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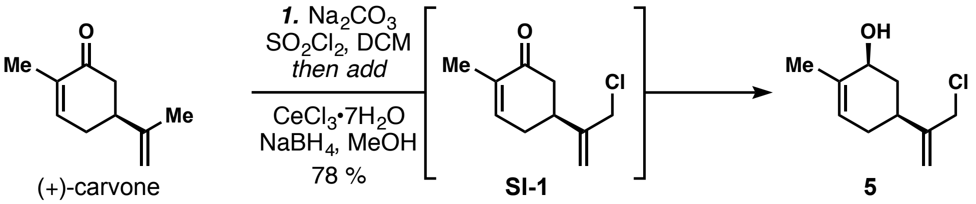
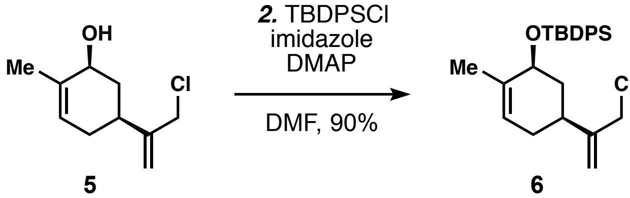
General Procedures

Unless otherwise stated, all reactions were performed in oven-dried or flame-dried glassware under an atmosphere of dry nitrogen or argon. Dry tetrahydrofuran (THF), *N*,*N*-dimethylformamide (DMF), dichloromethane (DCM), toluene, hexane, acetonitrile, and diethyl ether were obtained by passing these previously degassed solvents through activated alumina columns. Dry acetone was purchased from Fisher Chemical in Acroseal^{TM} bottles. Amine and alcohol reagents and solvents were distilled from calcium hydride prior to use. L-carvone, D-carvone, 2,2-dimethoxyacetaldehyde (60% in H_2O), and methyl acrylate was purchased from Sigma-Aldrich and used directly without further purification. Reactions were monitored by thin layer chromatography (TLC) on Silicycle Siliaplate^{TM} TLC G Glass-Backed Special for $KMnO_4$ (TLC-R10014BK-323, 250 µm thickness, F-254 indicator) and visualized by UV irradiation and staining with *p*-anisaldehyde, phosphomolybdic acid, or potassium permanganate developing agents. Volatile solvents were removed under reduced pressure using a rotary evaporator. Flash column chromatography was performed using Silicycle F60 silica gel (60Å, 230-400 mesh, 40-63 µm). Ethyl acetate and hexanes were purchased from Fisher Chemical and used for chromatography without further purification. Proton nuclear magnetic resonance (^{1}H NMR) and carbon nuclear magnetic resonance (^{13}C NMR) spectra were recorded on Bruker AVQ-400, AV-500, or AV-600 spectrometers operating at 400, 500, and 600 MHz for ^{1}H, and 100, 125, and 150 MHz for ^{13}C. Chemical shifts are reported in parts per million (ppm) with respect to the residual solvent signal $CDCl_3$ (^{1}H NMR: $\delta = 7.26$; ^{13}C NMR: $\delta = 77.16$) or DMSO-d_6 (^{1}H NMR: $\delta = 2.50$; ^{13}C NMR: $\delta = 39.52$). Peak multiplicities are reported as follows: s = singlet, d = doublet, t = triplet, q = quartet, p = pentet, dd = doublet of doublets, td = triplet of doublets, dt = doublet of triplets, ddd = doublet of doublet of doublets, ddt = doublet of doublet of triplets, ddq = doublet of doublet of quartets, dddd = doublet of doublet of doublet of doublets, m = multiplet, br = broad signal, app = apparent. Melting points were determined using MEl-TEMP^{TM} apparatus and are uncorrected. IR spectra were recorded on a Nicolet 380 FT-IR spectrometer. High-resolution mass spectra (HRMS) were obtained by the QB3/chemistry mass spectrometry facility at the University of California, Berkeley. Optical rotations were measured on a Perkin-Elmer 241 polarimeter. X-ray crystallographic analyses were performed at the UC-Berkeley College of Chemistry X-ray crystallography facility. All X-ray structures shown were obtained during preliminary studies conducted with (–)-carvone.

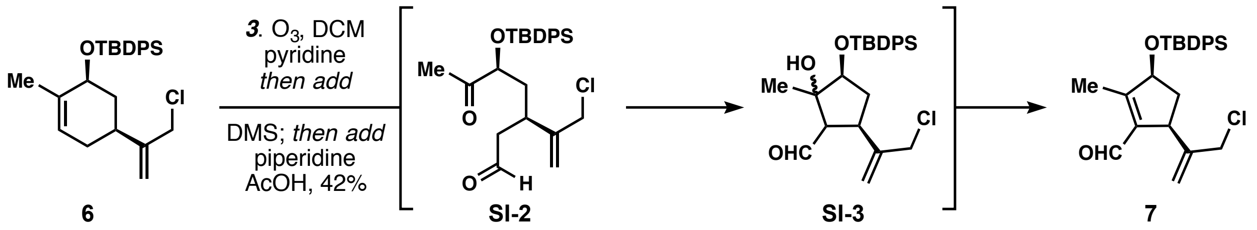


Chloro-carveol 5: An oven-dried 3 L three-necked flask equipped with a large stir bar was charged with D-carvone (30.0 g, 0.200 mol), sodium carbonate (63.6 g, 0.600 mol), and DCM (1 L). The resulting mixture was stirred vigorously at room temperature for 30 minutes, followed by slow addition of SO_2Cl_2 (20.0 mL, 0.247 mol) over 2 hours via a syringe pump. The reaction was monitored by TLC (EtOAc:hexane 1:4) and additional SO_2Cl_2 was added if necessary. After complete consumption of the starting material, methanol (1 L) and $CeCl_3$•$7H_2O$ (82.0 g, 0.220 mol) were added and the resulting mixture was stirred at room temperature for 30 minutes. The reaction was then cooled to 0 °C and $NaBH_4$ (22.8 g, 0.600 mol) was added in 4 portions over 1 hour. After the ketone intermediate **SI-1** was completely consumed as indicated by TLC, the reaction was quenched by addition of 1N aqueous HCl (300 mL) and H_2O (500 mL) sequentially. The aqueous layer was extracted with ethyl acetate (700 mL × 3). The combined organic layer was washed with brine, dried over $MgSO_4$, and concentrated *in vacuo*. The resulting crude was purified by column chromatography (EtOAc:hexane = 1:10 to 1:5), affording chloro-carveol **5** (29.2 g, 0.156 mol, 78%) as a light yellow oil: $[\alpha]_D^{20}$ = +37.4° (c 0.01 g/mL, $CHCl_3$); ^{1}H NMR (600 MHz, $CDCl_3$) δ 5.53 – 5.49 (m, 1H), 5.19 (s, 1H), 5.03 (s, 1H), 4.27 – 4.21 (m, 1H), 4.11 (s, 2H), 2.55 (ddd, J = 15.5, 8.0, 3.5 Hz, 1H), 2.24 (ddt, J = 12.2, 5.6, 2.3 Hz, 1H), 2.19 (dddd, J = 13.9, 6.9, 3.4, 1.6 Hz, 1H), 1.95 (ddq, J = 16.6, 10.8, 2.7 Hz, 1H), 1.77 (dd, J = 2.8, 1.5 Hz, 3H), 1.53 (td, J = 12.2, 9.6 Hz, 1H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 148.6, 136.4, 123.6, 113.9, 70.9, 47.6, 38.1, 36.9, 31.5, 19.0; IR (thin film, cm^{-1}) 3324, 2969, 2942, 2916, 2884, 2838, 1716, 1642, 1451, 1434, 1407, 1258; HRMS (EI+) calcd. for [$C_{10}H_{15}ClO$]: m/z 186.0811, found 186.0810.

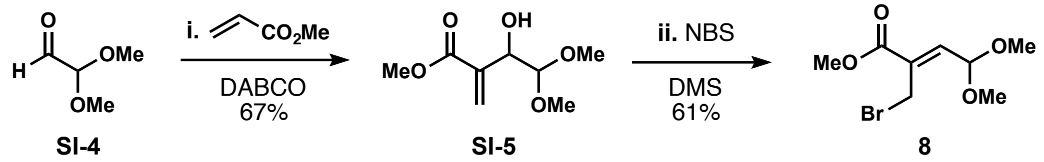
[Note: This compound is somewhat volatile and should not be placed under high vacuum for extended periods. On a 1-mmol scale, an 85% yield of product was obtained.]



Silyl ether 6: An oven-dried 1 L round-bottom flask was charged with a stir bar, chloro-carveol **5** (18.6 g, 0.100 mol), imidazole (20.4 g, 0.300 mol), and 4-dimethylaminopyridine (0.6 g, 0.005 mol). The flask was placed under vacuum and back-filled with N_2, followed by addition of dry DMF (500 mL). The resulting mixture was cooled to 0 °C, and TBDPSCl (32.8 g, 0.120 mol) was added slowly. The reaction was allowed to warm to room temperature and stirred overnight. After the reaction was complete as indicated by TLC, the reaction mixture was poured into a separation funnel charged with aqueous LiCl (10% w/w, 1 L). The aqueous layer was extracted with diethyl ether (500 mL × 3) and the combined organic phase was washed with H_2O (500 mL × 2), brine (500 mL), dried over $MgSO_4$, and concentrated *in vacuo*. The crude was purified by flash column chromatography (EtOAc:hexane = 1:100 to 1:30), affording silyl ether **6** (38.5 g, 0.0906 mol, 91%) as a colorless oil: $[\alpha]_D^{20}$ = +58.0° (c 0.01 g/mL, $CHCl_3$); ^1H NMR (600 MHz, $CDCl_3$) δ 7.75 – 7.69 (m, 4H), 7.45 – 7.40 (m, 2H), 7.40 – 7.35 (m, 4H), 5.43 (dq, *J* = 5.4, 1.7 Hz, 1H), 5.04 (s, 1H), 4.80 (s, 1H), 4.33 (br s, 1H), 3.92 (dd, *J* = 11.8, 1.0 Hz, 1H), 3.85 (dd, *J* = 11.8, 1.0 Hz, 1H), 2.29 – 2.20 (m, 1H), 2.06 (dddt, *J* = 16.9, 5.1, 3.0, 1.7 Hz, 1H), 1.88 (dddd, *J* = 14.4, 11.7, 5.4, 3.0 Hz, 1H), 1.83 (ddt, *J* = 12.5, 5.8, 2.3 Hz, 1H), 1.74 (dt, *J* = 2.6, 1.3 Hz, 3H), 1.48 (td, *J* = 12.5, 10.0 Hz, 1H), 1.08 (s, 9H); ^{13}C NMR (150 MHz, $CDCl_3$) δ 148.6, 137.7, 136.2, 136.2, 135.0, 134.0, 129.8, 129.7, 127.7, 127.5, 122.9, 113.4, 72.8, 47.3, 38.3, 36.2, 31.3, 27.3, 20.2, 19.7; IR (thin film, cm^{-1}) 3072, 3049, 2999, 2963, 2930, 2889, 2857, 1472, 1449, 1428; HRMS (EI+) calcd. for [$C_{26}H_{33}ClOSi$]: m/z 424.1989, found 424.1990.



Aldehyde 7: An oven-dried 1 L round-bottom flask equipped with a large stir bar was charged with silyl ether **6** (21.3 g, 50.1 mmol), pyridine (1.18 mL, 15.0 mmol), and DCM (500 mL). The reaction flask was connected to a Welsbach ozone generator through plastic tubing and a glass bubbler, and cooled to -78 °C over an acetone-dry ice bath. The system was purged with O_2 for 5 min, and ozone generation was initiated (5~6 psi, 1.6~1.8 L/min, 90 V). The reaction was monitored carefully by TLC (EtOAc:hexane 1:30), and disconnected from the ozone generator immediately after complete consumption of the starting material (20~40 min). The reaction was then bubbled with N_2 for 10 min, followed by the addition of dimethyl sulfide (7.35 mL, 100 mmol). The reaction was allowed to warm up to room temperature gradually and stirred for 8 hours. Piperidine (0.74 mL, 7.6 mmol) and acetic acid (0.58 mL, 10 mmol) were added to the reaction, which was heated at reflux for 16 hours. After complete conversion of the intermediates, the reaction mixture was filtered through a short column of silica gel (washed with DCM), concentrated *in vacuo*, and purified by flash column chromatography (EtOAc:hexane 1:30) to afford aldehyde **7** (9.16 g, 20.9 mmol, 42%) as a colorless oil: $[\alpha]_D^{20}$ = +12.3° (c 0.01 g/mL, $CHCl_3$); ^{1}H NMR (600 MHz, $CDCl_3$) δ 9.92 (s, 1H), 7.73 – 7.63 (m, 4H), 7.48 – 7.43 (m, 2H), 7.43 – 7.37 (m, 4H), 5.22 (s, 1H), 5.06 (s, 1H), 4.67 (ddt, *J* = 7.8, 5.5, 1.0 Hz, 1H), 4.23 (dd, *J* = 11.8, 1.2 Hz, 1H), 4.09 (dd, *J* = 11.8, 0.9 Hz, 1H), 3.36 (ddd, *J* = 8.4, 6.0, 2.1 Hz, 1H), 2.36 (ddd, *J* = 13.6, 8.4, 7.8 Hz, 1H), 2.03 (dd, *J* = 2.1, 1.0 Hz, 3H), 1.69 (ddd, *J* = 13.6, 6.0, 5.5 Hz, 1H), 1.10 (s, 9H); ^{13}C NMR (150 MHz, $CDCl_3$) δ 189.1, 161.7, 148.2, 139.1, 136.2, 136.1, 133.7, 133.6, 130.1, 130.0, 127.9, 127.8, 115.3, 80.5, 48.4, 44.9, 41.2, 27.1, 19.4, 12.3; IR (thin film, cm^{-1}) 3072, 3050, 2960, 2931, 2892, 2857, 1725, 1674, 1472, 1428; HRMS (EI+) calcd. for [$C_{26}H_{31}ClO_2Si$]: m/z 438.1782, found 438.1779.



Allyl bromide 8: This procedure was adapted from previous conditions reported by Hoffmann and co-workers.[1] (i) A 250 mL round-bottom flask equipped with a stir bar was charged with 2,2-dimethoxyacetaldehyde **SI-4** (70.0 g, 60% in H_2O, 0.400 mol), methyl acrylate (72.4 mL, 0.800 mol), and DABCO (44.0 g, 0.200 mol). The resulting mixture was stirred at room temperature for 2 days and concentrated *in vacuo*. The resulting oil was diluted with diethyl ether (500 mL) and washed with 1N HCl (300 mL), H_2O (300 mL), and brine (300 mL) sequentially. The organic phase was dried over Na_2SO_4 and concentrated *in vacuo*. The crude was purified by flash column chromatography (EtOAc:hexane 1:10 – 1:3), affording allyl alcohol **SI-5** (51.0 g, 0.268 mol, 67%) as a colorless oil, spectra data of which was in agreement with that previously reported by Myers and coworkers.[2]

(ii) A flame-dried 500 mL round-bottom flask was charged with a stir bar, *N*-Bromosuccinimide (22.0 g, 0.124 mol) and DCM (250 mL). The reaction was cooled to 0 °C, followed by the addition of dimethyl sulfide (10.0 mL, 0.139 mol) in DCM (75 mL). The resulting mixture was stirred at 0 °C for 20 min, and allyl alcohol **SI-5** (20.0 g, 0.105 mol) in DCM (75 mL) was added slowly. The reaction was allowed to warm to room temperature gradually and stirred overnight. After the reaction was complete as indicated by TLC (EtOAc:hexane 1:5), the reaction was quenched by the addition of sat. aqueous $NaHCO_3$ (200 mL). The aqueous phase was extracted with diethyl ether (200 mL × 2). The combined organic phase was washed with H_2O (300 mL) and brine (300 mL) sequentially, dried over Na_2SO_4, and concentratd *in vacuo*. The crude material was purified by flash column chromatography (EtOAc:hexane 1:15 – 1:5), affording allyl bromide **8** (16.1 g, 0.0636 mol, 61%) as a colorless oil: ^1H NMR (600 MHz, $CDCl_3$) δ 6.76 (d, *J* = 5.5 Hz, 1H), 5.20 (d, *J* = 5.5 Hz, 1H), 4.30 (s, 2H), 3.82 (s, 3H), 3.36 (s, 6H); ^{13}C NMR (150 MHz, $CDCl_3$) δ 165.7, 141.1, 133.0, 99.0, 52.9, 52.9, 52.6, 23.5; IR (thin film, cm^{-1}) 2997, 2955, 2907, 2832, 1722, 1654, 1438, 1371, 1329; HRMS (ESI) calcd. for $[C_8H_{13}{}^{79}BrNaO_4]^+$ $(M+Na)^+$: m/z 274.9895, found 274.9895, calcd. for $[C_8H_{13}{}^{81}BrNaO_4]^+$ $(M+Na)^+$: 276.9874, found 276.9877.

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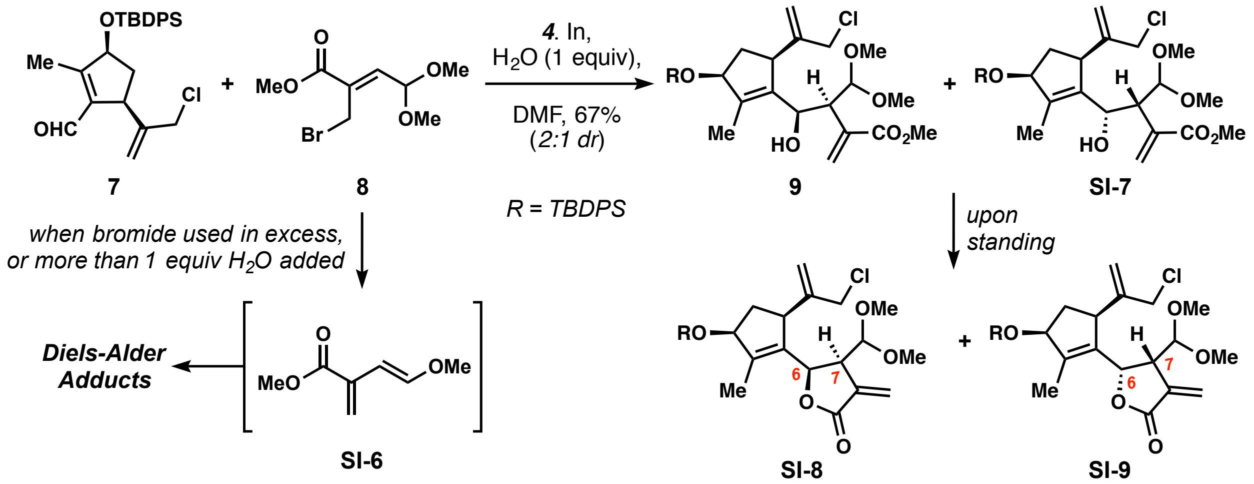
[1] H. Martin, R. Hoffmann, J. Rabe, *J. Org. Chem.* **1985**, *50*, 3849.
[2] J. Svenda, A. G. Myers, *Org. Lett.* **2009**, *11*, 2437.



Homoallylic Alcohol 9: A flame-dried 500 mL round-bottom flask equipped with a stir bar was charged with aldehyde **7** (14.0 g, 31.9 mmol), allyl bromide **8** (6.73 g, 26.6 mmol), and indium shot (4.58 g, 39.9 mmol). The flask was placed under vacuum and back-filled twice with N_2, followed by the addition of DMF (80 mL) and H_2O (0.48 mL, 26.6 mmol). The reaction was stirred vigorously at room temperature while bubbling with N_2 for 1 hour. The resulting mixture was stirred overnight and filtered through a pad of Celite®. The filtrate was diluted with H_2O (800 mL) and the aqueous layer was extracted with ethyl acetate (3 × 500 mL). The combined organic phase was washed with H_2O (500 mL × 2) and brine (500 mL), dried over Na_2SO_4, and concentrated *in vacuo*. The crude material was purified by flash column chromatography (EtOAc:hexane 1:20 to 1:10), affording recovered aldehyde **7** along with a mixture of homoallylic alcohols **9** and **SI-7** (11.0 g, 17.9 mmol, 67%, 2:1 *dr*). The diastereomeric ratio (*dr*) of **9** and **SI-7** was determined by ^{1}H NMR (See Figure S1). The products undergo lactonization upon standing to give **SI-8** and **SI-9**, respectively, and were therefore used immediately to the next step. The ^{1}H NMR coupling constant between the C-6/C-7 protons on **SI-8** and **SI-9** are 8.61 Hz and 8.43 Hz respectively implying that these compounds have the same relative configuration in this sector and thus the minor isomer has the structure depicted for **SI-7**.

When allyl bromide **8** was used in excess or more than 1 equivalent of H_2O was added, a mixture of Diels-Alder dimers derived from intermediate **SI-6** was obtained in addition to the aforementioned products. Compounds **9**, **SI-7**, **SI-8**, **SI-9** and dimerization products from **SI-6** are of similar polarity in various solvent systems, and thus inseparable.

[Notes: Lactonization of **SI-7** is faster than that of the desired diastereomer **9**, which is beneficial for the purpose of product separation in the next step. However, formation of large amounts of

SI-8 should be avoided. Lactones **SI-8** and **SI-9** are not reactive in the conditions of next step.]

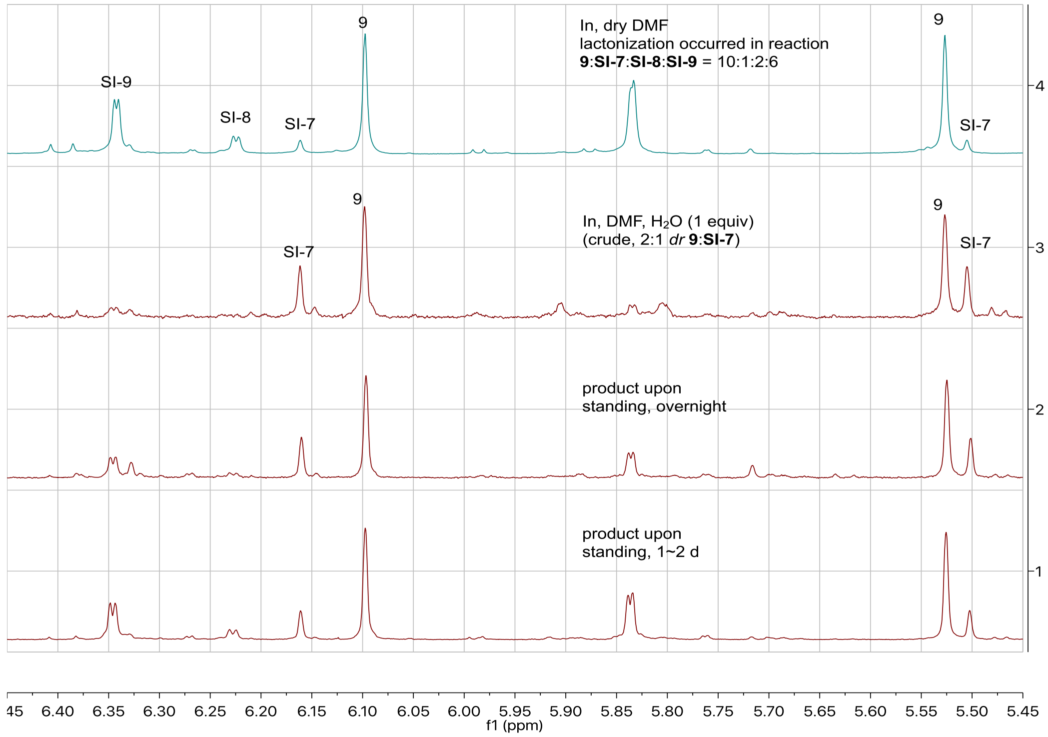
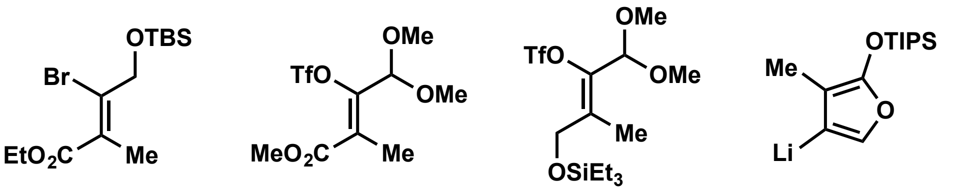


Figure S1. Ratio of products in the indium-mediated allylation reaction.

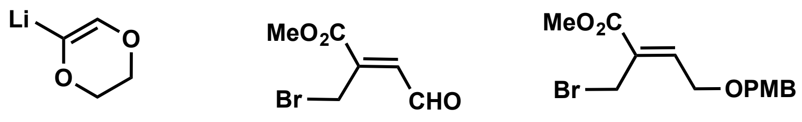


no desired pdt with $CrCl_2$, $NiCl_2$ *or* iPrMgCl *or* Zn

$CrCl_2$, $NiCl_2$ 45%, 7.5:1 dr at C-6 couldn't remove acetal after coupling

no desired pdt with $CrCl_2$, $NiCl_2$

product couldn't be elaborated to 7-membered ring

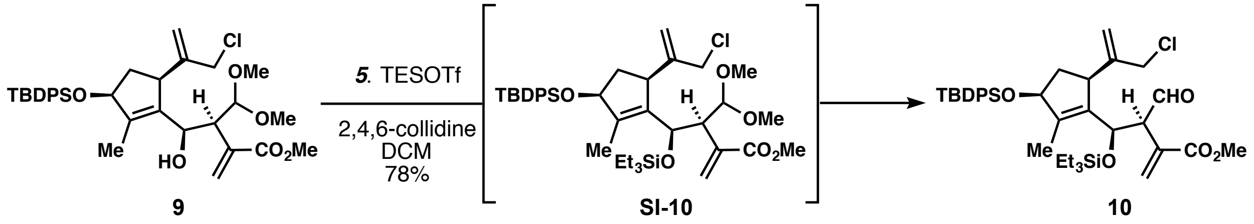


product couldn't be elaborated into 7-membered ring

no desired pdt with $CrCl_2$, $NiCl_2$

Zn, THF, *aq.* NH_4Cl, 89%, 1:1 dr *or* In, DMF, 77% 3:2 dr

Figure S2. A sampling of other reagents examined (besides **8**) in the nucleophilic addition to **7**.



