Supporting Information For

Mn(III)/TEMPO-Co-Mediated Tandem Azidation/1,2-Carbon Migration Reaction of Allylic Silyl Ethers

Zhi-Min Chen, Zhen Zhang, Yong-Qiang Tu,* Ming-Hui Xu, Fu-Min Zhang, Chen-Chen Li, and Shao-Hua Wang*

State Key Laboratory of Applied Organic Chemistry, Lanzhou University, Lanzhou; Collaborative Innovation Center of Chemical Science and Engineering, Tianjin, P. R. China

School of Pharmacy, Lanzhou University, Lanzhou 730000 P. R. China

E-mail: tuyq@lzu.edu.cn; wangshh@lzu.edu.cn

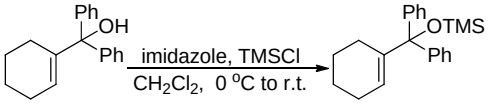
Context

General information:

All reactions under standard conditions were carried out under argon and monitored by thin-layer chromatography (TLC) on gel F_{254} plates. The silica gel (200-300 meshes) was used for column chromatography, and light petroleum ether (bp. 60~90 ^{o}C), dichloromethane, and ethyl acetate are used. All solvents were purified and dried by standard techniques. ^{1}H and ^{13}C NMR spectra were recorded in $CDCl_3$ solution or Acetone-d_6 solution on *Bruker* AM-400 MHz or *Varian Mercury*-600 MHz instruments and spectral data were reported in ppm relative to tetramethylsilane (TMS) as internal standard. Diastereoisomeric ratio was determined by ^{1}H NMR of the crude products. IR spectra were recorded on a Nicolet FT-170SX spectrometer. Mass spectra (MS) were measured on spectrometer by direct inlet at 70 eV and signals were given in m/z with relative intensity (%) in brackets. High-resolution mass spectral analysis (HRMS) data were measured on the Bruker ApexII by means of the ESI technique. The single crystal X-ray analysis was performed on an Agilent SuperNova Eos diffractometer. The substrates **1q**, **1r**, **1s**, and **1w** are known compounds.[1]

1. Experimental details for substrates and products

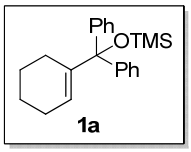
1.1 General procedure A: for the synthesis of allylic silyl ethers **1a-p** and **1t-v**:



13a **1a**

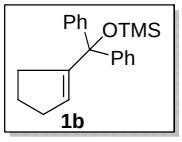
Known allylic alcohol **13a** (248 mg, 0.94 mmol) was dissolved in 8 mL of dry CH_2Cl_2 under argon followed by addition of imidazole (255 mg, 3.76 mmol) and TMSCl (0.30 mL, 2.35 mmol) at 0 ^{o}C. The reaction mixture was then stirred at room temperature. After the substrate disappeared completely (via thin-layer chromatography), the reaction mixture was quenched with 2 mL of water at 0 ^{o}C. Then, the organic layer was separated and aqueous layer was extracted with CH_2Cl_2 (5 mL × 3). The combined organic layer was washed with brine (10 mL), dried over anhydrous Na_2SO_4 and concentrated under vacuum. Purification of the residue by column chromatography on silica gel (petroleum/EtOAc 150:1) provided the compound **1a** (302

mg, 96% yield) as a colorless oil. Allylic silyl ethers **1b-p** and **1t-v** were prepared in the similar methods.



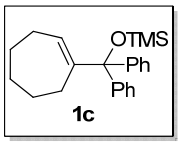
1a

^{1}H NMR (400 MHz, $CDCl_3$, ppm): δ 7.38-7.35 (m, 4H), 7.30-7.22 (m, 6H), 5.95 (dt, *J* = 2.0, 2.6 Hz, 1H), 2.17-2.13 (m, 2H), 1.80-1.76 (m, 2H), 1.58-1.50 (m, 4H), -0.15 (s, 9H); **^{13}C NMR** (100 MHz, $CDCl_3$, ppm): δ 145.2, 141.3, 128.8, 127.3, 126.8, 123.7, 85.4, 26.1, 25.4, 23.0, 22.3, 1.8; **IR** (neat) 2928, 1250, 1070, 840, 703 cm^{-1}; **MS** (EI) *m/z*(%) 336(M^+, 80), 255(70), 246(36), 73(100); **HRMS** (ESI) Calcd. for $C_{19}H_{19}$ $(M\text{-}TMSOH+H)^+$: 247.1481, Found 247.1478.



1b

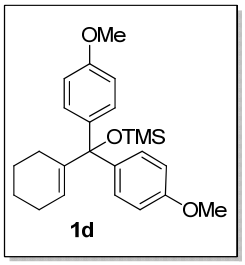
Prepared according to general procedure A with petroleum/EtOAc = 150:1 as eluent to afford **1b** (92% yield) as a colorless oil. **^{1}H NMR** (400 MHz, $CDCl_3$, ppm): δ 7.37-7.35 (m, 4H), 7.30-7.21 (m, 6H), 5.80 (d, *J* = 2.0 Hz, 1H), 2.37 (dt, *J* = 2.4, 7.2 Hz, 2H), 2.16 (dt, *J* = 1.6, 6.8 Hz, 2H), 1.91-1.83 (m, 2H), -0.14 (s, 9H); **^{13}C NMR** (100 MHz, $CDCl_3$, ppm): δ 149.1, 145.3, 128.3, 127.7, 127.5, 126.9, 82.9, 33.4, 32.3, 24.0, 1.8; **IR** (neat) 2954, 2926, 1250, 1070, 840, 702 cm^{-1}; **MS** (EI) *m/z*(%) 322(M^+, 13), 169(28), 158(30), 105(90), 85(45), 57(100); **HRMS** (ESI) Calcd. for $C_{18}H_{17}$ $(M\text{-}TMSOH+H)^+$: 233.1325, Found 233.1323.



1c

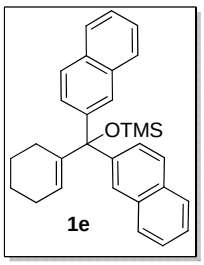
Prepared according to general procedure A with petroleum/EtOAc = 200:1 (silica gel column with triethylamine basification) as eluent to afford **1c** (85% yield) as a colorless oil. **^{1}H NMR** (400 MHz, $CDCl_3$, ppm): δ 7.44-7.41 (m, 4H), 7.35-7.26 (m, 6H), 6.21 (t, *J* = 6.8 Hz, 1H), 2.27-2.22 (m, 2H), 2.11-2.08 (m, 2H), 1.68-1.61 (m, 2H), 1.45-1.39 (m, 2H), 1.00-0.93 (m, 2H), -0.15 (s, 9H); **^{13}C NMR** (100 MHz, $CDCl_3$, ppm): δ148.4, 144.6, 129.1, 127.4, 127.2, 126.8,

86.1, 32.7, 30.6, 28.2, 26.6, 26.5, 1.8; **IR** (neat) 2924, 1250, 1103, 840, 702 cm^{-1}; **MS** (EI) *m/z*(%) 350(M^+, 15), 255(43), 105(100), 85(50), 71(70), 57(95); **HRMS** (ESI) Calcd. for $C_{20}H_{21}$ $(M\text{-}TMSOH+H)^+$: 261.1638, Found 261.1631.



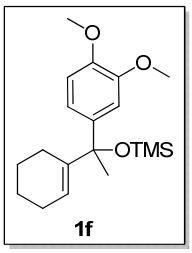
1d

Prepared according to general procedure A with petroleum/EtOAc = 50:1 as eluent to afford **1d** (83% yield) as a colorless oil. **^{1}H NMR** (400 MHz, Acetone-d_6, ppm): δ 7.30-7.27 (m, 4H), 6.89-6.86 (m, 4H), 5.96 (t, *J* = 4.0 Hz, 1H), 3.79 (s, 6H), 2.13-2.11 (m, 2H), 1.79-1.77 (m, 2H), 1.54-1.52 (m, 4H), -0.15 (s, 9H); **^{13}C NMR** (100 MHz, Acetone-d_6, ppm): δ 158.7, 142.0,137.1, 129.8, 122.5, 112.6, 84.7, 54.6, 25.9, 25.0, 22.8, 22.2, 1.1; **IR** (neat) 2931, 1508, 1250, 1175, 1071, 882, 840 cm^{-1}; **MS** (EI) *m/z*(%) 396(M^+, 30), 315(50), 306(100), 121(25), 73(80), 57(60); **HRMS** (ESI) Calcd. for $C_{21}H_{23}O_2(M\text{-}TMSOH+H)^+$: 307.1693, Found 307.1687.



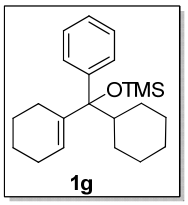
1e

Prepared according to general procedure A with petroleum/CH_2Cl_2 = 18:1 as eluent to afford **1e** (78% yield) as a colorless oil. **^{1}H NMR** (400 MHz, $CDCl_3$, ppm): δ 7.90-7.79 (m, 8H), 7.60 (dd, *J* = 2.0, 8.4 Hz, 2H), 7.52-7.46 (m, 4H), 6.06 (t, *J* = 4.0 Hz, 1H), 2.22-2.21 (m, 2H), 1.93-1.92 (m, 2H), 1.63-1.59 (m, 4H), -0.08 (s, 9H); **^{13}C NMR** (100 MHz, $CDCl_3$, ppm): δ 142.7, 141.4, 132.8, 132.5, 128.4, 127.4, 127.4, 126.9, 125.9, 125.8, 124.4, 85.8, 26.1, 25.5, 23.1, 22.3, 2.0; **IR** (neat) 2955, 2927, 1250, 1073, 952, 841,743 cm^{-1}; **MS** (EI) *m/z*(%) 436(M^+, 35), 355(40), 346(30), 73(100); **HRMS** (ESI) Calcd. for $C_{27}H_{23}$ $(M\text{-}TMSOH+H)^+$: 347.1794, Found 347.1785.



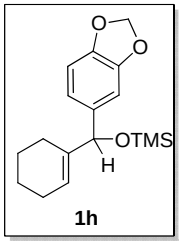
1f

Prepared according to general procedure A with petroleum/EtOAc = 20:1 as eluent to afford **1f** (81% yield) as a colorless oil. **^{1}H NMR** (400 MHz, $CDCl_3$, ppm): δ 6.96-6.89 (m, 2H), 6.78 (d, *J* = 8.4 Hz, 1H), 5.88 (s, 1H), 3.87 (s, 6H), 2.12-2.10 (m, 2H), 1.88-1.83 (m, 1H), 1.64 (s, 3H), 1.63-1.49 (m, 5H), 0.10 (s, 9H); **^{13}C NMR** (100 MHz, $CDCl_3$, ppm): δ 148.2, 147.3, 143.1, 141.0, 120.5, 117.5, 110.1, 109.4, 79.1, 55.8, 55.7, 28.9, 25.3, 24.5, 22.9, 22.4, 2.1; **IR** (neat) 3426, 2931, 1510, 1256, 1119, 1000, 840 cm^{-1}; **MS** (EI) *m/z*(%) 334(M^+, 30), 319(80), 253(95), 73(100); **HRMS** (ESI) Calcd. for $C_{19}H_{30}O_3Si_1(M+Na)^+$: 357.1856, Found 357.1851.



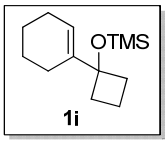
1g

Prepared according to general procedure A with petroleum/EtOAc = 200:1 as eluent to afford **1g** (92% yield) as a colorless oil. **^{1}H NMR** (400 MHz, $CDCl_3$, ppm): δ 7.30-7.15 (m, 5H), 5.90 (t, *J* = 4.0 Hz, 1H), 2.15-1.89 (m, 4H), 1.75-1.46 (m, 10H), 1.29-1.18 (m, 2H), 1.04-0.95 (m, 1H), 0.84-0.63 (m, 2H), 0.10 (s, 9H); **^{13}C NMR** (100 MHz, $CDCl_3$, ppm): δ 144.0, 139.5, 127.8, 126.7, 125.9, 123.6, 85.0, 44.7, 29.6 27.8, 26.9, 26.9, 26.7, 25.6, 25.5, 23.1, 22.4, 2.3; **IR** (neat) 2927, 2853, 1249, 1061, 880, 834, 753, 708 cm^{-1}; **MS** (EI) *m/z*(%) 342(M^+, <1), 259(100), 141(20), 73(90), 57(50), 55(45); **HRMS** (ESI) Calcd. for $C_{19}H_{25}(M-TMSOH+H)^+$: 253.1951, Found 253.1943.



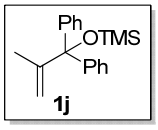
1h

Prepared according to general procedure A with petroleum/EtOAc = 100:1 as eluent to afford **1h** (83% yield) as a colorless oil. **^{1}H NMR** (400 MHz, Acetone-d_6, ppm): δ 6.88-6.86 (m, 2H), 6.83-6.80 (m, 1H), 6.02 (s, 2H), 5.88 (d, *J* = 0.8 Hz, 1H), 5.11 (s, 1H), 2.12-2.10 (m, 3H), 1.97-1.92 (m, 1H), 1.75-1.69 (m, 1H), 1.64-1.52 (m, 3H), 0.15 (s, 9H); **^{13}C NMR** (100 MHz, Acetone-d_6, ppm): δ 147.4, 146.4, 140.3, 137.8, 122.4, 119.2, 107.3, 106.4, 100.9, 78.2, 24.7, 23.0, 22.4, 22.4, -0.8; **IR** (neat) 2928, 1487, 1250, 1041, 886, 842 cm^{-1}; **MS** (EI) *m/z*(%) 304(M^+, 80), 274(30), 223(80), 115(35), 73(100), 57(35); **HRMS** (ESI) Calcd. for $C_{14}H_{15}O_2$(M-TMSOH+H)$^+$: 215.1067, Found 215.1062.



1i

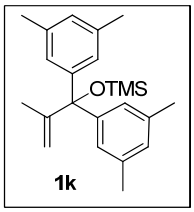
Prepared according to general procedure A with petroleum/EtOAc = 150:1 as eluent to afford **1i** (95% yield) as a colorless oil. **^{1}H NMR** (400 MHz, $CDCl_3$, ppm): δ 5.73 (t, *J* = 3.6 Hz, 1H), 2.30-2.23 (m, 2H), 2.14-2.02 (m, 6H), 1.74-1.55 (m, 5H), 1.47-1.38 (m, 1H), 0.09 (s, 9H); **^{13}C NMR** (100 MHz, $CDCl_3$, ppm): δ 139.5, 120.1, 79.1, 35.2, 25.2, 22.8, 22.8, 22.4, 13.3, 1.7; **IR** (neat) 2925, 1250, 1128, 840 cm^{-1}; **MS** (EI) *m/z*(%) 224(M^+, 15), 181(50), 73(100), 57(75), 55(80); **HRMS** (ESI) Calcd. for $C_{10}H_{15}$(M-TMSOH+H)$^+$: 135.1168, Found 135.1170.



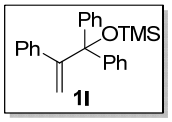
1j

Prepared according to general procedure A with petroleum/EtOAc = 150:1 as eluent to afford **1j** (96% yield) as a colorless oil. **^{1}H NMR** (400 MHz, $CDCl_3$, ppm): δ 7.47-7.44 (m, 4H), 7.36-28 (m, 6H), 5.35 (d, *J* = 1.6 Hz, 1H), 5.08 (s, 1H), 1.68 (s, 3H), -0.14 (s, 9H); **^{13}C NMR** (100 MHz,

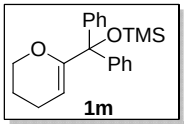
$CDCl_3$, ppm): δ 149.3, 144.3, 128.9, 127.5, 127.1, 113.1, 85.3, 20.4, 1.7; **IR** (neat) 2955, 2925, 1251, 1100, 839, 703 cm^{-1}; **MS** (EI) *m/z*(%) 296(M^+, 20), 281(40), 255(50), 85(50), 73(85), 57(100); **HRMS** (ESI) Calcd. for $C_{16}H_{15}$(M-TMSOH+H)$^+$: 207.1168, Found 207.1165.



Prepared according to general procedure A with petroleum/EtOAc = 150:1 as eluent to afford **1k** (95% yield) as a colorless oil. **^{1}H NMR** (400 MHz, $CDCl_3$, ppm): δ 7.14 (s, 4H), 7.01 (s, 2H), 5.41 (d, *J* = 1.6 Hz, 1H), 5.13 (s, 1H), 2.40 (s, 12H), 1.78 (s, 3H), -0.06 (s, 9H); **^{13}C NMR** (100 MHz, $CDCl_3$, ppm): δ 149.6, 144.4, 136.6, 128.5, 126.8, 112.8, 85.4, 21.5, 20.6, 1.7; **IR** (neat) 2955, 2920, 1250, 1100, 838, 703 cm^{-1}; **MS** (EI) *m/z*(%) 352(M^+, 40), 337(68), 311(100), 247(20), 73(75); **HRMS** (ESI) Calcd. for $C_{20}H_{22}$(M-TMSOH+H)$^+$:263.1794, Found 263.1789.

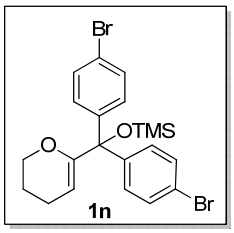


Prepared according to general procedure A with petroleum/CH_2Cl_2 = 12:1 as eluent to afford **1l** (83% yield) as a colorless oil. **^{1}H NMR** (400 MHz, $CDCl_3$, ppm): δ 7.44-7.41 (m, 4H), 7.29-7.22 (m, 6H), 7.15-7.06 (m, 3H), 7.02-6.98 (m, 2H), 5.47 (d, *J* = 1.6 Hz, 1H), 5.43 (d, *J* = 1.6 Hz, 1H), -0.24 (s, 9H); **^{13}C NMR** (100 MHz, $CDCl_3$, ppm): δ155.0, 144.8, 141.2, 129.2, 128.9, 127.4, 127.1, 127.0, 126.6, 117.3, 85.6, 1.7; **IR** (neat) 2955, 2925, 1251, 1072, 891, 839, 701 cm^{-1}; **MS** (EI) *m/z*(%) 358(M^+, 1), 255(100), 133(20), 73(98); **HRMS** (ESI) Calcd. for $C_{21}H_{17}$(M-TMSOH+H)$^+$: 269.1325, Found 269.1319.

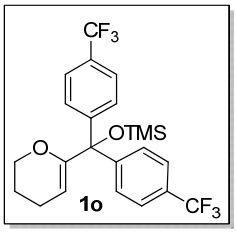


Prepared according to general procedure A with petroleum/EtOAc = 100:1 as eluent to afford **1m** (97% yield) as a colorless oil. **^{1}H NMR** (400 MHz, $CDCl_3$, ppm): δ 7.55-7.52 (m, 4H),

7.47-7.37 (m, 6H), 4.79 (t, *J* = 4.0 Hz, 1H), 4.17 (t, *J* = 5.2 Hz, 2H), 2.26-2.21 (m, 2H), 2.03-1.97 (m, 2H), 0.15 (s, 9H); **^{13}C NMR** (100 MHz, $CDCl_3$, ppm): δ 155.7, 145.6, 128.1, 127.3, 126.8, 100.4, 83.0, 65.9, 22.0, 20.4, 1.9; **IR** (neat) 2953, 1248, 1160, 1068, 885, 839, 700 cm^{-1}; **MS** (EI) *m/z*(%) 338(M^+, 20), 261(40), 248(45), 205(42), 105(30), 73(100); **HRMS** (ESI) Calcd. for $C_{21}H_{26}O_2Si_1(M+Na)^+$: 361.1594, Found 361.1589.

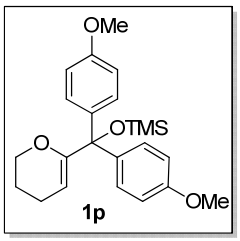


Prepared according to general procedure A with petroleum/EtOAc = 200:1 as eluent to afford **1n** (94% yield) as a colorless oil. **^{1}H NMR** (400 MHz, $CDCl_3$, ppm): δ 7.40 (d, *J* = 8.8 Hz, 4H), 7.21 (d, *J* = 8.8 Hz, 4H), 4.62 (t, *J* = 4.0 Hz, 1H), 3.99 (t, *J* = 5.2 Hz, 2H), 2.09-2.04 (m, 2H), 1.87-1.80 (m, 2H), -0.01 (s, 9H); **^{13}C NMR** (100 MHz, $CDCl_3$, ppm): δ 154.7, 144.2, 130.5, 129.9, 121.1, 101.1, 82.3, 66.0, 21.8, 20.3, 2.0; **IR** (neat) 2923, 1249, 1157, 1074, 844 cm^{-1}; **MS** (EI) *m/z*(%) 494(M^+, 10), 315(25), 235(25), 149(40), 97(55), 73(100); **HRMS** (ESI) Calcd. for $C_{18}H_{15}Br_2O_1(M-TMSOH+H)^+$: 406.9464, Found 406.9455.



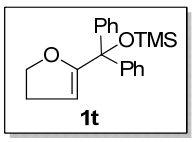
Prepared according to general procedure A with petroleum/EtOAc = 100:1 as eluent to afford **1o** (75% yield) as a colorless oil. **^{1}H NMR** (400 MHz, $CDCl_3$, ppm): δ 7.56 (d, *J* = 8.0 Hz, 4H), 7.47 (d, *J* = 8.0 Hz, 4H), 4.61 (t, *J* = 4.0 Hz, 1H), 4.03 (t, *J* = 5.2 Hz, 2H), 2.11-2.07 (m, 2H), 1.90-1.83 (m, 2H), 0.02 (s, 9H); **^{13}C NMR** (100 MHz, $CDCl_3$, ppm): δ 154.3, 148.9, 129.3 (q, *J* = 32.0 Hz), 128.3, 125.5, 124.5 (q, *J* = 3.7 Hz), 122.8, 101.9, 82.6, 66.1, 21.8, 20.3, 1.9; **IR** (neat) 2929, 1326, 1165, 1129, 907, 845 cm^{-1}; **MS** (EI) *m/z*(%) 474(M^+, 10), 431(18), 384(25), 329(25), 73(100), 55(30); **HRMS** (ESI) Calcd. for $C_{20}H_{15}F_6O_1(M-TMSOH+H)^+$: 385.1022,

Found 385.1015.



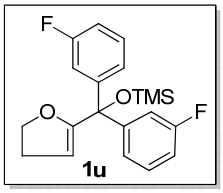
1p

Prepared according to general procedure A with petroleum/EtOAc = 10:1 as eluent to afford **1p** (90% yield) as a colorless oil. **^{1}H NMR** (400 MHz, Acetone-d_6, ppm): δ 7.44-7.39 (m, 4H), 7.02-6.97 (m, 4H), 4.77 (t, *J* = 4.0 Hz, 1H), 4.16 (t, *J* = 5.2 Hz, 2H), 3.94 (s, 6H), 2.24-2.19 (m, 2H), 2.01-1.94 (m, 2H), 0.15 (s, 9H); **^{13}C NMR** (100 MHz, Acetone-d_6, ppm): δ 158.6, 156.0, 137.9, 129.2, 112.3, 99.7, 82.4, 65.6, 54.5, 21.7, 20.0, 1.4; **IR** (neat) 2952, 1509, 1249, 1037, 840, 581 cm^{-1}; **MS** (EI) *m/z*(%) 398(M^+, 30), 315(60), 235(60), 135(45), 73(100); **HRMS** (ESI) Calcd. for $C_{23}H_{30}O_4Si_1(M+Na)^+$: 421.1806, Found 421.1802.



1t

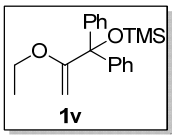
Prepared according to general procedure A with petroleum/EtOAc = 150:1 as eluent to afford **1t** (93% yield) as a colorless oil. **^{1}H NMR** (400 MHz, Acetone-d_6, ppm): δ 7.40-7.36 (m, 4H), 7.31-7.21 (m, 6H), 4.54 (t, *J* = 2.4 Hz, 1H), 4.44 (t, *J* = 9.2 Hz, 2H), 2.65 (dt, *J* = 9.2, 2.4 Hz, 2H), 0.03 (s, 9H); **^{13}C NMR** (100 MHz, Acetone-d_6, ppm): δ 161.2, 146.5, 128.4, 128.3, 127.9, 102.0, 90.8, 71.0, 30.6, 2.0; **IR** (neat) 2956, 1250, 1072, 885, 842, 700 cm^{-1}; **MS** (EI) *m/z*(%) 324(M^+, <1), 281(30), 255(50), 165(20), 105(50), 73(100); **HRMS** (ESI) Calcd. for $C_{20}H_{24}O_2Si_1(M+H)^+$: 325.1618, Found 325.1612.



1u

Prepared according to general procedure A with petroleum/EtOAc = 150:1 as eluent to afford **1u** (91% yield) as a colorless oil. **^{1}H NMR** (400 MHz, Acetone-d_6, ppm): δ 7.35 (dt, *J* = 6.4, 8.0 Hz,

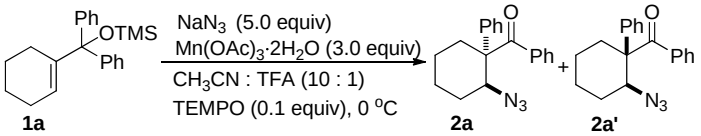
2H), 7.20-7.12 (m, 4H), 7.06-7.01 (m, 2H), 4.61 (t, *J* = 2.4 Hz, 1H), 4.49 (t, *J* = 9.2 Hz, 2H), 2.70 (dt, *J* = 9.2, 2.4 Hz, 2H), 0.07 (s, 9H); **^{13}C NMR** (100 MHz, Acetone-d_6, ppm): δ 163.5, 160.0 (d, *J* = 231.2 Hz), 147.9 (d, *J* = 6.6 Hz), 129.4 (d, *J* = 8.1 Hz), 123.3 (d, *J* = 2.8 Hz), 114.1 (d, *J* = 7.4 Hz), 113.8 (d, *J* = 5.3 Hz), 102.1, 79.0, 70.2, 29.6, 0.9; **IR** (neat) 2956, 1250, 1136, 844, 778 cm^{-1}; **MS** (EI) *m/z*(%) 360(M$^+$, 15), 317(100), 270(30), 123(33), 73(90); **HRMS** (ESI) Calcd. for $C_{17}H_{13}F_2O_1$(M-TMSOH+H)$^+$: 271.0929, Found 271.0926.



1v

Prepared according to general procedure A with petroleum/EtOAc = 20:1 (silica gel column with triethylamine basification) as eluent to afford **1v** (80% yield) as a colorless oil. **^{1}H NMR** (400 MHz, Acetone-d_6, ppm): δ 7.38-7.34 (m, 4H), 7.32-7.22 (m, 6H), 4.28 (d, *J* = 2.4 Hz, 1H), 4.10 (t, *J* = 2.0 Hz, 1H), 3.81 (q, *J* = 6.8 Hz, 2H), 1.22 (t, *J* = 6.8 Hz, 3H), -0.03 (s, 9H); **^{13}C NMR** (100 MHz, Acetone-d_6, ppm): δ 164.6, 145.5, 128.1, 127.2, 126.9, 85.5, 83.4, 63.2, 13.7, 1.1; **IR** (neat) 3419, 1624, 1250, 1117, 1073, 839, 700 cm^{-1}; **MS** (EI) *m/z*(%) 326(M$^+$, <1), 255(100), 239(10)，165(12), 105(15), 73(90); **HRMS** (ESI) Calcd. for $C_{20}H_{26}O_2Si_1$(M+H)$^+$: 327.1775, Found 327.1768.

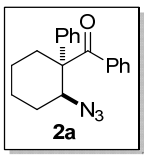
1.2 General procedure B: the azidation/1,2-migration reaction of allylic silyl ethers **1a-l**:



1a **2a** **2a'**

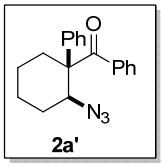
$Mn(OAc)_3{\cdot}2H_2O$ (0.6 mmol) was dissolved in 1.5 mL of CH_3CN under argon followed by addition of NaN_3 (1.0 mmol), TEMPO (0.02 mmol), then TFA (0.2 mL) was added at 0 °C. After 10–20 min, **1a** (0.2 mmol) in 0.5 mL of CH_3CN was added at 0 °C, and the reaction mixture was stirred at 0 °C under argon. When substrate **1a** was disappeared on TLC (about 0.5 h), the reaction mixture was quenched with 1.0 mL of saturated aqueous $NaHSO_3$, then warmed to room temperature, diluted with CH_2Cl_2, and extracted with CH_2Cl_2 (5 mL × 3). The combined organic layer was washed with saturated aqueous Na_2CO_3 and brine, dried over

anhydrous Na_2SO_4 and concentrated under vacuum. Purification of the residue by column chromatography on silica gel (petroleum/CH_2Cl_2 = 7:1-2:1) provided the pure products **2a** and **2a′**, respectively (52.7 mg, 86% total yield, d.r. = 6.3:1).



