Supporting Information For: Pd^{II}-Catalyzed Oxidative 1,1-Diarylation of Terminal Olefins

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General Considerations:

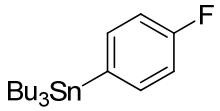
Dry dimethylacetamide (DMA) was purchased from Aldrich and stored over activated 3 Å molecular sieves (3 Å MS), Tetrahydrofuran (THF) and dichloromethane were dried before use by passing through a column of activated alumina. 3 Å MS used in diarylation reactions were powdered and activated by heating with a Bunsen burner while under vacuum. Terminal olefins were purchased from Aldrich or Acros, or synthesized according to the procedures referenced. Mg was purchased from Acros. Bu_3SnPh and Bu_3SnCl were purchased from Gelest Inc. Palladium(II) chloride was purchased from Pressure Chemicals. (*S*)-1-octene-3-ol was purchased from Fluka. $[Pd(allyl)Cl]_2$, $[Pd(I^iPr)Cl_2]_2$[1] and $Pd(I^iPr)(OTs)_2$[2] were synthesized according to literature procedures. ^{1}H-NMR spectra were obtained at 300 MHz, chemical shifts are reported in ppm, and referenced to the $CHCl_3$ singlet at 7.26 ppm or to the center peak of the CD_2Cl_2 triplet at 5.32 ppm. ^{13}C-NMR spectra were obtained at 75 MHz and referenced to the center line of the $CDCl_3$ triplet at 77.23 ppm, or the center line of the CD_2Cl_2 quintet at 54.00 ppm. The abbreviations s, d, t, dd, dt, m stand for the resonance multiplicities singlet, doublet, triplet, doublet 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. Flash chromatography was performed using EM reagent silica 60 (230-400 mesh). IR spectra were recorded using a Thermo Nicolet FT-IR. HRMS data were obtained on a Waters LCP Premier XE instrument by ESI/TOF. Chiral GC (gas chromatography) analysis was performed using a Hewlett Packard HP 6890 Series CG system fitted with a HP-Chiral permethylated β-cyclodextrin column. SFC (supercritical fluid chromatography) analysis was performed at 40 ºC, using a Thar instrument fitted with an AD-H column.

Synthesis of Terminal Olefin Substrates:

tert-Butyldimethyl((1-phenylbut-3-en-1-yl)oxy)silane (**1b**)[3], oct-1-en-3-yl acetate (**1c**)[4], and 11-choroundec-1-ene (**1e**)[5] were prepared following literature procedures and purity confirmed via ^{1}H NMR. (*S*)-1-Octene-3-ol was converted to **1c** using the same procedure as that used to synthesize racemic **1c**. The enantiomeric excess of **1c** was determined by chiral GC (see below).

Synthesis of Organostannane Reagents:

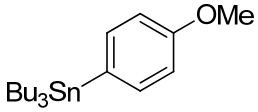
Tributyl(4-fluorophenyl)stannane (2a).



2a

Stannane **2a** was synthesized according to a previously reported procedure and purity confirmed *via* ^{1}H NMR.[6]

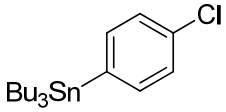
Tributyl(4-(methoxyphenyl)stannane (2b).



2b

Stannane **2b** was synthesized according to a previously reported procedure and purity confirmed *via* ^{1}H NMR.[7]

Tributyl(4-chlorophenyl)stannane (2e).

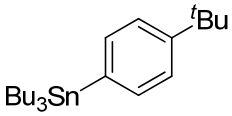


2e

Stannane **2e** was synthesized according to a previously reported procedure and purity confirmed *via* ^{1}H NMR.[8]

General Procedure for the Synthesis of Organnostannane Reagents:

Tributyl(4-(*tert*-butyl)phenyl)stannane (2c).

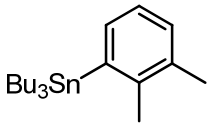


2c

To an oven-dried 50 mL round bottom flask equipped with a stir bar and water condenser was added 188 mg Mg (7.73 mmol, 1.70 equiv) and the flask was flushed with nitrogen before adding 5.0 mL THF. Two drops dibromoethane were added via syringe, followed by 1.07 g 1-bromo-4-(*tert*-butyl)benzene (5.00 mmol, 1.10 equiv) via syringe. The mixture was heated to reflux and stirred for 24 h. A separate dry 50 mL round bottom flask equipped with a stir bar and water condenser was flushed with nitrogen. The organometallic mixture was transferred from the first

flask to the second *via* cannula and the mixture was diluted with 5 mL THF. To this mixture, 1.48 g Bu_3SnCl (4.55 mmol) was added dropwise *via* syringe before heating the mixture to reflux and stirring for 24 h. The mixture was cooled to room temperature and 10 mL 1 M NaOH was added before stirring for 1 h. The mixture was transferred to a separatory funnel with 10 mL Et_2O. The aqueous layer was extracted three times with 10 mL Et_2O. The combined organic layers were washed with 25 mL H_2O and 25 mL brine before they were dried over Na_2SO_4. The mixture was filtered and the solvent removed *in vacuo*. The product was purified by silica gel flash chromatography eluting with hexanes and the ^1H NMR spectrum compared to that reported previously[10] to ensure purity. Yield: 92% (1.94 g).

Tributyl(2,3-dimethylphenyl)stannane (2f).

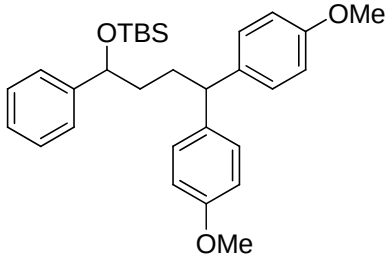


2f

The procedure used for the preparation of **2c** was used except 925 mg 1-bromo-2,3-dimethylbenzene (5.00 mmol, 1.10 equiv.) was added. The product was purified in the same way as **2c**. Yield 89% (1.59 g). R_f = 0.54 w/hexanes (silica), PMA stain: IR (neat) 3050, 2955, 2923, 2870, 2853, 1463l, 1418, 1376, 1340, 1071, 1014, 960, 874, 768, 712, 667, 597 cm^{-1}. ^1H-NMR (300 MHz, $CDCl_3$): δ 0.88 (t, *J* = 7.1 Hz, 9H), 1.03-1.08 (m, 6H), 1.34 (sextet, *J* = 7.1 Hz, 6H), 1.47-1.57 (m, 6H), 2.27 (s, 3H), 2.30 (s, 3H), 7.07-7.11 (m, 2H), 7.22-7.25 (m, 1H); ^{13}C-NMR {^1H} (75 MHz, $CDCl_3$): δ 10.5, 13.9, 21.2, 23.1, 27.7, 29.4, 125.6, 130.2, 134.5, 136.3, 142.7, 143.1.

General Procedure for Oxidative Diarylation Reaction:

(**4,4-bis(4-Methoxyphenyl)-1-phenylbutoxy)(*tert*-butyl)dimethylsilane (3b).**

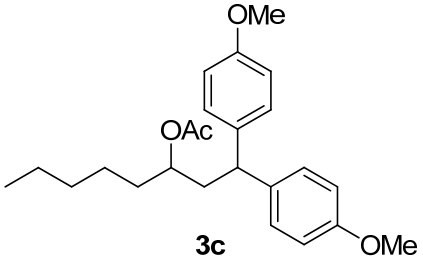


3b

To an oven-dried 50 mL round bottom Schlenk flask equipped with a stir bar was added 25 mg $Pd(I^iPr)(OTs)_2$ (0.030 mmol, 0.05 equiv.), 45 mg $Cu(OTf)_2$ (0.013 mmol, 0.25 equiv.), and 250 mg powdered freshly activated 3 Å MS. The flask was flushed with nitrogen before adding 2.50 mL DMA. A solution of 131 mg *tert*-butyldimethyl((1-phenylbut-3-en-1-yl)oxy)silane (**1b**) (0.50 mmol) was added in 1.50 mL DMA *via* syringe. A three-way joint was fitted with a balloon of O_2 and attached to the flask. The apparatus was evacuated and refilled with oxygen three times. The mixture was stirred under O_2 atmosphere for 5 minutes. To the stirred mixture was added 596 mg tributyl(4-methoxyphenyl)stannane (**2b**) (1.50 mmol, 3.00 equiv.) in 0.50 mL DMA *via* syringe. After 16 h the mixture was filtered through celite, rinsed with 15 mL Et_2O, and transferred to a separatory funnel. 15 mL distilled water was added, and the aqueous layer was extracted three times with 15 mL Et_2O. The combined organic extracts were washed twice with 15 mL distilled

water and 15 mL brine then dried over Na_2SO_4. The mixture was filtered and the solvent was removed *in vacuo*. The product was purified by silica gel flash chromatography eluting with 1% EtOAc/hexanes. For each substrate this procedure was performed at least twice and the average isolated yield is reported. Yield 82% (197 mg and 193 mg); R_f = 0.46 w/ 10% EtOAc/hexanes (silica), PMA stain: IR (neat) 2951, 2930, 2855, 1609, 1509, 1463, 1361, 1301, 1247, 1176, 1091, 1038, 835, 775, 701, 554 cm^{-1}. ^{1}H-NMR (300 MHz, $CDCl_3$): δ -0.17 (s, 3H), 0.00 (s, 3H), 0.88 (s, 9H), 1.52-1.72 (m, 2H), 1.86-2.08 (m, 2H, 3.74) (t, *J* = 7.8 Hz, 1H), 3.76 (s, 6H), 4.65 (dd, *J* = 6.9, 5.4 Hz, 1H), 6.78 (app d, *J* = 8.8 Hz, 4H), 7.05 (app d, *J* = 8.7 Hz, 4H), 7.19-7.29 (m, 5H); ^{13}C-NMR {^{1}H} (75 MHz, $CDCl_3$): δ -4.7, -4.4, 18.4, 26.1, 31.7, 39.3, 49.6, 55.4, 75.0, 113.9, 113.9, 126.1, 127.0, 128.2, 128.8, 128.8, 137.8, 137.9, 145.7, 157.9; HRMS $(M+Na)^+$ calcd.; 499.2644 obsd.; 499.2655.

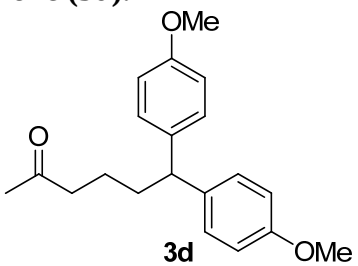
1,1-bis(4-Methoxyphenyl)octan-3-yl acetate (3c).



3c

The same procedure used to synthesize **3b** was used except 85 mg oct-1-en-3-yl acetate (**1c**) (0.50 mmol) was added, and the product was purified after 20 h by silica gel chromatography by eluting with 4% EtOAc/hexanes. Yield: 68% (123 mg and 139 mg); R_f = 0.37 w/ 10% EtOAc/hexanes (silica), PMA stain: IR (neat) 2955, 2932, 2859, 1734, 1609, 1509, 1464, 1374, 1302, 1246, 1177, 1036, 825, 668 cm^{-1}. ^{1}H-NMR (300 MHz, $CDCl_3$): δ 0.86 (t, *J* = 7.1 Hz, 3H), 1.14-1.30 (m, 6H), 1.48-1.58 (m, 2H), 1.94 (s, 3H), 2.17 (m, 1H), 2.28 (m, 1H), 3.76 (s, 3H), 3.77 (s, 3H), 3.90 (br t, *J* = 8.0 Hz, 1H), 4.77 (m, 1H), 6.81 (app d, *J* = 8.6 Hz, 2H), 6.83 (app d, *J* = 8.4 Hz, 2H), 7.09 (app d, *J* = 8.3 Hz, 2H), 7.17 (app d, *J* = 8.4 Hz, 2H); ^{13}C-NMR {^{1}H} (75 MHz, $CDCl_3$): δ 14.2, 21.3, 22.7, 24.8, 31.9, 34.5, 40.3, 46.3, 55.4, 55.4, 73.2, 114.0, 114.1, 128.7, 128.8, 137.1, 137.1, 158.0, 158.1, 170.9; HRMS $(M+Na)^+$ calcd.; 407.2198 obsd.; 407.2195.

6,6-bis(4-methoxyphenyl)hexan-2-one (3d).

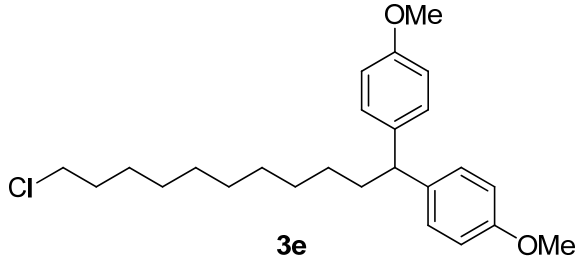


3d

The same procedure used to synthesize **3b** was used except 49 mg hex-5-en-2-one (**1d**) (0.50 mmol) was added, and the product was purified after 20 h by silica gel chromatography by eluting with 5% EtOAc/hexanes. Yield: 73% (112 mg and 115 mg); R_f = 0.45 w/ 10% EtOAc/hexanes (silica), PMA stain: IR (neat) 2998, 2934, 2835, 1713, 1608, 1583, 1509, 1462, 1442, 1358, 1301, 1245, 1176, 1034, 825, 552 cm^{-1}. ^{1}H-NMR (300 MHz, $CDCl_3$): δ 1.49-1.59 (m, 2H), 1.97 (tt, *J* = 7.6, 5.1, 2H), 2.09 (s, 3H), 2.44 (t, *J* = 7.3, 2H), 3.76 (s, 6H), 3.81 (t, *J* = 7.6, 1H), 6.82 (app d, *J* = 8.6 Hz, 4H), 7.13 (app d, *J* = 8.5 Hz, 4H); ^{13}C-NMR {^{1}H} (75 MHz, $CDCl_3$): δ 22.5, 30.0, 35.6,

43.8, 49.7, 55.4, 114.0, 128.7, 137.5, 158.0, 209.1; HRMS $(M+Na)^+$ calcd.; 335.1623 obsd.; 335.1635.

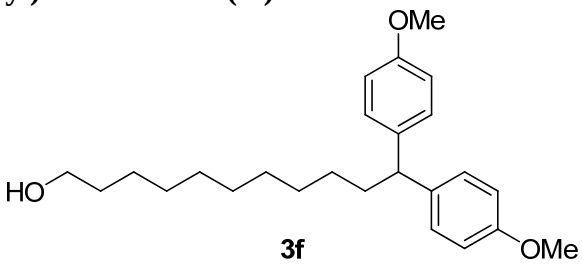
4,4'-(11-Chloroundecane-1,1-diyl)bis(methoxybenzene) (3e).



3e

The same procedure used to synthesize **3b** was used except 94 mg 11-chloroundec-1-ene (**1e**) (0.50 mmol) was added, and the product was purified after 20 h by silica gel chromatography by eluting with hexanes. Yield: 70% (149 mg and 132 mg); R_f = 0.40 w/ 5% EtOAc/hexanes (silica), PMA stain: IR (neat) 2996, 2927, 2854, 1609, 1509, 1497, 1463, 1441, 1301, 1246, 1218, 1177, 1037, 827, 668 cm^{-1}. ^{1}H-NMR (300 MHz, $CDCl_3$): δ 1.11-1.44 (m, 24H), 1.75 (tt, *J* = 7.8, 6.7 Hz, 2H), 1.96 (dt, *J* = 8.1, 7.8 Hz, 2H), 3.53 (t, *J* = 6.7 Hz, 2H) 3.77-3.85 (m, 8H), 6.82 (app d, *J* = 8.7 Hz, 4H), 6.86-6.95 (m, 2H), 7.14 (app d, *J* = 8.7 Hz, 4H); ^{13}C-NMR {^{1}H} (75 MHz, $CDCl_3$): δ 27.1, 28.2, 29.1, 29.6, 29.7, 29.7, 29.8, 32.8, 36.3, 45.4, 49.8, 55.4, 55.9, 113.9, 114.9, 119.7, 128.8, 138.1, 157.9; HRMS $(M+Ag)^+$ calcd.; 509.1377 obsd.; 509.1396.

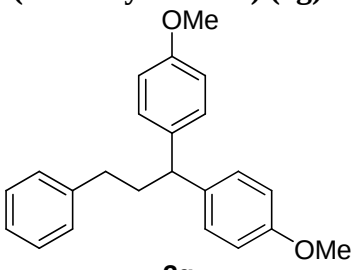
11,11-bis(4-Methoxyphenyl)undecan-1-ol (3f).



3f

The same procedure used to synthesize **3b** was used except 85 mg undec-10-en-1-ol (**1f**) (0.50 mmol) was added, and the product was purified after 22 h by silica gel chromatography by eluting with 10% EtOAc/hexanes. Yield: 57% (110 mg and 108 mg); R_f = 0.28 w/ 20% EtOAc/hexanes (silica), PMA stain: IR (neat) 3367, 2997, 2927, 2853, 1609, 1510, 1464, 1419, 1307, 1247, 1176, 1037, 824, 668, 589 cm^{-1}. ^{1}H-NMR (300 MHz, $CDCl_3$): δ 1.15-1.40 (m, 16H), 1.55 (tt, *J* = 7.1, 6.4 Hz, 2H), 1.96 (dt, *J* = 7.7, 6.6 Hz, 2H), 3.63 (t, *J* = 6.6 Hz, 2H), 3.79 (t, *J* = 8.5 Hz, 1H), 3.77 (s, 6H), 6.82 (app d, *J* = 8.6 Hz, 4H), 7.14 (app d, *J* = 8.5 Hz, 4H); ^{13}C-NMR {^{1}H} (75 MHz, $CDCl_3$): δ 25.9, 28.2, 29.6, 29.7, 29.7, 29.7, 29.8, 33.0, 36.3, 49.8, 55.4, 63.3, 113.9, 128.8, 138.1, 157.9; HRMS $(M+Ag)^+$ calcd.; 491.1715 obsd.; 491.1717.

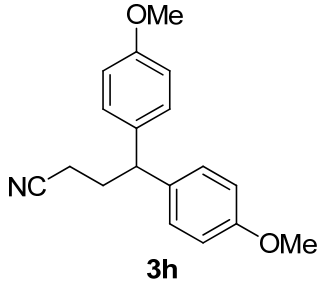
4,4'-(3-Phenylpropane-1,1-diyl)bis(methoxybenzene) (3g).



3g

The same procedure used to synthesize **3b** was used except 59 mg allyl benzene (**3g**) (0.50 mmol) was added, and the product was purified after 22 h by silica gel chromatography by eluting with 1% EtOAc/hexanes to give a mixture of regioisomeric products in a 7.2:1 ratio. Yield: 92% (155 mg and 150 mg); R_f = 0.44 w/ 5% EtOAc/hexanes (silica), PMA stain: IR (neat) 3026, 2999, 2932, 2834, 1609, 1510, 1455, 1301, 1246, 1176, 1036, 828, 700, 549 cm^{-1}. ^{1}H-NMR (300 MHz, $CDCl_3$): δ 2.18-2.35 (m, 2H), 2.48-2.59 (m, 2H), 3.75-3.85 (m, 7H), 6.80-6.84 (m, 3.6H), 7.04-7.07 (m, 0.5H), 7.13-7.30 (m, 9H); ^{13}C-NMR {^{1}H} (75 MHz, $CDCl_3$): δ 33.3, 34.3, 37.9, 49.1, 49.9, 55.4, 55.4, 113.9, 114.0, 126.0, 126.2, 128.0, 128.5, 128.6, 128.9, 129.0, 129.5, 134.4, 137.2, 137.6, 142.4, 145.5, 158.0, 158.1; HRMS $(M+K)^+$ calcd.; 371.1413 obsd.; 371.1429.

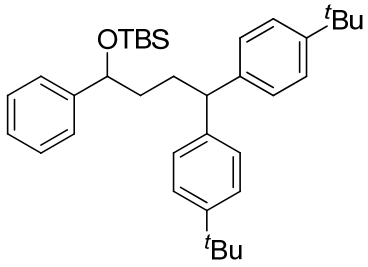
4,4-bis(4-Methoxyphenyl)butanenitrile (3h).



3h

The same procedure used to synthesize **3b** was used except 35 mg allyl cyanide **1h** (0.50 mmol) was added, and the product was purified after 20 h by silica gel chromatography by eluting with 5% EtOAc/hexanes to give the product which decomposes at room temperature. Yield: 27% (36 mg and 40 mg); R_f = 0.40 w/ 20% EtOAc/hexanes (silica), PMA stain: IR (neat) 2933, 2836, 2245, 1609, 1583, 1509, 1263, 1302, 1245, 1177, 1116, 1033, 828, 578, 552 cm^{-1}. ^{1}H-NMR (300 MHz, CD_2Cl_2): δ 2.23-2.36 (m, 4H), 3.76, (s, 6H), 3.94 (t, *J* = 7.8 Hz, 1H), 6.84 (app d, *J* = 8.8 Hz, 4H), 7.15 (app d, *J* = 8.6 Hz, 4H); ^{13}C-NMR {^{1}H} (75 MHz, CD_2Cl_2): δ 16.2, 31.8, 48.8, 55.7, 114.5, 120.1, 129.0, 136.0, 158.9; HRMS $(M+Na)^+$ calcd.; 304.1313 obsd.; 304.1318.

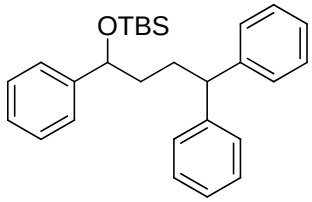
(4,4-bis(4-(tert-Butyl)phenyl)-1-phenylbutoxy)(tert-butyl)dimethylsilane (3i).



3i

The same procedure used to synthesize **3b** was used except 635 mg tributyl(4-(tert-butyl)phenyl)stannane (**2c**) (1.50 mmol) was added, and the product was purified after 20 h by silica gel chromatography by eluting with hexanes. Yield: 80% (206 mg and 214 mg); R_f = 0.79 w/ 5% EtOAc/hexanes (silica), PMA stain: IR (neat) 3026, 2903, 2859, 1510, 1493, 1471, 1462, 1407, 1362, 1257, 1092, 864, 836, 775, 700, 579 cm^{-1}. ^{1}H-NMR (300 MHz, $CDCl_3$): δ -0.17 (s, 3H), 0.00 (s, 3H), 0.87 (s, 9H), 1.27 (s, 18H) 1.55-1.75 (m, 2H), 1.96-2.09 (m, 2H), 3.75 (dd, *J* = 8.0, 8.0 Hz, 1H), 4.64 (dd, *J* = 5.5, 5.5 Hz, 1H), 7.09 (app d, *J* = 8.3 Hz, 4H), 7.39-7.27 (m, 9H); ^{13}C-NMR {^{1}H} (75 MHz, $CDCl_3$): δ -4.7, -4.5, 18.5, 26.1, 31.4, 31.6, 34.5, 39.2, 50.5, 75.0, 125.4, 125.4, 126.1, 127.0, 127.6, 127.6, 128.1, 142.4, 145.6, 148.7, 148.7; HRMS $(M+Na)^+$ calcd.; 551.3685 obsd.; 551.3686.

