 Supporting Information Veits, Wenz, Palmer, St. Amant, Hein and Read de Alaniz*

Cascade Rearrangement of Furylcarbinols with Hydroxylamines: Practical Access to Densely Functionalized Cyclopentane Derivatives

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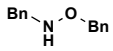
Materials and Methods. Unless stated otherwise, reactions were conducted in flame-dried glassware under an atmosphere of air using reagent grade solvents. All commercially obtained reagents were used as received. Reaction temperatures were controlled using an Heidolph temperature modulator, and unless stated otherwise, reactions were performed at room temperature (rt, approximately 23 ºC). Thin-layer chromatography (TLC) was conducted with E. Merck silica gel 60 F254 pre-coated plates, (0.25 mm) and visualized by exposure to UV light (254 nm) or stained with anisaldehyde and potassium permanganate. Flash column chromatography was performed using normal phase silica gel (60 Å, 0.040 – 0.063 mm, Geduran). ^{1}H NMR spectra were recorded on Varian spectrometers (at 500 or 600 MHz) and are reported

relative to deuterated solvent signals. Data for ^{1}H NMR spectra are reported as follows: chemical shift (δ ppm), multiplicity, coupling constant (Hz) and integration. ^{13}C NMR spectra were recorded on Varian Spectrometers (125 or 150 MHz). Data for ^{13}C NMR spectra are reported in terms of chemical shift (δ ppm), multiplicity, coupling constant (Hz). IR spectra were recorded on a Perkin Elmer Spectrum 100 FT/IR spectrometer and are reported in terms of frequency of absorption (cm^{-1}). Mass spectra were obtained from the UC Santa Barbara Mass Spectrometry Facility on a (Waters Corp.) Micromass QTOF2 with an electrospray ionization source. X-ray data were obtained from the UC Santa Barbara X-ray Facility.

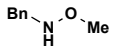
General Procedure for the Synthesis of Hydroxylamines: Hydroxylamines were synthesized following published procedures.[1]



2

***N*,*O*-Dibenzylhydroxylamine (2):**

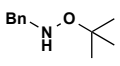
Colorless oil; **^{1}H NMR** (500 MHz, $CDCl_3$) δ 7.38 – 7.27 (m, 10H), 5.74 (s, 1H), 4.67 (s, 2H), 4.07 (s, 2H) ppm; **^{13}C NMR** (125 MHz, $CDCl_3$) δ 138.0, 137.7, 129.1, 128.6, 128.5, 128.5, 127.9, 127.6, 76.5, 56.7 ppm; **IR** (thin film) 3260, 3087, 3019, 2912, 2858, 1895, 1877, 1810, 1604, 1495, 1453, 1275, 1260, 988 cm^{-1}; **MS** (ESI) *m/z* 214.1219 (214.1232 calcd for $C_{14}H_{16}NO^{+}$ $[MH]^{+}$).



S-1

***N*-Benzyl-*O*-methylhydroxylamine (S-1):**

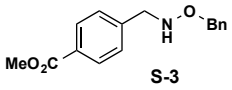
Colorless oil; **^{1}H NMR** (600 MHz, $CDCl_3$) δ 7.38 – 7.32 (m, 4H), 7.31 – 7.27 (m, 1H), 5.73 (s, 1H), 4.06 (s, 2H), 3.52 (s, 3H) ppm; **^{13}C NMR** (125 MHz, $CDCl_3$) δ 137.7, 129.0, 128.6, 127.6, 62.0, 56.4 ppm; **IR** (thin film) 3259, 3030, 2937, 2894, 2808, 1604, 1454, 1275, 1260, 992 cm^{-1}; **MS** (ESI) *m/z* 160.0737 (160.0738 calcd for $C_8H_{11}NNaO^{+}$ $[MNa]^{+}$).



S-2

***N*-Benzyl-*O*-(tert-butyl)hydroxylamine (S-2):**

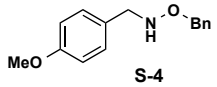
Colorless oil. **^{1}H NMR** (500 MHz, $CDCl_3$) δ 7.41 – 7.27 (m, 5H), 4.00 (s, 2H), 1.18 (s, 9H) ppm; **^{13}C NMR** (150 MHz, $CDCl_3$) δ 129.4, 128.5, 127.6, 57.8, 26.9 ppm; **IR** (thin film) 3255, 2975, 2929, 2863, 1947, 1876, 1806, 1603, 1454, 1360 cm^{-1}; **MS** (ESI) *m/z* 180.1362 (180.1383 calcd for $C_{11}H_{18}NO^+$ $[MH]^+$).



S-3

Methyl 4-(((benzyloxy)amino)methyl)benzoate (S-3):

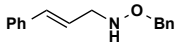
Colorless oil. **^{1}H NMR** (600 MHz, $CDCl_3$) δ 8.01 (d, *J* = 8.2 Hz, 2H), 7.43 (d, *J* = 8.0 Hz, 2H), 7.38 – 7.27 (m, 5H), 4.63 (s, 2H), 4.09 (s, 2H), 3.92 (s, 3H) ppm; **^{13}C NMR** (150 MHz, $CDCl_3$) δ 167.1, 143.3, 137.8, 129.8, 129.4, 128.9, 128.6, 128.5, 128.0, 76.6, 56.3, 52.2 ppm; **IR** (thin film) 3267, 3031, 2951, 1937, 1721, 1612 cm^{-1}; **MS** (ESI) *m/z* 294.1096 (294.1106 calcd for $C_{16}H_{17}NNaO_3^+$ $[MNa]^+$).



S-4

***O*-Benzyl-*N*-(4-methoxybenzyl)hydroxylamine (S-4):**

Colorless oil. **^{1}H NMR** (600 MHz, $CDCl_3$) δ 7.37 (d, *J* = 3.0 Hz, 4H), 7.35 – 7.32 (m, 1H), 7.30 (d, *J* = 8.5 Hz, 2H), 6.91 (d, *J* = 8.6 Hz, 2H), 5.68 (bs, 1H) 4.70 (s, 2H), 4.03 (s, 2H), 3.83 (s, 3H) ppm; **^{13}C NMR** (150 MHz, $CDCl_3$) δ 159.1, 138.0, 130.3, 129.7, 128.5, 128.4, 127.8, 113.9, 76.3, 56.0, 55.3 ppm; **IR** (thin film) 3261, 3031, 2910, 2859, 2060, 1883, 1612, 1513 cm^{-1}; **MS** (ESI) *m/z* 244.1319 (244.1332 calcd for $C_{15}H_{18}NO_2^+$ $[MH]^+$).

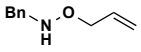


S-5

***O*-Benzyl-*N*-cinnamylhydroxylamine (S-5):**

Colorless oil; **^{1}H NMR** (600 MHz, $CDCl_3$) δ 7.41 – 7.29 (m, 9H), 7.27 – 7.21 (m, 1H), 6.58 (d, *J* = 16.0 Hz, 1H), 6.30 (dt, *J* = 15.9, 6.6 Hz, 1H), 5.61 (s, 1H), 4.76 (s, 2H), 3.72 (dd, *J* = 6.6, 1.3 Hz, 2H) ppm; **^{13}C NMR** (125 MHz, $CDCl_3$) δ 138.0, 137.1, 133.3,

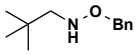
128.7, 128.6, 128.5, 128.0, 127.7, 126.5, 125.7, 76.5, 54.6 ppm; **IR** (thin film) 3258, 3061, 3028, 2910, 2853, 1877, 1598, 1494, 1453, 1361, 1275, 1260, 965^{-1}; **MS** (ESI) *m/z* 240.1381 (240.1388 calcd for $C_{16}H_{18}NO^+$ $[MH]^+$).



S-6

***O*-Allyl-*N*-benzylhydroxylamine (S-6):**

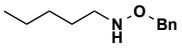
Colorless oil; **^{1}H NMR** (500 MHz, $CDCl_3$) δ 7.40 – 7.30 (m, 4H), 7.32 – 7.25 (m, 1H), 5.91 (ddt, *J* = 17.3, 10.4, 5.9 Hz, 1H), 5.72 (s, 1H), 5.26 (ddt, *J* = 17.3, 1.6, 1.6 Hz, 1H), 5.18 (ddt, *J* = 10.4, 2.0, 1.2 Hz, 1H), 4.17 (ddd, *J* = 6.0, 1.3, 1.3 Hz, 2H), 4.07 (s, 2H) ppm; **^{13}C NMR** (125 MHz, $CDCl_3$) δ 137.6, 134.6, 129.1, 128.5, 127.6, 117.7, 75.2, 56.7 ppm; **IR** (thin film) 3254, 3065, 3030, 2907, 2858, 1807, 1645, 1454, 1421, 1343, 1239, 988, 923 cm^{-1}; **MS** (ESI) *m/z* 186.0873 (186.0895 calcd for $C_{10}H_{13}NNaO^+$ $[MNa]^+$).



S-7

***O*-Benzyl-*N*-neopentylhydroxylamine (S-7):**

Colorless oil; **^{1}H NMR** (600 MHz, $CDCl_3$) δ 7.38 – 7.33 (m, 4H), 7.32 – 7.28 (m, 1H), 5.60 (s, 1H), 4.70 (s, 2H), 2.75 (s, 2H), 0.93 (s, 9H) ppm; **^{13}C NMR** (125 MHz, $CDCl_3$) δ 138.1, 128.6, 128.4, 127.8, 75.9, 63.6, 31.1, 28.3 ppm; **IR** (thin film) 3276, 3031, 2953, 2906, 2865, 1476, 1454, 1363, 1275, 1259, 978 cm^{-1}; **MS** (ESI) *m/z* 194.1523 (194.1545 calcd for $C_{12}H_{20}NO^+$ $[MH]^+$).

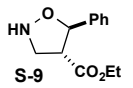


S-8

***O*-Benzyl-*N*-pentylhydroxylamine (S-8):**

Colorless oil; **^{1}H NMR** (600 MHz, $CDCl_3$) δ 7.39 – 7.33 (m, 4H), 7.32 – 7.27 (m, 1H), 5.54 (s, 1H), 4.71 (s, 2H), 2.93 (dd, *J* = 7.3, 7.3 Hz, 2H), 1.52 (dddd, *J* = 7.4, 7.4, 7.4, 7.4 Hz, 2H), 1.36 – 1.25 (m, 4H), 0.90 (dd, *J* = 6.8, 6.8 Hz, 3H) ppm; **^{13}C NMR** (125 MHz, $CDCl_3$) δ 138.2, 128.5, 128.5, 127.9, 76.3, 52.4, 29.5, 27.2, 22.7, 14.2 ppm; **IR** (thin

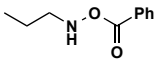
film) 3265, 3031, 2955, 2930, 1857, 1454, 1362, 1275, 1206, 998 cm^{-1}; **MS** (ESI) *m/z* 194.1535 (194.1545 calcd for $C_{12}H_{20}NO^+$ $[MH]^+$).



S-9

Ethyl (*trans*)-5-phenylisoxazolidine-4-carboxylate (S-9):

Prepared according to literature procedure.[2] Colorless oil. **^{1}H NMR** (600 MHz, Chloroform-d) δ 7.39 – 7.32 (m, 4H), 7.32 – 7.28 (m, 1H), 5.72 (s, 1H), 5.08 (d, J = 5.7 Hz, 1H), 4.27 – 4.12 (m, 2H), 3.57 (dd, J = 11.8, 3.3 Hz, 1H), 3.47 (dd, J = 11.8, 8.4 Hz, 1H), 3.35 – 3.20 (m, 1H), 1.27 (t, J = 7.2 Hz, 3H) ppm; **^{13}C NMR** (151 MHz, Chloroform-d) δ 173.2, 139.2, 128.7, 128.3, 126.2, 86.8, 61.4, 56.6, 53.7, 14.2 ppm; **IR** (thin film) 3229, 3065, 3034, 2983, 2942, 2906, 1886, 1813, 1729 cm^{-1}; **MS** (ESI) *m/z* 244.0942 (244.0950 calcd for $C_{12}H_{15}NO_3^+$ $[MH]^+$).

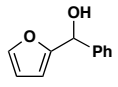


S-10

***O*-Benzoyl-*N*-propylhydroxylamine (S-10):**

Colorless oil. **^{1}H NMR** (600 MHz, $CDCl_3$) δ 8.03 (dd, *J* = 8.5, 1.4 Hz, 2H), 7.58 (t, *J* = 7.5 Hz, 1H), 7.46 (t, *J* = 7.8 Hz, 2H), 3.12 (t, *J* = 7.1 Hz, 2H), 1.66 (h, *J* = 7.4 Hz, 2H), 1.01 (t, *J* = 7.4 Hz, 3H) ppm; **^{13}C NMR** (150 MHz, $CDCl_3$) δ 167.1, 133.4, 129.5, 128.7, 128.6, 54.5, 20.7, 11.7 ppm; **IR** (thin film) 3239, 2963, 2936, 2876, 1765, 1716 cm^{-1}; **MS** (ESI) *m/z* 180.0997 (180.1019 calcd for $C_{10}H_{14}NO_2^+$ $[MH]^+$).

General Procedure for the Synthesis of Furylcarbinols: Furylcarbinols **1** and **S-12 – S-19** were prepared using standard synthetic chemistry from readily available commercial starting materials.

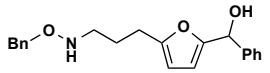


1

Furan-2-yl(phenyl)methanol (1):

Light yellow oil; **^{1}H NMR** (500 MHz, $CDCl_3$) δ 7.49 – 7.43 (m, 2H), 7.42 – 7.36 (m, 3H), 7.36 – 7.30 (m, 1H), 6.32 (dd, *J* = 3.2, 1.8 Hz, 1H), 6.12 (d, *J* = 3.3 Hz, 1H), 5.83 (d,

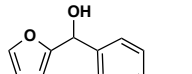
J = 4.0 Hz, 1H), 2.42 (d, *J* = 4.3 Hz, 1H) ppm; **^{13}C NMR** (150 MHz, $CDCl_3$) δ 156.1, 142.7, 140.9, 128.6, 128.2, 126.7, 110.4, 107.6, 70.3 ppm; **IR** (thin film) 3362, 3063, 3031, 2897, 1957, 1888, 1810, 1602, 1492, 1452, 1141, 1007 cm^{-1}; **MS** (EI^+) *m/z* 174.0685 (174.0681 calcd for $C_{11}H_{10}O_2^+$ $[M]^+$).



S-11

(5-(3-((Benzyloxy)amino)propyl)furan-2-yl)(phenyl)methanol (S-11):

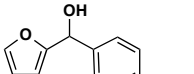
Light yellow oil; **^{1}H NMR** (500 MHz, $CDCl_3$) δ 7.47 – 7.42 (m, 2H), 7.39 – 7.28 (m, 8H), 5.94 (d, *J* = 3.1 Hz, 1H), 5.90 (d, *J* = 3.1 Hz, 1H), 5.76 (s, 1H), 4.70 (s, 2H), 2.95 (t, *J* = 7.0 Hz, 2H), 2.65 (t, *J* = 7.5 Hz, 2H), 1.85 (tt *J* = 7.3, 7.3 Hz, 2H) ppm; **^{13}C NMR** (125 MHz, $CDCl_3$) δ 156.0, 154.5, 141.1, 138.0, 128.5, 128.5, 128.5, 128.0, 127.9, 126.7, 108.4, 105.8, 76.4, 70.2, 51.5, 25.8 ppm; **IR** (thin film) 3382, 3087, 3062, 3030, 2910, 2858, 1955, 1885, 1453, 1190, 1010, 961 cm^{-1}; **MS** (ESI) *m/z* 360.1574 (360.1576 calcd for $C_{21}H_{23}NNaO_3^+$ $[MNa]^+$).



S-12

4-(Furan-2-yl(hydroxy)methyl)benzonitrile (S-12):

Yellow solid; **^{1}H NMR** (500 MHz, $CDCl_3$) δ 7.69 – 7.63 (m, 2H), 7.59 – 7.54 (m, 2H), 7.42 – 7.38 (m, 1H), 6.36 – 6.31 (m, 1H), 6.15 (d, *J* = 3.3 Hz, 1H), 5.88 (s, 1H), 2.69 (s, 1H) ppm; **^{13}C NMR** (150 MHz, $CDCl_3$) δ 154.7, 146.0, 143.2, 132.4, 127.3, 118.8, 111.8, 110.6, 108.1, 69.4 ppm; **IR** (thin film) 3418, 3122, 2879, 2228, 1927, 1808, 1609, 1504, 1410, 1141, 1009 cm^{-1}; **MS** (EI^+) *m/z* 199.0628 (199.0633 calcd for $C_{12}H_9O_2^+$ $[M]^+$).

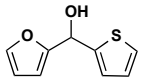


S-13

Furan-2-yl(4-methoxyphenyl)methanol (S-13):

Yellow oil. **^{1}H NMR** (600 MHz, $CDCl_3$) δ 7.38 (d, *J* = 0.8 Hz, 1H), 7.34 (d, *J* = 8.6 Hz, 2H), 6.90 (d, *J* = 8.7 Hz, 2H), 6.31 (dd, *J* = 3.2, 1.8 Hz, 1H), 6.11 (d, *J* = 3.2 Hz, 1H), 5.76 (s, 1H), 3.80 (s, 3H) ppm; **^{13}C NMR** (150 MHz, $CDCl_3$) δ 159.5, 156.3, 142.5,

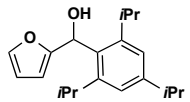
133.2, 128.1, 113.9, 110.3, 107.3, 69.9, 55.4 ppm; **IR** (thin film) 3402, 3001, 2957, 2935, 2910, 2837, 1610, 1586, 1510 cm^{-1}; **MS** (EI) *m/z* 204.0776 (204.0786 calcd for $C_{12}H_{12}O_3^+$ $[M]^+$).



S-14

Furan-2-yl(thiophen-2-yl)methanol (S-14):

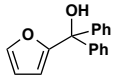
Yellow oil. **^{1}H NMR** (600 MHz, $CDCl_3$) δ 7.69 (d, *J* = 3.3 Hz, 1H), 7.38 (dd, *J* = 1.5, 0.7 Hz, 1H), 7.32 (d, *J* = 3.2 Hz, 1H), 6.35 – 6.30 (m, 2H), 6.08 (s, 1H), 4.79 (s, 1H) ppm; **^{13}C NMR** (150 MHz, $CDCl_3$) δ 171.7, 153.3, 143.1, 142.3, 119.9, 110.6, 108.4, 67.6 ppm; **IR** (thin film) 3119, 2852, 1766, 1621, 1503, 1432 cm^{-1}; MS (EI) *m/z* 180.0247 (180.0245 calcd for $C_9H_8O_2S^+$ $[M]^+$).



S-15

Furan-2-yl(2,4,6-triisopropylphenyl)methanol (S-15):

Brown solid; **^{1}H NMR** (500 MHz, $CDCl_3$) δ 7.39 (ddd, *J* = 1.8, 0.8, 0.8 Hz, 1H), 7.05 (s, 2H), 6.41 (d, *J* = 2.9 Hz, 1H), 6.31 (dd, *J* = 3.3, 1.8 Hz, 1H), 6.00 (ddd, *J* = 3.3, 1.1, 1.1 Hz, 1H), 3.35 (hept, *J* = 6.8 Hz, 2H), 2.89 (hept, *J* = 6.9 Hz, 1H), 2.32 (d, *J* = 3.5 Hz, 1H), 1.26 (d, *J* = 6.9 Hz, 6H), 1.20 (d, *J* = 6.8 Hz, 6H), 1.15 (d, *J* = 6.8 Hz, 6H) ppm; **^{13}C NMR** (150 MHz, $CDCl_3$) δ 156.4, 148.8, 142.0, 131.7, 122.2, 110.5, 106.6, 65.8, 34.3, 29.8, 25.1, 24.1, 24.1 ppm; IR (thin film) 3408, 2959, 2928, 2868, 1768, 1607, 1460, 1362, 1142, 1004 cm^{-1}; **MS** (EI^+) *m/z* 300.2096 (300.2089 calcd for $C_{20}H_{28}O_2^+$ $[M]^+$).

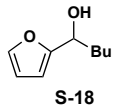


S-16

Furan-2-yldiphenylmethanol (S-16):

Yellow oil. **^{1}H NMR** (600 MHz, $CDCl_3$) δ 7.46 (s, 1H), 7.40 – 7.27 (m, 10H), 6.34 (d, *J* = 1.5 Hz, 1H), 5.94 (d, *J* = 3.2 Hz, 1H), 3.11 (s, 1H) ppm; **^{13}C NMR** (150 MHz, $CDCl_3$) δ 158.0, 144.7, 142.8, 128.1, 127.8, 127.3, 110.2, 109.8, 78.1 ppm; **IR** (thin film) 3410,

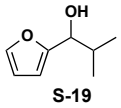
3061, 3028, 1957, 1888, 1813, 1725, 1675, 1598, 1554, 1490, 1447 cm^{-1}; **MS** (EI) *m/z* 250.0991 (250.0994 calcd for $C_{17}H_{14}O_2^+$ $[M]^+$).



S-18

1-(Furan-2-yl)pentan-1-ol (S-18):

Colorless oil; **^{1}H NMR** (500 MHz, $CDCl_3$) δ 7.37 (m, 1H), 6.32 (dd, *J* = 3.3, 1.8 Hz, 1H), 6.22 (d, *J* = 3.2 Hz, 1H), 4.66 (td, *J* = 6.7, 3.8 Hz, 1H), 1.91 (s, 1H), 1.88 – 1.80 (m, 2H), 1.47 – 1.23 (m, 4H), 0.90 (t, *J* = 7.1 Hz, 3H) ppm; **^{13}C NMR** (125 MHz, $CDCl_3$) δ 157.1, 142.0, 110.2, 105.9, 68.0, 35.4, 27.8, 22.6, 14.1 ppm; **IR** (thin film) 3360, 2956, 2932, 2861, 1597, 1505, 1466, 1149, 1007 cm^{-1}; **MS** (EI^+) *m/z* 154.0998 (154.0994 calcd for $C_9H_{14}O_2^+$ $[M]^+$).

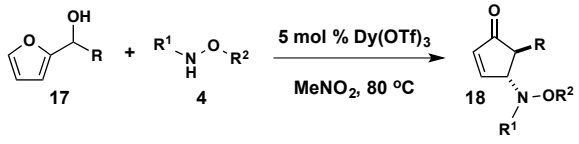


S-19

1-(Furan-2-yl)-2-methylpropan-1-ol (S-19):

Yellow oil; **^{1}H NMR** (600 MHz, $CDCl_3$) δ 7.37 (dd, *J* = 1.8, 0.9 Hz, 1H), 6.33 (dd, *J* = 3.2, 1.8 Hz, 1H), 6.23 (d, *J* = 3.2 Hz, 1H), 4.38 (d, *J* = 7.0 Hz, 1H), 2.11 (h, *J* = 6.8 Hz, 1H), 1.84 (s, 1H), 1.02 (d, *J* = 6.7 Hz, 3H), 0.86 (d, *J* = 6.8 Hz, 3H) ppm; **^{13}C NMR** (150 MHz, $CDCl_3$) δ 156.3, 141.8, 110.2, 106.6, 73.7, 33.5, 18.9, 18.4 ppm; **IR** (thin film) 3392, 2961, 2933, 2873, 1665, 1505, 1468 cm^{-1}; **MS** (EI) *m/z* 140.0840 (140.0837 calcd for $C_8H_{12}O_2^+$ $[M]^+$).

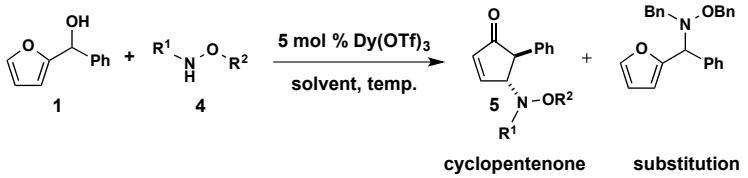
Synthesis of Substituted Cyclopentenones:



General Procedure for the Synthesis of Substituted Cyclopentenones: Furylcarbinol (**17**) and hydroxylamine (**4**) were stirred as a solution in $MeNO_2$ at rt. 5-10 mol %

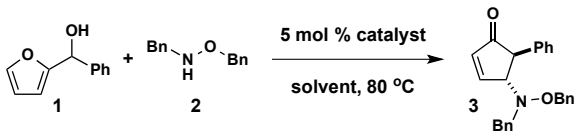
$Dy(OTf)_3$ was added to the reaction mixture, and the flask placed in an oil bath pre-heated at 80 °C. The reactions were monitored by TLC. Upon completion, the reaction was quenched with saturated $NaHCO_3$ at rt and extracted with EtOAc (3x). The combined organic layers were dried over $MgSO_4$, filtered and then concentrated *in vacuo*. The residue was purified by flash column chromatography to afford cyclopentenones (**18**).

Table S1. A small solvent screen was performed.



Solvent	Time	Temp.	Cyclopentenone Yield	Substitution Yield
Toluene	4 days	80 °C	71%	11%
CH_2Cl_2	4 days	40 °C	40%	41%
MeCN	18 h	80 °C	87%	0%
$MeNO_2$	1 h	80 °C	88%	0%

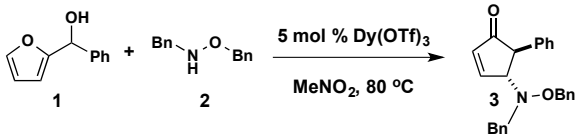
Table S2. Optimization of the rearrangement conditions.



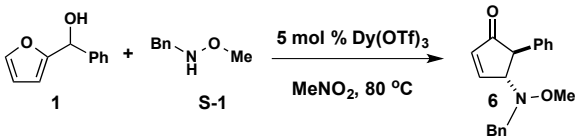
Solvent	Catalyst	Time	Cyclopentenone Yield[a]
MeCN	$Dy(OTf)_3$	18 h	87%
$MeNO_2$	$Dy(OTf)_3$	30 min	88%
$MeNO_2$	$Sc(OTf)_3$	20 min	76%
$MeNO_2$	$La(OTf)_3$	40 min	91%
$MeNO_2$	$Gd(OTf)_3$	30 min	88%
$MeNO_2$	$Yb(OTf)_3$	40 min	94%
$MeNO_2$	$DyCl_3$	10 h	54%
$MeNO_2$	PMA[b]	5 min	Decomp
$MeNO_2$	TsOH[c]	15 min	35%
$MeNO_2$	Amberlyst® 15[c]	6 h	35%

[a] Isolated yields. [b] PMA = phosphomolybdic acid. [c] 100 mol % of catalyst was used.

General Procedure for Table 1 optimization study: Furylcarbinol (**1**) and hydroxylamine (**2**) were stirred as a solution in MeCN or $MeNO_2$ at rt. The catalyst was added to the reaction mixture, and the flask placed in an oil bath pre-heated at 80 °C. The reactions were monitored by TLC. Upon completion, the reaction was quenched with saturated $NaHCO_3$ at rt and extracted with EtOAc (3x). The combined organic layers were dried over $MgSO_4$, filtered and then concentrated *in vacuo*. The residue was purified by flash column chromatography to afford cyclopentenones (**3**).

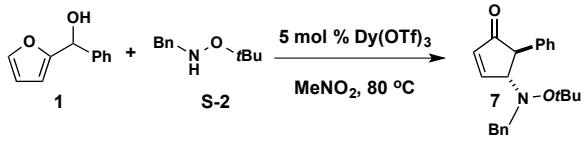


4-(Benzyl(benzyloxy)amino)-5-phenylcyclopent-2-en-1-one (3):
According to the general procedure, furan-2-yl(phenyl)methanol (38.2 mg, 0.220 mmol) and *N*,*O*-dibenzylhydroxylamine (2) (46.8 mg, 0.220 mmol) were treated with $Dy(OTf)_3$ (6.7 mg, 0.011 mmol) in $MeNO_2$ (2.2 mL). The resulting reaction mixture was heated to 80 ºC for 30 min. The reaction was then quenched at 23 ºC with saturated aqueous $NaHCO_3$ (5 mL) and extracted with ethyl acetate (3 × 5 mL). The combined organic layers were dried over $MgSO_4$, filtered and then concentrated *in vacuo*. The residue was purified by flash column chromatography to afford cyclopentenone **3** (71.6 mg, 88%) as a light orange/yellow solid. **^{1}H NMR** (600 MHz, $CDCl_3$) δ 7.61 (s, 1H), 7.36 – 7.20 (m, 9H), 7.15 – 7.04 (m, 6H), 6.33 (dd, *J* = 5.8, 1.9 Hz, 1H), 4.43 (d, *J* = 11.9 Hz, 1H), 4.41 (d, *J* = 10.2 Hz, 1H), 4.24 (ddd, *J* = 2.3, 2.3, 2.3 Hz, 1H), 4.01 (d, *J* = 12.6 Hz, 1H), 3.93 (s, 1H), 3.80 (d, *J* = 12.6 Hz, 1H) ppm; **^{13}C NMR** (125 MHz, $CDCl_3$) δ 207.1, 162.4, 139.0, 136.7, 136.6, 134.9, 129.9, 129.2, 129.1, 128.5, 128.4, 128.3, 128.3, 127.7, 127.2, 76.9, 73.9, 61.3, 52.7 ppm; **IR** (thin film) 3063, 3031, 2919, 1709, 1595, 1454, 1265, 1029, 975 cm^{-1}; **MS** (ESI) *m/z* 392.1636 (392.1626 calcd for $C_{25}H_{23}NNaO_2^+$ $[MNa]^+$).



4-(Benzyl(methoxy)amino)-5-phenylcyclopent-2-en-1-one (6):

According to the general procedure, furan-2-yl(phenyl)methanol (30.0 mg, 0.172 mmol) and *N*-benzyl-*O*-methylhydroxylamine (**S-1**) (23.6 mg, 0.172 mmol) were treated with $Dy(OTf)_3$ (5.2 mg, 0.0086 mmol) in $MeNO_2$ (1.8 mL). The resulting reaction mixture was heated to 80 ºC for 30 min. The reaction was then quenched at 23 ºC with saturated aqueous $NaHCO_3$ (5 mL) and extracted with ethyl acetate (3 × 5 mL). The combined organic layers were dried over $MgSO_4$, filtered and then concentrated *in vacuo*. The residue was purified by flash column chromatography to afford cyclopentenone **6** (46.2 mg, 91%) as an orange/brown solid. **^{1}H NMR** (600 MHz, $CDCl_3$) δ 7.76 (dd, *J* = 5.7, 2.3 Hz, 1H), 7.33 (dd, *J* = 7.4, 7.4 Hz, 2H), 7.29 – 7.24 (m, 1H), 7.23 – 7.21 (m, 3H), 7.12 (d, *J* = 7.2 Hz, 2H), 7.08 (s, 2H), 6.36 (dd, *J* = 5.7, 1.9 Hz, 1H), 4.21 (ddd, *J* = 2.3, 2.3, 2.3 Hz, 1H), 3.99 (d, *J* = 12.7 Hz, 1H), 3.87 (s, 1H), 3.74 (d, *J* = 12.7 Hz, 1H), 3.32 (s, 3H) ppm; **^{13}C NMR** (125 MHz, $CDCl_3$) δ 207.1, 162.1, 138.9, 136.7, 135.0, 129.7, 129.1, 128.5, 128.3, 127.6, 127.2, 73.9, 62.4, 60.9, 52.9 ppm; **IR** (thin film) 3062, 3030, 2934, 2812, 1709, 1595, 1454, 1266, 1040, 978 cm^{-1}; **MS** (ESI) *m/z* 316.1309 (316.1313 calcd for $C_{19}H_{19}NNaO_2^+$ $[MNa]^+$).



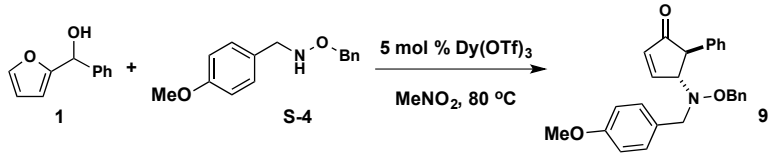
4-(Benzyl(tert-butoxy)amino)-5-phenylcyclopent-2-en-1-one (7):

According to the general procedure, furan-2-yl(phenyl)methanol (31.7 mg, 0.182 mmol) and *N*-benzyl-*O*-(*tert*-butyl)hydroxylamine (**S-2**) (32.7 mg, 0.182 mmol) were treated with $Dy(OTf)_3$ (5.54 mg, 0.0091 mmol) in $MeNO_2$ (1.8 mL). The resulting reaction mixture was heated to 80 ºC for 1 h. The reaction was then quenched at 23 ºC with saturated aqueous $NaHCO_3$ (5 mL) and extracted with ethyl acetate (3 × 5 mL). The combined organic layers were dried over $MgSO_4$, filtered and then concentrated *in vacuo*. The residue was purified by flash column chromatography to afford cyclopentenone **7** (46.2 mg, 76%) as a colorless oil. **^{1}H NMR** (600 MHz, $CDCl_3$) δ 7.68 – 7.63 (m, 1H), 7.35 – 7.25 (m, 3H), 7.19 – 7.03 (m, 5H), 6.79 (d, *J* = 7.5 Hz, 2H), 6.28 (d, *J* = 3.6 Hz, 1H), 4.19 – 4.08 (m, 3H), 3.80 (d, *J* = 12.7 Hz, 1H), 1.22 (s, 9H) ppm; **^{13}C NMR** (150 MHz, $CDCl_3$) δ 207.9, 164.9, 140.0, 136.9, 134.1, 129.4, 129.1, 128.7, 128.3, 127.5,

127.1, 78.0, 72.0, 62.8, 51.1, 28.1 ppm; **IR** (thin film) 3062, 3029, 2975, 2928, 2867, 1712, 1602 cm^{-1}; **MS** (ESI) *m/z* 358.1774 (358.1783 calcd for $C_{22}H_{25}NNaO_2^+$ $[MNa]^+$).

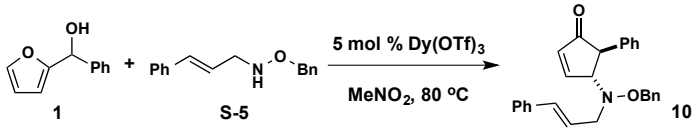
Methyl 4-(((benzyloxy)(4-oxo-5-phenylcyclopent-2-en-1-yl)amino)methyl)benzoate (8):

According to the general procedure, furan-2-yl(phenyl)methanol (28.8 mg, 0.166 mmol) and methyl 4-(((benzyloxy)amino)methyl)benzoate (**S-3**) (44.9 mg, 0.166 mmol) were treated with $Dy(OTf)_3$ (5.1 mg, 0.0084 mmol) in $MeNO_2$ (1.6 mL). The resulting reaction mixture was heated to 80 ºC for 1 h. The reaction was then quenched at 23 ºC with saturated aqueous $NaHCO_3$ (5 mL) and extracted with ethyl acetate (3 × 5 mL). The combined organic layers were dried over $MgSO_4$, filtered and then concentrated *in vacuo*. The residue was purified by flash column chromatography to afford cyclopentenone **8** (57.4 mg, 82%) as a white solid. **^{1}H NMR** (600 MHz, $CDCl_3$) δ 7.92 (d, *J* = 7.8 Hz, 2H), 7.62 (s, 1H), 7.33 (t, *J* = 7.3 Hz, 2H), 7.31 – 7.27 (m, 4H), 7.18 – 7.13 (m, 2H), 7.13 – 7.08 (m, 4H), 6.35 (dd, *J* = 5.8, 1.9 Hz, 1H), 4.47 – 4.37 (m, 2H), 4.24 (d, *J* = 2.3 Hz, 1H), 4.04 (d, *J* = 12.8 Hz, 1H), 3.94 (s, 1H), 3.91 (s, 3H), 3.84 (d, *J* = 12.8 Hz, 1H) ppm; **^{13}C NMR** (150 MHz, $CDCl_3$) δ 206.8, 167.0, 162.0, 141.9, 138.8, 136.5, 135.1, 129.8, 129.6, 129.6, 129.2, 129.2, 128.5, 128.5, 128.4, 127.3, 77.0, 74.1, 61.0, 52.7, 52.2 ppm; **IR** (thin film) 3084, 3031, 2950, 2910, 2874, 2275, 1738, 1718, 1701 cm^{-1}; **MS** (ESI) *m/z* 450.1665 (450.1682 calcd for $C_{27}H_{25}NNaO_4^+$ $[MNa]^+$).



4-((Benzyloxy)(4-methoxybenzyl)amino)-5-phenylcyclopent-2-en-1-one (9):

According to the general procedure, furan-2-yl(phenyl)methanol (19.7 mg, 0.113 mmol) and *O*-benzyl-*N*-(4-methoxybenzyl)hydroxylamine (**S-4**) (27.6 mg, 0.113 mmol) were treated with $Dy(OTf)_3$ (3.4 mg, 0.0057 mmol) in $MeNO_2$ (1.1 mL). The resulting reaction mixture was heated to 80 ºC for 2h. The reaction was then quenched at 23 ºC with saturated aqueous $NaHCO_3$ (5 mL) and extracted with ethyl acetate (3 × 5 mL). The combined organic layers were dried over $MgSO_4$, filtered and then concentrated *in vacuo*. The residue was purified by flash column chromatography to afford cyclopentenone **9** (34.4 mg, 76%) as a white solid. **^{1}H NMR** (600 MHz, $CDCl_3$) δ 7.59 (s, 1H), 7.36 – 7.26 (m, 6H), 7.20 – 7.14 (m, 2H), 7.11 (d, *J* = 7.5 Hz, 2H), 6.95 (s, 2H), 6.76 (d, *J* = 8.1 Hz, 2H), 6.33 (dd, *J* = 5.8, 2.1 Hz, 1H), 4.44 (s, 2H), 4.24 (d, *J* = 2.5 Hz, 1H), 3.96 (d, *J* = 12.5 Hz, 1H), 3.94 (s, 1H), 3.78 (s, 3H), 3.74 (d, *J* = 12.6 Hz, 1H) ppm; **^{13}C NMR** (150 MHz, $CDCl_3$) δ 207.2, 162.6, 159.2, 139.1, 136.8, 134.9, 131.1, 129.3, 129.1, 128.7, 128.6, 128.4, 128.3, 127.2, 113.7, 76.8, 73.6, 60.6, 55.4, 52.8 ppm; **IR** (thin film) 3030, 2930, 2837, 1884, 1712, 1611, 1513 cm^{-1}; **MS** (ESI) *m/z* 422.1716 (422.1732 calcd for $C_{26}H_{25}NNaO_3^+$ $[MNa]^+$).



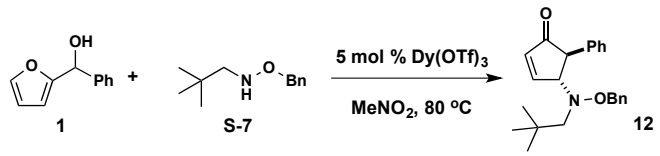
4-((Benzyloxy)(cinnamyl)amino)-5-phenylcyclopent-2-en-1-one (10):

According to the general procedure, furan-2-yl(phenyl)methanol (15.0 mg, 0.086 mmol) and *O*-benzyl-*N*-cinnamylhydroxylamine (**S-5**) (20.6 mg, 0.086 mmol) were treated with $Dy(OTf)_3$ (5.2 mg, 0.0086 mmol) in $MeNO_2$ (1.8 mL). The resulting reaction mixture was heated to 80 ºC for 1.5 h. The reaction was then quenched at 23 ºC with saturated aqueous $NaHCO_3$ (5 mL) and extracted with ethyl acetate (3 × 5 mL). The combined organic layers were dried over $MgSO_4$, filtered and then concentrated *in vacuo*. The residue was purified by flash column chromatography to afford cyclopentenone **10** (29.3 mg, 86%) as a light orange oil. **^{1}H NMR** (600 MHz, $CDCl_3$) δ 7.63 (s, 1H), 7.35 – 7.19 (m, 11H), 7.16 (d, *J* = 7.4 Hz, 2H), 7.11 (d, *J* = 7.2 Hz, 2H), 6.33 (dd, *J* = 5.8, 2.0 Hz, 1H), 6.12 (ddd, *J* = 14.7, 6.6, 6.6 Hz, 1H), 5.90 (d, *J* = 15.9 Hz, 1H), 4.69 (d, *J* = 10.7 Hz, 1H), 4.63 (d, *J* = 10.8 Hz, 1H), 4.37 (s, 1H), 3.87 (s, 1H), 3.69 (dd, *J* = 12.8, 6.1 Hz, 1H), 3.48 (dd, *J* = 13.0, 8.1 Hz, 1H) ppm; **^{13}C NMR** (125 MHz, $CDCl_3$) δ 207.1, 162.5, 139.0,

136.8, 136.7, 134.9, 134.9, 129.2, 129.1, 128.6, 128.6, 128.5, 128.3, 127.9, 127.2, 126.5, 123.9, 76.8, 73.6, 59.3, 52.4 ppm; **IR** (thin film) 3061, 3029, 2822, 2854, 1950, 1709, 1495, 1453, 1165, 1028, 968 cm^{-1}; **MS** (ESI) *m/z* 418.1766 (418.1783 calcd for $C_{27}H_{25}NNaO_2^+$ $[MNa]^+$).

4-((Allyloxy)(benzyl)amino)-5-phenylcyclopent-2-en-1-one (11):

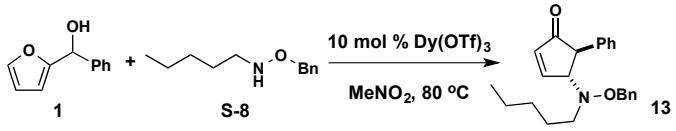
According to the general procedure, furan-2-yl(phenyl)methanol (100.0 mg, 0.57 mmol) and *O*-allyl-*N*-benzylhydroxylamine (**S-6**) (93.8 mg, 0.57 mmol) were treated with $Dy(OTf)_3$ (17.5 mg, 0.029 mmol) in $MeNO_2$ (5.7 mL). The resulting reaction mixture was heated to 80 ºC for 45 min. The reaction was then quenched at 23 ºC with saturated aqueous $NaHCO_3$ (10 mL) and extracted with ethyl acetate (3 × 10 mL). The combined organic layers were dried over $MgSO_4$, filtered and then concentrated *in vacuo*. The residue was purified by flash column chromatography to afford cyclopentenone **11** (173.5 mg, 95%) as an orange oil. **^{1}H NMR** (600 MHz, $CDCl_3$) δ 7.75 (dd, *J* = 6.0, 2.5 Hz, 1H), 7.33 (t, *J* = 7.4 Hz, 2H), 7.29 – 7.24 (m, 1H), 7.23 – 7.18 (m, 3H), 7.12 (d, *J* = 7.3 Hz, 2H), 7.07 (s, 2H), 6.36 (dd, *J* = 5.8, 2.0 Hz, 1H), 5.70 (dddd, *J* = 16.8, 10.3, 6.2, 6.2 Hz, 1H), 5.15 – 5.07 (m, 2H), 4.25 – 4.19 (m, 1H), 4.02 (d, *J* = 12.7 Hz, 1H), 4.00 – 3.89 (m, 3H), 3.78 (d, *J* = 12.7 Hz, 1H) ppm; **^{13}C NMR** (150 MHz, $CDCl_3$) δ 207.1, 162.3, 138.9, 136.6, 135.0, 133.5, 129.8, 129.1, 128.5, 128.3, 127.6, 127.2, 118.3, 75.9, 73.8, 61.4, 52.8 ppm; **IR** (thin film) 3063, 3029, 2916, 2858, 1708, 1495, 1454, 1165, 1029, 980 cm^{-1}; **MS** (ESI) *m/z* 342.1466 (342.1470 calcd for $C_{21}H_{21}NNaO_2^+$ $[MNa]^+$).



4-((Benzyloxy)(neopentyl)amino)-5-phenylcyclopent-2-en-1-one (12):

According to the general procedure, furan-2-yl(phenyl)methanol (30.0 mg, 0.172 mmol) and *O*-benzyl-*N*-neopentylhydroxylamine (**S-7**) (33.3 mg, 0.172 mmol) were treated with

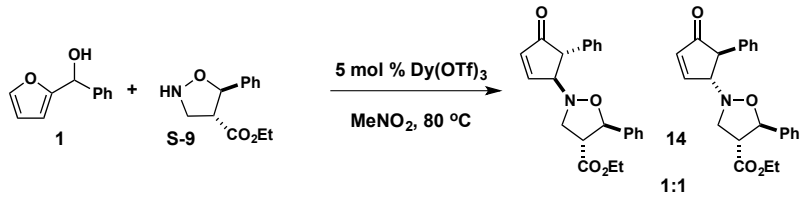
$Dy(OTf)_3$ (5.2 mg, 0.0085 mmol) in $MeNO_2$ (1.8 mL). The resulting reaction mixture was heated to 80 ºC for 45 min. The reaction was then quenched at 23 ºC with saturated aqueous $NaHCO_3$ (5 mL) and extracted with ethyl acetate (3 × 5 mL). The combined organic layers were dried over $MgSO_4$, filtered and then concentrated *in vacuo*. The residue was purified by flash column chromatography to afford cyclopentenone **12** (52.6 mg, 81%) as an orange oil. **^{1}H NMR** (500 MHz, $CDCl_3$) δ 7.80 (dd, *J* = 5.8, 2.3 Hz, 1H), 7.35 – 7.30 (m, 2H), 7.30 – 7.22 (m, 4H), 7.17 – 7.09 (m, 4H), 6.40 (dd, *J* = 5.8, 1.9 Hz, 1H), 4.70 (d, *J* = 10.5 Hz, 1H), 4.62 (d, *J* = 10.5 Hz, 1H), 4.38 (ddd, *J* = 2.3, 2.3, 2.3 Hz, 1H), 3.72 (d, *J* = 2.8 Hz, 1H), 2.65 (d, *J* = 14.1 Hz, 1H), 2.58 (d, *J* = 14.1 Hz, 1H), 0.94 (s, 9H) ppm; **^{13}C NMR** (125 MHz, $CDCl_3$) δ 207.3, 162.2, 139.2, 136.6, 135.4, 129.0, 128.7, 128.5, 128.3, 128.1, 127.1, 76.5, 75.1, 67.8, 53.5, 31.7, 28.5 ppm; **IR** (thin film) 3063, 3030, 2952, 2866, 1711, 1601, 1453, 1362, 1026, 981 cm^{-1}; **MS** (ESI) *m/z* 372.1932 (372.1939 calcd for $C_{23}H_{27}NNaO_2^+$ $[MNa]^+$).



4-((Benzyloxy)(pentyl)amino)-5-phenylcyclopent-2-en-1-one (13):

According to the general procedure, furan-2-yl(phenyl)methanol (15.0 mg, 0.086 mmol) and *O*-benzyl-*N*-pentylhydroxylamine (**S-8**) (16.7 mg, 0.086 mmol) were treated with $Dy(OTf)_3$ (5.2 mg, 0.0086 mmol) in $MeNO_2$ (0.9 mL). The resulting reaction mixture was heated to 80 ºC for 1 h. The reaction was then quenched at 23 ºC with saturated aqueous $NaHCO_3$ (5 mL) and extracted with ethyl acetate (3 × 5 mL). The combined organic layers were dried over $MgSO_4$, filtered and then concentrated *in vacuo*. The residue was purified by flash column chromatography to afford cyclopentenone **13** (22.8 mg, 76%) as an orange oil. **^{1}H NMR** (500 MHz, $CDCl_3$) δ 7.73 (dd, *J* = 5.8, 2.3 Hz, 1H), 7.32 (ddd, *J* = 7.7, 4.1 Hz, 5H), 7.27 – 7.22 (m, 3H), 7.13 – 7.08 (m, 2H), 6.36 (dd, *J* = 5.8, 1.9 Hz, 1H), 4.69 (d, *J* = 10.6 Hz, 1H), 4.64 (d, *J* = 10.7 Hz, 1H), 4.27 (ddd, *J* = 2.3, 2.3, 2.3 Hz, 1H), 3.77 (s, 1H), 2.87 (ddd, *J* = 12.5, 8.9, 5.6 Hz, 1H), 2.67 (ddd, *J* = 12.5, 8.8, 5.9 Hz, 1H), 1.57 – 1.41 (m, 2H), 1.29 – 1.20 (m, 4H), 0.89 – 0.81 (m, 3H) ppm; **^{13}C NMR** (125 MHz, $CDCl_3$) δ 207.3, 162.2, 139.1, 136.8, 135.0, 129.1, 128.9, 128.5, 128.3, 128.3,

127.1, 77.2, 75.1, 57.4, 52.8, 29.5, 27.1, 22.6, 14.1 ppm; **IR** (thin film) 3062, 3029, 2954, 2982, 2858, 1711, 1496, 1453, 1165, 1029, 982 cm^{-1}; **MS** (ESI) *m/z* 372.1937 (372.1939 calcd for $C_{23}H_{27}NNaO_2^+$ $[MNa]^+$).

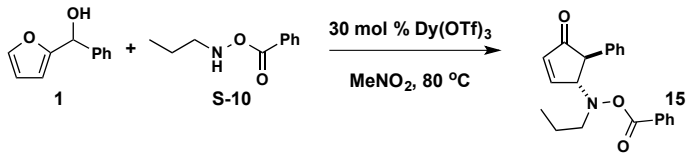


Ethyl 2-(4-oxo-5-phenylcyclopent-2-en-1-yl)-5-phenylisoxazolidine-4-carboxylate (14):

According to the general procedure, furan-2-yl(phenyl)methanol (33.7 mg, 0.194 mmol) and ethyl 5-phenylisoxazolidine-4-carboxylate (made according to literature procedure)[2] **S-9** (42.9 mg, 0.194 mmol) were treated with $Dy(OTf)_3$ (5.9 mg, 0.0097 mmol) in $MeNO_2$ (1.9 mL). The resulting reaction mixture was heated to 80 ºC for 1.25 h. The reaction was then quenched at 23 ºC with saturated aqueous $NaHCO_3$ (5 mL) and extracted with ethyl acetate (3 × 5 mL). The combined organic layers were dried over $MgSO_4$, filtered and then concentrated *in vacuo*. The residue was purified by flash column chromatography to afford cyclopentenone **14** (46.0 mg, 63%, 1:1 mixture of diastereomers) as a brown oil. Higher RF diastereomer **^{1}H NMR** (500 MHz, Toluene-d_8, 90 ºC) δ 7.45 – 7.30 (m, 3H), 7.21 – 6.94 (m, 8H), 6.02 (d, *J* = 5.8 Hz, 1H), 5.33 (d, *J* = 5.9 Hz, 1H), 4.09 (s, 1H), 3.94 – 3.75 (m, 2H), 3.52 (s, 1H), 3.19 – 3.08 (m, 2H), 3.08 – 3.00 (m, 1H), 3.04 (t, *J* = 8.1 Hz, 1H), 0.88 (t, *J* = 7.1 Hz, 3H) ppm; **^{13}C NMR** (200 MHz, Toluene-d_8, 70 ºC) 204.0, 171.6, 170.0, 159.8, 135.4, 129.2, 129.1, 128.6, 127.5, 126.8, 125.7, 81.8, 74.3, 61.3, 60.2, 57.0, 56.8, 56.1, 14.3 ppm; **IR** (thin film) 3063, 3030, 2981, 2927, 2852, 1714, 1597 cm^{-1}; **MS** (ESI) *m/z* 400.1516 (400.1525 calcd for $C_{23}H_{23}NNaO_4^+$ $[MNa]^+$).

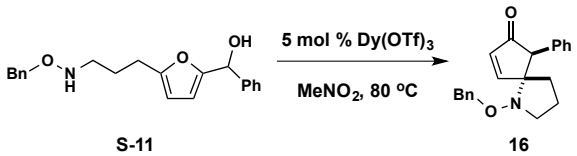
Lower RF diastereomer **^{1}H NMR** (500 MHz, Toluene-d_8, 90 ºC) δ 7.32 (d, *J* = 7.1 Hz, 3H), 7.19 – 7.10 (m, 2H), 7.10 – 6.95 (m, 6H), 6.02 (dd, *J* = 5.8, 1.6 Hz, 1H), 5.18 (d, *J* = 6.5 Hz, 1H), 4.06 (q, *J* = 2.5 Hz, 1H), 3.90 (dddd, *J* = 17.9, 10.8, 7.1, 3.7 Hz, 2H), 3.58 (d, *J* = 3.1 Hz, 1H), 3.37 (dd, *J* = 9.4, 5.2 Hz, 1H), 3.06 (ddd, *J* = 8.7, 6.5, 5.1 Hz, 1H), 2.78 (t, *J* = 9.1 Hz, 1H), 0.92 (t, *J* = 7.1 Hz, 3H) ppm; **^{13}C NMR** (125 MHz, Toluene-d_8,

90 ºC) 203.9, 171.5, 159.5, 159.3, 141.2, 139.4, 135.6, 135.6, 127.4, 127.0, 100.8, 82.1, 74.9, 61.3, 57.0, 56.5, 56.2, 24.5, 14.4 ppm; **IR** (thin film) 3063, 3030, 2981, 2925, 2852, 1714, 1597 cm^{-1}; **MS** (ESI) *m/z* 400.1508 (400.1525 calcd for $C_{23}H_{23}NNaO_4^+$ $[MNa]^+$).



4-((Benzoyloxy)(propyl)amino)-5-phenylcyclopent-2-en-1-one (15):

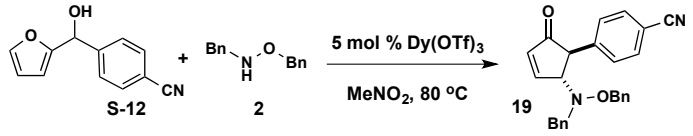
According to the general procedure, furan-2-yl(phenyl)methanol (28.3 mg, 0.163 mmol) and *O*-benzoyl-*N*-propylhydroxylamine (**S-10**) (29.1 mg, 0.163 mmol) were treated with 30 mol % $Dy(OTf)_3$ (29.8 mg, 0.0489 mmol) in MeCN (1.6 mL). The resulting reaction mixture was stirred at room temperature for 58 h. The reaction was then quenched with saturated aqueous $NaHCO_3$ (5 mL) and extracted with ethyl acetate (3 × 5 mL). The combined organic layers were dried over $MgSO_4$, filtered and then concentrated *in vacuo*. The residue was purified by flash column chromatography to afford cyclopentenone **15** (27.1 mg, 50%) as a yellow solid. **^{1}H NMR** (500 MHz, $CDCl_3$) δ 7.90 (dd, *J* = 8.3, 1.4 Hz, 2H), 7.84 (dd, *J* = 5.8, 2.4 Hz, 1H), 7.58 (dddd, *J* = 7.1, 7.1, 1.3, 1.3 Hz, 1H), 7.47 – 7.39 (m, 2H), 7.38 – 7.31 (m, 2H), 7.31 – 7.25 (m, 1H), 7.20 – 7.14 (m, 2H), 6.36 (dd, *J* = 5.8, 1.9 Hz, 1H), 4.56 (dd, *J* = 4.6, 2.3 Hz, 1H), 3.89 (d, *J* = 2.8 Hz, 1H), 3.16 – 3.09 (m, 1H), 2.91 (ddd, *J* = 12.7, 8.2, 6.8 Hz, 1H), 1.61 – 1.48 (m, 2H), 0.89 (t, *J* = 7.4 Hz, 3H) ppm; **^{13}C NMR** (125 MHz, $CDCl_3$) δ 206.2, 165.7, 160.9, 138.4, 135.7, 133.6, 129.6, 129.3, 128.7, 128.5, 128.2, 127.5, 76.0, 59.6, 52.7, 20.6, 11.6 ppm; **IR** (thin film) 3063, 3030, 2964, 2935, 2876, 1743, 1712 cm^{-1}; **MS** (ESI) *m/z* 358.1406 (358.1419 calcd for $C_{21}H_{21}NNaO_3^+$ $[MNa]^+$).



1-(Benzyloxy)-6-phenyl-1-azaspiro[4.4]non-8-en-7-one (16):

According to the general procedure, (5-(3-((benzyloxy)amino)propyl)furan-2-yl)(phenyl)methanol (**S-11**) (240 mg, 0.71 mmol) was treated with $Dy(OTf)_3$ (21.6 mg,

0.036 mmol) in $MeNO_2$ (7 mL). The resulting reaction mixture was heated to 80 ºC for 1 h. The reaction was then quenched at 23 ºC with saturated aqueous $NaHCO_3$ (5 mL) and extracted with ethyl acetate (3 × 5 mL). The combined organic layers were dried over $MgSO_4$, filtered and then concentrated *in vacuo*. The residue was purified by flash column chromatography to afford cyclopentenone **16** (185.6 mg, 82%) as a yellow oil. **^{1}H NMR** (500 MHz, $CDCl_3$) δ 7.54 (d, *J* = 5.8 Hz, 1H), 7.38 – 7.21 (m, 8H), 7.06 – 7.00 (m, 2H), 6.34 (d, *J* = 5.8 Hz, 1H), 4.73 (d, *J* = 11.4 Hz, 1H), 4.70 (d, *J* = 11.4 Hz, 1H), 4.00 (s, 1H), 3.28 – 3.20 (m, 1H), 3.10 (ddd, *J* = 10.2, 8.0, 4.3 Hz, 1H), 1.71 – 1.59 (m, 2H), 1.60 – 1.50 (m, 1H), 1.28 – 1.13 (m, 1H) ppm; **^{13}C NMR** (125 MHz, $CDCl_3$) δ 208.2, 165.5, 137.8, 137.6, 134.5, 130.2, 129.0, 128.6, 128.5, 128.2, 127.1, 78.5, 76.8, 56.6, 53.5, 29.5, 18.9 ppm; **IR** (thin film) 3061, 3029, 2940, 2865, 1707, 1594, 1496, 1453, 1342, 1208, 1032, 977, 918 cm^{-1}; **MS** (ESI) *m/z* 342.1477 (342.1470 calcd for $C_{21}H_{21}NNaO_2^+$ $[MNa]^+$).



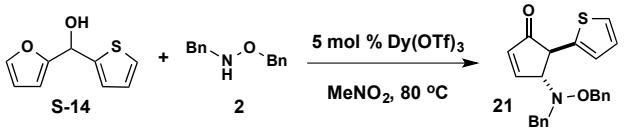
4-(2-(Benzyl(benzyloxy)amino)-5-oxocyclopent-3-en-1-yl)benzonitrile (19):

According to the general procedure, 4-(furan-2-yl(hydroxy)methyl)benzonitrile (34.4 mg, 0.172 mmol) and *N*,*O*-dibenzylhydroxylamine (**2**) (36.8 mg, 0.172 mmol) were treated with $Dy(OTf)_3$ (5.2 mg, 0.0086 mmol) in $MeNO_2$ (1.8 mL). The resulting reaction mixture was heated to 80 ºC for 17 h. The reaction was then quenched at 23 ºC with saturated aqueous $NaHCO_3$ (5 mL) and extracted with ethyl acetate (3 × 5 mL). The combined organic layers were dried over $MgSO_4$, filtered and then concentrated *in vacuo*. The residue was purified by flash column chromatography to afford cyclopentenone **19** (57.0 mg, 84%) as an orange oil. **^{1}H NMR** (500 MHz, $CDCl_3$) δ 7.63 – 7.56 (m, 3H), 7.32 – 7.22 (m, 6H), 7.16 (d, *J* = 8.1 Hz, 2H), 7.15 – 7.10 (m, 2H), 7.07 (s, 2H), 6.32 (dd, *J* = 5.8, 2.0 Hz, 1H), 4.45 (d, *J* = 10.9 Hz, 1H), 4.43 (d, *J* = 10.9 Hz, 1H), 4.22 (ddd, *J* = 2.3 Hz, 1H), 4.00 (d, *J* = 12.6 Hz, 1H), 3.95 (s, 1H), 3.78 (d, *J* = 12.5 Hz, 1H) ppm; **^{13}C NMR** (125 MHz, $CDCl_3$) δ 205.3, 162.3, 144.3, 136.5, 136.2, 134.7, 132.7, 129.6, 129.4, 129.4, 128.5, 128.5, 128.4, 128.0, 118.8, 111.1, 76.8, 73.1, 61.1, 52.6 ppm; **IR** (thin film)

3063, 3031, 2919, 2866, 2227, 1708, 1607, 1454, 1276, 1163, 1028, 972 cm^{-1}; **MS** (ESI) *m/z* 417.1573 (417.1579 calcd for $C_{26}H_{22}N_2NaO_2^+$ $[MNa]^+$).

4-(Benzyl(benzyloxy)amino)-5-(4-methoxyphenyl)cyclopent-2-en-1-one (20):

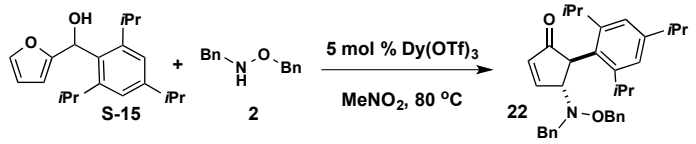
According to the general procedure, furan-2-yl(4-methoxyphenyl)methanol (23.1 mg, 0.113 mmol) and *N*,*O*-dibenzylhydroxylamine (**2**) (24.1 mg, 0.113 mmol) were treated with $Dy(OTf)_3$ (3.4 mg, 0.0057 mmol) in $MeNO_2$ (1.1 mL). The resulting reaction mixture was heated to 80 ºC for 30 min. The reaction was then quenched at 23 ºC with saturated aqueous $NaHCO_3$ (5 mL) and extracted with ethyl acetate (3 × 5 mL). The combined organic layers were dried over $MgSO_4$, filtered and then concentrated *in vacuo*. The residue was purified by flash column chromatography to afford cyclopentenone **20** (36.7 mg, 81%) as a yellow waxy solid. **^{1}H NMR** (600 MHz, $CDCl_3$) δ 7.61 (s, 1H), 7.31 – 7.27 (m, 3H), 7.28 – 7.23 (m, 3H), 7.15 – 7.09 (m, 4H), 7.02 (d, *J* = 8.6 Hz, 2H), 6.87 (d, *J* = 8.6 Hz, 2H), 6.32 (dd, *J* = 5.8, 1.9 Hz, 1H), 4.41 (s, 2H), 4.21 (dd, *J* = , 4.2, 2.1 Hz, 1H), 4.01 (d, *J* = 12.6 Hz, 1H), 3.88 (s, 1H), 3.81 (d, *J* = 12.6 Hz, 1H), 3.80 (s, 3H) ppm; **^{13}C NMR** (150 MHz, $CDCl_3$) δ 207.4, 162.2, 158.8, 136.7, 136.7, 134.9, 130.9, 130.0, 129.5, 129.3, 128.4, 128.4, 128.3, 127.7, 114.6, 77.0, 73.9, 61.4, 55.5, 52.0 ppm; **IR** (thin film) 3030, 2921, 2854, 1883, 1708, 1611, 1511 cm^{-1}; **MS** (ESI) *m/z* 422.1717 (422.1732 calcd for $C_{26}H_{25}NNaO_3^+$ $[MNa]^+$).



4-(Benzyl(benzyloxy)amino)-5-(thiophen-2-yl)cyclopent-2-en-1-one (21):

According to the general procedure, furan-2-yl(thiophen-2-yl)methanol (31.1 mg, 0.172 mmol) and *N*,*O*-dibenzylhydroxylamine (**2**) (36.8 mg, 0.172 mmol) were treated with $Dy(OTf)_3$ (5.2 mg, 0.0086 mmol) in $MeNO_2$ (1.8 mL). The resulting reaction mixture was heated to 80 ºC for 30 min. The reaction was then quenched at 23 ºC with saturated

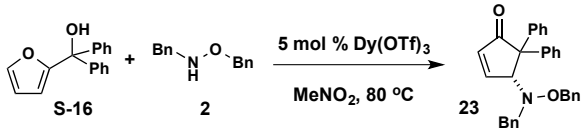
aqueous $NaHCO_3$ (5 mL) and extracted with ethyl acetate (3 × 5 mL). The combined organic layers were dried over $MgSO_4$, filtered and then concentrated *in vacuo*. The residue was purified by flash column chromatography to afford cyclopentenone **21** (59.2 mg, 92%) as a brown oil. **^{1}H NMR** (500 MHz, $CDCl_3$) δ 7.59 (s, 1H), 7.32 – 7.27 (m, 6H), 7.25 – 7.19 (m, 3H), 7.14 – 7.10 (m, 2H), 7.00 – 6.96 (m, 1H), 6.90 (d, *J* = 3.3 Hz, 1H), 6.31 (dd, *J* = 6.0, 1.8 Hz, 1H), 4.43 (d, *J* = 10.6 Hz, 1H), 4.40 (d, *J* = 10.6 Hz, 1H), 4.34 (ddd, *J* = 2.4, 2.4, 2.4 Hz, 1H), 4.20 (s, 1H), 4.06 (d, *J* = 12.7 Hz, 1H), 3.95 (d, *J* = 12.7 Hz, 1H) ppm; **^{13}C NMR** (125 MHz, $CDCl_3$) δ 204.7, 161.4, 140.1, 136.7, 136.5, 134.1, 129.9, 129.2, 128.6, 128.4, 128.3, 127.8, 127.2, 125.9, 124.7, 77.0, 74.1, 61.4, 47.6 ppm; **IR** (thin film) 3064, 3030, 2919, 2867, 1954, 1712, 1454, 1343, 1167, 1028, 972 cm^{-1}; **MS** (ESI) *m/z* 398.1188 (398.1191 calcd for $C_{23}H_{21}NNaO_2S^+$ $[MNa]^+$).



(4R,5S)-4-(Benzyl(benzyloxy)amino)-5-(2,4,6-triisopropylphenyl)cyclopent-2-en-1-one (22):

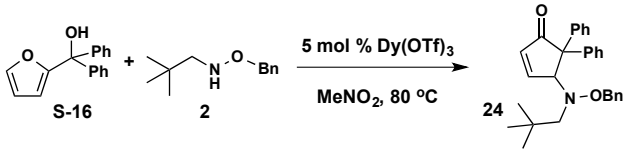
According to the general procedure, furan-2-yl(2,4,6-triisopropylphenyl)methanol (32.0 mg, 0.105 mmol) and *N*,*O*-dibenzylhydroxylamine (**2**) (22.5 mg, 0.105 mmol) were treated with $Dy(OTf)_3$ (3.2 mg, 0.0053 mmol) in $MeNO_2$ (1.0 mL). The resulting reaction mixture was heated to 80 ºC for 40 min. The reaction was then quenched at 23 ºC with saturated aqueous $NaHCO_3$ (5 mL) and extracted with ethyl acetate (3 × 5 mL). The combined organic layers were dried over $MgSO_4$, filtered and then concentrated *in vacuo*. The residue was purified by flash column chromatography to afford cyclopentenone **22** (41.7 mg, 80%) as a white solid. **^{1}H NMR** (600 MHz, $CDCl_3$) δ 7.39 – 7.30 (m, 4H), 7.28 (d, *J* = 7.3 Hz, 2H), 7.17 – 7.13 (m, 1H), 7.11 (t, *J* = 7.4 Hz, 2H), 7.07 (d, *J* = 1.9 Hz, 1H), 6.90 (d, *J* = 1.9 Hz, 1H), 6.67 (s, 2H), 6.31 (d, *J* = 4.7 Hz, 1H), 4.66 (d, *J* = 11.2 Hz, 1H), 4.63 – 4.53 (m, 2H), 4.03 (s, 1H), 3.99 (d, *J* = 12.2 Hz, 1H), 3.65 (d, *J* = 12.2 Hz, 1H), 3.57 (p, *J* = 6.8 Hz, 1H), 2.91 (hept, *J* = 6.9 Hz, 1H), 1.83 (hept, *J* = 6.7 Hz, 1H), 1.44 (d, *J* = 6.6 Hz, 3H), 1.29 (t, *J* = 7.1 Hz, 6H),z 1.25 (d, *J* = 6.8 Hz, 3H), 0.94 (d, *J* = 6.5 Hz, 3H), 0.65 (d, *J* = 5.6 Hz, 3H) ppm; **^{13}C NMR** (150 MHz, $CDCl_3$) δ 207.4, 160.9, 147.9, 147.7, 137.3, 136.3, 134.4, 130.7, 129.7, 129.2, 128.4, 128.3, 128.2, 127.5, 122.5,

121.4, 76.2, 72.6, 60.1, 48.3, 34.4, 30.7, 30.3, 29.9, 26.5, 24.4, 24.3, 24.2, 24.1, 22.2 ppm; **IR** (thin film) 3063, 3032, 2960, 2926, 2868, 1710, 1607 cm^{-1}; **MS** (ESI) *m/z* 518.3011 (518.3035 calcd for $C_{34}H_{41}NNaO_2^+$ $[MNa]^+$).



4-(Benzyl(benzyloxy)amino)-5,5-diphenylcyclopent-2-en-1-one (23):

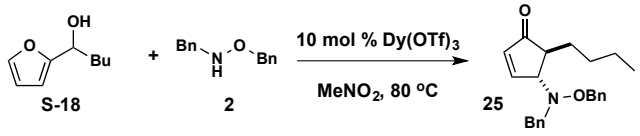
According to the general procedure, furan-2-yldiphenylmethanol (43.2 mg, 0.173 mmol) and *N*,*O*-dibenzylhydroxylamine (**2**) (36.8 mg, 0.173 mmol) were treated with $Dy(OTf)_3$ (5.3 mg, 0.0087 mmol) in $MeNO_2$ (1.7 mL). The resulting reaction mixture was heated to 80 ºC for 4 h. The reaction was then quenched at 23 ºC with saturated aqueous $NaHCO_3$ (5 mL) and extracted with ethyl acetate (3 × 5 mL). The combined organic layers were dried over $MgSO_4$, filtered and then concentrated *in vacuo*. The residue was purified by flash column chromatography to afford cyclopentenone **23** (58.4 mg, 76%) as a yellow oil. **^{1}H NMR** (500 MHz, Toluene-d_8, 90 °C) δ 7.58 (dd, *J* = 6.1, 2.8 Hz, 1H), 7.43 – 7.35 (m, 2H), 7.30 – 7.19 (m, 2H), 7.13 – 7.09 (m, 2H), 7.08 – 6.89 (m, 11H), 6.79 (d, *J* = 6.7 Hz, 2H), 6.32 (s, 1H), 6.02 (dd, *J* = 6.0, 1.4 Hz, 1H), 4.96 (s, 1H), 3.95 (d, *J* = 11.0 Hz, 1H), 3.76 (d, *J* = 10.9 Hz, 1H), 3.49 (dd, *J* = 20.3, 12.9 Hz, 2H) ppm; **^{13}C NMR** (125 MHz, Toluene-d_8, 90 °C) δ 205.0, 143.5, 142.1, 138.3, 135.3, 132.0, 131.8, 130.5, 130.4, 130.4, 128.7, 128.6, 128.5, 128.1, 128.0, 127.9, 127.3, 127.0, 75.8, 75.5, 63.6, 60.7 ppm; **IR** (thin film) 3087, 3060, 3030, 2922, 2858, 1952, 1883, 1808, 1709 cm^{-1}; **MS** (ESI) *m/z* 468.1920 (468.1940 calcd for $C_{31}H_{27}NNaO_2^+$ $[MNa]^+$).