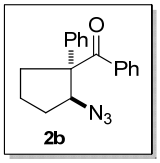
2a

mp 101-104 °C; **^{1}H NMR** (400 MHz, $CDCl_3$, ppm): δ 7.45-7.42 (m, 2H), 7.40-7.34 (m, 2H), 7.33-7.29 (m, 4H), 7.23-7.17 (m, 2H), 4.04 (s, 1H), 2.30 (t, *J* = 6.0 Hz, 2H), 2.18-2.09 (m, 1H), 2.02-1.94 (m, 1H), 1.77-1.66 (m, 1H), 1.50-1.35 (m, 3H); **^{13}C NMR** (100 MHz, $CDCl_3$, ppm): δ 202.7, 138.8, 137.9, 131.0, 128.8, 128.4, 127.8, 127.8, 127.5, 65.2, 58.2, 31.6, 26.8, 22.3, 21.2; **IR** (neat) 2935, 2106, 1680, 1253, 702 cm^{-1}; **MS** (EI) *m/z*(%) 305(M^+, 1), 209(2), 158(100), 105(90), 77(85); **HRMS** (ESI) Calcd. for $C_{19}H_{19}N_3O_1(M+Na)^+$: 328.1420, Found 328.1414.



2a'

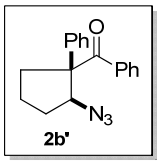
^{1}H NMR (400 MHz, $CDCl_3$, ppm): δ 7.45-7.35 (m, 6H), 7.31-7.20 (m, 4H), 4.56 (s, 1H), 2.44-2.33 (m, 2H), 2.21-2.11 (m, 1H), 1.97-1.93 (m, 1H), 1.64-1.47 (m, 3H), 1.10-0.97 (m, 1H); **^{13}C NMR** (100 MHz, $CDCl_3$, ppm): δ 204.0, 140.1, 137.7, 131.6, 129.3, 128.7, 128.0, 127.9, 126.9, 66.0, 58.7, 27.9, 27.7, 22.5, 20.1.



2b

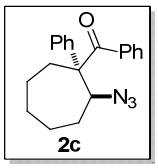
Prepared according to general procedure B with petroleum/CH_2Cl_2 = 8:1-1:1 as eluent to afford the pure products **2b** and **2b′** as a colorless oil, respectively (0.5 h, 69% total yield, d.r. = 4.7:1). **^{1}H NMR** (400 MHz, $CDCl_3$, ppm): δ 7.57 (d, *J* = 1.2 Hz, 2H), 7.40-7.33 (m, 5H), 7.30-7.24 (m, 3H), 4.59 (d, *J* = 5.2 Hz, 1H), 2.54-2.45 (m, 1H), 2.34-2.27 (m, 1H), 2.15-2.10 (m, 1H), 2.01-1.81 (m, 2H), 1.73-1.68 (m, 1H); **^{13}C NMR** (100 MHz, $CDCl_3$, ppm): δ 199.8, 140.0, 137.8, 131.8, 129.2, 128.8, 128.1, 127.5, 126.2, 69.8, 67.4, 34.0, 30.0, 20.6; **IR** (neat) 2956,

2107, 1675, 1254, 757, 702 cm^{-1}; **MS** (EI) *m/z*(%) 291(M^+, <1), 263 (3), 144(60), 105(100), 77(45), 57(35); **HRMS** (ESI) Calcd. for $C_{18}H_{17}N_3O_1(M+Na)^+$: 314.1264, Found 314.1264.



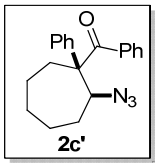
2b'

^{1}H NMR (400 MHz, $CDCl_3$, ppm): δ 7.61 (d, *J* = 7.2 Hz, 2H), 7.43-7.34 (m, 4H), 7.29-7.25 (m, 4H), 4.74 (t, *J* = 6.0 Hz, 1H), 2.76-2.67 (m, 1H), 2.32-2.24 (m, 1H), 2.21-2.12 (m, 1H), 2.04-1.94 (m, 1H), 1.83-1.73 (m, 1H), 1.71-1.60 (m, 1H); **^{13}C NMR** (100 MHz, $CDCl_3$, ppm): δ 201.0, 138.1, 135.2, 132.3, 129.9, 128.9, 128.1, 127.7, 126.3, 68.0, 66.5, 32.5, 29.2, 21.0.



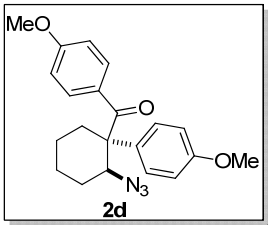
2c

Prepared according to general procedure B with petroleum/CH_2Cl_2 = 8:1-1:1 as eluent to afford the pure products **2c** and **2c′** as a colorless oil, respectively (0.5 h, 84% total yield, d.r. = 3.2:1). **^{1}H NMR** (400 MHz, $CDCl_3$, ppm): δ 7.40-7.29 (m, 8H), 7.26-7.20(m, 2H), 4.21 (dd, *J* = 2.0, 8.0 Hz, 1H), 2.41-2.34 (m, 1H), 2.32-2.23 (m, 2H), 2.12-2.05 (m, 1H), 1.87-1.82 (m, 1H), 1.59-1.54 (m, 5H); **^{13}C NMR** (100 MHz, $CDCl_3$, ppm): δ 201.7, 141.4, 138.2, 131.3, 128.9, 128.8, 128.0, 127.4, 127.4, 68.5, 61.5, 33.5, 29.5, 26.8, 22.7, 22.2; **IR** (neat) 2926, 2099, 1674, 1263, 1217, 702 cm^{-1}; **MS** (EI) *m/z*(%) 319(M^+, 1), 209(5), 105(100), 91(30), 77(45); **HRMS** (ESI) Calcd. for $C_{20}H_{21}N_3O_1(M+Na)^+$: 342.1577, Found 342.1570.



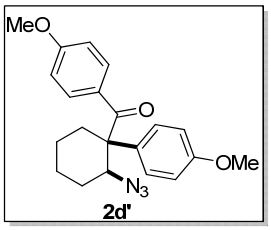
2c'

^{1}H NMR (400 MHz, $CDCl_3$, ppm): δ 7.44-7.33 (m, 8H), 7.27-7.21 (m, 2H), 4.57-4.54 (m, 1H), 2.48-2.43 (m, 2H), 2.15-2.08 (m, 2H), 1.79-1.75 (m, 1H), 1.63-1.533 (m, 3H), 1.47-1.43 (m, 1H), 1.19-1.16 (m, 1H); **^{13}C NMR** (100 MHz, $CDCl_3$, ppm): δ 202.7, 141.2, 137.4, 131.8, 129.1, 129.0, 128.0, 127.7, 127.1, 69.3, 62.0, 30.0, 29.3, 26.4, 22.1, 20.2.



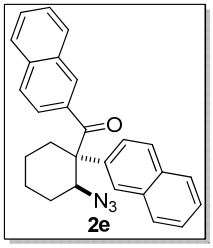
2d

Prepared according to general procedure B with petroleum/EtOAc = 80:1-40:1 as eluent to afford the pure products **2d** (12.3 mg) and **2d′** (52.6 mg) as a colorless oil, respectively (0.5 h, 83% total yield, d.r. = 4.3:1). **^{1}H NMR** (400 MHz, $CDCl_3$, ppm): δ 7.44-7.40 (m, 2H), 7.35-7.27 (m, 2H), 6.95-6.91 (m, 2H), 6.75-6.71 (m, 2H), 3.82 (s, 3H), 3.78 (m, 4H), 2.41-2.35 (m, 1H), 2.30-2.19 (m, 2H), 2.07-1.99 (m, 1H), 1.79-1.77 (m, 1H), 1.53-1.43 (m, 2H), 1.36-1.27 (m, 1H); **^{13}C NMR** (100 MHz, $CDCl_3$, ppm): δ 200.9, 162.0, 158.8, 131.9, 131.3, 130.0, 128.9, 114.2, 113.1, 66.7, 57.6, 55.3, 55.2, 32.9, 27.2, 23.3, 21.5; **IR** (neat) 2932, 2106, 1669, 1601, 1511, 1254, 1172, 1033, 734 cm^{-1}; **MS** (EI) *m/z*(%) 365(M^+, 1), 294 (8), 246(4), 85(50), 71(70), 57(100), 55(55); **HRMS** (ESI) Calcd. for $C_{21}H_{23}N_3O_3(M+Na)^+$: 388.1632, Found 388.1623.



2d'

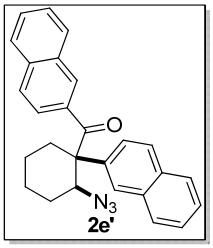
^{1}H NMR (400 MHz, $CDCl_3$, ppm): δ 7.38 (d, *J* = 8.8 Hz, 2H), 7.32 (d, *J* = 8.4 Hz, 2H), 6.95 (d, *J* = 9.2 Hz, 2H), 6.72 (d, *J* = 8.8 Hz, 2H), 4.48 (s, 1H), 3.83 (s, 3H), 3.78 (s, 3H), 2.39-2.35 (m, 2H), 2.23-2.14 (m, 1H), 1.95-1.92 (m, 1H), 1.63-1.59 (m, 1H), 1.55-1.46 (m, 2H), 1.10-0.97 (m, 1H); **^{13}C NMR** (100 MHz, $CDCl_3$, ppm): δ 202.1, 162.1, 159.1, 132.6, 131.3, 130.0, 128.0, 114.6, 113.2, 66.2, 57.8, 55.3, 55.2, 28.6, 27.7, 22.6, 20.2.



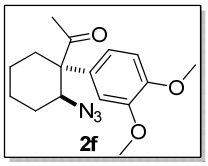
2e

Prepared according to general procedure B with petroleum/CH_2Cl_2 = 6:1-2:1 as eluent to afford

the pure products **2e** and **2e′** as a colorless oil, respectively (0.5 h, 91% total yield, d.r. = 3.8:1). **^{1}H NMR** (400 MHz, $CDCl_3$, ppm): δ 8.01 (d, *J* = 0.8 Hz, 1H), 7.93-7.87 (m, 4H), 7.75 (d, *J* = 8.8 Hz, 1H), 7.68-7.60 (m, 3H), 7.57-7.53 (m, 3H), 7.52-7.40 (m, 2H), 4.20 (s, 1H), 2.51 (t, *J* = 6.0 Hz, 2H), 2.31-2.22 (m, 1H), 2.16-2.05 (m, 1H), 1.84-1.78 (m, 1H), 1.58-1.46 (m, 3H); **^{13}C NMR** (100 MHz, $CDCl_3$, ppm): δ 202.8, 136.9, 135.3, 134.4, 133.5, 132.6, 132.1, 129.6, 129.3, 128.6, 128.2, 127.8, 127.7, 127.6, 127.5, 127.1, 126.5, 126.5, 126.4, 125.9, 125.2, 65.8, 58.7, 32.0, 27.1, 22.6, 21.5; **IR** (neat) 2926, 2102, 1676, 1258, 1125, 741 cm^{-1}; **MS** (EI) *m/z*(%) 405(M^+, 5), 342(30), 255(10), 169(27), 85(44), 71(70), 57(100); **HRMS** (ESI) Calcd. for $C_{27}H_{23}N_1O_1$ $(M-N_2+H)^+$: 378.1852, Found 378.1841.

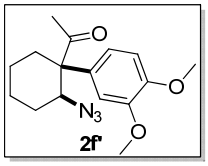


^{1}H NMR (400 MHz, $CDCl_3$, ppm): δ 8.00-7.88 (m, 5H), 7.76-7.73 (m, 1H), 7.67-7.62(m, 3H), 7.56-7.48 (m, 3H),7.45-7.38 (m, 2H), 4.74 (s, 1H), 2.62-2.58 (m, 2H), 2.34-2.24 (m, 1H), 2.06-2.01 (m, 1H), 1.68-1.56 (m, 3H), 1.20-1.08 (m, 1H); **^{13}C NMR** (100 MHz, $CDCl_3$, ppm): δ 203.7, 137.8, 134.9, 134.6, 133.7, 132.8, 132.1, 130.1, 129.3, 129.1, 128.3, 128.0, 127.7, 127.5, 126.5, 126.5, 126.4, 126.4, 125.0, 124.4, 66.0, 58.9, 28.4, 27.6, 22.7, 20.2.



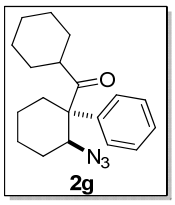
Prepared according to general procedure B with petroleum/EtOAc = 15:1-10:1 as eluent to afford the pure product **2f** and **2f′** as a colorless oil, respectively (0.5 h, 67% total yield, d.r. = 6.1:1). **^{1}H NMR** (400 MHz, $CDCl_3$, ppm): δ 6.92 (dd, *J* = 2.4, 8.4 Hz, 1H), 6.86 (d, *J* = 8.8 Hz, 1H), 6.79 (d, *J* = 2.0 Hz, 1H), 4.52 (s, 1H), 3.88 (s, 3H), 3.87 (s, 3H), 2.32-2.28 (m, 1H), 2.14-2.12 (m, 1H), 2.11-1.96 (m, 4H), 1.87-1.78 (m, 1H), 1.69-1.54 (m, 2H), 1.48-1.35 (m, 2H);

^{13}C NMR (100 MHz, $CDCl_3$, ppm): δ 208.0, 149.2, 148.3, 130.0, 120.0, 111.3, 110.7, 62.8, 58.3, 56.0, 55.8, 27.9, 26.0, 25.0, 21.1, 20.9; **IR** (neat) 2932, 2103, 1706, 1519, 1258, 1151, 1026 cm^{-1}; **MS** (EI) *m/z*(%) 303(M^+, 25), 260(30), 232(45), 218(50), 151(100), 71(55), 57(90), 55(70); **HRMS** (ESI) Calcd. for $C_{16}H_{21}N_3O_3(M+Na)^+$: 326.1475, Found 326.1467.



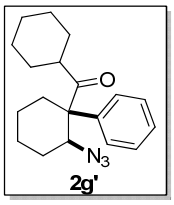
2f'

^{1}H NMR (400 MHz, $CDCl_3$, ppm): δ 6.88-6.86 (m, 2H), 6.76 (S, 1H), 4.50 (s, 1H), 3.89 (s, 3H), 3.88 (s, 3H), 2.33-2.29 (m, 1H), 2.21 (dt, *J* = 3.2, 13.6 Hz, 1H 1H), 2.07-1.97 (m, 1H), 1.94-1.86 (m, 4H), 1.56-1.49 (m, 2H), 1.27-1.13 (m, 1H); **^{13}C NMR** (100 MHz, $CDCl_3$, ppm): δ 209.1, 149.3, 148.7, 132.0, 119.0, 111.4, 109.6, 64.1, 59.3, 56.0, 55.8, 27.4, 27.3, 25.7, 23.1, 20.0.



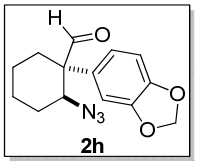
2g

Prepared according to general procedure B with petroleum/CH_2Cl_2 = 6:1-2:1 as eluent to afford the pure products **2g** and **2g′** as a colorless oil, respectively (1.0 h, 61% total yield, d.r. = 2.5:1). **^{1}H NMR** (400 MHz, $CDCl_3$, ppm): δ 7.38-7.33 (m, 4H), 7.29-7.27 (m, 1H), 4.73 (s, 1H), 2.60-2.52 (m, 1H), 2.46-2.41 (m, 1H), 2.16-2.08 (m, 1H), 2.00-1.95(m, 1H), 1.84-1.75 (m, 1H), 1.66-1.55 (m, 5H), 1.47-1.41 (m, 1H), 1.39-1.27 (m, 3H), 1.18-0.98 (m, 5H); **^{13}C NMR** (100 MHz, $CDCl_3$, ppm): δ 213.2, 137.1, 128.9, 127.9, 127.3, 62.3, 59.0, 45.7, 30.9, 29.8, 26.6, 25.9, 25.8, 25.6, 21.0, 20.6; **IR** (neat) 2932, 2361, 2104, 1702, 1259, 699 cm^{-1}; **MS** (EI) *m/z*(%) 311(M^+, 6), 158(33), 149(30), 105(60), 83(65), 57(85), 55(100); **HRMS** (ESI) Calcd. for $C_{19}H_{25}N_3O_1(M+Na)^+$: 334.1890, Found 334.1885.



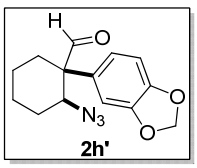
2g'

^{1}H NMR (400 MHz, $CDCl_3$, ppm): δ 7.39-7.35 (m, 2H), 7.32-7.26 (m, 3H), 4.51 (d, *J* = 1.6 Hz, 1H), 2.44-2.34 (m, 2H), 2.26-2.18 (m, 1H), 2.13-2.07 (m, 1H), 1.95-1.82 (m, 2H), 1.72-1.62 (m, 2H), 1.55-1.34 (m, 5H), 1.24-1.07 (m, 4H), 0.86-0.82 (m, 1H), 0.77-0.73 (m, 1H); **^{13}C NMR** (100 MHz, $CDCl_3$, ppm): δ 214.5, 139.3, 128.7, 127.7, 126.9, 64.2, 60.0, 46.6, 31.6, 29.9, 27.6, 26.6, 25.6, 25.6, 25.5, 23.7, 20.2.



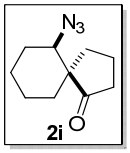
2h

Prepared according to general procedure B with petroleum/EtOAc = 100:1-50:1 as eluent to afford the pure products **2h** and **2h′** as a colorless oil, respectively (0.5 h, 64% total yield, d.r. = 2.1:1). **^{1}H NMR** (400 MHz, $CDCl_3$, ppm): δ 9.52 (s, 1H), 6.85-6.80 (m, 2H), 6.75 (dd, *J* = 2.0, 8.4 Hz, 1H), 5.98 (s, 2H), 4.24 (dd, *J* = 3.2, 8.0 Hz, 1H), 2.20-2.12 (m, 1H), 1.99-1.75 (m, 4H), 1.57-1.43 (m, 3H); **^{13}C NMR** (100 MHz, $CDCl_3$, ppm): δ 200.5, 148.6, 147.1, 130.5, 121.1, 108.7, 107.8, 101.4, 62.9, 56.9, 29.5, 27.1, 22.6, 21.4; **IR** (neat) 2926, 2101, 1719, 1245, 1041, 632 cm^{-1}; **MS** (EI) *m/z*(%) 273(M^+, 30), 216(60), 147(40), 135(100), 57(50); **HRMS** (ESI) Calcd. for $C_{14}H_{15}N_1O_3(M\text{-}N_2+H)^+$:246.1125, Found 246.1122.

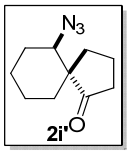


2h'

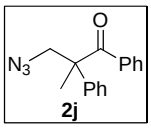
^{1}H NMR (400 MHz, $CDCl_3$, ppm): δ 9.22 (s, 1H), 6.85 (d, *J* = 8.0 Hz, 1H), 6.80 (d, *J* = 1.6 Hz, 1H) 6.76 (dd, *J* = 1.6, 8.0 Hz, 1H), 5.99 (s, 2H), 4.42 (s, 1H), 2.18-2.09 (m, 2H), 1.98-1.86 (m, 3H), 1.61-1.49 (m, 2H), 1.33-1.21 (m, 1H); **^{13}C NMR** (100 MHz, $CDCl_3$, ppm): δ 199.7, 148.5, 147.5, 130.0, 121.3, 108.7, 107.8, 101.4, 62.5, 57.7, 27.3, 25.8, 22.8, 19.6.



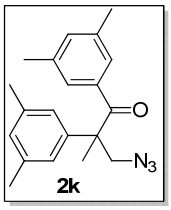
Prepared according to general procedure B with petroleum/ CH_2Cl_2 = 10:1-4:1 as eluent to afford the pure products **2i** and **2i′** as a colorless oil, respectively (0.5 h, 42% total yield, d.r. = 1.2:1). **^{1}H NMR** (400 MHz, $CDCl_3$, ppm): δ 3.33 (dd, *J* = 4.0, 11.2 Hz, 1H), 2.34-2.19 (m, 4H), 2.00-1.81 (m, 5H), 1.68-1.56 (m, 2H), 1.47-1.41 (m, 1H), 1.33-1.16 (m, 2H); **^{13}C NMR** (100 MHz, $CDCl_3$, ppm): δ 219.6, 64.9, 50.5, 39.7, 36.5, 32.9, 26.5, 24.1, 20.5, 18.7; **IR** (neat) 2931, 2099, 1733, 1260 cm^{-1}; **MS** (EI) *m/z*(%) 193(M^+, 10), 142(58), 105(60), 97(58), 81(65), 69(83), 55(100); **HRMS** (ESI) Calcd. for $C_{10}H_{15}N_1O_1(M\text{-}N_2+H)^+$:166.1226, Found 166.1225.



^{1}H NMR (400 MHz, $CDCl_3$, ppm): δ 3.70 (dd, *J* = 4.0, 11.6 Hz, 1H), 2.39-2.17 (m, 2H), 2.09-1.96 (m, 3H), 1.90-1.75 (m, 3H), 1.64-1.48 (m, 2H), 1.45-1.22 (m, 4H); **^{13}C NMR** (100 MHz, $CDCl_3$, ppm): δ 221.8, 63.7, 53.5, 38.4, 31.6, 27.7, 27.2, 24.3, 21.0, 19.0

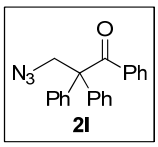


Prepared according to general procedure B with petroleum/CH_2Cl_2 = 6:1-2:1 as eluent to afford **2j** as a colorless oil (0.5 h, 71% yield). The reaction was carried out at -10 °C. **^{1}H NMR** (400 MHz, $CDCl_3$, ppm): δ 7.50-7.47(m, 2H), 7.42-7.32 (m, 6H), 7.27-7.22 (m, 2H), 3.87 (d, *J* = 12.0 Hz, 1H), 3.62 (d, *J* = 12.0 Hz, 1H), 1.75 (s, 3H); **^{13}C NMR** (100 MHz, $CDCl_3$, ppm): δ 201.8, 140.4, 135.7, 132.2, 129.6, 129.2, 128.1, 127.9, 126.4, 60.9, 55.1, 21.1; **IR** (neat) 2106, 1675, 1257, 975, 701 cm^{-1}; **MS** (EI) *m/z*(%) 265(M^+, <1), 181(15), 118(88), 105(100), 77(100), 51(30); **HRMS** (ESI) Calcd. for $C_{16}H_{15}N_3O_1(M+Na)^+$: 288.1107, Found 288.1107.



2k

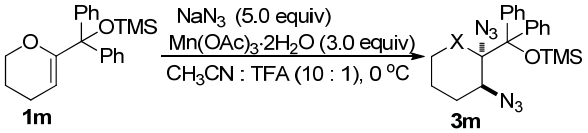
Prepared according to general procedure B with petroleum/CH_2Cl_2 = 4:1-1:1 as eluent to afford **2k** as a colorless oil (0.5 h, 84% yield). **^{1}H NMR** (400 MHz, $CDCl_3$, ppm): δ 7.10 (s, 2H), 7.05 (s, 1H), 6.98 (s, 1H), 6.95 (s, 2H), 3.92 (d, *J* = 12.0 Hz, 1H), 3.54 (d, *J* = 12.0 Hz, 1H), 2.32 (s, 6H), 2.21 (s, 6H), 1.71 (s, 3H); **^{13}C NMR** (100 MHz, $CDCl_3$, ppm): δ 202.5, 140.2, 138.6, 137.6, 136.3, 133.7, 129.4, 127.2, 124.1, 60.9, 55.0, 21.4, 21.2, 21.2; **IR** (neat) 2923, 2104, 1673, 1299, 1045, 703 cm^{-1}; **MS** (EI) *m/z*(%) 321(M^+, <1), 247(10), 146(55), 133(100), 105(25), 91(30), 73(80); **HRMS** (ESI) Calcd. for $C_{20}H_{23}N_3O_1$(M+Na)$^+$: 344.1733, Found 344.1730.



2l

Prepared according to general procedure B with petroleum/CH_2Cl_2 = 4:1-1:1 as eluent to afford **2l** as a colorless oil (0.5 h, 95% yield). **^{1}H NMR** (400 MHz, $CDCl_3$, ppm): δ 7.63 (dd, *J* = 1.2, 8.4 Hz, 2H), 7.46-7.32 (m, 11H), 7.27-7.32 (m, 2H), 4.21 (s, 2H); **^{13}C NMR** (100 MHz, $CDCl_3$, ppm): δ 199.8, 139.0, 136.5, 132.0, 130.0, 129.3, 128.6, 127.8, 127.7, 64.9, 60.7; **IR** (neat) 2103, 1676, 1495, 1446, 1228, 701 cm^{-1}; **MS** (EI) *m/z*(%) 327(M^+, 1), 271(12), 243(10), 180(80), 165(60), 105(100), 77(65); **HRMS** (ESI) Calcd. for $C_{21}H_{17}N_3O_1$(M+Na)$^+$: 350.1264, Found 350.1260.

1.3 General procedure C: the diazidation of allylic silyl ethers **1m-w**:

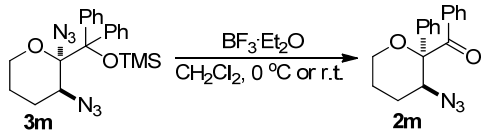


1m **3m**

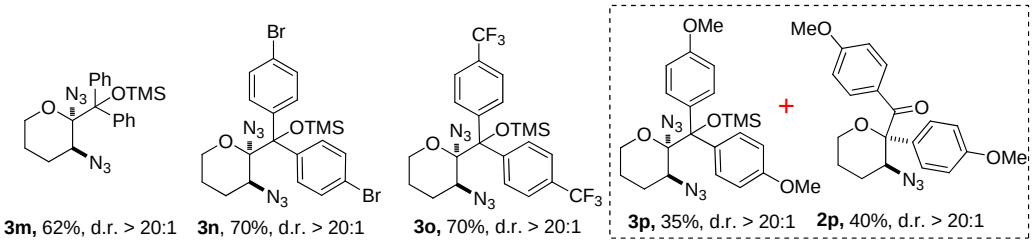
$Mn(OAc)_3·2H_2O$ (0.6 mmol) was dissolved in 1.5 mL of CH_3CN under argon followed by addition of NaN_3 (1.0 mmol) and TFA (0.2 mL) at 0 °C. After 10–20 min, **1m** (0.2 mmol) in 0.5 mL of CH_3CN was added at 0 °C, and the reaction mixture was stirred at 0 °C under argon.

When substrate **1m** was disappeared on TLC (about 2 h), the reaction mixture was quenched with 1.0 mL of saturated aqueous $NaHSO_3$, then warmed to room temperature, diluted with CH_2Cl_2, and extracted with CH_2Cl_2 (5 mL × 3). The combined organic layer was washed with saturated aqueous Na_2CO_3 and brine, dried over anhydrous Na_2SO_4 and concentrated under vacuum. Purification of the residue by column chromatography on silica gel (petroleum/CH_2Cl_2 = 10:1-4:1) provided the pure product **3m** as a white crystalline solid (52.3 mg, 62% yield).

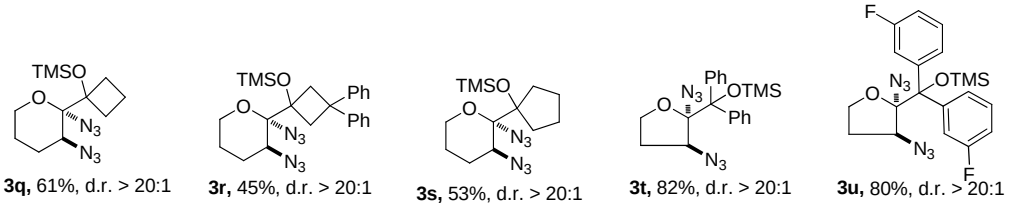
1.4 General procedure D: the semipinacol rearrangement reaction of 1,2-diazides **3m-w**:



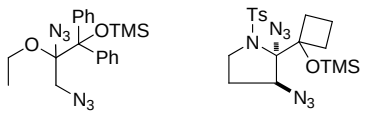
To a solution of **3m** (0.10 mmol, 42.2 mg) in CH_2Cl_2 (2.0 mL) at 0 °C was added $BF_3{\cdot}Et_2O$ (0.2 mmol) under argon. The reaction was monitored by TLC until the substrate **3m** disappeared completely. The reaction mixture was quenched with 1.0 mL of water. Then, the organic layer was separated and aqueous layer was extracted with CH_2Cl_2 (2 mL × 3). The combined organic layer was washed with brine (5 mL), dried over anhydrous Na_2SO_4 and concentrated under vacuum. Purification of the residue by column chromatography on silica gel (petroleum/CH_2Cl_2 = 3:1) provided the compound **2m** (27.0 mg, 88% yield) as a white crystalline solid.



