Supporting Information

Copper-Catalyzed, Stereoselective Cross-Coupling of Cyclic Allyl Boronic Acids with α-Diazoketones

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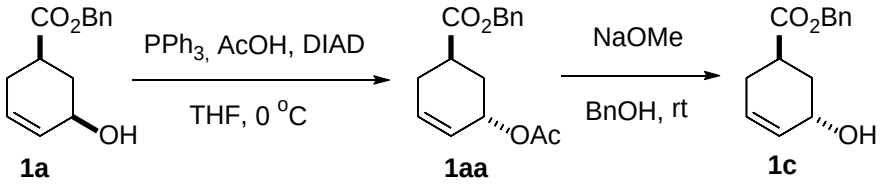
Contents:

General Information

All reactions were carried out under argon atmosphere. α-Diazoketones **3a-f**,[1, 2] *cis*- cyclic allyl alcohols **1a**,[3] **1b**,[4] and *trans*- cyclic allyl alcohol **1d** [5] were prepared according to published literature procedures. All other starting materials were obtained from commercial sources and used as received. ^{1}H NMR and ^{13}C NMR spectra were recorded in $CDCl_3$ (internal standard: 7.26 ppm, ^{1}H; 77.0 ppm, ^{13}C), DMSO-d_6 (internal standard: 2.50 ppm, ^{1}H; 39.5 ppm, ^{13}C) and acetone-d_6 (internal standard: 2.05 ppm, ^{1}H) using Brucker 400 MHz and 500 MHz spectrometers. The following abbreviations are used to designate signal multiplicity: s = singlet, d = doublet, t = triplet, q = quartet, m = multiplet, dd = doublet of doublet, ddd = doublet of doublet of doublet, dddd = doublet of doublet of doublet of doublet, dddt = doublet of doublet of doublet of triplet, dt = doublet of triplet, td = triplet of doublet, ddt = doublet of doublet of triplet, ddq = doublet of doublet of quartet, dtd = doublet of triplet of doublet, dtt = doublet of triplet of triplet, br = broad. ESI technique and mass analyzer type TOF were used for the high resolution mass (HRMS) measurements. For column chromatography, silica gel (35-70 microns) was used.

Experimental Procedures and Spectral Data

Synthesis of the cyclic allyl alcohol 1c



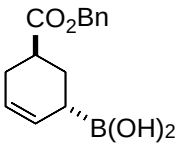
Benzyl *trans*-5-hydroxycyclohex-3-ene-1-carboxylate (1c). *cis*-Allylic alcohol **1a**[3] (0.93 g, 4 mmol) was dissolved in THF (16 mL) followed by the addition of PPh_3 (1.26 g, 4.8 mmol) and acetic acid (0.275 ml, 4.8 mmol). Then DIAD (0.945 mL, 4.8 mmol) was added dropwise to the mixture at 0 °C. Then the reaction mixture was stired at room temperature for 3 hours. Subsequently, methanol (0.4 mL) was added to quench the reaction mixture. The solvents were removed and a mixture of pentane and diethyl ether (1:1, 10 mL) was added to the residue. After filtration the solvents were evaporated and the crude was purified by silica gel column chromatography to yield 0.64 g of ester **1 aa** as a colorless oil (58%, *trans*:*cis*, 96:4) using pentane:EtOAc (10 : 1) as eluent. ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.43 – 7.30 (m, 5H), 6.00 (ddd, *J* = 9.9, 5.2, 2.5 Hz, 1H), 5.87 – 5.78 (m, 1H), 5.33 – 5.24 (m, 1H), 5.15 (s, 2H), 2.83 (dddd, *J* = 12.7, 11.0, 5.3, 3.1 Hz, 1H), 2.43 (dtt, *J* = 18.1, 5.3, 1.5 Hz, 1H), 2.29 – 2.16 (m, 2H), 2.04 (s, 3H), 1.87 (ddd, *J* = 14.3, 12.7, 4.3 Hz, 1H); ^{13}C NMR (101 MHz, $CDCl_3$): δ 174.8, 170.4, 135.9, 131.4, 128.6, 128.3, 128.1, 124.4, 66.4, 65.8, 35.2, 30.6, 27.6, 21.3; HRMS (pos. ESI) m/z: Calcd for $C_{16}H_{18}NaO_4$ $[M+Na]^+$ 297.1097. Found 297.1096.

Ester **1aa** (0.48 g, 1.75 mmol) was stirred in 10 mL benzyl alcohol in the presence of sodium methoxide (0.054 g, 1 mmol) for 6 h. After evaporation the residue was diluted with 10 mL diethyl ether and washed

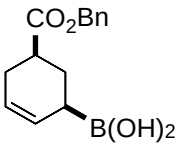
by a 5% aqueous solution of $NaHCO_3$ (10 mL). The organic layer was separated and dried over $MgSO_4$ and after evaporation the productwas purified by silica gel column chromatography (pentane:diethyl ether, 2:1). Compound **1c** was obtained as a colorless oil (0.25 g, 62%, *trans*:*cis*, 95:5). ^{1}H NMR (400 MHz, CDCl3): δ 7.40 – 7.28 (m, 5H), 5.89 (ddd, *J* = 10.0, 4.7, 2.2 Hz, 1H), 5.86 – 5.79 (m, 1H), 5.14 (s, 2H), 4.26 (br s, 1H), 2.85 (dddd, *J* = 12.3, 10.4, 5.3, 3.1 Hz, 1H), 2.37 (dt, *J* = 18.3, 5.1 Hz, 1H), 2.31 – 2.04 (m, 2H), 1.83 (ddd, *J* = 13.7, 12.2, 4.2 Hz, 1H), 1.71 (s, 1H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 175.3, 136.0, 129.5, 128.6, 128.2, 128.1, 128.0, 66.3, 63.2, 34.7, 33.7, 27.7.; HRMS (pos. ESI) m/z: Calcd for $C_{14}H_{16}NaO_3$ [M+Na]+ 255.0992. Found 255.0991.

Synthesis of the cyclic allyl boronic acids (2)

Method A: Allylic alcohol (1.0 mmol) was dissolved in a mixture of DMSO (0.9 mL) and H_2O (0.1 mL). To this mixture $Pd(CH_3CN)_4(BF_4)_2$ (5 mol %) and $B_2(OH)_4$ (1.2 equiv) were added in this order and the reaction mixture was stirred for 6h. Then, the reaction was allowed to stand two hours without stirring. The precipitated Pd-black was filtered off. (For this filtration we used syringe filter "Filtropur" 0.2 μm, PES membrane). The filtrate was collected in a Schlenk tube and the subsequent steps were carried out under Ar. Degassed CH_2Cl_2 (5 mL) was added to the filtrate and the solution was washed four times with degassed aqueous NaCl solution (20%, 5 mL). Then, the organic layer was transferred to a Straus flask and stored under Ar (glovebox recommended). To determine the yield and dr the allylboronic acid product was reacted with benzaldehyde. Assuming a quantitative formation of the homoallylic alcohol product the yield and the dr was determined by ^{1}H NMR using CH_2I_2 as internal standard.



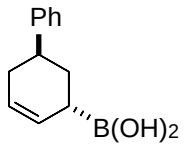
(*trans*-5-((benzyloxy)carbonyl)cyclohex-2-en-1-yl)boronic acid (2a) was prepared according to Method A from **1a (**232 mg, 1 mmol**)**. ^{1}H NMR yield: 52%, dr = 8:1. The ^{1}H NMR data is based on the analysis of the crude reaction mixture in $CDCl_3$/DMSO-d_6/D_2O: δ 7.38 – 7.24 (m, 5H), 5.83 – 5.71 (m, 1H), 5.69 – 5.59 (m, 1H), 5.15 – 5.04 (m, 2H), 2.76 – 2.63 (m, 1H), 2.29 – 2.20 (m, 2H), 2.15 – 2.04 (m, 1H), 1.92 – 1.79 (m, 2H).



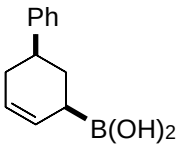
(*cis*-5-((benzyloxy)carbonyl)cyclohex-2-en-1-yl)boronic acid (2c) was prepared according to Method A from **1c (**232 mg, 1 mmol**)**. ^{1}H NMR yield: 47%, dr = 5.5:1. The ^{1}H NMR data is based on the analysis of the crude reaction mixture in $CDCl_3$/DMSO-d_6/D_2O: δ 7.37 – 7.19 (m, 5H), 5.72 (d, *J* = 10.0 Hz, 1H), 5.64 – 5.55 (m, 1H), 5.04 (s, 2H), 2.57 – 2.43 (m, 1H), 2.24 – 2.06 (m, 3H), 1.86 – 1.73 (m, 1H), 1.68 – 1.54 (m, 1H).

Method B: Allylic alcohol (1.0 mmol) was dissolved in a mixture of DMSO (0.9 mL) and H_2O (0.1 mL). To this mixture $Pd(CH_3CN)_4(BF_4)_2$ (5 mol %) and $B_2(OH)_4$ (1.2 equiv) were added in this order and the reaction mixture was stirred for 1h. Then, the reaction was allowed to stand two hours without stirring. The precipitated Pd-black was filtered off. The filtrate was collected in a Schlenk tube and the subsequent steps were carried out under Ar. The allylboronic acid product was precipitated by dropwise

addition of degassed aqueous solution of NaCl (20%, 4 mL) to the stirred solution of the filtrate. The solvent was removed and the precipitate was washed three times with degassed water (1 mL). The boronic acid product was dried in vacuum (about 30 minutes) and then it was stored in an argon filled glovebox.

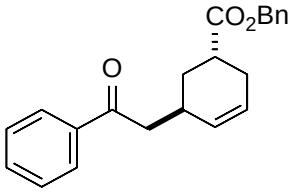


(*trans*-1,2,3,6-tetrahydro-[1,1'-biphenyl]-3-yl)boronic acid (2b) was prepared according to Method B from the corresponding *cis*- cyclic allyl alcohol **1b (**174 mg, 1 mmol**)**. Yield: 68% (137 mg), dr = 4:1. ^{1}H NMR (400 MHz, DMSO-d_6) δ 7.52 (s, 2H), 7.32 – 7.11 (m, 5H), 5.90 – 5.82 (m, 1H), 5.59 (ddt, *J* = 10.0, 4.6, 2.3 Hz, 1H), 2.91 – 2.79 (m, 1H), 2.21 – 2.12 (m, 1H), 2.10 – 2.02 (m, 1H), 1.97 – 1.92 (m, 1H), 1.78 – 1.63 (m, 2H); ^{13}C NMR (101 MHz, DMSO-d_6): δ 148.0, 130.5, 128.7, 127.2, 126.1, 123.7, 38.6, 33.2, 31.5. The ^{13}C shift of the boronated carbon is obscured because of the quadrupolar relaxation of the boron atom.[6] Because of the oxygen sensitivity of **2b** HRMS analysis was not carried out.



(*cis*-1,2,3,6-tetrahydro-[1,1'-biphenyl]-3-yl)boronic acid (2d) was prepared according to Method B from the corresponding *trans*- cyclic allyl alcohol **1d** (174 mg, 1 mmol). Yield: 56% (113 mg), dr = 4.5:1. ^{1}H NMR (400 MHz, DMSO-d_6) δ 7.53 (s, 2H), 7.33 – 7.13 (m, 5H), 5.82 – 5.73 (m, 1H), 5.67 – 5.55 (m, 1H), 2.71 – 2.58 (m, 1H), 2.21 – 1.98 (m, 2H), 1.96 – 1.74 (m, 2H), 1.72 – 1.60 (m, 1H); ^{13}C NMR (101 MHz, DMSO-d_6): δ 148.0, 129.9, 128.6, 127.1, 126.2, 124.5, 40.9, 33.5, 32.4. The ^{13}C shift of the boronated carbon is obscured because of the quadrupolar relaxation of the boron atom.[6] Because of the oxygen sensitivity of **2d** HRMS was not carried out.

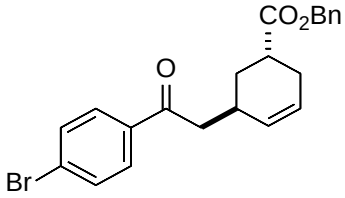
General procedure for cross-coupling of cyclic allyl boronic acids and α-diazoketones: CuTC (20 mol %, 0.02 mmol), the corresponding allyl boronic acid (0.12 mmol), and CH_2Cl_2 (5 mL) was added to a vial. After one minute the α-diazoketone (0.1 mmol) was added to the reaction mixture, which was subsequently stired at room temperature for 4 h. The dr of the product was determined by ^{1}H NMR analysis of the crude reaction product using CH_2I_2 as internal standard. The product was purified by silica gel chromatography.



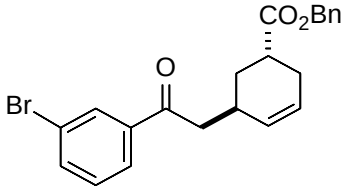
Benzyl *trans*-5-(2-oxo-2-phenylethyl)cyclohex-3-ene-1-carboxylate (4a). The compound was prepared according to the above general procedure. Product **4a** was isolated in 82% yield (27.4 mg, dr = 19:1) as a colorless oil using pentane:EtOAc (15:1) as eluent. ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.00 – 7.89 (m, 2H), 7.60 – 7.52 (m, 1H), 7.49 – 7.41 (m, 2H), 7.39 – 7.28 (m, 5H), 5.78 – 5.67 (m, 2H), 5.20 – 5.06 (m, 2H), 3.08 – 2.92 (m, 3H), 2.72 (dddd, *J* = 11.1, 8.2, 6.2, 3.2 Hz, 1H), 2.40 – 2.22 (m, 2H), 2.09 – 1.97 (m, 1H), 1.83 (dt, *J* = 13.5, 3.2 Hz, 1H); ^{1}H NMR (400 MHz, acetone-d_6) δ 8.07 – 7.99 (m, 2H), 7.65 – 7.59 (m, 1H), 7.55 – 7.47 (m, 2H), 7.40 – 7.28 (m, 5H), 5.79 – 5.61 (m, 2H), 5.12 (s, 2H), 3.18 – 3.04 (m, 2H), 2.97 – 2.88 (m, 1H), 2.85 – 2.78 (m, 1H), 2.30 – 2.24

(m, 2H), 1.96 (ddd, *J* = 13.3, 10.3, 5.8 Hz, 1H), 1.84 (ddd, *J* = 13.3, 4.2, 3.4 Hz, 1H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 198.8, 175.3, 137.1, 136.1, 133.1, 130.1, 128.62, 128.55, 128.15, 128.09, 128.06, 125.7. 66.3, 44.1, 36.3, 30.3, 29.6, 27.4; HRMS (pos. ESI) m/z: Calcd for $C_{22}H_{22}NaO_3$ $[M+Na]^+$ 357.1461. Found 357.1467.

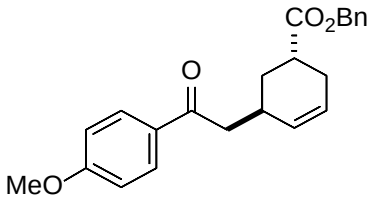
Benzyl *trans*-5-(2-oxo-2-phenylethyl)cyclohex-3-ene-1-carboxylate (4a) at 1 mmol scale. The above representative reaction was repeated at 1 mmol scale. CuTC (20 mol %, 0.2 mmol), allyl boronic acid **2a** (1.2 mmol), and CH_2Cl_2 (50 mL) was added to a round-bottom flask. After one minute the α-diazoketone **3a** (1.0 mmol) was added to the reaction mixture, which was subsequently stired at room temperature for 4 h. The solvent was removed under reduced pressure. The crude residue was purified by silica gel chromatography. Product **4a** was isolated in 70% yield (233 mg, dr = 16:1) as a colorless oil using pentane:EtOAc (15:1) as eluent. The NMR spectral data is identical to the above values for compound **4a**.



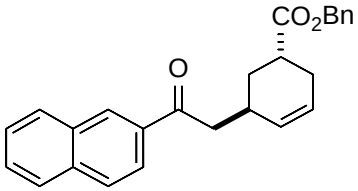
Benzyl *trans*-5-(2-(4-bromophenyl)-2-oxoethyl)cyclohex-3-ene-1-carboxylate (4b). The compound was prepared according to the above general procedure. Product **4b** was isolated in 73% yield (30.1 mg, dr = 12:1) as a colorless oil using pentane:EtOAc (20:1) as eluent. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.80 (d, *J* = 8.6 Hz, 2H), 7.58 (d, *J* = 8.6 Hz, 2H), 7.41 – 7.28 (m, 5H), 5.78 – 5.70 (m, 1H), 5.67 (d, *J* = 10.2 Hz, 1H), 5.19 – 5.06 (m, 2H), 3.03 – 2.85 (m, 3H), 2.70 (dddd, *J* = 11.0, 8.0, 6.2, 3.2 Hz, 1H), 2.40 – 2.20 (m, 2H), 2.09 – 1.97 (m, 1H), 1.85 – 1.75 (m, 1H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 197.7, 175.2, 136.0, 135.8, 131.9, 129.9, 129.6, 128.6, 128.3, 128.2, 128.1, 125.9, 66.3, 44.0, 36.2, 30.2, 29.6, 27.4; HRMS (pos. ESI) m/z: Calcd for $C_{22}H_{21}BrNaO_3$ $[M+Na]^+$ 435.0566. Found 435.0575.



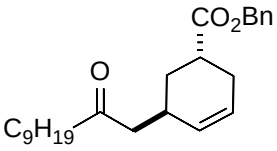
Benzyl *trans*-5-(2-(3-bromophenyl)-2-oxoethyl)cyclohex-3-ene-1-carboxylate (4c). The compound was prepared according to the above general procedure. Product **4c** was isolated in 78% yield (32.1 mg, dr = 12:1) as a colorless oil using pentane:EtOAc (20:1) as eluent for silica gel chromatography. ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.07 (t, *J* = 1.8 Hz, 1H), 7.86 (dt, *J* = 7.9, 1.3 Hz, 1H), 7.68 (ddd, *J* = 7.9, 2.0, 1.0 Hz, 1H), 7.41 – 7.28 (m, 6H), 5.79 – 5.71 (m, 1H), 5.68 (d, J = 10.2 Hz, 1H), 5.20 – 5.07 (m, 2H), 3.04 – 2.85 (m, 3H), 2.71 (dddd, *J* = 10.9, 8.0, 6.3, 3.2 Hz, 1H), 2.40 – 2.22 (m, 2H), 2.09 – 1.97 (m, 1H), 1.81 (dt, *J* = 12.6, 2.8 Hz, 1H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 197.3, 175.2, 138.8, 136.1, 135.9, 131.2, 130.2, 129.8, 128.6, 128.2, 128.1, 126.6, 126.0, 123.0, 66.3, 44.1, 36.2, 30.2, 29.4, 27.4; HRMS (pos. ESI) m/z: Calcd for $C_{22}H_{21}BrNaO_3$ $[M+Na]^+$ 435.0566. Found 435.0580.



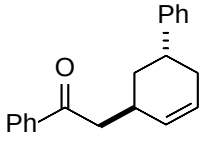
Benzyl *trans*-5-(2-(4-methoxyphenyl)-2-oxoethyl)cyclohex-3-ene-1-carboxylate (4d). The compound was prepared according to the above general procedure. Product **4d** was isolated in 67% yield (24.4 mg, dr = 15:1) as a colorless oil using pentane:EtOAc (20:1) as eluent for silica gel chromatography. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.93 (d, *J* = 8.9 Hz, 2H), 7.40 – 7.28 (m, 5H), 6.92 (d, *J* = 8.9 Hz, 2H), 5.79 – 5.66 (m, 2H), 5.20 – 5.05 (m, 2H), 3.86 (s, 3H), 3.02 – 2.85 (m, 3H), 2.71 (dddd, *J* = 10.9, 8.0, 6.4, 3.2 Hz, 1H), 2.38 – 2.23 (m, 2H), 2.07 – 1.96 (m, 1H), 1.83 (dt, *J* = 13.7, 3.4 Hz, 1H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 197.3, 175.3, 163.5, 136.1, 130.4, 130.28, 130.26, 128.5, 128.1, 128.0, 125.6, 113.7, 66.2, 55.5, 43.7, 36.3, 30.3, 29.8, 27.4; HRMS (pos. ESI) m/z: Calcd for $C_{23}H_{24}NaO_4$ $[M+Na]^+$ 387.1567. Found 387.1578.



Benzyl trans-5-(2-(naphthalen-2-yl)-2-oxoethyl)cyclohex-3-ene-1-carboxylate (4e). The compound was prepared according to the above general procedure. Product **4e** was isolated in 70% yield (26.9 mg, dr = 15:1) as a colorless oil using pentane:EtOAc (20:1) as eluent for silica gel chromatography. ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.50 – 8.43 (m, 1H), 8.03 (dd, *J* = 8.6, 1.8 Hz, 1H), 7.96 (dd, *J* = 8.1, 1.3 Hz, 1H), 7.92 – 7.85 (m, 2H), 7.58 (dddd, *J* = 20.6, 8.1, 6.9, 1.4 Hz, 2H), 7.41 – 7.27 (m, 5H), 5.81 – 5.71 (m, 2H), 5.21 – 5.07 (m, 2H), 3.23 – 2.99 (m, 3H), 2.77 (dddd, *J* = 10.9, 7.9, 6.4, 3.2 Hz, 1H), 2.42 – 2.26 (m, 2H), 2.14 – 2.02 (m, 1H), 1.89 (dt, *J* = 13.4, 3.5 Hz, 1H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 198.7, 175.3, 136.1, 135.6, 134.5, 132.5, 130.2, 129.8, 129.6, 128.54, 128.49, 128.15, 128.06, 127.8, 126.8, 125.8, 123.9, 66.3, 44.1, 36.3, 30.3, 29.8, 27.4; HRMS (pos. ESI) m/z: Calcd for $C_{26}H_{24}NaO_3$ $[M+Na]^+$ 407.1618. Found 407.1634.

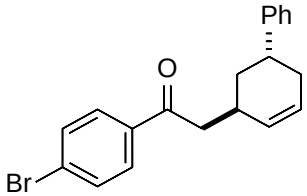


Benzyl *trans*-5-(2-oxoundecyl)cyclohex-3-ene-1-carboxylate (4f). The compound was prepared according to the above general procedure. Product **4f** was isolated in 67% yield (25.7 mg, dr = 11:1) as a colorless oil using pentane:diethyl ether (7:1) as eluent for silica gel chromatography. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.40 – 7.28 (m, 5H), 5.72 – 5.66 (m, 1H), 5.59 (ddt, *J* = 10.0, 4.0, 2.0 Hz, 1H), 5.13 (s, 2H), 2.79 (tdd, *J* = 8.0, 4.0, 2.1 Hz, 1H), 2.64 (dddd, *J* = 11.0, 8.0, 6.1, 3.2 Hz, 1H), 2.49 – 2.39 (m, 2H), 2.36 (d, J = 7.5 Hz, 2H), 2.31 – 2.23 (m, 2H), 1.95 (ddd, *J* = 13.4, 10.6, 5.9 Hz, 1H), 1.74 – 1.66 (m, 1H), 1.60 – 1.49 (m, 2H), 1.26 (s, 12H), 0.877 (t, *J* = 6.8 Hz, 3H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 209.8, 175.2, 136.1, 130.0, 128.6, 128.2, 128.0, 125.6, 66.2, 48.2, 43.4, 36.2, 31.9, 30.2, 29.43, 29.41, 29.3, 29.23, 29.18, 27.3, 23.8, 22.7, 14.1; HRMS (pos. ESI) m/z: Calcd for $C_{25}H_{36}NaO_3$ $[M+Na]^+$ 407.2557. Found 407.2561.

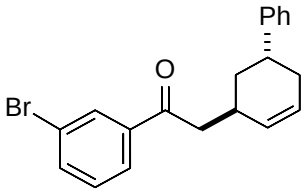


1-Phenyl-2-(*trans*-1,2,3,6-tetrahydro-[1,1'-biphenyl]-3-yl)ethan-1-one (4g). The compound was prepared according to the above general procedure. Product **4g** was isolated in 79% yield (21.8 mg, dr = >20:1) as a colorless oil using

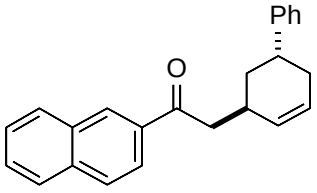
pentane:EtOAc (30:1) as eluent for silica gel chromatography. ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.01 – 7.96 (m, 2H), 7.60 – 7.55 (m, 1H), 7.50 – 7.44 (m, 2H), 7.34 – 7.28 (m, 2H), 7.27 – 7.19 (m, 3H), 5.89 – 5.83 (m, 1H), 5.78 (dddd, *J* = 8.5, 3.9, 2.4, 1.2 Hz, 1H), 3.18 – 3.05 (m, 2H), 3.06 – 2.99 (m, 1H), 2.93 (dddd, *J* = 12.3, 9.9, 5.3, 2.9 Hz, 1H), 2.39 – 2.30 (m, 1H), 2.18 (ddq, *J* = 17.6, 9.9, 2.4 Hz, 1H), 2.04 (ddd, *J* = 13.3, 11.9, 5.7 Hz, 1H), 1.86 – 1.76 (m, 1H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 199.3, 146.5, 137.2, 133.1, 130.3, 128.6, 128.4, 128.1, 127.4, 127.0, 126.1, 44.1, 35.9, 34.6, 33.2, 30.7; HRMS (pos. ESI) m/z: Calcd for $C_{20}H_{20}NaO$ $[M+Na]^+$ 299.1406. Found 299.1413.