Triethyl Silyl Aldehyde 10: This procedure was adapted from previous conditions reported by Kita and coworkers.[1]

A flame-dried 500 mL round-bottom flask equipped with a stir bar was charged with homoallylic alcohols **9** and **SI-7** (12.3 g, 20.1 mmol, 2:1 *dr* **9**:**SI-7**), 2,4,6-collidine (14.5 g, 120 mmol) and DCM (300 mL). The reaction was cooled to -78 °C in an acetone-dry ice bath and TESOTf (21.1 g, 80.0 mmol) was added dropwise. The reaction was allowed to warm gradually and stirred at approximately 0 °C for 24 hours. After the complete consumption of dimethyl acetal **SI-10** as indicated by TLC, the reaction was quenched by the addition of H_2O (50 mL) and stirred at room temperature for 30 min until the disappearance of polar collidine adducts on TLC (EtOAc:hexane 1:5). The resulting mixture was diluted with H_2O (200 mL) and the aqueous layer was extracted with DCM (200 mL × 3). The combined organic phase was washed with brine (300 mL), dried over $MgSO_4$, and concentrated *in vacuo*. The crude product was purified by flash column chromatography (EtOAc:hexane 1:30), affording triethyl silyl aldehyde **10** (7.05 g, 10.4 mmol, 78% from **9**) separated from its diastereomer as a light yellow oil: $[\alpha]_D^{20}$ = +25.0° (c 0.01 g/mL, $CHCl_3$); ^{1}H NMR (500 MHz, $CDCl_3$) δ 9.86 (d, *J* = 2.1 Hz, 1H), 7.68 – 7.62 (m, 4H), 7.45 – 7.41 (m, 2H), 7.39 – 7.35 (m, 4H), 6.17 (s, 1H), 5.58 (s, 1H), 5.36 (s, 1H), 5.27 (s, 1H), 5.18 (d, *J* = 9.9 Hz, 1H), 4.43 (dd, *J* = 7.6, 3.1 Hz, 1H), 4.31 (d, *J* = 12.5 Hz, 1H), 4.14 (d, *J* = 12.5 Hz, 1H), 3.64 (dd, *J* = 9.9, 2.1 Hz, 1H), 3.63 (s, 3H), 3.19 (ddd, *J* = 8.7, 4.3, 1.8 Hz, 1H), 2.09 (ddd, *J* = 14.0, 8.7, 7.6 Hz, 1H), 1.71 (ddd, *J* = 14.0, 4.3, 3.1 Hz, 1H), 1.46 (d, *J* = 1.8 Hz, 3H), 1.07 (s, 9H), 0.95 (t, *J* = 7.9 Hz, 9H), 0.66 – 0.56 (m, 6H); ^{13}C NMR (150 MHz, $CDCl_3$) δ 200.8, 166.1, 148.2, 141.1, 138.1, 136.2, 136.2, 134.7, 134.3, 134.2, 129.9, 129.8, 129.8, 127.7, 127.7, 116.3, 80.0, 68.2, 60.3, 52.3, 47.8, 47.6, 40.1, 27.1, 19.4, 12.7, 7.0, 4.9; IR (thin film, cm^{-1}) 3072, 2956, 2932, 2877, 2857, 1718, 1627, 1590, 1470, 1428; HRMS (ESI) calcd. for $[C_{38}H_{53}ClNaO_5Si_2]^+$ $(M+Na)^+$: m/z 703.3018, found 703.3025

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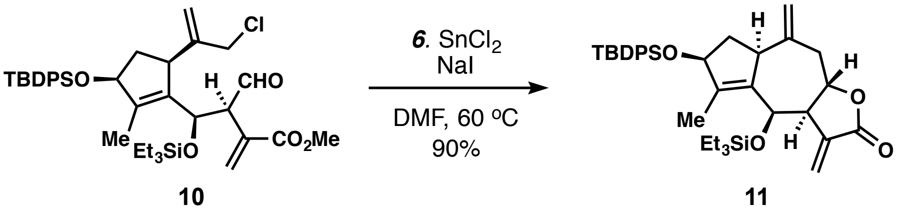
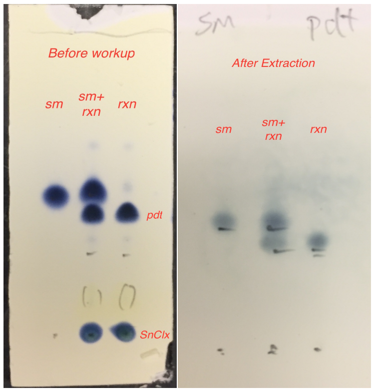
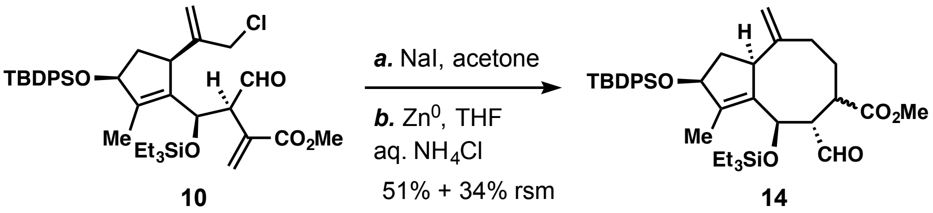
[1] H. Fujioka, T. Okitsu, Y. Sawama, N. Murata, R. Li, Y. Kita, *J. Am. Chem. Soc.* **2006**, *128*, 5930-5938.



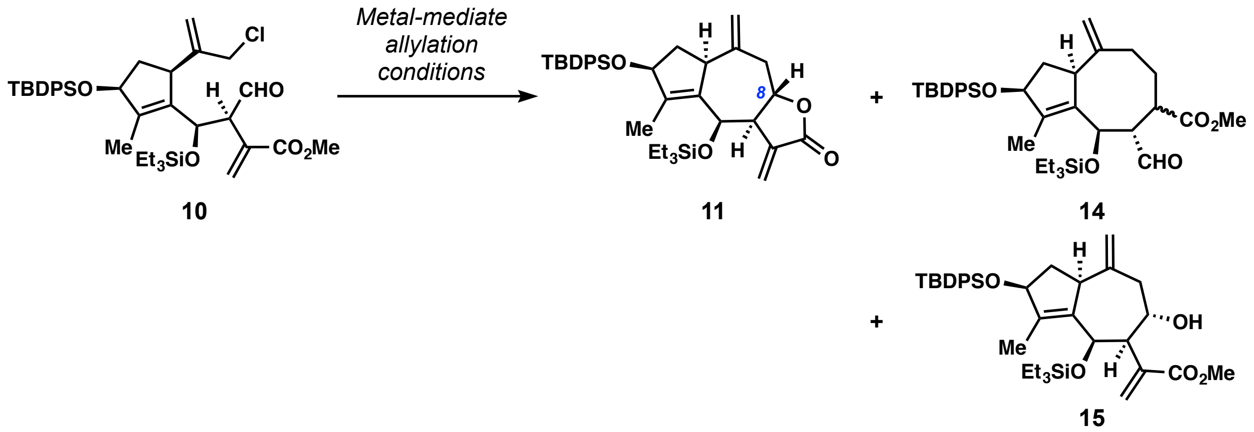


Unsaturated trans-lactone 11: A flame-dried 500 mL round-bottom flask was charged with a stir bar, NaI (14.9 g, 99.3 mmol) and anhydrous $SnCl_2$ (9.40 g, 49.6 mmol). The flask was placed under vacuum and back-filled twice with nitrogen, followed by the addition of degassed dry DMF (250 mL). The resulting mixture was covered by alumina foil to avoid light and stirred at room temperature for 30 min. The starting material **10** (7.60 g, 11.1 mmol) in dry DMF (50 mL) was degassed by bubbling of argon, and transferred to the reaction flask via syringe in one portion. The reaction was stirred in the dark at 60 ^{o}C for 12 hours. After complete consumption of the starting material as indicated by TLC (EtOAc:hexane 1:10, developed twice), the reaction was cooled to room temperature, diluted with ethyl acetate (100 mL), and quenched by addition of aq. NH_4F (10% w/w, 100 mL). The resulting mixture was diluted with H_2O (500 mL) and extracted with ethyl acetate (300 mL × 3). The combined organic phase was washed with H_2O (500 mL), brine (500 mL), dried over Na_2SO_4, and concentrated *in vacuo*. The crude was purified by flash column chromatography (EtOAc:hexane 1:20), affording unsaturated lactone **11** (6.18 g, 10.0 mmol, 90%) as a colorless oil: $[\alpha]^{20}_{D}$ = +57.9° (c 0.007 g/mL, $CHCl_3$); ^{1}H NMR (600 MHz, $CDCl_3$) δ 7.74 – 7.67 (m, 4H), 7.47 – 7.41 (m, 2H), 7.42 – 7.35 (m, 4H), 6.28 (d, *J* = 3.4 Hz, 1H), 5.52 (d, *J* = 3.1 Hz, 1H), 5.04 (s, 1H), 4.95 (s, 1H), 4.91 (s, 1H), 4.70 (ddd, *J* = 11.8, 9.8, 4.3 Hz, 1H), 4.57 (br t, *J* = 7.1 Hz, 1H), 3.06 (dd, *J* = 11.8, 4.3 Hz, 1H), 2.84 – 2.77 (m, 1H), 2.68 (ddd, *J* = 9.8, 3.4, 3.1 Hz, 1H), 2.22 (dd, *J* = 11.8, 11.8 Hz, 1H), 1.96 (ddd, *J* = 11.9, 6.1, 6.1 Hz, 1H), 1.85 (ddd, *J* = 11.9, 11.3, 8.2 Hz, 1H), 1.71 (dd, *J* = 2.5, 1.2 Hz, 3H), 1.11 (s, 9H), 0.89 (t, *J* = 7.9 Hz, 9H), 0.62 – 0.48 (m, 6H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 170.0, 142.4, 140.1, 139.5, 137.6, 136.1, 134.5, 134.2, 129.8, 127.7, 127.7, 119.5, 113.8, 78.6, 77.7, 63.6, 51.8, 48.8, 44.8, 39.3, 27.1, 19.5, 13.1, 7.1, 5.3; IR (thin film, cm^{-1}) 3072, 2963, 2930, 2889, 2857, 1472, 1449, 1428, 1343; HRMS (ESI) calcd. for $[C_{37}H_{50}NaO_4Si_2]^+$ $(M+Na)^+$: m/z 637.3140, found 637.3133.



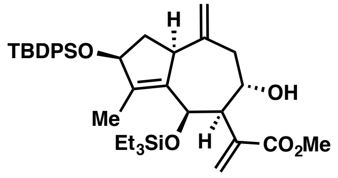
Cyclooctane 14: A flame-dried reaction tube was charged with a stir bar, triethyl silyl aldehyde **10** (34.0 mg, 0.0499 mmol), and NaI (75.0 mg, 0.500 mmol). The tube was placed under vacuum and back-filled twice with N_2, followed by addition of dry acetone (6 mL). The resulting mixture was stirred under cover of alumina foil at 40 °C overnight, and then concentrated *in vacuo*. The crude was re-dissolved in dry diethyl ether and filtered through a pad of Celite®. The filtrate was collected in another reaction tube wrapped by alumina foil and concentrated *in vacuo*. Activated zinc powder (32.0 mg, 0.496 mmol) and THF (2 mL) was added to the reaction followed by the addition of degassed saturated aq. NH_4Cl (1 mL). The reaction was vigorously stirred for 20 min and the aqueous layer was extracted with ethyl acetate (5 mL × 3). The combined organic phase was washed with H_2O (10 mL), dried over Na_2SO_4, and concentrated *in vacuo*. Flash column chromatography (EtOAc:hexane 1:20) afforded recovered **10** (11.5 mg, 0.0169 mmol, 34%) and cyclooctane **14** (16.5 mg, 0.0240 mmol, 51%, 5:2 *dr*) as a colorless oil that was an inseparable mixture of two diastereomers: IR (thin film, cm^{-1}) 3072, 2957, 2932, 2877, 2857, 1735, 1635, 1471, 1429; HRMS (EI) calcd. for [$C_{38}H_{54}O_5Si_2$]: m/z 646.3510, found 646.3503; Major diastereomer: ^1H NMR (600 MHz, $CDCl_3$) δ 9.93 (d, *J* = 2.1 Hz, 1H), 7.72 – 7.65 (m, 4H), 7.46 – 7.34 (m, 6H), 4.85 (br t, *J* = 1.7 Hz, 1H), 4.83 (br s, 1H), 4.63 – 4.57 (m, 1H), 4.21 (d, *J* = 10.4 Hz, 1H), 3.65 (s, 3H), 3.29 – 3.23 (m, 1H), 3.10 – 3.05 (m, 1H), 2.66 – 2.63 (m, 1H), 2.54 (d, *J* = 10.4 Hz, 1H), 2.12 (d, *J* = 9.2 Hz, 1H), 2.00 (dt, *J* = 13.3, 7.5 Hz, 1H), 1.87 (dd, *J* = 2.6, 1.1 Hz, 3H), 1.69 – 1.65 (m, 1H), 1.62 (ddd, *J* = 13.2, 7.9, 6.5 Hz, 1H), 1.59 – 1.54 (m, 1H), 1.09 (s, 9H), 0.81 (t, *J* = 8.0 Hz, 9H), 0.40 (q, *J* = 8.0 Hz, 6H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 206.1, 176.5, 146.9, 140.6, 139.3, 136.2, 136.1, 134.7, 134.2, 129.8, 129.7, 127.7, 127.6, 117.3, 80.5, 71.5, 58.4, 53.3, 52.2, 41.4, 37.6, 34.1, 27.2, 19.4, 12.7, 6.8, 4.6.

Table 1. Investigation of metal-mediated allylation conditions for synthesis of **11**.



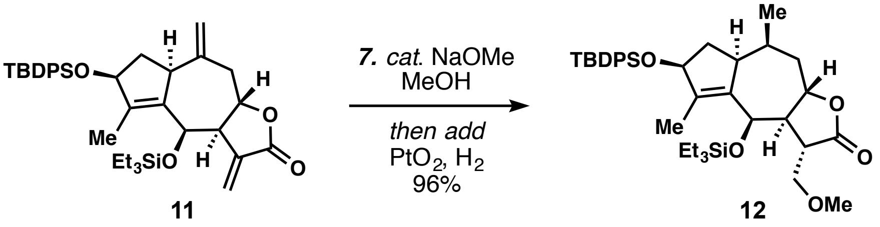
Entries	Conditions[a]	**11**	**14**	**15**	rsm
1	$CrCl_2$ (10 equiv), $NiCl_2$ (0.4 equiv) DMF, 60 °C	10% (2:1 *dr*)	17% (3.3:1 *dr*)	–	–
2	In^0 (5 equiv), NaI (10 equiv) DMF, 60 °C	13%[b]	–	–	–
3	*i.* NaI (10 equiv), acetone *ii.* SmI_2 (4.5 equiv), HMPA-THF (1:10), –78 °C	27% (2:1 *dr*)	17% (9:1 *dr*)	–	–
4	*i.* NaI (10 equiv), acetone *ii.* Zn^0 (10 equiv), THF, aq. NH_4Cl, rt	0%	51% (2.5:1 *dr*)	–	34%
5	*i.* NaI (10 equiv), acetone *ii.* Mg^0 (30 equiv), cat. $(CH_2Br)_2$, THF 0 °C to rt	0%	–	–	–
6	*i.* NaI (10 equiv), acetone *ii.* iPrMgCl (1.1 equiv), THF, 0 °C to rt	0%	–	–	–
7	*i.* NaI (10 equiv), acetone *ii.* $SnCl_2$ (5 equiv), DMF, rt	53%[b]	–	20%[b]	9%
8	$SnCl_2$ (4.5 equiv), NaI (9 equiv) DMF, 60 °C	90%[b]	–	–	–

[a] Reactions performed on 30-mg scale for entries 1-7, performed on 7-gram scale for entry 8; isolated yields reported; [b] Single diastereomer obtained; rsm = recovered starting material.

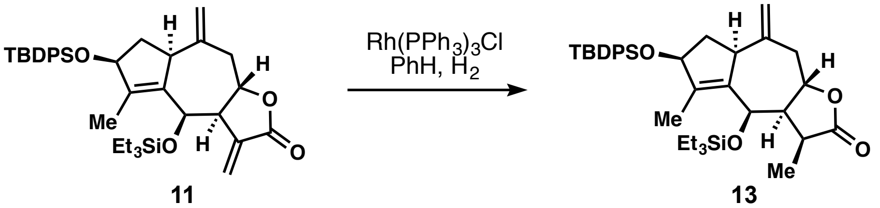


15

[From Entry 7, Table S1] Cycloheptanol methyl ester **15**, colorless oil: ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.71 – 7.65 (m, 4H), 7.45 – 7.40 (m, 2H), 7.40 – 7.34 (m, 4H), 6.30 (s, 1H), 5.80 (s, 1H), 4.95 (d, *J* = 1.8 Hz, 1H), 4.87 (d, *J* = 1.8 Hz, 1H), 4.57 (dd, *J* = 7.5, 6.8 Hz, 1H), 4.34 (d, *J* = 3.9 Hz, 1H), 3.90 (br s, 1H), 3.75 (s, 3H), 3.47 (t, *J* = 4.0 Hz, 1H), 3.00 – 2.91 (m, 1H), 2.66 (dd, *J* = 13.4, 2.6 Hz, 1H), 2.26 (dd, *J* = 13.4, 6.7 Hz, 1H), 2.17 (d, *J* = 8.0 Hz, 1H), 2.02 (ddd, *J* = 12.6, 6.8, 6.8 Hz, 1H), 1.68 (br s, 3H), 1.43 (ddd, *J* = 12.6, 9.7, 7.5 Hz, 1H), 1.08 (s, 9H), 0.86 (t, *J* = 8.0 Hz, 9H), 0.49 (qd, *J* = 8.0, 1.7 Hz, 6H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 169.0, 146.0, 141.9, 140.5, 136.1, 136.1, 136.0, 134.8, 134.3, 129.7, 129.7, 127.7, 127.6, 125.6, 115.2, 80.0, 77.4, 70.1, 69.1, 52.1, 51.3, 50.5, 41.2, 39.3, 27.2, 19.5, 13.4, 6.9, 4.8; IR (thin film, cm^{-1}) 3463, 3072, 3049, 2956, 2932, 2876, 2856, 1775, 1723, 1628, 1470, 1429; HRMS (EI) calcd. for [$C_{38}H_{54}O_5Si_2$]: m/z 646.3510, found 646.3505.

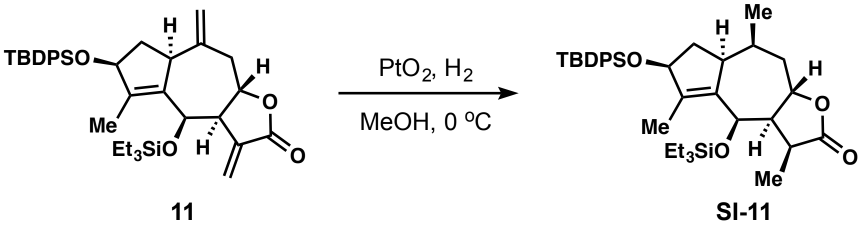


Mono-reduction product 12: A flame-dried 250 mL round-bottom flask was charged with a stir bar and unsaturated lactone **11** (6.18 g, 10.0 mmol). The flask was placed under vacuum and back-filled twice with nitrogen, followed by the addition of methanol (100 mL) and DCM (35 mL). NaOMe (54 mg, 1.0 mmol) was then added in one portion to the reaction and the resulting mixture was stirred at room temperature for 16 hours. The reaction was monitored by ^{1}H NMR with an aliquot (0.1 mL) concentrated *in vacuo*. After complete consumption of the starting material, acetic acid (60 mL, 1.0 mmol) and PtO$_2$ (227 mg, 1.00 mmol) were added sequentially to the reaction. The reaction mixture was bubbled with H$_2$ until a black suspension formed, and was stirred under 1 atmosphere of H$_2$ for 6 hours. After the reaction was complete as indicated by ^{1}H NMR, the reaction mixture was filtered through a pad of Celite® and concentrated *in vacuo*. The crude was purified by flash column chromatography (EtOAc:hexane 1:20), affording mono-reduction product **12** (6.23 g, 9.60 mmol, 96%) as a colorless oil: $[\alpha]_D^{20}$ = +48.8° (c 0.01 g/mL, CHCl$_3$); ^{1}H NMR (500 MHz, CDCl$_3$) δ 7.72 – 7.65 (m, 4H), 7.45 – 7.41 (m, 2H), 7.40 – 7.35 (m, 4H), 4.81 (ddd, *J* = 12.1, 10.2, 3.9 Hz, 1H), 4.64 (s, 1H), 4.52 (br t, *J* = 7.4 Hz, 1H), 3.65 (dd, *J* = 9.8, 4.8 Hz, 1H), 3.59 (dd, *J* = 9.8, 3.5 Hz, 1H), 3.30 (s, 3H), 2.81 (ddd, *J* = 12.0, 4.8, 3.5 Hz, 1H), 2.58 – 2.50 (m, 1H), 2.28 (ddd, *J* = 12.7, 3.9, 3.9 Hz, 1H), 2.14 (dd, *J* = 12.0, 10.2 Hz, 1H), 1.93 (ddd, *J* = 12.3, 7.4, 7.1 Hz, 1H), 1.89 – 1.81 (m, 1H), 1.65 – 1.63 (m, 3H), 1.61 (ddd, *J* = 12.7, 12.1, 3.9 Hz, 1H), 1.51 (ddd, *J* = 12.3, 9.9, 7.4 Hz, 1H), 1.08 (s, 9H), 1.03 (d, *J* = 7.3 Hz, 3H), 0.97 (t, *J* = 7.9 Hz, 9H), 0.72 – 0.57 (m, 6H); ^{13}C NMR (125 MHz, CDCl$_3$) δ 176.2, 143.1, 139.0, 136.1, 136.1, 134.6, 134.4, 129.7, 129.7, 127.6, 127.6, 79.4, 76.5, 68.9, 63.8, 59.4, 50.2, 50.0, 44.1, 40.9, 39.3, 31.5, 27.1, 19.4, 13.9, 13.0, 7.2, 5.7; IR (thin film, cm^{-1}) 3071, 2958, 2932, 2876, 2857, 1781, 1472, 1428, 1389; HRMS (EI) calcd. for [$C_{38}H_{56}O_5Si_2$]: m/z 648.3666, found 648.3660.

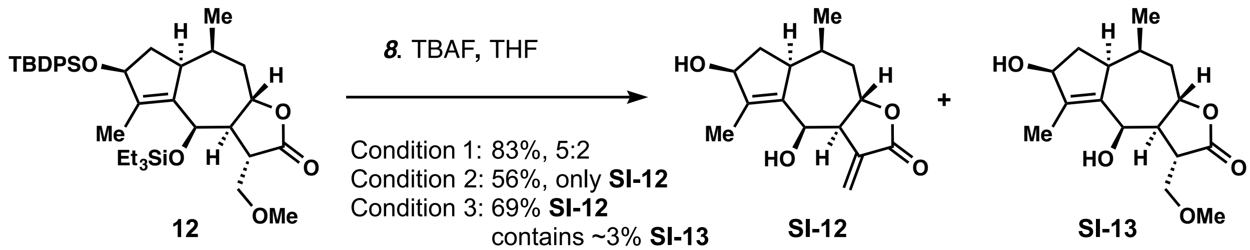


Methyl lactone 13: A flame-dried 25 mL round-bottom flask equipped with a stir bar was charged with unsaturated lactone **11** (560 mg, 0.911 mmol) and Wilkinson's catalyst (83.0 mg, 0.0897 mmol), followed by addition of anhydrous benzene (10 mL). The reaction mixture was bubbled with H_2 for 5 minutes, and was stirred under 1 atmosphere of H_2 for 1 hour. The reaction mixture was then concentrated *in vacuo* when TLC indicated full conversion of the starting material. The crude was purified by flash column chromatography (EtOAc:hexane 1:20), affording methyl lactone **13** (304 mg, 0.493 mmol, 54%) as a colorless oil: $[\alpha]^{20}_{D}$ = +62.0° (c 0.0025 g/mL, $CHCl_3$); ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.73 – 7.67 (m, 4H), 7.46 – 7.41 (m, 2H), 7.40 – 7.36 (m, 4H), 5.01 (s, 1H), 4.90 (s, 1H), 4.90 – 4.84 (m, 1H), 4.72 (s, 1H), 4.59 – 4.53 (m, 1H), 3.06 (dd, *J* = 11.6, 5.0 Hz, 1H), 2.80 (br s, 1H), 2.66 (app p, *J* = 7.8 Hz, 1H), 2.21 (dd, *J* = 10.5, 7.8 Hz, 1H), 2.11 (dd, *J* = 11.6, 11.6 Hz, 1H), 1.93 (dt, *J* = 11.6, 6.0 Hz, 1H), 1.83 (td, *J* = 11.6, 8.3 Hz, 1H), 1.69 (dd, *J* = 2.5, 1.1 Hz, 3H), 1.32 (d, *J* = 7.8 Hz, 3H), 1.10 (s, 9H), 0.94 (t, *J* = 8.0 Hz, 9H), 0.61 (q, *J* = 8.0 Hz, 6H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 179.6, 142.3, 140.1, 138.5, 136.1, 136.1, 134.6, 134.2, 129.8, 129.8, 127.7, 127.7, 113.4, 78.7, 77.6, 63.9, 49.7, 48.4, 45.4, 39.9, 39.3, 27.1, 19.5, 12.9, 12.4, 7.3, 5.6. IR (thin film, cm^{-1}) 3072, 2957, 2933, 2876, 2856, 1776, 1467, 1589, 1471, 1458; HRMS (EI) calcd. for [$C_{37}H_{52}O_4Si_2$]: m/z 616.3404, found 616.3400.

[When the reaction was not stopped after completion, over reduction could afford 0~10% double-reduction product **SI-11** (see below), which was inseparable from **13**.]



Double-reduction product SI-11: A flame-dried 10 mL round-bottom flask equipped with a stir bar was charged with unsaturated lactone **11** (21.0 mg, 0.0341 mmol) and PtO_2 (1.0 mg, 0.0044 mmol). The flask was placed under vacuum and back-filled with H_2. Anhydrous methanol (0.5 mL) was added and the reaction was cooled to 0 °C. The reaction mixture was bubbled with H_2 until a black suspension formed, and was then stirred under 1 atmosphere of H_2 for 2 hours. After the reaction was complete as indicated by TLC (EtOAc:hexane 1:5), the reaction mixture was filtered through a pad of Celite® and concentrated *in vacuo*. The crude was purified by flash column chromatography (EtOAc:hexane 1:20), affording double-reduction product **SI-11** (14.1 mg, 0.0228 mmol, 67%) as a colorless oil: $[\alpha]_D^{20}$ = +28.4° (c 0.005 g/mL, $CHCl_3$); ^{1}H NMR (600 MHz, $CDCl_3$) δ 7.73 – 7.65 (m, 4H), 7.46 – 7.40 (m, 2H), 7.41 – 7.34 (m, 4H), 5.04 (ddd, *J* = 11.5, 10.3, 4.2 Hz, 1H), 4.71 (s, 1H), 4.50 (br t, *J* = 7.2 Hz, 1H), 2.66 (app p, *J* = 8.0 Hz, 1H), 2.50 (dddd, *J* = 11.4, 7.0, 2.5, 2.5 Hz, 1H), 2.34 (ddd, *J* = 12.8, 4.2, 4.2 Hz, 1H), 2.08 (dd, *J* = 10.3, 8.7 Hz, 1H), 1.89 – 1.81 (m, 2H), 1.69 (dd, *J* = 2.5, 1.1 Hz, 3H), 1.59 – 1.48 (m, 2H), 1.35 (d, *J* = 7.8 Hz, 3H), 1.09 (s, 9H), 1.06 (d, *J* = 7.3 Hz, 3H), 1.00 (t, *J* = 8.0 Hz, 9H), 0.78 – 0.66 (m, 6H); ^{13}C NMR (150 MHz, $CDCl_3$) δ 179.9, 141.8, 139.7, 136.2, 136.1, 134.7, 134.4, 129.8, 129.7, 127.7, 127.6, 79.3, 77.1, 64.0, 49.7, 49.7, 42.2, 40.1, 39.7, 31.3, 27.1, 19.5, 13.9, 13.5, 13.2, 7.6, 5.9; IR (thin film, cm^{-1}) 3072, 3049, 2958, 2932, 2877, 2856, 1776, 1740, 1458, 1428; HRMS (EI) calcd. for [$C_{37}H_{54}O_4Si_2$]: m/z 618.3561, found 618.3548.

