Distinctive *meta*-Directing Group Effect for Iridium-Catalyzed 1,1-Diarylalkene Enantioselective Hydrogenation

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SUPPORTING INFORMATION

Table of Contents

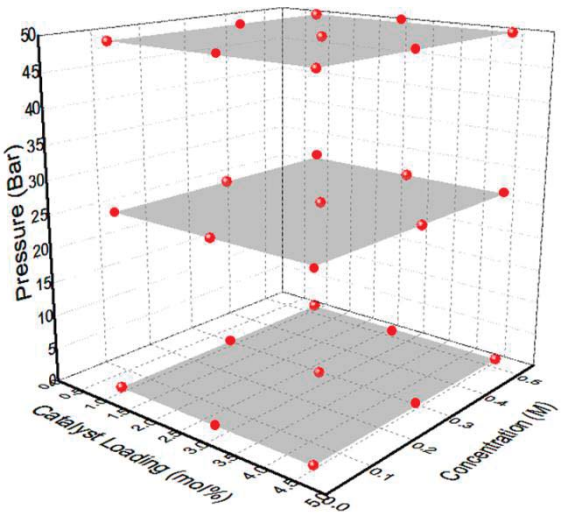
CONDITIONS OPTIMIZATION FOR (IrCODL)BAr_F-CATALYZED HYDROGENATION

Design of Experiments (DOE) principles were employed to identify the optimal conditions under which the (IrCOD**L**)BAr_F-catalyzed hydrogenations were performed. DOE principles indicate that by systematically varying experimental conditions across a range of interest and evaluating these changes' influence on some measureable outcome, the relationship between conditions' variations and outcome can be mathematically related.[1] From such a mathematical relationship, the optimal combination of assessed variables could be predicted.

With this foundation, we first identified quantifiable, modifiable conditions—catalyst loading, concentration, and pressure—to optimize enantiomeric excess (ee). Next, we identified our ranges of experimental interest for these variables based upon conditions typical of iridium-catalyzed hydrogenations reported in the literature: 1.1 mol% to 4.6 mol% catalyst loading, 0.03 M to 0.5 M in CH_2Cl_2, 1 to 50 bar H_2 pressure.[2] To understand the effect of variation across each of these ranges, we also incorporated into our experimental design a third point at the center of each variable's range, resulting in a 3x3x3 matrix.

While simultaneous optimization of each variable would be facilitated by evaluating each variable combination, this results in 27 experiments (SI Fig. 1), some of which provide redundant information. Instead, by selecting an appropriate experimental design matrix, we reduced the number of experiments performed and still gathered sufficient information to model the relationship between the modified variables and ee. Applying a face-centered cubic (FCC) design matrix to the 3x3x3 matrix allowed for a reduction in the number of experiments performed, from 27 to 15 experiments. The results of these 15 experiments, performed on substrate **1**, are reported in SI Table 1.

SI Figure 1. 3x3x3 experimental design matrix.



SI Figure 2. Face-centered cubic reduced experimental design matrix.

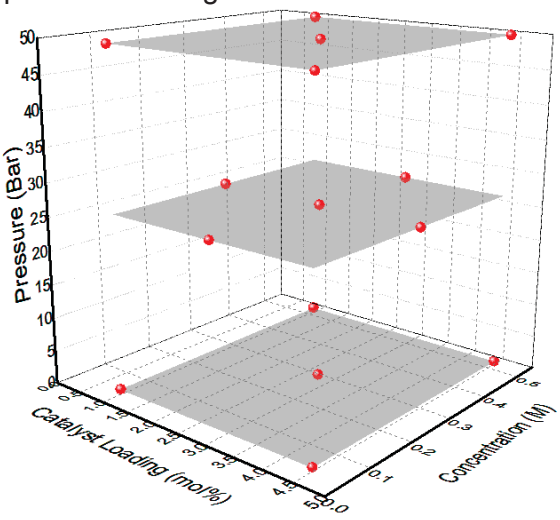


Table 1. Tabulation of results in the FCC design matrix.

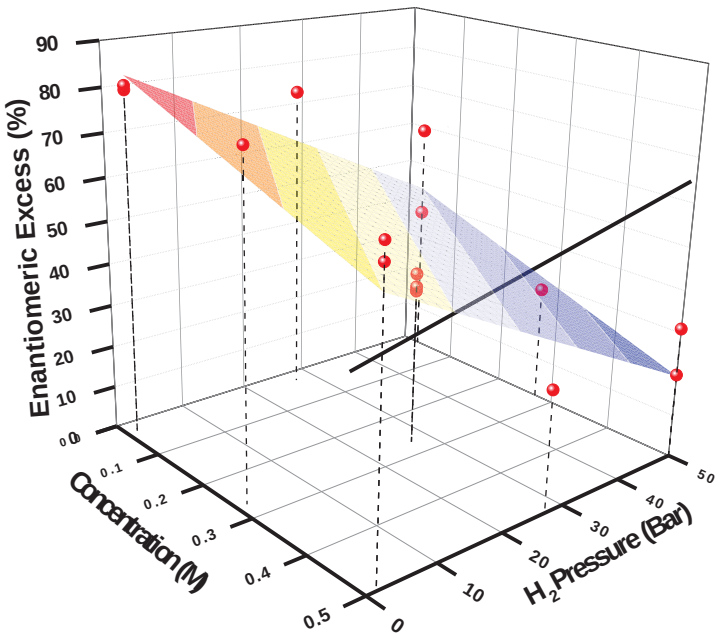
Entry	Catalyst Loading	Concentration (M)	H_2 (Bar)	Conversion[a]	ee[b]
1	1.1	0.028	1.4	57%	80%
2	4.6	0.028	1.4	>95%	81%
3	2.9	0.270	1.4	76%	77%
4	1.1	0.500	1.4	31%	65%
5	4.6	0.500	1.4	67%	69%
6	2.9	0.028	27	91%	74%
7	1.1	0.270	27	77%	37%
8	2.9	0.270	27	>95%	38%
9	4.6	0.270	27	>95%	41%
10	2.9	0.500	27	>95%	28%
11	1.1	0.028	50	59%	37%
12	4.6	0.028	50	>95%	59%
13	2.9	0.270	50	>95%	28%
14	1.1	0.500	50	>95%	20%
15	4.6	0.500	50	>95%	31%

[a]Conversions are representative of one experiment and measured by ^{1}H NMR. [b]ee's were measured by SFC fitted with a chiral stationary phase.

Performing standard stepwise regression analysis (using MATLAB®, R2010a, The MathWorks, Natick, MA) to relate ee to catalyst loading, concentration, and pressure yielded Eq. 1. According to p-value test, catalyst loading was a statistically insignificant variable to the model.

$$ee\% = 86 - 50\boldsymbol{Concentration} - 0.82\boldsymbol{Pressure} \qquad R^2=0.81 \qquad \text{Eq. 1}$$

SI Figure 3. Graphical representation of Eq. 1.



Through assessment of Eq. 1 and its graphical representation in SI Fig. 3., it is readily apparent that ee's increase as concentration and pressure decrease. The lowest pressure and concentration evaluated were 1.4 bar (20 psi) and 0.03 M in CH_2Cl_2, respectively. While catalyst loading had no statistically significant impact on ee, it did influence conversion of starting material to product. This influence is highlighted in the comparison of SI Table 1 entries 1 and 2, wherein concentration is 0.03 M, pressure is 1.4 bar, and catalyst loading is 1.1 mol% and 4.6 mol%, respectively. Of these two condition sets, only the latter afforded >95% conversion of starting material. Based on the results of this experiment, we performed further hydrogenation experiments under the conditions of 1 bar H_2, 0.03 M in CH_2Cl_2, and 4.6 mol% catalyst loading.

SYNTHETIC PROCEDURES

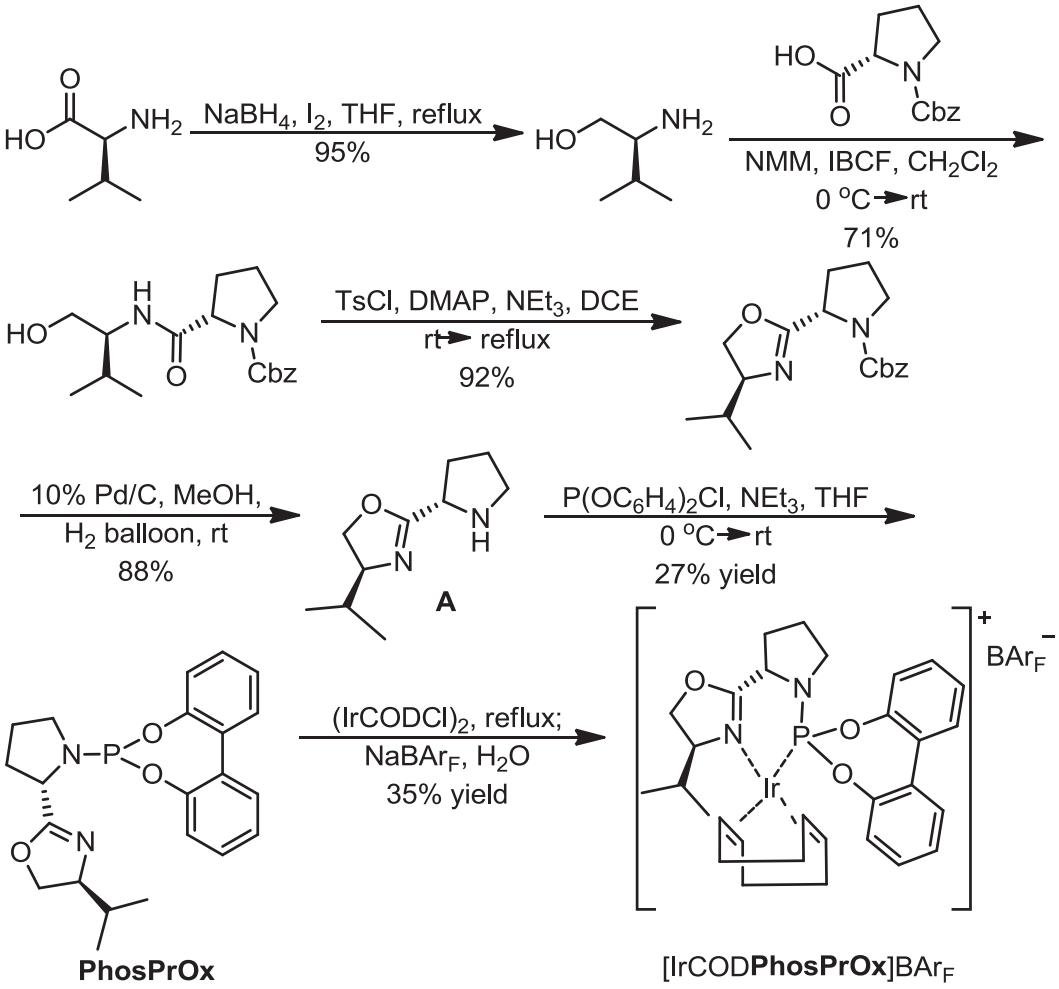
General Information

All glassware was dried in a 120 ºC oven or flame-dried and cooled under nitrogen or vacuum, unless otherwise noted. All reactions were performed under nitrogen, with stirring, unless otherwise noted. Tetrahydrofuran (THF), dichloromethane, and toluene were passed through an activated alumina column prior to use. Methanol was distilled from magnesium methoxide. Triethylamine was distilled from CaH_2. PCl_3 was purified via simple distillation. All other reagents were from commercial sources and were used as received, unless otherwise noted.

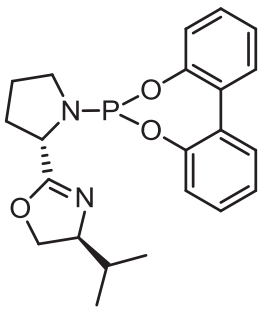
Thin-layer chromatography was performed using silica gel 60 F_{254} and the eluents indicated, then visualized via a 254 nm UV lamp and/or stained with phosphomolybdic acid, potassium permanganate, ninhydrin or vanillin. SiliaFlash® F60 40-63 µm silica gel or basic, activated alumina, Brockmann I (GFS Chemicals) was used for flash column chromatography, as designated. ^{1}H, ^{13}C, ^{19}F, and ^{31}P NMR spectra were acquired on a Varian Unity spectrometer at the MHz specified. Spectral referencing was performed relative to the $CHCl_3$ 7.26 ppm singlet (^{1}H NMR), the center peak of the $CHCl_3$ 77.16 ppm triplet (^{13}C NMR), the H_3PO_4 0 ppm singlet (^{31}P NMR, external standard), or the CF_3COOD -78.5 ppm singlet (^{19}F NMR, external standard). All multiplicities reported are apparent. Abbreviations s, d, t, q, p, sex, sep, dd, ddd, td, bs, and m represent the resonance multiplicities singlet, doublet, triplet, quartet, pentet, sextet, septet, doublet of doublets, doublet of doublets of doublets, triplet of doublets, broad singlet, and multiplet, respectively. Infrared (IR) spectroscopy data was obtained using a Nicolet 380 FT-IR instrument. High-resolution mass spectrometry (HRMS) data was obtained using an Agilent LCTOF. Melting points were measured using a Thomas Hoover Unimelt capillary melting point apparatus. All melting points are uncorrected. Super critical fluid chromatography (SFC) analysis was performed using a Thar instrument under the conditions indicated. High Performance Liquid Chromatography (HPLC) analysis was performed using a Hewlett-Packard instrument under the conditions indicated. Specific rotations were determined using a PerkinElmer 343 Polarimeter, the 589 nm wavelength (sodium D line), and a 1 dm cell path length, with concentrations given in units of g/100 mL.

CATALYST SYNTHESIS AND CHARACTERIZATION

The catalyst was synthesized according to previously published procedures.[3]



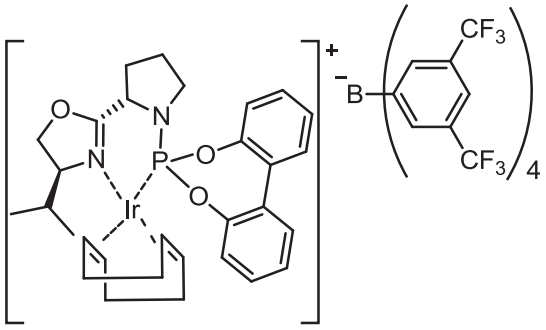
PhosPrOx: (*S*)-2-((*S*)-1-(dibenzo[d,f][1,3,2]dioxaphosphepin-6-yl)pyrrolidin-2-yl)-4-isopropyl-4,5-dihydrooxazole



Oxazoline **A** (2.244 mmol, 1.1 equiv.) was dissolved in THF (4.4 mL). After addition of NEt_3 (4.487 mmol, 2.2 equiv.), the solution was cooled to 0 °C, and the chlorophosphite (2.04 mL of a 1.0 M solution in THF, 1.0 equiv.) was added dropwise. The reaction was then allowed to warm to room temperature and stirred overnight. The phosphoramidite product was purified by flash silica-gel column chromatography (25% ethyl acetate in hexanes with 1% triethylamine) to give 27% yield, 0.176 g (0.443 mmol), of the clear, pale yellow, viscous oil **PhosPrOx**. TLC (30% ethyl acetate in hexanes) R_f=0.33. $[\alpha]_D^{20}$= -49.9 (c 2.50, $CHCl_3$). ^{1}H NMR (300 MHz, $CDCl_3$) δ: 0.86-1.01 (m, 6H), 1.64-1.94 (m, 3H), 1.96-2.18 (m, 2H), 2.92-3.05

(m, 1H), 3.16-3.30 (m, 1H), 3.91-4.11 (m, 2H), 4.25-4.35 (m, 1H), 4.47-4.55 (m, 1H), 7.14-7.25 (m, 4H), 7.28-7.38 (m, 2H), 7.42-7.44 (m, 1H), 7.44-7.47 (m, 1H). ^{13}C NMR (75 MHz, $CDCl_3$) δ:18.0 (s), 18.1 (s), 18.7 (s), 18.8 (s), 25.2 (s), 31.0 (d, *J*=5.0 Hz), 32.6 (s), 45.1 (s), 55.3 (s), 55.7 (s), 70.4 (s), 71.9 (s), 122.0 (s), 122.2 (s), 124.5 (s), 124.6 (s), 129.2 (s), 129.7 (s), 129.8 (s), 131.3 (d, *J*=2.6 Hz), 131.5 (d, *J*=3.5 Hz), 151.7 (d, *J*=4.1 Hz), 152.1 (d, *J*=5.5 Hz), 168.6 (d, *J*=1.5 Hz). ^{31}P NMR (121 MHz, $CDCl_3$, H_3PO_4 external standard) δ= [150.8 (s) and 150.6 (s)] ratio 4.5:1. IR: 2957, 2872, 2361, 1665, 1600, 1567, 1497, 1474, 1434, 1384, 1365, 1270, 1247, 1207, 1190, 1128, 1077, 1010, 979, 883, 868, 847, 764, 745, 731, 681, 645, 597, 547 cm^{-1}. HRMS $C_{22}H_{26}N_2O_3P$ $[M+H]^+$ calculated 397.1681, observed 397.1687.

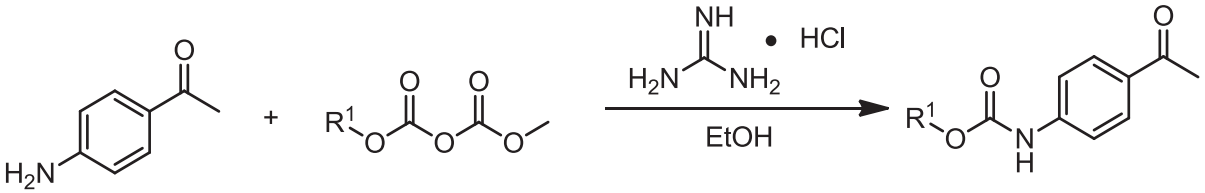
[IrCOD PhosPrOx**]BAr$_F$**



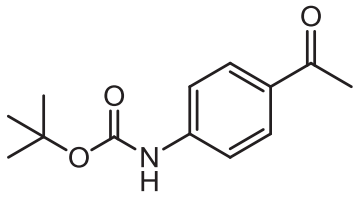
To an oven-dried Schlenk tube under nitrogen atmosphere was added **PhosPrOx** (0.399 mmol, 1 equiv.) and CH_2Cl_2 (8.3 mL). To this stirring solution, $(IrCODCl)_2$ (0.200 mmol, 0.5 equiv.) was added. The Schlenk tube was sealed, and the vessel was heated to 48 °C and stirred for 2 hrs. Next, the reaction mixture was cooled to room temperature, and $NaBAr_F$ (0.519 mmol, 1.3 equiv.) was added. After stirring approximately 10 minutes, 8 mL of water was added, and the mixture was stirred vigorously for about 30 mins. Then, the organic layer was extracted, washed twice with brine, and dried with Na_2SO_4. **[IrCOD**PhosPrOx**]BAr$_F$** was purified by flash silica-gel column chromatography (using 66% ethyl acetate in dichloromethane with 1% triethylamine) to give 35% yield, 0.111 g (0.071 mmol). TLC (66% ethyl acetate in dichloromethane) R_f=0.25. $[\alpha]_D^{20}$= -55.0 (c 0.20, $CHCl_3$). M.P.: 67-70 ºC. ^{1}H NMR (300 MHz, $CDCl_3$) δ: 0.90-1.06 (m, 6H), 1.55-1.76 (m, 2H), 1.76-1.91 (m, 2H), 1.91-2.20 (m, 5H), 2.23-2.47 (m, 4H), 2.71-2.92 (m, 1H), 3.06-3.15 (m, 1H), 3.15-3.27 (m, 1H), 3.69-3.82 (m, 1H), 3.98-4.11 (m, 1H), 4.39 (t, *J*=9.82 Hz, 1H), 4.50-4.63 (m, 1H), 4.83-4.95 (m, 1H), 5.08-5.23 (m, 1H), 5.26-5.39 (m, 1H), 7.17-7.24 (m, 2H), 7.30-7.53 (m, 6H), 7.55 (s, 4H), 7.73 (s, 8H). ^{13}C NMR (75 MHz, $CDCl_3$) δ: 14.7 (s), 17.9 (s), 26.1 (s), 26.1 (s), 26.5 (d, *J*=3.0 Hz), 27.2 (s), 27.3 (s), 29.5 (s), 31.3 (d, *J*=2.0 Hz), 32.9 (s), 35.4 (s), 35.5 (s), 46.8 (d, *J*=5.0 Hz), 56.5 (s), 56.8 (s), 63.3 (d, *J*=2.0 Hz), 65.8 (s), 69.8 (s), 71.8 (s), 101.8 (s), 102.0 (s), 104.7 (s), 104.9 (s), 117.6 (m), 119.3 (s), 120.9 (d, *J*=3.0 Hz), 121.7 (d, *J*=3.5 Hz), 122.9 (s), 126.5 (s), 126.6 (s), 127.0 (s), 128.8 (m), 129.2 (m), 109.7 (d, *J*=2.0 Hz), 130.1 (s), 130.1 (s), 130.4 (s), 130.5 (s), 134.9 (s), 148.7 (s), 148.8 (s), 150.2 (s), 150.4 (s), 160.9 (s), 161.5 (s), 162.2 (s), 162.8 (s), 174.9 (s), 175.0 (s). ^{19}F NMR (282 MHz, $CDCl_3$) δ: -63 (s). ^{31}P NMR (121 MHz, $CDCl_3$) δ: 104.6 (s). IR (thin film): 2964, 2361, 2338, 1611, 1501, 1478, 1436, 1390, 1353, 1274, 1119, 1096, 1045, 943, 914, 886, 839, 776, 735, 713, 682, 669, 614, 556 cm^{-1}. HRMS $C_{30}H_{37}N_2O_3PIr$ $[M]^+$ calculated 697.2171, observed 697.2176.

SUBSTRATE SYNTHESES AND CHARACTERIZATION

Synthesis of Carbamate S1

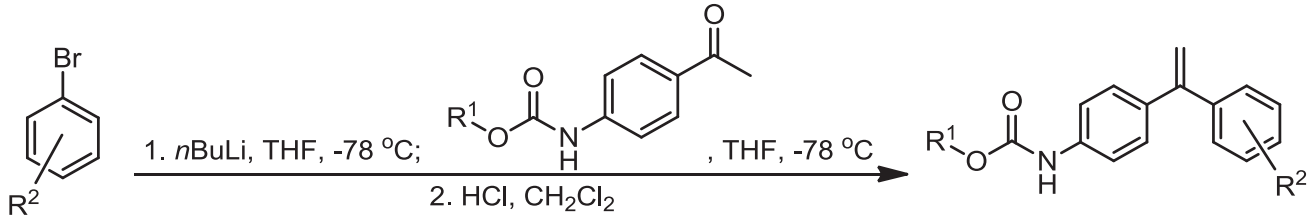


S1: *tert*-butyl (4-acetylphenyl)carbamate



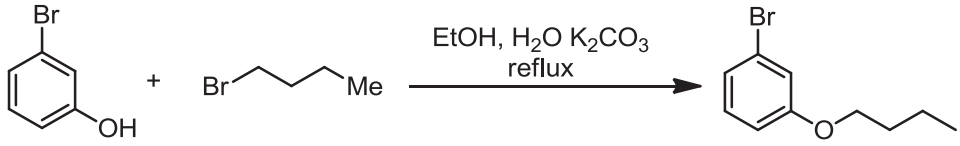
Carbamate **S1** was synthesized according to a published literature procedure.[4] Purity was assessed by comparison to published characterization data.[5]

Synthesis and Characterization of the 1,1-Terminal Alkenes 1-5



All bromobenzene starting materials used were commercially available and used as received, with the exception of 1-bromo-3-butoxybenzene, **S2**.

S2: 1-bromo-3-butoxybenzene



S2

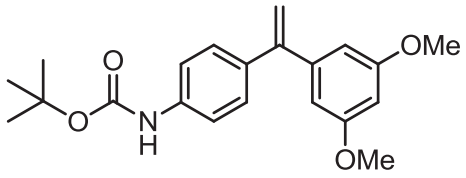
To a round-bottom flask was added 3-bromophenol (11.560 mmol, 1 equiv.), 1-bromobutane (17.340 mmol, 1.5 equiv.), 4.6 mL of ethanol (200 proof), 0.46 mL deionized H_2O, and potassium carbonate (16.180 mmol, 1.4 equiv.). After heating the reaction mixture to reflux for 20 hours, the reaction mixture was cooled, and the solvent was removed *in vacuo*. Diethyl ether was added to the remaining residue, followed by sequential washings with 1 M HCl (10 mL), H_2O (20 mL), 1 M NaOH (10 mL), and H_2O (20 mL). The organic phase was dried with Na_2SO_4. The solvent was removed and the product concentrated *in vacuo* to afford **S2**, a pale yellow liquid, in 45% yield, 1.201 g (5.241 mmol). TLC (10% ethyl acetate in hexanes) R_f=0.70. ^{1}H NMR (300 MHz, $CDCl_3$) δ: 0.98 (t, *J*=7.41 Hz, 3H), 1.42-1.56 (m, 2H), 1.70-1.82 (m, 2H), 3.94 (t, *J*=6.52 Hz, 2H), 6.80-6.86 (m, 1H), 7.03-7.09 (m, 2H), 7.09-7.17 (m, 1H). ^{13}C NMR (126 MHz, $CDCl_3$) δ: 14.0 (s), 19.3 (s), 31.3 (s), 68.0 (s), 113.7 (s), 117.8 (s), 122.9 (s), 123.6 (s), 130.6 (s), 160.1 (s). IR (thin film): 2958, 2933, 2872, 2360, 1589, 1572, 1466, 1424, 1389, 1324, 1304, 1283, 1242,

1226, 1167, 1157, 1124, 1091, 1065, 1027, 1010, 991, 974, 909, 890, 856, 841, 762, 737, 679, 601 cm^{-1}. HRMS $C_{10}H_{14}OBr$ $[M+H]^+$: calculated 229.0228, observed 229.0225.

General Procedure for the Synthesis of the Substrate Alkenes 1-5:

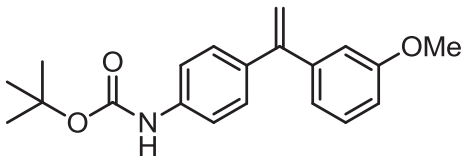
A round-bottom flask was charged with the corresponding bromobenzene (10.626 mmol, 2.5 equiv.). Under a nitrogen atmosphere, dry THF (24 mL) was added, and the reaction mixture was cooled to -78°C, followed by dropwise addition of *n*BuLi (10.626 mmol, 2.5 equiv.). After stirring at -78 °C for approximately 45 min., a solution of the corresponding acetophenone (4.250 mmol, 1 equiv.) in dry THF (9 mL) was added dropwise to the reaction mixture, which continued stirring at -78 °C for approximately 4 hrs. The reaction mixture was then quenched with H_2O. The organic phase was removed, and the aqueous phase was washed with EtOAc. The combined organic phases were dried with Na_2SO_4 and concentrated *in vacuo*. A solution of this product in 20 mL of CH_2Cl_2 (not dried) and 2 drops of concentrated HCl was stirred overnight. Next, H_2O was added to this solution, and the organic phase was extracted and subsequently washed with brine. Then, the combined aqueous phases were washed with CH_2Cl_2. The organic phase was dried with Na_2SO_4, concentrated *in vacuo*, and purified via flash-column chromatography.

1: *tert*-butyl (4-(1-(3,5-dimethoxyphenyl)vinyl)phenyl)carbamate



Substrate **1** was synthesized according to the above general procedure from 4.250 mmol of the corresponding acetophenone and purified via flash silica-gel column chromatography (using 30% ethyl acetate in hexanes) to give a white solid in 78% yield, 1.178 g (3.315 mmol). TLC (20% ethyl acetate in hexanes) R_f=0.36. M.P.: 76-79 °C ^{1}H NMR (300 MHz, $CDCl_3$) δ: 1.52 (s, 9H), 3.76 (s, 6H), 5.38 (d, *J*=1.24 Hz, 1H), 5.41 (d, *J*=1.24 Hz, 1H), 6.42-6.45 (m, 1H), 6.48 (d, *J*=2.33 Hz, 2H), 6.50 (bs, 1H), 7.27-7.35 (m, 4H). ^{13}C NMR (75 MHz, $CDCl_3$) δ: 28.4 (s), 55.4 (s), 80.7 (s), 100.0 (s), 106.7 (s), 113.6 (s), 118.2 (s), 128.9 (s), 135.9 (s), 138.1 (s), 143.9 (s), 149.5 (s), 152.8 (s), 160.6 (s). IR (thin film): 3333, 2976, 2837, 2360, 1728, 1701, 1589, 1521, 1456, 1422, 1406, 1392, 1366, 1348, 1314, 1230, 1204, 1154, 1051, 1027, 1015, 901, 840, 771, 731, 688, 668, 610 cm^{-1}. HRMS $C_{21}H_{25}NO_4Na$ $[M+Na]^+$ calculated 378.1681, observed 378.1690.

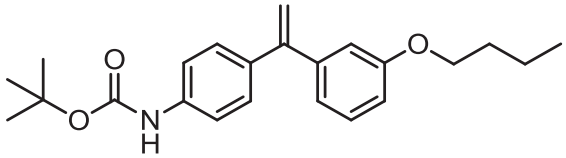
2: *tert*-butyl (4-(1-(3-methoxyphenyl)vinyl)phenyl)carbamate



Substrate **2** was synthesized according to the above general procedure from 3.190 mmol of the corresponding acetophenone and purified via flash silica-gel column chromatography (using 20% ethyl acetate in hexanes with 1% triethylamine) to give a clear, pale yellow liquid in 14% yield, 0.149 g (0.459 mmol). TLC (30% ethyl acetate in hexanes) R_f=0.56. ^{1}H NMR (300 MHz, $CDCl_3$) δ: 1.53 (s, 9H), 3.79 (s, 3H), 5.39 (d, *J*=1.24 Hz, 1H), 5.42 (d, *J*=1.24 Hz, 1H), 6.52 (bs, 1H), 6.83-6.96 (m, 3H), 7.20-7.36 (m, 5H). ^{13}C NMR (126 MHz, $CDCl_3$) δ: 28.5 (s), 55.4 (s), 80.8 (s), 113.4 (s), 113.7 (s), 114.0 (s), 118.3 (s), 121.1 (s), 129.0 (s), 129.2 (s), 136.2 (s), 138.1 (s), 143.2 (s), 149.5 (s), 152.8 (s), 159.6 (s). IR (thin film):

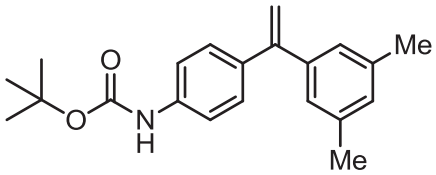
3331, 2976, 2360, 1727, 1700, 1608, 1584, 1519, 1454, 1429, 1404, 1392, 1367, 1313, 1285, 1228, 1155, 1049, 1015, 897, 841, 784, 745, 715, 684, 589 cm^{-1}. HRMS $C_{20}H_{23}NO_3Na$ $[M+Na]^+$ calculated 348.1576, observed 348.1575.

3: *tert*-butyl (4-(1-(3-butoxyphenyl)vinyl)phenyl)carbamate



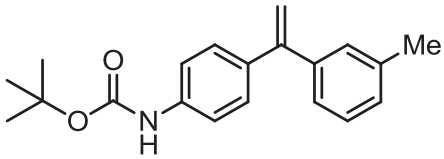
Substrate **3** was synthesized according to the above general procedure from 1.920 mmol of the corresponding acetophenone and purified via flash silica-gel column chromatography (using 10% ethyl acetate in hexanes) to give a clear, colorless liquid in 33% yield, 0.236 g (0.642 mmol). TLC (20% ethyl acetate in hexanes) R_f=0.54. ^{1}H NMR (500 MHz, $CDCl_3$) δ: 0.96 (t, *J*=7.33, 3H), 1.45-1.51 (m, 2H), 1.53 (s, 9H), 1.71-1.78 (m, 2H), 3.94 (t, *J*=6.60 Hz, 2H), 5.38 (d, *J*=1.47, 1H), 5.40 (d, *J*=1.47, 1H), 6.51 (bs, 1H), 6.84-6.88 (m, 2H), 6.88-6.92 (m, 1H), 7.22 (t, *J*=7.82, 1H), 7.26-7.30 (m, 2H), 7.32 (d, *J*=8.31, 2H). ^{13}C NMR (126 MHz, $CDCl_3$) δ= 14.0 (s), 19.4 (s), 28.5 (s), 31.5 (s), 67.8 (s), 80.8 (s), 113.6 (s), 113.9 (s), 114.7 (s), 118.3 (s), 120.9 (s), 129.0 (s), 129.2 (s), 136.3 (s), 138.1 (s), 143.1 (s), 149.5 (s), 152.8 (s), 159.1 (s). IR (thin film): 3333, 2959, 2932, 2871, 1729, 1700, 1584, 1518, 1435, 1404, 1392, 1366, 1313, 1285, 1224, 1153, 1050, 1027, 1014, 980, 933, 900, 840, 781, 733, 781, 733, 714, 683, 581 cm^{-1}. HRMS $C_{23}H_{29}NO_3Na$ $[M+Na]^+$ calculated 390.2045, observed 390.2048.

4: *tert*-butyl (4-(1-(3,5-dimethylphenyl)vinyl)phenyl)carbamate



Substrate **4** was synthesized according to the above general procedure from 3.190 mmol of the corresponding acetophenone and purified via flash silica-gel column chromatography (using 15% ethyl acetate in hexanes) to give a white solid in 95% yield, 0.978 g (3.023 mmol). TLC (20% ethyl acetate in hexanes) R_f=0.52. M.P.: 98-101 ºC. ^{1}H NMR (500 MHz, $CDCl_3$) δ: 1.54 (s, 9H), 2.31 (s, 6H), 5.36 (d, *J*=1.47 Hz, 1H), 5.38 (d, *J*=1.47 Hz, 1H), 6.55 (bs, 1H), 6.93-6.99 (m, 3H), 7.26-7.31 (m, 2H), 7.33 (d, *J*=8.79 Hz, 2H). ^{13}C NMR (500 MHz, $CDCl_3$) δ: 21.4 (s), 28.5 (s), 80.7 (s), 113.3 (s), 118.3 (s), 126.3 (s), 129.0 (s), 129.5 (s), 136.6 (s), 137.7 (s), 138.0 (s), 141.7 (s), 149.8 (s), 152.9 (s). IR (thin film): 3329, 2977, 2918, 2360, 1730, 1701, 1610, 1593, 1518, 1455, 1405, 1392, 1367, 1336, 1313, 1292, 1230, 1156, 1091, 1052, 1027, 1015, 894, 842, 771, 731, 686, 610, 542 cm^{-1}. HRMS $C_{21}H_{25}NO_2Na$ $[M+Na]^+$ calculated 346.1783, observed 346.1779.

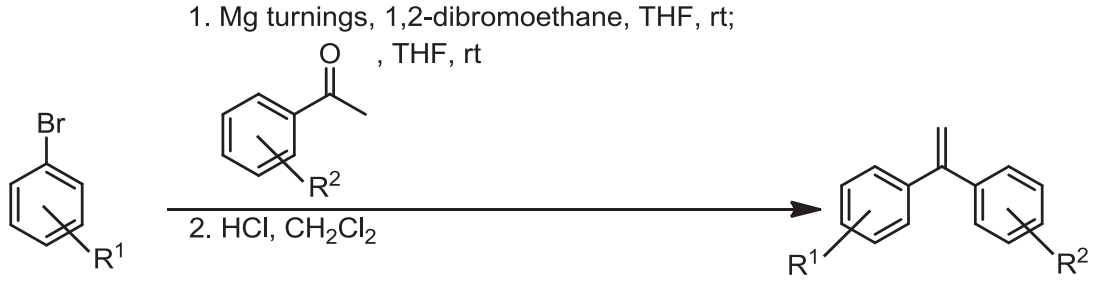
5: *tert*-butyl (4-(1-(m-tolyl)vinyl)phenyl)carbamate



Substrate **5** was synthesized according to the above general procedure from 3.190 mmol of the corresponding acetophenone and purified via flash silica-gel column chromatography (using 15% ethyl acetate in hexanes) to give product a yellow-white solid in 80% yield, 0.788 g (2.546 mmol). TLC (20% ethyl acetate in hexanes) R_f=0.52. M.P.: 93-94 ºC. ^{1}H NMR (500 MHz, $CDCl_3$) δ: 1.54 (s, 9H), 2.35 (s,

3H), 5.37 (d, *J*=1.47 Hz, 1H), 5.40 (d, *J*=1.47 Hz, 1H), 6.53 (bs, 1H), 7.12-7.14 (m, 1H), 7.14-7.16 (m, 2H), 7.20-7.25 (m, 1H), 7.26-7.28 (m, 1H), 7.28-7.30 (m, 1H), 7.33 (d, *J*=8.79 Hz, 2H). ^{13}C NMR (126 MHz, $CDCl_3$) δ: 21.6 (s), 28.5 (s), 80.8 (s), 113.4 (s), 118.3 (s), 125.6 (s), 128.2 (s), 128.6 (s), 129.0 (s), 129.1 (s), 136.5 (s), 137.8 (s), 138.0 (s), 141.7 (s), 149.7 (s), 152.9 (s). IR (thin film): 3329, 2977, 2929, 1729, 1699, 1610, 1585, 1518, 1454, 1403, 1392, 1367, 1313, 1290, 1231, 1155, 1052, 1027, 1015, 893, 841, 791. 744, 715, 683, 595 cm^{-1}. HRMS $C_{20}H_{23}NO_2Na$ $[M+Na]^+$ calculated 332.1626, observed 332.1622.

Synthesis and Characterization of the 1,1-Terminal Alkenes 6-8, S3-S10



General Procedure for Alkene Synthesis, Method A:

Mg turnings (13.200 mmol, 1.38 eq.) were ground with mortar and pestle until shiny and added to an oven-dried round-bottom flask. Under a nitrogen atmosphere, 3 mL of THF (distilled from sodium benzophenone) were added, and the heterogeneous mixture stirred for 5 min. at room temperature. After 2 drops of 1,2-dibromoethane* were added to the flask, the reaction mixture stirred for 10 minutes. Then, the respective bromobenzene derivative (12.000 mmol, 1.25 eq.) in THF (2 mL) was added all at once. After stirring 10 minutes at room temperature, 7 mL of THF were added. The reaction mixture was stirred for approximately 2 hours, at which time the respective acetophenone derivative (9.600 mmol, 1 eq.) in 10 mL of THF was added at room temperature, resulting in an exothermic reaction. After stirring overnight, the reaction mixture was quenched with H_2O and EtOAc was added. The organic phase was removed and subsequently washed twice with saturated $NH_4Cl_{(aq)}$ and once with brine. The resulting organic phase was dried with Na_2SO_4 and concentrated *in vacuo*. A solution of this product in 20 mL of CH_2Cl_2 (not dried prior to use) and 3 drops of concentrated HCl was stirred for 15-200 hours, as specified. Next, H_2O was added to this solution, and the organic phase was extracted and subsequently washed with brine. Then, the combined aqueous phases were washed with CH_2Cl_2. The organic phase was dried with Na_2SO_4, concentrated *in vacuo*. The crude product was purified via flash-column chromatography.

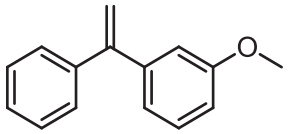
*Passed through a plug of activated, basic alumina prior to use.

General Procedure for Alkene Synthesis, Method B:

Mg turnings (13.200 mmol, 1.38 eq.) were ground with mortar and pestle until shiny and added to an oven-dried round-bottom flask. Under a nitrogen atmosphere, 3 mL of THF were added, and the heterogeneous mixture stirred for 5 min. at room temperature. After 2 drops of 1,2-dibromoethane* were added to the flask, the reaction mixture stirred for 10 minutes. Then, the respective bromobenzene derivative (12.000 mmol, 1.25 eq.) in THF (2 mL) was added all at once. After stirring 10 minutes at room temperature, 7 mL more of THF were added. The reaction mixture was stirred for approximately 2 hours, at which time the respective acetophenone derivative (9.600 mmol, 1 eq.) in 10 mL of THF was added at

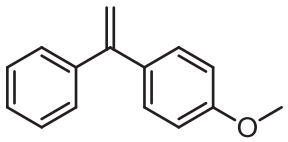
room temperature, resulting in an exothermic reaction. After stirring overnight, the reaction mixture was quenched with H_2O and EtOAc was added. The organic phase was removed and subsequently washed twice with saturated $NH_4Cl_{(aq)}$ and once with brine. The resulting organic phase was dried with Na_2SO_4, concentrated *in vacuo*, and passed through a silica column (using the same eluent as used for the final purification, unless otherwise noted) to remove the bulk of impurities. A solution of the resultant crude product in 20 mL of CH_2Cl_2 (not dried prior to use) and 3 drops of concentrated HCl was stirred for 15-96 hours, as specified. Next, H_2O was added to this solution, and the organic phase was extracted and subsequently washed with brine. Then, the combined aqueous phases were washed with CH_2Cl_2. The organic phase was dried with Na_2SO_4, concentrated *in vacuo*. The crude product was purified via flash-column chromatography.
*Passed through a plug of activated, basic alumina prior to use.

6: 1-methoxy-3-(1-phenylvinyl)benzene



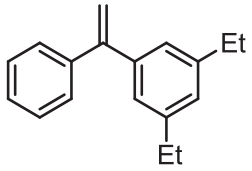
Substrate **6** was synthesized according to Method B from 9.6 mmol of 1-(3-methoxyphenyl)ethanone, stirring with HCl for 96 hours, and purified via flash silica-gel column chromatography (using 15% ethyl acetate in hexanes), affording a clear, colorless oil in 42% yield, 0.853 g (4.058 mmol). TLC (20% ethyl acetate in hexanes) R_f=0.55. ^{1}H NMR (300 MHz, $CDCl_3$) δ: 3.80 (s, 3H), 5.47 (s, 2H), 6.85-6.91 (m, 2H), 6.91-6.96 (m, 1H), 7.23-7.29 (m, 1H), 7.30-7.38 (m, 5H). ^{13}C NMR (126 MHz, $CDCl_3$) δ: 55.4 (s), 113.3 (s), 114.1 (s), 114.6 (s), 121.0 (s), 127.9 (s), 128.3 (s), 128.4 (s), 129.3 (s), 141.5 (s), 143.1 (s), 150.1 (s), 159.6 (s). IR (thin film): 3055, 3027, 2937, 2833, 2359, 2340, 1597, 1575, 1487, 1463, 1447, 1431, 1329, 1285, 1240, 1183, 1159, 1133, 1047, 898, 863, 777, 723, 699, 591, 549 cm^{-1}. HRMS $C_{15}H_{15}O$ $[M+H]^+$ calculated 211.1123, observed 211.1122.

7: 1-methoxy-4-(1-phenylvinyl)benzene



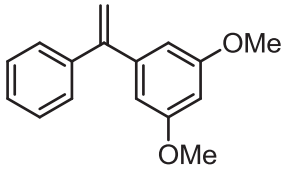
Substrate **7** was synthesized according to Method B from 9.6 mmol of 1-(4-methoxyphenyl)ethanone, stirring with HCl for 65 hours, and purified via flash silica-gel column chromatography (using 15% ethyl acetate in hexanes), affording a white solid in 19% yield, 0.379 g (1.801 mmol). TLC (20% ethyl acetate in hexanes) R_f= 0.53. M.P.: 68-72 °C. ^{1}H NMR (300 MHz, $CDCl_3$) δ: 3.84 (s, 3H), 5.37 (d, *J*=1.24 Hz, 1H), 5.41 (d, *J*=1.23 Hz, 1H), 6.85-6.88 (m, 1H), 6.88-6.91 (m, 1H), 7.26-7.40 (m, 7H). ^{13}C NMR (126 MHz, $CDCl_3$) δ: 55.4 (s), 113.1 (s), 113.6 (s), 127.8 (s), 128.3 (s), 128.4 (s), 129.5 (s), 134.1 (s), 141.9 (s), 149.6 (s), 159.5 (s). IR (thin film): 3093, 3031, 3005, 2951, 2904, 2835, 2536, 2359, 2341, 2029, 1967, 1907, 1811, 1781, 1715, 1663, 1601, 1572, 1506, 1491, 1456, 1441, 1415, 1328, 1314, 1288, 1245, 1178, 1161, 1151, 1116, 1082, 1069, 1027, 975, 963, 901, 841, 784, 747, 707, 681, 650, 625, 612, 580, 551 cm^{-1}. HRMS $C_{15}H_{15}O$ $[M+H]^+$ calculated 211.1123, observed 211.1124.

8: 1,3-diethyl-5-(1-phenylvinyl)benzene



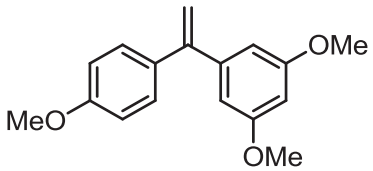
Substrate **8** was synthesized according to Method B (with the exception that THF distilled from sodium benzophenone was used) from 9.6 mmol of acetophenone (passed through a plug of activated, basic alumina prior to use), stirring with HCl for 40 hours, and purified via flash silica-gel column chromatography (using 15% ethyl acetate in hexanes for removal of bulk impurities prior to stirring in HCl and 100% hexanes for final purification), affording a clear, colorless liquid in 62% yield, 1.411 g (5.970 mmol). TLC (100% hexanes) R_f=0.30. ^{1}H NMR (300 MHz, $CDCl_3$) δ: 1.25 (t, *J*=7.55 Hz, 6H), 2.64 (q, *J*=7.60 Hz, 4H), 5.45-5.49 (m, 2H), 7.03 (s, 3H), 7.32-7.43 (m, 5H). ^{13}C NMR (126 MHz, $CDCl_3$) δ: 15.8 (s), 29.0 (s), 114.1 (s), 125.5 (s), 127.1 (s), 127.7 (s), 128.2 (s), 128.4 (s), 141.6 (s), 141.9 (s), 144.2 (s), 150.5 (s). IR (thin film): 3022, 2962, 2930, 2871, 2360, 2340, 1792, 1700, 1653, 1594, 1575, 1493, 1457, 1443, 1374, 1347, 1318, 1237, 1144, 1095, 1072, 1027, 893, 872, 776, 726, 699, 668, 613 cm^{-1}. HRMS $C_{18}H_{21}$ $[M+H]^+$ calculated 237.1643, observed 237.1639.

S3: 1,3-dimethoxy-5-(1-phenylvinyl)benzene



Substrate **S3** was synthesized according to Method A from 9.6 mmol of acetophenone (passed through through a plug of activated, basic alumina prior to use), stirring with HCl overnight, and purified via flash silica-gel column chromatography (using 2% acetone in hexanes), followed by bulb-to-bulb distillation vacuum distillation with heating, distilling off a lower-boiling impurity and affording a clear, yellow liquid in 15% yield, 0.350 g (1.455 mmol). TLC (20% ethyl acetate in hexanes) R_f= 0.51. ^{1}H NMR (500 MHz, $CDCl_3$) δ: 3.79 (s, 6H), 5.49 (s, 2H), 6.48 (t, *J*=2.44 Hz, 1H), 6.53 (d, *J*=1.95 Hz, 2H), 7.31-7.40 (m, 5H). ^{13}C NMR (126 MHz, $CDCl_3$) δ: 55.5 (s), 99.9 (s), 106.7 (s), 114.5 (s), 127.9 (s), 128.3 (s), 128.3 (s), 141.3 (s), 143.8 (s), 150.1 (s), 160.7 (s). IR (thin film): 2999, 2935, 2836, 1587, 1493, 1452, 1421, 1342, 1288, 1266, 1203, 1151, 1091, 1062, 1047, 1027, 992, 934, 899, 835, 777, 726, 697, 643, 615, 538 cm^{-1}. HRMS $C_{16}H_{17}O_2$ $[M+H]^+$ calculated 241.1229, observed 241.1225.

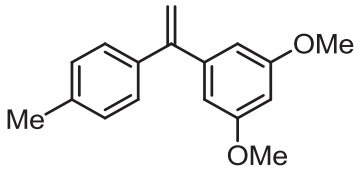
S4: 1,3-dimethoxy-5-(1-(4-methoxyphenyl)vinyl)benzene



Substrate **S4** was synthesized according to Method B from 9.6 mmol of 1-(4-methoxyphenyl)ethanone, stirring with HCl for 96 hours, and purified via flash silica-gel column chromatography (using 15% ethyl acetate in hexanes), affording a clear, colorless liquid in 39% yield, 1.021 g (3.777 mmol). TLC (15% ethyl acetate in hexanes) R_f=0.28. ^{1}H NMR (300 MHz, $CDCl_3$) δ: 3.78 (s, 6H), 3.83 (s, 3H), 5.36-5.39 (m, 1H), 5.40-5.42 (m, 1H), 6.44-6.48 (m, 1H), 6.49-6.54 (m, 2H), 6.84-6.91 (m, 2H), 7.28-7.34 (m, 2H). ^{13}C NMR (126 MHz, $CDCl_3$) δ: 55.4 (s), 55.5 (s), 99.9 (s), 106.7 (s), 113.1 (s), 113.6 (s), 129.5 (s), 133.8 (s),

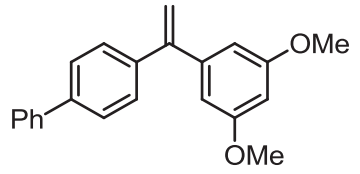
144.1 (s), 149.6 (s), 159.5 (s), 160.6 (s). IR (thin film): 2999, 2935, 2835, 2359, 1588, 1509, 1453, 1421, 1344, 1317, 1293, 1265, 1246, 1203, 1177, 1153, 1132, 1113, 1087, 1063, 1049, 1033, 992, 935, 896, 835, 813, 721, 689, 668, 595, 539 cm^{-1}. HRMS $C_{17}H_{19}O_3$ $[M+H]^+$ calculated 271.1334, observed 271.1331.

S5: 1,3-dimethoxy-5-(1-(*p*-tolyl)vinyl)benzene



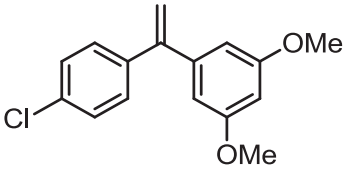
S5 was synthesized according to Method B (with the exception that THF distilled from sodium benzophenone was used) from 9.6 mmol of 1-(*p*-tolyl)ethanone, stirring with HCl for 40 hours, and purified via flash silica-gel column chromatography (using 15% ethyl acetate in hexanes), affording a clear, faintly yellow liquid in 21% yield, 0.514 g (2.020 mmol). TLC (15% ethyl acetate in hexanes) R_f= 0.44. ^{1}H NMR (500 MHz, $CDCl_3$) δ: 2.38 (s, 3H), 3.78 (s, 6H), 5.42 (d, *J*=1.02 Hz, 1H), 5.44 (d, *J*=0.98 Hz, 1H), 6.44-6.46 (m, 1H), 6.51 (d, *J*=1.96 Hz, 2H), 7.15 (d, *J*=8.31 Hz, 2H), 7.24-7.28 (m, 2H). ^{13}C NMR (126 MHz, $CDCl_3$) δ: 21.3 (s), 55.5 (s), 99.9 (s), 106.8 (s), 113.9 (s), 128.2 (s), 129.0 (s), 137.7 (s), 138.4 (s), 144.0 (s), 150.0 (s), 160.6 (s). IR (thin film): 2998, 2935, 2836, 2360, 1588, 1510, 1452, 1421, 1341, 1317, 1307, 1263, 1203, 1152, 1086, 1063, 1048, 1019, 992, 934, 899, 824, 730, 687, 646, 593, 538 cm^{-1}. HRMS $C_{17}H_{19}O_2$ $[M+H]^+$ calculated 255.1385, observed 255.1389.

