Electronic Supplementary Material (ESI) for Chemical Communications.

Supporting Information

Propargylic Cation-Induced Intermolecular Electrophilic Addition / Semipinacol Rearrangement

Hui Shao, Xiao-Ming Zhang, Shao-Hua Wang, Fu-Min Zhang, Yong-Qiang Tu,* Chao Yang

State Key Laboratory of Applied Organic Chemistry & College of Chemistry and Chemical Engineering, Lanzhou University, Lanzhou 730000, P. R. China

(E-mail: tuyq@lzu.edu.cn)

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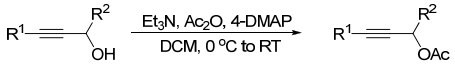
General Information:

All solvents were purified and dried by standard techniques, and distilled prior to use. All reactions under standard conditions were carried out under argon, dry atmosphere and monitored by thin-layer chromatography (TLC) on gel F_{254} plates. All products were purified through silica gel (200~300 mesh) or neutral alumina (200~300 mesh) column chromatography with light petroleum ether (bp. 60~90 ºC), ethyl acetate and dichloromethane as eluent. ^{1}H and ^{13}C NMR spectra were recorded in $CDCl_3$ solution or C_6D_6 solution on Bruker AM-400 MHz. The spectral data were reported in ppm and calibrated by using residual undeuterated solvent $CHCl_3$ (7.27 ppm), C_6H_6 (7.16 ppm), or tetramethylsilane (0.00 ppm) as internal reference for ^{1}H NMR and the deuterated solvent $CDCl_3$ (77.0 ppm) or C_6D_6 (128.4 ppm) as internal standard for ^{13}C NMR. The MS data were obtained with SHIMADZU GCMS-QP2010 SE by means of EI (70 eV) technique and signals were given in m/z with relative intensity (%) in brackets. IR spectra were recorded on Nicolet FT-170SX spectrometer. High-resolution mass spectral analysis (HRMS) data were determined on a Bruker Daltonics APEXII 47e FT-ICR spectrometer. The X-ray single-crystal determination was performed on an Agilent SuperNova Eos diffractometer. The substrates **S-1, S-2, S-3, S-7, S-8, S-10, S-11, S-12, 1a, 5a** are known compounds, and **S-9** is commercial available.

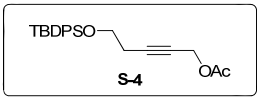
1. Experimental details for new compounds

1.1 General procedure A: for the preparation of a series of propargyl acetates:



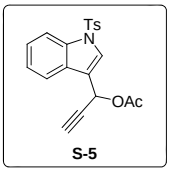
Substrate	R^1	R^2	Product	Yield (%)
S-1		H	**S-4**	90
S-2	H		**S-5**	85

To a stirred solution of the propargylic alcohol **S-1**[1] (3.38 g, 10.0 mmol) in DCM (35 mL) was successively added Et_3N (2.1 mL, 15.1 mmol), Ac_2O (1.42 mL, 15.0 mmol), and 4-DMAP (122 mg, 1.0mmol) at 0 ºC. The mixture was allowed to warm to room temperature and stirred for 2 h. After fully consumption of substrate **S-1**, the reaction was quenched with saturated aqueous $NaHCO_3$ and extracted with ethyl acetate (2 x 50 mL). The combined organic layer was washed with brine, dried over Na_2SO_4 and concentrated under vacuum. The crude product was purified by column chromatography (EtOAc: petroleum ether = 1:80) to give product **S-4** (3.42 g, 9.0 mmol, 90 %) as a colorless oil.



5-(*tert*-butyldiphenylsilyloxy)pent-2-ynyl acetate (**S-4**):

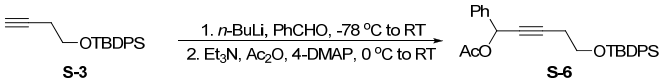
IR (neat) 2933, 2858, 2240, 1747, 1590, 1379, 1225, 1110, 823, 740, 705, 612 cm^{-1}; **^{1}H NMR** (400 MH_Z, $CDCl_3$) δ 7.76~7.74 (m, 4 H), 7.49~7.41 (m, 6 H), 4.69 (t, *J* = 2.0 Hz, 2 H), 3.84 (t, *J* = 7.0 Hz, 2 H), 2.57~2.54 (m, 2 H), 2.10 (s, 3 H), 1.13 (s, 9 H); **^{13}C NMR** (100 MH_Z, $CDCl_3$) δ 170.0, 135.5, 133.4, 129.6, 127.6, 84.4, 75.1, 62.1, 52.5, 26.7, 22.8, 20.6, 19.1; **EI MS** m/z (%) = 323 (22), 281 (57), 241 (90), 199 (100), 181 (61); **HRMS ESI** Calcd for $C_{23}H_{28}O_3Si$ $[M+NH_4]^+$: 398.2146, Found: 398.2143, Error: 0.8 ppm.



S-5

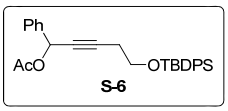
1-(1-tosyl-1*H*-indol-3-yl)prop-2-yn-1-yl acetate (**S-5**):

According to the general procedure A: **S-5** (85 % yield) was obtained as a yellow soild from **S-2**[2]. **mp**: 120-122 ºC; **IR** (neat) 3290, 3058, 2929, 2127, 1740, 1597, 1447, 1371, 1224, 1174, 976, 814, 746, 584 cm^{-1}; **^{1}H NMR** (400 MH_Z, $CDCl_3$) δ 7.97 (d, *J* = 8.0 Hz, 1 H), 7.82 (s, 1H), 7.77 (d, *J* = 8.0 Hz, 2H), 7.66 (d, *J* = 8.0 Hz, 1H), 7.33 (dd, *J* = 7.6 and 7.6 Hz, 1H), 7.25 (dd, *J* = 7.6 and 7.6 Hz, 1H), 7.16 (d, *J* = 8.0 Hz, 2 H), 6.70 (s, 1 H), 2.68 (s, 1 H), 2.26 (s, 3 H), 2.06 (s, 3 H); **^{13}C NMR** (100 MH_Z, $CDCl_3$) δ 169.4, 145.1, 135.1, 134.8, 129.8, 127.9, 126.8, 125.8, 125.1, 123.4, 120.0, 117.9, 113.5, 79.0, 74.8, 58.1, 21.3, 20.7; **EI MS** m/z (%) = 367 (M^+, 14), 307 (37), 155 (44), 91 (100), 65 (19); **HRMS ESI** Calcd for $C_{20}H_{17}NO_4S$ $[M+Na]^+$: 390.0770, Found: 390.0782, Error: 3.1 ppm.



S-3 **S-6**

Substrate **S-3**[3] (981 mg, 3.2 mmol) was dissolved in THF (15 mL) under argon at room temperature. The solution was cooled to -78 ºC and then *n*-BuLi (2.5 M in hexane, 1.4 mL, 3.5 mmol) was solwly added. The mixture was allowed to warm to room temperature and stirred for another 30 min. After the mixture was cooled to -78 ºC, benzaldehyde (0.36 mL, 3.5 mmol) was added and the mixture was stirred for an additional 2 h. Then the reaction was quenched with saturated aqueous NH_4Cl and extracted with ethyl acetate (2 x 40 mL). The combined organic layer was washed with brine, dried over Na_2SO_4 and concentrated under vacuum. Without purification, the crude product was dissolved in DCM (20 mL) at 0 ºC. Then Et_3N (0.65 mL, 4.7 mmol), Ac_2O (0.44 mL, 4.7 mmol), and 4-DMAP (39 mg, 0.32 mmol) were successively added to the solution. The cool bath was then removed, and the mixture was stirred at room temperature for 2 h. After fully consumption of substrate **S-3**, the reaction was quenched with saturated aqueous $NaHCO_3$ and extracted with ethyl acetate (2 x 50 mL). The combined organic layer was washed with brine, dried over Na_2SO_4 and concentrated under vacuum. The crude product was purified by column chromatography (EtOAc: petroleum ether = 1:80) to give product **S-6** (1.0 g, 2.2 mmol, 68 % yield of two steps) as a colorless oil.

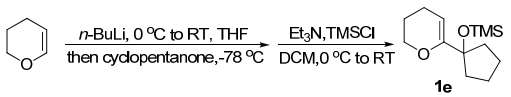


S-6

5-(*tert*-butyldiphenylsilyloxy)-1-phenylpent-2-ynyl acetate (**S-6**):

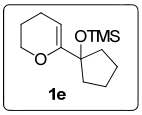
IR (neat) 3070, 2956, 2933, 2858, 2239, 1742, 1428, 1369, 1226, 1111, 823, 739, 703, 613 cm^{-1}; **^{1}H NMR** (400 MH_Z, $CDCl_3$) δ 7.91 (d, *J* = 6.0 Hz, 4 H), 7.74 (d, *J* = 6.8 Hz, 2 H), 7.55~7.44 (m, 9 H), 6.75 (s, 1 H), 4.00 (t, *J* = 6.2 Hz, 2 H), 2.72 (t, *J* = 6.2 Hz, 2 H), 2.16 (s, 3 H), 1.30 (s, 9 H); **^{13}C NMR** (100 MH_Z, $CDCl_3$) δ 169.2, 137.4, 135.3, 133.2, 129.5, 128.4, 128.3, 127.5, 127.4, 85.1, 77.8, 65.6, 61.8, 26.6, 22.8, 20.6, 18.9; **EI MS** m/z (%) = 399 (1), 357 (12), 319 (20), 199 (17), 141 (100); **HRMS ESI** Calcd for $C_{29}H_{32}O_3Si$ $[M+NH_4]^+$: 474.2459, Found: 474.2468, Error: 1.9 ppm.

1.2 General procedure B: for the preparation of a series of allylic silylethers **1b-1g**:



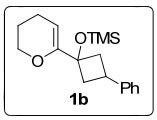
1e

To a stirred solution of 3, 4-dihydro-2*H*-pyran (4.6 mL, 50.0 mmol) in dry THF (60 mL) was slowly added *n*-BuLi (2.5 M in hexane, 5 mL, 12.5 mmol) at 0 ºC. Then the mixture was allowed to warm to room temperature. After stirring at the same temperature for 4 h, the mixture was cooled to -78 ºC and cyclopentanone (1.05 g, 12.5 mmol) in THF (20 mL) was added. The resulting solution was stirred at the same temperature for 0.5 h, then quenched with saturated aqueous NH_4Cl and extracted with ethyl acetate (2 x 150 mL). The combined organic layer was washed with water and brine, dried over Na_2SO_4 and concentrated under vacuum. Without purification, the crude product was dissolved in DCM (20 mL) at 0 ºC, then Et_3N (3.5 mL, 25.0 mmol) and TMSCl (2.4 mL, 18.7 mmol) were successively added to this solution. The mixture was allowed to warm to room temperature and stirred overnight. After fully consumption of the substrate, the reaction was quenched with saturated aqueous $NaHCO_3$ and extracted with ethyl acetate (2 x 60 mL). The combined organic layer was washed with brine, dried over Na_2SO_4 and concentrated under vacuum. The crude product was purified by flash column chromatography (EtOAc: petroleum ether = 1:200) to give product **1e** (1.68 g, 7.0 mmol, 56 % yield, two steps based on cyclopentanone) as a colorless oil.



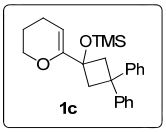
6-(1-trimethylsilyloxycyclopentyl)-3,4-dihydro-2*H*-pyran (**1e**):

IR (neat) 2956, 2872, 1669, 1450, 1249, 1067, 869, 840, 753 cm^{-1}; **^{1}H NMR** (400 MH_Z, $CDCl_3$) δ 4.80 (dd, *J* = 3.6 and 4.0 Hz, 1 H), 3.99 (dd, *J* = 5.2 and 5.2 Hz, 2 H), 2.04 (dd, *J* = 6.4 and 10.0 Hz, 2 H), 1.85~1.72 (m, 8 H), 1.62~1.60 (m, 2 H), 0.11 (s, 9 H); **^{13}C NMR** (100 MH_Z, $CDCl_3$) δ 156.9, 94.4, 84.6, 66.0, 38.5, 23.2, 22.3, 20.1, 2.0; **EI MS** m/z (%) = 240 (M^+, 1), 215 (19), 159 (43), 85 (40), 73 (100); **HRMS ESI** Calcd for $C_{13}H_{24}O_2Si$ $[M+H]^+$: 241.1618, Found: 241.1630, Error: 5.0 ppm.



6-(1-trimethylsilyloxy-3-phenylcyclobutyl)-3,4-dihydro-2*H*-pyran (**1b**):

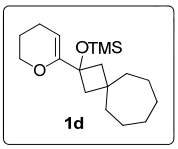
According to the general procedure B: **1b** (62 % yield, two steps) was obtained as a colorless oil from 3-phenylcyclobutanone[4]. **IR** (neat) 2950, 2870, 1941, 1868, 1801, 1667, 1603, 1495, 1246, 1119, 1090, 840, 753, 698 cm^{-1}; **^{1}H NMR** (400 MH_Z, $CDCl_3$) δ 7.07~6.91 (m, 5 H), 4.78 (dd, *J* = 3.6 and 3.6 Hz, 1 H), 3.83 (dd, *J* = 4.8 and 5.2 Hz, 2 H), 2.87~2.78 (m, 1 H), 2.62 (ddd, *J* = 2.8, 8.4 and 16.8 Hz, 2 H), 2.04 (ddd, *J* = 2.4, 9.2 and 19.2 Hz, 2 H), 1.88 (dd, *J* = 6.4 and 10.0 Hz, 2 H), 1.62~1.56 (m, 2 H), -0.06 (s, 9 H); **^{13}C NMR** (100 MH_Z, $CDCl_3$) δ 155.1, 144.8, 128.0, 126.3, 125.6, 95.2, 72.2, 65.8, 43.0, 31.2, 21.8, 20.0, 1.4; **EI MS** m/z (%) = 302 (M^+, 31), 198 (100), 155 (49), 141 (39), 73 (58); **HRMS ESI** Calcd for $C_{18}H_{26}O_2Si$ $[M+H]^+$: 303.1775, Found: 303.1771, Error: 1.3 ppm.



6-(1-trimethylsilyloxy-3,3-diphenylcyclobutyl)-3,4-dihydro-2*H*-pyran (**1c**):

According to the general procedure B: **1c** (55 % yield of two steps) was obtained as a colorless oil from 3,3-diphenylcyclobutanone[4]; **IR** (neat) 2948, 2875, 1948, 1876, 1821, 1709, 1599, 1493, 1250, 1083, 840, 753, 702 cm^{-1}; **^{1}H NMR** (400 MH_Z, $CDCl_3$) δ 7.49~7.37 (m, 8 H), 7.27~7.21 (m, 2 H), 4.76 (dd, *J* = 3.6 and 4.0 Hz, 1 H), 4.02 (dd, *J* = 4.8 and 5.2 Hz, 2 H), 3.57 (d, *J* = 12.6 Hz, 2 H), 3.08 (d, *J* = 12.6 Hz, 2 H), 1.90 (dd, *J* = 6.0 and 10.0 Hz, 2 H), 1.75~1.69 (m, 2 H), 0.23 (s, 9 H); **^{13}C NMR** (100 MH_Z, $CDCl_3$) δ 154.5, 151.0, 148.2, 128.2, 127.8,

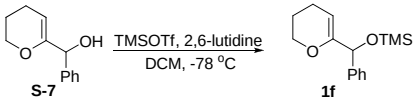
126.6, 125.9, 125.2, 125.1, 97.9, 72.7, 66.0, 47.5, 43.4, 21.7, 20.0, 1.5; **EI MS** m/z (%) = 378 (M^+, 16), 198 (100), 155 (35), 141 (38), 73 (55); **HRMS ESI** Calcd for $C_{24}H_{30}O_2Si$ $[M+H]^+$: 379.2088, Found: 379.2086, Error: 0.5 ppm.



6-(2-trimethylsilyloxyspiro[3.6]decan-2-yl)-3,4-dihydro-2*H*-pyran (**1d**):

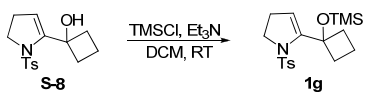
According to the general procedure B: **1d** (56 % yield of two steps) was obtained as a colorless oil from spiro[3.6]decan-2-one[5]; **IR** (neat) 2926, 2852, 1667, 1460, 1248, 1153, 1067, 840,754 cm^{-1}; **^{1}H NMR** (400 MH_Z, $CDCl_3$) δ 4.75 (dd, *J* = 3.6 and 3.6 Hz, 1 H)，3.95 (dd, *J* = 4.8 and 5.2 Hz, 2 H), 2.23 (d, *J* = 12.8 Hz, 2 H), 2.01 (dd, *J* = 6.0 and 10.0 Hz, 2 H), 1.84 (d, *J* = 12.8 Hz, 2 H), 1.75~1.65 (m, 4 H), 1.52~1.49 (m, 2 H), 1.43~1.34 (m, 8 H), 0.05 (s, 9 H); **^{13}C NMR** (100 MH_Z, $CDCl_3$) δ 157.1, 95.0, 72.2, 65.8, 46.3, 43.3, 40.6, 33.6, 27.5, 27.4, 23.0, 22.8, 21.9, 19.9, 1.5; **EI MS** m/z (%) = 308 (M^+, 18), 198 (100), 155 (30), 141 (33), 73 (44); **HRMS ESI** Calcd for $C_{18}H_{32}O_2Si$ $[M+K]^+$: 347.1803, Found: 347.1813, Error: 2.9 ppm.

6-(1-trimethylsilyloxybenzyl)-3,4-dihydro-2*H*-pyran (**1f**):



Substrate **S-7**[6] (500 mg, 2.63 mmol) was dissolved in DCM (8 mL) at room temperature. The solution was cooled to -78 ºC. Then 2, 6-lutidine (0.46 mL, 3.95 mmol) and TMSOTf (0.52 mL, 2.88 mmol) were successively added. After stirring at the same temperature for 0.5 h, the mixture was quenched with saturated aqueous $NaHCO_3$ and extracted with ethyl acetate (2 x 50 mL). The combined organic layer was washed with brine, dried over Na_2SO_4 and concentrated under vacuum. The crude product was purified by flash column chromatography (EtOAc: petroleum ether = 1:200) to give product **1f** (413 mg, 1.58 mmol, 60 %) as a colorless oil. **IR** (neat) 2955, 2929, 2870, 2850, 1678, 1493, 1452, 1251, 1159, 1098, 1066, 881, 840, 708 cm^{-1}; **^{1}H NMR** (400 MH_Z, $CDCl_3$) δ 7.13~6.94 (m, 5 H), 4.73 (s, 1 H), 4.58 (dd, *J* = 3.6 and 4.0 Hz, 1 H), 3.66 (ddd, *J* = 4.8, 10.4 and 22.4 Hz, 2 H), 1.77 (dd, *J* = 6.0 and 10.4 Hz, 2 H), 1.52~1.46 (m, 2 H), -0.15 (s, 9 H); **^{13}C NMR** (100 MH_Z, $CDCl_3$) δ 155.2, 142.2, 127.9, 127.1, 126.4, 97.3, 74.9, 66.3, 22.3, 20.0, 0.1; **EI MS** m/z (%) = 262 (M^+,56), 219 (41), 205 (17), 185 (28), 73 (100); **HRMS ESI** Calcd for $C_{15}H_{22}NO_2Si$ $[M+H]^+$: 263.1462, Found: 263.1466, Error: 1.5 ppm.

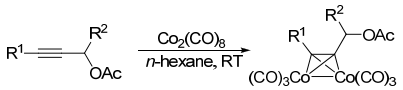
5-(1-trimethylsilyloxy-(cyclobutyl))-1-tosyl-2,3-dihydro-1*H*-pyrrole (**1g**)

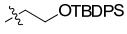
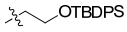


To a stirred solution of substrate **S-8**[7] (100 mg, 0.341 mmol) in DCM (2.5 mL) was successively added Et_3N (0.095 mL, 0.68 mmol) and TMSCl (0.064 mL, 0.511 mmol) at room temperature. After stirring for an additional 27 h, the mixture was quenched with saturated aqueous $NaHCO_3$ and extracted with ethyl acetate (2 x 30 mL). The combined organic layer was washed with brine, dried over Na_2SO_4 and concentrated under vacuum. The crude product was purified by flash column chromatography (EtOAc: petroleum ether = 1:30) to give product **1g** (71 mg, 0.195 mmol, 57 % yield, 80 % yield based on consumed starting material) as a colorless oil. **IR** (neat) 2953, 1633,

1356, 1250, 1166, 1142, 1092, 992, 839 cm^{-1}; **^{1}H NMR** (400 MH_Z, C_6D_6+CCl_4) δ 7.71 (d, *J* = 8.0 Hz, 2 H), 7.03 (d, *J* = 8.0 Hz, 2 H), 5.17 (brs, 1 H), 3.59 (dd, *J* = 8.4 and 8.4 Hz, 2 H), 2.47 (dd, *J* = 8.4 and 8.4 Hz, 2 H), 2.28 (dd, *J* = 9.6 and 20.4 Hz, 2 H), 2.21 (s, 3 H), 1.84 (dd, *J* = 6.0 and 8.4 Hz, 2 H), 1.70~1.63 (m, 1 H), 1.41 (ddd, *J* = 8.4, 8.8 and 28.0 Hz, 1 H), 0.10 (s, 9 H); **^{13}C NMR** (100 MH_Z, C_6D_6+CCl_4) δ 150.7, 142.9, 138.0, 129.6, 128.7, 115.1, 96.9 (CCl_4), 75.9, 52.4, 38.6, 28.1, 22.1, 14.2, 3.1; **EI MS** m/z (%) = 365 (M^+, 1), 258 (22), 210 (100), 91 (18), 73 (62); **HRMS ESI** Calcd for $C_{18}H_{27}NO_3SSi$ $[M+H]^+$: 366.1554, Found: 366.1565, Error: 3.0 ppm.

1.3 General procedure C: for the preparation of a series of hexacarbonyldicobalt alkyne complexes:

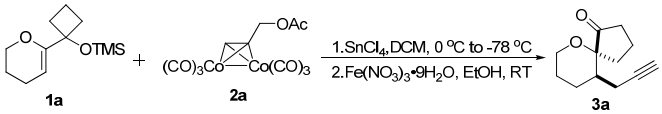


Entry	Substrate	R^1	R^2
1	**S-4**		H
2[a]	**S-5**	H	
3	**S-6**		Ph
4	**S-9**	H	H
5	**S-10**[8]	Ph	H
6	**S-11**[9]	H	Ph

[a] Reaction solvent was DCM.

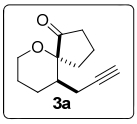
To a stirred solution of alkyne (0.31 mmol) in *n*-hexane (5 mL) was added octacarbonyldicobalt (116 mg, 0.34 mmol). The mixture was stirred at room temperature for 3-4 h and then filtered through a pad of neutral alumina (Et_2O as eluent). Without purification, the crude product was concentrated under vacuum immediately for subsequent reaction.

1.4 General procedure D: for the Nicholas/semipinocal reaction of dihydropyran-type and dihydropyrrole-type allylic silylethers **1a-g**:



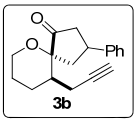
Cobalt complex **2a** (crude, 93 mg, about 0.24 mmol) was dissolved in DCM (1.6 mL), followed by addtion of $SnCl_4$ (1 M in DCM, 0.23 mL, 0.23 mmol) at 0 ºC. After stirring at the same temperature for 1.5 h, the mixture was cooled to -78 ºC and **1a**[10] (50 mg, 0.22 mmol) in DCM (2 mL) was added. The resulting mixture was allowed to stir for an additional 10 min and filtered through a plug of silica gel (DCM: EtOAc = 1:1, 30 mL). The filtrate was concentrated under vacuum. The crude product was purified by flash column chromatography (EtOAc: petroleum ether = 1:100) to give cobalt complex intermediate. Then cobalt complex was immediately dissolved in ethanol (5 mL), and $Fe(NO_3)_3·9H_2O$ (404 mg, 1.0 mmol) was added to the solution at room temperature. After stirring at the same temperature for 2-3 h, the reaction was quenched with water and extracted with ethyl acetate (2 x 30 mL). The combined organic layer was washed with water and brine, dried over Na_2SO_4 and concentrated under vacuum.

The crude product was purified by flash column chromatography (EtOAc: petroleum ether = 1:50) to give product **3a** (30 mg, 0.156 mmol, 71 % yield of two steps) as a white soild.



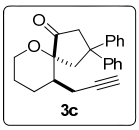
10-(prop-2-ynyl)-6-oxaspiro[4.5]decan-1-one (**3a**):

mp: 36-38 ºC; **IR** (neat) 3291, 2949, 2873, 2118, 1735, 1157, 1084, 638 cm^{-1}; **^{1}H NMR** (400 MH_Z, $CDCl_3$) δ 3.69~3.58 (m, 2 H), 2.43~2.36 (m, 1 H), 2.27~2.20 (m, 2 H), 2.16~1.77 (m, 9 H), 1.68~1.54 (m, 2 H); **^{13}C NMR** (100 MH_Z, $CDCl_3$) δ 214.8, 82.7, 80.1, 69.7, 63.3, 37.9, 37.5, 35.6, 24.9, 24.3, 20.3, 17.6; **EI MS** m/z (%) = 192 (M^+, 7), 135 (93), 121 (100), 93 (63), 79 (90); **HRMS ESI** Calcd for $C_{12}H_{16}O_2$ $[M+H]^+$: 193.1223, Found: 193.1227, Error: 2.1 ppm.



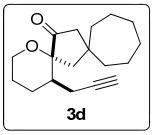
3-phenyl-10-(prop-2-ynyl)-6-oxaspiro[4.5]decan-1-one (**3b**):

According to the general procedure D: **3b** (44 mg, 0.164 mmol, 75 % yield of two steps) was obtained as a white soild from **1b** (67 mg, 0.22 mmol). **mp**: 59-61 ºC; **IR** (neat) 3294, 2929, 2872, 2116, 1734, 1544, 1224, 1073, 755, 700, 643 cm^{-1}; **^{1}H NMR** (400 MH_Z, $CDCl_3$) δ 7.34~7.31 (m, 2 H), 7.24~7.23 (m, 3 H), 3.78~3.76 (m, 1 H), 3.71~3.60 (m, 2 H), 2.83 (ddd, *J* = 2.4, 7.6 and 18.8 Hz, 1 H), 2.38~2.17 (m, 4 H), 2.14~2.07 (m, 1 H), 2.01~1.88 (m, 4 H), 1.68~1.64 (m, 2 H); **^{13}C NMR** (100 MH_Z, $CDCl_3$) δ 212.8, 143.1, 128.6, 126.7, 126.6, 82.5, 81.2, 70.0, 63.3, 46.1, 44.1, 38.2, 36.9, 25.8, 24.8, 21.1; **EI MS** m/z (%) = 268 (M^+, 17), 135 (100), 121 (45), 93 (36), 79 (49); **HRMS ESI** Calcd for $C_{18}H_{20}O_2$ $[M+Na]^+$: 291.1356, Found: 291.1353, Error: 1.0 ppm.



3,3-diphenyl-10-(prop-2-ynyl)-6-oxaspiro[4.5]decan-1-one (**3c**):

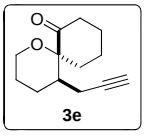
According to the general procedure D: **3c** (57 mg, 0.166 mmol, 75 % yield of two steps) was obtained as a colorless oil from **1c** (83 mg, 0.22 mmol). **IR** (neat) 3301, 2944, 2873, 2117, 1736, 1599, 1446, 1083, 1067, 737, 710, 642 cm^{-1}; **^{1}H NMR** (400 MH_Z, $CDCl_3$) δ 7.30~7.22 (m, 2 H), 7.21~7.10 (m, 8 H), 3.74~3.68 (m, 1 H), 3.50~3.48 (m, 1 H), 3.34 (d, *J* = 17.6 Hz, 1 H), 3.04~2.92 (m, 3 H), 2.06~1.88 (m, 5 H), 1.77~1.70 (m, 1 H), 1.64~1.52 (m, 2 H); **^{13}C NMR** (100 MH_Z, $CDCl_3$) δ 213.1, 148.3, 147.6, 128.6, 128.1, 126.8, 126.5, 126.4, 125.9, 82.4, 80.4, 69.9, 62.9, 51.9, 48.9, 47.8, 39.1, 24.2, 24.0, 19.8 ; **EI MS** m/z (%) = 344 (M^+, 6), 305 (7), 149 (34), 135 (100), 79 (54); **HRMS ESI** Calcd for $C_{24}H_{24}O_2$ $[M+H]^+$: 345.1849, Found: 345.1861, Error: 3.5 ppm.



3,3-cycloheptyl-10-(prop-2-ynyl)-6-oxaspiro[4.5]decan-1-one (**3d**):

According to the general procedure D: **3d** (39 mg, 0.142 mmol, 65 % yield of two steps) was obtained as a white soild from **1d** (68 mg, 0.22 mmol). **mp**: 49-51 ºC; **IR** (neat) 3307, 3291, 2925, 2854, 2118, 1731, 1462, 1446, 1086, 1071, 969, 632 cm^{-1}; **^{1}H NMR** (400 MH_Z, $CDCl_3$) δ 3.76 (ddd, *J* = 2.8, 10.8 and 11.6 Hz, 1 H), 3.67~3.62 (m, 1 H), 2.45~2.40 (m, 1 H), 2.26 (ddd, *J* = 2.8, 4.0 and 16.8 Hz, 1 H), 2.09~2.02 (m, 3 H), 1.98~1.84 (m, 4 H), 1.80~1.72 (m, 2 H), 1.69~1.45 (m, 13 H); **^{13}C NMR** (100 MH_Z, $CDCl_3$) δ 215.9, 82.5, 81.2, 69.8, 63.0, 53.8, 48.6, 43.3, 41.4,

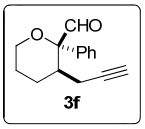
39.4, 39.1, 29.1, 28.8, 24.8, 24.2, 23.4, 22.9, 20.5 ; **EI MS** m/z (%) = 274 (M^+, 12), 231 (26), 135 (100), 121 (55), 79 (50); **HRMS ESI** Calcd for $C_{18}H_{26}O_2$ $[M+H]^+$: 275.2006, Found: 275.2007, Error: 0.4 ppm.



3e

5-(prop-2-ynyl)-1-oxaspiro[5.5]undecan-7-one (**3e**):

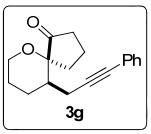
According to the general procedure D: **3e** (26 mg, 0.126 mmol, 57 % yield of two steps) was obtained as a white soild from **1e** (53 mg, 0.22 mmol). **mp**: 41-43 ºC; **IR** (neat) 3295, 2944, 2862, 2116, 1713, 1451, 1434, 1087, 1073, 991, 634 cm^{-1}; **^{1}H NMR** (400 MH_Z, $CDCl_3$) δ 3.84~3.82 (m, 1 H), 3.31~3.24 (m, 1 H), 2.72 (ddd, *J* = 6.0, 12.4 and 12.4 Hz, 1 H), 2.53 (ddd, *J* = 2.4, 10.4 and 17.2 Hz, 1 H), 2.33 (ddd, *J* = 2.8, 3.2 and 17.2 Hz, 1 H), 2.18~2.15 (m, 1 H), 2.07~1.96 (m, 5 H), 1.87~1.82 (m, 1 H), 1.80~1.72 (m, 1 H), 1.63~1.58 (m, 5 H); **^{13}C NMR** (100 MH_Z, $CDCl_3$) δ 213.2, 83.8, 81.4, 68.9, 63.7, 42.7, 40.0, 38.4, 27.9, 25.2, 24.4, 20.2, 20.0 ; **EI MS** m/z (%) = 206 (M^+, 17), 155 (26), 147 (66), 105 (67), 75 (100); **HRMS ESI** Calcd for $C_{13}H_{18}O_2$ $[M+Na]^+$: 229.1199 , Found: 229.1200, Error: 0.4 ppm.



3f

2-phenyl-3-(prop-2-ynyl)tetrahydro-2*H*-pyran-2-carbaldehyde (**3f**):

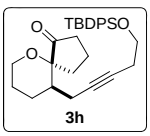
According to the general procedure D: **3f** (16 mg, 0.07 mmol, 31 % yield of two steps) was obtained as a colorless oil from **1f** (58 mg, 0.22 mmol). **IR** (neat) 3296, 2944, 2882, 2117, 1716, 1680, 1449, 1276, 1072, 761, 708, 640 cm^{-1}; **^{1}H NMR** (400 MH_Z, $CDCl_3$) δ 9.42 (s, 1 H), 7.45~7.39 (m, 4 H), 7.38~7.32 (m, 1 H), 3.82 (dd, *J* = 5.2 and 5.6 Hz, 2 H), 2.73~2.66 (m, 1 H), 2.62~2.56 (m, 1 H), 2.41~2.36 (m, 1 H), 1.99 (dd, *J* = 2.4 and 2.8 Hz, 1 H), 1.94~1.80(m, 3 H), 1.49~1.43 (m, 1 H); **^{13}C NMR** (100 MH_Z, $CDCl_3$) δ 199.4, 135.4, 129.1, 128.4, 127.1, 85.4, 82.6, 69.9, 63.9, 37.8, 22.8, 21.9, 18.1 ; **EI MS** m/z (%) = 199 (12), 123 (7), 105 (100), 91 (6), 77 (42); **HRMS ESI** Calcd for $C_{15}H_{16}O_2$ $[M+H]^+$: 229.1223, Found: 229.1234, Error: 4.8 ppm.



