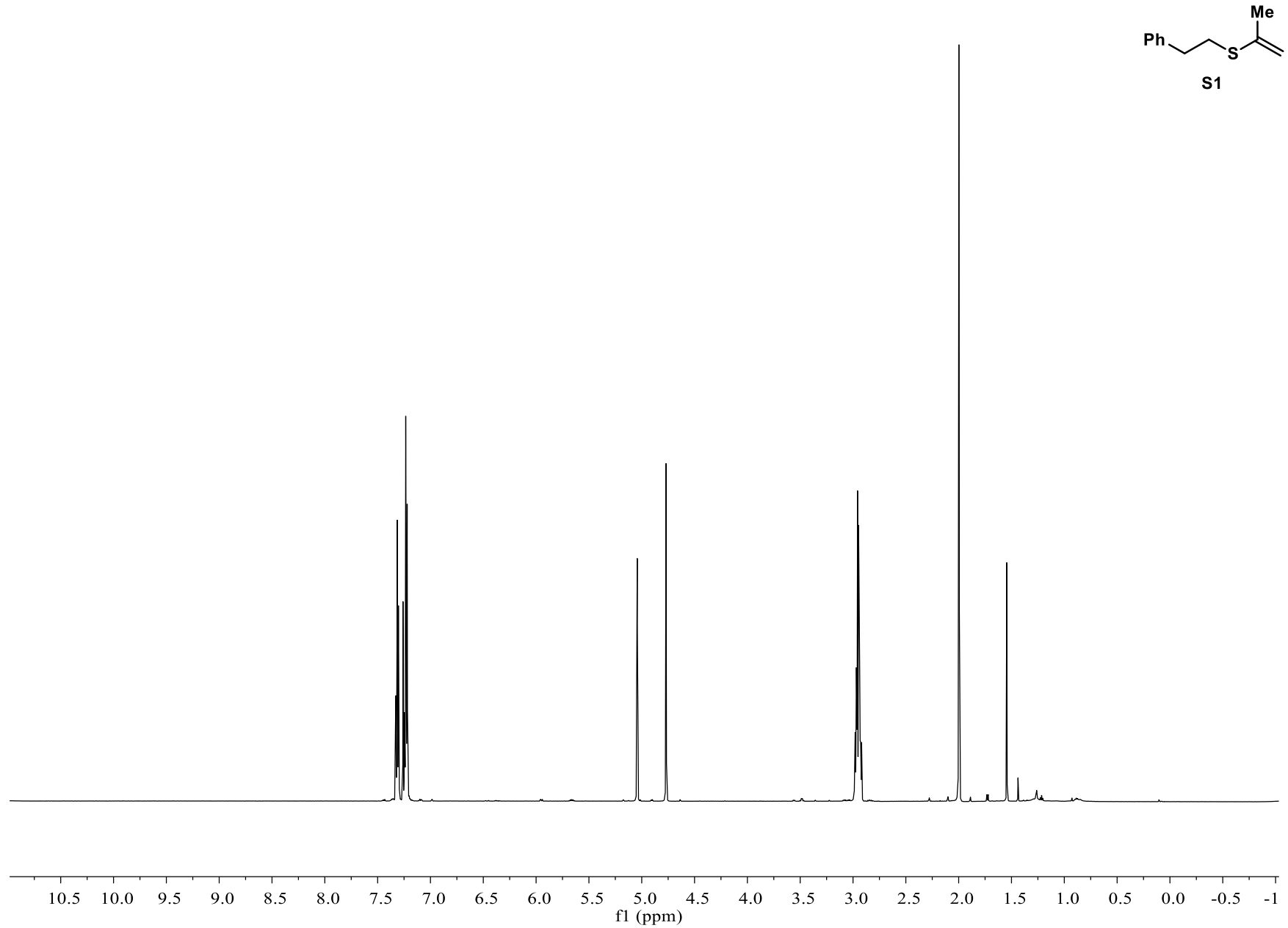
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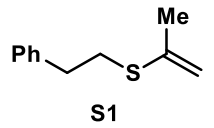
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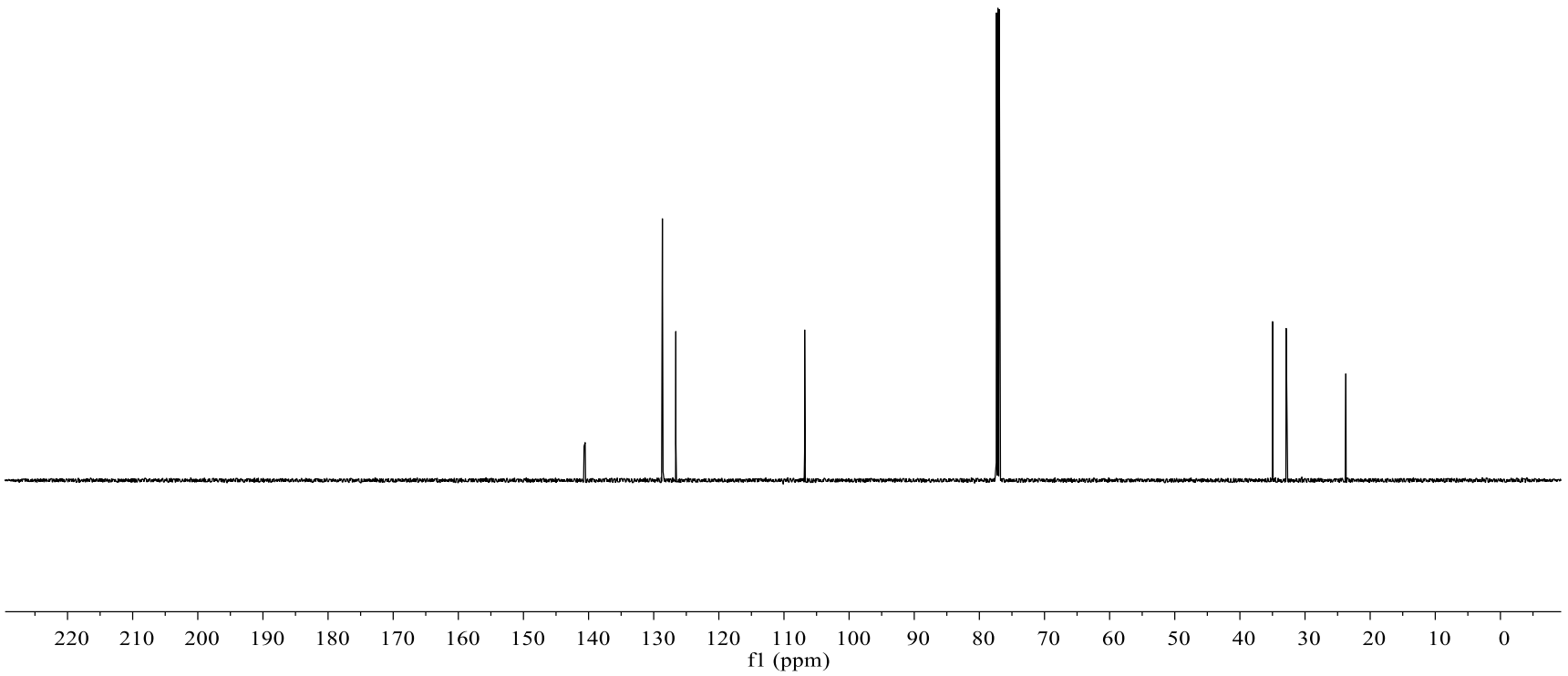
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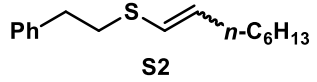
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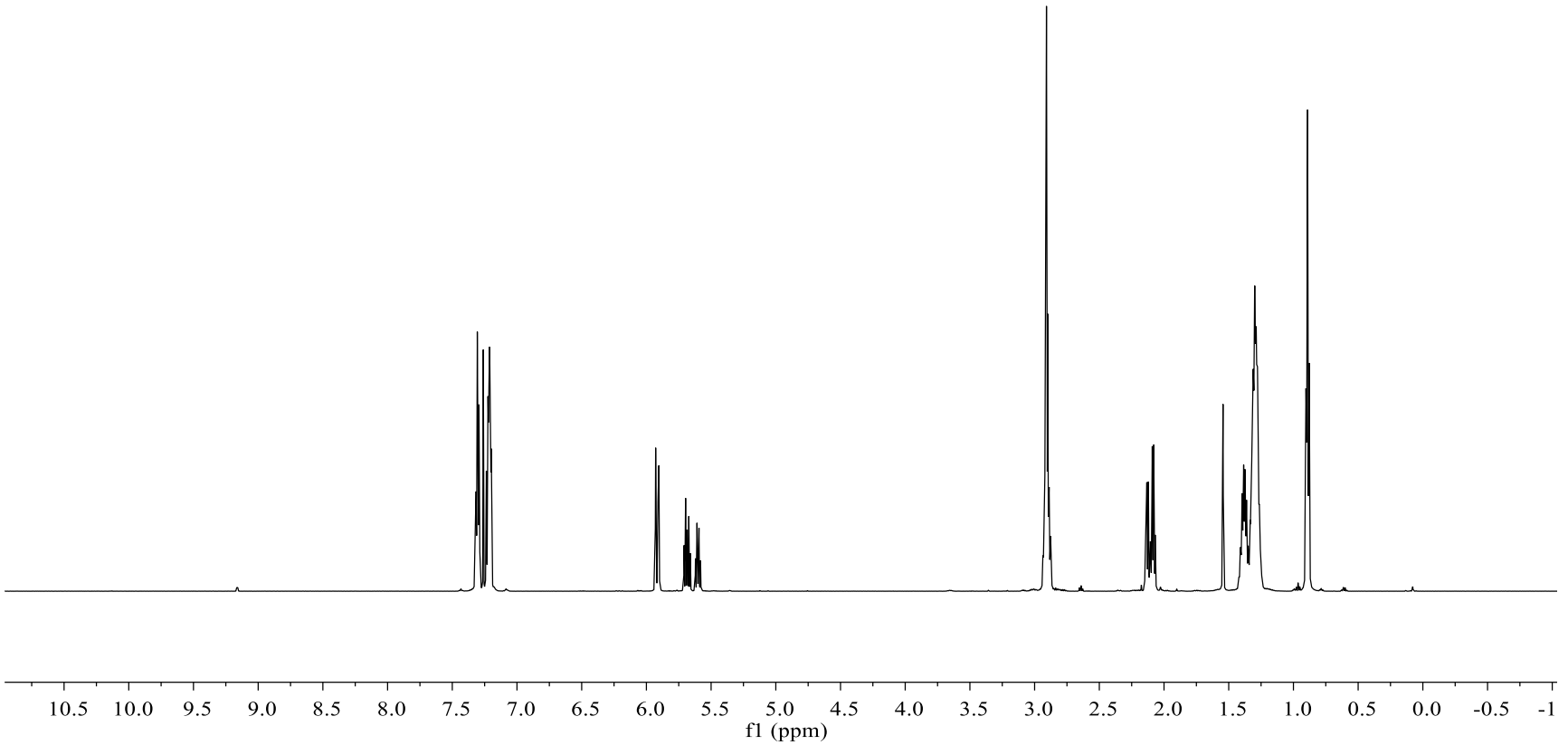
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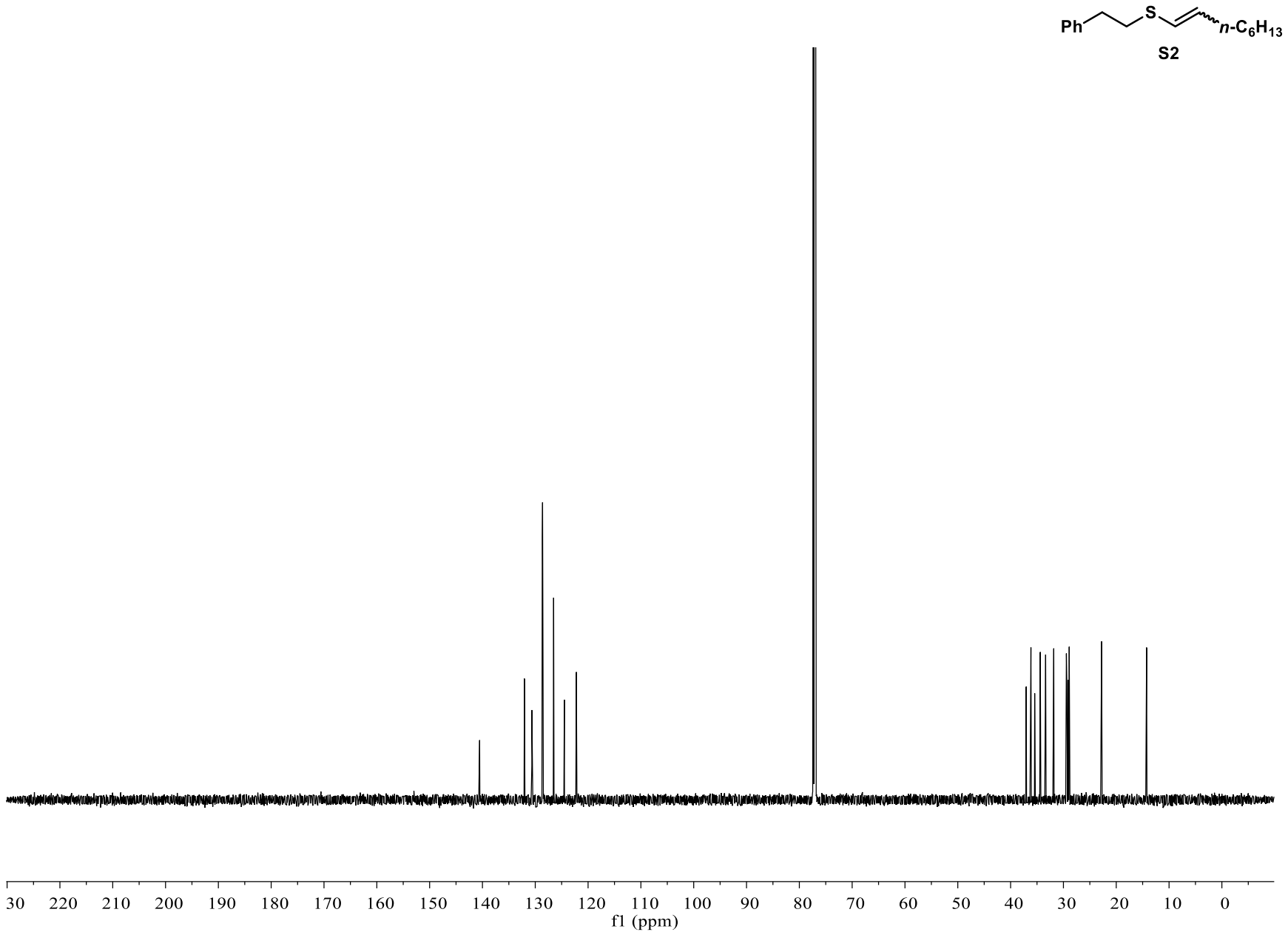
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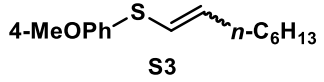
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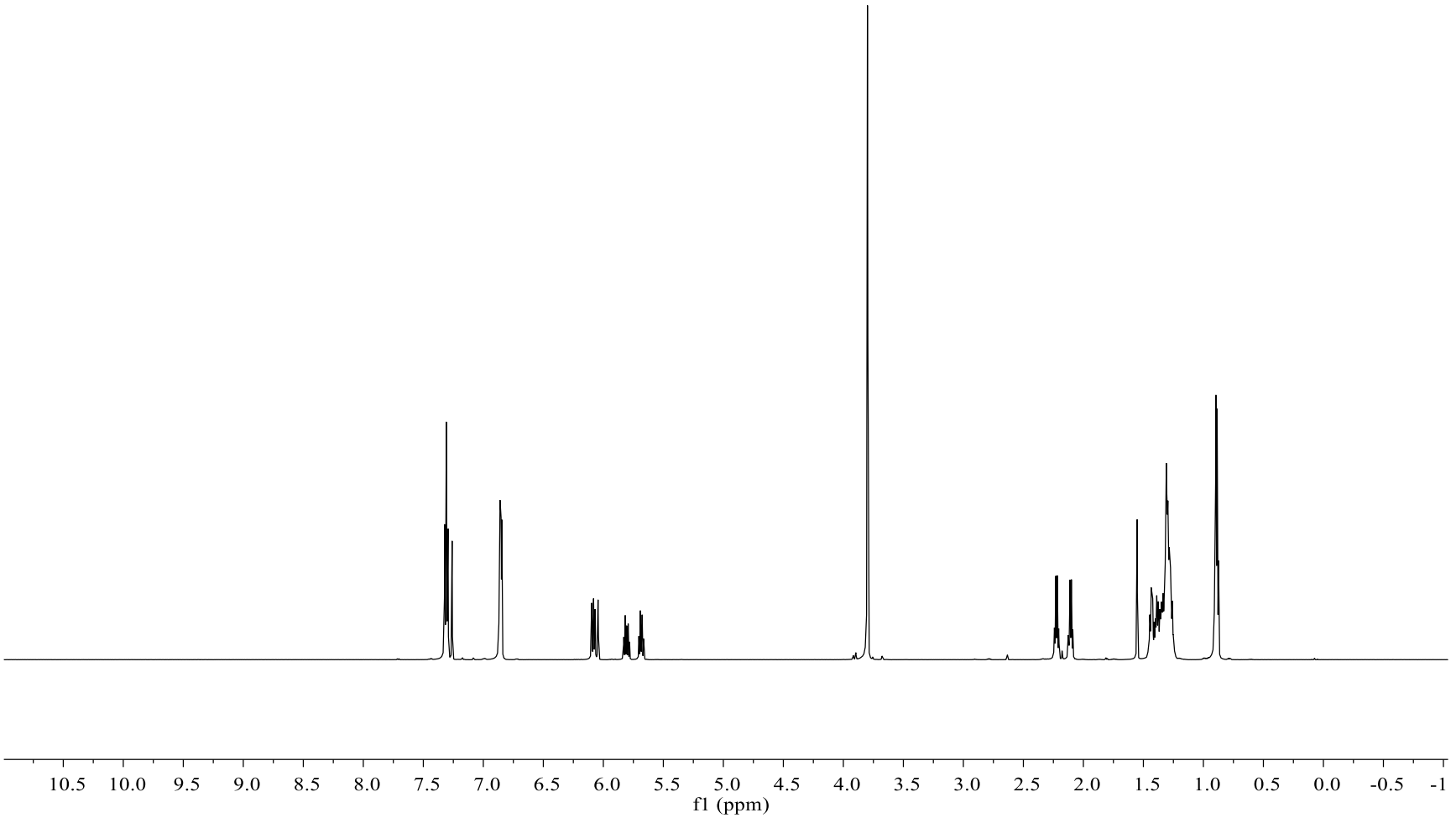
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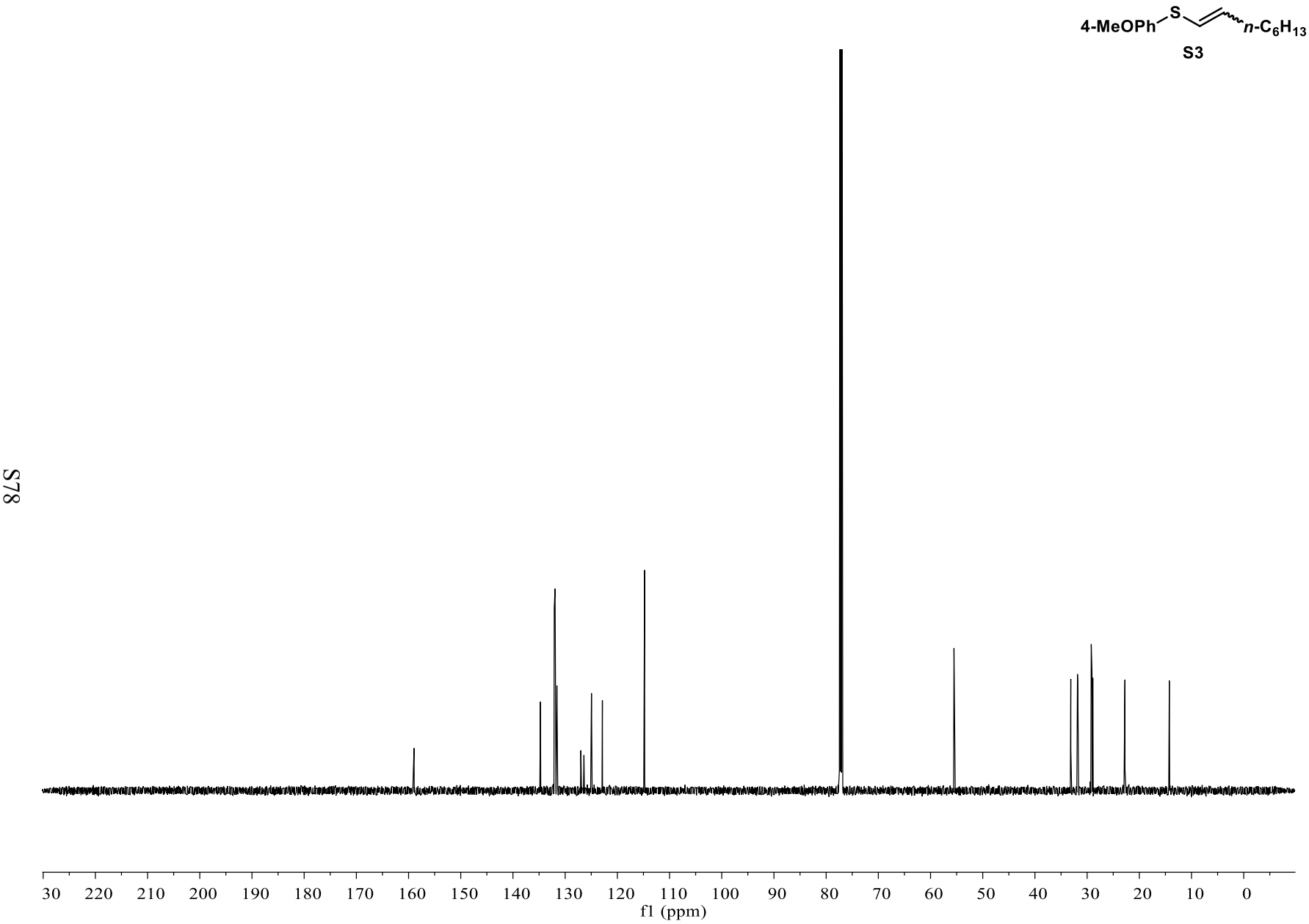
2.0
1.5
1.0
0.5
0.0
-0.5
-1
f1 (ppm)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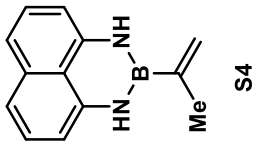
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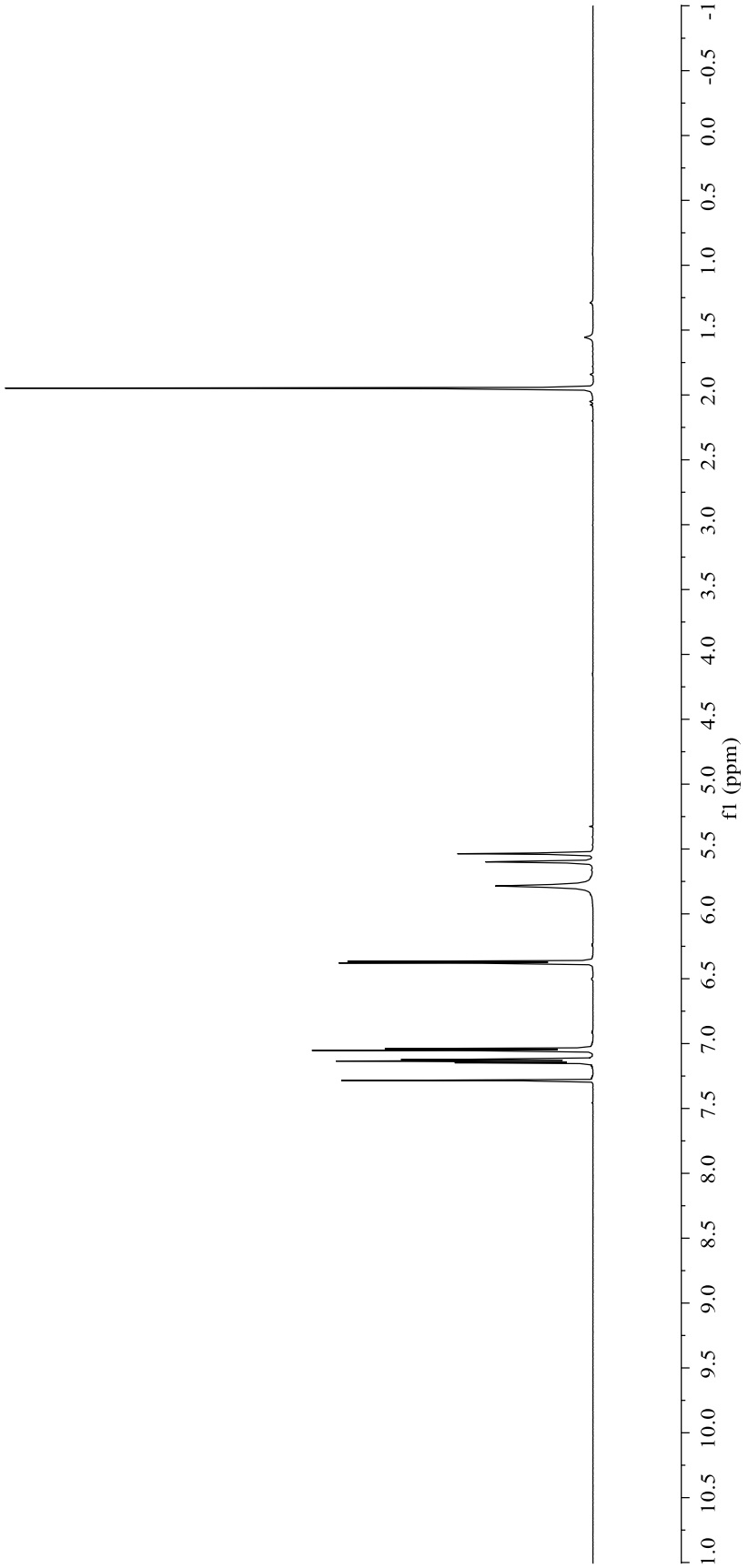
B
NH
Me

S4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4.5
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1.5
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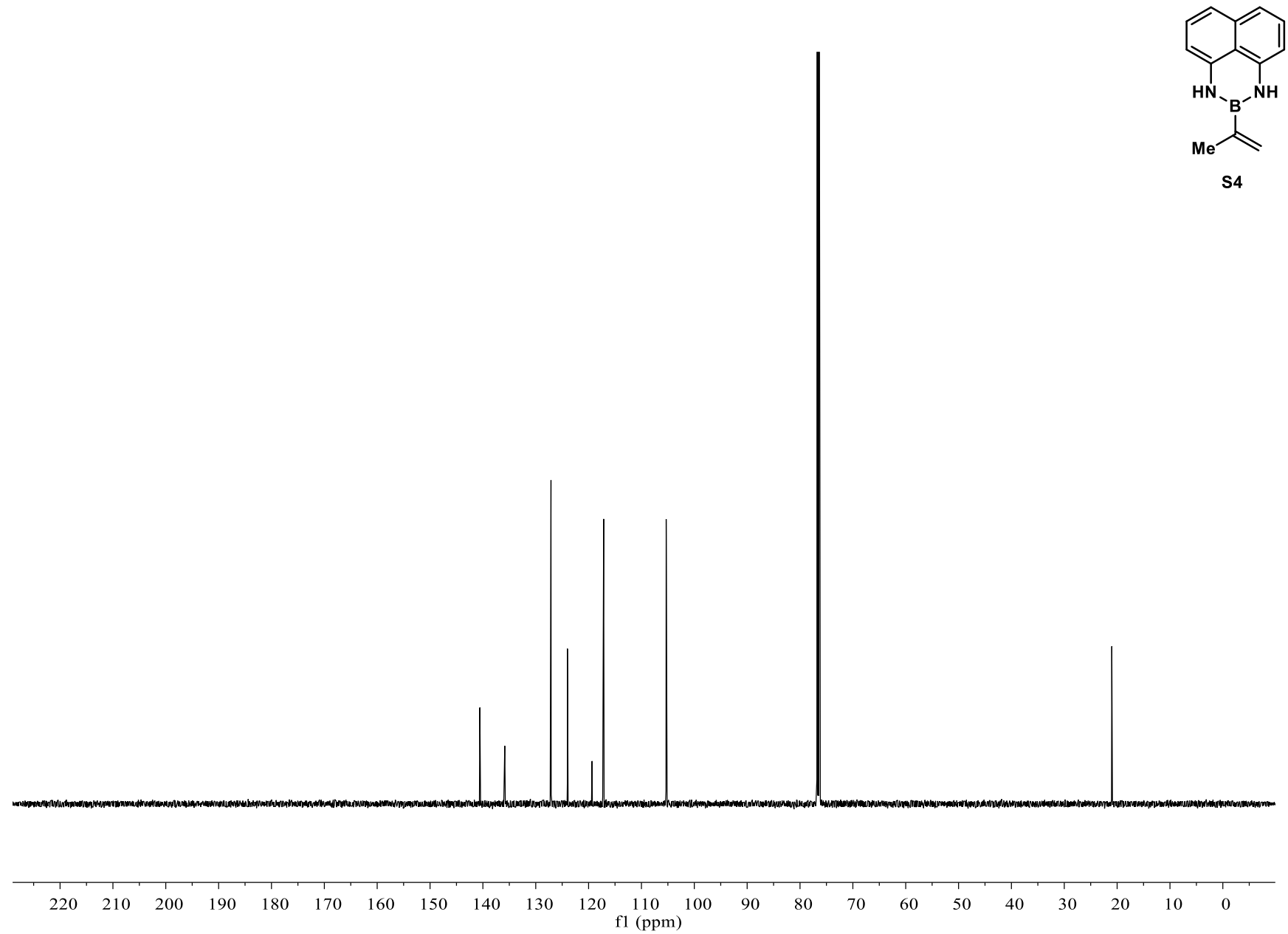
0.5
0.0
-0.5
-1
f1 (ppm)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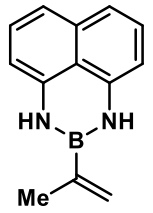
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B
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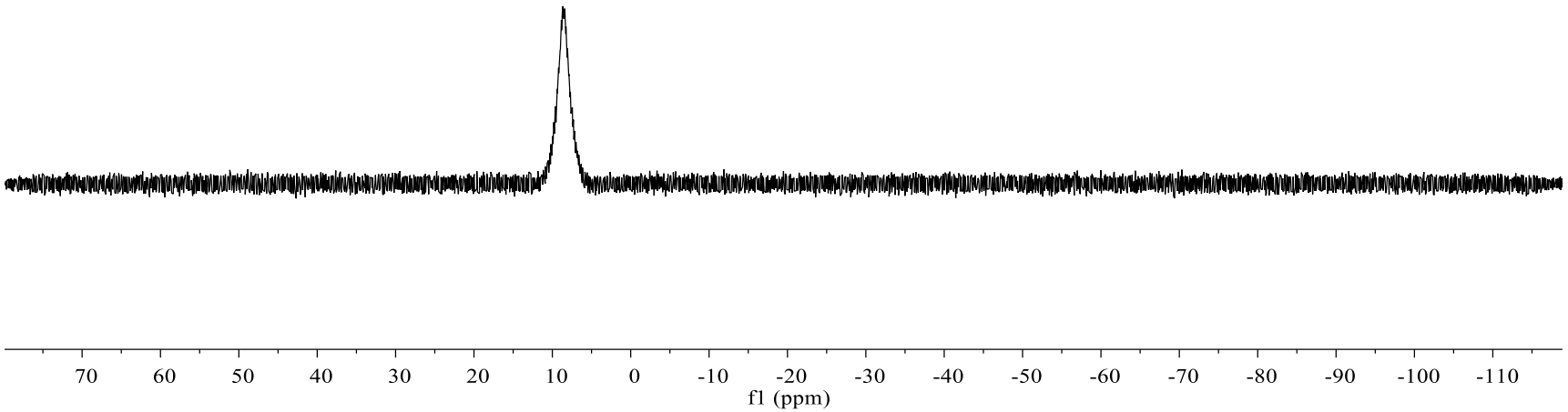
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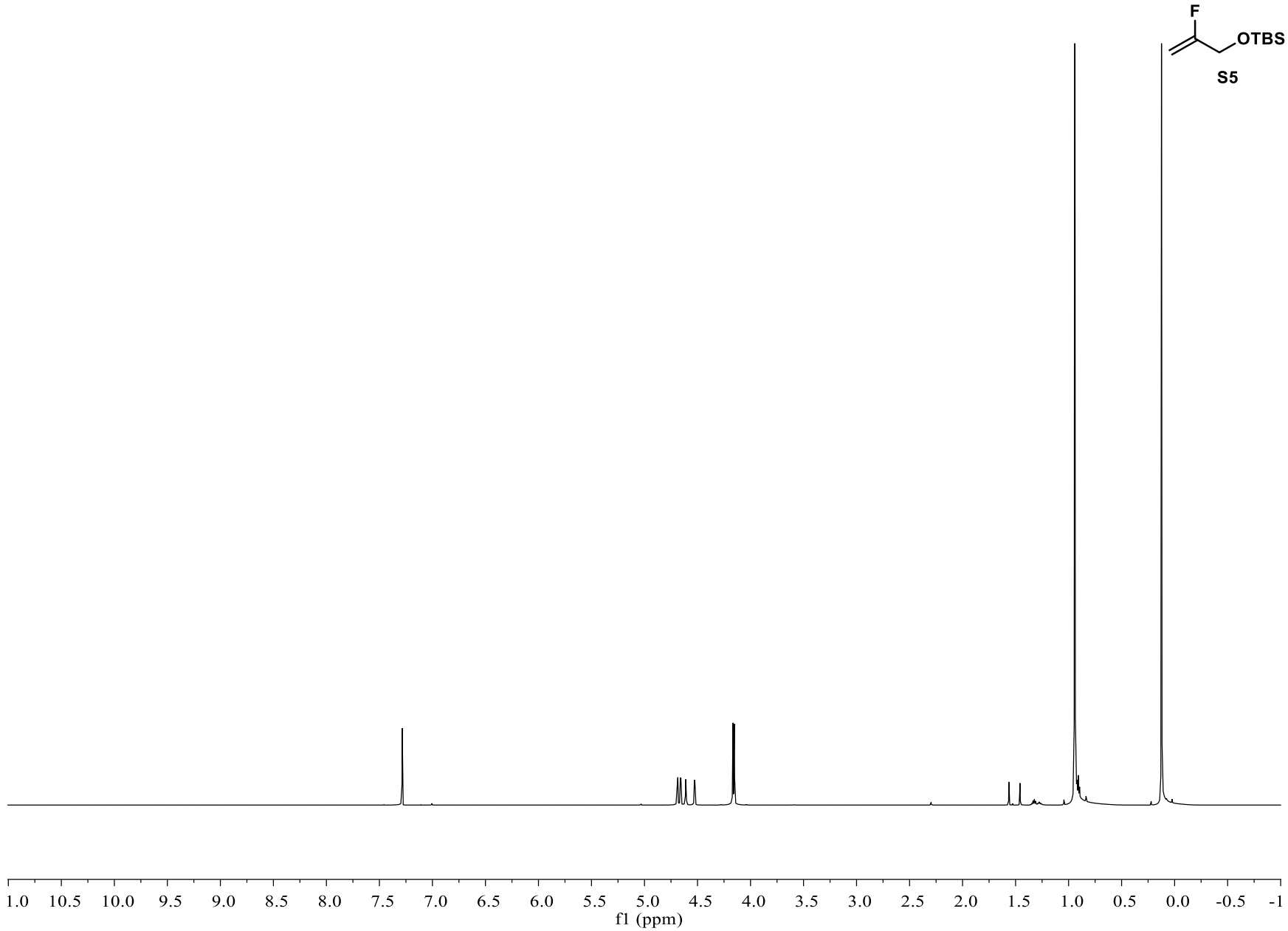
f1 (ppm)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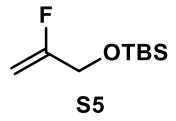
f1 (ppm)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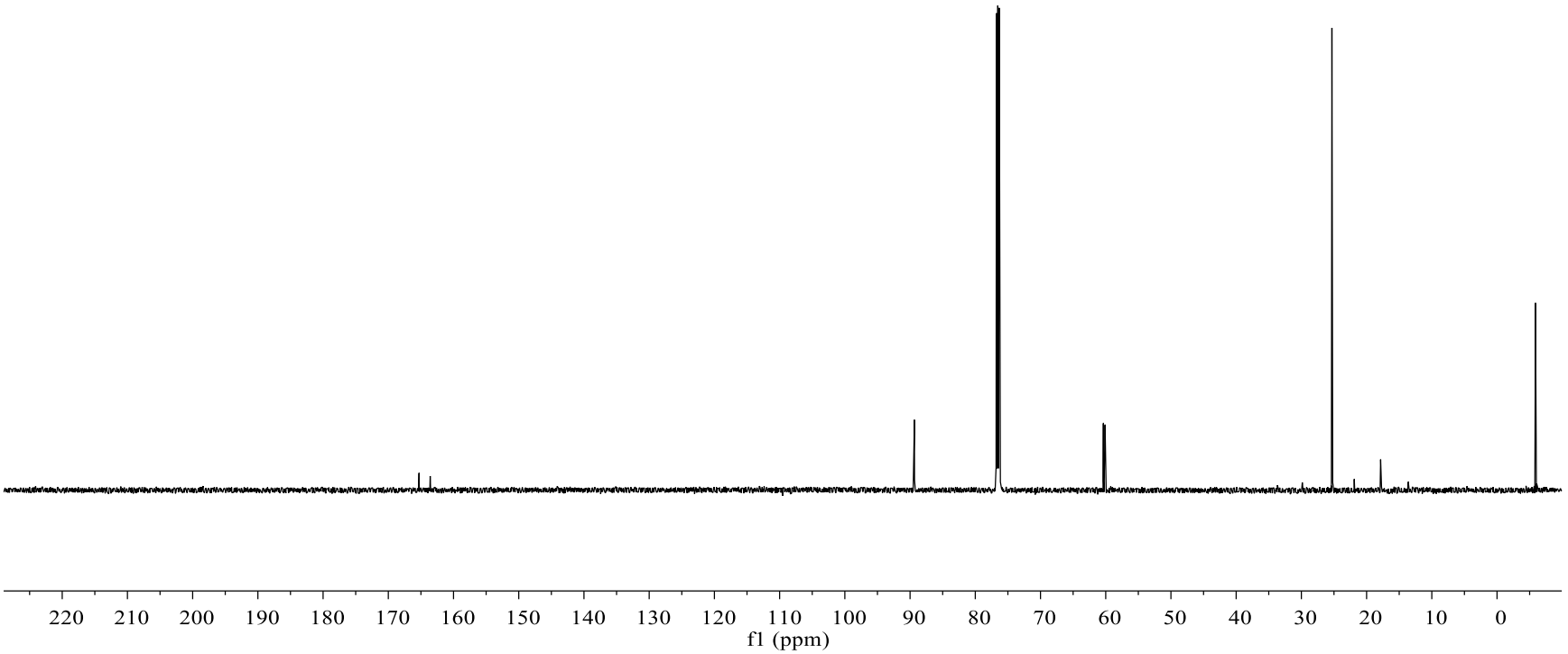
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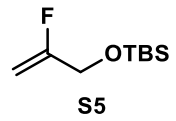
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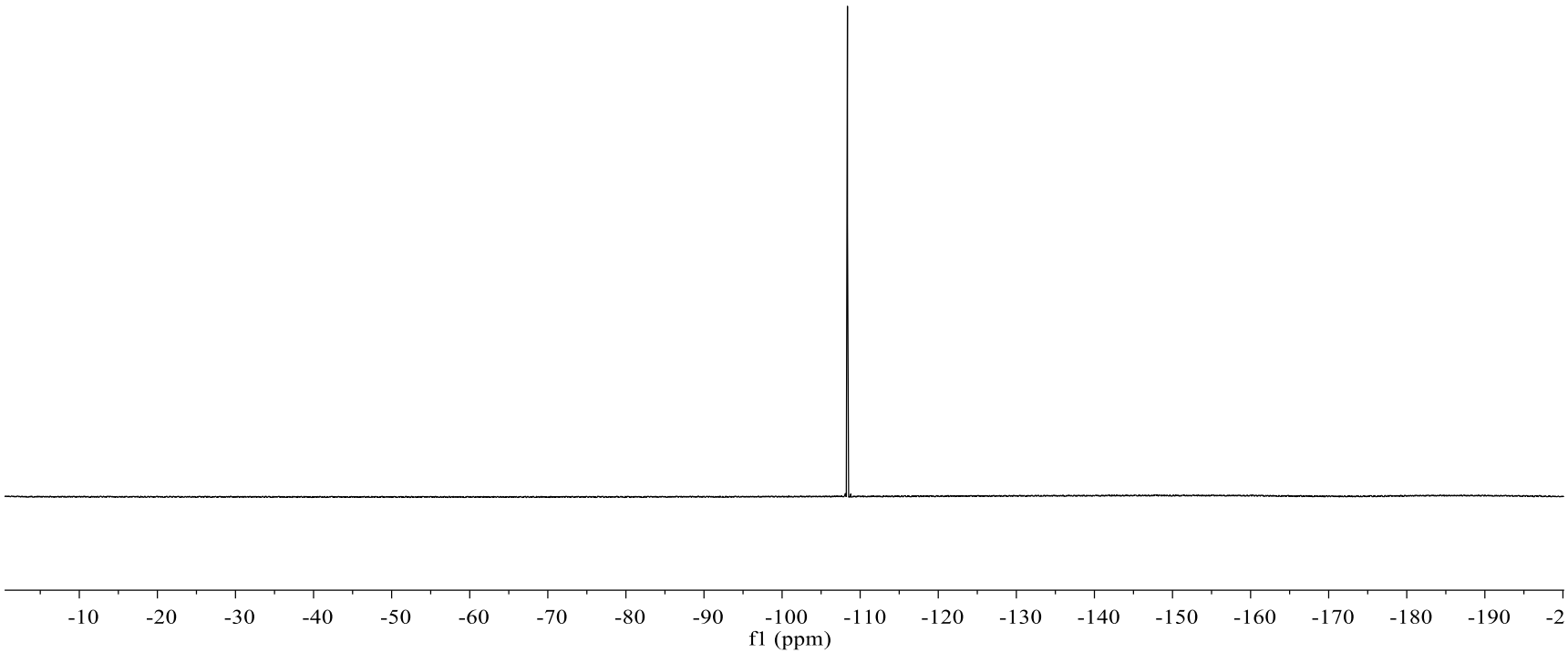
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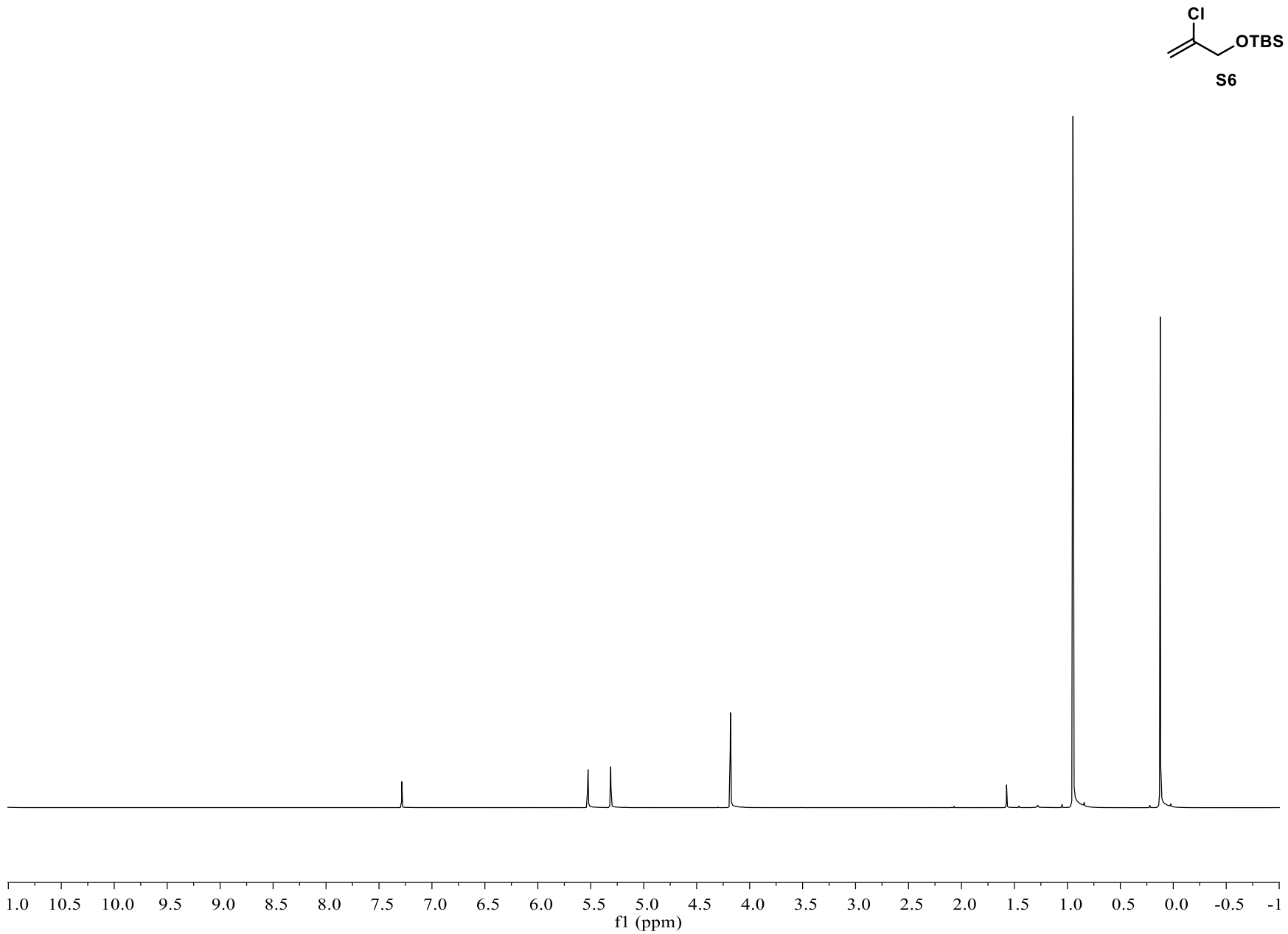
f1 (ppm)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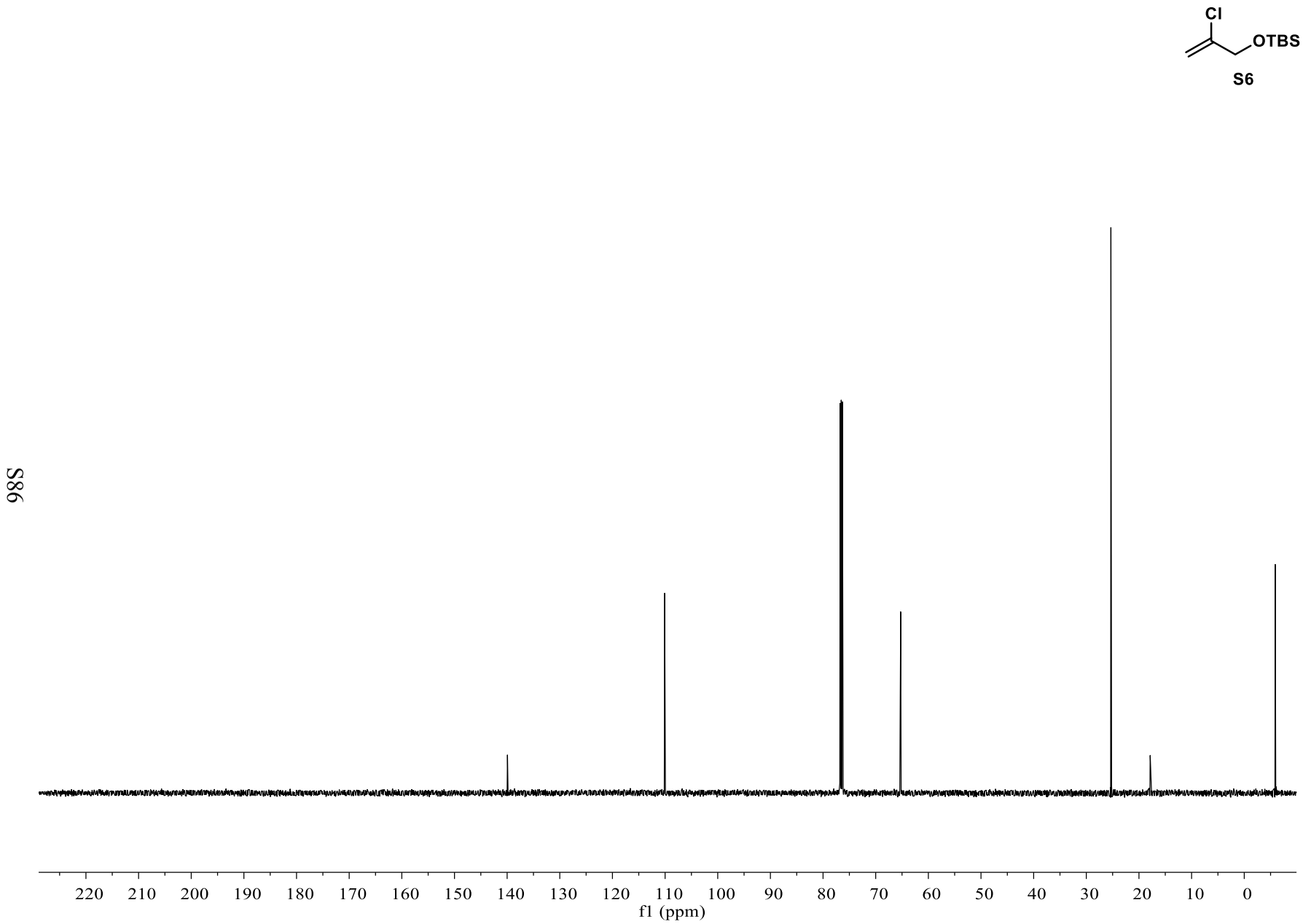
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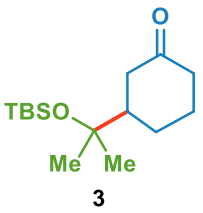

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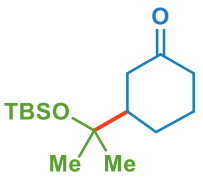
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Me
Me