S6: 4-(1-(3,5-dimethoxyphenyl)vinyl)-1,1'-biphenyl



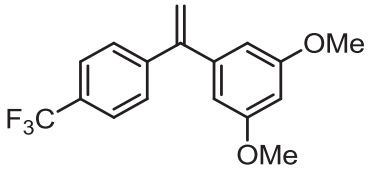
Substrate **S6** was synthesized according to Method B from 9.6 mmol of 1-(3,5-dimethoxyphenyl)ethanone, stirring with HCl for 100 hours, and purified via flash silica-gel column chromatography (using 15% ethyl acetate in hexanes), affording a white solid in 52% yield, 1.580 g (4.995 mmol). TLC (10% ethyl acetate in hexanes) R_f= 0.32. M.P.: 73-75 ^{o}C. ^{1}H NMR (300 MHz, $CDCl_3$) δ: 3.79 (s, 6H), 5.49 (d, *J*=1.24 Hz, 1H), 5.54 (d, *J*=1.23 Hz, 1H), 6.46-6.49 (m, 1H), 6.54 (d, *J*=2.33 Hz, 2H), 7.32-7.40 (m, 1H), 7.42-7.49 (m, 4H), 7.55-7.65 (m, 4H). ^{13}C NMR (126 MHz, $CDCl_3$) δ: 55.5 (s), 100.0 (s), 106.8 (s), 114.6 (s), 127.0 (s), 127.2 (s), 127.5 (s), 128.7 (s), 128.9 (s), 140.2 (s), 140.7 (s), 140.9 (s), 143.8 (s), 149.7 (s), 160.7 (s). IR (thin film): 3028, 2999, 2935, 2836, 2361, 2338, 1589, 1486, 1453, 1422, 1350, 1307, 1272, 1259, 1204, 1154, 1064, 1049, 1007, 935, 902, 846, 794, 771, 742, 718, 697, 668, 617 cm^{-1}. HRMS $C_{22}H_{21}O_2$ $[M+H]^+$ calculated 317.1542, observed 317.1540.

S7: 1-(1-(4-chlorophenyl)vinyl)-3,5-dimethoxybenzene



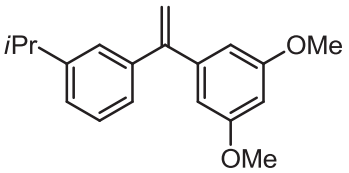
Substrate **S7** was synthesized according to Method B from 9.6 mmol of 1-(4-chlorophenyl)ethanone, stirring with HCl for 100 hours, and purified via flash silica-gel column chromatography (using 15% ethyl acetate in hexanes), affording a clear, pale yellow liquid in 43% yield, 1.144 g (4.165 mmol). TLC (10% ethyl acetate in hexanes) R_f=0.37. ^{1}H NMR (300 MHz, $CDCl_3$) δ: 3.77 (s, 6H), 5.44 (d, *J*=1.10 Hz, 1H), 5.47 (d, *J*=1.10 Hz, 1H), 6.46 (s, 3H), 7.27-7.33 (m, 4H). ^{13}C NMR (126 MHz, $CDCl_3$) δ: 55.5 (s), 100.1 (s), 106.7 (s), 114.9 (s), 128.5 (s), 129.7 (s), 133.8 (s), 139.8 (s), 143.3 (s), 149.0 (s), 160.7 (s). IR (thin film): 3000, 2936, 2837, 2362, 2338, 1589, 1489, 1454, 1422, 1350, 1275, 1204, 1155, 1093, 1064, 1050, 1013, 935, 903, 835, 787, 717, 688, 668 cm^{-1}. HRMS $C_{16}H_{16}O_2Cl$ $[M+H]^+$ calculated 275.0839, observed 275.0836.

S8: 1,3-dimethoxy-5-(1-(4-(trifluoromethyl)phenyl)vinyl)benzene



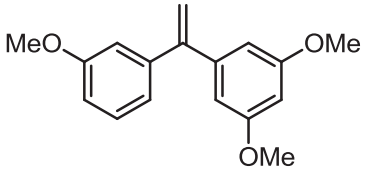
Substrate **S8** was synthesized according to Method B from 9.6 mmol of 1-(4-(trifluoromethyl)phenyl)ethanone, stirring in HCl approximately 10 days, and purified via flash silica-gel column chromatography (using 15% ethyl acetate in hexanes), affording a clear, yellow liquid in 4% yield, 0.117 g (0.379 mmol). TLC (15% ethyl acetate in hexanes) R_f=0.37. ^{1}H NMR (300 MHz, $CDCl_3$) δ: 3.79 (s, 6H), 5.53 (d, *J*=0.83 Hz, 1H), 5.59 (d, *J*=0.82 Hz, 1H), 6.47-6.51 (m, 3H), 7.48 (d, *J*=8.65 Hz, 2H), 7.61 (dd, *J*=8.10 Hz, 0.55 Hz, 2H). ^{13}C NMR (126 MHz, $CDCl_3$) δ: 55.5 (s), 100.1 (s), 106.7 (s), 116.2 (s), 124.4 (q, *J*=272.8 Hz), 125.3 (q, *J*=3.78 Hz), 128.7 (s), 129.9 (q, *J*=32.3 Hz), 142.9 (s), 144.9 (s), 149.0 (s), 160.9 (s). ^{19}F NMR (282 MHz, $CDCl_3$) δ: -63. IR (thin film): 2938, 2839, 2360, 2341, 1591, 1457, 1423, 1324, 1268, 1206, 1157, 1124, 1089, 1065, 1016, 908, 849, 744, 689, 668, 648 cm^{-1}. HRMS $C_{17}H_{16}O_2F_3$ $[M+H]^+$ calculated 309.1102, observed 309.1100.

S9: 1-(1-(3-isopropylphenyl)vinyl)-3,5-dimethoxybenzene



Substrate **S9** was synthesized according to Method B from 9.6 mmol of 1-(3,5-dimethoxyphenyl)ethanone, stirring with HCl for 44 hours, and purified via flash silica-gel column chromatography (using 15% ethyl acetate in hexanes), affording a clear, yellow liquid in 54% yield, 1.477 g (5.229 mmol). TLC (15% ethyl acetate in hexanes) R_f=0.49. ^{1}H NMR (300 MHz, $CDCl_3$) δ: 1.25 (d, *J*=6.87 Hz, 6H), 2.90 (sep, *J*=6.86 Hz, 1H), 3.77 (s, 6H), 5.46 (s, 2H), 6.44-6.47 (m, 1H), 6.50-6.54 (m, 2H), 7.14-7.21 (m, 2H), 7.21-7.29 (m, 2H). ^{13}C NMR (75 MHz, $CDCl_3$) δ: 24.2 (s), 34.2 (s), 55.5 (s), 100.0 (s), 106.7 (s), 114.4 (s), 125.9 (s), 126.0 (s), 126.6 (s), 128.2 (s), 141.1 (s), 143.9 (s), 148.8 (s), 150.3 (s), 160.6 (s). IR (thin film): 2959, 2837, 2175, 1980, 1591, 1455, 1422, 1351, 1279, 1204, 1156, 1065, 1050, 897, 836, 802, 707, 636 cm^{-1}. HRMS $C_{19}H_{23}O_2$ $[M+H]^+$ calculated 283.1698, observed 283.1695.

S10: 1,3-dimethoxy-5-(1-(3-methoxyphenyl)vinyl)benzene



Substrate **S10** was synthesized according to Method B from 9.6 mmol of 1-(3,5-dimethoxyphenyl)ethanone, stirring with HCl for 44 hours, and purified via flash silica-gel column chromatography (using 15% ethyl acetate in hexanes), affording a clear, colorless liquid in 62% yield, 1.606 g (5.941 mmol). TLC (15% ethyl acetate in hexanes) R_f=0.36. ^{1}H NMR (300 MHz, $CDCl_3$) δ: 3.77 (s, 6H), 3.80 (s, 3H), 5.46 (s, 2H), 6.42-6.45 (m, 1H), 6.49 (d, *J*=2.33 Hz, 2H), 6.84-6.96 (m, 3H), 7.21-7.28 (m, 1H). ^{13}C NMR (75 MHz, $CDCl_3$) δ: 55.3 (s), 55.5 (s), 100.0 (s), 106.7 (s), 113.3 (s), 114.0 (s), 114.7 (s), 120.9 (s), 129.2 (s), 142.7 (s), 143.6 (s), 150.0 (s), 159.5 (s), 160.6 (s). IR (thin film): 2999, 2937, 2835, 1586, 1486, 1453, 1422, 1346, 1317, 1284, 1249, 1227, 1203, 1153, 1063, 1046, 993, 940, 926, 904, 882, 838, 786, 730, 706, 688, 630 cm^{-1}. HRMS $C_{17}H_{19}O_3$ $[M+H]^+$ calculated 271.1334, observed 271.1328.

HYDROGENATION METHODS AND 1,1-DIARYLETHANE PRODUCT CHARACTERIZATION

Asymmetric hydrogenation was carried out according to Method C or D, as noted for each product. For characterization purposes, pure product samples were obtained and characterized according to one of the below procedures: Method C, Method D, or the General Racemic Hydrogenation Procedure.

General Asymmetric Hydrogenation Procedure, Method C:

To a 5 mL oven-dried, screw-top vial, equipped with a stirbar and cooled under nitrogen, was added (IrCOD**L**)BAr_F (0.003 mmol, 0.046 eq.). The vial was fitted with a screw-cap septum and placed under a nitrogen atmosphere. A solution of the corresponding alkene (0.056 mmol, 1 eq.) in CH_2Cl_2 (2 mL) was added. The nitrogen inlet was removed and replaced with a needle open to the atmosphere. After placing the vial in a high-pressure reactor vessel, the vessel was evacuated and refilled with hydrogen gas to 15 psi three to five times. Then, the reaction was allowed to stir for 15 hours at room temperature, at which time the pressure in the vessel was slowly released. The solvent was evaporated, and then 1:1 diethyl ether:pentane was added. This solution was passed through a short silica column, to remove the catalyst, and concentrated *in vacuo*. Conversion of starting material to product was then measured by ^{1}H NMR, and enantiomeric excess was measured by SFC or HPLC, as indicated.

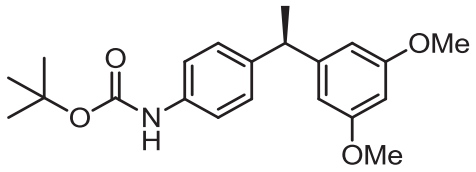
General Asymmetric Hydrogenation Procedure, Method D:

To a 5 mL oven-dried, screw-top vial, equipped with a stirbar and cooled under nitrogen, was added the corresponding alkene substrate (0.056 mmol, 1 eq.). The vial was fitted with a screw-cap septum and placed under a nitrogen atmosphere. 2 mL of a standard solution of (IrCOD**L**)BAr_F in CH_2Cl_2 (0.001 M) was added. The nitrogen inlet was removed and replaced with a needle, open to the atmosphere. After placing the vial in a high-pressure reactor vessel, the vessel was evacuated and refilled with hydrogen gas to 15 psi three to five times. Then, the reaction was allowed to stir for 15 hours at room temperature, at which time the pressure in the vessel was slowly released. The solvent was evaporated, and then 1:1 diethyl ether:pentane was added. This solution was passed through a short silica column, to remove the catalyst, and concentrated *in vacuo*. Conversion of starting material to product was then measured by ^{1}H NMR, and enantiomeric excess was measured by SFC or HPLC, as indicated.

General Racemic Hydrogenation Procedure:
To an oven-dried round bottom flask, equipped with a stirbar and cooled nitrogen, was added 10% palladium on carbon (0.011 mmol, 0.2 eq.). After bringing the flask under nitrogen atmosphere, the corresponding alkene (0.056 mmol, 1 eq.) in 0.3 mL of ethyl acetate was added to the flask. Using a hydrogen-filled balloon, the flask was subsequently evacuated and refilled with hydrogen three times, and the reaction was stirred, under balloon-pressure of hydrogen, overnight. Finally, the solvent was evaporated, and the remaining residue was taken up in 1:1 diethyl ether:pentane, passed through a short silica column, and concentrated *in vacuo*.

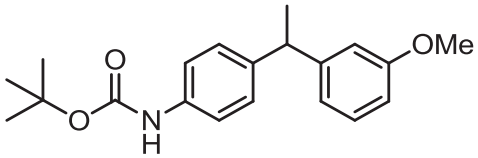
Assignment of Absolute Configuration
Absolute configurations were assigned by comparison of the optical rotation for that reported of (*R*)-(+)-4-(1-(3,5-dimethoxyphenyl)ethyl)-1,1'-biphenyl.[6]

S11: (*R*)-(+)-*tert*-butyl (4-(1-(3,5-dimethoxyphenyl)ethyl)phenyl)carbamate



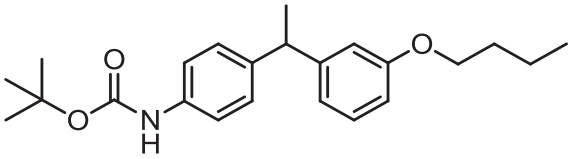
S11 was synthesized according to Method C to afford ^{1}H NMR conversions of 88% (run 1) and 89% (run 2), and er's of 92:8 and 92:8, respectively. Absolute configuration was assigned by analogy (*vide supra*). $[\alpha]_D^{20} = +2.8$ (*c* 0.84, $CHCl_3$). The purity of **S23** was assessed by comparison to published characterization data.[7] Enantiomers were separated by SFC on a Chiralpak AD-H column (4.6 mm x 250 mm, 5 µm particle size) under the following conditions: 38 °C, 20% isopropyl alcohol, 2 mL min^{-1}, 160 Bar. R_T = 12.05 min, 13.77 min.

S12: *tert*-butyl (4-(1-(3-methoxyphenyl)ethyl)phenyl)carbamate



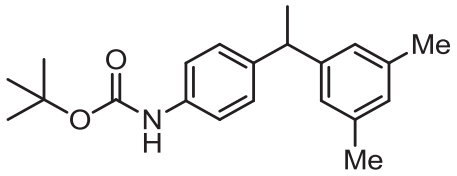
S12 was synthesized according to Method C to afford ^{1}H NMR conversions of 64% (run 1) and 54% (run 2), and er's of 74:26 and 74:26, respectively. TLC (20% ethyl acetate in hexanes) R_f=0.44. M.P.: 76-79 ºC. ^{1}H NMR (500 MHz, $CDCl_3$) δ: 1.51 (s, 9H), 1.59 (d, *J*=7.33 Hz, 3H), 3.77 (s, 3H), 4.07 (q, *J*=7.33 Hz, 1H), 6.41 (bs, 1H), 6.72 (ddd, *J*=8.30 Hz, 2.44 Hz, 0.97 Hz, 1H), 6.75 (t, *J*=2.20 Hz, 1H), 6.79 (dt, *J*=8.31 Hz, 0.98 Hz, 1H), 7.14 (d, *J*=8.79 Hz, 2H), 7.19 (t, *J*=7.82 Hz, 1H), 7.24-7.28 (m, 2H). ^{13}C NMR (126 MHz, $CDCl_3$) δ: 22.0 (s), 28.5 (s), 44.3 (s), 55.3 (s), 80.5 (s), 111.1 (s), 113.8 (s), 118.8 (s), 120.2 (s), 128.2 (s), 129.4 (s), 136.4 (s), 141.1 (s), 148.3 (s), 153.0 (s), 159.7 (s). IR (thin film): 3334, 2969, 2931, 2359, 1699, 1594, 1520, 1486, 1454, 1435, 1410, 1392, 1366, 1313, 1231, 1155, 1051, 1016, 900, 836, 777, 741, 696 cm^{-1}. HRMS $C_{20}H_{25}NO_3Na$ $[M+Na]^+$ calculated 350.1732, observed 350.1732. Enantiomers were separated by HPLC on a Chiralpak AD-H column (4.6 mm x 250 mm, 5 µm particle size) under the following conditions: ambient temperature, 10% isopropyl alcohol in hexanes, 0.9 mL min^{-1}. R_T = 9.76 min, 10.69 min.

S13: *tert*-butyl (4-(1-(3-butoxyphenyl)ethyl)phenyl)carbamate



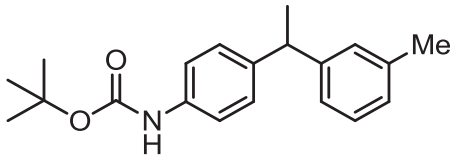
S13 was synthesized according to Method C to afford ^{1}H NMR conversions of 66% (run 1) and 66% (run 2) and er's of 75:25 and 75:25, respectively. TLC (20% ethyl acetate in hexanes) R_f= 0.48. ^{1}H NMR (500 MHz, $CDCl_3$) δ: 0.96 (t, *J*=7.33 Hz, 3H), 1.45-1.53 (m, 11H), 1.59 (d, *J*=7.33 Hz, 3H), 1.69-1.79 (m, 2H), 3.91 (t, *J*=6.35 Hz, 2H), 4.06 (q, *J*=7.33 Hz, 1H), 6.41 (bs, 1H), 6.70 (dd, *J*=8.31 Hz, 2.45 Hz, 1H), 6.73-6.79 (m, 2H), 7.11-7.19 (m, 3H), 7.22-7.29 (m, 2H). ^{13}C NMR (126 MHz, $CDCl_3$) δ: 14.0 (s), 19.4 (s), 22.0 (s), 28.5 (s), 31.5 (s), 44.3 (s), 67.7 (s), 80.5 (s), 111.6 (s), 114.4 (s), 118.8 (s), 120.0 (s), 128.2 (s), 129.3 (s), 136.4 (s), 141.2 (s), 148.2 (s), 153.0 (s), 159.3 (s). IR (thin film):3335, 2962, 2931, 2872, 2359, 1727, 1699, 1594, 1520, 1486, 1453, 1410, 1391, 1367, 1313, 1228, 1155, 1052, 1028, 1016, 974, 904, 835, 775, 740, 696 cm^{-1}. HRMS $C_{23}H_{31}NO_3Na$ $[M+Na]^+$ calculated 392.2202, observed 392.2210. Enantiomers were separated by HPLC on a Chiralpak AD-H column (4.6 mm x 250 mm, 5 μm particle size) under the following conditions: ambient temperature, 5% isopropyl alcohol in hexanes, 0.9 mL min^{-1}. R_T = 9.74 min, 10.51 min.

S14: *tert*-butyl (4-(1-(3,5-dimethylphenyl)ethyl)phenyl)carbamate



S14 was synthesized according to Method C to afford ^{1}H NMR conversions of 71% (run 1) and 68% (run 2) and er's of 64:36 and 62:38, respectively. TLC (20% ethyl acetate in hexanes) R_f= 0.53. ^{1}H NMR (500 MHz, $CDCl_3$) δ: 1.51 (s, 9H), 1.58 (d, *J*=7.33 Hz, 3H), 2.27 (s, 6H), 4.02 (q, *J*=7.33 Hz, 1H), 6.40 (bs, 1H), 6.81 (s, 3H), 7.12-7.18 (m, 2H), 7.26 (d, *J*=8.31 Hz, 2H). ^{13}C NMR (126 MHz, $CDCl_3$) δ: 21.5 (s), 22.1 (s), 28.5 (s), 44.2 (s), 80.5 (s), 118.8 (s), 125.5 (s), 127.8 (s), 128.2 (s), 136.3 (s), 137.9 (s), 141.5 (s), 146.6 (s), 153.0 (s). IR (thin film): 3334, 2969, 2929, 2360, 2167, 1728, 1700, 1596, 1521, 1455, 1410, 1392, 1367, 1313, 1232, 1159, 1051, 1028, 1017, 901, 835, 771, 702, 543 cm^{-1}. HRMS $C_{21}H_{27}NO_2Na$ $[M+Na]^+$ calculated 348.1939, observed 348.1946. Enantiomers were separated by SFC on a Chiralcel OD column (4.6 mm x 250 mm) under the following conditions: 28 ^{o}C, 10% isopropyl alcohol, 3 mL min^{-1}. R_T = 4.36 min, 14.58 min.

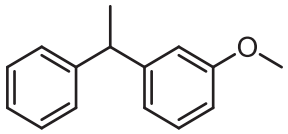
S15: *tert*-butyl (4-(1-(m-tolyl)ethyl)phenyl)carbamate



S15 was synthesized according to Method C to afford ^{1}H NMR conversions of 57% (run 1) and 50% (run 2) and er's of 49:51 and 52:48, respectively. TLC (20% ethyl acetate in hexanes) R_f=0.54. ^{1}H NMR (500 MHz, $CDCl_3$) δ: 1.51 (s, 9H), 1.60 (d, *J*=7.33 Hz, 3H), 2.31 (s, 3H), 4.07 (q, *J*=7.33 Hz, 1H), 6.41 (bs, 1H), 6.97-7.03 (m, 3H), 7.12-7.19 (m, 3H), 7.23-7.29 (m, 2H). ^{13}C NMR (126 MHz, $CDCl_3$) δ: 21.6 (s), 22.1 (s), 28.5 (s), 44.2 (s), 80.5 (s), 118.8 (s), 124.7 (s), 126.9 (s), 128.2 (s), 128.4 (s), 128.5 (s), 136.4 (s), 138.0 (s), 141.4 (s), 146.6 (s), 153.0 (s). IR (thin film): 3334, 2972, 2929, 2362, 1728, 1699, 1594,

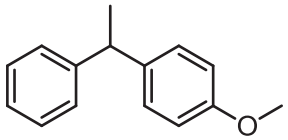
1521, 1455, 1410, 1392, 1367, 1314, 1233, 1158, 1054, 1017, 902, 837, 779, 741, 703, 552 cm^{-1}. HRMS $C_{20}H_{25}NO_2Na$ $[M+Na]^+$ calculated 334.1783, observed 334.1784. Enantiomers for run 1 were separated by HPLC on a Chiralpak AD-H column (4.6 mm x 250 mm, 5 µm particle size) under the following conditions: ambient temperature, 3% isopropyl alcohol in hexanes, 0.9 mL min^{-1}. R_T = 10.39 min, 11.40 min. Enantiomers for run 2 were separated by SFC on a Chiralcel OZ-H column (4.6 mm x 250 mm, 5 µm particle size) under the following conditions: 40 ^oC, 5% isopropyl alcohol, 2 mL min^{-1}. R_T = 9.66 min, 11.01 min.

S16: 1-methoxy-3-(1-phenylethyl)benzene



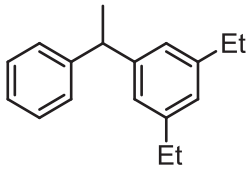
S16, a previously reported molecule,[8] was synthesized according to Method D to afford ^1H NMR conversions of >95% (run 1) and >95% (run 2) and er's of 73:27 and 75:25, respectively. Enantiomers were separated by SFC on a Chiralcel OJ-H column (4.6 mm x 250 mm) under the following conditions: 40 ^oC, 1% methanol, 4 mL min^{-1}. R_T = 10.71 min, 11.66 min.

S17: 1-methoxy-4-(1-phenylethyl)benzene



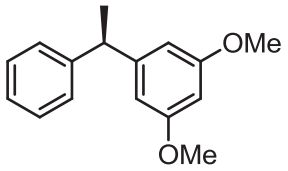
S17, a previously reported molecule,[6] was synthesized according to Method D to afford ^1H NMR conversions of >95% (run 1) and >95% (run 2) and er's of 52:48 and 54:46, respectively. Enantiomers were separated by SFC on a Chiralcel OJ-H column (4.6 mm x 250 mm) under the following conditions: 40 ^oC, 1% methanol, 4 mL min^{-1}. R_T = 10.71 min, 11.66 min.

S18: 1,3-diethyl-5-(1-phenylvinyl)benzene



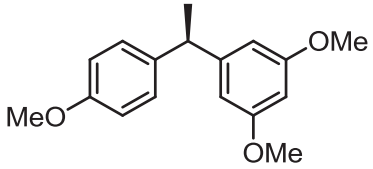
S18 was synthesized according to Method D to afford ^1H NMR conversions of >95% (run 1) and >95% (run 2) and er's of 49:51 and 48:52, respectively. TLC (10% ethyl acetate in hexanes) R_f=0.63. ^1H NMR (300 MHz, $CDCl_3$) δ: 1.21 (t, *J*=7.62 Hz, 6H), 1.63 (d, *J*=7.28 Hz, 3H), 2.59 (q, *J*=7.60 Hz, 4H), 4.11 (q, *J*=7.19 Hz, 1H), 6.88 (s, 3H), 7.14-7.32 (m, 5H). ^{13}C NMR (126 MHz, $CDCl_3$) δ: 15.8 (s), 22.2 (s), 29.0 (s), 45.0 (s), 124.7 (s), 125.3 (s), 126.0 (s), 127.8 (s), 128.4 (s), 144.3 (s), 146.4 (s), 146.8 (s). IR (thin film): 3024, 2964, 2931, 2872, 2359, 2341, 1599, 1495, 1458, 1373, 1319, 1067, 1030, 868, 762, 711, 699, 668 cm^{-1}. HRMS $C_{18}H_{22}Ag$ $[M+Ag]^+$ calculated 345.0772, observed 345.0797. Enantiomers were separated by SFC on a Chiralcel OJ-H column (4.6 mm x 250 mm) under the following conditions: 40 ^oC, 0% co-solvent, 2 mL min^{-1}. R_T = 5.75 min, 6.21 min.

9: (*R*)-(–)-1,3-diethyl-5-(1-phenylethyl)benzene



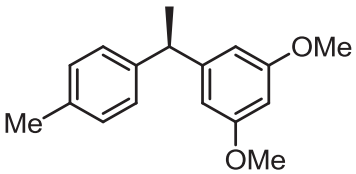
Product **9** was synthesized according to Method D to afford ^{1}H NMR conversions of >95% (run 1) and >95% (run 2) and er's of 92:8 and 93:7, respectively. Absolute configuration was assigned by analogy (*vide supra*). TLC (10% ethyl acetate in hexanes) R_f= 0.33. $[\alpha]_D^{20} =$ -2.5 (*c* 0.40, $CHCl_3$). ^{1}H NMR (500 MHz, $CDCl_3$) δ: 1.63 (d, *J*=7.33 Hz, 3H), 3.76 (s, 6H), 4.09 (q, *J*=7.33 Hz, 1H), 6.31 (t, *J*=2.44 Hz, 1H), 6.40 (d, *J*=2.45 Hz, 2H), 7.19 (t, *J*=7.33 Hz, 1H), 7.24 (d, *J*=7.33 Hz, 2H), 7.27-7.31 (m, 2H). ^{13}C NMR (126 MHz, $CDCl_3$) δ: 21.9 (s), 45.1 (s), 55.4 (s), 97.8 (s), 106.2 (s), 126.2 (s), 127.7 (s), 128.5 (s), 146.2 (s), 149.0 (s), 160.9 (s). IR (thin film): 2964, 2934, 2836, 2359, 1594, 1495, 1457, 1427, 1345, 1322, 1289, 1204, 1153, 1070, 1042, 1029, 990, 927, 834, 764, 703, 668, 540 cm^{-1}. HRMS $C_{16}H_{19}O_2$ $[M+H]^+$ calculated 243.1385, observed 243.1388. Enantiomers were separated by SFC on a Chiralpak AD-H column (4.6 mm x 250 mm, 5 µm particle size) under the following conditions: 32 °C, gradient 5%-50% methanol over 10 min., 3 mL min^{-1}. R_T = 2.92 min, 3.36 min.

10: (*R*)-(+)-1,3-dimethoxy-5-(1-(4-methoxyphenyl)ethyl)benzene



Product **10** was synthesized according to Method D to afford ^{1}H NMR conversions of >95% (run 1) and >95% (run 2) and er's of 91:9 and 92:8, respectively. Absolute configuration was assigned by analogy (*vide supra*). TLC (10% ethyl acetate in hexanes) R_f=0.24. $[\alpha]_D^{20} =$ +5.0 (*c* 0.48, $CHCl_3$). ^{1}H NMR (300 MHz, $CDCl_3$) δ: 1.59 (d, *J*=7.14 Hz, 3H), 3.75 (s, 6H), 3.78 (s, 3H), 4.03 (q, *J*=7.23 Hz, 1H), 6.27-6.31 (m, 1H), 6.34-6.39 (m, 2H), 6.79-6.85 (m, 2H), 7.11-7.18 (m, 2H). ^{13}C NMR (126 MHz, $CDCl_3$) δ: 22.1 (s). 44.3 (s), 55.4 (s), 97.7 (s), 106.0 (s), 113.9 (s), 128.6 (s), 138.3 (s), 149.4 (s), 158.0 (s), 160.8 (s). IR (thin film): 2962, 2934, 2835, 2360, 2341, 1653, 1606, 1595, 1540, 1559, 1540, 1511, 1458, 1428, 1373, 1302, 1247, 1204, 1179, 1154, 1117, 1074, 1035, 927, 831, 810, 695, 668 cm^{-1}. HRMS $C_{17}H_{21}O_3$ $[M+H]^+$ calculated 273.1491, observed 273.1483. Enantiomers were separated by SFC on a Chiralcel OJ-H column (4.6 mm x 250 mm) under the following conditions: 40 °C, 3% methanol, 4 mL min^{-1}. R_T = 5.66 min, 6.37 min.

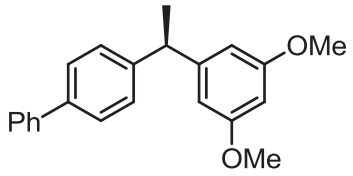
11: (*R*)-(+)-1,3-dimethoxy-5-(1-(*p*-tolyl)ethyl)benzene



Product **11:** was synthesized according to Method D to afford ^{1}H NMR conversions of >95% (run 1) and >95% (run 2) and er's of 88:12 and 89:11, respectively. Absolute configuration was assigned by analogy (*vide supra*). TLC (10% ethyl acetate in hexanes) R_f=0.35. $[\alpha]_D^{20} =$ +0.9 (*c* 0.55, $CHCl_3$). ^{1}H NMR (300 MHz, $CDCl_3$) δ: 1.60 (d, *J*=7.28 Hz, 3H), 2.31 (s, 3H), 3.76 (s, 6H), 4.05 (q, *J*=7.19 Hz, 1H), 6.29-6.32 (m,

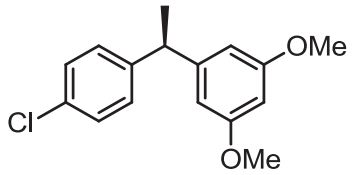
1H), 6.38-6.42 (m, 2H), 7.07-7.16 (m, 4H). ^{13}C NMR (126 MHz, $CDCl_3$) δ: 21.1 (s), 22.0 (s), 44.8 (s), 55.4 (s), 97.7 (s), 106.1 (s), 127.5 (s), 129.2 (s), 135.7 (s), 143.2 (s), 149.2 (s), 160.8 (s). IR (thin film): 2964, 2933, 2836, 2360, 1595, 1513, 1458, 1427, 1344, 1289, 1204, 1155, 1076, 1043, 1021, 991, 927, 818, 740, 695, 668, 544 cm^{-1}. HRMS $C_{17}H_{21}O_2$ $[M+H]^+$ calculated 257.1542, observed 257.1536. Enantiomers were separated by SFC on a Chiralcel OJ-H column (4.6 mm x 250 mm) under the following conditions: 40 °C, 3% methanol, 4 mL min^{-1}. R_T = 4.45 min, 4.99 min.

12: (*R*)-(+)-4-(1-(3,5-dimethoxyphenyl)ethyl)-1,1'-biphenyl



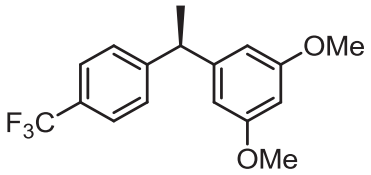
Product **12** was synthesized according to Method D to afford ^{1}H NMR conversions of >95% (run 1) and >95% (run 2) and er's of 89:11 and 89:11, respectively. Absolute configuration previously reported (*vide supra*). TLC (10% ethyl acetate in hexanes) R_f=0.33. $[\alpha]_D^{20}$ = +11.4 (*c* 0.57, $CHCl_3$). ^{1}H NMR (300 MHz, $CDCl_3$) δ: 1.66 (d, *J*=7.14 Hz, 3H), 3.77 (s, 6H), 4.13 (q, *J*=7.23 Hz, 1H), 6.31-6.34 (m, 1H), 6.44 (d, *J*=2.33 Hz, 2H), 7.28-7.37 (m, 3H), 7.38-7.47 (m, 2H), 7.48-7.61 (m, 4H). ^{13}C NMR (126 MHz, $CDCl_3$) δ: 21.9 (s), 44.9 (s), 55.4 (s), 97.8 (s), 106.2 (s), 127.2 (s), 127.2 (s), 127.3 (s), 128.1 (s), 128.8 (s), 139.1 (s), 141.1 (s), 145.3 (s), 148.9 (s), 160.9 (s). IR (thin film): 3027, 2964, 2933, 2835, 2361, 2338, 2210, 2176, 2159, 1595, 1486, 1458, 1427, 1345, 1288, 1204, 1154, 1076, 1045, 1008, 927, 835, 767, 738, 697, 668, 549 cm^{-1}. HRMS $C_{22}H_{23}O_2$ $[M+H]^+$ calculated 319.1698, observed 319.1706. Enantiomers were separated by SFC on a Chiralcel AY-H column (4.6 mm x 250 mm, 5 µm particle size) under the following conditions: 40 °C, gradient 5%-50% methanol over 10 min., 3 mL min^{-1}. R_T = 5.40 min, 6.12 min.

13: (*R*)-(+)-1-(1-(4-chlorophenyl)ethyl)-3,5-dimethoxybenzene



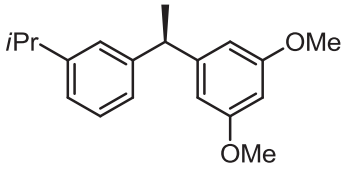
Product **13** was synthesized according to Method D to afford ^{1}H NMR conversions of >95% (run 1) and >95% (run 2) and er's of 96:4 and 96:4, respectively. Absolute configuration was assigned by analogy (*vide supra*). TLC (10% ethyl acetate in hexanes) R_f=0.39. $[\alpha]_D^{20}$ = +4.5 (*c* 0.71, $CHCl_3$). ^{1}H NMR (300 MHz, $CDCl_3$) δ: 1.59 (d, *J*=7.28 Hz, 3H), 3.76 (s, 6H), 4.05 (q, *J*=7.23 Hz, 1H), 6.31-6.34 (m, 1H), 6.33-3.37 (m, 2H), 7.12-7.18 (m, 2H), 7.21-7.27 (m, 2H). ^{13}C NMR (126 MHz, $CDCl_3$) δ: 21.8 (s), 44.5 (s), 55.4 (s), 97.9 (s), 106.1 (s), 128.6 (s), 129.0 (s), 131.9 (s), 144.7 (s), 148.4 (s), 160.9 (s). IR (thin film): 2965, 2934, 2836, 2361, 2337, 1595, 1491, 1458, 1427, 1407, 1344, 1288, 1204, 1155, 1092, 1075, 1042, 1014, 928, 829, 782, 730, 697, 668 cm^{-1}. HRMS $C_{16}H_{17}ClO_2$ $[M+H]^+$ calculated 277.0995, observed 277.0995. Enantiomers were separated by SFC on a Chiralpak AD-H column (4.6 mm x 250 mm, 5 µm particle size) under the following conditions: 40 °C, 3% methanol, 4 mL min^{-1}. R_T = 3.16 min, 5.89 min.

14: (*R*)-(–)-1,3-dimethoxy-5-(1-(4-(trifluoromethyl)phenyl)ethyl)benzene



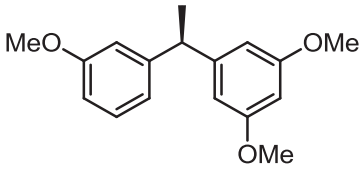
Product **14** was synthesized according to Method D to afford ^{1}H NMR conversions of >95% (run 1) and >95% (run 2) and er's of 96:4 and 97:3, respectively. Absolute configuration was assigned by analogy (*vide supra*). TLC (15% ethyl acetate in hexanes) R_f= 0.43. $[\alpha]_D^{20} =$ -2.6 (*c* 0.69, $CHCl_3$). ^{1}H NMR (300 MHz, $CDCl_3$) δ: 1.63 (d, *J*=7.28 Hz, 3H), 3.76 (s, 6H), 4.13 (q, *J*=7.28 Hz, 1H), 6.31-6.34 (m, 1H), 6.34-6.37 (m, 2H), 7.33 (dd, *J*=8.10 Hz, 0.69 Hz, 2H), 7.53 (d, *J*=8.10 Hz, 2H). ^{13}C NMR (126 MHz, $CDCl_3$) δ: 21.6 (s), 45.0 (s), 55.4 (s), 98.0 (s), 106.2 (s), 124.4 (q, *J*=272.5 Hz), 125.5 (q, *J*=3.8 Hz), 128.0 (s), 128.5 (q, *J*=32.4 Hz), 147.8 (s), 150.3 (m), 161.0 (s). ^{19}F NMR (282 MHz, $CDCl_3$) δ: -63. IR (thin film): 2967, 2839, 2360, 1596, 1459, 1429, 1325, 1205, 1159, 1118, 1068, 1043, 1017, 928, 841, 742, 698, 668, 611 cm^{-1}. HRMS $C_{17}H_{18}O_2F_3$ $[M+H]^+$ calculated 311.1259, observed 311.1253. Enantiomers were separated by SFC on a Chiralpak AD-H column (4.6 mm x 250 mm) under the following conditions: 40 ^{o}C, 2% methanol, 2 mL min^{-1}, 160 Bar. R_T = 3.65 min, 4.62 min.

15: (*R*)-(–)-1-(1-(3-isopropylphenyl)ethyl)-3,5-dimethoxybenzene



Product **15** was synthesized according to Method D to afford ^{1}H NMR conversions of >95% (run 1) and >95% (run 2) and er's of 85:15 and 86:14, respectively. Absolute configuration was assigned by analogy (*vide supra*). TLC (15% ethyl acetate in hexanes) R_f=0.50. $[\alpha]_D^{20} =$ -3.1 (*c* 0.70, $CHCl_3$). ^{1}H NMR (300 MHz, $CDCl_3$) δ: 1.24 (d, *J*=6.87 Hz, 6H), 1.62 (d, *J*=7.28 Hz, 3H), 2.88 (sep, *J*=6.91 Hz, 1H), 3.76 (s, 6H), 4.07 (q, *J*=7.23 Hz, 1H), 6.30 (t, *J*=2.20 Hz, 1H), 6.41 (dd, *J*=2.33 Hz, 0.55 Hz, 2H), 7.02-7.09 (m, 2H), 7.09-7.12 (m, 1H), 7.18-7.25 (m, 1H). ^{13}C NMR (75 MHz, $CDCl_3$) δ: 22.0 (s), 24.2 (s), 24.2 (s), 34.3 (s), 45.2 (s), 55.4 (s), 97.7 (s), 106.1 (s), 124.1 (s), 125.1 (s), 126.1 (s), 128.4 (s), 146.0 (s), 149.0 (s), 149.2 (s), 160.8 (s). IR (thin film): 2960, 2836, 2364, 1596, 1459, 1427, 1345, 1289, 1204, 1154, 1071, 1043, 928, 832, 796, 707, 668 cm^{-1}. HRMS $C_{19}H_{25}O_2$ $[M+H]^+$ calculated 285.1855, observed 285.1862. Enantiomers were separated by SFC on a Chiralcel OJ-H column (4.6 mm x 250 mm) under the following conditions: 27 ^{o}C, 0% cosolvent, 4 mL min^{-1}. R_T = 3.21 min, 3.76 min.

16: (*R*)-(–)-1,3-dimethoxy-5-(1-(3-methoxyphenyl)ethyl)benzene

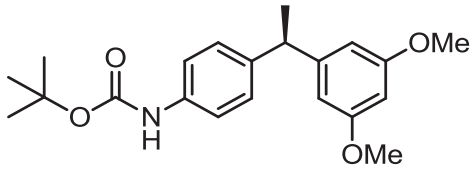


Product **16** was synthesized according to Method D to afford ^{1}H NMR conversions of >95% (run 1) and >95% (run 2) and er's of 71:29 and 71:29, respectively. Absolute configuration was assigned by analogy (*vide supra*). TLC (15% ethyl acetate in hexanes) R_f= 0.38. $[\alpha]_D^{20} =$ -1.3 (*c* 0.61, $CHCl_3$). ^{1}H NMR (300

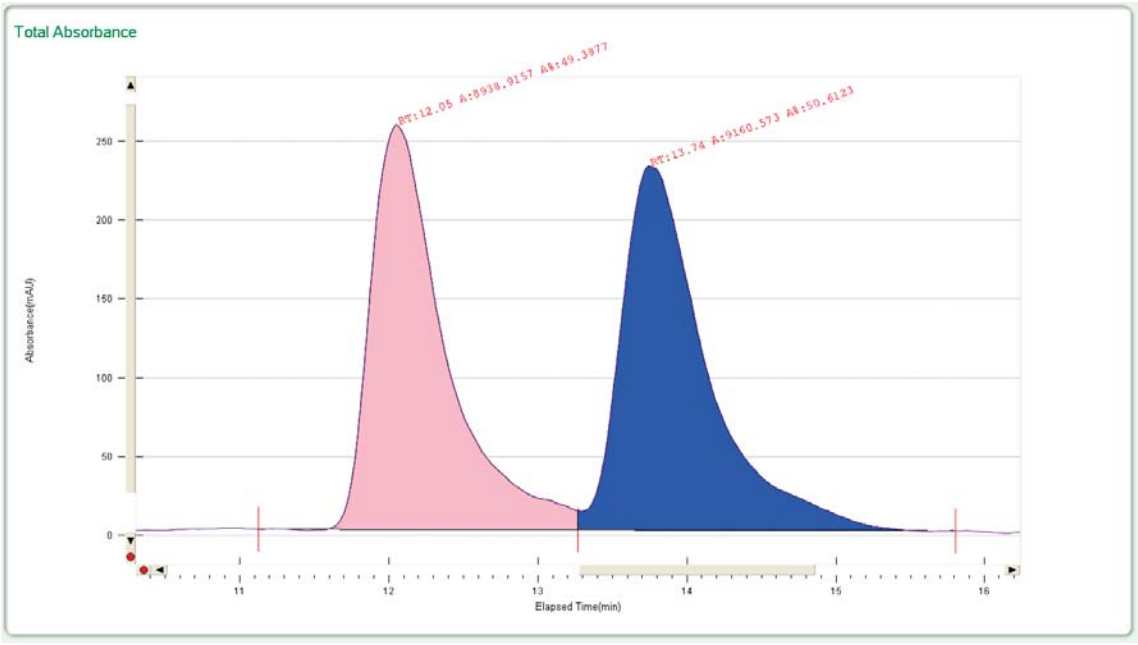
MHz, $CDCl_3$) δ: 1.60 (d, *J*=7.14 Hz, 3H), 3.75 (s, 6H), 3.78 (s, 3H), 4.05 (q, *J*=7.14 Hz, 1H), 6.29-6.31 (m, 1H), 6.39 (d, *J*=2.33 Hz, 2H), 6.73 (ddd, *J*=8.17 Hz, 2.54 Hz, 0.96 Hz, 1H), 6.76-6.80 (m, 1H), 6.83 (dt, *J*=7.69 Hz, 0.82 Hz, 1H), 7.17-7.23 (m, 1H). ^{13}C NMR (75 MHz, $CDCl_3$) δ: 21.8 (s), 45.1 (s), 55.3 (s), 55.4 (s), 97.8 (s), 106.1 (s), 111.1 (s), 113.8 (s), 120.1 (s), 129.4 (s), 147.8 (s), 148.8 (s), 159.7 (s), 160.8 (s). IR (thin film): 2964, 2835, 2362, 1595, 1486, 1458, 1428, 1318, 1287, 1263, 1204, 1154, 1040, 928, 834, 782, 735, 708 cm^{-1}. HRMS $C_{17}H_{21}O_3$ $[M+H]^+$ calculated 273.1491, observed 273.1503. Enantiomers were separated by SFC on a Chiralcel OJ-H column (4.6 mm x 250 mm) under the following conditions: 24 ^oC, 0% cosolvent, 2 mL min^{-1}. R_T = 15.55 min, 17.48 min.

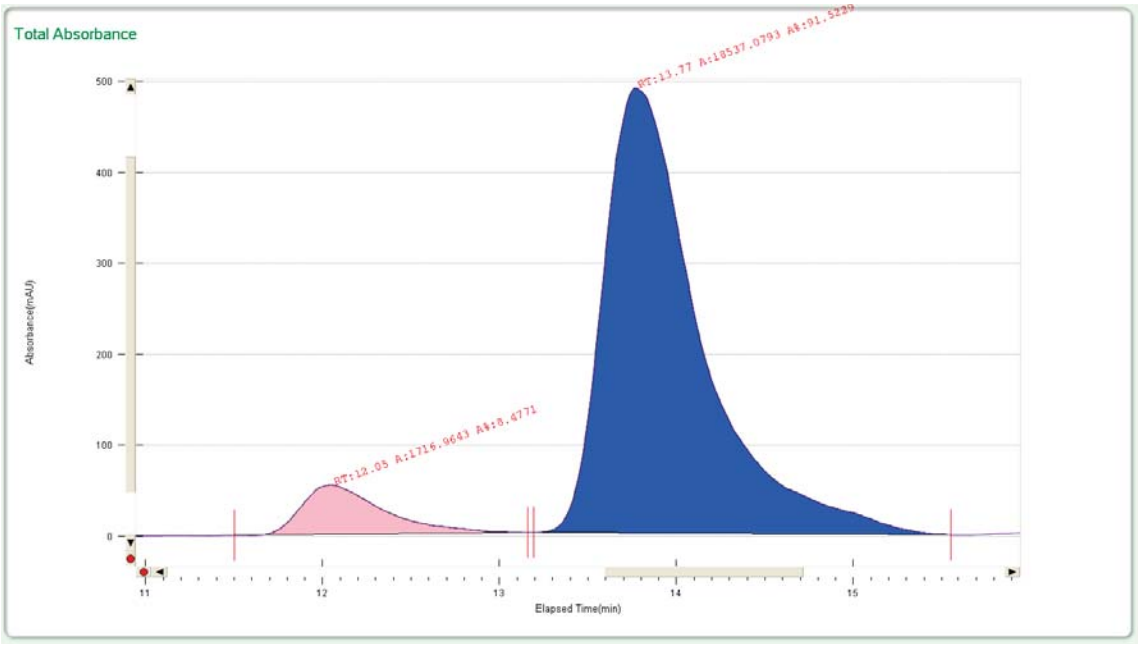
HPLC AND SFC TRACES

S11: (*R*)-(+)-*tert*-butyl (4-(1-(3,5-dimethoxyphenyl)ethyl)phenyl)carbamate

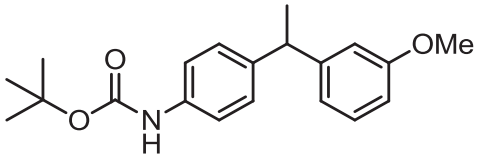


Enantiomers were separated by SFC on a Chiralpak AD-H column (4.6 mm x 250 mm, 5 µm particle size) under the following conditions: 40 °C, 20% isopropyl alcohol, 2 mL min^{-1}, 160 Bar. R_T = 12.05 min, 13.77 min.



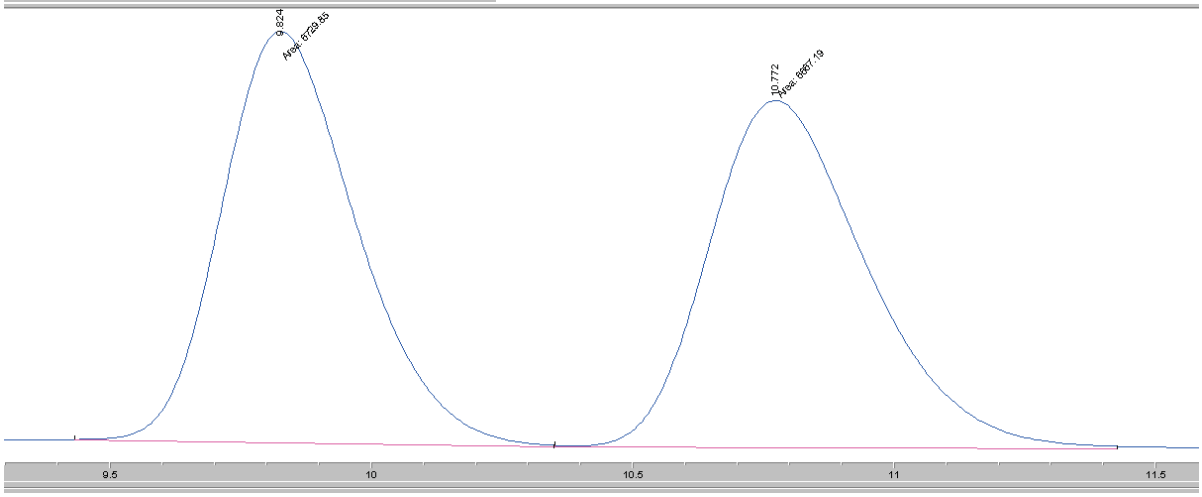


S12: *tert*-butyl (4-(1-(3-methoxyphenyl)ethyl)phenyl)carbamate

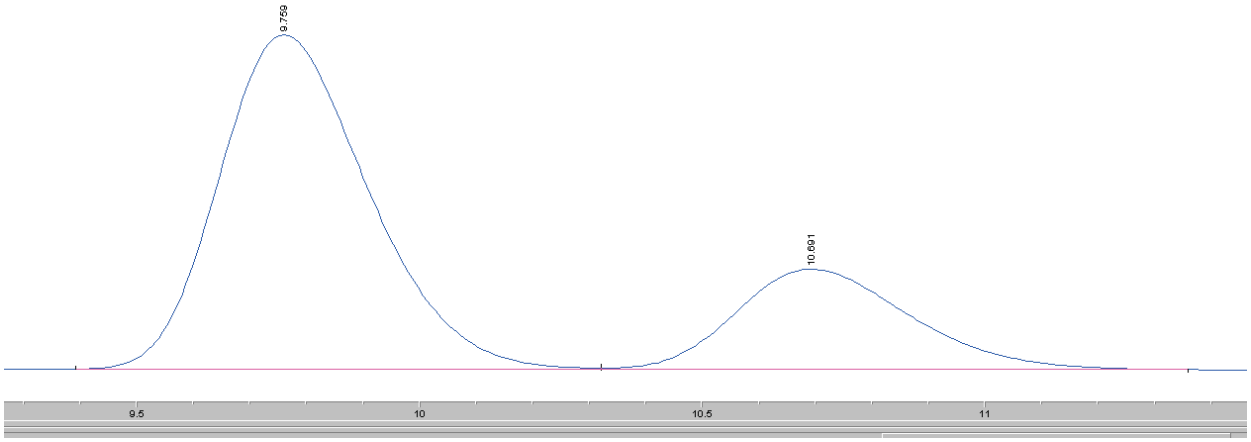


Enantiomers were separated by HPLC on a Chiralpak AD-H column (4.6 mm x 250 mm, 5 µm particle size) under the following conditions: ambient temperature, 10% isopropyl alcohol in hexanes, 0.9 mL min^{-1}. R_T = 9.76 min, 10.69 min.