1-(4-Bromophenyl)-2-(*trans*-1,2,3,6-tetrahydro-[1,1'-biphenyl]-3-yl)ethan-1-one (4h). The compound was prepared according to the above general procedure. Product **4h** was isolated in 68% yield (24.1 mg, dr = 15:1) as a colorless oil using pentane:EtOAc (20:1) as eluent for silica gel chromatography. ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.09 (t, *J* = 1.8 Hz, 1H), 7.88 (dt, *J* = 7.8, 1.4 Hz, 1H), 7.68 (ddd, *J* = 7.9, 2.1, 1.1 Hz, 1H), 7.38 – 7.28 (m, 3H), 7.27 – 7.16 (m, 3H), 5.91 – 5.80 (m, 1H), 5.75 (dddd, *J* = 11.2, 3.8, 2.5, 1.2 Hz, 1H), 3.15 – 2.85 (m, 4H), 2.34 (dtd, *J* = 17.8, 5.0, 1.4 Hz, 1H), 2.17 (ddq, *J* = 17.6, 9.8, 2.4 Hz, 1H), 2.03 (ddd, *J* = 13.3, 11.8, 5.6 Hz, 1H), 1.85 – 1.73 (m, 1H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 198.1, 146.3, 135.9, 131.9, 130.1, 129.6, 128.4, 128.2, 127.6, 127.0, 126.1, 44.1, 35.9, 34.6, 33.1, 30.7; HRMS (pos. ESI) m/z: Calcd for $C_{20}H_{19}BrNaO$ $[M+Na]^+$ 377.0511. Found 377.0502.

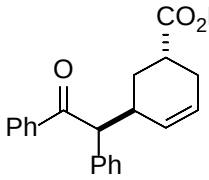


1-(3-Bromophenyl)-2-(*trans*-1,2,3,6-tetrahydro-[1,1'-biphenyl]-3-yl)ethan-1-one (4i). The compound was prepared according to the above general procedure. Product **4i** was isolated in 72% yield (25.6 mg, dr = 14:1) as a colorless oil using pentane:EtOAc (20:1) as eluent for silica gel chromatography. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.87 – 7.79 (m, 2H), 7.63 – 7.57 (m, 2H), 7.34 – 7.27 (m, 2H), 7.25 – 7.15 (m, 3H), 5.88 – 5.82 (m, 1H), 5.78 – 5.72 (m, 1H), 3.14 – 2.85 (m, 4H), 2.34 (dtd, *J* = 17.9, 5.0, 1.4 Hz, 1H), 2.17 (ddq, *J* = 17.6, 9.9, 2.4 Hz, 1H), 2.02 (ddd, *J* = 13.2, 11.7, 5.6 Hz, 1H), 1.82 – 1.73 (m, 1H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 197.8, 146.3, 139.0, 135.9, 131.2, 130.2, 130.0, 128.4, 127.6, 127.0, 126.6, 126.2, 123.0, 44.2, 35.9, 34.6, 33.1, 30.6; HRMS (pos. ESI) m/z: Calcd for $C_{20}H_{19}BrNaO$ $[M+Na]^+$ 377.0511. Found 377.0506.

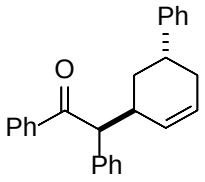


1-(naphthalen-2-yl)-2-(*trans*-1,2,3,6-tetrahydro-[1,1'-biphenyl]-3-yl)ethan-1-one (4j). The compound was prepared according to the above general procedure. Product **4j** was isolated in 65% yield (21.2 mg, dr = 10:1) as a colorless oil using pentane:EtOAc (20:1) as eluent for silica gel chromatography. ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.49 (s, 1H), 8.05 (dd, *J* = 8.6, 1.8 Hz, 1H), 7.98 (d, *J* = 8.1 Hz, 1H), 7.93 – 7.86 (m, 2H), 7.59 (dddd, *J* = 18.5, 8.2, 6.9, 1.5 Hz, 2H), 7.35 – 7.23 (m, 4H), 7.23 – 7.17 (m, 1H), 5.92 – 5.85 (m, 1H), 5.85 – 5.79 (m, 1H), 3.31 – 3.17 (m, 2H), 3.08 (s, 1H), 3.03 –

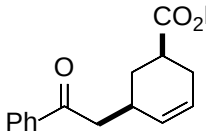
2.91 (m, 1H), 2.42 – 2.32 (m, 1H), 2.20 (ddq, *J* = 17.7, 10.0, 2.3 Hz, 1H), 2.07 (ddd, *J* = 13.3, 11.7, 5.8 Hz, 1H), 1.91 – 1.82 (m, 1H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 199.2, 146.5, 135.6, 134.6, 132.6, 130.4, 129.8, 129.6, 128.5, 128.45, 128.41, 127.8, 127.4, 127.0, 126.8, 126.1, 123.9, 44.2, 36.0, 34.7, 33.2, 30.9; HRMS (pos. ESI) m/z: Calcd for $C_{24}H_{22}NaO$ $[M+Na]^+$ 349.1563. Found 349.1576.



Benzyl *trans*-5-(2-oxo-1,2-diphenylethyl)cyclohex-3-ene-1-carboxylate (4k). The compound was prepared according to the above general procedure. Product **4k** was isolated in 32% yield (13.2 mg, four diasteremers were observed in a ratio of 20 : 4 : 4 : 1, the trans-**4k** being the major diastereomer) as a colorless oil using pentane:diethyl ether (7:1) as eluent for silica gel chromatography. NMR spectral data for the major isomer of **4k**: ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.01 – 7.91 (m, 2H), 7.54 – 7.45 (m, 1H), 7.42 – 7.25 (m, 11H), 7.24 – 7.17 (m, 1H), 5.68 (dtd, *J* = 10.3, 3.7, 2.0 Hz, 1H), 5.21 – 5.13 (m, 1H), 5.13 – 5.03 (m, 2H), 4.47 (d, *J* = 10.8 Hz, 1H), 3.28 (ddq, *J* = 9.8, 5.9, 2.0 Hz, 1H), 2.74 (dtd, *J* = 10.4, 7.0, 3.1 Hz, 1H), 2.36 – 2.22 (m, 2H), 2.07 (ddd, *J* = 13.6, 10.4, 5.8 Hz, 1H), 1.78 (dt, *J* = 13.6, 3.7 Hz, 1H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 199.3, 175.1, 137.3, 137.2, 136.1, 133.0, 129.0, 128.9, 128.67, 128.65, 128.58, 128.56, 128.1, 127.9, 127.3, 126.5, 66.2, 58.2, 36.65, 36.60, 29.6, 27.5; HRMS (pos. ESI) m/z: Calcd for $C_{28}H_{26}NaO_3$ $[M+Na]^+$ 433.1774. Found 433.1770.

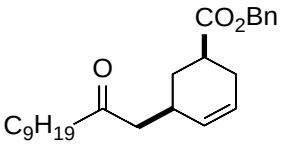


1,2-Diphenyl-2-(*trans*-1,2,3,6-tetrahydro-[1,1'-biphenyl]-3-yl)ethan-1-one (4l). The compound was prepared according to the above general procedure. Product **4l** was isolated in 30% yield (10.6 mg, four diasteremers were observed in a ratio of 55 : 9.8 : 4.6 : 1, the trans-**4l** being the major diastereomer) as a white solid (m.p. 144 – 145 °C) using pentane:diethyl ether (30:1) as eluent for silica gel chromatography. NMR spectral data for the major isomer of **4l**: ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.03 – 7.92 (m, 2H), 7.54 – 7.46 (m, 1H), 7.44 – 7.34 (m, 4H), 7.34 – 7.27 (m, 2H), 7.27 – 7.21 (m, 3H), 7.19 – 7.11 (m, 3H), 5.85 – 5.75 (m, 1H), 5.28 – 5.15 (m, 1H), 4.67 (d, *J* = 10.8 Hz, 1H), 3.32 (br s, 1H), 3.01 – 2.87 (m, 1H), 2.40 – 2.29 (m, 1H), 2.16 (ddq, *J* = 17.7, 10.0, 2.5 Hz, 1H), 2.05 (ddd, *J* = 13.7, 11.9, 5.9 Hz, 1H), 1.83 – 1.74 (m, 1H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 199.6, 146.3, 137.5, 137.3, 133.0, 129.0, 128.9, 128.8, 128.6, 128.5, 128.4, 128.0, 127.2, 126.9, 126.1, 58.1, 37.8, 36.2, 34.1, 33.2.; HRMS (pos. ESI) m/z: Calcd for $C_{26}H_{24}NaO$ $[M+Na]^+$ 375.1719. Found 375.1715.

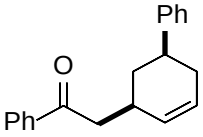


Benzyl *cis*-5-(2-oxo-2-phenylethyl)cyclohex-3-ene-1-carboxylate (5a). The compound was prepared according to the above general procedure. Product **5a** was isolated in 41% yield (13.7 mg, dr = 5:1) as a colorless oil using pentane:EtOAc (15:1) as eluent for silica gel chromatography. Spectral data for the major isomer of **5a**: ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.99 – 7.91 (m, 2H), 7.61 – 7.53 (m, 1H), 7.50 – 7.43 (m, 2H), 7.39 – 7.29 (m, 5H), 5.77 – 5.66 (m, 1H), 5.62 – 5.54 (m, 1H), 5.17 – 5.08 (m, 2H), 3.03 – 2.89 (m, 3H), 2.72 (dddd, *J* = 12.7, 11.1, 5.5, 2.7 Hz, 1H), 2.41 – 2.29 (m, 1H), 2.29 – 2.17 (m, 2H), 1.38 (td, *J* = 12.6, 10.8

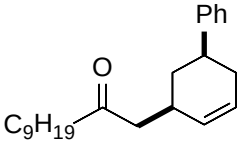
Hz, 1H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 198.9, 175.3, 137.1, 136.1, 133.1, 130.6, 128.63, 128.56, 128.2, 128.07, 128.06, 125.8, 66.2, 44.6, 39.7, 32.1, 32.0, 27.8; HRMS (pos. ESI) m/z: Calcd for $C_{22}H_{22}NaO_3$ $[M+Na]^+$ 357.1461. Found 357.1471.



Benzyl *cis*-5-(2-oxoundecyl)cyclohex-3-ene-1-carboxylate (5b). The compound was prepared according to the above general procedure except that the reaction was performed using 0.2 mmol of **2c** and 0.1 mmol of **3f**. Product **5b** was isolated in 45% yield (17.4 mg, dr = 4:1) as a colorless oil using pentane:diethyl ether (7:1) as eluent for silica gel chromatography. Spectral data for the major isomer of **5b**: ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.41 – 7.28 (m, 5H), 5.68 (ddt, *J* = 9.9, 4.9, 2.4 Hz, 1H), 5.51 – 5.41 (m, 1H), 5.18 – 5.07 (m, 2H), 2.84 – 2.59 (m, 2H), 2.49 – 2.24 (m, 5H), 2.24 – 2.17 (m, 1H), 2.17 – 2.09 (m, 1H), 1.61 – 1.49 (m, 2H), 1.34 – 1.18 (m, 13H), 0.88 (t, *J* = 6.9 Hz, 3H). ^{13}C NMR (101 MHz, $CDCl_3$). ^{13}C NMR (101 MHz, $CDCl_3$) δ 210.0, 175.3, 136.1, 130.5, 128.6, 128.2, 128.0, 125.7, 66.2, 48.7, 43.6, 39.6, 31.88, 31.86, 31.6, 29.42, 29.41, 29.3, 29.2, 27.7, 23.8, 22.7, 14.1; HRMS (pos. ESI) m/z: Calcd for $C_{25}H_{36}NaO_3$ $[M+Na]^+$ 407.2557. Found 407.2558.

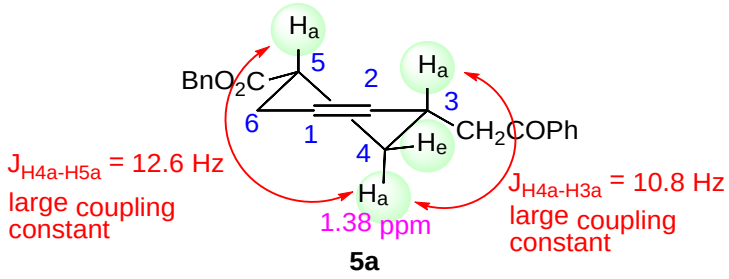


1-Phenyl-2-(*cis*-1,2,3,6-tetrahydro-[1,1'-biphenyl]-3-yl)ethan-1-one (5c). The compound was prepared according to the above general procedure except that the reaction was stirred for overnight. Product **5c** was isolated in 69% yield (19.1 mg, dr = 3:1) as a colorless oil using pentane:EtOAc (30:1) as eluent for silica gel chromatography. Spectral data for the major isomer of **5c**: ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.04 – 7.90 (m, 2H), 7.60 – 7.52 (m, 1H), 7.51 – 7.43 (m, 2H), 7.30 (dd, *J* = 8.0, 6.9 Hz, 2H), 7.25 – 7.17 (m, 3H), 5.90 – 5.75 (m, 1H), 5.72 – 5.58 (m, 1H), 3.15 – 2.96 (m, 3H), 2.91 (ddq, *J* = 15.3, 7.9, 2.6 Hz, 1H), 2.38 – 2.26 (m, 1H), 2.22 – 2.07 (m, 2H), 1.49 (td, *J* = 12.6, 10.5 Hz, 1H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 199.3, 146.7, 137.2, 133.1, 130.7, 128.6, 128.4, 128.1, 127.4, 126.9, 126.1, 44.9, 40.4, 37.1, 33.7, 33.6; HRMS (pos. ESI) m/z: Calcd for $C_{20}H_{20}NaO$ $[M+Na]^+$ 299.1406. Found 299.1418.



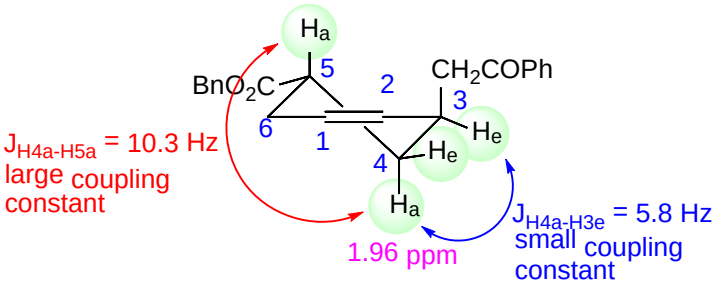
1-(*cis*-1,2,3,6-tetrahydro-[1,1'-biphenyl]-3-yl)undecan-2-one (5d). The compound was prepared according to the above general procedure except that the reaction was stirred for overnight. Product **5d** was isolated in 51% yield (16.7 mg, dr = 3:1) as a colorless oil using pentane:EtOAc (30:1) as eluent for silica gel chromatography. Spectral data for the major isomer of **5d**: ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.34 – 7.27 (m, 2H), 7.25 – 7.16 (m, 3H), 5.86 – 5.73 (m, 1H), 5.59 – 5.49 (m, 1H), 2.97 – 2.76 (m, 2H), 2.60 – 2.46 (m, 1H), 2.46 – 2.35 (m, 3H), 2.34 – 2.23 (m, 1H), 2.19 – 2.06 (m, 1H), 2.04 – 1.91 (m, 1H), 1.61 – 1.52 (m, 2H), 1.38 (td, *J* = 12.5, 10.9 Hz, 1H), 1.32 – 1.19 (m, 12H), 0.88 (t, *J* = 6.8 Hz, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 210.3, 146.7, 130.6, 128.4, 127.3, 126.8, 126.1, 49.1, 43.6, 40.4, 36.9, 33.6, 33.2, 31.9, 29.43, 29.42, 29.27, 29.25, 23.8, 22.7, 14.1; HRMS (pos. ESI) m/z: Calcd for $C_{23}H_{34}NaO$ $[M+Na]^+$ 349.2507. Found 349.2508.

Determination of the stereochemistry of 4a and 5a: The connectivity of carbons and hydrogens were determined by COSY and HSQC techniques. Afterwards the stereochemistry of **4a** and **5a** was determined by analysis of their 400 MHz ^{1}H NMR spectra. In compound **5a** H_{4a} resonating at 1.38 ppm has a dt coupling pattern with coupling constants of 10.8 Hz and 12.6 Hz, respectively. The (pseudo) triplet coupling (12.6 Hz) was assigned to the diaxial couplings of H_{5a} and H_{4a} and the geminal coupling of H_{4a} and H_{4e}, while the doublet coupling (10.8 Hz) was assigned to the diaxial coupling of H_{3a} and H_{4a} . Since H_{5a} and H_{3a} are in axial position, the two functional groups COOBn (at C5) and CH_2COPh (at C3) must be in equatorial positions. This means that the realative configuration of these two groups is cis.



5a

We have also assigned the coupling constants of H_{4a} in compound **4a**, which is the diastereomer of **5a**. ^{1}H NMR spectrum of **4a** gave sharper signals and higher resolution in aceton-d_6 than in $CDCl_3$, and therefore, our assignment is based on the ^{1}H NMR spectrum of **4a** in aceton-d_6. The H_{4a} of compound **4a** resonates at 1.96 ppm and it shows a ddd coupling pattern of 13.3, 10.3 and 5.8 Hz. The largest coupling (13.3 Hz) was assigned to the geminal coupling between H_{4a} and H_{4e}. The coupling constant of 10.3 Hz was assigned to a diaxial coupling between H_{4a} and H_{5a}, while the smallest coupling constant of 5.8 Hz was assigned to the H_{4a} and H_{3e} interaction. According to this assignment the relative configuration of the two functional groups COOBn (at C5) and CH_2COPh (at C3) is trans. This assigment is also in line with the litereture data reported for analog compounds.[7]



