Supporting Information For: The Palladium-Catalyzed Anti-Markovnikov Hydroalkylation of Allylic Alcohol Derivatives

*Ryan J. DeLuca and Matthew S. Sigman**

Department of Chemistry, University of Utah, 315 S. 1400 East, Salt Lake City, UT 84112-085

E-mail: sigman@chem.utah.edu

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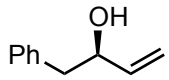
General Considerations:

Dry dimethylacetamide (DMA) was purchased from Aldrich and stored over activated 3 Å molecular sieves (3 Å MS). 3 Å MS used in hydroalkylation reactions were powdered and activated by heating with a Bunsen burner while under vacuum. Granular Iodine was purchased from J.T. Baker. Unless otherwise noted all chemicals were purchased from Aldrich or Acros and used without further purification. All melting points are uncorrected and recorded on Thomas Hoover Unimelt capillary melting point apparatus. ^{1}H-NMR spectra were obtained at 300 MHz, 400 MHz or 500 MHz, chemical shifts are reported in ppm, and referenced to the $CHCl_3$ singlet at 7.26 ppm. ^{13}C-NMR spectra were obtained at 75MHz, 100 MHz or 126 MHz and referenced to the center peak of the $CHCl_3$ at 77.23 ppm. All multiplicities reported are apparent. The abbreviations s, d, t, quint, dd, ddd, dt,

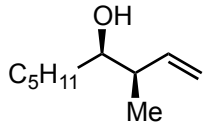
m stand for the resonance multiplicities singlet, doublet, triplet, quintet, doublet of doublets, doublet of doublets of doublets, doublet of triplets and multiplet, respectively. Thin-layer chromatography was performed with EMD silica gel 60 F254 plates eluting with solvents indicated, visualized by a 254 nm UV lamp and stained with phosphomolybdic acid (PMA). Flash chromatography was performed using EM reagent silica 60 (230-400 mesh). GC separations were performed with an HP6890 GC with a flame ionization detector equipped with a DB-5 column using a 50:1 split. IR spectra were recorded using a Thermo Nicolet FT-IR. HRMS data were obtained on a Waters LCP Premier XE instrument by ESI/TOF. SFC (supercritical fluid chromatography) analysis was performed at 28 °C, using a Thar instrument fitted with AY-H and OD columns.

Preparation of Substrates:

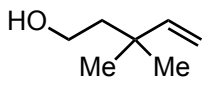
(*R*)-1-phenylbut-3-en-2-ol: This compound was prepared according to the literature procedure.[1] Analytical data matches the literature.



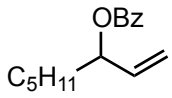
3-methylnon-1-en-4-ol: This compound was prepared according to the literature procedure.[2,3] Analytical data matches the literature.



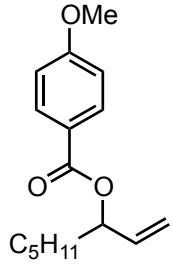
3,3-dimethylpent-4-en-1-ol: This compound was prepared according to the literature procedure.[4-6] Analytical data matches the literature.

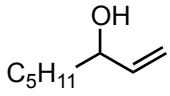


oct-1-en-3-yl benzoate (1a): This compound was prepared according to the literature procedure.[7] Analytical data matches the literature.[8]

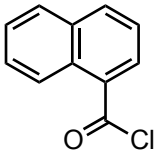


oct-1-en-3-yl 4-methoxybenzoate (1b): This compound was prepared according to the literature procedure.[9] Analytical data matches the literature.

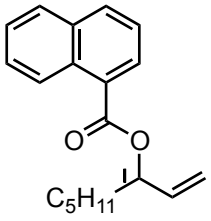




S1



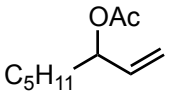
pyridine



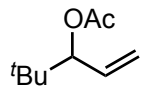
1c

Oct-1-en-3-yl 1-naphthoate (1c): To a dry 25 mL round-bottom flask equipped with a stirbar under N_2 were added 2.3 mL of 1-octen-3-ol **S1** (15.0 mmol, 1.0 equiv.) and 4.5 mL of pyridine and the solution was cooled to 0 °C. Next, 2.5 mL of 1-naphthoyl chloride (16.5 mmol, 1.1 equiv.) was added dropwise via syringe and the resulting solution was allowed to warm to room temperature and stirred overnight. The solution was then quenched with H_2O (20 mL) and diluted with DCM (15 mL). The layers were separated and the organic layer was washed with H_2O (20 mL). The combined aqueous layers were washed with DCM (3 × 20 mL). The combined organic layers were then washed with brine (30 mL), dried over Na_2SO_4, decanted, and concentrated *in vacuo*. The product was purified by silica gel flash chromatography eluting with 7% diethyl ether in hexanes to give the product as a colorless oil in 88% yield. R_f = 0.4 (7% Et_2O in hexanes). ^{1}H NMR (400 MHz, $CDCl_3$): δ 0.93 (t, *J* = 6.8 Hz, 3H), 1.30-1.55 (m, 6H), 1.74-1.95 (m, 2H), 5.27 (d, *J* = 10.8 Hz, 1H), 5.42 (d, *J* = 17.2 Hz, 1H), 5.64 (q, *J* = 6.5 Hz, 1H), 5.99 (m, 1H), 7.49-7.57 (m, 2H), 7.60-7.66 (m, 1H), 7.89 (d, *J* = 8.4 Hz, 1H), 8.02 (d, *J* = 8.4 Hz, 1H), 8.23 (d, *J* = 7.6 Hz, 1H), 8.97 (d, *J* = 8.8 Hz, 1H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 14.2, 22.7, 25.0, 31.8, 34.6, 75.7, 117.0, 124.7, 126.0, 126.3, 127.8(2), 128.7, 130.1, 131.6, 133.4, 134.1, 136.9, 167.0. IR (neat): 2929, 2858, 1709, 1593, 1509, 1462, 1274, 1238, 1193, 1131, 1029, 927, 778, 653 cm^{-1}. HRMS $(M+Na)^+$: calcd. 305.1517, obsvd. 305.1519.

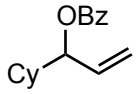
oct-1-en-3-yl acetate (1d): This compound was prepared according to the literature procedure.[10] Analytical data matches the literature.



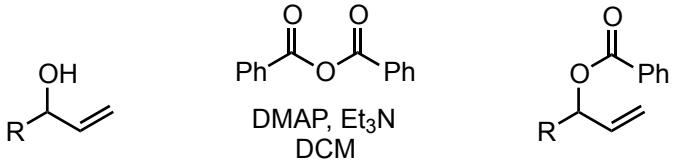
4,4-dimethylpent-1-en-3-yl acetate (1e): This compound was prepared according to the literature procedure.[11] Analytical data matches the literature.



1-cyclohexylallyl benzoate (1f): This compound was prepared according to the literature procedure.[12] Analytical data matches the literature.

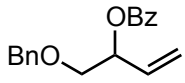


General Procedure for Benzoyl Protection

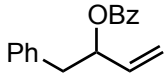


Into a dry 250 mL round-bottom flask equipped with a stirbar were added the alcohol (10.0 mmol, 1.0 equiv.), 244 mg of DMAP (2.0 mmol, 0.20 equiv.), 1.8 mL of Et_3N (13.0 mmol, 1.3 equiv) and 50 mL of DCM. The flask was equipped with a septum and connected to a N_2 line. The resulting mixture was cooled to 0 °C, and 3.40 g of benzoic anhydride (15.0 mmol, 1.5 equiv.) was dissolved in 5 mL of DCM and added dropwise. The mixture was allowed to warm to room temperature and was stirred overnight. The solution was then washed with sat. aq. NH_4Cl (50 mL) and H_2O (50 mL). The combined aqueous layers were extracted with DCM (50 mL). The combined organic layers were then washed with brine (30 mL), dried over Na_2SO_4, decanted, and concentrated *in vacuo*. The product was purified by silica gel flash column chromatography.

1-(benzyloxy)but-3-en-2-yl benzoate (1g): The general procedure for benzoyl protection was followed. The product was purified by silica gel flash chromatography eluting with 10% diethyl ether in hexanes to give the product as a colorless oil in 85% yield. R_f = 0.3 (10% EtOAc in hexanes). ^{1}H NMR (400 MHz, $CDCl_3$): δ 0.73 (dd, *J* = 10.5, 4.4 Hz, 1H), 0.78 (dd, *J* = 10.5, 6.6 Hz, 1H), 4.61 (d, *J* = 12.4 Hz, 1H), 4.67 (d, *J* = 12.4 Hz, 1H), 5.33 (d, *J* = 10.8 Hz, 1H), 5.46 (d, *J* = 17.2 Hz, 1H), 5.80 (m, 1H), 6.00 (ddd, *J* = 17.1, 10.8, 6.1 Hz, 1H), 7.27-7.38 (m, 5H), 7.44-7.73 (m, 3H), 8.11-8.15 (m, 2H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 71.5, 73.3, 73.9, 118.1, 127.7, 127.8, 128.5(2), 129.8, 130.4, 133.1, 133.5, 138.1, 165.8. IR (neat): 3063, 3030, 2860, 1787, 1716, 1601, 1584, 1494, 1451, 1314, 1265, 1096, 1025, 987, 933, 736, 708, 696 cm^{-1}. HRMS $(M+Na)^+$: calcd. 305.1154, obsvd. 305.1156.

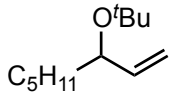


1-phenylbut-3-en-2-yl benzoate (1h): The general procedure for benzoyl protection was followed. The product was purified by silica gel flash chromatography eluting with 10% ethyl acetate in hexanes to give the product as a colorless oil in 86% yield. R_f = 0.4 (10% EtOAc in hexanes).

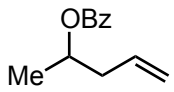


^{1}H NMR (400 MHz, $CDCl_3$): δ 3.03 (dd, *J* = 13.9, 6.2 Hz, 1H), 3.12 (dd, *J* = 13.9, 7.2 Hz, 1H), 5.19 (d, *J* = 10.8 Hz, 1H), 5.29 (d, *J* = 17.2 Hz, 1H), 5.72 (q, *J* = 6.5 Hz, 1H), 5.92 (ddd, *J* = 17.1, 10.7, 6.3 Hz, 1H), 7.17-7.32 (m, 5H), 7.42 (t, *J* = 7.6 Hz, 2H), 7.54 (t, *J* = 7.2 Hz, 1H), 8.03 (d, *J* = 6.8 Hz, 2H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 41.2, 75.8, 117.2, 126.7, 128.5(2), 129.7, 129.8, 130.6, 133.0, 135.9, 137.0, 165.8. IR (neat): 3062, 3029, 2923, 1714, 1601, 1451, 1264, 1108, 983, 697 cm^{-1}. HRMS $(M+Na)^+$: calcd. 275.1048, obsvd. 275.1049.

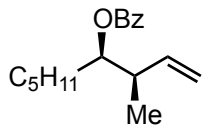
3-(*tert*-butoxy)oct-1-ene (1o): This compound was prepared according to the literature procedure.[13] The product was purified by silica gel flash chromatography eluting with 2% diethyl ether in hexanes to give the product as a colorless oil in 63% yield. R_f = 0.5 (5% EtOAc in Hexanes). ^{1}H NMR (400 MHz, $CDCl_3$): δ 0.87 (t, *J* = 7.0 Hz, 3H), 1.17 (s, 9H), 1.21-1.52 (m, 8H), 3.87 (q, *J* = 6.3 Hz, 1H), 4.99 (d, *J* = 10.8 Hz, 1H), 5.09 (d, *J* = 17.2 Hz, 1H), 5.80 (ddd, *J* = 17.2, 10.5, 6.6 Hz, 1H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 14.3, 22.9, 25.6, 28.9, 32.1, 37.6, 73.4, 74.0, 113.5, 143.1. IR (neat): 3734, 3076, 2959, 2931, 2860, 1733, 1464, 1388, 1195, 1054, 915, 681 cm^{-1}. HRMS $(M+H)^+$: calcd. 185.1905, obsvd. 185.1911.



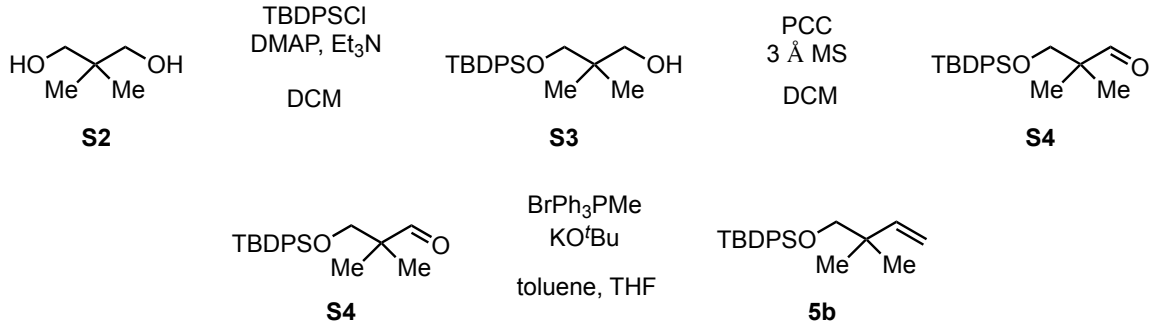
pent-4-en-2-yl benzoate (3a): This compound was prepared according to the literature procedure.[14] Analytical data matches the literature.



3-methylnon-1-en-4-yl benzoate (5a): The general procedure for benzoyl protection was followed. The product was purified by silica gel flash chromatography eluting with 5% ethyl acetate in hexanes to give the product as a colorless oil in 85% yield. R_f = 0.3 (5% EtOAc in hexanes). ^{1}H NMR (400 MHz, $CDCl_3$): δ 0.86 (t, *J* = 7.0 Hz, 3H), 1.09 (d, *J* = 7.2 Hz, 3H), 1.22-1.43 (m, 6H), 1.66 (q, *J* = 7.2 Hz, 2H), 2.50-2.60 (m, 1H), 5.02-5.16 (m, 3H), 5.83 (ddd, *J* = 17.4, 10.2, 7.4 Hz, 1H) 7.42-7.47 (m, 2H), 7.53-7.58 (m, 1H), 8.03-8.08 (m, 2H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 14.2, 15.5, 22.7, 25.4, 31.7, 31.9, 41.8, 77.7, 115.4, 128.5, 129.8, 130.9, 132.9, 140.2, 166.5. IR (neat): 2931, 2860, 1715, 1451, 1268, 1108, 1069, 707, 1105 cm^{-1}. HRMS $(M+Na)^+$: calcd. 283.1674, obsvd. 283.1682.



Substrate Procedure A



Into a dry 250 mL round-bottom flask equipped with a stirbar were added 4.00 g of 2,2-dimethylpropane-1,3-diol **S2** (38.4 mmol, 3.0 equiv.), 280 mg of DMAP (2.50 mmol, 0.20 equiv.), 2.4 mL of Et_3N (17.2 mmol, 1.3 equiv), and 60 mL of DCM. The flask was equipped with a septum and connected to a N_2 line. The resulting mixture was cooled to 0° C, and 3.2 mL of TBDPSCl (13.0 mmol, 1.0 equiv.) was added dropwise. The mixture was allowed to warm to room temperature and was allowed to stir overnight. The solution was then washed with sat. aq. NH_4Cl (50 mL) and H_2O (50 mL). The combined aqueous layers were extracted with DCM (50 mL). The combined organic layers were then washed with brine (30 mL), dried over Na_2SO_4, decanted, and concentrated *in vacuo*. The product was purified by silica gel flash column chromatography to give 2.89 g of product in 65% yield.[15]

Into a dry 100 mL round-bottom flask equipped with a stirbar were added 2.20 g of pyridinium chlorochromate (PCC) (10.0 mmol, 1.5 equiv.), 500 mg of powdered 3 Å molecular sieves, and 30 mL of DCM. To this mixture was then added 2.28 g of 3-((*tert*-butyldiphenylsilyl)oxy)-2,2-dimethylpropan-1-ol **S3** (6.67 mmol, 1.0 equiv.) and the reaction stirred for 30 min. The reaction was passed through a small plug of silica resulting in 1.93 g of aldehyde product in 85% yield, which was used immediately in the next step.[15]

To a dry 100 mL round-bottomed flask equipped with a stirbar under N_2 were added 1.57 g of methyltriphenylphosphonium bromide (4.40 mmol, 1.2 equiv.) and 20 mL of toluene. To this solution, 494 mg of KO^{t}Bu (4.40 mmol, 1.2 equiv.) in 3.0 mL of THF was added dropwise via a syringe. The reaction mixture was stirred for 4 h. The mixture was cooled to -78° C and 1.25 g of 3-((*tert*-butyldiphenylsilyl)oxy)-2,2-dimethylpropanal **S4** (3.67 mmol, 1.0 equiv.) was added dropwise. The mixture was allowed to warm to room temperature and was stirred for 1 h. Upon completion by TLC analysis, the reaction was quenched with 10 mL of sat. aq. NH_4Cl. The mixture was diluted with diethyl ether (50 mL) and washed with H_2O (2 × 10 mL) and brine (20 mL). The organic layer was dried over Na_2SO_4, decanted, and concentrated *in vacuo*. The crude reaction mixture was purified by silica gel flash column chromatography.

***tert*-butyl((2,2-dimethylbut-3-en-1-yl)oxy)diphenylsilane (5b)**: This compound was prepared using substrate procedure A. The product was purified by silica gel flash chromatography eluting with 2% ethyl acetate in hexanes to give the product as a colorless oil in 90% yield. R_f = 0.7 (5% EtOAc in hexanes). ^{1}H NMR (400 MHz, $CDCl_3$): δ 1.10 (s, 6H), 1.12 (s, 9H), 3.44 (s, 2H), 5.00-5.09 (m, 2H), 5.94 (dd, *J* = 17.6, 10.8 Hz, 1H), 7.40-7.49 (m, 6H), 7.70-7.75 (m, 4H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 19.7, 24.0, 27.1, 39.5, 72.7, 111.9, 127.8, 129.8, 134.1, 136.0, 146.2. IR (neat): 3071, 2959, 2930, 2857, 1472, 1471, 1427, 1360, 1105, 1089, 908, 733, 699, 612 cm^{-1}. HRMS $(M+H)^+$: calcd. 339.2144, obsvd. 339.2143.

2,2-dimethylbut-3-en-1-yl benzoate (5c): This compound was prepared using substrate procedure A with the modification that the alcohol was protected using benzoic anhydride instead of TBDPSCl.[16] The product was purified by silica gel flash chromatography eluting with 10% ethyl acetate in hexanes to give the product as a colorless oil in 91% yield. R_f = 0.3 (10% EtOAc in hexanes). ^{1}H NMR (500 MHz, $CDCl_3$): δ 1.15 (s, 6H), 4.11 (s, 2H), 5.05 (dd, *J* = 10.8, 1.2 Hz, 1H), 5.10 (dd, *J* = 17.5, 1.2 Hz, 1H), 5.90 (dd, *J* = 17.5, 10.8 Hz, 1H), 7.42-7.45 (m, 2H), 7.53-7.56 (m, 1H), 8.04-8.07 (m, 2H). ^{13}C NMR (125 MHz, $CDCl_3$): δ 24.2, 37.7, 72.6, 112.7, 128.5, 129.7, 130.6, 133.0, 144.7, 166.6. IR (neat): 2966, 1717, 1644, 1601, 1452, 1365, 1314, 1267, 1175, 1109, 1026, 706, 686, 671 cm^{-1}. HRMS $(M+H)^+$: calcd. 205.1229, obsvd. 205.1232.

3,3-dimethylpent-4-en-1-yl benzoate (5d): The general procedure for benzoyl protection was followed. The product was purified by silica gel flash chromatography eluting with 5% ethyl acetate in hexanes to give the product as a colorless oil in 98% yield. R_f = 0.6 (10% EtOAc in hexanes). ^{1}H NMR (300 MHz, $CDCl_3$): δ 1.10 (s, 6H), 1.81 (t, *J* = 7.2 Hz, 2H), 4.32 (t, *J* = 7.3 Hz, 2H), 4.95-5.02 (m, 2H), 5.83 (dd, *J* = 17.6, 10.9 Hz, 1H), 7.41-7.48 (m, 2H), 7.52-7.59 (m, 1H), 8.00-8.05 (m, 2H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 27.3, 36.0, 40.8, 62.7, 111.4, 128.5, 129.7, 130.7, 133.0, 147.5, 173.2. IR (neat): 2962, 1715, 1602, 1451, 1268, 1109, 1069, 912, 707 cm^{-1}. HRMS $(M+H)^+$: calcd. 219.1385, obsvd. 219.1388.

(*R*)-1-phenylbut-3-en-2-yl benzoate: The general procedure for benzoyl protection was followed. The product was purified by silica gel flash chromatography eluting with 10% ethyl acetate in hexanes to give the product as a colorless oil in 86% yield. R_f = 0.4 (10% EtOAc in hexanes). ^{1}H NMR (400 MHz, $CDCl_3$): δ 3.03 (dd, *J* = 13.9, 6.2 Hz, 1H), 3.12 (dd, *J* = 13.9, 7.2 Hz, 1H),

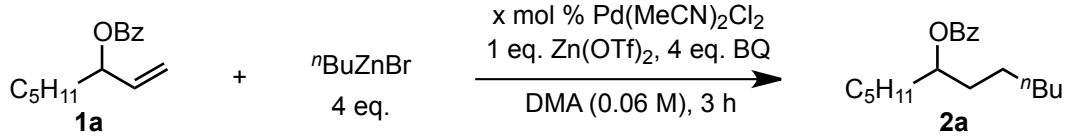
5.19 (d, J = 10.8 Hz, 1H), 5.29 (d, J = 17.2 Hz, 1H), 5.72 (q, J = 6.5 Hz, 1H), 5.92 (ddd, J = 17.1, 10.7, 6.3 Hz, 1H), 7.17-7.32 (m, 5H), 7.42 (t, J = 7.6 Hz, 2H), 7.54 (t, J = 7.2 Hz, 1H), 8.03 (d, J = 6.8 Hz, 2H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 41.2, 75.8, 117.2, 126.7, 128.5(2), 129.7, 129.8, 130.6, 133.0, 135.9, 137.0, 165.8. IR (neat): 3062, 3029, 2923, 1714, 1601, 1451, 1264, 1108, 983, 697 cm^{-1}. HRMS $(M+Na)^+$: calcd. 275.1048, obsvd. 275.1049.

General Procedure for the Synthesis of Organozinc Reagents: A 25-mL round-bottomed flask was charged with 0.98 g of zinc powder (15.00 mmol, 1.50 equiv.) and heated to 80 °C under high vacuum for 3 hours. After back-filling with argon, DMA (to give a total volume of 10 mL) and then 76.1 mg of iodine (0.30 mmol, 0.03 equiv.) were added. After the red color of iodine had faded (usually 3-5 minutes), the freshly distilled alkyl halide (10.00 mmol) was added. The colorless reaction mixture was stirred for 16 hours at 80 °C (the disappearance of the alkyl halide and the formation of the organozinc reagent can be monitored by ^{1}H NMR). The gray solution (~1.0 M) was transferred into a dry Schlenk flask via cannula. These organozinc solutions can be stored at room temperature under a dry atmosphere for several weeks without deterioration.[17,18]

Optimization for the Hydroalkylation Reaction:

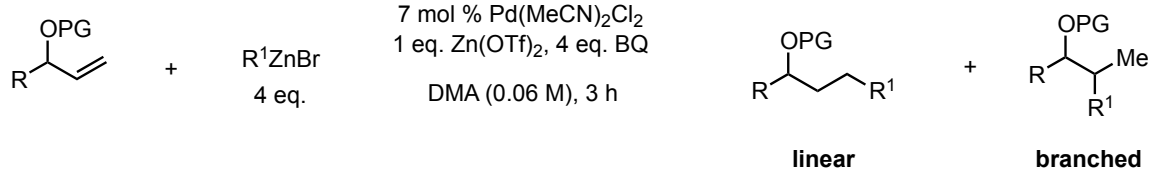
The general procedure A described below was used with the following modifications. The reaction was performed on 0.10 mmol scale with ~10 wt% undecane used as an internal standard. After 3 h aliquots (~50 μL) were taken, passed through a small silica pipet with ethyl acetate and analyzed for conversion and product formation by gas chromatography. The modifications described below were applied in order to optimize the reaction.

Modifications:



entry	x	temp.	additive	% yield[a]
1	6	0 °C	3 Å MS	69
2	7	0 °C	3 Å MS	74
3	**7**	**0 °C**	**--**	**79**
4	7	RT	--	54
5	7	-10 °C	--	61

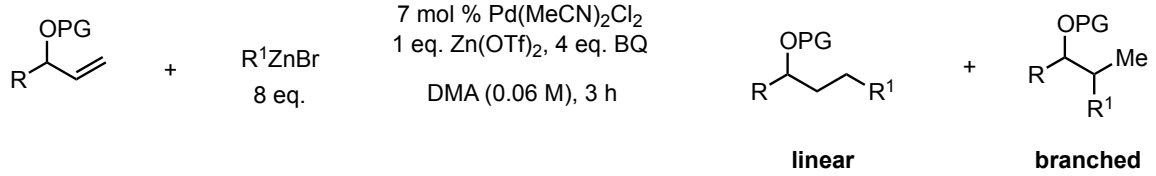
General Procedure A for the Hydroalkylation of Protected Alcohols:



Into a 25 mL round-bottom flask equipped with a stirbar were added 9 mg of $Pd(MeCN)_2Cl_2$ (0.035 mmol, 0.07 equiv.), 216 mg of benzoquinone (2.0 mmol, 4.0 equiv.) and 182 mg of $Zn(OTf)_2$ (0.5 mmol, 1.0 equiv.). The flask was equipped with a rubber septum and argon line and the system was flushed with argon for 15 minutes. Dry DMA (6.0 mL) was then added to the reaction flask using a syringe. The substrate (0.5 mmol, 1.0 equiv.) was then added to the flask via a syringe. The flask was placed in an ice-water bath. The solution was stirred for 5 minutes, after which time 2.0 mL of alkylzinc bromide (2.0 mmol, 4.0 equiv.) was then added dropwise to the cooled solution. The reaction mixture was then stirred for 3 hours at 0 °C.