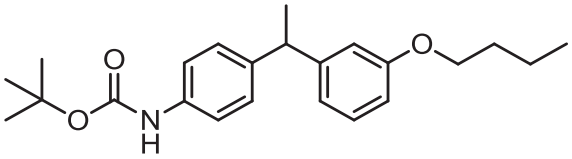
#	Time	Area	Height	Width	Area%	Symmetry
1	9.824	6729.8	374.1	0.2998	50.234	0.765
2	10.772	6667.2	315.7	0.352	49.766	0.727



#	Time	Area	Height	Width	Area%	Symmetry
1	9.759	4620.5	250.4	0.2833	73.970	0.745
2	10.691	1626	75.3	0.332	26.030	0.733

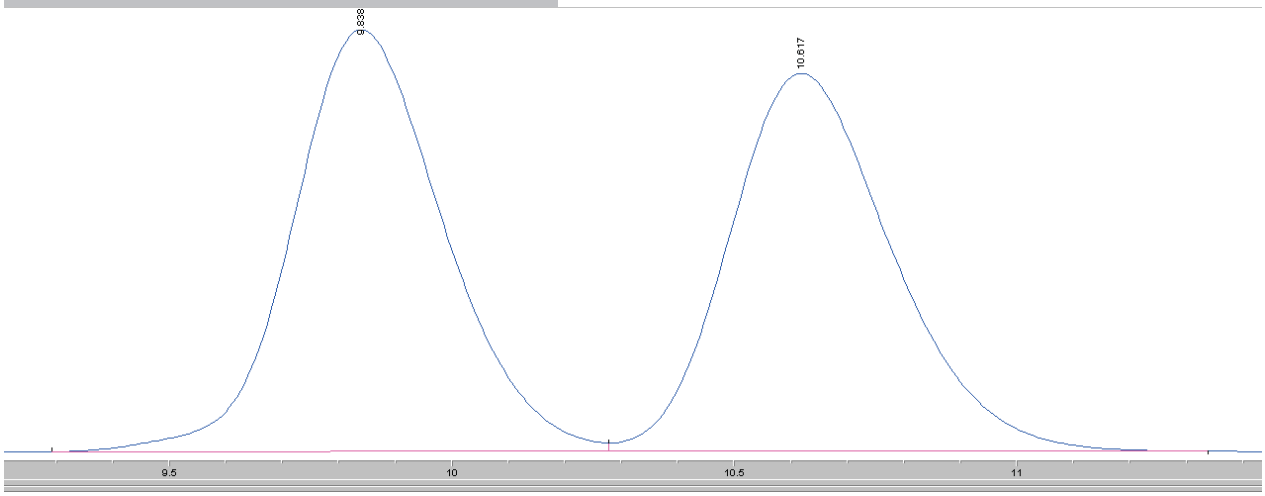


S13: *tert*-butyl (4-(1-(3-butoxyphenyl)ethyl)phenyl)carbamate

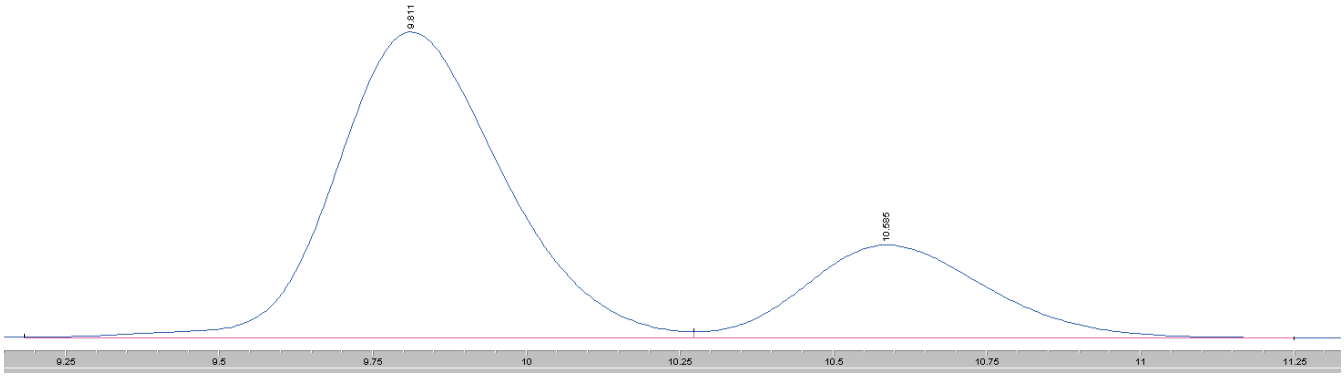


Enantiomers were separated by HPLC on a Chiralpak AD-H column (4.6 mm x 250 mm, 5 µm particle size) under the following conditions: ambient temperature, 5% isopropyl alcohol in hexanes, 0.9 mL min^{-1}. R_T = 9.74 min, 10.51 min.

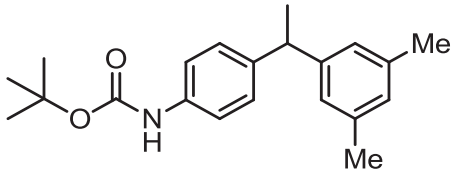
#	Time	Area	Height	Width	Area%	Symmetry
1	9.838	6464.9	346.3	0.2858	50.915	0.825
2	10.617	6232.5	310.4	0.3082	49.085	0.771



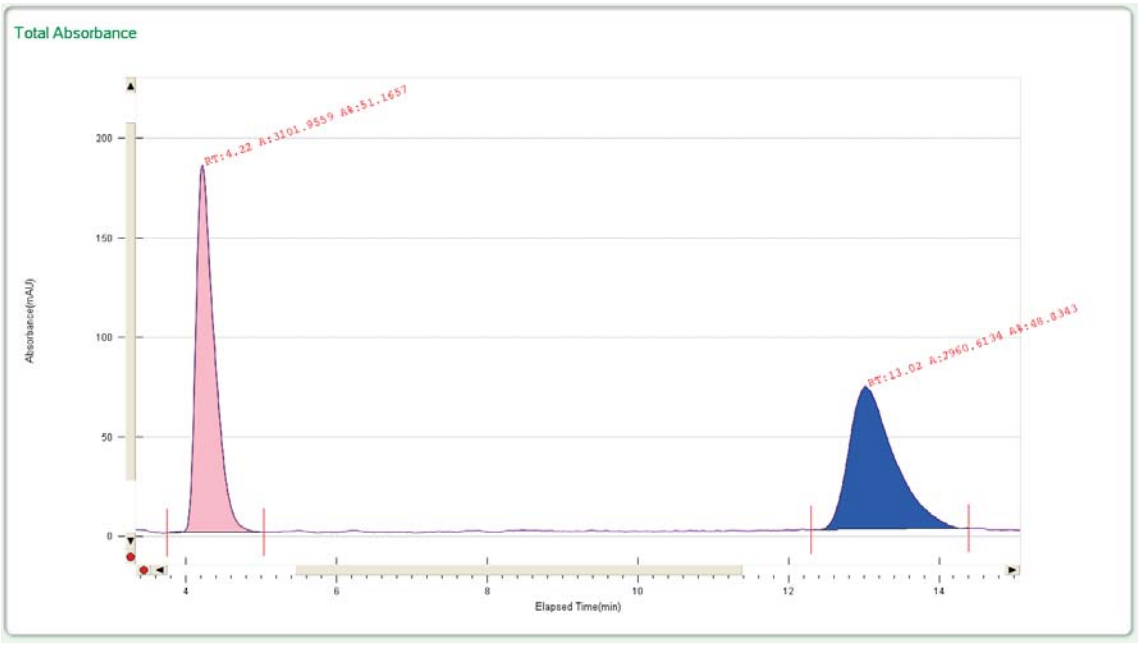
#	Time	Area	Height	Width	Area%	Symmetry
1	9.811	7086	373.2	0.2915	75.093	0.795
2	10.585	2350.2	113.4	0.3219	24.907	0.784

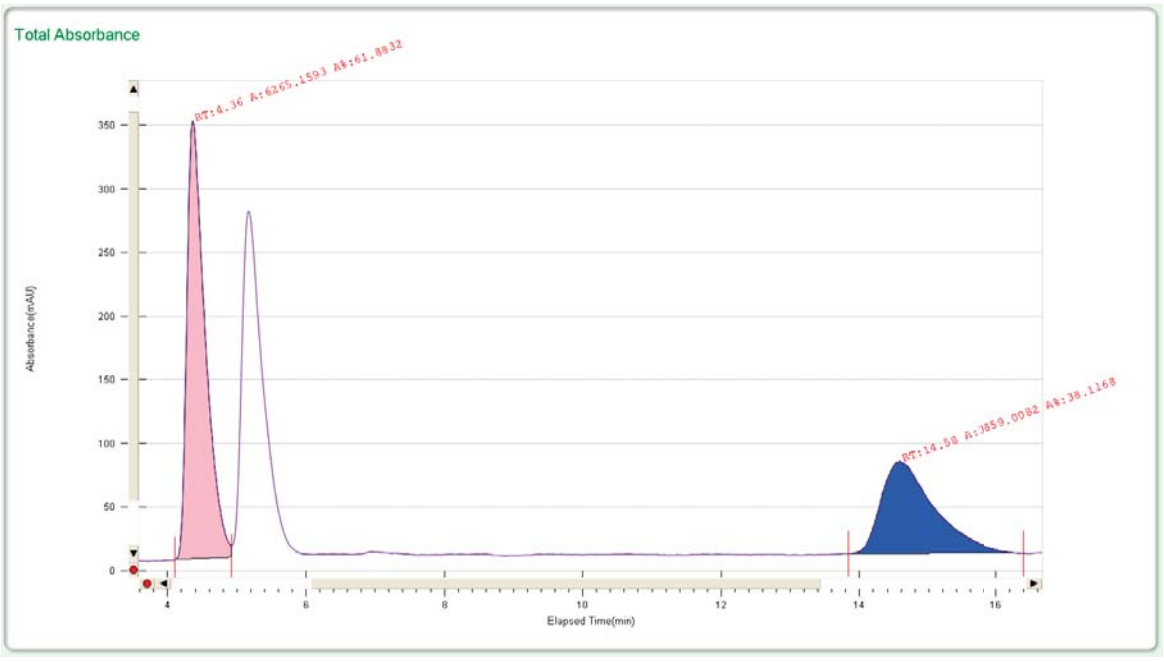


S14: *tert*-butyl (4-(1-(3,5-dimethylphenyl)ethyl)phenyl)carbamate

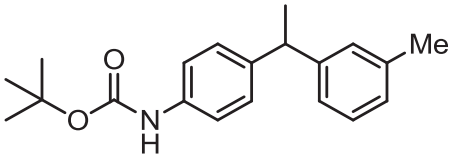


Enantiomers were separated by SFC on a Chiralcel OD column (4.6 mm x 250 mm) under the following conditions: 28 °C, 10% isopropyl alcohol, 3 mL min^{-1}, 160 bar. R_T = 4.36 min, 14.58 min.



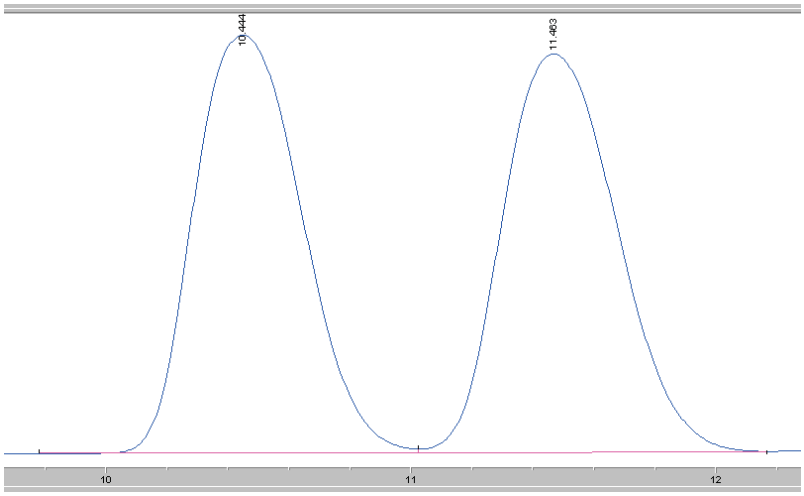


S15: *tert*-butyl (4-(1-(m-tolyl)ethyl)phenyl)carbamate

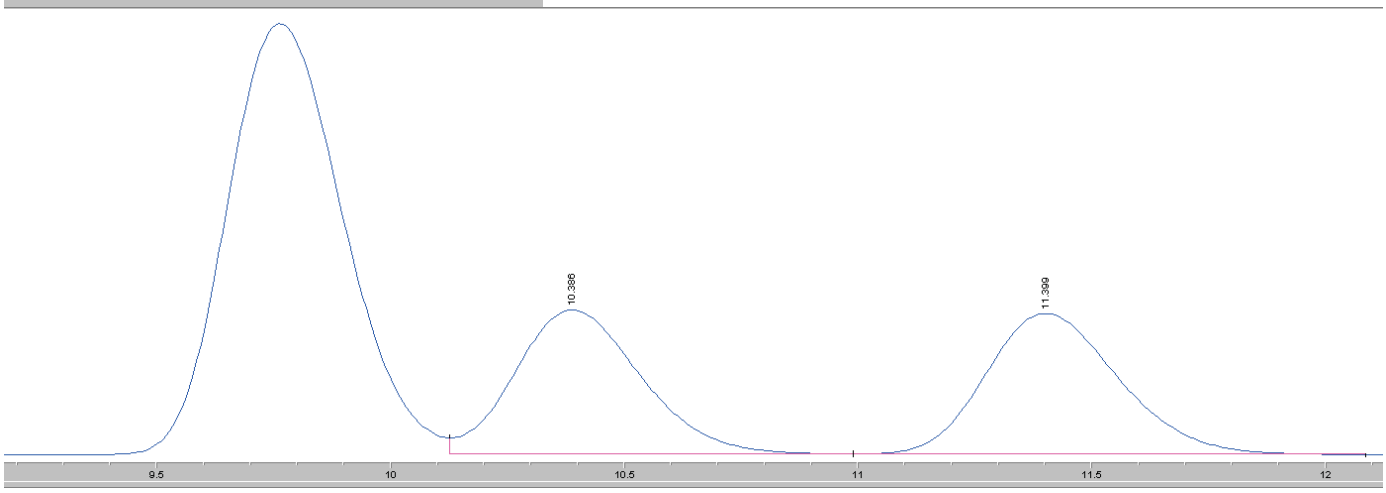


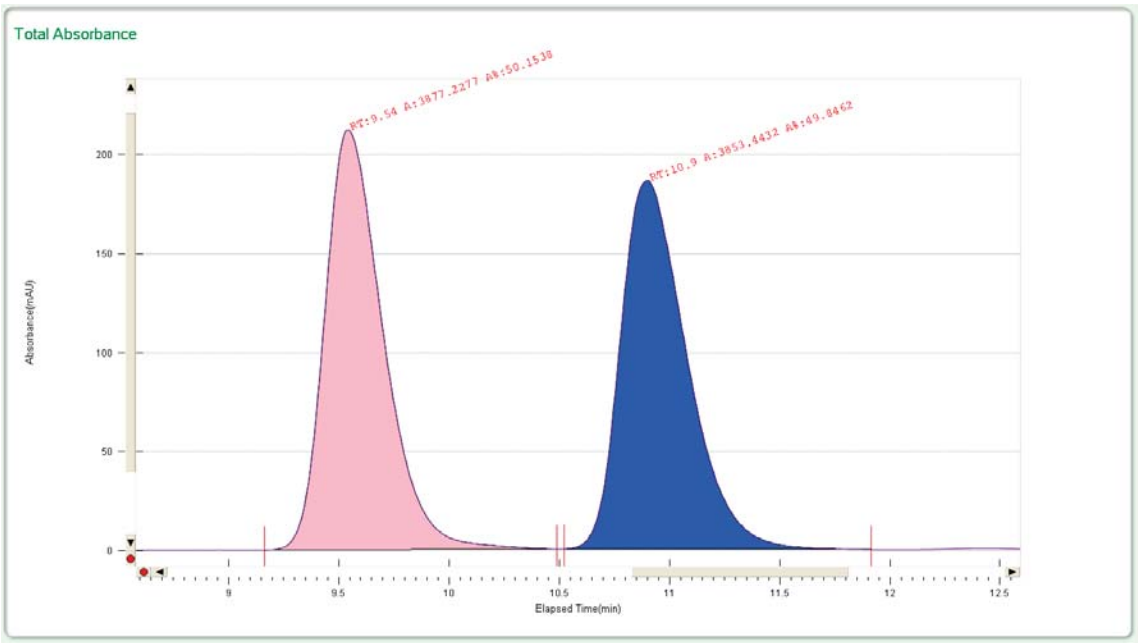
Enantiomers for run 1 were separated by HPLC on a Chiralpak AD-H column (4.6 mm x 250 mm, 5 µm particle size) under the following conditions: ambient temperature, 3% isopropyl alcohol in hexanes, 0.9 mL min^{-1}. R_T = 10.39 min, 11.40 min. Enantiomers for run 2 were separated by SFC on a Chiralcel OZ-H column (4.6 mm x 250 mm, 5 µm particle size) under the following conditions: 40 ^oC, 5% isopropyl alcohol, 2 mL min^{-1}, 160 bar. R_T = 9.66 min, 11.01 min.

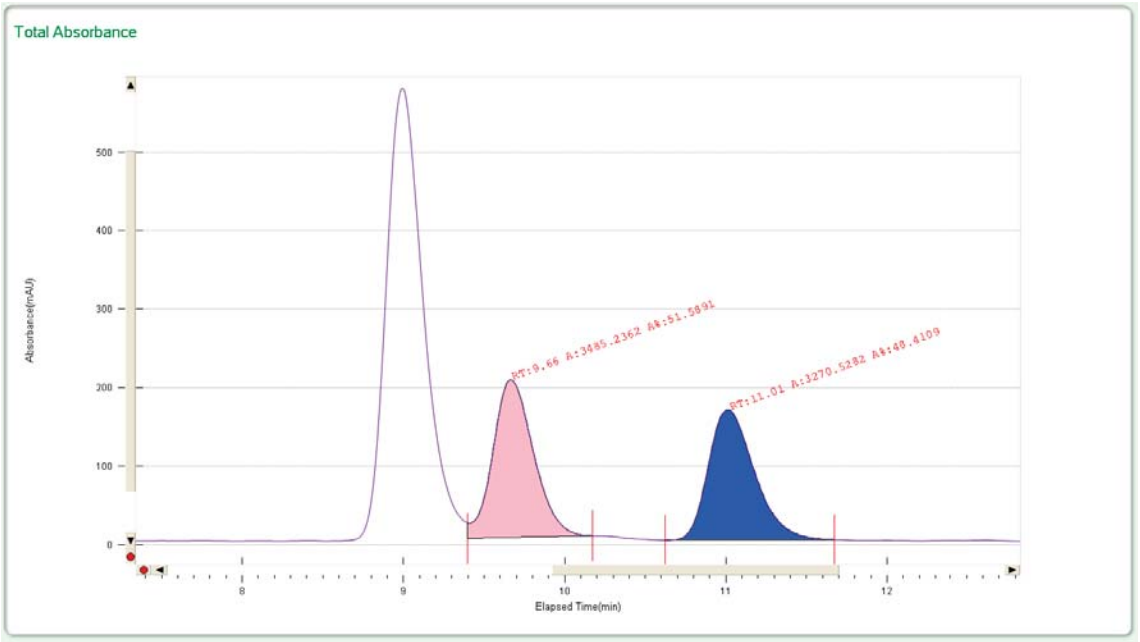
#	Time	Area	Height	Width	Area%	Symmetry
1	10.444	46560	1895.8	0.3965	49.748	0.791
2	11.463	47031.3	1807.7	0.4215	50.252	0.775



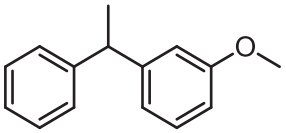
#	Time	Area	Height	Width	Area%	Symmetry
1	10.386	8421.8	446.1	0.2923	49.374	0.79
2	11.399	8635.2	435.3	0.3074	50.626	0.789



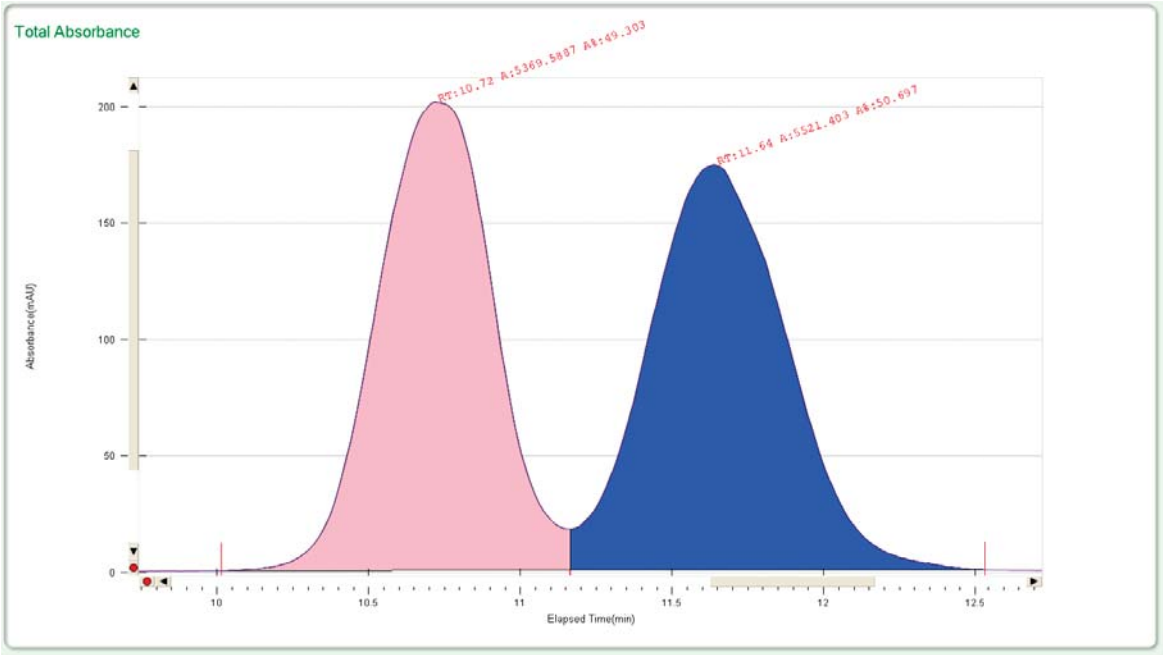

Total Absorbance
RT:9.54 A:3877.2277 A%:50.1538
RT:10.9 A:3853.4432 A%:49.8462
Absorbance(mAU)
Elapsed Time(min)

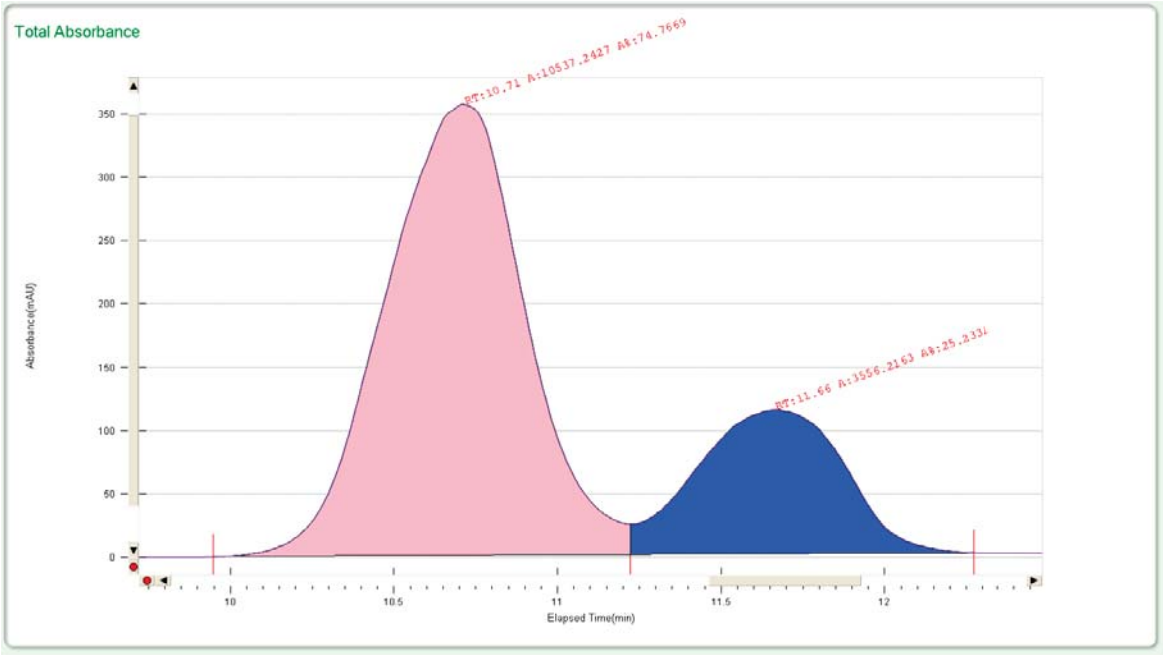

Total Absorbance
RT:9.66 A:3485.2362 A%:51.5891
RT:11.01 A:3270.5282 A%:48.4109
Absorbance(mAU)
Elapsed Time(min)

S16: 1-methoxy-3-(1-phenylethyl)benzene

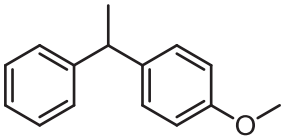


Enantiomers were separated by SFC on a Chiralcel OJ-H column (4.6 mm x 250 mm) under the following conditions: 40 ^{o}C, 1% methanol, 4 mL min^{-1}, 160 bar. R_T = 10.71 min, 11.66 min.

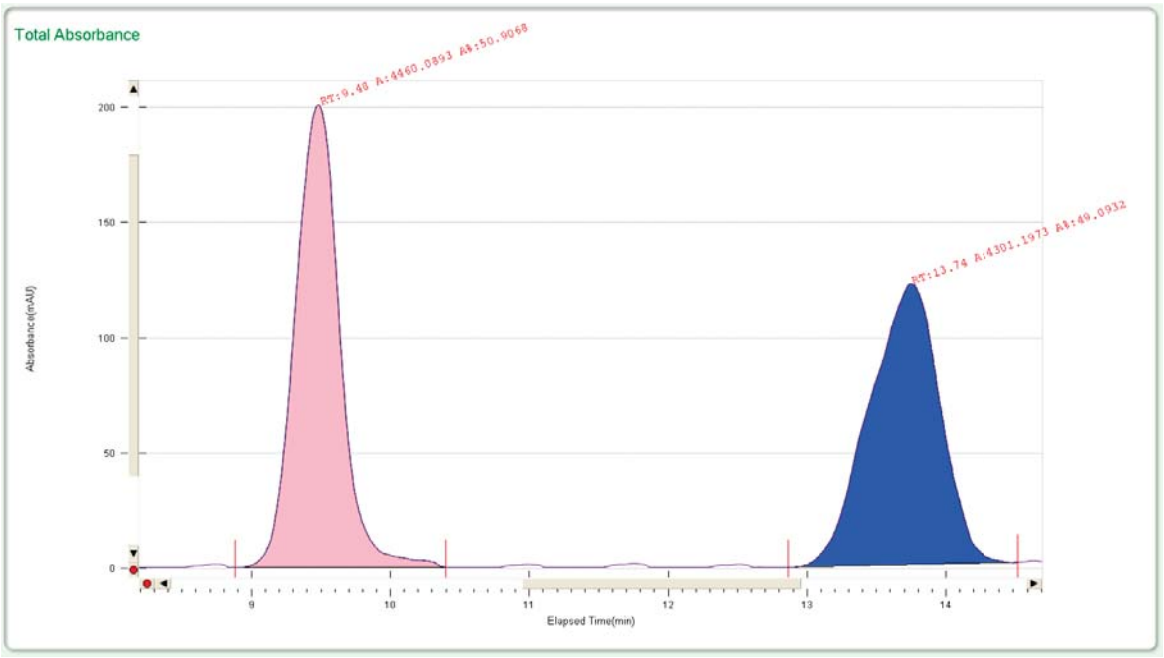


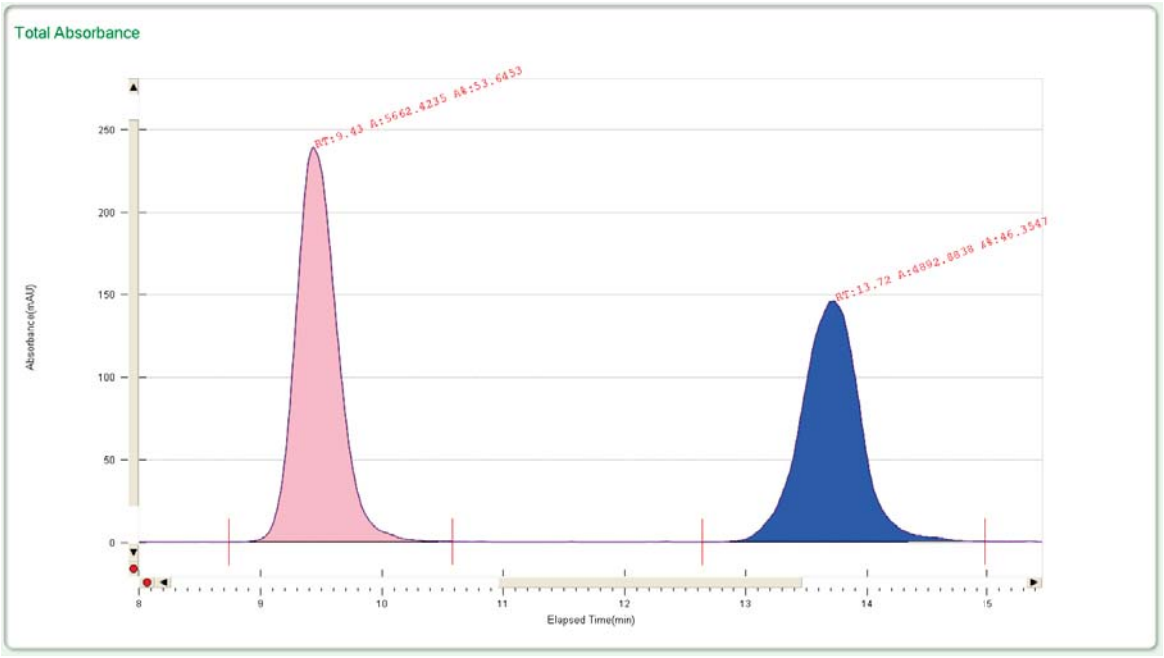


S17: 1-methoxy-4-(1-phenylethyl)benzene

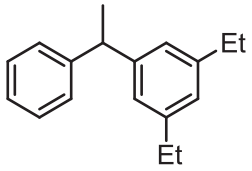


Enantiomers were separated by SFC on a Chiralcel OJ-H column (4.6 mm x 250 mm) under the following conditions: 40 ^{o}C, 1% methanol, 4 mL min^{-1}, 160 bar. R_T = 10.71 min, 11.66 min.

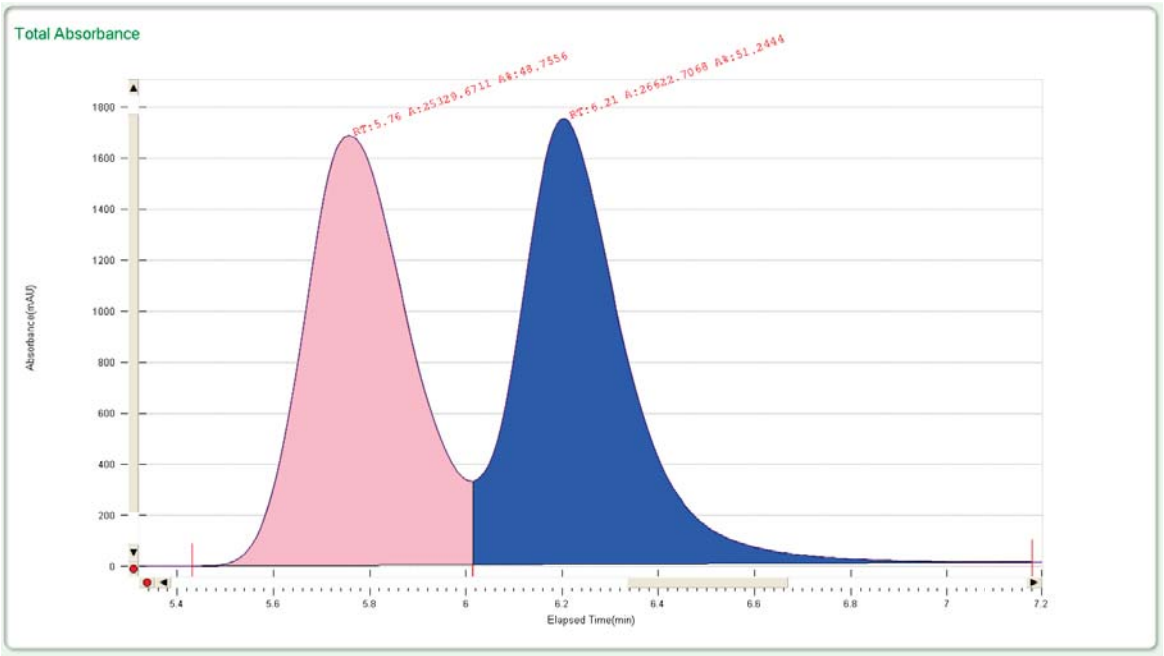


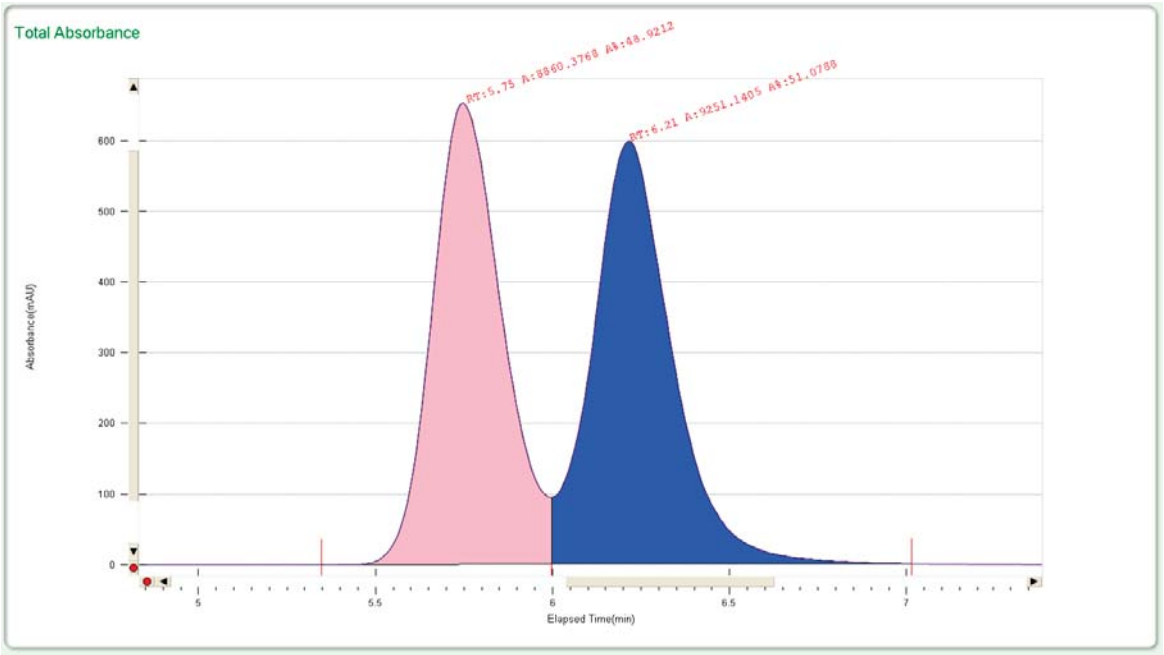


S18: 1,3-diethyl-5-(1-phenylvinyl)benzene

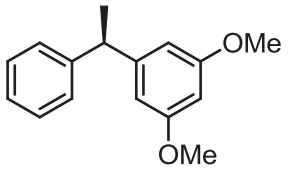


Enantiomers were separated by SFC on a Chiralcel OJ-H column (4.6 mm x 250 mm) under the following conditions: 40 °C, 0% co-solvent, 2 mL min^{-1}, 160 bar. R_T = 5.75 min, 6.21 min.

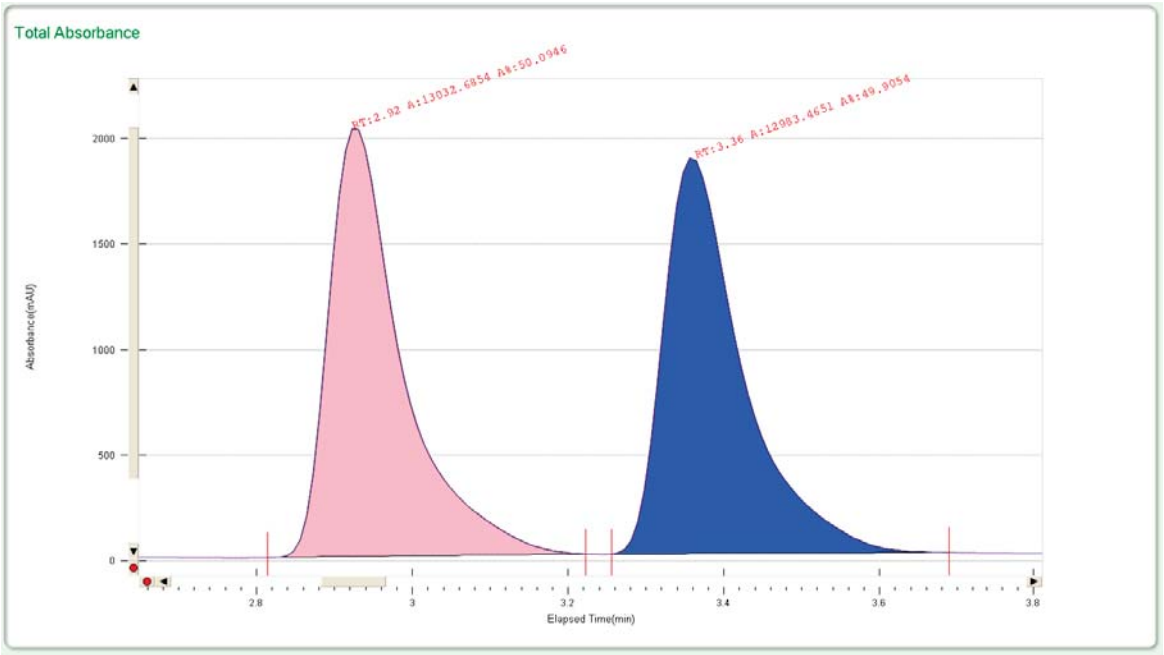


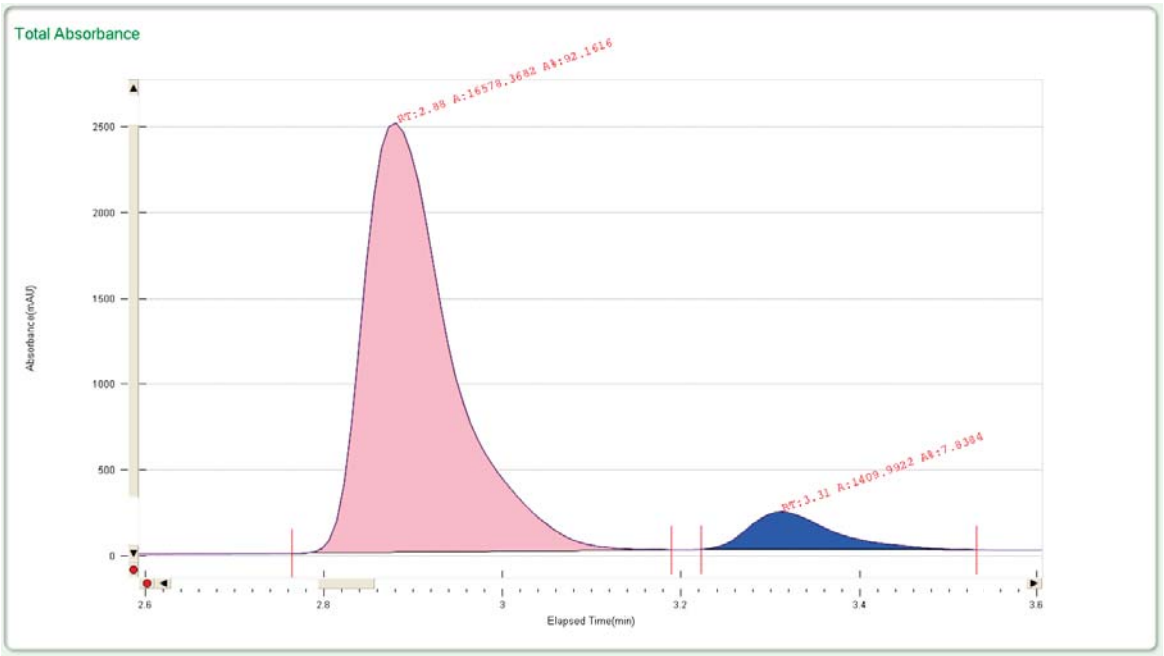


9: (*R*)-(–)-1,3-diethyl-5-(1-phenylethyl)benzene

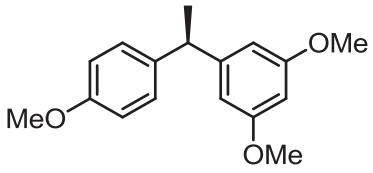


Enantiomers were separated by SFC on a Chiralpak AD-H column (4.6 mm x 250 mm, 5 µm particle size) under the following conditions: 32 °C, gradient 5%-50% methanol over 10 min., 3 mL min^{-1}, 160 bar. R_T = 2.92 min, 3.36 min.

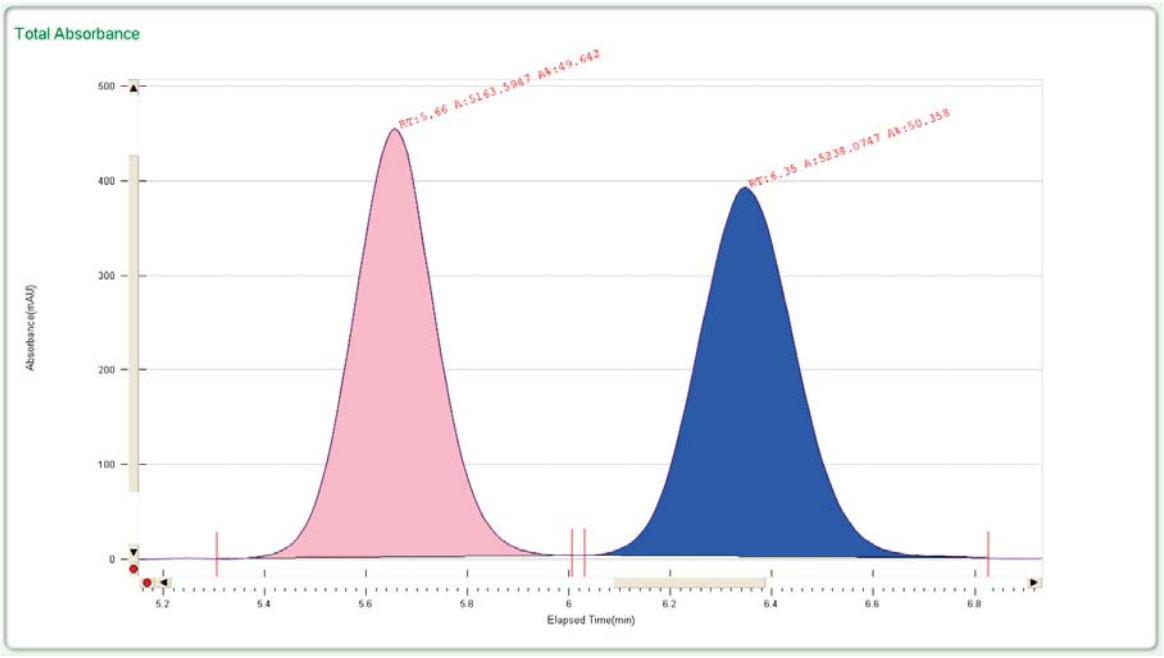


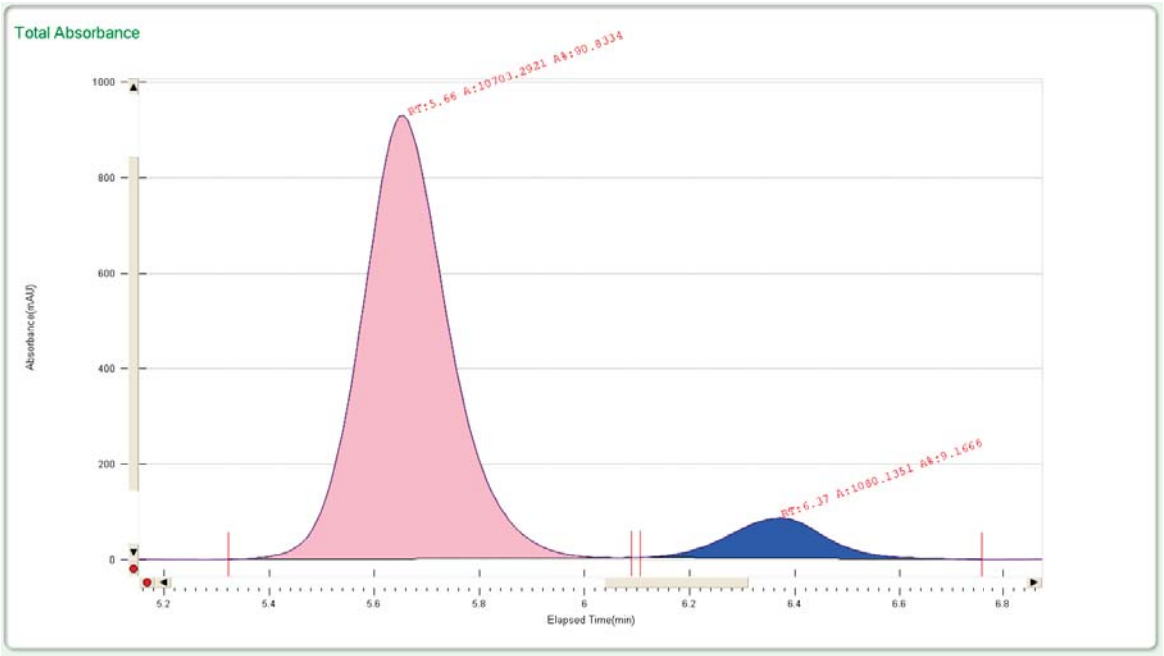


10: (*R*)-(+)-1,3-dimethoxy-5-(1-(4-methoxyphenyl)ethyl)benzene

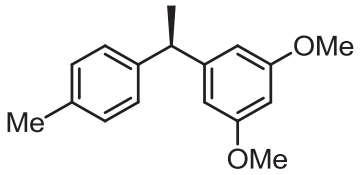


Enantiomers were separated by SFC on a Chiralcel OJ-H column (4.6 mm x 250 mm) under the following conditions: 40 °C, 3% methanol, 4 mL min^{-1}, 160 bar. R_T = 5.66 min, 6.37 min.

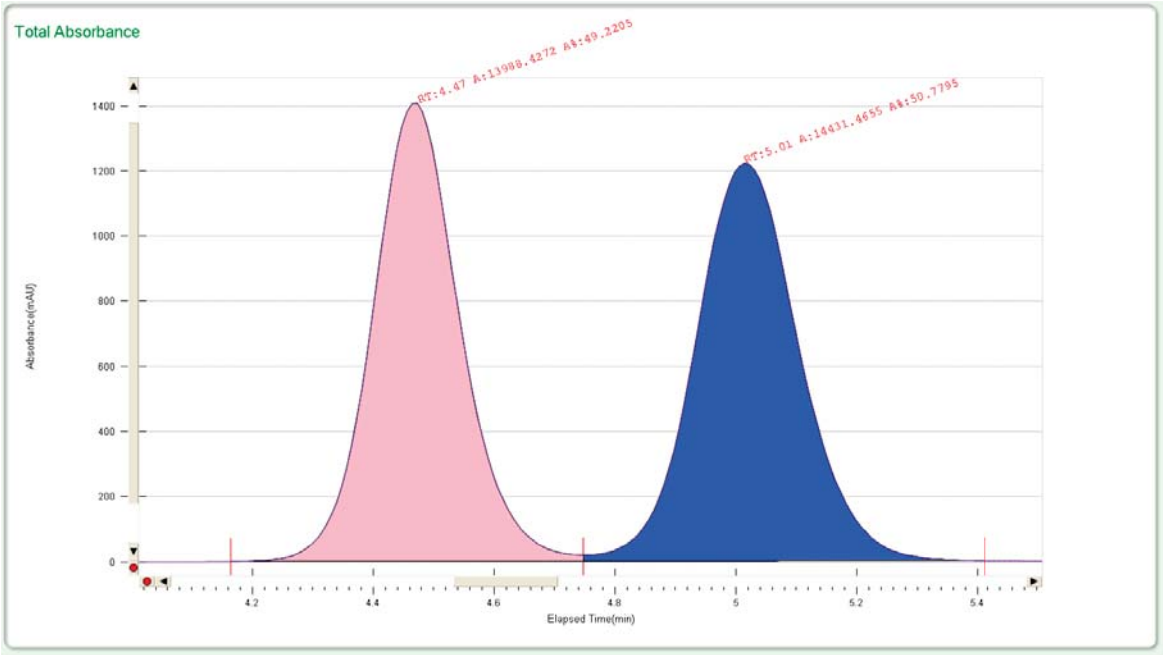


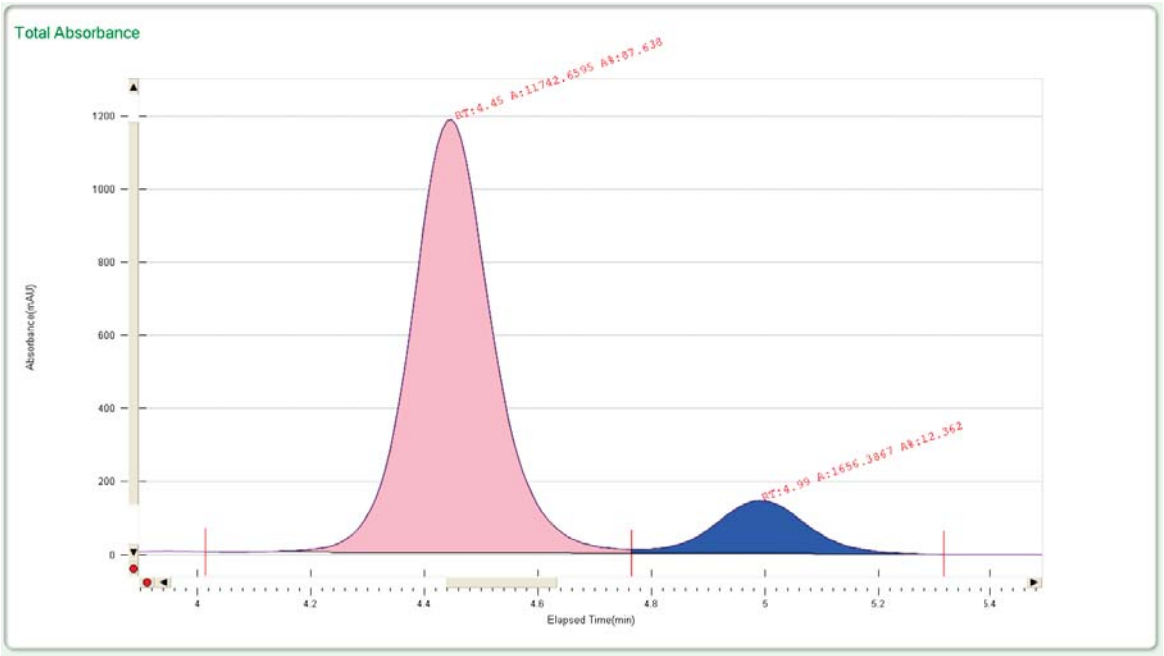


11: (*R*)-(+)-1,3-dimethoxy-5-(1-(*p*-tolyl)ethyl)benzene

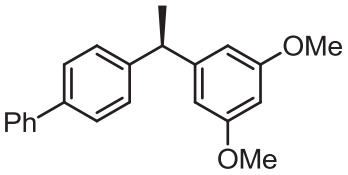


Enantiomers were separated by SFC on a Chiralcel OJ-H column (4.6 mm x 250 mm) under the following conditions: 40 °C, 3% methanol, 4 mL min^{-1}, 160 bar. R_T = 4.45 min, 4.99 min.