3

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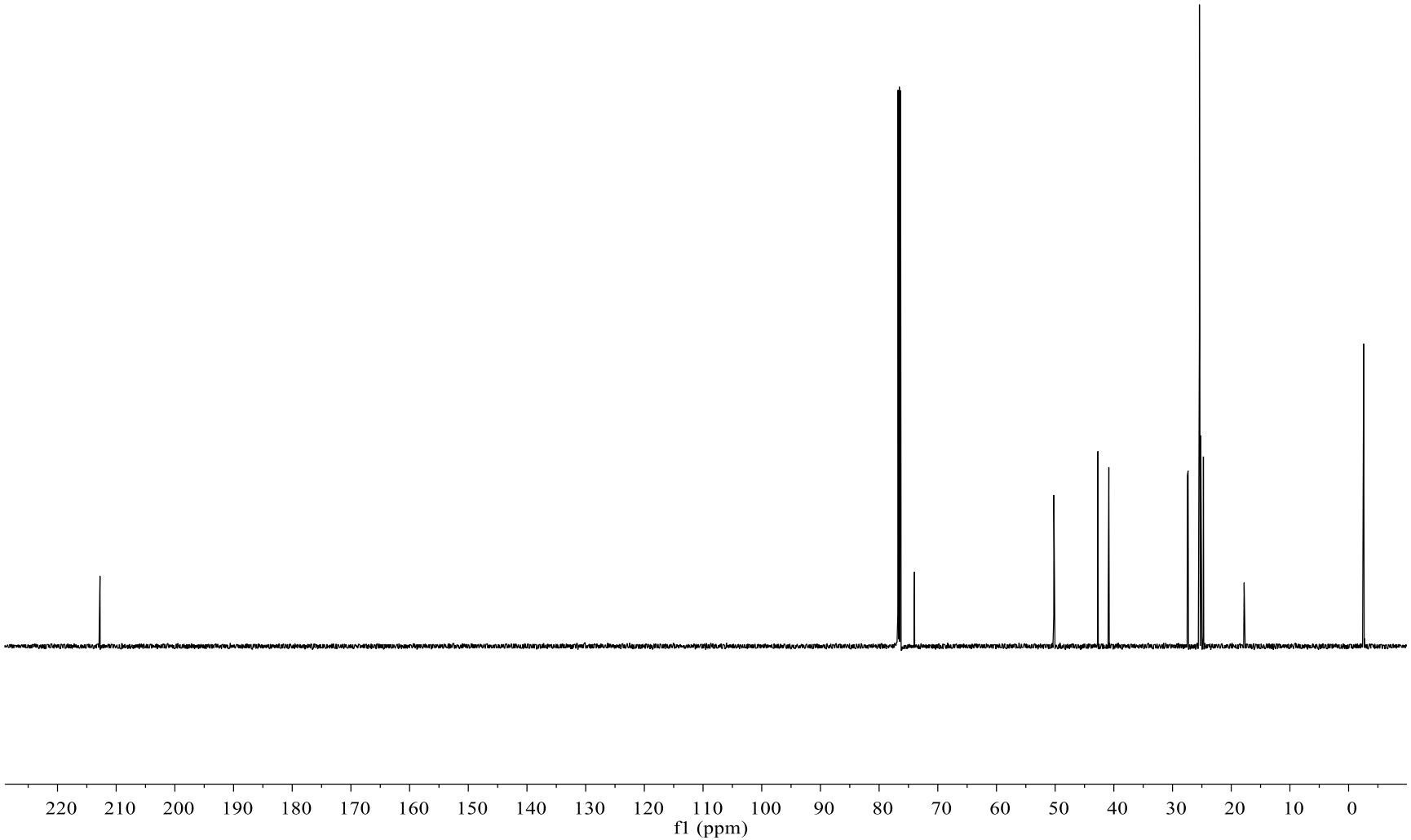
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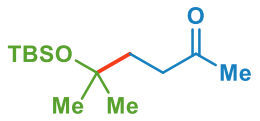
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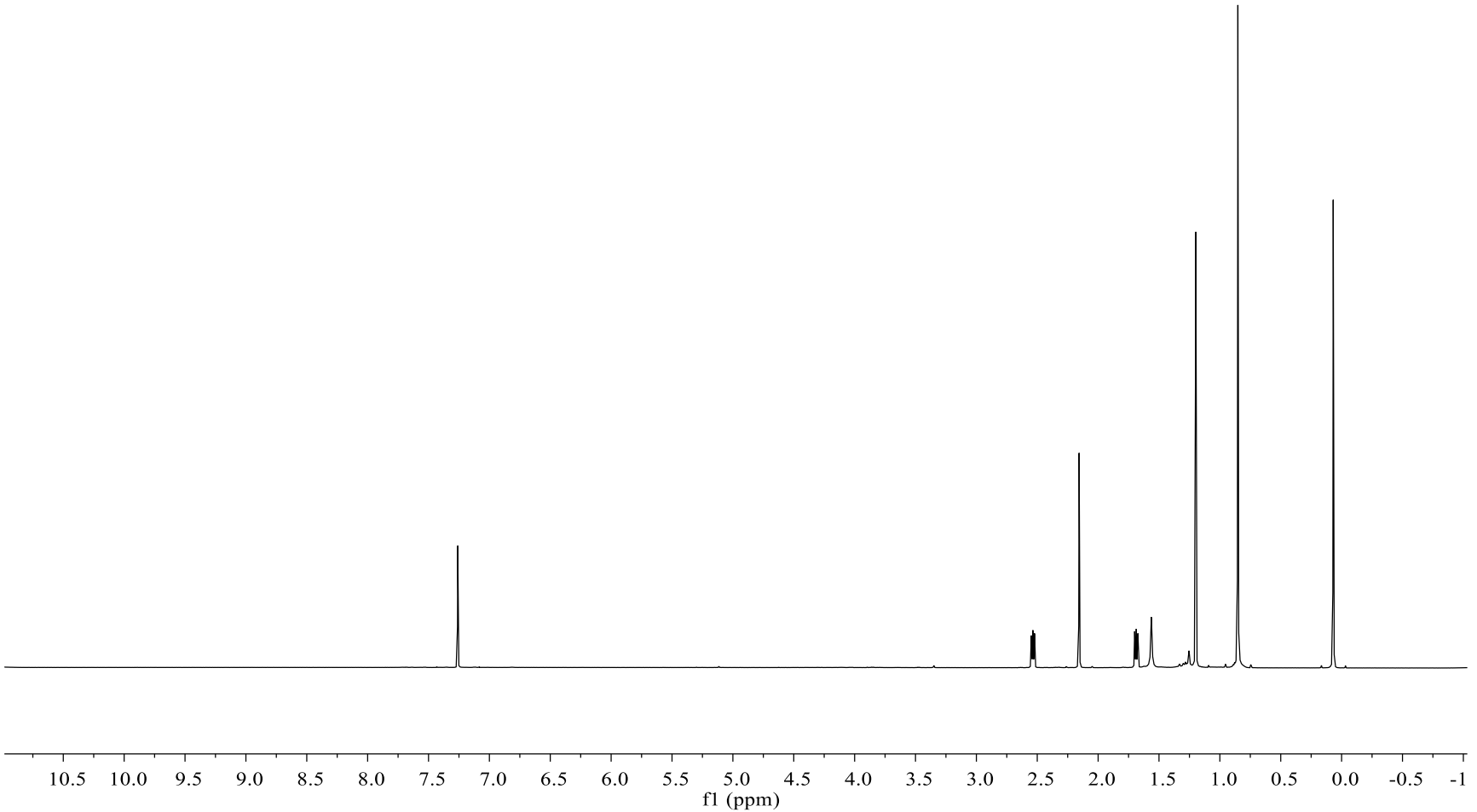
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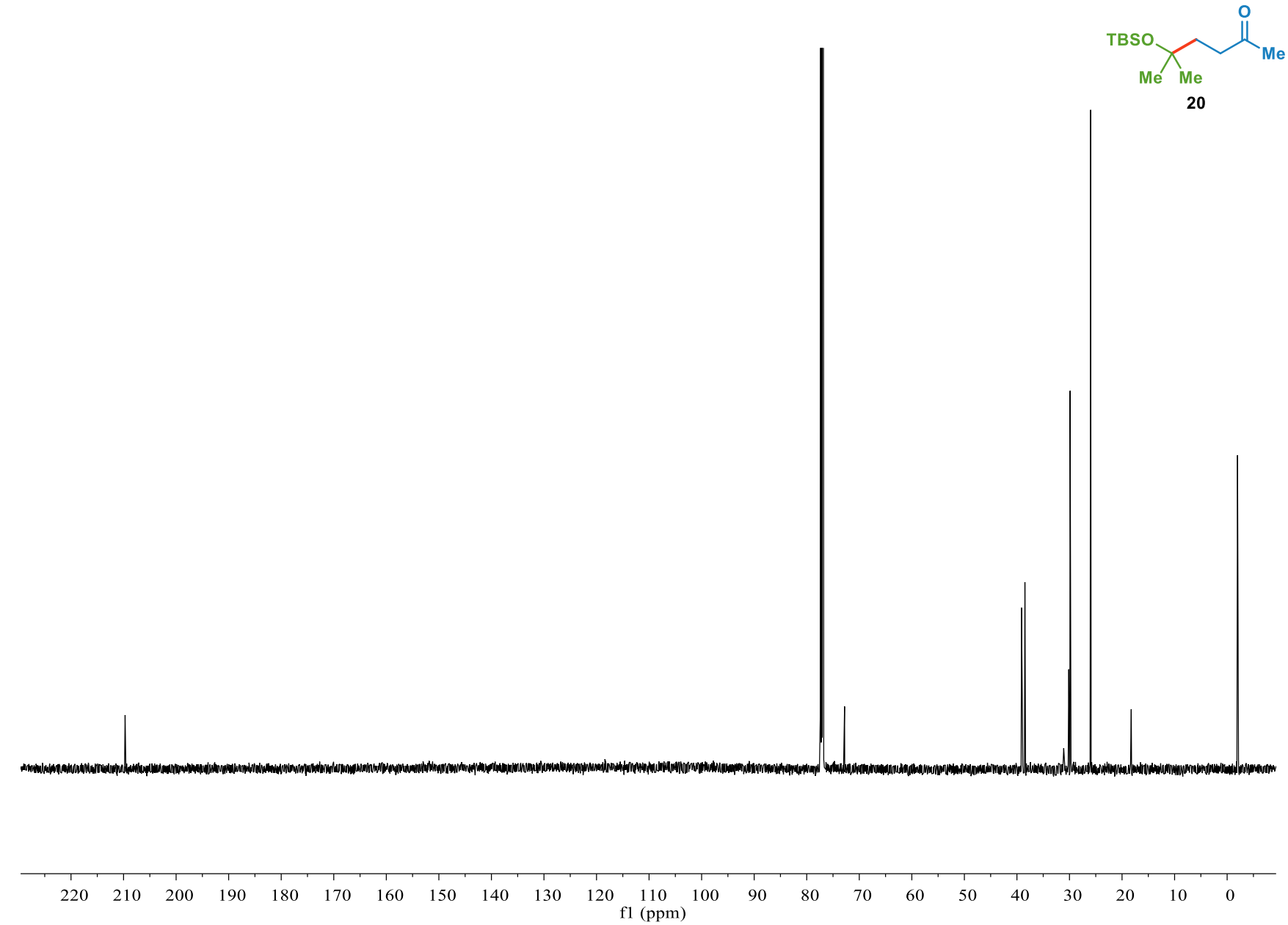
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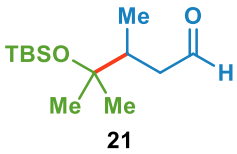
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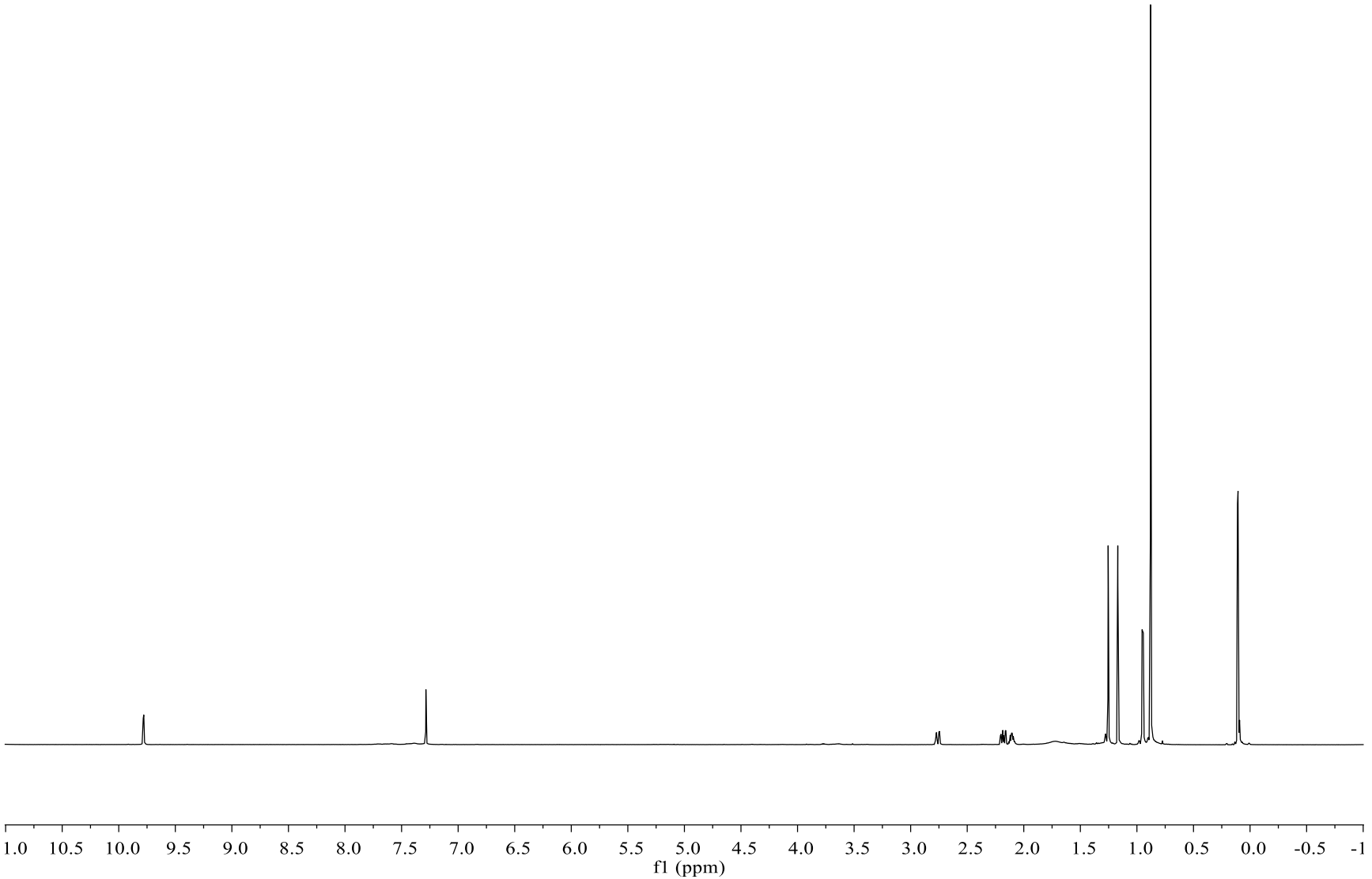
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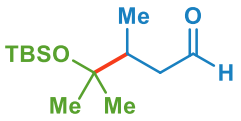
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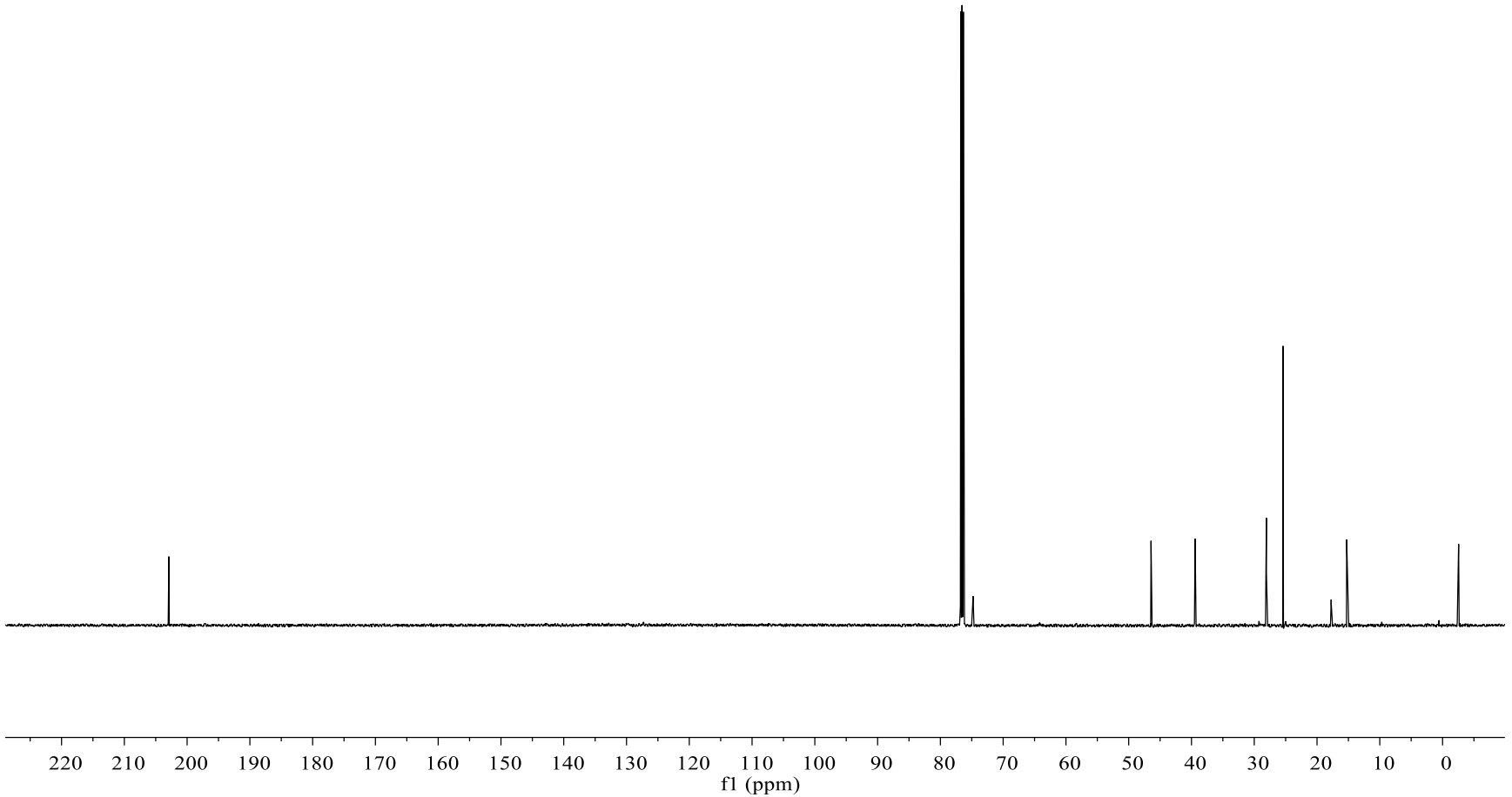
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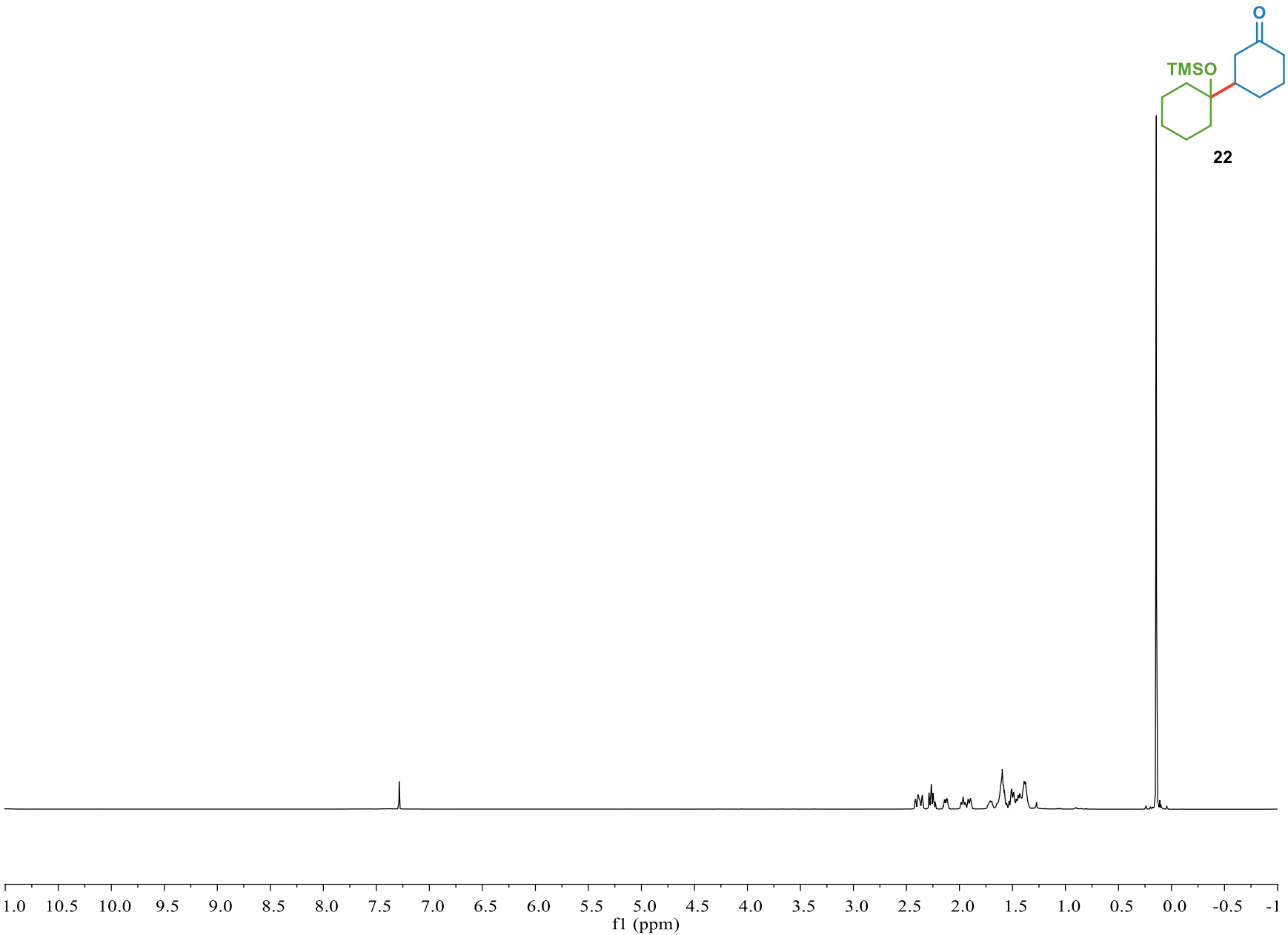
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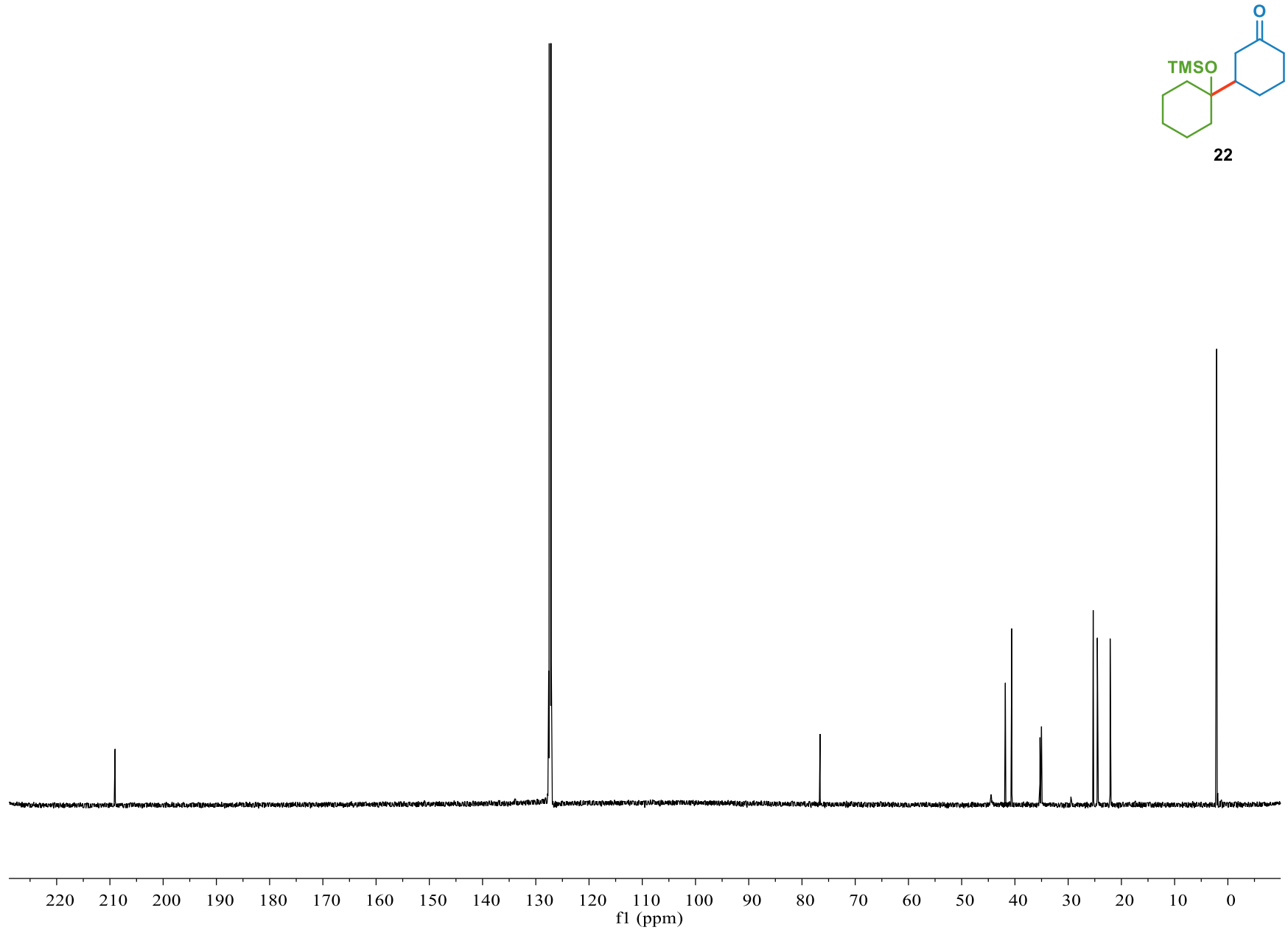
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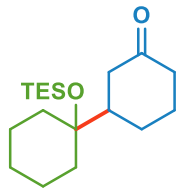
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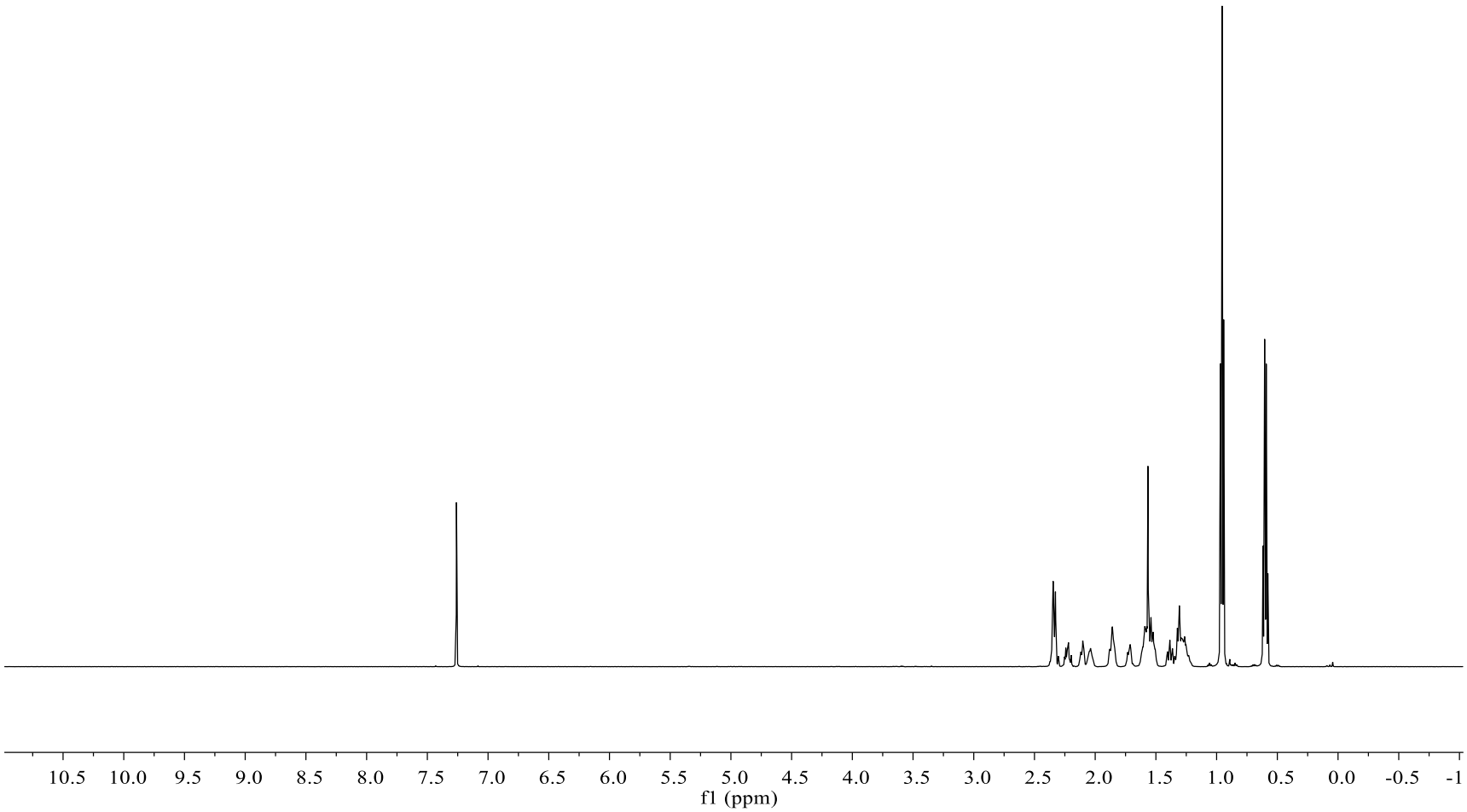
23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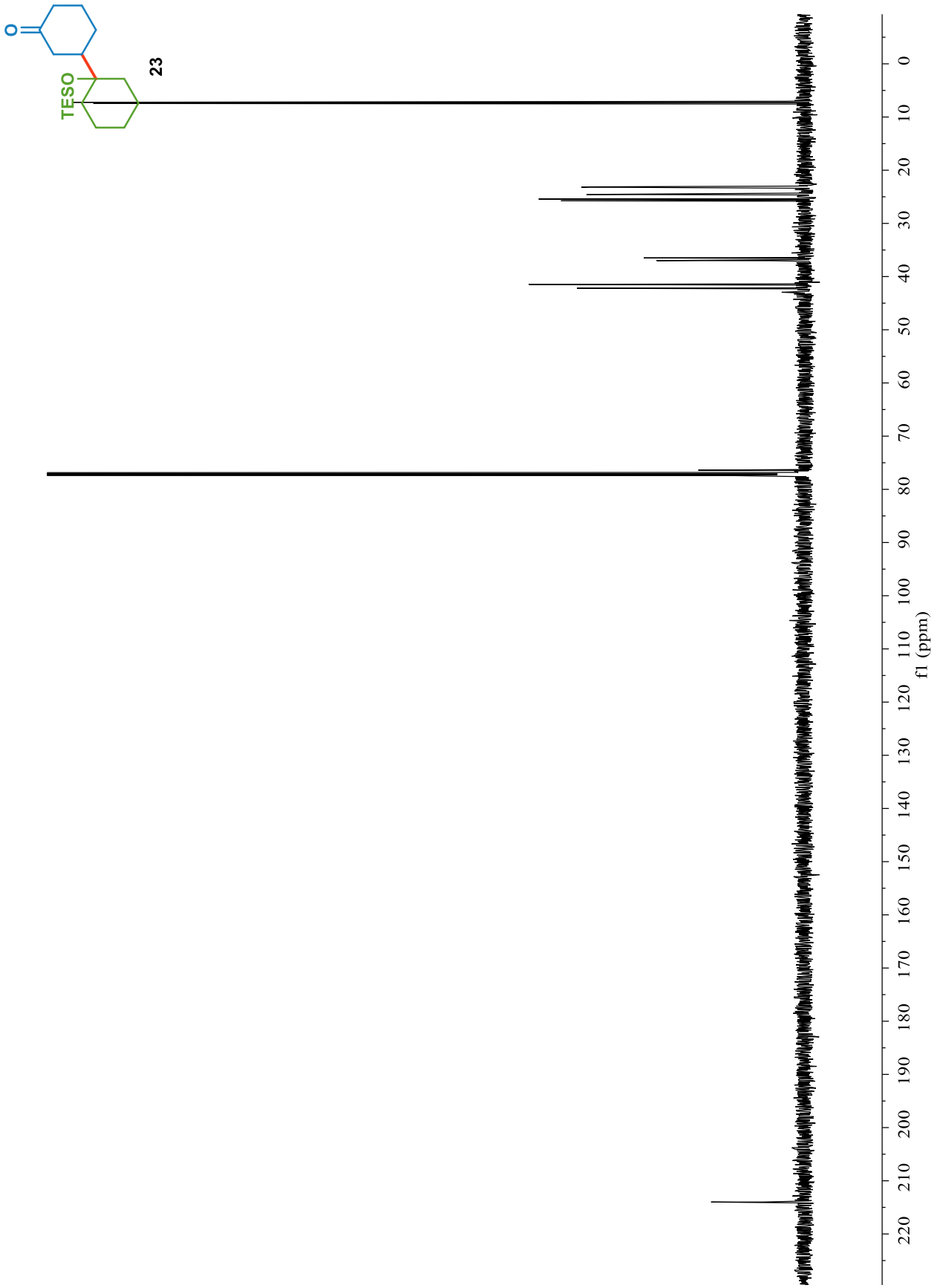
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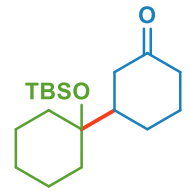
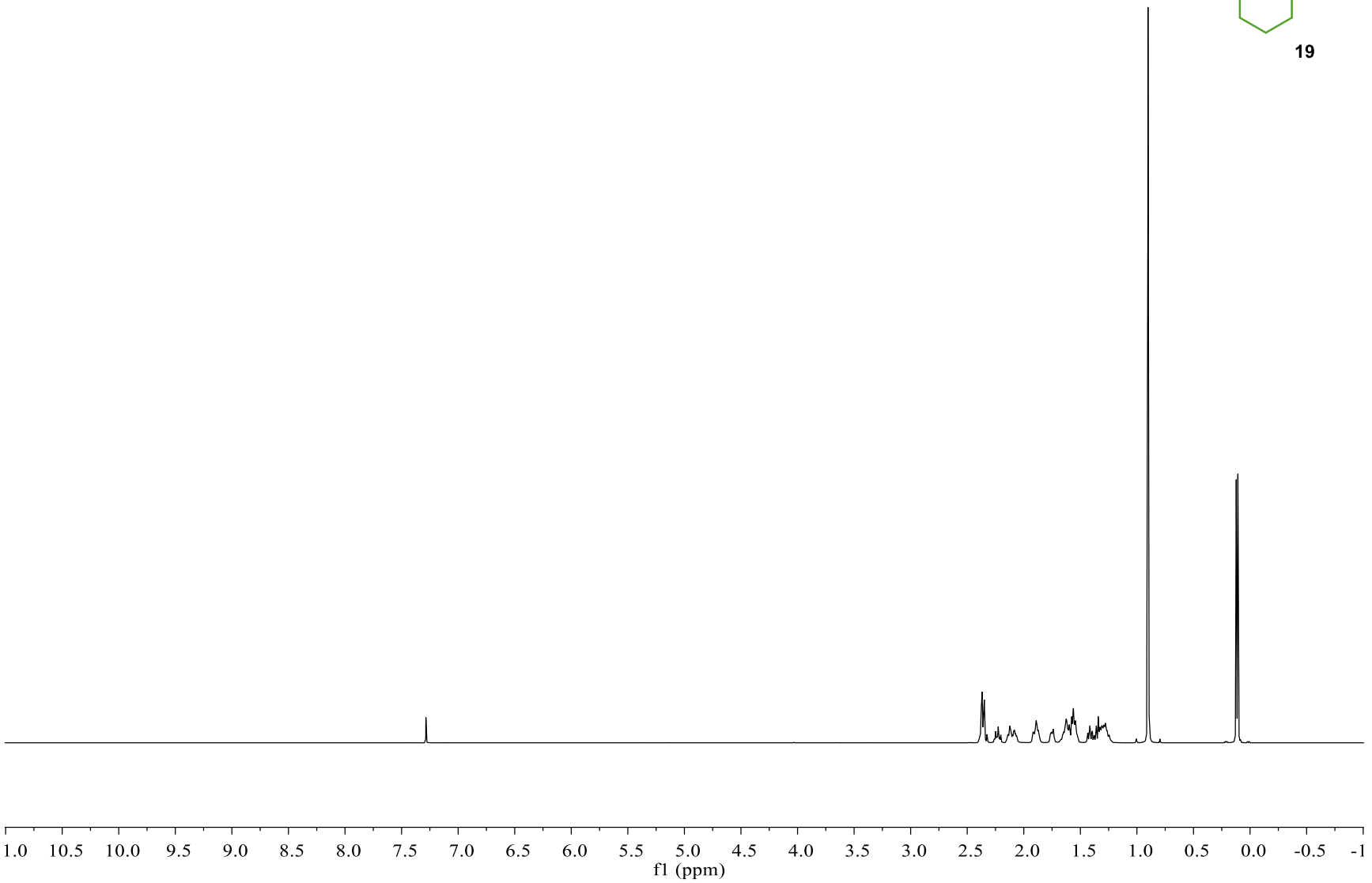
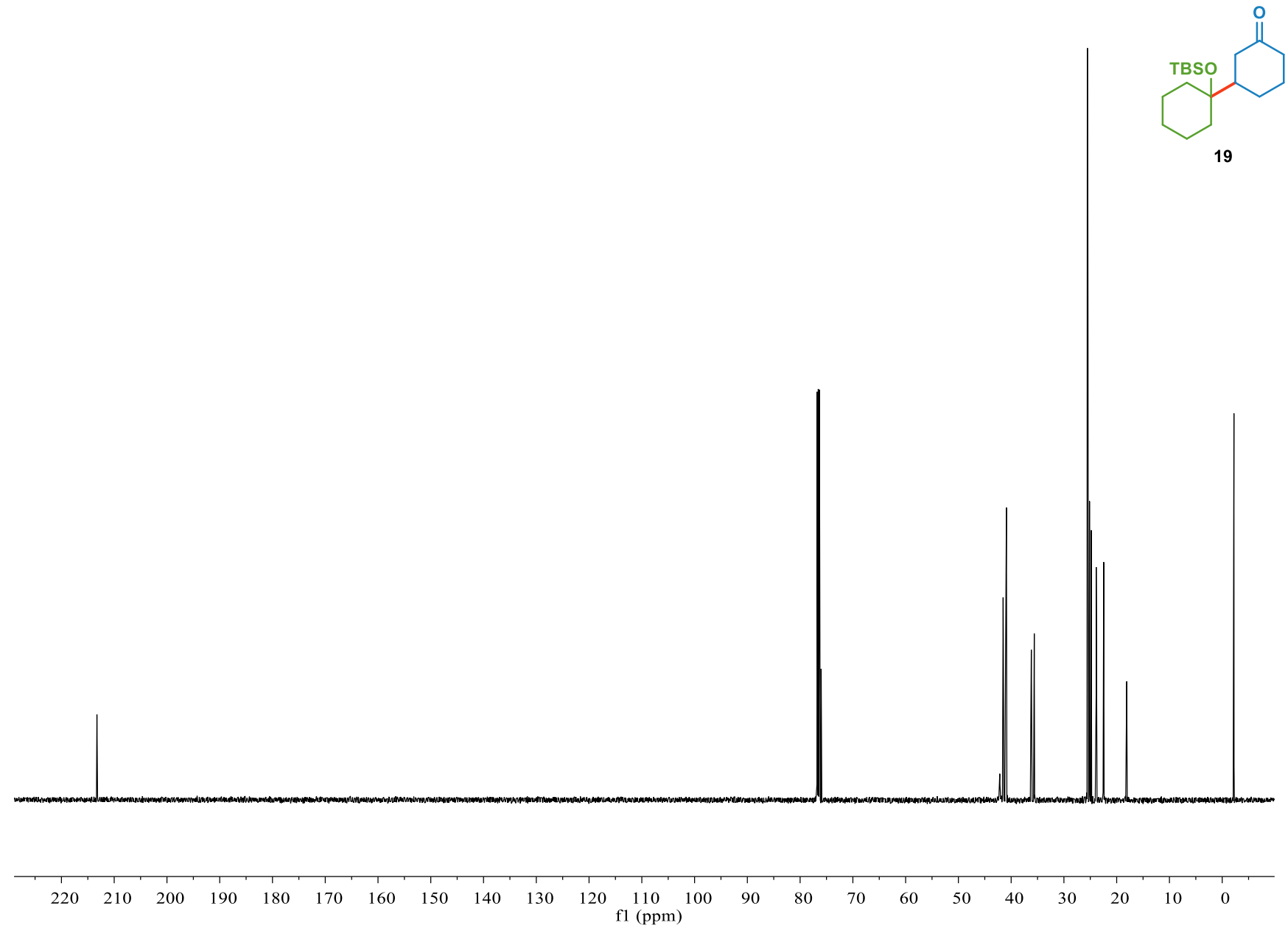
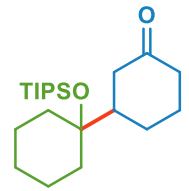
140
150
160
170
180
190
200
210
220
f1 (ppm)


O
TBSO

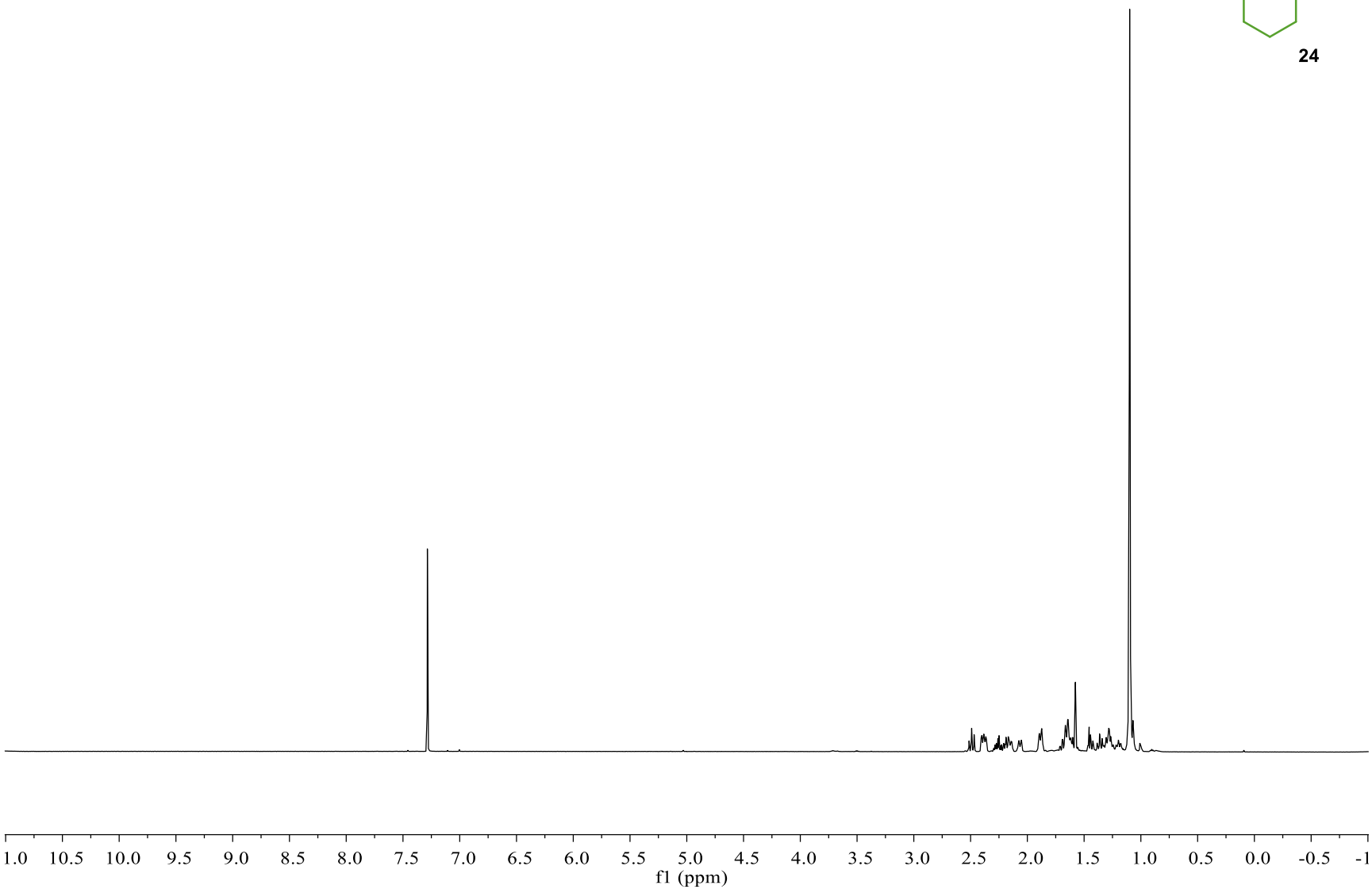
19

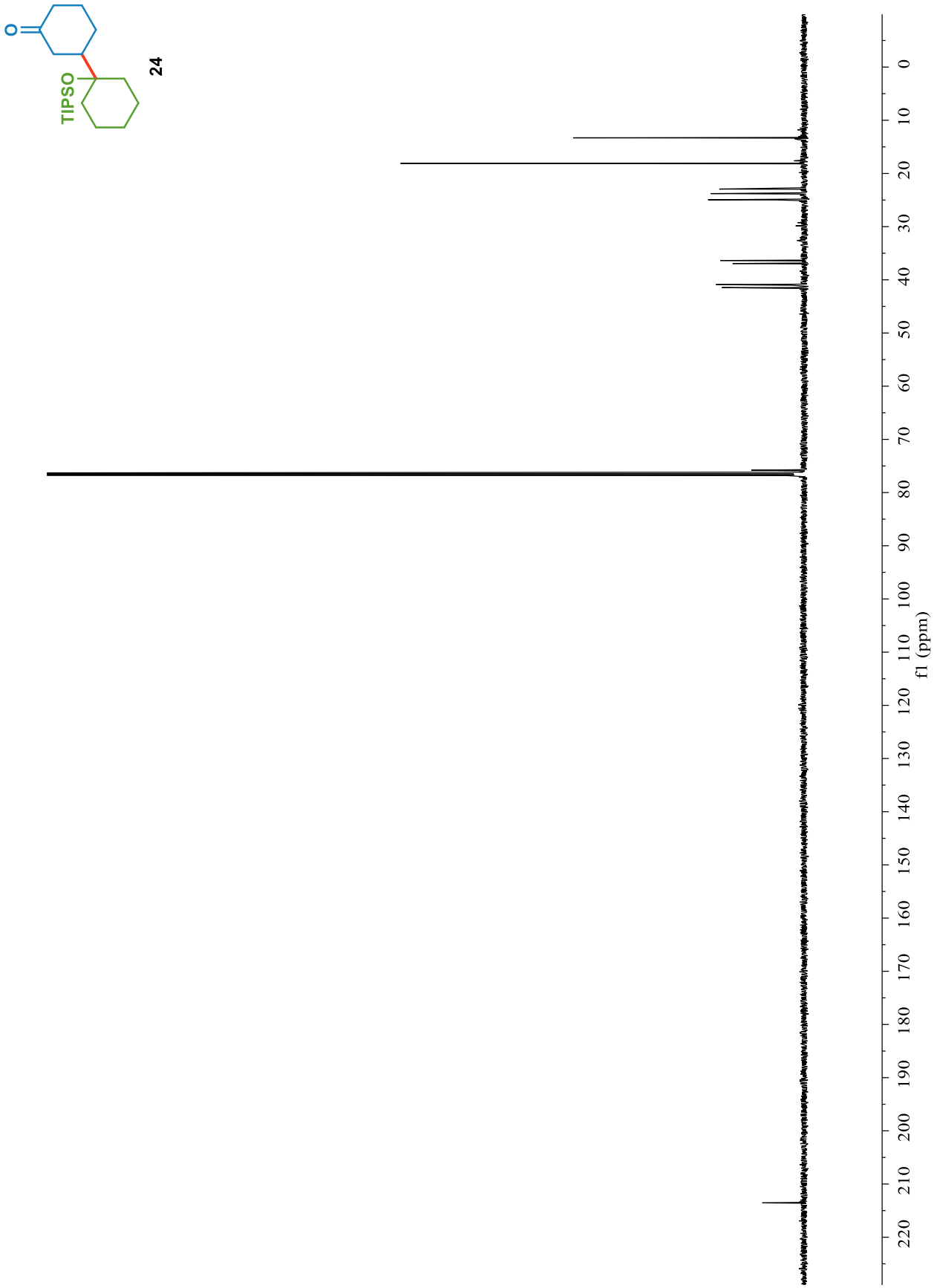

1.0 10.5 10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0 -0.5 -1
f1 (ppm)

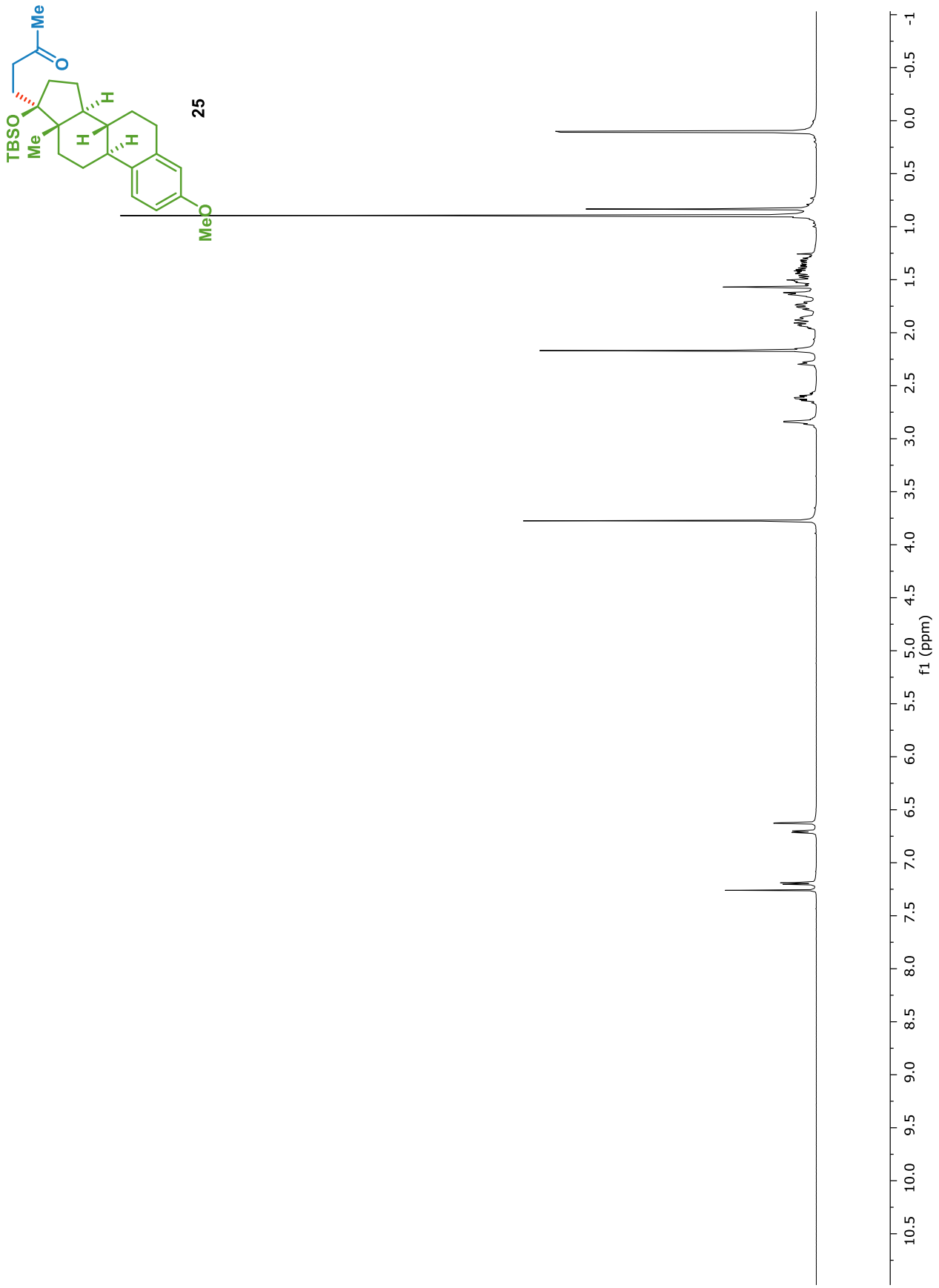

O
TBSO
19
220 210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
f1 (ppm)

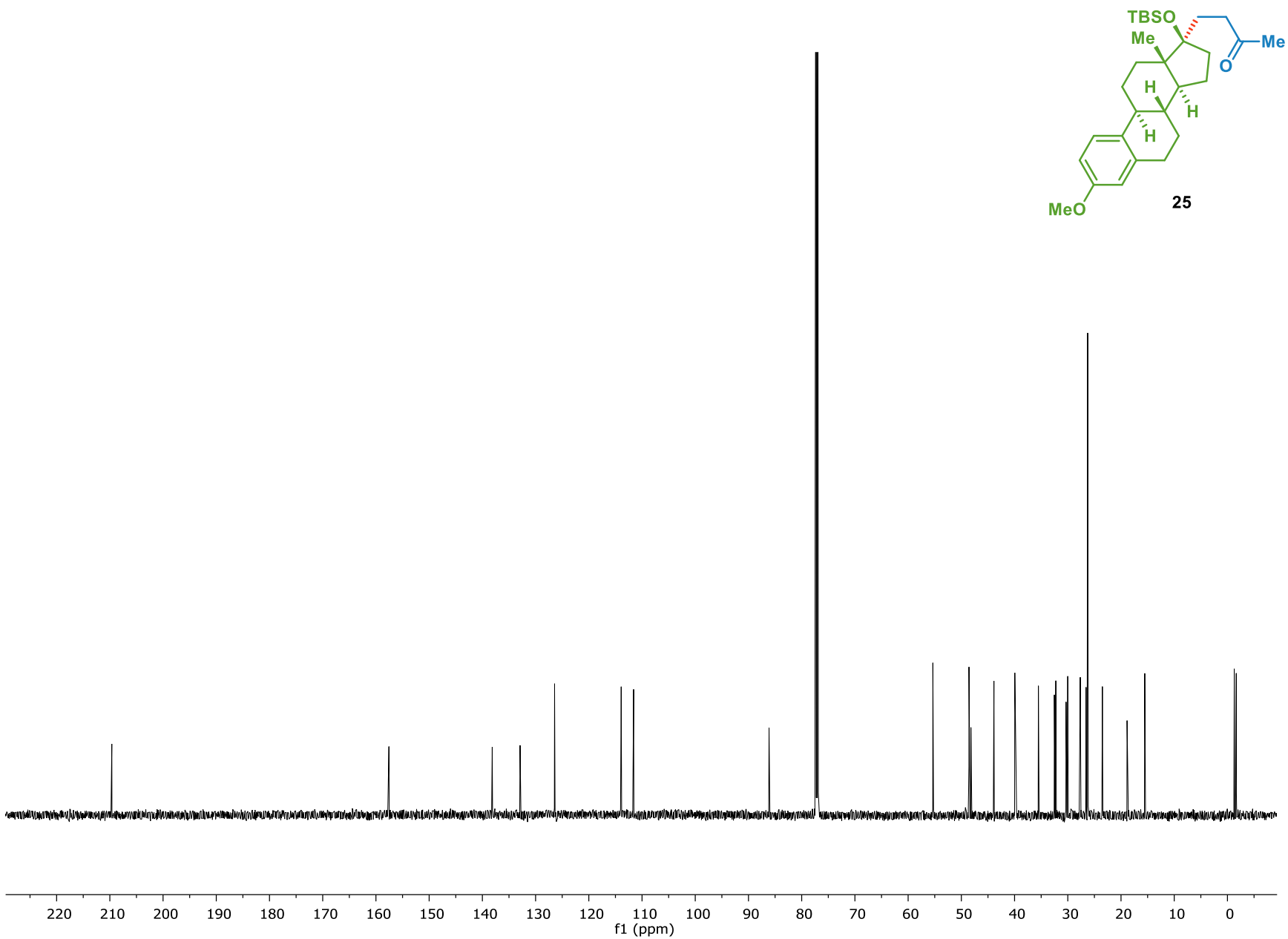

O
TIPSO

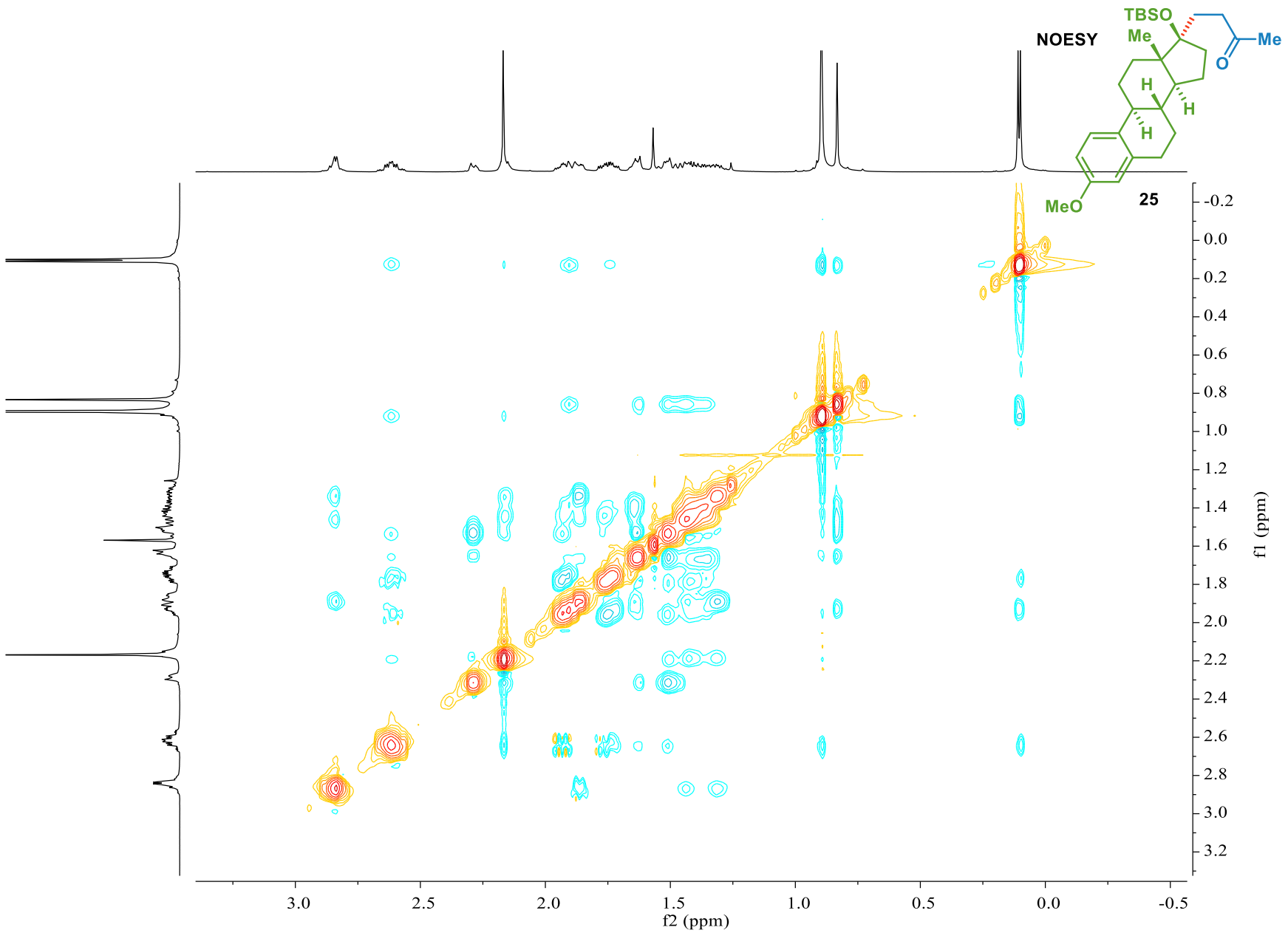
24

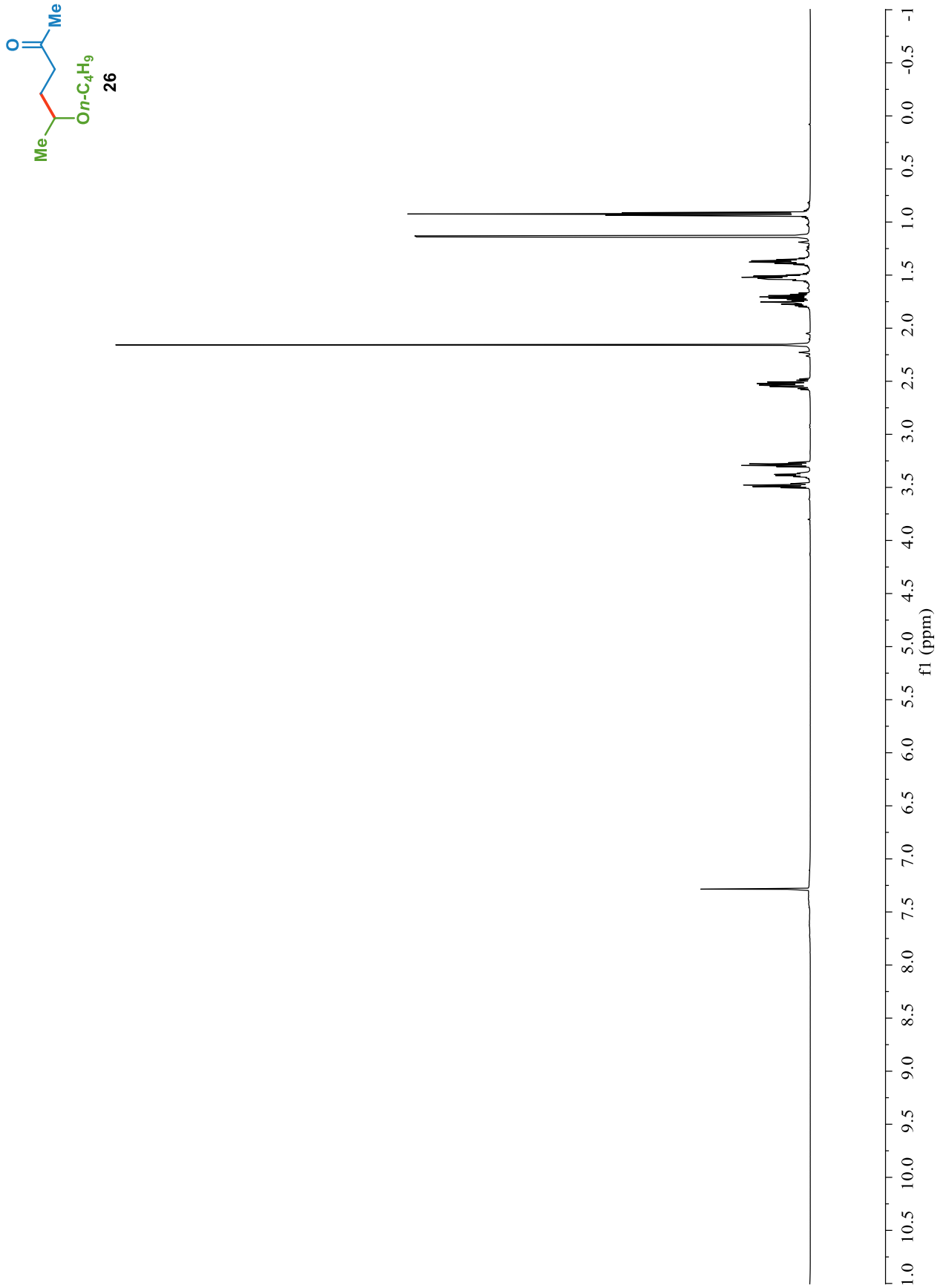

1.0 10.5 10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0 -0.5 -1
f1 (ppm)

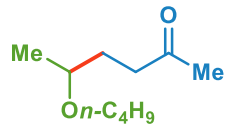

O
TIPSO
24
0
10
20
30
40
50
60
70
80
90
100
110
120
130
140
150
160
170
180
190
200
210
220
f1 (ppm)


Me
O
TBSO
Me
H
H
H
25
MeO
10.5
10.0
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
-0.5
-1
f1 (ppm)

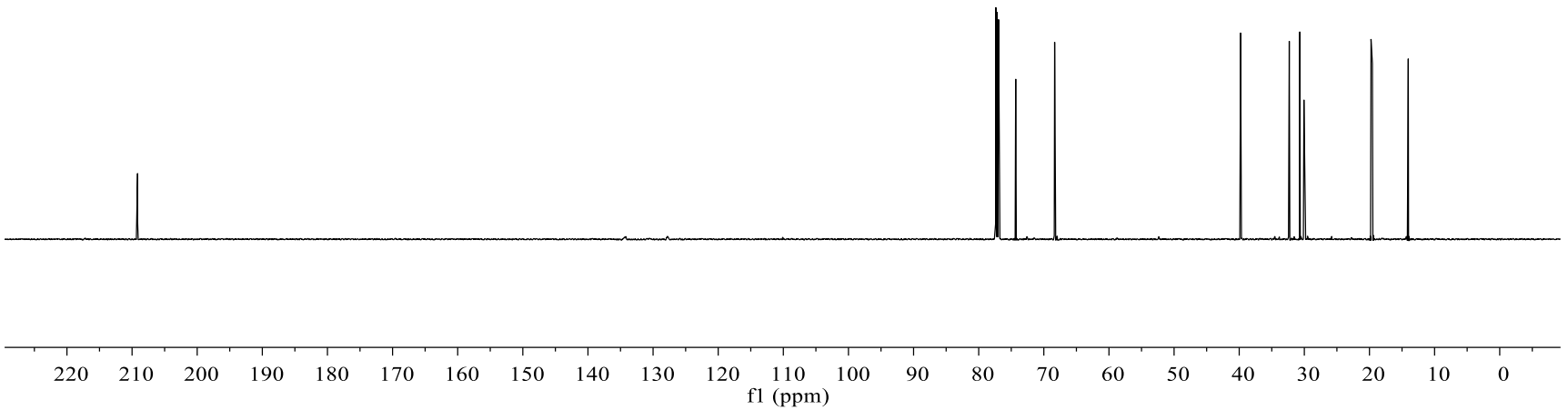

TBSO
Me
Me
O
H
H
H
MeO
25
220
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)

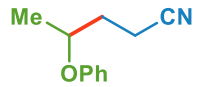

NOESY
TBSO
Me
Me
O
H
H
H
MeO
25
-0.2
0.0
0.2
0.4
0.6
0.8
1.0
1.2
1.4
1.6
1.8
2.0
2.2
2.4
2.6
2.8
3.0
3.2
f1 (ppm)
3.0
2.5
2.0
1.5
1.0
0.5
0.0
-0.5
f2 (ppm)


O
Me
On-C4H9
Me
26
1.0
10.5
10.0
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
-0.5
-1
f1 (ppm)

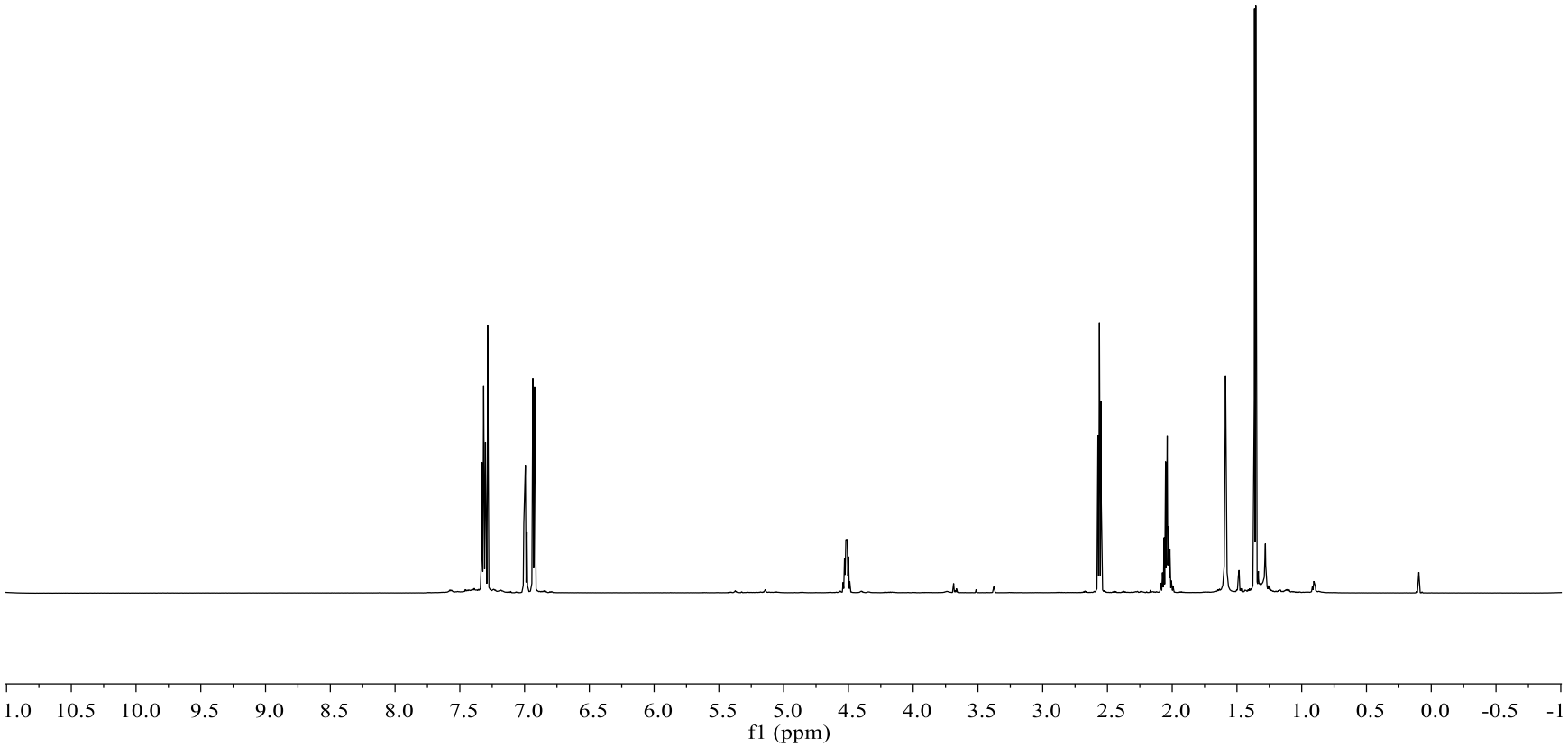

O
Me
Me
On-C4H9

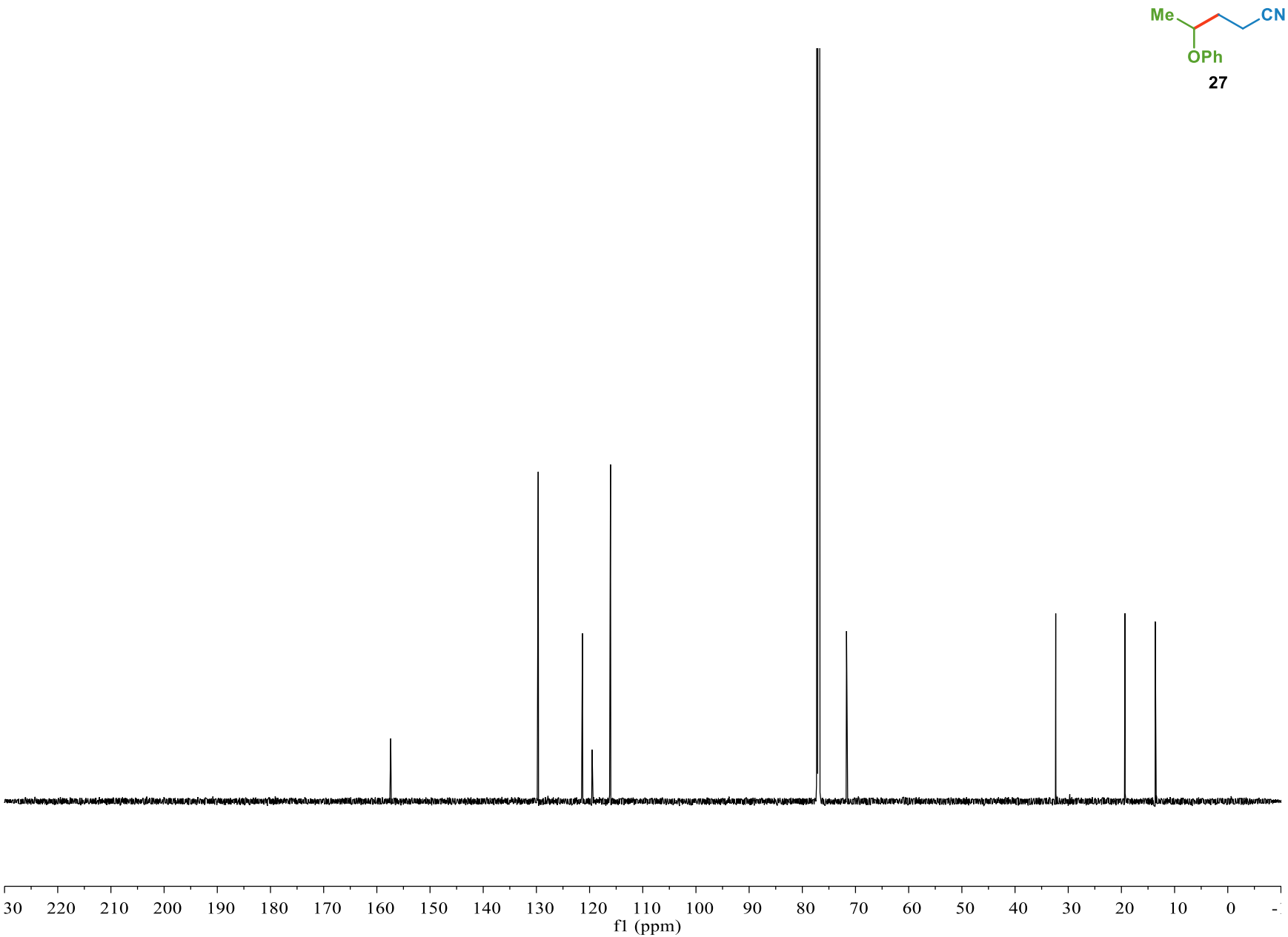
26

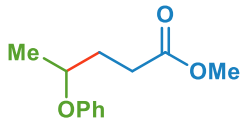

220 210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
f1 (ppm)