After this time, the reaction was diluted with diethyl ether (100 mL) and filtered through celite. The filtrate was transferred to a separatory funnel and washed with saturated NH_4Cl (30 mL). The organic layer was separated and washed with H_2O (2 x 30 mL) followed by brine (10 mL). The organic layer was then dried over anhydrous Na_2SO_4. After filtration, the solvents were removed via *in vacuo* rotary evaporation. The product was purified by silica gel flash chromatography.

General Procedure B for the Hydroalkylation of Protected Alcohols:



Into a 25 mL round-bottom flask equipped with a stirbar were added 9 mg of $Pd(MeCN)_2Cl_2$ (0.035 mmol, 0.07 equiv.), 216 mg of benzoquinone (2.0 mmol, 4.0 equiv.) and 182 mg of $Zn(OTf)_2$ (0.5 mmol, 1.0 equiv.). The flask was equipped with a rubber septum and argon line and the system was flushed with argon for 15 minutes. Dry DMA (4.0 mL) was then added to the reaction flask using a syringe. The substrate (0.5 mmol, 1.0 equiv.) was then added to the flask via a syringe. The flask was placed in an ice-water bath. The solution was stirred for 5 minutes, after which time 4.0 mL of

alkylzinc bromide (4.0 mmol, 8.0 equiv.) was then added dropwise to the cooled solution. The reaction mixture was then stirred for 3 hours at 0 °C.

After this time, the reaction was diluted with diethyl ether (100 mL) and filtered through celite. The filtrate was transferred to a separatory funnel and washed with saturated NH_4Cl (30 mL). The organic layer was separated and washed with H_2O (2 x 30 mL) followed by brine (10 mL). The organic layer was then dried over anhydrous Na_2SO_4. After filtration, the solvents were removed via *in vacuo* rotary evaporation. The product was purified by silica gel flash chromatography.

Product Purification/Characterization data:

Table 2, entry 1 (dodecan-6-yl benzoate) (2a). The general procedure A was used. The product was purified by silica gel flash chromatography eluting with 5% ethyl acetate in hexanes to give the product as a slightly yellow oil in 73% yield, >20:1 (linear:branched). R_f = 0.5 (10% EtOAc in hexanes). ^{1}H NMR (300 MHz, $CDCl_3$): δ 0.87 (m, 6H), 1.18-1.43 (m, 14H), 1.66 (m, 4H), 5.13 (quint, *J* = 6.2 Hz, 1H), 7.40-7.59 (m, 3H), 8.03-8.08 (m, 2H). ^{13}C NMR (75 MHz, $CDCl_3$): δ 14.2, 14.3, 22.8(2), 25.2, 25.5, 29.5, 32.0(2), 34.4(2), 75.3, 128.5, 129.7, 131.1, 132.9, 166.6. IR (neat): 2927, 2858, 1715, 1451, 1269, 1109, 1026, 708, 669 cm^{-1}. HRMS $(M+Na)^+$: calcd. 313.2144, obsvd. 313.2139.

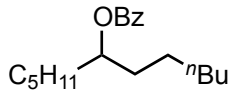


Table 2, entry 2 (dodecan-6-yl 4-methoxybenzoate) (2b). The general procedure A was used. The product was purified by silica gel flash chromatography eluting with 10% diethyl ether in hexanes to give the product as a colorless oil in 72% yield, >20:1 (linear:branched). R_f = 0.4 (10% Et_2O in hexanes). ^{1}H NMR (400 MHz, $CDCl_3$): δ 0.83-0.89 (m, 6H), 1.21-1.43 (m, 14H), 1.57-1.71 (m, 4H), 3.85 (s, 3H), 5.07-5.12 (m, 1H), 6.91 (d, *J* = 8.5 Hz, 2H), 8.00 (d, *J* = 9 Hz, 2H). ^{13}C NMR (125 MHz, $CDCl_3$): δ 14.2, 14.3, 22.8(2), 25.2, 25.6, 29.5, 31.9, 32.0, 34.4, 34.5, 55.6, 74.9, 113.7, 123.6, 131.7, 163.4, 166.3. IR (neat): 2929, 2858, 1705, 1606, 1510, 1253, 1166, 1111, 1032, 846, 731 cm^{-1}. HRMS $(M+Na)^+$: calcd. 343.2249, obsvd. 343.2251.

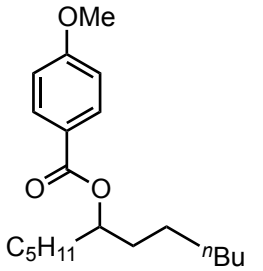
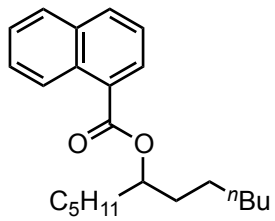


Table 2, entry 3 (dodecan-6-yl 1-naphthoate) (2c). The general procedure A was used. The product was purified by silica gel flash chromatography eluting with 5% ethyl acetate in hexanes to give the product as a



colorless oil in 65% yield, >20:1 (linear:branched). R_f = 0.5 (5% EtOAc in hexanes). ^{1}H NMR (500 MHz, $CDCl_3$): δ 0.85-0.94 (m, 6H), 1.24-1.52 (m, 14H), 1.66-1.82 (m, 4H), 5.24-5.31 (m, 1H), 7.48-7.56 (m, 2H), 7.59-7.64 (m, 1H), 7.89 (d, *J* = 8.2 Hz, 1H), 8.01 (d, *J* = 8.2 Hz, 1H), 8.16 (d, *J* = 8.0 Hz, 1H), 8.92 (d, *J* = 8.6 Hz, 1H). ^{13}C NMR (125 MHz, $CDCl_3$): δ 14.2, 14.3, 22.7, 22.8, 25.3, 25.7, 29.5, 32.0(2), 34.5(2), 75.4, 124.7, 126.1, 126.3, 127.8, 128.3, 128.7, 129.9, 131.6, 133.1, 134.0, 167.6. IR (neat): 2953, 2927, 2857, 1709, 1509, 1460, 1275, 1238, 1194, 1135, 1003, 779 cm^{-1}. HRMS $(M+Na)^+$: calcd. 363.2300, obsvd. 363.2306.

Table 2, entry 4 (dodecan-6-yl acetate) (2d). The general procedure A was used. The product was purified by silica gel flash chromatography eluting with 5% ethyl acetate in hexanes to give the product as a colorless oil in 47% yield, >20:1 (linear:branched). R_f = 0.3 (5% EtOAc in hexanes). ^{1}H NMR (500 MHz, $CDCl_3$): δ 0.77-0.90 (m, 6H), 1.16-1.55 (m, 18H), 2.03 (s, 3H), 4.79-4.89 (m, 1H). ^{13}C NMR (125 MHz, $CDCl_3$): δ 14.2, 14.3, 21.5, 22.7, 22.8, 25.2, 25.5, 29.4, 31.9, 32.0, 34.2, 34.3 74.7, 171.1. IR (neat): 2927, 2858, 1736, 1458, 1371, 1237, 1123, 1019, 725, 608 cm^{-1}. HRMS $(M+Na)^+$: calcd. 251.1987, obsvd. 251.1993.

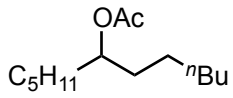


Table 2, entry 5 (2,2-dimethylnonan-3-yl acetate) (2e). The general procedure A was used. The product was purified by silica gel flash chromatography eluting with 5% ethyl acetate in hexanes to give the product as a colorless oil in 46% yield, >20:1 (linear:branched). R_f = 0.4 (5% EtOAc in hexanes). ^{1}H NMR (300 MHz, $CDCl_3$): δ 0.83-0.90 (m, 12H), 1.17-1.55 (m, 10H), 2.05 (s, 3H), 4.71 (dd, *J* = 10.3, 2.6 Hz, 1H). ^{13}C NMR (75 MHz, $CDCl_3$): δ 14.3, 21.3, 22.8, 26.1, 26.6, 29.5, 29.8, 32.0, 34.7, 81.1, 171.4. IR (neat): 2955, 2925, 2857, 1736, 1466, 1369, 1239, 1018, 961, 604 cm^{-1}. HRMS $(M+Na)^+$: calcd. 237.1831, obsvd. 237.1826.

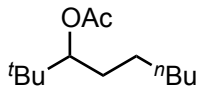


Table 2, entry 6 (1-cyclohexylheptyl benzoate) (2f). The general procedure A was used. The product was purified by silica gel flash chromatography eluting with 2% diethyl ether in hexanes to give the product as a colorless oil in 72% yield, >20:1 (linear:branched). R_f = 0.3 (2% Et_2O in Hexanes). ^{1}H NMR (300 MHz, $CDCl_3$): δ 0.85 (t, *J* = 6.8 Hz, 3H), 1.04-1.40 (m, 13H), 1.56-1.84 (m, 8H), 5.00 (q, *J* = 6.1 Hz, 1H) 7.40-7.47 (m, 2H), 7.52-7.58 (m, 1H), 8.03-8.08 (m, 2H). ^{13}C NMR (75 MHz, $CDCl_3$): δ 14.2, 22.8, 25.7, 26.3, 26.4, 26.6, 28.3, 29.4, 29.5, 31.5, 31.9, 41.6, 78.8, 128.5, 129.8, 131.0, 132.9, 166.6. IR (neat): 2924, 2852, 1714, 1449, 1267, 1110, 1068, 707 cm^{-1}. HRMS $(M+Na)^+$: calcd. 325.2144, obsvd. 325.2148.

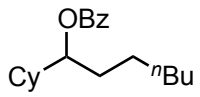


Table 2, entry 7 (1-(benzyloxy)octan-2-yl benzoate) (2g). The general procedure A was used. The product was purified by silica gel flash chromatography eluting with 10% diethyl ether in hexanes to give the product as a colorless oil in 78% yield, >20:1 (linear:branched). R_f = 0.4 (10% Et_2O in hexanes). ^1H NMR (300 MHz, $CDCl_3$): δ 0.86 (t, *J* = 6.8 Hz, 3H), 1.17-1.40 (m, 8H), 1,75 (q, *J* = 7.4 Hz, 2H), 3.59-3.69 (m, 2H), 4.53 (d, *J* = 12.3 Hz, 1H), 4.61 (d, *J* = 12.0 Hz, 1H), 5.31 (m, 1H), 7.24-7.33 (m, 5H), 7.41-7.48 (m, 2H), 7.53-7.60 (m, 1H), 8.04-8.10 (m, 2H). ^{13}C NMR (125 MHz, $CDCl_3$): δ 14.3, 22.8, 25.5, 29.4, 31.2, 31.9, 71.4, 73.3, 73.7, 127.8, 128.4, 128.5, 129.9, 130.8, 133.0, 138.4, 166.4. IR (neat): 2926, 2856, 1714, 1601, 1451, 1268, 1097, 709 cm^{-1}. HRMS $(M+H)^+$: calcd. 341.2117, obsvd. 341.2119.

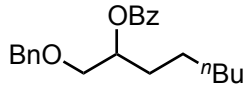


Table 2, entry 8 (1-phenyloctan-2-yl benzoate) (2h). The general procedure A was used. The product was purified by silica gel flash chromatography eluting with 10% diethyl ether in hexanes to give the product as a colorless oil in 67% yield, >20:1 (linear:branched). R_f = 0.3 (10% Et_2O in hexanes). ^1H NMR (400 MHz, $CDCl_3$): δ 0.82-0.90 (m, 3H), 1.17-1.49 (m, 8H), 1.61-1.76 (m, 2H), 2.95 (dd, *J* = 14.0, 6.2 Hz, 1H), 3.05 (dd, *J* = 13.6, 6.2 Hz, 1H), 5.34 (quint, *J* = 6.2 Hz, 1H), 7.17-7.32 (m, 5H), 7.40-7.59 (m, 3H), 8.03 (d, *J* = 7.2 Hz, 2H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 14.2, 22.8, 25.6, 29.3, 31.9, 33.7, 40.8, 75.7, 126.6, 128.5(2), 129.7, 130.9, 132.9, 137.8, 166.3. IR (neat): 2926, 2856, 1713, 1450, 1268, 1109, 1068, 1068, 1025, 708, 698 cm^{-1}. HRMS $(M+Na)^+$: calcd. 333.1831, obsvd. 333.1830.

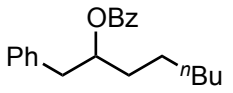


Table 2, entry 9 (14-chlorotetradecan-6-yl benzoate) (2i). The general procedure B was used. The product was purified by silica gel flash chromatography eluting with 5% ethyl acetate in hexanes to give the product as a slightly yellow oil in 63% yield, >20:1 (linear:branched). R_f = 0.3 (5% EtOAc in hexanes). ^1H NMR (500 MHz, $CDCl_3$): δ 0.87 (t, *J* = 7.0 Hz, 3H), 1.23-1.44 (m, 16H), 1.59-1.78 (m, 6H), 3.50 (t, *J* = 6.8 Hz, 2H), 5.10-5.16 (m, 1H), 7.44 (t, *J* = 7.8 Hz, 2H), 7.52-7.56 (m, 1H), 8.05 (d, *J* = 7.0 Hz, 2H). ^{13}C NMR (125 MHz, $CDCl_3$): δ 14.2, 22.7, 25.2, 25.5, 27.0, 28.9, 29.5, 29.6, 32.0, 32.8, 34.4, 45.3, 75.2, 76.4, 128.5, 129.7, 131.1, 132.8, 166.5. IR (neat): 2928, 2856, 1713, 1450, 1270, 1109, 709 cm^{-1}. HRMS $(M+Na)^+$: calcd. 375.2067, obsvd. 375.2073.

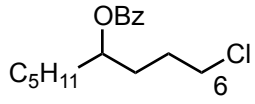


Table 2, entry 10 (1-cyclohexylnonan-4-yl 1-naphthoate) (2j). The general procedure A was used. The product was purified by silica gel flash chromatography eluting with 5% diethyl ether in hexanes to give the product as a colorless oil in 63% yield, >20:1 (linear:branched). R_f = 0.7 (10% Et_2O in hexanes). ^{1}H NMR (300 MHz, $CDCl_3$): δ 0.77-0.94 (m, 5H), 1.08-1.80 (s, 22H), 5.20-5.31 (m, 1H), 7.46-7.63 (m, 3H), 7.88 (d, *J* = 8.0 Hz, 1H), 8.01 (d, *J* = 8.0 Hz, 1H), 8.14 (dd, *J* = 7.4, 1.3 Hz, 1H), 8.89 (d, *J* = 8.7 Hz, 1H). ^{13}C NMR (125 MHz, $CDCl_3$): δ 14.2, 22.8, 22.9, 25.4, 26.6, 26.9, 30.5, 32.0, 33.6(2), 34.5, 34.8, 37.6, 37.8, 75.4, 124.7, 126.0, 126.3, 127.8, 128.3, 128.7, 129.8, 131.6, 133.1, 134.0, 167.7. IR (neat): 2920, 2849, 1709, 1509, 1447, 1275, 1238, 1195, 1133, 1003, 779 cm^{-1}. HRMS $(M+Na)^+$: calcd. 403.2613, obsvd. 403.2619.

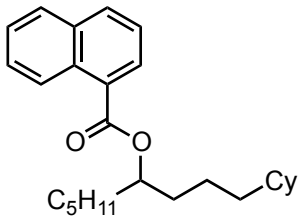


Table 2, entry 11 (14-(pivaloyloxy)tetradecan-6-yl 1-naphthoate) (2k). The general procedure A was used. The product was purified by silica gel flash chromatography eluting with 5% ethyl acetate in hexanes to give the product as a colorless oil in 61% yield, >20:1 (linear:branched). R_f = 0.2 (5% EtOAc in hexanes). ^{1}H NMR (300 MHz, $CDCl_3$): δ 0.88 (t, *J* = 7.2 Hz, 3H), 1.18 (s, 9H), 1.25-1.49 (m, 16H), 1.55-1.81 (m, 6H), 4.02 (t, *J* = 6.6 Hz, 2H), 5.21-5.29 (m, 1H), 7.46-7.63 (m, 3H), 7.88 (d, *J* = 8.0 Hz, 1H), 8.01 (d, *J* = 8.0 Hz, 1H), 8.14 (dd, *J* = 7.4, 1.3 Hz, 1H), 8.89 (d, *J* = 8.7 Hz, 1H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 14.2, 22.8, 25.4, 25.7, 26.1, 27.4, 28.8, 29.4, 29.6, 29.7, 30.5, 32.0, 34.5, 38.9, 64.6, 75.3, 124.7, 126.0, 126.3, 127.8, 128.3, 128.7, 129.9, 131.6, 133.2, 134.1, 167.6, 178.8. IR (neat): 2928, 2856, 1725, 1710, 1509, 1460, 1277, 1239, 1152, 1136, 781 cm^{-1}. HRMS $(M+Na)^+$: calcd. 491.3137, obsvd. 491.3147.

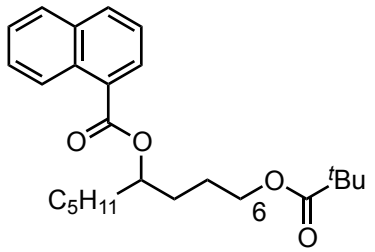
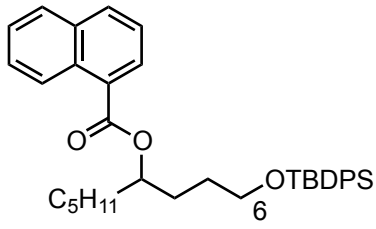


Table 2, entry 12 (14-((*tert*-butyldiphenylsilyl)oxy)tetradecan-6-yl 1-naphthoate) (2l). The general procedure B was used. The product was purified by silica gel flash chromatography eluting with 5% ethyl acetate in hexanes to give the product as a colorless oil in 76% yield, >20:1 (linear:branched). R_f = 0.4 (5% EtOAc in hexanes). ^{1}H NMR (300 MHz, $CDCl_3$): δ 0.91 (t, *J* = 7.2 Hz, 3H), 1.07 (s, 9H), 1.23-1.61 (m, 18H), 1.67-1.98 (m, 4H), 3.66 (t, *J* = 6.5 Hz, 2H), 5.24-5.33 (m, 1H), 7.33-7.73 (m, 13H), 7.88 (d, *J* = 8.2 Hz, 1H), 8.01 (d, *J* = 8.4 Hz, 1H), 8.14 (dd, *J* = 7.4, 1.3 Hz, 1H), 8.89 (d, *J* = 8.7 Hz, 1H). ^{13}C NMR (75 MHz, $CDCl_3$): δ



14.3, 19.4, 22.8, 25.4, 25.7, 25.9, 27.1 29.5, 29.7, 29.8, 31.9, 32.8, 34.5(2), 64.1, 75.3, 124.7, 126.0, 126.3, 127.8(2), 128.2, 128.7, 129.7, 129.9, 131.6, 133.2, 134.0, 134.3, 135.8, 167.6. IR (neat): 2928, 2855, 1709, 1461, 1239, 1135, 1109, 1004, 780, 737, 699, 612 cm^{-1}. HRMS $(M+Na)^+$: calcd. 645.3740, obsvd. 645.3746.

Table 2, entry 13 (14-(benzoyloxy)tetradecan-6-yl 1-naphthoate) (2m). The general procedure B was used. The product was purified by silica gel flash chromatography eluting with 5% diethyl ether in hexanes to give the product as a colorless oil in 66% yield, >20:1 (linear:branched). R_f = 0.2 (5% Et_2O in Hexanes). ^1H NMR (400 MHz, $CDCl_3$): δ 0.89 (t, *J* = 7.2 Hz, 3H), 1.27-1.53 (m, 16H), 1.65-1.83 (m, 6H), 4.30 (t, *J* = 6.4 Hz, 2H), 5.22-5.31 (m, 1H), 7.43-7.63 (m, 6H), 7.88 (d, *J* = 8.2 Hz, 1H), 8.01-8.07 (m, 3H), 8.14 (dd, *J* = 7.4, 1.3 Hz, 1H), 8.89 (d, *J* = 8.8 Hz, 1H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 14.2, 22.8, 25.3, 25.6, 26.2, 28.9, 29.4, 29.6, 29.7, 30.5, 32.0, 34.5, 75.3, 65.3, 124.7, 126.0, 126.3, 127.7, 128.2, 128.5, 128.7, 129.7, 129.9, 130.7, 131.6, 132.9, 133.1, 134.0, 166.8, 167.6. IR (neat): 2927, 2855, 1710, 1509, 1451, 1270, 1135, 781, 709 cm^{-1}. HRMS $(M+H)^+$: calcd. 489.3005, obsvd. 489.3022.

Table 2, entry 14 (14-morpholino-14-oxotetradecan-6-yl 1-naphthoate) (2n). The general procedure B was used. The product was purified by silica gel flash chromatography eluting with 10% methanol in dichloromethane to give the product as a colorless oil in 59% yield, >20:1 (linear:branched). R_f = 0.4 (10% MeOH in DCM). ^1H NMR (300 MHz, $CDCl_3$): δ 0.88 (t, *J* = 7.1 Hz, 3H), 1.21-1.48 (m, 14H), 1.55-1.80 (m, 6H), 2.27 (t, *J* = 7.7 Hz, 2H), 3.42 (t, *J* = 4.8 Hz, 2H), 3.56-3.67 (m, 6H), 5.20-5.29 (m, 1H), 7.46-7.43 (m, 3H), 7.88 (d, *J* = 8.0 Hz, 1H), 8.01 (d, *J* = 8.0 Hz, 1H), 8.14 (dd, *J* = 7.4, 1.3 Hz, 1H), 8.89 (d, *J* = 8.7 Hz, 1H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 14.2, 22.8, 25.4(2), 25.6, 29.5, 29.7, 32.0, 33.3, 34.5, 42.1, 46.3, 66.9, 67.2, 75.3, 124.7, 126.0, 126.4, 127.8, 128.2, 128.7, 129.9, 131.6, 133.2, 134.1, 167.6, 172.0. IR (neat): 3853, 3743, 2928, 2855, 1707, 1652, 1456, 1275, 1242, 1136, 1116, 784, 668 cm^{-1}. HRMS $(M+H)^+$: calcd. 468.3114, obsvd. 468.3127.

Table 2, entry 15 (6-(*tert*-butoxy)dodecane) (2o). The general procedure A was used. The product was purified by silica gel flash chromatography eluting with 5% ethyl acetate in hexanes to give the product as a colorless oil

in 35% yield, >20:1 (linear:branched). R_f = 0.6 (5% EtOAc in hexanes). ^{1}H NMR (500 MHz, $CDCl_3$): δ 0.82-0.91 (m, 6H), 1.18 (s, 9H), 1.20-1.45 (m, 18H), 3.40 (quint, J = 5.7 Hz, 1H). ^{13}C NMR (125 MHz, $CDCl_3$): δ 14.3(2), 22.9,(2), 25.5, 25.8, 29.1, 29.9, 32.1, 32.5, 36.6, 36.6, 71.5, 73.2. IR (neat): 2955, 2927, 2857, 1459, 1386, 1360, 1194, 1042, 1016, 723 cm^{-1}. HRMS $(M+H)^+$: calcd. 243.2688, obsvd. 243.2693.

Table 3, entry 1 (7-methyltridecan-6-yl benzoate) (6a). The general procedure A was used. The product was purified by silica gel flash chromatography eluting with 5% ethyl acetate in hexanes to give the product as a colorless oil in 46% yield, >20:1 (linear:branched). R_f = 0.4 (5% EtOAc in hexanes). ^{1}H NMR (400 MHz, $CDCl_3$): δ 0.83-0.92 (m, 6H), 0.99 (d, J = 6.8, 3H), 1.11-1.49 (m, 16H), 1.55-1.82 (m, 3H), 5.11 (dt, J = 8.4, 4.3 Hz, 1H), 7.41-7.47 (m, 2H), 7.52-7.57 (m, 1H), 8.04-8.08 (m, 2H). ^{13}C NMR (125 MHz, $CDCl_3$): δ 14.2, 14.3, 14.7, 22.7, 22.8, 25.7, 27.4, 29.7, 31.6, 32.0(2), 33.3, 36.6, 78.2, 128.5, 129.8, 131.2, 132.9, 166.6. IR (neat): 2955, 2925, 2856, 1715, 1450, 1269, 1108, 708 cm^{-1}. HRMS $(M+Na)^+$: calcd. 341.2457, obsvd. 341.2466.

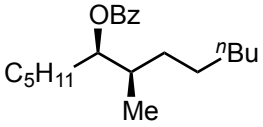


Table 3, entry 2 (*tert*-butyl((2,2-dimethyloctyl)oxy)diphenylsilane) (6b). The general procedure A was used. The product was purified by silica gel flash chromatography eluting with 2% ethyl acetate in hexanes to give the product as a colorless oil in 84% yield, >20:1 (linear:branched). R_f = 0.8 (5% EtOAc in hexanes). ^{1}H NMR (300 MHz, $CDCl_3$): δ 0.87-0.94 (m, 9H), 1.09 (s, 9H), 1.16-1.38 (m, 10H), 3.33 (s, 2H), 7.36-7.48 (m, 6H), 7.66-7.72 (m, 4H) ^{13}C NMR (75 MHz, $CDCl_3$): δ 14.4, 19.7, 22.9, 24.1, 24.5, 27.1, 30.6, 32.2, 35.8, 39.1, 72.4, 127.7, 129.7, 134.3, 135.9. IR (neat): 2955, 2928, 2856, 1471, 1427, 1105, 818, 698, 613 cm^{-1}. HRMS $(M+Na)^+$: calcd. 419.2746, obsvd. 419.2758.

