Total Synthesis of Propolisbenzofuran B

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1. General Methods

All reactions were carried out under a nitrogen atmosphere in flame-dried glassware with magnetic stirring unless otherwise stated. THF, Et_2O and CH_2Cl_2 were purified by passage through a bed of activated alumina.[1] Reagents were purified prior to use unless otherwise stated following the guidelines of Armarego and Chai.[2] Purification of reaction products was carried out by flash chromatography using EM Reagent silica gel 60 (230-400 mesh). Analytical thin layer chromatography was performed on EM Reagent 0.25 mm silica gel 60-F plates. Visualization was accomplished with UV light and anisaldehyde stain, ceric ammonium molybdate stain, or potassium permanganate stain followed by heating. Film infrared spectra were recorded using a Bruker Tensor ATR. ^{1}H-NMR spectra were recorded on a Bruker Avance III 500 (500 MHz) or Varian Inova 400 (400 MHz) spectrometer and are reported in ppm using solvent as an internal standard ($CDCl_3$ at 7.26 ppm). Data are reported as (app = apparent, obs = obscured, s = singlet, d = doublet, t = triplet, q = quartet, p = pentet, h = hextet, sep = septet, o = octet, m = multiplet, b = broad; coupling constant(s) in Hz; integration. Proton-decoupled ^{13}C-NMR spectra were recorded on a Bruker Avance III 500 (500 MHz) spectrometer and are reported in ppm using solvent as an internal standard ($CDCl_3$ at 77.00 ppm). Mass spectra data were obtained on an Agilent 6210 Time-of-Flight LC/MS and a Thermo Finnegan Mat 900 XL High Resolution Magnetic Sector.

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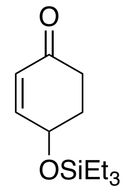
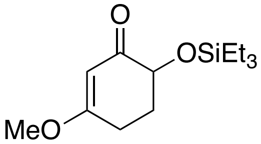
[1] A. B. Pangborn, M. A. Giardello, R. H. Grubbs, R. K. Rosen, F. J. Timmers, *Organometal*. 1996, **15**, 1518–1520.
[2] W. L. F. Armarego, C. L. L. Chai, *Purification of Laboratory Chemicals;* 5th Ed., Butterworth-Heinemann, 2003.

2. Experiment Procedures



4-((Triethylsilyl)oxy)cyclohex-2-en-1-one (4): To a solution of 4-hydroxycyclohex-2-en-1-one (3 g, 27.2 mmol, 1 equiv.),[3] and TES-Cl (5 mL, 29.9 mmol, 1.1 equiv.), in DCM (100 mL) at 0 °C was added Hünig's base (12.3 mL, 70.7 mmol, 2.5 equiv.). The reaction mixture was then left to warm to room temperature overnight. The reaction was then quenched with $NaHCO_3$ and the aqueous phase extracted in DCM (3x 100 mL). The combined organic layers were washed with brine and dried over Na_2SO_4. The crude product was purified by flash chromatography (silica gel, 5% EtOAc/hexanes) to afford the title compound (5.42g, 23.9 mmol, 88% yield) as a pale yellow oil: IR (film) 2954, 2876, 1687, 1382, 1246, 1095, 1001, 839, 726, cm^{-1}; ^{1}H NMR (500 MHz, $CDCl_3$) δ 6.84 (dt, J = 10.3, 2.0 Hz, 1H), 5.93 (ddd, J = 10.2, 2.0, 1.1 Hz, 1H), 4.52 (ddt, J = 9.3, 4.6, 2.1 Hz, 1H), 2.57 (dtd, J = 16.9, 4.5, 1.1 Hz, 1H), 2.35 (ddd, J = 16.9, 13.0, 4.7 Hz, 1H), 2.22 (dqd, J = 13.0, 4.7, 1.7 Hz, 1H), 2.01 (tdd, J = 13.0, 9.2, 4.3 Hz, 1H), 0.98 (t, J = 7.9 Hz, 10H), 0.65 (q, J = 8.0 Hz, 6H); ^{13}C NMR (126 MHz, $CDCl_3$) δ 199.0, 154.2, 128.8, 66.9, 35.7, 33.2, 6.9, 4.9; HRMS (EI): Exact mass calcd for $C_{12}H_{22}$ NaO_2Si [M+Na]$^+$, 226.1389. Found 249.1289.



3-Methoxy-6-((triethylsilyl)oxy)cyclohex-2-en-1-one (S1): To a solution of LDA (prepared from 14.33 mL, 102.3 mmol, 1.2 equiv. *i*-Pr_2NH and 93.74 mmol, 1.1 equiv. of *n*-BuLi) in 200 mL of THF at –78 °C was added **18** (10.75 g, 85.22 mmol, 1 equiv.) in 100 mL THF. After 30 mins at –78 °C TES-Cl (15.7 mL, 93.74 mmol, 1.1 equiv.) was added dropwise. The reaction was stirred at –78 °C for 1 hour and slowly warmed to room temperature over 2.5 hours. The reaction was then washed with mL 1M pH 7 buffer (300 mL), extracted in pentanes (3x 300 mL), washed with brine, and dried with Na_2SO_4. The crude product was carried forward without purification.

To a pre-stirred suspension of *m*-CPBA (29.3 g, 170 mmol, 2 equiv.) and $NaHCO_3$ (28.6 g, 340 mmol, 4 equiv.) in 500 mL EtOAc at 0 °C was added the prepared enol silane (crude: 20.4g, 85 mmol, 1 equiv.) in 100 mL of EtOAc. The reaction was stirred vigorously and allowed to warm to room temperature overnight. The precipitate was filtered off and the filtrate washed with 500 mL 10 % $Na_2S_2O_3$ (aqueous) and extracted in EtOAc (3x 400 mL). The combined organic extracts were washed with 1 L saturated $NaHCO_3$ (aqueous), 1 L H_2O, and 1 L brine and then dried with Na_2SO_4 and hexanes. The crude mixture was purified by flash column chromatography (silica gel, 10%–33% EtOAc/hexanes) to afford the title compound (19.4 g, 75.7 mmol, 89% yield) as a clear oil: IR (film) 2952, 1679, 1606, 1378, 1230, 1140, 988, 866, 726 cm^{-1}; ^{1}H NMR (500 MHz, $CDCl_3$) δ 5.33 – 5.27 (m, 1H), 4.07 (dd, J = 9.8, 4.5 Hz, 1H), 3.68 (s, 3H), 2.56 (dt, J = 17.6, 5.2 Hz, 1H), 2.45 (dddd, J = 17.7, 9.5, 5.2, 1.2 Hz, 1H), 2.14 – 1.95 (m, 2H), 0.96 (t, J = 7.9 Hz, 10H), 0.73 – 0.55 (m, 6H); ^{13}C NMR (126 MHz, $CDCl_3$) δ 197.7, 177.3, 100.6, 72.6, 56.0, 30.7, 27.3, 7.0, 5.0; HRMS (ESI): Exact mass calcd for $C_{13}H_{24}NaO_3Si$ [M+Na]$^+$, 279.1387. Found 279.1395.

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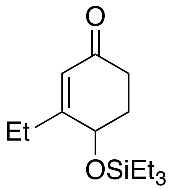
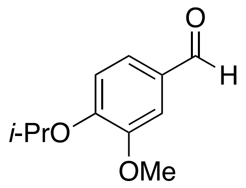
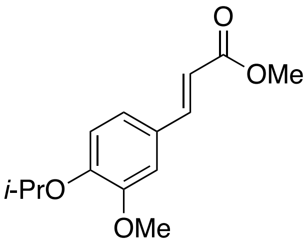
[3] S. J. Danishefsky and B. Simoneau, *J. Am. Chem. Soc.*, 1989, **111**, 2599-2604.



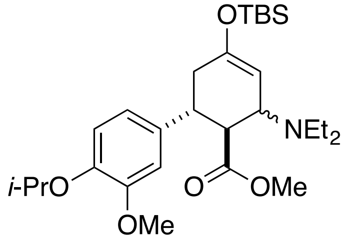
3-Ethyl-4-((triethylsilyl)oxy)cyclohex-2-en-1-one (19): To a solution of EtMgBr (23.4 mmol, 2 equiv.) and LiCl (1.24 g, 29.3 mmol, 2.5 equiv.) in 180 mL THF at 0 °C was added a solution of **S1** (3.0 g, 11.7 mmol, 1 equiv.) in 60 mL THF. The reaction was warmed to room temperature over 1.5 hours. The reaction was then quenched with a 50% solution of H_2O/brine (200 mL), extracted in EtOAc (3x 200 mL), and the combined organic layers washed with 0.33 M HCl (300 mL), brine (300 mL) and dried with Na_2SO_4 The crude product was purified by flash column chromatography (silica gel, 10% EtOAc/hexanes) to afford the title compound (2.66 g, 10.45 mmol, 89%); IR (film) 2955, 2876, 1673, 1103, 991, 724 cm^{-1}; ^1H NMR (500 MHz, $CDCl_3$) δ 6.84 (dt, *J* = 10.3, 2.0 Hz, 1H), 5.93 (ddd, *J* = 10.3, 2.0, 1.1 Hz, 1H), 4.52 (ddt, *J* = 9.3, 4.6, 2.1 Hz, 1H), 2.57 (dtd, *J* = 16.8, 4.4, 1.1 Hz, 1H), 2.35 (ddd, *J* = 16.9, 13.0, 4.7 Hz, 1H), 2.22 (dqd, *J* = 13.0, 4.7, 1.7 Hz, 1H), 2.01 (tdd, *J* = 13.1, 9.3, 4.3 Hz, 1H), 0.98 (t, *J* = 7.9 Hz, 9H), 0.65 (q, *J* = 8.0 Hz, 6H); ^{13}C NMR (126 MHz, $CDCl_3$) δ 199.30 169.1, 124.4, 69.0, 35.0, 32.8, 26.5, 11.4, 7.0, 5.1. HRMS (EI): Exact mass calcd for $C_{14}H_{26}NaO_2Si$ $[M+Na]^+$, 277.1594. Found 277.1603.



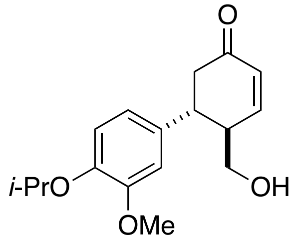
4-Isopropoxy-3-methoxybenzaldehyde (S2): To a suspension of vanillin (15.2g, 100 mmol), K_2CO_3 (27.6g, 200 mmol), and KI (spatula tip) in ethanol (50 mL) was added *i*-PrBr (14 mL, 150 mmol). This solution was heated at reflux for 4 days. The suspension was cool and filtered and the filter cake washed with DCM. The filtrate was condensed and purified by flash chromatography (silica gel, 100% DCM) to afford the title compound (38.9 g, 198 mmol, 99%) as a viscous yellow oil: IR (film) 2978, 1680, 1581, 1503, 1261, 1131, 1030, 947, 729 cm^{-1}; ^1H NMR (500 MHz, $CDCl_3$) δ 9.84 (s, 1H), 7.46 – 7.39 (m, 2H), 6.97 (d, *J* = 8.1 Hz, 1H), 4.69 (hept, *J* = 6.1 Hz, 1H), 3.92 (s, 3H), 1.43 (d, *J* = 6.1 Hz, 6H); ^{13}C NMR (126 MHz, $CDCl_3$) δ 191.1, 153.2, 150.5, 129.8, 126.8, 112.9, 109.6, 71.5, 56.2, 22.0; HRMS (EI): Exact mass calcd for $C_{11}H_{14}NaO_3$ $[M+Na]^+$, 217.0835. Found 217.0846.



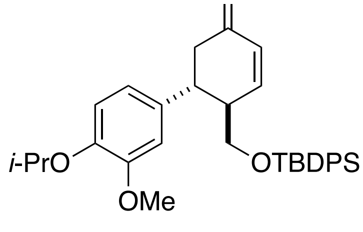
Methyl (*E*)-3-(4-isopropoxy-3-methoxyphenyl)acrylate (6): To a suspension of NaH (8.2 g, 207 mmol, 1.2 equiv., 60% dispersion) in 1 L THF at 0 °C was added methyl diethylphosphonoacetate (39.9 g, 190 mmol, 1.1 equiv.). After stirring at 0 °C for 15 min the reaction mixture became homogenous and **S2** was added in 50 mL THF. The reaction was left to warm to room temperature overnight. The reaction mixture was diluted with 300 mL DCM and washed with brine (500 mL). The product was extracted in DCM (2x 500 mL), washed again with brine (1 L), and dried with Na_2SO_4. The product was recrystallized from Et_2O/pentanes to afford the title compound (34.4 g, 137.3 mmol, 90% yield) as a white crystalline solid: IR (film) 2982, 1694, 1595, 1507, 1252, 1146, 1031 cm^{-1}; ^1H NMR (500 MHz, $CDCl_3$) δ 7.63 (d, *J* = 15.9 Hz, 1H), 7.15 – 6.97 (m, 2H), 6.87 (d, *J* = 8.3 Hz, 1H), 6.30 (d, *J* = 15.9 Hz, 1H), 4.60 (p, *J* = 6.1 Hz, 1H), 3.88 (s, 3H), 3.80 (s, 3H), 1.39 (d, *J* = 6.1 Hz, 6H); ^{13}C NMR (126 MHz, $CDCl_3$) δ 167.89, 150.31, 149.71, 145.02, 127.34, 122.56, 115.42, 114.45, 110.45, 71.35, 56.10, 51.78, 22.12; HRMS (EI): Exact mass calcd for $C_{14}H_{18}NaO_4$ $[M+Na]^+$, 273.1097. Found 273.1105.



Methyl (±)-5-((*tert*-butyldimethylsilyl)oxy)-3-(diethylamino)-4'-isopropoxy-3'-methoxy-1,2,3,6-tetrahydro-[1,1'-biphenyl]-2-carboxylate (S3): To a solution of **7** (12 g, 47 mmol, 1 equiv.) in 75 mL of toluene was added solid **6** (23.5 g, 94 mmol, 2 equiv.) in one portion. The reaction was heated to 90 °C for 3 days. The reaction mixture was then cooled and condensed to minimal toluene. Excess starting material (11.6 g) was precipitated out with Et_2O/pentanes. The mother liquor was then further purified by column chromatography (silica gel, 10% EtOAc/hexanes with 1% triethylamine) to afford the title compound (20 g, 39.5 mmol, 84%) as a viscous yellow oil: IR (film) 2959, 1735, 1663, 1514, 1464, 1371, 1257, 1160, 909, 838, 729 cm^{-1}; ^1H NMR (500 MHz, $CDCl_3$) δ 6.80 (dd, *J* = 11.8, 8.0 Hz, 1H), 6.76 – 6.62 (m, 2H), 4.89 (t, *J* = 1.8 Hz, 1H), 4.47 (p, *J* = 6.0 Hz, 1H), 3.84 (s, 3H), 3.35 (s, 3H), 3.06 (td, *J* = 11.6, 5.5 Hz, 1H), 2.67 (dd, *J* = 11.8, 10.1 Hz, 1H), 2.54 (dq, *J* = 12.9, 7.3 Hz, 2H), 2.37 (dq, *J* = 13.4, 6.8 Hz, 2H), 2.33 – 2.17 (m, 2H), 1.34 (d, *J* = 6.0 Hz, 6H), 0.98 (dt, *J* = 9.8, 7.0 Hz, 6H), 0.91 (d, *J* = 1.7 Hz, 11H), 0.15 (d, *J* = 4.7 Hz, 6H); ^{13}C NMR (126 MHz, $CDCl_3$) δ 175.04, 151.18, 150.20, 146.02, 135.49, 119.40, 115.93, 111.74, 103.72, 71.47, 60.05, 56.12, 52.15, 51.18, 44.55, 43.16, 38.43, 25.77, 22.25, 18.11, 14.91, -4.40; HRMS (EI): Exact mass calcd for $C_{28}H_{47}NNaO_5Si$ $[M+Na]^+$, 528.3116. Found 528.3113.

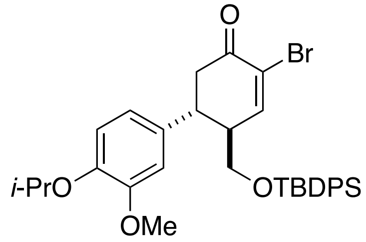


(±)-6-(Hydroxymethyl)-4'-isopropoxy-3'-methoxy-1,6-dihydro-[1,1'-biphenyl]-3(2*H*)-one (**8**): To a suspension of $LiAlH_4$ (2.9 g, 77.2 mmol, 2 equiv.) in 140 mL Et_2O at –78 °C was added **S3** (19.5 g, 38.6 mmol, 1 equiv.) in a solution of 50 mL Et_2O. The reaction was stirred at –78 °C for 4 h and warmed to 0 °C. The reaction was carefully quenched with Rochelle’s salt and stirred vigorously at 0 °C for 30 mins. This suspension was then extracted with Et_2O (3x 300 mL), washed with brine (1 L), and dried with Na_2SO_4. The product was condensed and then taken up in 75 mL MeCN. To this solution was added 18 mL of HF (10%, MeCN) and the reaction was stirred at room temperature overnight. The crude mixture was quenched with a 50% solution of saturated $NaHCO_3$ and brine (100 mL), extracted in EtOAc (3x 150 mL), washed with brine (500 mL), and dried with hexanes and Na_2SO_4. The crude product was purified by flash chromatography (silica gel, 20% EtOAc/hexanes) and then crystalized from Et_2O/pentanes to afford the title compound (8.6 g, 29.6 mmol, 77% yield) as a white solid: IR (film) 3416, 2937, 1651, 1514, 1242, 1137, 1036, 859 cm^{-1}; ^1H NMR (500 MHz, $CDCl_3$) δ 7.09 (dd, *J* = 10.1, 2.1 Hz, 1H), 6.85 (d, *J* = 7.9 Hz, 1H), 6.79 – 6.71 (m, 2H), 6.17 (dd, *J* = 10.3, 2.7 Hz, 1H), 4.50 (dh, *J* = 12.6, 6.3 Hz, 1H), 3.85 (s, 3H), 3.78 – 3.62 (m, 1H), 3.49 (dt, *J* = 10.6, 6.1 Hz, 1H), 3.16 (ddd, *J* = 13.0, 10.5, 4.8 Hz, 1H), 2.77 (dddt, *J* = 10.6, 6.3, 4.3, 2.5 Hz, 1H), 2.73 – 2.56 (m, 2H), 1.38 – 1.31 (m, 6H); ^{13}C NMR (126 MHz, $CDCl_3$) δ 199.1, 151.7, 150.6, 146.6, 134.7, 130.4, 119.4, 115.9, 111.2, 71.54, 63.4, 56.2, 45.5, 45.4, 43.1, 22.3; HRMS (EI): Exact mass calcd for $C_{17}H_{22}NaO_4$ $[M+Na]^+$, 313.141. Found 313.1408.



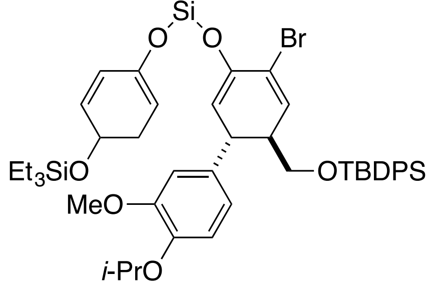
(±)-6-(((*tert*-Butyldiphenylsilyl)oxy)methyl)-4'-isopropoxy-3'-methoxy-1,6-dihydro-[1,1'-biphenyl]-3(2*H*)-one (**S4**): To a solution of **8** (6.65 g, 22.9 mmol, 1 equiv.) in 100 mL DMF at 0 °C was added solid imidazole (1.87 g, 27.5 mmol, 1.2 equiv.) in one portion. After stirring at 0 °C for 10 mins, TBDPS-Cl (6.47

mL, 25.2 mmol, 1.1 equiv.) was added over 5 mins. The reaction was left warming to room temperature for 2 hours, then diluted with 100 mL 50% EtOAc/Hexanes and quenched with 1M HCl (200 mL). The product was then extracted in 50% EtOAc/Hexanes (3x 200 mL), washed with brine (800 mL), and dried with hexanes and Na$_2$SO$_4$. The crude product was purified by elution through a silica plug (20% EtOAc/hexanes) to afford the title compound (10.4 g, 19.7 mmol, 86%, 95% on smaller scale) as an extremely viscous pale yellow oil: IR (film) 2931, 2857, 1677, 1512, 1264, 1138, 822, 700 cm^{-1}; ^{1}H NMR (500 MHz, CDCl$_3$) δ 7.54 (ddt, *J* = 20.1, 6.8, 1.4 Hz, 4H), 7.45 – 7.37 (m, 2H), 7.38 – 7.29 (m, 4H), 7.09 – 6.99 (m, 1H), 6.78 (d, *J* = 8.2 Hz, 1H), 6.68 (d, *J* = 2.1 Hz, 1H), 6.64 (dd, *J* = 8.2, 2.1 Hz, 1H), 6.16 (dd, *J* = 10.2, 2.7 Hz, 1H), 4.49 (p, *J* = 6.1 Hz, 1H), 3.76 (s, 3H), 3.65 (dd, *J* = 10.2, 3.5 Hz, 1H), 3.60 – 3.48 (m, 1H), 3.28 (td, *J* = 10.8, 6.6 Hz, 1H), 2.79 – 2.67 (m, 1H), 2.67 – 2.57 (m, 2H), 1.37 (d, *J* = 6.1 Hz, 6H), 1.03 (s, 9H); ^{13}C NMR (126 MHz, CDCl$_3$) δ 199.4, 153.0, 150.4, 146.3, 135.7, 135.6, 134.9, 133.3, 133.2, 130.0, 130.0, 129.9, 127.9, 127.8, 119.3, 115.9, 111.4, 71.5, 63.9, 56.0, 45.7, 45.5, 42.7, 27.0, 22.3, 19.5; HRMS (EI): Exact mass calcd for C$_{33}$H$_{41}$O$_4$Si [M+H]$^+$, 529.2769. Found 529.2781.

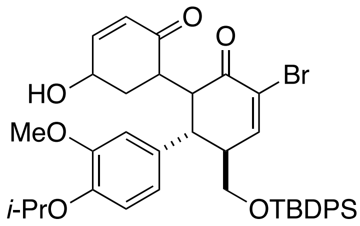


(±)-4-Bromo-6-(((*tert*-butyldiphenylsilyl)oxy)methyl)-4'-isopropoxy-3'-methoxy-1,6-dihydro-[1,1'-biphenyl]-3(2*H*)-one (**5**): To a solution of **S4** (10.4 g, 19.7 mmol, 1 equiv.) in 35 mL CCl$_4$ at 0 °C was added a solution of Br$_2$ (1.06 mL, 10 mmol, 1.05 equiv.) dropwise. The reaction turned reddish-brown upon complete addition of the solution and was stirred at 0 °C for 45 mins before NEt$_3$ (5.5 mL, 39.4 mmol, 2 equiv.) was added slowly. The reaction was warmed to room temperature and stirred overnight. The crude reaction mixture was quenched with 1M HCl (50 mL), extracted in DCM (3x 50 mL), washed with brine (200 mL), and dried with Na$_2$SO$_4$. The crude product was then purified by flash column chromatography (10% EtOAc/hexanes) to provide an extremely viscous pale yellow oil, which upon lyophillization, afforded the title compound (10.0 g, 16.5 mmol, 84 %, 98% on smaller scale) as a white powder: IR (film) 2930, 2855, 1691, 1589, 1513, 1463, 1264, 1105, 822, 700 cm^{-1} ^{1}H NMR (500 MHz, CDCl$_3$) δ 7.63 – 7.55 (m, 2H), 7.55 – 7.51 (m, 2H), 7.46 – 7.39 (m, 3H), 7.39 – 7.31 (m, 4H), 6.78 (d, *J* = 8.2 Hz, 1H), 6.66 (d, *J* = 2.1 Hz, 1H), 6.62 (dd, *J* = 8.1, 2.0 Hz, 1H), 4.55 – 4.42 (m, 1H), 3.77 (s, 3H), 3.62 (dd, *J* = 10.3, 3.6 Hz, 1H), 3.54 (dd, *J* = 10.3, 5.6 Hz, 1H), 3.34 (ddd, *J* = 14.3, 10.4, 4.3 Hz, 1H), 2.93 – 2.71 (m, 3H), 1.37 (d, *J* = 6.1 Hz, 6H), 1.05 (s, 9H); ^{13}C NMR (126 MHz, CDCl$_3$) δ 191.00, 153.21, 135.72, 135.57, 133.64, 132.96, 130.08, 129.97, 127.99, 127.90, 123.99, 119.18, 115.84, 111.29, 71.52, 63.55, 56.04, 48.55, 45.24, 42.51, 26.97, 22.26, 19.43; HRMS (ESI): Exact mass calcd for C$_{33}$H$_{39}$BrNaO$_4$Si [M+Na]$^+$, 629.1693. Found 629.1690.

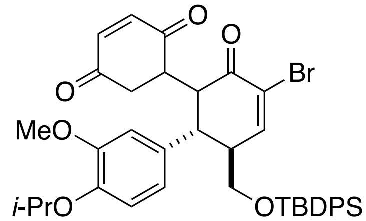
First route to propolisbenzofuran B:



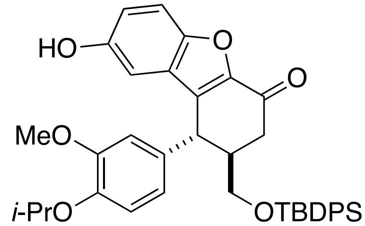
(((±)-4-Bromo-5-((diisopropyl((4-((triethylsilyl)oxy)cyclohexa-1,5-dien-1-yl)oxy)silyl)oxy)-4'-isopropoxy-3'-methoxy-1,2-dihydro-[1,1'-biphenyl]-2-yl)methoxy)(*tert*-butyl)diphenylsilane (**10**): To a solution of freshly prepared LDA (prepared from 0.84 mL, 6 mmol, 1.2 equiv. of *i*-Pr$_2$NH and 5.5 mmol, 1.1 equiv. of *n*-BuLi) in 7 mL THF at –78 °C was added a solution of **4** (1.13 g, 5 mmol, 1 equiv.) in 3 mL THF. After 10 mins, this solution was cannulated at –78 °C through an insulated cannula to a solution of *i*-Pr_2SiCl_2 (1.08 mL, 6 mmol, 1.1 equiv.), DMPU (1.81 mL, 15 mmol, 3.0 equiv.), and 20 mL THF at –78 °C over 3 hours. After complete addition, the reaction was monitored by TLC until the starting material was consumed. To a second solution of LDA (prepared from 0.84 mL, 6 mmol, 1.2 equiv., *i*-Pr_2NH and 5.5 mmol, 1.1 equiv. of *n*-BuLi) in 7 mL THF at –78 °C was added a solution of **5** (3.04 g, 5 mmol, 1 equiv.) in 8 mL THF. After 10 mins, this solution was cannulated at –78 °C through an insulated cannula to the *in situ* solution of chlorosilylenol ether at –78 °C over 2 hours. Upon complete addition the reaction was slowly warmed to 0 °C and then room temperature while monitored by TLC until complete consumption of starting material was observed. The reaction was then diluted with pentanes (60 mL) washed with 1M pH 7 buffer (100 mL), extracted with pentanes (3x 100 mL), washed with brine (400 mL), and dried with Na_2SO_4. The crude product could be purified by rapid flash column chromatography (3–5% EtOAc and 3% NEt_3 in hexanes) to afford the title compound (3.98 g, 4.2 mmol, 84%) as a viscous, colorless oil: IR (film) 2952, 2868, 1511, 1463, 1427, 1224, 1105, 1004, 907, 732 cm^{-1}; ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.73 – 7.57 (m, 4H), 7.53 – 7.31 (m, 6H), 6.88 – 6.74 (m, 2H), 6.71 (ddd, *J* = 8.1, 4.4, 2.0 Hz, 1H), 6.11 (dd, *J* = 4.8, 1.6 Hz, 1H), 5.90 – 5.65 (m, 2H), 5.19 (d, *J* = 4.8 Hz, 1H), 5.14 – 4.93 (m, 1H), 4.63 – 4.28 (m, 2H), 3.80 (q, *J* = 2.3 Hz, 3H), 3.69 – 3.48 (m, 2H), 2.65 (dd, *J* = 7.4, 5.2 Hz, 1H), 2.46 – 2.19 (m, 3H), 1.39 (d, *J* = 6.1 Hz, 6H), 1.19 – 0.82 (m, 32H), 0.61 (dq, *J* = 12.0, 8.0 Hz, 6H); ^{13}C NMR (126 MHz, $CDCl_3$) δ 150.2, 146.6, 145.9, 143.8, 135.6, 133.5, 132.5, 129.7, 127.7, 125.9, 119.7, 115.5, 111.4, 106.8, 101.9, 101.0, 71.4, 65.9, 63.6, 55.8, 48.0, 32.1, 26.9, 22.2, 19.3, 17.2, 15.3, 12.3, 6.8, 4.8; HRMS (EI): Exact mass calcd for $C_{51}H_{74}BrO_6Si_3$ $[M+H]^+$, 945.3971. Found 945.397.



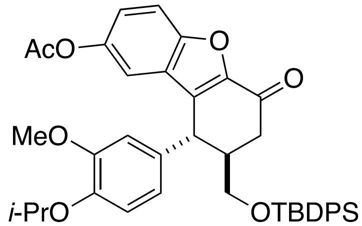
(±)-3-Bromo-5-(((*tert*-butyldiphenylsilyl)oxy)methyl)-5'-hydroxy-6-(4-isopropoxy-3-methoxyphenyl)-[1,1'-bi(cyclohexane)]-3,3'-diene-2,2'-dione (**11**): To a well-stirred suspension of CAN (2.41 g, 2 mmol, 2.2 equiv.), $NaHCO_3$ (0.739 g, 8.8 mmol, 4.4 equiv.), DMSO (0.284 mL, 4 mmol, 2 equiv.), and 66 mL MeCN at 0 °C was added a solution of **10** (1.90 g, 2 mmol, 1 equiv.) in 11 mL EtCN at 0 °C dropwise. The reaction suspension faded from an orange-red to light yellow upon addition and was stirred warming to room temperature for 1.5 hours. The reaction mixture was then quenched with 1M HCl (100 mL), extracted in $CHCl_3$ (3x 100 mL), washed with brine (100 mL) and dried with Na_2SO_4. This was condensed to minimal $CHCl_3$ and taken up in 6 mL MeCN. This solution was then treated with 2 mL HF (10% MeCN) and stirred at room temperature overnight. The reaction mixture was quenched with 50% saturated $NaHCO_3$ and brine (25 mL), extracted in EtOAc (3x 25 mL), washed with brine (100 mL), and dried with Na_2SO_4. The crude product was purified by flash column chromatography (silica gel, 20%–50% then 100% EtOAc/hexanes) to afford the title compound (0.710 g, 1.0 mmol, 50%) as an tan foamy solid: IR (film) 2930, 1674, 1508, 1382, 1261, 1110, 843, 700 cm^{-1}; ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.53 (dq, *J* = 7.9, 1.8 Hz, 4H), 7.45 (d, *J* = 2.2 Hz, 1H), 7.41 (td, *J* = 7.3, 1.8 Hz, 2H), 7.37 – 7.29 (m, 4H), 6.80 – 6.67 (m, 2H), 6.65 – 6.50 (m, 2H), 5.86 (dd, *J* = 42.0, 10.0 Hz, 1H), 4.55 – 4.41 (m, 1H), 4.42 – 4.29 (m, 1H), 3.92 – 3.76 (m, 1H), 3.72 (s, 3H), 3.57 – 3.40 (m, 2H), 2.92 – 2.75 (m, 1H), 2.69 (s, 1H), 2.12 – 1.91 (m, 1H), 1.83 (ddd, *J* = 12.8, 5.9, 3.7 Hz, 1H), 1.72 (d, *J* = 9.1 Hz, 0H), 1.66 – 1.49 (m, 0H), 1.48 – 1.38 (m, 1H), 1.35 (t, *J* = 6.5 Hz, 6H), 1.04 (d, *J* = 1.8 Hz, 9H); ^{13}C NMR (126 MHz, $CDCl_3$) δ 199.1, 191.6, 152.2, 151.7, 150.3, 146.4, 144.9, 135.6, 133.2, 132.9, 130.9, 129.9, 129.1, 127.8, 123.6, 115.7, 71.2, 67.7, 63.8, 62.9, 55.9, 49.5, 49.3, 43.7, 40.0, 26.8, 22.1, 19.3; HRMS (EI): Exact mass calcd for $C_{39}H_{45}BrNaO_6Si$ $[M+Na]^+$, 739.2066. Found 739.2068.



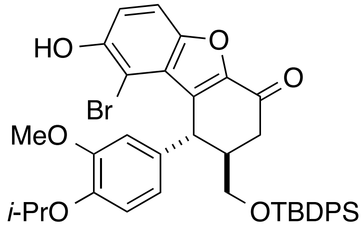
(±)-3'-Bromo-5'-(((*tert*-butyldiphenylsilyl)oxy)methyl)-6'-(4-isopropoxy-3-methoxyphenyl)-[1,1'-bi(cyclohexane)]-3,3'-diene-2,2',5-trione (**12**): To a suspension of **11** (0.706 g, 0.99 mmol, 1 equiv.) and 4Å molecular sieves (0.500 g) in 15 mL DCM was added solid NMO (0.233 g, 1.97 mmol, 2 equiv.) in one portion. After stirring for 30 mins the reaction was cooled to 0 °C and TPAP (0.070 g, 0.2 mmol, 0.20 equiv.) was added in one portion. After 5 mins the reaction was warmed to room temperature and stirred for 2 hours. The crude reaction mixture was filtered through a pad of silica gel and washed with EtOAc. The crude product was then purified through flash column chromatography (silica gel, 10% EtOAc/hexane) to afford the title compound (0.635 g, 0.89 mmol, 90%) as a tan foam: IR (film) 2981, 1679, 1509, 1262, 1110, 839, 701 cm^{-1}; ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.53 (tq, *J* = 6.4, 2.8, 2.2 Hz, 4H), 7.49 – 7.44 (m, 1H), 7.44 – 7.38 (m, 2H), 7.38 – 7.30 (m, 4H), 6.89 – 6.28 (m, 3H), 4.48 (dq, *J* = 12.1, 6.2 Hz, 1H), 3.86 (t, *J* = 12.2 Hz, 1H), 3.80 – 3.64 (m, 3H), 3.55 (dd, *J* = 10.2, 3.5 Hz, 1H), 3.48 (dd, *J* = 10.3, 6.3 Hz, 1H), 3.38 (dd, *J* = 16.3, 11.1 Hz, 1H), 2.96 – 2.77 (m, 2H), 2.77 – 2.63 (m, 1H), 2.59 (dd, *J* = 16.3, 6.3 Hz, 1H), 1.37 (d, *J* = 6.0 Hz, 6H), 1.05 (d, *J* = 8.1 Hz, 10H); ^{13}C NMR (126 MHz, $CDCl_3$) δ 197.9, 197.8, 191.3, 152.6, 150.5, 146.9, 141.5, 141.2, 140.7, 140.6, 135.7, 135.6, 133.2, 132.9, 131.6, 130.0, 123.0, 128.0, 127.9, 123.3, 123.1, 115.6, 71.4, 63.7, 56.0, 49.4, 46.9, 44.4, 34.8, 27.0, 25.4, 22.3, 19.4. HRMS (EI): Exact mass calcd for $C_{39}H_{43}BrNaO_6Si$ $[M+Na]^+$, 737.1904. Found 737.1901.