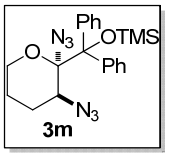
3m, 62%, d.r. > 20:1 **3n**, 70%, d.r. > 20:1 **3o,** 70%, d.r. > 20:1 **3p,** 35%, d.r. > 20:1 **2p,** 40%, d.r. > 20:1



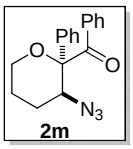
3q, 61%, d.r. > 20:1 **3r,** 45%, d.r. > 20:1 **3s,** 53%, d.r. > 20:1 **3t,** 82%, d.r. > 20:1 **3u,** 80%, d.r. > 20:1



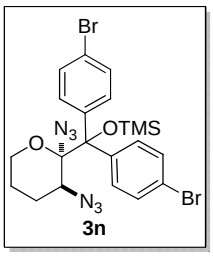
3v, 62% **3w,** 46%, d.r. > 20:1



mp 110.0-112.8 °C; **^{1}H NMR** (400 MHz, $CDCl_3$, ppm): δ 7.78-7.75 (m, 2H), 7.71-7.68 (m, 2H), 7.42-7.40 (m, 3H), 7.34-7.32 (m, 3H), 4.31-4.27 (m, 1H), 4.08-4.01 (m, 1H), 3.19 (s, 1H), 2.31-2.12 (m, 2H), 2.01-1.97 (m, 1H), 1.64-1.59 (m,1H), -0.08 (s, 9H); **^{13}C NMR** (100 MHz, $CDCl_3$, ppm): δ 143.2, 142.6, 131.2, 129.1, 127.6, 127.5, 127.0, 126.9, 96.8, 88.1, 63.6, 56.0, 24.8, 19.1, 1.8; **IR** (neat) 2115, 2101, 1252, 1070, 877, 703 cm^{-1}; **MS** (EI) *m/z*(%) 422(M^+, <1), 255(100), 239(30), 165(35), 105(50), 73(95); **HRMS** (ESI) Calcd. for $C_{21}H_{26}N_6O_2Si_1(M+Na)^+$: 445.1779, Found 445.1770.

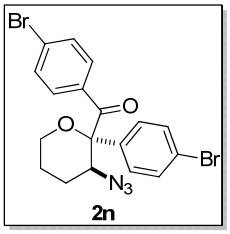


mp 81.5-83.0 °C; **^{1}H NMR** (400 MHz, $CDCl_3$, ppm): δ 7.97 (d, *J* = 7.6 Hz, 2H), 7.48 (d, *J* = 7.6 Hz, 2H), 7.47-7.43 (m, 1H), 7.40-7.36 (m, 2H), 7.34-7.29 (m, 3H), 3.90-3.80 (m, 2H), 3.62-3.55 (m, 1H), 2.32-2.22 (m, 1H), 2.11-2.03 (m, 1H), 1.98-1.89 (m, 1H), 1.82-1.71(m, 1H); **^{13}C NMR** (100 MHz, $CDCl_3$, ppm): δ 199.5, 138.5, 135.2, 132.7, 130.2, 128.6, 128.2, 127.9, 126.2, 85.9, 64.7, 63.9, 24.7, 23.7; **IR** (neat) 2108, 1679, 1256, 1077, 701 cm^{-1}; **MS** (EI) *m/z*(%) 307(M^+, <1), 202(50), 188(42), 160(40), 105(100), 77(95), 51(40); **HRMS** (ESI) Calcd. for $C_{18}H_{17}N_3O_2(M+Na)^+$: 330.1213, Found 330.1207.



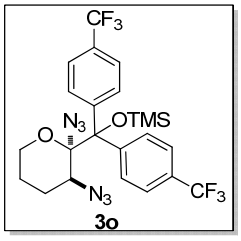
Prepared according to general procedure C with petroleum/CH_2Cl_2 = 10:1-8:1 as eluent to afford **3n** as a colorless oil (2 h, 70% yield). **^{1}H NMR** (400 MHz, $CDCl_3$, ppm): δ 7.55 (d, *J* = 8.8 Hz, 2H), 7.50-7.43 (m, 4H), 7.38 (d, *J* = 8.8 Hz, 2H), 4.24-4.20 (m, 1H), 4.00-3.93 (s, 1H),

3.09 (s, 1H), 2.24-2.02 (m, 2H), 1.97-1.93 (m, 1H), 1.60-1.55 (m, 1H), -0.14 (s, 9H); **^{13}C NMR** (100 MHz, $CDCl_3$, ppm): δ 142.0, 141.4, 133.0, 130.7, 130.3, 130.1, 122.2, 122.0, 96.4, 87.5, 63.7, 55.8, 26.9, 19.0, 1.9; **IR** (neat) 2926, 2115, 1252, 1087, 1011, 884, 740 cm^{-1}; **MS** (EI) *m/z*(%) 580(M^+, 1), 308(100), 240(30), 149(40), 75(95), 55(90); **HRMS** (ESI) Calcd. for $C_{21}H_{24}BrN_4O_2Si_1(M\text{-}N_2+H)^+$: 553.0088, Found 553.0080.



2n

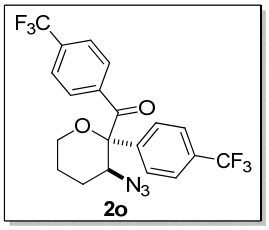
Prepared according to general procedure D with petroleum/CH_2Cl_2 = 6:1-1:1 as eluent to afford **2n** as a colorless oil (76% yield). **^{1}H NMR** (400 MHz, $CDCl_3$, ppm): δ 7.82 (dt, *J* = 2.0, 9.2 Hz, 2H), 7.66-7.44 (m, 4H), 7.34 (dt, *J* = 2.0, 8.8 Hz, 2H), 3.88-3.83 (m, 1H), 3.66-3.63 (m, 1H), 3.57-3.50 (m, 1H), 2.29-2.24 (m, 1H), 2.09-2.04 (m, 1H), 1.95-1.90 (m, 1H), 1.82-1.77 (m, 1H); **^{13}C NMR** (100 MHz, $CDCl_3$, ppm): δ 198.1, 137.5, 133.4, 131.8, 131.8, 131.4, 128.3, 127.8, 122.7, 85.4, 64.4, 64.2, 24.6, 23.8; **IR** (neat) 2927, 2108, 1684, 1251, 1075, 813, 741 cm^{-1}; **MS** (EI) *m/z*(%) 464(M^+, <1), 308(20), 185(40), 75(100), 57(60), 55(50); **HRMS** (ESI) Calcd. for $C_{18}H_{15}BrN_3O_2(M+Na)^+$: 487.9403, Found 487.9399.



3o

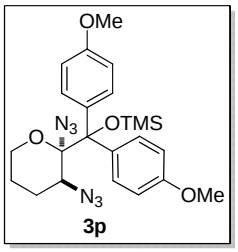
Prepared according to general procedure C with petroleum/CH_2Cl_2 = 10:1-8:1 as eluent to afford **3o** as a colorless oil (2 h, 70% yield). **^{1}H NMR** (400 MHz, $CDCl_3$, ppm): δ 7.79 (d, *J* = 8.0 Hz, 2H), 7.72 (d, *J* = 8.4 Hz, 2H), 7.63 (d, *J* = 8.0 Hz, 2H), 7.54 (d, *J* = 8.4 Hz, 2H), 4.28-4.24 (m, 1H), 4.00 (dt, *J* = 2.4, 12.0 Hz, 1H), 3.16 (s, 1H), 2.26-2.05 (m, 2H), 2.01-1.96 (m, 1H), 1.63-1.59(m,1H), -0.13 (s, 9H); **^{13}C NMR** (100 MHz, $CDCl_3$, ppm): δ 146.9, 146.1, 131.4, 130.4, 130.1, 130.1, 129.8, 129.5, 129.1, 125.5, 125.4, 124.2, 124.2, 124,2, 124.0, 124.0, 122.8,

122.7, 96.4, 87.6, 63.8, 55.8, 27.0, 19.0, 1.8; **IR** (neat) 2925, 2109, 1326, 1259, 1168, 882, 843, 800 cm^{-1}; **MS** (EI) *m/z*(%) 558(M^+, 1), 392(30), 391(95), 299(55), 73(100), 57(45); **HRMS** (ESI) Calcd. for $C_{23}H_{24}F_6N_4O_2Si_1(M\text{-}N_2+H)^+$: 531.1645, Found 531.1641.



2o

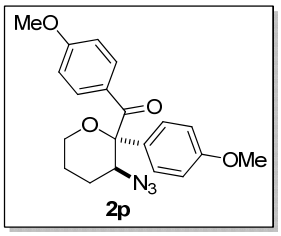
Prepared according to general procedure D with petroleum/EtOAc = 150:1-130:1 as eluent to afford **2o** as a colorless oil (43% yield). **^{1}H NMR** (400 MHz, $CDCl_3$, ppm): δ 8.03 (d, *J* = 8.4 Hz, 2H), 7.67-7.58 (m, 6H), 3.92-3.85 (m, 1H), 3.81-3.78 (m, 1H), 3.62-3.55 (m, 1H), 2.34-2.24 (m, 1H), 2.12-2.05 (m, 1H), 2.03-1.94 (m, 1H), 1.86-1.76 (m, 1H); **^{13}C NMR** (150 MHz, $CDCl_3$, ppm): δ 198.4, 141.9, 137.6, 134.2, 134.0, 130.8, 130.5, 127.4, 126.7, 125.8, 125.8, 125.1, 85.7, 64.2, 64.0, 24.5, 23.4; **IR** (neat) 2926, 2111, 1691, 1169, 1326, 1130, 1069, 1018 cm^{-1}; **MS** (EI) *m/z*(%) 443(M^+, <1), 270(30), 173(100), 145(70), 69(70), 55(50); **HRMS** (ESI) Calcd. for $C_{20}H_{15}F_6N_1O_2(M\text{-}N_2+H)^+$: 416.1080, Found 416.1071.



3p

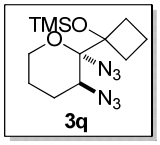
Prepared according to general procedure C with petroleum/CH_2Cl_2 = 5:1-1:1(**3p**) then petroleum/EtOAc = 10:1 (**2p**) as eluent to afford **3p** (0.5-2.0 h, 35% yield) and **2p** (0.5-2.0 h, 40% yield) as a colorless oil. Compound **3p**: **^{1}H NMR** (400 MHz, $CDCl_3$, ppm): δ 7.63 (dd, *J* = 2.0, 7.2 Hz, 2H), 7.52 (dd, *J* = 2.0, 6.8 Hz, 2H), 6.88 (d, *J* = 8.8 Hz, 2H), 6.78 (d, *J* = 9.2 Hz, 2H), 4.24-4.19 (m, 1H), 3.95 (dt, *J* = 2.4, 12.0 Hz, 1H), 3.85 (s, 3H), 3.83 (s, 3H), 3.05 (s, 1H), 2.25-2.04 (m, 2H), 1.94-1.90 (m, 1H), 1.57-1.52(m, 1H), -0.15 (s, 9H); **^{13}C NMR** (100 MHz, $CDCl_3$, ppm): δ 158.9, 158.8, 135.3, 134.9, 132.6, 130.3, 112.3, 112.0, 97.0, 87.5, 63.6, 56.0, 55.1, 55.1, 24.8, 19.1, 1.8; **IR** (neat) 2955, 2113, 1608, 1252, 1038, 881, 842, 735 cm^{-1}; **MS** (EI)

m/z(%) 482(M^+, 15), 235(25), 111(35), 94(45), 73(85), 57(100), 55(90); **HRMS** (ESI) Calcd. for $C_{23}H_{30}N_6O_4Si_1(M+Na)^+$: 505.1990, Found 505.1984.



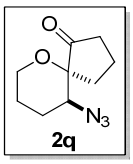
2p

Prepared according to general procedure D with petroleum/EtOAc = 50:1-30:1 as eluent to afford **2p** as a colorless oil (89% yield). **^{1}H NMR** (400 MHz, $CDCl_3$, ppm): δ 8.03-8.00 (m, 2H), 7.41-7.27 (m, 2H), 6.90-6.86 (m, 2H), 6.81-6.76 (m, 2H), 3.89-3.79 (m, 7H), 3.67-3.52 (m, 2H), 2.33-2.22 (m, 1H), 2.10-2.02 (m, 1H), 1.95-1.80 (m, 1H), 1.79-1.75(m, 1H); **^{13}C NMR** (100 MHz, $CDCl_3$, ppm): δ 197.7, 163.1, 159.3, 132.8, 131.1, 127.9, 127.4, 113.9, 113.1, 85.6, 65.1, 63.9, 55.3, 55.2, 24.8, 24.1; **IR** (neat) 2927, 2109, 1672, 1599, 1252, 1173, 1034, 825, 734 cm^{-1}; **MS** (EI) *m/z*(%) 367(M^+, 10), 315(15), 235(20), 135(25), 97(40), 73(60), 57(85), 55(100); **HRMS** (ESI) Calcd. for $C_{20}H_{21}N_3O_4(M+Na)^+$: 390.1424, Found 390.1418.



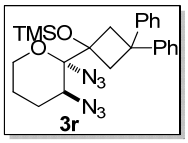
3q

Prepared according to general procedure C with petroleum/CH_2Cl_2 = 10:1-8:1 as eluent to afford **3q** as a colorless oil (9.0 equiv of TFA was added, 0.5 h, 61% yield). **^{1}H NMR** (400 MHz, $CDCl_3$, ppm): δ 3.89 (t, *J* = 2.4 Hz, 1H), 3.84 (dd, *J* = 2.0, 9.6 Hz, 2H), 2.93-2.89 (m, 1H), 2.66-2.60 (m, 1H), 2.22-2.14 (m, 2H), 2.07-2.00 (m, 1H), 1.94-1.83 (m, 3H), 1.73-1.66 (m, 1H), 1.42-1.38 (m, 1H), 0.28 (s, 9H); **^{13}C NMR** (100 MHz, $CDCl_3$, ppm): δ 93.5, 83.8, 63.1, 57.2, 33.3, 31.3, 25.4, 19.1, 13.4, 2.0; **IR** (neat) 2103, 1253, 1147, 844, 758 cm^{-1}; **MS** (EI) *m/z*(%) 310(M^+, <1), 143(35), 73(100), 55(20); **HRMS** (ESI) Calcd. for $C_{12}H_{23}N_4O_2Si_1(M-N_2+H)^+$: 283.1585, Found 283.1582.



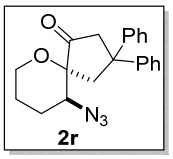
2q

Prepared according to general procedure D with petroleum/EtOAc = 50:1 as eluent to afford **2q** as a colorless oil (87% yield). **^{1}H NMR** (400 MHz, $CDCl_3$, ppm): δ 3.76-3.64 (m, 2H), 3.46 (dd, *J* = 5.2, 12.0 Hz, 1H), 2.51-2.37 (m, 2H), 2.27-2.15 (m, 2H), 2.06-1.64 (m, 6H); **^{13}C NMR** (100 MHz, $CDCl_3$, ppm): δ 214.6, 77.9, 62.6, 59.8, 38.4, 35.8, 24.7, 23.6, 18.0; **IR** (neat) 2103, 1740, 1251, 1070 cm^{-1}; **MS** (EI) *m/z*(%) 195(M^+, 5), 149(35), 123(37), 97(55), 73(85), 57(100), 55(90); **HRMS** (ESI) Calcd. for $C_9H_{13}N_3O_2(M+H)^+$: 196.1081, Found 196.1078.



3r

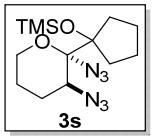
Prepared according to general procedure C with petroleum/CH_2Cl_2 = 10:1-8:1 as eluent to afford **3r** as a colorless oil (9.0 equiv of TFA was added, 1.0 h, 45% yield). **^{1}H NMR** (400 MHz, $CDCl_3$, ppm): δ 7.40 (dd, *J* = 1.2, 8.4 Hz, 2H), 7.30-7.17 (m, 6H), 7.13-7.08 (m, 1H), 7.06-7.01 (m, 1H), 3.74-3.69 (m, 2H), 3.67-3.60 (m, 1H), 3.54-3.49 (m, 2H), 3.14-3.07 (m, 2H), 2.04-1.96 (m, 1H), 1.89-1.76 (m, 2H), 1.35-1.30 (m, 1H), -0.09 (s, 9H); **^{13}C NMR** (100 MHz, $CDCl_3$, ppm): δ 150.4, 150.0, 128.3, 127.9, 126.4, 125.7, 125.4, 124.9, 93.2, 80.0, 62.9, 57.4, 47.1, 44.1, 43.5, 25.1, 18.9, 1.7; **IR** (neat) 2926, 2104, 1252, 1117, 902, 843, 704 cm^{-1}; **MS** (EI) *m/z*(%) 462(M^+, <1), 255(15), 149(40), 97(40),71(55), 57(100), 55(90); **HRMS** (ESI) Calcd. for $C_{24}H_{30}N_3O_2Si_1(M-HN_3+H)^+$: 420.2102, Found 420.2097.



2r

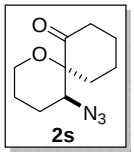
Prepared according to general procedure D with petroleum/EtOAc = 50:1 as eluent to afford **2r** as a colorless oil (81% yield). **^{1}H NMR** (400 MHz, $CDCl_3$, ppm): δ 7.32-7.28 (m, 2H), 7.25-7.20 (m, 7H), 7.29-7.09 (m, 1H), 3.86 (dt, *J* = 2.8, 12.0 Hz, 1H), 3.49-3.36 (m, 3H), 3.08 (d, *J* = 14.0 Hz, 1H), 2.96 (d, *J* = 15.6 Hz, 1H), 2.80 (dd, *J* = 2.8, 14.0 Hz,, 1H), 2.40-2.29 (m, 1H), 2.02-1.97 (m, 1H), 1.76-1.57 (m, 2H); **^{13}C NMR** (100 MHz, $CDCl_3$, ppm): δ 213.6, 148.6, 146.7, 128.6, 128.1, 127.0, 126.4, 126.3, 126.0, 78.4, 62.2, 60.5, 53.2, 48.5, 48.1, 24.3, 23.6; **IR** (neat) 2103, 1740, 1264, 1047, 752, 700 cm^{-1}; **MS** (EI) *m/z*(%) 347(M^+, 1), 317(12), 149(27),

111(30), 97(50), 73(70), 55(100); **HRMS** (ESI) Calcd. for $C_{21}H_{21}N_3O_2Si_1(M+Na)^+$: 370.1526, Found 370.1523.



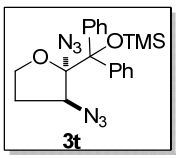
3s

Prepared according to general procedure C with petroleum/CH_2Cl_2 = 12:1-10:1 as eluent to afford **3s** as a colorless oil (9.0 equiv of TFA was added, 1.0 h, 53% yield). **^{1}H NMR** (400 MHz, $CDCl_3$, ppm): δ 3.96 (t, *J* = 2.8 Hz, 1H), 3.84-3.72 (m, 2H), 2.47 (td, *J* = 4.8, 8.8 Hz, 1H), 2.18-1.90 (m, 2H), 1.90-1.70 (m, 7H), 1.70-1.40 (m, 1H), 1.38-1.37 (m, 1H), 0.21 (s, 9H); **^{13}C NMR** (100 MHz, $CDCl_3$, ppm): δ 95.2, 92.2, 63.2, 57.3, 37.2, 36.3, 26.0, 24.2, 19.0, 2.2; **IR** (neat) 2957, 2104, 1253, 1105, 912, 842 cm^{-1}; **MS** (EI) *m/z*(%) 324(M^+, 5), 157(40), 97(35), 73(100), 57(83), 55(95); **HRMS** (ESI) Calcd. for $C_{13}H_{24}N_4O_2Si_1$ $(M-N_2+H)^+$: 297.1741, Found 297.1737.



2s

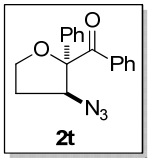
Prepared according to general procedure D with petroleum/EtOAc = 50:1-20:1 as eluent to afford **2s** as a colorless oil (60% yield). **^{1}H NMR** (400 MHz, $CDCl_3$, ppm): δ 3.82-3.78 (m, 1H), 3.25 (td, *J* = 3.2, 11.2 Hz, 1H), 3.05 (dd, *J* = 4.4, 11.2 Hz, 1H), 2.70 (td, *J* = 6.0, 12.8 Hz, 1H), 2.34-2.22 (m, 2H), 2.15-2.10 (m, 1H), 2.08-1.91 (m, 3H), 1.86-1.59 (m, 5H); **^{13}C NMR** (100 MHz, $CDCl_3$, ppm): δ 211.1, 80.1, 63.3, 62.3, 39.9, 37.8, 27.5, 24.9, 23.8, 20.0; **IR** (neat) 2928, 2104, 1721, 1254, 1073, 990, 735 cm^{-1}; **MS** (EI) *m/z*(%) 209(M^+, 1), 149(30), 97(40), 73(90), 57(100), 55(98); **HRMS** (ESI) Calcd. for $C_{10}H_{15}N_3O_2(M+Na)^+$: 232.1056, Found 232.1052.



3t

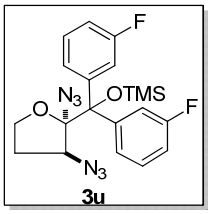
Prepared according to general procedure C with petroleum/CH_2Cl_2 = 10:1-8:1 as eluent to afford **3t** as a colorless oil (1.0 h, 82% yield). **^{1}H NMR** (400 MHz, $CDCl_3$, ppm): δ 7.71-7.65

(m, 4H), 7.36-7.28 (m, 6H), 4.45-4.35 (m, 2H), 3.58 (s, 1H), 2.51 (m, 1H), 2.12-2.10 (m, 1H), 0.01 (s, 9H); **IR** (neat) 2107, 1252, 1105, 841, 703 cm^{-1}; **MS** (EI) *m/z*(%) 408(M^+, <1), 255(100), 165(15), 105(20), 73(98); **HRMS** (ESI) Calcd. for $C_{20}H_{24}N_6O_2Si_1(M+Na)^+$: 431.1622, Found 431.1614.



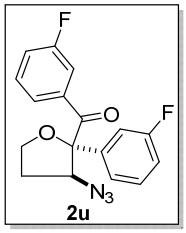
2t

Prepared according to general procedure D with petroleum/EtOAc = 50:1 as eluent to afford **2t** as a colorless oil (70% yield). **^{1}H NMR** (400 MHz, $CDCl_3$, ppm): δ 8.05-8.04 (m, 2H), 7.71-7.68 (m, 2H), 7.50-7.46 (m, 1H), 7.42-7.34 (m, 4H), 7.33-7.28 (m, 1H), 4.64 (d, *J* = 4.0 Hz, 1H), 4.38-4.27 (m, 2H), 2.07-1.92 (m, 2H); **^{13}C NMR** (100 MHz, $CDCl_3$, ppm): δ 198.6, 139.0, 136.0, 132.8, 130.1, 128.9, 128.3, 127.9, 125.4, 96.3, 71.0, 67.7, 29.7; **IR** (neat) 2926, 2105, 1674, 1267, 1114, 752, 701 cm^{-1}; **MS** (EI) *m/z*(%) 293(M^+, <1), 255(25), 188(50), 105(100), 77(90), 51(20); **HRMS** (ESI) Calcd. for $C_{17}H_{15}N_3O_2(M+Na)^+$: 316.1056, Found 316.1053.

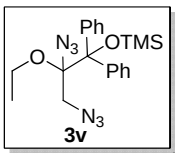


3u

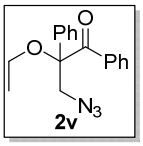
Prepared according to general procedure C with petroleum/CH_2Cl_2 = 10:1-8:1 as eluent to afford **3u** as a colorless oil (1.0 h, 80% yield). **^{1}H NMR** (400 MHz, $CDCl_3$, ppm): δ 7.12-7.01 (m, 6H), 6.76-6.72 (m, 2H), 4.19 (t, *J* = 8.8 Hz, 1H), 4.08-4.05 (m, 1H), 2.27-2.25 (m, 1H), 1.88-1.86 (m, 1H), -0.22 (m, 9H); **IR** (neat) 2108, 1252, 1104, 1014, 843, 772 cm^{-1}; **MS** (EI) *m/z*(%) 444(M^+, 1), 291(75), 73(100); **HRMS** (ESI) Calcd. for $C_{20}H_{22}F_2N_3O_2Si_1(M-HN_3+H)^+$: 402.1444, Found 402.1436.



Prepared according to general procedure D with petroleum/EtOAc = 50:1 as eluent to afford **2u** as a colorless oil (41% yield). **^{1}H NMR** (400 MHz, $CDCl_3$, ppm): δ 7.86-7.82 (m, 1H), 7.80-7.75 (m, 1H), 7.47-7.44 (m, 1H), 7.42-7.33 (m, 3H), 7.23-7.71 (m, 1H), 7.05-6.99 (m, 1H), 4.61 (d, J = 3.6 Hz, 1H), 4.38-4.28 (m, 2H), 2.08-2.01 (m, 1H), 2.00-1.95 (m, 1H); **^{13}C NMR** (100 MHz, $CDCl_3$, ppm): δ 197.2, 163.9 (d, J_F = 96.0 Hz), 161.4 (d, J_F = 96.0 Hz), 141.5 (d, J_F = 7.0 Hz), 137.6 (d, J_F = 7.0 Hz), 130.6 (d, J_F = 8.0 Hz), 129.6 (q, J_F = 7.0 Hz), 125.9 (d, J_F = 3.0 Hz), 121.1 (d, J_F = 3.0 Hz), 120.0 (d, J_F = 21.0 Hz), 117.1(d, J_F = 23.0 Hz), 115.5 (d, J_F = 21.0 Hz), 112.8 (d, J_F = 23.0 Hz), 95.9, 71.0, 68.0, 29.7; **IR** (neat) 2112, 1679, 1270, 1115, 775 cm^{-1}; **MS** (EI) *m/z*(%) 329(M^+, 1), 317(80), 270(30), 149(30), 123(50), 73(100), 57(90), 55(70); **HRMS** (ESI) Calcd. for $C_{17}H_{13}F_2N_1O_2(M\text{-}N_2+H)^+$: 302.0987, Found 302.0983.

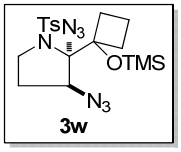


Prepared according to general procedure C with petroleum/CH_2Cl_2 = 6:1-4:1 as eluent to afford **3v** as a colorless oil (1.0 h, 62% yield). **^{1}H NMR** (400 MHz, $CDCl_3$, ppm): δ 7.57-7.53 (m, 2H), 7.49-7.45 (m, 2H), 7.30-7.23 (m, 6H), 4.03-3.94 (m, 1H), 3.82-3.71 (m, 2H), 3.16 (d, J = 13.6 Hz, 1H), 1.20 (t, J = 7.2 Hz, 3H), -0.1 (s, 9H); **^{13}C NMR** (100 MHz, $CDCl_3$, ppm): δ 143.5, 143.0, 130.4, 128.8, 127.7, 127.5, 127.3, 127.3, 96.6, 86.3, 61.9, 54.9, 15.5, 1.7; **IR** (neat) 2977, 2120, 1105, 842, 702 cm^{-1}; **MS** (EI) *m/z*(%) 410(M^+, 1), 255(100), 239(10), 165(10), 73(70); **HRMS** (ESI) Calcd. for $C_{20}H_{26}N_3O_2Si_1(M\text{-}HN_3+H)^+$: 368.1789, Found 368.1784.



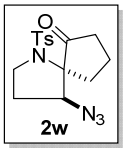
Prepared according to general procedure D with petroleum/CH_2Cl_2 = 1:1 as eluent to afford **2v**

as a colorless oil (86% yield). **^{1}H NMR** (400 MHz, $CDCl_3$, ppm): δ 7.99 (d, *J* = 7.6 Hz, 2H), 7.55 (d, *J* = 7.2 Hz, 2H), 7.46 (t, *J* = 7.6 Hz, 1H), 7.39 (t, *J* = 7.6 Hz, 2H), 7.34-7.29 (m, 3H), 4.19 (d, *J* = 13.6 Hz, 1H), 3.83-3.73 (m, 2H), 3.34-3.26 (m, 1H), 1.18 (t, *J* = 6.8 Hz, 3H); **^{13}C NMR** (100 MHz, $CDCl_3$, ppm): δ 199.7, 138.9, 134.1, 133.2, 130.1, 128.7, 128.2, 128.1, 125.3, 86.9, 60.7, 54.8, 15.1; **IR** (neat) 2102, 1676, 1246, 1112, 1075, 702 cm^{-1}; **MS** (EI) *m/z*(%) 295(M^+, <1), 239(12), 190(40), 105(100), 77(50); **HRMS** (ESI) Calcd. for $C_{17}H_{17}N_1O_2(M\text{-}N_2+H)^+$: 268.1332, Found 268.1330.