4-((Benzyloxy)(neopentyl)amino)-5,5-diphenylcyclopent-2-en-1-one (24):

According to the general procedure, furan-2-yldiphenylmethanol (100.0 mg, 0.40 mmol) and *O*-benzyl-*N*-neopentylhydroxylamine (**S-7**) (77.2 mg, 0.40 mmol) were treated with $Dy(OTf)_3$ (12.2 mg, 0.020 mmol) in $MeNO_2$ (4.0 mL). The resulting reaction mixture was

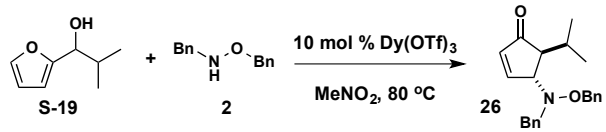
heated to 80 ºC for 18 h. The reaction was then quenched at 23 ºC with saturated aqueous $NaHCO_3$ (5 mL) and extracted with ethyl acetate (3 × 5 mL). The combined organic layers were dried over $MgSO_4$, filtered and then concentrated *in vacuo*. The residue was purified by flash column chromatography to afford cyclopentenone **24** (142.0 mg, 83%) as a brown/orange solid. **^{1}H NMR** (500 MHz, toluene-d_8, 80 °C) δ 7.58 (dd, *J* = 6.1, 2.7 Hz, 1H), 7.54 – 7.50 (m, 2H), 7.18 (d, *J* = 7.5 Hz, 2H), 7.03 (m, 11H) 6.02 (dd, *J* = 6.0, 1.4 Hz, 1H), 4.92 (s, 1H), 4.28 (d, *J* = 11.1 Hz, 1H), 3.86 (s, 1H), 2.55 (d, *J* = 13.9 Hz, 1H), 2.25 (d, *J* = 13.8 Hz, 1H), 0.71 (s, 9H) ppm; **^{13}C NMR** (125 MHz, toluene-d_8, 80 °C) δ 204.5, 158.1, 143.9, 141.3, 138.0, 135.0, 131.8, 131.6, 128.5, 128.4, 128.2, 127.6, 126.9, 126.7, 77.2, 73.2, 67.7, 62.9, 31.7, 28.7, 24.2 ppm; **IR** (thin film) 3059, 2953, 2868, 1707, 1494, 1444, 1265, 1037, 1029, 949 cm^{-1}; **MS** (ESI) *m/z* 448.2231 (448.2252 calcd for $C_{29}H_{31}NNaO_2^+$ $[MNa]^+$).



4-(Benzyl(benzyloxy)amino)-5-butylcyclopent-2-en-1-one (25):

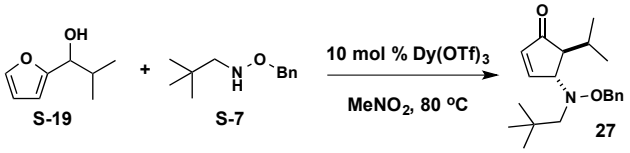
According to the general procedure, 1-(furan-2-yl)pentan-1-ol (26.5 mg, 0.172 mmol) and *N*,*O*-dibenzylhydroxylamine (**2**) (36.7 mg, 0.172 mmol) were treated with $Dy(OTf)_3$ (10.5 mg, 0.0172 mmol) in $MeNO_2$ (1.8 mL). The resulting reaction mixture was heated to 80 ºC for 48 h. The reaction was then quenched at 23 ºC with saturated aqueous $NaHCO_3$ (5 mL) and extracted with ethyl acetate (3 × 5 mL). The combined organic layers were dried over $MgSO_4$, filtered and then concentrated *in vacuo*. The residue was purified by flash column chromatography to afford cyclopentenone **25** (31.8 mg, 53%) as a dark yellow oil. **^{1}H NMR** (500 MHz, $CDCl_3$) δ 7.66 (dd, *J* = 5.9, 2.0 Hz, 1H), 7.42 (d, *J* = 7.2 Hz, 2H), 7.37 (t, *J* = 7.2 Hz, 2H), 7.35 – 7.31 (m, 1H), 7.29 – 7.24 (m, 3H), 7.11 – 7.05 (m, 2H), 6.26 (dd, *J* = 5.8, 1.4 Hz, 1H), 4.34 (s, 2H), 3.98 (d, *J* = 12.9 Hz, 1H), 3.95 (d, *J* = 13.1 Hz, 1H), 3.91 (s, 1H), 2.53 (s, 1H), 1.76 – 1.65 (m, 1H), 1.63 – 1.51 (m, 1H), 1.35 – 1.23 (m, 4H), 0.88 (dd, *J* = 6.9 Hz, 3H) ppm; **^{13}C NMR** (125 MHz, $CDCl_3$) δ 209.9, 160.8, 137.4, 136.7, 135.7, 129.8, 129.1, 128.5, 128.4, 128.2, 127.8, 76.9, 71.7, 60.7, 47.2, 30.0, 28.9, 23.0, 14.0 ppm; **IR** (thin film) 3063, 3031, 2955, 2928, 2858,

1707, 1454, 1359, 1176, 1028, 976 cm^{-1}; **MS** (ESI) *m/z* 372.1941 (372.1939 calcd for $C_{23}H_{27}NNaO_2^+$ $[MNa]^+$).



(4-(Benzyl(benzyloxy)amino)-5-isopropylcyclopent-2-en-1-one (26):

According to the general procedure, 1-(furan-2-yl)-2-methylpropan-1-ol (12.1 mg, 0.086 mmol) and *N*,*O*-dibenzylhydroxylamine (**2**) (18.4 mg, 0.086 mmol) were treated with $Dy(OTf)_3$ (5.2 mg, 0.0086 mmol) in $MeNO_2$ (0.9 mL). The resulting reaction mixture was heated to 80 ºC for 24 h. The reaction was then quenched at 23 ºC with saturated aqueous $NaHCO_3$ (5 mL) and extracted with ethyl acetate (3 × 5 mL). The combined organic layers were dried over $MgSO_4$, filtered and then concentrated *in vacuo*. The residue was purified by flash column chromatography to afford cyclopentenone **26** (14.4 mg, 50%) as a light orange oil. **^{1}H NMR** (500 MHz, $CDCl_3$) δ 7.74 (dd, *J* = 5.7, 2.1 Hz, 1H), 7.36 (m, 5H), 7.28 – 7.22 (m, 3H), 7.09 – 7.01 (m, 2H), 6.26 (dd, *J* = 5.8, 1.3 Hz, 1H), 4.33 (s, 2H), 4.00 – 3.87 (m, 3H), 2.41 (s, 1H), 2.19 (dqq, *J* = 13.9, 6.9, 4.5 Hz, 1H), 0.94 (d, *J* = 6.9 Hz, 3H), 0.83 (d, *J* = 6.8 Hz, 3H) ppm; **^{13}C NMR** (125 MHz, $CDCl_3$) δ 209.7, 160.8, 137.5, 136.7, 136.6, 129.8, 129.1, 128.5, 128.4, 128.2, 127.8, 77.0, 68.9, 60.5, 52.9, 29.0, 20.2, 18.8 ppm; **IR** (thin film) 3063, 3031, 2957, 2928, 2872, 1703, 1454, 1367, 1181, 1028, 963 cm^{-1}; **MS** (ESI) *m/z* 358.1787 (358.1783 calcd for $C_{22}H_{25}NNaO_2^+$ $[MNa]^+$).

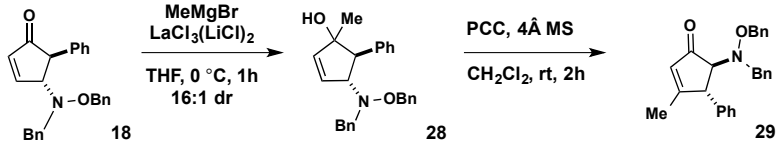


4-((Benzyloxy)(neopentyl)amino)-5-isopropylcyclopent-2-en-1-one (27):

According to the general procedure, 1-(furan-2-yl)-2-methylpropan-1-ol (20.0 mg, 0.140 mmol) and *O*-benzyl-*N*-neopentylhydroxylamine (**S-7**) (27.6 mg, 0.140 mmol) were treated with $Dy(OTf)_3$ (8.7 mg, 0.014 mmol) in $MeNO_2$ (1.4 mL). The resulting reaction mixture was heated to 80 ºC for 96 h. The reaction was then quenched at 23 ºC with saturated aqueous $NaHCO_3$ (5 mL) and extracted with ethyl acetate (3 × 5 mL). The

combined organic layers were dried over $MgSO_4$, filtered and then concentrated *in vacuo*. The residue was purified by flash column chromatography to afford cyclopentenone **27** (22.6 mg, 51%) as an orange oil. **^{1}H NMR** (500 MHz, $CDCl_3$) δ 7.80 (dd, *J* = 5.8, 2.1 Hz, 1H), 7.36 – 7.27 (m, 5H), 6.27 (dd, *J* = 5.9, 1.6 Hz, 1H), 4.79 (d, *J* = 10.6 Hz, 1H), 4.73 (d, *J* = 10.6 Hz, 1H), 4.15 (s, 1H), 2.55 (d, *J* = 14.3 Hz, 1H), 2.34 (d, *J* = 14.0 Hz, 1H), 2.27 (dqq, *J* = 13.8, 6.9, 4.1 Hz, 1H), 2.15 (s, 1H), 1.04 (d, *J* = 7.0 Hz, 3H), 0.97 (s, 9H), 0.87 (d, *J* = 6.8 Hz, 3H) ppm; **^{13}C NMR** (125 MHz, $CDCl_3$) δ 209.5, 161.9, 137.0, 136.8, 128.6, 128.5, 128.1, 74.6, 69.1, 66.0, 53.4, 31.6, 28.8, 28.6, 20.5, 18.6 ppm; **IR** (thin film) 3065, 3032, 2955, 2870, 1705, 1463, 1362, 1027, 976 cm^{-1}; **MS** (ESI) *m/z* 338.2093 (338.2096 calcd for $C_{20}H_{29}NNaO_2^+$ $[MNa]^+$).

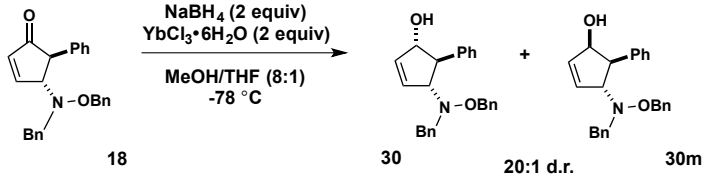
Selected Functionalization of the Cyclopentenone Scaffold:



5-(Benzyl(benzyloxy)amino)-3-methyl-4-phenylcyclopent-2-en-1-one (29):

Adapted from literature procedure.[3] In a flame dried round bottom flask with magnetic stirrer under N_2 atmosphere, 4-(benzyl(benzyloxy)amino)-5-phenylcyclopent-2-en-1-one **3** was dissolved in 0.5 mL dry THF followed by the addition of 0.6 M $LaCl_3(LiCl)_2$ in THF (0.0939 mmol, 157 μL) and stirring at room temperature for 1 hour. The reaction mixture was cooled to 0 ºC and 3.0 M methylmagnesium bromide in diethyl ether (0.188 mmol, 63 μL) was added. Stirring at 0 ºC continued until complete as determined by thin layer chromatography. Upon completion, the reaction was quenched with saturated aqueous NH_4Cl (5 mL) then extracted with EtOAc (3 x 5 mL). The combined organic layers were dried over $MgSO_4$, filtered and then concentrated *in vacuo*. The crude reaction mixture contained allylic alcohol **28** in 16:1 dr as determined by ^{1}H NMR spectroscopy**.** The crude reaction mixture was passed through a silica gel plug using 3:1 hexanes : ethyl acetate and used as is for the subsequent reaction. 80% Yield of crude material.

Adapted from literature procedure.[4] In a 10 mL round bottom flask containing a magnetic stir bar under N_2 atmosphere, 4Å mol sieves (500 mg) and pyridinium chlorochromate (PCC) (27.2 mg, 0.126 mmol) were added to anhydrous CH_2Cl_2 (1 mL) followed by addition of 4-(benzyl(benzyloxy)amino)-1-methyl-5-phenylcyclopent-2-en-1-ol **28** (24.3 mg, 0.063 mmol). Reaction was stirred until complete (2 h) as determined by thin layer chromatography. Upon completion, 5 mL Et_2O was added, and the residual solids were decanted off (3 x). The decanted liquid was transferred to a separatory funnel containing 5 mL 2M NaOH and extracted with Et_2O (3 x 5 mL). The combined organic layers were dried over $MgSO_4$, filtered and then concentrated *in vacuo*. The residue was purified by flash column chromatography (1% EtOAc in toluene) to afford cyclopentenone **29** (18.4 mg, 70%) (56% yield over 2 steps) as a colorless oil. **^{1}H NMR** (600 MHz, $CDCl_3$) δ 7.36 – 7.30 (m, 2H), 7.31 – 7.24 (m, 3H), 7.21 – 7.16 (m, 3H), 7.14 – 7.08 (m, 7H), 6.16 (s, 1H), 4.65 (d, *J* = 10.3 Hz, 1H), 4.42 (d, *J* = 10.3 Hz, 1H), 4.33 (s, 1H), 4.10 (d, *J* = 12.4 Hz, 1H), 3.93 (d, *J* = 12.4 Hz, 1H), 3.62 (d, *J* = 2.7 Hz, 1H), 1.85 (s, 3H) ppm; **^{13}C NMR** (150 MHz, $CDCl_3$) δ 205.3, 179.1, 141.0, 137.0, 136.5, 130.7, 130.0, 129.3, 129.3, 128.4, 128.2, 128.1, 128.1, 127.6, 127.4, 76.5, 76.5, 60.8, 51.4, 18.2 ppm; **IR** (thin film) 3405, 3063, 3030, 2924, 2857, 1953, 1880, 1810, 1711, 1623 cm^{-1}; **MS** (ESI) *m/z* 406.1795 (406.1783 calcd for $C_{26}H_{25}NNaO_2^+$ $[MNa]^+$).

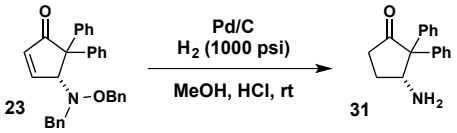


4-(Benzyl(benzyloxy)amino)-5-phenylcyclopent-2-en-1-ol (30 and **30m):**

4-(Benzyl(benzyloxy)amino)-5-phenylcyclopent-2-en-1-one (**18**) (231 mg, 0.63 mmol) and $YbCl_3$•$6H_2O$ (387.5 mg, 1.25 mmol) was dissolved in 3 mL THF, then 23 mL MeOH was added and the solution stirred while cooling to -78 ºC. $NaBH_4$ (47.3 mg, 1.25 mmol) was added in one portion and the reaction was stirred at -78 ºC until complete (1 h) as determined by thin layer chromatography (2:1 hexanes:ethyl acetate, stained with

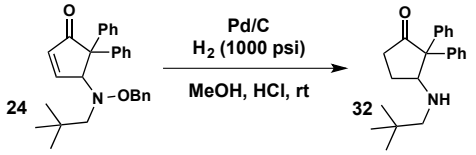
anisaldehyde). The reaction was then quenched with saturated aqueous NH_4Cl (5 mL) and extracted with ethyl acetate (3 × 10 mL). The combined organic layers were dried over $MgSO_4$, filtered and then concentrated *in vacuo*. The residue (20:1 dr as determined by ^{1}H NMR of crude mixture) was purified by flash column chromatography (15:1 → 9:1 → 6:1 hexanes:ethyl acetate) to afford cyclopentenone **30** (174 mg, 78%) as a colorless oil. *Major Diastereomer:* **^{1}H NMR** (600 MHz, $CDCl_3$) δ 7.36 – 7.27 (m, 10H), 7.23 (t, *J* = 7.4 Hz, 1H), 7.17 (d, *J* = 7.2 Hz, 2H), 7.15 – 7.09 (m, 2H), 6.24 – 6.19 (m, 1H), 6.19 – 6.14 (m, 1H), 4.48 (s, 1H), 4.43 (d, *J* = 9.8 Hz, 1H), 4.29 (d, *J* = 9.8 Hz, 1H), 4.06 (d, *J* = 12.7 Hz, 1H), 3.96 (q, *J* = 2.1 Hz, 1H), 3.85 (d, *J* = 12.7 Hz, 1H), 3.44 (s, 1H), 2.49 (s, 1H) ppm; **^{13}C NMR** (150 MHz, $CDCl_3$) δ 144.5, 137.4, 137.0, 136.1, 134.4, 130.1, 129.5, 128.9, 128.5, 128.4, 128.3, 127.6, 127.0, 126.4, 83.4, 78.2, 77.3, 61.4, 53.1 ppm; **IR** (thin film) 3414, 3062, 3030, 2878, 1602, 1495, 1454 cm^{-1}; **MS** (ESI) *m/z* 394.1785 (394.1783 calcd for $C_{25}H_{25}NNaO_2^+$ $[MNa]^+$).

Minor Diastereomer: **^{1}H NMR** (600 MHz, Chloroform-d) δ 7.37 – 7.31 (m, 2H), 7.32 – 7.21 (m, 12H), 7.03 (s, 2H), 6.31 (d, J = 6.4 Hz, 1H), 6.12 (d, J = 5.8 Hz, 1H), 4.96 (d, J = 6.8 Hz, 1H), 4.49 – 4.40 (m, 1H), 4.40 – 4.24 (m, 2H), 3.89 (d, J = 12.9 Hz, 1H), 3.82 – 3.71 (m, 2H). ppm; **^{13}C** NMR (150 MHz, Chloroform-d) δ 139.0, 137.0, 135.8, 135.4, 130.0, 129.4, 129.1, 128.8, 128.3, 128.2, 128.0, 127.4, 127.1, 77.7, 77.0, 76.5, 61.6 ppm; **IR** (thin film) 3413, 3062, 3003, 2919, 1602, 1495, 1454, 1361 cm^{-1}; **MS** (ESI) *m/z* 394.1769 (394.1783 calcd for $C_{25}H_{25}NNaO_2^+$ $[MNa]^+$).



3-Amino-2,2-diphenylcyclopentan-1-one (31): In a 20 mL vial, 4-(benzyl(benzyloxy)amino)-5,5-diphenylcyclopent-2-en-1-one **23** (13.4 mg, 0.0301 mmol) was dissolved in MeOH (1.5 mL), followed by addition of Palladium on carbon (10 wt%) (1.6 mg, 0.0015 mmol). One drop of 12M HCl from an 18 gauge needle was added prior to placing the vial into the pressure vessel. The reaction mixture was placed under H_2 gas at 70 bar for 48h. The reaction mixture was filtered over Celite. The Celite

pad was rinsed with ethyl acetate (3 x 5mL). The organic layer was then quenched with saturated aqueous $NaHCO_3$ (5 mL) and extracted with ethyl acetate (3 x 5 ml). The combined organic layers were dried with Na_2SO_4, filtered and then concentrated *in vacuo* to afford **31** (7.6 mg, quantitative yield) as a clear oil. **^{1}H NMR** (600 MHz, $CDCl_3$) δ 7.41 (d, *J* = 7.6 Hz, 2H), 7.36 – 7.31 (m, 2H), 7.29 – 7.24 (m, 3H), 7.24 – 7.19 (m, 1H), 7.11 (d, *J* = 8.0 Hz, 2H), 4.37 (t, *J* = 4.5 Hz, 1H), 2.75 – 2.60 (m, 1H), 2.46 – 2.29 (m, 2H), 1.83 – 1.74 (m, 1H), 1.69 (bs, 2H) ppm; **^{13}C NMR** (150 MHz, $CDCl_3$) δ 216.3, 140.5, 139.8, 129.7, 128.8, 128.6, 128.2, 127.3, 127.0, 66.7, 56.4, 36.0, 27.5 ppm; **IR** (thin film) 3372, 3302, 3086, 3057, 3032, 2925, 2855, 1763, 1672 cm^{-1}; **MS** (EI) *m/z* 251.1305 (251.1310 calcd for $C_{17}H_{17}NO^+$ $[M]^+$).



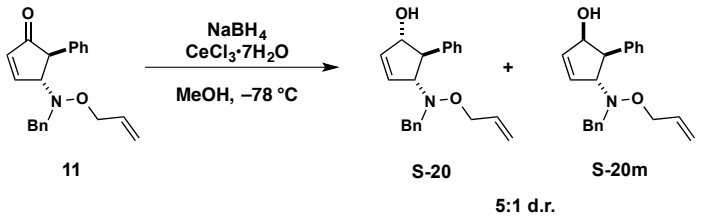
3-(Neopentylamino)-2,2-diphenylcyclopentan-1-one (32):

In a 20 mL vial, 4-((benzyloxy)(neopentyl)amino)-5,5-diphenylcyclopent-2-en-1-one **24** (41.5 mg, 0.098 mmol) was dissolved in MeOH (1.5 mL), followed by addition of Palladium on carbon (10 wt%) (5.2 mg, 0.0049 mmol). One drop of 12M HCl from an 18 gauge needle was added prior to placing the vial into the pressure vessel. The reaction mixture was placed under H_2 gas at 70 bar for 48h. The reaction mixture was filtered over Celite. The Celite pad was rinsed with ethyl acetate (3 x 5mL). The organic layer was then quenched with saturated aqueous $NaHCO_3$ (5 mL) and extracted with ethyl acetate (3 x 5 mL). The combined organic layers were dried over Na_2SO_4, filtered and then concentrated *in vacuo* to afford **32** (31.3 mg, quantitative yield) as a brown oil.

^{1}H NMR (600 MHz, $CDCl_3$) δ 7.45 (d, *J* = 7.3 Hz, 2H), 7.31 (t, *J* = 7.8 Hz, 2H), 7.28 – 7.21 (m, 3H), 7.20 (d, *J* = 7.5 Hz, 3H), 3.94 (t, *J* = 4.3 Hz, 1H), 2.63 (ddd, *J* = 18.9, 9.0, 7.2 Hz, 1H), 2.46 (d, *J* = 11.1 Hz, 1H), 2.28 (ddd, *J* = 18.8, 9.1, 4.5 Hz, 1H), 2.22 (d, *J* = 11.0 Hz, 1H), 2.19 (dddd, *J* = 11.5, 9.1, 5.9, 3.5 Hz, 1H), 1.89 (dddd, *J* = 13.4, 9.1, 4.4, 4.4 Hz, 1H), 1.29 (s, 1H), 0.76 (s, 9H) ppm; **^{13}C NMR** (150 MHz, $CDCl_3$) δ 216.6, 140.4, 140.0, 66.3, 63.4, 59.8, 35.5, 31.7, 29.8, 27.7, 23.8 ppm; **IR** (thin film) 3347, 3087, 3058,

3031, 2951, 2864, 1737, 1599 cm^{-1}; **MS** (EI) *m/z* 321.2096 (321.2093 calcd for $C_{22}H_{27}NO^{+}$ $[M]^{+}$).

Synthesis of Allylic Alcohols:



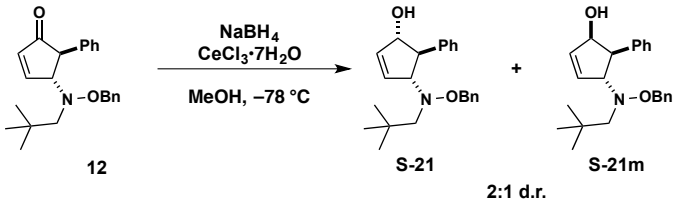
11 S-20 S-20m

5:1 d.r.

4-((Allyloxy)(benzyl)amino)-5-phenylcyclopent-2-en-1-ol (S-20):

A solution of **11** (300.0 mg, 0.94 mmol) in MeOH (22 mL) was treated with $CeCl_3 \bullet 7H_2O$ (384.9 mg, 1.03 mmol) and stirred at rt for 20 min. The solution was cooled to –78 °C and subsequently treated with $NaBH_4$ (46.2 mg, 1.22 mmol) and stirred at this temperature until the reaction was complete by TLC. The reaction was quenched with H_2O, and allowed to come to rt before removal of the solvent and extracting with EtOAc (3 x 10 mL). The combined organic phases were dried over $MgSO_4$, filtered and then concentrated *in vacuo*. ^{1}H NMR analysis of the crude reaction mixture indicated a 5:1 mixture of diastereomers. The residue was purified by flash column chromatography to afford the separated allylic alcohols **S-20** and **S-20m** (286.8 mg, 95% combined yield) as yellow oils. *Major diastereomer*: **^{1}H NMR** (500 MHz, $CDCl_3$) δ 7.32 – 7.27 (m, 2H), 7.27 – 7.24 (m, 5H), 7.25 – 7.18 (m, 1H), 7.18 – 7.13 (m, 2H), 6.19 (ddd, *J* = 5.7, 1.9, 1.9 Hz, 1H), 6.11 (dd, *J* = 5.7, 2.3 Hz, 1H), 5.70 (dddd, *J* = 16.8, 10.3, 6.3, 6.3 Hz, 1H), 5.17 – 5.08 (m, 1H), 5.13–5.11 (m, 1H), 4.48 (d, *J* = 6.1 Hz, 1H), 4.04 (d, *J* = 12.7 Hz, 1H), 3.96 – 3.90 (m, 1H), 3.90 – 3.83 (m, 2H), 3.81 (d, *J* = 12.8 Hz, 1H), 3.43 (s, 1H), 2.65 (s, 1H) ppm; **^{13}C NMR** (125 MHz, $CDCl_3$) δ 144.4, 137.3, 137.1, 134.4, 133.0, 130.0, 128.9, 128.3, 127.5, 127.0, 126.5, 119.0, 83.3, 78.0, 76.0, 61.4, 53.3 ppm; **IR** (thin film) 3413, 3061, 3029, 2918, 2851, 1601, 1494, 1453, 1344, 1080, 1027, 995, 925 cm^{-1}; **MS** (ESI) *m/z* 344.1605 (344.1626 calcd for $C_{21}H_{23}NNaO_2$ $[MNa]^{+}$). *Minor diastereomer*: **^{1}H NMR** (600 MHz, $CDCl_3$) δ 7.33 (t, *J* = 7.5 Hz, 2H), 7.29 – 7.18 (m, 8H), 6.27 (d, *J* = 4.3 Hz, 1H), 6.11 – 6.05 (m, 1H), 5.63 (dddd, *J* = 16.7, 10.4, 6.3, 6.3 Hz, 1H), 5.07 – 5.00 (m, 2H), 4.92 (d, *J* = 5.9 Hz, 1H), 4.40 – 4.36 (m, 1H), 3.90 – 3.82 (m, 3H), 3.76 – 3.68 (m,

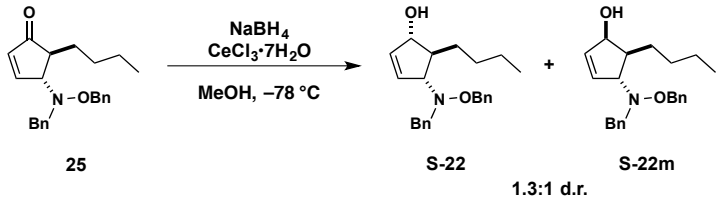
2H), 1.25 (d, *J* = 12.8 Hz, 1H) ppm; **^{13}C NMR** (125 MHz, $CHCl_3$) δ 139.0, 137.7, 135.9, 135.2, 133.8, 129.8, 129.4, 128.8, 128.2, 127.4, 127.1, 117.9, 77.6, 76.2, 75.9, 61.6, 50.8 ppm; **IR** (thin film) 3425, 3061, 3029, 2917, 2865, 1602, 1494, 1453, 1342, 1069, 1029, 994 $^{-1}$; **MS** (ESI) *m/z* 344.1636 (344.1626 calcd for $C_{21}H_{23}NNaO_2$ $[MNa]^+$).



4-((Benzyloxy)(neopentyl)amino)-5-phenylcyclopent-2-en-1-ol (S-21 and **S-21m):**

A solution of **12** (52.6 mg, 0.15 mmol) in MeOH (3.6 mL) was treated with $CeCl_3$•$7H_2O$ (61.7 mg, 0.17 mmol) and stirred at rt for 20 min. The solution was cooled to –78 °C and subsequently treated with $NaBH_4$ (7.4 mg, 0.20 mmol) and stirred at this temperature until the reaction was complete as judged by TLC. The reaction was quenched with H_2O and allowed to come to rt before extracting with EtOAc (3x 6 mL). The combined organic phases were dried over $MgSO_4$, filtered and then concentrated *in vacuo*. ^{1}H NMR analysis of the crude reaction mixture indicated a 2:1 mixture of diastereomers. The residue was purified by flash column chromatography to afford the separated allylic alcohols **S-21** and **S-21m** (37.1 mg, 70% combined yield) as yellow oils. *Major diastereomer*: **^{1}H NMR** (500 MHz, $CDCl_3$) δ 7.33 – 7.27 (m, 5H), 7.23 – 7.19 (m, 3H), 7.16 – 7.11 (m, 2H), 6.18 (dd, *J* = 5.7, 2.1 Hz, 1H), 6.15 (ddd, *J* = 5.7, 1.8, 1.8 Hz, 1H), 4.76 (d, *J* = 10.0 Hz, 1H), 4.58 (d, *J* = 9.9 Hz, 1H), 4.45 (s, 1H), 3.95 (s, 1H), 3.25 (dd, *J* = 2.6, 2.6 Hz, 1H), 2.82 (d, *J* = 14.1 Hz, 1H), 2.60 (d, *J* = 14.1 Hz, 1H), 2.33 (s, 1H), 0.95 (s, 9H) ppm; **^{13}C NMR** (125 MHz, $CDCl_3$) δ 144.9, 136.7, 136.2, 134.6, 129.1, 128.9, 128.6, 128.3, 127.0, 126.3, 83.3, 80.9, 75.6, 69.0, 53.9, 31.7, 28.7 ppm; **IR** (thin film) 3408, 3086, 3061, 3029, 2951, 2903, 2866, 1945, 1804, 1602, 1453, 1360, 1209, 1020, 1011, 909 cm^{-1}; **MS** (ESI) *m/z* 374.2069 (374.2096 calcd for $C_{23}H_{29}NNaO_2^+$ $[MNa]^+$). *Minor Diastereomer*: **^{1}H NMR** (600 MHz, $CDCl_3$) δ 7.34 (t, *J* = 7.5 Hz, 2H), 7.30 – 7.24 (m, 6H), 7.14 (d, *J* = 6.0 Hz, 2H), 6.30 (d, *J* = 5.6 Hz, 1H), 6.13 – 6.04 (m, 1H), 4.92 (d, *J* = 6.5 Hz, 1H), 4.66 – 4.60 (m, 2H), 4.56 (s, 1H), 3.53 (dd, *J* = 6.2 Hz, 1H), 2.61 (d, *J* = 14.2 Hz, 1H), 2.48 (d, *J* = 14.2 Hz, 1H), 1.25 (s, 1H), 0.89 (s, 9H) ppm; **^{13}C NMR** (125

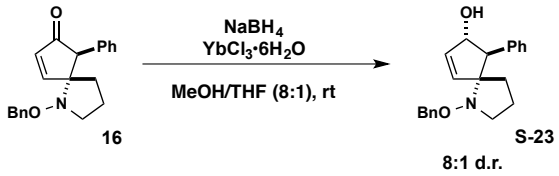
MHz, $CDCl_3$) δ 139.3, 137.2, 136.1, 135.5, 129.4, 128.8, 128.6, 128.4, 127.9, 127.0, 78.4, 77.4, 74.8, 67.6, 50.4, 31.6, 28.6 ppm; **IR** (thin film) 3412, 3086, 3061, 3030, 2951, 2904, 2865, 1947, 1807, 1602, 1453, 1361, 1208, 1027, 910 cm^{-1}; **MS** (ESI) *m/z* 374.2097 (374.2096 calcd for $C_{23}H_{29}NNaO_2^+$ $[MNa]^+$).



4-(Benzyl(benzyloxy)amino)-5-butylcyclopent-2-en-1-ol (S-22 and **S-22m):**

A solution of **25** (145.5 mg, 0.42 mmol) in MeOH (10 mL) was treated with $CeCl_3$•$7H_2O$ (170.6 mg, 0.45 mmol) and stirred at rt for 20 min. The solution was cooled to –30 °C and subsequently treated with $NaBH_4$ (20.5 mg, 0.54 mmol) and stirred at this temperature until the reaction was complete by TLC. The reaction was quenched with H_2O and allowed to come to rt before extracting with EtOAc (3x 10 mL). The combined organic phases were dried over $MgSO_4$, filtered and then concentrated *in vacuo*. ^{1}H NMR analysis of the crude reaction mixture indicated a 1.3:1 mixture of diastereomers. The residue was purified by flash column chromatography to afford the separated allylic alcohols **S-22** and **S-22m** (132.6 mg, 90% combined yield) as a yellow oil (major) and light orange solid (minor). *Major diastereomer*: **^{1}H NMR** (600 MHz, $CDCl_3$) δ 7.43 (d, *J* = 7.2 Hz, 2H), 7.36 (t, *J* = 7.4 Hz, 2H), 7.31 (t, *J* = 7.3 Hz, 1H), 7.25 (d, *J* = 5.9 Hz, 3H), 7.08 – 7.05 (m, 2H), 6.03 (d, *J* = 5.3 Hz, 1H), 5.99 – 5.95 (m, 1H), 4.35 (d, *J* = 9.7 Hz, 1H), 4.24 – 4.18 (m, 1H), 4.15 (d, *J* = 8.4 Hz, 1H), 3.96 (d, *J* = 12.8 Hz, 1H), 3.86 (d, *J* = 12.8 Hz, 1H), 3.51 (s, 1H), 2.28 (s, 1H), 2.15 (s, 1H), 1.42 – 1.27 (m, 6H), 0.90 (dd, *J* = 7.0, 7.0 Hz, 3H) ppm; **^{13}C NMR** (125 MHz, $CDCl_3$) δ 137.9, 136.7, 136.1, 133.0, 130.0, 129.5, 128.5, 128.4, 128.3, 127.6, 80.9, 77.2, 76.1, 61.3, 46.9, 33.6, 30.1, 23.0, 14.2 ppm; **IR** (thin film) 3422, 3087, 3062, 3031, 2955, 2926, 2856, 1496, 1454, 1359, 1209, 1028, 1000 cm^{-1}; **MS** (ESI) *m/z* 374.2101 (374.2096 calcd for $C_{23}H_{29}NNaO_2$ $[MNa]^+$). *Minor Diastereomer*: **^{1}H NMR** (600 MHz, $CDCl_3$) δ 7.39 (d, *J* = 7.2 Hz, 2H), 7.33 (t, *J* = 7.3 Hz, 2H), 7.29 (d, *J* = 7.2 Hz, 1H), 7.28 – 7.21 (m, 3H), 7.11 – 7.02 (m, 2H), 6.24 (d, *J* = 5.2 Hz, 1H), 6.06 (ddd, *J* = 5.8, 2.1, 2.1 Hz, 1H), 4.78 (d, *J* = 5.6 Hz, 1H), 4.34 (s, 2H),

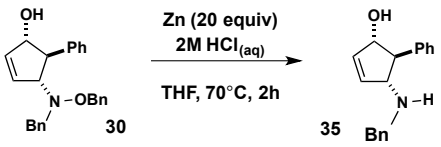
3.93 (d, *J* = 13.0 Hz, 1H), 3.85 (d, *J* = 13.0 Hz, 1H), 3.80 (s, 1H), 2.13 (dddd, *J* = 12.5, 6.1, 6.1, 6.1 Hz, 1H), 1.64 – 1.54 (m, 1H), 1.52 – 1.45 (m, 1H), 1.45 – 1.38 (m, 1H), 1.37 – 1.28 (m, 3H), 1.14 (s, 1H), 0.91 (dd, *J* = 7.1, 7.1 Hz, 3H) ppm; **^{13}C NMR** (125 MHz, $CDCl_3$) δ 138.3, 137.2, 136.0, 134.7, 129.8, 129.1, 128.3, 127.9, 127.4, 76.7, 76.2, 76.1, 60.3, 44.6, 31.0, 27.5, 23.2, 14.3 ppm; **IR** (thin film) 3376, 3089, 3064, 3033, 2956, 2930, 2872, 2859, 1606, 1496, 1454, 1362, 1265, 1210, 1028, 906 cm^{-1}; **MS** (ESI) *m/z* 374.2087 (374.2096 calcd for $C_{23}H_{29}NNaO_2$ $[MNa]^+$).



1-(Benzyloxy)-6-phenyl-1-azaspiro[4.4]non-8-en-7-ol (S-23):

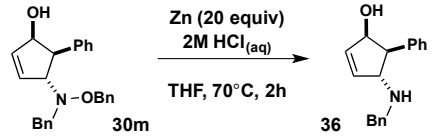
A solution of **16** (85.0 mg, 0.27 mmol) in MeOH (3.6 mL) and THF (0.4 mL) was treated with $YbCl_3$•$6H_2O$ (206.4 mg, 0.53 mmol) and stirred at rt for 20 min. The solution was subsequently treated with $NaBH_4$ (20.1 mg, 0.53 mmol) and stirred at this temperature until the reaction was complete by TLC. The reaction was quenched with saturated NH_4Cl and extracted with EtOAc (3 x 10 mL). The combined organic phases were dried over $MgSO_4$, filtered and then concentrated *in vacuo*. The residue was purified by flash column chromatography to afford allylic alcohol **S-23** (66.5 mg, 77%, isolated as an inseparable mixture of diastereomers with 8:1 d.r.) as a light yellow oil. *Major*: **^{1}H NMR** (500 MHz, $CDCl_3$) δ 7.39 – 7.28 (m, 8H), 7.27 – 7.22 (m, 2H), 6.18 (dd, *J* = 5.7, 1.9 Hz, 1H), 6.02 (d, *J* = 5.3 Hz, 1H), 5.19 (dd, *J* = 6.3, 6.3 Hz, 1H), 4.80 – 4.67 (m, 2H), 3.68 (d, *J* = 7.0 Hz, 1H), 3.17 – 2.99 (m, 2H), 1.70 – 1.60 (m, 2H), 1.59 – 1.49 (m, 1H), 1.49 – 1.38 (m, 1H) ppm; **^{13}C NMR** (125 MHz, $CDCl_3$) δ138.2, 137.9, 137.6, 137.2, 130.6, 128.9, 128.5, 128.4, 127.9, 127.1, 83.0, 78.3, 76.6, 54.7, 53.3, 30.6, 19.3 ppm; **IR** (thin film) 3413, 3086, 3059, 3029, 2940, 2866, 1601, 1494, 1453, 1362, 1208, 1080, 1026, 974 cm^{-1}; **MS** (ESI) *m/z* 344.1640 (344.1626 calcd for $C_{21}H_{23}NNaO_2$ $[MNa]^+$).

Reductive N–O bond cleavage:



4-(Benzylamino)-5-phenylcyclopent-2-en-1-ol (35):

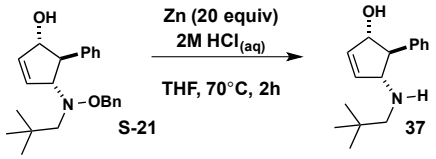
4-(Benzyl(benzyloxy)amino)-5-phenylcyclopent-2-en-1-ol **30** (13.3 mg, 0.036 mmol) was dissolved in 0.5 mL THF, followed by addition of 6-9 micron Zn powder (46.8 mg, 0.716 mmol). Next, 2M HCl (1 mL) in H_2O was added and the solution was heated to 70 ºC. Reaction was stirred until complete (2 h) as determined by thin layer chromatography. The reaction was then quenched by the addition of 4M $NaOH_{(aq)}$ until pH 14 was reached and extracted with ethyl acetate (3 × 5 mL). The combined organic layers were dried over Na_2SO_4, filtered and then concentrated *in vacuo*. The residue was purified by flash column chromatography (3% MeOH in CH_2Cl_2) to afford the free amine **35** (9.5 mg, quantitative yield) as a colorless oil. **^{1}H NMR** (600 MHz, $CDCl_3$) δ 7.32 (t, *J* = 7.5 Hz, 2H), 7.28 – 7.22 (m, 4H), 7.19 (t, *J* = 7.2 Hz, 4H), 6.00 (t, *J* = 7.0 Hz, 2H), 4.64 (d, *J* = 4.5 Hz, 1H), 3.84 – 3.77 (m, 2H), 3.73 (d, *J* = 13.1 Hz, 1H), 3.18 (s, 2H), 3.00 (t, *J* = 4.9 Hz, 1H) ppm; **^{13}C NMR** (150 MHz, $CDCl_3$) δ 143.0, 138.9, 135.6, 134.5, 128.9, 128.6, 127.6, 127.4, 126.8, 83.9, 69.6, 62.0, 51.3 ppm; **IR** (thin film) 3294, 3061, 3028, 2922, 2854, 1951, 1877, 1810, 1734, 1602, 1495 cm^{-1}; **MS** (ESI) *m/z* 288.1371 (288.1371 calcd for $C_{18}H_{19}NNaO^+$ $[MNa]^+$).



4-(Benzylamino)-5-phenylcyclopent-2-en-1-ol (36):

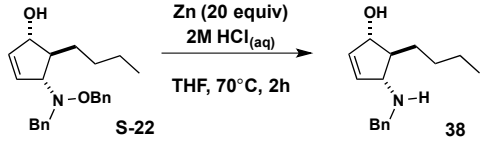
A solution of **S-30m** (20.0 mg, 0.062 mmol) in THF (1.9 mL) was treated with Zn (81.4 mg, 1.2 mmol), followed by slow addition of 3.7 mL 2M HCl. The reaction was placed in an oil bath at 70 °C and stirred until no starting material was observed by TLC. The reaction was then cooled to rt, quenched with saturated $NaHCO_3$, then the pH was adjusted to 9 using 3 M NaOH before extraction with EtOAc (3 x 5 mL). The combined

organic phases were dried over Na_2SO_4, filtered, and solvent removed *in vacuo*. The residue was purified by flash column chromatography to afford **36** (11.7 mg, 98%) as a light yellow solid. **^{1}H NMR** (500 MHz, $CDCl_3$) δ 7.37 – 7.32 (m, 2H), 7.31 – 7.27 (m, 3H), 7.27 – 7.24 (m, 2H), 7.24 – 7.18 (m, 3H), 6.21 (dd, *J* = 5.8, 1.7 Hz, 1H), 6.04 (ddd, *J* = 5.8, 2.2, 2.2 Hz, 1H), 4.84 (ddd, *J* = 6.3, 2.1, 2.1 Hz, 1H), 4.31 (dddd, *J* = 6.6, 1.8, 1.8, 1.8 Hz, 1H), 3.77 (s, 2H), 3.23 (dd, *J* = 6.4, 6.4 Hz, 1H), 1.57 (s, 2H) ppm; **^{13}C NMR** (125 MHz, $CDCl_3$) δ 140.1, 138.7, 138.2, 133.2, 129.4, 128.8, 128.5, 128.3, 127.2, 127.2, 77.3, 67.2, 57.8, 52.4 ppm; **IR** (thin film) 3302, 3059, 3027, 2901, 2851, 1601, 1553, 1493, 1453, 1319, 1094, 1070, 1028 cm^{-1}; **MS** (ESI) *m/z* 288.1354 (288.1364 calcd for $C_{18}H_{19}NNaO$ $[MNa]^+$).



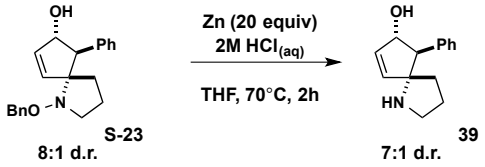
4-(Neopentylamino)-5-phenylcyclopent-2-en-1-ol (37):

A solution of **S-21** (7.6 mg, 0.022 mmol) in THF (0.7 mL) was treated with Zn (28.3 mg, 0.43 mmol), followed by slow addition of 1.3 mL 2M HCl. The reaction was placed in an oil bath at 70 °C and stirred until no starting material was observed by TLC. The reaction was then cooled to rt, quenched with saturated $NaHCO_3$, then the pH was adjusted to ~10 using 3 M NaOH before extraction with EtOAc (3 x 5 mL). The combined organic phases were dried over Na_2SO_4, filtered, and solvent removed *in vacuo*. The residue was purified by flash column chromatography to afford **37** (3.1 mg, 58%) as a yellow oil. **^{1}H NMR** (600 MHz, $CDCl_3$) δ 7.32 (t, *J* = 7.3 Hz, 2H), 7.27 – 7.20 (m, 3H), 6.08 (d, *J* = 5.7 Hz, 1H), 6.01 (d, *J* = 5.2 Hz, 1H), 4.68 (s, 1H), 3.80 – 3.75 (m, 1H), 2.99 – 2.94 (m, 1H), 2.39 (s, 2H), 1.28 (s, 1H), 1.25 (s, 1H), 0.89 (s, 9H) ppm; **^{13}C NMR** (125 MHz, $CDCl_3$) δ 143.0, 136.7, 133.9, 129.0, 127.4, 126.9, 84.1, 71.4, 59.2, 31.4, 29.9, 27.9 ppm; **IR** (thin film) 3293, 3061, 3028, 2953, 2926, 2855, 1555, 1467, 1453, 1363, 1079, 1013, 906 cm^{-1}; **MS** (ESI) *m/z* 246.1853 (246.1858 calcd for $C_{16}H_{24}NO$ $[MH]^+$).



4-(Benzylamino)-5-butylcyclopent-2-en-1-ol (38):

A solution of **S-22** (30.2 mg, 0.086 mmol) in THF (2.6 mL) was treated with Zn (112.4 mg, 1.7 mmol), followed by slow addition of 5.2 mL 2M HCl. The reaction was placed in an oil bath at 70 °C and stirred for 40 min, until no starting material was observed by TLC. The reaction was then cooled to rt, quenched with saturated $NaHCO_3$, then the pH was adjusted to ~10 using 3 M NaOH before extraction with EtOAc (3 x 5 mL). The combined organic phases were dried over Na_2SO_4, filtered, and solvent removed *in vacuo*. The residue was purified by flash column chromatography to afford **38** (17.3 mg, 82%) as a yellow oil. **^{1}H NMR** (500 MHz, $CDCl_3$) δ 7.37 – 7.30 (m, 4H), 7.28 – 7.23 (m, 1H), 5.97 – 5.91 (m, 1H), 5.89 (ddd, *J* = 5.7, 1.7, 1.7 Hz, 1H), 4.32 – 4.27 (m, 1H), 3.84 (d, *J* = 2.0 Hz, 2H), 3.34 – 3.28 (m, 1H), 2.53 (s, 2H), 1.79 (dddd, *J* = 10.0, 3.6, 3.6, 3.6 Hz, 1H), 1.56 – 1.28 (m, 6H), 0.91 (dd, *J* = 7.1, 7.1 Hz, 3H) ppm; **^{13}C NMR** (125 MHz, $CDCl_3$) δ 139.5, 135.7, 134.4, 128.6, 128.5, 127.4, 81.6, 67.9, 54.7, 51.8, 33.1, 30.1, 23.1, 14.2 ppm; **IR** (thin film) 3290, 3059, 2039, 2955, 2924, 2855, 1454, 1354, 1073, 1027, 996 cm^{-1}; **MS** (ESI) *m/z* 268.1662 (268.1677 calcd for $C_{16}H_{23}NNaO$ $[MNa]^+$).

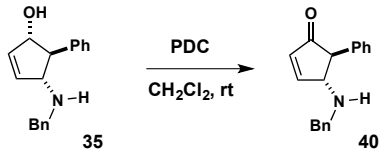


6-Phenyl-1-azaspiro[4.4]non-8-en-7-ol (39):

A solution of (**S-23**) (66.5 mg, 0.21 mmol, as an 8:1 mixture of diastereomers) in 6.4 mL THF was treated with zinc (274.7 mg, 4.2 mmol), followed by dropwise addition of 2M HCl (12.7 mL). The reaction was placed in an oil bath heated to 70 °C and stirred for 2 hours. The reaction was then cooled to rt, quenched with saturated $NaHCO_3$, then the pH

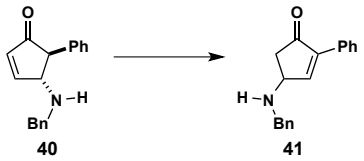
was adjusted to ~10 using 3M NaOH before extraction with EtOAc (3 x 10 mL). The combined organic phases were dried over Na_2SO_4, filtered, and solvent removed *in vacuo*. The residue was purified by flash column chromatography to afford **39** (34.3 mg, 77%) as a yellow oil and an inseparable 7:1 mixture of diastereomers. *Major*: **^{1}H NMR** (500 MHz, $CDCl_3$) δ 7.32 – 7.23 (m, 5H), 6.04 (d, *J* = 5.8 Hz, 1H), 6.01 (dd, *J* = 5.8, 1.9 Hz, 1H), 5.13 (ddd, *J* = 6.4, 1.6, 1.6 Hz, 1H), 3.37 (d, *J* = 6.4 Hz, 1H), 2.94 (ddd, *J* = 10.4, 7.9, 5.0 Hz, 1H), 2.84 (ddd, *J* = 10.6, 6.8, 6.8 Hz, 1H), 2.14 (bs, 3H), 1.73 – 1.46 (m, 5H) ppm; **^{13}C NMR** (125 MHz, $CDCl_3$) δ 140.6, 138.0, 134.7, 130.7, 128.4, 127.2, 77.7, 76.6, 61.0, 45.7, 34.8, 25.7 ppm; **IR** (thin film) 3363, 3060, 3029, 2922, 2852, 1600, 1554, 1455, 1387, 1104, 1083, 1033 cm^{-1}; **MS** (ESI) *m/z* 216.1393 (216.1388 calcd for $C_{14}H_{18}NO$ $[MH]^+$).

Allylic Oxidation:



4-(Benzylamino)-5-phenylcyclopent-2-en-1-one (40):

A solution of (**35**) (50.0 mg, 0.19 mmol) in 1.9 mL dry DMF was treated with pyridinium dichromate (PDC) (354 mg, 0.94 mmol) and stir ed at rt for 2 h. The reaction was quenched with water (20 mL) and diluted with EtOAc (5 mL). The phases were separated, and the aqueous phase extracted with EtOAc (3 x 5 mL). Subsequently, the combined organic phases were washed with H_2O (5 x 5 mL) and brine (2 x 5 mL). The organic layer was dried over $MgSO_4$, filtered and solvent removed *in vacuo* to give the crude, desired product **40** (35 mg, 70%) as a yellow oil. **^{1}H NMR** (600 MHz, $CDCl_3$) δ 7.68 (s, 1H), 7.42 – 7.03 (m, 10H), 6.31 (s, 1H), 4.13 (s, 1H), 3.91 (d, *J* = 12.8 Hz, 1H), 3.82 (d, *J* = 12.3 Hz, 1H), 3.41 (s, 1H), 2.19 (bs, 1H) ppm; **^{13}C NMR** (125 MHz, $CDCl_3$) δ 207.1, 163.3, 139.4, 138.4, 134.0, 129.0, 128.6, 128.3, 127.4, 127.3, 67.3, 60.6, 51.9 ppm; **IR** (thin film) 3085, 3061, 3029, 2925, 2853, 1705, 1494, 1453, 1265 cm^{-1}; **MS** (ESI) *m/z* 264.1376 (264.1388 calcd for $C_{18}H_{18}NO$ $[MH]^+$).



4-(Benzylamino)-2-phenylcyclopent-2-en-1-one (41):

Upon purification on silica, exposure to base, or standing at rt, **40** isomerizes to the more thermodynamically stable cyclopentenone **41**. **^{1}H NMR** (500 MHz, $CDCl_3$) δ 7.71 (d, *J* = 2.6 Hz, 1H), 7.71 – 7.65 (m, 2H), 7.41 – 7.32 (m, 7H), 7.32 – 7.27 (m, 1H), 4.08 (ddd, *J* = 5.9, 2.5, 2.5 Hz, 1H), 3.95 (d, *J* = 13.0 Hz, 1H), 3.91 (d, *J* = 13.0 Hz, 1H), 2.91 (dd, *J* = 18.5, 6.2 Hz, 1H), 2.43 (dd, *J* = 18.5, 2.4 Hz, 1H), 1.63 (bs, 2H) ppm; **^{13}C NMR** (125 MHz, $CDCl_3$) δ 205.2, 157.9, 143.9, 139.7, 131.1, 129.0, 128.8, 128.6, 128.4, 127.5, 55.3, 52.1, 44.3 ppm; **IR** (thin film) 3086, 3059, 3029, 2925, 2851, 1704, 1598, 1577, 1494, 1452, 1265 cm^{-1}; **MS** (ESI) *m/z* 264.1374 (264.1388 calcd for $C_{18}H_{18}NO$ $[MH]^+$).

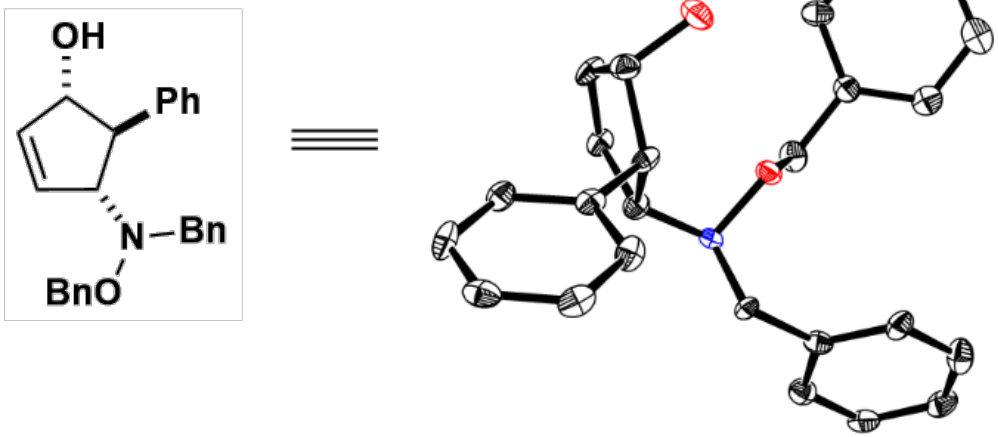
Crystallographic Experimental Section

A colorless crystal of approximate dimensions 0.3*0.1*0.1 mm was mounted on a glass fiber and transferred to a Bruker Kappa Apex II diffractometer. The APEX2 program was used to determine the unit cell parameters and data collection (15 sec / frame, 0.3 deg. /frame).[2] The data were collected at 100K. The raw frame data were processed using APEX2 program.[2] The absorption correction was applied using program SADABS.[3] Subsequent calculations were carried out using SHELXTL program.[4] The structure was solved by direct methods and refined on F^2 by full-matrix least-squares techniques. Hydrogen atomic positions were theoretically calculated. At convergence, wR2= 0.1517 and GOF = 0.957 for 274 variables refined against 4375 reflections, while R1= 0.0620 for 3625 reflections with I>2σ(I). All ORTEP diagrams have been drawn with 50% probability ellipsoids.

Crystals were prepared by slow vapor diffusion using hexanes and ethyl acetate.

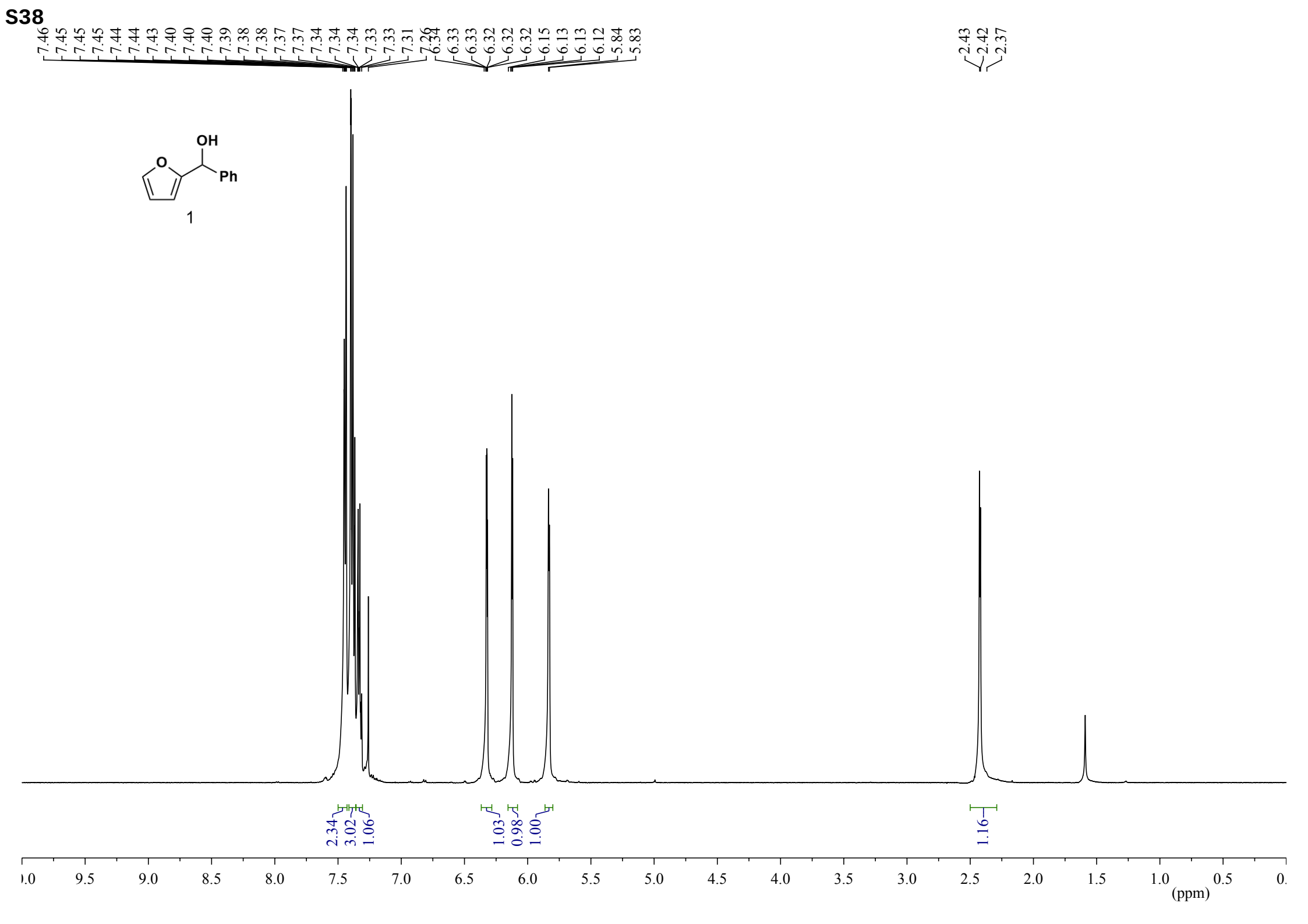
The crystal structure data can be obtained free of charge from the Cambridge Crystallographic Data Centre www.ccdc.cam.ac.uk/data_request/cif

Compound # 30 CCDC 986010



References:

