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The Enantioselective Total Synthesis of Laurendecumallene B

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Supporting Information Section

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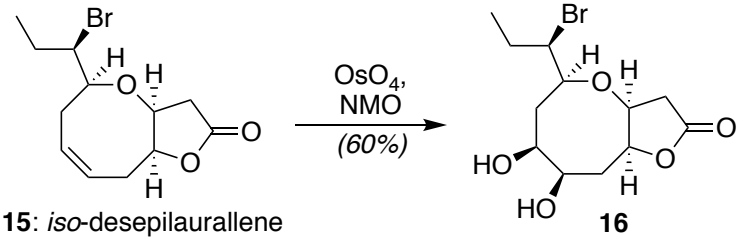
Experimental Data for Compounds

A. General Procedures. All reactions were carried out under an argon atmosphere with dry solvents under anhydrous conditions, unless otherwise noted. Dry tetrahydrofuran (THF), toluene, diethyl ether (Et_2O) dichloromethane (CH_2Cl_2), and acetonitrile (CH_3CN) were obtained by passing commercially available pre-dried, oxygen-free formulations through activated alumina columns. Yields refer to chromatographically and spectroscopically (^1H and ^{13}C NMR) homogeneous materials, unless otherwise stated. Reagents were purchased at the highest commercial quality and used without further purification, unless otherwise stated. Reactions were magnetically stirred and monitored by thin-layer chromatography (TLC) carried out on 0.25 mm E. Merck silica gel plates (60F-254) using UV light as visualizing agent, and an ethanolic solution of phosphomolybdic acid and cerium sulfate or a solution of $KMnO_4$ in aq. $NaHCO_3$ and heat as developing agents. SiliCycle silica gel (60, academic grade, particle size 0.040–0.063 mm) was used for flash column chromatography. Preparative thin-layer chromatography separations were carried out on 0.50 mm E. Merck silica gel plates (60F-254). NMR spectra were recorded on Bruker 500 MHz instruments and calibrated using residual undeuterated solvent as an internal reference. The following abbreviations were used to explain the multiplicities: s = singlet, d = doublet, t = triplet, q = quartet, br = broad, app = apparent. IR spectra were recorded on a Perkin-Elmer 1000 series FT-IR spectrometer. High-resolution mass spectra (HRMS) were recorded on Agilent 6244 Tof-MS using ESI (Electrospray Ionization) at the University of Chicago Mass Spectroscopy Core Facility.

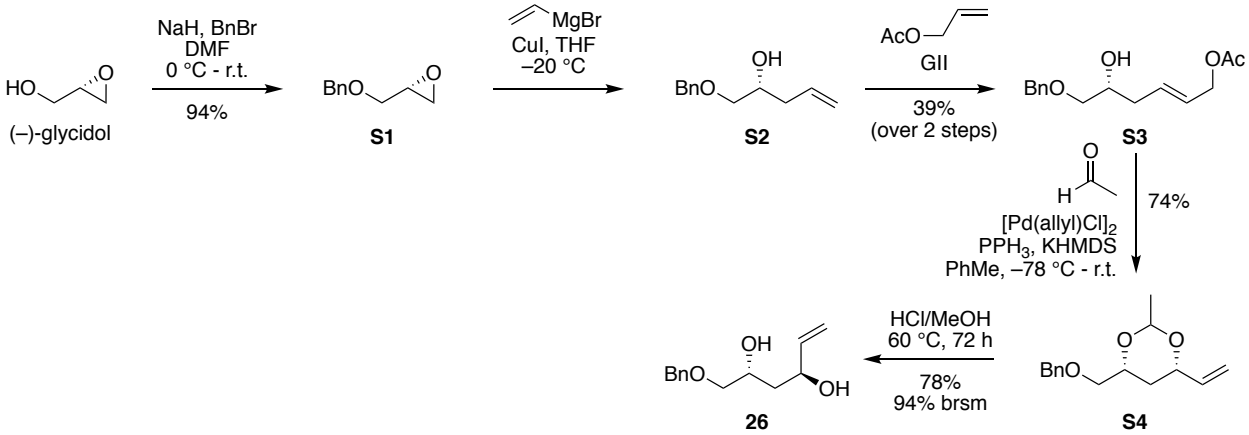
B. Abbreviations. THF = tetrahydrofuran, Et_2O = diethyl ether, EtOAc = ethyl acetate, DMP = Dess–Martin periodinane, Et_3N = triethylamine, BDSB = bromodiethylsulfonium bromopentachloroantimonate(V), GII = Grubbs Catalyst®, 2nd generation, HGII = Hoveyda-Grubbs Catalyst®, 2nd generation.

C. Synthesis of Laurendecumallene B



15: *iso*-desepilaurallene **16**

Diol 16. To a solution of *rac*-alkene **15**[1] (29.5 mg, 0.102 mmol, 1.0 equiv) in acetone (1.0 mL) and H_2O (0.2 mL) at 25 °C was added NMO (24.0 mg, 0.204 mmol, 2.0 equiv) and then the reaction was allowed to stir at 25 °C for 20 min. Next, OsO_4 (0.05 mL, 2.5% by weight in *t*-BuOH, 0.004 mmol, 0.04 equiv) was added and the reaction mixture was stirred at 25 °C for 2 h. Upon completion, the reaction contents were quenched by the addition of saturated aqueous Na_2SO_3 (5 mL), diluted with CH_2Cl_2 (10 mL), and poured into a separatory funnel. The two phases were separated, and the aqueous layer was extracted with CH_2Cl_2 (3 × 10 mL). The combined organic extracts were then dried (Na_2SO_4), filtered, and concentrated. Purification of the resultant residue by flash column chromatography (silica gel, CH_2Cl_2:MeOH, 30:1→25:1→20:1) afforded diol **16** (18.4 mg, 0.057 mmol, 56% yield) as a gray powder. **16**: R_f = 0.25 (silica gel, CH_2Cl_2:MeOH, 20:1); IR (film) ν_{max} 3421, 2971, 2921, 2852, 1825, 1751, 1653, 1507, 1465, 994 cm^{-1}; ^1H NMR (500 MHz, DMSO-d_6) δ 4.58 (dt, *J* = 10.9, 4.3 Hz, 1 H), 4.38 (dd, *J* = 7.0, 4.3 Hz, 1 H), 4.15 (dt, *J* = 9.8, 3.7 Hz, 1 H), 3.73 (tt, *J* = 8.6, 3.3 Hz, 3 H), 3.34 (br s, 2 H), 3.03 (dd, *J* = 18.1, 7.0 Hz, 1 H), 2.31 (d, *J* = 18.1 Hz, 1 H), 2.17 (ddd, *J* = 14.7, 11.1, 8.5 Hz, 1 H), 2.02–1.91 (m, 2 H), 1.87 (ddd, *J* = 14.7, 7.3, 3.3 Hz, 1 H), 1.69 (ddd, *J* = 14.7, 9.7, 7.3 Hz, 1 H), 1.54 (d, *J* = 14.6 Hz, 1 H), 0.98 (t, *J* = 7.2 Hz, 3 H); ^{13}C NMR (125 MHz, DMSO-d_6) δ 175.1, 83.6, 80.5, 77.6, 69.7, 68.1, 63.4, 37.9, 35.1, 32.1, 27.0, 12.2; HRMS (CI) calcd for $C_{12}H_{20}BrO_5$ $[M+H]^+$ 323.0496, found 323.0476.



Epoxide S1. To a solution of (*S*)-(–)-glycidol (3.60 mL, 4.00 g, 54.0 mmol, 1.0 equiv) in DMF (21.6 mL) at 25 °C was added BnBr (8.35 mL, 12.0 g, 70.2 mmol, 1.3 equiv) and then the reaction was cooled to 0 °C. Next, NaH (2.81 g, 60% by weight in mineral oil, 70.2 mmol, 1.3 equiv) was added and the reaction mixture was stirred at 0 °C for 5 min before allowing the solution to warm to 25 °C over 10 min. Upon completion, the reaction contents were quenched by the addition of saturated aqueous NH_4Cl (100 mL), diluted with EtOAc (50 mL), and poured into a separatory funnel. The two phases were separated, and the aqueous layer was extracted with EtOAc (3 × 100 mL). The combined organic extracts were then dried (Na_2SO_4), filtered,

and concentrated. Purification of the resultant residue by flash column chromatography (silica gel, hexanes:EtOAc, 8:1) afforded the desired epoxide **S1** (8.37 g, 50.97 mmol, 94% yield) as a colorless liquid. **S1**: R_f = 0.60 (silica gel, hexanes:EtOAc, 4:1); IR (film) ν_{max} 3030, 2998, 2861, 1495, 1454, 1254, 1095, 1028, 899, 739 cm^{-1}; ^1H NMR (500 MHz, $CDCl_3$) δ 7.39–7.25 (m, 5 H), 4.59 (dd, 2 H), 3.77 (dd, *J* = 11.4, 3.0 Hz, 1 H), 3.45 (q, *J* = 11.5, 5.9 Hz, 1 H), 3.20 (m, 1 H), 2.81 (t, *J* = 4.6 Hz, 1 H), 2.63 (dd, *J* = 5.0, 2.7 Hz, 1 H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 137.8, 128.4, 127.7, 73.3, 70.8, 50.9, 44.3; HRMS (ES) calcd for $C_{20}H_{25}O_4$ $[2M+H]^+$ 329.1754, found 329.1751; $[\alpha]_D^{24}$ = +2.4° (*c* = 1.0, $CHCl_3$).

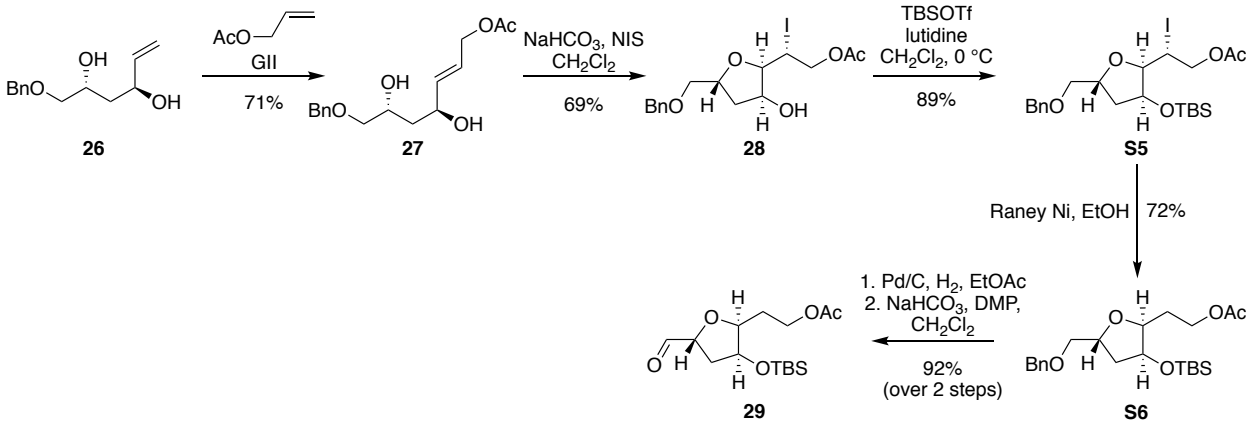
Alcohol S2. To a solution of epoxide **S1** (8.27 g, 50.4 mmol, 1.0 equiv) in THF (50 mL) at –20 °C was added CuI (2.40 g, 12.6 mmol, 0.25 equiv) and then the reaction mixture was stirred at –20 °C for 5 min. Next, vinylmagnesium bromide (60.4 mL, 1.0 M in THF, 60.4 mmol, 1.2 equiv) was added dropwise and the resultant mixture was stirred for an additional 10 min at –20 °C. Upon completion, the reaction contents were quenched by the addition of saturated aqueous NH_4Cl (100 mL), diluted with EtOAc (50 mL), and poured into a separatory funnel. The two phases were separated, and the aqueous layer was extracted with EtOAc (3 × 100 mL). The combined organic extracts were then dried (Na_2SO_4), filtered, and concentrated. Purification of the resultant residue by flash column chromatography (silica gel, hexanes:EtOAc, 10:1) afforded the desired alcohol **S2** (11.0 g, 57.16 mmol, 114% yield) as a colorless liquid containing inseparable impurities (~15%) that were ultimately removed in the next step. [Note: at this point, the impurities were only separable by preparative TLC, CH_2Cl_2:Et_2O, 20:1. Therefore, a sample of the so-obtained fully pure compound was utilized for characterization purposes.] **S2**: R_f = 0.30 (silica gel, hexanes:EtOAc, 8:1); IR (film) ν_{max} 3431, 3066, 3030, 2907, 2861, 1453, 1207, 1101, 996, 915, 698 cm^{-1}; ^1H NMR (500 MHz, $CDCl_3$) δ 7.39–7.28 (m, 5 H), 5.88–5.78 (m, 1 H), 5.15–5.07 (m, 2 H), 4.56 (s, 2 H), 3.89 (dq, *J* = 6.9, 3.5 Hz, 1 H), 3.52 (dd, *J* = 9.5, 3.4 Hz, 1 H), 3.38 (dd, *J* = 9.5, 7.4 Hz, 1 H), 2.36 (s, 1 H), 2.27 (t, *J* = 6.8 Hz, 2 H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 137.9, 134.2, 128.5, 127.8, 127.7, 117.7, 73.9, 73.4, 69.7, 37.9; HRMS (CI) calcd for $C_{12}H_{17}O_2$ $[M+H]^+$ 193.1230, found 193.1229; $[\alpha]_D^{24}$ = –2.5° (*c* = 1.0, $CHCl_3$).

Alkene S3. To neat alcohol **S2** (10.9 g, 56.7 mmol, 1.0 equiv) at 25 °C was added allyl acetate (36.7 mL, 340.14 mmol, 6.00 equiv) and the Grubbs 2nd generation initiator (1.44 g, 1.70 mmol, 0.03 equiv). The resultant brown mixture was stirred at 25 °C for 4 h. Upon completion, the reaction mixture was purified directly by flash column chromatography (silica gel, hexanes:EtOAc, 5:1→1:1) to yield the resultant alkene **S3** (5.18 g, 19.59 mmol, 39% yield over 2 steps as calculated against starting 50.4 mmol of **S1**) as a clear brown liquid. **S3**: R_f = 0.20 (silica gel, hexanes:EtOAc, 4:1); IR (film) ν_{max} 3455, 2905, 2862, 1737, 1454, 1382, 1365, 1236, 1096, 1027, 699 cm^{-1}; ^1H NMR (500 MHz, $CDCl_3$) δ 7.38–7.28 (m, 5 H), 5.83–5.76 (m, 1 H), 5.71–5.62 (m, 1 H), 4.56 (s, 2 H), 4.52 (d, *J* = 6.3 Hz, 2 H), 3.88 (tt, *J* = 7.0, 3.4 Hz, 1 H), 3.51 (dd, *J* = 9.5, 3.4 Hz, 1 H), 3.37 (dd, *J* = 9.5, 7.4 Hz, 1 H), 2.27 (t, *J* = 6.9 Hz, 2 H), 2.06 (s, 3 H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 170.8, 137.8, 131.3, 128.5, 127.8, 127.7, 126.9, 73.8, 73.4, 69.7, 64.9, 36.3, 21.0; HRMS (ES) calcd for $C_{15}H_{21}O_4$ $[M+H]^+$ 265.1442, found 265.1426; $[\alpha]_D^{26}$ = –1.3° (*c* = 1.0, $CHCl_3$).

Protected diol S4. To a solution of alkene **S3** (5.11 g, 19.3 mmol, 1.0 equiv) in toluene (19.3 mL) at –78 °C was added acetaldehyde (19.3 mL, 34.4 mmol, 1.78 equiv), Ph_3P (1.52 g, 5.80 mmol, 0.3 equiv), $[Pd(allyl)Cl]_2$ (0.706 g, 1.93 mmol, 0.1 equiv), and KHMDS (9.66 mL, 1.0 M in THF, 9.66 mmol, 0.5 equiv). The resultant yellow mixture was allowed to warm to 25 °C and was stirred for an additional 2 h. Upon completion, the reaction contents were quenched by the addition of saturated aqueous NH_4Cl (50 mL), diluted with EtOAc (25 mL), and

poured into a separatory funnel. The two phases were separated, and the aqueous layer was extracted with EtOAc (3 × 50 mL). The combined organic extracts were then dried (Na_2SO_4), filtered, and concentrated. Purification of the resultant residue by flash column chromatography (silica gel, hexanes:EtOAc, 15:1) afforded the desired protected diol **S4** (3.54 g, 14.26 mmol, 74% yield) as a pale yellow liquid. **S4**: R_f = 0.60 (silica gel, hexanes:EtOAc, 3:1); IR (film) ν_{max} 3453, 2991, 2939, 2864, 1721, 1453, 1376, 1113, 994, 920, 699 cm^{-1}; ^1H NMR (500 MHz, $CDCl_3$) δ 7.37–7.27 (m, 5 H), 5.87 (ddd, *J* = 16.7, 10.6, 5.7 Hz, 1 H), 5.28 (dq, *J* = 17.3, 1.3 Hz, 1 H), 5.16 (dq, *J* = 10.6, 1.2 Hz, 1 H), 4.80 (q, *J* = 5.1 Hz, 1 H), 4.63–4.54 (m, 2 H), 4.17–4.12 (m, 1 H), 3.95–3.90 (m, 1 H), 3.56 (dd, *J* = 10.1, 6.3 Hz, 1 H), 3.44 (dd, *J* = 10.2, 4.4 Hz, 1 H), 1.61–1.57 (m, 1 H), 1.48–1.43 (m, 1 H), 1.40–1.38 (m, 3 H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 138.0, 137.7, 128.4, 127.8, 127.7, 115.8, 98.5, 76.6, 75.2, 73.5, 72.8, 33.1, 21.1; HRMS (CI/ES): No molecular ion peak was observed; $[\alpha]_D^{24}$ = –6.9° (*c* = 1.0, $CHCl_3$).

Diol 26. Protected diol **S4** (3.50 g, 14.1 mmol, 1.0 equiv) was diluted in a solution of HCl/MeOH (282 mL, 1:3) before warming to 60 °C. The solution was allowed to stir at 60 °C for 72 h. Although full conversion was not observed at this time based on TLC analysis, the reaction contents were diluted with CH_2Cl_2 (100 mL) and poured into a separatory funnel. The two phases were separated, and the aqueous layer was extracted with CH_2Cl_2 (3 × 250 mL). The combined organic extracts were then dried (Na_2SO_4), filtered, and concentrated. Purification of the resultant residue by flash column chromatography (silica gel, hexanes:EtOAc, 3:1→1:1) afforded recovered protected diol **S4** (0.582 g, 2.34 mmol) along with the desired diol **26** (2.44 g, 10.99 mmol,78% yield, 94% yield based on recovered starting material) as a pale yellow oil. **26**: R_f = 0.15 (silica gel, hexanes:EtOAc, 3:1); IR (film) ν_{max} 3382, 2912, 2862, 1453, 1324, 1096, 1027, 992, 924, 737, 698 cm^{-1}; ^1H NMR (500 MHz, $CDCl_3$) δ 7.38–7.28 (m, 5 H), 5.87 (ddd, *J* = 16.7, 10.4, 5.8 Hz, 1 H), 5.32–5.24 (m, 1 H), 5.10 (dt, *J* = 10.5, 1.4 Hz, 1 H), 4.56 (s, 2 H), 4.39 (d, *J* = 6.4 Hz, 1 H), 4.14–4.04 (m, 1 H), 3.48 (dd, *J* = 9.4, 3.8 Hz, 1 H), 3.40 (dd, *J* = 9.4, 7.1 Hz, 1 H), 3.09 (s, 1 H), 3.00 (d, *J* = 2.8 Hz, 1 H), 1.68–1.64 (m, 2 H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 140.4, 137.8, 128.5, 127.9, 127.8, 114.6, 74.2, 73.4, 72.8, 70.7, 39.5; HRMS (CI/ES): No molecular ion peak was observed; $[\alpha]_D^{24}$ = –1.3° (*c* = 1.0, $CHCl_3$).



Alkene 27. To neat diol **26** (2.42 g, 10.9 mmol, 1.0 equiv) at 25 °C was added allyl acetate (11.8 mL, 109.0 mmol, 10.00 equiv) and the Grubbs 2nd generation initiator (0.280 g, 0.33 mmol, 0.03 equiv). The resultant brown mixture was stirred at 25 °C for 4 h. Upon completion, the reaction mixture was directly purified by flash column chromatography (silica gel, hexanes:EtOAc, 4:1→1:2) to afford recovered diol **26** (0.701 g, 3.16 mmol) along with the desired alkene **27** (1.73 g, 5.87 mmol, 54% yield, 76% yield based on recovered starting

material) as a colorless oil. The recovered diol **26** was subjected to the same conditions, yielding an additional batch of the desired alkene **27** (0.561 g, 1.91 mmol, 60% yield, 75% yield based on recovered starting material, 71% combined yield over two iterations of the process). **27**: R_f = 0.40 (silica gel, hexanes:EtOAc, 1:1); IR (film) ν_{max} 3406, 2862, 1736, 1453, 1365, 1241, 1098, 1027, 971, 738 cm^{-1}; ^1H NMR (500 MHz, $CDCl_3$) δ 7.43–7.27 (m, 5 H), 5.81 (ddd, *J* = 16.4, 6.9, 4.7 Hz, 2 H), 4.55 (d, *J* = 4.7 Hz, 4 H), 4.42 (d, *J* = 6.1 Hz, 1 H), 4.10–4.03 (m, 1 H), 3.46 (dd, *J* = 9.4, 3.7 Hz, 1 H), 3.42–3.37 (m, 1 H), 3.36 (d, *J* = 3.6 Hz, 1 H), 3.03 (d, *J* = 2.9 Hz, 1 H), 2.06 (s, 3 H), 1.67–1.62 (t, 2 H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 170.8, 137.7, 136.4, 128.5, 127.9, 127.8, 124.3, 74.2, 73.4, 71.6, 70.8, 64.2, 39.4, 20.9; HRMS (ES) calcd for $C_{16}H_{23}O_5$ $[M+H]^+$ 295.1547, found 295.1542; $[\alpha]_D^{24}$ = –0.9° (*c* = 1.0, $CHCl_3$).

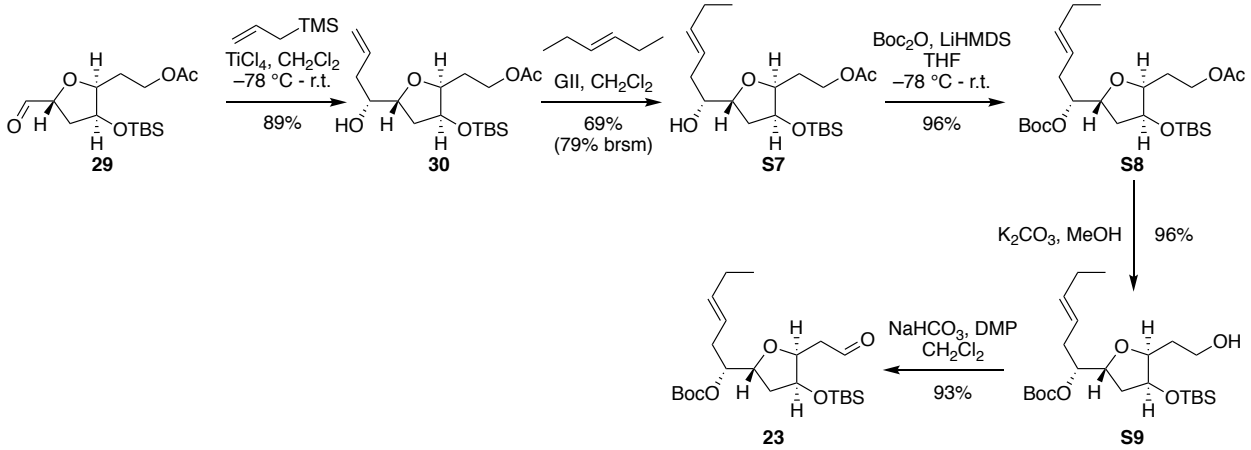
***trans* THF alcohol 28.** To a solution of alkene **27** (2.26 g, 7.68 mmol, 1.0 equiv) in CH_2Cl_2 (25.6 mL) at 25 °C was added $NaHCO_3$ (3.87 g, 46.1 mmol, 6.0 equiv) and *N*-iodosuccinimide (4.32 g, 19.2 mmol, 2.5 equiv). The resultant pink colored reaction mixture was allowed to stir for 8 h. Upon completion, the reaction contents were directly concentrated. Purification of the resultant residue by flash column chromatography (silica gel, hexanes:EtOAc, 4:1→3:1) afforded the desired *trans* THF alcohol **28** (2.23 g, 5.31 mmol, 69% yield) as a clear pink oil. **28**: R_f = 0.60 (silica gel, hexanes:EtOAc, 1:1); IR (film) ν_{max} 3459, 2926, 2861, 1742, 1453, 1379, 1240, 1054, 1029, 737, 699 cm^{-1}; ^1H NMR (500 MHz, $CDCl_3$) δ 7.37–7.26 (m, 5 H), 4.60–4.52 (m, 5 H), 4.37 (dd, *J* = 12.2, 6.6 Hz, 1 H), 4.29–4.24 (m, 1 H), 4.20 (dd, *J* = 10.6, 2.8 Hz, 1 H), 3.53 (dd, *J* = 10.5, 3.6 Hz, 1 H), 3.45 (dd, *J* = 10.5, 4.9 Hz, 1 H), 2.10 (s, 3 H), 2.07–2.03 (m, 2 H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 170.5, 138.2, 128.4, 127.6, 127.5, 83.4, 79.0, 74.1, 73.3, 72.3, 67.1, 37.0, 27.1, 20.9; HRMS (ES) calcd for $C_{48}H_{63}I_3O_{15}Na$ $[3M+Na]^+$ 1283.1202, found 1283.1241; $[\alpha]_D^{24}$ = +20.4° (*c* = 1.0, $CHCl_3$).

TBS protected alcohol S5. To a solution of *trans* THF alcohol **28** (2.20 g, 5.23 mmol, 1.0 equiv) in CH_2Cl_2 (17.4 mL) at 0 °C was added TBSOTf (1.51 mL, 8.37 mmol, 1.6 equiv) and 2,6-lutidine (2.42 mL, 20.9 mmol, 4.0 equiv). The resultant reaction mixture was then stirred at 0 °C for 1 h. Upon completion, the reaction contents were quenched by the addition of saturated aqueous NH_4Cl (50 mL), diluted with CH_2Cl_2 (25 mL), and poured into a separatory funnel. The two phases were separated, and the aqueous layer was extracted with CH_2Cl_2 (3 × 50 mL). The combined organic extracts were then dried (Na_2SO_4), filtered, and concentrated. Purification of the resultant residue by flash column chromatography (silica gel, hexanes:EtOAc, 15:1) afforded the desired TBS protected alcohol **S5** (2.49 g, 4.65 mmol, 89% yield) as a colorless liquid. **S5**: R_f = 0.80 (silica gel, hexanes:EtOAc, 4:1); IR (film) ν_{max} 2953, 2928, 2885, 2856, 1746, 1471, 1454, 1361, 1237, 1055, 937, 837 cm^{-1}; ^1H NMR (500 MHz, $CDCl_3$) δ 7.37–7.27 (m, 5 H), 4.59–4.56 (m, 3 H), 4.53 (t, *J* = 3.0 Hz, 1 H), 4.48 (q, *J* = 4.5 Hz, 1 H), 4.40 (dd, *J* = 12.1, 6.7 Hz, 1 H), 4.26 (dd, *J* = 6.8, 3.0 Hz, 1 H), 4.18 (dd, *J* = 10.4, 2.6 Hz, 1 H), 3.52 (dd, *J* = 10.5, 3.7 Hz, 1H), 3.45 (dd, *J* = 10.5, 5.0 Hz, 1 H), 2.10 (s, 3 H), 1.99–1.88 (m, 2 H), 0.92 (s, 9 H), 0.20 (s, 3 H), 0.13 (s, 3 H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 170.6, 138.3, 128.4, 127.6 (2 C), 84.5, 79.0, 74.1, 73.4, 72.5, 67.3, 37.8, 27.2, 25.9, 21.0, 18.0, –4.1, –4.4; HRMS (CI/ES): No molecular ion peak was observed; $[\alpha]_D^{24}$ = +35.7° (*c* = 1.0, $CHCl_3$).

Deiodinated *trans* THF S6. A suspension of Raney Nickel (reagent grade, 30 mL of an aqueous slurry, excess) was added to a round bottom flask under an Ar atmosphere and rinsed with EtOH (3 × 20 mL, removing the solvent each time with a Pasteur pipette). Next, to a solution of TBS protected alcohol **S5** (2.46 g, 4.61 mmol, 1.0 equiv) in EtOH (20.0 mL) at 25 °C was slowly added the above prepared Raney Nickel suspension in EtOH. The resultant suspension was then stirred vigorously at 25 °C for 10 min. Upon completion, the reaction

mixture was filtered through Celite, rinsed with EtOAc (150 mL), and the filtrate was concentrated. The resultant crude material was purified by flash column chromatography (silica gel, hexanes:EtOAc, 12:1) to afford the deiodinated *trans* THF **S6** (1.35 g, 3.31 mmol, 72% yield). **S6**: R_f = 0.30 (silica gel, hexanes:EtOAc, 8:1); IR (film) ν_{max} 2955, 2929, 2897, 2857, 1740, 1472, 1363, 1242, 1093, 1058, 836 cm^{-1}; ^1H NMR (500 MHz, $CDCl_3$) δ 7.37–7.26 (m, 5 H), 4.58 (s, 2 H), 4.40–4.34 (m, 1 H), 4.28 (q, *J* = 3.2 Hz, 1 H), 4.22 (dt, *J* = 11.0, 6.3 Hz, 1 H), 4.15 (ddd, *J* = 11.0, 7.6, 6.2 Hz, 1 H), 3.97 (ddd, *J* = 8.3, 5.0, 3.4 Hz, 1 H), 3.54–3.46 (m, 2 H), 2.03 (s, 3 H), 1.95–1.84 (m, 4 H), 0.89 (s, 9 H), 0.07 (d, *J* = 4.6 Hz, 6 H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 171.1, 138.4, 128.3, 127.6, 127.5, 79.7, 76.3, 73.4, 73.3, 72.6, 62.2, 38.3, 29.0, 25.7, 21.0, 18.0, –4.5, –5.1; HRMS (CI/ES): No molecular ion peak was observed; $[\alpha]_D^{24}$ = +9.6° (*c* = 1.0, $CHCl_3$).

***trans* THF aldehyde 29.** Pd/C (0.443 g, 10% by weight, 0.42 mmol, 0.13 equiv) was carefully added to a solution of deiodinated *trans* THF **S6** (1.33 g, 3.25 mmol, 1.0 equiv) in EtOAc (46.0 mL) at 25 °C. The resultant suspension was then purged by direct bubbling with a balloon of H_2 gas for 2 h at 25 °C. Upon completion, the reaction contents were filtered through a short pad of Celite and washed with EtOAc (200 mL). The filtrate was concentrated directly to afford the desired crude alcohol as a colorless oil. Pressing forward without any additional purification, the so-obtained alcohol (3.25 mmol assumed) was dissolved in CH_2Cl_2 (32.5 mL) at 25 °C and solid $NaHCO_3$ (1.36 g, 16.3 mmol, 5.0 equiv) and Dess–Martin periodinane (1.52 g, 3.58 mmol, 1.1 equiv) were added sequentially. The resultant mixture was stirred at 25 °C for 30 min. Upon completion, the reaction contents were concentrated directly and the resultant residue was purified by flash column chromatography (silica gel, hexanes:EtOAc, 2:1→1:1) to afford the desired aldehyde **29** (0.942 g, 2.98 mmol, 92% yield over 2 steps) as a colorless liquid. **29**: R_f = 0.60 (silica gel, hexanes:EtOAc, 1:1); IR (film) ν_{max} 2955, 2929, 2899, 2857, 1738, 1472, 1463, 1364, 1252, 1052, 836 cm^{-1}; ^1H NMR (500 MHz, $CDCl_3$) δ 9.69 (d, *J* = 2.1 Hz, 1 H), 4.48 (d, *J* = 2.2 Hz, 1 H), 4.33–4.30 (m, 1 H), 4.29–4.23 (m, 1 H), 4.21–4.16 (m, 1 H), 4.00 (ddd, *J* = 8.2, 4.5, 3.2 Hz, 1 H), 2.14–2.08 (m, 2 H), 2.06 (s, 3 H), 1.99 (dd, *J* = 8.5, 5.9 Hz, 1 H), 1.89 (ddd, *J* = 7.9, 6.4, 4.5 Hz, 1 H), 0.89 (s, 9 H), 0.09 (d, *J* = 6.8 Hz, 6 H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 202.7, 171.1, 81.3, 81.2, 72.7, 61.9, 37.3, 28.9, 25.7, 21.0, 18.0, –4.6, –5.1; HRMS (CI/ES): No molecular ion peak was observed; $[\alpha]_D^{24}$ = +19.2° (*c* = 1.0, $CHCl_3$).



Allylic Alcohol 30. To a solution of *trans* THF aldehyde **29** (0.919 g, 2.90 mmol, 1.0 equiv) in CH_2Cl_2 (29.0 mL) at –78 °C was slowly added $TiCl_4$ (0.320 mL, 2.90 mmol, 1.0 equiv) and the resultant mixture was stirred at –78 °C for 5 min. Next, allyltrimethylsilane (0.69 mL,

4.35 mmol, 1.50 equiv) was added dropwise, and the reaction mixture was allowed to stir at –78 °C for a further 30 min. Upon completion, the reaction contents were quenched by the addition of saturated aqueous NH_4Cl (50 mL), diluted with CH_2Cl_2 (25 mL), and poured into a separatory funnel. The two phases were separated, and the aqueous layer was extracted with CH_2Cl_2 (3 × 50 mL). The combined organic extracts were then dried (Na_2SO_4), filtered, and concentrated. Purification of the resultant residue by flash column chromatography (silica gel, hexanes:EtOAc, 5:1→4:1) afforded the desired allylic alcohol **30** (0.928 g, 2.59 mmol, 89% yield) as a colorless oil. **30**: R_f = 0.40 (silica gel, hexanes:EtOAc, 2:1); IR (film) ν_{max} 3468, 2929, 2857, 1739, 1643, 1472, 1364, 1256, 1048, 940, 775 cm^{-1}; ^1H NMR (500 MHz, $CDCl_3$) δ 5.94–5.84 (m, 1 H), 5.16–5.07 (m, 2 H), 4.28 (q, *J* = 3.4, 3.0 Hz, 1 H), 4.25–4.14 (m, 2 H), 4.10–4.04 (m, 1 H), 3.93–3.88 (m, 1 H), 3.47 (ddd, *J* = 7.4, 4.8, 2.1 Hz, 1 H), 2.27–2.22 (m, 2 H), 2.05 (s, 3 H), 1.94 (tt, *J* = 11.6, 4.2 Hz, 1 H), 1.90–1.87 (m, 2 H), 1.85–1.78 (m, 1 H), 0.89 (s, 9 H), 0.07 (d, *J* = 5.6 Hz, 6 H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 171.2, 134.7, 117.3, 79.8, 79.8, 73.9, 73.3, 62.2, 38.4, 38.3, 29.1, 25.7, 21.1, 18.0, –4.5, –5.0; HRMS (CI) calcd for $C_{15}H_{35}O_5Si$ $[M+H]^+$ 359.2256, found 359.2248; $[\alpha]_D^{24}$ = +5.3° (*c* = 1.0, $CHCl_3$).