3g

10-(3-phenylprop-2-ynyl)-6-oxaspiro[4.5]decan-1-one (**3g**):

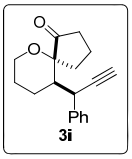
According to the general procedure D: **3g** (42 mg, 0.157 mmol, 71 % yield of two steps) was obtained as a white soild from **1a** (50 mg, 0.22 mmol). **mp**: 92-94 ºC; **IR** (neat) 2955, 2925, 2870, 2378, 1734, 1598, 1462, 1276, 1083, 1072, 1022, 756, 692 cm^{-1}; **^{1}H NMR** (400 MH_Z, $CDCl_3$) δ 7.40~7.38 (m, 2 H), 7.29~7.27 (m, 3 H), 3.74~3.64 (m, 2 H), 2.51~2.46 (m, 1 H), 2.44~2.29 (m, 3 H), 2.22~2.13 (m, 1 H), 2.10~1.96 (m, 4 H), 1.92~1.81 (m, 2 H), 1.74~1.60(m, 2 H); **^{13}C NMR** (100 MH_Z, $CDCl_3$) δ 214.9, 131.4, 128.2, 127.7, 123.7, 88.3, 82.0, 80.1, 63.3, 38.4, 37.6, 35.8, 25.1, 24.6, 21.4, 17.7; **EI MS** m/z (%) = 268 (M^+, 3), 197 (93), 191 (89), 115 (100), 55 (44); **HRMS ESI** Calcd for $C_{18}H_{20}O_2$ $[M+Na]^+$: 291.1356, Found: 291.1354, Error: 0.7 ppm.



3h

10-(5-(*tert*-butyldiphenylsilyloxy)pent-2-ynyl)-6-oxaspiro[4.5]decan-1-one (**3h**):

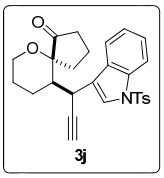
According to the general procedure D: **3h** (70 mg, 0.148 mmol, 67 % yield of two steps) was obtained as a colorless oil from **1a** (50 mg, 0.22 mmol). **IR** (neat) 2934, 2862, 2373, 1735, 1589, 1428, 1105, 1081, 821, 740, 703 cm^{-1}; **^{1}H NMR** (400 MH_Z, $CDCl_3$) δ 7.75~7.69 (m, 4 H), 7.46~7.38 (m, 6 H), 3.76 (dd, *J* = 6.8 and 7.2 Hz, 2 H), 3.70~3.61 (m, 2 H), 2.44~2.34 (m, 3 H), 2.26~2.18 (m, 2 H), 2.15~1.92 (m, 5 H), 1.86~1.77 (m, 3 H), 1.65~1.55 (m, 2 H), 1.07 (s, 9 H); **^{13}C NMR** (100 MH_Z, $CDCl_3$) δ 214.9, 135.5, 134.8, 133.6, 129.6, 129.5, 127.6, 80.1, 79.4, 78.6, 63.2, 62.7, 38.4, 37.6, 35.7, 26.7, 26.5, 25.0, 24.3, 22.9, 20.7, 19.1, 17.6; **EI MS** m/z (%) = 417 (30), 387 (75), 199 (100), 135 (35), 91 (46); **HRMS ESI** Calcd for $C_{30}H_{38}O_3Si$ $[M+Na]^+$: 497.2482, Found: 497.2493, Error: 2.2 ppm.



3i

10-(1-phenylprop-2-ynyl)-6-oxaspiro[4.5]decan-1-one (**3i**):

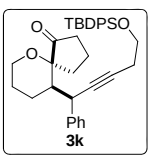
According to the general procedure D: **3i** (41 mg, 0.153 mmol, 70 % yield of two steps) was obtained as a white soild from **1a** (50 mg, 0.22 mmol). **mp**: 74-76 ºC; **IR** (neat) 3286, 2954, 2873, 2112, 1733, 1599, 1452, 1083, 1031, 765, 702, 631 cm^{-1}; **^{1}H NMR** (400 MH_Z, $CDCl_3$) δ 7.30~7.24 (m, 5 H), 3.62~3.61 (m, 2 H), 3.52 (dd, *J* = 10.8 and 10.8 Hz, 1 H), 3.09~3.01 (m, 1 H), 2.45~2.28 (m, 3 H), 2.18~2.01 (m, 2 H), 1.90~1.88 (m, 2 H), 1.74~1.65 (m, 1 H), 1.52~1.40 (m, 2 H), 1.34~1.31 (m, 1 H); **^{13}C NMR** (100 MH_Z, $CDCl_3$) δ 214.8, 140.4, 128.5, 128.4, 127.1, 86.9, 80.5, 73.3, 62.9, 43.4, 39.2, 37.4, 36.8, 25.1, 24.2, 17.8; **EI MS** m/z (%) = 268 (M^+, 6), 211 (28), 197 (42), 115 (100), 55 (43); **HRMS ESI** Calcd for $C_{18}H_{20}O_2$ $[M+H]^+$: 269.1536, Found: 269.1545, Error: 3.3 ppm.



3j

10-(1-(1-tosyl-1*H*-indol-3-yl) prop-2-ynyl)-6-oxaspiro[4.5]decan-1-one (**3j**):

According to the general procedure D: **3j** (67 mg, 0.145 mmol, 66 % yield of two steps) was obtained as a white soild from **1a** (50 mg, 0.22 mmol). **mp**: 180-182 ºC; **IR** (neat) 3292, 2955, 2925, 2870, 2113, 1732, 1597, 1447, 1372, 1174, 1121, 1086, 812, 747, 675, 577 cm^{-1}; **^{1}H NMR** (400 MH_Z, $CDCl_3$) δ 8.02 (d, *J* = 8.0 Hz, 1 H), 7.78 (d, *J* = 8.0 Hz, 2 H), 7.72 (d, *J* = 8.0 Hz, 1 H), 7.51 (s, 1 H), 7.36 (dd, *J* = 7.2 and 7.2 Hz, 1 H), 7.29 (dd, *J* = 7.2 and 7.2 Hz, 1 H), 7.23 (d, *J* = 8.0 Hz, 2 H), 3.88 (dd, *J* = 2.4 and 8.8 Hz, 1 H), 3.68~3.64 (m, 1 H), 3.55 (ddd, *J* = 2.8, 10.8 and 10.8 Hz, 1 H), 3.07~3.02 (m, 1 H), 2.47~2.37 (m, 2 H), 2.36 (s, 3 H), 2.33~2.30 (m, 2 H) , 2.14~2.10 (m, 1 H), 1.96~1.90 (m, 2 H) , 1.78~1.71 (m, 1 H), 1.51~1.45 (m, 1 H), 1.42~1.35 (m, 1 H), 1.33~1.28 (m, 1 H); **^{13}C NMR** (100 MH_Z, $CDCl_3$) δ 214.9, 144.9, 135.5, 135.1, 129.8, 129.3, 126.8, 124.8, 124.3, 123.2, 121.2, 120.4, 113.9, 85.1, 80.5, 73.2, 62.9, 41.9, 37.3, 36.7, 30.5, 25.1, 24.4, 21.5, 17.7; **EI MS** m/z (%) = 461 (M^+, 10), 308 (92), 155 (46), 91 (100), 55 (32); **HRMS ESI** Calcd for $C_{27}H_{27}NO_4S$ $[M+Na]^+$: 484.1553, Found: 484.1558, Error: 1.0 ppm.

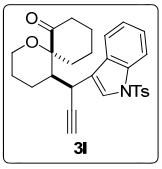


3k

10-(5-(*tert*-butyldiphenylsilyloxy)-1-phenylpent-2-ynyl)-6-oxaspiro[4.5]decan-1-one (**3k**):

According to the general procedure D: **3k** (73 mg, 0.133 mmol, 60 % yield of two steps) was obtained as a colorless oil from **1a** (50 mg, 0.22 mmol). **IR** (neat) 2955, 2933, 2858, 2363, 2343, 1735, 1428, 1110, 1083, 823,

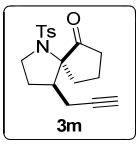
739, 703 cm^{-1}; **^{1}H NMR** (400 MH_Z, $CDCl_3$) δ 7.65 (d, *J* = 6.0 Hz, 4 H), 7.43~7.33 (m, 6 H), 7.26~7.20 (m, 5 H), 3.70 (dd, *J* = 6.8 and 7.2 Hz, 2 H), 3.62~3.47 (m, 3 H), 3.08~3.00 (m, 1 H), 2.41 (ddd, *J* = 2.0, 6.8 and 6.8 Hz, 2 H), 2.35~2.31 (m, 1 H), 2.25~2.16 (m, 1 H), 2.08~1.92 (m, 2 H), 1.82~1.64 (m, 3 H), 1.50~1.23 (m, 3 H), 1.04 (s, 9 H); **^{13}C NMR** (100 MH_Z, $CDCl_3$) δ 214.7, 141.5, 135.5, 133.5, 129.6, 128.4, 128.3, 127.7, 126.8, 84.1, 82.3, 80.3, 62.8, 62.4, 44.0, 39.8, 37.5, 37.2, 26.8, 25.3, 24.6, 23.1, 19.1, 17.9; **EI MS** m/z (%) = 493 (88), 463 (59), 199 (100), 135 (88), 91 (73); **HRMS ESI** Calcd for $C_{36}H_{42}O_3Si$ $[M+Na]^+$: 573.2795, Found: 573.2791, Error: 0.7 ppm.



3l

5-(1-(1-tosyl-1*H*-indol-3-yl) prop-2-ynyl)-1-oxaspiro[5.5]undecan-7-one (**3l**):

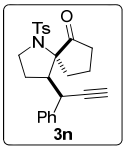
According to the general procedure D: **3l** (34 mg, 0.072 mmol, 33 % yield of two steps) was obtained as a white soild from **1e** (53 mg, 0.22 mmol). **mp**: 94-96 ºC; **IR** (neat) 3296, 2944, 2862, 2113, 1710, 1598, 1447, 1371, 1174, 744, 672 cm^{-1}; **^{1}H NMR** (400 MH_Z, $CDCl_3$) δ 7.97 (d, *J* = 8.0 Hz, 1 H), 7.87 (d, *J* = 8.0 Hz, 1 H), 7.73 (d, *J* = 8.0 Hz, 2 H), 7.54 (s, 1 H), 7.32~7.25 (m, 2 H), 7.17 (d, *J* = 8.0 Hz, 2 H), 4.28 (dd, *J* = 2.0 and 9.2 Hz, 1 H), 3.76 (d, *J* = 10.4 Hz, 1 H), 3.13 (ddd, *J* = 2.4, 8.4 and 8.8 Hz, 1 H), 2.83~2.76 (m, 2 H), 2.31 (s, 3 H), 2.28~2.23 (m, 2 H), 2.12~2.04 (m, 3 H), 1.92 (dd, *J* = 10.0, and 10.8 Hz, 1 H), 1.78~1.63 (m, 2 H), 1.43~1.34 (m, 3 H), 1.01~0.99 (m, 1 H); **^{13}C NMR** (100 MH_Z, $CDCl_3$) δ 213.9, 144.8, 135.4, 135.2, 130.0, 129.7, 126.8, 124.7, 124.7, 123.2, 122.0, 120.8, 113.9, 86.8, 82.4, 71.8, 63.7, 47.8, 40.6, 40.4, 29.4, 27.9, 26.0, 24.5, 21.5, 20.3; **EI MS** m/z (%) = 475 (M^+, 1), 321 (11), 308 (75), 155 (46), 91 (100); **HRMS ESI** Calcd for $C_{28}H_{29}NO_4S$ $[M+H]^+$: 476.1890, Found: 476.1901, Error: 2.3 ppm.



3m

4-(prop-2-ynyl)-1-tosyl-1-azaspiro[4.4]nonan-6-one (**3m**):

According to the general procedure D: **3m** (44 mg, 0.133 mmol, 60 % yield of two steps) was obtained as a yellow foam from **1g** (81 mg, 0.22 mmol). **IR** (neat) 3294, 2962, 2884, 2119, 1746, 1329, 1269, 1157, 817, 665 cm^{-1}; **^{1}H NMR** (400 MH_Z, $CDCl_3$) δ 7.79 (d, *J* = 8.0 Hz, 2 H), 7.29 (d, *J* = 8.0 Hz, 2 H), 3.45 (ddd, *J* = 4.0, 8.4 and 8.4 Hz, 1 H), 3.16 (dd, *J* = 8.0 and 15.6 Hz, 1 H), 2.76 (ddd, *J* = 8.0, 12.0 and 12.4 Hz, 1 H), 2.57~2.47 (m, 1 H), 2.42 (s, 3 H), 2.35~2.28 (m, 2 H), 2.26~1.96 (m, 7 H), 1.86~1.74 (m, 1 H); **^{13}C NMR** (100 MH_Z, $CDCl_3$) δ 215.6, 143.3, 137.0, 129.3, 127.6, 81.9, 75.3, 70.1, 48.1, 45.7, 37.5, 36.8, 29.5, 21.4, 19.7, 18.3; **EI MS** m/z (%) = 331 (M^+, 2), 303 (43), 275 (24), 210 (14), 120 (100); **HRMS ESI** Calcd for $C_{18}H_{21}NO_3S$ $[M+H]^+$: 332.1315, Found: 332.1312, Error: 0.9 ppm.

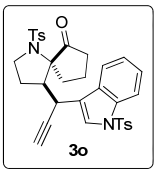


3n

4-(1-phenylprop-2-ynyl)-1-tosyl-1-azaspiro[4.4]nonan-6-one (**3n**):

According to the general procedure D: **3n** (55 mg, 0.135 mmol, 61 % yield of two steps) was obtained as a white soild from **1g** (81 mg, 0.22 mmol). **mp**: 175-177 ºC; **IR** (neat) 3282, 2957, 2881, 2371, 1744, 1598, 1330, 1156, 736, 703, 681 cm^{-1}; **^{1}H NMR** (400 MH_Z, $CDCl_3$) δ 7.79 (d, *J* = 8.0 Hz, 2 H), 7.30 (d, *J* = 8.0 Hz, 2 H), 7.26~7.17 (m, 5 H), 3.52 (dd, *J* = 2.0 and 10.8 Hz, 1 H), 3.24 (dd, *J* = 8.0 and 15.6 Hz, 1 H), 3.09 (dd, *J* = 7.2 and 15.6 Hz, 1

H), 2.82~2.74 (m, 1 H), 2.61~2.53 (m, 3 H), 2.45~2.39 (m,1 H), 2.42 (s, 3 H), 2.30~2.26 (m, 2 H), 2.13~2.01 (m, 1 H), 1.59 (ddd, *J* = 6.8, 13.2 and 13.6 Hz, 1 H) , 1.41 (ddd, *J* = 6.4, 12.4 and 12.8 Hz,1 H); **^{13}C NMR** (100 MH_Z, $CDCl_3$) δ 217.3, 143.2, 139.8, 137.3, 129.4, 128.7, 127.9, 127.6, 127.4, 85.5, 75.0, 73.0, 56.9, 46.1, 38.2, 38.0, 37.2, 28.8, 21.4, 18.4; **EI MS** m/z (%) = 407 (M^+, 1), 379 (56), 196 (100), 155 (46), 91 (86); **HRMS ESI** Calcd for $C_{24}H_{25}NO_3S$ $[M+H]^+$: 408.1628, Found: 408.1640, Error: 2.9 ppm.



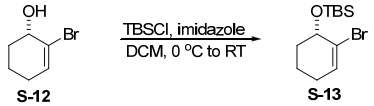
3o

1-tosyl-4-(1-(1-tosyl-1*H*-indol-3-yl) prop-2-ynyl)-1-azaspiro[4.4]nonan-6-one (**3o**):

According to the general procedure D: **3o** (95 mg, 0.158 mmol, 72 % yield of two steps) was obtained as a yellow soild from **1g** (81 mg, 0.22 mmol). **mp**: 102-104 ºC; **IR** (neat) 3293, 2960, 2881, 2116, 1743, 1598, 1371, 1174, 1157, 738, 704, 676 cm^{-1}; **^{1}H NMR** (400 MH_Z, $CDCl_3$) δ 7.96 (d, *J* = 8.0 Hz, 1 H), 7.82 (d, *J* = 8.0 Hz, 2 H), 7.69 (d, *J* = 8.0 Hz, 2 H), 7.58 (d, *J* = 8.0 Hz, 1 H), 7.38 (s, 1 H), 7.33~7.26 (m, 3 H), 7.21~7.14 (m, 3 H), 3.82 (d, *J* = 9.2 Hz, 1 H), 3.24~3.21 (m, 1 H), 3.05 (dd, *J* = 7.2 and 15.6 Hz, 1 H), 2.82~2.75 (m, 2 H), 2.58~2.56 (m, 2 H), 2.43 (s, 3 H), 2.47~2.20 (m, 3 H), 2.28 (s, 3 H), 2.06 (dd, 8.8 and 20.0 Hz, 1 H), 1.59 (dd, 6.8 and 12.8 Hz, 1 H), 1.36 (dd, 6.0 and 12.4 Hz,1 H); **^{13}C NMR** (100 MH_Z, $CDCl_3$) δ 217.0, 145.0, 143.3, 137.0, 135.3, 134.8, 129.7, 129.4, 128.5, 127.5, 126.6, 125.0, 124.1, 123.2, 120.2, 120.1, 113.9, 83.7, 74.9, 72.7, 54.9, 46.0, 38.1, 37.9, 28.7, 28.5, 21.4, 21.3, 18.3; **EI MS** m/z (%) = 600 (M^+, 1), 445 (15), 389 (36), 308 (23), 91 (100); **HRMS ESI** Calcd for $C_{33}H_{32}N_2O_5S_2$ $[M+Na]^+$: 623.1645, Found: 623.1638, Error: 1.1 ppm.

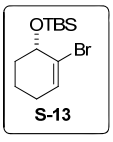
1.5 The preparation of cyclohexenone-type allylic silylether 5b:

1-(2-bromocyclohex-2-enyl) *tert*-butyldimethylsilyl ether (**S-13**):



S-12 **S-13**

Allylic alcohol **S-12**[11] (4.72 g, 26.8 mmol) was dissolved in DCM (108 mL) at 0 ºC. Then imidazole (4.37 g, 64.3 mmol) and TBSCl (4.82 g, 32.0 mmol) were successively added. The cool bath was then removed and the mixture was stirred at room temperature for 4 h. After fully consumption of the substrate, the reaction was quenched with water and extracted with ethyl acetate (2 x 100 mL). The combined organic layer was washed with brine, dried over Na_2SO_4 and concentrated under vacuum. The crude product was purified by column chromatography (EtOAc: petroleum ether = 1:100) to give product **S-13** (7.34 g, 25.3 mmol, 94 %) as a colorless oil.

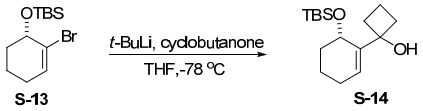


S-13

IR (neat) 2951, 2930, 2859, 2857, 2178, 1643, 1586, 1472, 1362, 1252, 1165, 1093, 1021, 836, 776 cm^{-1}; **^{1}H NMR** (400 MH_Z, $CDCl_3$) δ 6.15 (dd, *J* = 4.0 and 4.0 Hz, 1 H), 4.20 (dd, *J* = 4.0 and 4.0 Hz, 1 H), 2.16~2.10 (m, 1 H), 2.05~1.97 (m, 1 H), 1.86~1.74 (m, 3 H), 1.61~1.56 (m, 1 H), 0.93 (s, 9 H), 0.18 (s, 3 H), 0.12 (s, 3 H); **^{13}C NMR** (100 MH_Z, $CDCl_3$) δ 132.0, 125.8, 70.6, 33.7, 27.8, 25.8, 18.1, 17.2, -4.5, -4.7; **EI MS** m/z (%) = 235 (99), 233 (100), 139 (63), 137 (62), 79 (53), 75 (70); **HRMS ESI** Calcd for $C_{12}H_{23}BrOSi$ $[M+K]^+$: 329.0333, Found:

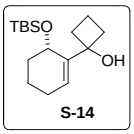
329.0340, Error: 2.1 ppm.

1-(6-(*tert*-butyldimethylsilyloxy)cyclohex-1-enyl)cyclobutanol (**S-14**):



S-13 **S-14**

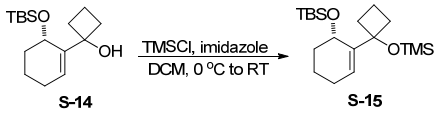
To a stirred solution of vinyl bromine substrate **S-13** (2.98 g, 10.3 mmol) in dry THF (50 mL) was added *t*-BuLi (1.6 M in hexane, 14.1 mL, 22.6 mmol) under argon at -78 °C. After 20 min, cyclobutanone (0.86 g, 12.3 mmol) was added to the solution and the mixture was stirred at the same temperature for another 1h. Then the reaction was quenched with water and extracted with ethyl acetate (2 x 100 mL). The combined organic layer was washed with brine, dried over Na_2SO_4 and concentrated under vacuum. The crude product was purified by column chromatography (EtOAc: petroleum ether = 1:150 to 1:80) to give product **S-14** (2.30 g, 8.2 mmol, 79 %) as a colorless oil.



S-14

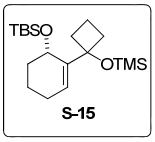
IR (neat) 3507, 3445, 2936, 2859, 1658, 1469, 1360, 1254, 1125, 1064, 835, 776 cm^{-1}; **^{1}H NMR** (400 MH_Z, $CDCl_3$) δ 5.85 (dd, *J* = 3.6 and 3.6 Hz, 1 H)，4.57 (dd, *J* = 4.8 and 4.8 Hz, 1 H), 4.17 (s, 1 H), 2.44~2.37 (m, 1 H), 2.14 (dd, *J* = 7.2 and 8.0 Hz, 2 H), 2.11~1.94 (m, 3 H), 1.88~1.68 (m, 4 H), 1.54~1.39 (m, 2 H), 0.88 (s, 9 H), 0.12 (s, 6 H); **^{13}C NMR** (100 MH_Z, $CDCl_3$) δ 139.7, 124.7, 78.1, 67.7, 35.6, 32.9, 32.8, 25.8, 25.1, 18.8, 17.8, 13.2, -3.6, -4.7; **EI MS** m/z (%) = 225 (21), 133 (53), 105 (48), 91 (66), 75 (100); **HRMS ESI** Calcd for $C_{16}H_{30}O_2Si$ $[M+Na]^+$: 305.1907, Found: 305.1904, Error: 1.0 ppm.

1-(2-(1-(trimethylsilyloxy)cyclobutyl)cyclohex-2-enyl) *tert*-butyldimethylsilyl ether (**S-15**):



S-14 **S-15**

Allylic alcohol **S-14** (1.48 g, 5.25 mmol) was dissolved in DCM (50 mL) at 0 ºC, and then imidazole (0.86 g, 12.6 mmol), TMSCl (0.8 mL, 6.3 mmol) were successively added to the solution. The cool bath was removed and the reation mixture was stirred at room temperature for 0.5 h. After fully consumption of the substrate, the reaction was quenched with water and extracted with ethyl acetate (2 x 60 mL). The combined organic layer was washed with brine, dried over Na_2SO_4 and concentrated under vacuum. The crude product was purified by flash column chromatography (EtOAc: petroleum ether = 1:200) to give product **S-15** (1.72 g, 4.86 mmol, 93 %) as a colorless oil.

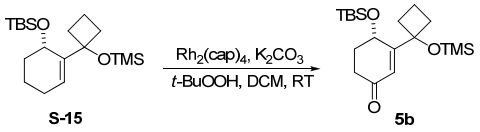


S-15

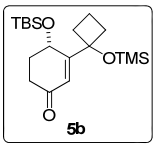
IR (neat) 2951, 2858, 1656, 1471, 1251, 1136, 1086, 1013, 838, 773 cm^{-1}; **^{1}H NMR** (400 MH_Z, $CDCl_3$) δ 5.82 (dd, *J* = 3.6 and 3.6 Hz, 1 H), 4.55 (dd, *J* = 3.2 and 3.2 Hz, 1 H), 2.52~2.40 (m, 2 H), 2.21~2.12 (m, 3 H), 2.02~1.96 (m, 1 H), 1.89~1.70 (m, 3 H), 1.54~1.48 (m, 3 H), 0.91 (s, 9 H), 0.10 (s, 6 H), 0.08 (s, 9 H); **^{13}C NMR** (100 MH_Z,

$CDCl_3$) δ 141.6, 123.1, 79.1, 64.1, 38.7, 34.6, 32.6, 26.1, 25.7, 18.0, 16.8, 13.6, 1.9，-4.1, -4.3; **EI MS** m/z (%) = 297 (37), 223 (24), 147 (100), 133 (66), 73 (69); **HRMS ESI** Calcd for $C_{19}H_{38}O_2Si_2$ $[M+K]^+$: 393.2042, Found: 393.2058, Error: 4.1 ppm.

4-(*tert*-butyldimethylsilyloxy)-3-(1-(trimethylsilyloxy)cyclobutyl)cyclohex-2-enone (**5b**)[12]:

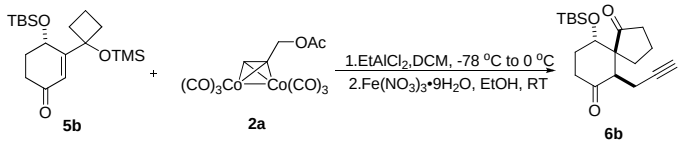


To a stirred solution of substrate **S-15** (1.1 g, 3.1 mmol) in DCM (13 mL) was added K_2CO_3 (222 mg, 1.6 mmol), $Rh_2(cap)_4$ (2.1 mg, 0.003 mmol) and *t*-BuOOH (5 M in decane, 3.1 mL, 15.5 mmol) sequentially at room temperature. The mixture was stirred at the same temperature for 1.5 h under oxygen atmosphere. Then another $Rh_2(cap)_4$ (2.1 mg, 0.003 mmol) and *t*-BuOOH (5 M in decane, 3.1 ml, 15.5 mmol) were added to the solution at the same condition. After 1.5 h, the same procedure was repeated again. After stirring for 4 h, the solution was filtered through a short silica gel column (DCM: EtOAc = 1:1, 150 mL) and concentrated under vacuum. The crude product was purified by flash column chromatography (EtOAc: petroleum ether = 1:200) to give product **5b** (883 mg, 2.4 mmol, 77 %) as a white soild.



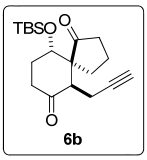
mp: 38-40 ºC; **IR** (neat) 2955, 2931, 2858, 1683, 1471, 1252, 1140, 1068, 985, 840, 776 cm^{-1}; **^{1}H NMR** (400 MH_Z, $CDCl_3$) δ 5.96 (s, 1 H,)，4.76 (dd, *J* = 3.2 and 3.2 Hz, 1 H), 2.80~2.71 (m, 1 H), 2.50~2.36 (m, 2 H), 2.32~2.21 (m, 3 H), 2.09~2.02 (m, 1 H), 1.98~1.90 (m, 1 H), 1.81~1.71 (m, 1 H), 1.60~1.48 (m, 1 H), 0.85 (s, 9 H), 0.09 (s, 3 H), 0.08 (s, 3 H), 0.07 (s, 9 H); **^{13}C NMR** (100 MH_Z, $CDCl_3$) δ 200.6, 164.4, 122.8, 77.6, 63.2, 38.7, 34.2, 32.1, 31.4, 25.7, 17.9, 12.9, 1.7，-4.6, -4.6; **EI MS** m/z (%) = 368 (M^+, 3), 311 (20), 221 (21), 147 (100), 119 (28); **HRMS ESI** Calcd for $C_{19}H_{36}O_3Si_2$ $[M+H]^+$: 369.2276 Found: 369.2273, Error: 0.8 ppm.

1.6 General procedure E: for the Nicholas/semipinocal reaction of cyclohexenone-type allylic silylethers **5a** and **5b:**



A mixture of cobalt complex **2a** (crude, 93 mg, about 0.24 mmol) and enone **5b** (81 mg, 0.22 mmol) was dissolved in DCM (3.6 mL) at -78 ºC, followed by addition of $EtAlCl_2$ (1.8 M in toluene, 0.16 mL, 0.29 mmol). Then the mixture was immediately moved to ice bath and stirred for another 6-7 h. Next, the mixture was filtered throuth a plug of silica gel (DCM: EtOAc = 1:1, 30 mL), and the filtrate was concentrated under vacuum. The crude product was purified by flash column chromatography (EtOAc: petroleum ether = 1:15) to give cobalt complex intermediate. Then cobalt complex was dissolved in ethanol (5 mL), and $Fe(NO_3)_3{\cdot}9H_2O$ (404 mg, 1.0 mmol) was added to the solution at room temperature. After 2-3 h, the reaction was quenched with water and extracted with ethyl acetate (2 x 30 mL). The combined organic layer was washed with water and brine, dried over Na_2SO_4 and

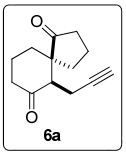
concentrated under vacuum. The crude product was purified by flash column chromatography (EtOAc: petroleum ether = 1:15) to give product **6b** (44 mg, 0.132 mmol, 60 % yield of two steps) as a colorless oil.



10-(*tert*-butyldimethylsilyloxy)-6-(prop-2-ynyl)spiro[4.5]decane-1,7-dione (**6b**):

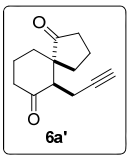
IR (neat) 3310, 2956, 2858, 2120, 1733, 1469, 1257, 1097, 860, 838, 669 cm^{-1}; **^{1}H NMR** (400 MH_Z, $CDCl_3$) δ 4.00 (dd, *J* = 4.4 and 10.8 Hz, 1 H), 2.71~2.66 (m, 1 H), 2.49~2.40 (m, 2 H), 2.38~2.21 (m, 4 H), 2.17~1.75 (m, 7 H), 0.83 (s, 9 H) , 0.10 (s, 3 H), 0.04 (s, 3 H); **^{13}C NMR** (100 MH_Z, $CDCl_3$) δ 220.2, 205.7, 83.2, 76.5, 69.2, 59.5, 53.6, 40.4, 37.9, 32.5, 29.9, 25.8, 19.7, 18.0, 14.6, -4.1, -4.8; **EI MS** m/z (%) = 277 (37), 193 (25), 157 (28), 129 (21), 75 (100); **HRMS ESI** Calcd for $C_{19}H_{30}O_3Si$ $[M+H]^+$: 335.2037, Found: 335.2036, Error: 0.3 ppm.

According to the general procedure E: Two separable diastereomers **6a** (20 mg, 0.098 mmol, 45 %) and **6a'** (9 mg, 0.044 mmol, 20 %) were obtained as white solids from **5a**[13] (52 mg, 0.22 mmol).



6-(prop-2-ynyl)spiro[4.5]decane-1,7-dione (**6a**):

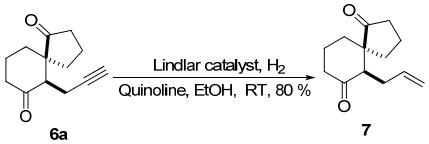
mp: 107-109 ºC; **IR** (neat) 3271, 2942, 2900, 2112, 1726, 1707, 1251, 698, 664 cm^{-1}; **^{1}H NMR** (400 MH_Z, $CDCl_3$) δ 2.80 (ddd, *J* = 2.8, 6.8 and 17.6 Hz, 1 H), 2.54~2.40 (m, 2 H), 2.38~2.23 (m, 3 H), 2.21~2.12 (m, 1 H), 2.07~2.02 (m, 1 H), 2.02~1.96 (m, 2 H), 1.94~1.91 (m, 2 H), 1.87~1.79 (m, 3 H), 1.69~1.62 (m, 1 H); **^{13}C NMR** (100 MH_Z, $CDCl_3$) δ 219.0, 207.4, 83.0, 69.5, 56.2, 54.0, 39.6, 37.7, 35.2, 32.0, 21.2, 18.6, 14.6; **EI MS** m/z (%) = 204 (M^+, 6), 110 (100), 95 (61), 91 (55), 55 (56); **HRMS ESI** Calcd for $C_{13}H_{16}O_2$ $[M+H]^+$: 205.1223, Found: 205.1232, Error: 4.4 ppm.



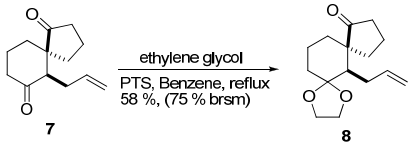
6-(prop-2-ynyl)spiro[4.5]decane-1,7-dione (**6a'**):

mp: 75-77 ºC; **IR** (neat) 3299, 2952, 2870, 2119, 1736, 1713, 1268, 1186, 1159, 736, 639 cm^{-1}; **^{1}H NMR** (400 MH_Z, $CDCl_3$) δ 3.07 (t, *J* = 6.8 Hz, 1 H), 2.55 (ddd, *J* = 2.8, 8.0 and 16.8 Hz, 1 H), 2.44~2.39 (m, 2 H), 2.38~2.31 (m, 1 H), 2.31~2.22 (m, 1 H), 2.09~2.06 (m, 1 H), 1.99~1.95 (m, 1 H), 1.94~1.89 (m, 2 H), 1.87~1.80 (m, 2 H), 1.79~1.68 (m, 3 H) , 1.67~1.60 (m, 1 H); **^{13}C NMR** (100 MH_Z, $CDCl_3$) δ 219.0, 209.5, 81.9, 70.4, 56.9, 52.7, 41.4, 37.3, 32.9, 27.6, 23.6, 18.9, 15.1; **EI MS** m/z (%) = 204 (M^+, 13), 148 (47), 110 (100), 91 (86), 55 (83); **HRMS ESI** Calcd for $C_{13}H_{16}O_2$ $[M+H]^+$: 205.1223, Found: 205.1230, Error: 3.4 ppm.