Me
CN
OPh

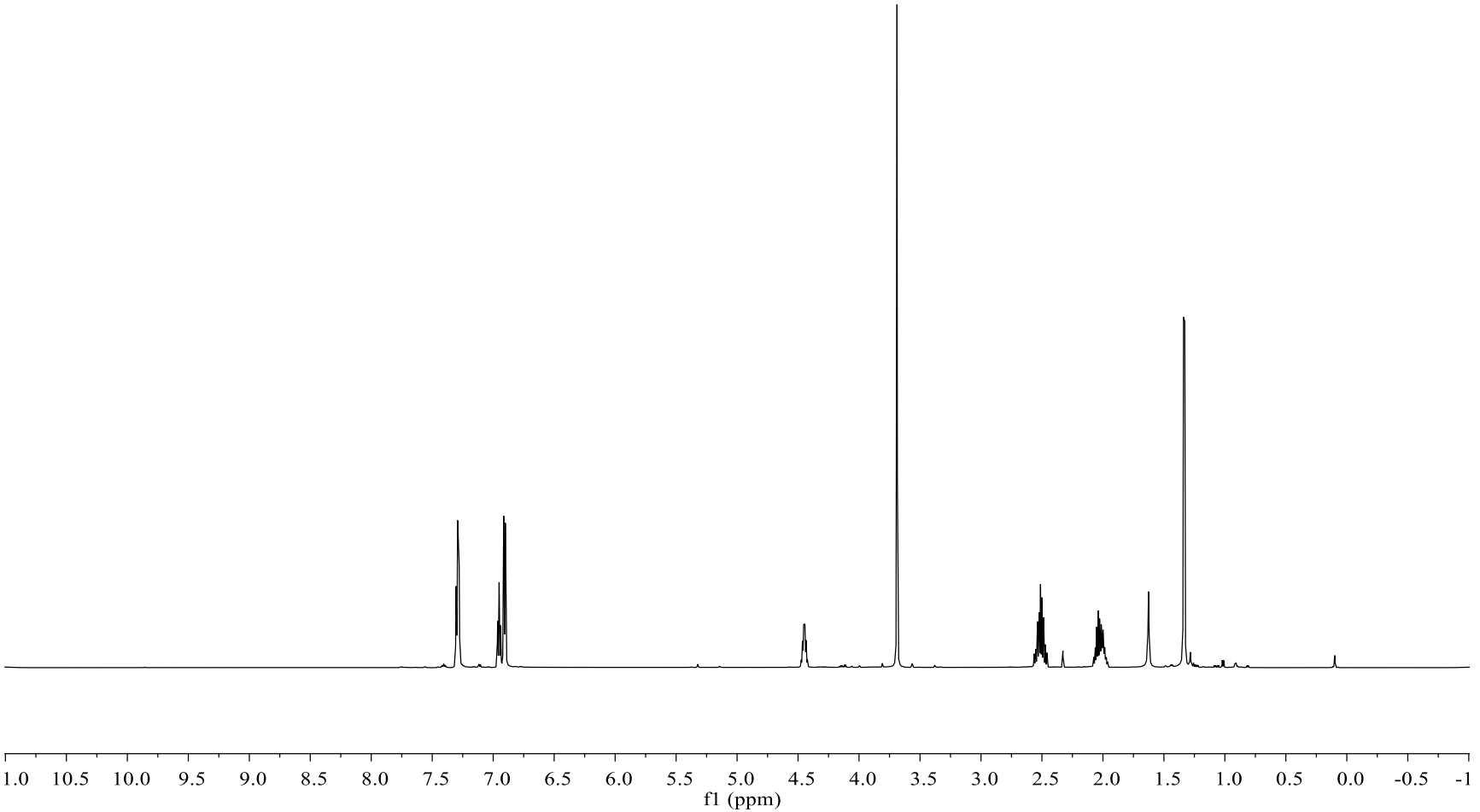
27

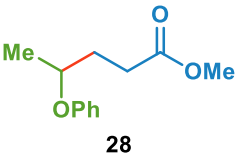

1.0
10.5
10.0
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
-0.5
-1
f1 (ppm)


Me
CN
OPh
27
30 220 210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
f1 (ppm)

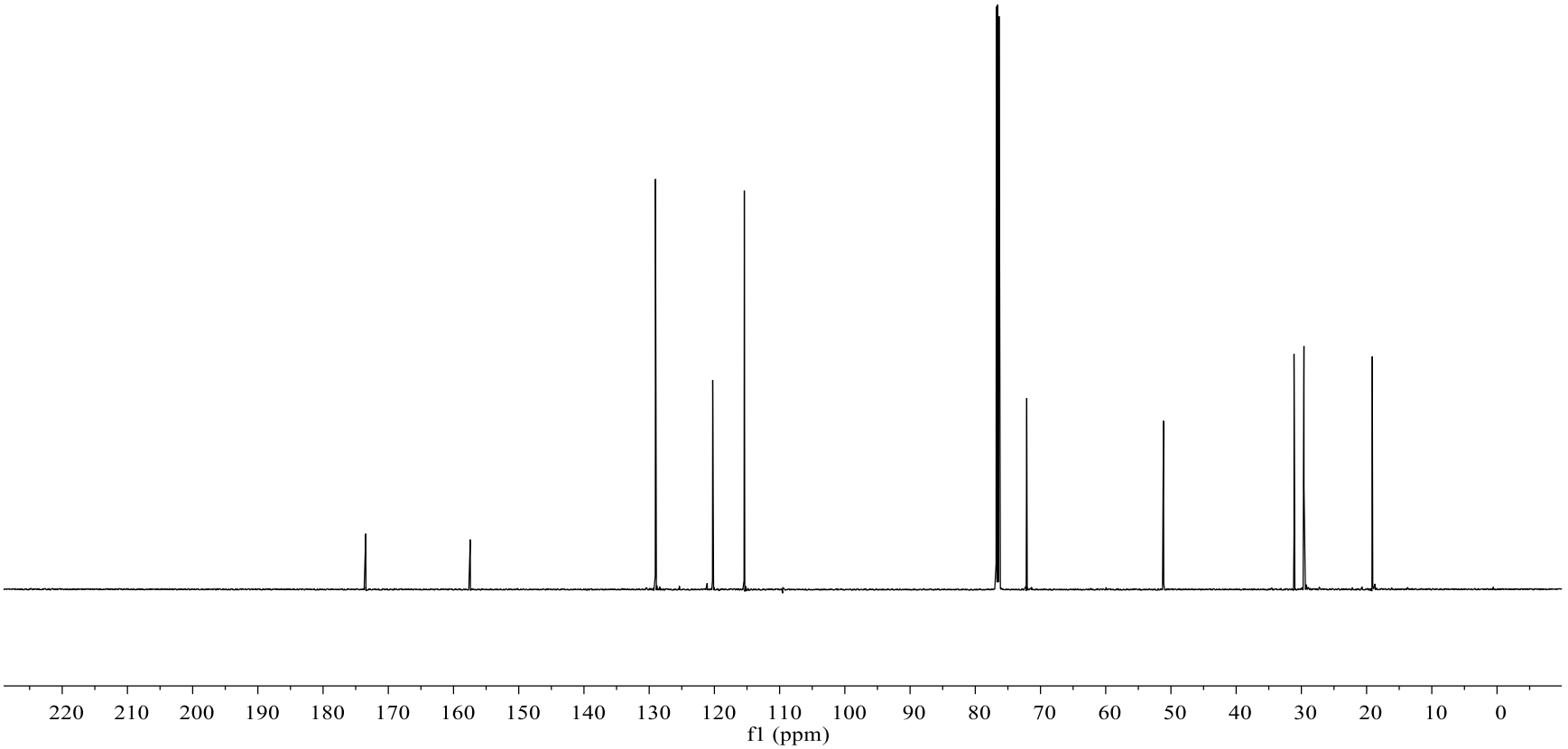

Me
O
OMe
OPh

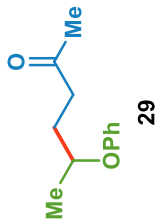
28


1.0
10.5
10.0
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
-0.5
-1
f1 (ppm)

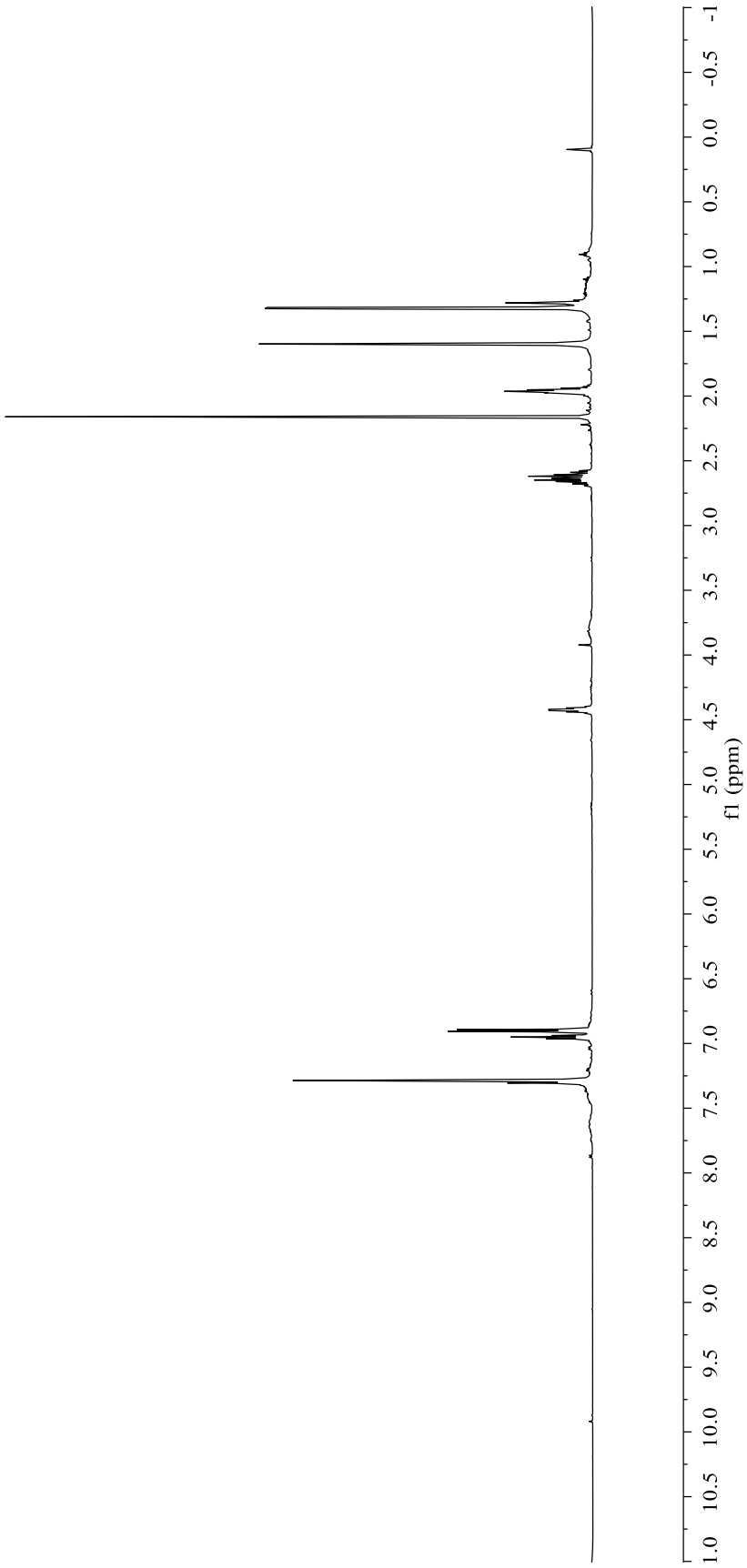

O
Me
OMe
OPh

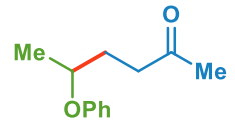
28


220
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)


O
Me
OPh
Me

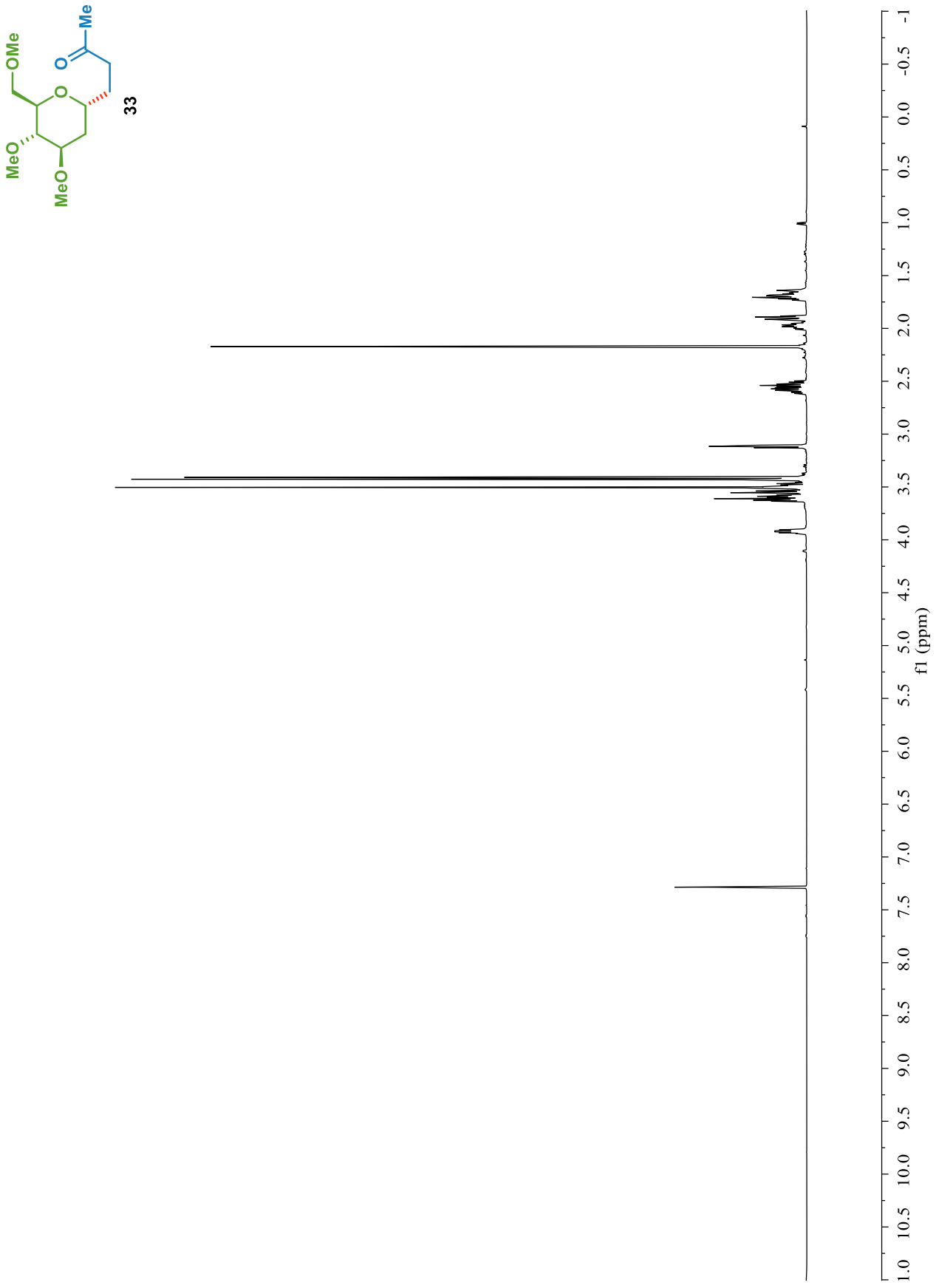
29

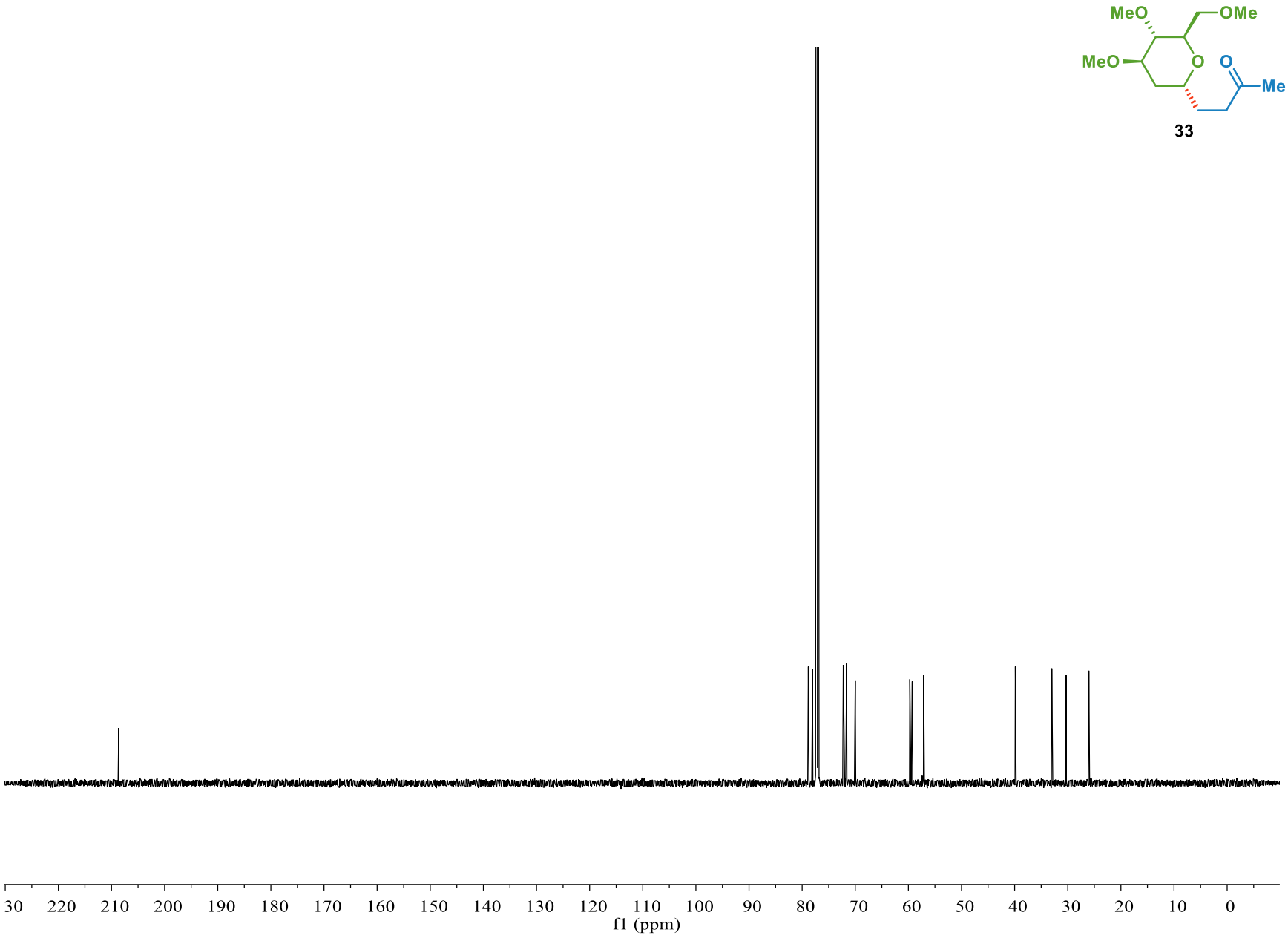

1.0
10.5
10.0
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
-0.5
-1
f1 (ppm)

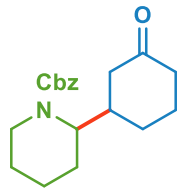

O
Me
Me
OPh

29

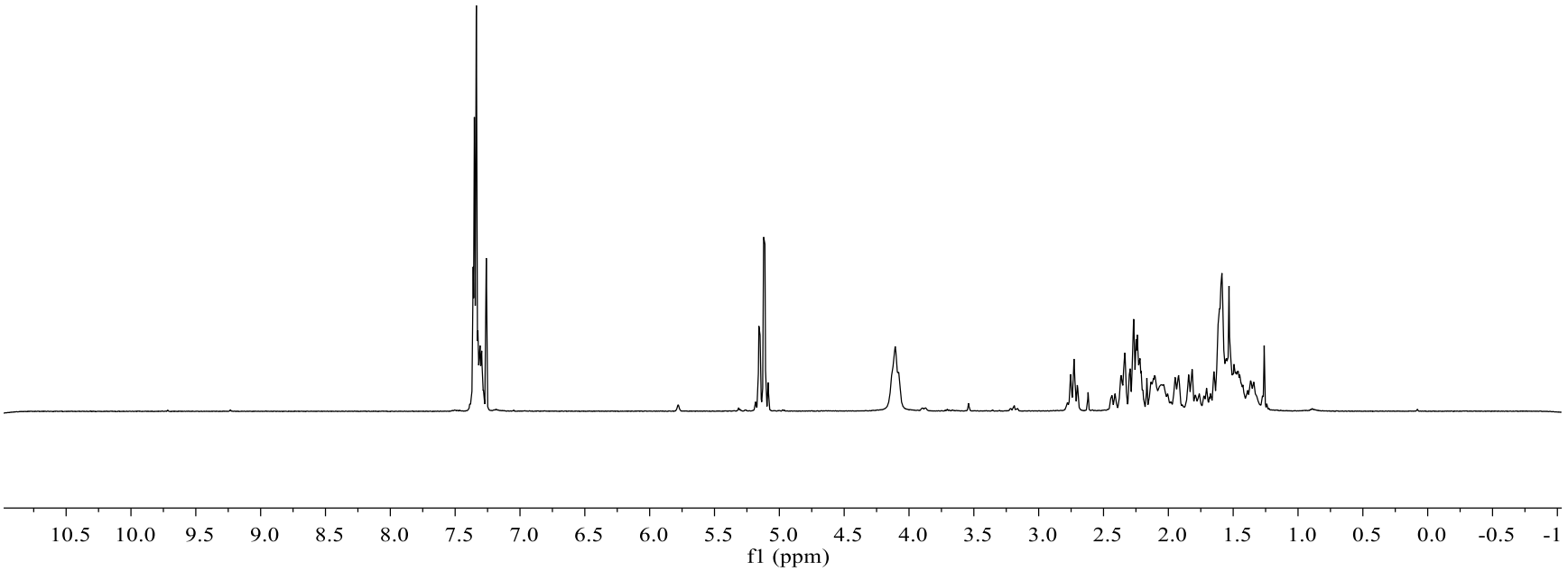
30 220 210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
f1 (ppm)

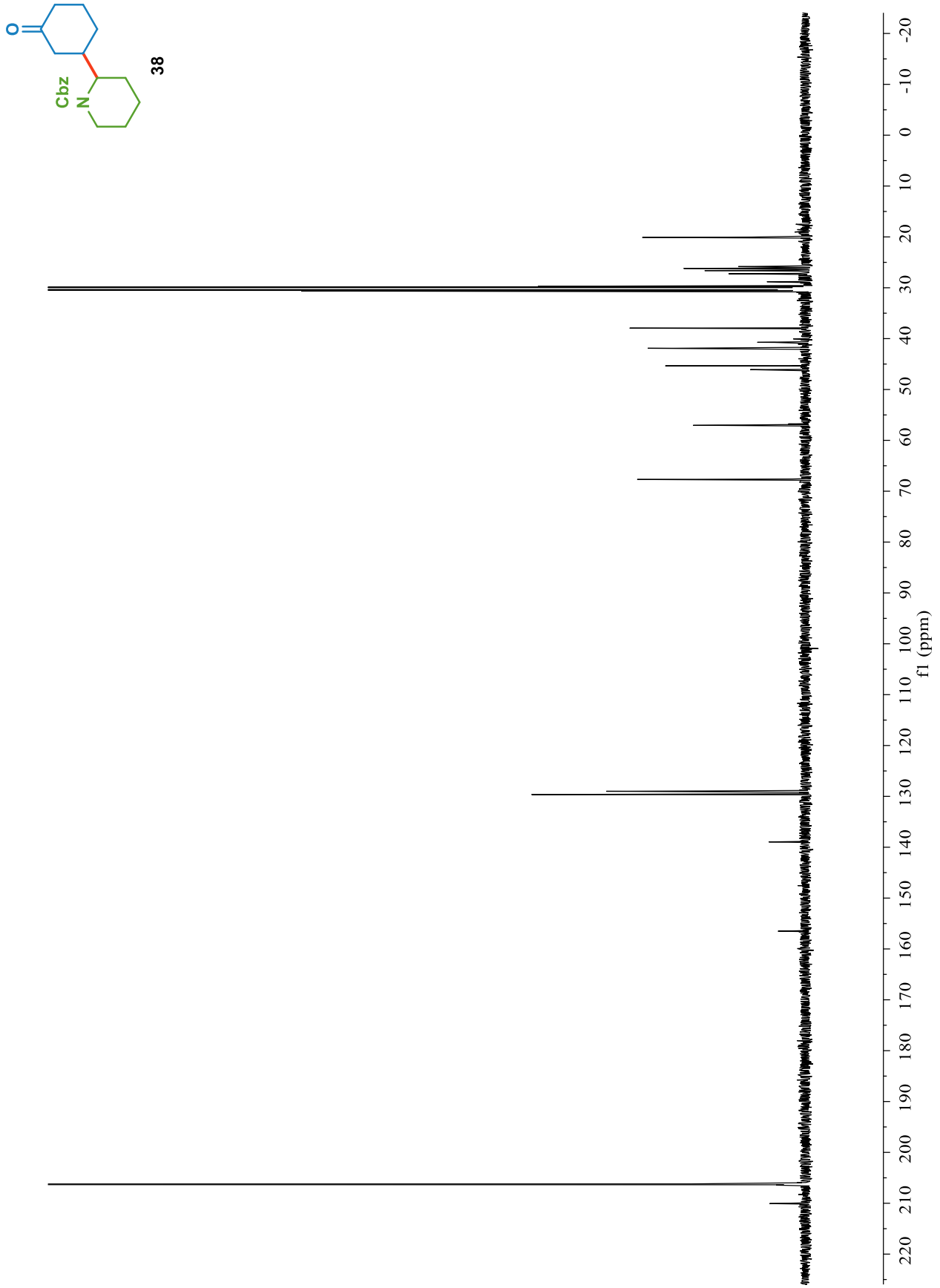

OMe
MeO
MeO
O
O
Me
33
1.0
10.5
10.0
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
-0.5
-1
f1 (ppm)

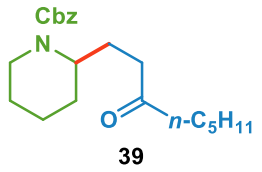

MeO
OMe
MeO
O
O
Me
33
30
220
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)


O
Cbz
N

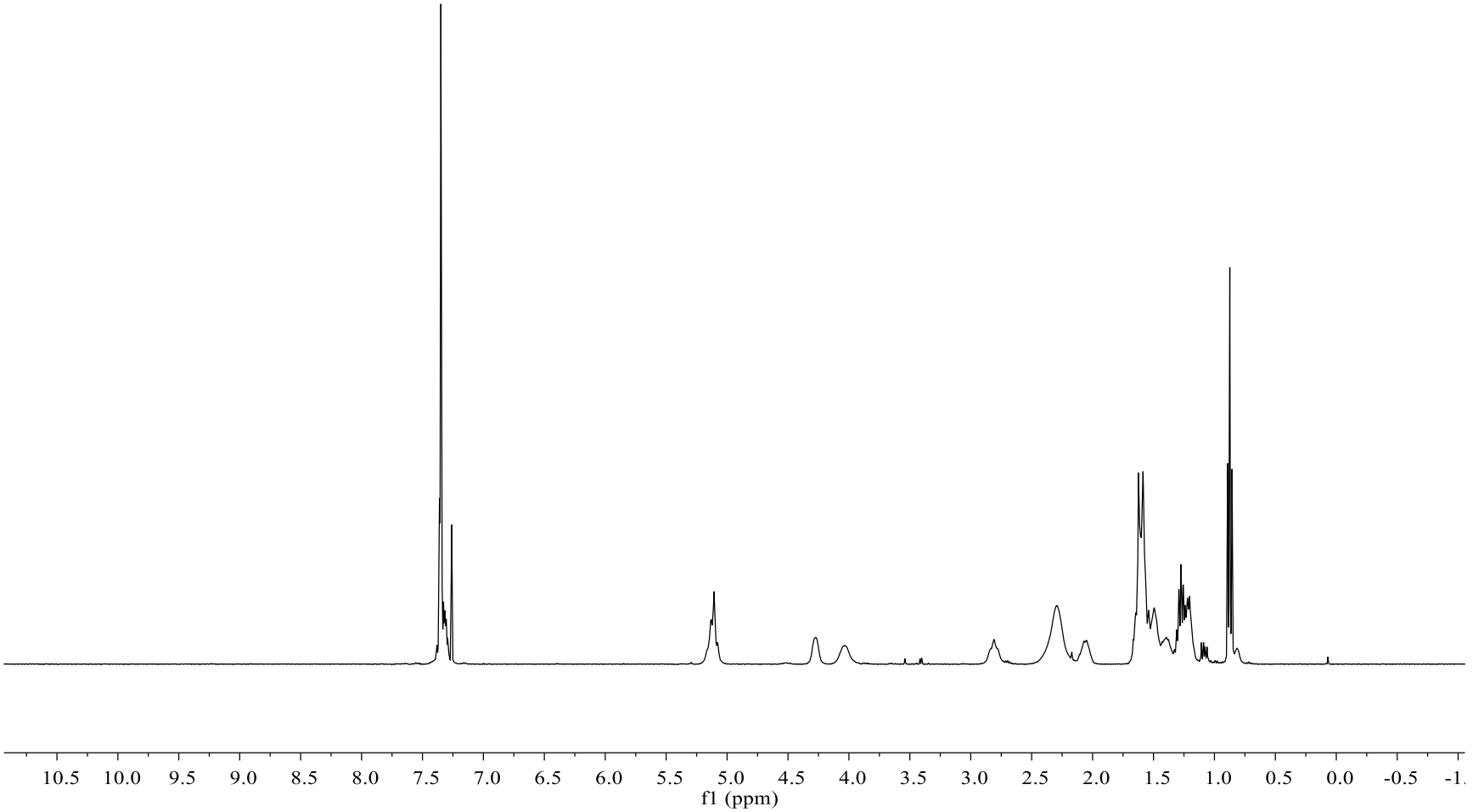
38

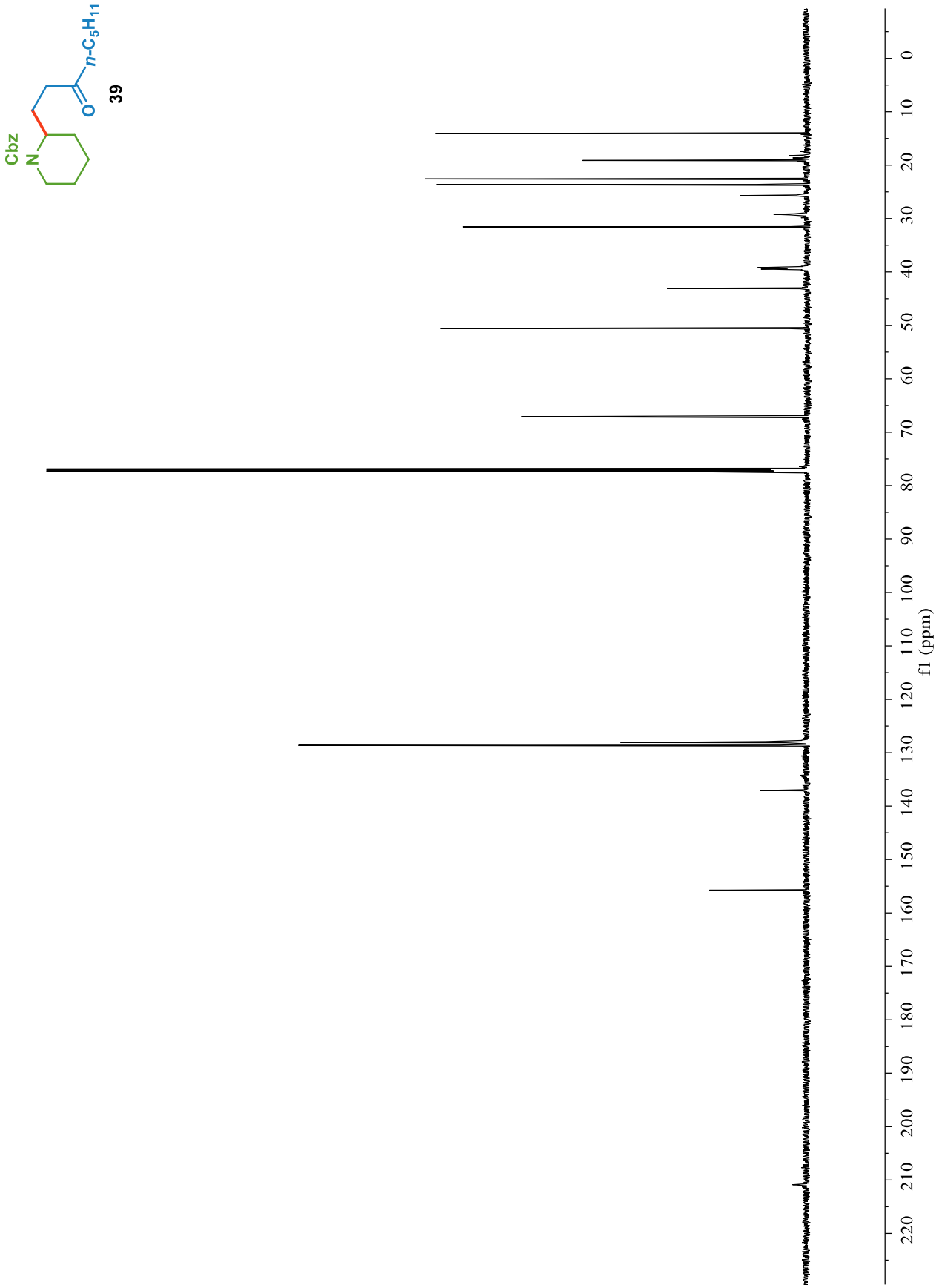

10.5 10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0 -0.5 -1
f1 (ppm)

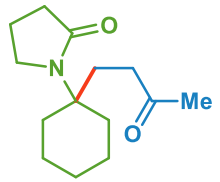

O
Cbz
N
38
f1 (ppm)


Cbz
N
O
n-C5H11

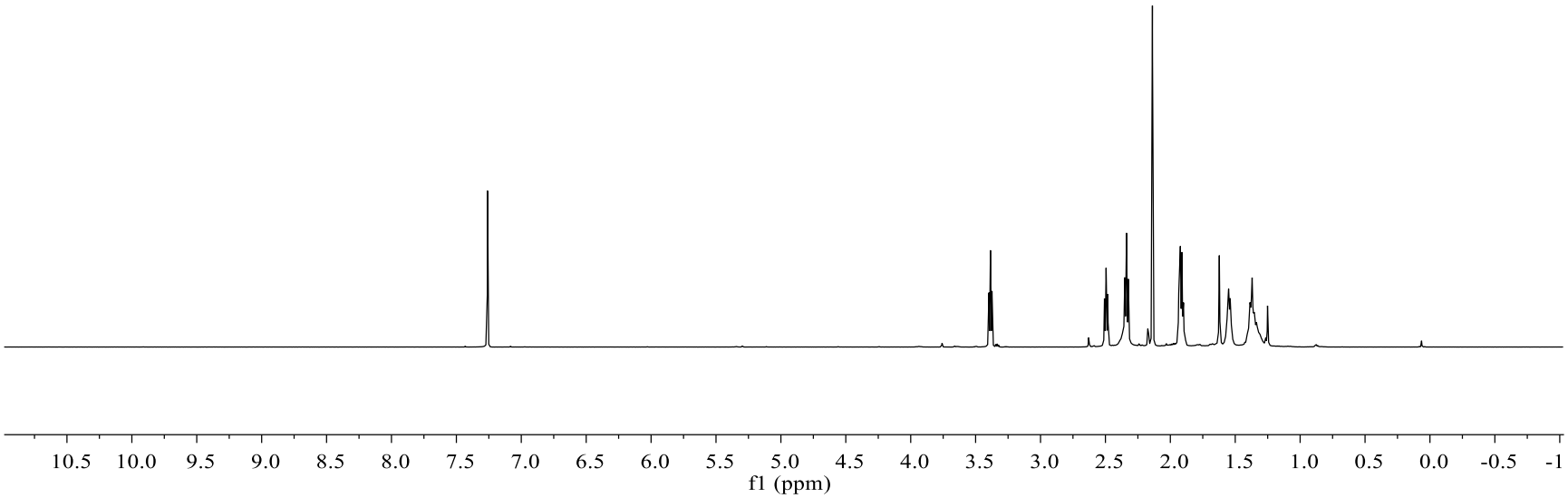
39

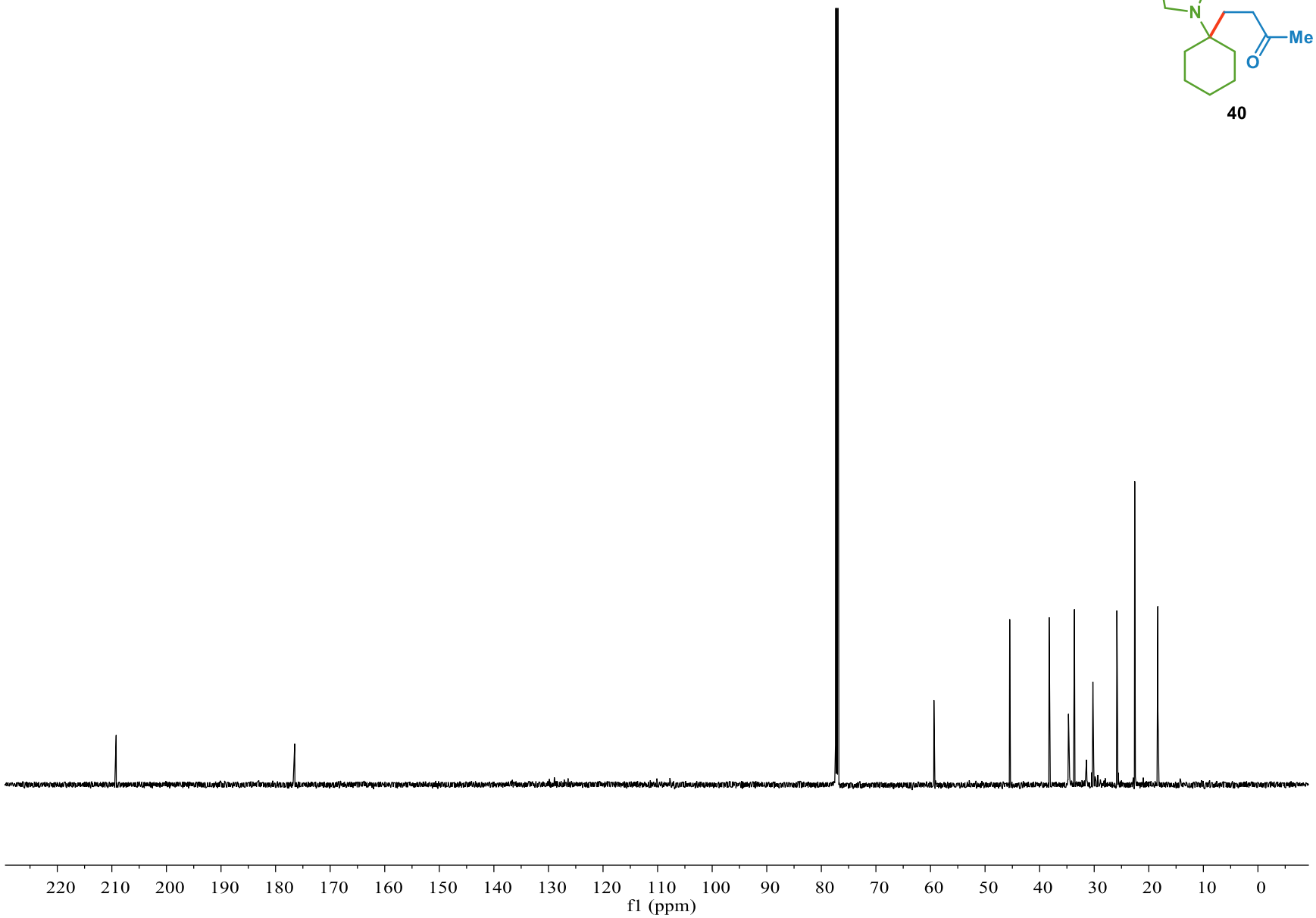

10.5 10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0 -0.5
f1 (ppm)

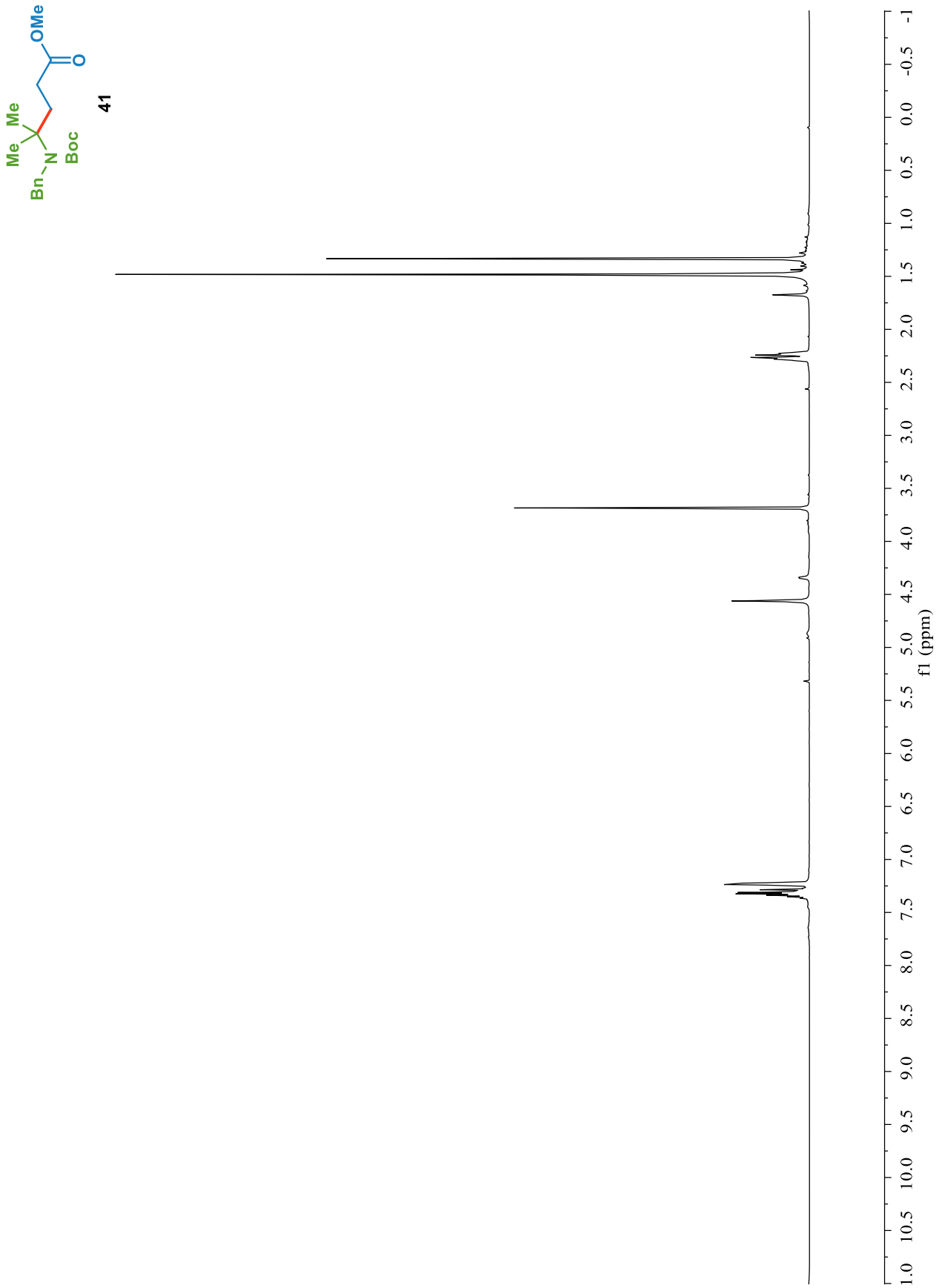

Cbz
N
O
n-C5H11
39
f1 (ppm)

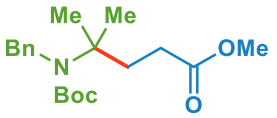

O
N
Me
O

40

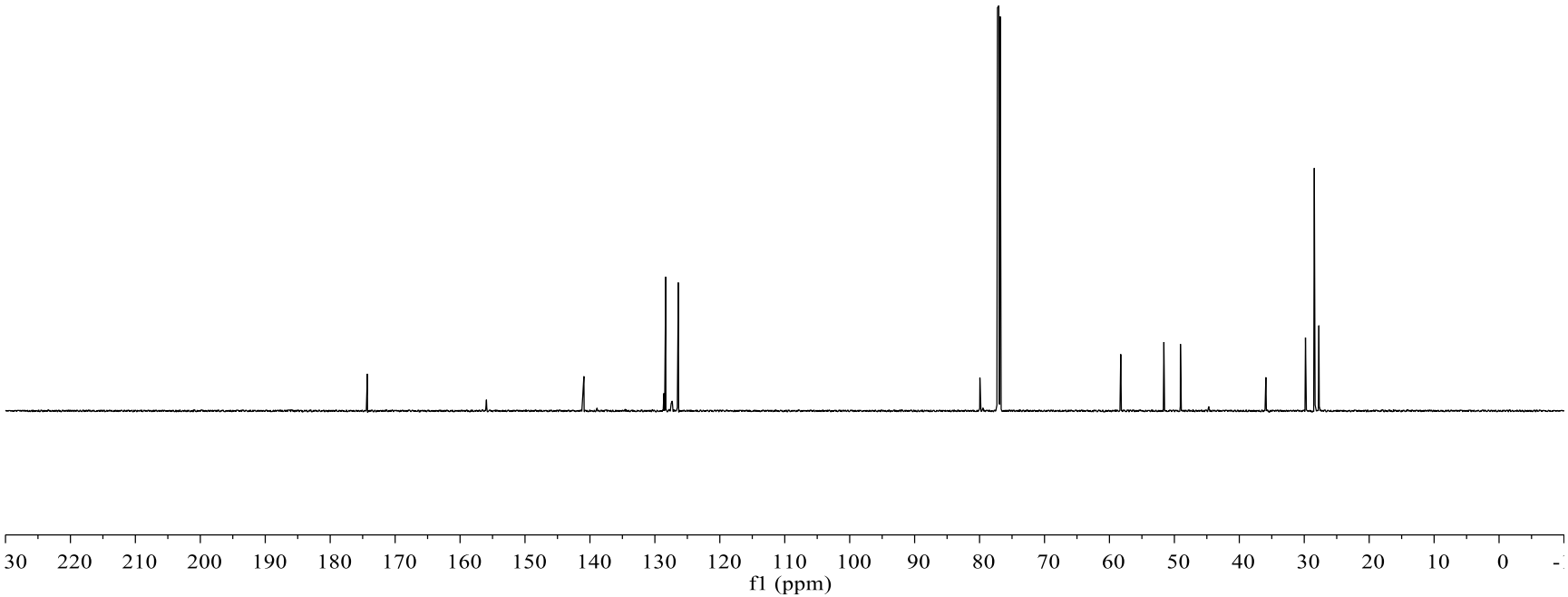

10.5 10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0 -0.5 -1
f1 (ppm)

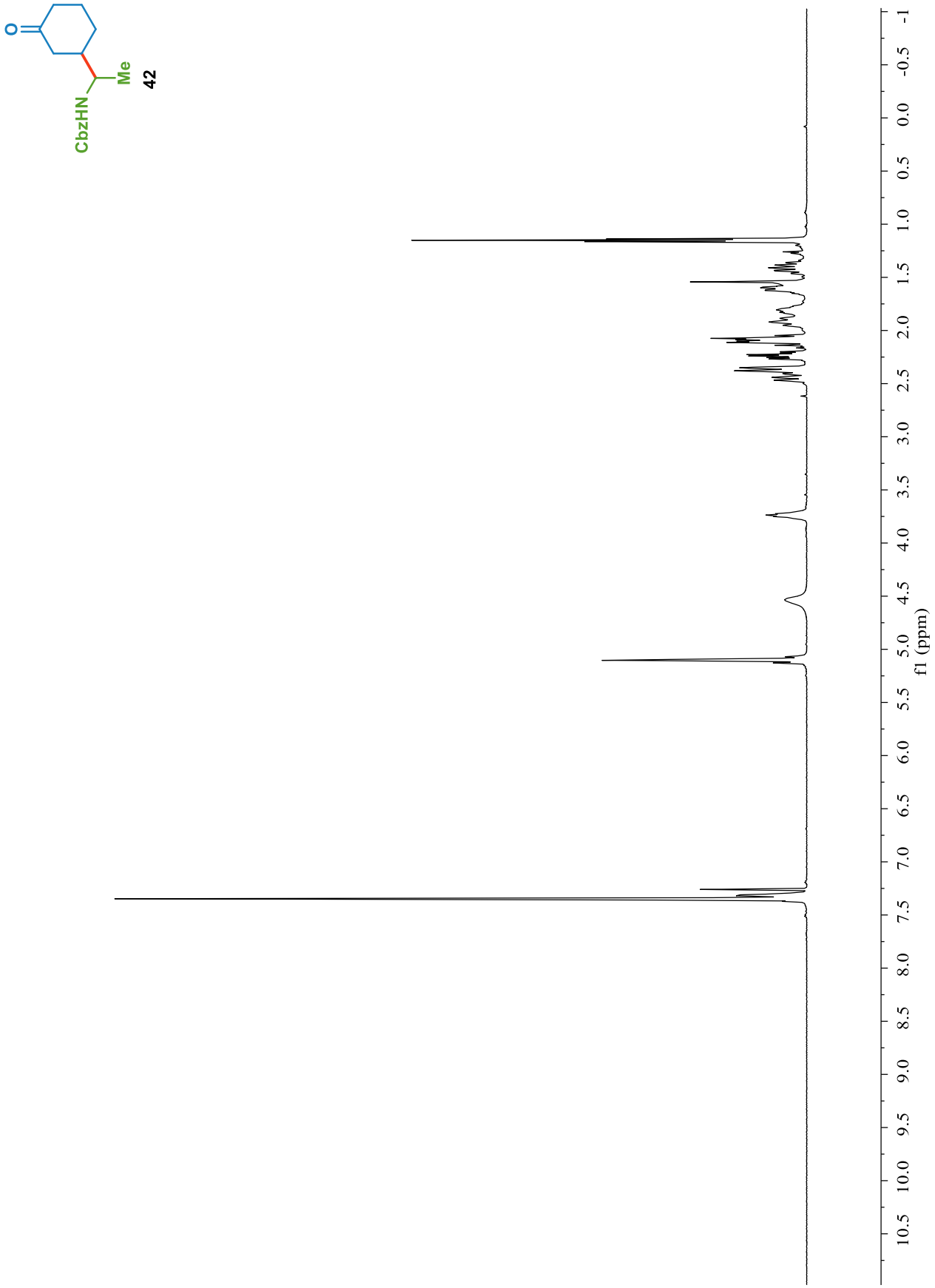

O
N
Me
O
40
220 210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
f1 (ppm)

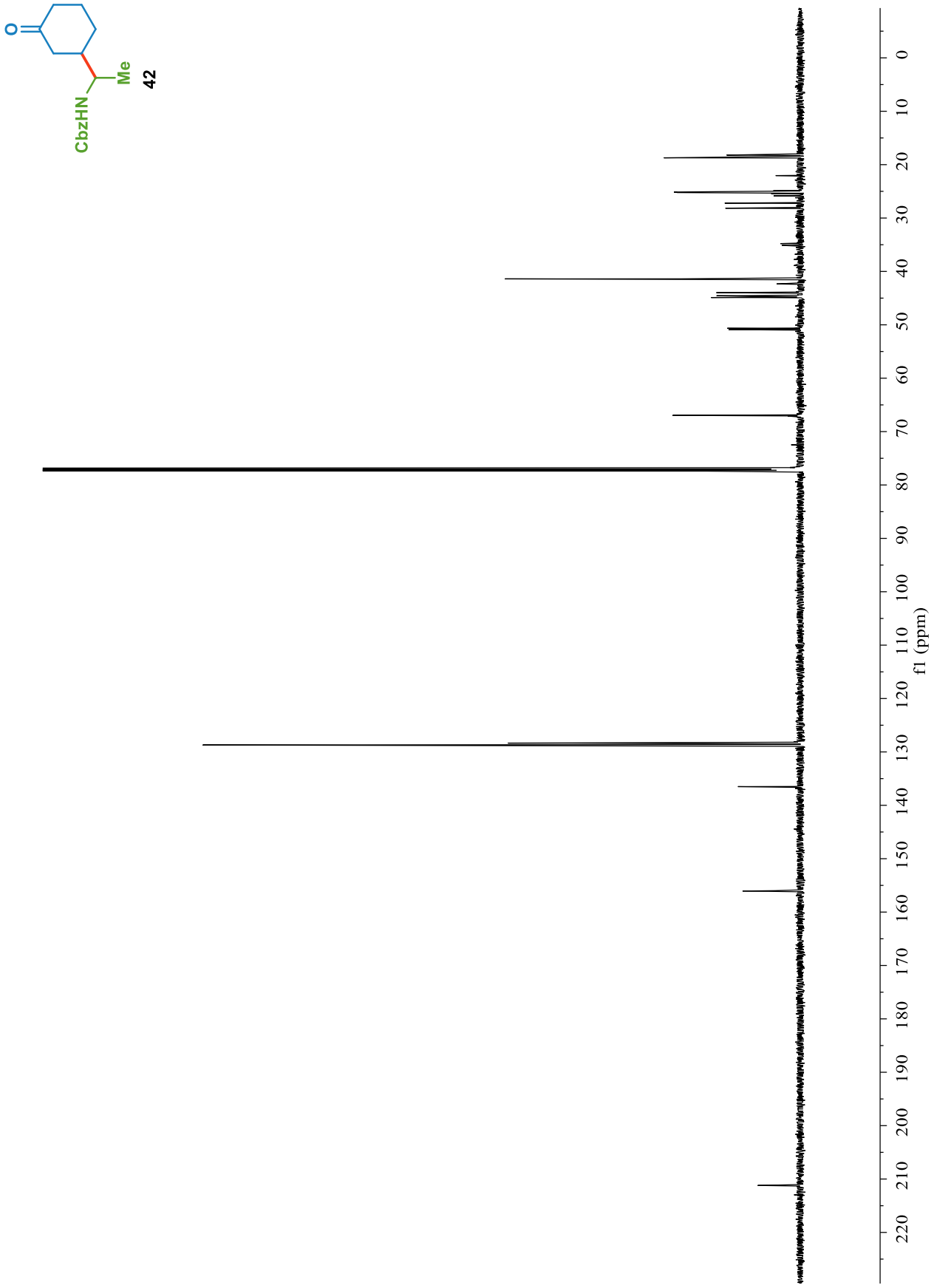

OMe
O
Me
Me
Bn
N
Boc
41
f1 (ppm)
1.0
10.5
10.0
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
-0.5
-1

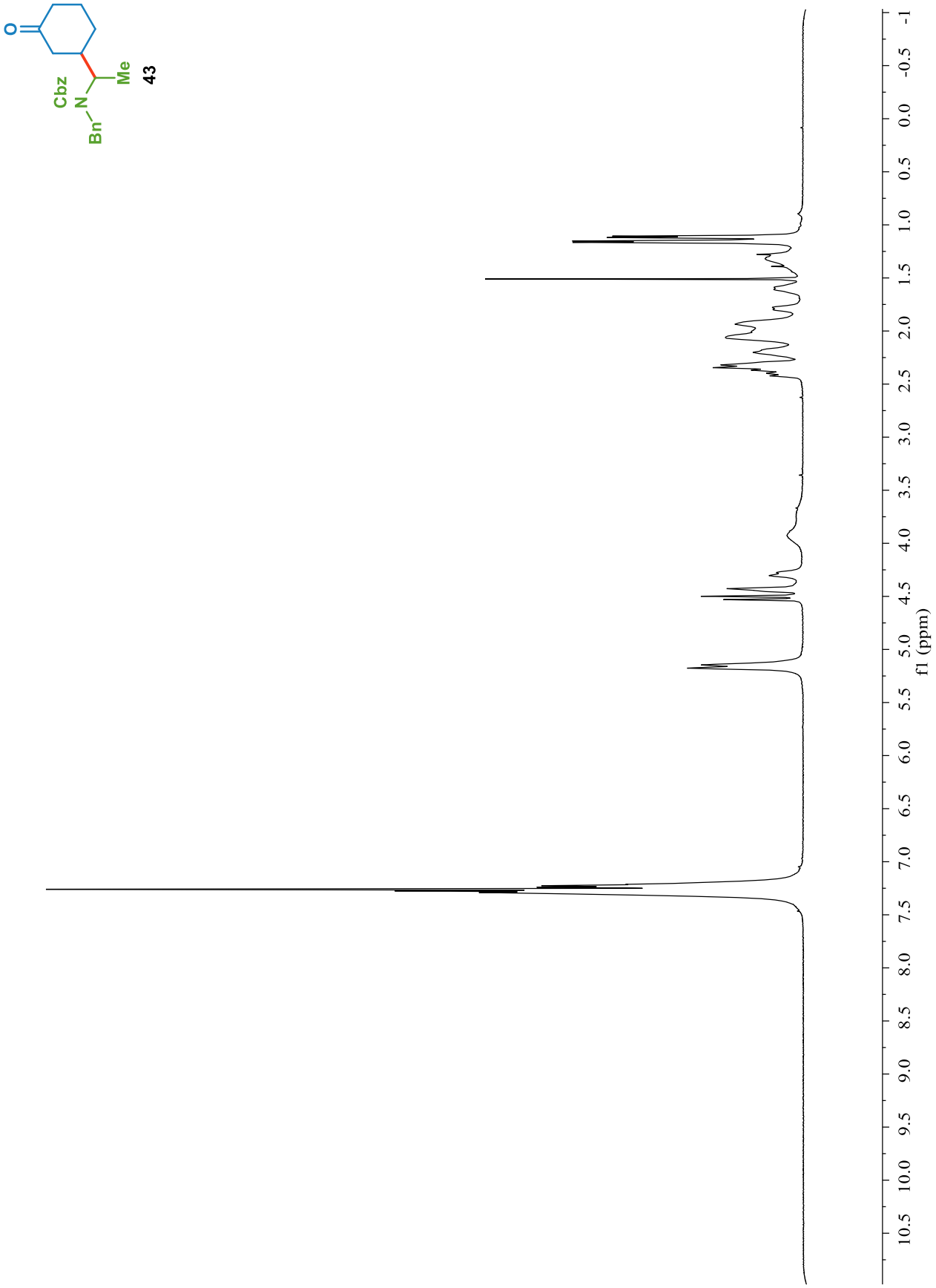

Me
Me
Bn
N
Boc
OMe
O

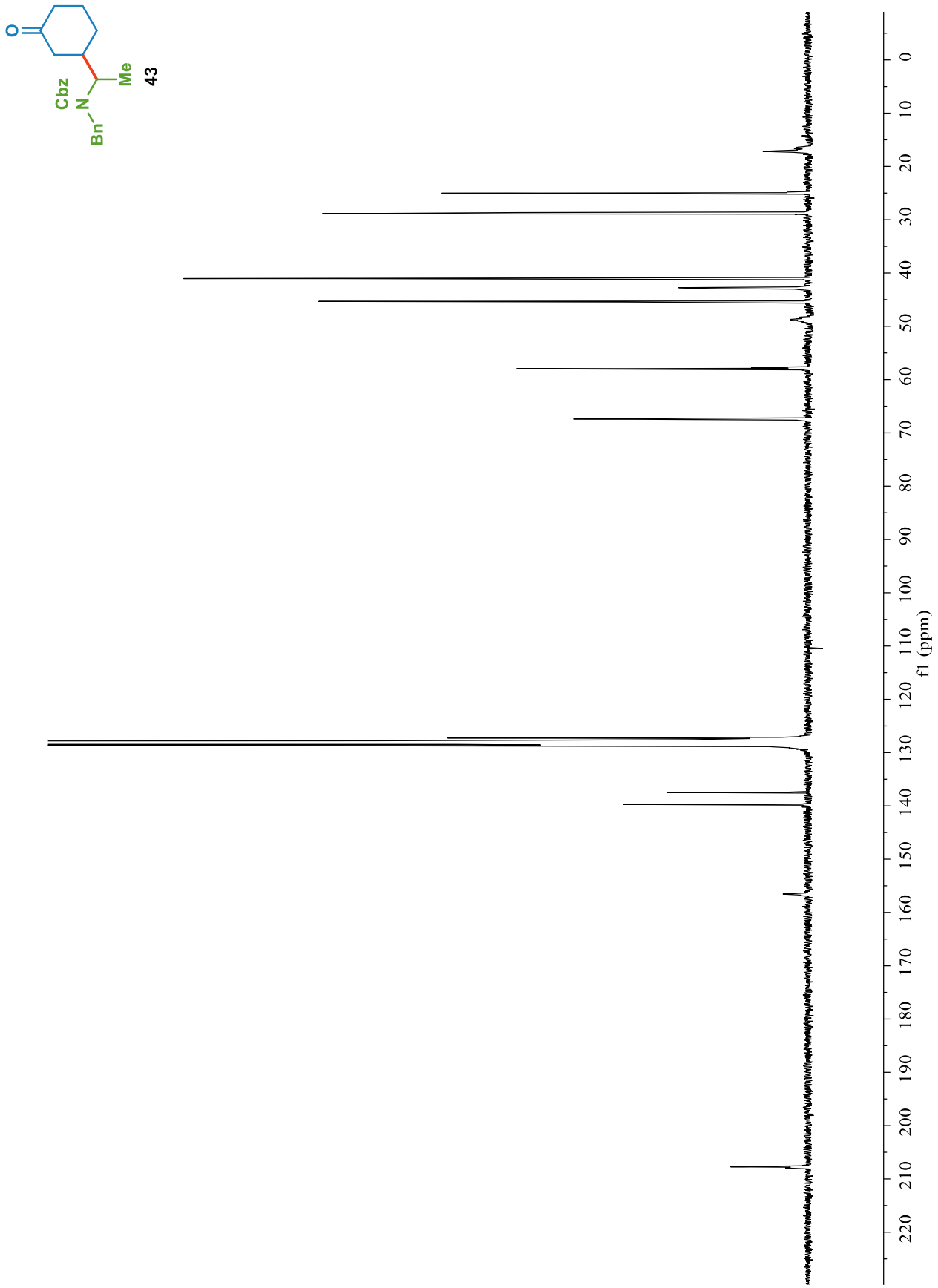
41

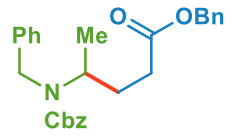

30
220
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)