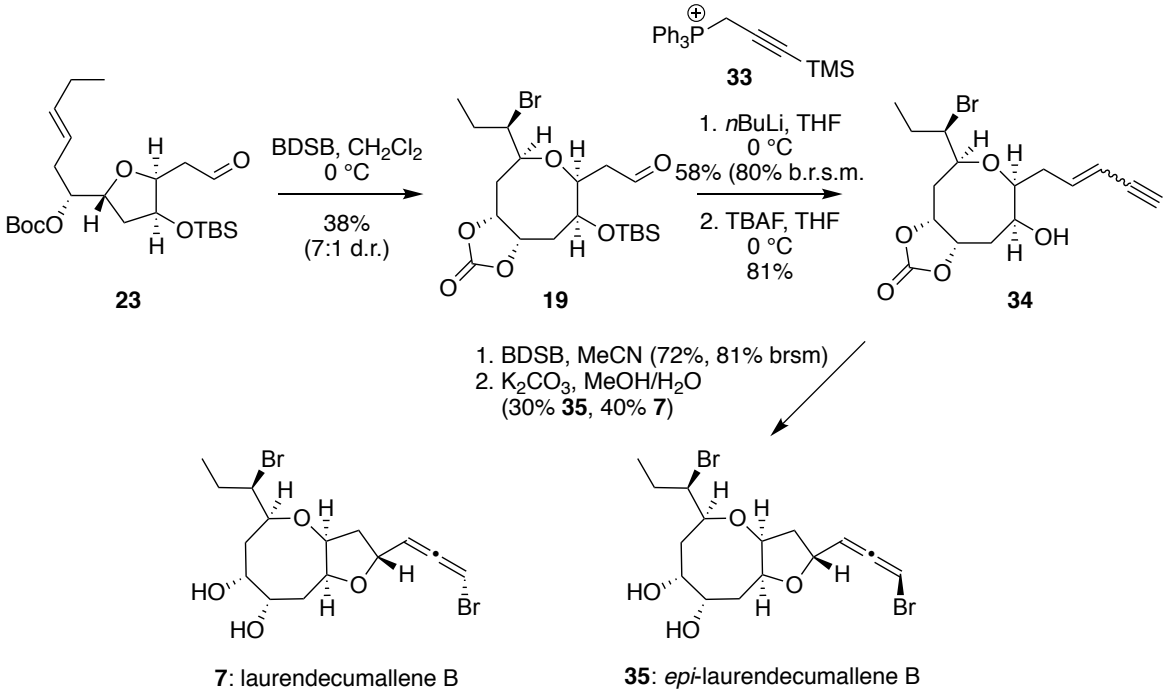
***trans* THF alkene S7.** To a solution of allylic alcohol **30** (0.910 g, 2.54 mmol, 1.0 equiv) in CH_2Cl_2 (5.1 mL) at 25 °C was added *trans*-3-hexene (2.53 mL, 20.3 mmol, 8.0 equiv) and the Grubbs 2nd generation initiator (0.110 g, 0.13 mmol, 0.05 equiv). The resultant mixture was stirred at 25 °C for 8 h. Upon completion, the reaction contents were concentrated directly and the resultant residue was purified by flash column chromatography (silica gel, hexanes:EtOAc, 10:1) to afford recovered allyl alcohol **30** (0.111 g, 0.31 mmol) and the desired alkene **S7** (0.684 g, 1.76 mmol, 69% yield, 79% yield based on recovered starting material) as a colorless oil. **S7**: R_f = 0.50 (silica gel, hexanes:EtOAc, 2:1); IR (film) ν_{max} 3468, 2958, 2929, 2857, 1741, 1463, 1364, 1251, 1048, 971, 941, 836 cm^{-1}; ^1H NMR (500 MHz, $CDCl_3$) δ 5.64–5.40 (m, 2 H), 4.30–4.26 (m, 1 H), 4.19 (tdd, *J* = 13.8, 11.0, 6.0 Hz, 2 H), 4.07 (tt, *J* = 7.9, 5.0 Hz, 1 H), 3.91 (dq, *J* = 8.2, 4.0 Hz, 1 H), 3.42 (dq, *J* = 7.2, 5.1 Hz, 1 H), 2.25 (dd, *J* = 5.1, 3.3 Hz, 1 H), 2.18 (q, *J* = 7.2, 6.5 Hz, 2 H), 2.09–2.00 (m, 5 H), 1.98–1.91 (m, 1 H), 1.90–1.85 (m, 2 H), 1.84–1.78 (m, 1 H), 1.60 (s, 1 H), 1.02–0.94 (m, 3 H), 0.90 (d, *J* = 4.8 Hz, 9 H), 0.08 (t, *J* = 5.1 Hz, 6 H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 171.2, 135.2, 124.6, 79.8, 79.7, 73.9, 73.7, 62.2, 38.3, 37.1, 29.1, 25.7, 25.6, 21.1, 18.0, 13.7, –4.5, –5.0; HRMS (CI/ES): No molecular ion peak was observed; $[\alpha]_D^{24}$ = +5.4° (*c* = 1.0, $CHCl_3$).

***trans* THF protected allylic alcohol S8.** To a solution of alkene **S7** (0.682 g, 1.75 mmol, 1.0 equiv) in THF (11.7 mL) at –78 °C was added Boc_2O (0.7634 g, 3.50 mmol, 2.0 equiv) and LiHMDS (2.28 mL, 1.0 M in THF, 2.28 mmol, 1.3 equiv) and the resultant reaction mixture was allowed to warm to 25 °C over 8 h. Upon completion, the reaction contents were quenched by the addition of saturated aqueous NH_4Cl (25 mL), diluted with CH_2Cl_2 (15 mL), and poured into a separatory funnel. The two phases were separated, and the aqueous layer was extracted with CH_2Cl_2 (3 × 15 mL). The combined organic extracts were then dried (Na_2SO_4), filtered, and concentrated. Purification of the resultant residue by flash column chromatography (silica gel, hexanes:EtOAc, 15:1→10:1) afforded the desired protected allylic alcohol **S8** (0.819 g, 1.68 mmol, 96% yield) as a colorless oil. **S8**: R_f = 0.65 (silica gel, hexanes:EtOAc, 6:1); IR (film) ν_{max} 2958, 2931, 2857, 1740, 1472, 1463, 1367, 1279, 1254, 1165, 1052, 836 cm^{-1}; ^1H NMR (500 MHz, $CDCl_3$) δ 5.60–5.52 (m, 1 H), 5.38 (dtd, *J* = 16.9, 6.4, 1.6 Hz, 1 H), 4.60 (dt, *J* = 6.9, 5.4 Hz, 1 H), 4.30–4.26 (m, 1 H), 4.24–4.16 (m, 2 H), 4.15–4.08 (m, 1 H), 3.97–3.92 (m, 1 H), 2.40–2.27 (m, 2 H), 2.04 (s, 3 H), 2.02–1.95 (m, 2 H), 1.94–1.86 (m, 2 H), 1.80 (dtt, *J* = 13.6, 9.2, 4.7 Hz, 2 H), 1.47 (s, 9 H), 0.95 (t, *J* = 7.4 Hz, 3 H), 0.88 (s, 9 H), 0.06 (d, *J* = 4.3 Hz, 6 H);

^{13}C NMR (125 MHz, $CDCl_3$) δ 171.1, 153.6, 135.6, 123.4, 81.7, 79.4, 77.9, 77.4, 73.4, 62.3, 38.1, 34.4, 28.9, 27.8, 25.7, 25.6, 21.0, 18.0, 13.6, –4.6, –5.0; HRMS (ES) calcd for $C_{25}H_{47}O_7Si$ $[M+H]^+$ 487.3093, found 487.3089; $[\alpha]_D^{24}$ = +2.3° (*c* = 1.0, $CHCl_3$).

***trans* THF primary alcohol S9.** To a solution of protected allylic alcohol **S8** (0.799 g, 1.64 mmol, 1.0 equiv) in MeOH (10.9 mL) at 25 °C was added K_2CO_3 (1.36 g, 9.84 mmol, 6.0 equiv). The resultant white solution was stirred at 25 °C for 2 h. Upon completion, the reaction contents were quenched by the addition of saturated aqueous NH_4Cl (25 mL), diluted with EtOAc (15 mL), and poured into a separatory funnel. The two phases were separated, and the aqueous layer was extracted with EtOAc (3 × 15 mL). The combined organic extracts were then dried (Na_2SO_4), filtered, and concentrated. Purification of the resultant residue by flash column chromatography (silica gel, hexanes:EtOAc, 6:1→4:1) afforded the desired primary alcohol **S9** (0.701 g, 1.58 mmol, 96% yield) as a colorless liquid. **S9**: R_f = 0.40 (silica gel, hexanes:EtOAc, 4:1); IR (film) ν_{max} 3448, 2958, 2930, 2857, 1739, 1472, 1368, 1255, 1166, 1057, 835 cm^{-1}; ^{1}H NMR (500 MHz, $CDCl_3$) δ 5.60–5.52 (m, 1 H), 5.41–5.33 (m, 1 H), 4.61 (q, *J* = 6.2 Hz, 1 H), 4.28–4.20 (m, 2 H), 4.02 (dt, *J* = 10.2, 3.3 Hz, 1 H), 3.76 (q, *J* = 5.9 Hz, 2 H), 2.65 (t, *J* = 6.1 Hz, 1 H), 2.28 (t, *J* = 6.8 Hz, 2 H), 2.03–1.95 (m, 2 H), 1.93–1.87 (m, 2 H), 1.79 (ddd, *J* = 13.1, 8.6, 4.7 Hz, 1 H), 1.67–1.57 (m, 2 H), 1.48 (s, 9 H), 0.95 (q, *J* = 7.3 Hz, 3 H), 0.88 (s, 9 H), 0.06 (d, *J* = 4.5 Hz, 6 H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 153.8, 135.7, 123.2, 81.9, 81.7, 78.0, 77.6, 74.0, 61.1, 38.0, 34.1, 31.9, 27.8, 25.7, 25.6, 18.1, 13.7, –4.7, –5.0; HRMS (CI) calcd for $C_{23}H_{42}O_5SiNa$ $[M+Na–H_2O]^+$ 450.2727, found 450.2716; $[\alpha]_D^{24}$ = +5.2° (*c* = 1.0, $CHCl_3$).

***trans* THF aldehyde 23.** To a solution of primary alcohol **S9** (0.680 g, 1.53 mmol, 1.0 equiv) in CH_2Cl_2 (10.2 mL) at 25 °C was sequentially added solid $NaHCO_3$ (0.643 g, 7.65 mmol, 5.00 equiv) and Dess–Martin periodinane (0.713 g, 1.68 mmol, 1.1 equiv). The resultant mixture was stirred at 25 °C for 30 min. Upon completion, the reaction contents were concentrated directly and the resultant residue was purified by flash column chromatography (silica gel, hexanes:EtOAc, 10:1) to afford the desired aldehyde **23** (0.631 g, 1.43 mmol, 93% yield) as a colorless liquid. **23**: R_f = 0.65 (silica gel, hexanes:EtOAc, 4:1); IR (film) ν_{max} 2958, 2931, 2857, 1738, 1472, 1368, 1279, 1255, 1165, 1077, 836 cm^{-1}; ^{1}H NMR (500 MHz, $CDCl_3$) δ 9.79 (t, *J* = 1.8 Hz, 1 H), 5.61–5.51 (m, 1 H), 5.41–5.32 (m, 1 H), 4.61 (dt, *J* = 6.9, 5.2 Hz, 1 H), 4.42–4.39 (m, 1 H), 4.33 (td, *J* = 6.4, 3.5 Hz, 1 H), 4.25 (dt, *J* = 9.4, 6.0 Hz, 1 H), 2.68 (ddd, *J* = 6.6, 3.0, 1.8 Hz, 2 H), 2.35–2.29 (m, 2 H), 2.03–1.96 (m, 2 H), 1.94–1.82 (m, 2 H), 1.47 (s, 9 H), 0.95 (t, *J* = 7.4 Hz, 3 H), 0.86 (s, 9 H), 0.06 (s, 3 H), 0.01 (s, 3 H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 201.5, 153.5, 135.8, 123.2, 81.8, 78.1, 77.7, 77.7, 73.3, 44.1, 37.9, 34.4, 27.8, 25.7, 25.5, 18.0, 13.6, –4.7, –5.1; HRMS (ES) calcd for $C_{23}H_{43}O_6Si$ $[M+H]^+$ 443.2831, found 443.2834; $[\alpha]_D^{24}$ = +14.0° (*c* = 1.0, $CHCl_3$).



Bromoether aldehyde 19. To a solution of aldehyde **23** (0.603 g, 1.36 mmol, 1.0 equiv) in CH_2Cl_2 (27.2 mL) at 0 °C was added BDSB[2] (0.895 g, 1.63 mmol, 1.2 equiv). The resultant orange solution was stirred at 0 °C for 10 min. Upon completion, the reaction contents were quenched by the addition of saturated aqueous NH_4Cl (50 mL), diluted with CH_2Cl_2 (25 mL), and poured into a separatory funnel. The two phases were separated, and the aqueous layer was extracted with CH_2Cl_2 (3 × 25 mL). The combined organic extracts were then dried (Na_2SO_4), filtered, and concentrated. Purification of the resultant residue by flash column chromatography (silica gel, hexanes:EtOAc, 8:1→5:1) afforded the desired bromoether aldehyde **19** as a mixture of two inseparable diastereomers (0.241 g, 0.52 mmol, d.r. = 7:1, 38% yield) as a pale yellow oil. **19**: R_f = 0.50 (silica gel, hexanes:EtOAc, 2:1); IR (film) ν_{max} 2930, 2856, 1801, 1724, 1463, 1360, 1256, 1179, 1074, 833, 777 cm^{-1}; ^1H NMR (500 MHz, $CDCl_3$) δ 9.80 (s, 1 H), 5.24 (dd, *J* = 10.8, 7.1 Hz, 1 H), 4.98–4.92 (m, 1 H), 3.88 (dd, *J* = 8.8, 5.9 Hz, 3 H), 3.81–3.75 (m, 1 H), 2.95–2.84 (m, 2 H), 2.40–2.23 (m, 3 H), 2.05–1.95 (m, 2 H), 1.57 (d, *J* = 3.9 Hz, 1 H), 1.04 (t, *J* = 7.3 Hz, 3 H), 0.93 (s, 9 H), 0.12 (s, 3 H), 0.07 (s, 3 H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 199.8, 154.3, 78.9, 76.6, 76.1, 75.4, 70.5, 56.5, 47.7, 35.1, 29.5, 28.2, 25.8, 18.1, 12.2, –4.4, –5.0; HRMS (CI/ES) calcd for $C_{38}H_{66}BrO_{12}Si_2$ $[2M]^+$ 928.2460, found 928.2415; $[\alpha]_D^{24}$ = –6.5° (*c* = 1.0, $CHCl_3$).

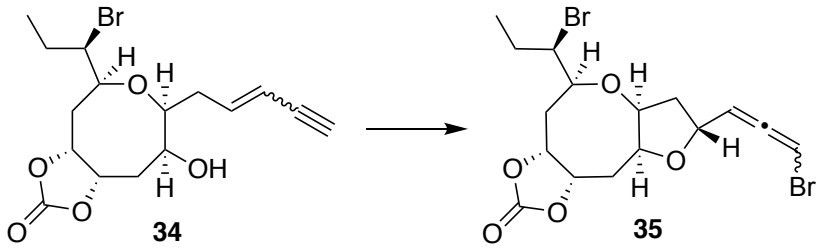
***E/Z* Bromoether enyne 34.** To a solution of Wittig salt **33** (0.390 g, 0.86 mmol, 1.80 equiv; prepared according to the literature procedure reported by Diederich and co-workers[3] with all the spectroscopic data matching that reported in Ref. 3) in THF (12.0 mL) was added *n*-BuLi (0.48 mL, 1.6 M in hexanes, 0.77 mmol, 1.6 equiv) dropwise at 0 °C. The resultant dark solution was stirred at 0 °C for 30 min before a solution of bromoether aldehyde **19** (0.225 g, 0.48 mmol, 1.0 equiv) in THF (12.0 mL) was added in a single portion at 0 °C. Upon completion, the reaction contents were quenched by the addition of saturated aqueous NH_4Cl (50 mL), diluted with CH_2Cl_2 (25 mL), and poured into a separatory funnel. The two phases were separated, and the aqueous layer was extracted with CH_2Cl_2 (3 × 25 mL). The combined organic extracts were then dried (Na_2SO_4), filtered, and concentrated. Purification of the resultant residue by flash

column chromatography (silica gel, hexanes:EtOAc, 8:1→5:1) afforded recovered aldehyde **19** (59.6 mg, 0.13 mmol) and the desired protected enyne (0.158 g, 0.28 mmol, *E/Z* = 2:1, 58% yield, 80% yield b.r.s.m.) as a colorless oil and as inseparable *E/Z* isomers. Pressing forward, to a solution of protected enyne (0.145 g, 0.26 mmol, 1.0 equiv) in THF (10.4 mL) at 0 °C was added TBAF (0.52 mL, 1.0 M in THF, 0.52 mmol, 2.0 equiv) and the reaction mixture was stirred at 0 °C for 5 min. Upon completion, the reaction contents were quenched by the addition of saturated aqueous NH_4Cl (25 mL), diluted with EtOAc (15 mL), and poured into a separatory funnel. The two phases were separated, and the aqueous layer was extracted with EtOAc (3 × 15 mL). The combined organic extracts were then dried (Na_2SO_4), filtered, and concentrated. Purification of the resultant residue by flash column chromatography (silica gel, hexanes:EtOAc, 3:1→2:1) afforded the desired bromoether enyne **34** (78.0 mg, 0.21 mmol, *E*/*Z* = 2:1, 81% yield) as a colorless oil and as a mixture of inseparable *E/Z* isomers. **34**: R_f = 0.20 (silica gel, hexanes:EtOAc, 2:1); IR (film) ν_{max} 3469, 3288, 2925, 2360, 2339, 1797, 1458, 1358, 1192, 1047, 962, 779 cm^{-1}; ^1H NMR (500 MHz, $CDCl_3$) δ 6.15 (dt, *J* = 15.5, 7.6 Hz, 0.66 H), 6.00 (d, *J* = 10.8 Hz, 0.33 H), 5.61 (ddt, *J* = 15.9, 14.2, 2.1 Hz, 1 H), 5.26–5.17 (m, 1 H), 4.96 (dtd, *J* = 15.5, 8.3, 7.7, 3.5 Hz, 1 H), 3.94 (t, *J* = 6.5 Hz, 1 H), 3.83 (dtd, *J* = 9.6, 7.0, 3.6 Hz, 1 H), 3.66 (dd, *J* = 9.7, 5.6 Hz, 1 H), 3.46–3.39 (m, 1 H), 2.87 (dd, *J* = 15.4, 3.2 Hz, 1 H), 2.79–2.59 (m, 0.66 H), 2.54–2.41 (m, 1.33 H), 2.35–2.10 (m, 4 H), 1.91 (d, *J* = 6.8 Hz, 1 H), 1.75–1.64 (m, 1 H), 1.08 (td, *J* = 7.2, 1.6 Hz, 3 H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 154.1, 140.5, 112.8, 83.3, 80.6, 78.9, 76.1, 75.1, 68.7, 56.1, 36.2, 35.2, 33.1, 29.2, 28.6, 12.1 (only one isomer reported); HRMS (CI/ES): No molecular ion peak was observed; $[\alpha]_D^{24}$ = +4.8° (*c* = 0.8, $CHCl_3$).

Laurendecumallene B (7) and *epi*-laurendecumallene B (35). To a solution of enyne **34** (66.2 mg, 0.18 mmol, 1.0 equiv) in MeCN (9.0 mL) at 25 °C was added BDSB[2] (0.121 g, 0.22 mmol, 1.2 equiv) and the reaction mixture was stirred at 25 °C for 2 h. Upon completion, the reaction contents were quenched by the addition of saturated aqueous NH_4Cl (25 mL), diluted with EtOAc (15 mL), and poured into a separatory funnel. The two phases were separated, and the aqueous layer was extracted with EtOAc (3 × 15 mL). The combined organic extracts were then dried (Na_2SO_4), filtered, and concentrated. Purification of the resultant residue by flash column chromatography (silica gel, hexanes:EtOAc, 4:1→2:1) afforded recovered enyne **34** (7.9 mg, 0.021 mmol) and the desired protected diol bromoallene (56.6 mg, 0.13 mmol, *R*/*S* = 1.0:1.3, 72% yield, 81% yield based on recovered starting material) as a colorless oil and as a mixture of inseparable epimers. Pressing forward, to a solution of protected diol bromoallene (44.9 mg, 0.099 mmol, 1.0 equiv) in MeOH (9.9 mL) and H_2O (1.0 mL) at 25 °C was added K_2CO_3 (0.137 g, 0.99 mmol, 10 equiv). The resultant mixture was stirred for 2 h at 25 °C. Upon completion, the reaction contents were quenched by the addition of saturated aqueous NH_4Cl (25 mL), diluted with EtOAc (15 mL), and poured into a separatory funnel. The two phases were separated, and the aqueous layer was extracted with EtOAc (3 × 15 mL). The combined organic extracts were then dried (Na_2SO_4), filtered, and concentrated. Purification of the resultant residue by preparative thin-layer chromatography (silica gel, CH_2Cl_2:Et_2O, 1:1) over six consecutive full development iterations afforded the undesired *epi*-laurendecumallene B (**35**, 12.6 mg, 0.030 mmol, 30% yield) and desired laurendecumallene B (**7**, 17.1 mg, 0.040 mmol, 40% yield), both as colorless oils. **35**: R_f = 0.65 (silica gel, hexanes:EtOAc, 2:1); IR (film) ν_{max} 3403, 3055, 2922, 2851, 1958, 1557, 1437, 1334, 1194, 1106, 1064, 869 cm^{-1}; ^1H NMR (500 MHz, $CDCl_3$) δ 6.09 (dd, J = 5.7, 1.7 Hz, 1 H), 5.43 (t, *J* = 6.0 Hz, 1 H), 4.77 (m, 1 H), 4.31 (d, *J* = 6.6 Hz, 1 H), 4.20 (m, 1 H), 4.17 (m, 1 H), 4.10 (m, 1 H), 3.87 (m, 1 H), 3.82 (m, 1 H), 2.42 (ddd, *J* = 15.8, 7.4, 2.1 Hz, 1 H), 2.20 (dd, *J* = 12.4, 7.4 Hz, 1 H), 2.07–2.06 (m, 3 H), 2.01 (m, 1

H), 1.96 (m, 1 H), 1.77 (m, 1 H), 1.06 (t, J = 7.2 Hz, 3 H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 201.6, 101.9, 81.3, 78.6, 78.5, 74.0, 73.9, 70.7, 69.0, 60.8, 40.1, 35.2, 32.4, 27.4, 12.1; HRMS (ES) calcd for $C_{15}H_{22}Br_2O_4Na$ $[M+Na]^+$ 446.9785, found 446.9763; $[\alpha]_D^{24}$ = –82.2° (c = 1.0, $CHCl_3$). **7**: R_f = 0.65 (silica gel, hexanes:EtOAc, 2:1); IR (film) ν_{max} 3405, 3056, 2933, 1959, 1438, 1335, 1196, 1065, 868, 659 cm^{-1}; ^{1}H NMR (500 MHz, $CDCl_3$) δ 6.06 (dd, J = 5.7, 1.9 Hz, 1 H), 5.45 (t, J = 5.7 Hz, 1 H), 4.77 (m, 1 H), 4.31 (d, J = 8.3 Hz, 1 H), 4.20 (m, 1 H), 4.18 (m, 1 H), 4.10 (m, 1 H), 3.87 (m, 1 H), 3.82 (m, 1 H), 2.42 (dd, J = 15.0, 7.9 Hz, 1 H), 2.19 (m, 1 H), 2.08–2.03 (m, 3 H), 2.01 (m, 1 H), 1.97 (m, 1 H), 1.77 (m, 1 H), 1.06 (t, J = 7.2 Hz, 3 H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 201.2, 102.2, 81.2, 78.7, 78.5, 74.1, 73.5, 70.6, 69.0, 60.8, 40.1, 35.2, 32.4, 27.4, 12.2; HRMS (ES) calcd for $C_{15}H_{22}Br_2O_4Na$ $[M+Na]^+$ 446.9785, found 446.9761; $[\alpha]_D^{24}$ = +117.4° (c = 0.33, $CHCl_3$). [Note: The same optical rotation value was observed with c = 1.0].

Table S1. Screening of Cyclization Conditions to Generate **S10**.[a]



Entry	Reagent	Solvent	Temperature (°C)	*E*-/*Z*-[a]	Yield (%)
1	TBCO	MeCN	23	1 : 1	63%
2	TBCO	benzene	23	1 : 1	decomp.
3	BDSB	HFIP	23	1 : 1	54%
4	BDSB	MeCN	23	1 : 1	75%
5	BDSB	MeCN	23	2 : 1	72% (81% brsm)
6	BDSB	$EtNO_2$	–78 to 23	2 : 1	52% (78% brsm)
7	BDSB	$MeNO_2$	0 to 23	2 : 1	34%

[a] Starting ratio of enyne isomers; in all cases product **35** was generated as an ~1:1 mixture of *R*-/*S*-bromoallenes based on crude NMR. For the actual case run on scale, the final ratio was 1.3:1 after isolation.

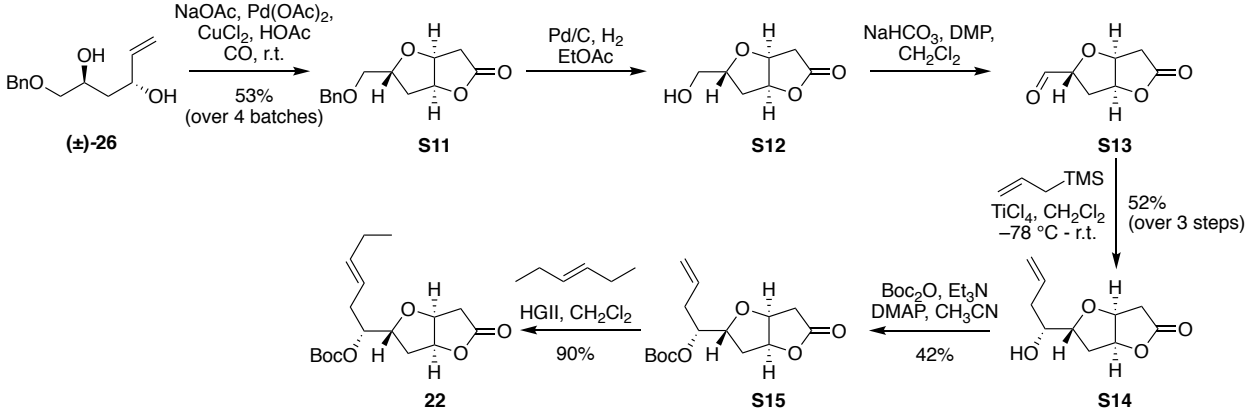
Table S2. Comparative ^{1}H NMR data for laurendecumallene B (**7**)

Natural (Wang)[4] (500 MHz, $CDCl_3$)	Synthetic (this work) (500 MHz, $CDCl_3$)
6.06 (dd, *J* = 5.7, 1.7 Hz, 1 H)	6.06 (dd, *J* = 5.7, 1.9 Hz, 1 H)
5.45 (dd, *J* = 5.7, 5.7 Hz, 1 H)	5.45 (t, *J* = 5.7 Hz, 1 H)
4.77 (m, 1 H)	4.77 (m, 1 H)
4.31 (br d, *J* = 7.3 Hz, 1 H)	4.31 (d, *J* = 8.3 Hz, 1 H)
4.20 (m, 1 H)	4.20 (m, 1 H)
4.18 (m, 1 H)	4.18 (m, 1 H)
4.10 (m, 1 H)	4.10 (m, 1 H)
3.87 (m, 1 H)	3.87 (m, 1 H)
3.82 (m, 1 H)	3.82 (m, 1 H)
2.42 (ddd, *J* = 15.8, 7.3, 1.6 Hz, 1 H)	2.42 (dd, *J* = 15.0, 7.9 Hz, 1 H)
2.19 (ddd, *J* = 13.2, 6.6, 1.8 Hz, 1 H)	2.19 (m, 1 H)
2.07–2.03 (m, 3 H)	2.08–2.03 (m, 3 H)
2.01 (m, 1 H)	2.01 (m, 1 H)
1.97 (m, 1 H)	1.97 (m, 1 H)
1.77 (m, 1 H)	1.77 (m, 1 H)
1.06 (t, *J* = 7.2 Hz, 3 H)	1.06 (t, *J* = 7.2 Hz, 3 H)

Table S3. Comparative ^{13}C NMR data for laurendecumallene B (**7**)

Natural (Wang)[4] (125 MHz, $CDCl_3$)	Synthetic (this work) (125 MHz, $CDCl_3$)
201.3	201.2
102.3	102.2
81.3	81.2
78.8	78.7
78.5	78.5
74.0	74.1
73.4	73.5
70.7	70.6
69.1	69.0
60.8	60.8
40.2	40.1
35.2	35.2
32.5	32.4
27.4	27.4
12.1	12.2

D. Synthesis of Bicyclic Lactone (22)



Bicyclic lactone S11. A flame-dried flask was charged with NaOAc (0.371 g, 4.26 mmol, 3.0 equiv) and $CuCl_2$ (0.565 g, 4.26 mmol, 3.0 equiv) before being flushed with CO and evacuated three times. The CO balloon was then transferred to the flask, followed by the addition of AcOH (7.1 mL). A solution of diol (±)-**26** (0.316 g, 1.42 mmol, 1.0 equiv) in AcOH (7.1 mL) was then added, followed by $Pd(OAc)_2$ (0.031 g, 0.14 mmol, 0.1 equiv). The resultant suspension was then purged by direct bubbling with a balloon of CO gas for 1 h at 25 °C. Upon completion, the reaction contents were filtered through a short pad of Celite and washed with EtOAc (150 mL). This procedure was repeated a total of 4 times with a combined starting mass of diol (±)-**26** of 1.272 g (5.72 mmol). The filtrates were combined and concentrated directly and the resultant residue was purified by flash column chromatography (silica gel, hexanes:EtOAc, 4:1 → 3:2) to afford the desired bicyclic lactone **S11** (0.750 g, 3.01 mmol, 53% yield over 4 batches) as a slightly yellow oil. **S11**: R_f = 0.23 (silica gel, hexanes:EtOAc, 3:2); IR (film) ν_{max} 3064, 3030, 2935, 2863, 1781, 1496, 1453, 1402, 1352, 1257, 1181, 1148, 1077, 1050, 912, 831, 700 cm^{-1}; ^1H NMR (500 MHz, $CDCl_3$) δ 7.39–7.27 (m, 5 H), 5.11 (t, *J* = 4.8 Hz, 1H), 4.86–4.83 (m, 1 H), 4.57 (s, 2 H), 4.37 (m, 1 H), 3.62 (dd, *J* = 10.5, 3.1 Hz, 1 H), 3.48 (dd, *J* = 10.5, 5.0 Hz, 1 H), 2.74–2.70 (m, 2 H), 2.34 (dd, *J* = 14.0, 5.8 Hz, 1 H), 2.09–2.01 (m, 1 H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 175.6, 137.9, 128.4, 127.7, 127.6, 84.7, 78.5, 77.9, 73.5, 71.5, 36.7, 34.8; HRMS (CI) calcd for $C_{14}H_{17}O_4$ $[M+H]^+$ 249.1127, found 249.1123.

Allylic alcohol S14. Pd/C (0.187 g, 10% by weight, 0.18 mmol, 0.06 equiv) was carefully added to a solution of bicyclic lactone **S11** (0.749 g, 3.01 mmol, 1.0 equiv) in EtOAc (30.1 mL) at 25 °C. The resultant suspension was then purged by direct bubbling with a balloon of H_2 gas for 0.5 h and then stirred under a H_2 atmosphere for 10 h at 25 °C. Upon completion, the reaction contents were filtered through a short pad of Celite and washed with EtOAc (200 mL). The filtrate was concentrated directly to afford the desired crude alcohol as a colorless oil. Pressing forward without any additional purification, the so-obtained alcohol (3.01 mmol assumed) was dissolved in CH_2Cl_2 (30.1 mL) at 25 °C and solid $NaHCO_3$ (1.26 g, 15.05 mmol, 5.0 equiv) and Dess–Martin periodinane (1.40 g, 3.31 mmol, 1.1 equiv) were added sequentially. The resultant mixture was stirred at 25 °C for 20 min. Upon completion, the reaction contents were concentrated directly and the resultant residue was purified by flash column chromatography twice (silica gel, CH_2Cl_2:MeOH, 30:1, *then* silica gel, pure EtOAc) to afford the desired aldehyde **S13** with inseparable impurities as a colorless liquid. Pushing forward, to a solution of aldehyde **S13** (0.437 g, 2.80 mmol, 1.0 equiv) in CH_2Cl_2 (28.0 mL) at –78 °C was slowly added $TiCl_4$ (0.31 mL, 2.80 mmol, 1.0 equiv) and the resultant mixture was stirred at –78 °C for 10 min. Next, allyltrimethylsilane (0.67 mL, 4.20 mmol, 1.50 equiv) was added dropwise,

and the reaction mixture was allowed to stir at –78 °C for a further 20 min. The reaction was then warmed to 25 °C and stirred for a further 10 min. Upon completion, the reaction contents were quenched by the addition of saturated aqueous Rochelle's Salt (50 mL), diluted with CH_2Cl_2 (25 mL), and poured into a separatory funnel. The two phases were separated, and the aqueous layer was extracted with CH_2Cl_2 (3 × 50 mL). The combined organic extracts were then dried (Na_2SO_4), filtered, and concentrated. Purification of the resultant residue by flash column chromatography (silica gel, CH_2Cl_2:MeOH, 40:1) afforded the desired allylic alcohol **S14** (0.309 g, 1.56 mmol, 52% yield over 3 steps) as a colorless oil. **S14**: R_f = 0.17 (silica gel, CH_2Cl_2:MeOH, 20:1); IR (film) ν_{max} 3466, 3076, 2924, 1780, 1641, 1435, 1402, 1356, 1181, 1150, 1064, 919, 838 cm^{-1}; ^1H NMR (500 MHz, $CDCl_3$) δ 5.84 (ddt, *J* = 17.5, 10.1, 7.2 Hz, 1 H), 5.18–5.11 (m, 3 H), 4.82 (t, *J* = 5.2 Hz, 1 H), 4.11 (dd, *J* = 9.9, 5.0 Hz, 1 H), 3.56 (t, *J* = 5.8 Hz, 1 H), 2.78–2.67 (m, 2 H), 2.35–2.28 (m, 2 H), 2.22–2.12 (m, 1 H), 2.06 (m, 1 H); ^{13}C NMR (125 MHz, $CDCl_3$) δ175.5, 133.9, 118.3, 84.9, 81.0, 78.5, 72.1, 38.8, 36.8, 34.9; HRMS (CI/ES) calcd for $C_{10}H_{15}O_4$ $[M+H]^+$ 199.0970, found 199.0961.