3w

Prepared according to general procedure C with petroleum/EtOAc = 40:1-20:1 as eluent to afford **3w** as a colorless oil (9.0 equiv of TFA was added, 1.0 h, 46% yield). **^{1}H NMR** (400 MHz, $CDCl_3$, ppm): δ 7.86 (d, *J* = 8.4 Hz, 2H), 7.31 (d, *J* = 8.0 Hz, 2H), 3.90 (t, *J* = 7.2 Hz, 1H), 3.59-3.52 (m, 1H), 3.49-3.42 (m, 1H), 3.12-3.03 (m, 2H), 2.44 (s, 3H), 2.34-2.21 (m, 2H), 2.09-1.82 (m, 4H), 0.29 (s, 9H); **^{13}C NMR** (100 MHz, $CDCl_3$, ppm): δ 143.8, 136.6, 129.5, 128.3, 89.7, 84.4, 68.9, 48.7, 33.6, 33.5, 26.9, 21.5, 13.8, 2.1; **IR** (neat) 2958, 2110, 1258, 1162, 1097, 846, 667 cm^{-1}; **MS** (EI) *m/z*(%) 449(M^+, 1), 317(35), 149(28), 95(37), 73(100), 57(77), 55(70); **HRMS** (ESI) Calcd. for $C_{18}H_{27}N_7O_3S_1(M+Na)^+$: 472.1558, Found 472.1552.

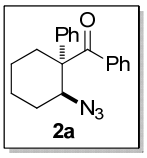


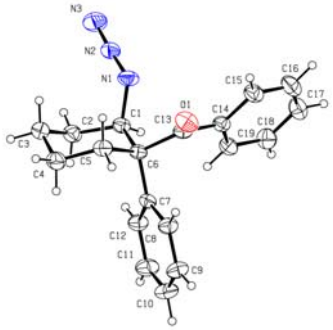
2w

Prepared according to general procedure D with petroleum/EtOAc = 10:1-6:1 as eluent to afford **2w** as a colorless oil (90% yield). **^{1}H NMR** (400 MHz, $CDCl_3$, ppm): δ 7.79 (d, *J* = 8.4 Hz, 2H), 7.31 (d, *J* = 8.0 Hz, 2H), 3.87 (t, *J* = 6.4 Hz, 1H), 3.50-3.44 (m, 2H), 2.93-2.84 (m, 1H), 2.52-2.39 (m, 5H), 2.32-2.16 (m, 3H), 2.11-2.05 (m, 1H), 1.95-1.89 (m, 1H); **^{13}C NMR** (100 MHz, $CDCl_3$, ppm): δ 213.4, 143.6, 136.8, 129.5, 127.6, 74.3, 68.8, 45.7, 36.4, 35.7, 29.3, 21.5, 18.1; **IR** (neat) 2107, 1752, 1334, 1157, 666, 596, 548 cm^{-1}; **MS** (EI) *m/z*(%) 334(M^+, 15), 149(30), 84(50), 73(75),57(100), 55(90); **HRMS** (ESI) Calcd. for $C_{15}H_{18}N_4O_3S_1(M+Na)^+$:

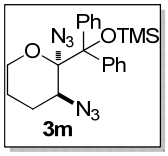
357.0992, Found 357.0985.

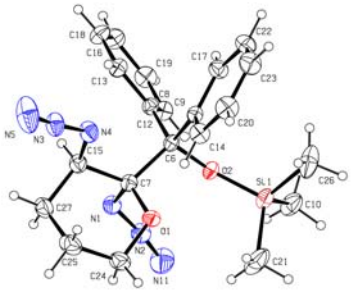
2. X-Ray ellipsoid plots of 2a, 3m and 2m



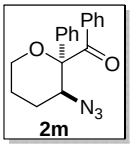


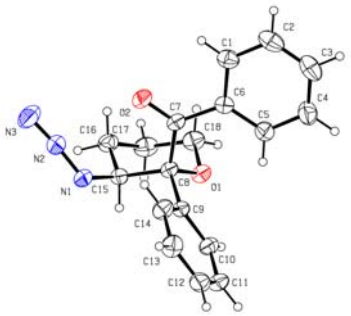
The structure of compound **2a** was corroborated by single-crystal. The crystal structure has been deposited at the Cambridge Crystallographic Data Centre and allocated the deposition number: 997264.





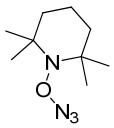
The structure of compound **3m** was corroborated by single-crystal. The crystal structure has been deposited at the Cambridge Crystallographic Data Centre and allocated the deposition number: 997265.



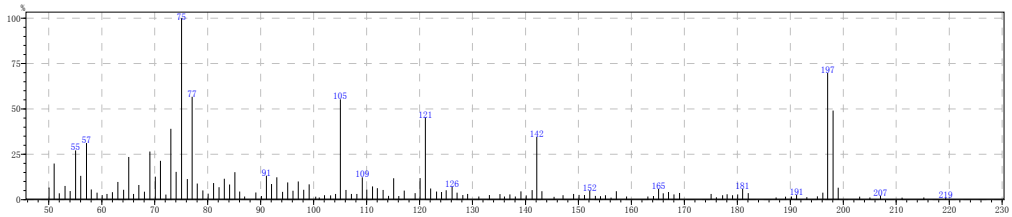


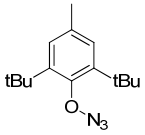
The structure of compound **2m** was corroborated by single-crystal. The crystal structure has been deposited at the Cambridge Crystallographic Data Centre and allocated the deposition number: 997266.

3. Mechanistic studies

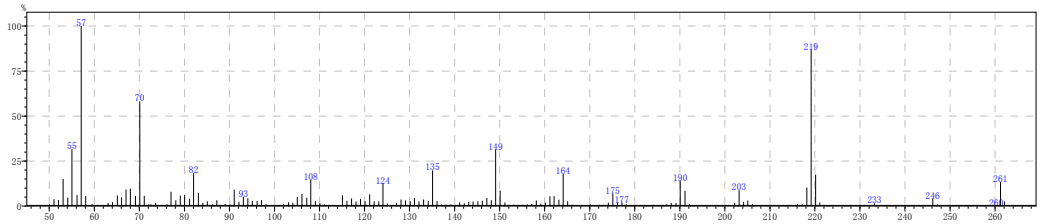


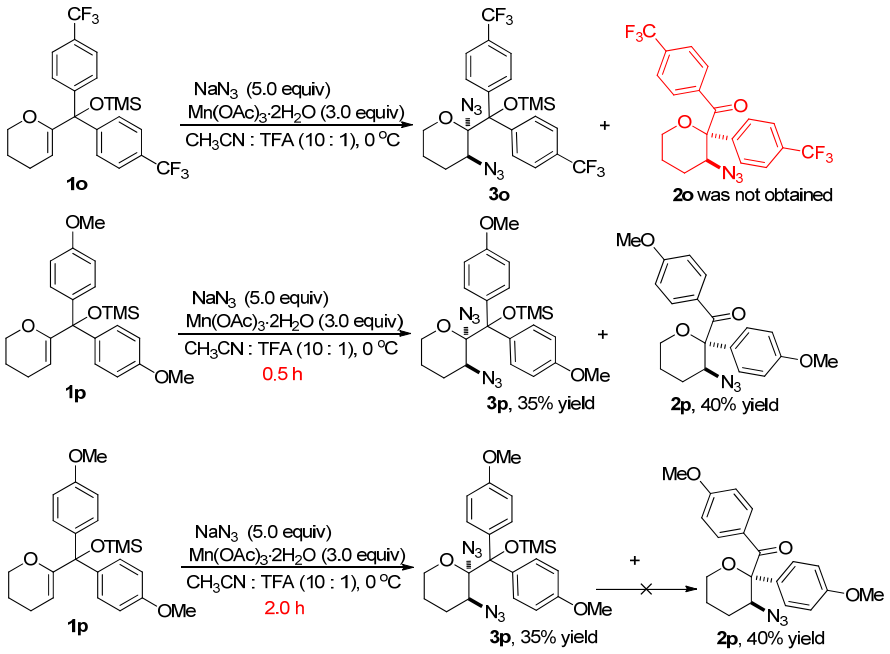
Chemical Formula: $C_9H_{18}N_4O$
m/z: 198.15 (100.0%), 199.15 (11.5%)





Chemical Formula: $C_{15}H_{23}N_3O$
m/z: 261.18 (100.0%), 262.19 (16.5%), 263.19 (1.5%), 262.18 (1.1%)





Based on previous literatures,[2] electron-rich phenyl groups are prior to migrate in cationic rearrangements, whereas electron-poor phenyl groups are prior to migrate in radical rearrangements. In the course of our experiments, the substrate **1p** with the more electron-rich aryl groups could give **3p** and rearrangement product **2p**, whereas the substrate **1o** with more electron-deficient aryl groups did not give the rearrangement product **2o**. Additionally, while the reaction time was extended to 2.0 h, the amount of **2p** has not changed. Therefore, we also ruled out the product **2p** was got from **3p** under the standard conditions. When the amount of NaN_3 was reduced (1.5 equiv), the yields of **3p** and **2p** were reduced but the ratio of **2p** and **3p** was not changed. Considering the above results, we speculated that the diazidation reaction might proceed through only one possible way with a cyclic oxonium intermediate.

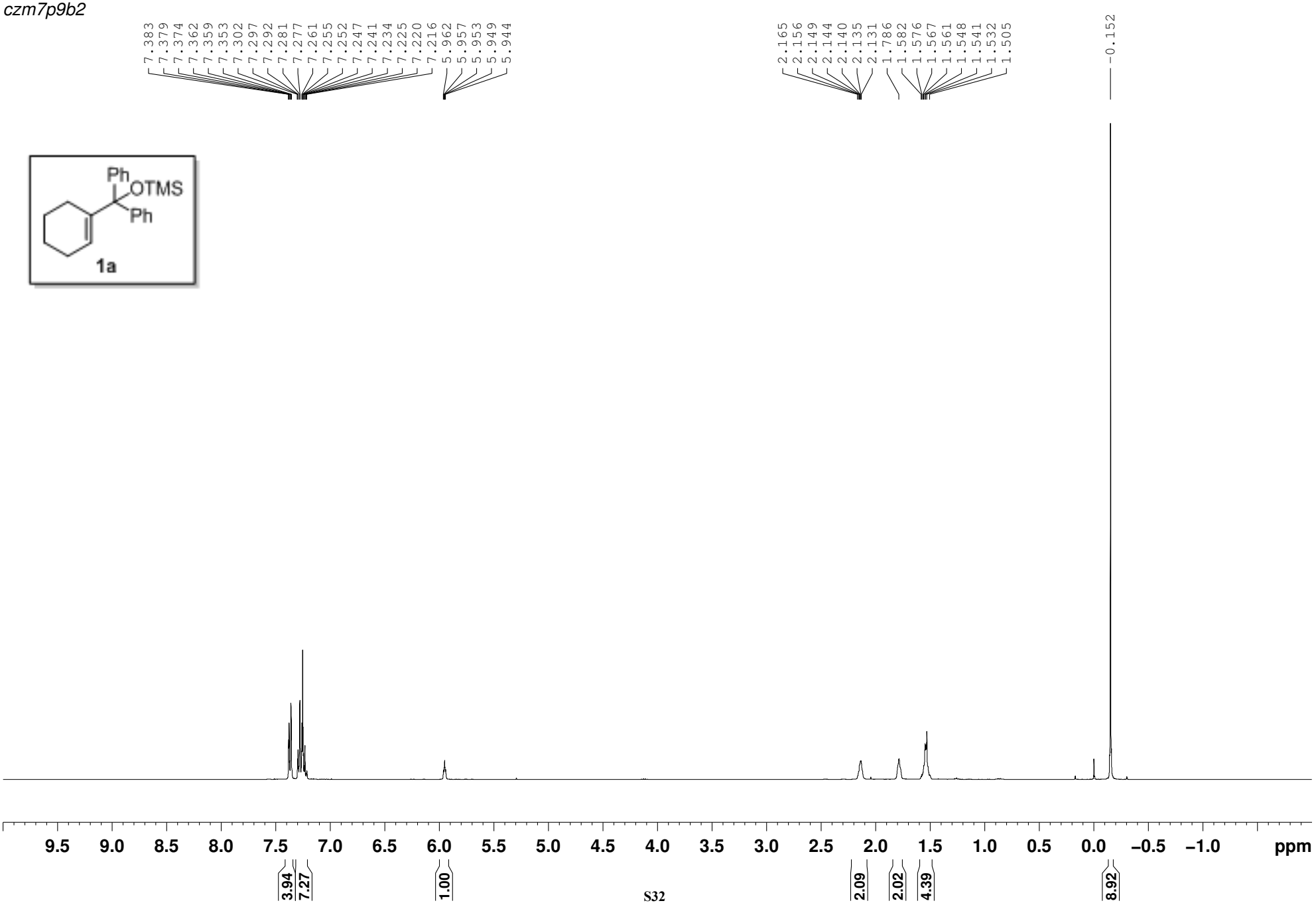
Reference

1. The substrates **1q**, **1r**, **1s**, and **1w**, see: H. Shao, X.-M. Zhang, S.-H. Wang, F.-M. Zhang, Y.-Q. Tu, C. Yang, *Chem. Commun.* 2014, **50**, 5691.

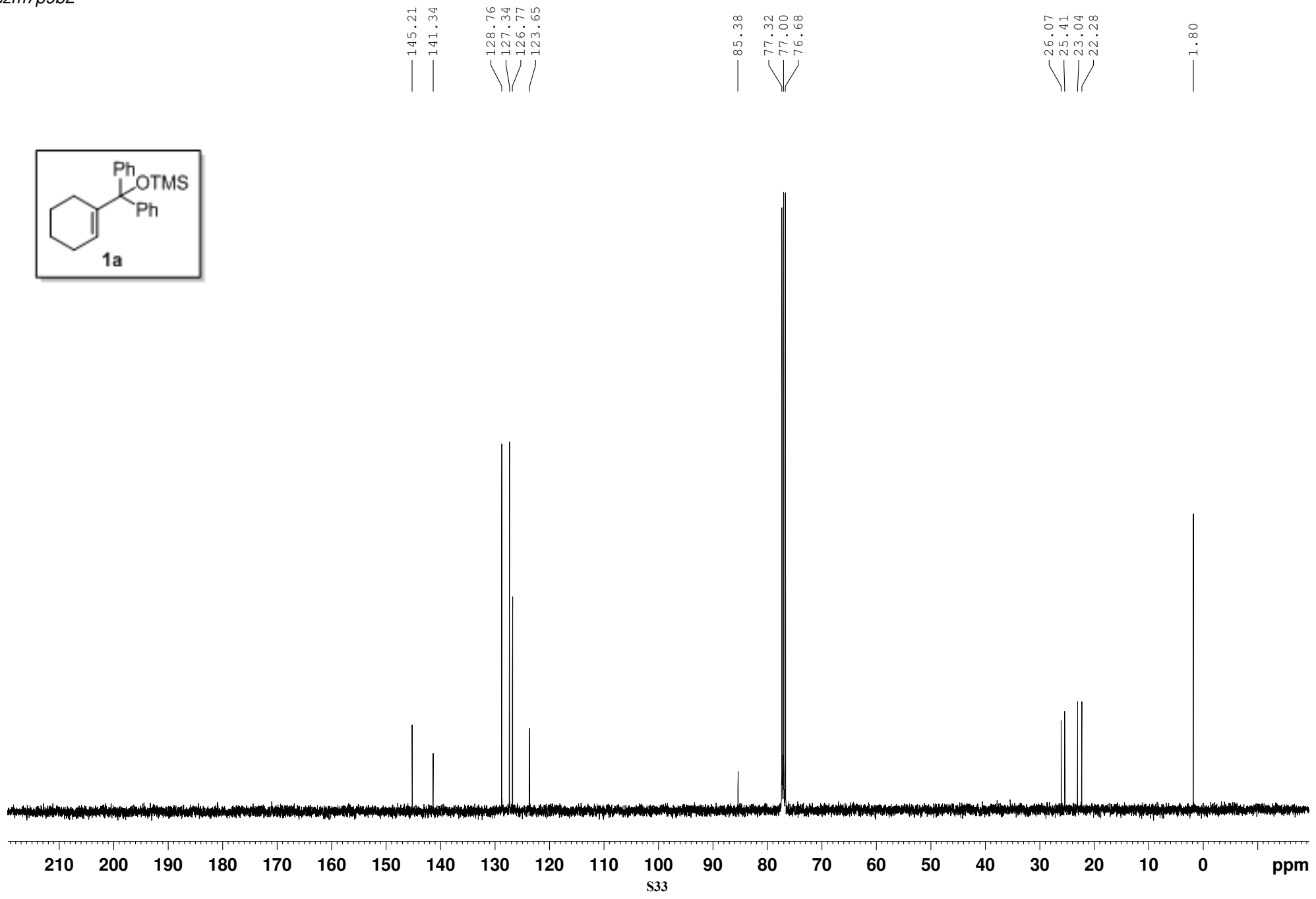
2. (a) X. Liu, F. Xiong, X. Huang, L. Xu, P. Li, X. Wu, *Angew. Chem. Int. Ed.* 2013, **52**, 6962; (b) A. Studer, M. Bossart, *Tetrahedron* 2001, **57**, 9649.

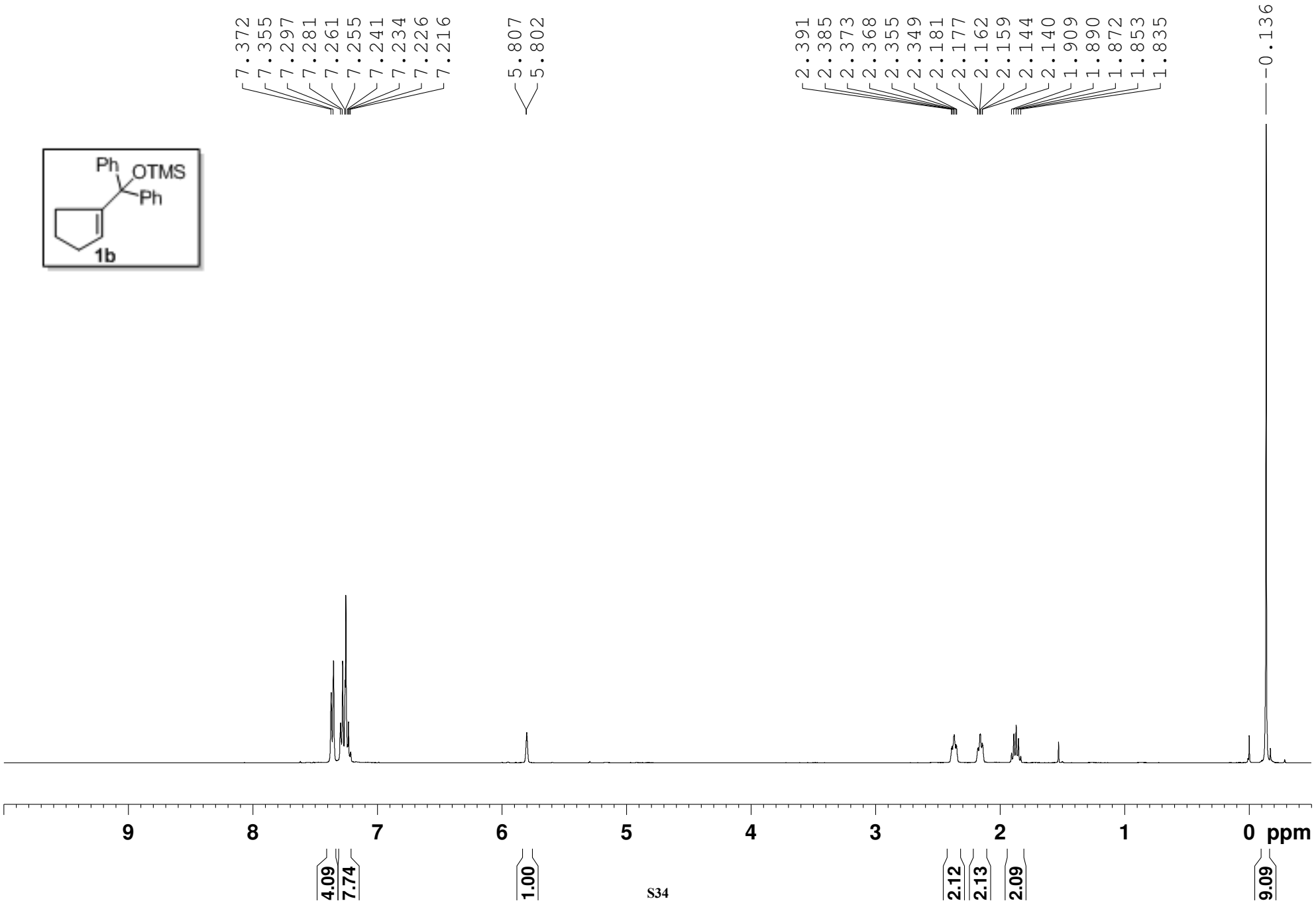
4. NMR spectra of substrates and products

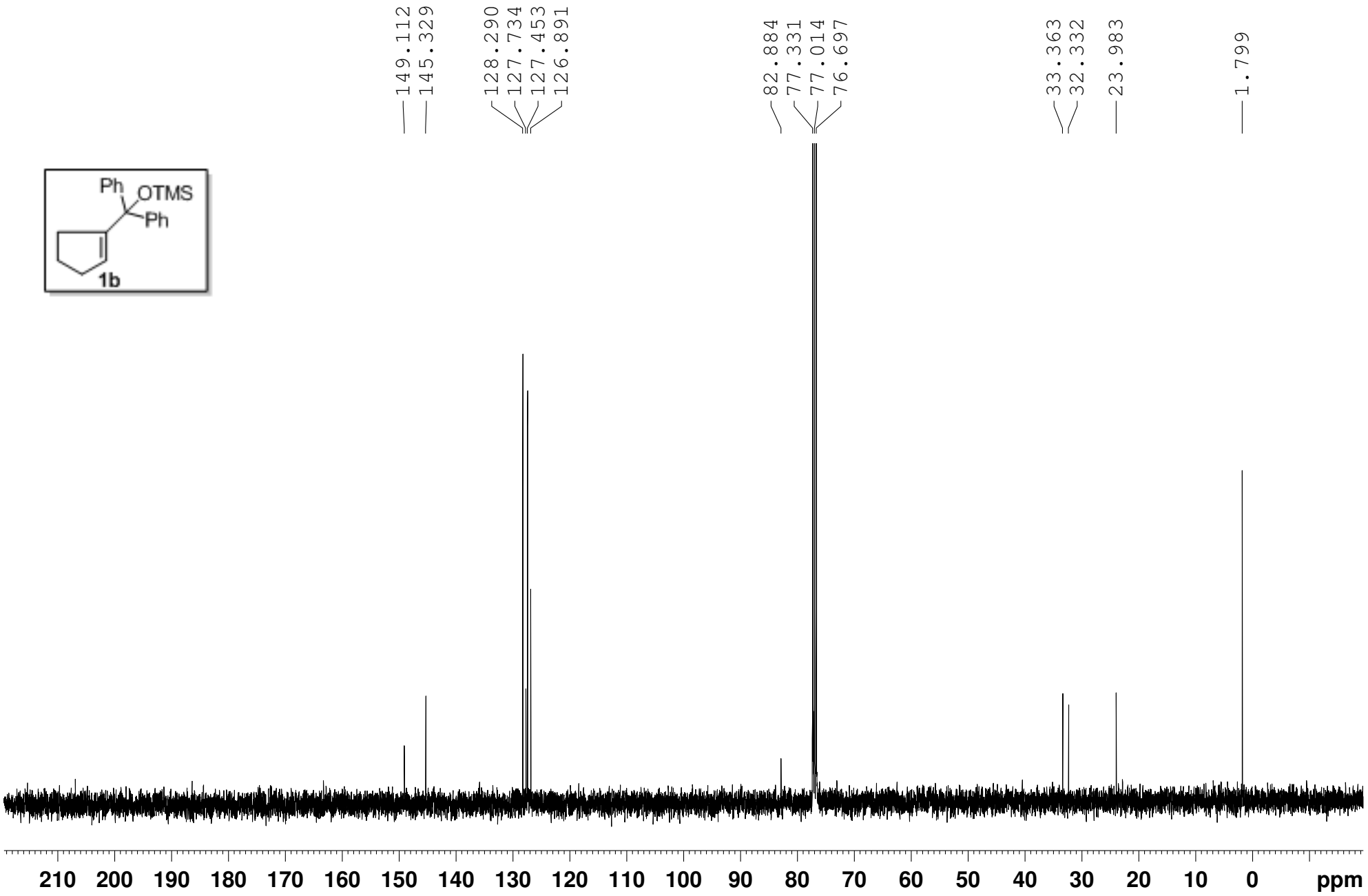
czm7p9b2


7.383
7.379
7.374
7.362
7.359
7.353
7.302
7.297
7.292
7.281
7.277
7.261
7.255
7.252
7.247
7.241
7.234
7.225
7.220
7.216
5.962
5.957
5.953
5.949
5.944
2.165
2.156
2.149
2.144
2.140
2.135
2.131
1.786
1.582
1.576
1.567
1.561
1.548
1.541
1.532
1.505
0.152
Ph
OTMS
Ph
1a
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
−0.5
−1.0
ppm
3.94
7.27
1.00
2.09
2.02
4.39
8.92

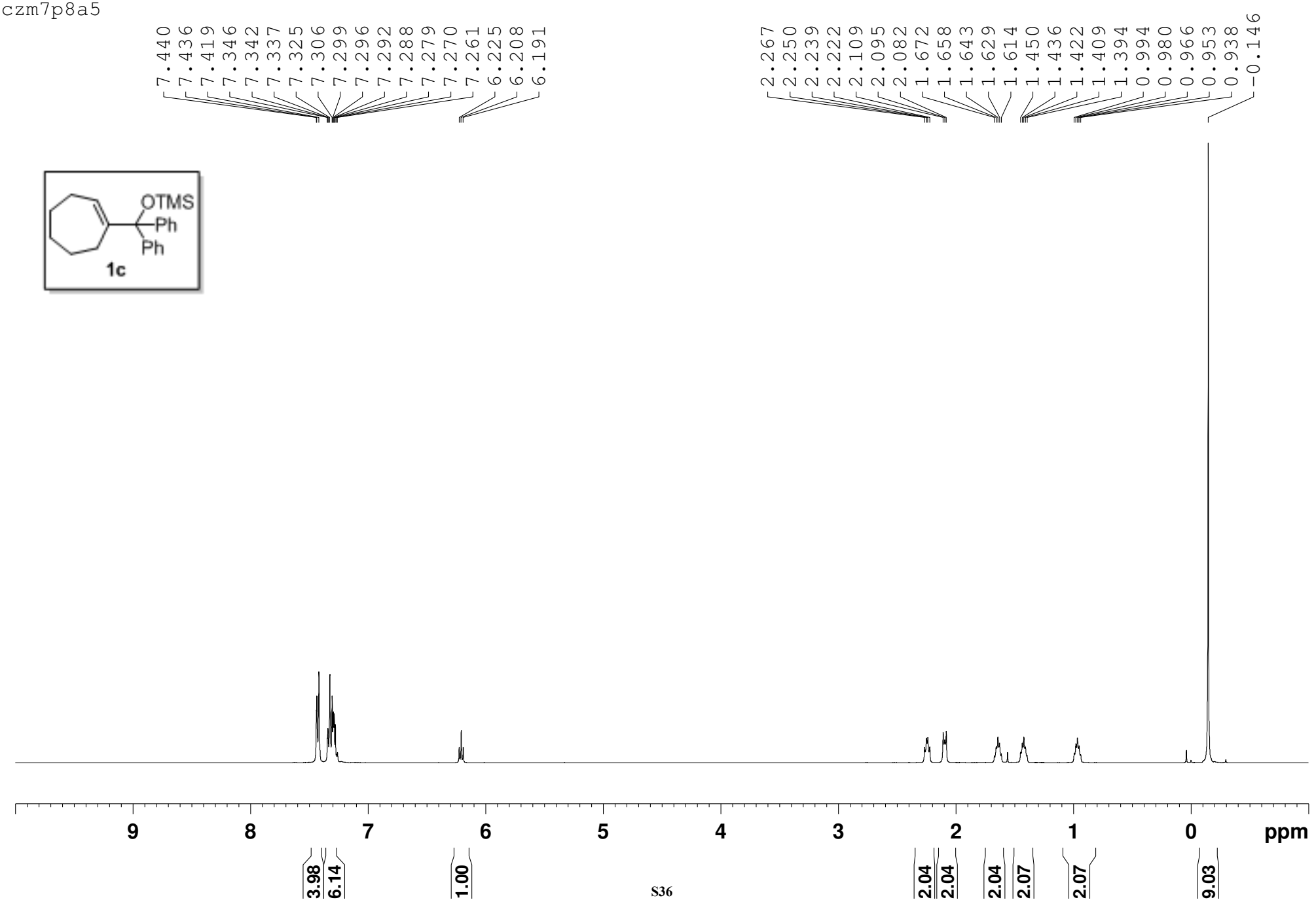
czm7p9b2


145.21
141.34
128.76
127.34
126.77
123.65
85.38
77.32
77.00
76.68
26.07
25.41
23.04
22.28
1.80
Ph
OTMS
Ph
1a
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
ppm