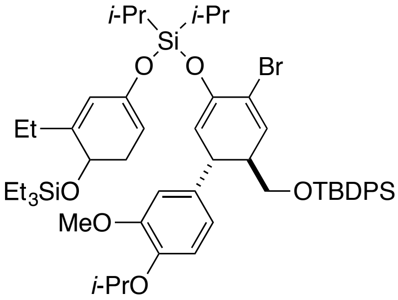
(±)-2-(((*tert*-Butyldiphenylsilyl)oxy)methyl)-8-hydroxy-1-(4-isopropoxy-3-methoxyphenyl)-2,3-dihydrodibenzo[*b*,*d*]furan-4(1*H*)-one (**14**): To a solution of **12** (0.251 g, 0.351 mmol, 1 equiv.) in 22 mL of DCM at 0 °C was added TMSOTf (0.063 mL, 0.351 mmol, 1.0 equiv.) dropwise. The reaction mixture turned deep blue upon complete addition and was monitored by TLC for 1 hour while slowly warming to room temperature and was stirred at room temperature for 2 hours. The reaction was then quenched with $NaHCO_3$ (2x 25 mL), the combined aqueous layers back extracted with DCM (3x 25 mL), the combined organic extracts washed with brine (100 mL), and dried with Na_2SO_4. The crude material was then purified by flash column chromatography (silica gel, 15%–33% EtOAc/hexanes) to afford the title compound (0.154 g, 0.243 mmol, 69%) as a white solid: IR (film) 3274, 2955, 2858, 1654, 1504, 1256, 1211, 1112, 736 cm^{-1}; ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.58 (ddt, *J* = 9.5, 6.8, 1.5 Hz, 4H), 7.45 – 7.38 (m, 3H), 7.33 (ddd, *J* = 8.3, 7.2, 6.1 Hz, 4H), 6.95 (dd, *J* = 9.0, 2.6 Hz, 1H), 6.85 – 6.79 (m, 1H), 6.72 (d, *J* = 6.8 Hz, 2H), 6.05 (d, *J* = 2.6 Hz, 1H), 4.71 (s, 1H), 4.55 (hept, *J* = 6.1 Hz, 1H), 4.46 (d, *J* = 9.6 Hz, 1H), 3.67 (s, 3H), 3.62 (dd, *J* = 10.5, 3.8 Hz, 1H), 3.50 (dd, *J* = 10.5, 3.0 Hz, 1H), 3.07 (dd, *J* = 16.8, 12.1 Hz, 1H), 2.79 (dd, *J* = 16.8, 3.9 Hz, 1H), 2.57 (ddq, *J* = 13.1, 10.5, 3.6 Hz, 1H), 1.39 (dd, *J* = 6.1, 2.6 Hz, 6H), 1.08 (s, 9H); ^{13}C NMR (126 MHz, $CDCl_3$) δ 188.4, 151.8, 151.5, 150.4, 148.1, 146.5, 136.1, 135.5, 133.2, 132.8, 132.5, 129.9, 129.8, 127.8, 127.7, 126.9, 121.1, 118.4, 115.6, 113.4, 112.2, 107.0, 71.4, 63.7, 55.8, 47.9, 41.8, 41.6, 26.9, 22.1, 19.4. HRMS (EI): Exact mass calcd for $C_{39}H_{42}NaO_6Si$ $[M+Na]^+$, 657.2648. Found 657.2642.



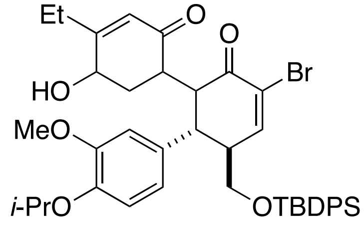
(±)-8-(((*tert*-Butyldiphenylsilyl)oxy)methyl)-9-(4-isopropoxy-3-methoxyphenyl)-6-oxo-6,7,8,9-tetrahydrodibenzo[*b*,*d*]furan-2-yl acetate (**15**): To a solution of **14** (0.140 g, 0.22 mmol, 1 equiv.), and DMAP (6 mg, 0.05 mmol, 0.20 equiv.) in 10 mL DCM at 0 °C was added pyridine (0.039 mL, 0.49 mmol, 2.2 equiv.). After 5 mins at 0 °C, Ac_2O (0.083 mL, 0.88 mmol, 4 equiv.) was added dropwise. The reaction was warmed to room temperature and stirred for 1 hour then quenched with 1M HCl (10 mL), extracted in DCM (3x 10 mL), washed with brine (40 mL), and dried with Na_2SO_4. The crude material was then purified by flash column chromatography (silica gel, 20% EtOAc/hexanes) to afford the title compound (0.128 g, 0.19 mmol, 86%) as an amorphous yellow solid: IR (film) 2930, 2857, 1759, 1681, 1510, 1371, 1208, 1105, 700 cm^{-1}; ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.78 – 7.49 (m, 4H), 7.46 – 7.37 (m, 2H), 7.38 – 7.28 (m, 4H), 7.20 – 7.01 (m, 1H), 6.96 – 6.76 (m, 1H), 6.80 – 6.61 (m, 2H), 6.33 (d, *J* = 2.4 Hz, 1H), 4.68 – 4.27 (m, 2H), 3.68 (s, 3H), 3.64 (dd, *J* = 10.6, 3.9 Hz, 1H), 3.57 – 3.42 (m, 1H), 3.09 (dd, *J* = 16.8, 12.3 Hz, 1H), 2.79 (dd, *J* = 16.8, 3.8 Hz, 1H), 2.57 (ddq, *J* = 13.2, 10.4, 3.6 Hz, 1H), 2.23 (s, 3H), 1.43 – 1.30 (m, 6H), 1.09 (s, 9H); ^{13}C NMR (125 MHz, $CDCl_3$): δ 188.6, 169.8, 154.0, 150.8, 148.5, 146.6, 136.5, 135.7, 135.6, 135.4, 133.3, 132.9, 132.5, 130.0, 129.9, 127.9, 127.8, 127.0, 123.3, 121.2, 116.4, 115.6, 113.5, 112.3, 71.7, 63.7, 56.0, 48.1, 41.9, 41.8, 27.1, 27.0, 22.2, 21.2, 19.6; HRMS (ESI): Exact mass calcd for $C_{41}H_{45}O_7Si$ [M+H]$^+$, 677.2929. Found 677.2930.



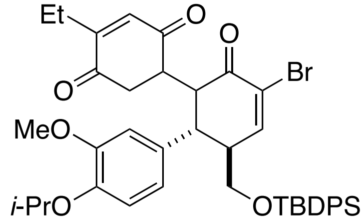
(±)-9-Bromo-2-(((tert-butyldiphenylsilyl)oxy)methyl)-8-hydroxy-1-(4-isopropoxy-3-methoxyphenyl)-2,3-dihydrodibenzo[*b*,*d*]furan-4(1H)-one (17): To a solution of **14** (15 mg, 0.024 mmol, 1 equiv.) in 1 mL of toluene at – 30 °C was added Br_2 (1.3 μL, 0.024 mmol, 1 equiv.). The reaction mixture was cooled to – 78 °C and *tert*-butylamine (5 μL, 0.048 mmol, 2 equiv.) was added in 0.5 mL of toluene. The reaction mixture was left to warm to room temperature and stirred for 18 hours. The reaction mixture was quenched with H_2O (1 mL), washed with 1 M HCl (1 mL), extracted in DCM (3x 1 mL), washed with brine and dried with $MgSO_4$. The crude mixture was purified by flash column chromatography (silica gel, 20% EtOAc/hexanes) to afford the title compound (7.5 mg, 0.007 mmol, 42%); IR (film) 3415, 2931, 2857, 1683, 1510, 1470, 1427, 1387, 1260, 1112, 703 cm^{-1}; ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.58 (ddd, *J* = 7.8, 3.6, 1.5 Hz, 2H), 7.55 – 7.45 (m, 3H), 7.36 – 7.28 (m, 4H), 7.13 – 7.06 (m, 1H), 6.79 – 6.69 (m, 2H), 6.50 (dd, *J* = 8.2, 2.1 Hz, 1H), 5.46 (s, 1H), 5.19 (d, *J* = 1.6 Hz, 1H), 4.52 – 4.40 (m, 2H), 3.79 (s, 3H), 3.76 (d, *J* = 5.5 Hz, 1H), 3.73 – 3.63 (m, 1H), 2.86 (dd, *J* = 17.4, 5.4 Hz, 1H), 2.68 (dd, *J* = 9.7, 5.1 Hz, 1H), 2.37 (dd, *J* = 17.4, 2.4 Hz, 1H), 1.35 (d, *J* = 6.0 Hz, 6H), 1.07 (d, *J* = 8.0 Hz, 9H); ^{13}C NMR (126 MHz, $CDCl_3$) δ 187.2, 151.2, 150.6, 149.5, 148.5, 146.4, 135.5, 135.4, 133.8, 132.9, 132.8, 131.9, 129.9, 129.8, 129.7, 127.8, 127.7, 127.6, 127.5, 125.9, 119.9, 118.1, 115.2, 113.1, 112.0, 101.4, 65.9, 65.4, 56.1, 55.9, 47.1, 38.8, 36.8, 26.9, 26.8, 26.7, 22.1, 19.4, 19.2, 15.3. HRMS (ESI): Exact mass calcd for $C_{39}H_{42}BrO_6Si$ [M+H]$^+$, 713.1929. Found 713.1934.



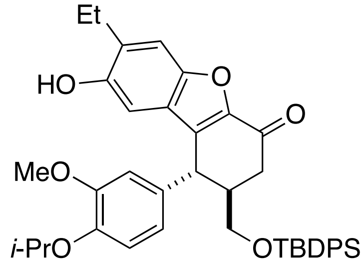
(((±)-4-Bromo-5-((((5-ethyl-4-((triethylsilyl)oxy)cyclohexa-1,5-dien-1-yl)oxy)diisopropylsilyl)oxy)-4'-isopropoxy-3'-methoxy-1,2-dihydro-[1,1'-biphenyl]-2-yl)methoxy)(*tert*-butyl)diphenylsilane (**20**): To a solution of freshly prepared LDA (prepared from 0.672 mL, 4.8 mmol, 1.2 equiv. of *i*-Pr$_2$NH and 4.4 mmol, 1.1 equiv. of *n*-BuLi) in 50 mL THF at –78 °C was added a solution of **19** (1.02 g, 4 mmol, 1 equiv.) in 25 mL THF. After this, the solution was cannulated at –78 °C through an insulated cannula to a solution of *i*-Pr$_2$SiCl$_2$ (0.866 mL, 4.8 mmol, 1.2 equiv.), DMPU (1.45 mL, 12 mmol, 3.0 equiv.), and 175 mL THF at –78 °C over 3 hours. After complete addition, the reaction was monitored by TLC until starting material was consumed. To a second solution of LDA (prepared from 0.672 mL, 4.8 mmol, 1.2 equiv. of *i*-Pr$_2$NH and 4.4 mmol, 1.1 equiv. of *n*-BuLi) in 50 mL THF at –78 °C was added a solution of **5** (2.44 g, 4 mmol, 1 equiv.) in 25 mL THF. After 10 mins this solution was cannulated at –78 °C through an insulated cannula to the *in situ* solution of chlorosilane at –78 °C over 2 hours. Upon complete addition the reaction was slowly warmed to 0 °C and then room temperature while monitored by TLC until complete consumption of starting material was observed. The reaction was then washed with 1M pH 7 buffer (300 mL), extracted with pentanes (3x 300 mL), washed with brine (1 L), and dried with Na$_2$SO$_4$. The crude product could be purified by rapid flash column chromatography (3–5% EtOAc and 3% NEt$_3$ in hexanes) to afford the title compound (3.82 g, 3.9 mmol, 98 %) as a viscous, colorless oil: IR (film) 2950, 2867, 1511, 1463, 1262, 1107, 998, 731, 700 cm^{-1}; ^{1}H NMR (500 MHz, CDCl$_3$) δ 7.61 (ddt, *J* = 10.8, 7.8, 1.5 Hz, 3H), 7.44 – 7.38 (m, 2H), 7.37 (s, 0H), 6.85 – 6.60 (m, 3H), 6.08 (dd, *J* = 5.0, 2.1 Hz, 1H), 5.85 – 5.70 (m, 1H), 5.29 (q, *J* = 7.0 Hz, 1H), 5.21 – 5.10 (m, 1H), 4.46 (dtd, *J* = 12.1, 6.1, 2.9 Hz, 1H), 4.22 – 4.05 (m, 1H), 3.84 – 3.65 (m, 4H), 3.65 – 3.51 (m, 2H), 2.60 (ddq, *J* = 14.2, 6.6, 5.1, 4.3 Hz, 1H), 2.48 – 2.36 (m, 0H), 2.32 (dqt, *J* = 18.1, 9.0, 4.4 Hz, 1H), 2.26 – 2.11 (m, 1H), 2.07 – 1.89 (m, 1H), 1.83 – 1.66 (m, 1H), 1.58 (t, *J* = 7.4 Hz, 2H), 1.42 – 1.30 (m, 7H), 1.10 – 1.01 (m, 15H), 0.98 – 0.87 (m, 9H), 0.64 – 0.53 (m, 5H); ^{13}C NMR (126 MHz, CDCl$_3$) δ 150.2, 147.3, 146.6, 146.5, 145.9, 143.8, 136.8, 135.5, 133.5, 133.4, 130.1, 129.7, 127.7, 119.7, 119.6, 119.5, 119.5, 115.5, 111.4, 106.8, 99.1, 99.1, 71.4, 68.6, 68.5, 65.9, 63.6, 55.7, 48.0, 40.4, 32.6, 26.9, 25.5, 25.5, 22.2, 22.2, 19.3, 17.3, 17.3, 17.2, 17.2, 17.1, 15.3, 13.0, 12.3, 12.2, 12.0, 6.9, 6.8, 6.4, 5.0, 4.9; HRMS (ESI): Exact mass calcd for $C_{53}H_{78}BrO_6Si_3$ [M+H]$^+$, 973.4284. Found 973.4296.



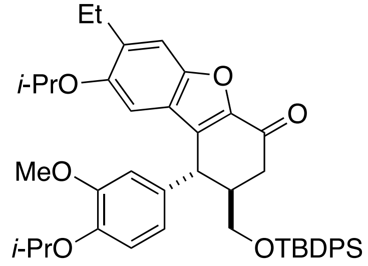
(±)-3-Bromo-5-(((*tert*-butyldiphenylsilyl)oxy)methyl)-4'-ethyl-5'-hydroxy-6-(4-isopropoxy-3-methoxyphenyl)-[1,1'-bi(cyclohexane)]-3,3'-diene-2,2'-dione (**21**): To a suspension of CAN (4.31 g, 7.86 mmol, 2.2 equiv.), NaHCO$_3$ (1.32 g, 15.72 mmol, 4.4 equiv.), DMSO (0.507 mL, 7.14 mmol, 2 equiv.) in 117 mL MeCN at 0 °C was added a solution of **20** (4.48 g, 3.57 mmol, 1 equiv.) in 19.5 mL EtCN at 0 °C dropwise. The reaction suspension faded from an orange-red to light yellow upon addition and was stirred warming to room temperature for 1.5 hours. The reaction mixture was then quenched with 1M HCl (150 mL), extracted in CHCl$_3$ (3x 150 mL), washed with brine and dried with Na$_2$SO$_4$. This was condensed to minimal CHCl$_3$ and taken up in 18 mL MeCN. This solution was then treated with 6 mL HF (10% MeCN) and stirred at room temperature overnight. The reaction mixture was quenched with 50% saturated NaHCO$_3$ and brine (100 mL), extracted in EtOAc (3x 100 mL), washed with brine (300 mL), and dried with Na_2SO_4. The crude product was purified by flash column chromatography (silica gel, 20%–50% then 100% EtOAc/hexanes) to afford the title compound (1.28 g, 1.72 mmol, 48%) as an tan foamy solid: IR (film) 2930, 2856, 1663, 1505, 1371, 1262, 1106, 822, 700 cm^{-1}; ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.53 (ddd, J = 8.0, 2.6, 1.5 Hz, 4H), 7.46 (d, J = 2.1 Hz, 1H), 7.44 – 7.37 (m, 2H), 7.33 (q, J = 7.1 Hz, 4H), 6.71 (t, J = 9.0 Hz, 1H), 6.65 – 6.50 (m, 2H), 5.72 (s, 1H), 4.47 (dt, J = 12.2, 6.1 Hz, 1H), 4.26 (s, 0H), 4.14 (dt, J = 6.0, 2.7 Hz, 1H), 3.72 (s, 3H), 3.52 (dt, J = 10.3, 3.7 Hz, 1H), 2.80 (ddt, J = 12.9, 6.6, 2.7 Hz, 1H), 2.65 (s, 1H), 2.46 – 2.15 (m, 2H), 1.99 (dt, J = 10.7, 4.8 Hz, 0H), 1.81 (dd, J = 15.0, 11.6 Hz, 1H), 1.35 (dd, J = 7.6, 6.0 Hz, 7H), 1.09 – 0.99 (m, 13H); ^{13}C NMR (126 MHz, $CDCl_3$) δ 199.3, 191.8, 191.5, 168.0, 162.2, 151.7, 150.4, 146.5, 135.7, 135.6, 133.3, 133.3, 133.1, 133.0, 130.0, 129.9, 127.9, 127.9, 127.8, 125.8, 124.8, 123.8, 115.8, 71.3, 69.6, 66.8, 63.9, 63.9, 56.0, 49.6, 49.4, 44.3, 39.2, 28.0, 27.0, 27.0, 25.5, 22.3 22.2, 22.1, 19.4, 11.5, 11.1; HRMS (EI): Exact mass calcd for $C_{41}H_{49}BrNaO_6Si$ [M+Na]$^+$, 769.2359. Found 769.2372.



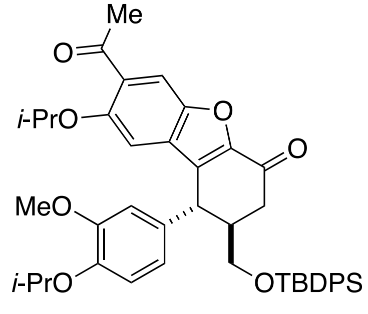
(±)-3'-Bromo-5'-(((*tert*-butyldiphenylsilyl)oxy)methyl)-4-ethyl-6'-(4-isopropoxy-3-methoxyphenyl)-[1,1'-bi(cyclohexane)]-3,3'-diene-2,2',5-trione (**S5**): To a solution of **21** (0.596 g, 0.80 mmol, 1 equiv.) in 40 mL DCM at room temperature was added a crushed mixture of PCC (0.690 g, 3.2 mmol, 4 equiv.) and silica gel (0.690 g) in one portion. The suspension was stirred vigorously at room temperature for 4 hrs. The reaction was filtered through a pad of silica gel and washed with 200 mL EtOAc. The crude product was purified by flash column chromatography (silica gel, 20% EtOAc/hexanes) to afford the title compound (0.566 g, 0.76 mmol, 95%) as a tan foam: IR (film) 2981, 2930, 2857, 1673, 1507, 1426, 1260, 1105, 822, 700 cm^{-1}; ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.62 – 7.26 (m, 16H), 6.80 – 6.68 (m, 1H), 6.63 – 6.52 (m, 2H), 6.53 – 6.37 (m, 2H), 4.48 (dq, J = 12.2, 6.0 Hz, 1H), 3.94 – 3.80 (m, 1H), 3.81 – 3.69 (m, 3H), 3.69 – 3.57 (m, 2H), 3.59 – 3.42 (m, 3H), 3.44 – 3.32 (m, 1H), 2.81 (ddt, J = 12.6, 6.2, 3.2 Hz, 1H), 2.71 – 2.64 (m, 1H), 2.63 – 2.49 (m, 1H), 2.47 – 2.28 (m, 3H), 1.42 – 1.18 (m, 10H), 1.15 – 0.97 (m, 18H), 0.88 (t, J = 7.0 Hz, 1H), 0.46 (s, 1H); ^{13}C NMR (126 MHz, $CDCl_3$) δ 198.3, 198.1, 191.5, 155.5, 152.5, 152.4, 150.0, 147.1, 146.8, 145.9, 136.9, 135.7, 135.7, 135.6, 135.6, 133.3, 133.2, 133.0, 133.0, 132.8, 130.0, 130.0, 129.9, 129.8, 128.0, 128.0, 127.9, 127.9, 127.8, 127.8, 127.8, 124.0, 123.4, 116.9, 115.7, 71.4, 71.3, 63.9, 63.8, 56.0, 55.9, 49.4, 48.0, 47.0, 44.7, 27.1, 27.0, 22.6, 22.4, 22.3, 22.2, 22.1, 19.4, 19.4, 13.8, 11.4; HRMS (EI): Exact mass calcd for $C_{41}H_{47}BrNaO_6Si$ [M+Na]$^+$, 767.2203. Found 767.2207.



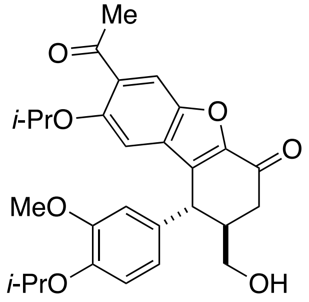
(±)-2-(((*tert*-Butyldiphenylsilyl)oxy)methyl)-7-ethyl-8-hydroxy-1-(4-isopropoxy-3-methoxyphenyl)-2,3-dihydrodibenzo[*b*,*d*]furan-4(1*H*)-one (**22**): To a stirred solution of **S5** (23 mg, 0.03 mmol, 1 equiv.) in 2.5 mL of DCM at 0 °C was added TMSOTf (8 μL, 0.046 mmol, 1.5 equiv.) dropwise. The reaction mixture turned deep blue upon complete addition and was monitored by TLC for 1 hour while slowly warming to room temperature over 2 hours. The reaction was then quenched with $NaHCO_3$ (2x 3 mL), the combined aqueous layers back extracted with DCM (3x 5 mL), the combined organic extracts washed with brine (20 mL), and dried with Na_2SO_4. The crude material was then purified by flash column chromatography (silica gel, 15%–33% EtOAc/hexanes) to afford the title compound (13 mg, 0.019 mmol, 65%) as a white solid: IR (film) 3449, 2974, 29, 30, 2857, 1656, 1566, 1450, 1251, 1110, 701 cm^{-1}; ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.65 – 7.55 (m, 5H), 7.45 – 7.25 (m, 9H), 6.83 (d, *J* = 8.0 Hz, 1H), 6.79 – 6.68 (m, 2H), 5.95 (s, 1H), 4.60 – 4.46 (m, 2H), 4.44 (d, *J* = 9.7 Hz, 1H), 3.68 (s, 4H), 3.67 – 3.55 (m, 3H), 3.58 – 3.42 (m, 2H), 3.06 (dd, *J* = 16.8, 12.1 Hz, 1H), 2.77 (dd, *J* = 16.8, 3.8 Hz, 5H), 2.69 (q, *J* = 7.4 Hz, 2H), 2.65 – 2.48 (m, 1H), 1.45 – 1.31 (m, 9H), 1.28 – 1.18 (m, 7H), 1.08 (s, 11H); ^{13}C NMR (126 MHz, $CDCl_3$) δ 188.2, 152.0, 150.4, 150.4, 150.3, 147.5, 146.5, 136.5, 135.7, 135.6, 135.6, 134.7, 133.3, 132.9, 132.8, 130.0, 129.9, 127.9, 127.8, 124.5, 121.1, 115.6, 115.5, 112.4, 112.4, 106.4, 71.4, 63.8, 55.9, 48.0, 42.1, 41.7, 27.0, 24.2, 22.3, 22.2, 19.5, 13.9; HRMS (EI): Exact mass calcd for $C_{41}H_{46}NaO_6Si$ [M+Na]$^+$, 685.2961. Found 685.2968.



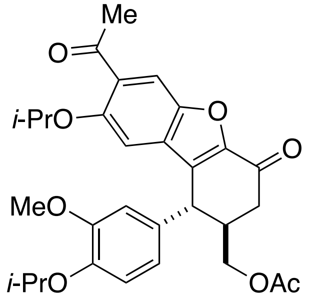
(±)-2-(((*tert*-Butyldiphenylsilyl)oxy)methyl)-7-ethyl-8-isopropoxy-1-(4-isopropoxy-3-methoxyphenyl)-2,3-dihydrodibenzo[*b*,*d*]furan-4(1*H*)-one (S6): To a solution of **22** (0.40 g, 0.060 mmol, 1 equiv.) and *i*-PrI (0.060 mL, 0.60 mmol, 10 equiv.) in 1 mL acetone was added solid K_2CO_3 (0.025 g, 0.180 mmol, 3 equiv.). The reaction was then heated to reflux and stirred vigorously for 4 days with an additional portion of K_2CO_3 (0.025 g, 0.180 mmol, 3 equiv.) added after 2 days. The reaction was cooled and diluted with 3 mL DCM, washed with saturated NH_4Cl (3 mL), extracted in Et_2O (3x 3 mL) and dried with Na_2SO_4. The crude product was purified by flash column chromatography (silica gel, 10% EtOAc/hexanes) to afford the title compound (0.025 g, 0.035 mmol, 59% yield), and recovered starting material (0.015 g, 0.23 mmol, 38% yield), both as white solids: IR (film) 2974, 2930, 2857, 1677, 1510, 1449, 1383, 1217, 1111, 950, 702 cm^{-1}; 1H NMR (500 MHz, $CDCl_3$) δ 7.59 (ddd, *J* = 8.1, 4.6, 1.4 Hz, 4H), 7.47 – 7.28 (m, 8H), 6.93 – 6.80 (m, 1H), 6.76 (d, *J* = 6.7 Hz, 2H), 5.90 (s, 1H), 4.65 – 4.37 (m, 2H), 4.01 (dt, *J* = 12.1, 6.1 Hz, 1H), 3.73 – 3.58 (m, 4H), 3.53 (td, *J* = 10.2, 2.8 Hz, 1H), 3.09 (dd, *J* = 16.7, 12.4 Hz, 1H), 2.78 (dd, *J* = 16.7, 3.9 Hz, 1H), 2.63 (dddd, *J* = 20.5, 10.1, 8.0, 5.5 Hz, 3H), 1.39 (dd, *J* = 6.1, 2.2 Hz, 6H), 1.28 – 1.13 (m, 6H), 1.14 – 0.95 (m, 13H); ^{13}C NMR (126 MHz, $CDCl_3$) δ 188.0, 152.3, 151.5, 150.5, 147.0, 146.7, 137.7, 136.9, 135.5, 135.5, 133.2, 132.9, 132.8, 129.9, 129.8, 127.8, 127.7, 127.7, 124.1, 121.2, 115.5, 112.4, 112.2, 104.1, 71.4, 69.9, 63.7, 56.0, 47.8, 42.1, 41.7, 26.9, 24.4, 22.1, 22.1, 22.1, 22.0, 21.4, 19.4, 14.0; HRMS (EI): Exact mass calcd for $C_{44}H_{53}O_6Si$ [M+H]$^+$, 705.3606. Found 705.3607.



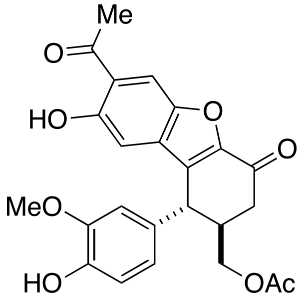
(±)-7-Acetyl-2-(((*tert*-butyldiphenylsilyl)oxy)methyl)-8-isopropoxy-1-(4-isopropoxy-3-methoxyphenyl)-2,3-dihydrodibenzo[*b*,*d*]furan-4(1*H*)-one (23): To a suspension of CrO_3 (0.054 g, 0.538 mmol, 20 equiv.) in 2 mL DCM at –25 °C was added 3,5-dimethylpyrazole (0.052 g, 0.538 mmol, 20 equiv.) in one portion. After stirring at –25 °C for 20 mins a solution of **S6** in 1 mL DCM at – 25 °C was added. The reaction was warmed to – 10 °C and stirred overnight before warming to room temperature. The reaction was directly purified by flash column chromatography (silica gel, 10% – 20% EtOAc/hexanes) to afford the title compound (6.2 mg, 0.0086 mmol, 32%) and recovered starting material (12.5 mg, 0.018 mmol, 67%) both as a white solid: IR (film) 2978, 2930, 2856, 1686, 1511, 1444, 1211, 1112 cm^{-1}; ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.81 (s, 1H), 7.59 (ddd, *J* = 8.1, 3.2, 1.5 Hz, 4H), 7.47 – 7.37 (m, 2H), 7.37 – 7.29 (m, 4H), 6.86 (d, *J* = 8.0 Hz, 1H), 6.81 – 6.70 (m, 2H), 6.00 (s, 1H), 4.65 – 4.41 (m, 2H), 4.10 (p, *J* = 6.0 Hz, 1H), 3.75 – 3.58 (m, 4H), 3.52 (dd, *J* = 10.6, 2.8 Hz, 1H), 3.12 (dd, *J* = 16.8, 12.6 Hz, 1H), 2.80 (dd, *J* = 16.8, 3.8 Hz, 1H), 2.68 – 2.61 (m, 1H), 2.58 (s, 3H), 1.40 (dd, *J* = 6.0, 2.0 Hz, 7H), 1.26 (d, *J* = 6.0 Hz, 4H), 1.13 – 1.01 (m, 13H); ^{13}C NMR (126 MHz, $CDCl_3$) δ 200.1, 188.5, 153.1, 150.8, 150.5, 149.5, 147.0, 135.8, 135.7, 135.6, 133.3, 132.9, 132.4, 131.5, 130.1, 129.9, 127.9, 127.9, 121.3, 115.5, 114.1, 112.4, 105.7, 71.5, 71.0, 63.7, 56.1, 47.8, 42.1, 42.0, 32.0, 27.1, 22.2, 22.2, 22.1, 21.3, 19.6; HRMS (EI): Exact mass calcd for $C_{44}H_{51}O_7Si$ [M+H]$^+$, 719.3399. Found 719.3395.



(±)-7-Acetyl-2-(hydroxymethyl)-8-isopropoxy-1-(4-isopropoxy-3-methoxyphenyl)-2,3-dihydrodibenzo[*b*,*d*]furan-4(1*H*)-one (S7): A solution of **23** (10 mg, 0.0013 mmol, 1 equiv.) was stirred in 1 mL of a 20% HF solution in MeCN overnight. The reaction was then diluted with 2 mL DCM, quenched with $NaHCO_3$ (3 mL), extracted in DCM (3 x 5 mL), washed with brine (15 mL) and dried with $MgSO_4$. The crude product was purified by flash column chromatography (silica gel, 50% EtOAc/hexanes) to afford the title compound (5.5 mg, 0.0113, 99% yield) as a white solid: IR (film) 3475, 2977, 2929, 1678, 1510, 1444, 1384, 1213, 1110, 1035 cm^{-1}; ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.80 (s, 1H), 6.90 (d, *J* = 8.2 Hz, 1H), 6.83 (dd, *J* = 8.2, 2.0 Hz, 1H), 6.77 (d, *J* = 2.0 Hz, 1H), 5.99 (s, 1H), 4.54 (p, *J* = 6.1 Hz, 1H), 4.33 (d, *J* = 10.2 Hz, 1H), 4.10 (p, *J* = 6.0 Hz, 1H), 3.77 (s, 3H), 3.65 (d, *J* = 3.9 Hz, 2H), 2.99 – 2.80 (m, 2H), 2.72 – 2.60 (m, 1H), 2.57 (s, 3H), 1.39 (dd, *J* = 6.1, 1.6 Hz, 7H), 1.25 (d, *J* = 6.0 Hz, 4H), 1.08 (d, *J* = 6.0 Hz, 3H); ^{13}C NMR (126 MHz, $CDCl_3$) δ 200.1, 188.0, 153.1, 150.8, 150.4, 149.5, 147.1, 135.6, 132.3, 131.5, 129.8, 121.3, 115.3, 114.1, 112.2, 105.6, 71.5, 71.0, 63.1, 56.3, 47.4, 42.2, 41.6, 32.0, 22.2, 22.2, 22.1, 21.3; HRMS (EI): Exact mass calcd for $C_{28}H_{33}O_7$ [M+H]$^+$, 481.2221. Found 481.2217.

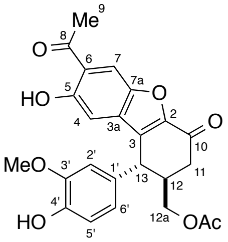


((±)-7-Acetyl-8-isopropoxy-1-(4-isopropoxy-3-methoxyphenyl)-4-oxo-1,2,3,4-tetrahydrodibenzo[*b*,*d*]furan-2-yl)methyl acetate (S8): To a solution of **S7** (10 mg, 0.021 mmol, 1 equiv.), and DMAP (0.5 mg, 0.004 mmol, 0.20 equiv.) in 2 mL DCM at 0 °C was added pyridine (6 μL, 0.046 mmol, 2.2 equiv.). After 5 mins at 0 °C, Ac_2O (8 μL, 0.084 mmol, 4 equiv.) was added dropwise. The reaction was warmed to room temperature and stirred for 1 hour. The reaction was then diluted with 2 mL DCM, quenched with NH_4Cl (2 mL), extracted in DCM (3x 2 mL), washed with brine (8 mL), and dried with Na_2SO_4. The crude material was then purified by flash column chromatography (silica gel, 20% EtOAc/hexanes) to afford the title compound (9.7 mg, 0.019 mmol, 88%) as an amorphous yellow solid: IR (film) 2978, 2933, 1740, 1682, 1511, 1444, 1384, 1233, 1111, 1037 cm^{-1}; ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.80 (s, 1H), 6.90 (d, *J* = 8.2 Hz, 1H), 6.83 (dd, *J* = 8.2, 2.0 Hz, 1H), 6.77 (d, *J* = 2.0 Hz, 1H), 5.99 (s, 1H), 4.54 (hept, *J* = 6.1 Hz, 1H), 4.33 (d, *J* = 10.2 Hz, 1H), 4.10 (p, *J* = 6.0 Hz, 1H), 3.77 (s, 3H), 3.65 (d, *J* = 3.9 Hz, 2H), 3.03 – 2.75 (m, 2H), 2.66 (tdd, *J* = 10.1, 8.4, 4.4 Hz, 1H), 2.57 (s, 3H), 1.43 – 1.34 (m, 7H), 1.25 (d, *J* = 6.0 Hz, 4H), 1.08 (d, *J* = 6.0 Hz, 3H); ^{13}C NMR (126 MHz, $CDCl_3$) δ 200.1, 188.0, 153.1, 150.8, 150.4, 149.5, 147.1, 135.6, 132.3, 131.5, 129.8, 121.3, 115.3, 114.1, 112.2, 105.6, 71.5, 71.0, 63.9, 56.3, 47.4, 42.2, 41.6, 32.0, 22.2, 22.2, 22.1, 21.3; HRMS (ESI): Exact mass calcd for $C_{30}H_{35}O_8$ $[M+H]^+$, 523.2326. Found 523.2319.