[1] (a) L. Grierson, M. J. Perkins, *Tetrahedron Lett.* 1993, **34**, 7463-7464.
(b) G. E. Keck, T. T. Wager, S. F. McHardy, *Tetrahedron* 1999, **55**, 11755-11772.
(c) S. G. Davies, C. J. Goodwin, D. Hepworth, P. M. Roberts, J. E. Thomson, *J. Org. Chem.* 2010, **75**, 1214-1227.
[2] W. G. Dauben, D. M. Michno, *J. Org. Chem.* 1977, **42**, 682-685.
[3] A. Krasovskiy, F. Kopp, P. Knochel, *Angew. Chem. Int. Ed.* 2006, **45**, 497-500.
[4] R. S. Jones, J. Sutherland, D. F. Weaver, *Synth. Commun.* 2003, **33**, 43-51.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OH
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Ph
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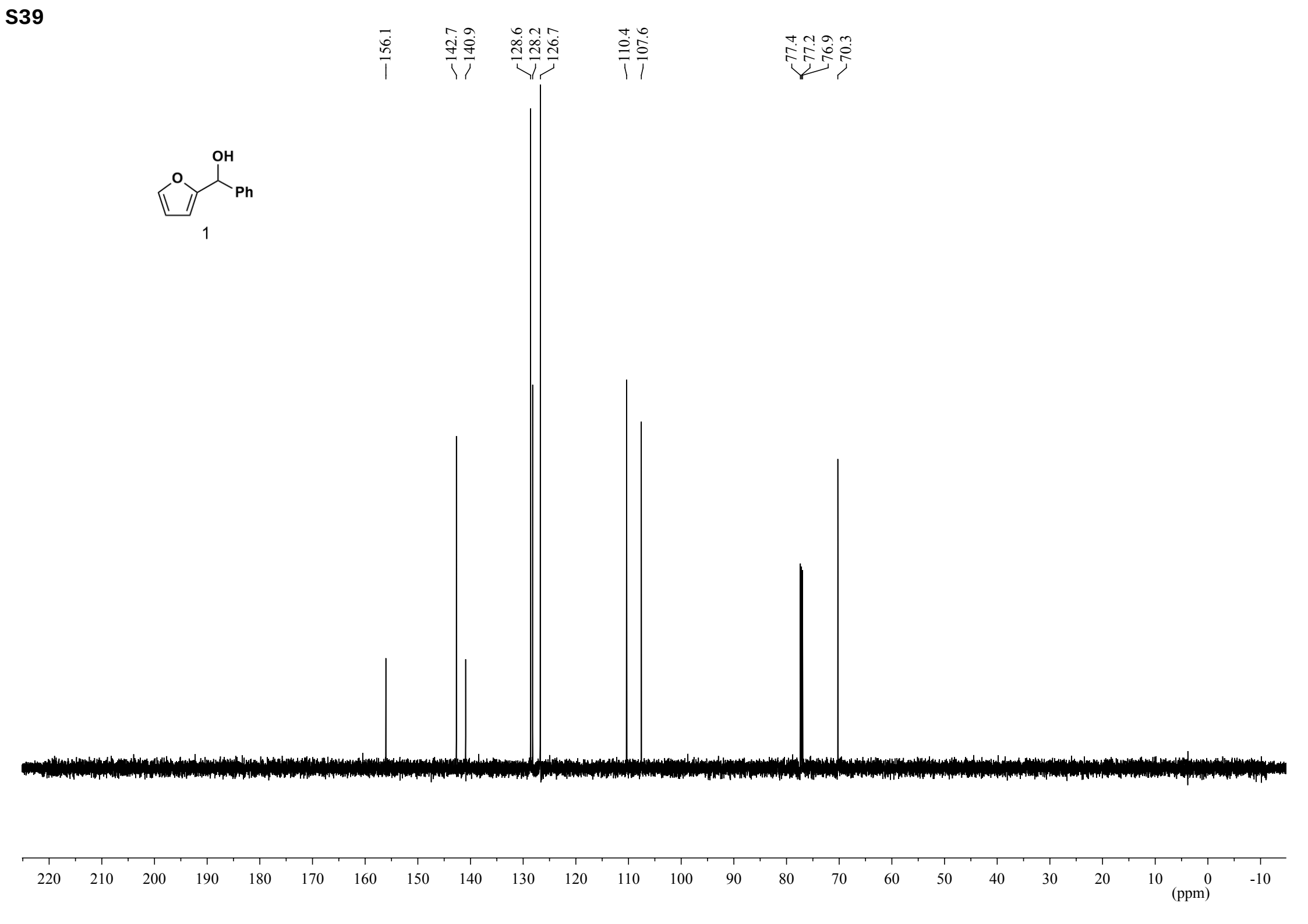
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200
190
180
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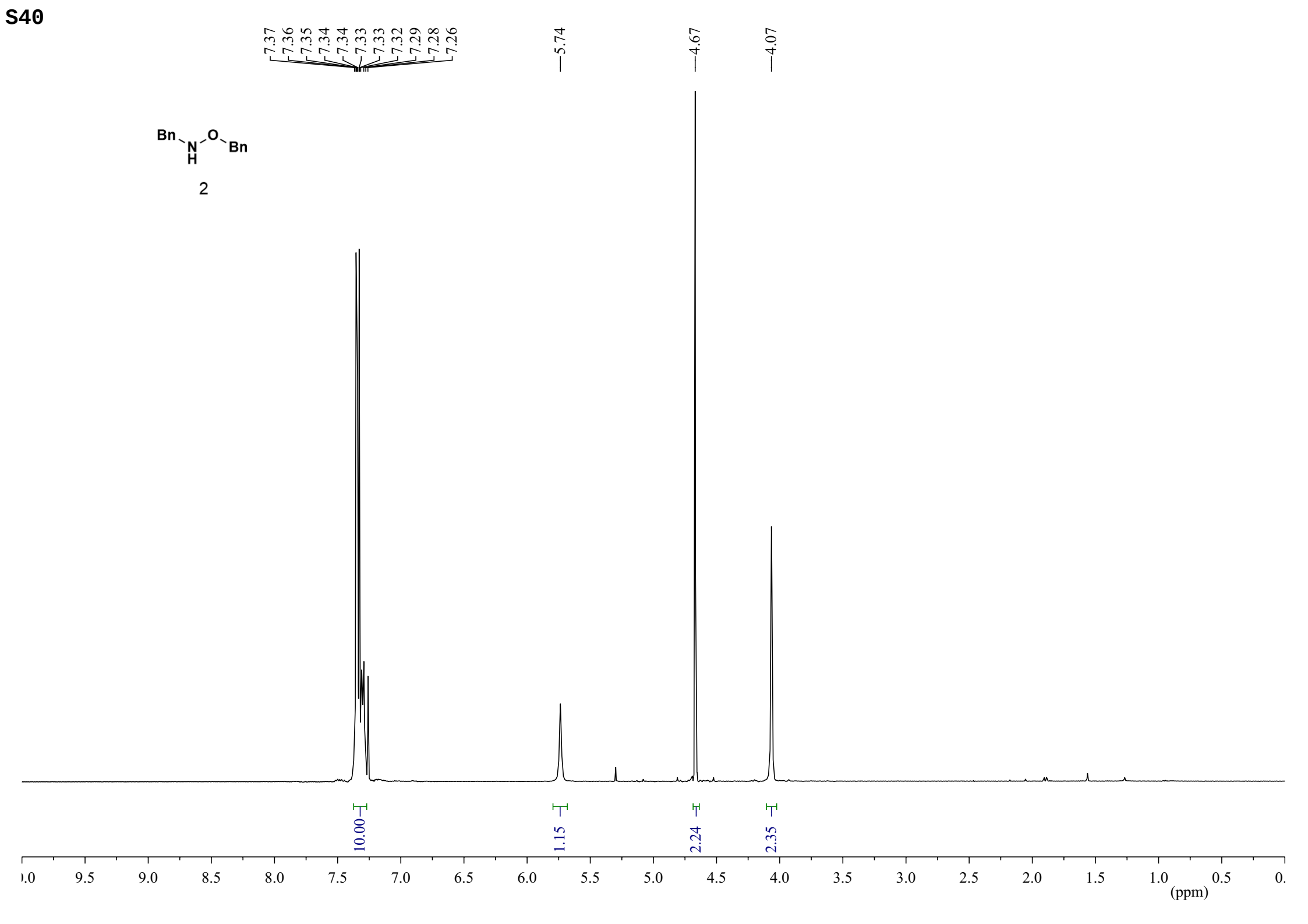
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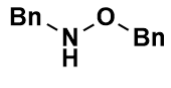
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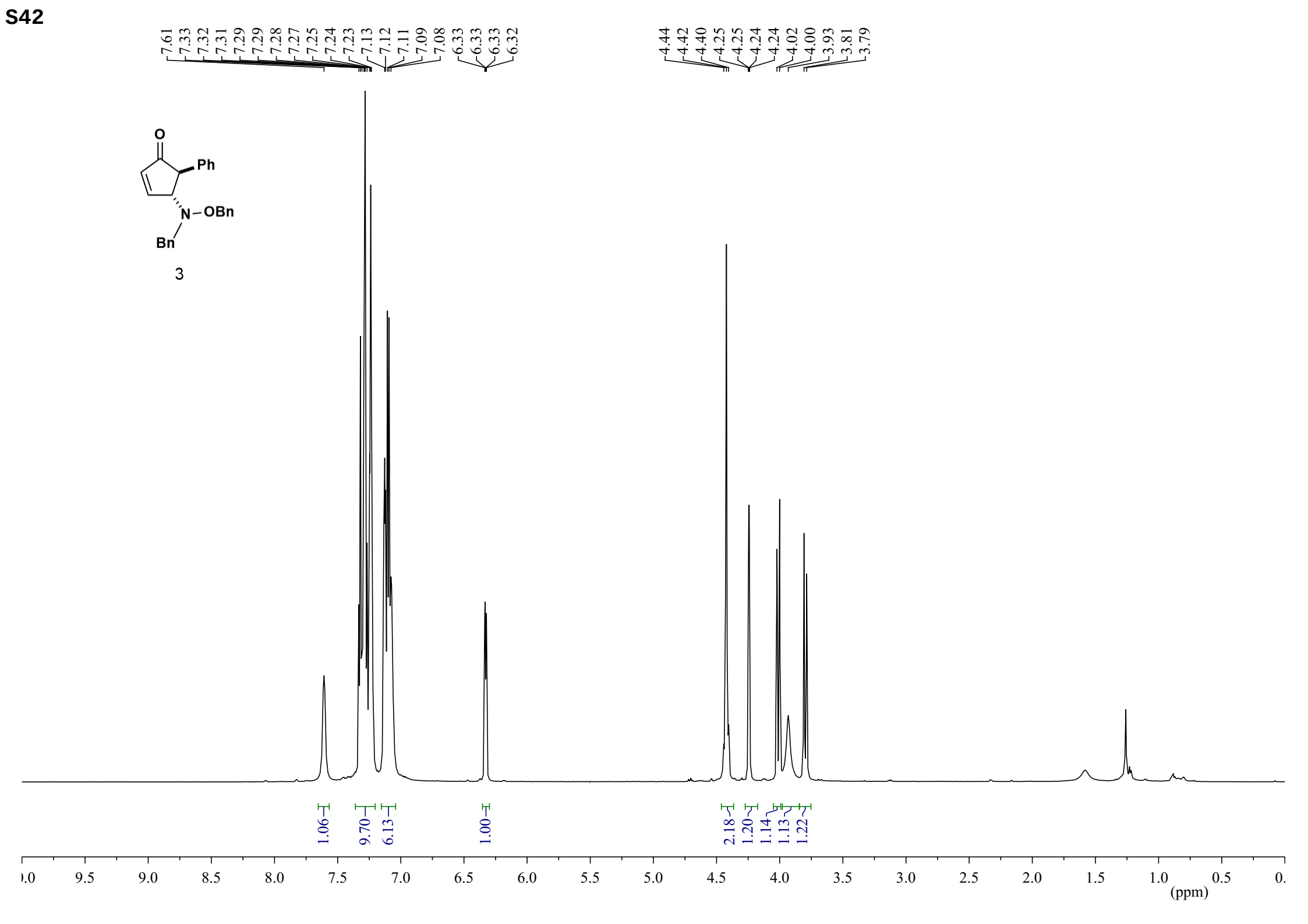
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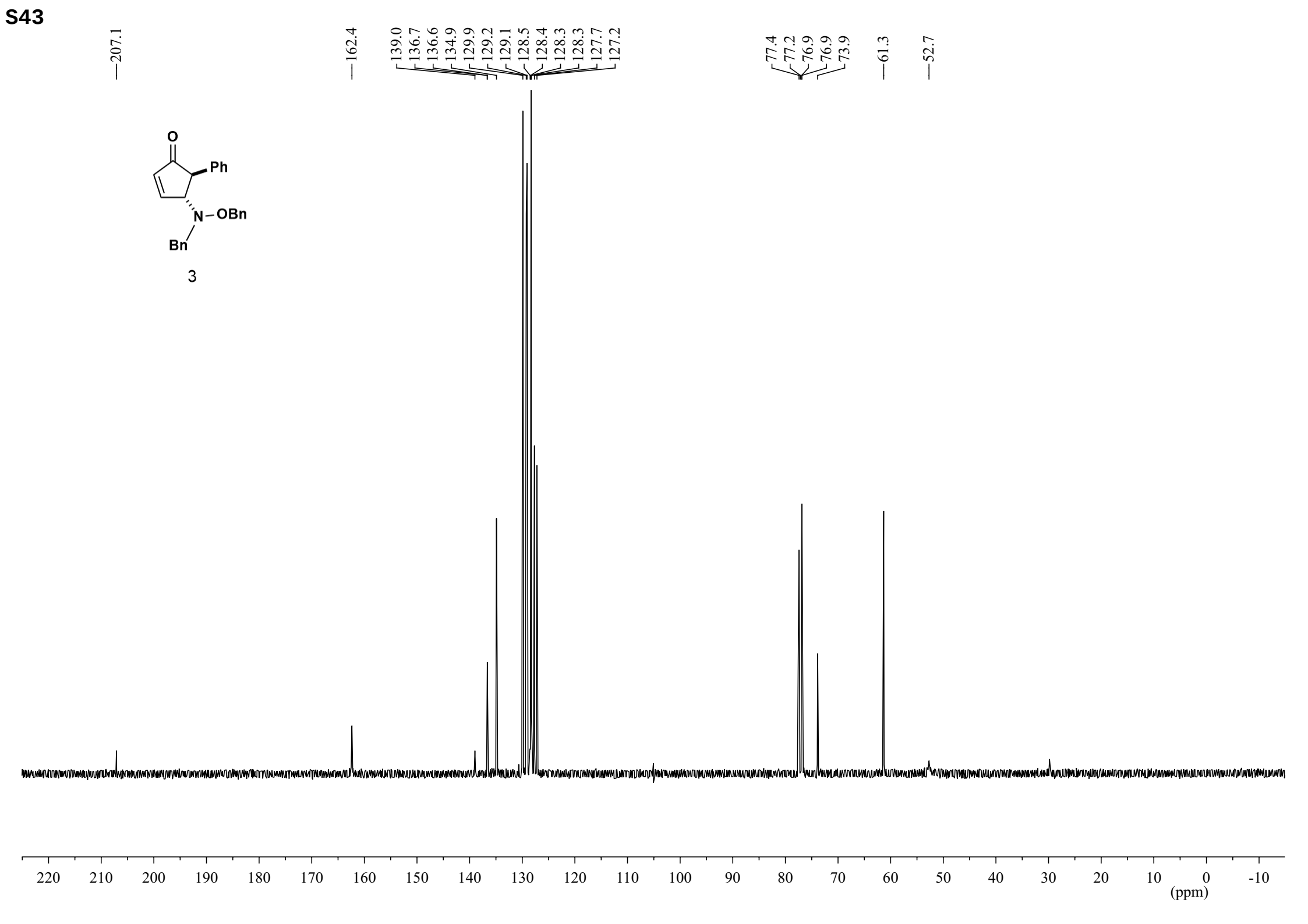
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Bn
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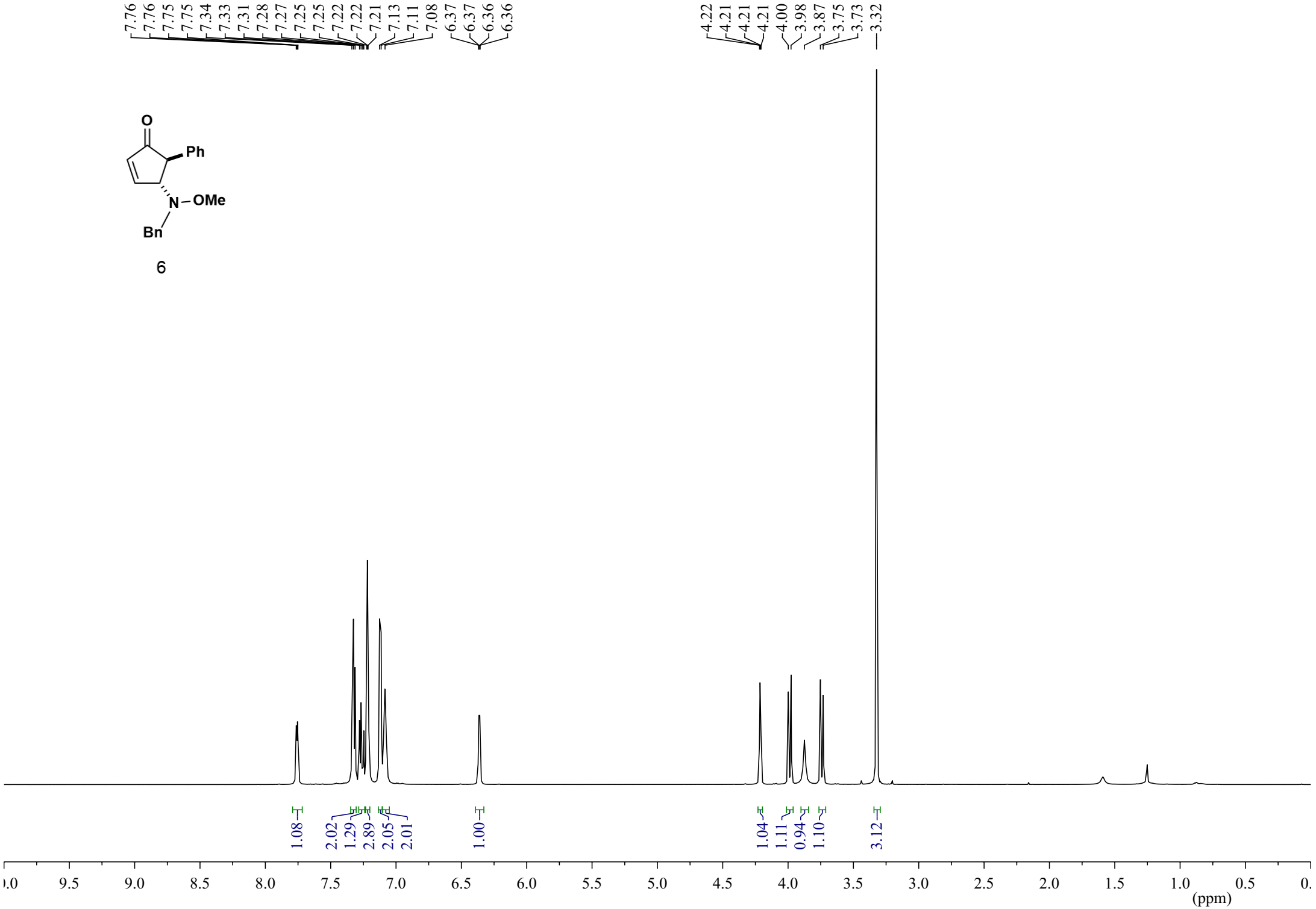
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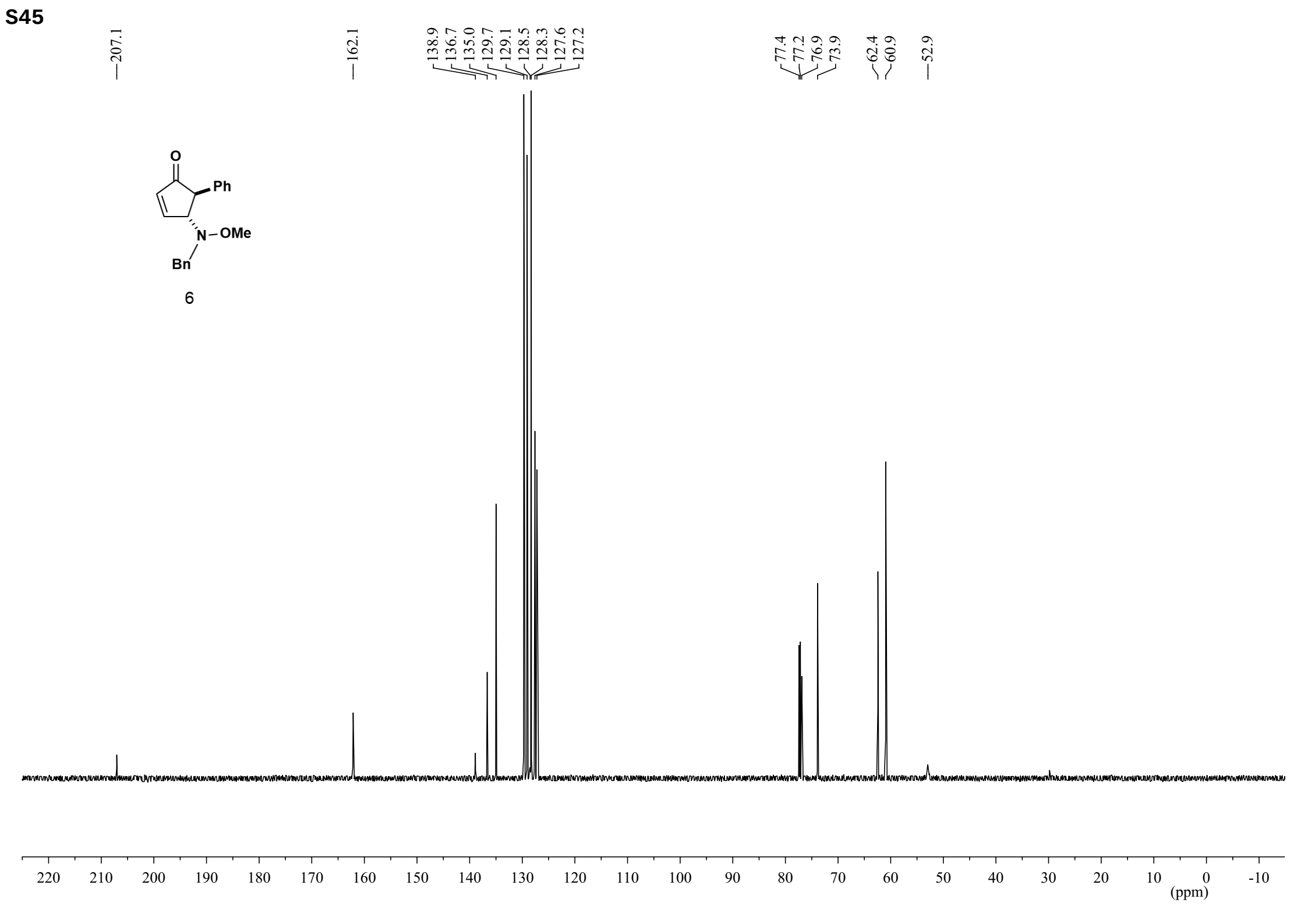
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OMe
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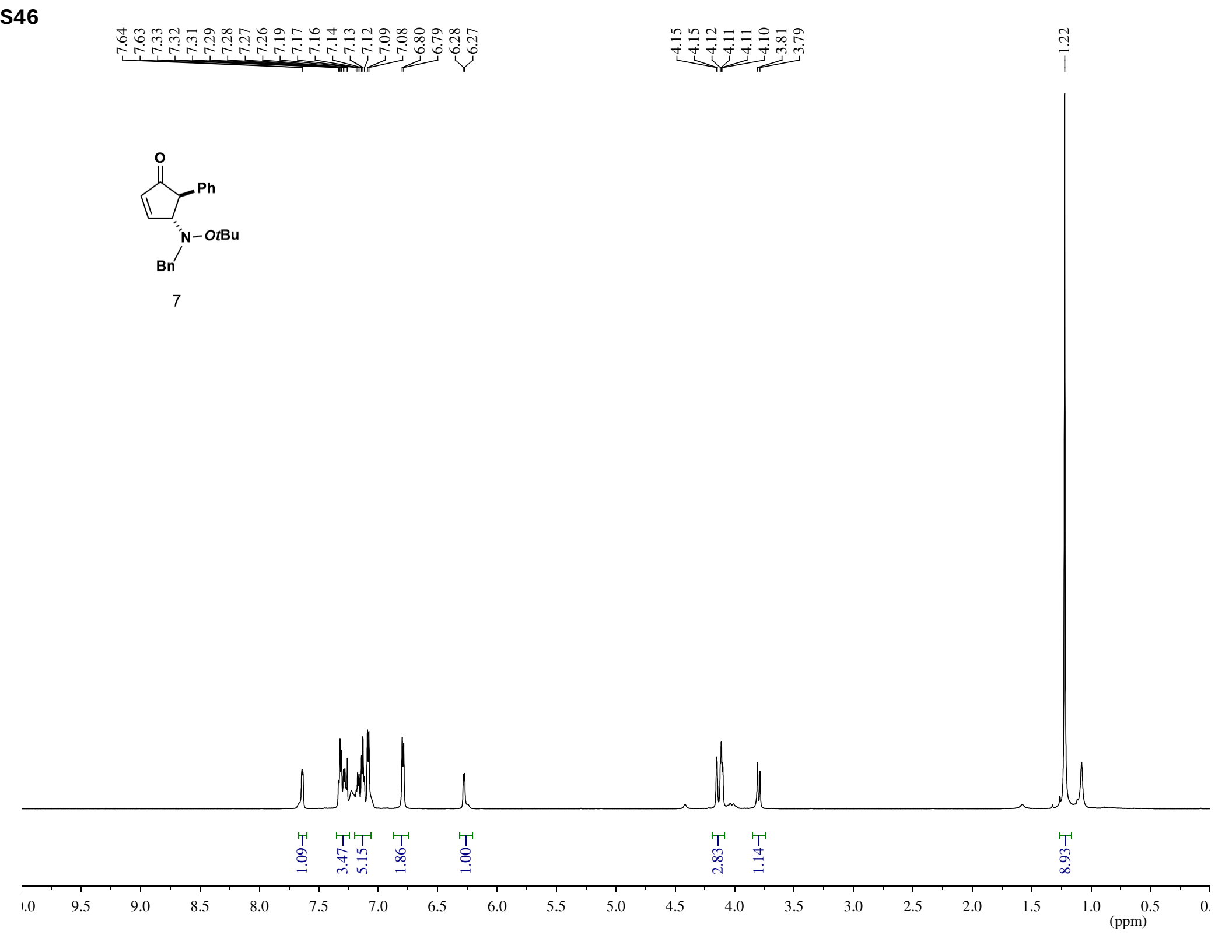
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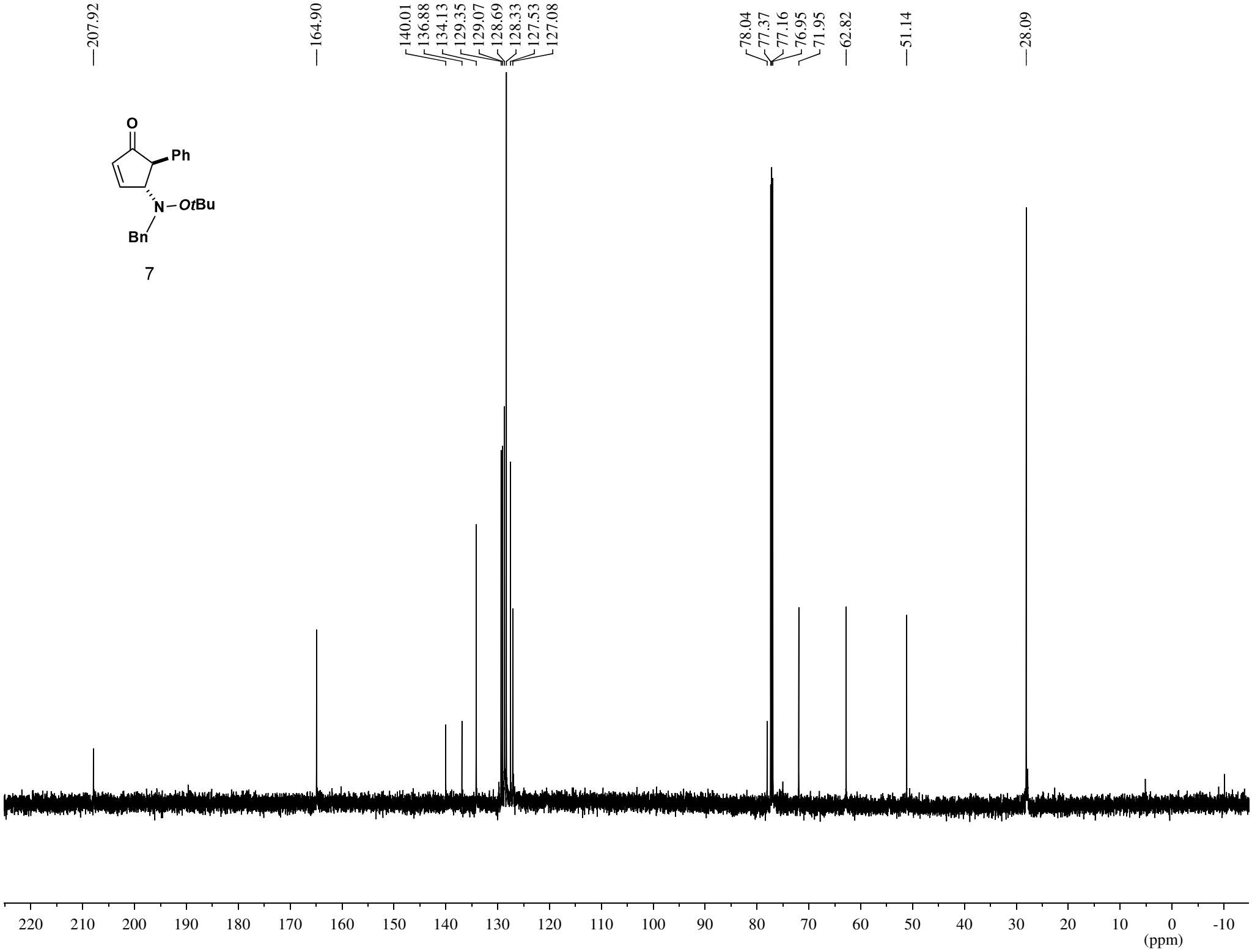
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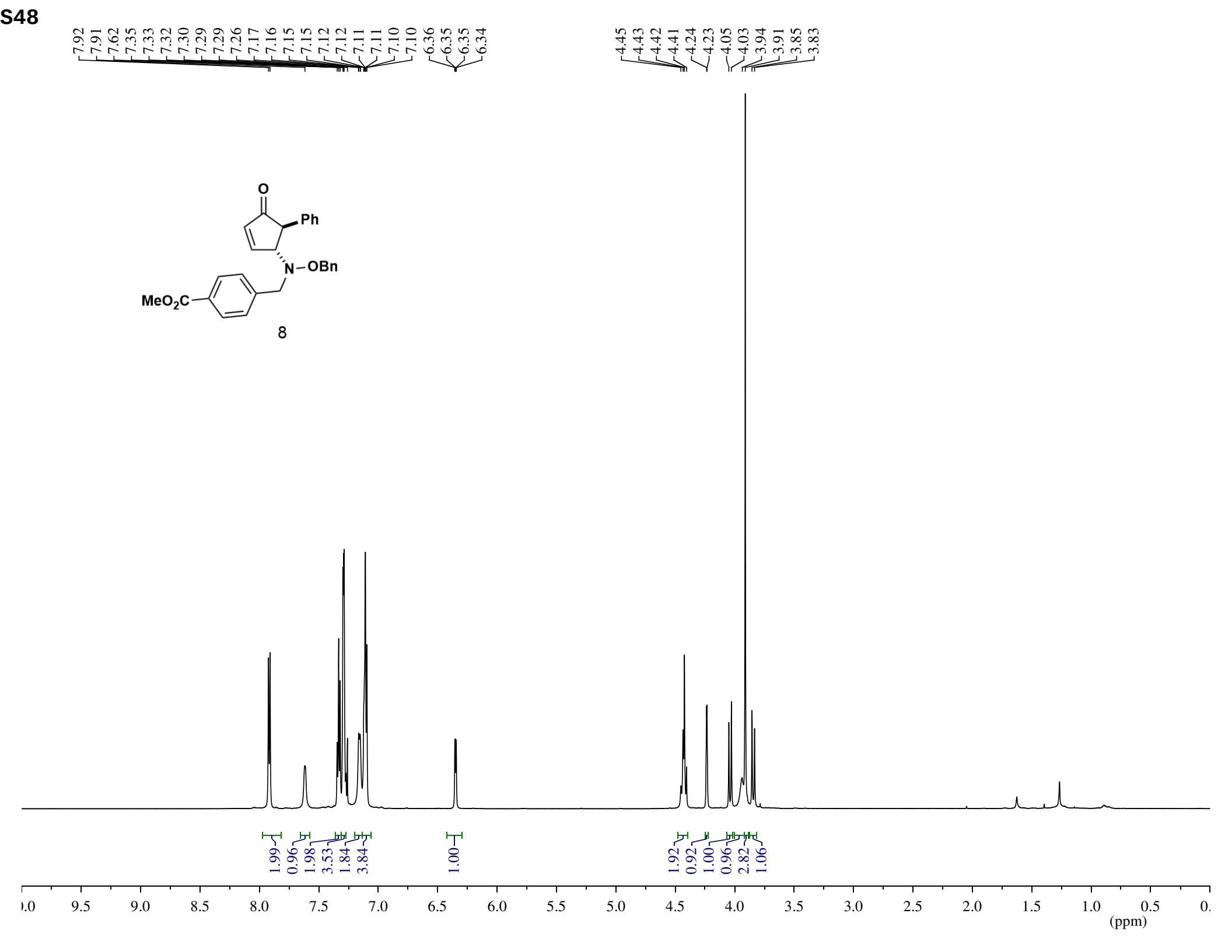
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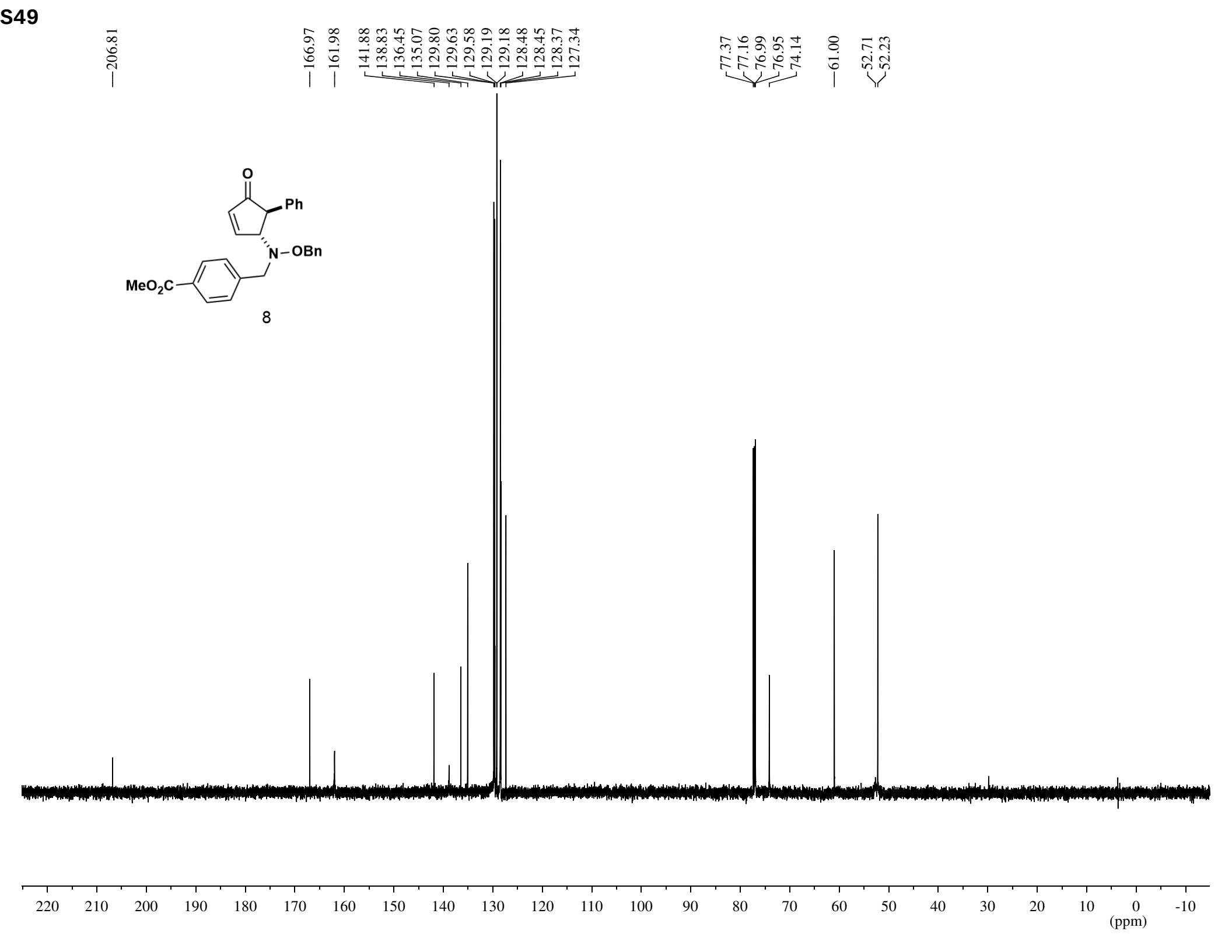
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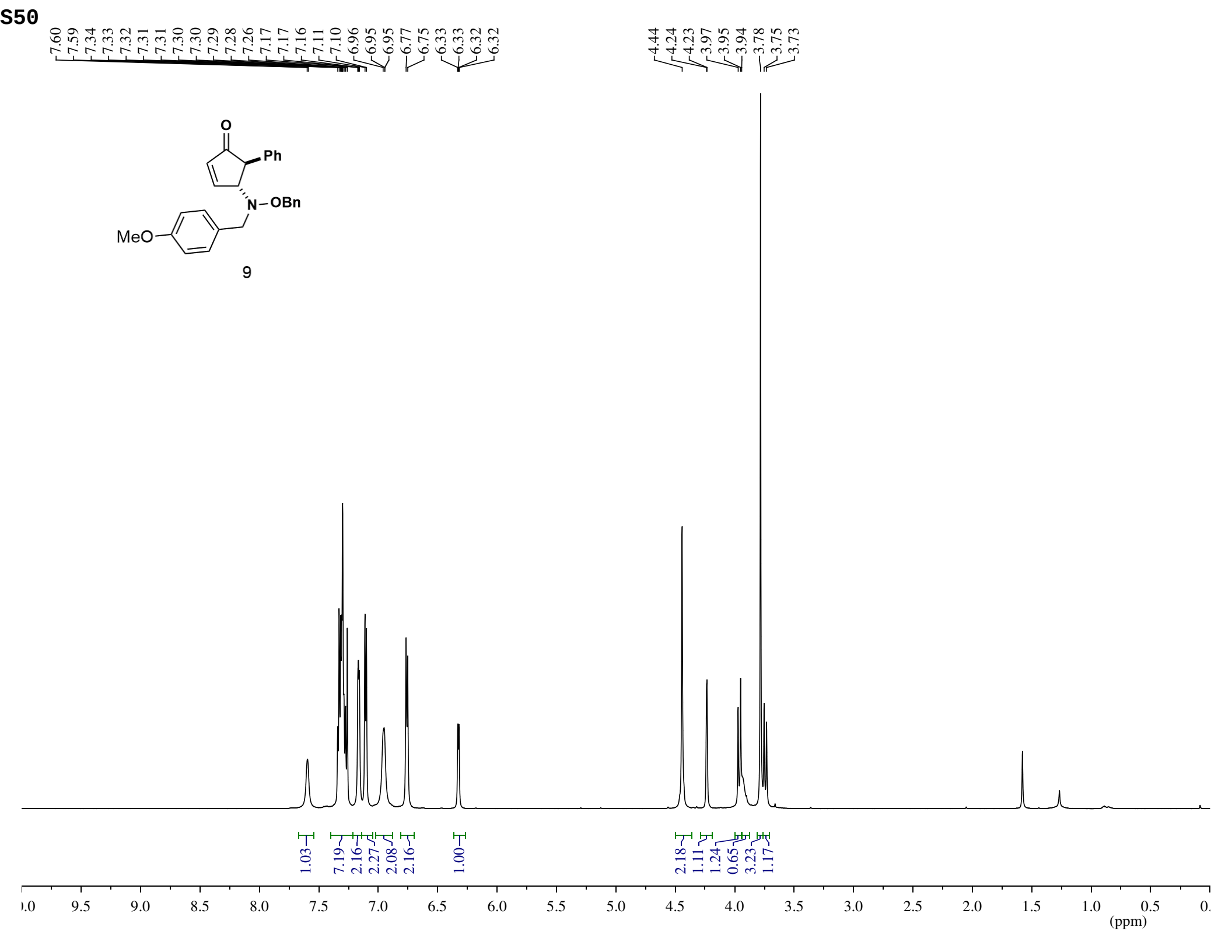
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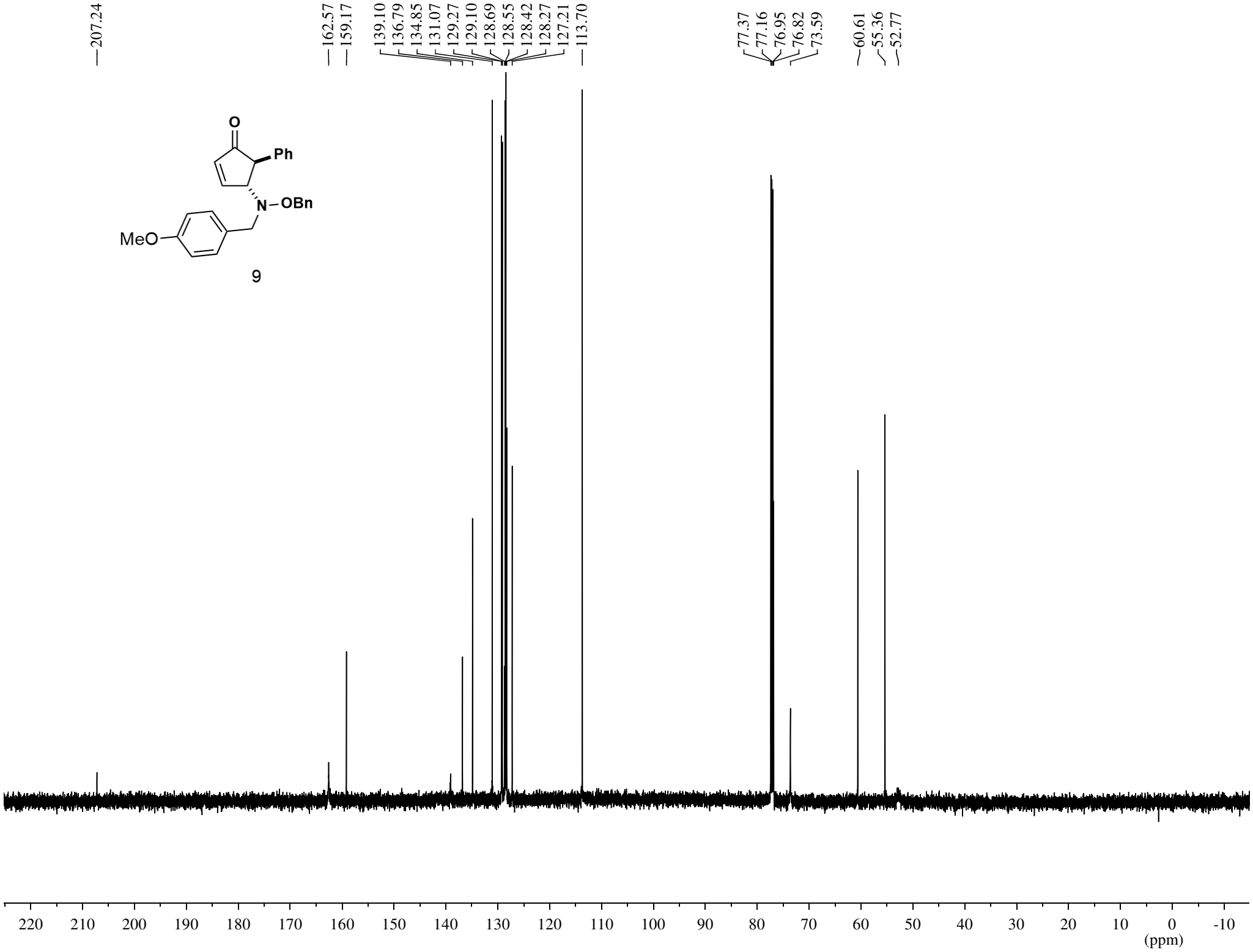
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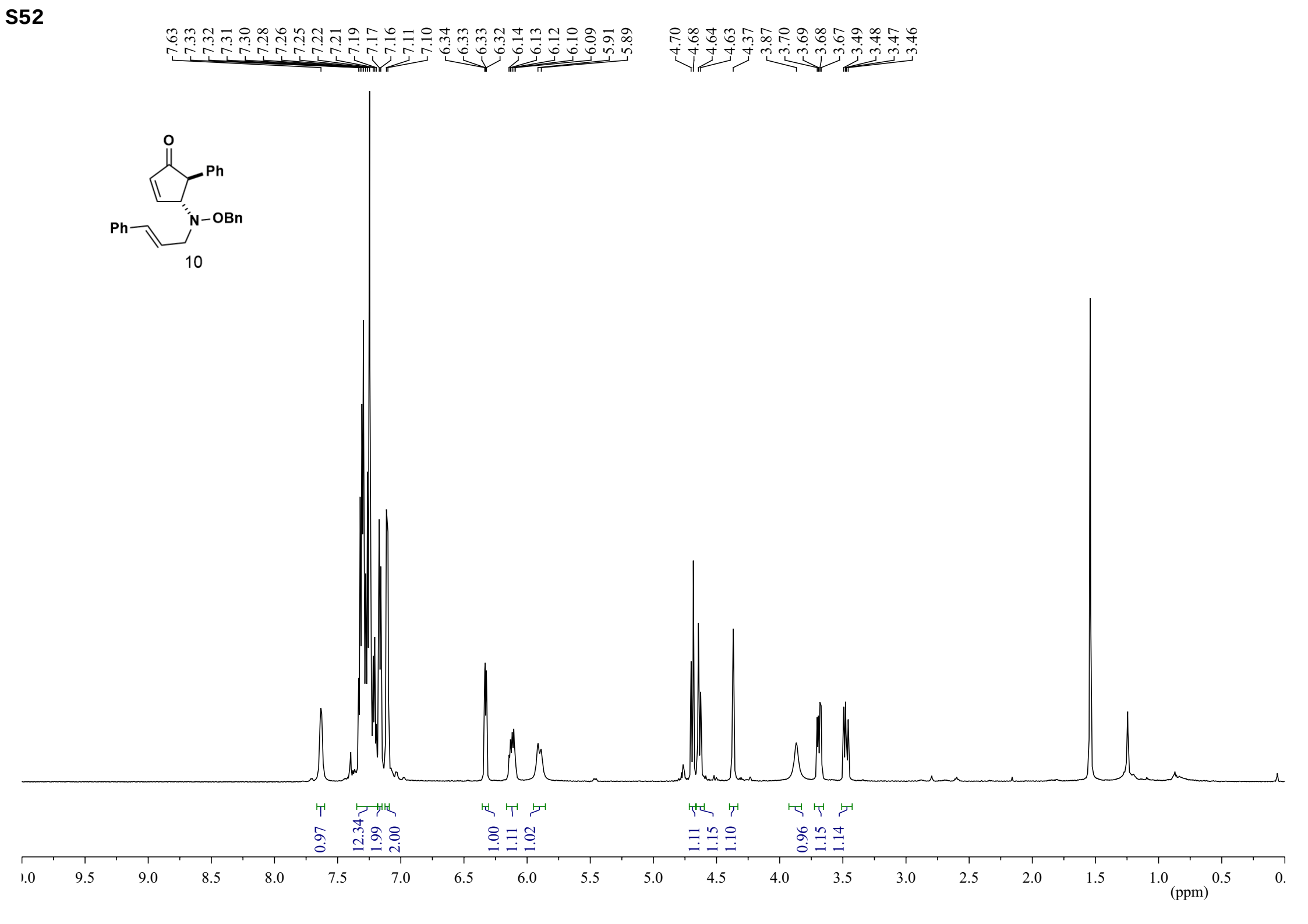
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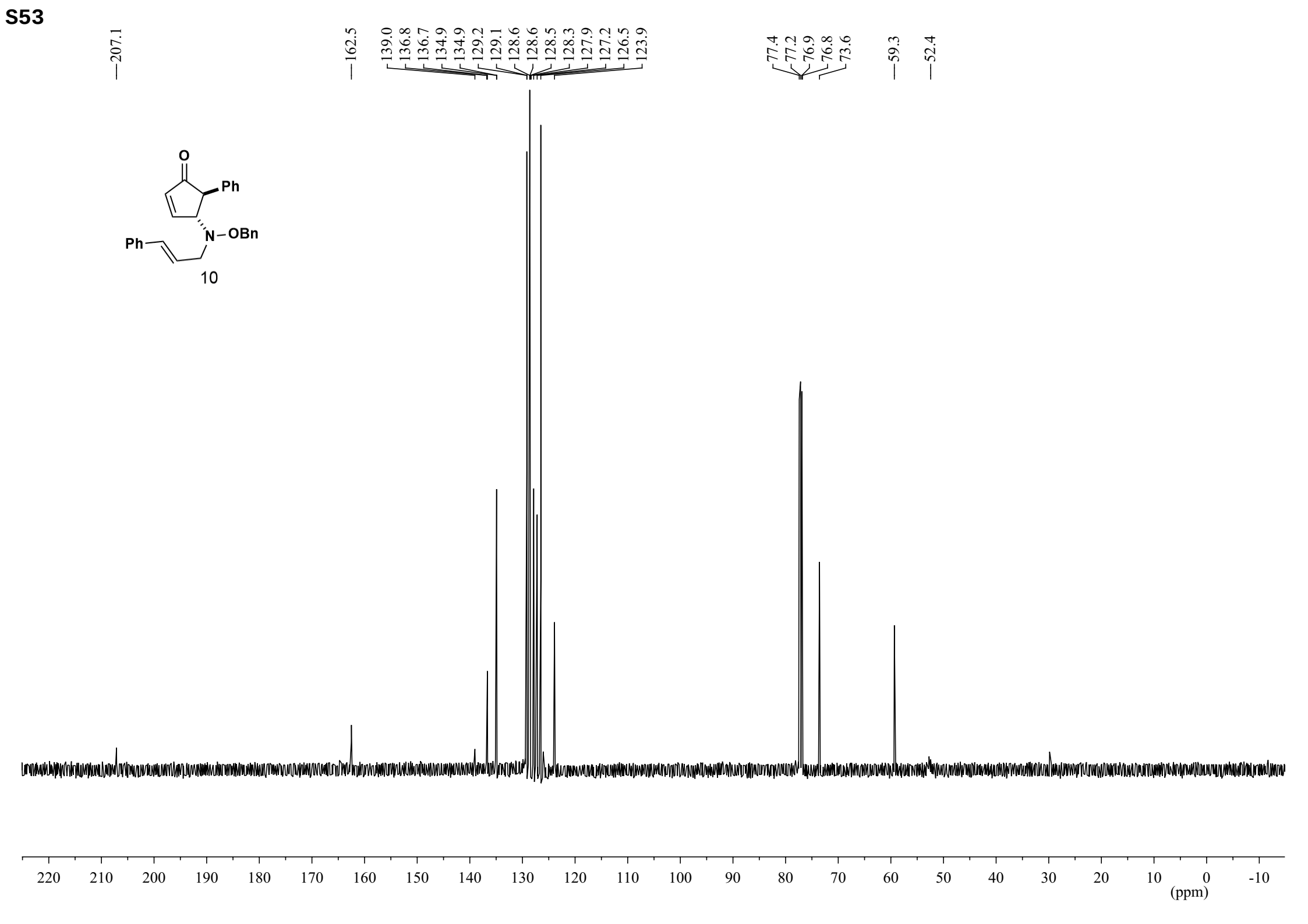
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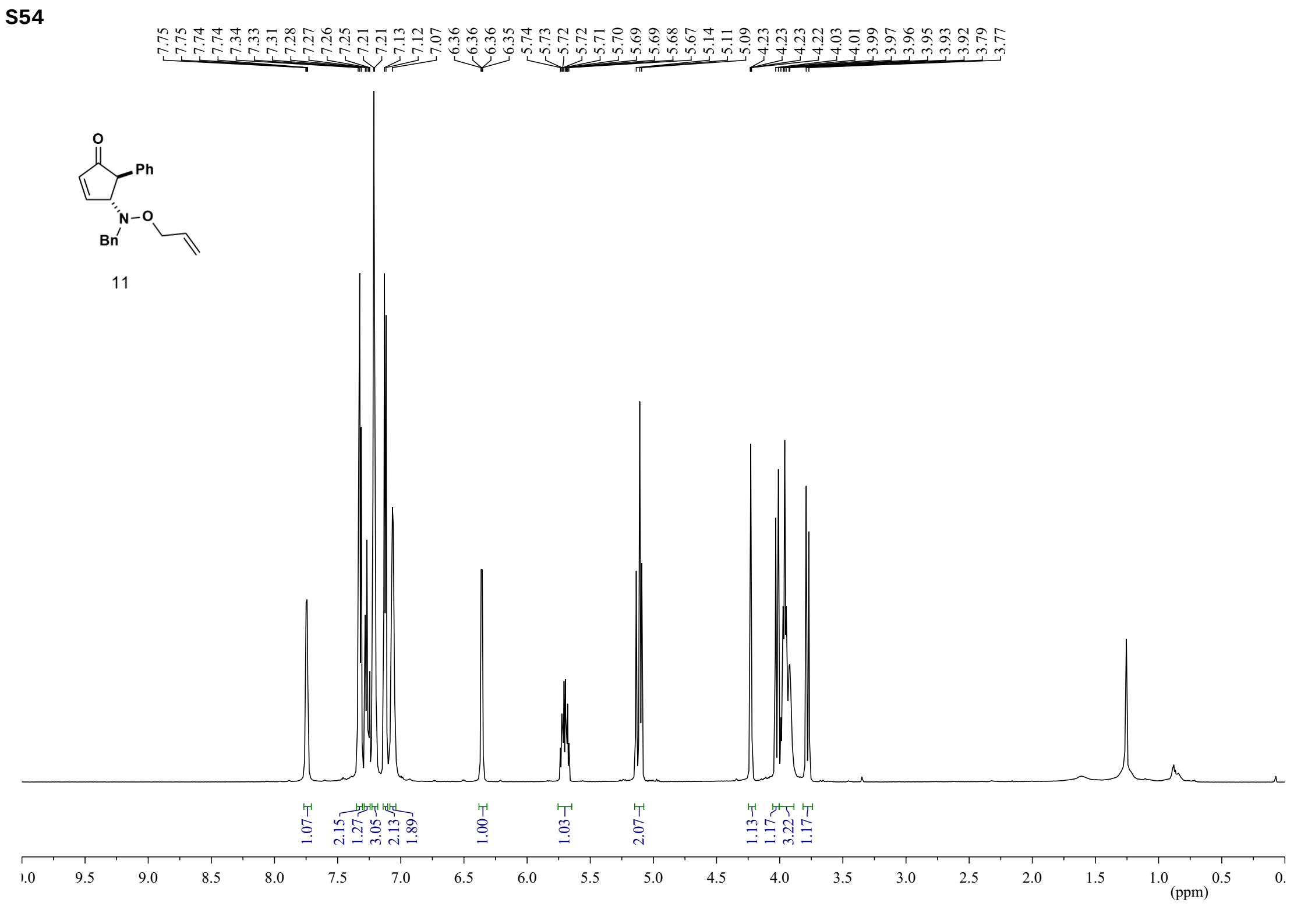
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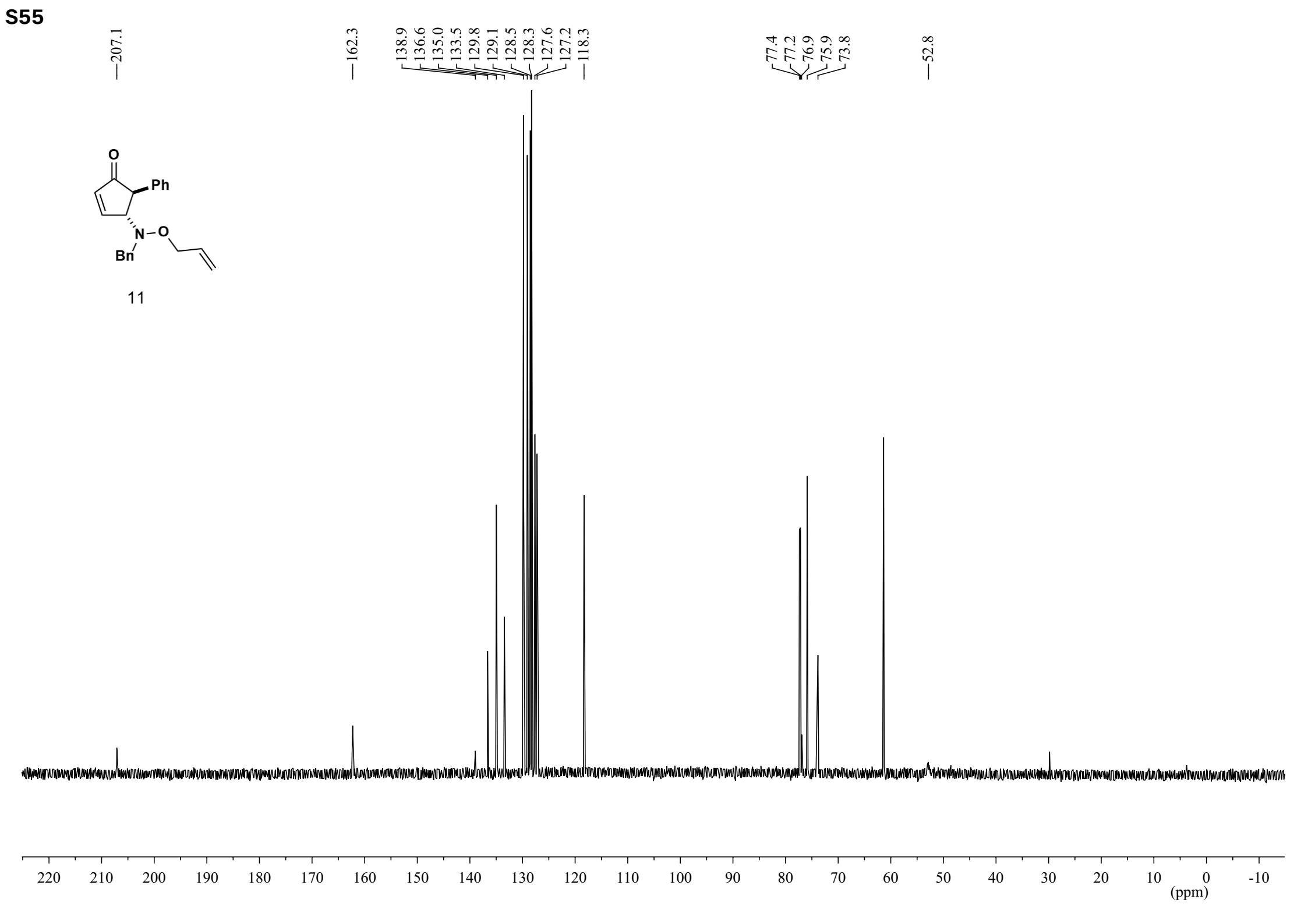
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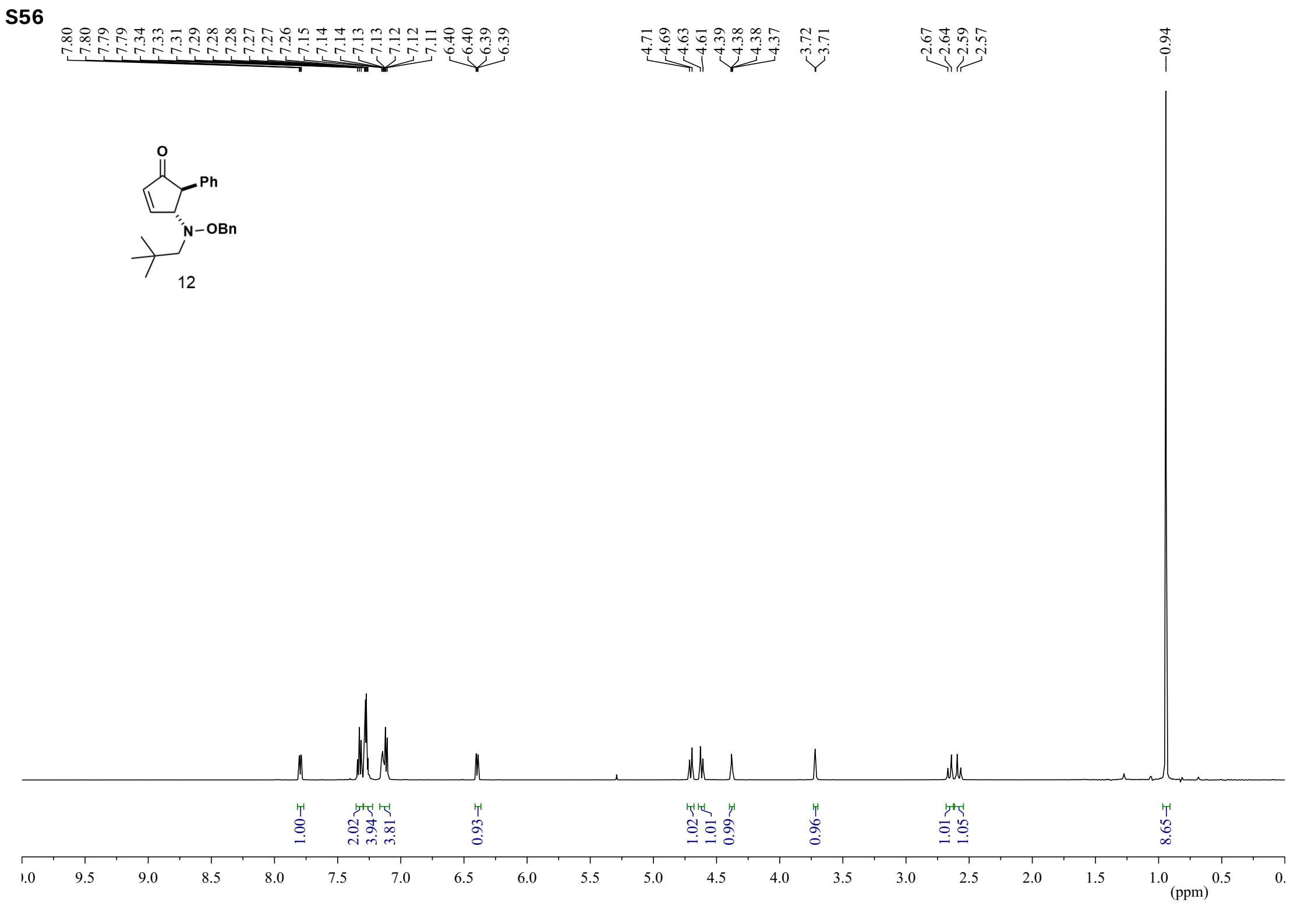
11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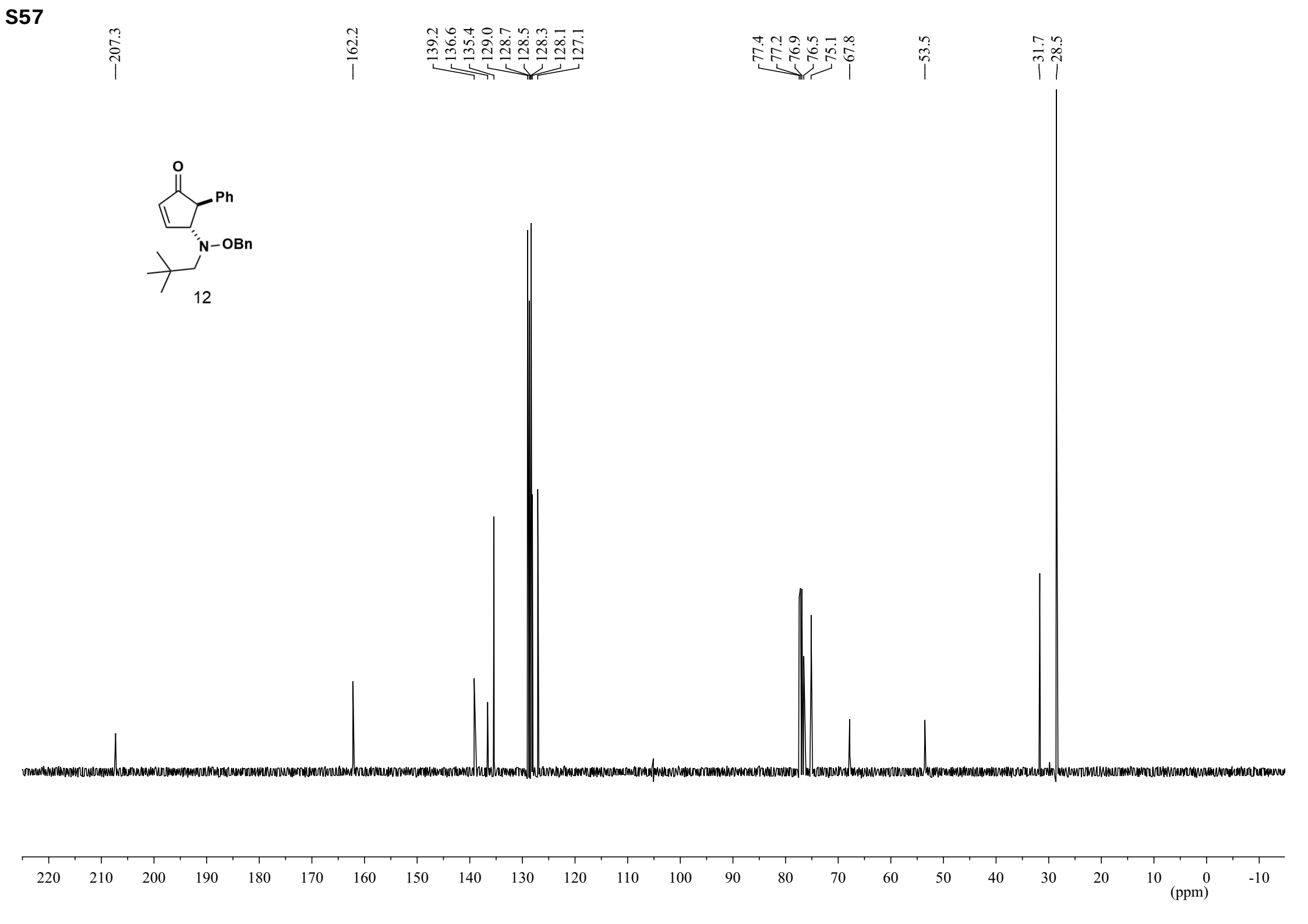
6.39
6.39
4.71
4.69
4.63
4.61
4.39
4.38
4.38
4.37
3.72
3.71
2.67
2.64
2.59
2.57
0.94
O
Ph
N–OBn
12
1.00
2.02
3.94
3.81
0.93
1.02
1.01
0.99
0.96
1.01
1.05
8.65
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
(ppm)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162.2
139.2
136.6
135.4
129.0
128.7
128.5
128.3
128.1
127.1
77.4
77.2
76.9
76.5
75.1
67.8
53.5
31.7
28.5
O
Ph
N–OBn
12
220
210
200
190
180
170
160
150
140
130
120
110
100
90
80
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60
50
40
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20
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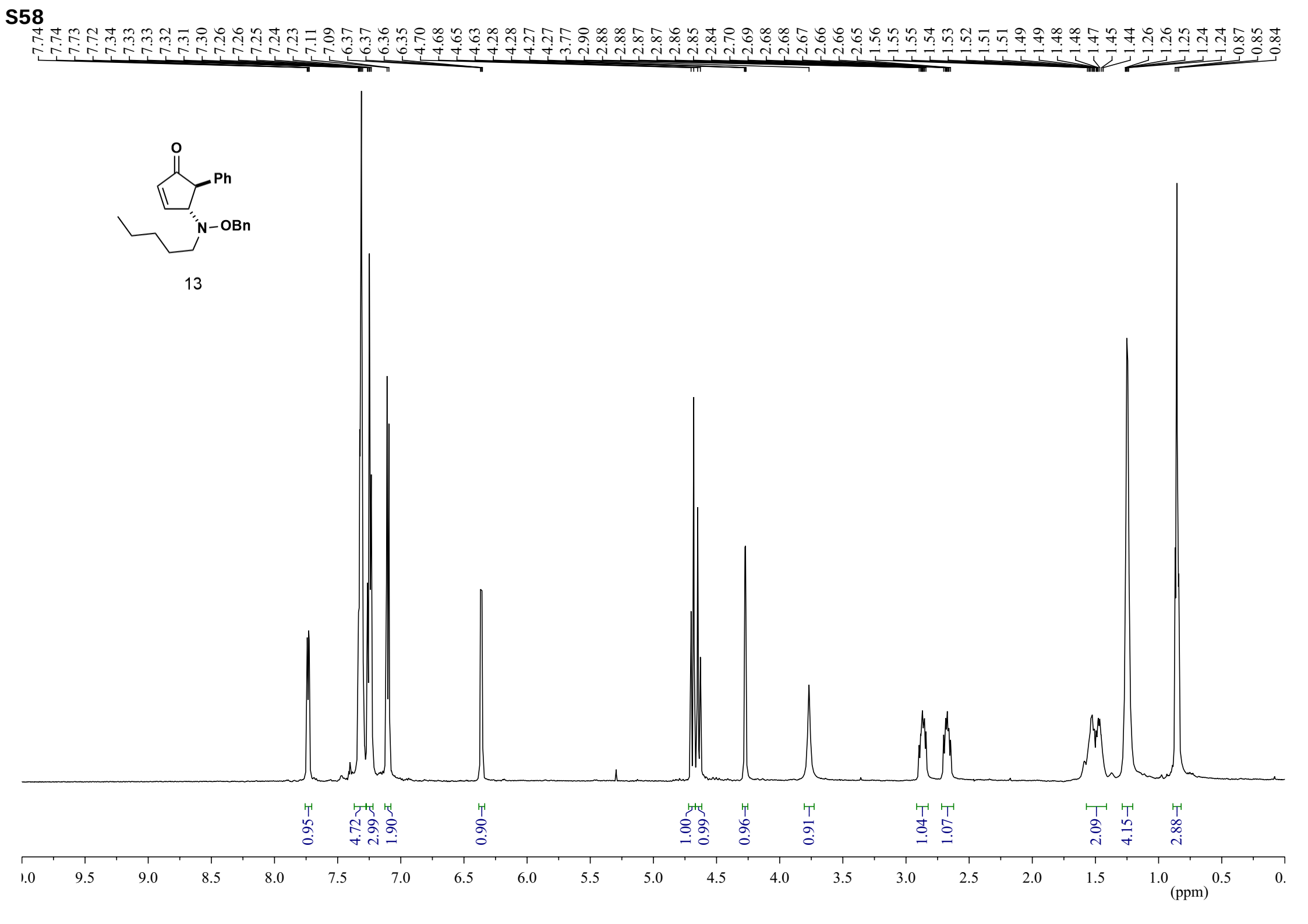
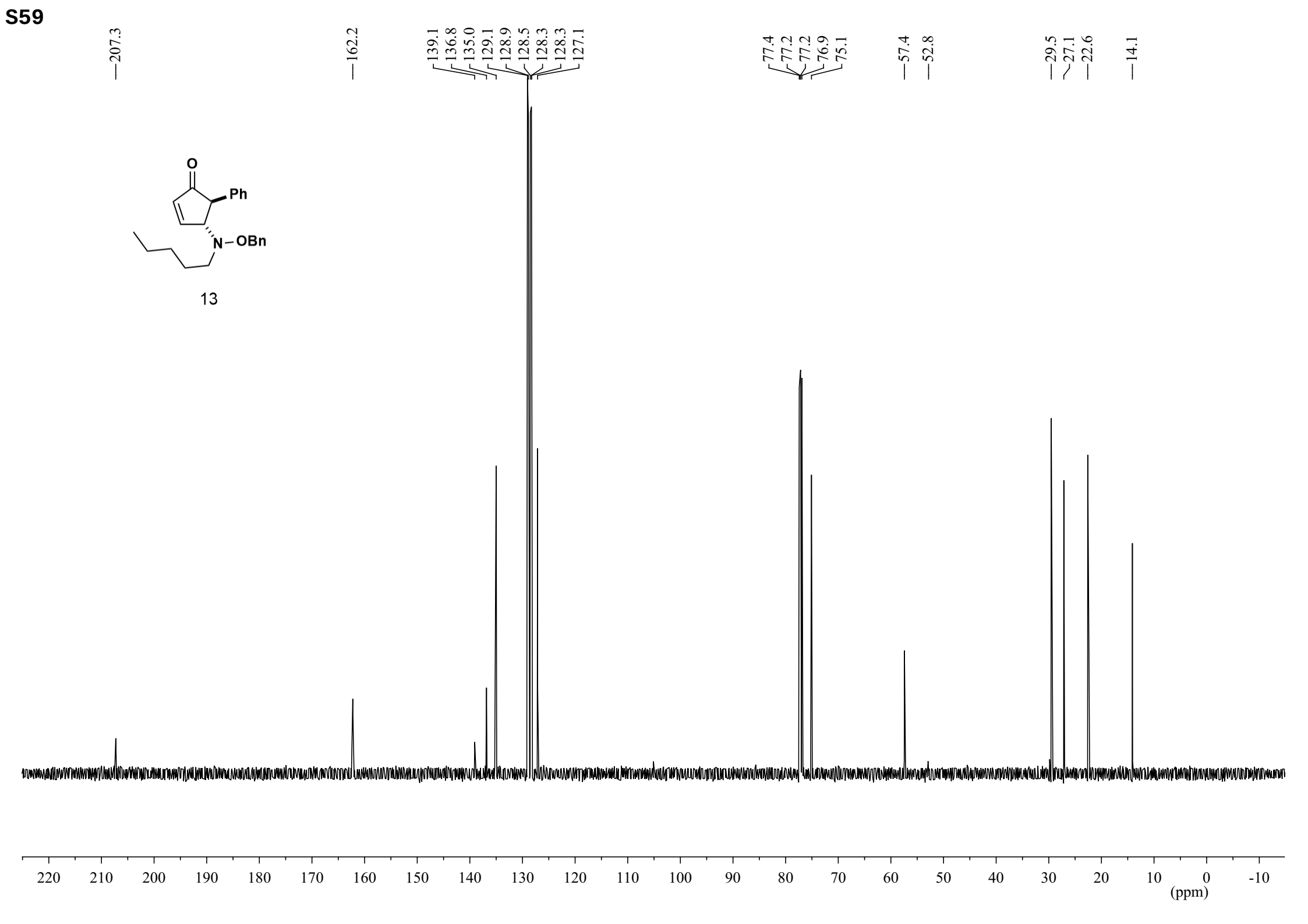
0
-10
(ppm)


7.74 7.74 7.73 7.72 7.34 7.33 7.33 7.32 7.31 7.30 7.26 7.26 7.25 7.24 7.23 7.11 7.09 6.37 6.37 6.36 6.35 4.70 4.68 4.65 4.63 4.28 4.28 4.27 4.27 3.77 2.90 2.88 2.88 2.87 2.87 2.86 2.85 2.84 2.70 2.69 2.68 2.68 2.67 2.66 2.66 2.65 1.56 1.55 1.55 1.54 1.53 1.52 1.51 1.51 1.49 1.49 1.48 1.48 1.47 1.45 1.44 1.26 1.26 1.25 1.24 1.24 0.87 0.85 0.84
O
Ph
N–OBn
13
0.95
4.72
2.99
1.90
0.90
1.00
0.99
0.96
0.91
1.04
1.07
2.09
4.15
2.88
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
(ppm)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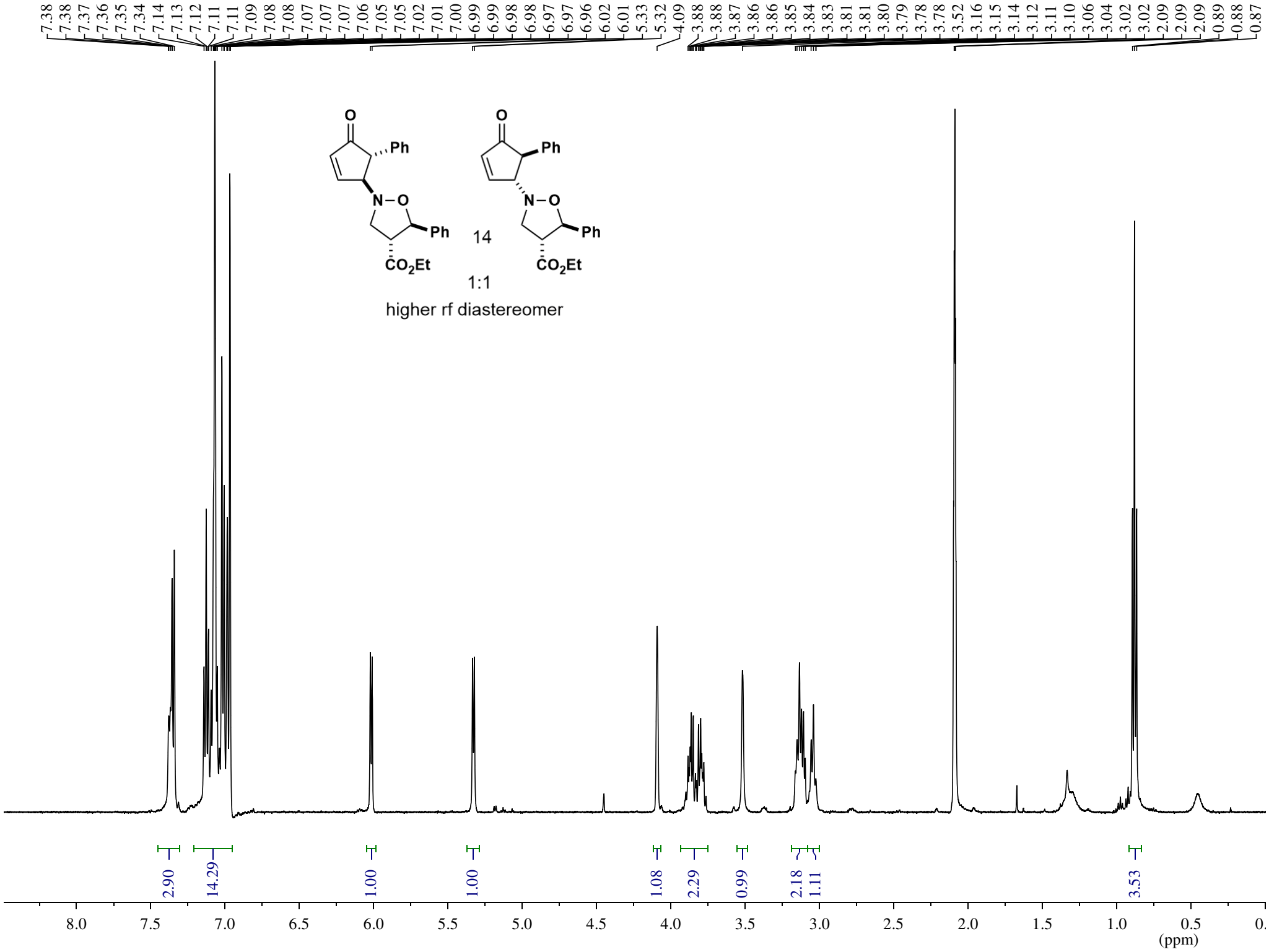
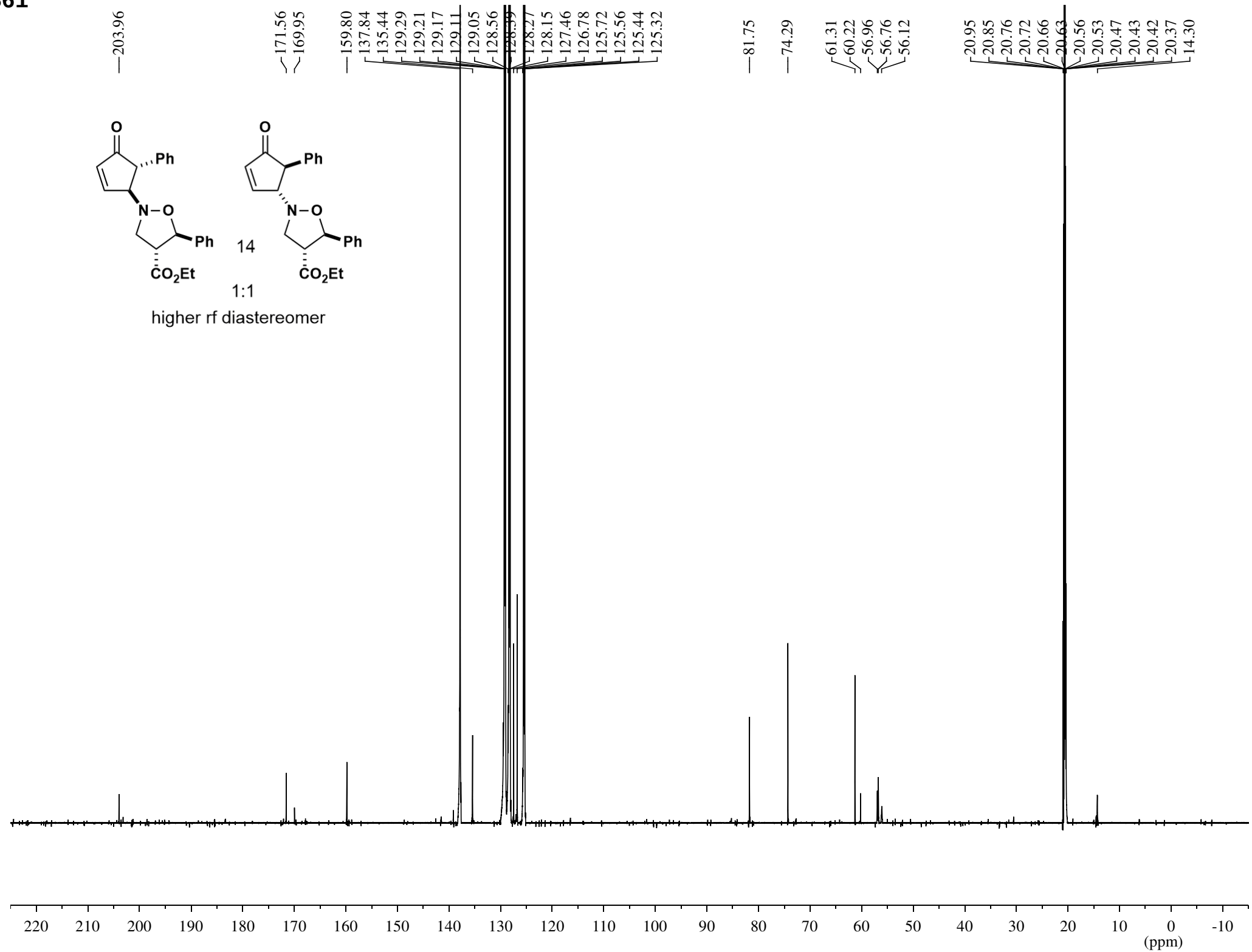
139.1
136.8
135.0
129.1
128.9
128.5
128.3
128.3
127.1
77.4
77.2
77.2
76.9
75.1
57.4
52.8
29.5
27.1
22.6
14.1
O
Ph
N–OBn
13
220
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
-10
(ppm)