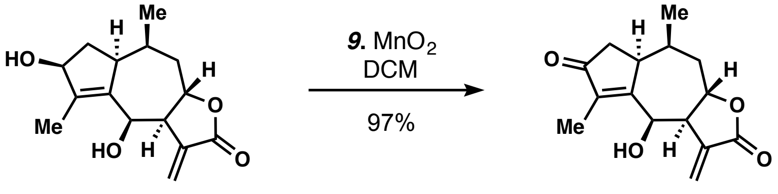


Diol SI-12: [Condition 1] A flame-dried reaction tube was charged with a stir bar and mono-reduction product **12** (100 mg, 0.154 mmol) in THF (1 mL). The reaction was cooled to 0 °C and TBAF (0.46 mL, 0.46 mmol, 1M in THF) was added dropwise. The resulting mixture was warmed to room temperature and stirred overnight. After the reaction was complete as indicated by TLC (pure EtOAc), acetic acid (54 μL) was added to quench the reaction. The reaction mixture was concentrated *in vacuo*, and the crude was purified by flash column chromatography (EtOAc:hexane 3:1), affording a mixture of **SI-12** and **SI-13** (33.9 mg, 0.128 mmol, 83%, 5:2 **SI-12**:**SI-13**). The mixture could be separated by preparative TLC (acetone:toluene 1:4, developed 3 times).

[Condition 2] Mono-reduction product **12** (28 mg, 0.043 mmol) was treated similarly with TBAF (0.13 mL, 0.13 mmol, 1M in THF) as in Condition 1. After desilylation was complete as indicated by TLC, the reaction was cooled to 0 °C and LiHMDS (0.13 mL, 0.13 mmol, 1M in THF) was added dropwise. The resulting mixture was further stirred for 20 minutes, followed by addition of acetic acid (25 μL) to quench the reaction. The crude was purified by flash column chromatography affording diol **SI-12** (6.4 mg, 0.024 mmol, 56%) without any **SI-13** observed.

[Condition 3] A flame-dried 250 mL round-bottom flask was charged with a stir bar and mono-reduction product **12** (3.90 g, 6.00 mmol) in THF (100 mL). TBAF (24 mL, 24 mmol, 1 M in THF) was added at 0 °C and the resulting mixture was stirred for 24 hours at room temperature. Acetic acid (0.5 mL) was added to the reaction. The reaction mixture was concentrated *in vacuo* and then re-dissolved in DCM (20 mL) and toluene (120 ml). DBU (1.0 mL, 6.6 mmol) was added to the reaction and the flask was equipped with a reflux condenser and heated at 120 °C for 24 hours. The crude after concentrating *in vacuo* was purified by flash column chromatography (pure EtOAc), affording diol **SI-12** (1.09 g, 4.12 mmol, 69%) which contained up to 3% **SI-13**.

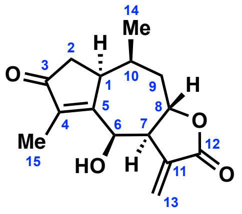
Diol **SI-12**, colorless oil: $[\alpha]_D^{20}$ = +96.8° (c 0.005 g/mL, MeOH); ^{1}H NMR (600 MHz, CDCl$_3$) δ 6.37 (d, *J* = 3.4 Hz, 1H), 5.64 (d, *J* = 3.1 Hz, 1H), 4.91 (s, 1H), 4.80 (ddd, *J* = 12.6, 9.6, 3.7 Hz, 1H), 4.52 (dd, J = 8.0, 5.1 Hz, 1H), 2.87 – 2.82 (m, 1H), 2.80 (dddd, J = 9.6, 3.4, 3.1, 1.6 Hz, 1H), 2.53 (ddd, J = 14.0, 8.4, 8.0 Hz, 1H), 2.39 (ddd, J = 12.6, 3.7, 3.7 Hz, 1H), 2.06 – 1.99 (m, 1H), 1.90 (d, J = 2.2 Hz, 3H), 1.80 (ddd, J = 12.6, 12.6, 3.7 Hz, 1H), 1.41 (ddd, J = 14.0, 6.1, 5.1 Hz, 1H), 0.98 (d, J = 7.3 Hz, 3H); ^{13}C NMR (150 MHz, $CDCl_3$) δ 169.8, 145.1, 139.4, 137.1, 120.4, 79.0, 75.6, 63.5, 51.2, 50.4, 40.9, 38.8, 32.8, 13.5, 12.6; IR (thin film, cm^{-1}) 3448, 2960, 2924, 2877, 2855, 1748, 1662, 1463, 1404, 1384; HRMS (EI) calcd. for [$C_{15}H_{20}O_4$]: m/z 264.1362, found 264.1355. [Note: Diol **SI-12** is unstable in chloroform at room temperature.]



SI-12 **1**

Mikanokryptin (1): An oven-dried 100 mL round bottom flask was charged with a stir bar, diol **SI-12** (1.088 g, 4.116 mmol), and DCM (50 mL). Activated MnO_2 (10.7 g, 123 mmol) was added in one portion. The resulting mixture was stirred vigorously at room temperature for 16 hours. The reaction was monitored by TLC (pure EtOAc), and filtered through a pad of Celite® when complete conversion was observed. The filtrate was concentrated *in vacuo*, affording spectroscopically pure mikanokryptin (1.051 g, 4.007 mmol, 97%) as a light-yellow to white solid: mp 230.5 – 232.4 °C; $[\alpha]^{20}_{D}$ = +235.0° (lit. +264°, c 0.00098 g/mL, MeOH); ^{1}H NMR (600 MHz, $CDCl_3$) δ 6.46 (d, J = 3.5 Hz, 1H), 5.70 (d, J = 3.1 Hz, 1H), 5.17 (br s, 1H), 4.80 (ddd, J = 12.6, 9.6, 3.5 Hz, 1H), 3.15 – 3.10 (m, 1H), 3.06 (dddd, J = 9.6, 3.5, 3.1, 1.9 Hz, 1H), 2.67 (ddd, J = 19.1, 6.9, 1.1 Hz, 1H), 2.45 (ddd, J = 12.8, 3.5, 3.5 Hz, 1H), 2.34 – 2.27 (m, 1H), 2.19 (dd, J = 19.1, 1.9 Hz, 1H), 1.94 (ddd, J = 12.8, 12.6, 4.1 Hz, 1H), 1.92 (dd, J = 2.1, 0.9 Hz, 3H), 0.85 (d, J = 7.3 Hz, 3H); ^{1}H NMR (600 MHz, DMSO-d_6) δ 6.20 (d, J = 3.4 Hz, 1H), 5.80 (d, J = 3.1 Hz, 1H), 5.74 (d, J = 6.5 Hz, 1H), 5.09 (d, J = 6.5 Hz, 1H), 4.64 (ddd, J = 12.5, 9.4, 3.4 Hz, 1H), 3.24 – 3.14 (m, 2H), 2.55 (dd, J = 19.0, 6.7 Hz, 1H), 2.21 (ddd, J = 12.0, 3.4, 3.4 Hz, 1H), 2.19 – 2.15 (m, 1H), 2.05 (dd, J = 19.0, 1.9 Hz, 1H), 1.94 (ddd, J = 12.5, 12.0, 4.0 Hz, 1H), 1.76 (d, J = 1.0 Hz, 3H), 0.73 (d, J = 7.1 Hz, 3H); ^{13}C NMR (150 MHz, DMSO-d_6) δ 207.2, 172.5, 169.5, 141.5, 136.5, 120.8, 75.0, 62.7, 49.5, 44.2, 40.9, 39.4, 32.4, 12.5, 8.6; IR (thin film, cm^{-1}) 3434, 2961, 2924, 2882, 1762, 1679, 1633, 1450, 1407, 1385, 1325; HRMS (EI) calcd. for [$C_{15}H_{18}O_4$]: m/z 262.1205, found 262.1207.

Table S2. ^{1}H NMR comparison of natural and synthetic mikanokryptin (**1**).



mikanokryptin (**1**)

	mikanokryptin (**1**)[1]	mikanokryptin (**1**) this work[2]	mikanokryptin (**1**)[3]	mikanokryptin (**1**) this work
C	90 MHz, *d*-DMSO	600 MHz, *d*-DMSO	200 MHz, 95% $CDCl_3$ – 5% *d*-DMSO	600 MHz, $CDCl_3$
1	3.16 (m, 1H)	3.19 (m, 1H)	3.12 (ddddd, *J* = 6.8, 2.2, 2.0, 2.0, 1.0 Hz, 1H)	3.12 (m, 1H)
2α	obscured signal	2.55 (dd, *J* = 19.0, 6.7 Hz, 1H)	2.65 (ddd, *J* = 19.1, 6.8, 1.1 Hz, 1H)	2.67 (ddd, *J* = 19.1, 6.9, 1.1 Hz, 1H)
2β	obscured signal	2.05 (dd, *J* = 19.0, 1.9 Hz, 1H)	2.17 (dd, *J* = 19.1, 2.0 Hz, 1H)	2.19 (dd, *J* = 19.1, 1.9 Hz, 1H)
6	5.10 (br d, *J* = 6.2 Hz, 1H)	5.09 (d, *J* = 6.5 Hz, 1H)	5.13 (ddddd, *J* = 5.6, 3.5, 1.1, 1.0, 0.8 Hz, 1H)	5.17 (br s, 1H)
7	3.16 (m, 1H)	3.19 (m, 1H)	3.01 (dddd, *J* = 9.6, 3.5, 3.4, 3.0 Hz, 1H)	3.06 (dddd, *J* = 9.6, 3.5, 3.1, 1.9 Hz, 1H)
8	4.66 (ddd, *J* = 12, 10, 3.7 Hz, 1H)	4.64 (ddd, *J* = 12.5, 9.4, 3.4 Hz, 1H)	4.84 (ddd, *J* = 12.1, 9.6, 3.5 Hz, 1H)	4.80 (ddd, *J* = 12.6, 9.6, 3.5 Hz, 1H)
9α	obscured signal	1.94 (ddd, *J* = 12.5, 12.0, 4.0 Hz, 1H)	1.92 (ddd, *J* = 12.6, 12.1, 3.9 Hz, 1H)	1.94 (ddd, *J* = 12.8, 12.6, 4.1 Hz, 1H)
9β	obscured signal	2.21 (ddd, *J* = 12.0, 3.4, 3.4 Hz, 1H)	2.42 (ddd, *J* = 12.6, 3.5, 3.5 Hz, 1H)	2.45 (ddd, *J* = 12.8, 3.5, 3.5 Hz, 1H)
10	obscured signal	2.17 (m, 1H)	2.29 (dddd, *J* = 7.3, 3.9, 3.5, 2.2 Hz, 1H)	2.31 (m, 1H)
13_{cis}	6.24 (d, *J* = 3.5 Hz, 1H)	6.20 (d, *J* = 3.4 Hz, 1H)	6.40 (d, *J* = 3.4 Hz, 1H)	6.46 (d, *J* = 3.5 Hz, 1H)
13_{trans}	5.81 (d, *J* = 3.1 Hz, 1H)	5.80 (d, *J* = 3.1 Hz, 1H)	5.72 (d, *J* = 3.0 Hz, 1H)	5.70 (d, *J* = 3.1 Hz, 1H)
14	0.69 (d, *J* = 7.2 Hz, 1H)	0.73 (d, *J* = 7.1 Hz, 3H)	1.90 (dd, *J* = 2.0, 0.8 Hz, 3H)	1.92 (dd, *J* = 2.1, 0.9 Hz, 3H)
15	1.74 (dd, *J* = 1, 0.9 Hz, 1H)	1.76 (d, *J* = 1.0 Hz, 3H)	0.86 (d, *J* = 7.3 Hz, 3H)	0.85 (d, *J* = 7.3 Hz, 3H)
OH	5.60 (d, *J* = 6.2 Hz, 1H)	5.74 (d, *J* = 6.5 Hz, 1H)	4.54 (d, *J* = 5.6 Hz, 1H)	not observed

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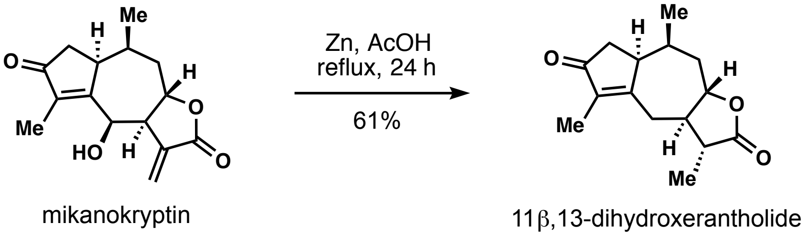
[1] W. Herz, A. Srinivasan, P. S. Kalyanaraman, *Phytochemistry* **1975**, *14*, 233.

[2] Crystallographic Analysis of synthetic **1** matches with that reported in: M. J. Bovill, M. H. P. Guy, G. A. Sim, D. N. J. White, W. Herz, *J. Chem. Soc., Perkin Trans. 2* **1979**, 53.

[3] W. F. Reynolds, R. G. Enriquez, M. A. Chavez, A. L. Silba, M. A. Martinez, *Can. J. Chem.* **1985**, *63*, 849. Standard inversion-recovery pulse sequence was utilized by choosing a delay time (0.88 s) for which the methyl signal is nulled. For details, see the original paper.



11β,13-dihydroxerantholide: This procedure was adapted from previous conditions reported by Barton and coworkers.[1]

A flame-dried reaction tube equipped with a stir bar was charged with mikanokryptin (26.0 mg, 0.0991 mmol) and activated zinc powder (98 mg, 1.5 mmol). The tube was placed under vacuum and back-filled with N_2, followed by the addition of degassed acetic acid (0.8 mL). The reaction was heated at 120 °C for 24 hours, diluted with ethyl acetate and filtered through a pad of Celite®. The filtrate was concentrated *in vacuo* and purified by flash column chromatography (EtOAc:hexane 1:1), affording 11β,13-dihydroxerantholide (15.0 mg, 0.0604 mmol, 61%) as a colorless oil: $[\alpha]_D^{20}$ = +153.1° (c= 0.01 g/mL, $CHCl_3$); ^{1}H NMR (600 MHz, $CDCl_3$) δ 4.15 (ddd, *J* = 12.1, 10.0, 3.7 Hz, 1H), 3.13 (dq, *J* = 6.6, 2.0 Hz, 1H), 2.98 (ddd, *J* = 19.0, 3.2, 1.6 Hz, 1H), 2.62 (ddd, *J* = 19.0, 6.6, 1.2 Hz, 1H), 2.42 – 2.34 (m, 3H), 2.29 – 2.23 (m, 1H), 2.13 – 2.06 (m, 2H), 1.81 (ddd, *J* = 12.1, 12.1, 4.1 Hz, 1H), 1.70 (q, *J* = 1.5 Hz, 3H), 1.28 (d, *J* = 7.0 Hz, 3H), 0.73 (d, *J* = 7.3 Hz, 3H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 207.2, 178.1, 170.6, 139.5, 81.4, 48.1, 45.2, 42.1, 41.4, 40.5, 33.0, 31.4, 13.0, 13.0, 8.3; IR (thin film, cm^{-1}) 2965, 2931, 2876, 1771, 1695, 1636, 1456, 1383; HRMS (ESI) calcd. for $[C_{15}H_{20}NaO_3]^+$ $(M+Na)^+$: m/z 271.1310, found 271.1315.

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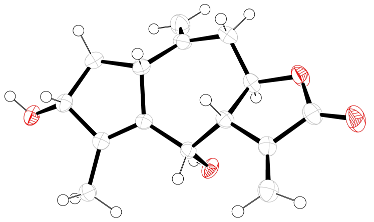
[1] D. H. R. Barton, J. E. D. Levisalles, *J. Chem. Soc.* **1958**, 4518-4523.

X-Ray Crystallographic Analysis of Desilylated (–)-11



A colorless blade 0.070 x 0.040 x 0.020 mm in size was mounted on a Cryoloop with Paratone oil. Data were collected in a nitrogen gas stream at 100(2) K using and scans. Crystal-to-detector distance was 60 mm and exposure time was 5 seconds per frame using a scan width of 2.0°. Data collection was 100.0% complete to 67.000° in θ. A total of 22793 reflections were collected covering the indices, -8<=*h*<=8, -9<=*k*<=9, -15<=*l*<=14. 2366 reflections were found to be symmetry independent, with an R_{int} of 0.0609. Indexing and unit cell refinement indicated a primitive, monoclinic lattice. The space group was found to be P 21 (No. 4). The data were integrated using the Bruker SAINT software program and scaled using the SADABS software program. Solution by iterative methods (SHELXT-2014) produced a complete heavy-atom phasing model consistent with the proposed structure. All non-hydrogen atoms were refined anisotropically by full-matrix least-squares (SHELXL-2014). 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. Absolute stereochemistry was unambiguously determined to be *R* at C1, C3, C7, and C10, and *S* at C6, respectively.

Table 1. Crystal data and structure refinement for Desilylated (–)-11.

X-ray ID	maimone75	
Sample/notebook ID	XH_183_tbaf	
Empirical formula	C15 H18 O4	
Formula weight	262.29	
Temperature	100(2) K	
Wavelength	1.54178 Å	
Crystal system	Monoclinic	
Space group	P 21	
Unit cell dimensions	a = 6.7293(2) Å	α= 90°.
	b = 7.8229(2) Å	β= 101.647(2)°.
	c = 12.5521(4) Å	γ = 90°.
Volume	647.17(3) Å^3	
Z	2	
Density (calculated)	1.346 Mg/m^3	
Absorption coefficient	0.796 mm^{-1}	
F(000)	280	
Crystal size	0.070 x 0.040 x 0.020 mm^3	
Theta range for data collection	3.595 to 68.310°.	
Index ranges	-8<=h<=8, -9<=k<=9, -15<=l<=14	
Reflections collected	22793	
Independent reflections	2366 [R(int) = 0.0609]	
Completeness to theta = 67.000°	100.0 %	
Absorption correction	Semi-empirical from equivalents	
Max. and min. transmission	0.929 and 0.795	
Refinement method	Full-matrix least-squares on F^2	
Data / restraints / parameters	2366 / 1 / 175	
Goodness-of-fit on F^2	1.070	
Final R indices [I>2sigma(I)]	R1 = 0.0391, wR2 = 0.0958	
R indices (all data)	R1 = 0.0420, wR2 = 0.0980	
Absolute structure parameter	0.07(10)	
Extinction coefficient	n/a	
Largest diff. peak and hole	0.245 and -0.147 e.Å^{-3}	

Table 2. Atomic coordinates (x 10^4) and equivalent isotropic displacement parameters ($Å^2$x 10^3) for maimone75. U(eq) is defined as one third of the trace of the orthogonalized U^{ij} tensor.

	x	y	z	U(eq)
C(1)	3592(4)	2776(3)	2431(2)	24(1)
C(2)	4225(4)	1126(3)	3061(2)	27(1)
C(3)	2723(4)	934(3)	3818(2)	25(1)
C(4)	2224(4)	2767(3)	4032(2)	23(1)
C(5)	2657(4)	3791(3)	3254(2)	22(1)
C(6)	2056(4)	5653(3)	3144(2)	22(1)
C(7)	1731(4)	6226(3)	1953(2)	23(1)
C(8)	592(4)	7864(4)	1641(2)	25(1)
C(9)	1523(4)	8701(4)	802(2)	31(1)
C(10)	3699(4)	6517(4)	1540(2)	27(1)
C(11)	4542(4)	4963(4)	1075(2)	30(1)
C(12)	5241(4)	3644(4)	1951(2)	27(1)
C(13)	1249(4)	3212(4)	4963(2)	30(1)
C(14)	-1064(4)	8497(4)	1939(2)	32(1)
C(15)	7196(5)	3252(4)	2233(3)	39(1)
O(1)	3213(3)	7836(3)	702(2)	33(1)
O(2)	3494(3)	19(2)	4790(2)	29(1)
O(3)	3510(3)	6735(2)	3824(2)	30(1)
O(4)	963(3)	9956(3)	265(2)	41(1)

Table 3. Bond lengths [Å] and angles [°] for maimone75.

C(1)-C(12)	1.525(4)	C(8)-C(9)	1.483(4)
C(1)-C(2)	1.529(4)	C(9)-O(4)	1.207(4)
C(1)-C(5)	1.534(4)	C(9)-O(1)	1.351(4)
C(1)-H(1)	1.0000	C(10)-O(1)	1.463(3)
C(2)-C(3)	1.528(4)	C(10)-C(11)	1.509(4)
C(2)-H(2A)	0.9900	C(10)-H(10)	1.0000
C(2)-H(2B)	0.9900	C(11)-C(12)	1.512(4)
C(3)-O(2)	1.420(3)	C(11)-H(11A)	0.9900
C(3)-C(4)	1.509(4)	C(11)-H(11B)	0.9900
C(3)-H(3)	1.0000	C(12)-C(15)	1.327(4)
C(4)-C(5)	1.340(4)	C(13)-H(13A)	0.9800
C(4)-C(13)	1.492(4)	C(13)-H(13B)	0.9800
C(5)-C(6)	1.511(4)	C(13)-H(13C)	0.9800
C(6)-O(3)	1.438(3)	C(14)-H(14A)	0.9500
C(6)-C(7)	1.533(4)	C(14)-H(14B)	0.9500
C(6)-H(6)	1.0000	C(15)-H(15A)	0.9500
C(7)-C(8)	1.503(4)	C(15)-H(15B)	0.9500
C(7)-C(10)	1.533(3)	O(2)-H(2)	0.8400
C(7)-H(7)	1.0000	O(3)-H(3A)	0.8400
C(8)-C(14)	1.339(4)		

C(12)-C(1)-C(2)	115.6(2)	O(2)-C(3)-C(2)	114.3(2)
C(12)-C(1)-C(5)	117.7(2)	C(4)-C(3)-C(2)	102.5(2)
C(2)-C(1)-C(5)	101.4(2)	O(2)-C(3)-H(3)	109.1
C(12)-C(1)-H(1)	107.1	C(4)-C(3)-H(3)	109.1
C(2)-C(1)-H(1)	107.1	C(2)-C(3)-H(3)	109.1
C(5)-C(1)-H(1)	107.1	C(5)-C(4)-C(13)	128.7(3)
C(3)-C(2)-C(1)	104.7(2)	C(5)-C(4)-C(3)	110.4(2)
C(3)-C(2)-H(2A)	110.8	C(13)-C(4)-C(3)	120.7(2)
C(1)-C(2)-H(2A)	110.8	C(4)-C(5)-C(6)	123.3(2)
C(3)-C(2)-H(2B)	110.8	C(4)-C(5)-C(1)	111.1(2)
C(1)-C(2)-H(2B)	110.8	C(6)-C(5)-C(1)	125.2(2)
H(2A)-C(2)-H(2B)	108.9	O(3)-C(6)-C(5)	112.1(2)
O(2)-C(3)-C(4)	112.4(2)	O(3)-C(6)-C(7)	110.7(2)

C(5)-C(6)-C(7)	110.7(2)
O(3)-C(6)-H(6)	107.7
C(5)-C(6)-H(6)	107.7
C(7)-C(6)-H(6)	107.7
C(8)-C(7)-C(6)	117.9(2)
C(8)-C(7)-C(10)	102.4(2)
C(6)-C(7)-C(10)	114.2(2)
C(8)-C(7)-H(7)	107.2
C(6)-C(7)-H(7)	107.2
C(10)-C(7)-H(7)	107.2
C(14)-C(8)-C(9)	122.0(3)
C(14)-C(8)-C(7)	130.7(3)
C(9)-C(8)-C(7)	107.1(2)
O(4)-C(9)-O(1)	121.9(3)
O(4)-C(9)-C(8)	128.8(3)
O(1)-C(9)-C(8)	109.2(2)
O(1)-C(10)-C(11)	109.7(2)
O(1)-C(10)-C(7)	105.4(2)
C(11)-C(10)-C(7)	115.4(2)
O(1)-C(10)-H(10)	108.7
C(11)-C(10)-H(10)	108.7
C(7)-C(10)-H(10)	108.7
C(10)-C(11)-C(12)	110.7(2)
C(10)-C(11)-H(11A)	109.5
C(12)-C(11)-H(11A)	109.5
C(10)-C(11)-H(11B)	109.5
C(12)-C(11)-H(11B)	109.5
H(11A)-C(11)-H(11B)	108.1
C(15)-C(12)-C(11)	119.9(3)
C(15)-C(12)-C(1)	123.5(3)
C(11)-C(12)-C(1)	116.5(2)
C(4)-C(13)-H(13A)	109.5
C(4)-C(13)-H(13B)	109.5
H(13A)-C(13)-H(13B)	109.5
C(4)-C(13)-H(13C)	109.5
H(13A)-C(13)-H(13C)	109.5
H(13B)-C(13)-H(13C)	109.5
C(8)-C(14)-H(14A)	120.0
C(8)-C(14)-H(14B)	120.0
H(14A)-C(14)-H(14B)	120.0
C(12)-C(15)-H(15A)	120.0
C(12)-C(15)-H(15B)	120.0
H(15A)-C(15)-H(15B)	120.0
C(9)-O(1)-C(10)	110.9(2)
C(3)-O(2)-H(2)	109.5
C(6)-O(3)-H(3A)	109.5

Symmetry transformations used to generate equivalent atoms:

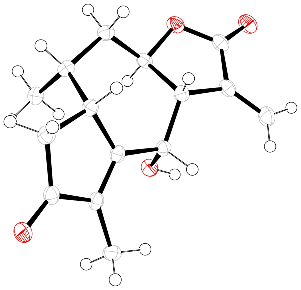
Table 4. Anisotropic displacement parameters ($Å^2 x 10^3$) for maimone75. The anisotropic displacement factor exponent takes the form: $-2\pi^2[h^2a^{*2}U^{11} + ... + 2 h k a^* b^* U^{12}]$

	U^{11}	U^{22}	U^{33}	U^{23}	U^{13}	U^{12}
C(1)	25(1)	24(1)	23(1)	-4(1)	4(1)	0(1)
C(2)	28(1)	25(1)	28(2)	-5(1)	4(1)	2(1)
C(3)	28(1)	23(1)	22(1)	-2(1)	-1(1)	-3(1)
C(4)	22(1)	24(1)	21(1)	-1(1)	0(1)	-1(1)
C(5)	21(1)	24(1)	18(1)	-3(1)	2(1)	-2(1)
C(6)	25(1)	22(1)	19(1)	0(1)	4(1)	-1(1)
C(7)	24(1)	27(1)	18(1)	-1(1)	2(1)	-2(1)
C(8)	29(1)	27(1)	17(1)	0(1)	-2(1)	-3(1)
C(9)	31(1)	37(2)	22(1)	5(1)	1(1)	-1(1)
C(10)	27(1)	31(1)	23(1)	5(1)	5(1)	-1(1)
C(11)	30(1)	37(2)	24(1)	1(1)	9(1)	-2(1)
C(12)	29(1)	30(1)	25(1)	-4(1)	10(1)	-1(1)
C(13)	39(1)	26(1)	25(1)	4(1)	10(1)	3(1)
C(14)	32(1)	35(2)	27(1)	5(1)	1(1)	4(1)
C(15)	33(2)	41(2)	44(2)	4(2)	12(1)	0(1)
O(1)	36(1)	38(1)	28(1)	12(1)	11(1)	3(1)
O(2)	36(1)	20(1)	29(1)	1(1)	0(1)	-1(1)
O(3)	42(1)	20(1)	23(1)	-2(1)	-4(1)	1(1)
O(4)	44(1)	43(1)	34(1)	18(1)	5(1)	7(1)

Table 5. Hydrogen coordinates (x 10^4) and isotropic displacement parameters ($Å^2$x 10^3) for maimone75.

	x	y	z	U(eq)
H(1)	2463	2478	1810	29
H(2A)	4135	139	2560	33
H(2B)	5632	1213	3484	33
H(3)	1471	351	3417	30
H(6)	734	5778	3383	27
H(7)	967	5295	1500	28
H(10)	4753	6974	2152	32
H(11A)	5699	5304	744	36
H(11B)	3484	4459	497	36
H(13A)	993	4446	4962	44
H(13B)	2152	2889	5647	44
H(13C)	-39	2595	4891	44
H(14A)	-1676	9512	1609	38
H(14B)	-1625	7931	2479	38
H(15A)	8152	3799	1885	46
H(15B)	7639	2424	2784	46
H(2)	3567	-1025	4647	43
H(3A)	4422	6129	4199	44

X-Ray Crystallographic Analysis of (–)-Mikanokryptin



A colorless plate 0.050 x 0.040 x 0.020 mm in size was mounted on a Cryoloop with Paratone oil. Data were collected in a nitrogen gas stream at 100(2) K using and scans. Crystal-to-detector distance was 60 mm and exposure time was 10 seconds per frame using a scan width of 2.0°. Data collection was 99.4% complete to 67.000° in θ. A total of 33715 reflections were collected covering the indices, -8<=*h*<=11, -12<=*k*<=12, -16<=*l*<=16. 2328 reflections were found to be symmetry independent, with an R_{int} of 0.0306. Indexing and unit cell refinement indicated a primitive, orthorhombic lattice. The space group was found to be P 21 21 21 (No. 19). The data were integrated using the Bruker SAINT software program and scaled using the SADABS software program. Solution by iterative methods (SHELXT-2014) produced a complete heavy-atom phasing model consistent with the proposed structure. All non-hydrogen atoms were refined anisotropically by full-matrix least-squares (SHELXL-2014). 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. Absolute stereochemistry was unambiguously determined to be *R* at C1, C7, C10, and C12, and *S* at C6, respectively.