4a

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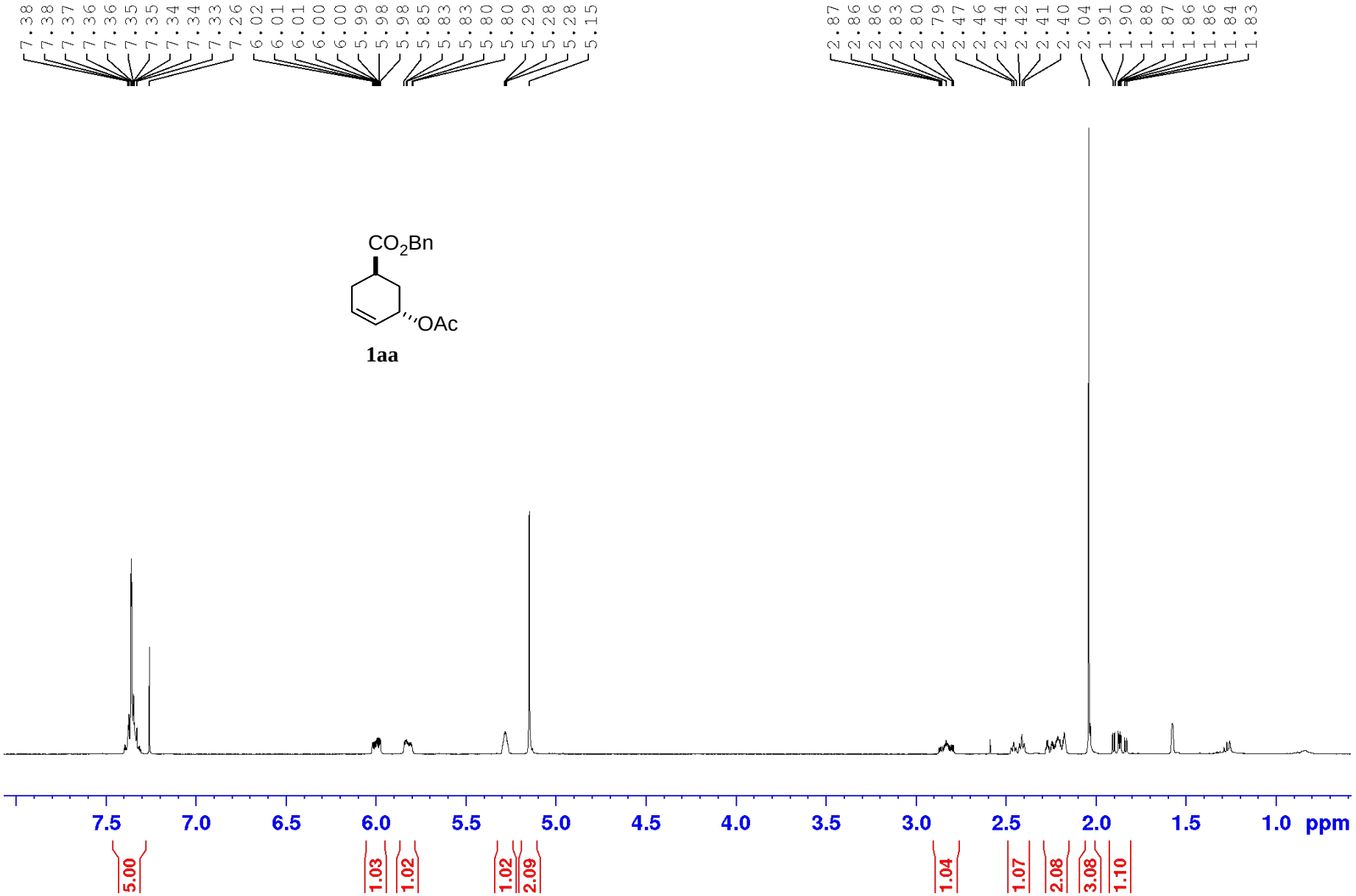
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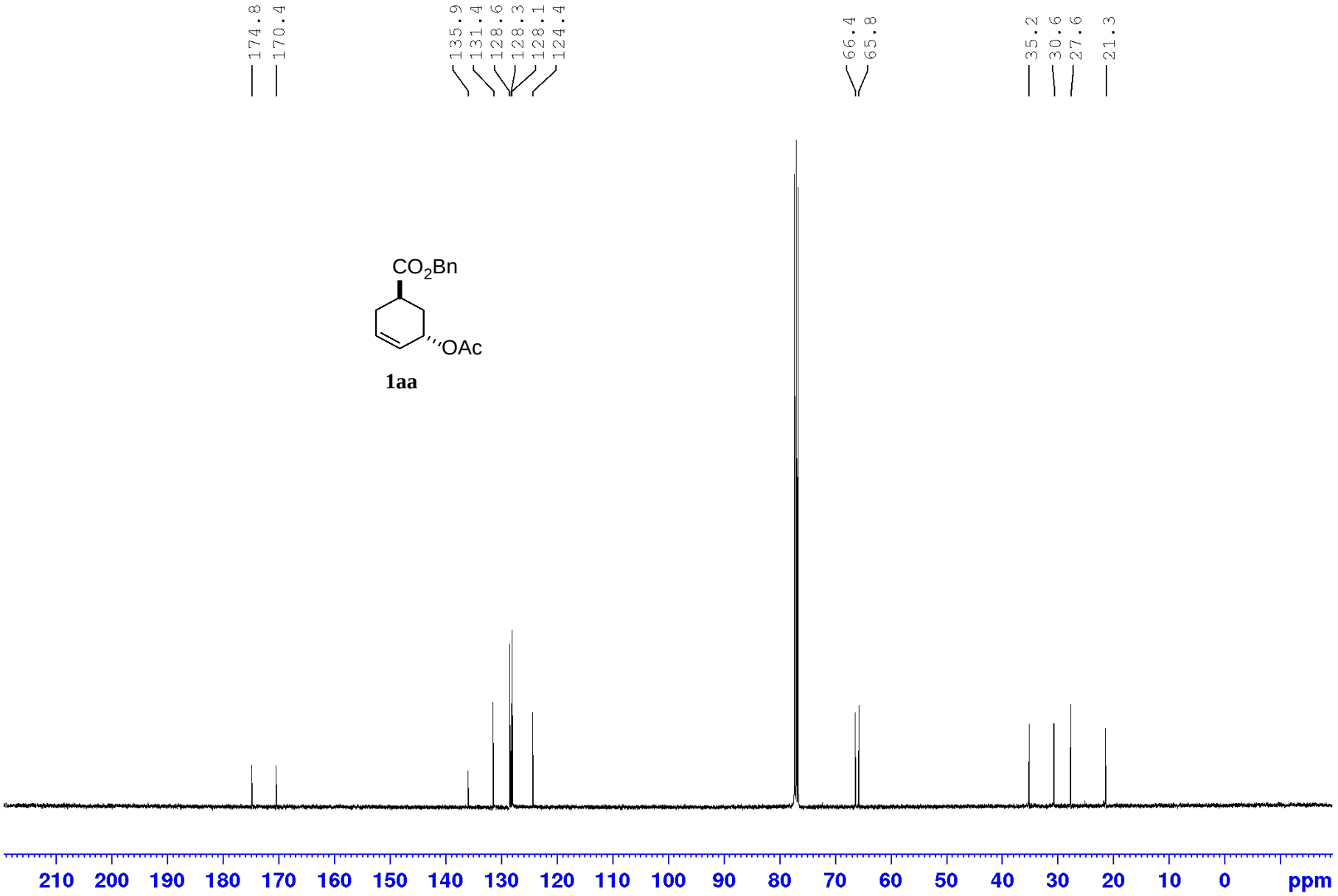
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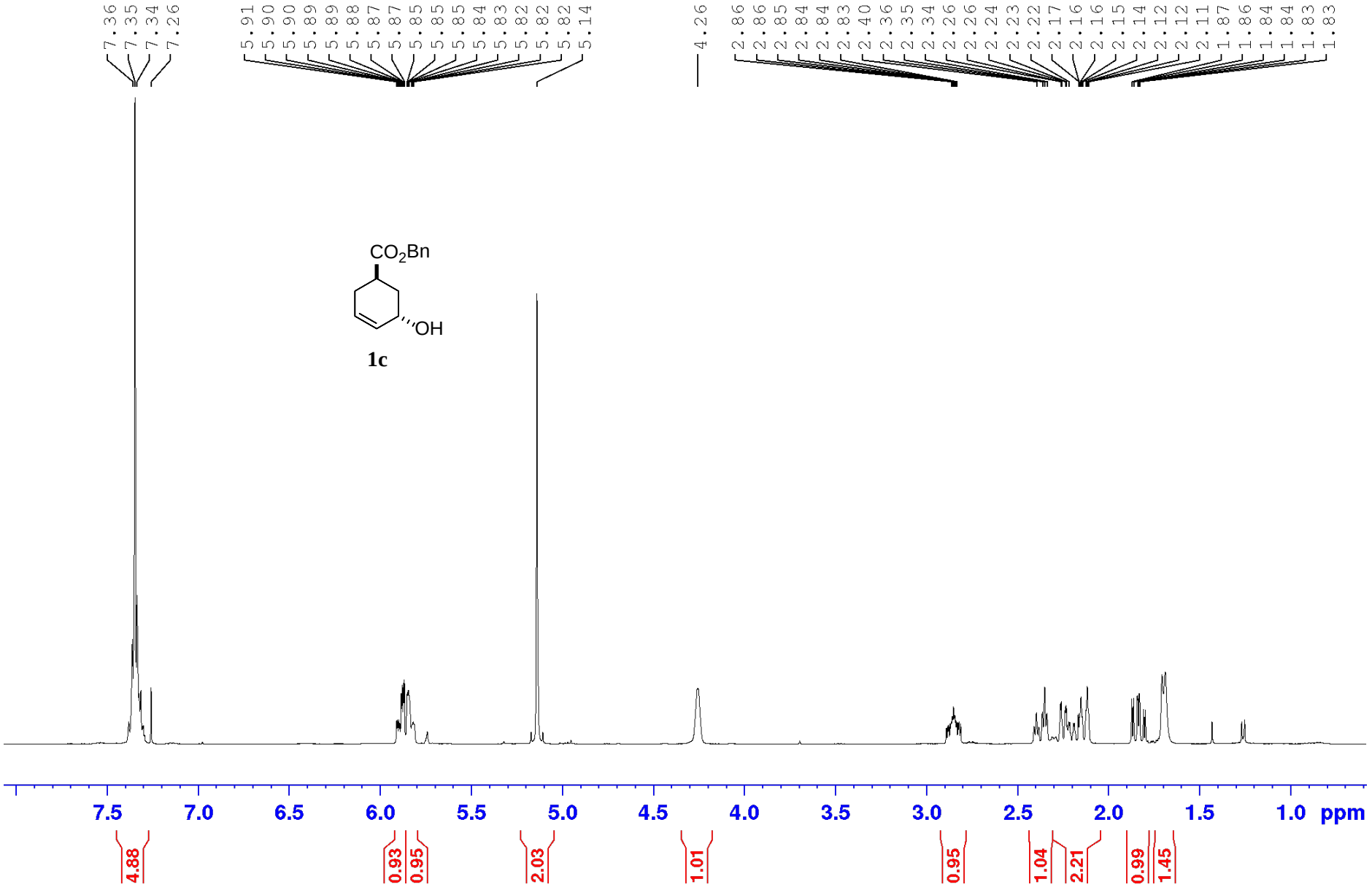
1aa
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 ppm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7.35
7.34
7.26
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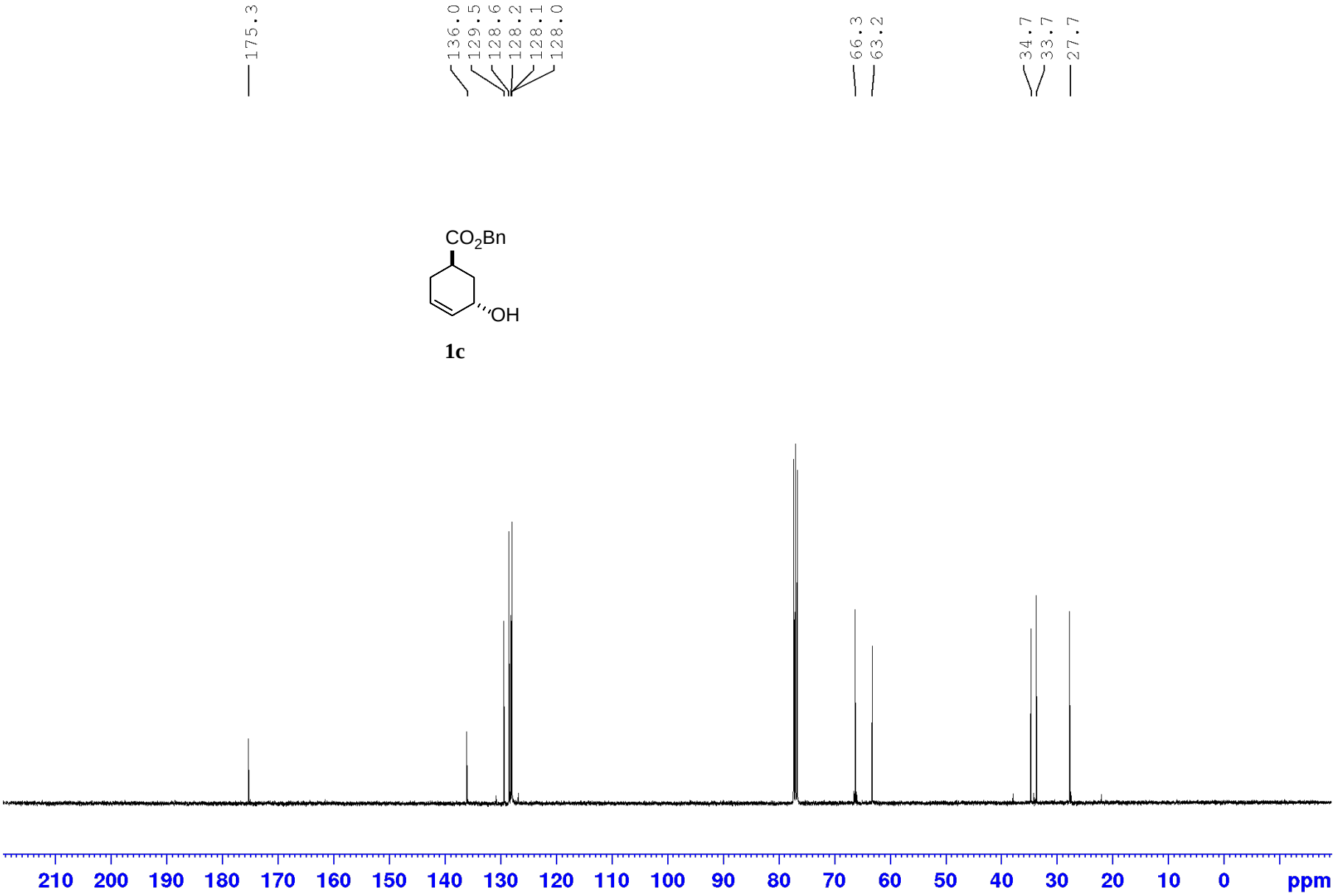
5.90
5.90
5.89
5.89
5.88
5.87
5.87
5.85
5.85
5.85
5.84
5.83
5.82
5.82
5.14
4.26
2.86
2.86
2.85
2.84
2.84
2.83
2.40
2.36
2.35
2.34
2.26
2.26
2.24
2.23
2.22
2.17
2.16
2.16
2.15
2.14
2.12
2.12
2.11
1.87
1.86
1.84
1.84
1.83
1.83
CO2Bn
OH
1c
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
ppm
4.88
0.93
0.95
2.03
1.01
0.95
1.04
2.21
0.99
1.45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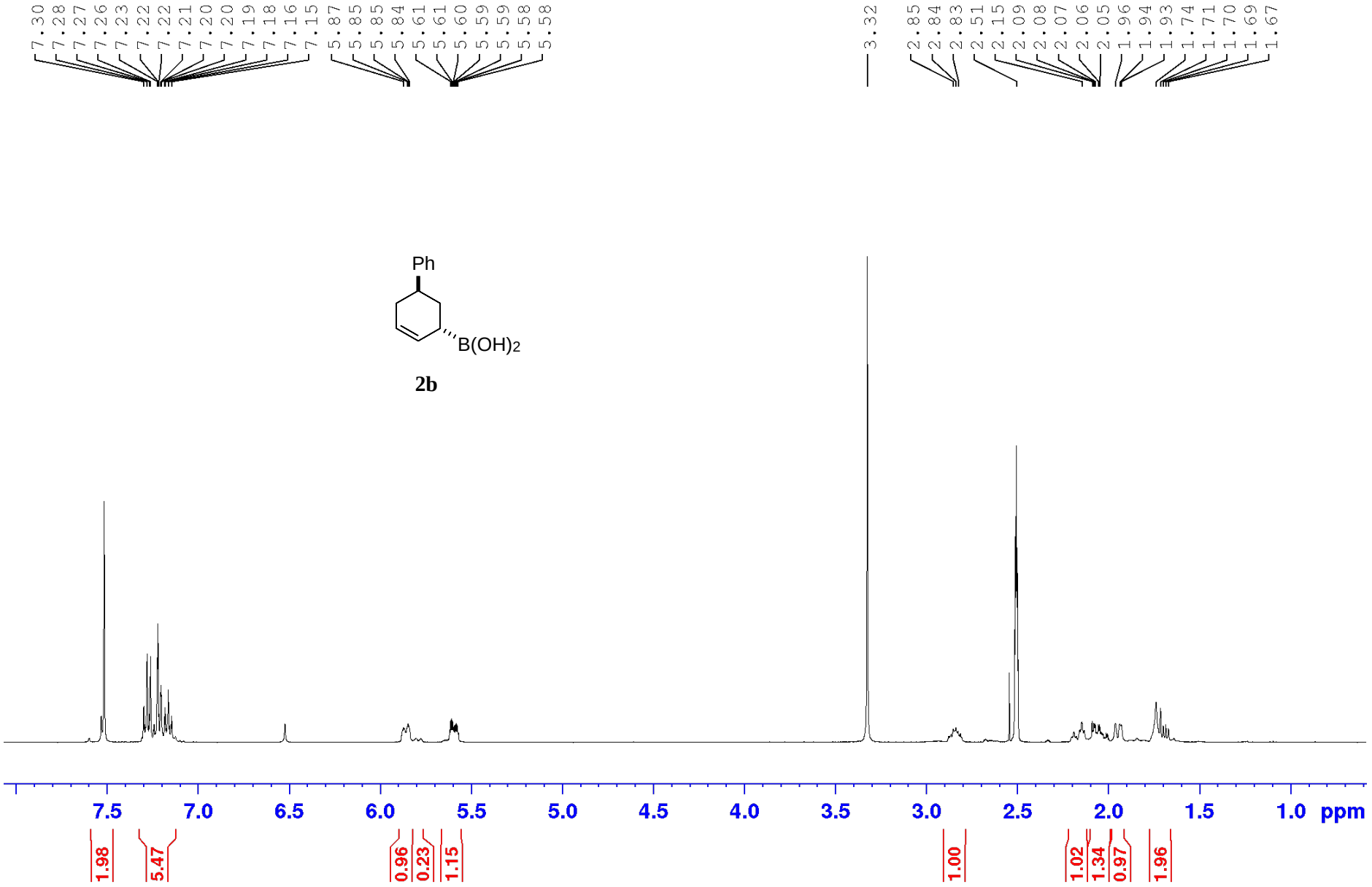
136.0
129.5
128.6
128.2
128.1
128.0
66.3
63.2
34.7
33.7
27.7
CO2Bn
OH
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 ppm

1c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7.28
7.27
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7.22
7.22
7.21
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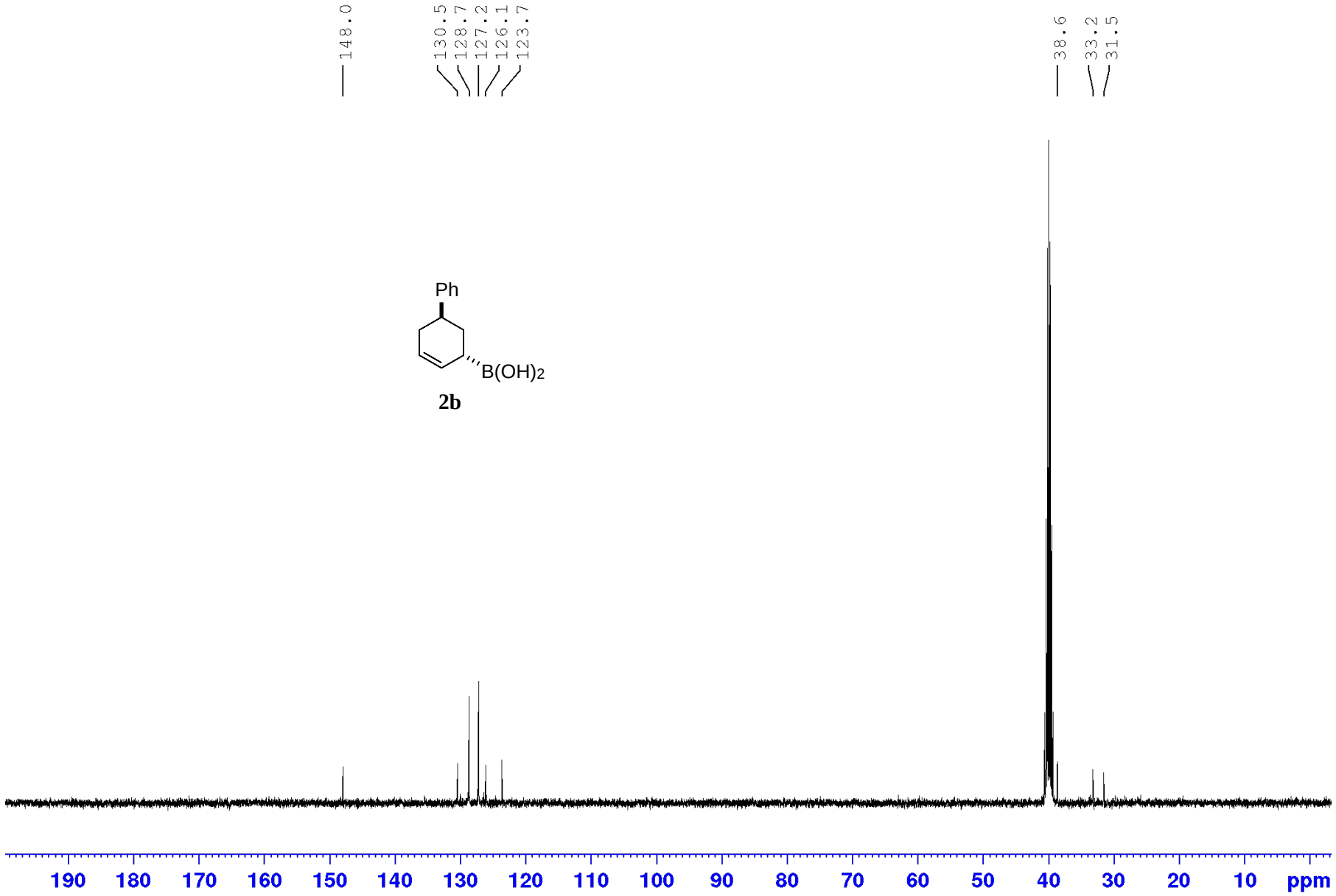
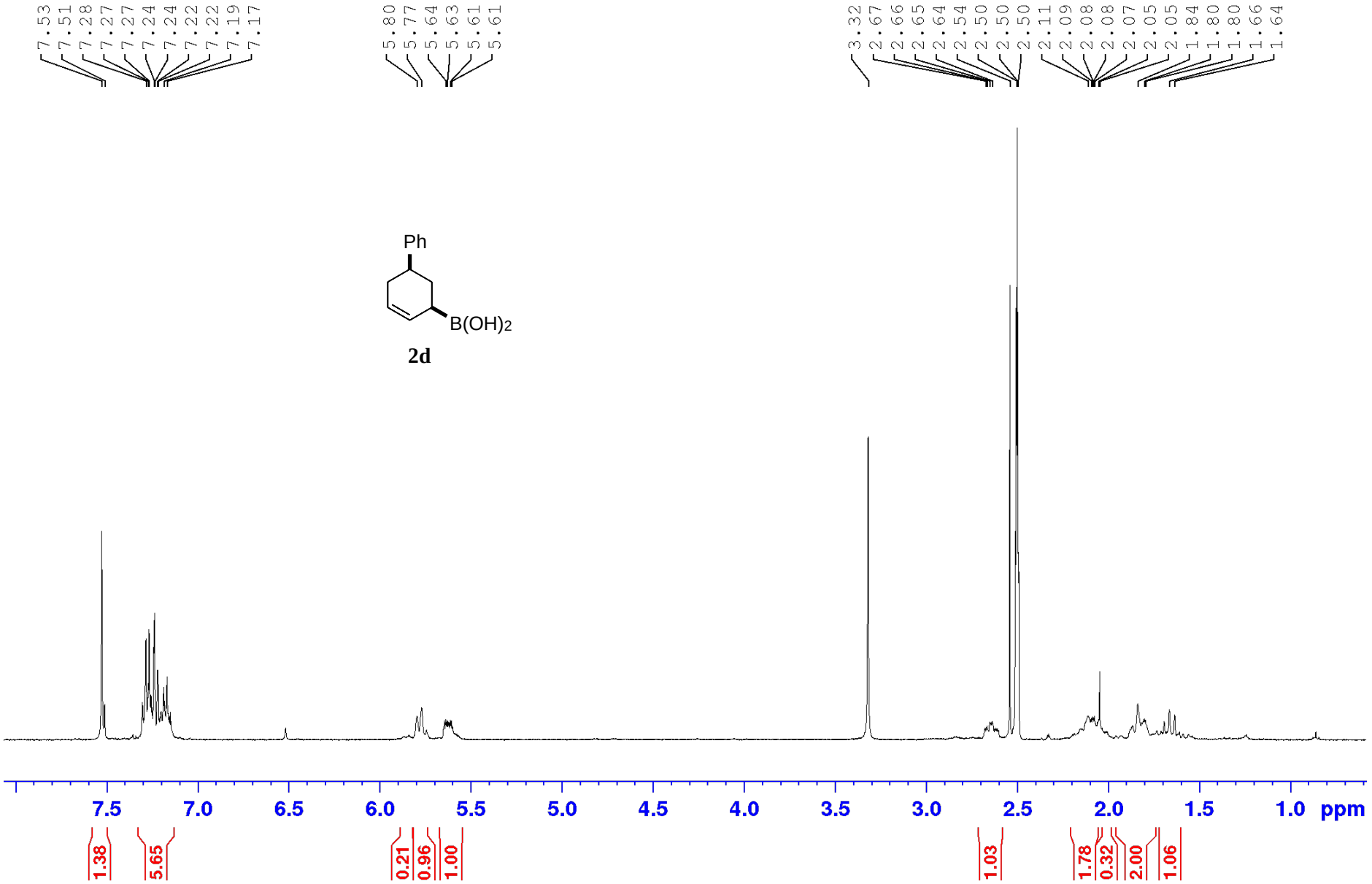
7.20
7.19
7.18
7.16
7.15
5.87
5.85
5.85
5.84
5.61
5.61
5.60
5.59
5.59
5.58
5.58
3.32
2.85
2.84
2.83
2.51
2.15
2.09
2.08
2.07
2.06
2.05
1.96
1.94
1.93
1.74
1.71
1.70
1.69
1.67
Ph
B(OH)2
2b
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
ppm
1.98
5.47
0.96
0.23
1.15
1.00
1.02
1.34
0.97
1.96


148.0
130.5
128.7
127.2
126.1
123.7
38.6
33.2
31.5
Ph
B(OH)2
2b
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
ppm


7.53
7.51
7.28
7.27
7.27
7.24
7.24
7.22
7.22
7.19
7.17
5.80
5.77
5.64
5.63
5.61
5.61
3.32
2.67
2.66
2.65
2.64
2.54
2.50
2.50
2.50
2.11
2.09
2.08
2.08
2.07
2.05
2.05
1.84
1.80
1.80
1.66
1.64
Ph
B(OH)2
2d
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
ppm
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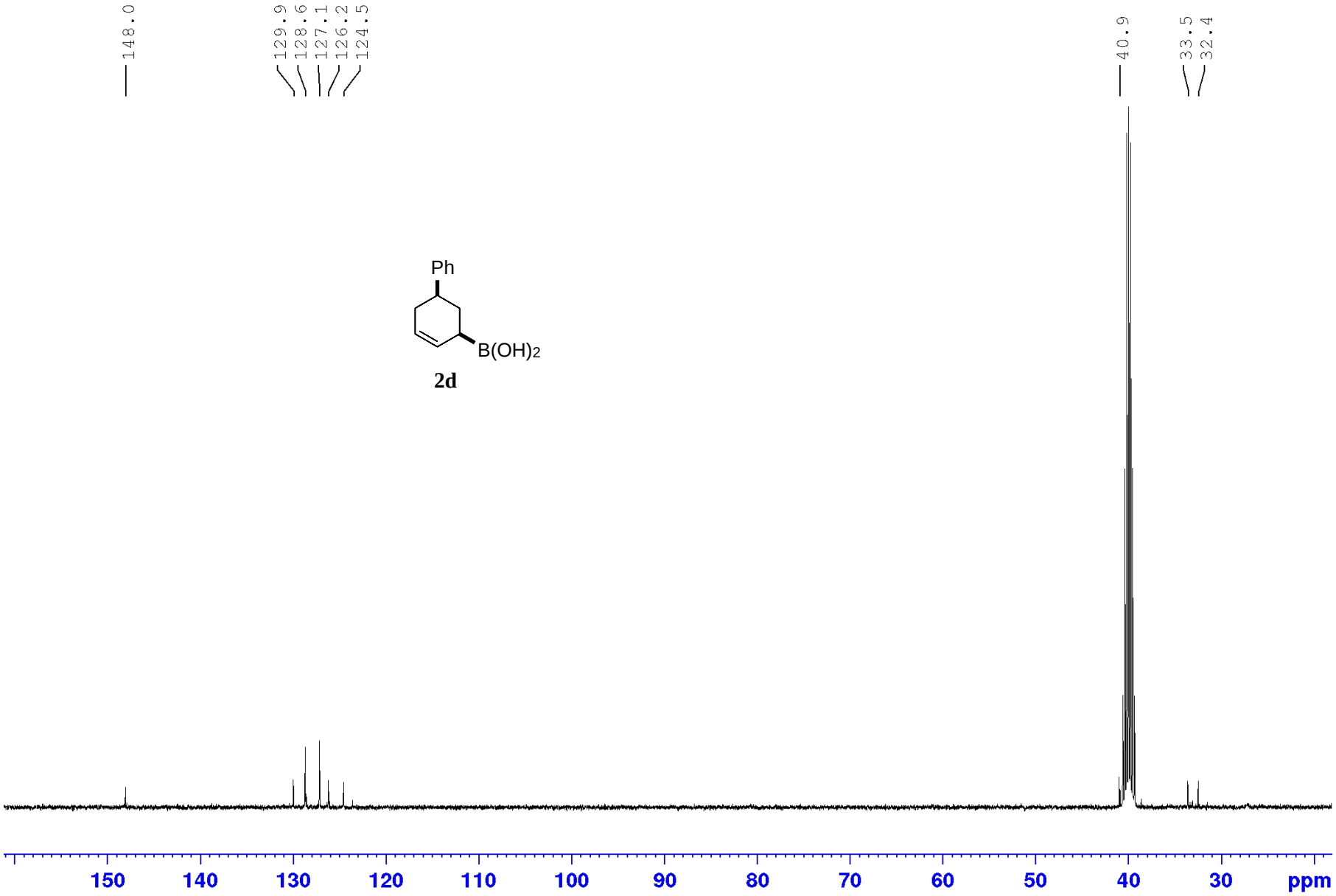
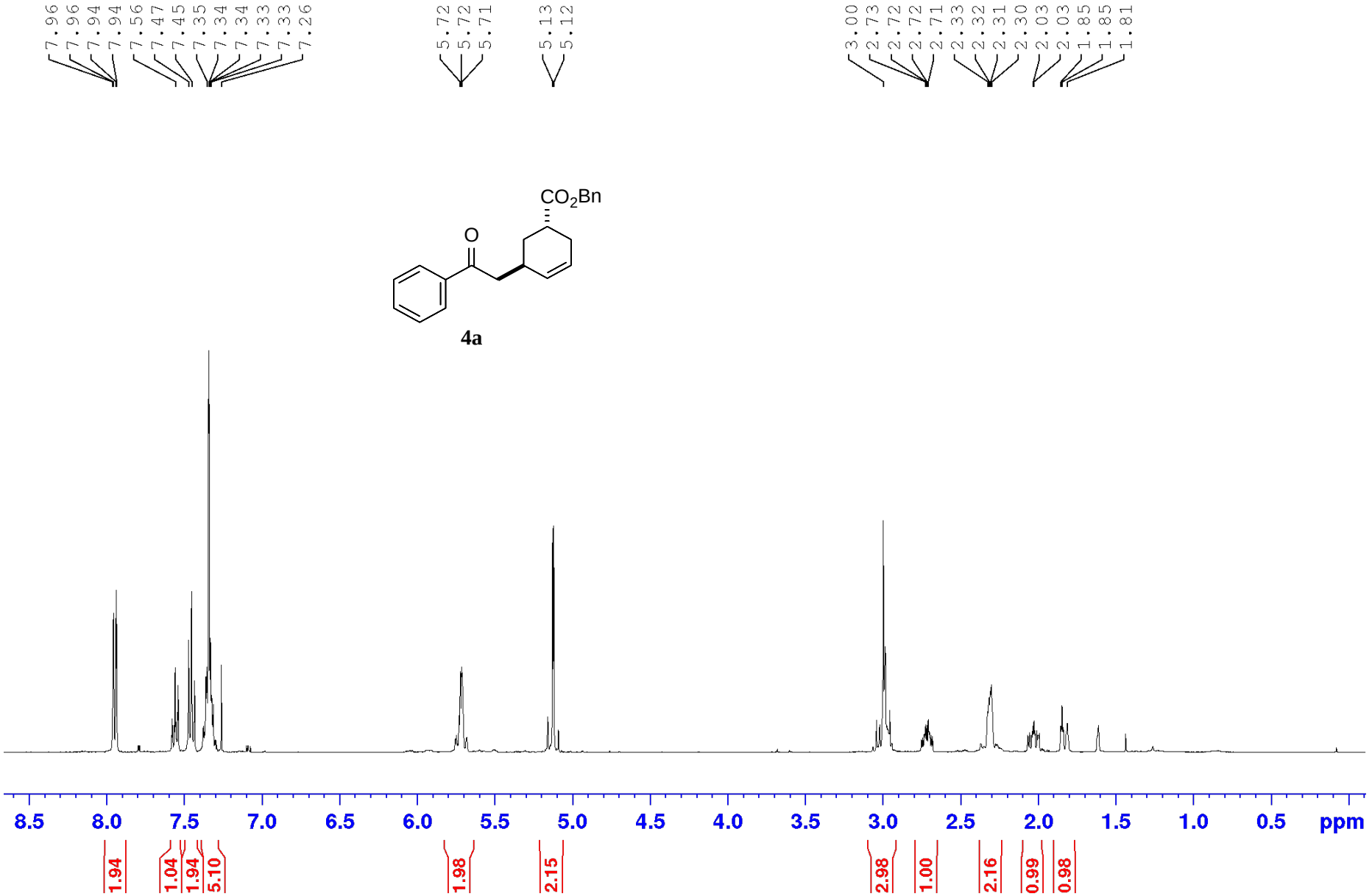
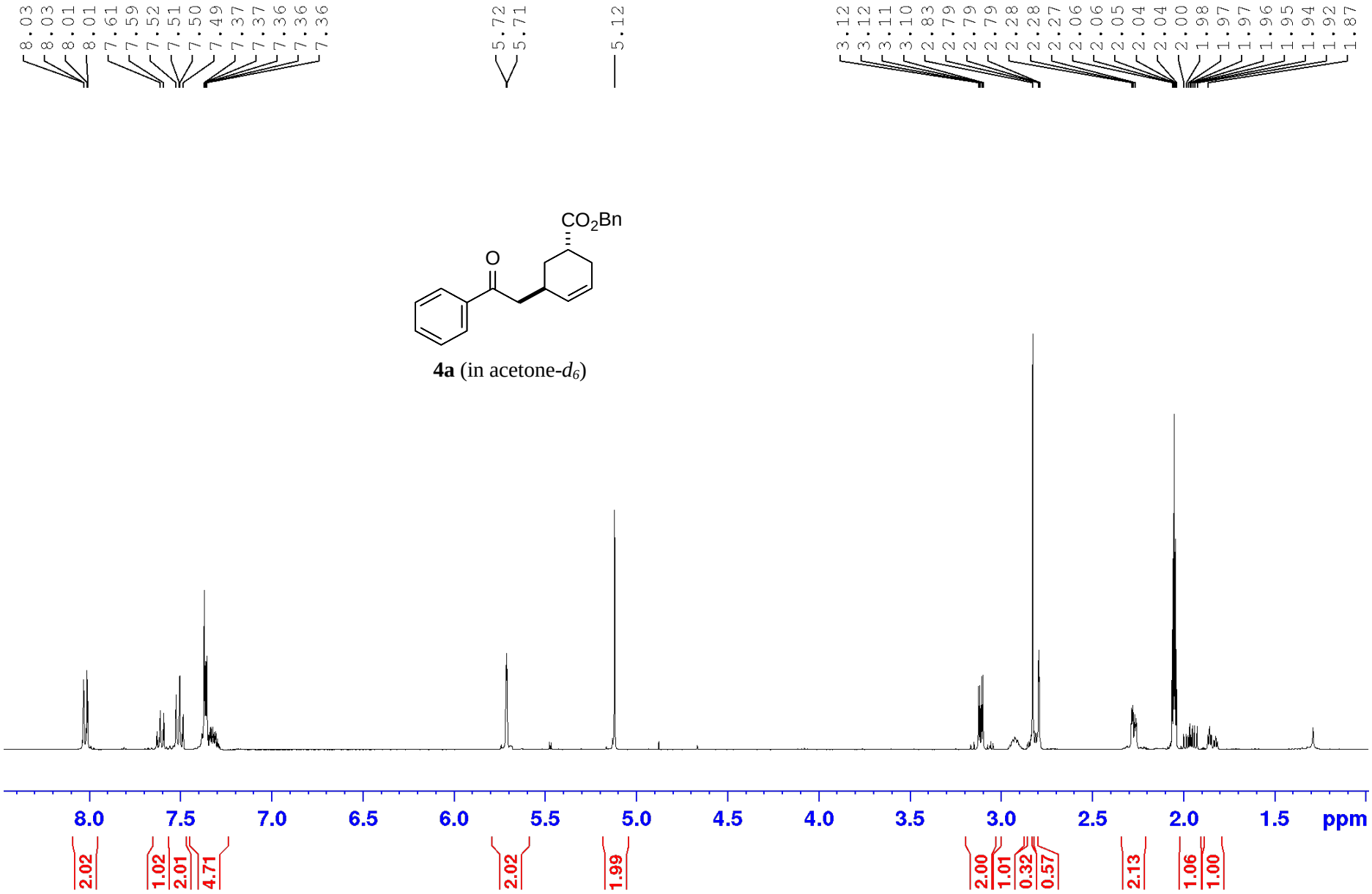
5.65
0.21
0.96
1.00
1.03
1.78
0.32
2.00
1.06