Protected allylic alcohol S15. To a solution of allylic alcohol **S14** (0.182 g, 0.92 mmol, 1.0 equiv) in CH_3CN (9.2 mL) at 25 °C was added Boc_2O (0.220 g, 1.01 mmol, 1.1 equiv), Et_3N (0.39 mL, 2.76 mmol, 3.0 equiv), and DMAP (0.010 g, 0.09 mmol, 0.1 equiv) and the resultant reaction mixture was stirred at 25 °C for 8 h. Upon completion, the reaction contents were quenched by the addition of saturated aqueous NH_4Cl (25 mL), diluted with CH_2Cl_2 (15 mL), and poured into a separatory funnel. The two phases were separated, and the aqueous layer was extracted with CH_2Cl_2 (3 × 15 mL). The combined organic extracts were then dried (Na_2SO_4), filtered, and concentrated. Purification of the resultant residue by flash column chromatography (silica gel, hexanes:EtOAc, 5:1 → 3:1) afforded the desired protected allylic alcohol **S15** (0.116 g, 0.39 mmol, 42% yield) as a white amorphous solid. **S15**: R_f = 0.15 (silica gel, hexanes:EtOAc, 3:1); IR (film) ν_{max} 2984, 2929, 1786, 1739, 1460, 1395, 1369, 1279, 1255, 1160, 750 cm^{-1}; ^1H NMR (500 MHz, $CDCl_3$) δ 5.77 (td, *J* = 10.1, 7.1 Hz, 1 H), 5.18–5.08 (m, 3 H), 4.83 (ddd, *J* = 5.7, 4.3, 1.4 Hz, 1 H), 4.68 (td, *J* = 6.5, 4.5 Hz, 1 H), 4.26 (ddd, *J* = 9.2, 6.0, 4.6 Hz, 1 H), 2.77–2.65 (m, 2 H), 2.45–2.34 (m, 3 H), 1.94 (m, 1 H), 1.48 (s, 9 H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 175.5, 153.3, 132.6, 118.6, 84.4, 82.4, 78.7, 78.3, 76.5, 36.6, 35.7, 34.8, 27.8; HRMS (ES) calcd for $C_{15}H_{23}O_6$ $[M+H]^+$ 299.1495, found 299.1445.

Bicyclic lactone alkene 22. To a solution of protected allylic alcohol **S15** (0.116 g, 0.39 mmol, 1.0 equiv) in CH_2Cl_2 (3.9 mL) at 25 °C was added *trans*-3-hexene (0.29 mL, 2.34 mmol, 6.0 equiv) and the Hoveyda–Grubbs 2nd generation initiator (0.013 g, 0.02 mmol, 0.05 equiv). The resultant mixture was stirred at 25 °C for 1 h. Upon completion, the reaction contents were quenched by the addition of saturated aqueous NH_4Cl (15 mL), diluted with CH_2Cl_2 (10 mL), and poured into a separatory funnel. The two phases were separated, and the aqueous layer was extracted with CH_2Cl_2 (3 × 15 mL). The combined organic extracts were then dried (Na_2SO_4), filtered, and concentrated. Purification of the resultant residue by flash column chromatography (silica gel, hexanes:EtOAc, 4:1) to afford the desired bicyclic lactone **22** (0.115 g, 0.35 mmol, 90% yield) as a slightly purple solid. **22**: R_f = 0.17 (silica gel, hexanes:EtOAc, 3:1); IR (film) ν_{max} 2966, 2935, 1788, 1741, 1460, 1395, 1369, 1279, 1255, 1162, 1074, 968, 846 cm^{-1}; ^1H NMR (500 MHz, $CDCl_3$) δ 5.61–5.50 (m, 1 H), 5.38–5.27 (m, 1 H), 5.10 (t, *J* = 4.6 Hz, 1 H), 4.86 (td, *J* = 6.6, 4.3 Hz, 1 H), 4.77 (td, *J* = 4.5, 1.9 Hz, 1 H), 4.23 (ddd, *J* = 9.8, 5.8, 4.2 Hz, 1 H), 2.77–2.63 (m, 2 H), 2.35 (dd, *J* = 14.1, 5.8 Hz, 1 H), 2.29–2.23 (m, 2 H), 2.14 (ddd, *J* = 14.3, 9.5, 5.2 Hz, 1 H), 2.00 (tdd, *J* = 7.7, 6.2, 1.5 Hz, 2 H), 1.47 (s, 9 H), 0.96 (td, *J* = 7.5, 5.4 Hz, 3 H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 175.5, 153.1, 136.2, 122.6, 84.6, 82.2, 79.3, 78.5, 76.2, 36.8,

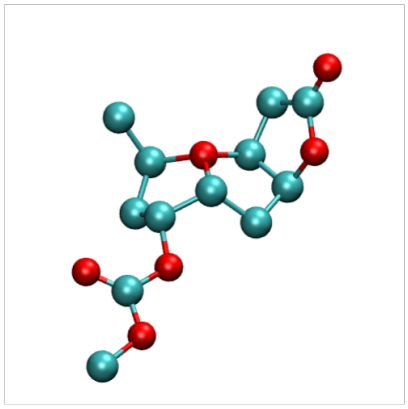
34.6, 33.3, 27.8, 25.5, 13.6; HRMS (CI/ES) calcd for $C_{17}H_{27}O_6$ $[M+H]^+$ 327.1808, found 327.1802.

E. Computational General Information

DFT optimizations were performed through Gaussian 09 on the Midway2 Cluster at the University of Chicago's Research Computing Center. Ground state geometry optimizations and free energies (kcal/mol) were determined using the B3LYP/cc-pVDZ level of theory in the gas phase at 298K. All ground state structures display no imaginary frequencies.

F. Minimized Structures

24 – lactone



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Thermal correction to Gibbs Free Energy= 0.242399
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Sum of electronic and thermal Energies= -918.349076
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1 1

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H	-4.42549000	0.36628900	1.14216100
H	-3.77202300	1.32325500	-0.20503600
C	-2.01476600	-1.30122200	0.90038800
O	-2.82874600	-1.76080000	-0.18291000
O	-1.21804900	0.79011500	0.08512800
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C	-0.25571100	-0.29881700	-0.38859100
C	-0.53415800	-1.44968100	0.56486200
H	-2.29591100	-1.82952100	1.82439900
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H	0.07321500	-1.37168500	1.47811400
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C	-0.43737700	2.06518500	0.51842300
C	0.96442500	1.51447200	0.71519600
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O	-4.59140500	-1.03344800	-1.39772200
C	3.36941100	-0.24967500	-0.21847700
H	-0.17621300	2.79220200	-1.52065200
H	-0.12415100	4.02747300	-0.24069800
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O	4.12885700	-1.27619300	0.11312300
C	5.55118800	-1.08210000	-0.09697200
O	3.69994700	0.82056100	-0.66761100
H	5.90876900	-0.23282400	0.50143200
H	5.75298300	-0.89797700	-1.16109600
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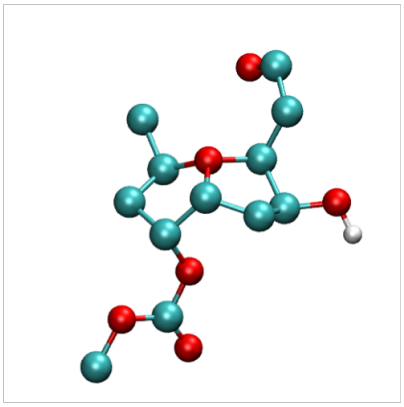
25 – aldehyde



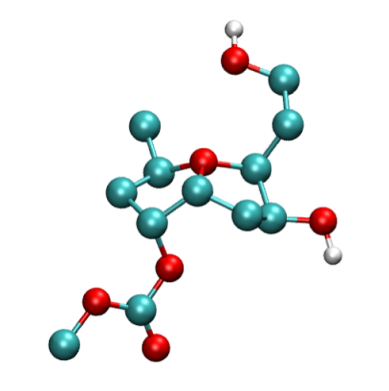
Zero-point correction= 0.308678 (Hartree/Particle)
Thermal correction to Energy= 0.327302
Thermal correction to Enthalpy= 0.328246
Thermal correction to Gibbs Free Energy= 0.261242
Sum of electronic and zero-point Energies= -919.533630
Sum of electronic and thermal Energies= -919.515006
Sum of electronic and thermal Enthalpies= -919.514061
Sum of electronic and thermal Free Energies= -919.581066

1 1

C	-3.29699600	0.62307100	0.26990900
C	-4.26350400	-0.43336500	-0.23014500

C	-1.90081100	0.50792400	-0.31398900
H	-3.29481400	0.62627800	1.37347600
H	-3.70021400	1.61042900	-0.01931300
C	-1.04145100	1.78717000	-0.21707400
O	-1.87758600	2.90656500	-0.37634800
O	-1.09888800	-0.49808000	0.48370600
H	-1.94719000	0.08857200	-1.32617700
C	-0.09833400	0.22998800	1.40819800
C	-0.39369000	1.70014400	1.18354100
H	-0.25582300	1.74682100	-0.98680400
H	-1.10773900	2.07898600	1.92846500
H	0.52732000	2.29535000	1.24114500
C	1.24582700	-0.33854600	0.96848100
H	-0.35398800	-0.13543200	2.41008200
C	-0.37680200	-1.65985000	-0.25933000
C	0.90800100	-1.77041500	0.54800200
C	-1.27372100	-2.86902300	-0.28574400
H	1.71516400	-2.21572800	-0.04831400
H	0.75409800	-2.40025800	1.43859500
H	1.97924400	-0.29676900	1.78438000
O	1.68281400	0.44353100	-0.15168600
O	-3.97451000	-1.26875900	-1.05647900
C	2.99822300	0.44489900	-0.54583500
H	-5.28991400	-0.37685300	0.20377400
H	-1.37355900	3.62952900	-0.77730100
H	-1.51151000	-3.21009700	0.73326700
H	-0.72739600	-3.67817000	-0.79807400
H	-2.20196000	-2.67682100	-0.83788900
H	-0.18705100	-1.24822700	-1.26041400
O	3.73188200	-0.38678400	0.20199500
C	5.14644900	-0.41538500	-0.12940300
H	5.58540200	0.58016900	0.02069500
H	5.27972500	-0.72425500	-1.17483800
H	5.58720000	-1.14606200	0.55729000
O	3.36177000	1.13013700	-1.45640100

S16 – Free Alcohol



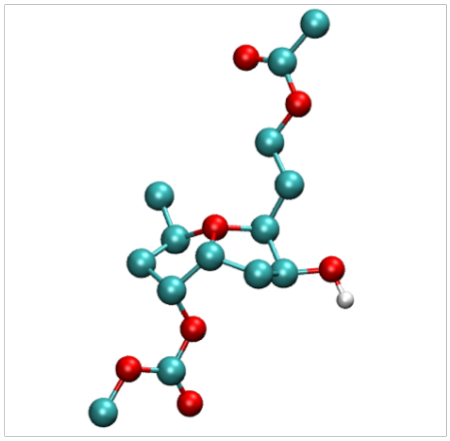
Zero-point correction= 0.332858 (Hartree/Particle)
Thermal correction to Energy= 0.352024
Thermal correction to Enthalpy= 0.352968
Thermal correction to Gibbs Free Energy= 0.283881
Sum of electronic and zero-point Energies= -920.718684
Sum of electronic and thermal Energies= -920.699518
Sum of electronic and thermal Enthalpies= -920.698574
Sum of electronic and thermal Free Energies= -920.767661

1 1

C	-3.24328900	0.77164200	0.19824000
C	-4.30677900	-0.21914400	-0.25270600
C	-1.87047600	0.60563200	-0.43828500
H	-3.15241900	0.74263100	1.29645500
H	-3.57341100	1.78841000	-0.06604900
C	-0.94206700	1.83277700	-0.29737200
O	-1.70314000	3.00123600	-0.46872100
O	-1.07696900	-0.46623800	0.28651700
H	-1.93893300	0.24814800	-1.47416700
C	-0.10524600	0.18998200	1.29199400
C	-0.34005600	1.67921500	1.11777900
H	-0.13501800	1.75624100	-1.04369700
H	-1.06052000	2.05710100	1.85613800
H	0.60061400	2.23606500	1.21895400
C	1.24677000	-0.39813500	0.90025900
H	-0.42776800	-0.21012200	2.26047400
C	-0.33155000	-1.53882500	-0.53523600
C	0.89183100	-1.77532600	0.33687100
C	-1.23169100	-2.72299000	-0.77223800
H	1.72186400	-2.20059100	-0.24215900
H	0.65335000	-2.47119800	1.15693500
H	1.91957700	-0.45244900	1.76573900
O	1.79788000	0.45001800	-0.11827700
O	-3.91457300	-1.52522500	0.15128300
C	3.13815500	0.42548400	-0.40942900

H	-1.12287300	3.71815300	-0.76362000
H	-1.54402800	-3.17883500	0.17755000
H	-0.65863700	-3.46418600	-1.35314400
H	-2.13288300	-2.45203100	-1.33417300
H	-0.05706100	-1.02158800	-1.46636000
O	3.78128400	-0.48970500	0.32564900
C	5.21512000	-0.55041600	0.10283500
H	5.67562500	0.41142000	0.36600900
H	5.42121600	-0.78215000	-0.95073100
H	5.57425200	-1.34966100	0.76016300
O	3.59929500	1.15961200	-1.23404800
H	-4.43276200	-0.15704700	-1.35320400
H	-5.26968100	0.07337500	0.20397000
H	-4.65504700	-2.12865200	-0.01059000

S17 – Acetate-protected alcohol



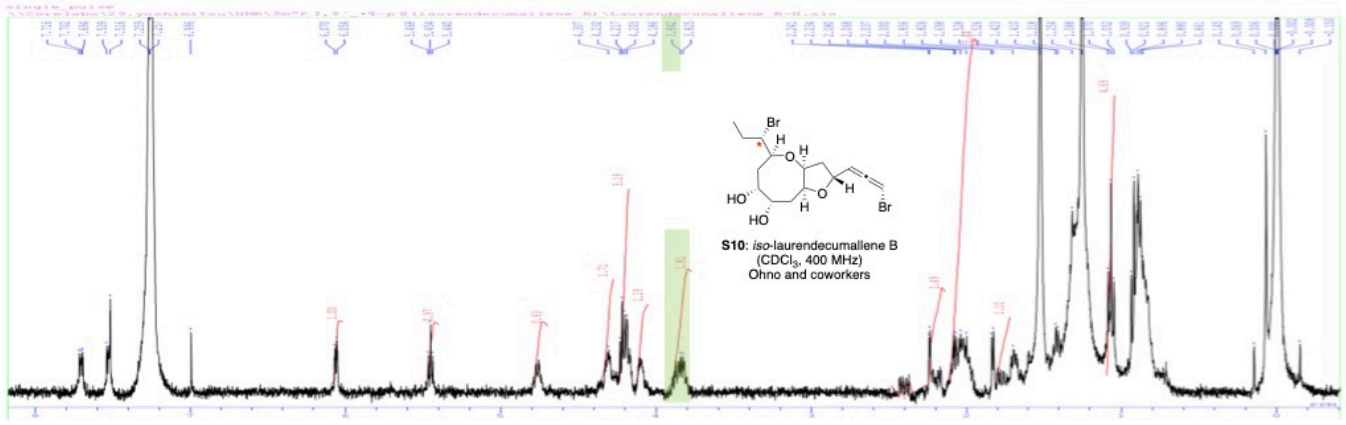
Zero-point correction= 0.369805 (Hartree/Particle)
Thermal correction to Energy= 0.392585
Thermal correction to Enthalpy= 0.393529
Thermal correction to Gibbs Free Energy= 0.314822
Sum of electronic and zero-point Energies= -1073.351401
Sum of electronic and thermal Energies= -1073.328622
Sum of electronic and thermal Enthalpies= -1073.327678
Sum of electronic and thermal Free Energies= -1073.406384

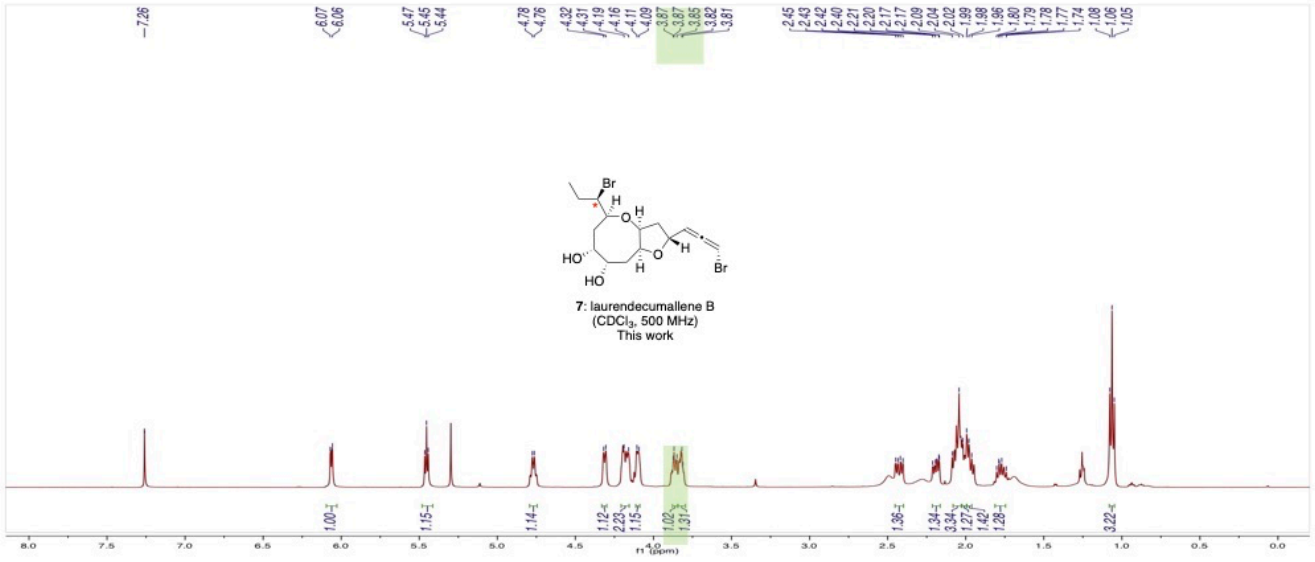
1 1

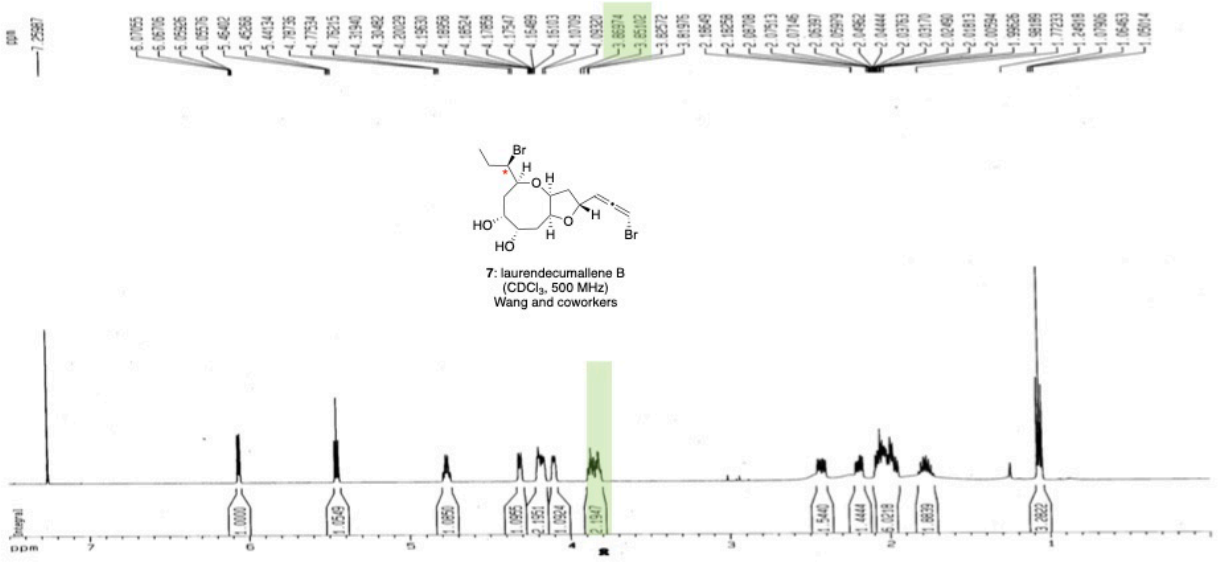
C	-2.16165300	1.10317000	-0.09337600
C	-3.11515300	-0.05470300	-0.34888600
C	-0.75359300	0.85395400	-0.59391900
H	-2.15519500	1.35797100	0.97859300
H	-2.51416900	2.00435600	-0.61926900
C	0.24765300	2.00271900	-0.34779000
O	-0.42831600	3.22299500	-0.50842000
O	-0.13063300	-0.29422300	0.18790800
H	-0.74772600	0.50509400	-1.63535900

C	0.84430000	0.25459900	1.25470800
C	0.75422700	1.76029200	1.09411100
H	1.09013900	1.89946300	-1.04992100
H	0.03152700	2.19064500	1.80100000
H	1.73428500	2.22723200	1.25902200
C	2.14789900	-0.46029700	0.91698700
H	0.43565300	-0.12456600	2.19900400
C	0.53240300	-1.45542300	-0.58141200
C	1.68404800	-1.80477500	0.34963900
C	-0.48965600	-2.53265700	-0.84180100
H	2.49349800	-2.31593500	-0.18765900
H	1.34147600	-2.46381200	1.16319300
H	2.78288400	-0.56935600	1.80568800
O	2.80545000	0.32343000	-0.08828600
O	-4.40884900	0.37080200	0.08435300
C	4.15027600	0.18326000	-0.32917400
H	0.20928500	3.91125500	-0.74779000
H	-0.90969000	-2.92519100	0.09597400
H	0.01645400	-3.36043800	-1.36466500
H	-1.30804800	-2.18726100	-1.48840500
H	0.90207000	-0.98930200	-1.50601600
O	4.68481200	-0.77589900	0.43501800
C	6.11630100	-0.96078400	0.26722600
H	6.64682700	-0.03977000	0.54404300
H	6.34072600	-1.21700000	-0.77681000
H	6.38024800	-1.78291600	0.94113500
O	4.69992500	0.86874800	-1.14075400
H	-3.15079200	-0.31665500	-1.42172600
H	-2.82265700	-0.96289100	0.20018700
C	-5.36380600	-0.61406300	0.08319200
C	-6.69564300	-0.07414000	0.52331800
H	-6.59910800	0.43468600	1.49415900
H	-7.41849600	-0.89488800	0.59193200
H	-7.04940200	0.67427900	-0.20320500
O	-5.11181400	-1.74859200	-0.24357500

G. Physical NMR Comparison







When comparing the NMR spectrum of the natural product from the Wang group,[4] it can be seen that the distinctive ^{1}H NMR signal of the proton at the red-starred position is reported to be at 3.87 ppm, which is what we observe as well. The tentatively assigned product from the Ohno group reports this signal at 3.83–3.84,[5] which although close, lends credence to the actual construction of *iso*-laurendecumallene B (**S10**). Furthermore, the position alpha to the red-starred carbon on the exocyclic sidechain is reported by the Wang group to have two peaks, one at 2.01 ppm and the other at 1.77 ppm. Our reported spectrum is in line with this observation, whereas the Fujii/Ohno group observes signals at 2.00, 1.83, and 1.70 ppm. These are all subtle differences; however, it is our belief that these are representative of **S10** and not **7**.

H. References

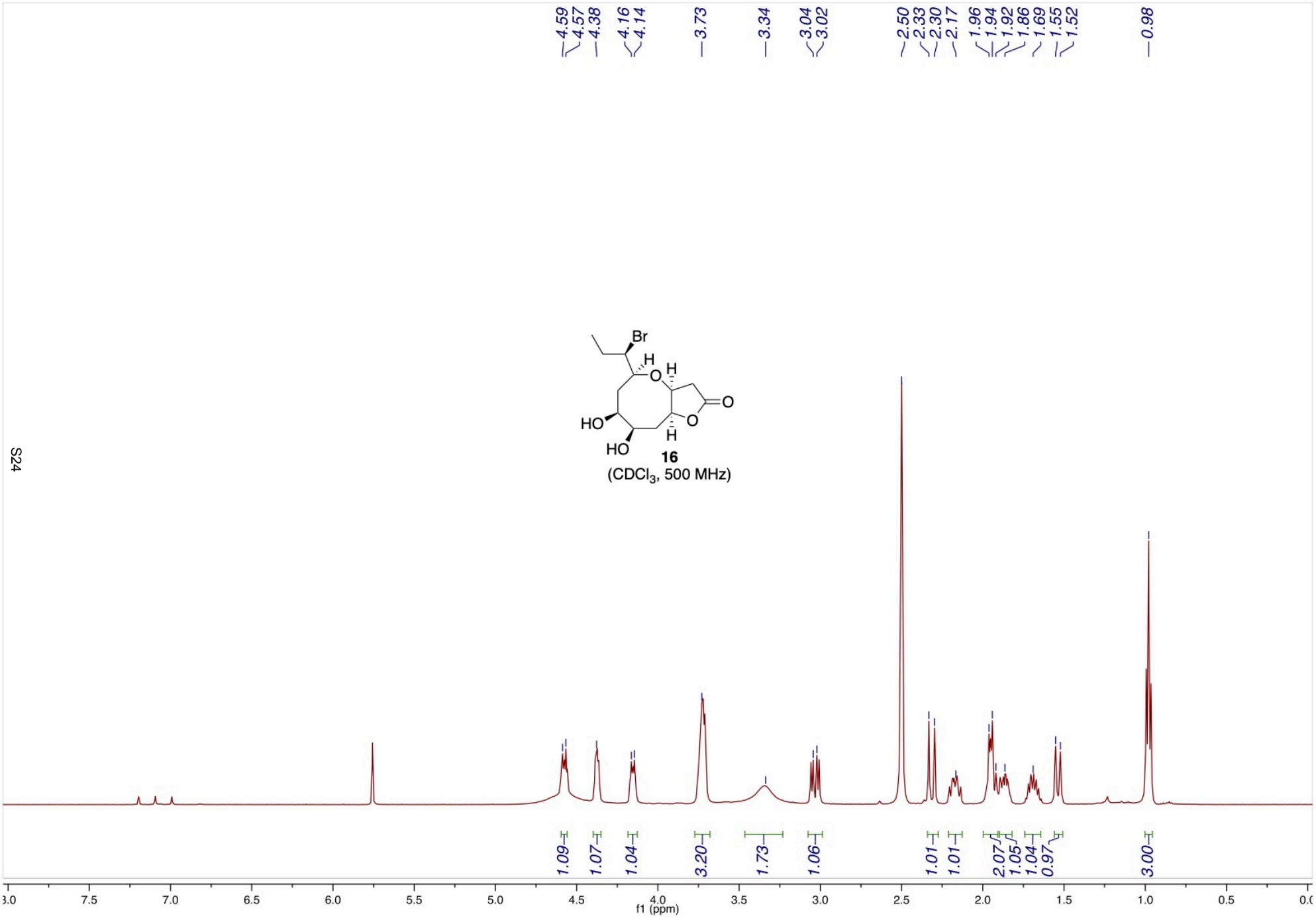
1 Y.-A. Zhang, N. Yaw and S. A. Snyder, *J. Am. Chem. Soc.* 2019, **141**, 7776.

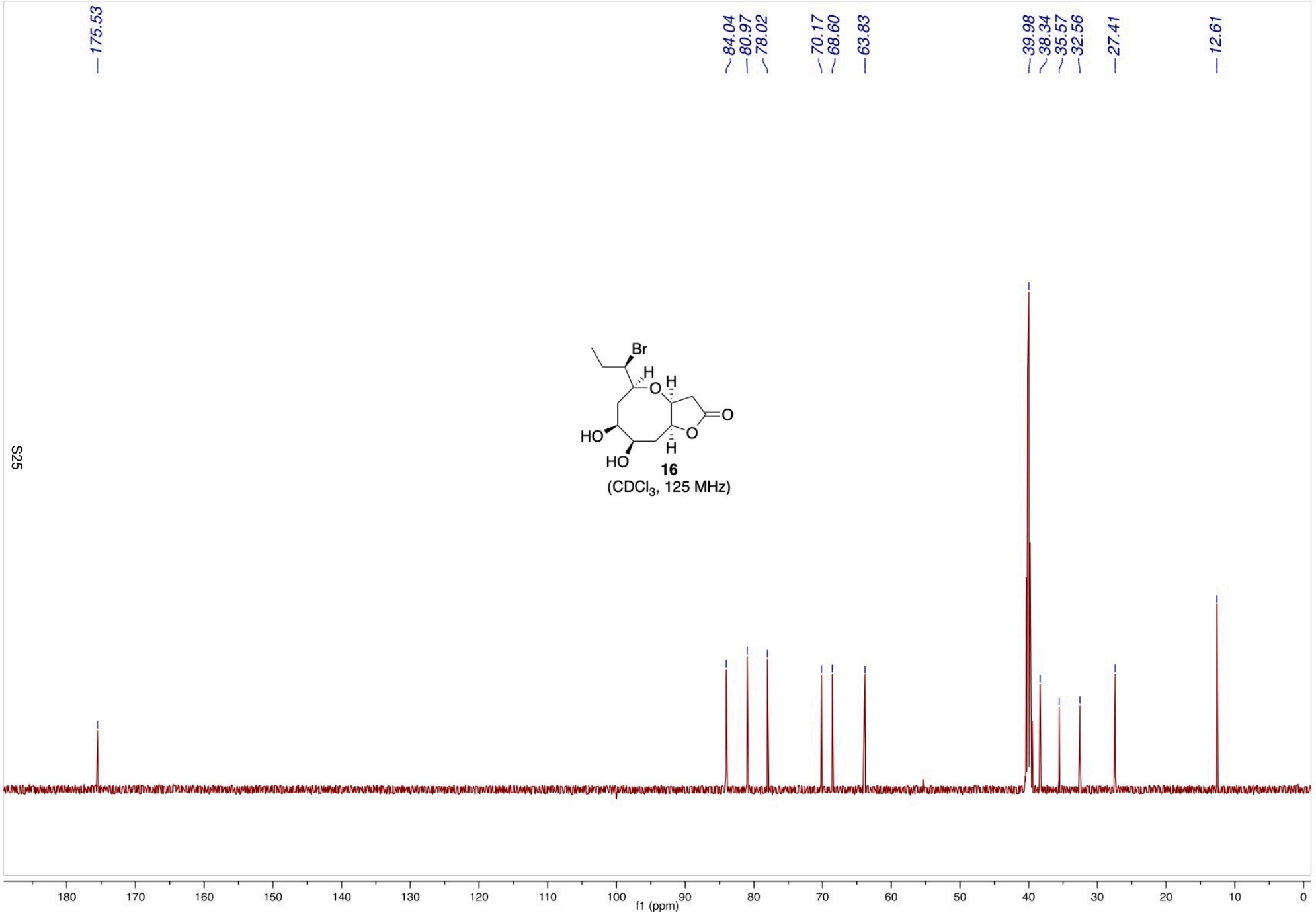
2 (*a*) S. A. Snyder and D. S. Treitler, *Angew. Chem. Int. Ed.* 2009, **48**, 7899; (*b*) S. A. Snyder and D. S. Treitler, *Org. Synth.* 2011, **88**, 54.

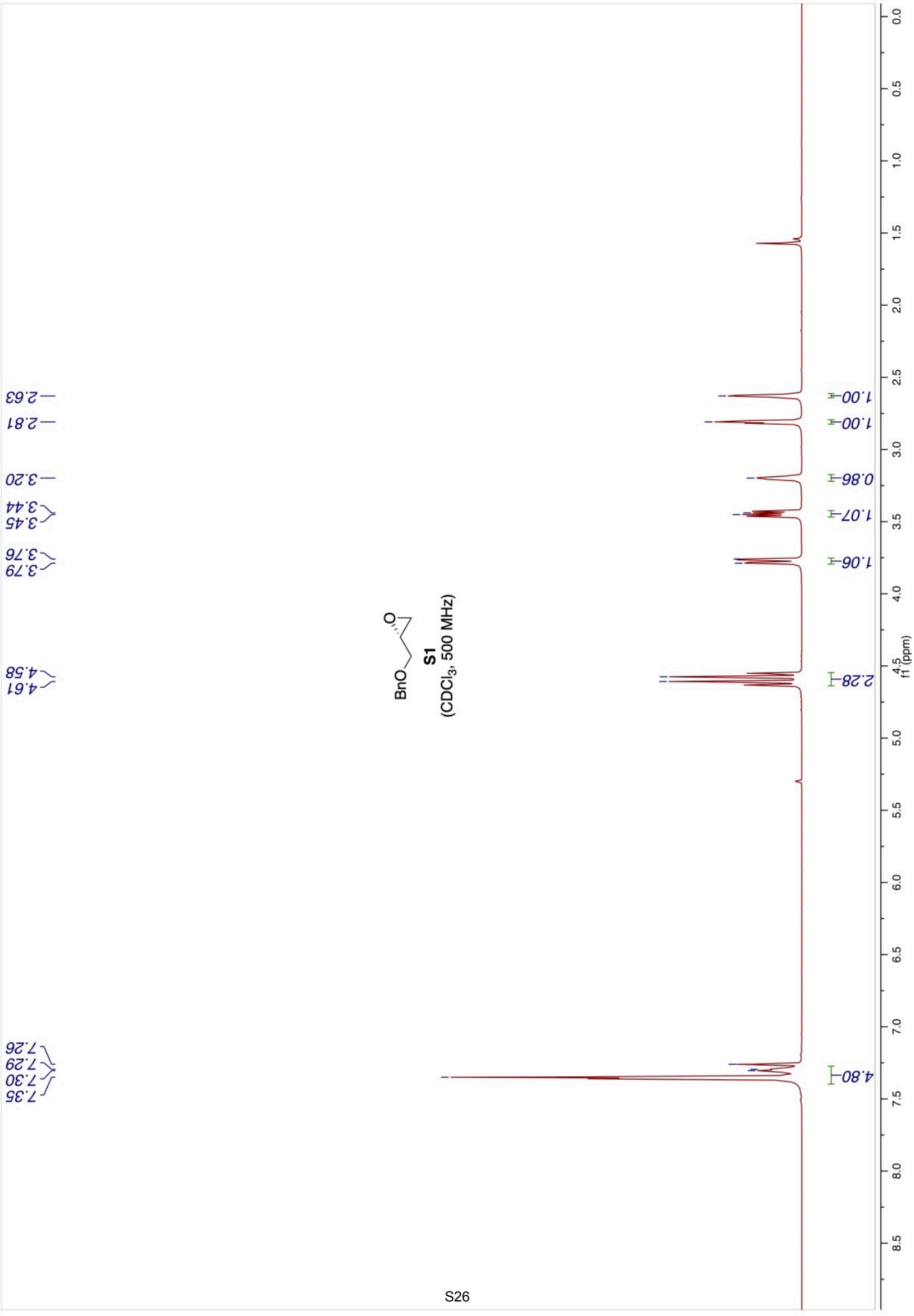
3 M. Zürcher, F. Hof, L. Barandun, A. Schütz, W. B. Schweizer, S. Meyer, D. Bur and F. Diederich, *Eur. J. Org. Chem.* 2009, **2009**, 1707.