1.7 Synthesis towards the tricyclic unit of daphlongamine E:

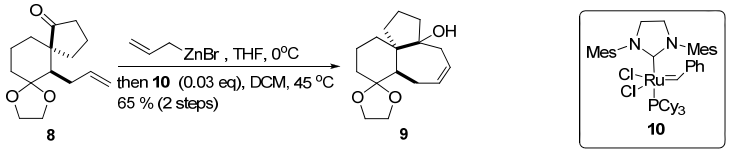


To a stirred solution of substrate **6a** (222 mg, 1.09 mmol) in EtOH (15 mL) at room temperature was added Lindlar Pd catalyst (56 mg) and quinoline (0.56 mL, 4.7 mmol) sequentially. The mixture was stirred at room temperature for 20 min at hydrogen atmosphere. Then the solution was filtered through filter membrane (DCM: EtOAc = 1:1, 20 mL). The filtrate was diluted with ethyl acetate (50 mL) and the organic layer was washed with 5 % aqueous HCl, saturated aqueous $NaHCO_3$ and brine. The organic phase was dried over Na_2SO_4 and concentrated under vacuum. The crude product was purified by flash column chromatography (EtOAc: petroleum ether = 1:20) to give product **7** (179 mg, 0.869 mmol, 80 %) as a white solid. **mp**: 36-38 ºC; **IR** (neat) 3074, 2956, 2925, 2870, 2853, 1732, 1712, 1639, 1456, 1163, 990, 914 cm^{-1}; **^{1}H NMR** (400 MH_Z, $CDCl_3$) δ 5.76~5.66 (m, 1 H), 5.01~4.92 (m, 2 H), 2.54~2.44 (m, 2 H), 2.32~2.08 (m, 7 H), 1.99~1.88 (m, 3 H), 1.82~1.72 (m, 2 H), 1.58~1.51 (m, 1 H); **^{13}C NMR** (100 MH_Z, $CDCl_3$) δ 219.2, 209.7, 136.5, 115.9, 55.6, 54.3, 39.6, 37.8, 35.1, 31.1, 30.1, 21.8, 18.6; **EI MS** m/z (%) = 206 (M^+, 23), 151 (18), 110 (100), 97 (47), 79 (30); **HRMS ESI** Calcd for $C_{13}H_{18}O_2$ $[M+H]^+$: 207.1380, Found: 207.1377, Error: 1.4 ppm.



7 **8**

The flame dried round bottom flask with a Dean-Stark apparatus and a condenser was charged with the solution of substrate **7** (178 mg, 0.864 mmol) in benzene (5 mL), ethylene glycol (0.39 mL, 6.9 mmol) and anhydrous PTS (30 mg, 0.17 mmol). The mixture was refluxed for 0.5 h, during which time the water produced was collected in the Dean-Stark apparatus. Then the residue was diluted with ethyl acetate (50 mL), and the organic layer was washed with saturated aqueous $NaHCO_3$ and brine. The organic phase was dried over Na_2SO_4 and concentrated under vacuum. The crude product was purified by flash column chromatography (EtOAc: petroleum ether = 1:50) to give product **8** (126 mg, 0.504 mmol, 58 % yield, 75 % yield based on consumed starting material) as a white soild. **mp**: 39-41 ºC; **IR** (neat) 3076, 2955, 2925, 2869, 2854, 1734, 1460, 1377, 1090, 1026, 949, 914, 740 cm^{-1}; **^{1}H NMR** (400 MH_Z, $CDCl_3$) δ 5.72~5.63 (m, 1 H), 4.90~4.84 (m, 2 H), 3.96~3.90 (m, 2 H), 3.90~3.86 (m, 2 H), 2.85~2.79 (m, 1 H), 2.29~2.22 (m, 3 H), 2.17~2.08 (m, 1 H), 1.89~1.85(m, 1 H), 1.84~1.79 (m, 2 H), 1.76~1.72 (m, 1 H), 1.67~1.56 (m, 3 H), 1.56~1.45 (m, 2 H), 1.07 (d, J = 13.6 Hz, 1 H); **^{13}C NMR** (100 MH_Z, $CDCl_3$) δ 220.7, 139.4, 114.5, 111.0, 64.3, 63.6, 52.5, 43.9, 37.7, 35.2, 31.5, 30.2, 28.9, 19.8, 17.8; **EI MS** m/z (%) = 250 (M^+, 2), 196 (20), 112 (59), 99 (100), 55 (27); **HRMS ESI** Calcd for $C_{15}H_{22}O_3$ $[M+H]^+$: 251.1642, Found: 251.1643, Error: 0.4 ppm.

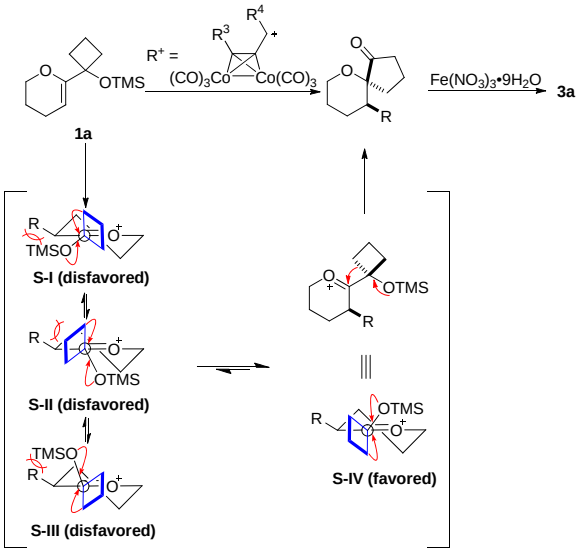


8 **9** **10**

To a stirred solution of substrate **8** (86 mg, 0.344 mmol) in THF (1.6 mL) was added allylic zinc bromide (1.187 M in THF, 0.44 mL, 0.52 mmol)[14] under argon at 0 ºC, and the mixture was stirred at the same temperature for 3 h. Then the reaction was quenched with water and extracted with ethyl acetate (2 x 40 mL). The combined organic layer was washed with brine, dried over Na_2SO_4 and concentrated under vacuum. Without purification, the crude product was dissolved in DCM (2.5 mL), and then Grubbs II catalyst **10** (9 mg, 0.011 mmol) was added. After refluxing for 2-3 h, the mixture was concentrated under vacuum. The crude product was purified by flash column chromatography (EtOAc: petroleum ether = 1:30) to give product **9** (59 mg, 0.223 mmol, 65 % yield of two steps) as a white soild. **mp**: 105-107 ºC; **IR** (neat) 3563, 3015, 2951, 2926, 2873, 1455, 1357, 1297, 1091, 1024 cm^{-1}; **^{1}H NMR** (400 MH_Z, $CDCl_3$) δ 5.87 (dd, J = 7.6 and 10.4 Hz, 1H), 5.45 (dd, J = 8.4 and 10.4 Hz, 1 H), 3.92~3.82 (m,

4 H), 2.76 (d, *J* = 16.0 Hz, 1 H), 2.39~2.29 (m, 3 H), 2.23~2.11 (m, 2 H), 2.07~1.99 (m, 1 H), 1.88~1.78(m, 2 H), 1.66~1.59 (m, 2 H), 1.56~1.49 (m, 4 H), 1.47~1.44 (m, 1 H), 1.42~1.34 (m, 1 H), 1.24 (d, *J* = 14.0 Hz, 1 H); **^{13}C NMR** (100 MH_Z, $CDCl_3$) δ 132.7, 125.7, 111.2, 84.9, 64.1, 63.4, 49.8, 49.5, 39.4, 39.0, 35.0, 31.1, 26.2, 23.5, 19.4, 17.8; **EI MS** m/z (%) = 246 (M^+, 11), 133 (22), 112 (62), 99 (100), 85 (39), 71 (51); **HRMS ESI** Calcd for $C_{16}H_{24}O_3$ $[M+Na]^+$: 287.1618, Found: 287.1614, Error: 1.5 ppm.

2. Proposed stereo-controlling mechanism from 1a-1f to 3a-3l:



Since the substrate **1a** with a dihydropyran ring would form an oxonium intermediate after coupling with Nicholas cation, four conformations of oxonium intermediates were possible for the following 1,2-migration process. Because of the clear steric hindrance existed in forms **S-I** to **S-III**, the rearrangement took the favorable form **S-IV** to give compound **3a** after decomplexation.

References:

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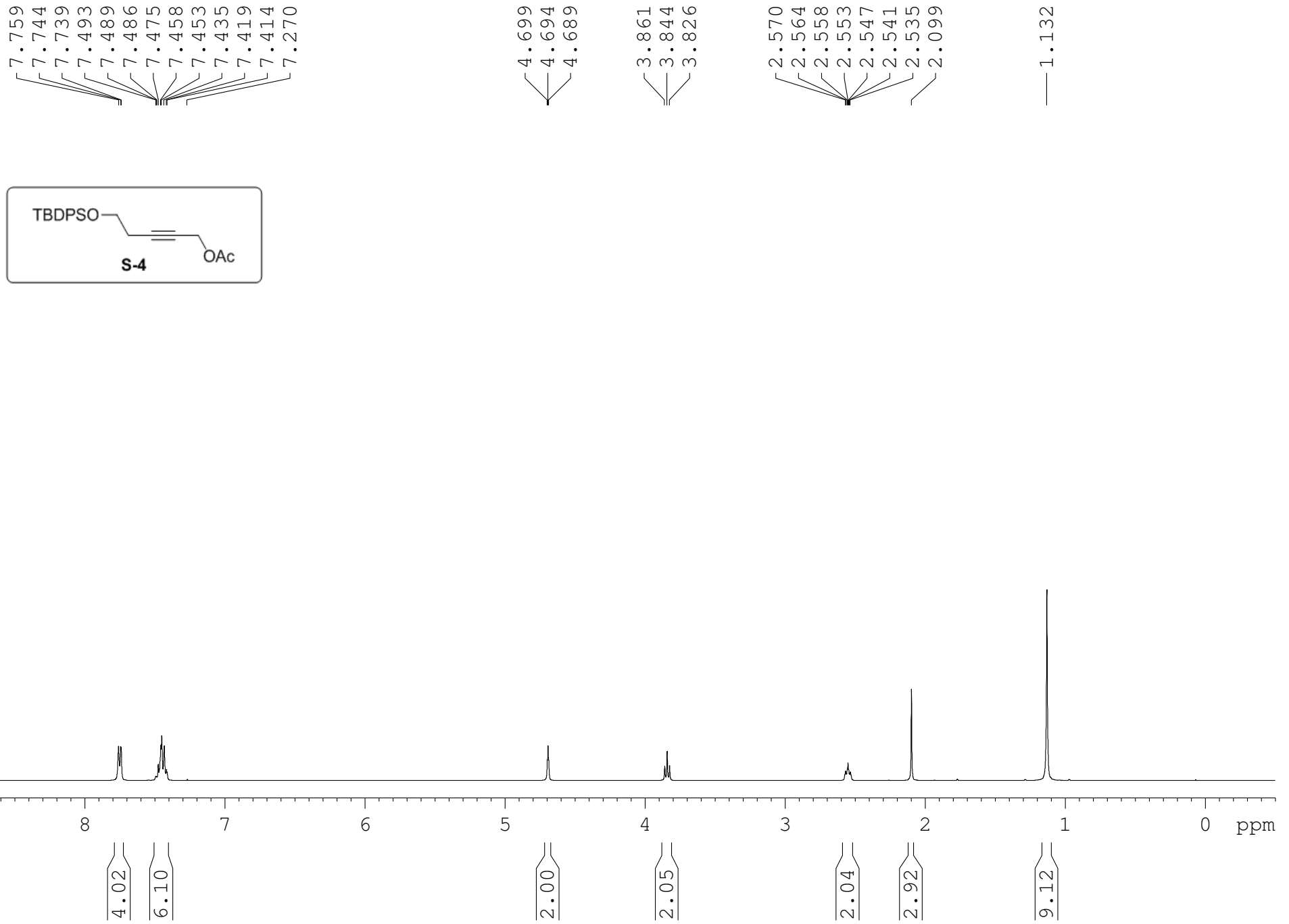
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2.547
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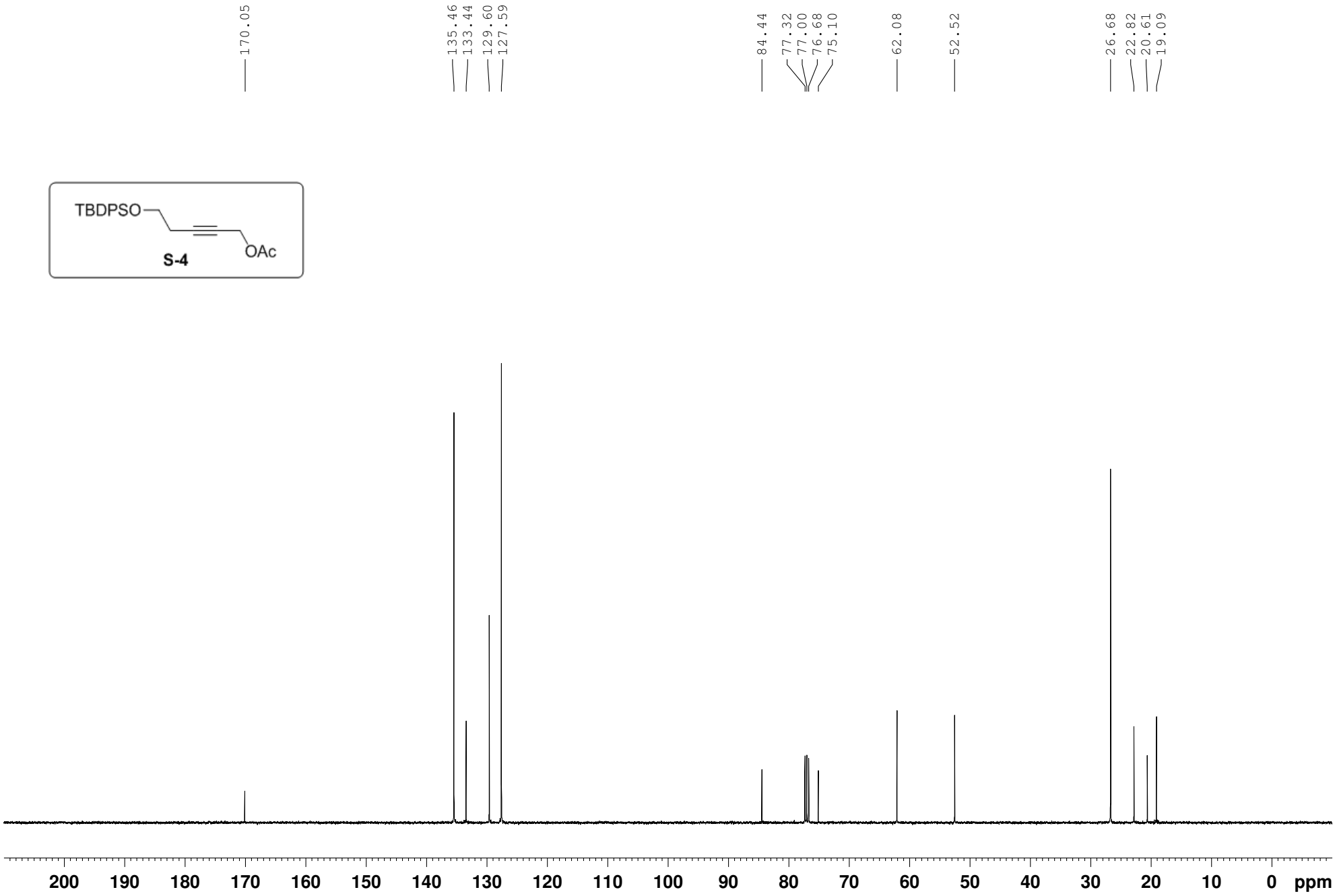
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20.61
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OAc
S-4
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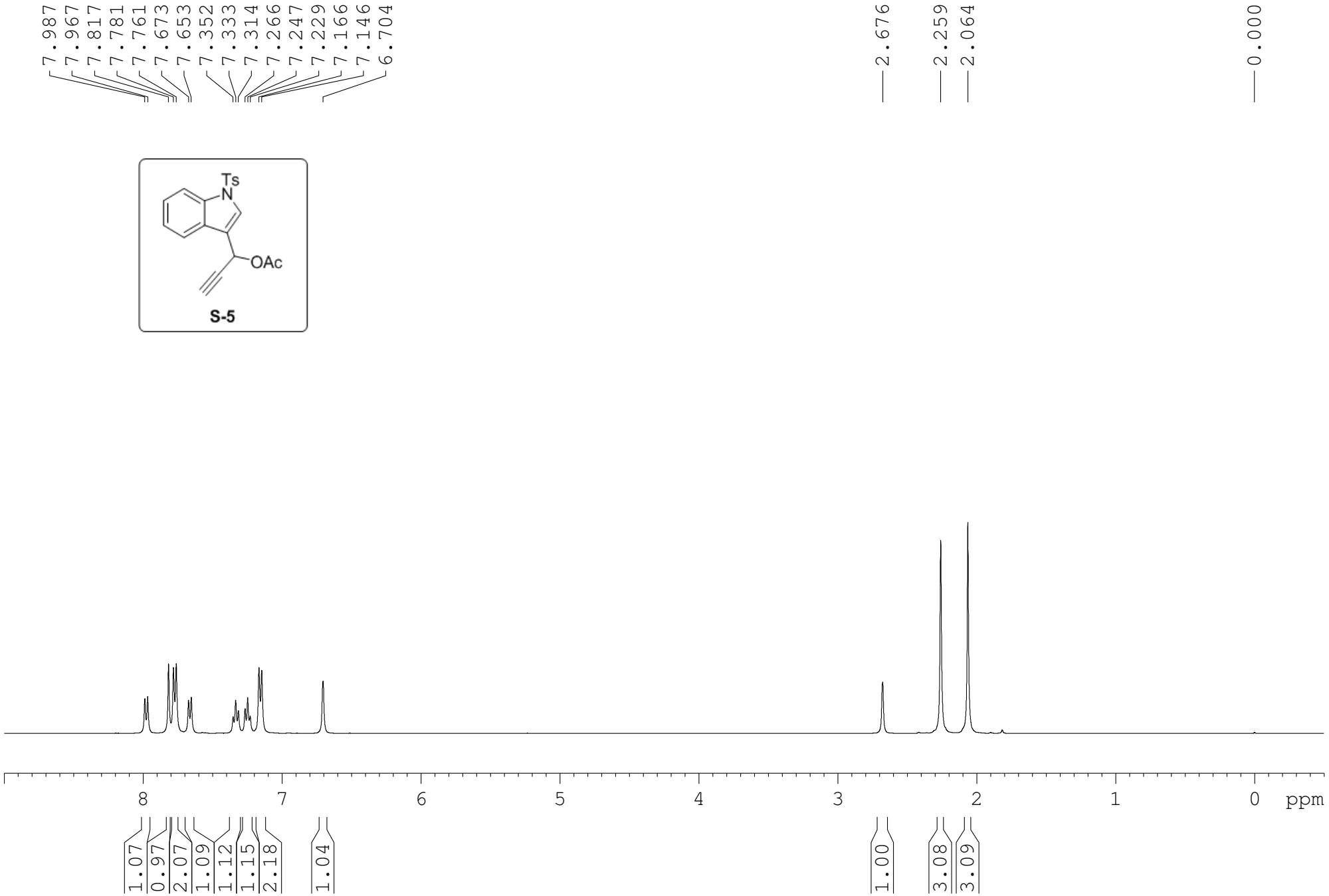
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OAc
S-5
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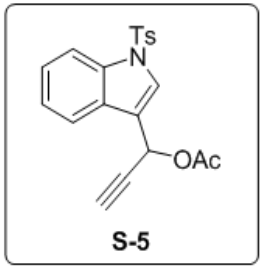
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OAc

S-5

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113.53
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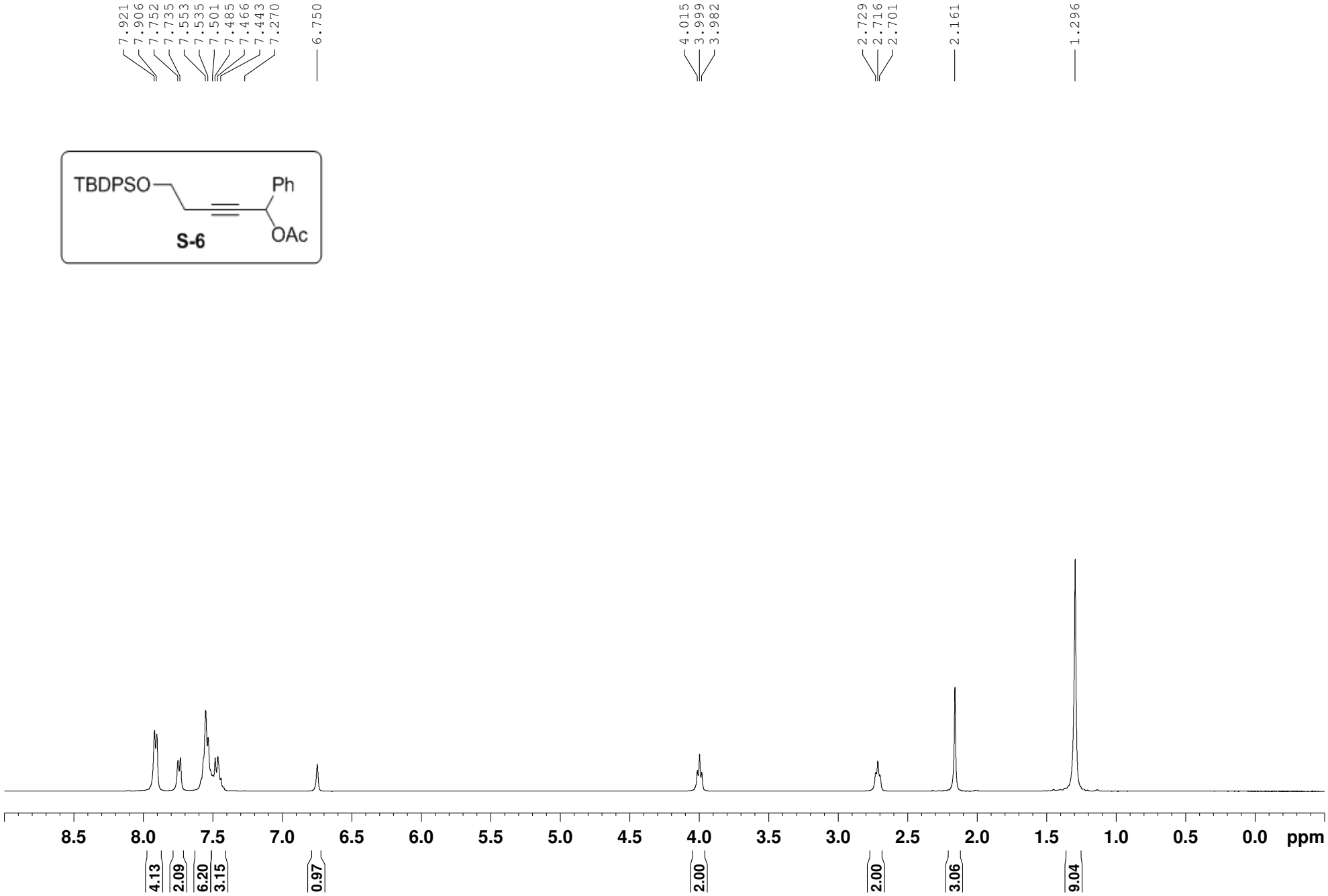
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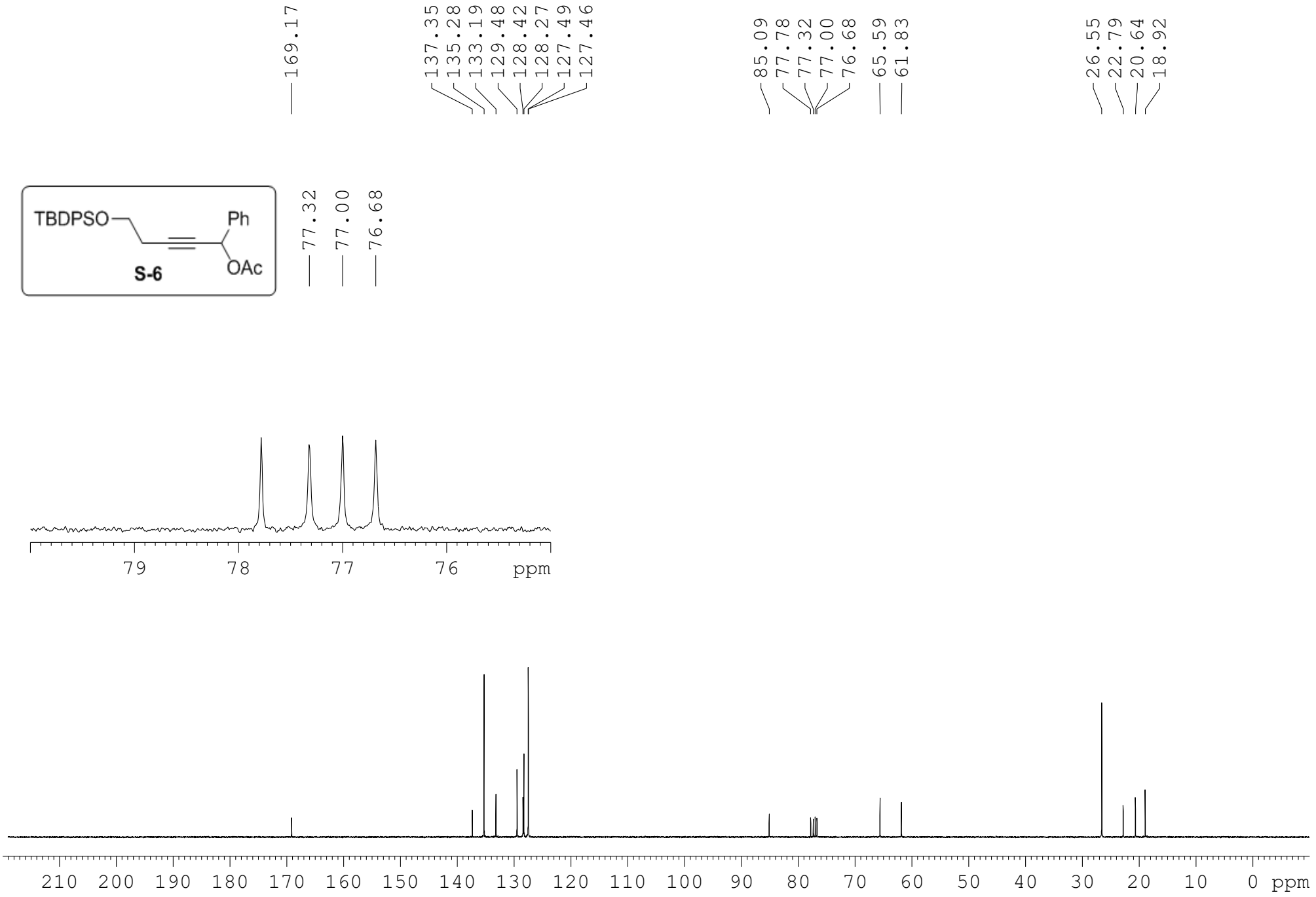
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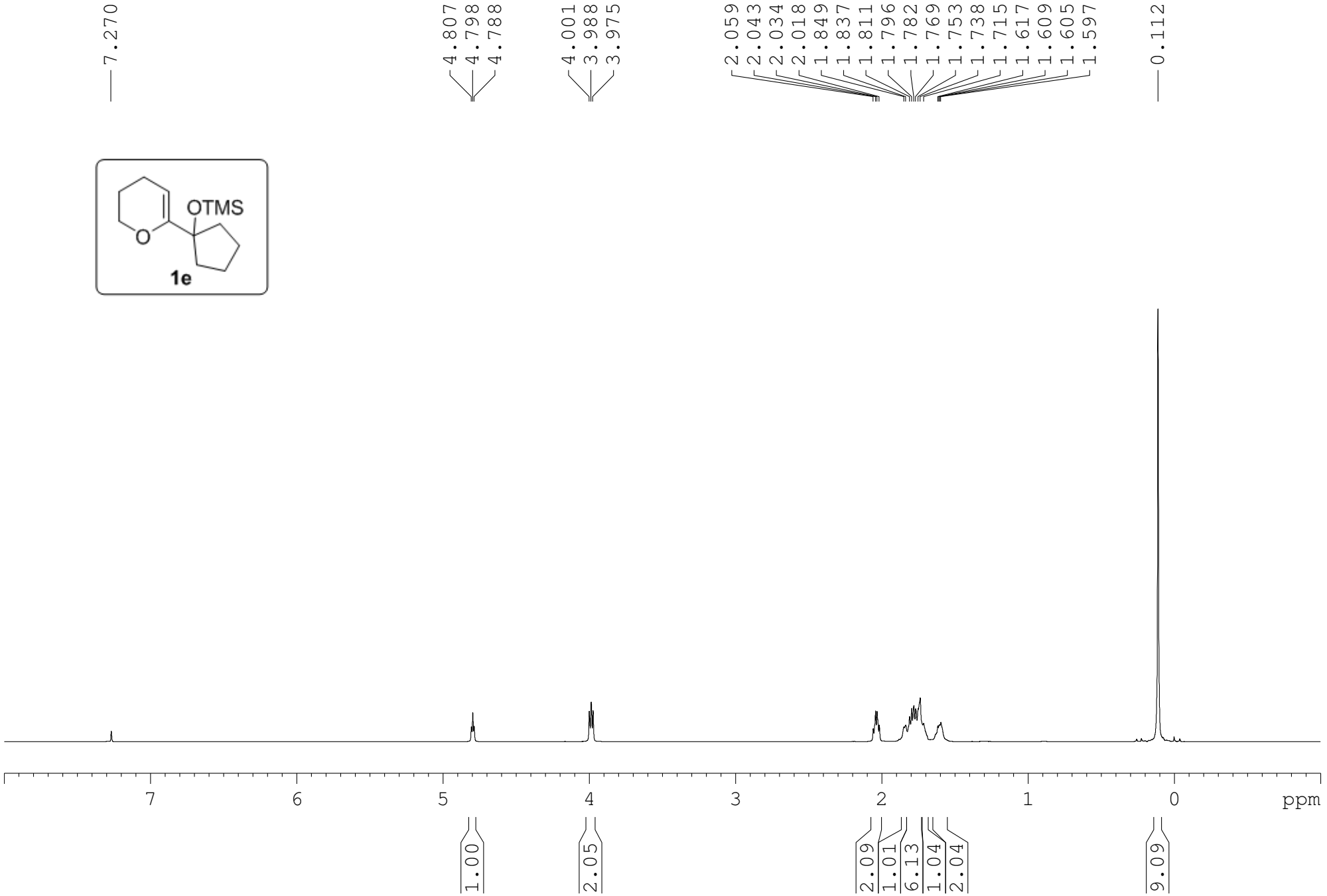
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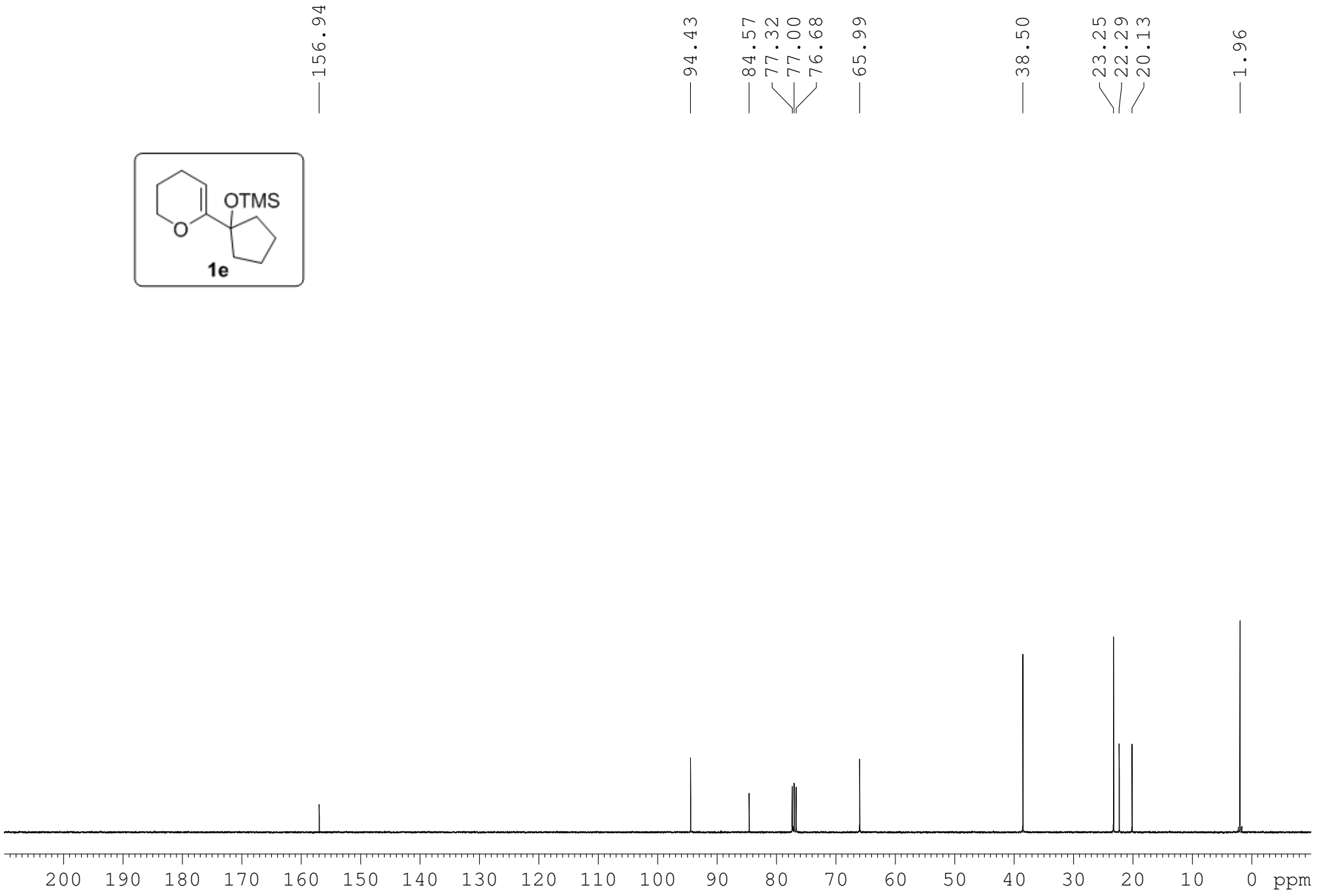
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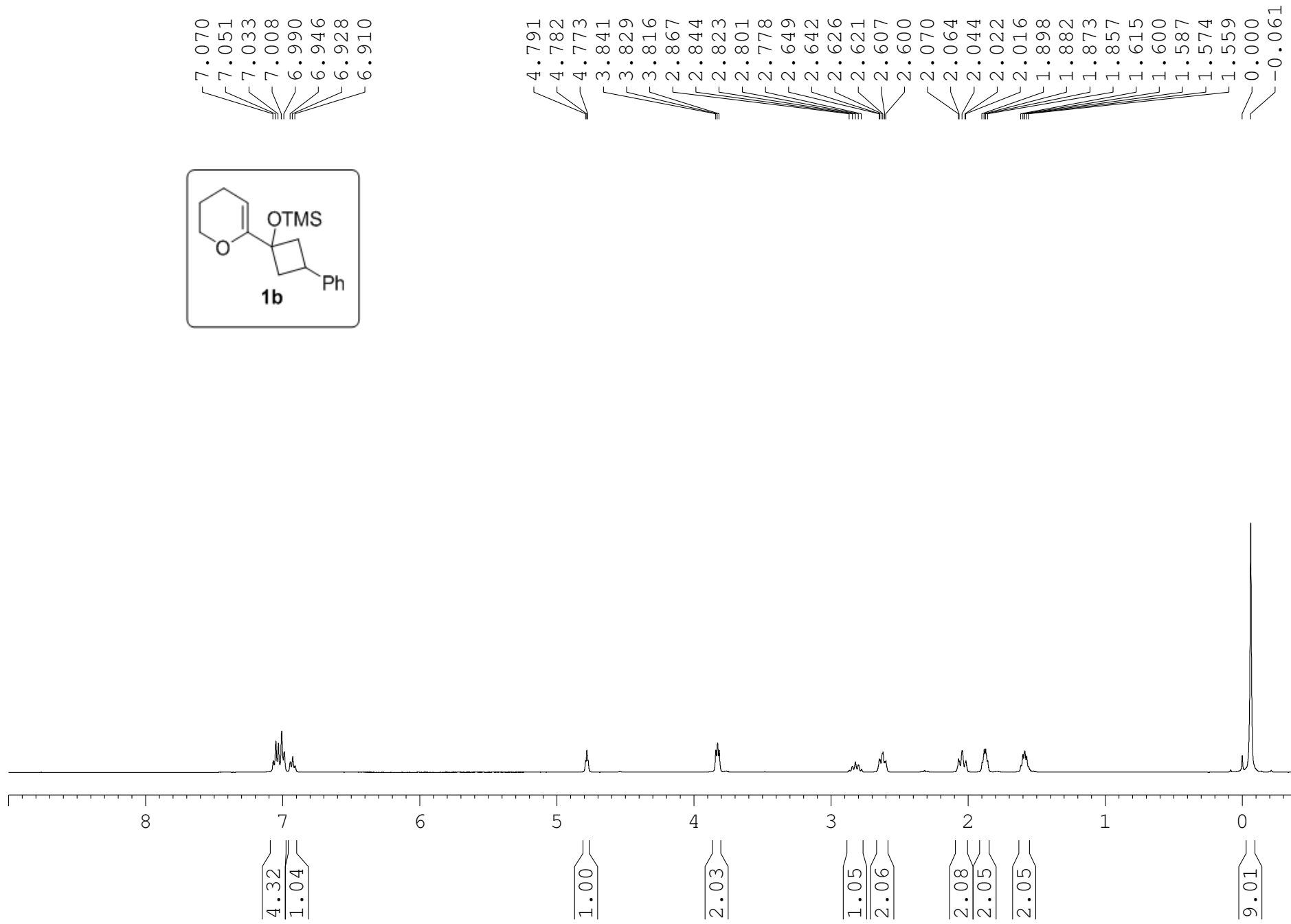
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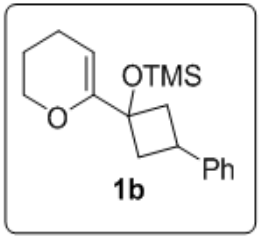