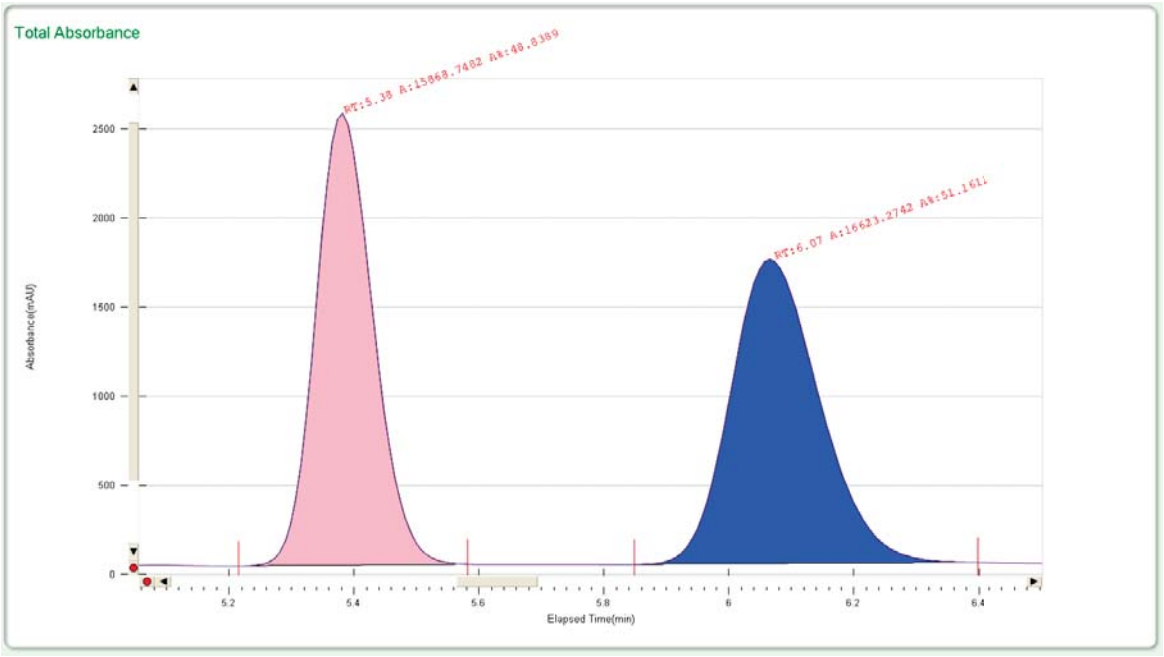


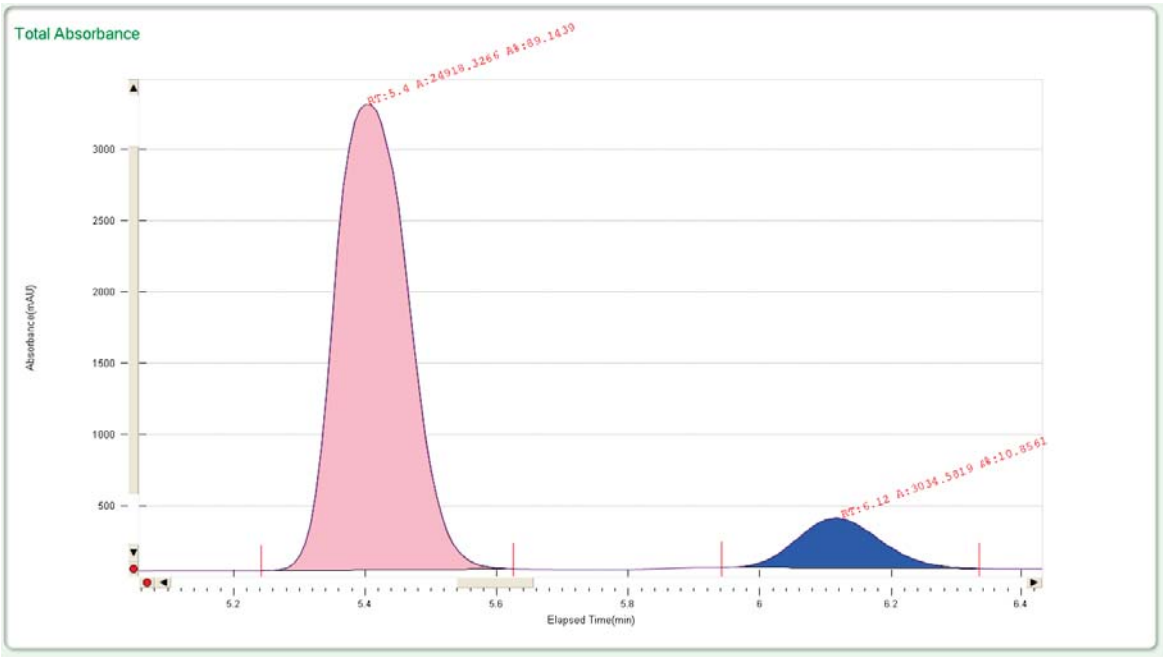


12: (*R*)-(+)-4-(1-(3,5-dimethoxyphenyl)ethyl)-1,1'-biphenyl

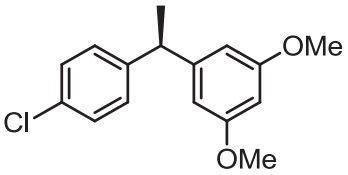


Enantiomers were separated by SFC on a Chiralcel AY-H column (4.6 mm x 250 mm, 5 µm particle size) under the following conditions: 40 °C, gradient 5%-50% methanol over 10 min., 3 mL min^{-1}, 160 bar. R_T = 5.40 min, 6.12 min.

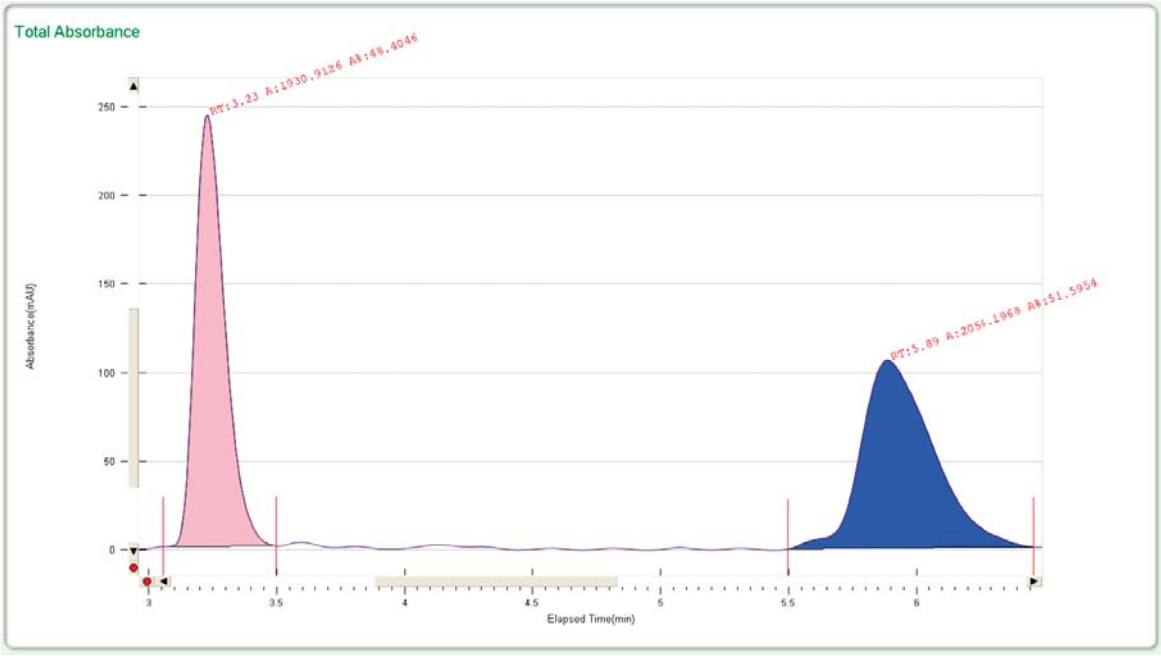


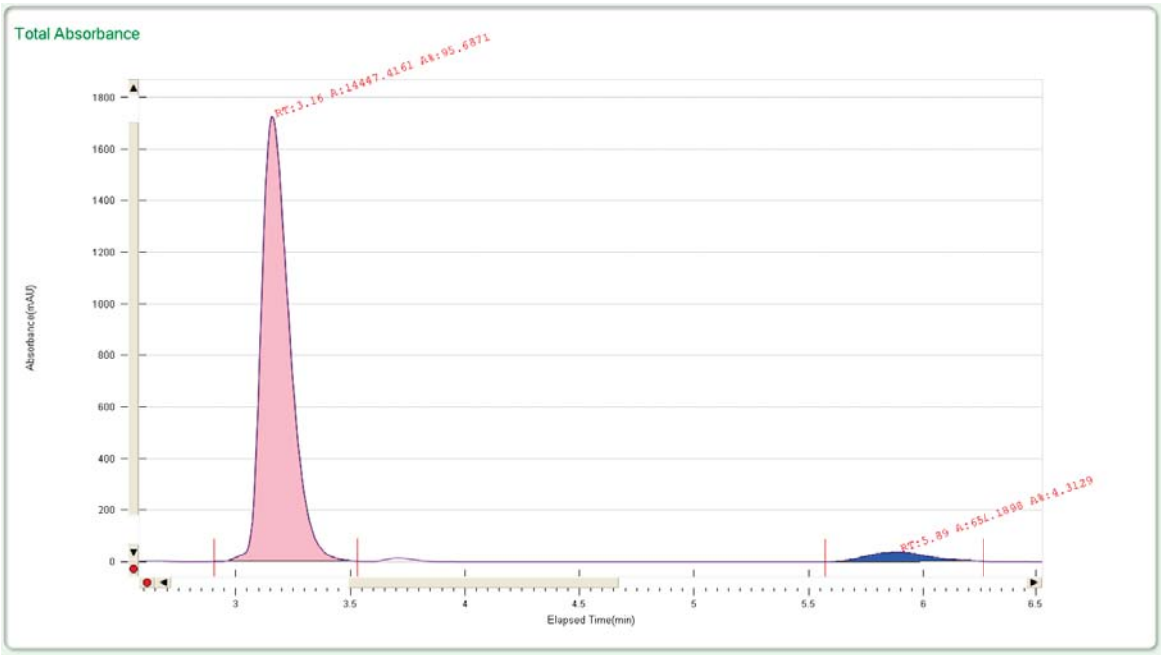


13: (*R*)-(+)-1-(1-(4-chlorophenyl)ethyl)-3,5-dimethoxybenzene

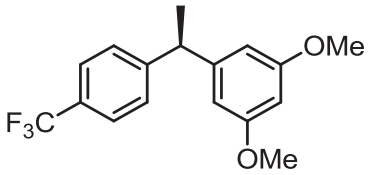


Enantiomers were separated by SFC on a Chiralpak AD-H column (4.6 mm x 250 mm, 5 µm particle size) under the following conditions: 40 °C, 3% methanol, 4 mL min^{-1}, 160 bar. R_T = 3.16 min, 5.89 min.

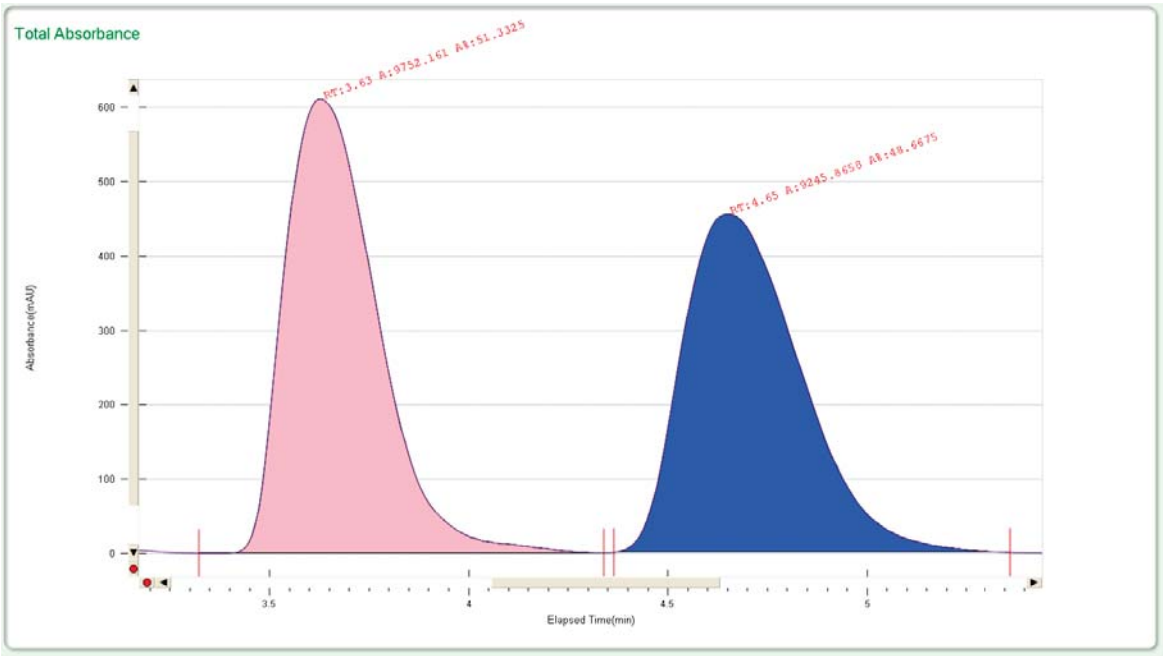


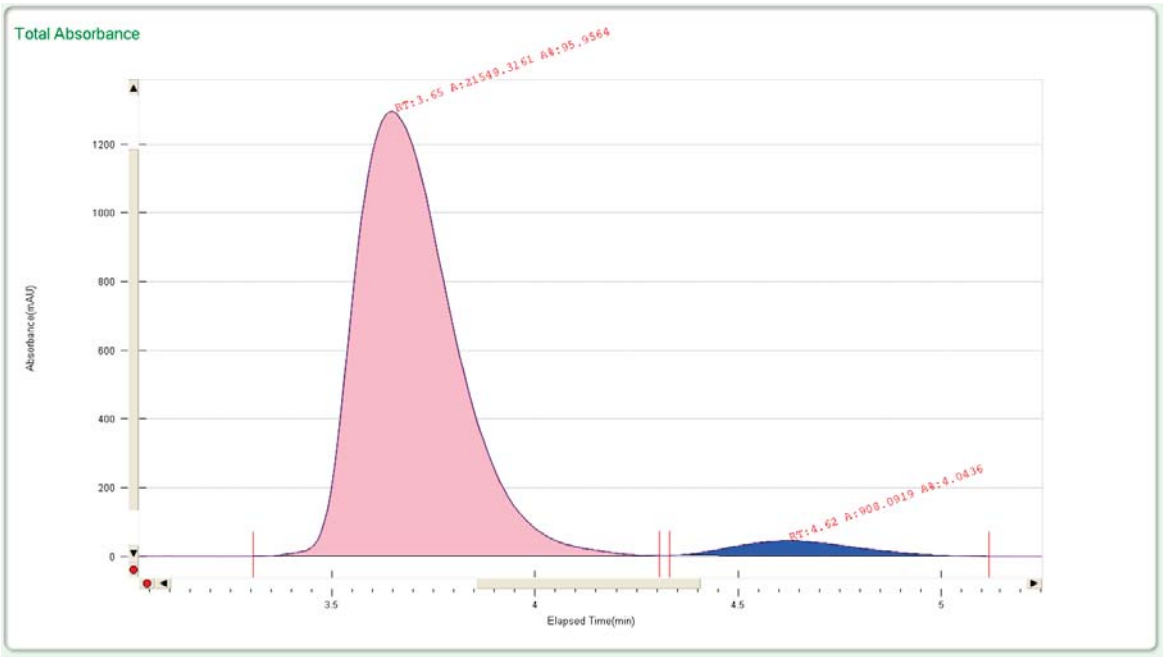


14: (*R*)-(–)-1,3-dimethoxy-5-(1-(4-(trifluoromethyl)phenyl)ethyl)benzene

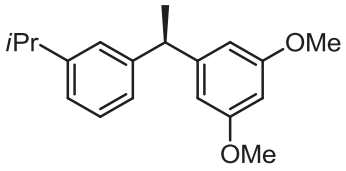


Enantiomers were separated by SFC on a Chiralpak AD-H column (4.6 mm x 250 mm) under the following conditions: 40 °C, 2% methanol, 2 mL min^{-1}, 160 Bar. R_T = 3.65 min, 4.62 min.

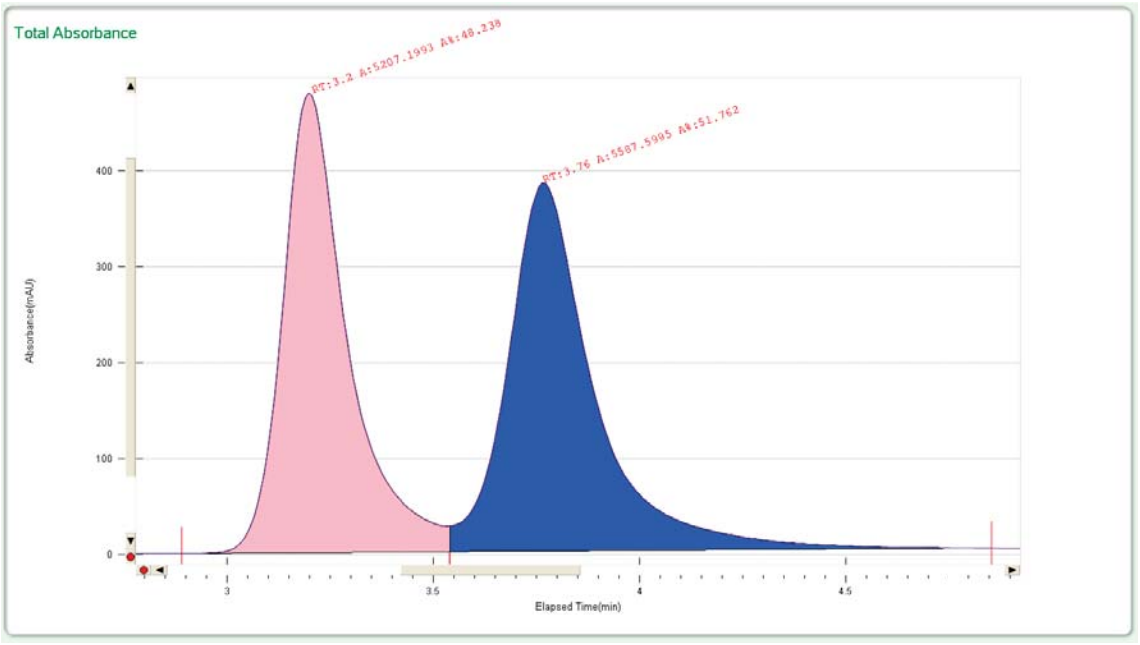


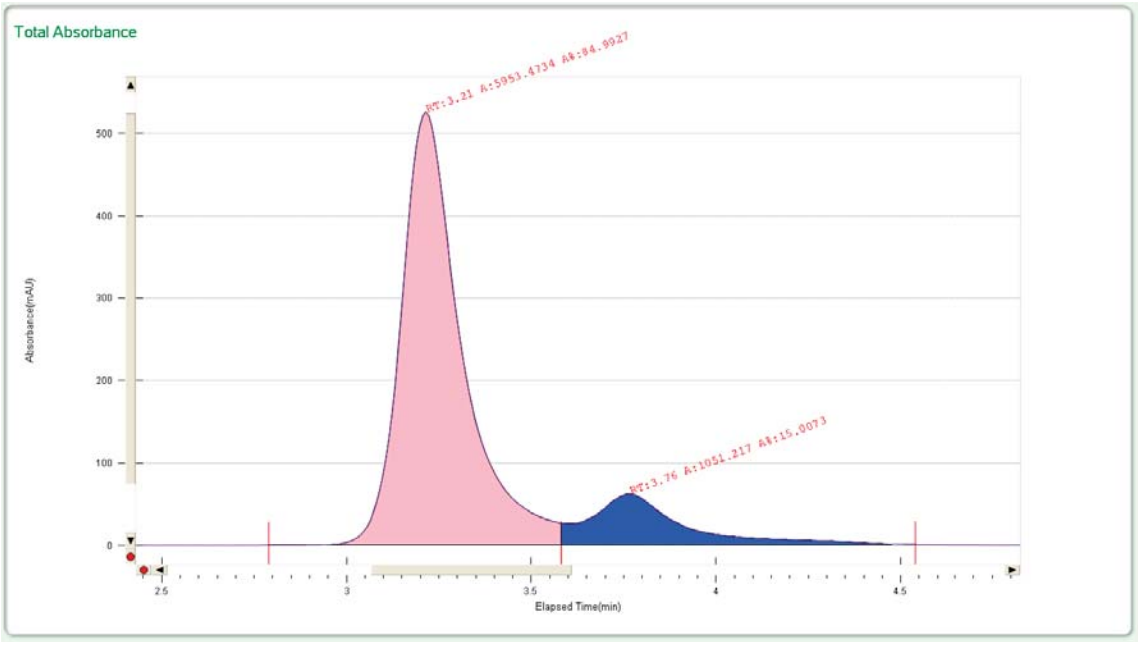


15: (*R*)-(–)-1-(1-(3-isopropylphenyl)ethyl)-3,5-dimethoxybenzene

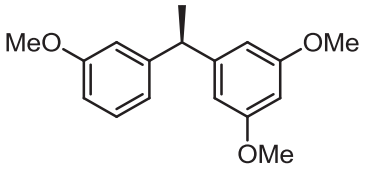


Enantiomers were separated by SFC on a Chiralcel OJ-H column (4.6 mm x 250 mm) under the following conditions: 27 °C, 0% cosolvent, 4 mL min^{-1}. R_T = 3.21 min, 3.76 min.

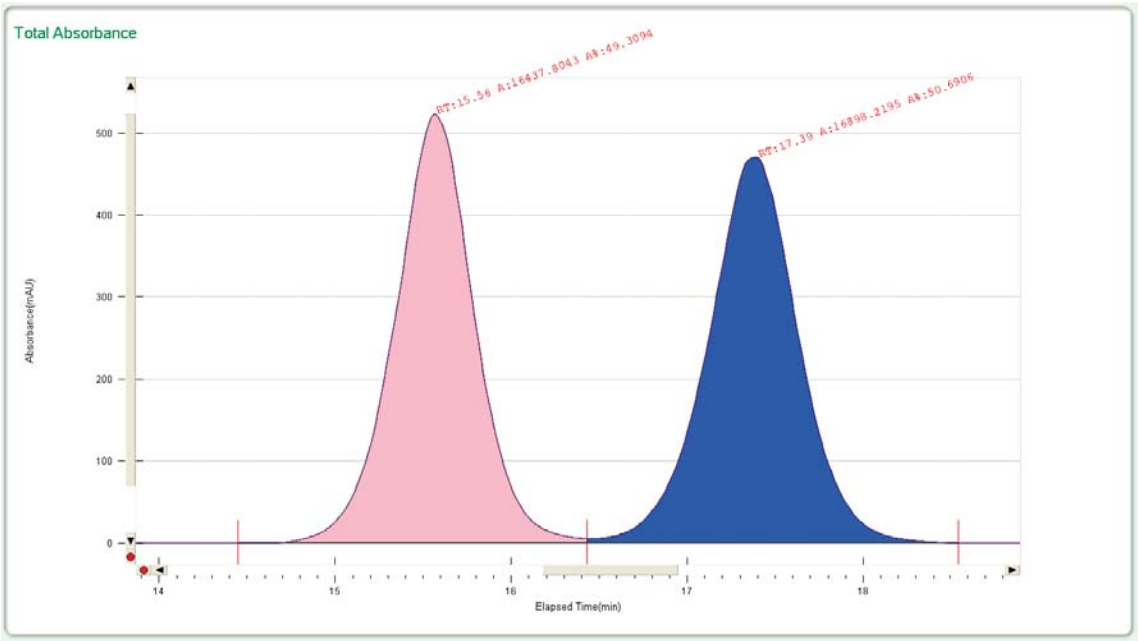


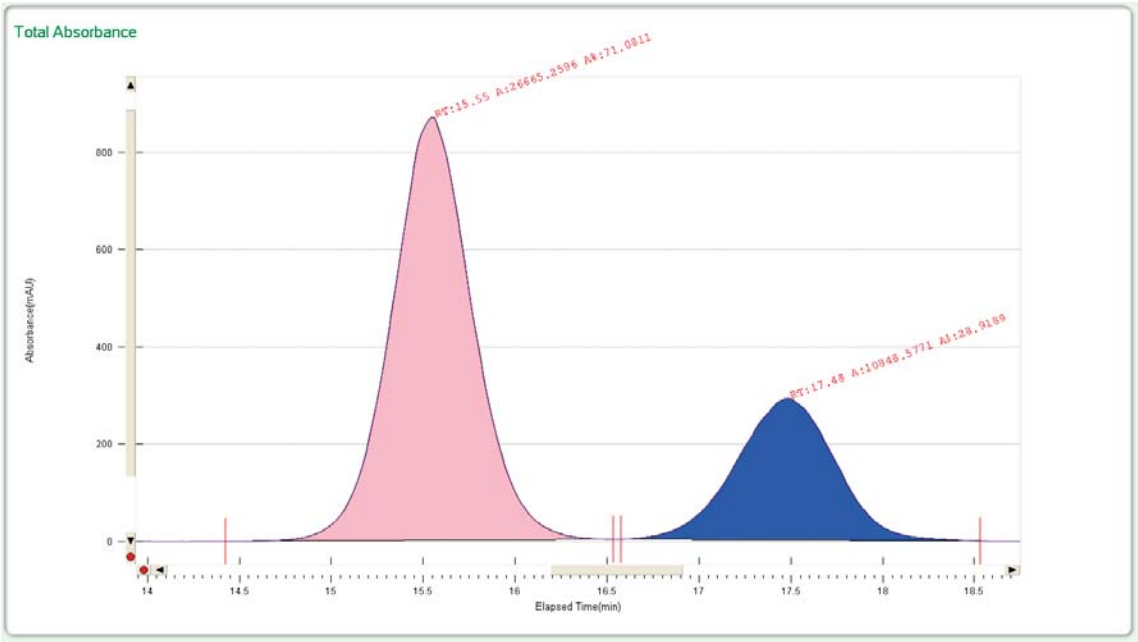


16: (*R*)-(–)-1,3-dimethoxy-5-(1-(3-methoxyphenyl)ethyl)benzene



Enantiomers were separated by SFC on a Chiralcel OJ-H column (4.6 mm x 250 mm) under the following conditions: 24 °C, 0% cosolvent, 2 mL min^{-1}. R_T = 15.55 min, 17.48 min.





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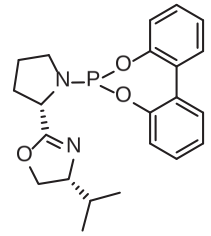
N
P
O
O
O
N

PhosPrOx

9
8
7
6
5
4
3
2
1
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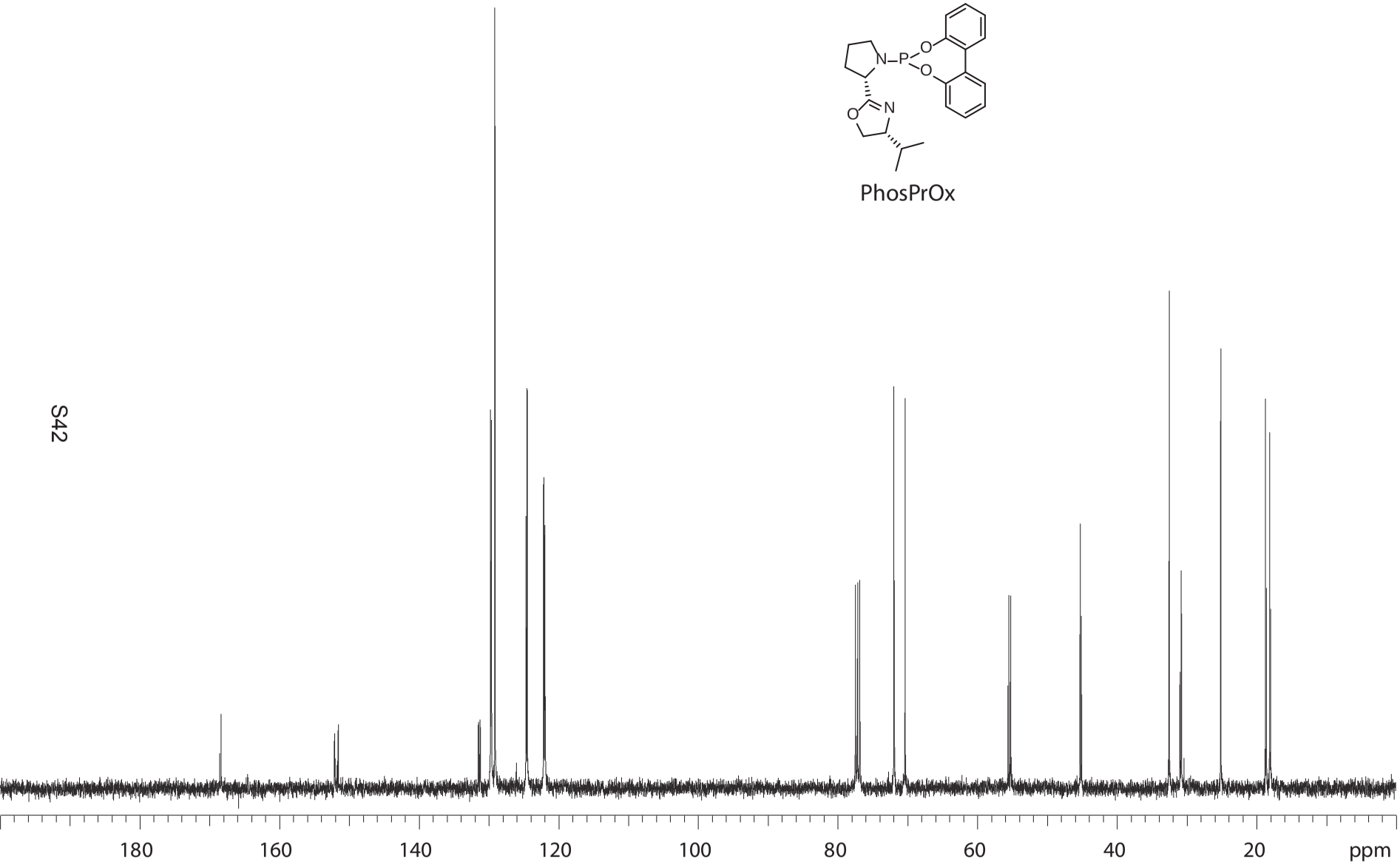
2.07
0.92
1.01
0.98
1.02
1.00
0.97
2.07
3.50
6.23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60
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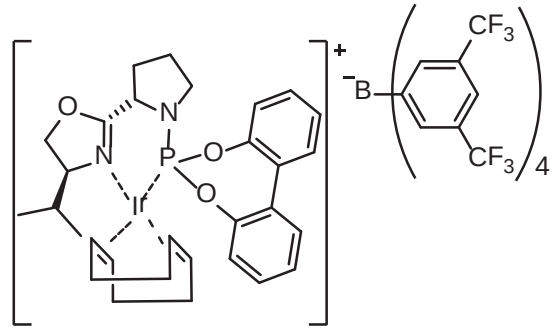
20
ppm



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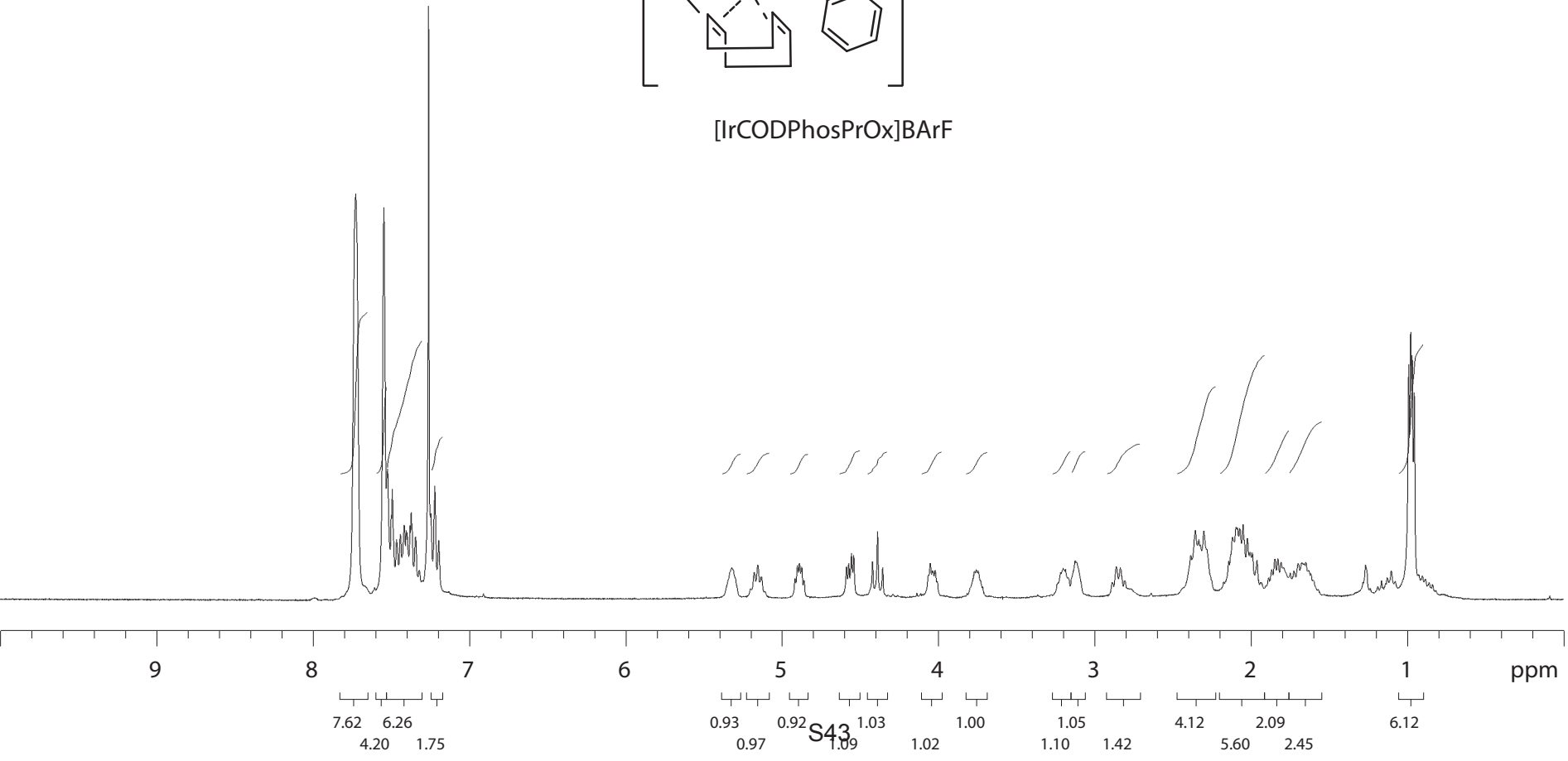

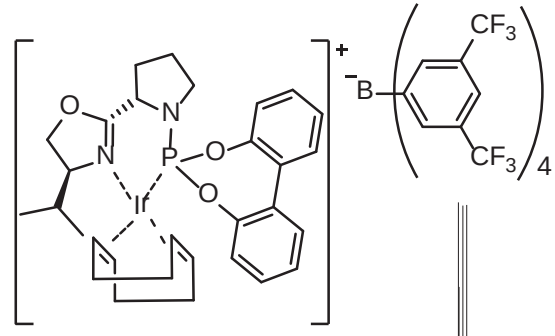

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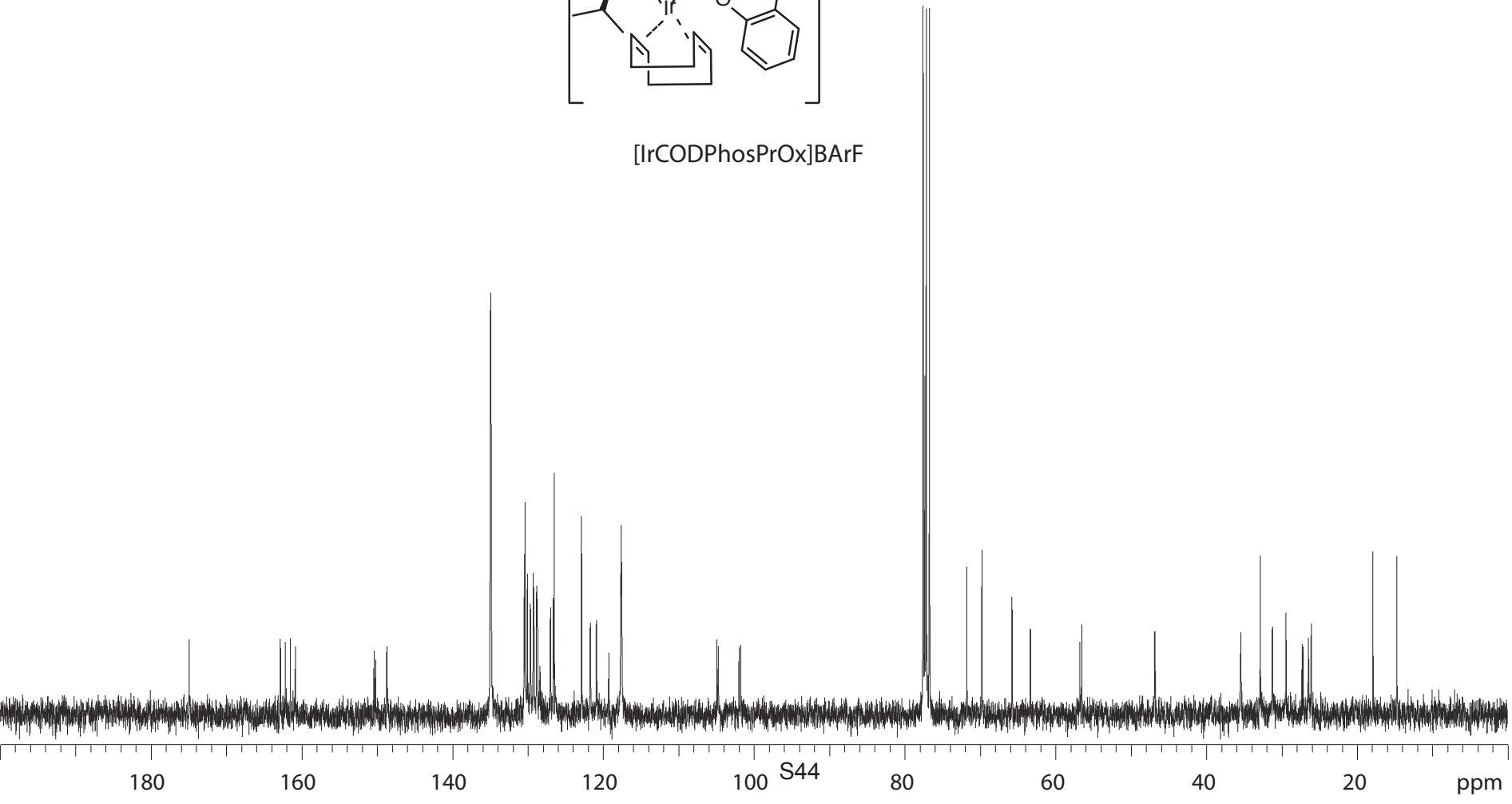