7.38 7.38 7.37 7.36 7.35 7.34 7.14 7.13 7.12 7.11 7.11 7.09 7.08 7.08 7.07 7.07 7.07 7.06 7.05 7.05 7.02 7.01 7.00 6.99 6.99 6.98 6.98 6.97 6.97 6.96 6.02 6.01 5.33 5.32 4.09 3.88 3.88 3.87 3.86 3.86 3.85 3.84 3.83 3.81 3.81 3.80 3.79 3.78 3.78 3.52 3.16 3.15 3.14 3.12 3.11 3.10 3.06 3.04 3.02 3.02 2.09 2.09 2.09 0.89 0.88 0.87
O
Ph
N–O
Ph
CO2Et
14
1:1
higher rf diastereomer
2.90
14.29
1.00
1.00
1.08
2.29
0.99
2.18
1.11
3.53
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
(ppm)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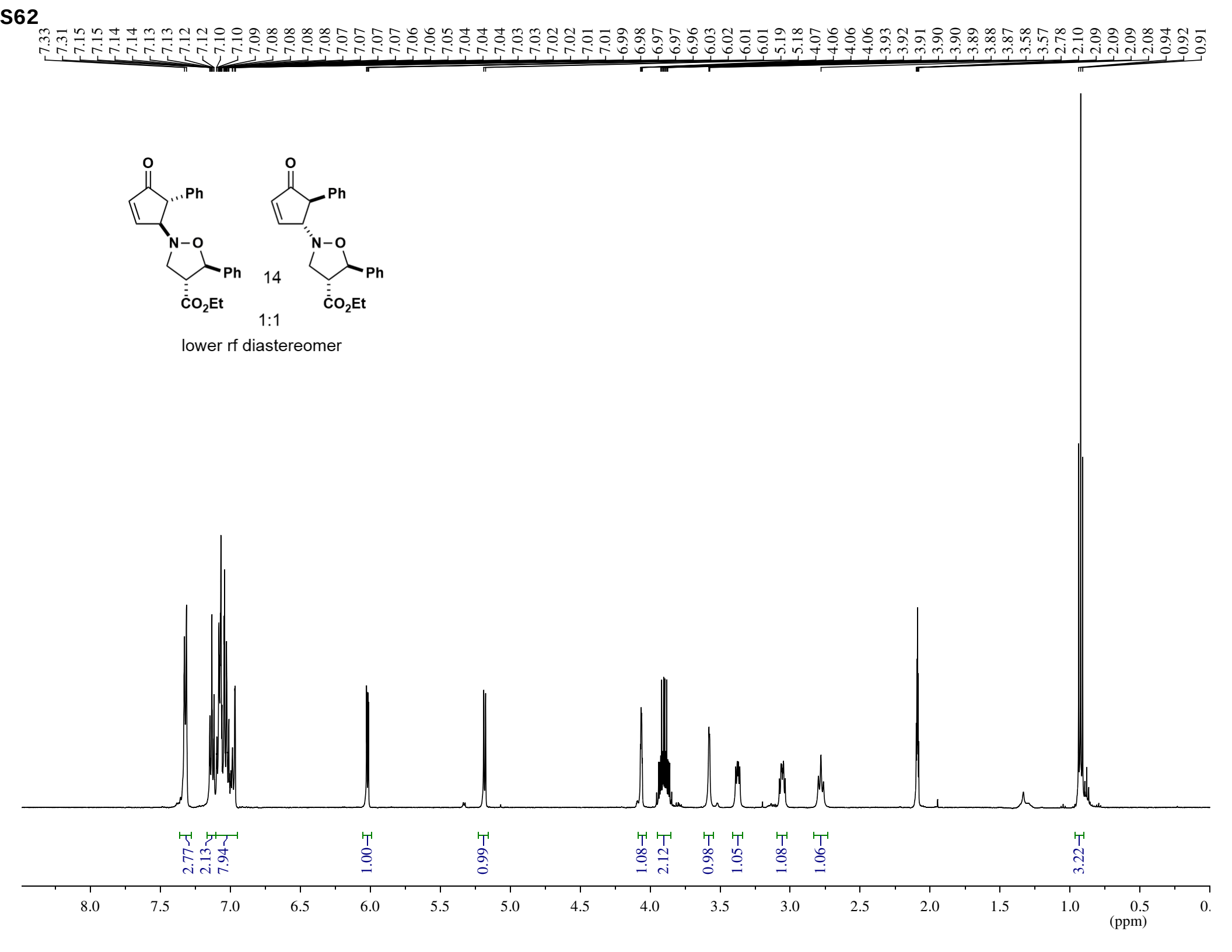
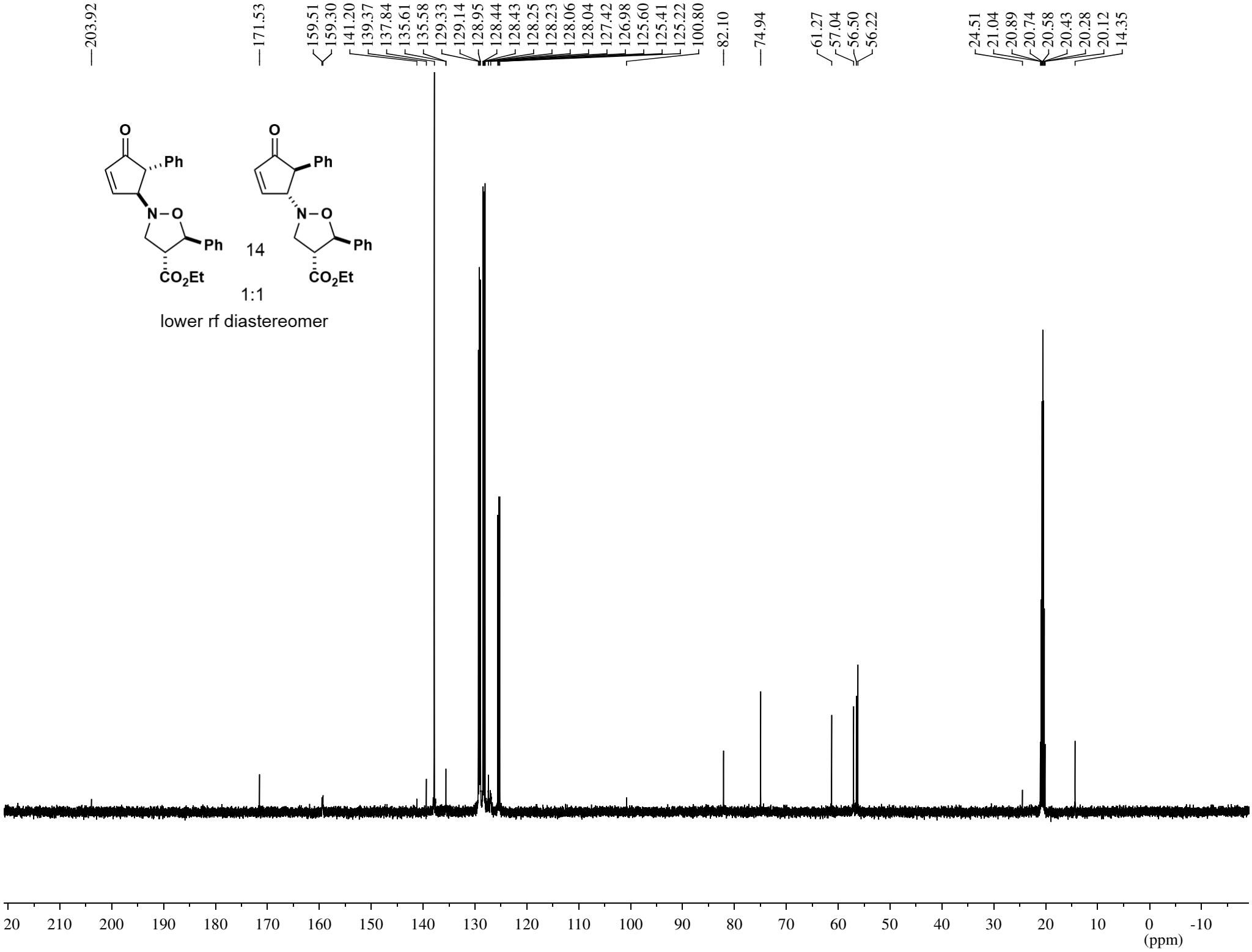
171.56
169.95
159.80
137.84
135.44
129.29
129.21
129.17
129.11
129.05
128.56
128.39
128.27
128.15
127.46
126.78
125.72
125.56
125.44
125.32
81.75
74.29
61.31
60.22
56.96
56.76
56.12
20.95
20.85
20.76
20.72
20.66
20.63
20.56
20.53
20.47
20.43
20.42
20.37
14.30
O
Ph
N–O
Ph
CO2Et
14
1:1
higher rf diastereomer
220
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
-10
(ppm)


7.33 7.31 7.15 7.15 7.14 7.14 7.13 7.13 7.12 7.12 7.10 7.10 7.09 7.08 7.08 7.08 7.08 7.07 7.07 7.07 7.07 7.06 7.06 7.05 7.04 7.04 7.04 7.03 7.03 7.02 7.02 7.01 7.01 6.99 6.98 6.97 6.97 6.96 6.03 6.02 6.01 6.01 5.19 5.18 4.07 4.06 4.06 4.06 3.93 3.92 3.91 3.90 3.90 3.89 3.88 3.87 3.58 3.57 2.78 2.10 2.09 2.09 2.09 2.08 0.94 0.92 0.91
O
Ph
N–O
Ph
CO2Et
14
1:1
lower rf diastereomer
2.77 2.13 7.94 1.00 0.99 1.08 2.12 0.98 1.05 1.08 1.06 3.22
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
(ppm)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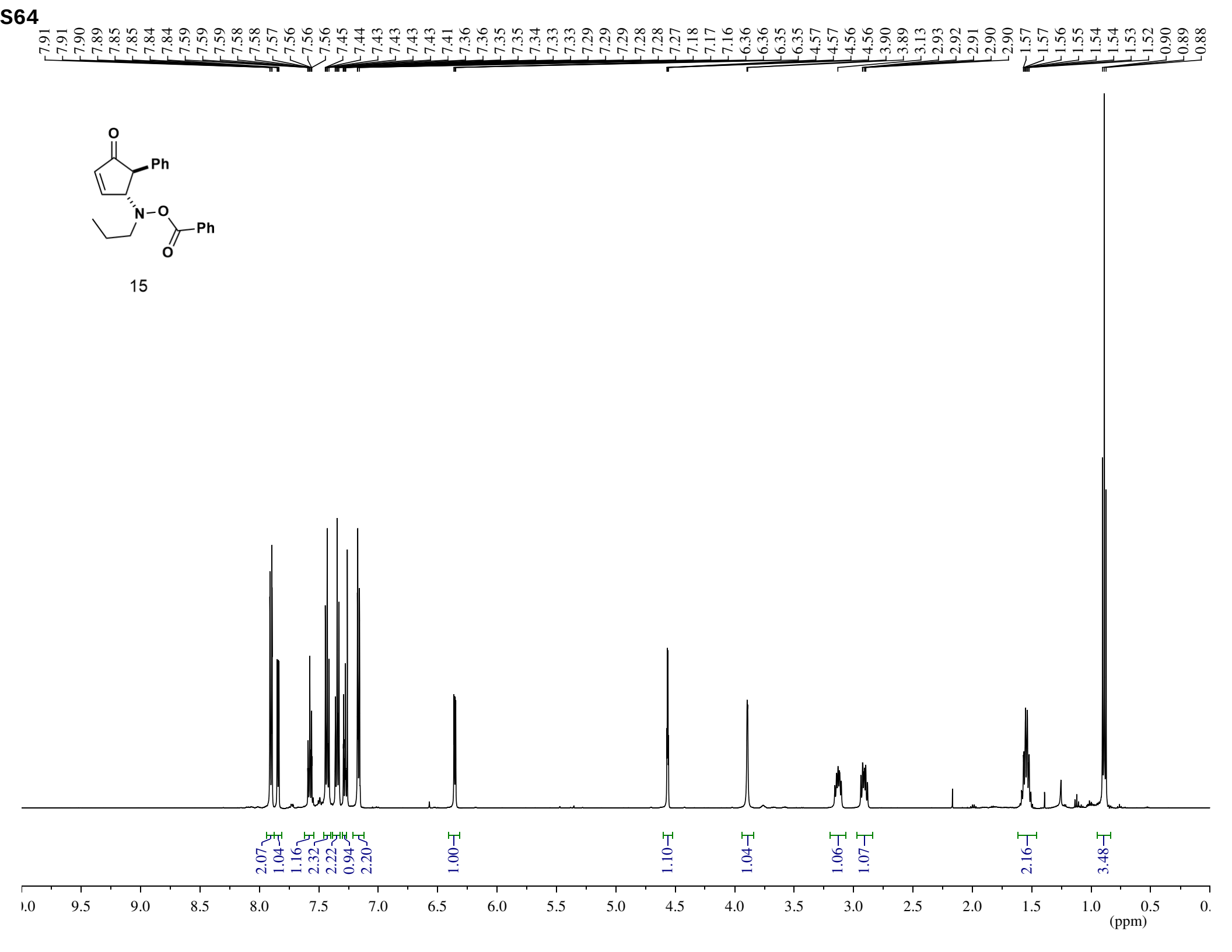
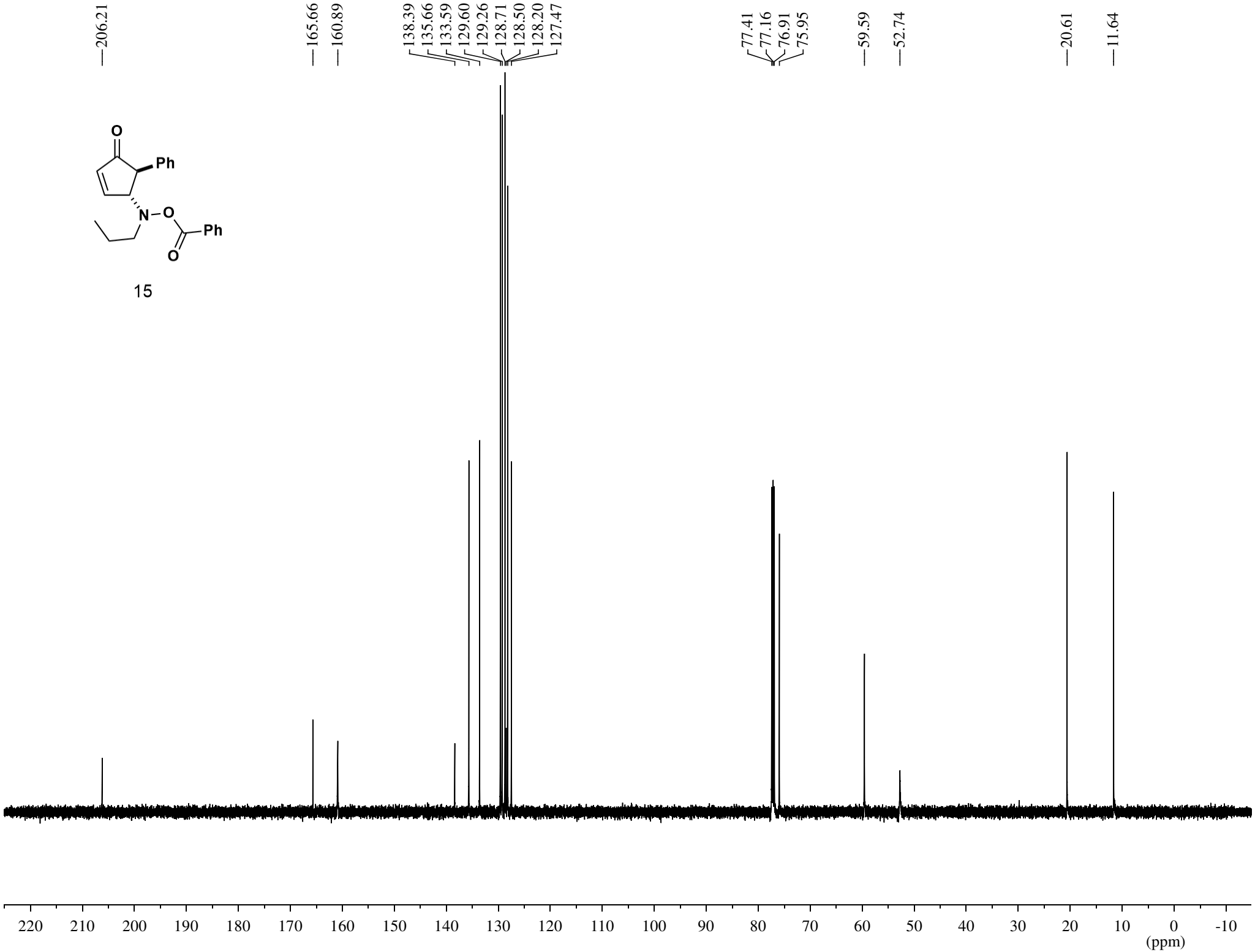
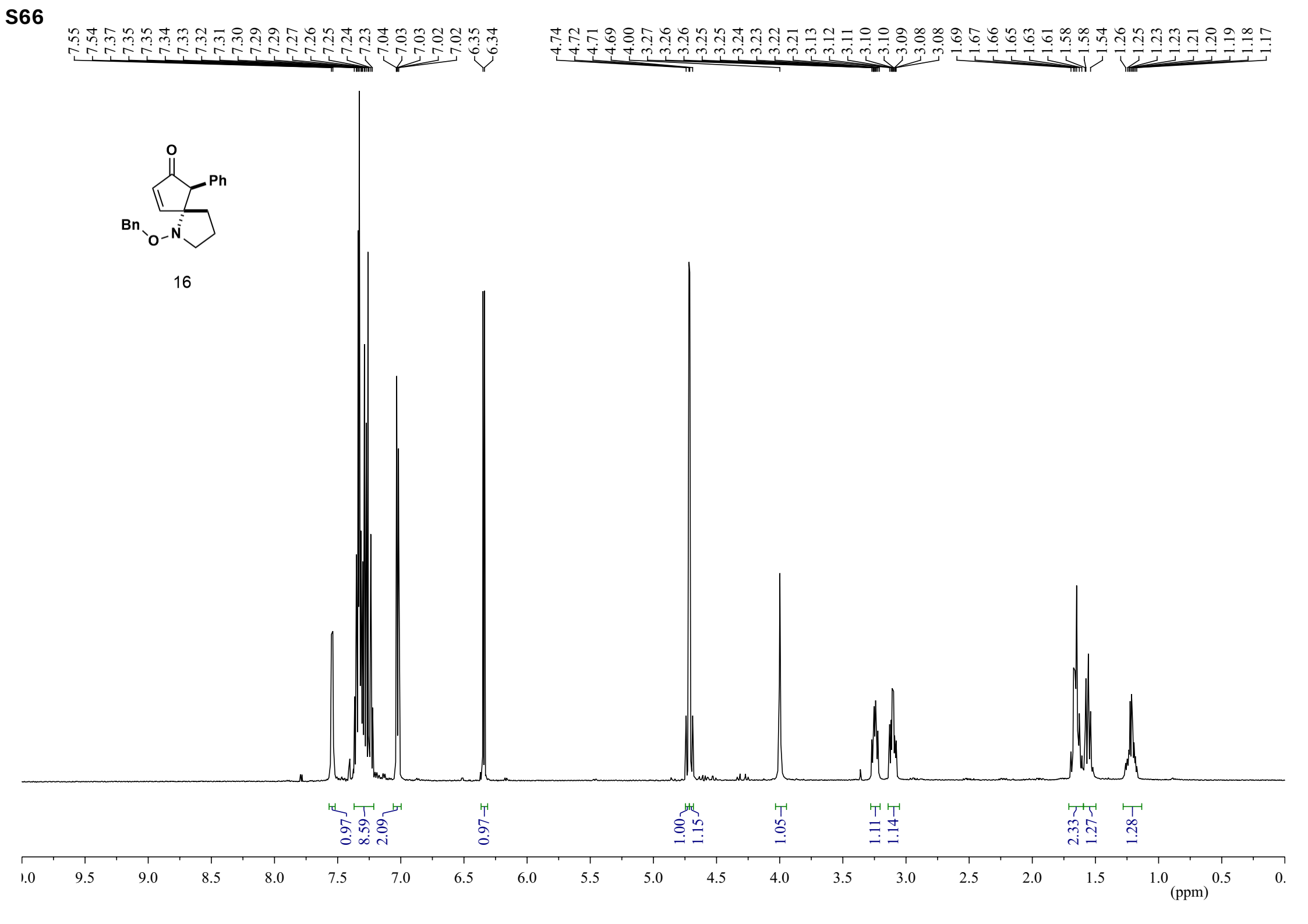
171.53
159.51
159.30
141.20
139.37
137.84
135.61
135.58
129.33
129.14
128.95
128.44
128.43
128.25
128.23
128.06
128.04
127.42
126.98
125.60
125.41
125.22
100.80
82.10
74.94
61.27
57.04
56.50
56.22
24.51
21.04
20.89
20.74
20.58
20.43
20.28
20.12
14.35
O
Ph
N–O
Ph
CO2Et
14
1:1
lower rf diastereomer
20
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
-10
(ppm)

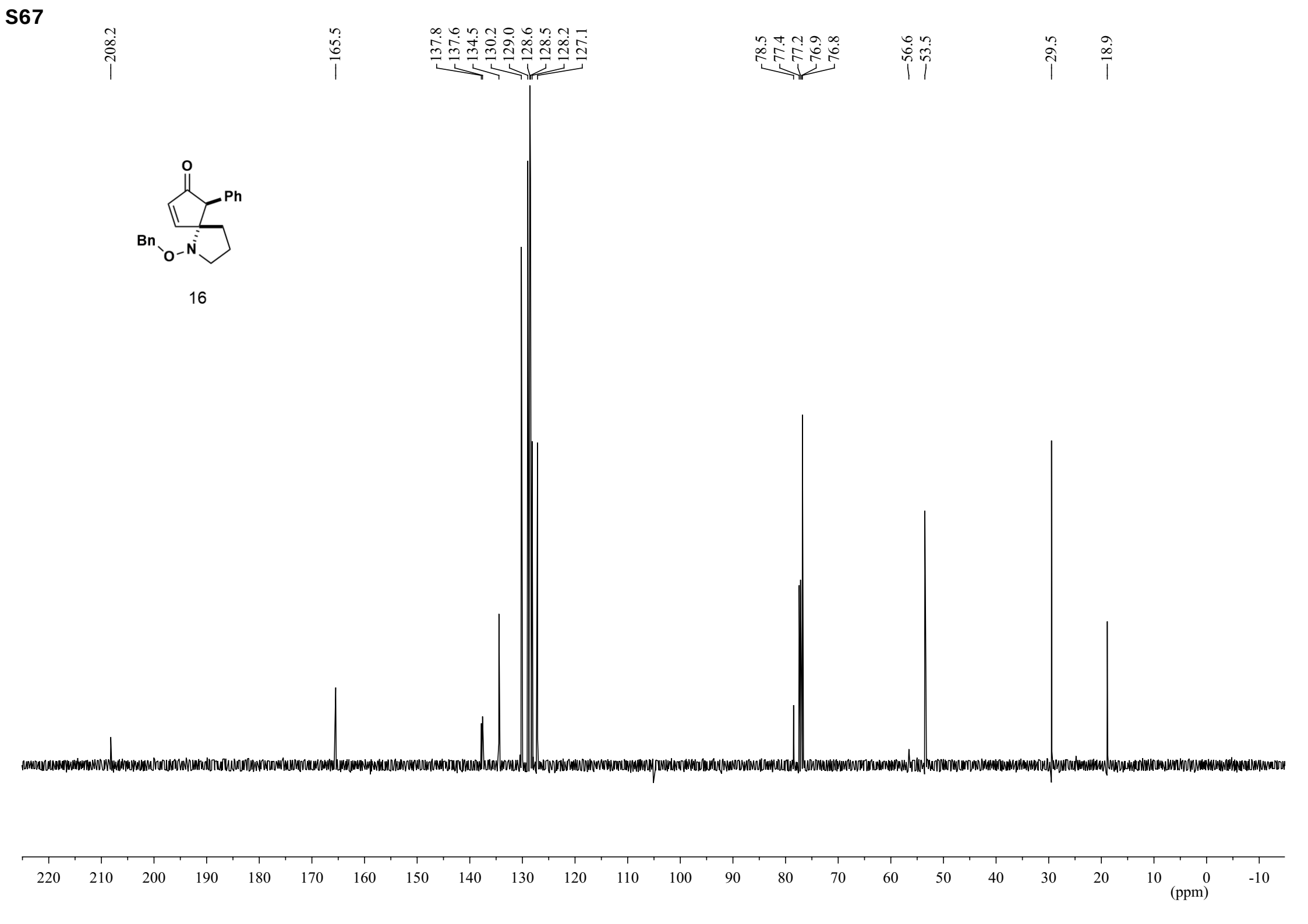

7.91 7.91 7.90 7.89 7.85 7.85 7.84 7.84 7.59 7.59 7.59 7.58 7.58 7.57 7.56 7.56 7.56 7.45 7.44 7.43 7.43 7.43 7.43 7.41 7.36 7.36 7.35 7.35 7.34 7.33 7.33 7.29 7.29 7.29 7.28 7.28 7.27 7.18 7.17 7.16 6.36 6.36 6.35 6.35 4.57 4.57 4.56 4.56 3.90 3.89 3.13 2.93 2.92 2.91 2.90 2.90 1.57 1.57 1.56 1.55 1.54 1.54 1.53 1.52 0.90 0.89 0.88
O
Ph
N
O
Ph
O
15
2.07 1.04 1.16 2.32 2.22 0.94 2.20 1.00 1.10 1.04 1.06 1.07 2.16 3.48
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
(ppm)

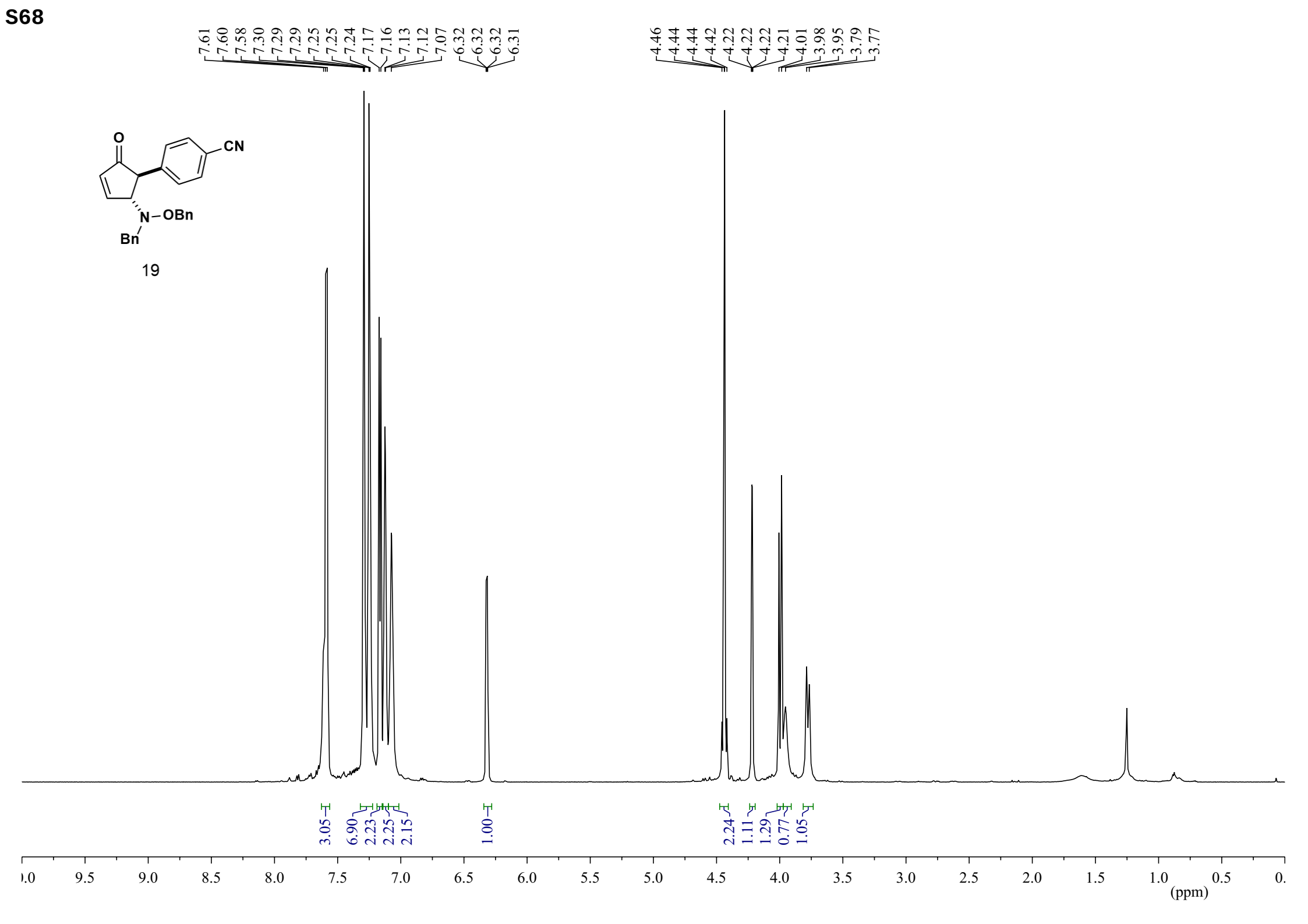

206.21
165.66
160.89
138.39
135.66
133.59
129.60
129.26
128.71
128.50
128.20
127.47
77.41
77.16
76.91
75.95
59.59
52.74
20.61
11.64
O
Ph
N
O
Ph
O
220
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
-10
(ppm)

15

S66


7.55 7.54 7.37 7.35 7.35 7.34 7.33 7.32 7.31 7.30 7.29 7.29 7.27 7.26 7.25 7.24 7.23 7.04 7.03 7.03 7.02 7.02 6.35 6.34
4.74 4.72 4.71 4.69 4.00 3.27 3.26 3.26 3.25 3.25 3.24 3.23 3.22 3.21 3.13 3.12 3.11 3.10 3.10 3.09 3.08 3.08
1.69 1.67 1.66 1.65 1.63 1.61 1.58 1.58 1.54 1.26 1.25 1.23 1.23 1.21 1.20 1.19 1.18 1.17
O
Ph
Bn
O
N
16
0.97 8.59 2.09 0.97 1.00 1.15 1.05 1.11 1.14 2.33 1.27 1.28
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
(ppm)


208.2
165.5
137.8
137.6
134.5
130.2
129.0
128.6
128.5
128.2
127.1
78.5
77.4
77.2
76.9
76.8
56.6
53.5
29.5
18.9
O
Ph
Bn
O
N
16
220
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
-10
(ppm)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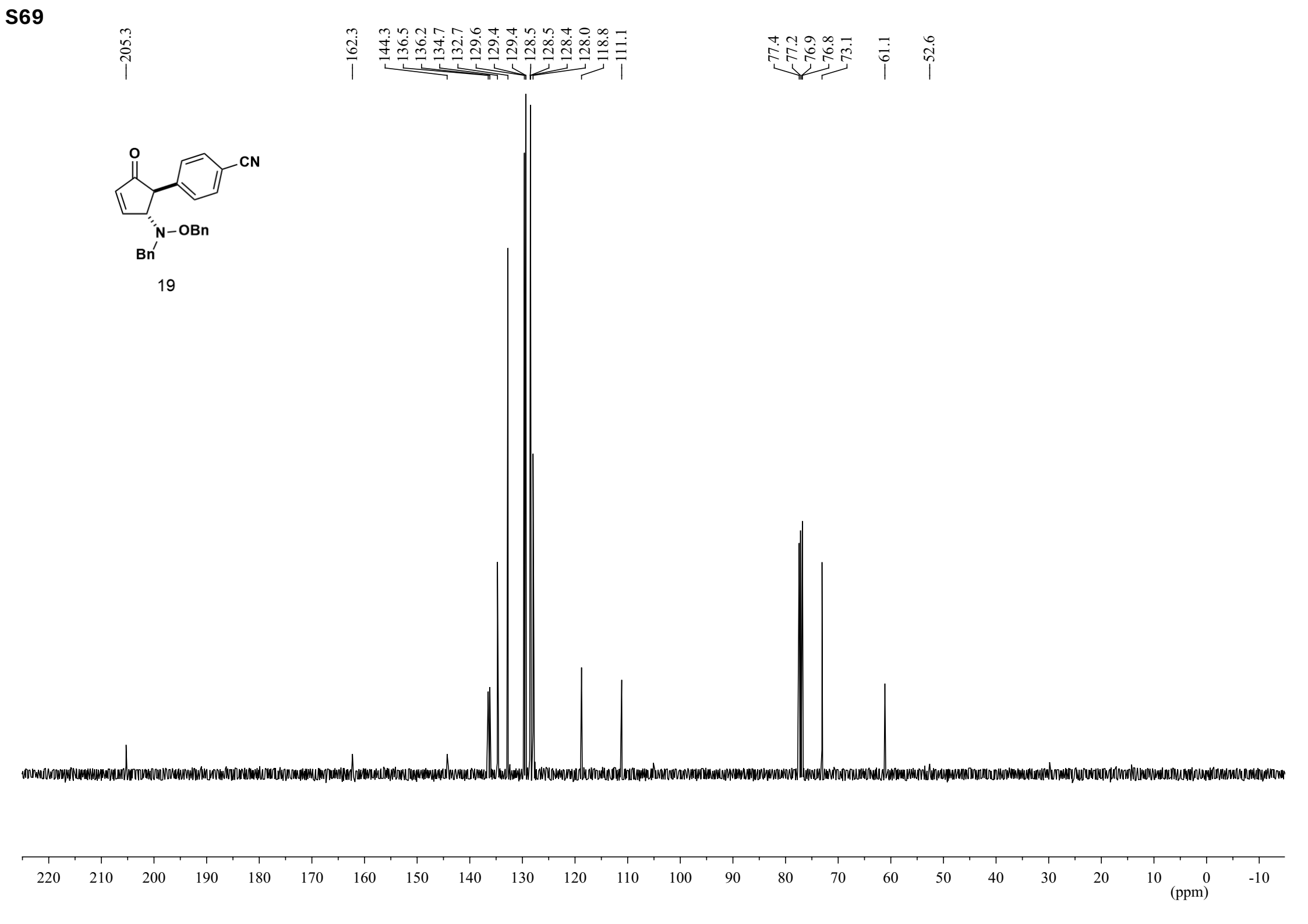
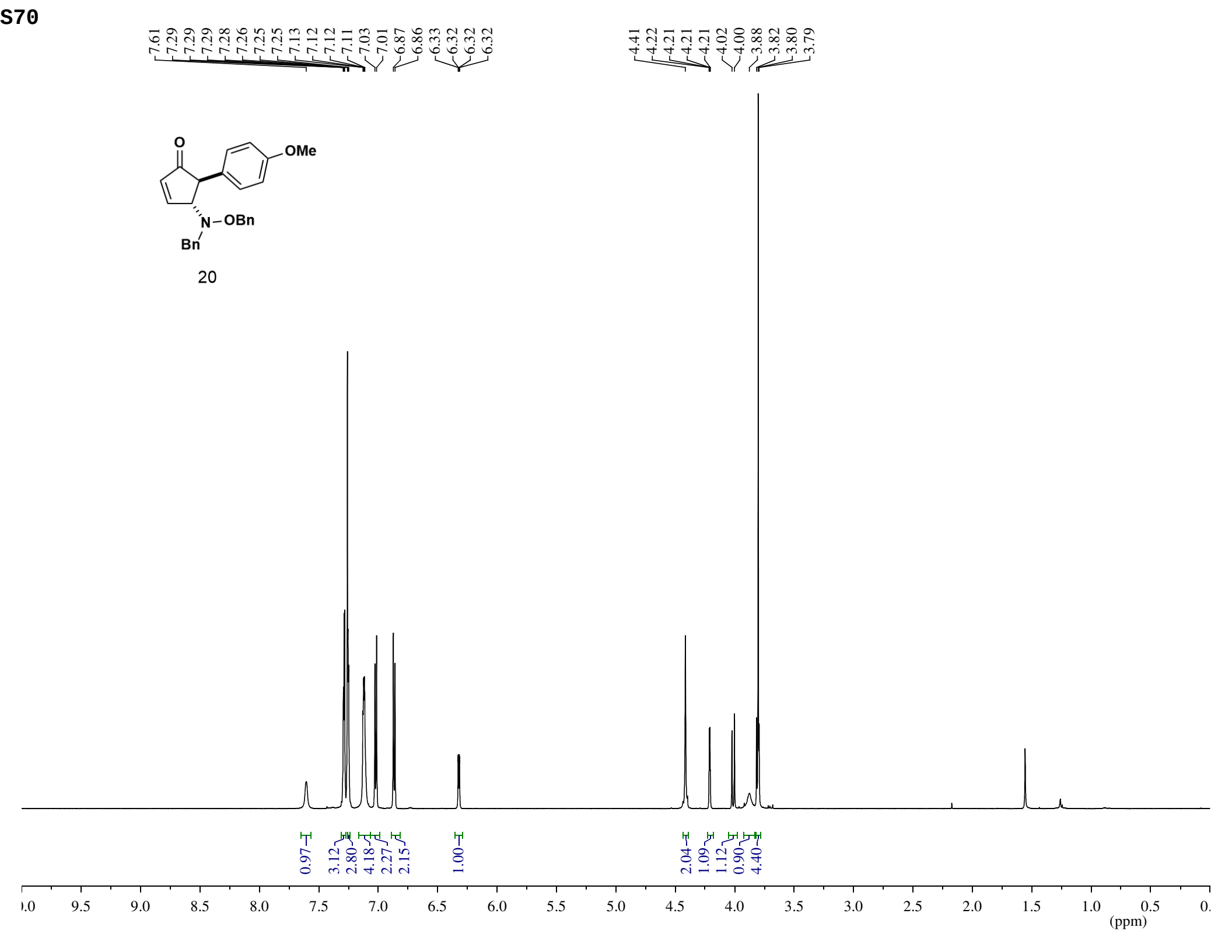
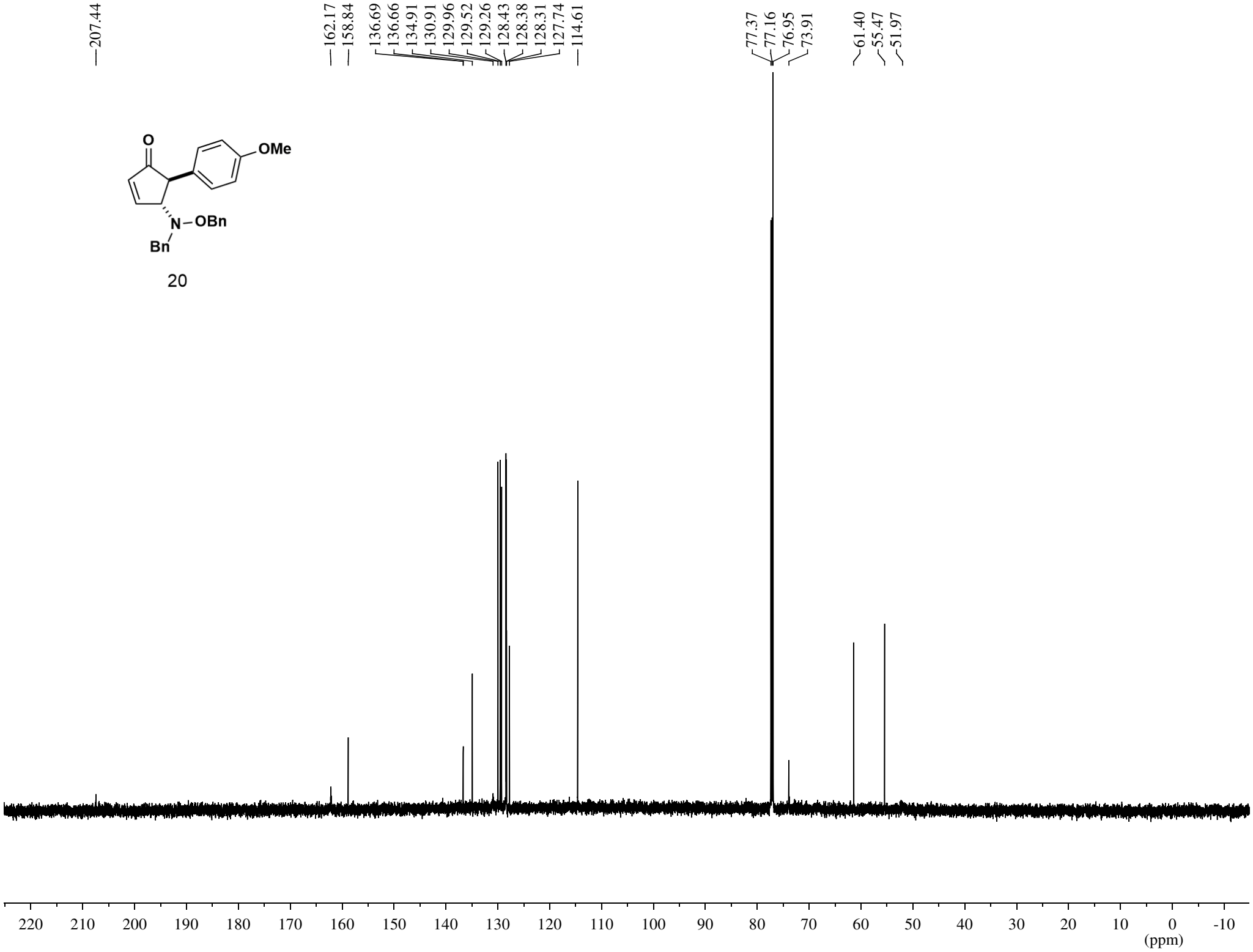
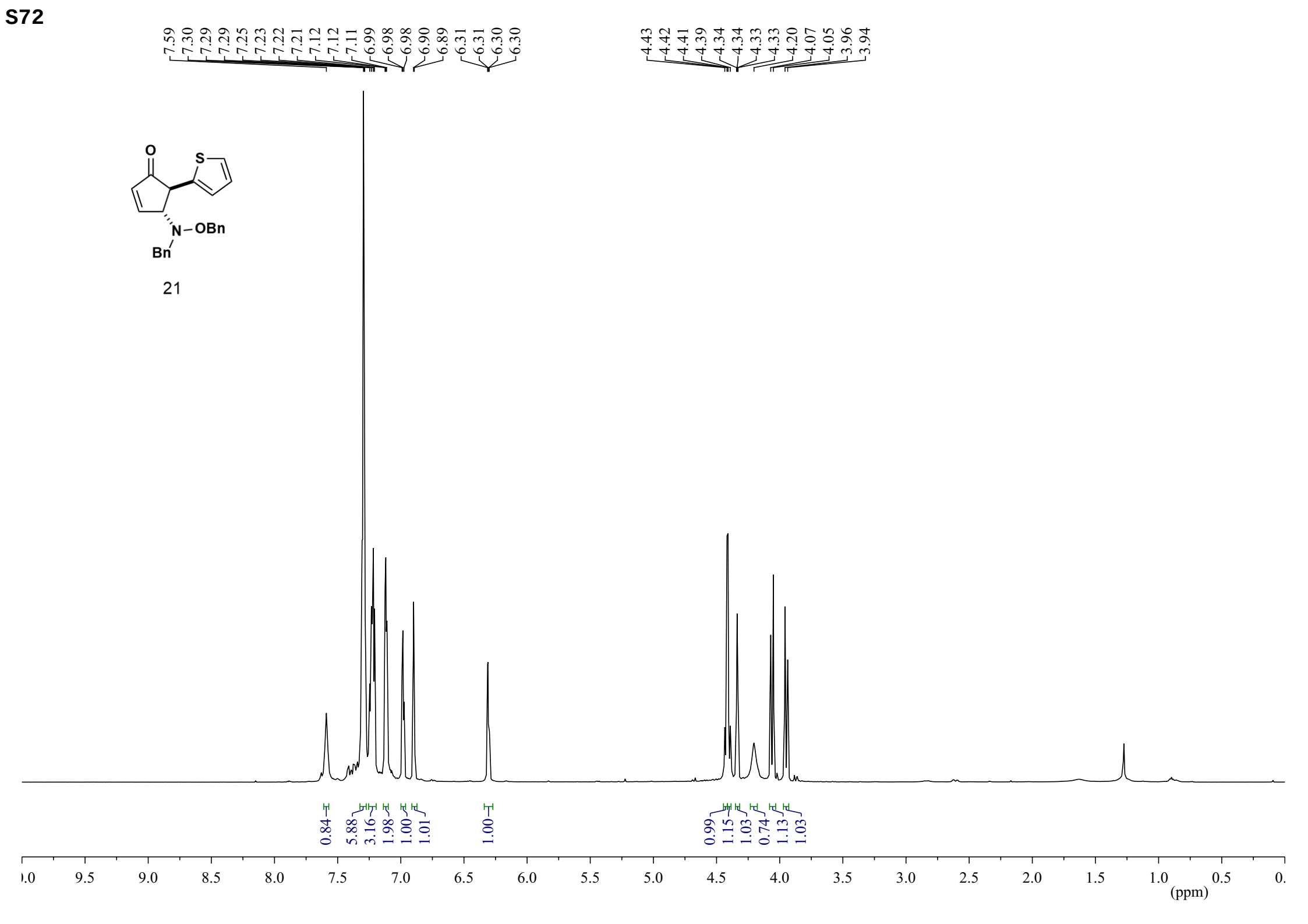
7.60
7.58
7.30
7.29
7.29
7.25
7.25
7.24
7.17
7.16
7.13
7.12
7.07
6.32
6.32
6.32
6.31
4.46
4.44
4.44
4.42
4.22
4.22
4.22
4.21
4.01
3.98
3.95
3.79
3.77
O
CN
N–OBn
Bn
19
3.05
6.90
2.23
2.25
2.15
1.00
2.24
1.11
1.29
0.77
1.05
(ppm)

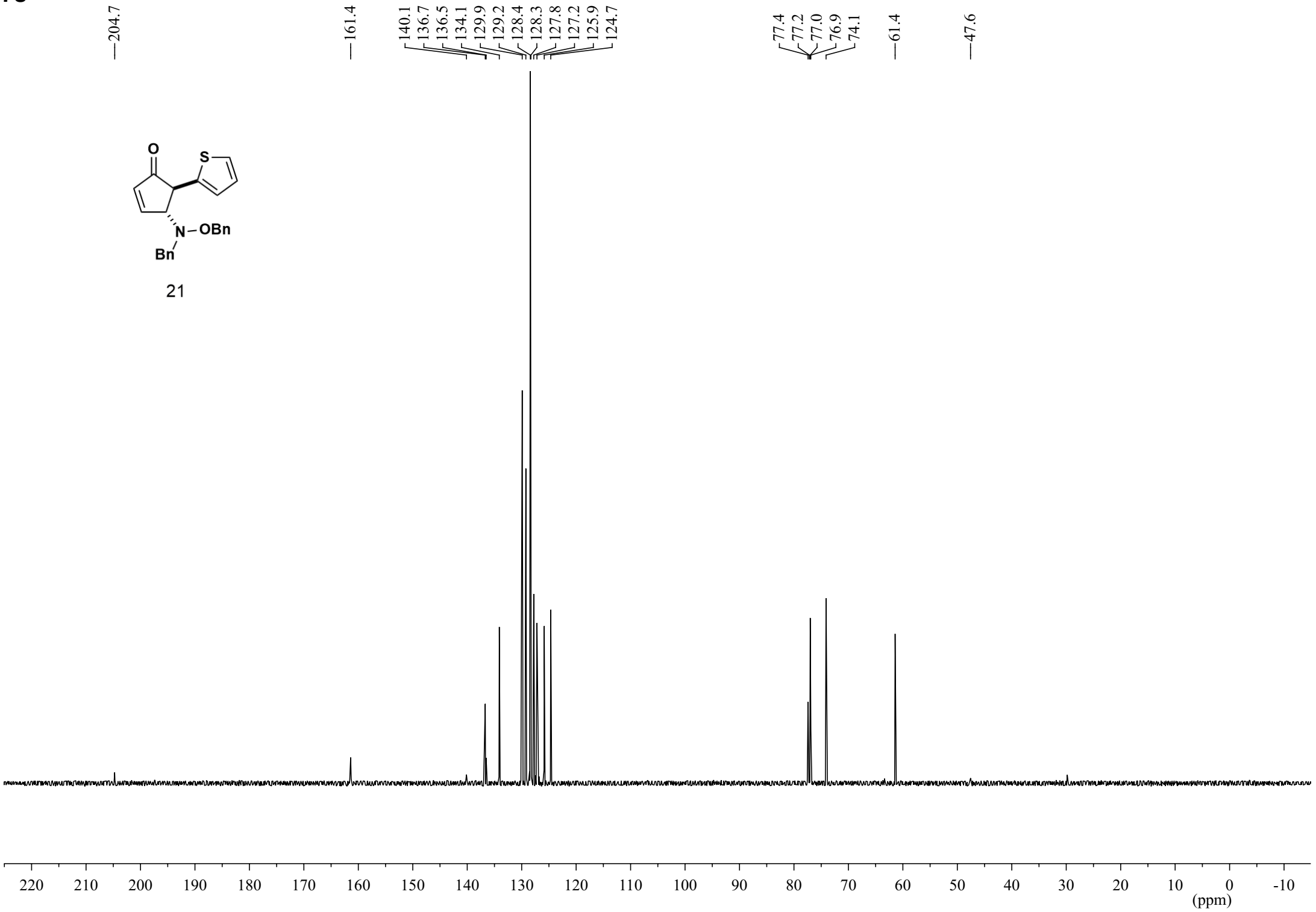

205.3
162.3
144.3
136.5
136.2
134.7
132.7
129.6
129.4
129.4
128.5
128.5
128.4
128.0
118.8
111.1
77.4
77.2
76.9
76.8
73.1
61.1
52.6
O
CN
N–OBn
Bn
19
220
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
-10
(ppm)


7.61
7.29
7.29
7.29
7.28
7.26
7.25
7.25
7.13
7.12
7.12
7.11
7.03
7.01
6.87
6.86
6.33
6.32
6.32
6.32
4.41
4.22
4.21
4.21
4.21
4.02
4.00
3.88
3.82
3.80
3.79
O
OMe
N–OBn
Bn
0.97
3.12
2.80
4.18
2.27
2.15
1.00
2.04
1.09
1.12
0.90
4.40
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
(ppm)

20


207.44
162.17
158.84
136.69
136.66
134.91
130.91
129.96
129.52
129.26
128.43
128.38
128.31
127.74
114.61
77.37
77.16
76.95
73.91
61.40
55.47
51.97
O
OMe
N–OBn
Bn
20
220
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
-10
(ppm)


7.59
7.30
7.29
7.29
7.25
7.23
7.22
7.21
7.12
7.12
7.11
6.99
6.98
6.98
6.90
6.89
6.31
6.31
6.30
6.30
4.43
4.42
4.41
4.39
4.34
4.34
4.33
4.33
4.20
4.07
4.05
3.96
3.94
O
S
N–OBn
Bn
21
0.84
5.88
3.16
1.98
1.00
1.01
1.00
0.99
1.15
1.03
0.74
1.13
1.03
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
(ppm)


204.7
161.4
140.1
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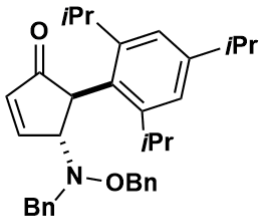
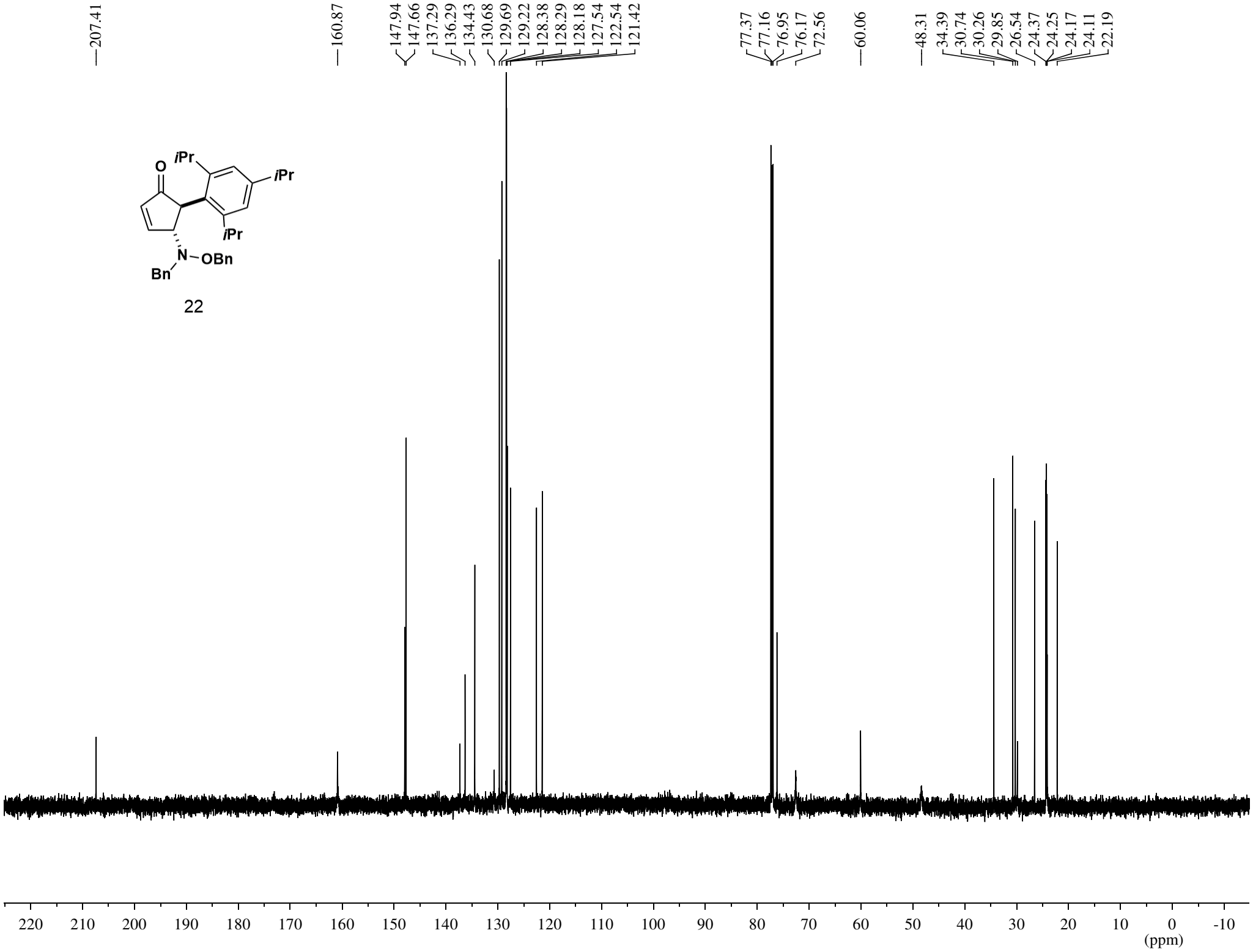
136.5
134.1
129.9
129.2
128.4
128.3
127.8
127.2
125.9
124.7
77.4
77.2
77.0
76.9
74.1
61.4
47.6
O
S
N–OBn
Bn
220
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
-10
(ppm)

21

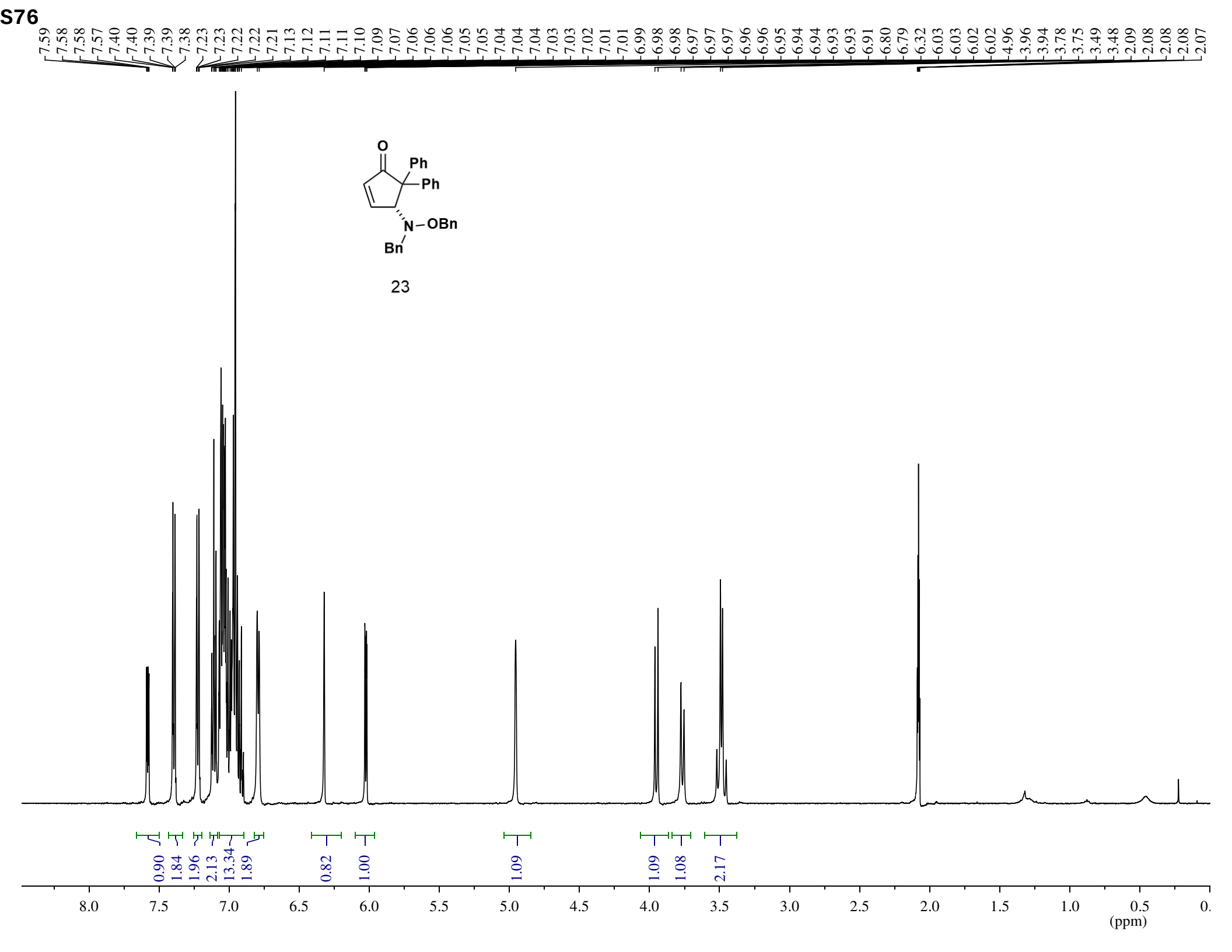


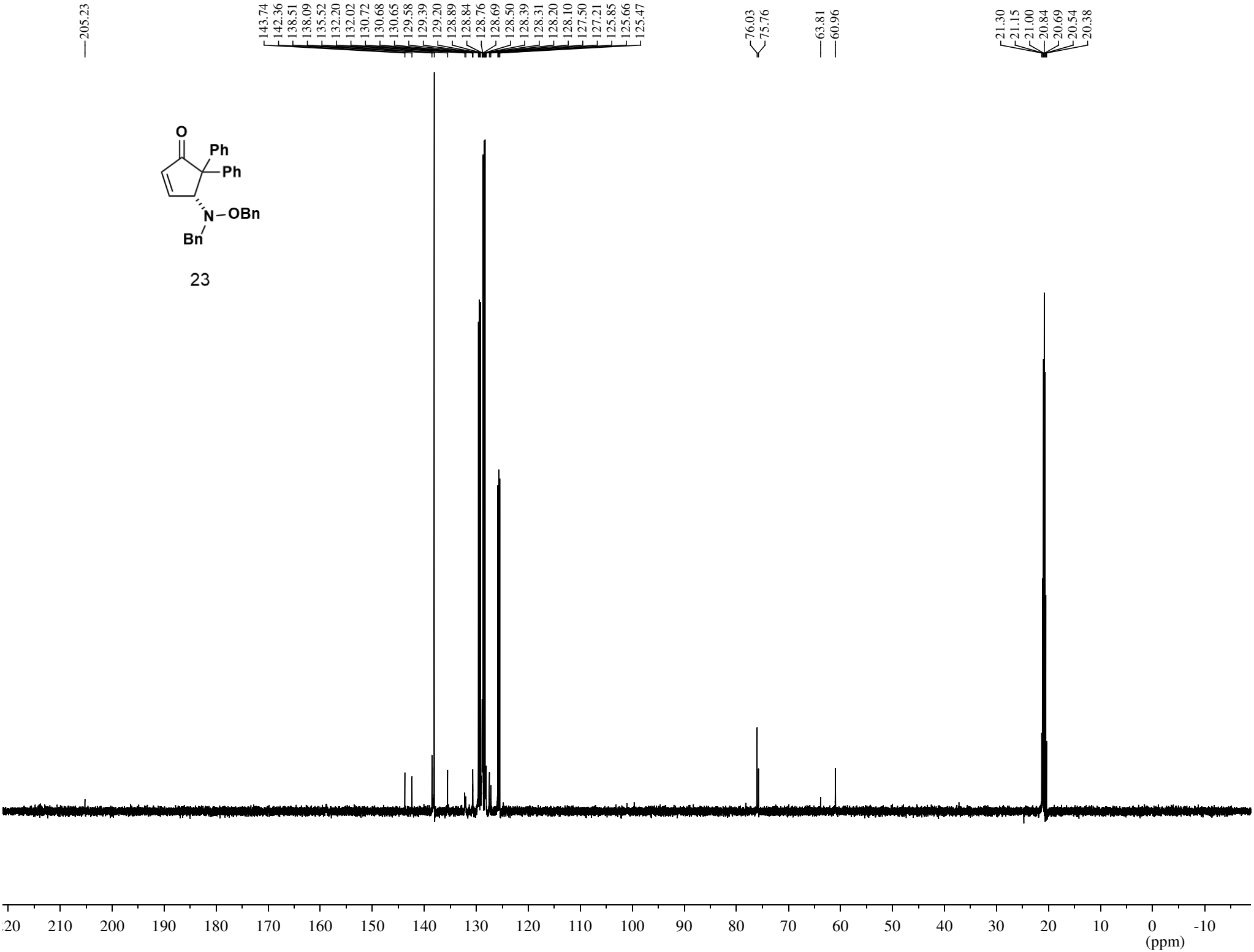
22

(ppm)


207.41
160.87
147.94
147.66
137.29
136.29
134.43
130.68
129.69
129.22
128.38
128.29
128.18
127.54
122.54
121.42
77.37
77.16
76.95
76.17
72.56
60.06
48.31
34.39
30.74
30.26
29.85
26.54
24.37
24.25
24.17
24.11
22.19
O
iPr
iPr
iPr
N
OBn
Bn
220
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
-10
(ppm)