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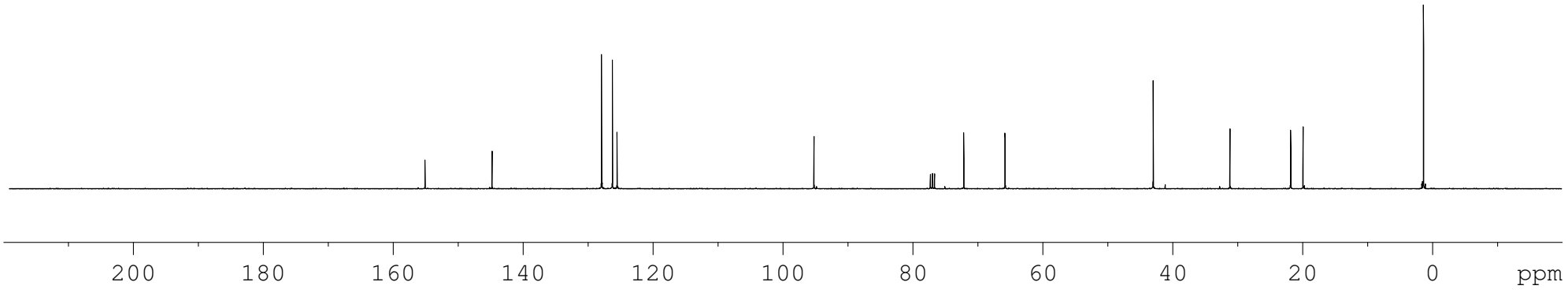

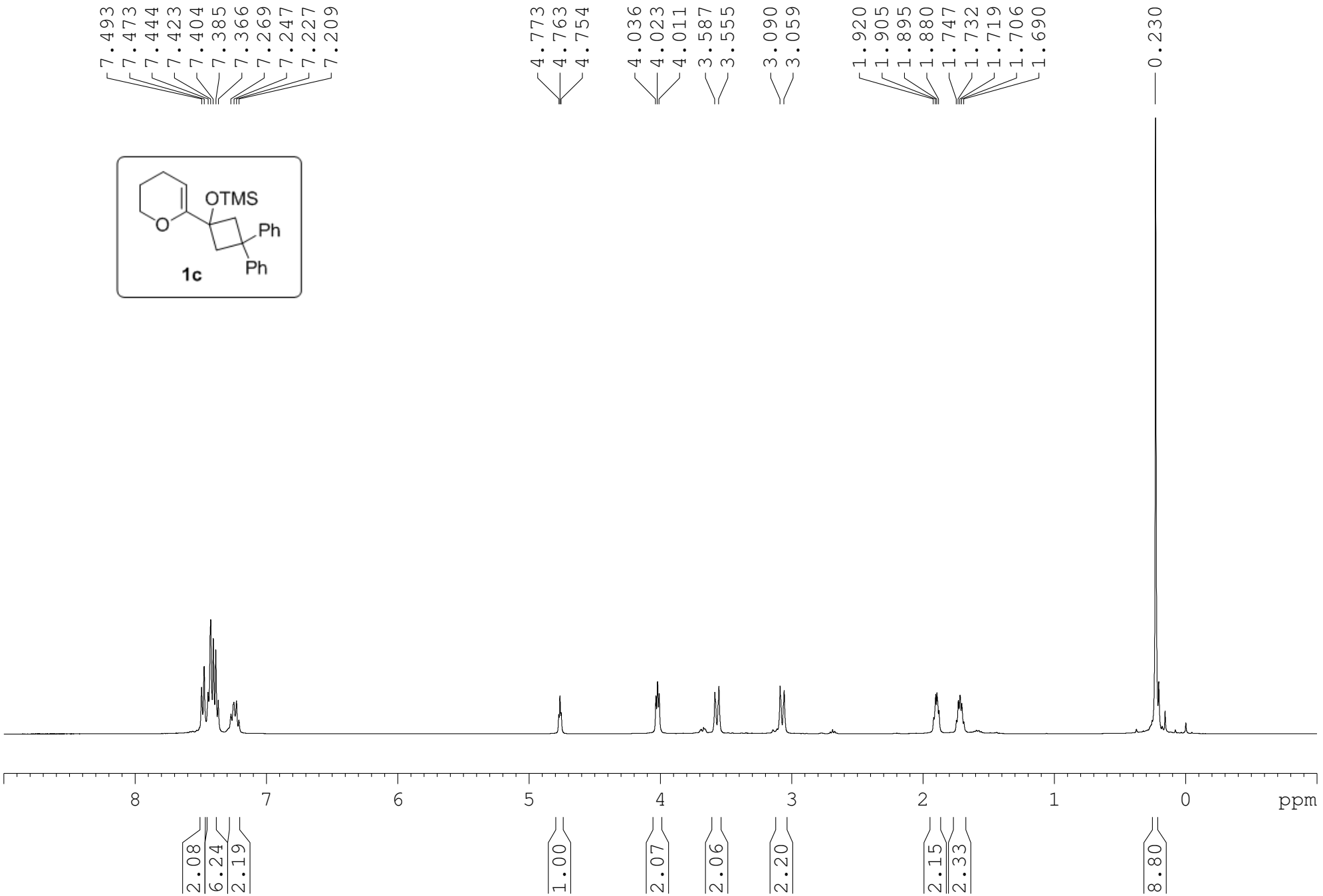
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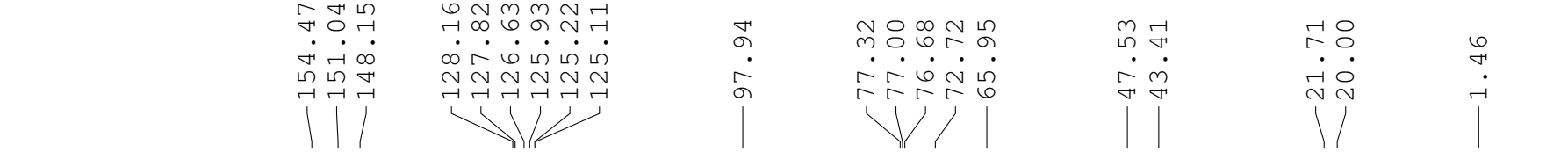
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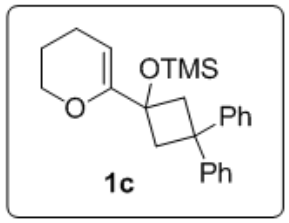
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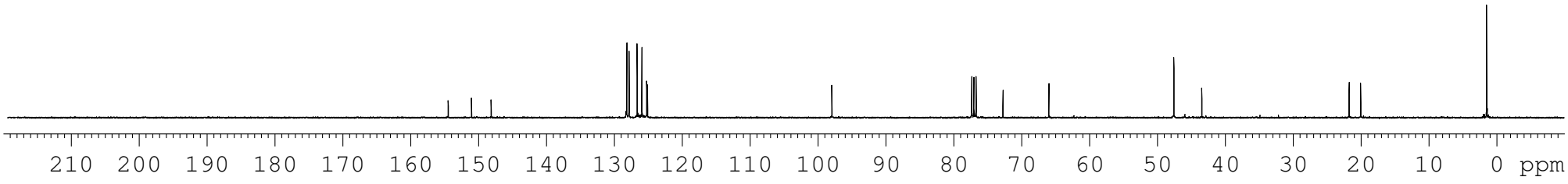
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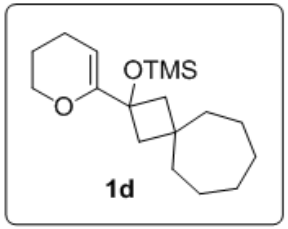
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2.021
2.006
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6.0
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5.0
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3.5
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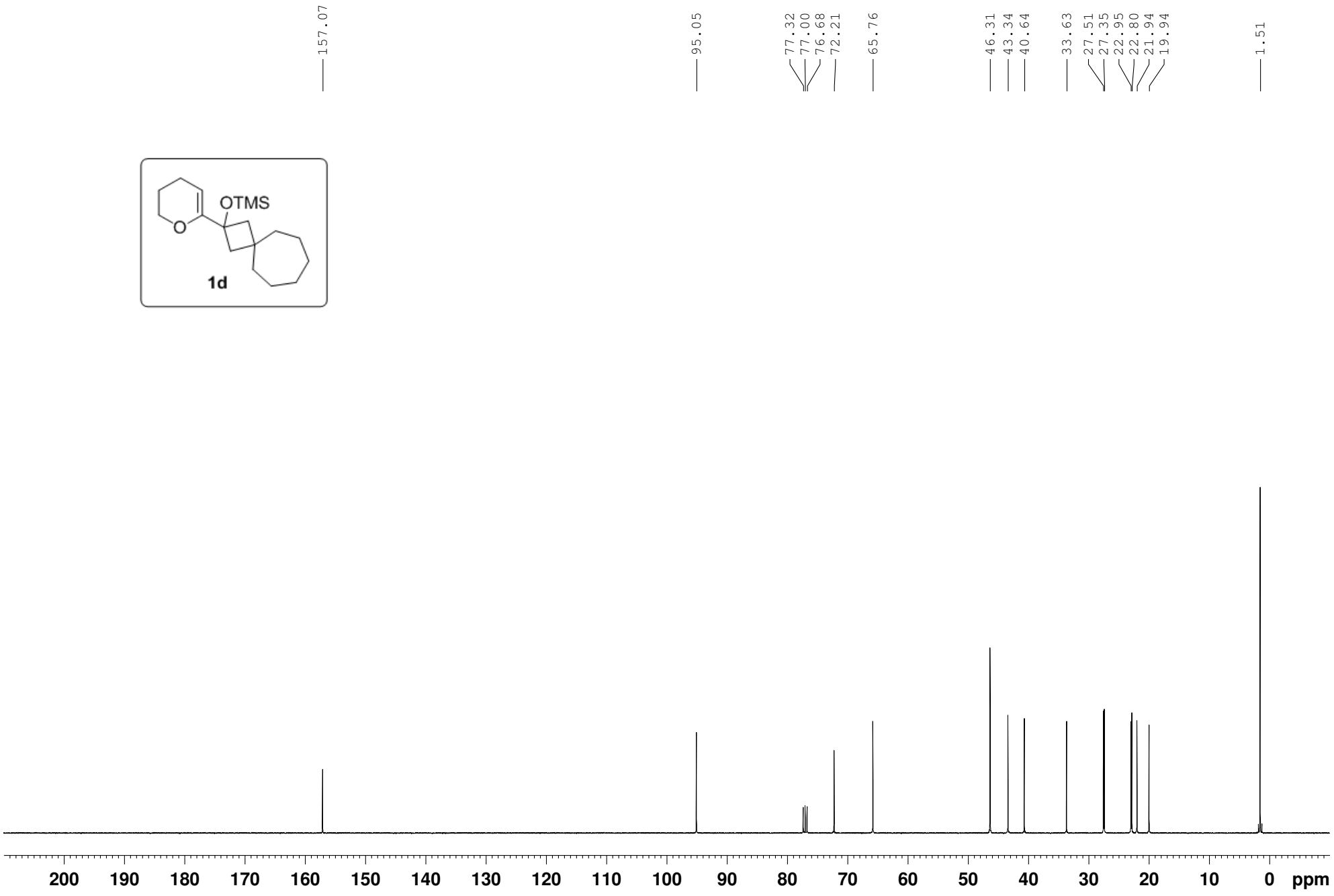
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22.95
22.80
21.94
19.94
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OTMS
O
1d
200
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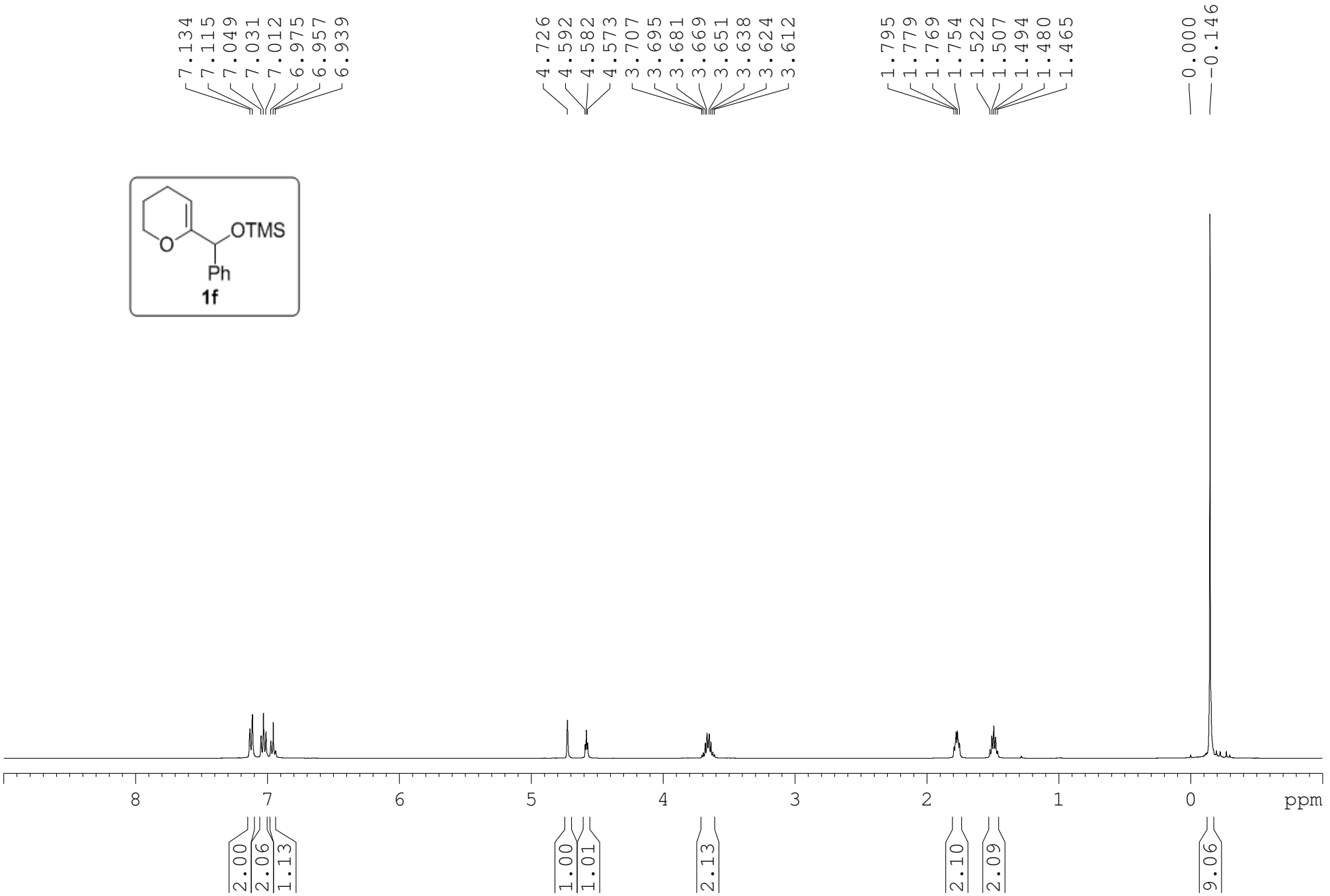
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1.779
1.769
1.754
1.522
1.507
1.494
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0.000
-0.146
OTMS
Ph
1f
8
7
6
5
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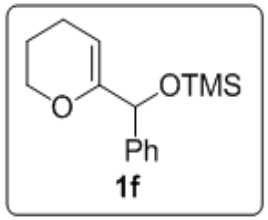
2.09
9.06


OTMS
Ph
1f

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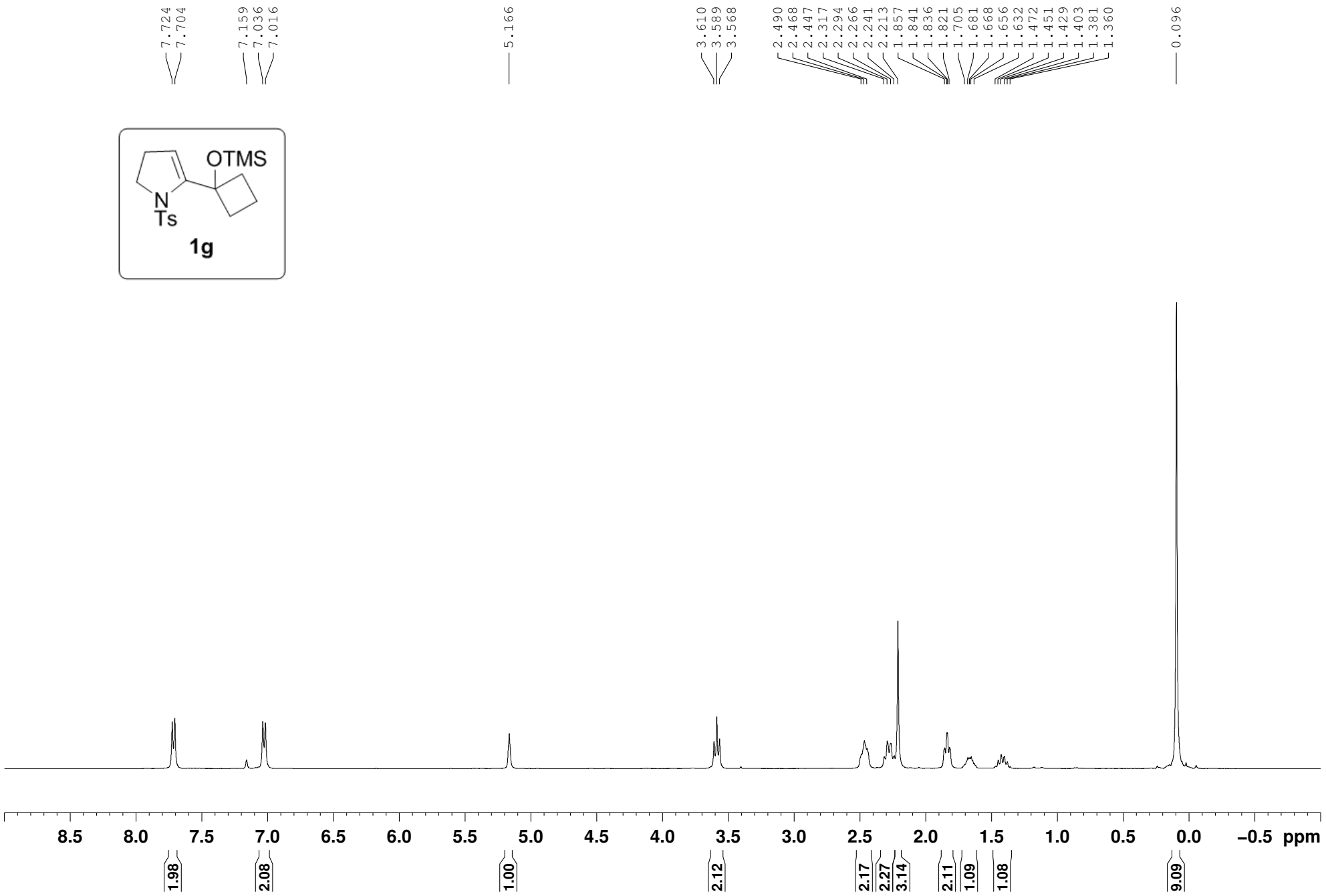
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2.317
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2.241
2.213
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1.841
1.836
1.821
1.705
1.681
1.668
1.656
1.632
1.472
1.451
1.429
1.403
1.381
1.360
0.096
OTMS
N
Ts
1g
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
−0.5
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3.14
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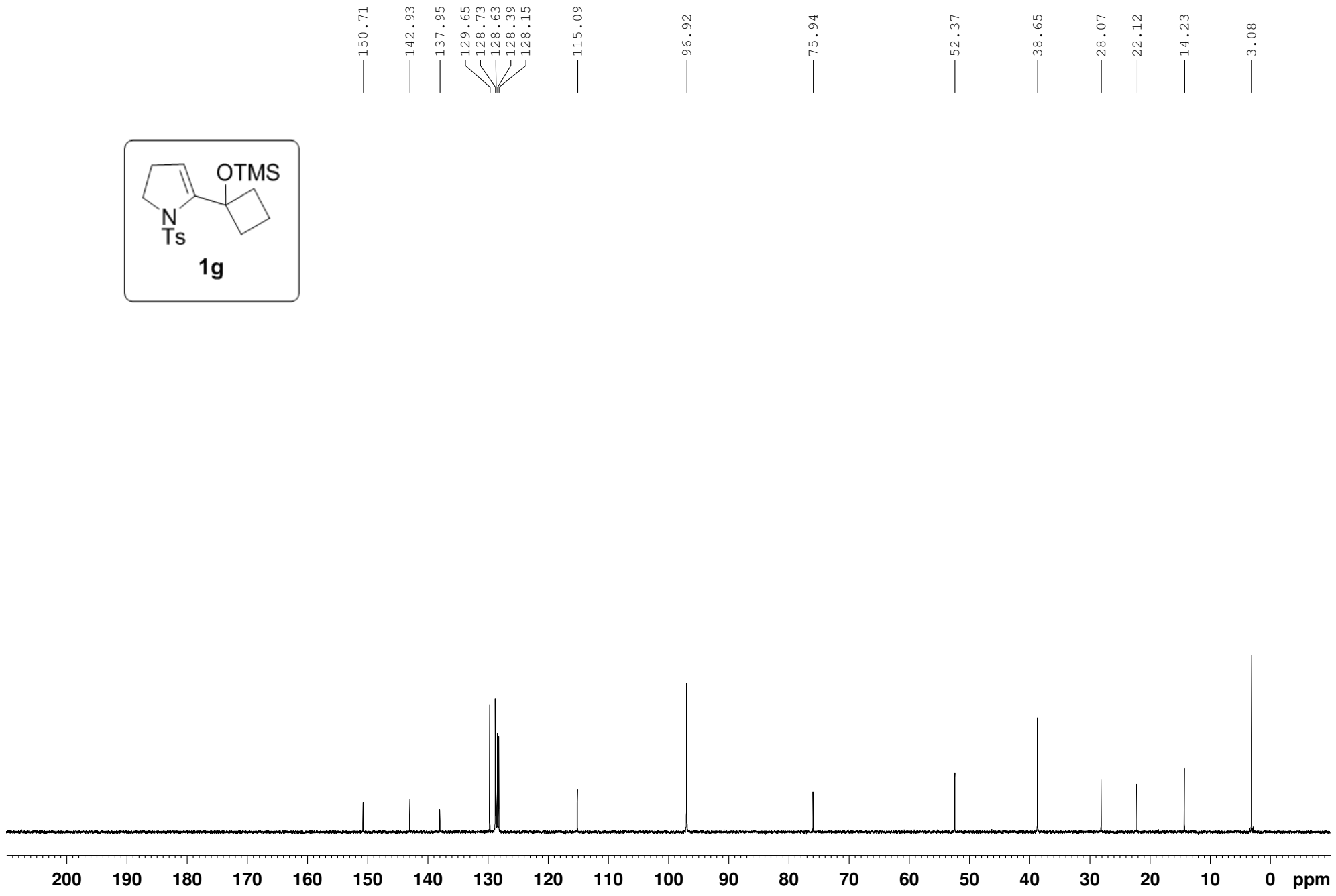
1.08
9.09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128.15
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96.92
75.94
52.37
38.65
28.07
22.12
14.23
3.08
OTMS
N
Ts
1g
200
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140
130
120
110
100
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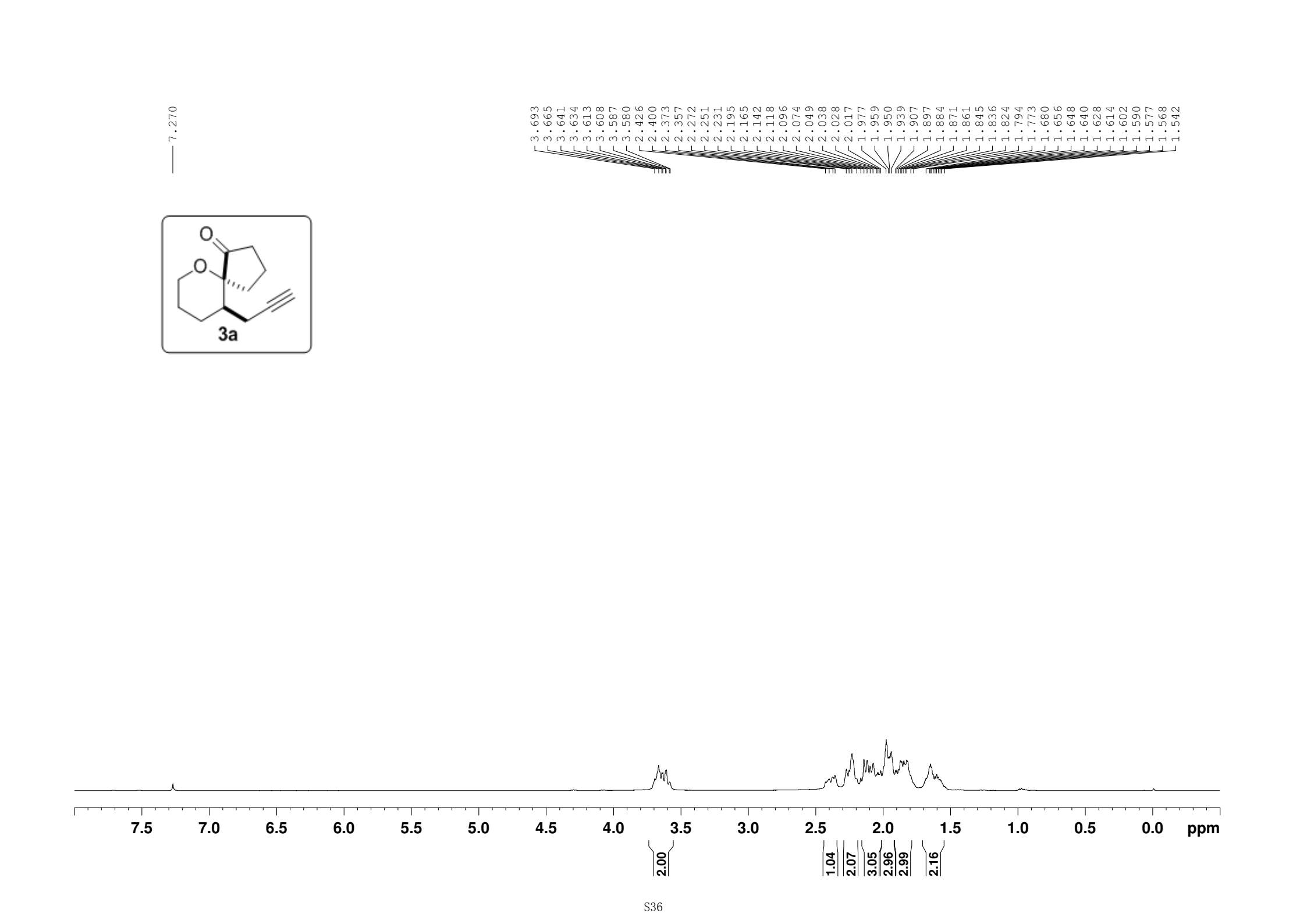
ppm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2.231
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2.142
2.118
2.096
2.074
2.049
2.038
2.028
2.017
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1.824
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1.680
1.656
1.648
1.640
1.628
1.614
1.602
1.590
1.577
1.568
1.542
O
O
3a
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6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
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0.0
ppm
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2.07
3.05
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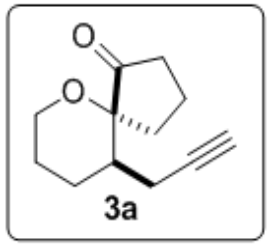
2.16