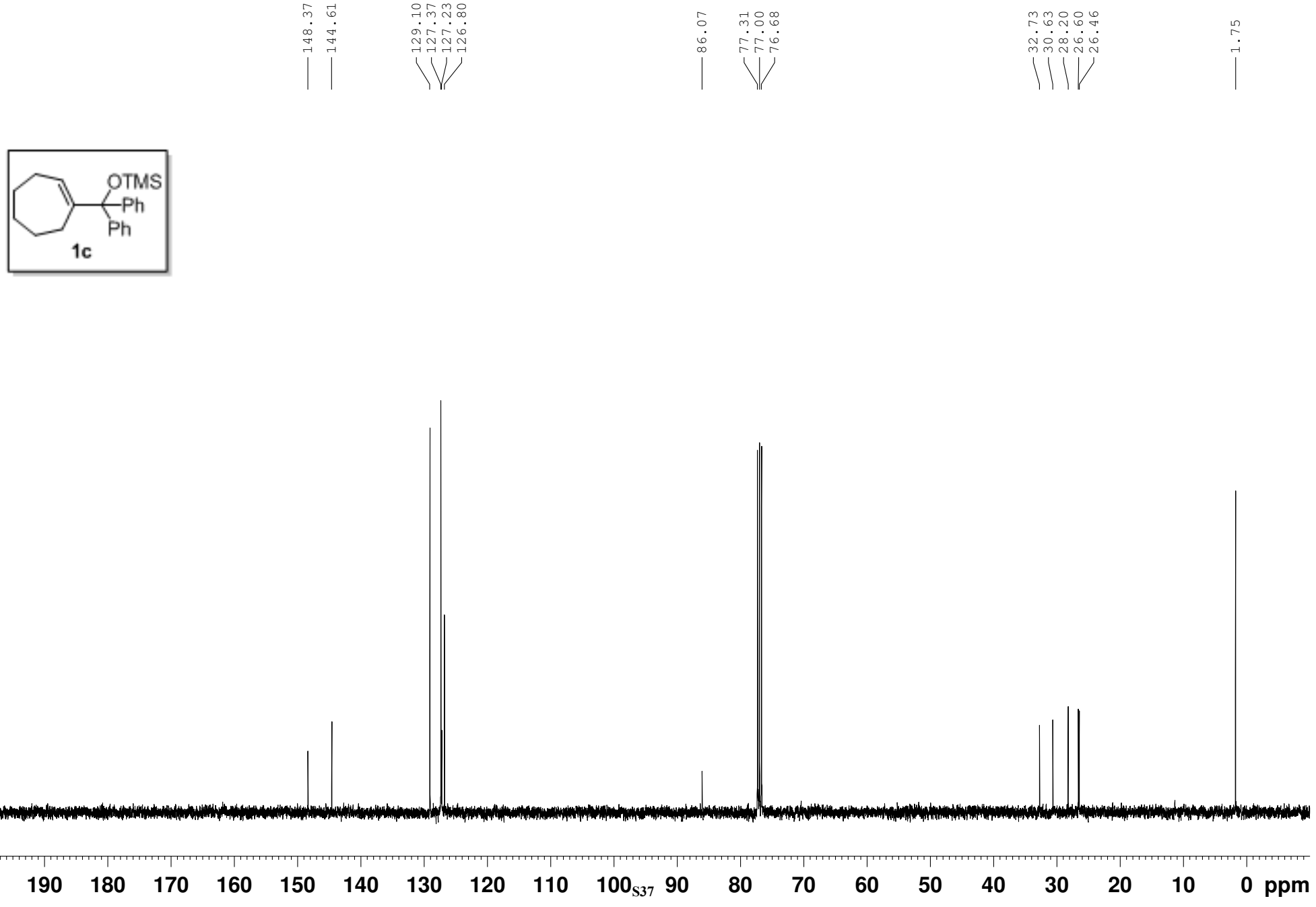

7.372
7.355
7.297
7.281
7.261
7.255
7.241
7.234
7.226
7.216
5.807
5.802
2.391
2.385
2.373
2.368
2.355
2.349
2.181
2.177
2.162
2.159
2.144
2.140
1.909
1.890
1.872
1.853
1.835
0.136
Ph
OTMS
Ph
1b
9
8
7
6
5
4
3
2
1
0 ppm
4.09
7.74
1.00
2.12
2.13
2.09
9.09


149.112
145.329
128.290
127.734
127.453
126.891
82.884
77.331
77.014
76.697
33.363
32.332
23.983
1.799
Ph
OTMS
Ph
1b
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 ppm

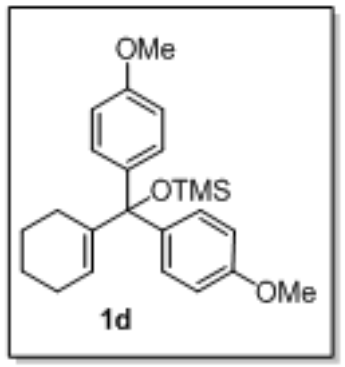
czm7p8a5


7.440
7.436
7.419
7.346
7.342
7.337
7.325
7.306
7.299
7.296
7.292
7.288
7.279
7.270
7.261
6.225
6.208
6.191
2.267
2.250
2.239
2.222
2.109
2.095
2.082
1.672
1.658
1.643
1.629
1.614
1.450
1.436
1.422
1.409
1.394
0.994
0.980
0.966
0.953
0.938
-0.146
OTMS
Ph
Ph
1c
9
8
7
6
5
4
3
2
1
0
ppm
3.98
6.14
1.00
2.04
2.04
2.04
2.07
2.07
9.03

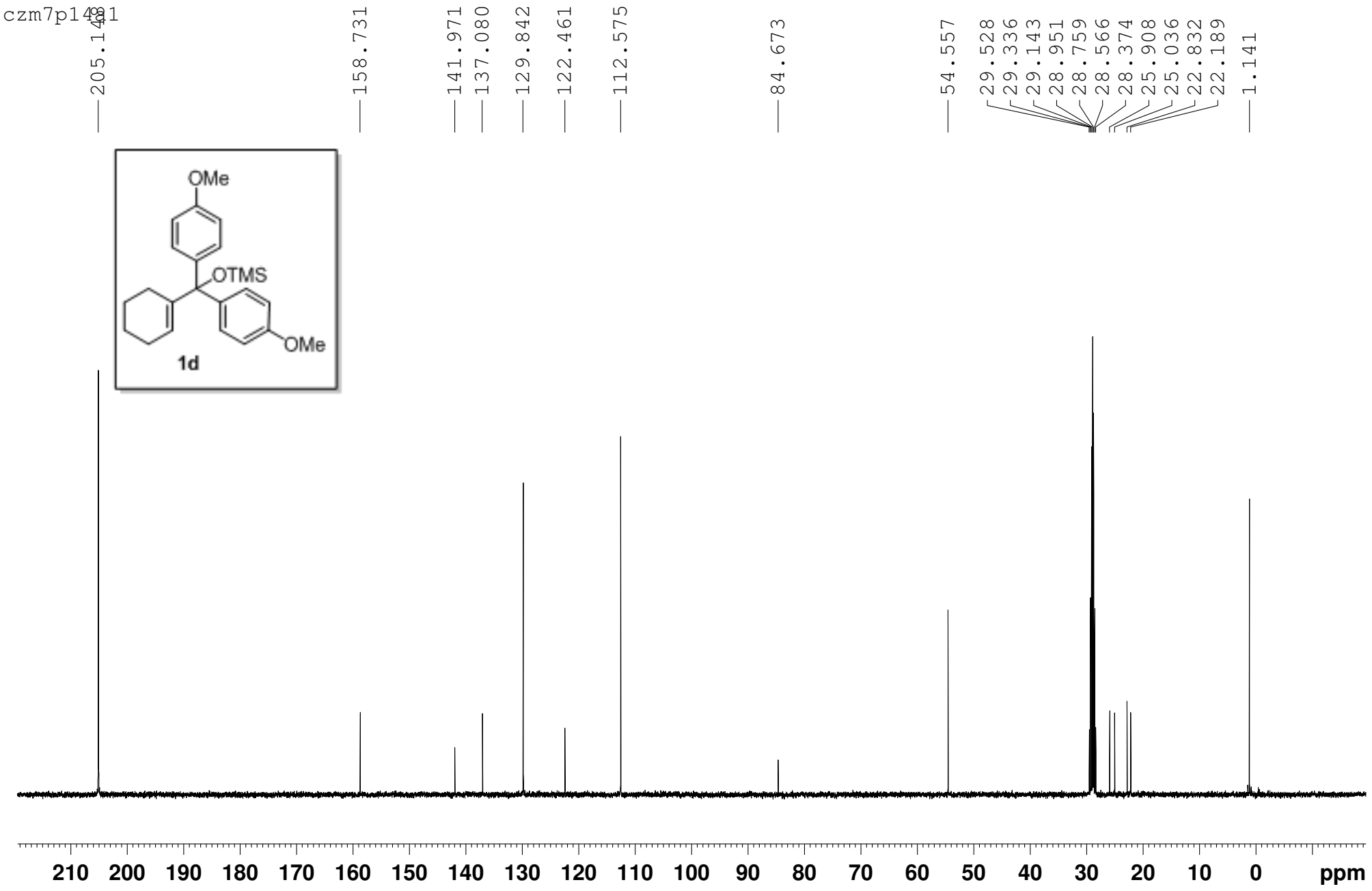
czm7p8a5


148.37
144.61
129.10
127.37
127.23
126.80
86.07
77.31
77.00
76.68
32.73
30.63
28.20
26.60
26.46
1.75
OTMS
Ph
Ph
1c
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
ppm

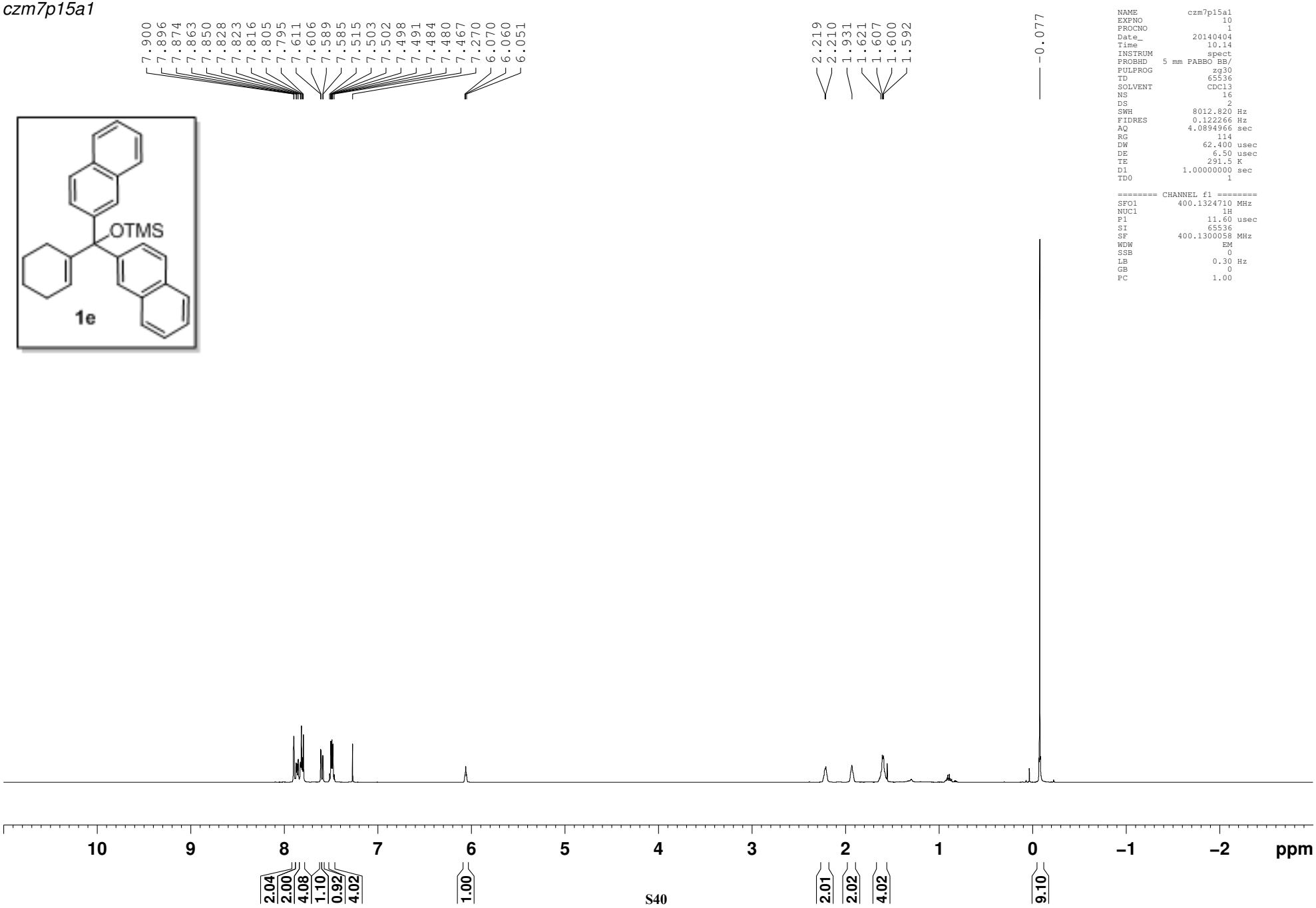
czm7p14a1


OMe
OTMS
OMe
1d

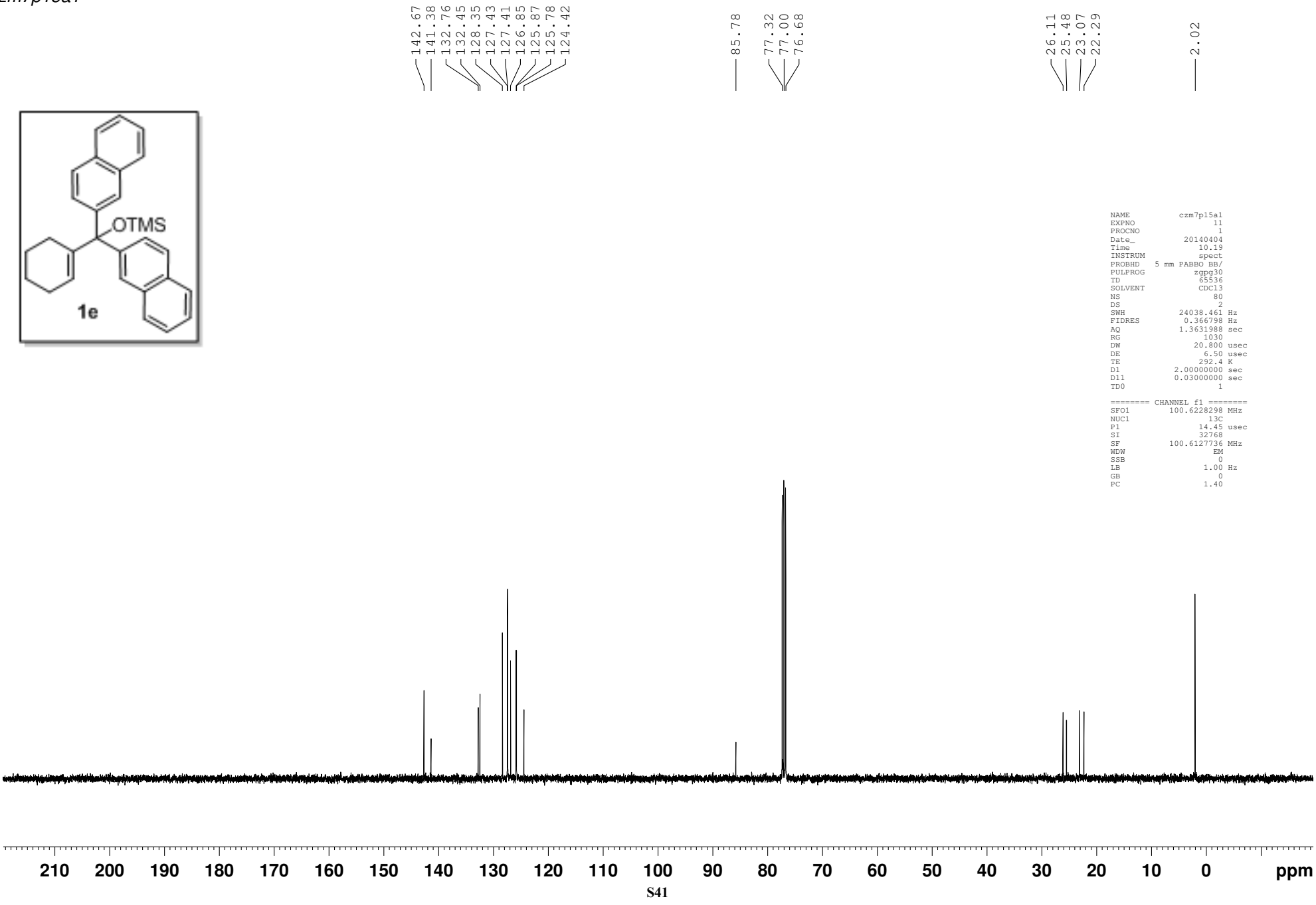
7.296
7.279
7.274
6.886
6.869
6.864
5.971
5.962
5.952
3.792
2.126
2.061
2.055
2.050
2.045
2.039
1.783
1.536
1.529
1.522
0.149
9
8
7
6
5
4
3
2
1
0 ppm
4.11
4.10
1.00
6.19
2.25
2.22
4.42
9.23


czm7p1481
205.148
158.731
141.971
137.080
129.842
122.461
112.575
84.673
54.557
29.528
29.336
29.143
28.951
28.759
28.566
28.374
25.908
25.036
22.832
22.189
1.141
OMe
OTMS
OMe
1d
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 ppm

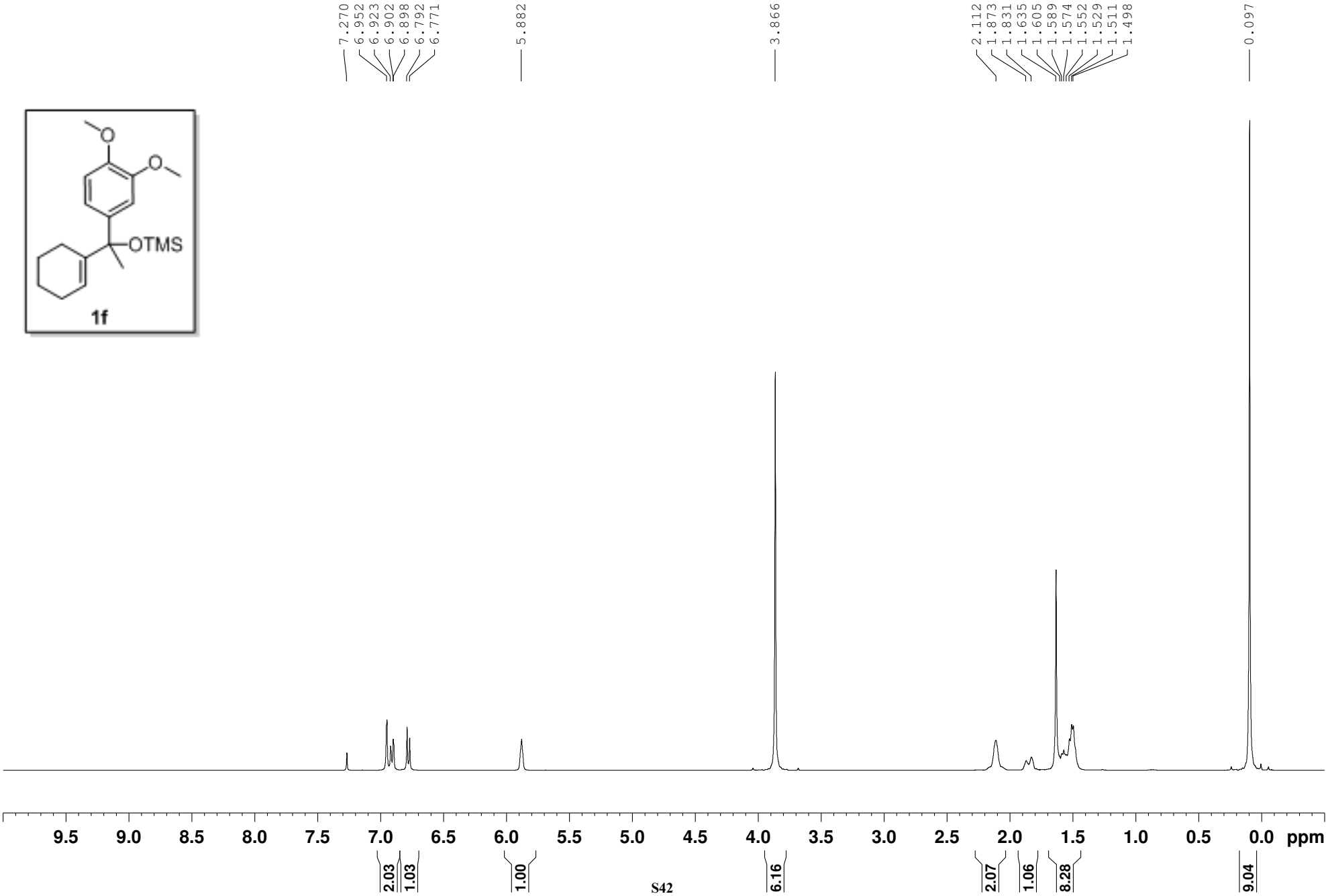
czm7p15a1


7.900
7.896
7.874
7.863
7.850
7.828
7.823
7.816
7.805
7.795
7.611
7.606
7.589
7.585
7.515
7.503
7.502
7.498
7.491
7.484
7.480
7.467
7.270
6.070
6.060
6.051
2.219
2.210
1.931
1.621
1.607
1.600
1.592
0.077
OTMS
1e
NAME czm7p15a1
EXPNO 10
PROCNO 1
Date_ 20140404
Time 10.14
INSTRUM spect
PROBHD 5 mm PABBO BB/
PULPROG zg30
TD 65536
SOLVENT CDC13
NS 16
DS 2
SWH 8012.820 Hz
FIDRES 0.122266 Hz
AQ 4.0894966 sec
RG 114
DW 62.400 usec
DE 6.50 usec
TE 291.5 K
D1 1.00000000 sec
TD0 1
======== CHANNEL f1 ========
SFO1 400.1324710 MHz
NUC1 1H
P1 11.60 usec
SI 65536
SF 400.1300058 MHz
WDW EM
SSB 0
LB 0.30 Hz
GB 0
PC 1.00
10
9
8
7
6
5
4
3
2
1
0
–1
–2
ppm
2.04
2.00
4.08
1.10
0.92
4.02
1.00
2.01
2.02
4.02
9.10

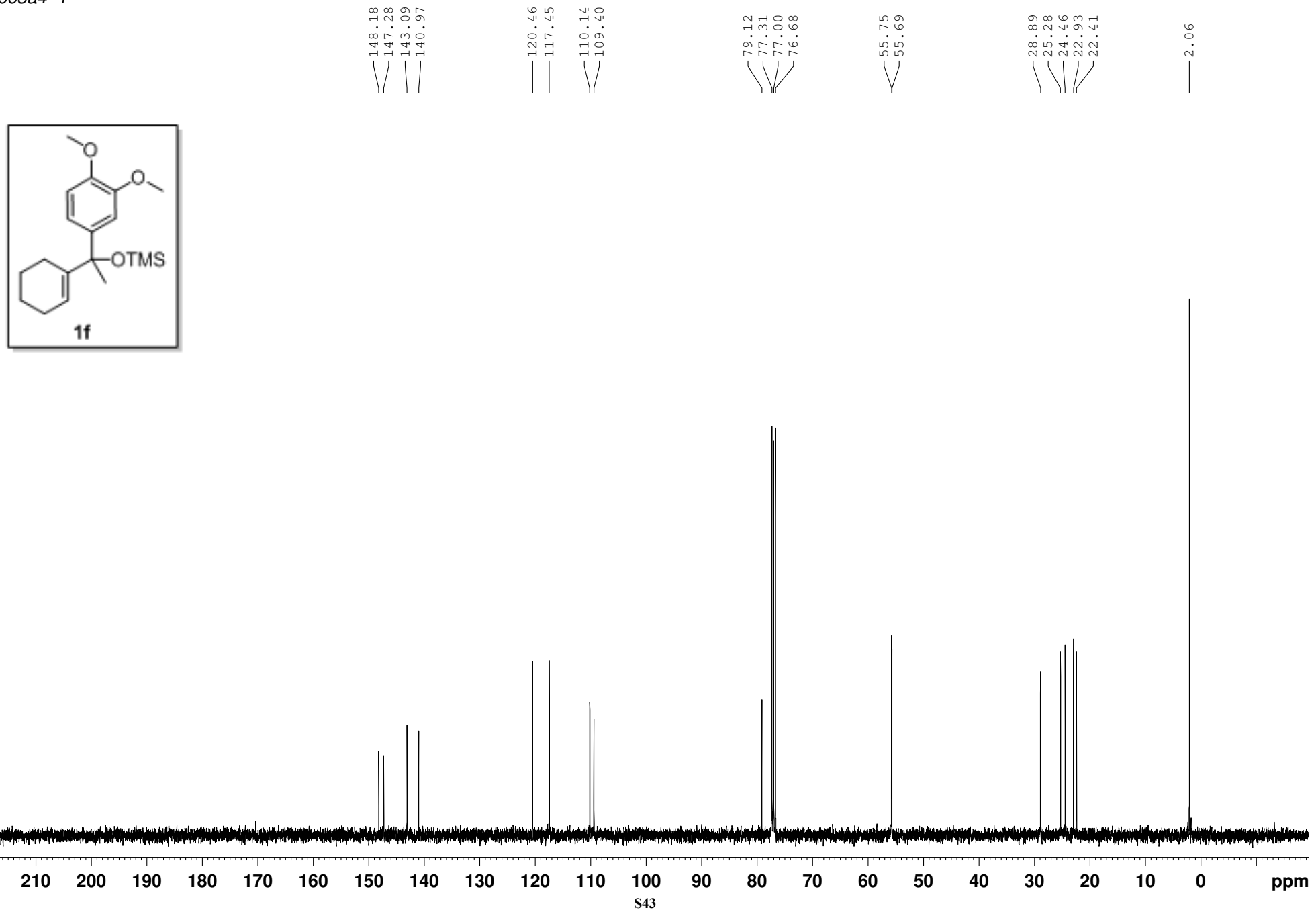
czm7p15a1


142.67
141.38
132.76
132.45
128.35
127.43
127.41
126.85
125.87
125.78
124.42
85.78
77.32
77.00
76.68
26.11
25.48
23.07
22.29
2.02
OTMS
1e
NAME czm7p15a1
EXPNO 11
PROCNO 1
Date_ 20140404
Time 10.19
INSTRUM spect
PROBHD 5 mm PABBO BB/
PULPROG zgpg30
TD 65536
SOLVENT CDC13
NS 80
DS 2
SWH 24038.461 Hz
FIDRES 0.366798 Hz
AQ 1.3631988 sec
RG 1030
DW 20.800 usec
DE 6.50 usec
TE 292.4 K
D1 2.00000000 sec
D11 0.03000000 sec
TD0 1
======== CHANNEL f1 ========
SFO1 100.6228298 MHz
NUC1 13C
P1 14.45 usec
SI 32768
SF 100.6127736 MHz
WDW EM
SSB 0
LB 1.00 Hz
GB 0
PC 1.40
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 ppm

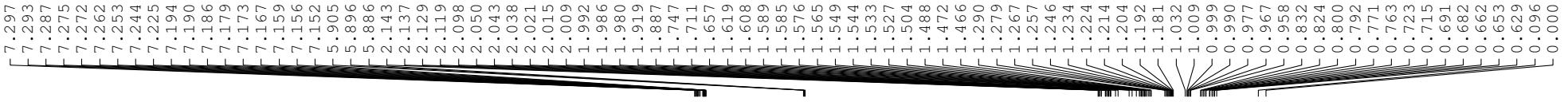
zz2p63a4–1

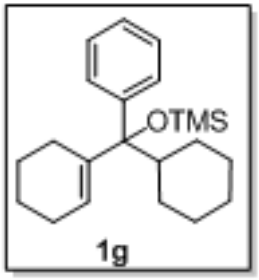

7.270
6.952
6.923
6.902
6.898
6.792
6.771
5.882
3.866
2.112
1.873
1.831
1.635
1.605
1.589
1.574
1.552
1.529
1.511
1.498
0.097
OTMS
1f
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
ppm
2.03
1.03
1.00
6.16
2.07
1.06
8.28
9.04

zz2p63a4–1


148.18
147.28
143.09
140.97
120.46
117.45
110.14
109.40
79.12
77.31
77.00
76.68
55.75
55.69
28.89
25.28
24.46
22.93
22.41
2.06
OTMS
1f
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
ppm