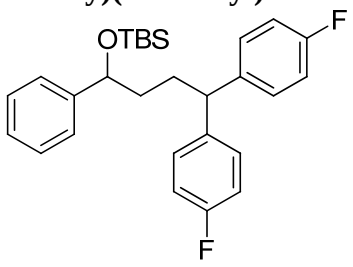
***tert*-Butyldimethyl(1,4,4-triphenylbutoxy)silane (3j):**



3j

The same procedure used to synthesize **3b** was used except 551 mg Bu_3SnPh (**2d**) (1.50 mmol) was added, and the product was purified after 23 h by silica gel chromatography by eluting with hexanes. Yield: 75% (158 mg and 151 mg); R_f = 0.09 w/ hexanes (silica), PMA stain: IR (neat) 3061, 3026, 2950, 2928, 2856, 1600, 1506, 1493, 1471, 1451, 1361, 1255, 1093, 1070, 979, 862, 835, 804, 775, 698, 547 cm^{-1}. ^{1}H-NMR (300 MHz, $CDCl_3$): δ -0.17 (s, 3H), 0.00 (s, 3H), 0.89 (s, 9H), 1.56-1.74 (m, 2H), 1.96-2.19 (m, 2H), 3.83 (dd, *J* = 7.8, 7.8 Hz, 1H), 4.67 (dd, *J* = 5.0, 6.6 Hz, 1H), 7.02-7.30 (m, 15H); ^{13}C-NMR {^{1}H} (75 MHz, $CDCl_3$): δ -4.7, -4.5, 18.4, 26.1, 31.3, 39.2, 51.4, 75.0, 126.1, 126.2, 127.0, 128.0, 128.1, 128.2, 128.6, 128.6, 145.2, 145.3, 145.6; HRMS $(M+Na)^+$ calcd.: 439.2433 obsd.: 439.2439.

(4,4-bis(4-Fluorophenyl)-1-phenylbutoxy)(tert-butyl)dimethylsilane (3k).

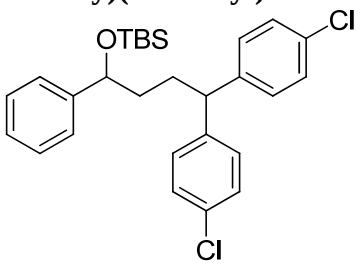


3k

The same procedure used to synthesize **3b** was used except 578 mg tributyl(4-fluorophenyl)stannane (**2a**) (1.50 mmol) was added, and the product was purified after 48 h by silica gel chromatography by eluting with hexanes. Yield: 66% (150 mg). The reaction to reproduce this yield was performed using 121 mg *tert*-butyldimethyl((1-phenylbut-3-en-1-yl)oxy)silane (**1b**) (0.46 mmol) with 532 mg **2a** (1.38 mmol) and was purified in the same way. Yield: 59% (123 mg); R_f = 0.74 w/ 20% acetone/hexanes (silica), PMA stain: IR (neat) 3035, 2952, 2929, 2857, 1604, 1471, 1361, 1256, 1225, 1157, 1092, 979, 864, 835, 776, 700, 548 cm^{-1}. ^{1}H-NMR (300 MHz, $CDCl_3$): δ -0.16 (s, 3H), 0.00 (s, 3H), 0.88 (s, 9H), 1.51-1.71 (m, 2H), 1.89-

2.12 (m, 2H), 3.79 (dd, *J* = 8.0, 8.0 Hz, 1H), 4.66 (dd, *J* = 5.2, 6.4 Hz, 1H), 6.93 (app t, *J* = 8.7 Hz, 4H), 7.02 (app d, *J* = 8.6 Hz, 2H), 7.09 (app d, *J* = 8.6 Hz, 2H), 7.20-7.35 (m, 5H); ^{13}C-NMR {^{1}H} (75 MHz, $CDCl_3$): δ -4.7, -4.5, 18.4, 26.1, 31.6, 39.1, 49.8, 74.8, 115.4 (d, J^2 = 21.2 Hz), 115.4 (d, J^2 = 21.1 Hz), 126.0, 127.1, 128.2, 129.2 (d, J^3 = 2.5 Hz), 129.3 (d, J^3 = 3.0 Hz), 140.7 (d, J^4 = 3.0 Hz), 140.8 (d, J^4 = 2.5 Hz), 145.4, 161.5 (d, J^1 = 244.2 Hz); HRMS $(M+Ag)^+$ calcd.; 559.1398 obsd.: 559.1406.

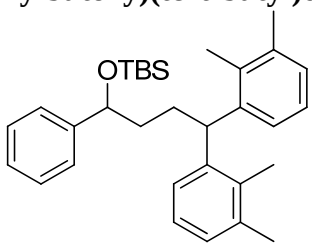
(4,4-bis(4-Chlorophenyl)-1-phenylbutoxy)(*tert*-butyl)dimethylsilane (3l).



3l

The same procedure used to synthesize **3b** was used except 602 mg tributyl(4-chlorophenyl)stannane (**2e**) (1.50 mmol) was added, and the product was purified after 48 h by silica gel chromatography by eluting with hexanes. Yield: 45% (109 mg). The reaction to reproduce this yield was performed using 110 mg *tert*-butyldimethyl((1-phenylbut-3-en-1-yl)oxy)silane (**2b**) (0.42 mmol) with 505 mg **2e** (1.28 mmol) and was purified in the same way. Yield: 46% (93 mg); R_f = 0.56 w/ 5% acetone/5% benzene/hexanes (silica), PMA stain: IR (neat) 3027, 2952, 2928, 2884, 2856, 1491, 1471, 1462, 1389, 1361, 1256, 1206, 1014, 978, 836, 775, 700, 546 cm^{-1}. ^{1}H-NMR (300 MHz, $CDCl_3$): δ -0.16 (s, 3H), 0.01 (s, 3H), 0.89 (s, 9H), 1.51-1.71 (m, 2H), 1.89-2.13 (m, 2H), 3.78 (dd, *J* = 7.7, 7.7 Hz, 1H), 4.66 (dd, *J* = 5.0, 6.6 Hz, 1H), 7.05 (app d, *J* = 8.7 Hz, 4H), 7.20-7.31 (m, 9H),; ^{13}C-NMR {^{1}H} (75 MHz, $CDCl_3$): δ -4.7, -4.4, 18.4, 26.1, 31.2, 39.0, 50.5, 74.8, 126.0, 127.2, 128.3, 128.8, 138.8, 129.3, 129.3, 132.2, 143.2, 143.3, 145.3; HRMS $(M+Ag)^+$ calcd.; 591.0807 obsd.; 591.0818.

(4,4-bis(2,3-Dimethylphenyl)-1-phenylbutoxy)(tert-butyl)dimethylsilane (3n).

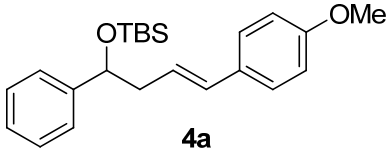


3m

The same procedure used to synthesize **3b** was used except 593 mg tributyl(2,3-dimethylphenyl)stannane (**2f**) (1.50 mmol) was added, and the product was purified after 72 h by silica gel chromatography by eluting with hexanes. 62 mg (47%) **1b** was recovered each experiment. Yield: 26% (65 mg and 57 mg); R_f = 0.57 w/ 10% EtOAc/hexanes (silica), PMA stain: IR (neat) 3064, 3026, 2951, 2928, 2856, 1585, 1493, 1471, 1461, 1386, 1361, 1255, 1094, 1071, 1027, 1006, 977, 837, 776, 745, 724, 700, 548 cm^{-1}. ^{1}H-NMR (300 MHz, $CDCl_3$): δ -0.17 (s, 3H), 0.00 (s, 3H), 0.89 (s, 9H), 1.70-1.90 (m, 4H), 2.06 (s, 3H), 2.10 (s, 3H), 2.24 (s, 3H), 2.25 (s, 3H), 4.23 (dd, *J* = 7.4, 7.4 Hz, 1H), 4.67 (dd, *J* = 5.0, 5.0 Hz, 1H), 6.81-6.87 (m, 2H), 6.96-

6.99 (m, 4H), 7.20-7.27 (m, 5H); ^{13}C-NMR {^{1}H} (75 MHz, $CDCl_3$): δ -4.7, -4.5, 15.0, 18.4, 21.3, 26.1, 30.8, 39.5, 43.7, 75.0, 125.3, 125.3, 125.4, 126.2, 127.0, 127.7, 127.7, 128.1, 134.8, 134.9, 136.8, 142.9, 142.9, 145.4; HRMS $(M+Ag)^+$ calcd.; 579.2212 obsd.; 579.2230.

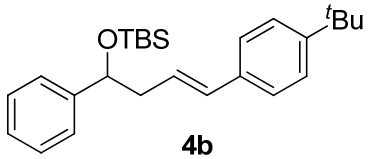
(*E*)-*tert*-Butyl((4-(4-methoxyphenyl)-1-phenylbut-3-en-1-yl)oxy)dimethylsilane (4a).



4a

Isolated as a side product from the reaction used to synthesize **3b**. Material was a mixture of **4a** and an isomeric compound. Yield: 13% (30 mg and 18 mg); R_f = 0.71 w/ 10% EtOAc/hexanes (silica), PMA stain: IR (neat) 3031, 2954, 2928, 2856, 1608, 1540, 1511, 1471, 1464, 1362, 1293, 1249, 1174, 1091, 1039, 1005, 966, 939, 837, 776, 753, 700, 668 cm^{-1}. ^{1}H-NMR (300 MHz, $CDCl_3$): δ -0.16 (s, 0.35H), -0.12 (s, 3H), 0.01 (s, 3H), 0.05 (s, 0.24H), 0.91 (s, 1H), 0.88 (s, 9H), 2.48-2.57 (m, 2H), 3.31 (br d, *J* = 6.6 Hz, 0.31H), 3.80 (s, 3H), 4.72 (dd, *J* = 5.1, 7.2 Hz, 1H), 5.17 (d, *J* = 6 Hz, 0.25H), 6.05 (dt, *J* = 15.8, 7.2 Hz, 1H), 6.32 (d, *J* = 15.8 Hz, 1H), 6.83 (app d, *J* = 8.8 Hz, 2H), 7.04-7.09 (m, 0.66H) 7.23-7.33 (m, 7H); ^{13}C-NMR {^{1}H} (75 MHz, $CDCl_3$): δ -4.7, -4.6, 18.5, 26.0, 26.1, 27.7, 29.9, 35.1, 37.8, 40.7, 44.9, 55.5, 75.1, 75.6, 75.5, 113.8, 114.0, 114.1, 125.2, 126.0, 126.1, 127.0, 127.1, 127.3, 128.2, 128.2, 128.3, 129.4, 129.7, 130.8, 131.6, 135.1, 145.5, 158.9; HRMS $(M+Ag)^+$ calcd.; 475.1223 obsd.; 475.1212.

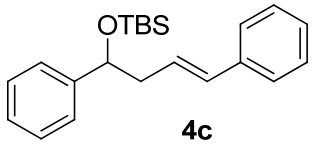
(*E*)-*tert*-Butyl((4-(4-(*tert*-butyl)phenyl)-1-phenylbut-3-en-1-yl)oxy)dimethylsilane (4b).



4b

Isolated as a side product from the reaction used to synthesize **3i**. Yield: 13% (27 mg and 22 mg); R_f = 0.84 w/ 5% EtOAc/hexanes (silica), PMA stain: IR (neat) 3028, 2956, 2928, 2902, 2856, 1514, 1493, 1471, 1462, 1363, 1256, 1202, 1090, 1069, 1005, 967, 939, 836, 806, 776, 700, 556 cm^{-1}. ^{1}H-NMR (300 MHz, $CDCl_3$): δ -0.12 (s, 3H), 0.03 (s, 3H), 0.90 (s, 9H), 1.30 (s, 9H), 2.50-2.61 (m, 2H), 4.73 (dd, *J* = 5.1, 7.2 Hz, 1H), 6.16 (dt, *J* = 15.8, 7.2 Hz, 1H), 6.36 (d, *J* = 15.9 Hz, 1H), 7.23-7.32 (m, 9H); ^{13}C-NMR {^{1}H} (75 MHz, $CDCl_3$): δ -4.6, -4.5, 18.5, 26.1, 31.5, 31.6, 45.0, 75.5, 125.6, 125.9, 126.1, 126.5, 127.2, 128.2, 132.0, 135.2, 145.4, 150.8; HRMS $(M+Ag)^+$ calcd.; 501.1743 obsd.; 501.1758.

(*E*)-*tert*-Butyl((1,4-diphenylbut-3-en-1-yl)oxy)dimethylsilane (4c).

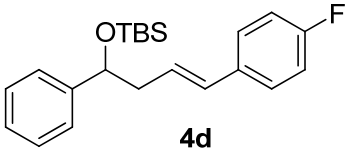


4c

Isolated as a side product from the reaction used to synthesize **3j**. Yield: 9 % (12 mg and 18 mg); R_f = 0.16 w/ hexanes (silica), PMA stain: IR (neat) 3061, 3027, 2954, 2928, 2894, 2855, 1734, 1700, 1653, 1599, 1540, 1521, 1506, 1494, 1472, 1437, 1362, 1256, 1215, 1086, 1070, 1005, 836, 776, 743, 699, 540 cm^{-1}. ^{1}H-NMR (300 MHz, $CDCl_3$): δ -0.12 (s, 3H), 0.02 (s, 3H), 0.88 (s, 9H), 2.51-2.59 (m, 2H), 4.74 (dd, *J* = 5.0, 7.4 Hz, 1H), 6.21 (dt, *J* = 15.9, 7.2 Hz, 1H), 6.38 (d, *J* = 15.9 Hz, 1H), 7.19-7.33 (m, 10H); ^{13}C-NMR {^{1}H} (75 MHz, $CDCl_3$): δ -4.7, -4.5, 18.5, 26.0, 45.0,

75.4, 126.0, 126.2, 127.1, 127.2, 127.4, 128.3, 128.7, 132.3, 137.9, 145.4; HRMS $(M+Ag)^+$ calcd.; 445.1117 obsd.; 445.1124.

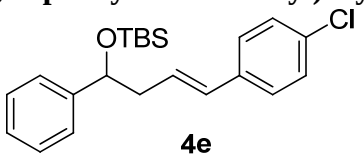
(*E*)-*tert*-Butyl((4-(4-fluorophenyl)-1-phenylbut-3-en-1-yl)oxy)dimethylsilane (4d).



4d

Isolated as a side product from the reaction used to synthesize **3k**. Yield: 18 % (26 mg and 34 mg); R_f = 0.78 w/ 20% acetone/hexanes (silica), PMA stain: IR (neat) 3030, 2954, 2928, 2856, 1653, 1602, 1508, 1471, 1463, 1362, 1256, 1230, 1157, 1090, 1005, 966, 939, 810, 796, 776, 700, 569 cm^{-1}. ^{1}H-NMR (300 MHz, $CDCl_3$): δ -0.13 (s, 3H), 0.01 (s, 3H), 0.88 (s, 9H), 2.50-2.60 (m, 2H), 4.73 (dd, *J* = 5.0, 7.4 Hz, 1H), 6.11 (dt, *J* = 15.9, 7.1 Hz, 1H), 6.33 (d, *J* = 15.9 Hz, 1H), 6.97 (app t, *J* = 8.9 Hz, 2H), 7.22-7.33 (m, 7H); ^{13}C-NMR {^{1}H} (75 MHz, $CDCl_3$): δ -4.7, -4.5, 18.4, 26.0, 44.9, 75.3, 115.6 (d, J^2 = 21.7 Hz), 126.0, 127.1, 127.1, 127.2, 127.6 (d, J^3 = 8.1 Hz), 128.3, 131.1, 134.1 (d, J^4 = 3.5 Hz), 145.3, 162.2 (d, J^1 = 245.6 Hz); HRMS $(M+Ag)^+$ calcd.; 463.1023 obsd.; 463.1032.

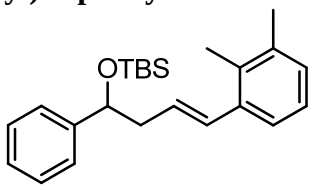
(*E*)-*tert*-Butyl((4-(4-chlorophenyl)-1-phenylbut-3-en-1-yl)oxy)dimethylsilane (4e).



4e

Isolated as a side product from the reaction used to synthesize **3l**. Yield: 36 % (63 mg and 58 mg); R_f = 0.68 w/ 5% acetone/5% benzene/hexanes (silica), PMA stain: IR (neat) 3028, 2954, 2928, 2895, 2856, 1491, 1471, 1462, 1453, 1404, 1388, 1361, 1256, 1091, 1068, 1012, 966, 938, 836, 776, 700, 548 cm^{-1}. ^{1}H-NMR (300 MHz, $CDCl_3$): δ -0.13 (s, 3H), 0.00 (s, 3H), 0.88 (s, 9H), 2.50-2.60 (m, 2H), 4.74 (dd, *J* = 5.0, 7.3 Hz, 1H), 6.17 (dt, *J* = 15.9, 7.2 Hz, 1H), 6.33 (d, *J* = 15.9 Hz, 1H), 7.32 (app d, *J* = 4.4 Hz, 4 H), 7.20-7.27 (m, 5H); ^{13}C-NMR {^{1}H} (75 MHz, $CDCl_3$): δ -4.7, -4.4, 18.4, 26.0, 44.9, 75.3, 126.0, 127.3, 127.4, 128.1, 128.3, 128.8, 131.2, 132.7, 136.5, 145.2; HRMS $(M+Ag)^+$ calcd.; 479.0727 obsd.; 479.0747.

(*E*)-*tert*-Butyl((4-(2,3-dimethylphenyl)-1-phenylbut-3-en-1-yl)oxy)dimethylsilane (4f).

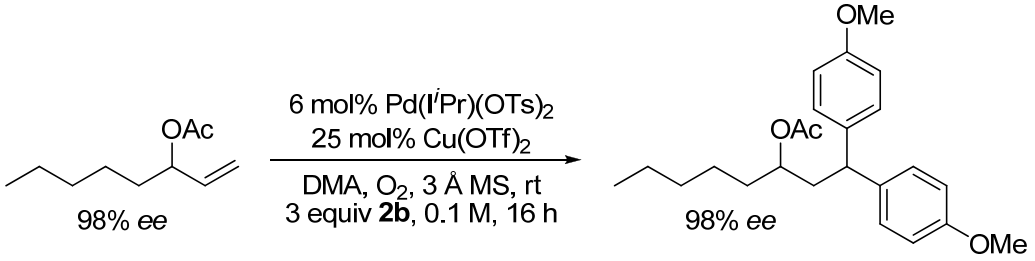


4f

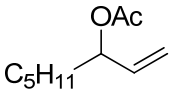
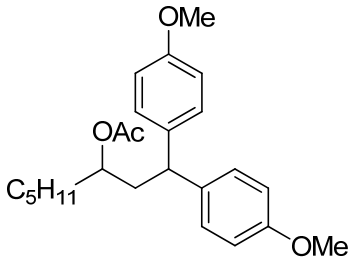
Isolated as a side product from the reaction used to synthesize **3m**. Yield: 26 % (52 mg and 43 mg); R_f = 0.63 w/ 10% EtOAc/hexanes (silica), PMA stain: IR (neat) 3027, 2954, 2928, 2895, 2856, 1653, 1559, 1506, 1491, 1471, 1387, 1362, 1256, 1091, 1068, 1005, 969, 940, 854, 775, 699, 668 cm^{-1}. ^{1}H-NMR (300 MHz, $CDCl_3$): δ -0.12 (s, 3H), 0.04 (s, 3H), 0.88 (s, 9H), 2.15 (s, 3H), 2.27 (s, 3H), 2.55-2.62 (m, 2H), 4.77 (dd, *J* = 5.6, 5.6 Hz, 1H), 5.96 (dt, *J* = 15.6, 7.1 Hz, 1H), 6.58 (d, *J* = 15.6 Hz, 1H), 7.03 (app d, *J* = 5.1 Hz, 2H) 7.17-7.34 (m, 6H); ^{13}C-NMR {^{1}H} (75 MHz, $CDCl_3$): δ -4.6, -4.5, 15.5, 18.4, 20.8, 26.1, 45.2, 75.4, 124.2, 125.6, 126.1, 127.1, 128.2,

128.7, 128.8, 131.3, 133.9, 136.8, 137.5, 145.3; HRMS $(M+Ag)^+$ calcd.; 473.1430 obsd.; 473.1436.

Evaluation of enantiomeric excess retention:



The same procedure used to synthesize racemic **3c** was used except 24 mg (*S*)-oct-1-en-3-yl acetate (**1c**) (0.14 mmol) was added, and the product was purified after 16 h by silica gel chromatography by eluting with 4% EtOAc/hexanes. The purified product was evaluated for enantiomeric excess using chiral SFC (see below).

compound	method	retention times (min)
	GC. hold 100 °C 25 min	6.5 and 6.9 min
	SFC. 5% MeOH 1.5 mL/min	5.5 and 6.1 min