Table 1. Crystal data and structure refinement for maimone80.

X-ray ID	maimone80	
Sample/notebook ID	XH_5_MK	
Empirical formula	C15 H18 O4	
Formula weight	262.29	
Temperature	100(2) K	
Wavelength	1.54178 Å	
Crystal system	Orthorhombic	
Space group	P 21 21 21	
Unit cell dimensions	a = 9.3552(7) Å	α= 90°.
	b = 10.2688(8) Å	β= 90°.
	c = 13.2963(11) Å	γ = 90°.
Volume	1277.33(17) Å^3	
Z	4	
Density (calculated)	1.364 Mg/m^3	
Absorption coefficient	0.807 mm^{-1}	
F(000)	560	
Crystal size	0.050 x 0.040 x 0.020 mm^3	
Theta range for data collection	5.443 to 68.347°.	
Index ranges	-8<=h<=11, -12<=k<=12, -16<=l<=16	
Reflections collected	33715	
Independent reflections	2328 [R(int) = 0.0306]	
Completeness to theta = 67.000°	99.4 %	
Absorption correction	Semi-empirical from equivalents	
Max. and min. transmission	0.929 and 0.891	
Refinement method	Full-matrix least-squares on F^2	
Data / restraints / parameters	2328 / 0 / 175	
Goodness-of-fit on F^2	1.061	
Final R indices [I>2sigma(I)]	R1 = 0.0277, wR2 = 0.0733	
R indices (all data)	R1 = 0.0280, wR2 = 0.0736	
Absolute structure parameter	0.06(3)	
Extinction coefficient	n/a	
Largest diff. peak and hole	0.216 and -0.134 e.Å^{-3}	

Table 2. Atomic coordinates (x 10^4) and equivalent isotropic displacement parameters ($Å^2$x 10^3) for maimone80. U(eq) is defined as one third of the trace of the orthogonalized U^{ij} tensor.

	x	y	z	U(eq)
C(1)	6651(2)	8272(2)	4010(1)	19(1)
C(2)	5999(2)	8121(2)	5067(1)	22(1)
C(3)	6217(2)	6714(2)	5361(1)	20(1)
C(4)	7002(2)	6068(2)	4545(1)	19(1)
C(5)	7277(2)	6927(2)	3809(1)	18(1)
C(6)	8167(2)	6600(2)	2892(1)	18(1)
C(7)	8424(2)	7775(2)	2212(1)	18(1)
C(8)	9426(2)	7537(2)	1344(1)	21(1)
C(9)	8866(2)	8303(2)	480(1)	22(1)
C(10)	7072(2)	8261(2)	1686(1)	19(1)
C(11)	6222(2)	9273(2)	2252(1)	20(1)
C(12)	5539(2)	8746(2)	3223(1)	20(1)
C(13)	7433(2)	4665(2)	4608(1)	24(1)
C(14)	10588(2)	6812(2)	1299(2)	28(1)
C(15)	4406(2)	7707(2)	3000(2)	23(1)
O(1)	7597(1)	8839(1)	740(1)	23(1)
O(2)	5846(2)	6217(1)	6156(1)	26(1)
O(3)	7478(1)	5564(1)	2367(1)	22(1)
O(4)	9391(2)	8479(1)	-335(1)	28(1)

Table 3. Bond lengths [Å] and angles [°] for maimone80.

C(1)-C(5)	1.524(2)	C(9)-O(4)	1.204(2)
C(1)-C(2)	1.539(2)	C(9)-O(1)	1.354(2)
C(1)-C(12)	1.554(2)	C(10)-O(1)	1.475(2)
C(1)-H(1)	1.0000	C(10)-C(11)	1.510(3)
C(2)-C(3)	1.511(3)	C(10)-H(10)	1.0000
C(2)-H(2A)	0.9900	C(11)-C(12)	1.539(3)
C(2)-H(2B)	0.9900	C(11)-H(11A)	0.9900
C(3)-O(2)	1.224(2)	C(11)-H(11B)	0.9900
C(3)-C(4)	1.469(2)	C(12)-C(15)	1.533(3)
C(4)-C(5)	1.343(3)	C(12)-H(12)	1.0000
C(4)-C(13)	1.498(3)	C(13)-H(13A)	0.9800
C(5)-C(6)	1.514(2)	C(13)-H(13B)	0.9800
C(6)-O(3)	1.426(2)	C(13)-H(13C)	0.9800
C(6)-C(7)	1.527(2)	C(14)-H(14A)	0.9500
C(6)-H(6)	1.0000	C(14)-H(14B)	0.9500
C(7)-C(8)	1.507(3)	C(15)-H(15A)	0.9800
C(7)-C(10)	1.529(2)	C(15)-H(15B)	0.9800
C(7)-H(7)	1.0000	C(15)-H(15C)	0.9800
C(8)-C(14)	1.320(3)	O(3)-H(3)	0.8400
C(8)-C(9)	1.488(3)		

C(5)-C(1)-C(2)	102.79(14)	O(2)-C(3)-C(2)	125.74(17)
C(5)-C(1)-C(12)	115.01(14)	C(4)-C(3)-C(2)	107.98(15)
C(2)-C(1)-C(12)	112.37(15)	C(5)-C(4)-C(3)	109.69(17)
C(5)-C(1)-H(1)	108.8	C(5)-C(4)-C(13)	128.42(17)
C(2)-C(1)-H(1)	108.8	C(3)-C(4)-C(13)	121.86(16)
C(12)-C(1)-H(1)	108.8	C(4)-C(5)-C(6)	123.08(16)
C(3)-C(2)-C(1)	106.20(15)	C(4)-C(5)-C(1)	113.23(16)
C(3)-C(2)-H(2A)	110.5	C(6)-C(5)-C(1)	123.65(15)
C(1)-C(2)-H(2A)	110.5	O(3)-C(6)-C(5)	108.13(14)
C(3)-C(2)-H(2B)	110.5	O(3)-C(6)-C(7)	111.78(14)
C(1)-C(2)-H(2B)	110.5	C(5)-C(6)-C(7)	112.80(15)
H(2A)-C(2)-H(2B)	108.7	O(3)-C(6)-H(6)	108.0
O(2)-C(3)-C(4)	126.24(18)	C(5)-C(6)-H(6)	108.0

C(7)-C(6)-H(6)	108.0
C(8)-C(7)-C(6)	115.03(15)
C(8)-C(7)-C(10)	102.52(14)
C(6)-C(7)-C(10)	113.49(14)
C(8)-C(7)-H(7)	108.5
C(6)-C(7)-H(7)	108.5
C(10)-C(7)-H(7)	108.5
C(14)-C(8)-C(9)	123.56(18)
C(14)-C(8)-C(7)	129.77(18)
C(9)-C(8)-C(7)	106.68(16)
O(4)-C(9)-O(1)	121.86(18)
O(4)-C(9)-C(8)	129.12(19)
O(1)-C(9)-C(8)	109.02(16)
O(1)-C(10)-C(11)	108.87(15)
O(1)-C(10)-C(7)	104.25(14)
C(11)-C(10)-C(7)	115.55(14)
O(1)-C(10)-H(10)	109.3
C(11)-C(10)-H(10)	109.3
C(7)-C(10)-H(10)	109.3
C(10)-C(11)-C(12)	113.30(15)
C(10)-C(11)-H(11A)	108.9
C(12)-C(11)-H(11A)	108.9
C(10)-C(11)-H(11B)	108.9
C(12)-C(11)-H(11B)	108.9
H(11A)-C(11)-H(11B)	107.7
C(15)-C(12)-C(11)	111.65(15)
C(15)-C(12)-C(1)	112.06(15)
C(11)-C(12)-C(1)	113.37(15)
C(15)-C(12)-H(12)	106.4
C(11)-C(12)-H(12)	106.4
C(1)-C(12)-H(12)	106.4
C(4)-C(13)-H(13A)	109.5
C(4)-C(13)-H(13B)	109.5
H(13A)-C(13)-H(13B)	109.5
C(4)-C(13)-H(13C)	109.5
H(13A)-C(13)-H(13C)	109.5
H(13B)-C(13)-H(13C)	109.5
C(8)-C(14)-H(14A)	120.0
C(8)-C(14)-H(14B)	120.0
H(14A)-C(14)-H(14B)	120.0
C(12)-C(15)-H(15A)	109.5
C(12)-C(15)-H(15B)	109.5
H(15A)-C(15)-H(15B)	109.5
C(12)-C(15)-H(15C)	109.5
H(15A)-C(15)-H(15C)	109.5
H(15B)-C(15)-H(15C)	109.5
C(9)-O(1)-C(10)	110.28(14)
C(6)-O(3)-H(3)	109.5

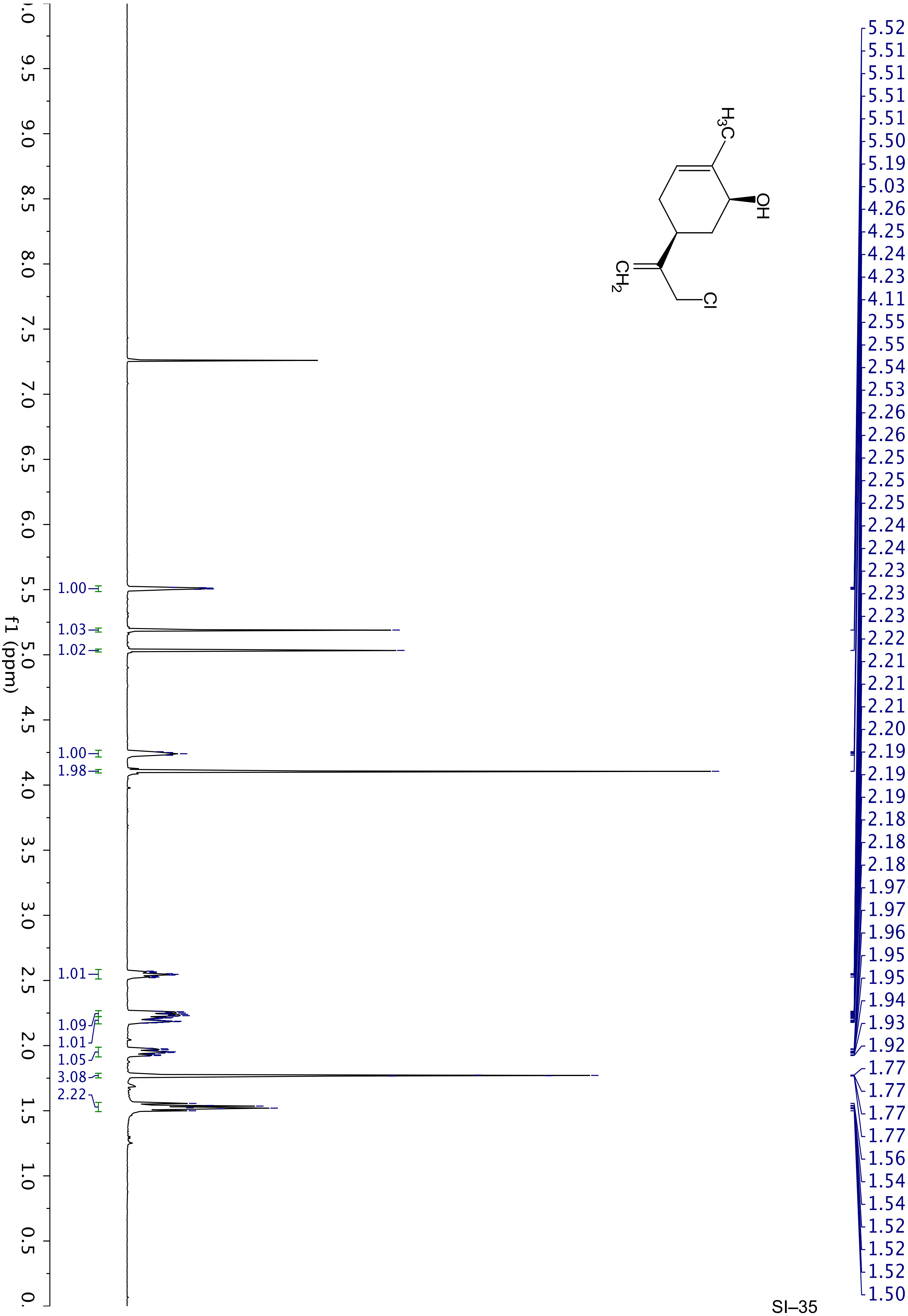
Symmetry transformations used to generate equivalent atoms:

Table 4. Anisotropic displacement parameters (Å^{2}x 10^3) for maimone80. The anisotropic displacement factor exponent takes the form: $-2\pi^2[h^2a^{*2}U^{11} + ... + 2 h k a^* b^* U^{12}]$

	U^{11}	U^{22}	U^{33}	U^{23}	U^{13}	U^{12}
C(1)	19(1)	20(1)	17(1)	-2(1)	0(1)	1(1)
C(2)	24(1)	24(1)	19(1)	-2(1)	2(1)	4(1)
C(3)	16(1)	25(1)	19(1)	0(1)	-2(1)	-1(1)
C(4)	15(1)	24(1)	19(1)	-1(1)	-1(1)	1(1)
C(5)	14(1)	22(1)	19(1)	-1(1)	-3(1)	0(1)
C(6)	16(1)	20(1)	18(1)	0(1)	-1(1)	0(1)
C(7)	18(1)	20(1)	18(1)	-1(1)	0(1)	-1(1)
C(8)	21(1)	23(1)	18(1)	-1(1)	0(1)	-6(1)
C(9)	23(1)	22(1)	21(1)	-1(1)	-1(1)	-7(1)
C(10)	20(1)	20(1)	17(1)	3(1)	-1(1)	-4(1)
C(11)	21(1)	18(1)	22(1)	2(1)	-3(1)	1(1)
C(12)	20(1)	19(1)	21(1)	0(1)	-2(1)	3(1)
C(13)	27(1)	22(1)	22(1)	4(1)	2(1)	3(1)
C(14)	24(1)	35(1)	25(1)	2(1)	7(1)	1(1)
C(15)	18(1)	25(1)	27(1)	1(1)	0(1)	1(1)
O(1)	25(1)	26(1)	18(1)	5(1)	-1(1)	-2(1)
O(2)	26(1)	31(1)	21(1)	4(1)	6(1)	2(1)
O(3)	25(1)	19(1)	21(1)	-4(1)	3(1)	-1(1)
O(4)	32(1)	33(1)	20(1)	4(1)	3(1)	-5(1)

Table 5. Hydrogen coordinates (x 10^4) and isotropic displacement parameters (Å^{2}x 10^3) for maimone80.

	x	y	z	U(eq)
H(1)	7449	8919	4044	22
H(2A)	6484	8706	5551	27
H(2B)	4968	8338	5056	27
H(6)	9117	6277	3129	22
H(7)	8818	8500	2631	22
H(10)	6441	7502	1527	23
H(11A)	5459	9612	1808	25
H(11B)	6860	10009	2425	25
H(12)	5022	9495	3539	24
H(13A)	6589	4112	4517	35
H(13B)	7859	4492	5268	35
H(13C)	8133	4473	4080	35
H(14A)	11116	6759	690	33
H(14B)	10898	6342	1875	33
H(15A)	4843	6992	2620	35
H(15B)	3633	8093	2602	35
H(15C)	4020	7371	3634	35
H(3)	8074	5185	1996	32



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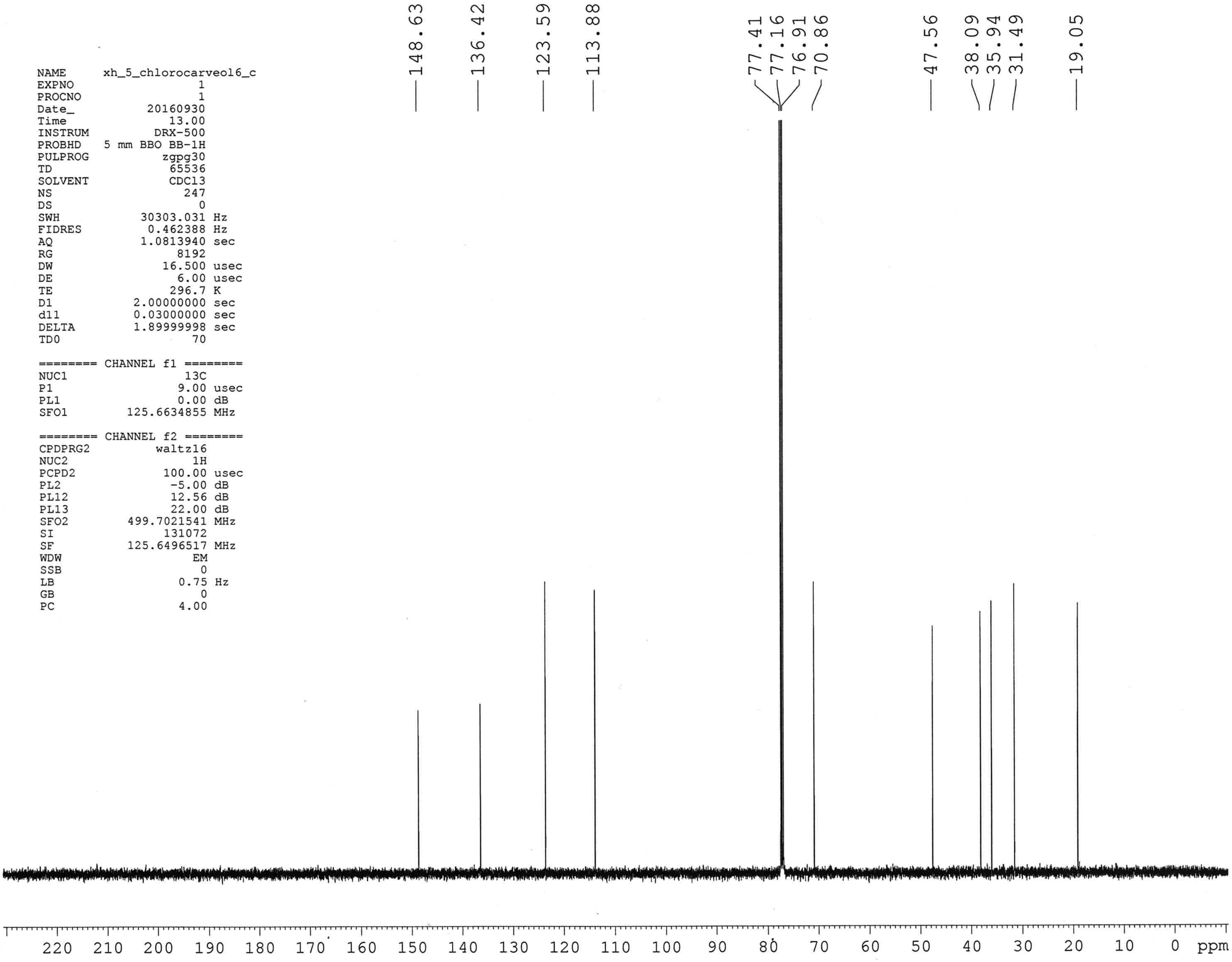