Propolisbenzofuran B (**1**): To a solution of **S8** (21.7 mg, 0.042 mmol, 1 equiv.) in 1 mL DCM at 0 °C was added solid $AlCl_3$ (16.8 mg, 0.126 mmol, 3 equiv.) in one portion. After 10 mins the reaction was warmed to room temperature and monitored by TLC. After 12 hours the reaction was quenched with saturated NH_4Cl (1 mL), extracted in DCM (3x 5mL), washed with brine (10 mL), and dried with $MgSO_4$. The crude product was purified by flash column chromatography (silica gel, 50% EtOAc/hexanes) to afford the title compound (15.8 mg, 0.036 mmol, 86%) as a yellow solid which matched the published spectral data (see Table S1): IR (film) 3428, 2927, 1738, 1663, 1645, 1516, 1431, 1368, 1241, 1035 cm^{-1}; ^1H NMR (500 MHz, acetone-d_6) δ 11.82 (s, 1H), 8.24 (s, 1H), 7.73 (d, J = 11.9 Hz, 1H), 7.07 – 6.98 (m, 1H), 6.88 (d, J = 1.7 Hz, 2H), 6.14 (s, 1H), 4.35 (d, J = 9.9 Hz, 1H), 4.17 – 3.95 (m, 2H), 3.75 (s, 3H), 2.96 (dddd, J = 15.2, 8.2, 5.4, 4.1 Hz, 1H), 2.83 – 2.79 (m, 4H), 2.76 (s, 3H); ^1H NMR (500 MHz, $CDCl_3$) δ 11.84 (s, 1H), 7.93 (s, 1H), 7.36 (s, 1H), 6.92 (d, J = 8.0 Hz, 1H), 6.73 (dd, J = 8.1, 2.0 Hz, 1H), 6.63 (d, J = 2.0 Hz, 1H), 6.26 (s, 1H), 4.18 (d, J = 9.7 Hz, 1H), 4.04 (dd, J = 4.3, 2.5 Hz, 2H), 3.80 (s, 3H), 2.97 – 2.87 (m, 1H), 2.84 – 2.73 (m, 1H), 2.70 (s, 4H), 2.08 (s, 3H); ^{13}C NMR (126 MHz, acetone-d_6) δ 205.9, 187.6, 171.0, 158.3, 151.9, 149.6, 149.0, 147.3, 135.1, 134.2, 131.7, 122.6, 120.6, 116.2, 115.7, 115.7, 112.9, 110.1, 65.3, 56.4, 45.0, 43.2, 42.4, 27.4, 20.7; ^{13}C NMR (126 MHz, $CDCl_3$) δ 204.2, 187.5, 170.8, 157.7, 150.8, 149.0, 147.2, 145.7, 134.4, 133.1, 130.3, 121.7, 120.0, 115.2, 114.2, 110.4, 110.2, 77.2, 64.7, 56.1, 44.6, 42.8, 41.6, 27.2, 20.9; HRMS (EI): Exact mass calcd for $C_{24}H_{23}O_8$ $[M+H]^+$, 439.1387. Found 439.1380.

3. Tabulated Natural Product Data

Table S1. 			**propolisbenzofuran B (1)**	
C	^{1}H NMR Natural Sample[4] 400 MHz d_6- acetone δ	^{13}C NMR Natural Sample[4] 100 MHz d_6-acetone δ	^{1}H NMR Synthetic Sample 500 MHz d_6- acetone δ	^{13}C NMR Synthetic Sample (126 MHz, d_6- acetone) δ
2	–	151.7	–	151.8
3	–	135.0	–	135.1
3a	–	134.0	–	134.1
4	6.13 s	110.0	6.14 s	110.0
5	–	158.2	–	158.2
OH-5	11.81 s	–	11.82 (s, 1H)	–
6	–	120.5	–	120.6
7	8.21 s	115.5	8.24 (s, 1H)	115.6
7a	–	149.5	–	149.6
8	–	205.8	–	205
9	2.75 s	27.3	2.76 (s, 3H)	27.4
10	–	187.5	–	187.6
11	2.86 m (2H)	42.3	2.81 m (2H)	42.4
12	2.94 m	44.9	2.96 m	44.9
12a	4.05 m (2H)	65.2	4.05 (t, *J* = 4.5 Hz, 2H)	65.2
13	4.33 d (*J* = 9.9 Hz)	43.1	4.35 d (*J* = 9.9 Hz)	43.1
1’	–	131.6	–	131.7
2’	7.02 d (*J* = 2.0 Hz)	112.9	7.03 b s	112.9
3’	–	148.9	–	148.9
4’	–	147.2	–	147.2
OH-4’	8.01 b s	–	7.75 s	–
5’	6.89 (d *J* = 8.0 Hz)	116.1	6.88 (d, *J* = 1.7 Hz, 2H)	116.1
6’	6.87 (dd *J* = 8.0, 2.0 Hz)	122.5		122.5
OMe	3.73 s	56.3	3.75 s	56.3
OAc	2.03 s	20.6; 170.8	2.04 s	20.7

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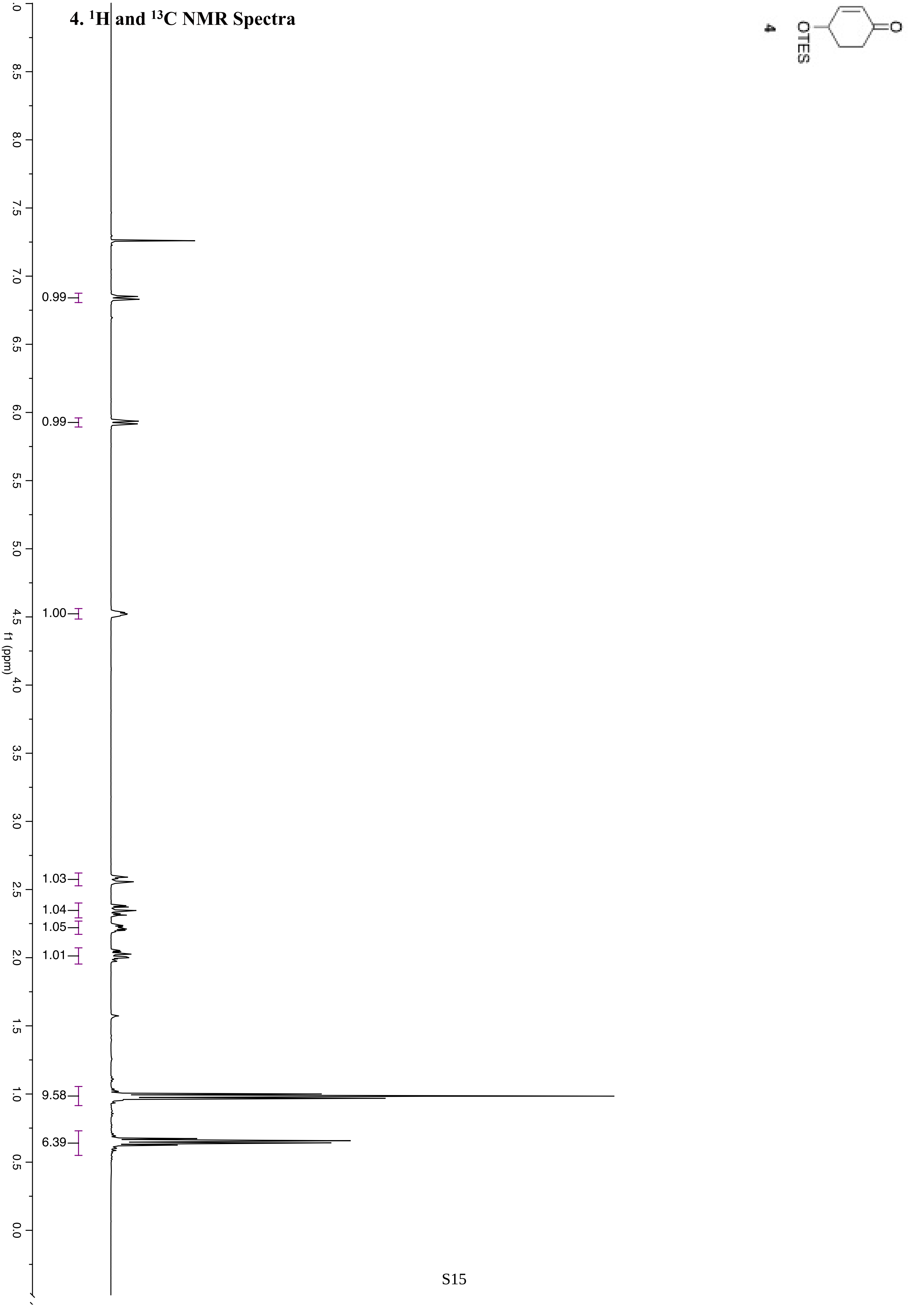
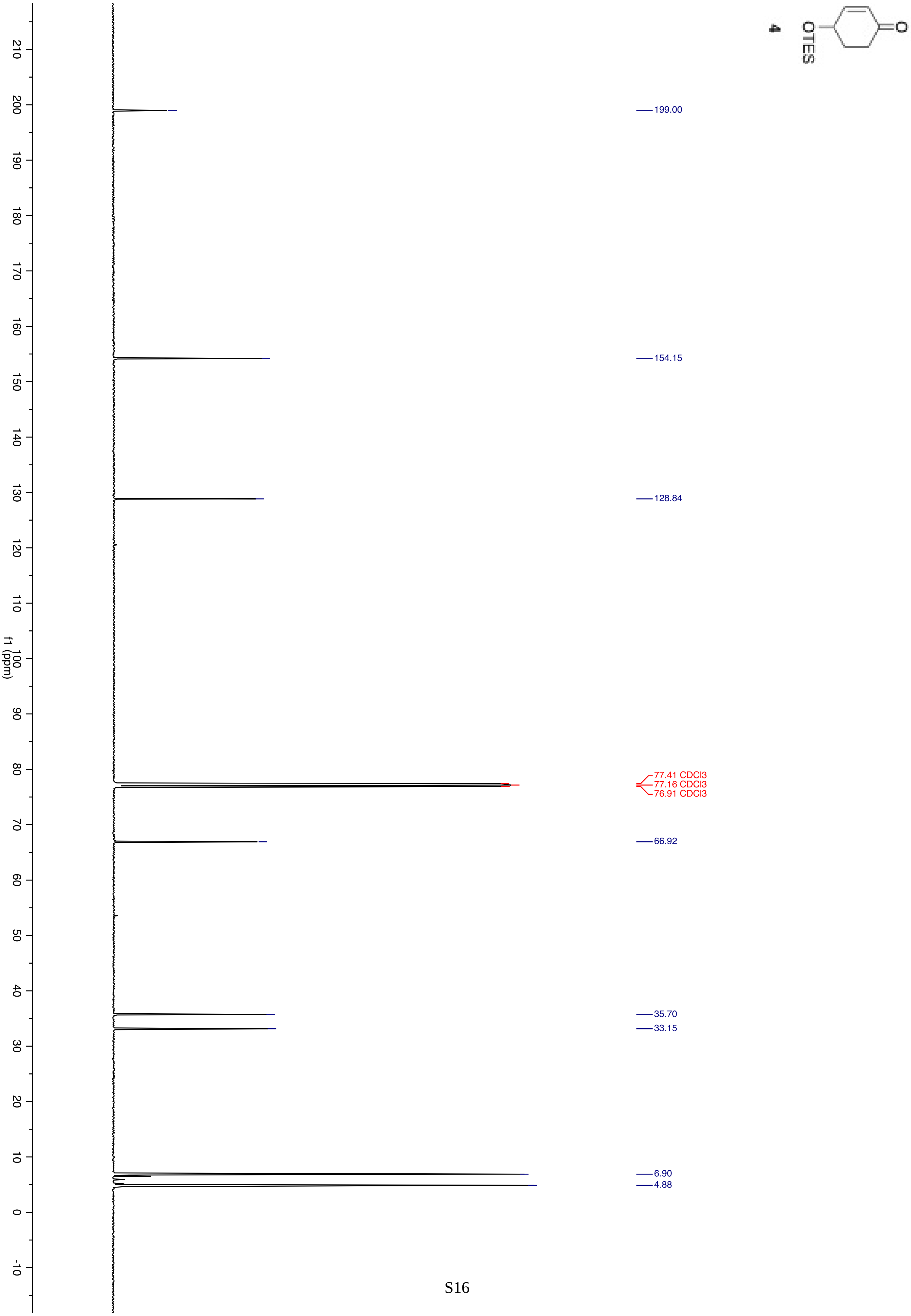
[4] A. H. Banskota, Y. Tezuka, K. Midorikawa, K. Matsushige and S. Kadota, *J. Nat. Prod.*, 2000, **63**, 1277-1279

4. ^{1}H and ^{13}C NMR Spectra

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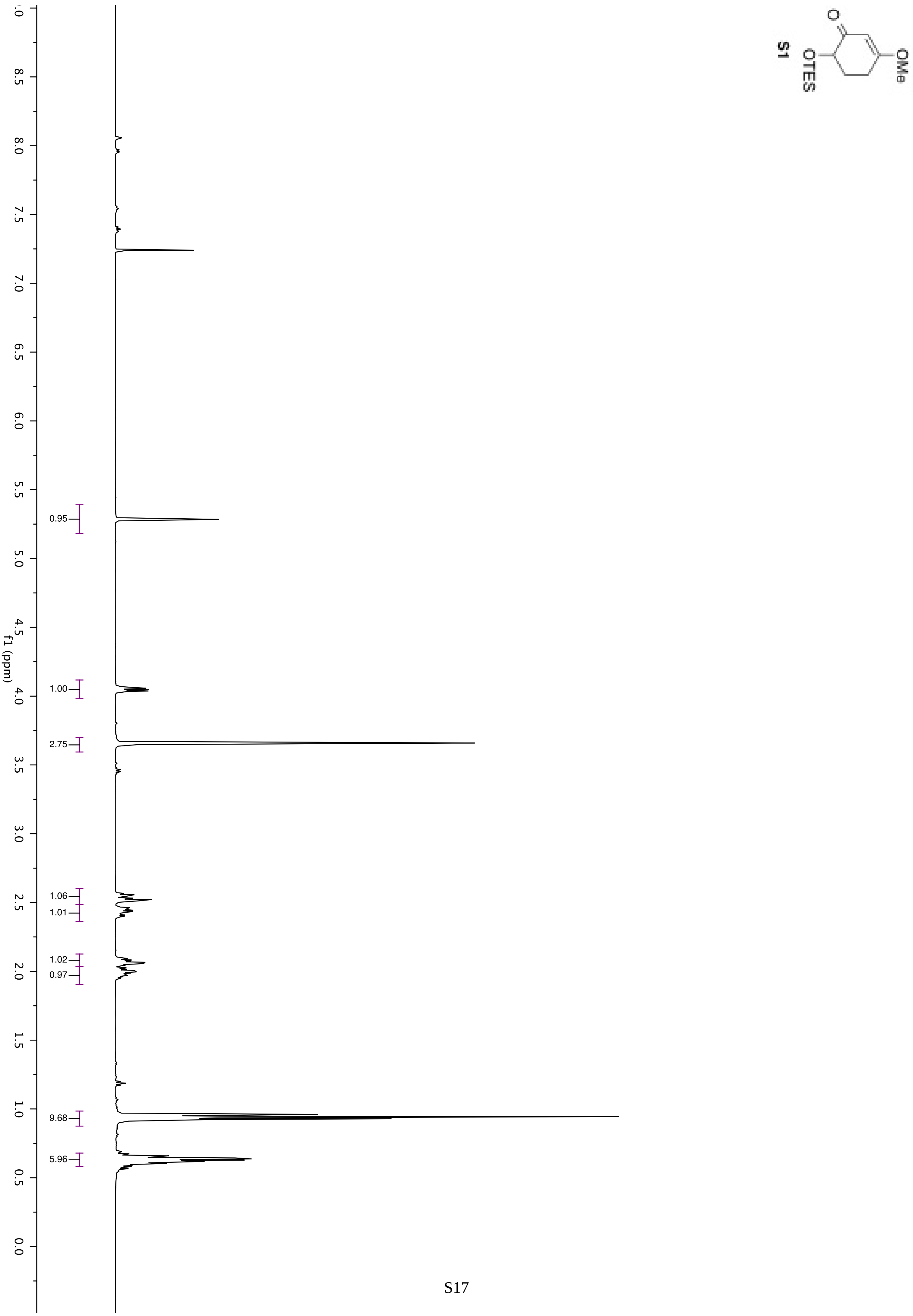
O
4
199.00
154.15
128.84
77.41 CDCl3
77.16 CDCl3
76.91 CDCl3
66.92
35.70
33.15
6.90
4.88
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
-10
f1 (ppm)


O
OMe
OTES
S1
.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)
0.95
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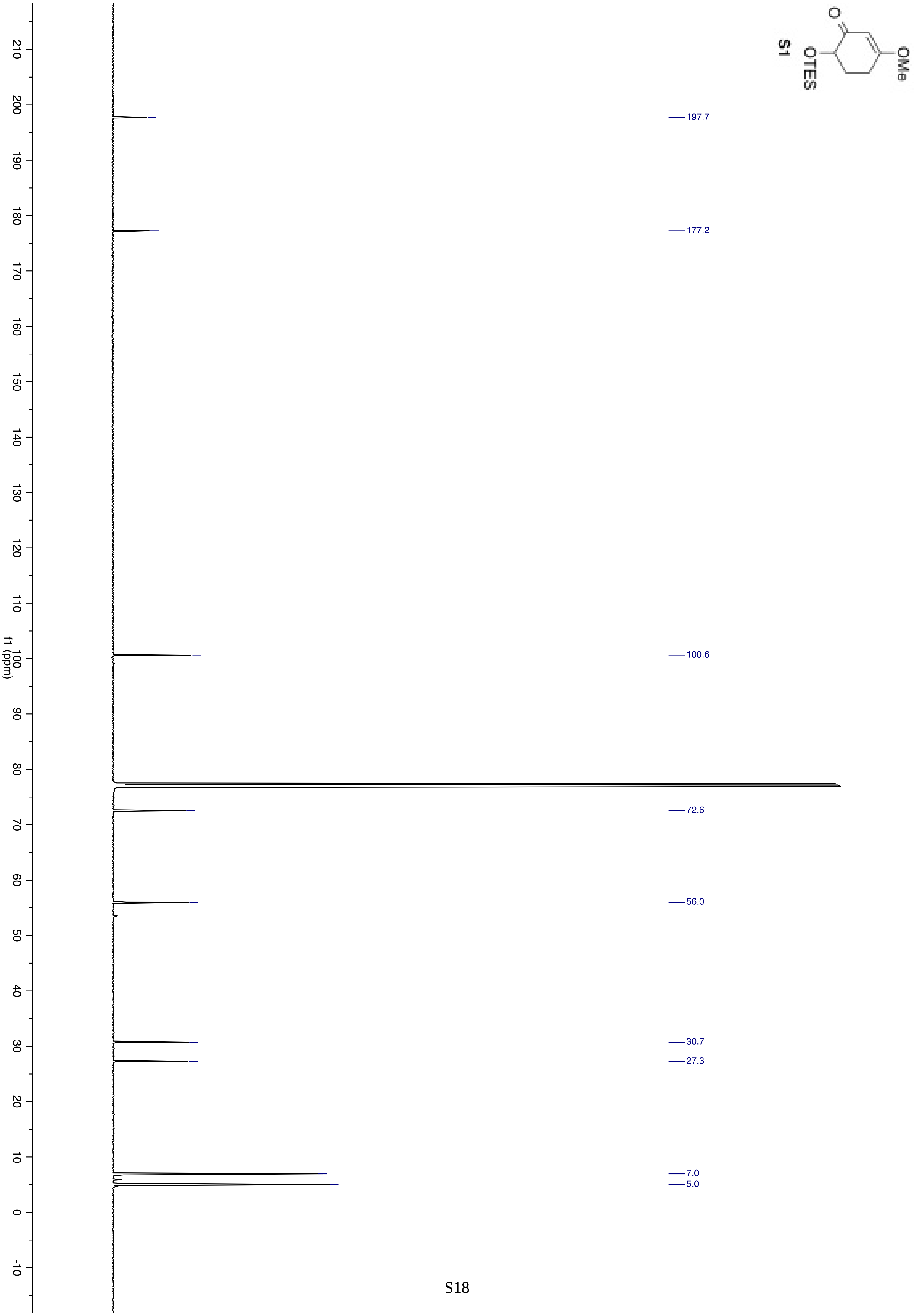
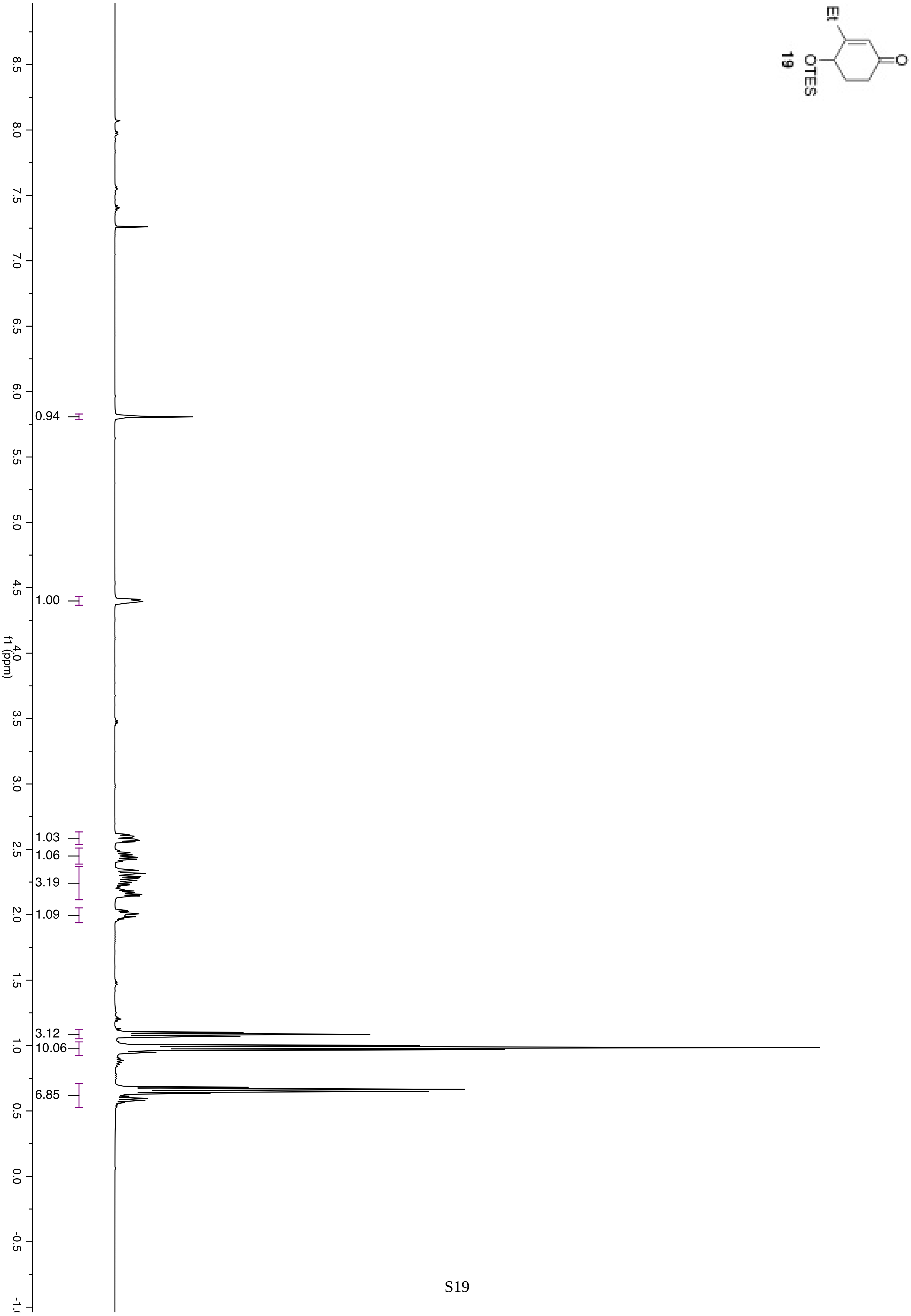
2.75
1.06
1.01
1.02
0.97
9.68
5.96



S1
OTES
OMe
O
197.7
177.2
100.6
72.6
56.0
30.7
27.3
7.0
5.0
f1 (ppm)
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
-10


Et
OTES
O
19
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8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
-0.5
-1.0
f1 (ppm)
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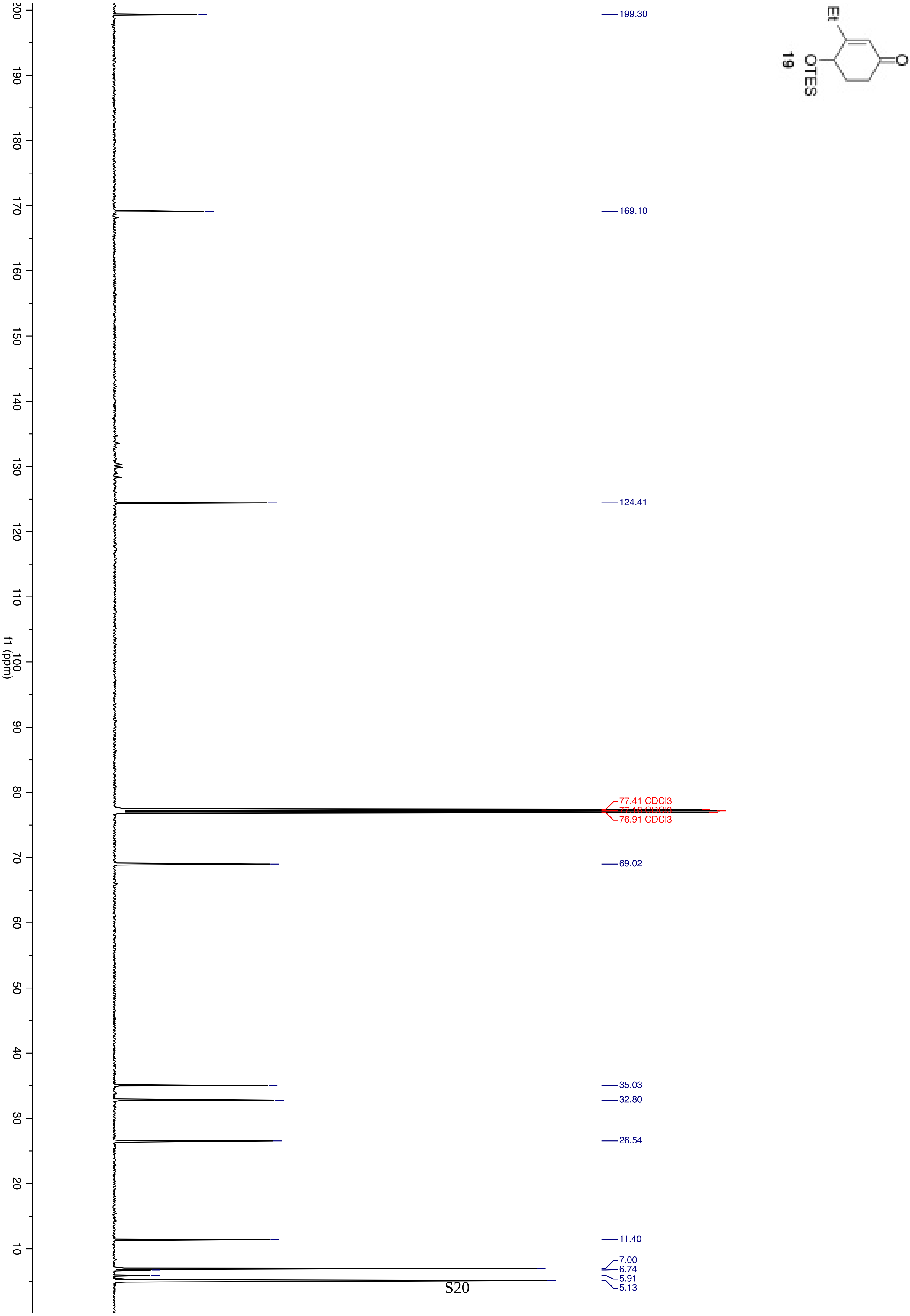
1.00
1.03
1.06
3.19
1.09
3.12
10.06
6.85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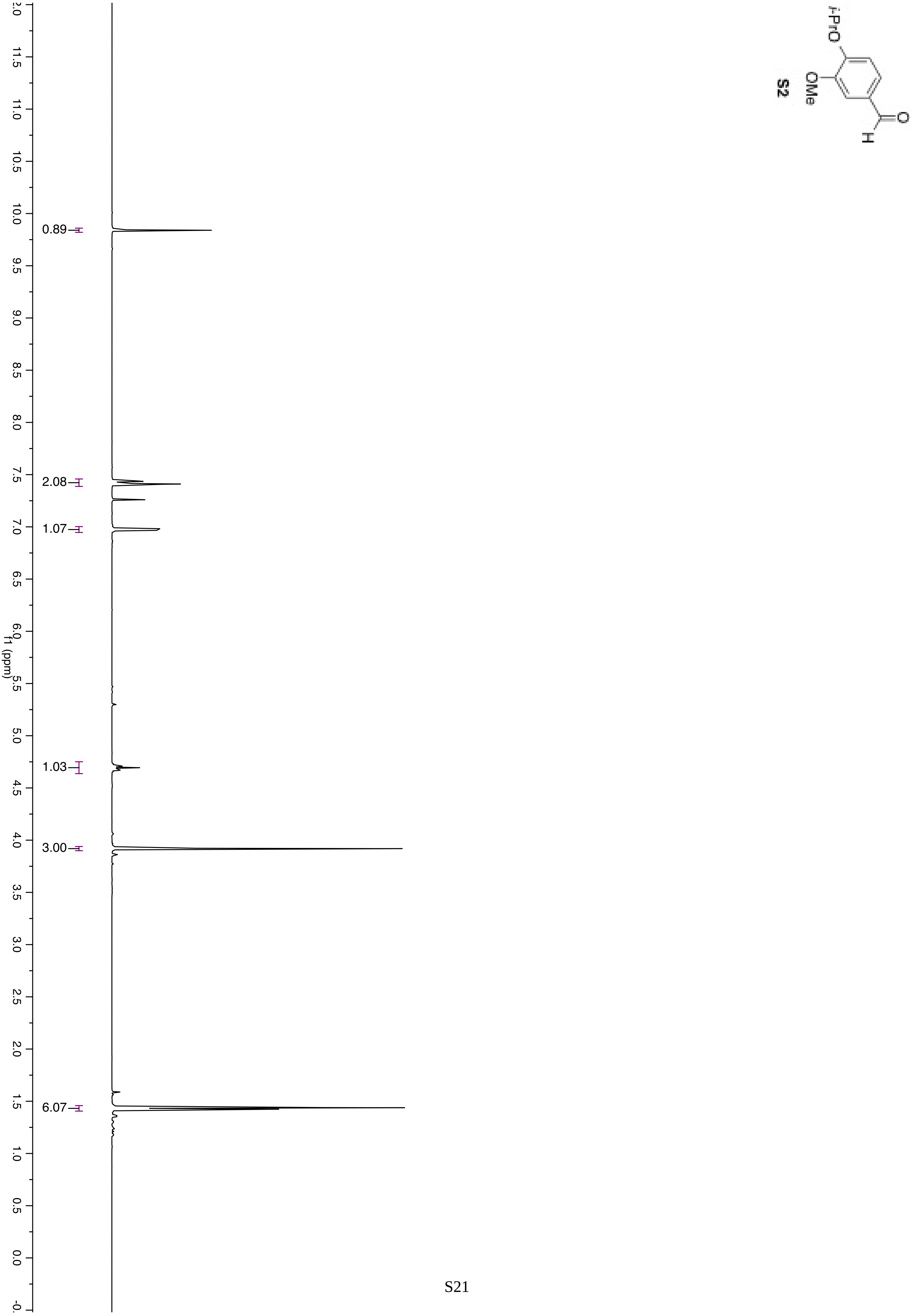
169.10
124.41
77.41 CDCl3
77.16 CDCl3
76.91 CDCl3
69.02
35.03
32.80
26.54
11.40
7.00
6.74
5.91
5.13
f1 (ppm)
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
Et
O
OTES