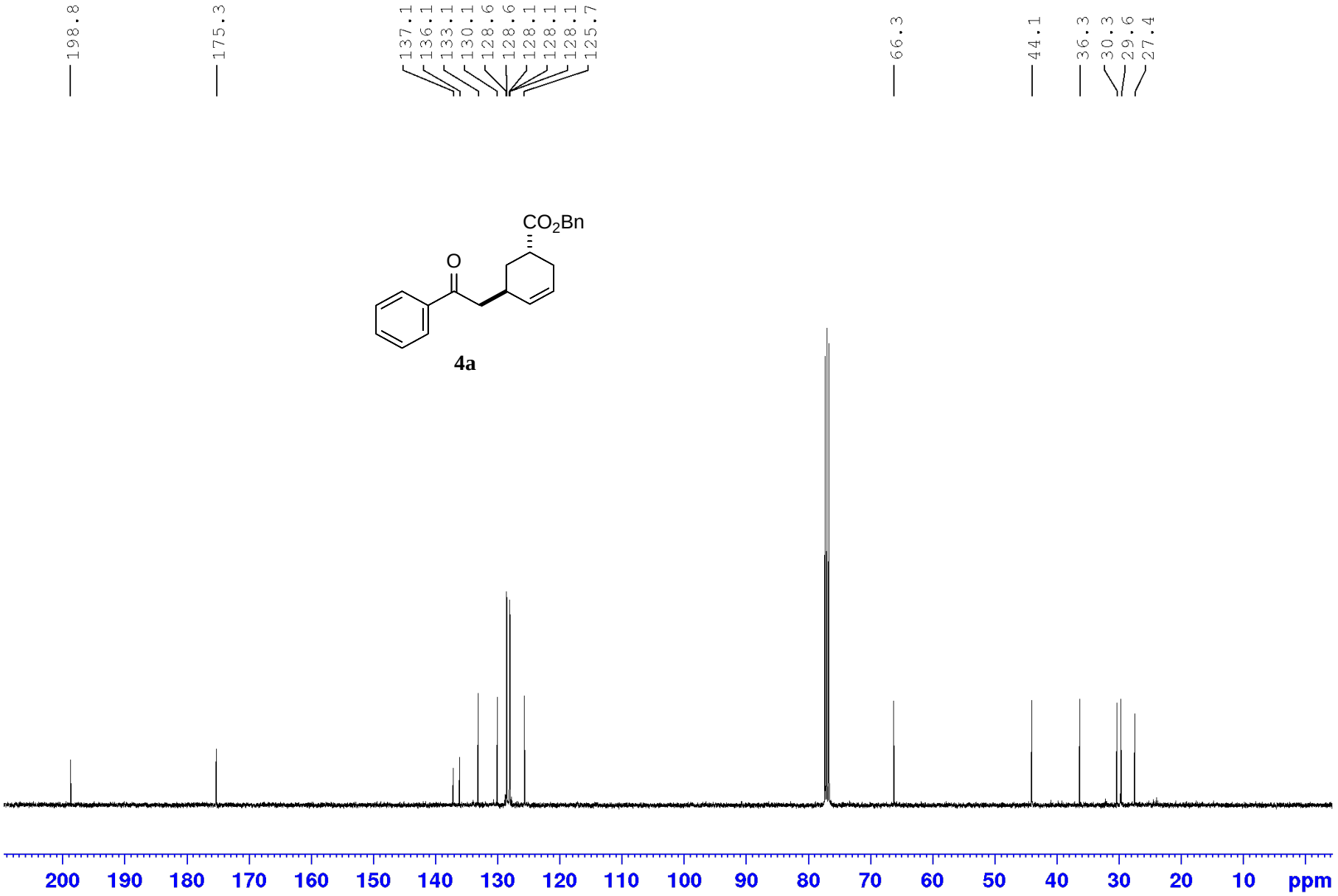

148.0
129.9
128.6
127.1
126.2
124.5
40.9
33.5
32.4
Ph
B(OH)2
150
140
130
120
110
100
90
80
70
60
50
40
30
ppm

2d

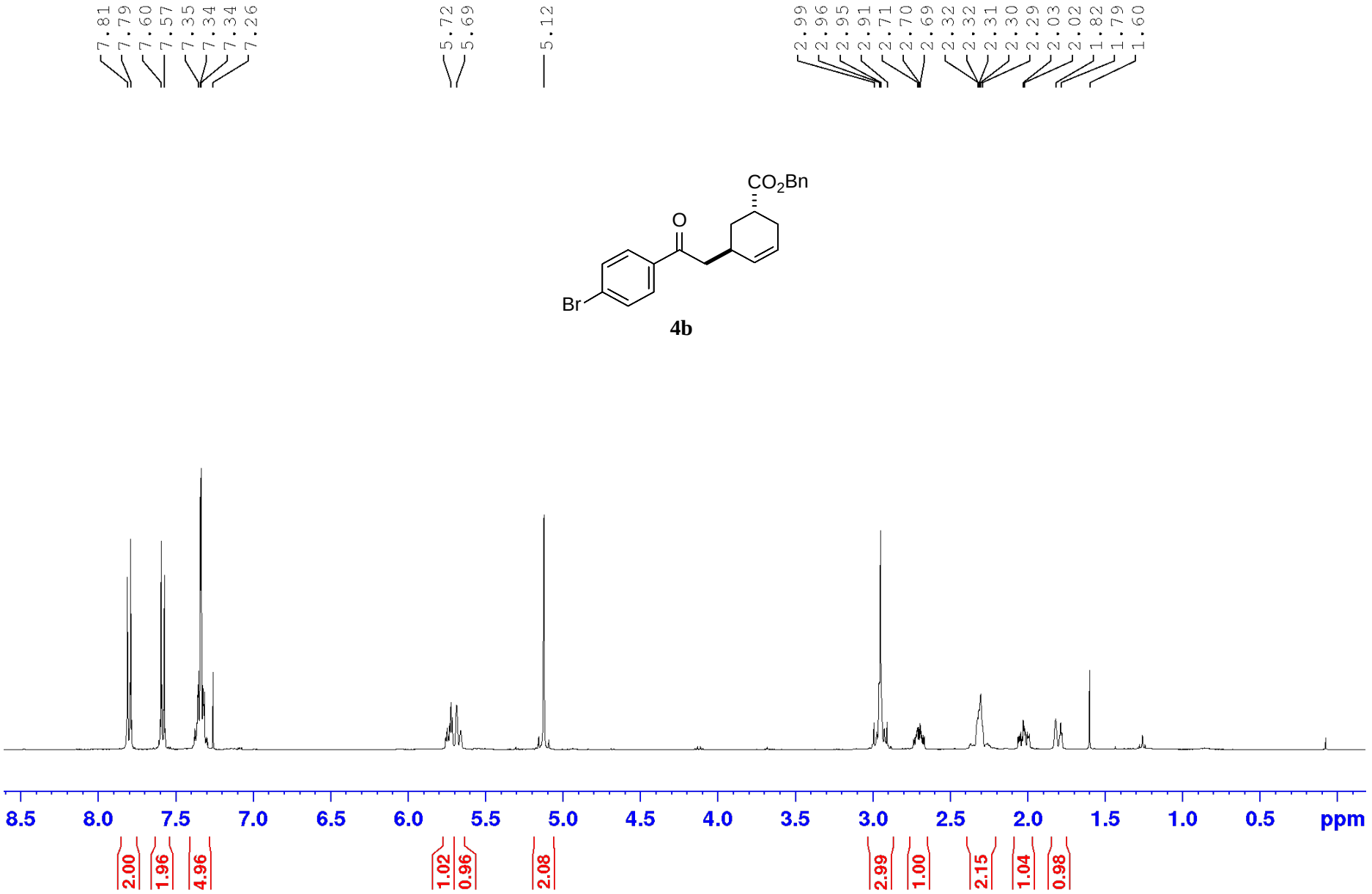

7.96
7.96
7.94
7.94
7.56
7.47
7.45
7.35
7.34
7.34
7.33
7.33
7.26
5.72
5.72
5.71
5.13
5.12
3.00
2.73
2.72
2.72
2.71
2.33
2.32
2.31
2.30
2.03
2.03
1.85
1.85
1.81
CO2Bn
O
4a
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
ppm
1.94
1.04
1.94
5.10
1.98
2.15
2.98
1.00
2.16
0.99
0.98



4a (in acetone-d_6)


198.8
175.3
137.1
136.1
133.1
130.1
128.6
128.6
128.1
128.1
128.1
125.7
66.3
44.1
36.3
30.3
29.6
27.4
CO2Bn
O
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
ppm

4a


7.81
7.79
7.60
7.57
7.35
7.34
7.34
7.26
5.72
5.69
5.12
2.99
2.96
2.95
2.91
2.71
2.70
2.69
2.32
2.32
2.31
2.30
2.29
2.03
2.02
1.82
1.79
1.60
CO2Bn
O
Br
4b
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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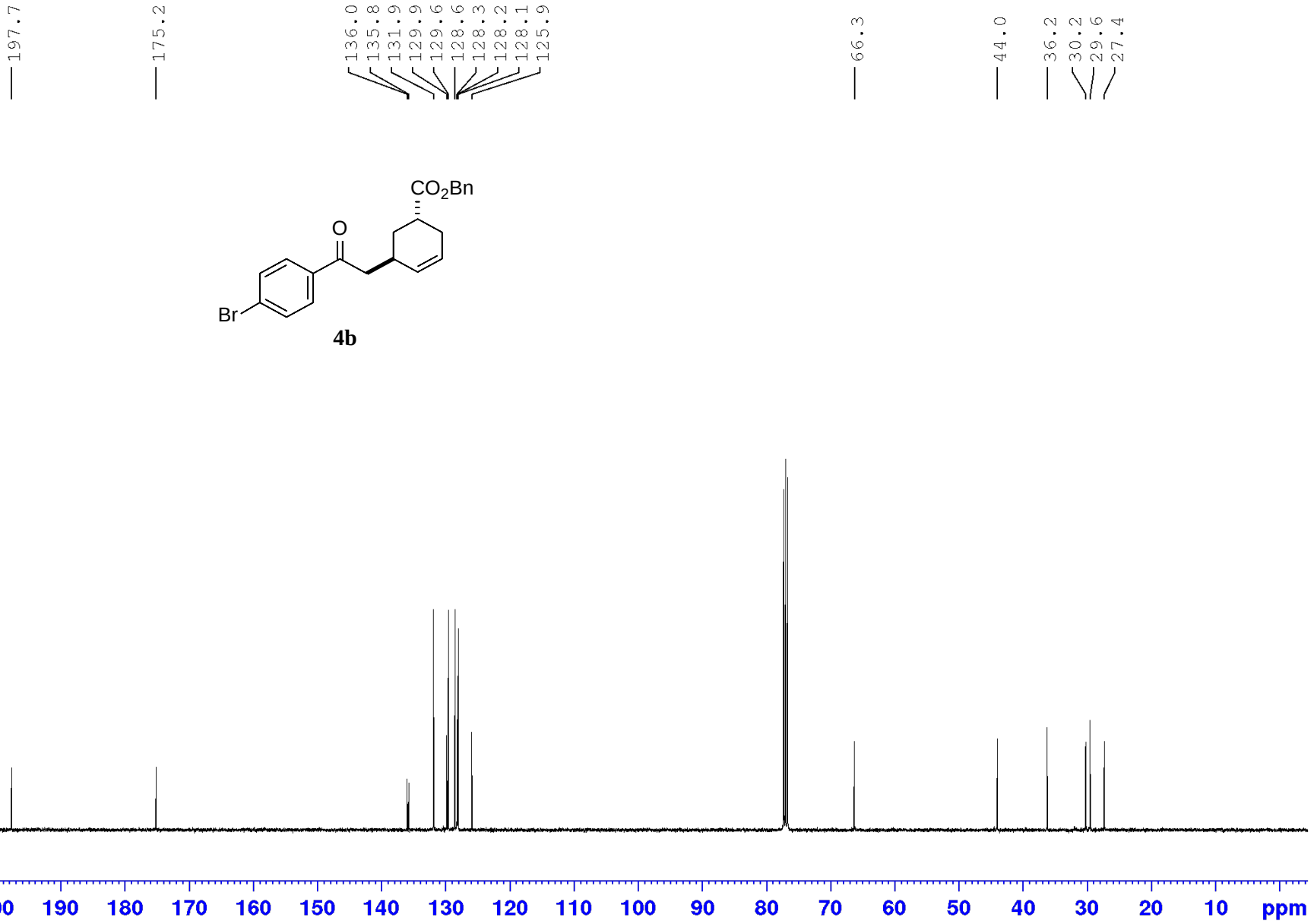
1.96
4.96
1.02
0.96
2.08
2.99
1.00
2.15
1.04
0.98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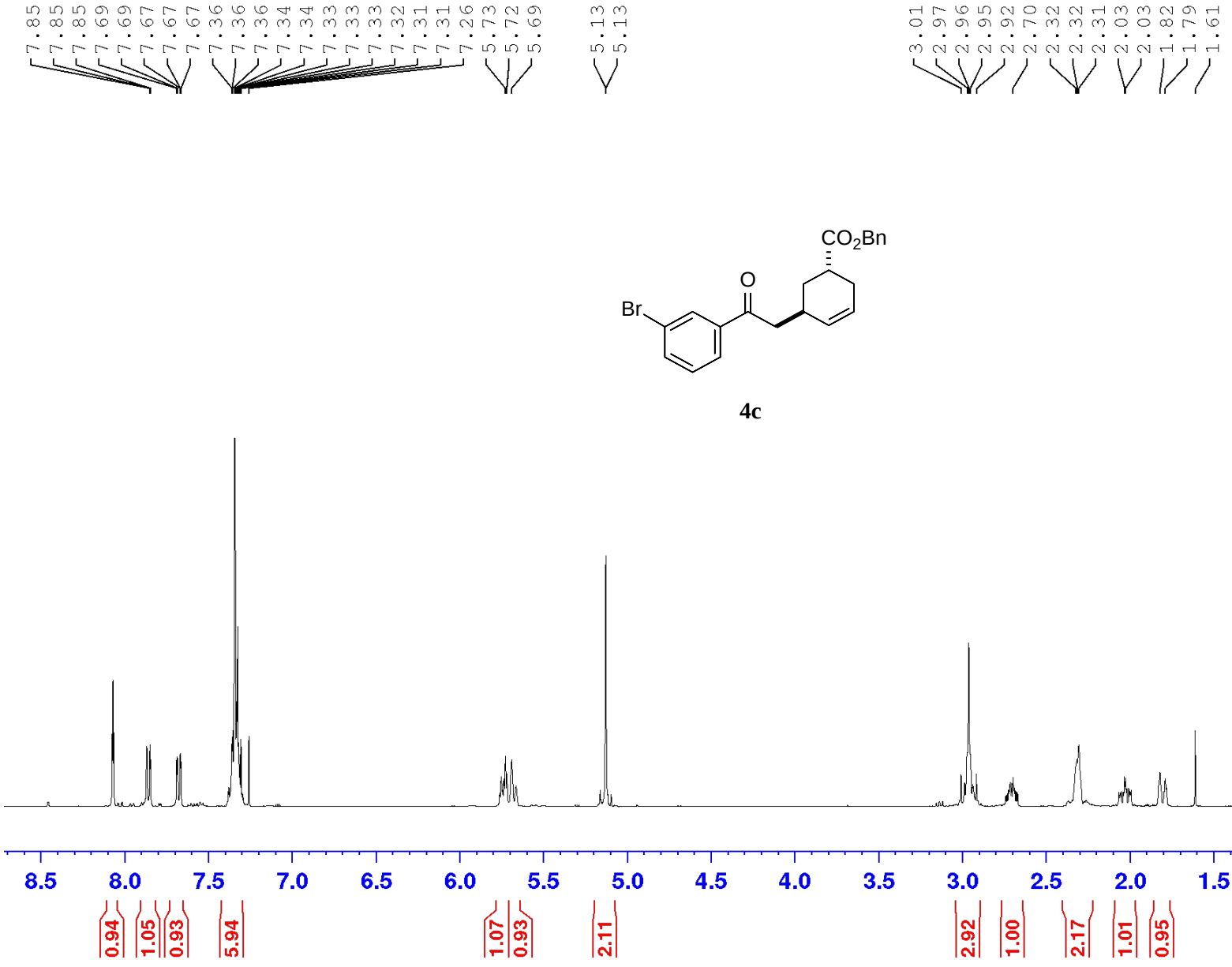
175.2
136.0
135.8
131.9
129.9
129.6
128.6
128.3
128.2
128.1
125.9
66.3
44.0
36.2
30.2
29.6
27.4
CO2Bn
O
Br
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
ppm

4b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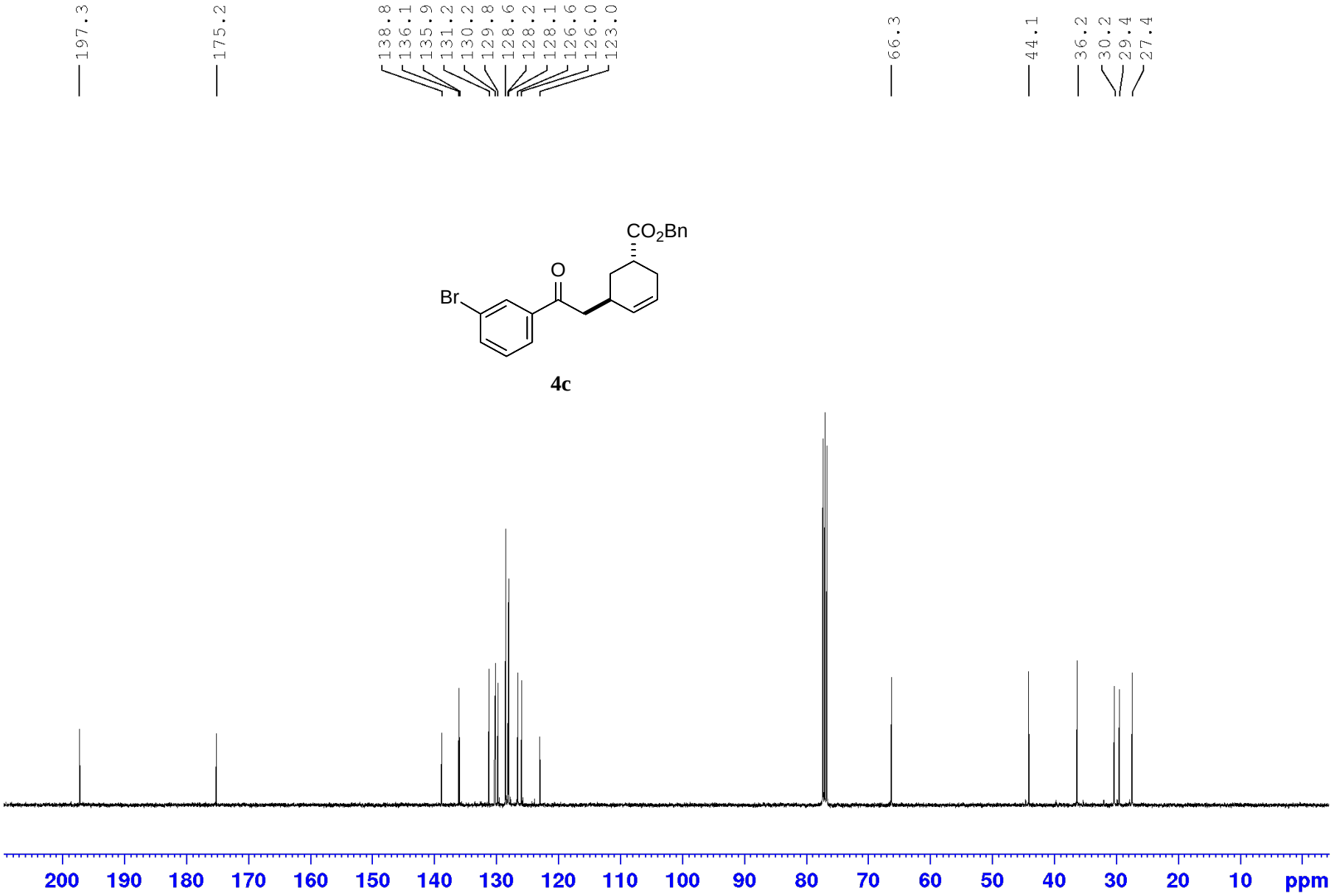
7.85
7.85
7.69
7.69
7.67
7.67
7.67
7.36
7.36
7.36
7.34
7.34
7.33
7.33
7.33
7.32
7.31
7.31
7.26
5.73
5.72
5.69
5.13
5.13
3.01
2.97
2.96
2.95
2.92
2.70
2.32
2.32
2.31
2.03
2.03
1.82
1.79
1.61
CO2Bn
O
Br
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
ppm
0.94
1.05
0.93
5.94
1.07
0.93
2.11
2.92
1.00
2.17
1.01
0.95