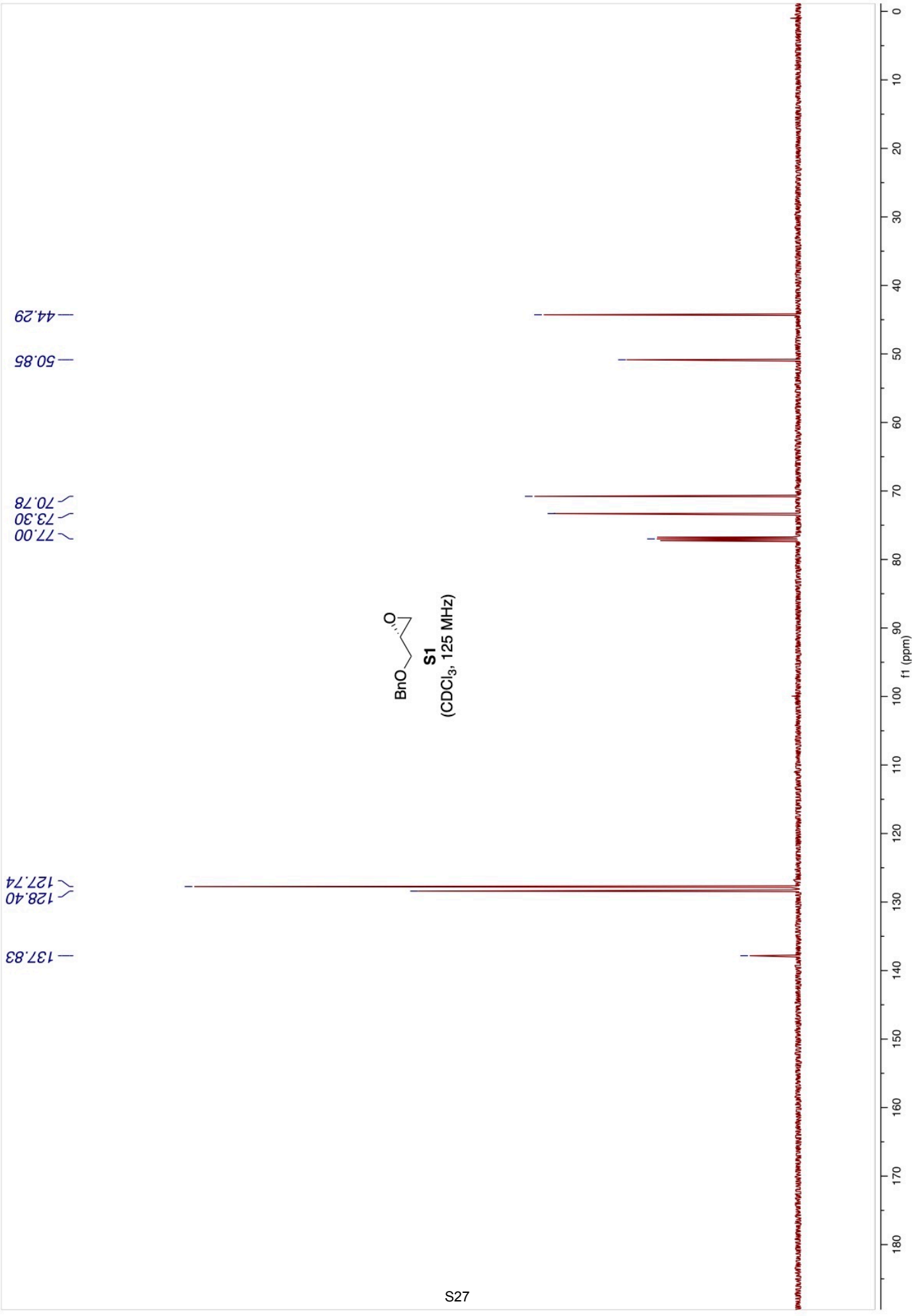
4 N.-Y. Ji, X.-M. Li, K. Li and B.-G. Wang, *J. Nat. Prod.* 2007, **70**, 1499.

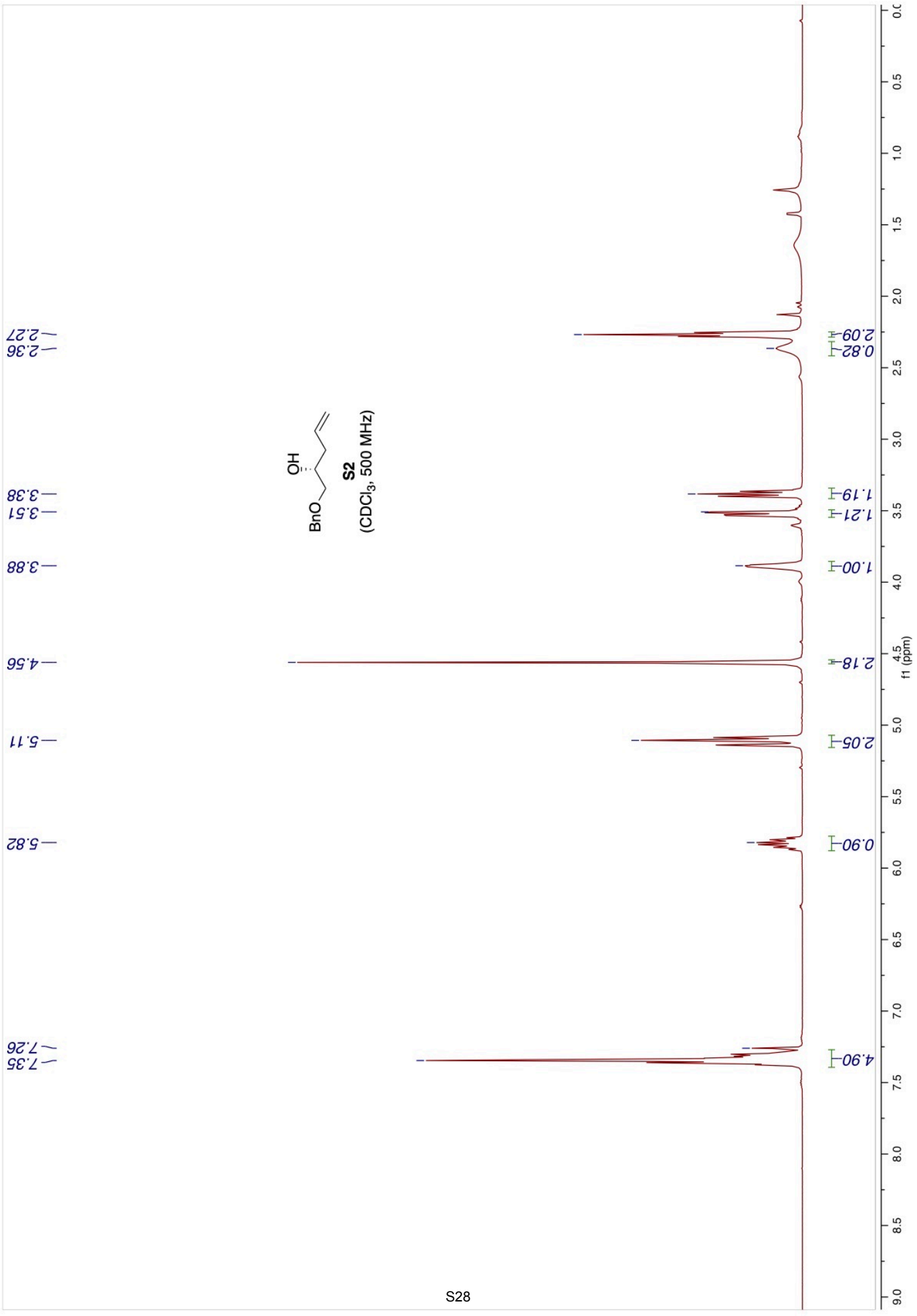
5 Y. Yoshimitsu, S. Inuki, S. Oishi, N. Fujii and H. Ohno, *Org. Lett.* 2013, **15**, 3046.

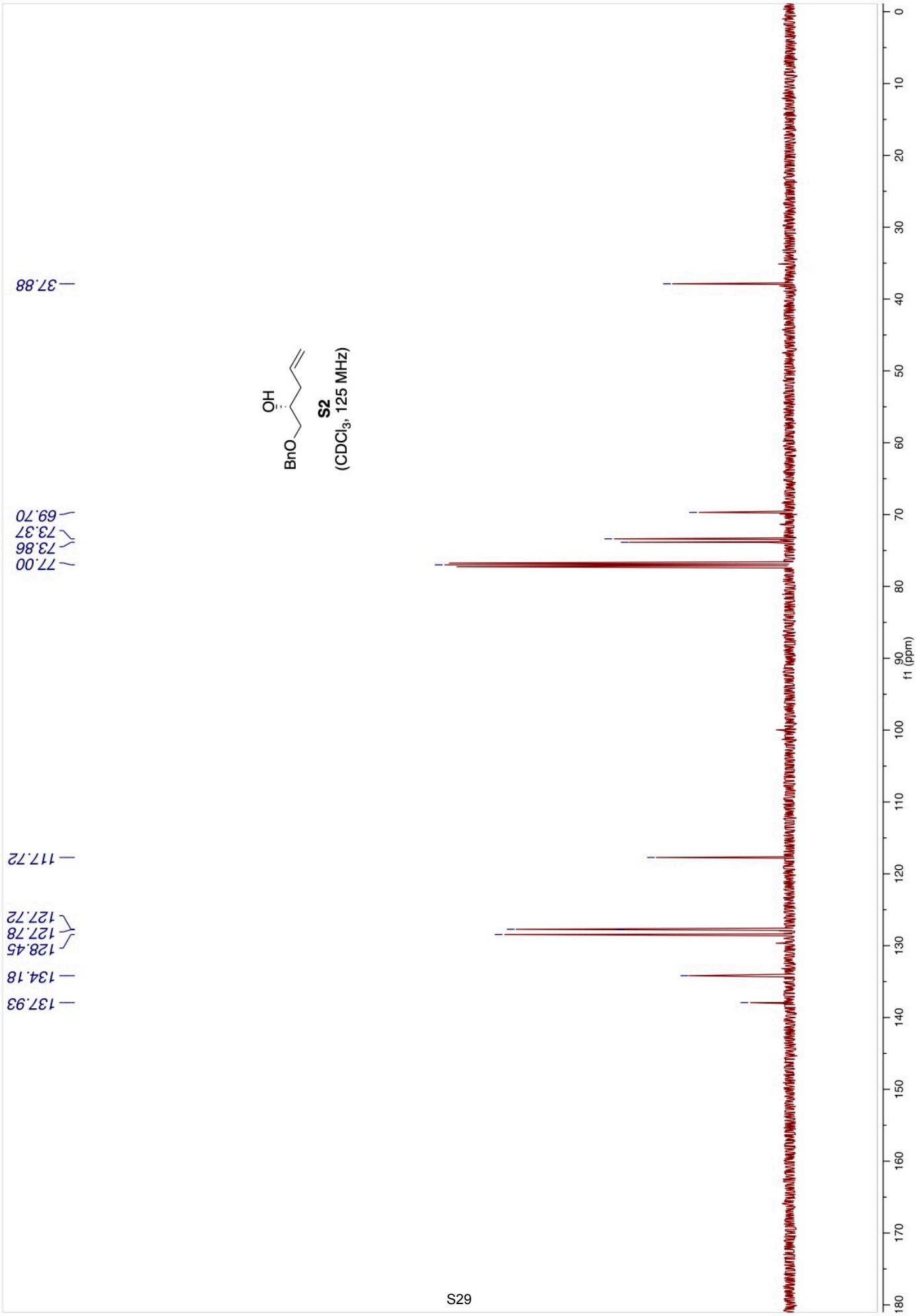

4.59
4.57
4.38
4.16
4.14
3.73
3.34
3.04
3.02
2.50
2.33
2.30
2.17
1.96
1.94
1.92
1.86
1.69
1.55
1.52
0.98
Br
H
O
H
HO
HO
O
O
H
16
(CDCl3, 500 MHz)
1.09
1.07
1.04
3.20
1.73
1.06
1.01
1.01
2.07
1.05
1.04
0.97
3.00
f1 (ppm)

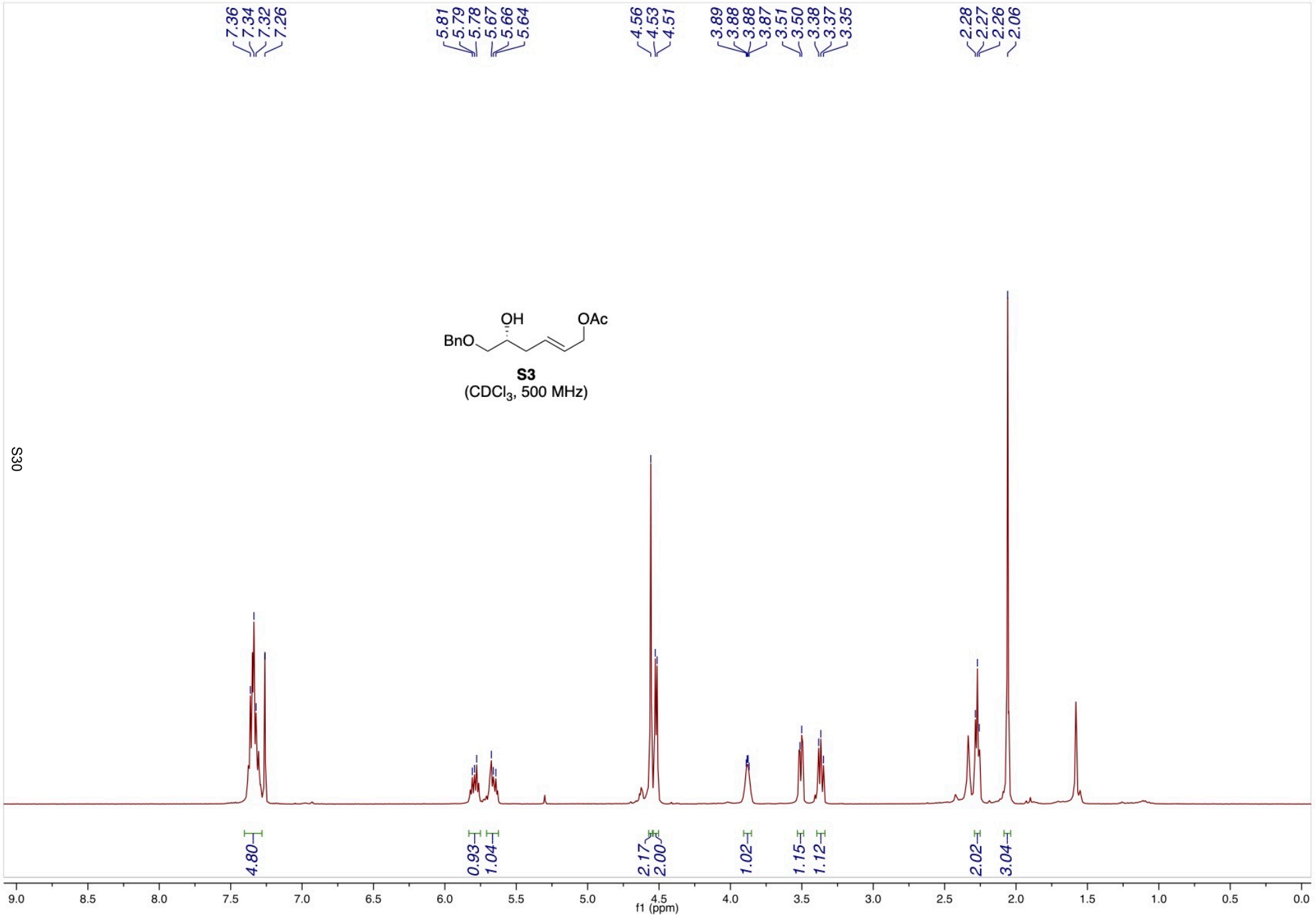

175.53
84.04
80.97
78.02
70.17
68.60
63.83
39.98
38.34
35.57
32.56
27.41
12.61
Br
H
O
H
HO
O
O
H
HO
16
(CDCl3, 125 MHz)
S25
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)

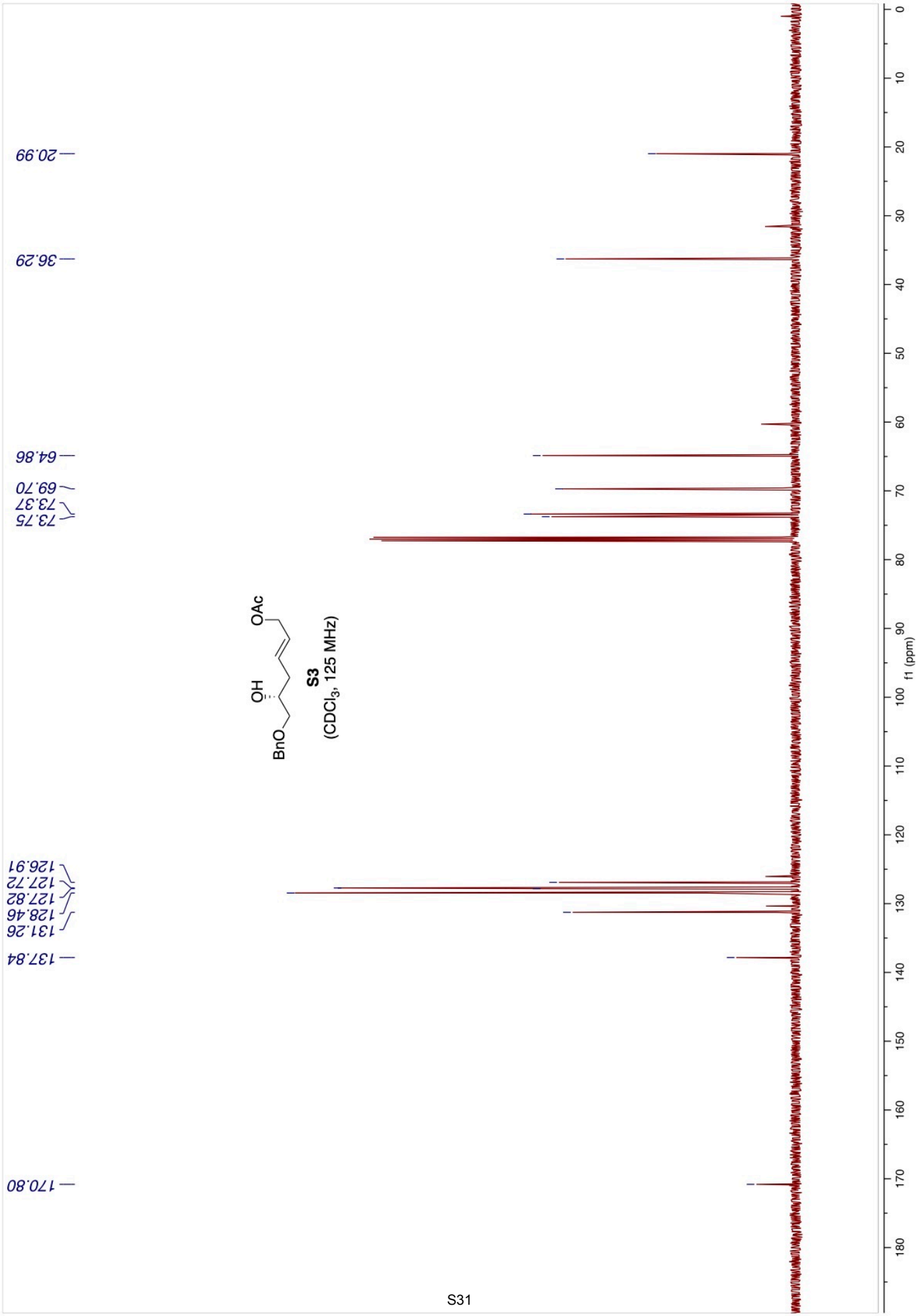

BnO
O
S1
(CDCl3, 500 MHz)
7.35
7.30
7.29
7.26
4.61
4.58
3.79
3.76
3.45
3.44
3.20
2.81
2.63
4.80
2.28
1.06
1.07
0.86
1.00
1.00
f1 (ppm)

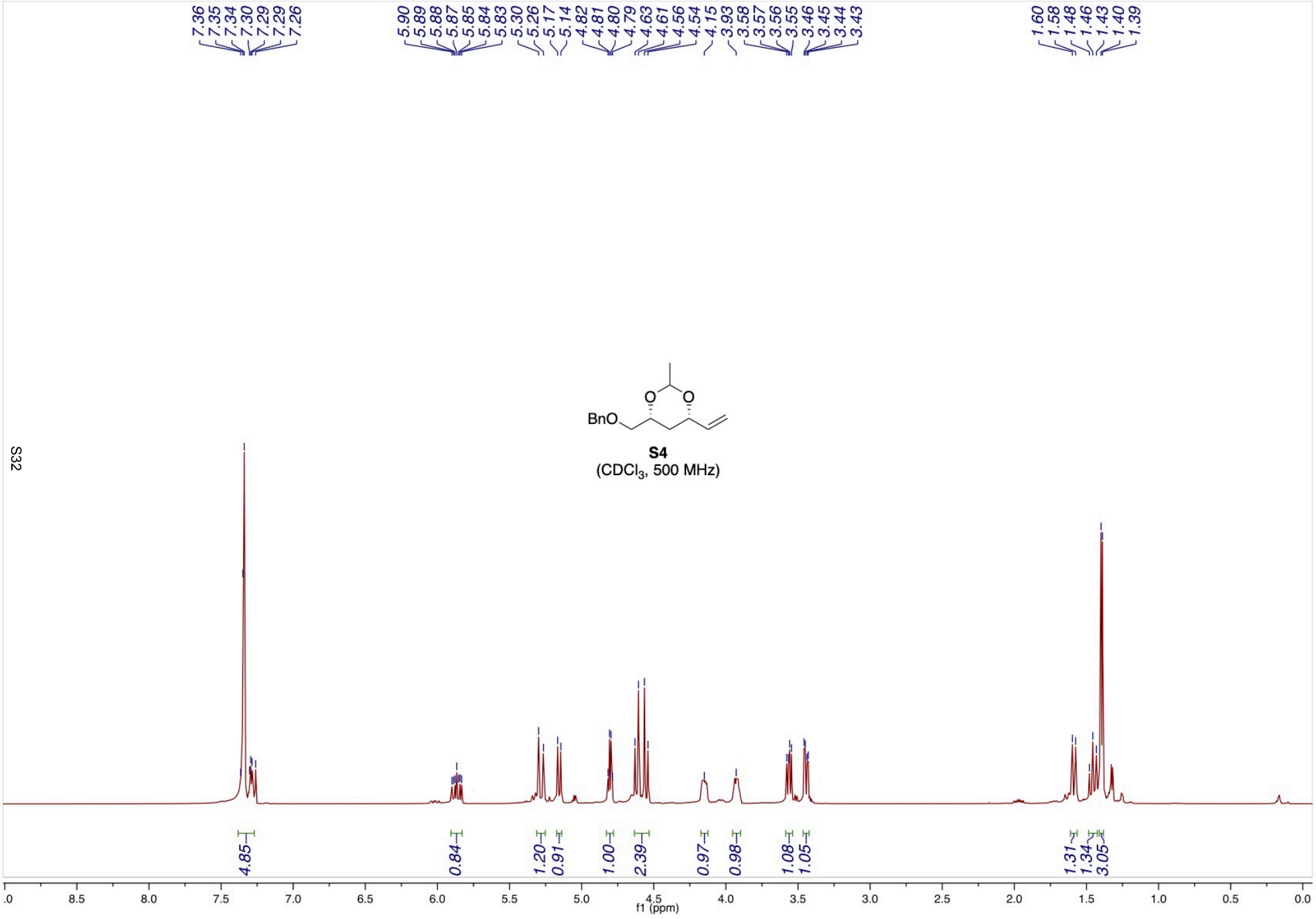

137.83
128.40
127.74
77.00
73.30
70.78
50.85
44.29
BnO
O
S1
(CDCl3, 125 MHz)
f1 (ppm)


OH
BnO
S2
(CDCl3, 500 MHz)
7.35
7.26
5.82
5.11
4.56
3.88
3.51
3.38
2.36
2.27
4.90
0.90
2.05
2.18
1.00
1.21
1.19
0.82
2.09
f1 (ppm)

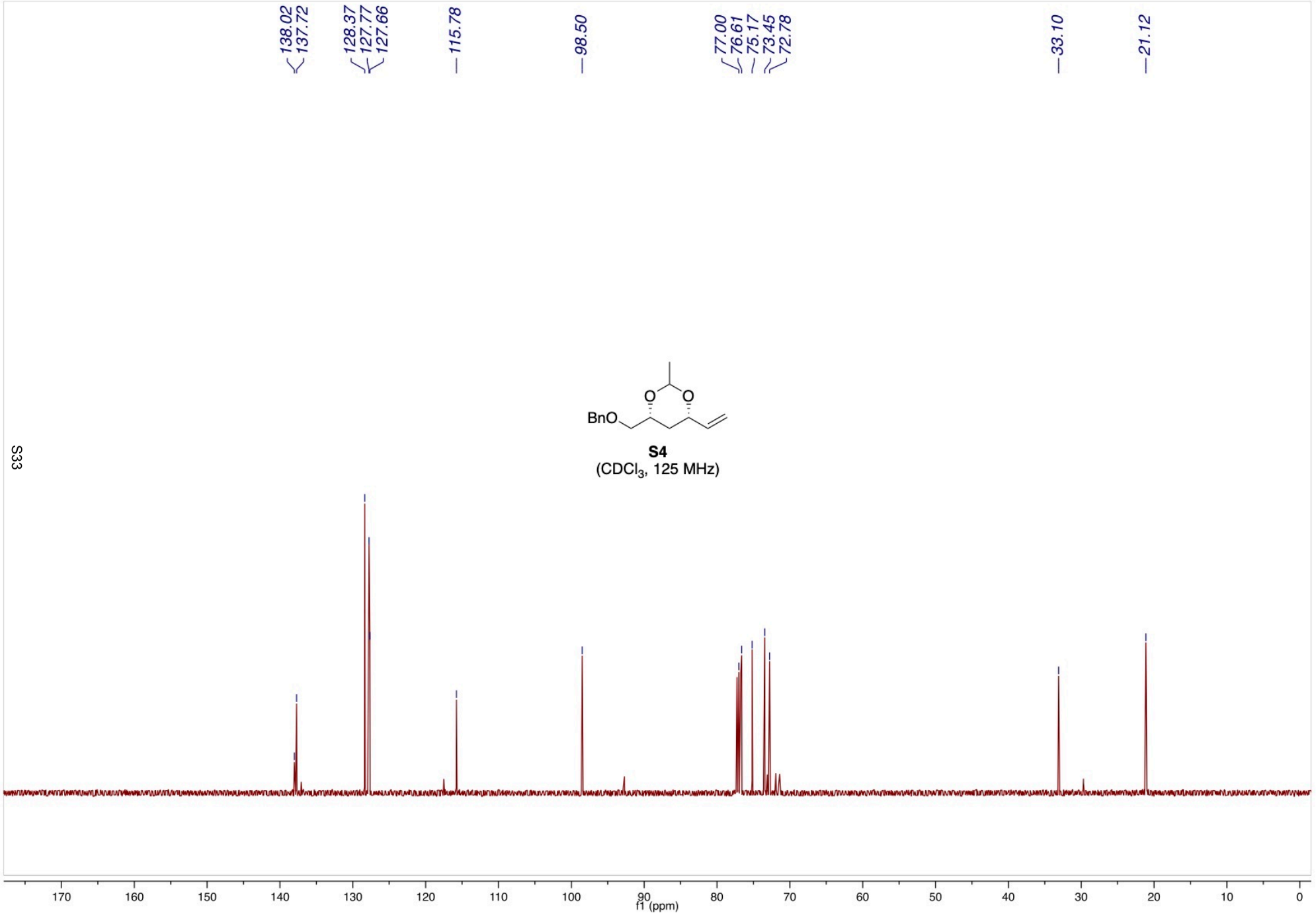

OH
BnO
S2
(CDCl3, 125 MHz)
37.88
69.70
73.37
73.86
77.00
117.72
127.72
127.78
128.45
134.18
137.93
f1 (ppm)


7.36
7.34
7.32
7.26
5.81
5.79
5.78
5.67
5.66
5.64
4.56
4.53
4.51
3.89
3.88
3.88
3.87
3.51
3.50
3.38
3.37
3.35
2.28
2.27
2.26
2.06
OH
OAc
BnO
S3
(CDCl3, 500 MHz)
S30
4.80
0.93
1.04
2.17
2.00
1.02
1.15
1.12
2.02
3.04
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)

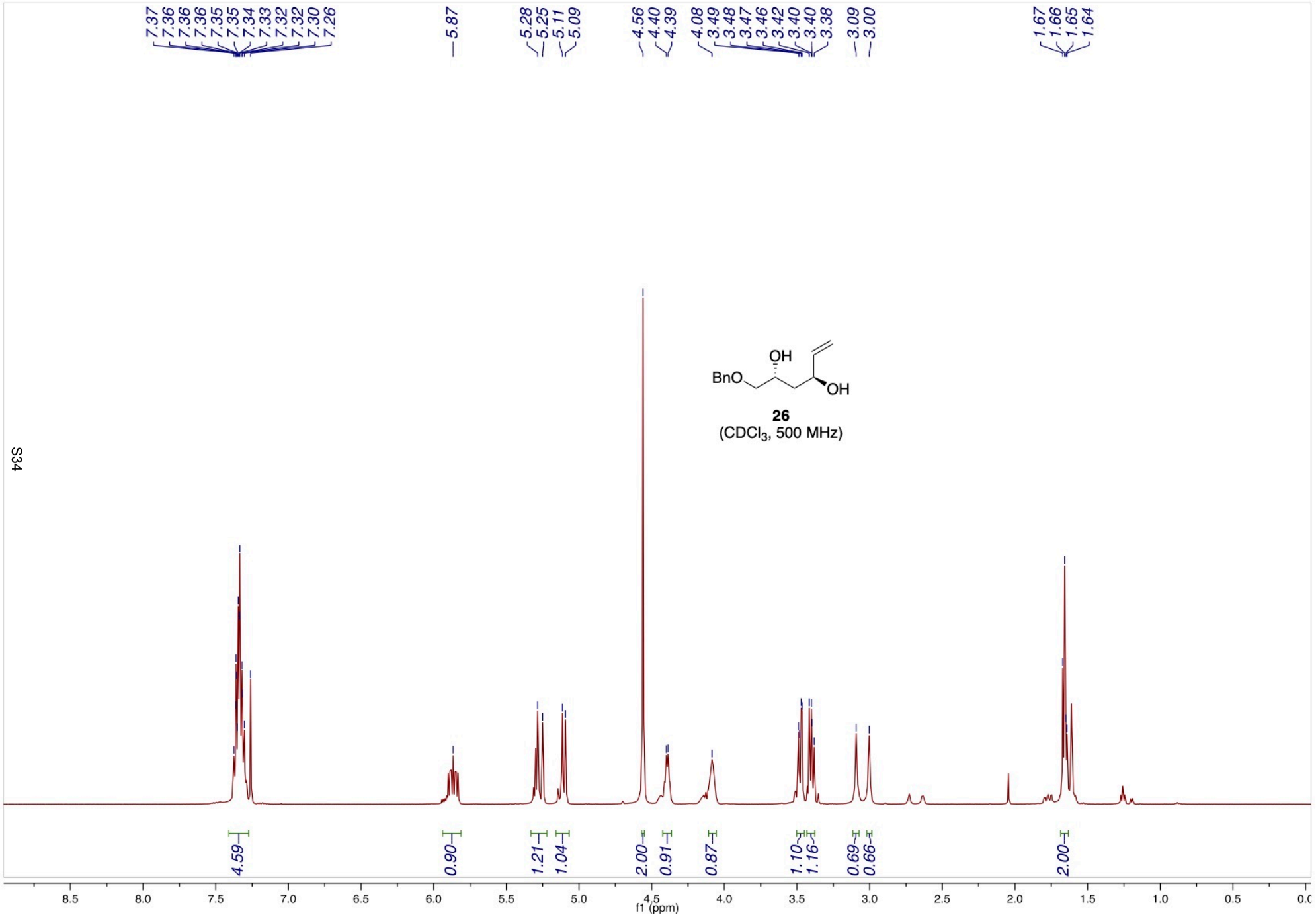

OAc
OH
BnO
S3
(CDCl3, 125 MHz)
20.99
36.29
64.86
69.70
73.37
73.75
126.91
127.72
127.82
128.46
131.26
137.84
170.80
f1 (ppm)

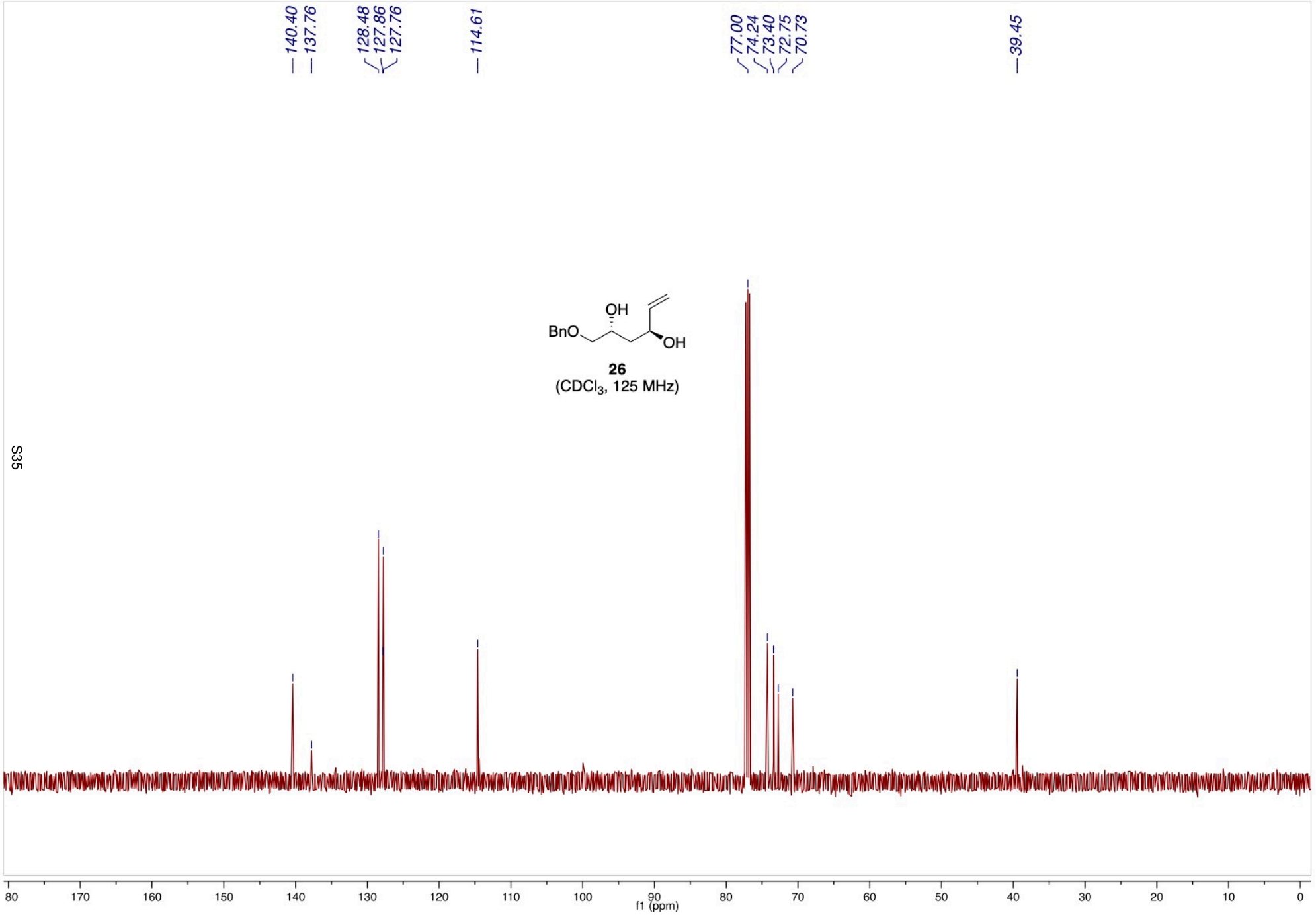


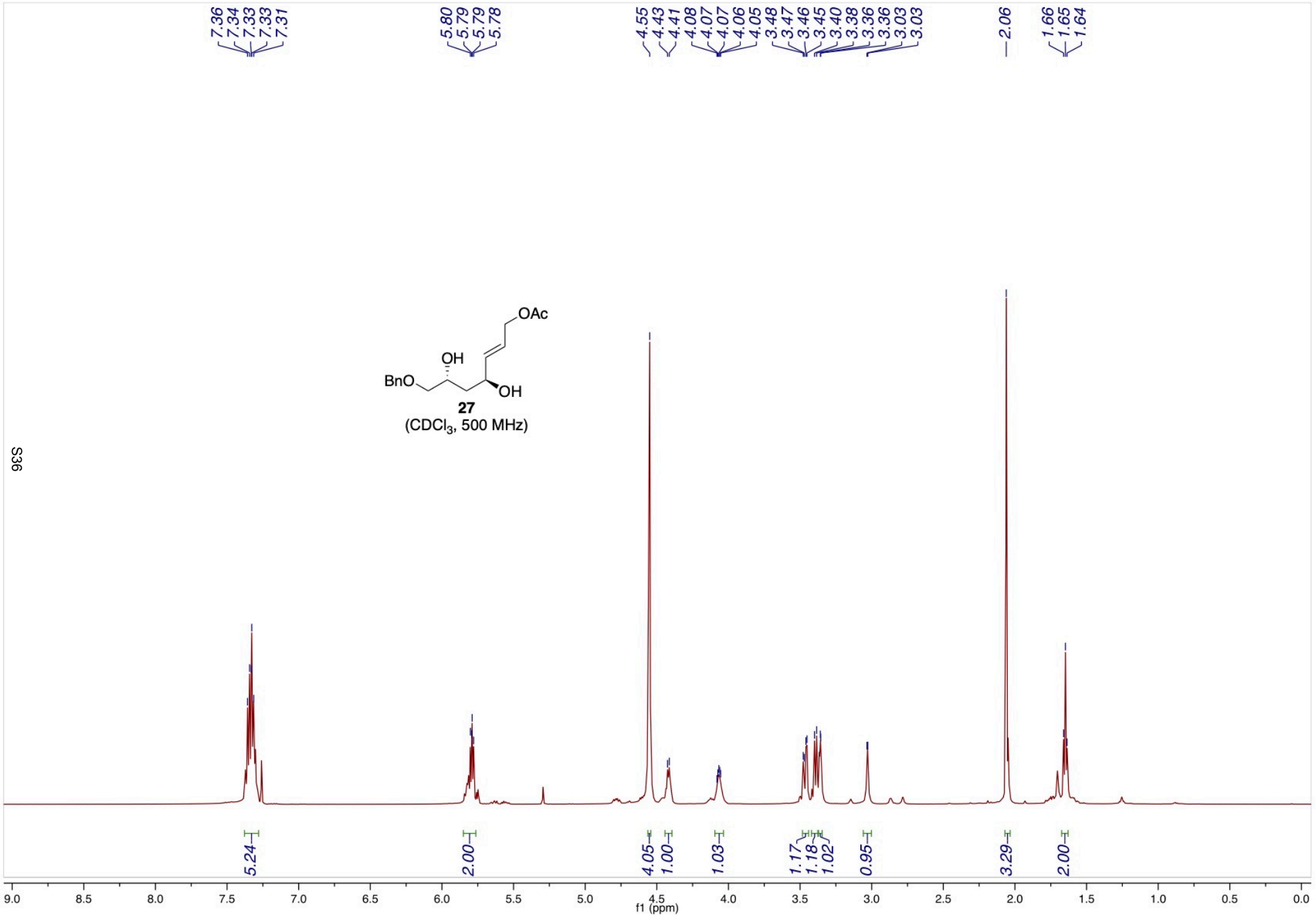
S4
($CDCl_3$, 500 MHz)