O
CbzHN
Me
42
10.5
10.0
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
-0.5
-1
f1 (ppm)

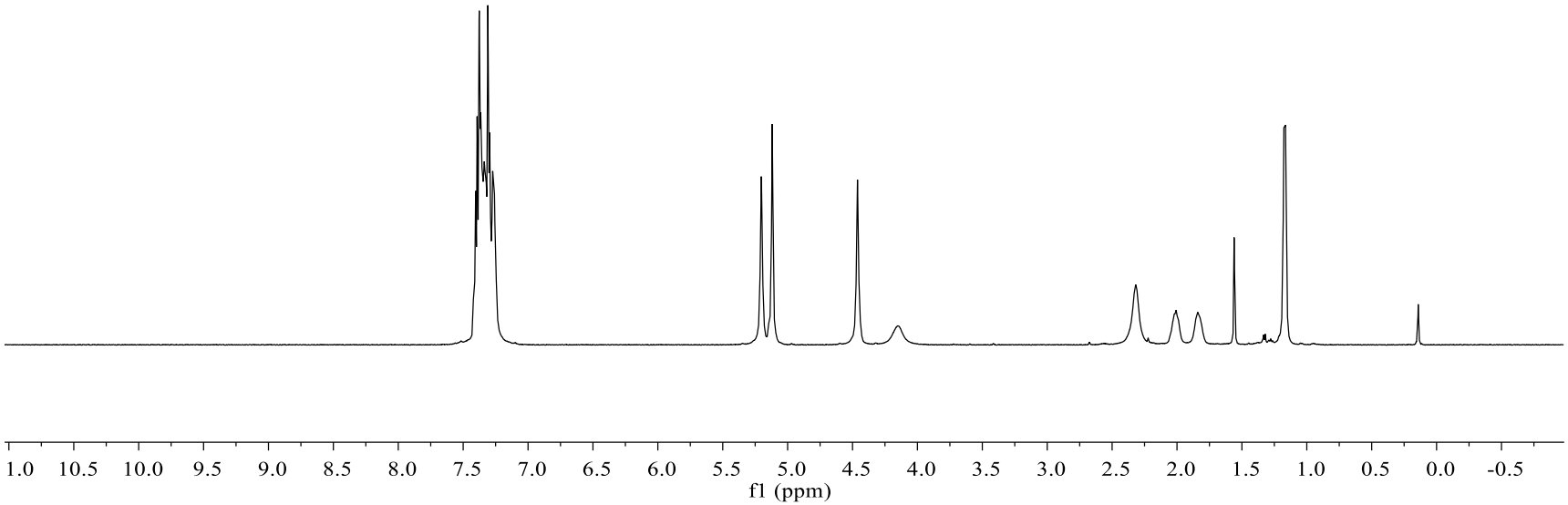

O
CbzHN
Me
42
f1 (ppm)
220
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0

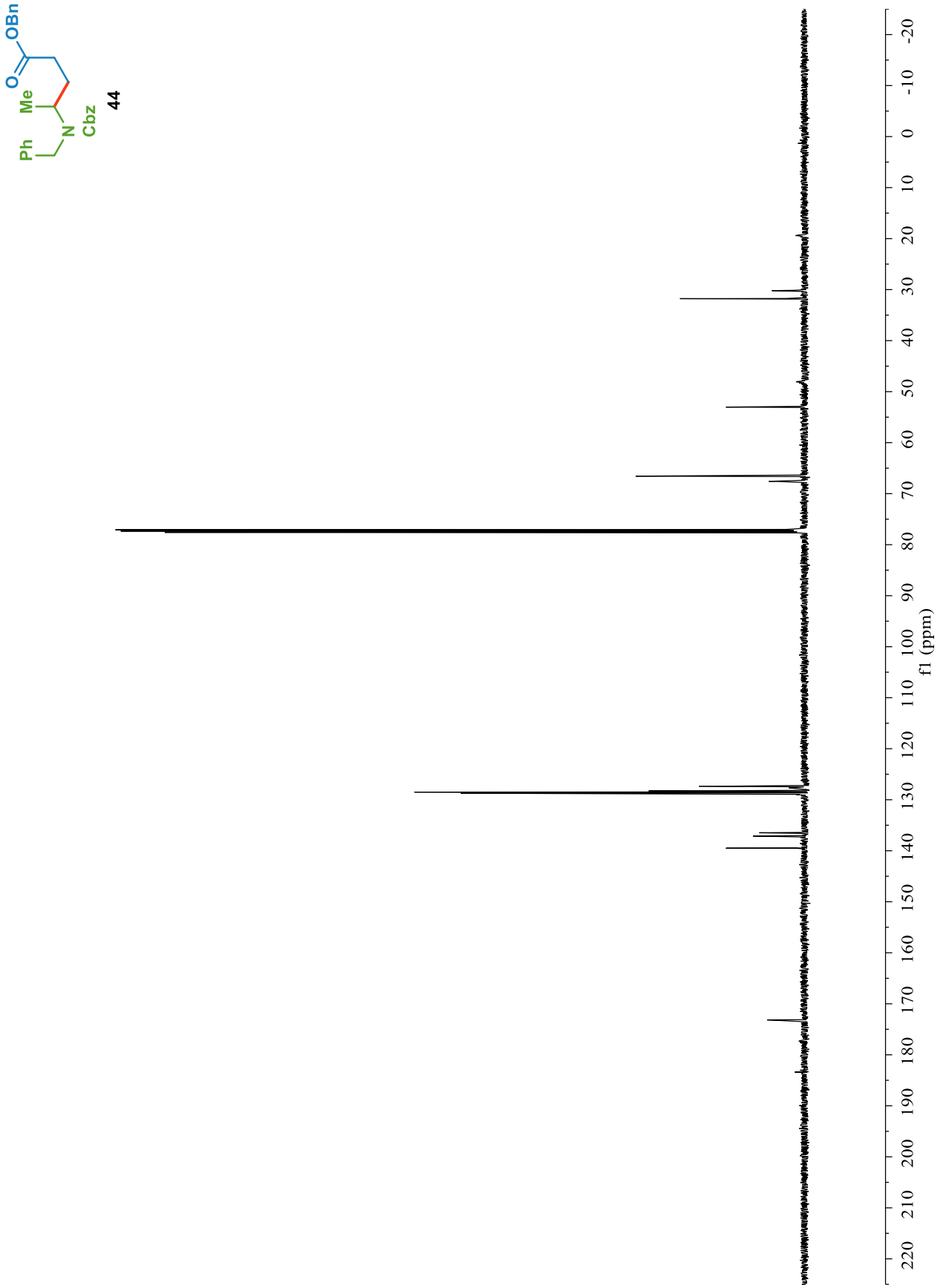

O
Cbz
N
Bn
Me
43
10.5
10.0
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
-0.5
-1
f1 (ppm)

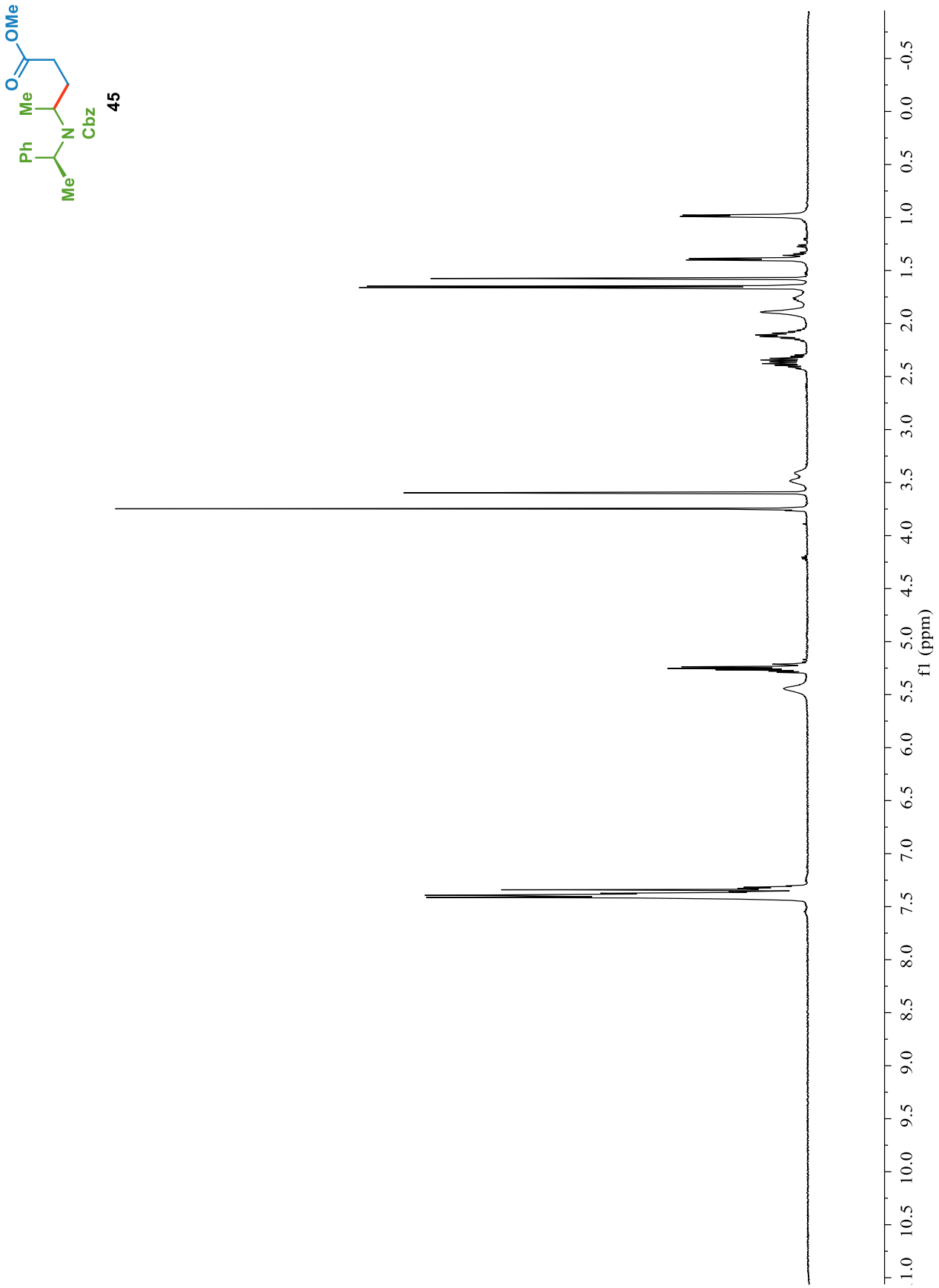

O
Cbz
N
Bn
Me
43
f1 (ppm)
0
10
20
30
40
50
60
70
80
90
100
110
120
130
140
150
160
170
180
190
200
210
220

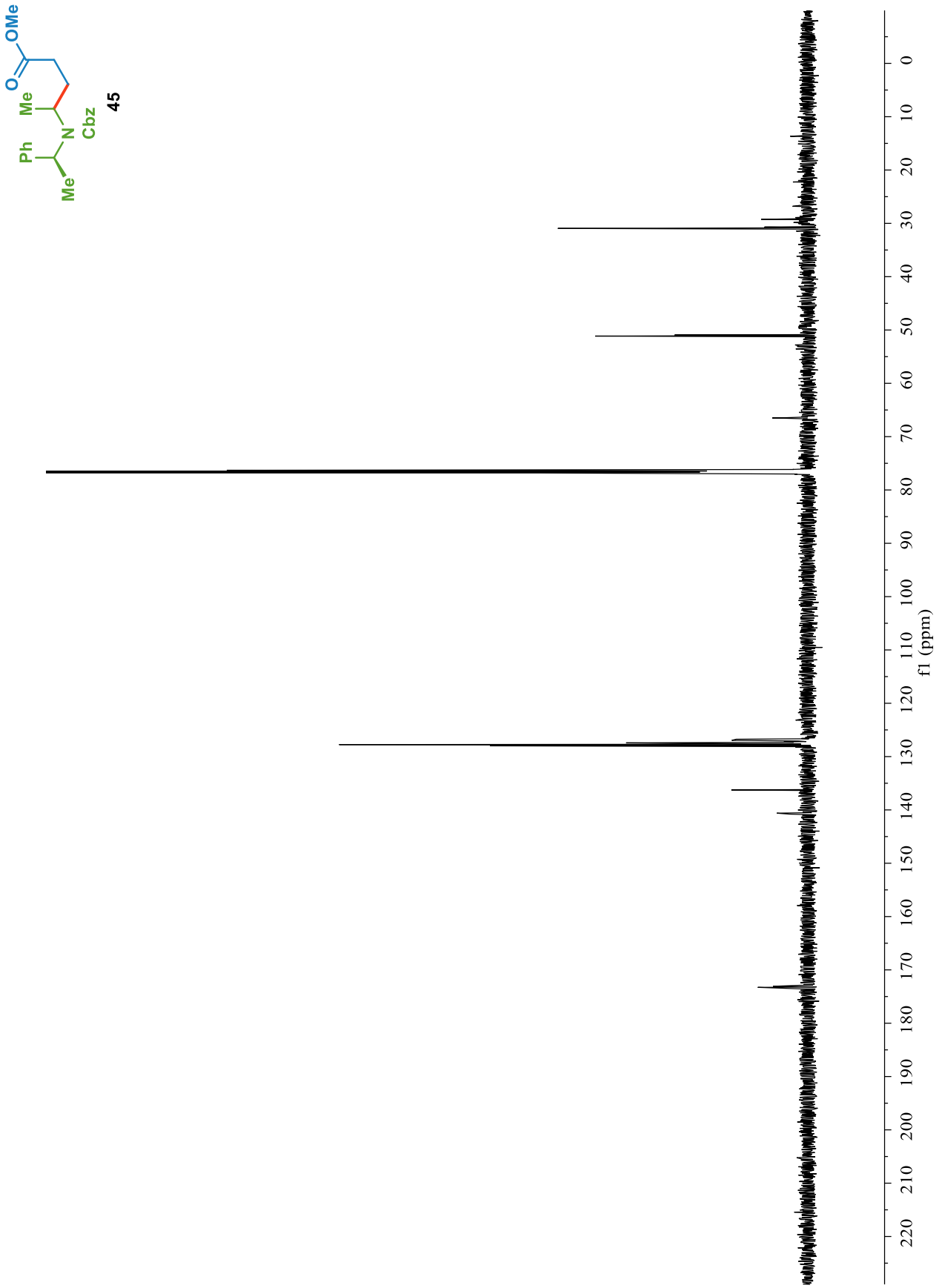

Ph
Me
O
OBn
N
Cbz

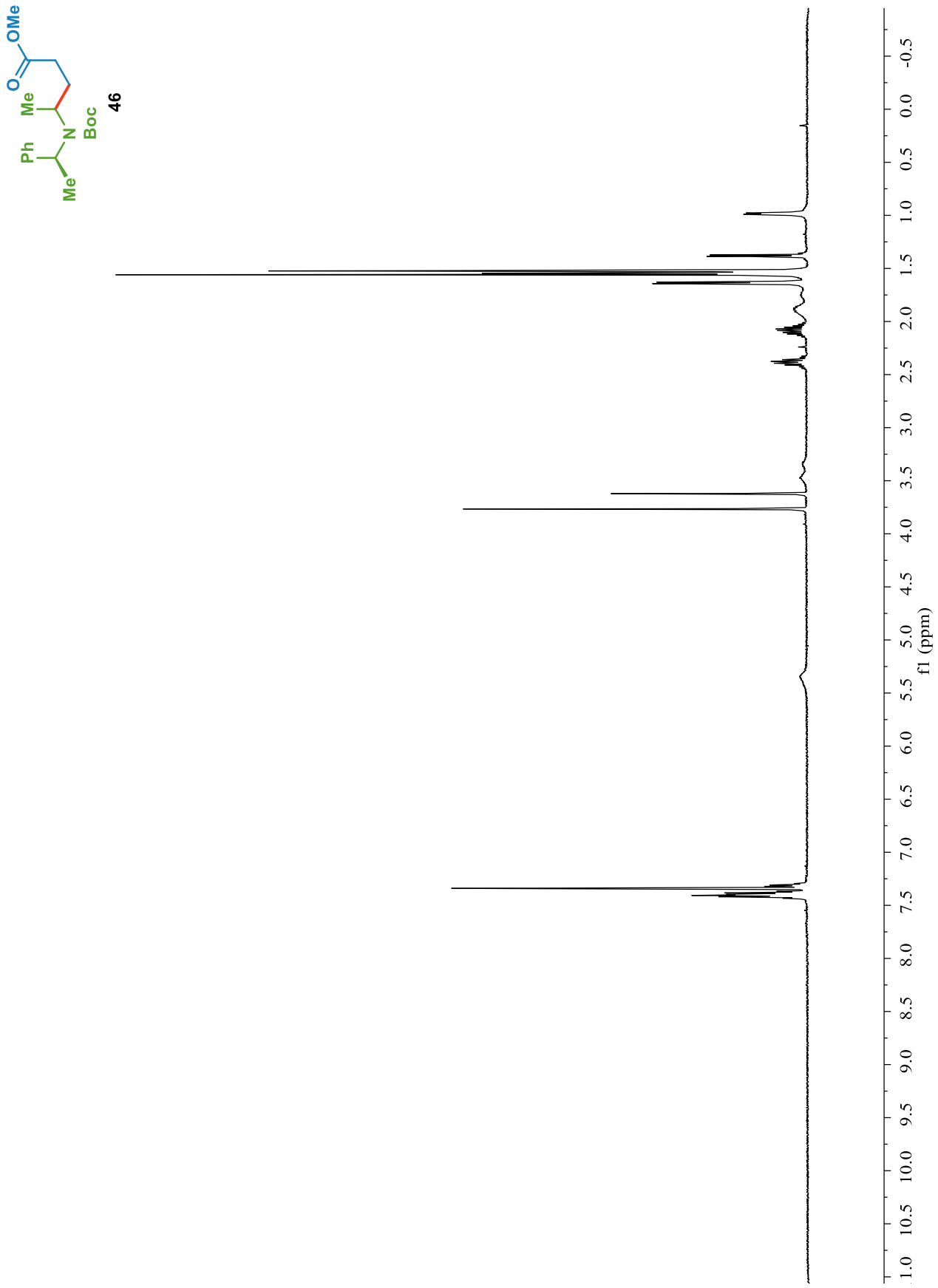
44

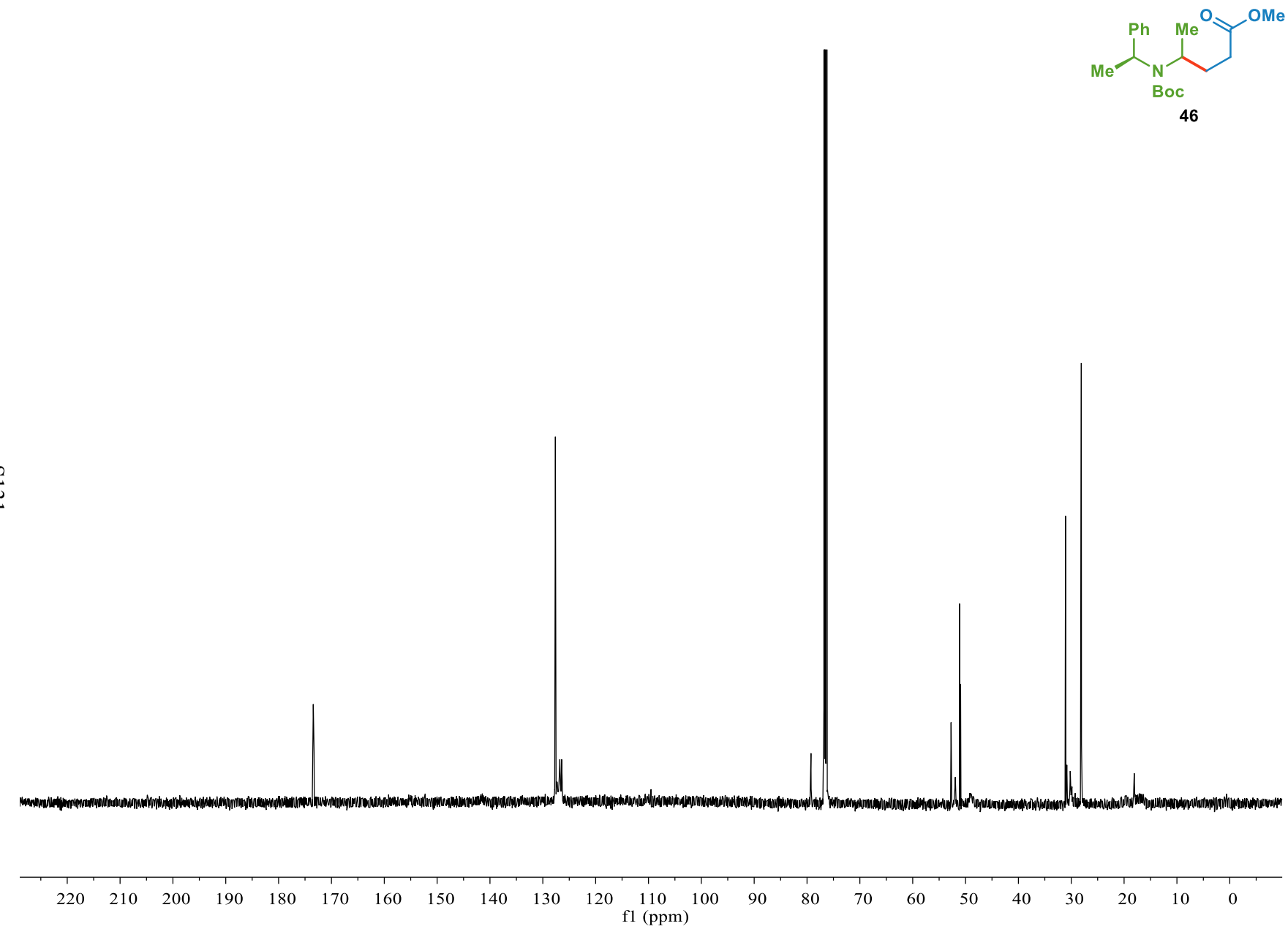

1.0
10.5
10.0
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
-0.5
f1 (ppm)

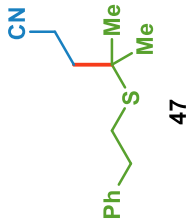

OBn
O
Me
Ph
N
Cbz
44
f1 (ppm)


OMe
O
Me
Ph
N
Cbz
Me
45
f1 (ppm)
1.0
10.5
10.0
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
-0.5

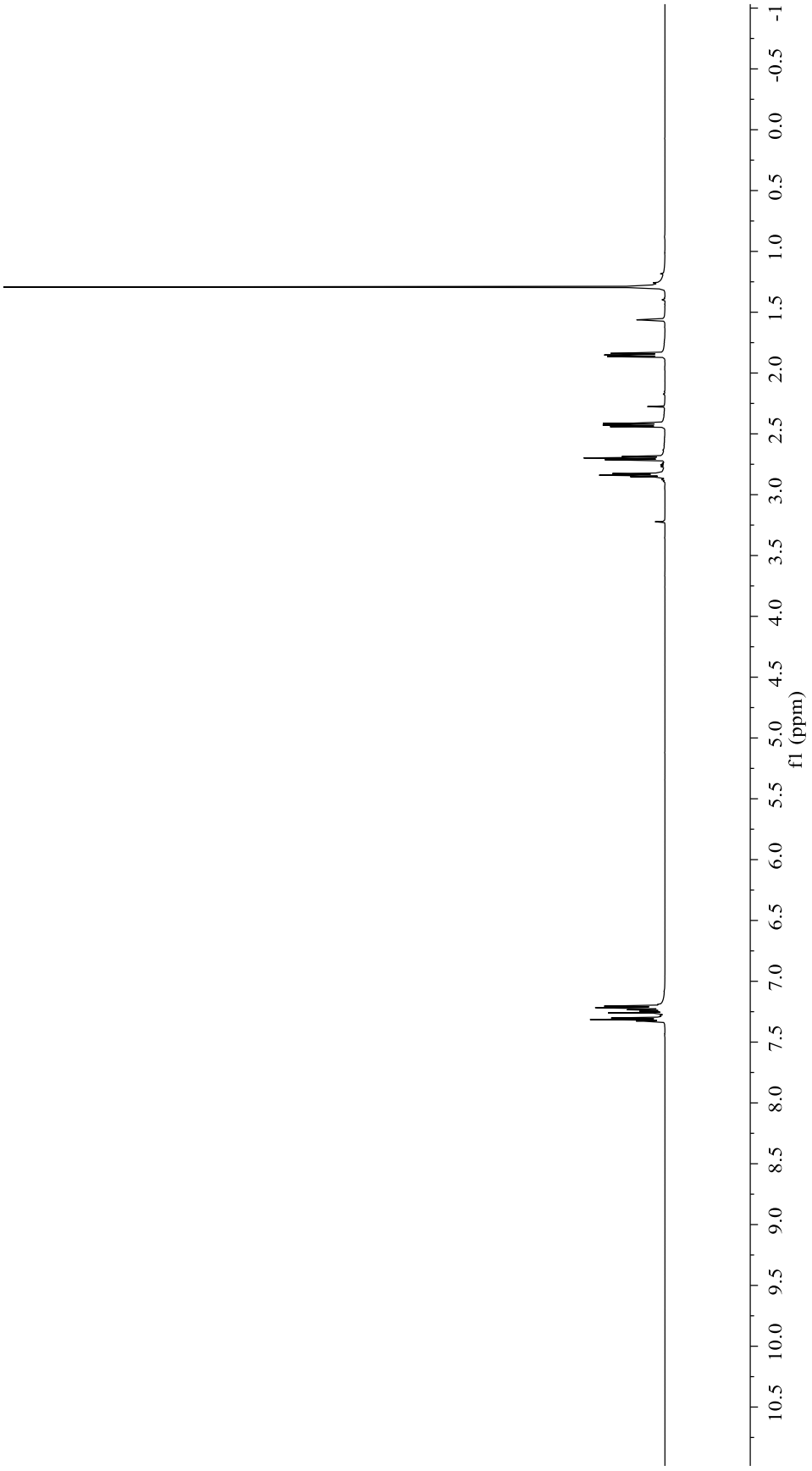

OMe
O
Me
Ph
N
Cbz
Me
45
f1 (ppm)
0
10
20
30
40
50
60
70
80
90
100
110
120
130
140
150
160
170
180
190
200
210
220

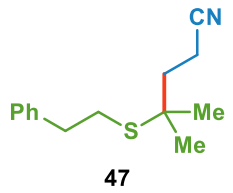

OMe
O
Me
Ph
N
Boc
Me
46
1.0
10.5
10.0
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
-0.5
f1 (ppm)


Ph
Me
O
OMe
Me
N
Boc
46
220 210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
f1 (ppm)

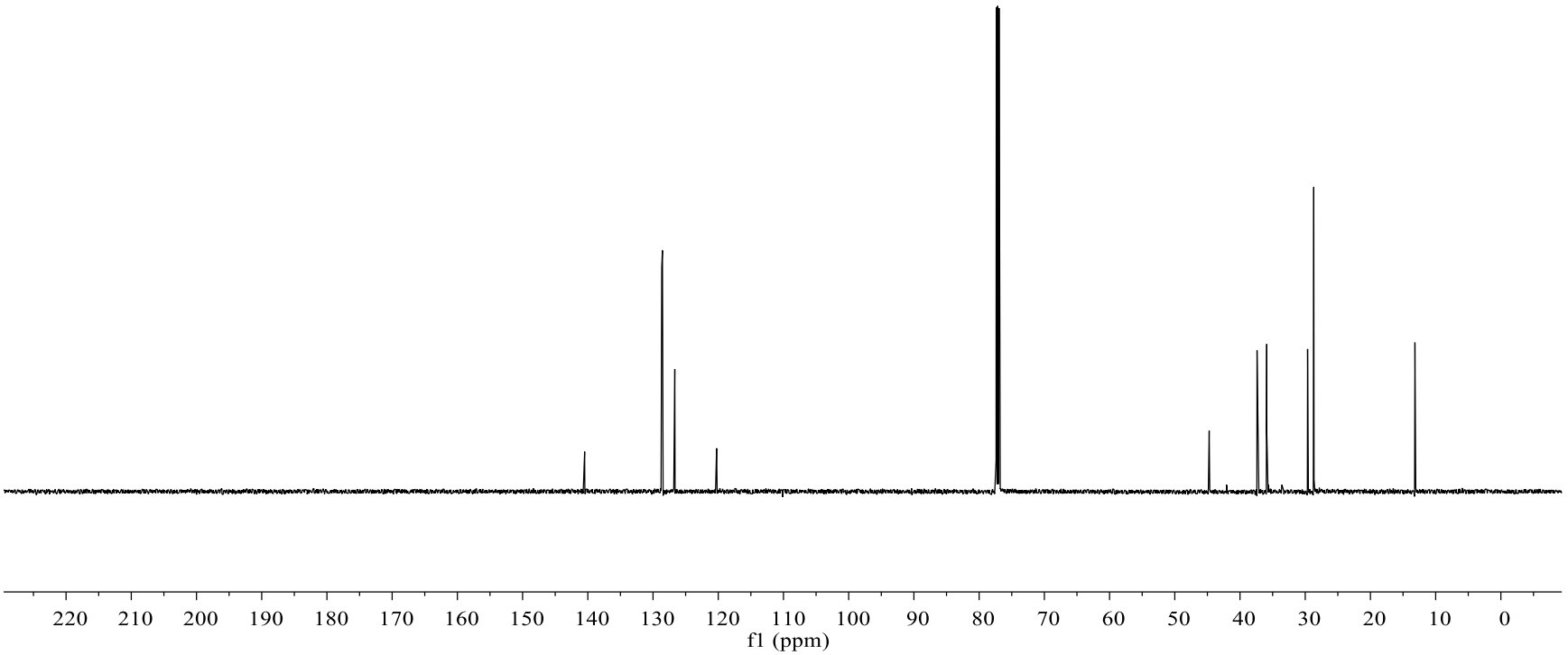

CN
Me
Me
S
Ph

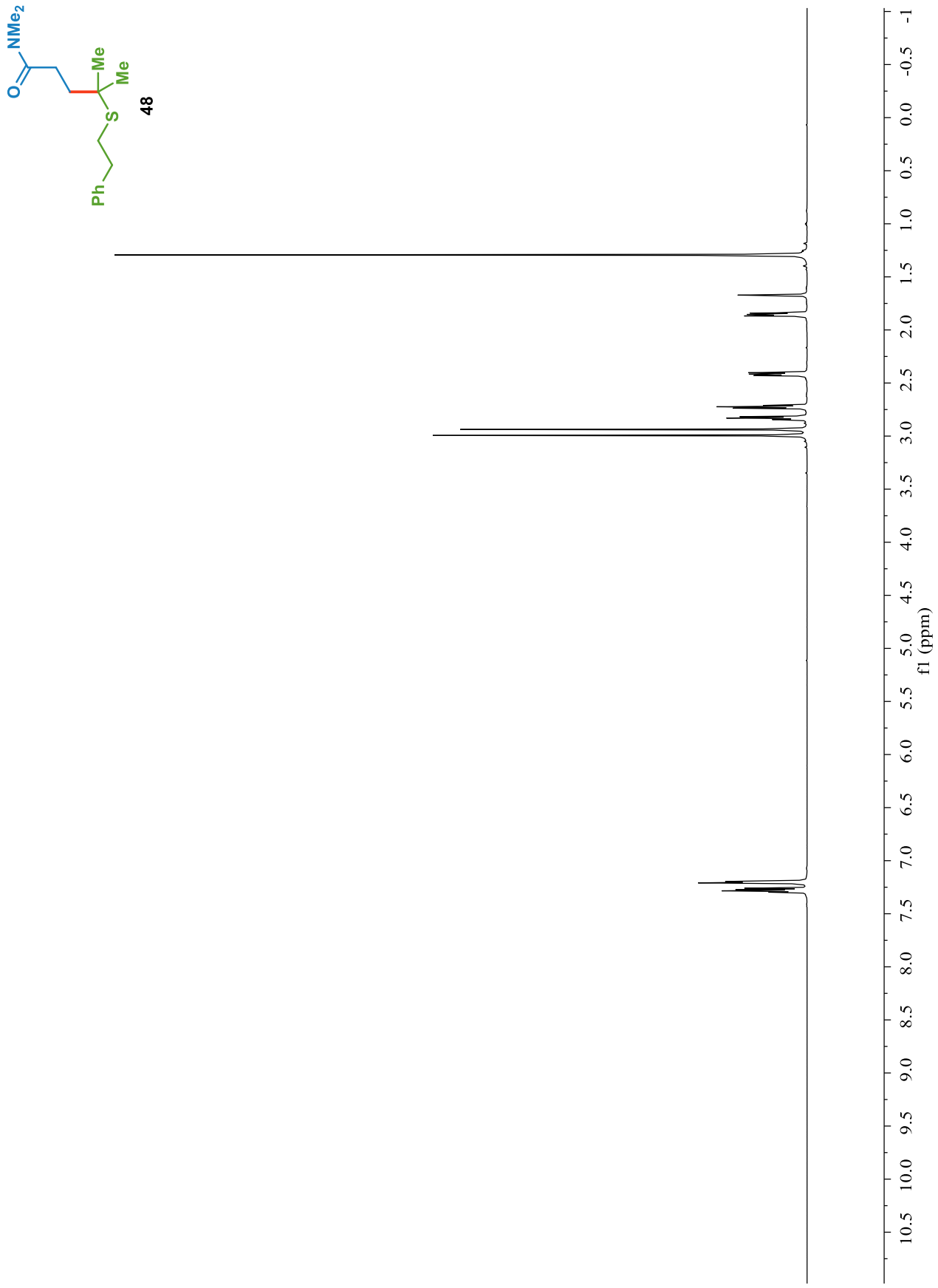
47

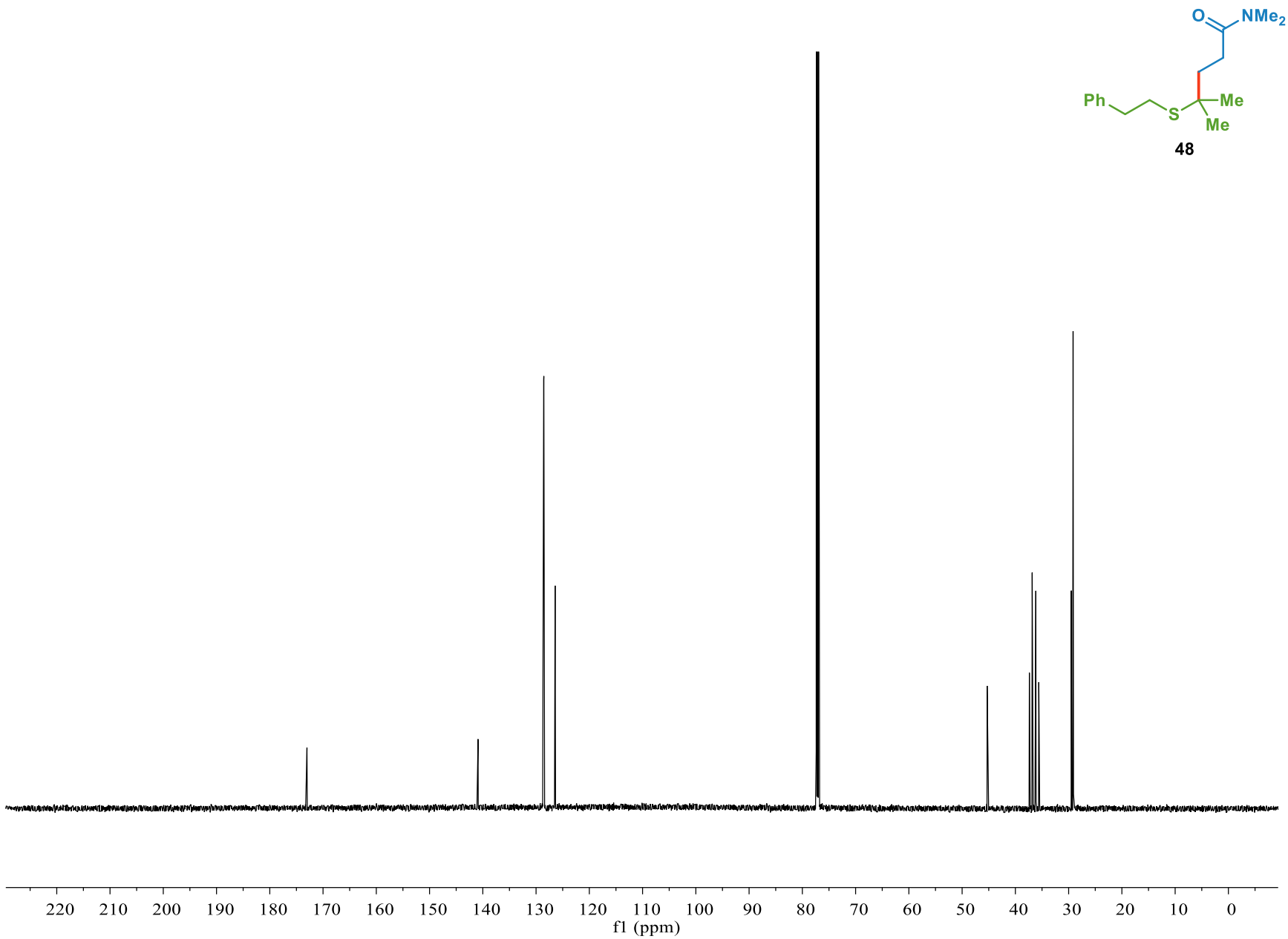

10.5
10.0
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
-0.5
-1
f1 (ppm)

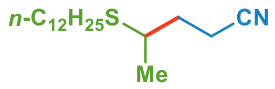

CN
Ph
S
Me
Me

47

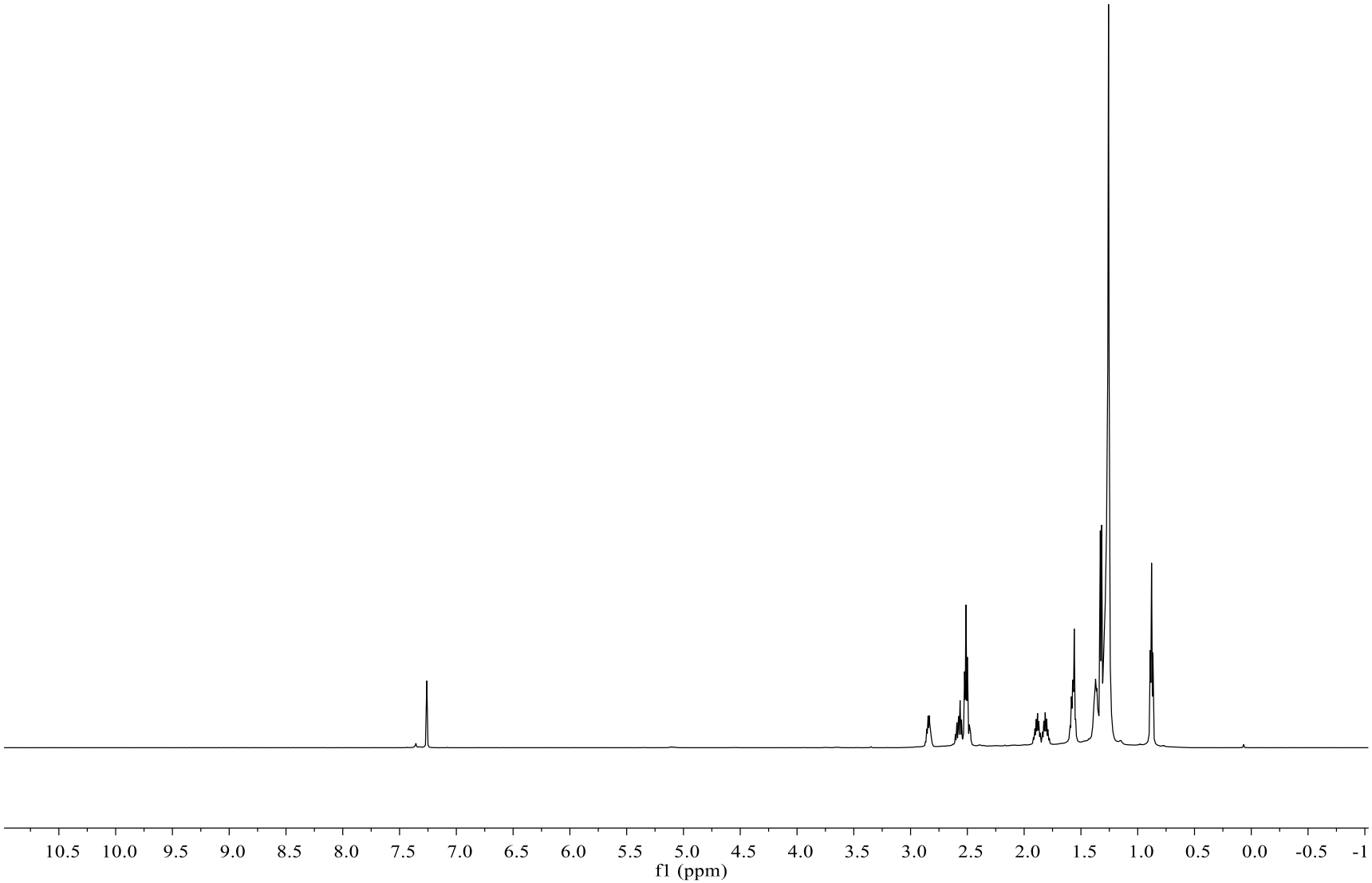

220 210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
f1 (ppm)

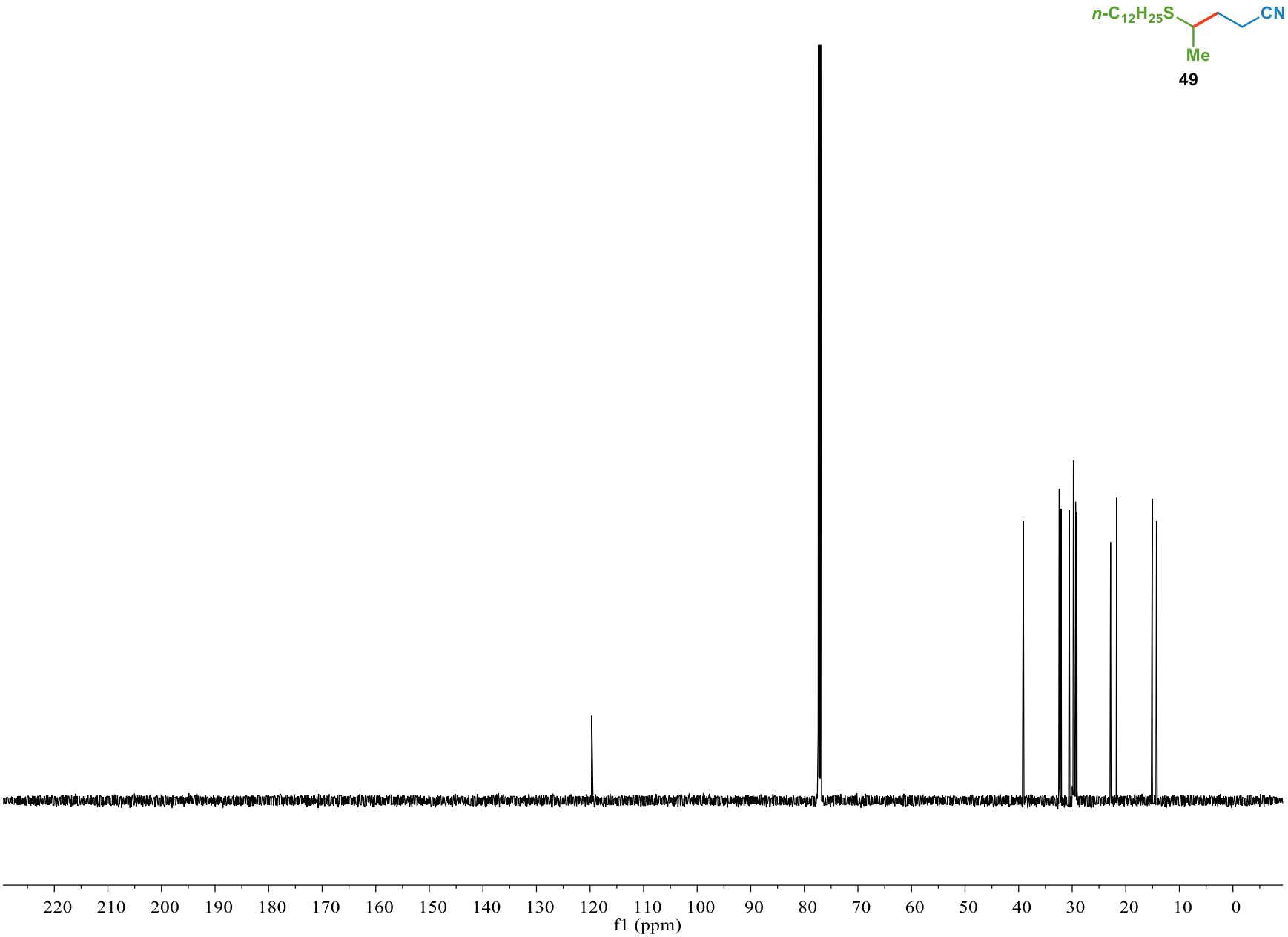

NMe2
O
Me
Me
S
Ph
48
10.5
10.0
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
-0.5
-1
f1 (ppm)

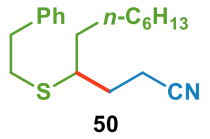

O
NMe2
Ph
S
Me
Me
48
220 210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
f1 (ppm)


n-C12H25S
CN
Me

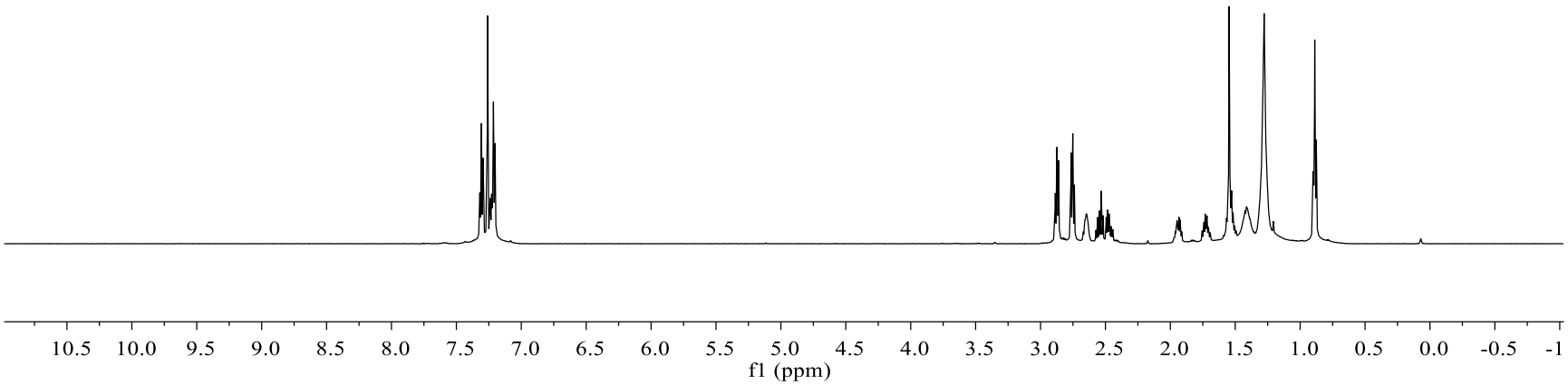
49

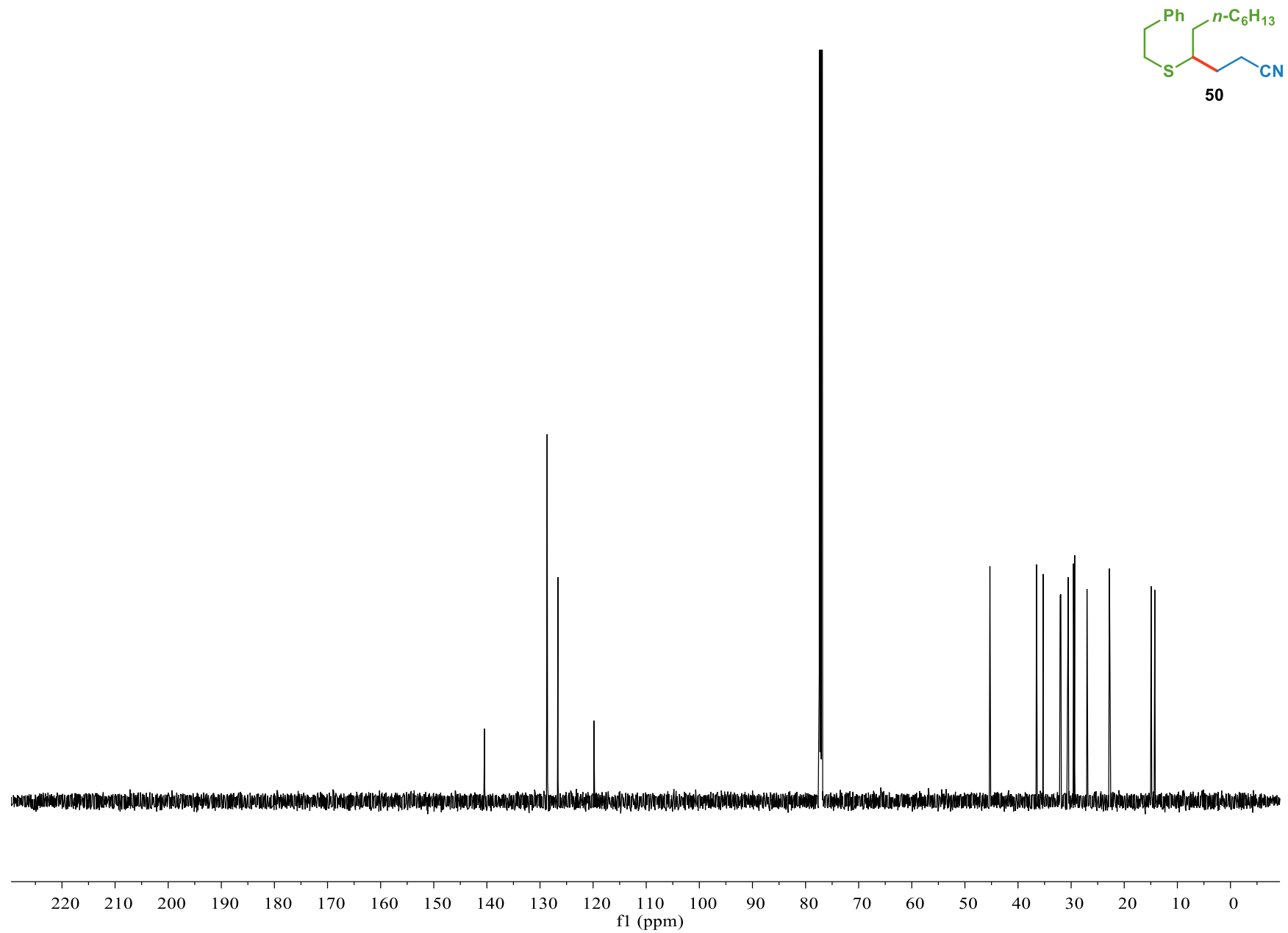

10.5 10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0 -0.5 -1
f1 (ppm)

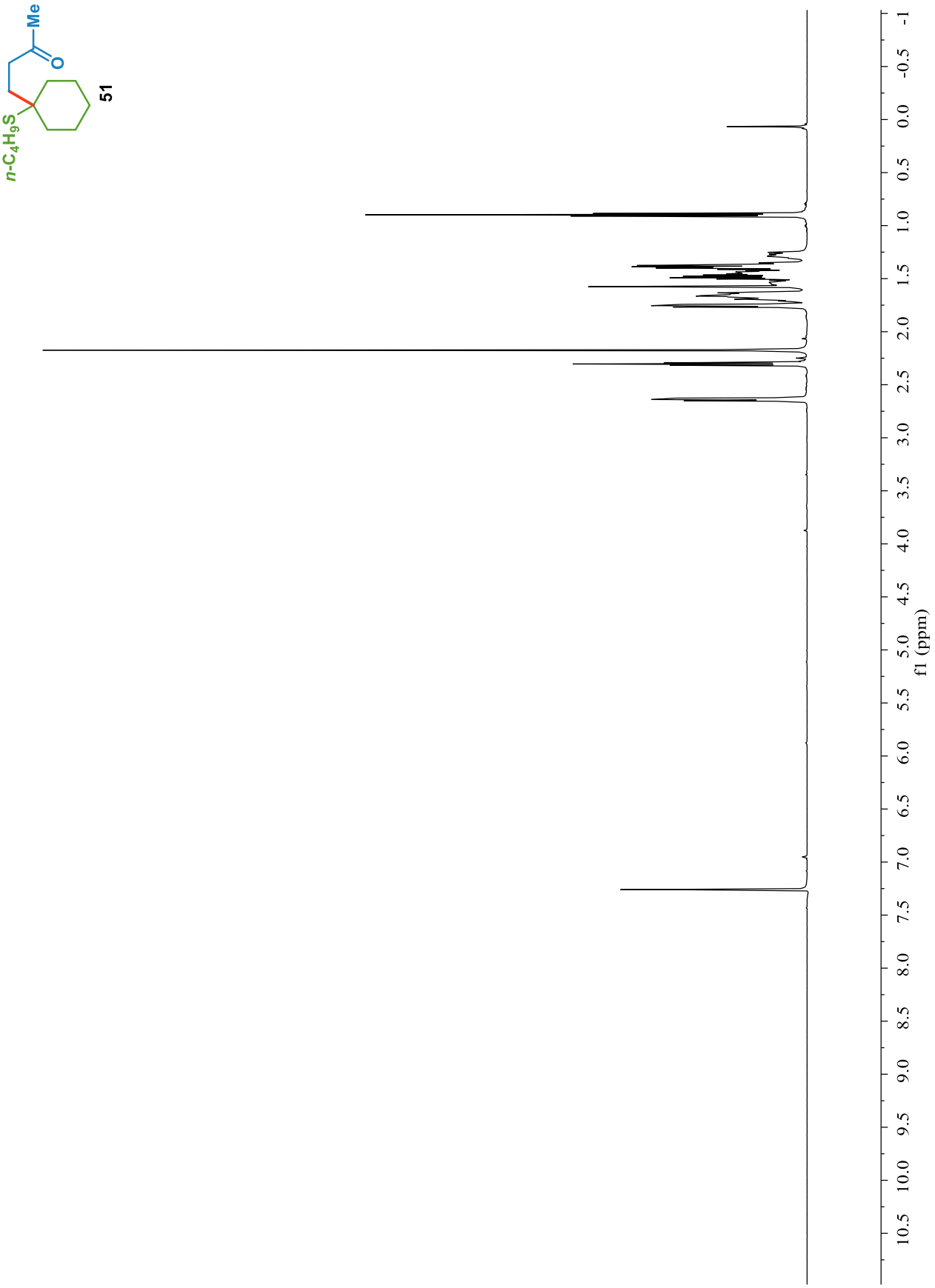

n-C12H25S
CN
Me
49
220 210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
f1 (ppm)

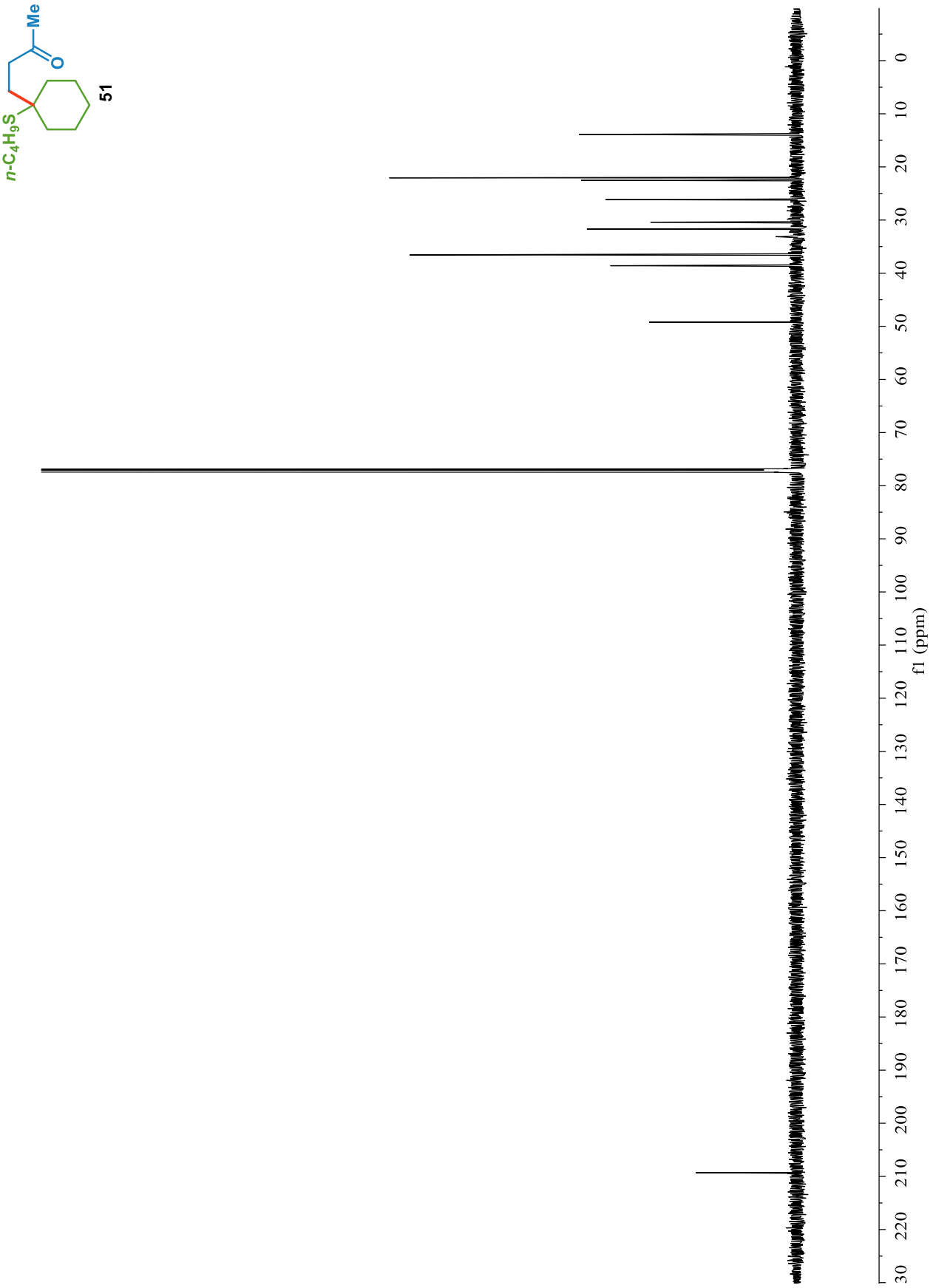

Ph
n-C6H13
S
CN

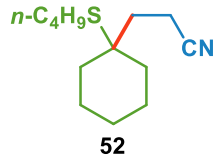
50


10.5 10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0 -0.5 -1
f1 (ppm)