4c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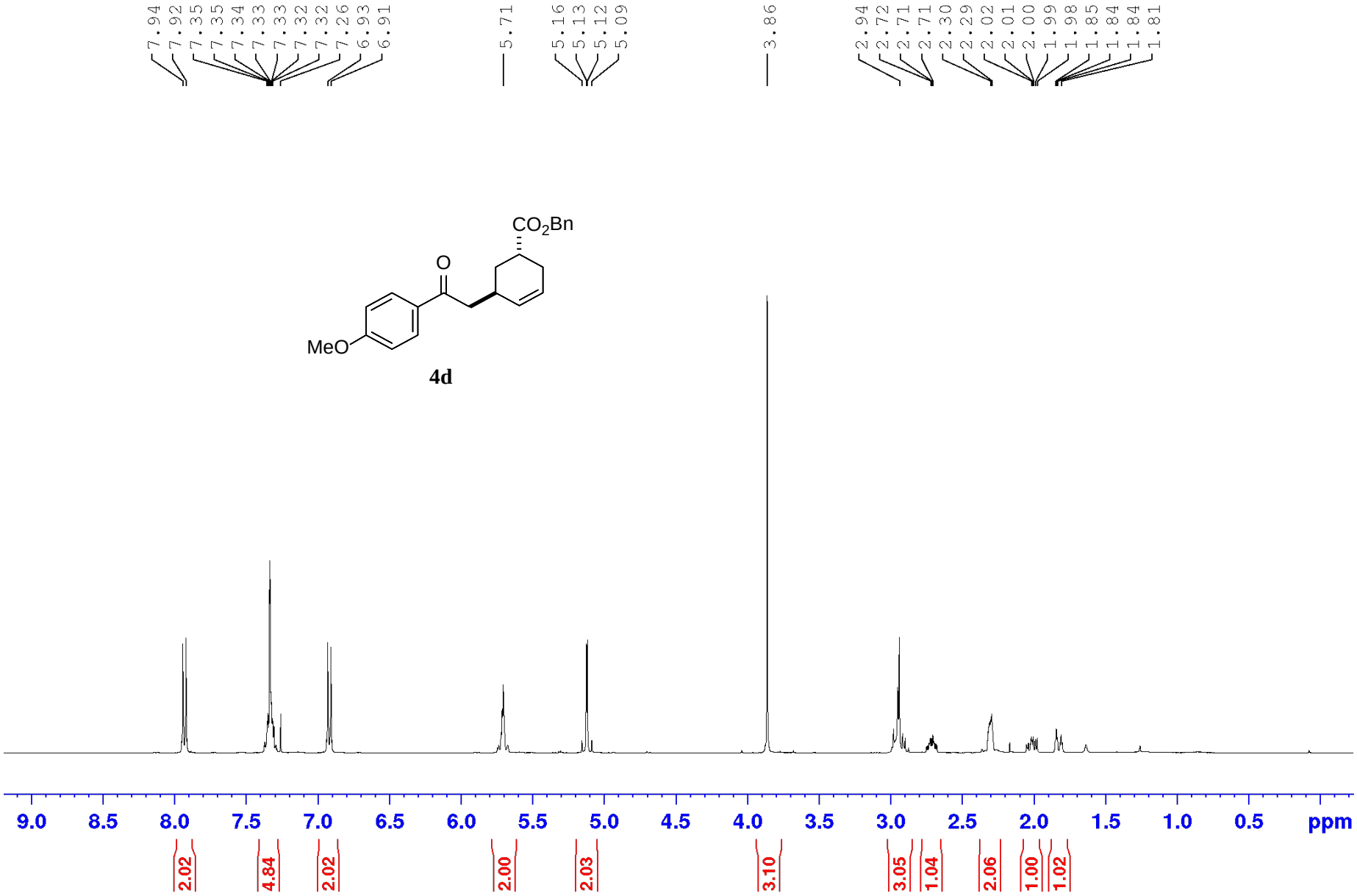
175.2
138.8
136.1
135.9
131.2
130.2
129.8
128.6
128.2
128.1
126.6
126.0
123.0
66.3
44.1
36.2
30.2
29.4
27.4
CO2Bn
O
Br
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
ppm

4c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7.92
7.35
7.35
7.34
7.33
7.33
7.32
7.32
7.26
6.93
6.91
5.71
5.16
5.13
5.12
5.09
3.86
2.94
2.72
2.71
2.71
2.30
2.29
2.02
2.01
2.00
1.99
1.98
1.85
1.84
1.84
1.81
CO2Bn
O
MeO
4d
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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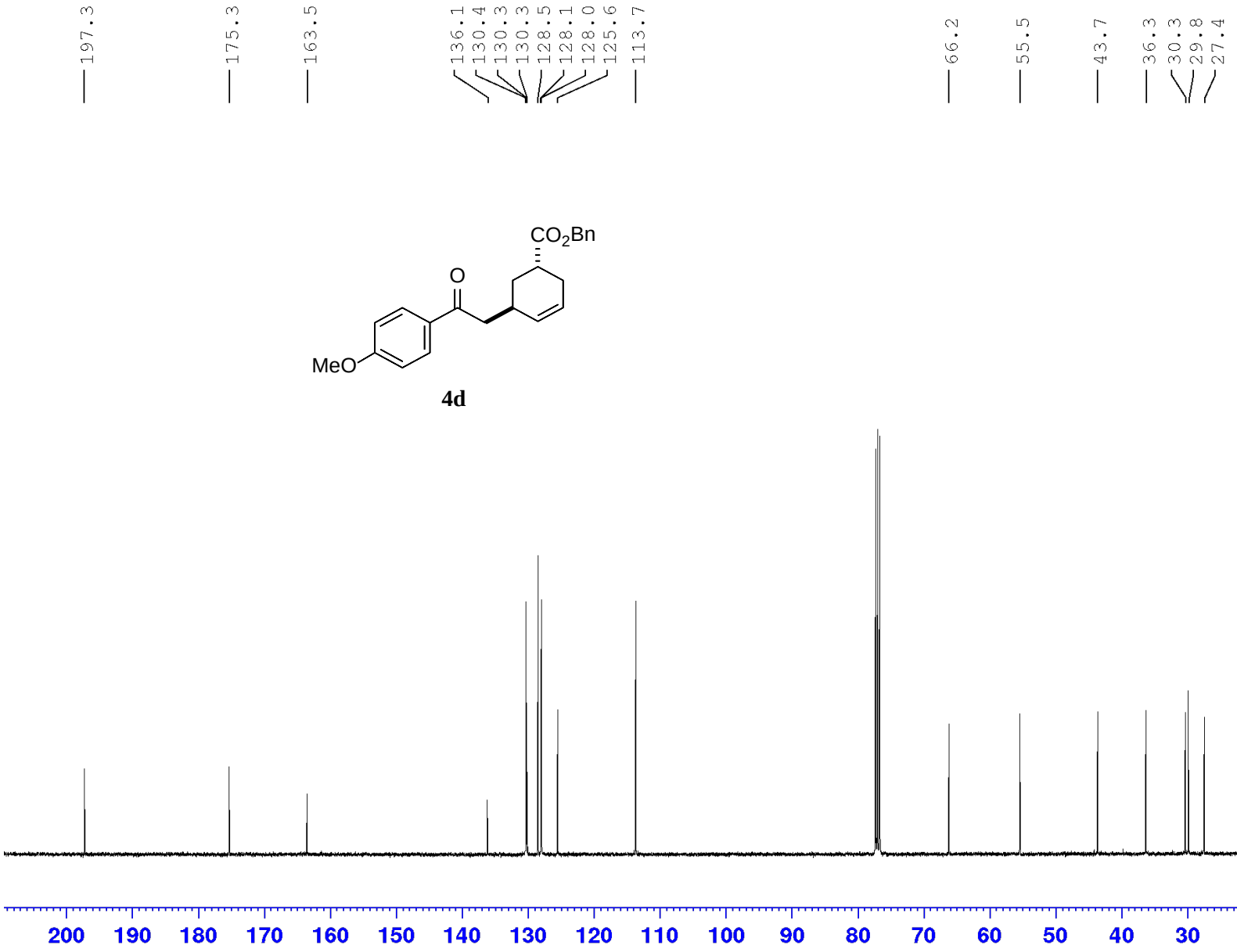
4.84
2.02
2.00
2.03
3.10
3.05
1.04
2.06
1.00
1.02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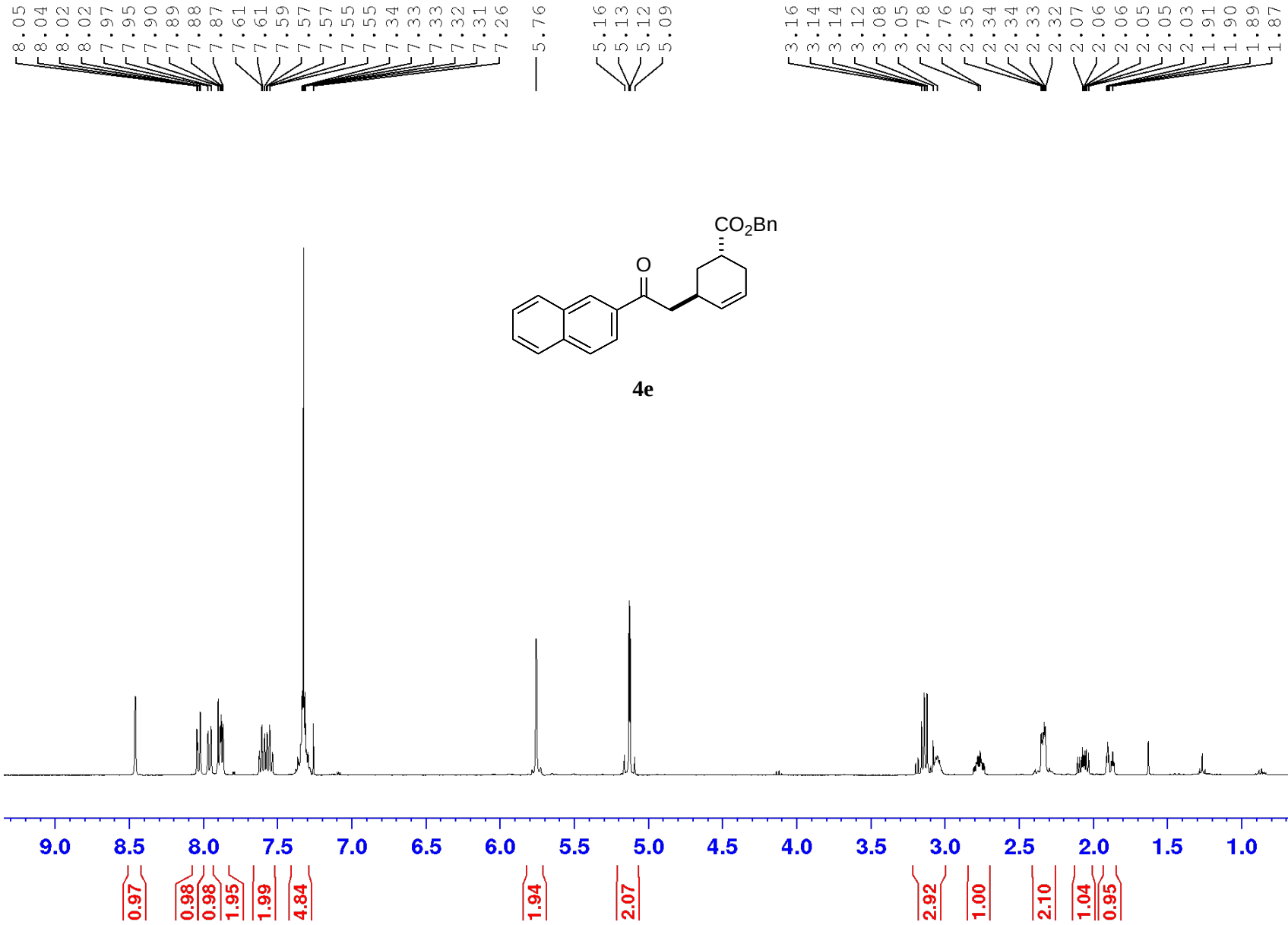
175.3
163.5
136.1
130.4
130.3
130.3
128.5
128.1
128.0
125.6
113.7
66.2
55.5
43.7
36.3
30.3
29.8
27.4
CO2Bn
O
MeO
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
ppm

4d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8.04
8.02
8.02
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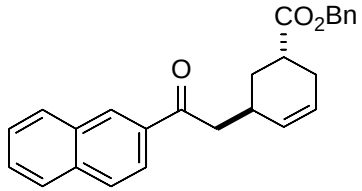
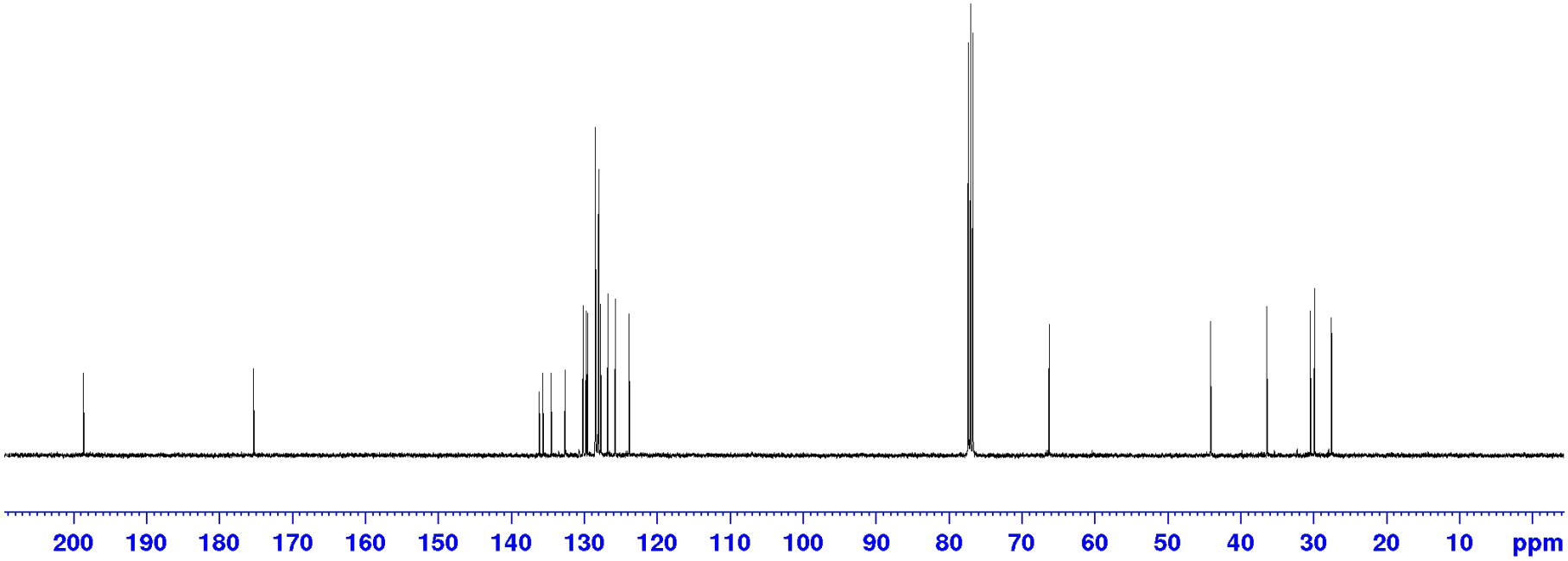
7.95
7.90
7.89
7.88
7.87
7.61
7.61
7.59
7.57
7.57
7.55
7.55
7.34
7.33
7.33
7.32
7.31
7.26
5.76
5.16
5.13
5.12
5.09
3.16
3.14
3.14
3.12
3.08
3.05
2.78
2.76
2.35
2.34
2.34
2.33
2.32
2.07
2.06
2.06
2.05
2.05
2.03
1.91
1.90
1.89
1.87
CO2Bn
O
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
ppm
0.97
0.98
0.98
1.95
1.99
4.84
1.94
2.07
2.92
1.00
2.10
1.04
0.95

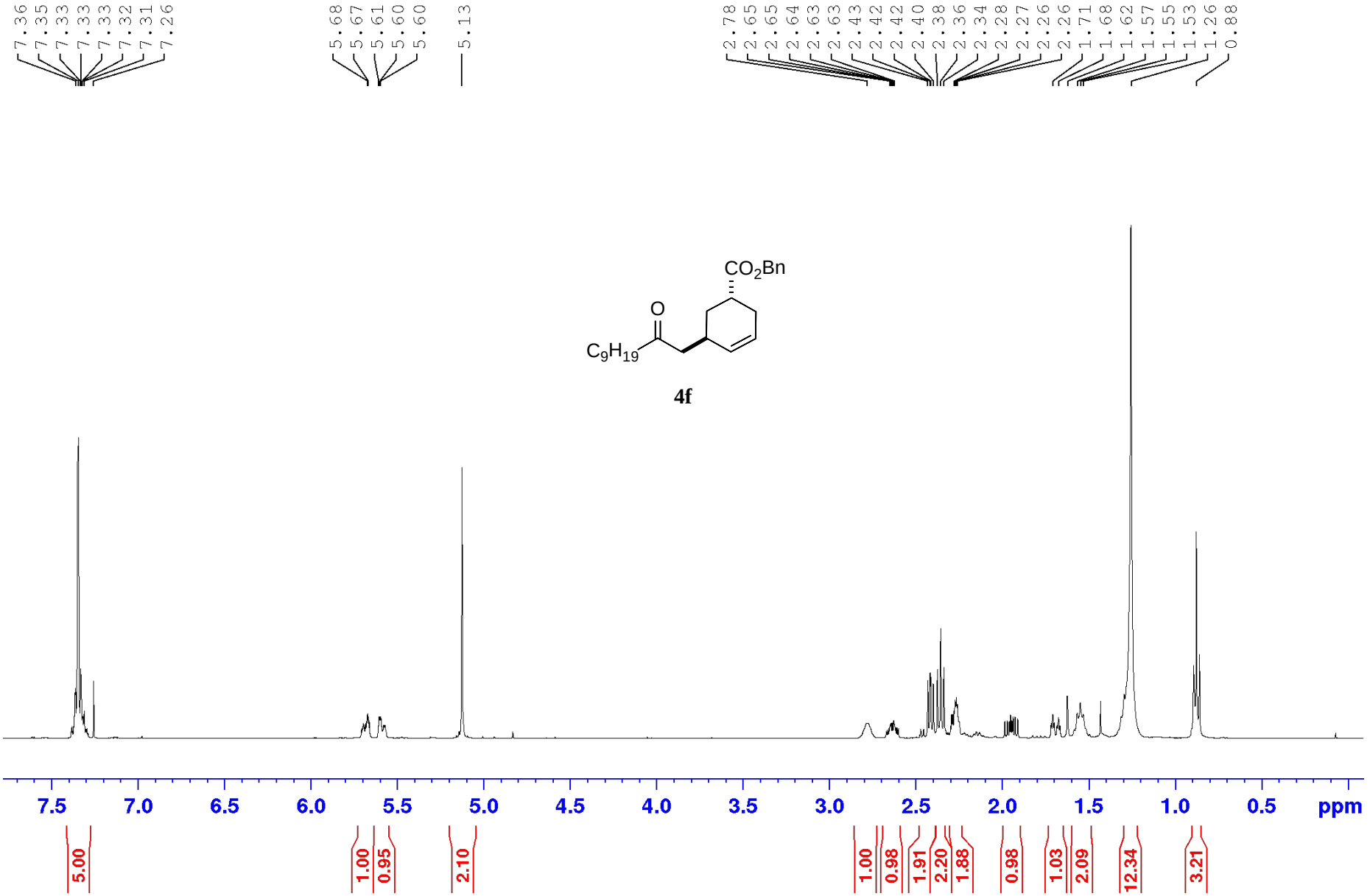
4e

198.7
175.3
136.1
135.6
134.5
132.5
130.2
129.8
129.6
128.5
128.5
128.1
128.1
127.8
126.8
125.8
123.9
66.3
44.1
36.3
30.3
29.8
27.4



4e

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7.33
7.33
7.33
7.32
7.31
7.26
5.68
5.67
5.61
5.60
5.60
5.13
2.78
2.65
2.65
2.64
2.63
2.63
2.43
2.42
2.42
2.40
2.38
2.36
2.34
2.28
2.27
2.26
2.26
1.71
1.68
1.62
1.57
1.55
1.53
1.26
0.88
CO2Bn
O
C9H19
4f
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
5.00
1.00
0.95
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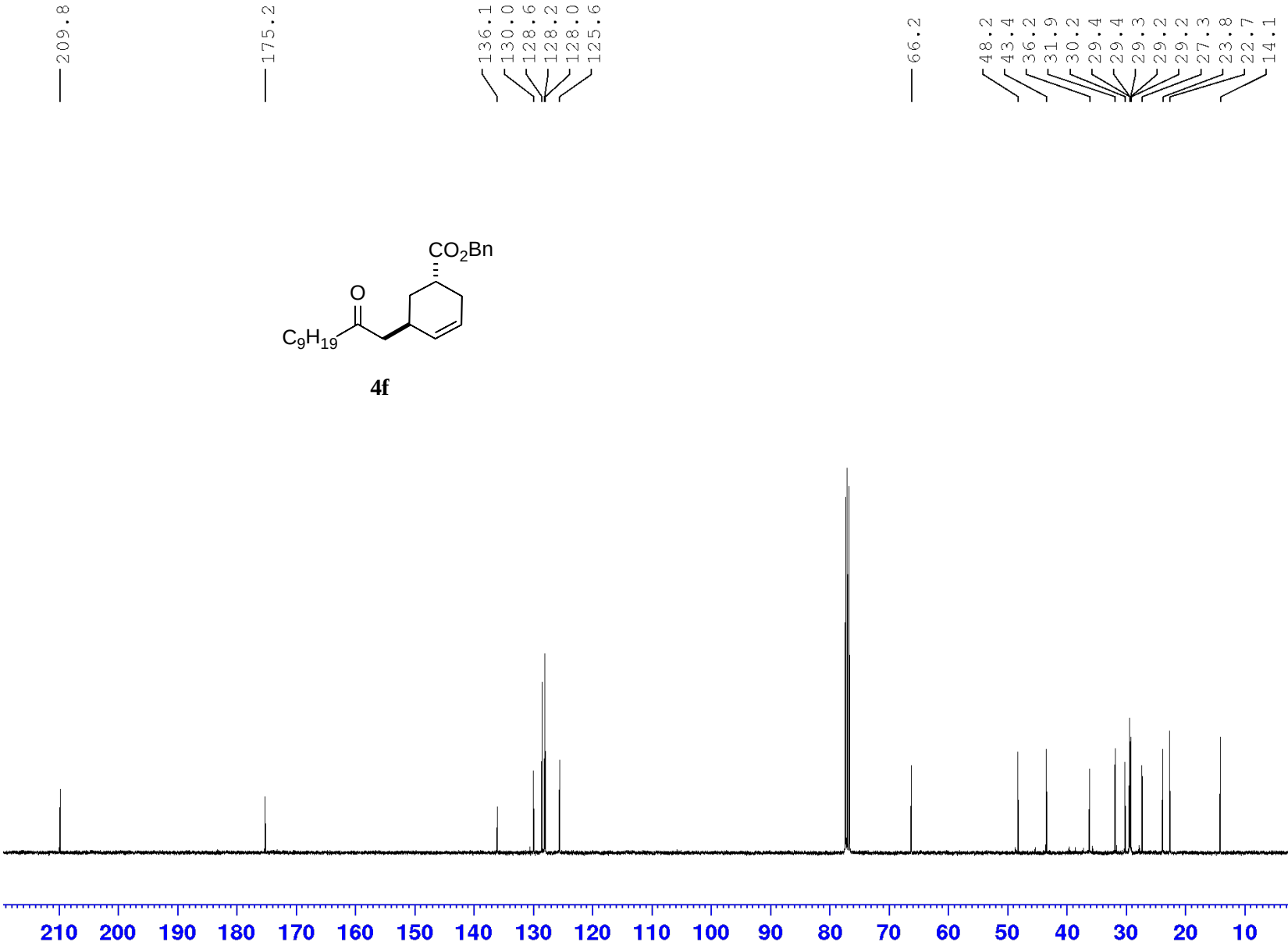
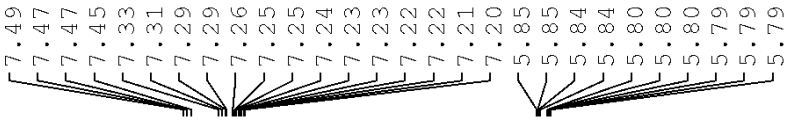
1.00
0.98
1.91
2.20
1.88
0.98
1.03
2.09
12.34
3.21


209.8
175.2
136.1
130.0
128.6
128.2
128.0
125.6
66.2
48.2
43.4
36.2
31.9
30.2
29.4
29.4
29.3
29.2
29.2
27.3
23.8
22.7
14.1
CO2Bn
O
C9H19
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 ppm