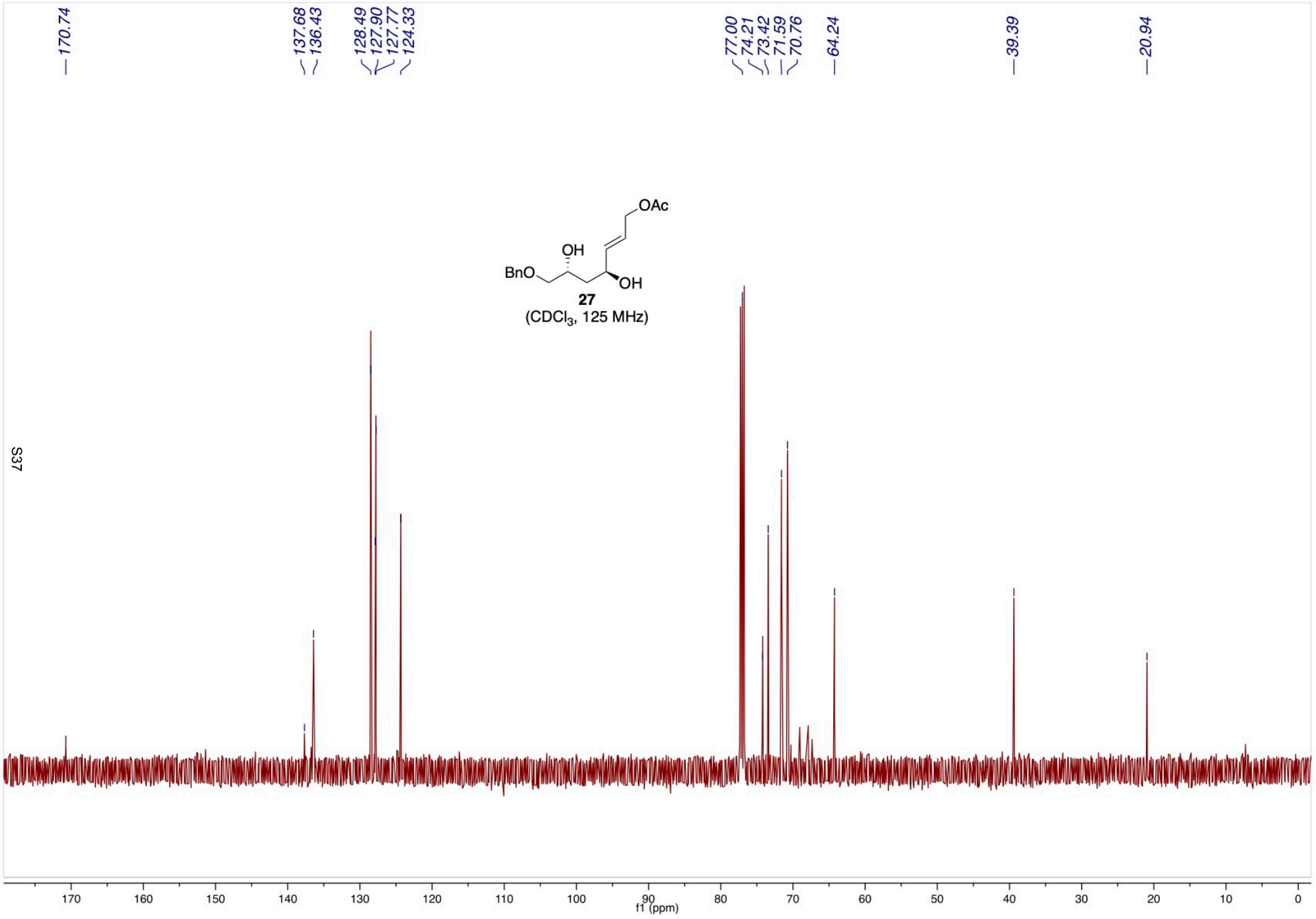


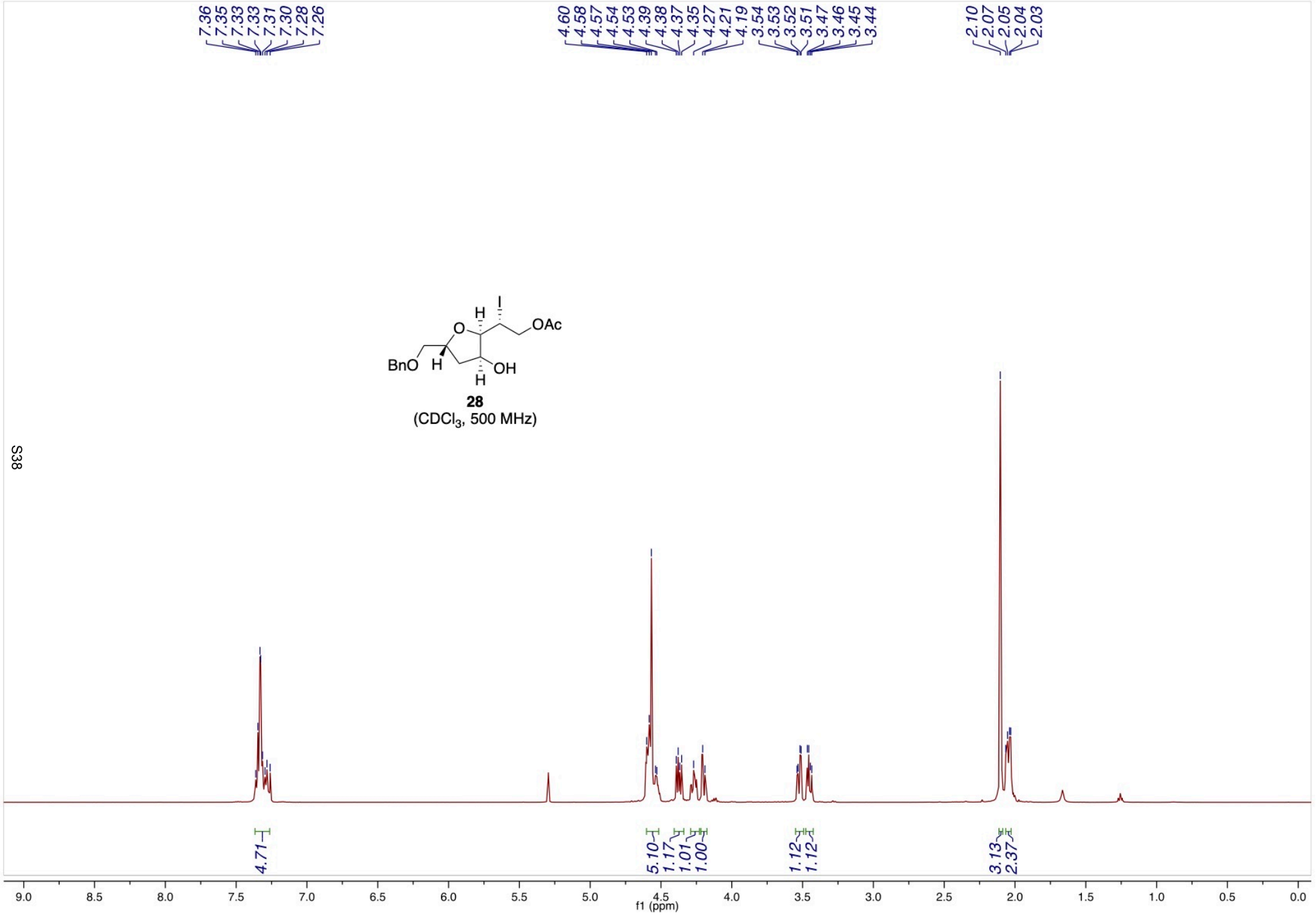
S4
($CDCl_3$, 125 MHz)

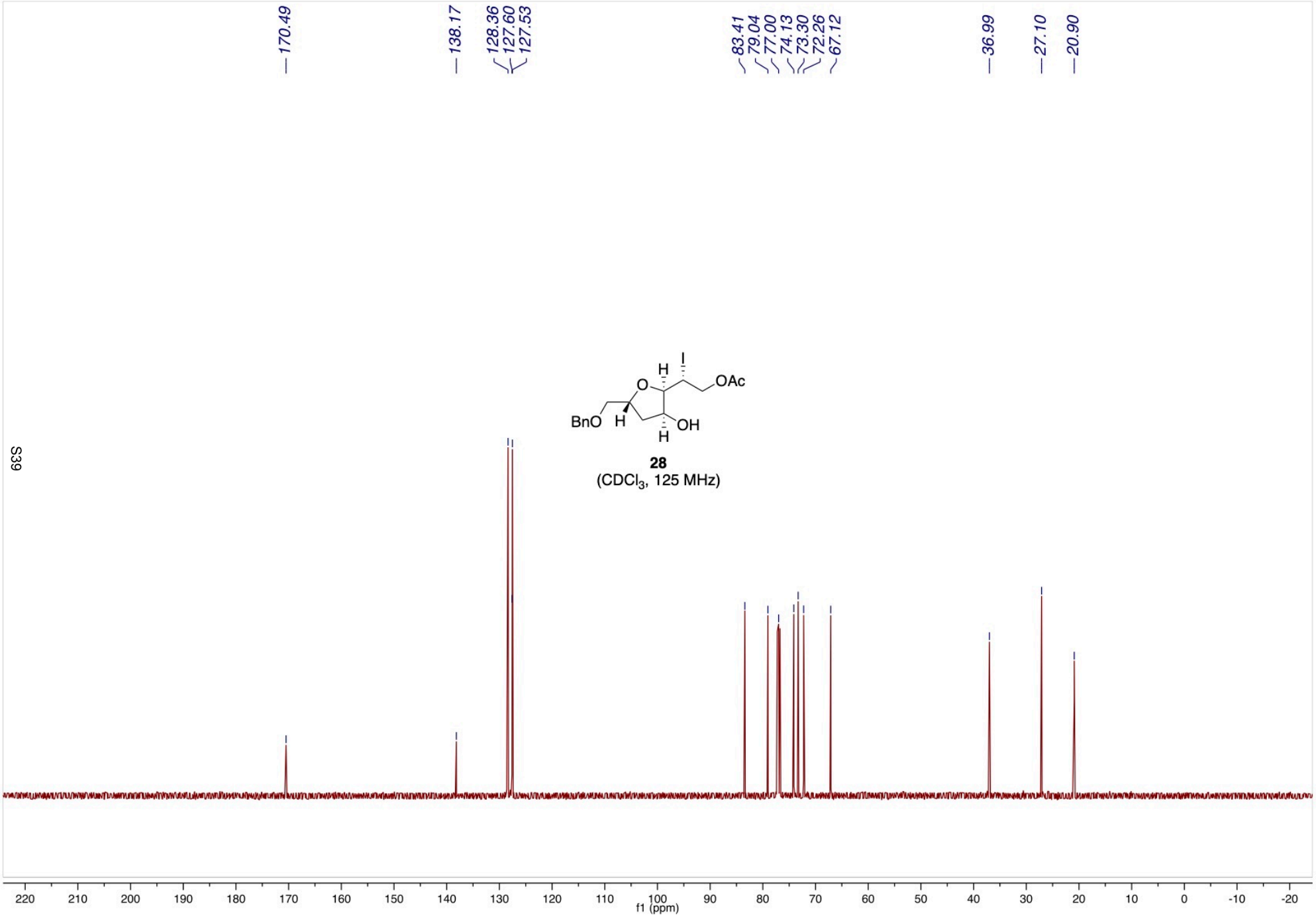

7.37
7.36
7.36
7.35
7.35
7.34
7.33
7.32
7.32
7.30
7.26
5.87
5.28
5.25
5.11
5.09
4.56
4.40
4.39
4.08
3.49
3.48
3.47
3.46
3.42
3.40
3.40
3.38
3.09
3.00
1.67
1.66
1.65
1.64
OH
BnO
OH
26
(CDCl3, 500 MHz)
4.59
0.90
1.21
1.04
2.00
0.91
0.87
1.10
1.16
0.69
0.66
2.00
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
f1 (ppm)


140.40
137.76
128.48
127.86
127.76
114.61
77.00
74.24
73.40
72.75
70.73
39.45
OH
BnO
OH
26
(CDCl3, 125 MHz)
f1 (ppm)

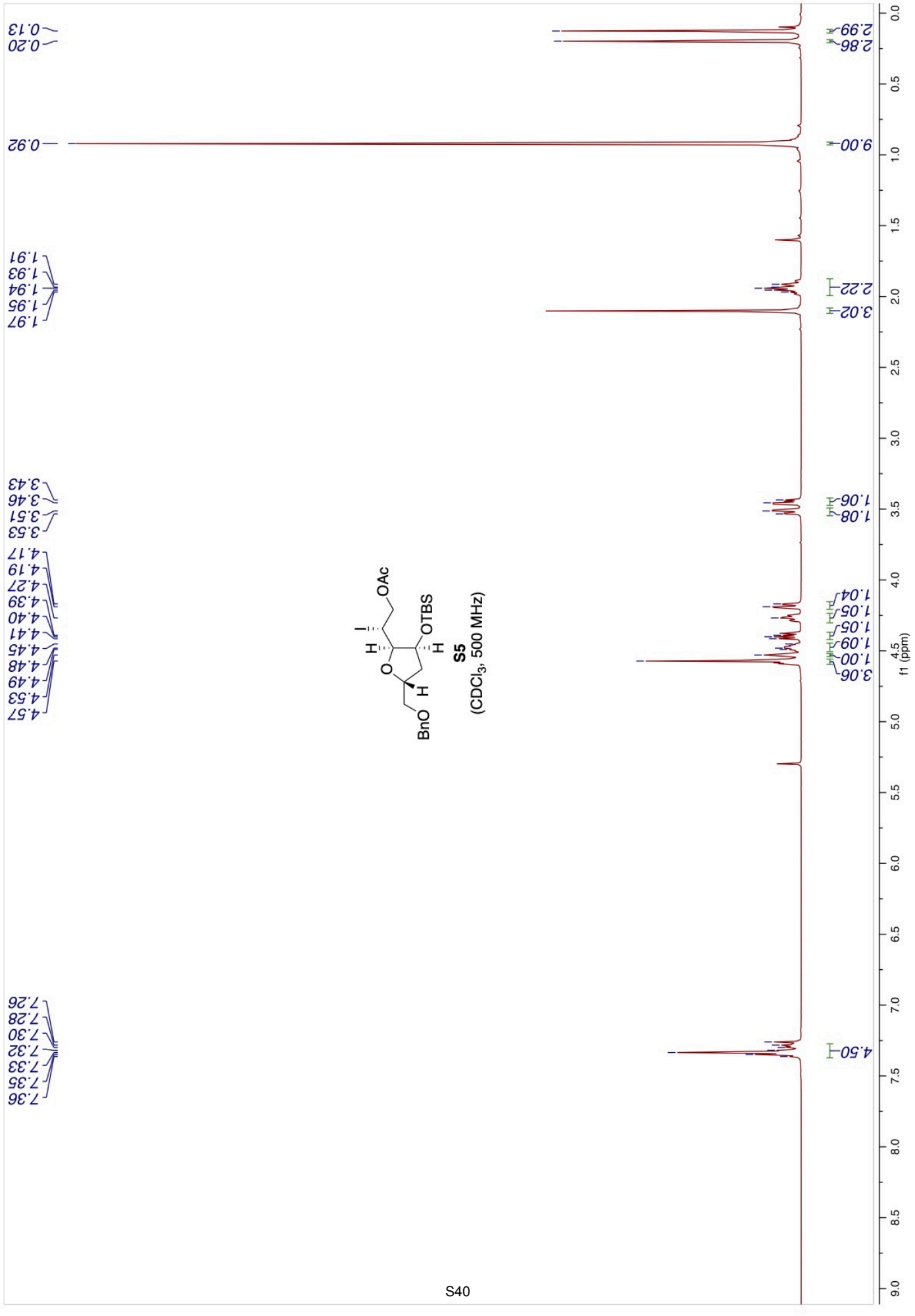

7.36
7.34
7.33
7.33
7.31
5.80
5.79
5.79
5.78
4.55
4.43
4.41
4.08
4.07
4.07
4.06
4.05
3.48
3.47
3.46
3.45
3.40
3.38
3.36
3.36
3.03
3.03
2.06
1.66
1.65
1.64
OAc
OH
BnO
OH
27
(CDCl3, 500 MHz)
S36
5.24
2.00
4.05
1.00
1.03
1.17
1.18
1.02
0.95
3.29
2.00
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
f1 (ppm)

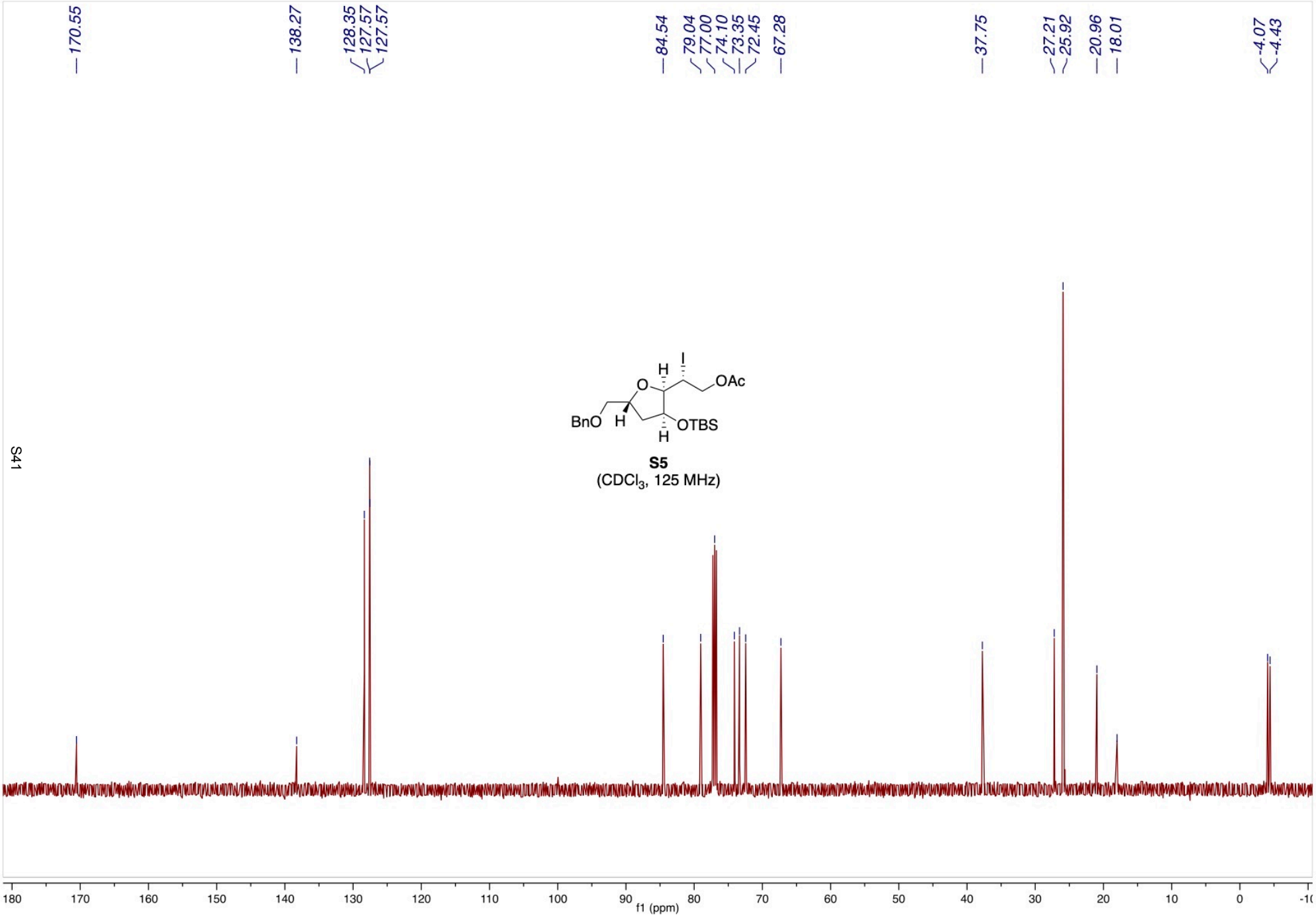

170.74
137.68
136.43
128.49
127.90
127.77
124.33
77.00
74.21
73.42
71.59
70.76
64.24
39.39
20.94
OAc
OH
BnO
OH
27
(CDCl3, 125 MHz)
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)

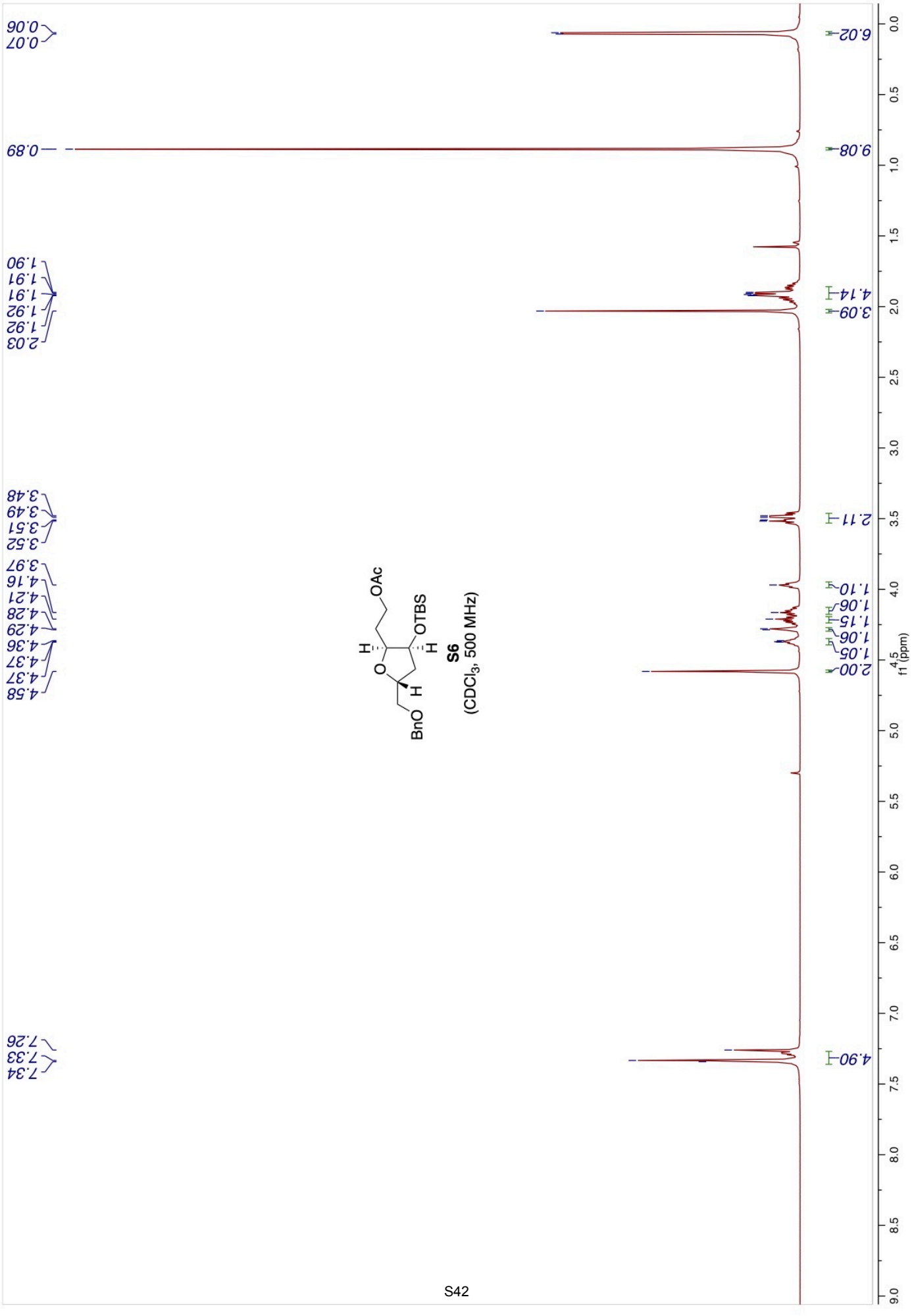

7.36
7.35
7.33
7.33
7.31
7.30
7.28
7.26
4.60
4.58
4.57
4.54
4.53
4.39
4.38
4.37
4.35
4.27
4.21
4.19
3.54
3.53
3.52
3.51
3.47
3.46
3.45
3.44
2.10
2.07
2.05
2.04
2.03
BnO
H
O
H
I
OAc
OH
H
28
(CDCl3, 500 MHz)
4.71
5.10
1.17
1.01
1.00
1.12
1.12
3.13
2.37
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
f1 (ppm)

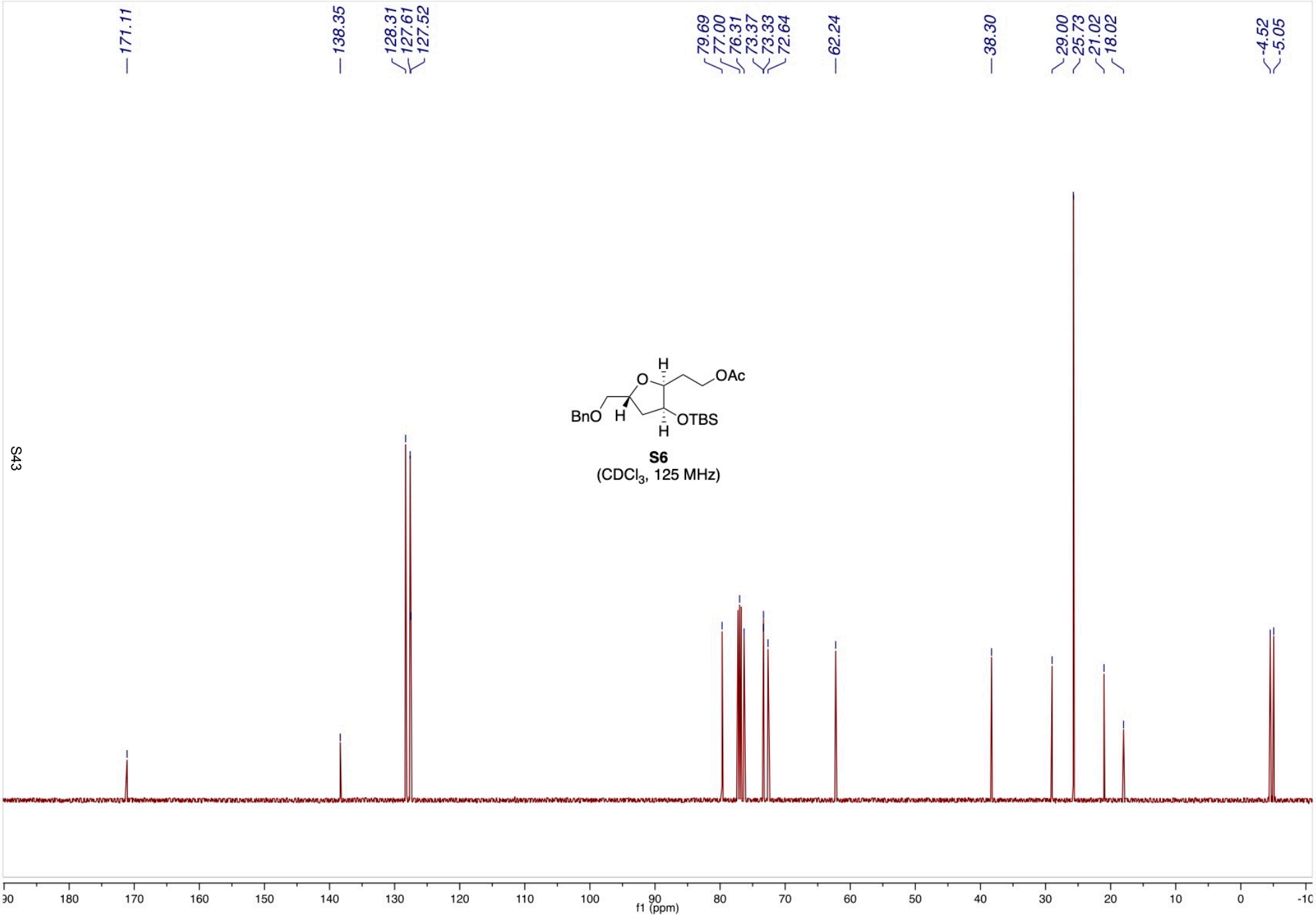


28
($CDCl_3$, 125 MHz)

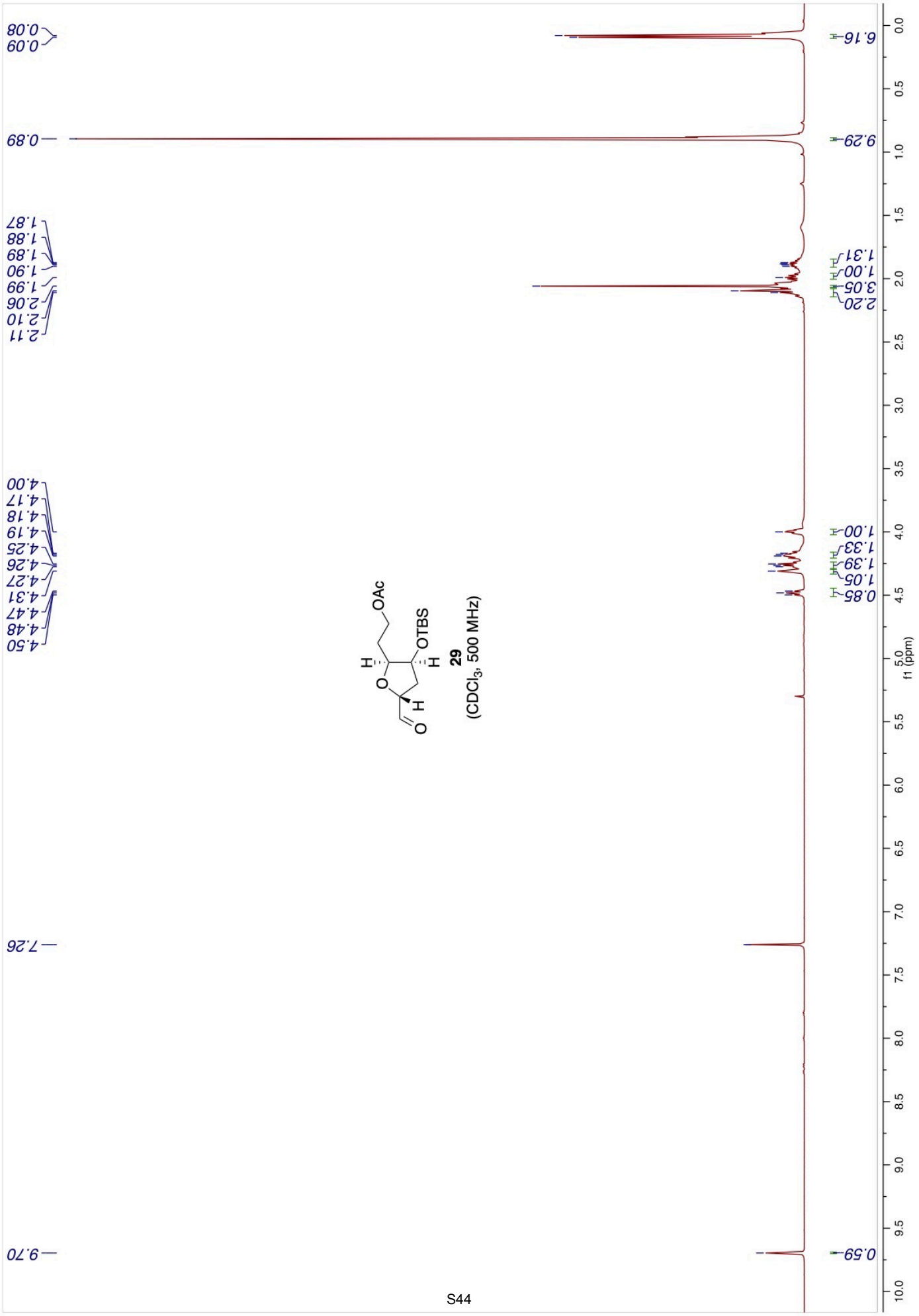

OAc
I
H
OTBS
O
H
H
BnO
S5
(CDCl3, 500 MHz)
f1 (ppm)