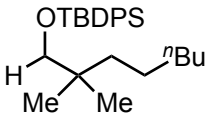


Table 3, entry 3 (2,2-dimethyloctyl benzoate) (6c). The general procedure A was used. The product was purified by silica gel flash chromatography eluting with 5% diethyl ether in hexanes to give the product as a colorless oil in 81% yield, >20:1 (linear:branched). R_f = 0.6 (10% Et_2O in hexanes). ^{1}H NMR (300 MHz, $CDCl_3$): δ 0.88 (t, J = 6.3 Hz, 3H), 1.00 (s, 6H), 1.25-1.40 (m, 10H), 4.04 (s, 2H), 7.41-7.49 (m, 2H), 7.53-7.59 (m, 1H), 8.03-8.09 (m, 2H). ^{13}C NMR (75 MHz, $CDCl_3$): δ 14.3, 22.8, 23.9, 24.7, 30.4, 32.0, 34.2, 39.6, 73.1, 128.5, 129.7, 130.7, 133.0, 166.8. IR (neat): 2956, 2928, 2857, 1719, 1602, 1601, 1470, 1393, 1266, 1175, 1111, 1069, 1026, 970, 707, 686, 673 cm^{-1}. HRMS $(M+Na)^+$: calcd. 285.1831, obsvd. 285.1827.

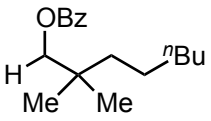
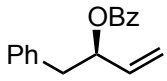
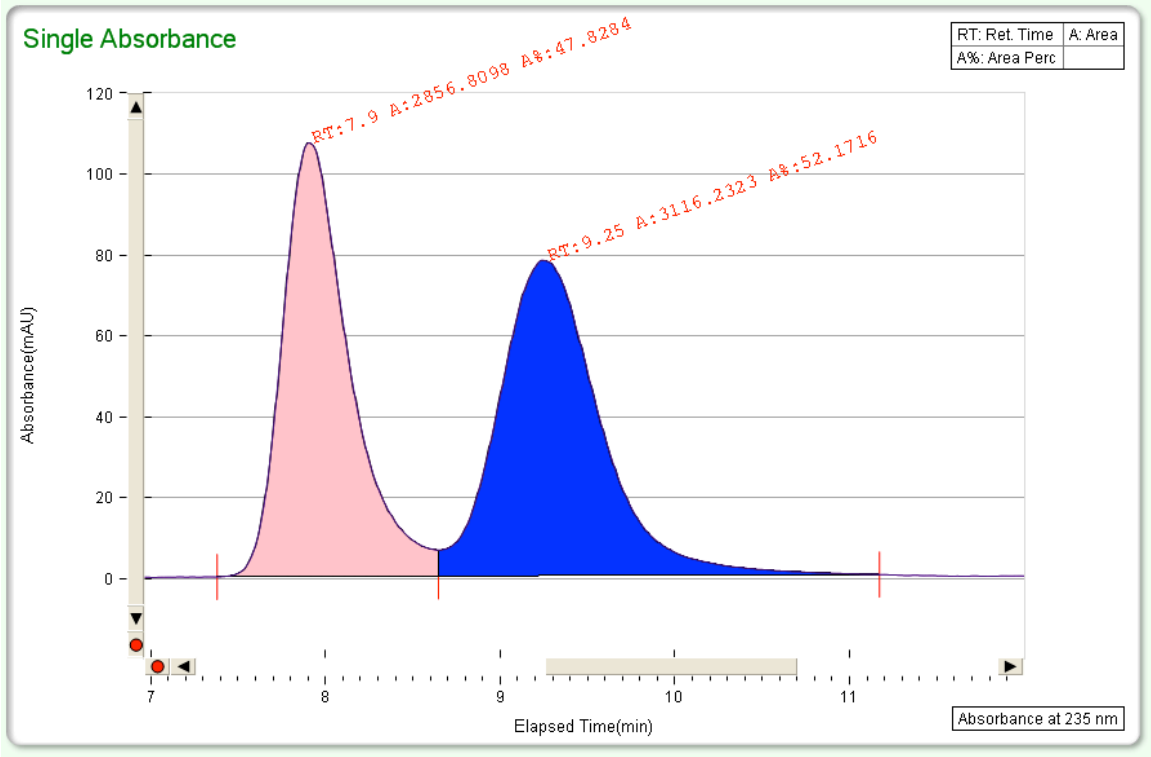
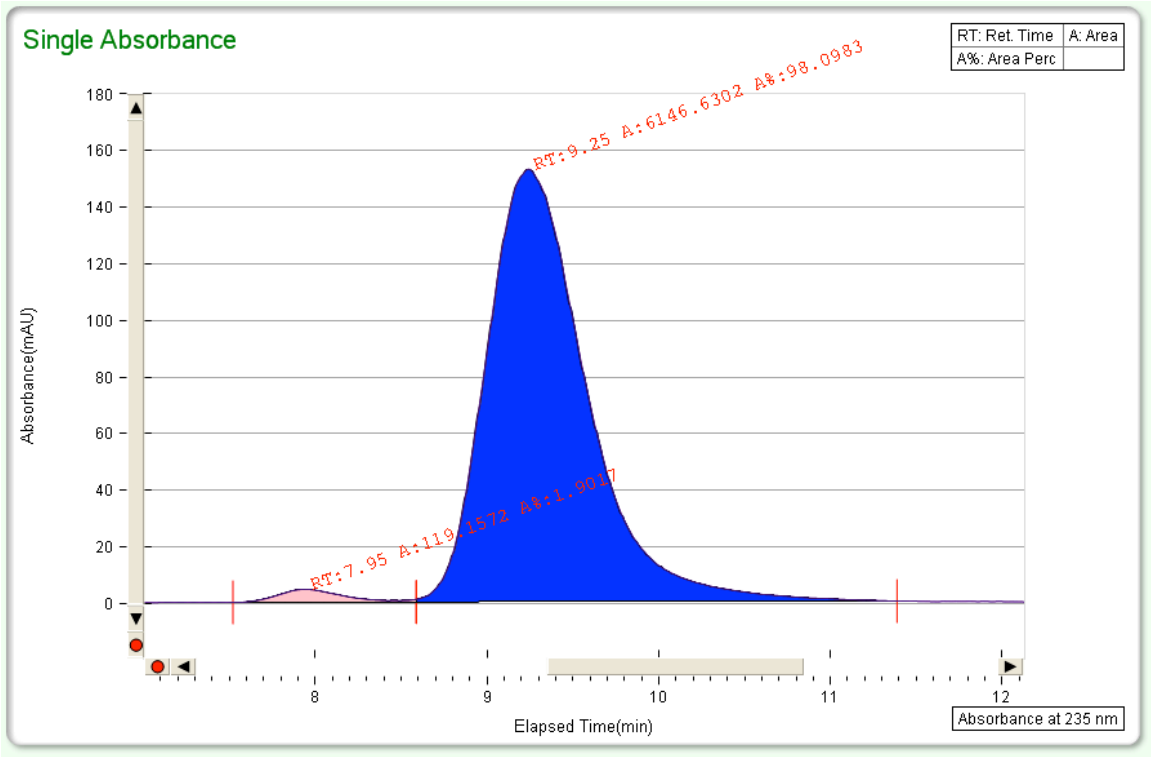


Table 3, entry 4 (3,3-dimethylpent-4-en-1-yl benzoate) (6d). The general procedure A was used. The product was purified by silica gel flash chromatography eluting with 5% ethyl acetate in hexanes to give the product as a colorless oil in 75% yield, >20:1 (linear:branched). R_f = 0.4 (5% EtOAc in hexanes). ^{1}H NMR (500 MHz, $CDCl_3$): δ 0.88 (t, *J* = 6.8 Hz, 3H), 0.95 (s, 6H), 1.24-1.32 (m, 10H), 1.70 (t, *J* = 7.4 Hz, 2H), 4.36 (t, *J* = 7.3 Hz, 2H), 7.43 (t, *J* = 7.7 Hz, 2H), 7.55 (t, *J* = 7.5 Hz, 1H), 8.04 (d, *J* = 8.0 Hz, 2H). ^{13}C NMR (125 MHz, $CDCl_3$): δ 14.3, 22.9, 24.2, 27.7, 30.4, 32.1, 32.5, 40.0, 42.6, 62.7, 128.5, 130.8, 133.0, 166.9. IR (neat): 2955, 2927, 2857, 1718, 1451, 1269, 1110, 707 cm^{-1}. HRMS $(M+Na)^+$: calcd. 299.1987, obsvd. 299.1988.

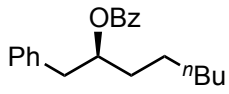
Separation of enantiomers by SFC. ChiraCel AY-H column, isochratic 2 mL/min, 1% IPA, 160 bar, 28 °C, 7.9 min (minor), 9.3 min (major).

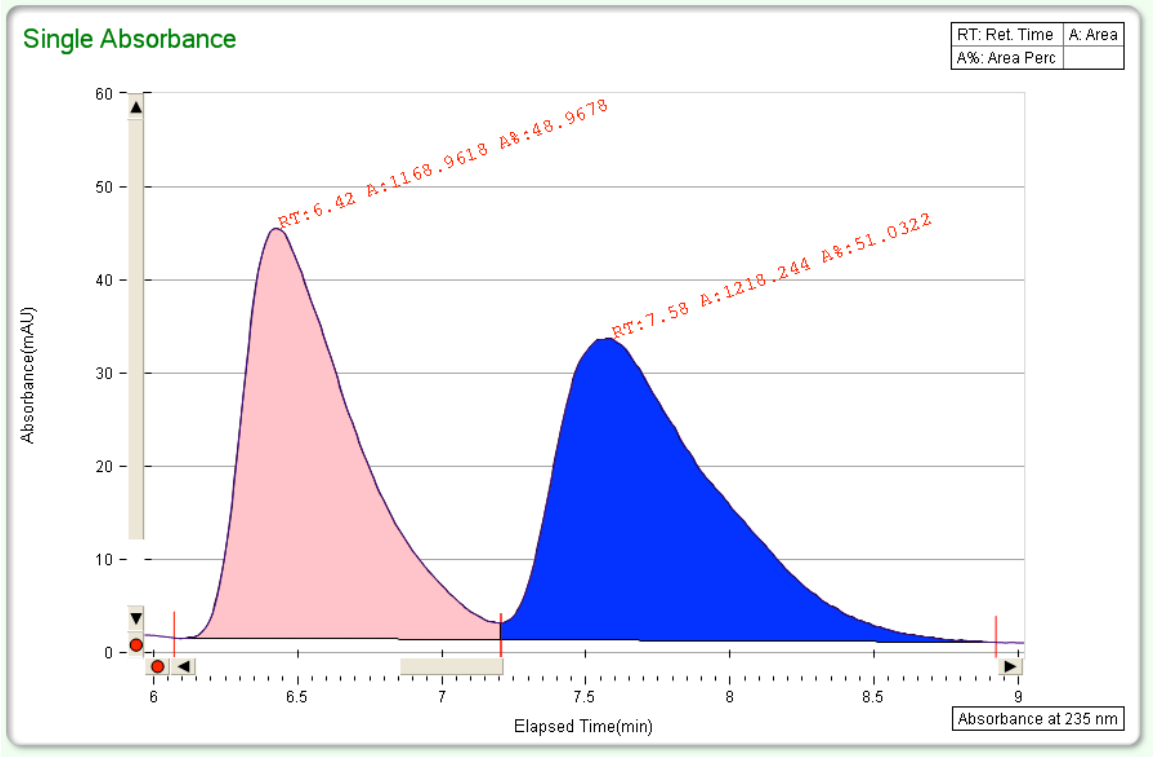


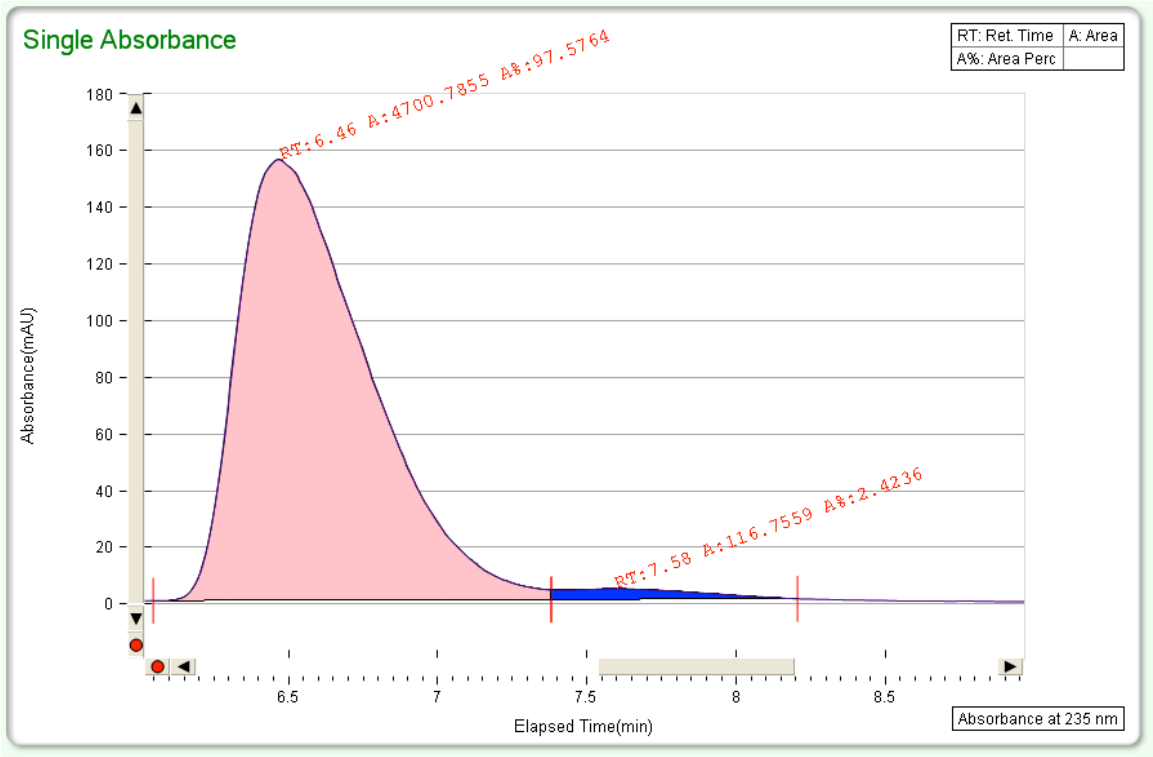




Separation of enantiomers by SFC. ChiraCel OD column, isochratic 3 mL/min, 1% IPA, 160 bar, 28 °C, 6.4 min (major), 7.6 min (minor).







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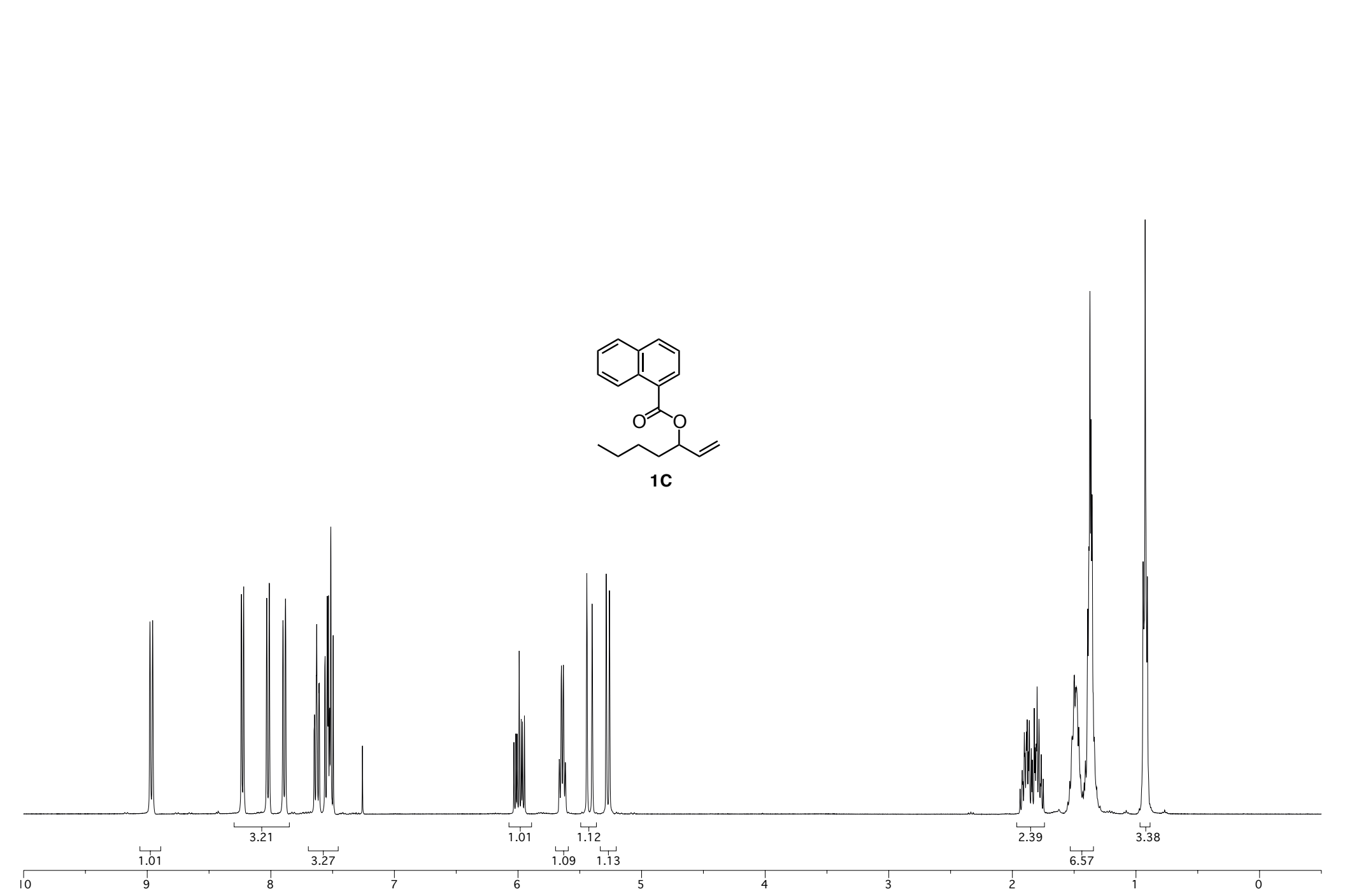
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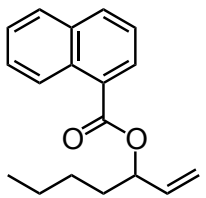

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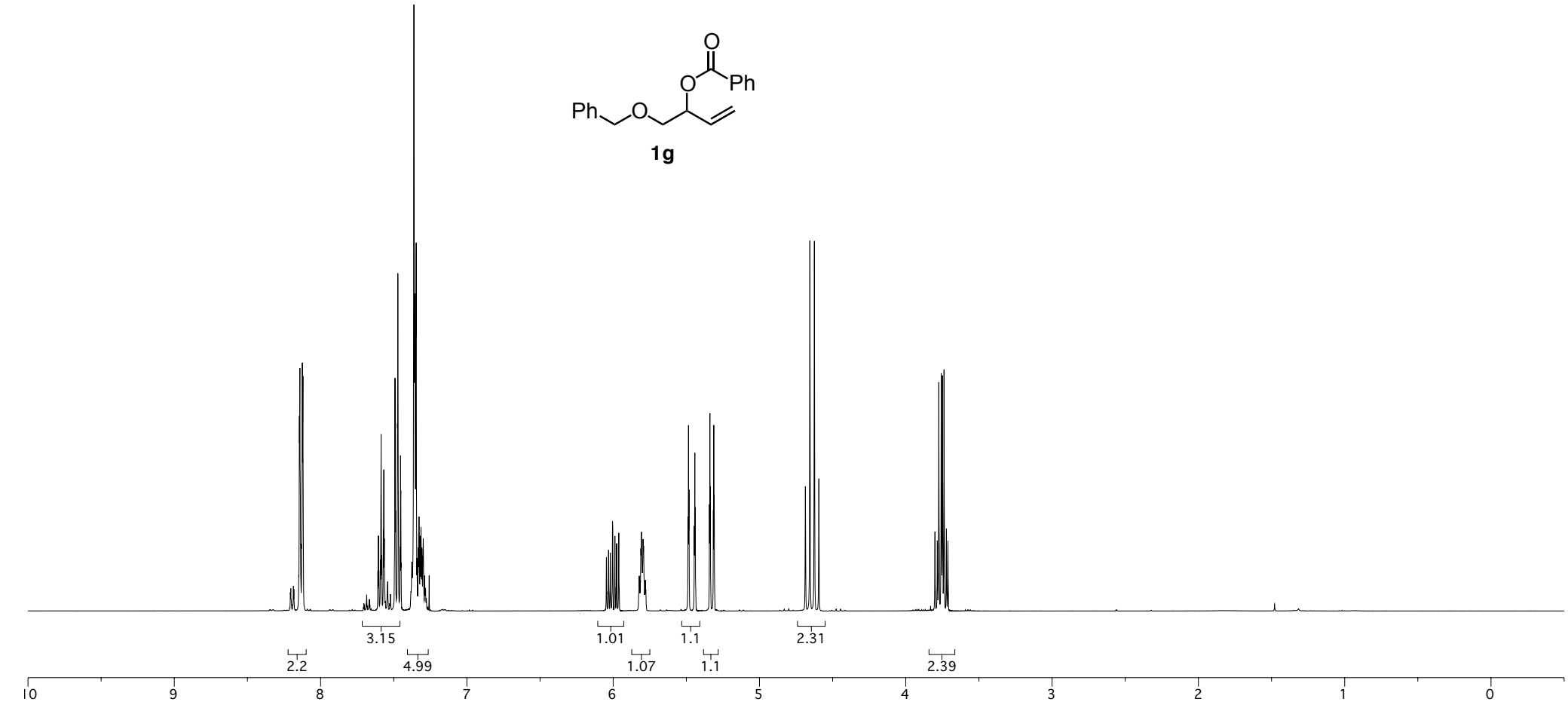
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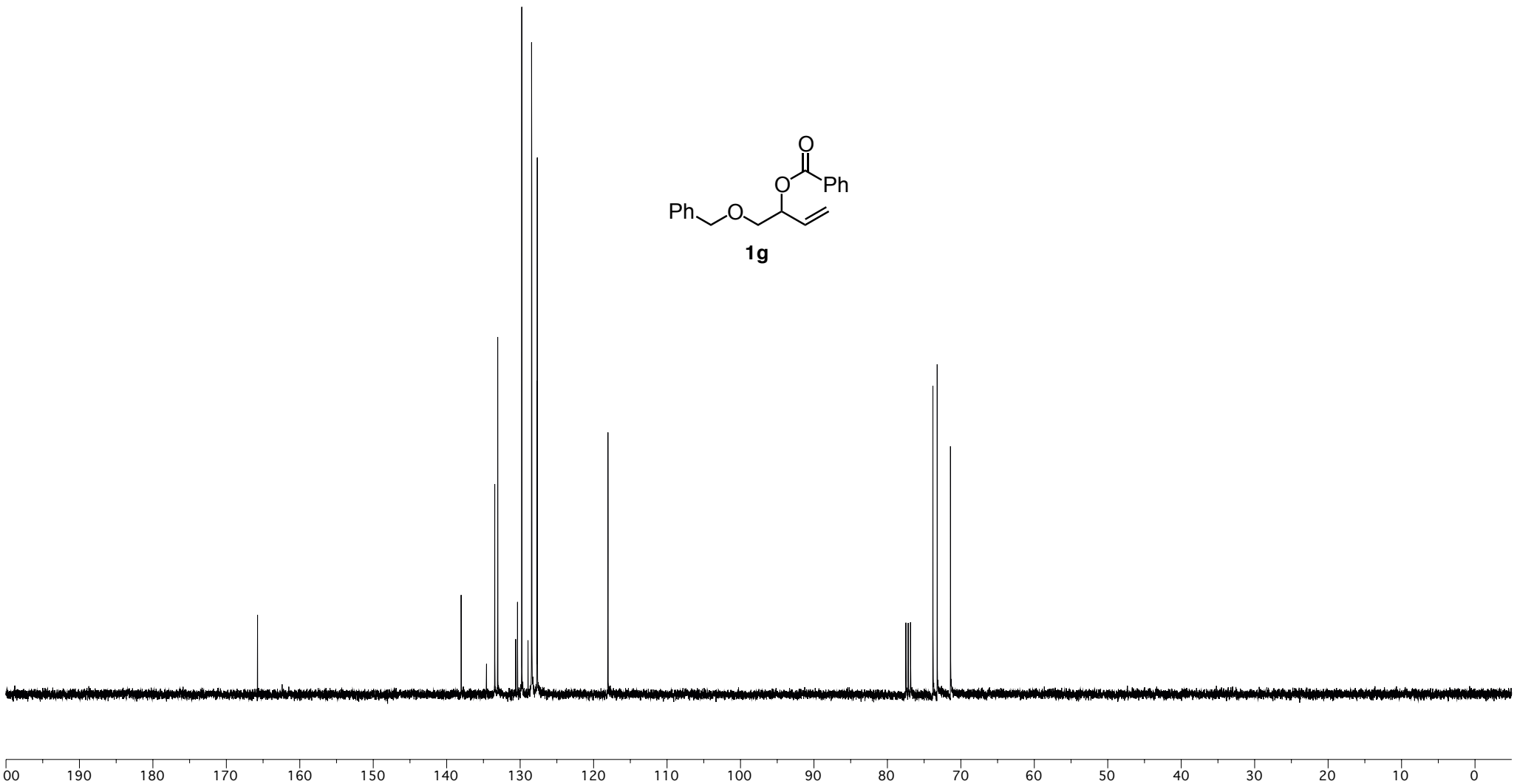
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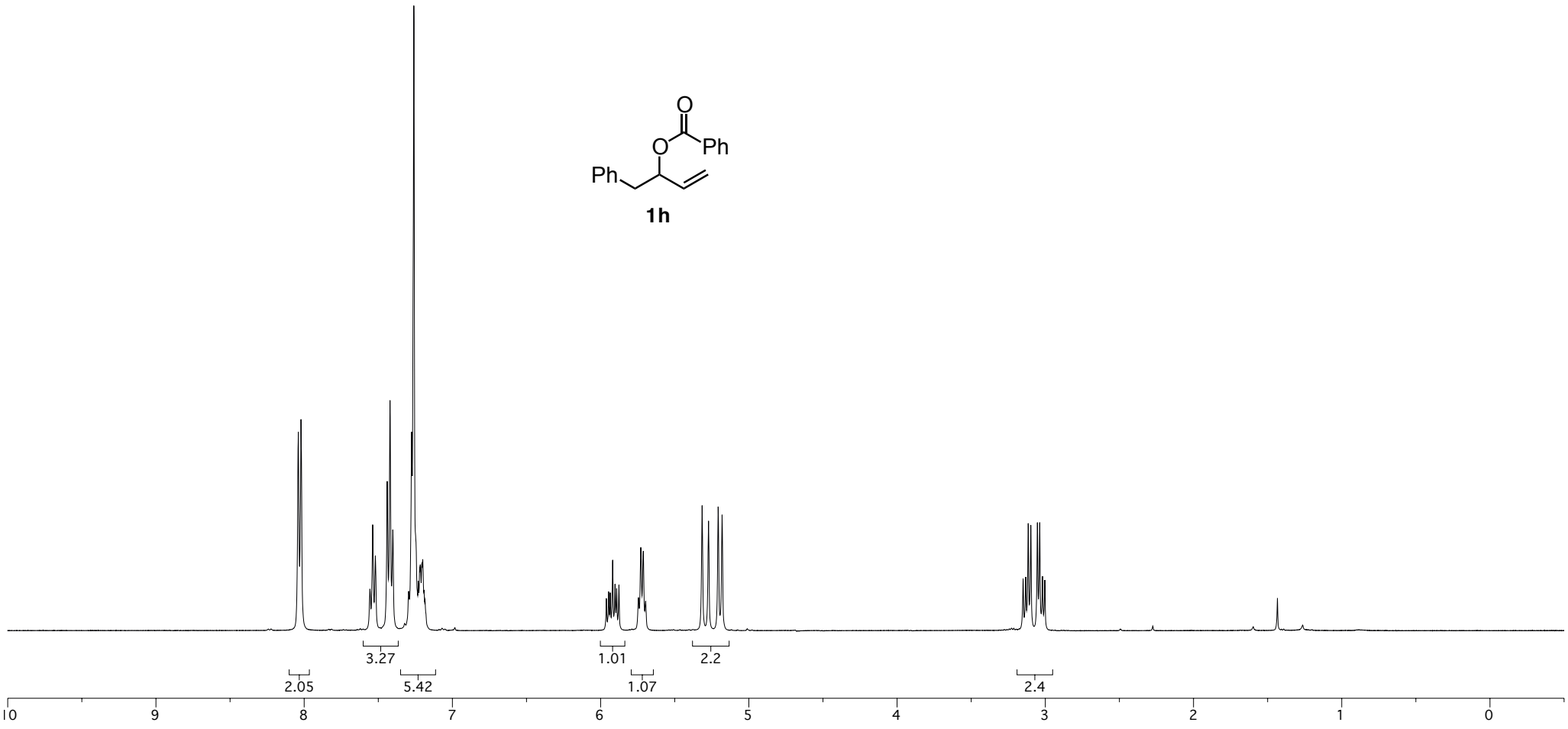
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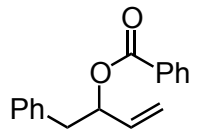