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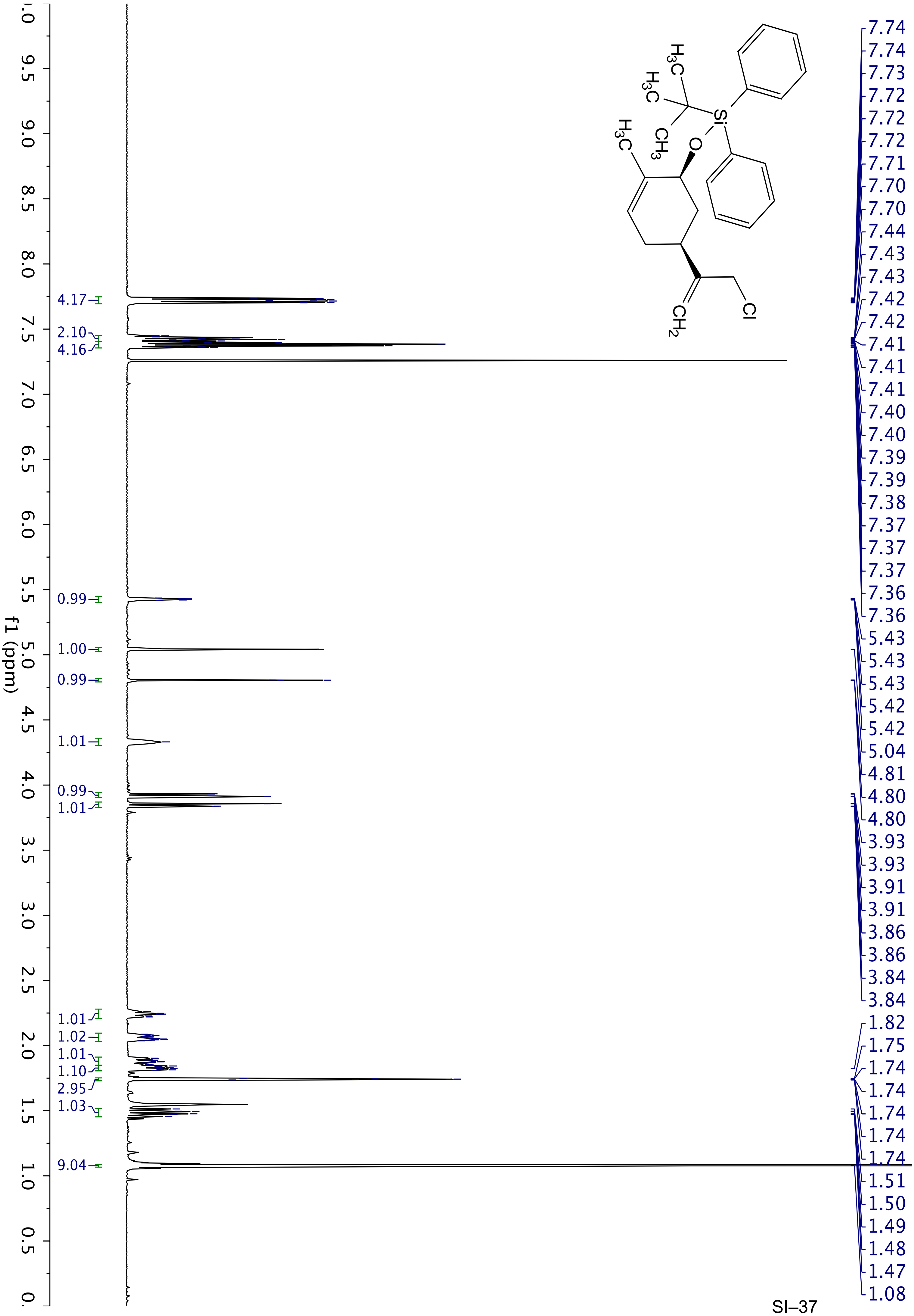
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Cl
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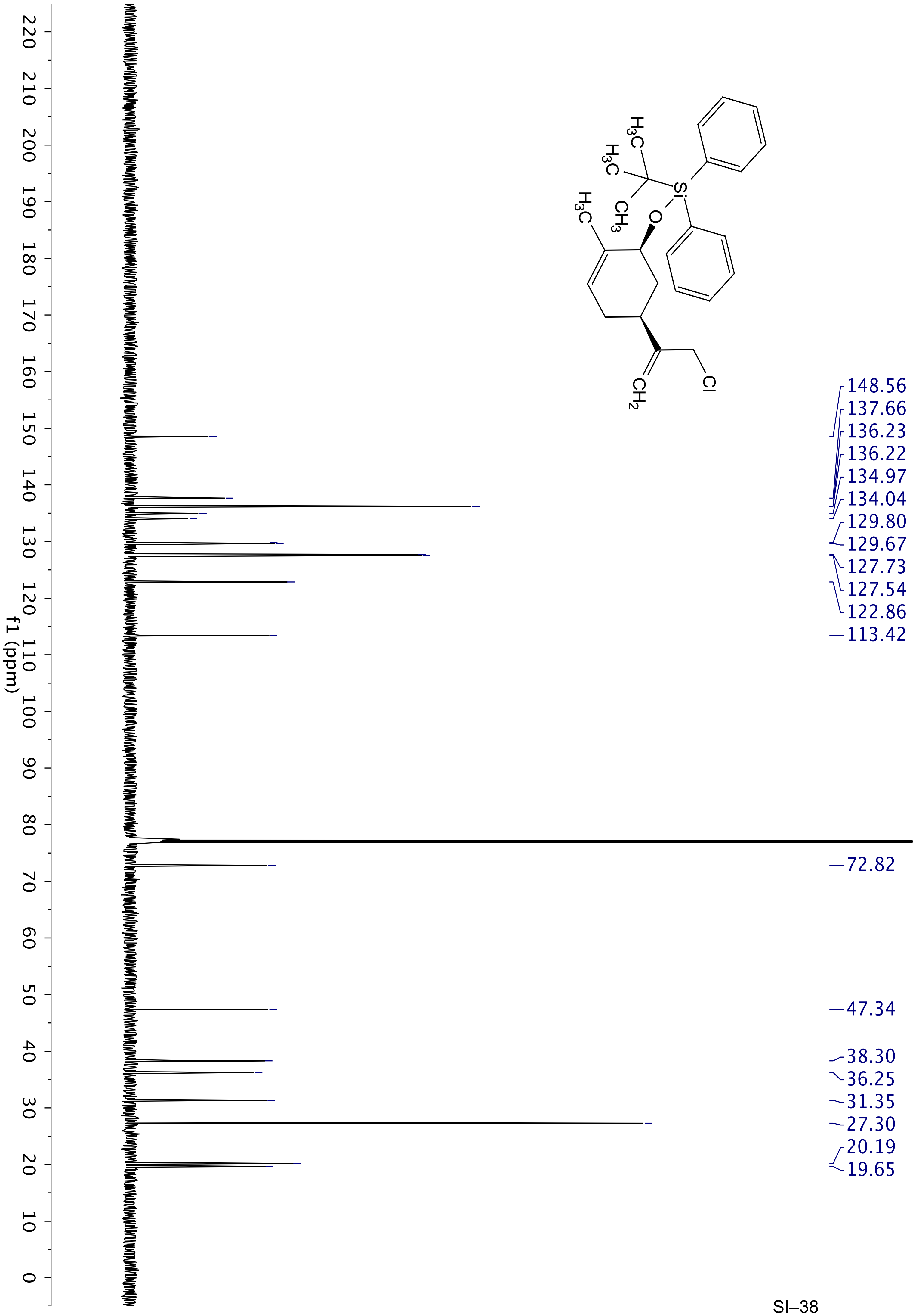
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31.35
27.30
20.19
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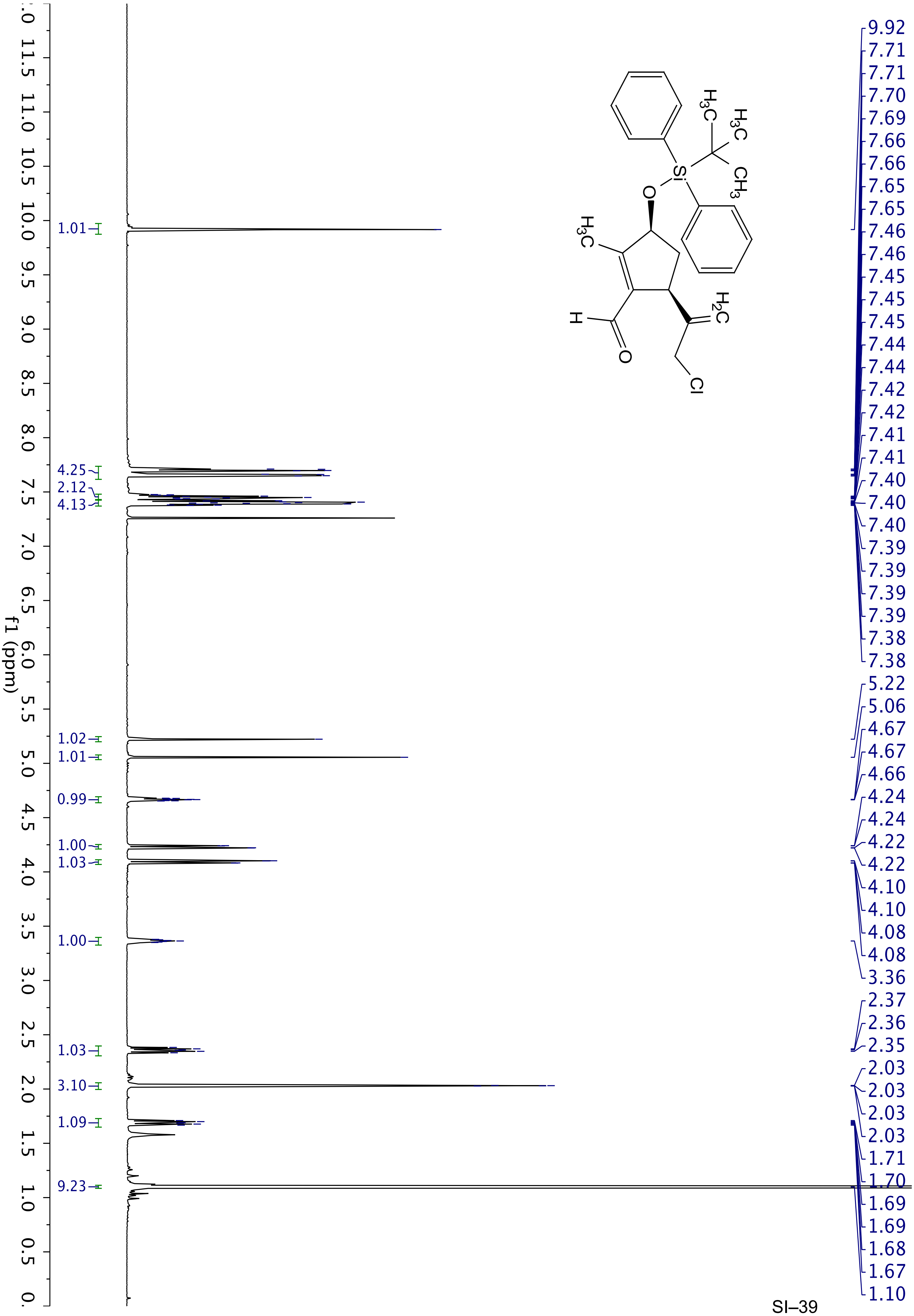9.92
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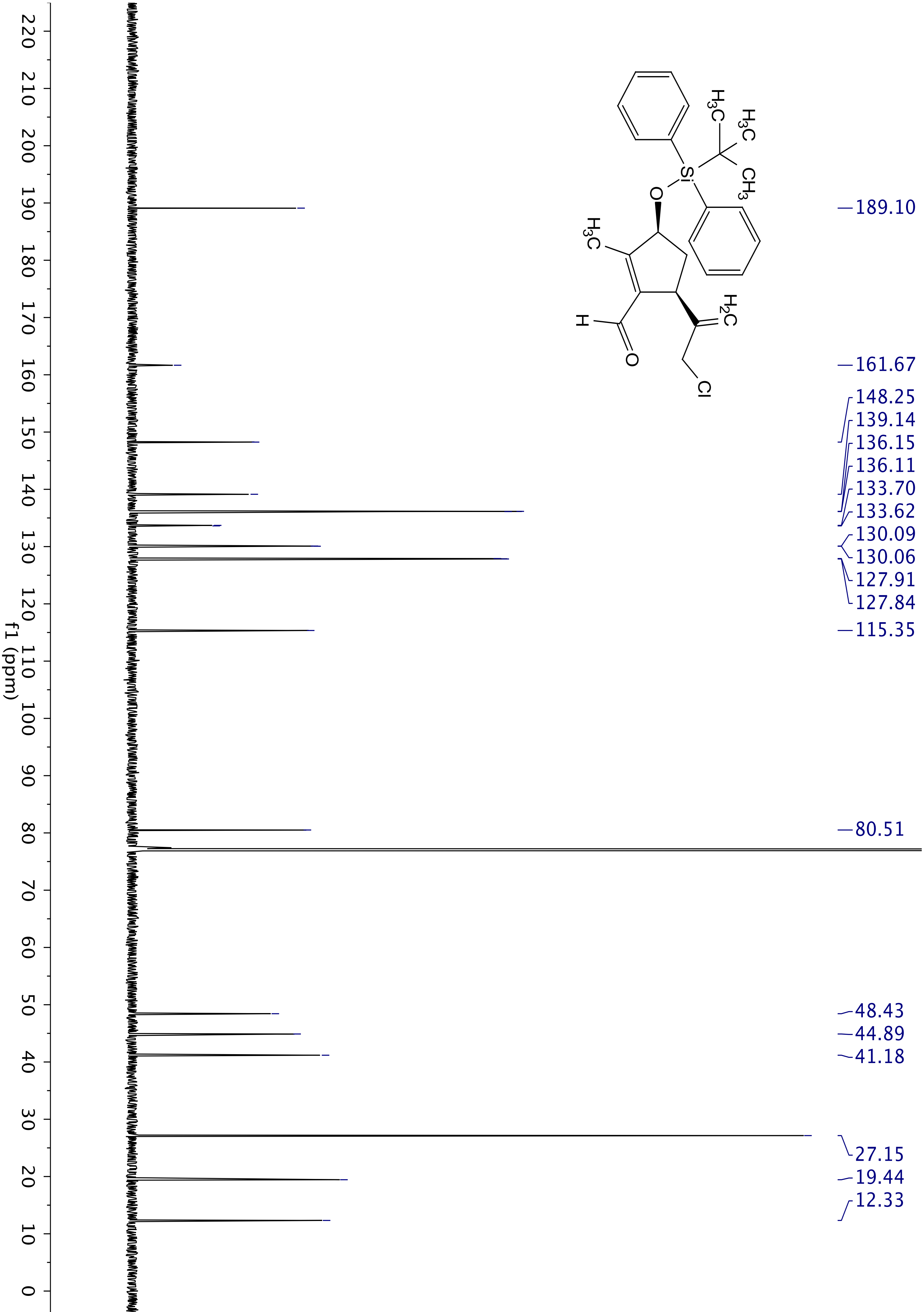
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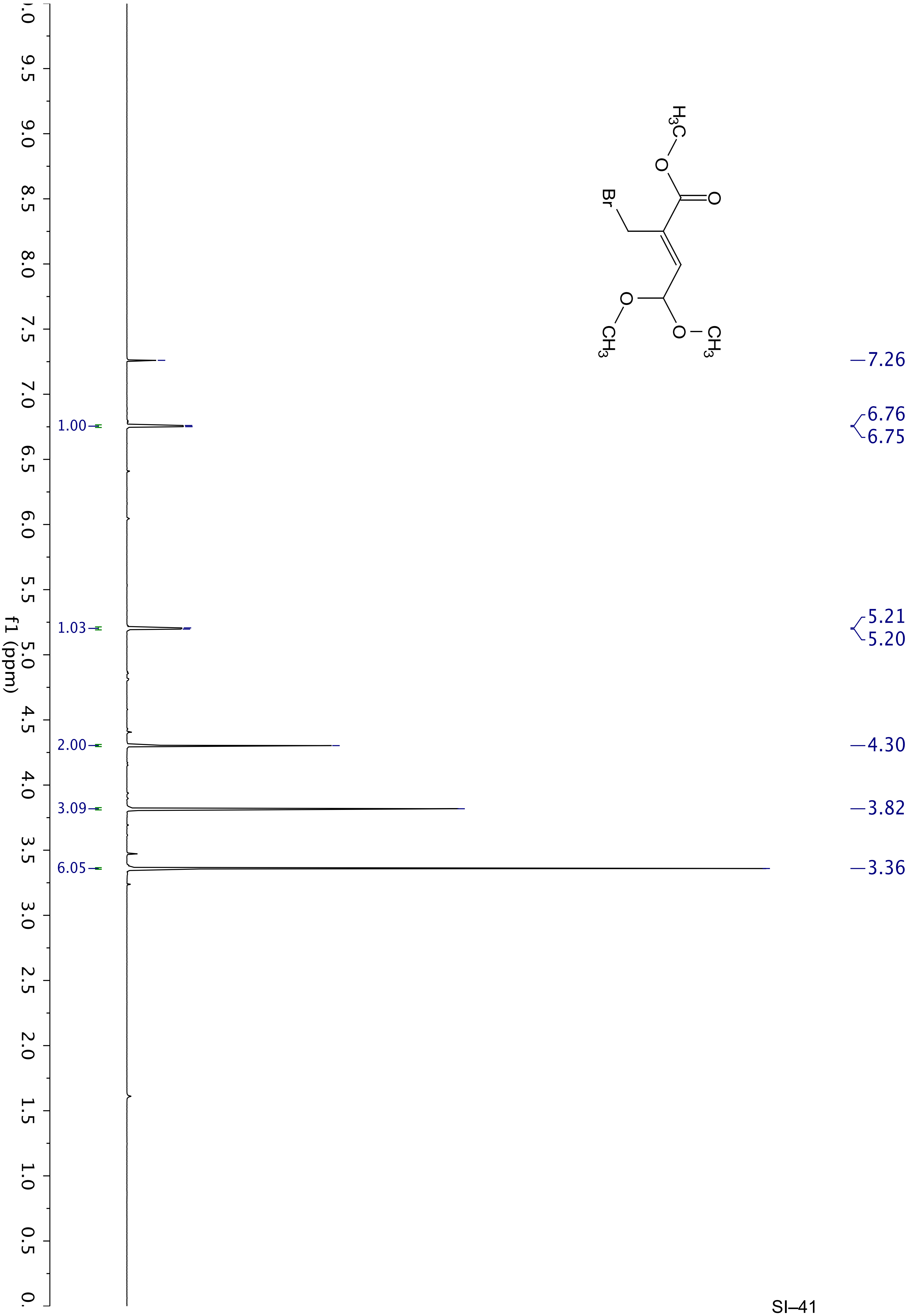
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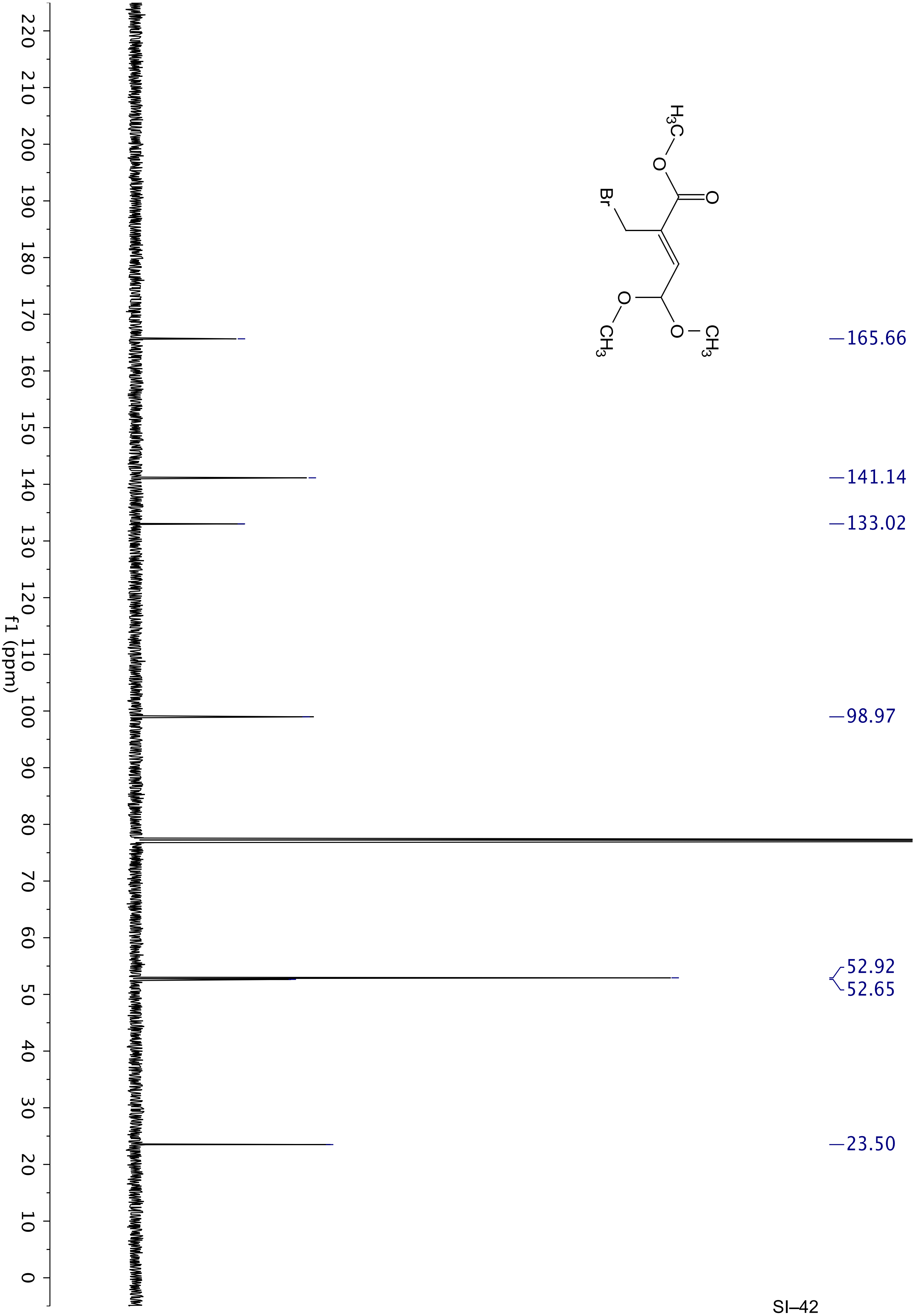
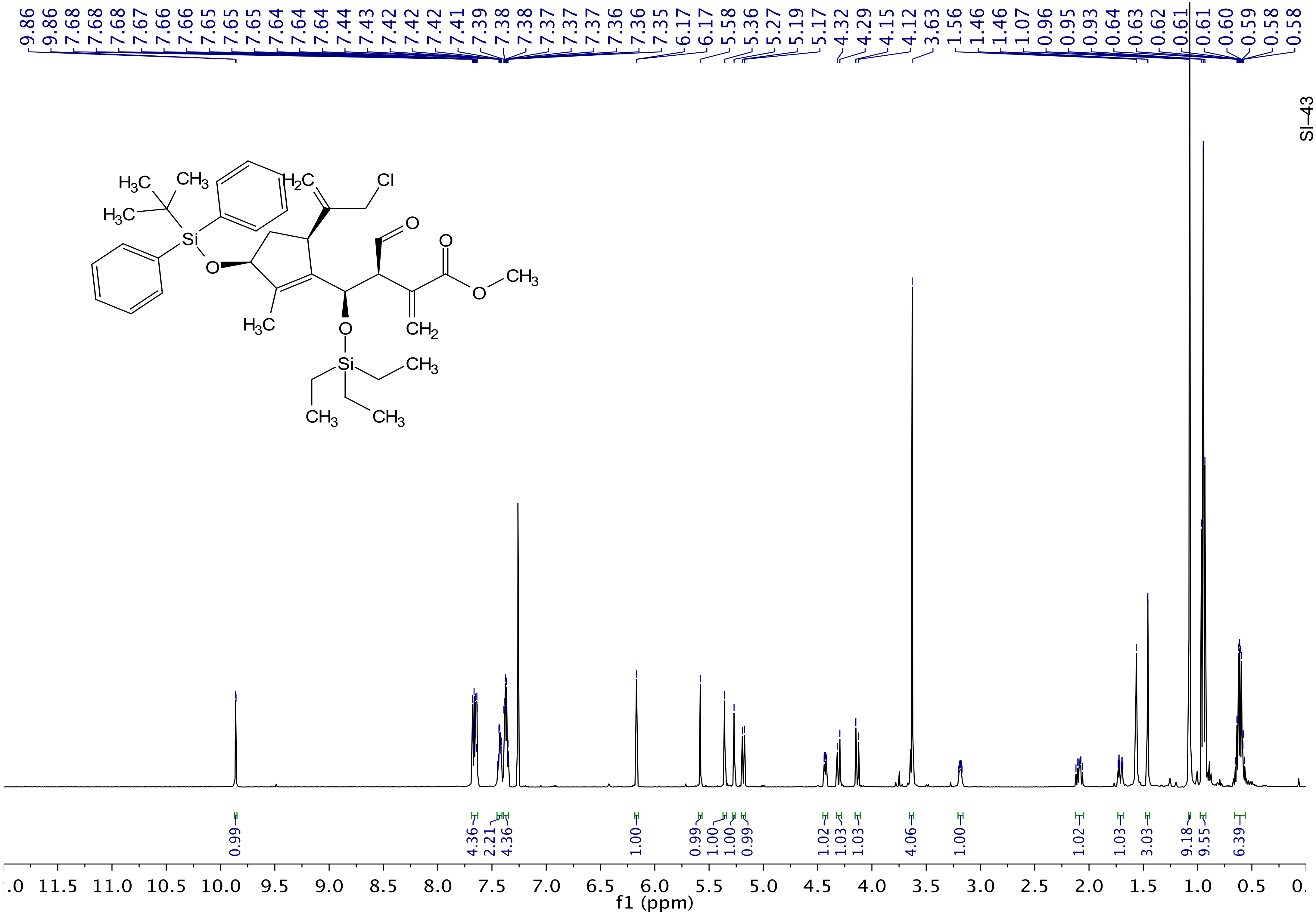
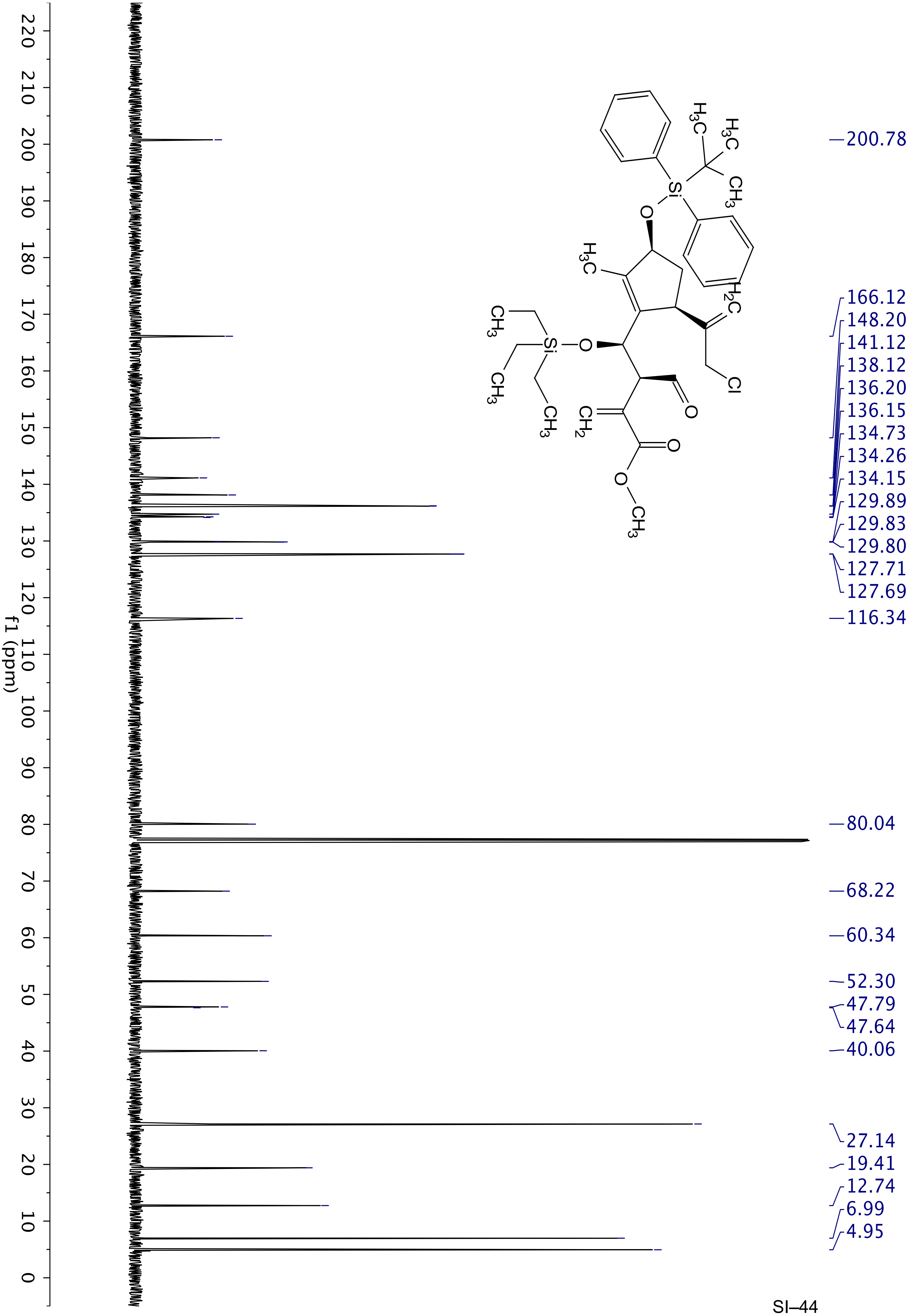
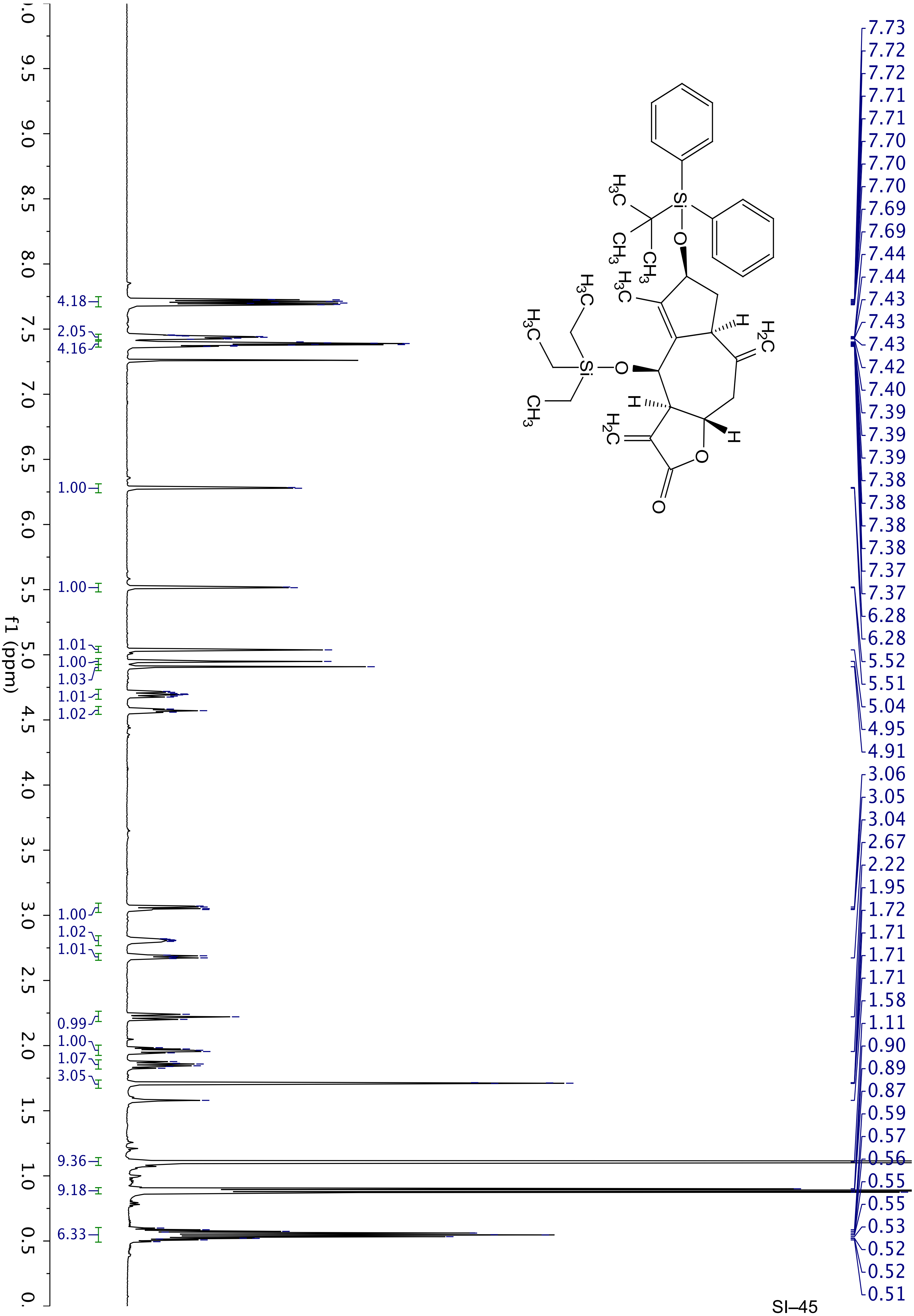
0.