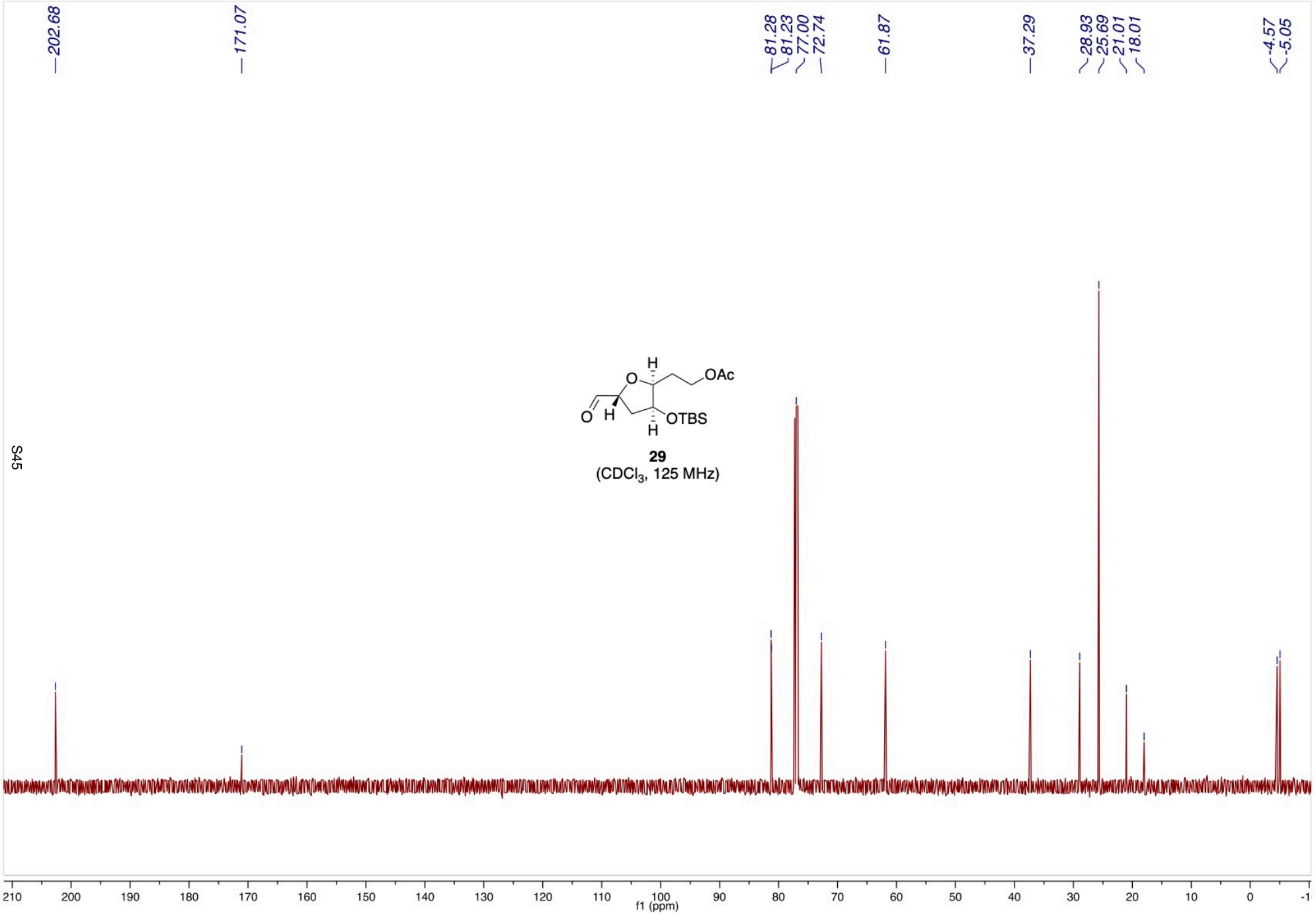

170.55
138.27
128.35
127.57
127.57
84.54
79.04
77.00
74.10
73.35
72.45
67.28
37.75
27.21
25.92
20.96
18.01
-4.07
-4.43
H
I
O
OAc
BnO
H
OTBS
H
S5
(CDCl3, 125 MHz)
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
-10
f1 (ppm)

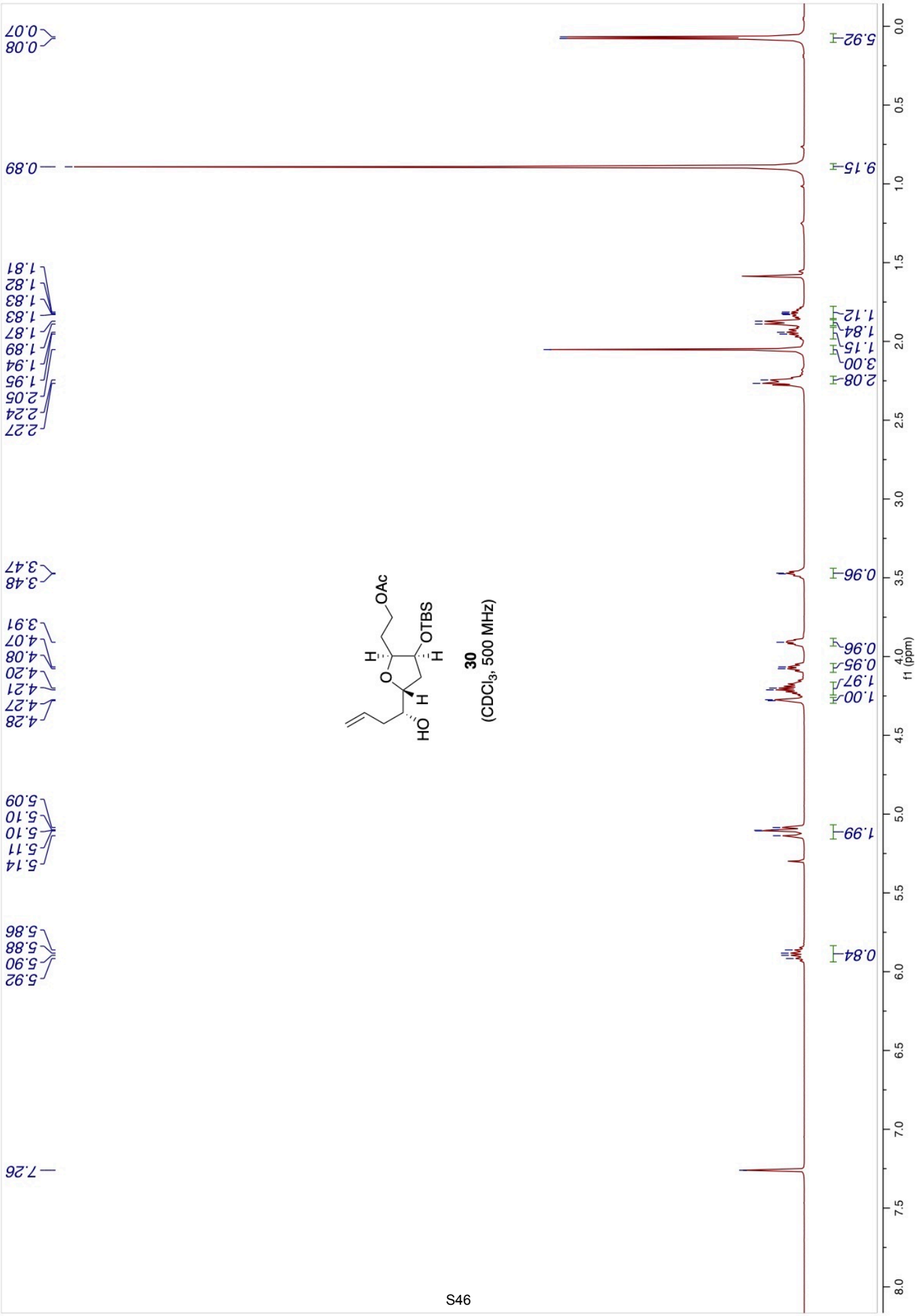

OAc
OTBS
H
H
H
O
BnO
S6
(CDCl3, 500 MHz)
0.07
0.06
0.89
2.03
1.92
1.92
1.91
1.91
1.90
3.52
3.51
3.49
3.48
3.97
4.16
4.21
4.28
4.29
4.36
4.37
4.37
4.58
7.34
7.33
7.26
6.02
9.08
4.14
3.09
2.11
1.10
1.06
1.15
1.06
1.05
2.00
4.90
f1 (ppm)

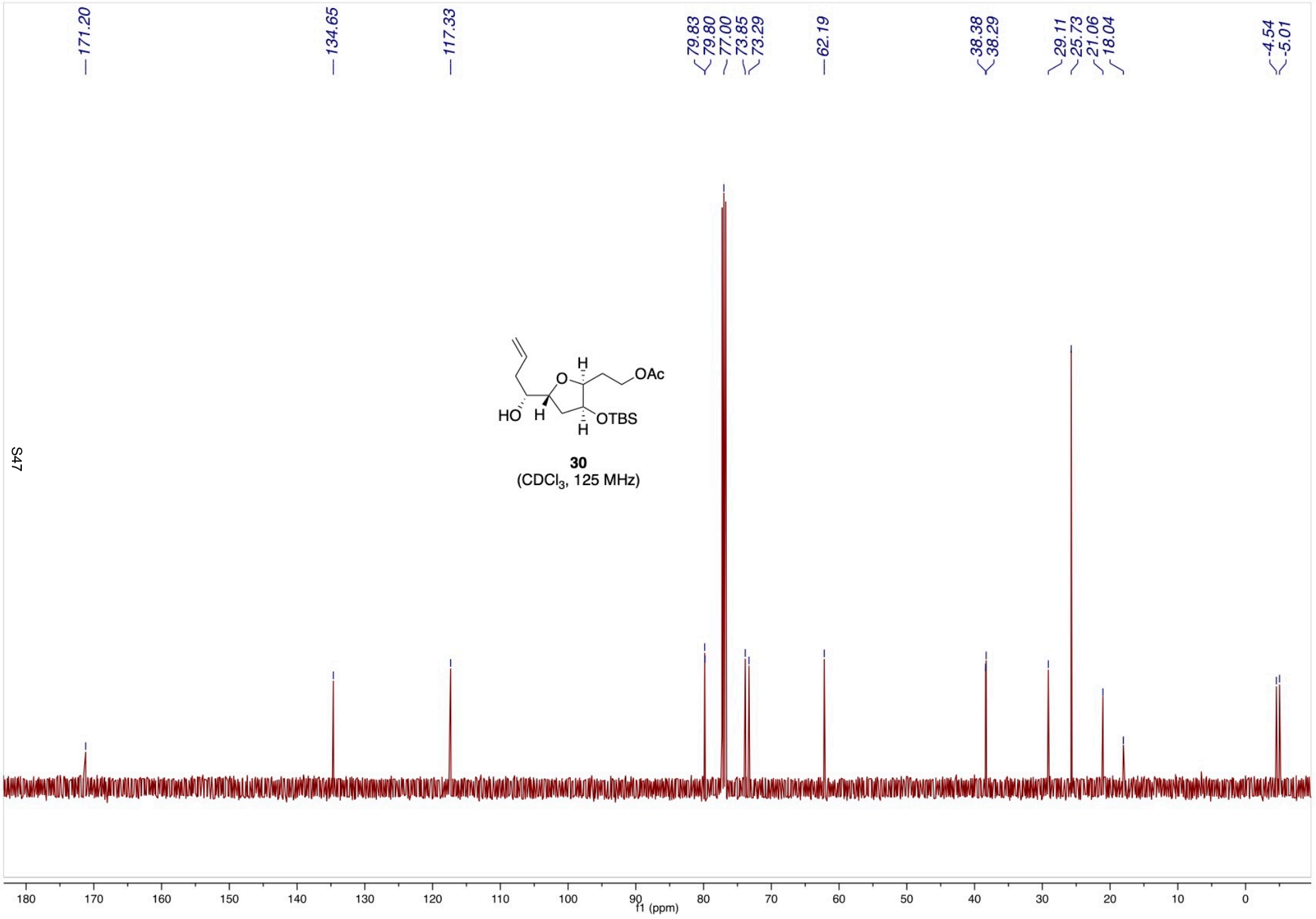


S6
($CDCl_3$, 125 MHz)

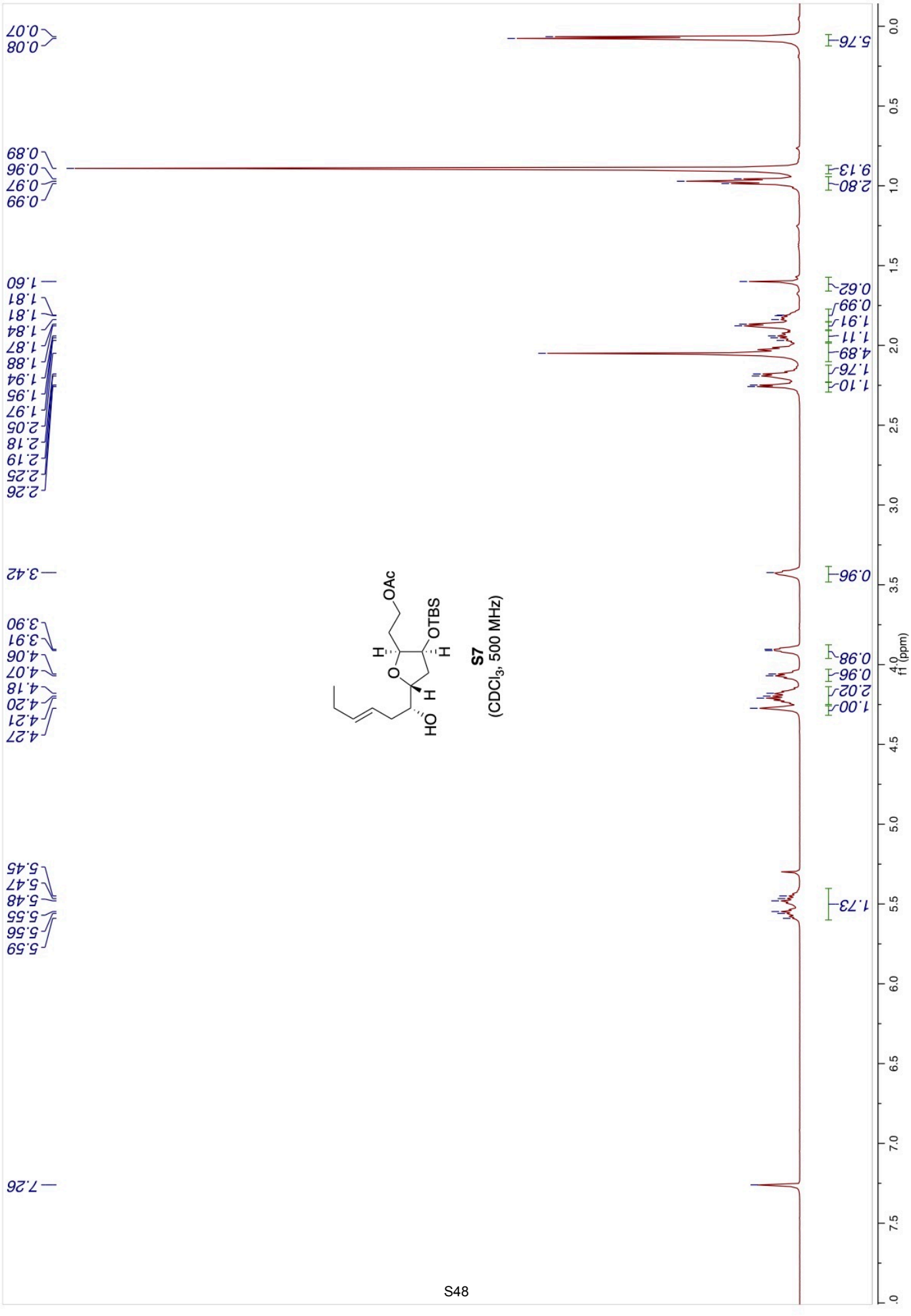

OAc
OTBS
H
H
O
O
H
29
(CDCl3, 500 MHz)
f1 (ppm)

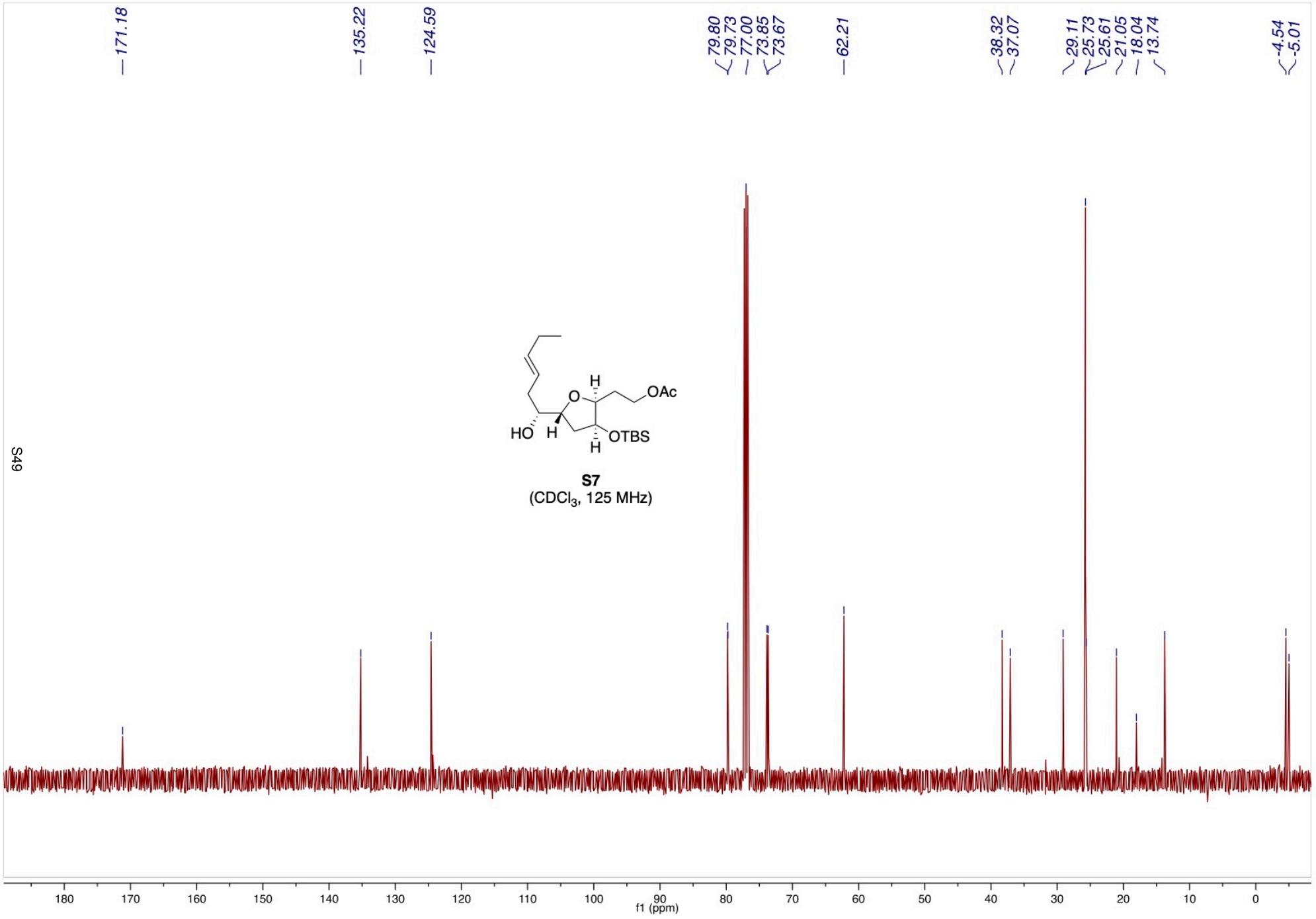

202.68
171.07
81.28
81.23
77.00
72.74
61.87
37.29
28.93
25.69
21.01
18.01
-4.57
-5.05
O
H
OAc
O
H
OTBS
H
29
(CDCl3, 125 MHz)
f1 (ppm)

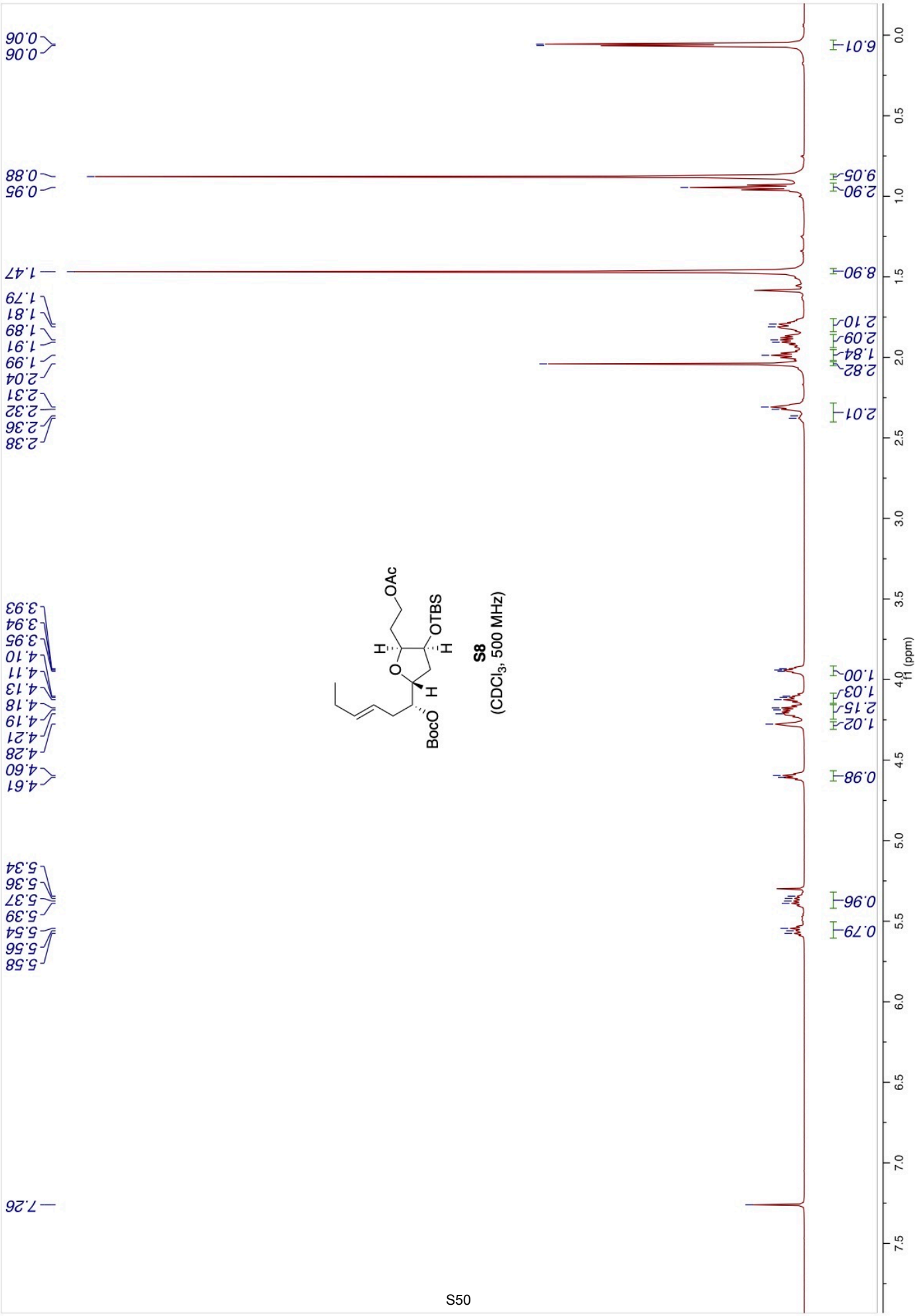

OAc
OTBS
H
H
O
H
HO
30
(CDCl3, 500 MHz)
f1 (ppm)

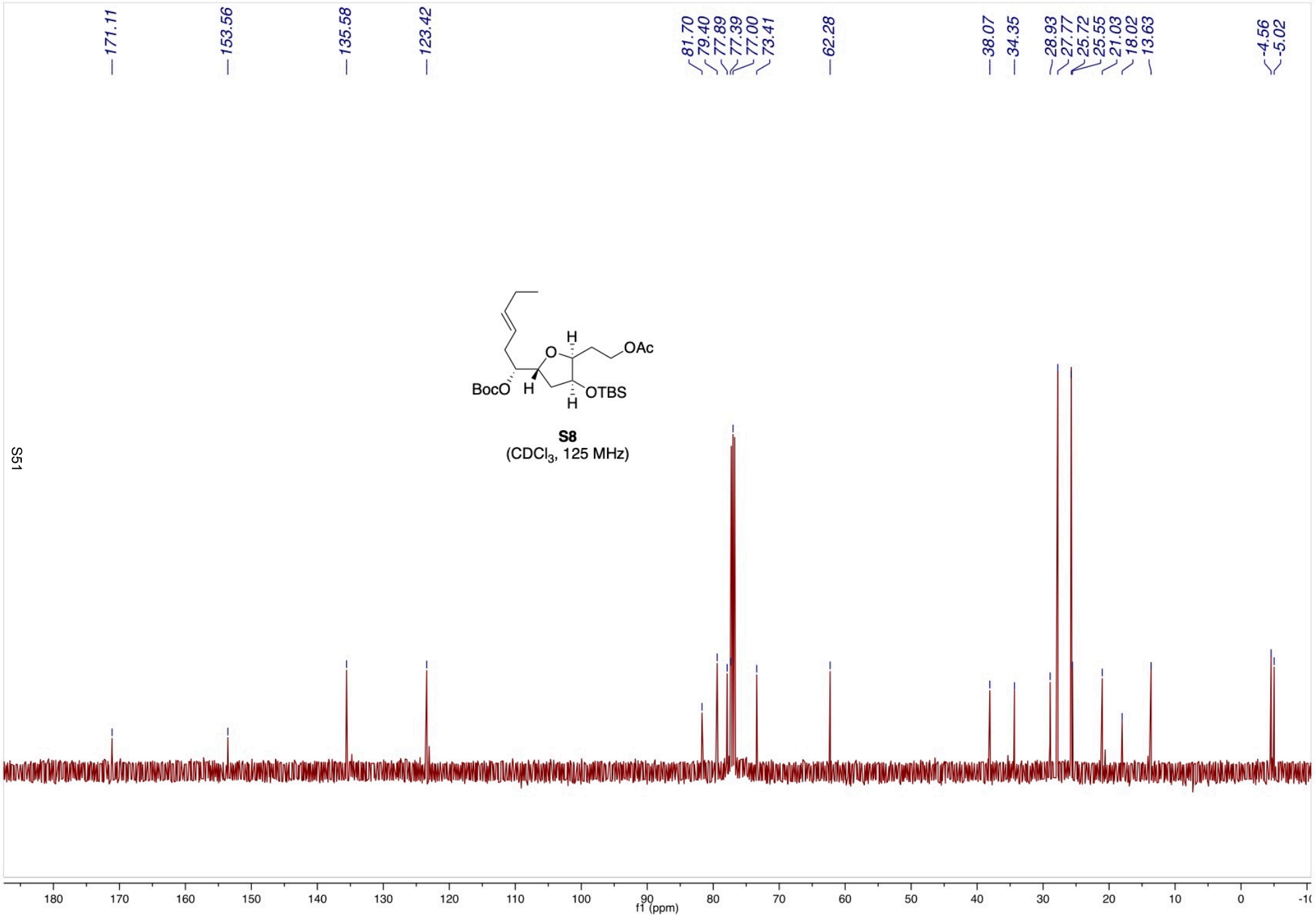


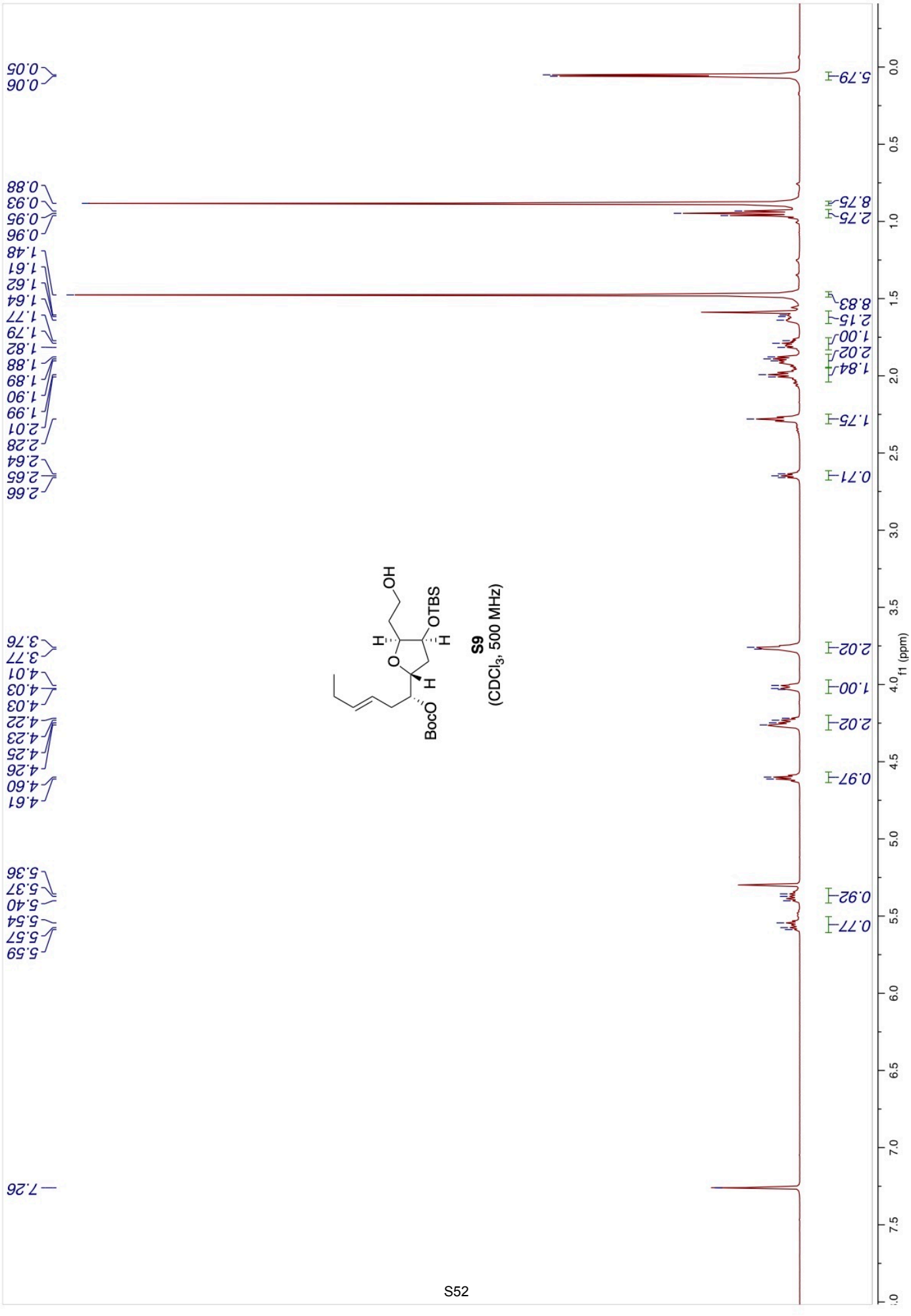
30
($CDCl_3$, 125 MHz)

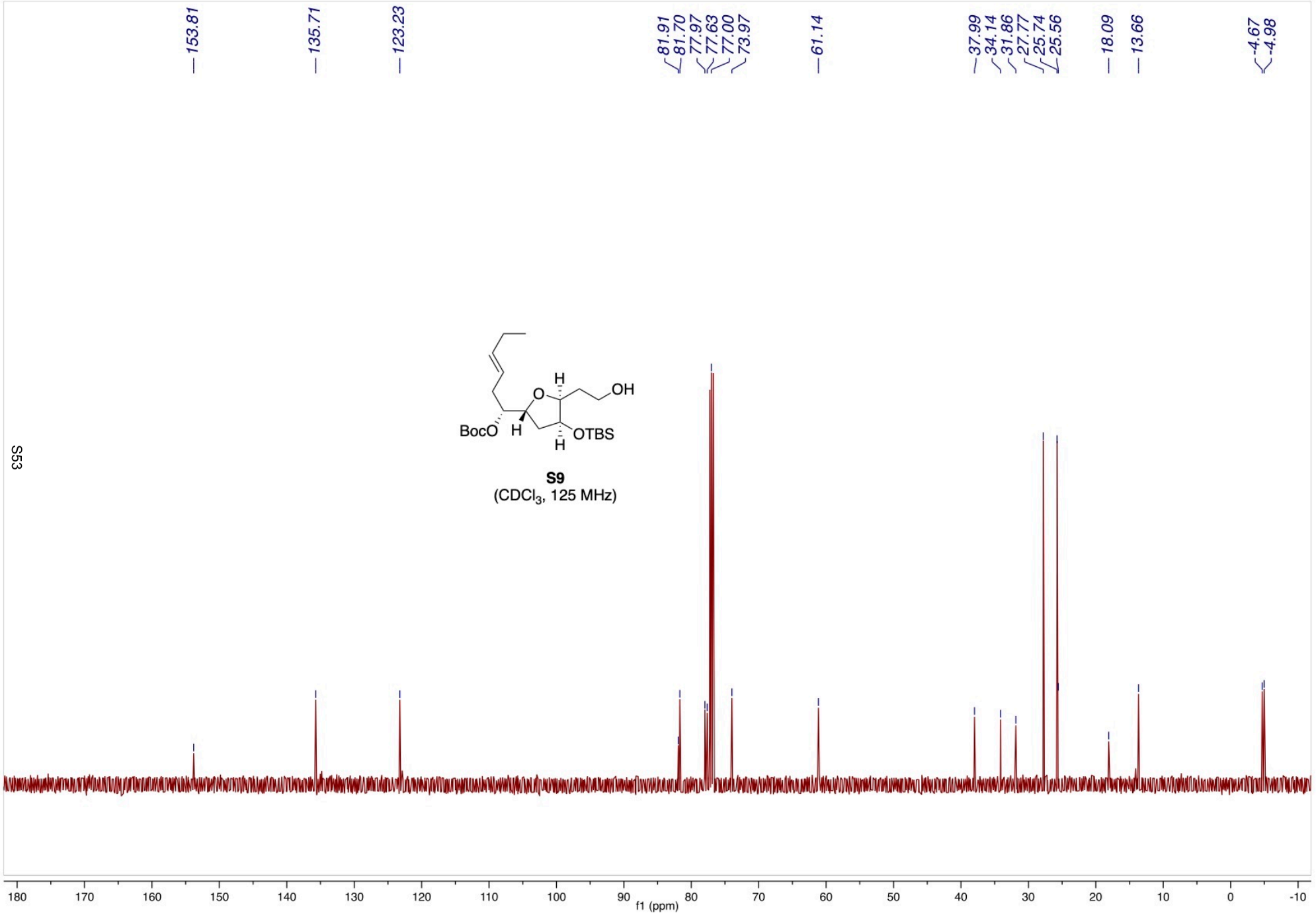

OAc
OTBS
H
O
H
HO
H
S7
(CDCl3, 500 MHz)
f1 (ppm)