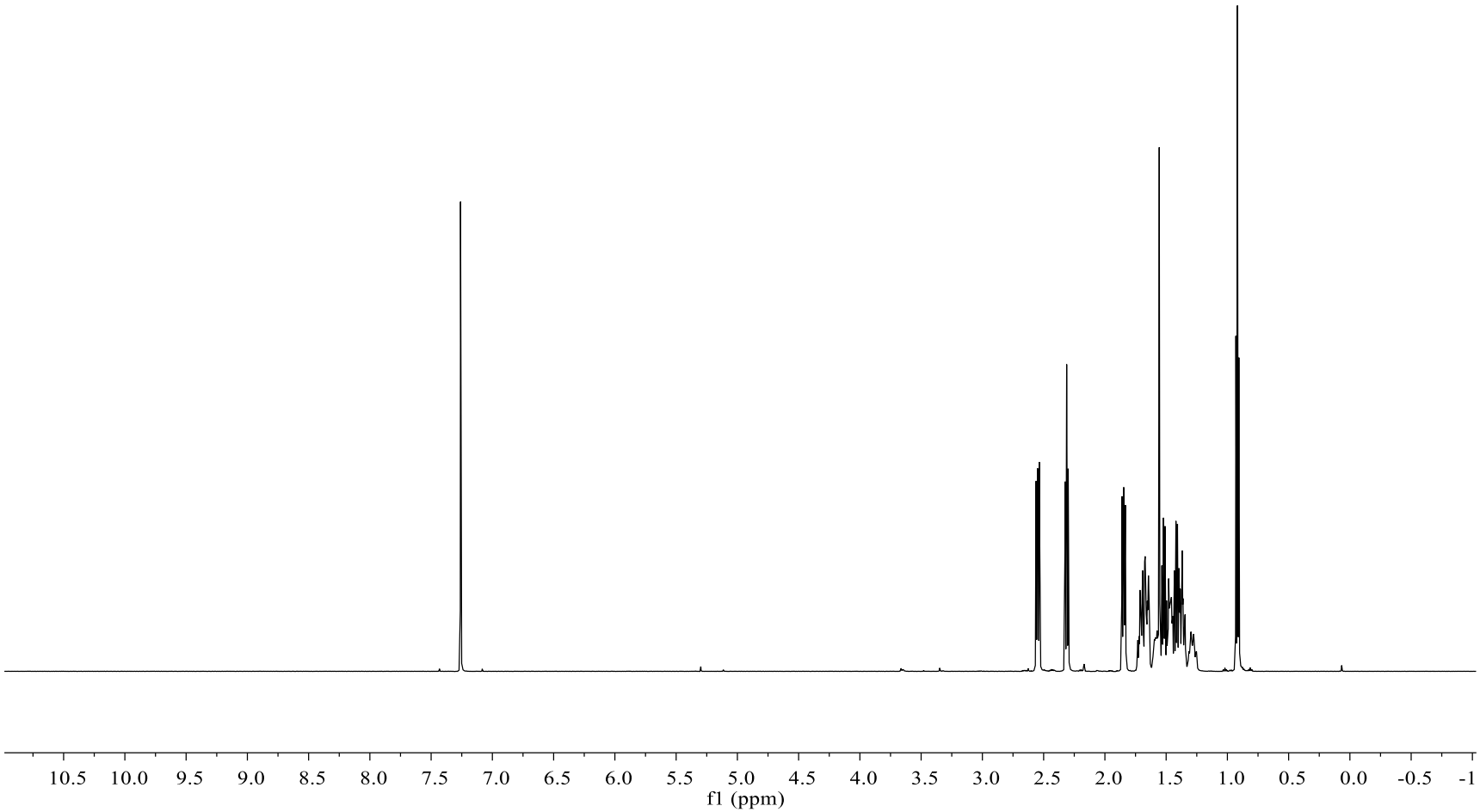

Ph
n-C6H13
S
CN
50
220 210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
f1 (ppm)

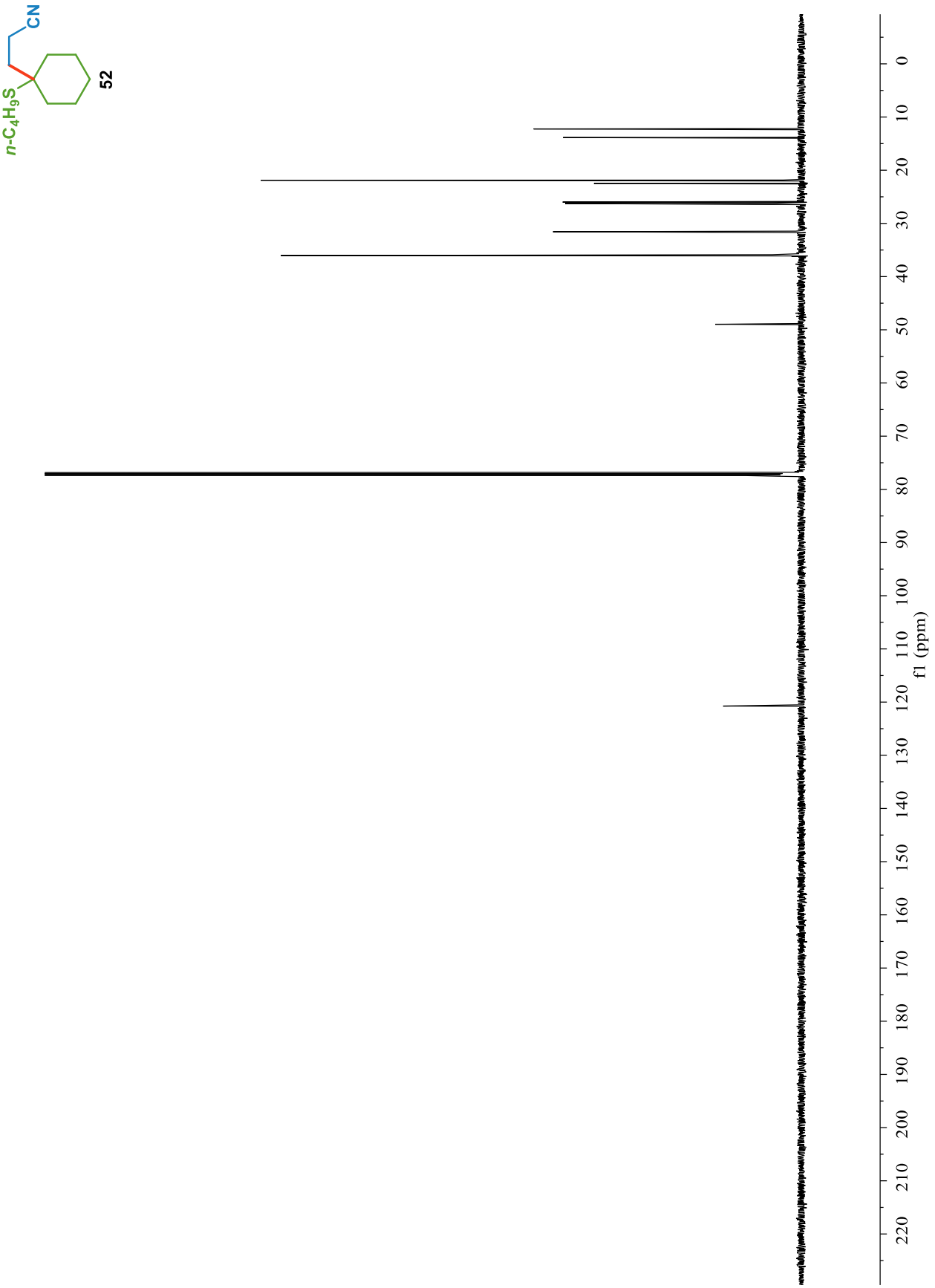

Me
O
n-C4H9S
51
10.5
10.0
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
-0.5
-1
f1 (ppm)

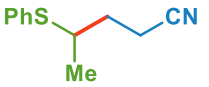

Me
O
n-C4H9S
51
f1 (ppm)


n-C4H9S
CN

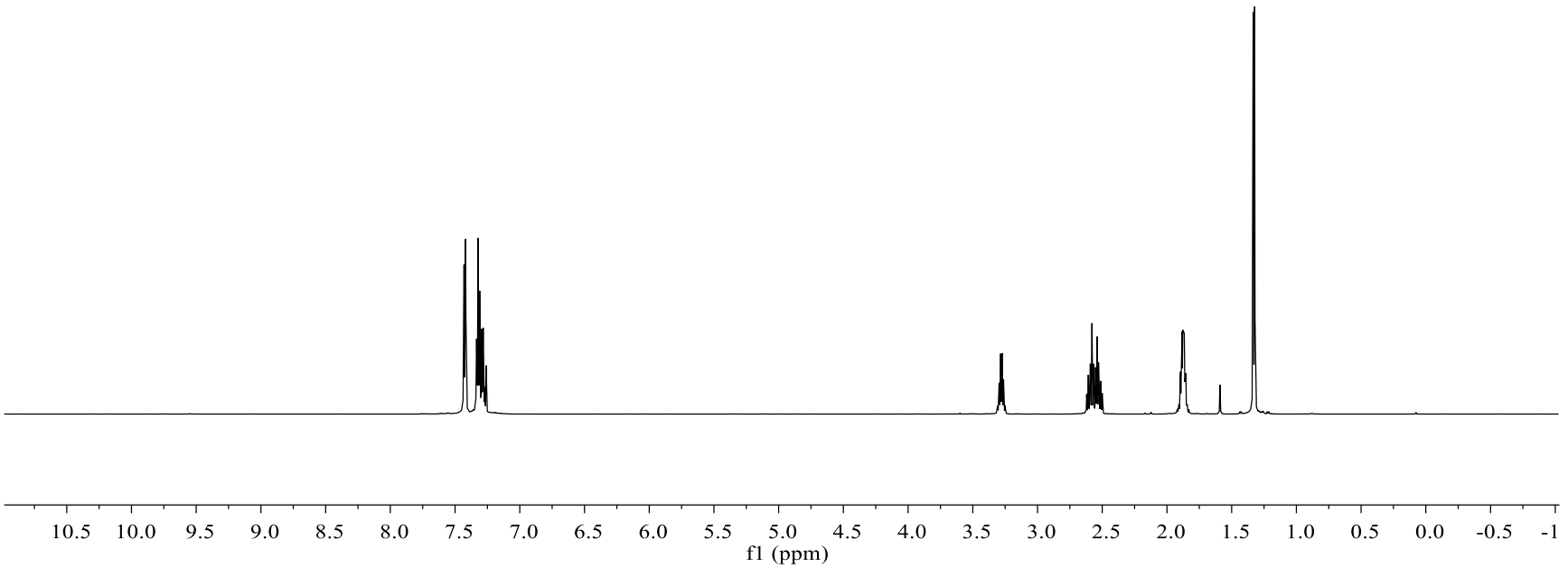
52

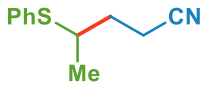

10.5 10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0 -0.5 -1
f1 (ppm)


CN
n-C4H9S
52
0
10
20
30
40
50
60
70
80
90
100
110
120
130
140
150
160
170
180
190
200
210
220
f1 (ppm)

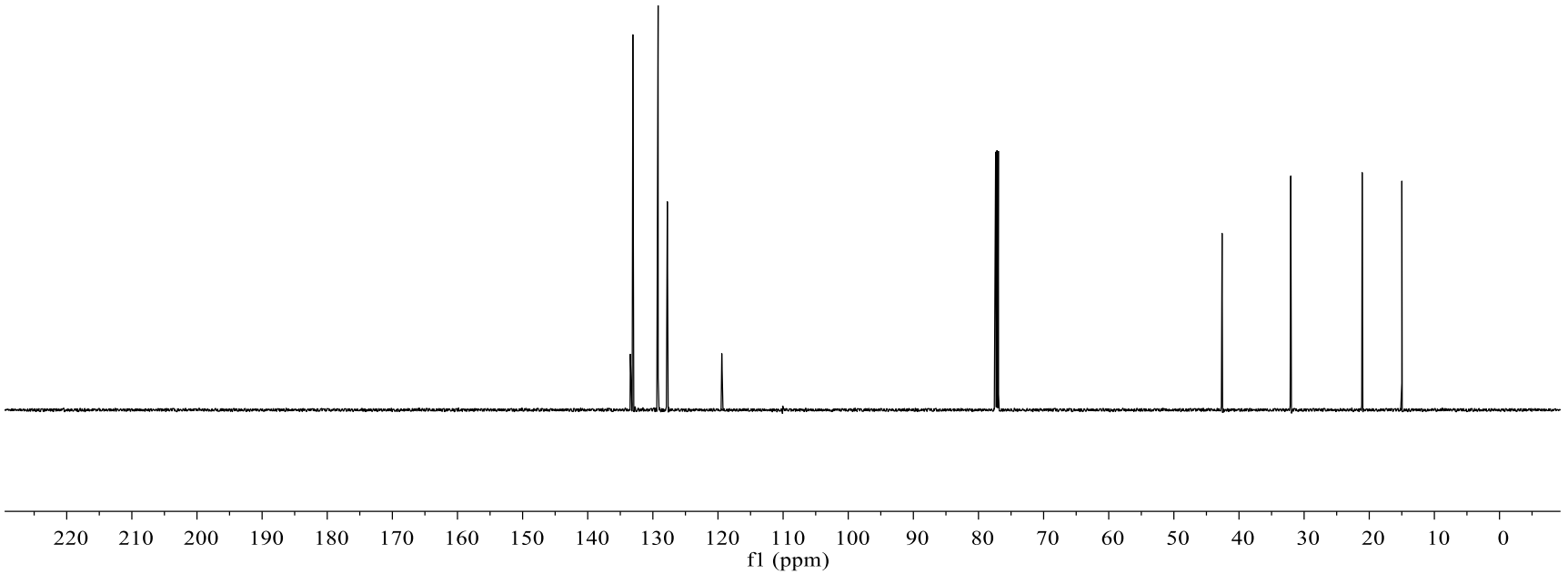

PhS
CN
Me

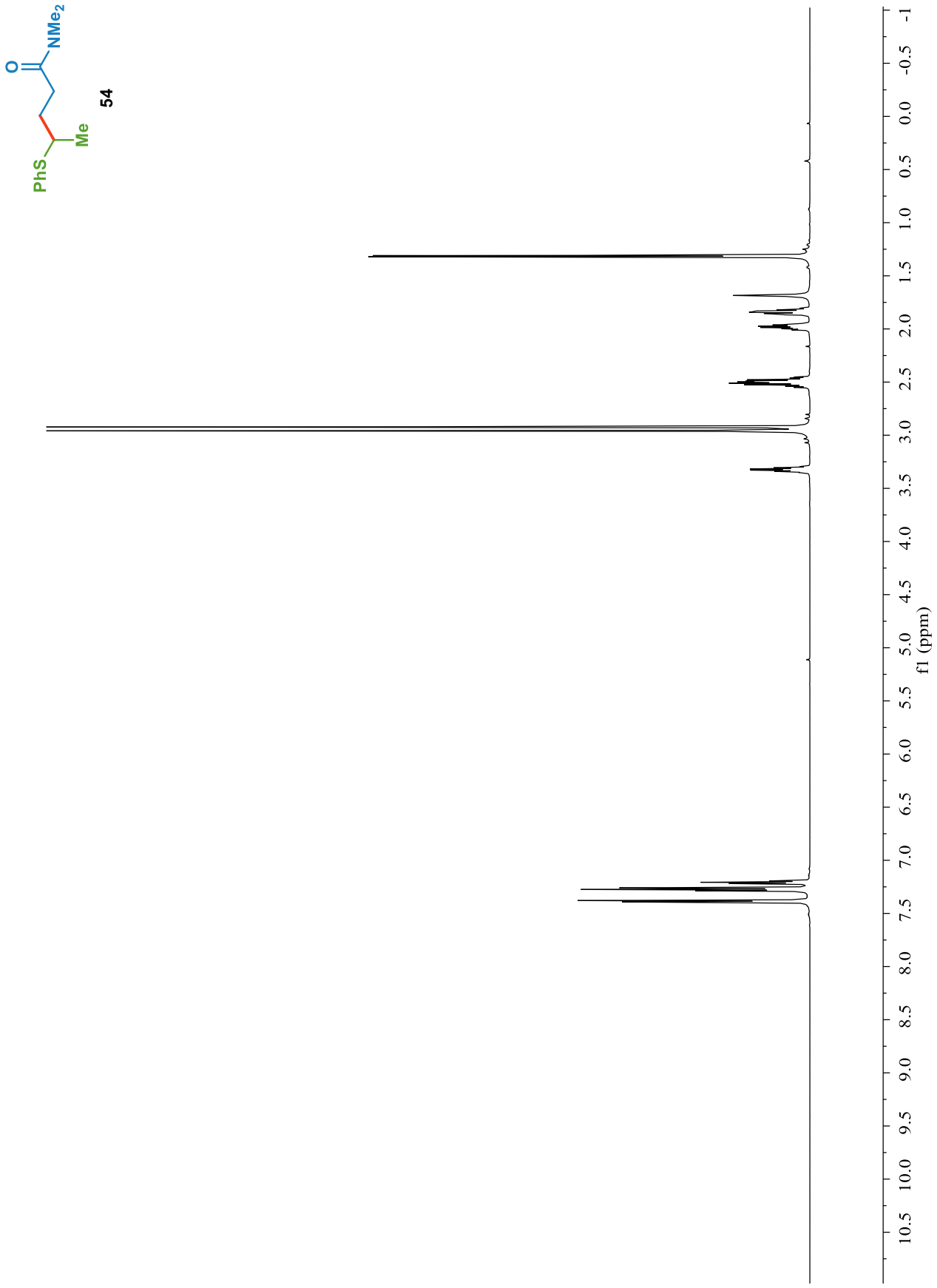
53

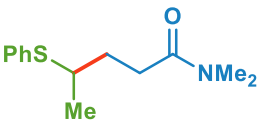

10.5 10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0 -0.5 -1
f1 (ppm)


PhS
CN
Me

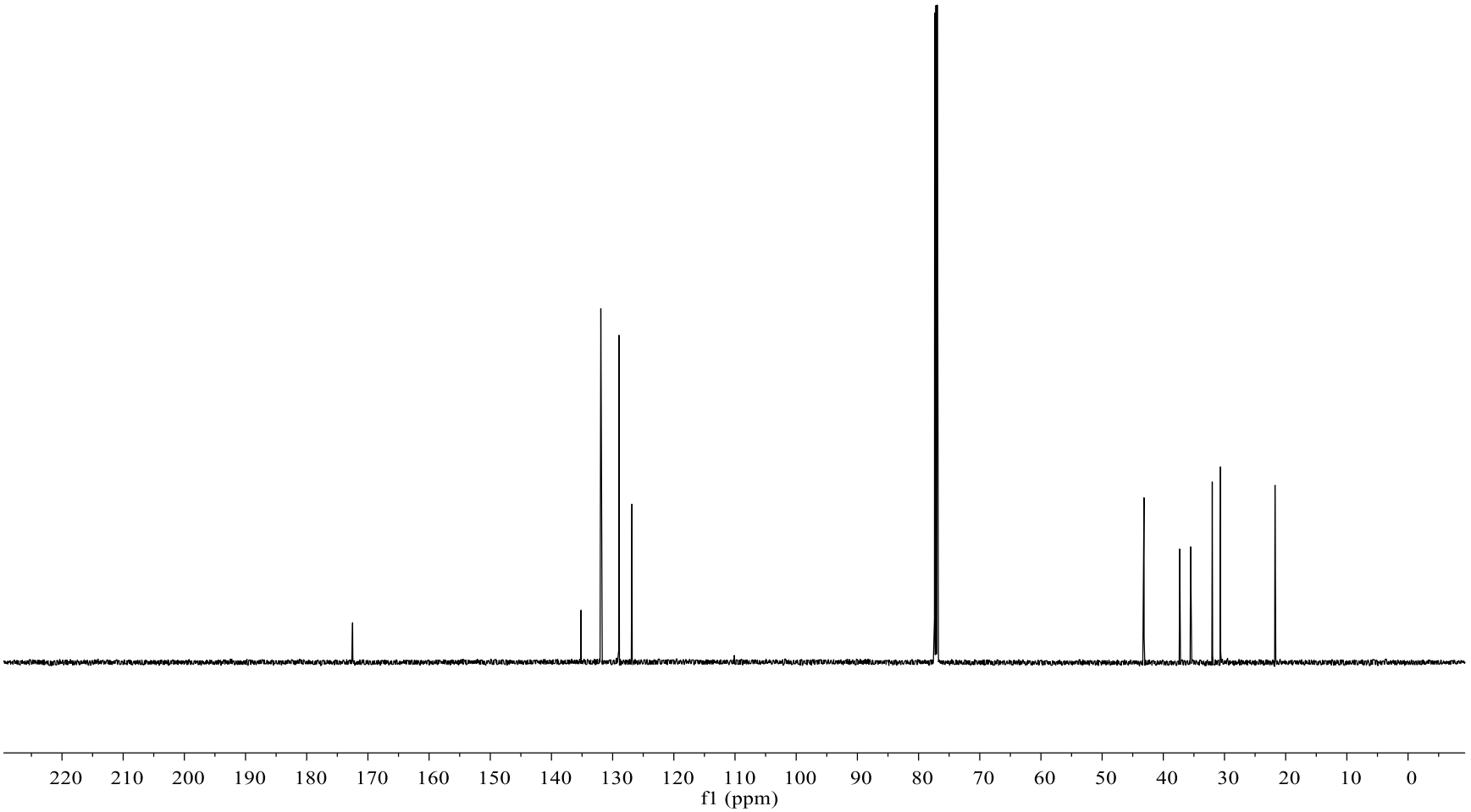
53

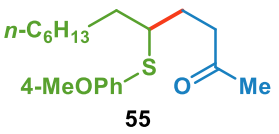

220 210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
f1 (ppm)


O
NMe2
PhS
Me
54
10.5
10.0
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
-0.5
-1
f1 (ppm)

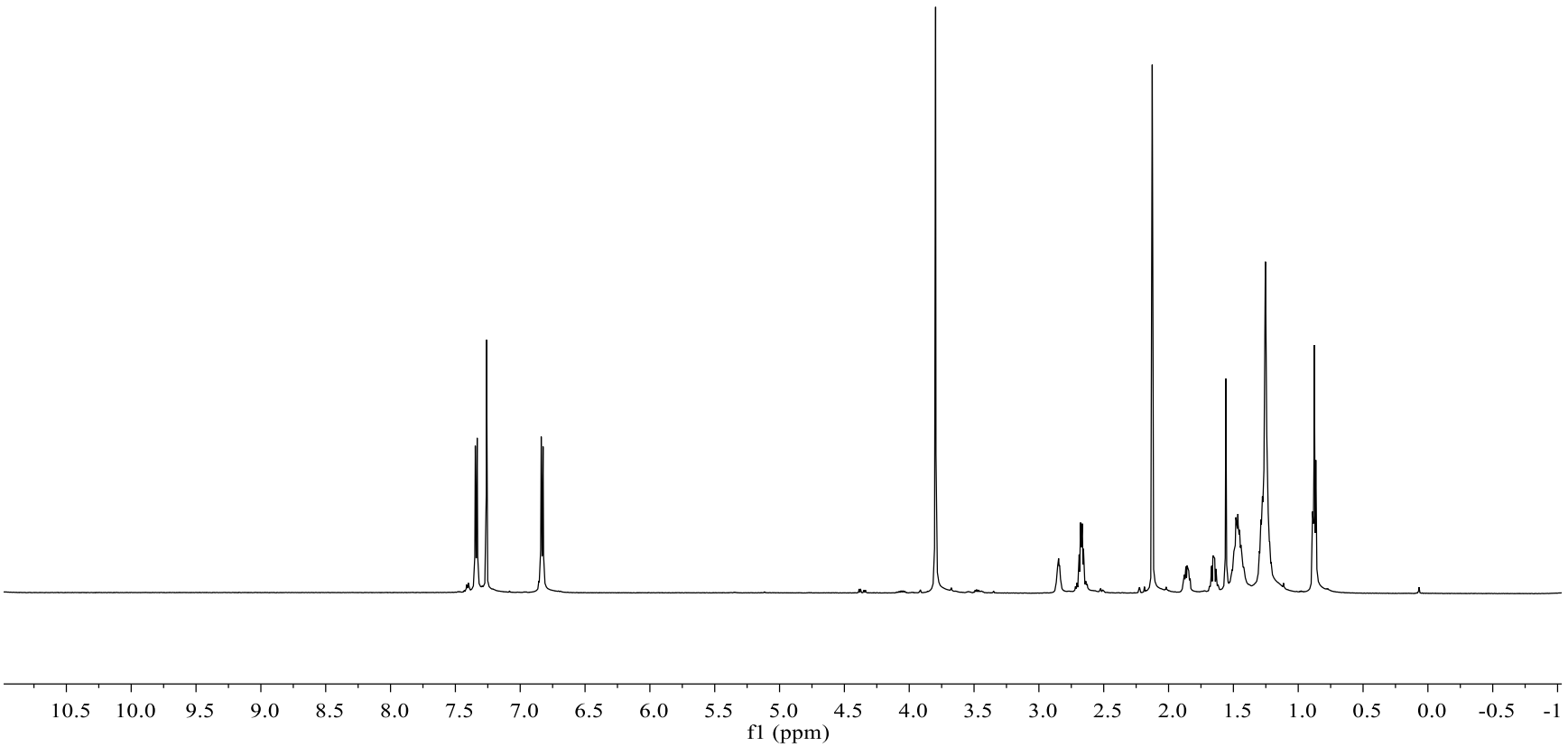

PhS
Me
O
NMe2

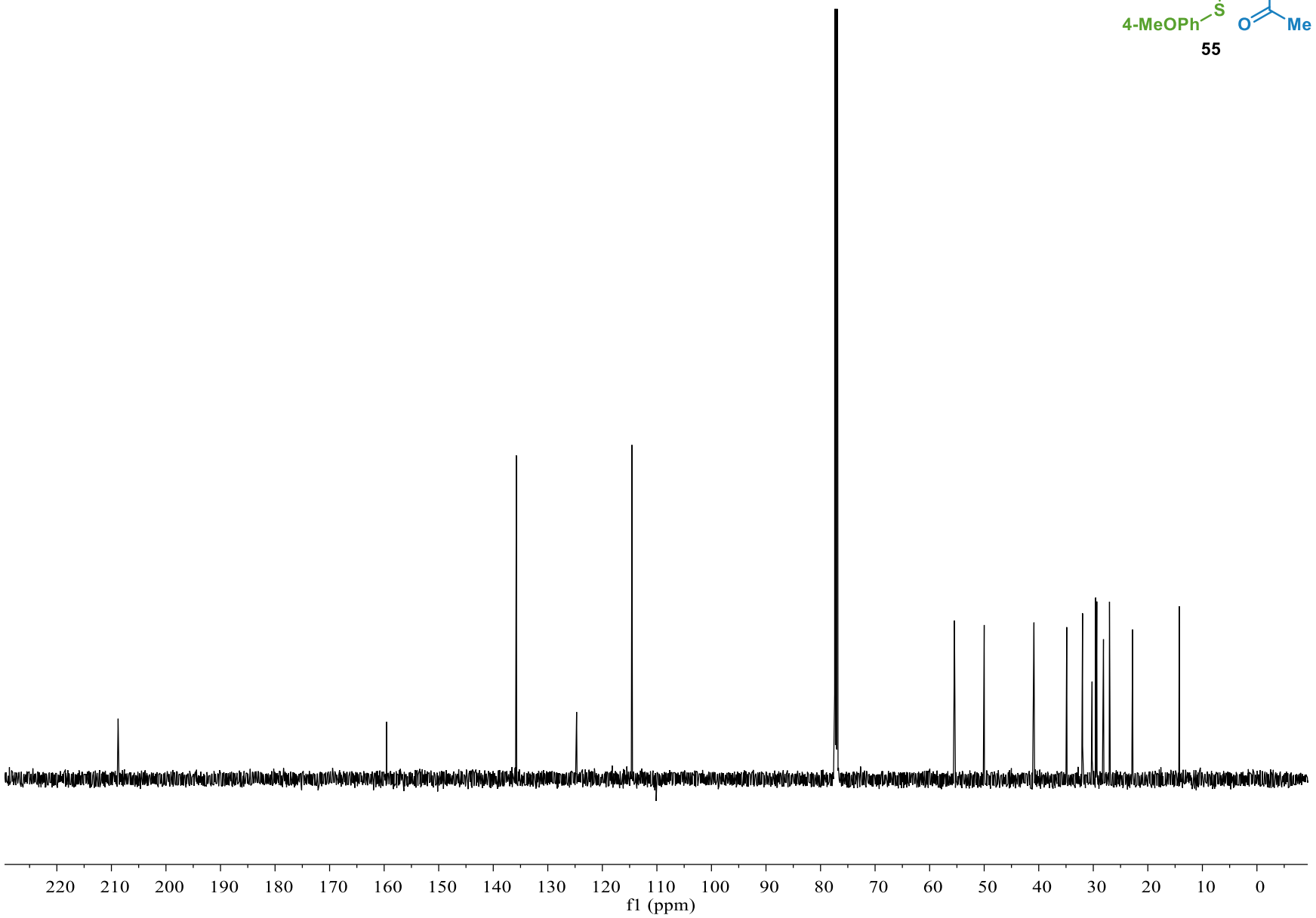
54

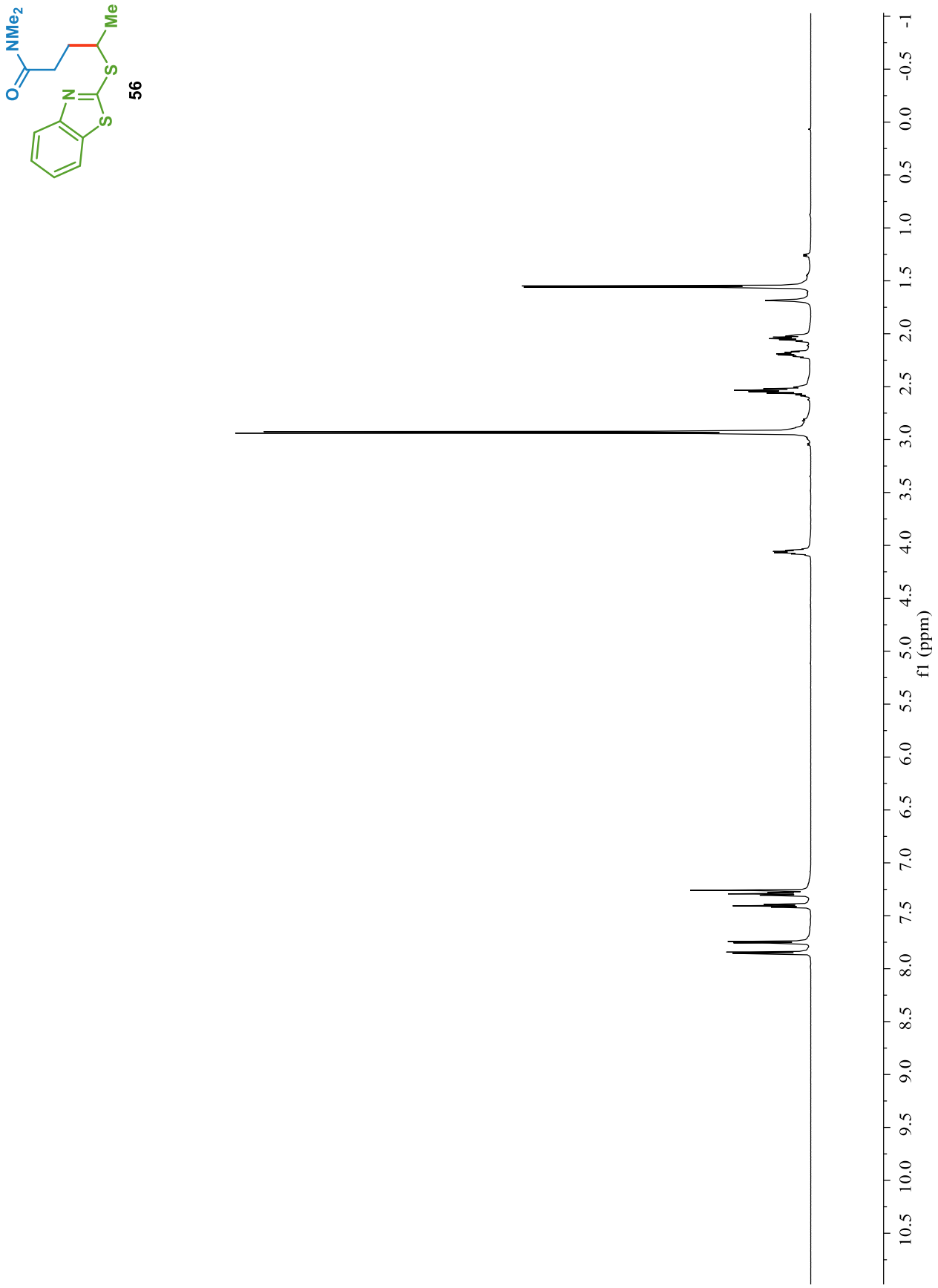

220
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)

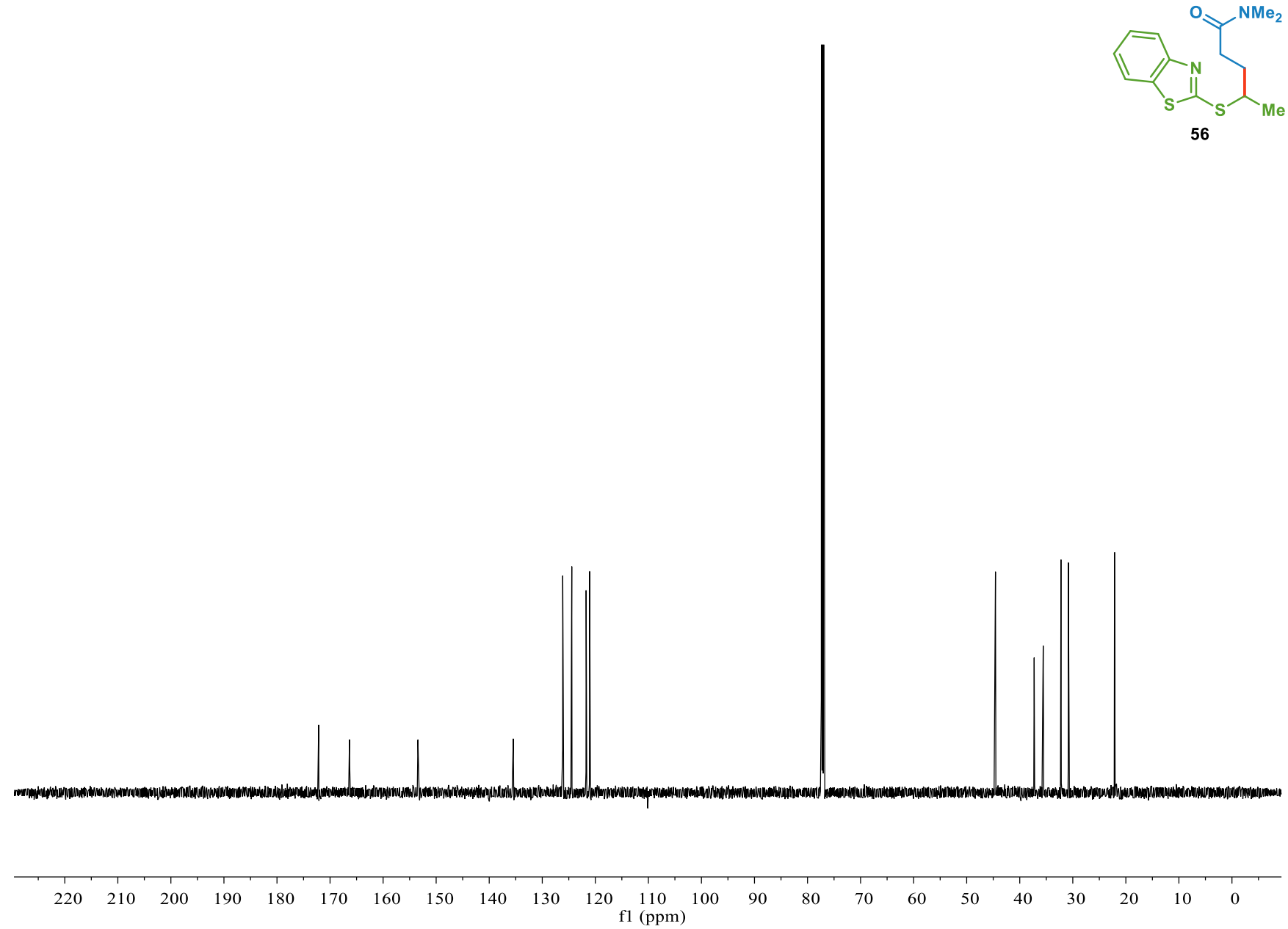

n-C6H13
S
4-MeOPh
O
Me

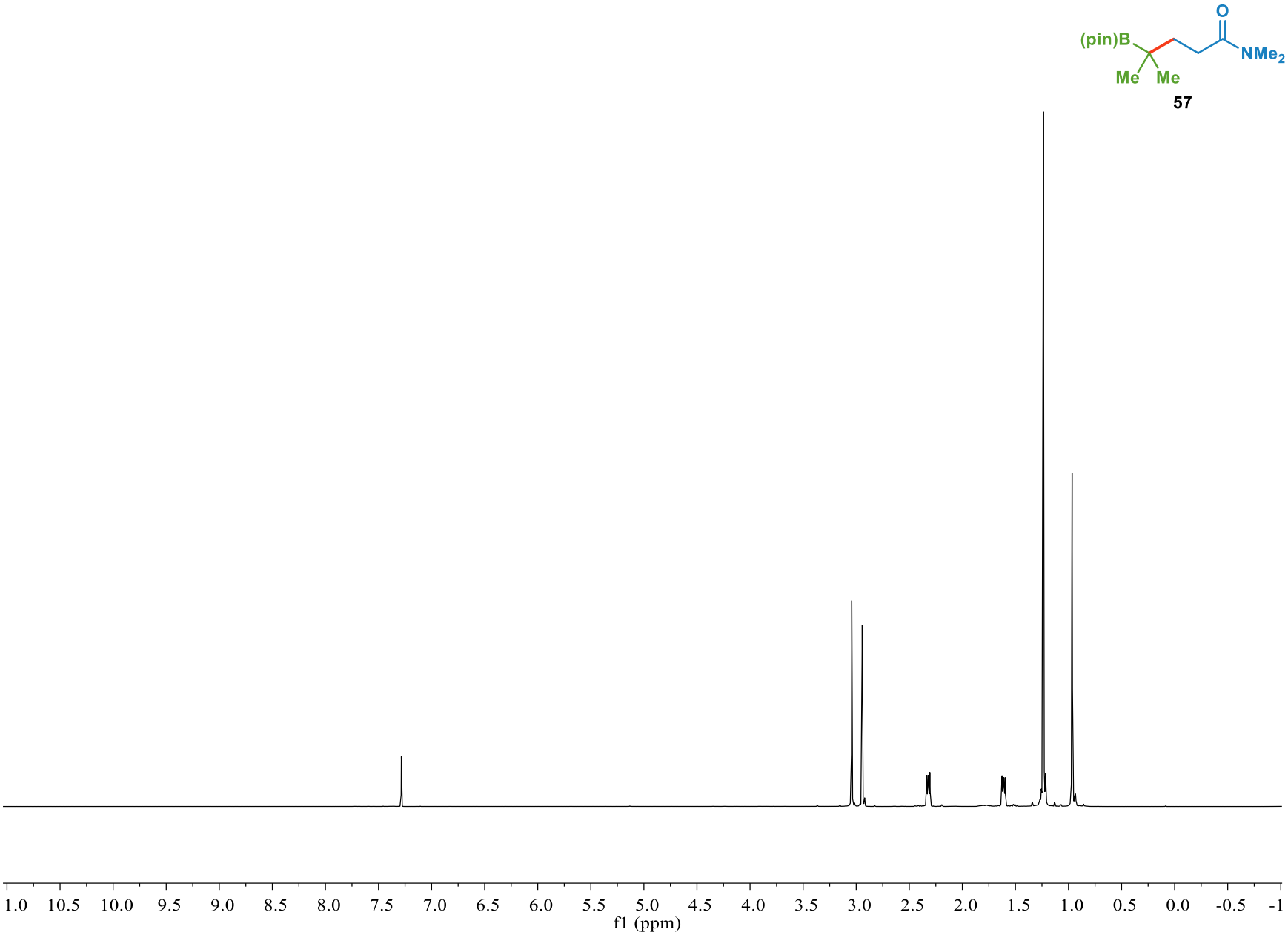
55

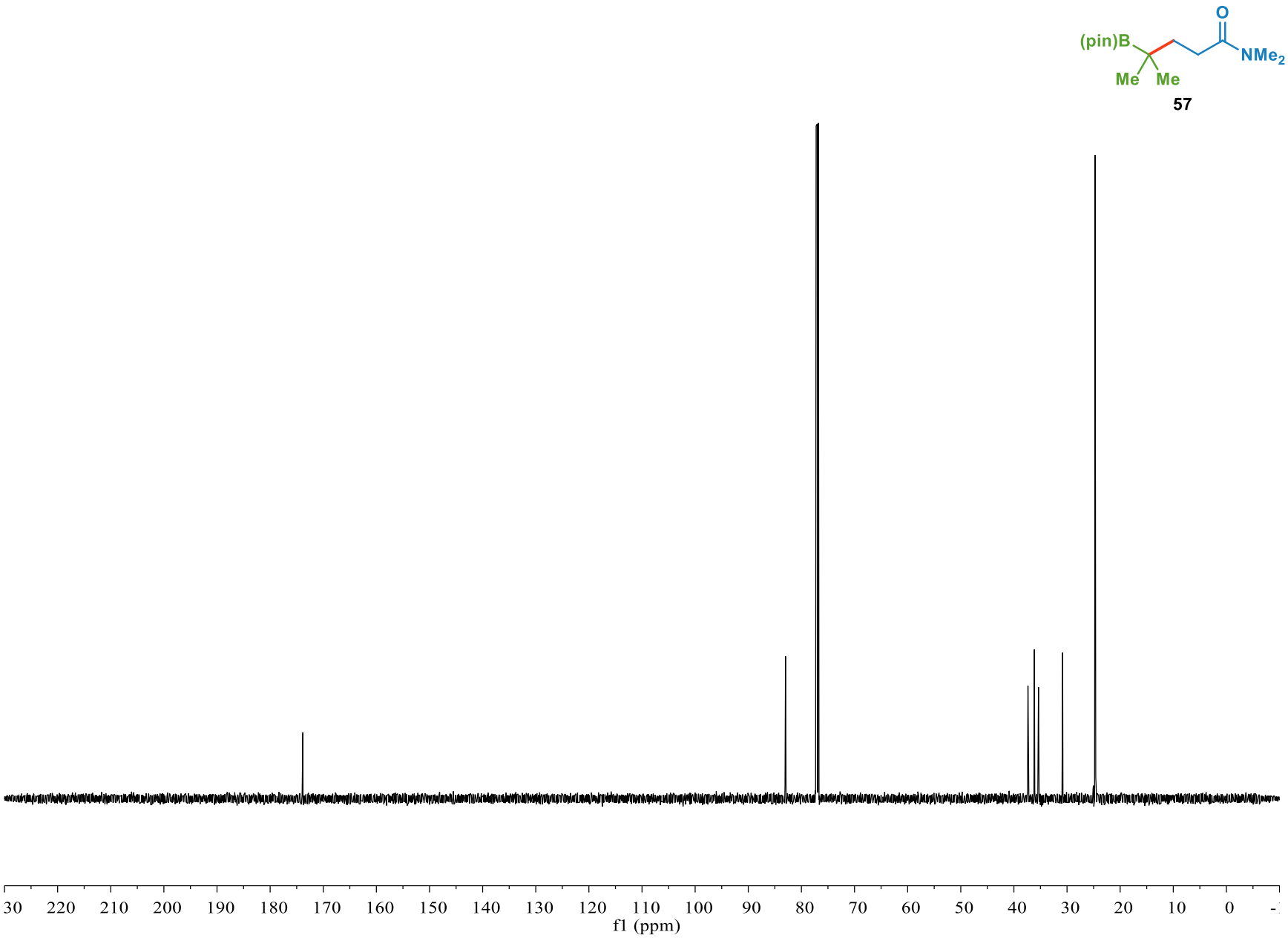

10.5 10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0 -0.5 -1
f1 (ppm)

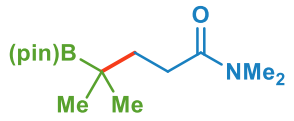

n-C6H13
S
4-MeOPh
O
Me
55
220 210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
f1 (ppm)


NMe2
O
N
S
S
Me
56
10.5
10.0
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
-0.5
-1
f1 (ppm)

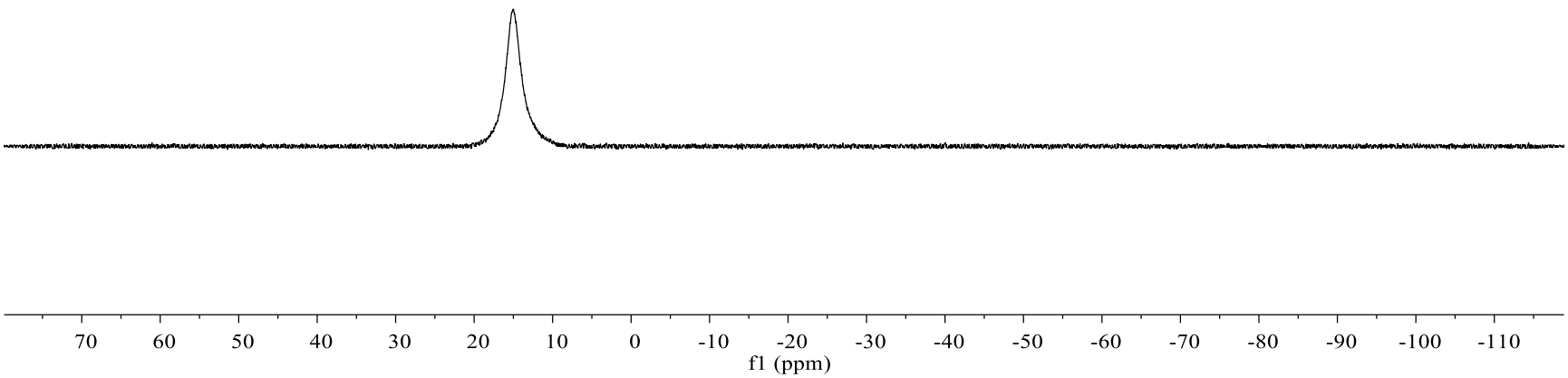

O
NMe2
N
S
S
Me
56
220
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)

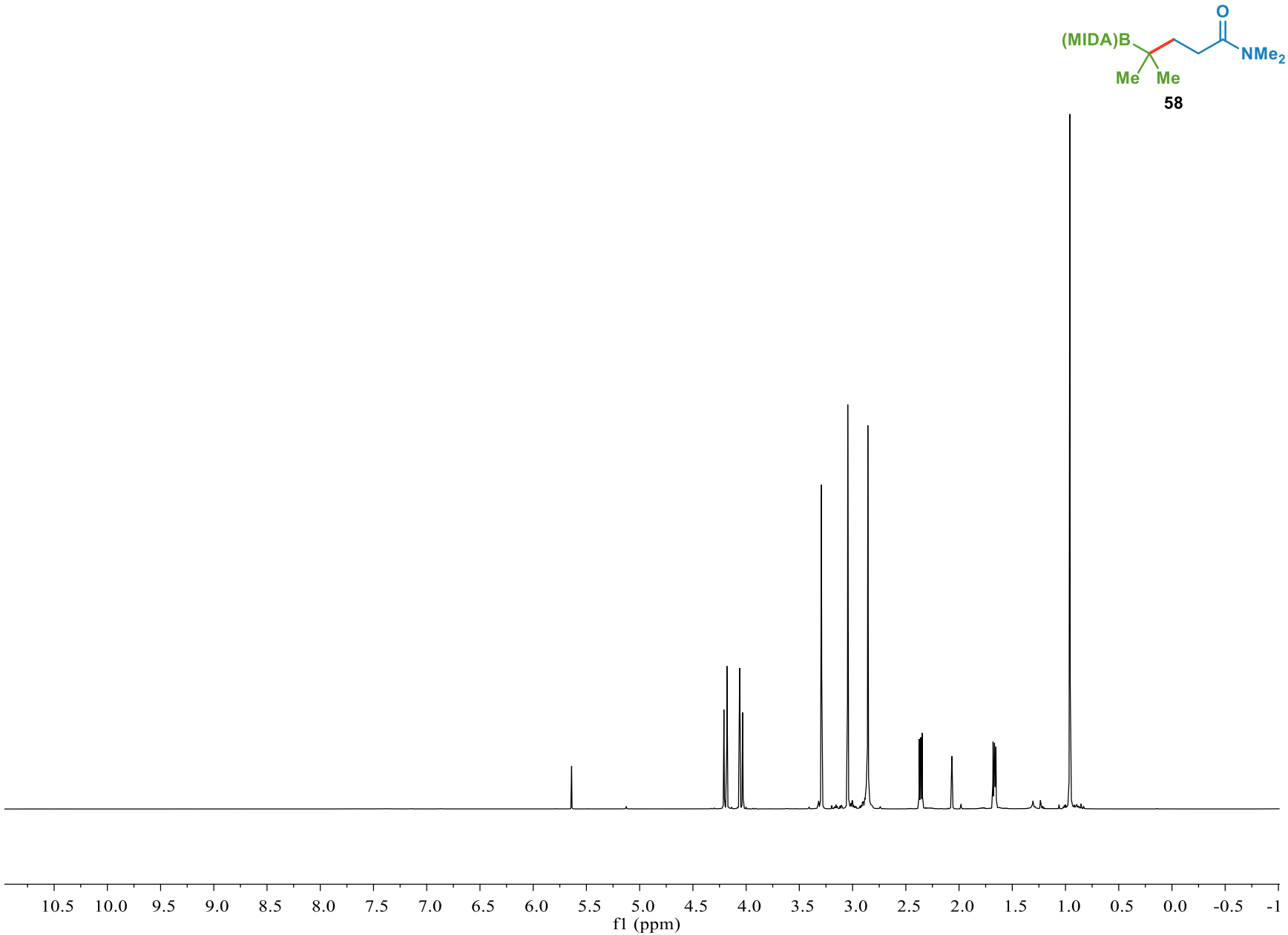

O
(pin)B
NMe2
Me
Me
57
1.0
10.5
10.0
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
-0.5
-1
f1 (ppm)

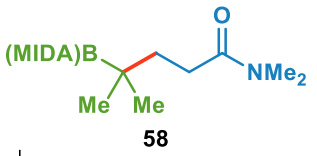

O
(pin)B
NMe2
Me
Me
57
30
220
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)


O
(pin)B
NMe2
Me
Me

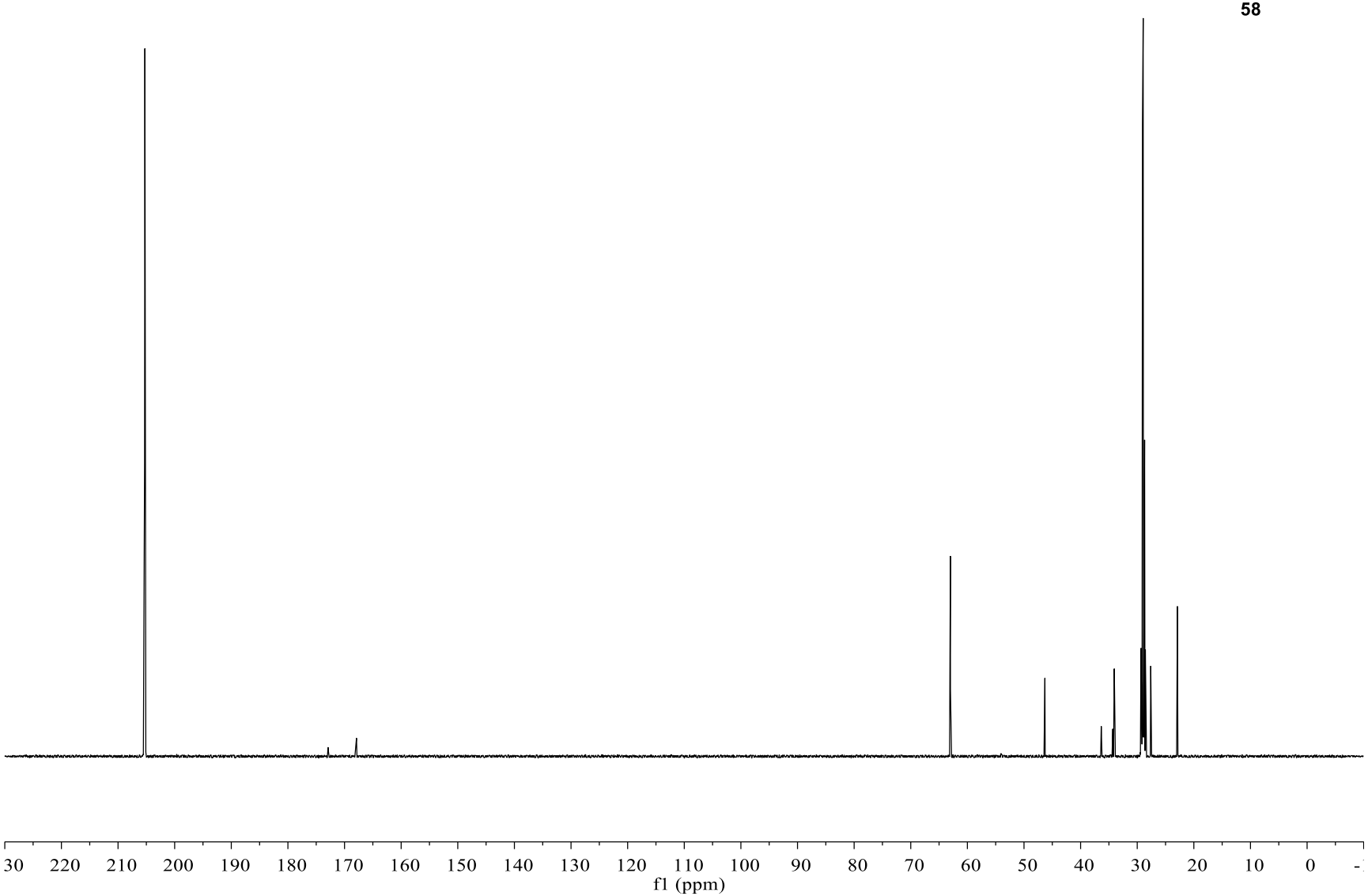
57

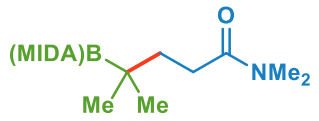

70
60
50
40
30
20
10
0
-10
-20
-30
-40
-50
-60
-70
-80
-90
-100
-110
f1 (ppm)


O
(MIDA)B
NMe2
Me
Me
58
10.5
10.0
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
-0.5
-1
f1 (ppm)

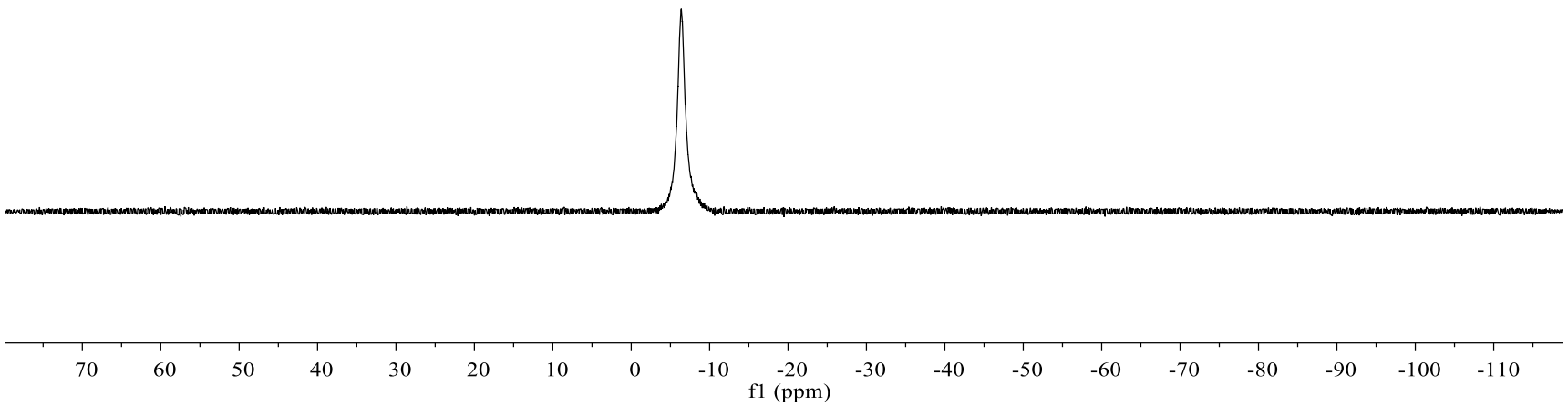

O
(MIDA)B
NMe2
Me
Me

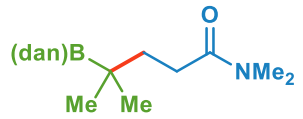
58


30 220 210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
f1 (ppm)

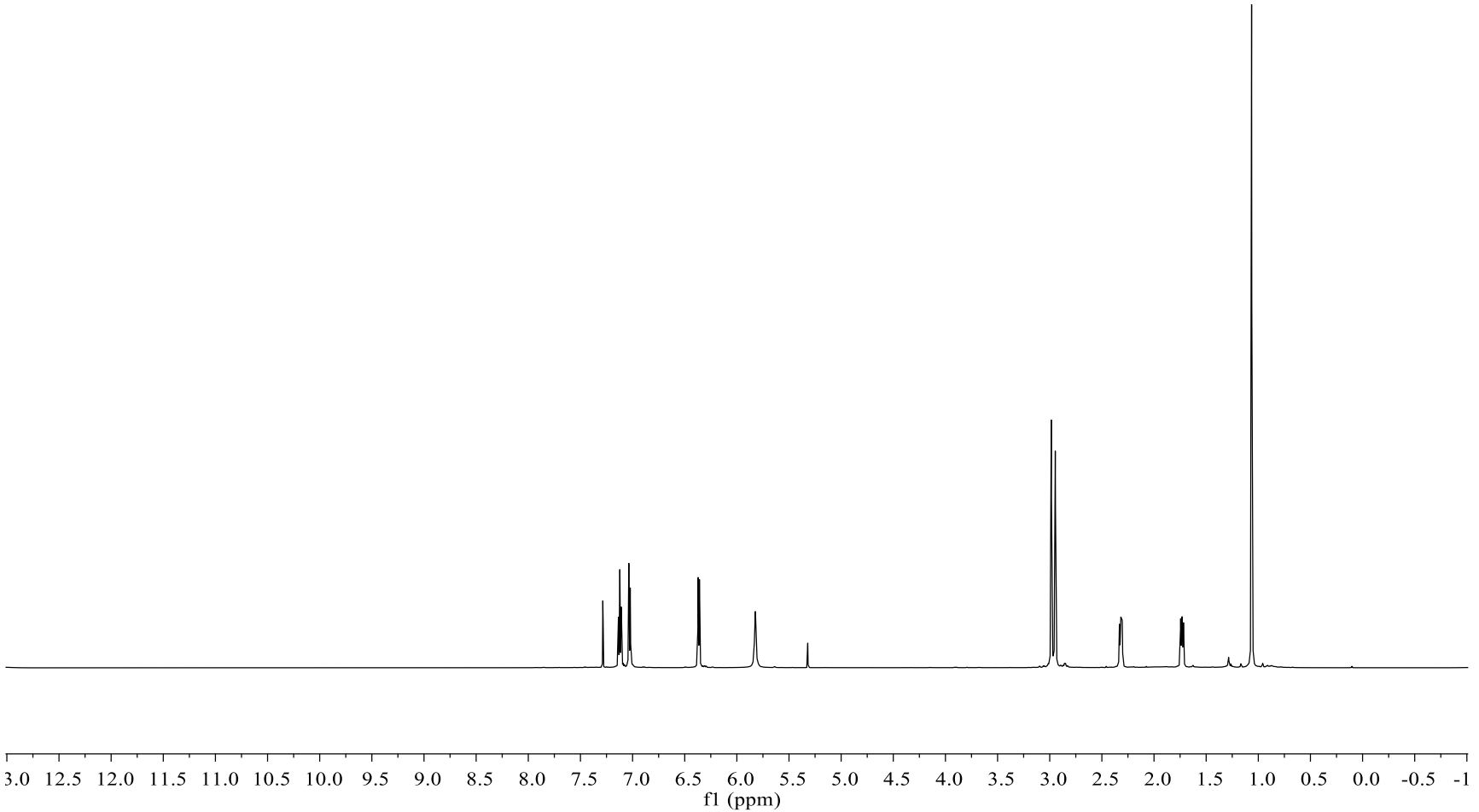

(MIDA)B
Me
Me
O
NMe2

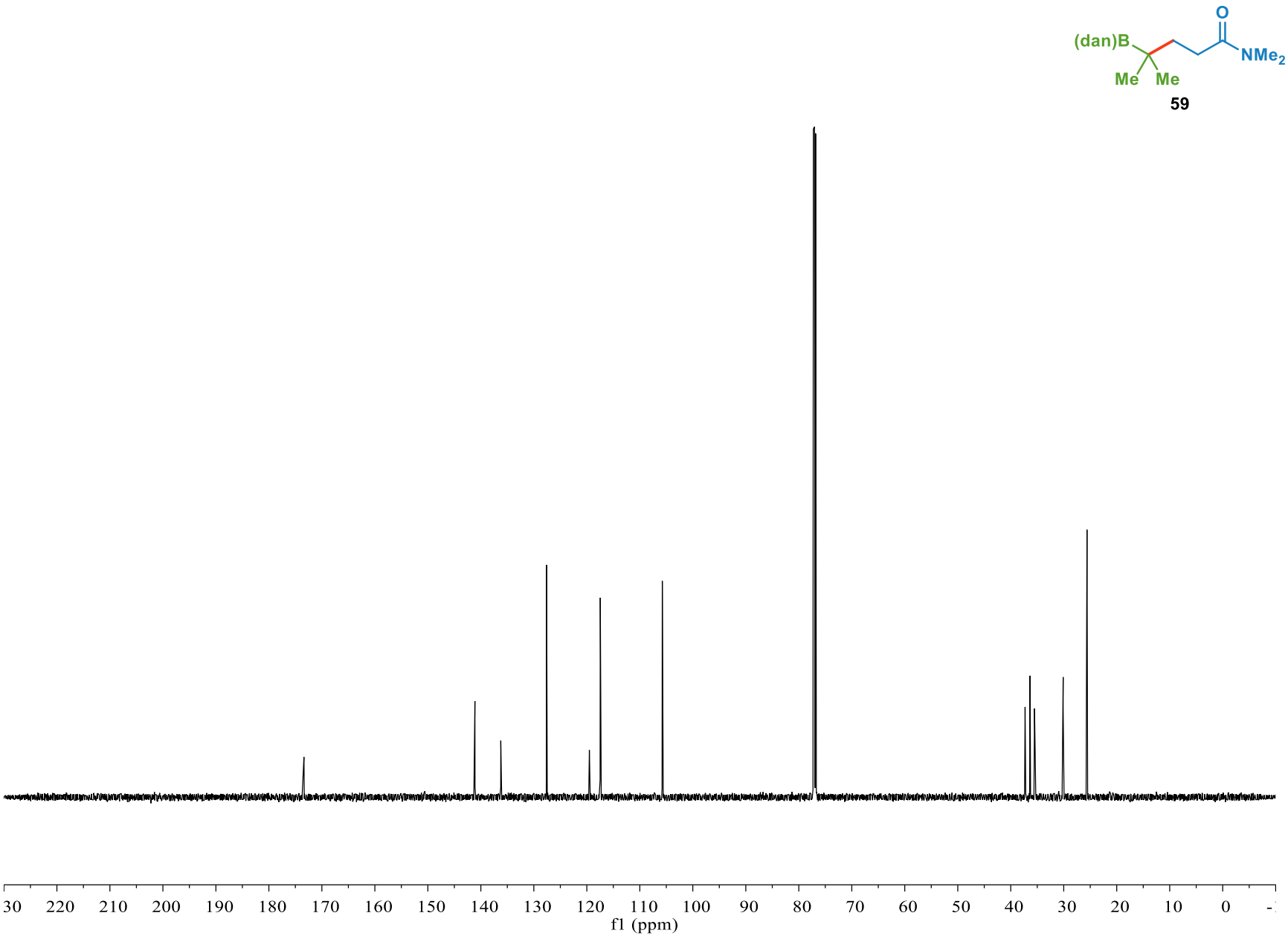
58

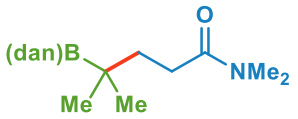

70
60
50
40
30
20
10
0
-10
-20
-30
-40
-50
-60
-70
-80
-90
-100
-110
f1 (ppm)