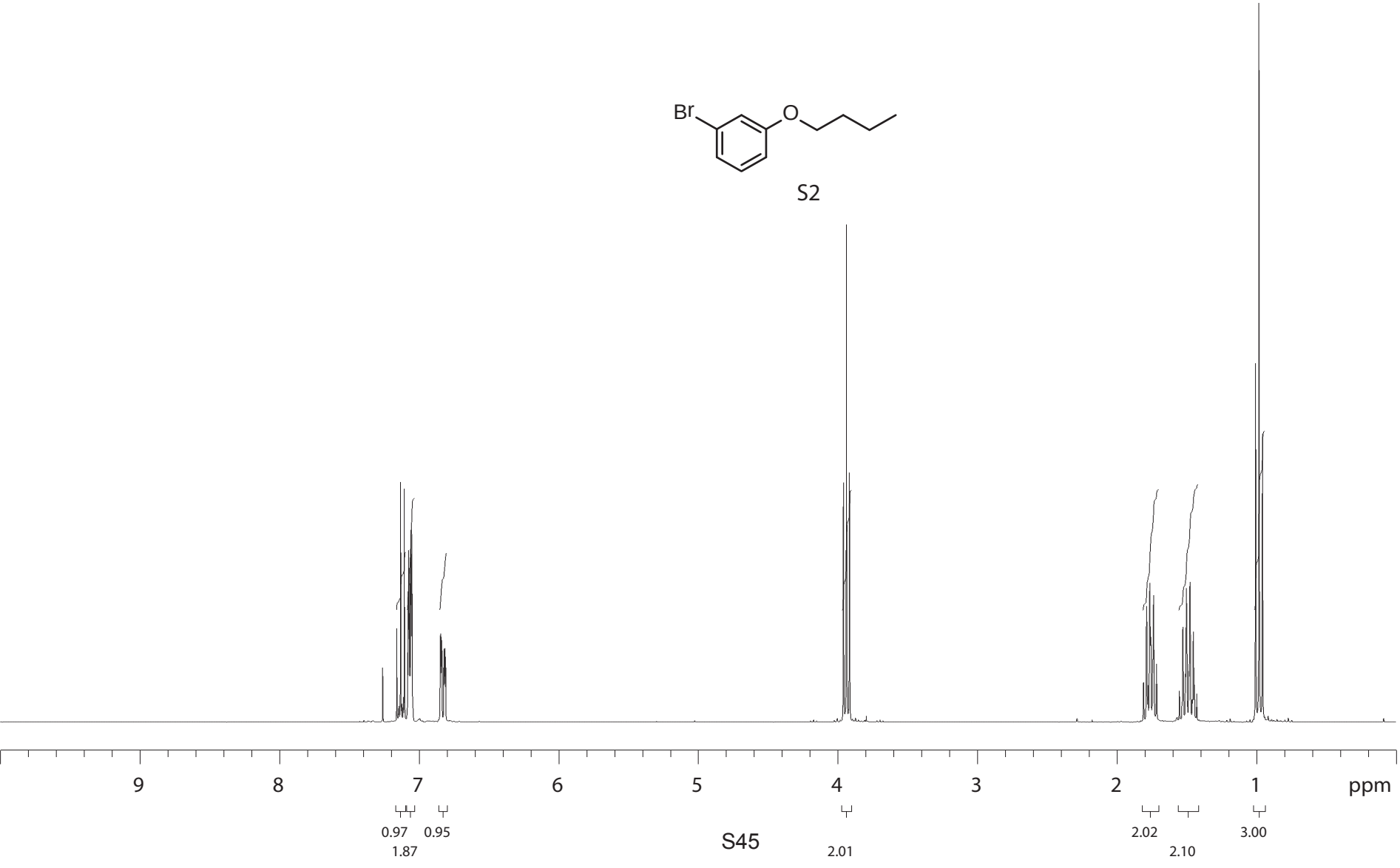
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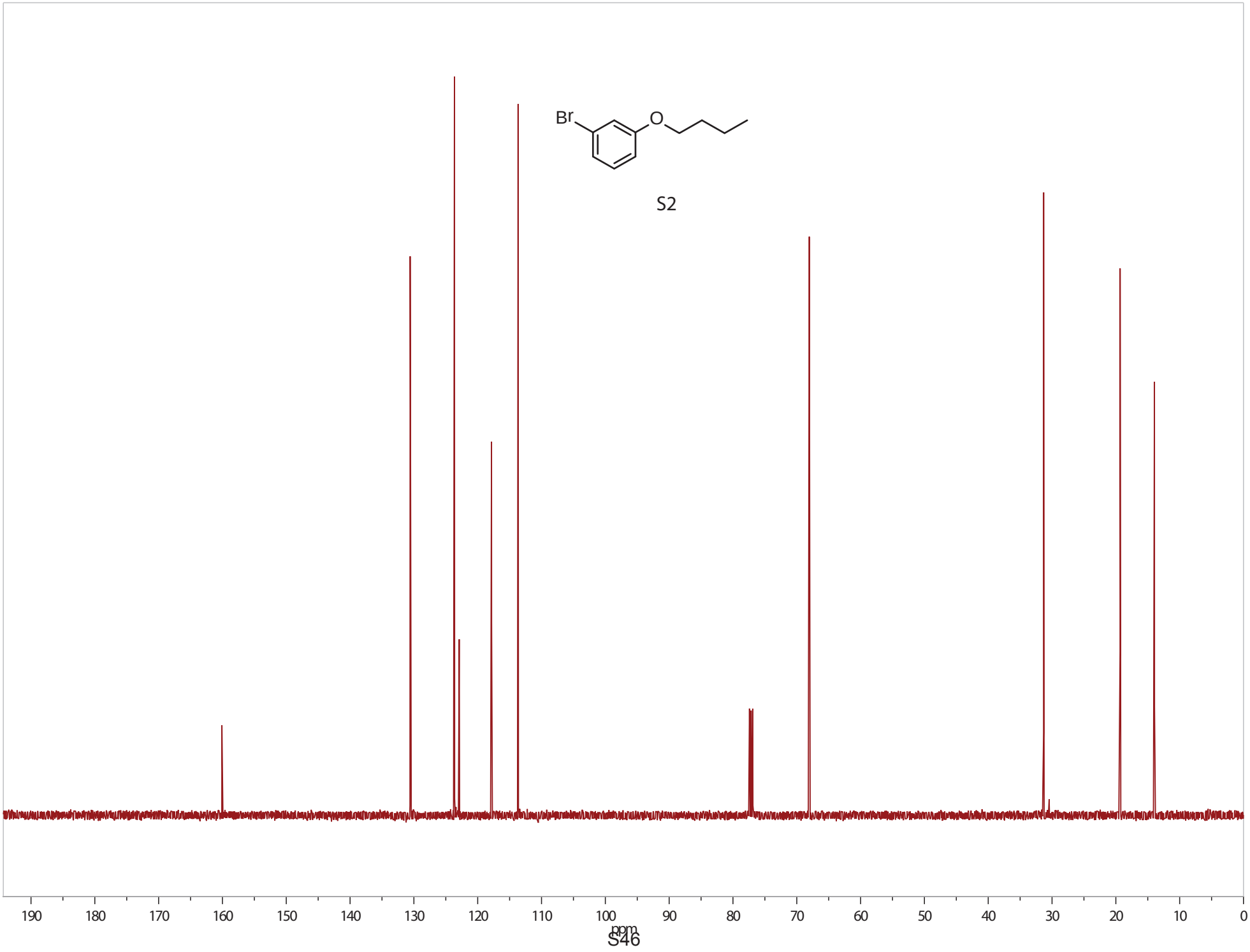
3.00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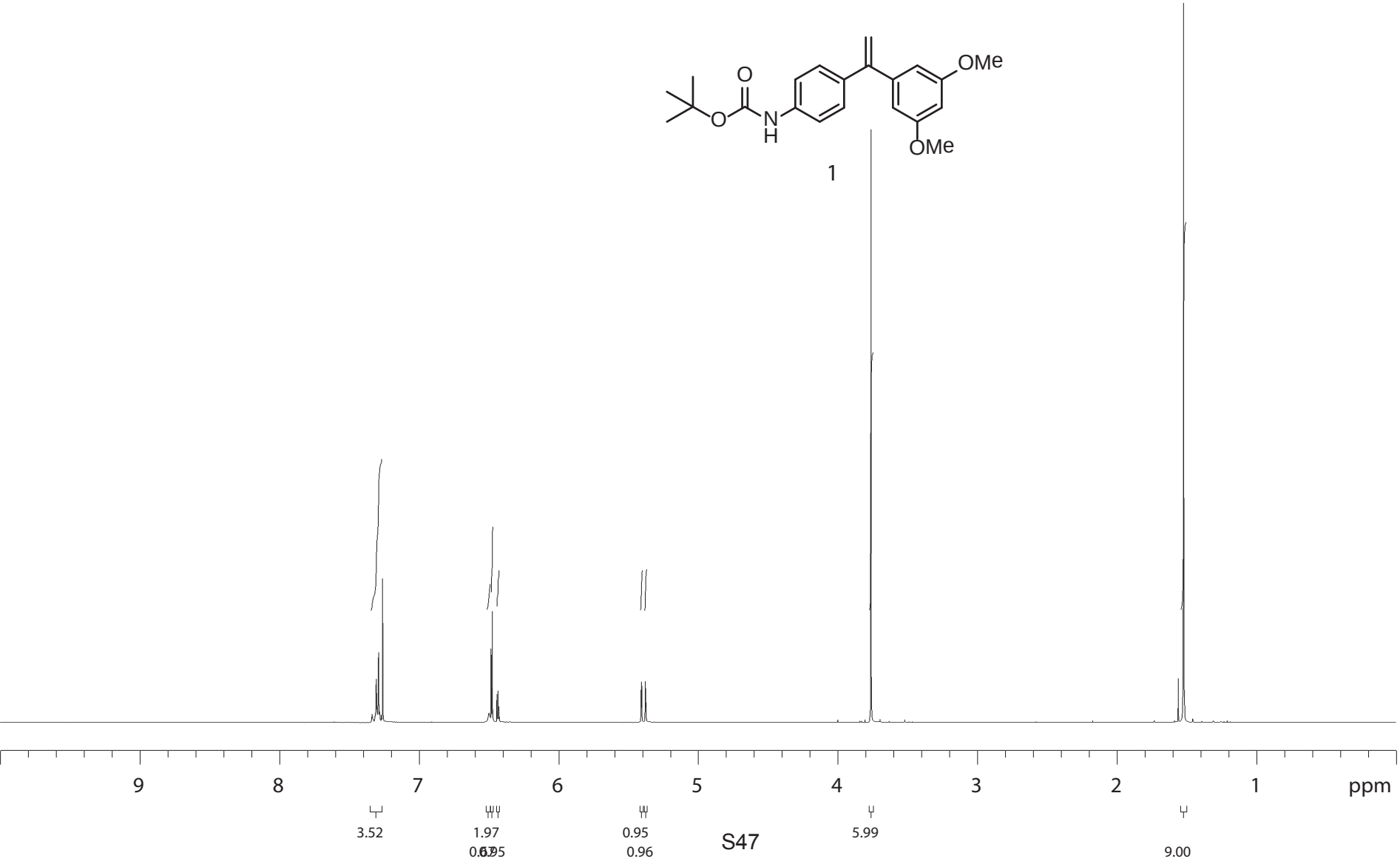
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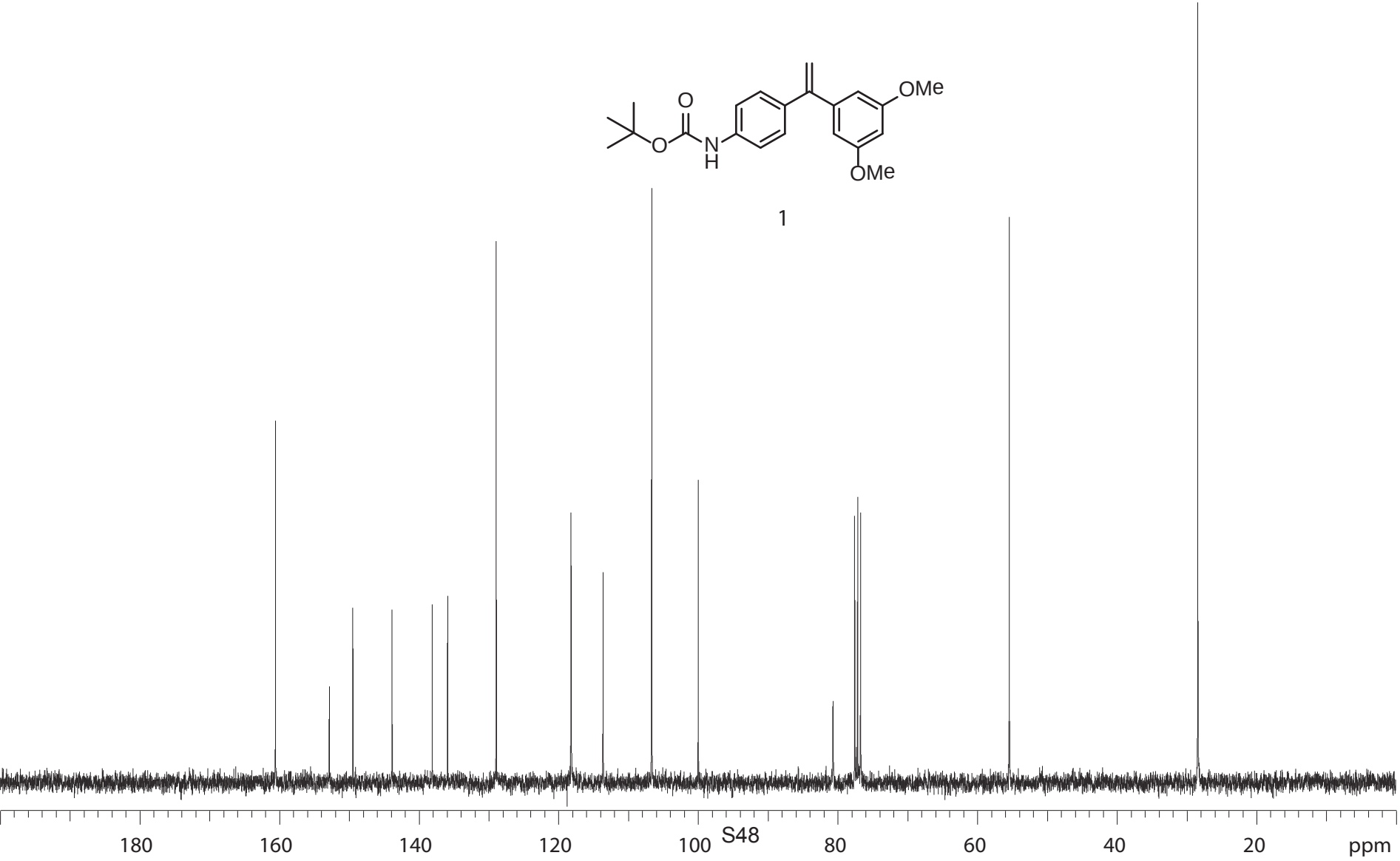
0.96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H
OMe
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80
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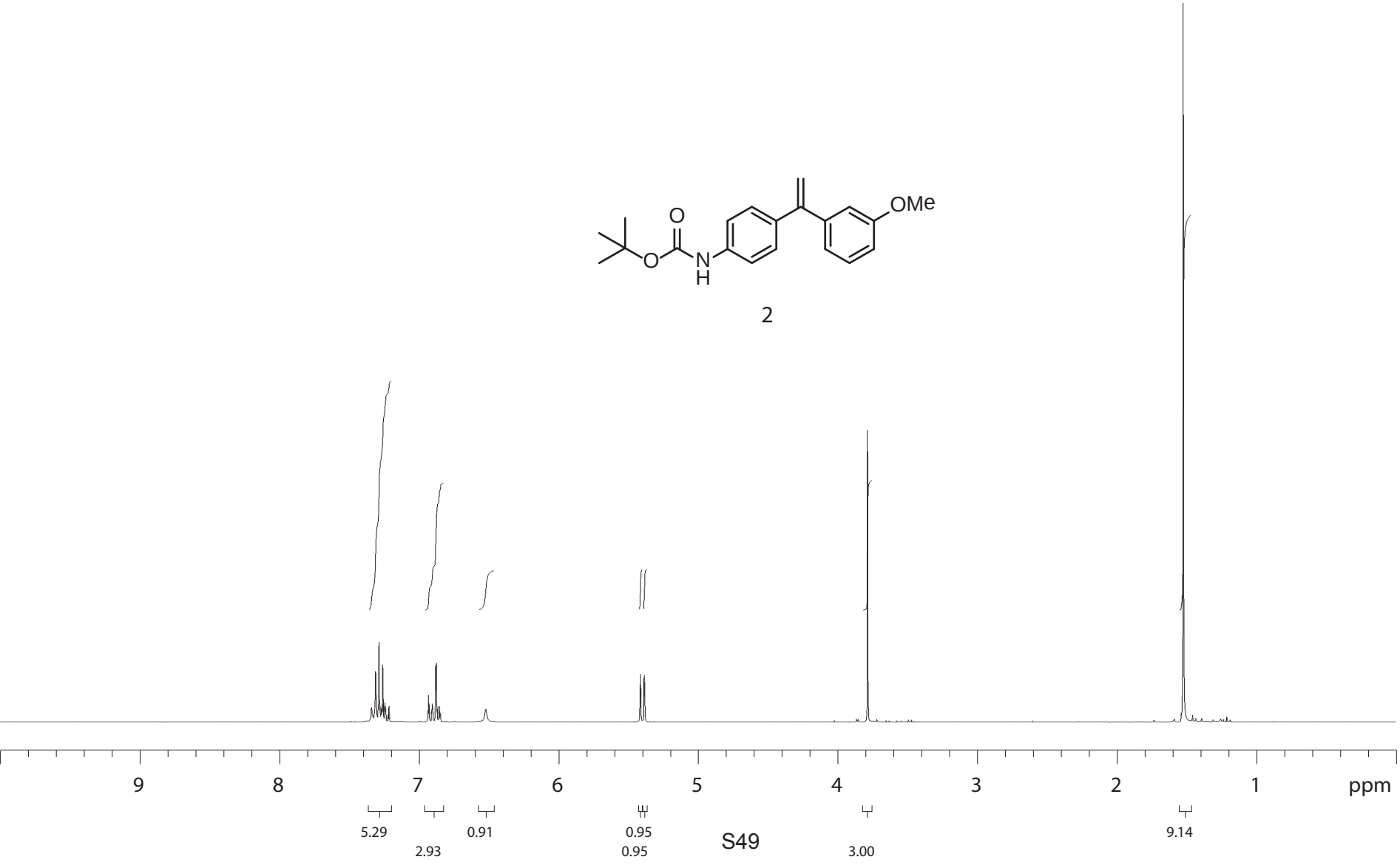
ppm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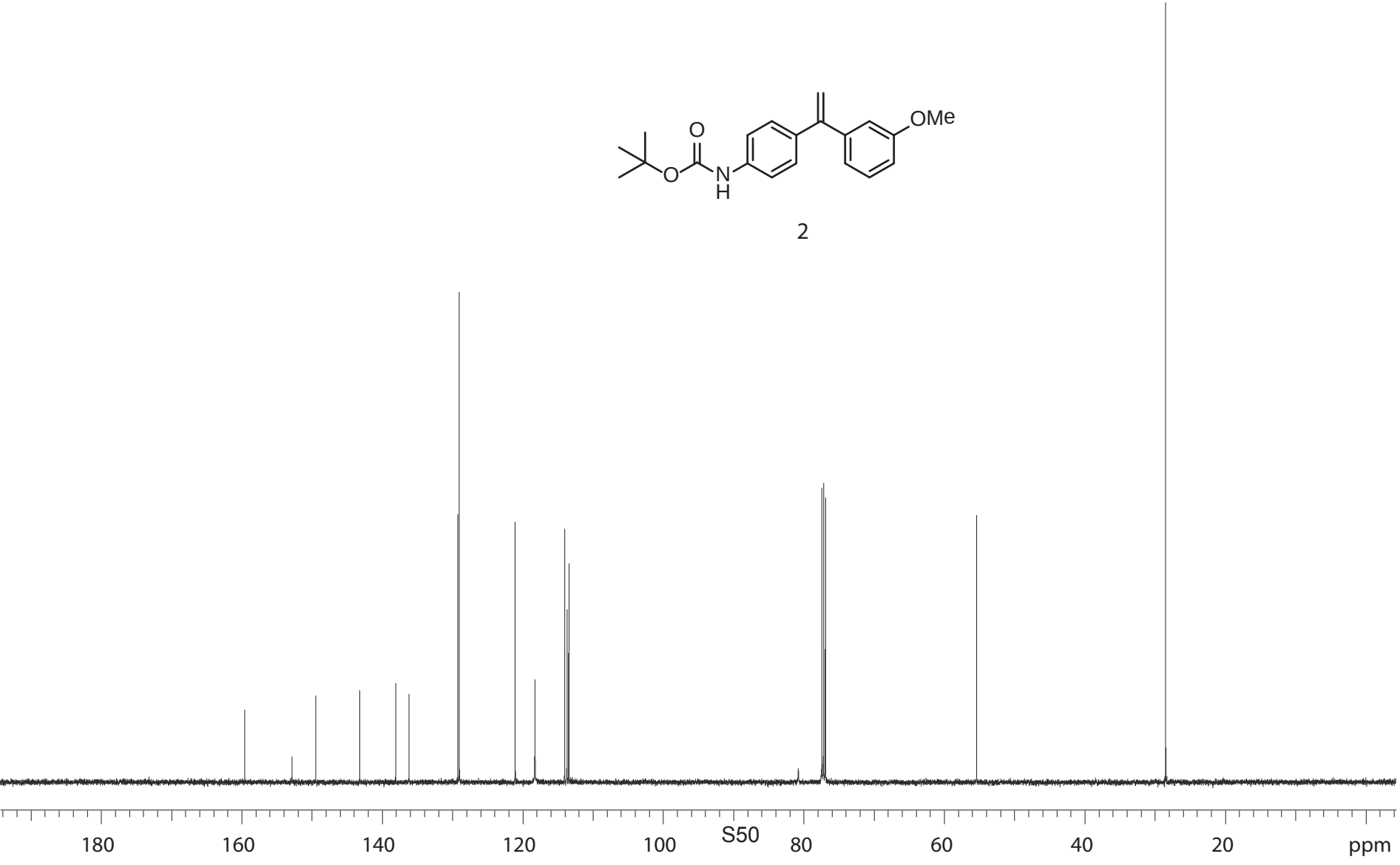
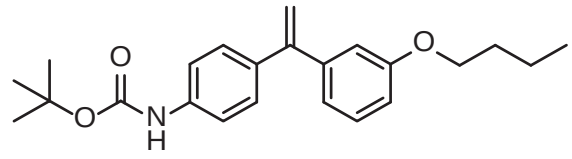


2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O
N
H
O

3

9
8
7
6
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4
3
2
1
ppm
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8.90
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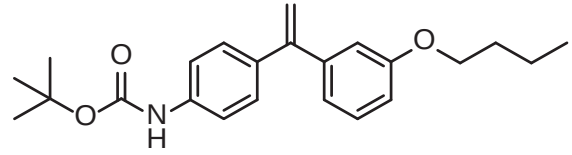

3

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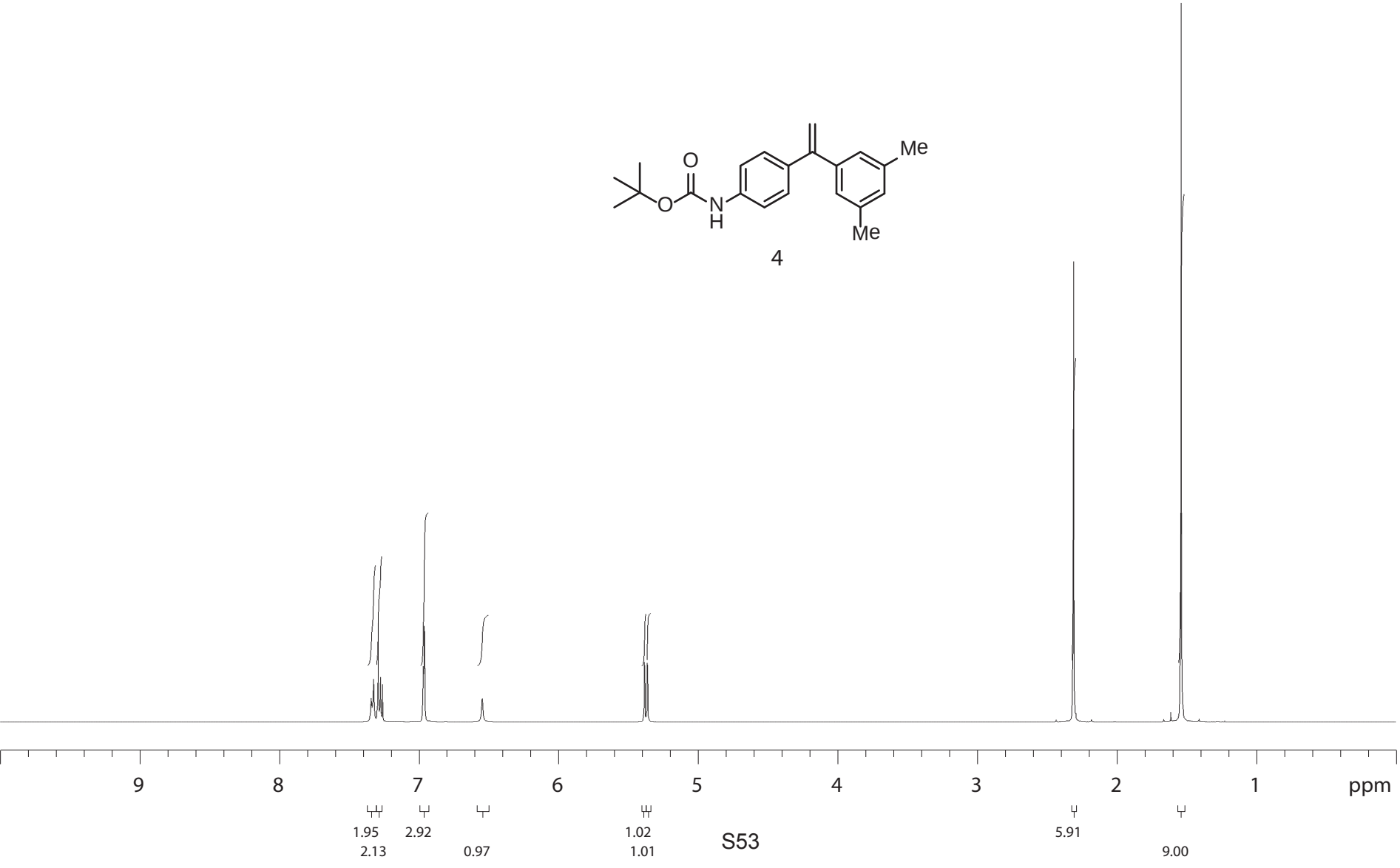
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ppm
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2.92
0.97
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1.01
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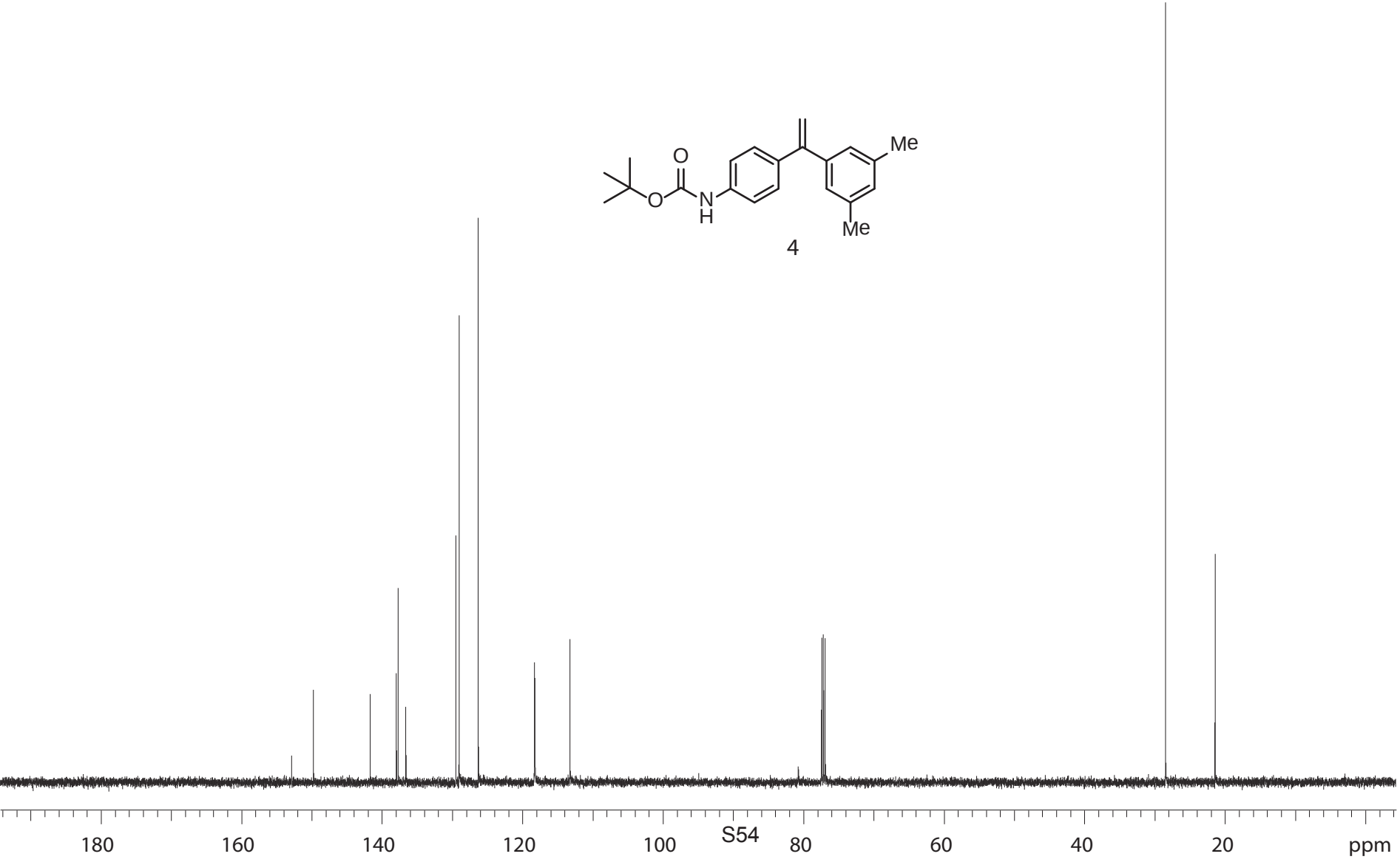
9.00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Me
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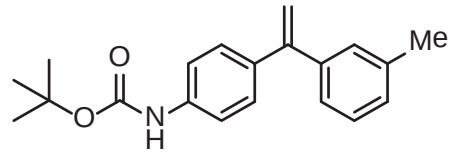