19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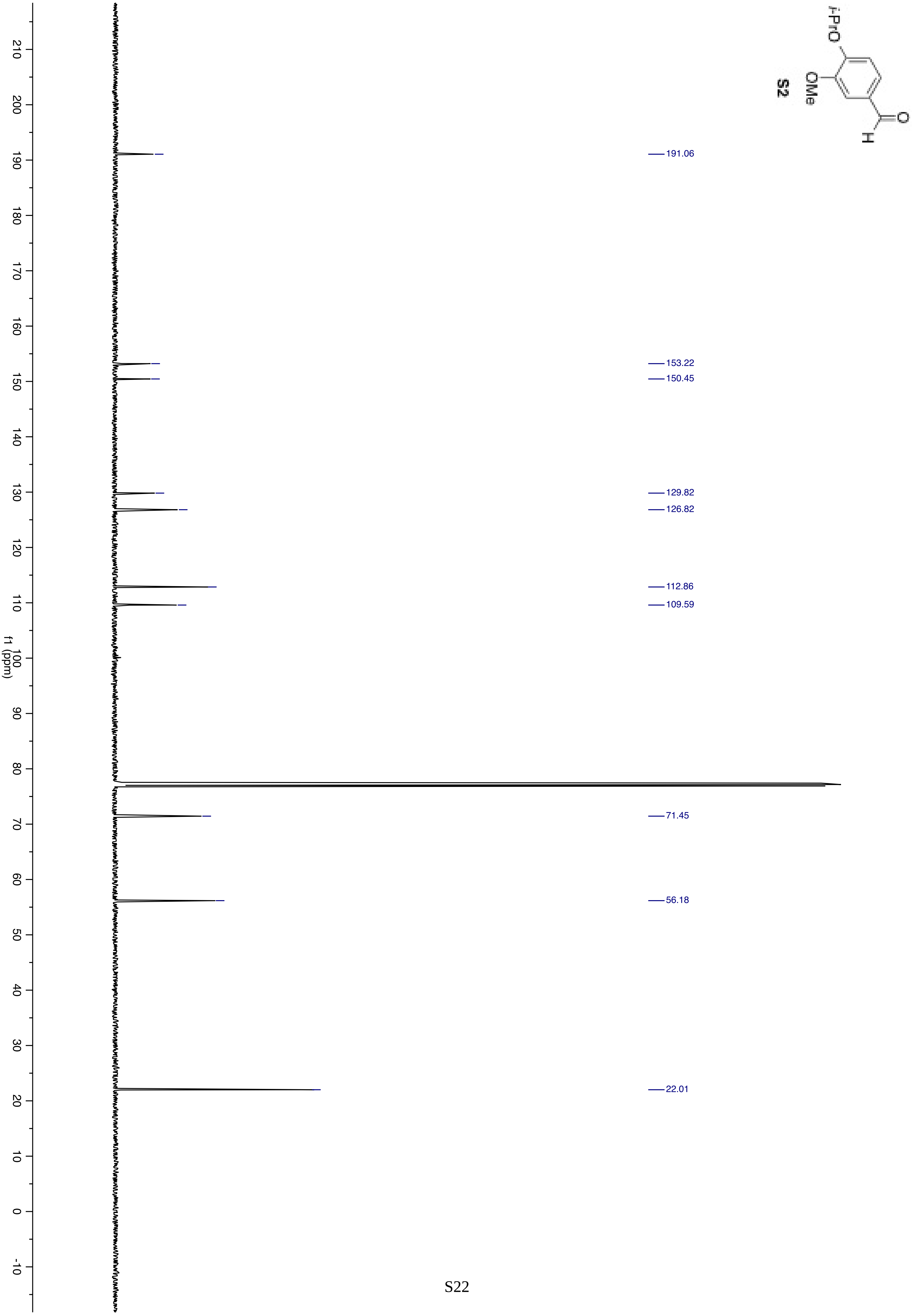
OMe
H
O
S2
12.0
11.5
11.0
10.5
10.0
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
-0.
f1 (ppm)
0.89
2.08
1.07
1.03
3.00
6.07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OMe
O
H
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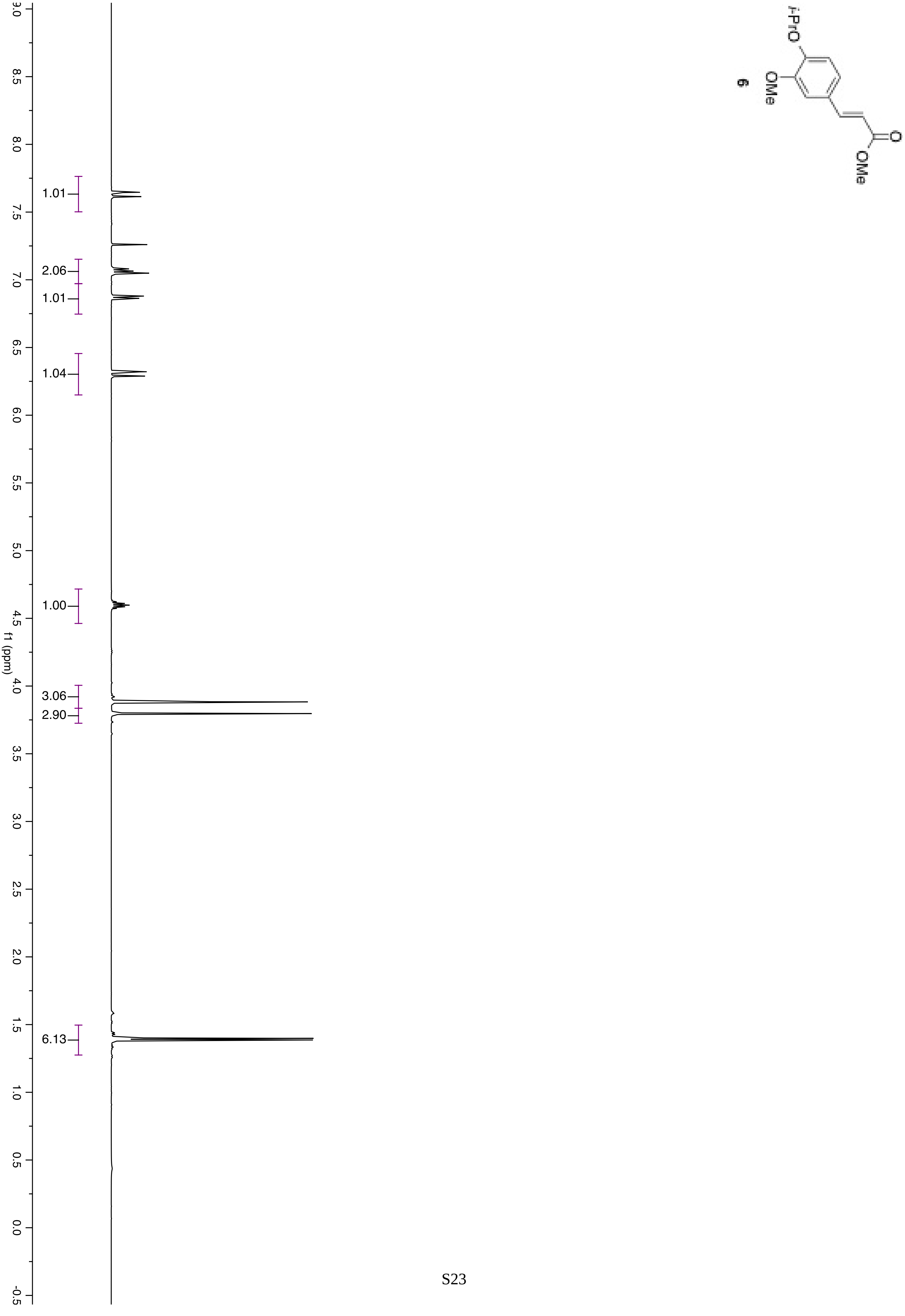
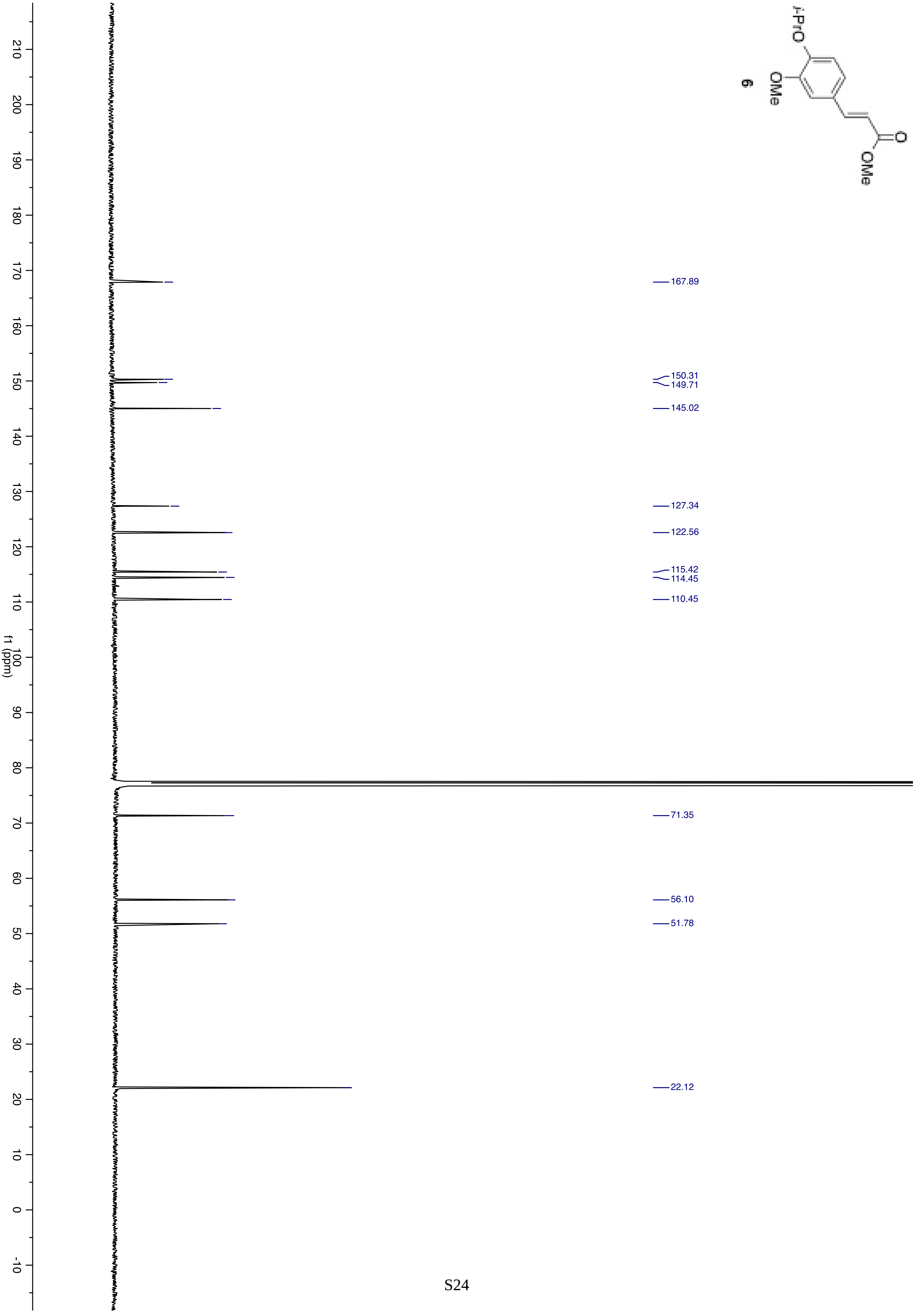
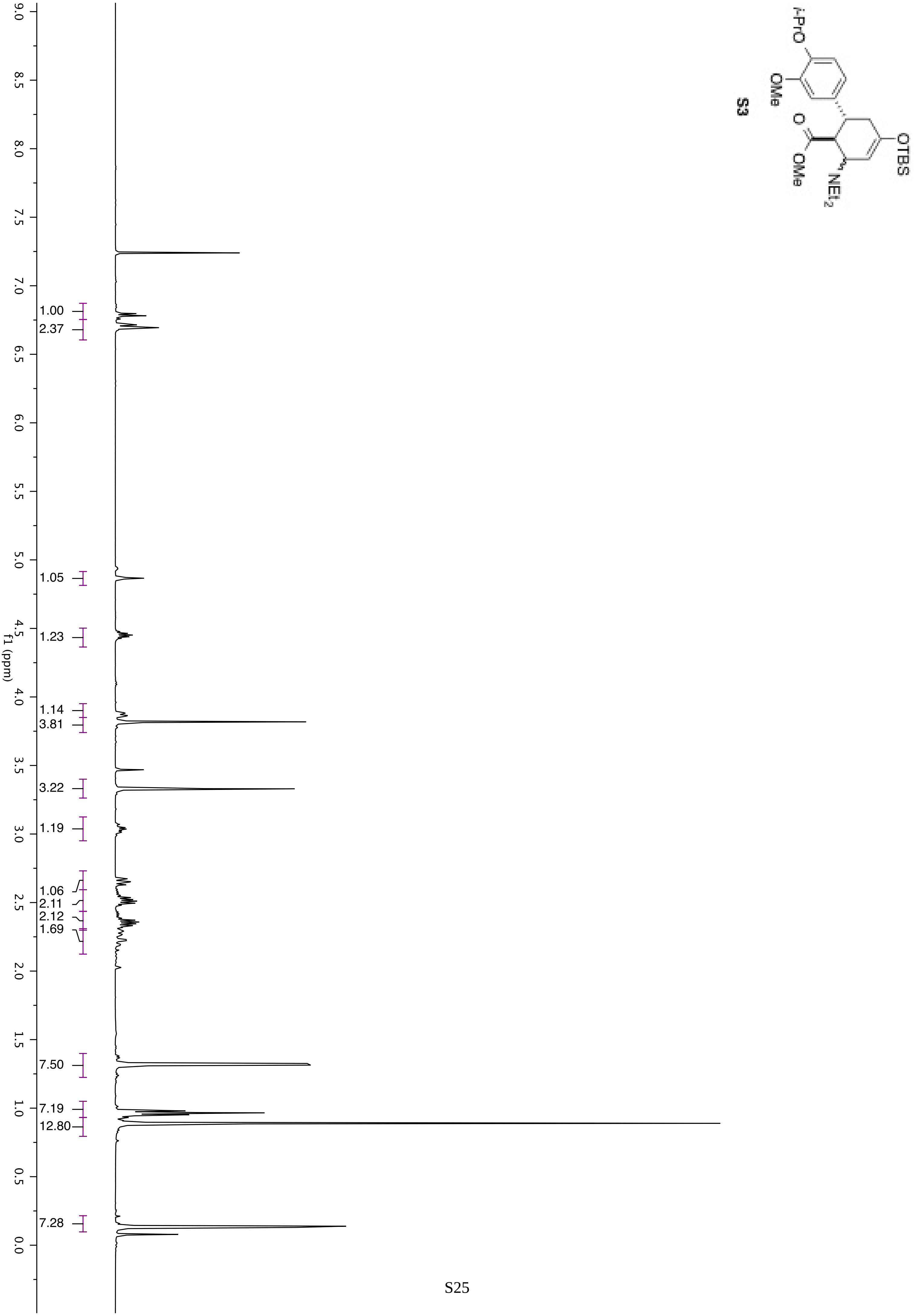
153.22
150.45
129.82
126.82
112.86
109.59
71.45
56.18
22.01
f1 (ppm)
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
-10

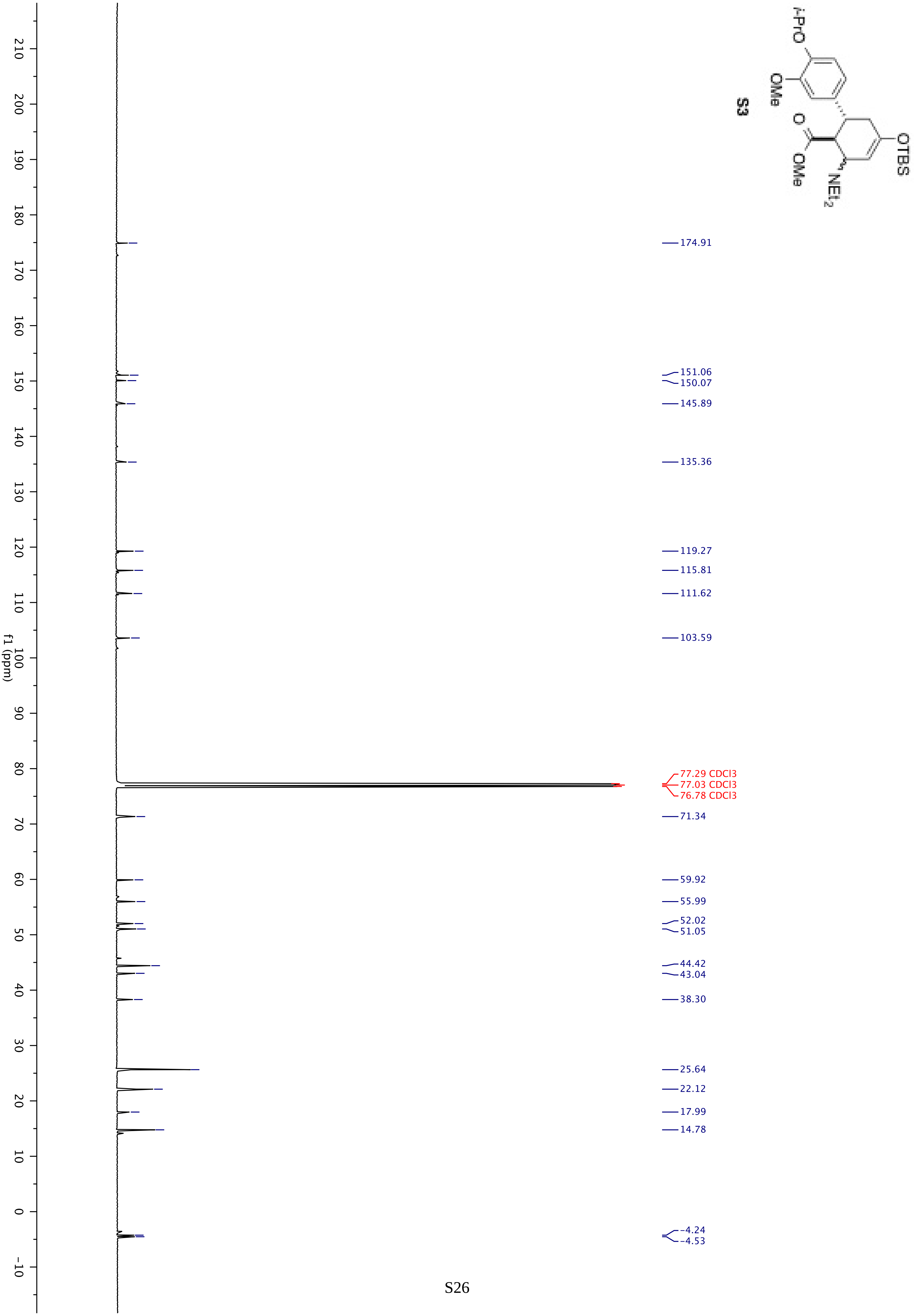
S2


i-PrO
OMe
6
O
OMe
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
-0.5
f1 (ppm)
1.01
2.06
1.01
1.04
1.00
3.06
2.90
6.13


i-PrO
OMe
O
OMe
6
167.89
150.31
149.71
145.02
127.34
122.56
115.42
114.45
110.45
71.35
56.10
51.78
22.12
210
200
190
180
170
160
150
140
130
120
110
100
f1 (ppm)
90
80
70
60
50
40
30
20
10
0
-10

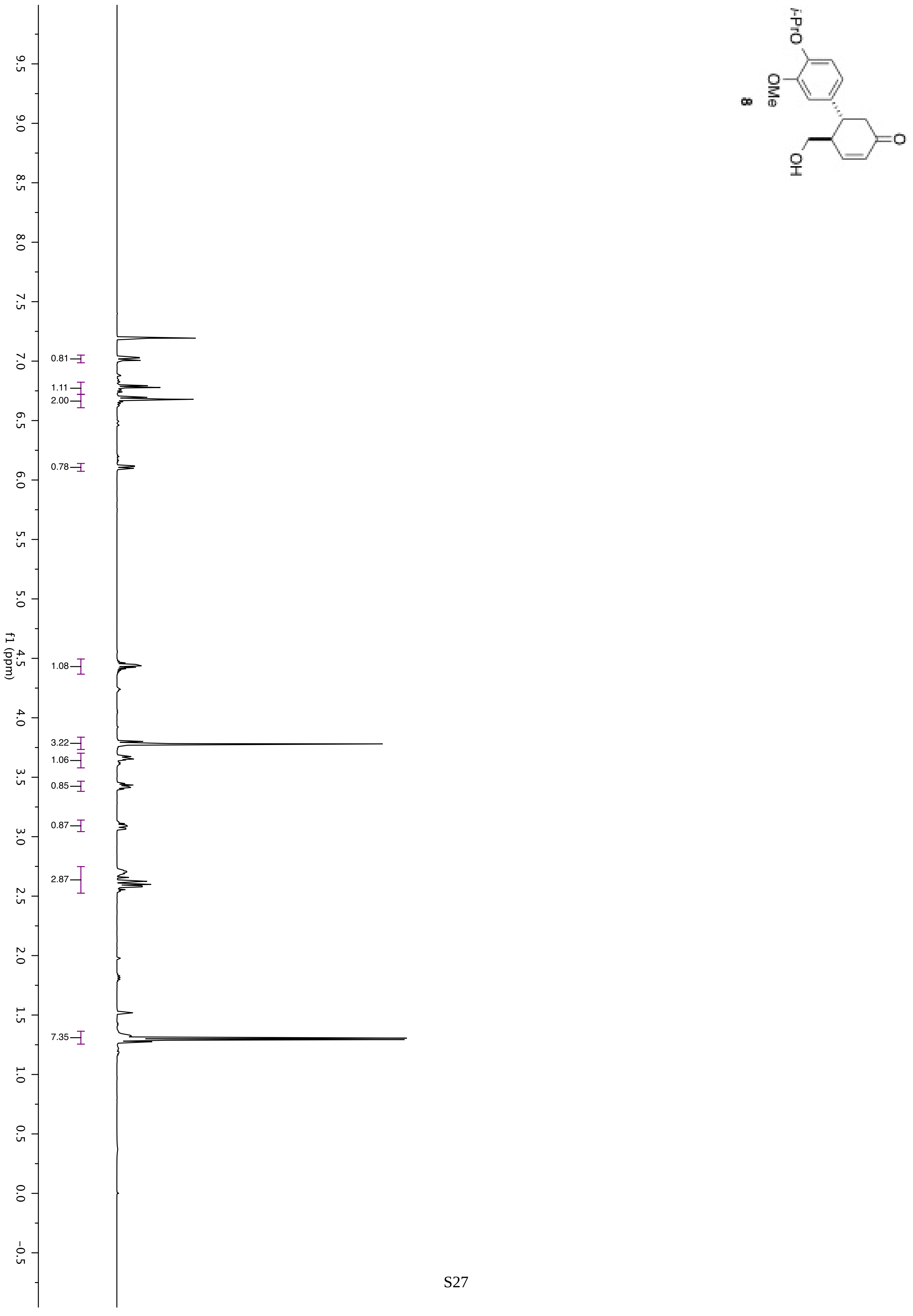

OTBS
NEt$_2$
OMe
O
i-PrO
OMe
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
f1 (ppm)
1.00
2.37
1.05
1.23
1.14
3.81
3.22
1.19
1.06
2.11
2.12
1.69
7.50
7.19
12.80
7.28

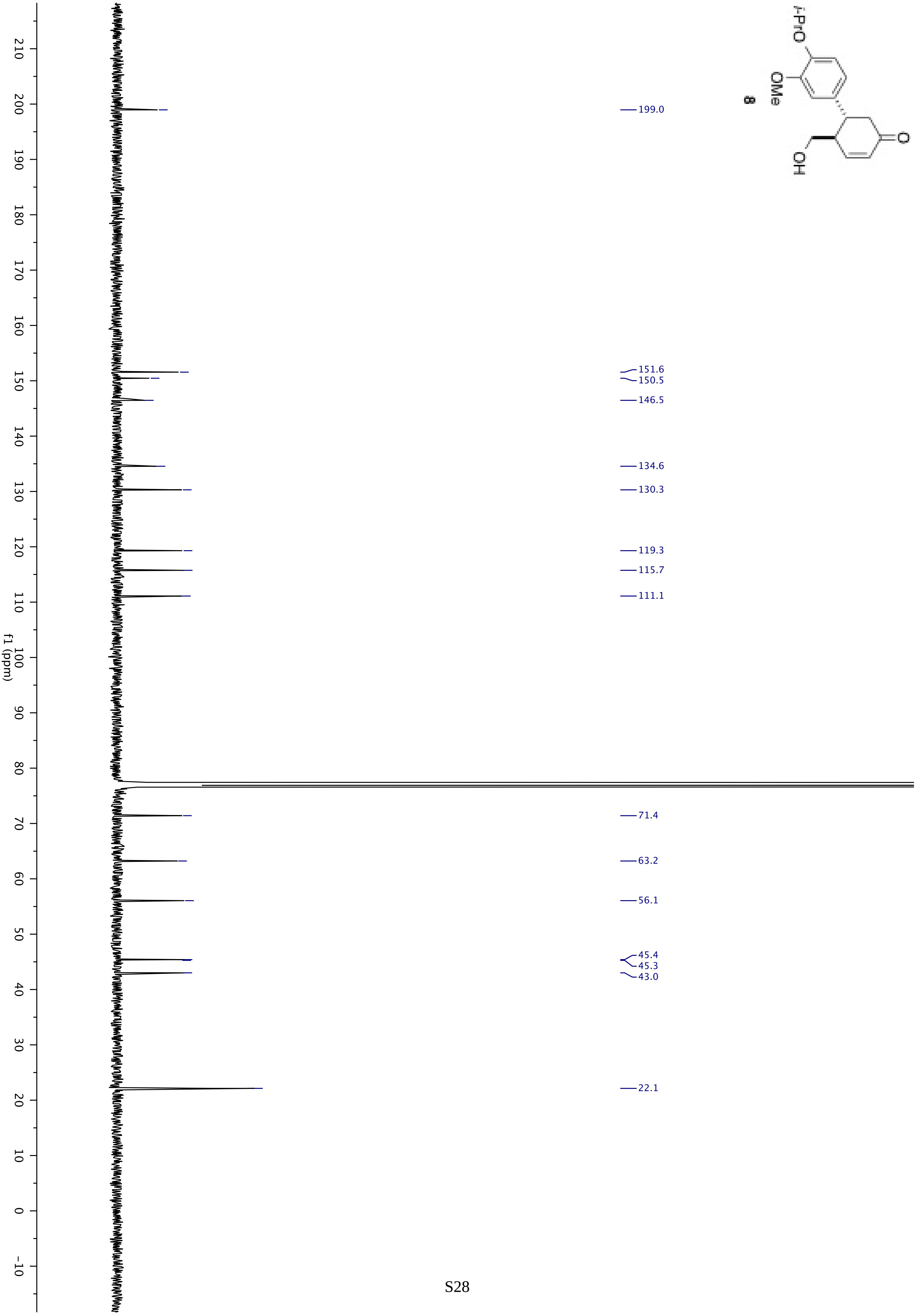
S3

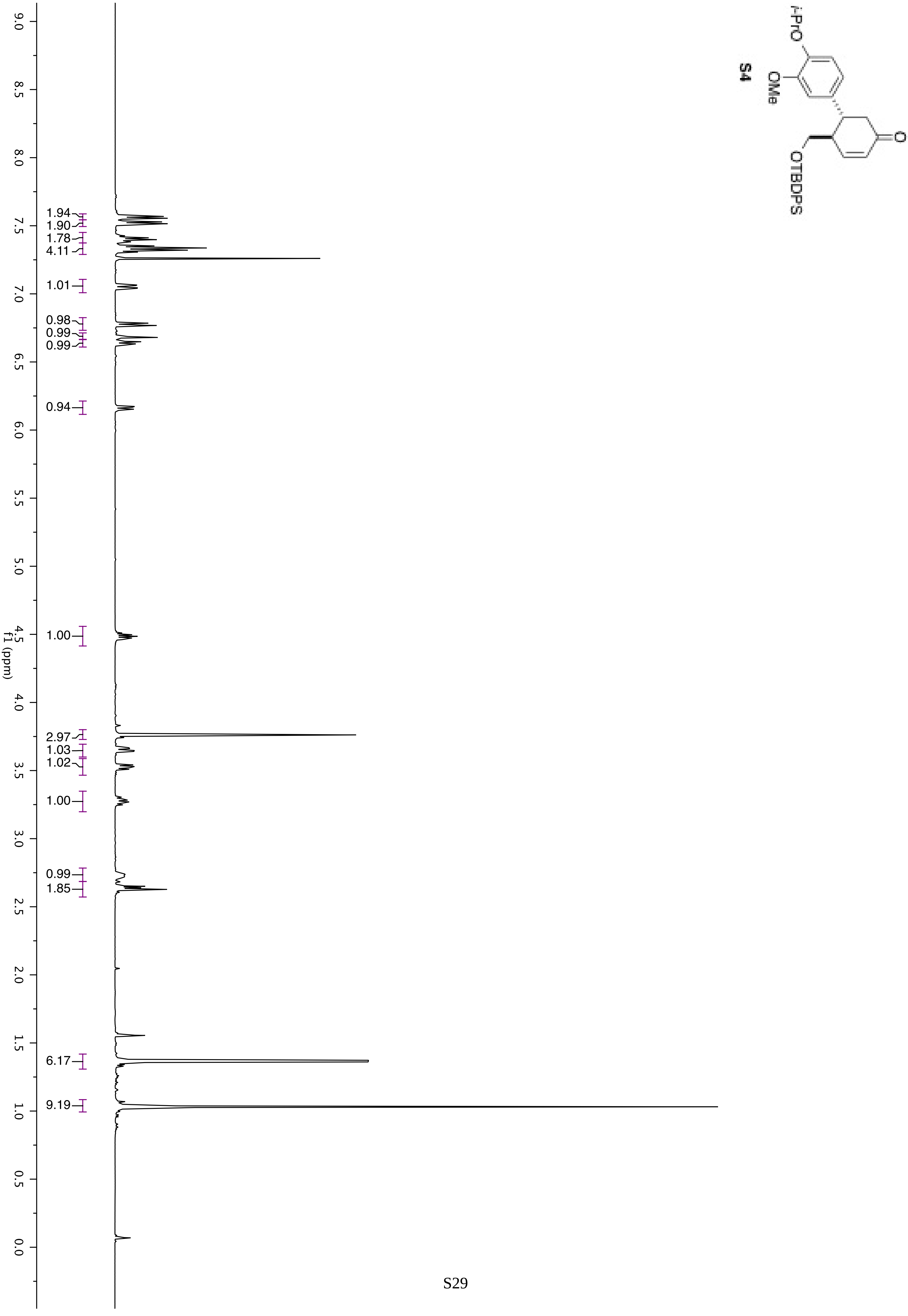


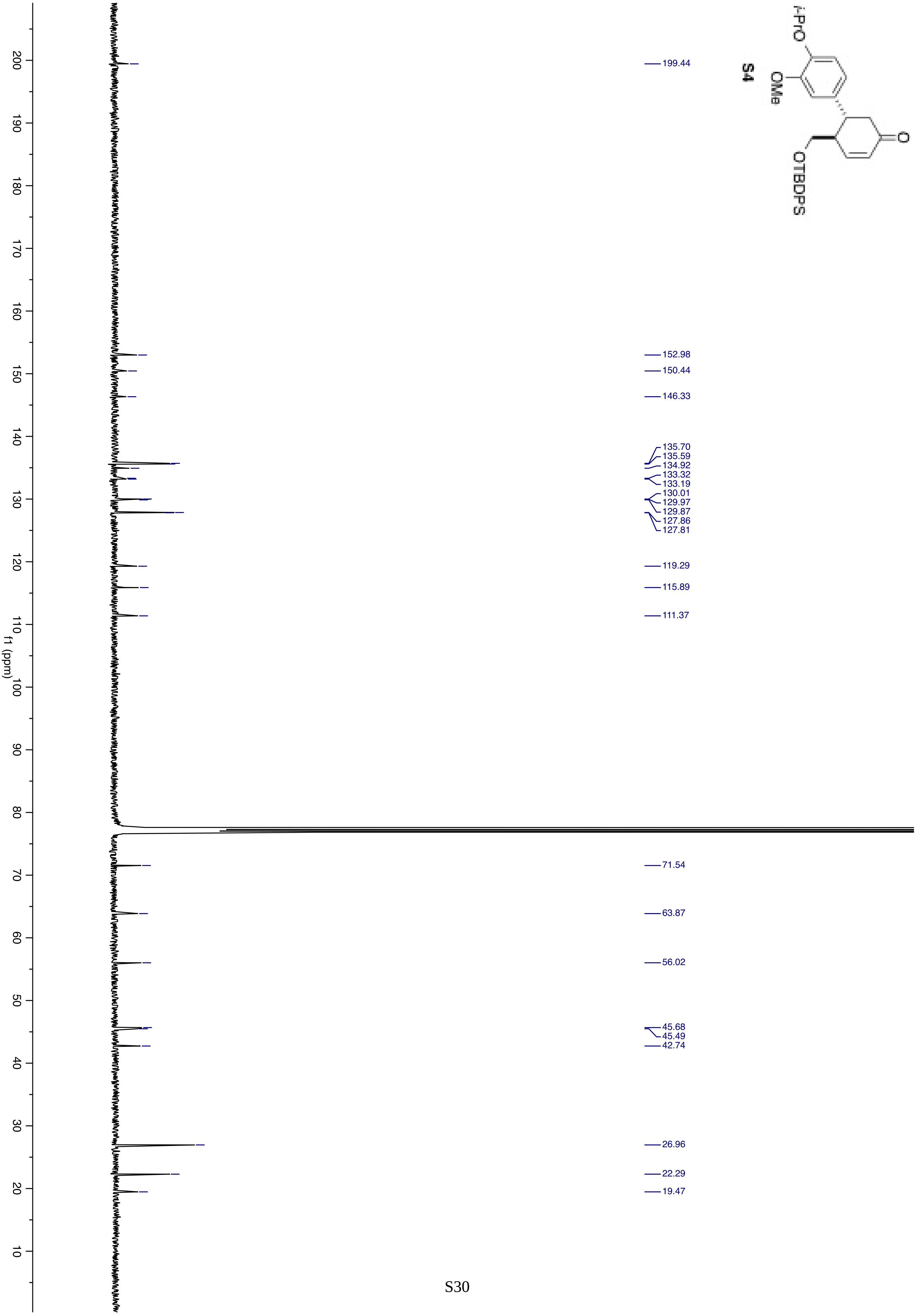
S3

i-PrO
OMe
O
OMe
OTBS
NEt$_2$
174.91
151.06
150.07
145.89
135.36
119.27
115.81
111.62
103.59
77.29 CDCl3
77.03 CDCl3
76.78 CDCl3
71.34
59.92
55.99
52.02
51.05
44.42
43.04
38.30
25.64
22.12
17.99
14.78
−4.24
−4.53
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
−10
f1 (ppm)