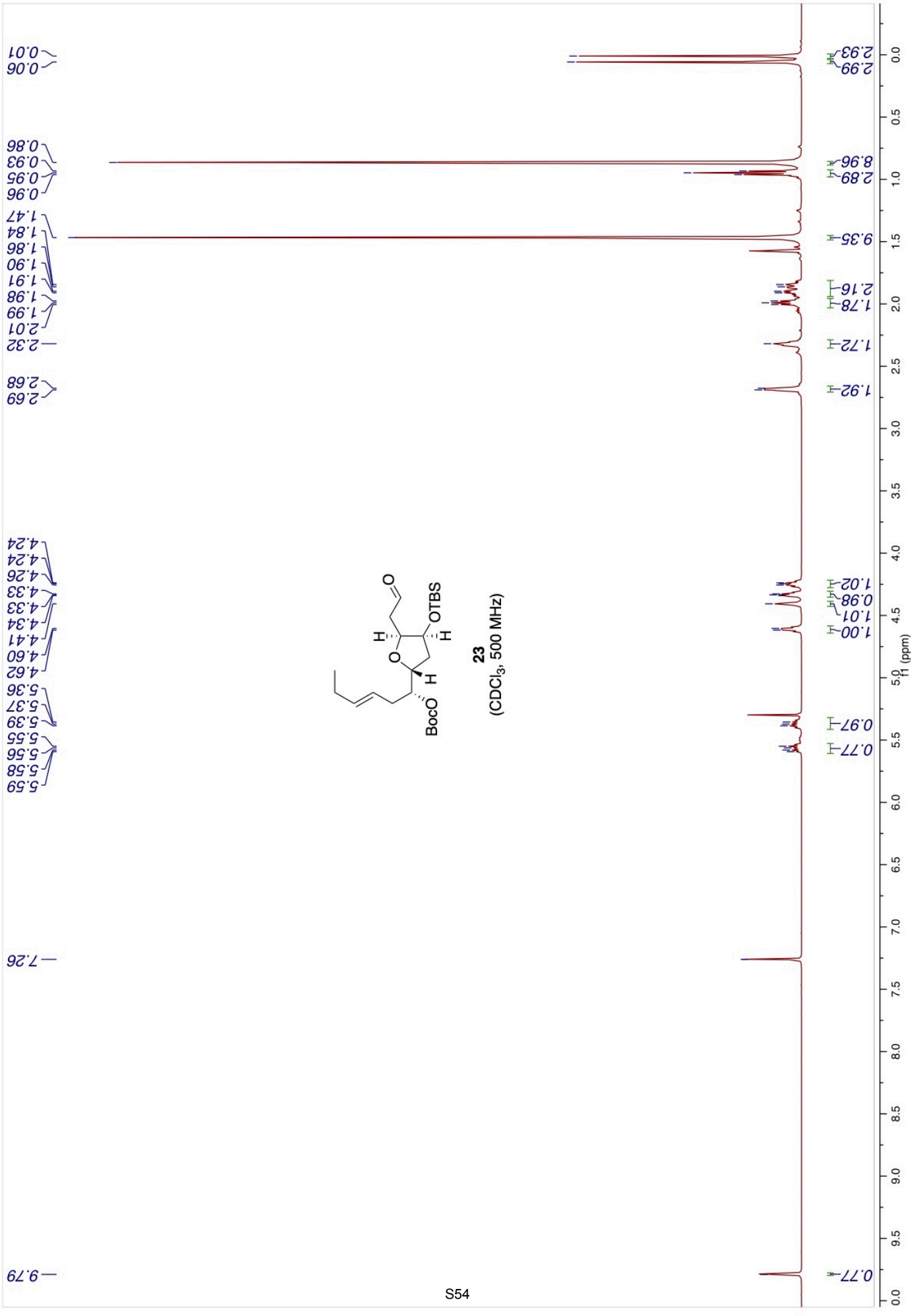

171.18
135.22
124.59
79.80
79.73
77.00
73.85
73.67
62.21
38.32
37.07
29.11
25.73
25.61
21.05
18.04
13.74
-4.54
-5.01
HO
H
O
H
OAc
OTBS
H
S7
(CDCl3, 125 MHz)
f1 (ppm)

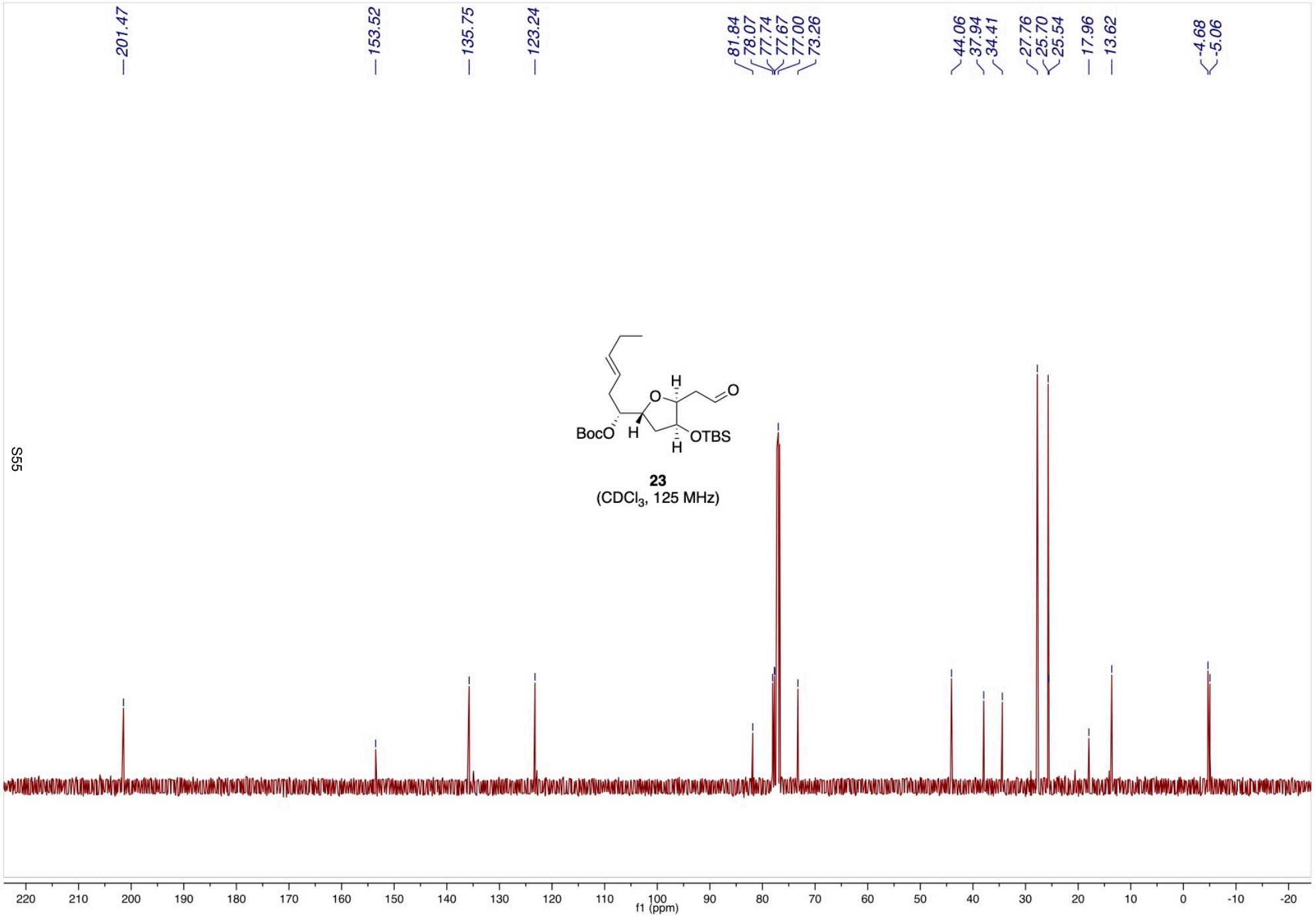

OAc
OTBS
H
H
O
H
BocO
S8
(CDCl3, 500 MHz)
f1 (ppm)


171.11
153.56
135.58
123.42
81.70
79.40
77.89
77.39
77.00
73.41
62.28
38.07
34.35
28.93
27.77
25.72
25.55
21.03
18.02
13.63
-4.56
-5.02
OAc
BocO
H
O
OTBS
S8
(CDCl3, 125 MHz)
f1 (ppm)

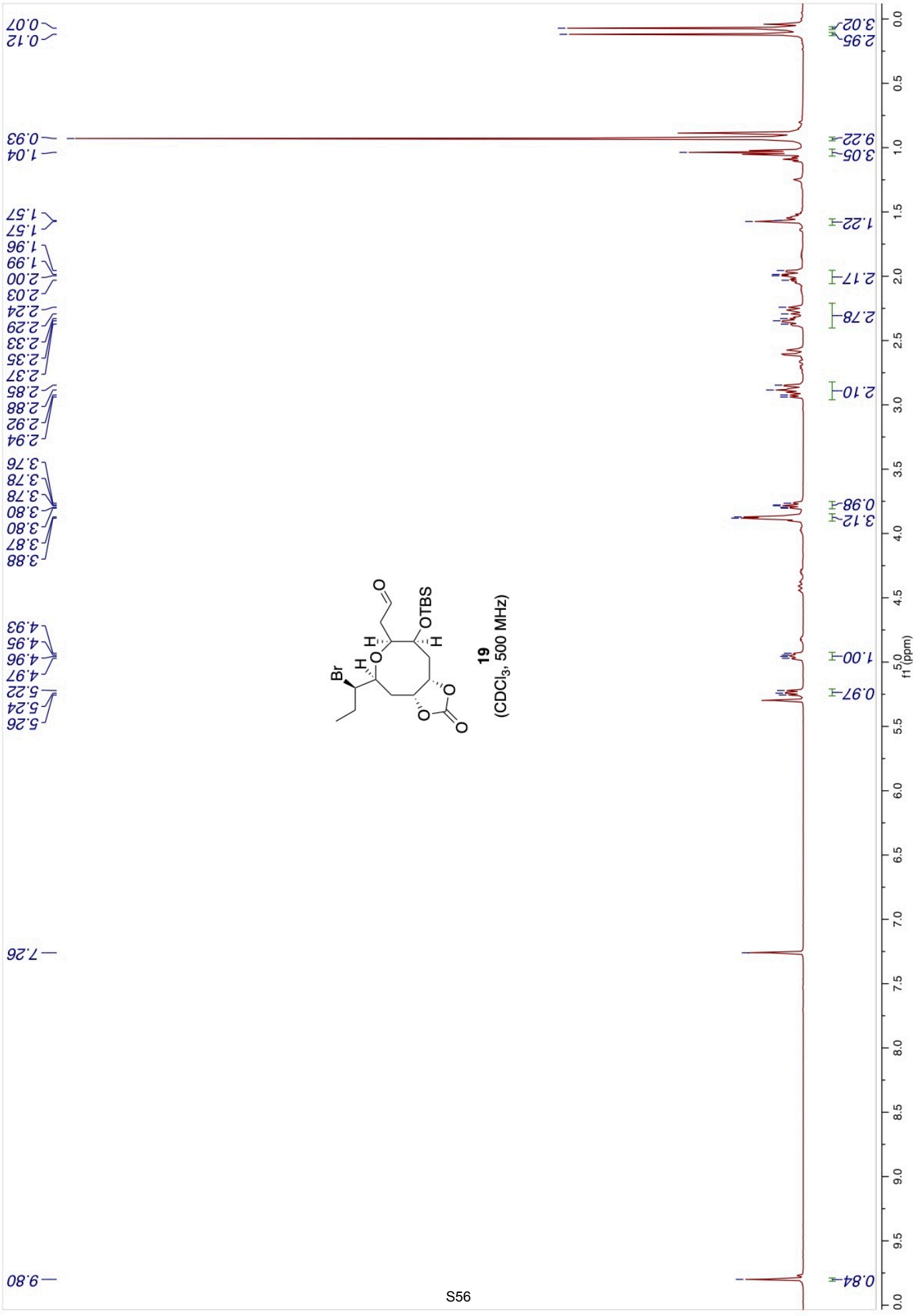

OH
OTBS
H
H
O
H
BocO
S9
(CDCl3, 500 MHz)
f1 (ppm)

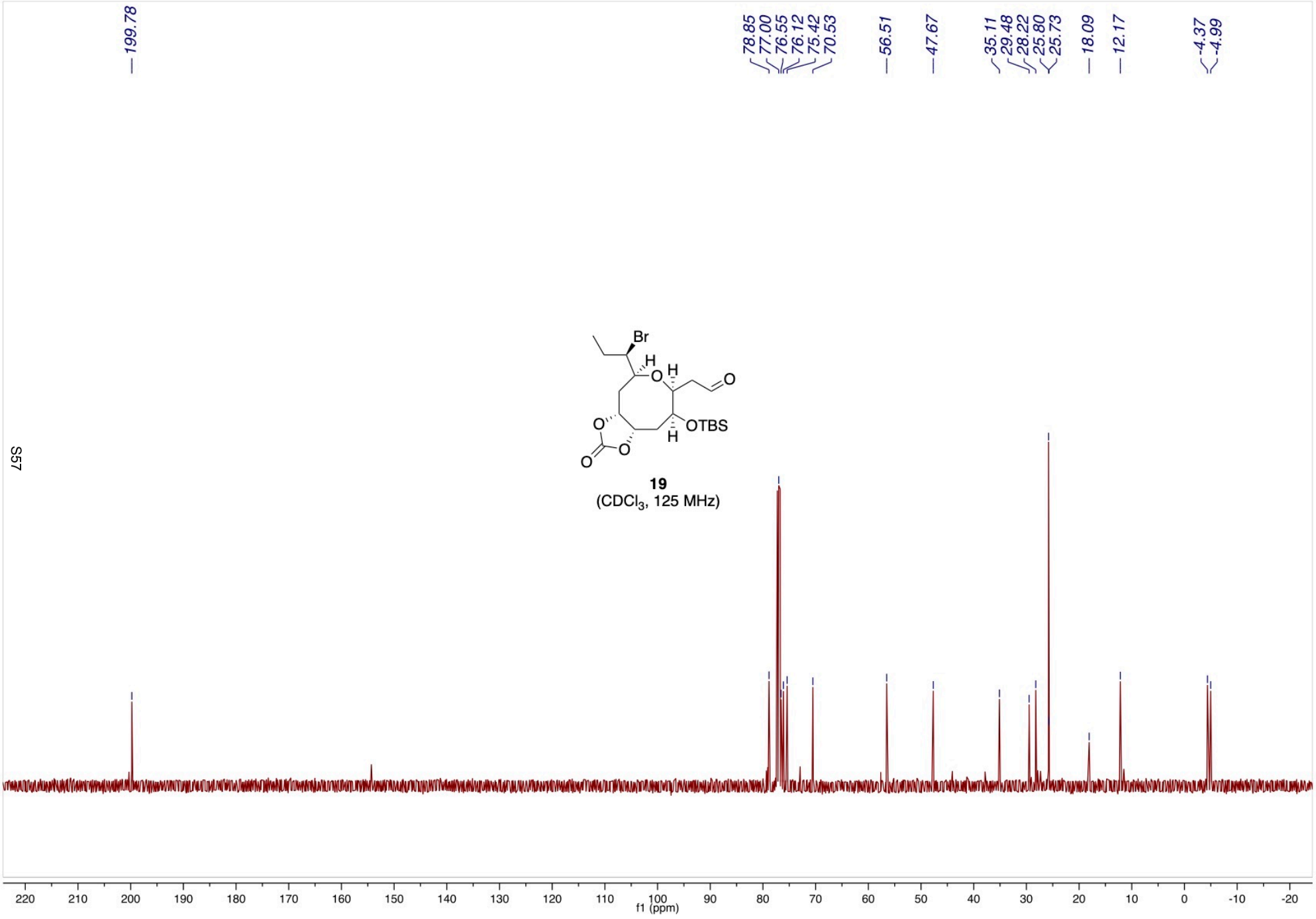

153.81
135.71
123.23
81.91
81.70
77.97
77.63
77.00
73.97
61.14
37.99
34.14
31.86
27.77
25.74
25.56
18.09
13.66
-4.67
-4.98
BocO
H
O
H
OH
H
OTBS
S9
(CDCl3, 125 MHz)
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
-10
f1 (ppm)

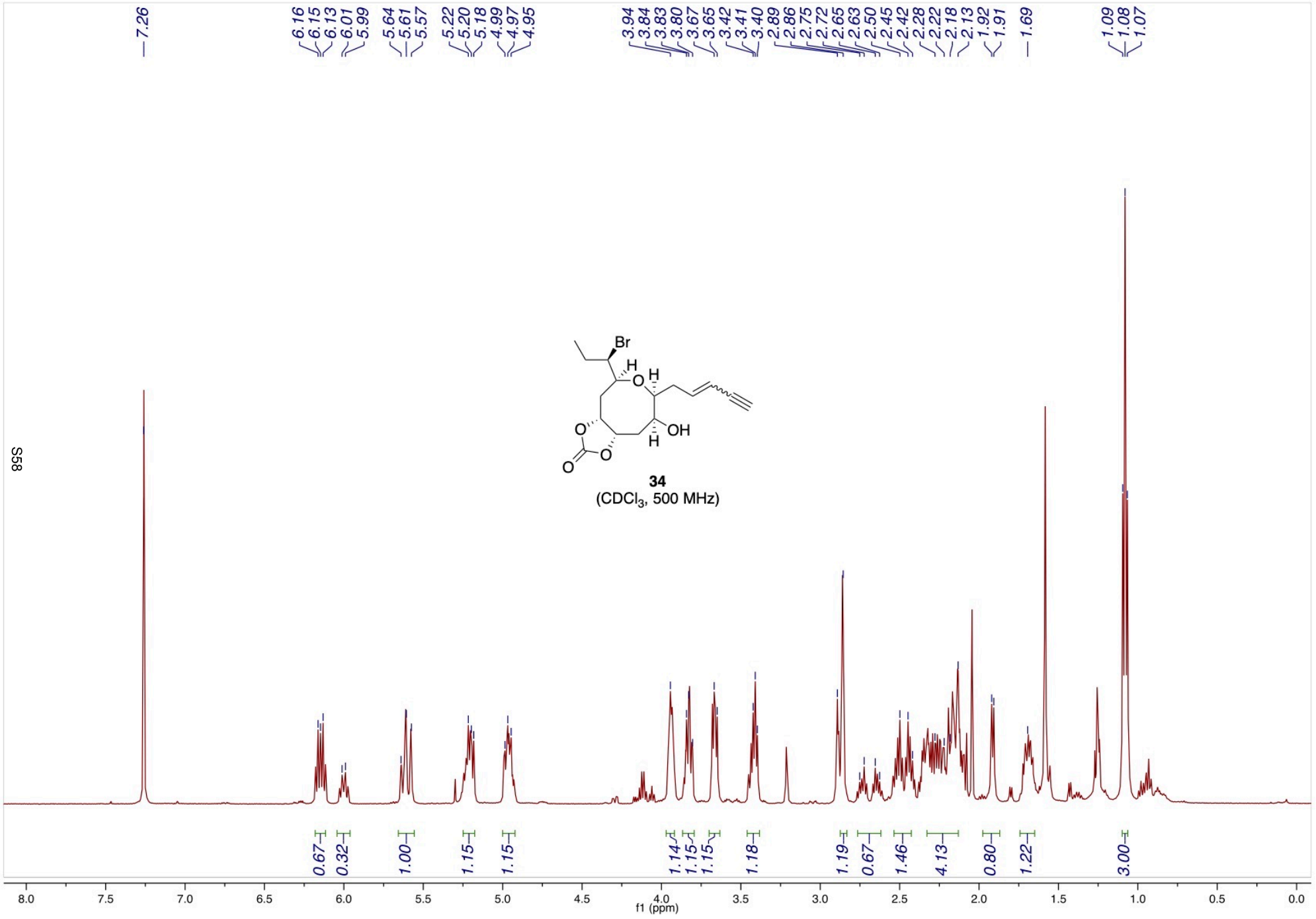

BocO
H
O
H
OTBS
O
23
(CDCl3, 500 MHz)
f1 (ppm)



23
($CDCl_3$, 125 MHz)

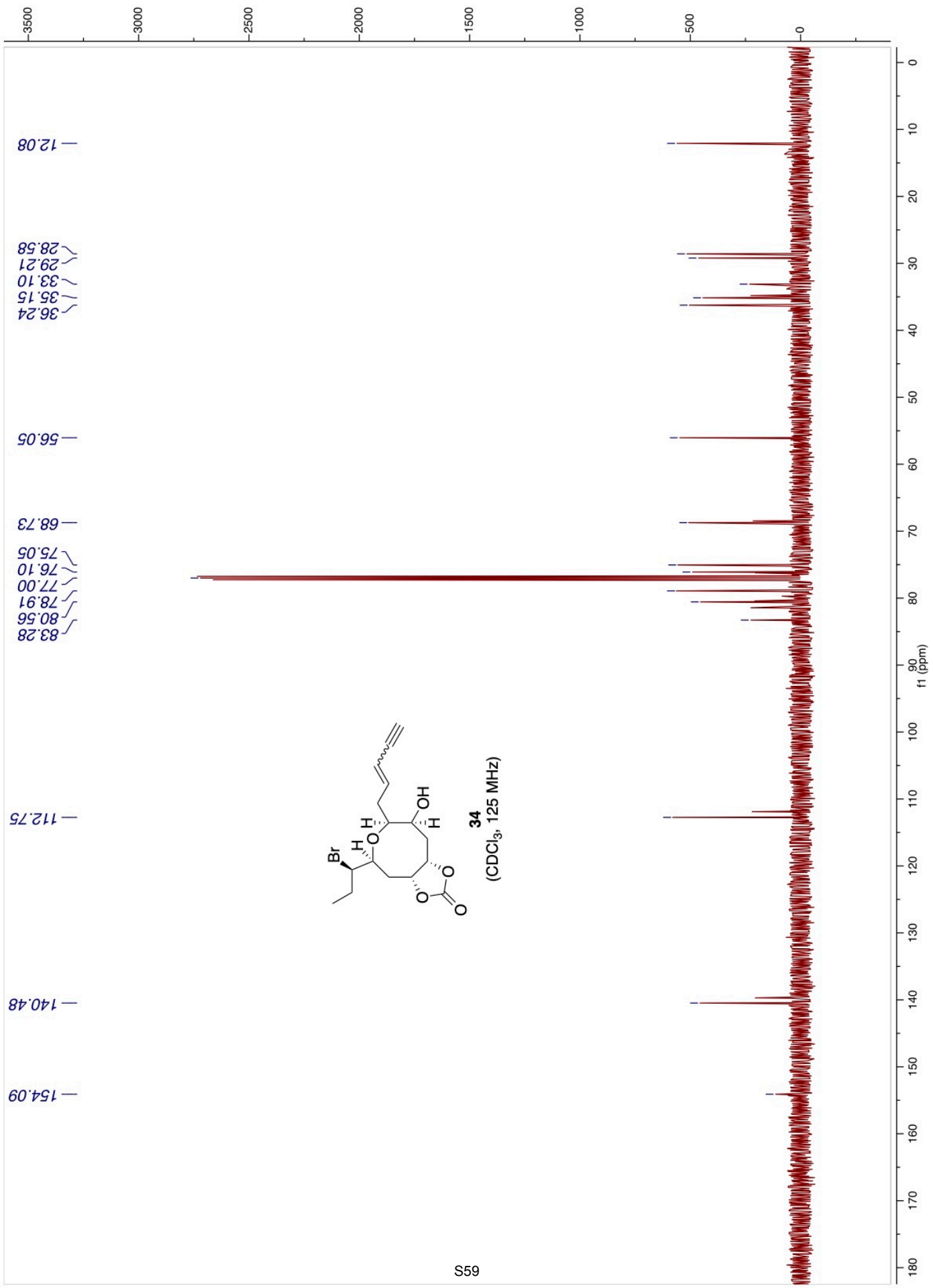

OTBS
Br
O
H
H
O
O
O
O
19
(CDCl3, 500 MHz)
f1 (ppm)

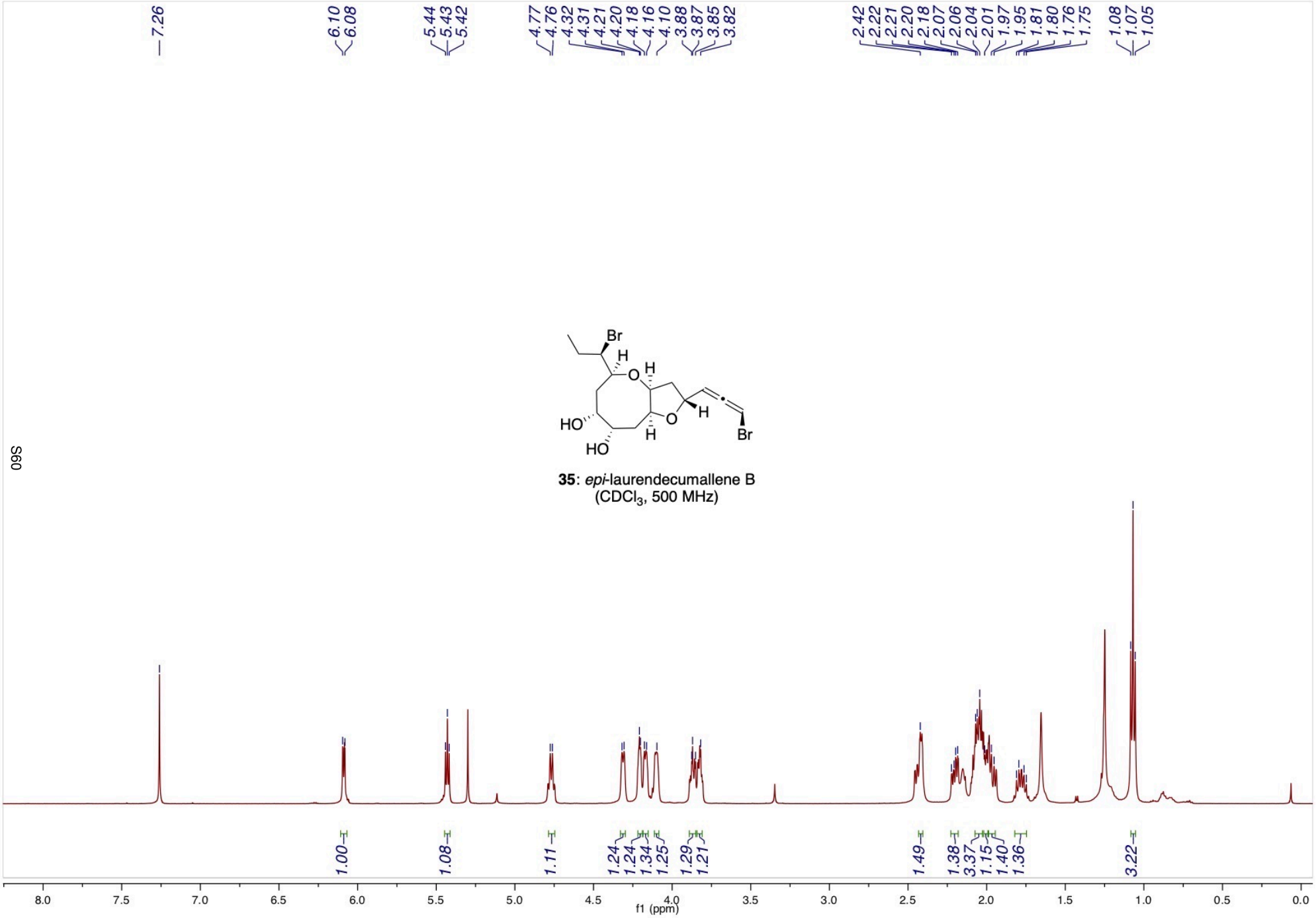

199.78
78.85
77.00
76.55
76.12
75.42
70.53
56.51
47.67
35.11
29.48
28.22
25.80
25.73
18.09
12.17
-4.37
-4.99
Br
H
O
H
O
O
O
O
O
OTBS
H
O
19
(CDCl3, 125 MHz)
220
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
-10
-20
f1 (ppm)



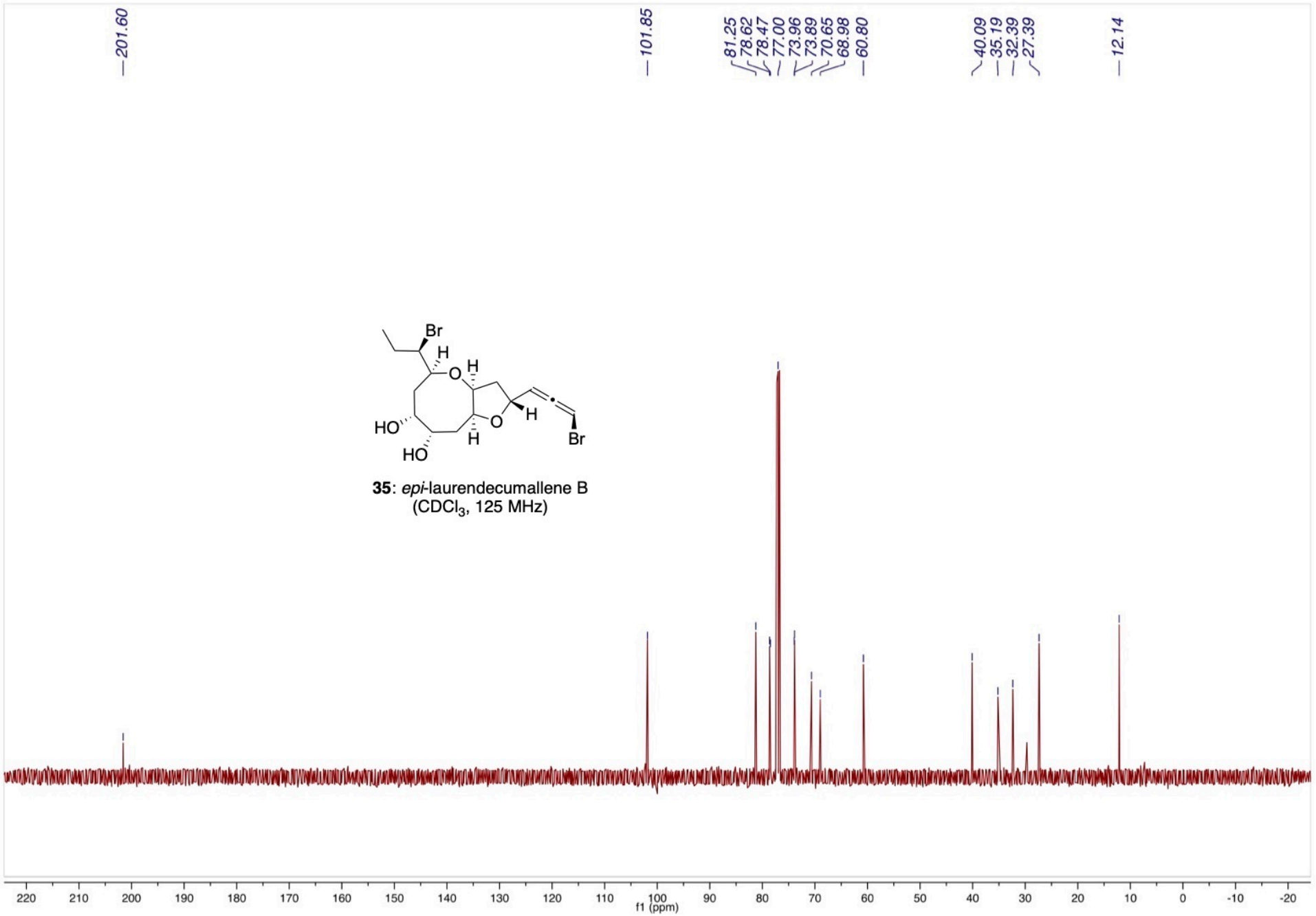
S58

34
($CDCl_3$, 500 MHz)

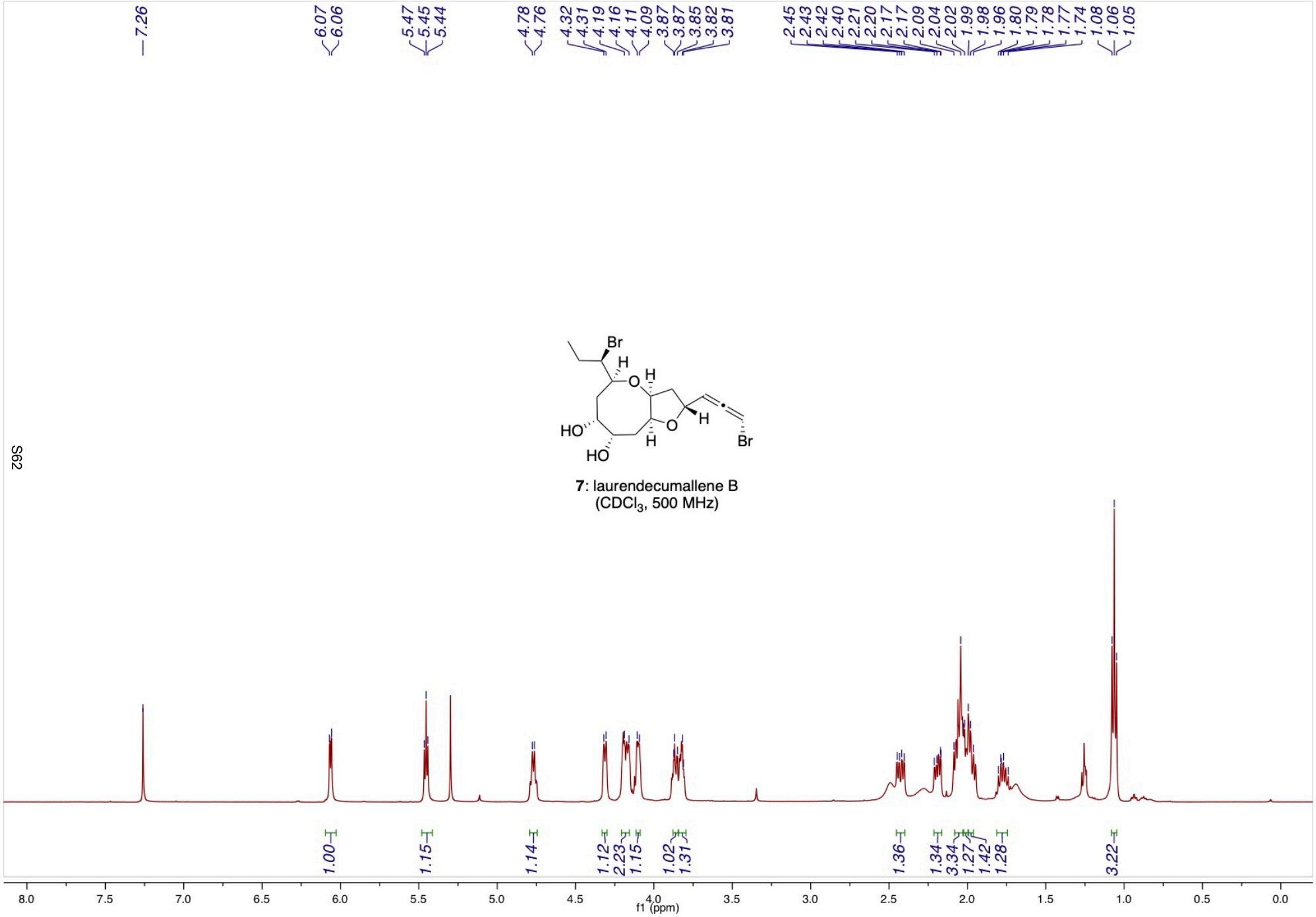

12.08
28.58
29.21
33.10
35.15
36.24
56.05
68.73
75.05
76.10
77.00
78.91
80.56
83.28
112.75
140.48
154.09
Br
H
O
H
OH
H
O
O
O
O
34
(CDCl3, 125 MHz)
f1 (ppm)