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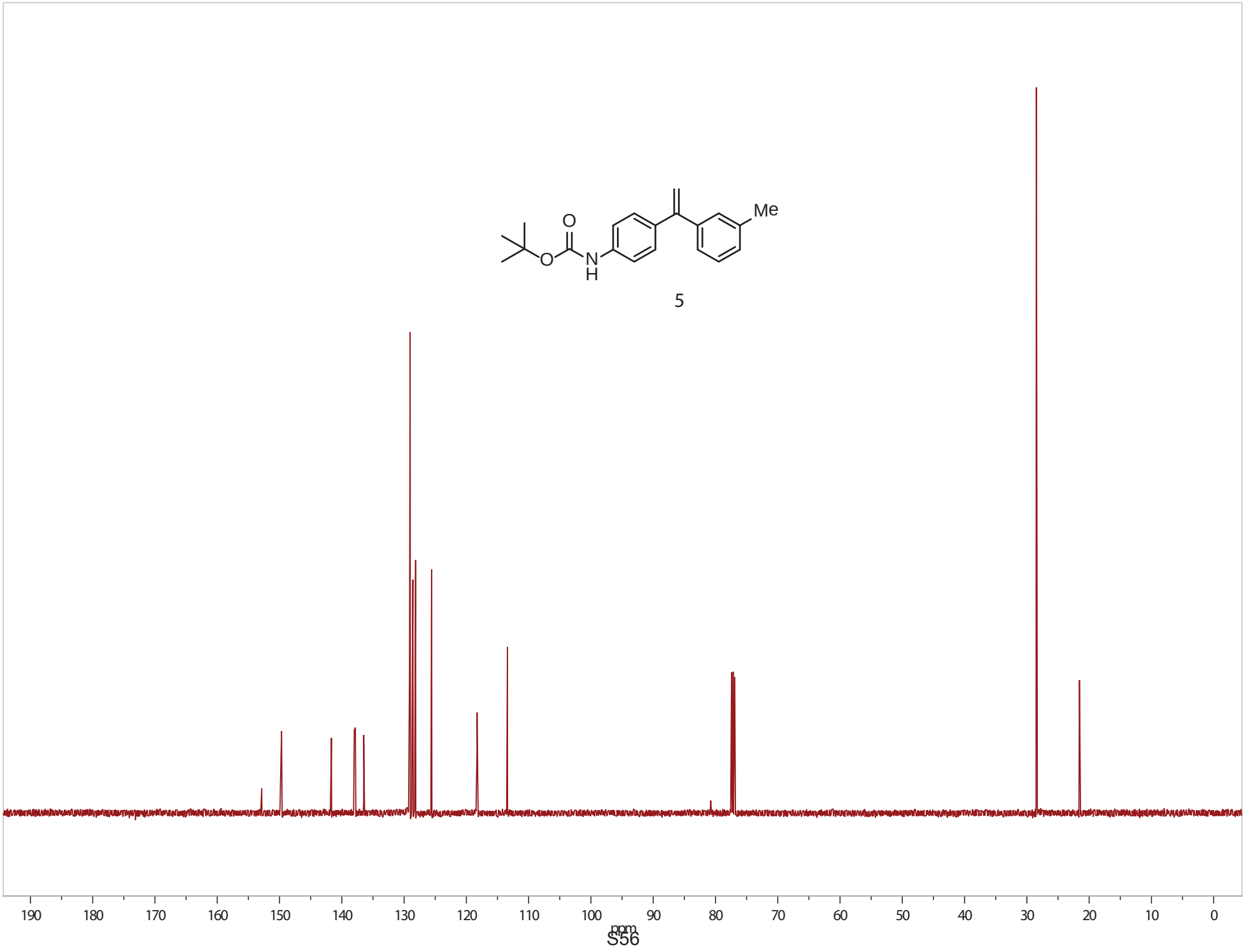
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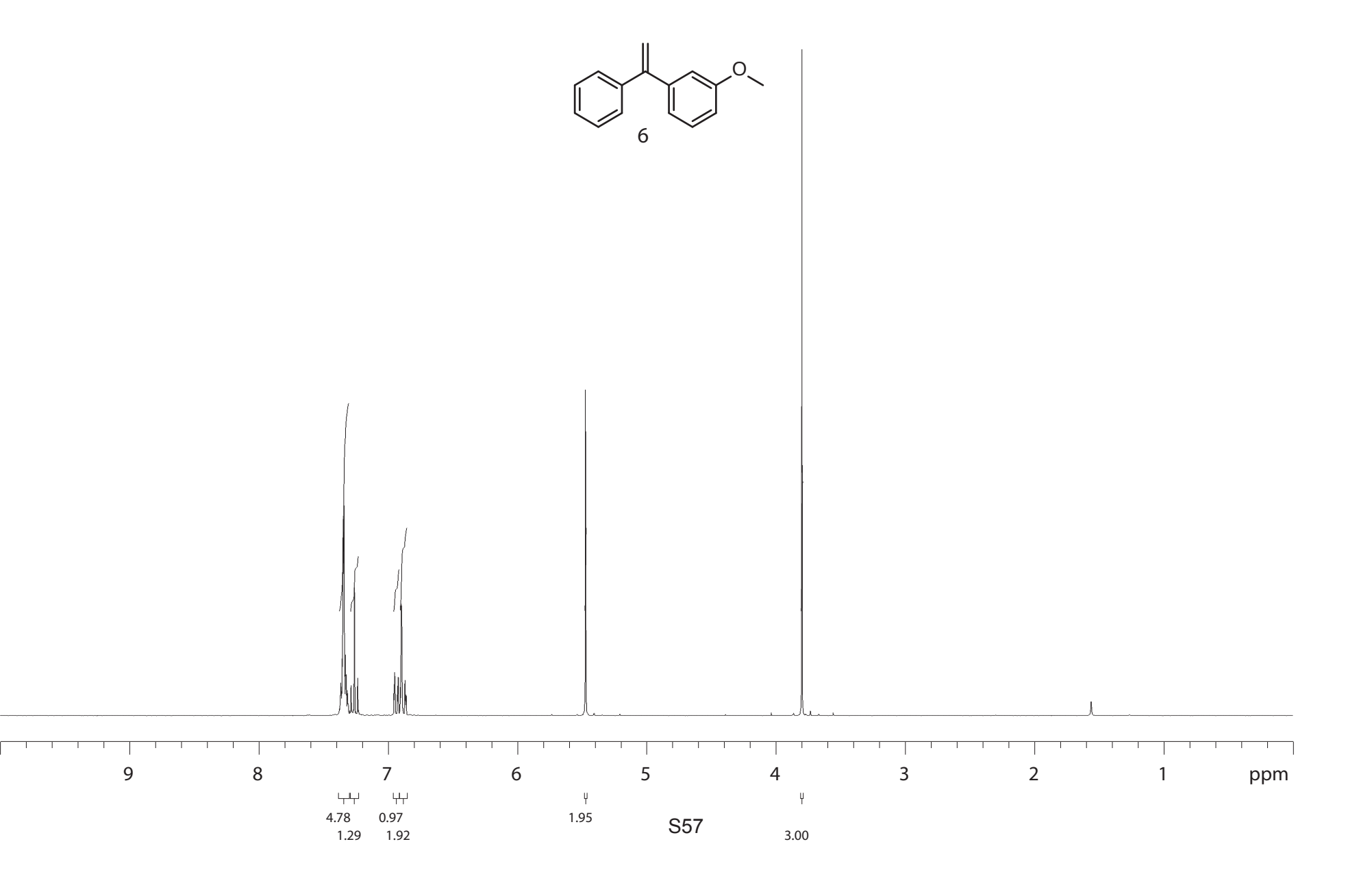
O
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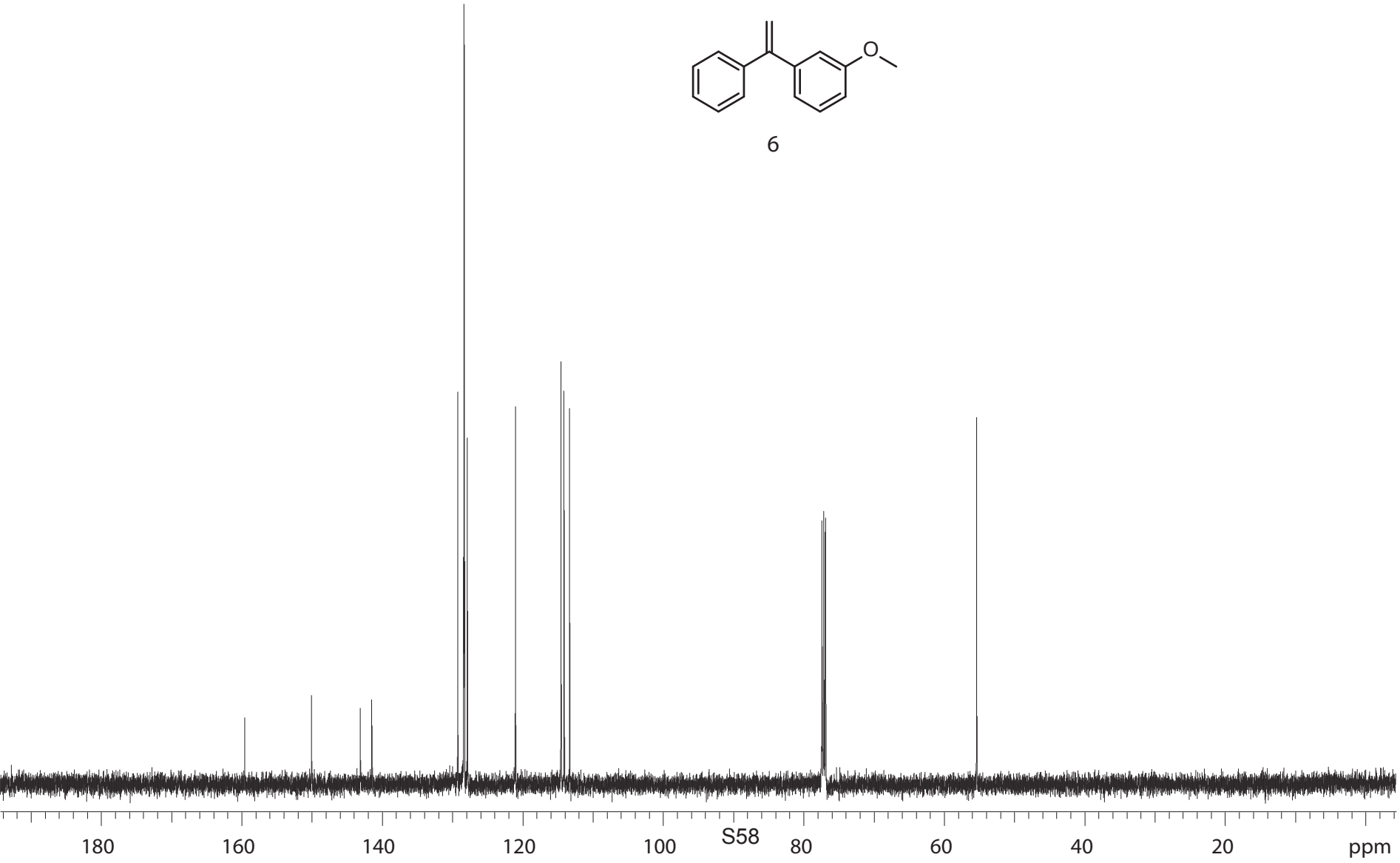
1.95
3.00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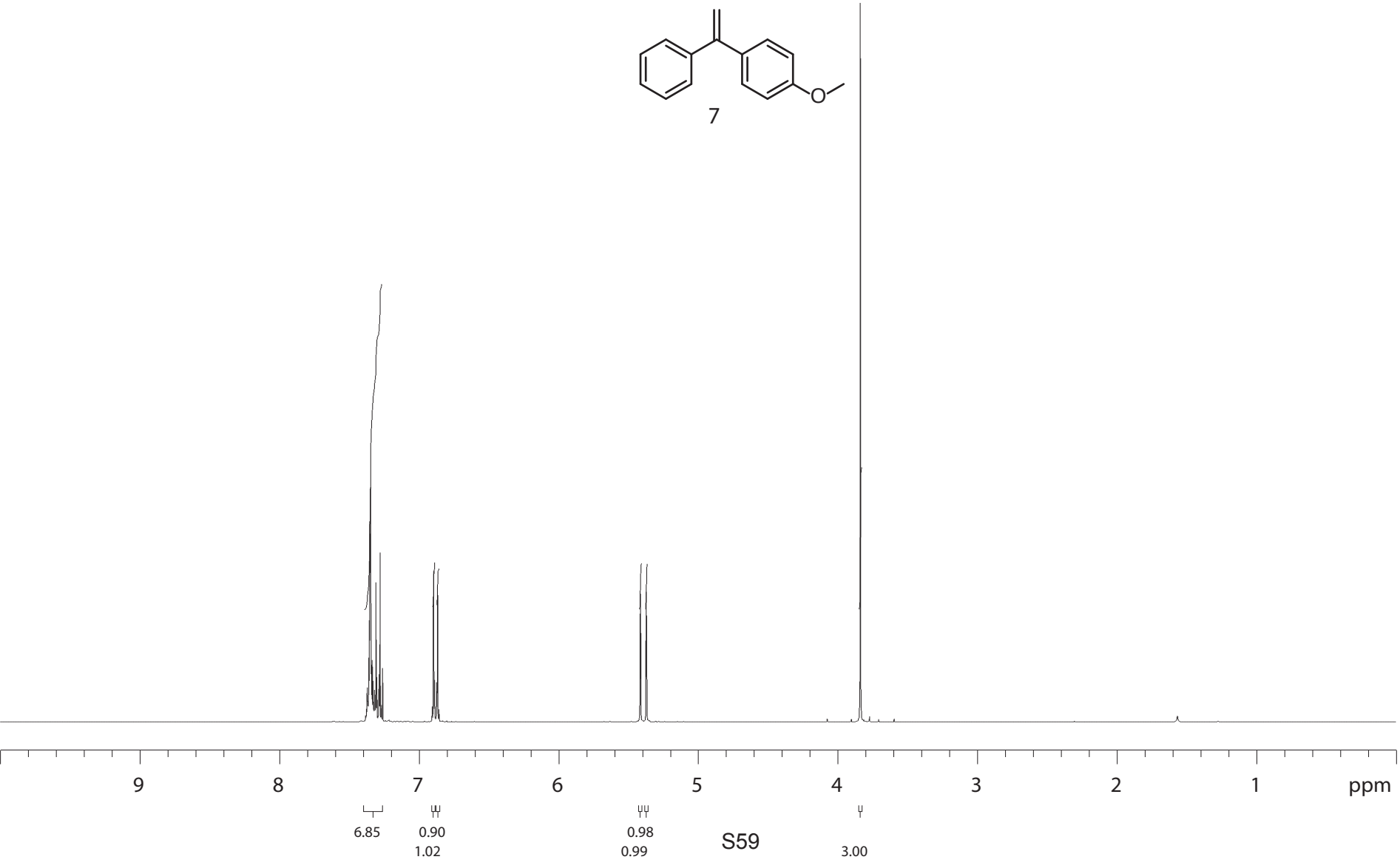
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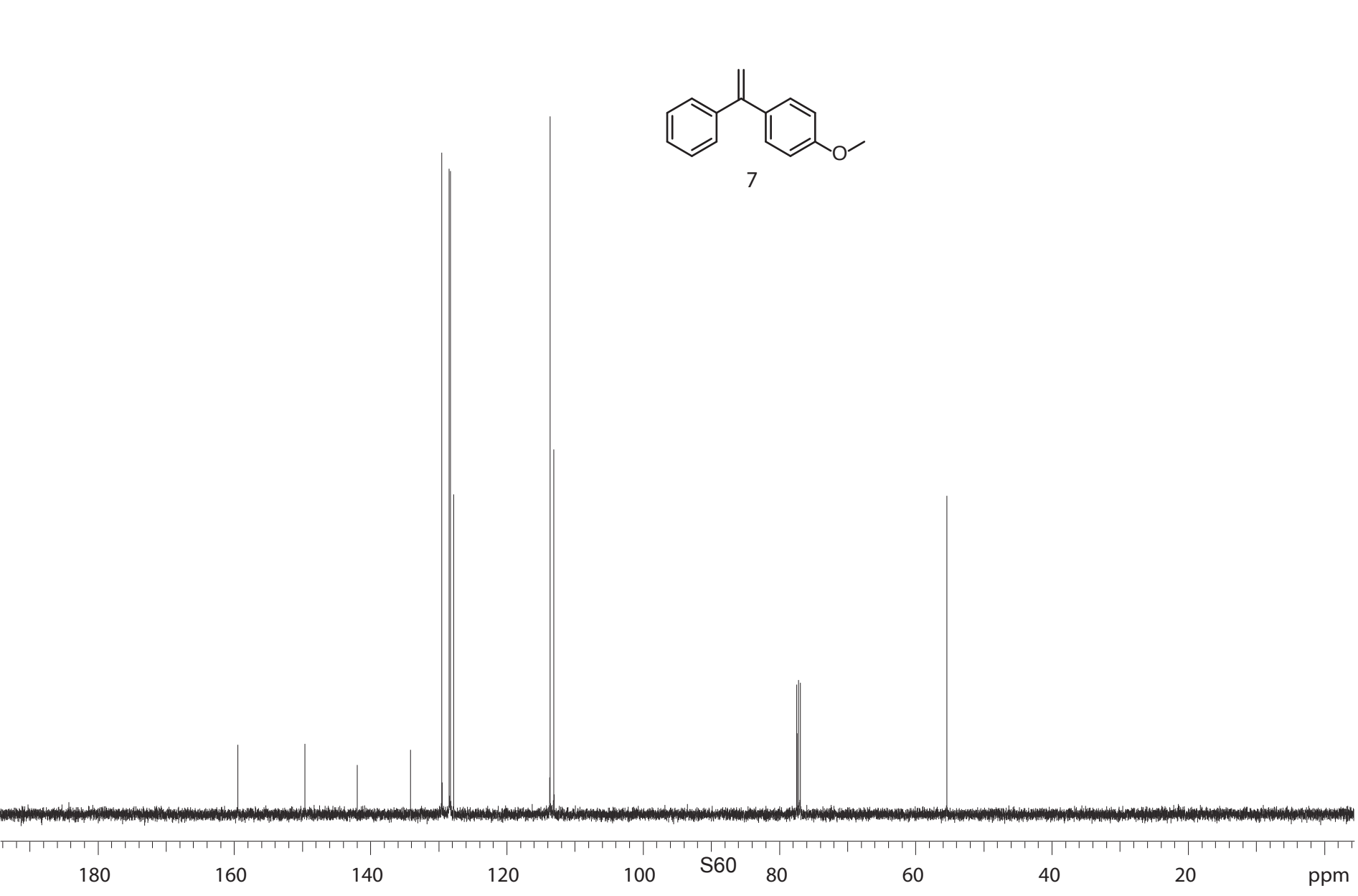
3.00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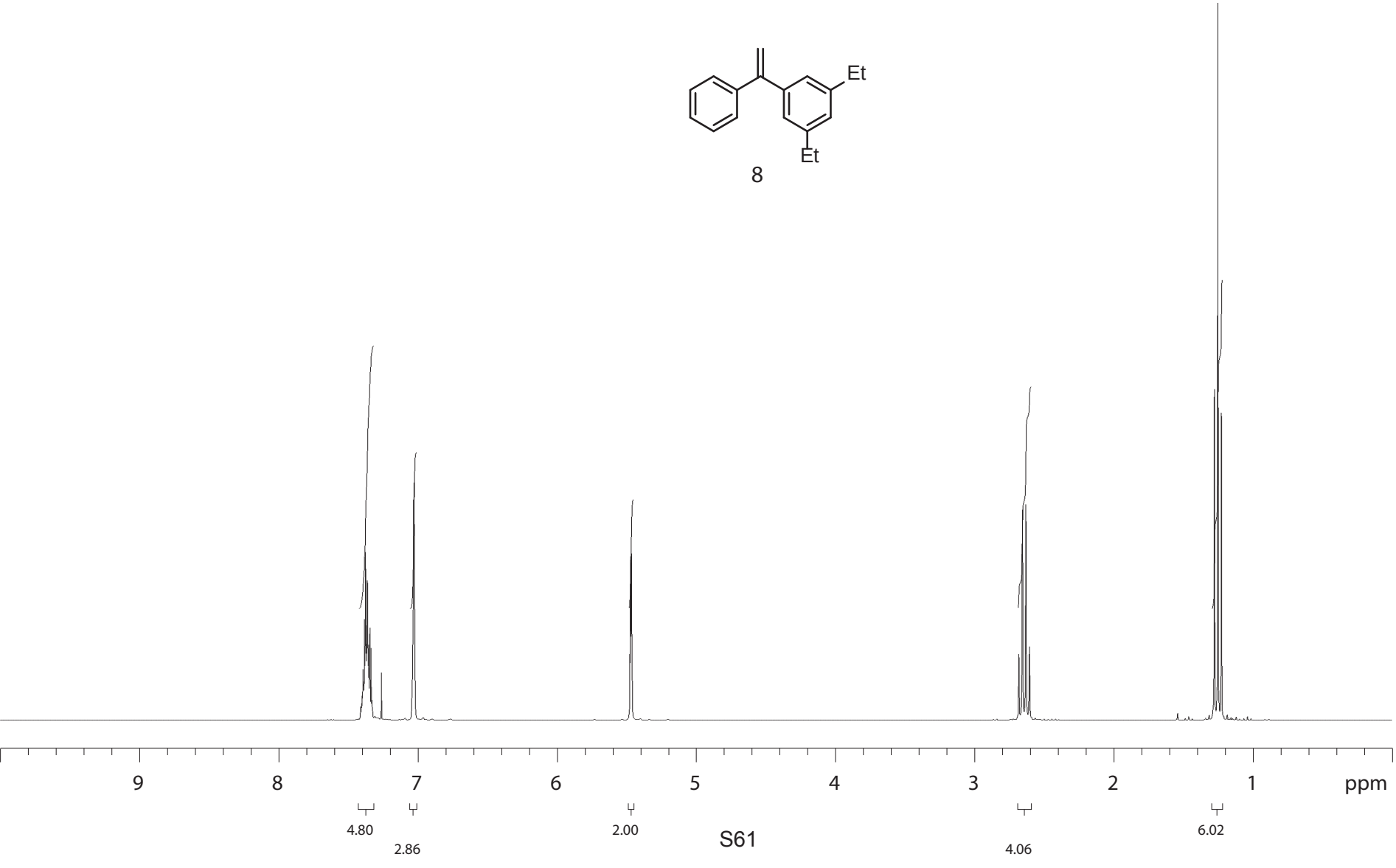
Et
Et
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4
3
2
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ppm
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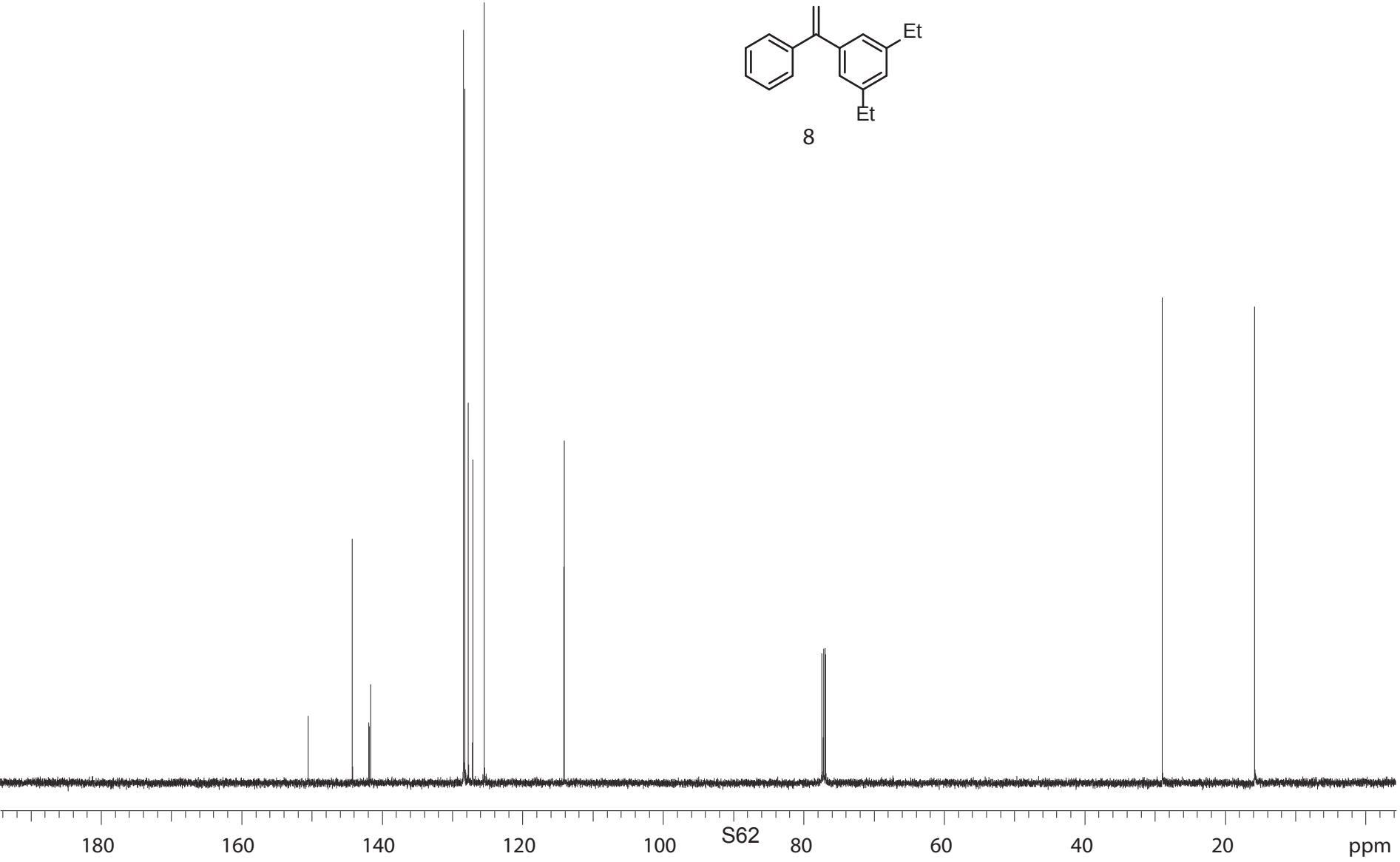
4.06
6.02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Et
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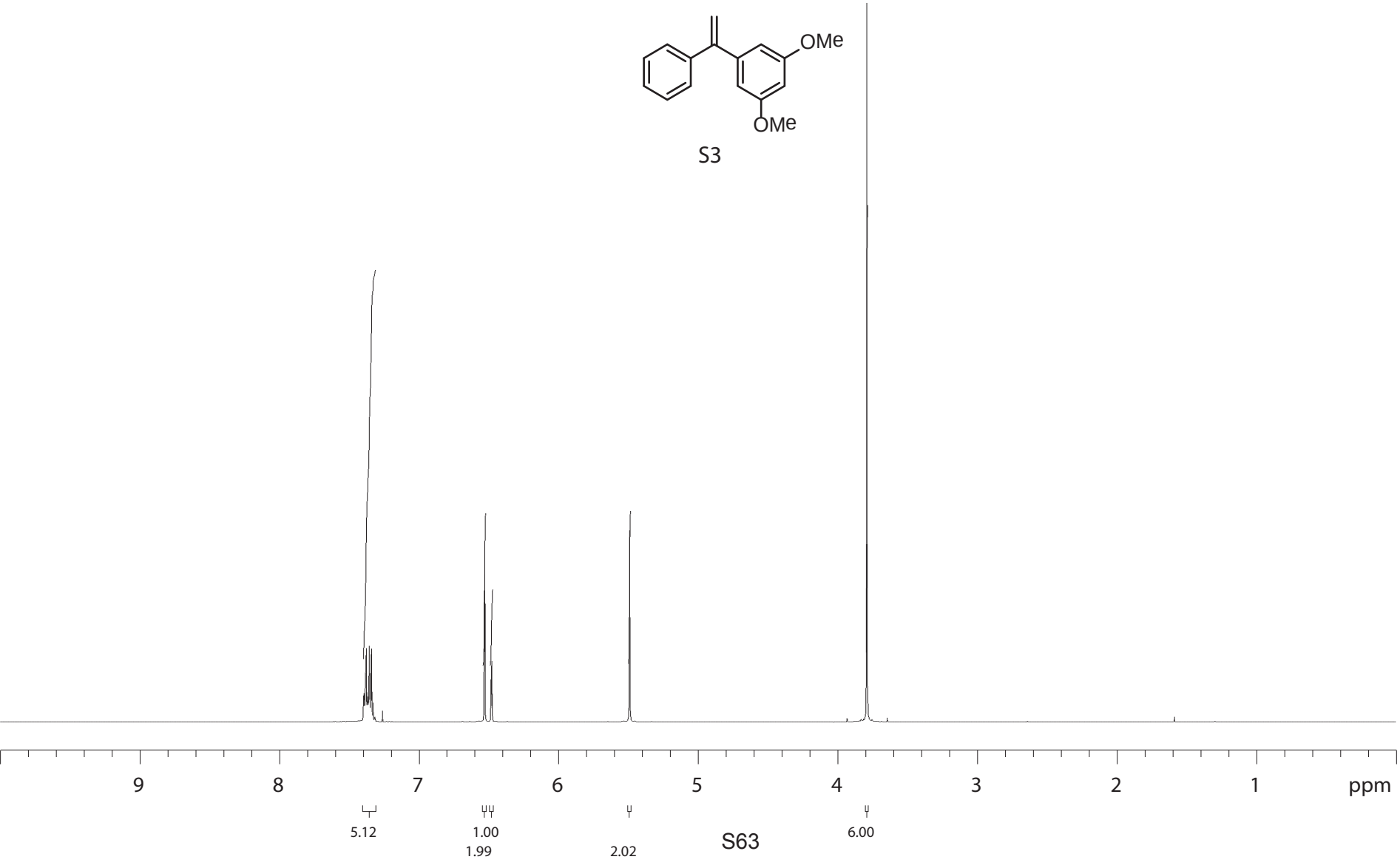
OMe
OMe
S3
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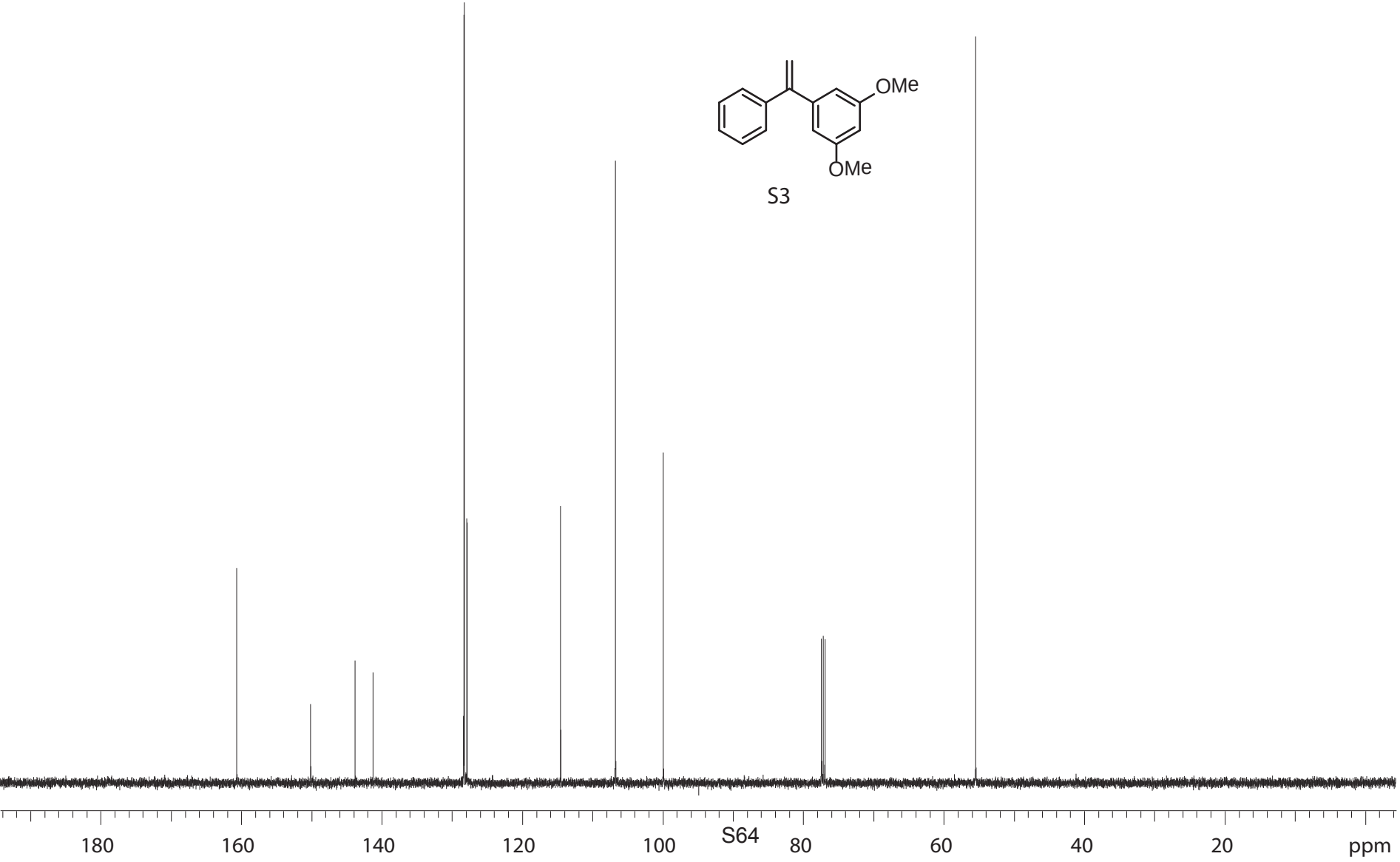
2.02
6.00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OMe
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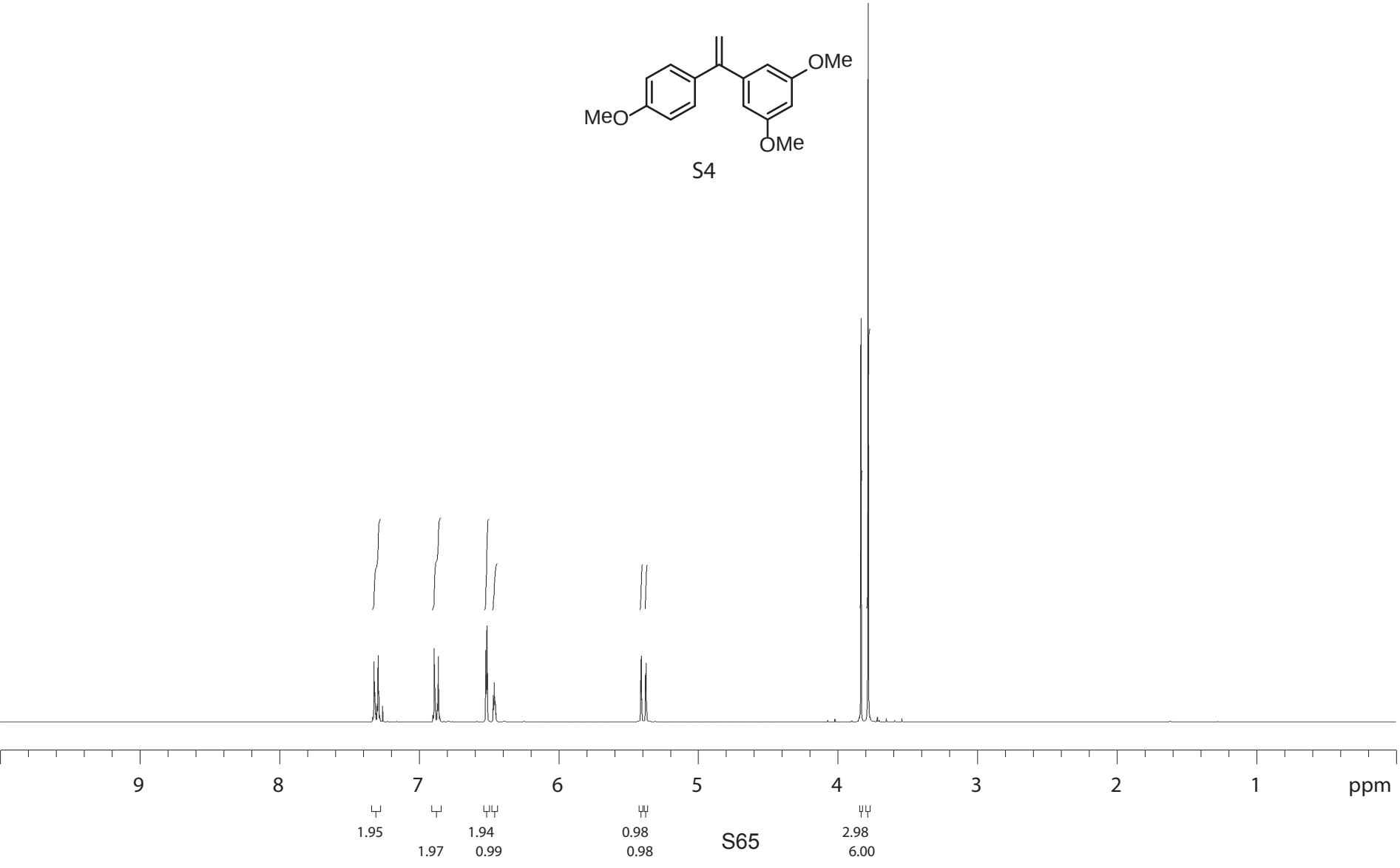
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MeO
OMe
S4
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8
7
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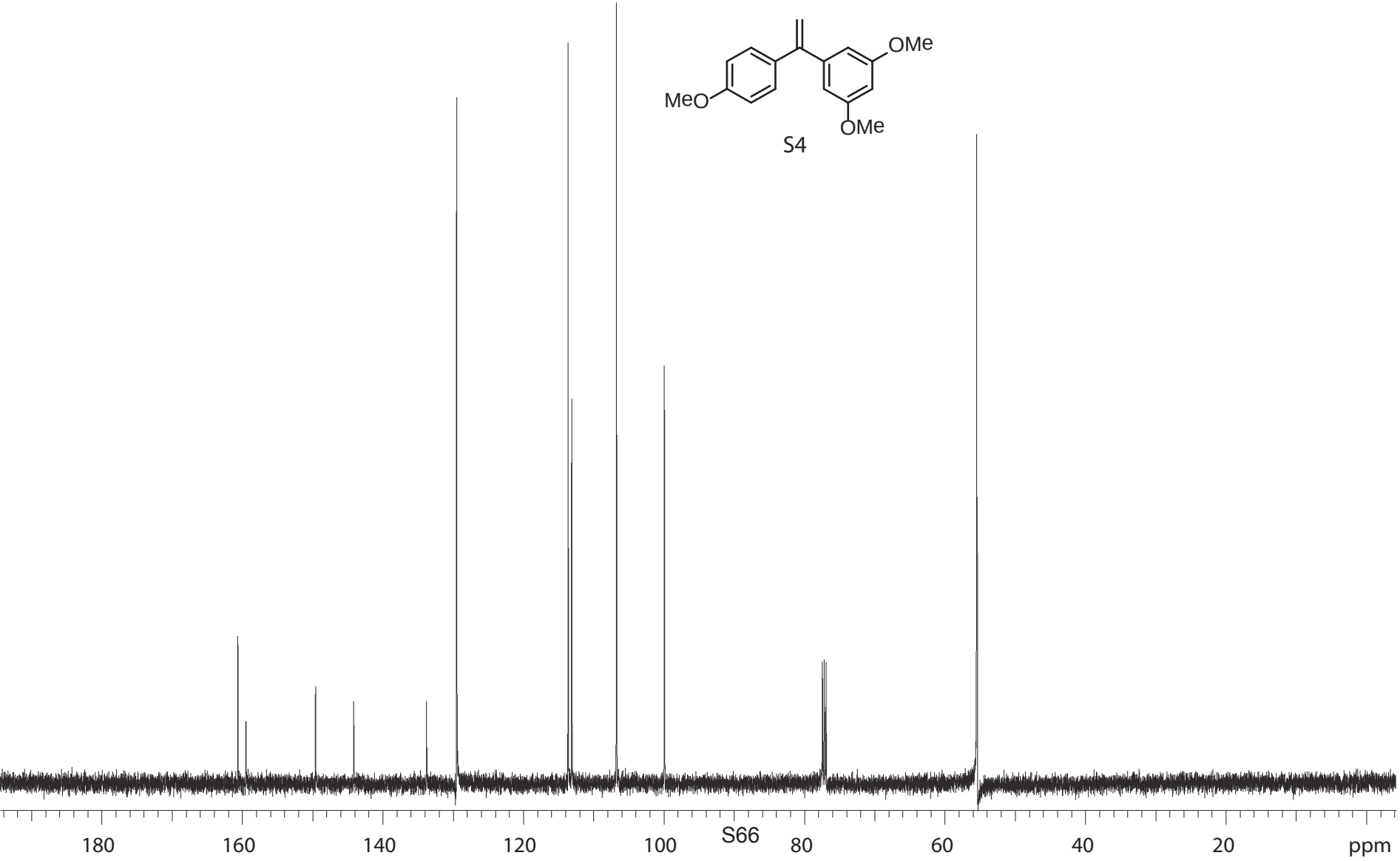
1.94
0.99
0.98
0.98
2.98
6.00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MeO
OMe
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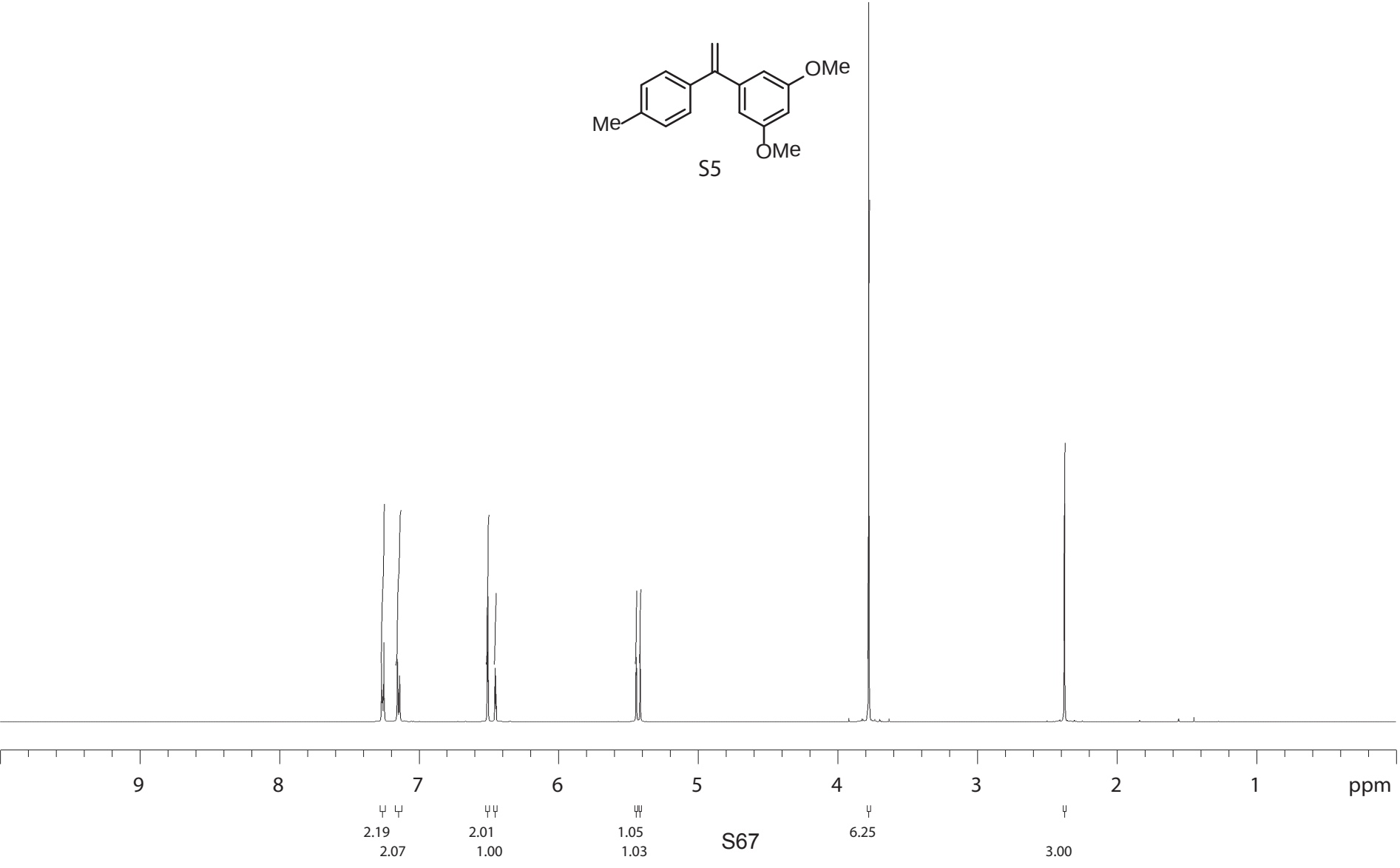
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Me
OMe
S5
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7
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5
4
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2
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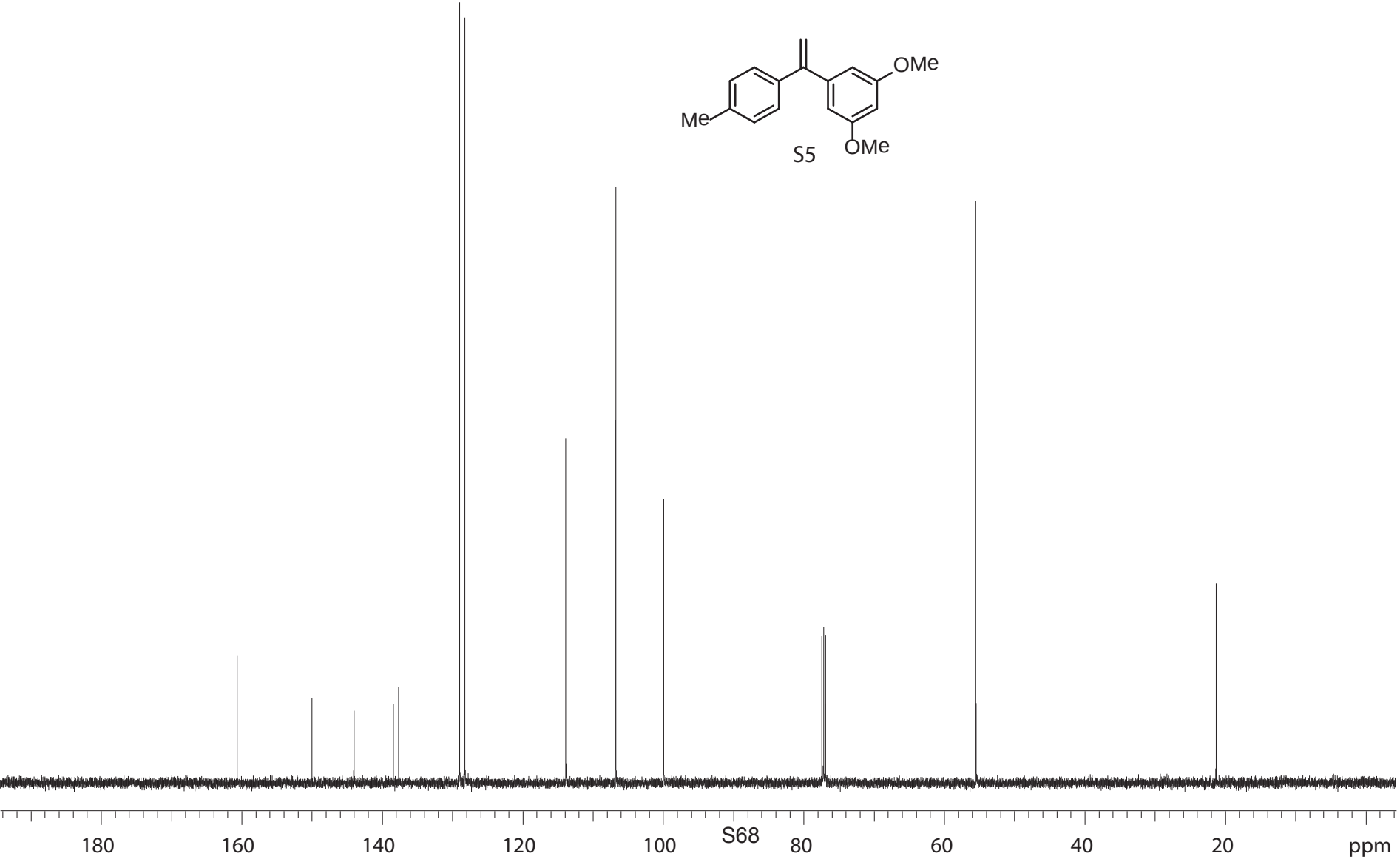
1.00
1.05
1.03
6.25
3.00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Me
OMe
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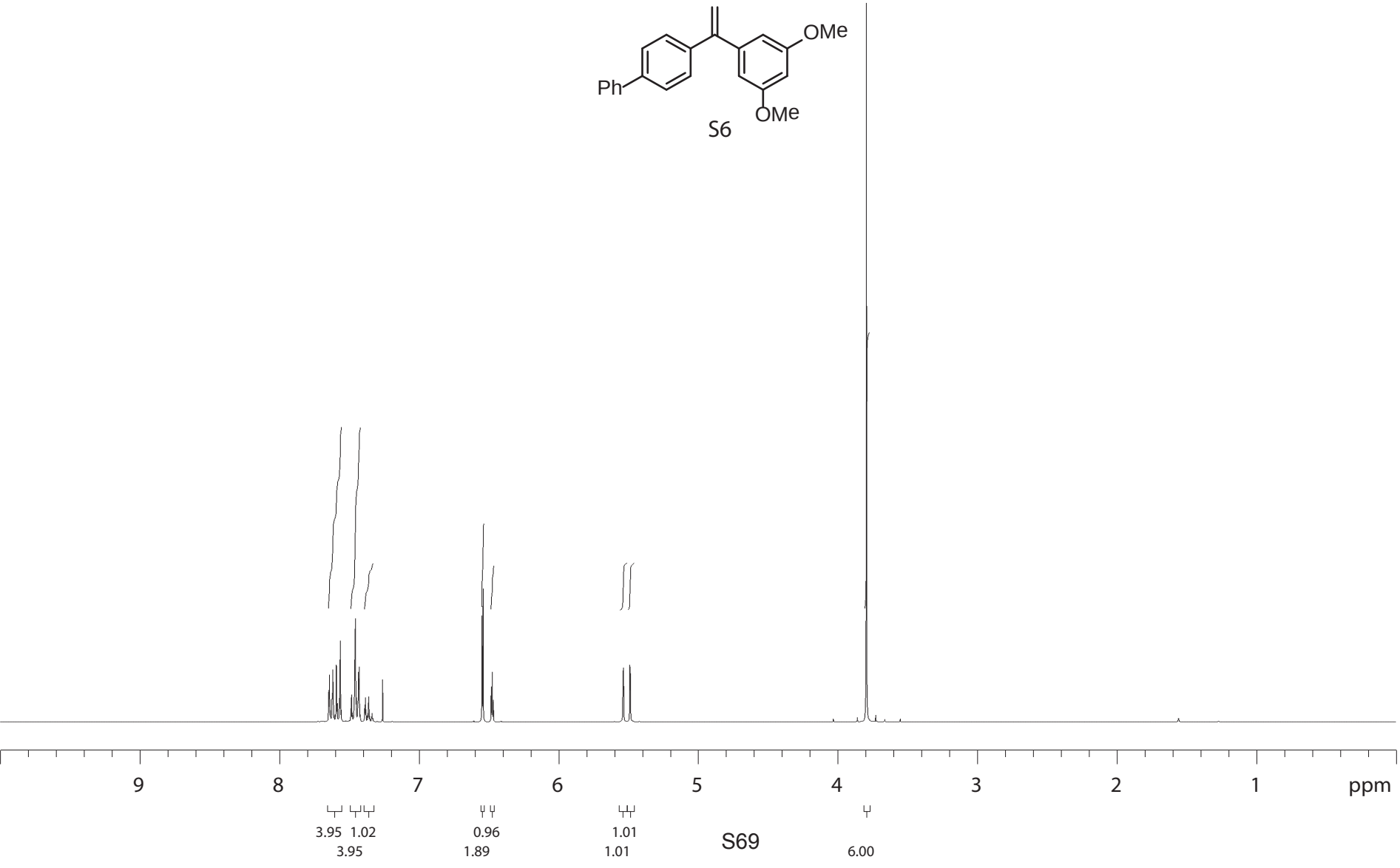
ppm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Ph
OMe
S6
9
8
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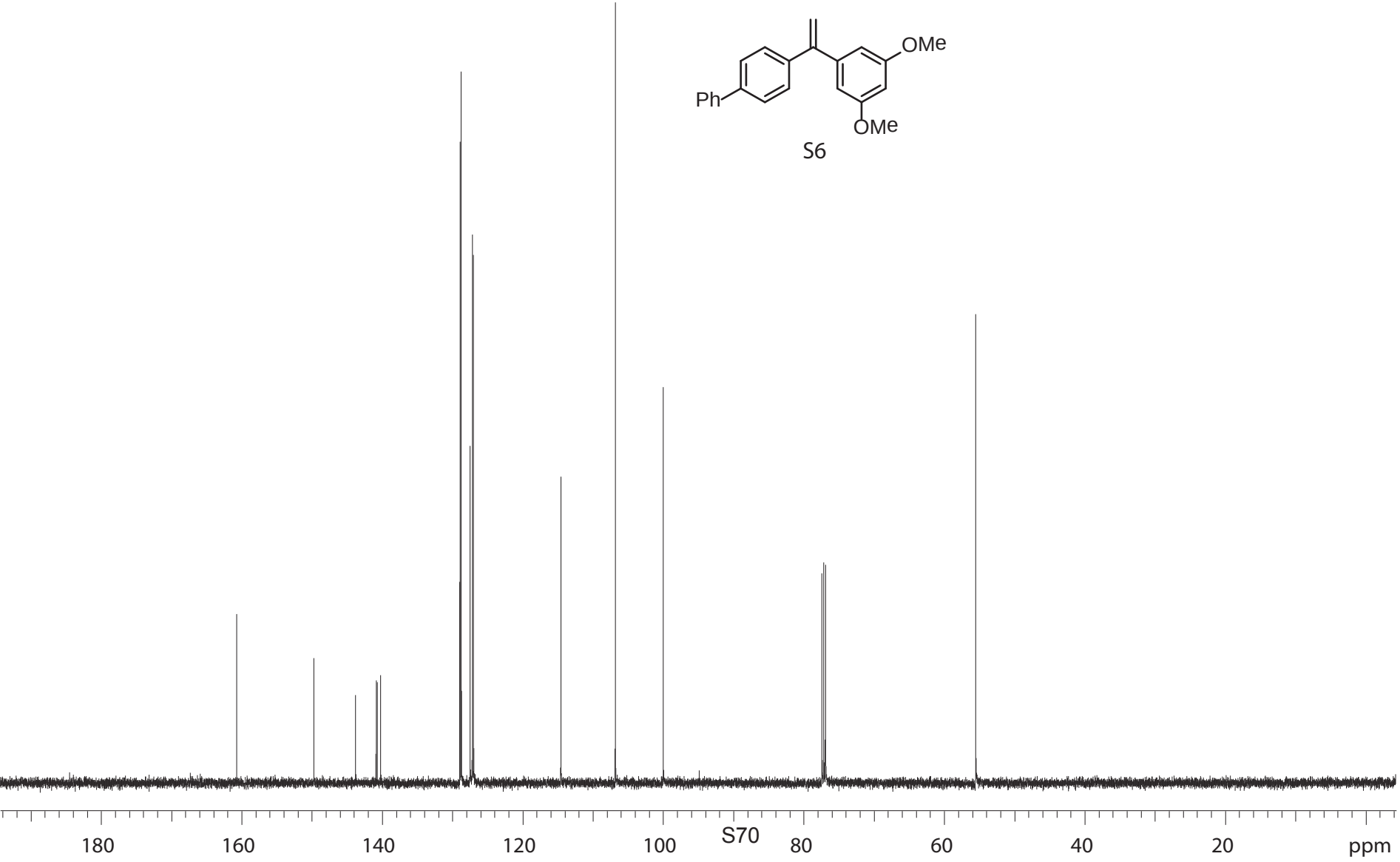
2
1
ppm
3.95 1.02
3.95
0.96
1.89
1.01
1.01
6.00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Ph
OMe
S6
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160
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120
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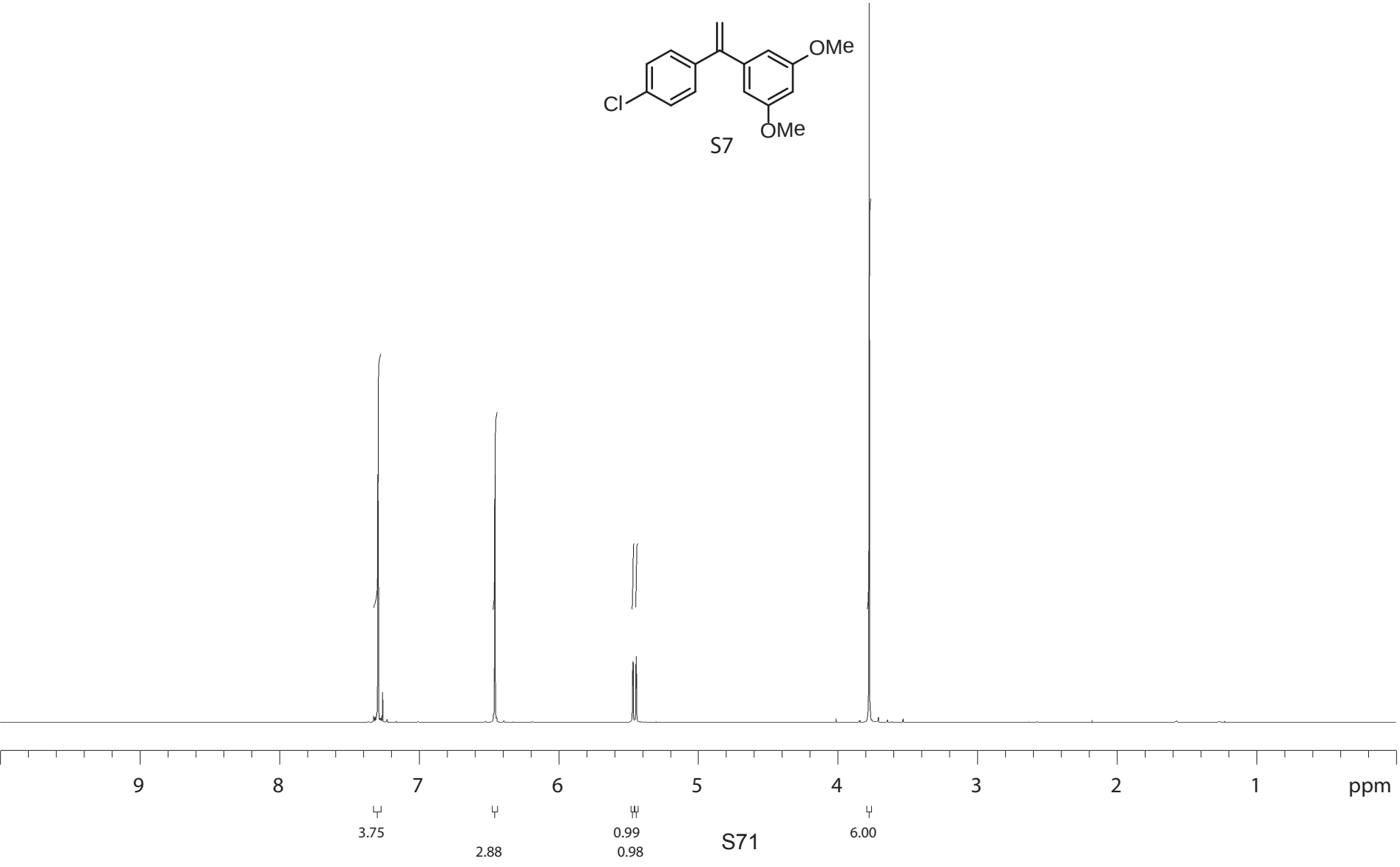
ppm


OMe
Cl
OMe
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2
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ppm
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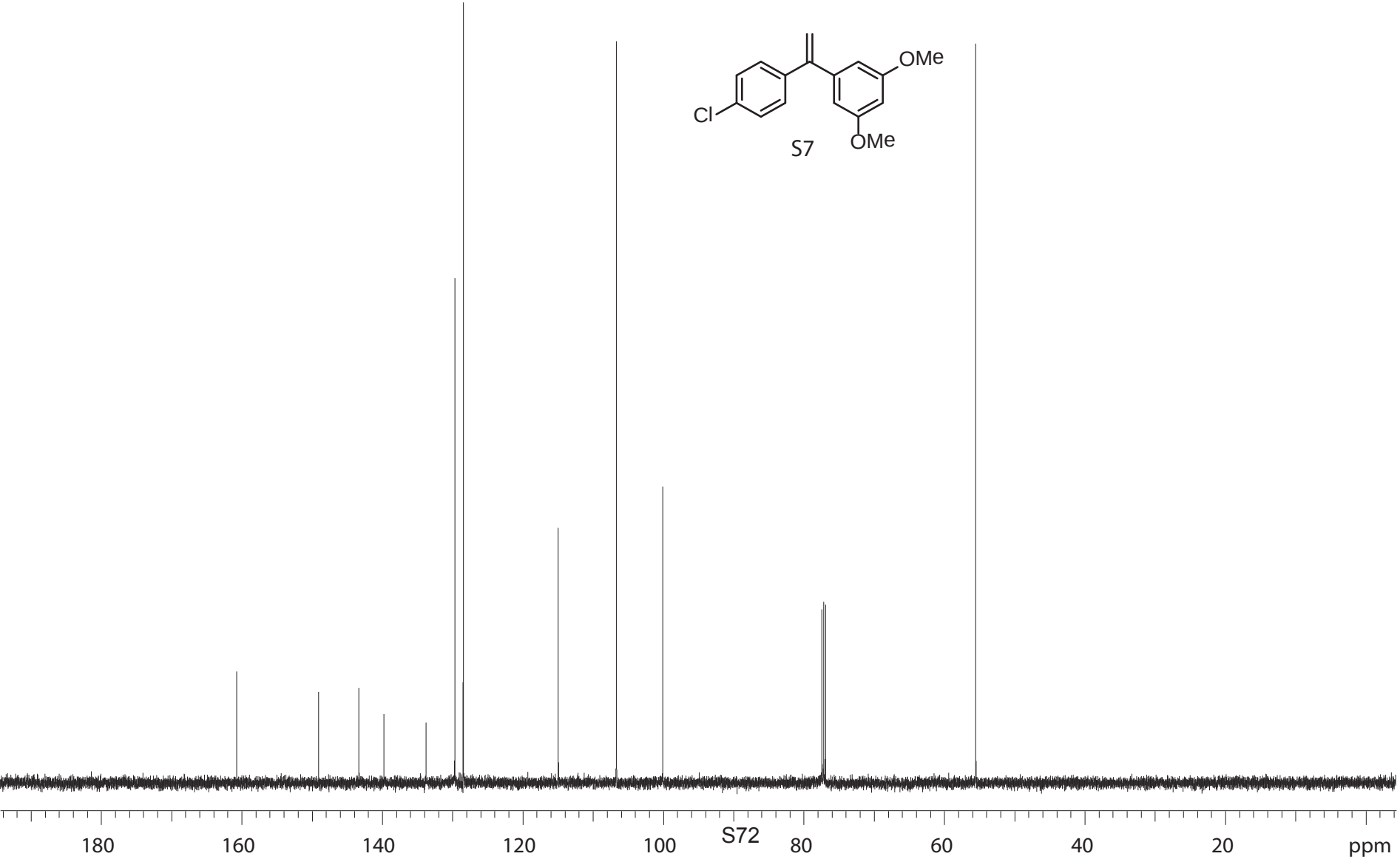
0.99
0.98
6.00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Cl
OMe
S7
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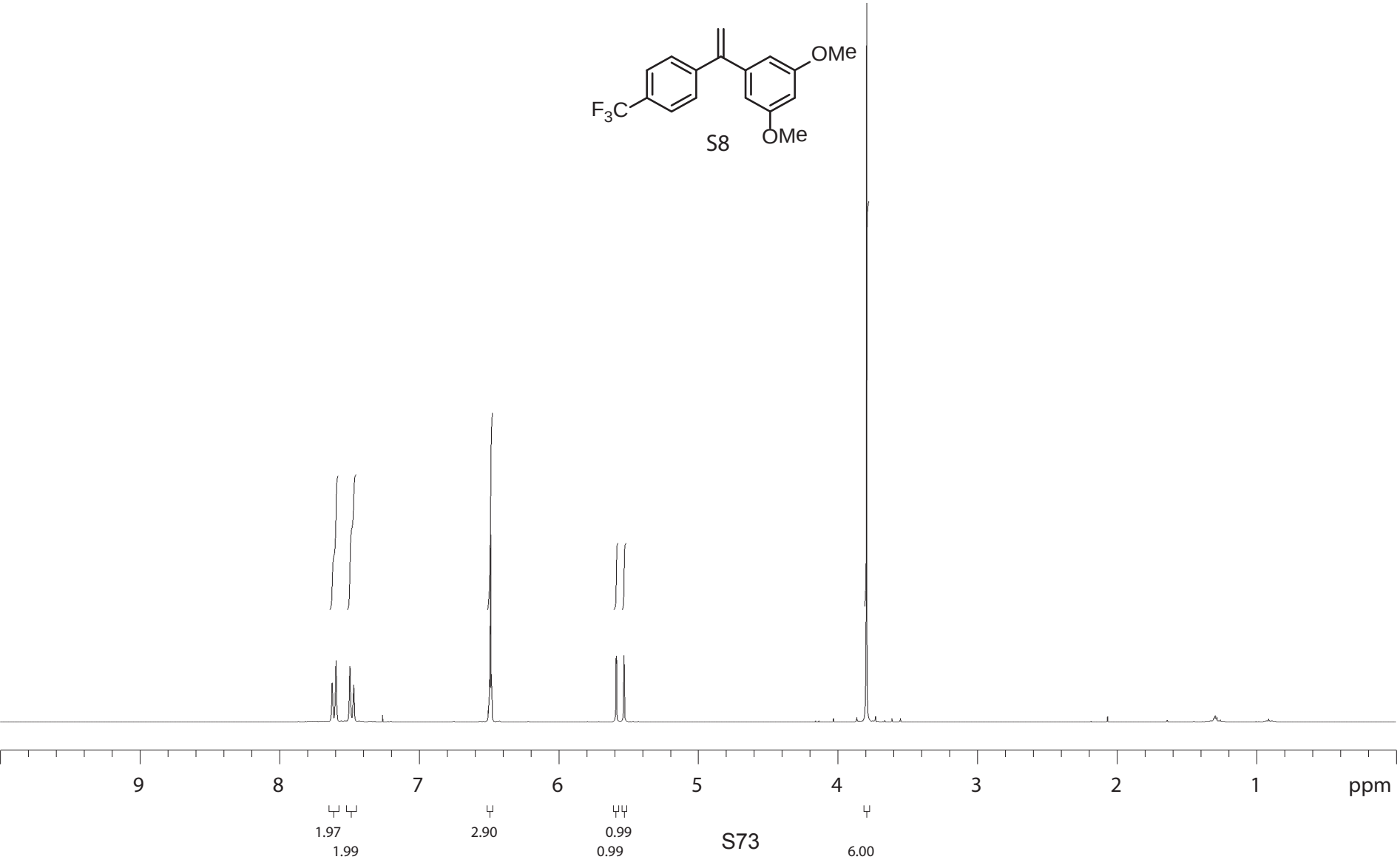
20
ppm


OMe
F3C
OMe
S8
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8
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4
3
2
1
ppm
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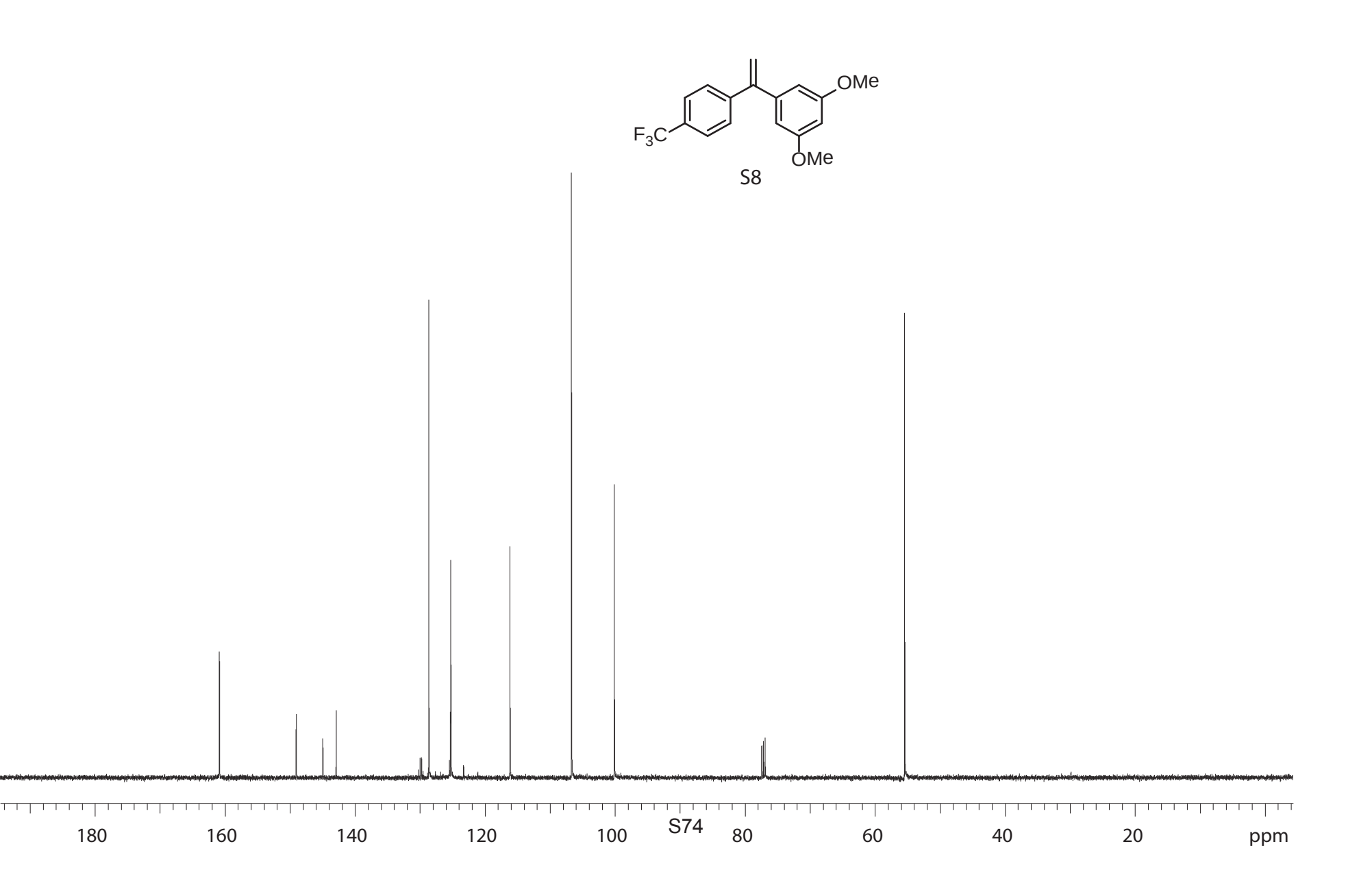
1.99
2.90
0.99
0.99
6.00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F3C
OMe
S8
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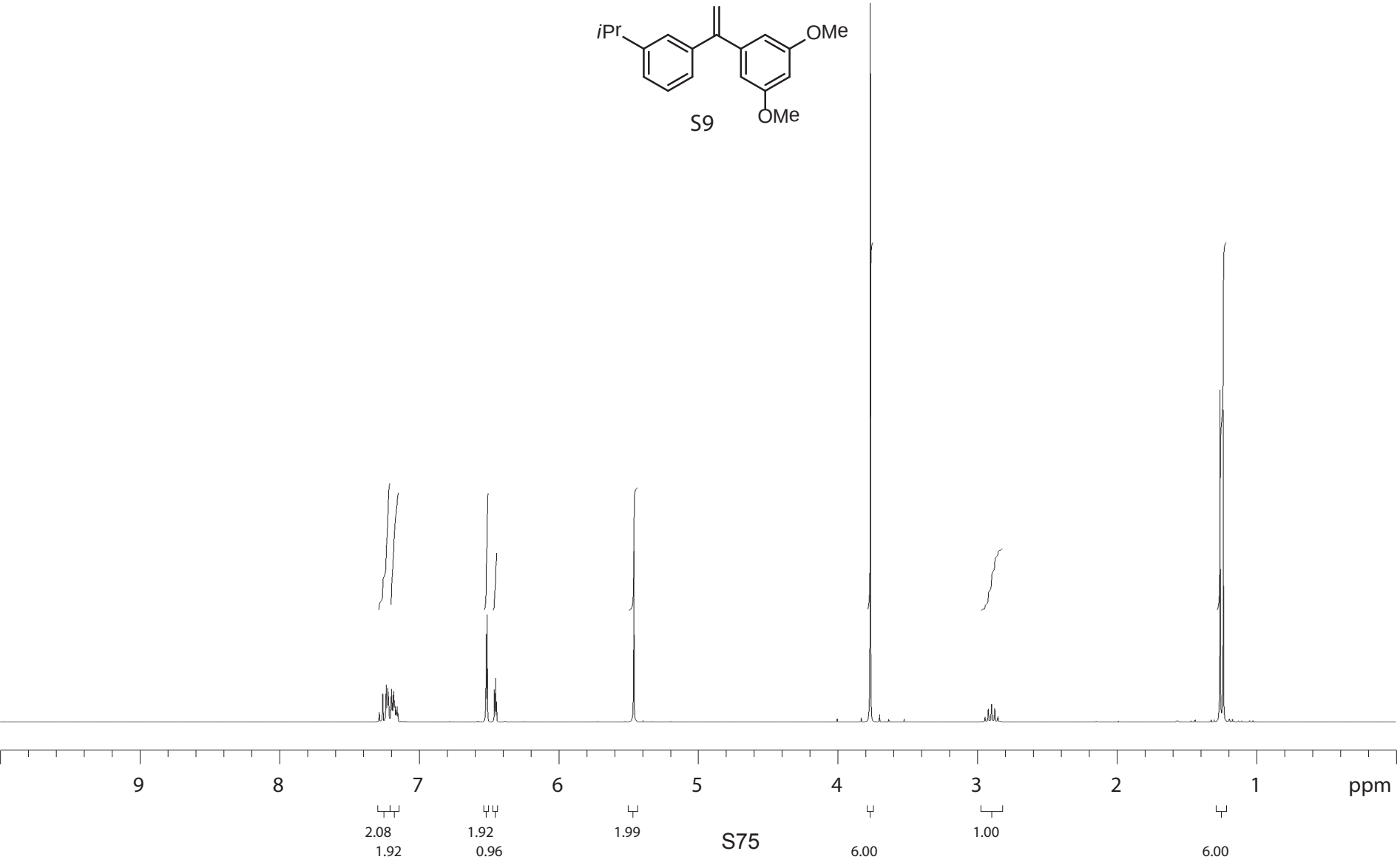
ppm


iPr
OMe
OMe
S9
9
8
7
6
5
4
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2
1
ppm
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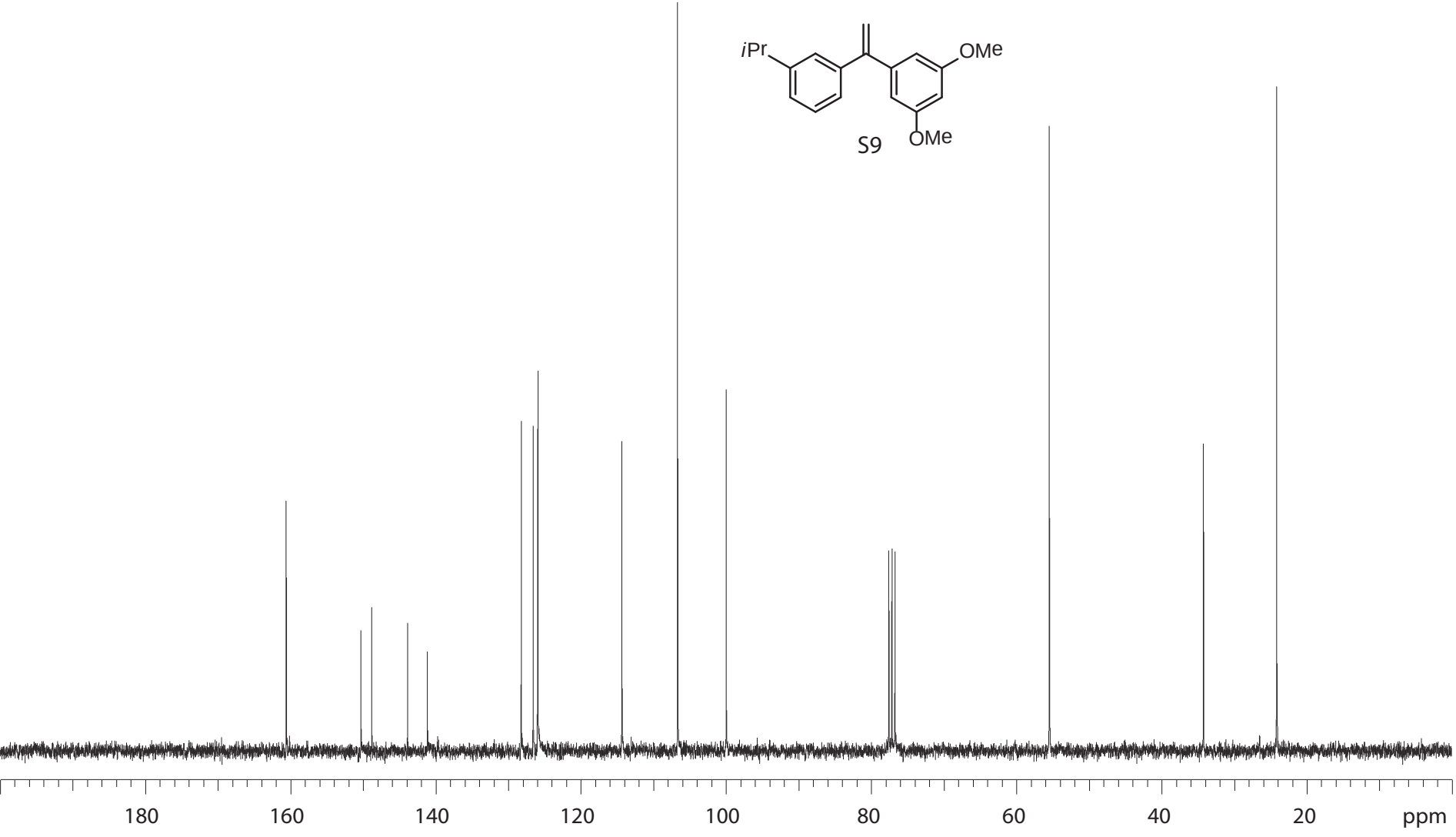
0.96
1.99
6.00
1.00
6.00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OMe
OMe
S9
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120
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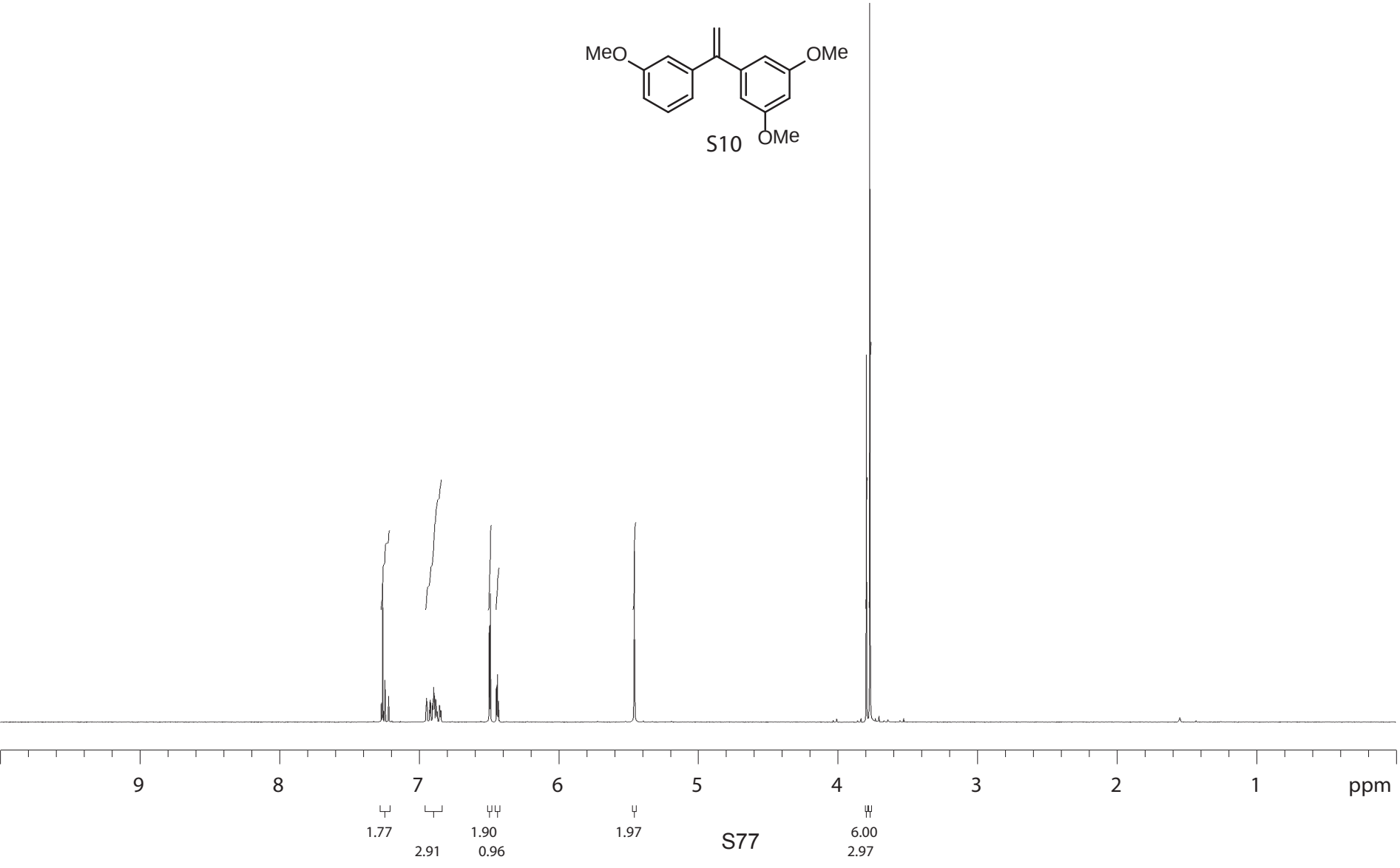
20
ppm