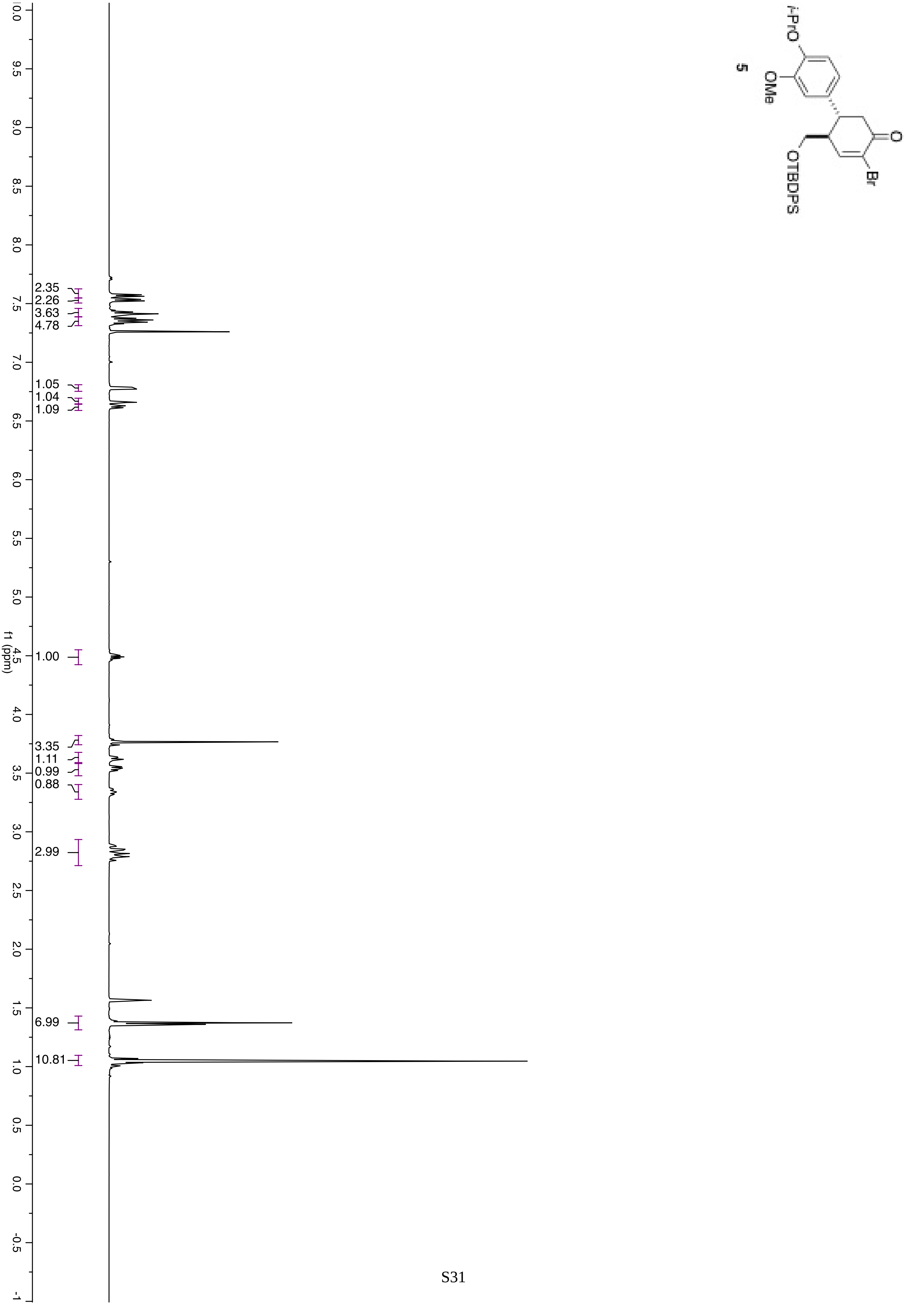

i-PrO
OMe
8
OH
O
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
f1 (ppm)
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
−0.5
0.81
1.11
2.00
0.78
1.08
3.22
1.06
0.85
0.87
2.87
7.35


i-PrO
OMe
OH
O
8
199.0
151.6
150.5
146.5
134.6
130.3
119.3
115.7
111.1
71.4
63.2
56.1
45.4
45.3
43.0
22.1
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
−10
f1 (ppm)

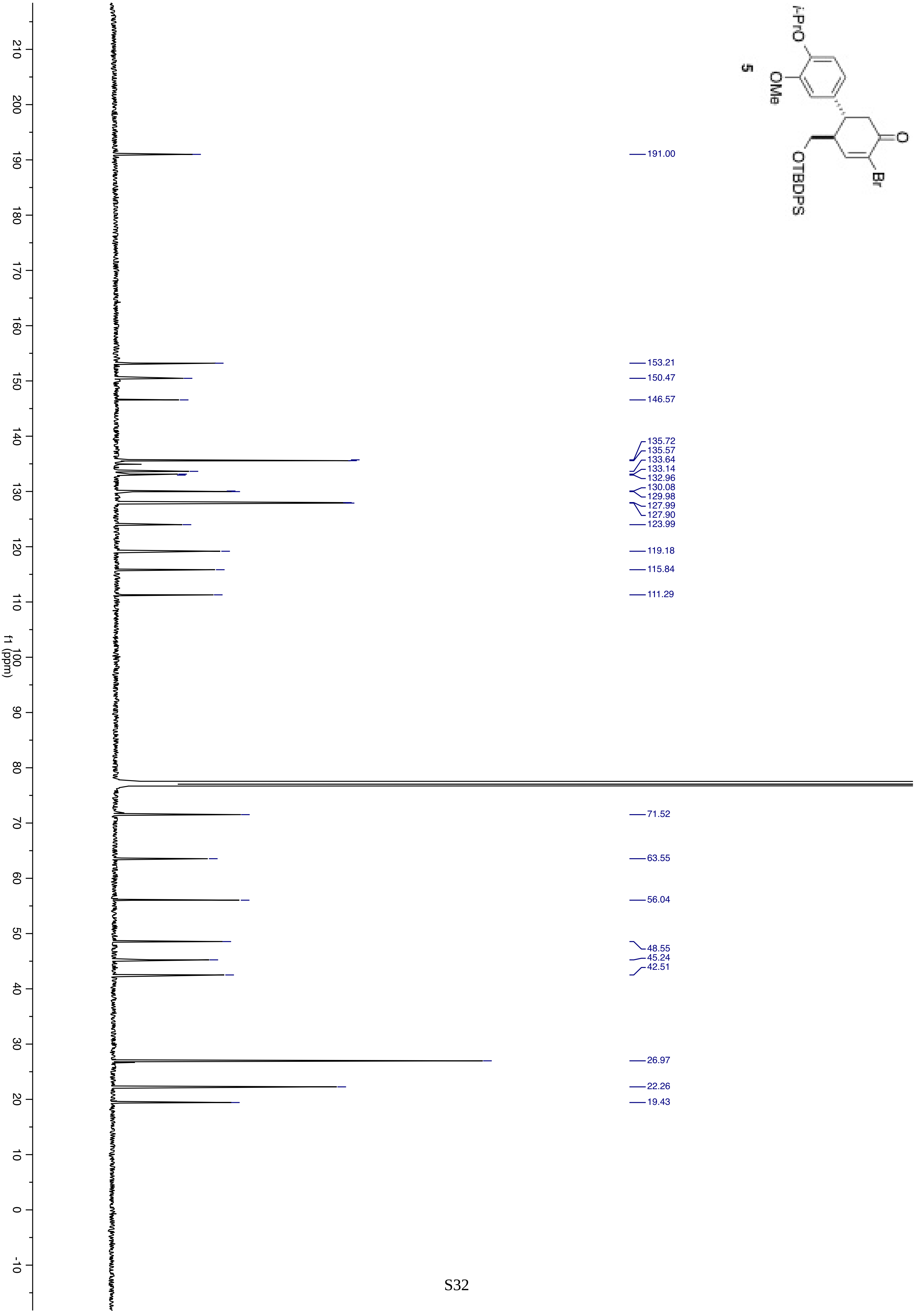

i-PrO
OMe
O
OTBDPS
S4
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
f1 (ppm)
1.94
1.90
1.78
4.11
1.01
0.98
0.99
0.99
0.94
1.00
2.97
1.03
1.02
1.00
0.99
1.85
6.17
9.19


S4

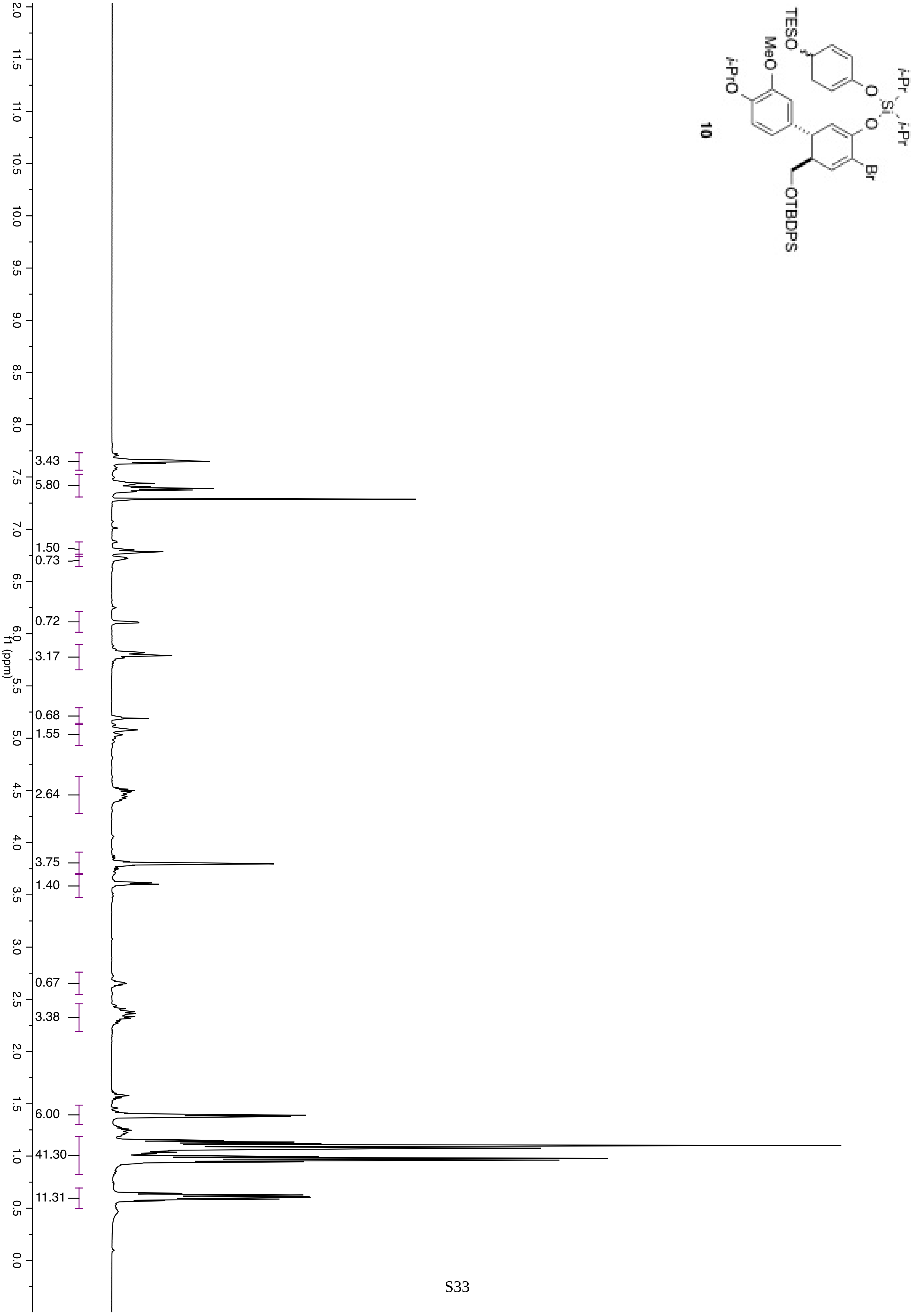
i-PrO
OMe
OTBDPS
O
199.44
152.98
150.44
146.33
135.70
135.59
134.92
133.32
133.19
130.01
129.97
129.87
127.86
127.81
119.29
115.89
111.37
71.54
63.87
56.02
45.68
45.49
42.74
26.96
22.29
19.47
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
f1 (ppm)



i-PrO
OMe
O
Br
OTBDPS
5
2.35
2.26
3.63
4.78
1.05
1.04
1.09
1.00
3.35
1.11
0.99
0.88
2.99
6.99
10.81
10.0
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
f1 (ppm)
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
-0.5
-1

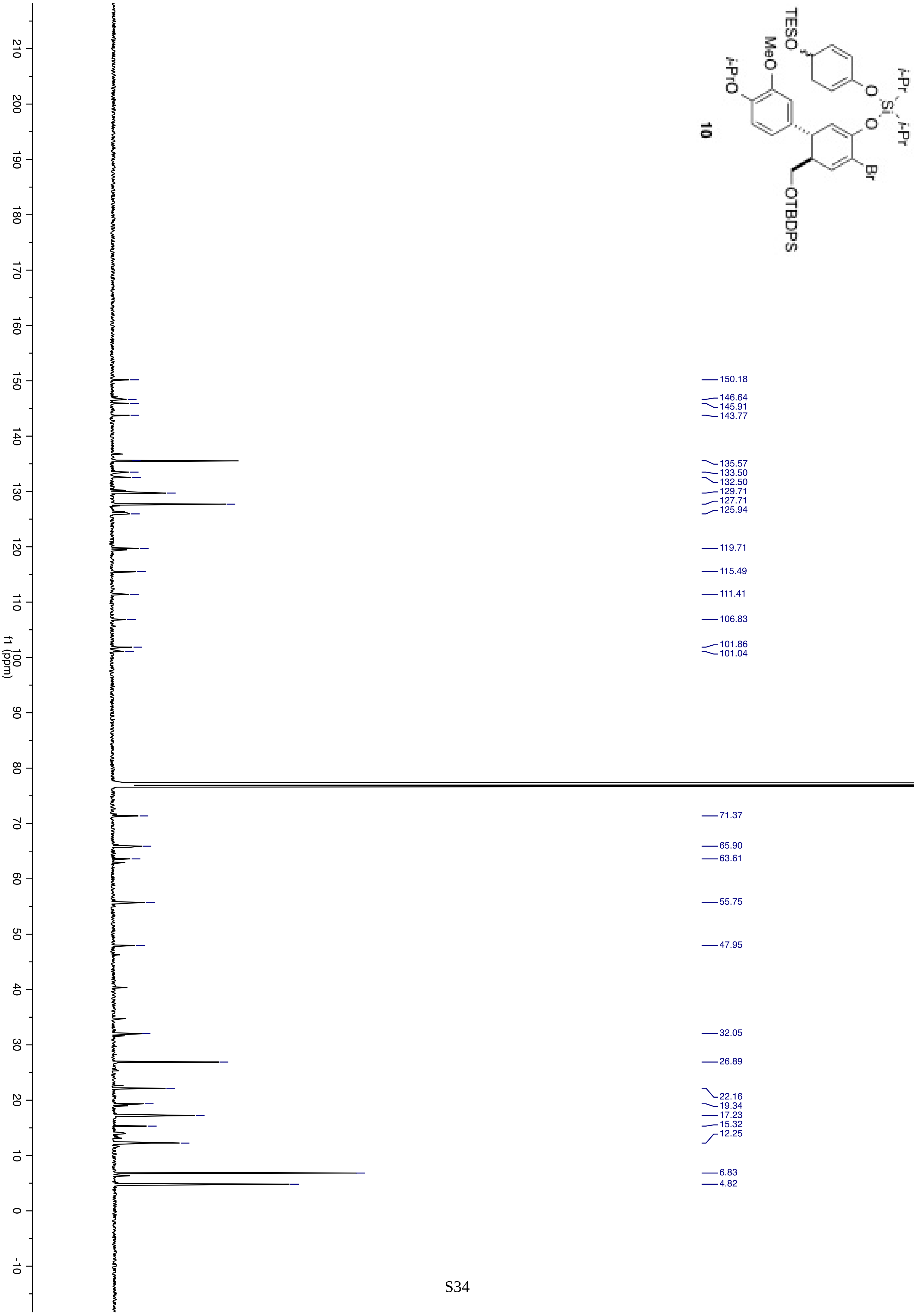


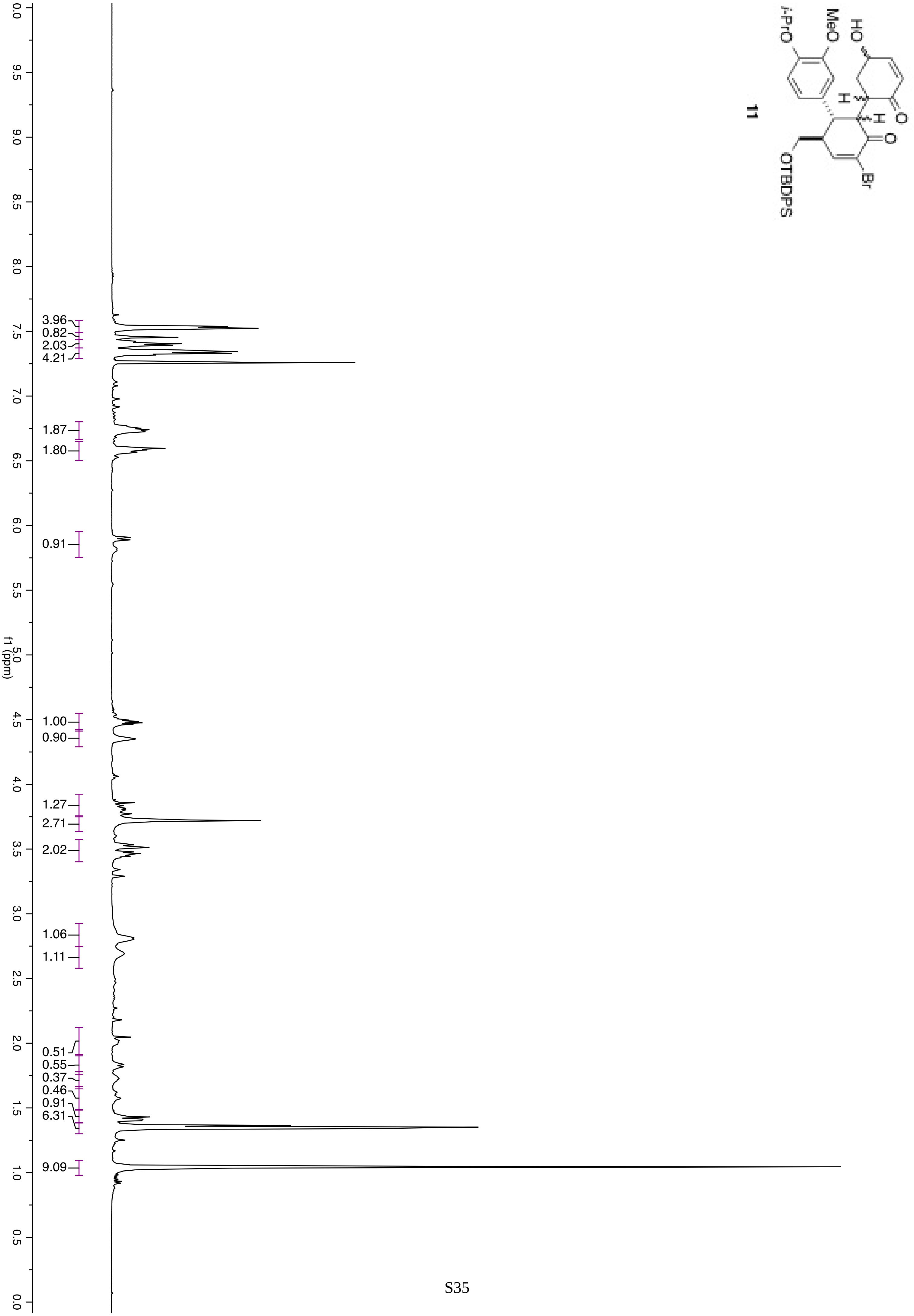
i-PrO
OMe
5
O
Br
OTBDPS
191.00
153.21
150.47
146.57
135.72
135.57
133.64
133.14
132.96
130.08
129.98
127.99
127.90
123.99
119.18
115.84
111.29
71.52
63.55
56.04
48.55
45.24
42.51
26.97
22.26
19.43
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
-10
f1 (ppm)



10

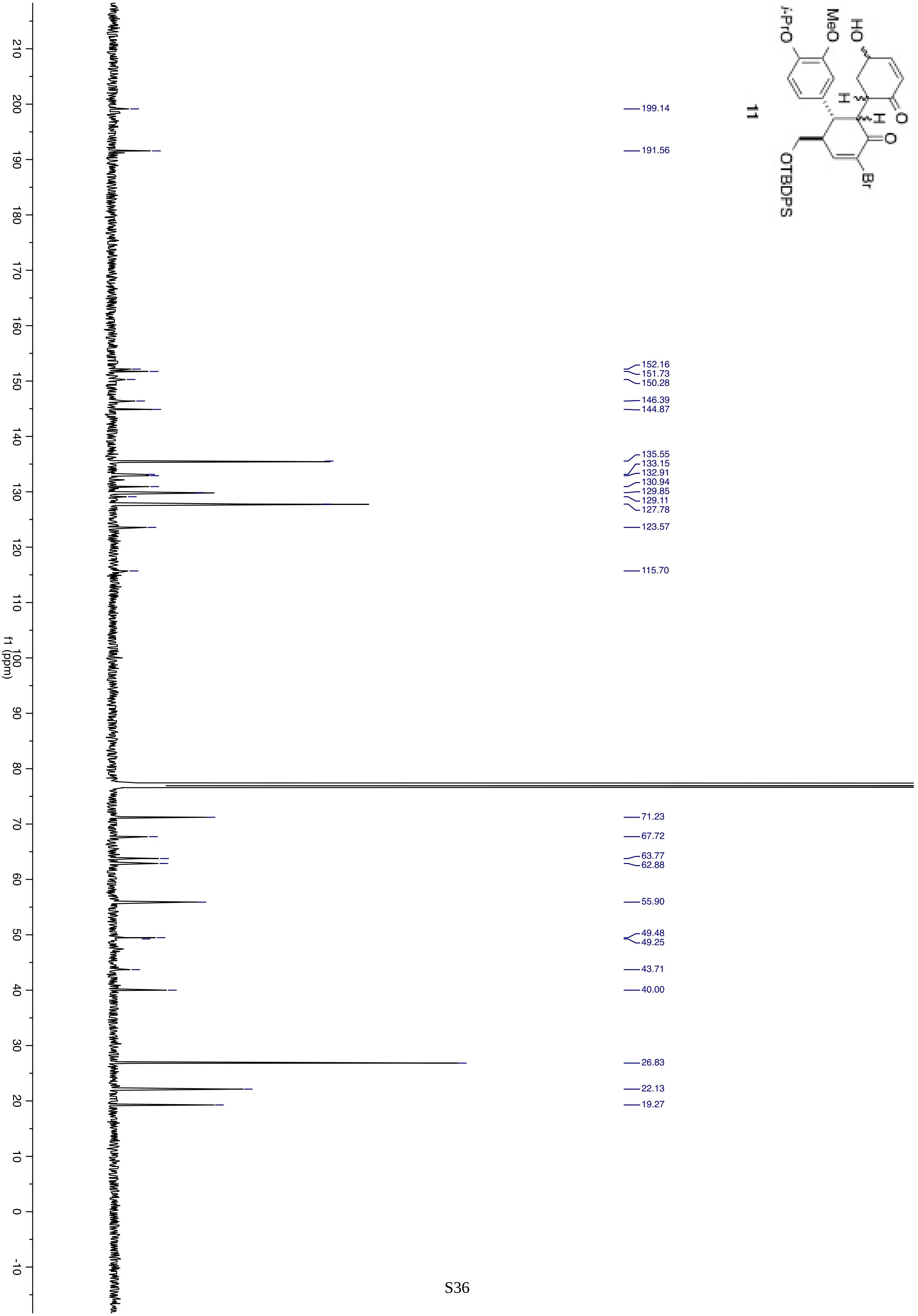
12.0
11.5
11.0
10.5
10.0
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
f1 (ppm)
3.43
5.80
1.50
0.73
0.72
3.17
0.68
1.55
2.64
3.75
1.40
0.67
3.38
6.00
41.30
11.31


10
TESO
MeO
i-PrO
i-Pr
Si
i-Pr
O
O
Br
OTBDPS
150.18
146.64
145.91
143.77
135.57
133.50
132.50
129.71
127.71
125.94
119.71
115.49
111.41
106.83
101.86
101.04
71.37
65.90
63.61
55.75
47.95
32.05
26.89
22.16
19.34
17.23
15.32
12.25
6.83
4.82
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
-10
f1 (ppm)

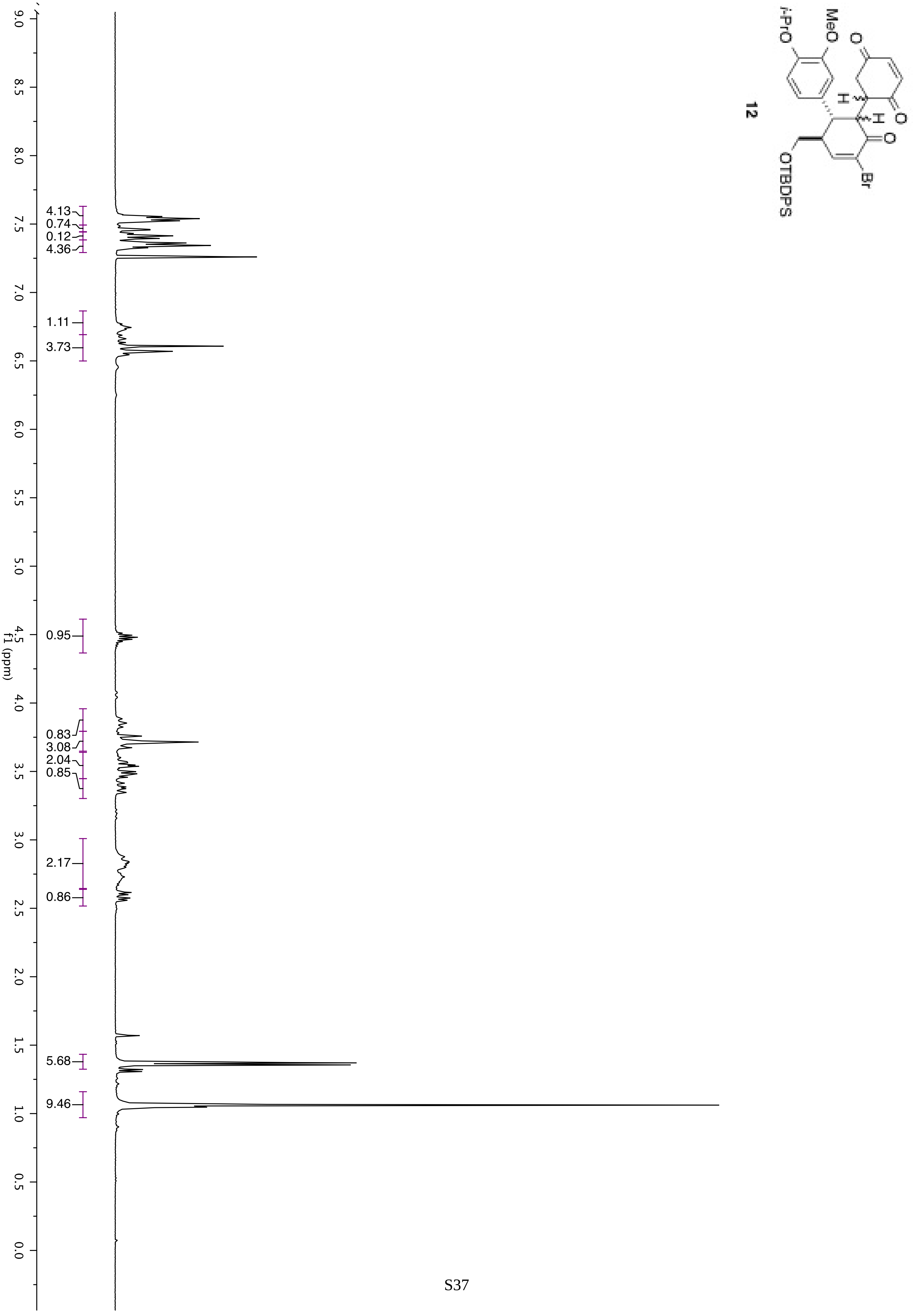


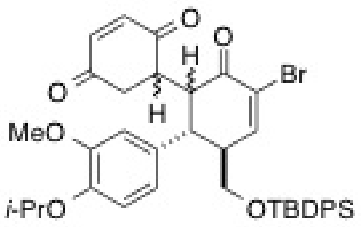
11

HO
MeO
i-PrO
H
H
O
O
Br
OTBDPS
3.96
0.82
2.03
4.21
1.87
1.80
0.91
1.00
0.90
1.27
2.71
2.02
1.06
1.11
0.51
0.55
0.37
0.46
0.91
6.31
9.09
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)

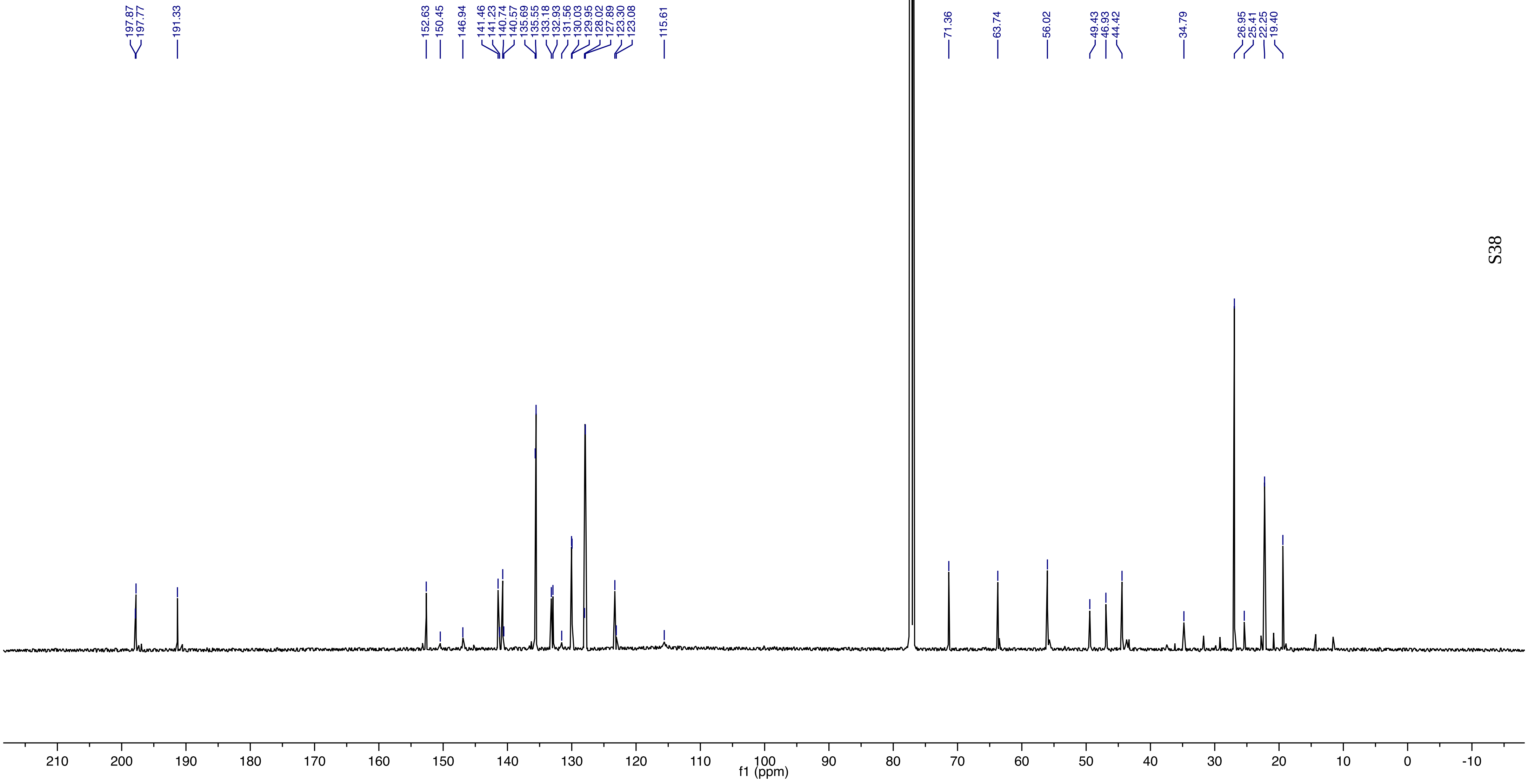

HO
MeO
i-PrO
H
H
O
O
Br
OTBDPS
199.14
191.56
152.16
151.73
150.28
146.39
144.87
135.55
133.15
132.91
130.94
129.85
129.11
127.78
123.57
115.70
71.23
67.72
63.77
62.88
55.90
49.48
49.25
43.71
40.00
26.83
22.13
19.27
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
-10
f1 (ppm)