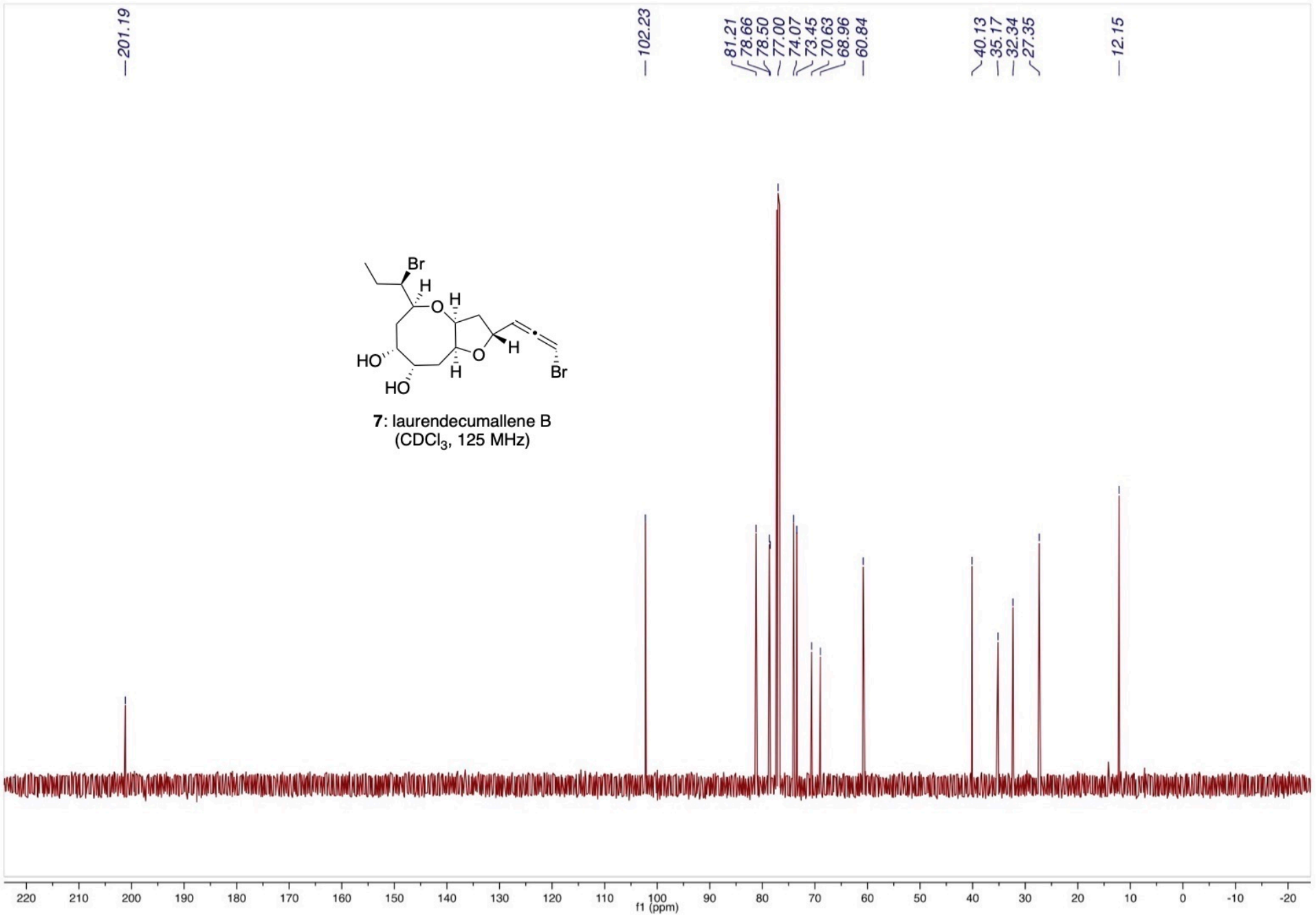
35: *epi*-laurendecumallene B
($CDCl_3$, 500 MHz)

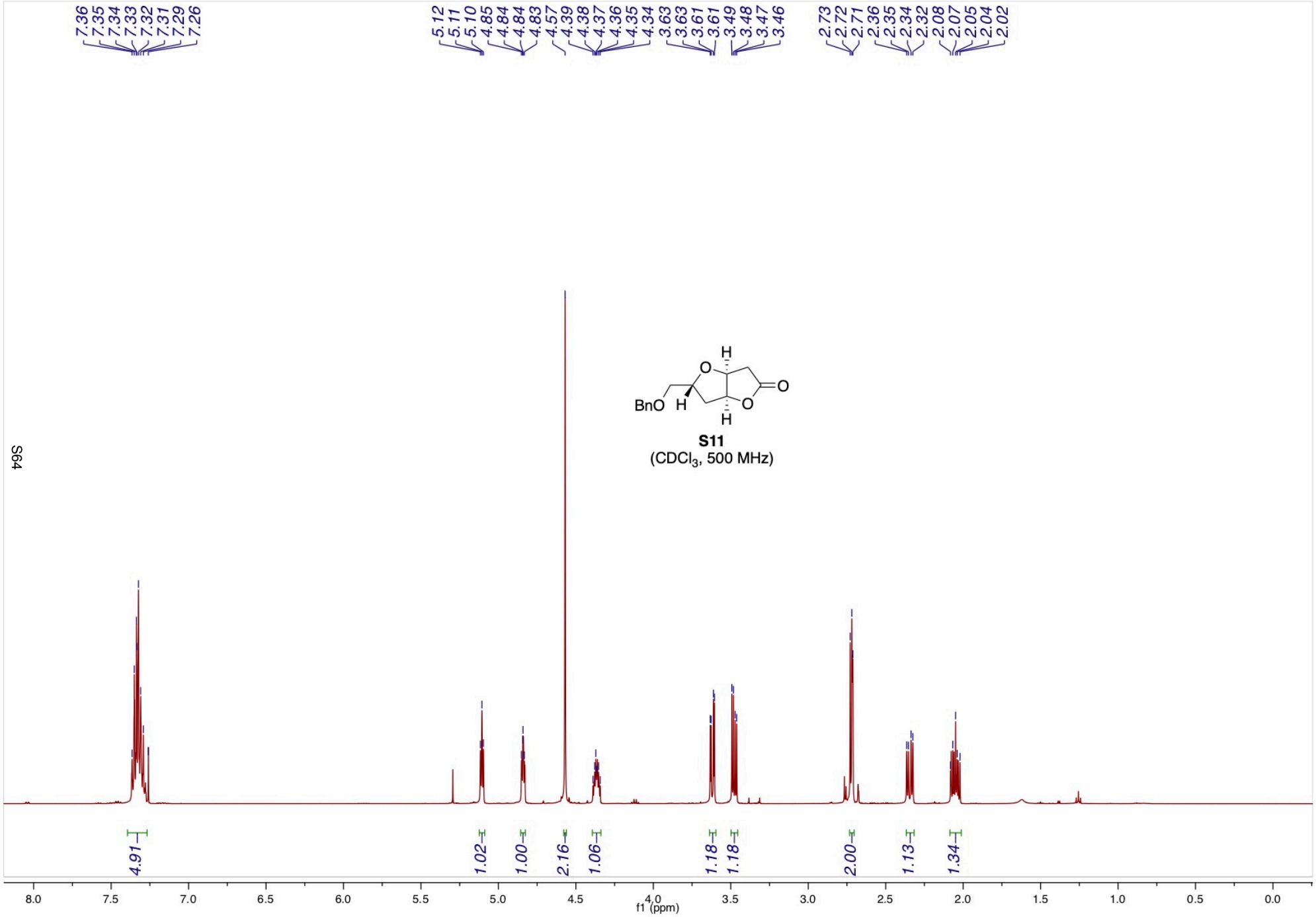


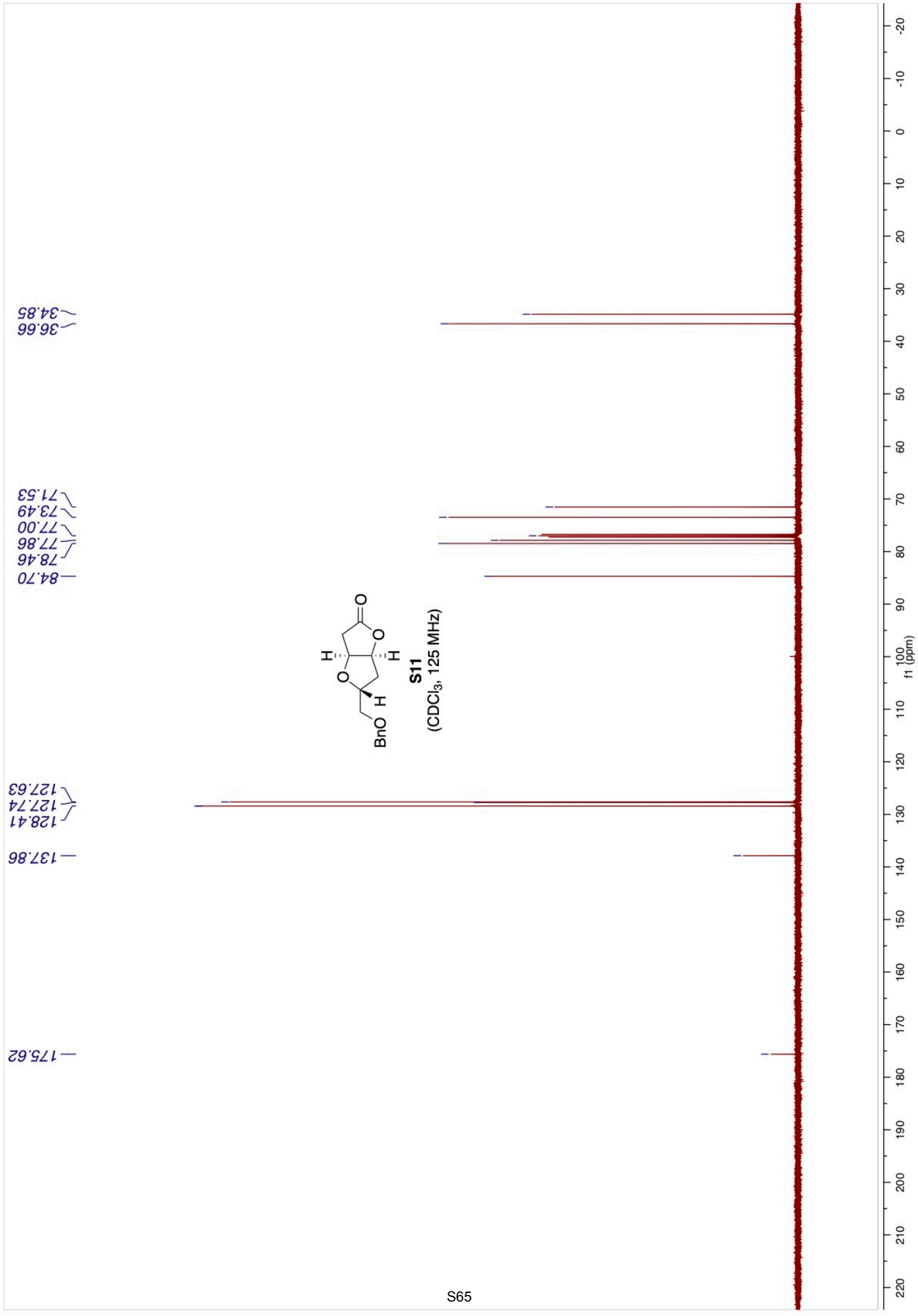
35: *epi*-laurendecumallene B
($CDCl_3$, 125 MHz)

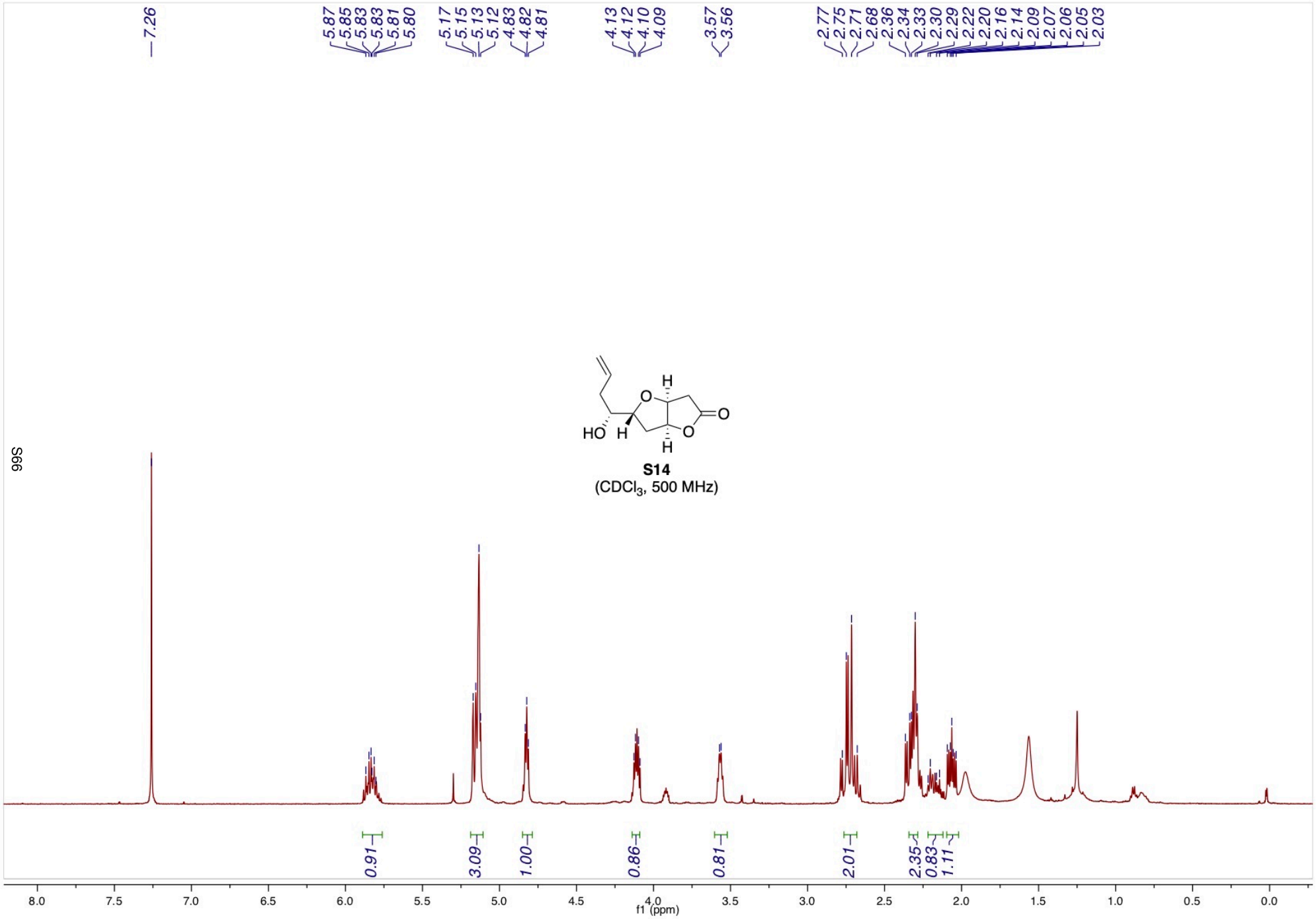


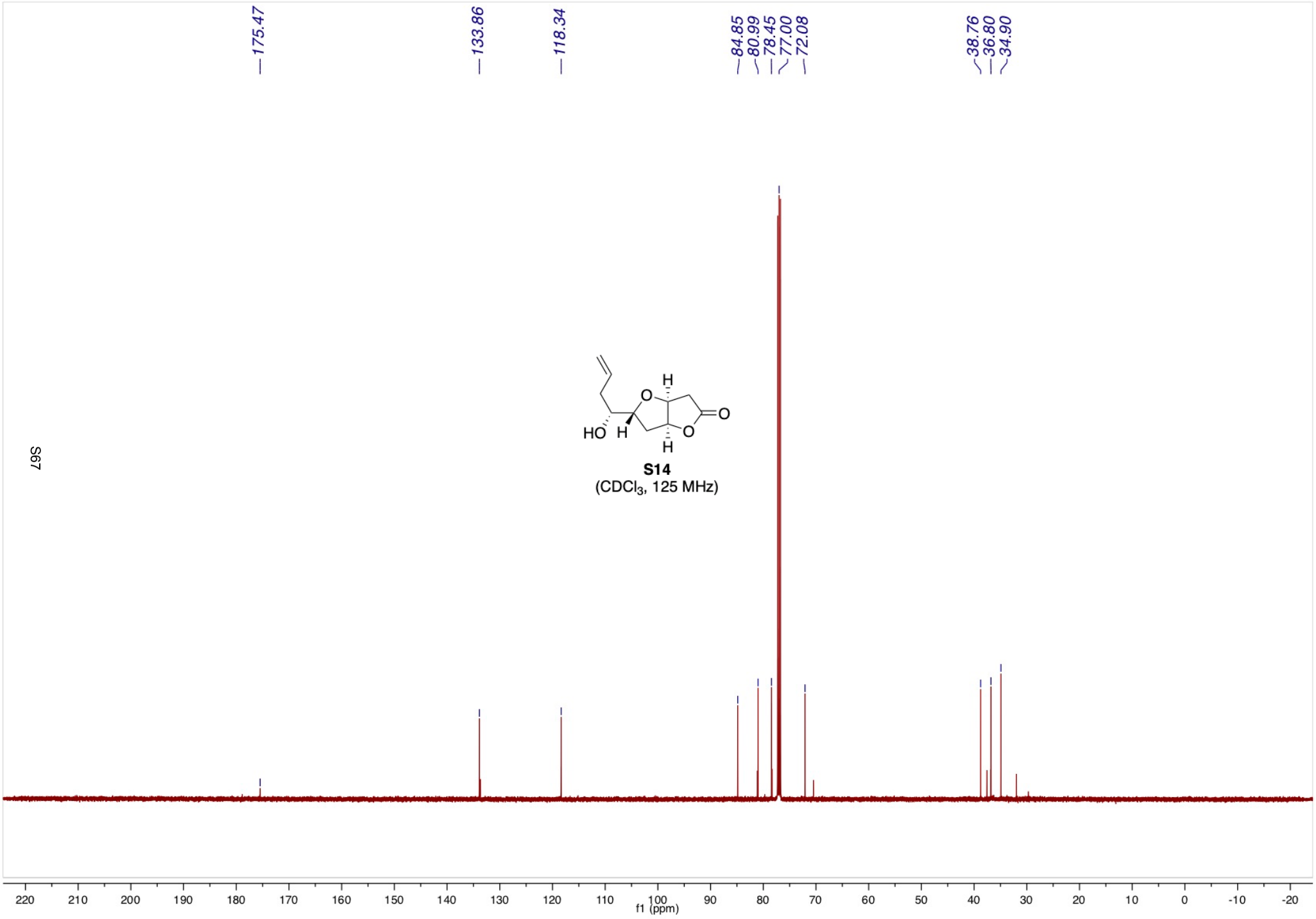
7: laurendecumallene B
($CDCl_3$, 500 MHz)

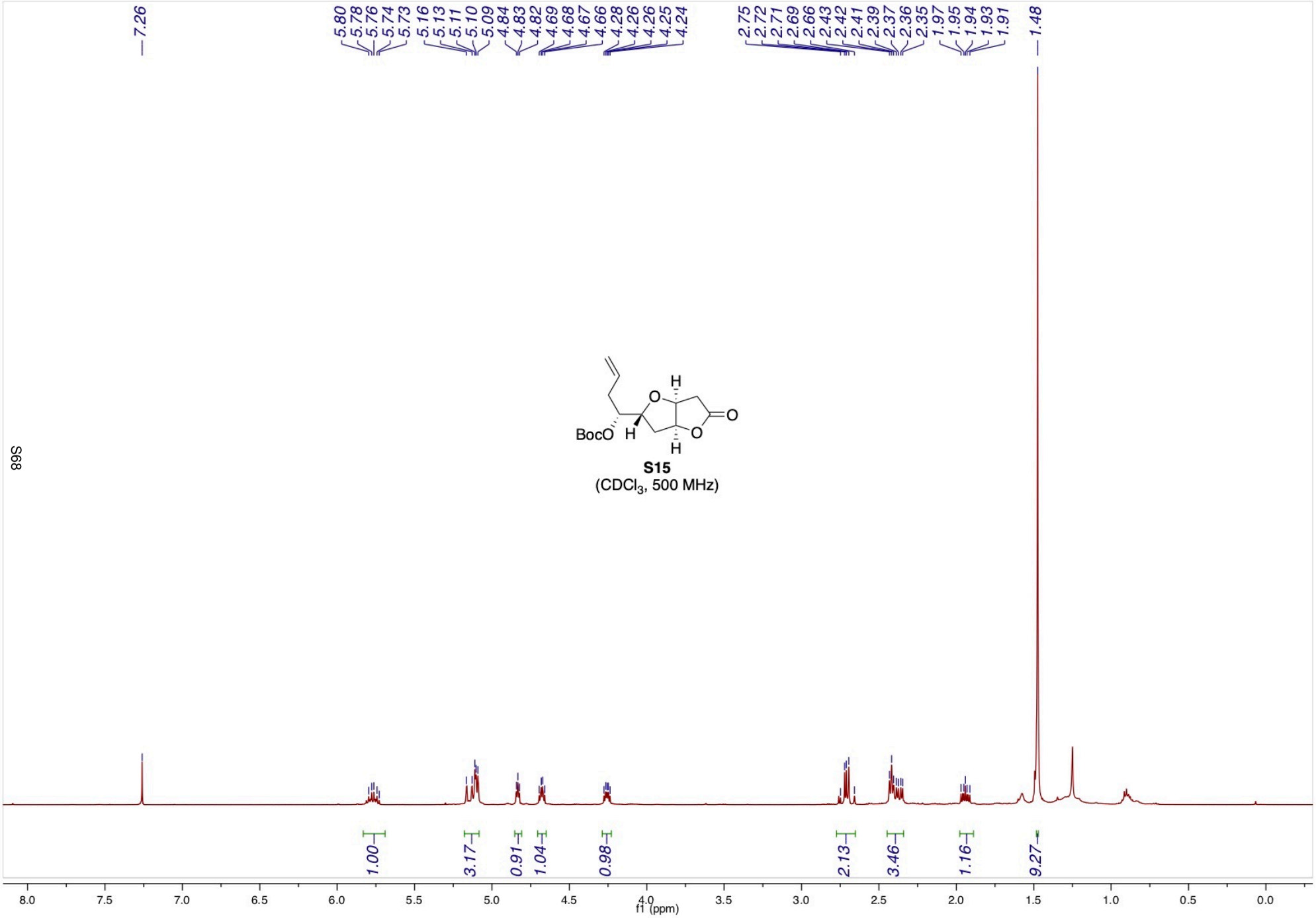

201.19
102.23
81.21
78.66
78.50
77.00
74.07
73.45
70.63
68.96
60.84
40.13
35.17
32.34
27.35
12.15
Br
H
O
H
HO
O
H
H
HO
Br
7: laurendecumallene B
(CDCl3, 125 MHz)
f1 (ppm)


7.36
7.35
7.34
7.33
7.32
7.31
7.29
7.26
5.12
5.11
5.10
4.85
4.84
4.84
4.83
4.57
4.39
4.38
4.37
4.36
4.35
4.34
3.63
3.63
3.61
3.61
3.49
3.48
3.47
3.46
2.73
2.72
2.71
2.36
2.35
2.34
2.32
2.08
2.07
2.05
2.04
2.02
BnO
H
O
O
H
O
H
S11
(CDCl3, 500 MHz)
4.91
1.02
1.00
2.16
1.06
1.18
1.18
2.00
1.13
1.34
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)

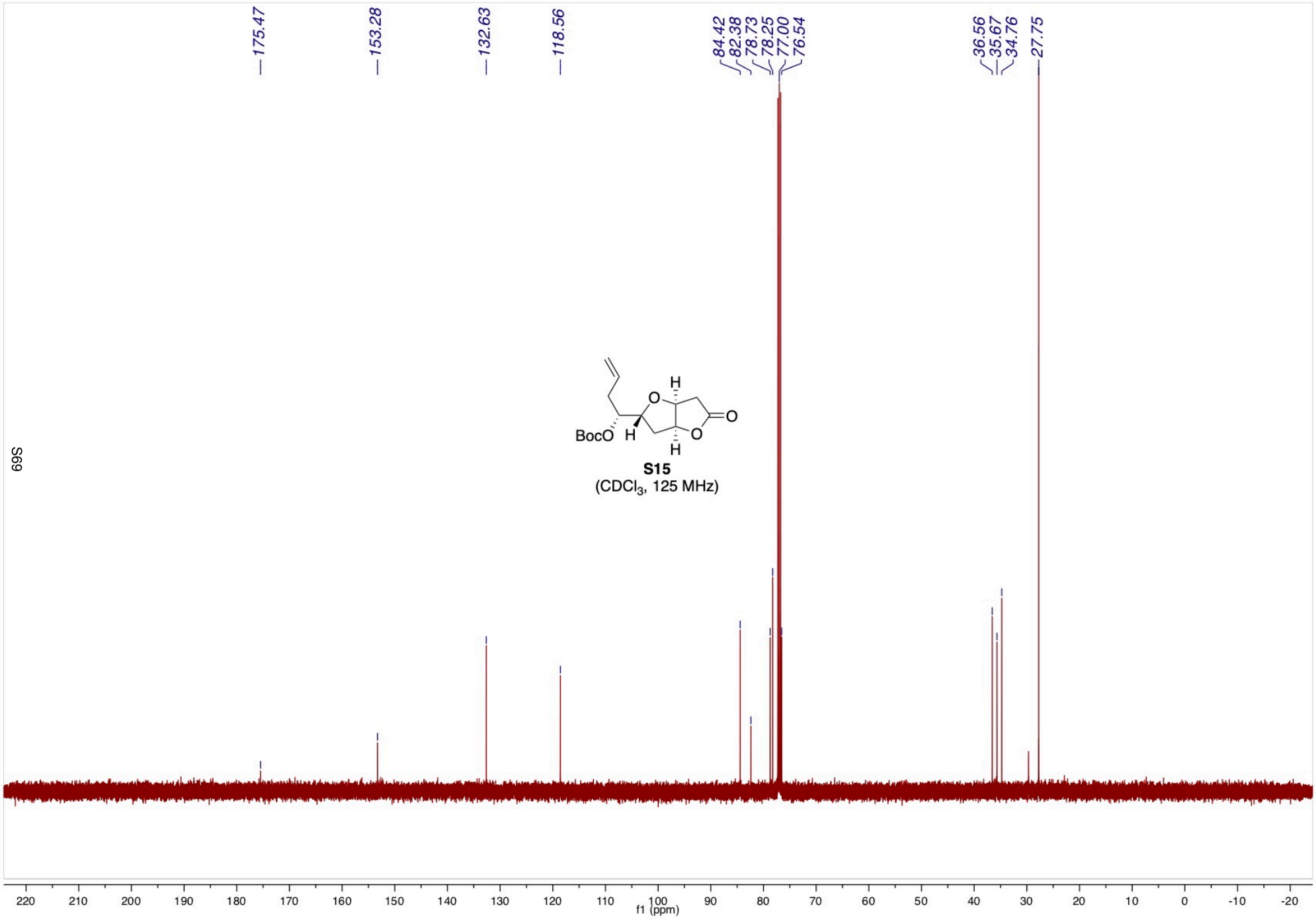

175.62
137.86
128.41
127.74
127.63
84.70
78.46
77.86
77.00
73.49
71.53
36.66
34.85
BnO
H
H
H
O
O
O
S11
(CDCl3, 125 MHz)
f1 (ppm)

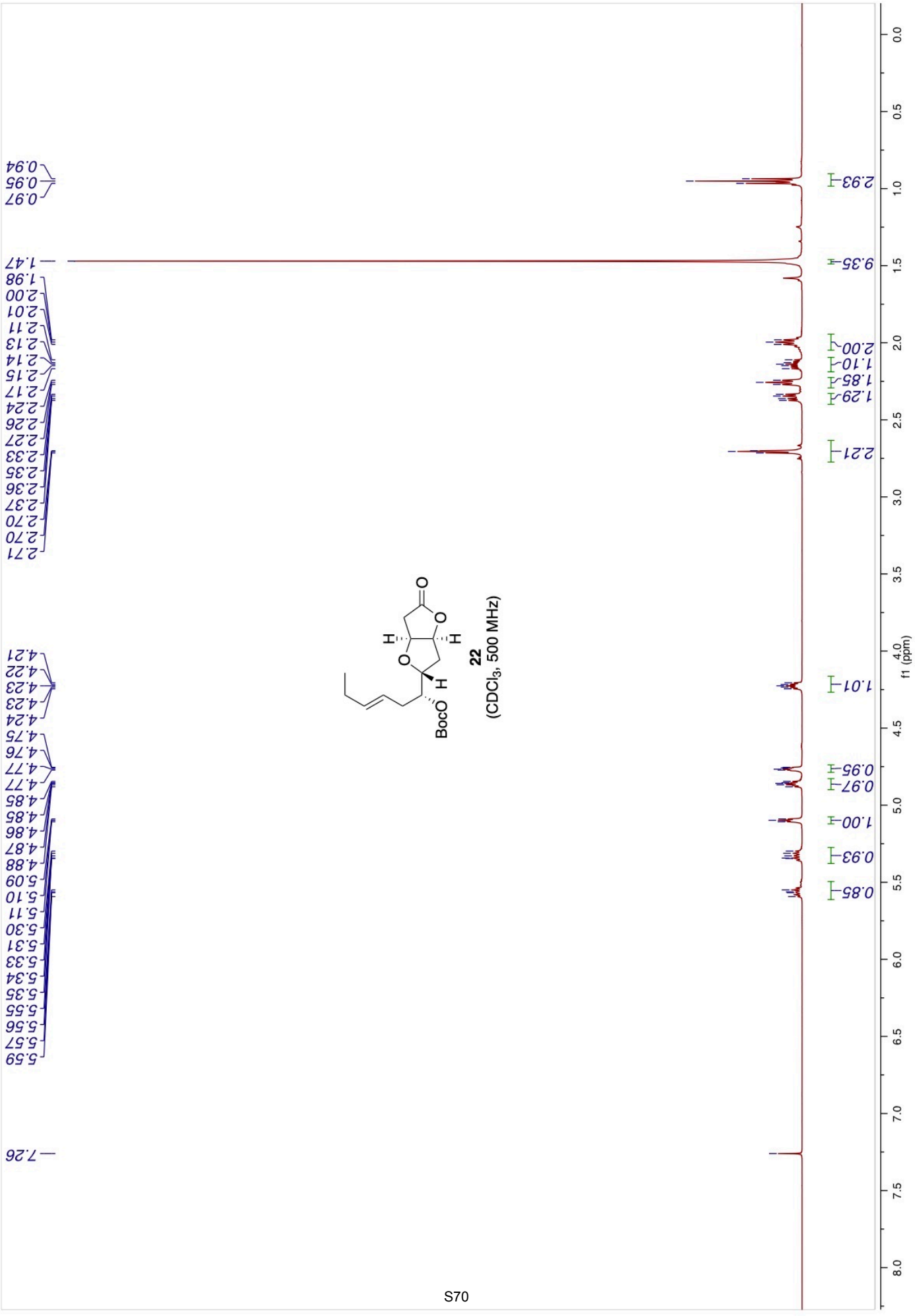

7.26
5.87
5.85
5.83
5.83
5.81
5.80
5.17
5.15
5.13
5.12
4.83
4.82
4.81
4.13
4.12
4.10
4.09
3.57
3.56
2.77
2.75
2.71
2.68
2.36
2.34
2.33
2.30
2.29
2.22
2.20
2.16
2.14
2.09
2.07
2.06
2.05
2.03
HO
H
O
H
O
O
H
S66
S14
(CDCl3, 500 MHz)
0.91
3.09
1.00
0.86
0.81
2.01
2.35
0.83
1.11
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
f1 (ppm)

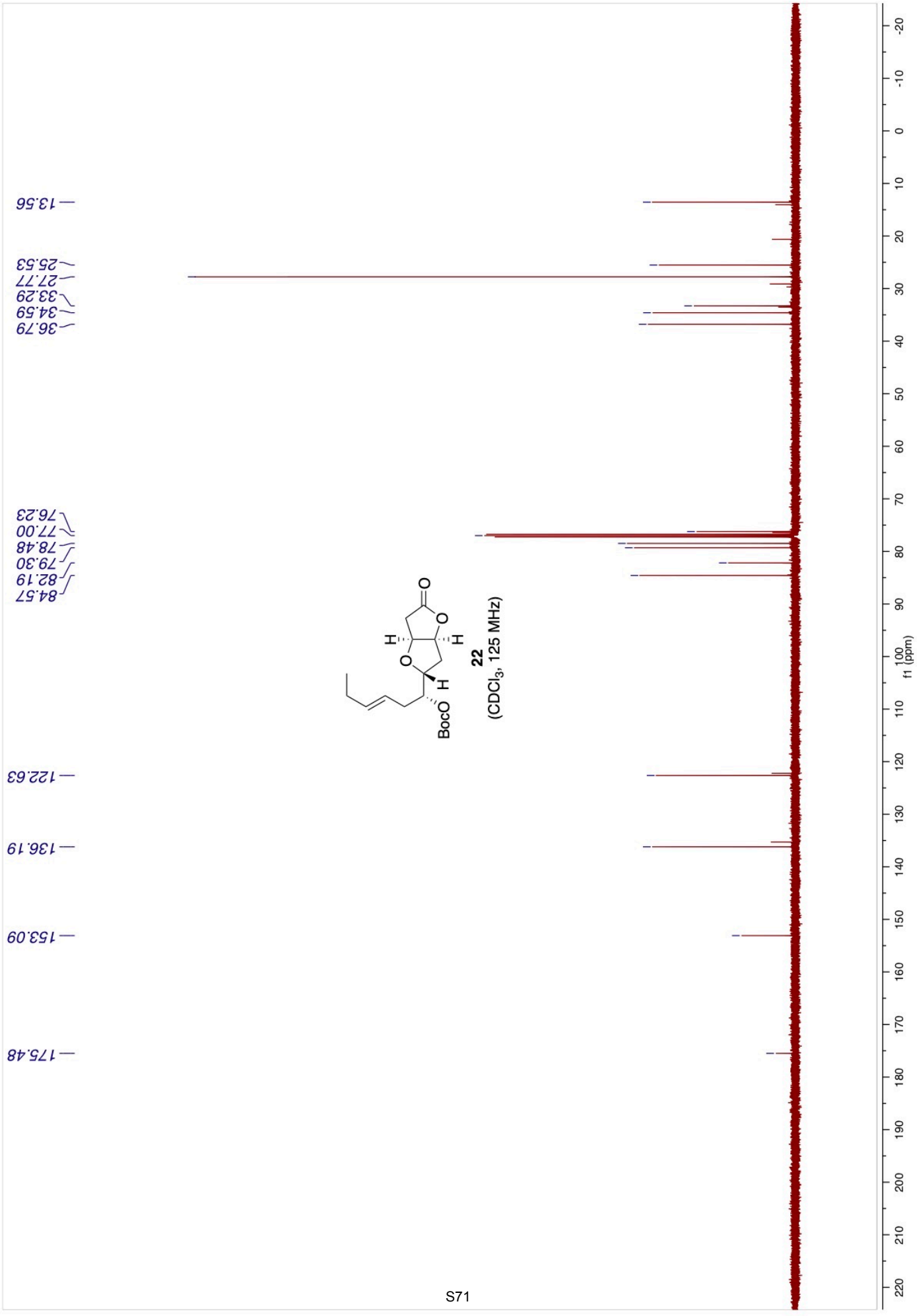

175.47
133.86
118.34
84.85
80.99
78.45
77.00
72.08
38.76
36.80
34.90
HO
H
O
H
O
O
H
S14
(CDCl3, 125 MHz)
S67
220
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
-10
-20
f1 (ppm)



S15
($CDCl_3$, 500 MHz)


175.47
153.28
132.63
118.56
84.42
82.38
78.73
78.25
77.00
76.54
36.56
35.67
34.76
27.75
BocO
H
O
O
O
H
H
S15
(CDCl3, 125 MHz)
f1 (ppm)


22
(CDCl3, 500 MHz)
BocO
H
O
H
O
O
f1 (ppm)


175.48
153.09
136.19
122.63
84.57
82.19
79.30
78.48
77.00
76.23
36.79
34.59
33.29
27.77
25.53
13.56
BocO
H
O
O
H
H
O
22
(CDCl3, 125 MHz)
f1 (ppm)