O
(dan)B
NMe2
Me
Me

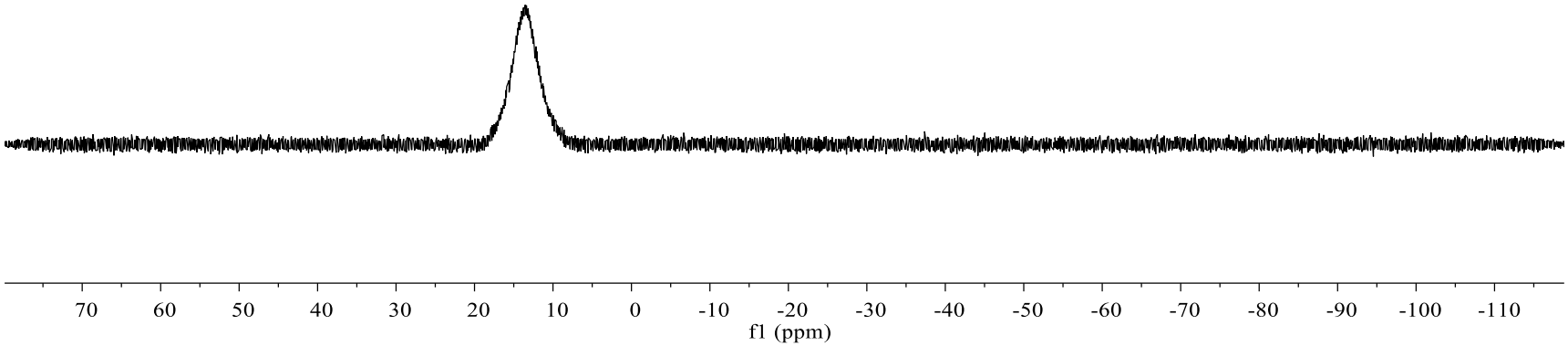
59

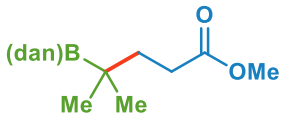

3.0 12.5 12.0 11.5 11.0 10.5 10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0 -0.5 -1
f1 (ppm)


O
(dan)B
NMe2
Me
Me
59
30
220
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)

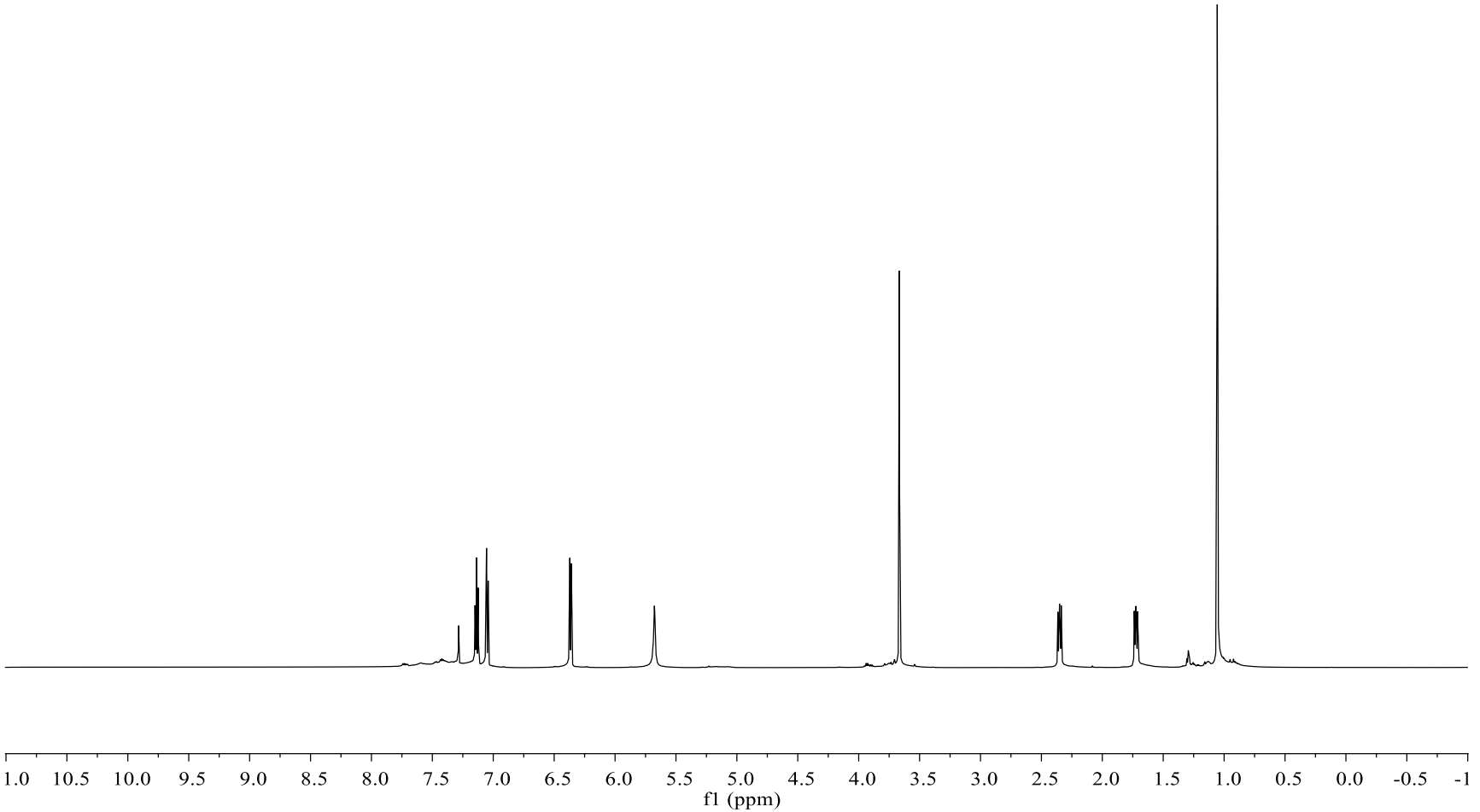

O
(dan)B
NMe2
Me
Me

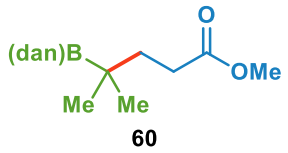
59


70
60
50
40
30
20
10
0
-10
-20
-30
-40
-50
-60
-70
-80
-90
-100
-110
f1 (ppm)

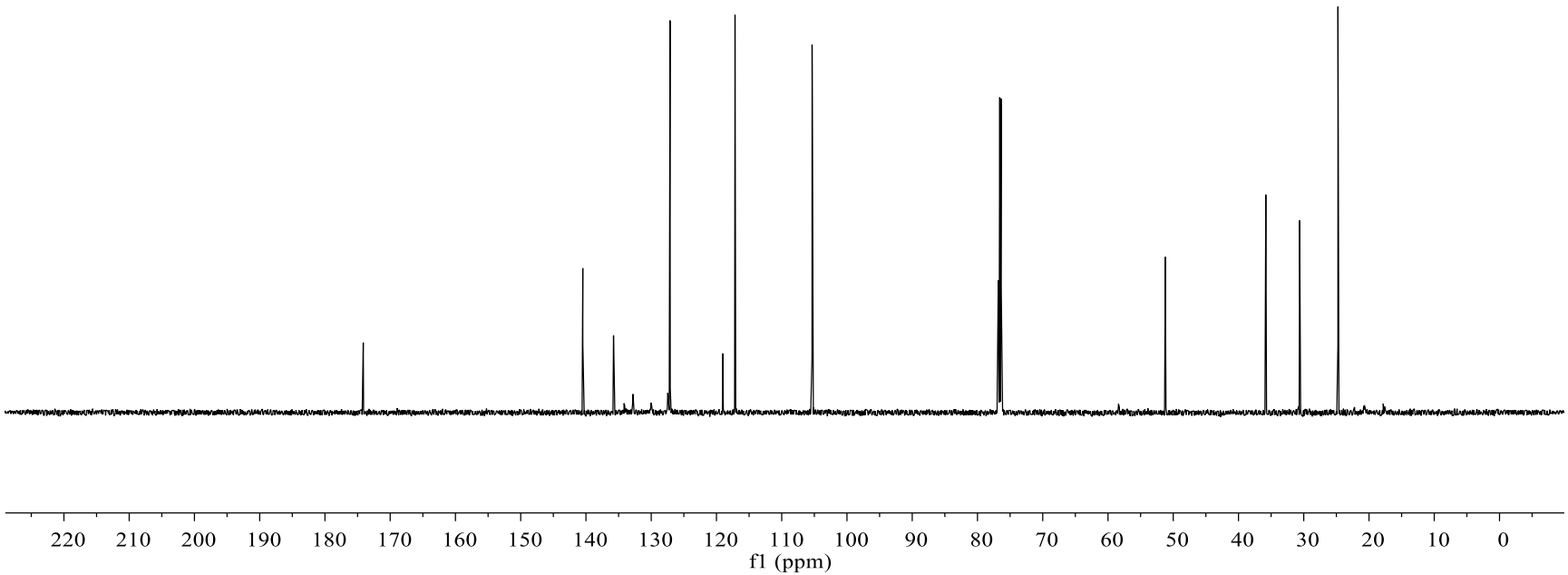

O
(dan)B
OMe
Me
Me

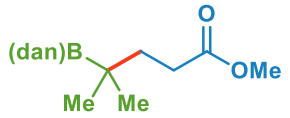
60


1.0
10.5
10.0
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
-0.5
-1
f1 (ppm)

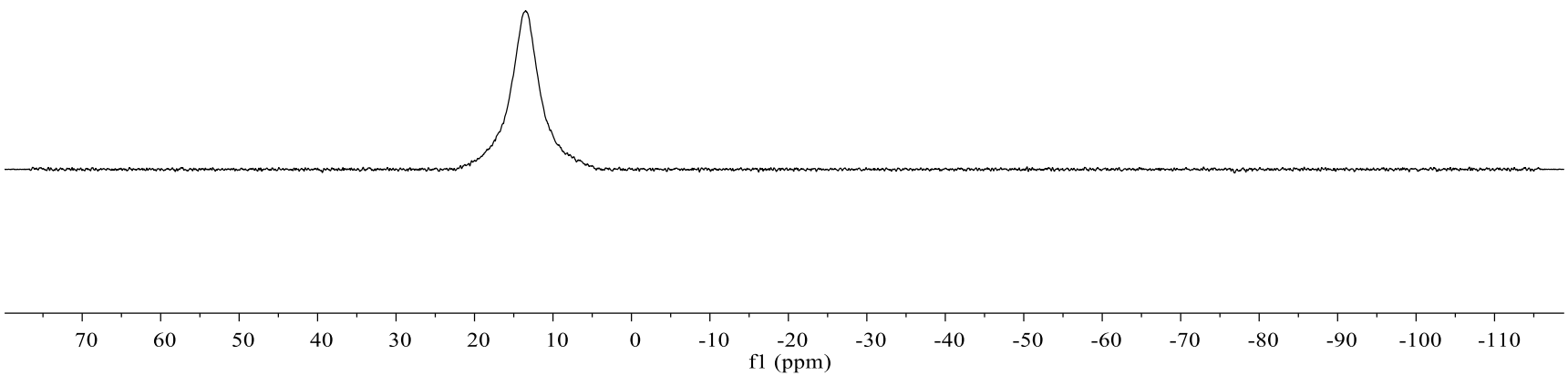

O
(dan)B
OMe
Me
Me

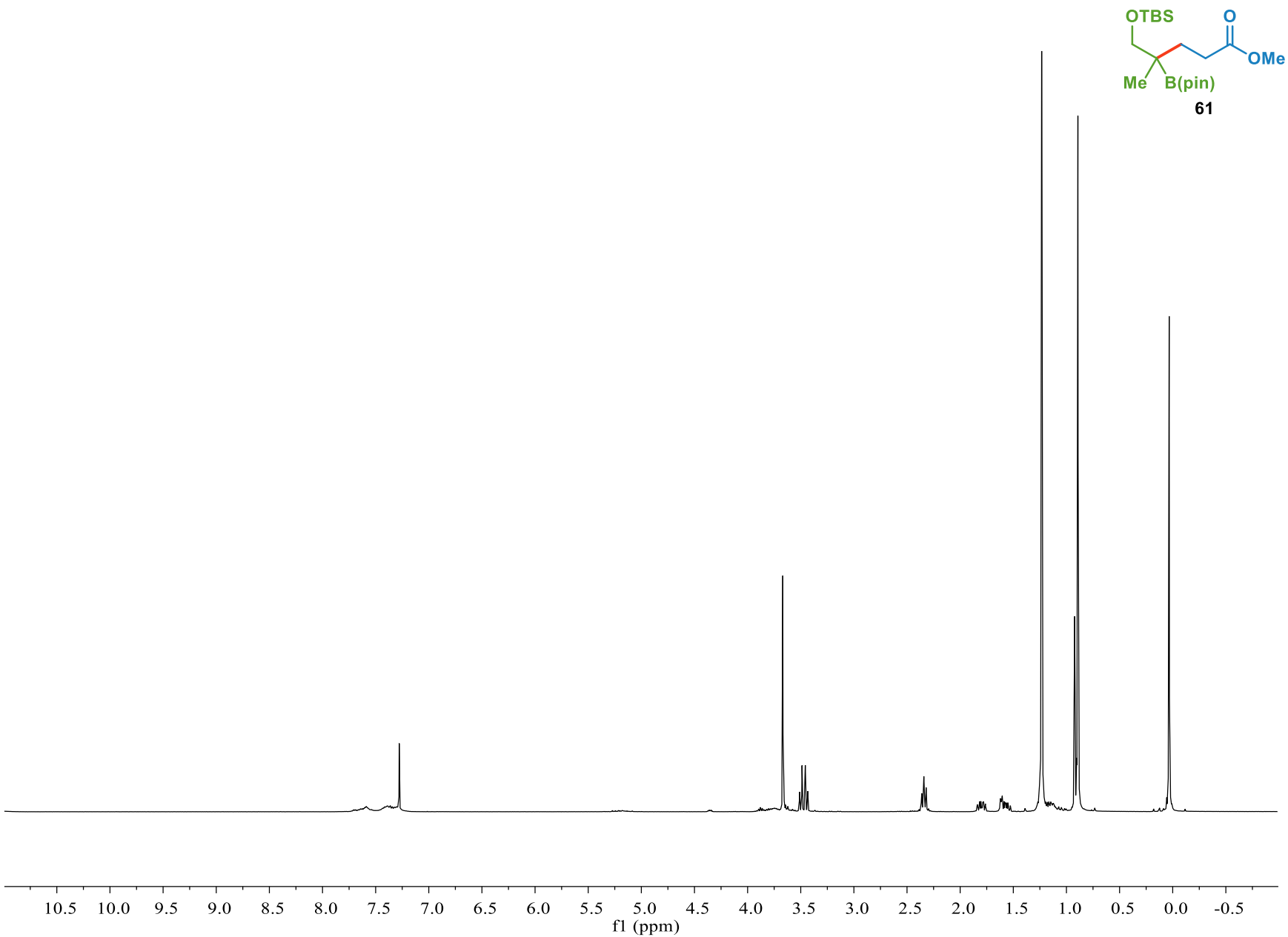
60

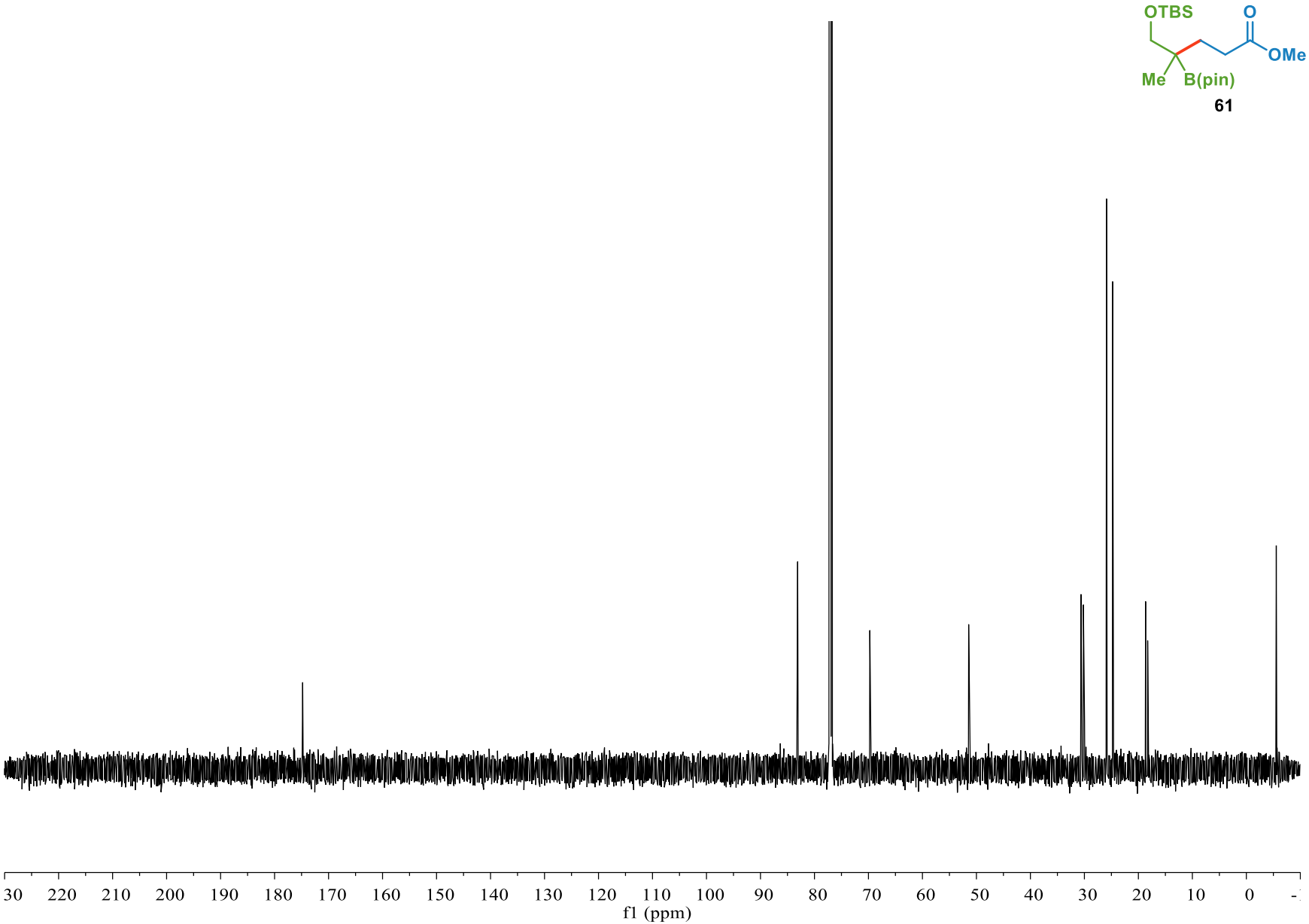

220
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)

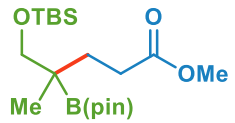

O
(dan)B
OMe
Me
Me

60

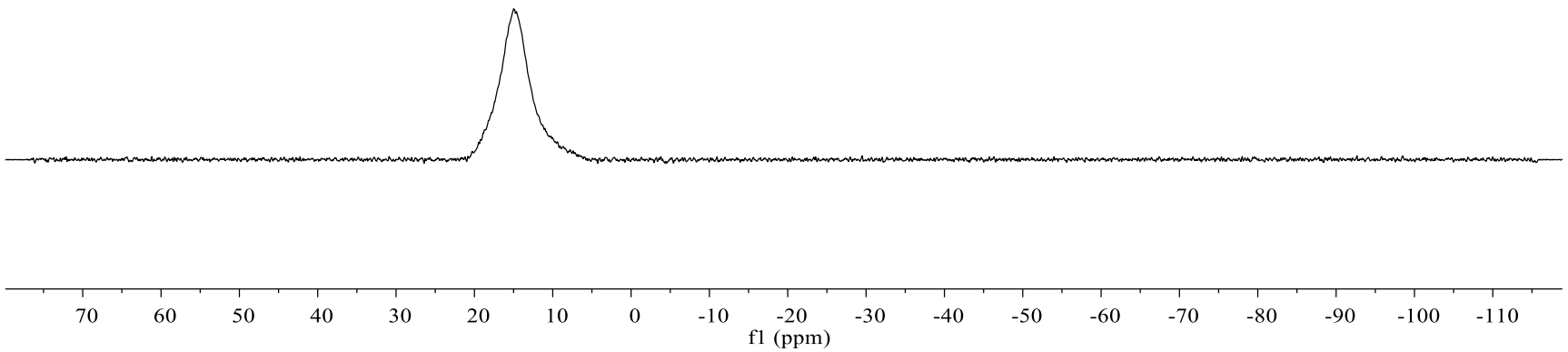

70
60
50
40
30
20
10
0
-10
-20
-30
-40
-50
-60
-70
-80
-90
-100
-110
f1 (ppm)


OTBS
O
OMe
Me
B(pin)
61
10.5 10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0 -0.5
f1 (ppm)


OTBS
O
OMe
Me
B(pin)
61
30 220 210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
f1 (ppm)


OTBS
O
OMe
Me
B(pin)

61


70
60
50
40
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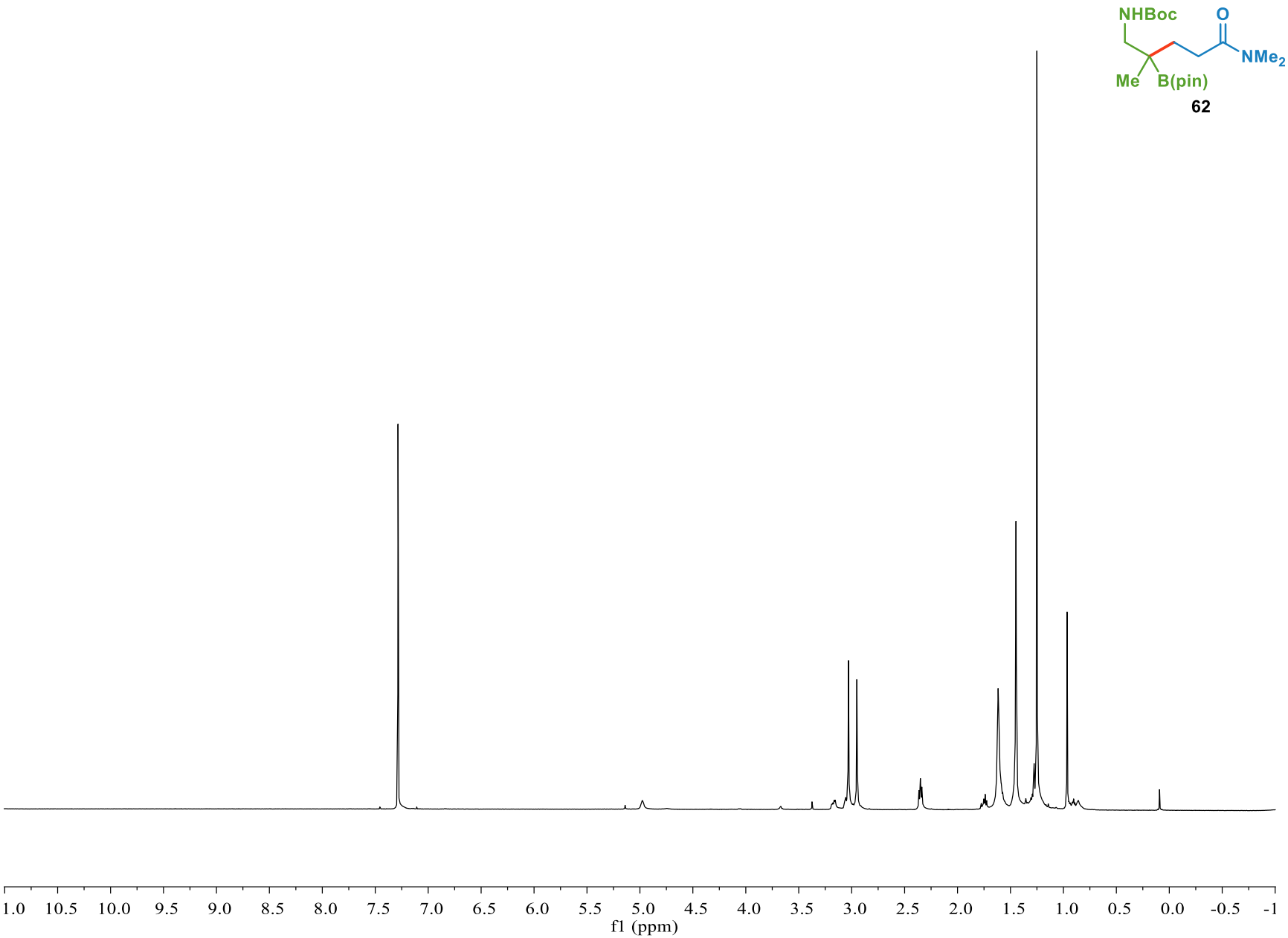
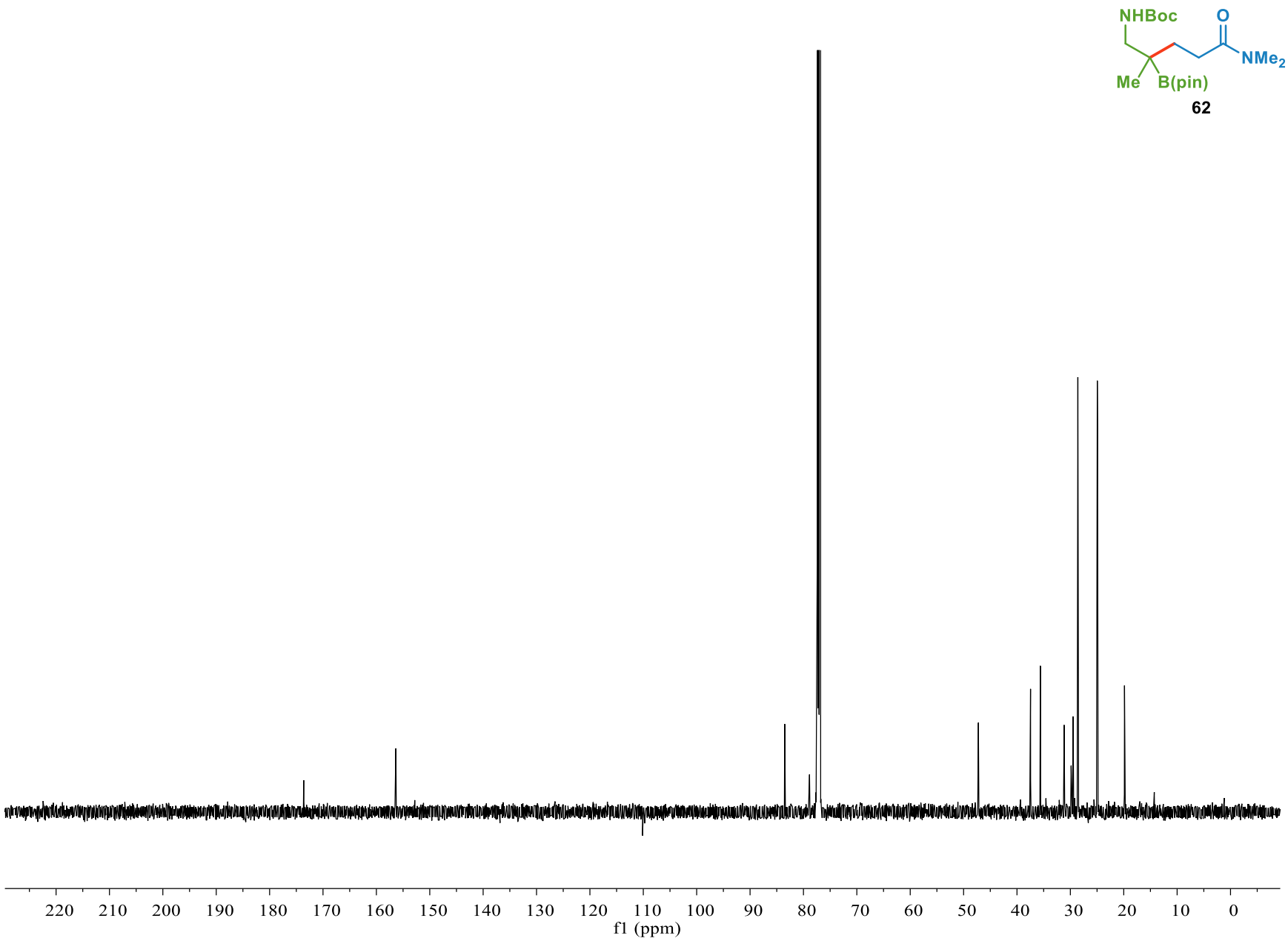
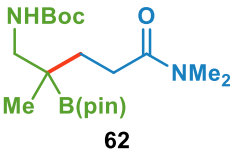
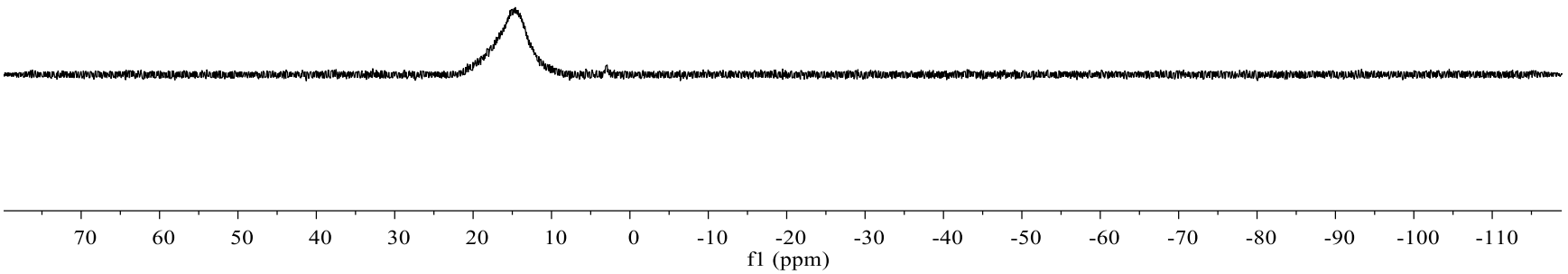
20
10
0
-10
-20
-30
-40
-50
-60
-70
-80
-90
-100
-110
f1 (ppm)

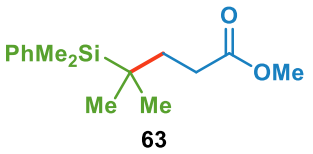

NHBoc
O
NMe2
Me
B(pin)
62
1.0
10.5
10.0
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
-0.5
-1
f1 (ppm)


NHBoc
O
NMe2
Me
B(pin)
62
220 210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
f1 (ppm)

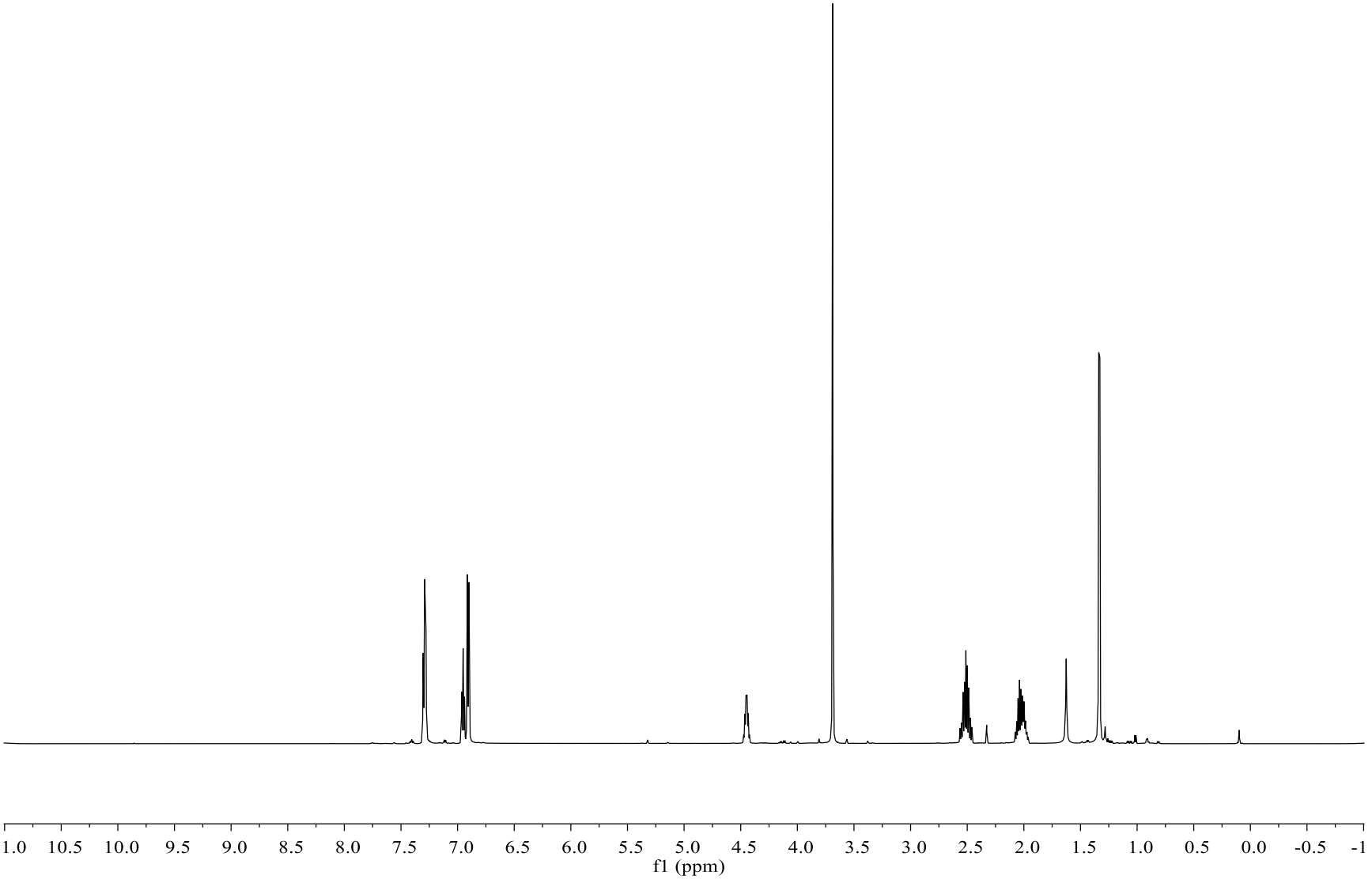

NHBoc
O
NMe2
Me
B(pin)

62


70
60
50
40
30
20
10
0
-10
-20
-30
-40
-50
-60
-70
-80
-90
-100
-110
f1 (ppm)

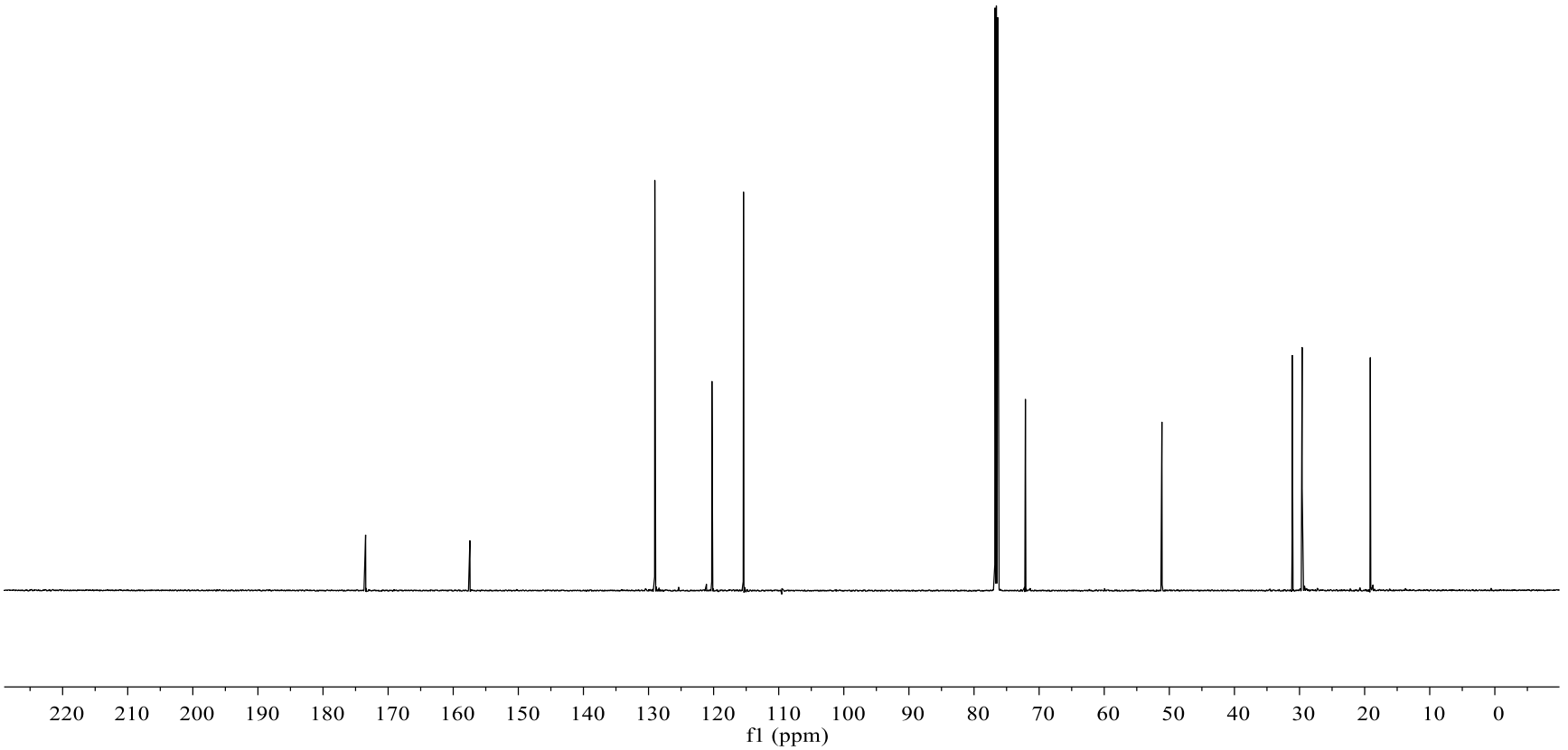

O
PhMe2Si
OMe
Me
Me

63


1.0
10.5
10.0
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
-0.5
-1
f1 (ppm)

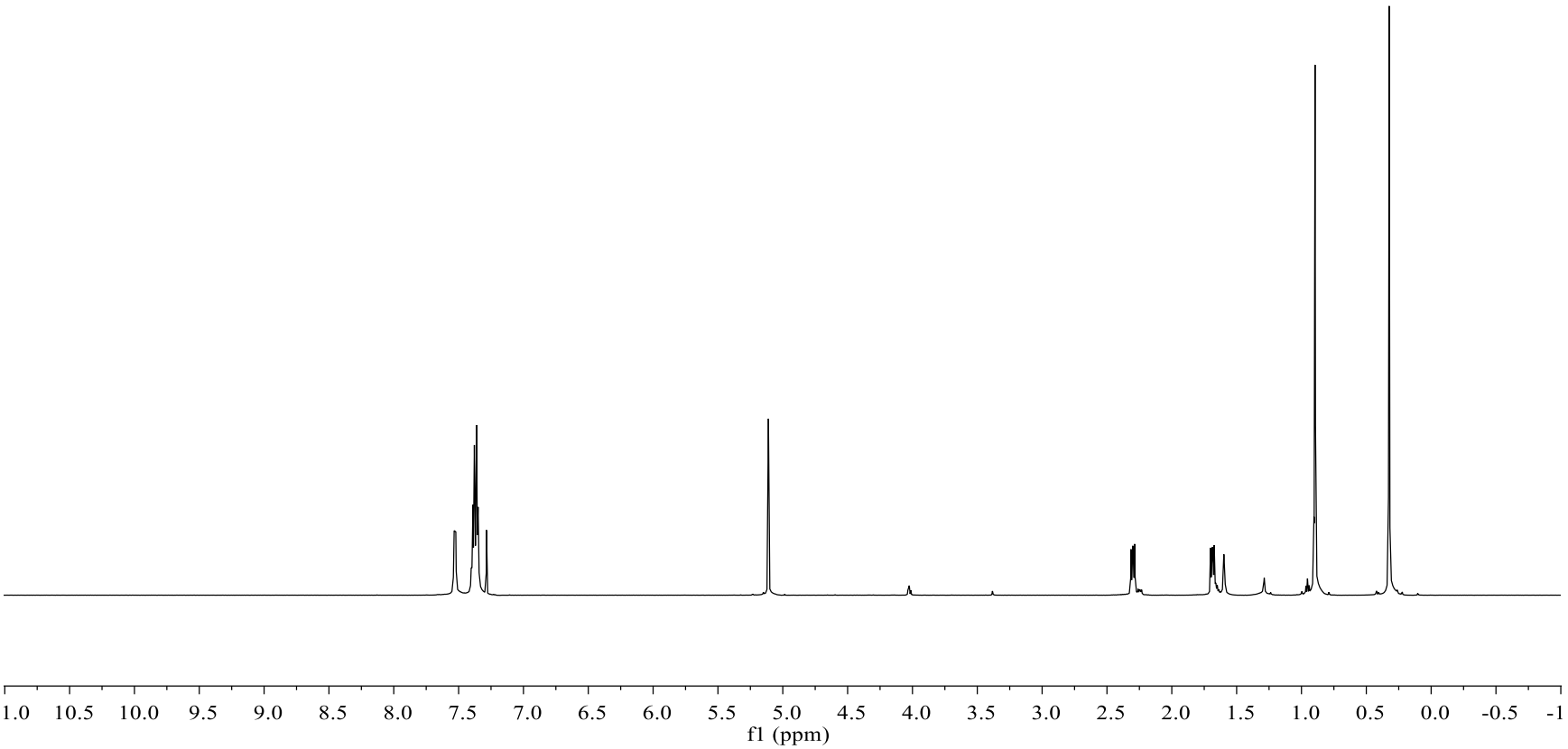

O
PhMe2Si
OMe
Me
Me

63


220
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)


O
PhMe2Si
OBn
Me
Me

64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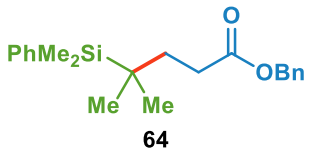
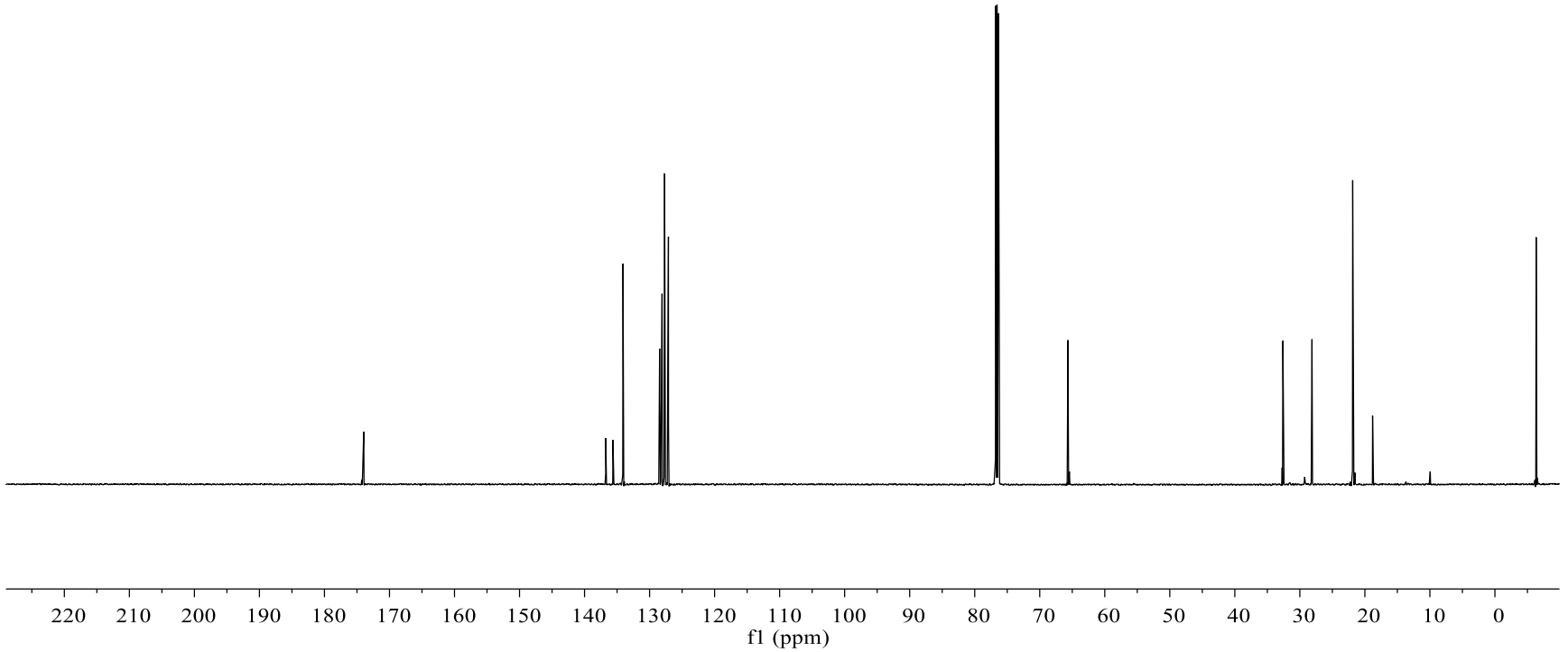
10.0
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
-0.5
-1
f1 (ppm)

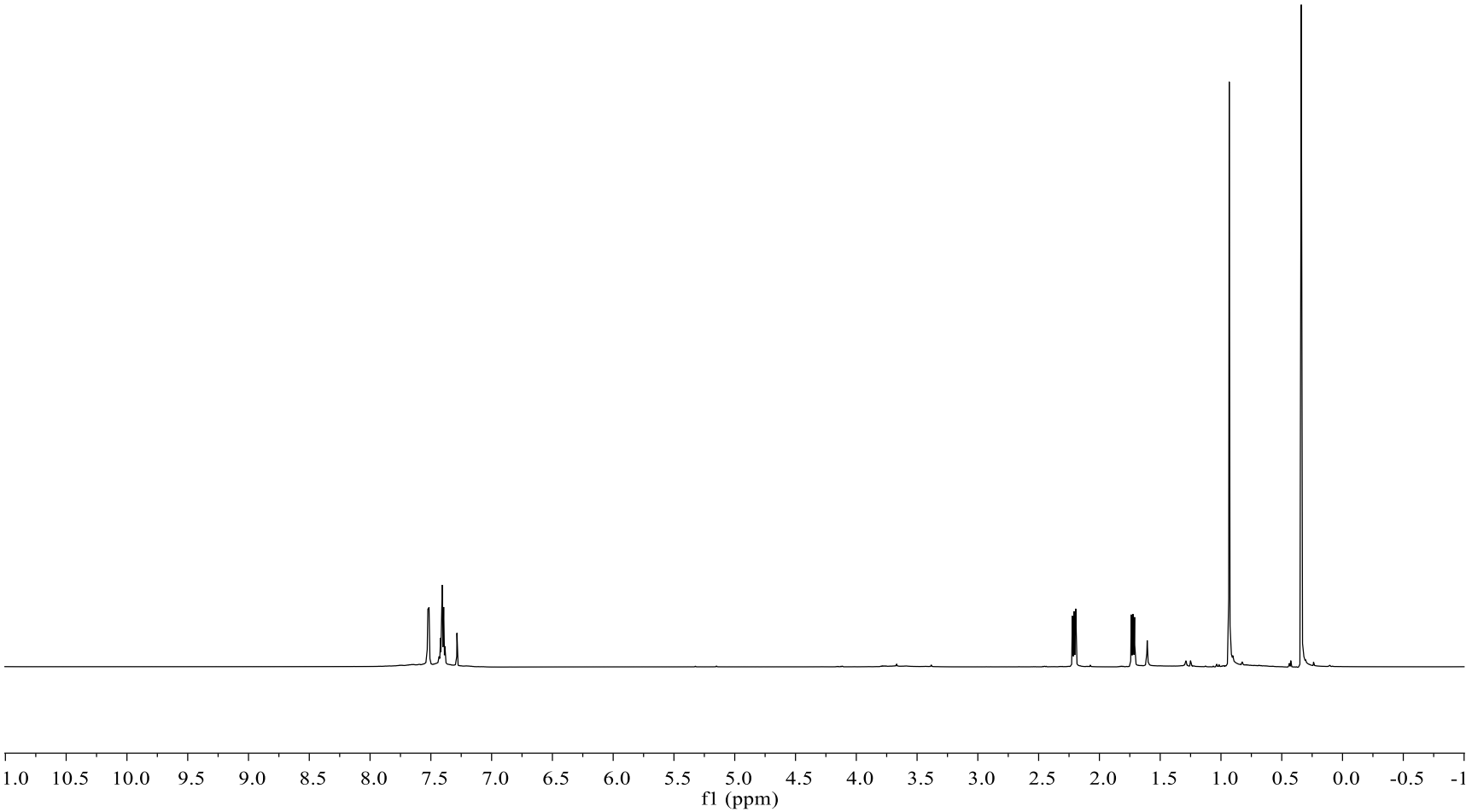

O
PhMe2Si
OBn
Me
Me

64


220
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)

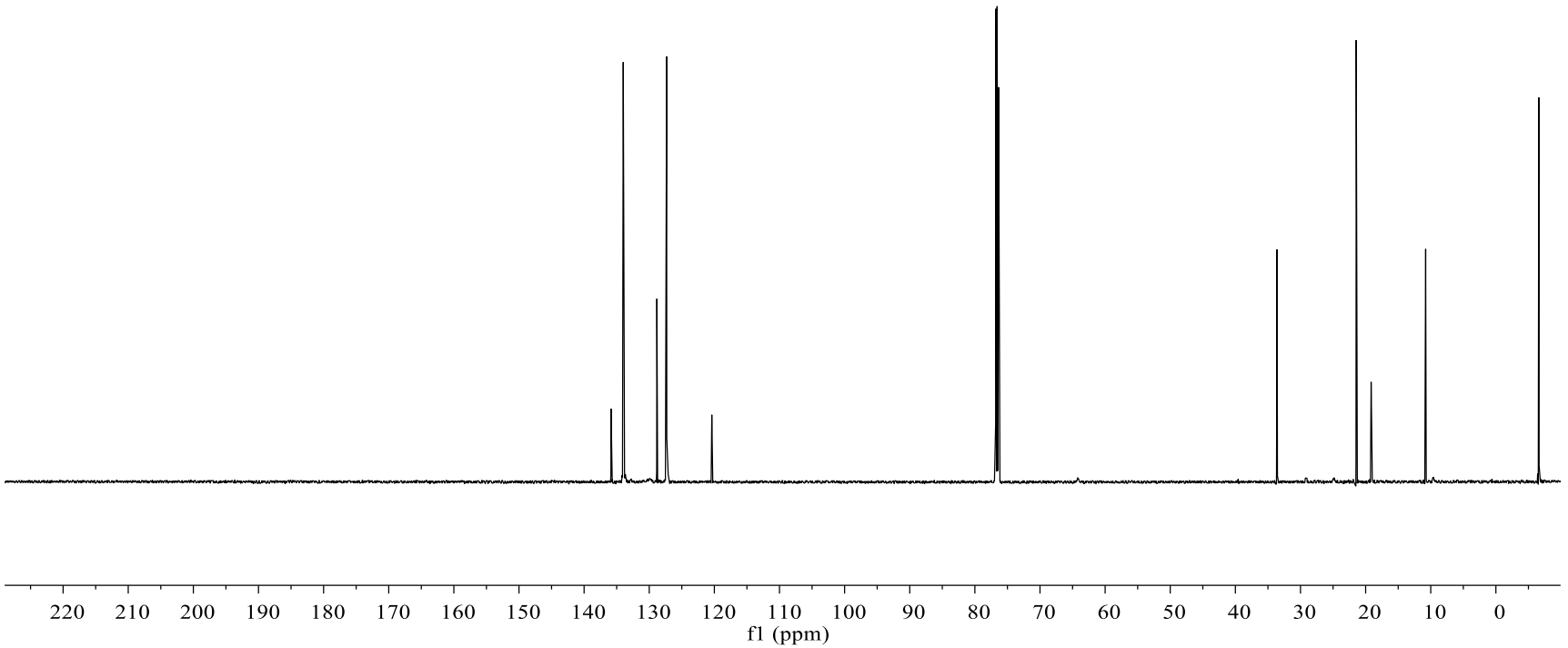

PhMe2Si
CN
Me
Me

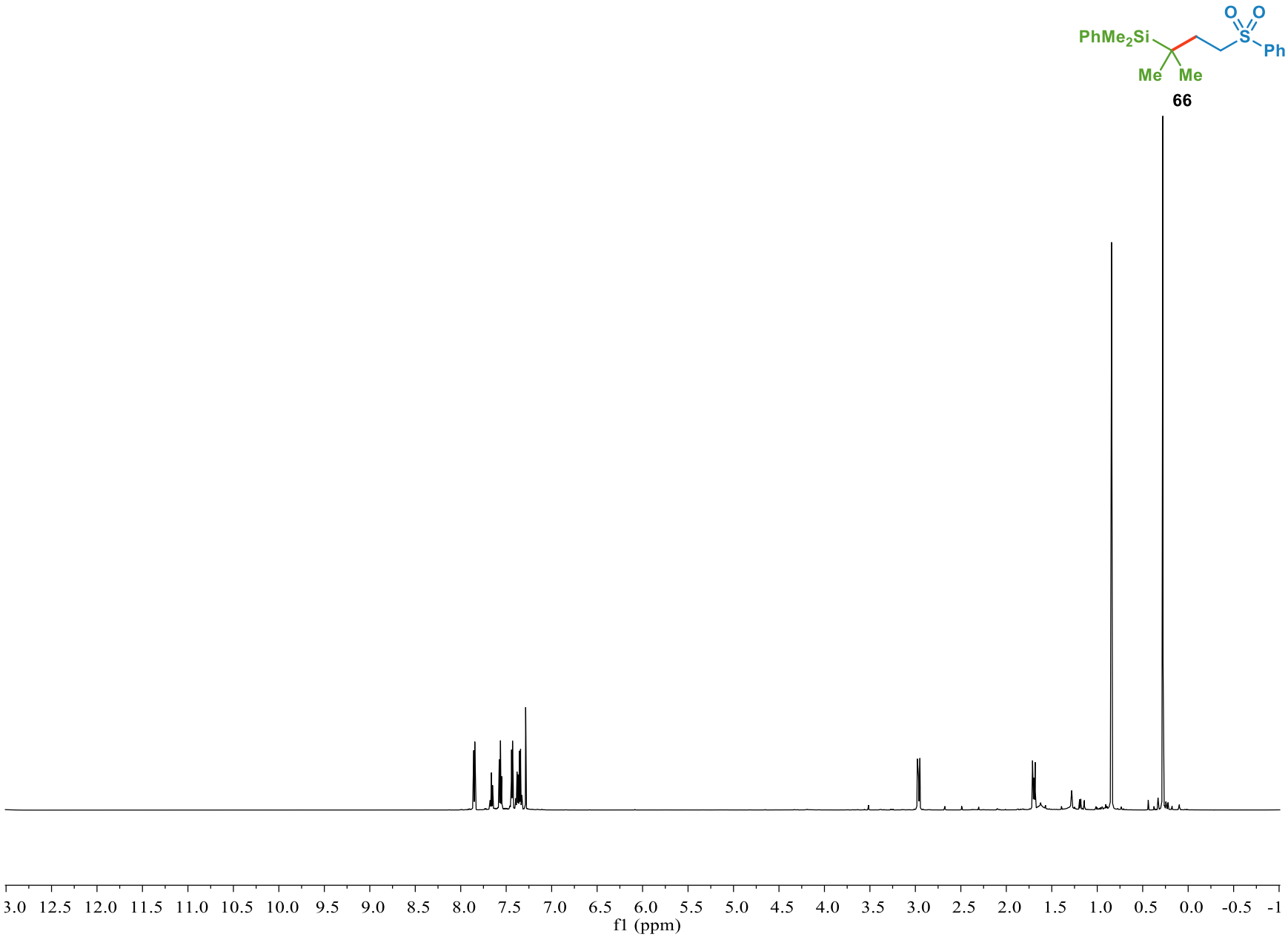
65

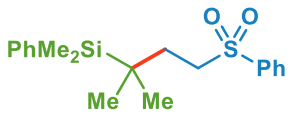

1.0
10.5
10.0
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
-0.5
-1
f1 (ppm)


PhMe2Si
CN
Me
Me

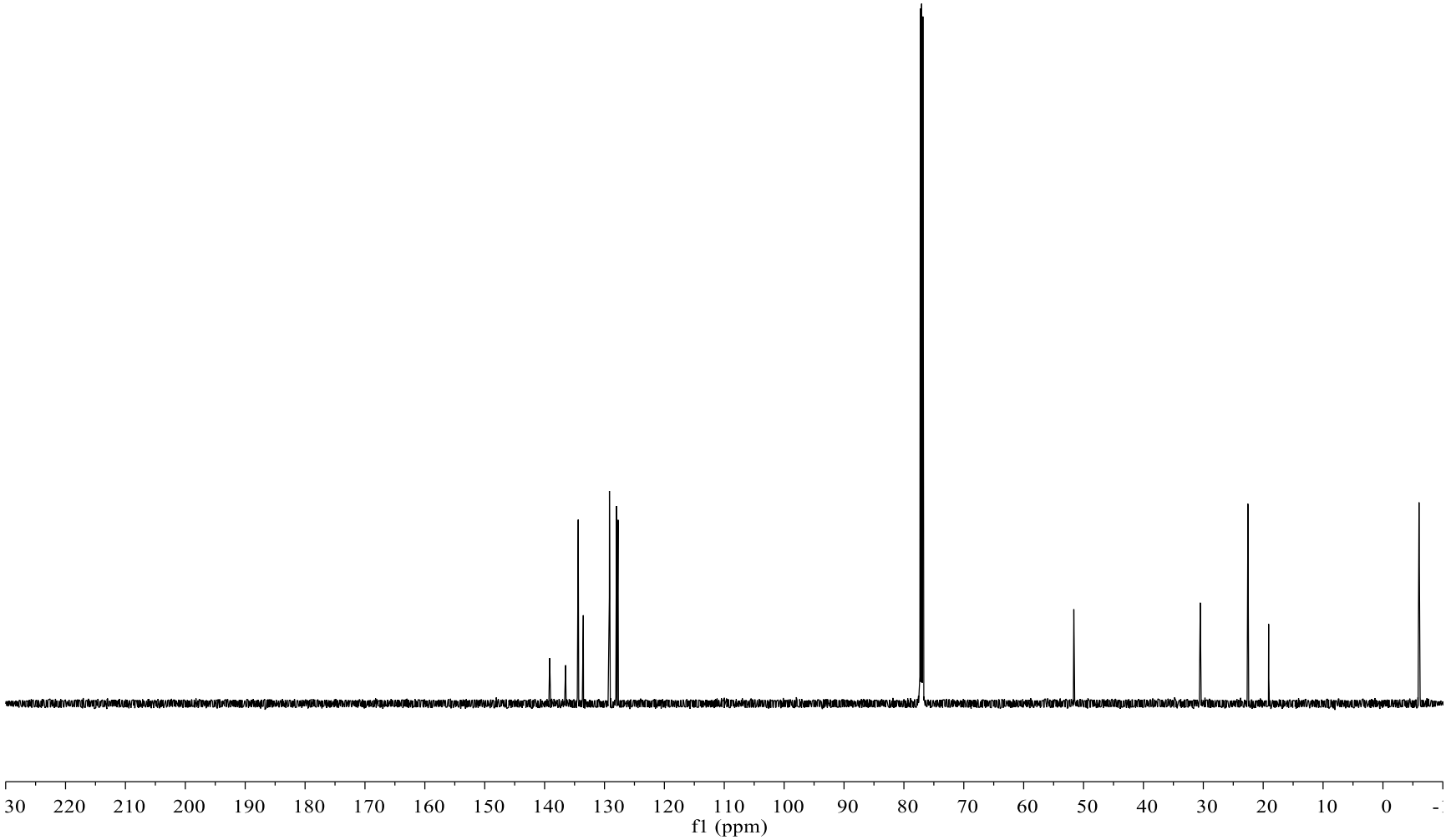
65


220
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)