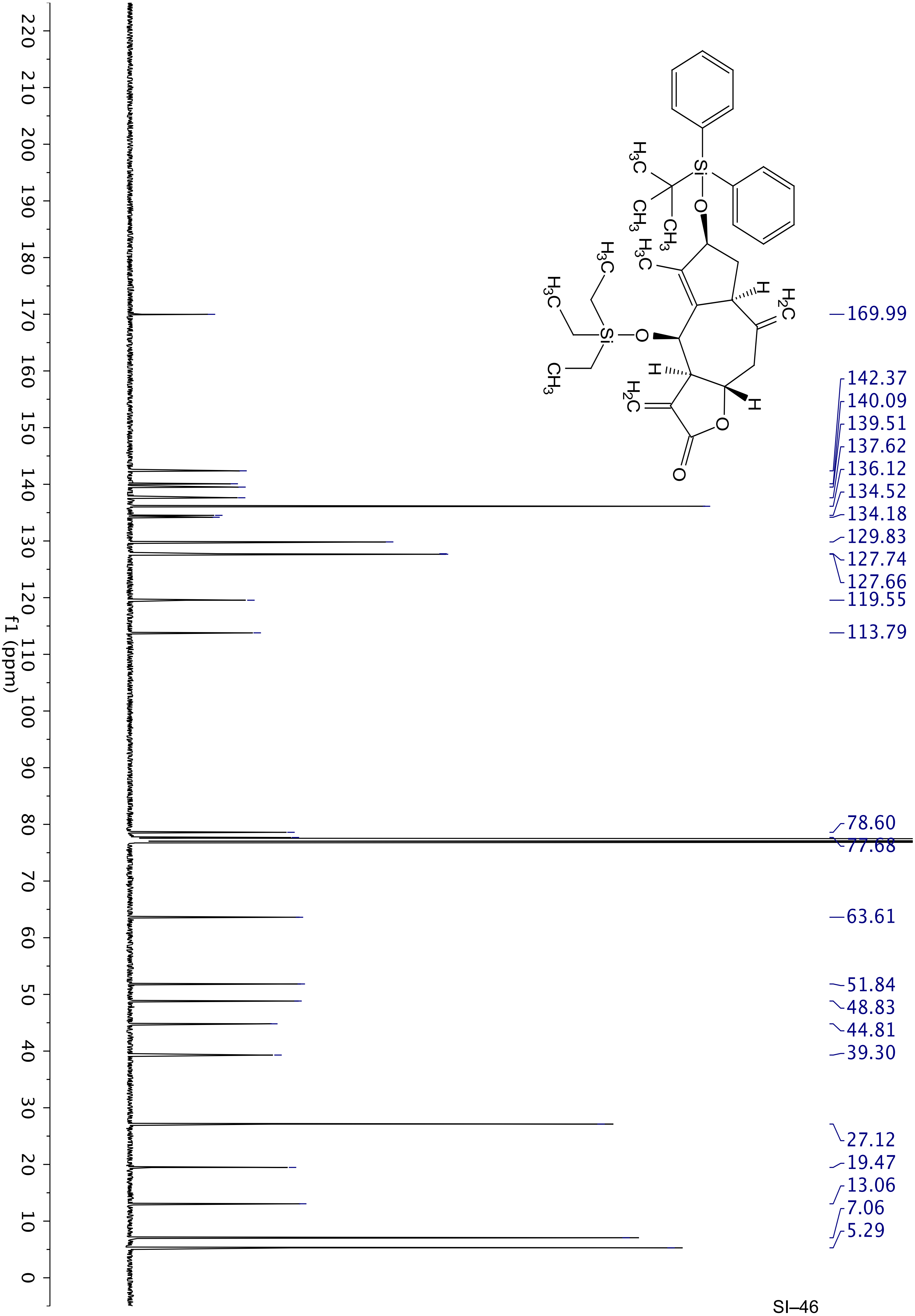


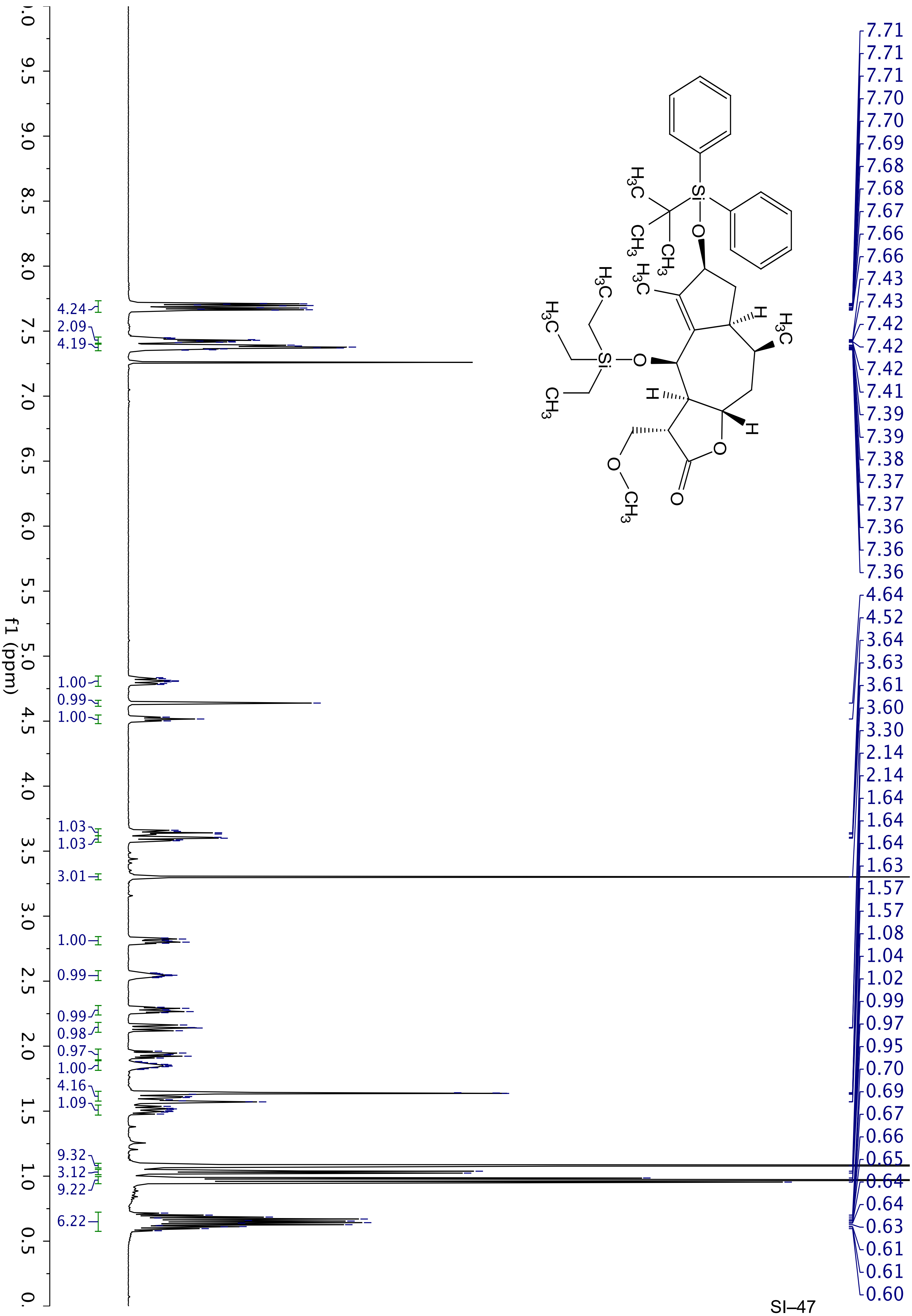
165.66
141.14
133.02
98.97
52.92
52.65
23.50
f1 (ppm)
220
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
H3C
O
O
Br
O
O
CH3
CH3

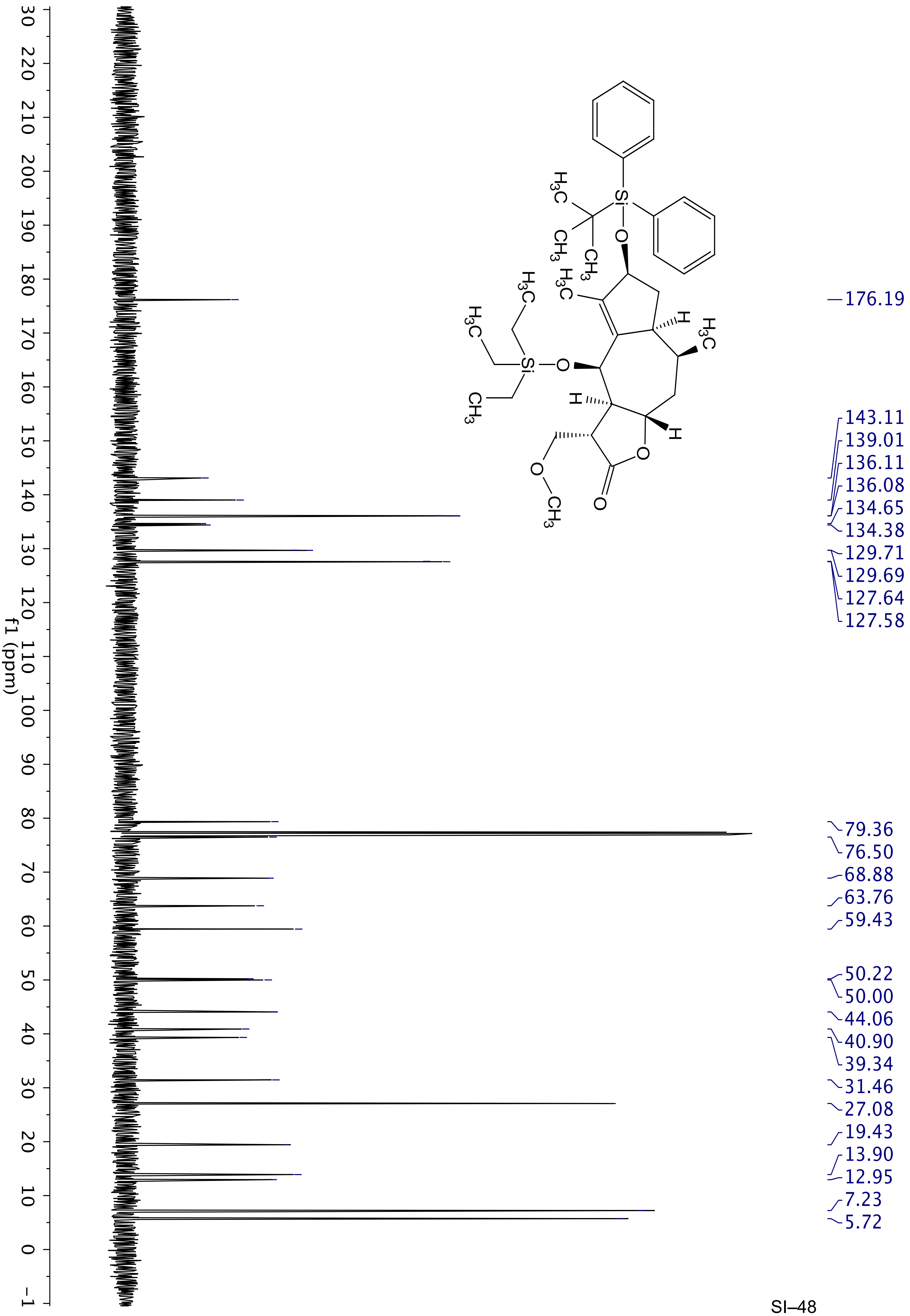

9.86
9.86
7.68
7.68
7.68
7.67
7.66
7.66
7.65
7.65
7.65
7.64
7.64
7.64
7.44
7.43
7.42
7.42
7.42
7.41
7.39
7.38
7.38
7.37
7.37
7.37
7.36
7.36
7.35
6.17
6.17
5.58
5.36
5.27
5.19
5.17
4.32
4.29
4.15
4.12
3.63
1.56
1.46
1.46
1.07
0.96
0.95
0.93
0.64
0.63
0.62
0.61
0.61
0.60
0.59
0.58
0.58
H3C
CH3
H3C
Si
O
H2C
Cl
O
O
O
CH3
H3C
O
CH2
Si
CH3
CH3
CH3
0.99
4.36
2.21
4.36
1.00
0.99
1.00
1.00
0.99
1.02
1.03
1.03
4.06
1.00
1.02
1.03
3.03
9.18
9.55
6.39
.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.
f1 (ppm)

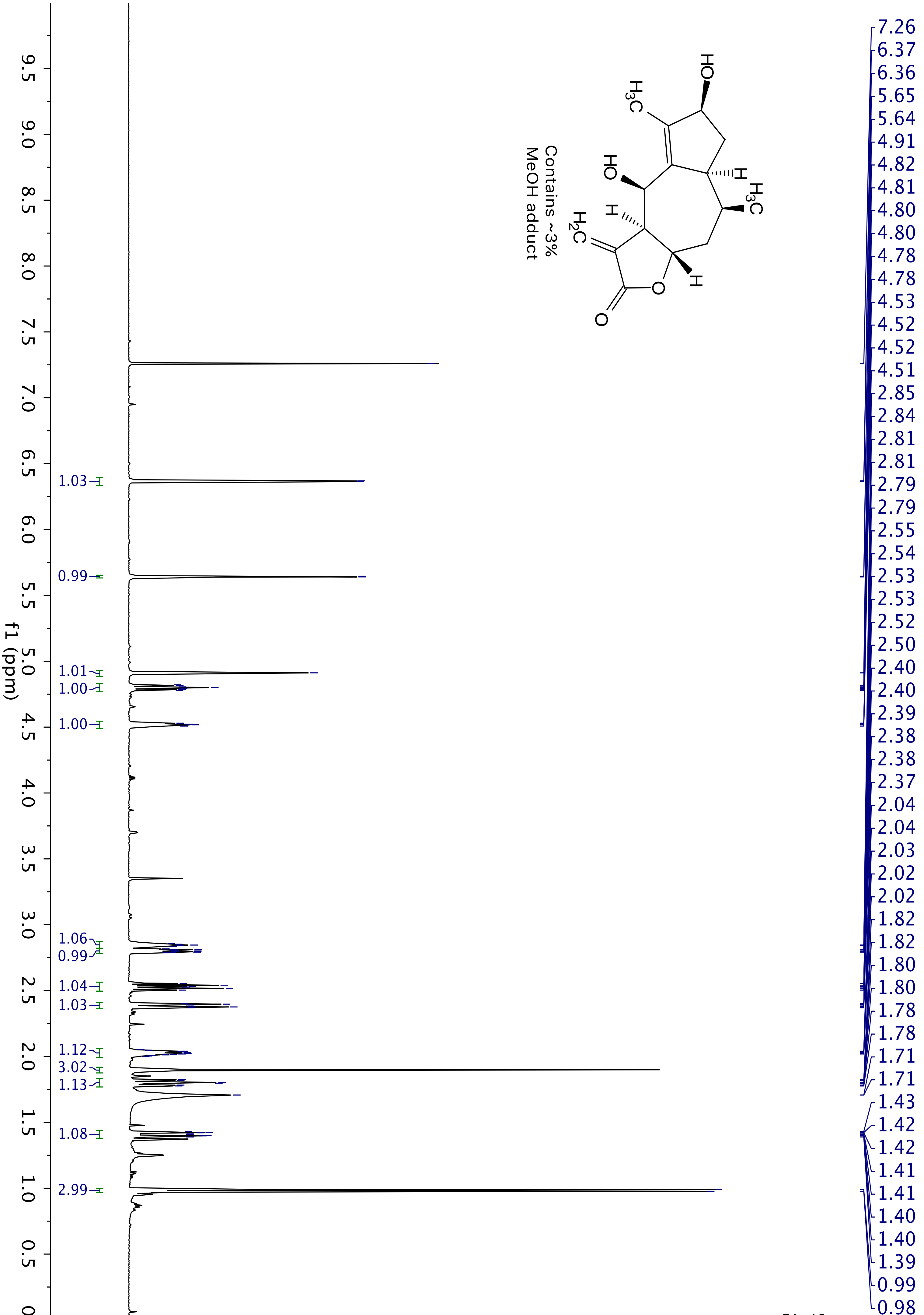

200.78
166.12
148.20
141.12
138.12
136.20
136.15
134.73
134.26
134.15
129.89
129.83
129.80
127.71
127.69
116.34
80.04
68.22
60.34
52.30
47.79
47.64
40.06
27.14
19.41
12.74
6.99
4.95
220
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)
Si
O
H3C
H3C
CH3
H3C
H2C
CH3
Si
O
CH3
CH3
CH2
O
O
O
CH3
Cl

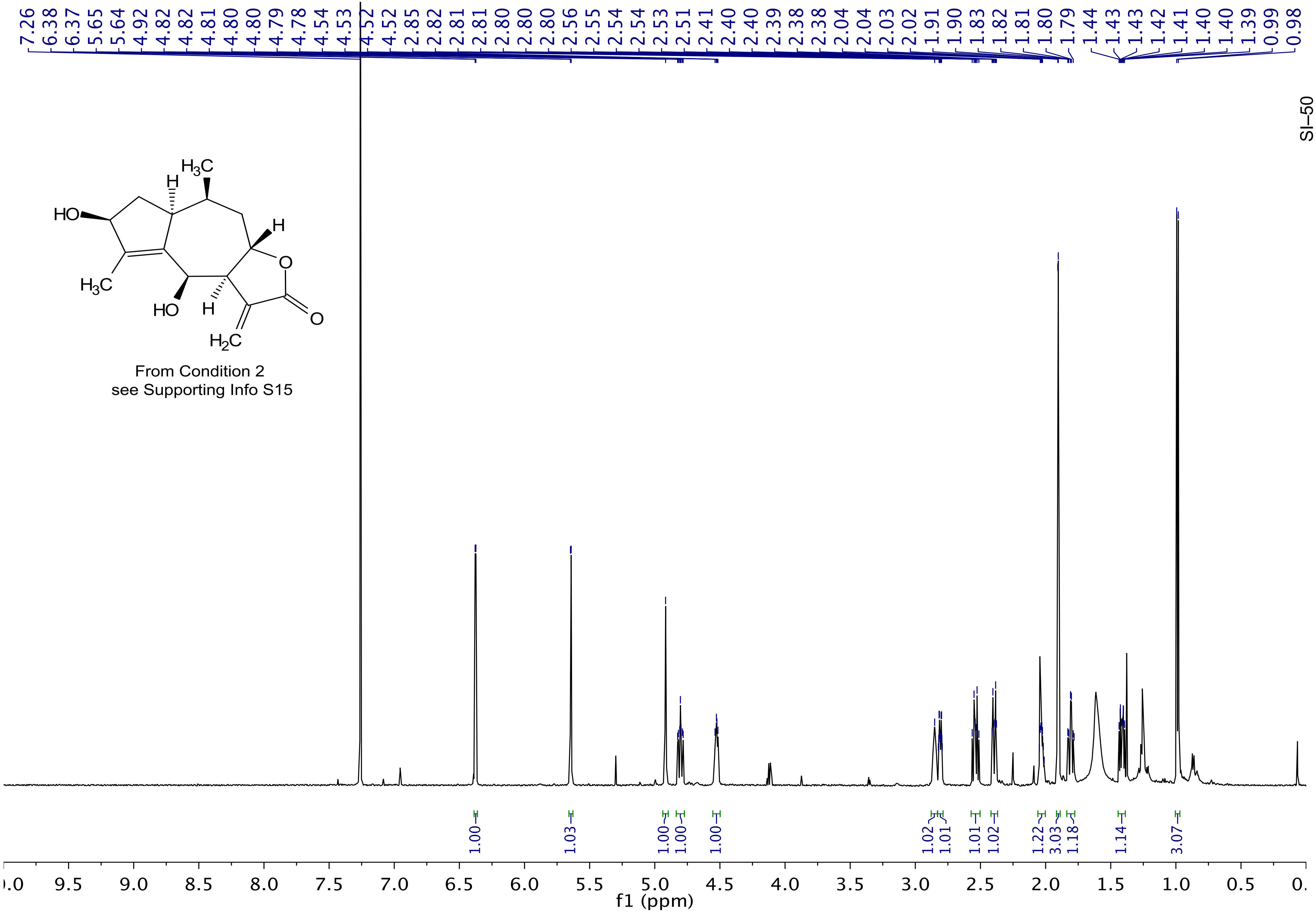

7.73
7.72
7.72
7.71
7.71
7.70
7.70
7.70
7.69
7.69
7.44
7.44
7.43
7.43
7.43
7.42
7.40
7.39
7.39
7.39
7.38
7.38
7.38
7.38
7.37
7.37
6.28
6.28
5.52
5.51
5.04
4.95
4.91
3.06
3.05
3.04
2.67
2.22
1.95
1.72
1.71
1.71
1.71
1.58
1.11
0.90
0.89
0.87
0.59
0.57
0.56
0.55
0.55
0.53
0.52
0.52
0.51
4.18
2.05
4.16
1.00
1.00
1.01
1.00
1.03
1.01
1.02
1.00
1.02
1.01
0.99
1.00
1.07
3.05
9.36
9.18
6.33
f1 (ppm)
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
Si
O
H3C
CH3
CH3
H3C
H3C
H3C
Si
O
CH3
H
H2C
H
H2C
H
O
O


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)
169.99
142.37
140.09
139.51
137.62
136.12
134.52
134.18
129.83
127.74
127.66
119.55
113.79
78.60
77.68
63.61
51.84
48.83
44.81
39.30
27.12
19.47
13.06
7.06
5.29
Si
O
H3C
CH3
CH3
H3C
H3C
H3C
Si
O
CH3
H
H2C
H
H2C
H
O
O

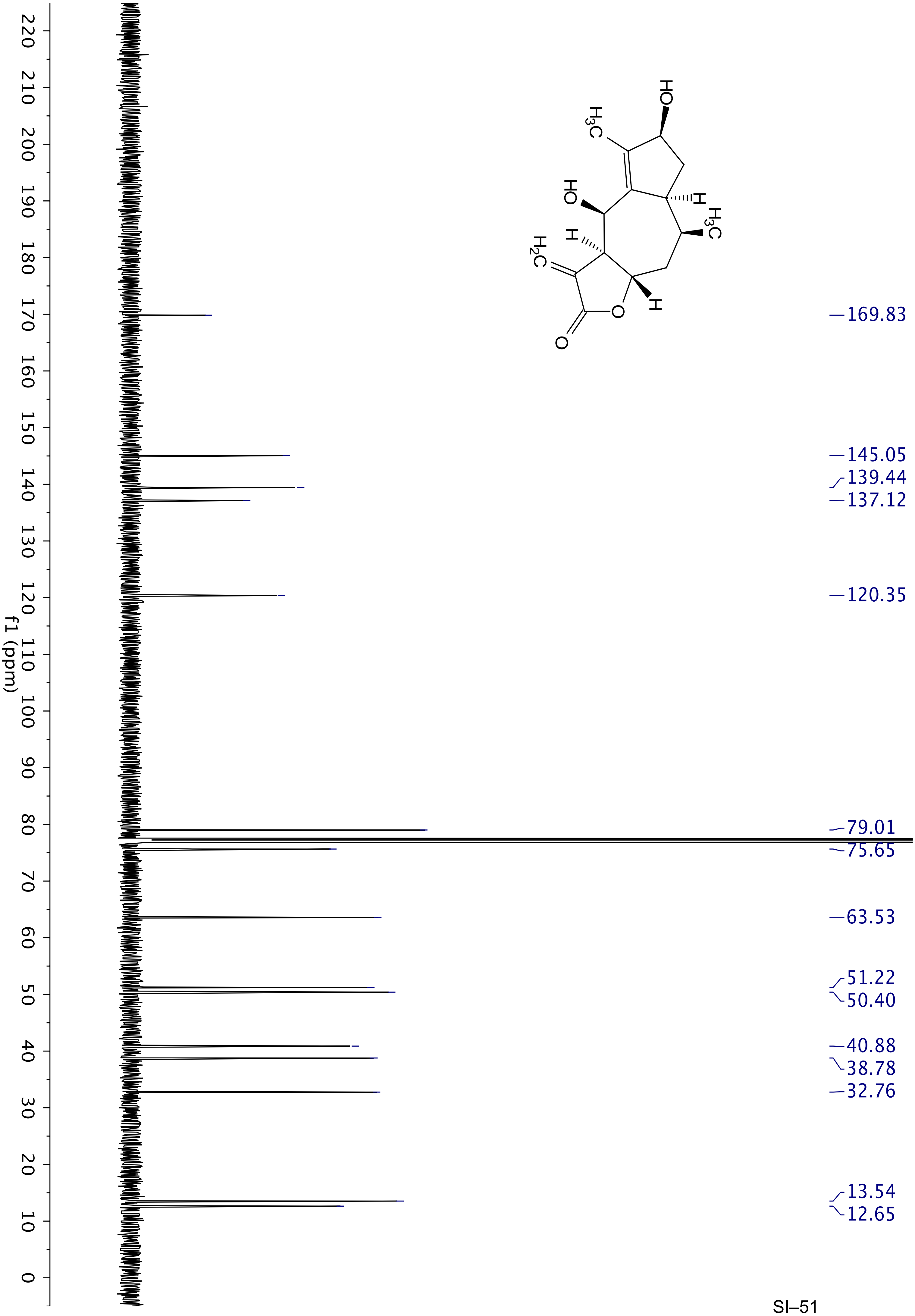

7.71
7.71
7.71
7.70
7.70
7.69
7.68
7.68
7.67
7.66
7.66
7.43
7.43
7.42
7.42
7.42
7.41
7.39
7.39
7.38
7.37
7.37
7.36
7.36
7.36
4.64
4.52
3.64
3.63
3.61
3.60
3.30
2.14
2.14
1.64
1.64
1.64
1.63
1.57
1.57
1.08
1.04
1.02
0.99
0.97
0.95
0.70
0.69
0.67
0.66
0.65
0.64
0.64
0.63
0.61
0.61
0.60
4.24
2.09
4.19
1.00
0.99
1.00
1.03
1.03
3.01
1.00
0.99
0.99
0.98
0.97
1.00
4.16
1.09
9.32
3.12
9.22
6.22
f1 (ppm)
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
Si
O
H_3C
CH_3
CH_3
H_3C
H
H_3C
H_3C
H_3C
Si
O
CH_3
H
H
O
O
O
CH_3


176.19
143.11
139.01
136.11
136.08
134.65
134.38
129.71
129.69
127.64
127.58
79.36
76.50
68.88
63.76
59.43
50.22
50.00
44.06
40.90
39.34
31.46
27.08
19.43
13.90
12.95
7.23
5.72
230
220
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
-1
f1 (ppm)
Si
O
H_3C
CH_3
CH_3
H_3C
H_3C
H_3C
CH_3
H_3C
H
H
H
O
O
O
O
O
Si
CH_3