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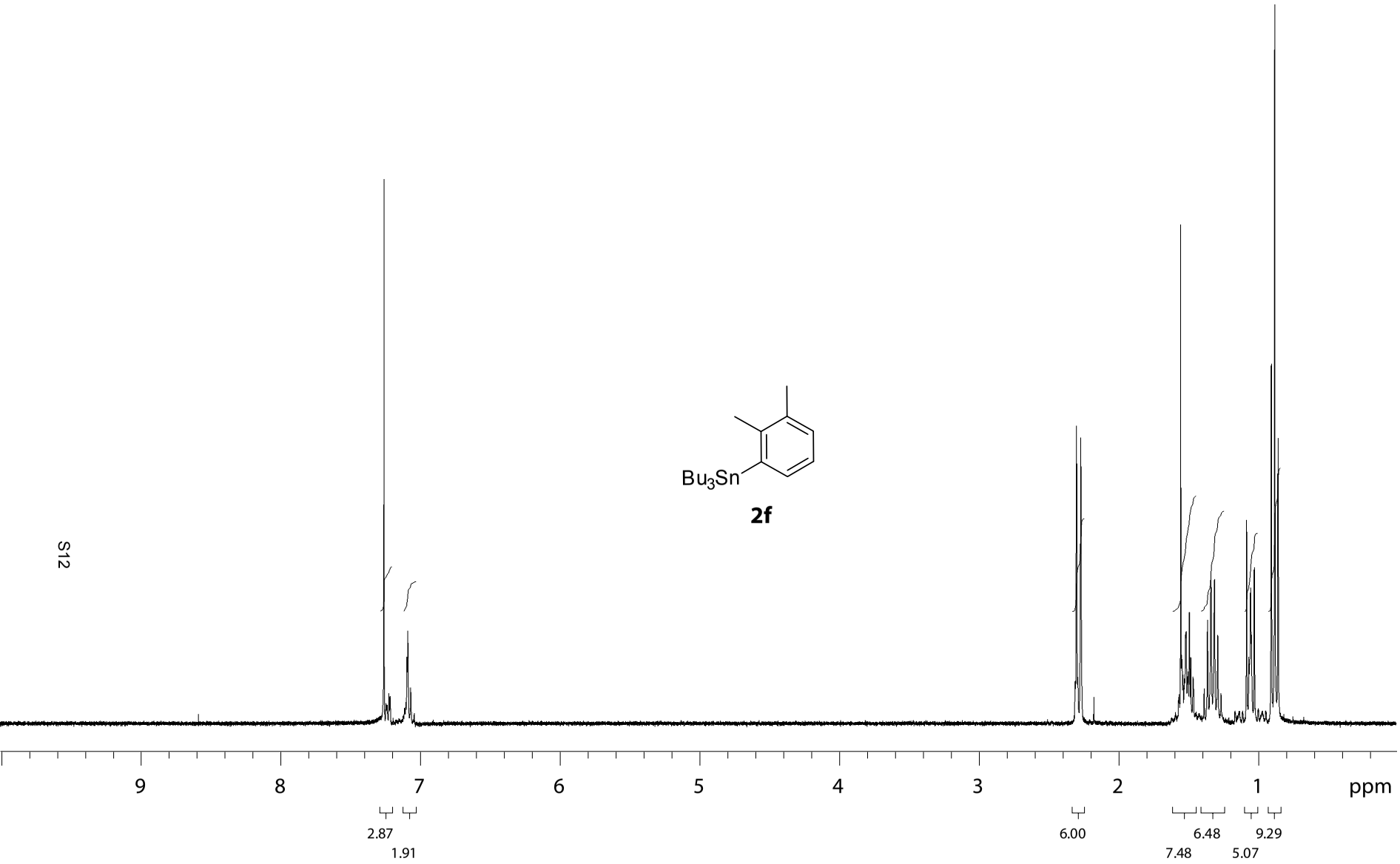
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7
6
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4
3
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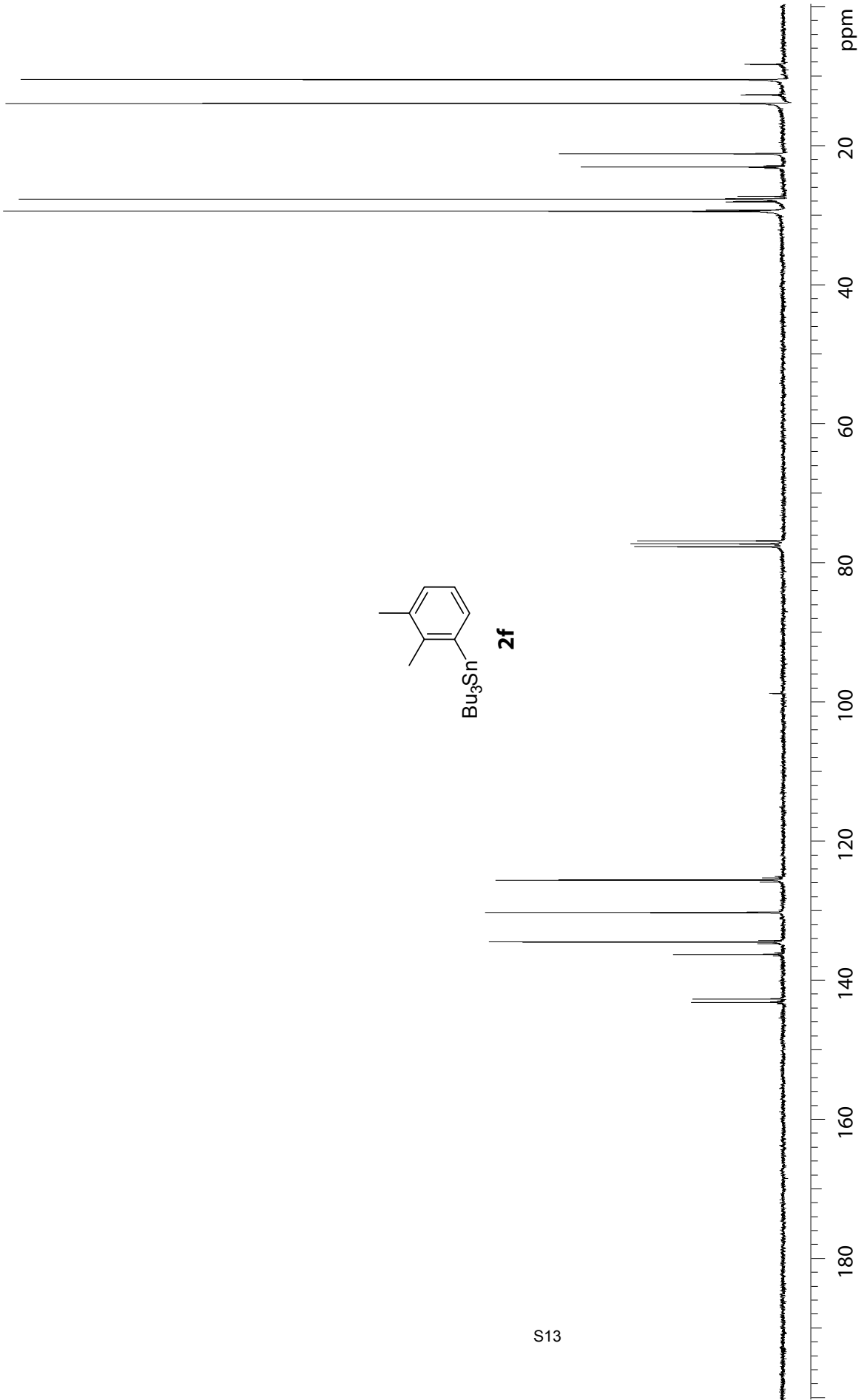
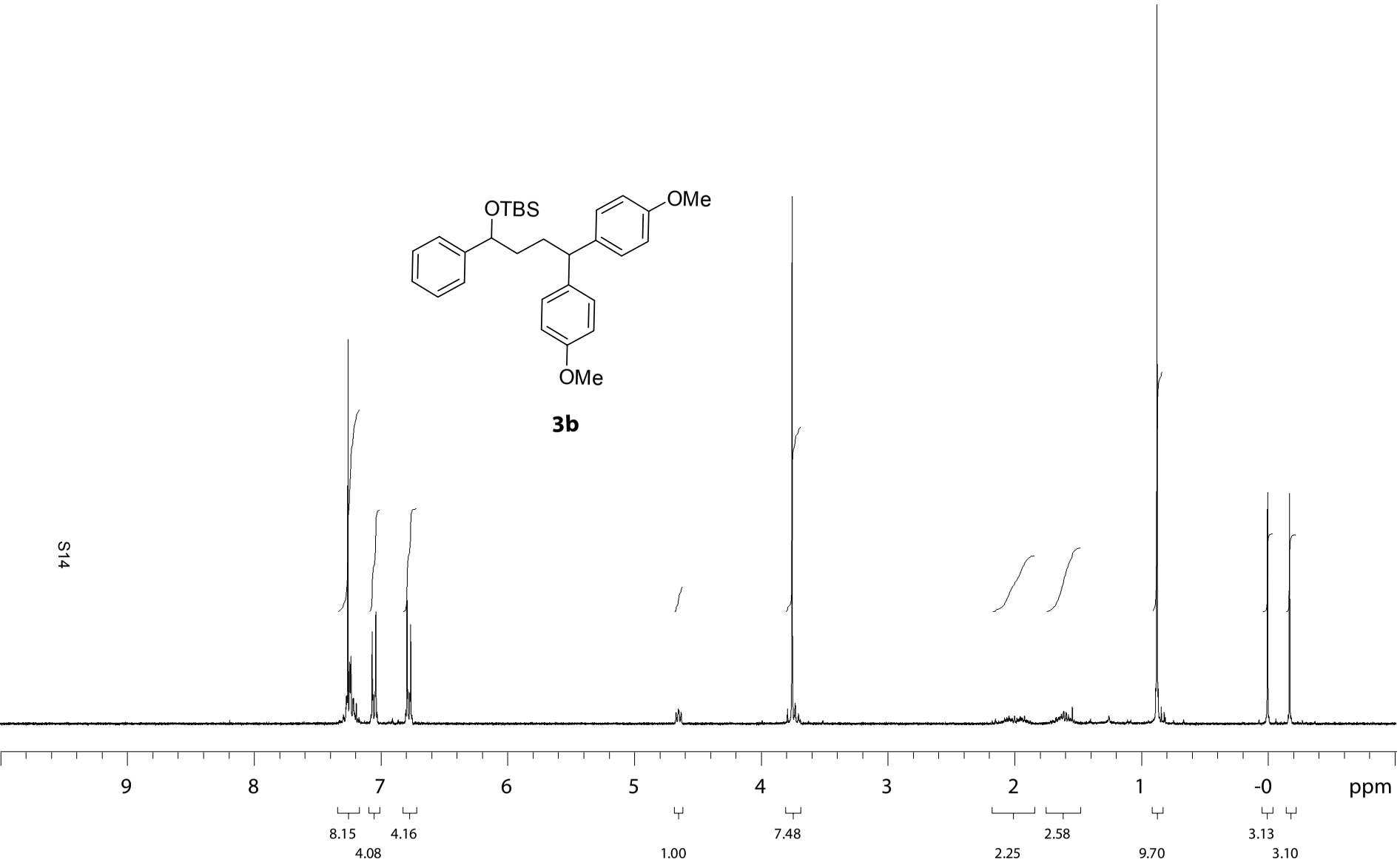
5.07
9.29