4f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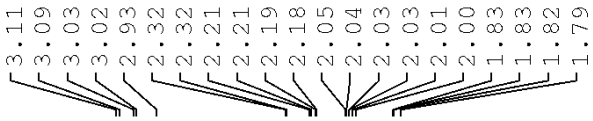
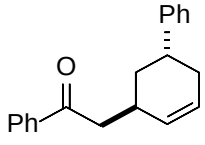
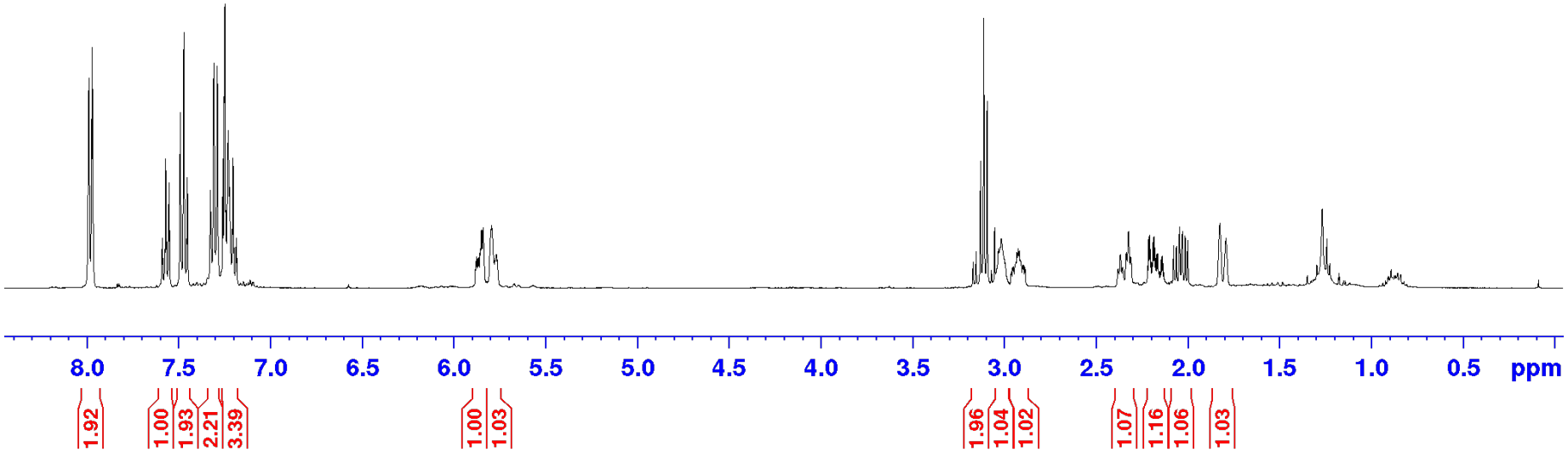
7.47
7.47
7.45
7.33
7.31
7.29
7.29
7.26
7.25
7.25
7.24
7.23
7.23
7.22
7.22
7.21
7.20
5.85
5.85
5.84
5.84
5.80
5.80
5.80
5.79
5.79
5.79


3.11
3.09
3.03
3.02
2.93
2.32
2.32
2.21
2.21
2.19
2.18
2.05
2.04
2.03
2.03
2.01
2.00
1.83
1.83
1.82
1.79


Ph
O
Ph

4g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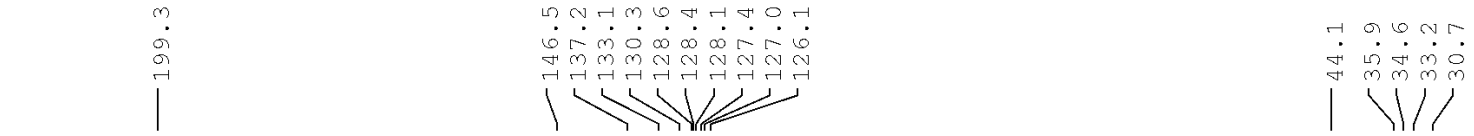
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
ppm
1.92
1.00
1.93
2.21
3.39
1.00
1.03
1.96
1.04
1.02
1.07
1.16
1.06
1.03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128.1
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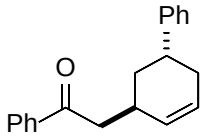
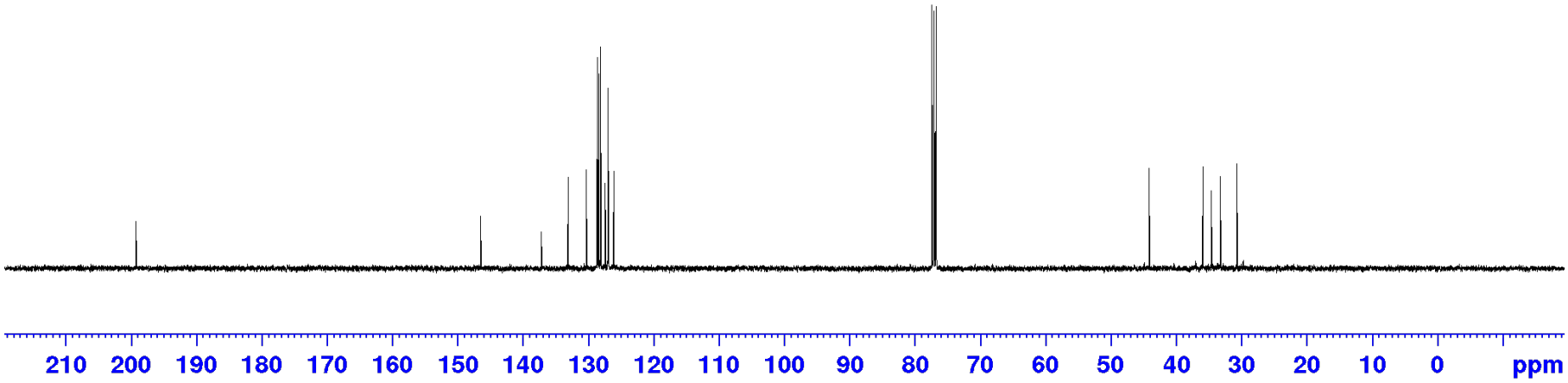
34.6
33.2
30.7


Ph
O
Ph

4g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200
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180
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150
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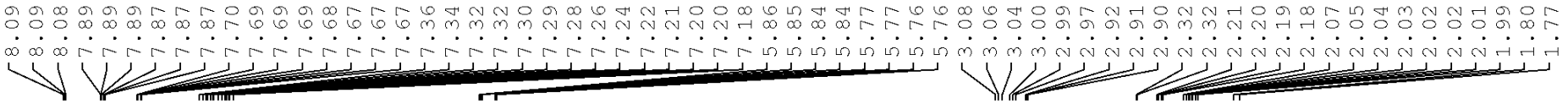
130
120
110
100
90
80
70
60
50
40
30
20
10
0
ppm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8.09
8.08
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7.87
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7.70
7.69
7.69
7.69
7.68
7.67
7.67
7.67
7.36
7.34
7.32
7.32
7.30
7.29
7.28
7.26
7.24
7.22
7.21
7.20
7.20
7.18
5.86
5.85
5.84
5.84
5.77
5.77
5.76
5.76
3.08
3.06
3.04
3.00
2.99
2.97
2.92
2.91
2.90
2.32
2.32
2.21
2.20
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2.03
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2.02
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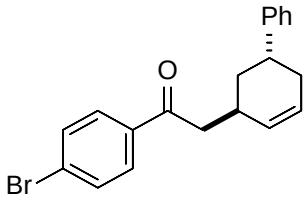
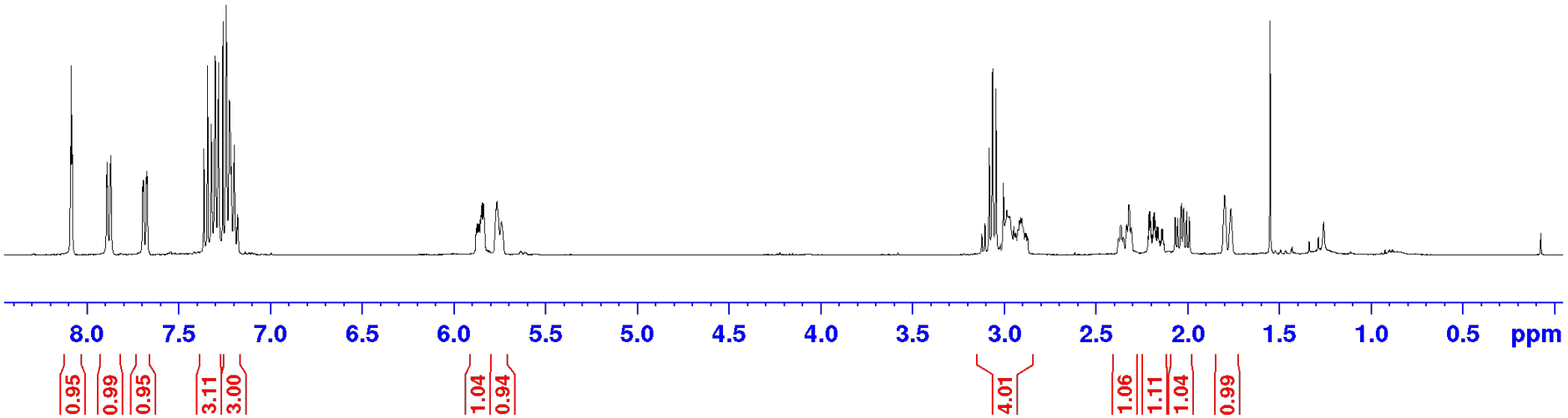
1.80
1.77


Ph
O
Br

4h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4.5
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3.5
3.0
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2.0
1.5
1.0
0.5
ppm
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0.99
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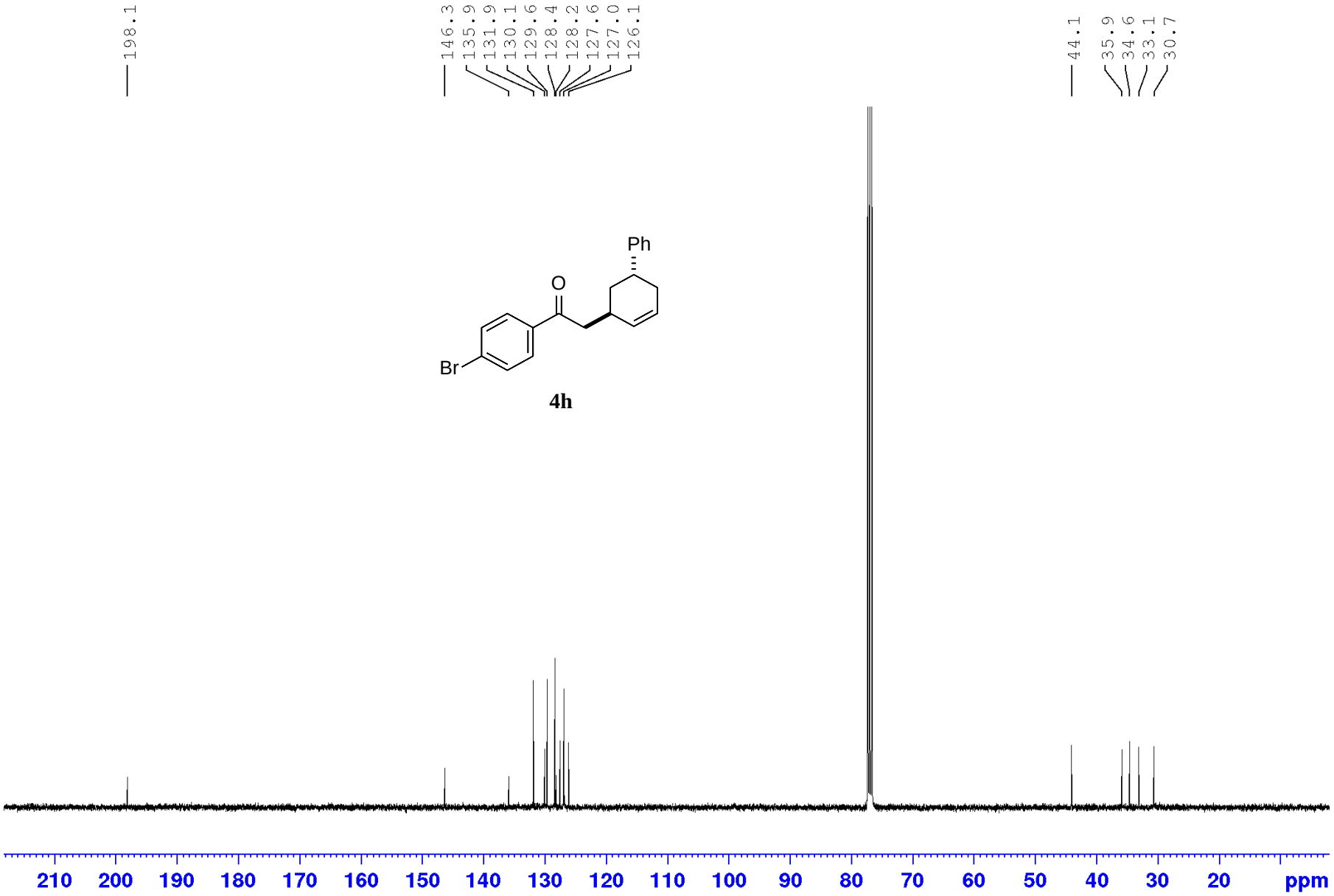
3.11
3.00
1.04
0.94
4.01
1.06
1.11
1.04
0.99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146.3
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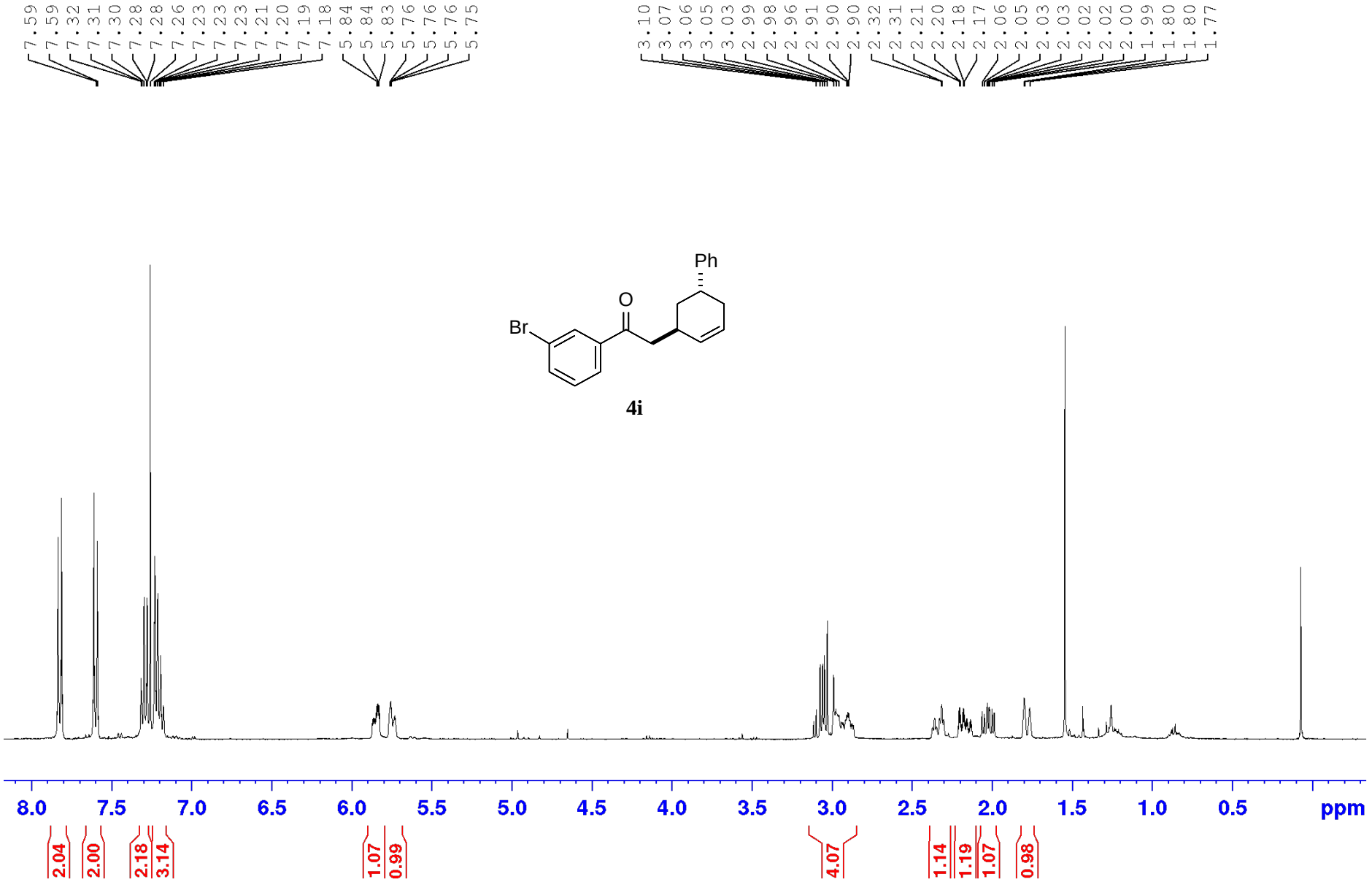
130.1
129.6
128.4
128.2
127.6
127.0
126.1
44.1
35.9
34.6
33.1
30.7
Ph
O
Br
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
ppm

4h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7.28
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7.23
7.21
7.20
7.19
7.18
5.84
5.84
5.83
5.76
5.76
5.76
5.75
3.10
3.07
3.06
3.05
3.03
2.99
2.98
2.96
2.91
2.90
2.90
2.32
2.31
2.21
2.20
2.18
2.17
2.06
2.05
2.03
2.03
2.02
2.02
2.00
1.99
1.80
1.80
1.77
Ph
O
Br
4i
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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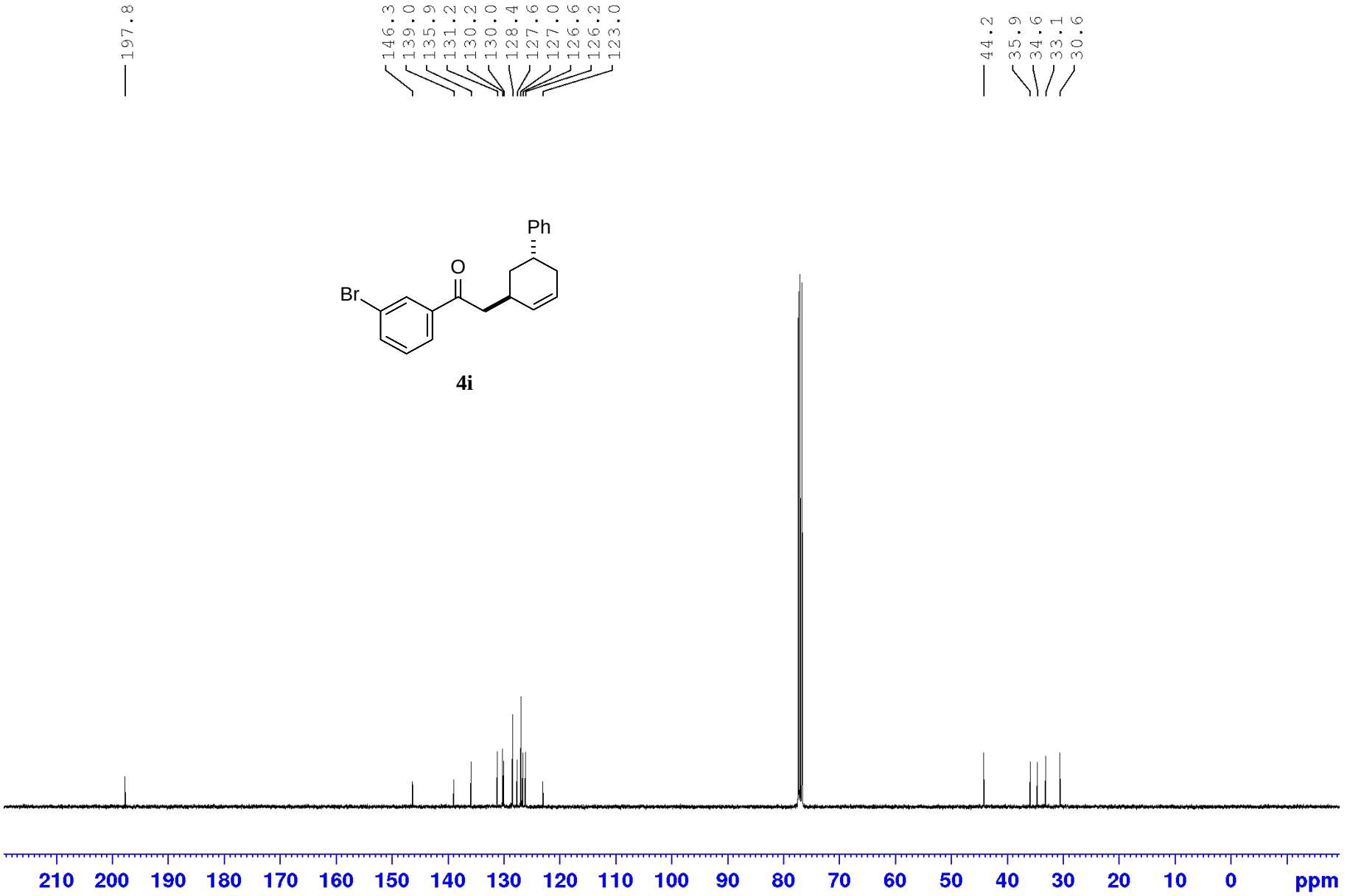
2.18
3.14
1.07
0.99
4.07
1.14
1.19
1.07
0.98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146.3
139.0
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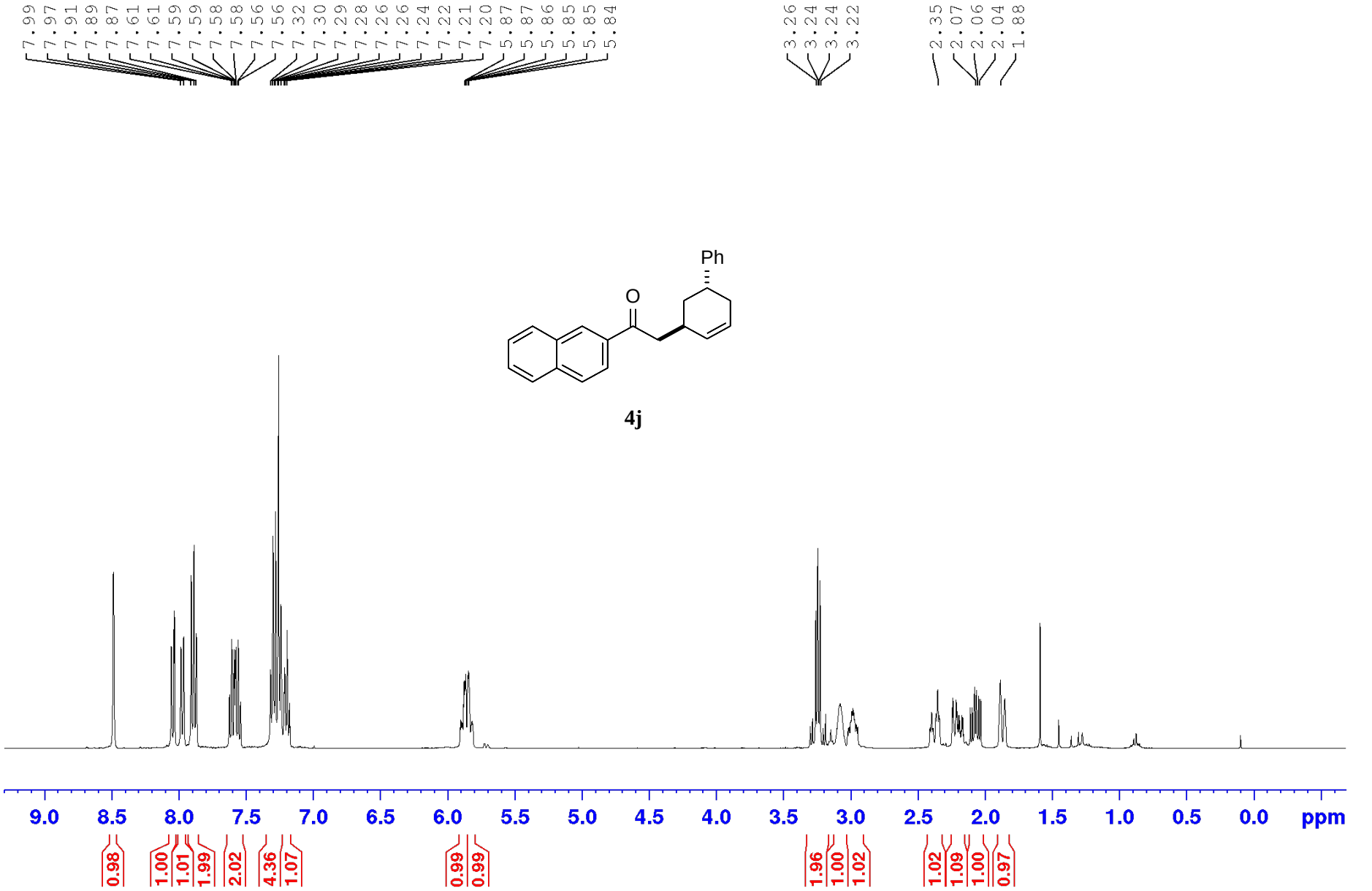
131.2
130.2
130.0
128.4
127.6
127.0
126.6
126.2
123.0
44.2
35.9
34.6
33.1
30.6
Ph
O
Br
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 ppm