MeO
OMe
OMe
S10
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2
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ppm
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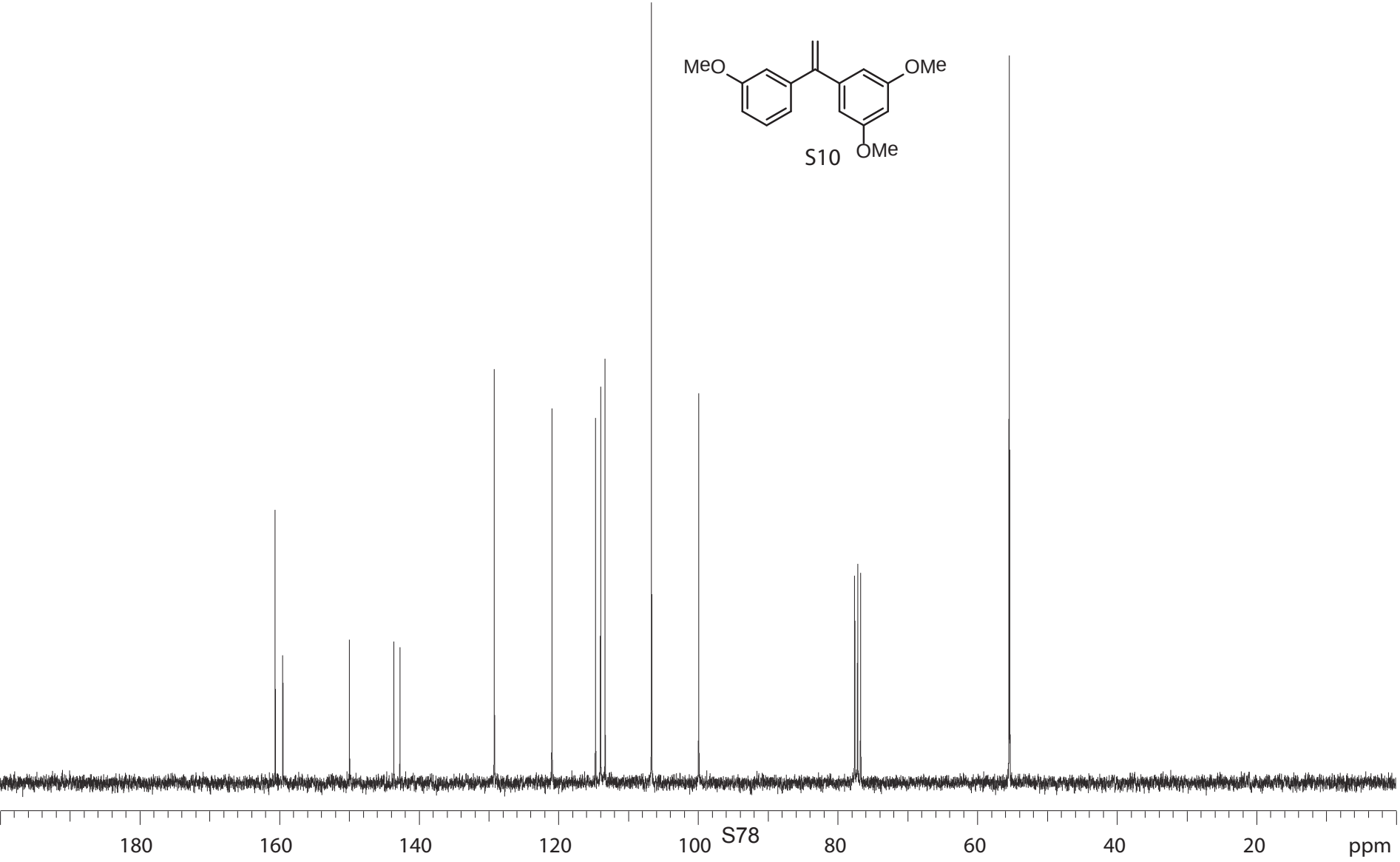
2.91
1.90
0.96
1.97
6.00
2.97
S77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OMe
OMe
S10
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120
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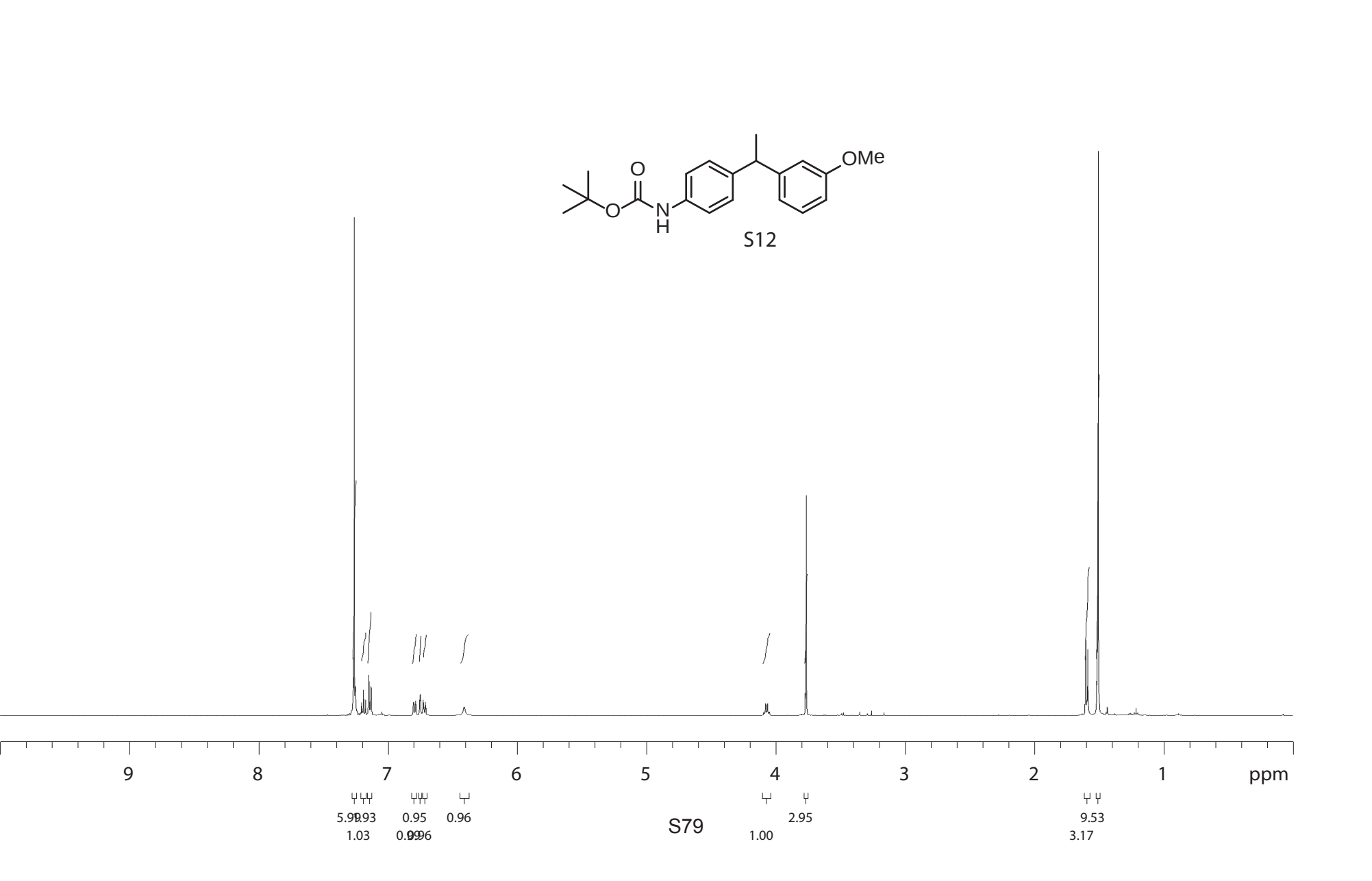
40
20
ppm


OMe
O
O
N
H
S12
9
8
7
6
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ppm
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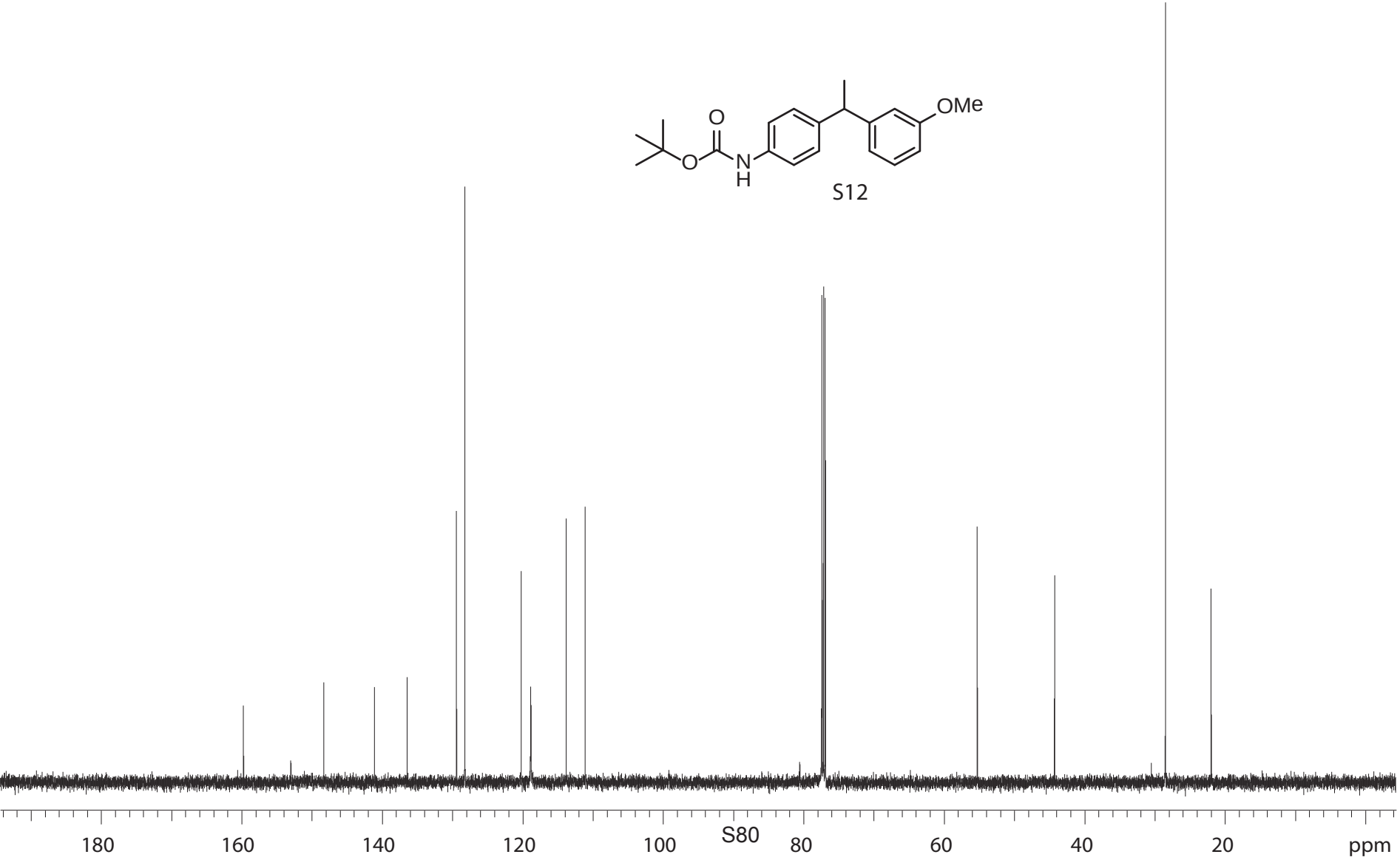
1.03
1.93
0.95
0.96
1.00
2.95
9.53
3.17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N
H
OMe
S12
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140
120
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60
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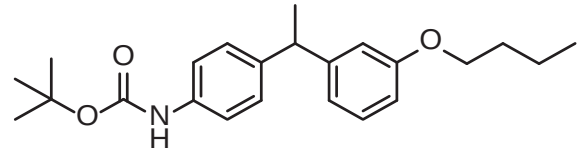
20
ppm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O
N
H
O

S13

9
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7
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5
4
3
2
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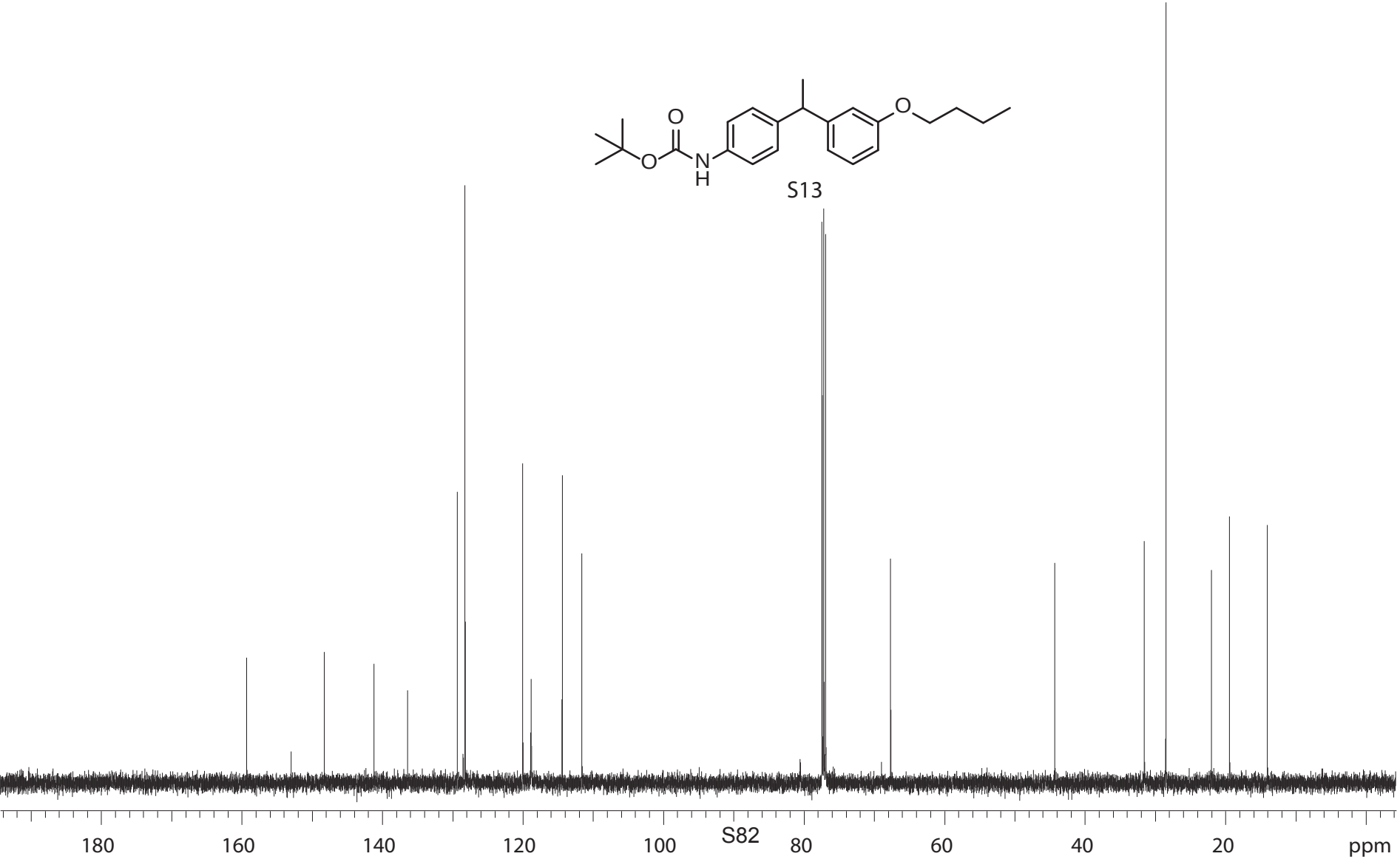
0.88
2.03
1.01
3.33
2.07
11.00
3.00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O
S13
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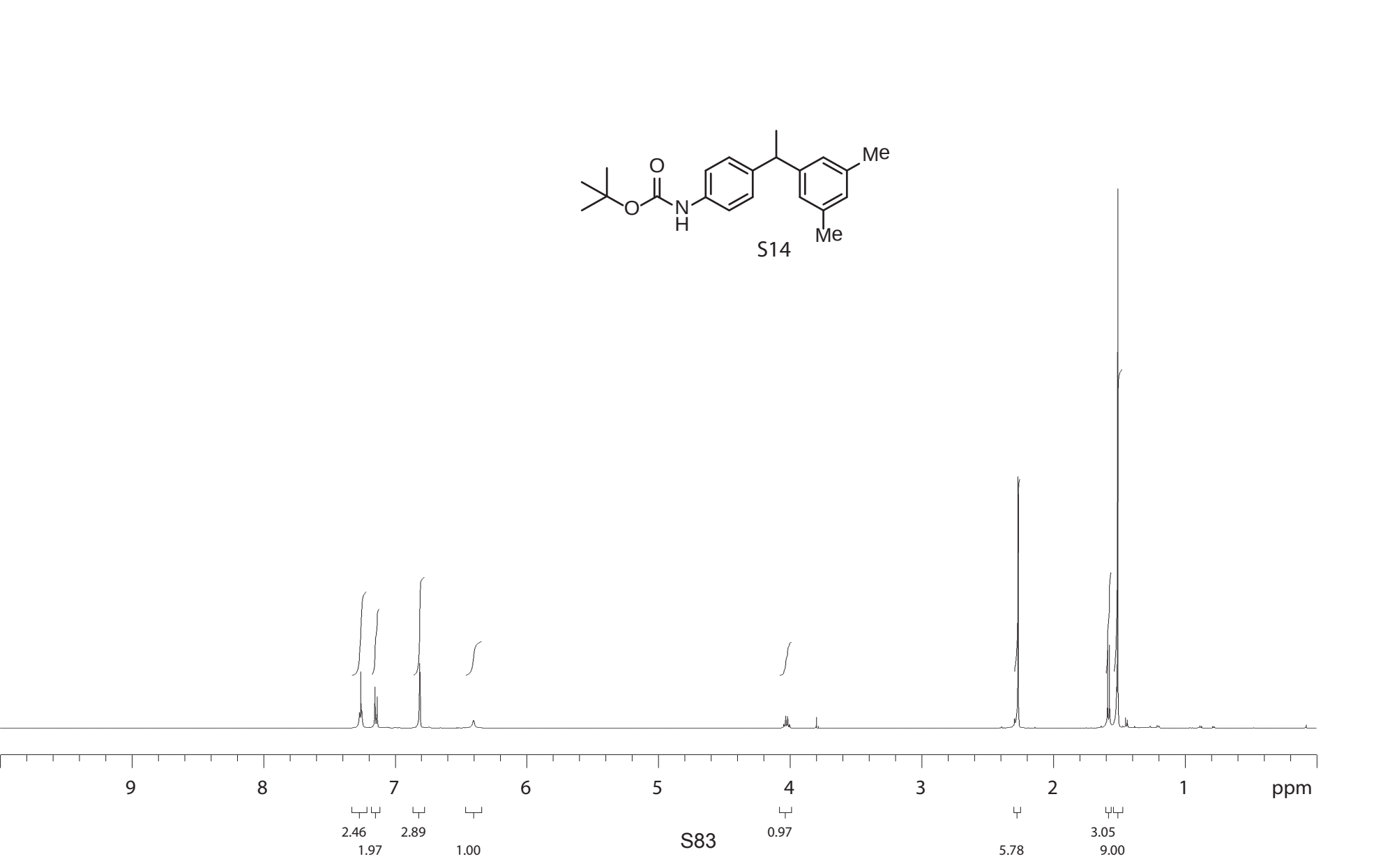
20
ppm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H
Me
Me
S14
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1
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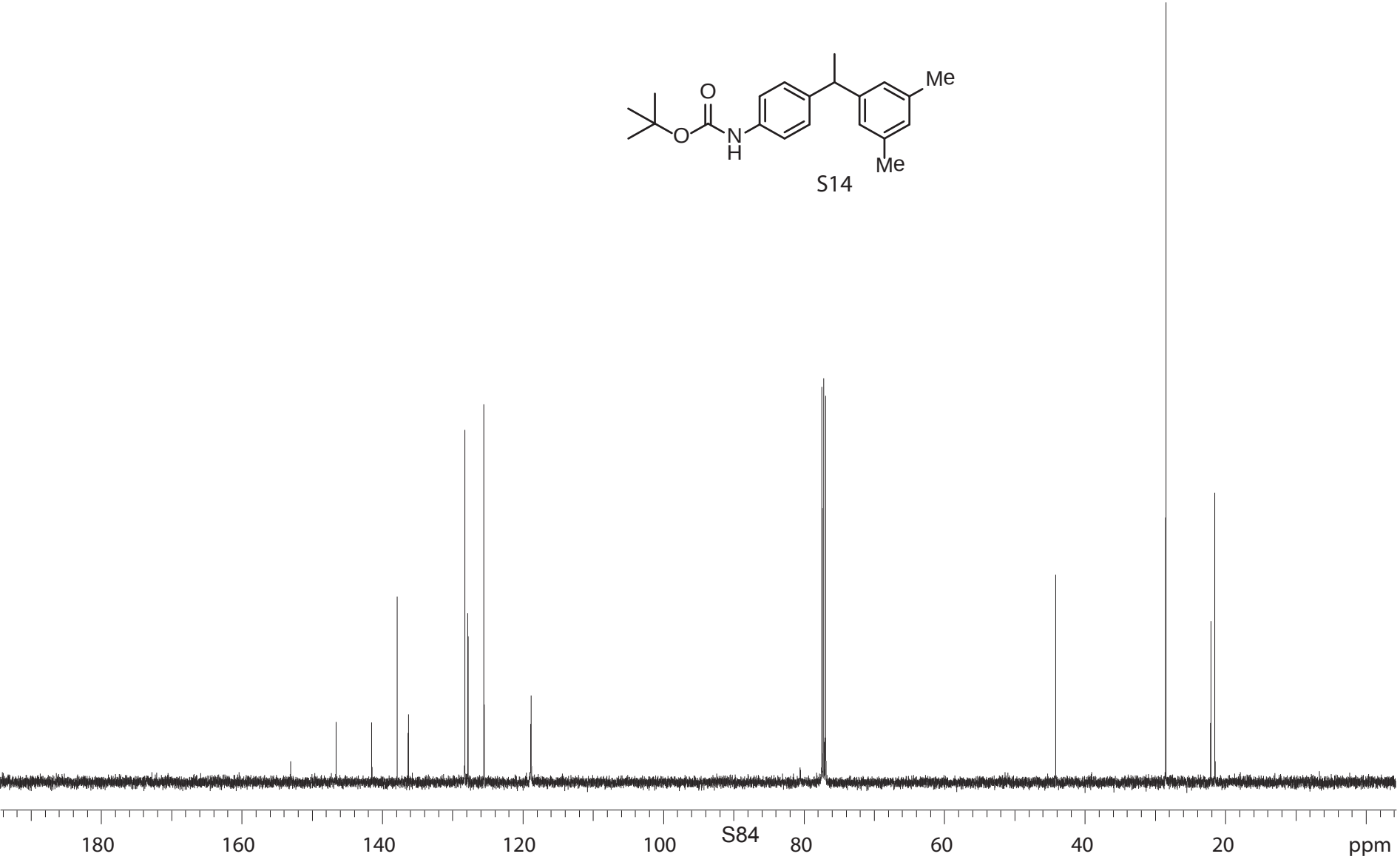
9.00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O
N
H
Me
Me
S14
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140
120
100
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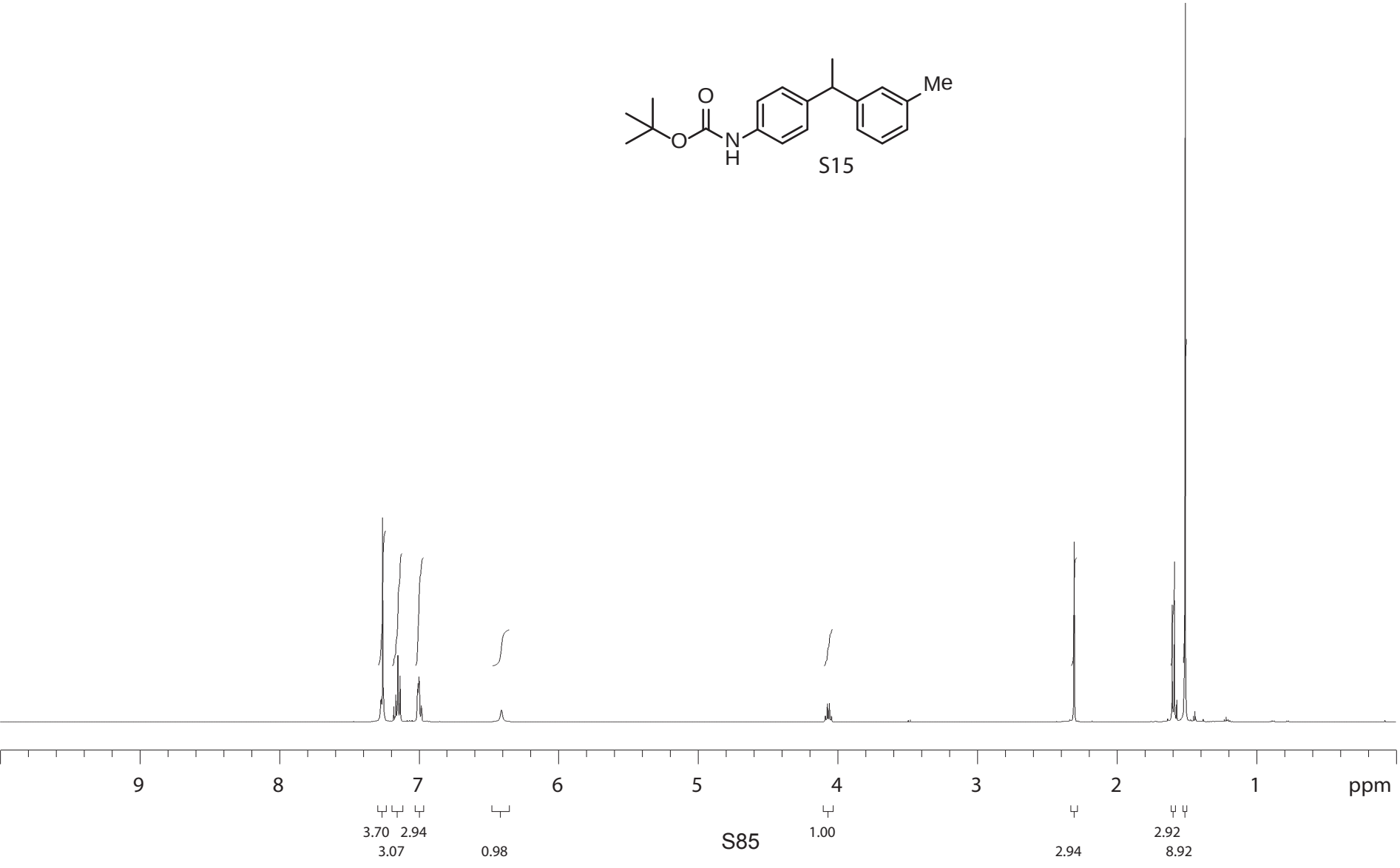
60
40
20
ppm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N
H
Me
S15
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8
7
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1
ppm
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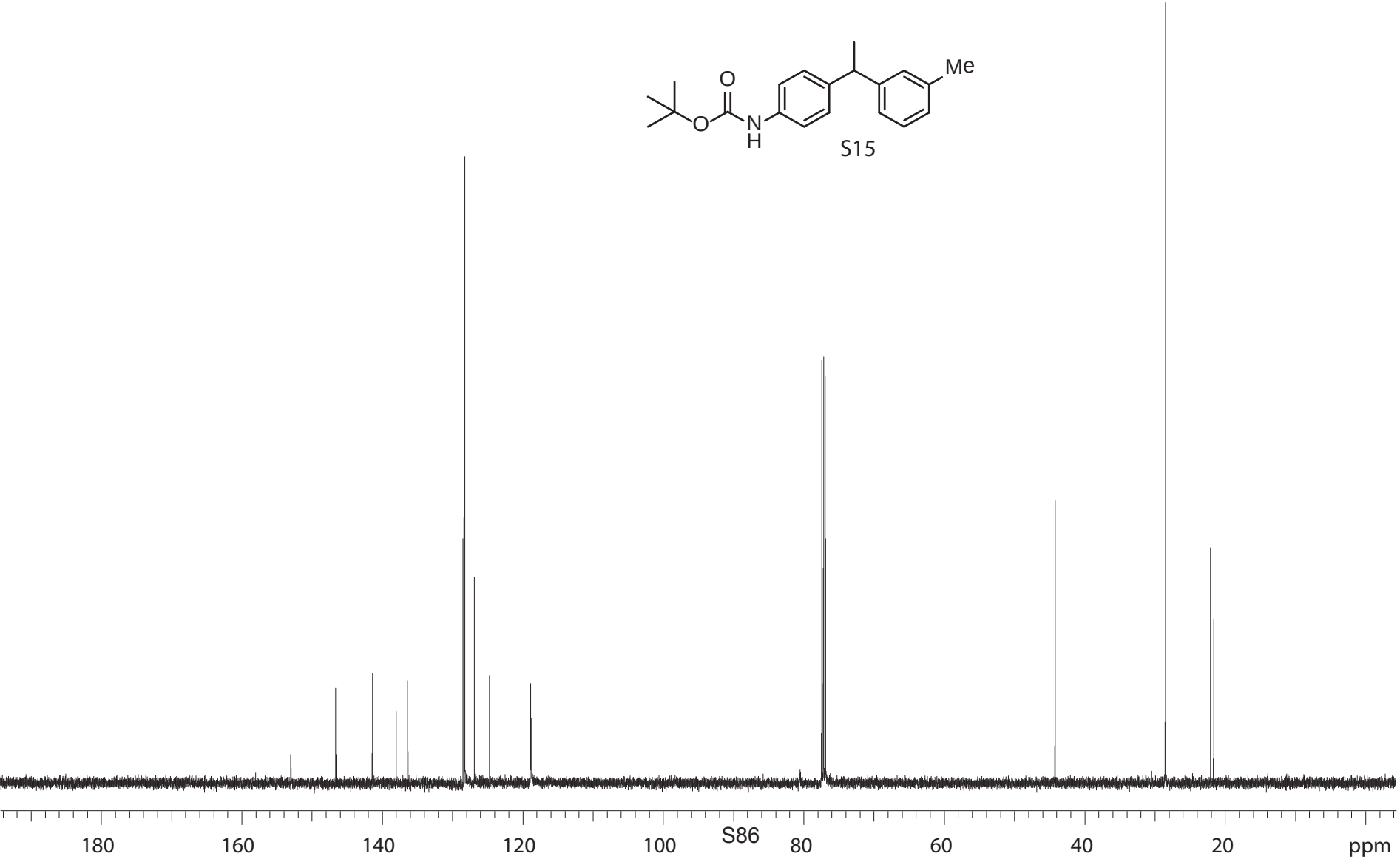
3.07
0.98
1.00
2.94
2.92
8.92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H
Me
S15
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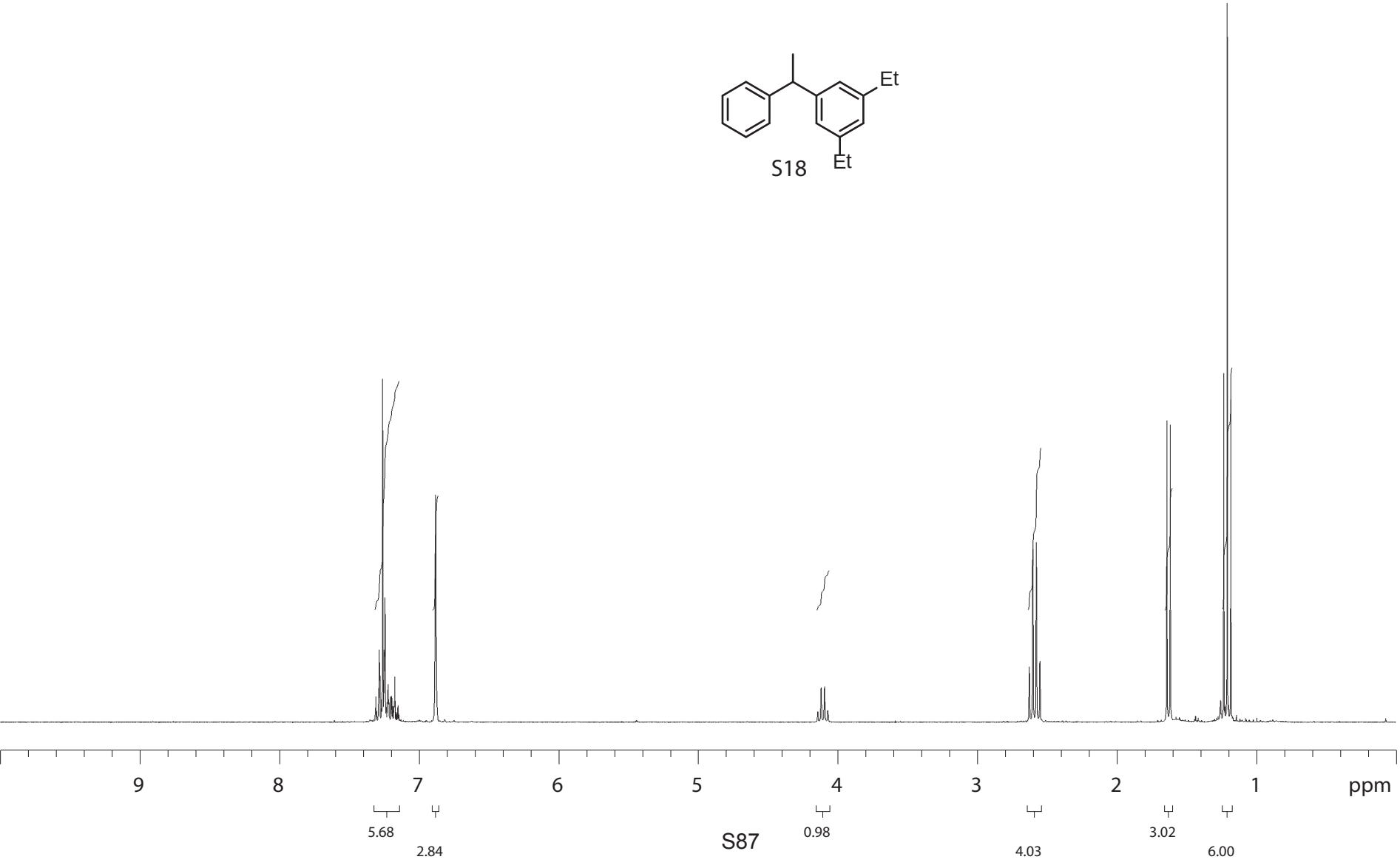
40
20
ppm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Et
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ppm
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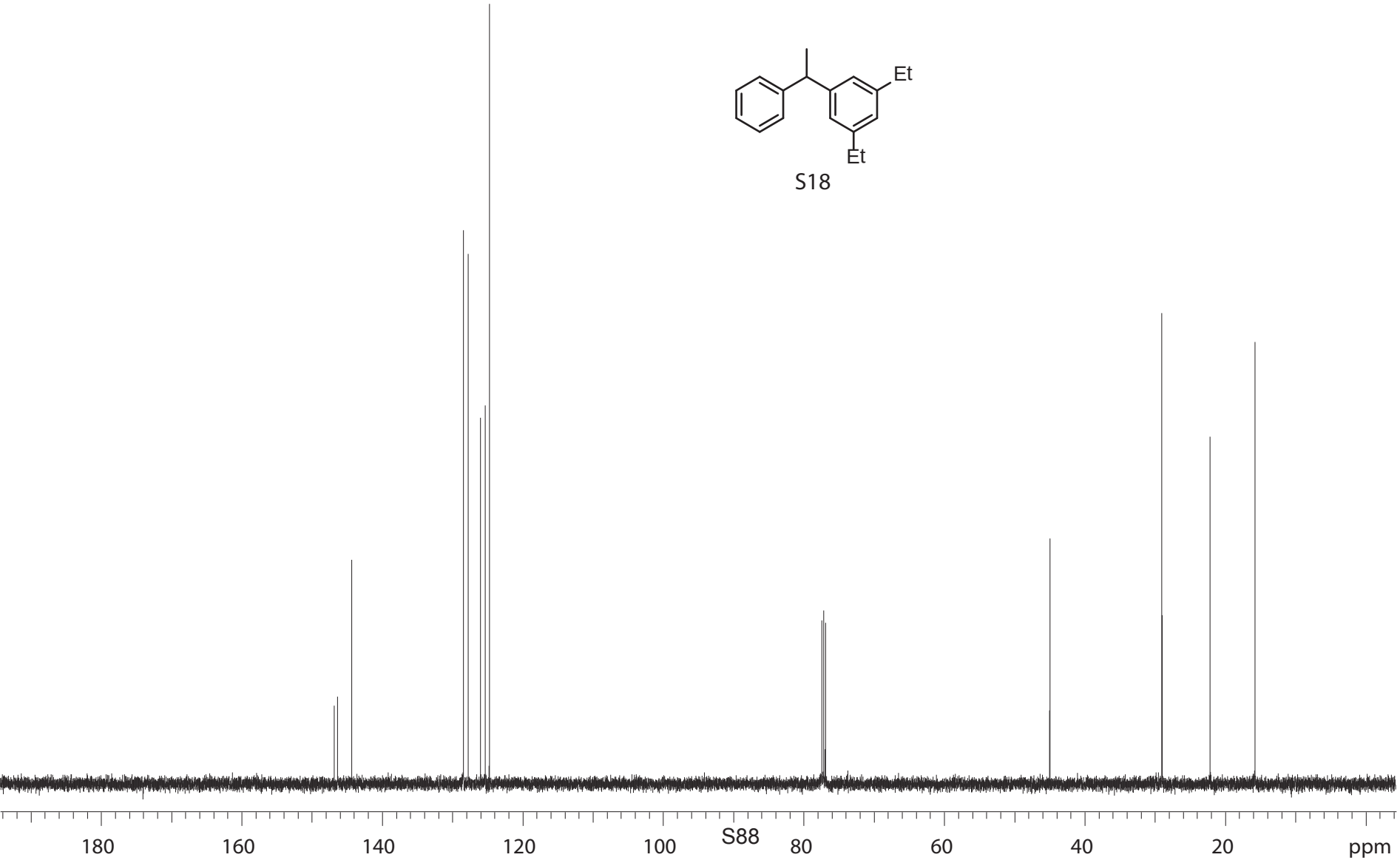
3.02
6.00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Et
S18
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120
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60
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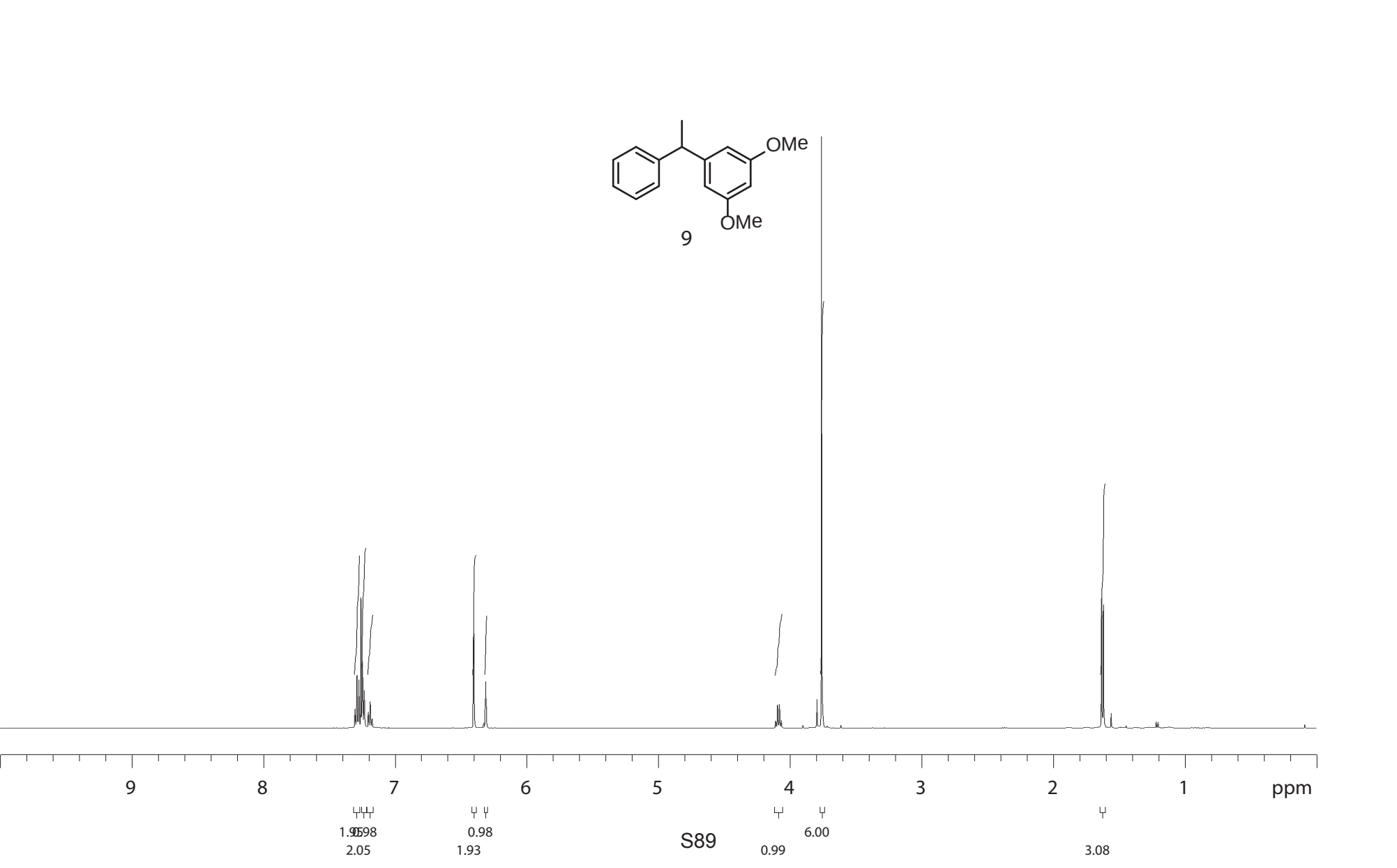
ppm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OMe
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9
8
7
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ppm
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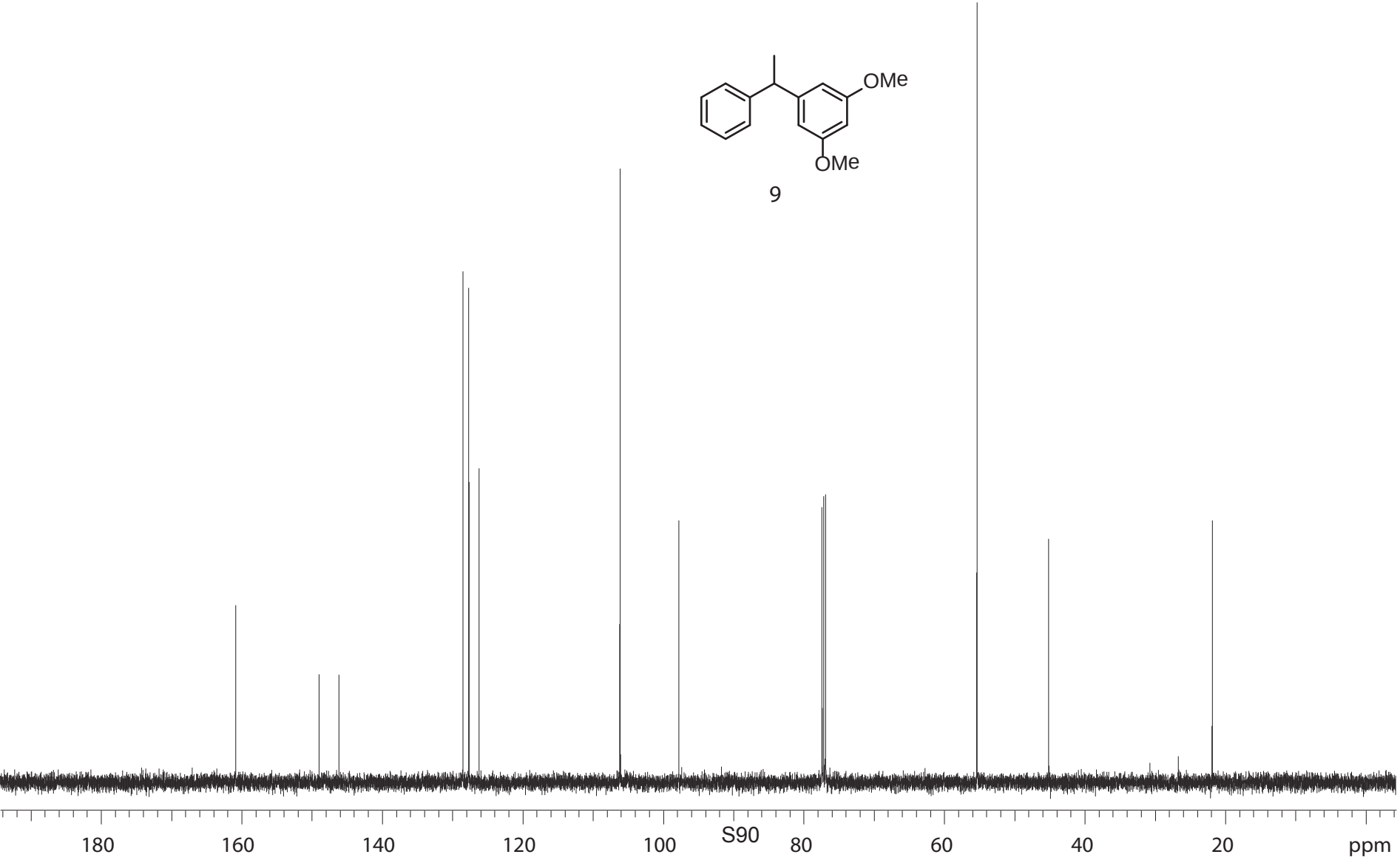
2.05
0.98
1.93
0.99
6.00
3.08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OMe
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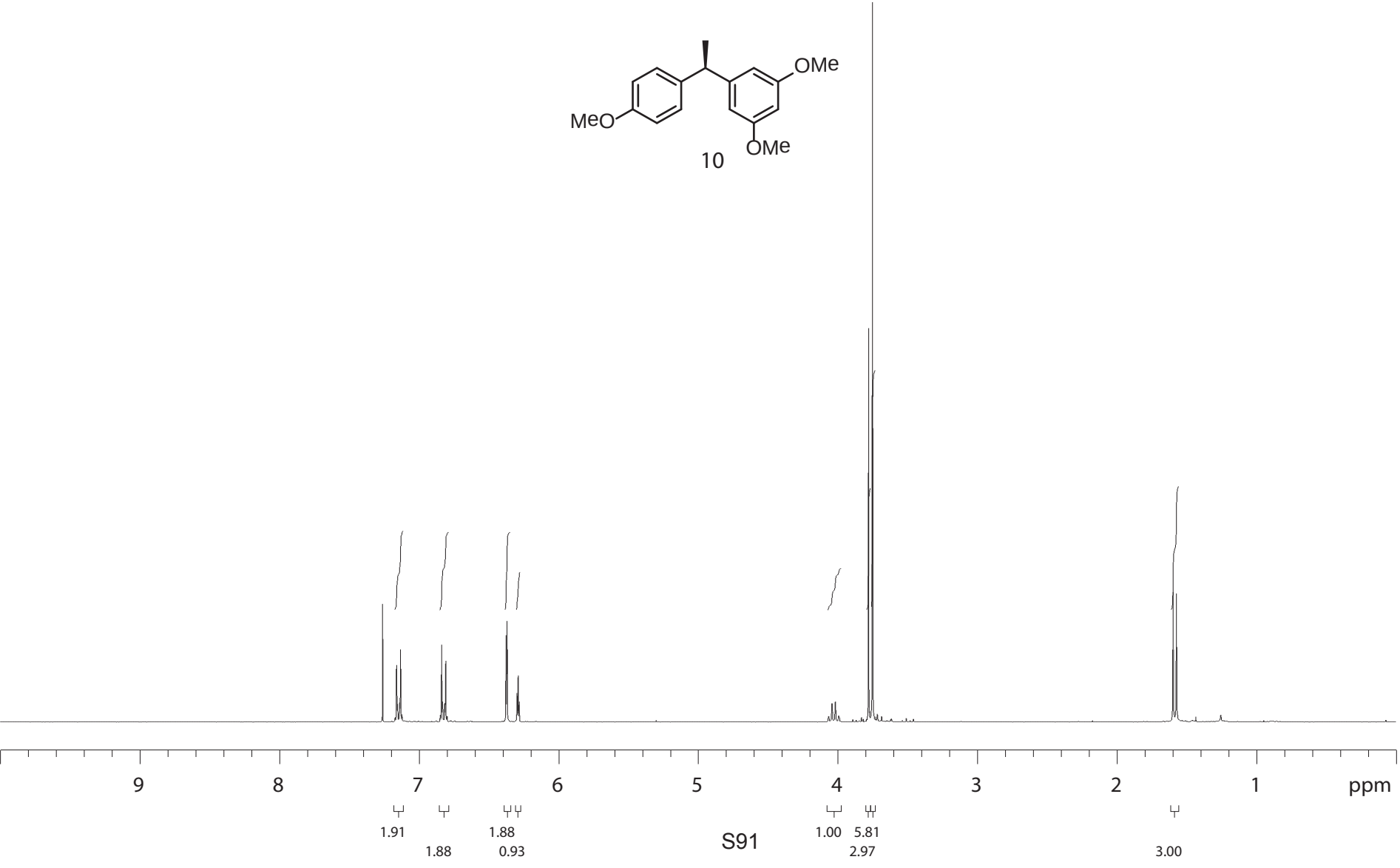
20
ppm