2f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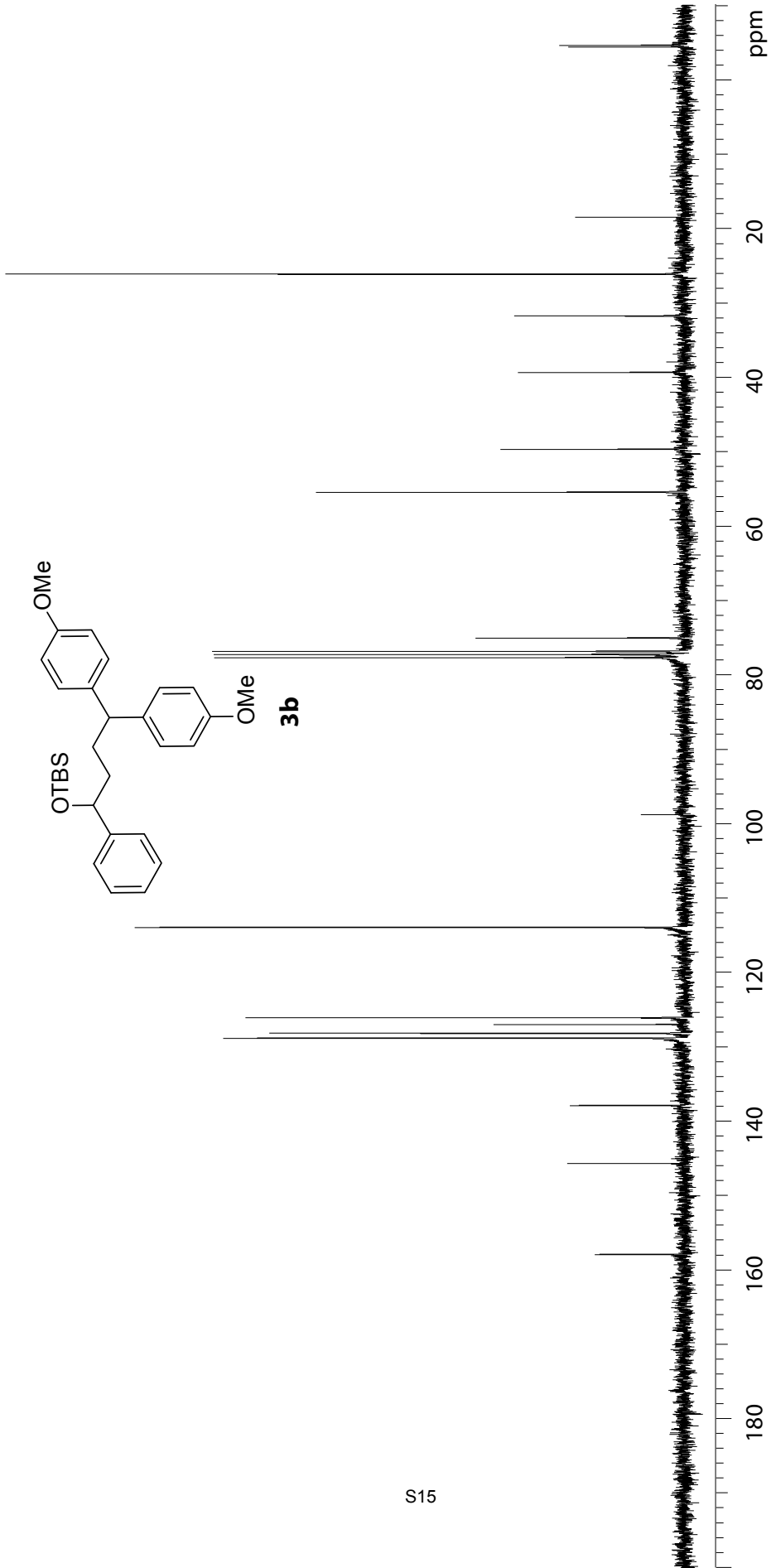
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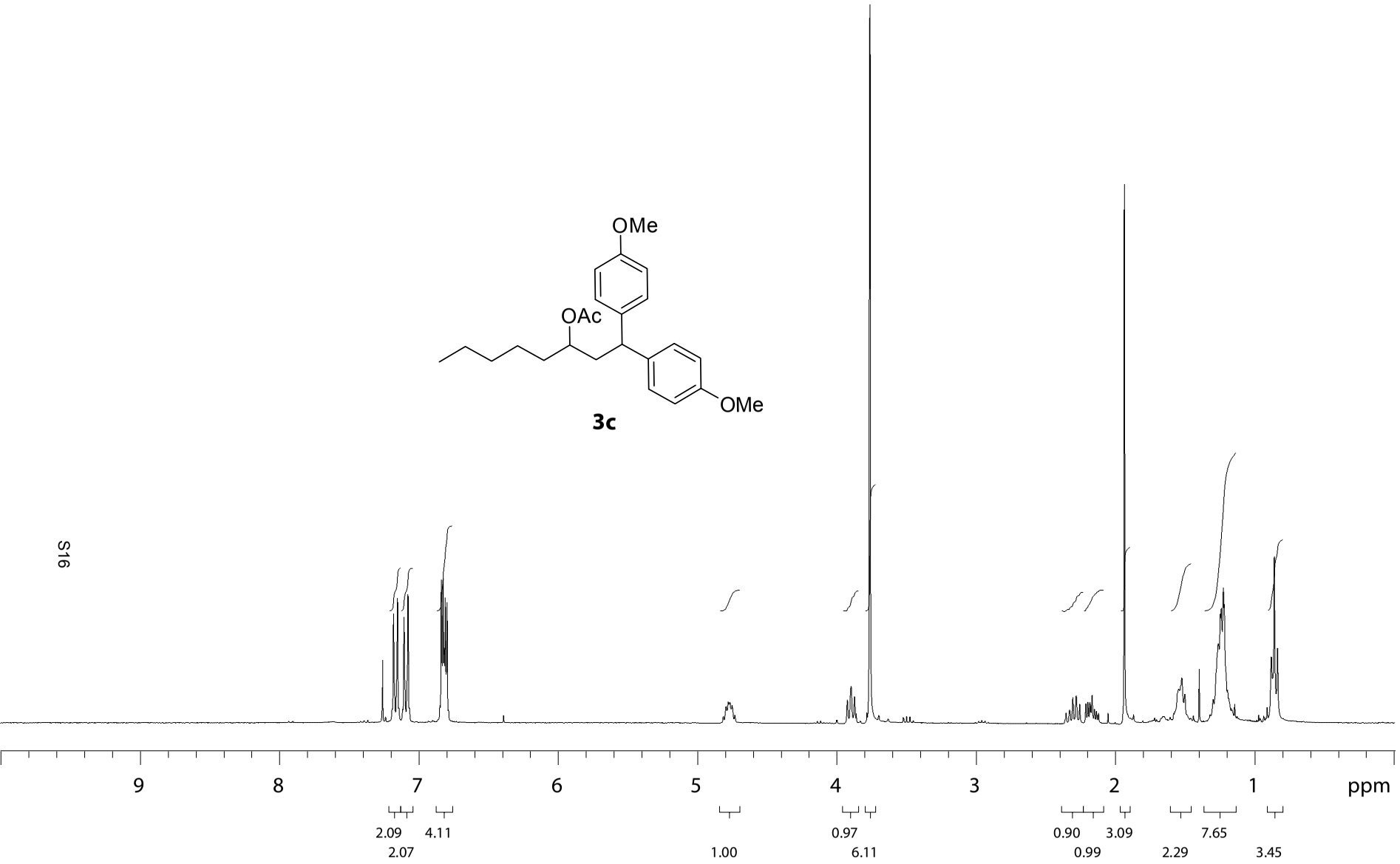
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ppm
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0.97
6.11
0.90
3.09
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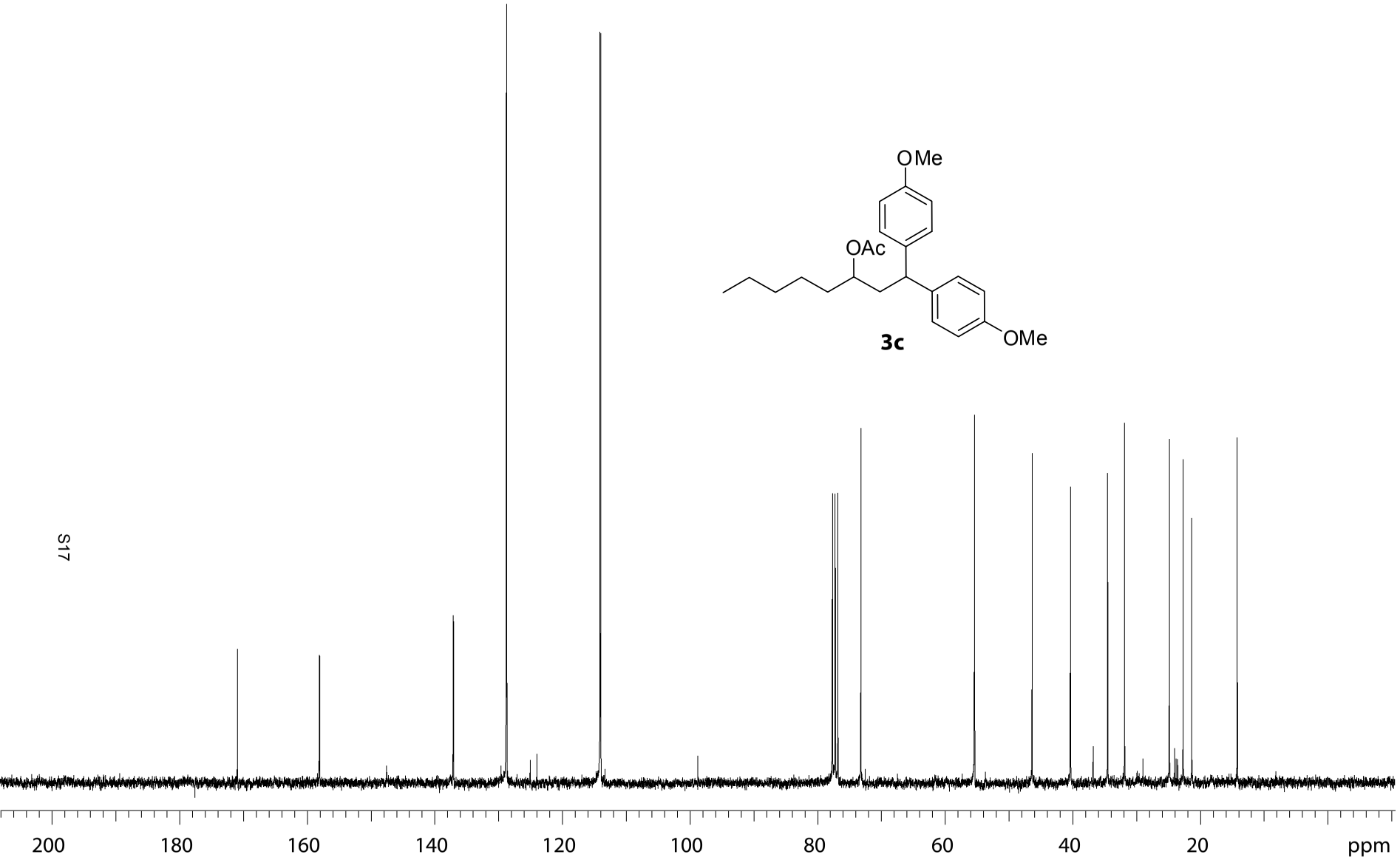
7.65
3.45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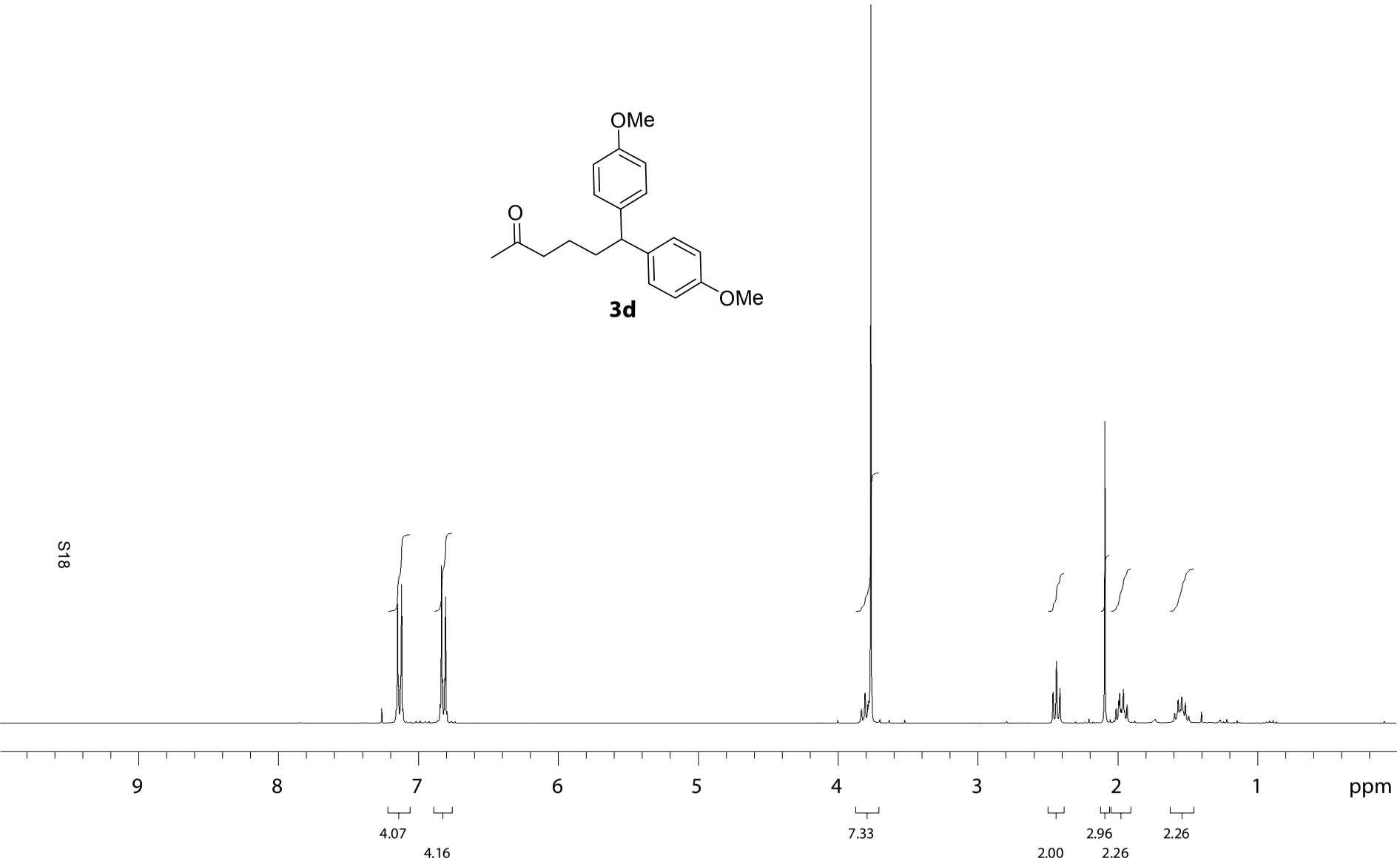
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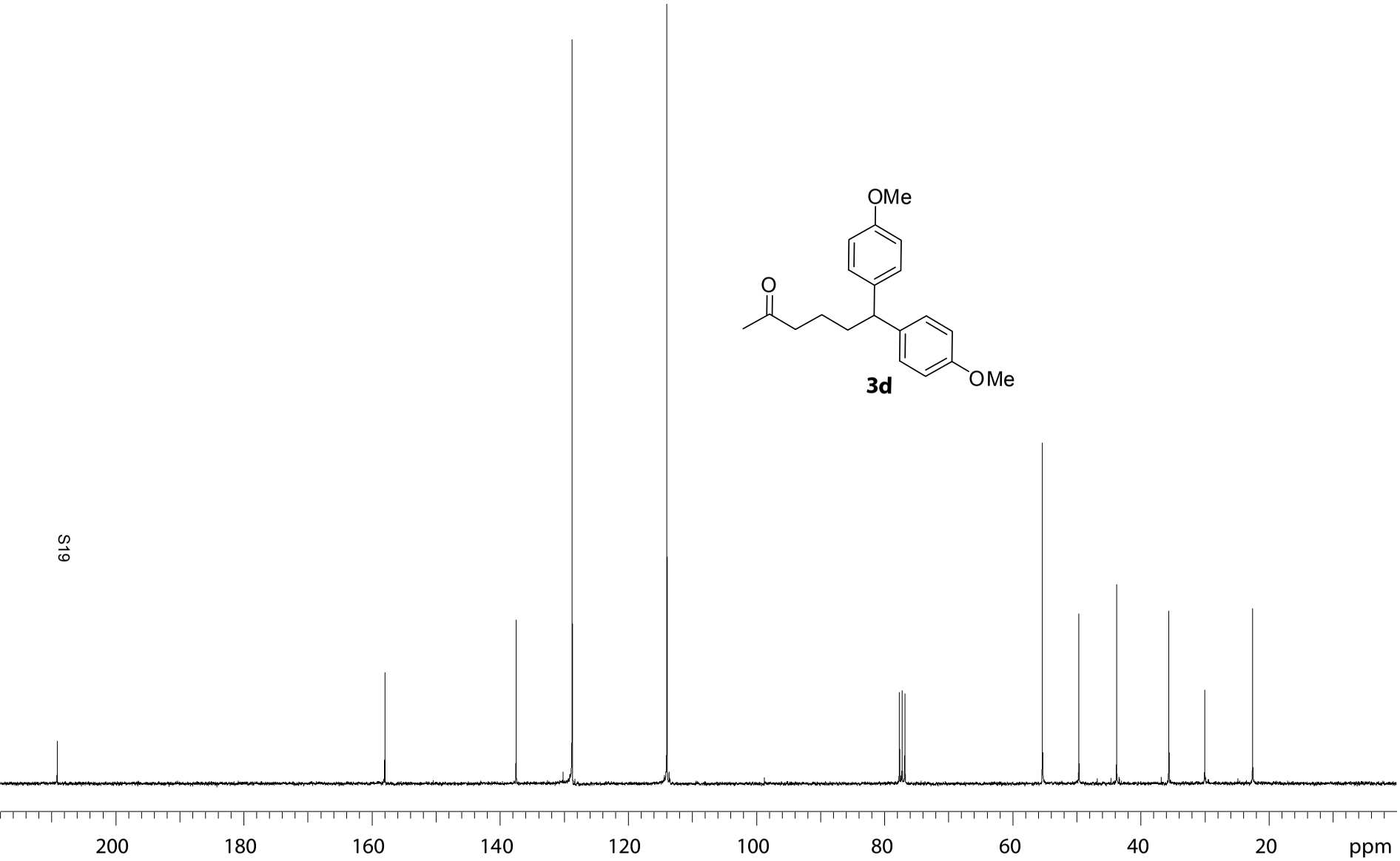
2.26
2.26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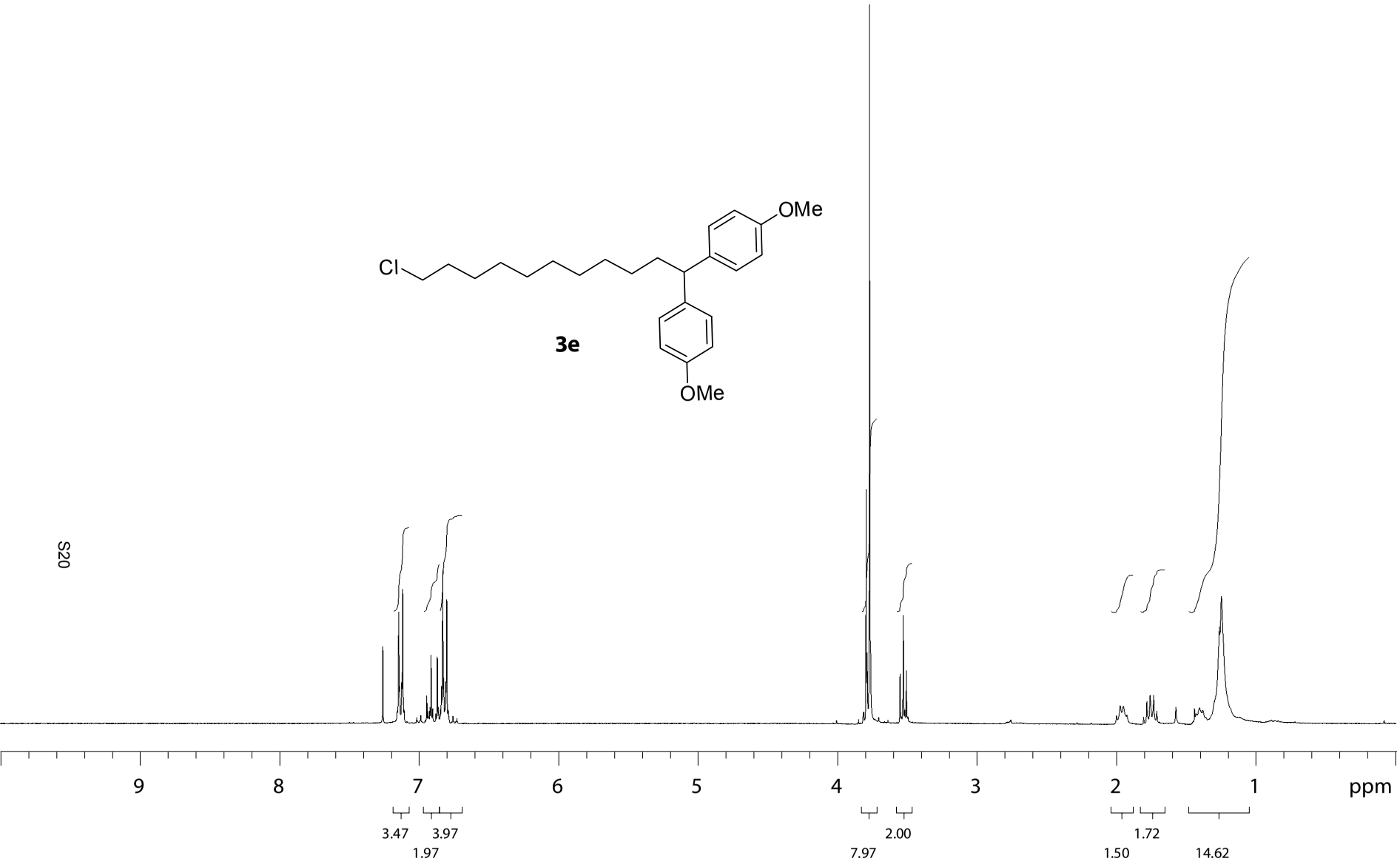
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7.97
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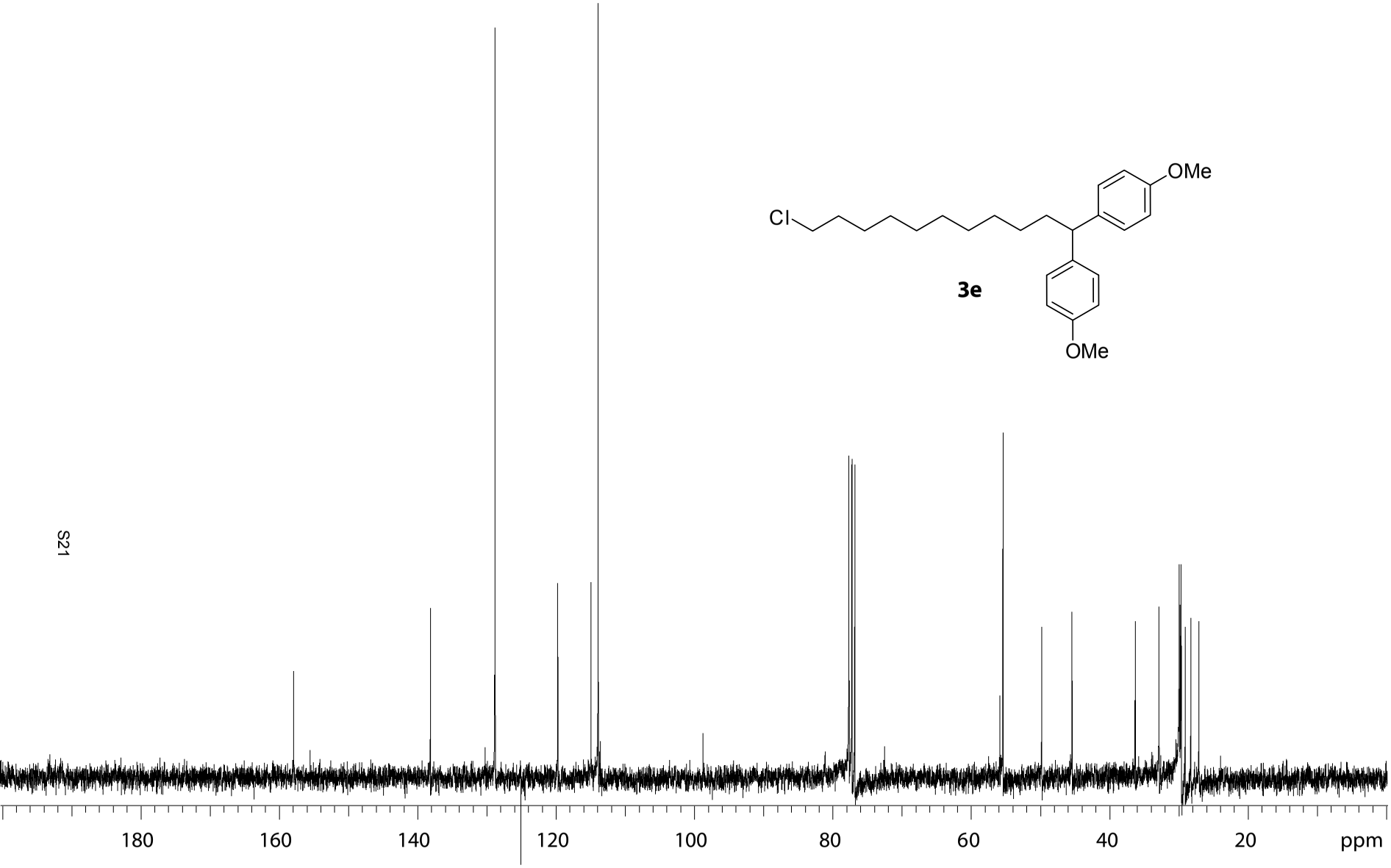
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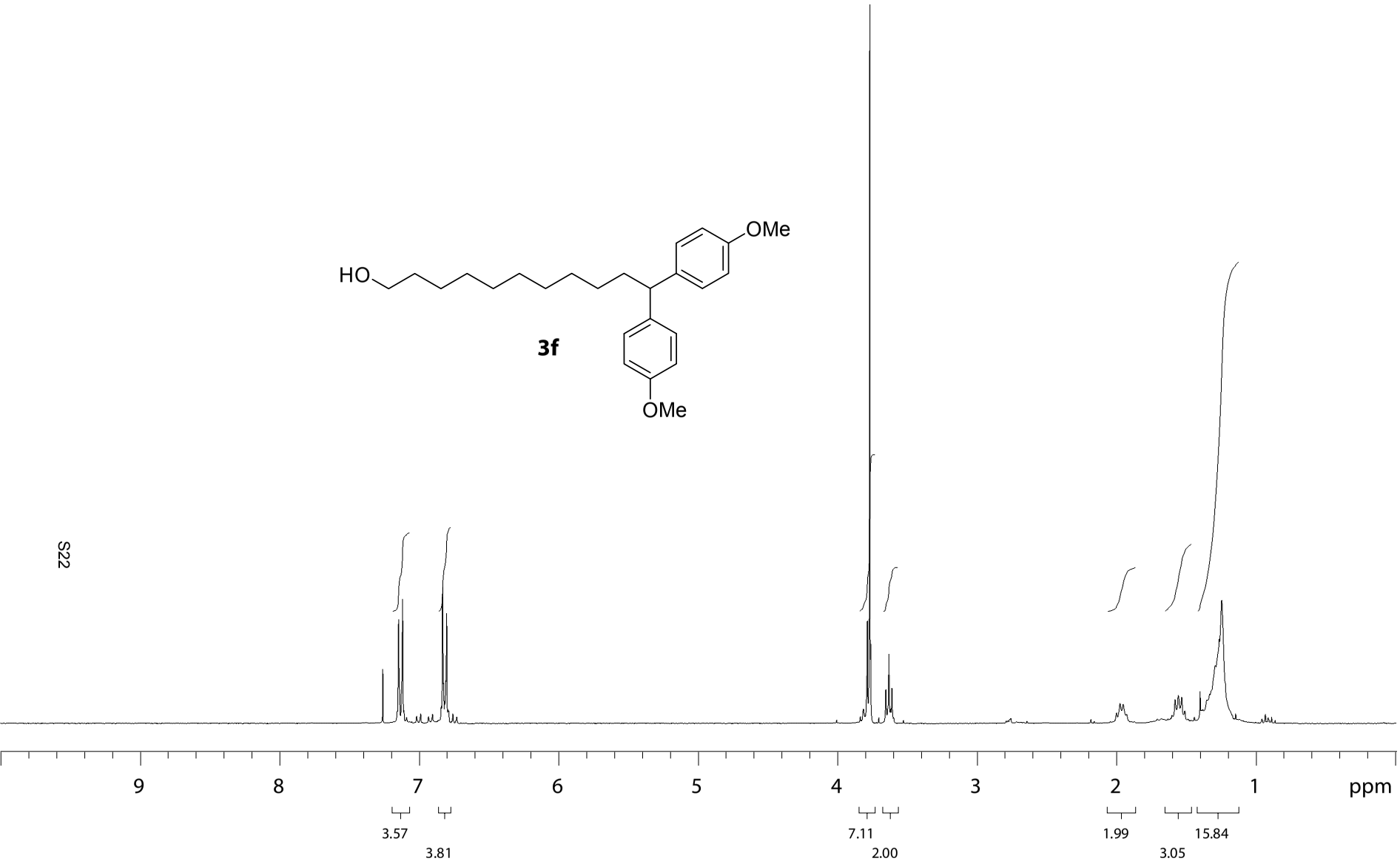
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OMe