4i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7.91
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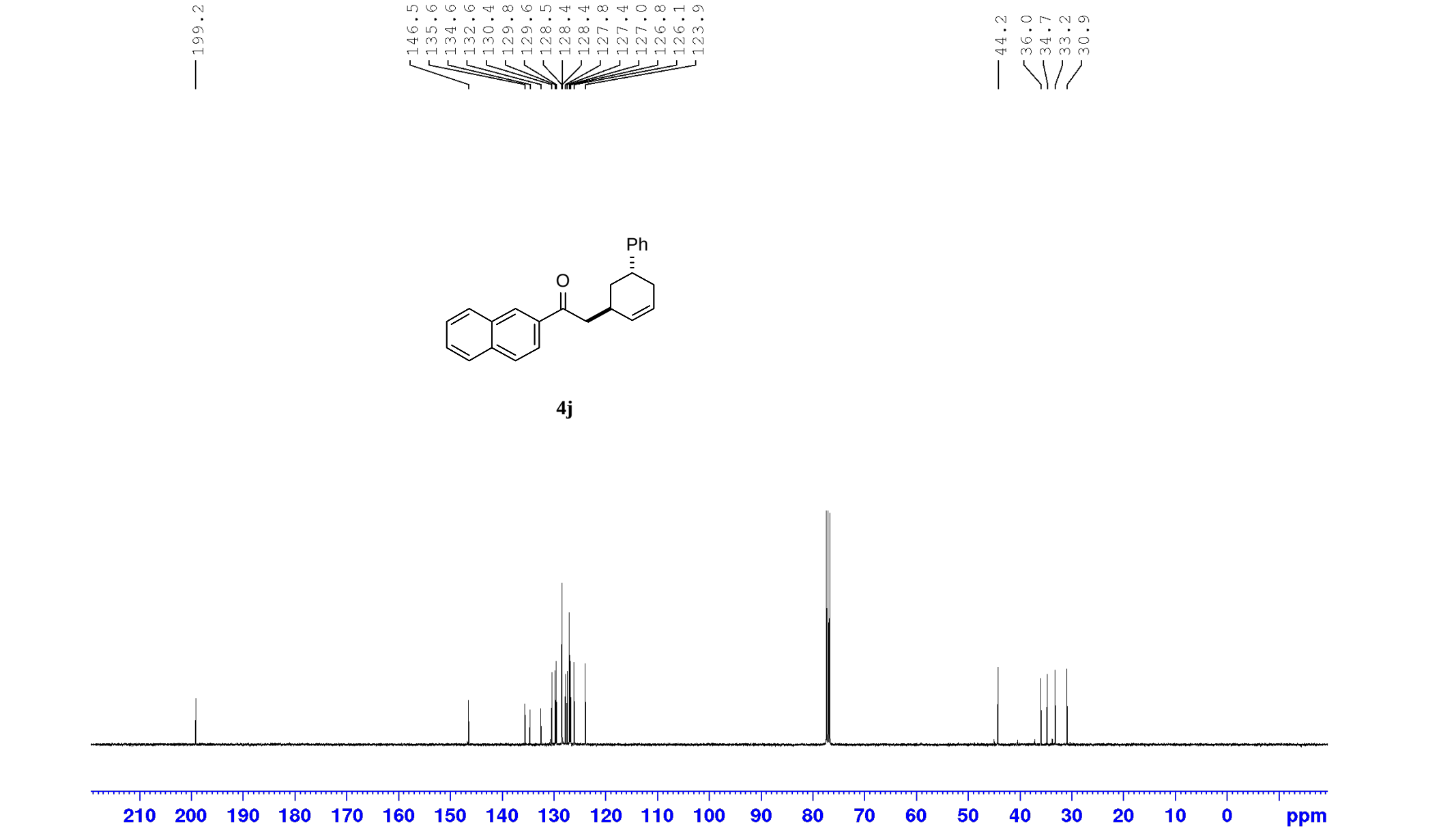
7.61
7.61
7.59
7.59
7.58
7.58
7.56
7.56
7.32
7.30
7.29
7.28
7.26
7.26
7.24
7.22
7.21
7.20
5.87
5.87
5.86
5.85
5.85
5.84
3.26
3.24
3.24
3.22
2.35
2.07
2.06
2.04
1.88
Ph
O
4j
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
ppm
0.98
1.00
1.01
1.99
2.02
4.36
1.07
0.99
0.99
1.96
1.00
1.02
1.02
1.09
1.00
0.97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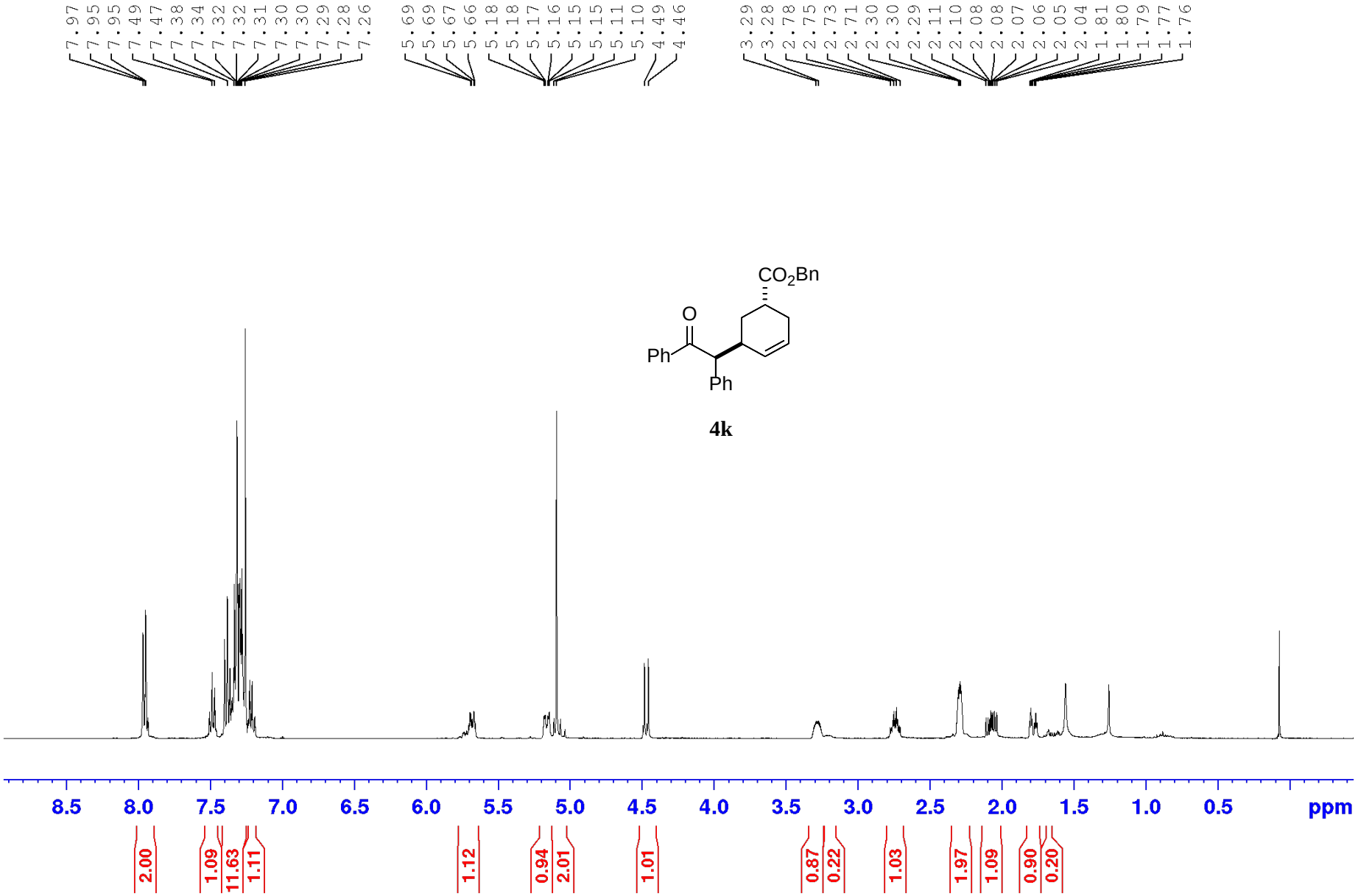
146.5
135.6
134.6
132.6
130.4
129.8
129.6
128.5
128.4
128.4
127.8
127.4
127.0
126.8
126.1
123.9
44.2
36.0
34.7
33.2
30.9
Ph
O
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
ppm

4j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7.95
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7.34
7.32
7.32
7.31
7.30
7.30
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7.28
7.26
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5.69
5.67
5.66
5.18
5.18
5.17
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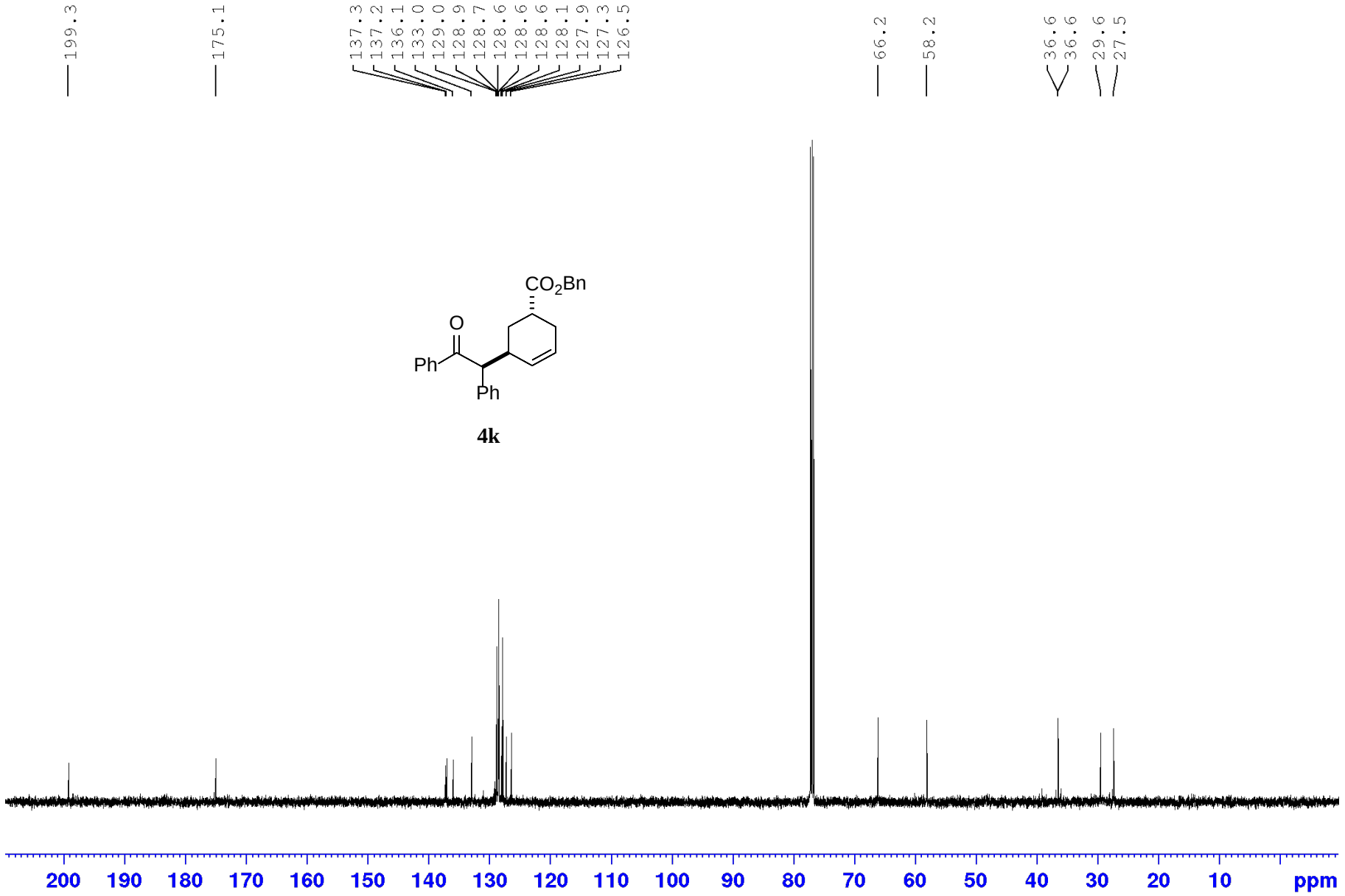
5.15
5.11
5.10
4.49
4.46
3.29
3.28
2.78
2.75
2.73
2.71
2.30
2.30
2.29
2.11
2.10
2.08
2.08
2.07
2.06
2.05
2.04
1.81
1.80
1.79
1.77
1.76
CO2Bn
O
Ph
Ph
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
ppm
2.00
1.09
11.63
1.11
1.12
0.94
2.01
1.01
0.87
0.22
1.03
1.97
1.09
0.90
0.20

4k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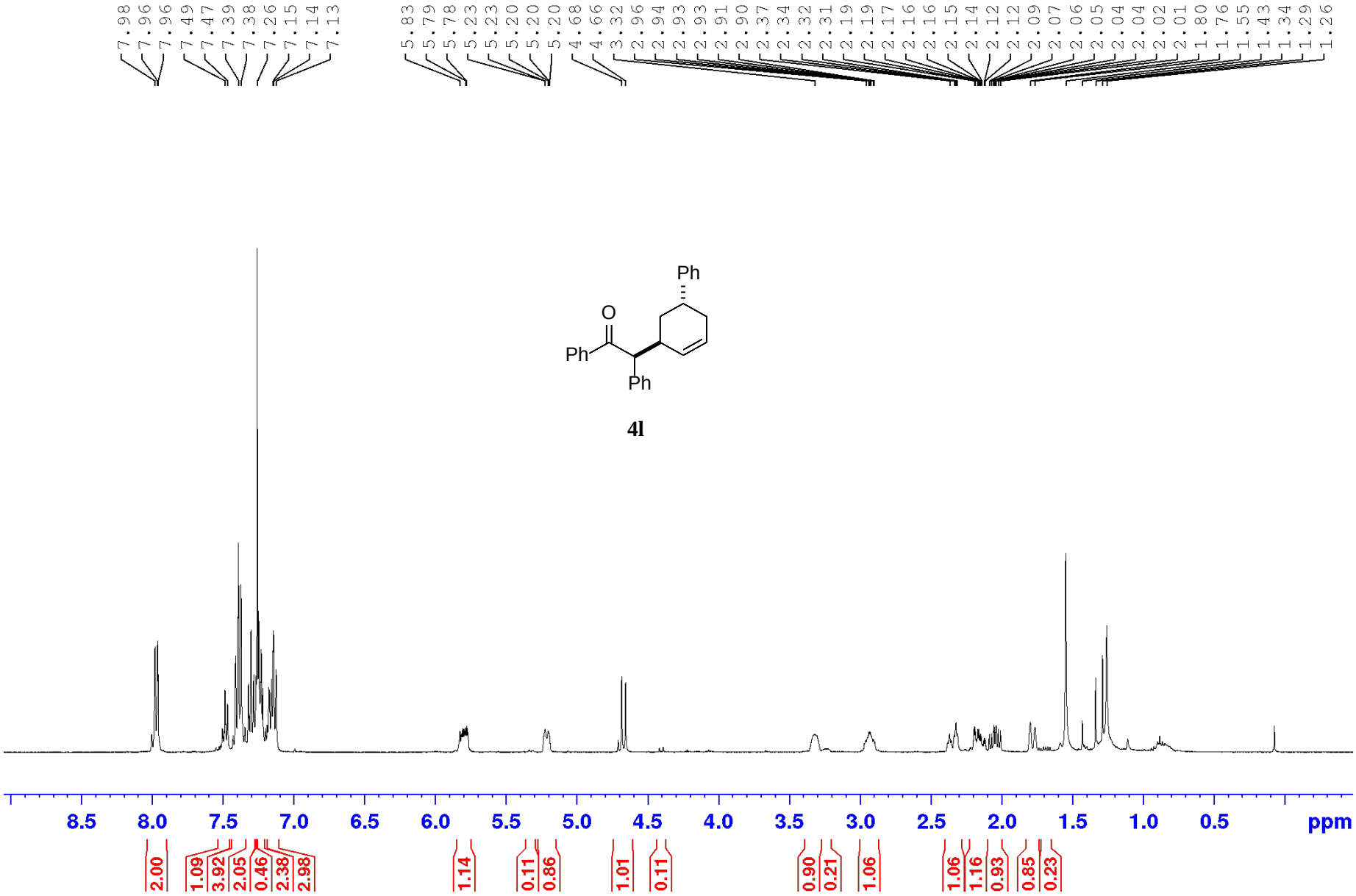
137.2
136.1
133.0
129.0
128.9
128.7
128.6
128.6
128.6
128.1
127.9
127.3
126.5
66.2
58.2
36.6
36.6
29.6
27.5
CO2Bn
O
Ph
Ph
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
ppm

4k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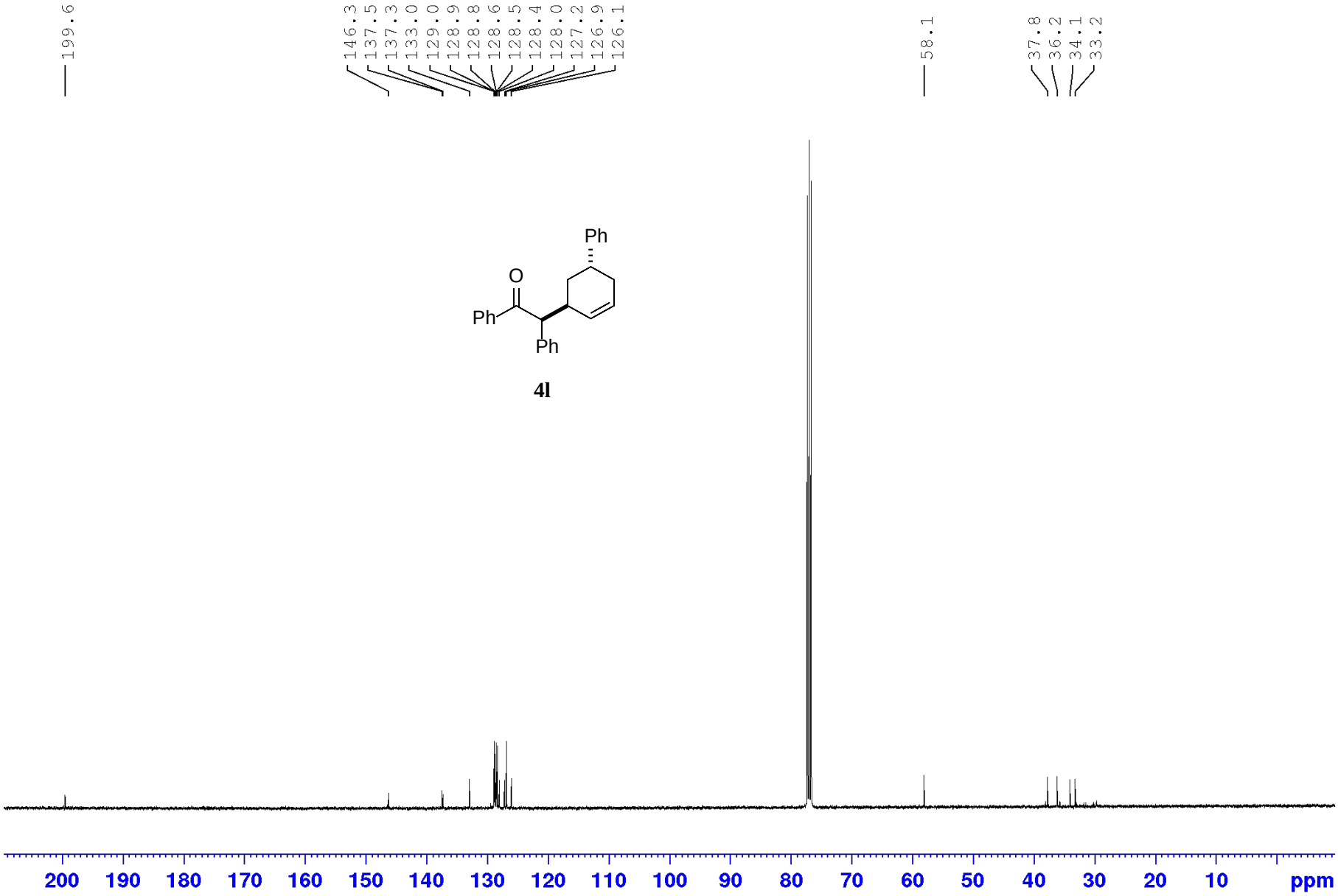
5.83 5.79 5.78 5.23 5.23 5.20 5.20 5.20 4.68 4.66 3.32 2.96 2.94 2.93 2.93 2.91 2.90 2.37 2.34 2.32 2.31 2.19 2.19 2.17 2.16 2.16 2.15 2.14 2.12 2.12 2.09 2.07 2.06 2.05 2.04 2.04 2.02 2.01 1.80 1.76 1.55 1.43 1.34 1.29 1.26
Ph
O
Ph
Ph
8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 ppm
2.00 1.09 3.92 2.05 0.46 2.38 2.98 1.14 0.11 0.86 1.01 0.11 0.90 0.21 1.06 1.06 1.16 0.93 0.85 0.23

4l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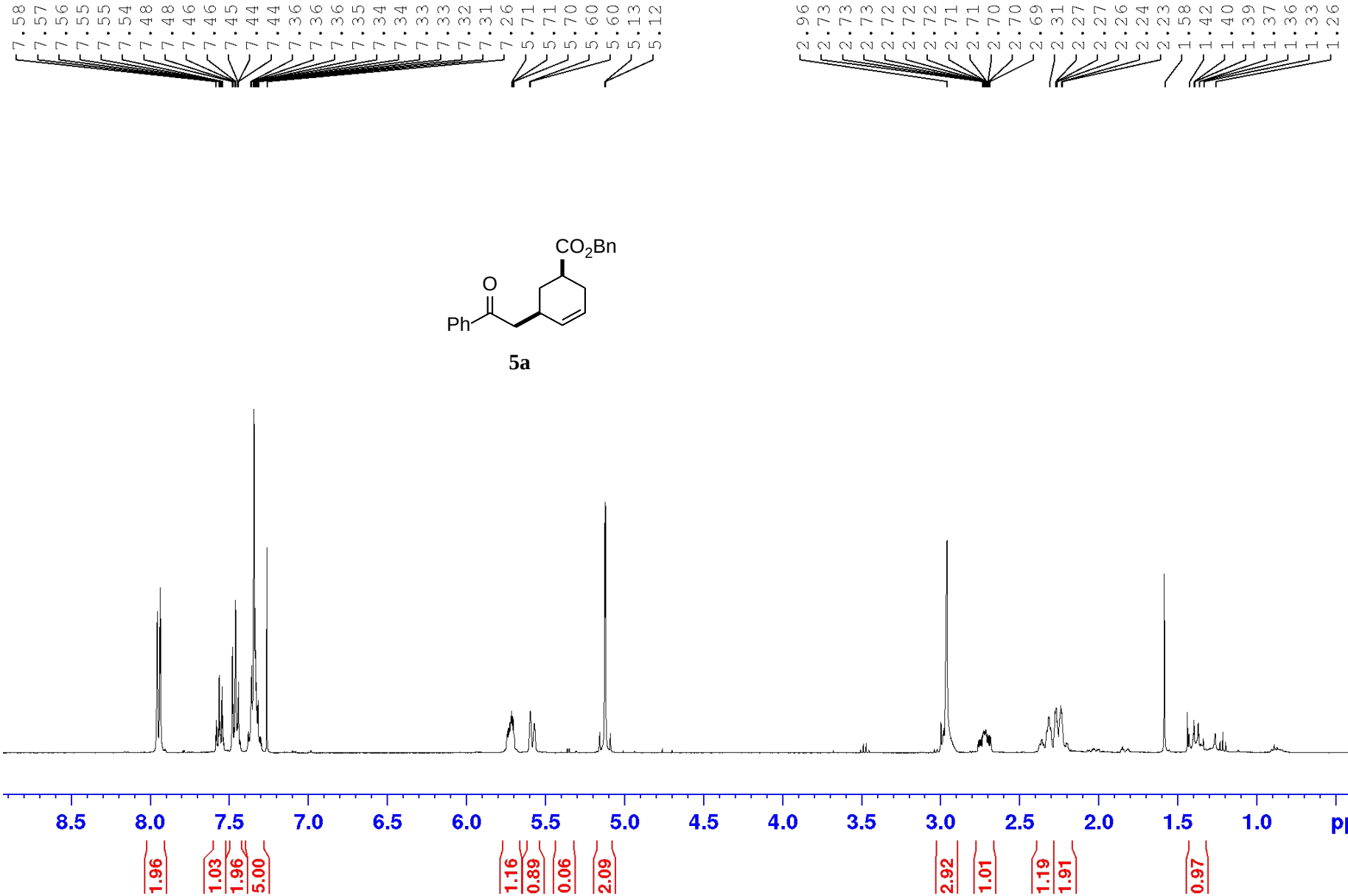
137.5
137.3
133.0
129.0
128.9
128.8
128.6
128.5
128.4
128.0
127.2
126.9
126.1
58.1
37.8
36.2
34.1
33.2
Ph
O
Ph
Ph
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
ppm