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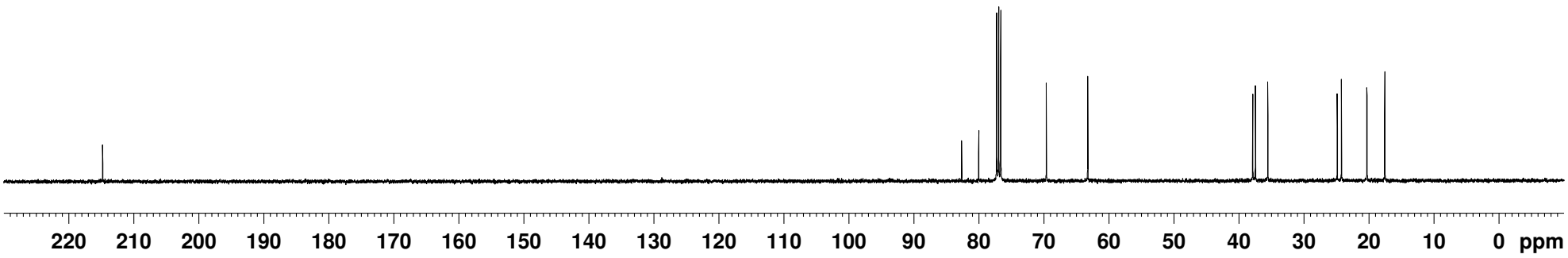
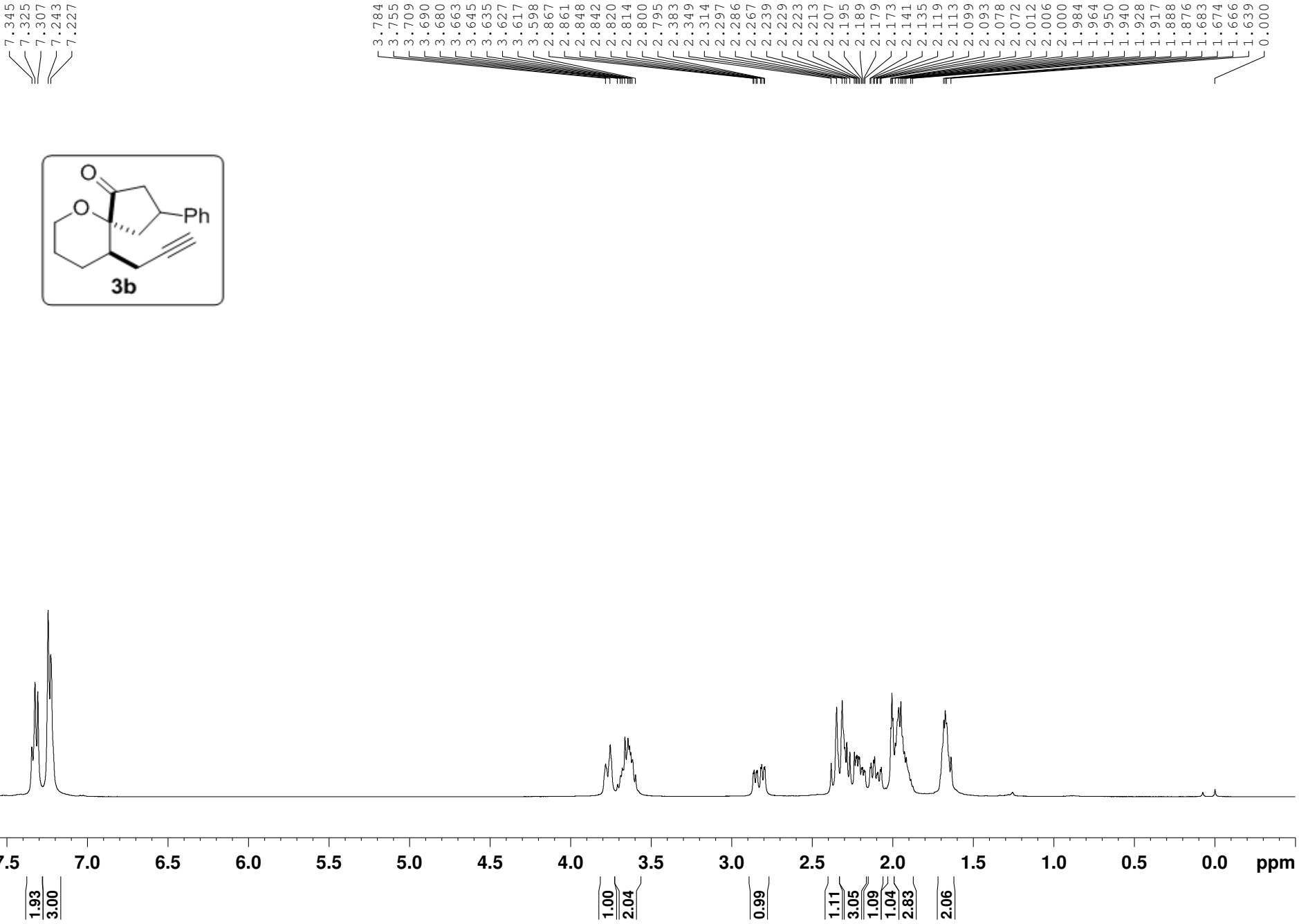
24.28
20.34
17.61

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3.627
3.617
3.598
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2.814
2.800
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2.383
2.349
2.314
2.297
2.286
2.267
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2.229
2.223
2.213
2.207
2.195
2.189
2.179
2.173
2.141
2.135
2.119
2.113
2.099
2.093
2.078
2.072
2.012
2.006
2.000
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1.964
1.950
1.940
1.928
1.917
1.888
1.876
1.683
1.674
1.666
1.639
0.000
O
O
Ph
3b
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6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
ppm
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1.00
2.04
0.99
1.11
3.05
1.09
1.04
2.83
2.06

212.78
143.07
128.64
126.71
126.63
82.47
81.19
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70.01
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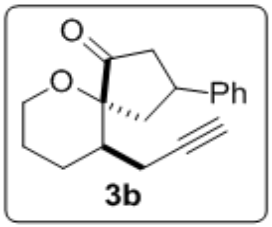
24.79
21.05



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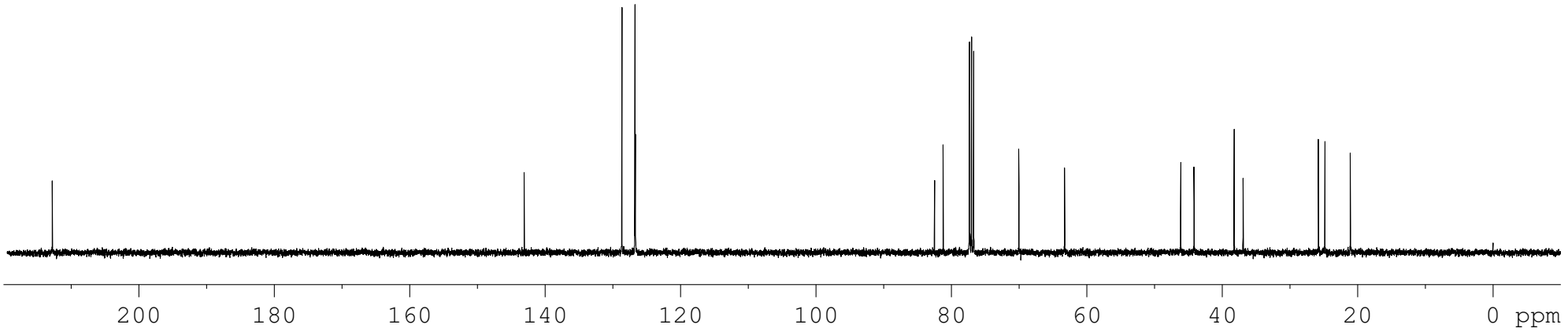

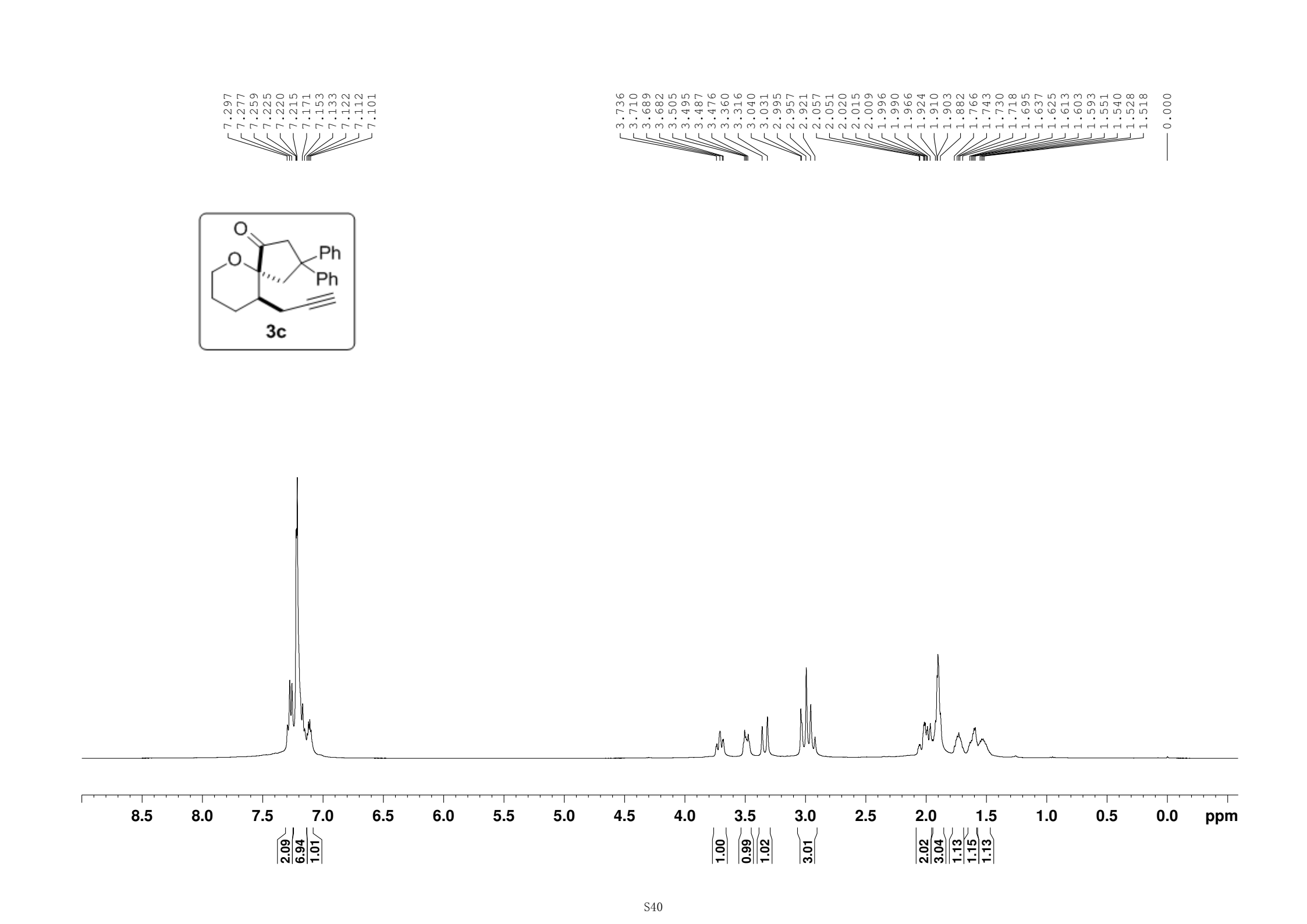
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7.101
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3.710
3.689
3.682
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3.495
3.487
3.476
3.360
3.316
3.040
3.031
2.995
2.957
2.921
2.057
2.051
2.020
2.015
2.009
1.996
1.990
1.966
1.924
1.910
1.903
1.882
1.766
1.743
1.730
1.718
1.695
1.637
1.625
1.613
1.603
1.593
1.551
1.540
1.528
1.518
0.000
O
O
Ph
Ph
3c
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7.5
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6.5
6.0
5.5
5.0
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4.0
3.5
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1.0
0.5
0.0
ppm
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1.00
0.99
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3.01
2.02
3.04
1.13
1.15
1.13

213.08
148.29
147.59
128.58
128.11
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126.54
126.38
125.92
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80.35
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24.04
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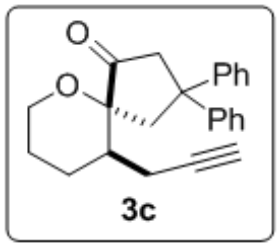

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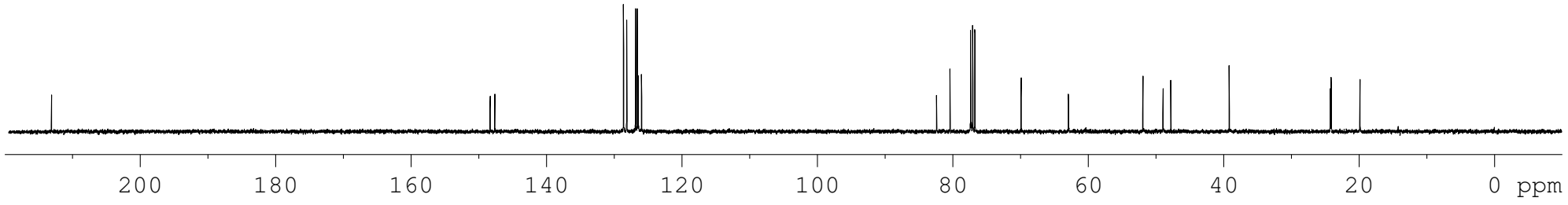

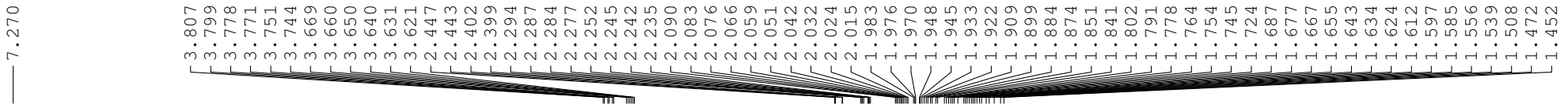
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2.443
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2.284
2.277
2.252
2.245
2.242
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2.083
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2.066
2.059
2.051
2.042
2.032
2.024
2.015
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1.976
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1.945
1.933
1.922
1.909
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1.874
1.851
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1.778
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1.754
1.745
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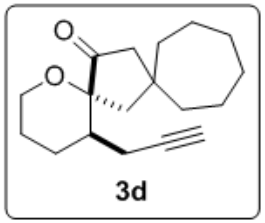
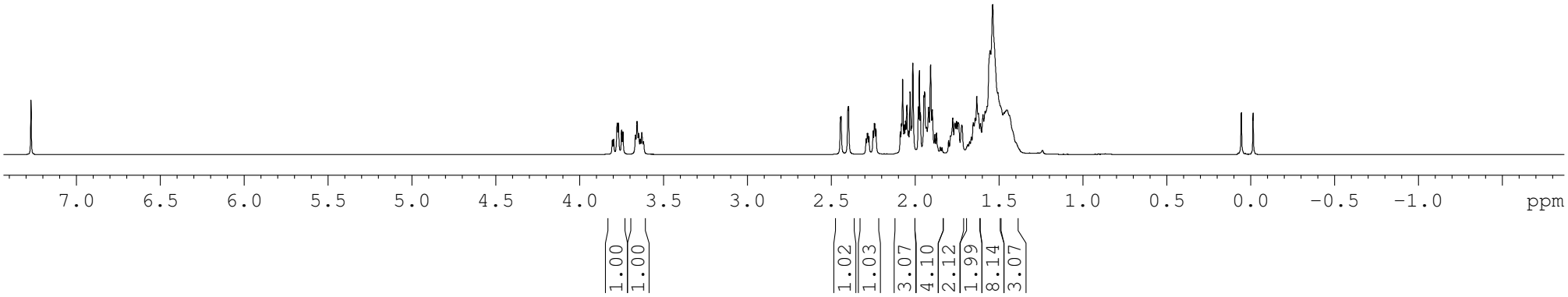
1.452


O
O
3d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1.0
0.5
0.0
−0.5
−1.0
ppm
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1.00
1.02
1.03
3.07
4.10
2.12
1.99
8.14
3.07

215.87

82.52
81.23
77.31
77.00
76.68
69.77
63.03
53.81
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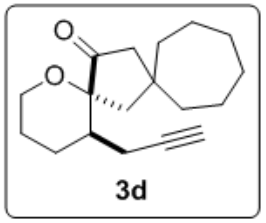
20.48



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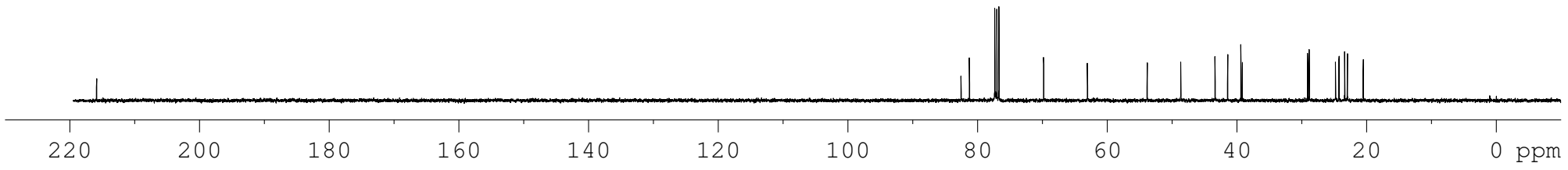

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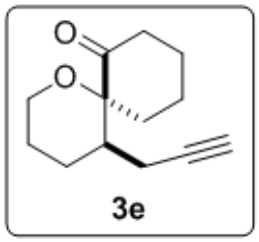

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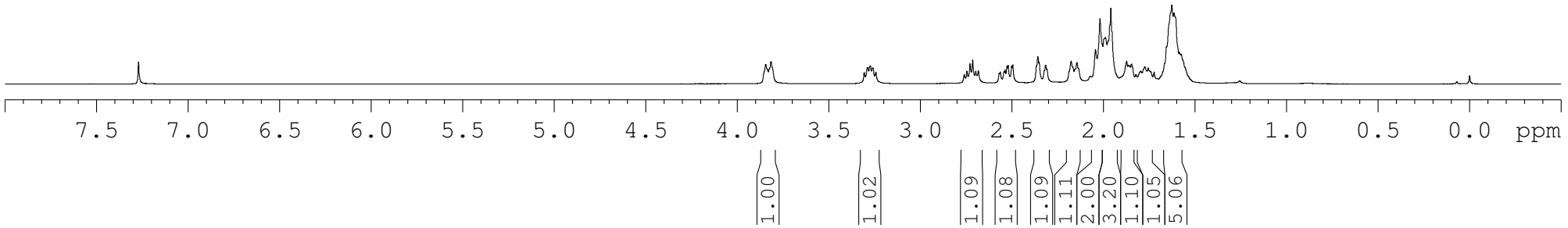

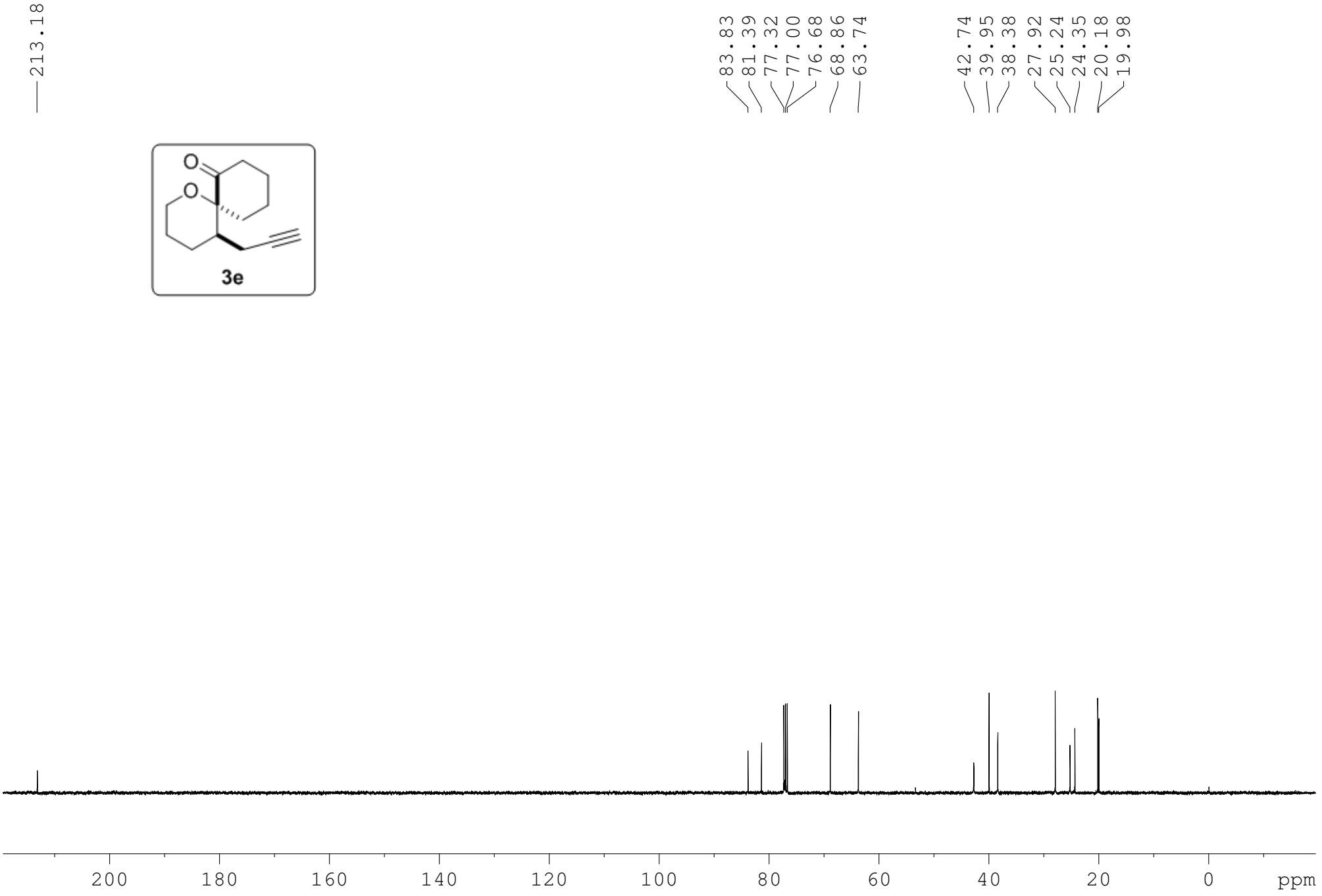
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25.24
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O
O
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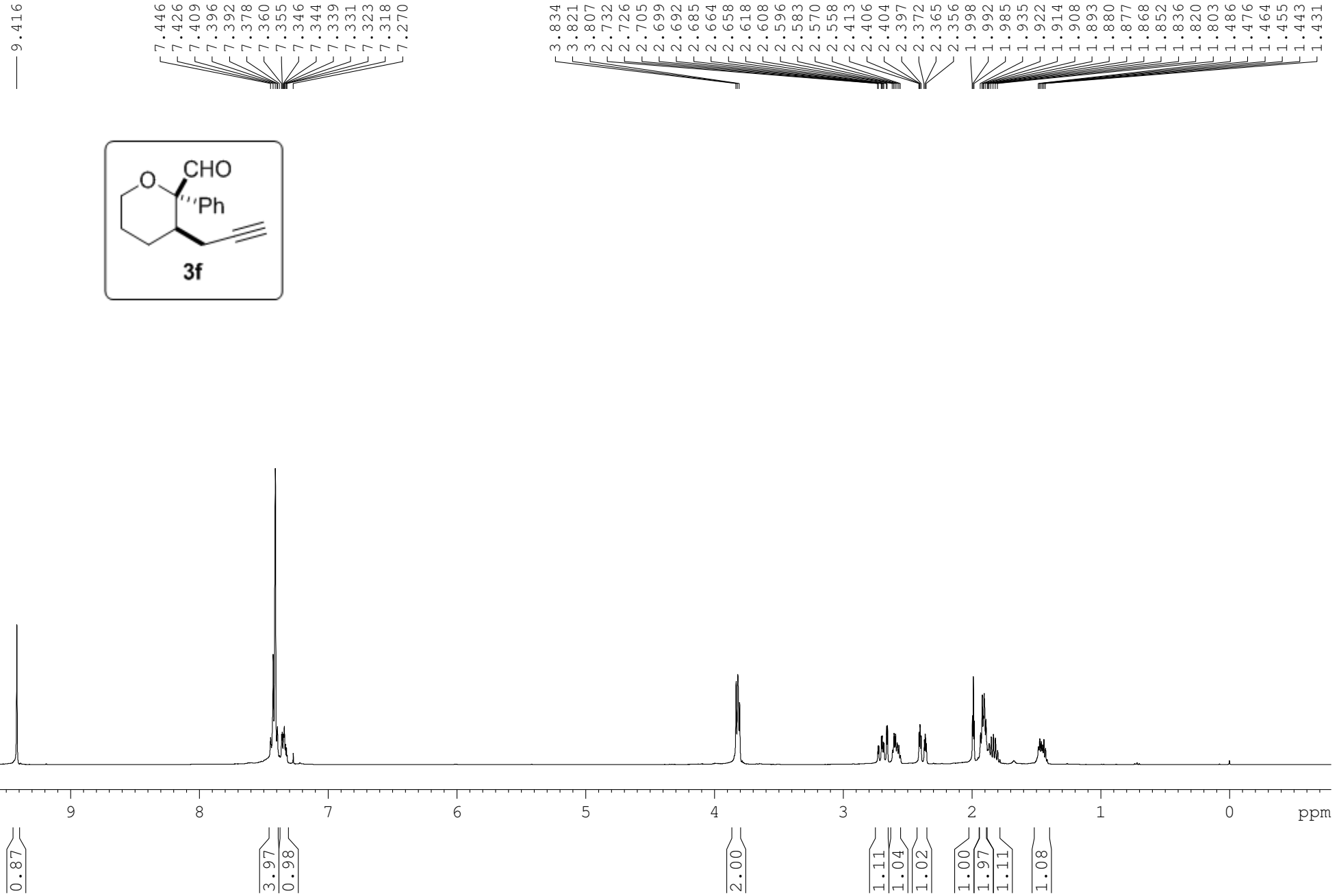
120
100
80
60
40
20
0
ppm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1.908
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1.803
1.486
1.476
1.464
1.455
1.443
1.431
O
CHO
Ph
3f
9
8
7
6
5
4
3
2
1
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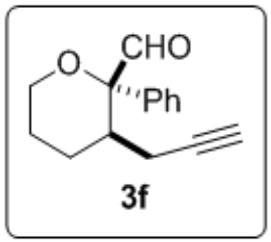
1.08



3f

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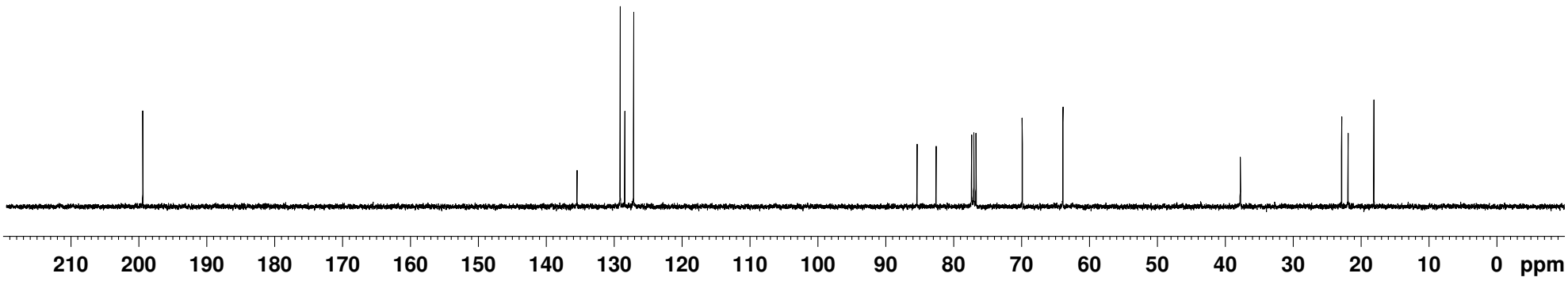
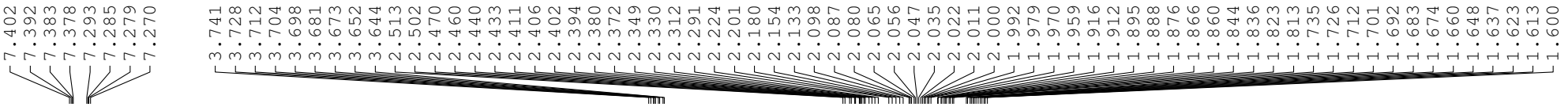
18.07

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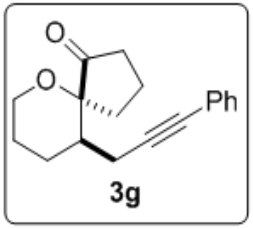
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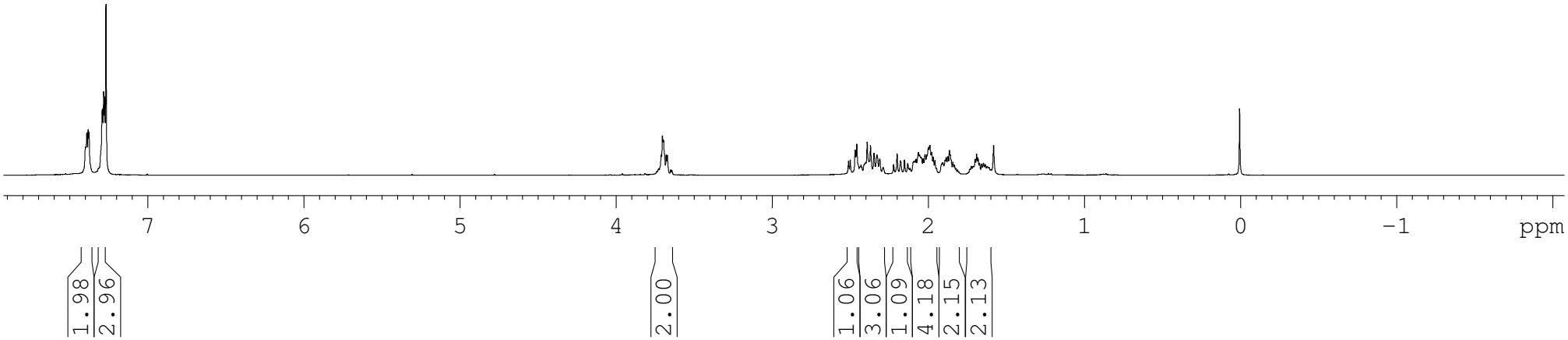
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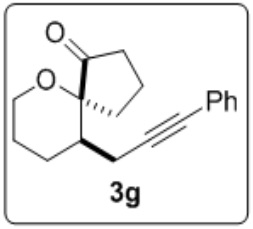

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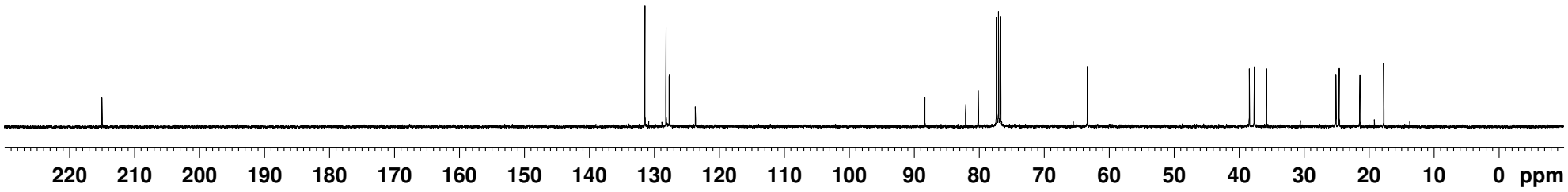