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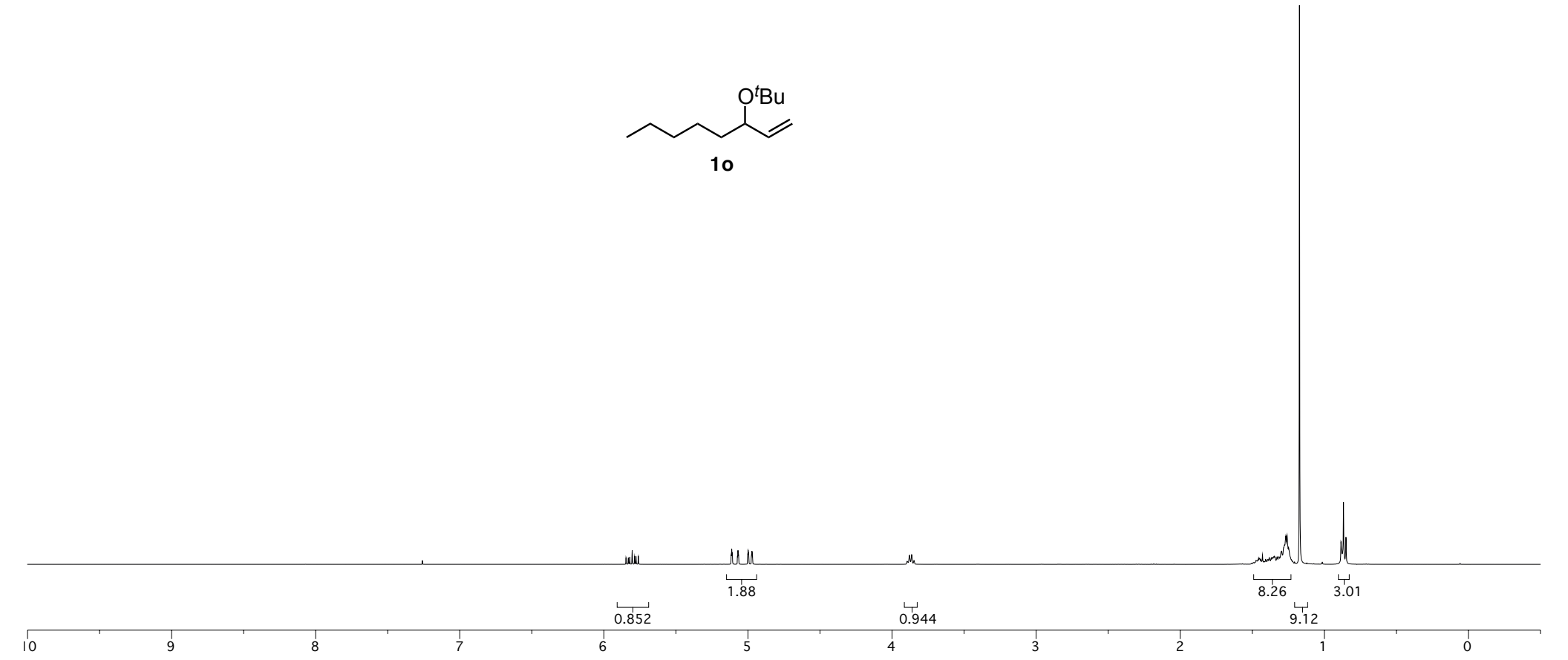
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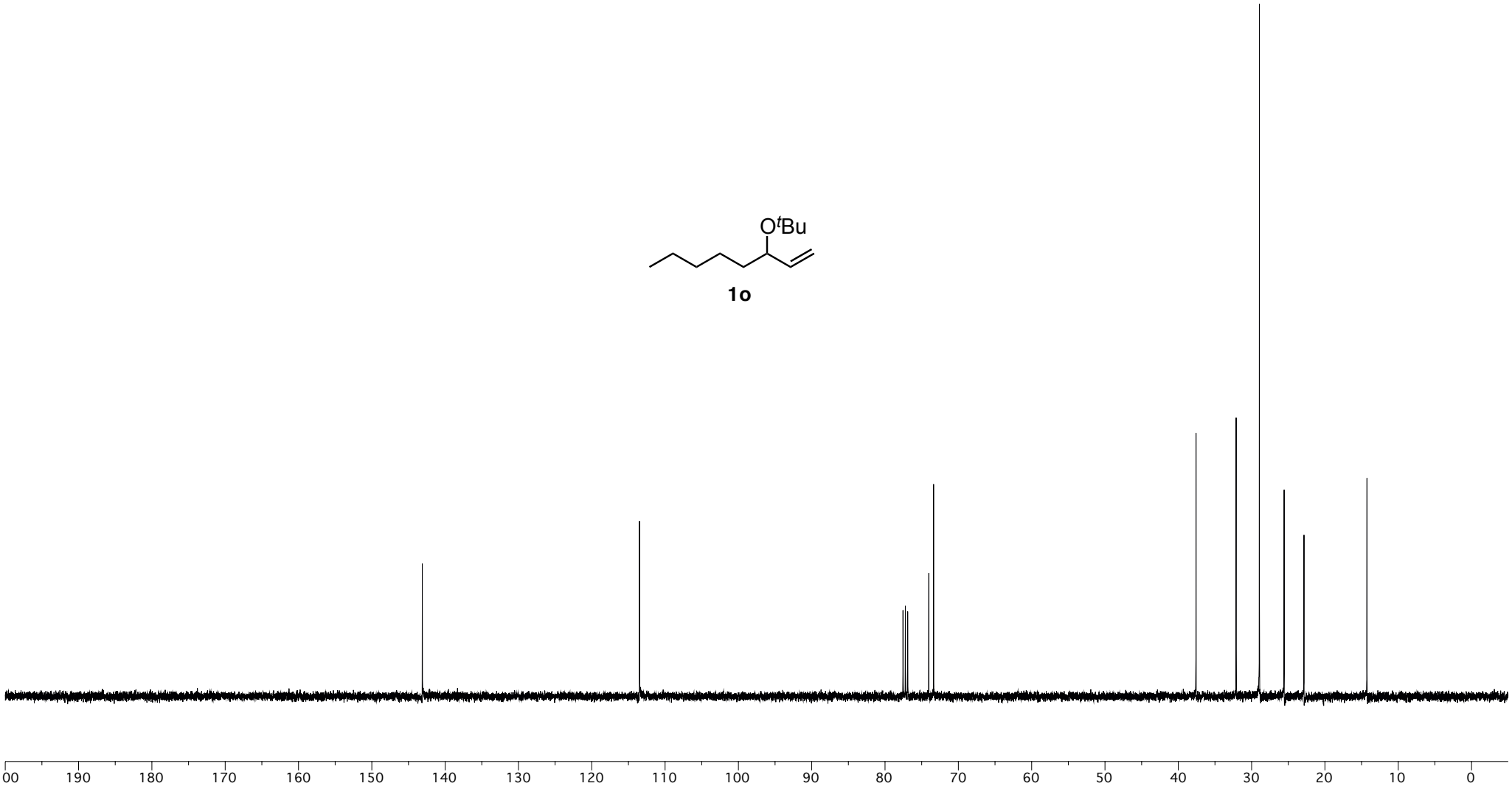
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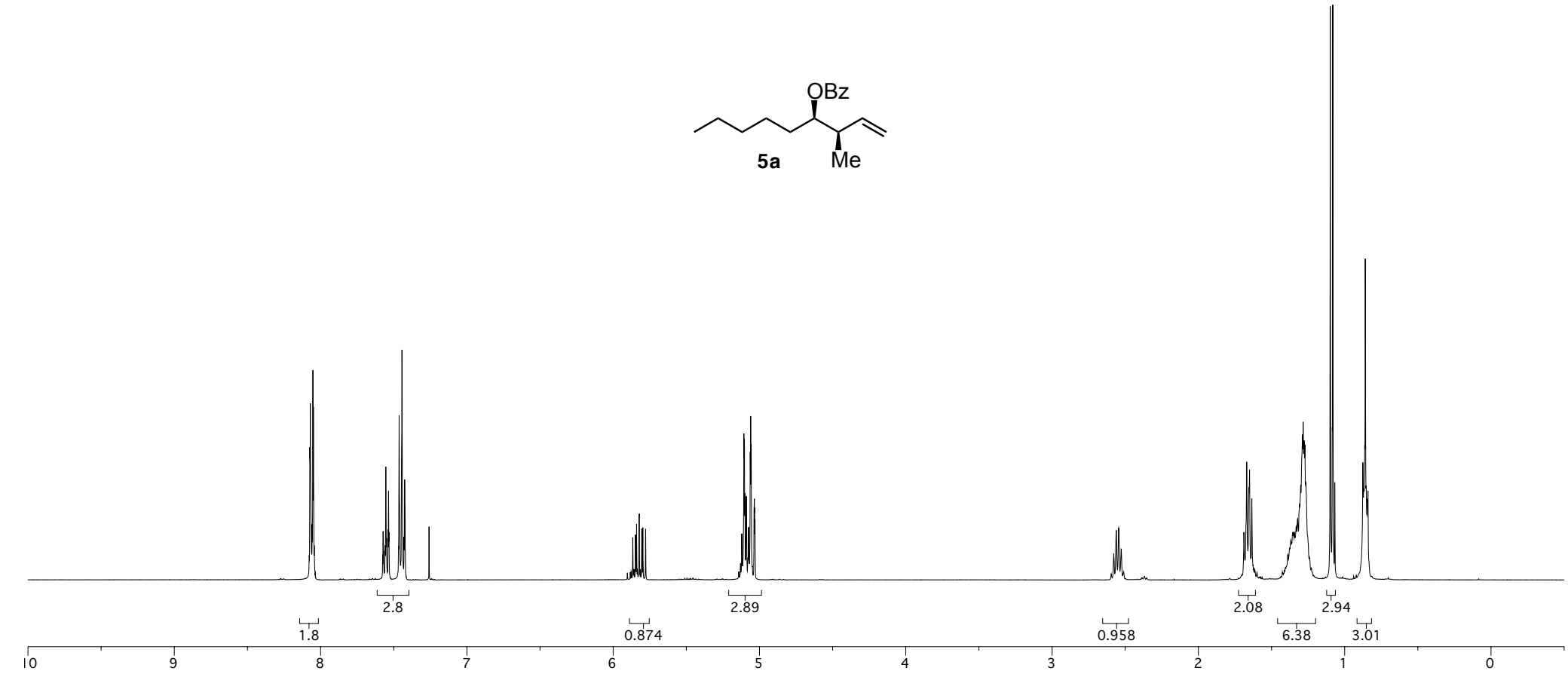
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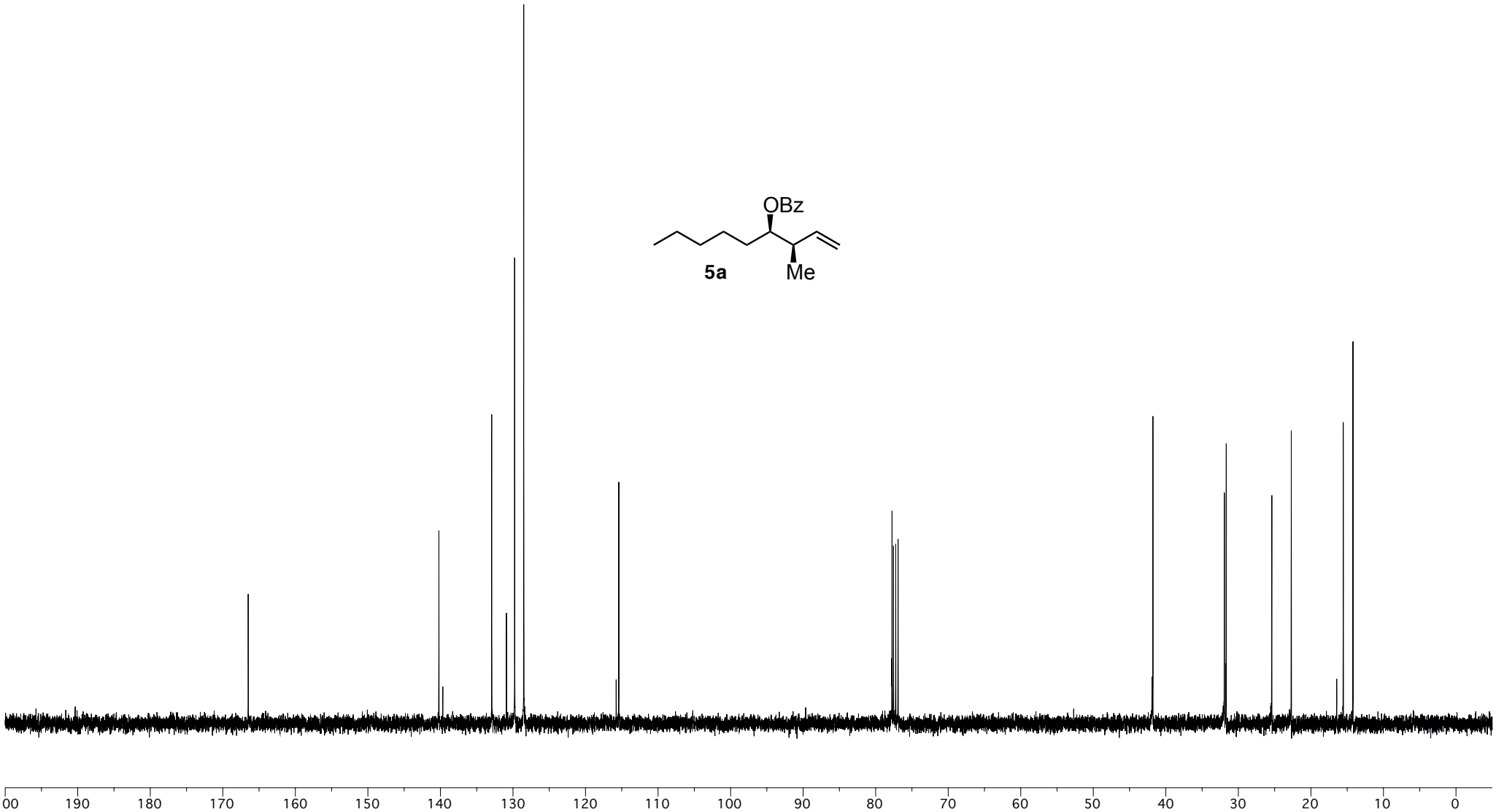
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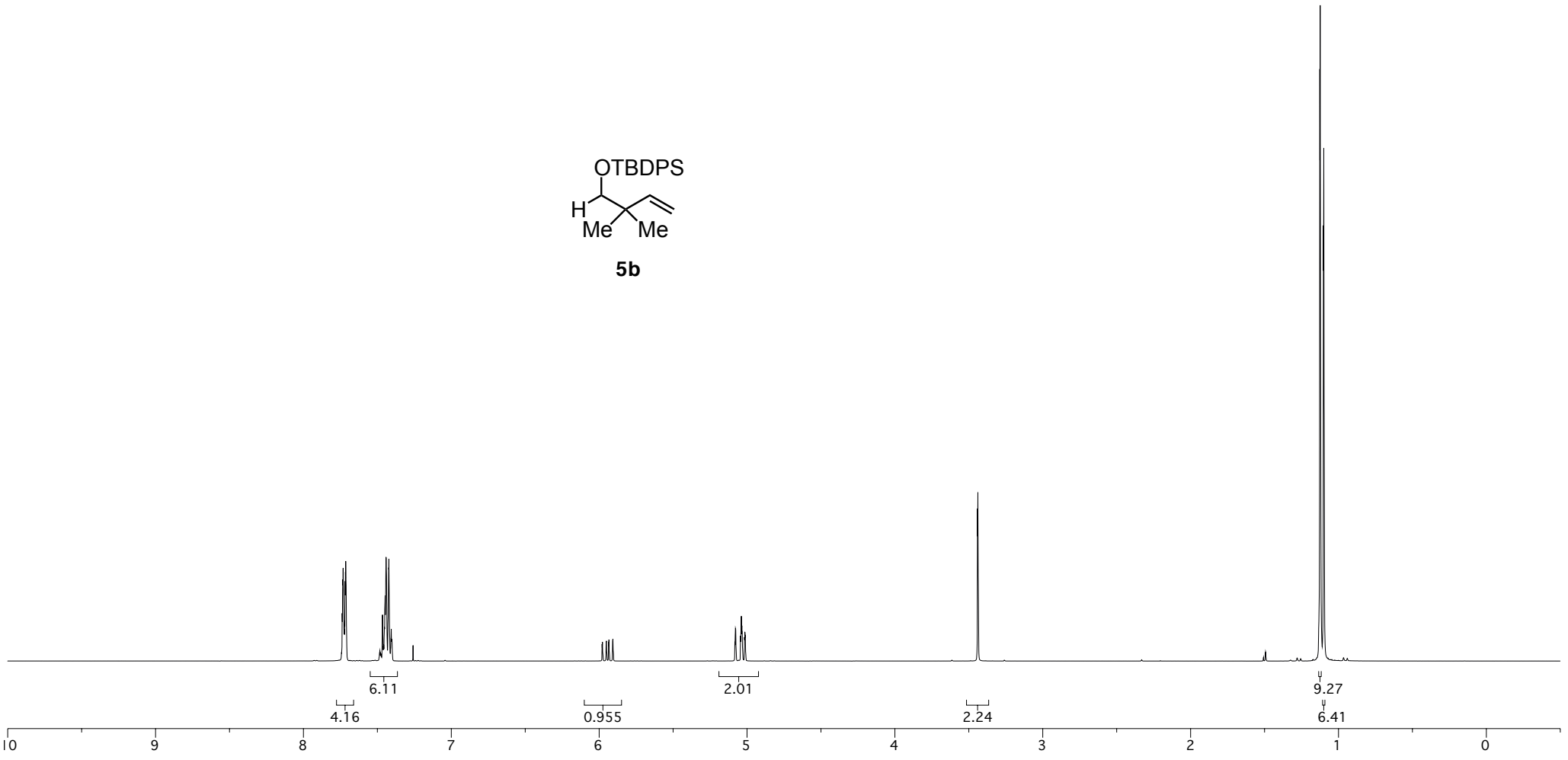
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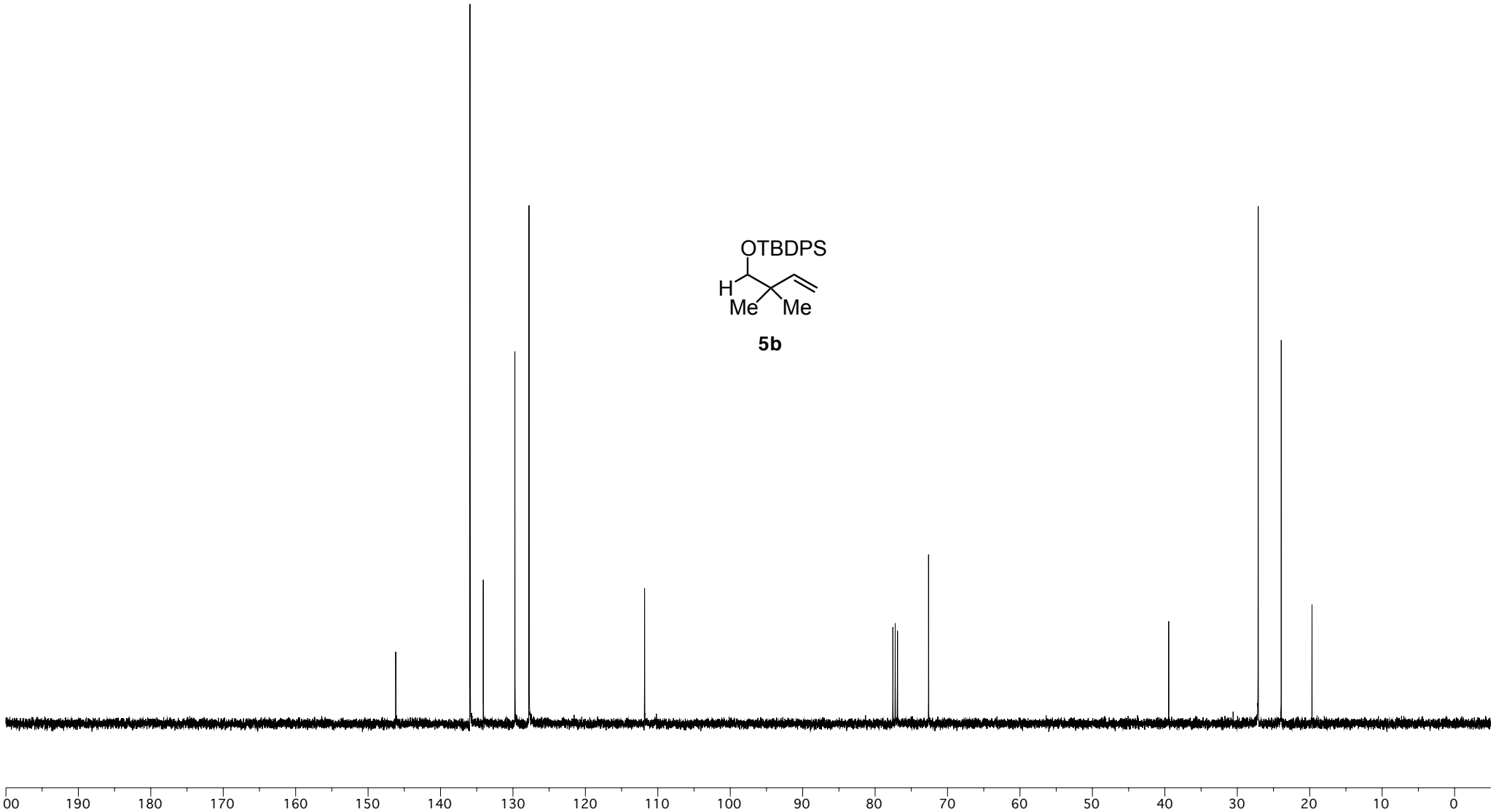
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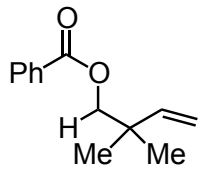

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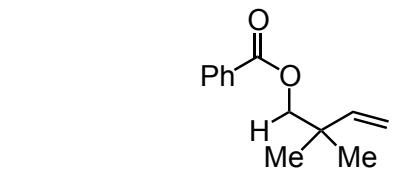
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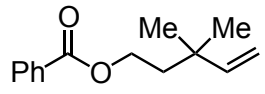

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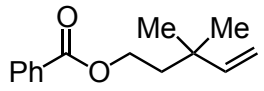
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Me
Me
Ph
O