OMe
MeO
OMe
10
9
8
7
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4
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2
1
ppm
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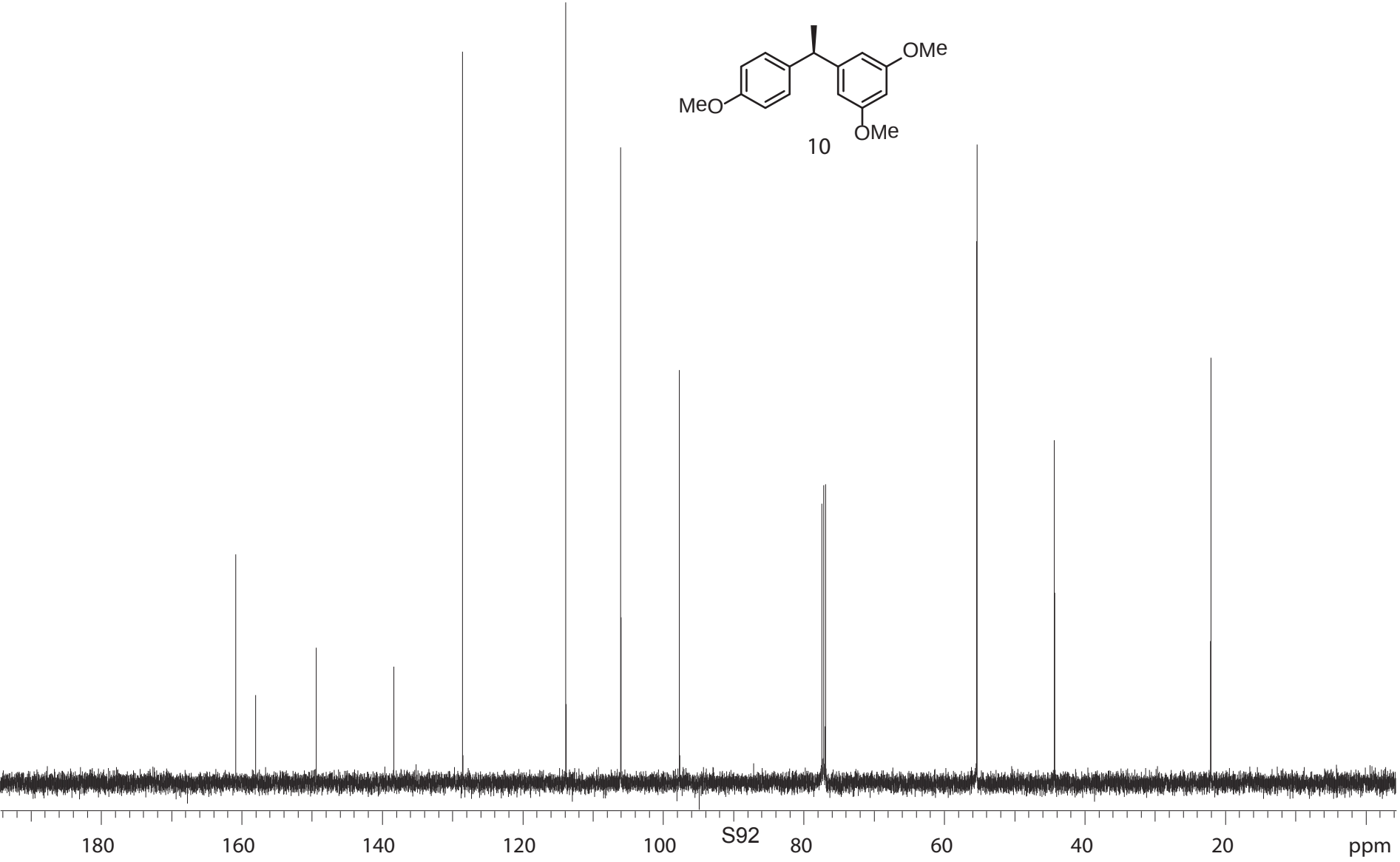
1.88
0.93
1.00
5.81
2.97
3.00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MeO
OMe
10
180
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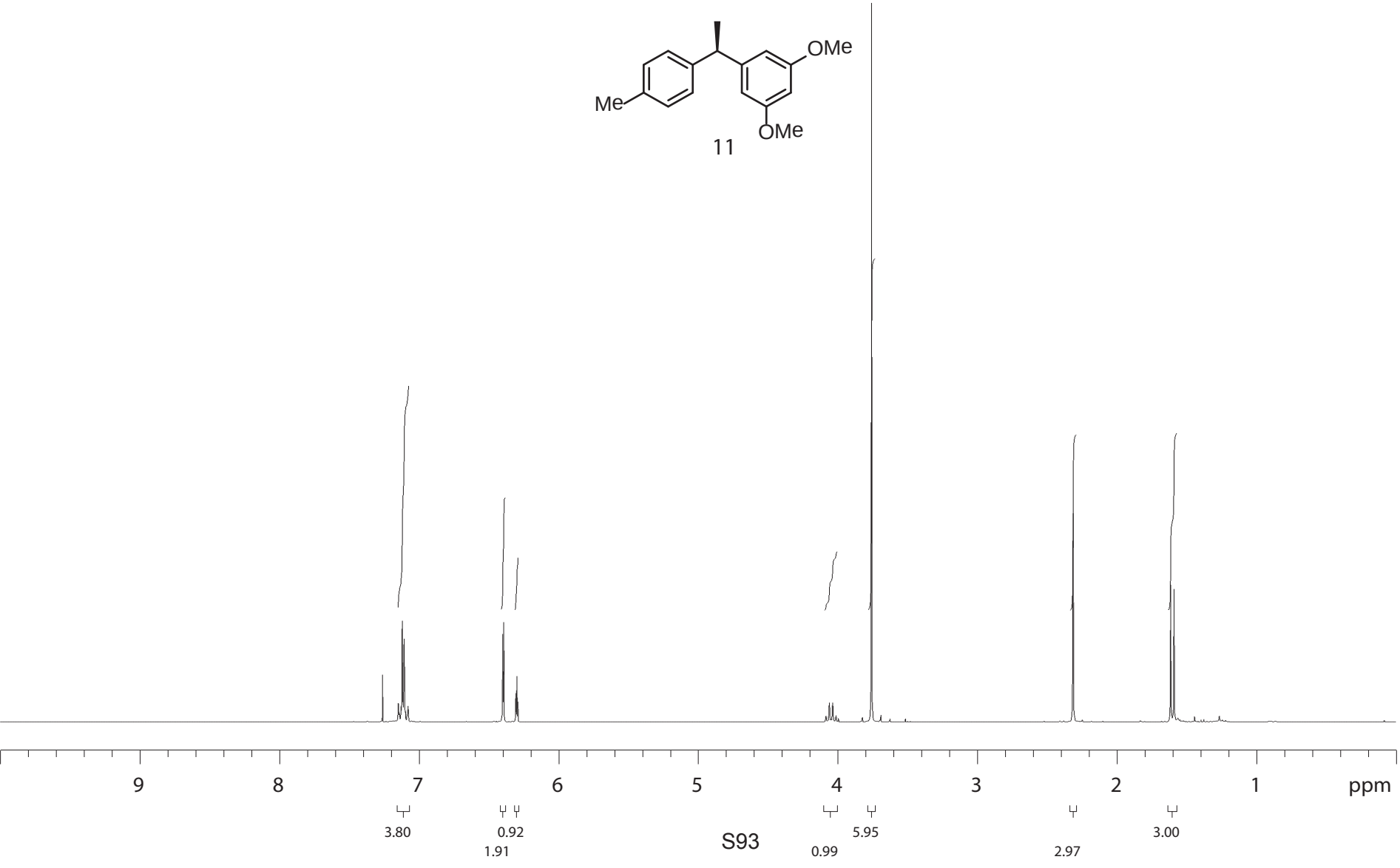
140
120
100
80
60
40
20
ppm


OMe
Me
OMe
11
9
8
7
6
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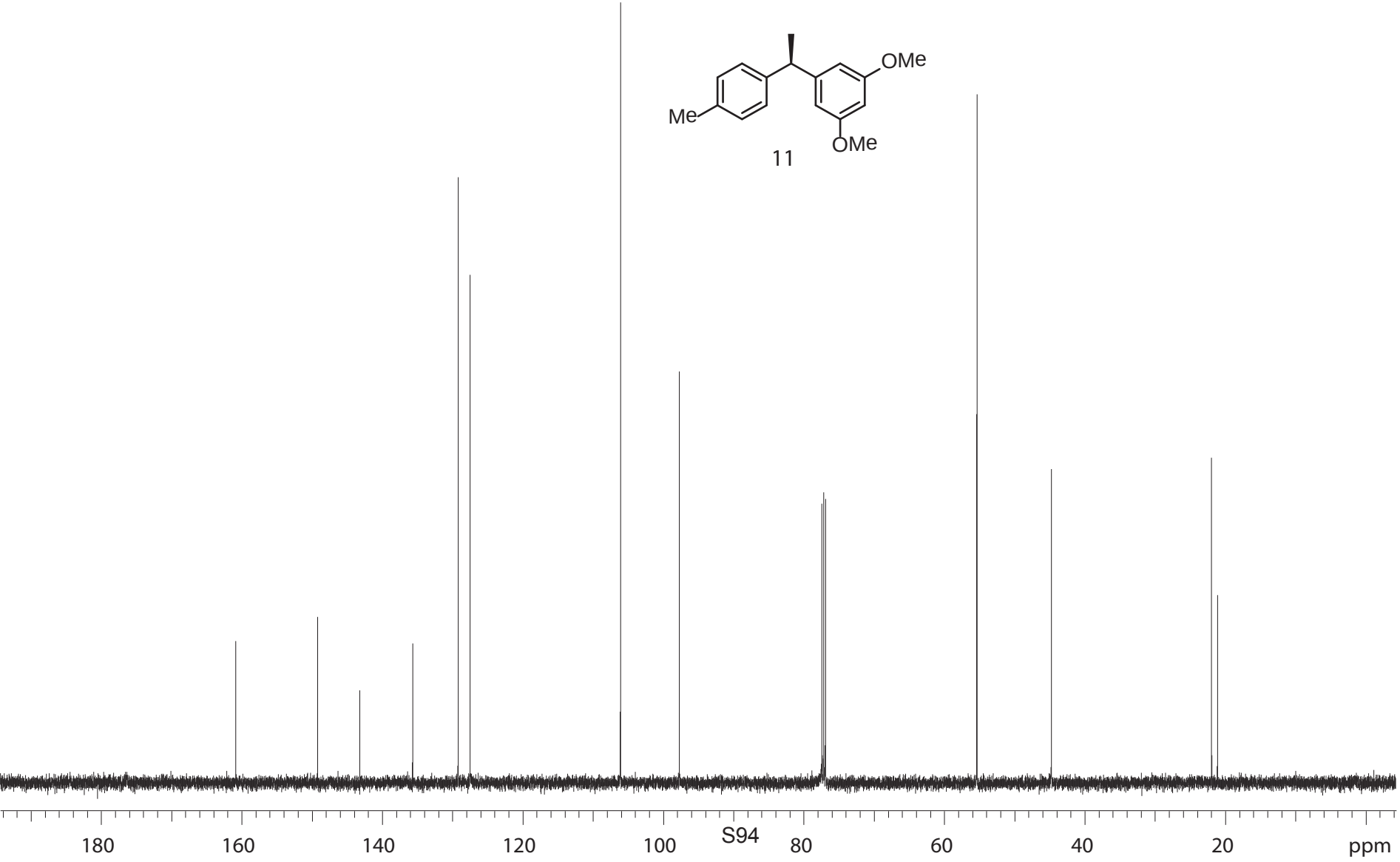
3
2
1
ppm
3.80
0.92
1.91
0.99
5.95
2.97
3.00


OMe
Me
OMe
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120
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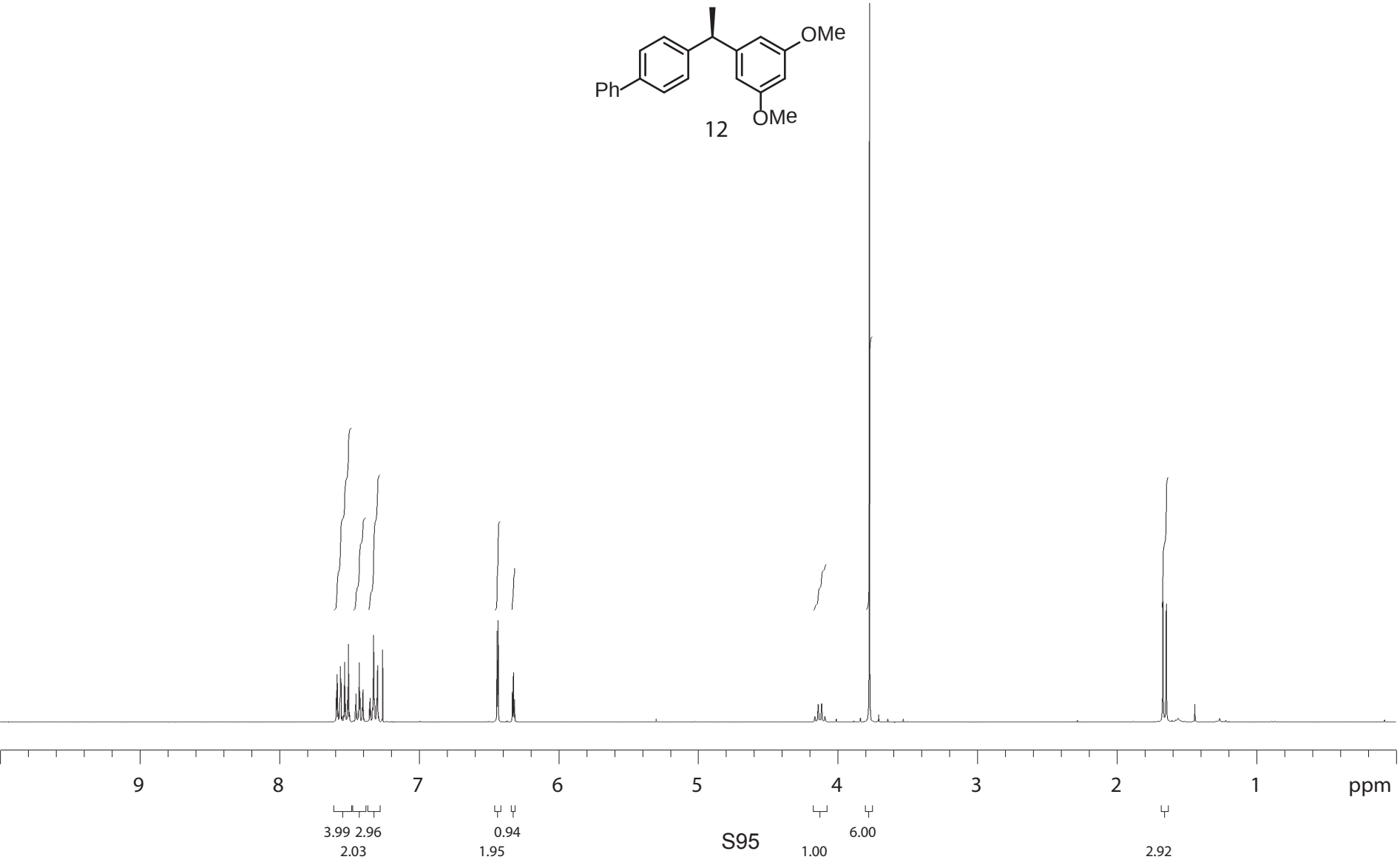
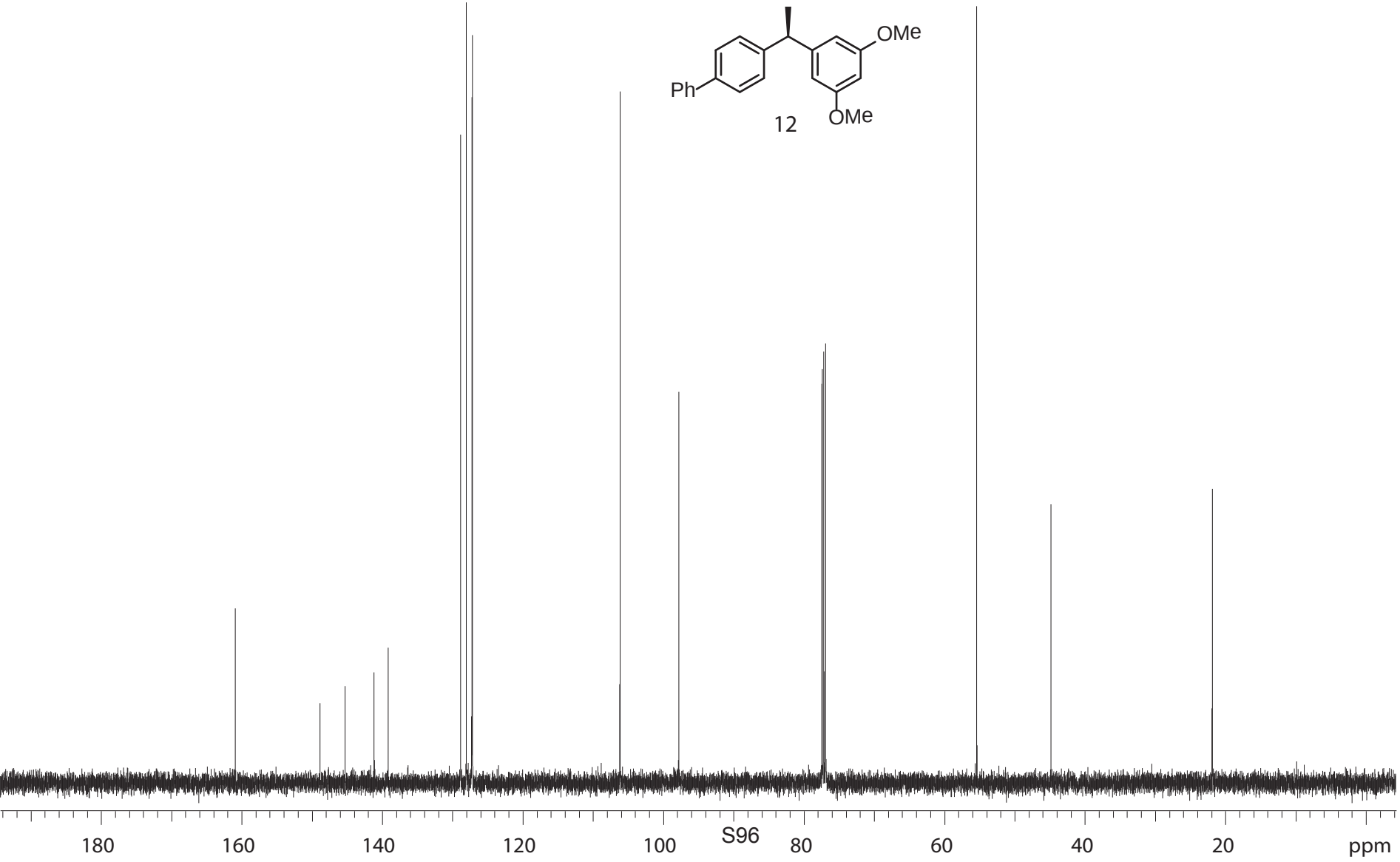
20
ppm


OMe
Ph
OMe
12
9
8
7
6
5
4
3
2
1
ppm
3.99 2.96
2.03
0.94
1.95
6.00
1.00
2.92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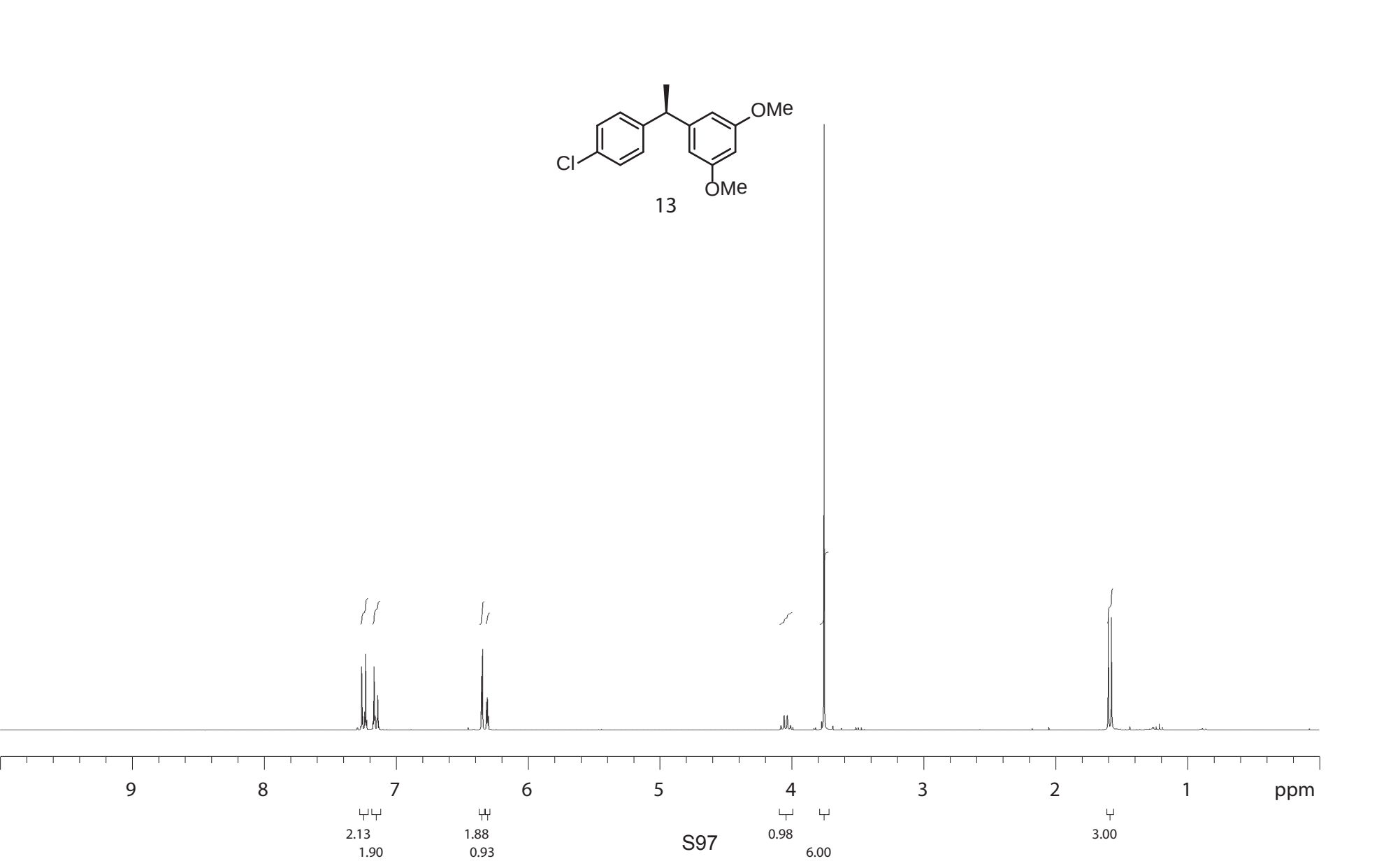
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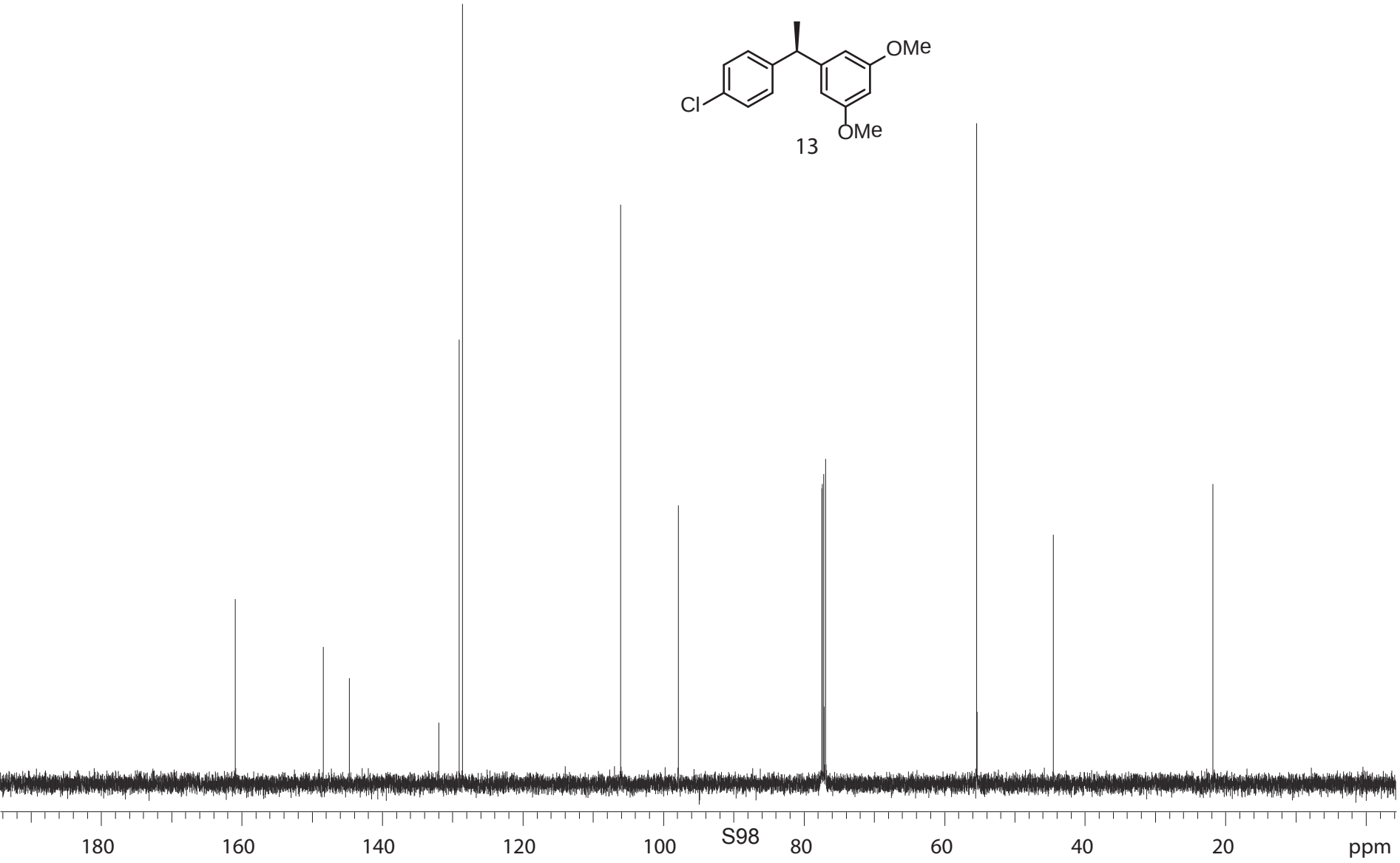
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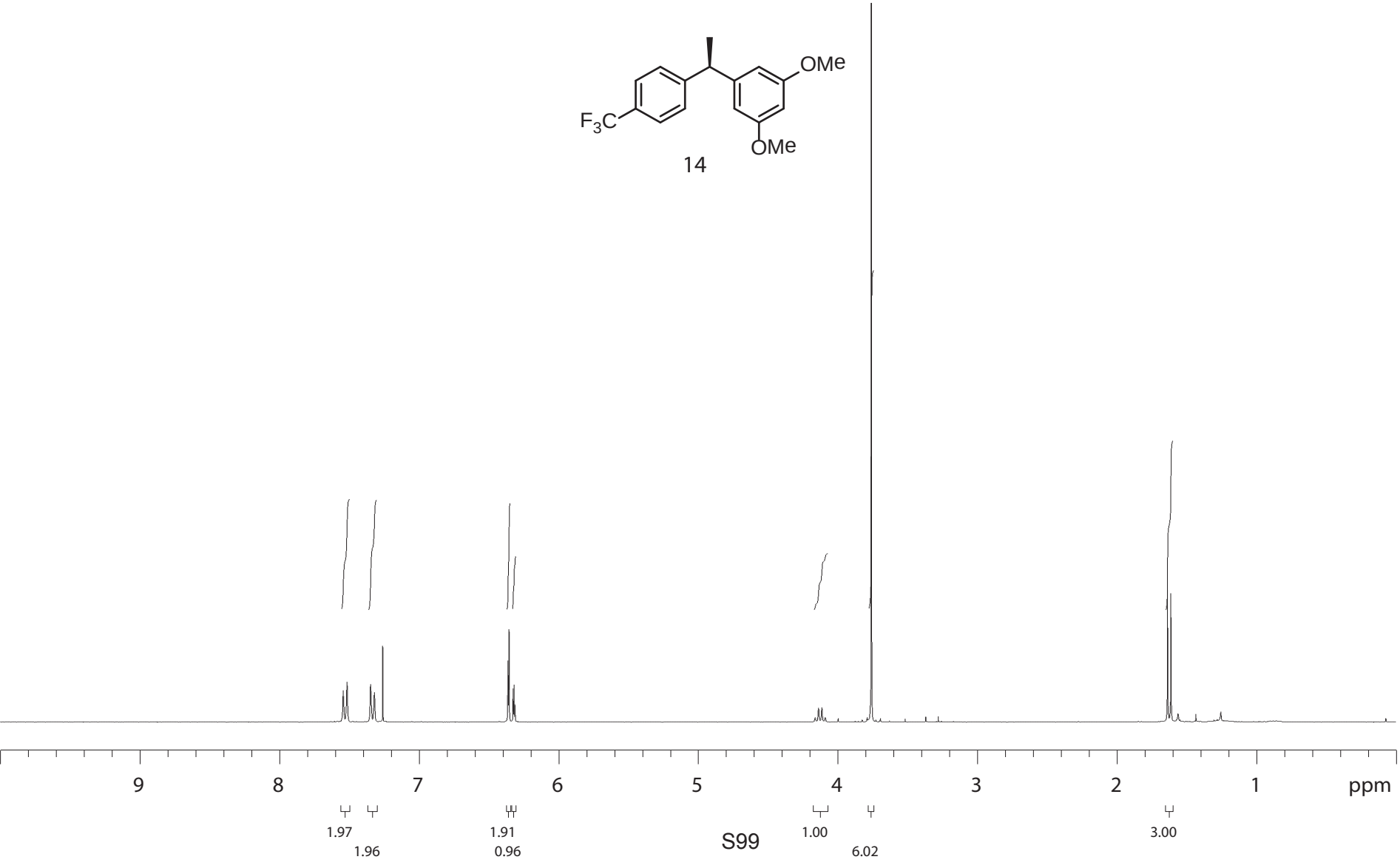
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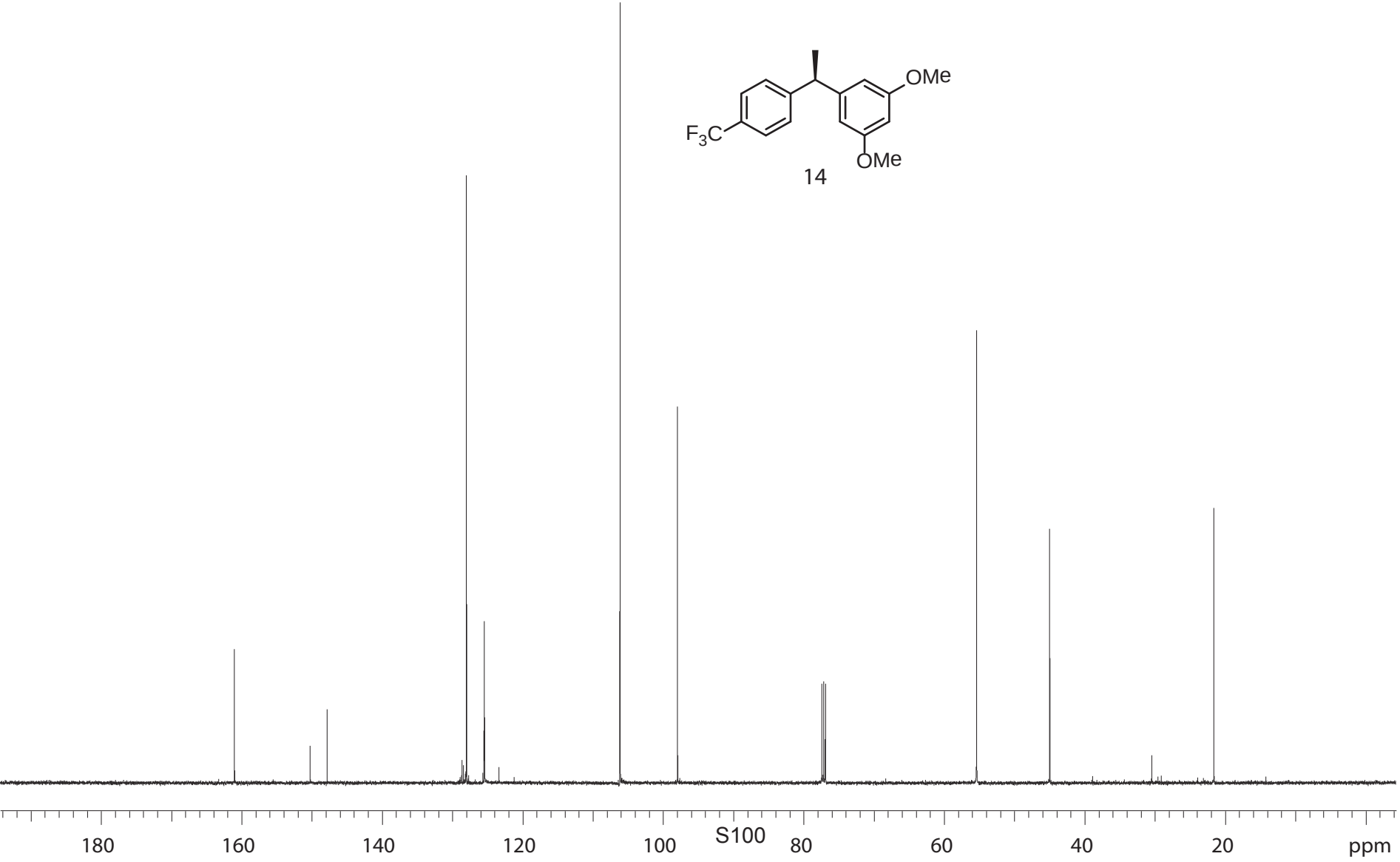
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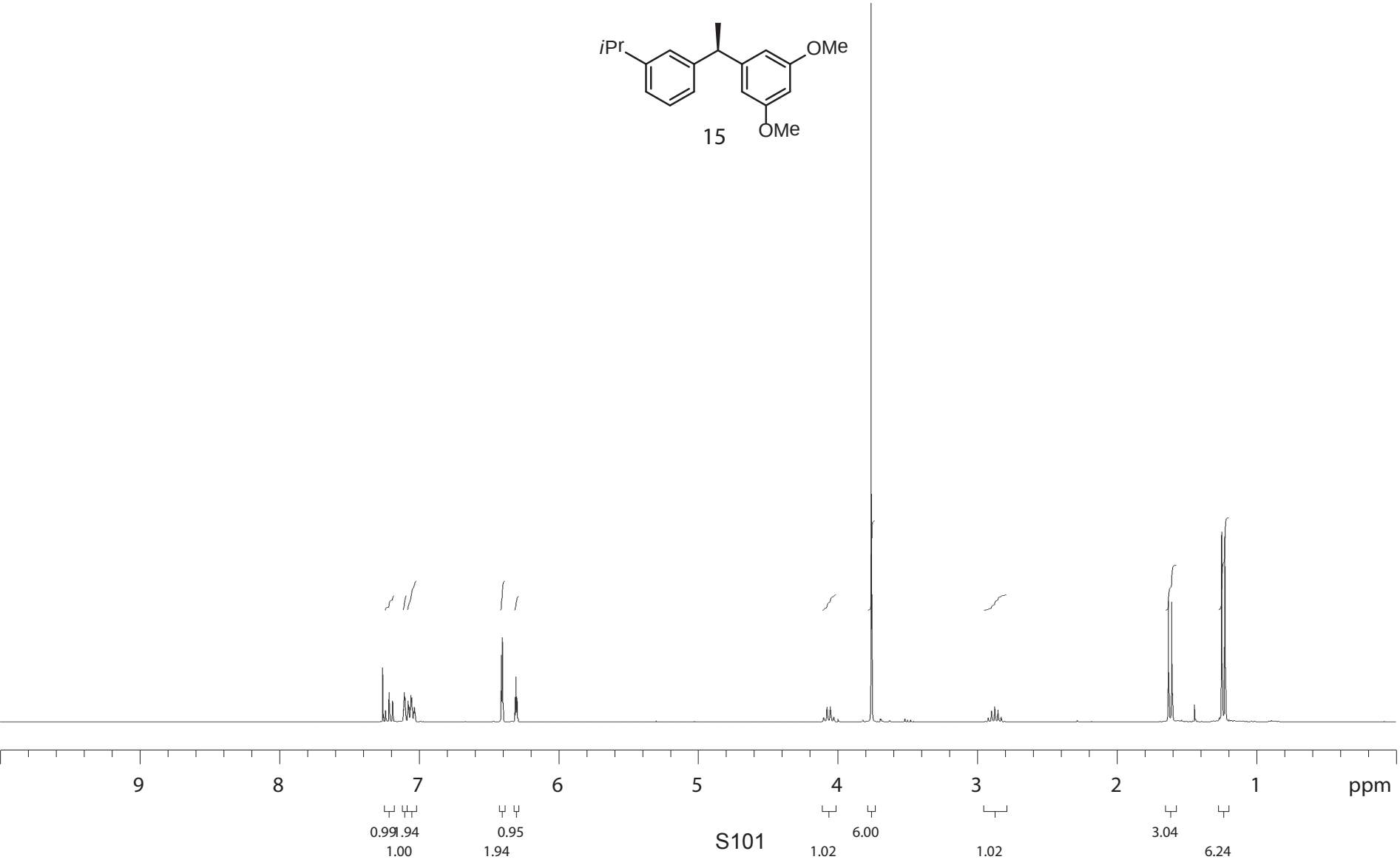
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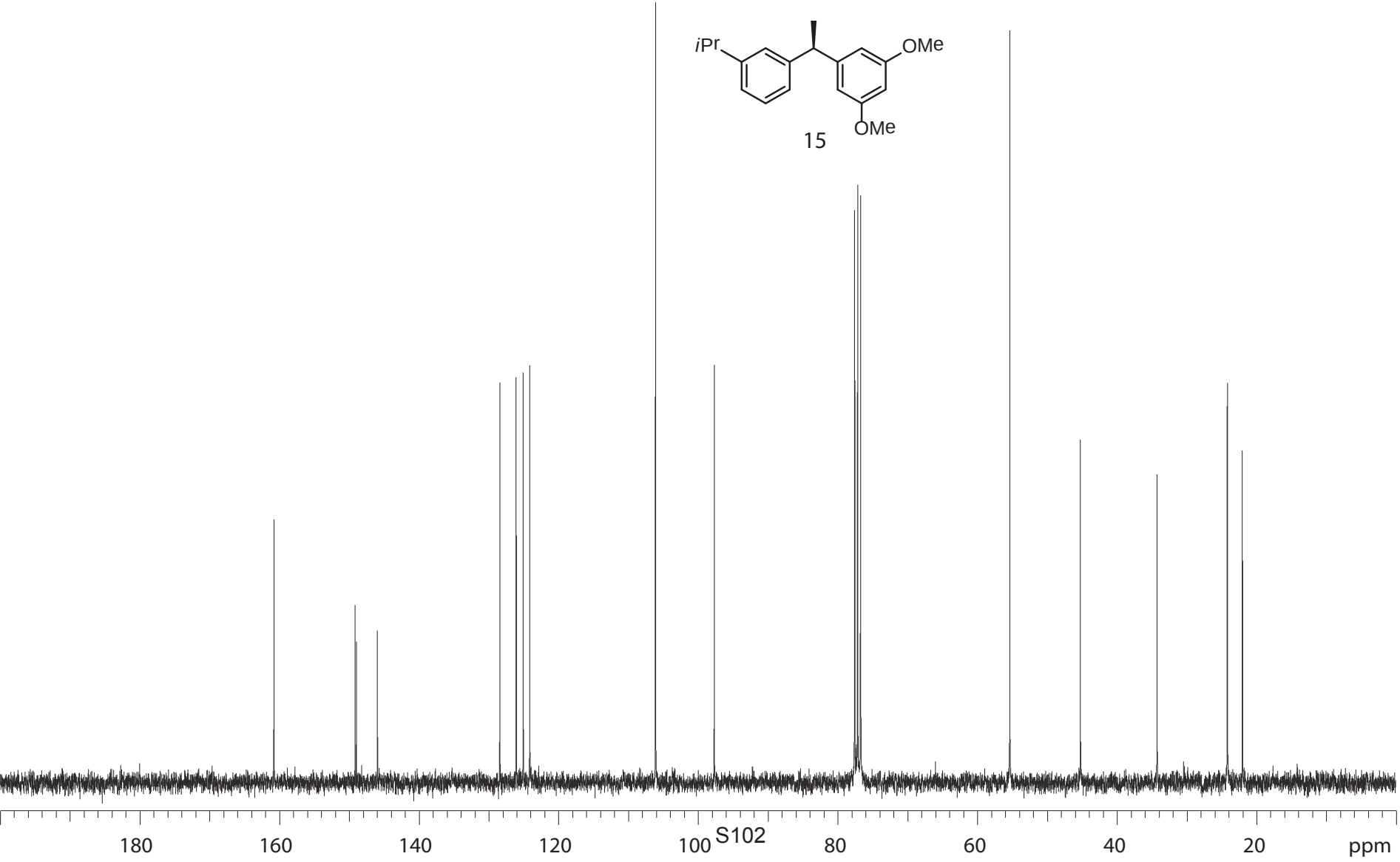
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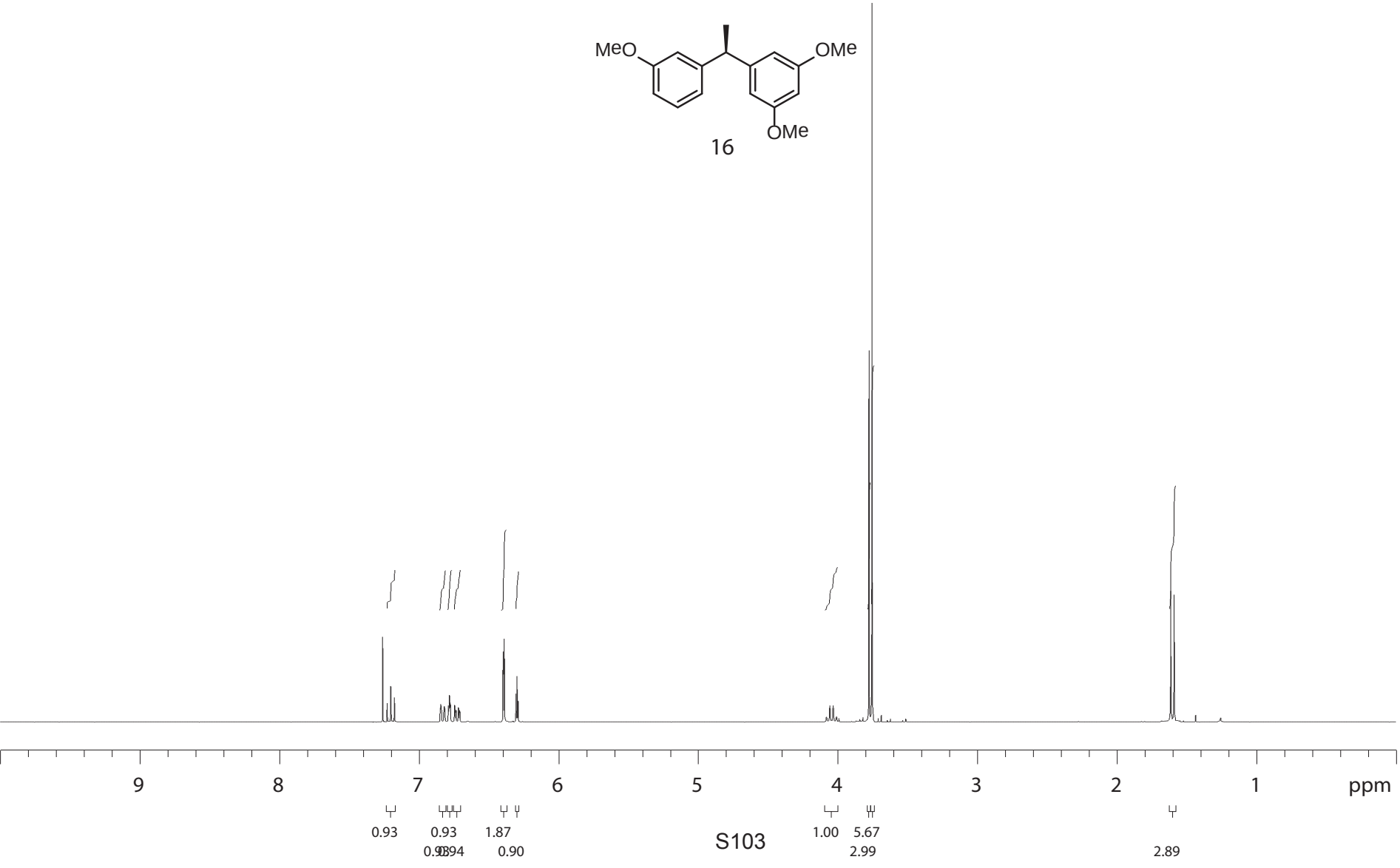
ppm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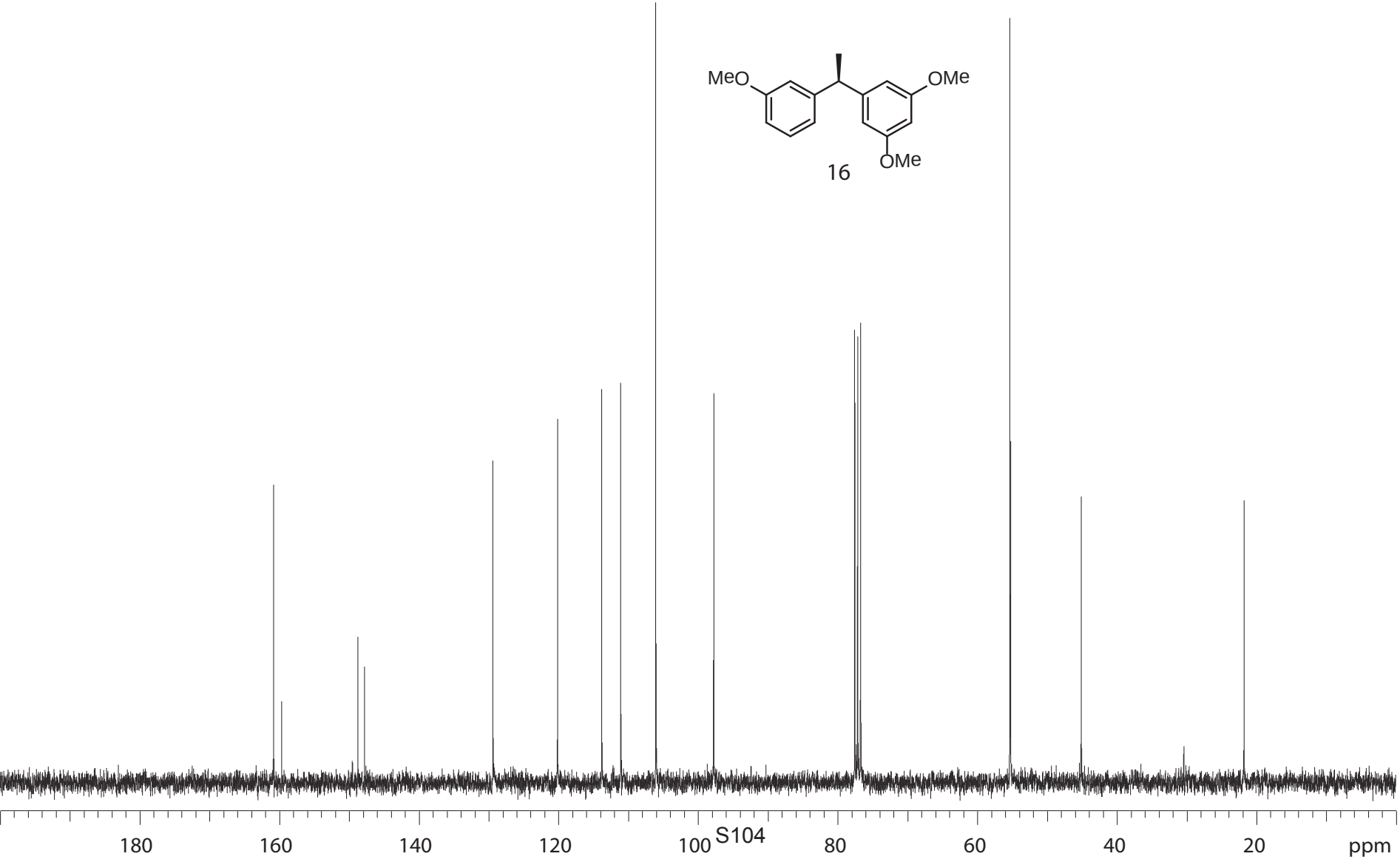
MeO
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OMe
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ppm