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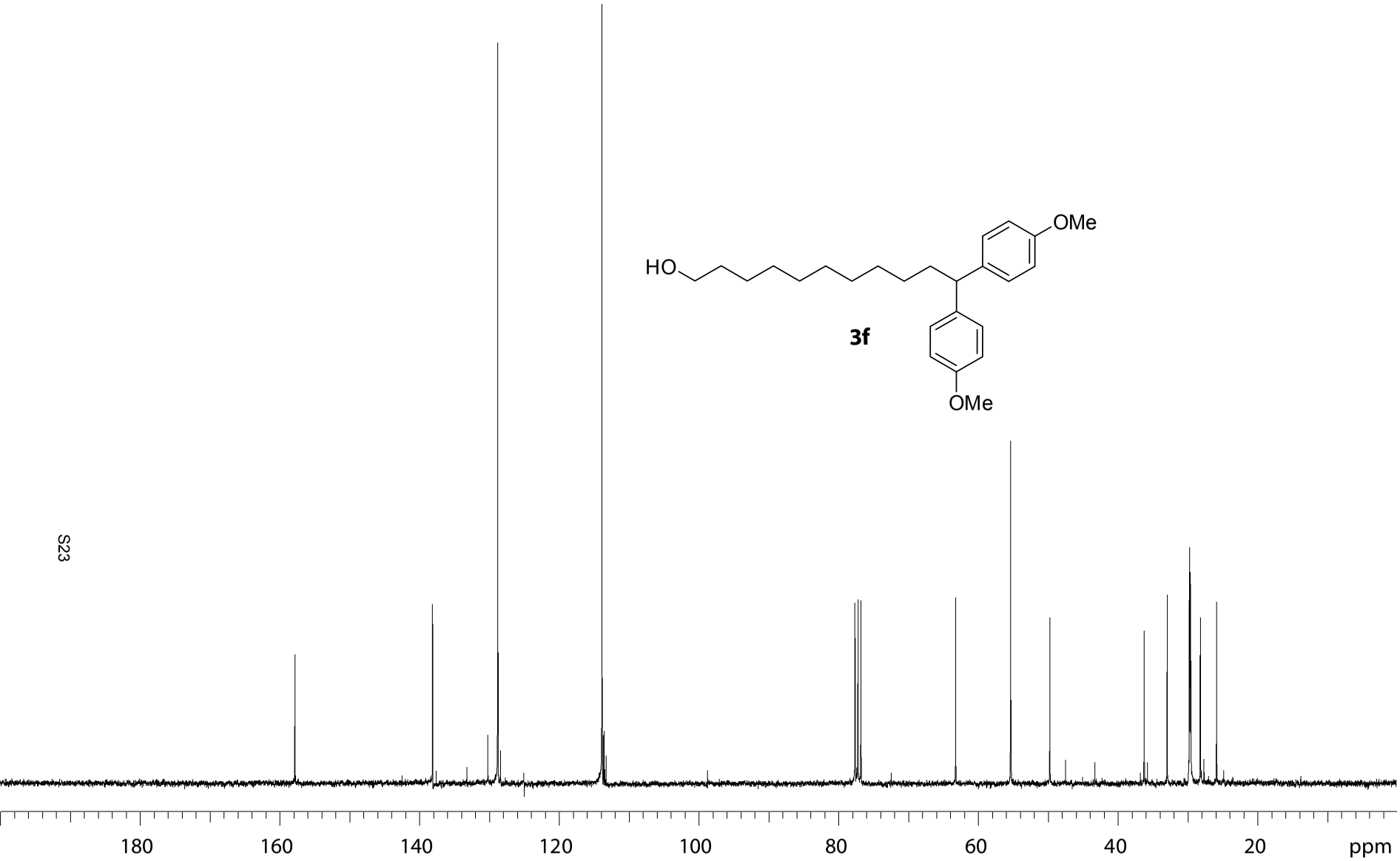
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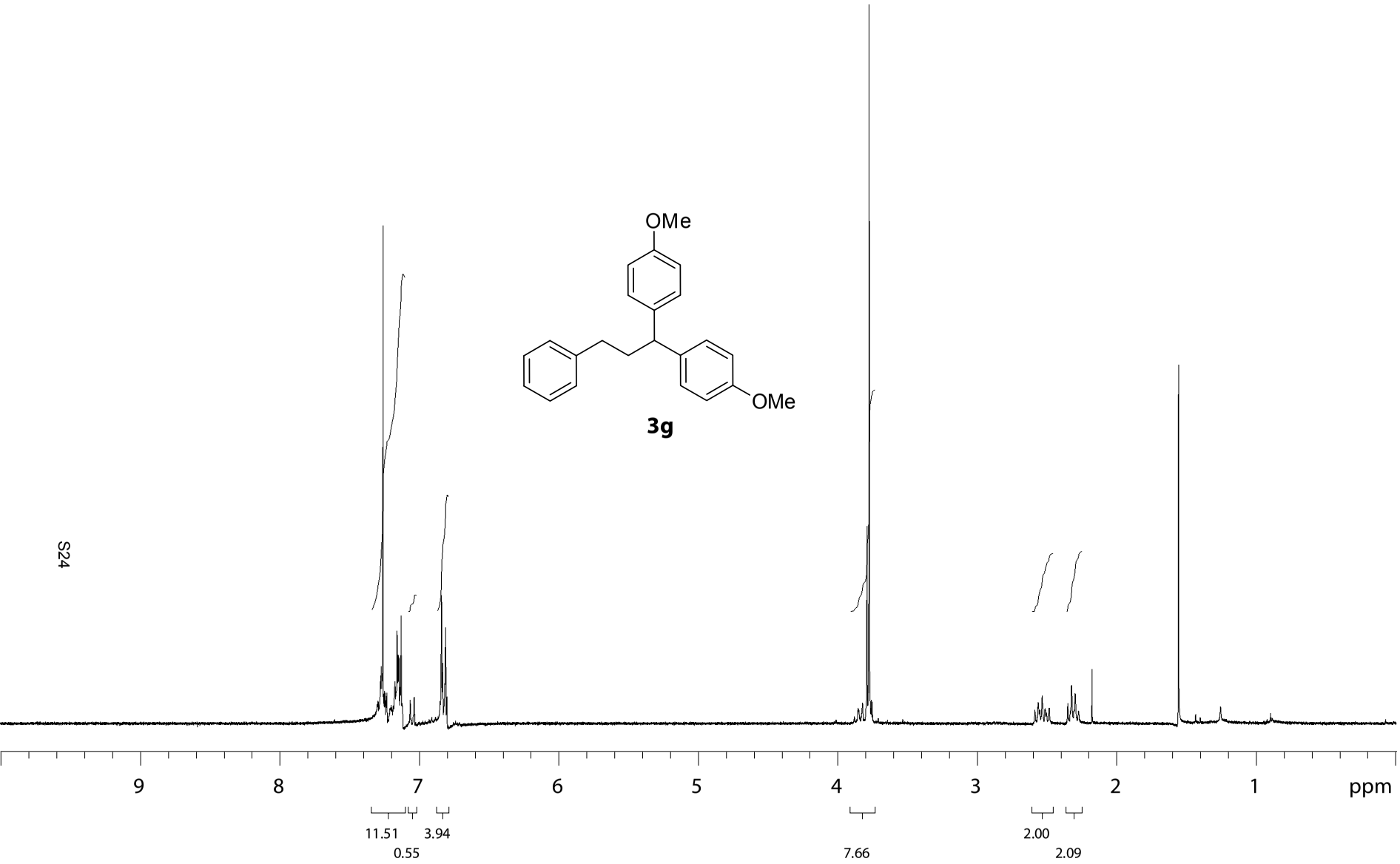
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OMe
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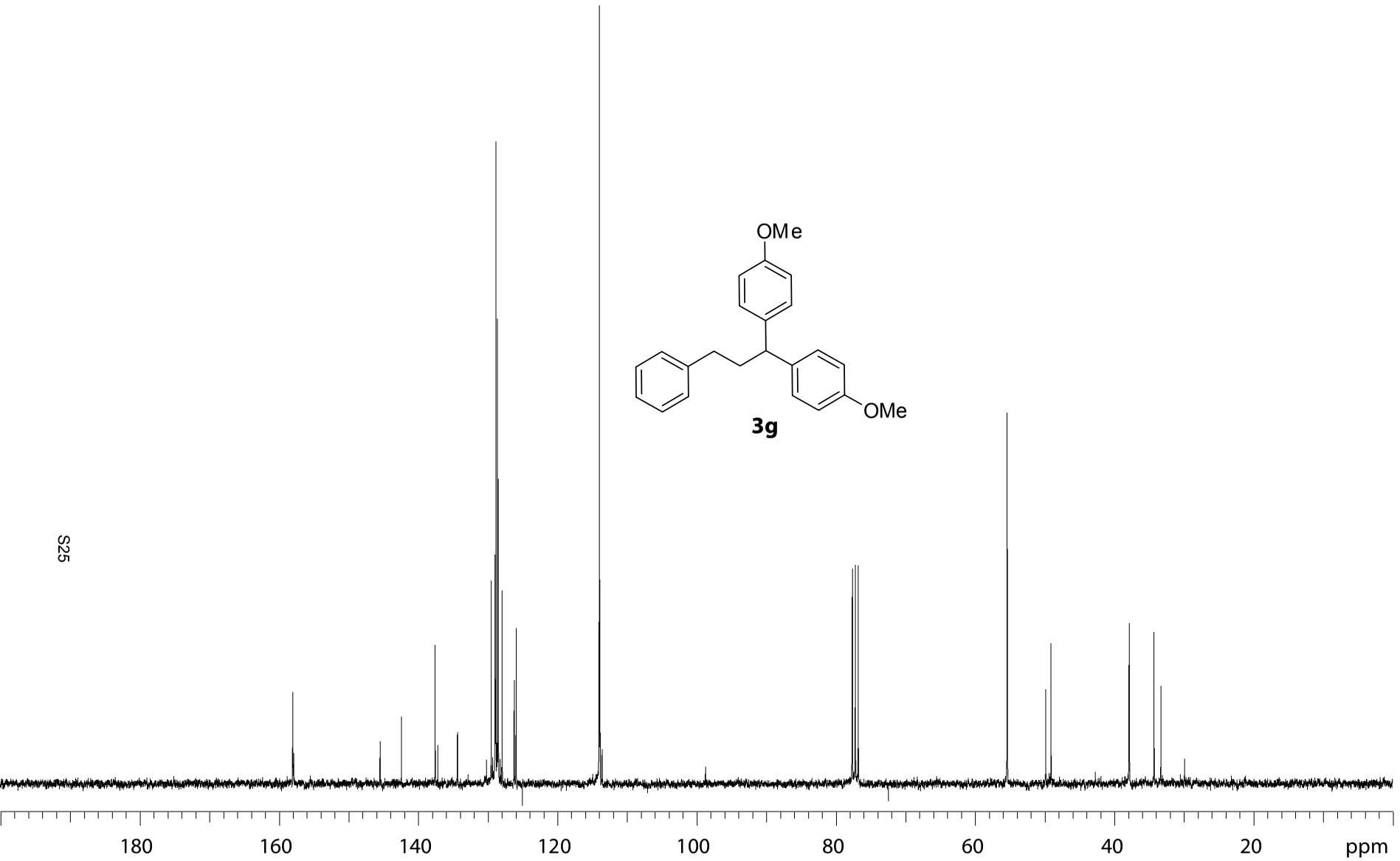
2.09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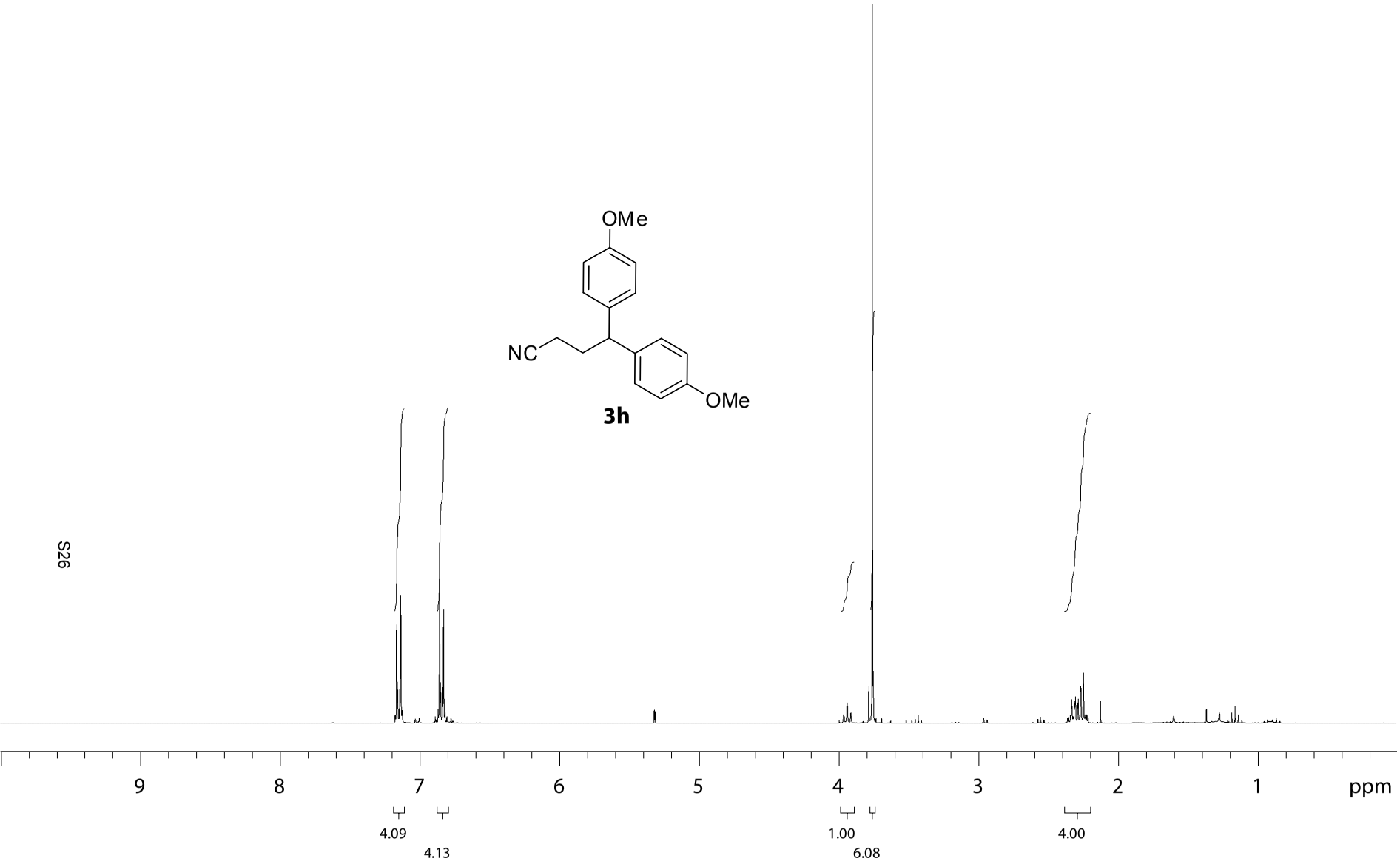
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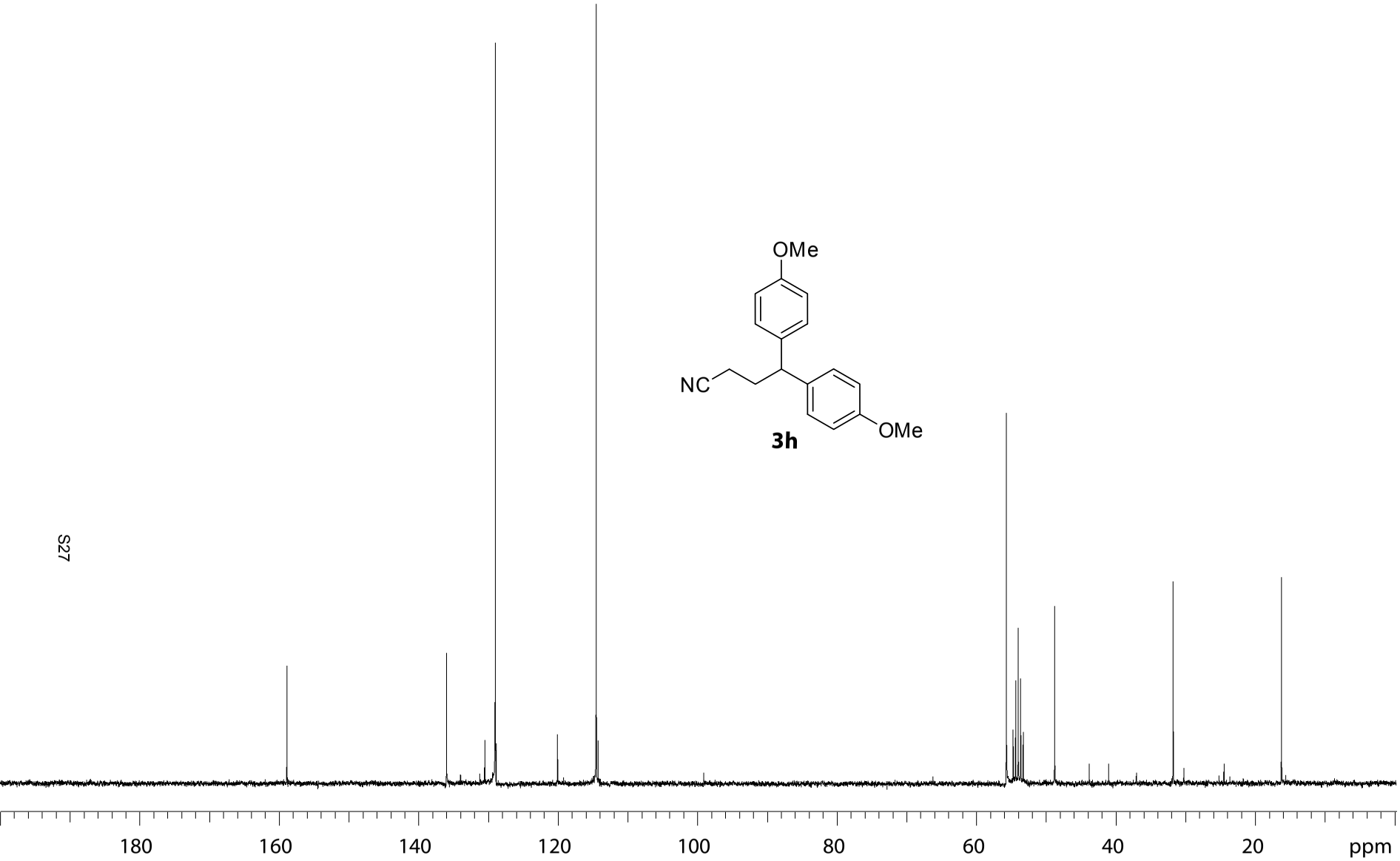
4.00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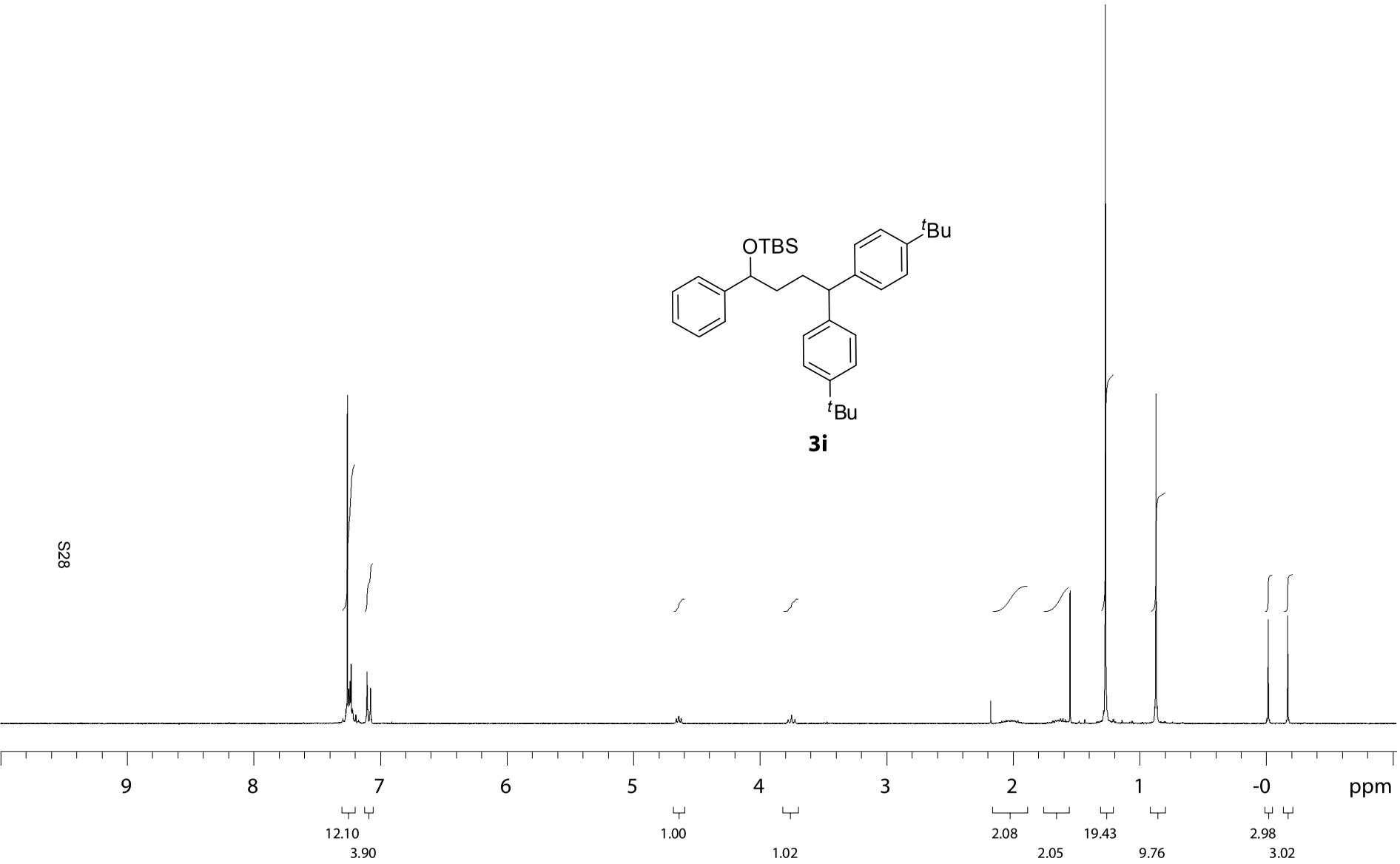
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tBu
3i
S28
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8
7
6
5
4
3
2
1
-0
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1.00
1.02
2.08
2.05
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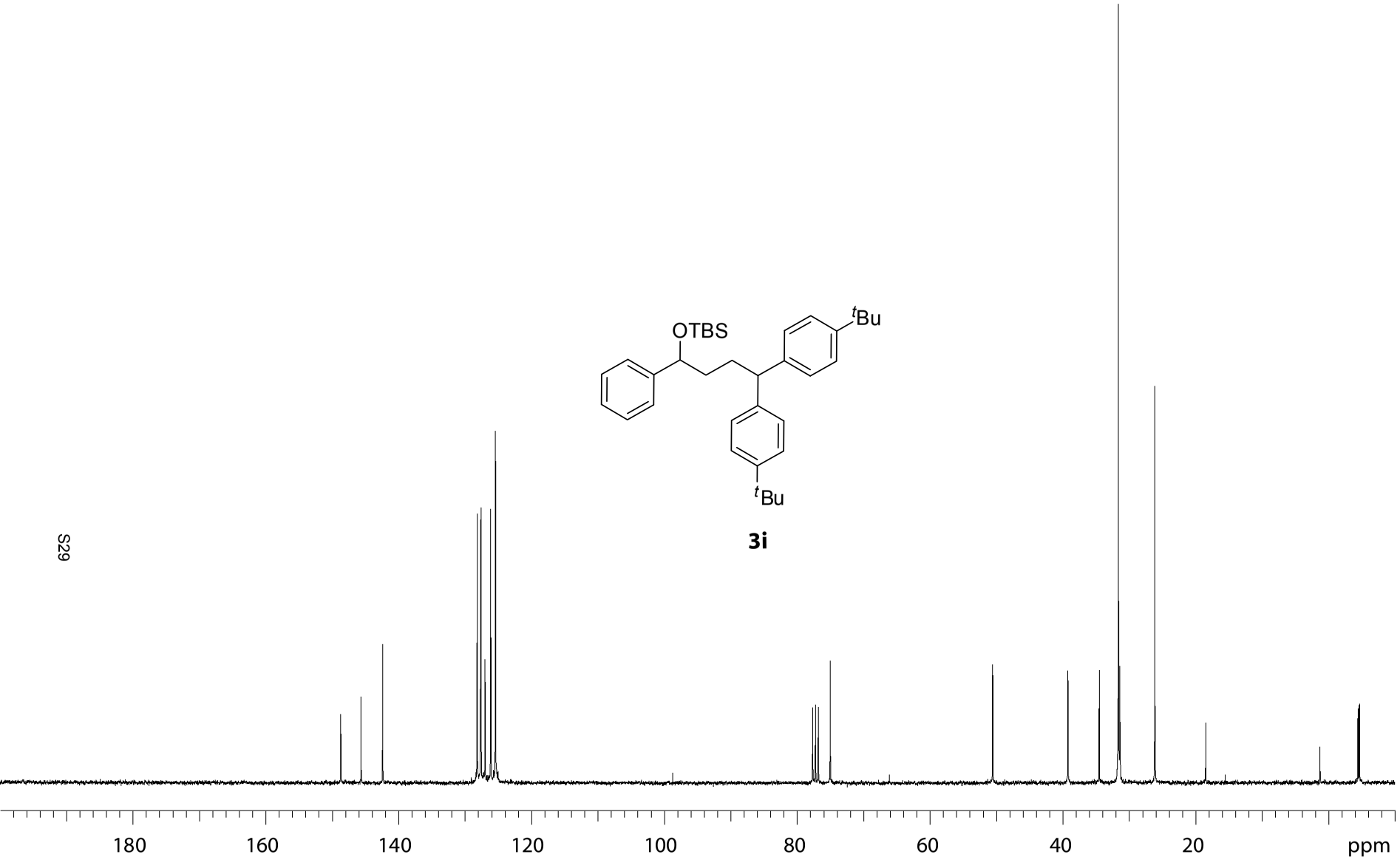
9.76
2.98
3.02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tBu