5d

190
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140
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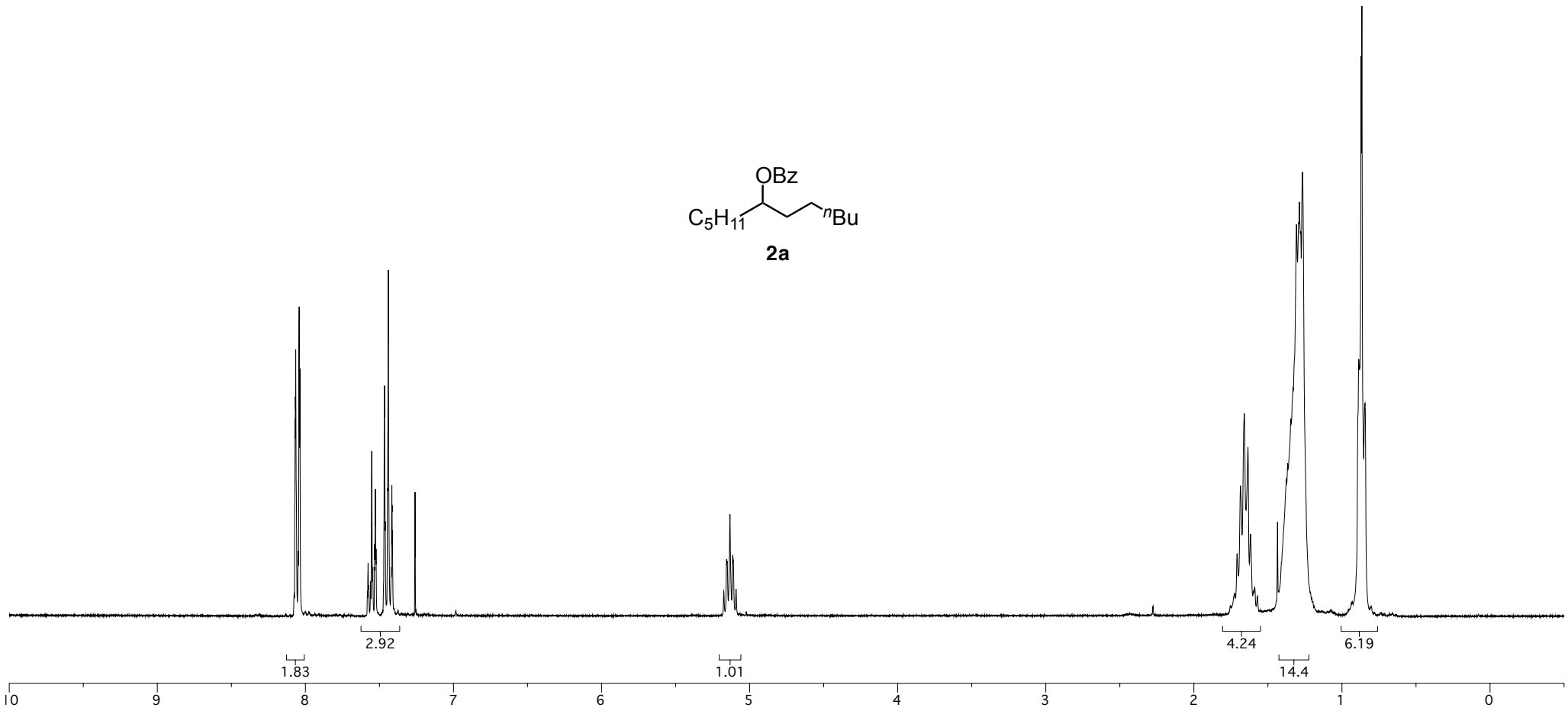
OBz
C5H11
nBu
2a
1.83
2.92
1.01
4.24
14.4
6.19
10
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7
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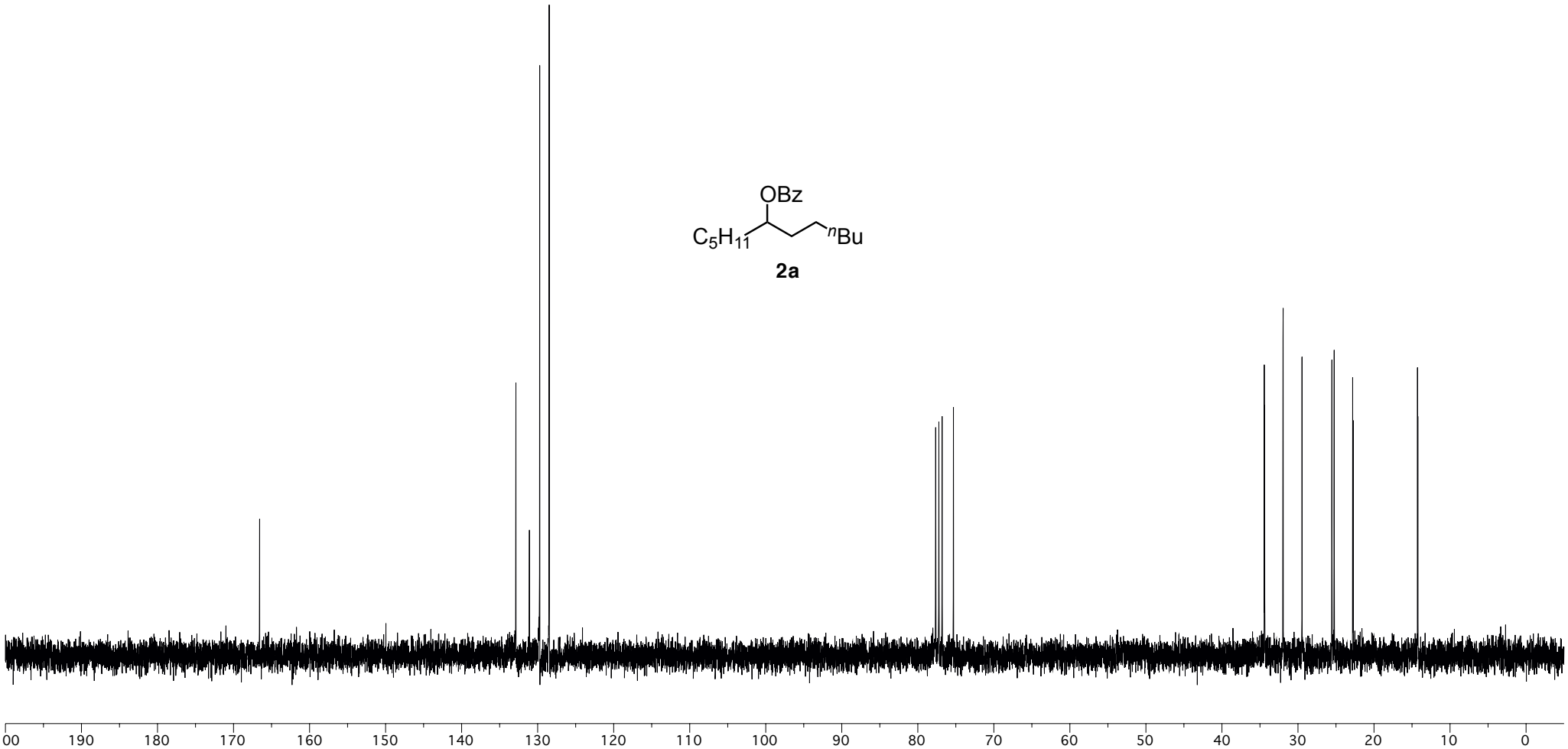
OBz
C5H11
nBu
2a
00
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180
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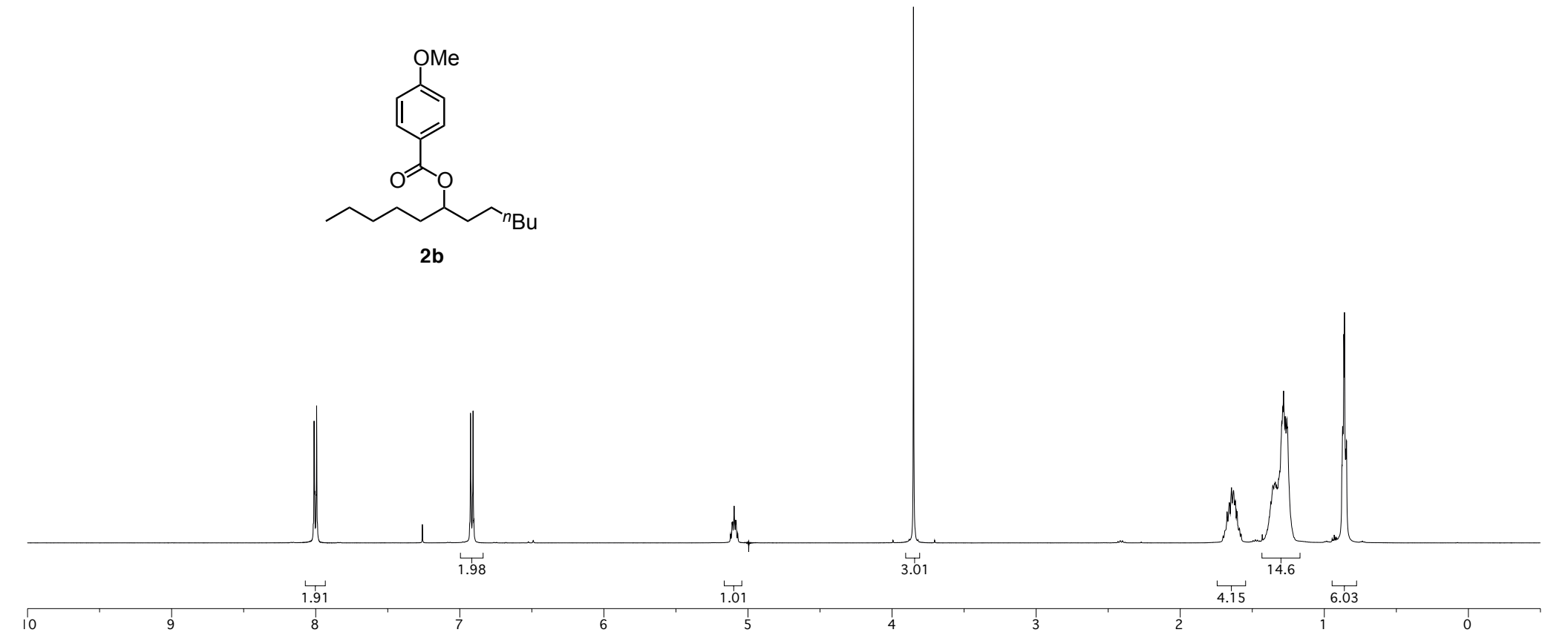
OMe
O
O
nBu
2b
1.91
1.98
1.01
3.01
4.15
14.6
6.03
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7
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3
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1
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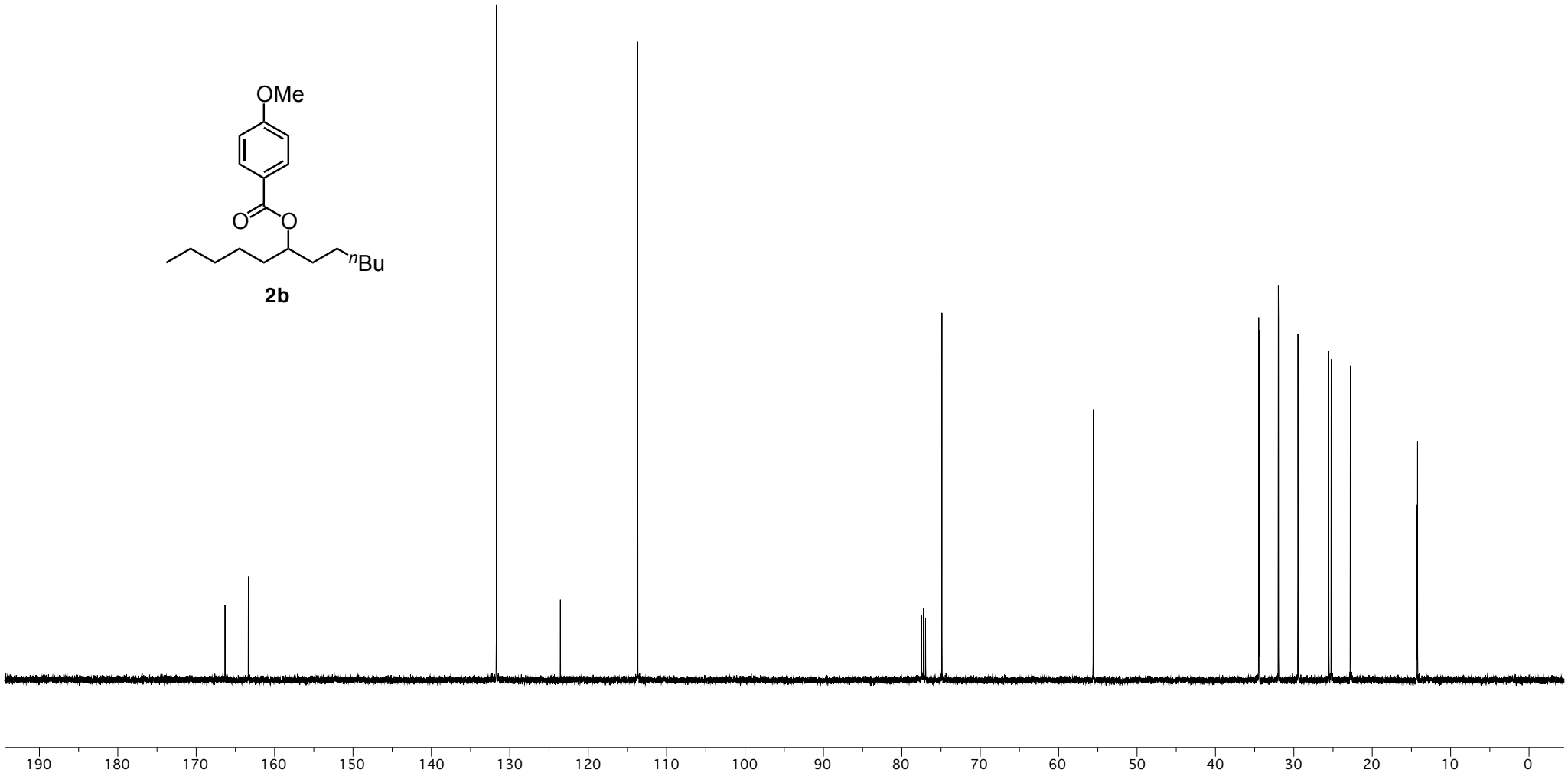
OMe
O
O
nBu
2b
190
180
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140
130
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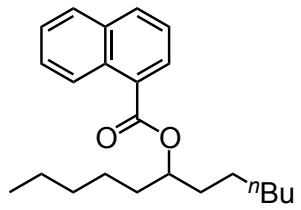
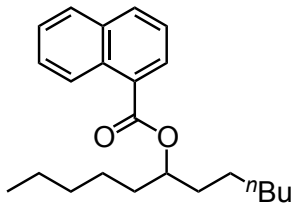
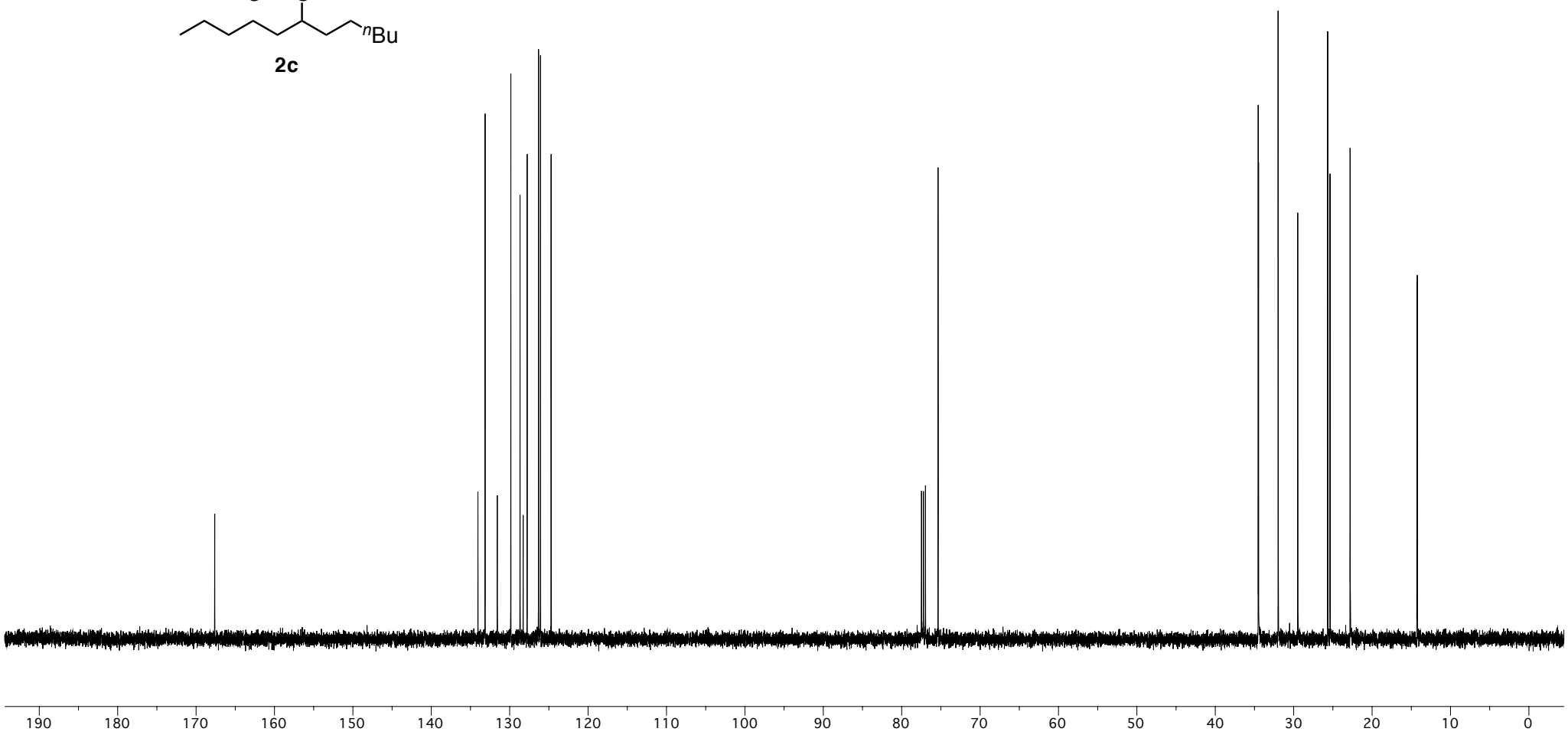


2c


O
O
nBu

2c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180
170
160
150
140
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120
110
100
90
80
70
60
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30
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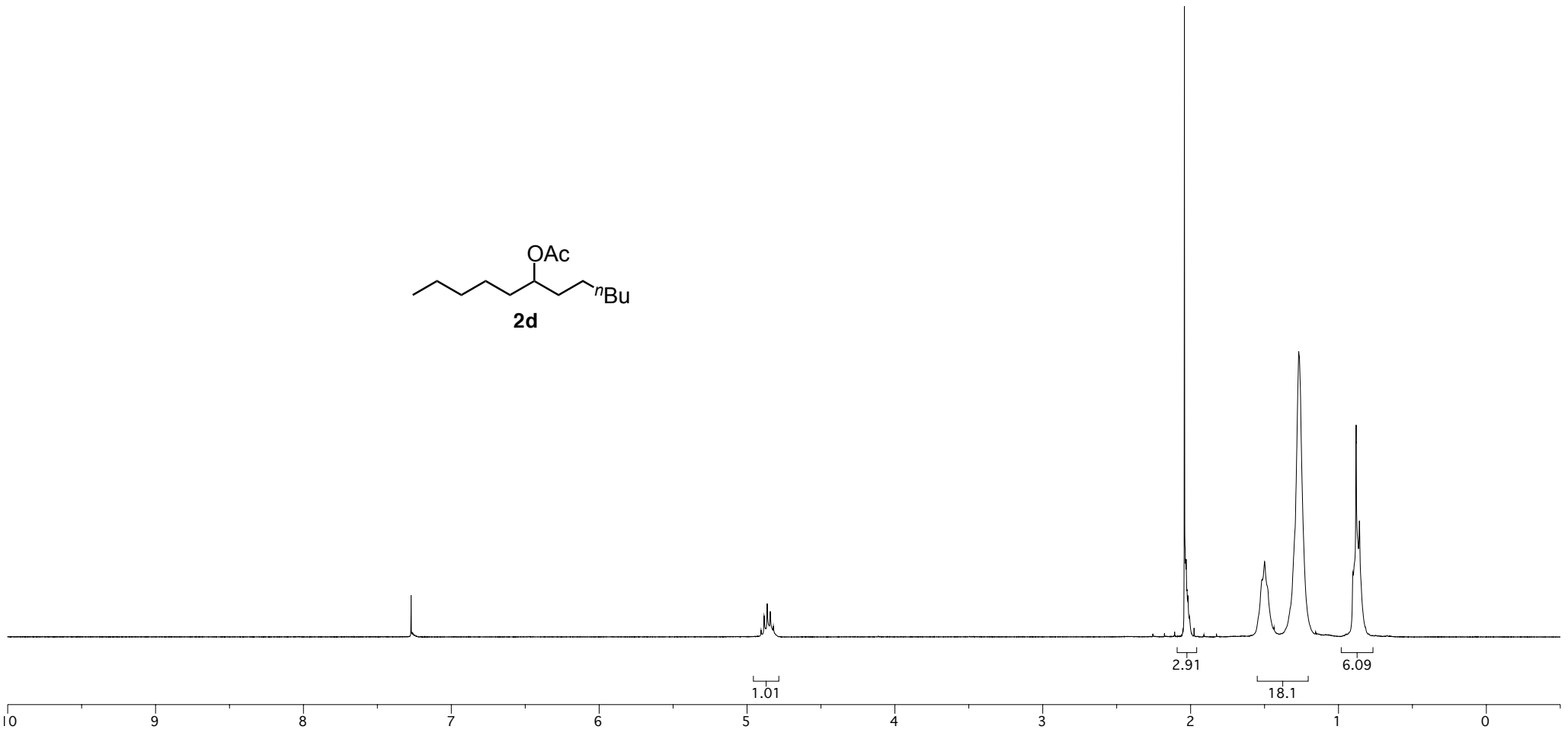
10
0


OAc
nBu
2d
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2.91
18.1
6.09
10
9
8
7
6
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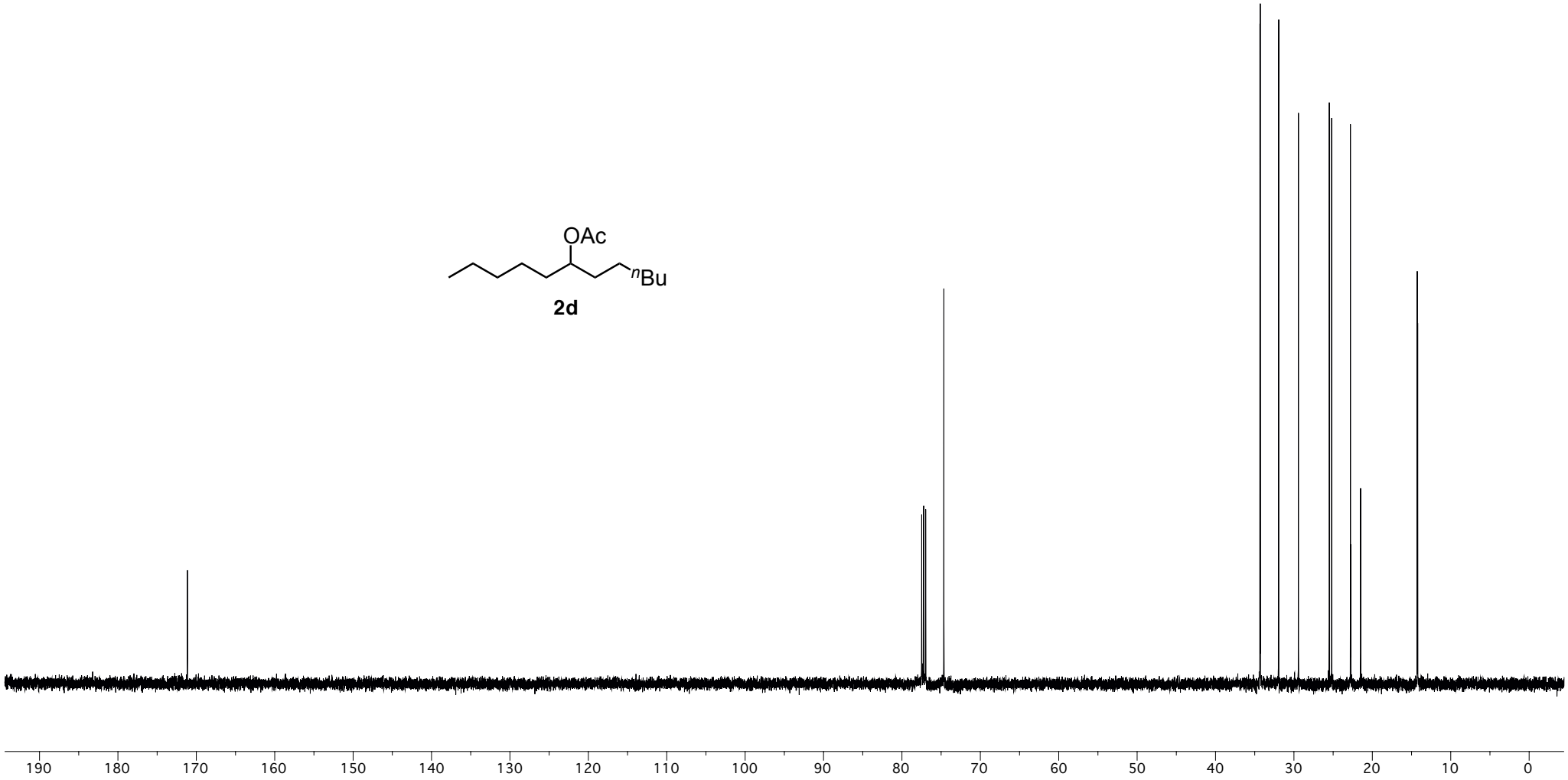
3
2
1
0