22


7.59 7.58 7.58 7.57 7.40 7.40 7.39 7.39 7.38 7.23 7.23 7.22 7.22 7.21 7.13 7.12 7.11 7.11 7.10 7.09 7.07 7.06 7.06 7.06 7.05 7.05 7.04 7.04 7.04 7.03 7.03 7.02 7.01 7.01 6.99 6.98 6.98 6.97 6.97 6.97 6.96 6.96 6.95 6.94 6.94 6.93 6.93 6.91 6.80 6.79 6.32 6.03 6.03 6.02 6.02 4.96 3.96 3.94 3.78 3.75 3.49 3.48 2.09 2.08 2.08 2.08 2.07
O
Ph
Ph
N–OBn
Bn
23
0.90 1.84 1.96 2.13 13.34 1.89 0.82 1.00 1.09 1.09 1.08 2.17
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
(ppm)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127.21
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125.66
125.47
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75.76
63.81
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21.15
21.00
20.84
20.69
20.54
20.38
O
Ph
Ph
N–OBn
Bn
23
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210
200
190
180
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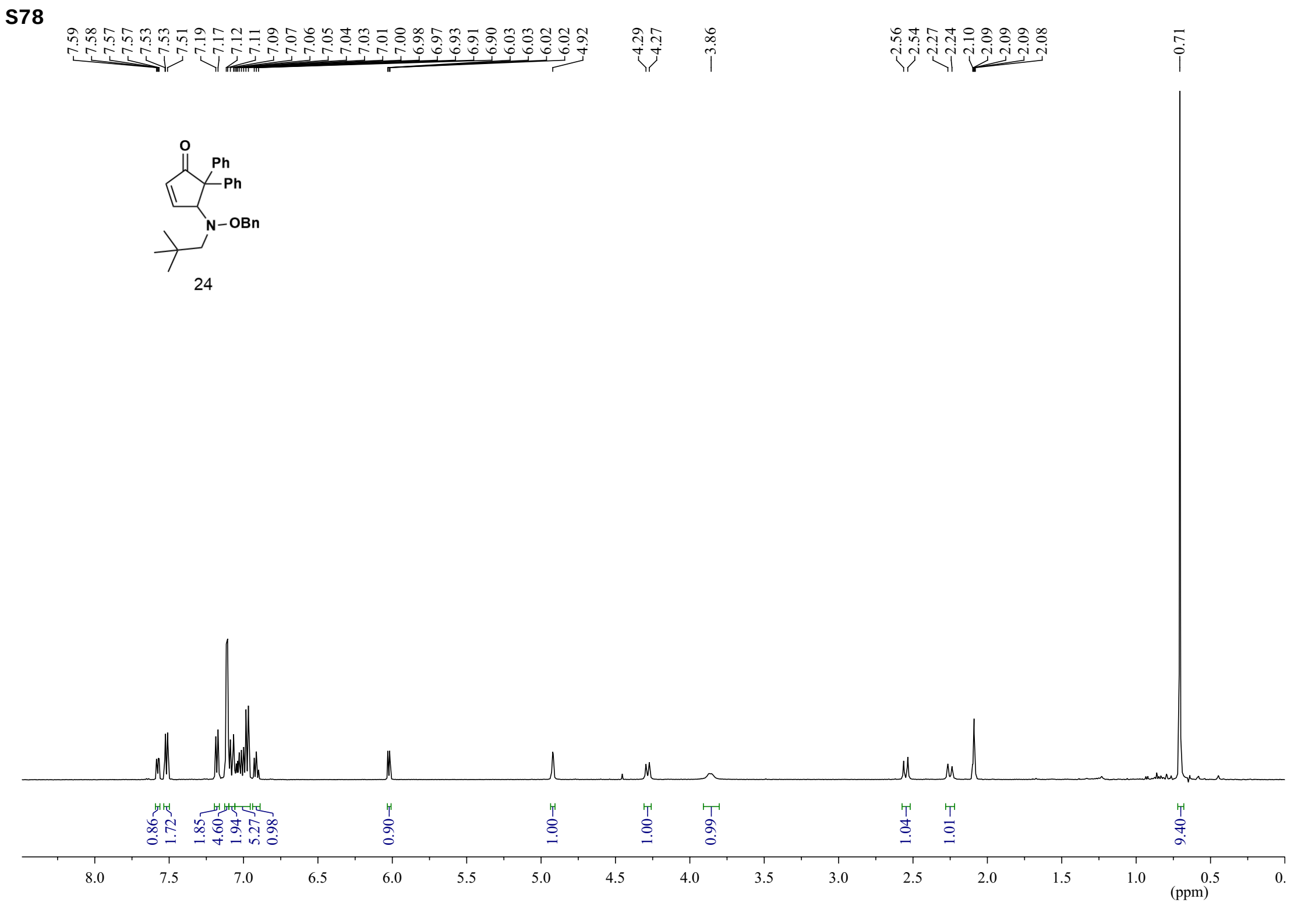
(ppm)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7.09
7.07
7.06
7.05
7.04
7.03
7.01
7.00
6.98
6.97
6.93
6.91
6.90
6.03
6.03
6.02
6.02
4.92
4.29
4.27
3.86
2.56
2.54
2.27
2.24
2.10
2.09
2.09
2.09
2.08
0.71
O
Ph
Ph
N–OBn
24
0.86
1.72
1.85
4.60
1.94
5.27
0.98
0.90
1.00
1.00
0.99
1.04
1.01
9.40
8.0
7.5
7.0
6.5
6.0
5.5
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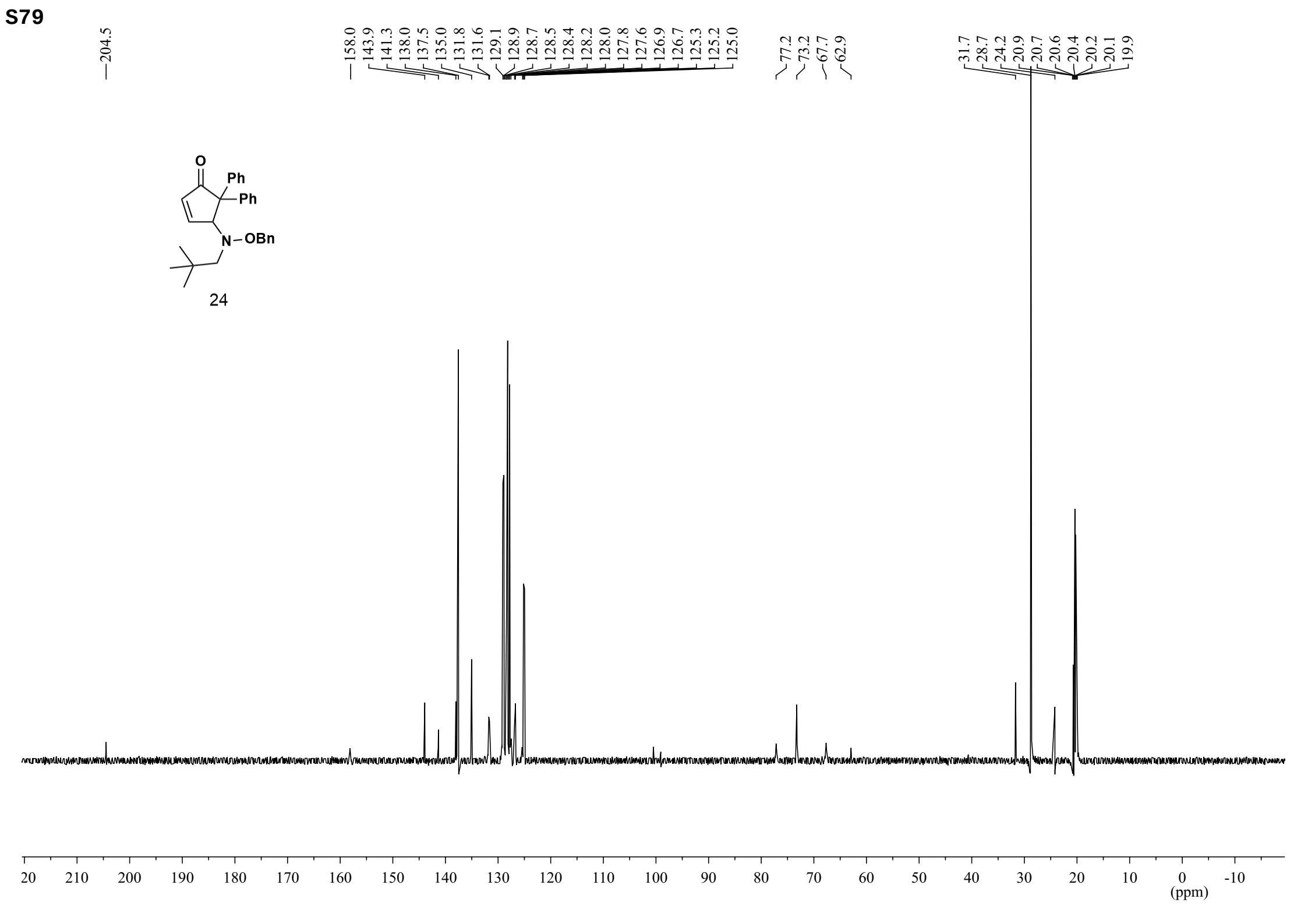
(ppm)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128.7
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128.4
128.2
128.0
127.8
127.6
126.9
126.7
125.3
125.2
125.0
77.2
73.2
67.7
62.9
31.7
28.7
24.2
20.9
20.7
20.6
20.4
20.2
20.1
19.9
O
Ph
Ph
N–OBn
24
20
210
200
190
180
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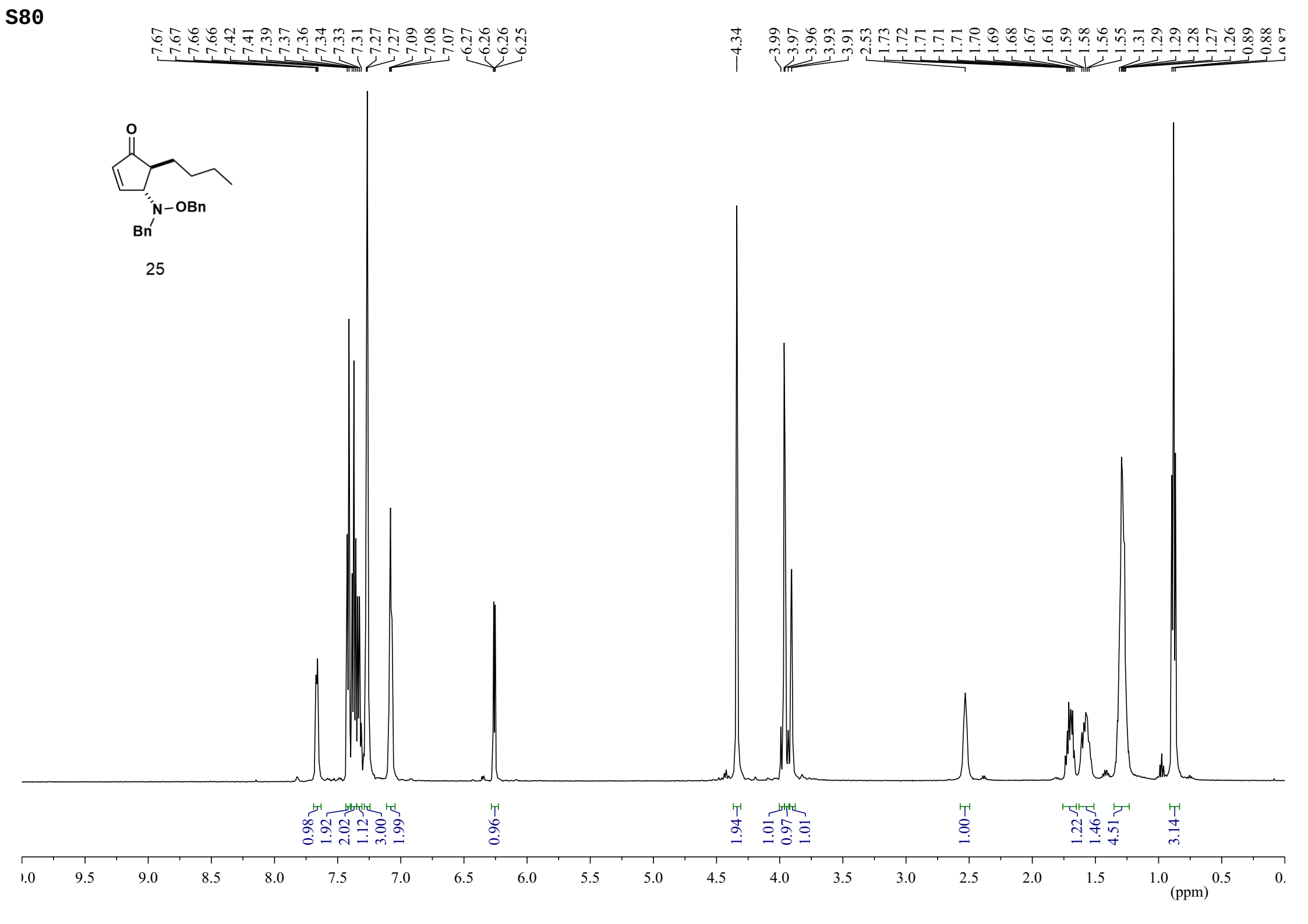
(ppm)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7.66
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7.39
7.37
7.36
7.34
7.33
7.31
7.27
7.27
7.09
7.08
7.07
6.27
6.26
6.26
6.25
4.34
3.99
3.97
3.96
3.93
3.91
2.53
1.73
1.72
1.71
1.71
1.71
1.70
1.69
1.68
1.67
1.61
1.59
1.58
1.56
1.55
1.31
1.29
1.29
1.28
1.27
1.26
0.89
0.88
O
N–OBn
Bn
25
0.98
1.92
2.02
1.12
3.00
1.99
0.96
1.94
1.01
0.97
1.01
1.00
1.22
1.46
4.51
3.14
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
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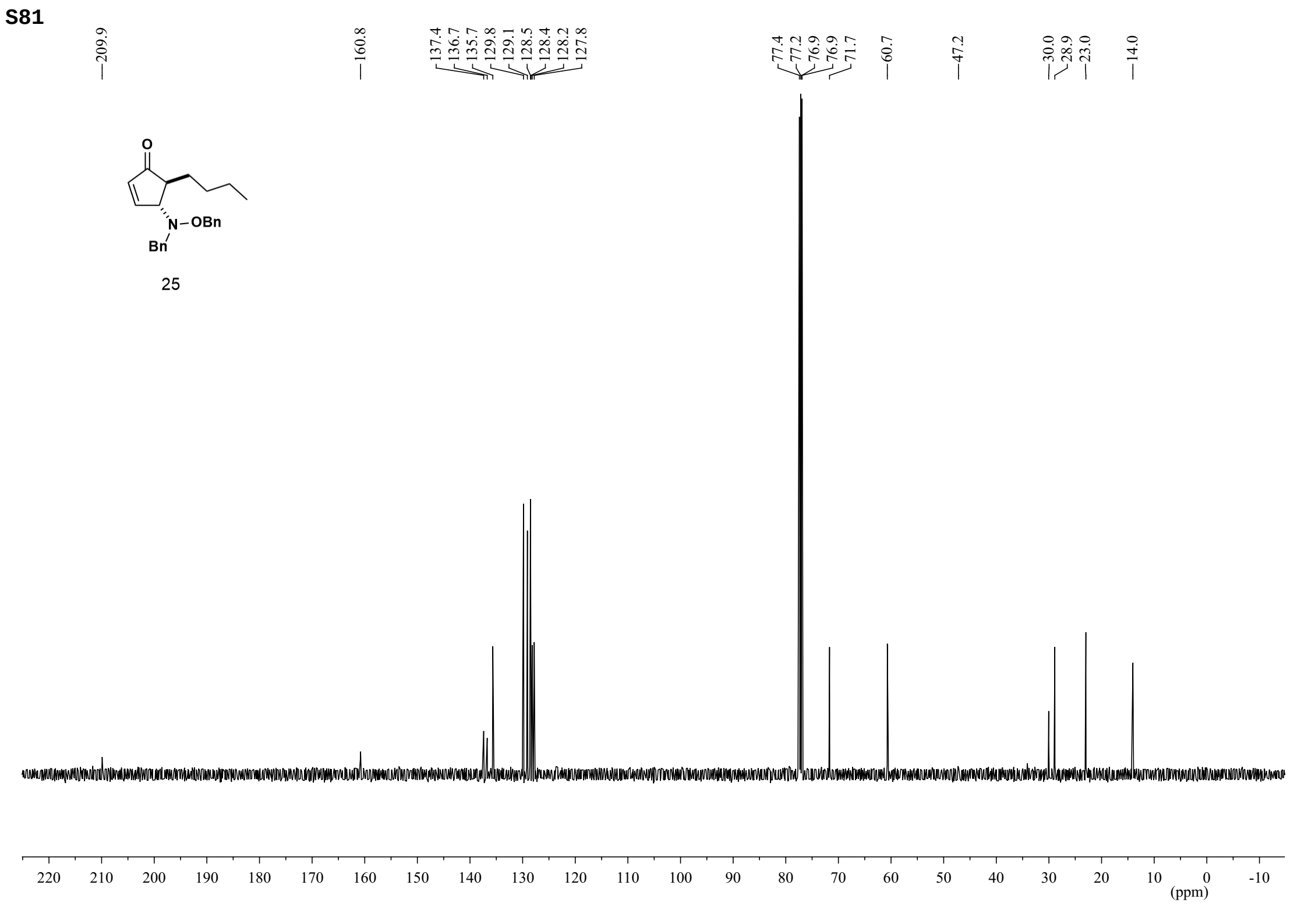
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
(ppm)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160.8
137.4
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129.1
128.5
128.4
128.2
127.8
77.4
77.2
76.9
76.9
71.7
60.7
47.2
30.0
28.9
23.0
14.0
O
N–OBn
Bn
25
220
210
200
190
180
170
160
150
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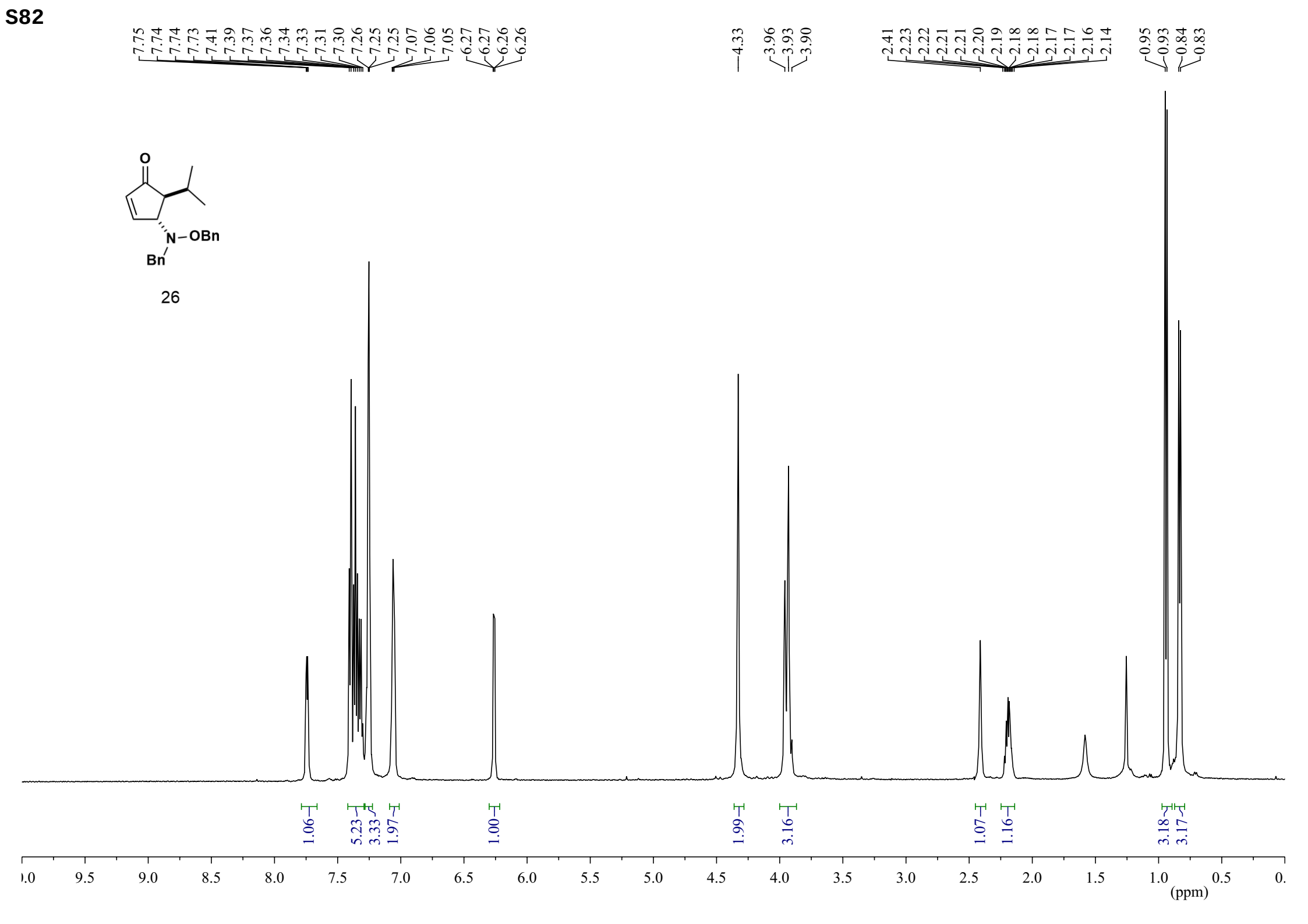
130
120
110
100
90
80
70
60
50
40
30
20
10
0
-10
(ppm)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7.74
7.74
7.73
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7.36
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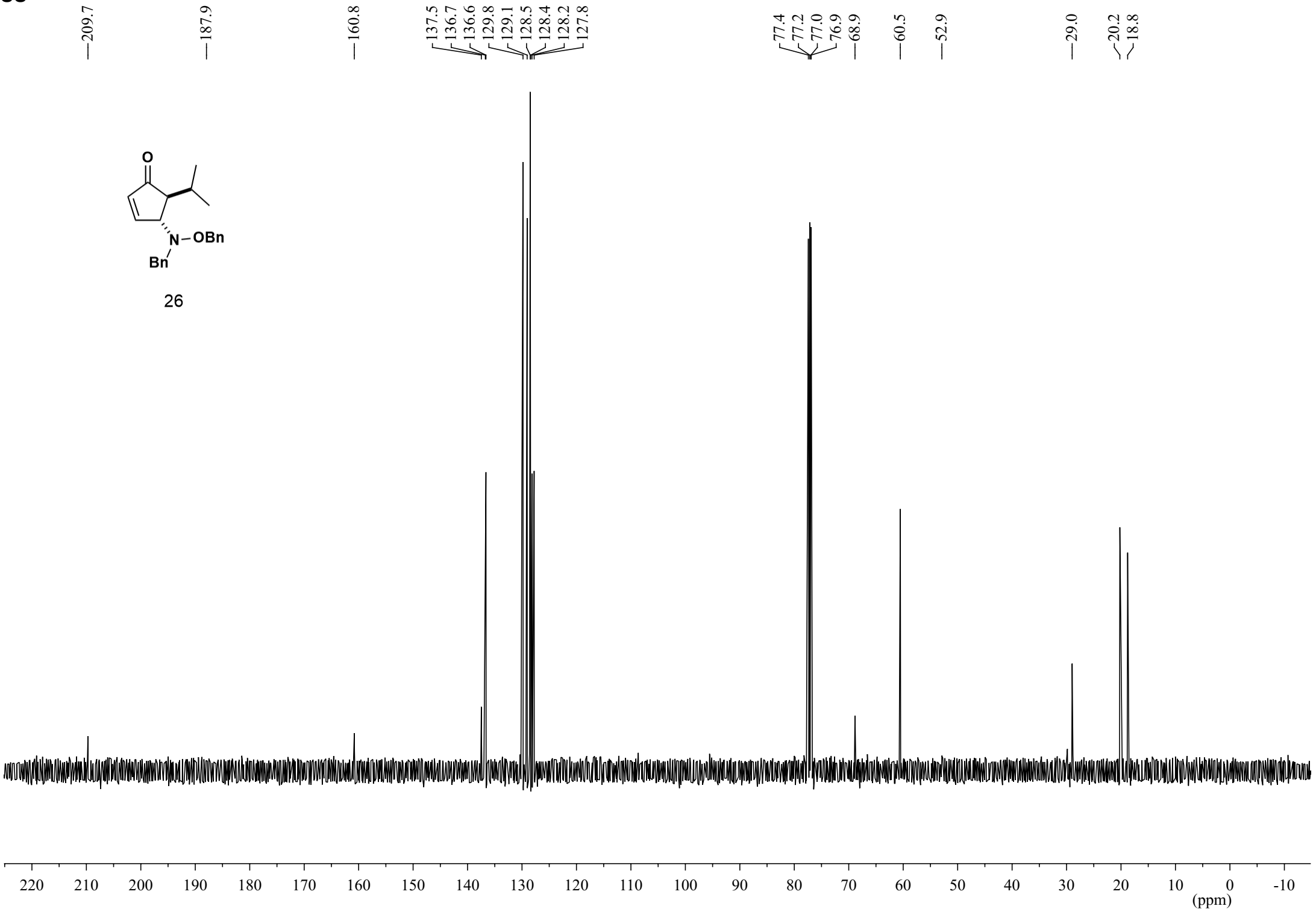
7.33
7.31
7.30
7.26
7.25
7.25
7.07
7.06
7.05
6.27
6.27
6.26
6.26
4.33
3.96
3.93
3.90
2.41
2.23
2.22
2.21
2.21
2.20
2.19
2.18
2.18
2.17
2.17
2.16
2.14
0.95
0.93
0.84
0.83
O
N–OBn
Bn
26
1.06
5.23
3.33
1.97
1.00
1.99
3.16
1.07
1.16
3.18
3.17
(ppm)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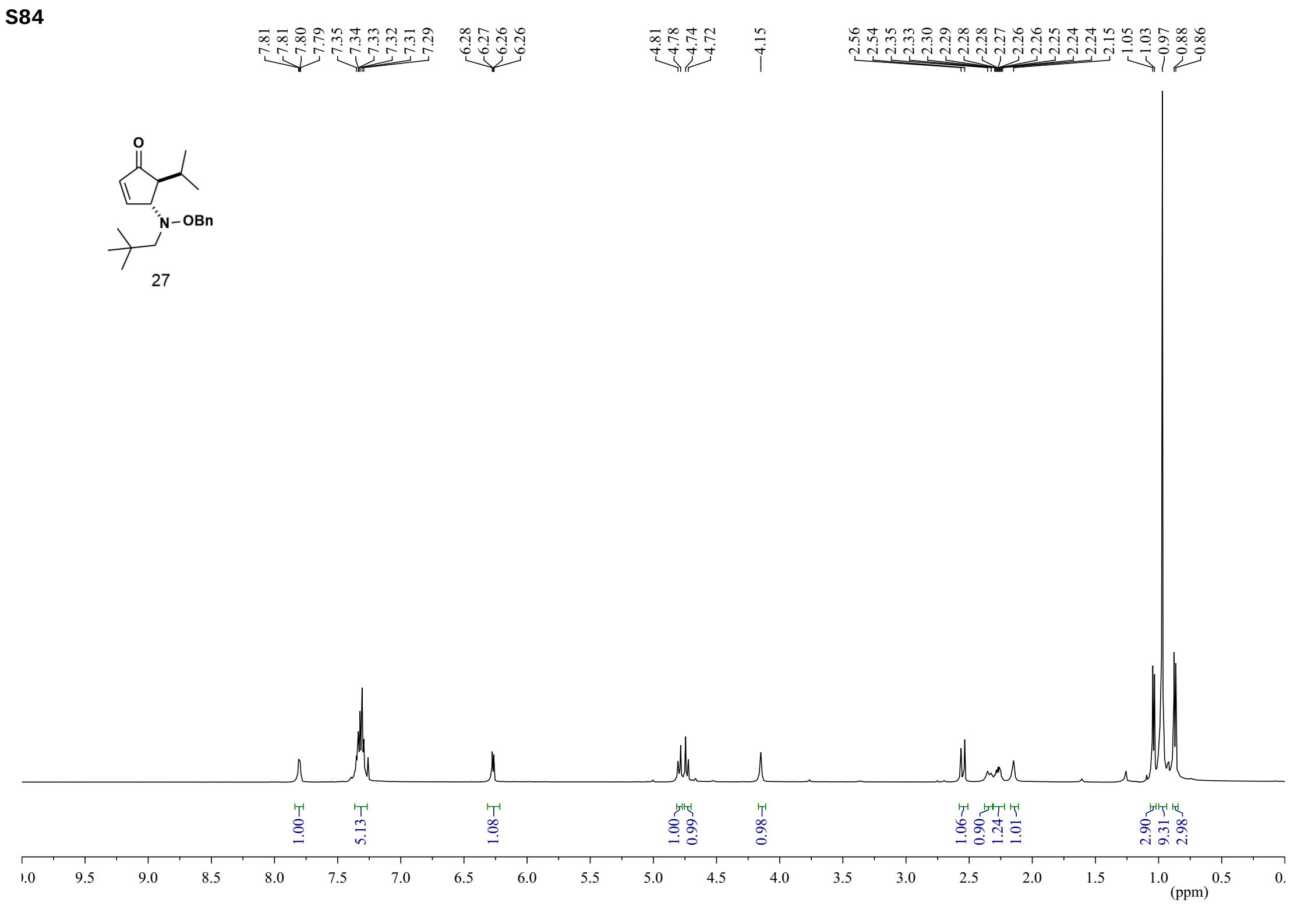
136.7
136.6
129.8
129.1
128.5
128.4
128.2
127.8
77.4
77.2
77.0
76.9
68.9
60.5
52.9
29.0
20.2
18.8
O
N–OBn
Bn
26
220
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
-10
(ppm)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7.81
7.80
7.79
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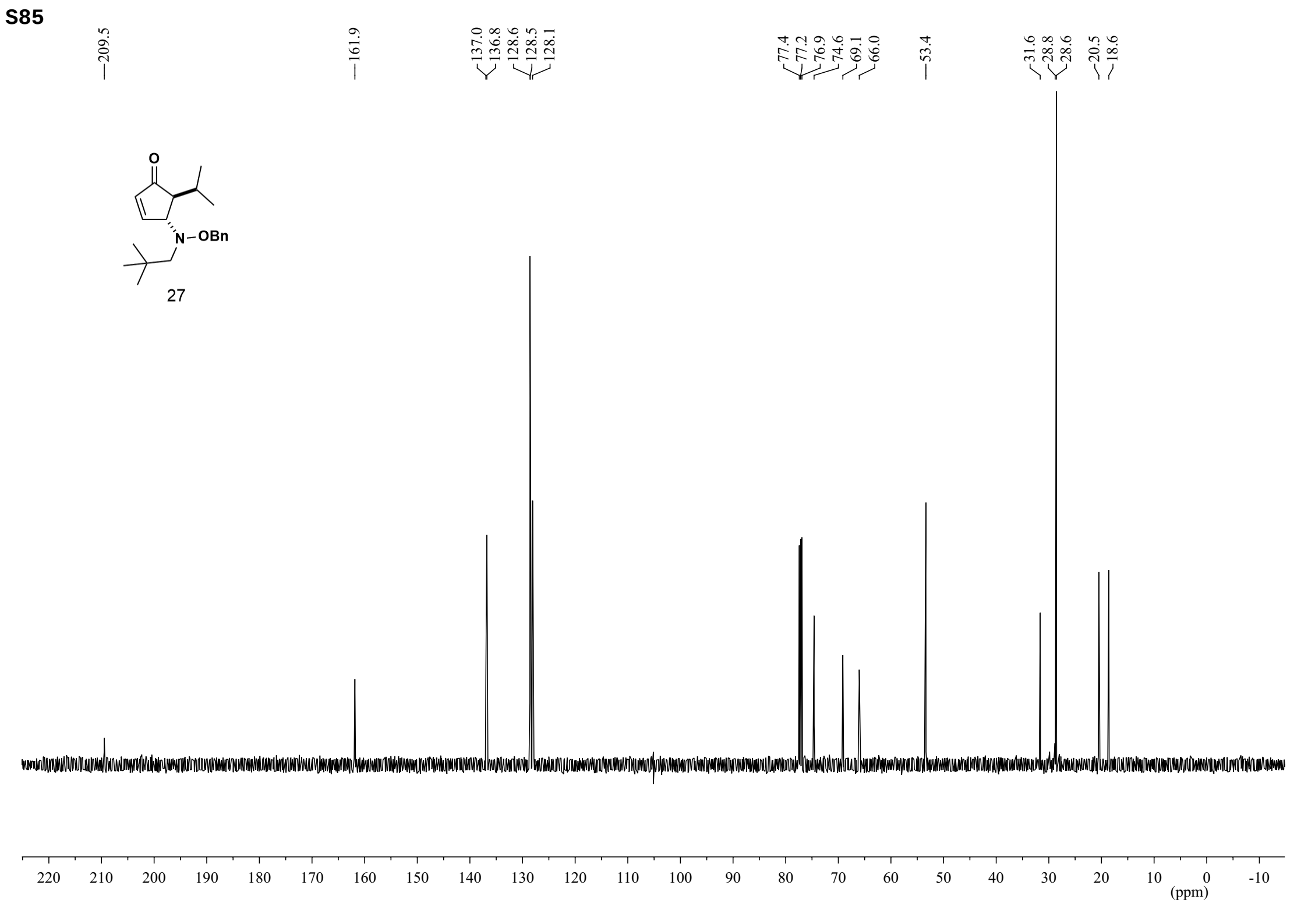
7.34
7.33
7.32
7.31
7.29
6.28
6.27
6.26
6.26
4.81
4.78
4.74
4.72
4.15
2.56
2.54
2.35
2.33
2.30
2.29
2.28
2.28
2.27
2.26
2.26
2.25
2.24
2.24
2.15
1.05
1.03
0.97
0.88
0.86
O
N–OBn
27
1.00
5.13
1.08
1.00
0.99
0.98
1.06
0.90
1.24
1.01
2.90
9.31
2.98
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
(ppm)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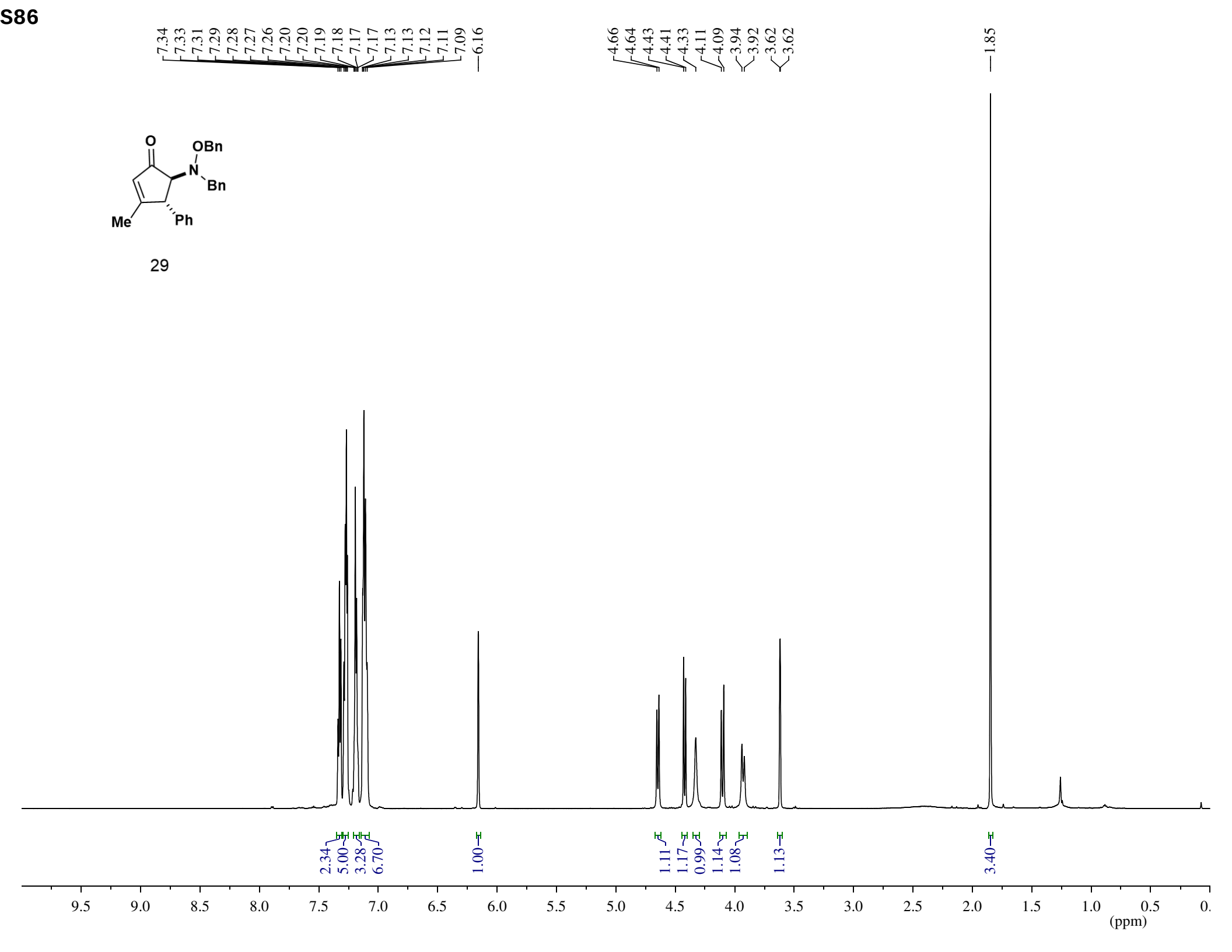
136.8
128.6
128.5
128.1
77.4
77.2
76.9
74.6
69.1
66.0
53.4
31.6
28.8
28.6
20.5
18.6
O
N–OBn
27
220
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
-10
(ppm)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7.29
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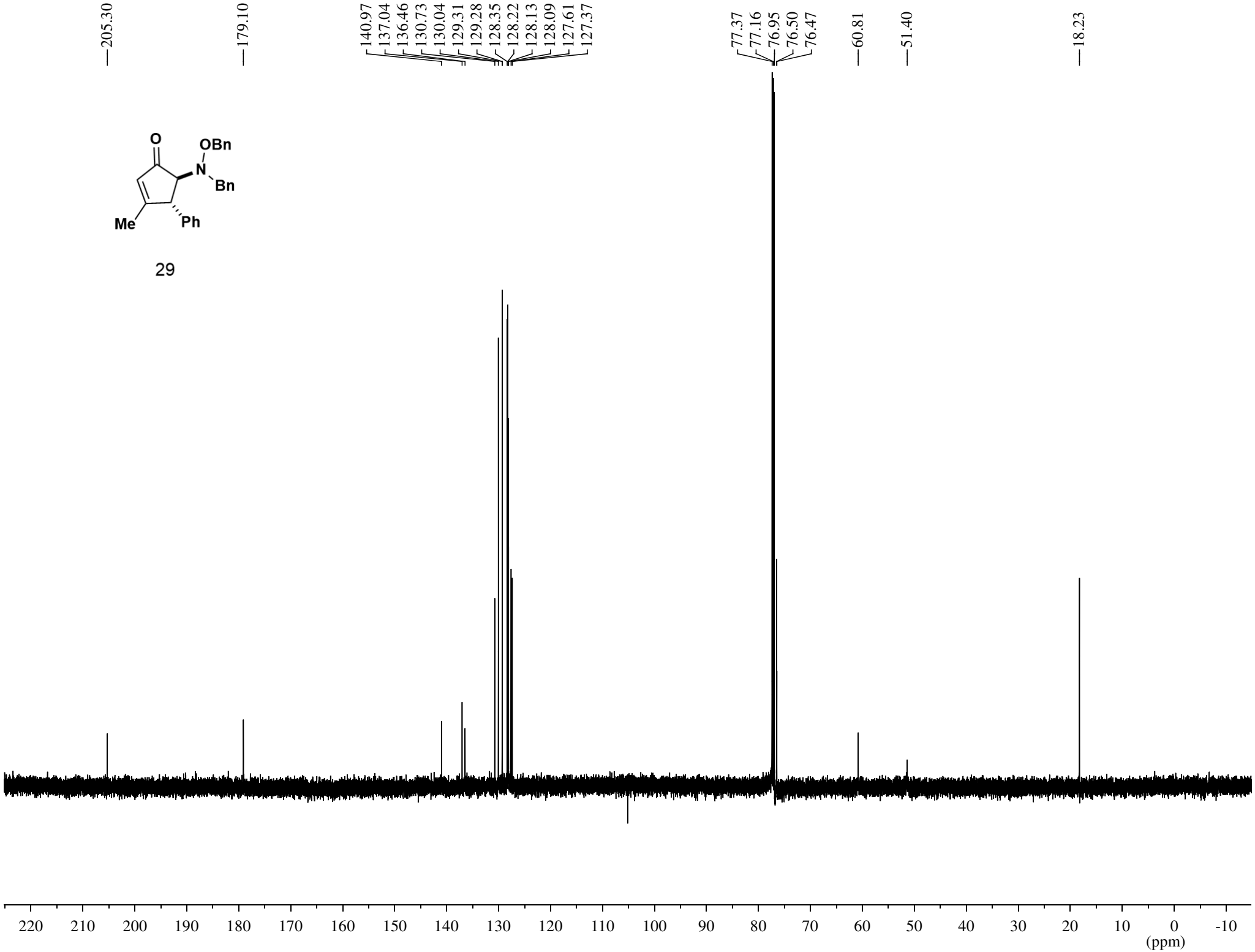
7.27
7.26
7.20
7.20
7.19
7.18
7.17
7.17
7.13
7.13
7.12
7.11
7.09
6.16
4.66
4.64
4.43
4.41
4.33
4.11
4.09
3.94
3.92
3.62
3.62
1.85
O
OBn
N
Bn
Me
Ph
29
2.34
5.00
3.28
6.70
1.00
1.11
1.17
0.99
1.14
1.08
1.13
3.40
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
(ppm)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130.73
130.04
129.31
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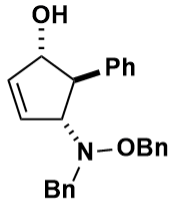
128.22
128.13
128.09
127.61
127.37
77.37
77.16
76.95
76.50
76.47
60.81
51.40
18.23
O
OBn
N
Bn
Me
Ph
29
220
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
-10
(ppm)


OH
Ph
N–OBn
Bn

30

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7.32
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7.23
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7.18
7.17
7.16
7.14
7.13
7.12
6.22
6.21
6.21
6.21
6.17
6.17
6.17
6.16
4.48
4.44
4.42
4.30
4.28
4.07
4.04
3.96
3.96
3.95
3.95
3.86
3.84
3.44
2.49
10.25
1.02
2.14
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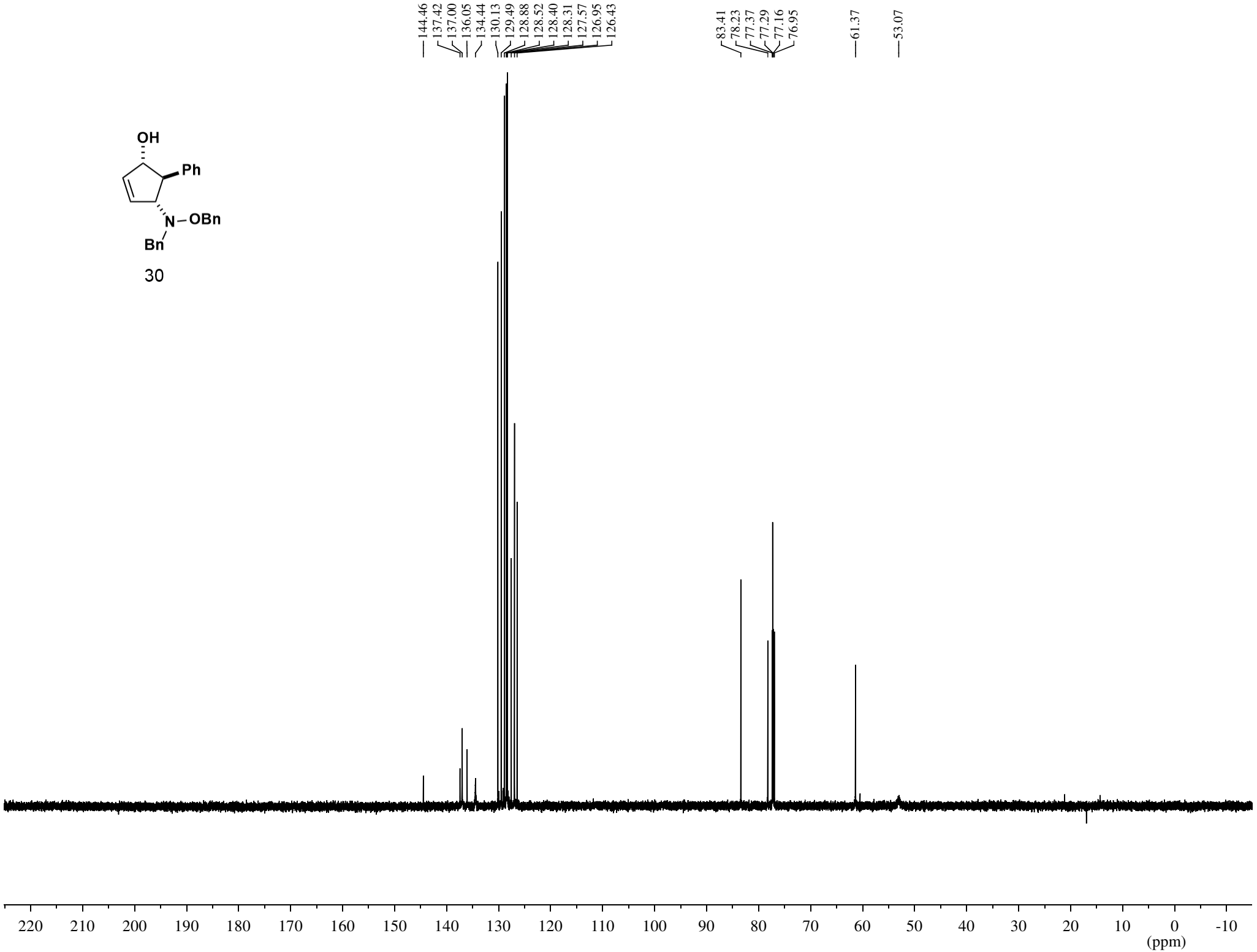
1.00
1.01
1.01
1.05
0.99
1.03
1.05
1.05
1.03
0.92
(ppm)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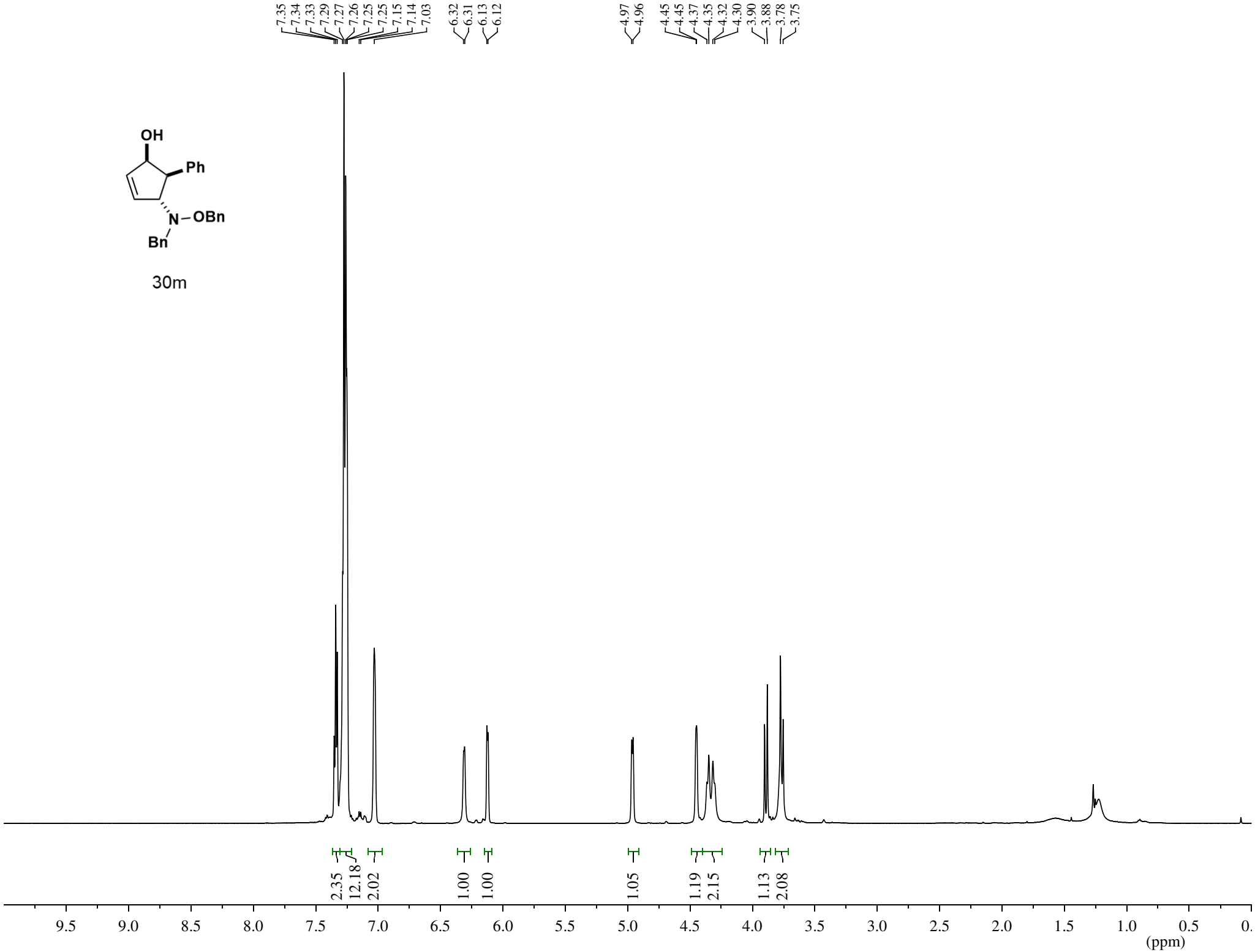
128.40
128.31
127.57
126.95
126.43
83.41
78.23
77.37
77.29
77.16
76.95
61.37
53.07
OH
Ph
N–OBn
Bn
30
220
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
-10
(ppm)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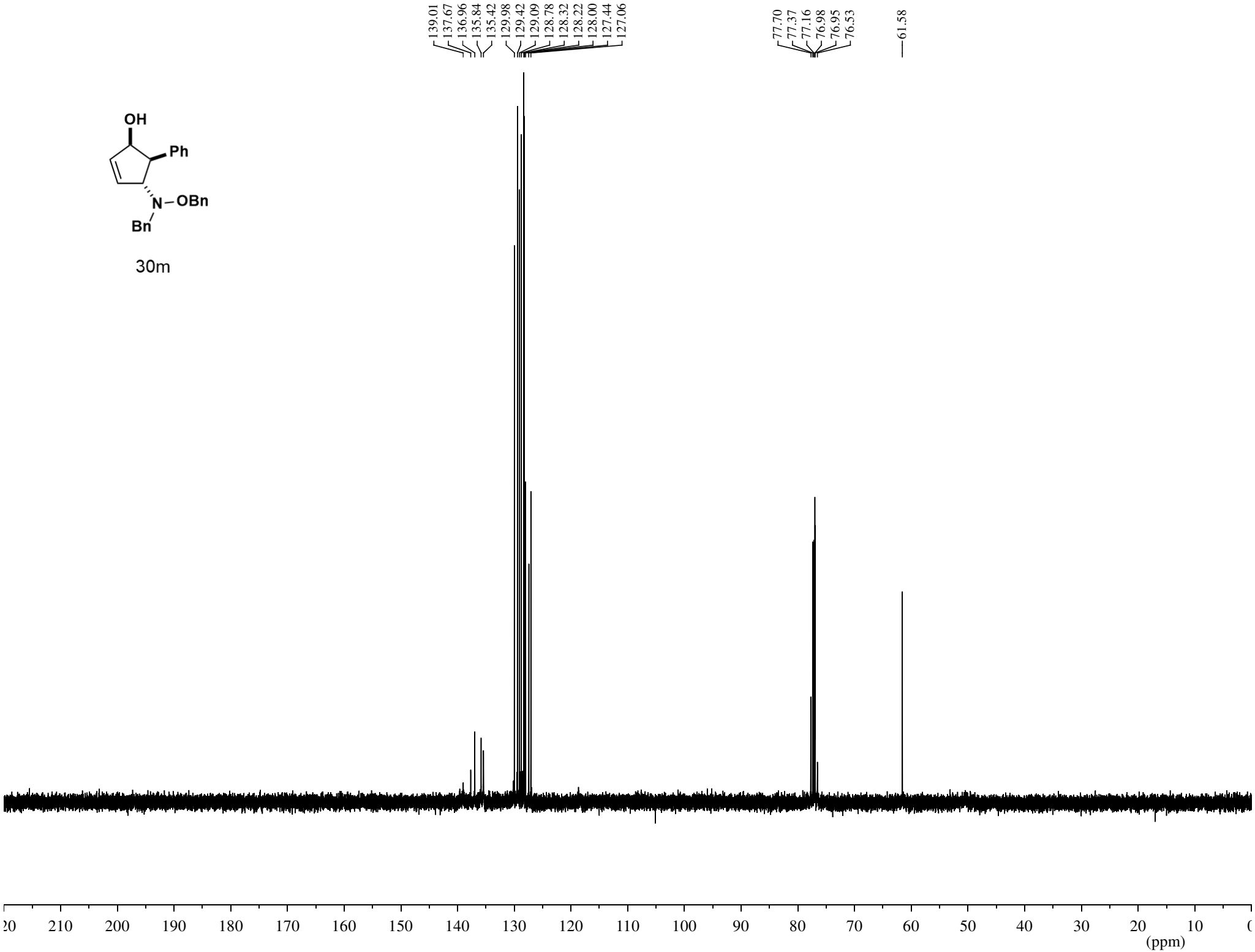
7.25
7.15
7.14
7.03
6.32
6.31
6.13
6.12
4.97
4.96
4.45
4.45
4.37
4.35
4.32
4.30
3.90
3.88
3.78
3.75
OH
Ph
N–OBn
Bn
30m
2.35
12.18
2.02
1.00
1.00
1.05
1.19
2.15
1.13
2.08
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
(ppm)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137.67
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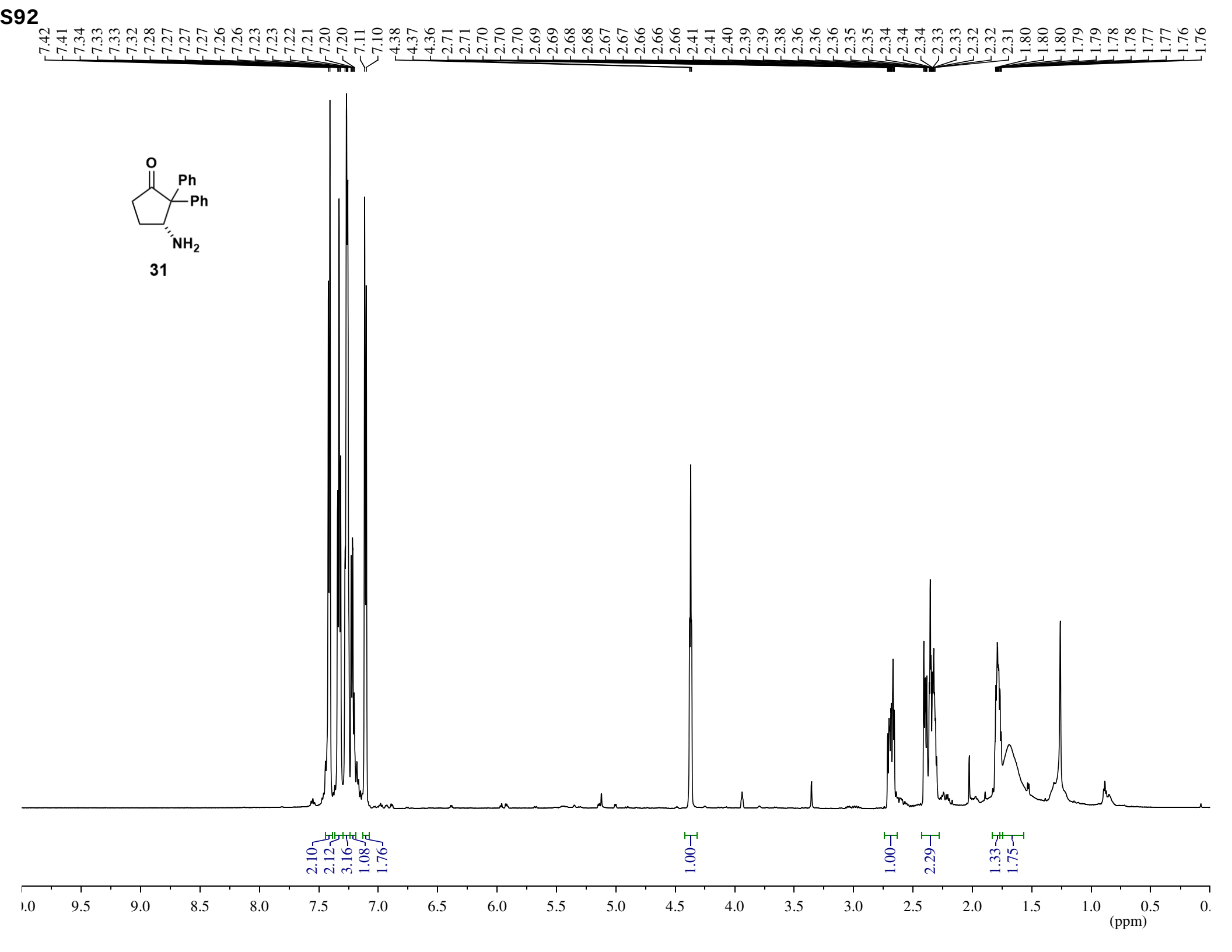
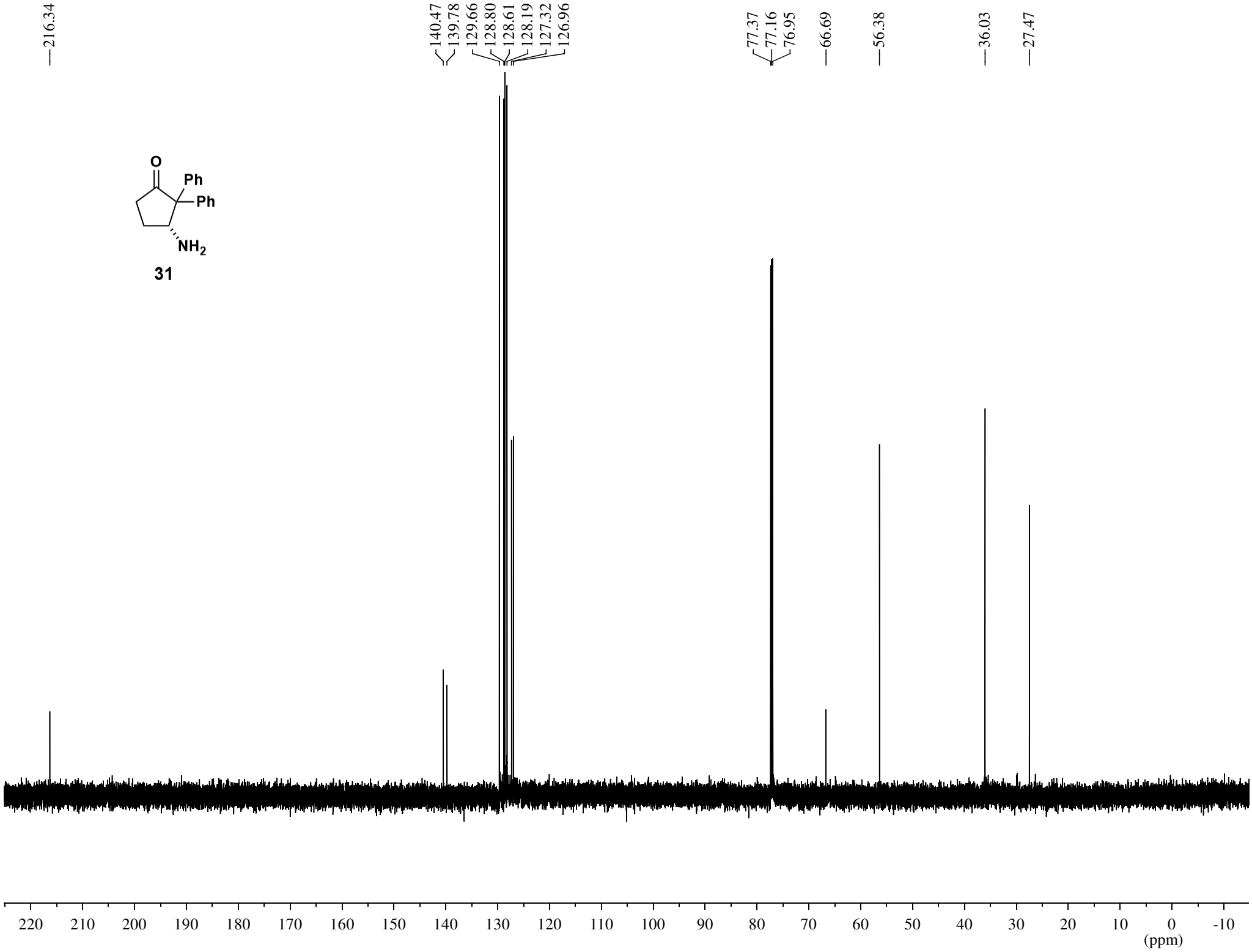
135.84
135.42
129.98
129.42
129.09
128.78
128.32
128.22
128.00
127.44
127.06
77.70
77.37
77.16
76.98
76.95
76.53
61.58
OH
Ph
N–OBn
Bn
30m
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
(ppm)


7.42 7.41 7.34 7.33 7.33 7.32 7.28 7.27 7.27 7.27 7.26 7.26 7.23 7.23 7.22 7.21 7.20 7.20 7.11 7.10
4.38 4.37 4.36 2.71 2.71 2.70 2.70 2.70 2.69 2.69 2.68 2.68 2.67 2.67 2.66 2.66 2.66 2.41 2.41 2.40 2.39 2.39 2.38 2.36 2.36 2.36 2.35 2.35 2.34 2.34 2.34 2.33 2.33 2.32 2.32 2.31 1.80 1.80 1.80 1.79 1.79 1.78 1.78 1.77 1.77 1.76 1.76
O
Ph
Ph
NH2
31
2.10
2.12
3.16
1.08
1.76
1.00
1.00
2.29
1.33
1.75
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
(ppm)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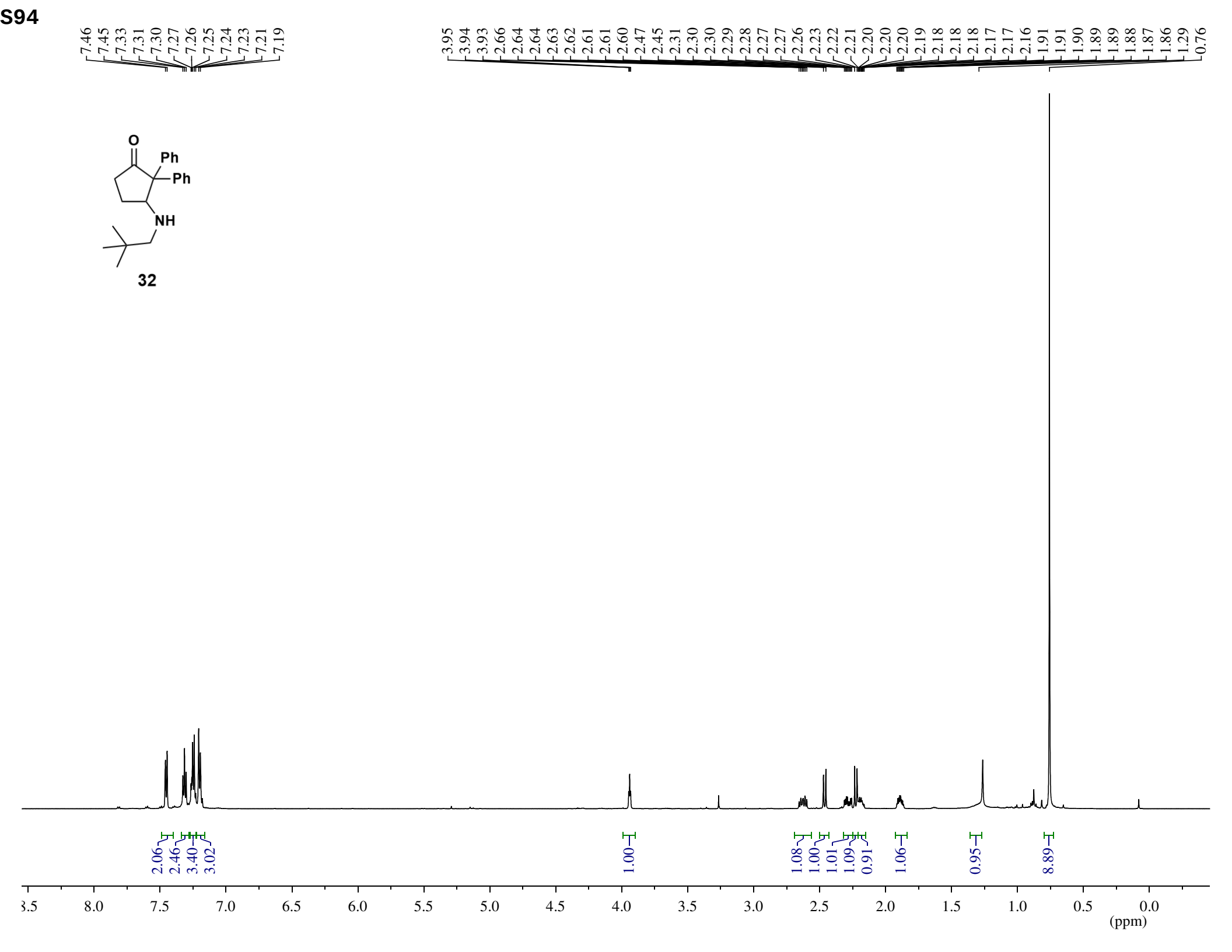
128.61
128.19
127.32
126.96
77.37
77.16
76.95
66.69
56.38
36.03
27.47
O
Ph
Ph
NH2
31
220
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
-10
(ppm)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7.27
7.26
7.25
7.24
7.23
7.21
7.19
3.95
3.94
3.93
2.66
2.64
2.64
2.63
2.62
2.61
2.61
2.60
2.47
2.45
2.31
2.30
2.30
2.29
2.28
2.27
2.27
2.26
2.23
2.22
2.21
2.20
2.20
2.20
2.19
2.18
2.18
2.18
2.17
2.17
2.16
1.91
1.91
1.90
1.89
1.89
1.88
1.87
1.86
1.29
0.76
O
Ph
Ph
NH
32
2.06
2.46
3.40
3.02
1.00
1.08
1.00
1.01
1.09
0.91
1.06
0.95
8.89
8.0
7.5
7.0
6.5
6.0
5.5
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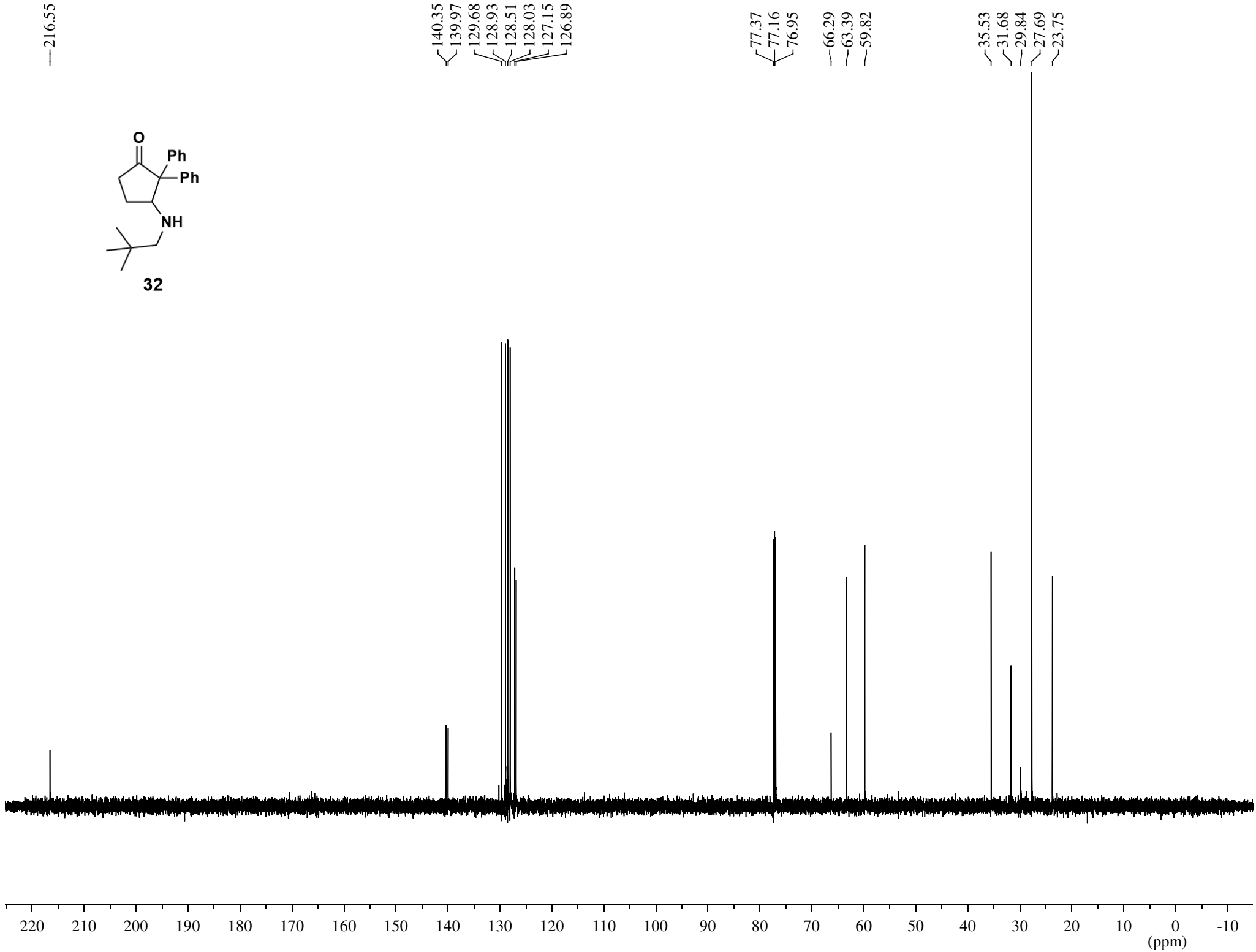
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
(ppm)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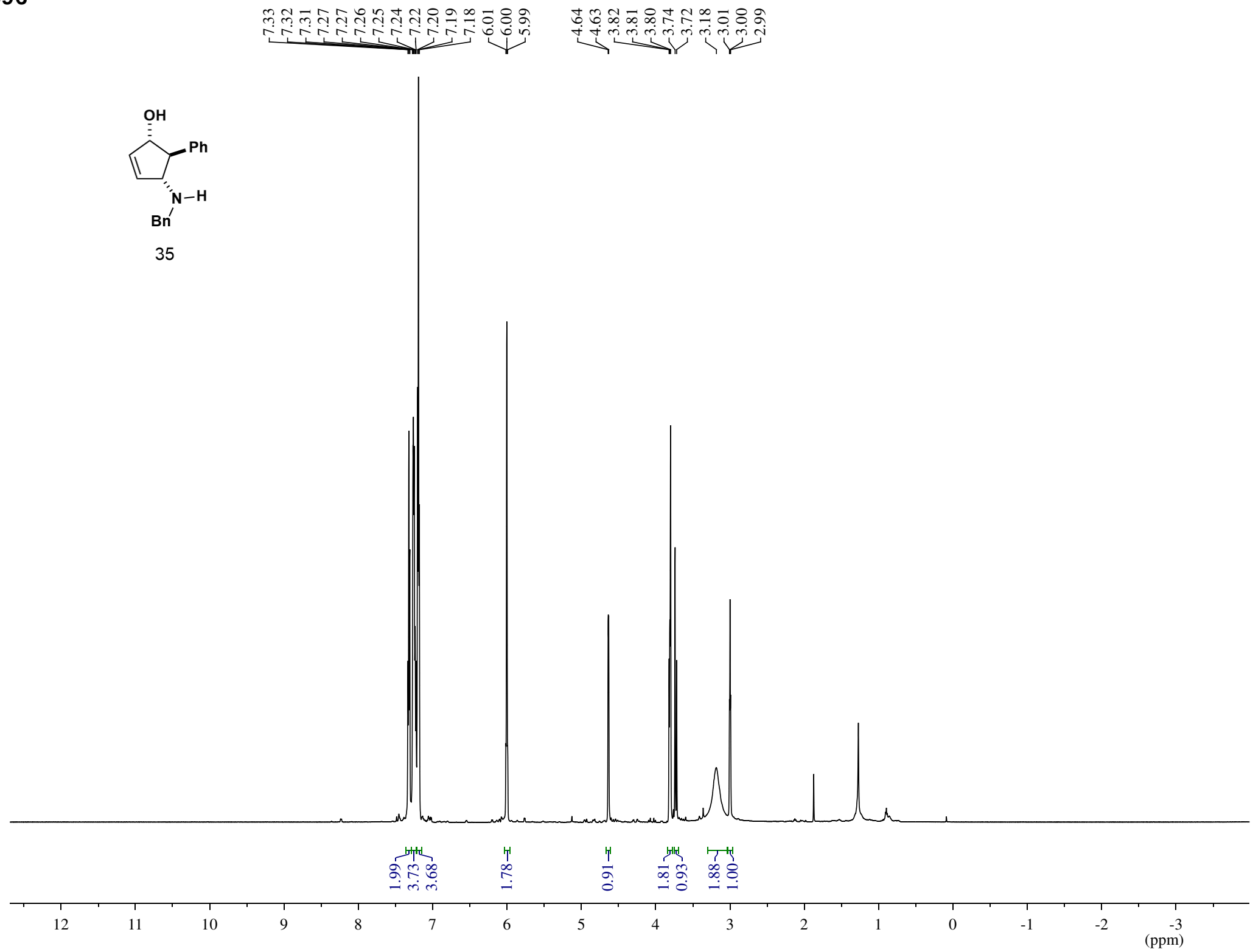
128.51
128.03
127.15
126.89
77.37
77.16
76.95
66.29
63.39
59.82
35.53
31.68
29.84
27.69
23.75
O
Ph
Ph
NH
32
220
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
-10
(ppm)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7.32
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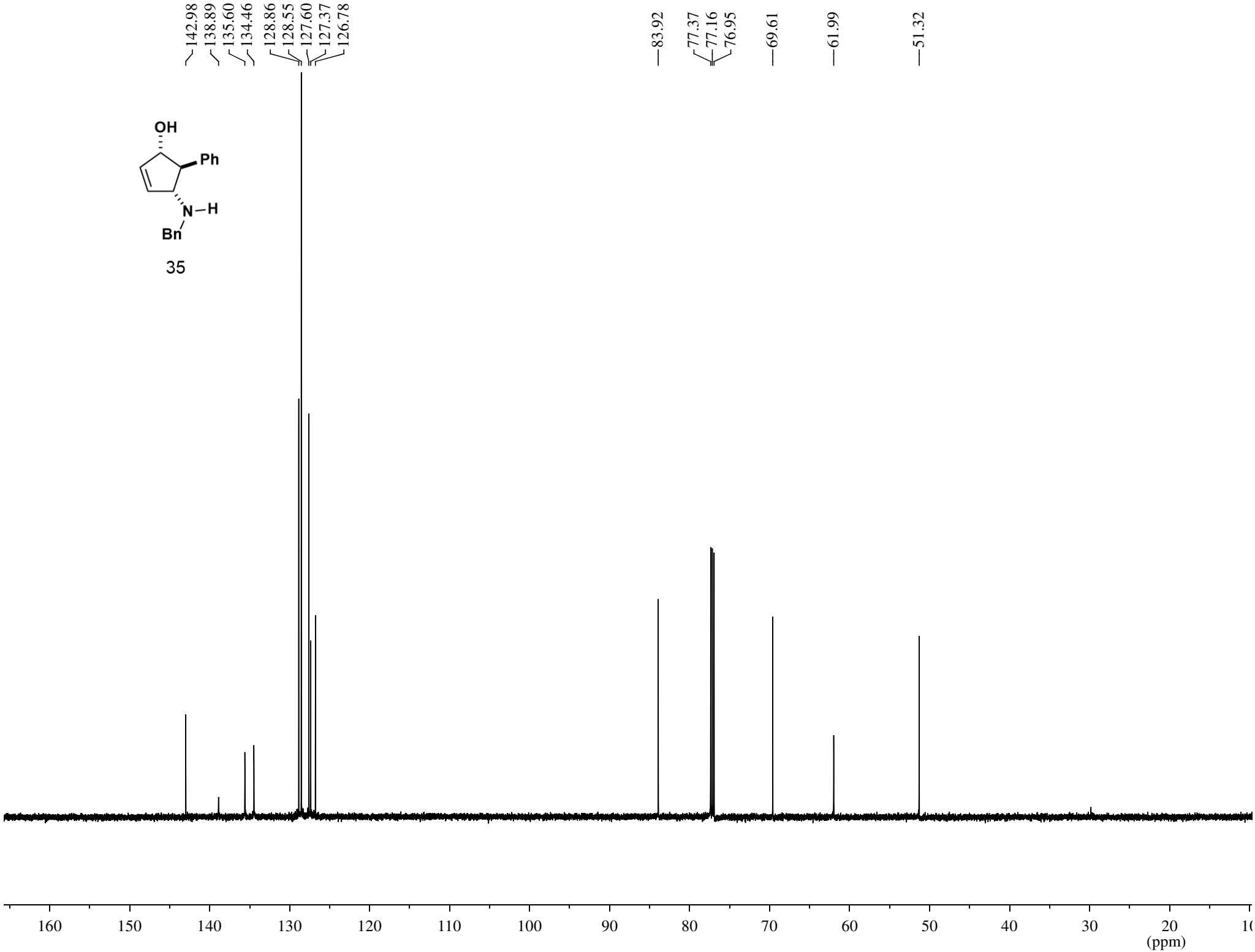
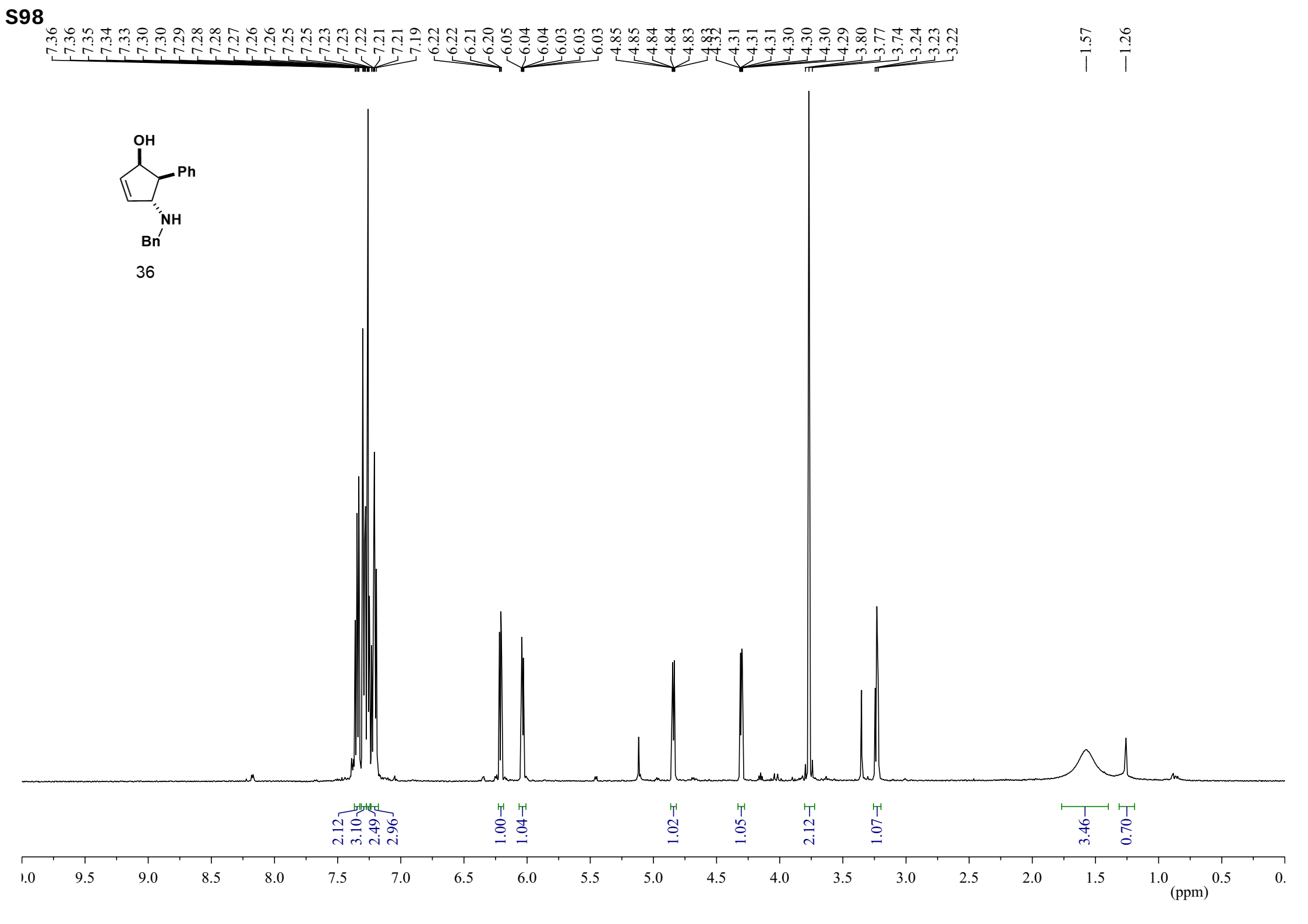
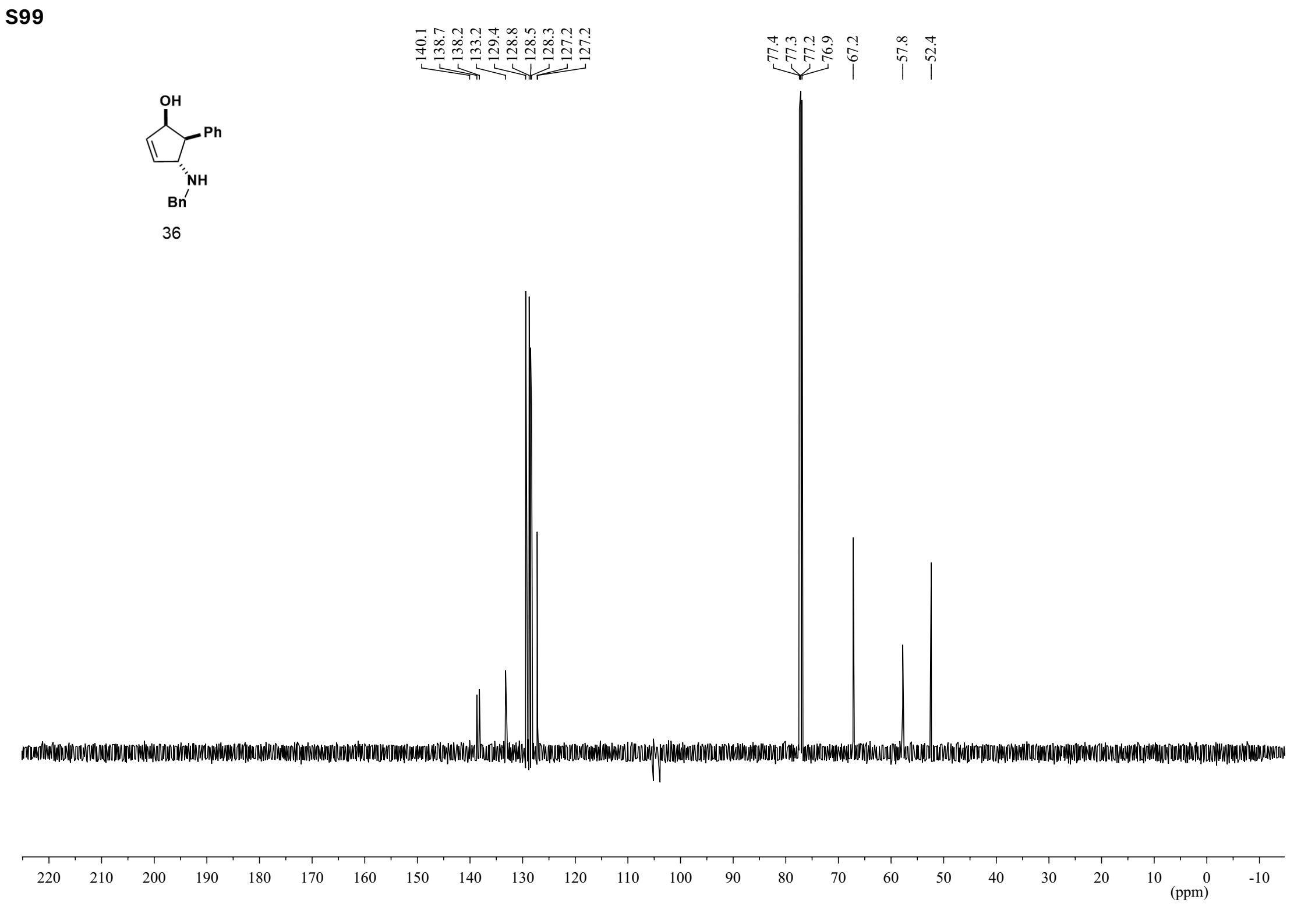
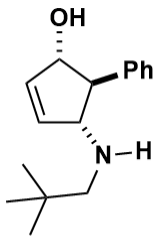
7.26
7.25
7.24
7.22
7.20
7.19
7.18
6.01
6.00
5.99
4.64
4.63
3.82
3.81
3.80
3.74
3.72
3.18
3.01
3.00
2.99
OH
Ph
N–H
Bn
35
1.99
3.73
3.68
1.78
0.91
1.81
0.93
1.88
1.00
12
11
10
9
8
7
6
5
4
3
2
1
0
-1
-2
-3
(ppm)


142.98
138.89
135.60
134.46
128.86
128.55
127.60
127.37
126.78
83.92
77.37
77.16
76.95
69.61
61.99
51.32
OH
Ph
N–H
Bn
35
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
(ppm)


7.36
7.36
7.35
7.34
7.33
7.30
7.30
7.29
7.28
7.28
7.27
7.26
7.26
7.25
7.25
7.23
7.23
7.22
7.21
7.21
7.19
6.22
6.22
6.21
6.20
6.05
6.04
6.04
6.03
6.03
6.03
4.85
4.85
4.84
4.84
4.83
4.83
4.32
4.31
4.31
4.31
4.30
4.30
4.30
4.29
3.80
3.77
3.74
3.24
3.23
3.22
1.57
1.26
OH
Ph
NH
Bn
36
2.12
3.10
2.49
2.96
1.00
1.04
1.02
1.05
2.12
1.07
3.46
0.70
(ppm)


140.1
138.7
138.2
133.2
129.4
128.8
128.5
128.3
127.2
127.2
77.4
77.3
77.2
76.9
67.2
57.8
52.4
OH
Ph
NH
Bn
36
220
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
-10
(ppm)

S100



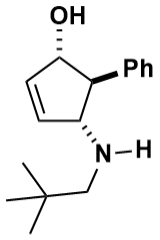
37

7.33 7.32 7.31 7.26 7.25 7.23 7.22 6.09 6.08 6.02 6.01 4.68 3.77 3.77 2.97 2.97 2.96 2.39 1.28 1.25 0.89

2.06 2.89 1.01 1.00 1.06 1.03 1.01 2.17 0.83 2.00 9.39

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.