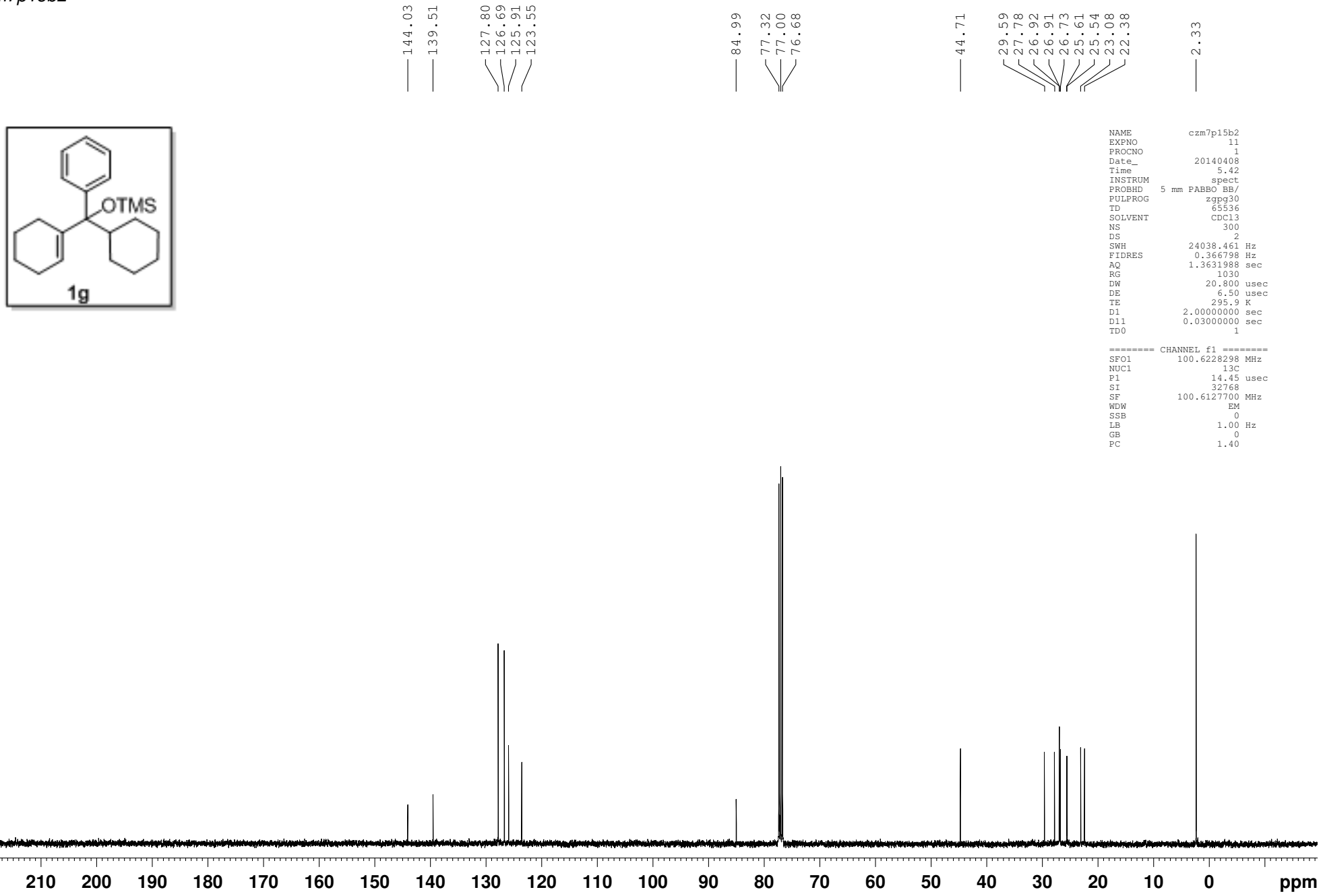
czm7p15b2


7.297
7.293
7.287
7.275
7.272
7.262
7.253
7.244
7.225
7.194
7.190
7.186
7.179
7.173
7.167
7.159
7.156
7.152
5.905
5.896
5.886
2.143
2.137
2.129
2.119
2.098
2.050
2.043
2.038
2.021
2.015
2.009
1.992
1.986
1.980
1.919
1.887
1.747
1.711
1.657
1.619
1.608
1.589
1.585
1.576
1.565
1.549
1.544
1.533
1.527
1.504
1.488
1.472
1.466
1.290
1.279
1.267
1.257
1.246
1.234
1.224
1.214
1.204
1.192
1.181
1.032
1.009
0.999
0.990
0.977
0.967
0.958
0.832
0.824
0.800
0.792
0.771
0.763
0.723
0.715
0.691
0.682
0.662
0.653
0.629
0.096
0.000

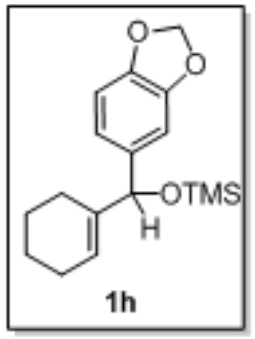

OTMS
1g

NAME czm7p15b2
EXPNO 10
PROCNO 1
Date_ 20140408
Time 5.24
INSTRUM spect
PROBHD 5 mm PABBO BB/
PULPROG zg30
TD 65536
SOLVENT CDCl3
NS 16
DS 2
SWH 8012.820 Hz
FIDRES 0.122266 Hz
AQ 4.0894966 sec
RG 144
DW 62.400 usec
DE 6.50 usec
TE 295.0 K
D1 1.00000000 sec
TD0 1
======== CHANNEL f1 ========
SFO1 400.1324710 MHz
NUC1 1H
P1 11.40 usec
SI 65536
SF 400.1300122 MHz
WDW EM
SSB 0
LB 0.30 Hz
GB 0
PC 1.00
16 15 14 13 12 11 10 9 8 7 6 5 4 3 2 1 0 −1 −2 ppm
4.71 0.99 1.00 2.06 1.12 1.05 5.14 2.10 3.49 2.13 1.11 1.05 1.02 8.88

czm7p15b2


144.03
139.51
127.80
126.69
125.91
123.55
84.99
77.32
77.00
76.68
44.71
29.59
27.78
26.92
26.91
26.73
25.61
25.54
23.08
22.38
2.33
OTMS
1g
NAME czm7p15b2
EXPNO 11
PROCNO 1
Date_ 20140408
Time 5.42
INSTRUM spect
PROBHD 5 mm PABBO BB/
PULPROG zgpg30
TD 65536
SOLVENT CDCl3
NS 300
DS 2
SWH 24038.461 Hz
FIDRES 0.366798 Hz
AQ 1.3631988 sec
RG 1030
DW 20.800 usec
DE 6.50 usec
TE 295.9 K
D1 2.00000000 sec
D11 0.03000000 sec
TD0 1
======== CHANNEL f1 ========
SFO1 100.6228298 MHz
NUC1 13C
P1 14.45 usec
SI 32768
SF 100.6127700 MHz
WDW EM
SSB 0
LB 1.00 Hz
GB 0
PC 1.40
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 ppm

czm7p15b3

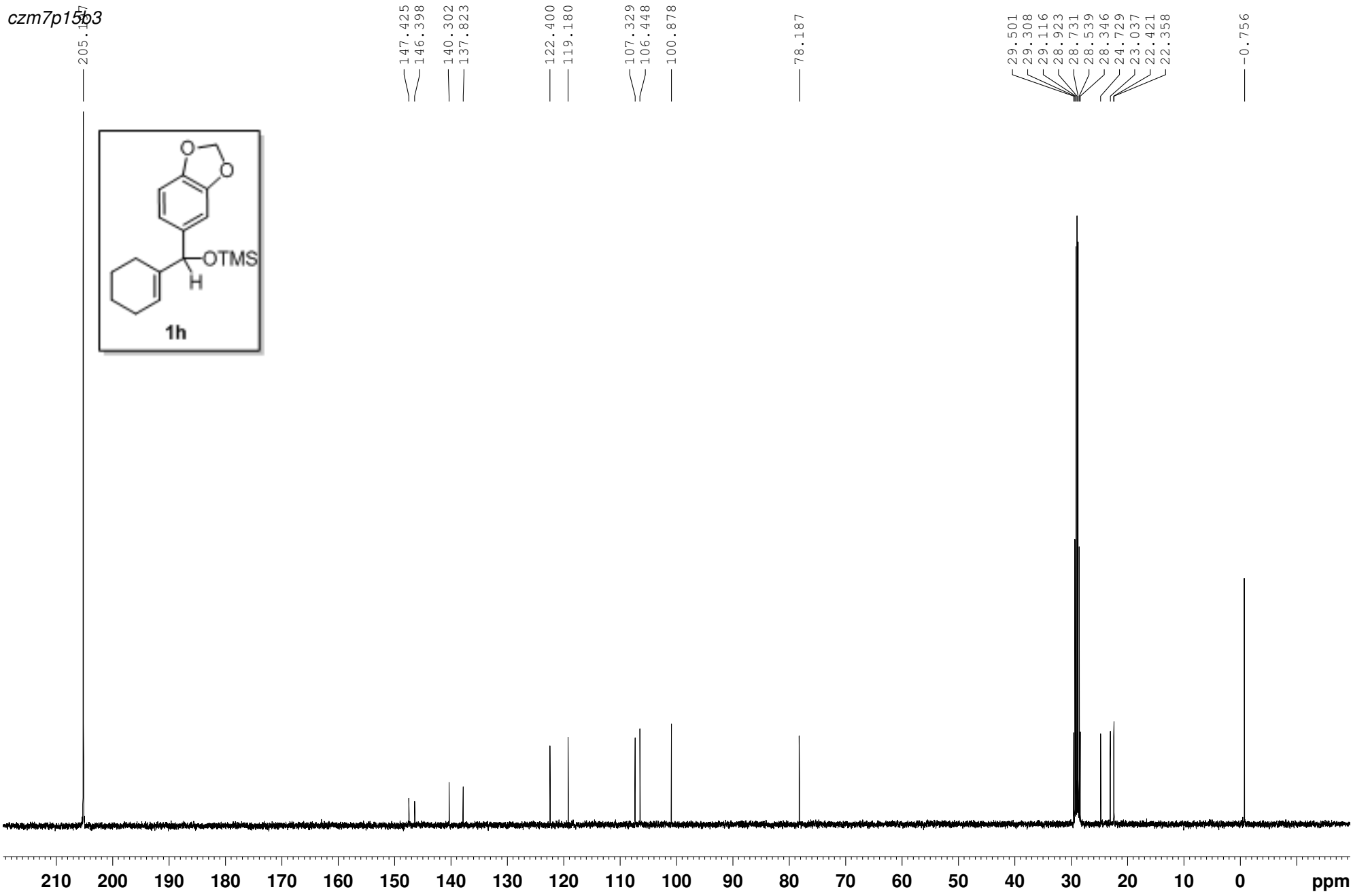


1h

6.880 6.875 6.866 6.865 6.862 6.829 6.821 6.815 6.808 6.016 5.880 5.878 5.113 2.120 2.115 2.109 2.104 2.099 1.971 1.961 1.947 1.933 1.928 1.923 1.745 1.733 1.721 1.695 1.690 1.686 1.637 1.628 1.621 1.605 1.596 1.586 1.580 1.573 1.559 1.549 1.543 1.537 1.533 1.522 0.149

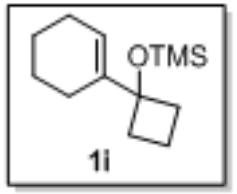
9 8 7 6 5 4 3 2 1 0 −1 ppm

1.98 1.03 2.00 1.00 0.98 2.88 1.06 1.08 4.07 8.82


czm7p15b3
205.107
147.425
146.398
140.302
137.823
122.400
119.180
107.329
106.448
100.878
78.187
29.501
29.308
29.116
28.923
28.731
28.539
28.346
24.729
23.037
22.421
22.358
-0.756
OTMS
H
1h
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
ppm

czm7p20a1

7.270 5.735 5.726 5.717 2.291 2.284 2.276 2.270 2.268 2.261 2.254 2.247 2.240 2.232 2.137 2.131 2.113 2.107 2.100 2.090 2.083 2.076 2.070 2.060 2.056 2.040 2.025 2.021 1.736 1.728 1.720 1.712 1.704 1.693 1.686 1.678 1.671 1.662 1.657 1.648 1.644 1.634 1.629 1.612 1.606 1.591 1.584 1.578 1.572 1.564 1.550 1.468 1.445 1.423 1.400 1.397 1.376 0.085

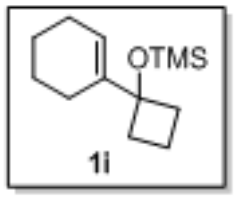


1i

15 14 13 12 11 10 9 8 7 6 5 4 3 2 1 0 –1 –2 ppm

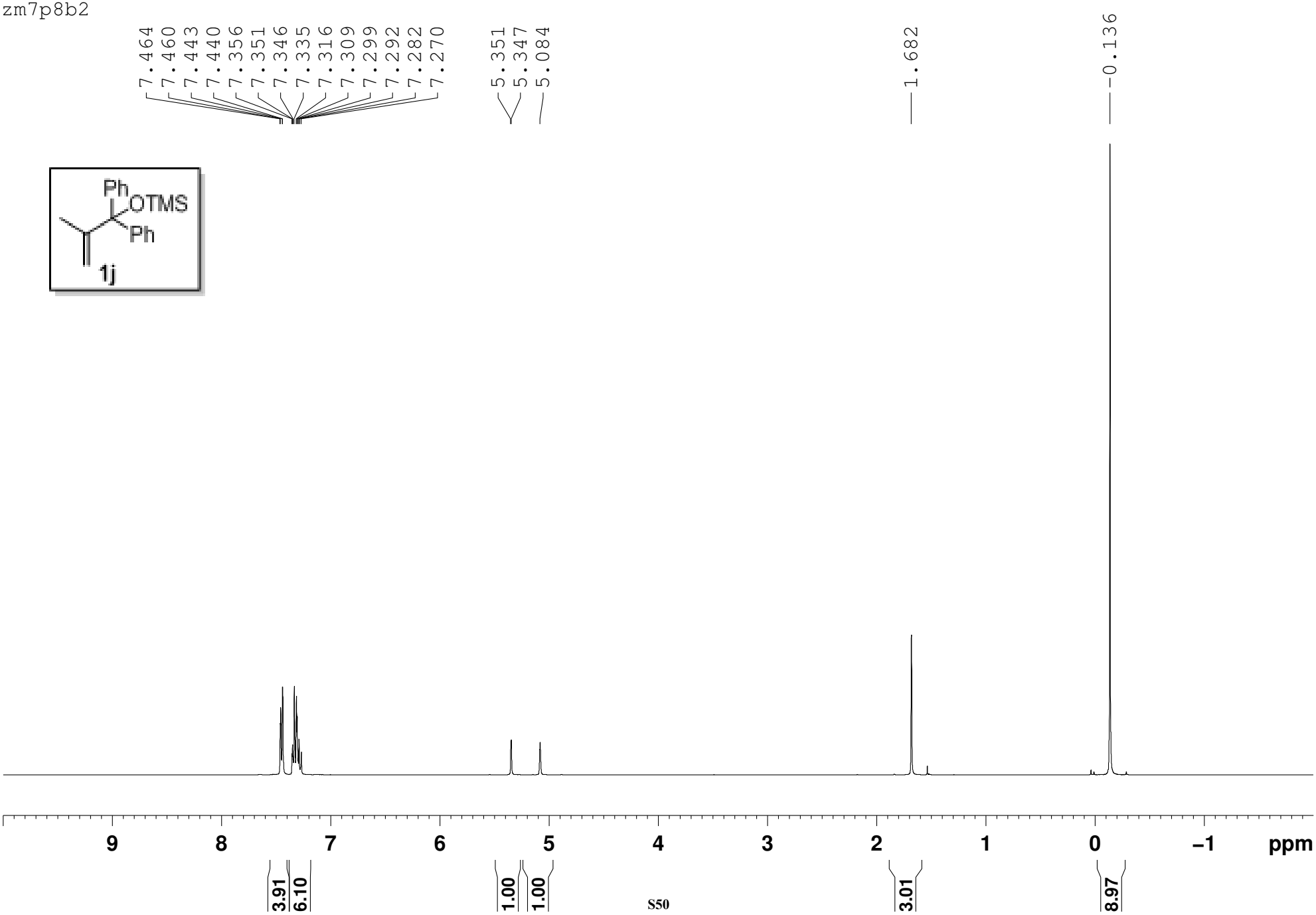
1.00 2.10 6.17 5.42 1.10 8.87

czm7p20a1-C


OTMS
1i

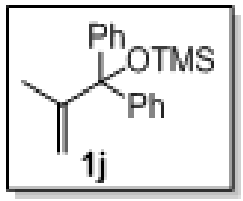
139.516
120.052
79.099
77.314
76.997
76.679
35.221
25.218
22.833
22.765
22.387
13.275
1.703
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 ppm

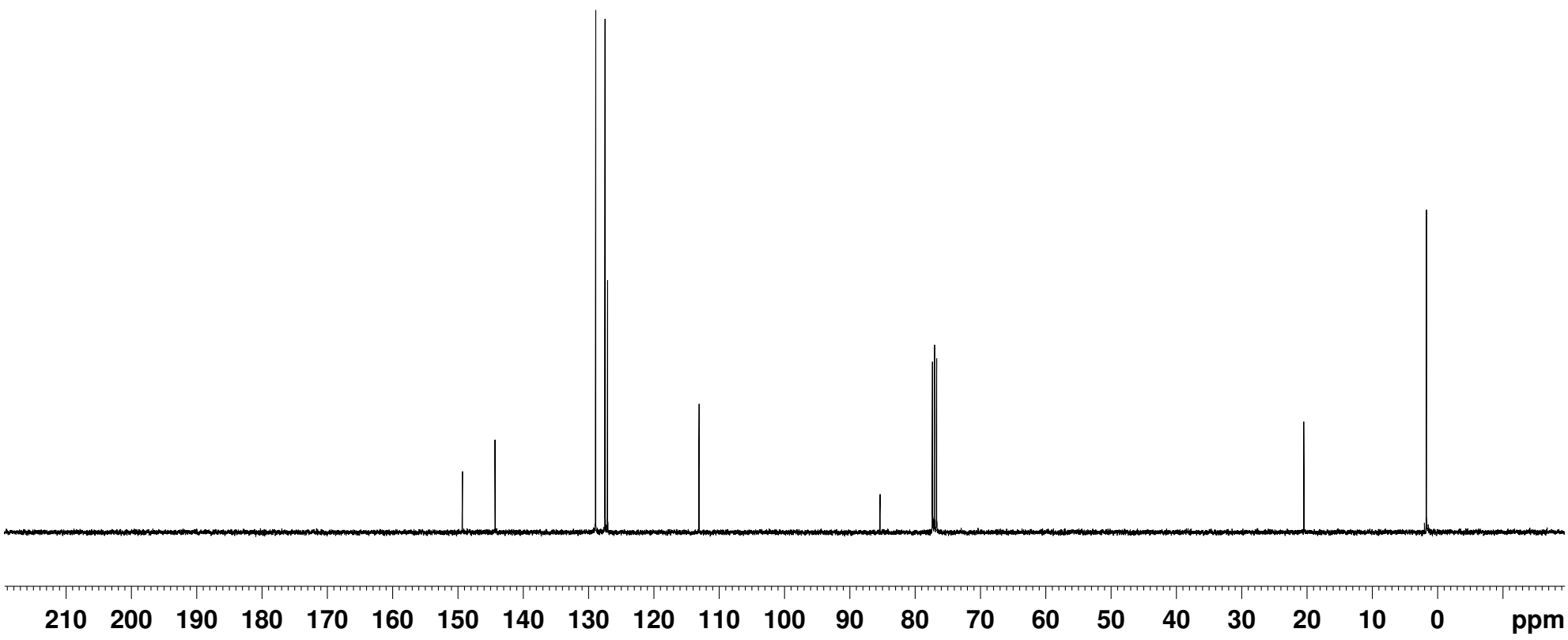
czm7p8b2


7.464
7.460
7.443
7.440
7.356
7.351
7.346
7.335
7.316
7.309
7.299
7.292
7.282
7.270
5.351
5.347
5.084
1.682
0.136
Ph
OTMS
Ph
1j
9
8
7
6
5
4
3
2
1
0
−1
ppm
3.91
6.10
1.00
1.00
3.01
8.97

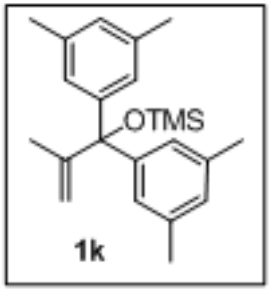
czm7p8b2

149.301
144.303
128.884
127.456
127.054
113.062
85.348
77.317
77.000
76.682
20.425
1.657



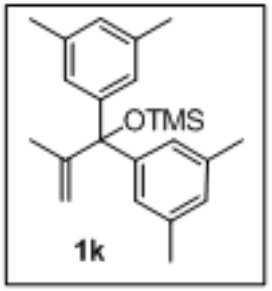


czm7p10b2


OTMS
1k

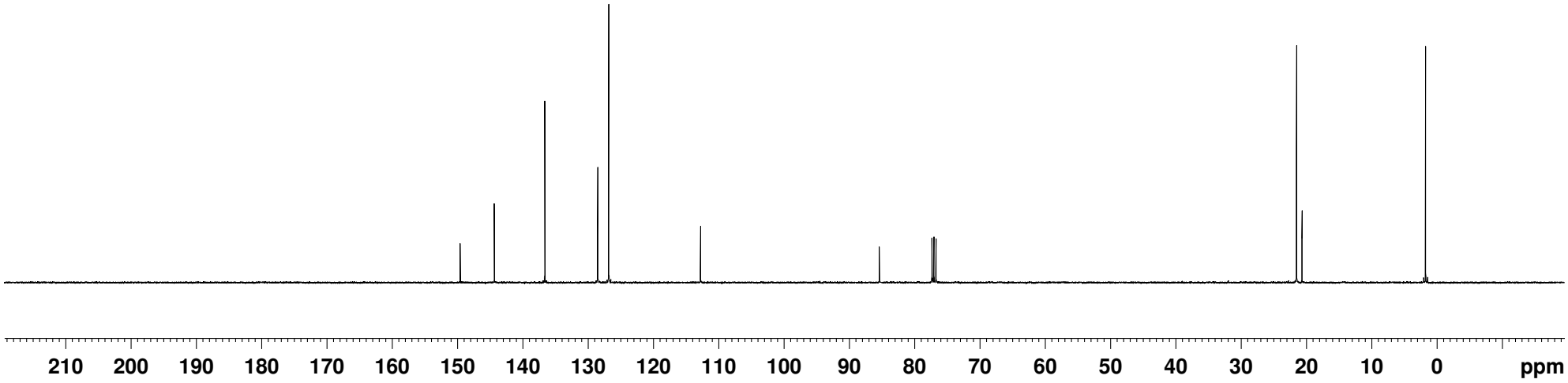
7.270
7.138
7.008
5.417
5.413
5.130
2.401
1.776
0.056
9
8
7
6
5
4
3
2
1
0
−1
ppm
4.03
2.04
1.00
1.00
12.13
3.08
9.15

czm7p10b2

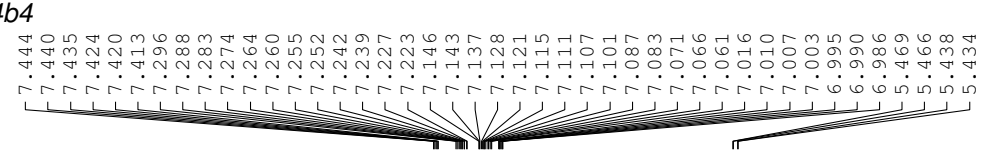


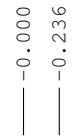
149.57
144.35
136.61
128.51
126.83
112.76
85.38
77.32
77.00
76.68
21.47
20.63
1.70

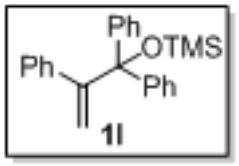
```
NAME                czm7p10b2
EXPNO                      11
PROCNO                      1
Date_              20140321
Time                   18.29
INSTRUM                spect
PROBHD     5 mm PABBO BB/
PULPROG             zgpg30
TD                       65536
SOLVENT                  CDCl3
NS                          60
DS                           2
SWH                  24038.461 Hz
FIDRES               0.366798 Hz
AQ                   1.3631988 sec
RG                         822
DW                   20.800 usec
DE                    6.00 usec
TE                       300.1 K
D1                   2.00000000 sec
D11                  0.03000000 sec
TD0                          1

======== CHANNEL f1 ========
SFO1               100.6228298 MHz
NUC1                       13C
P1                       12.00 usec
SI                       32768
SF                 100.6127780 MHz
WDW                        EM
SSB                         0
LB                       1.00 Hz
GB                          0
PC                       1.40
```