OAc
nBu
2d
190
180
170
160
150
140
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120
110
100
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70
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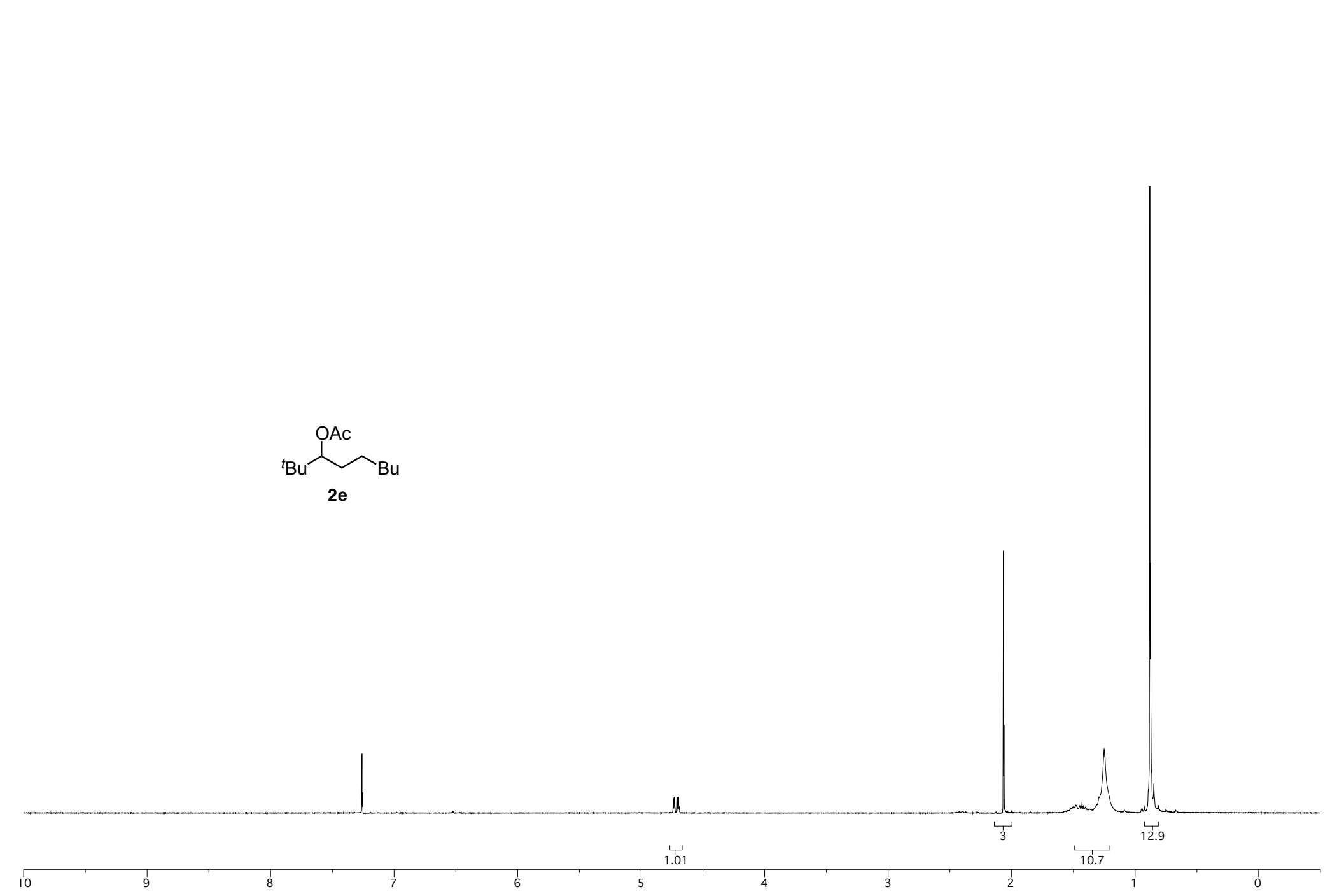
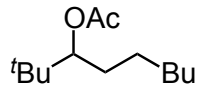
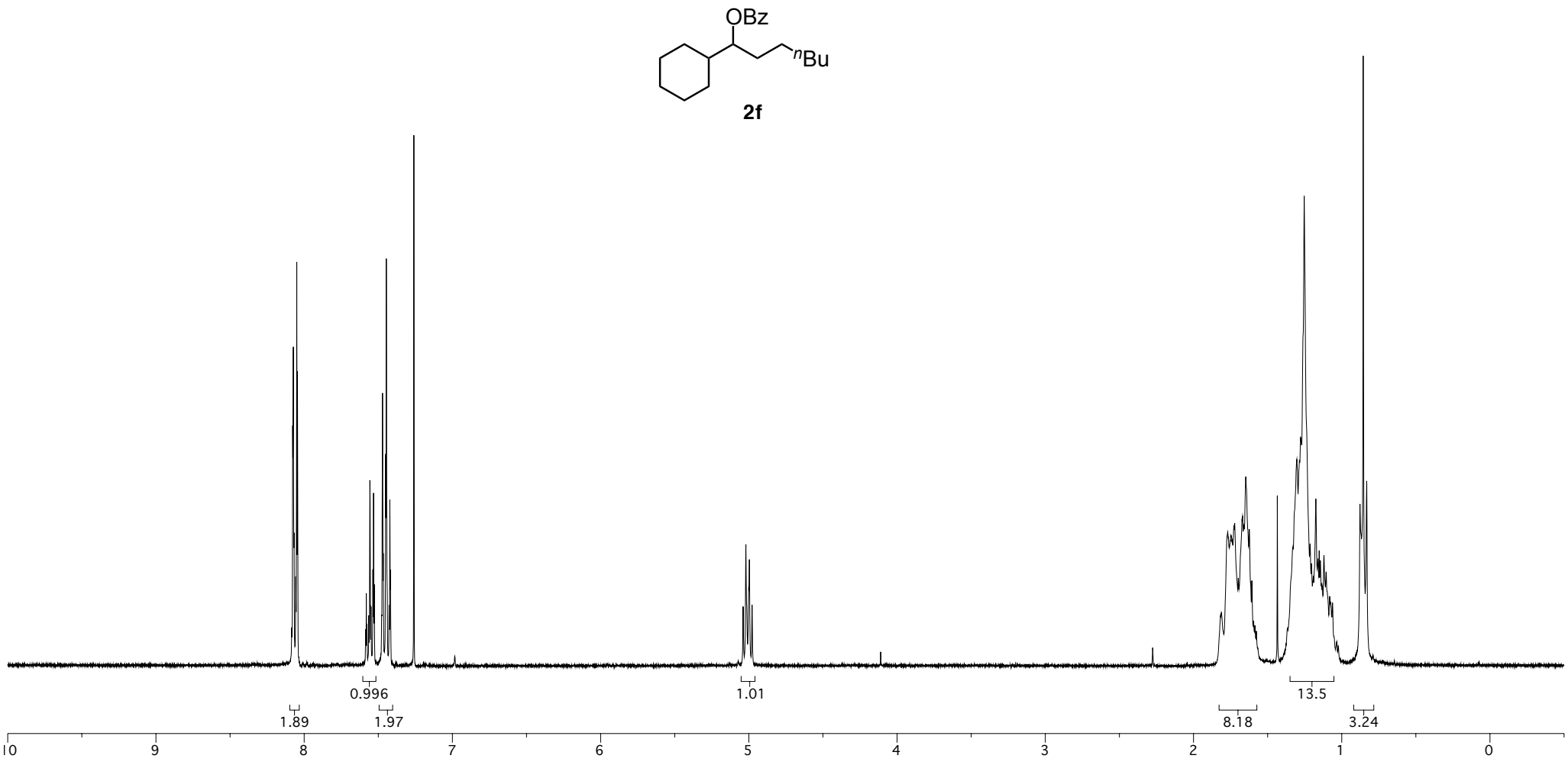
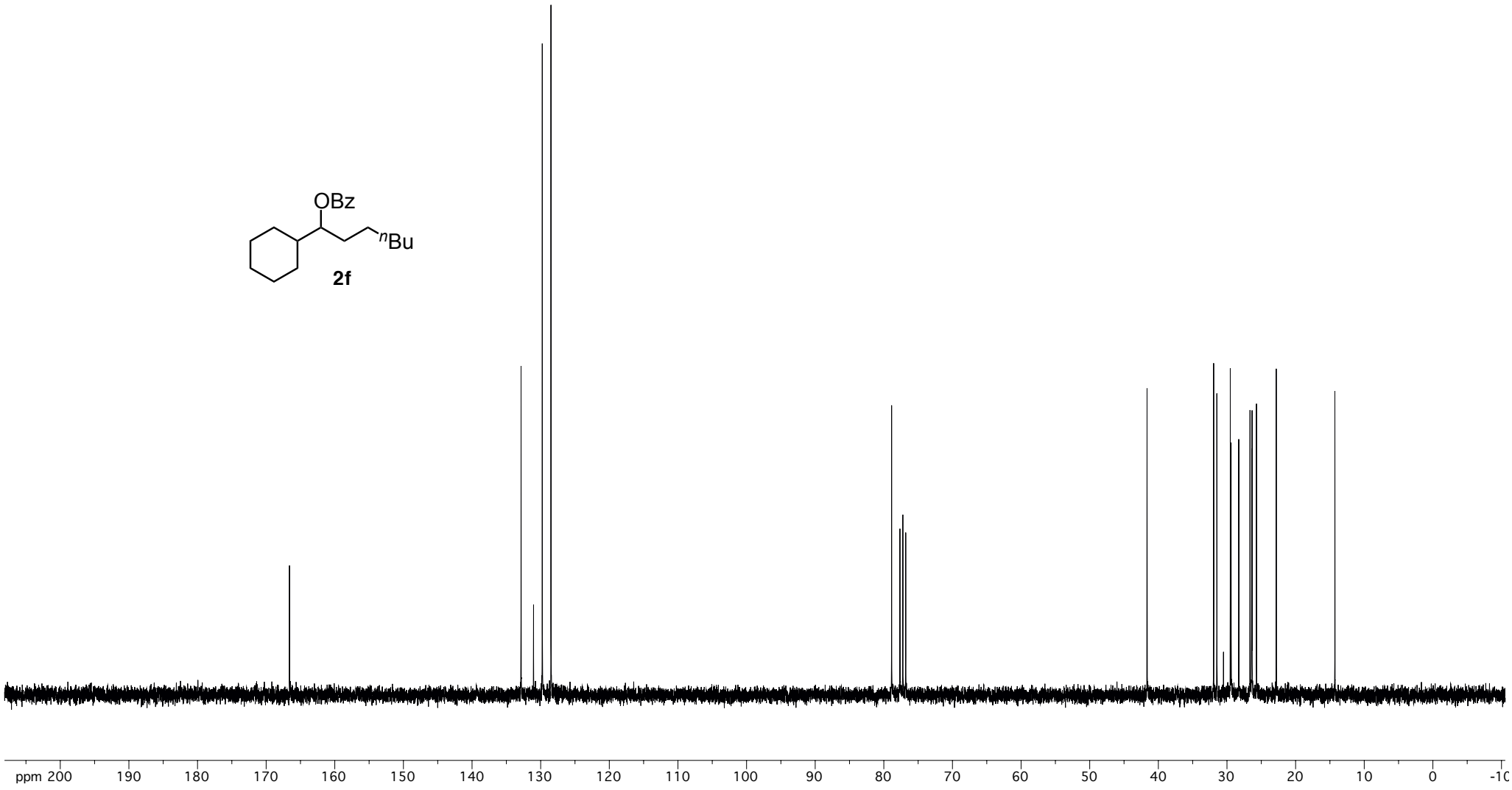
10
0

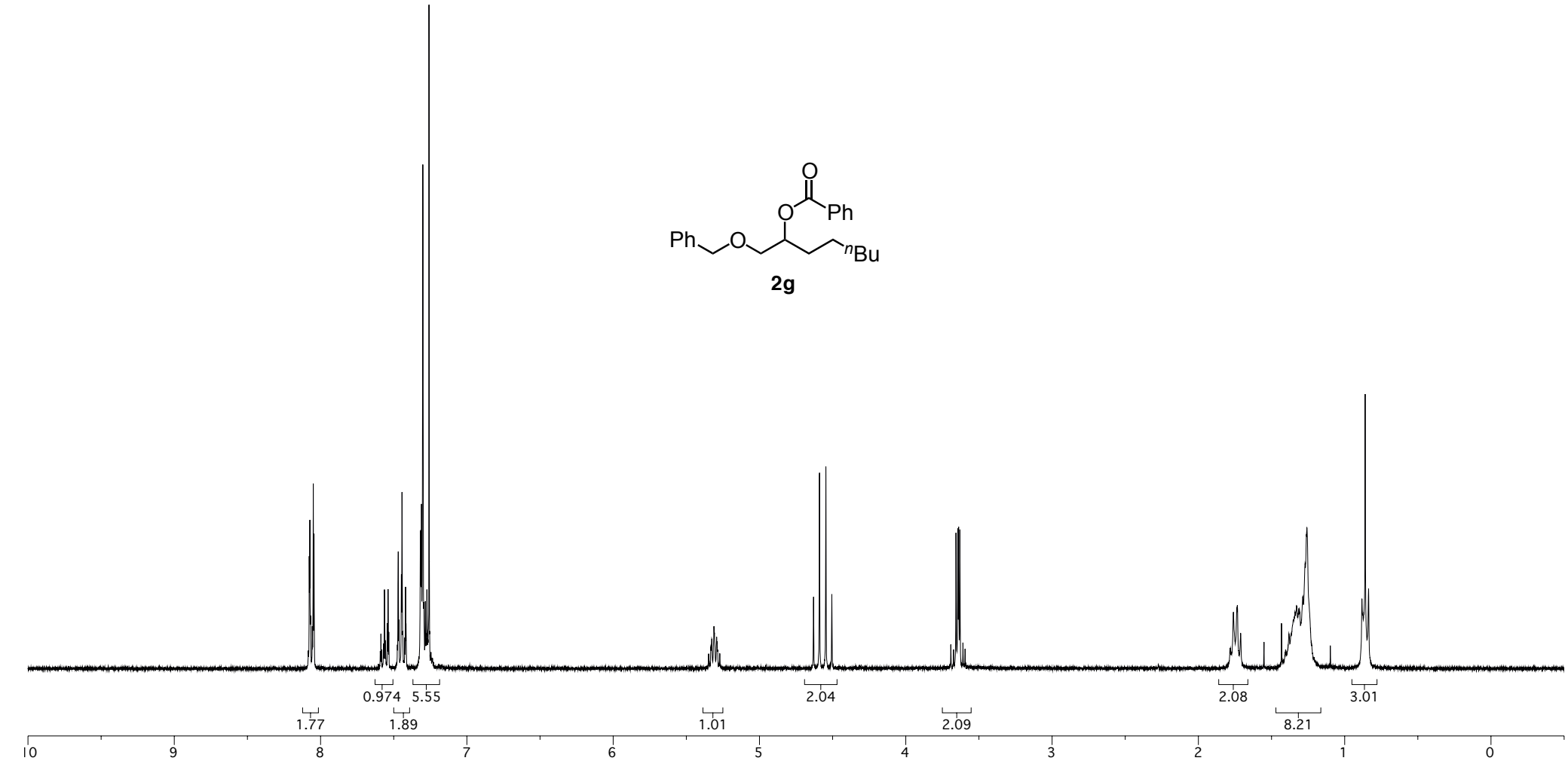

OAc
tBu
Bu
2e
1.01
3
10.7
12.9
10
9
8
7
6
5
4
3
2
1
0

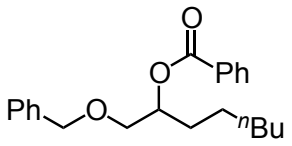


2e

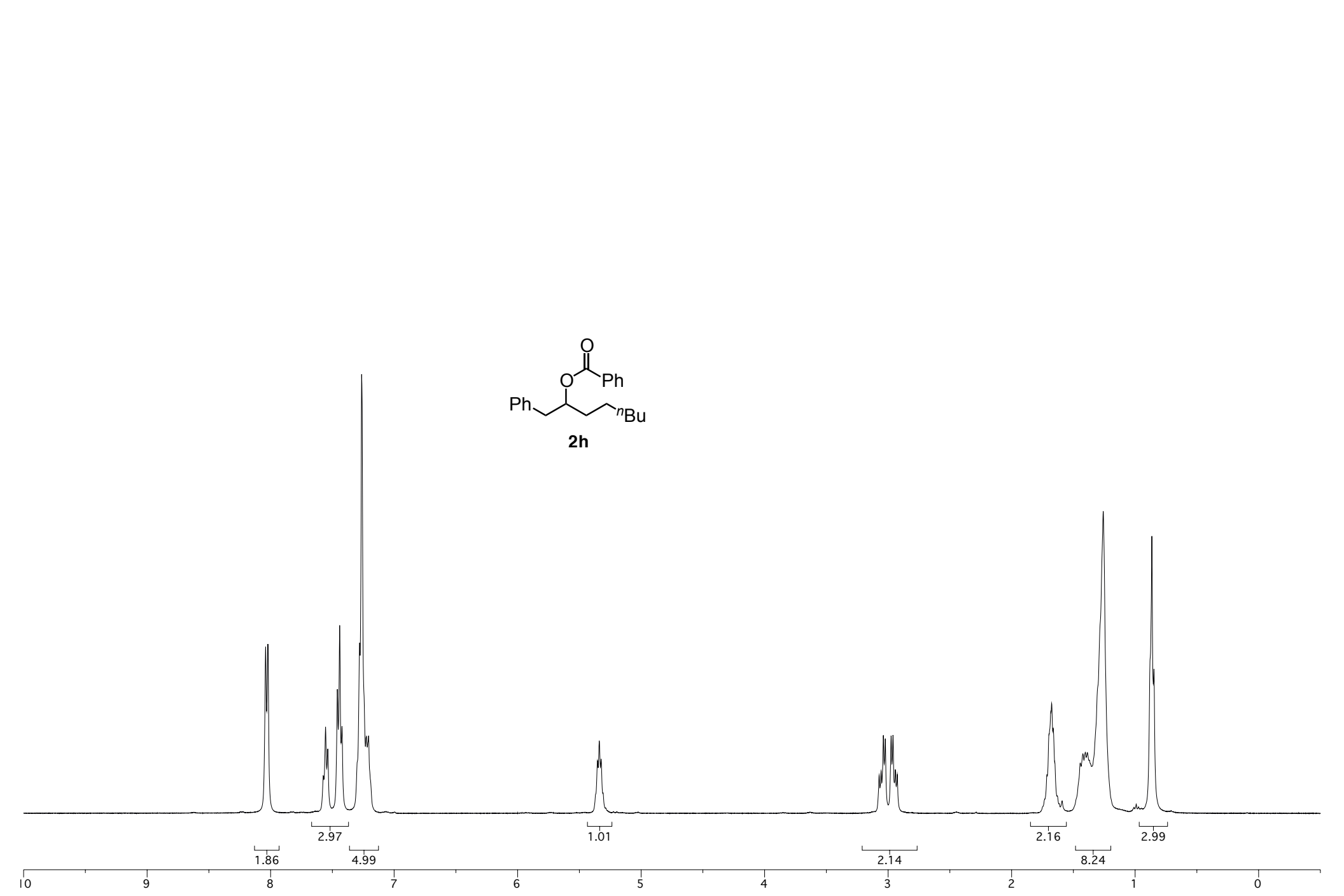

OBz
nBu
2f
1.89
0.996
1.97
1.01
8.18
13.5
3.24
10
9
8
7
6
5
4
3
2
1
0

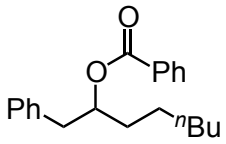

OBz
nBu
2f
ppm 200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
-10


O
O
Ph
Ph
O
nBu
2g
1.77
0.974
1.89
5.55
1.01
2.04
2.09
2.08
8.21
3.01
10
9
8
7
6
5
4
3
2
1
0

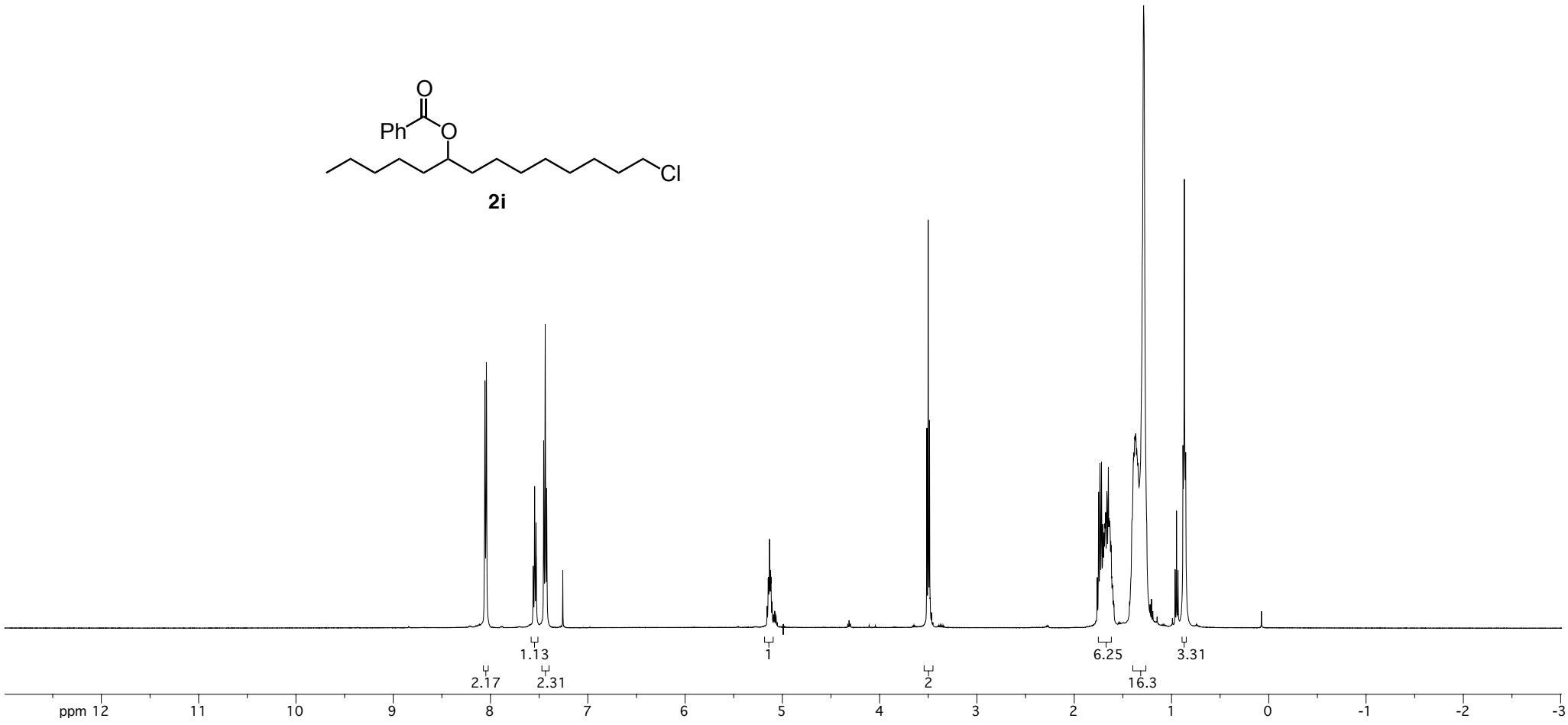


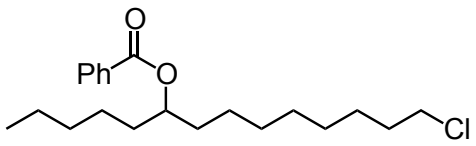
2g


O
O
Ph
Ph
nBu
2h
1.86
2.97
4.99
1.01
2.14
2.16
8.24
2.99
10
9
8
7
6
5
4
3
2
1
0

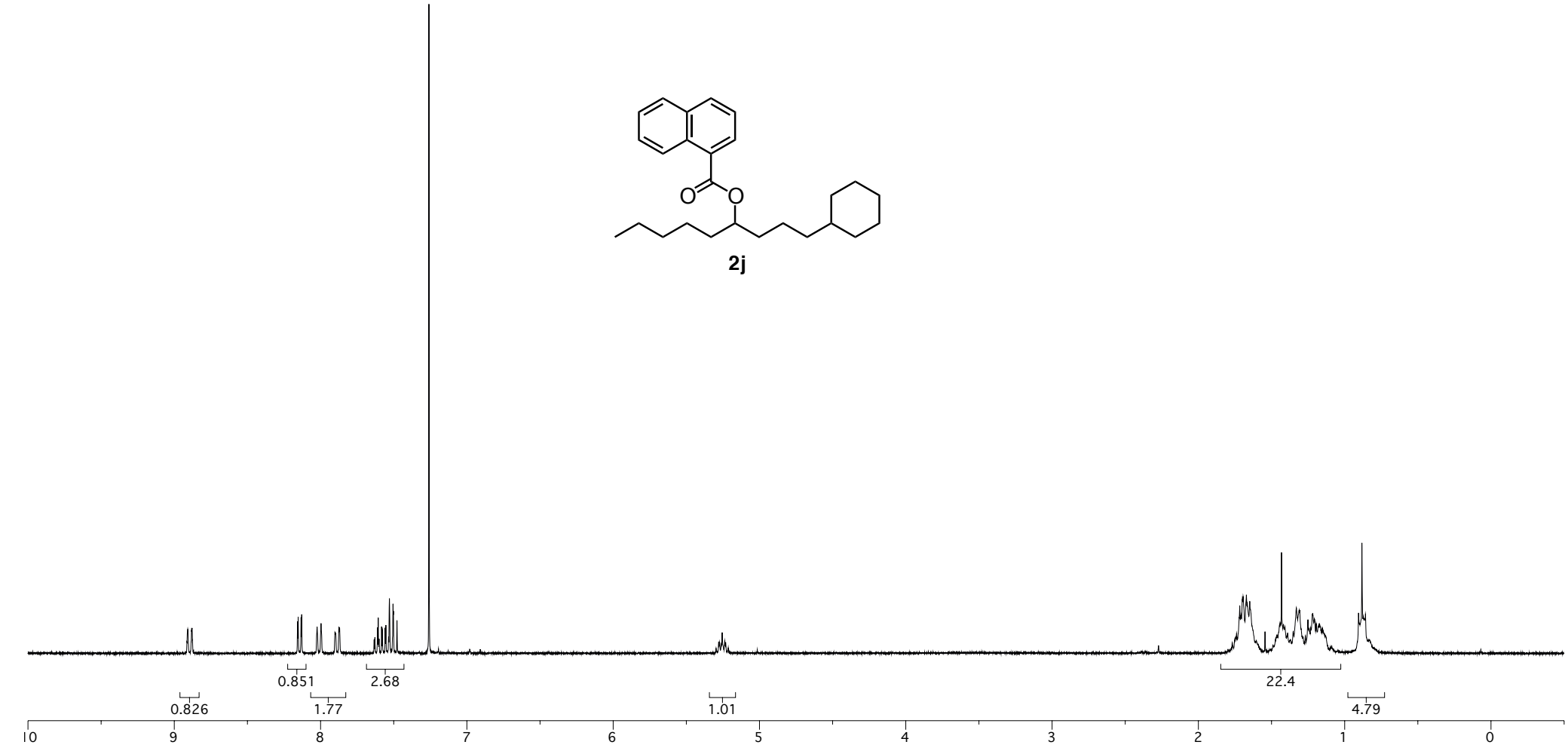


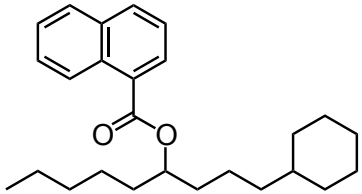
2h


O
Ph
O
Cl
2i
2.17
1.13
2.31
1
2
6.25
16.3
3.31
ppm 12
11
10
9
8
7
6
5
4
3
2
1
0
-1
-2
-3