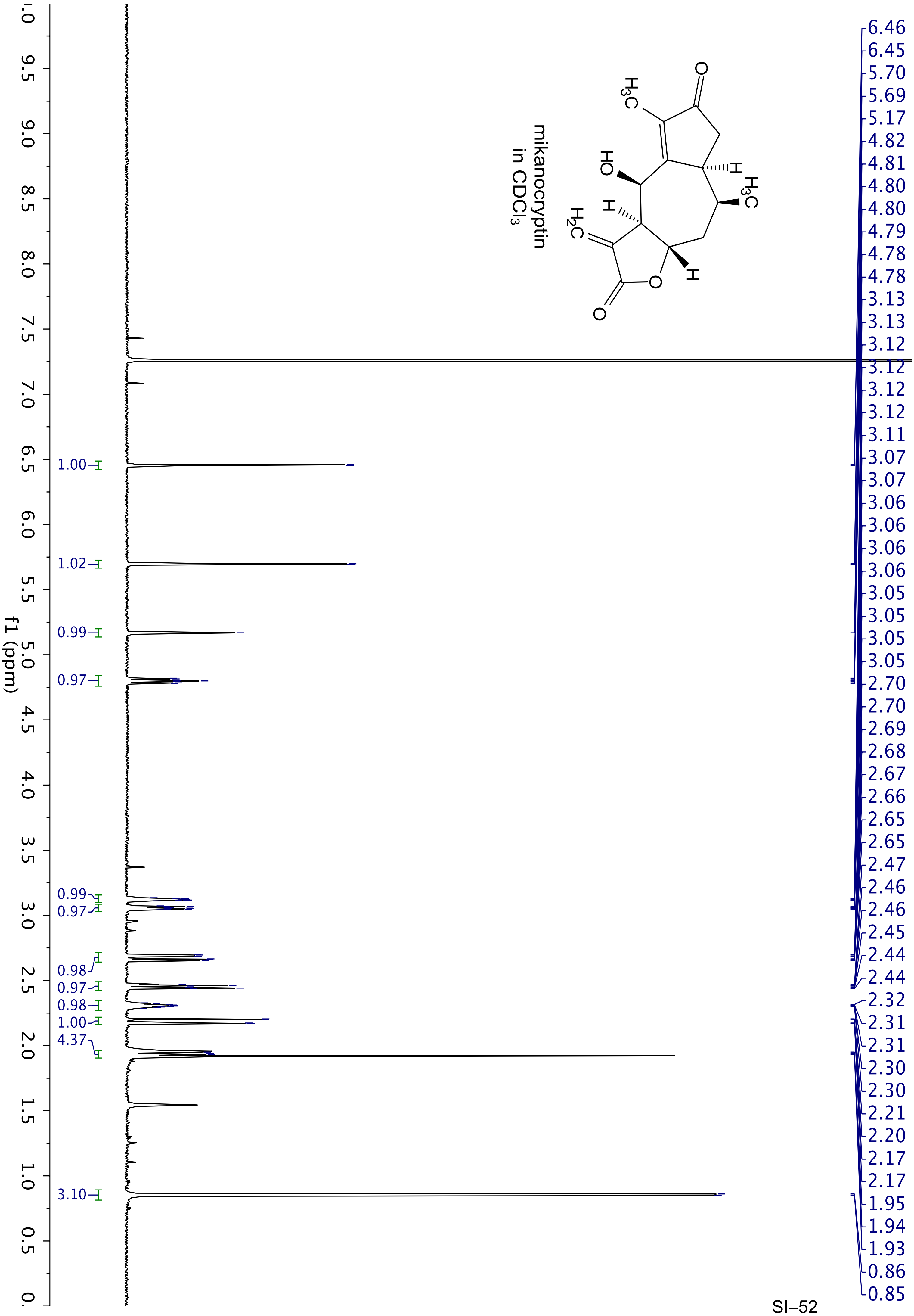

Contains ~3% MeOH adduct
HO
H3C
HO
H
H3C
H
H2C
H
O
O
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.
f1 (ppm)
1.03
0.99
1.01
1.00
1.00
1.06
0.99
1.04
1.03
1.12
3.02
1.13
1.08
2.99
7.26
6.37
6.36
5.65
5.64
4.91
4.82
4.81
4.80
4.80
4.78
4.78
4.53
4.52
4.52
4.51
2.85
2.84
2.81
2.81
2.79
2.79
2.55
2.54
2.53
2.53
2.52
2.50
2.40
2.40
2.39
2.38
2.38
2.37
2.04
2.04
2.03
2.02
2.02
1.82
1.82
1.80
1.80
1.78
1.78
1.71
1.71
1.43
1.42
1.42
1.41
1.41
1.40
1.40
1.39
0.99
0.98

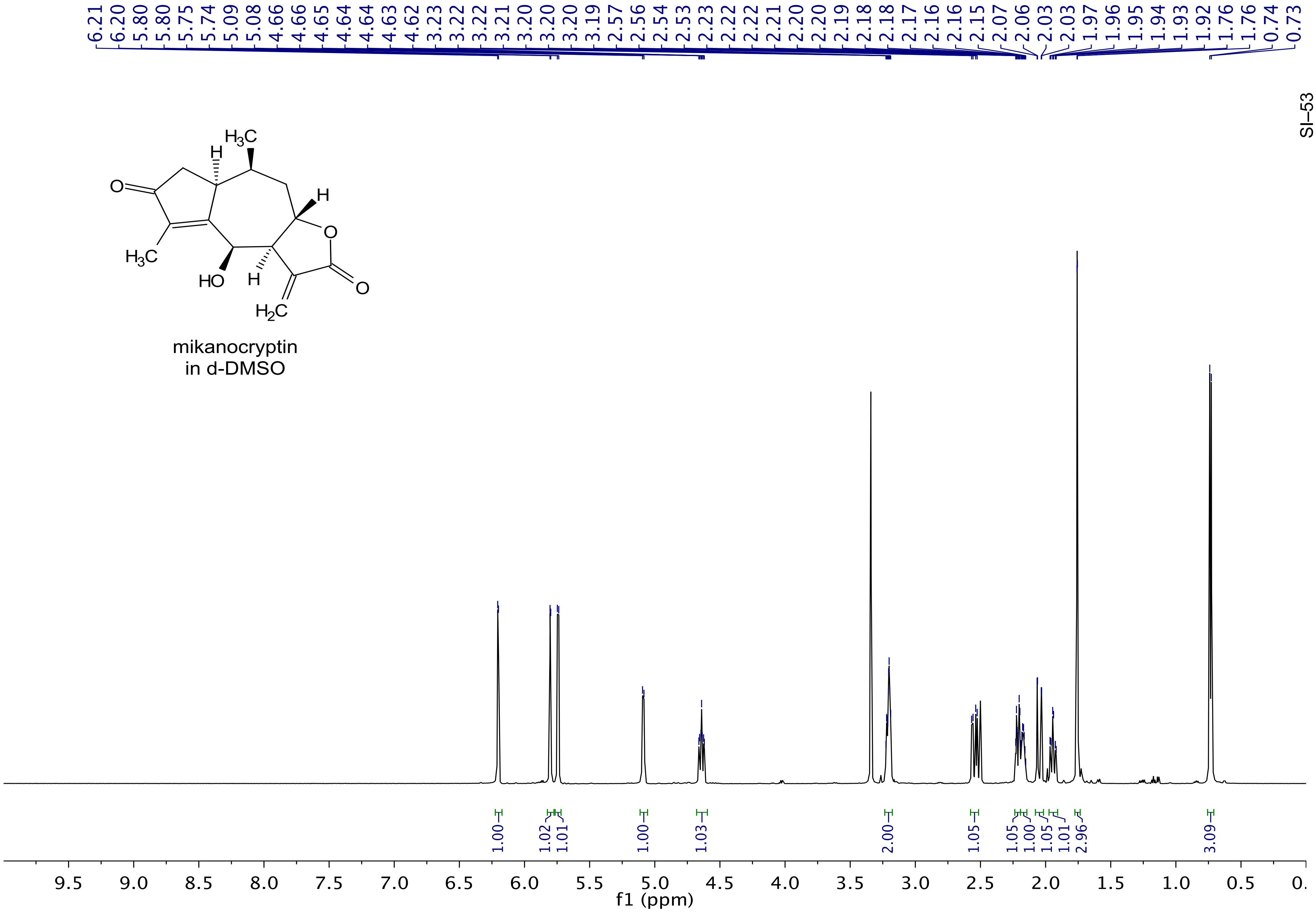


From Condition 2
see Supporting Info S15

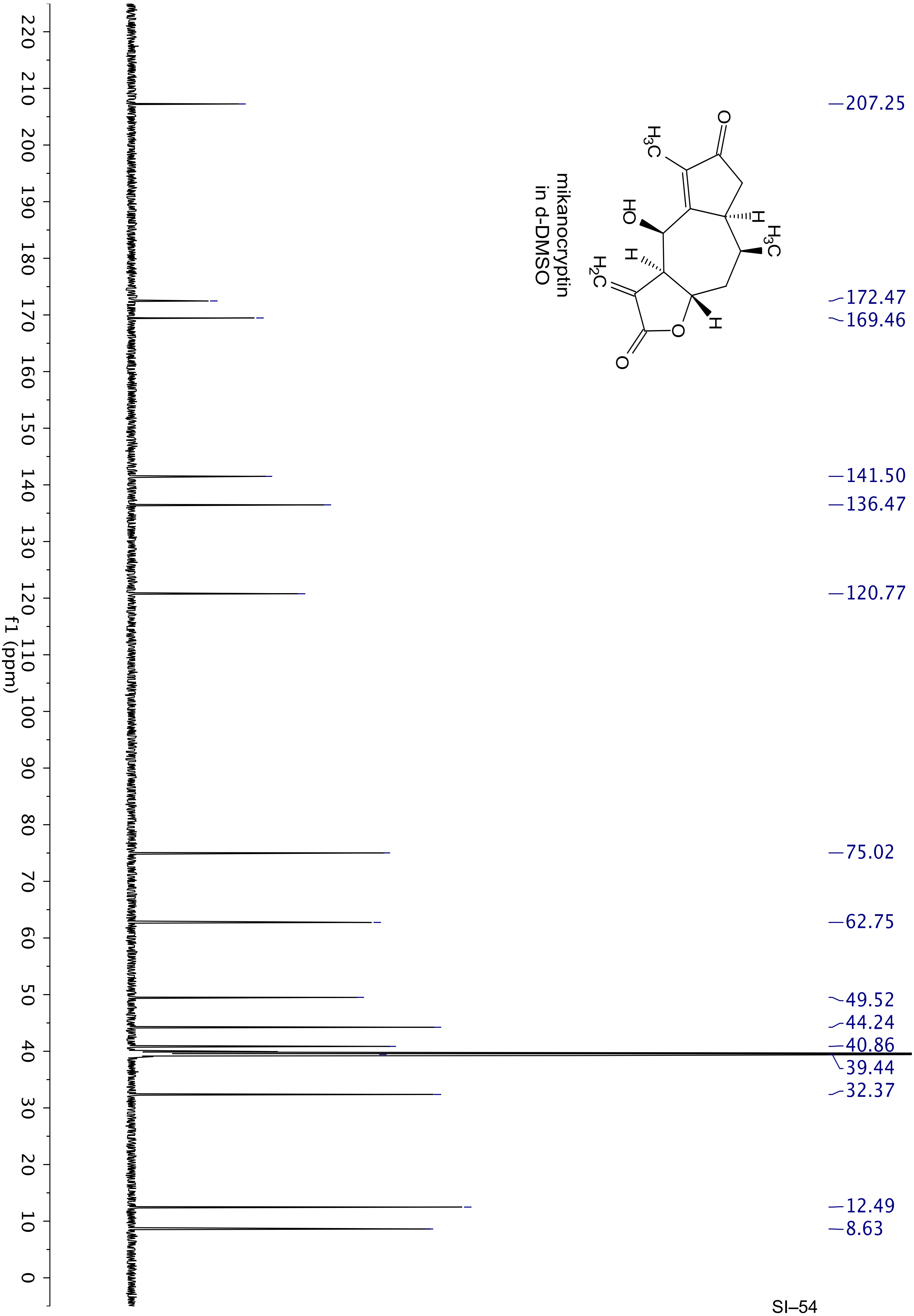


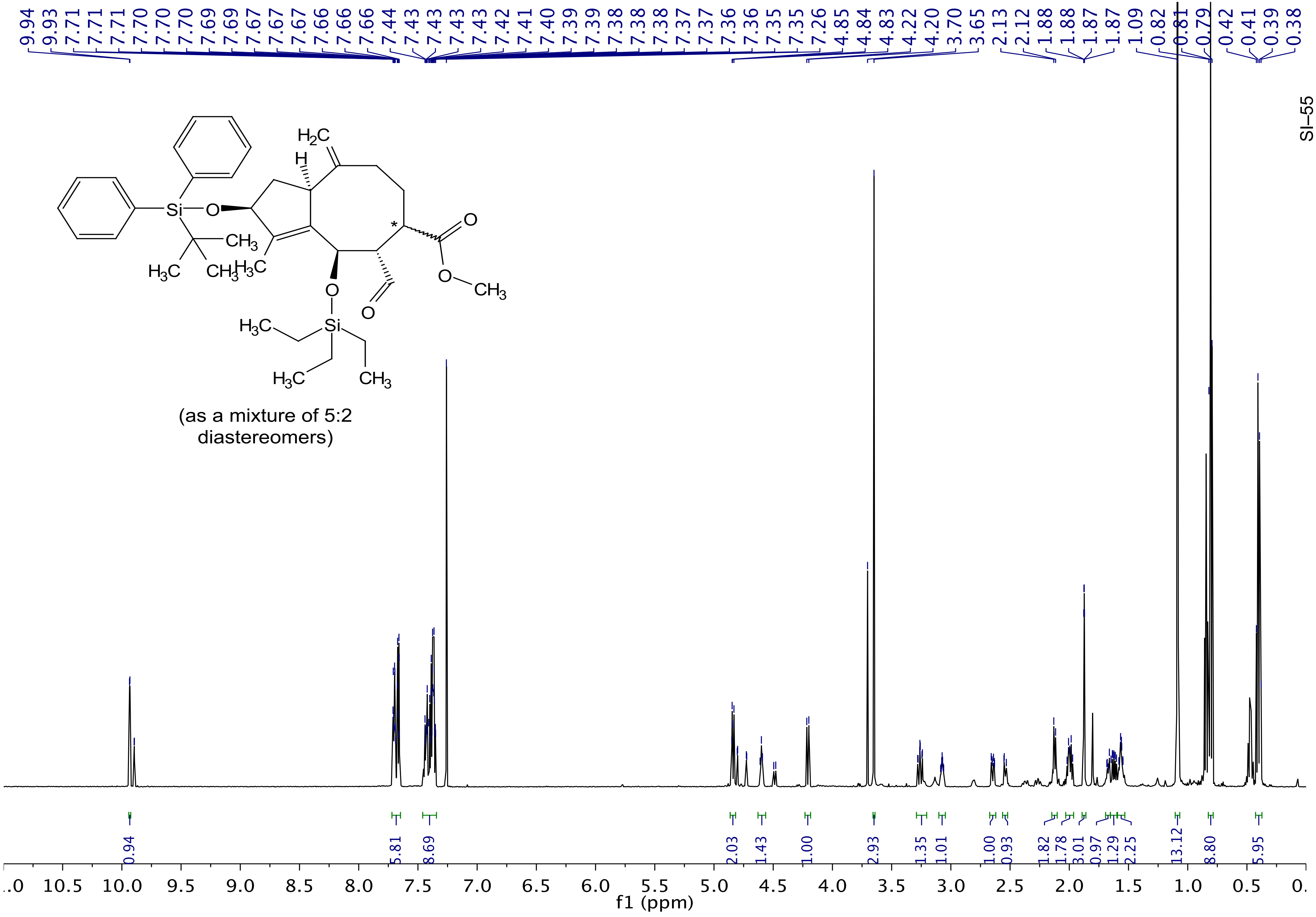
169.83
145.05
139.44
137.12
120.35
79.01
75.65
63.53
51.22
50.40
40.88
38.78
32.76
13.54
12.65
f1 (ppm)
220
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
HO
H_3C
HO
H
H_3C
H
H_2C
H
O
O

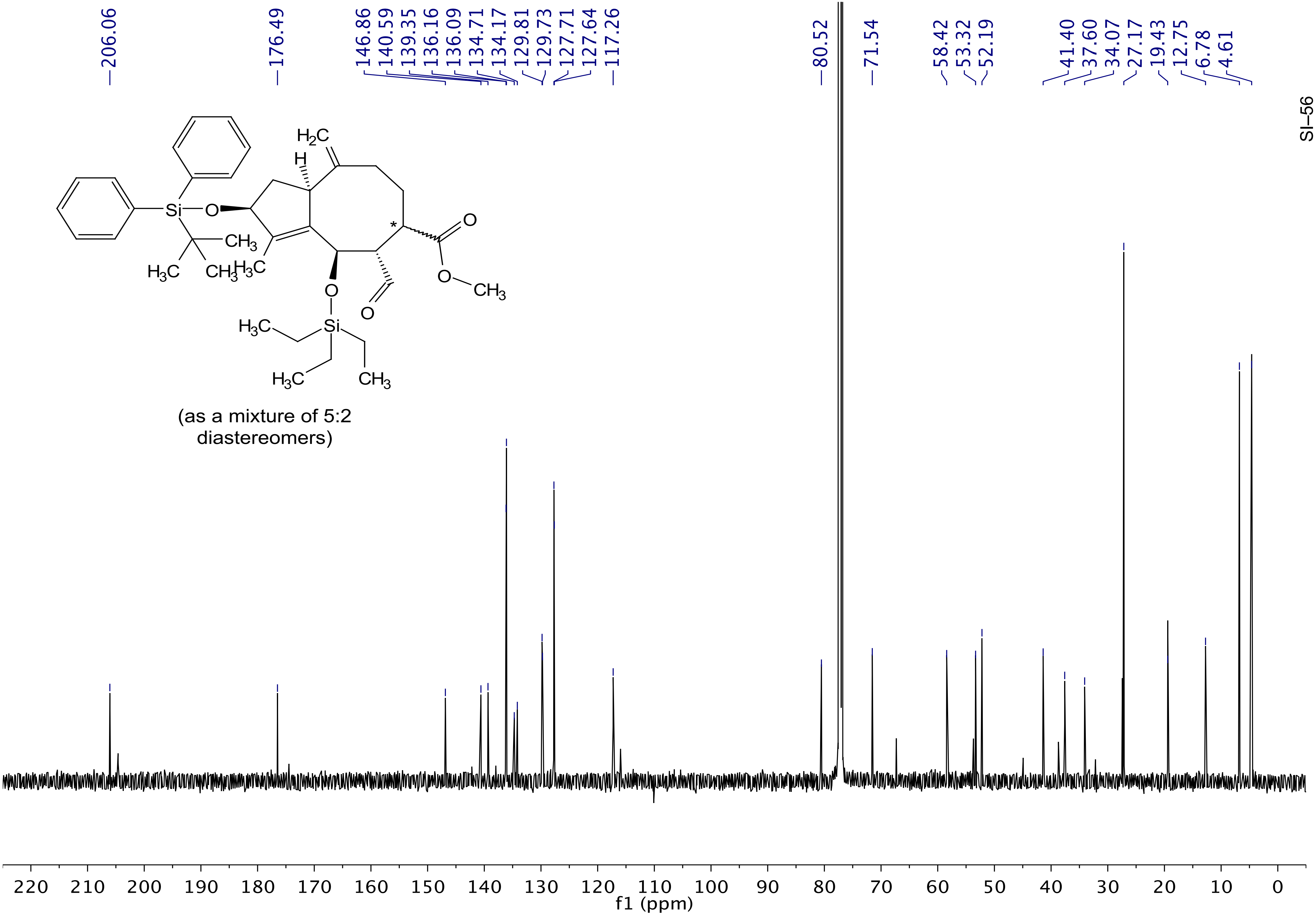

mikanocryptin
in CDCl3
O
H3C
HO
H
H3C
H2C
H
O
O
6.46
6.45
5.70
5.69
5.17
4.82
4.81
4.80
4.80
4.79
4.78
4.78
3.13
3.13
3.12
3.12
3.12
3.12
3.11
3.07
3.07
3.06
3.06
3.06
3.06
3.05
3.05
3.05
3.05
2.70
2.70
2.69
2.68
2.67
2.66
2.65
2.65
2.47
2.46
2.46
2.45
2.44
2.44
2.32
2.31
2.31
2.30
2.30
2.21
2.20
2.17
2.17
1.95
1.94
1.93
0.86
0.85
1.00
1.02
0.99
0.97
0.99
0.97
0.98
0.97
0.98
1.00
4.37
3.10
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
f1 (ppm)

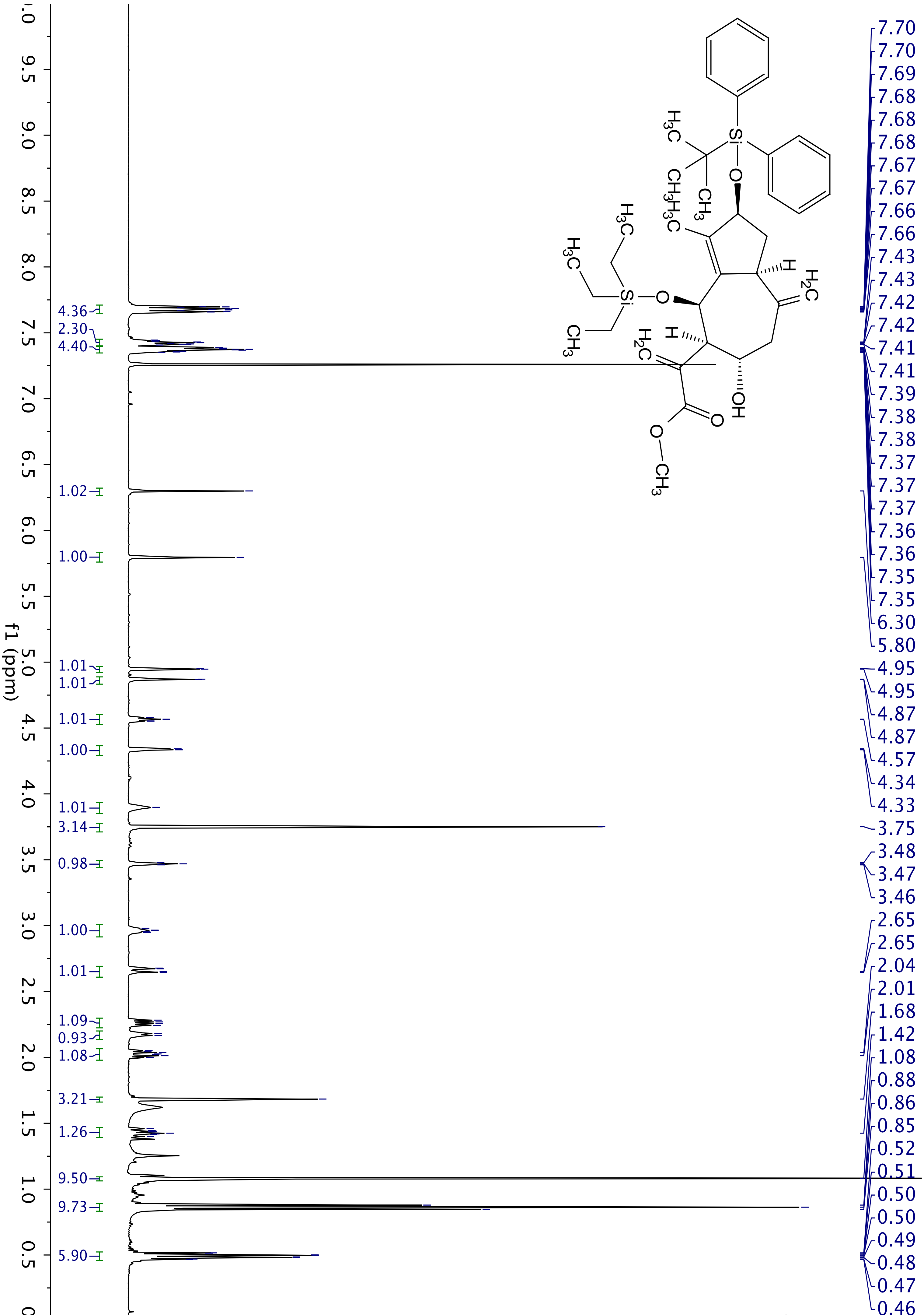


mikanocryptin
in d-DMSO

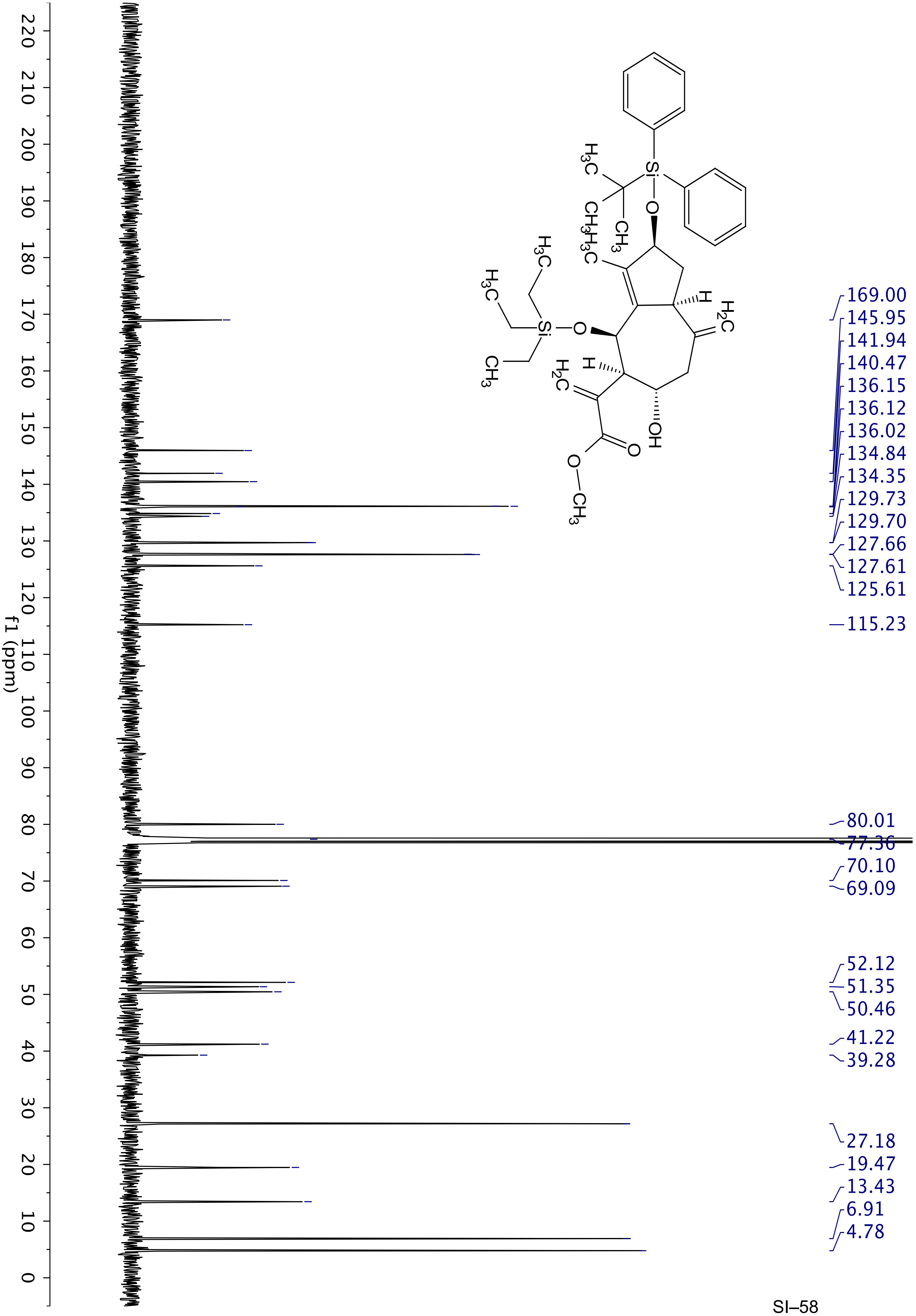

mikanocryptin
in d-DMSO
207.25
172.47
169.46
141.50
136.47
120.77
75.02
62.75
49.52
44.24
40.86
39.44
32.37
12.49
8.63
f1 (ppm)
220
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
O
H3C
HO
H
H3C
H2C
H
H
O
O