4l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7.45
7.44
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7.34
7.34
7.33
7.33
7.32
7.31
7.26
5.71
5.71
5.70
5.60
5.60
5.13
5.12
2.96
2.73
2.73
2.73
2.72
2.72
2.72
2.71
2.71
2.70
2.70
2.69
2.31
2.27
2.27
2.26
2.24
2.23
1.58
1.42
1.40
1.39
1.37
1.36
1.33
1.26
CO2Bn
O
Ph
5a
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
ppm
1.96
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0.06
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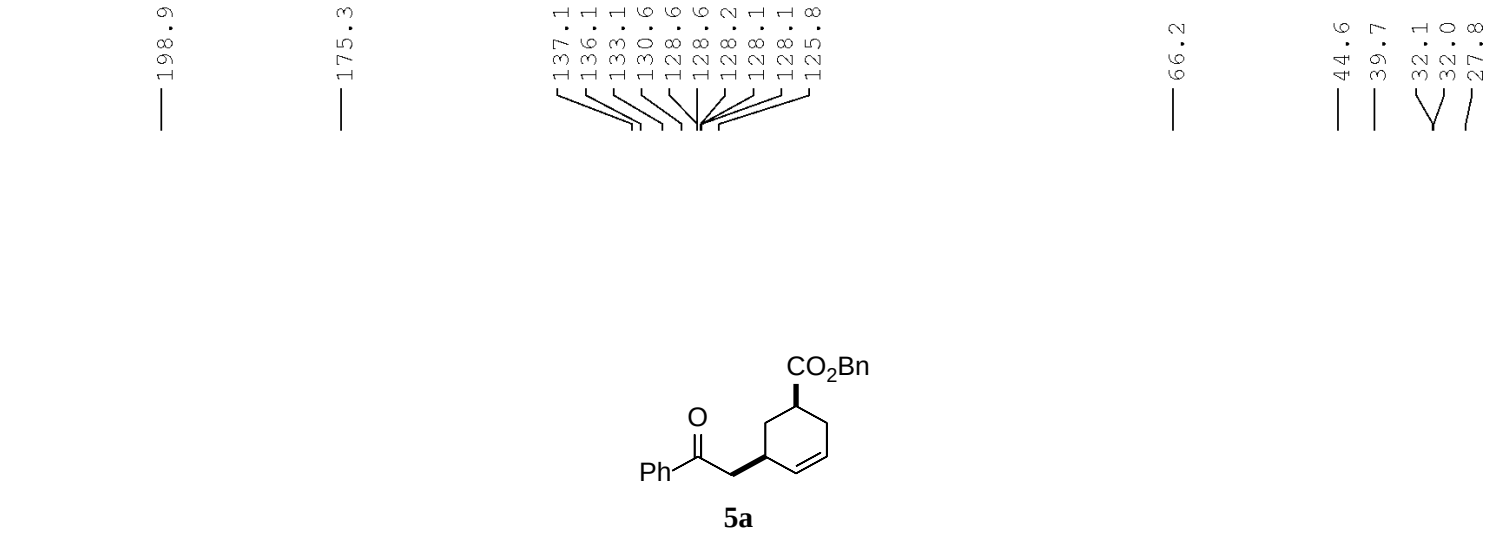
2.92
1.01
1.19
1.91
0.97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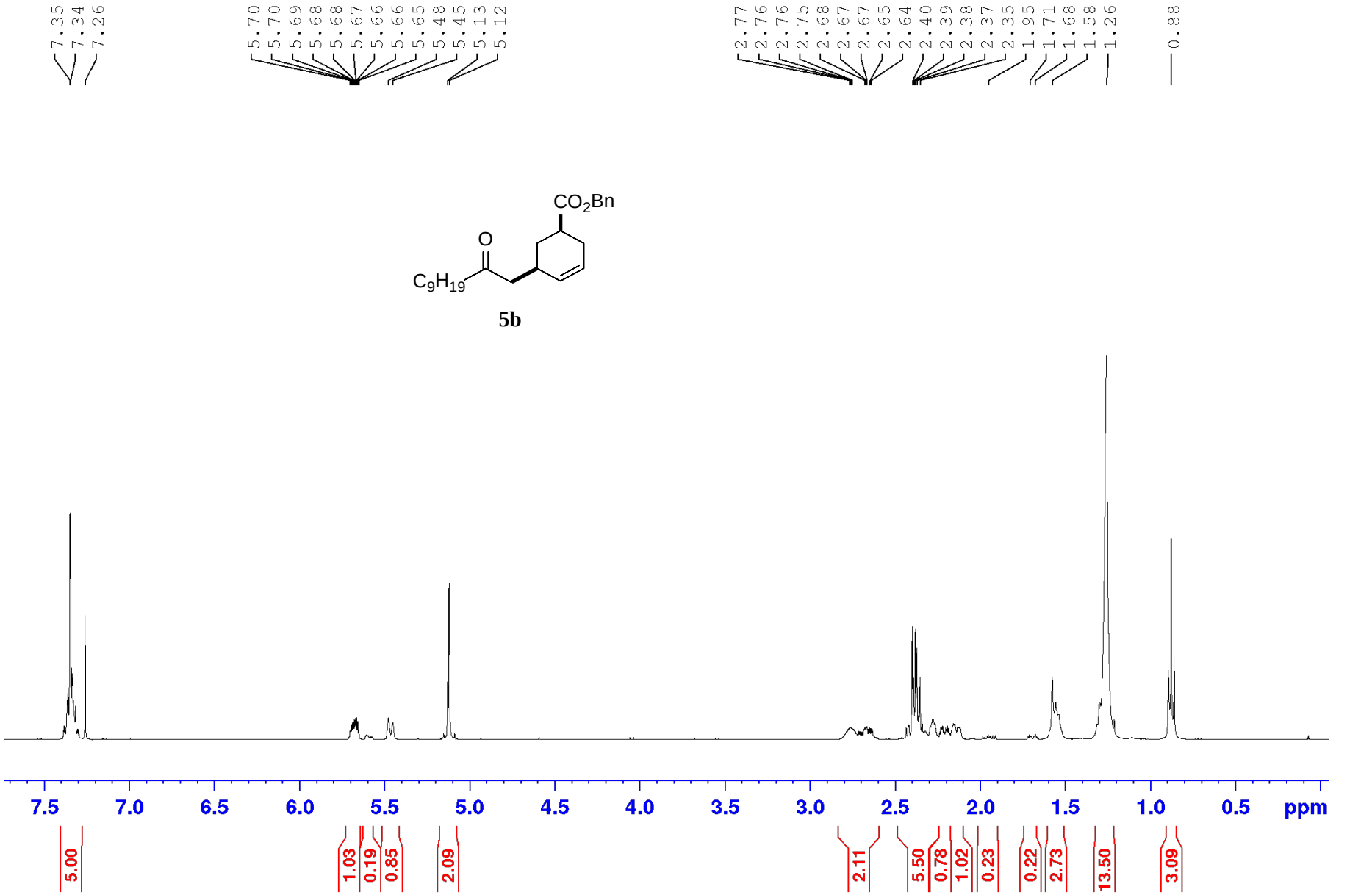
136.1
133.1
130.6
128.6
128.6
128.2
128.1
128.1
125.8
66.2
44.6
39.7
32.1
32.0
27.8
CO2Bn
O
Ph
5a
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 ppm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5.65
5.48
5.45
5.13
5.12
2.77
2.76
2.76
2.75
2.68
2.67
2.67
2.65
2.64
2.40
2.39
2.38
2.37
2.35
1.95
1.71
1.68
1.58
1.26
0.88
CO2Bn
O
C9H19
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
5.00
1.03
0.19
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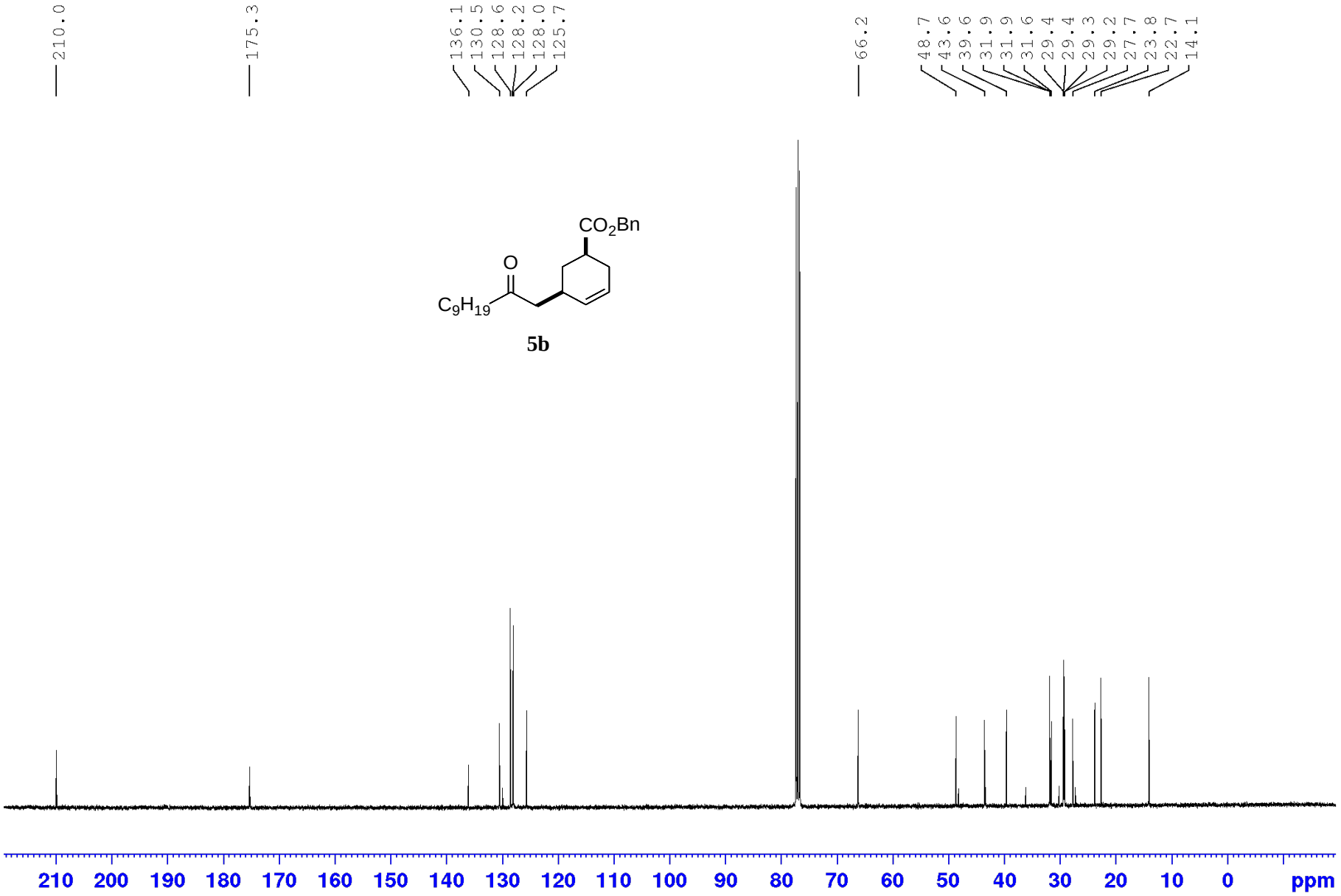
2.11
5.50
0.78
1.02
0.23
0.22
2.73
13.50
3.09

5b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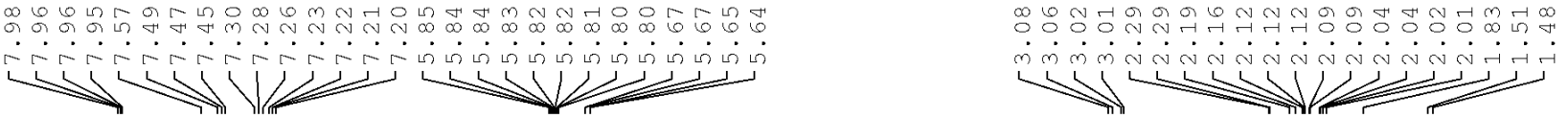
128.6
128.2
128.0
125.7
66.2
48.7
43.6
39.6
31.9
31.9
31.6
29.4
29.4
29.3
29.2
27.7
23.8
22.7
14.1
CO2Bn
O
C9H19
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 ppm

5b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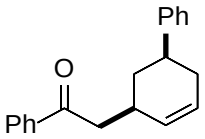
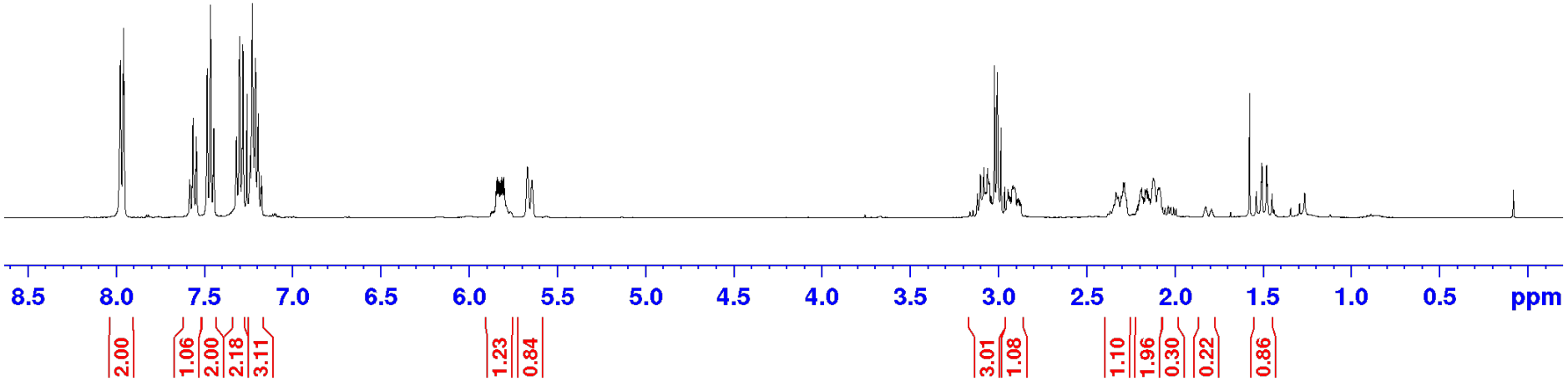
7.28
7.26
7.23
7.22
7.21
7.20
5.85
5.84
5.84
5.83
5.82
5.82
5.81
5.80
5.80
5.67
5.67
5.65
5.64
3.08
3.06
3.02
3.01
2.29
2.29
2.19
2.16
2.12
2.12
2.12
2.09
2.09
2.04
2.04
2.02
2.01
1.83
1.51
1.48


Ph
O
Ph

5c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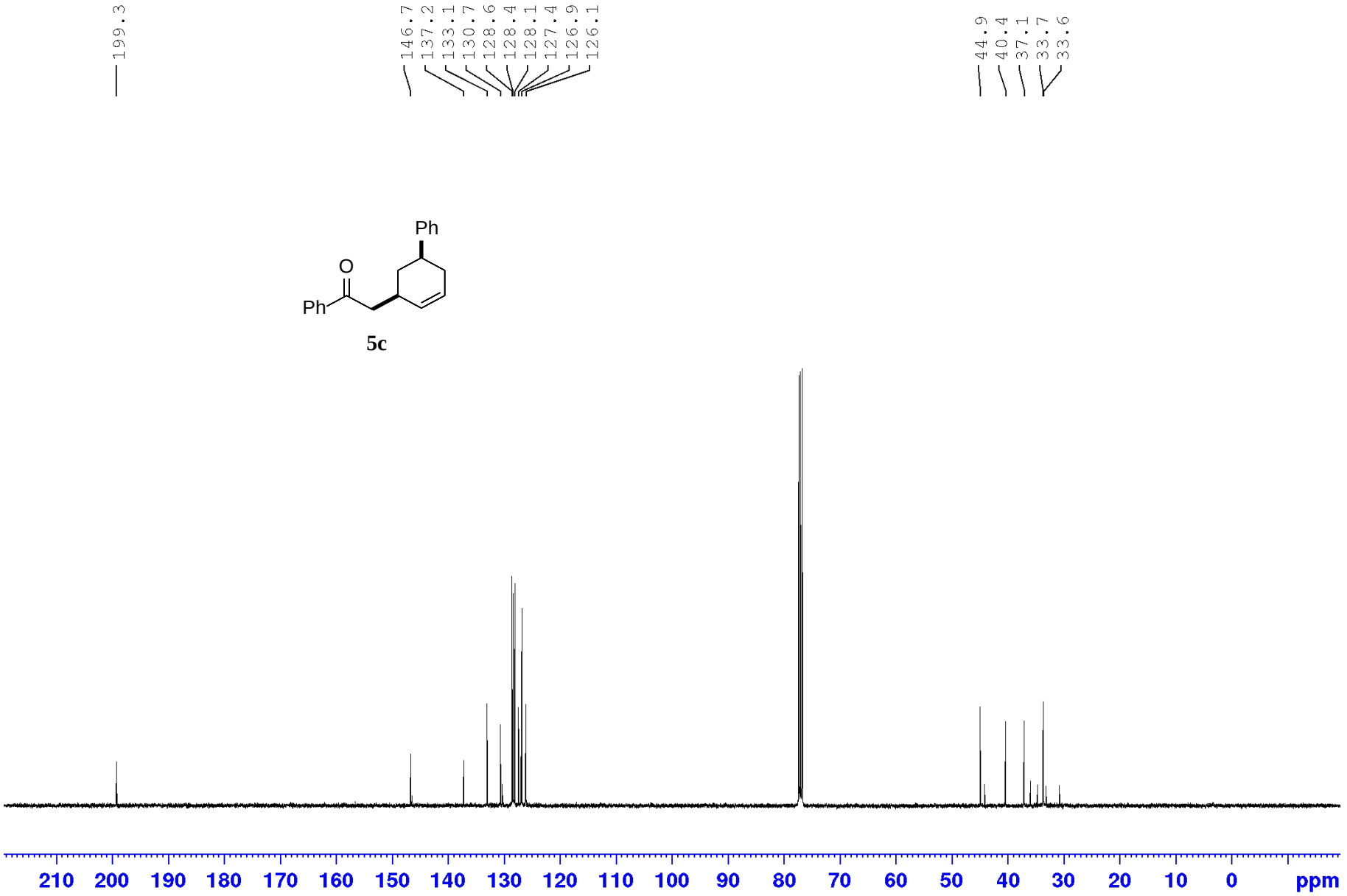
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
ppm
2.00
1.06
2.00
2.18
3.11
1.23
0.84
3.01
1.08
1.10
1.96
0.30
0.22
0.86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146.7
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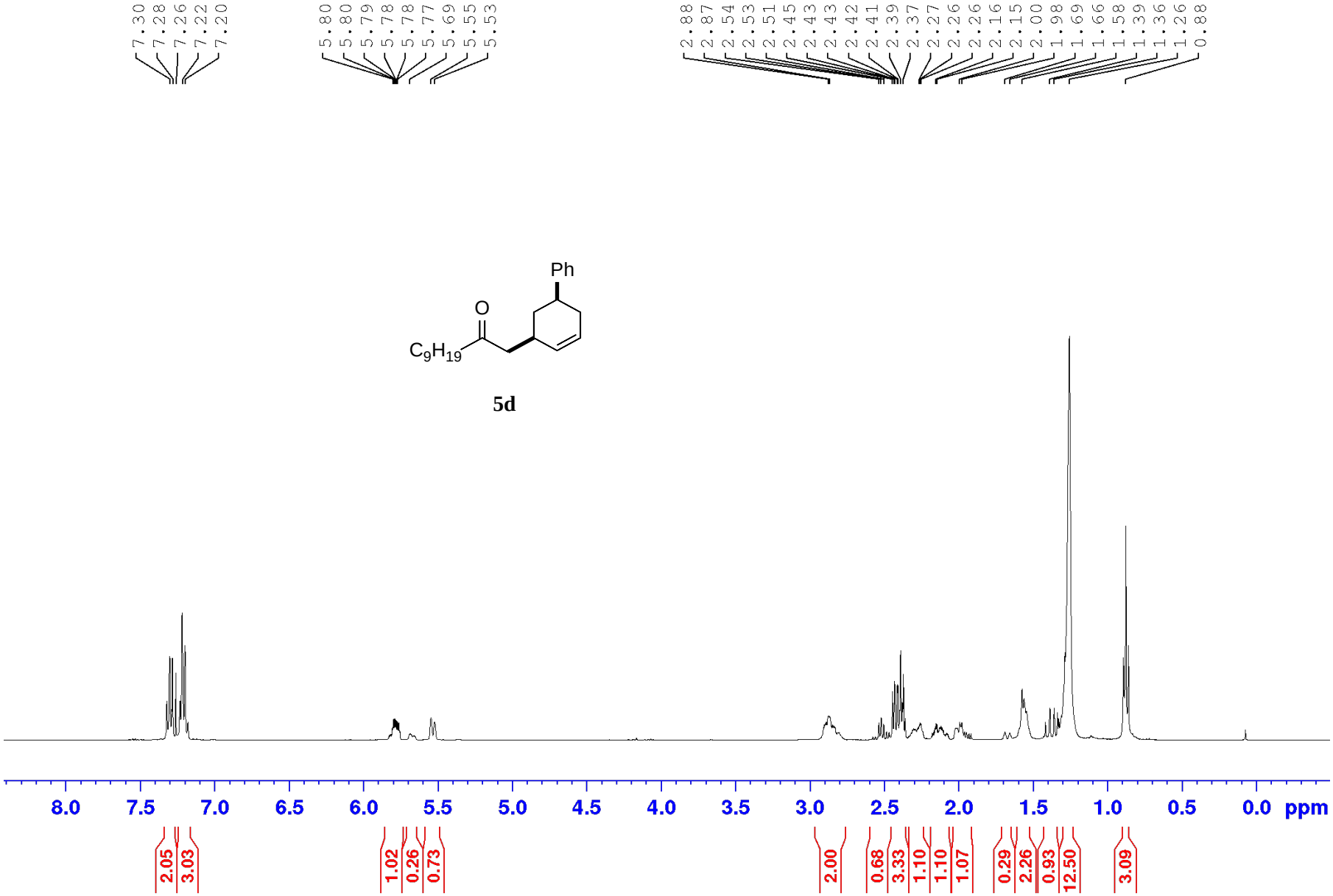
133.1
130.7
128.6
128.4
128.1
127.4
126.9
126.1
44.9
40.4
37.1
33.7
33.6
Ph
O
Ph
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 ppm

5c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7.26
7.22
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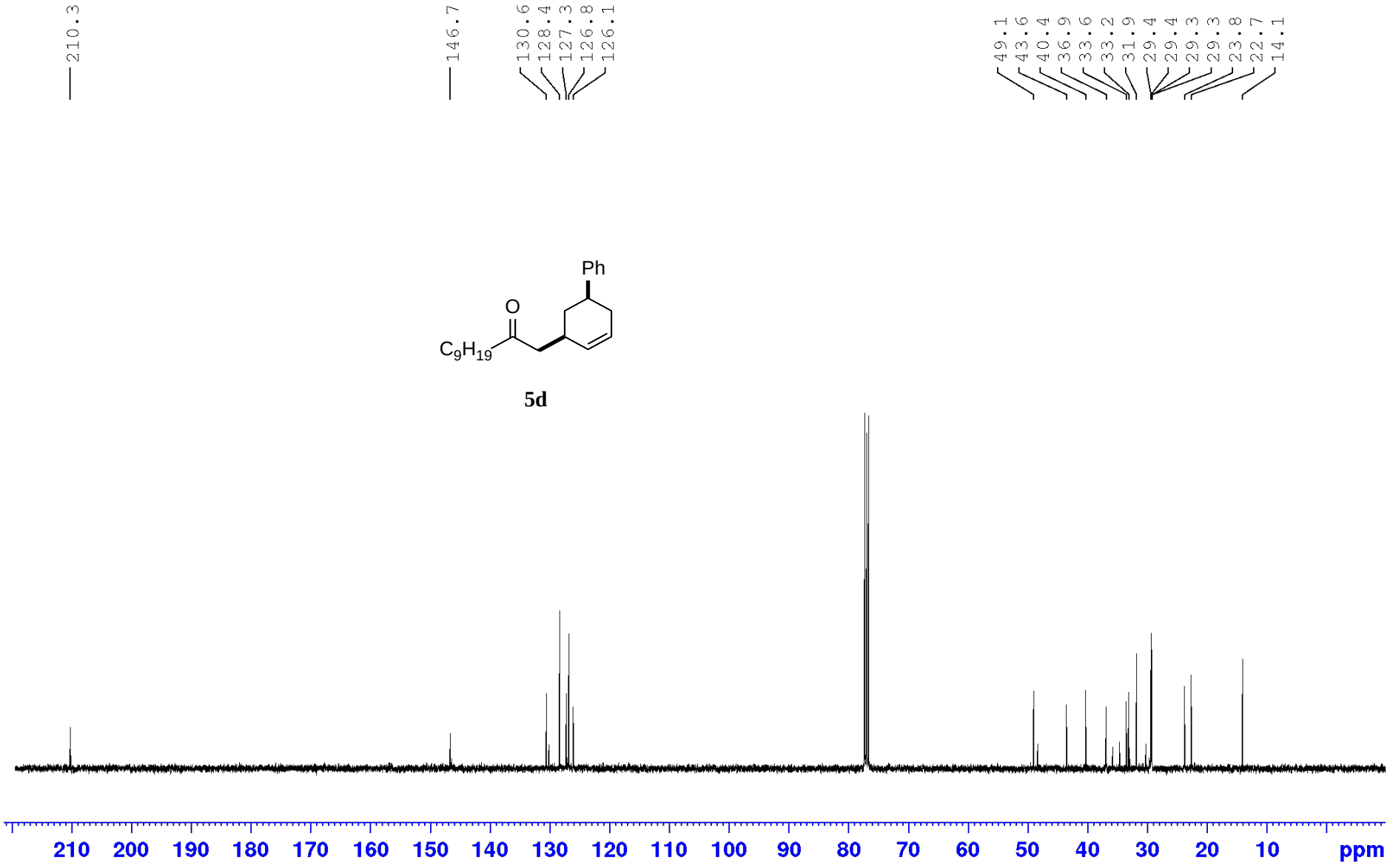
5.80
5.79
5.78
5.78
5.77
5.69
5.55
5.53
2.88
2.87
2.54
2.53
2.51
2.45
2.43
2.43
2.42
2.41
2.39
2.37
2.27
2.26
2.26
2.16
2.15
2.00
1.98
1.69
1.66
1.58
1.39
1.36
1.26
0.88
Ph
O
C9H19
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
ppm
2.05
3.03
1.02
0.26
0.73
2.00
0.68
3.33
1.10
1.10
1.07
0.29
2.26
0.93
12.50
3.09

5d


210.3
146.7
130.6
128.4
127.3
126.8
126.1
49.1
43.6
40.4
36.9
33.6
33.2
31.9
29.4
29.4
29.3
29.3
23.8
22.7
14.1
Ph
O
C9H19
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
ppm

5d