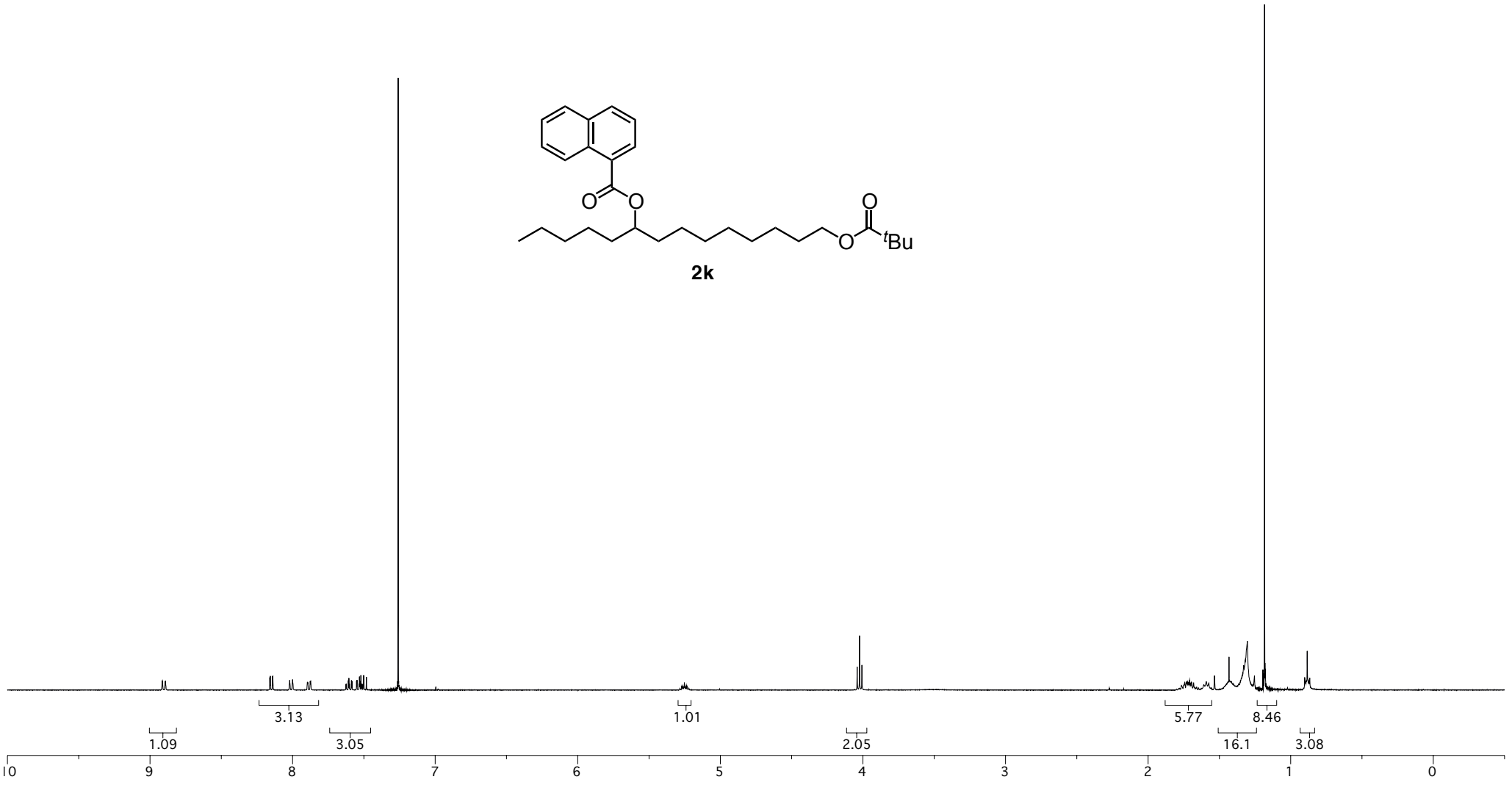


2i

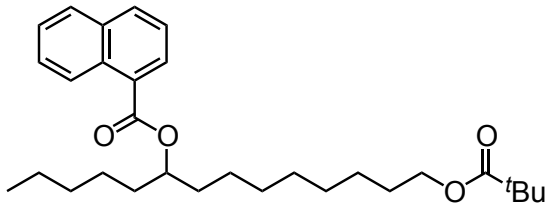

2j
0.826
0.851
1.77
2.68
1.01
22.4
4.79
10
9
8
7
6
5
4
3
2
1
0



2j

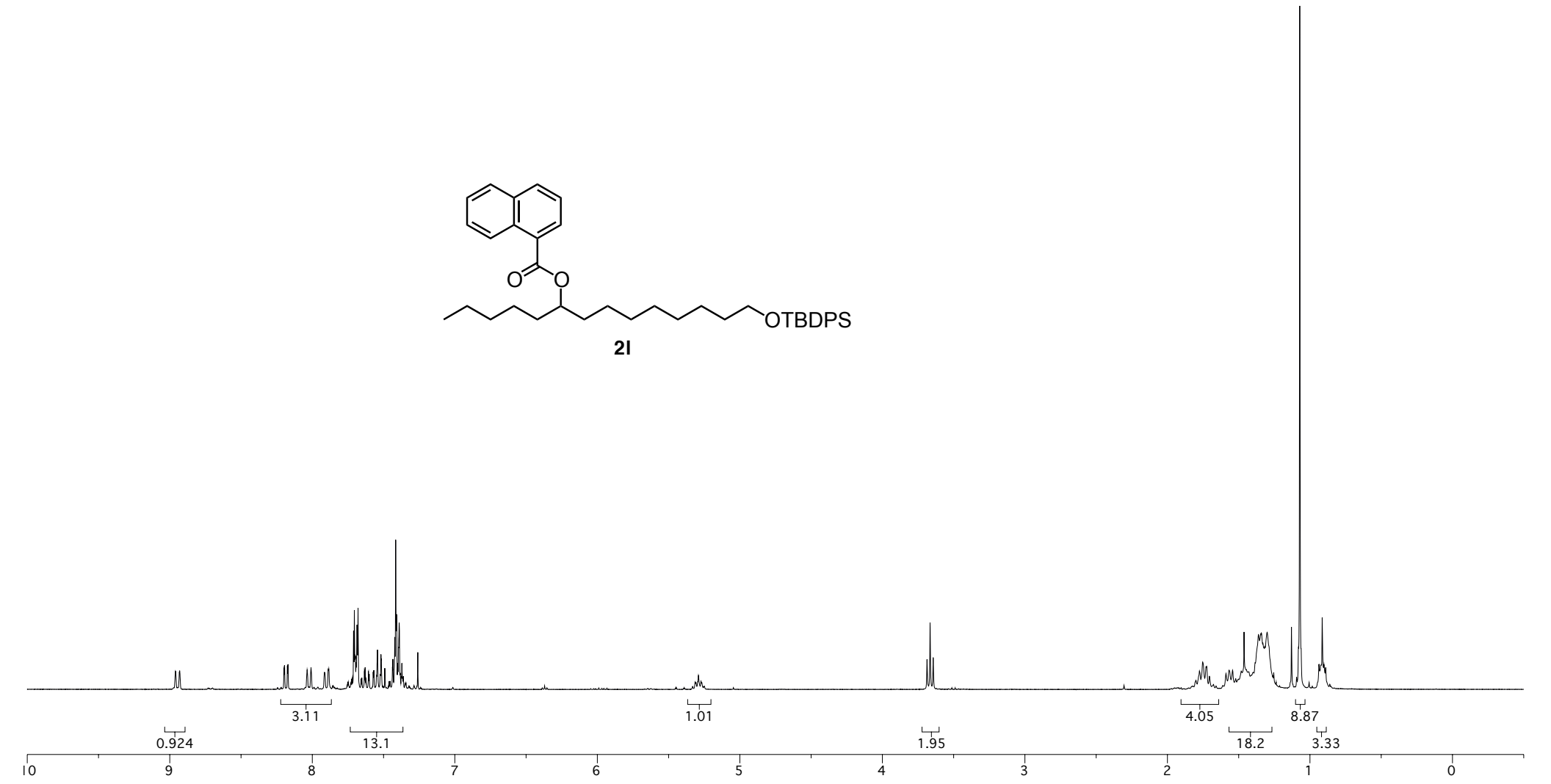


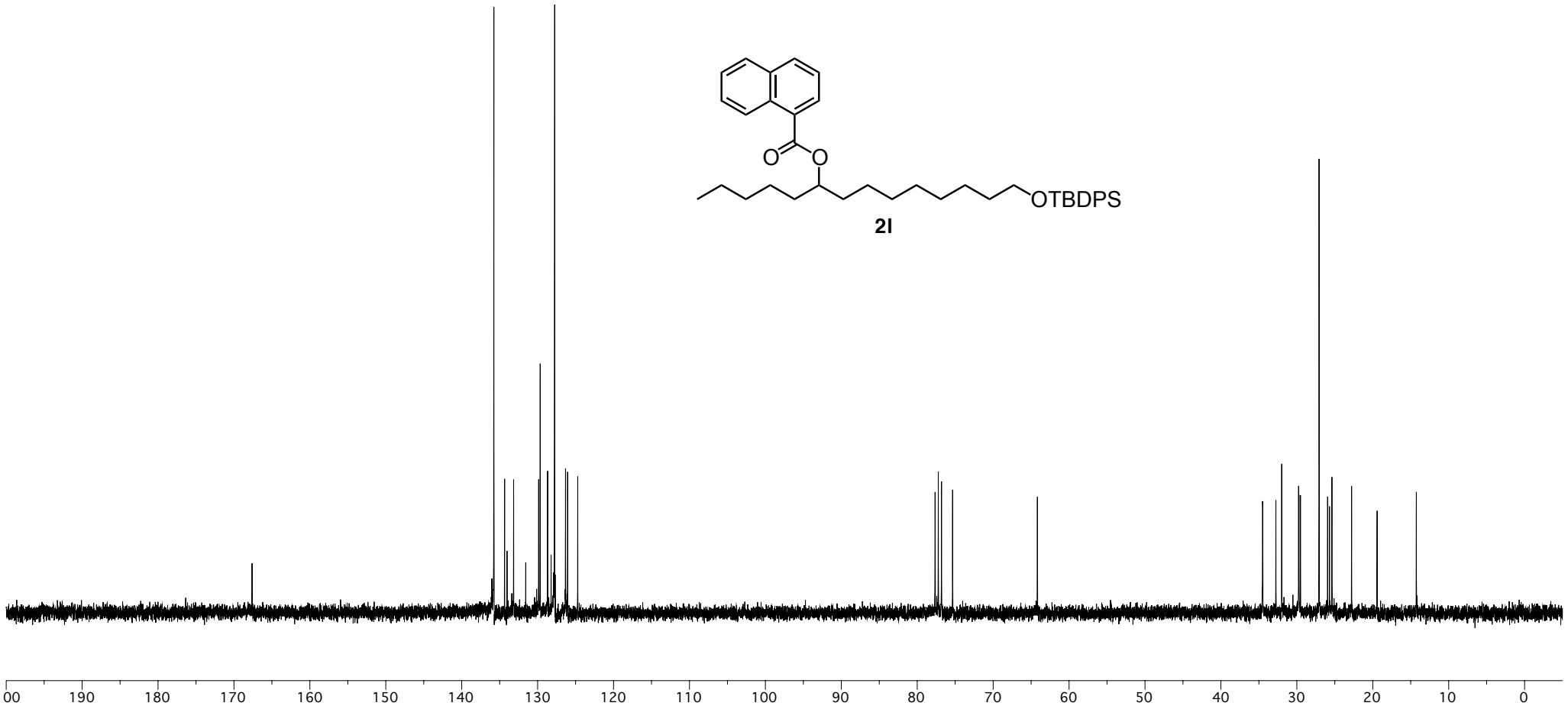
2k


O
O
O
O
tBu

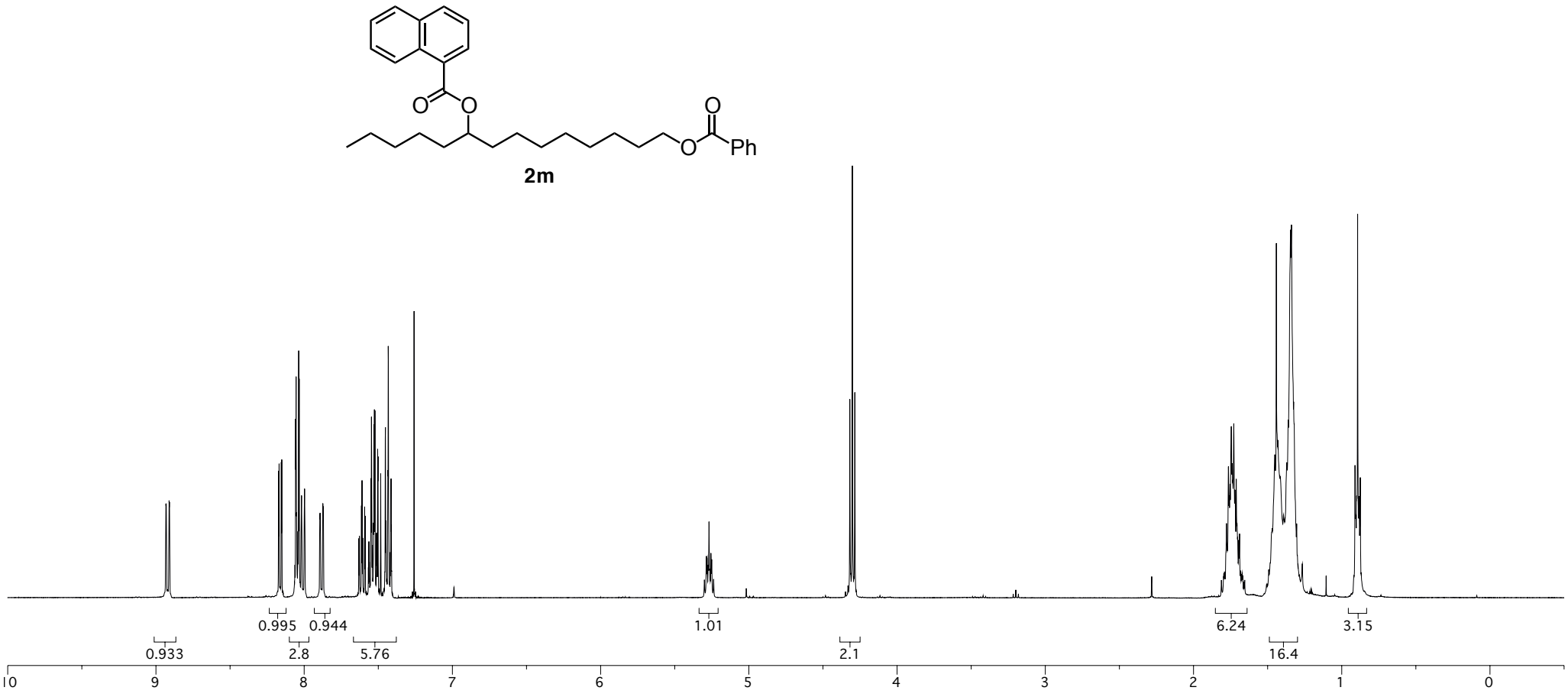
2k

00
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0

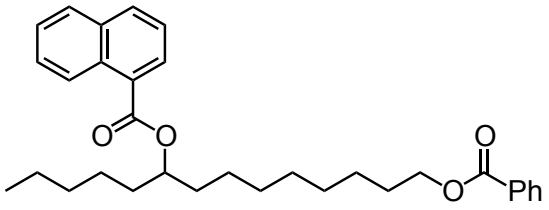

OTBDPS
2l
3.11
13.1
1.01
1.95
4.05
18.2
8.87
3.33
0.924
10
9
8
7
6
5
4
3
2
1
0



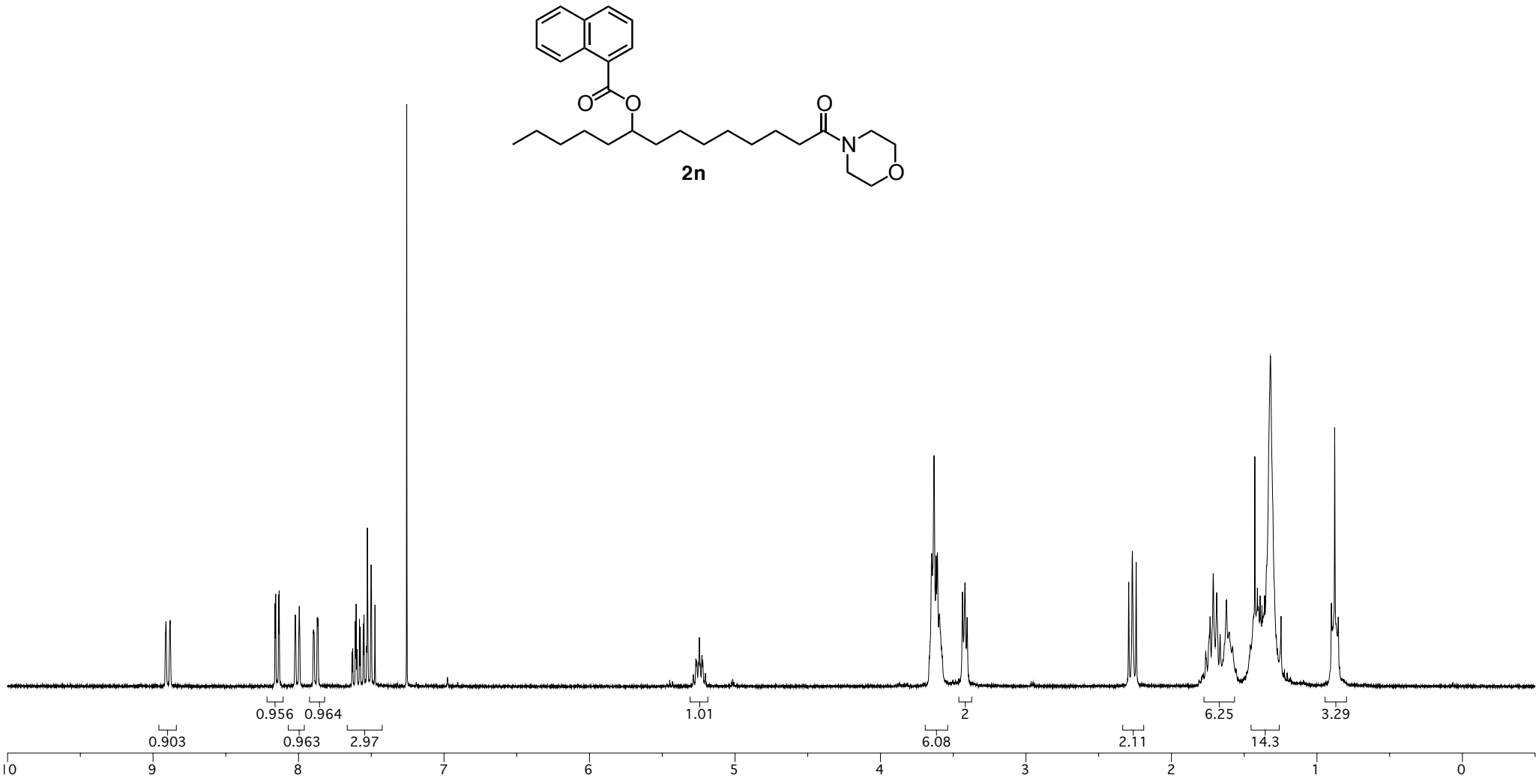
2l

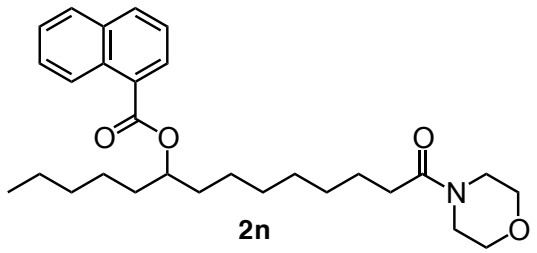


2m



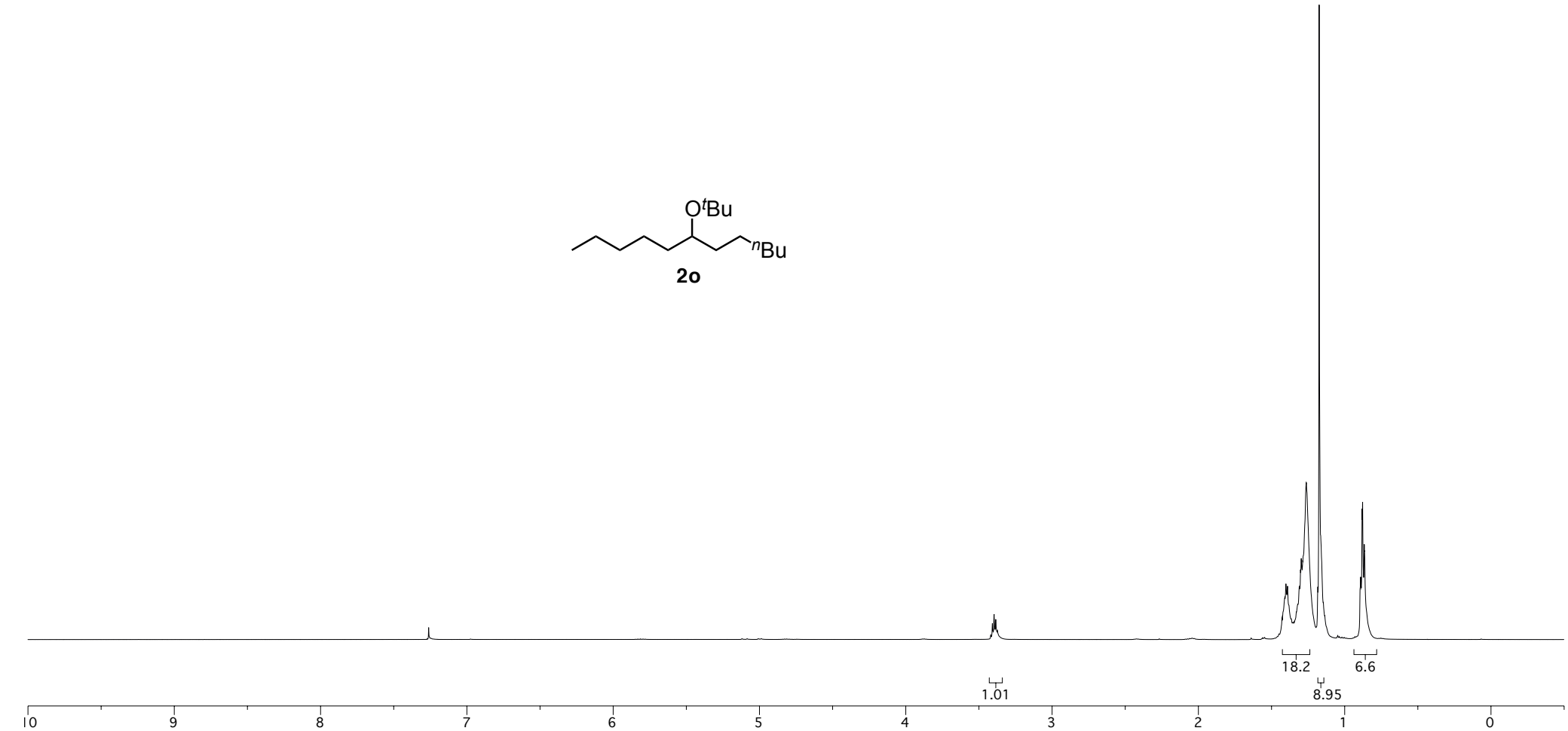
2m


O
O
O
N
O
2n
0.903
0.956
0.963
0.964
2.97
1.01
6.08
2
2.11
6.25
14.3
3.29
10
9
8
7
6
5
4
3
2
1
0

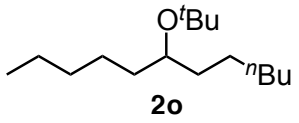

O
O
O
N
O

2n

00
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0

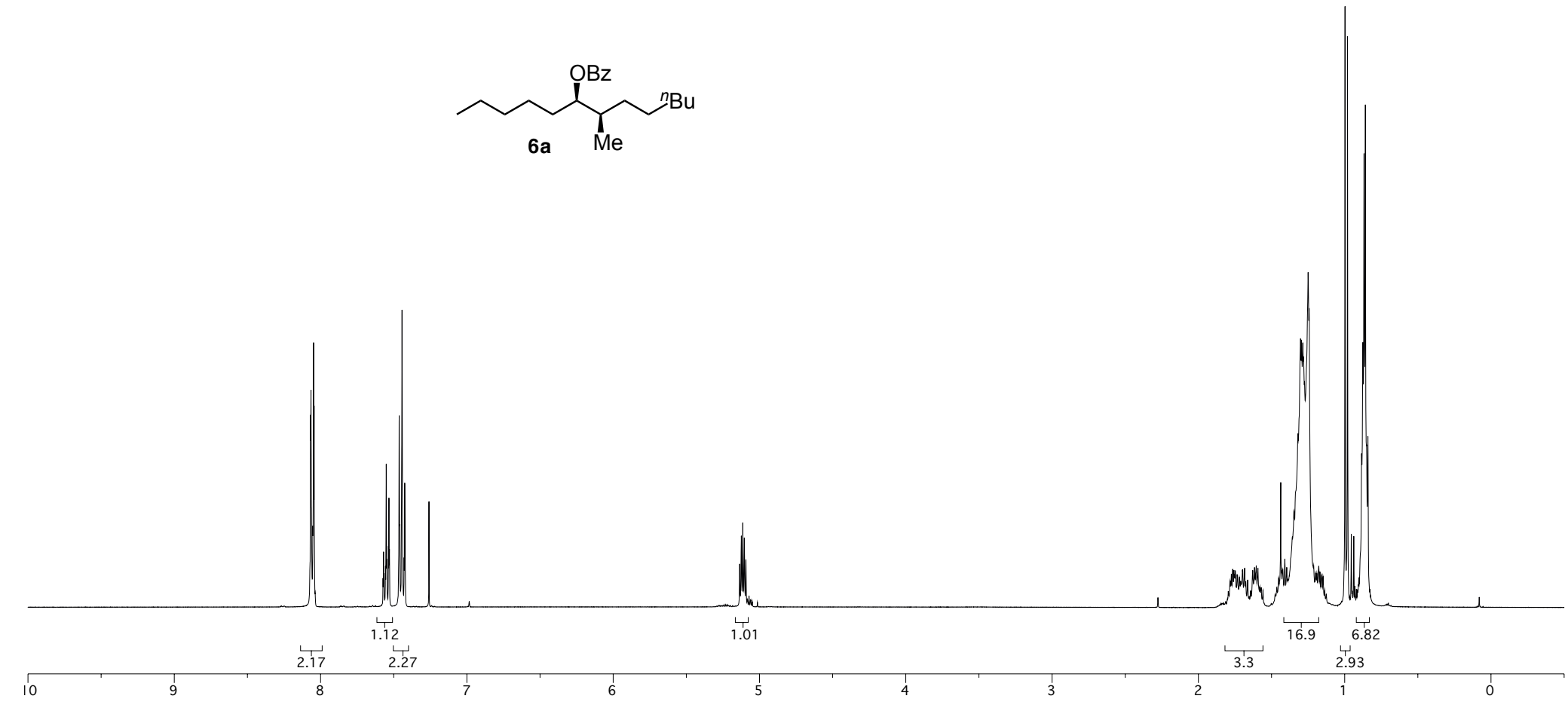


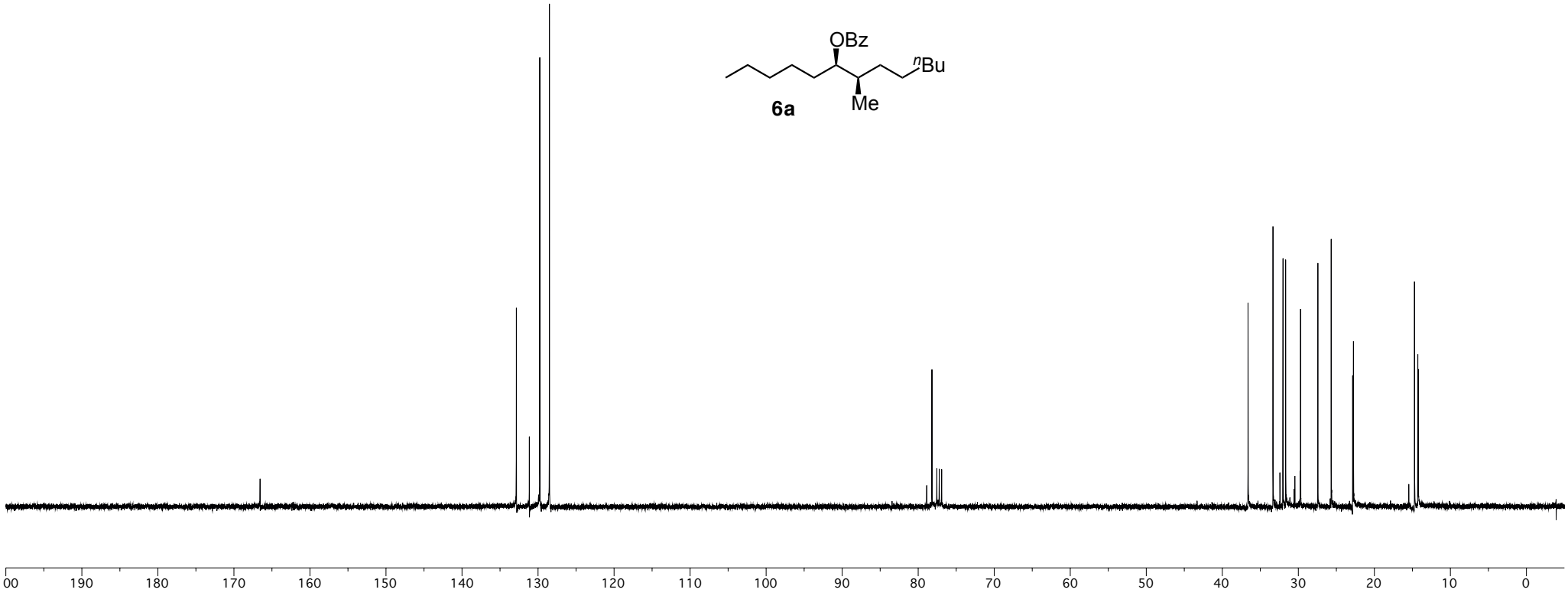