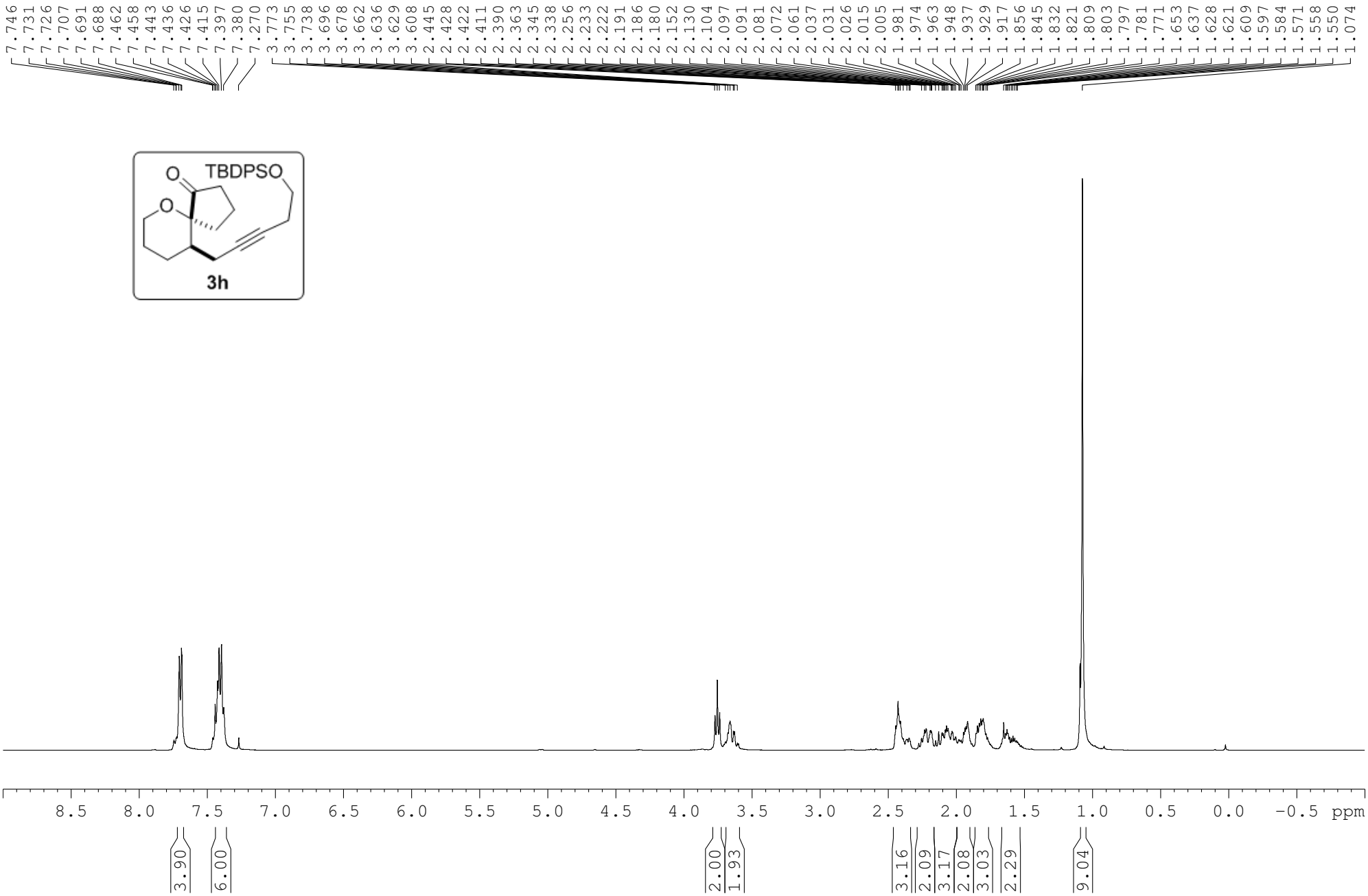
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1.074
O
TBDPSO
O
3h
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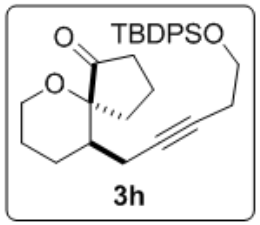

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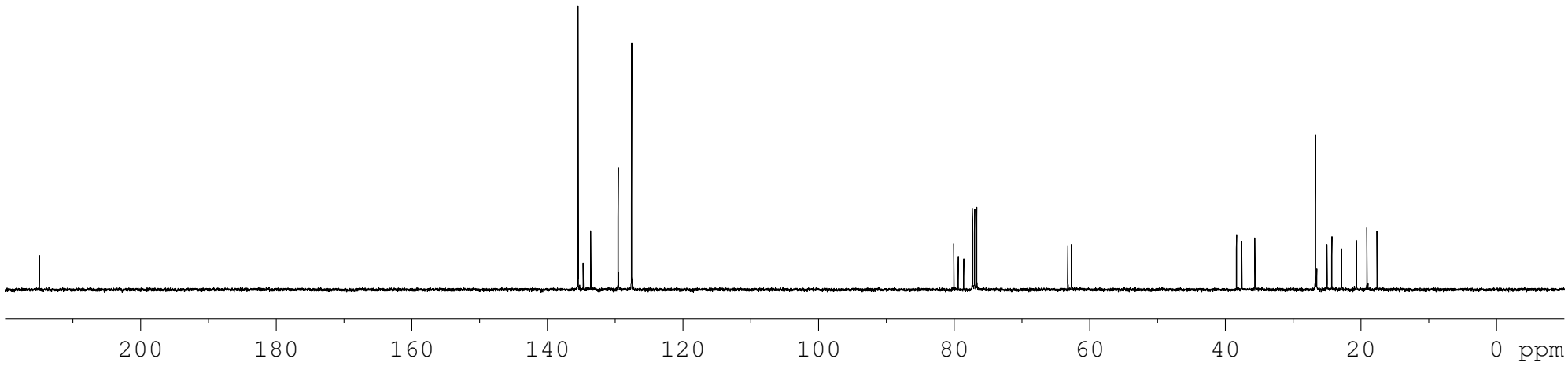

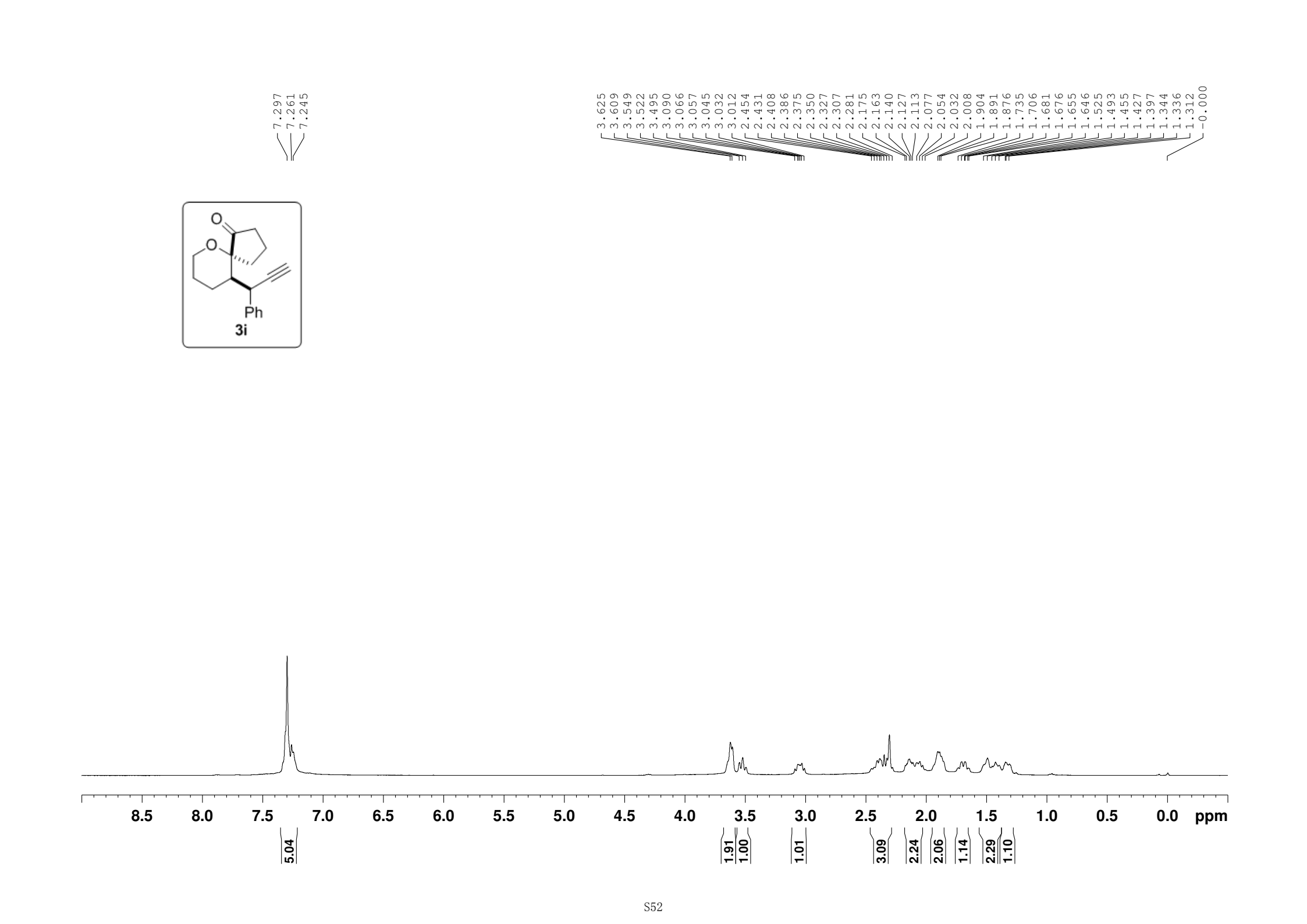
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2.350
2.327
2.307
2.281
2.175
2.163
2.140
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2.008
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1.427
1.397
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1.336
1.312
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O
O
Ph
3i
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7.0
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4.0
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2.29
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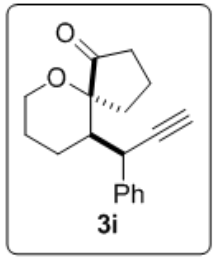

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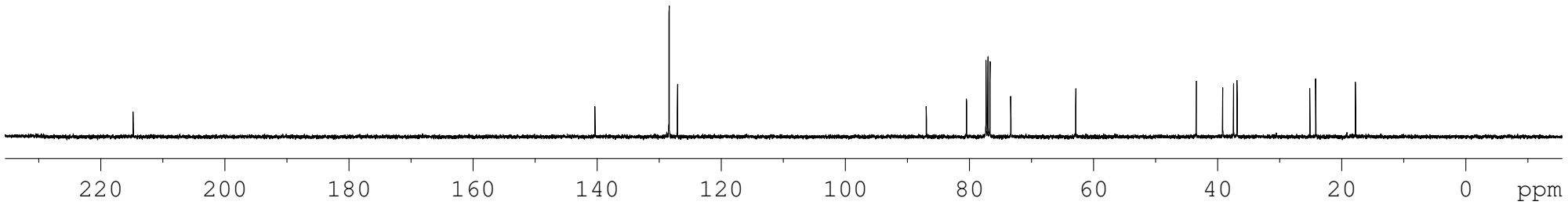

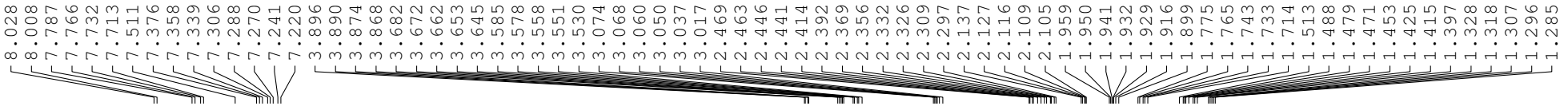
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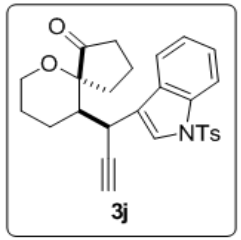
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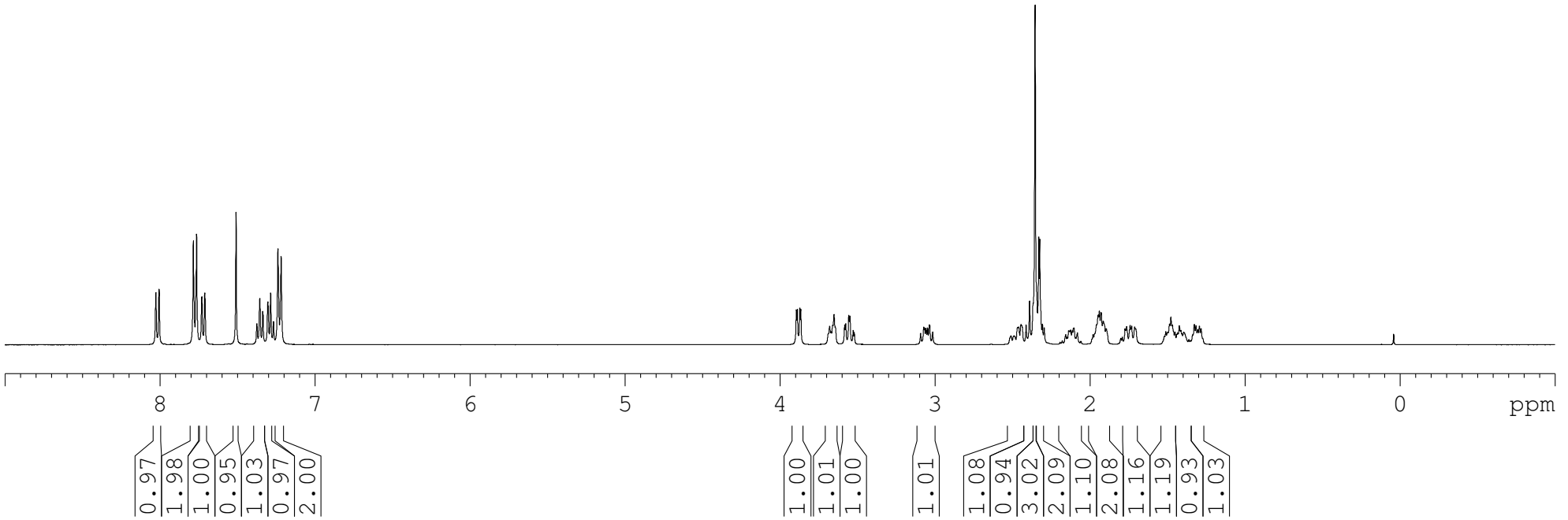
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2.08
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0.93
1.03

214.90

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113.92

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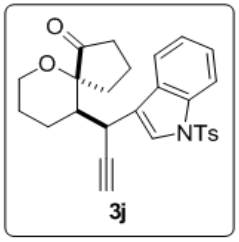

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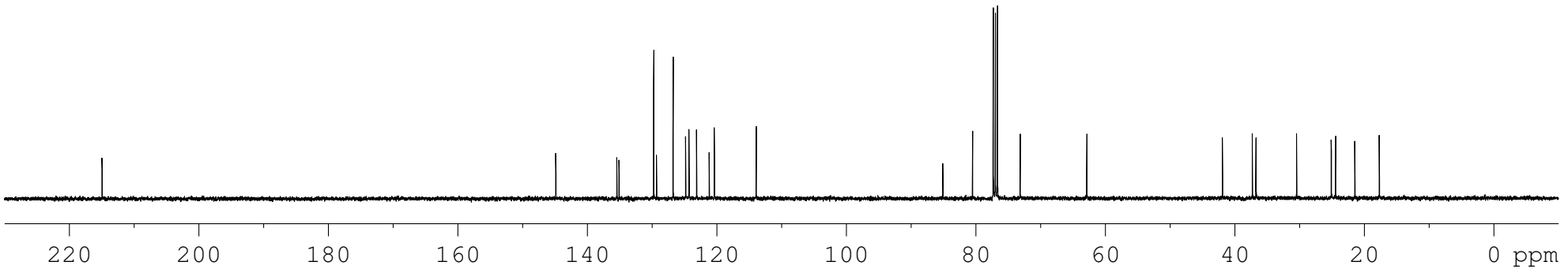

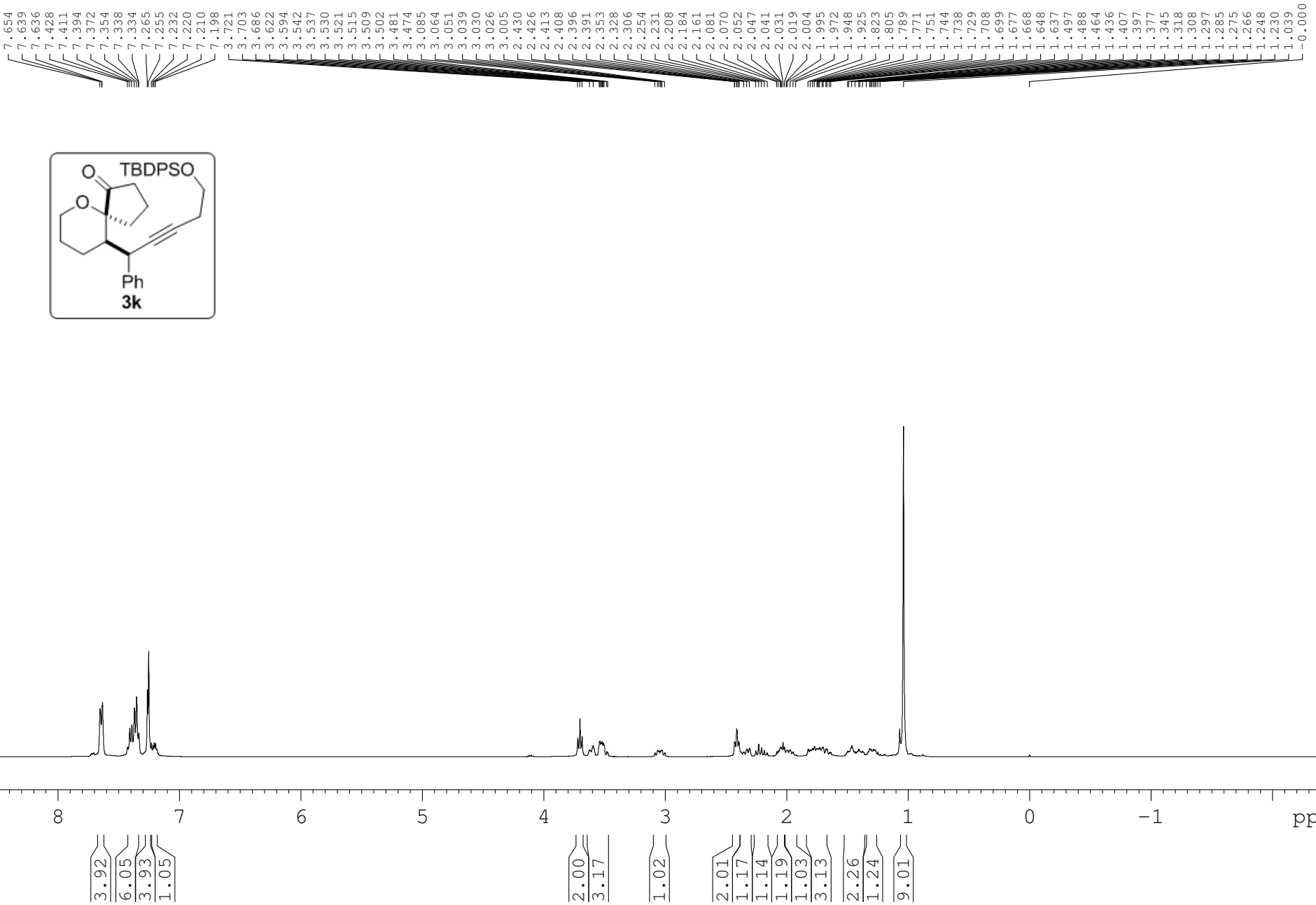
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TBDPSO
O
Ph
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−1
ppm
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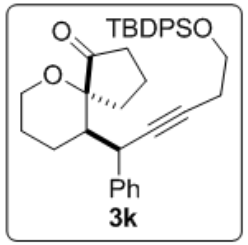

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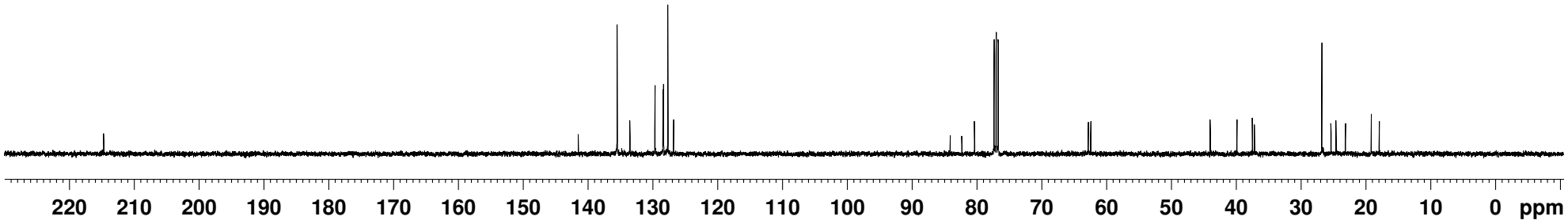

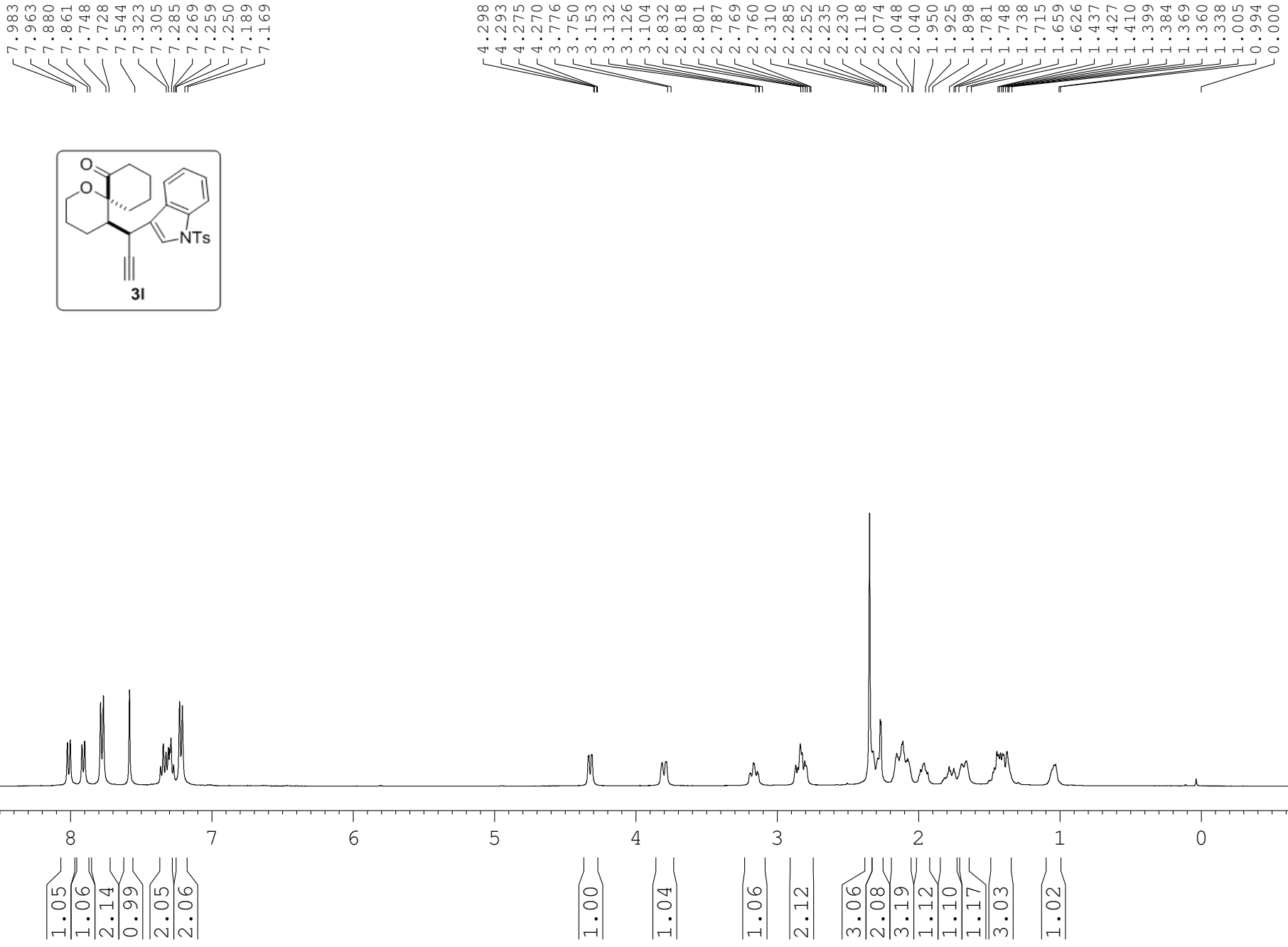
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7.169
4.298
4.293
4.275
4.270
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1.005
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0.000
O
O
NTs
3l
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7
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5
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1.06
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2.08
3.19
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1.10
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3.03
1.02

213.93

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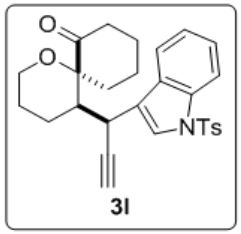

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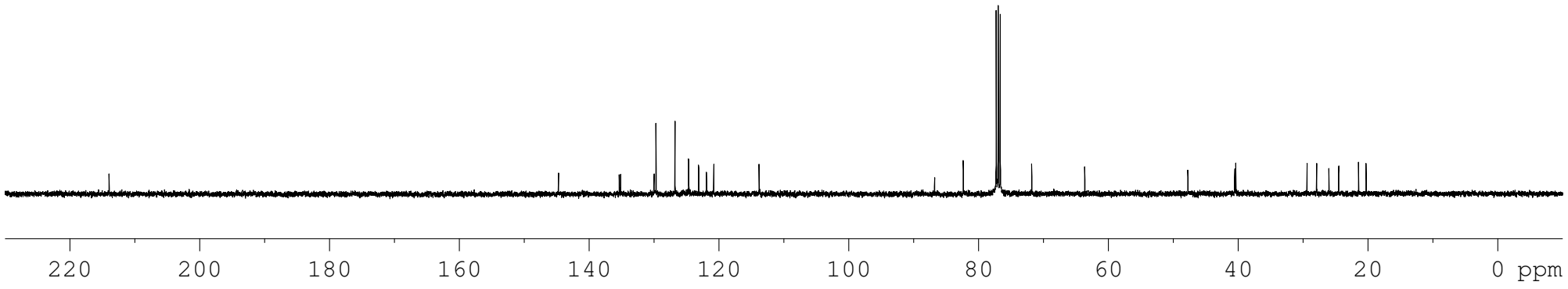

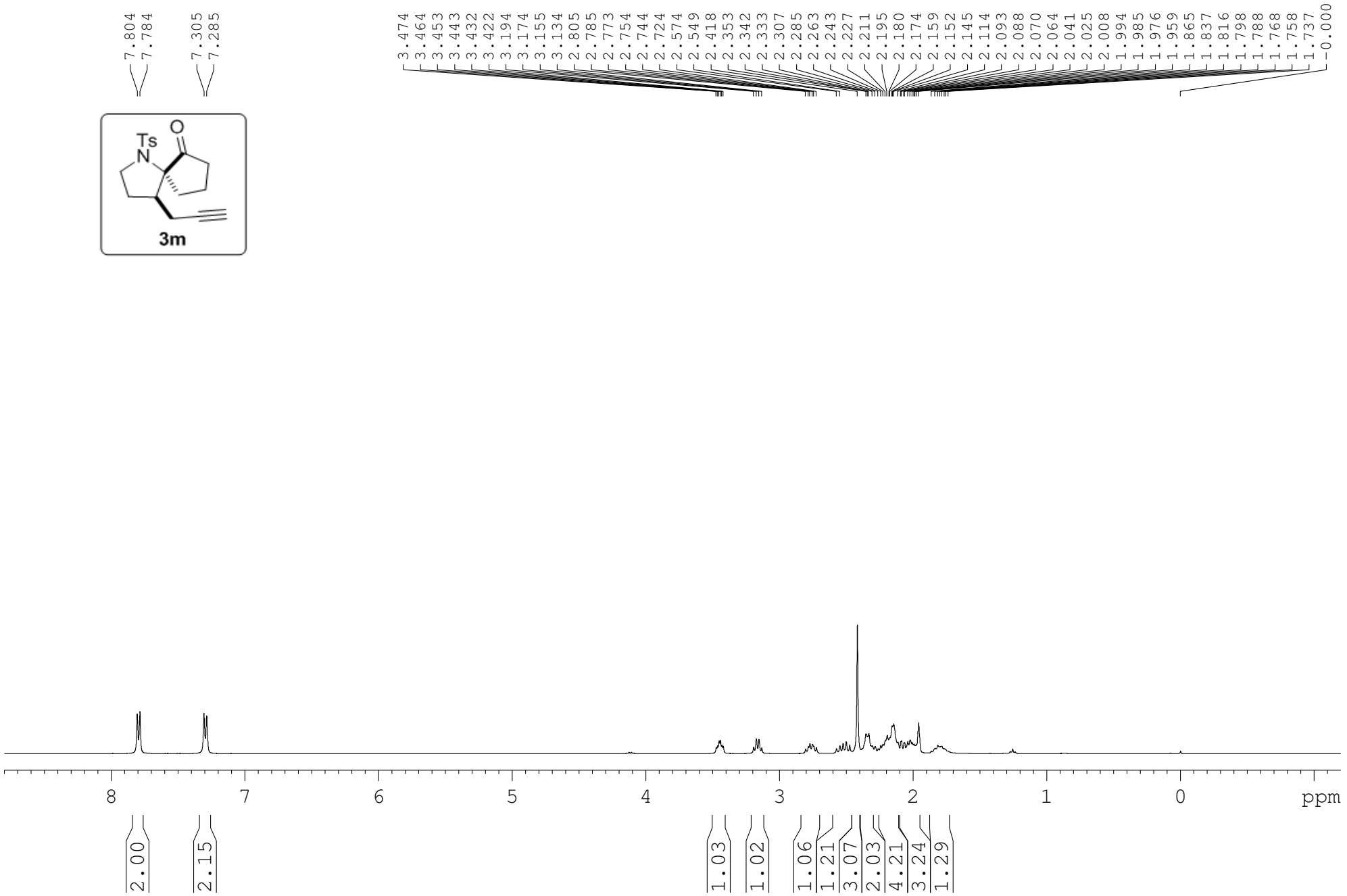
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O
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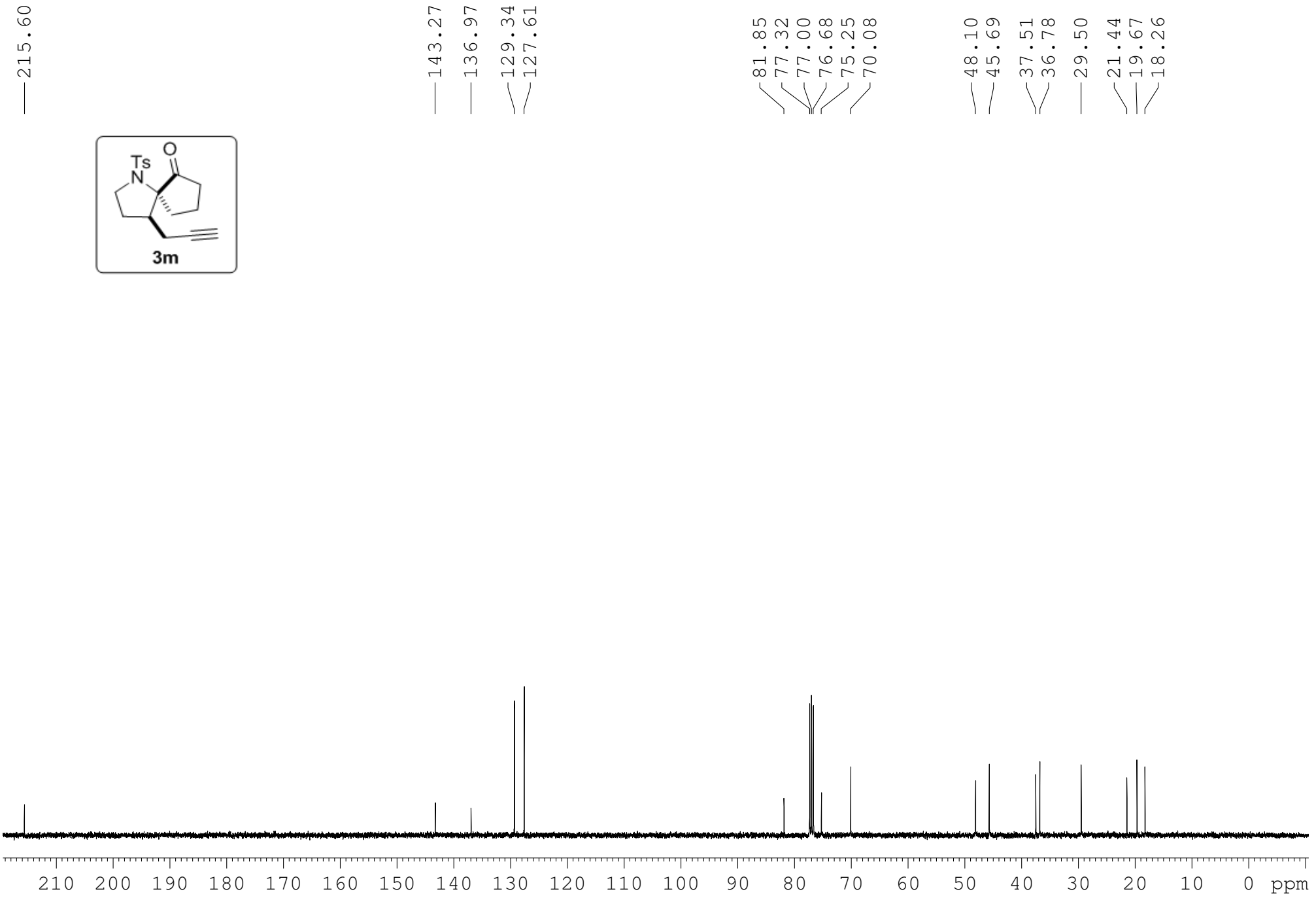
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N
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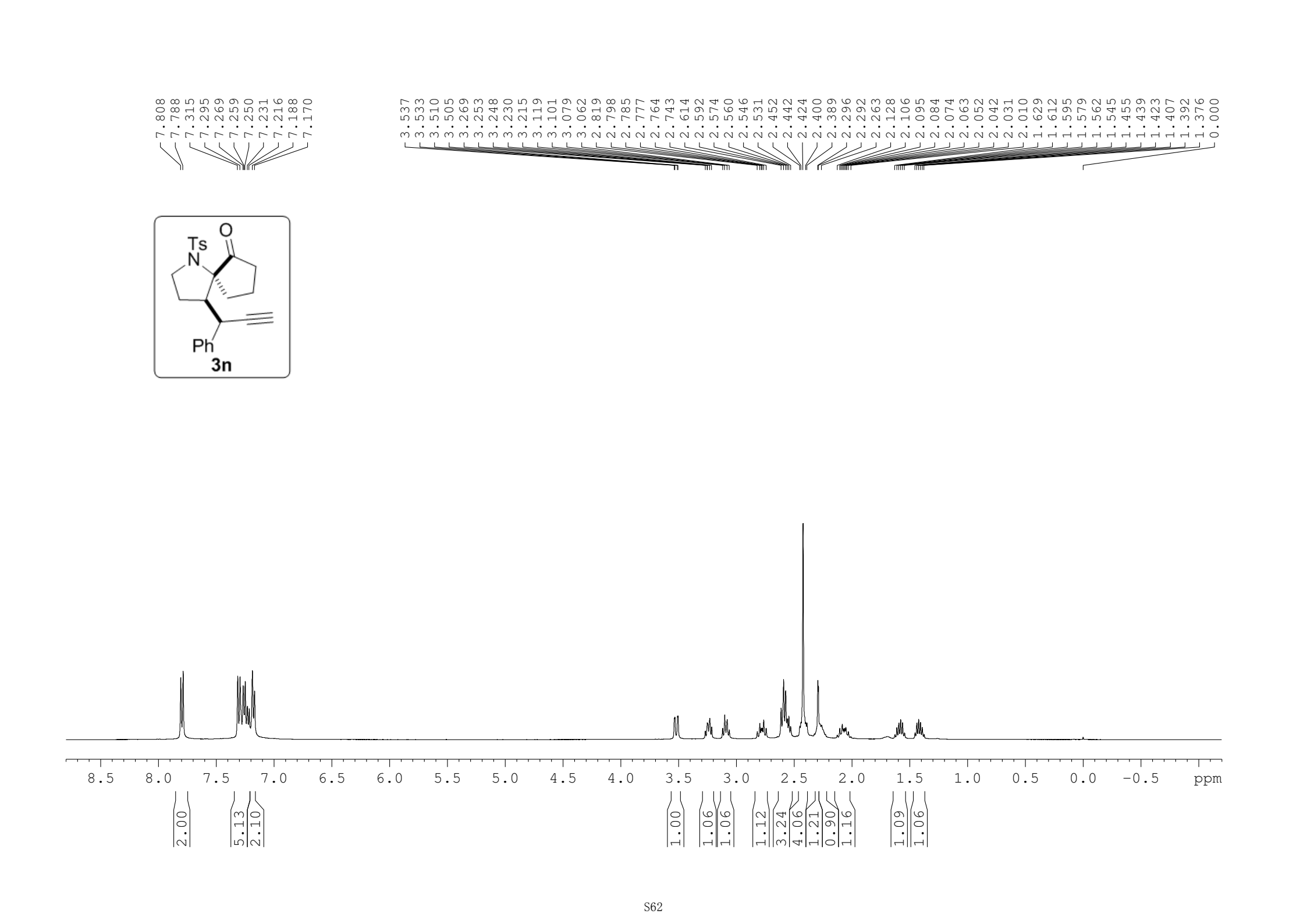
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1.455
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1.376
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Ts
N
O
Ph
3n
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0.0
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ppm
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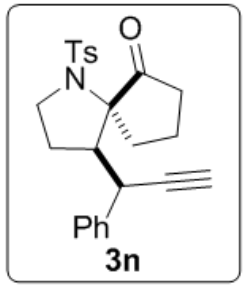
1.06