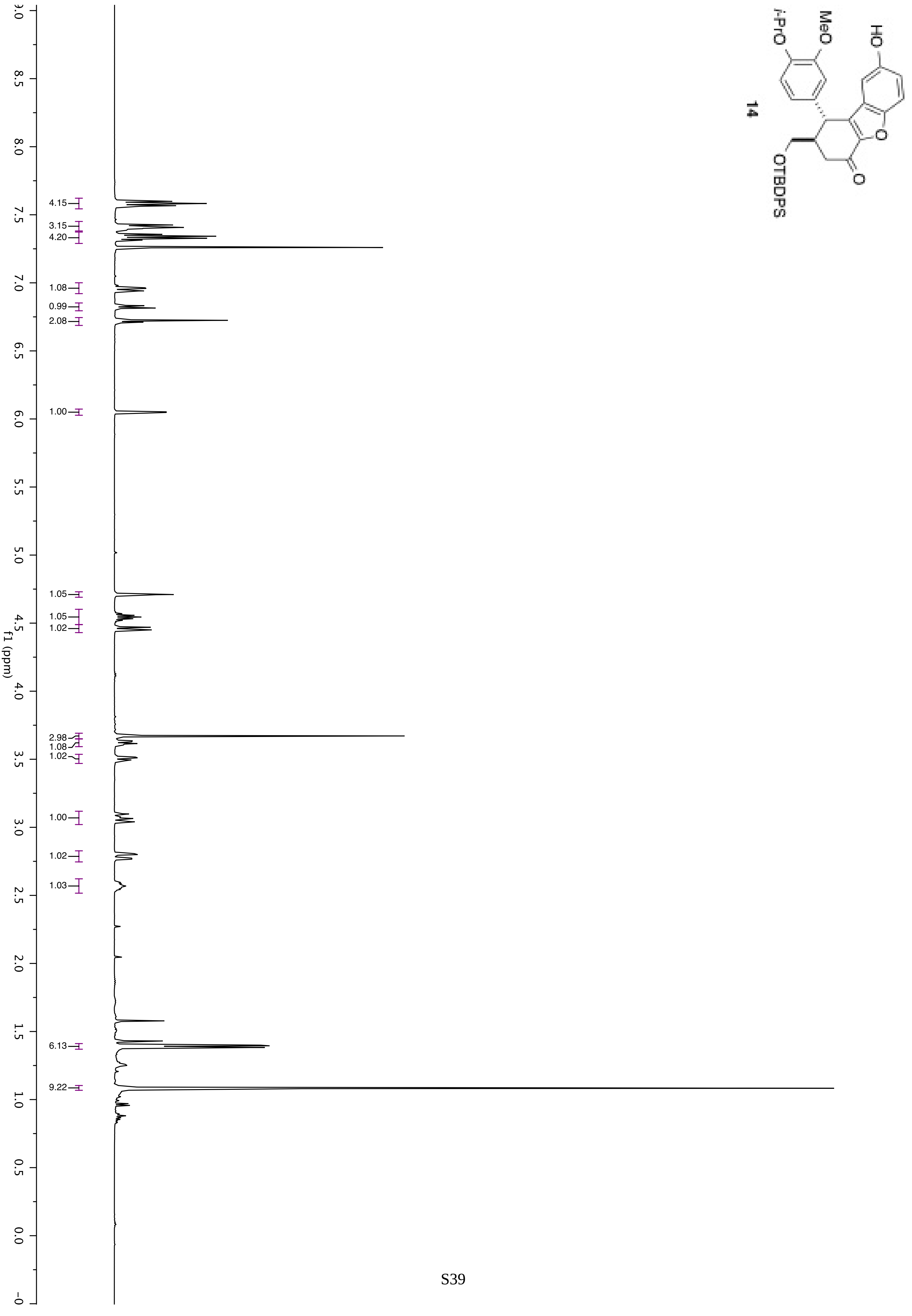
11

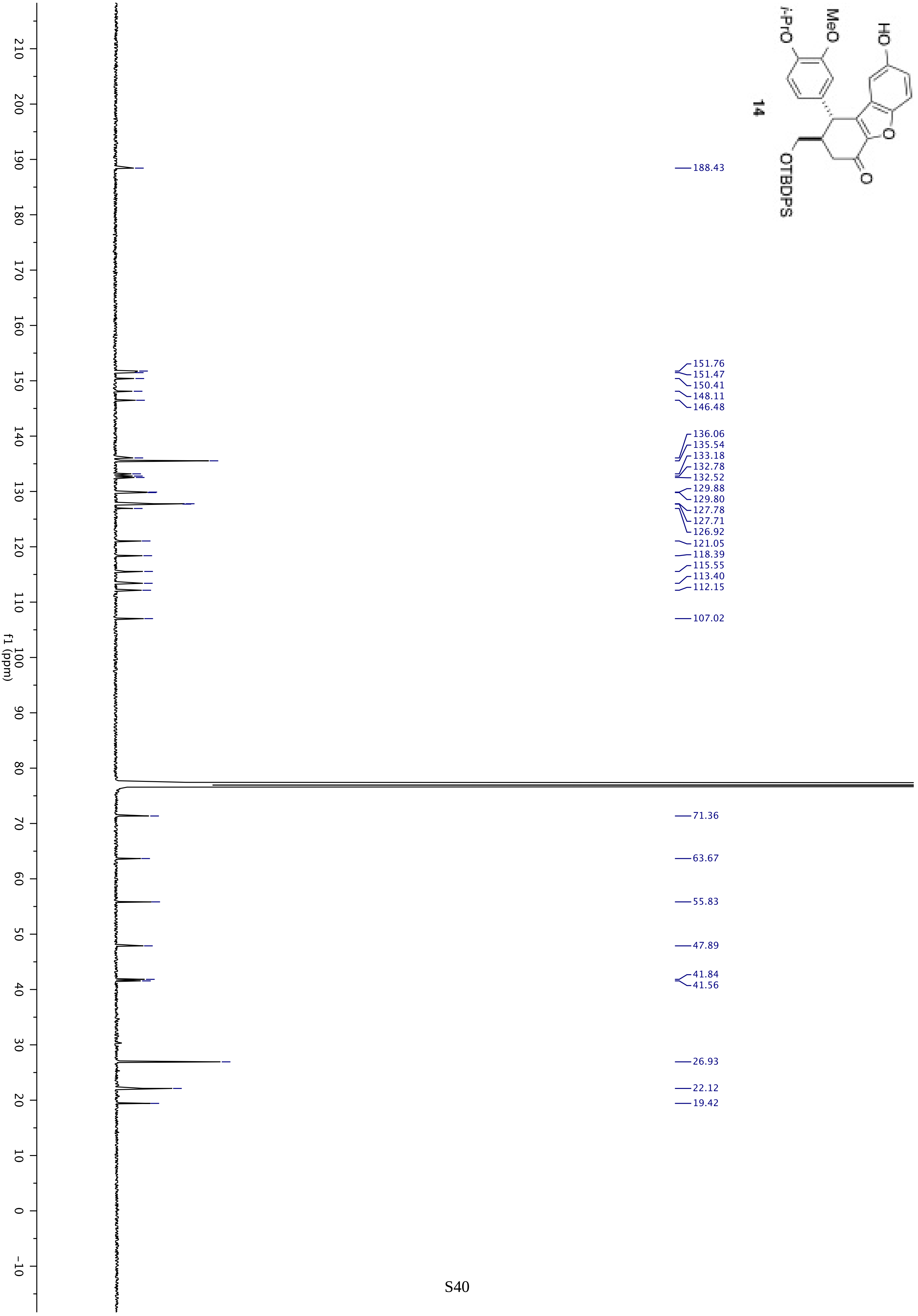

12
MeO
i-PrO
O
O
O
H
H
Br
OTBDPS
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
f1 (ppm)
4.13
0.74
0.12
4.36
1.11
3.73
0.95
0.83
3.08
2.04
0.85
2.17
0.86
5.68
9.46

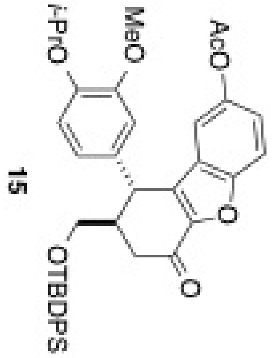

O
O
O
H
H
Br
MeO
i-PrO
OTBDPS

12

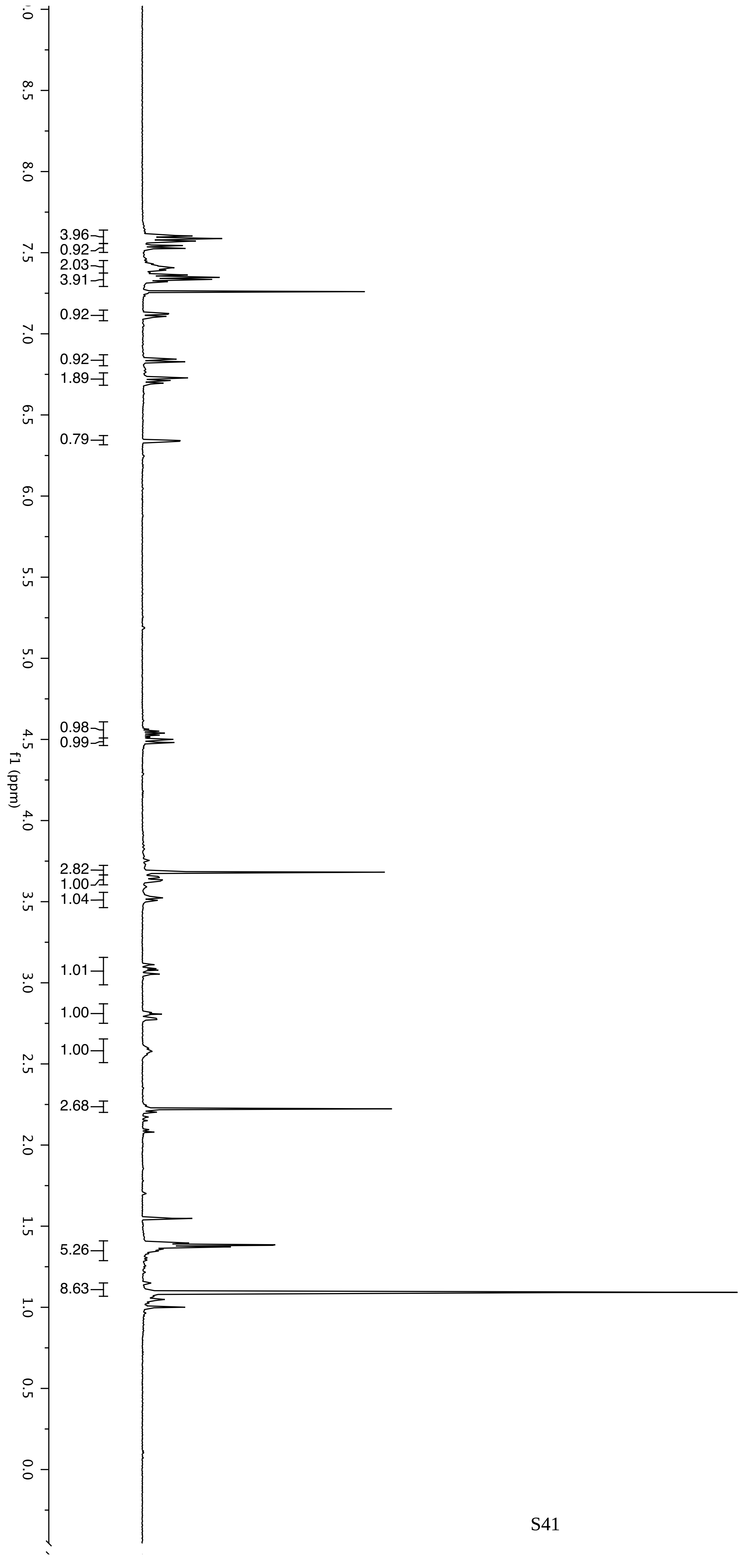

197.87
197.77
191.33
152.63
150.45
146.94
141.46
141.23
140.74
140.57
135.69
135.55
133.18
132.93
131.56
130.03
129.95
128.02
127.89
123.30
123.08
115.61
71.36
63.74
56.02
49.43
46.93
44.42
34.79
26.95
25.41
22.25
19.40
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
-10
f1 (ppm)


HO
MeO
i-PrO
O
O
OTBDPS
14
4.15
3.15
4.20
1.08
0.99
2.08
1.00
1.05
1.05
1.02
2.98
1.08
1.02
1.00
1.02
1.03
6.13
9.22
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)

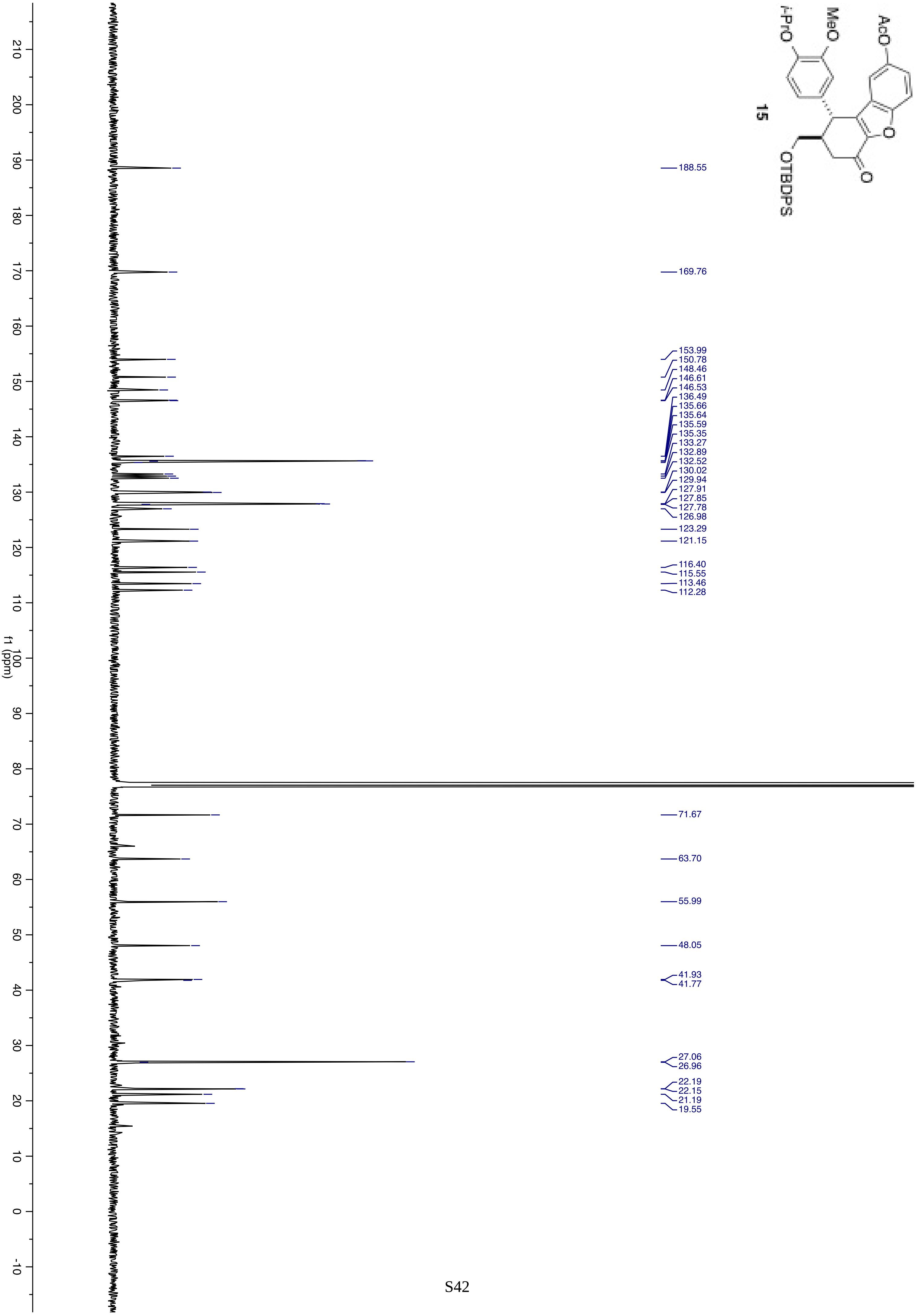

HO
MeO
i-PrO
O
O
OTBDPS
14
188.43
151.76
151.47
150.41
148.11
146.48
136.06
135.54
133.18
132.78
132.52
129.88
129.80
127.78
127.71
126.92
121.05
118.39
115.55
113.40
112.15
107.02
71.36
63.67
55.83
47.89
41.84
41.56
26.93
22.12
19.42
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
−10
f1 (ppm)

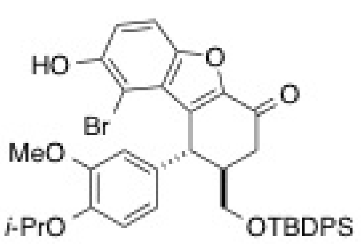


15

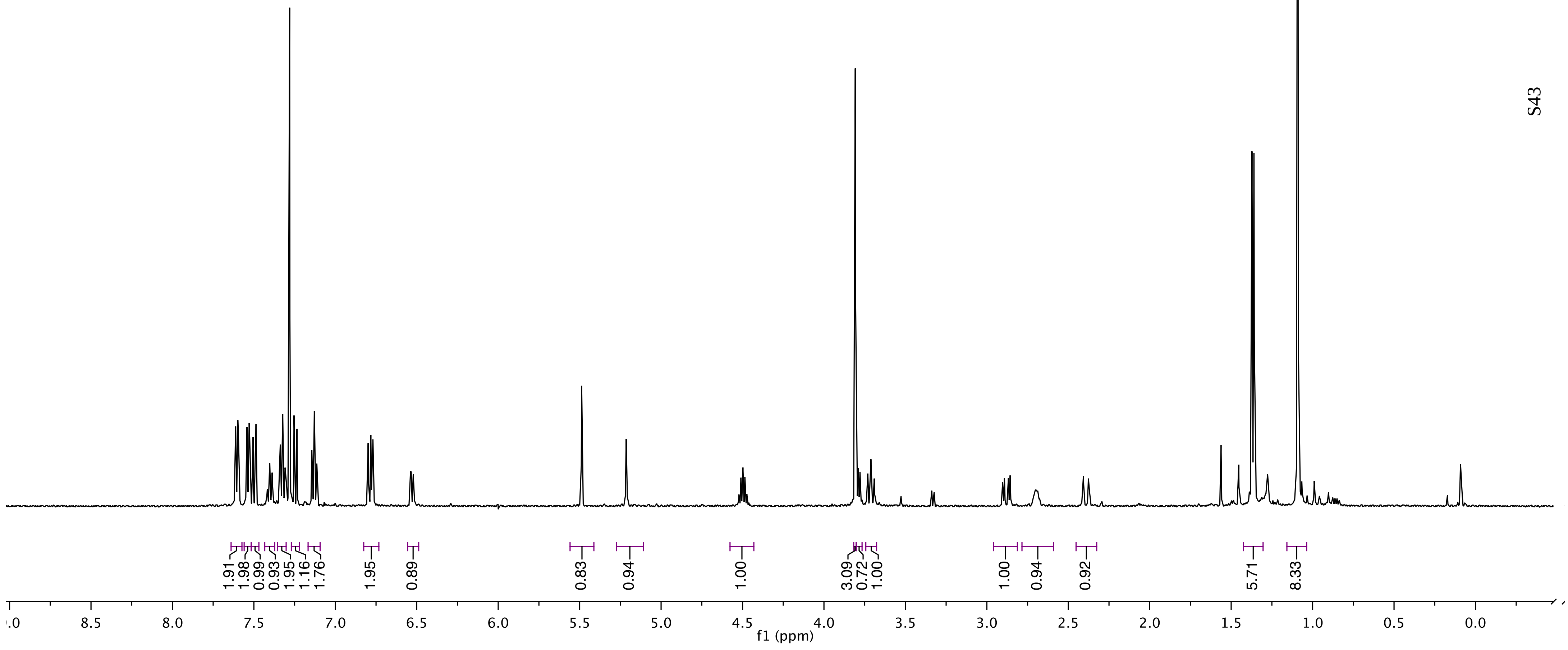


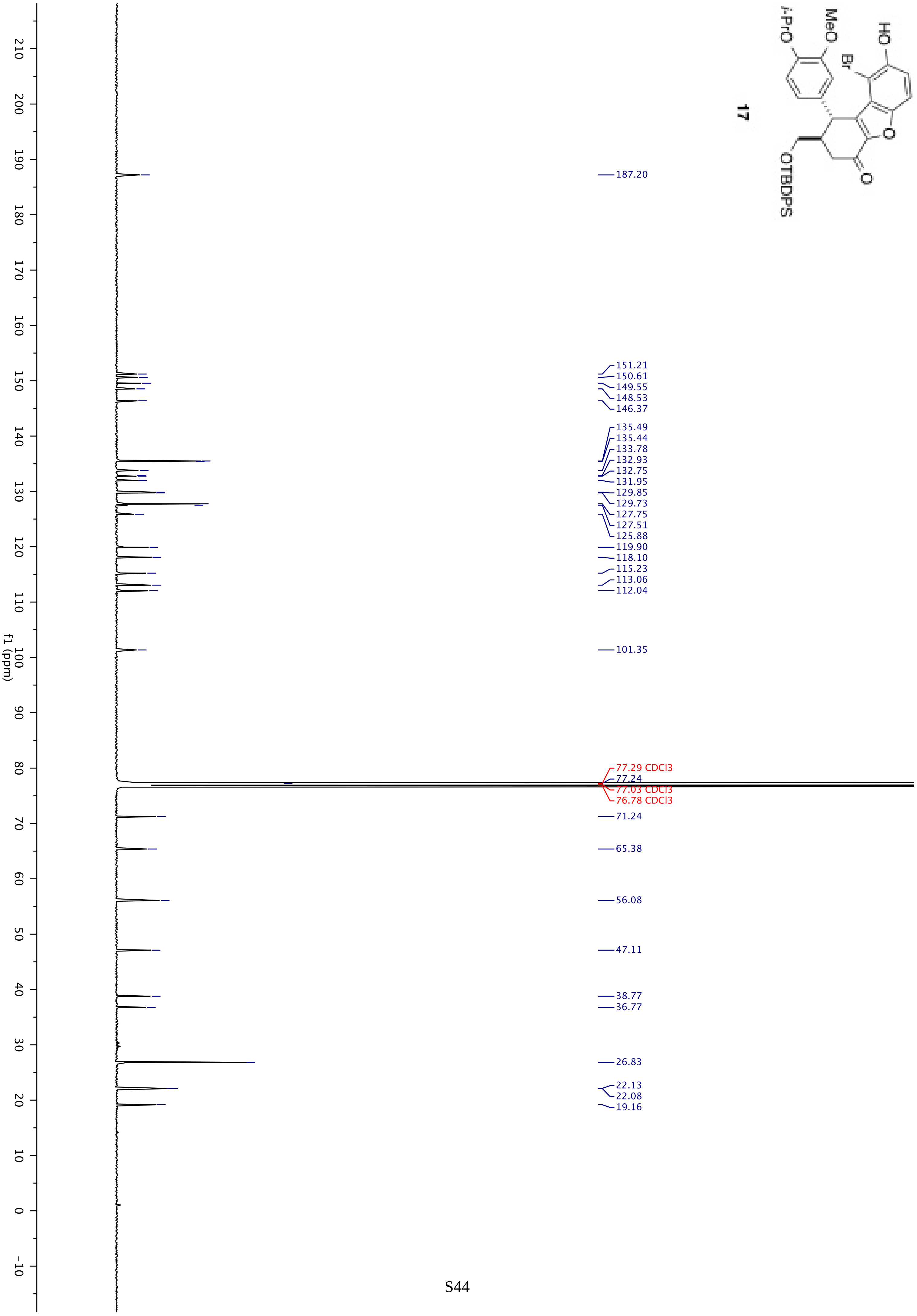
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
f1 (ppm)
3.96
0.92
2.03
3.91
0.92
0.92
1.89
0.79
0.98
0.99
2.82
1.00
1.04
1.01
1.00
1.00
2.68
5.26
8.63


AcO
O
O
MeO
i-PrO
OTBDPS
15
188.55
169.76
153.99
150.78
148.46
146.61
146.53
136.49
135.66
135.64
135.59
135.35
133.27
132.89
132.52
130.02
129.94
127.91
127.85
127.78
126.98
123.29
121.15
116.40
115.55
113.46
112.28
71.67
63.70
55.99
48.05
41.93
41.77
27.06
26.96
22.19
22.15
21.19
19.55
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
-10
f1 (ppm)

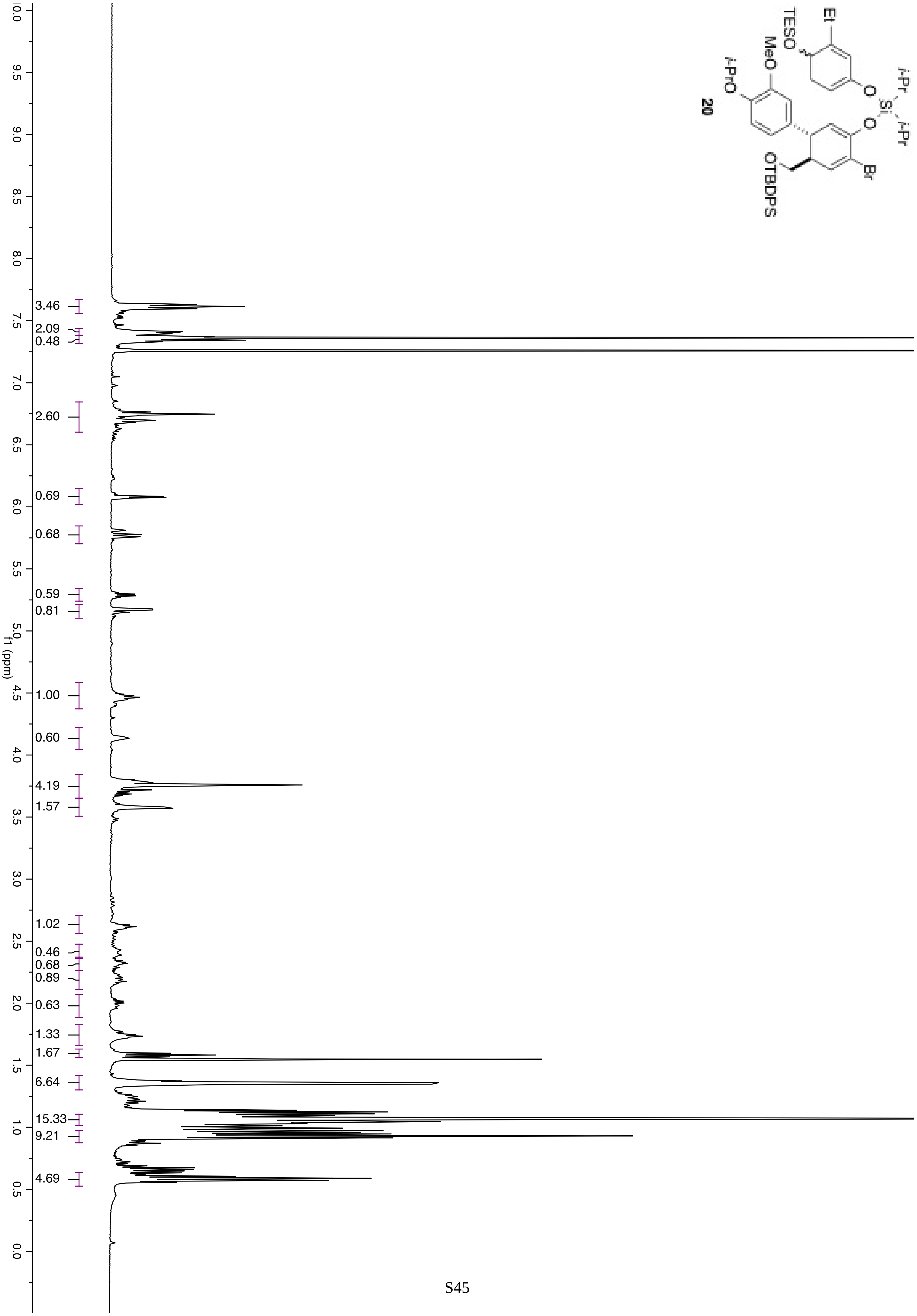


17

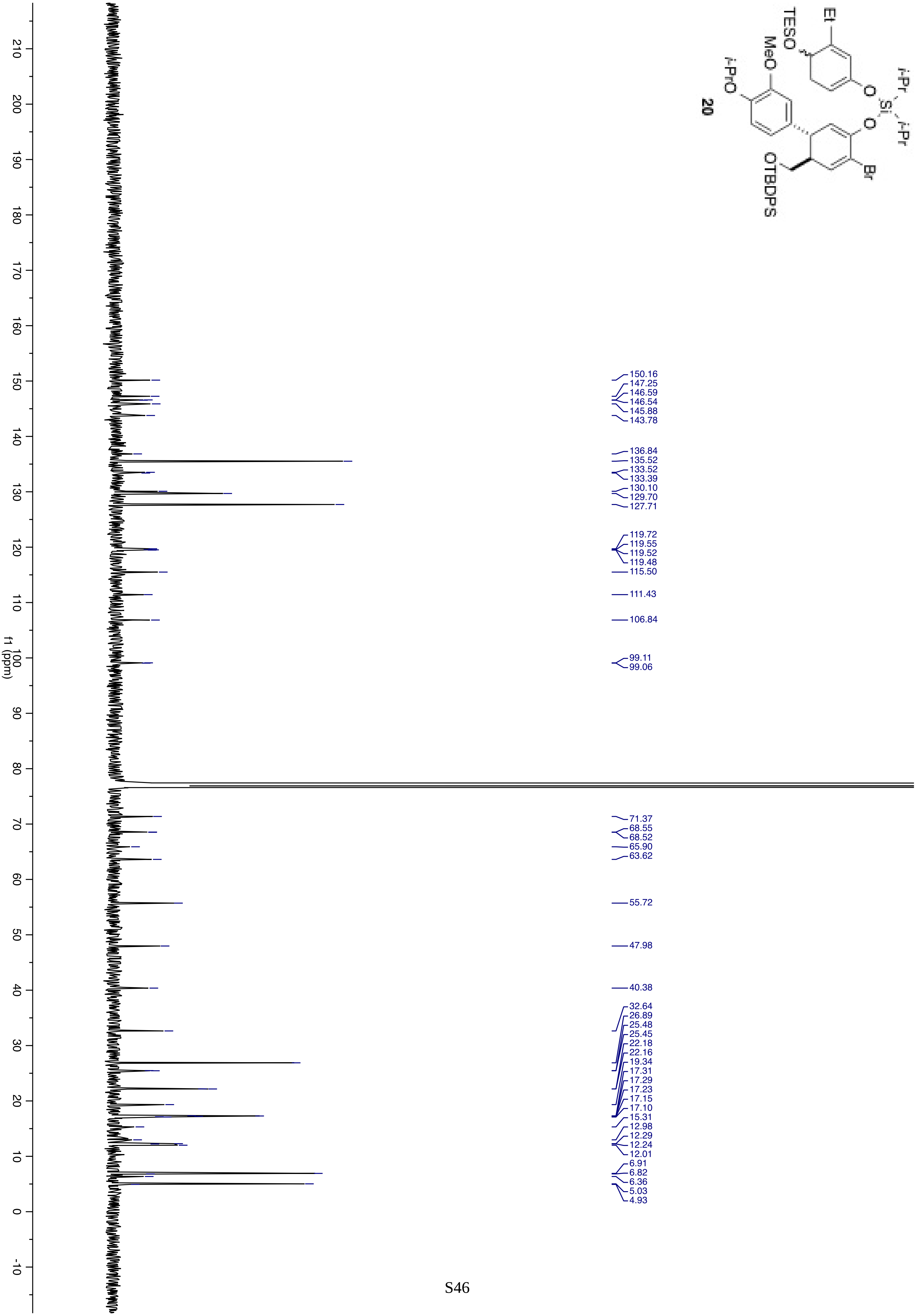

1.91
1.98
0.99
0.93
1.95
1.16
1.76
1.95
0.89
0.83
0.94
1.00
3.09
0.72
1.00
1.00
0.94
0.92
5.71
8.33
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
f1 (ppm)

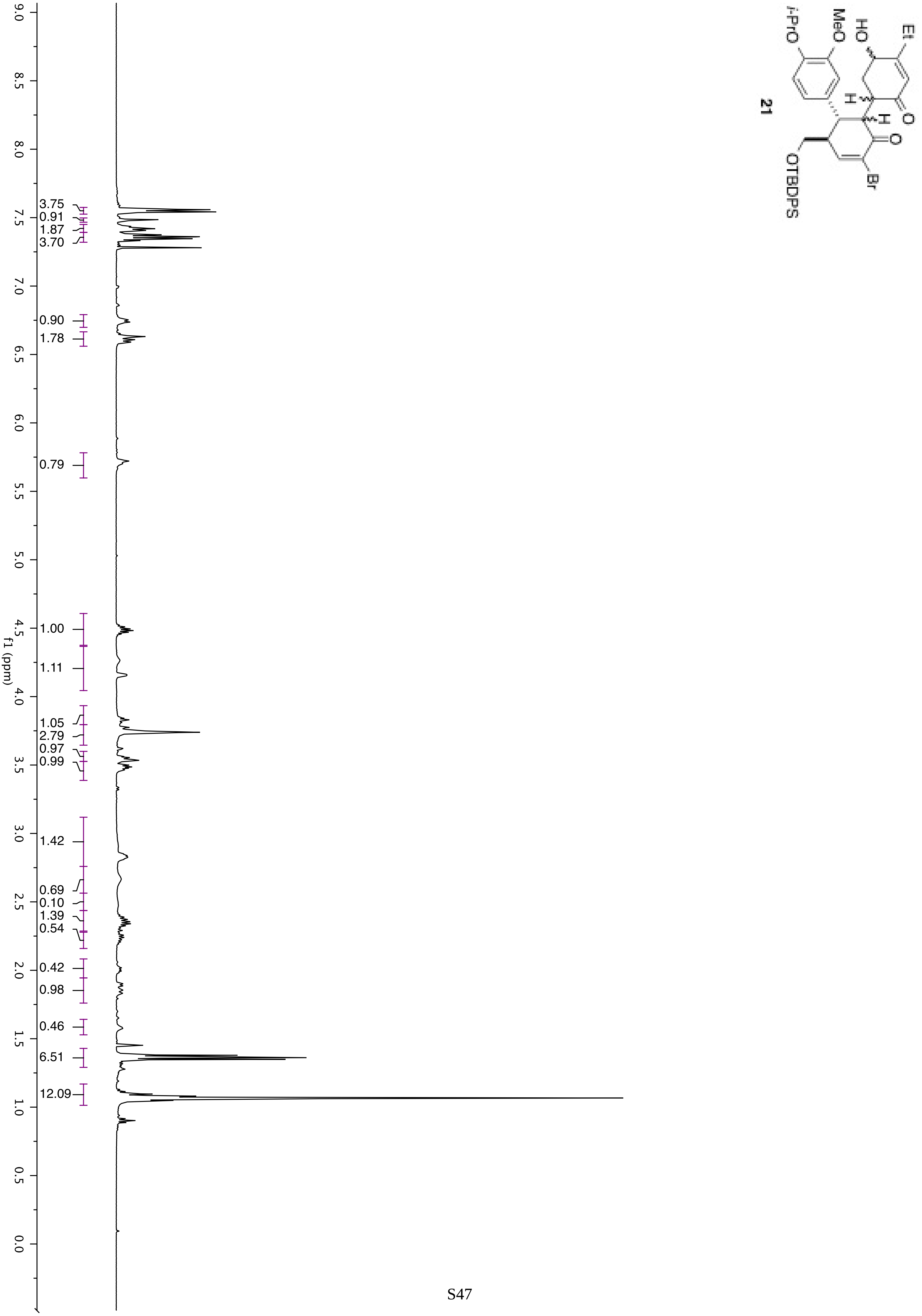


17
HO
Br
O
O
MeO
i-PrO
OTBDPS
187.20
151.21
150.61
149.55
148.53
146.37
135.49
135.44
133.78
132.93
132.75
131.95
129.85
129.73
127.75
127.51
125.88
119.90
118.10
115.23
113.06
112.04
101.35
77.29 CDCl3
77.24
77.03 CDCl3
76.78 CDCl3
71.24
65.38
56.08
47.11
38.77
36.77
26.83
22.13
22.08
19.16
f1 (ppm)
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
-10