2o

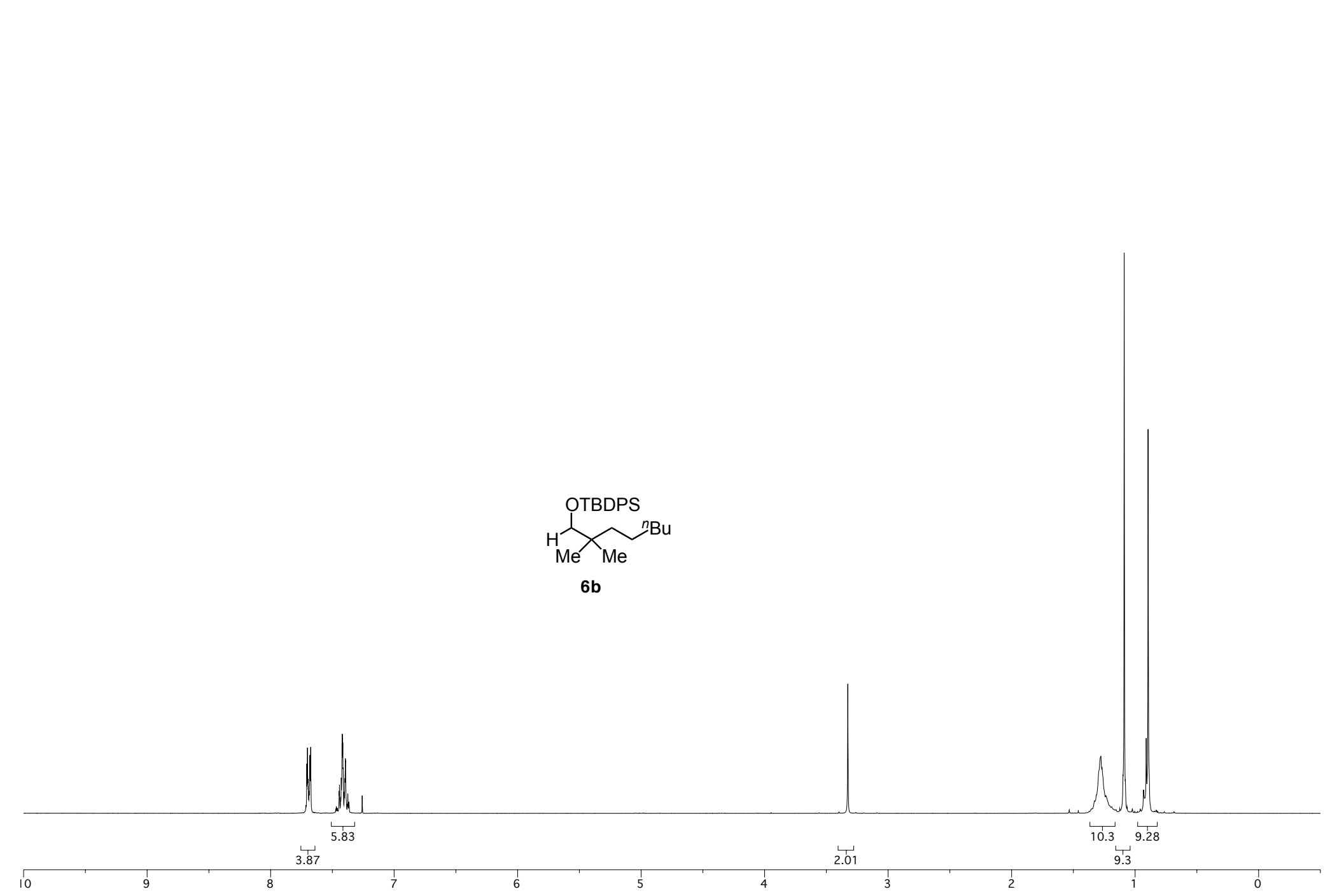

O^{t}Bu
^{n}Bu

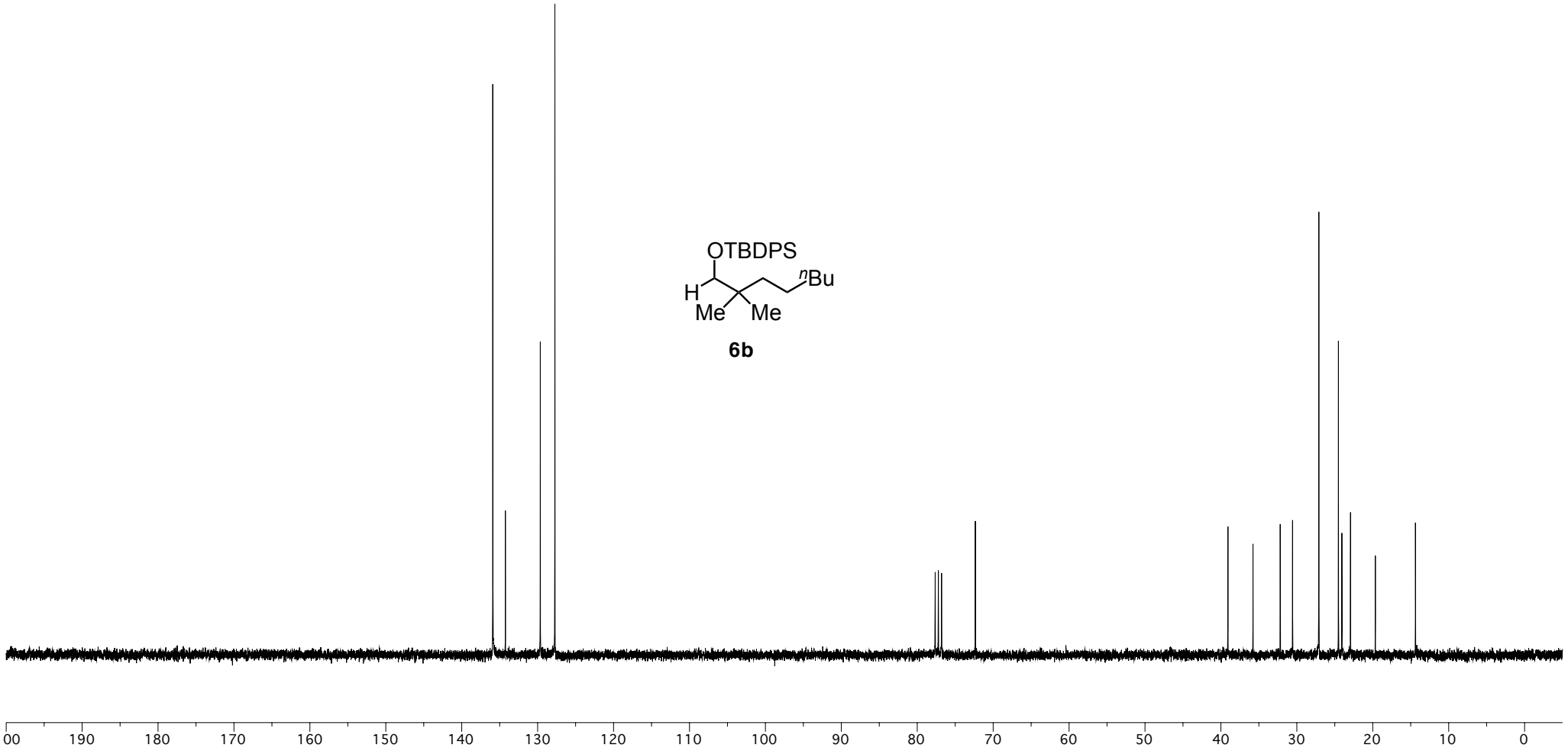
2o

190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0


OBz
nBu
Me
6a
2.17
1.12
2.27
1.01
3.3
16.9
2.93
6.82
10
9
8
7
6
5
4
3
2
1
0

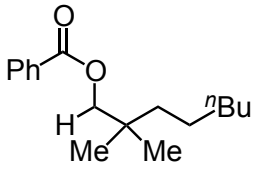

OBz
nBu
Me
6a
00
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0


OTBDPS
H
Me
Me
nBu
6b
3.87
5.83
2.01
10.3
9.3
9.28
10
9
8
7
6
5
4
3
2
1
0


OTBDPS
H
nBu
Me
Me

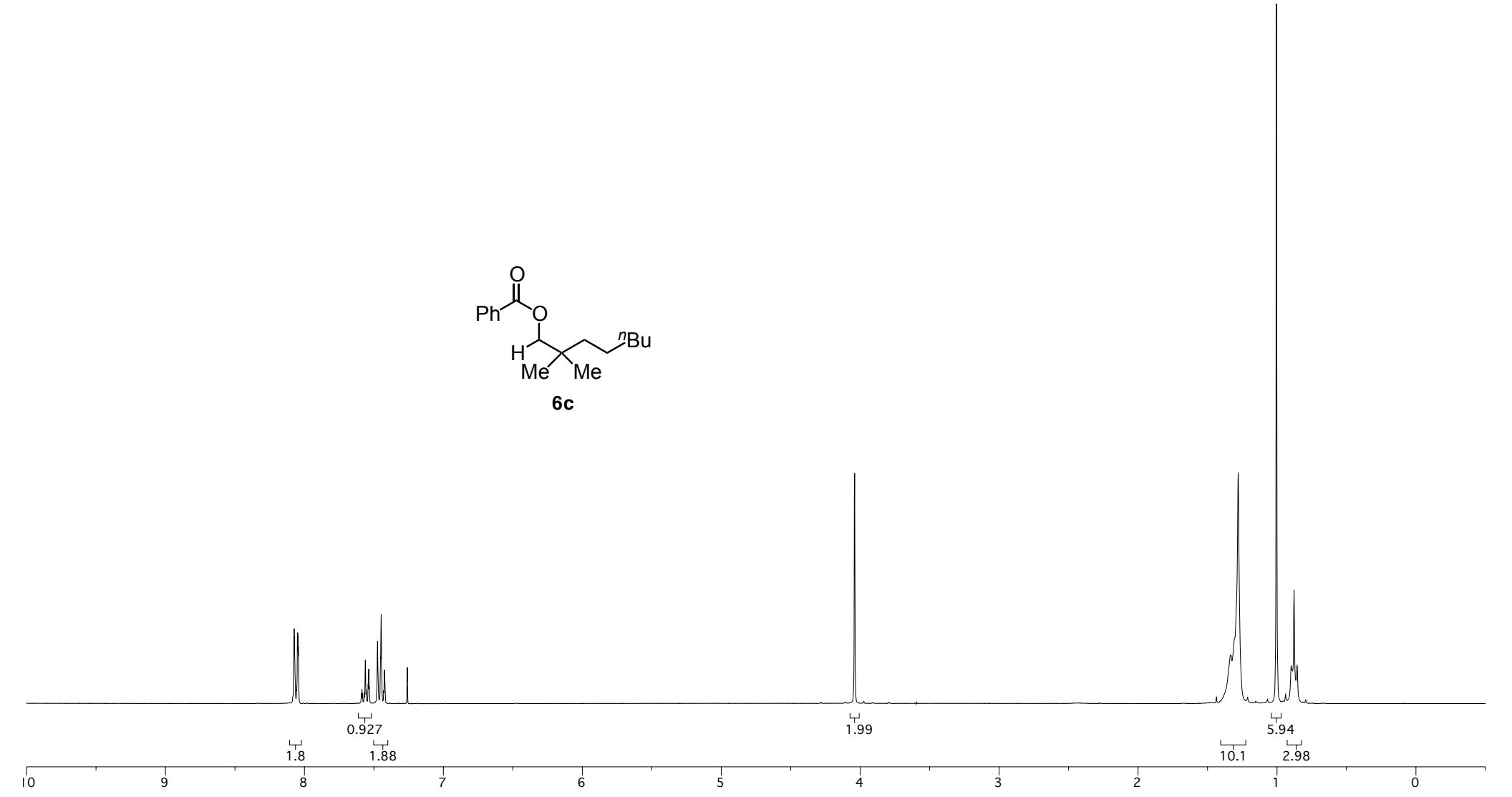
6b

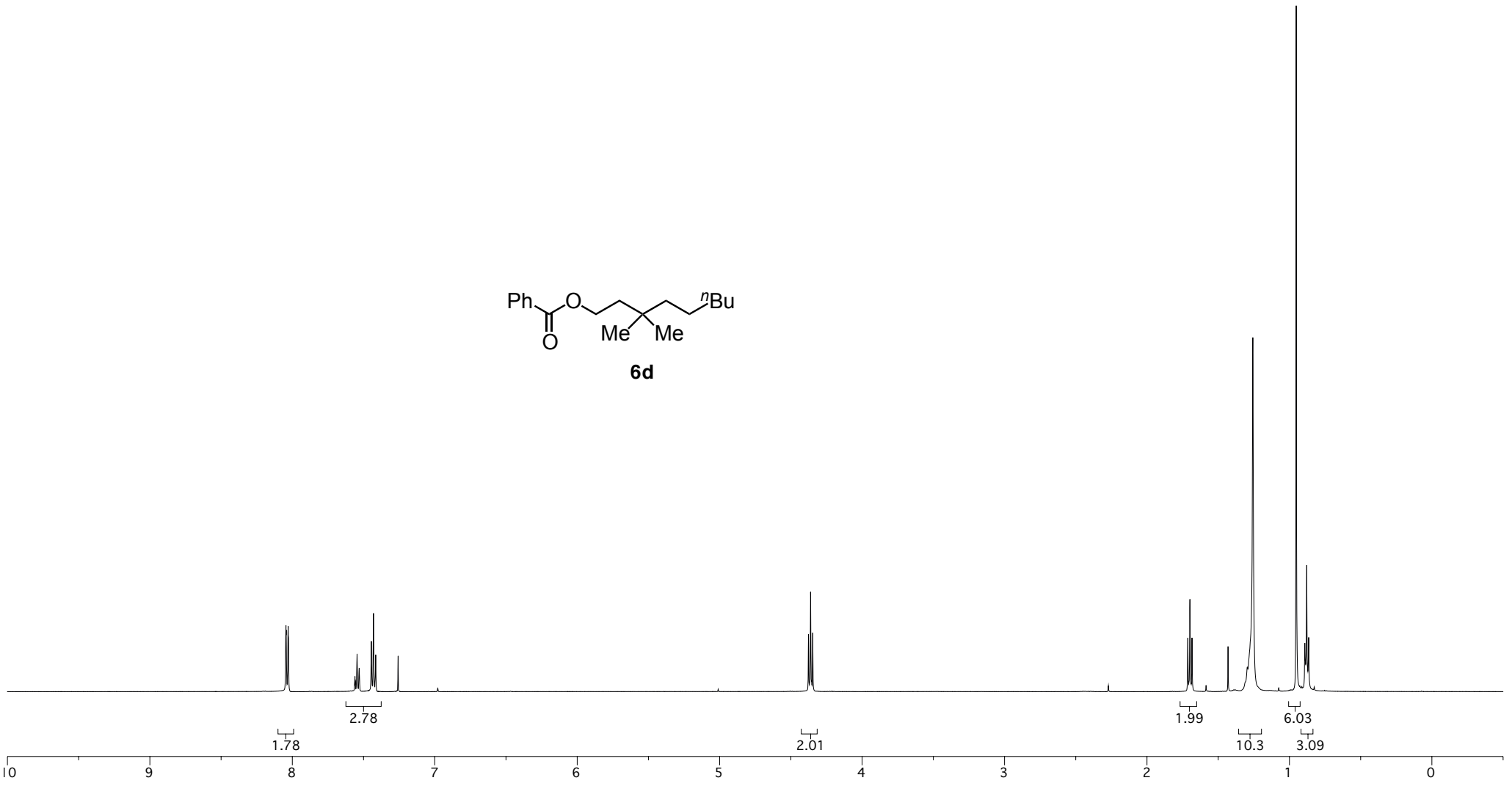
00
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0

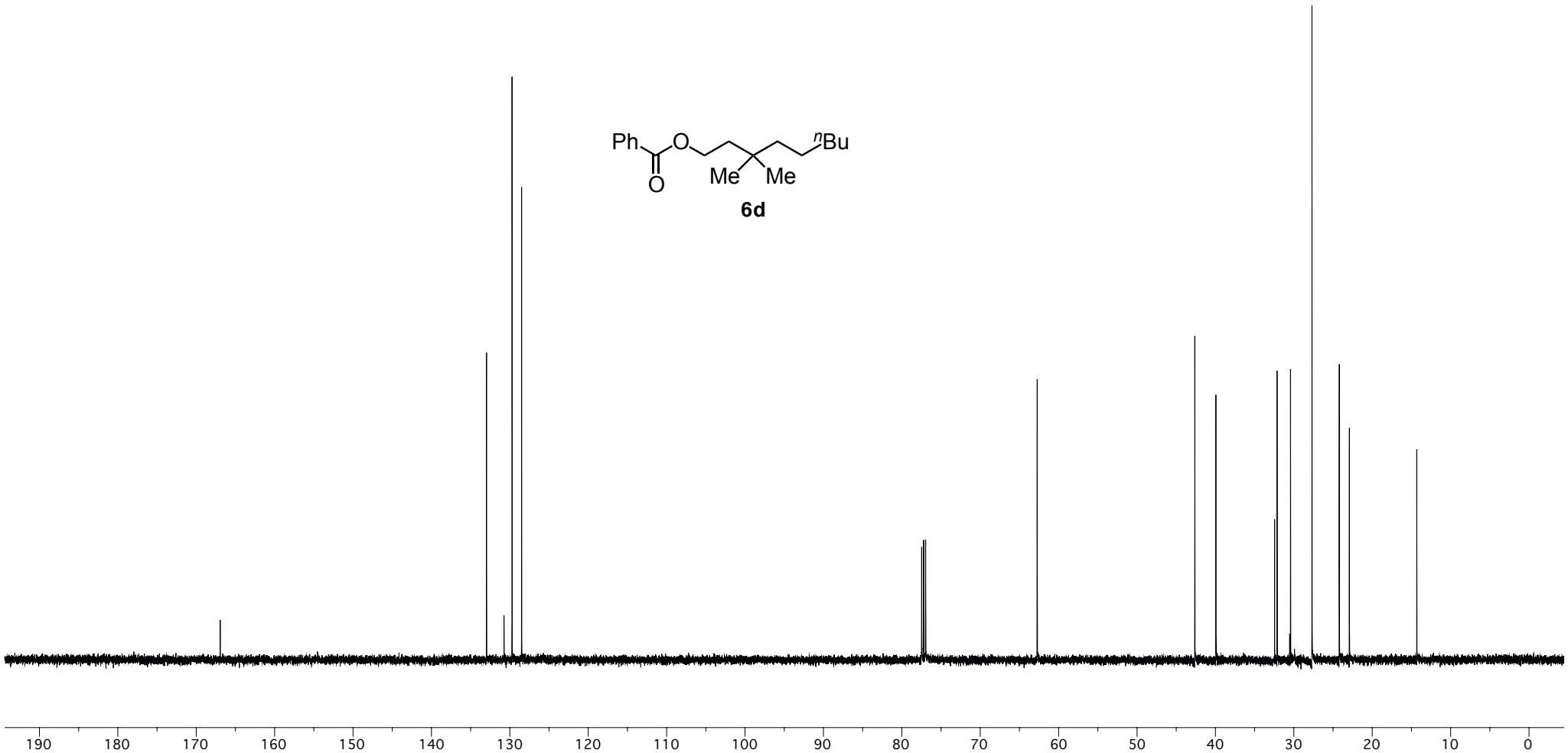

O
Ph
O
H
Me
Me
nBu

6c

ppm 200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
-10


O
Ph
O
H
Me
Me
nBu
6c
1.8
0.927
1.88
1.99
10.1
5.94
2.98
10
9
8
7
6
5
4
3
2
1
0


Ph
O
O
Me
Me
nBu
6d
1.78
2.78
2.01
1.99
10.3
6.03
3.09
10
9
8
7
6
5
4
3
2
1
0



6d