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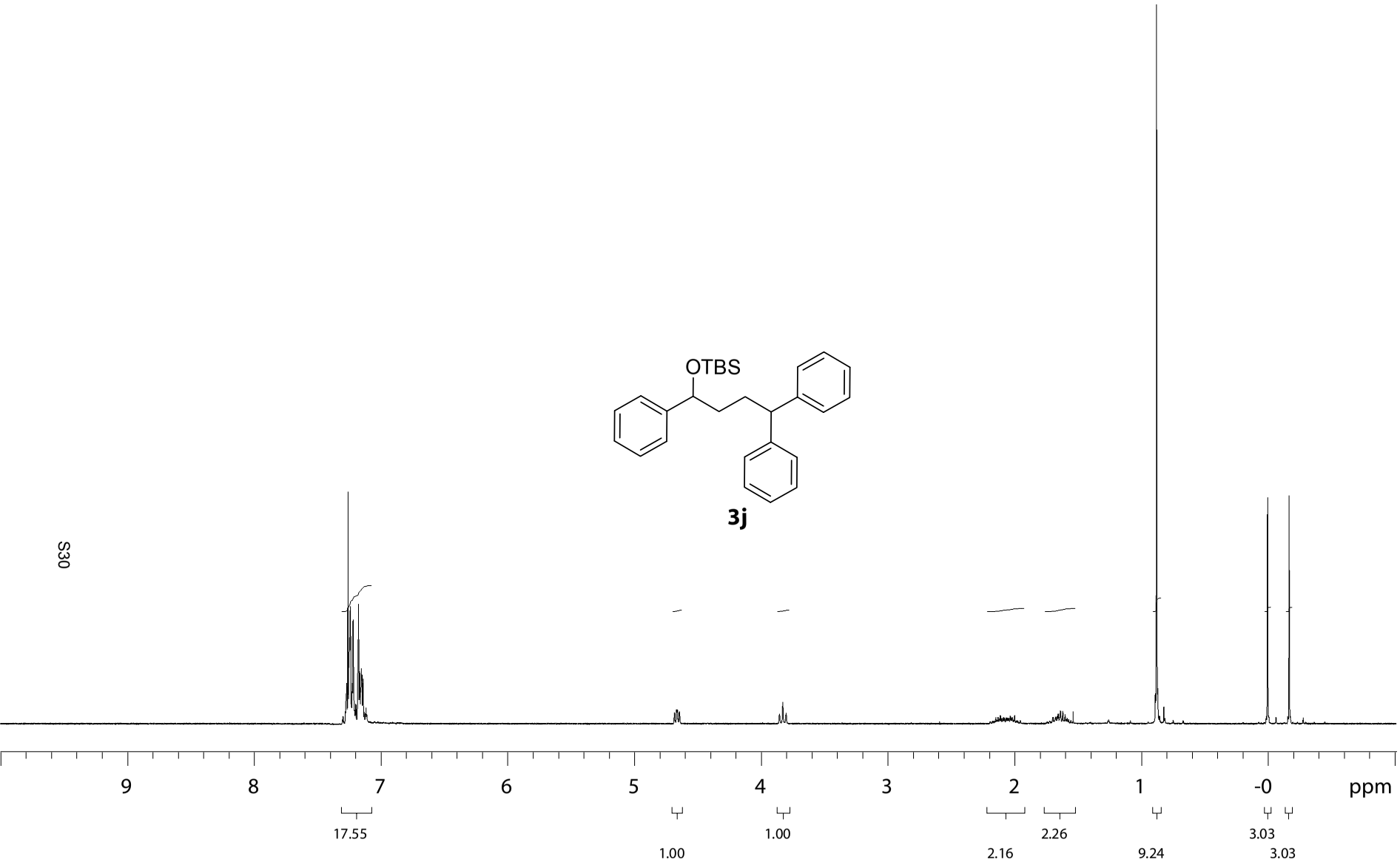
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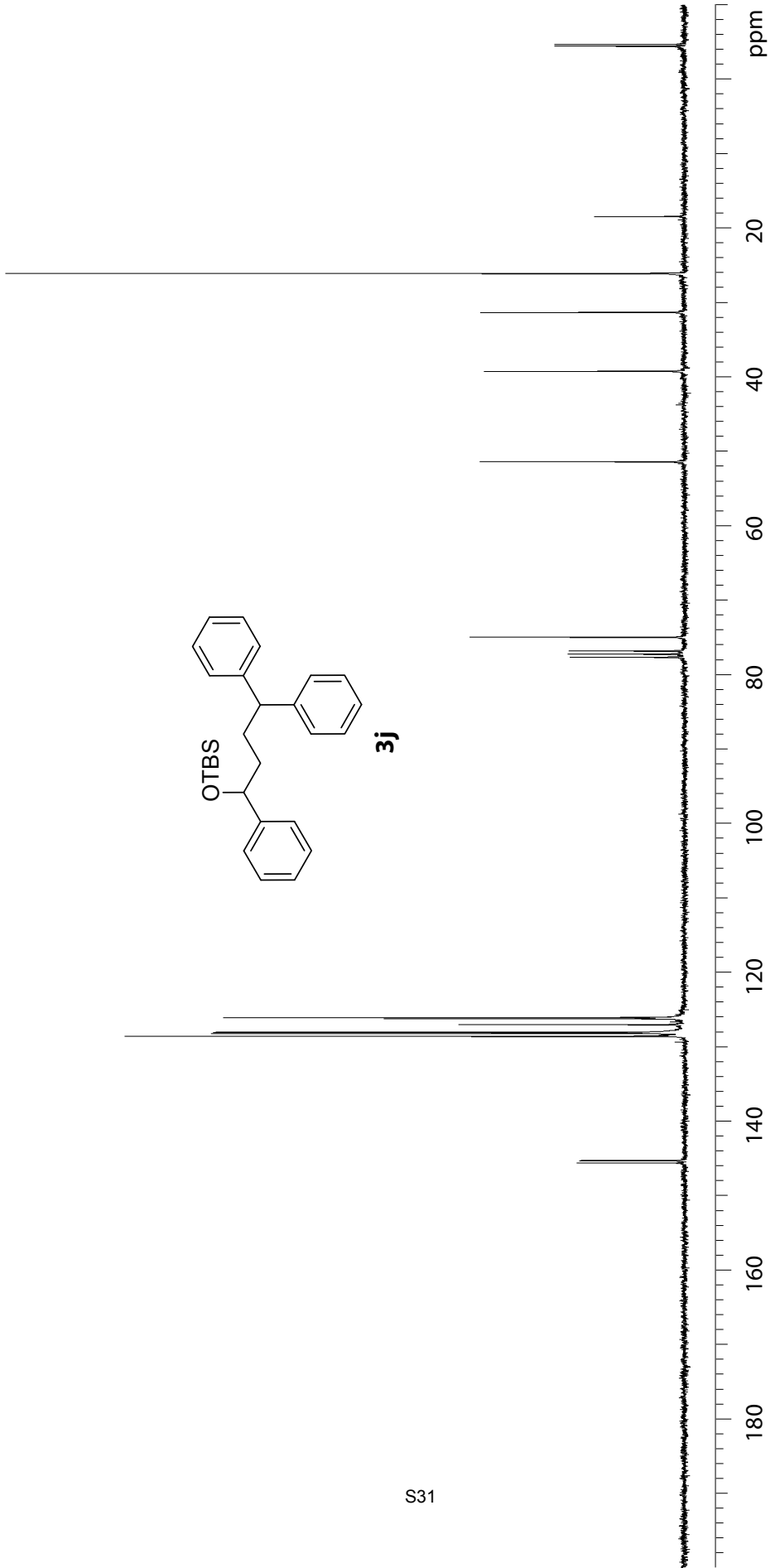
3.03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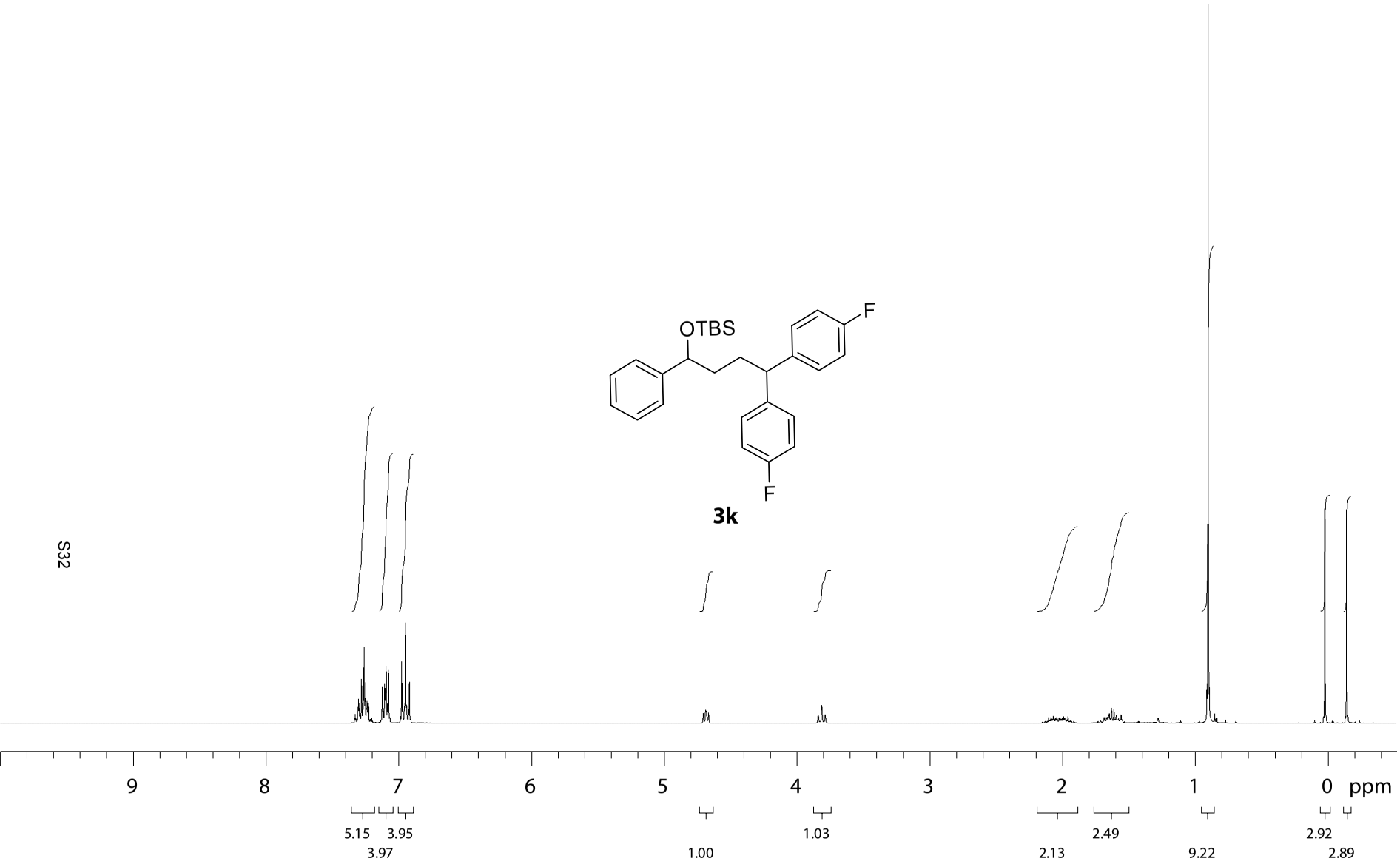
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F
3k
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8
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6
5
4
3
2
1
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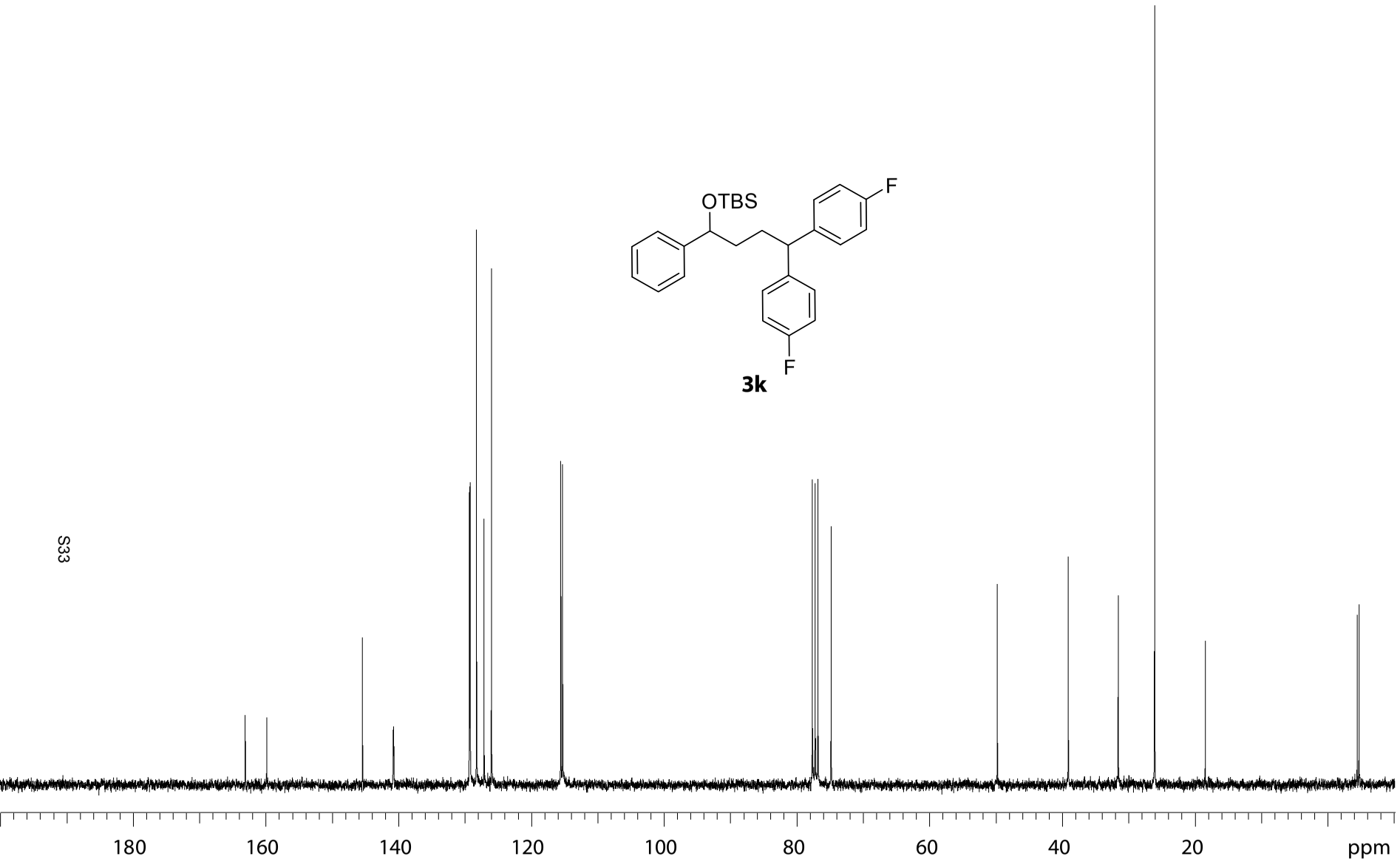
3.97
1.00
1.03
2.13
2.49
9.22
2.92
2.89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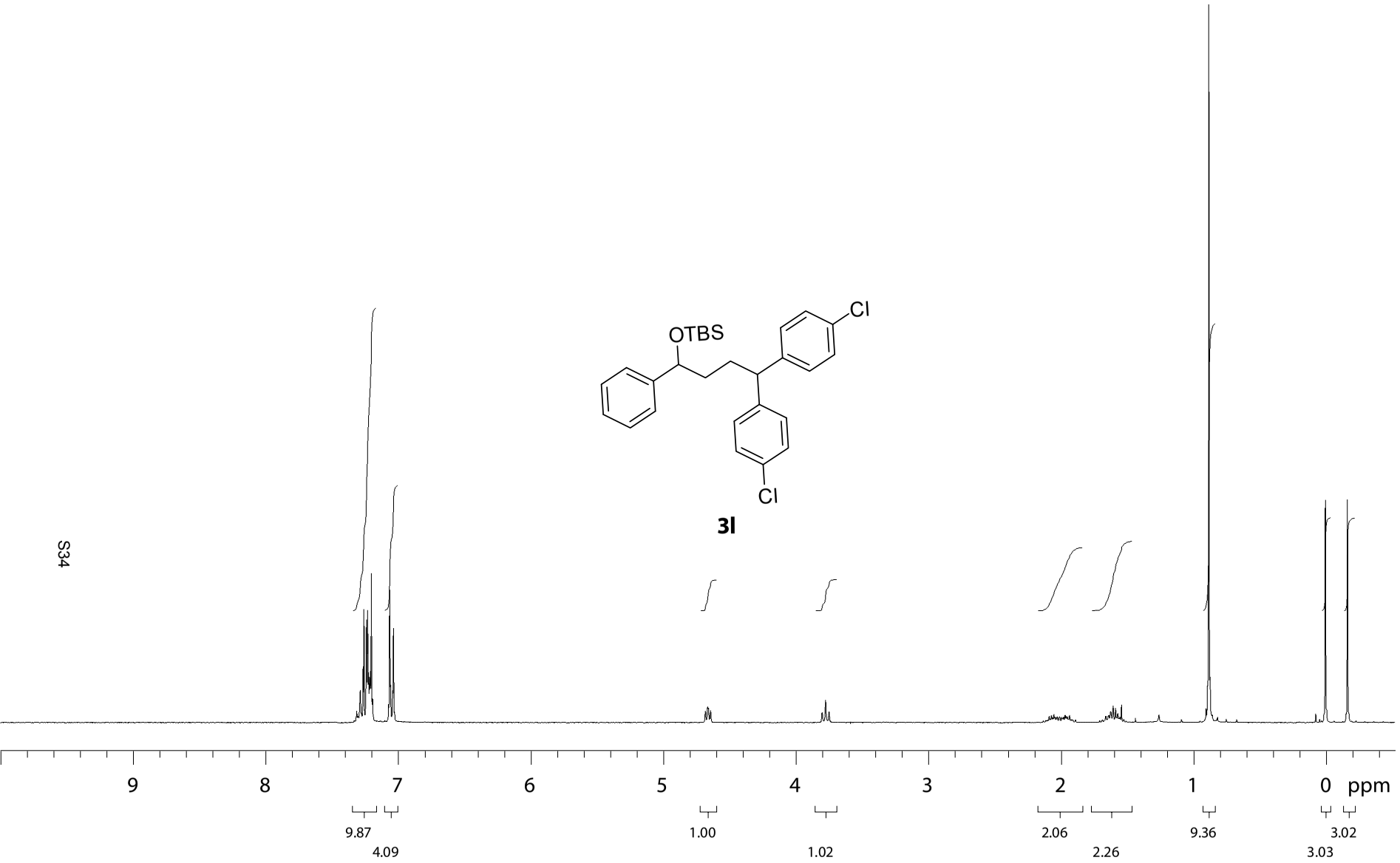
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Cl
Cl
3l
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7
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5
4
3
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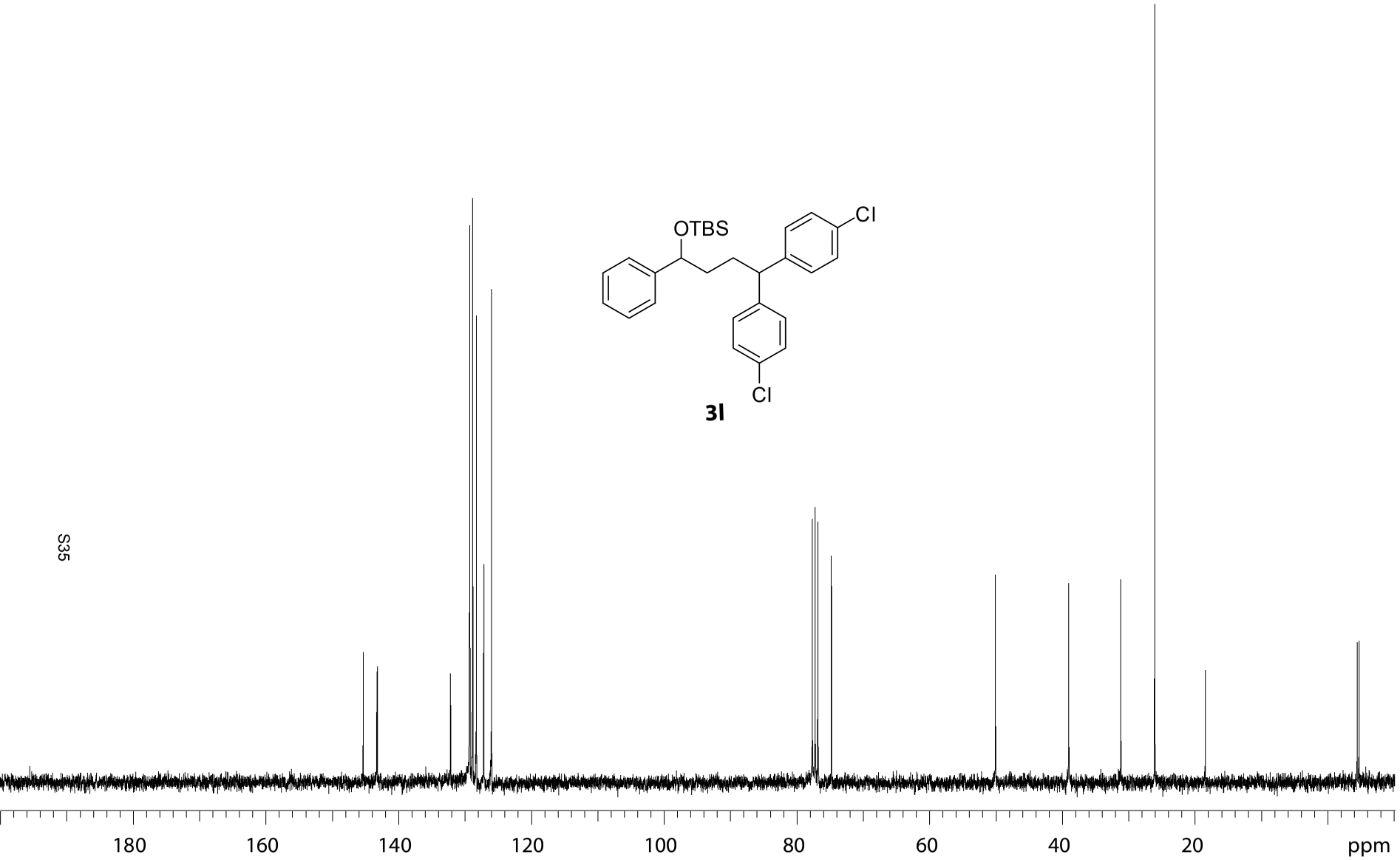
1.02