PhMe2Si
Me
Me
O
O
S
Ph
66
3.0 12.5 12.0 11.5 11.0 10.5 10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0 -0.5 -1
f1 (ppm)

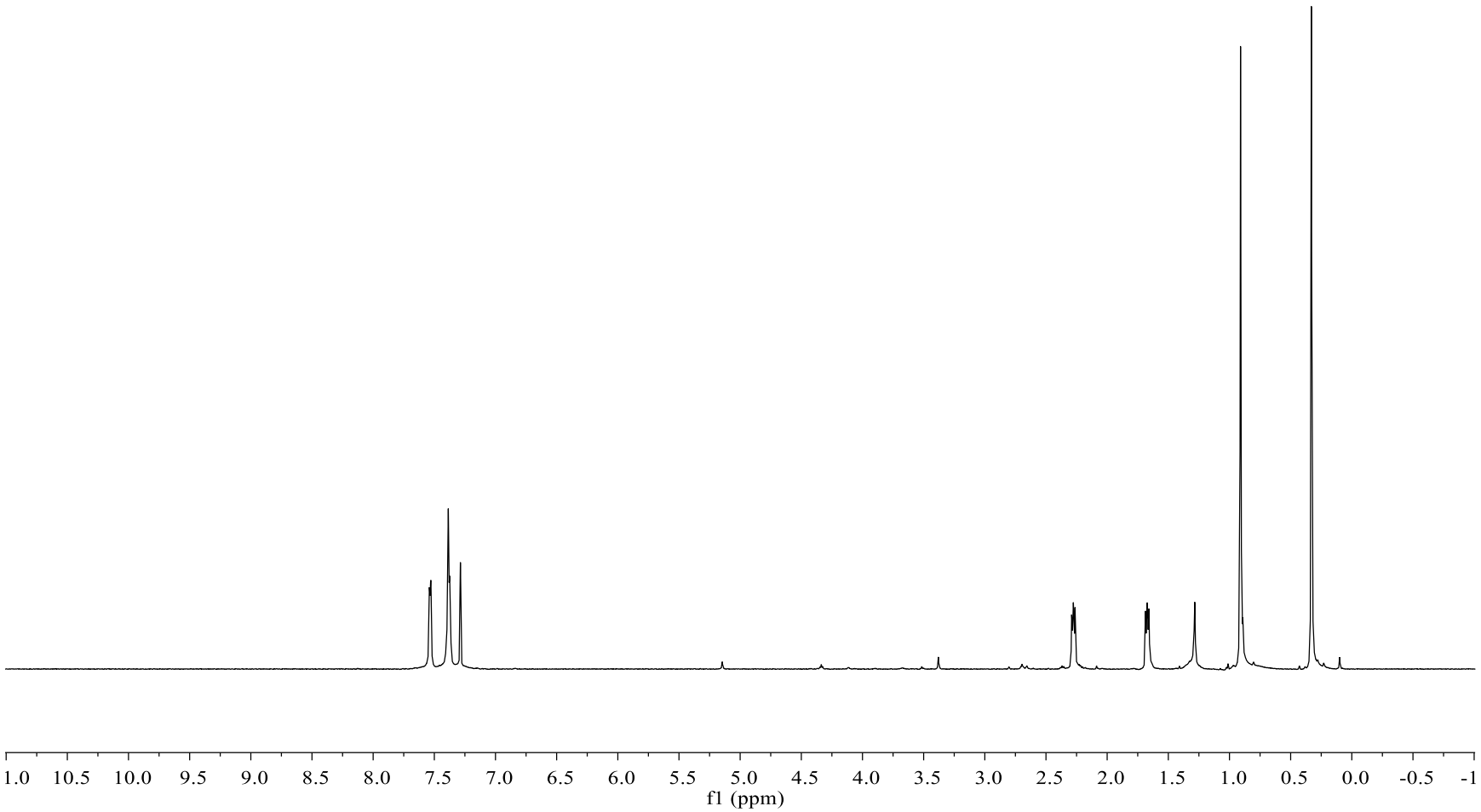

PhMe2Si
Me
Me
O
O
S
Ph

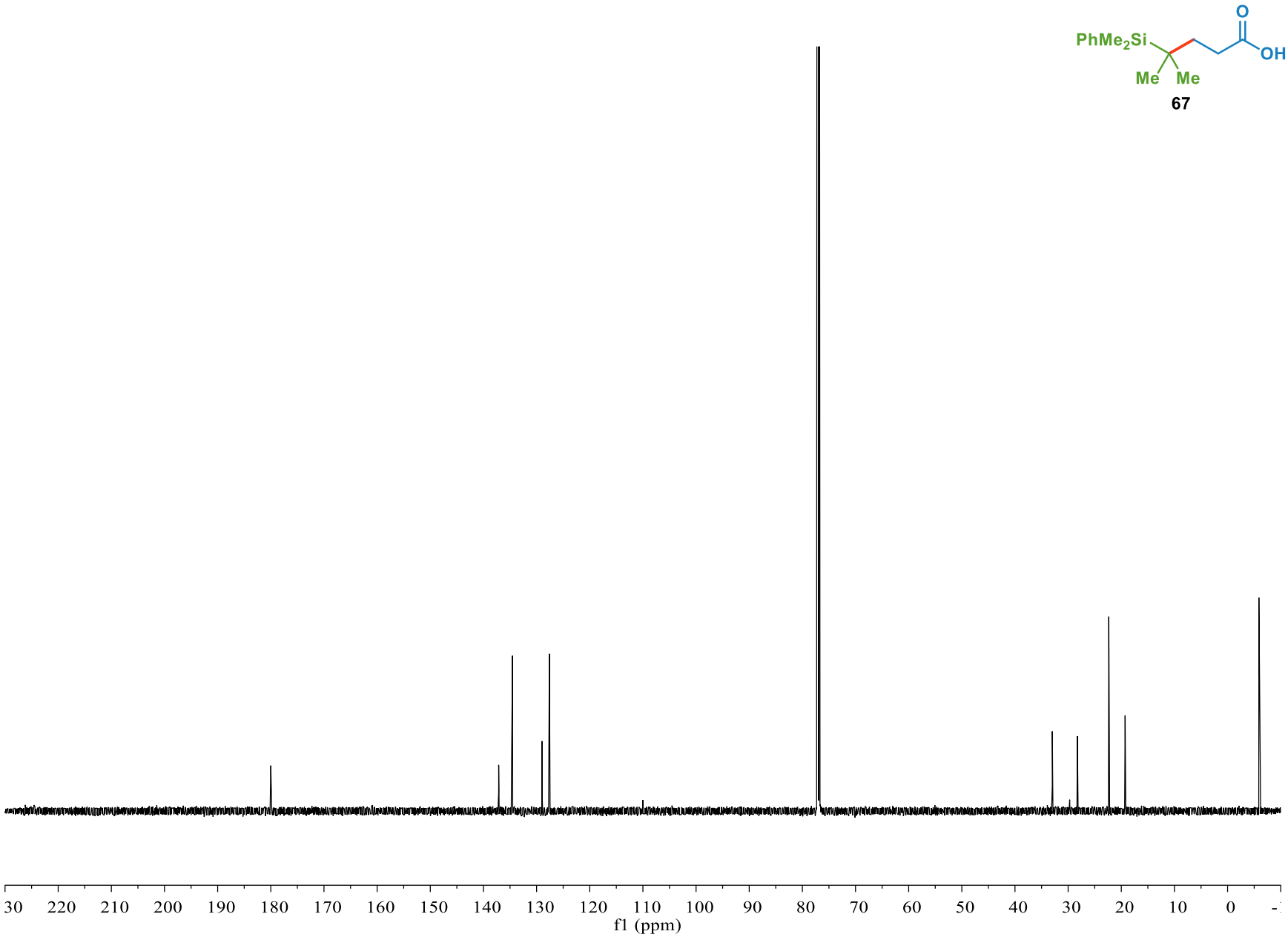
66

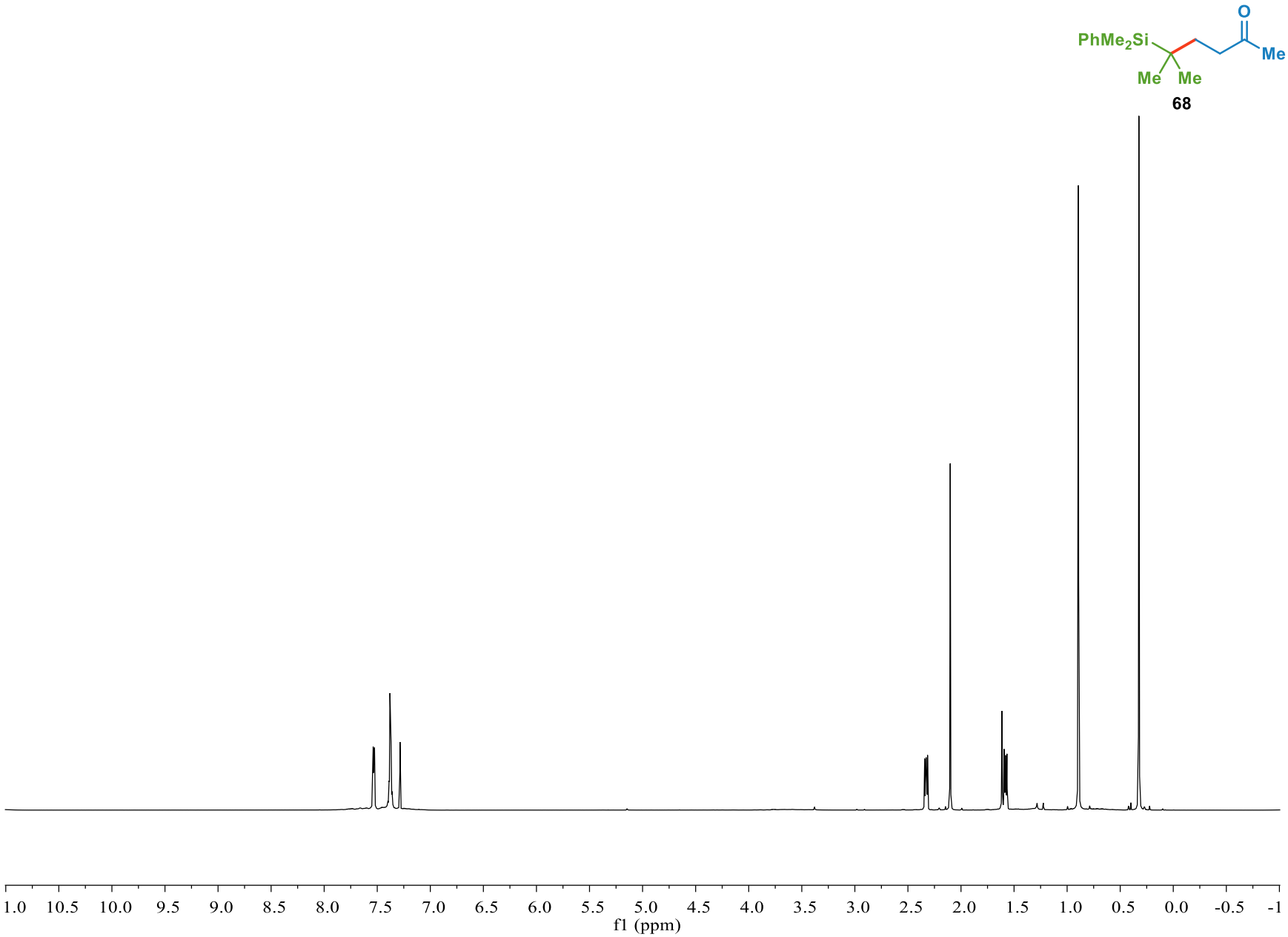

30
220
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)

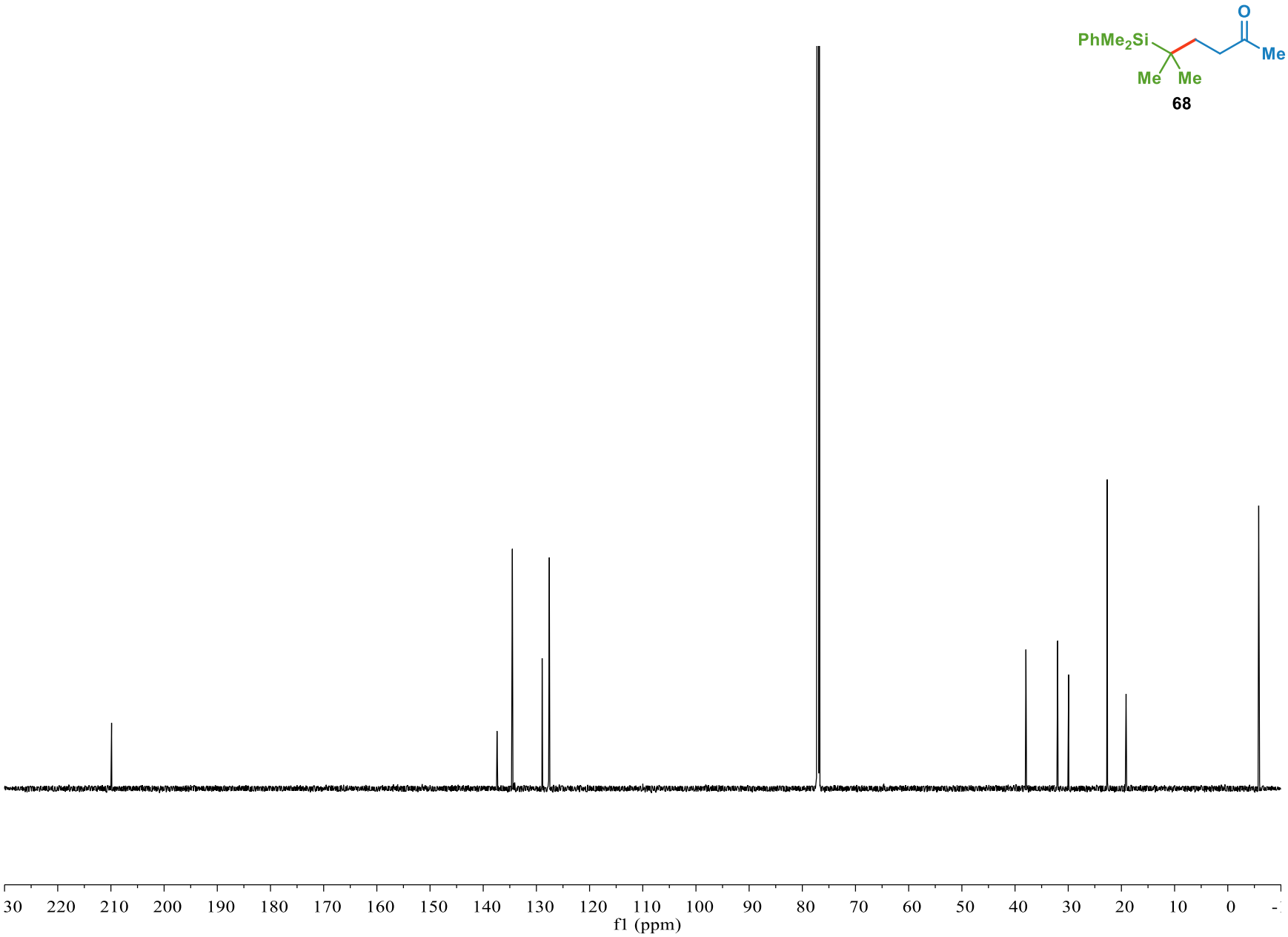

O
PhMe2Si
OH
Me
Me

67


1.0
10.5
10.0
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
-0.5
-1
f1 (ppm)

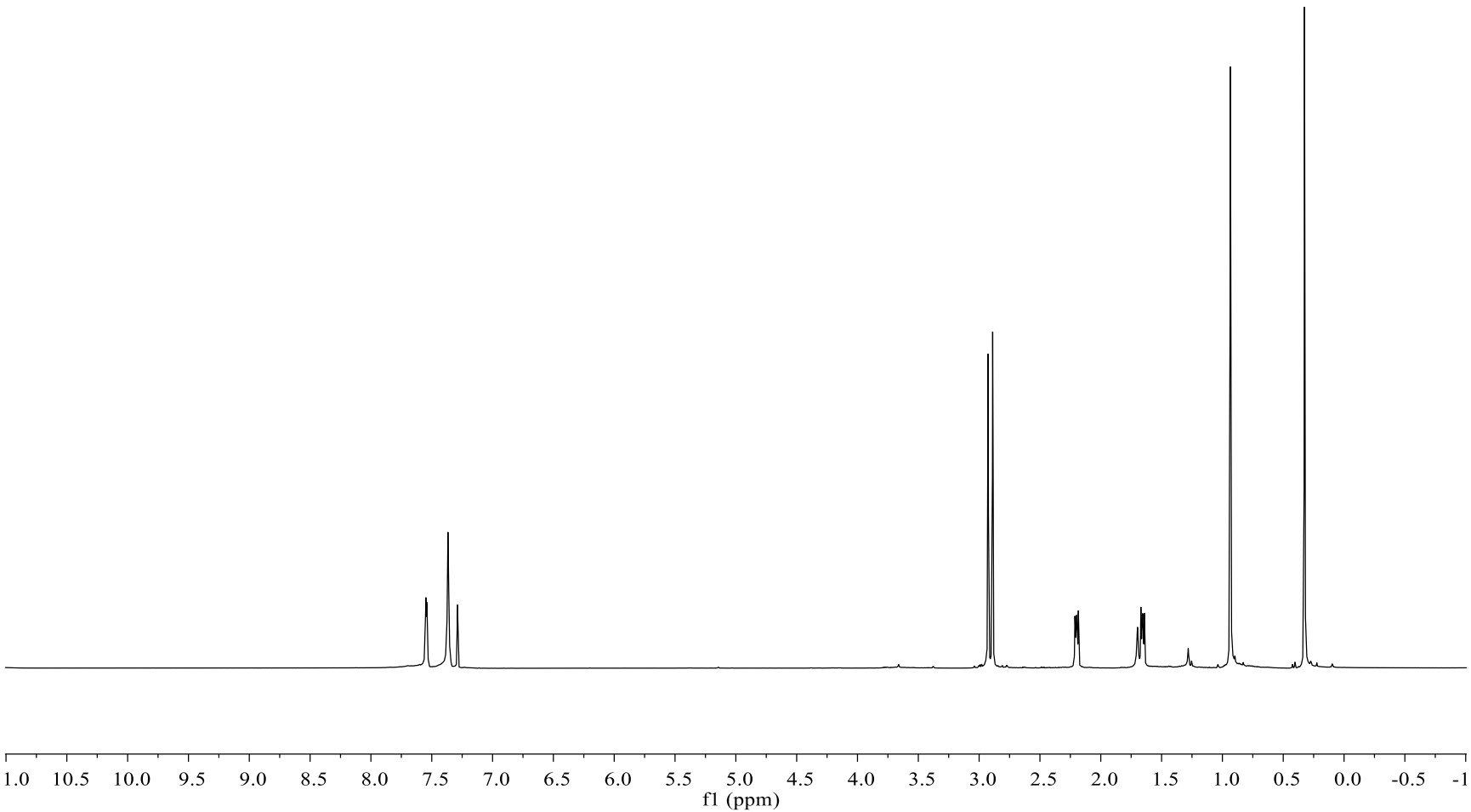

PhMe2Si
Me
Me
O
OH
67
30
220
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)


PhMe2Si
Me
Me
O
Me
68
1.0
10.5
10.0
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
-0.5
-1
f1 (ppm)


PhMe2Si
Me
Me
O
Me
68
30 220 210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
f1 (ppm)

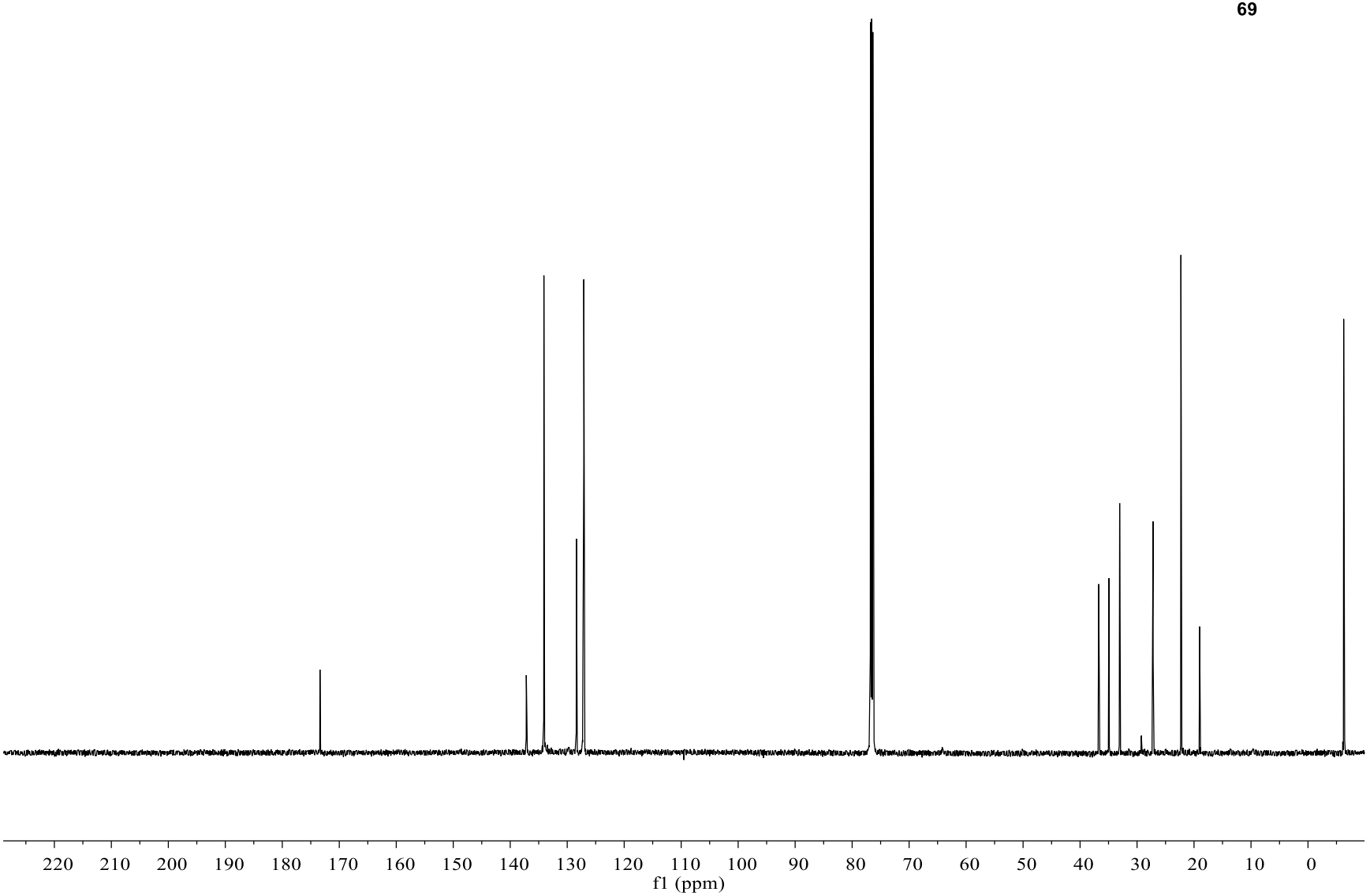

O
PhMe2Si
NMe2
Me
Me

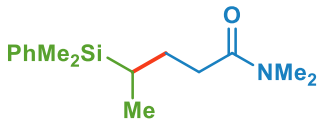
69


1.0
10.5
10.0
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
-0.5
-1
f1 (ppm)

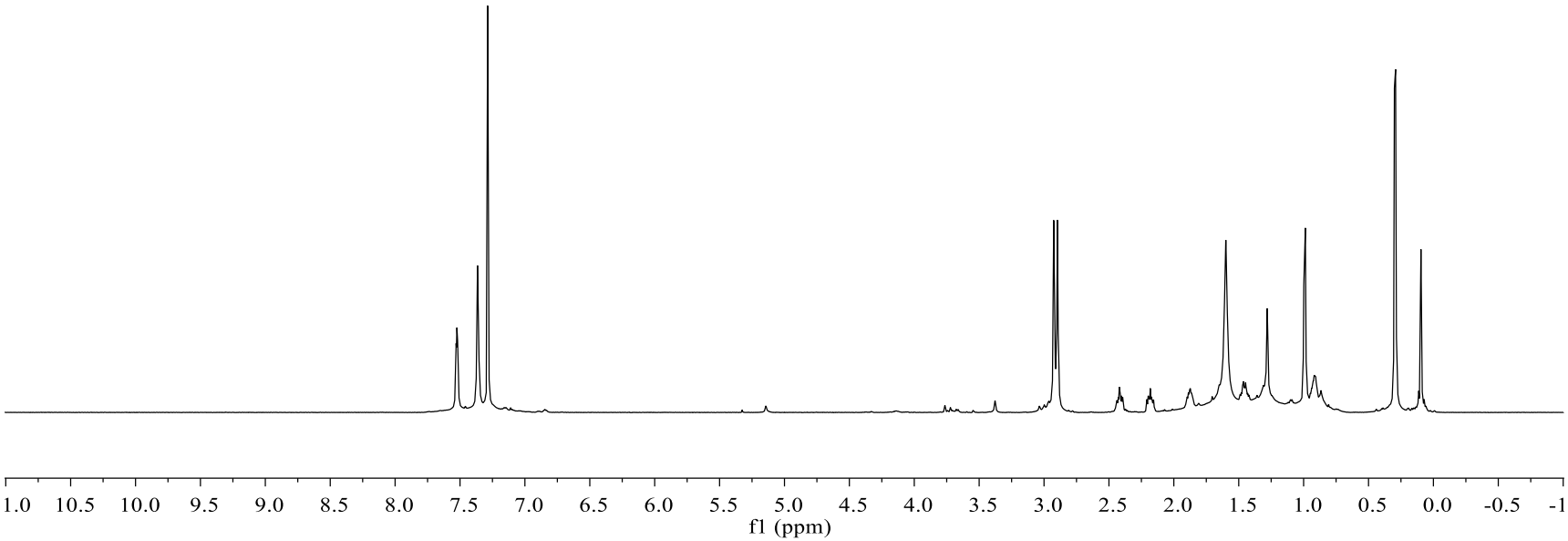

O
PhMe2Si
NMe2
Me
Me

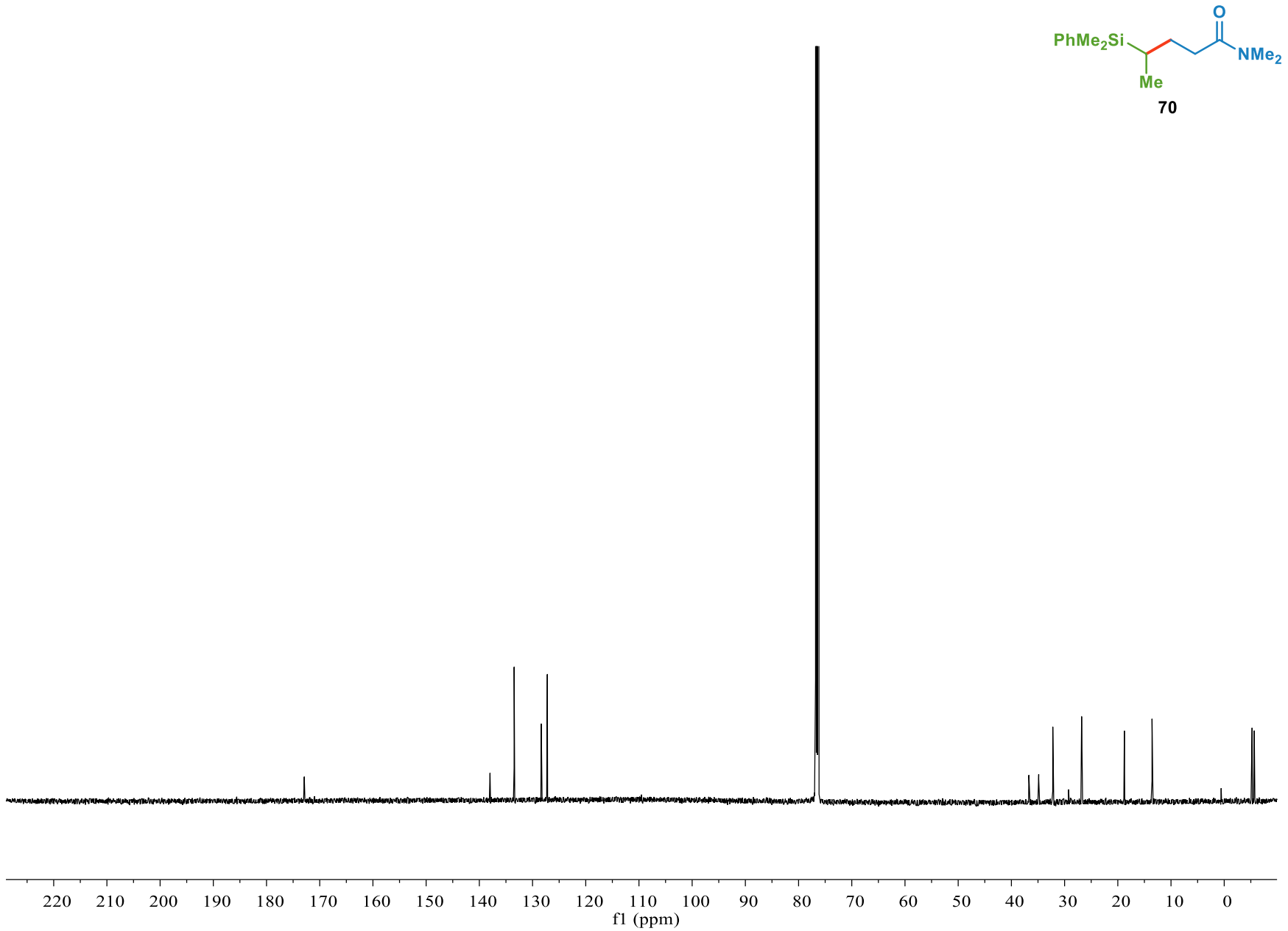
69

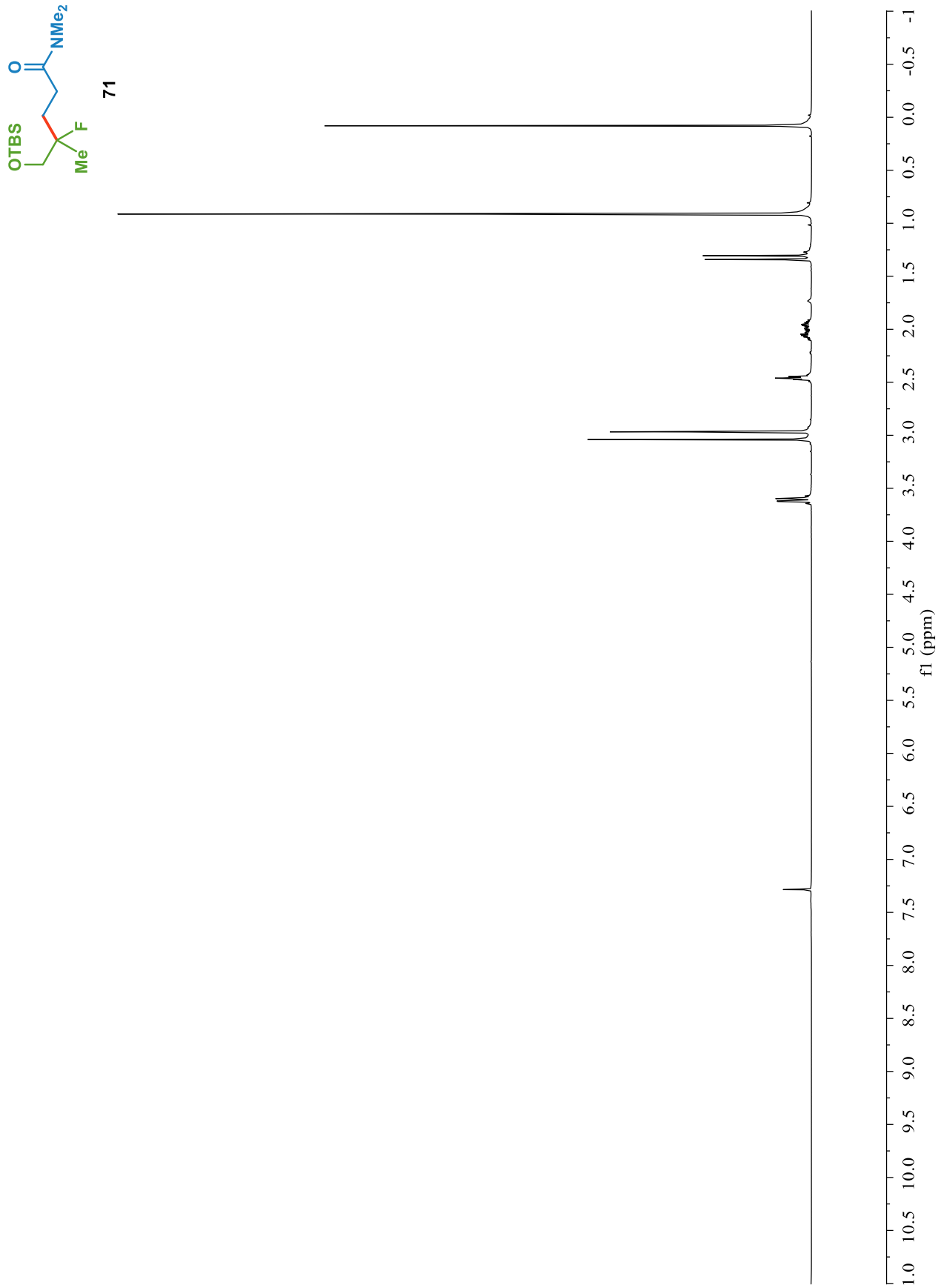

220
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)

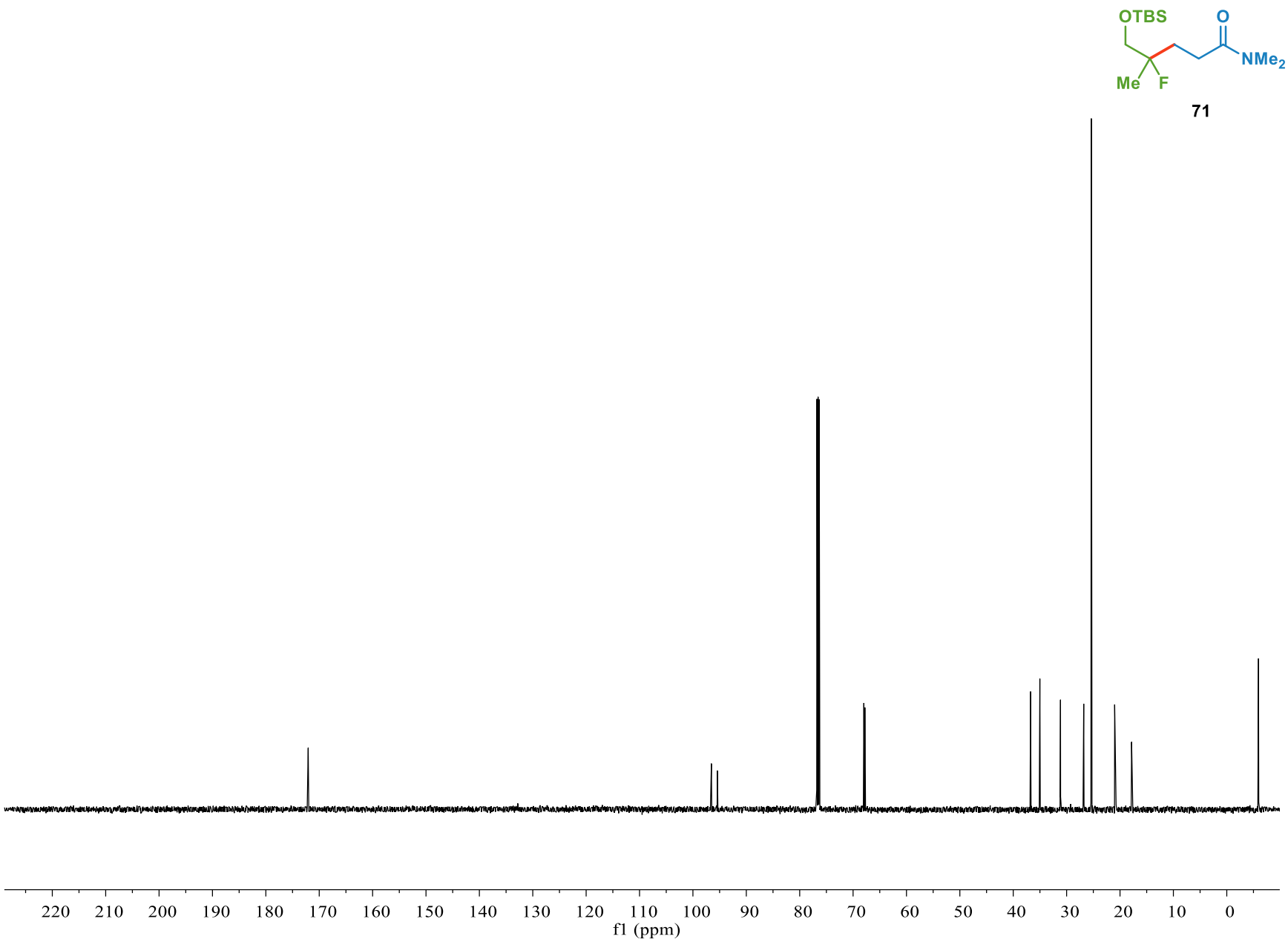

O
PhMe2Si
NMe2
Me

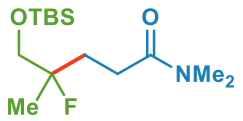
70


1.0 10.5 10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0 -0.5 -1
f1 (ppm)

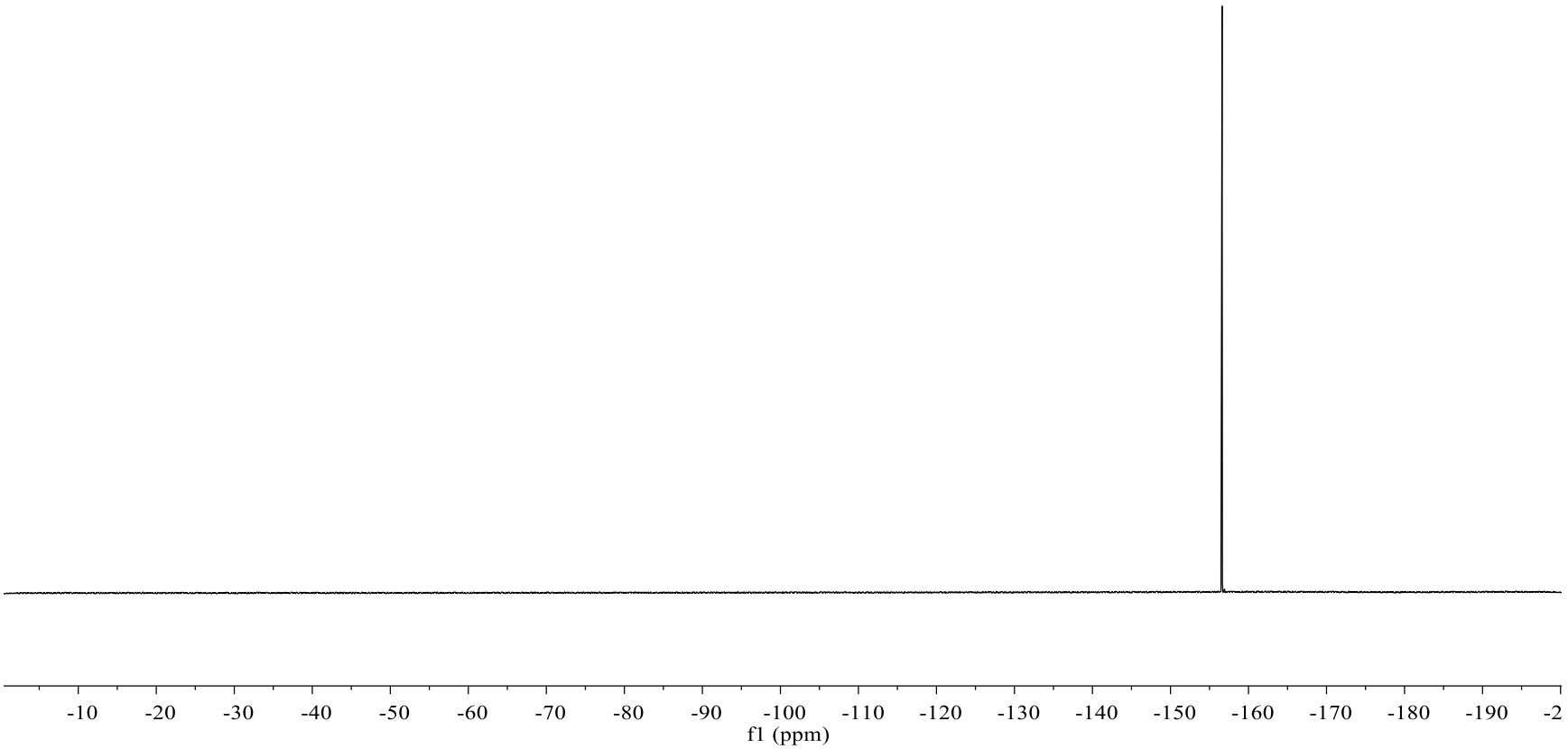

PhMe2Si
Me
O
NMe2
70
220 210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
f1 (ppm)

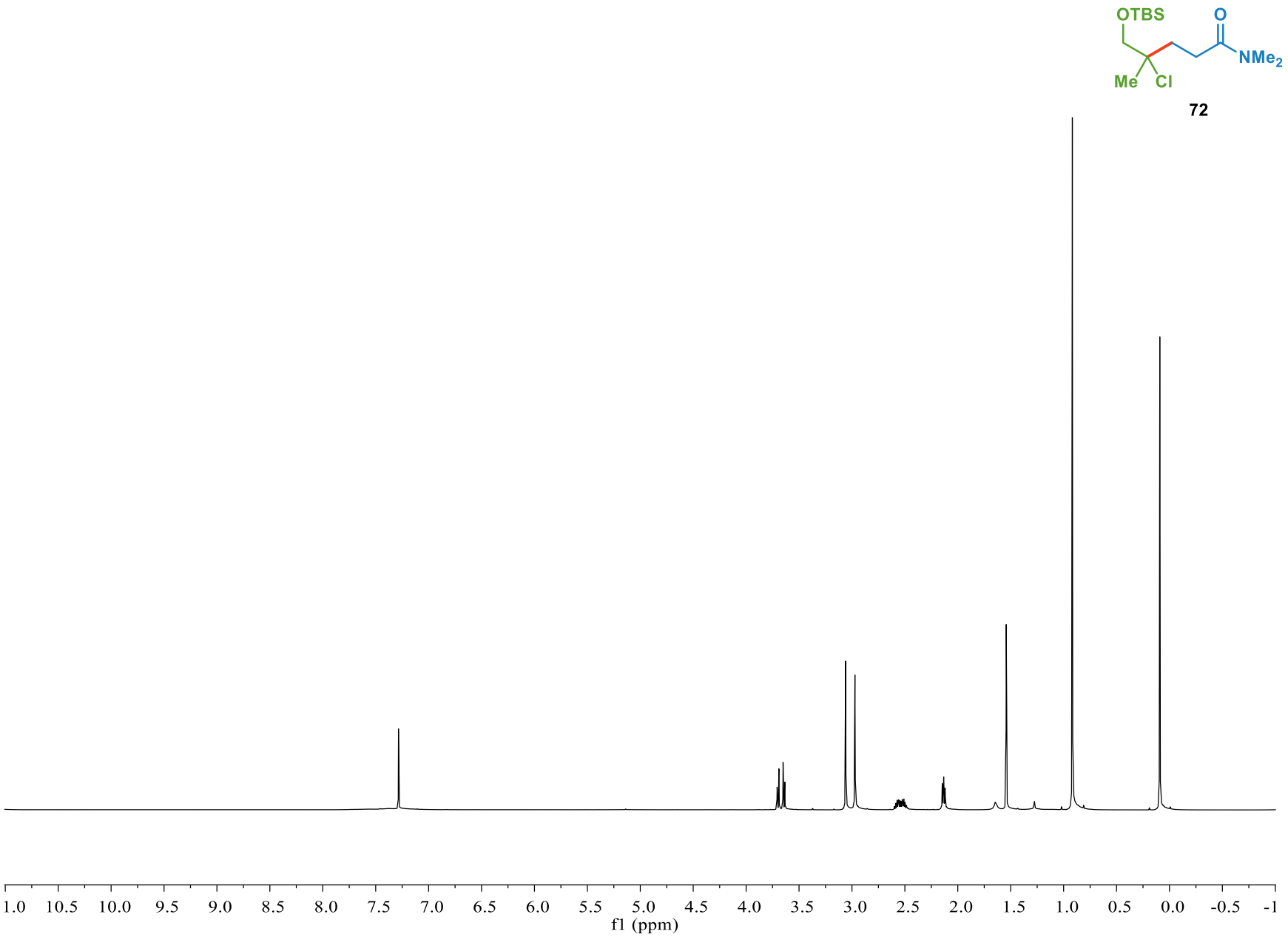

OTBS
O
NMe2
Me
F
71
f1 (ppm)

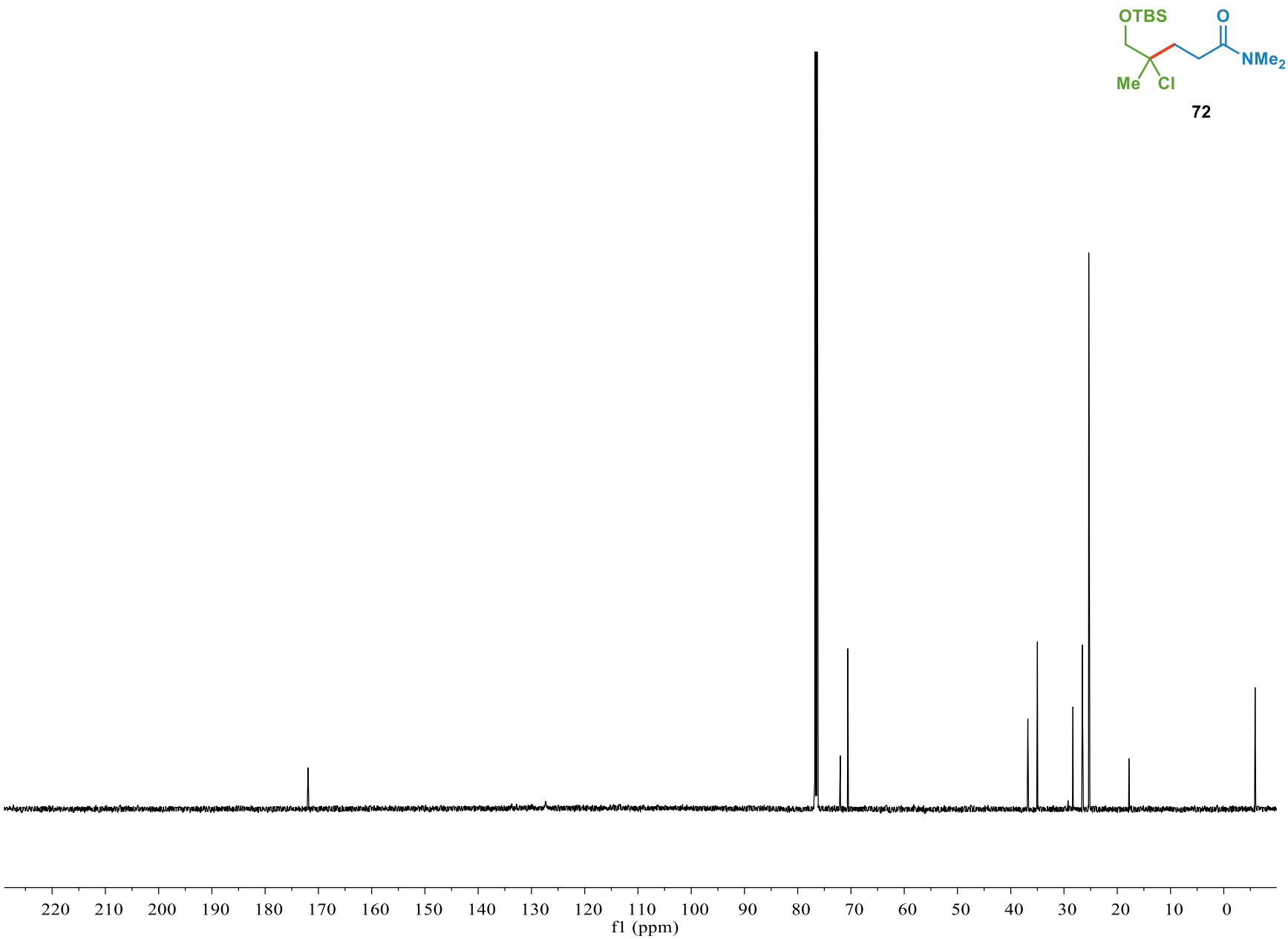

OTBS
O
NMe2
Me
F
71
220
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)

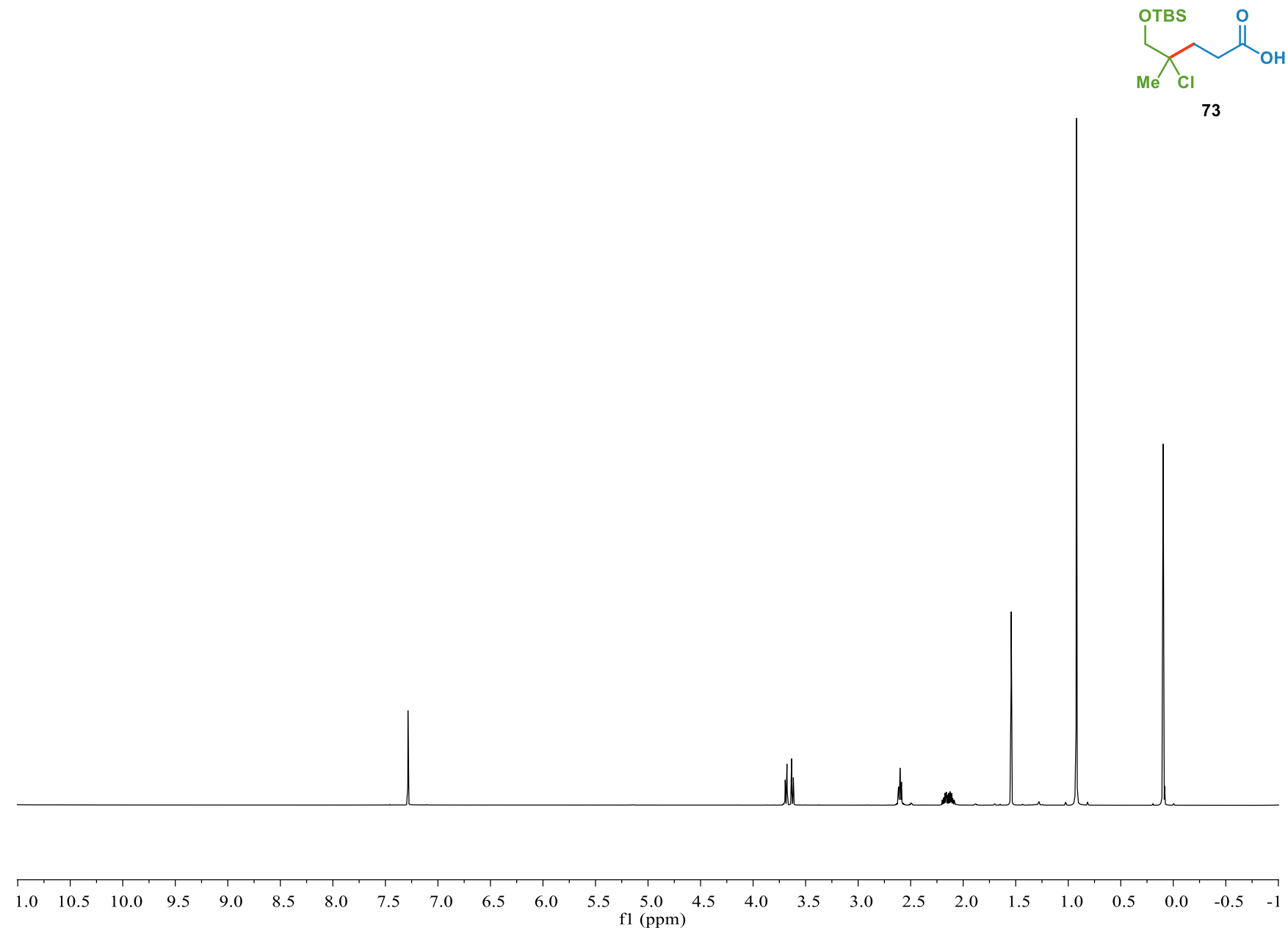

OTBS
O
NMe2
Me
F

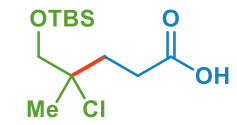
71


-10
-20
-30
-40
-50
-60
-70
-80
-90
-100
-110
-120
-130
-140
-150
-160
-170
-180
-190
-2
f1 (ppm)

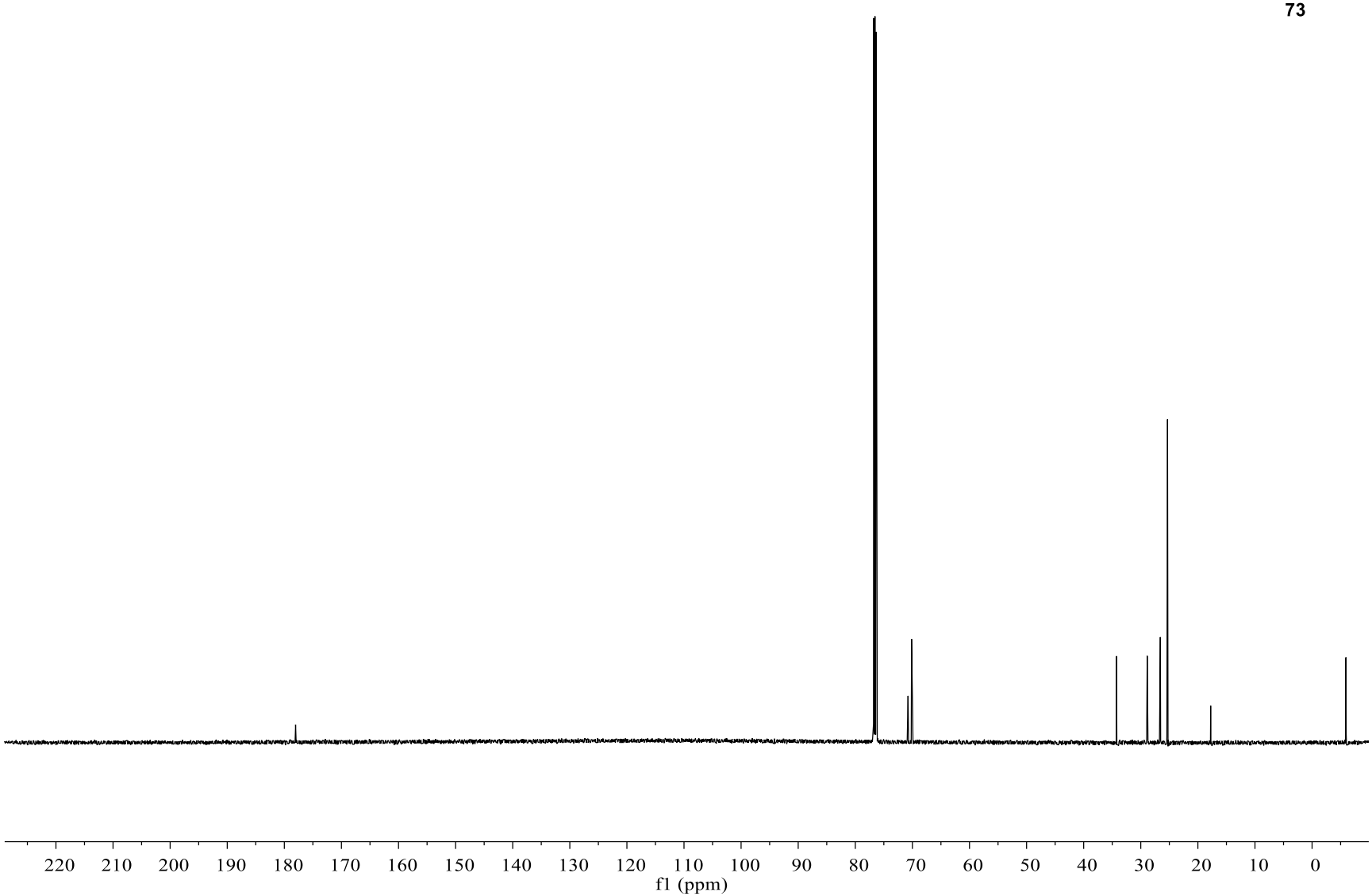

OTBS
O
NMe2
Me
Cl
72
1.0
10.5
10.0
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
-0.5
-1
f1 (ppm)

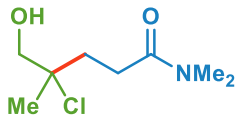

OTBS
O
NMe2
Me
Cl
72
220
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)


OTBS
O
OH
Me
Cl
73
1.0
10.5
10.0
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
-0.5
-1
f1 (ppm)