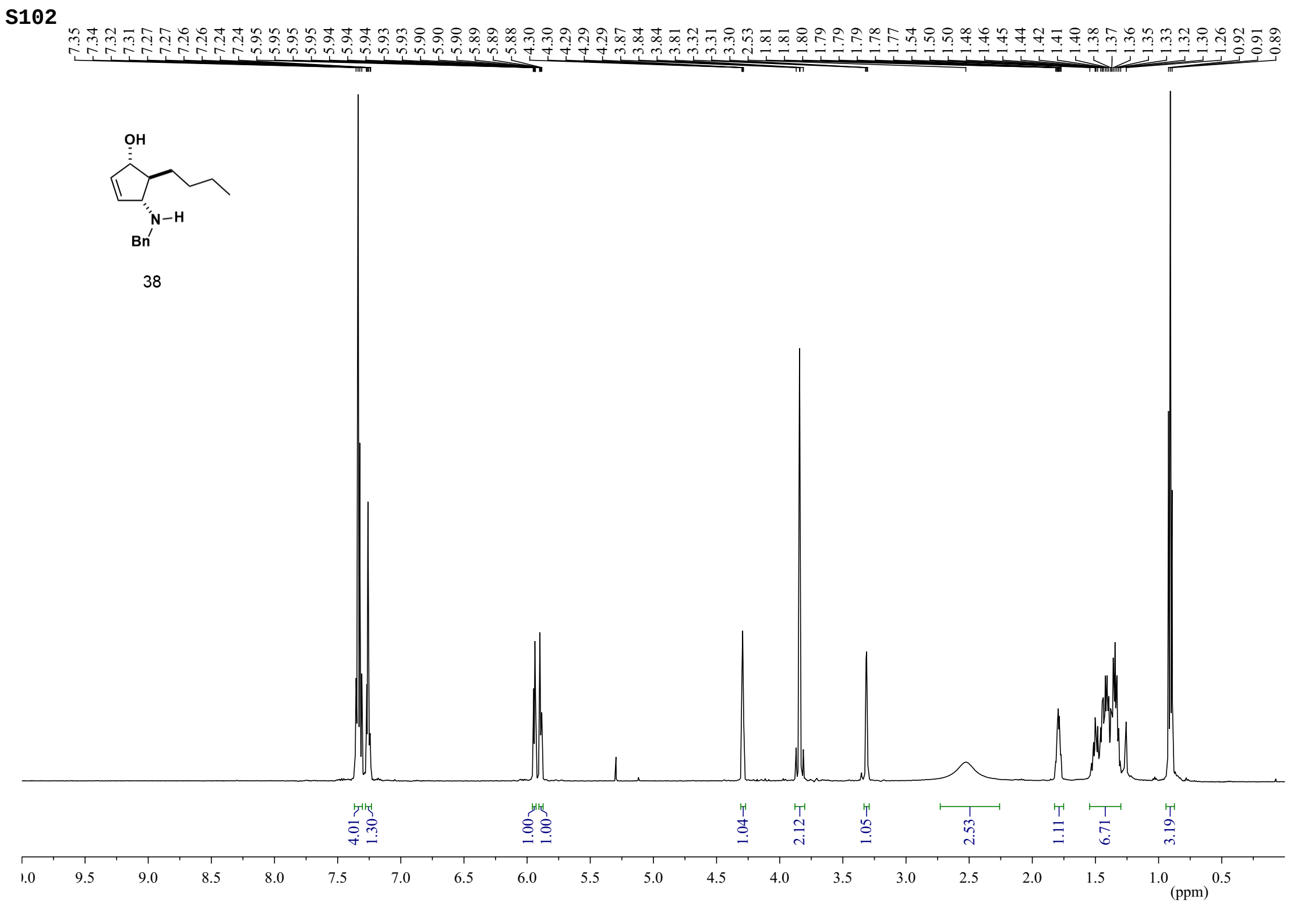
(ppm)

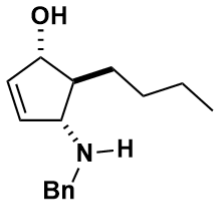

OH
Ph
N–H

37

143.0
136.7
133.9
129.0
127.4
126.9
84.1
77.4
77.2
76.9
71.4
59.2
31.4
29.9
27.9
220
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
-10
(ppm)

S102

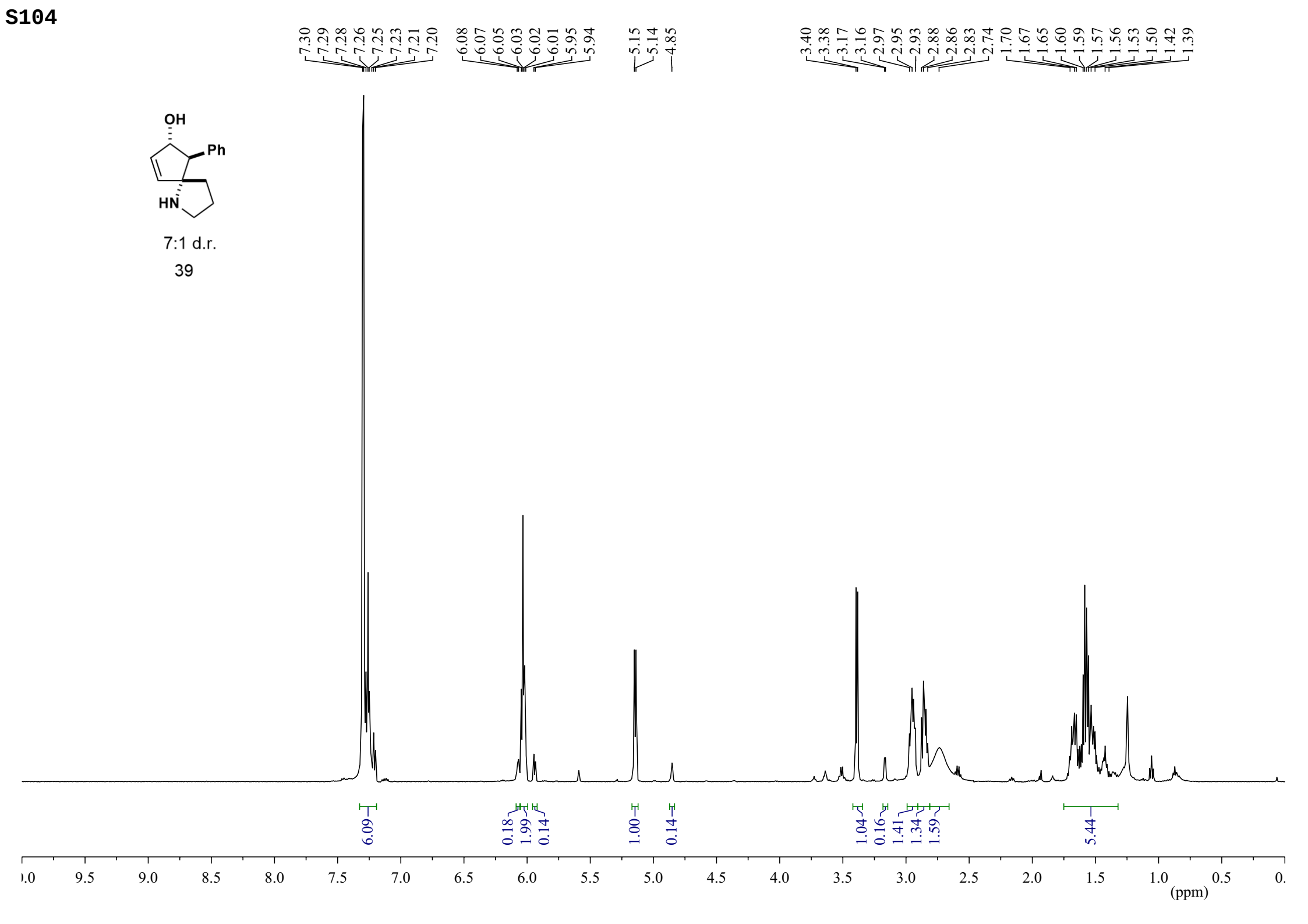

7.35 7.34 7.32 7.31 7.27 7.27 7.26 7.26 7.24 7.24 5.95 5.95 5.95 5.95 5.94 5.94 5.94 5.93 5.93 5.90 5.90 5.90 5.89 5.89 5.88 4.30 4.30 4.29 4.29 4.29 3.87 3.84 3.84 3.81 3.32 3.31 3.30 2.53 1.81 1.81 1.80 1.79 1.79 1.79 1.78 1.77 1.54 1.50 1.50 1.48 1.46 1.45 1.44 1.42 1.41 1.40 1.38 1.37 1.36 1.35 1.33 1.32 1.30 1.26 0.92 0.91 0.89
OH
N–H
Bn
38
4.01
1.30
1.00
1.00
1.04
2.12
1.05
2.53
1.11
6.71
3.19
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
(ppm)


OH
N–H
Bn

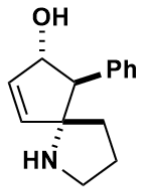
38

139.5
135.7
134.4
128.6
128.5
127.4
81.6
77.4
77.2
76.9
67.9
54.7
51.8
33.1
30.1
23.1
14.2
220
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
-10
(ppm)

S104


7.30
7.29
7.28
7.26
7.25
7.23
7.21
7.20
6.08
6.07
6.05
6.03
6.02
6.01
5.95
5.94
5.15
5.14
4.85
3.40
3.38
3.17
3.16
2.97
2.95
2.93
2.88
2.86
2.83
2.74
1.70
1.67
1.65
1.60
1.59
1.57
1.56
1.53
1.50
1.42
1.39
OH
Ph
HN
7:1 d.r.
39
6.09
0.18
1.99
0.14
1.00
0.14
1.04
0.16
1.41
1.34
1.59
5.44
(ppm)

S105

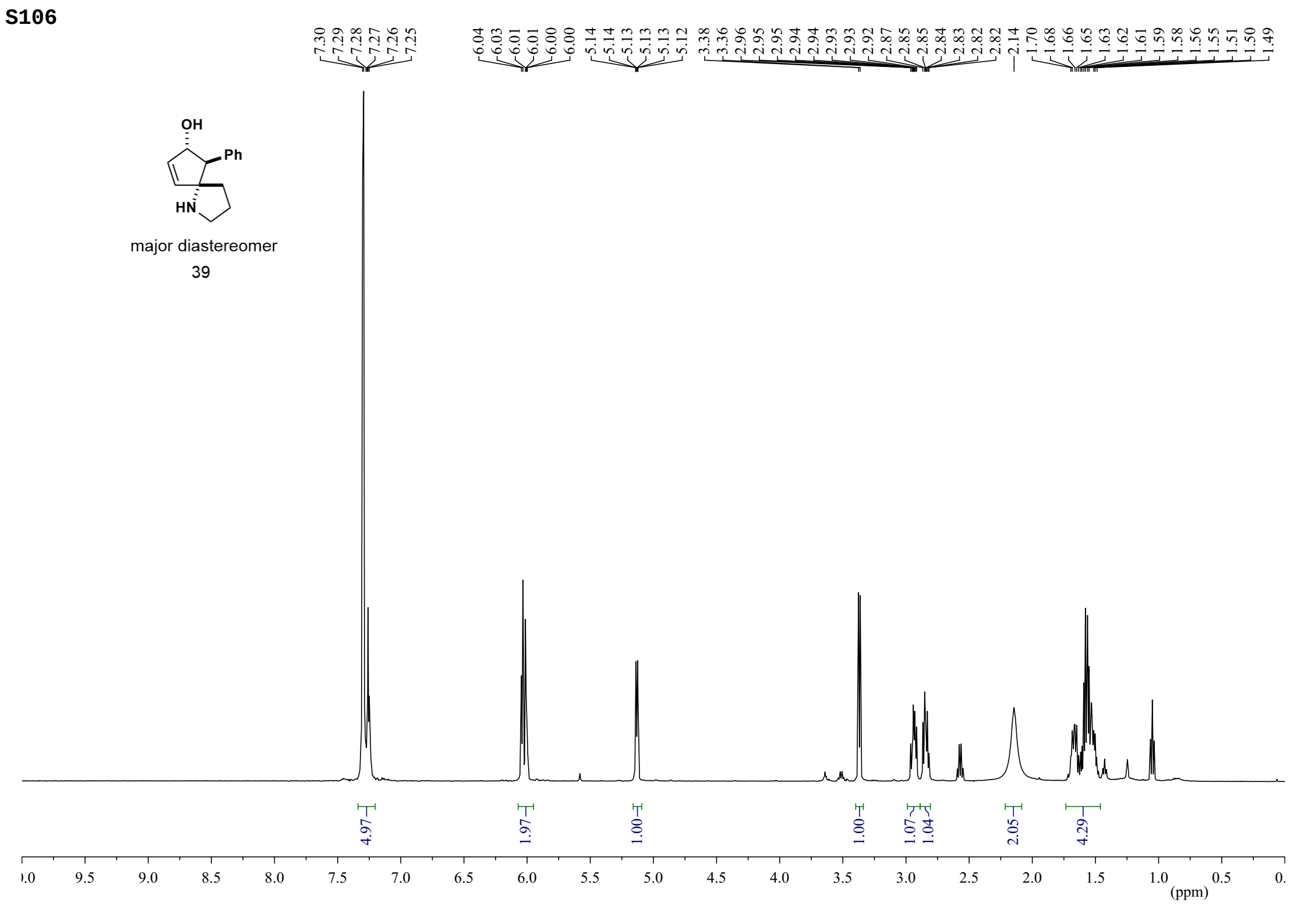

OH
Ph
HN

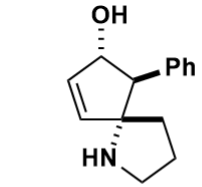
7:1 d.r.

39

140.4
140.3
139.0
138.0
134.8
134.5
130.7
128.8
128.4
128.4
127.1
126.9
81.3
77.6
77.4
77.2
76.9
76.7
76.4
64.2
60.8
45.6
45.1
34.7
32.7
25.6
25.0
220
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
-10
(ppm)

S106

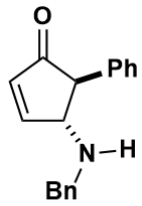

7.30
7.29
7.28
7.27
7.26
7.25
6.04
6.03
6.01
6.01
6.00
6.00
5.14
5.14
5.13
5.13
5.13
5.12
3.38
3.36
2.96
2.95
2.95
2.94
2.94
2.93
2.93
2.92
2.87
2.85
2.85
2.84
2.83
2.82
2.82
2.14
1.70
1.68
1.66
1.65
1.63
1.62
1.61
1.59
1.58
1.56
1.55
1.51
1.50
1.49
OH
Ph
HN
major diastereomer
39
4.97
1.97
1.00
1.00
1.07
1.04
2.05
4.29
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
(ppm)



major diastereomer

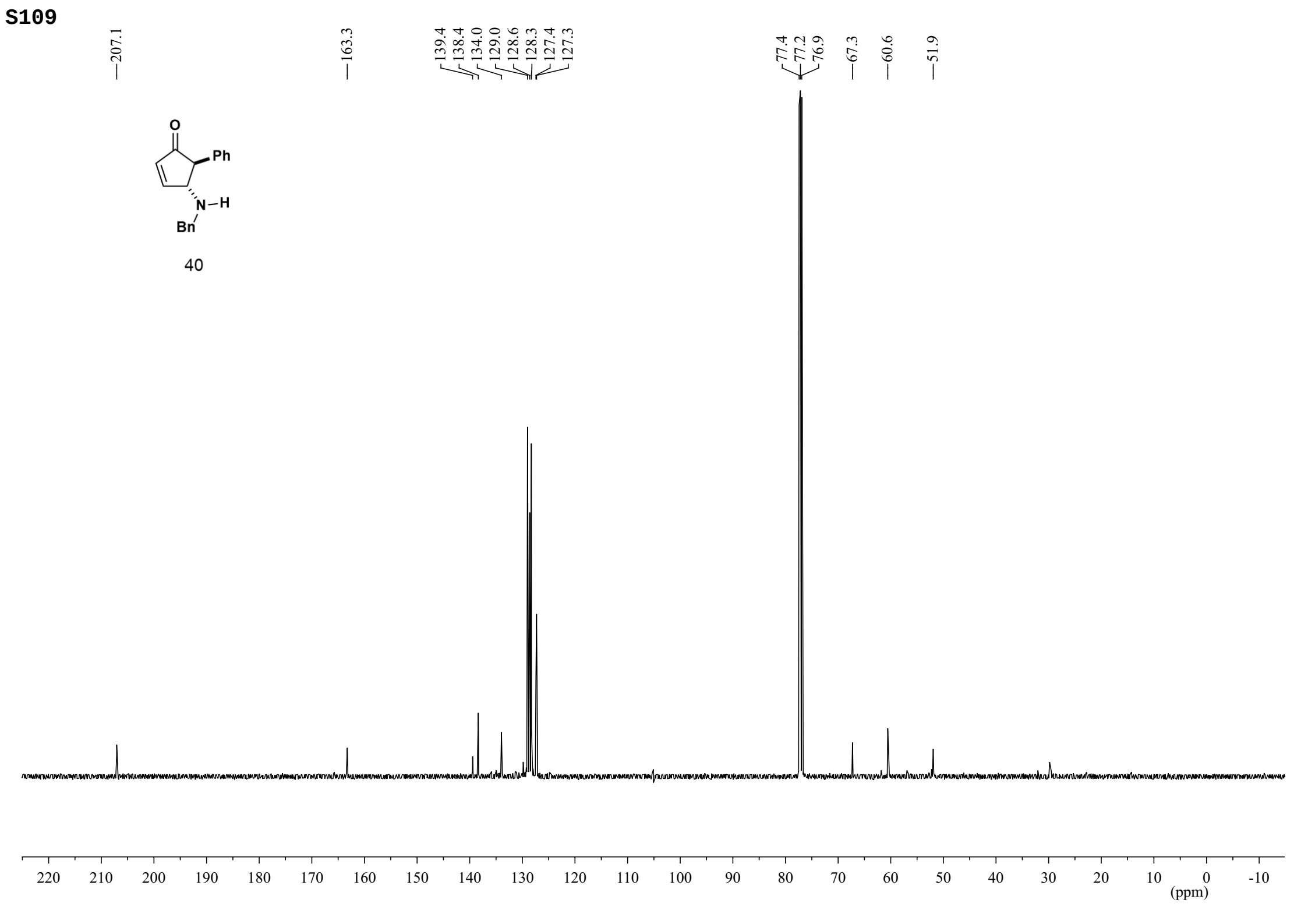
39

S108


O
Ph
N–H
Bn

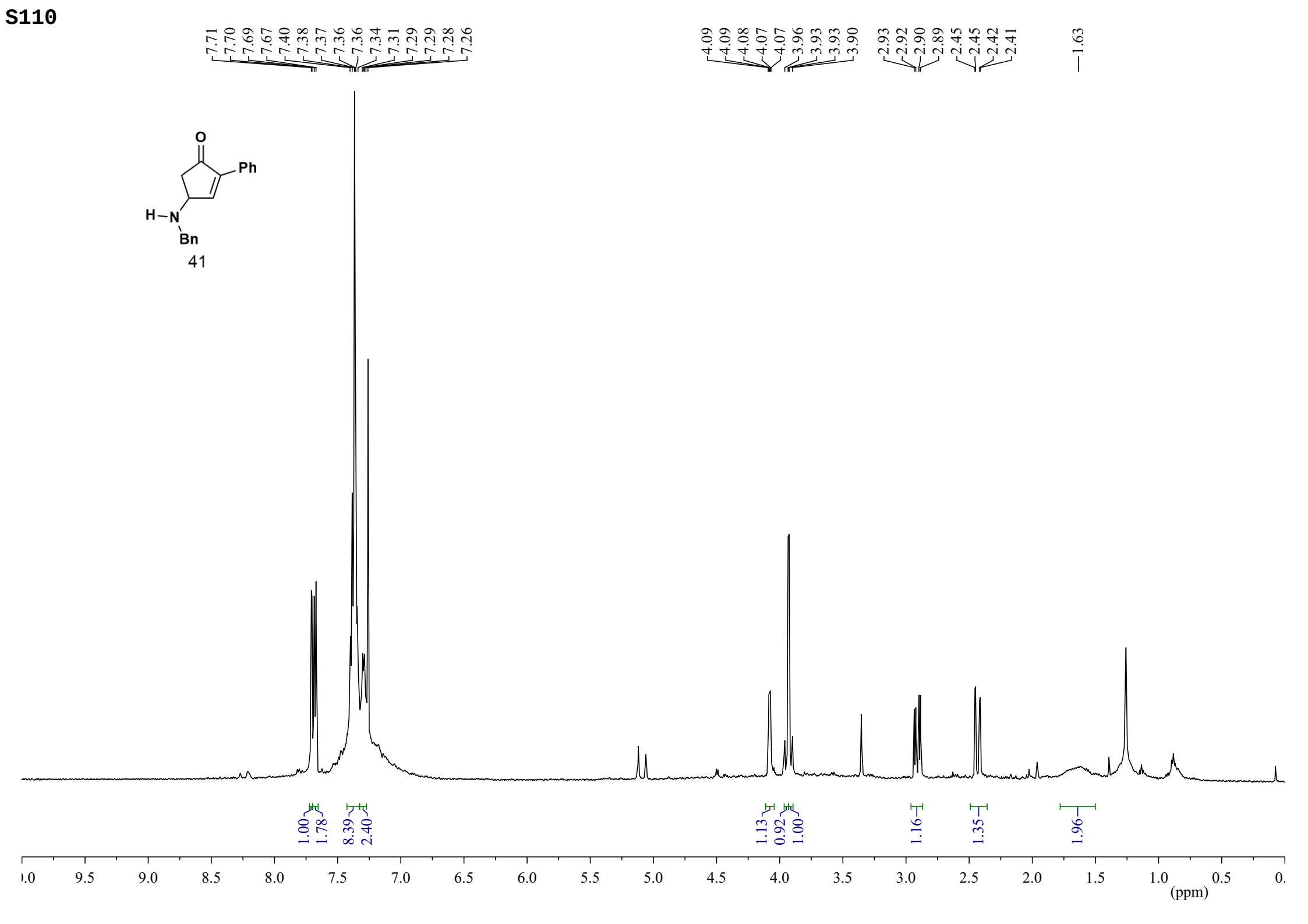
40

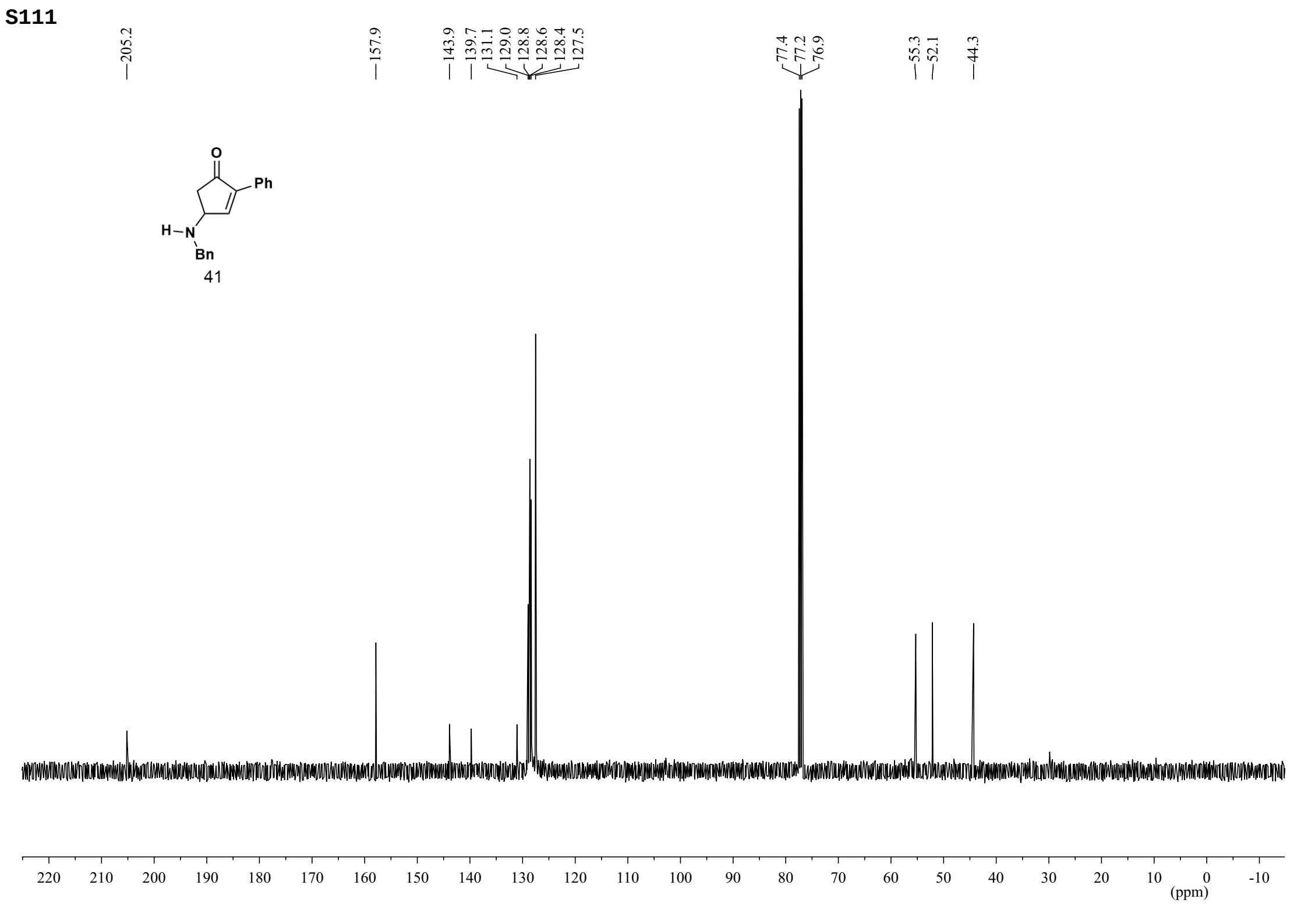
7.68
7.36
7.34
7.33
7.30
7.28
7.26
7.24
7.21
7.13
7.12
6.31
4.13
3.92
3.90
3.83
3.81
3.41
2.19
1.01
12.39
1.00
1.04
1.12
1.17
1.32
1.35
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
(ppm)


207.1
163.3
139.4
138.4
134.0
129.0
128.6
128.3
127.4
127.3
77.4
77.2
76.9
67.3
60.6
51.9
O
Ph
N–H
Bn
220
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
-10
(ppm)

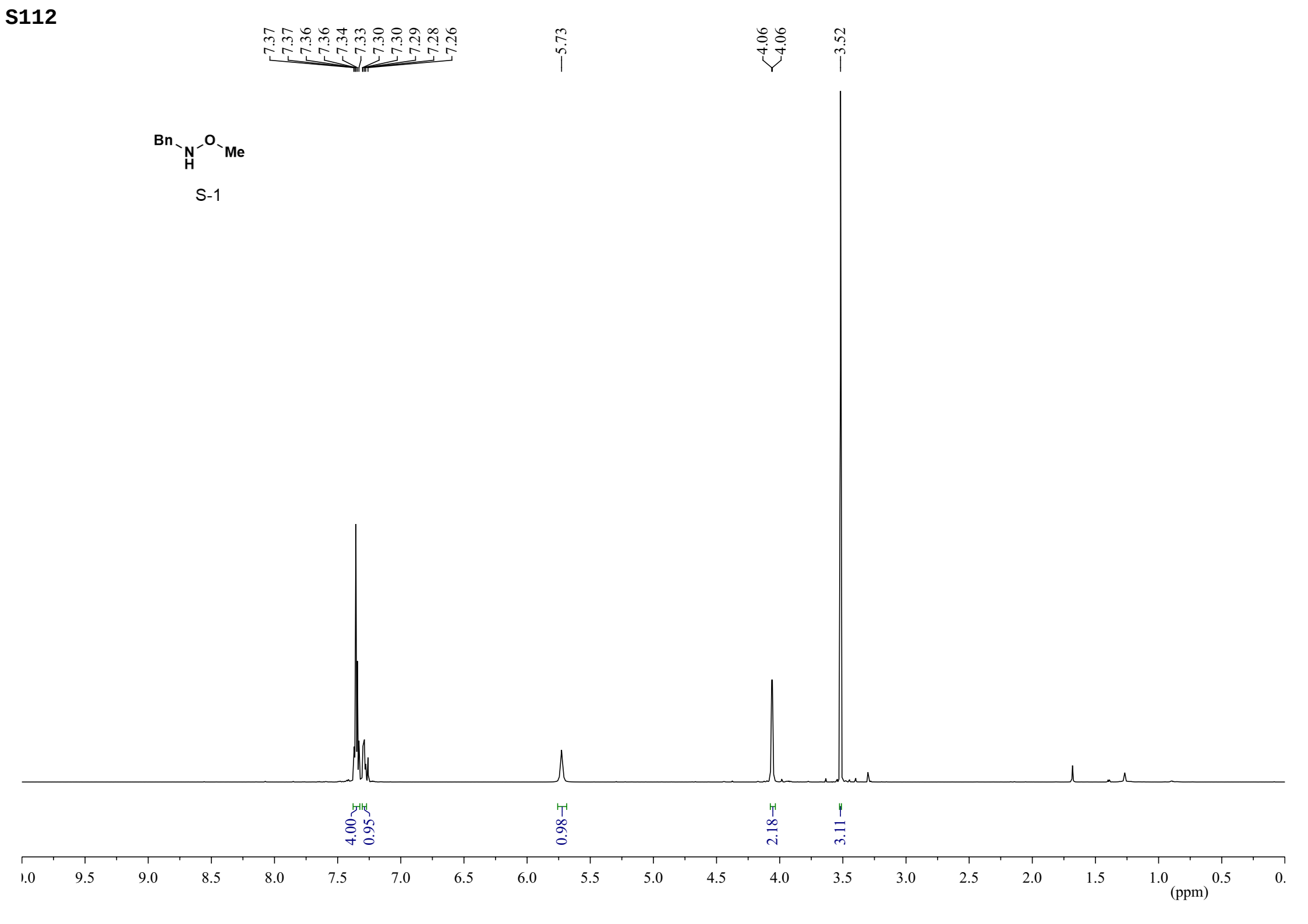
40

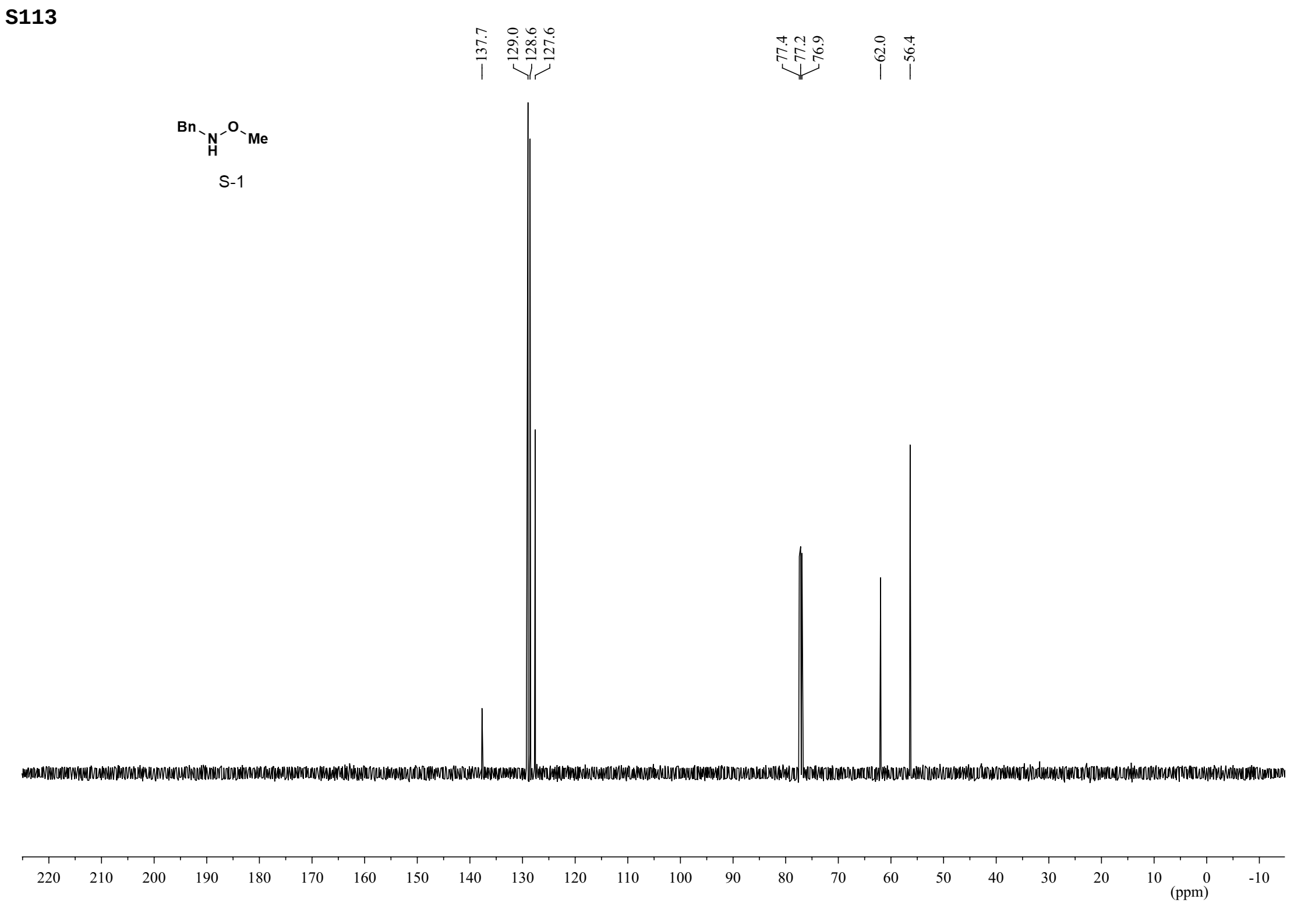
S110

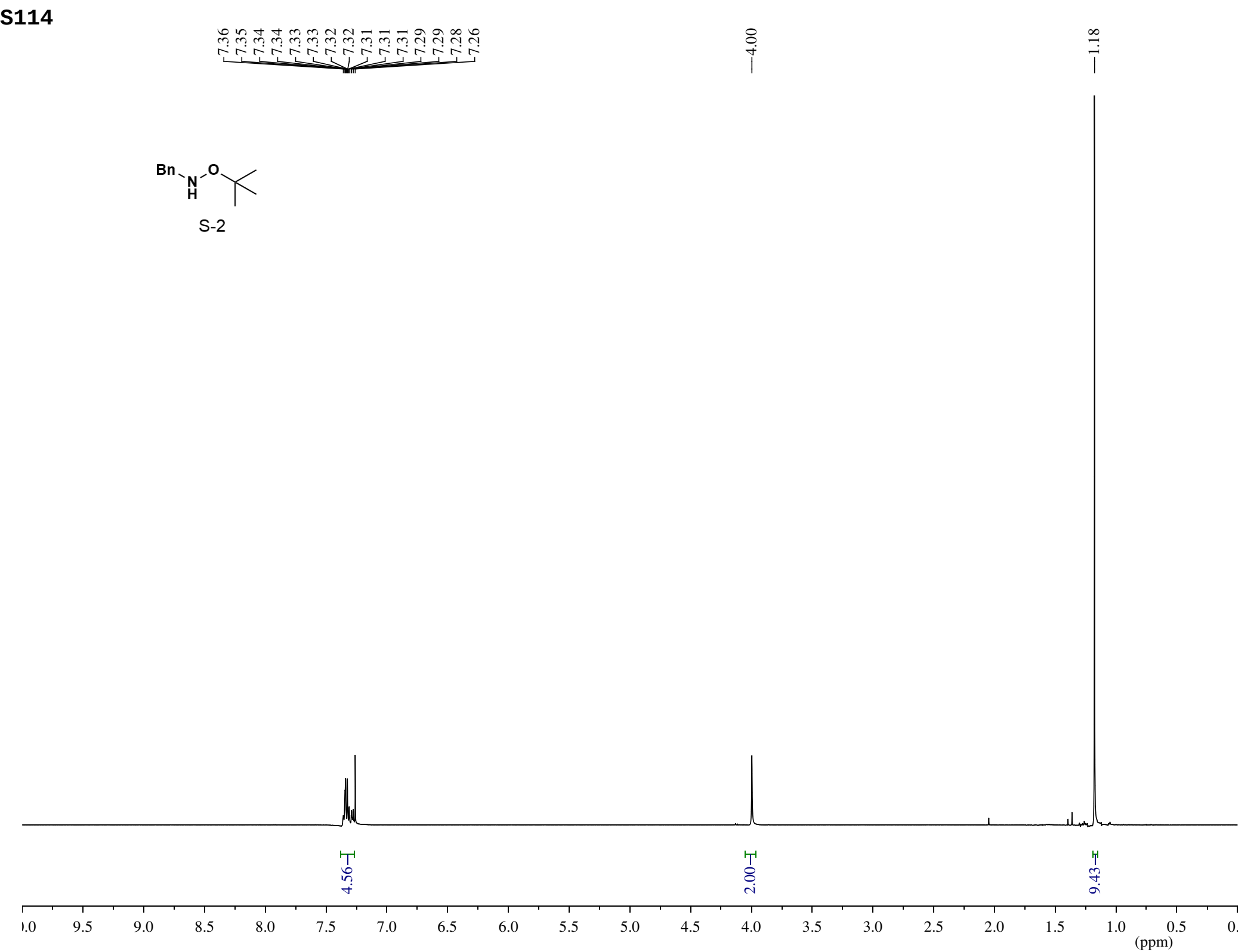

7.71
7.70
7.69
7.67
7.40
7.38
7.37
7.36
7.36
7.34
7.31
7.29
7.29
7.28
7.26
4.09
4.09
4.08
4.07
4.07
3.96
3.93
3.93
3.90
2.93
2.92
2.90
2.89
2.45
2.45
2.42
2.41
1.63
O
Ph
H–N
Bn
41
1.00
1.78
8.39
2.40
1.13
0.92
1.00
1.16
1.35
1.96
(ppm)

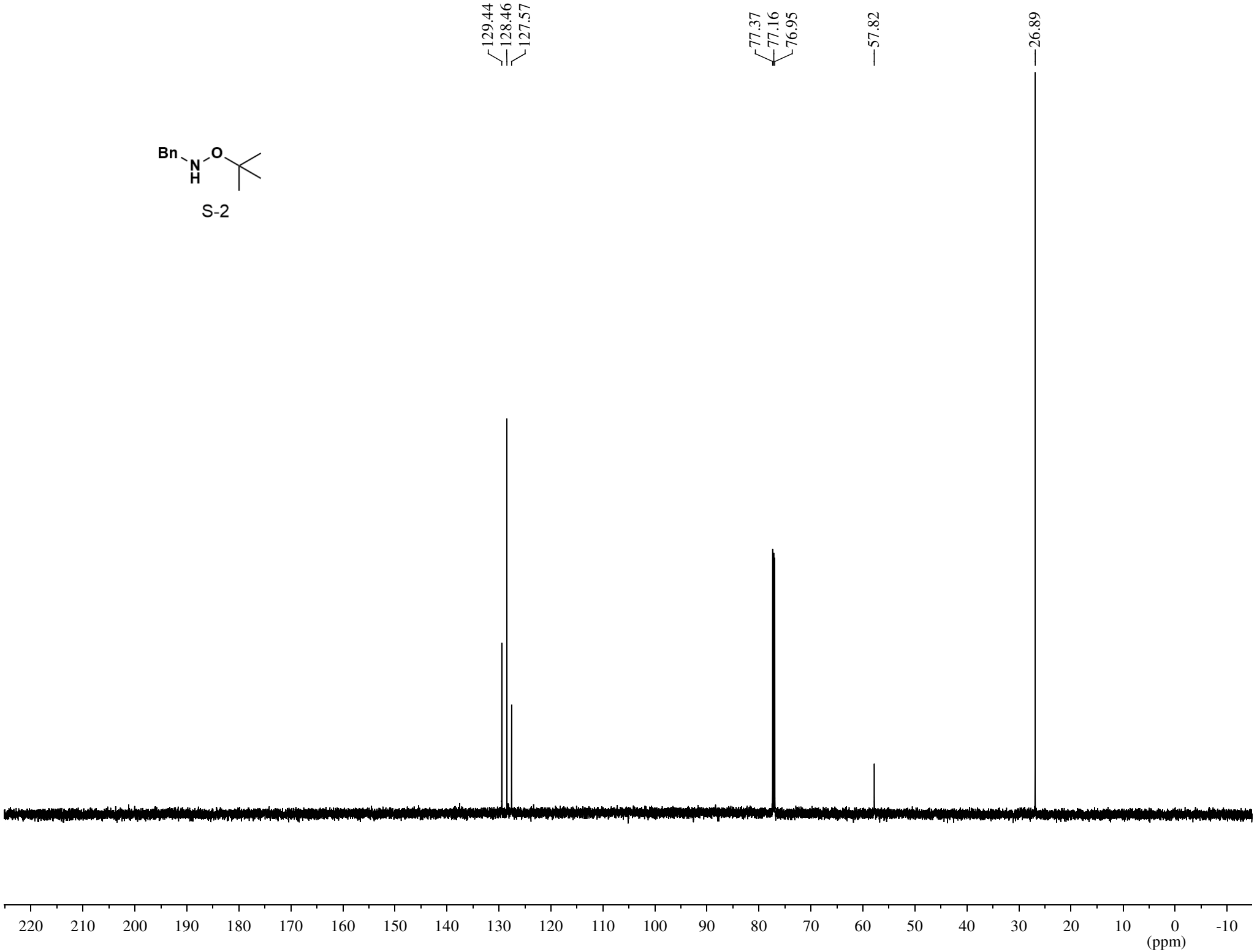

205.2
157.9
143.9
139.7
131.1
129.0
128.8
128.6
128.4
127.5
77.4
77.2
76.9
55.3
52.1
44.3
O
Ph
H–N
Bn
41
220
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
-10
(ppm)

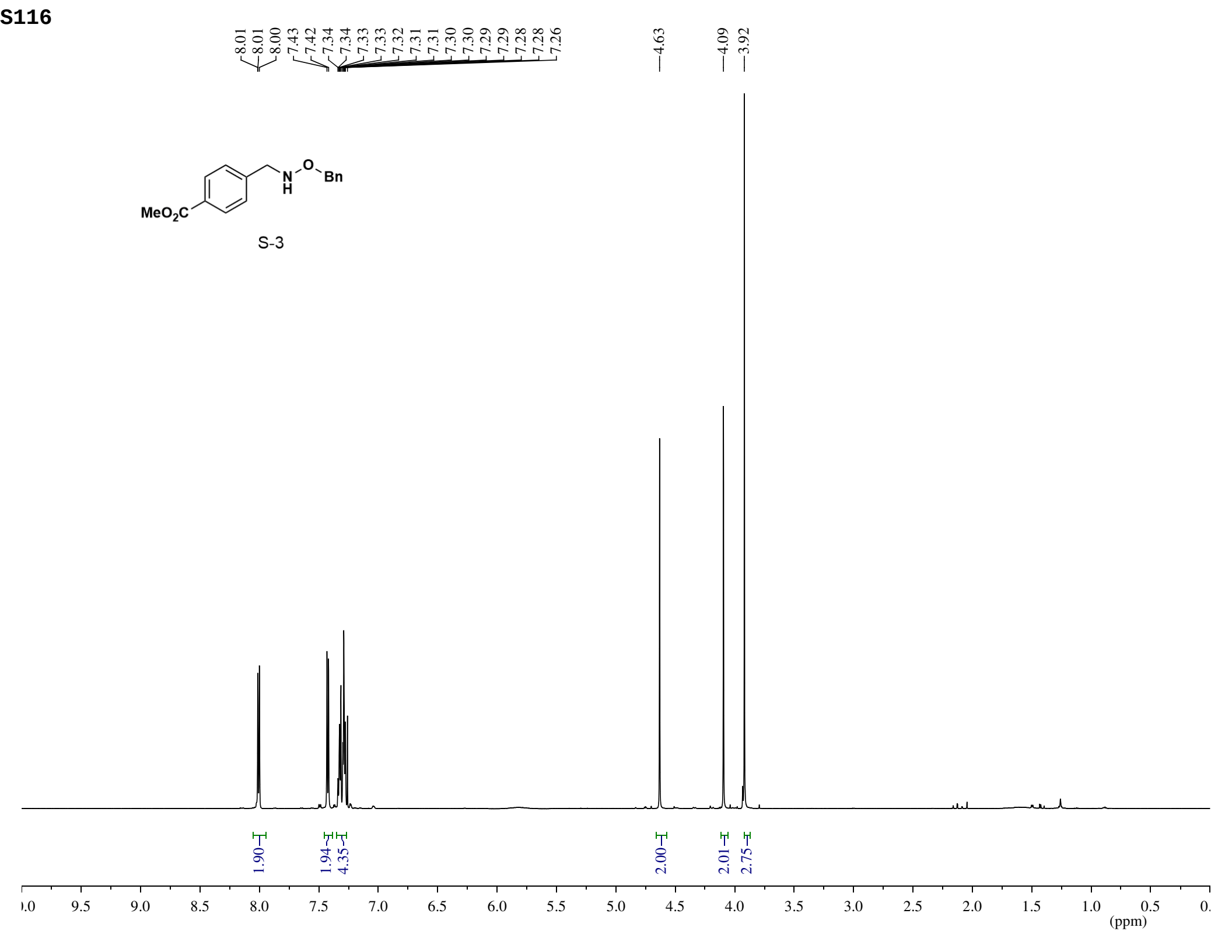
S112

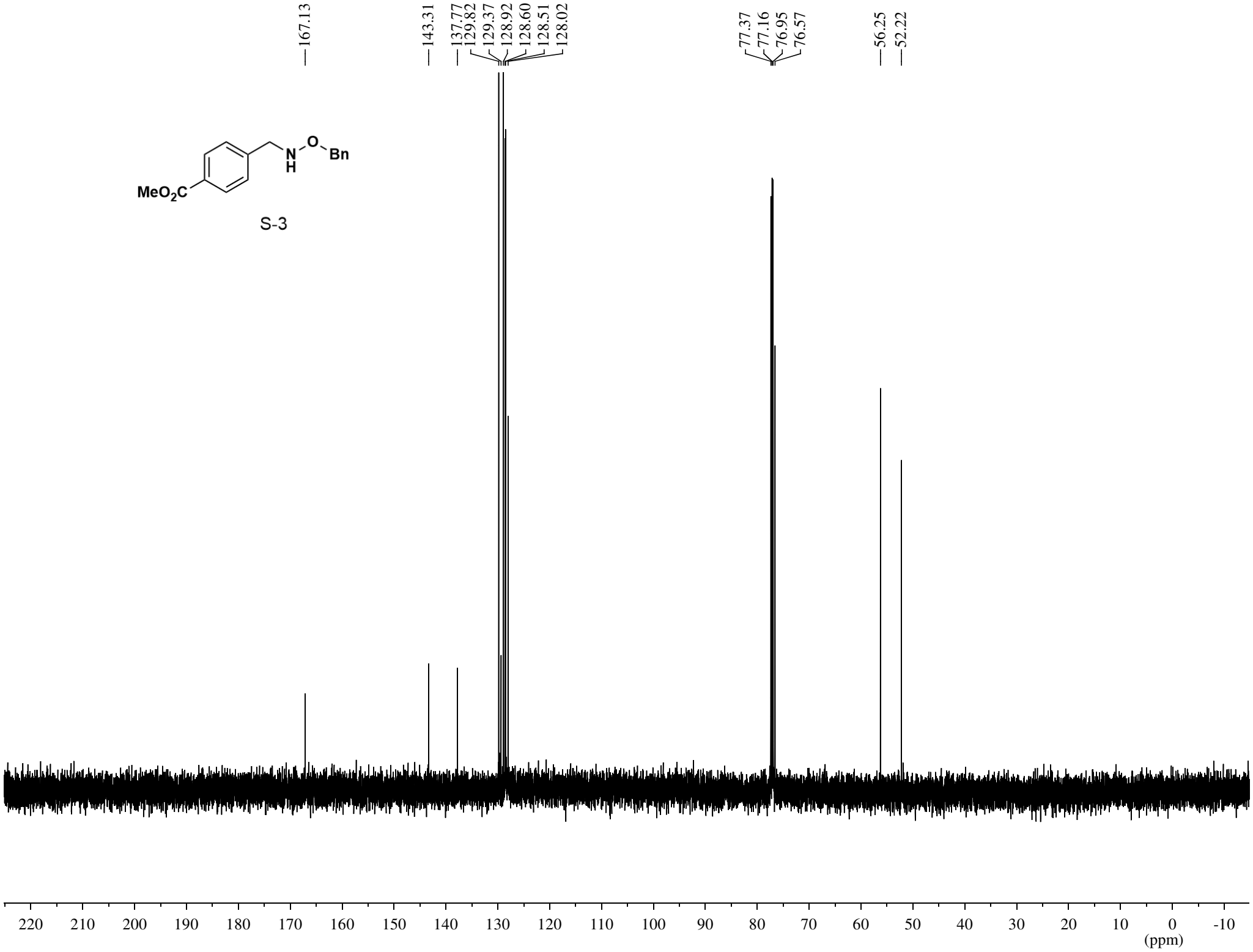

7.37
7.37
7.36
7.36
7.34
7.33
7.30
7.30
7.29
7.28
7.26
5.73
4.06
4.06
3.52
Bn
N
H
O
Me
S-1
4.00
0.95
0.98
2.18
3.11
(ppm)

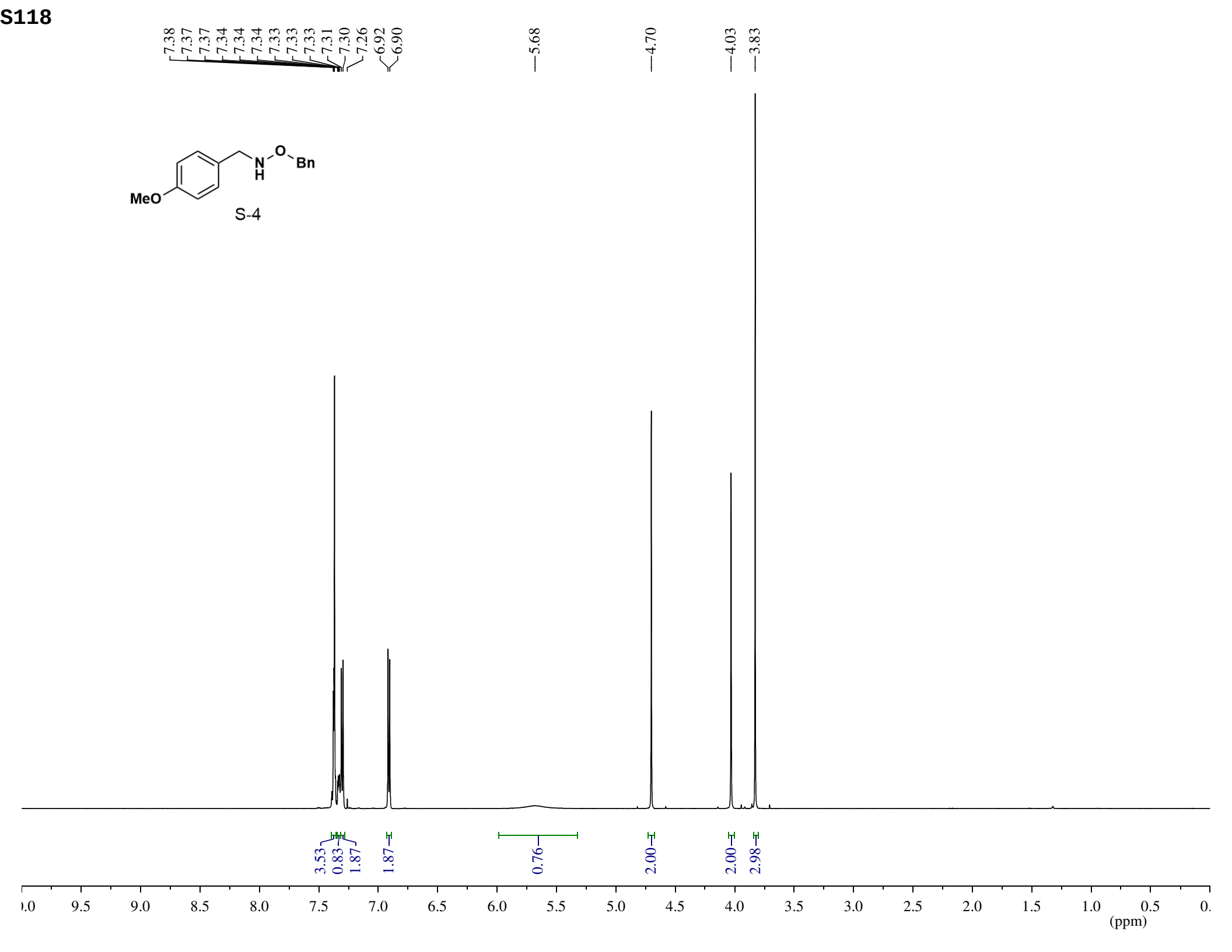

137.7
129.0
128.6
127.6
77.4
77.2
76.9
62.0
56.4
Bn
N
H
O
Me
S-1
220
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
-10
(ppm)

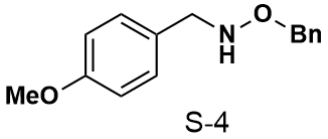

7.36
7.35
7.34
7.34
7.33
7.33
7.32
7.32
7.31
7.31
7.31
7.29
7.29
7.28
7.26
4.00
1.18
Bn
N
H
O
S-2
4.56
2.00
9.43
(ppm)


129.44
128.46
127.57
77.37
77.16
76.95
57.82
26.89
Bn
N
H
O
S-2
220
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
-10
(ppm)


8.01
8.01
8.00
7.43
7.42
7.34
7.34
7.33
7.33
7.32
7.31
7.31
7.30
7.30
7.29
7.29
7.28
7.28
7.26
4.63
4.09
3.92
MeO2C
N
H
O
Bn
S-3
1.90
1.94
4.35
2.00
2.01
2.75
(ppm)


167.13
143.31
137.77
129.82
129.37
128.92
128.60
128.51
128.02
77.37
77.16
76.95
76.57
56.25
52.22
MeO2C
N
H
O
Bn
S-3
220
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
-10
(ppm)

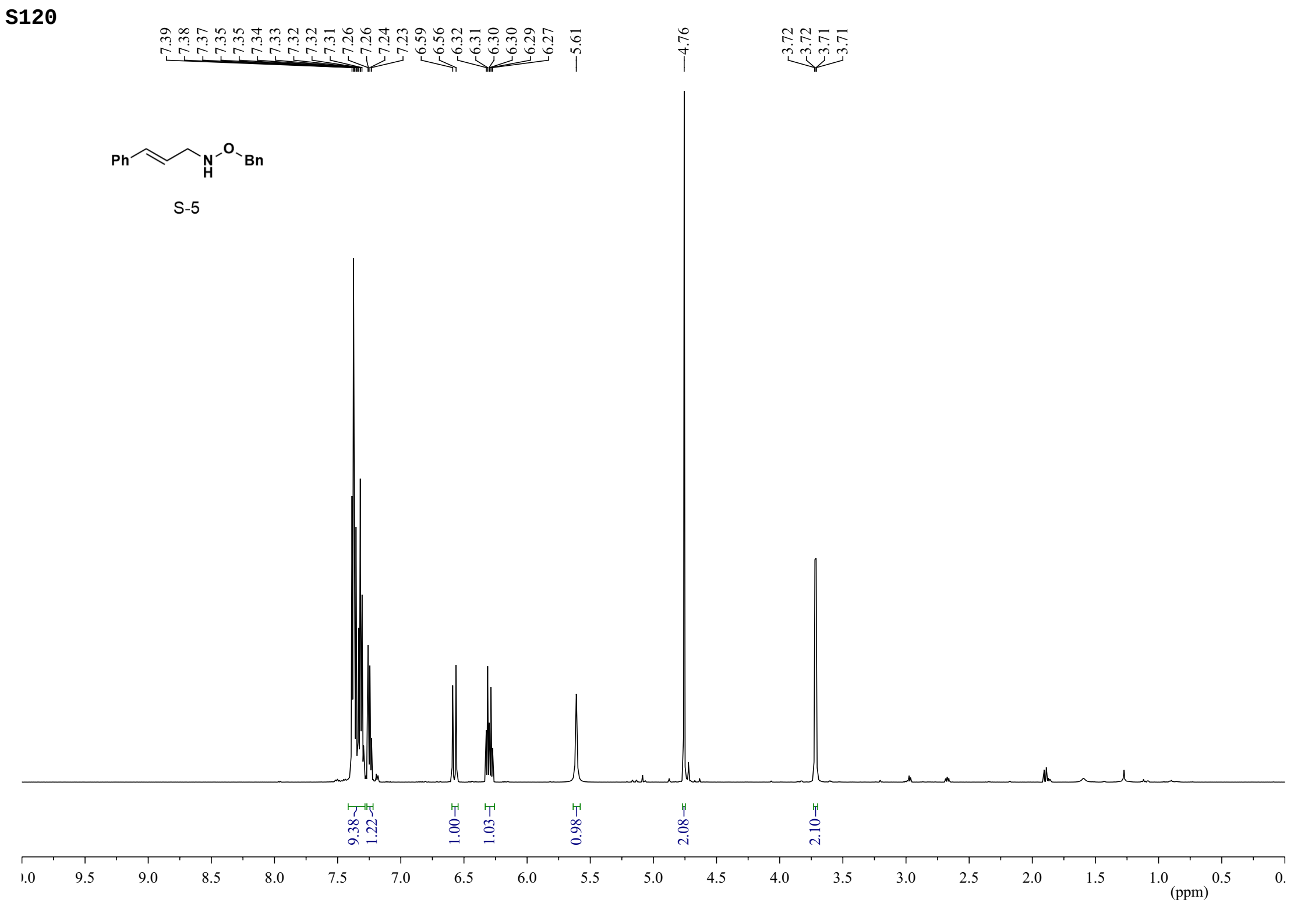

7.38
7.37
7.37
7.34
7.34
7.34
7.33
7.33
7.33
7.31
7.30
7.26
6.92
6.90
5.68
4.70
4.03
3.83
MeO
N
H
O
Bn
S-4
3.53
0.83
1.87
1.87
0.76
2.00
2.00
2.98
(ppm)