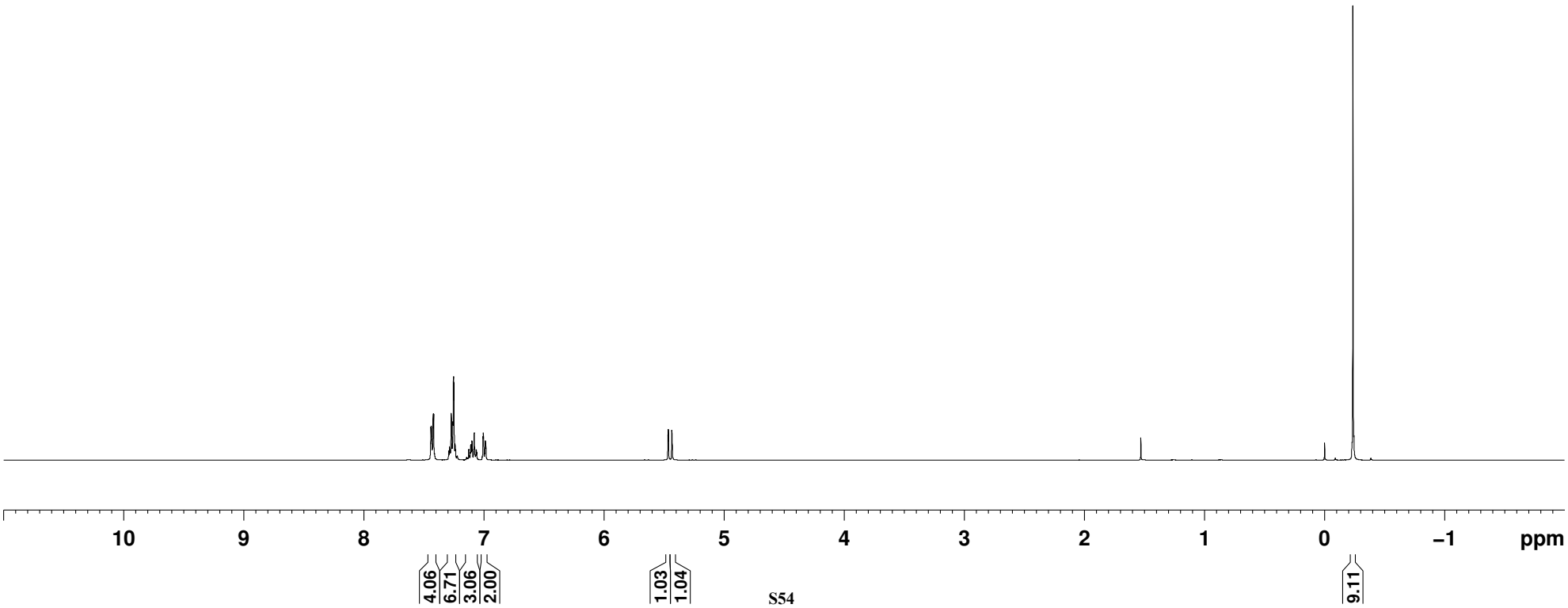
czm7p14b4



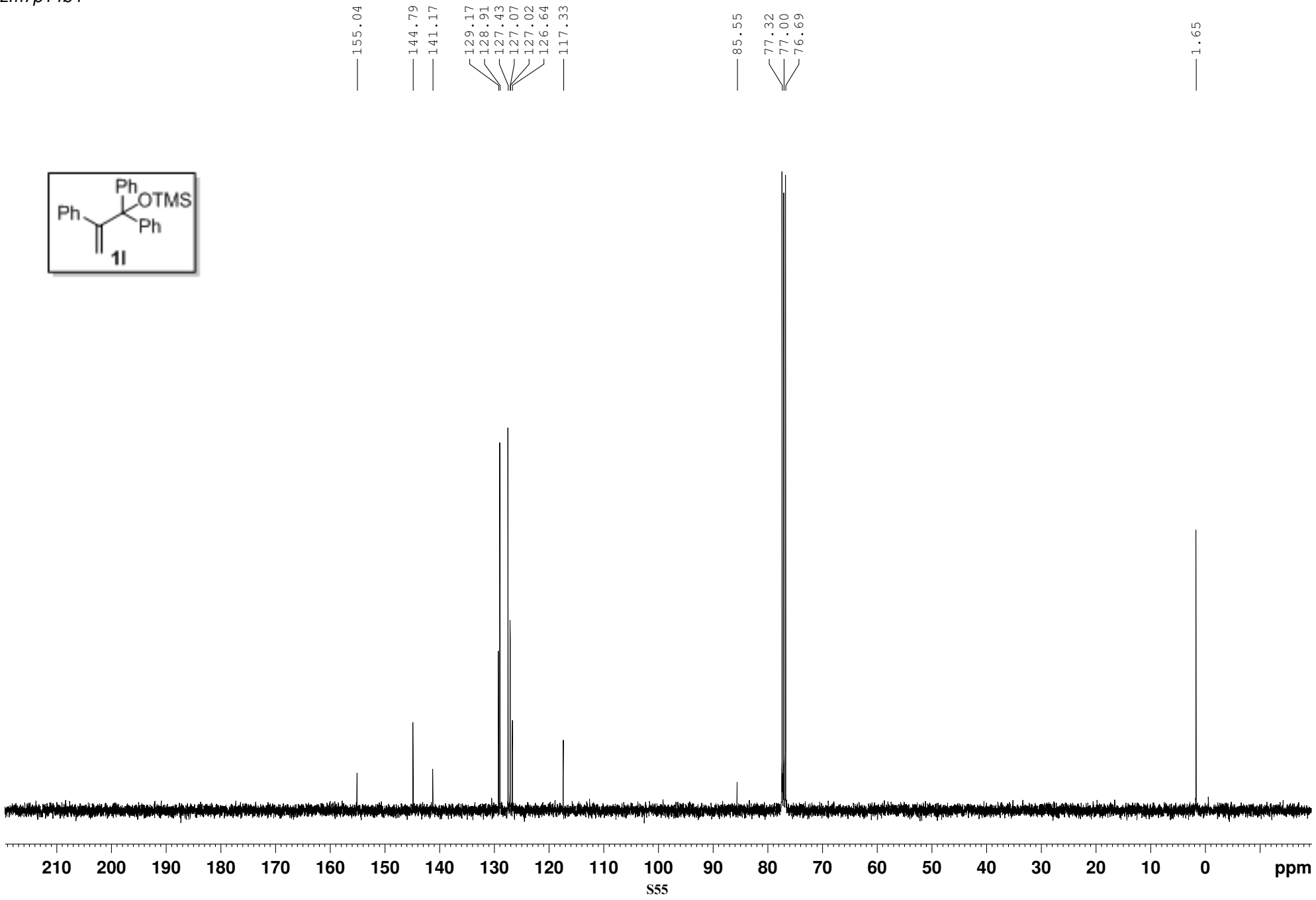




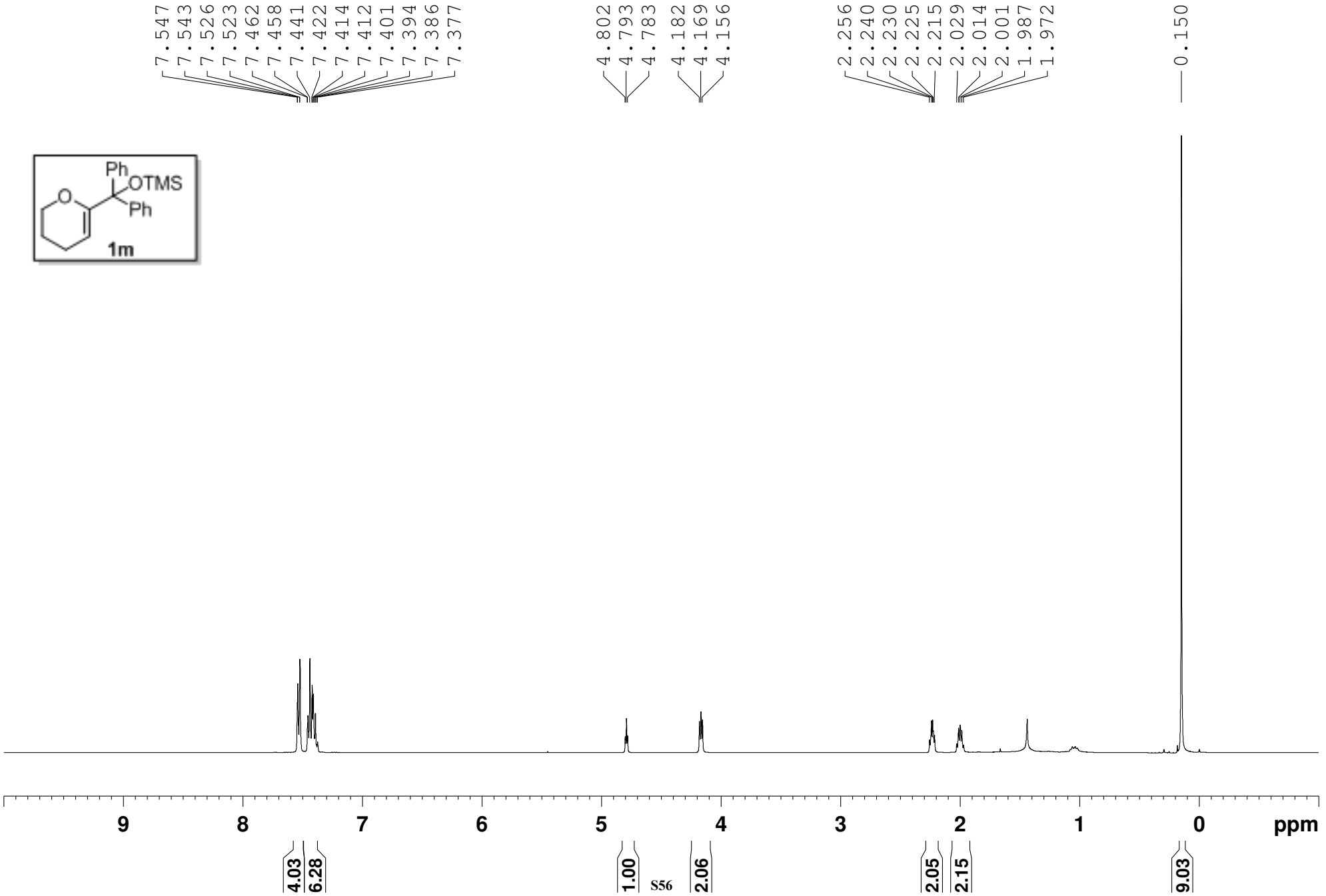

```
NAME            czm7p14b4
EXPNO                  10
PROCNO                  1
Date_            20140404
Time                10.25
INSTRUM             spect
PROBHD   5 mm PABBO BB/
PULPROG             zg30
TD                 65536
SOLVENT            CDCl3
NS                    16
DS                     2
SWH             8012.820 Hz
FIDRES          0.122266 Hz
AQ              4.0894966 sec
RG                   203
DW                62.400 usec
DE                 6.50 usec
TE                291.4 K
D1             1.00000000 sec
TD0                    1

======== CHANNEL f1 ========
SFO1         400.1324710 MHz
NUC1                   1H
P1                 11.60 usec
SI                 65536
SF           400.1300130 MHz
WDW                   EM
SSB                    0
LB                  0.30 Hz
GB                     0
PC                  1.00
```



czm7p14b4

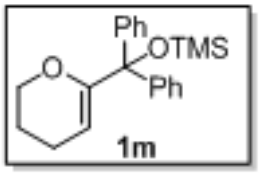

155.04
144.79
141.17
129.17
128.91
127.43
127.07
127.02
126.64
117.33
85.55
77.32
77.00
76.69
1.65
Ph
OTMS
Ph
Ph
1l
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
ppm

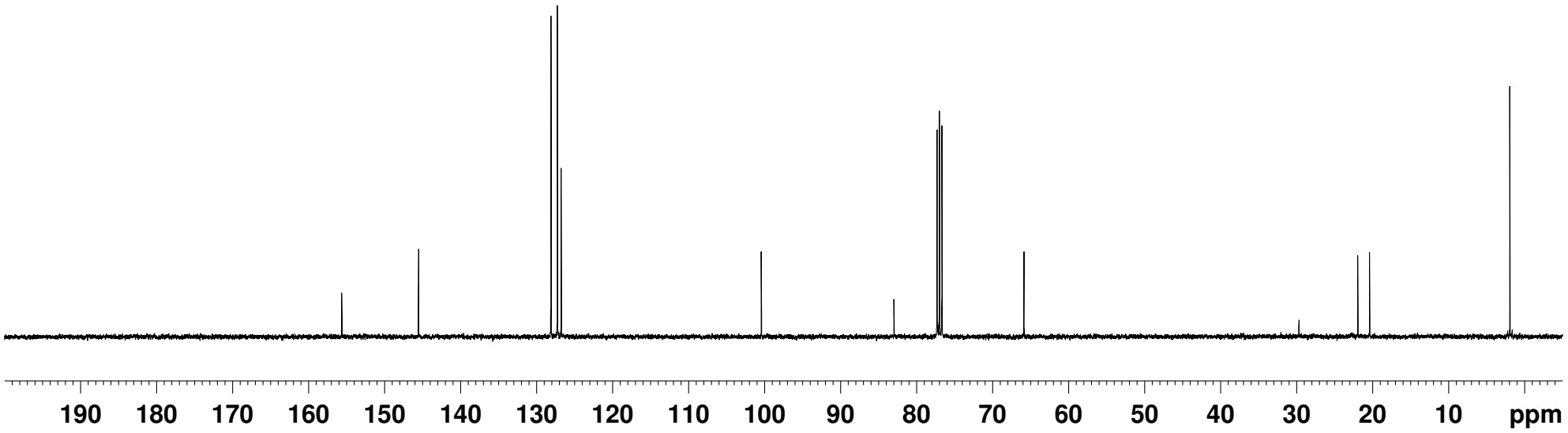
czm7p8a-4


7.547
7.543
7.526
7.523
7.462
7.458
7.441
7.422
7.414
7.412
7.401
7.394
7.386
7.377
4.802
4.793
4.783
4.182
4.169
4.156
2.256
2.240
2.230
2.225
2.215
2.029
2.014
2.001
1.987
1.972
0.150
Ph
OTMS
Ph
O
1m
9
8
7
6
5
4
3
2
1
0
ppm
4.03
6.28
1.00
2.06
2.05
2.15
9.03

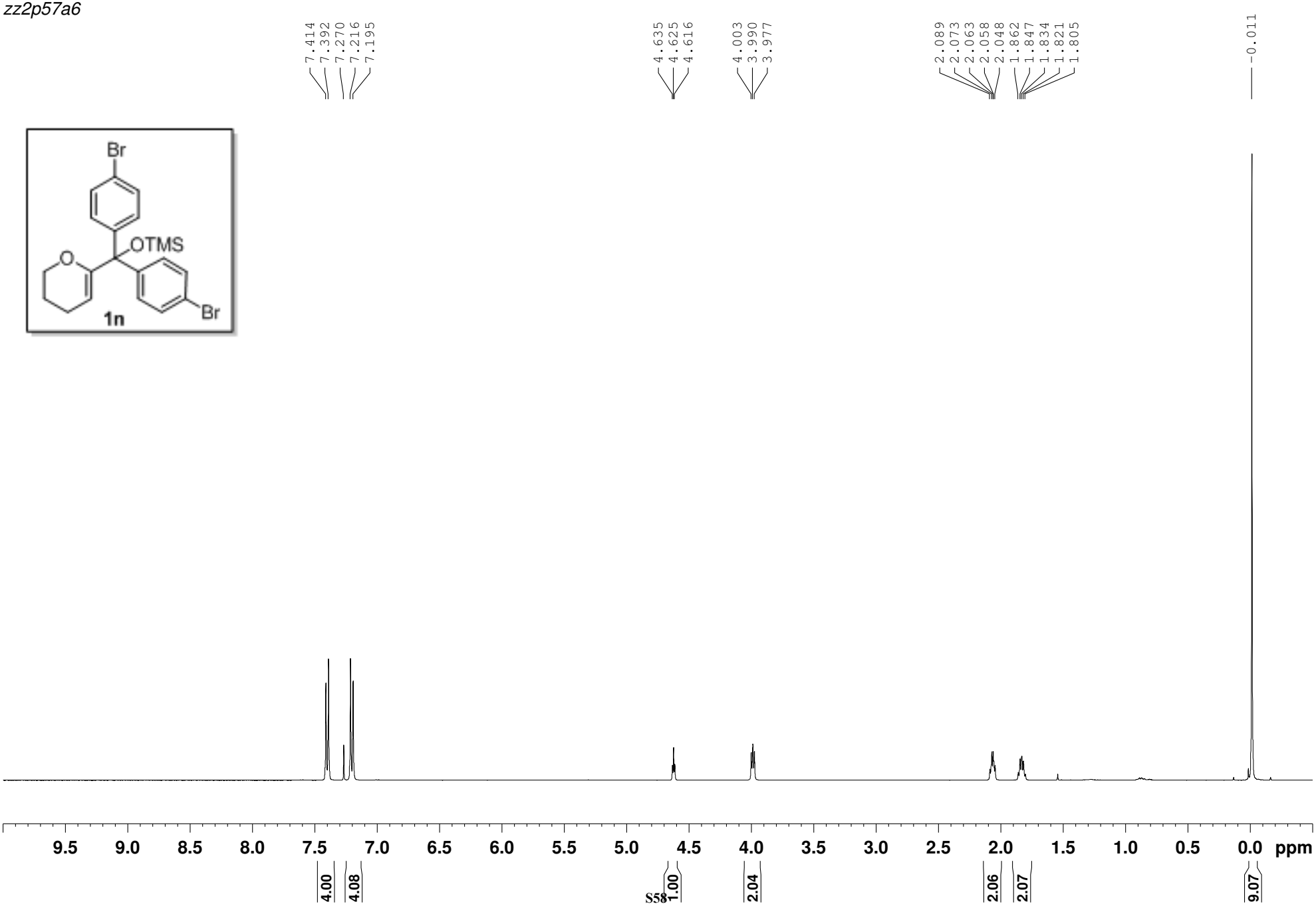
czm7p8a-4

155.659
145.554
128.125
127.275
126.778
100.448
82.992
77.317
77.000
76.682
65.880
21.952
20.399
1.942

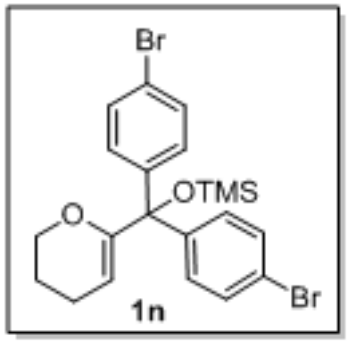




zz2p57a6

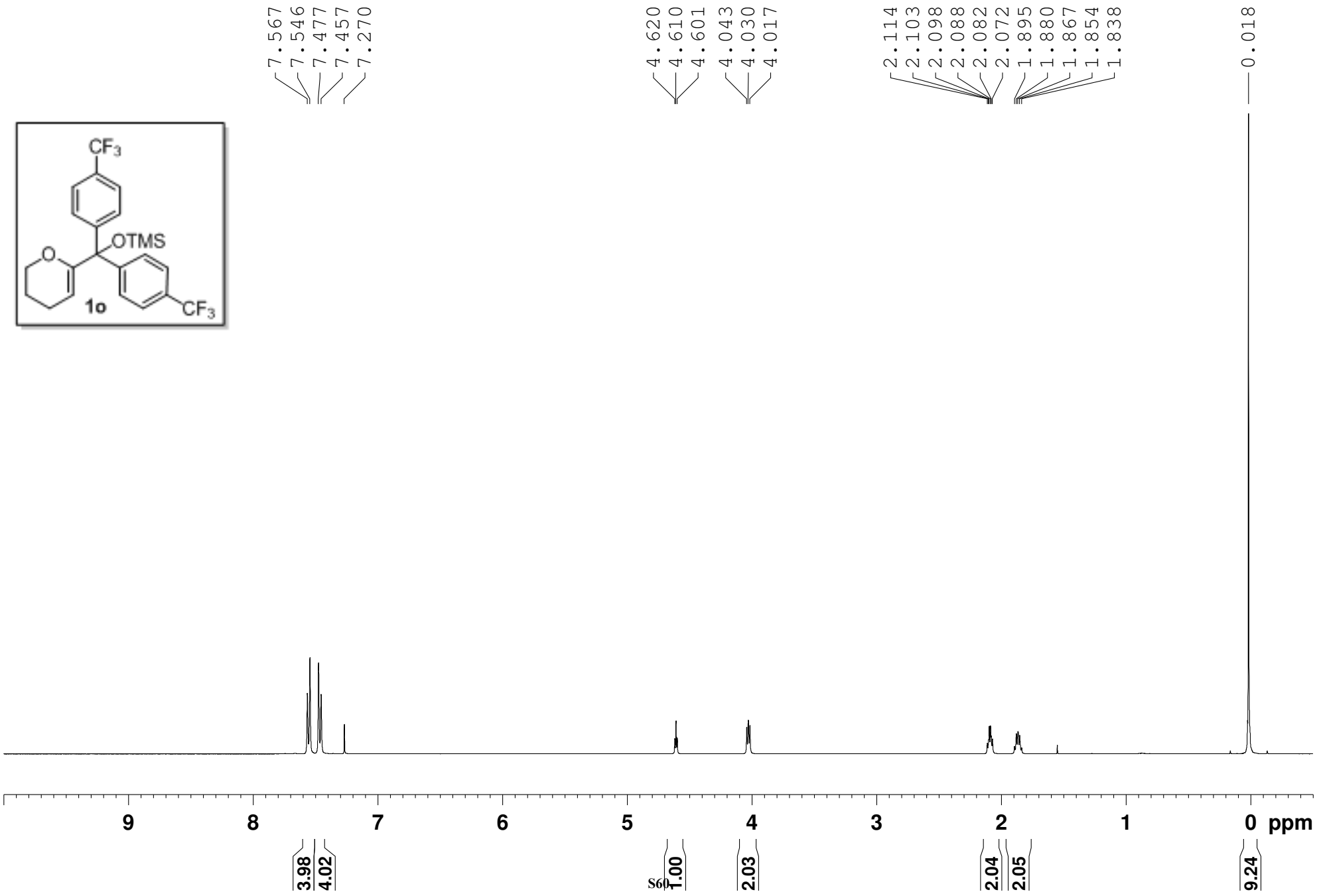

7.414
7.392
7.270
7.216
7.195
4.635
4.625
4.616
4.003
3.990
3.977
2.089
2.073
2.063
2.058
2.048
1.862
1.847
1.834
1.821
1.805
-0.011
Br
OTMS
O
Br
1n
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
ppm
4.00
4.08
1.00
2.04
2.06
2.07
9.07

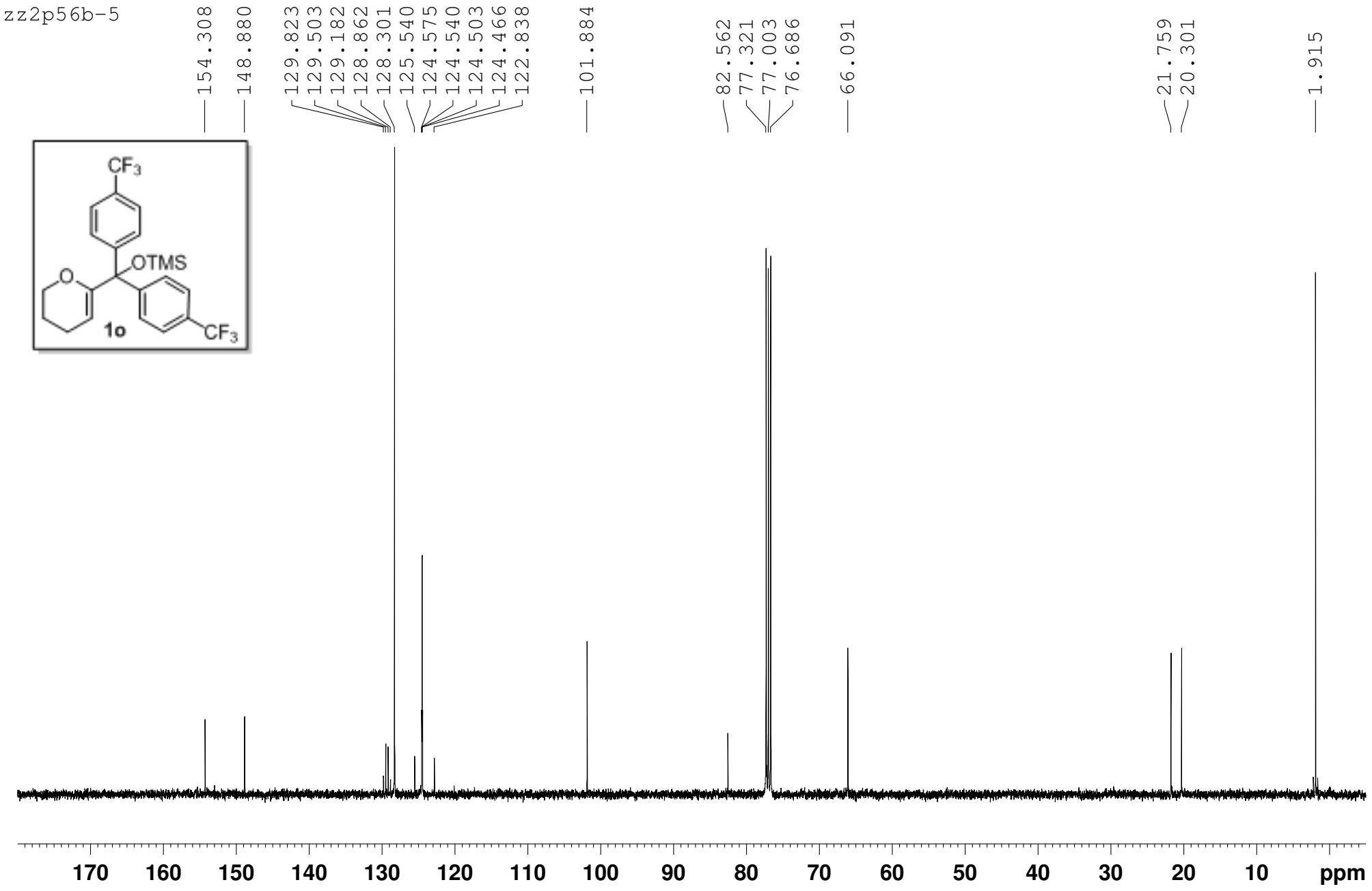
zz2p57a6


Br
OTMS
O
Br
1n

154.71
144.24
130.53
129.85
121.12
101.06
82.31
77.32
77.00
76.68
66.00
21.83
20.31
1.95
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 ppm

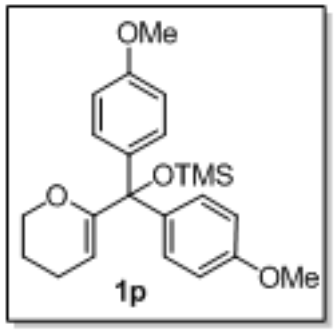
zz2p56b-5


7.567
7.546
7.477
7.457
7.270
4.620
4.610
4.601
4.043
4.030
4.017
2.114
2.103
2.098
2.088
2.082
2.072
1.895
1.880
1.867
1.854
1.838
0.018
CF3
OTMS
O
1o
CF3
9
8
7
6
5
4
3
2
1
0 ppm
3.98
4.02
1.00
2.03
2.04
2.05
9.24

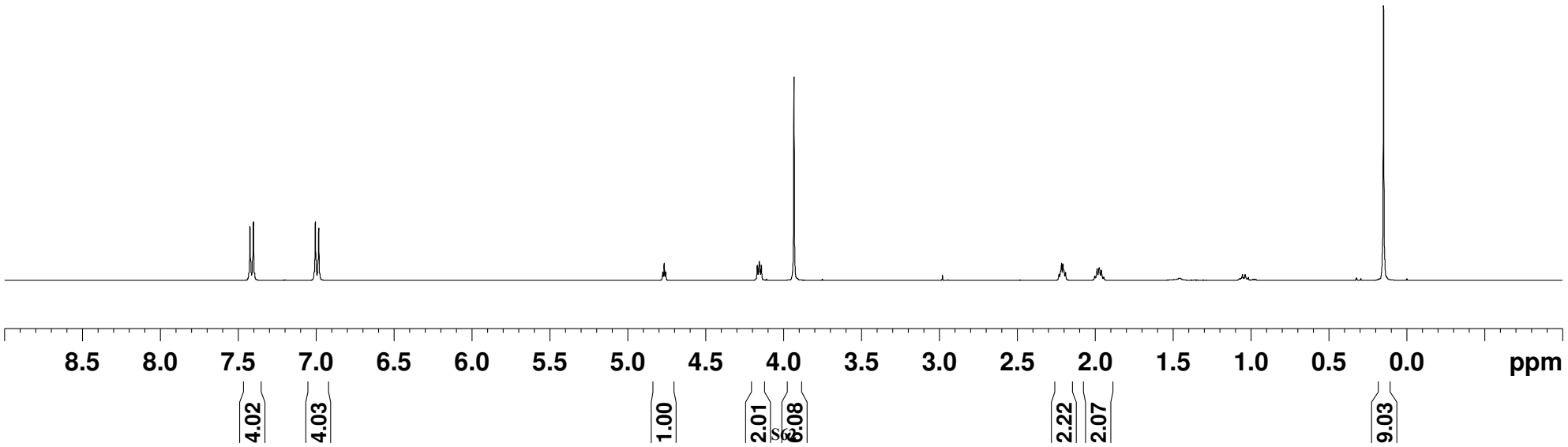

zz2p56b-5
154.308
148.880
129.823
129.503
129.182
128.862
128.301
125.540
124.575
124.540
124.503
124.466
122.838
101.884
82.562
77.321
77.003
76.686
66.091
21.759
20.301
1.915
CF3
OTMS
O
1o
CF3
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
ppm

czm7p16a2

7.434
7.426
7.422
7.409
7.404
7.397
7.014
7.007
7.002
6.990
6.985
6.978
4.777
4.767
4.758
4.169
4.157
4.144
3.934
2.233
2.216
2.207
2.201
2.191
2.003
1.988
1.976
1.962
1.946
0.149