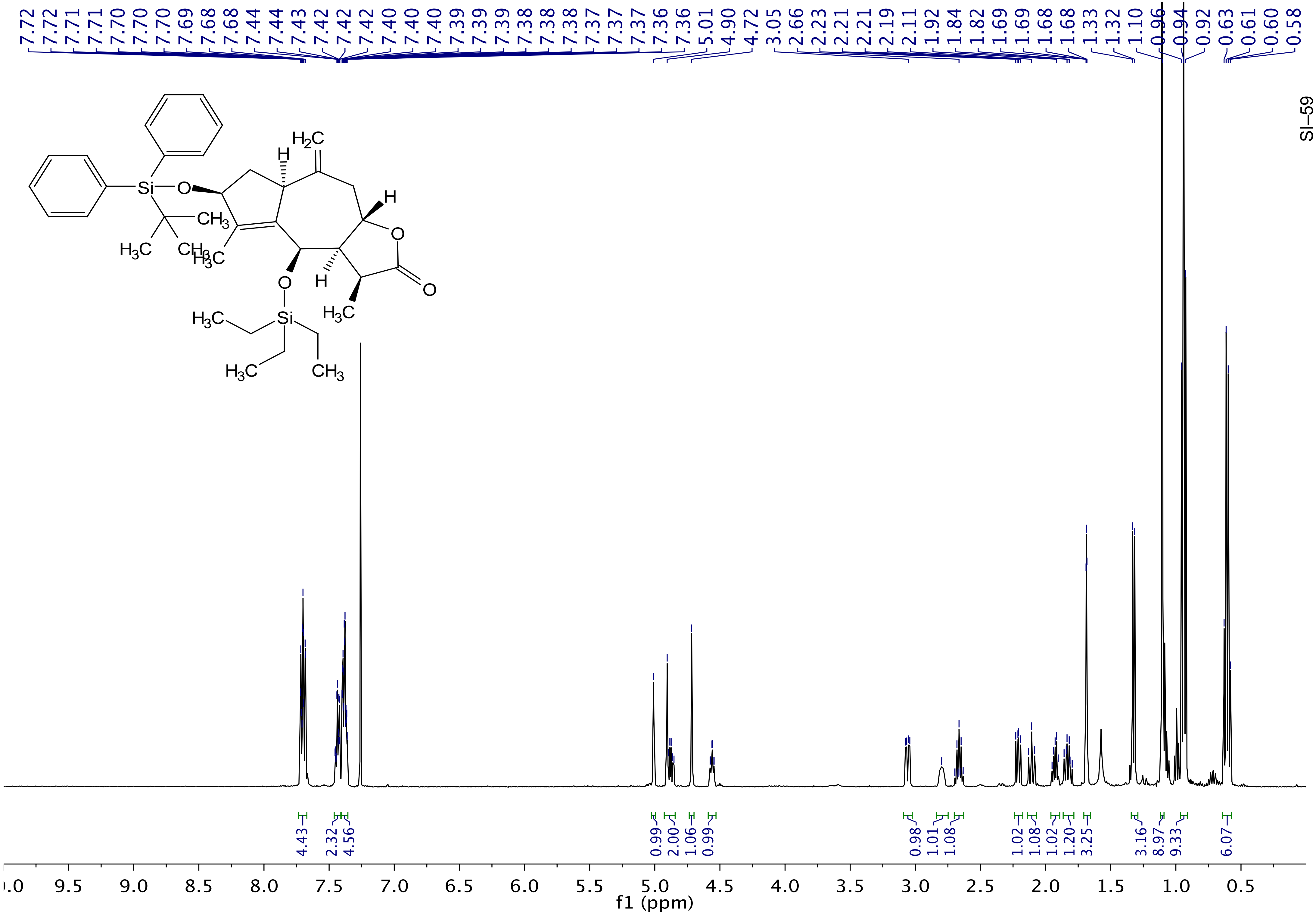

9.94
9.93
7.71
7.71
7.71
7.70
7.70
7.70
7.69
7.69
7.67
7.67
7.67
7.66
7.66
7.66
7.44
7.43
7.43
7.43
7.43
7.42
7.41
7.40
7.39
7.39
7.38
7.38
7.38
7.37
7.37
7.36
7.36
7.35
7.35
7.26
4.85
4.84
4.83
4.22
4.20
3.70
3.65
2.13
2.12
1.88
1.88
1.87
1.87
1.09
0.82
0.81
0.79
0.42
0.41
0.39
0.38
H2C
H
Si
O
CH3
H3C
CH3
H3C
O
O
CH3
O
O
Si
H3C
H3C
CH3
*
(as a mixture of 5:2
diastereomers)
0.94
5.81
8.69
2.03
1.43
1.00
2.93
1.35
1.01
1.00
0.93
1.82
1.78
3.01
0.97
1.29
2.25
13.12
8.80
5.95
.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.
f1 (ppm)

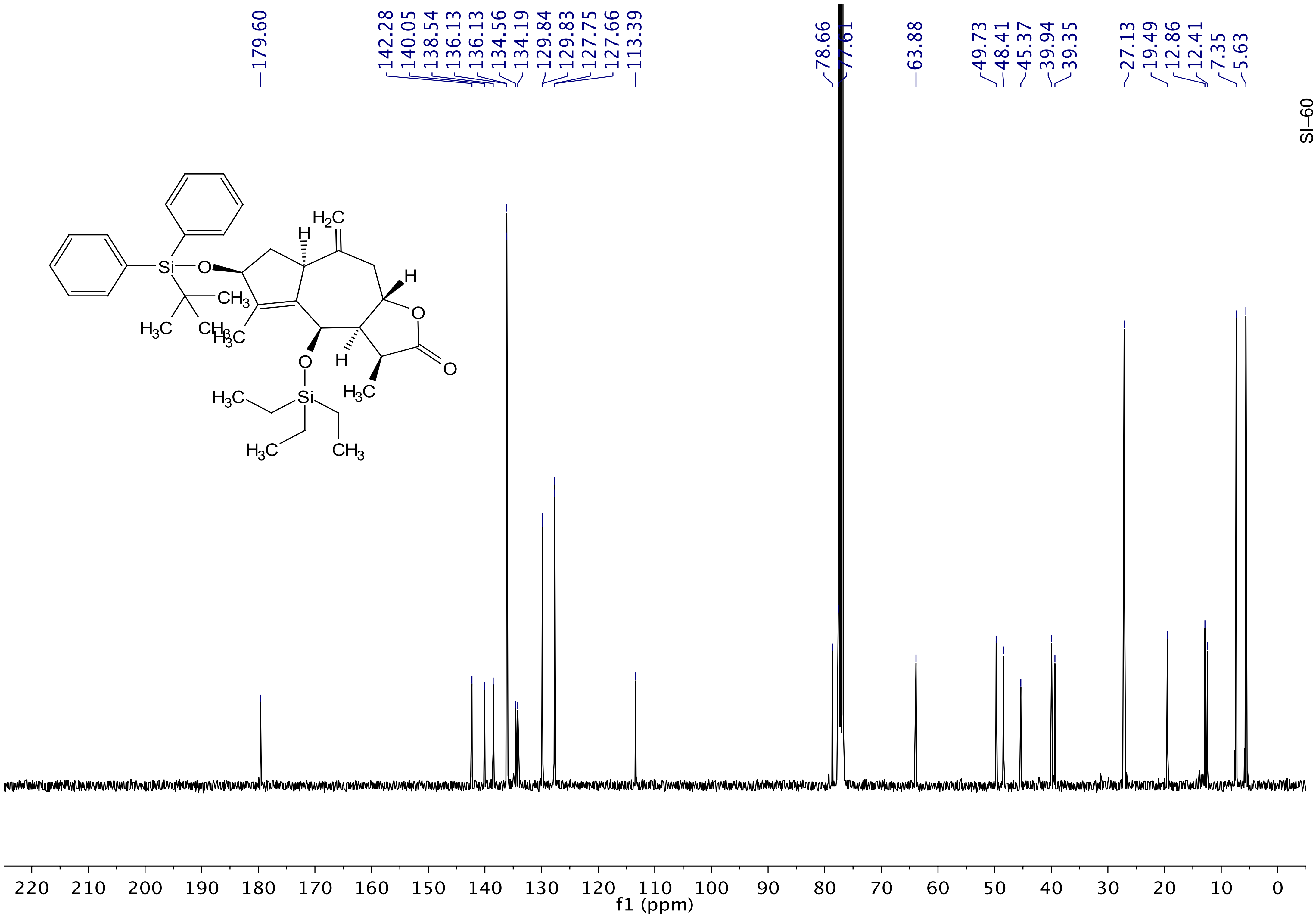

(as a mixture of 5:2 diastereomers)



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
f1 (ppm)
4.36
2.30
4.40
1.02
1.00
1.01
1.01
1.01
1.00
1.01
3.14
0.98
1.00
1.01
1.09
0.93
1.08
3.21
1.26
9.50
9.73
5.90
7.70
7.70
7.69
7.68
7.68
7.68
7.67
7.67
7.66
7.66
7.43
7.43
7.42
7.42
7.41
7.41
7.39
7.38
7.38
7.37
7.37
7.37
7.36
7.36
7.35
7.35
6.30
5.80
4.95
4.95
4.87
4.87
4.57
4.34
4.33
3.75
3.48
3.47
3.46
2.65
2.65
2.04
2.01
1.68
1.42
1.08
0.88
0.86
0.85
0.52
0.51
0.50
0.50
0.49
0.48
0.47
0.46
Si
O
H3C
CH3
H3C
CH3
H3C
H
H2C
H3C
H3C
Si
O
CH3
H
H2C
OH
O
O
CH3


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)
169.00
145.95
141.94
140.47
136.15
136.12
136.02
134.84
134.35
129.73
129.70
127.66
127.61
125.61
115.23
80.01
77.36
70.10
69.09
52.12
51.35
50.46
41.22
39.28
27.18
19.47
13.43
6.91
4.78
Si
O
H3C
CH3
CH3
H3C
H
H2C
O
Si
H3C
H3C
CH3
H
H2C
OH
O
O
CH3


7.72
7.72
7.71
7.71
7.70
7.70
7.70
7.69
7.68
7.68
7.44
7.44
7.43
7.42
7.42
7.42
7.40
7.40
7.40
7.39
7.39
7.39
7.38
7.38
7.38
7.37
7.37
7.37
7.36
7.36
5.01
4.90
4.72
3.05
2.66
2.23
2.21
2.21
2.19
2.11
1.92
1.84
1.82
1.69
1.69
1.68
1.68
1.33
1.32
1.10
0.96
0.94
0.92
0.63
0.61
0.60
0.58
H2C
H
H
Si
O
O
CH3
H3C
CH3
H3C
O
H
O
O
Si
H3C
H3C
H3C
CH3
4.43
2.32
4.56
0.99
2.00
1.06
0.99
0.98
1.01
1.08
1.02
1.08
1.02
1.20
3.25
3.16
8.97
9.33
6.07
.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
f1 (ppm)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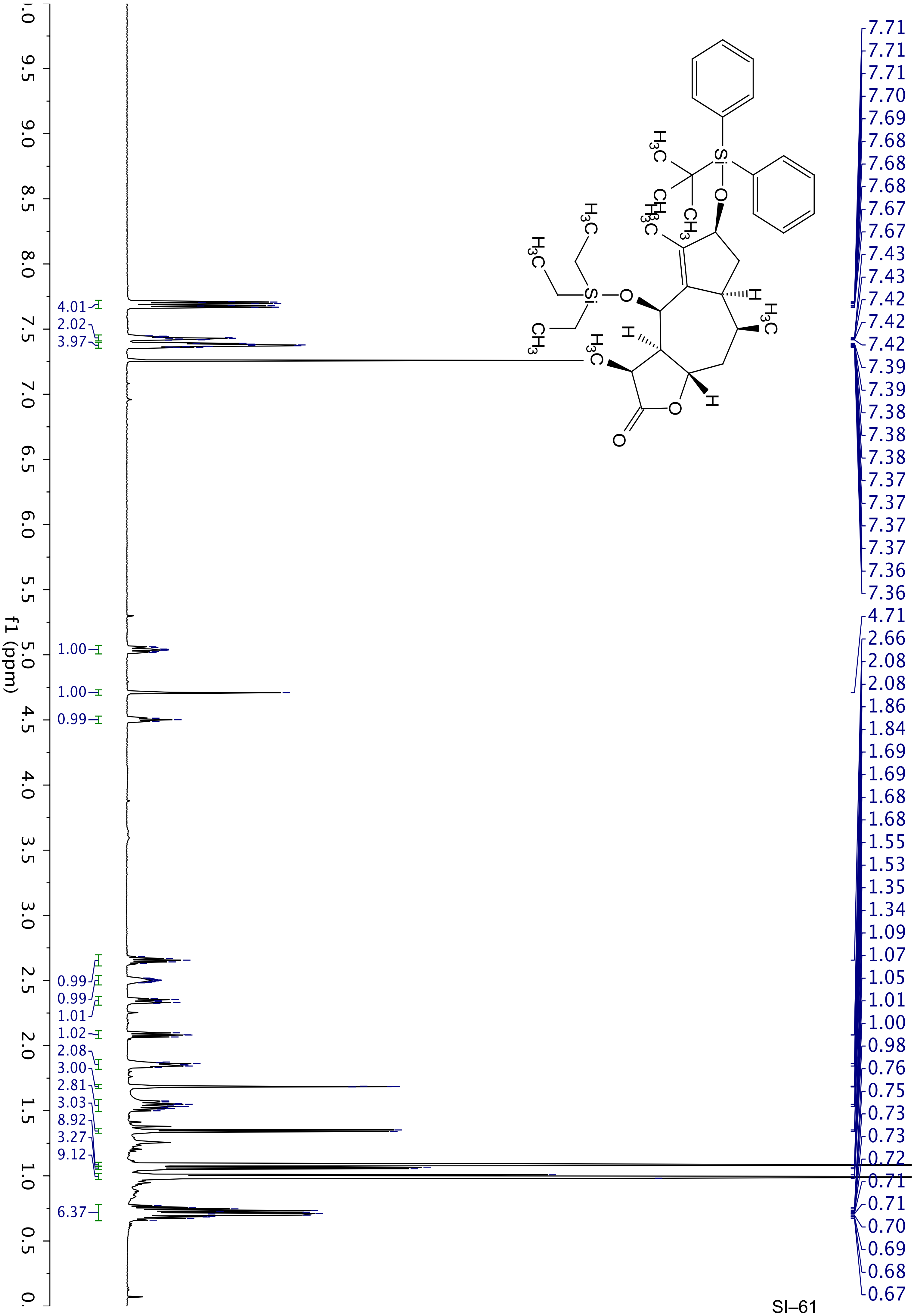
142.28
140.05
138.54
136.13
136.13
134.56
134.19
129.84
129.83
127.75
127.66
113.39
78.66
77.61
63.88
49.73
48.41
45.37
39.94
39.35
27.13
19.49
12.86
12.41
7.35
5.63
Si
O
CH_3
H_3C
CH_3
H_3C
H_2C
H
H
O
O
H
O
Si
H_3C
H_3C
CH_3
H_3C
220 210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
f1 (ppm)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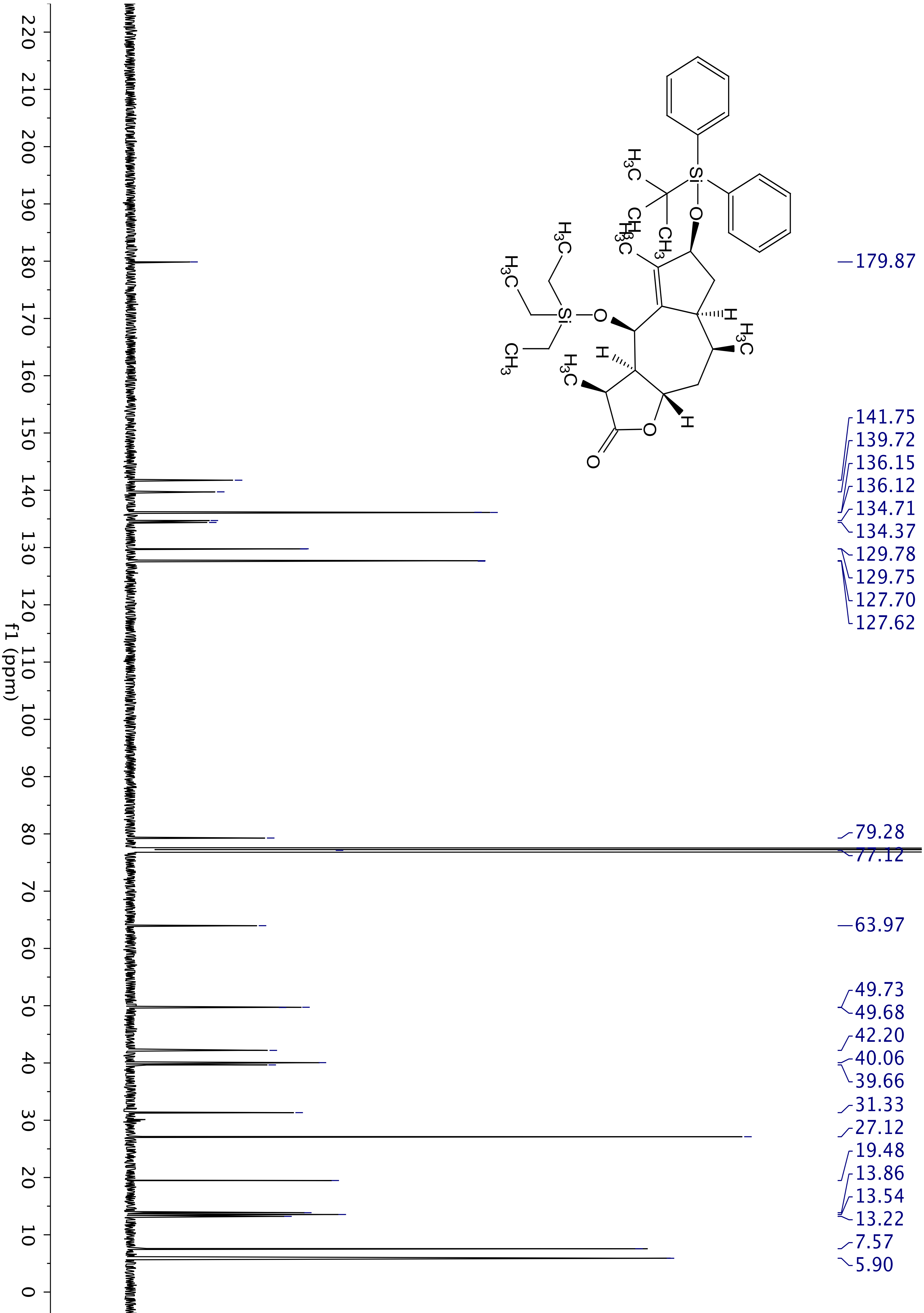
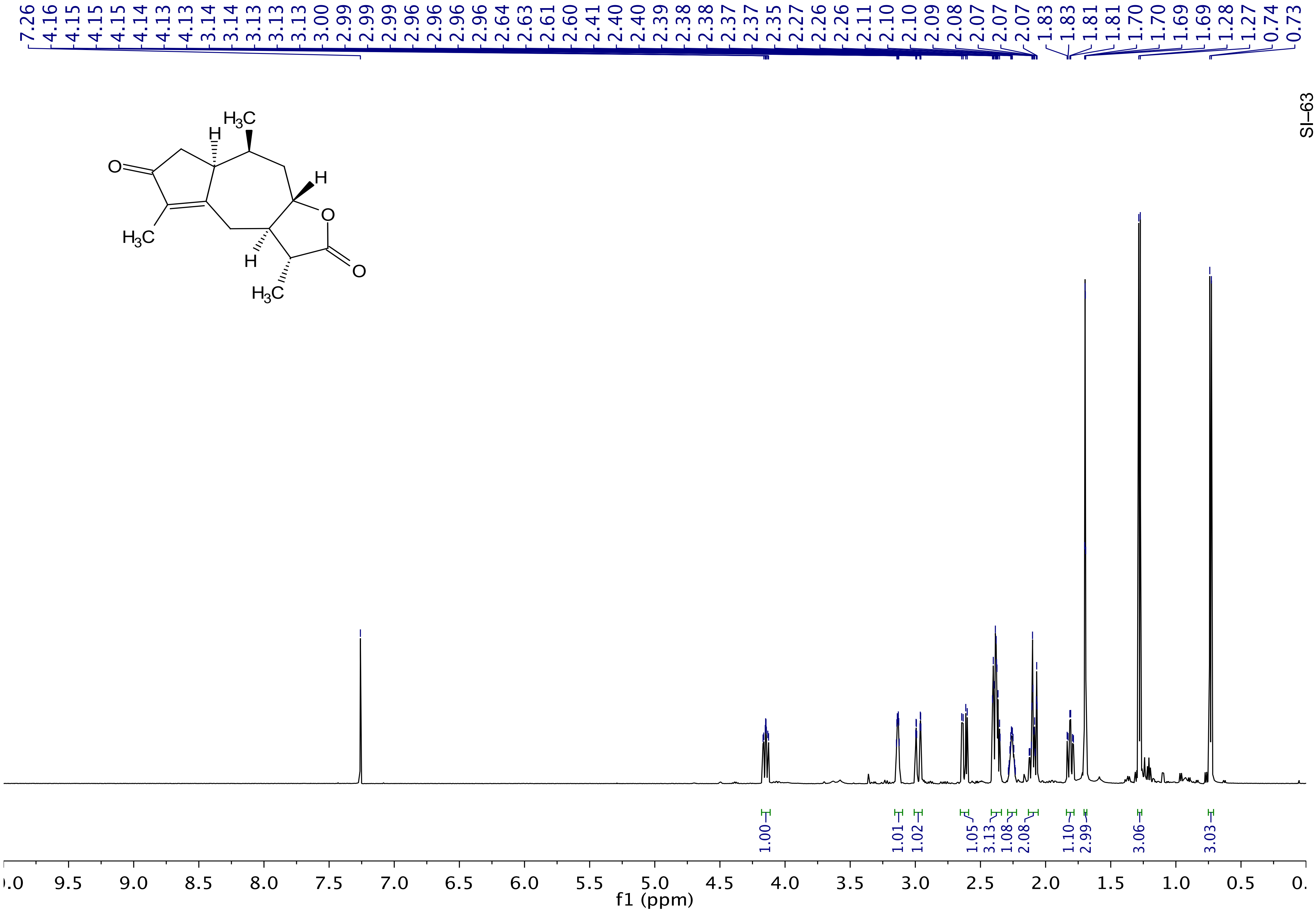
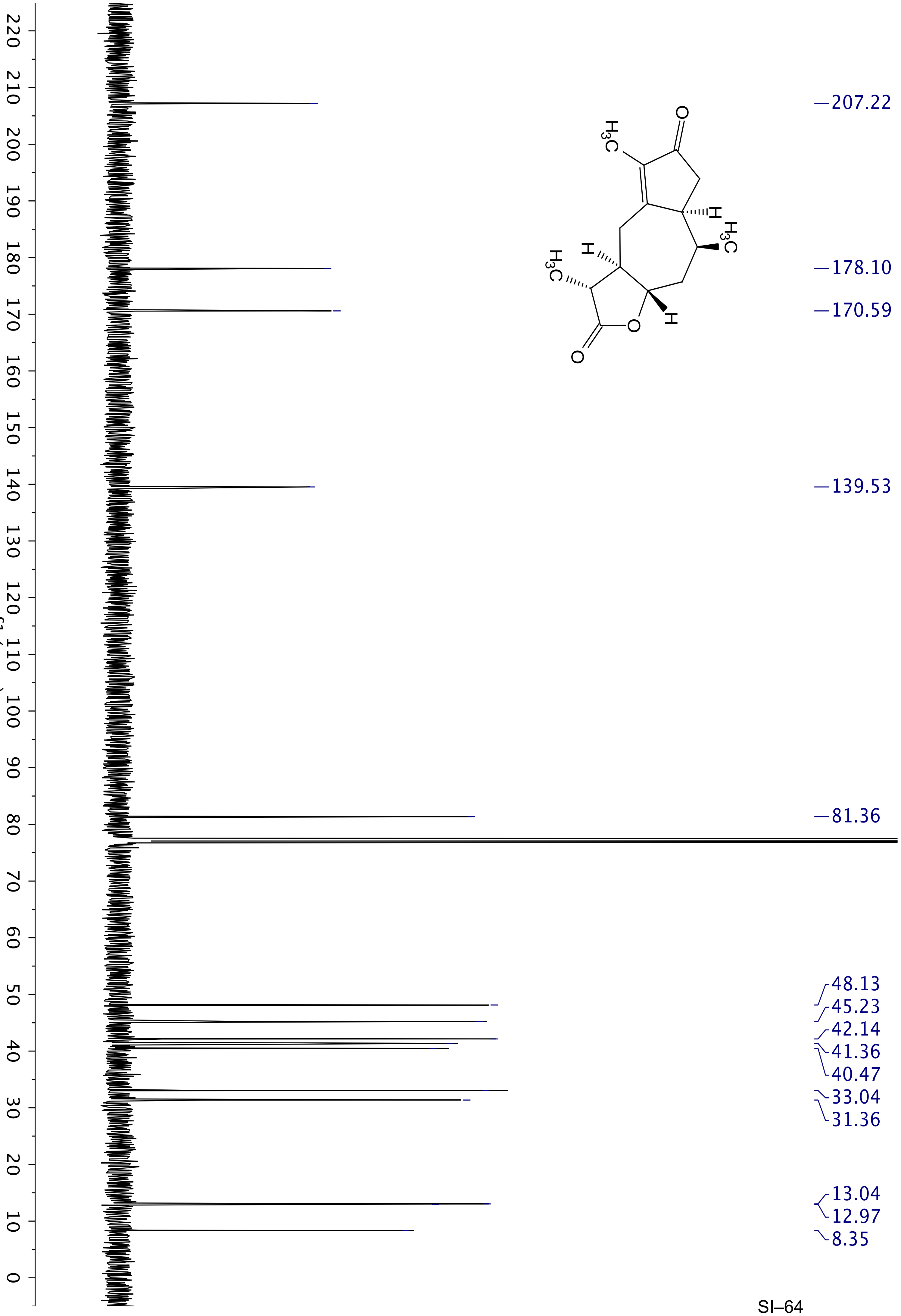
7.71
7.71
7.70
7.69
7.68
7.68
7.68
7.67
7.67
7.43
7.43
7.42
7.42
7.42
7.39
7.39
7.38
7.38
7.38
7.37
7.37
7.37
7.37
7.36
7.36
4.71
2.66
2.08
2.08
1.86
1.84
1.69
1.69
1.68
1.68
1.55
1.53
1.35
1.34
1.09
1.07
1.05
1.01
1.00
0.98
0.76
0.75
0.73
0.73
0.72
0.71
0.71
0.70
0.69
0.68
0.67
4.01
2.02
3.97
1.00
1.00
0.99
0.99
0.99
1.01
1.02
2.08
3.00
2.81
3.03
8.92
3.27
9.12
6.37
f1 (ppm)
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
Si
O
H
H
H
O
O
H_3C
CH_3


179.87
141.75
139.72
136.15
136.12
134.71
134.37
129.78
129.75
127.70
127.62
79.28
77.12
63.97
49.73
49.68
42.20
40.06
39.66
31.33
27.12
19.48
13.86
13.54
13.22
7.57
5.90
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)
Si
O
H3C
CH3
Si
O
H3C
CH3
H
H3C
H
H3C
H
O
O


7.26
4.16
4.15
4.15
4.15
4.14
4.13
4.13
3.14
3.14
3.13
3.13
3.13
3.00
2.99
2.99
2.99
2.96
2.96
2.96
2.96
2.64
2.63
2.61
2.60
2.41
2.40
2.40
2.39
2.38
2.38
2.37
2.37
2.35
2.27
2.26
2.26
2.11
2.10
2.10
2.09
2.08
2.07
2.07
2.07
1.83
1.83
1.81
1.81
1.70
1.70
1.69
1.69
1.28
1.27
0.74
0.73
H3C
H
H
O
O
H3C
H
O
H3C
1.00
1.01
1.02
1.05
3.13
1.08
2.08
1.10
2.99
3.06
3.03
.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.
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
f1 (ppm)
207.22
178.10
170.59
139.53
81.36
48.13
45.23
42.14
41.36
40.47
33.04
31.36
13.04
12.97
8.35
O
H_3C
H
H_3C
H
H_3C
H
O
O