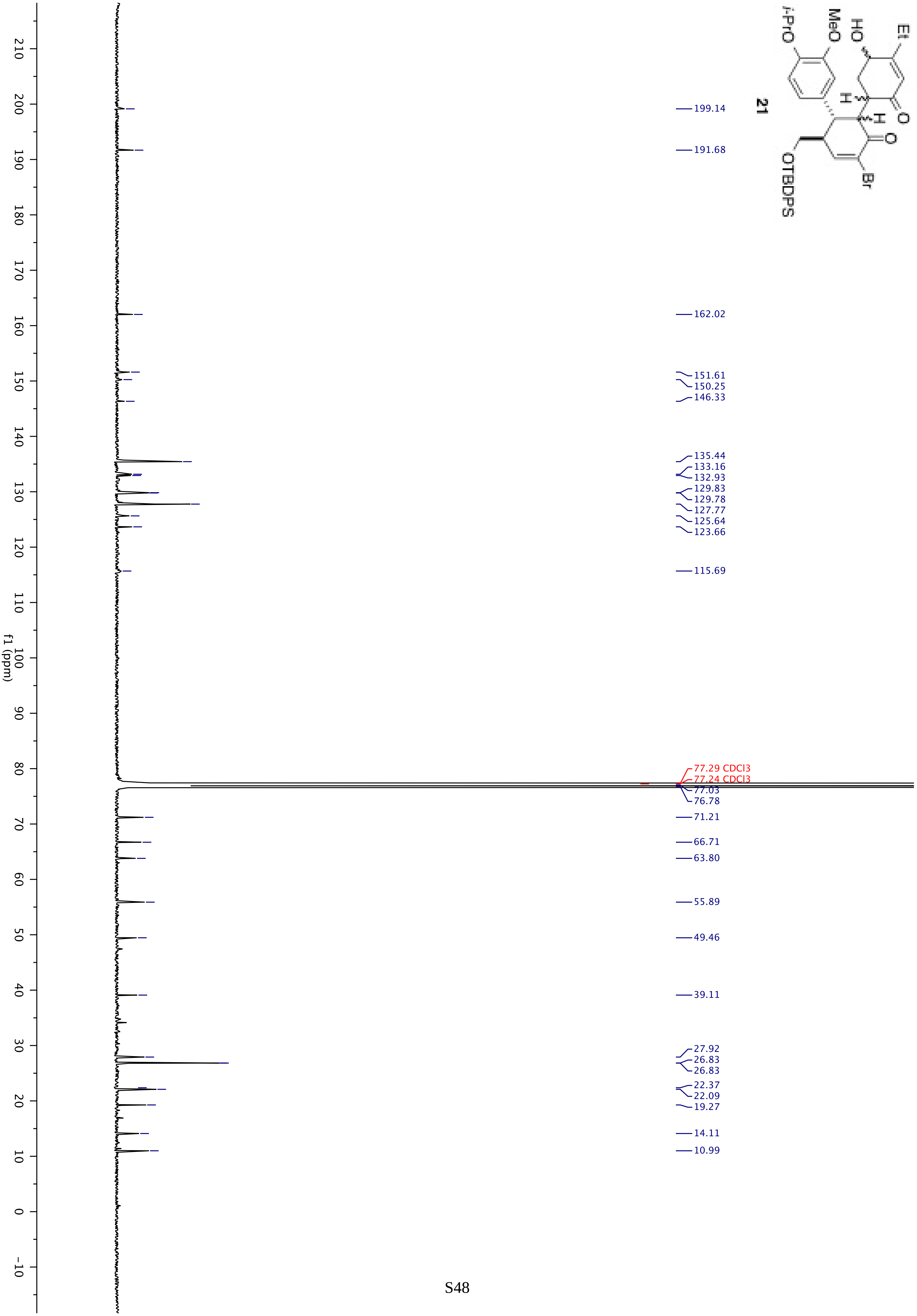
Et
TESO
MeO
i-PrO
i-Pr
Si
i-Pr
O
O
Br
OTBDPS
10.0
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
f1 (ppm)
3.46
2.09
0.48
2.60
0.69
0.68
0.59
0.81
1.00
0.60
4.19
1.57
1.02
0.46
0.68
0.89
0.63
1.33
1.67
6.64
15.33
9.21
4.69

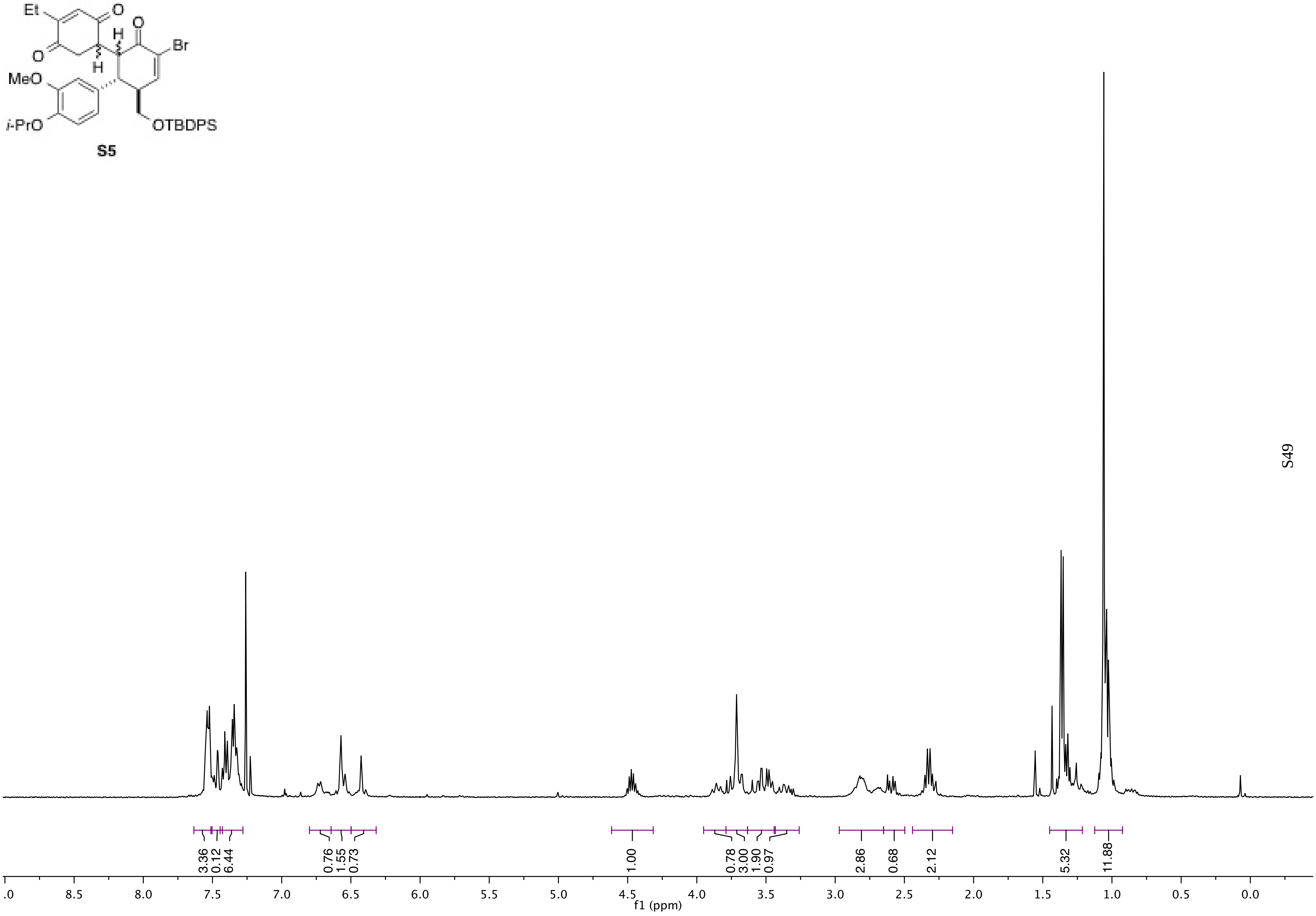
20


Et
TESO
i-Pr
Si
i-Pr
O
O
Br
MeO
i-PrO
OTBDPS
20
150.16
147.25
146.59
146.54
145.88
143.78
136.84
135.52
133.52
133.39
130.10
129.70
127.71
119.72
119.55
119.52
119.48
115.50
111.43
106.84
99.11
99.06
71.37
68.55
68.52
65.90
63.62
55.72
47.98
40.38
32.64
26.89
25.48
25.45
22.18
22.16
19.34
17.31
17.29
17.23
17.15
17.10
15.31
12.98
12.29
12.24
12.01
6.91
6.82
6.36
5.03
4.93
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
-10
f1 (ppm)

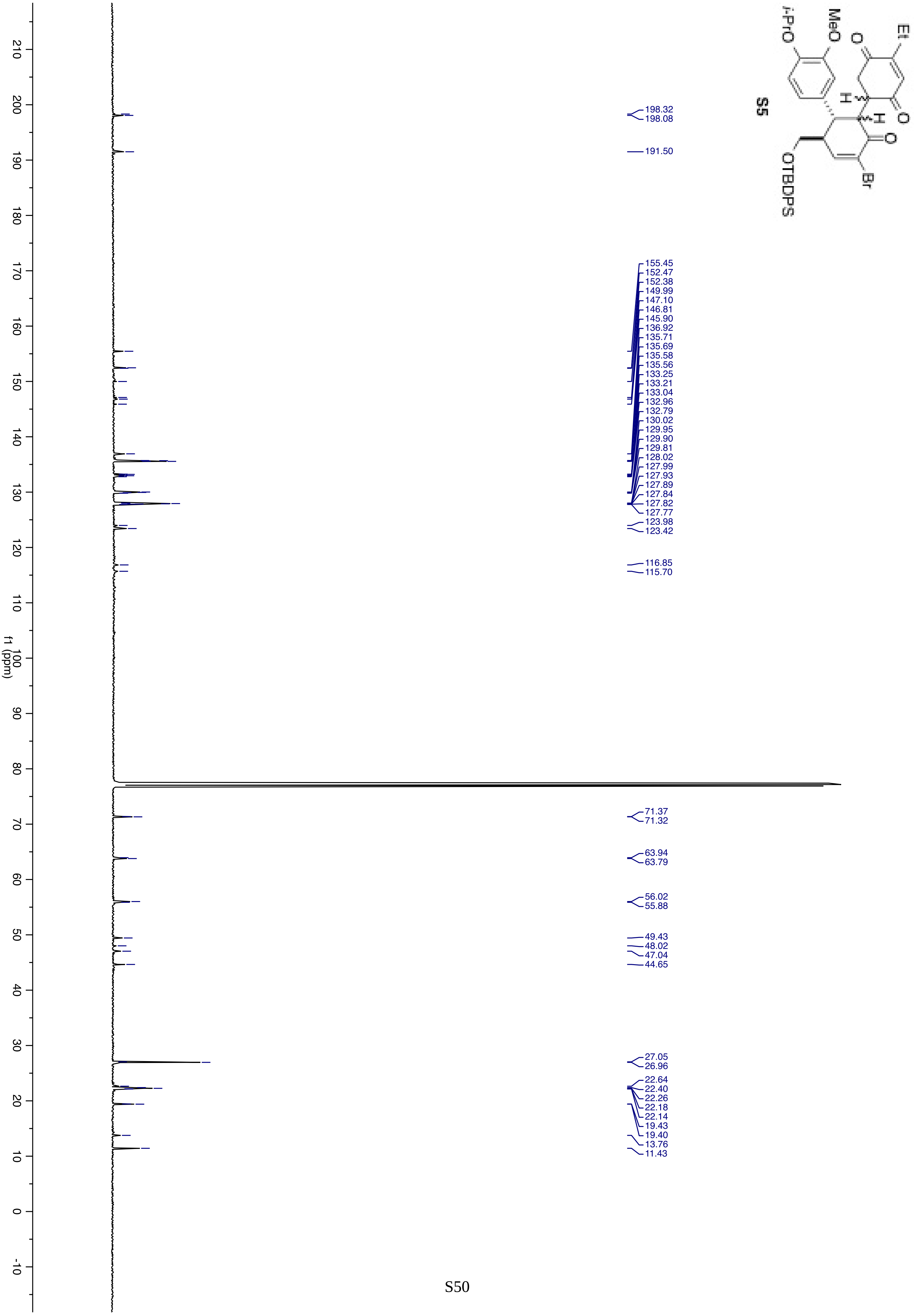

Et
HO
MeO
i-PrO
O
H
H
O
Br
OTBDPS
3.75
0.91
1.87
3.70
0.90
1.78
0.79
1.00
1.11
1.05
2.79
0.97
0.99
1.42
0.69
0.10
1.39
0.54
0.42
0.98
0.46
6.51
12.09
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
f1 (ppm)

21

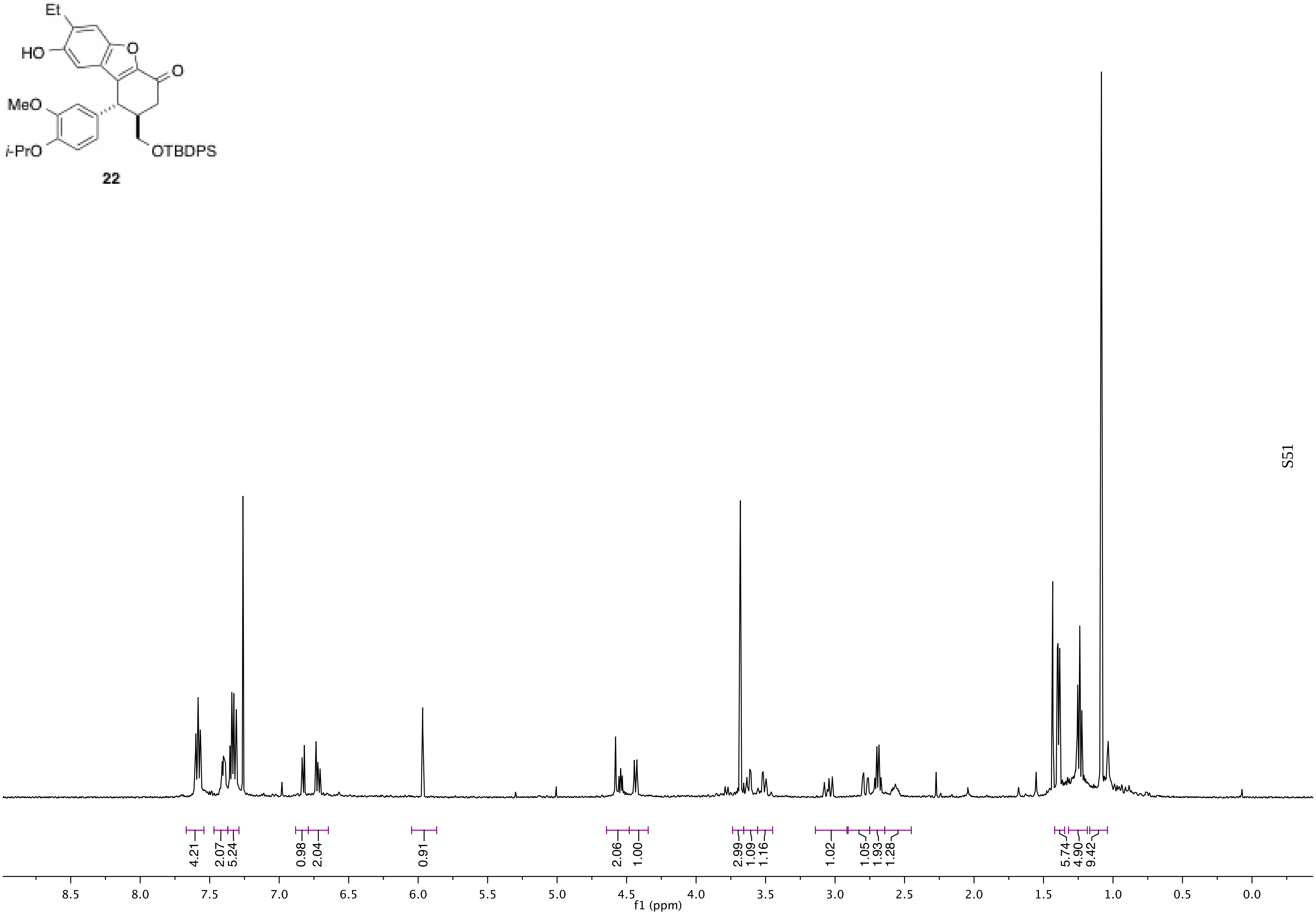

21
Et
HO
MeO
i-PrO
O
H
H
O
Br
OTBDPS
199.14
191.68
162.02
151.61
150.25
146.33
135.44
133.16
132.93
129.83
129.78
127.77
125.64
123.66
115.69
77.29 CDCl3
77.24 CDCl3
77.03
76.78
71.21
66.71
63.80
55.89
49.46
39.11
27.92
26.83
26.83
22.37
22.09
19.27
14.11
10.99
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
−10
f1 (ppm)


Et
O
O
H
H
O
Br
MeO
i-PrO
OTBDPS
3.36
0.12
6.44
0.76
1.55
0.73
1.00
0.78
3.00
1.90
0.97
2.86
0.68
2.12
5.32
11.88
.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)

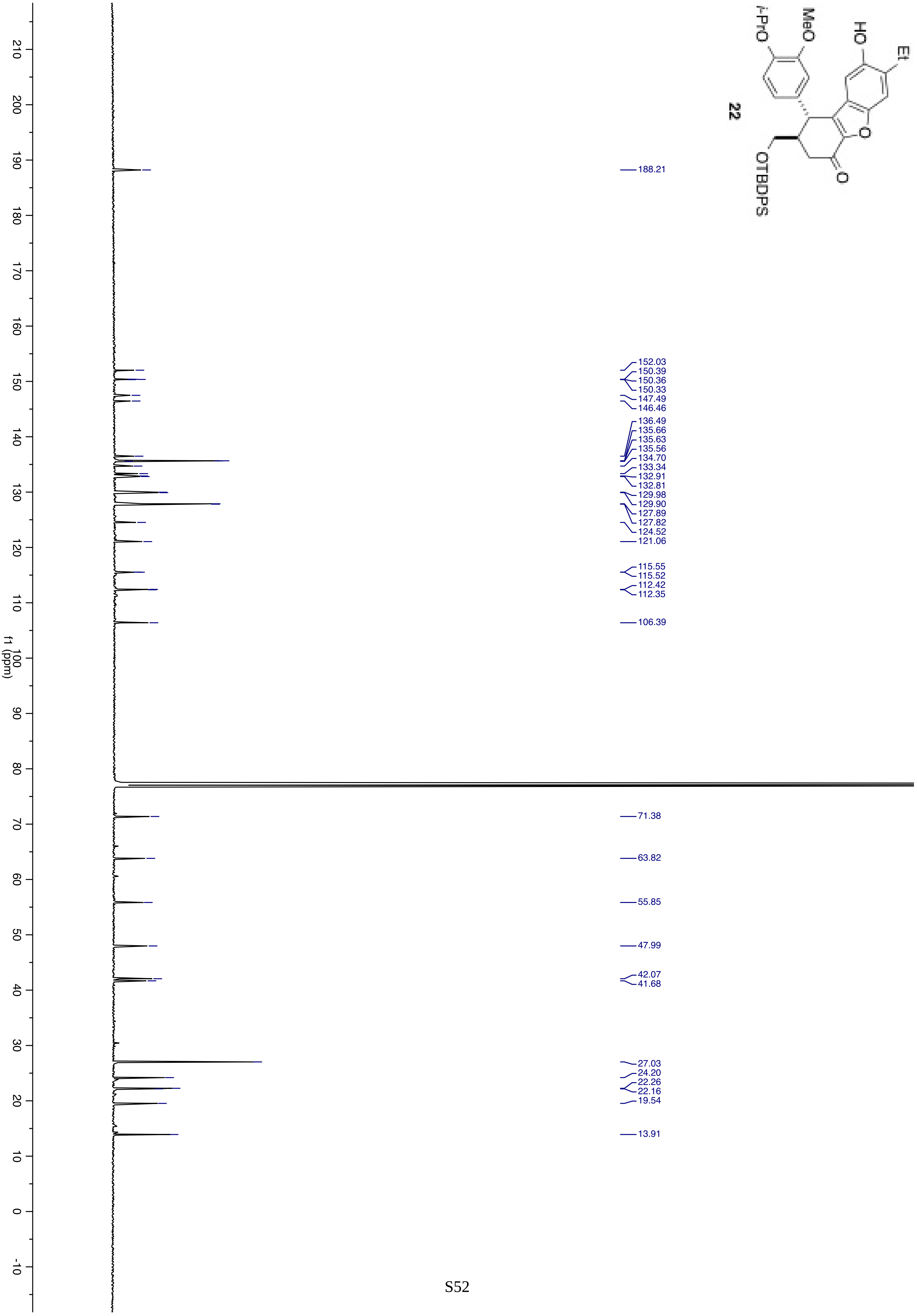
S5

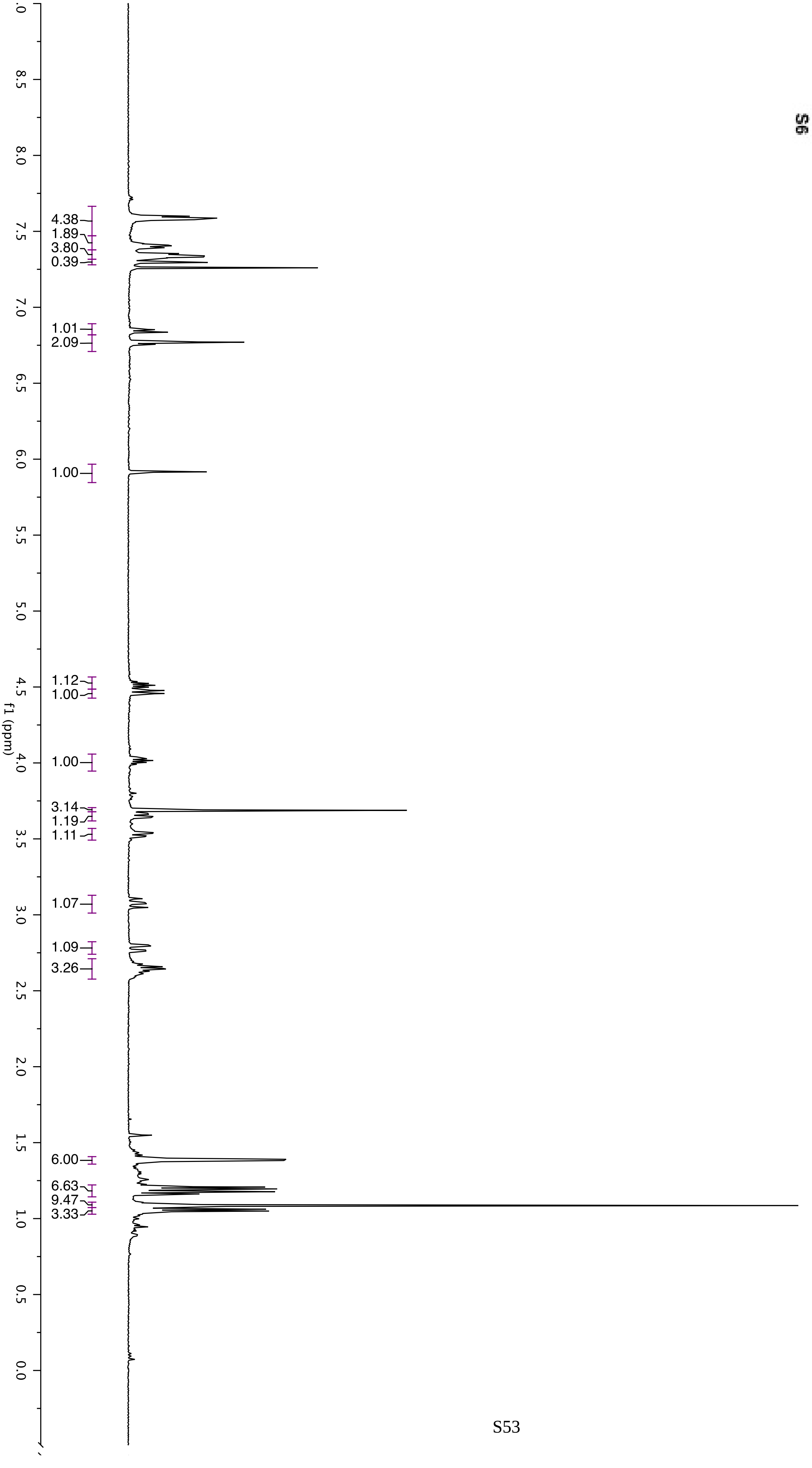

S5

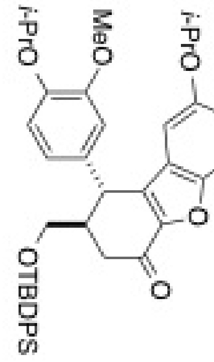
Et
O
O
MeO
i-PrO
H
H
O
Br
OTBDPS
198.32
198.08
191.50
155.45
152.47
152.38
149.99
147.10
146.81
145.90
136.92
135.71
135.69
135.58
135.56
133.25
133.21
133.04
132.96
132.79
130.02
129.95
129.90
129.81
128.02
127.99
127.93
127.89
127.84
127.82
127.77
123.98
123.42
116.85
115.70
71.37
71.32
63.94
63.79
56.02
55.88
49.43
48.02
47.04
44.65
27.05
26.96
22.64
22.40
22.26
22.18
22.14
19.43
19.40
13.76
11.43
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
-10
f1 (ppm)


Et
HO
O
O
MeO
i-PrO
OTBDPS
4.21
2.07
5.24
0.98
2.04
0.91
2.06
1.00
2.99
1.09
1.16
1.02
1.05
1.93
1.28
5.74
4.90
9.42
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)

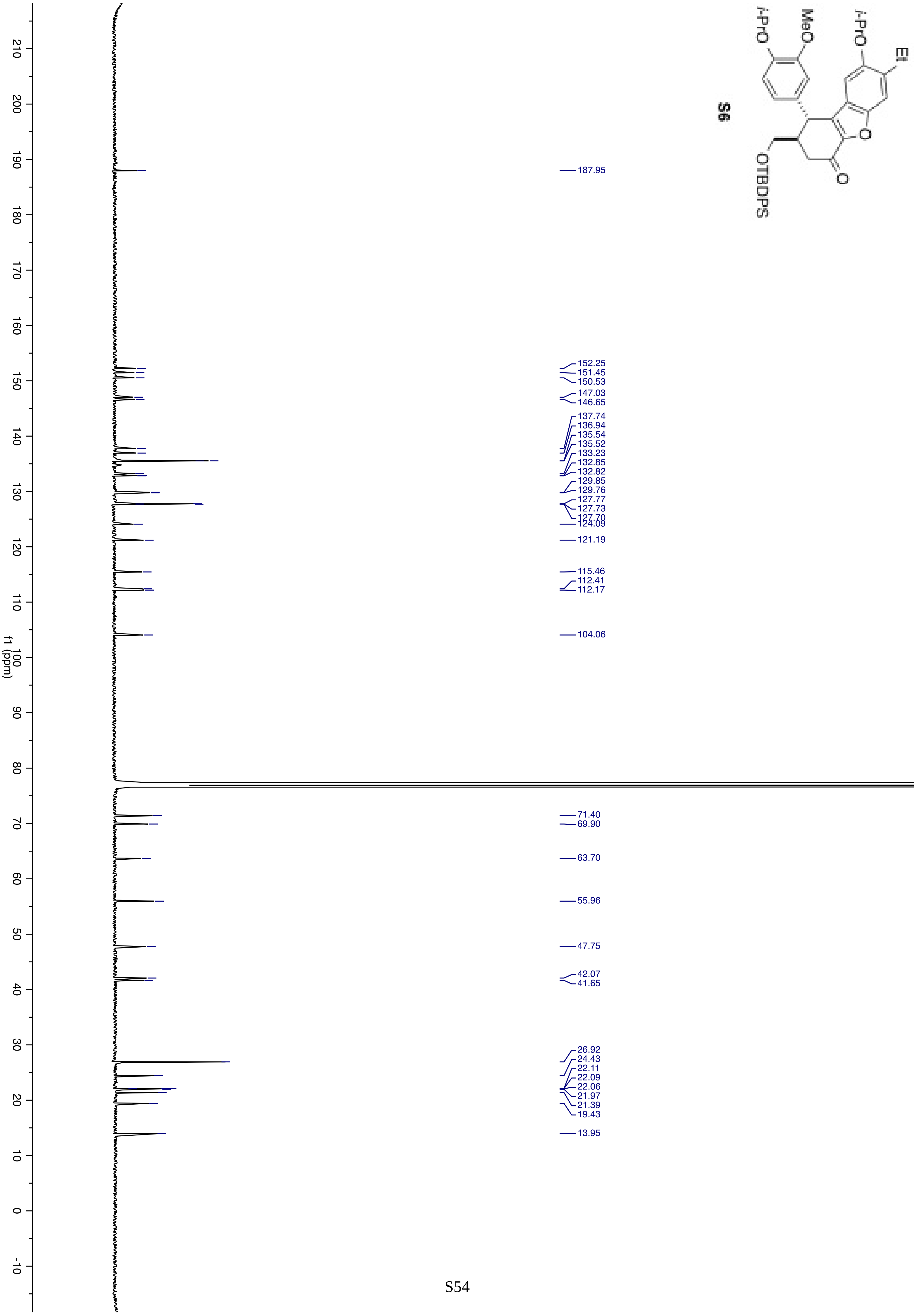
22


22
Et
HO
MeO
i-PrO
O
OTBDPS
188.21
152.03
150.39
150.36
150.33
147.49
146.46
136.49
135.66
135.63
135.56
134.70
133.34
132.91
132.81
129.98
129.90
127.89
127.82
124.52
121.06
115.55
115.52
112.42
112.35
106.39
71.38
63.82
55.85
47.99
42.07
41.68
27.03
24.20
22.26
22.16
19.54
13.91
f1 (ppm)
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
-10


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)
4.38
1.89
3.80
0.39
1.01
2.09
1.00
1.12
1.00
1.00
3.14
1.19
1.11
1.07
1.09
3.26
6.00
6.63
9.47
3.33

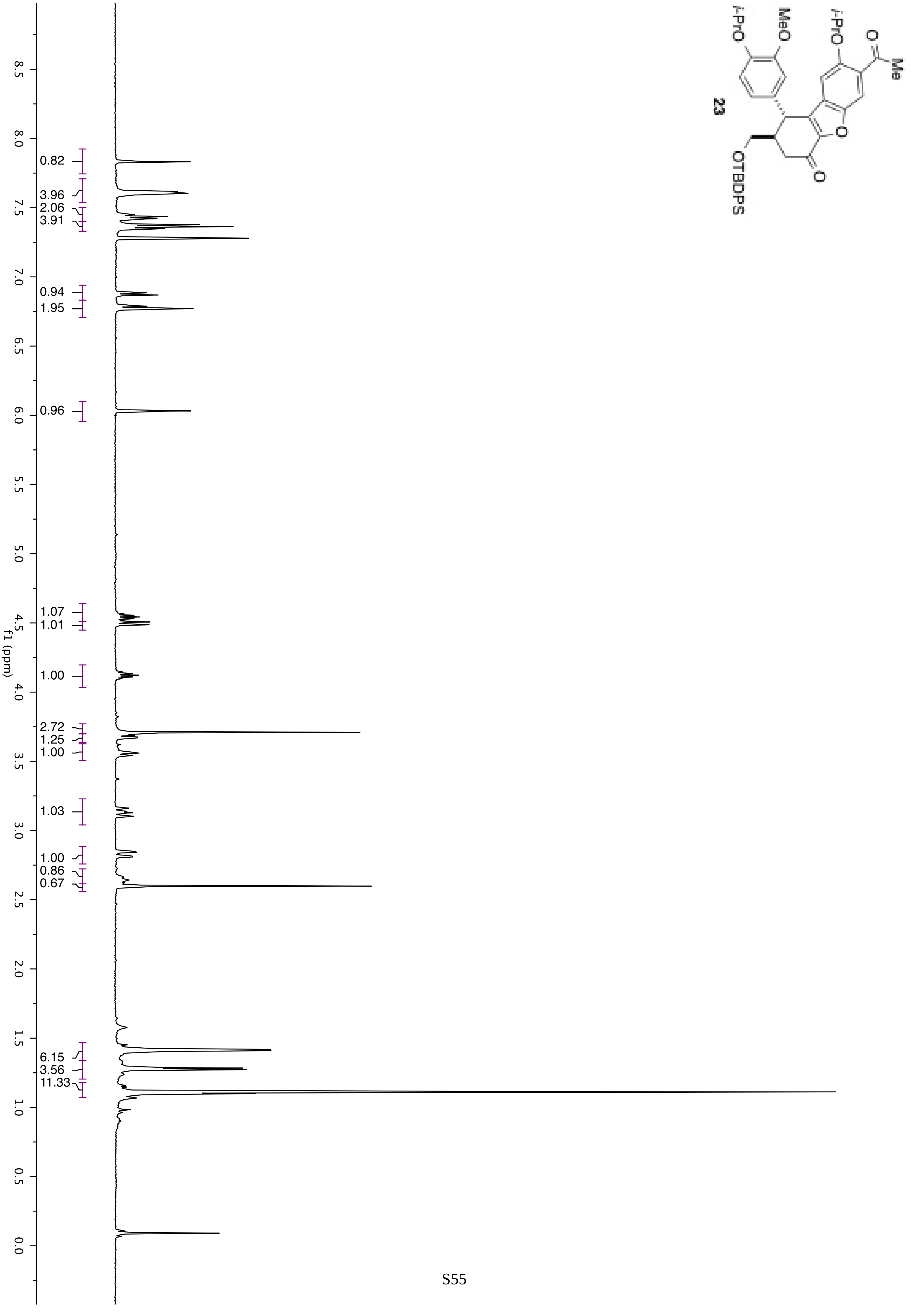

Et
i-PrO
O
O
MeO
i-PrO
OTBDPS

S6



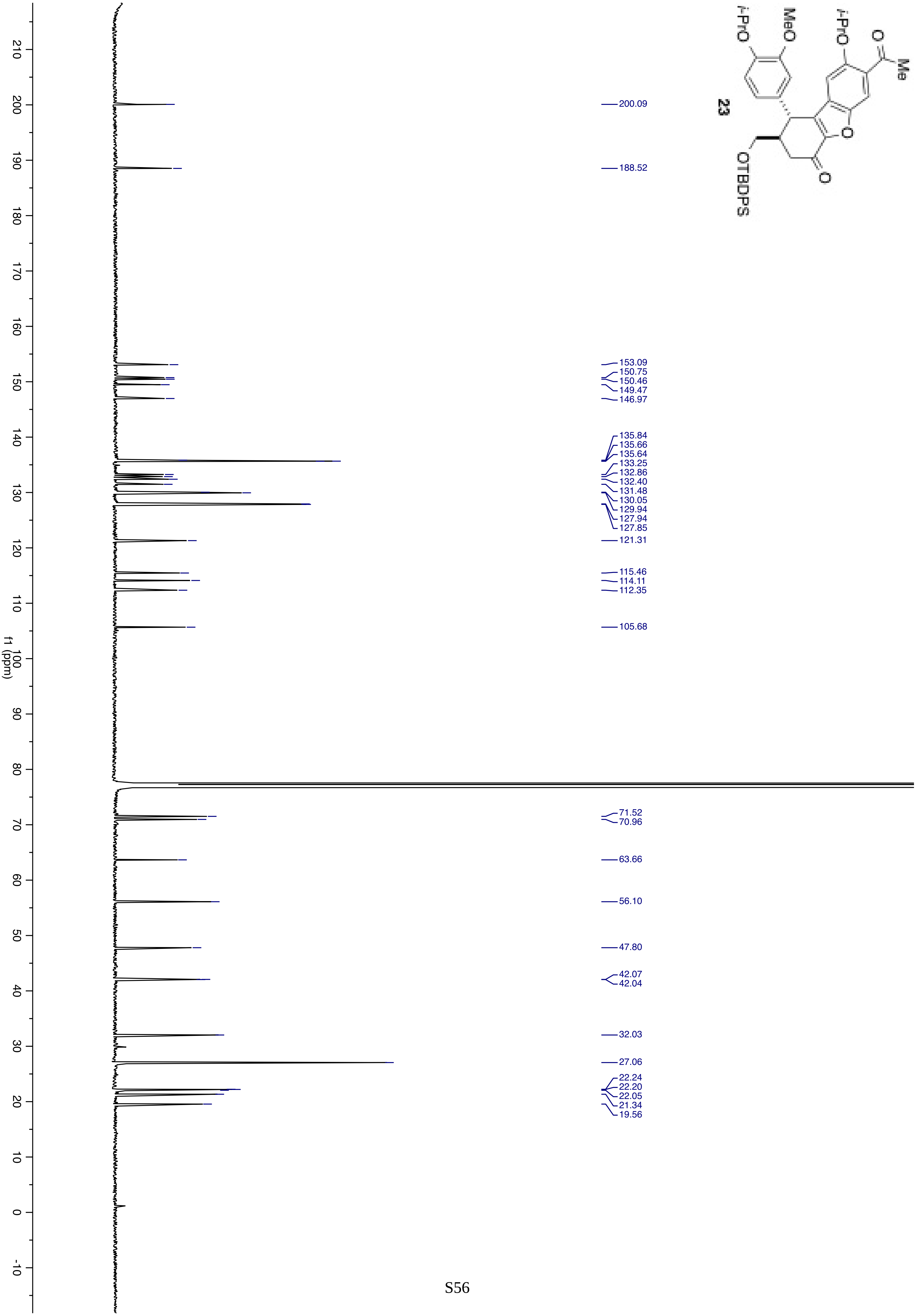
i-PrO
MeO
i-PrO
Et
O
O
OTBDPS
187.95
152.25
151.45
150.53
147.03
146.65
137.74
136.94
135.54
135.52
133.23
132.85
132.82
129.85
129.76
127.77
127.73
127.70
124.09
121.19
115.46
112.41
112.17
104.06
71.40
69.90
63.70
55.96
47.75
42.07
41.65
26.92
24.43
22.11
22.09
22.06
21.97
21.39
19.43
13.95
f1 (ppm)
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
-10