2.06
2.26
9.36
3.02
3.03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Cl
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60
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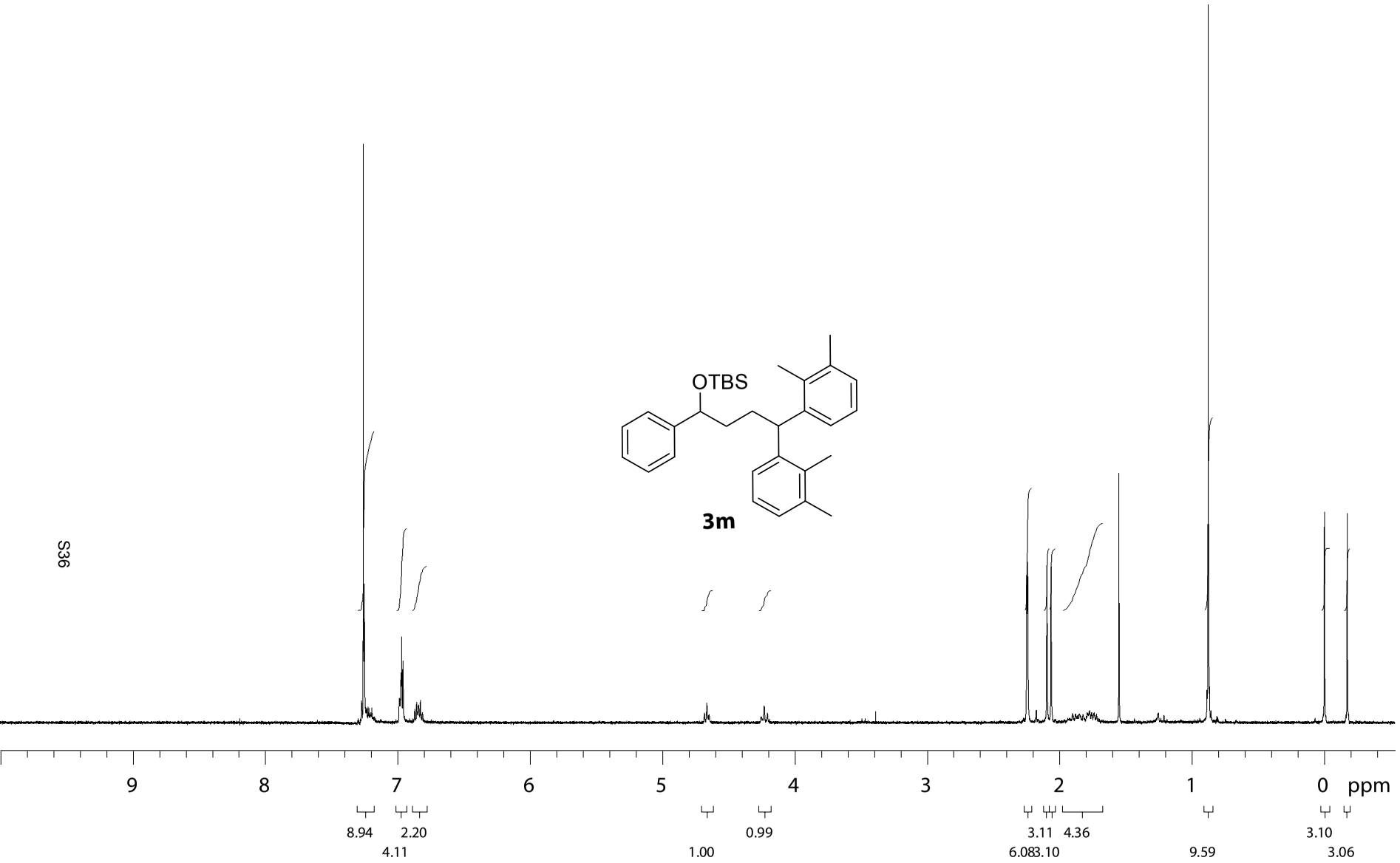
ppm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3m
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7
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5
4
3
2
1
0
ppm
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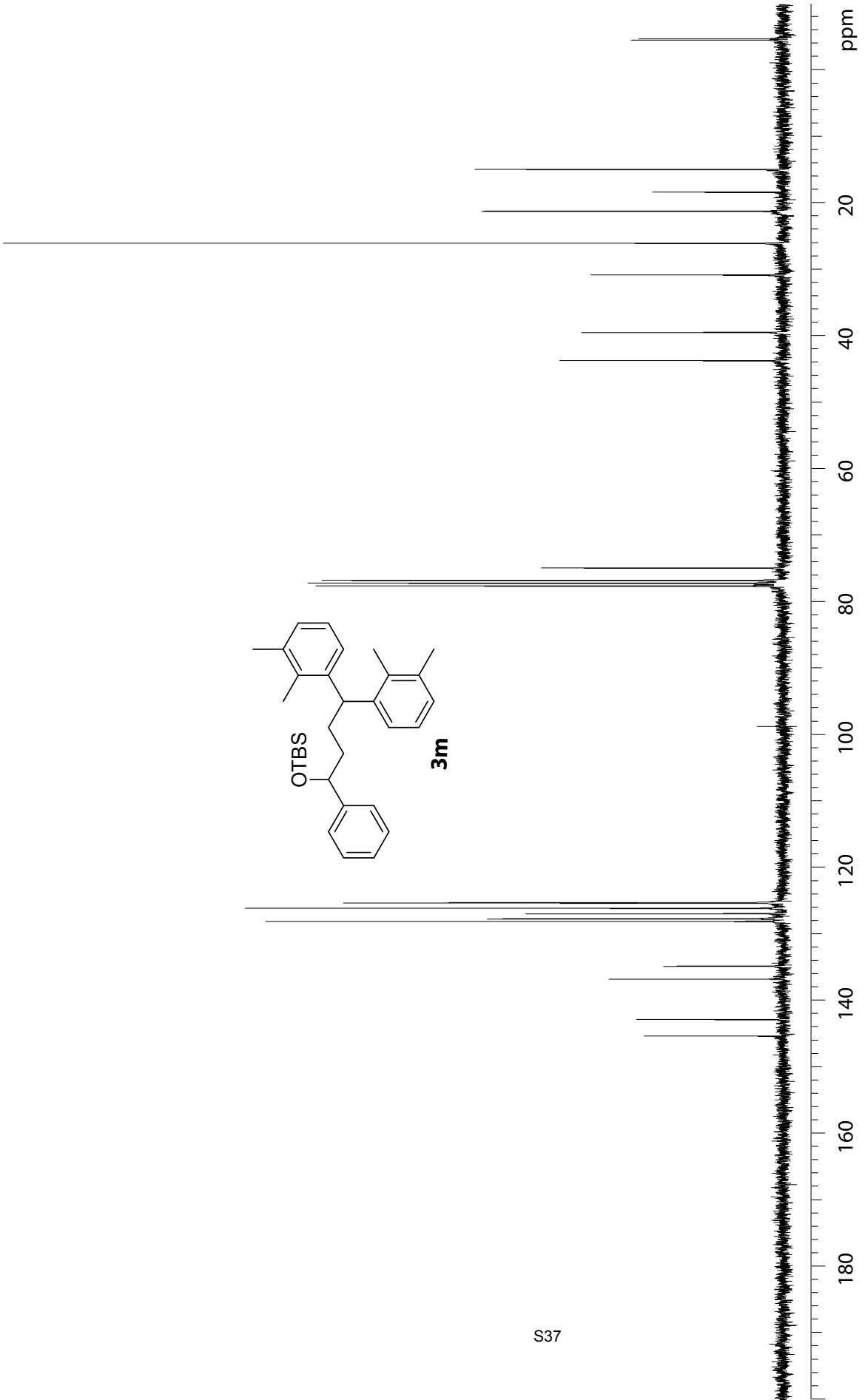
6.08
3.10
9.59
3.10
3.06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ppm
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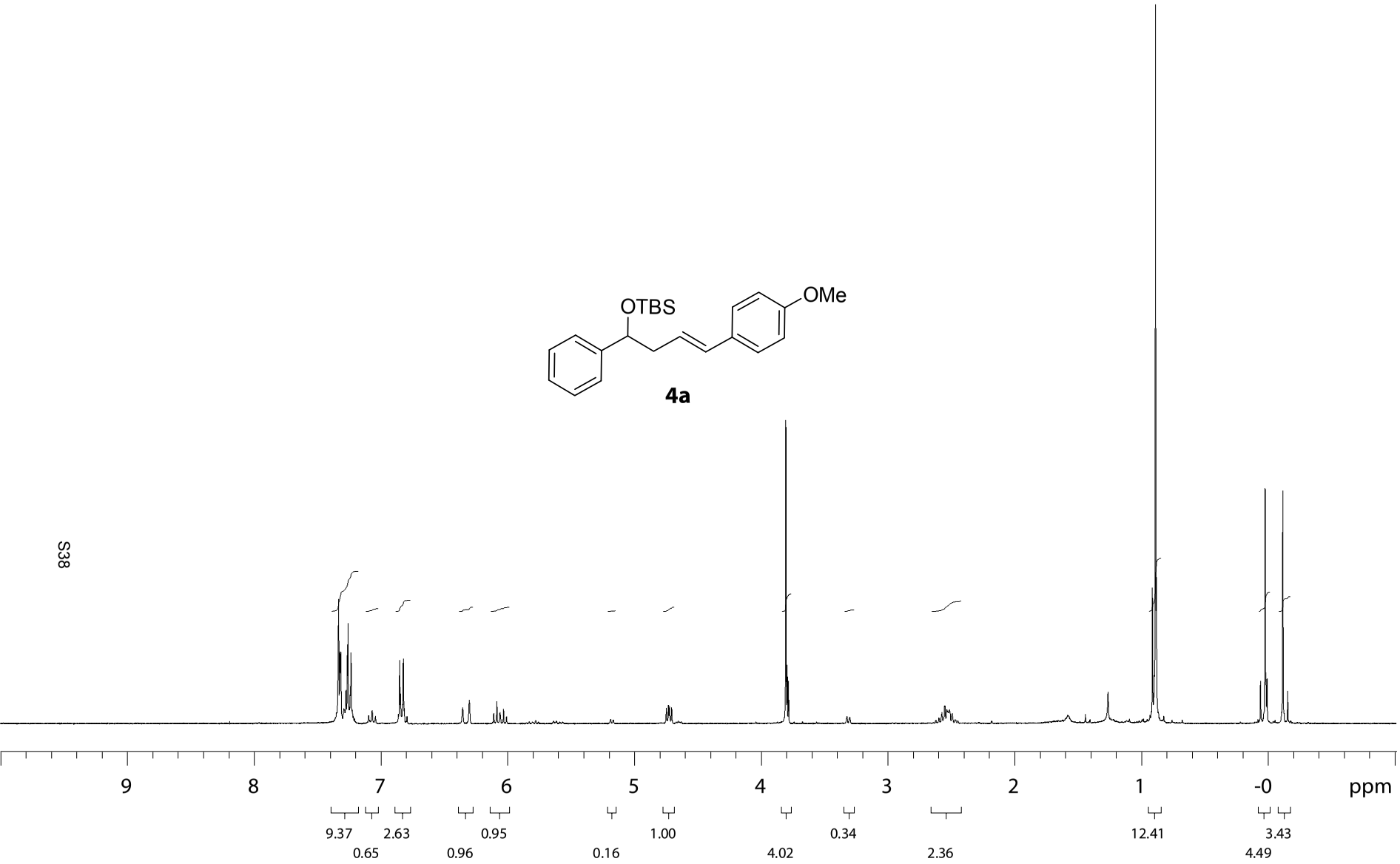
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6
5
4
3
2
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-0
ppm
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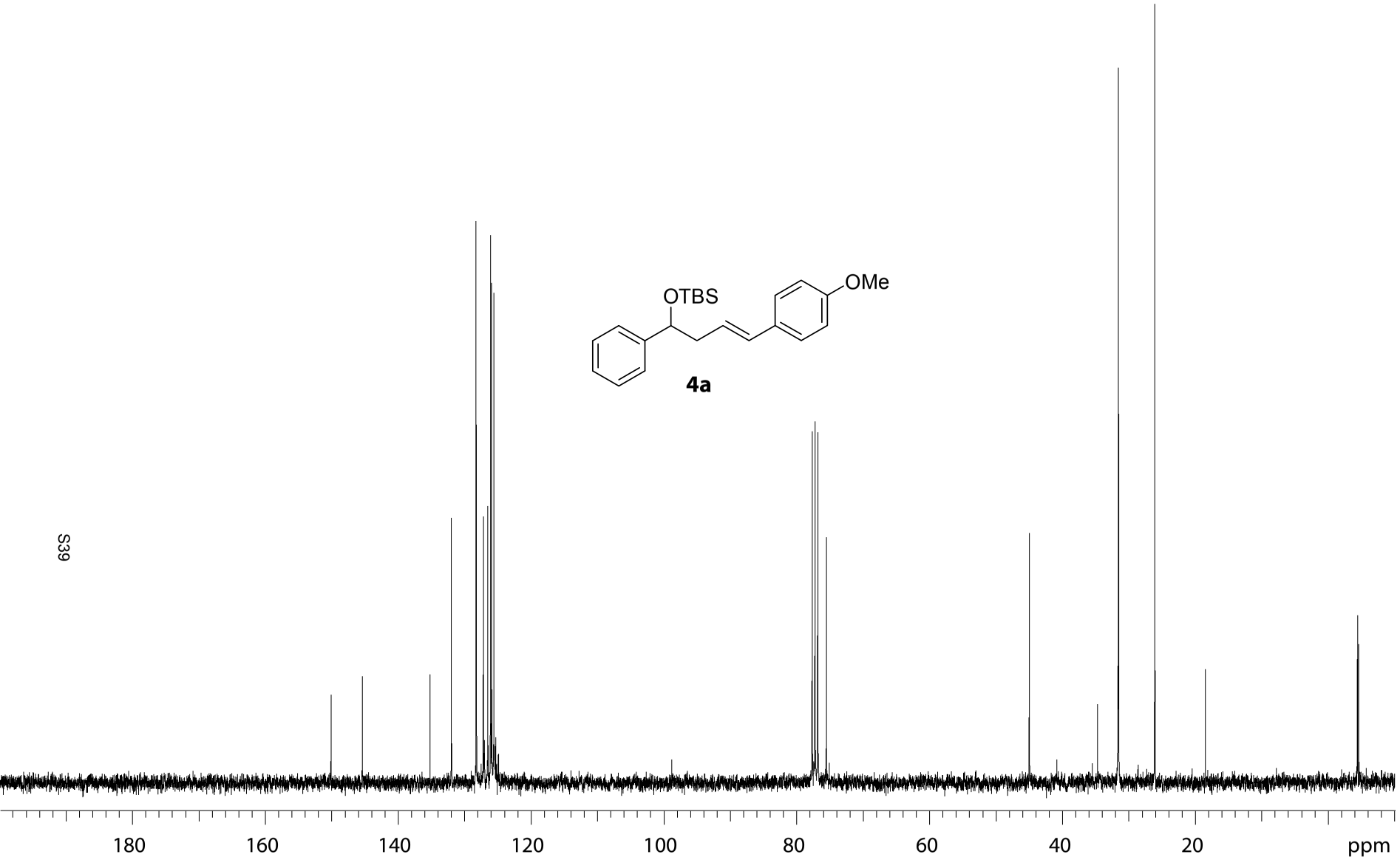
4.49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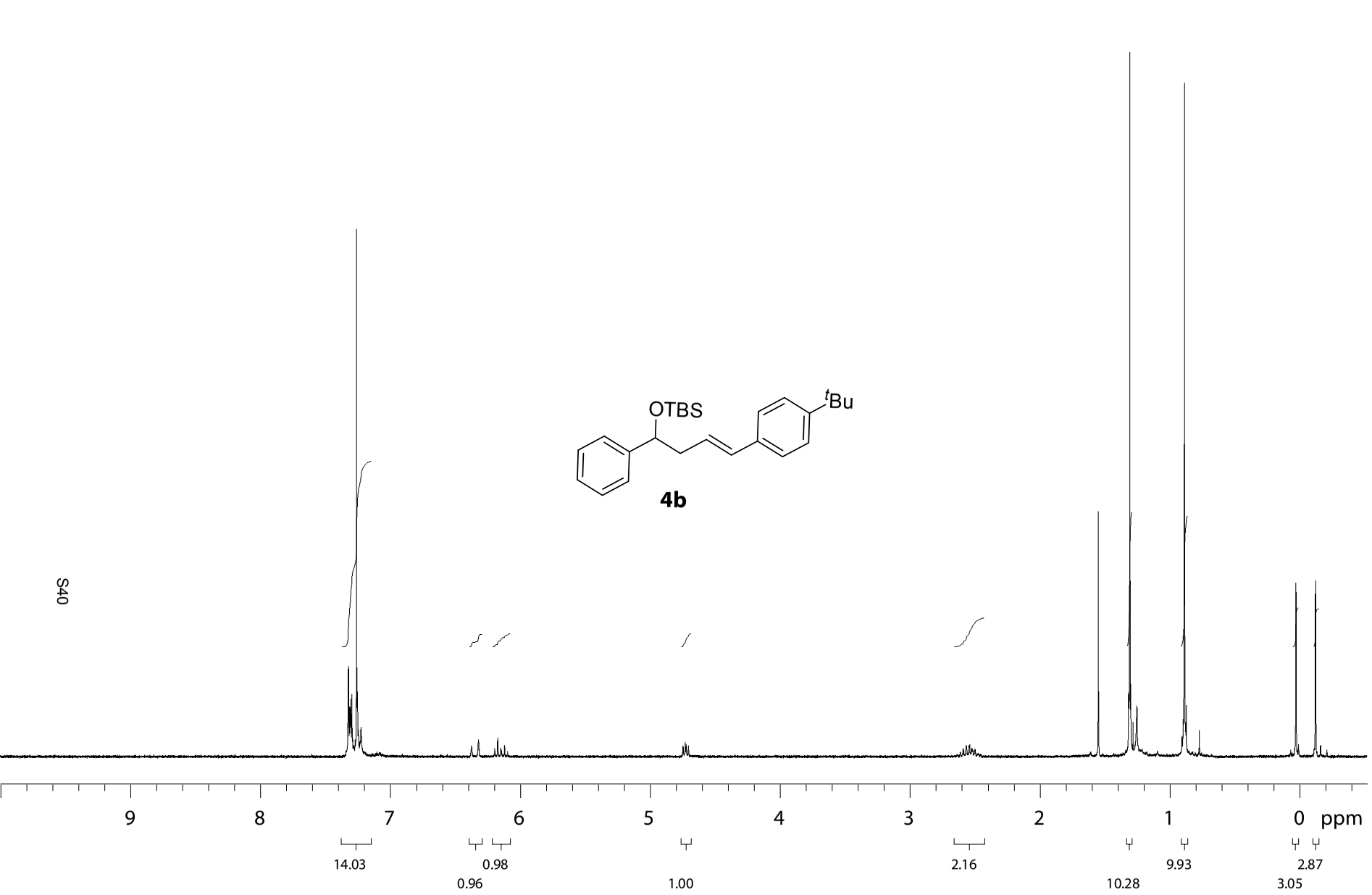