3n

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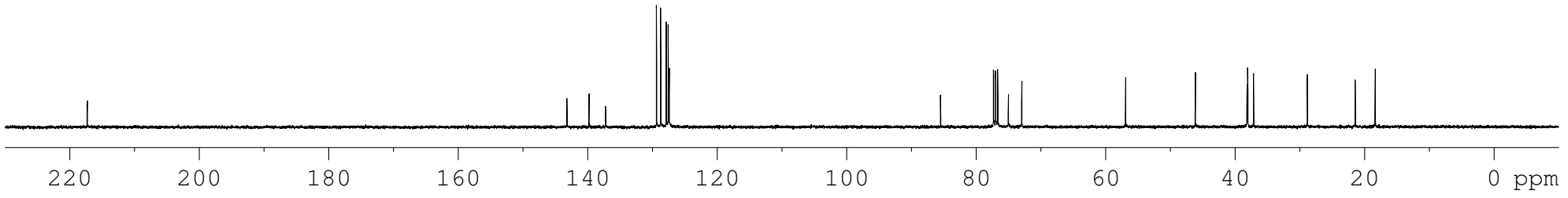

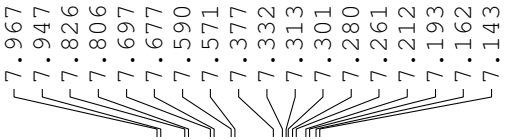
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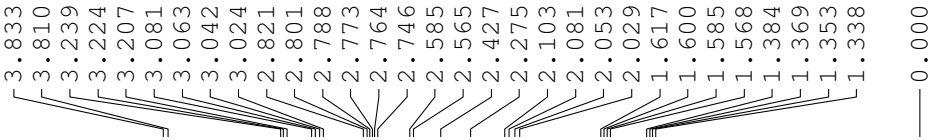
7.280
7.261
7.212
7.193
7.162
7.143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3.810
3.239
3.224
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3.081
3.063
3.042
3.024
2.821
2.801
2.788
2.773
2.764
2.746
2.585
2.565
2.427
2.275
2.103
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1.568
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1.338
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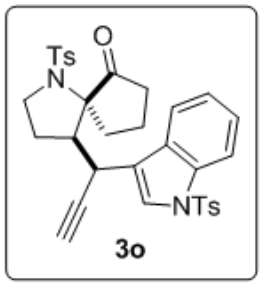
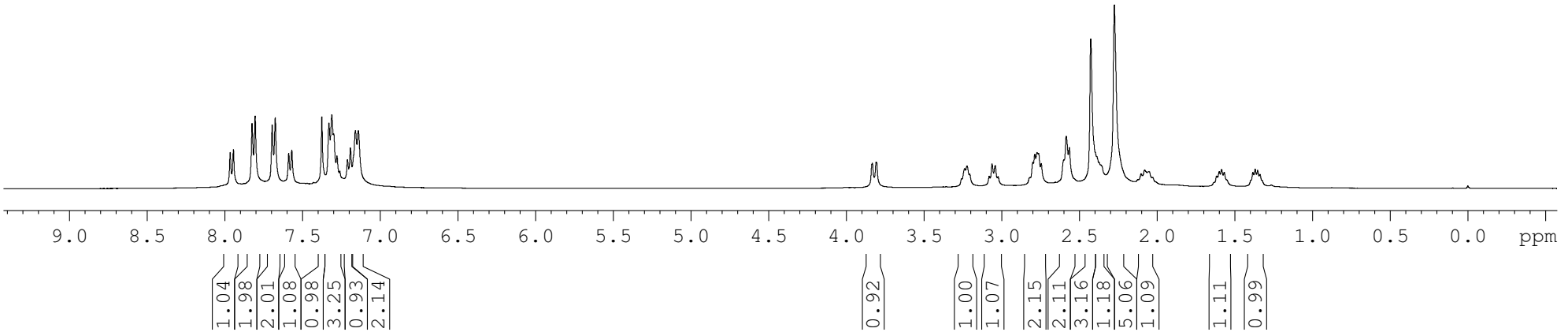

Ts
N
O
NTs
3o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6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
ppm
1.04
1.98
2.01
1.08
0.98
3.25
0.93
2.14
0.92
1.00
1.07
2.15
2.11
3.16
1.18
5.06
1.09
1.11
0.99

216.95

145.01
143.31
137.04
135.34
134.78
129.74
129.38
128.52
127.48
126.60
125.00
124.07
123.16
120.24
120.09
113.85

83.69
77.32
77.00
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72.69

54.92

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38.07
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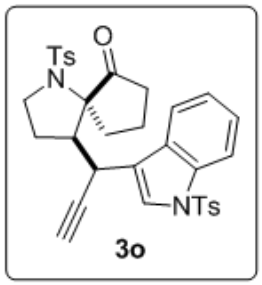
21.33
18.28



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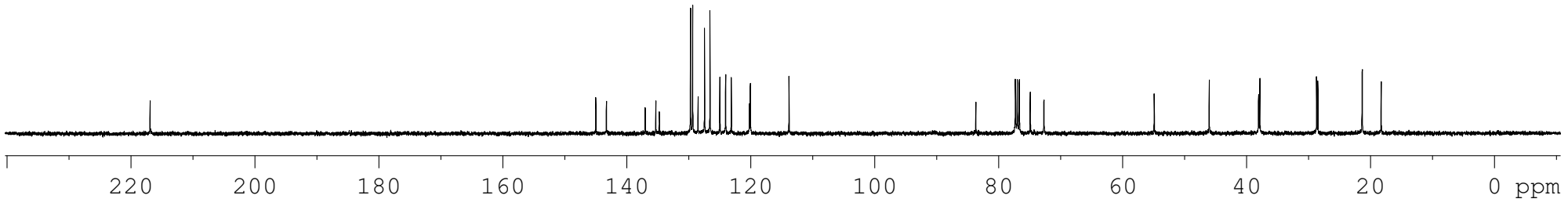

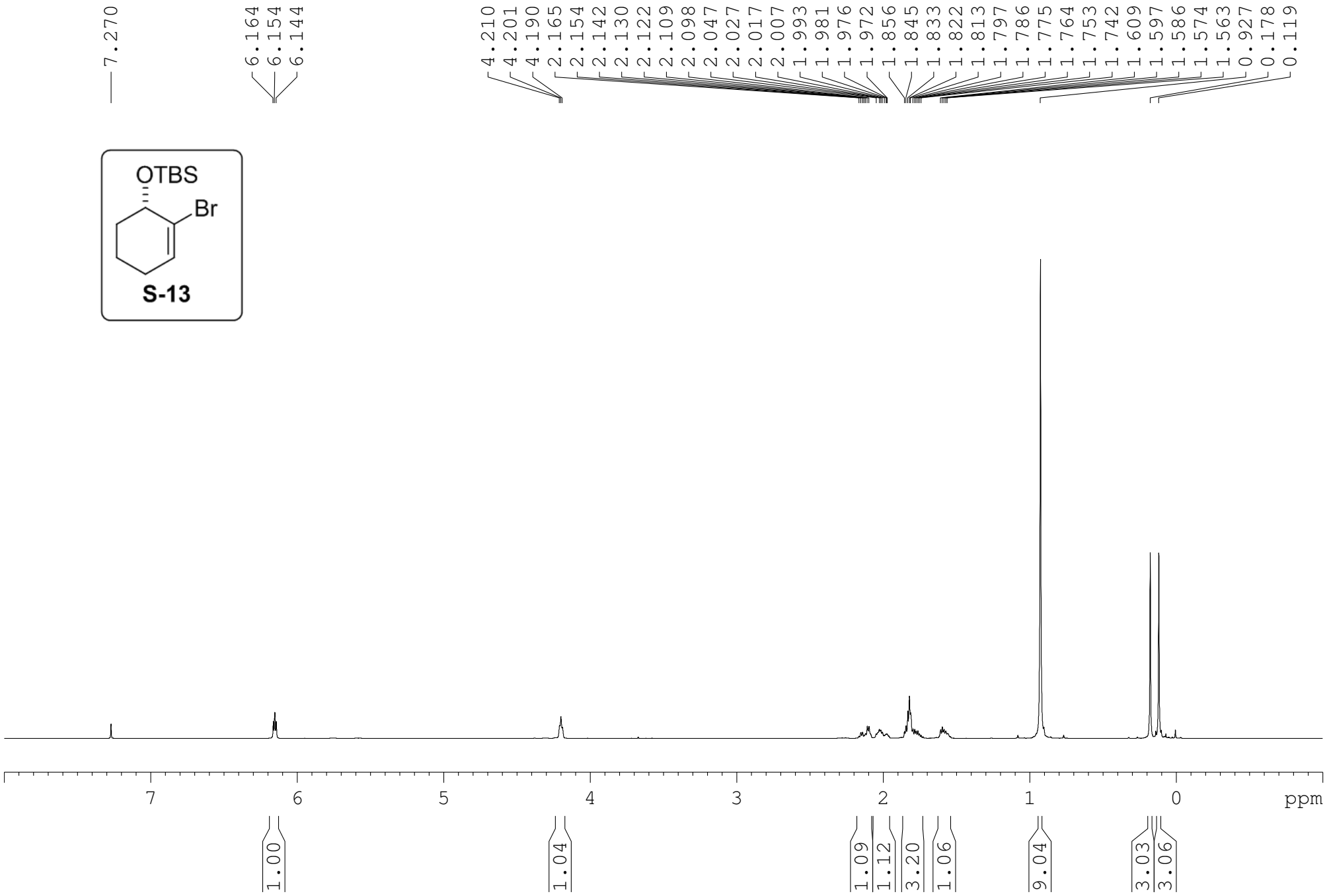
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6.154
6.144
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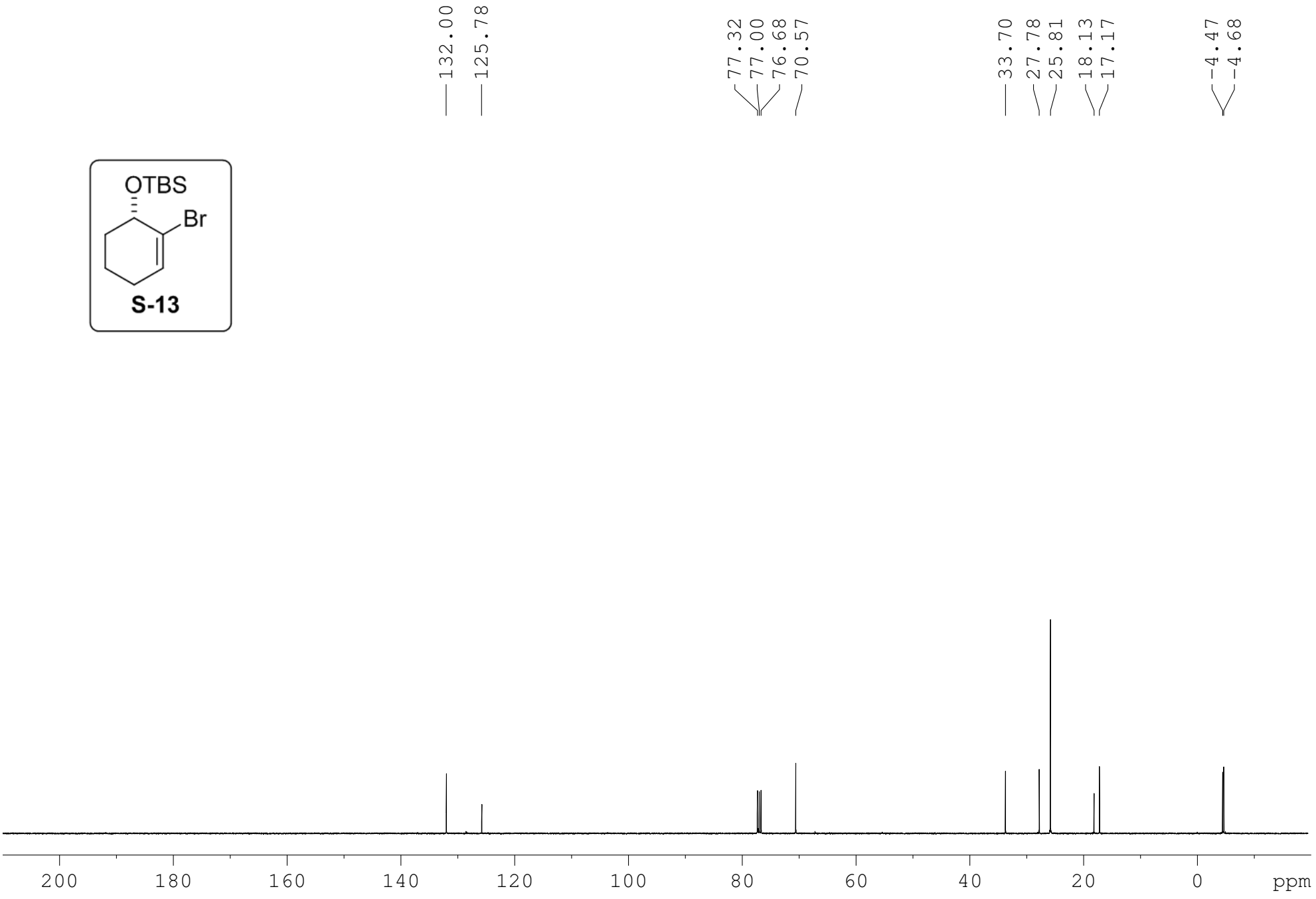
4.201
4.190
2.165
2.154
2.142
2.130
2.122
2.109
2.098
2.047
2.027
2.017
2.007
1.993
1.981
1.976
1.972
1.856
1.845
1.833
1.822
1.813
1.797
1.786
1.775
1.764
1.753
1.742
1.609
1.597
1.586
1.574
1.563
0.927
0.178
0.119
OTBS
Br
S-13
7
6
5
4
3
2
1
0
ppm
1.00
1.04
1.09
1.12
3.20
1.06
9.04
3.03
3.06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77.32
77.00
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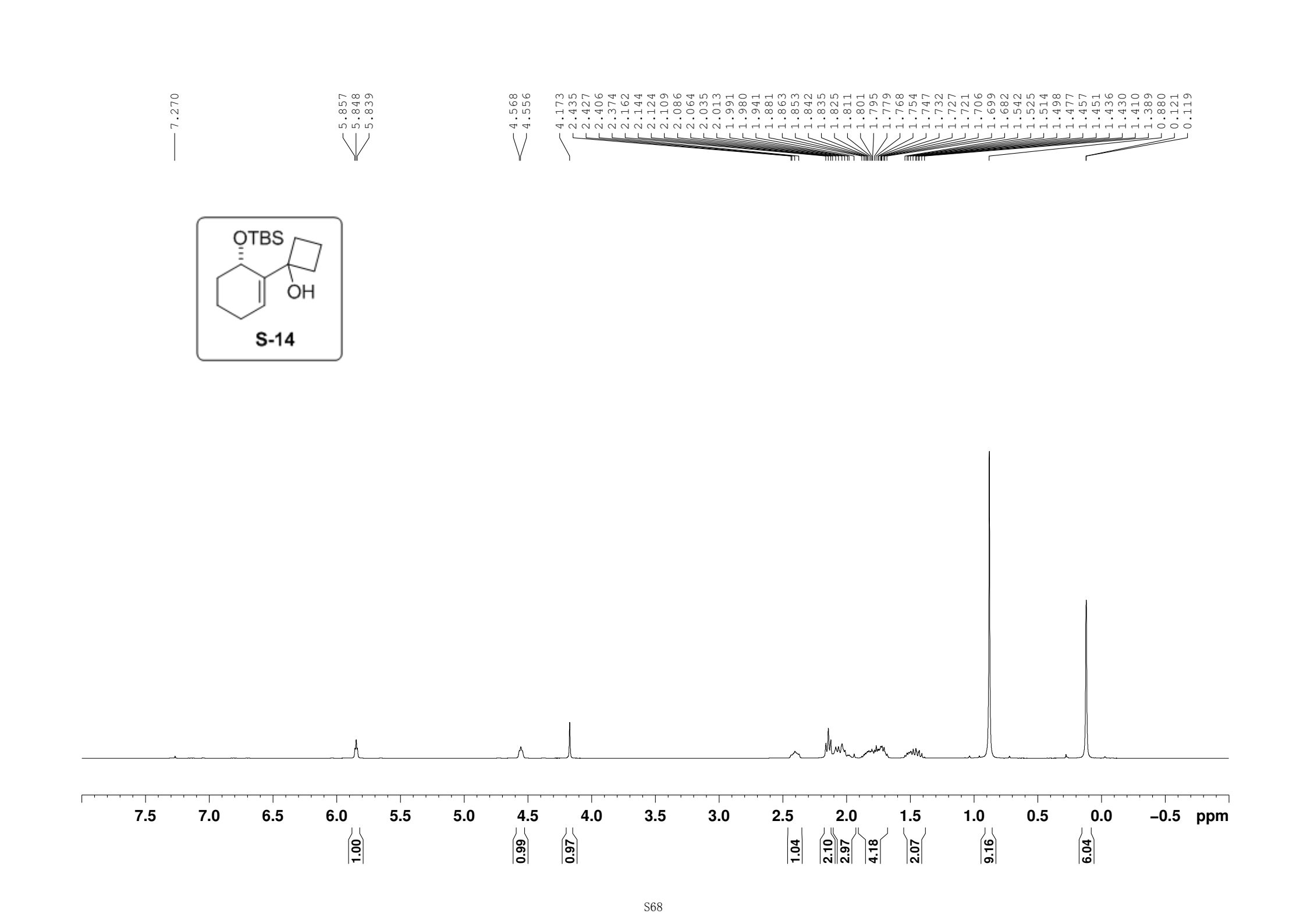
70.57
33.70
27.78
25.81
18.13
17.17
-4.47
-4.68
OTBS
Br
S-13
200
180
160
140
120
100
80
60
40
20
0
ppm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5.839
4.568
4.556
4.173
2.435
2.427
2.406
2.374
2.162
2.144
2.124
2.109
2.086
2.064
2.035
2.013
1.991
1.980
1.941
1.881
1.863
1.853
1.842
1.835
1.825
1.811
1.801
1.795
1.779
1.768
1.754
1.747
1.732
1.727
1.721
1.706
1.699
1.682
1.542
1.525
1.514
1.498
1.477
1.457
1.451
1.436
1.430
1.410
1.389
0.880
0.121
0.119
OTBS
OH
S-14
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
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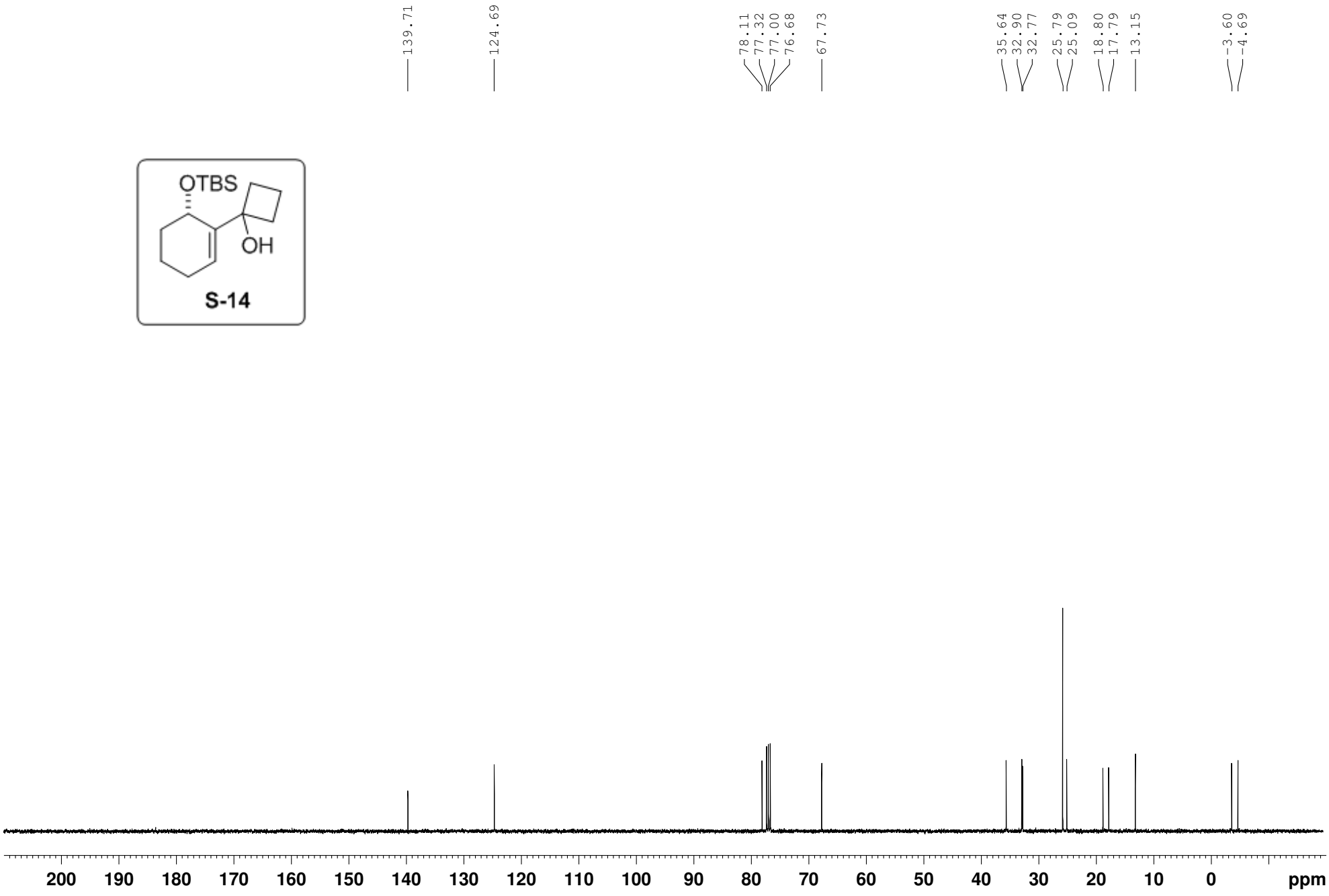
0.99
0.97
1.04
2.10
2.97
4.18
2.07
9.16
6.04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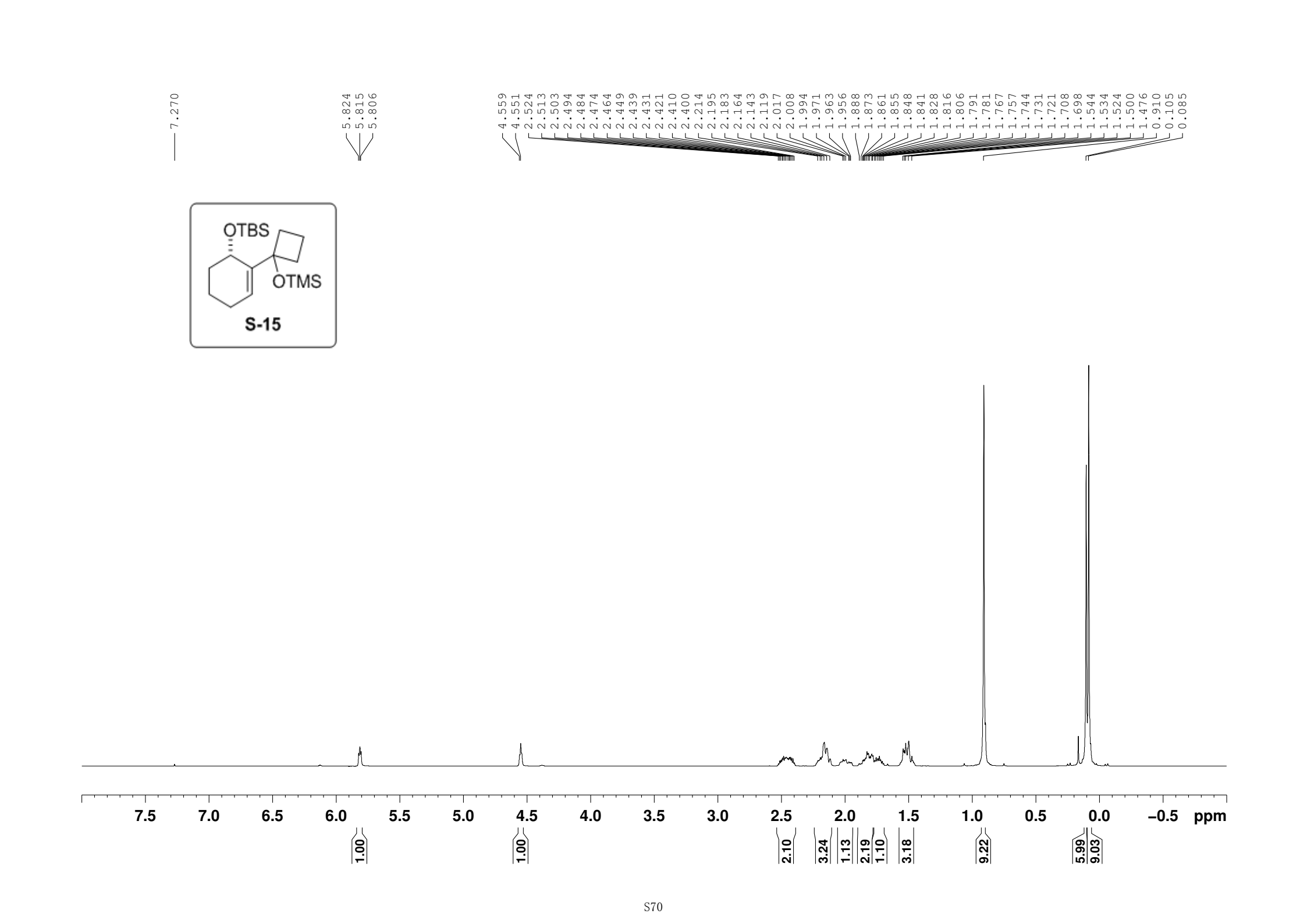
76.68
67.73
35.64
32.90
32.77
25.79
25.09
18.80
17.79
13.15
-3.60
-4.69
OTBS
OH
S-14
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
ppm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2.513
2.503
2.494
2.484
2.474
2.464
2.449
2.439
2.431
2.421
2.410
2.400
2.214
2.195
2.183
2.164
2.143
2.119
2.017
2.008
1.994
1.971
1.963
1.956
1.888
1.873
1.861
1.855
1.848
1.841
1.828
1.816
1.806
1.791
1.781
1.767
1.757
1.744
1.731
1.721
1.708
1.698
1.544
1.534
1.524
1.500
1.476
0.910
0.105
0.085
OTBS
OTMS
S-15
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
−0.5
ppm
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1.00
2.10
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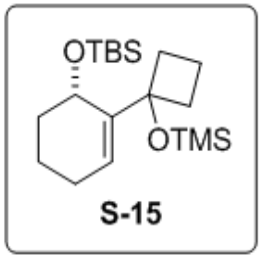
1.13
2.19
1.10
3.18
9.22
5.99
9.03