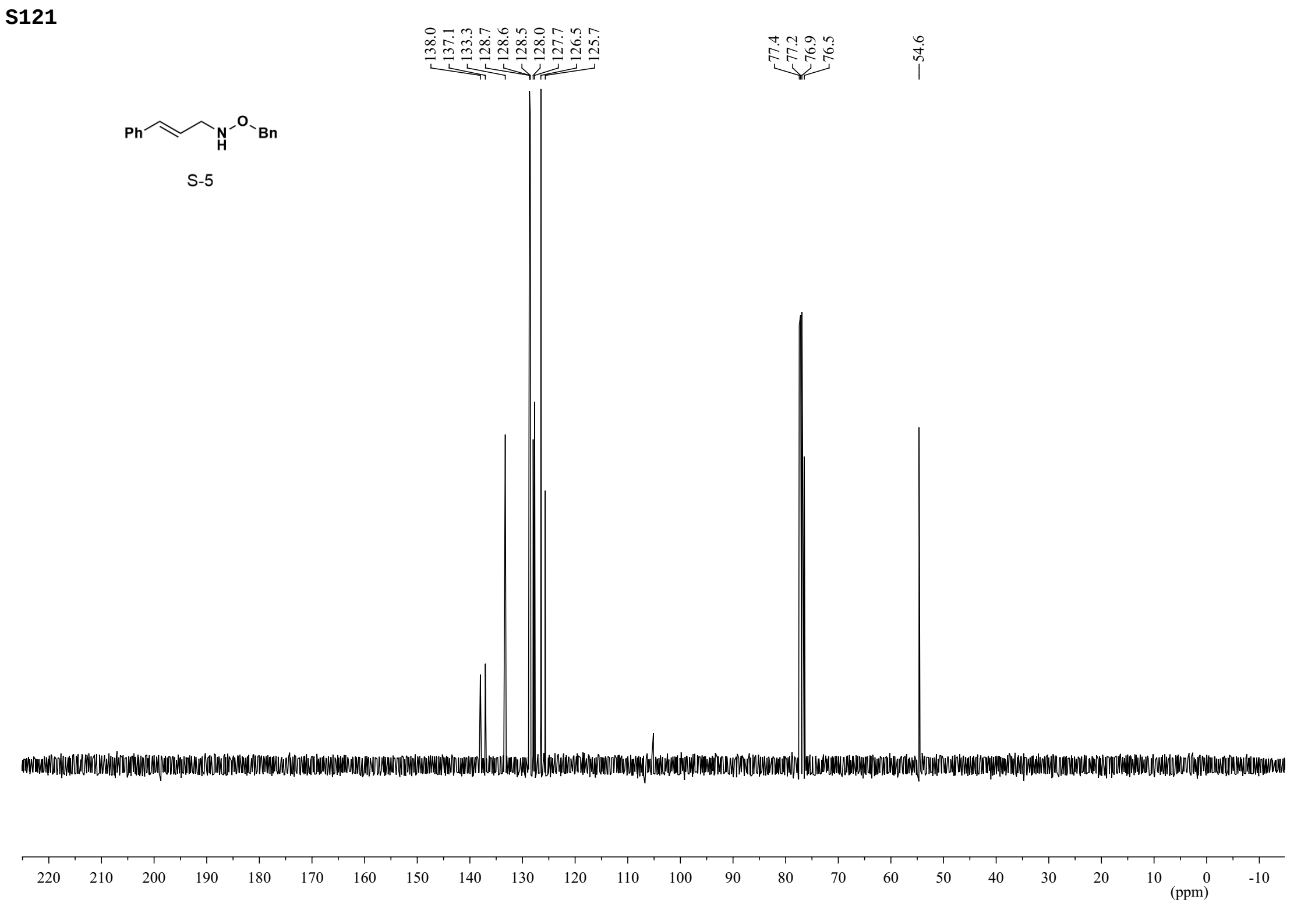

MeO
N
H
O
Bn

S-4

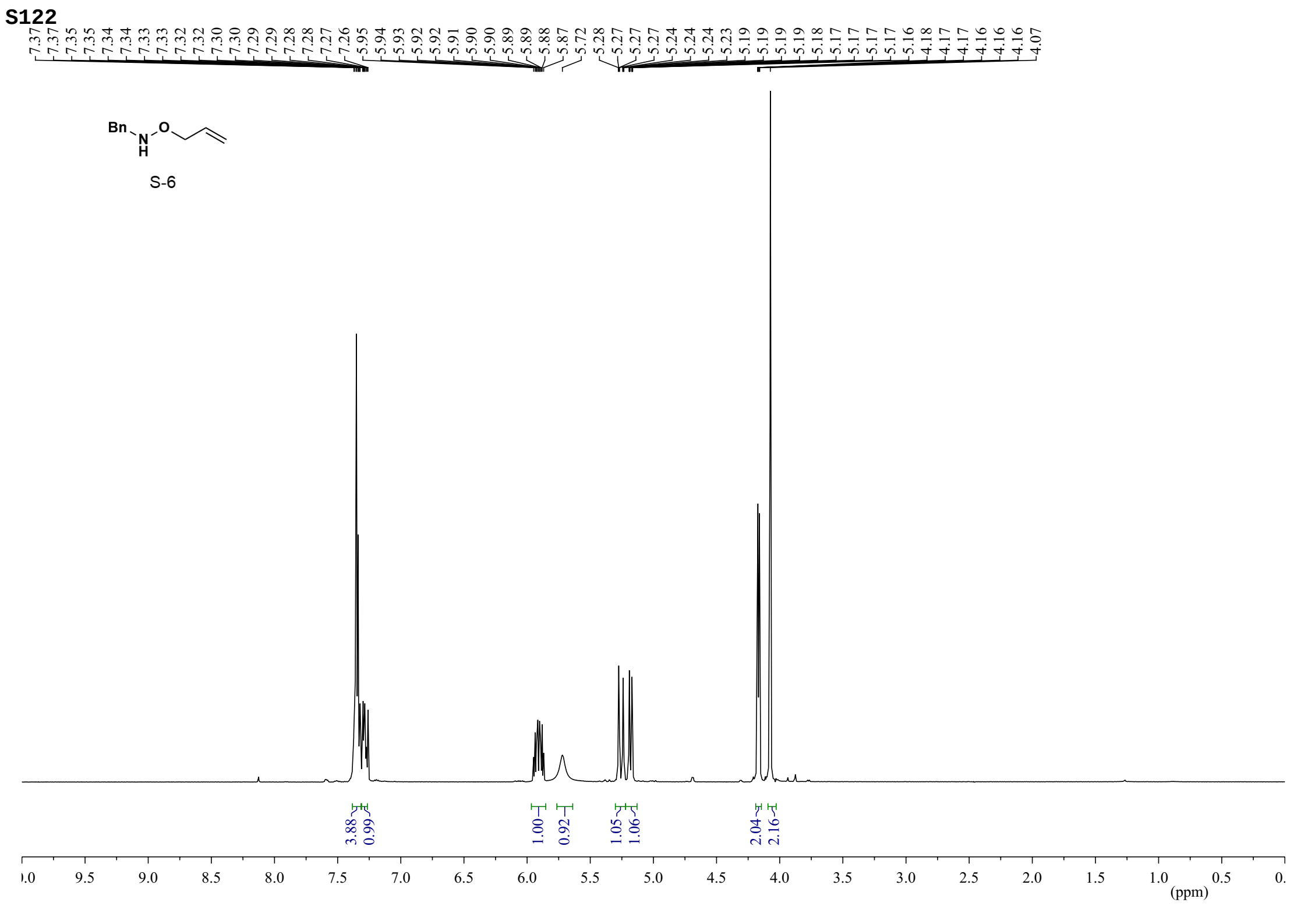
159.06
138.01
130.28
129.69
128.52
128.39
127.82
113.86
77.37
77.16
76.95
76.32
55.97
55.29
220
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
-10
(ppm)

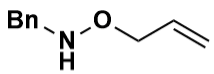
S120


7.39
7.38
7.37
7.35
7.35
7.34
7.33
7.32
7.32
7.31
7.26
7.26
7.24
7.23
6.59
6.56
6.32
6.31
6.30
6.30
6.29
6.27
5.61
4.76
3.72
3.72
3.71
3.71
Ph
N
H
O
Bn
S-5
9.38
1.22
1.00
1.03
0.98
2.08
2.10
(ppm)


138.0
137.1
133.3
128.7
128.6
128.5
128.0
127.7
126.5
125.7
77.4
77.2
76.9
76.5
54.6
Ph
N
H
O
Bn
S-5
220
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
-10
(ppm)

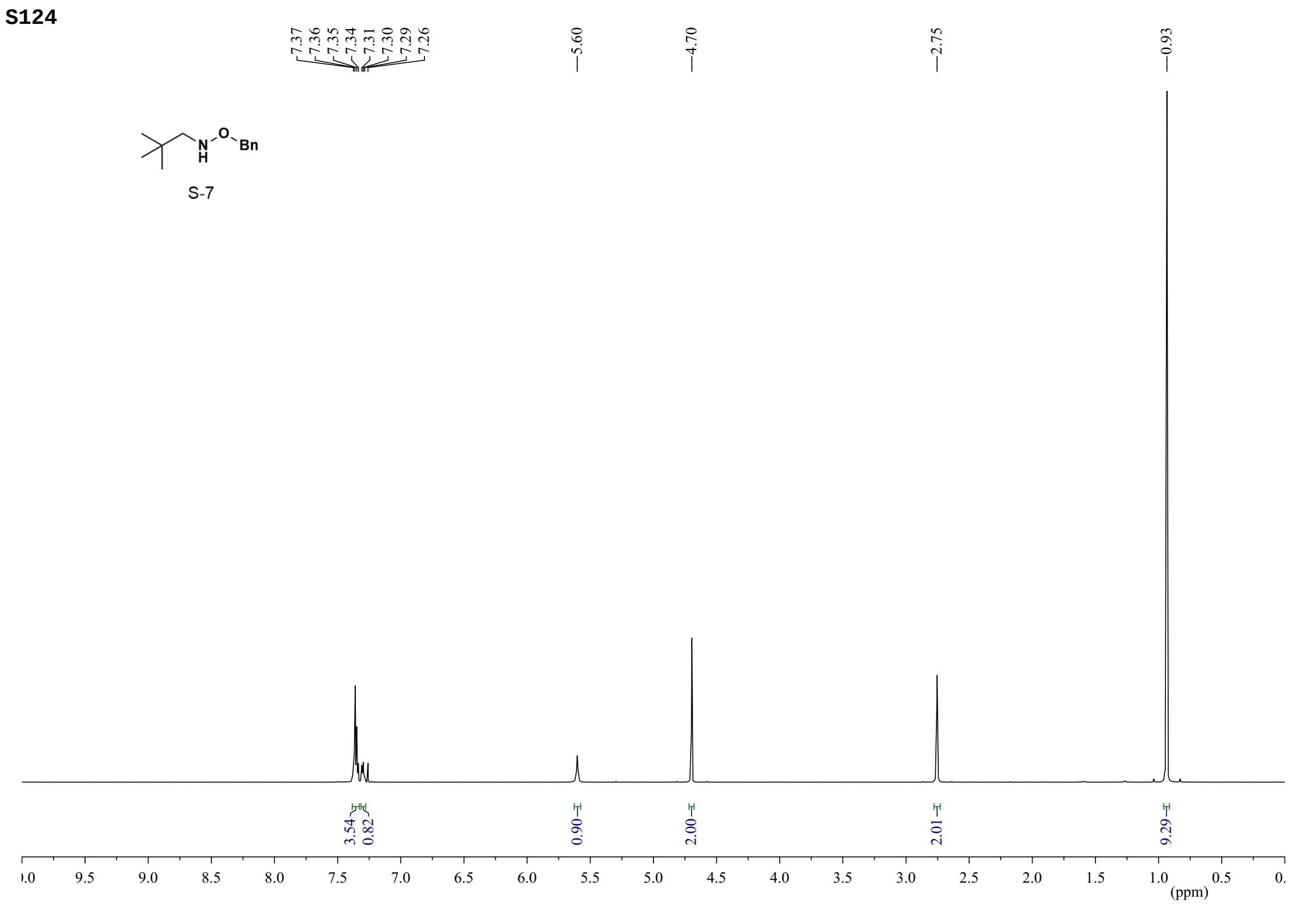
S122

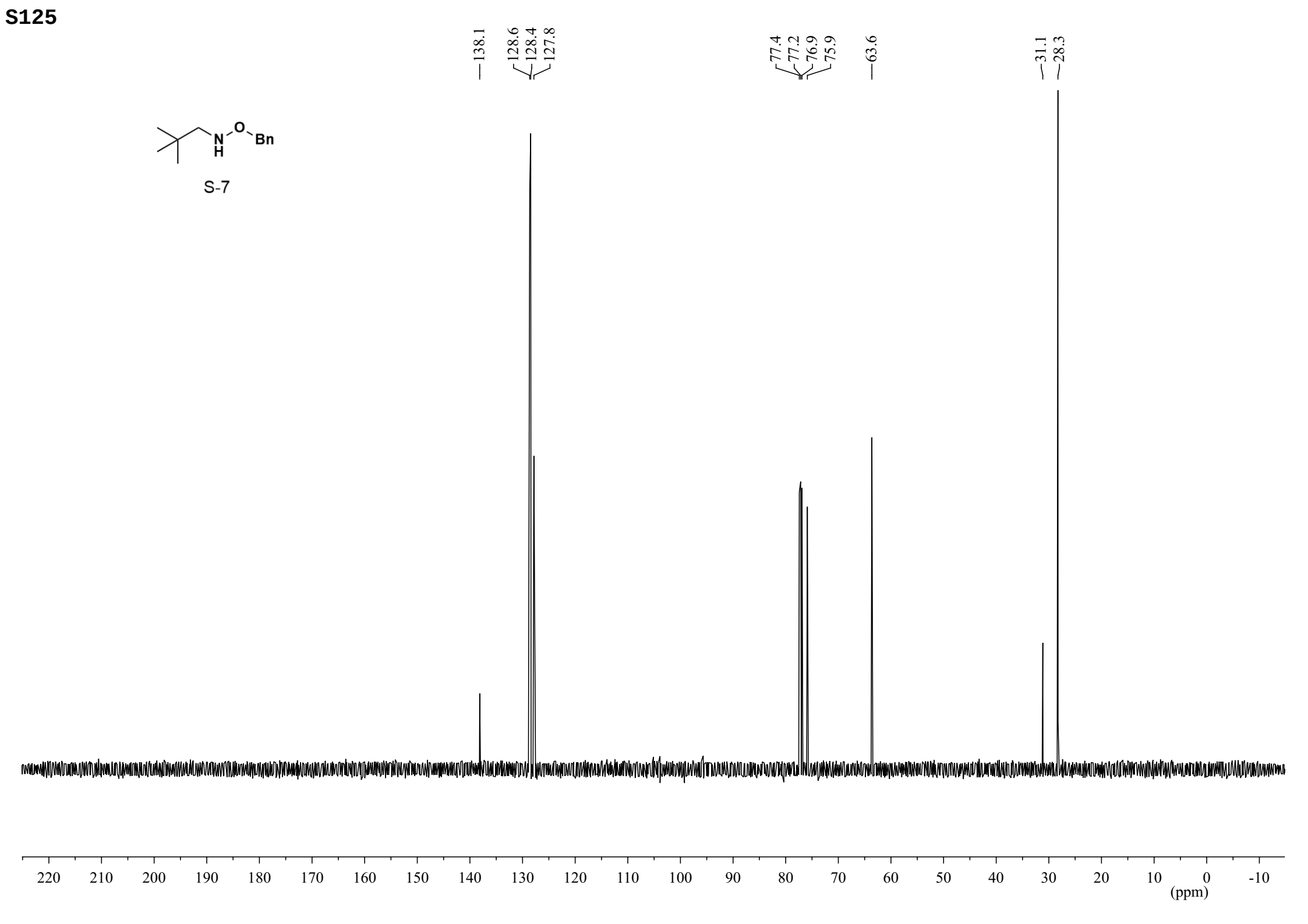

7.37
7.37
7.35
7.35
7.34
7.34
7.33
7.33
7.32
7.32
7.30
7.30
7.29
7.29
7.28
7.28
7.27
7.26
5.95
5.94
5.93
5.92
5.92
5.91
5.90
5.90
5.89
5.89
5.88
5.87
5.72
5.28
5.27
5.27
5.27
5.24
5.24
5.24
5.23
5.19
5.19
5.19
5.19
5.18
5.17
5.17
5.17
5.17
5.16
4.18
4.17
4.17
4.16
4.16
4.16
4.07
Bn
N
H
O
S-6
3.88
0.99
1.00
0.92
1.05
1.06
2.04
2.16
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
(ppm)


Bn
N
H
O

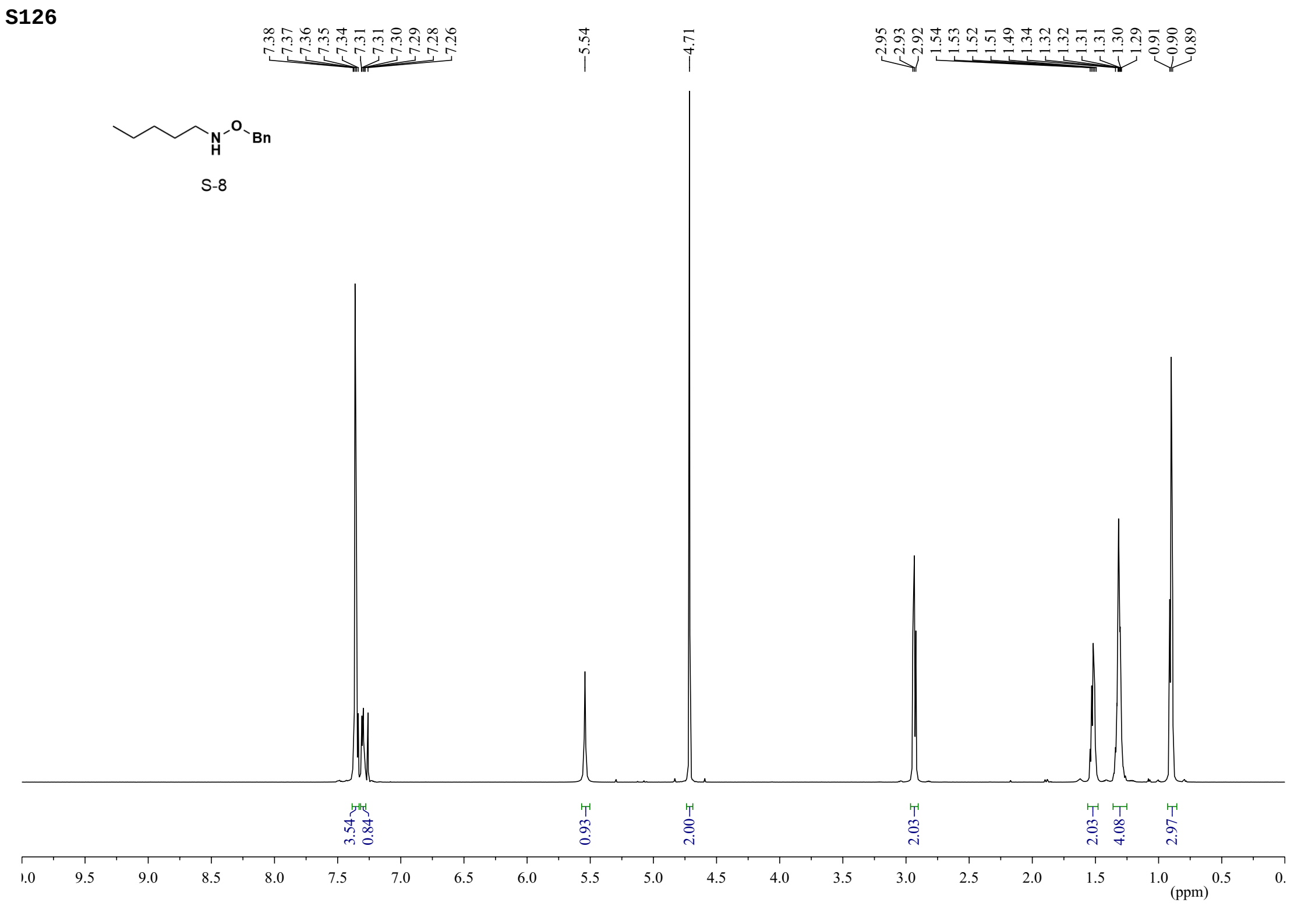
S-6

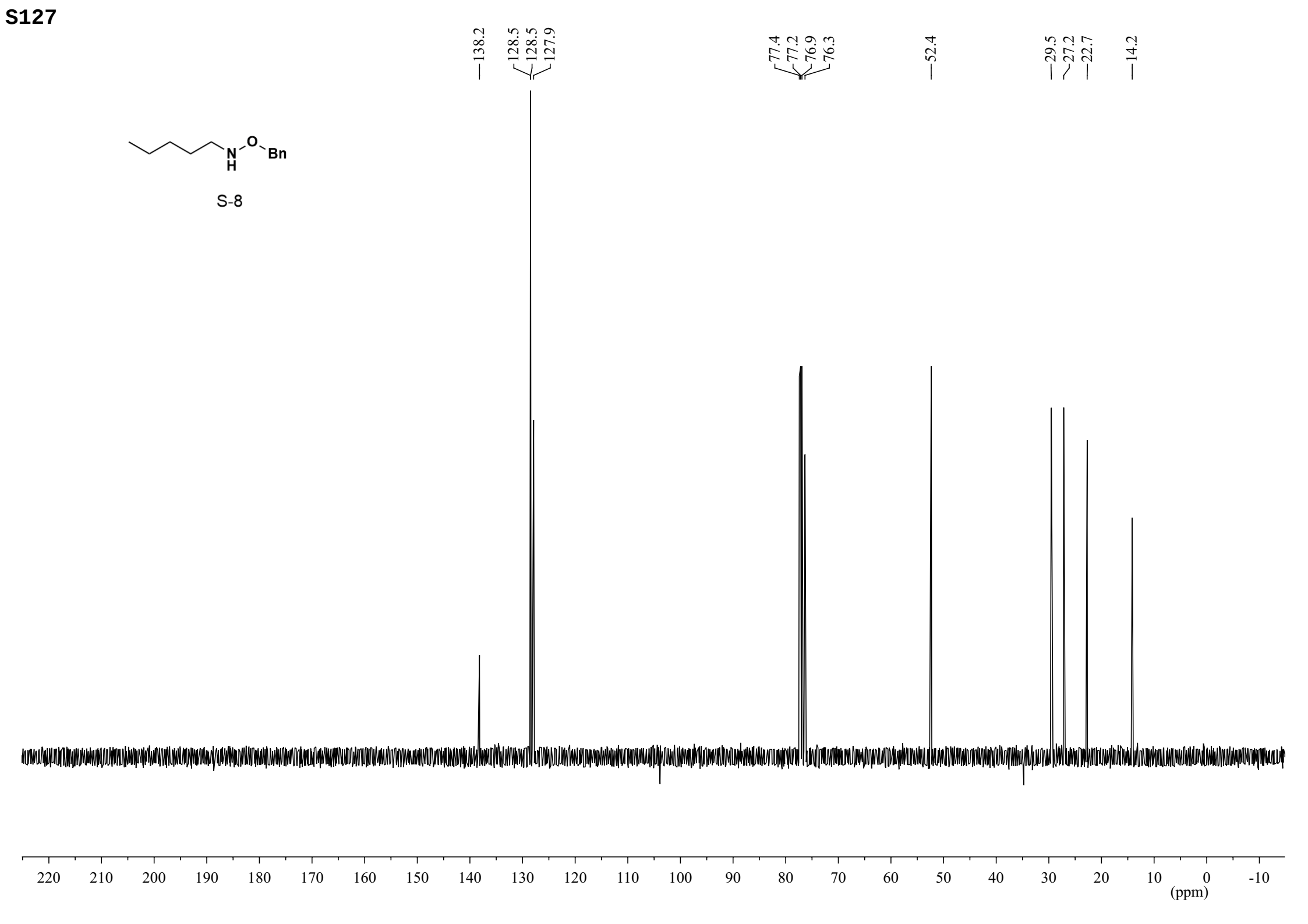
137.6
134.6
129.1
128.5
127.6
117.7
77.4
77.2
76.9
75.2
56.7
220
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
-10
(ppm)


7.37
7.36
7.35
7.34
7.31
7.30
7.29
7.26
5.60
4.70
2.75
0.93
N
H
O
Bn
S-7
3.54
0.82
0.90
2.00
2.01
9.29
(ppm)

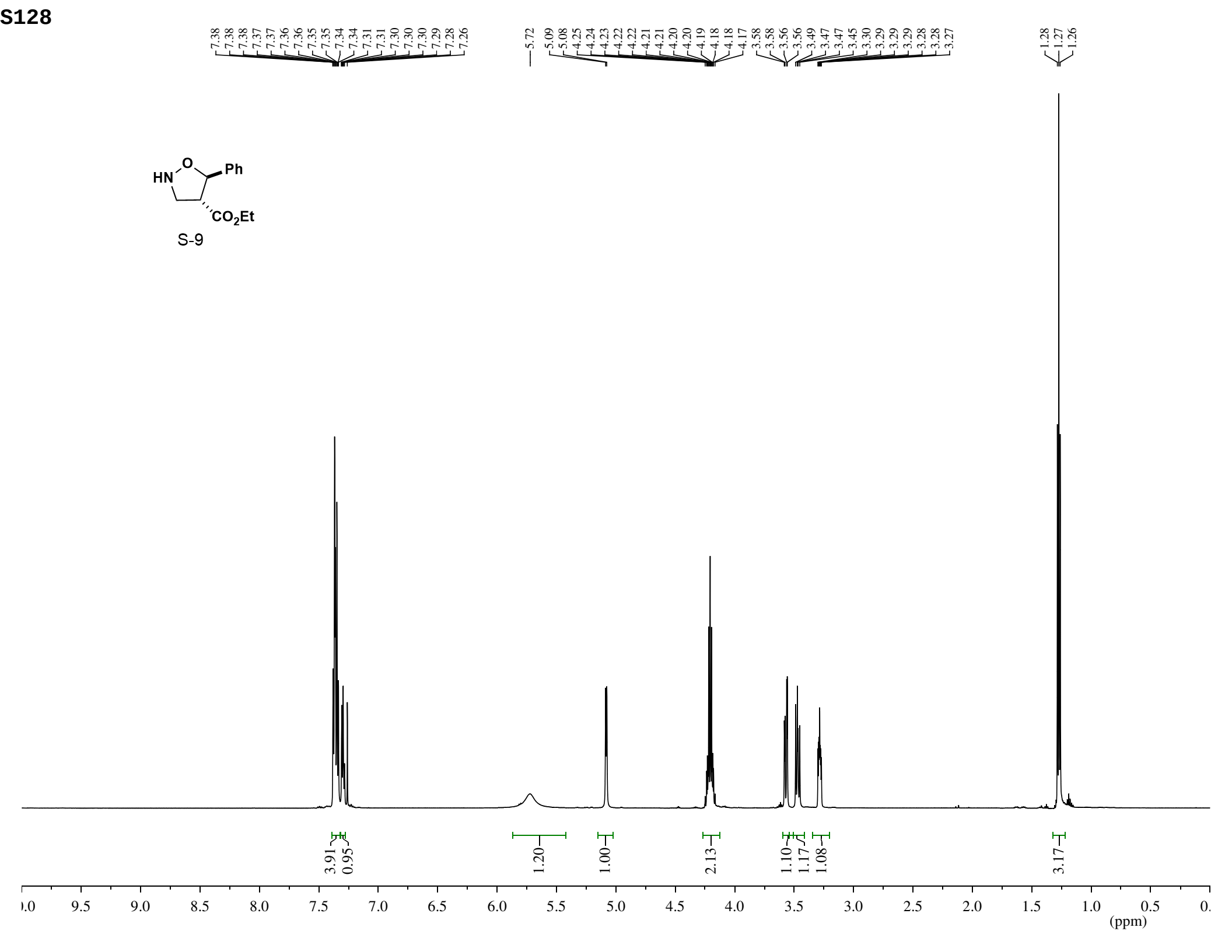

138.1
128.6
128.4
127.8
77.4
77.2
76.9
75.9
63.6
31.1
28.3
N
H
O
Bn
S-7
220
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
-10
(ppm)

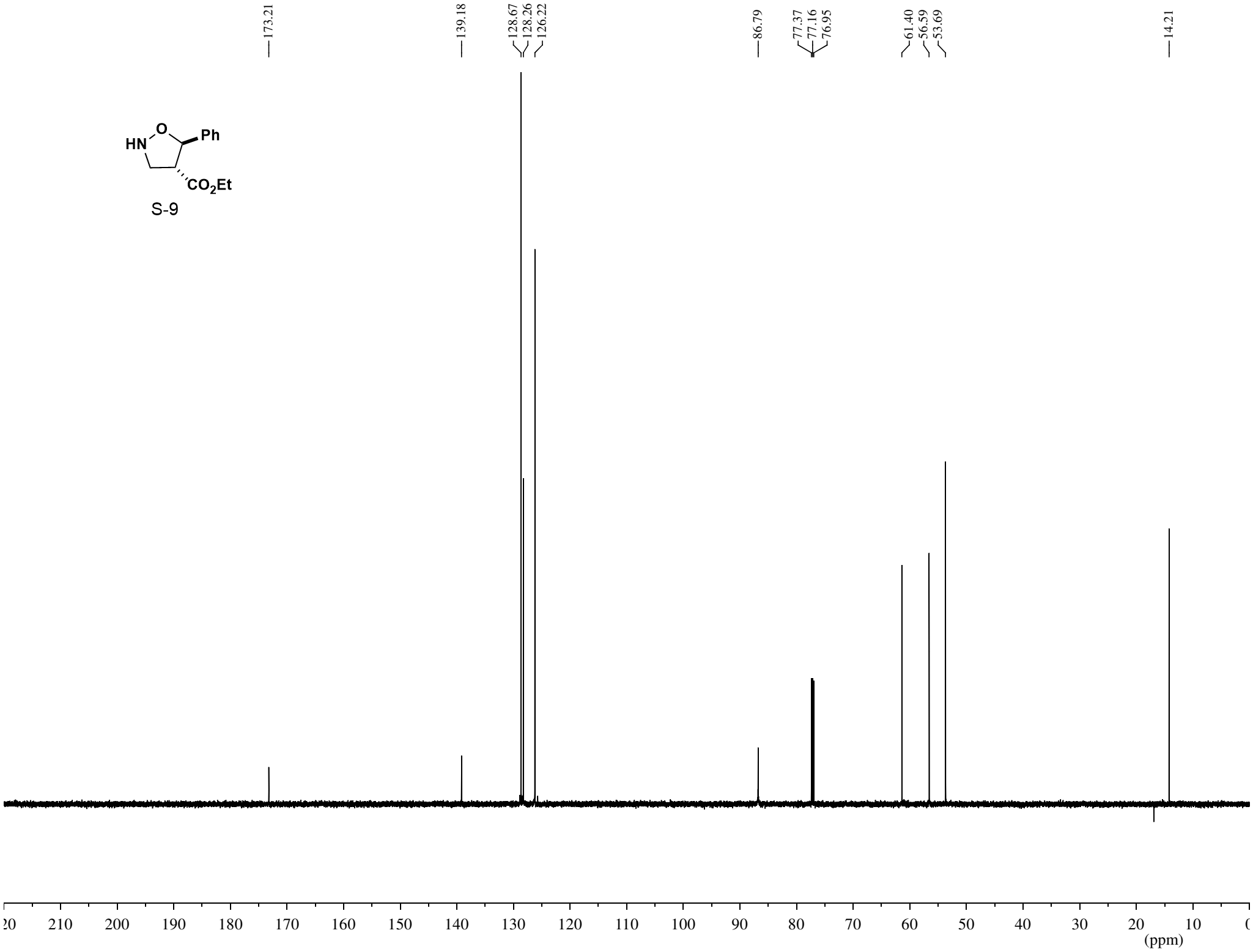
S126


7.38
7.37
7.36
7.35
7.34
7.31
7.31
7.30
7.29
7.28
7.26
5.54
4.71
2.95
2.93
2.92
1.54
1.53
1.52
1.51
1.49
1.34
1.32
1.32
1.31
1.31
1.30
1.29
0.91
0.90
0.89
O
N
H
Bn
S-8
3.54
0.84
0.93
2.00
2.03
2.03
4.08
2.97
(ppm)

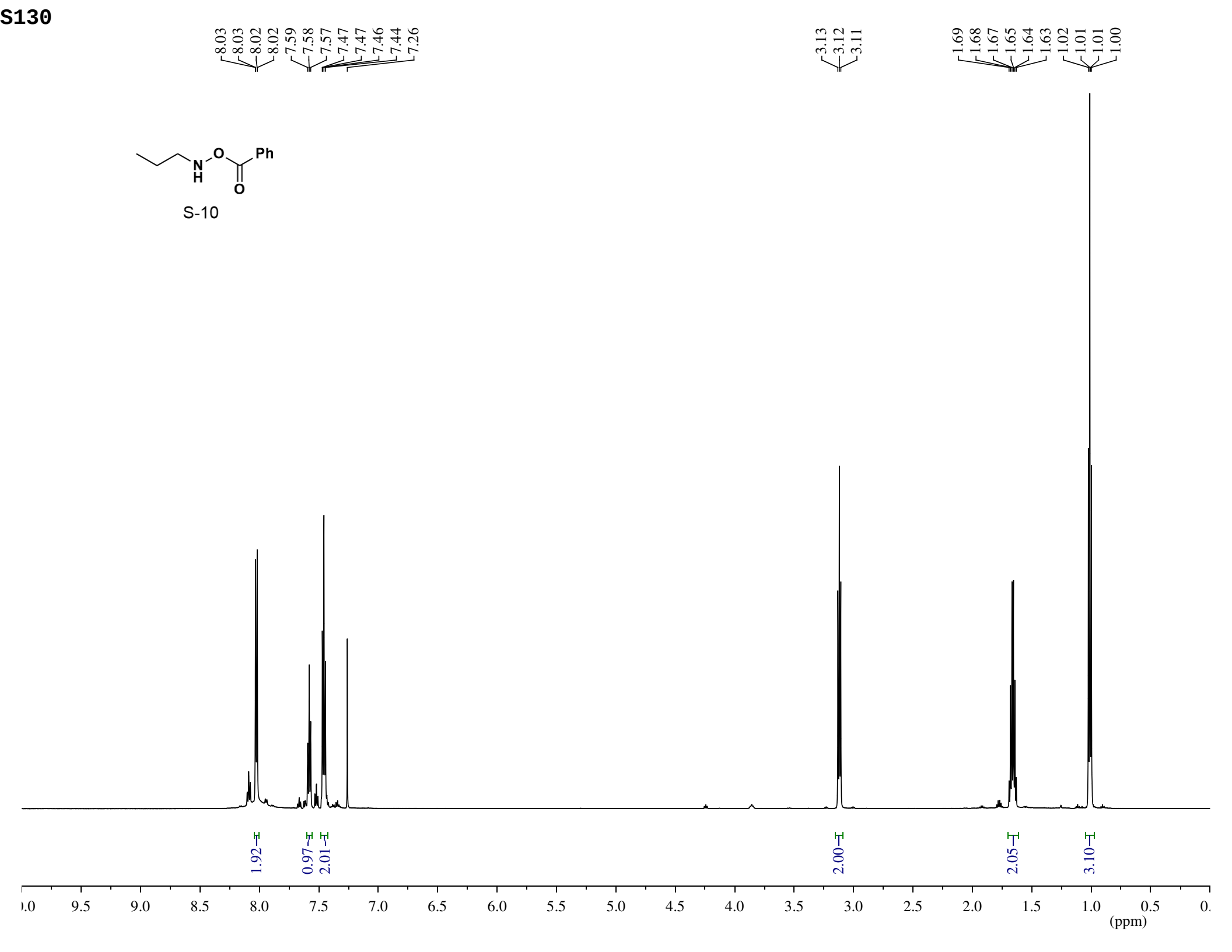

138.2
128.5
128.5
127.9
77.4
77.2
76.9
76.3
52.4
29.5
27.2
22.7
14.2
O
N
H
Bn
S-8
220
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
-10
(ppm)

S128

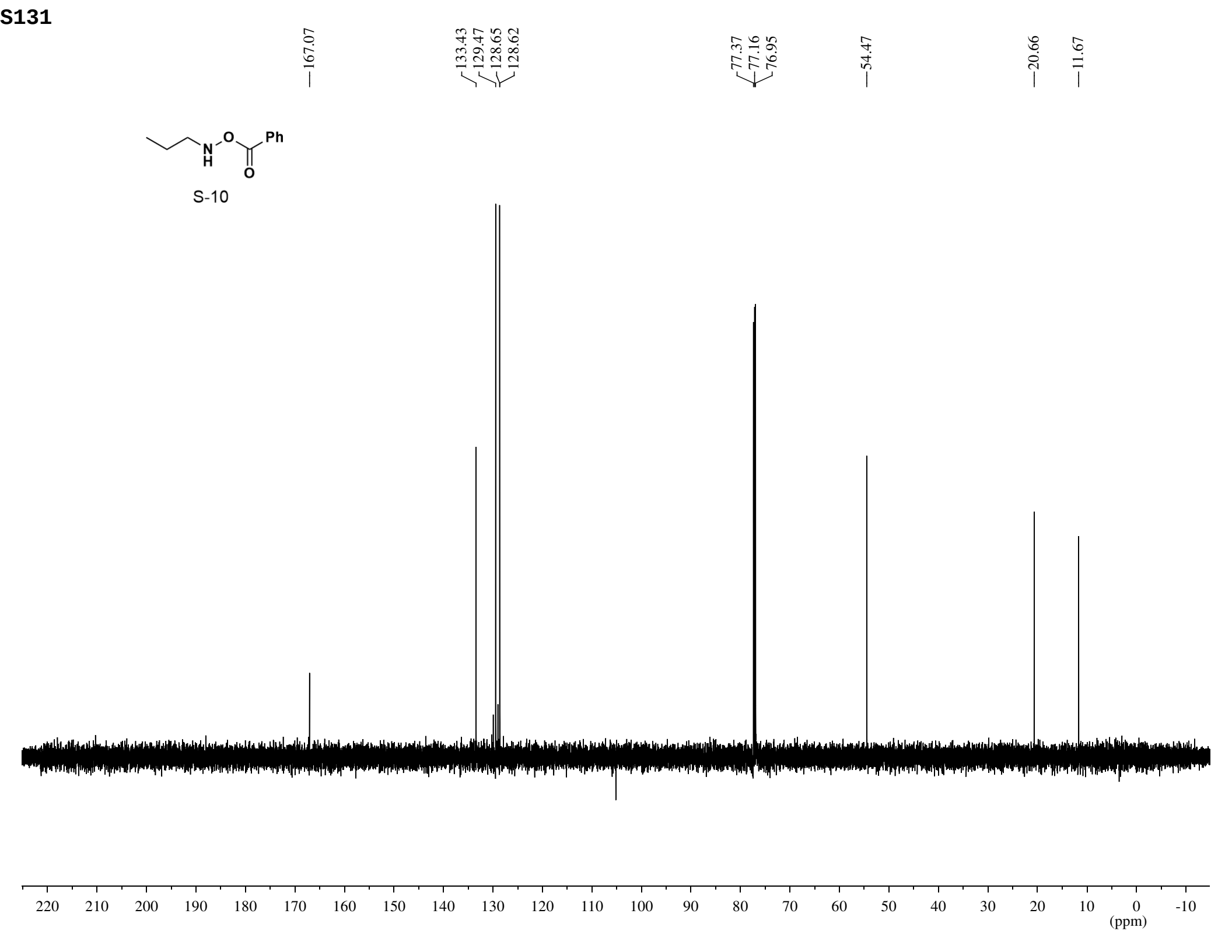

7.38 7.38 7.38 7.37 7.37 7.36 7.36 7.35 7.35 7.34 7.34 7.31 7.31 7.30 7.30 7.30 7.29 7.28 7.26
5.72
5.09 5.08 4.25 4.24 4.23 4.22 4.22 4.21 4.21 4.20 4.20 4.19 4.18 4.18 4.17
3.58 3.58 3.56 3.56 3.49 3.47 3.47 3.45 3.30 3.29 3.29 3.29 3.28 3.28 3.27
1.28 1.27 1.26
HN
O
Ph
CO2Et
S-9
3.91
0.95
1.20
1.00
2.13
1.10
1.17
1.08
3.17
(ppm)


173.21
139.18
128.67
128.26
126.22
86.79
77.37
77.16
76.95
61.40
56.59
53.69
14.21
HN
O
Ph
CO2Et
S-9
(ppm)

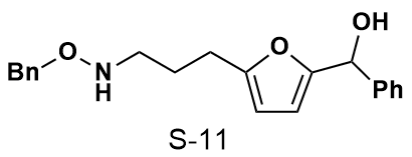
S130


8.03
8.03
8.02
8.02
7.59
7.58
7.57
7.47
7.47
7.46
7.44
7.26
3.13
3.12
3.11
1.69
1.68
1.67
1.65
1.64
1.63
1.02
1.01
1.01
1.00
Ph
O
N
H
O
S-10
1.92
0.97
2.01
2.00
2.05
3.10
(ppm)

S131


167.07
133.43
129.47
128.65
128.62
77.37
77.16
76.95
54.47
20.66
11.67
N
H
O
O
Ph
S-10
220
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
-10
(ppm)

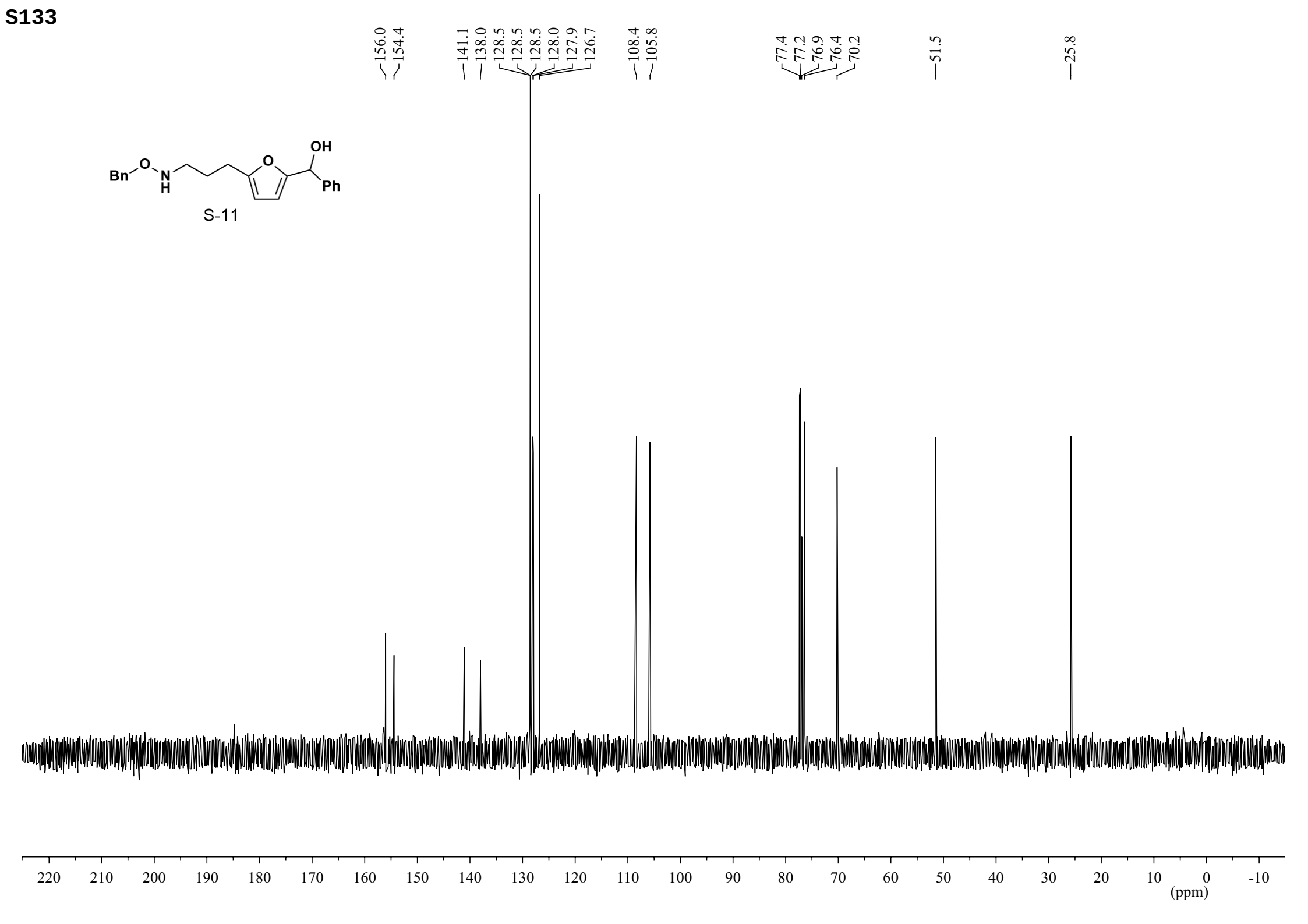
S132

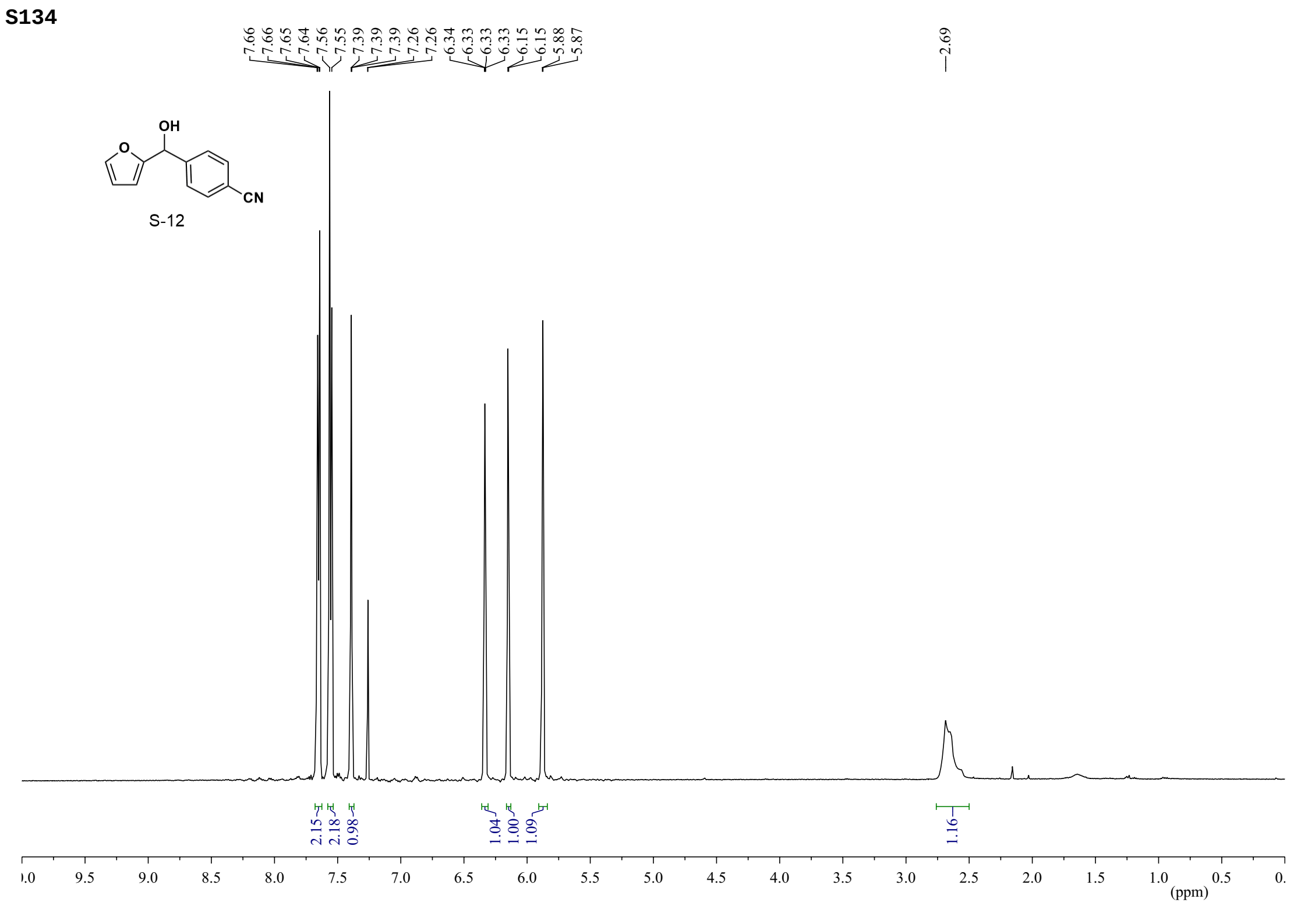

Bn
O
N
H
O
OH
Ph

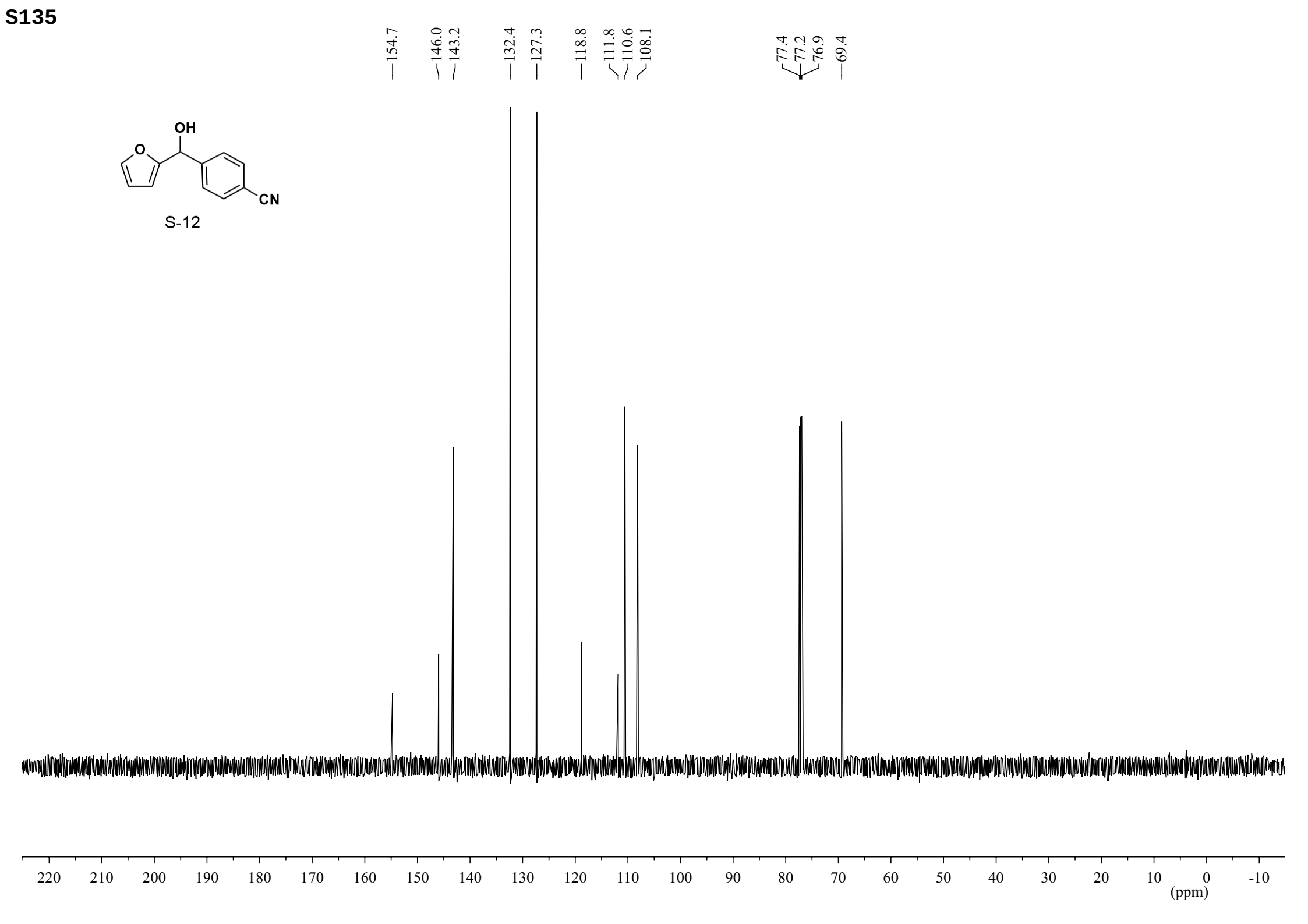
S-11

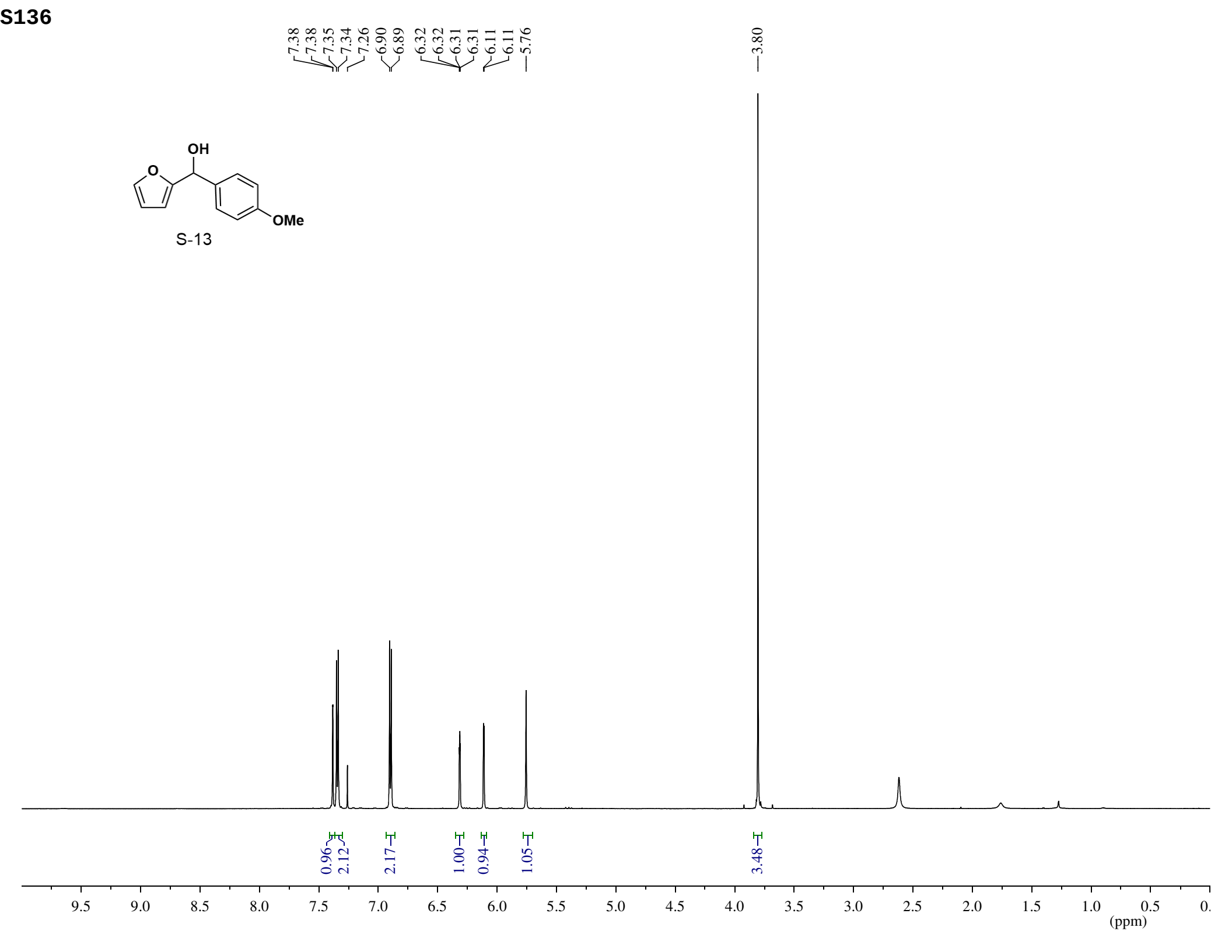
7.44
7.43
7.38
7.37
7.36
7.35
7.33
7.31
7.31
7.30
7.29
7.26
5.95
5.94
5.91
5.90
5.76
4.70
2.96
2.95
2.94
2.67
2.65
2.64
1.88
1.86
1.85
1.84
1.83
2.02
7.93
1.00
1.01
1.06
1.91
2.03
2.03
2.10
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
(ppm)

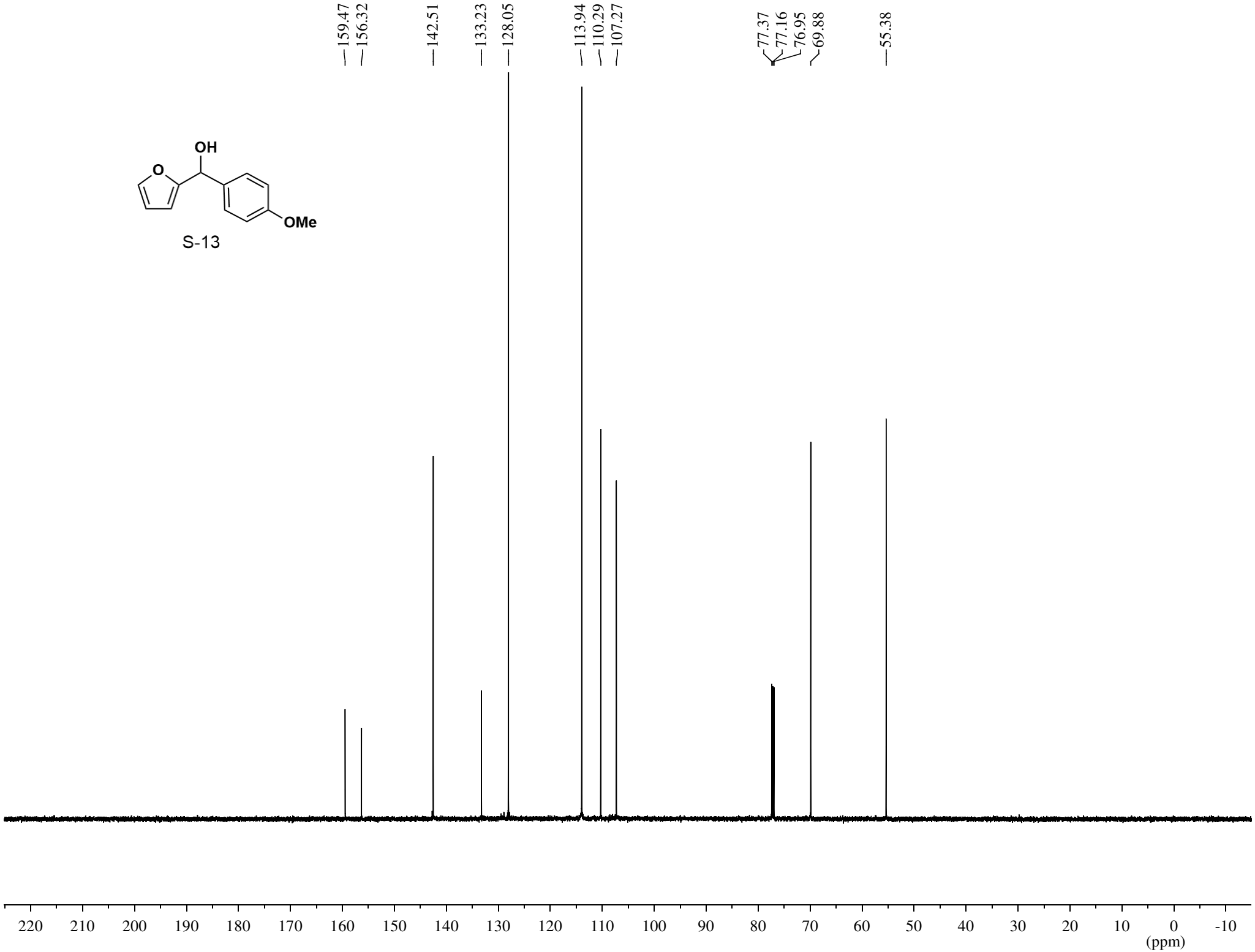
S133

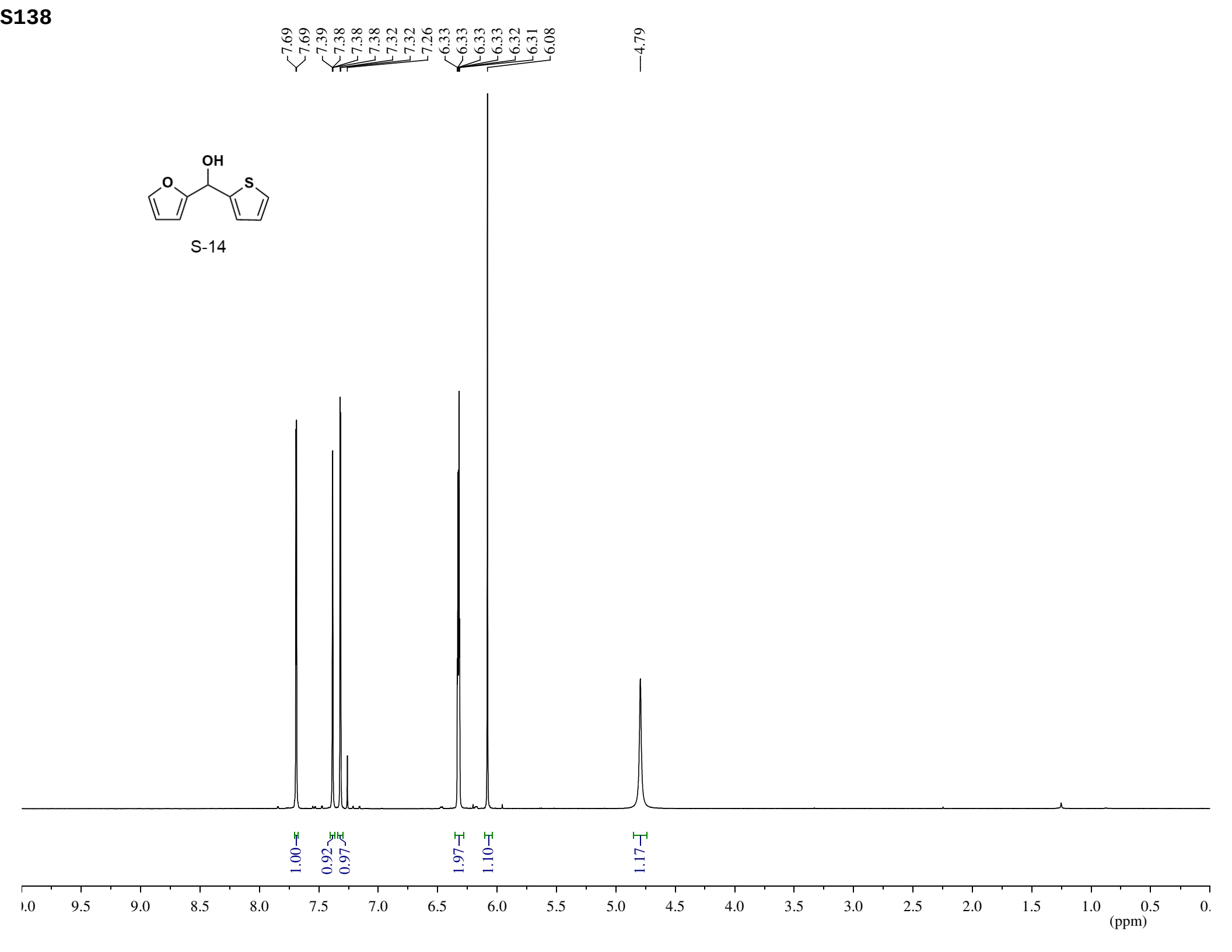

156.0
154.4
141.1
138.0
128.5
128.5
128.5
128.0
127.9
126.7
108.4
105.8
77.4
77.2
76.9
76.4
70.2
51.5
25.8
Bn
O
N
H
O
OH
Ph
S-11
220
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
-10
(ppm)

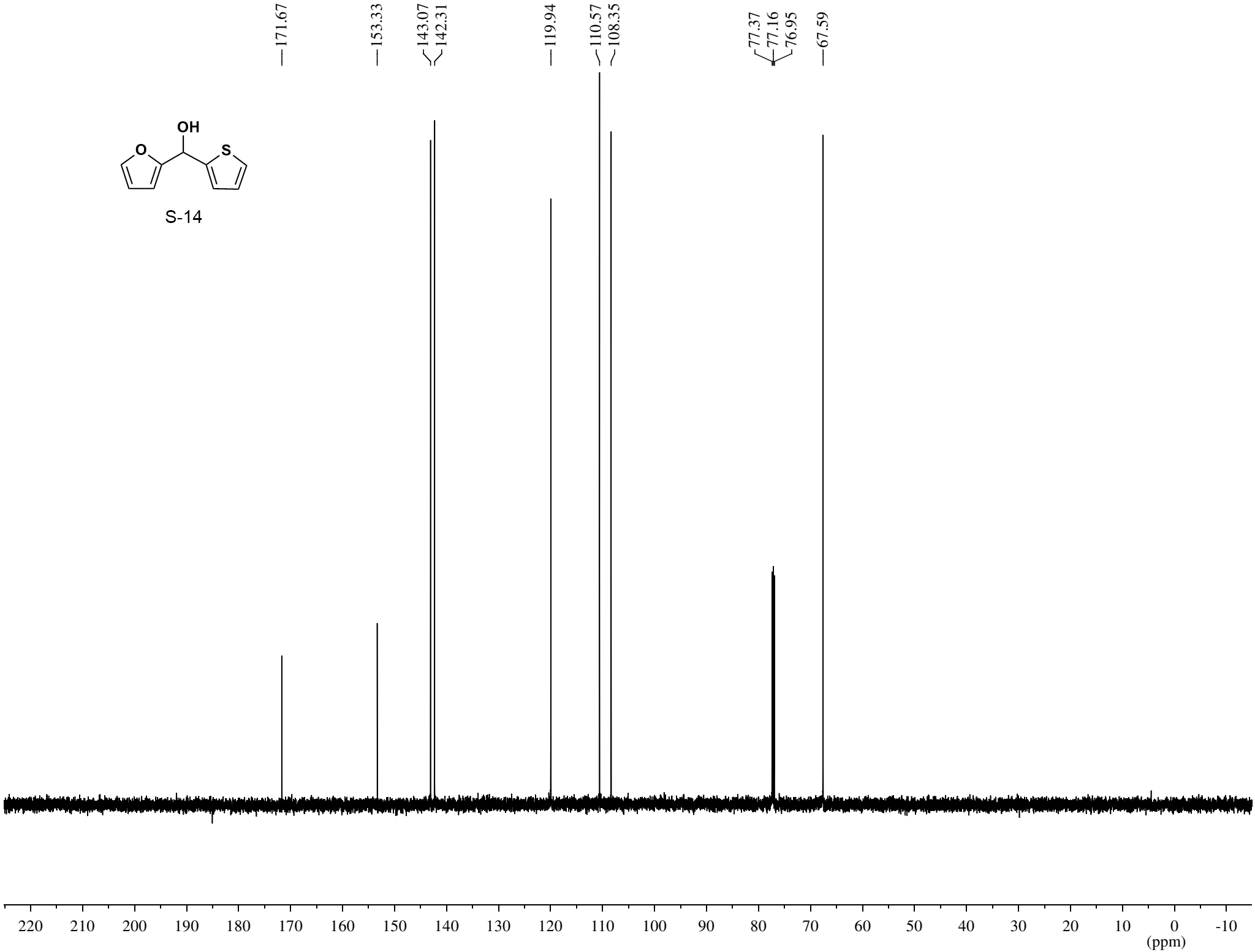

7.66
7.66
7.65
7.64
7.56
7.55
7.39
7.39
7.39
7.26
7.26
6.34
6.33
6.33
6.33
6.15
6.15
5.88
5.87
2.69
OH
O
CN
S-12
2.15
2.18
0.98
1.04
1.00
1.09
1.16
(ppm)


154.7
146.0
143.2
132.4
127.3
118.8
111.8
110.6
108.1
77.4
77.2
76.9
69.4
OH
O
CN
S-12
220
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
-10
(ppm)

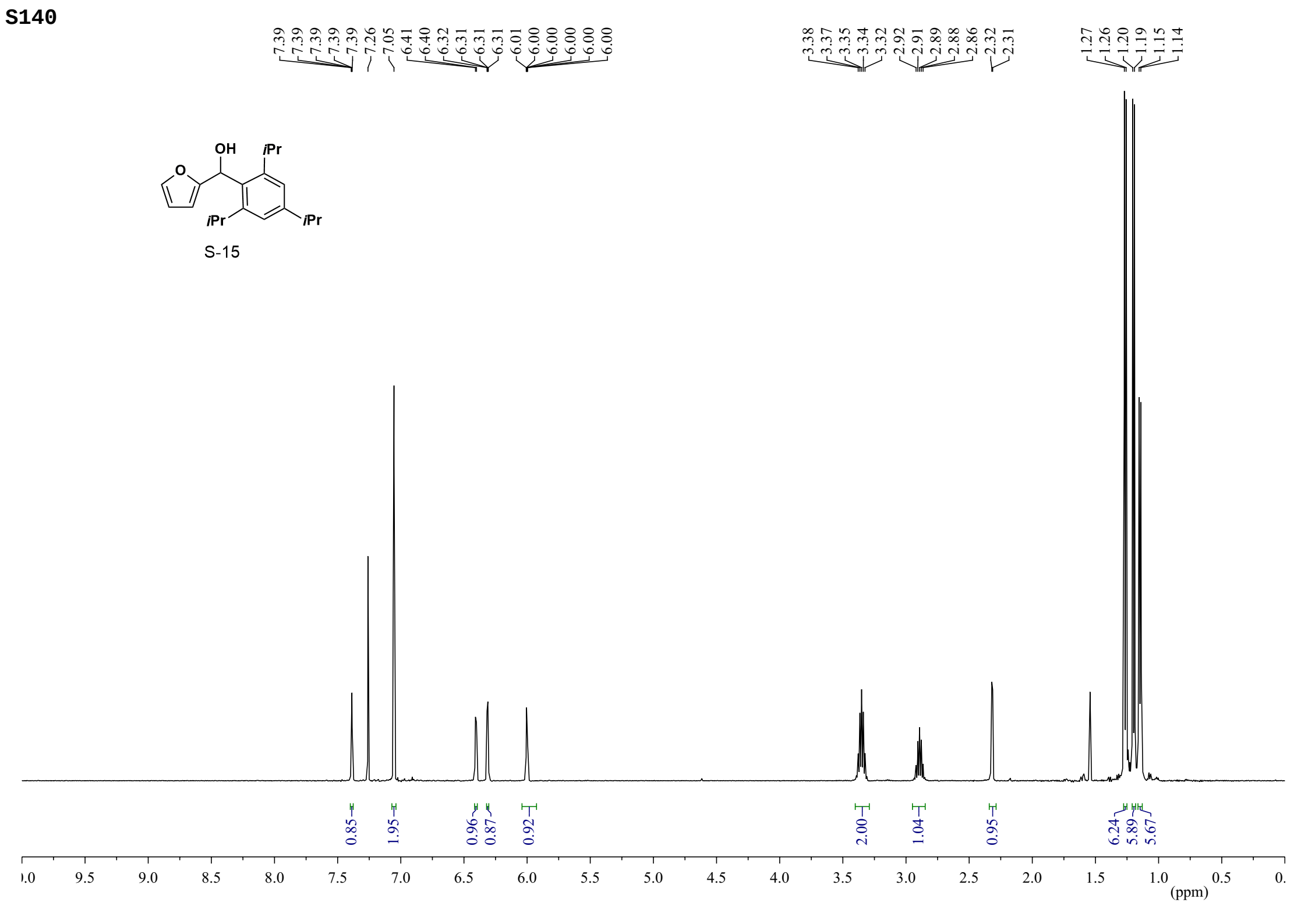

7.38
7.38
7.35
7.34
7.26
6.90
6.89
6.32
6.32
6.31
6.31
6.11
6.11
5.76
3.80
OH
O
OMe
S-13
0.96
2.12
2.17
1.00
0.94
1.05
3.48
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
(ppm)