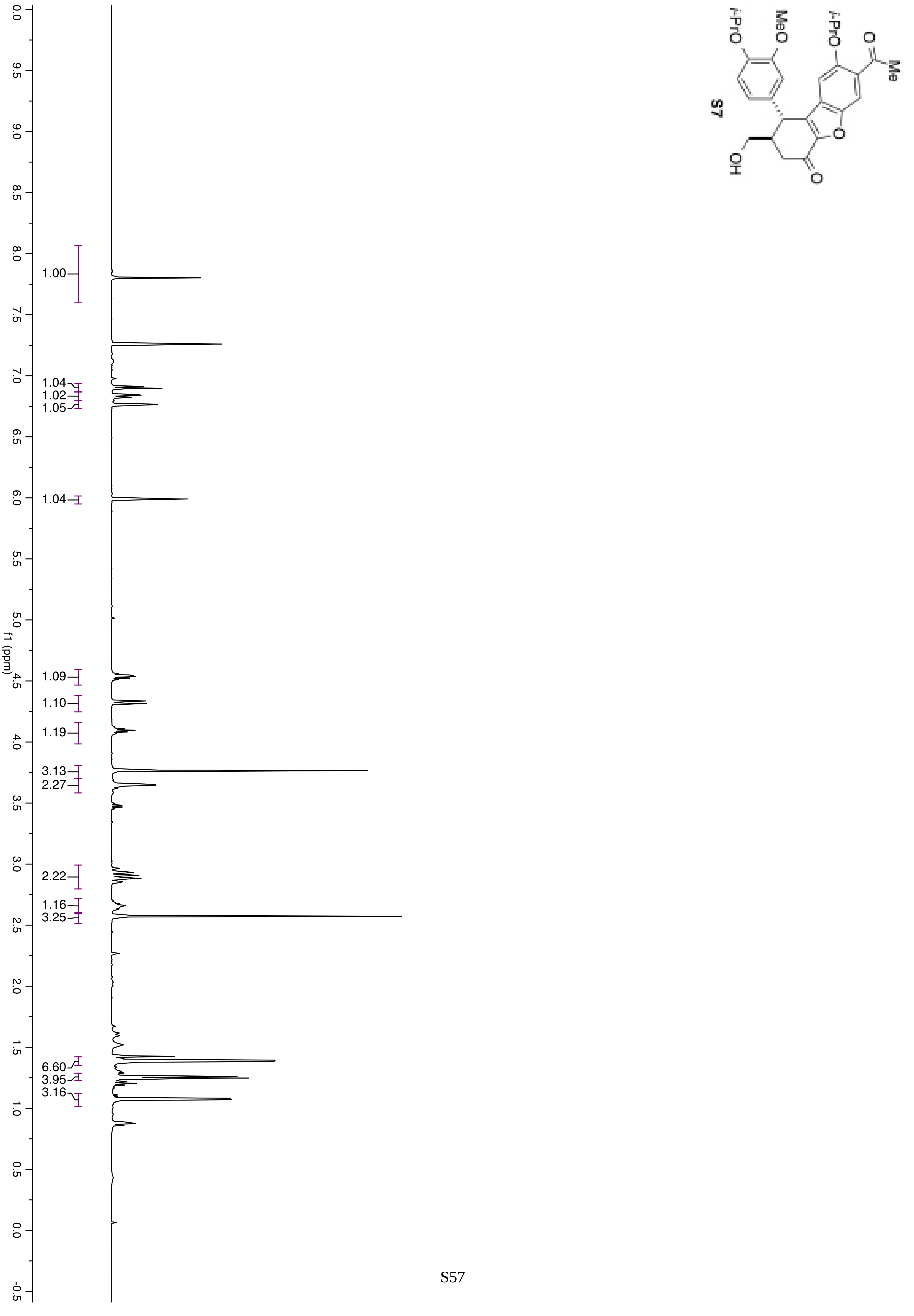
S6



23

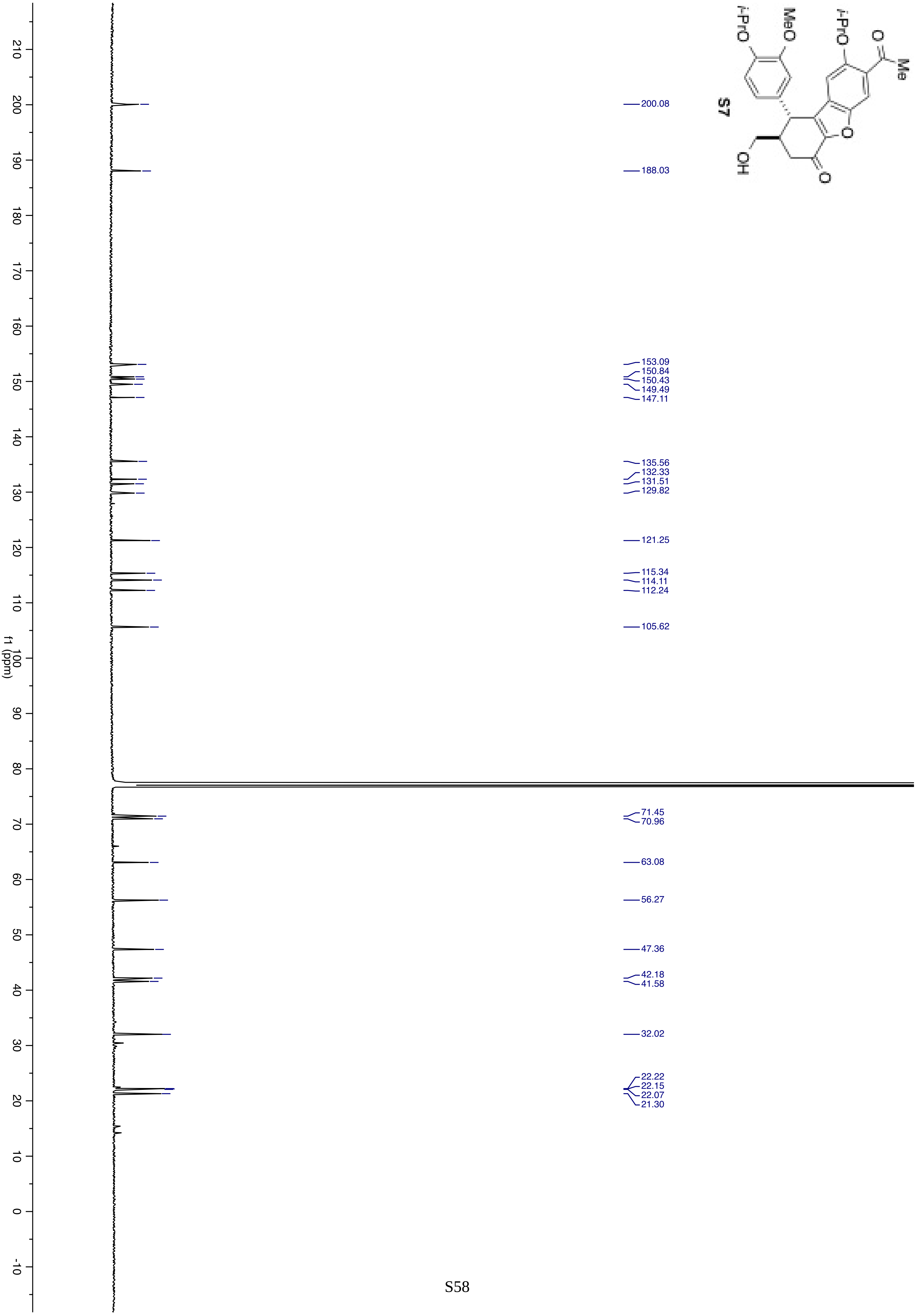
i-PrO
MeO
i-PrO
O
Me
O
O
OTBDPS
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
f1 (ppm)
0.82
3.96
2.06
3.91
0.94
1.95
0.96
1.07
1.01
1.00
2.72
1.25
1.00
1.03
1.00
0.86
0.67
6.15
3.56
11.33


23
i-PrO
MeO
i-PrO
O
Me
O
O
OTBDPS
200.09
188.52
153.09
150.75
150.46
149.47
146.97
135.84
135.66
135.64
133.25
132.86
132.40
131.48
130.05
129.94
127.94
127.85
121.31
115.46
114.11
112.35
105.68
71.52
70.96
63.66
56.10
47.80
42.07
42.04
32.03
27.06
22.24
22.20
22.05
21.34
19.56
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
-10
f1 (ppm)

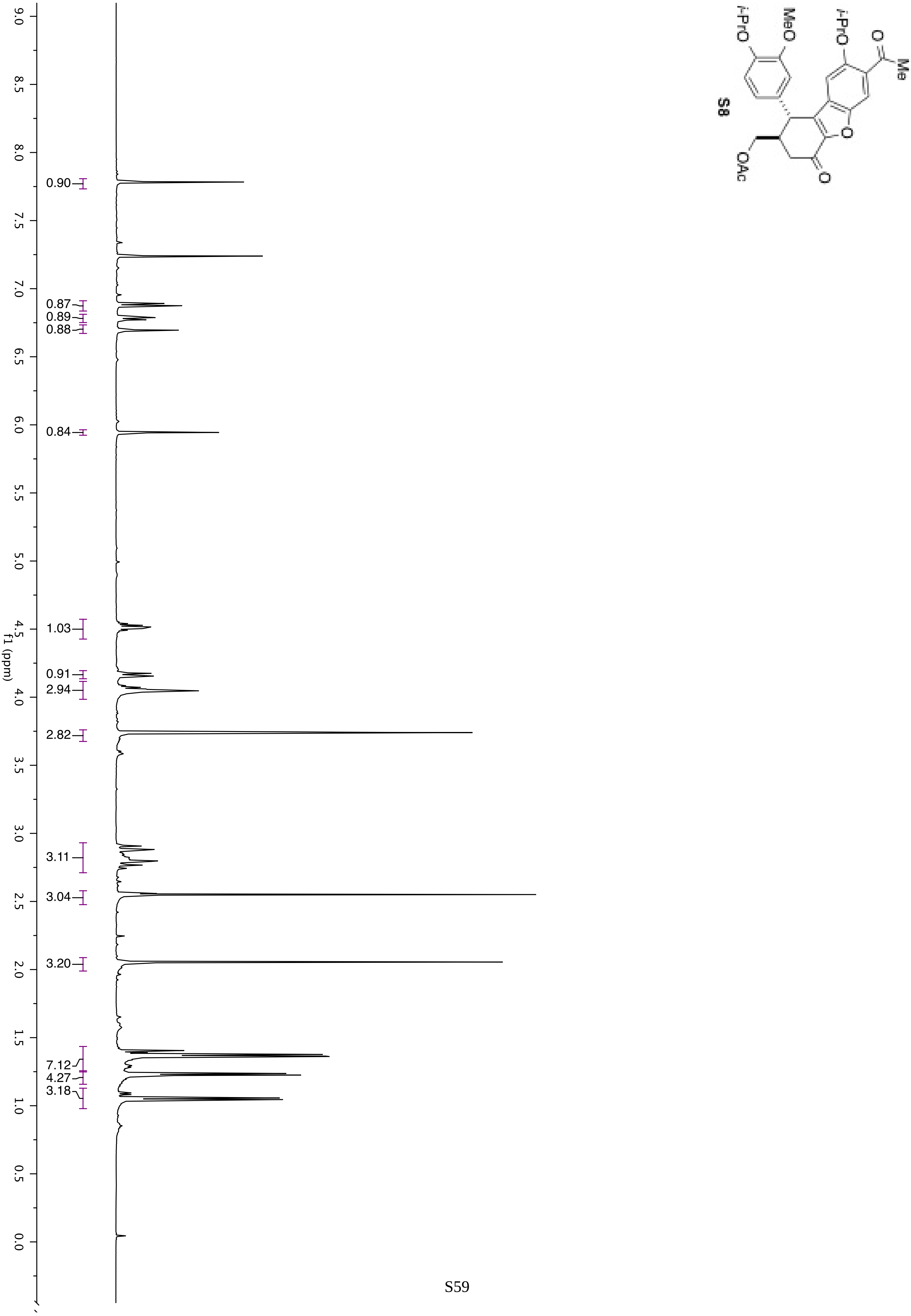


i-PrO
MeO
i-PrO
O
Me
O
O
OH
10.0
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
-0.5
f1 (ppm)
1.00
1.04
1.02
1.05
1.04
1.09
1.10
1.19
3.13
2.27
2.22
1.16
3.25
6.60
3.95
3.16

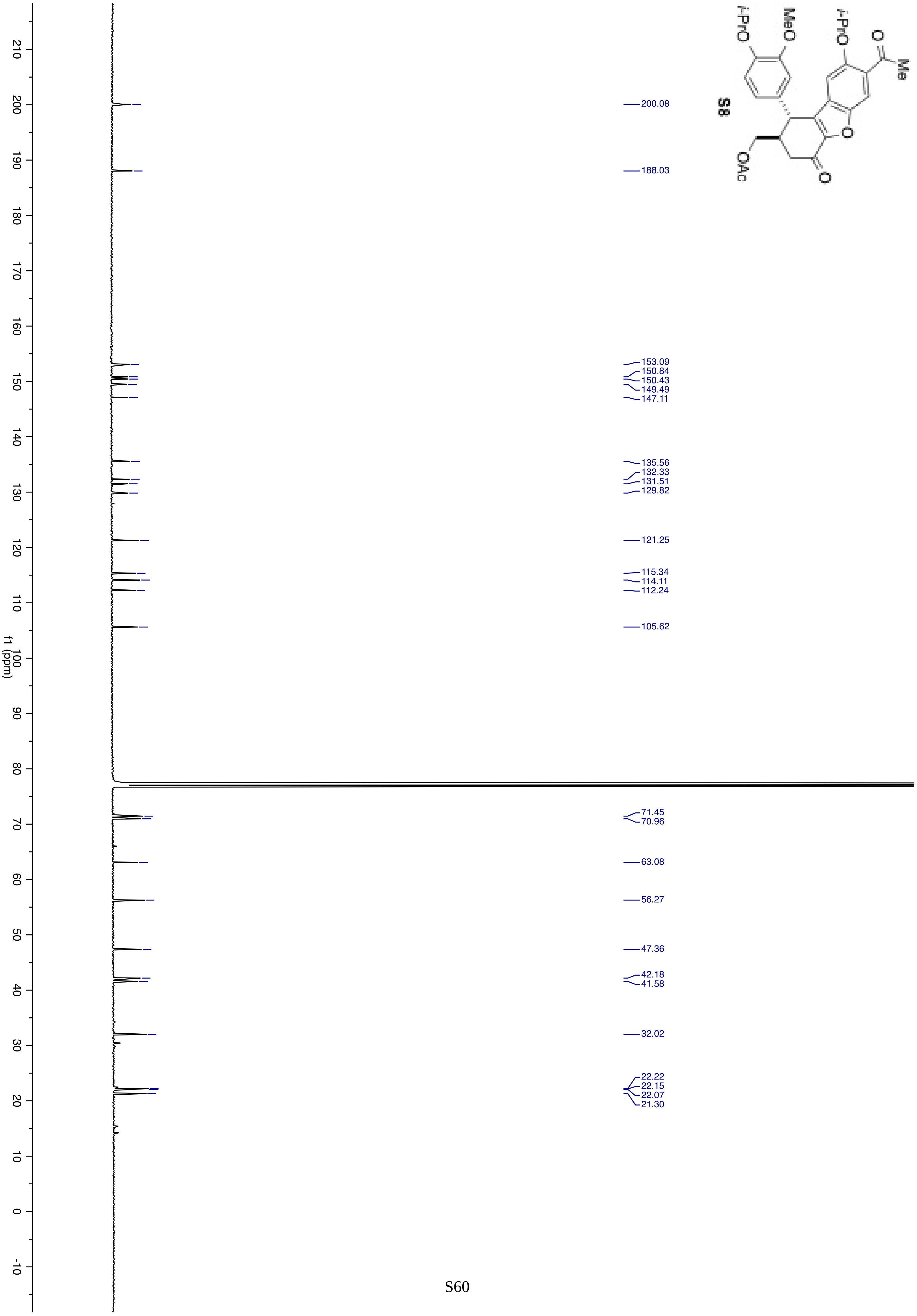
S7


200.08
188.03
153.09
150.84
150.43
149.49
147.11
135.56
132.33
131.51
129.82
121.25
115.34
114.11
112.24
105.62
71.45
70.96
63.08
56.27
47.36
42.18
41.58
32.02
22.22
22.15
22.07
21.30
f1 (ppm)
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
-10
i-PrO
MeO
i-PrO
O
Me
O
O
OH

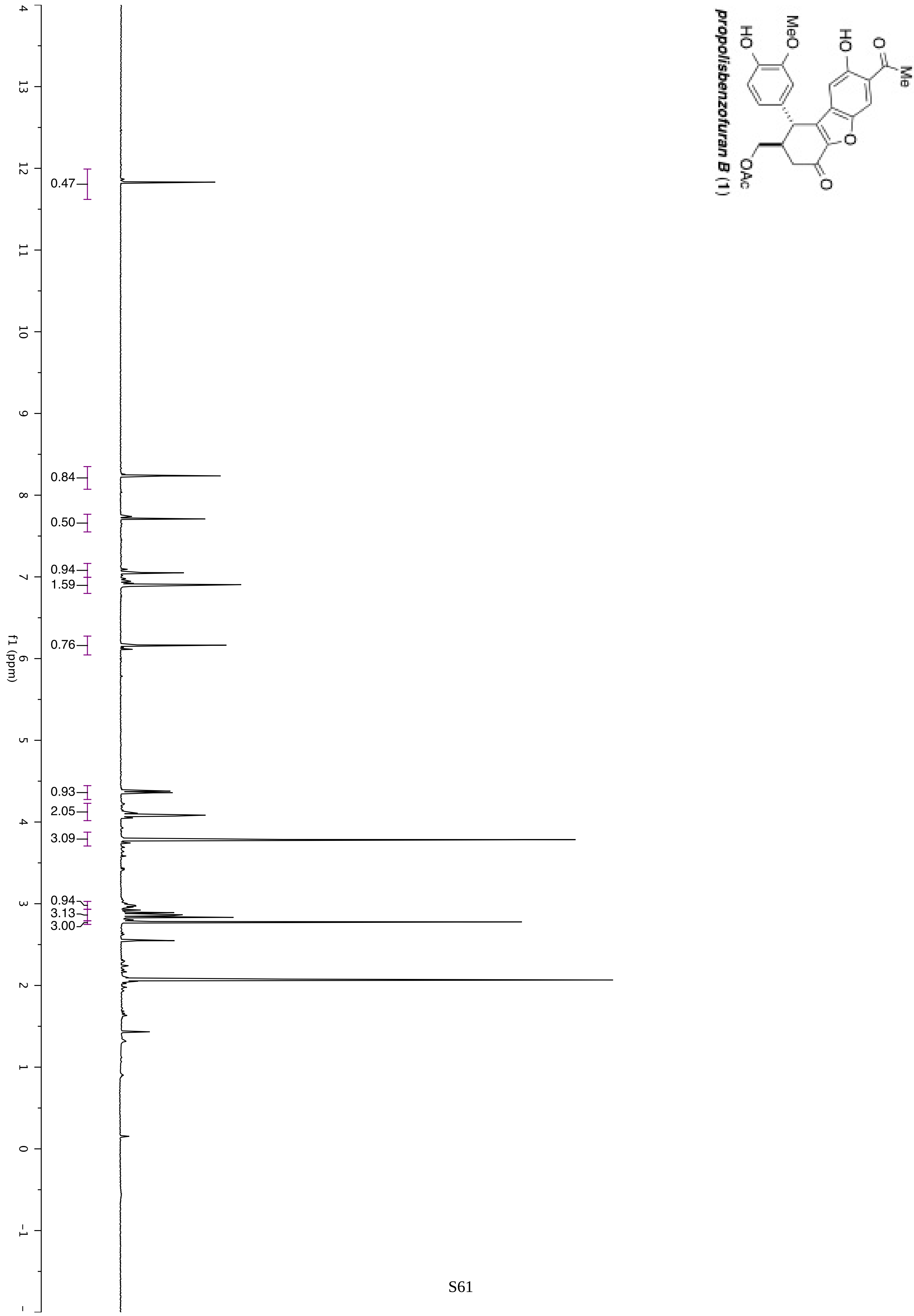
S7

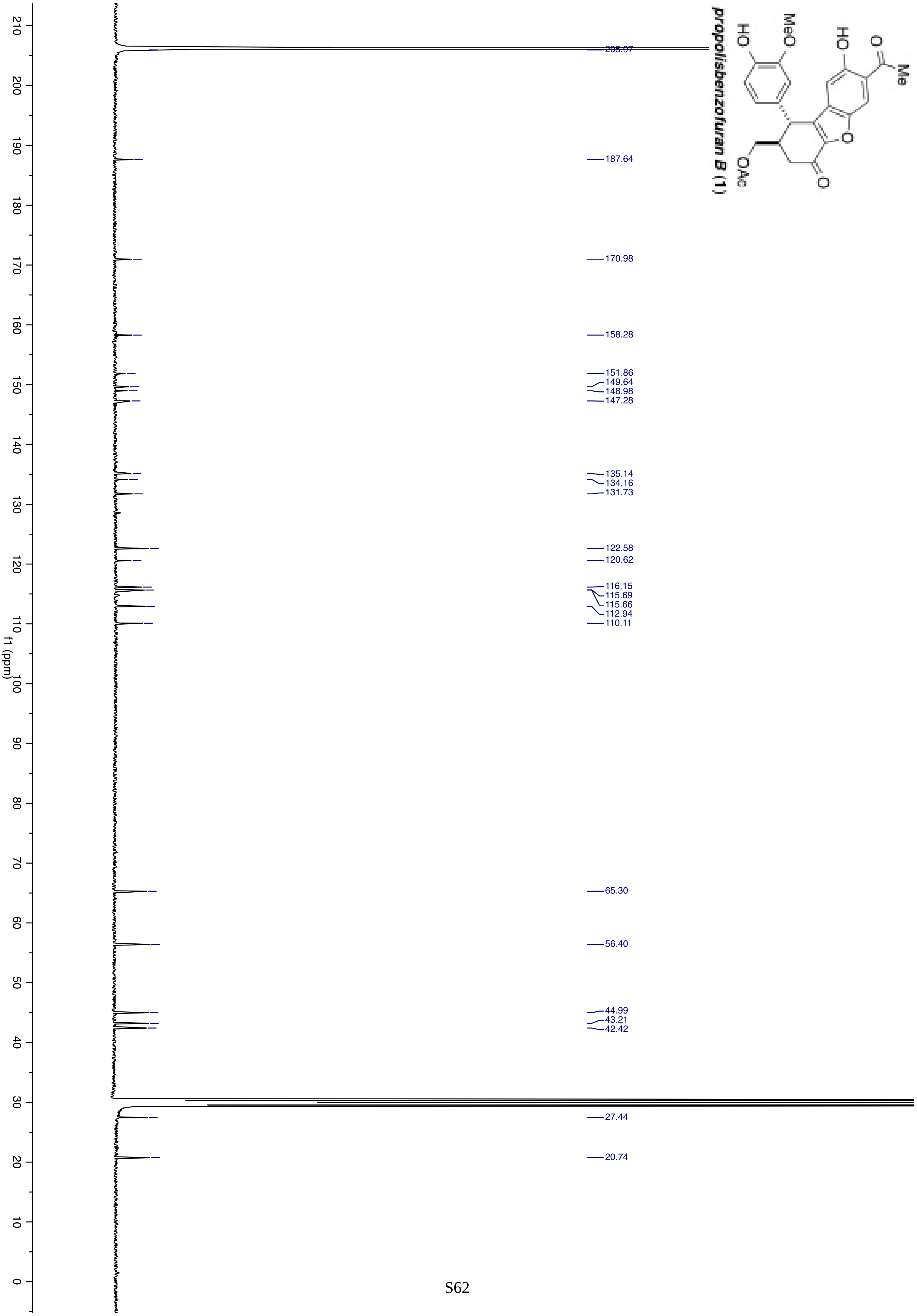

9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
f1 (ppm)
0.90
0.87
0.89
0.88
0.84
1.03
0.91
2.94
2.82
3.11
3.04
3.20
7.12
4.27
3.18
Me
O
i-PrO
MeO
i-PrO
O
O
OAc

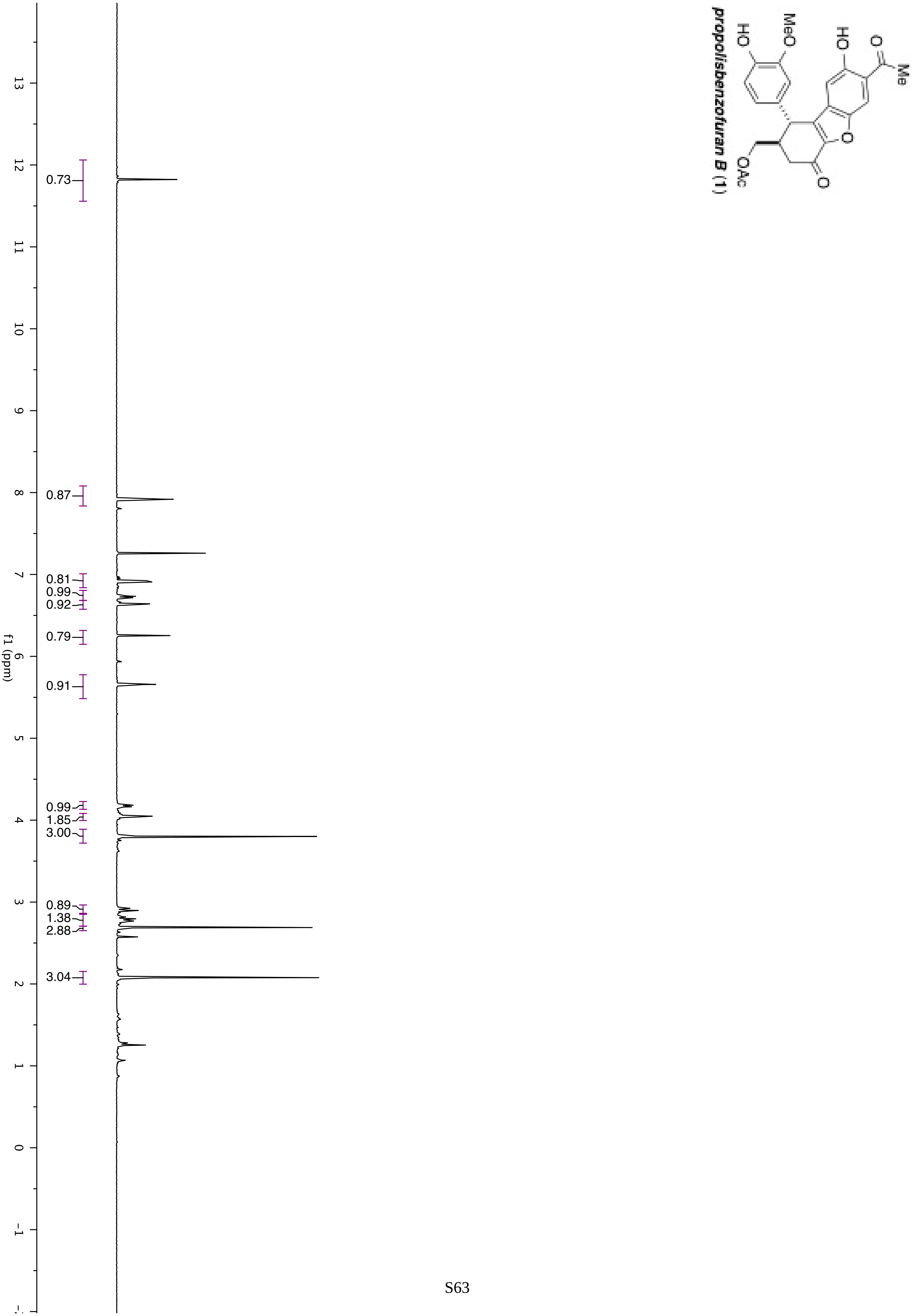
S8

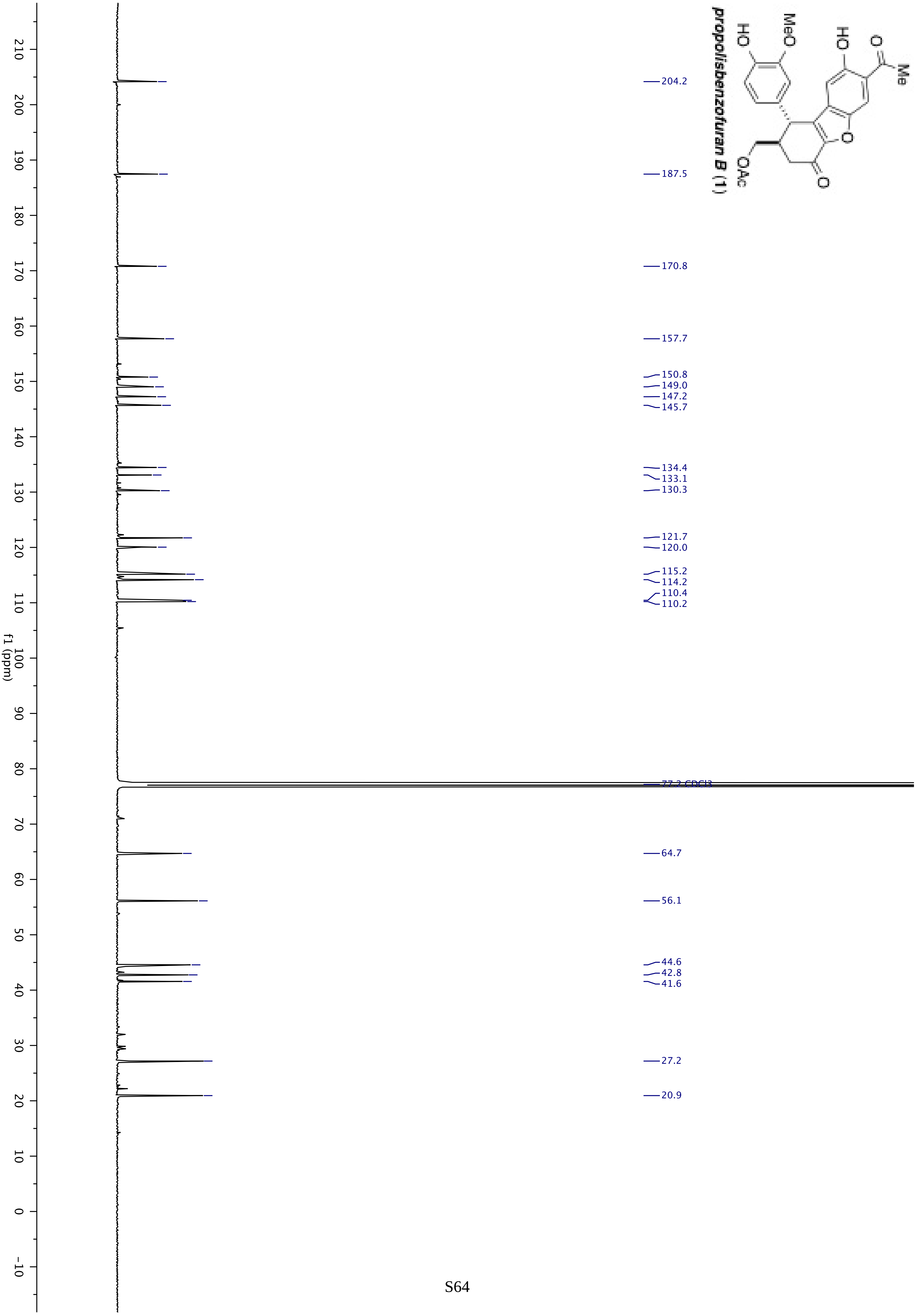

S8

200.08
188.03
153.09
150.84
150.43
149.49
147.11
135.56
132.33
131.51
129.82
121.25
115.34
114.11
112.24
105.62
71.45
70.96
63.08
56.27
47.36
42.18
41.58
32.02
22.22
22.15
22.07
21.30
f1 (ppm)
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
-10
i-PrO
MeO
i-PrO
O
Me
O
O
OAc


propolisbenzofuran B (1)
Me
O
HO
O
O
MeO
HO
OAc
0.47
0.84
0.50
0.94
1.59
0.76
0.93
2.05
3.09
0.94
3.13
3.00
14
13
12
11
10
9
8
7
6
5
4
3
2
1
0
−1
f1 (ppm)


propolisbenzofuran B (1)


propolisbenzofuran B (1)
Me
O
HO
O
O
MeO
HO
OAc
f1 (ppm)
13
12
11
10
9
8
7
6
5
4
3
2
1
0
-1
0.73
0.87
0.81
0.99
0.92
0.79
0.91
0.99
1.85
3.00
0.89
1.38
2.88
3.04


propolisbenzofuran B (1)
Me
O
HO
O
O
MeO
HO
OAc
204.2
187.5
170.8
157.7
150.8
149.0
147.2
145.7
134.4
133.1
130.3
121.7
120.0
115.2
114.2
110.4
110.2
77.2 CDCl3
64.7
56.1
44.6
42.8
41.6
27.2
20.9
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
−10
f1 (ppm)