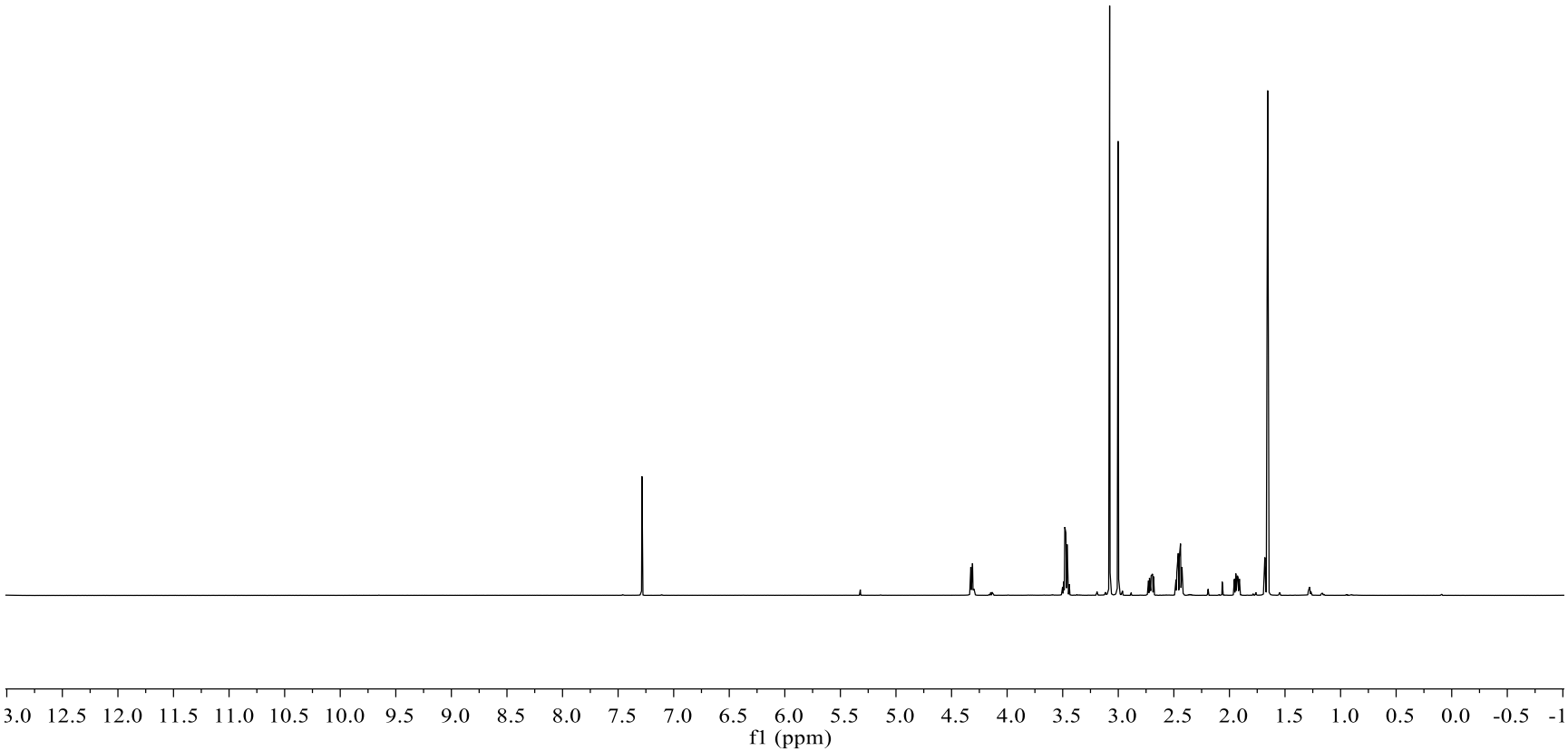

OTBS
O
OH
Me
Cl

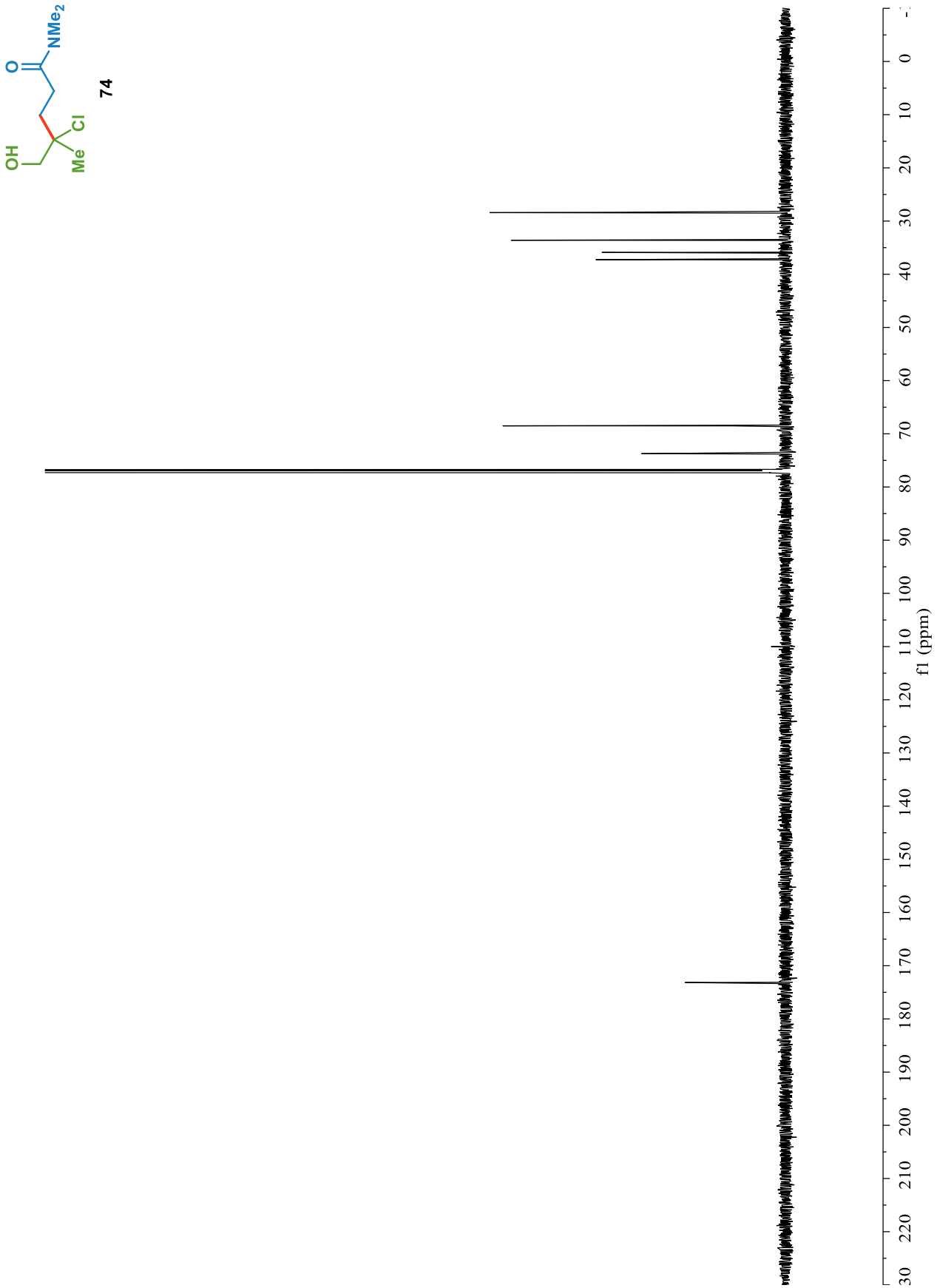
73

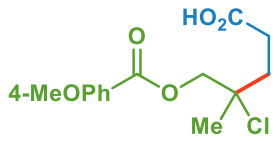

220
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)


OH
O
NMe2
Me
Cl

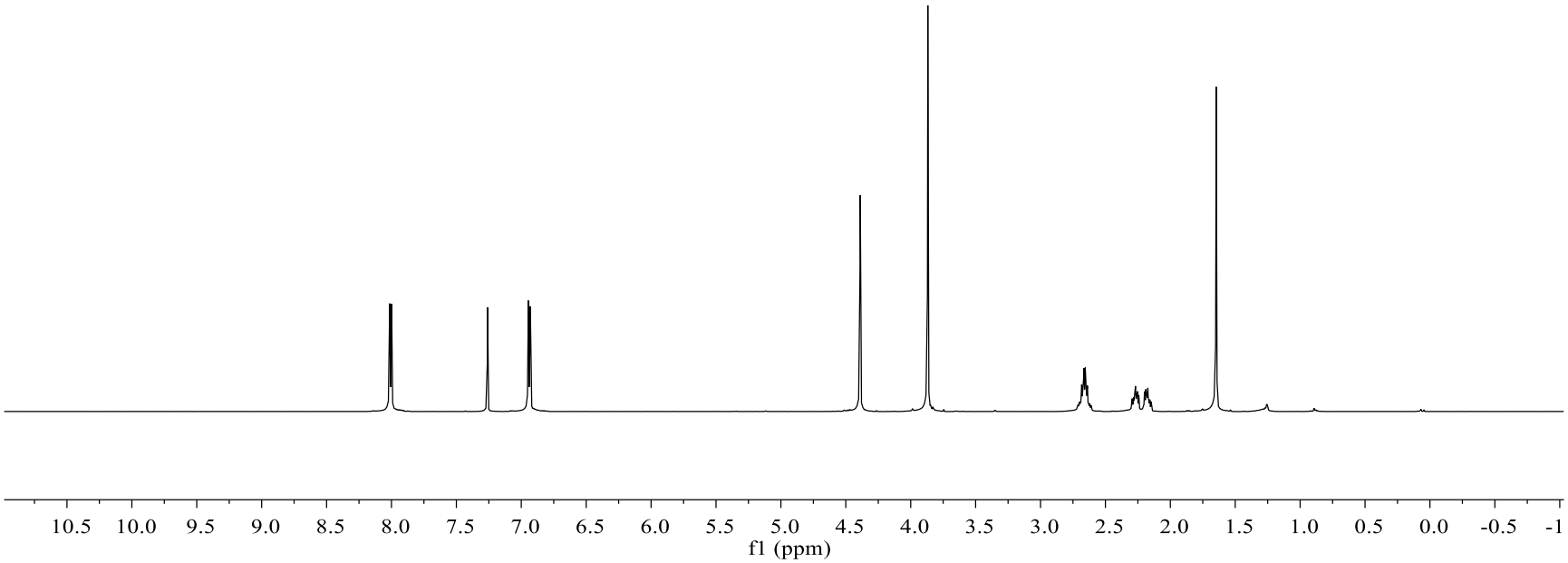
74

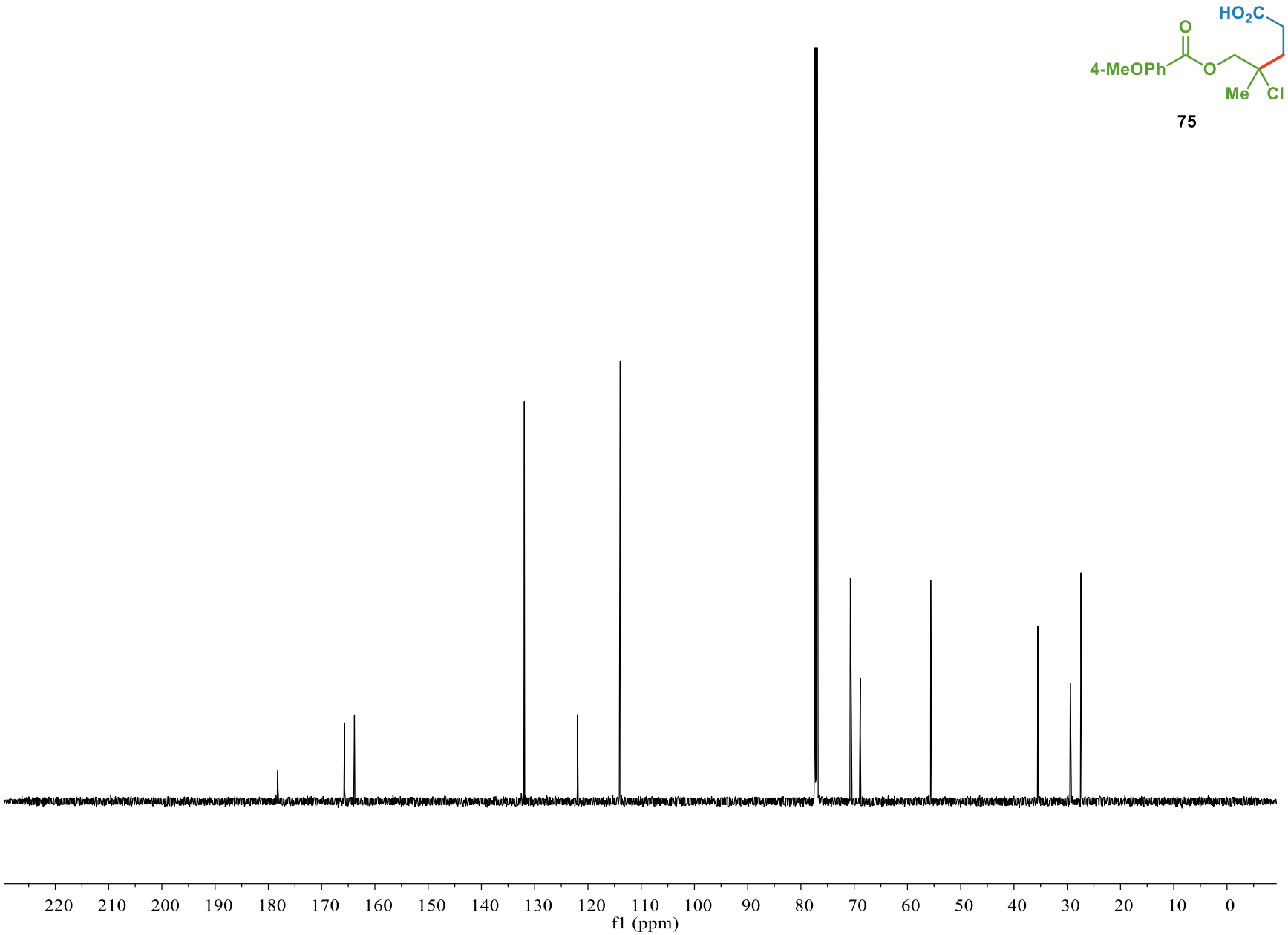

3.0 12.5 12.0 11.5 11.0 10.5 10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0 -0.5 -1
f1 (ppm)

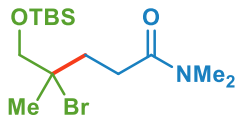

O
NMe2
OH
Cl
Me
74
f1 (ppm)


HO2C
O
4-MeOPh
O
Me
Cl

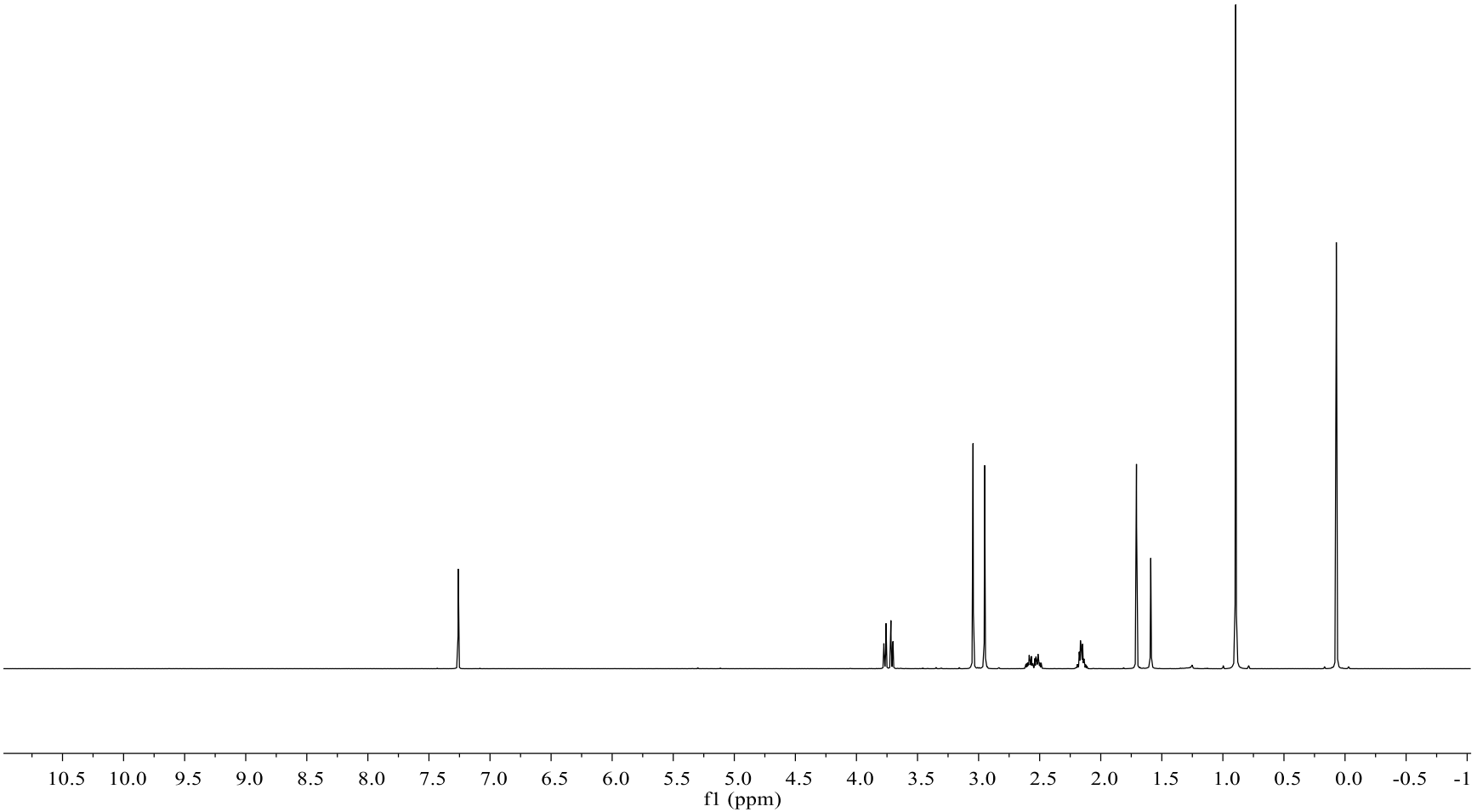
75

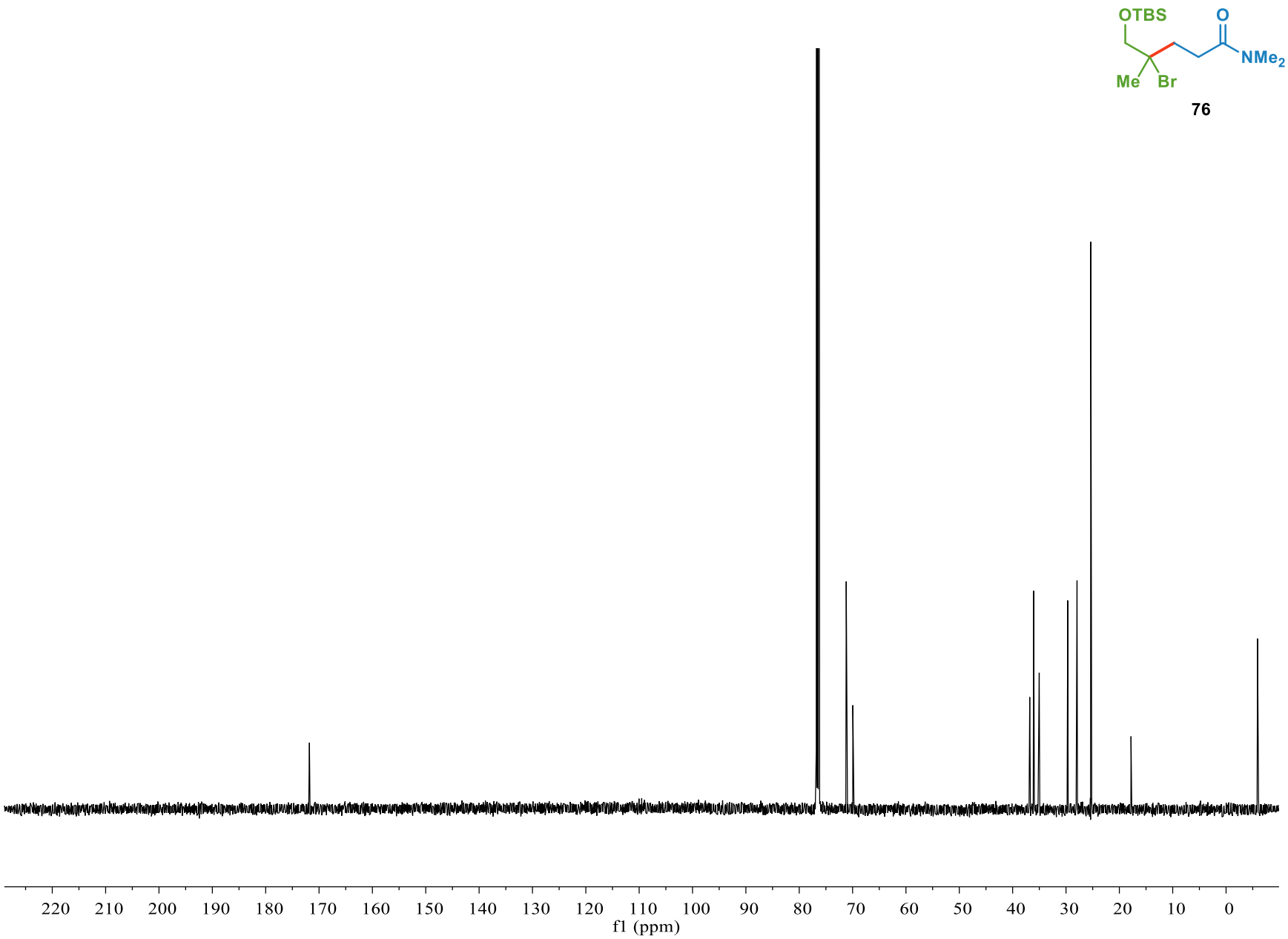

10.5 10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0 -0.5 -1
f1 (ppm)

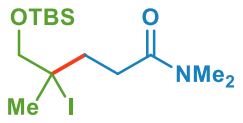

HO2C
O
4-MeOPh
O
Me
Cl
75
220 210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
f1 (ppm)


OTBS
O
NMe2
Me
Br

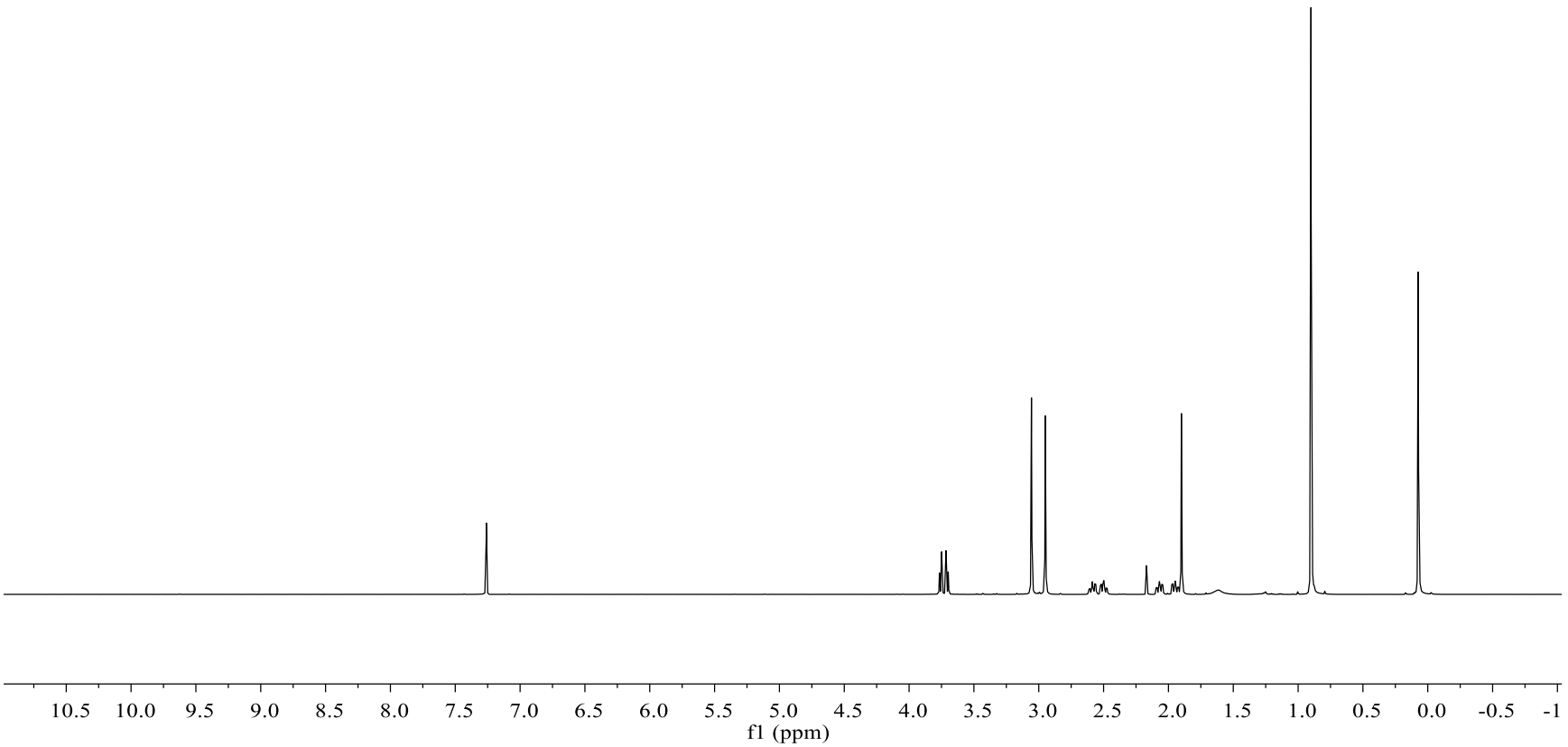
76

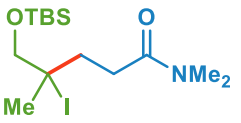

10.5
10.0
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
-0.5
-1
f1 (ppm)


OTBS
O
NMe2
Me
Br
76
220
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)

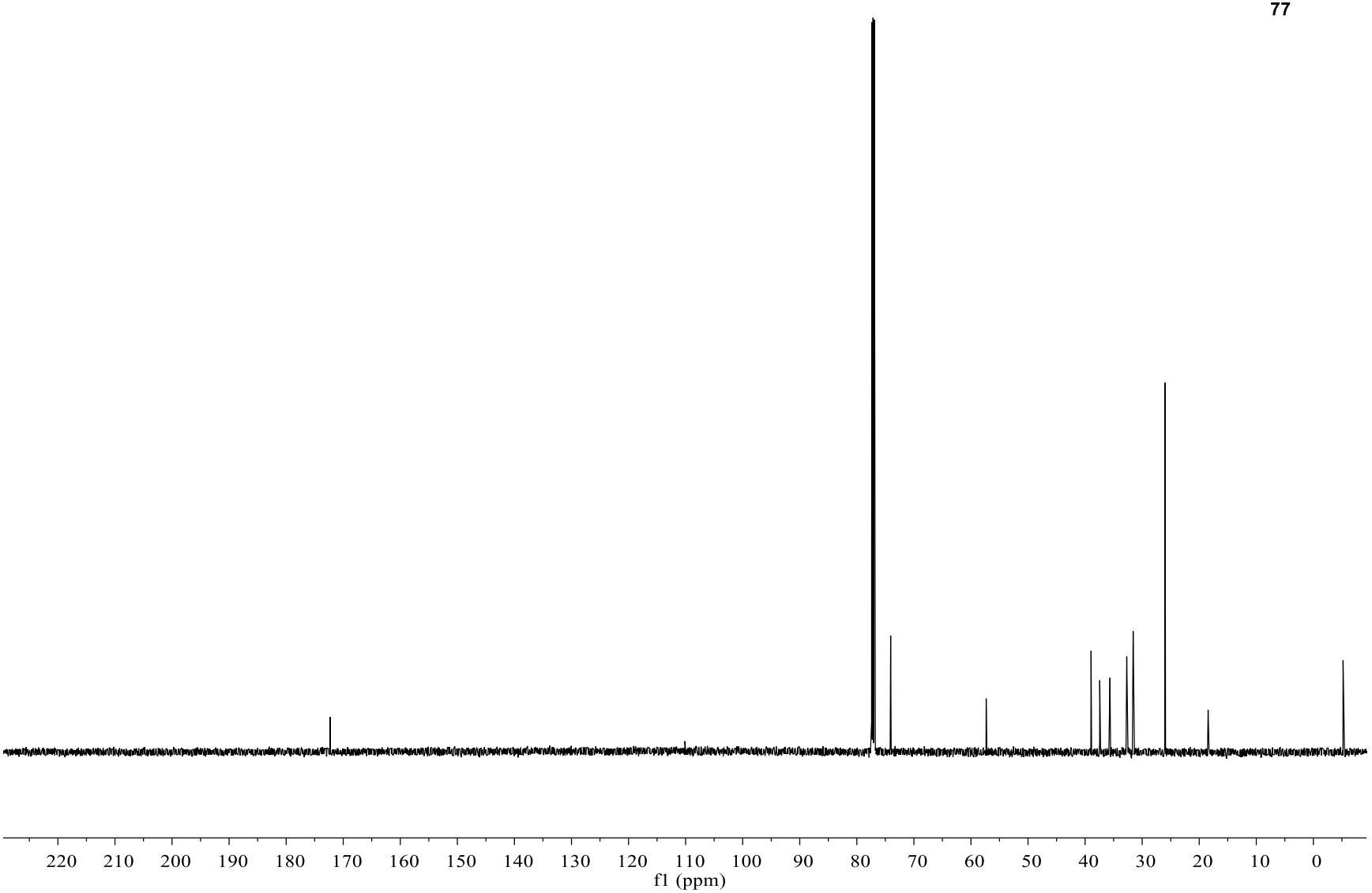

OTBS
O
NMe2
Me
I

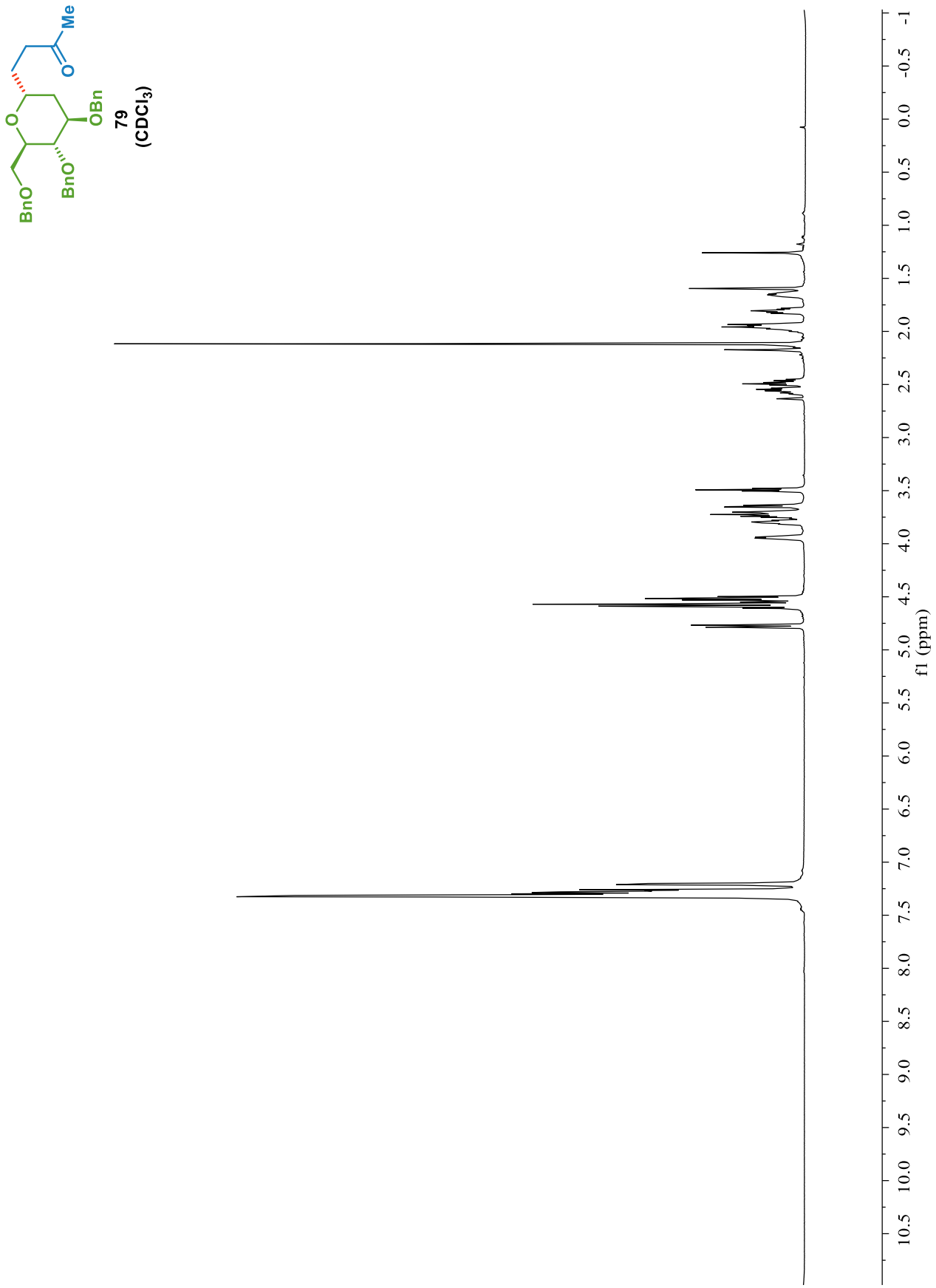
77

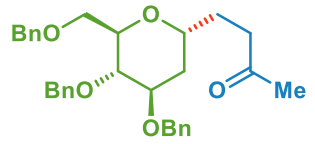

10.5 10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0 -0.5 -1
f1 (ppm)


OTBS
O
NMe2
Me
I

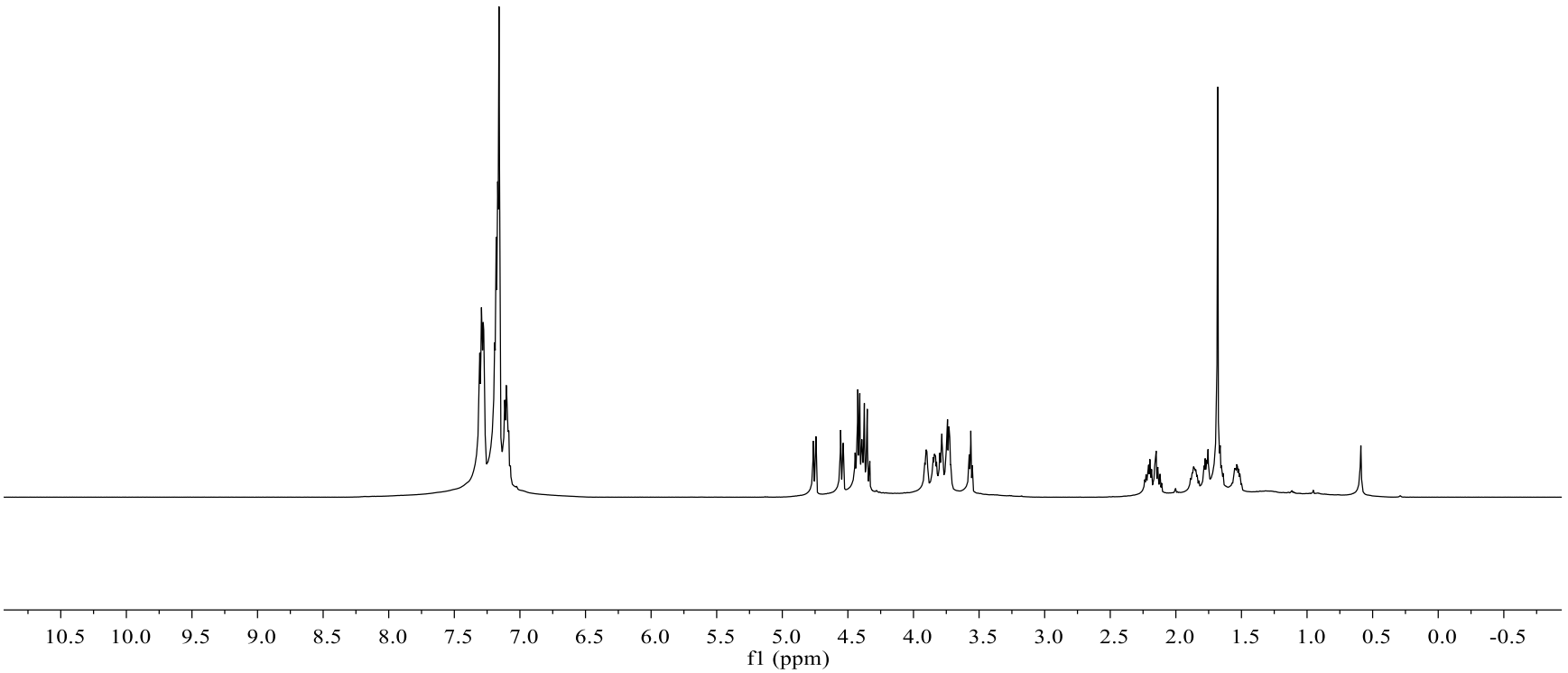
77

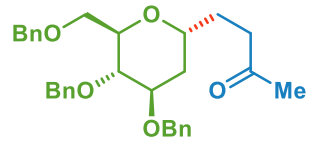

220
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)


79
(CDCl3)
BnO
BnO
OBn
O
O
Me
10.5
10.0
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
-0.5
-1
f1 (ppm)

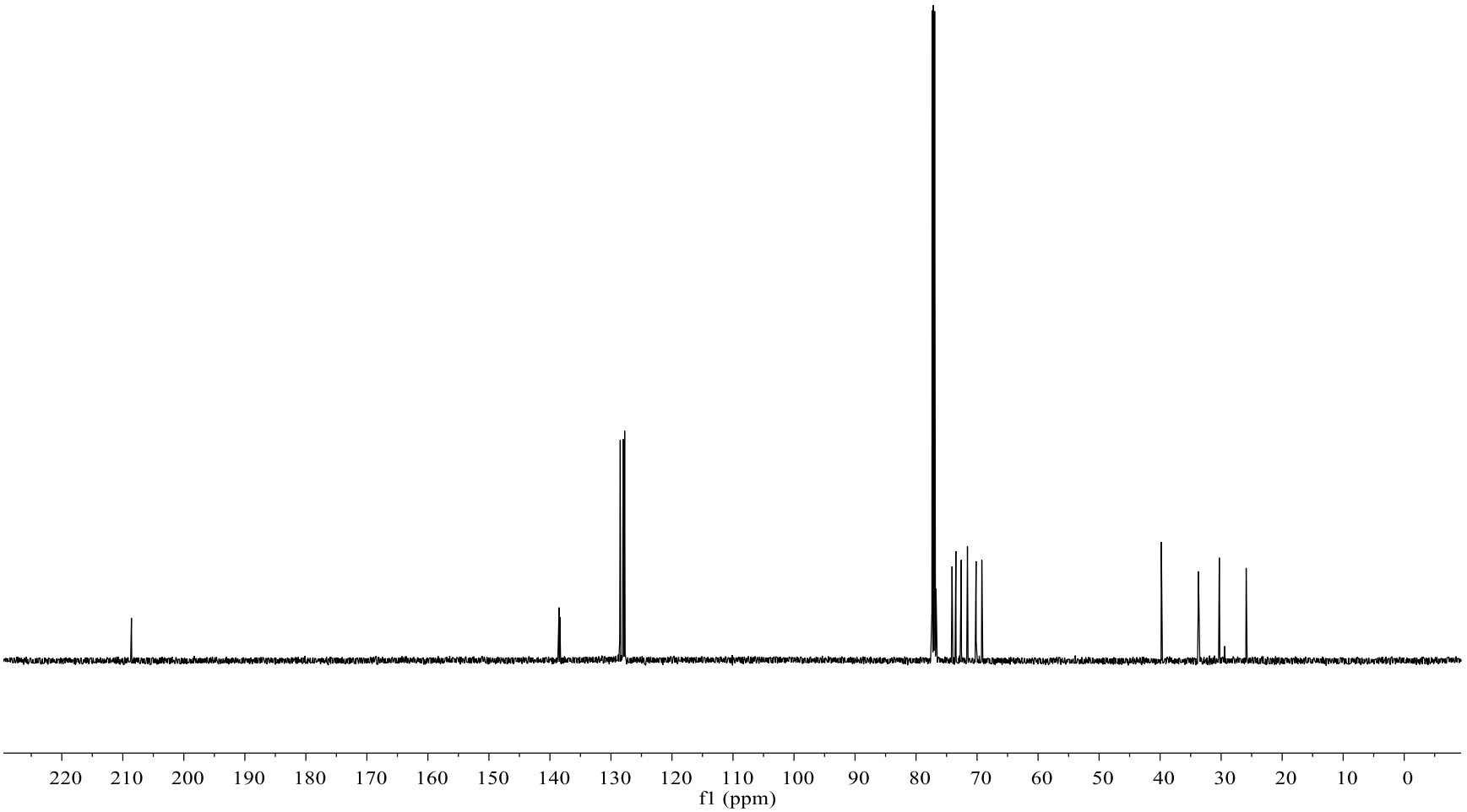

BnO
O
BnO
OBn
O
Me

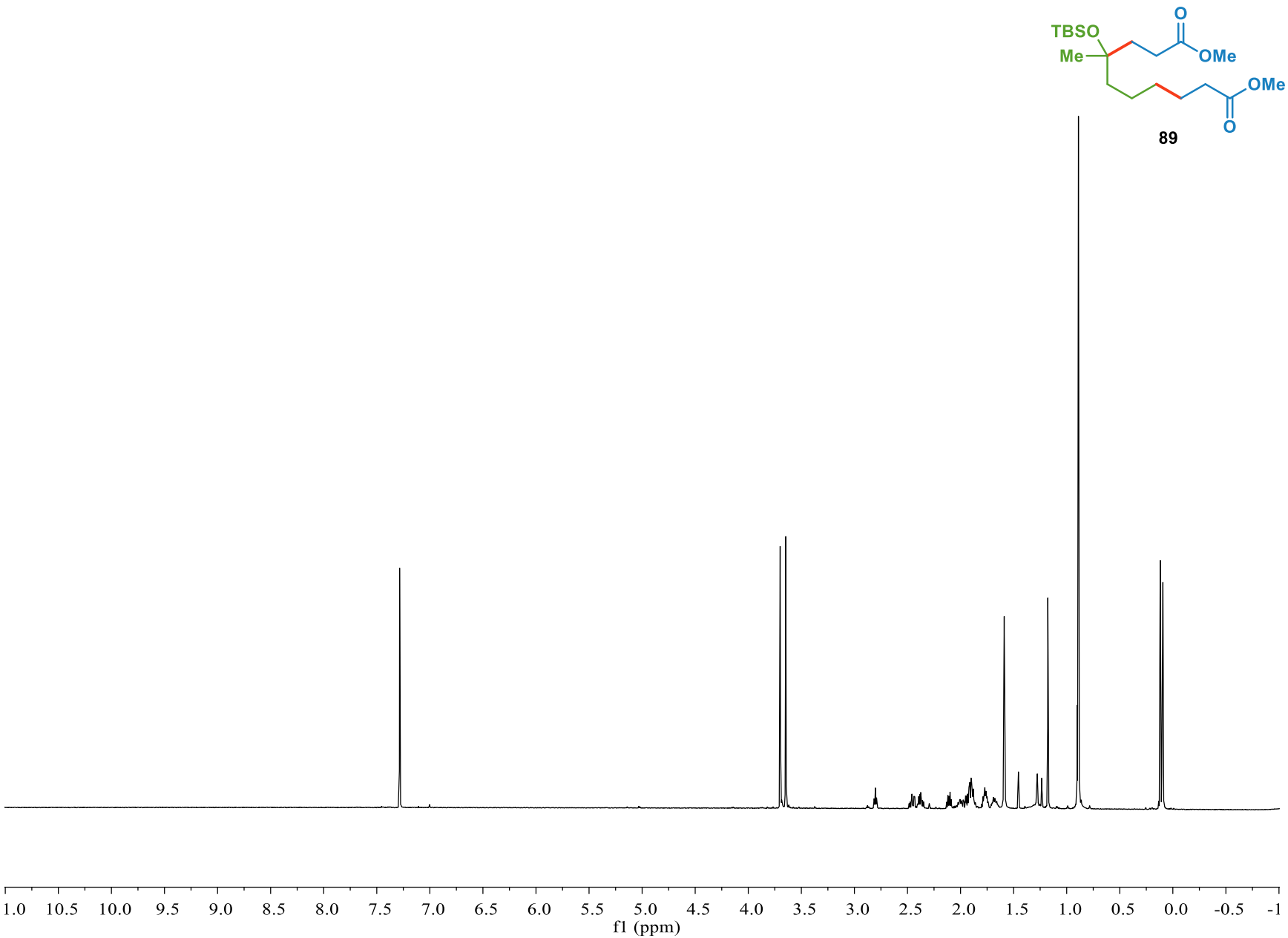
79
(C_6D_6)

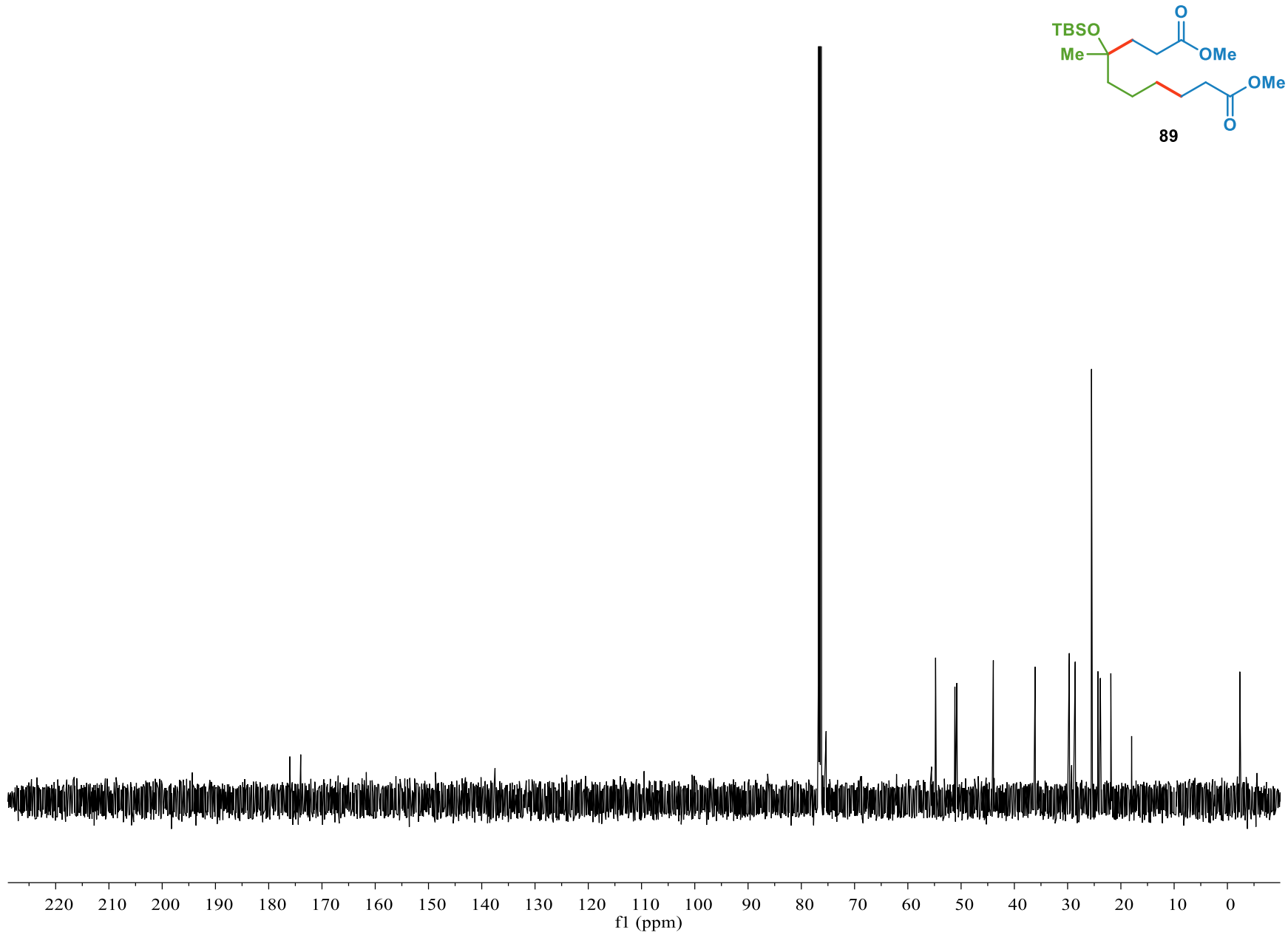

10.5
10.0
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
-0.5
f1 (ppm)

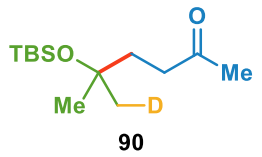

BnO
O
BnO
OBn
O
Me

79

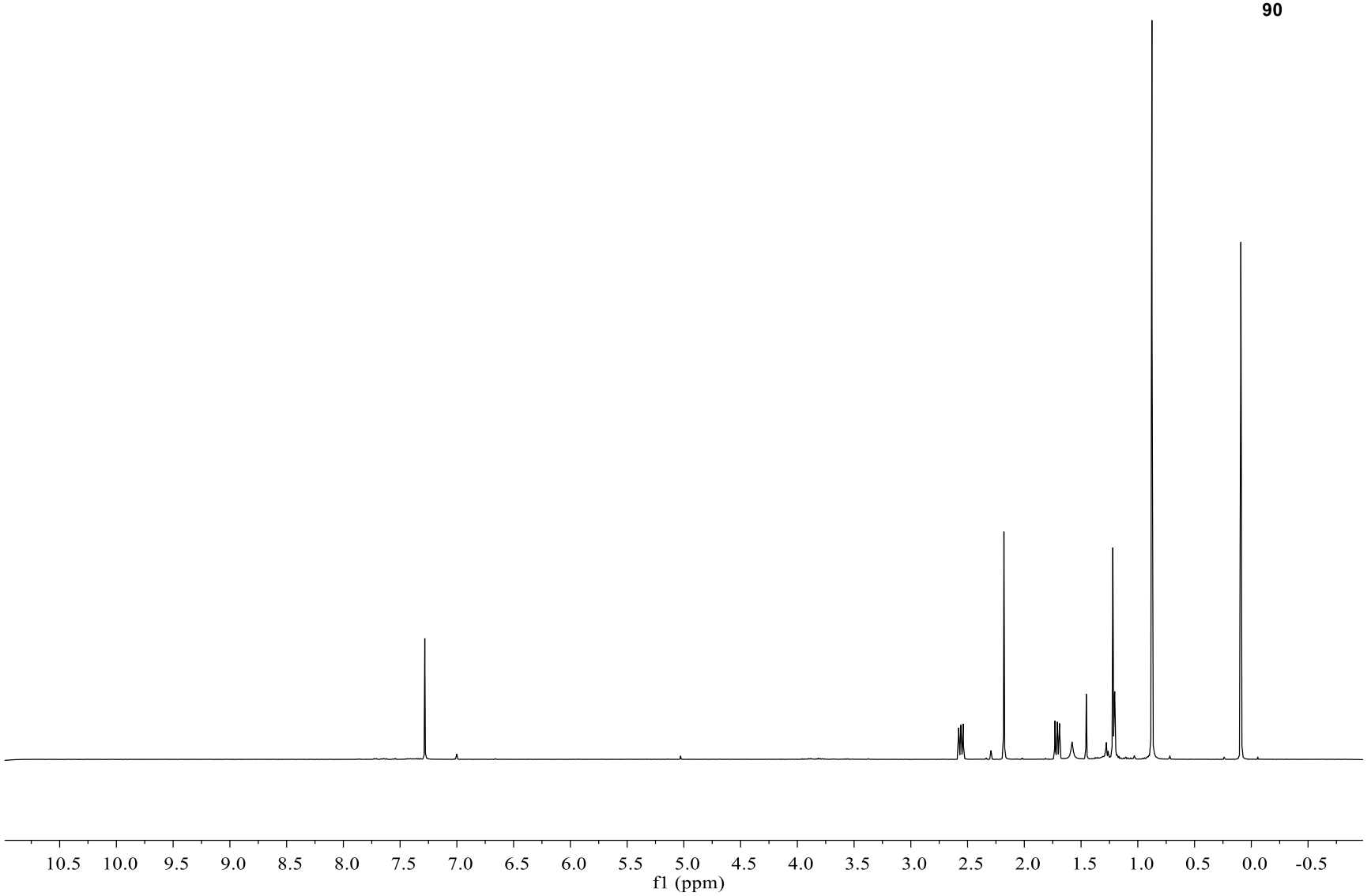

220
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)

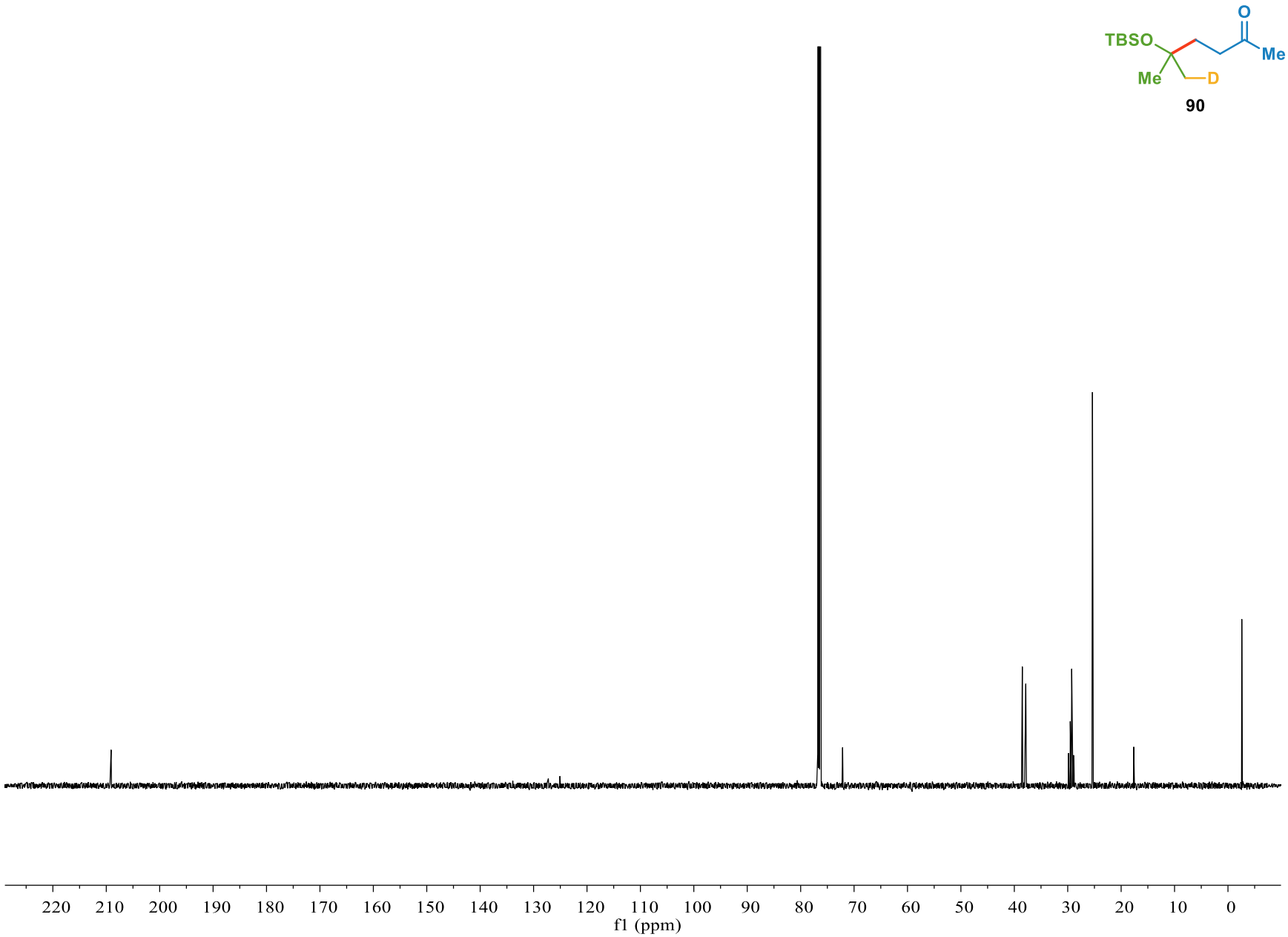

TBSO
Me
O
OMe
OMe
O
89
1.0 10.5 10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0 -0.5 -1
f1 (ppm)

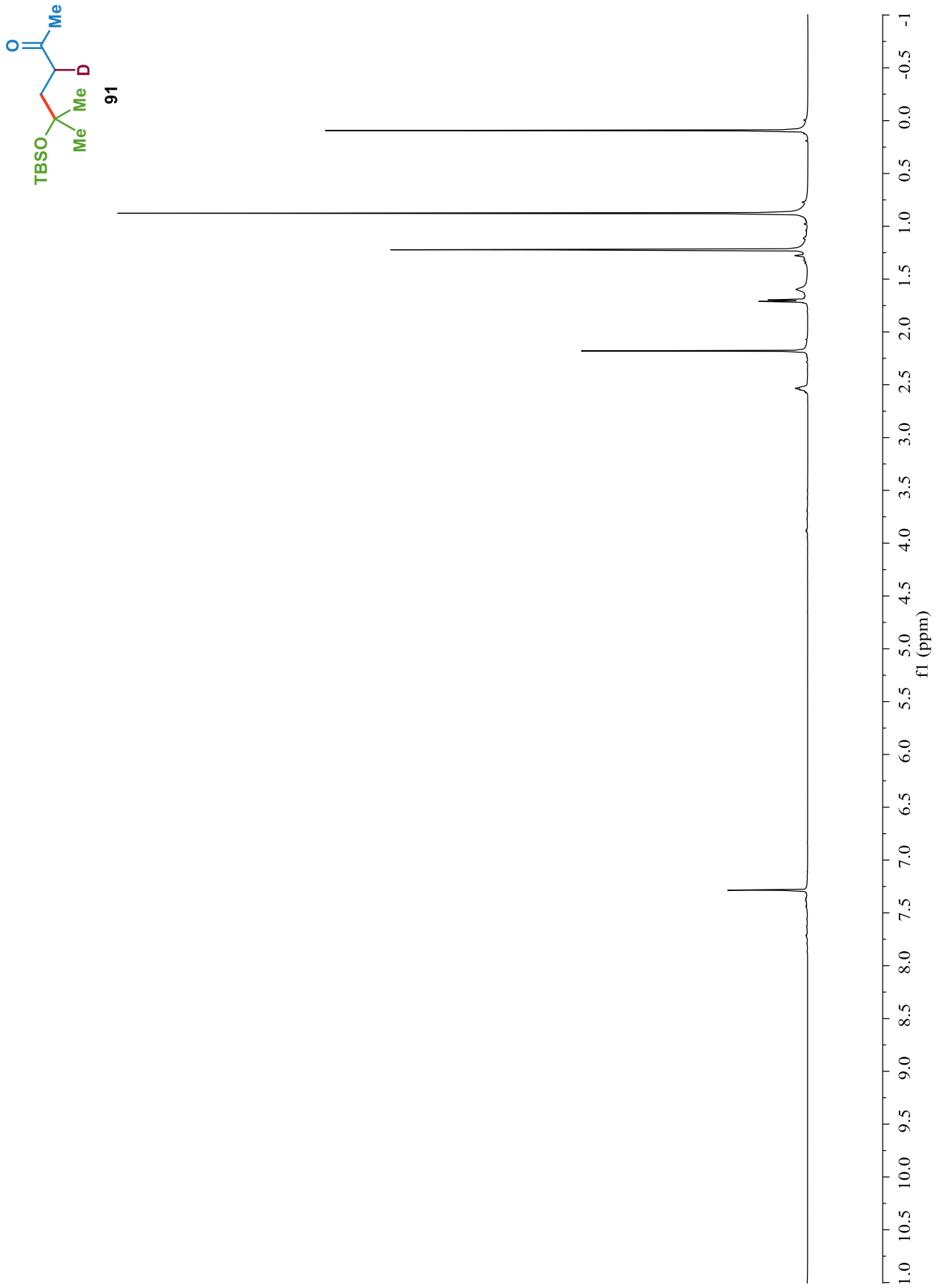

TBSO
Me
O
OMe
OMe
O
89
220 210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
f1 (ppm)

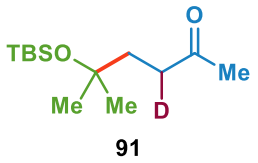

O
TBSO
Me
Me
D

90


10.5
10.0
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
-0.5
f1 (ppm)


TBSO
Me
Me
D
O
90
220 210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
f1 (ppm)


O
Me
D
Me
Me
TBSO
91
1.0
10.5
10.0
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
-0.5
-1
f1 (ppm)


TBSO
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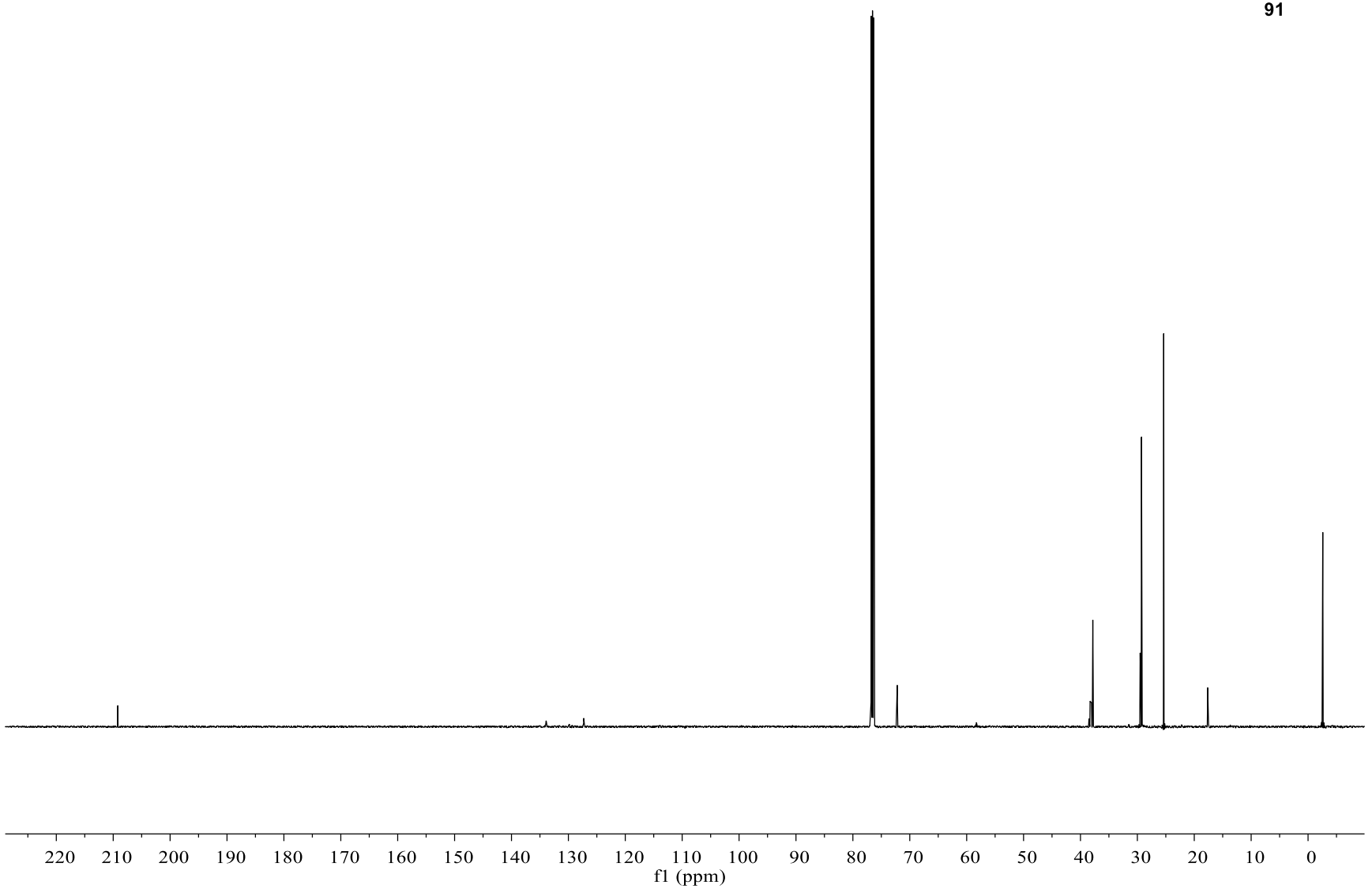
91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