20
ppm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1.00
2.16
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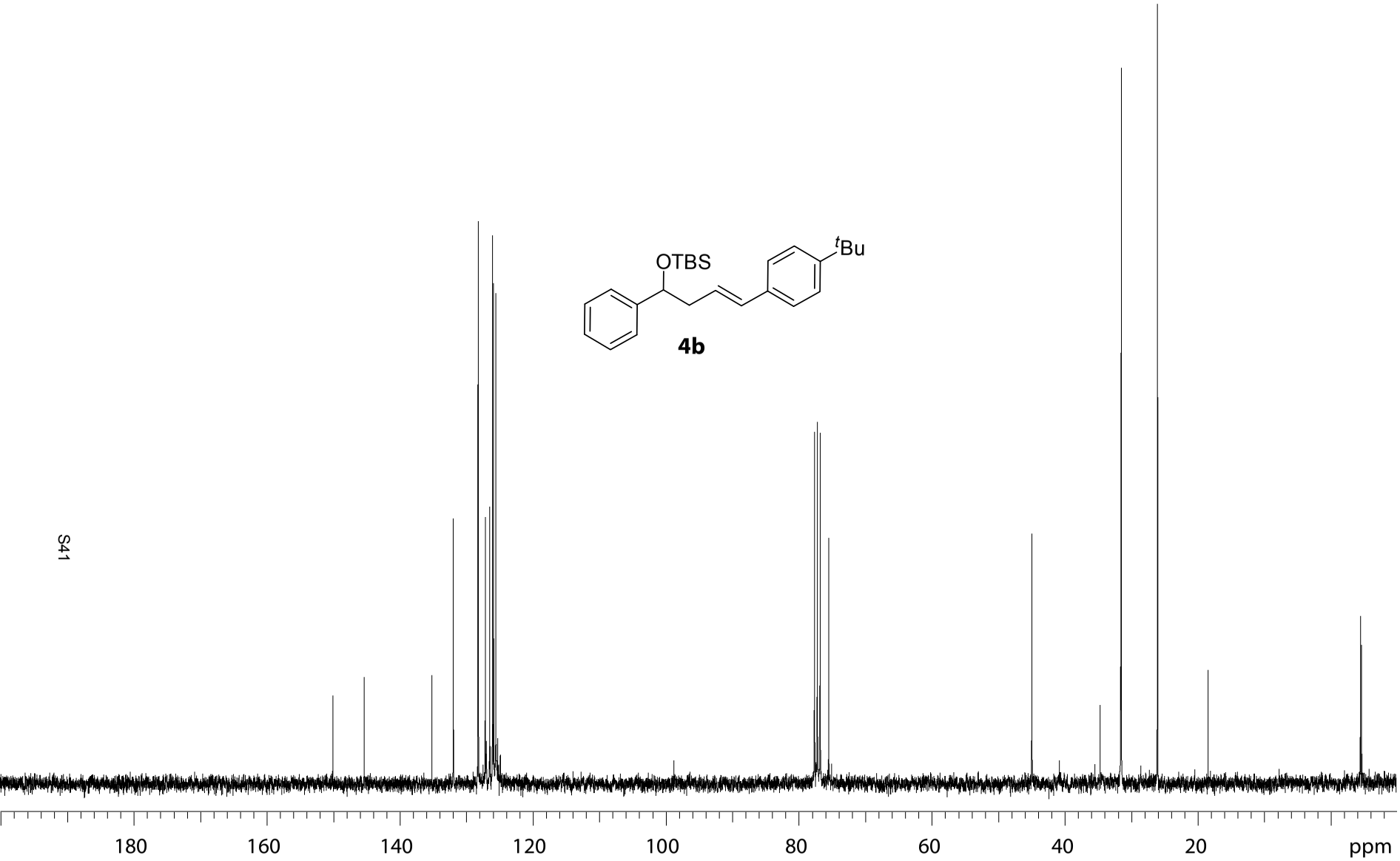
3.05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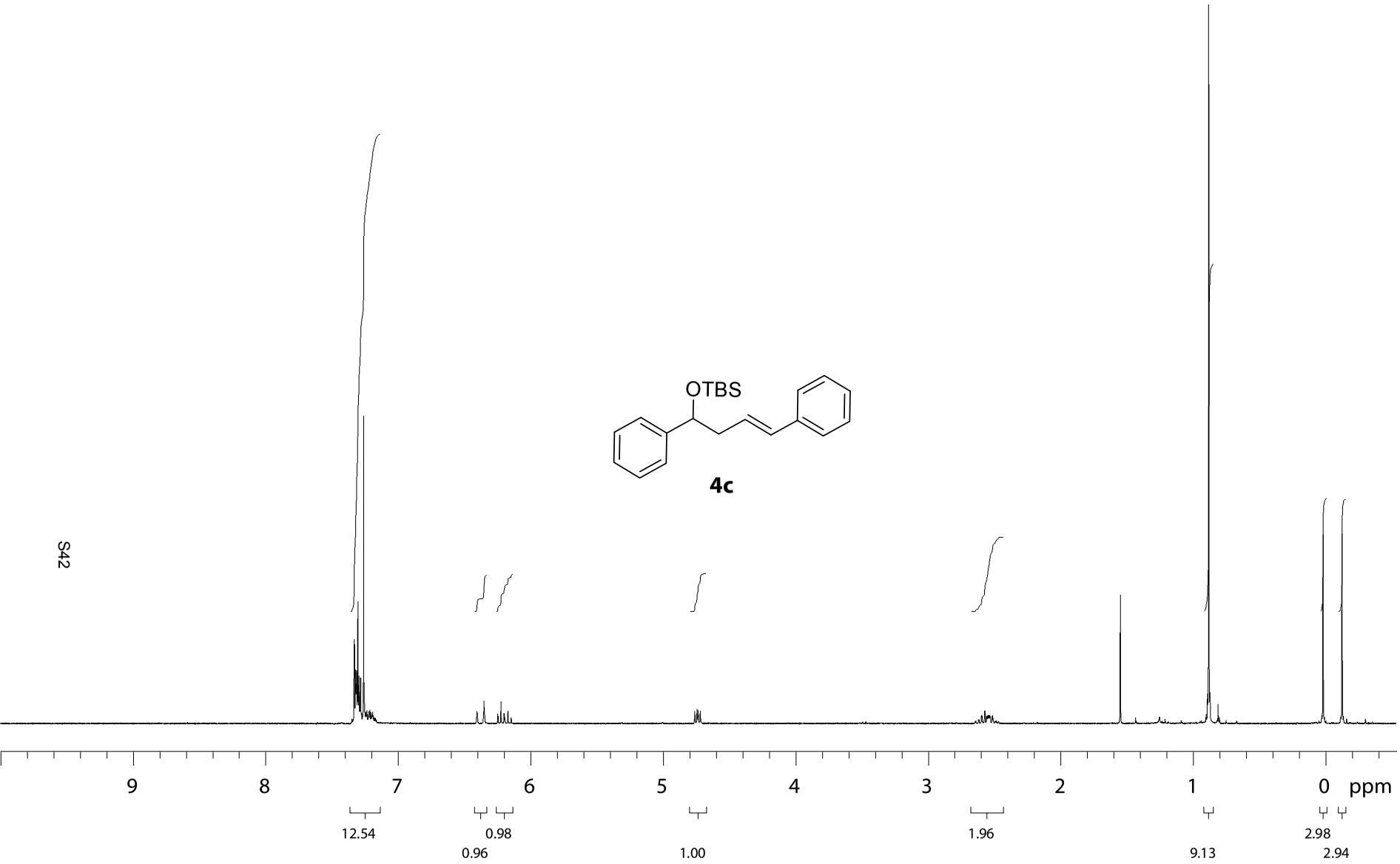
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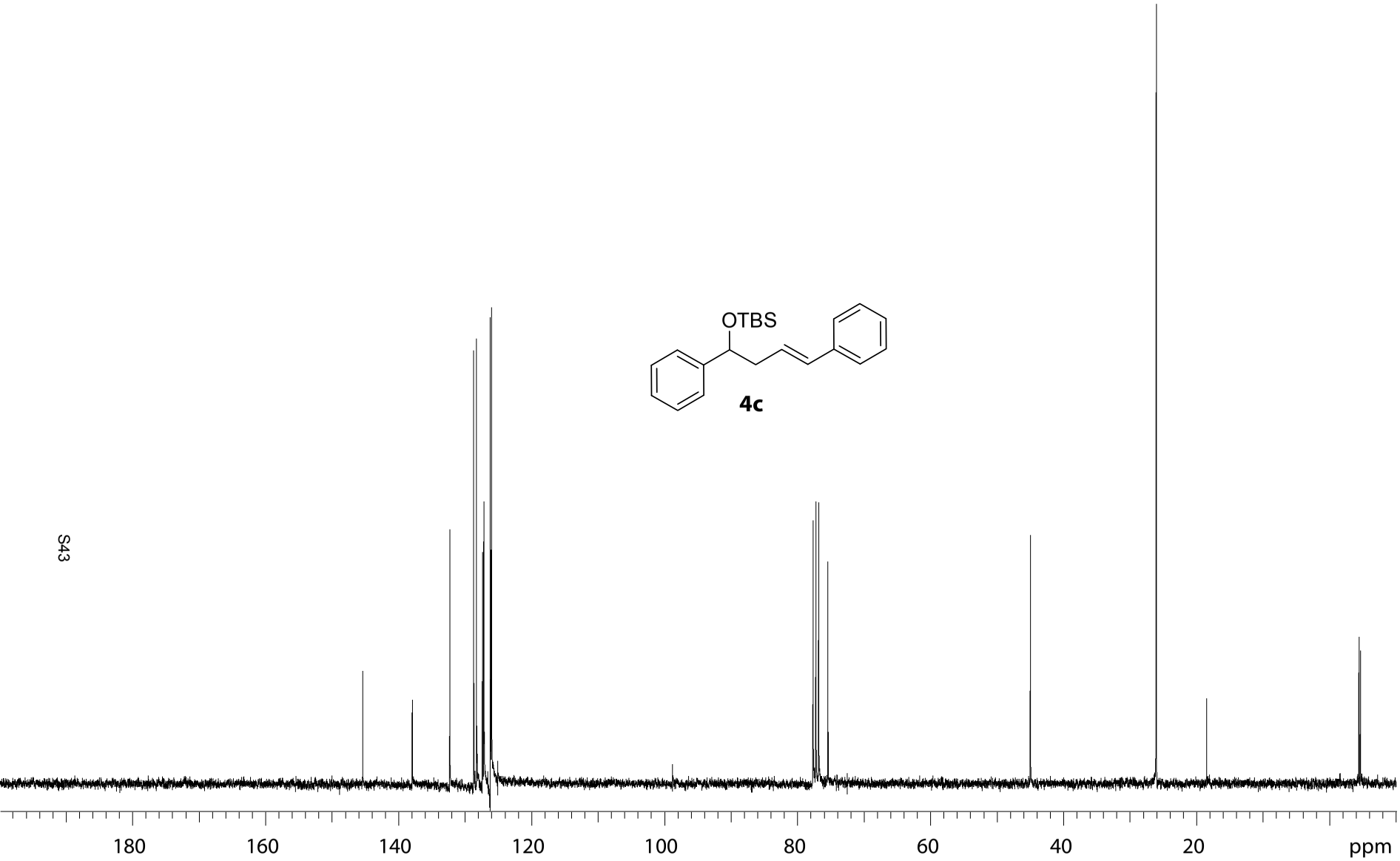
2.98
2.94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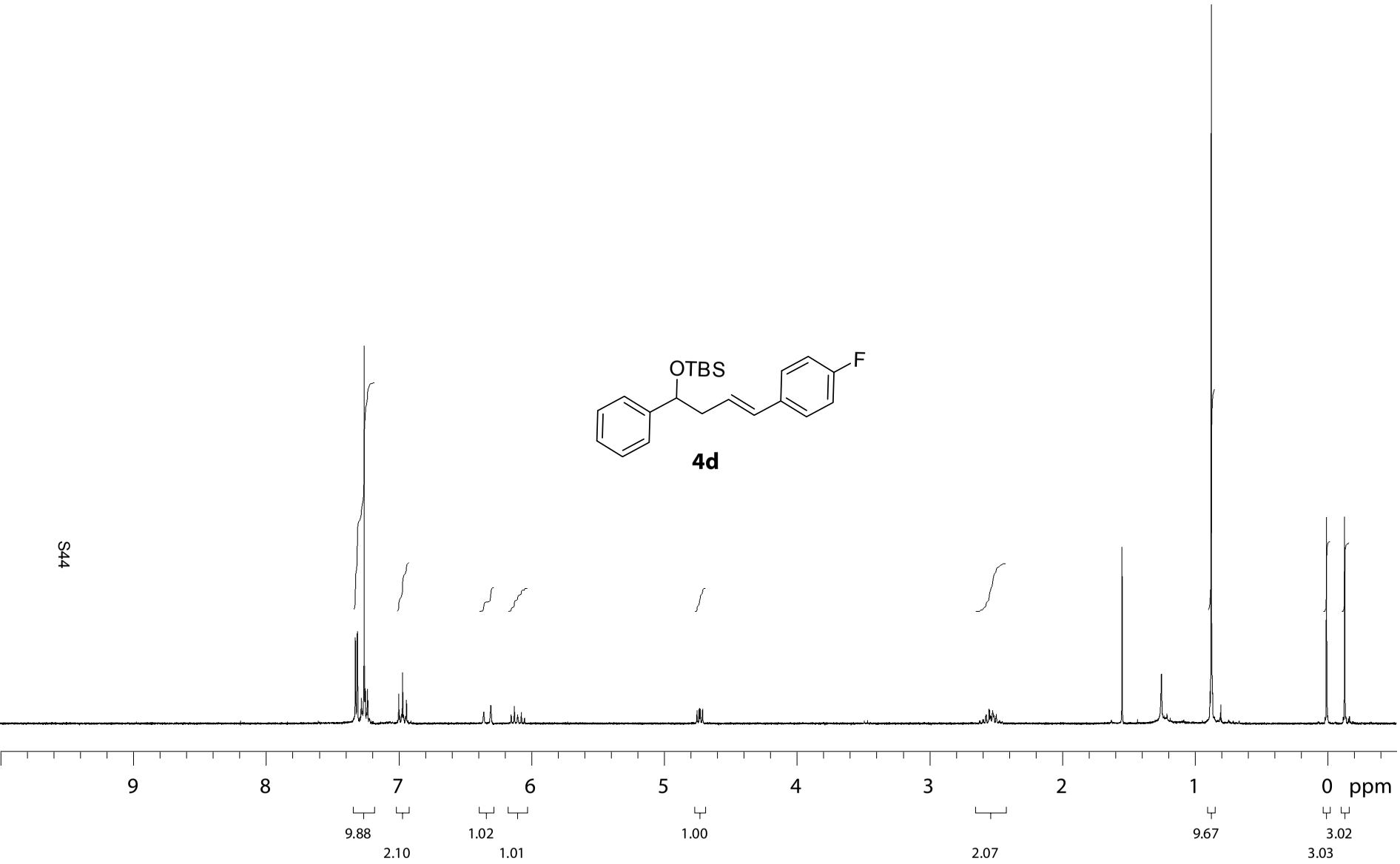
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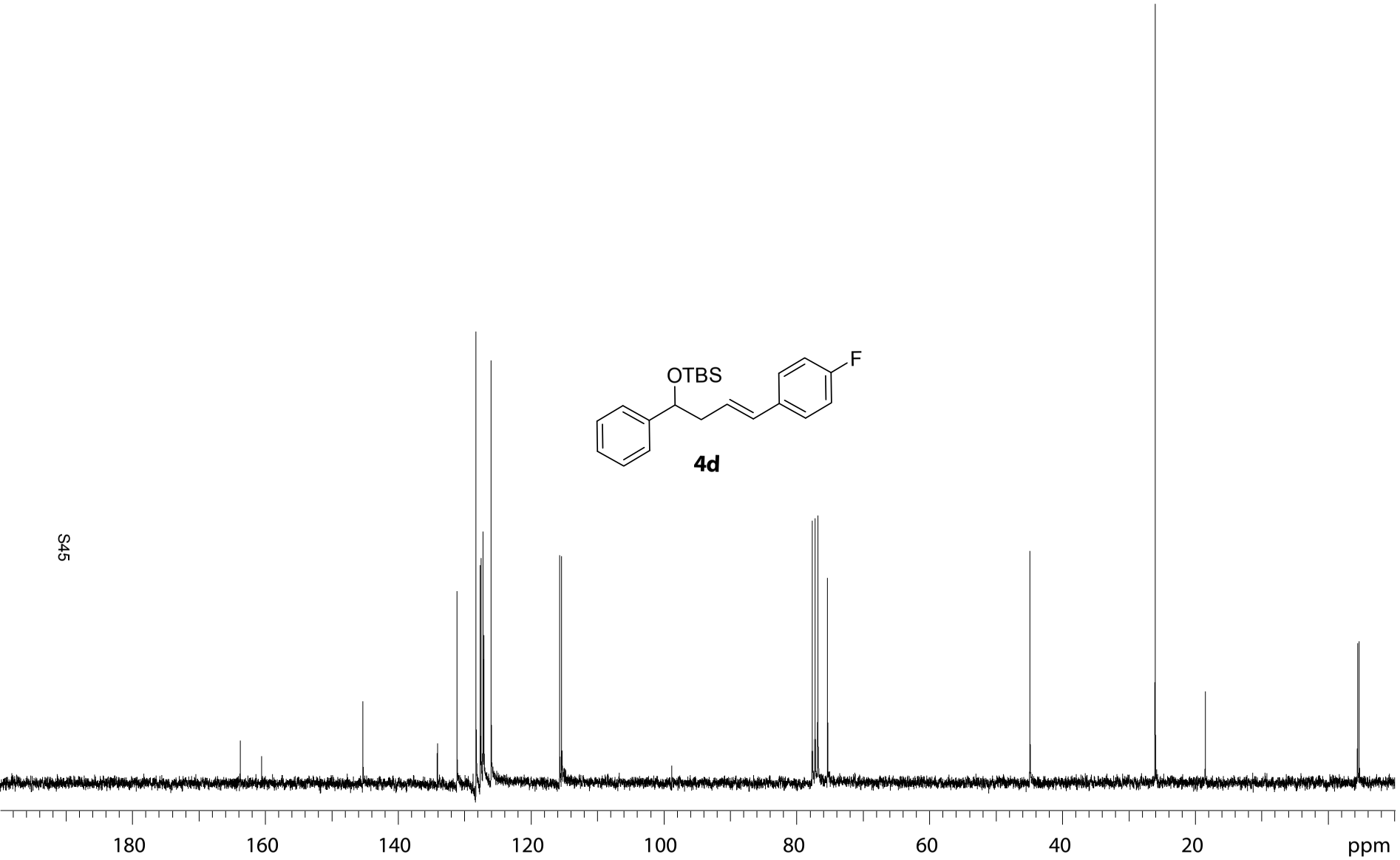
3.03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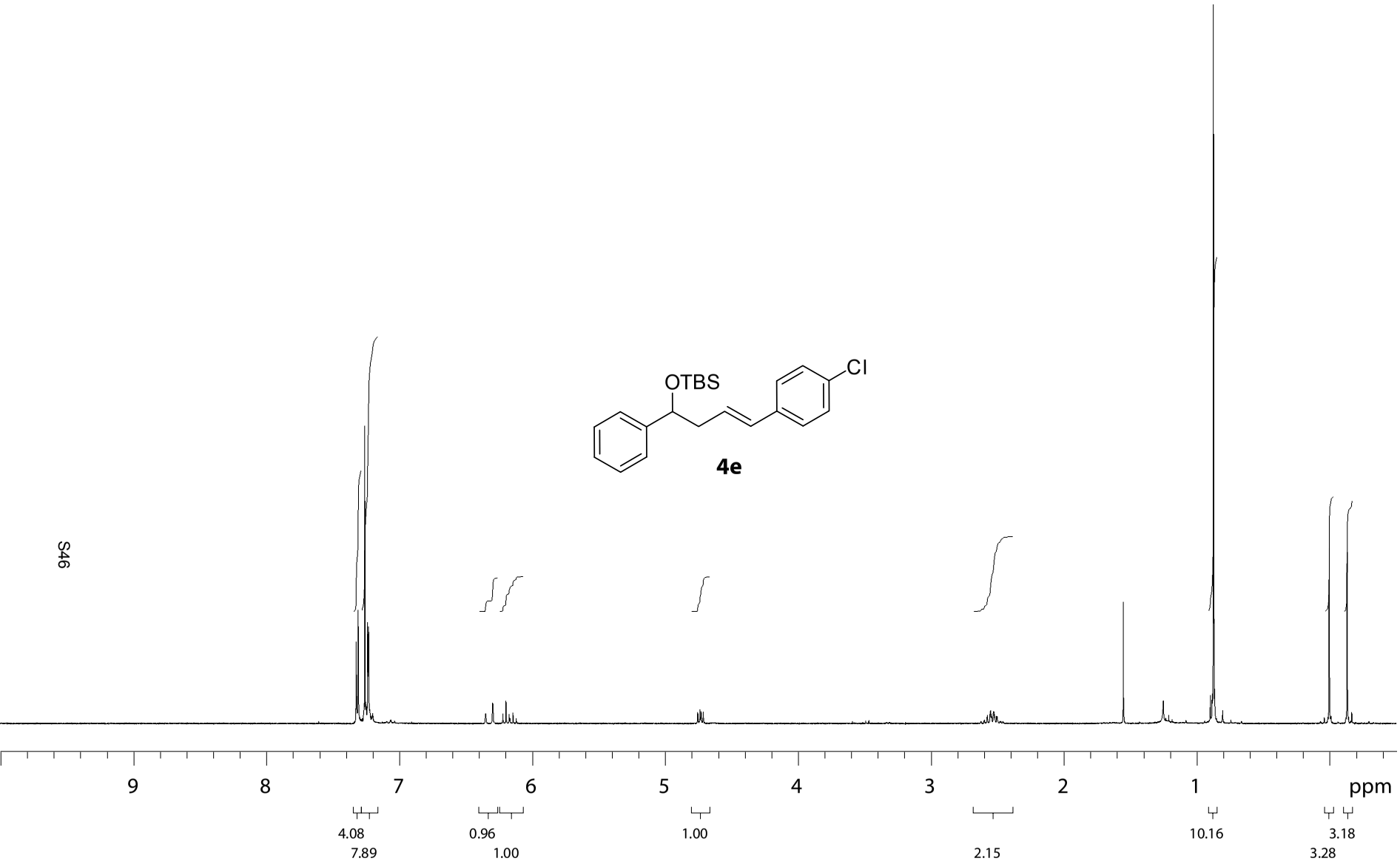
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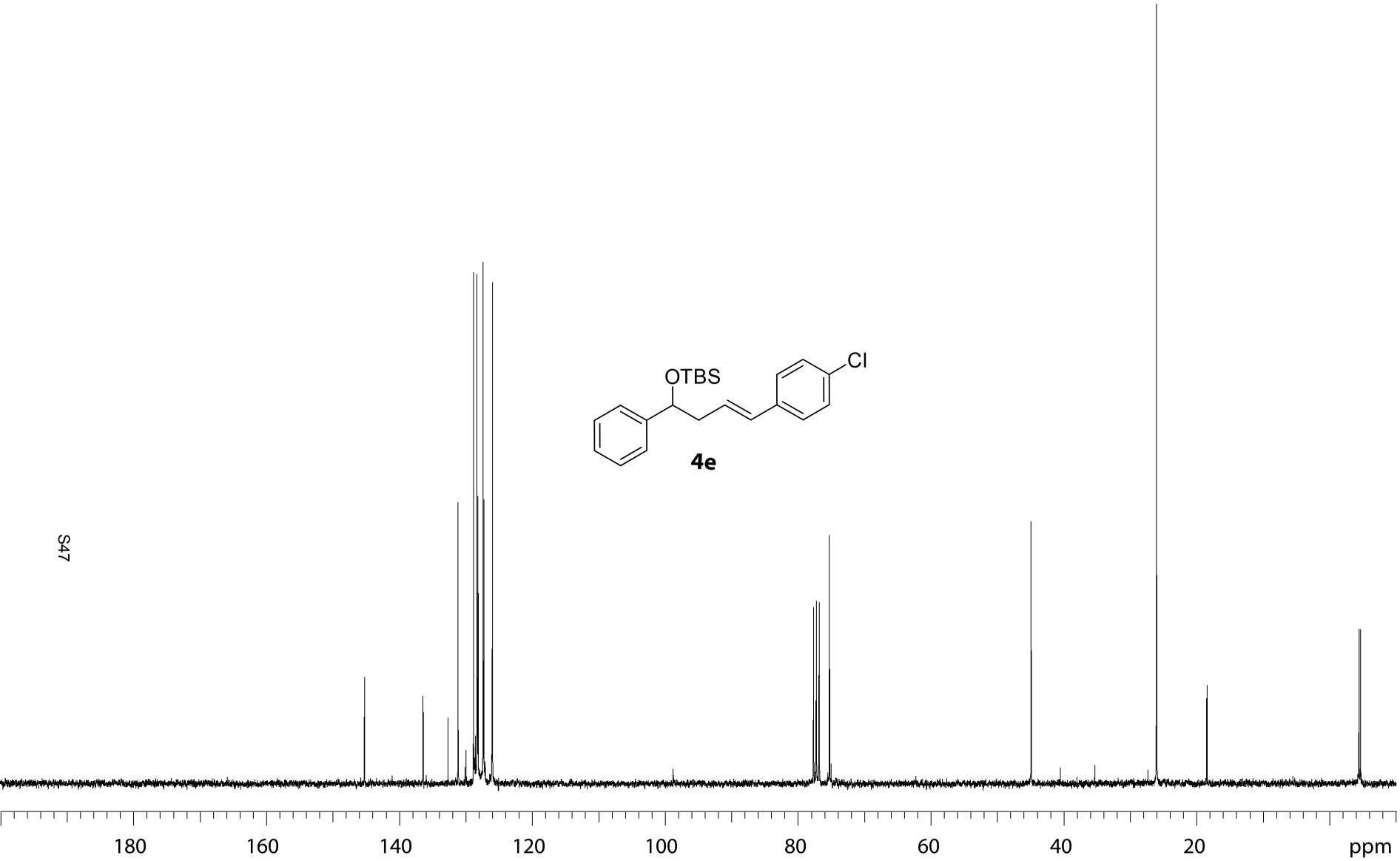
3.28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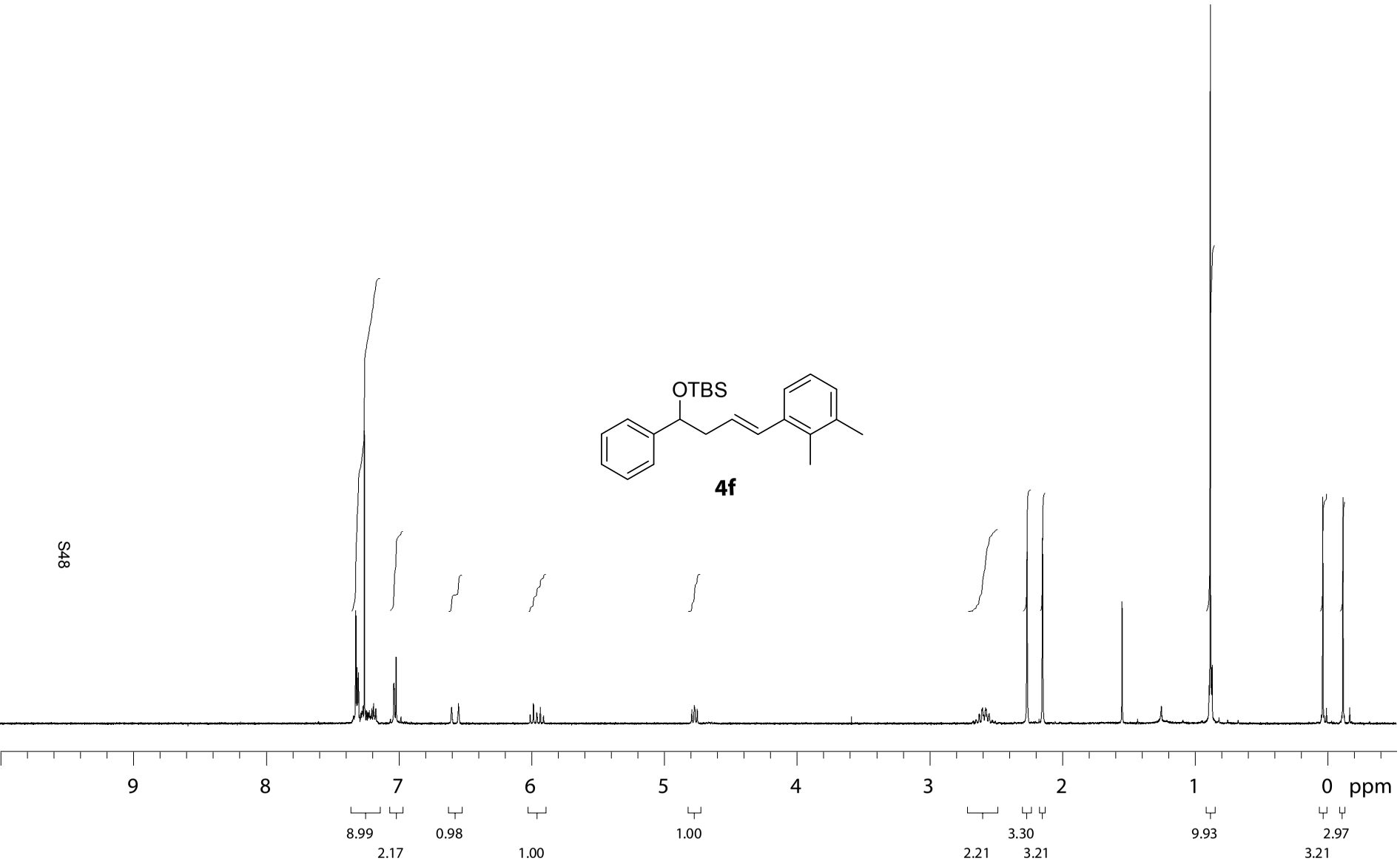
ppm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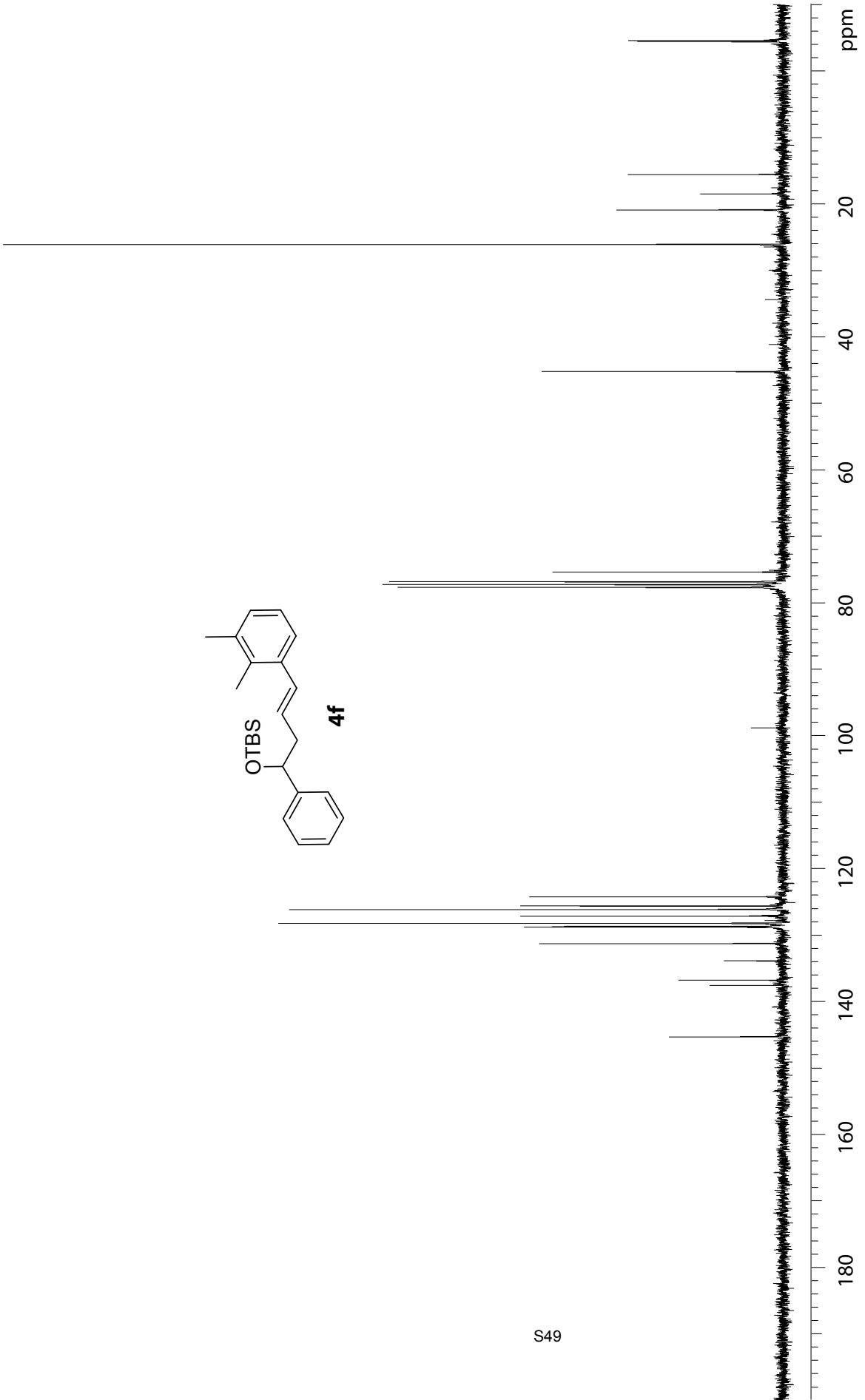
3.21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