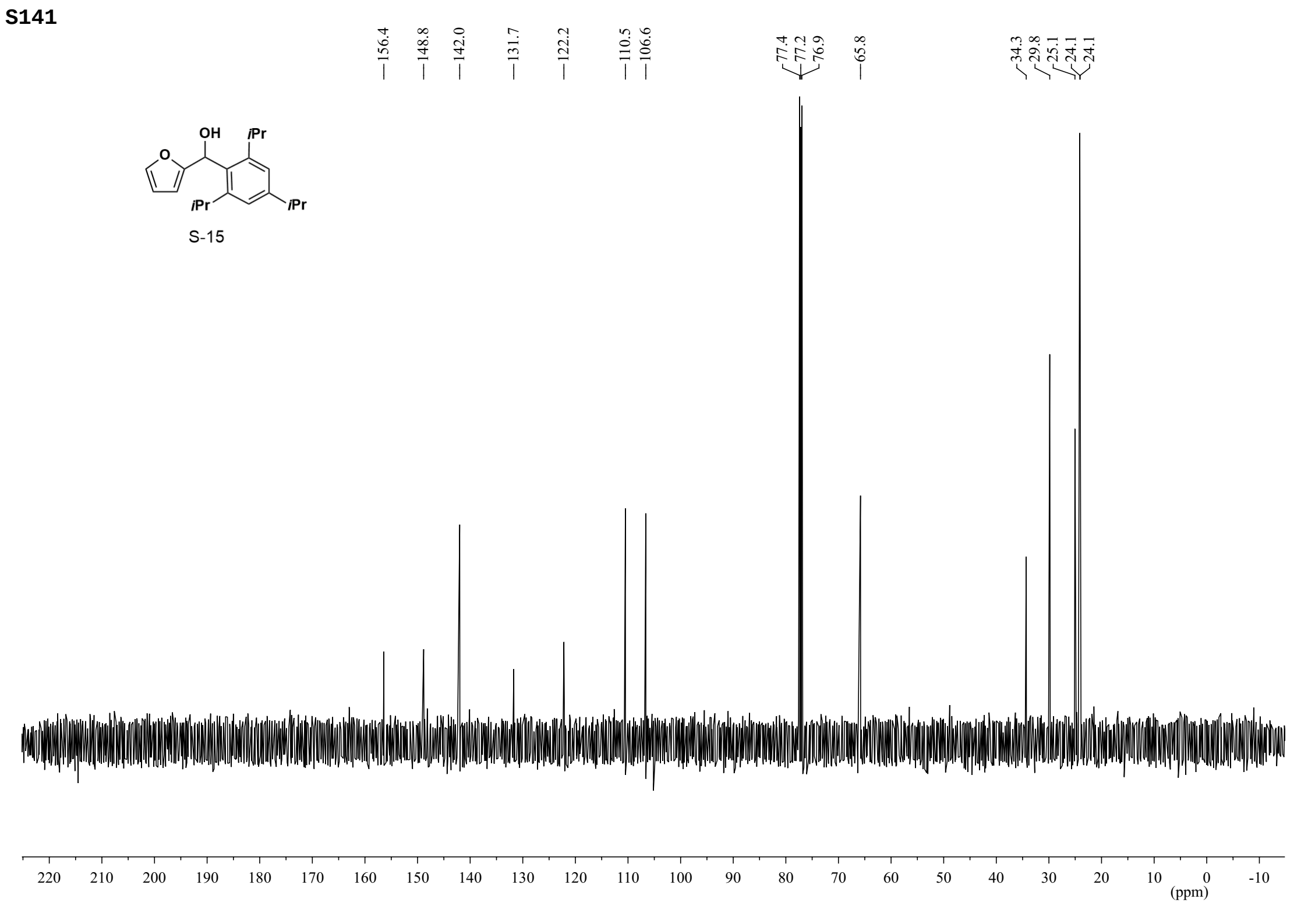

159.47
156.32
142.51
133.23
128.05
113.94
110.29
107.27
77.37
77.16
76.95
69.88
55.38
OH
O
OMe
S-13
220
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
-10
(ppm)

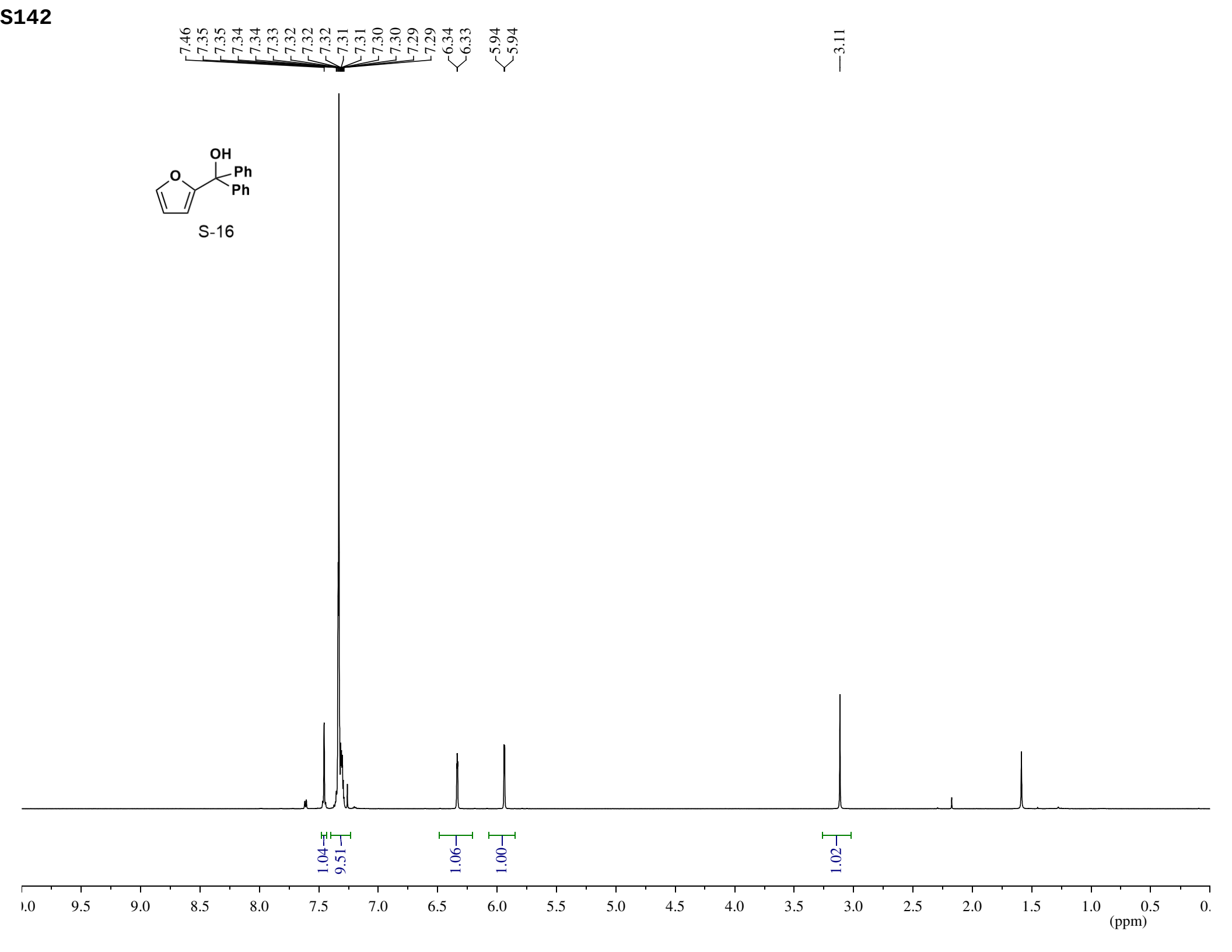

7.69
7.69
7.39
7.38
7.38
7.38
7.32
7.32
7.26
6.33
6.33
6.33
6.33
6.32
6.31
6.08
4.79
OH
O
S
S-14
1.00
0.92
0.97
1.97
1.10
1.17
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
(ppm)

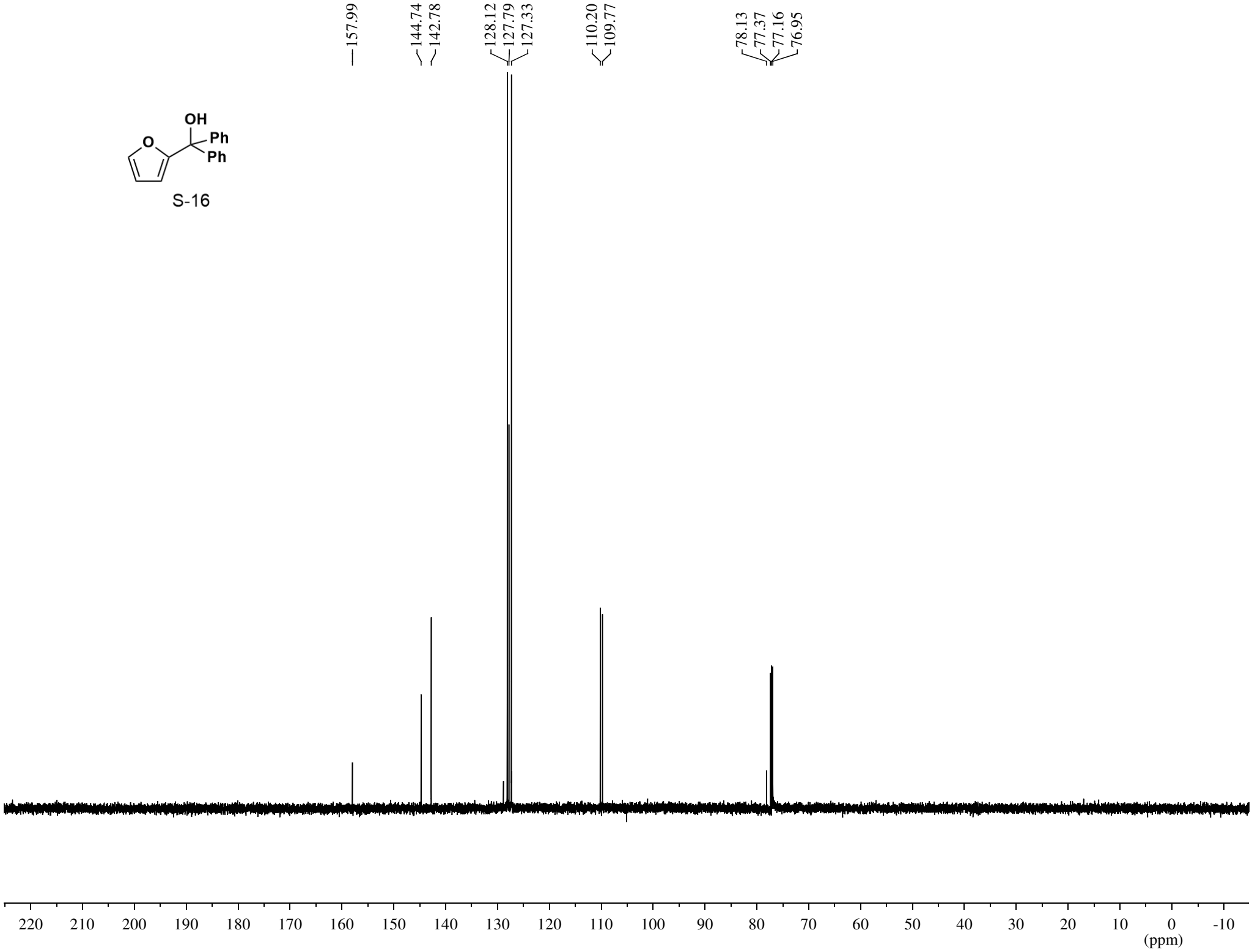

171.67
153.33
143.07
142.31
119.94
110.57
108.35
77.37
77.16
76.95
67.59
OH
O
S
S-14
220
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
-10
(ppm)

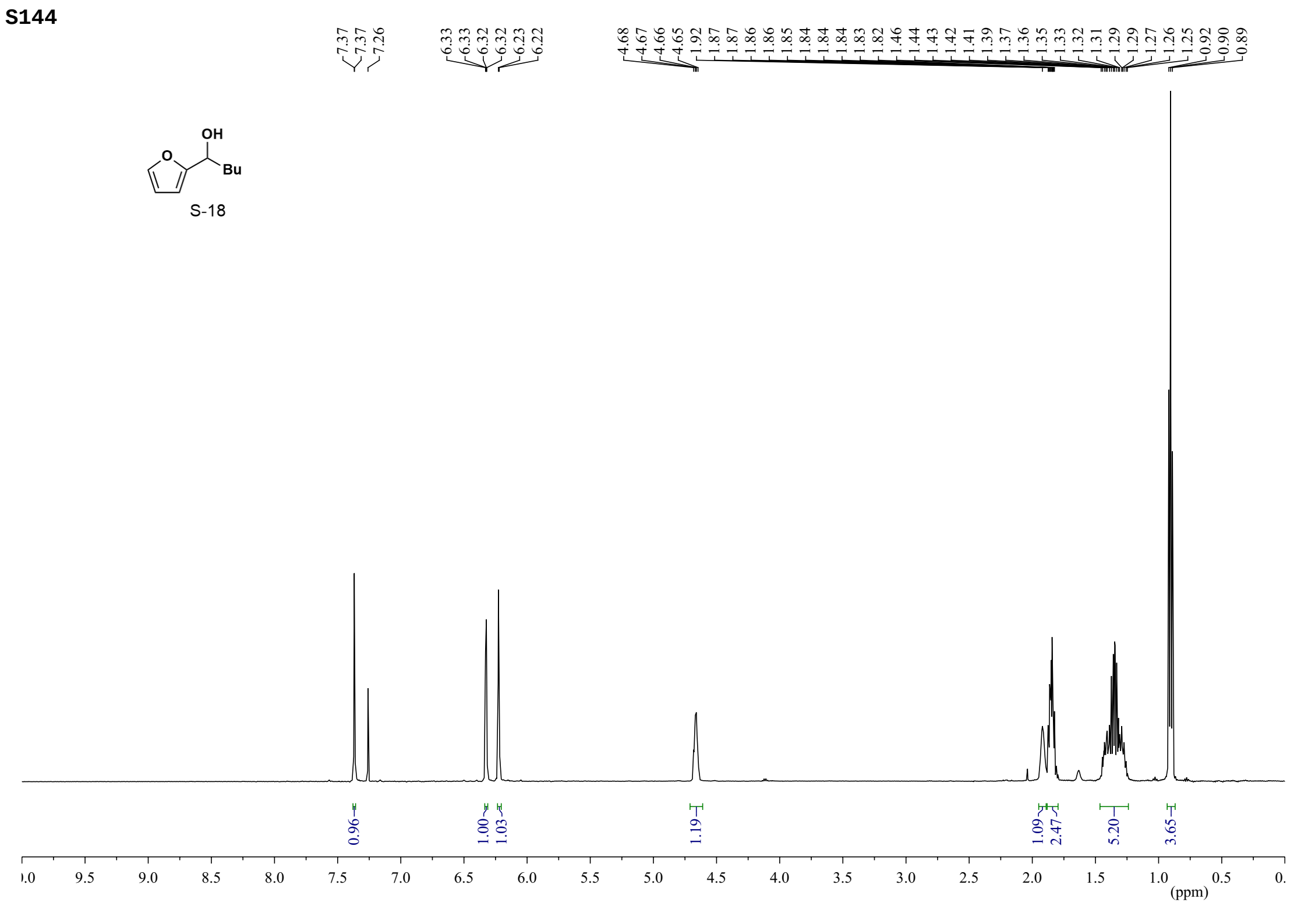
S140

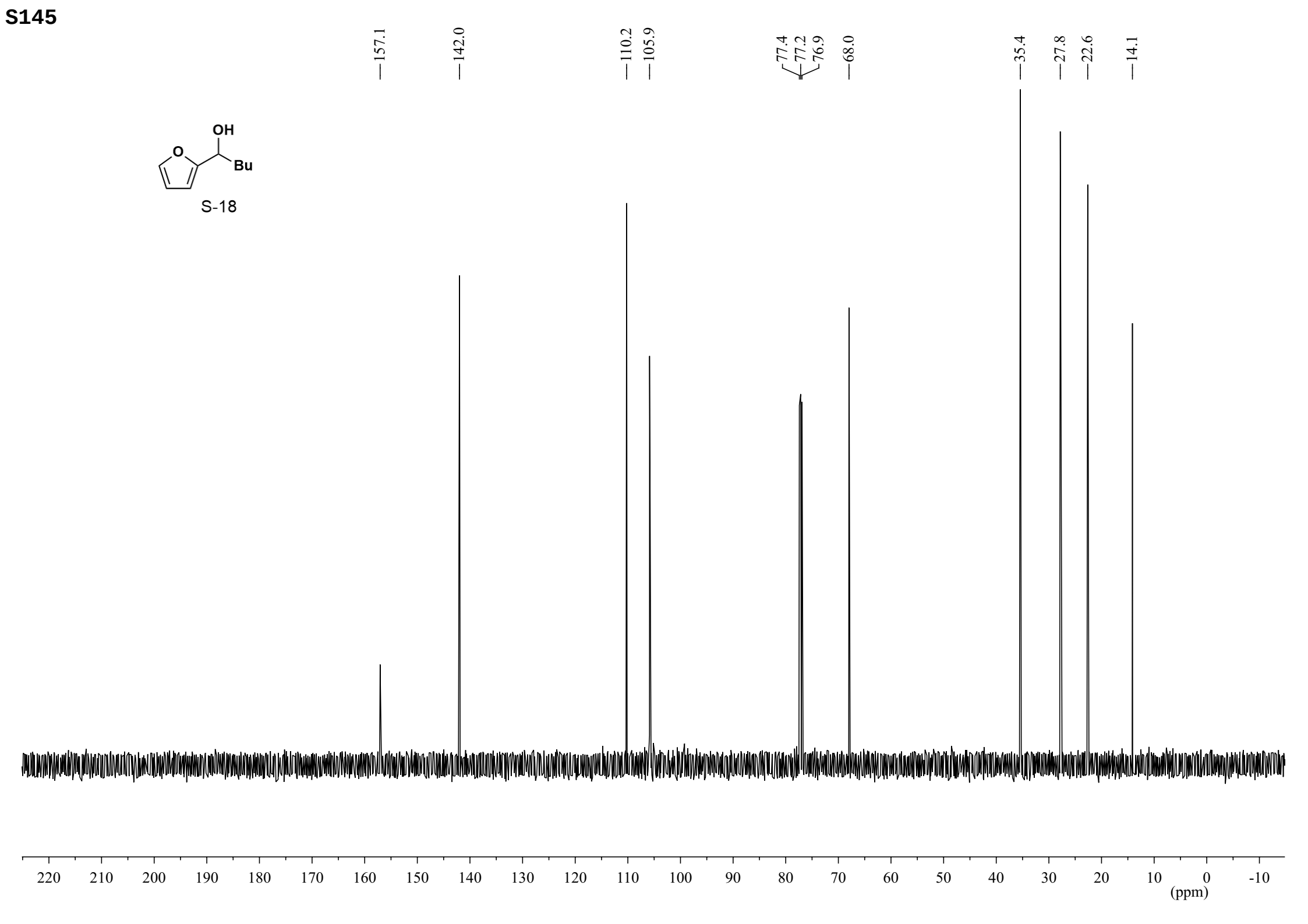

7.39
7.39
7.39
7.39
7.39
7.26
7.05
6.41
6.40
6.32
6.31
6.31
6.31
6.01
6.00
6.00
6.00
6.00
6.00
3.38
3.37
3.35
3.34
3.32
2.92
2.91
2.89
2.88
2.86
2.32
2.31
1.27
1.26
1.20
1.19
1.15
1.14
OH
iPr
iPr
iPr
O
S-15
0.85
1.95
0.96
0.87
0.92
2.00
1.04
0.95
6.24
5.89
5.67
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
(ppm)

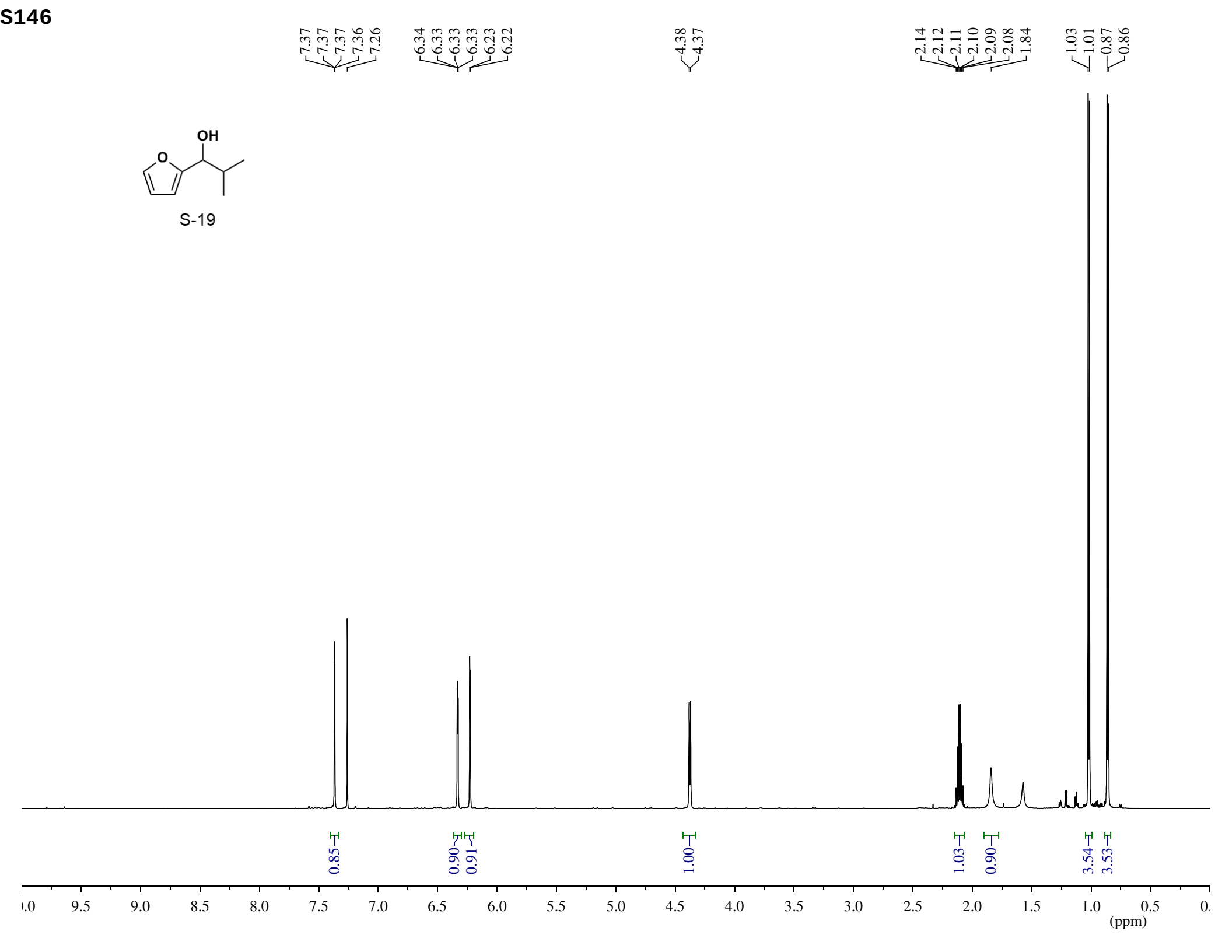

156.4
148.8
142.0
131.7
122.2
110.5
106.6
77.4
77.2
76.9
65.8
34.3
29.8
25.1
24.1
24.1
OH
iPr
iPr
iPr
O
S-15
220
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
-10
(ppm)

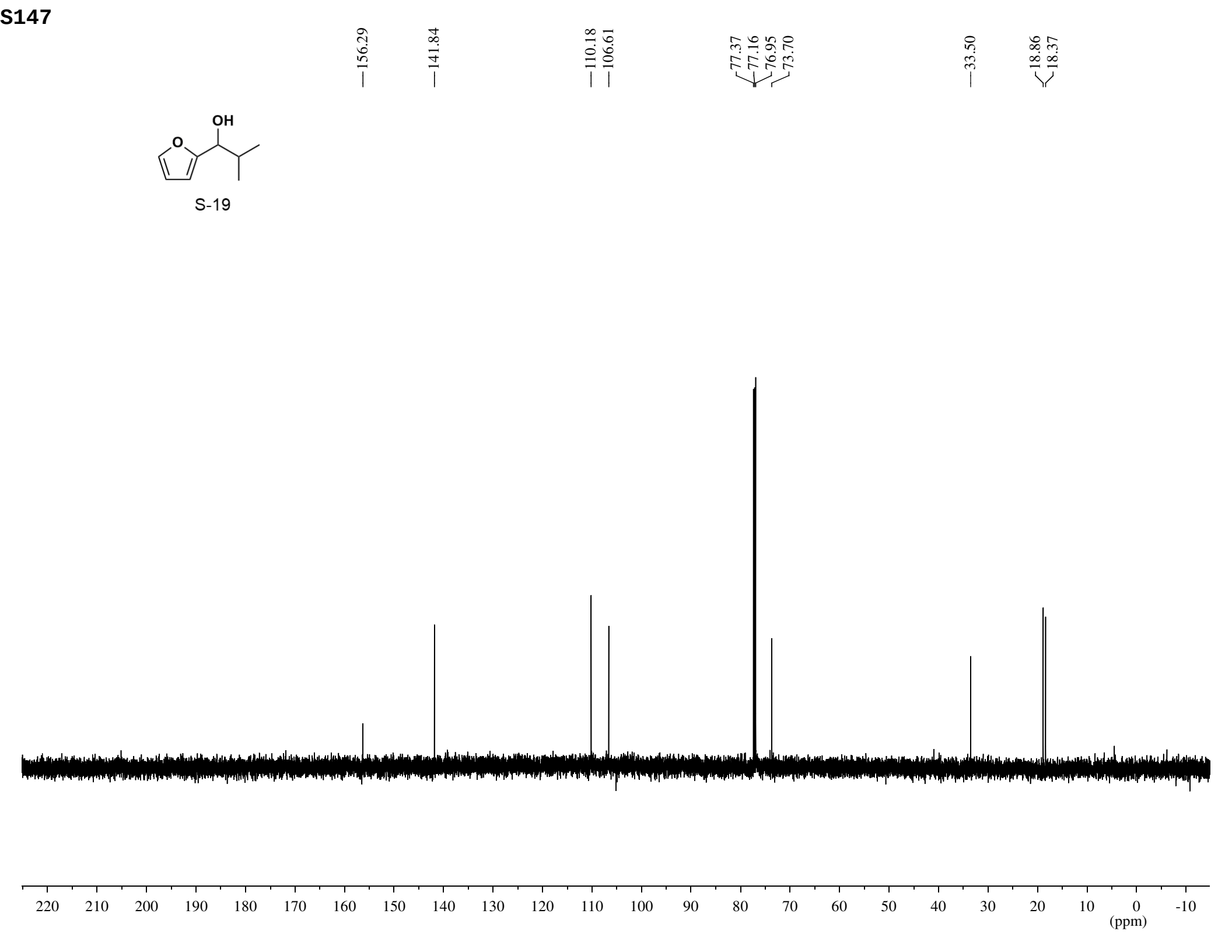

7.46
7.35
7.35
7.34
7.34
7.33
7.32
7.32
7.32
7.31
7.31
7.30
7.30
7.29
7.29
6.34
6.33
5.94
5.94
3.11
OH
Ph
Ph
O
S-16
1.04
9.51
1.06
1.00
1.02
(ppm)

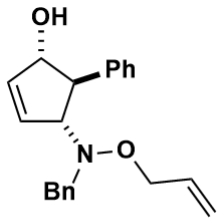

157.99
144.74
142.78
128.12
127.79
127.33
110.20
109.77
78.13
77.37
77.16
76.95
OH
Ph
Ph
O
S-16
220
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
-10
(ppm)


7.37
7.37
7.26
6.33
6.33
6.32
6.32
6.23
6.22
4.68
4.67
4.66
4.65
1.92
1.87
1.87
1.86
1.86
1.85
1.84
1.84
1.84
1.83
1.82
1.46
1.44
1.43
1.42
1.41
1.39
1.37
1.36
1.35
1.33
1.32
1.31
1.29
1.29
1.27
1.26
1.25
0.92
0.90
0.89
OH
O
Bu
S-18
0.96
1.00
1.03
1.19
1.09
2.47
5.20
3.65
(ppm)


157.1
142.0
110.2
105.9
77.4
77.2
76.9
68.0
35.4
27.8
22.6
14.1
OH
O
Bu
S-18
220
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
-10
(ppm)

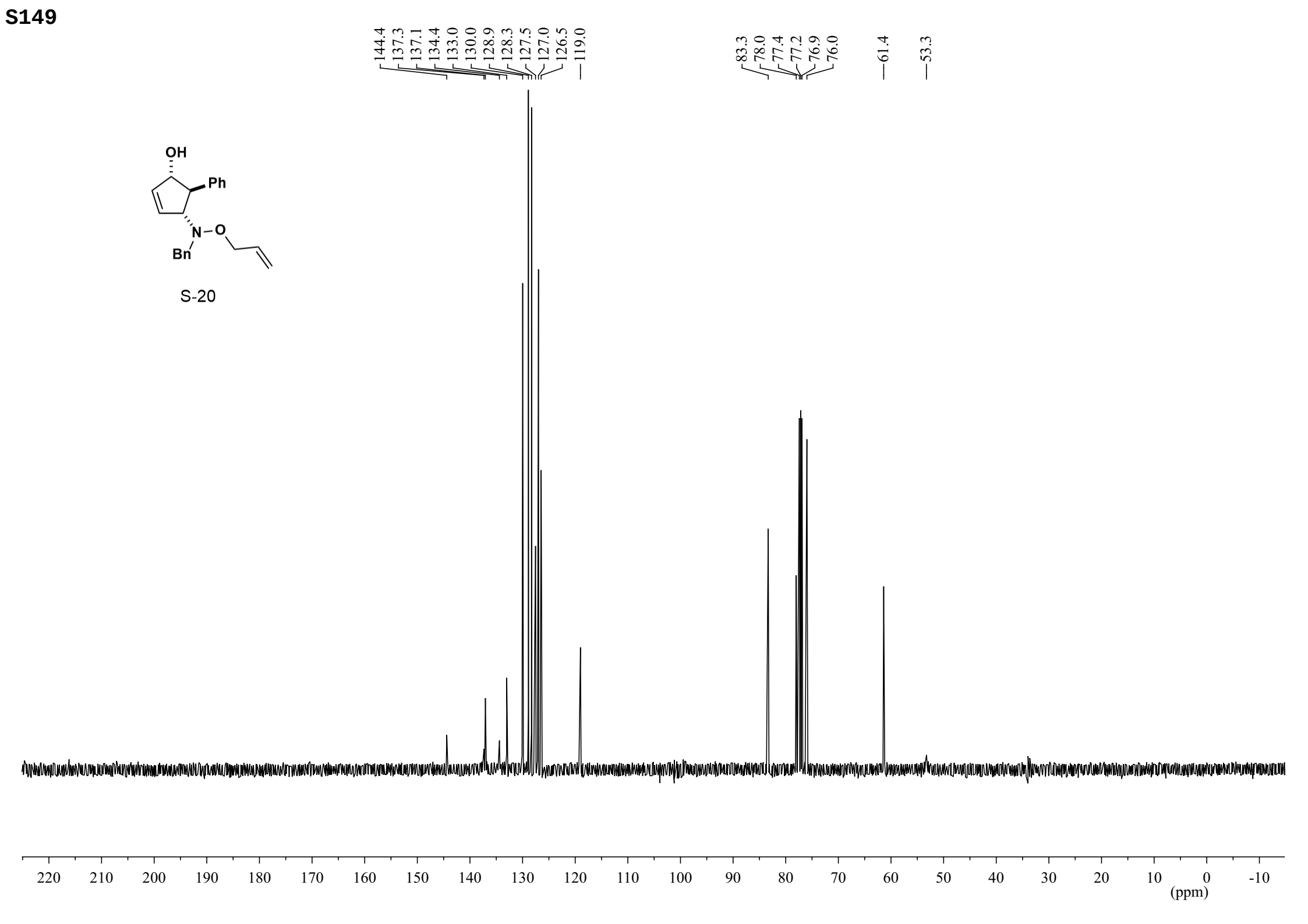

7.37
7.37
7.37
7.36
7.26
6.34
6.33
6.33
6.33
6.23
6.22
4.38
4.37
2.14
2.12
2.11
2.10
2.09
2.08
1.84
1.03
1.01
0.87
0.86
OH
O
S-19
0.85
0.90
0.91
1.00
1.03
0.90
3.54
3.53
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
(ppm)


156.29
141.84
110.18
106.61
77.37
77.16
76.95
73.70
33.50
18.86
18.37
OH
O
S-19
220
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
-10
(ppm)

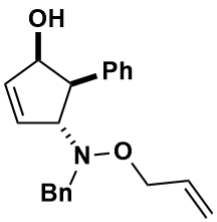

OH
Ph
N
O
Bn

S-20

7.31 7.29 7.28 7.26 7.23 7.21 7.20 7.17 7.15
6.20 6.19 6.19 6.19 6.18 6.18 6.12 6.12 6.11 6.11 6.09
5.74 5.72 5.72 5.71 5.70 5.69 5.68 5.68 5.67 5.66 5.16 5.16 5.16 5.15 5.12 5.11 5.10 5.10
4.49 4.47 4.05 4.03 3.95 3.94 3.93 3.91 3.88 3.88 3.87 3.86 3.82 3.80 3.43 2.65
2.23 4.90 1.18 2.09 1.00 1.06 1.04 0.53 0.96 0.49 1.09 1.05 1.12 2.12 1.22 1.06 0.95
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
(ppm)

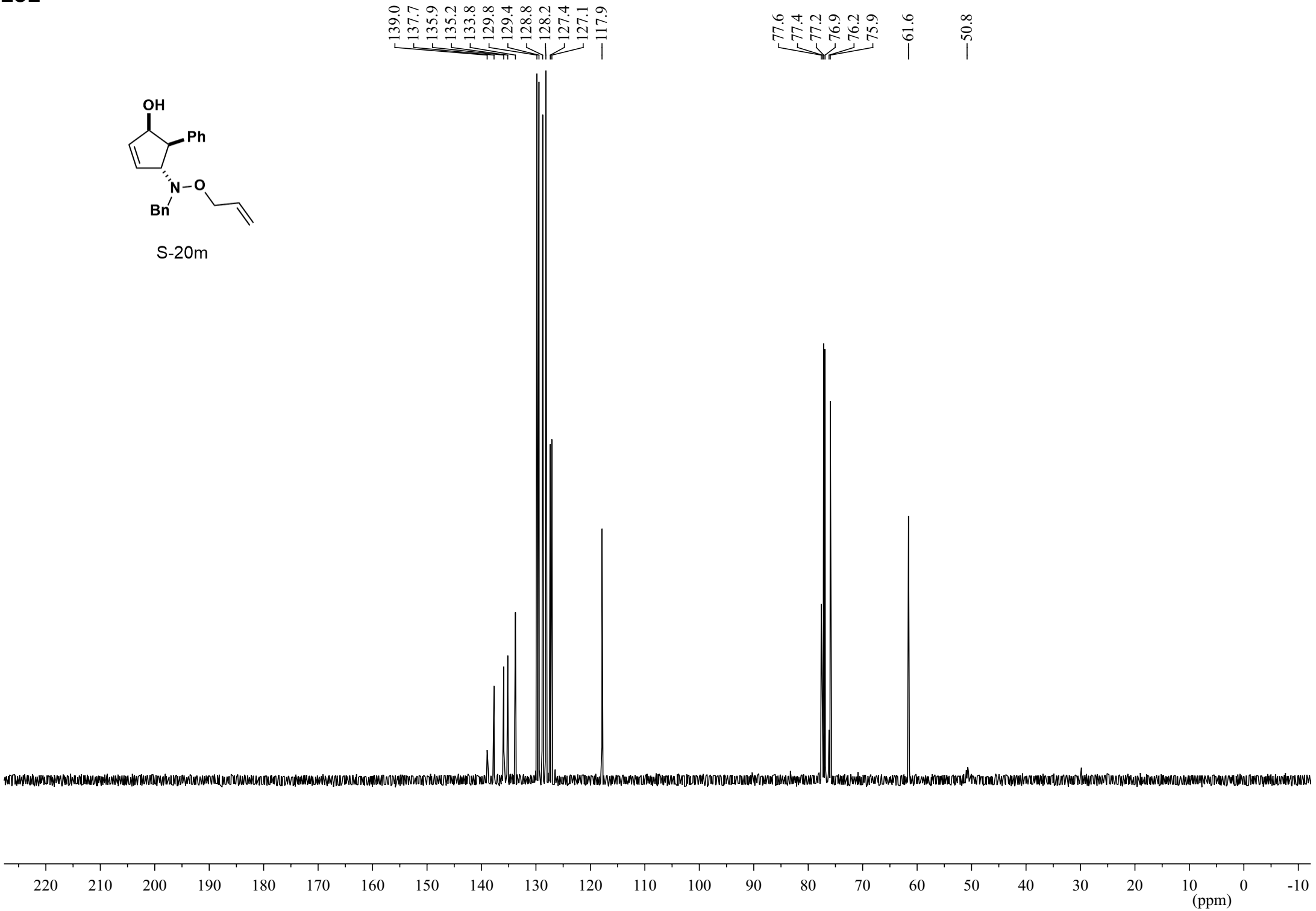

144.4
137.3
137.1
134.4
133.0
130.0
128.9
128.3
127.5
127.0
126.5
119.0
83.3
78.0
77.4
77.2
76.9
76.0
61.4
53.3
OH
Ph
N
O
Bn
S-20
220
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
-10
(ppm)

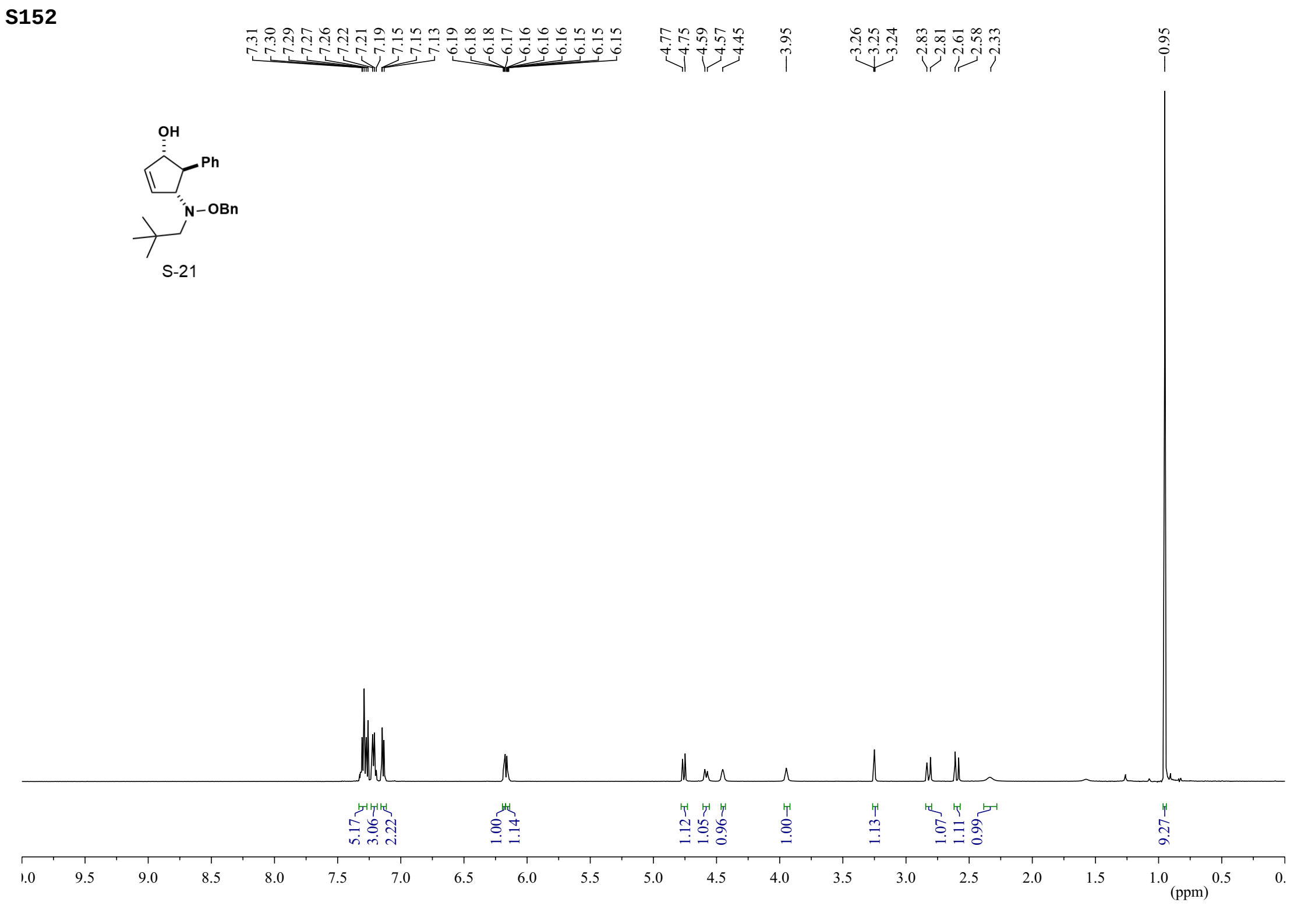
S150

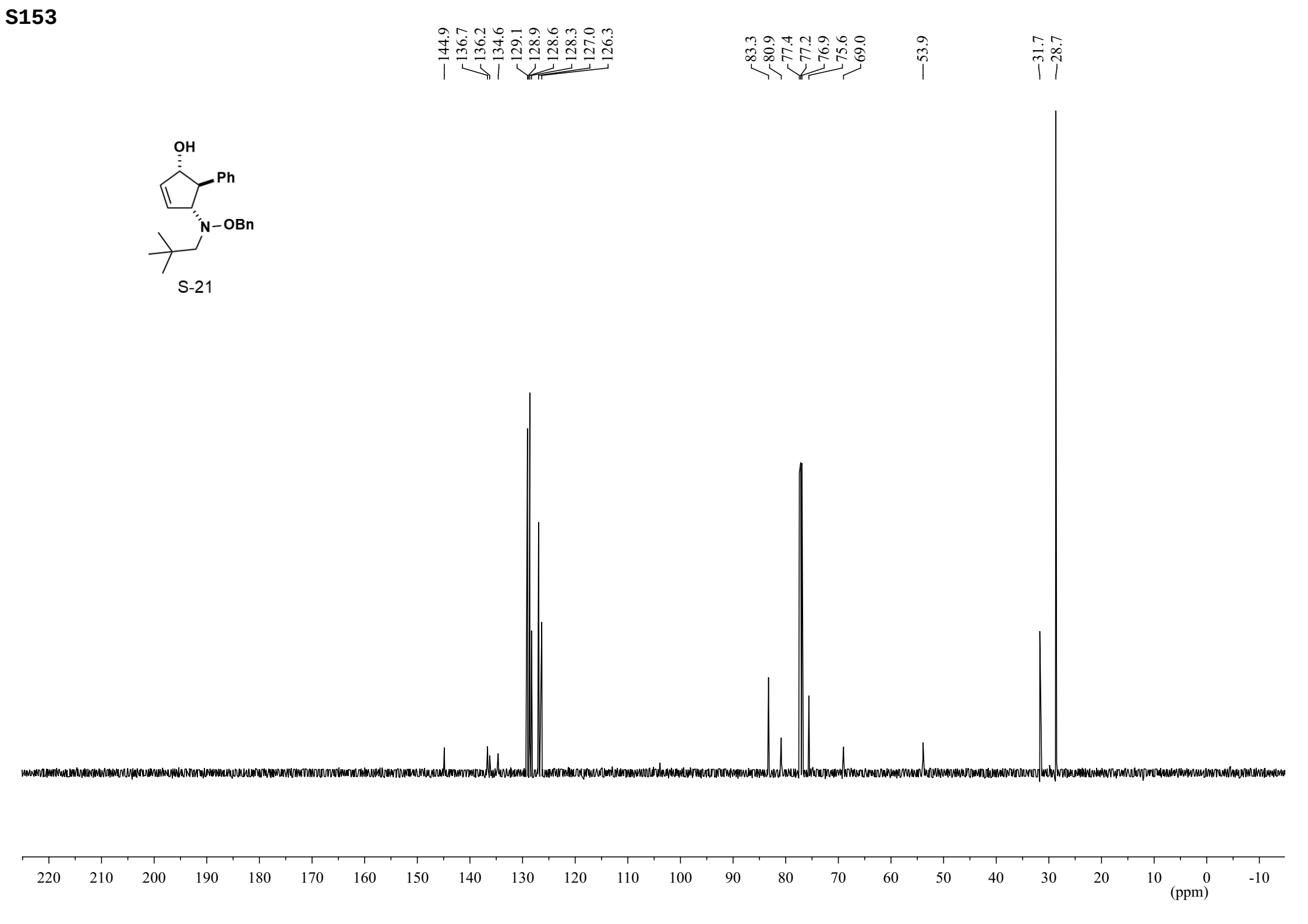

OH
Ph
N
O
Bn

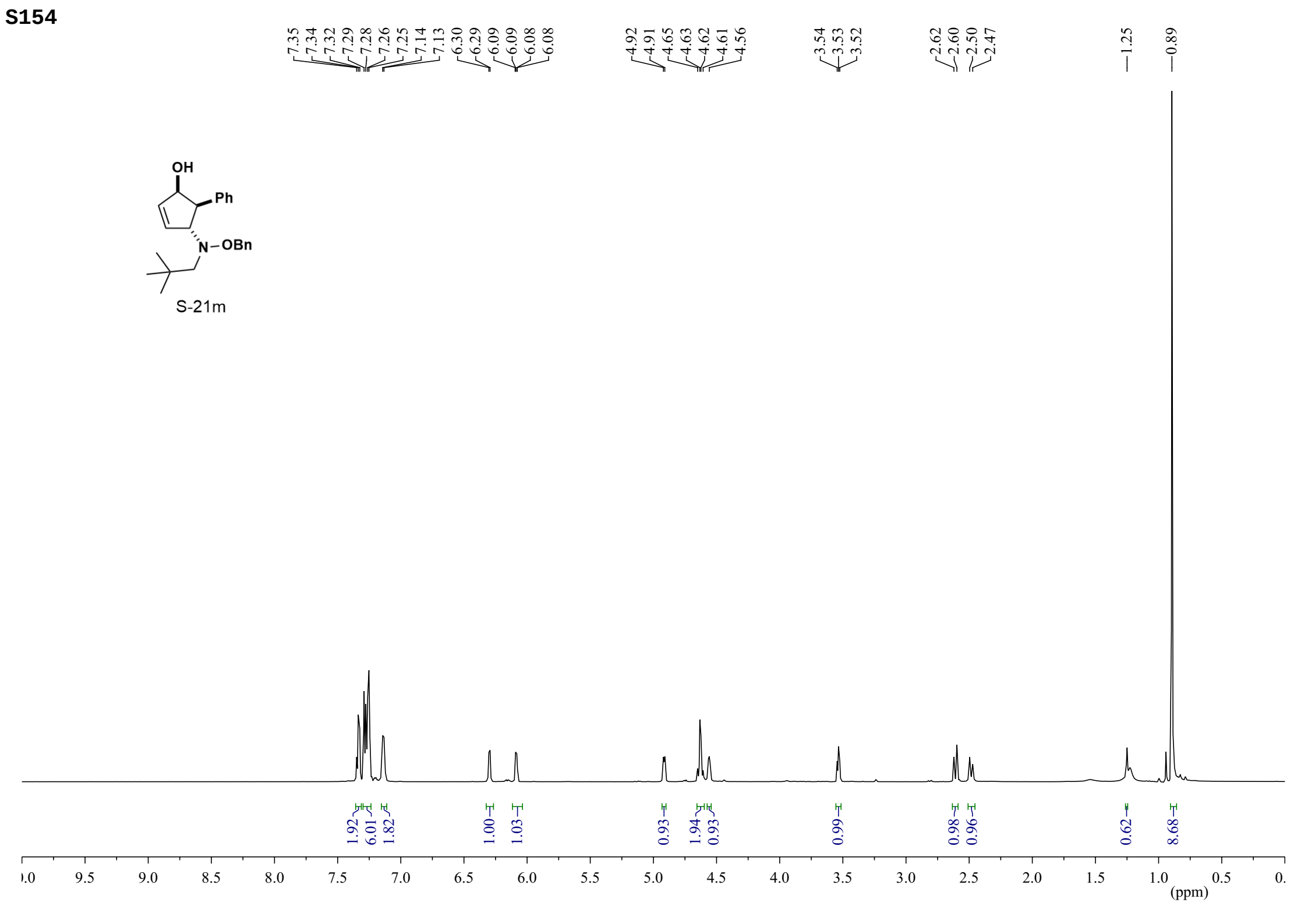
S-20m

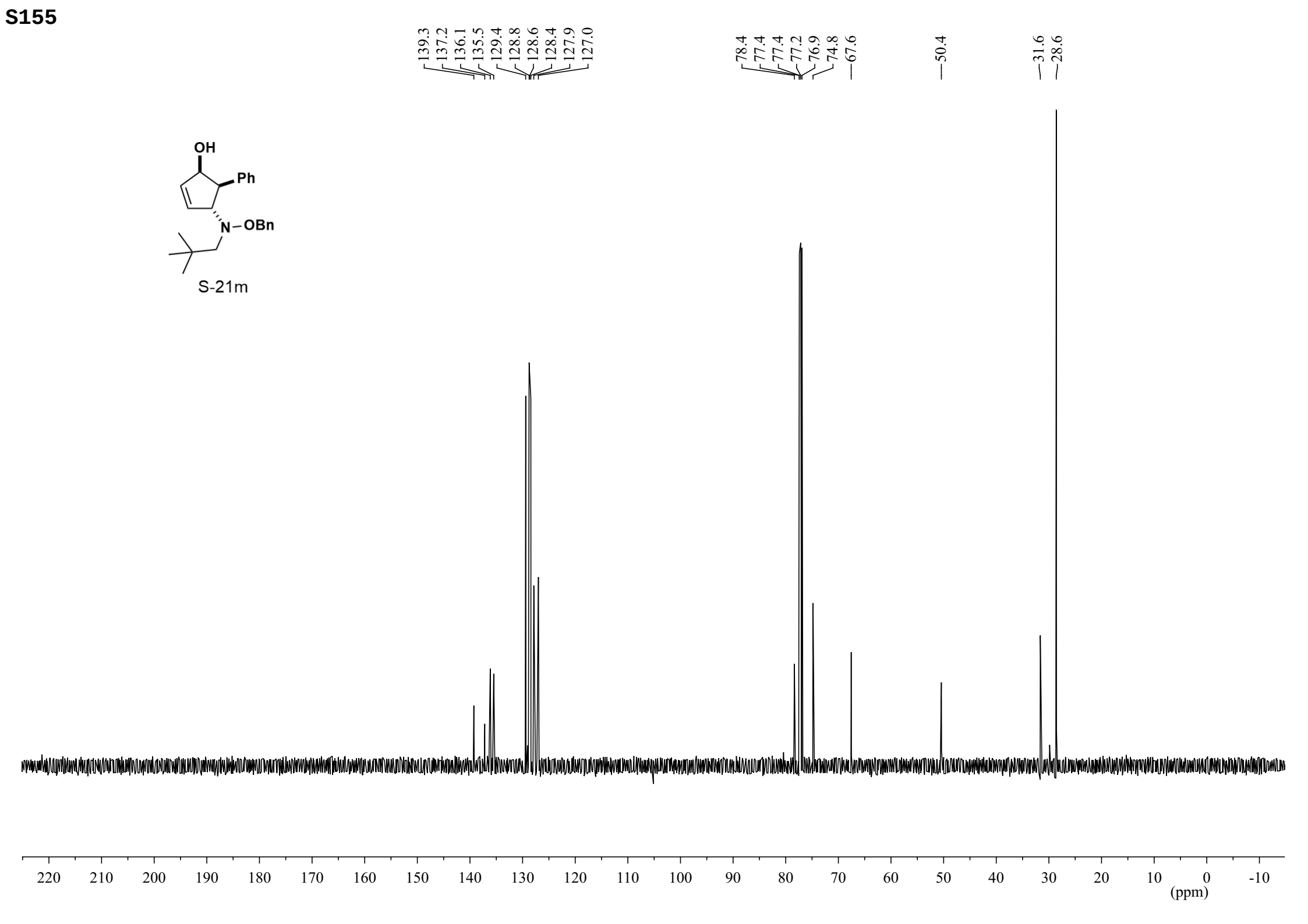
7.34
7.33
7.32
7.28
7.26
7.25
7.23
7.22
6.27
6.27
6.09
6.08
5.66
5.65
5.65
5.64
5.64
5.62
5.62
5.61
5.61
5.60
5.05
5.03
5.02
5.02
4.93
4.92
4.39
4.39
4.39
4.38
4.38
3.87
3.85
3.75
3.73
1.26
1.24
2.04
8.16
1.00
1.03
1.01
1.94
0.97
1.04
3.08
2.06
1.62
(ppm)


139.0
137.7
135.9
135.2
133.8
129.8
129.4
128.8
128.2
127.4
127.1
117.9
77.6
77.4
77.2
76.9
76.2
75.9
61.6
50.8
OH
Ph
N
O
Bn
S-20m
220
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
-10
(ppm)

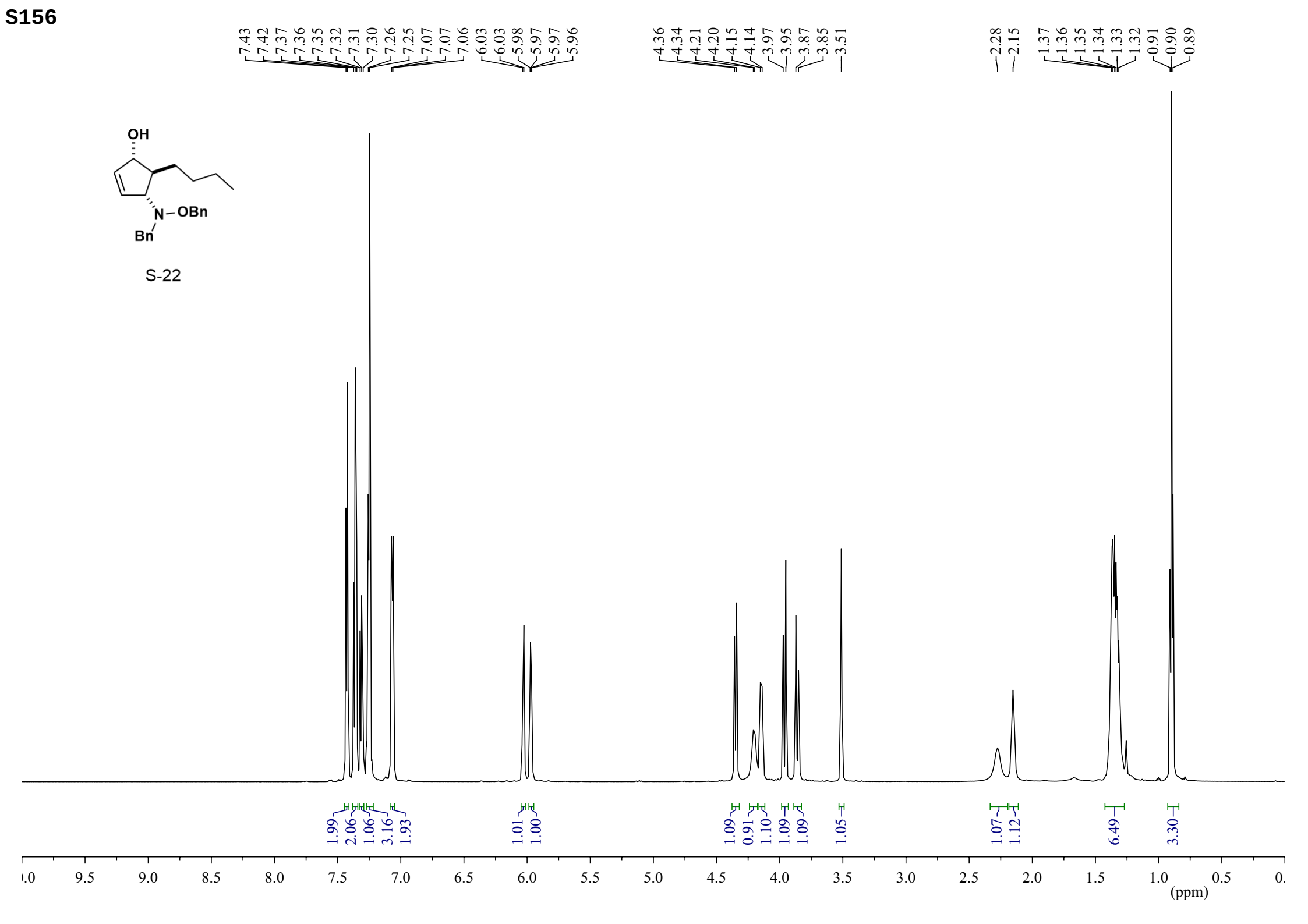

7.31
7.30
7.29
7.27
7.26
7.22
7.21
7.19
7.15
7.15
7.13
6.19
6.18
6.18
6.17
6.16
6.16
6.16
6.15
6.15
6.15
4.77
4.75
4.59
4.57
4.45
3.95
3.26
3.25
3.24
2.83
2.81
2.61
2.58
2.33
0.95
OH
Ph
N–OBn
S-21
5.17
3.06
2.22
1.00
1.14
1.12
1.05
0.96
1.00
1.13
1.07
1.11
0.99
9.27
(ppm)


144.9
136.7
136.2
134.6
129.1
128.9
128.6
128.3
127.0
126.3
83.3
80.9
77.4
77.2
76.9
75.6
69.0
53.9
31.7
28.7
OH
Ph
N–OBn
S-21
220
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
-10
(ppm)

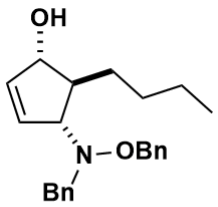

7.35
7.34
7.32
7.29
7.28
7.26
7.25
7.14
7.13
6.30
6.29
6.09
6.09
6.08
6.08
4.92
4.91
4.65
4.63
4.62
4.61
4.56
3.54
3.53
3.52
2.62
2.60
2.50
2.47
1.25
0.89
OH
Ph
N–OBn
S-21m
1.92
6.01
1.82
1.00
1.03
0.93
1.94
0.93
0.99
0.98
0.96
0.62
8.68
(ppm)


139.3
137.2
136.1
135.5
129.4
128.8
128.6
128.4
127.9
127.0
78.4
77.4
77.4
77.2
76.9
74.8
67.6
50.4
31.6
28.6
OH
Ph
N–OBn
S-21m
220
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
-10
(ppm)

S156


7.43
7.42
7.37
7.36
7.35
7.32
7.31
7.30
7.26
7.25
7.07
7.07
7.06
6.03
6.03
5.98
5.97
5.97
5.96
4.36
4.34
4.21
4.20
4.15
4.14
3.97
3.95
3.87
3.85
3.51
2.28
2.15
1.37
1.36
1.35
1.34
1.33
1.32
0.91
0.90
0.89
OH
N–OBn
Bn
S-22
1.99
2.06
1.06
3.16
1.93
1.01
1.00
1.09
0.91
1.10
1.09
1.09
1.05
1.07
1.12
6.49
3.30
(ppm)

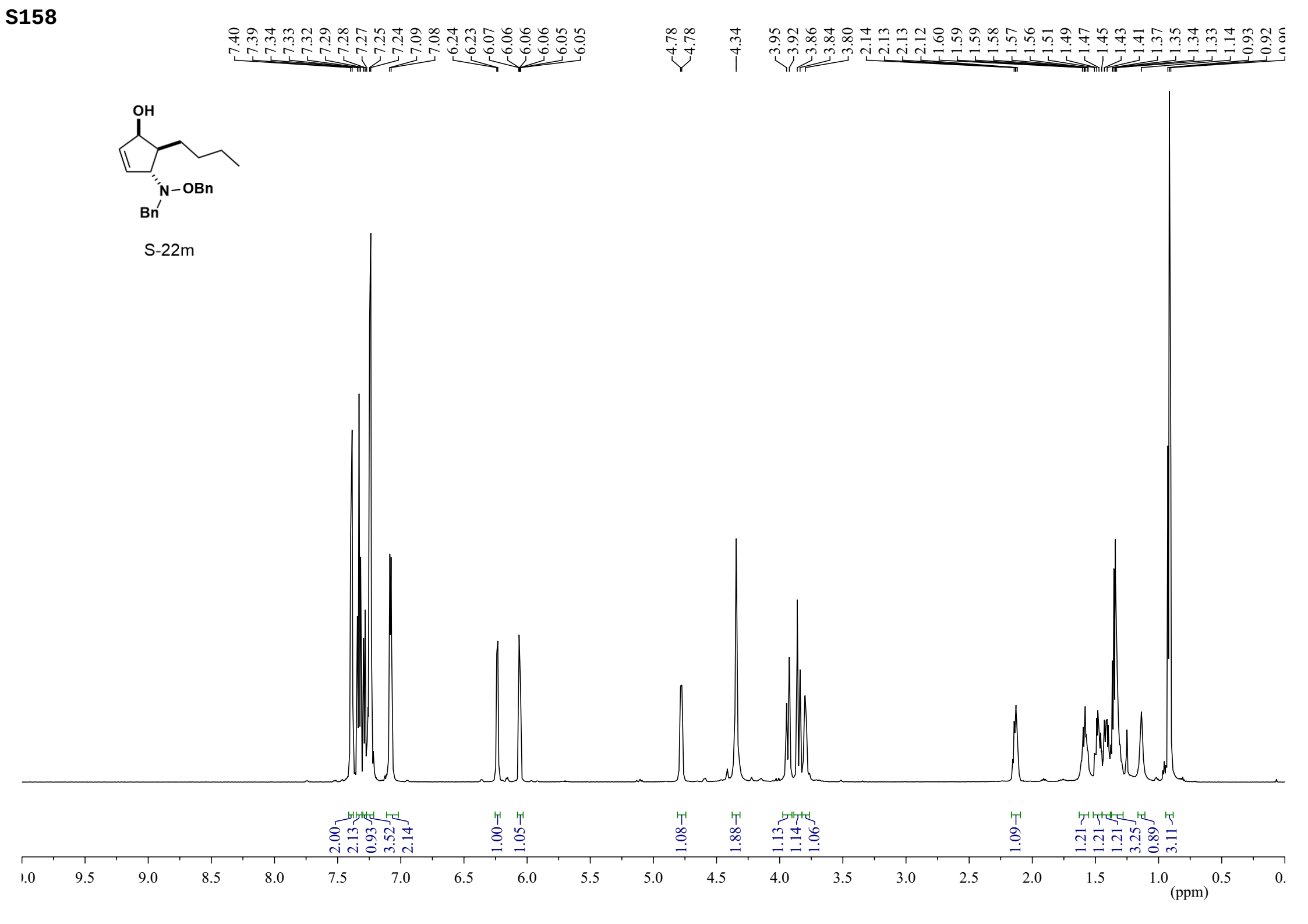
S157

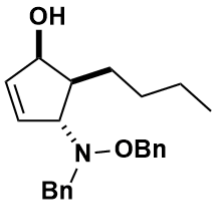

OH
N–OBn
Bn

S-22

137.9
136.7
136.1
133.0
130.0
129.5
128.5
128.4
128.3
127.6
80.9
77.4
77.2
77.2
76.9
76.1
61.3
46.9
33.6
30.1
23.0
14.2
220
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
-10
(ppm)

S158

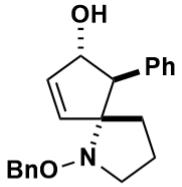

7.40
7.39
7.34
7.33
7.32
7.29
7.28
7.27
7.25
7.24
7.09
7.08
6.24
6.23
6.07
6.06
6.06
6.06
6.05
6.05
4.78
4.78
4.34
3.95
3.92
3.86
3.84
3.80
2.14
2.13
2.13
2.12
1.60
1.59
1.59
1.58
1.57
1.56
1.51
1.49
1.47
1.45
1.43
1.41
1.37
1.35
1.34
1.33
1.14
0.93
0.92
OH
N–OBn
Bn
S-22m
2.00
2.13
0.93
3.52
2.14
1.00
1.05
1.08
1.88
1.13
1.14
1.06
1.09
1.21
1.21
1.21
3.25
0.89
3.11
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
(ppm)


OH
N–OBn
Bn

S-22m

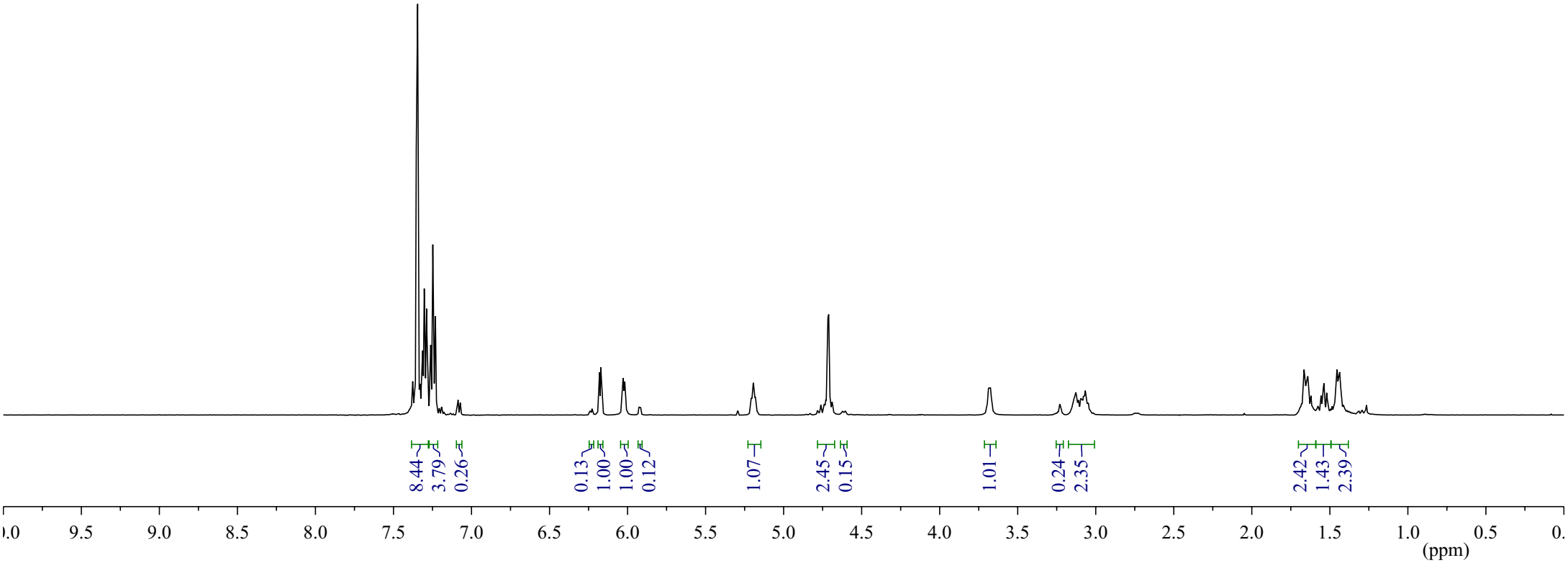
138.3
137.2
136.0
134.7
129.8
129.1
128.3
127.9
127.4
77.4
77.2
76.9
76.7
76.2
76.1
60.3
44.6
31.0
27.5
23.2
14.3
220
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
-10
(ppm)

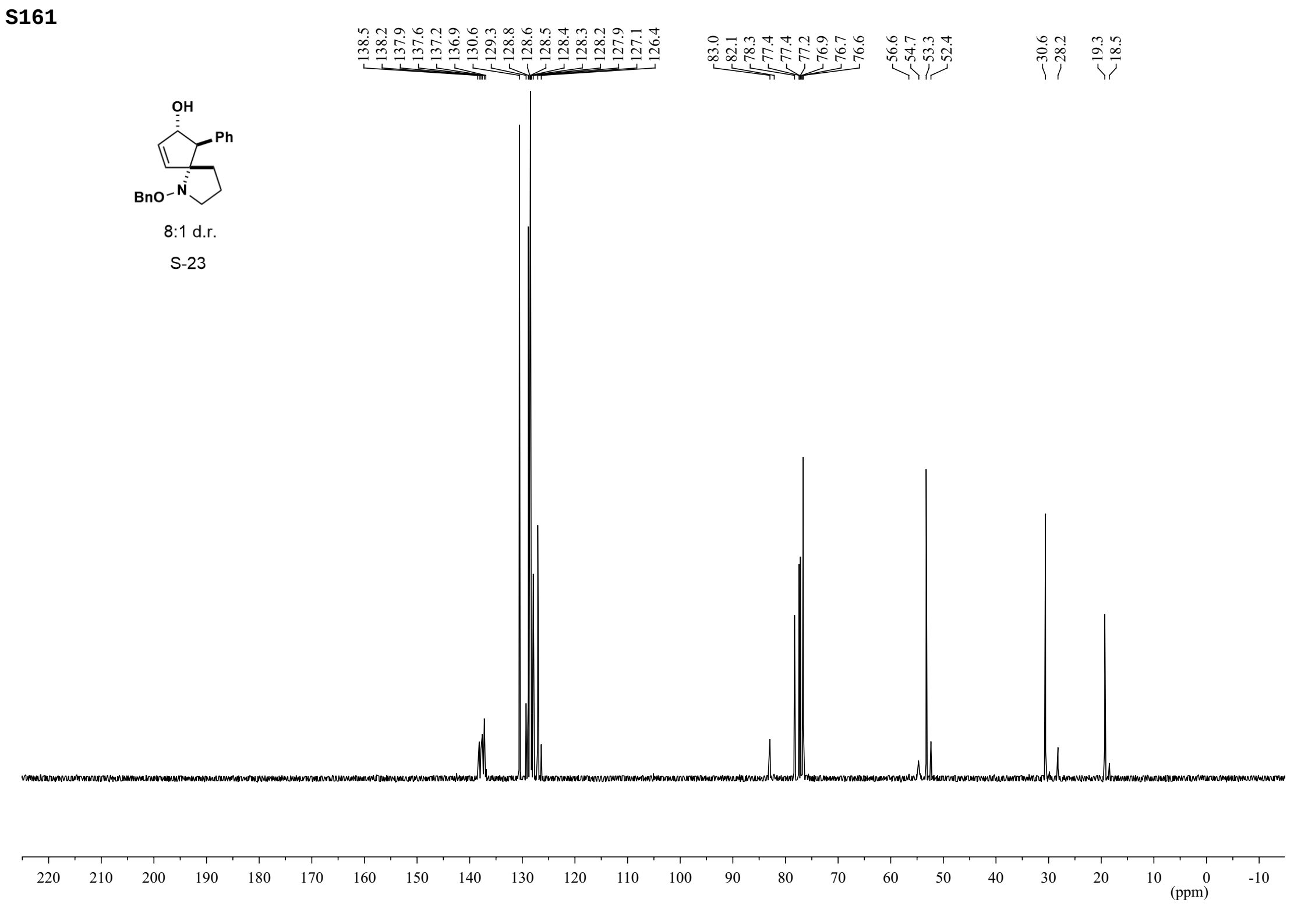
S160



8:1 d.r.

S-23




138.5
138.2
137.9
137.6
137.2
136.9
130.6
129.3
128.8
128.6
128.5
128.4
128.3
128.2
127.9
127.1
126.4
83.0
82.1
78.3
77.4
77.4
77.2
76.9
76.7
76.6
56.6
54.7
53.3
52.4
30.6
28.2
19.3
18.5
OH
Ph
BnO
N
8:1 d.r.
S-23
220
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
-10
(ppm)