OTBS
OTMS
S-15

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79.07
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77.00
76.69
64.13
38.74
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32.60
26.07
25.67
18.05
16.75
13.55
1.92
-4.10
-4.28
200
190
180
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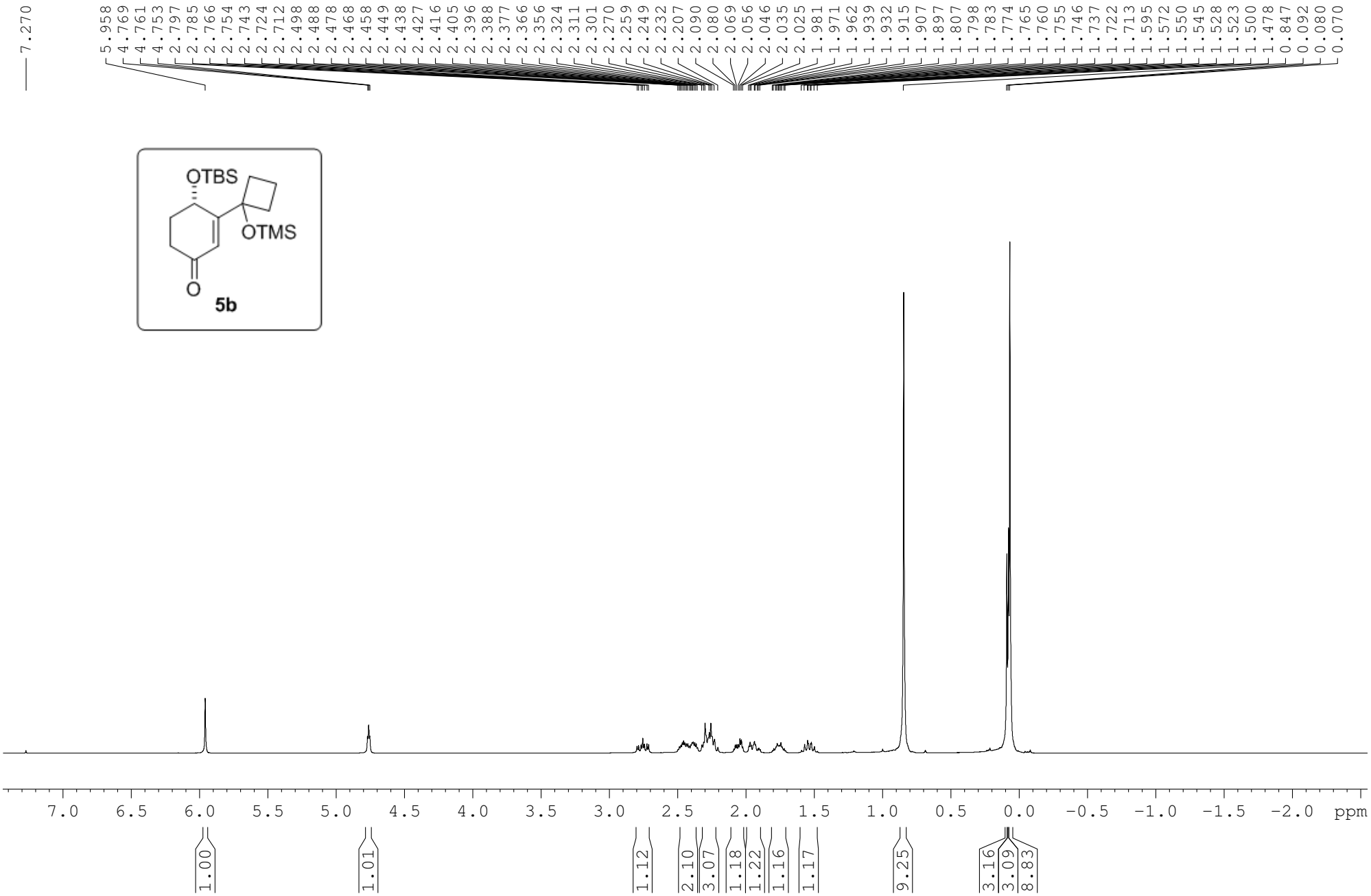
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
ppm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2.724
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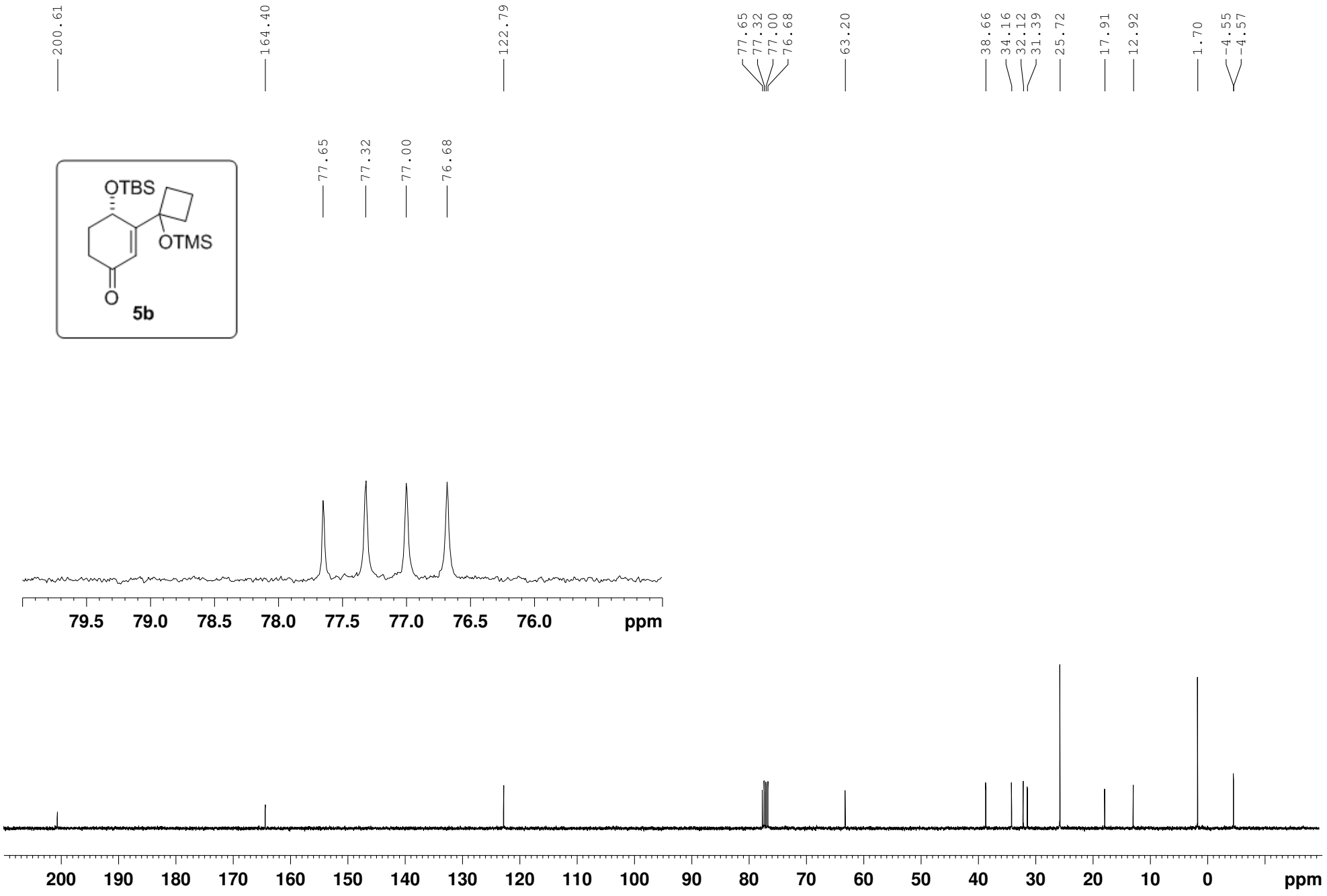
2.478
2.468
2.458
2.449
2.438
2.427
2.416
2.405
2.396
2.388
2.377
2.366
2.356
2.324
2.311
2.301
2.270
2.259
2.249
2.232
2.207
2.090
2.080
2.069
2.056
2.046
2.035
2.025
1.981
1.971
1.962
1.939
1.932
1.915
1.907
1.897
1.807
1.798
1.783
1.774
1.765
1.760
1.755
1.746
1.737
1.722
1.713
1.595
1.572
1.550
1.545
1.528
1.523
1.500
1.478
0.847
0.092
0.080
0.070
OTBS
OTMS
O
5b
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
-0.5
-1.0
-1.5
-2.0
ppm
1.00
1.01
1.12
2.10
3.07
1.18
1.22
1.16
1.17
9.25
3.16
3.09
8.83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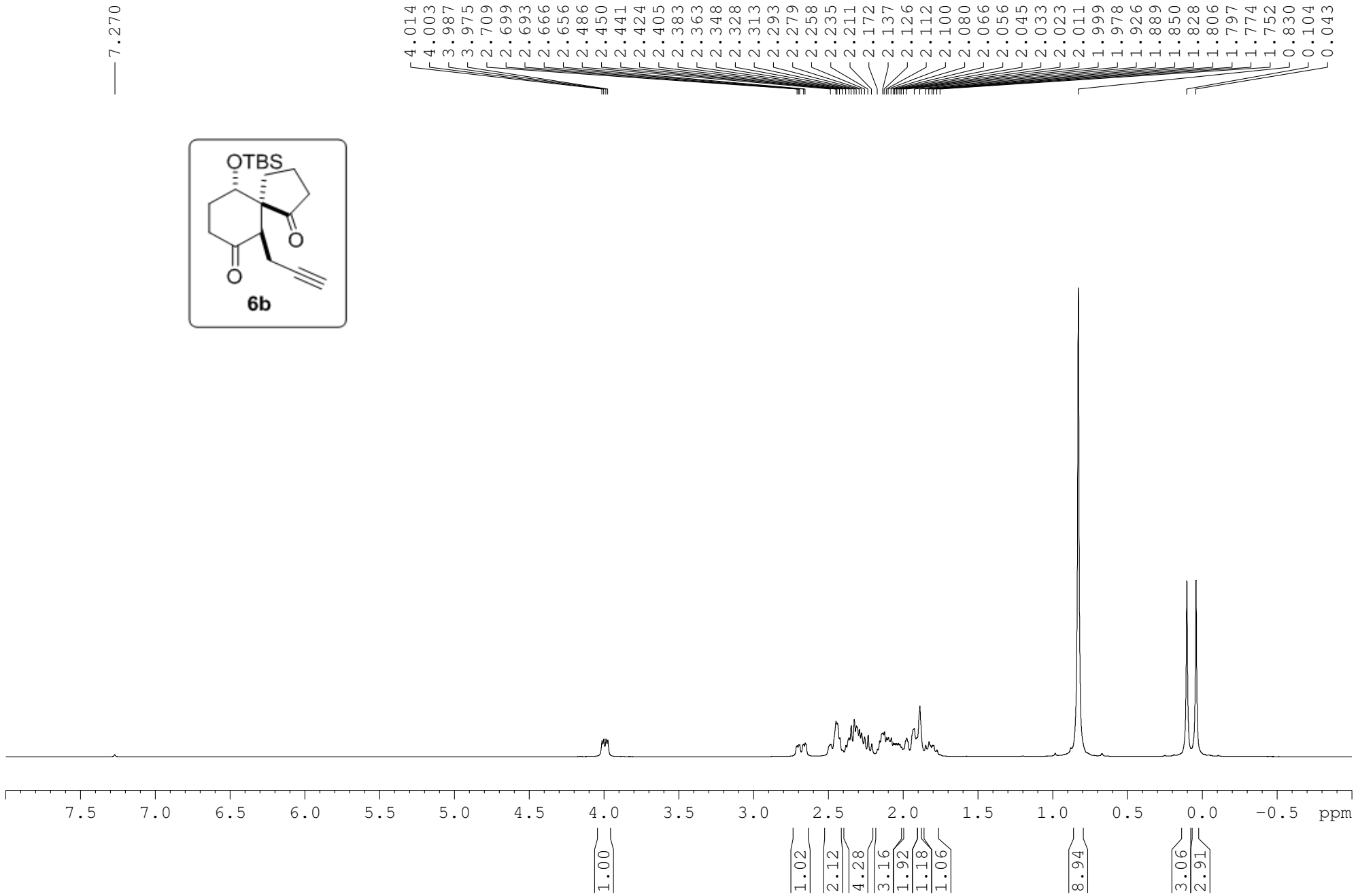
122.79
77.65
77.32
77.00
76.68
63.20
38.66
34.16
32.12
31.39
25.72
17.91
12.92
1.70
-4.55
-4.57
OTBS
OTMS
O
5b
79.5
79.0
78.5
78.0
77.5
77.0
76.5
76.0
ppm
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
ppm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2.441
2.424
2.405
2.383
2.363
2.348
2.328
2.313
2.293
2.279
2.258
2.235
2.211
2.172
2.137
2.126
2.112
2.100
2.080
2.066
2.056
2.045
2.033
2.023
2.011
1.999
1.978
1.926
1.889
1.850
1.828
1.806
1.797
1.774
1.752
0.830
0.104
0.043
OTBS
O
O
6b
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
-0.5
ppm
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2.12
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3.16
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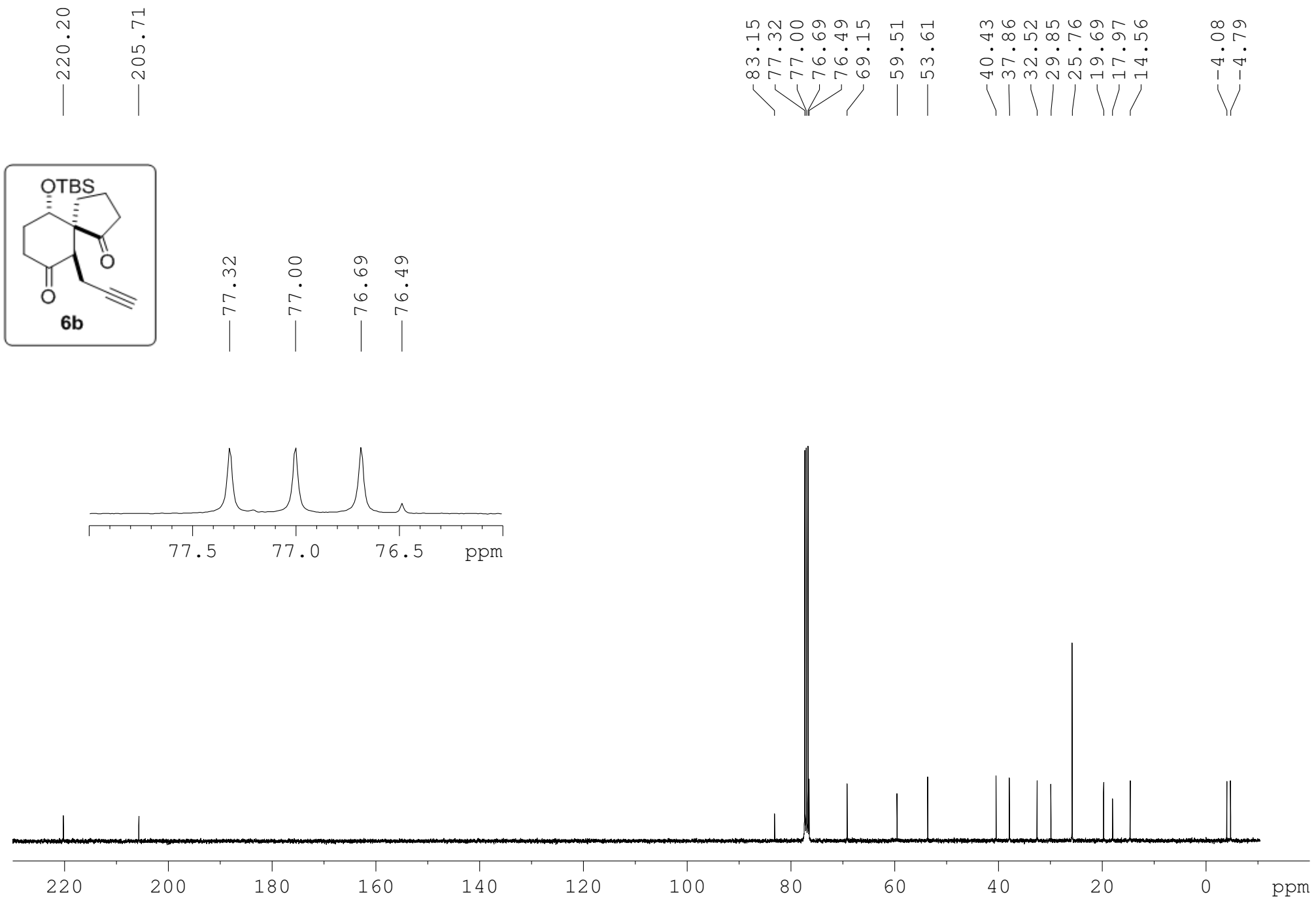
1.18
1.06
8.94
3.06
2.91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76.69
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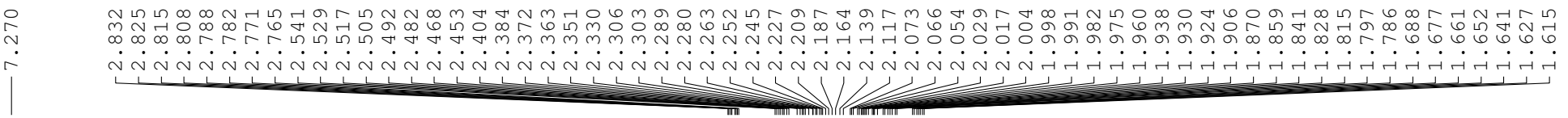
69.15
59.51
53.61
40.43
37.86
32.52
29.85
25.76
19.69
17.97
14.56
-4.08
-4.79
OTBS
O
O
6b
77.32
77.00
76.69
76.49
77.5
77.0
76.5
ppm
220
200
180
160
140
120
100
80
60
40
20
0
ppm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2.808
2.788
2.782
2.771
2.765
2.541
2.529
2.517
2.505
2.492
2.482
2.468
2.453
2.404
2.384
2.372
2.363
2.351
2.330
2.306
2.303
2.289
2.280
2.263
2.252
2.245
2.227
2.209
2.187
2.164
2.139
2.117
2.073
2.066
2.054
2.029
2.017
2.004
2.004
1.998
1.991
1.982
1.975
1.960
1.938
1.930
1.924
1.906
1.870
1.859
1.841
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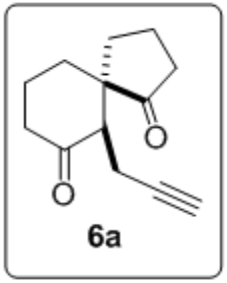
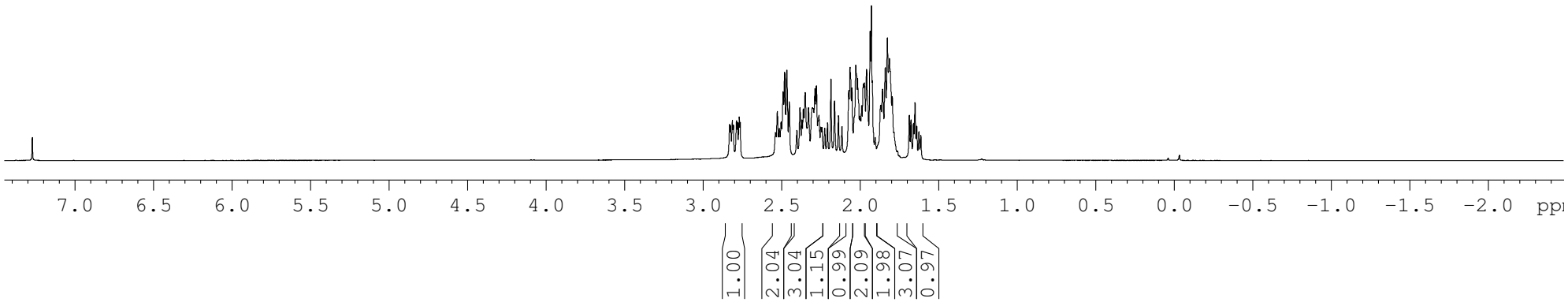
1.661
1.652
1.641
1.627
1.615


O
O
6a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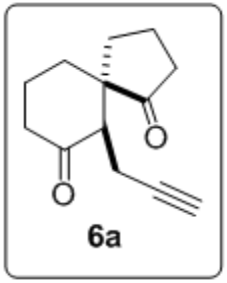
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
-0.5
-1.0
-1.5
-2.0
ppı
1.00
2.04
3.04
1.15
0.99
2.09
1.98
3.07
0.97


O
O
6a

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207.36
82.97
77.32
77.00
76.68
69.45
56.16
53.95
39.63
37.68
35.19
32.00
21.17
18.64
14.62
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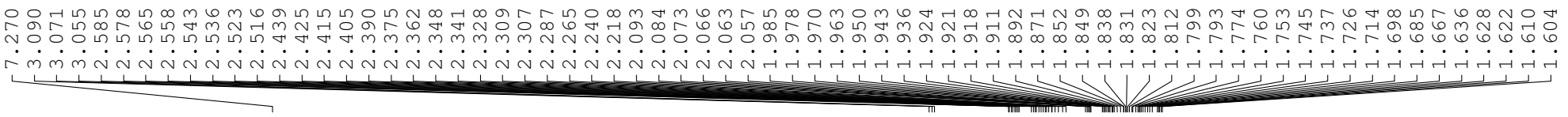
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2.578
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2.543
2.536
2.523
2.516
2.439
2.425
2.415
2.405
2.390
2.375
2.362
2.348
2.341
2.328
2.309
2.307
2.287
2.265
2.240
2.218
2.093
2.084
2.073
2.066
2.063
2.057
1.985
1.978
1.970
1.963
1.950
1.943
1.936
1.924
1.921
1.918
1.911
1.892
1.871
1.852
1.849
1.838
1.831
1.823
1.812
1.799
1.793
1.774
1.760
1.753
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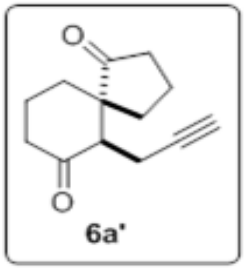
1.604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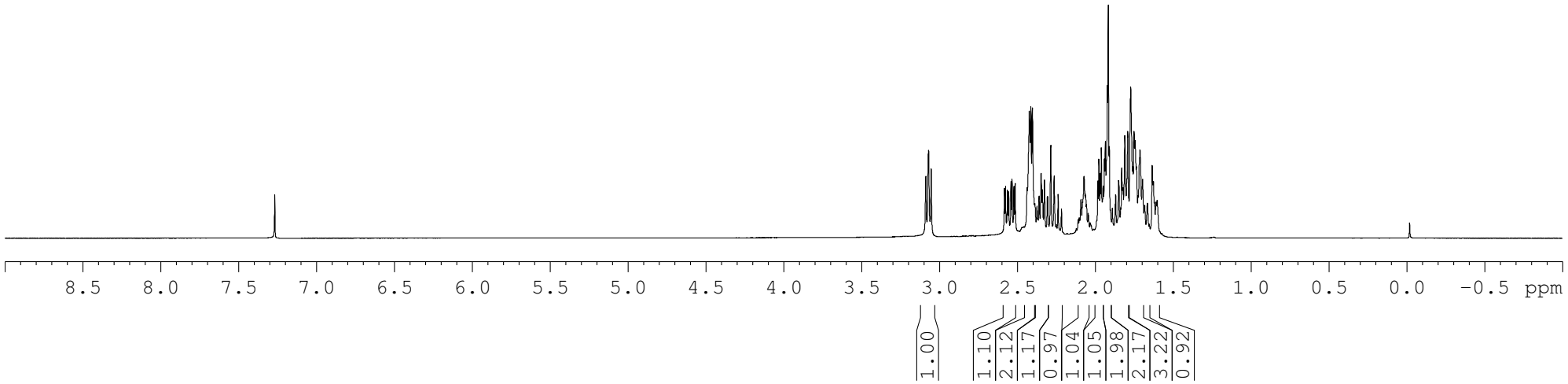
6a'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6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
-0.5
ppm
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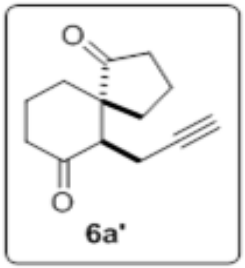
2.12
1.17
0.97
1.04
1.05
1.98
2.17
3.22
0.92


O
O
6a'

218.97
209.45
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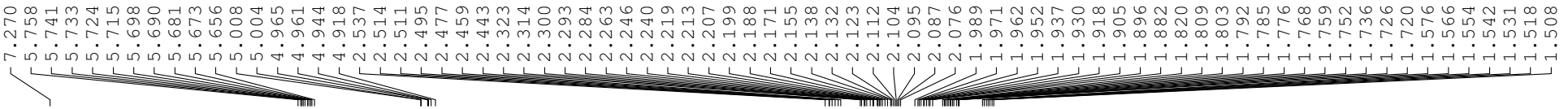
77.00
76.68
70.40
56.93
52.72
41.44
37.30
32.88
27.60
23.57
18.89
15.13
220 210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 ppm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5.741
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5.690
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5.673
5.656
5.008
5.004
4.965
4.961
4.944
4.918
2.537
2.514
2.511
2.495
2.477
2.459
2.443
2.323
2.314
2.300
2.293
2.284
2.263
2.246
2.240
2.219
2.213
2.207
2.199
2.188
2.171
2.155
2.138
2.132
2.123
2.112
2.104
2.095
2.087
2.076
1.989
1.971
1.962
1.952
1.937
1.930
1.918
1.905
1.896
1.882
1.820
1.809
1.803
1.792
1.785
1.776
1.768
1.759
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1.720
1.576
1.566
1.554
1.542
1.531
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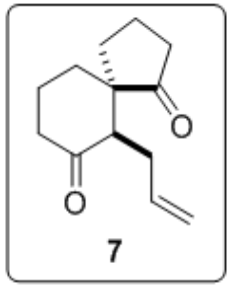
1.508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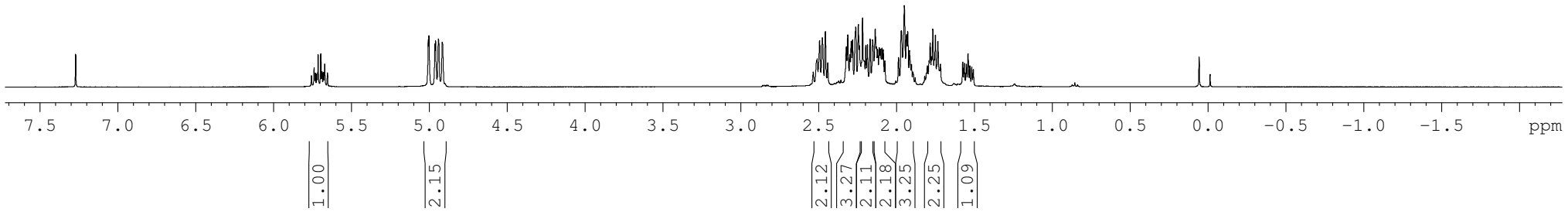
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6.5
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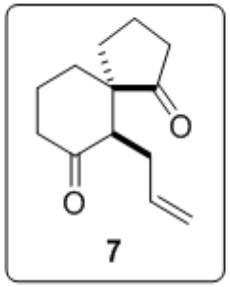
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
-0.5
-1.0
-1.5
ppm
1.00
2.15
2.12
3.27
2.11
2.18
3.25
2.25
1.09

219.23
209.69
136.54
115.91
77.32
77.00
76.68
55.57
54.32
39.55
37.76
35.09
31.10
30.11
21.77
18.55



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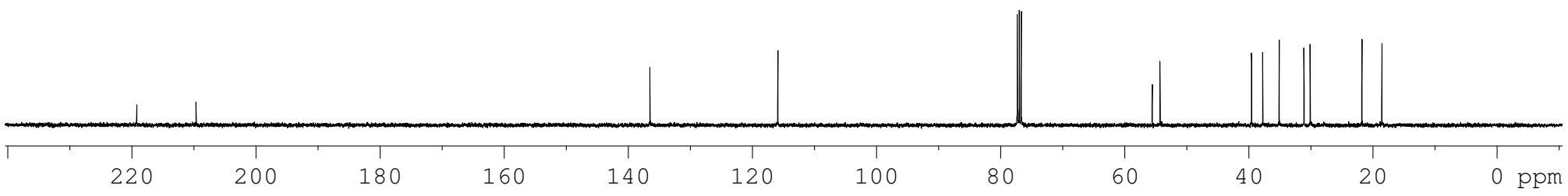

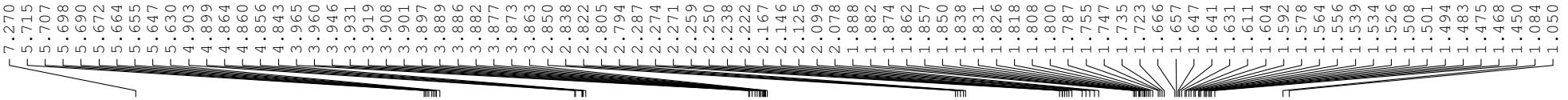
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5.715
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5.672
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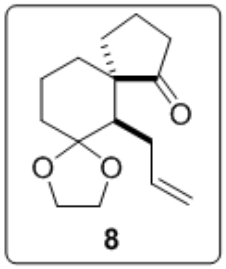
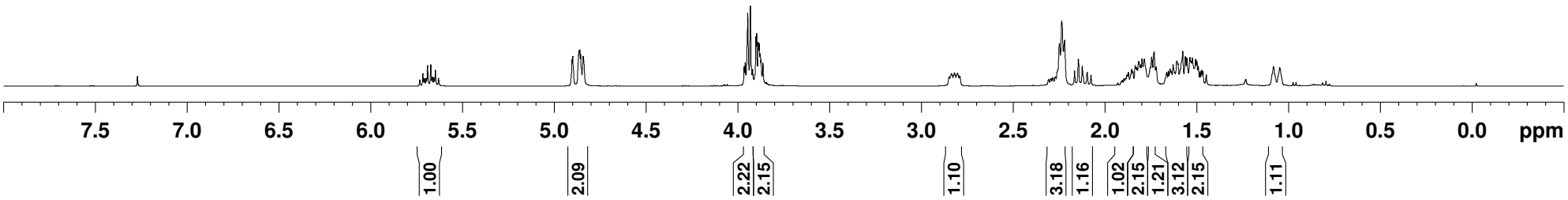
5.655
5.647
5.630
4.903
4.899
4.864
4.860
4.856
4.843
3.965
3.960
3.946
3.931
3.919
3.908
3.901
3.897
3.889
3.886
3.882
3.877
3.873
3.863
2.850
2.838
2.822
2.805
2.794
2.287
2.274
2.271
2.259
2.250
2.238
2.222
2.167
2.146
2.125
2.099
2.078
1.888
1.882
1.874
1.862
1.857
1.850
1.838
1.831
1.826
1.818
1.808
1.800
1.787
1.755
1.747
1.735
1.723
1.666
1.657
1.647
1.641
1.631
1.611
1.604
1.592
1.578
1.564
1.556
1.539
1.534
1.526
1.508
1.501
1.494
1.483
1.475
1.468
1.450
1.084
1.050


O
O
O
8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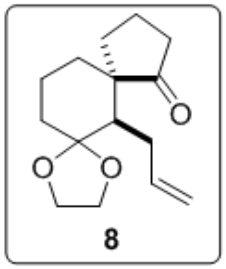
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
ppm
1.00
2.09
2.22
2.15
1.10
3.18
1.16
1.02
2.15
1.21
3.12
2.15
1.11

220.69
139.44
114.54
110.95
77.31
77.00
76.68
64.32
63.64
52.47
43.92
37.71
35.16
31.46
30.15
28.87
19.78
17.82



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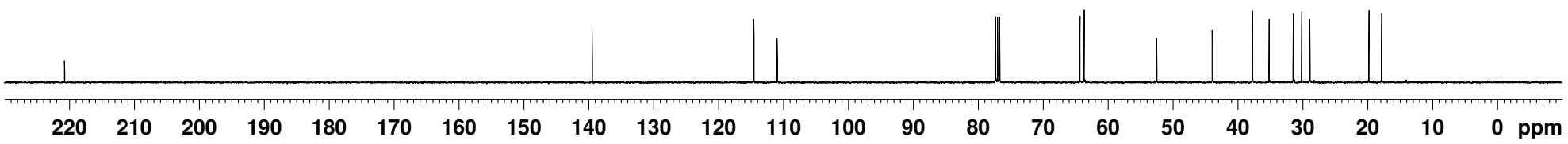

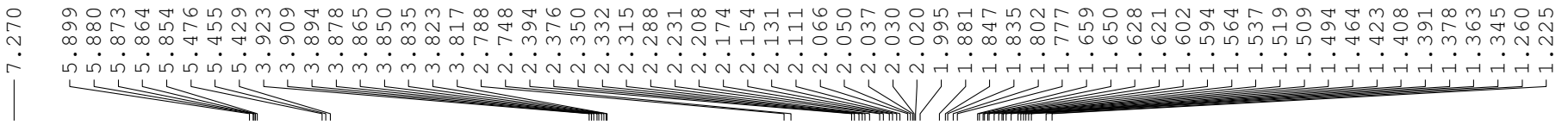
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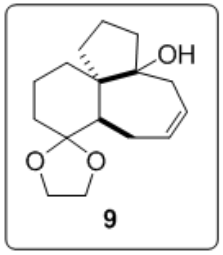
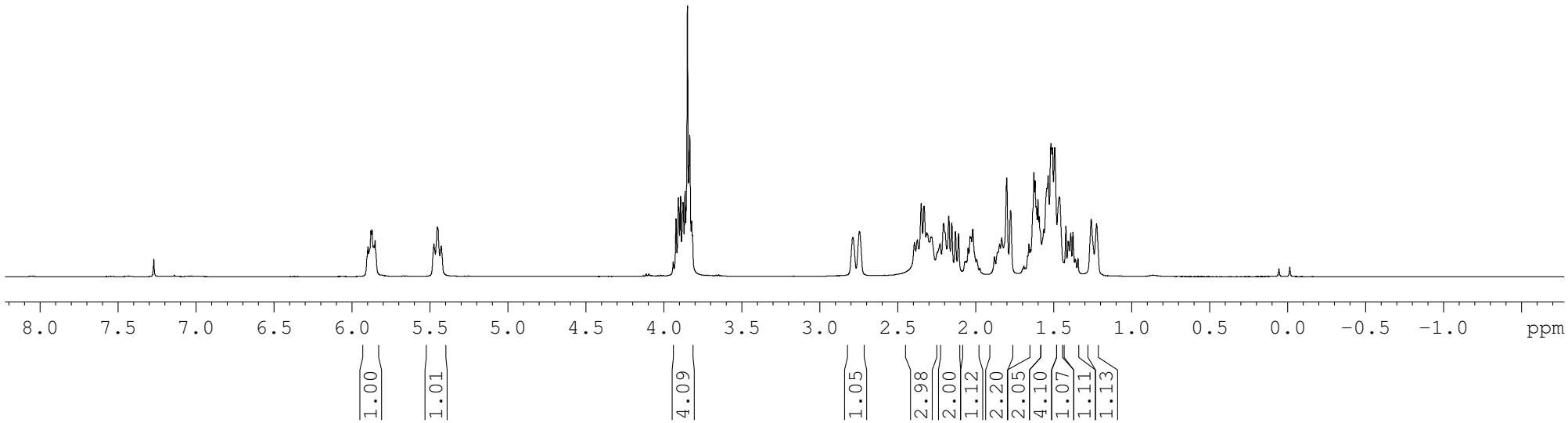
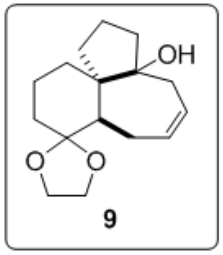
5.854
5.476
5.455
5.429
3.923
3.909
3.894
3.878
3.865
3.850
3.835
3.823
3.817
2.788
2.748
2.394
2.376
2.350
2.332
2.315
2.288
2.231
2.208
2.174
2.154
2.131
2.111
2.066
2.050
2.037
2.030
2.020
1.995
1.881
1.847
1.835
1.802
1.777
1.659
1.650
1.628
1.621
1.602
1.594
1.564
1.537
1.519
1.509
1.494
1.464
1.423
1.408
1.391
1.378
1.363
1.345
1.260
1.225


OH
O
O

9


8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
-0.5
-1.0
ppm
1.00
1.01
4.09
1.05
2.98
2.00
1.12
2.20
2.05
4.10
1.07
1.11
1.13



132.74
125.69
111.15
84.91
77.32
77.00
76.69
64.12
63.45
49.84
49.52
39.44
38.95
35.03
31.06
26.20
23.48
19.42
17.76