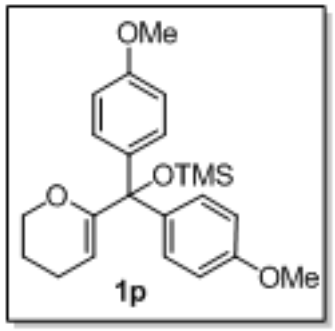


1p

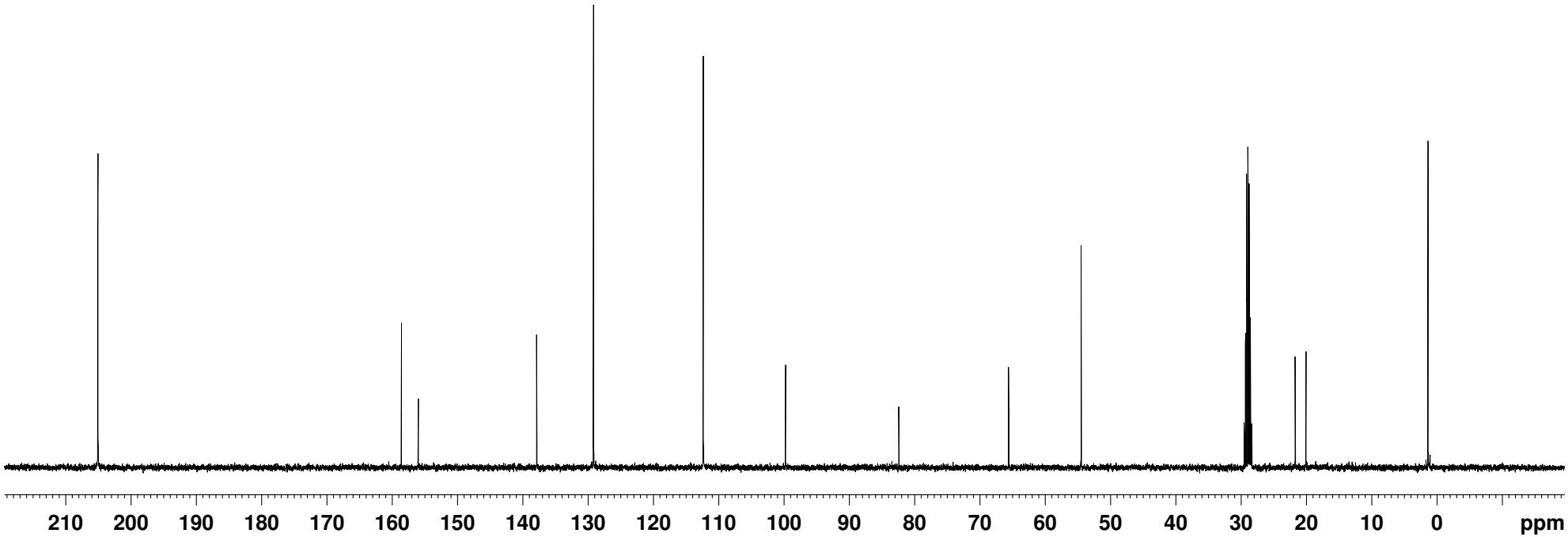


czm7p16a2

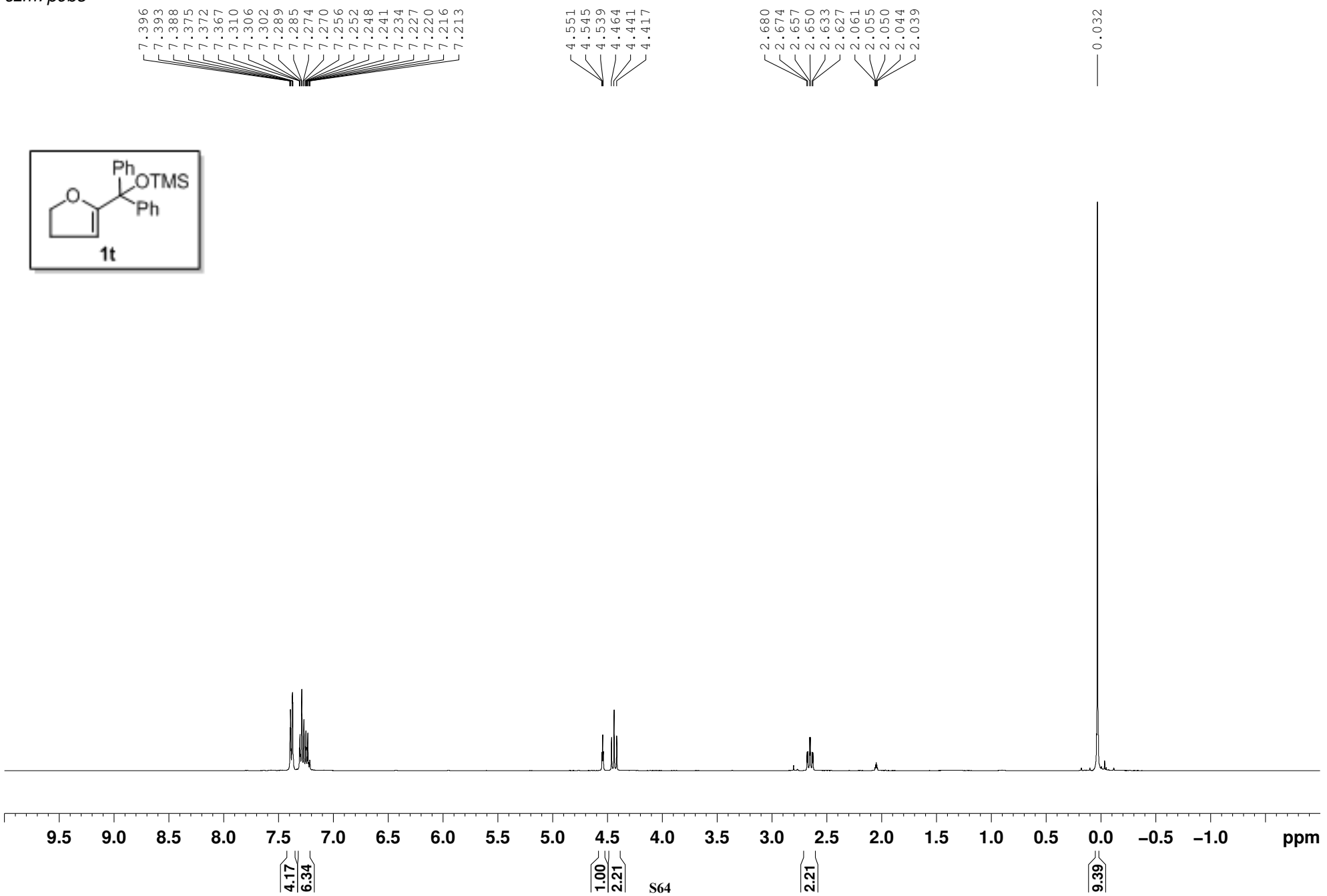
205.06
158.57
155.99
137.85
129.15
112.34
99.74
82.39
65.58
54.47
29.49
29.30
29.11
28.92
28.72
28.53
28.34
21.70
20.04
1.35



1p

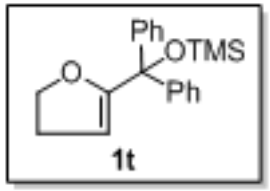


czm7p9b3

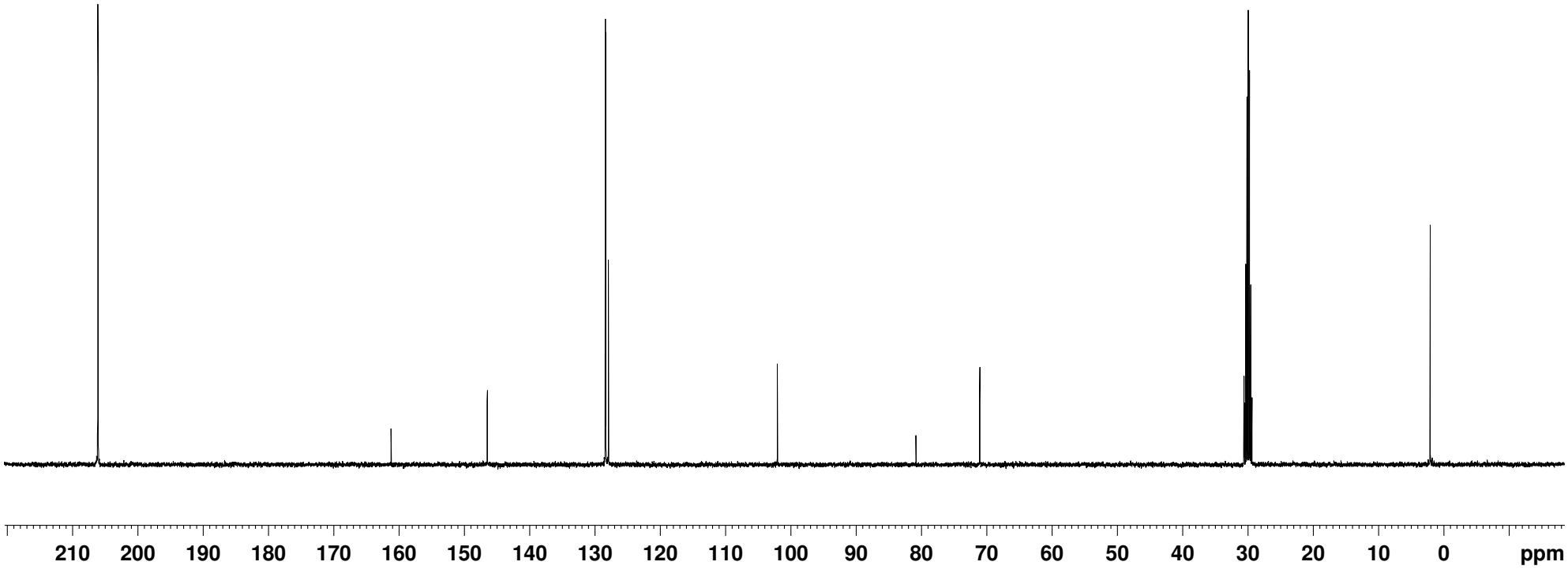

7.396
7.393
7.388
7.375
7.372
7.367
7.310
7.306
7.302
7.289
7.285
7.274
7.270
7.256
7.252
7.248
7.241
7.234
7.227
7.220
7.216
7.213
4.551
4.545
4.539
4.464
4.441
4.417
2.680
2.674
2.657
2.650
2.633
2.627
2.061
2.055
2.050
2.044
2.039
0.032
Ph
OTMS
Ph
O
1t
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
−0.5
−1.0
ppm
4.17
6.34
1.00
2.21
2.21
9.39

czm7p9b3

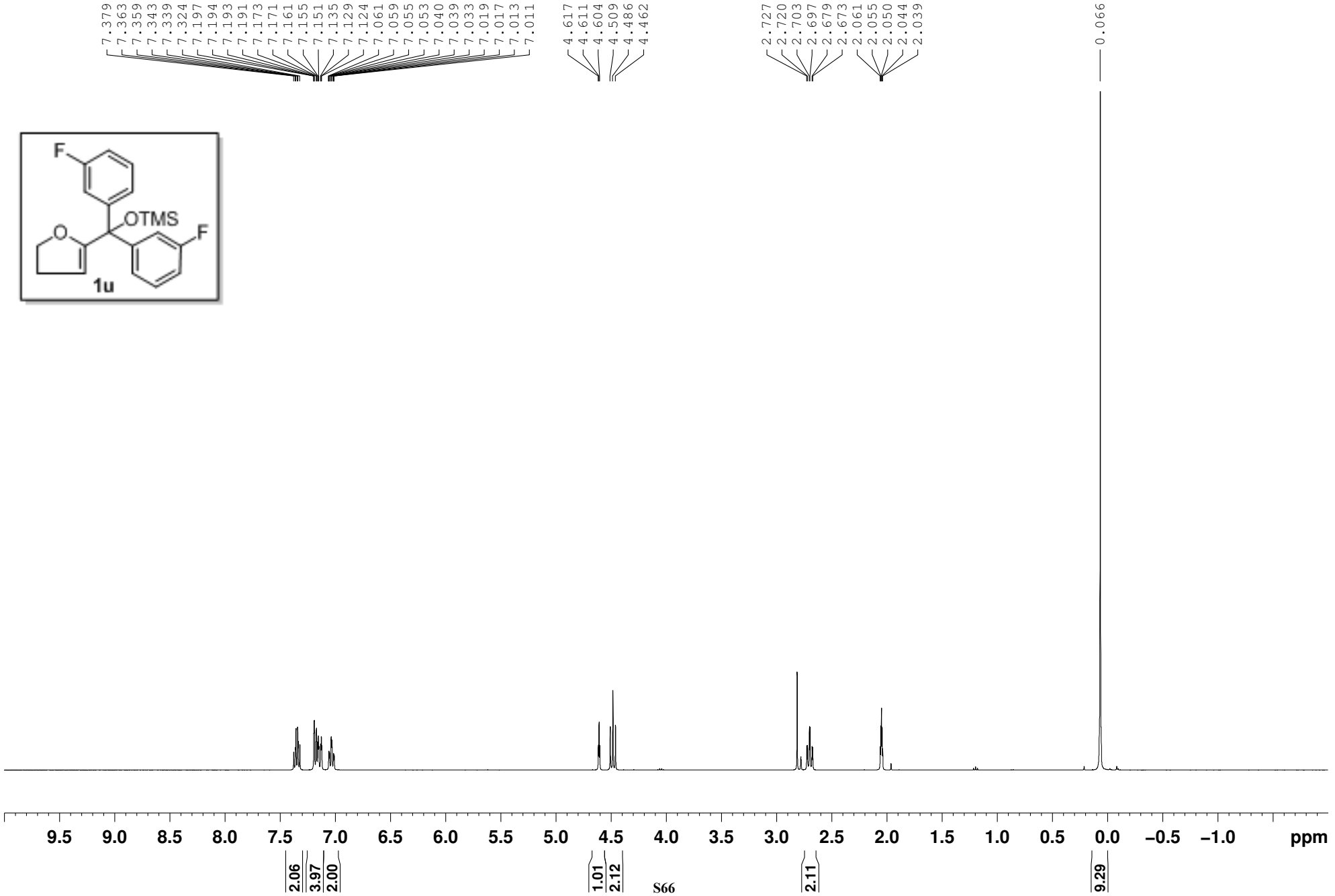
206.09
161.20
146.47
128.37
128.31
127.91
102.03
80.80
71.04
30.57
30.50
30.31
30.11
29.92
29.73
29.54
29.34
2.03

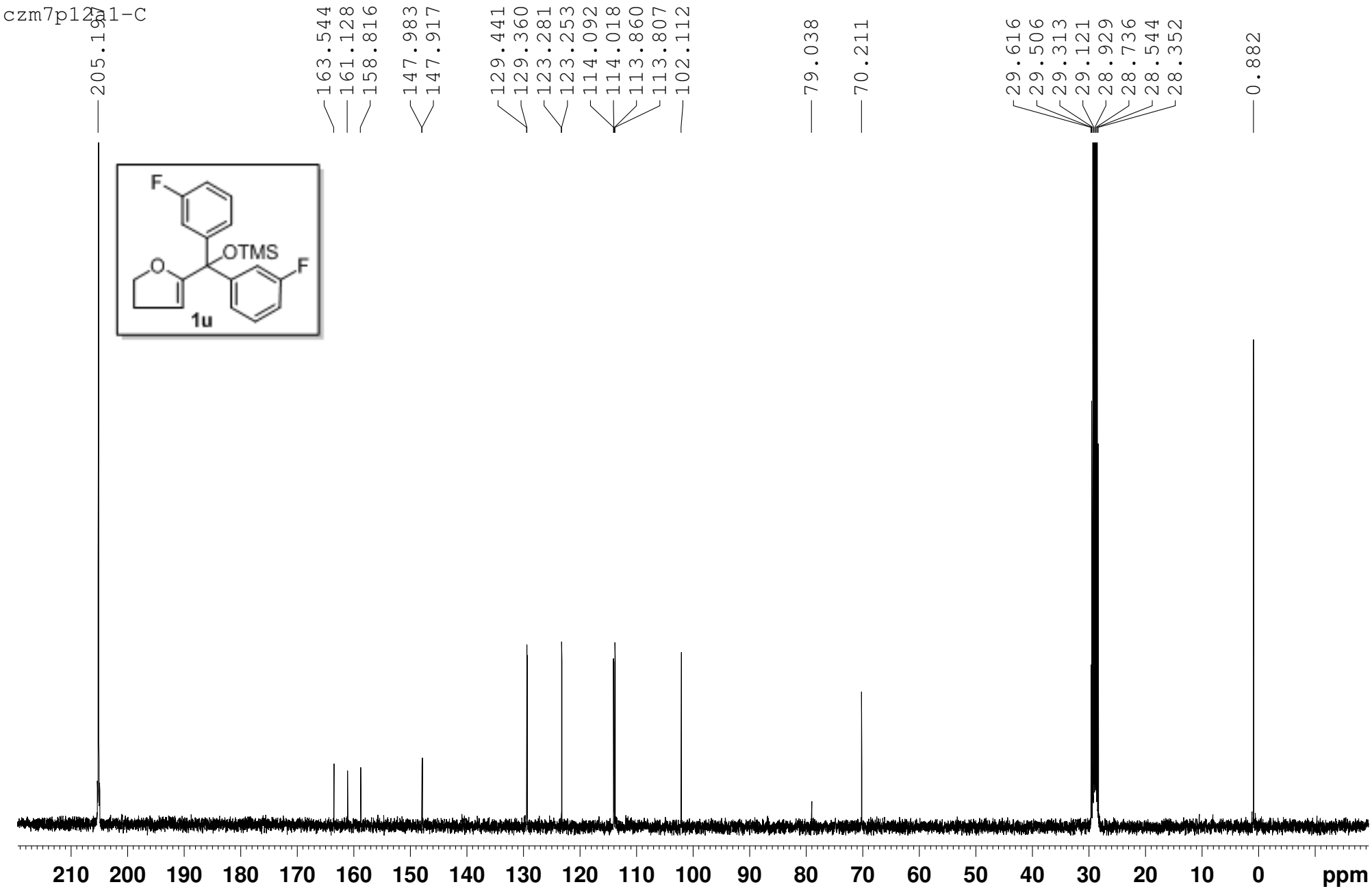


1t

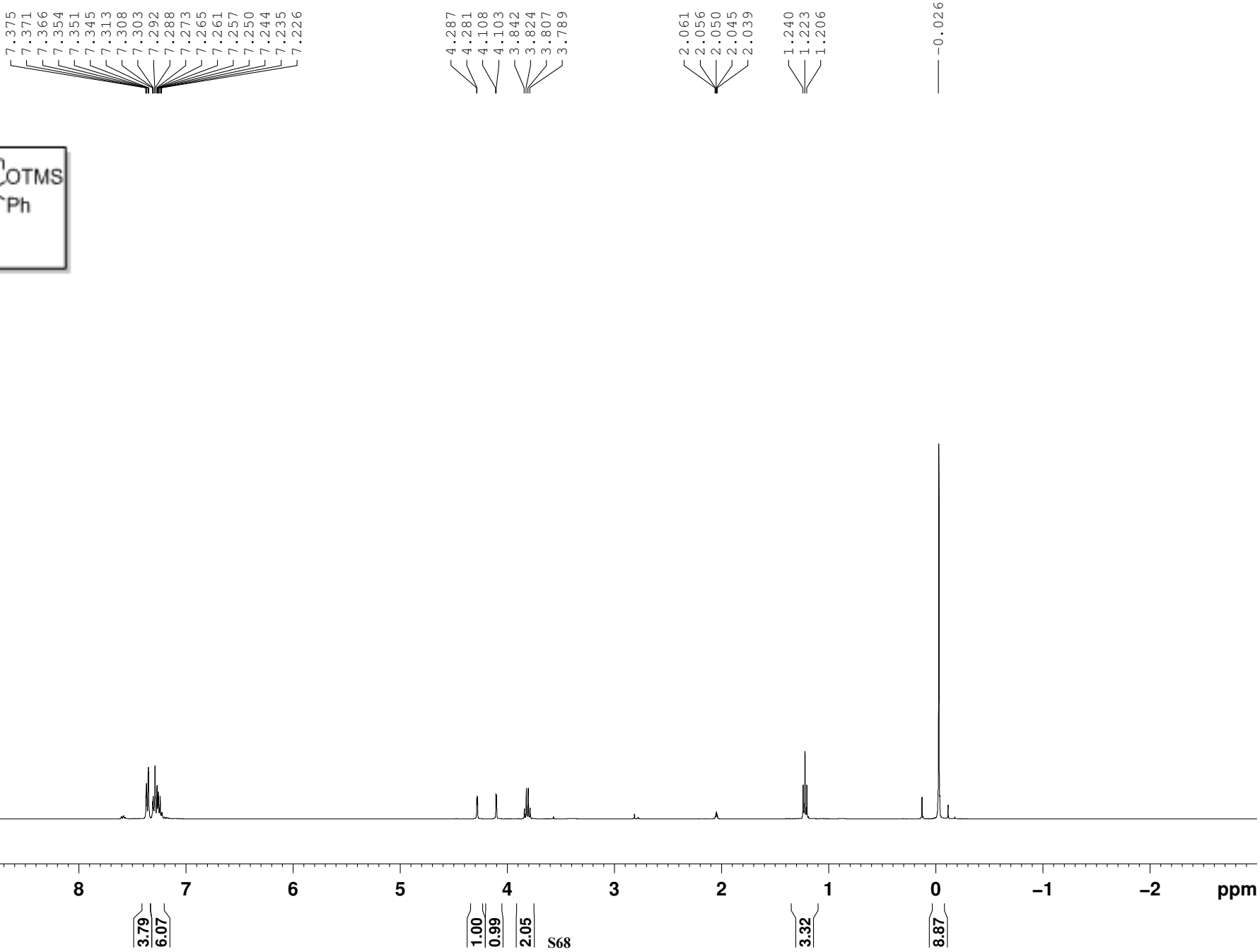


czm7p12a1


7.379
7.363
7.359
7.343
7.339
7.324
7.197
7.194
7.193
7.191
7.173
7.171
7.161
7.155
7.151
7.135
7.129
7.124
7.061
7.059
7.055
7.053
7.040
7.039
7.033
7.019
7.017
7.013
7.011
4.617
4.611
4.604
4.509
4.486
4.462
2.727
2.720
2.703
2.697
2.679
2.673
2.061
2.055
2.050
2.044
2.039
0.066
F
OTMS
O
F
1u
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
−0.5
−1.0
ppm
2.06
3.97
2.00
1.01
2.12
2.11
9.29

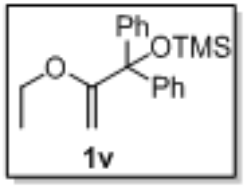

czm7p12a1-C
205.199
163.544
161.128
158.816
147.983
147.917
129.441
129.360
123.281
123.253
114.092
114.018
113.860
113.807
102.112
79.038
70.211
29.616
29.506
29.313
29.121
28.929
28.736
28.544
28.352
0.882
F
OTMS
O
F
1u
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 ppm

czm7p16a1

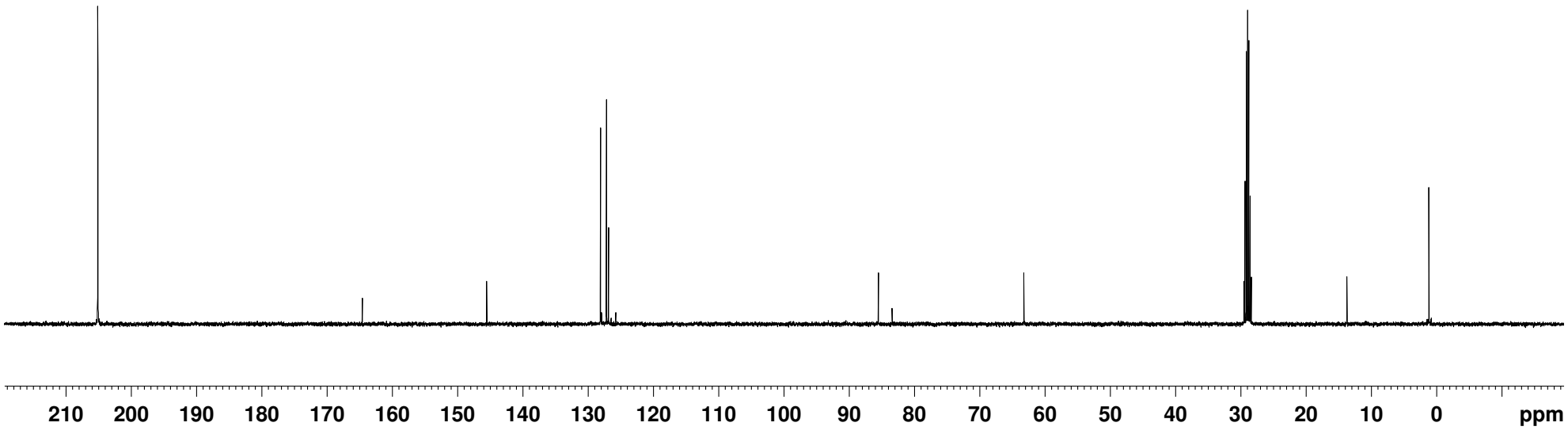

7.375
7.371
7.366
7.354
7.351
7.345
7.313
7.308
7.303
7.292
7.288
7.273
7.265
7.261
7.257
7.250
7.244
7.235
7.226
4.287
4.281
4.108
4.103
3.842
3.824
3.807
3.789
2.061
2.056
2.050
2.045
2.039
1.240
1.223
1.206
-0.026
Ph
OTMS
O
Ph
1v
9
8
7
6
5
4
3
2
1
0
–1
–2
ppm
3.79
6.07
1.00
0.99
2.05
3.32
8.87

czm7p16a1

205.11
164.57
145.52
128.08
127.17
126.85
85.49
83.39
63.20
29.50
29.31
29.12
28.92
28.73
28.54
28.34
13.69
1.14



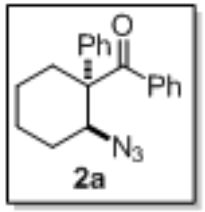
1v



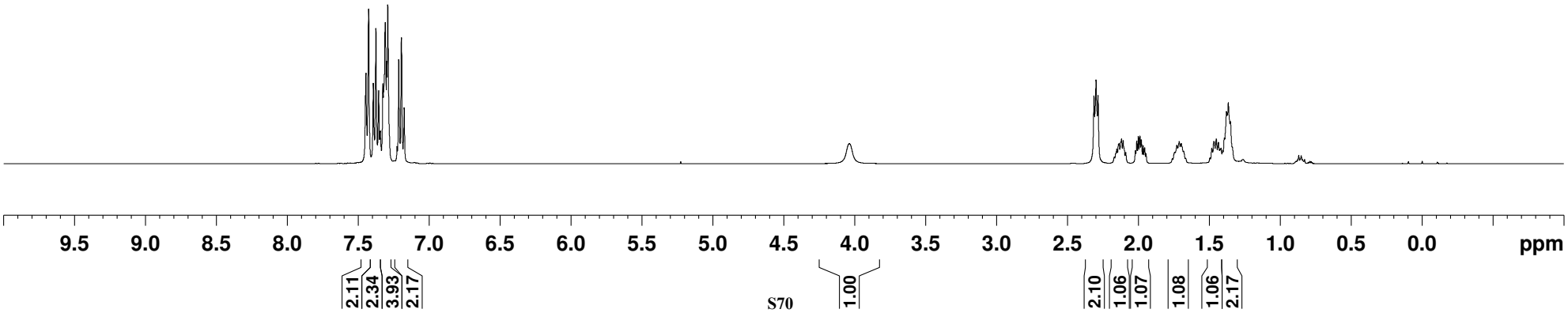
czm7p8a3

7.447
7.429
7.395
7.377
7.357
7.346
7.327
7.322
7.318
7.311
7.300
7.293
7.228
7.216
7.197
7.178

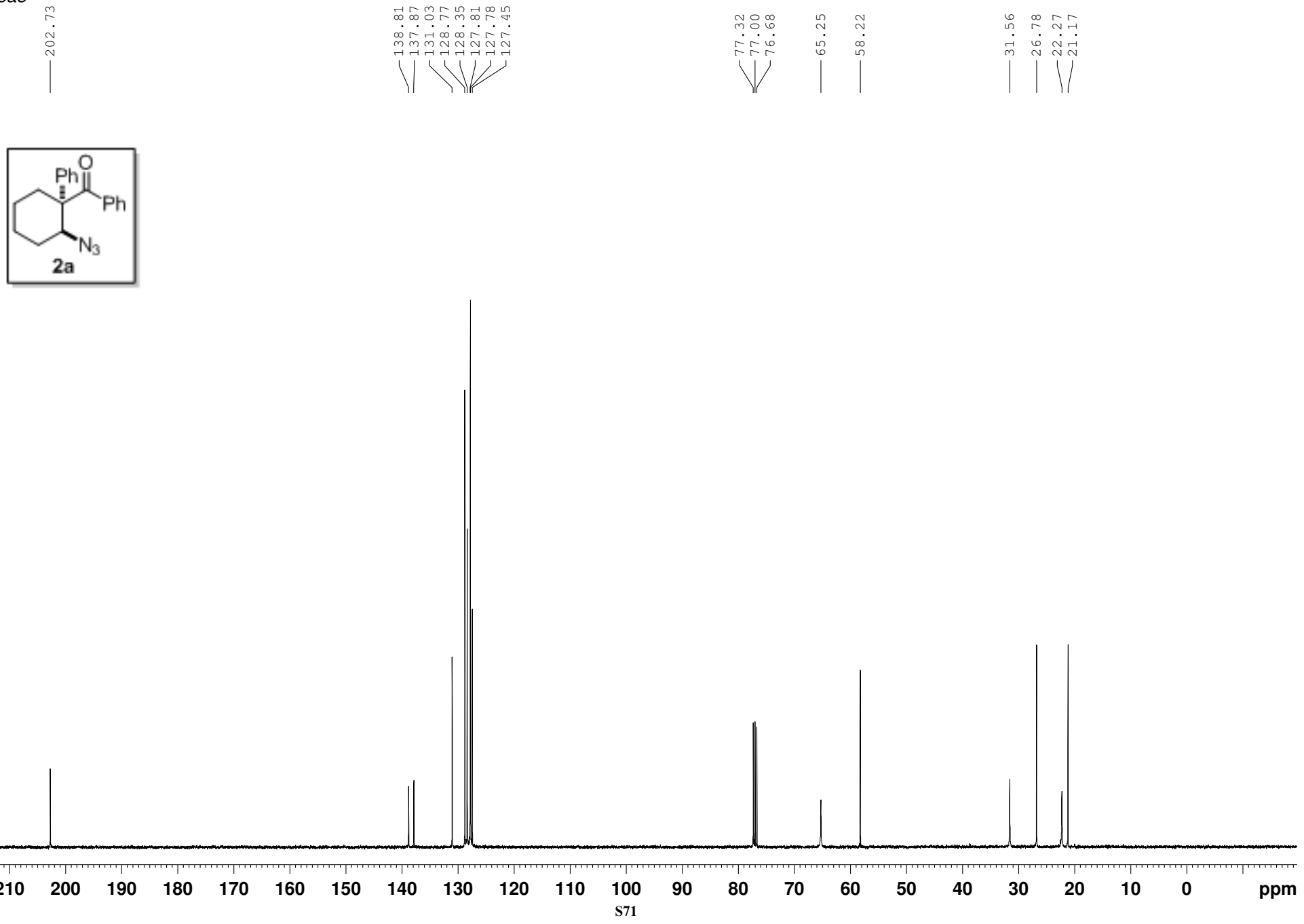
4.039
2.314
2.300
2.285
2.172
2.154
2.142
2.137
2.120
2.108
2.090
2.022
2.012
2.002
1.990
1.980
1.967
1.957
1.947
1.762
1.746
1.730
1.713
1.699
1.681
1.667
1.497
1.483
1.469
1.452
1.437
1.424
1.419
1.407
1.395
1.380
1.367
1.352
0.000



2a

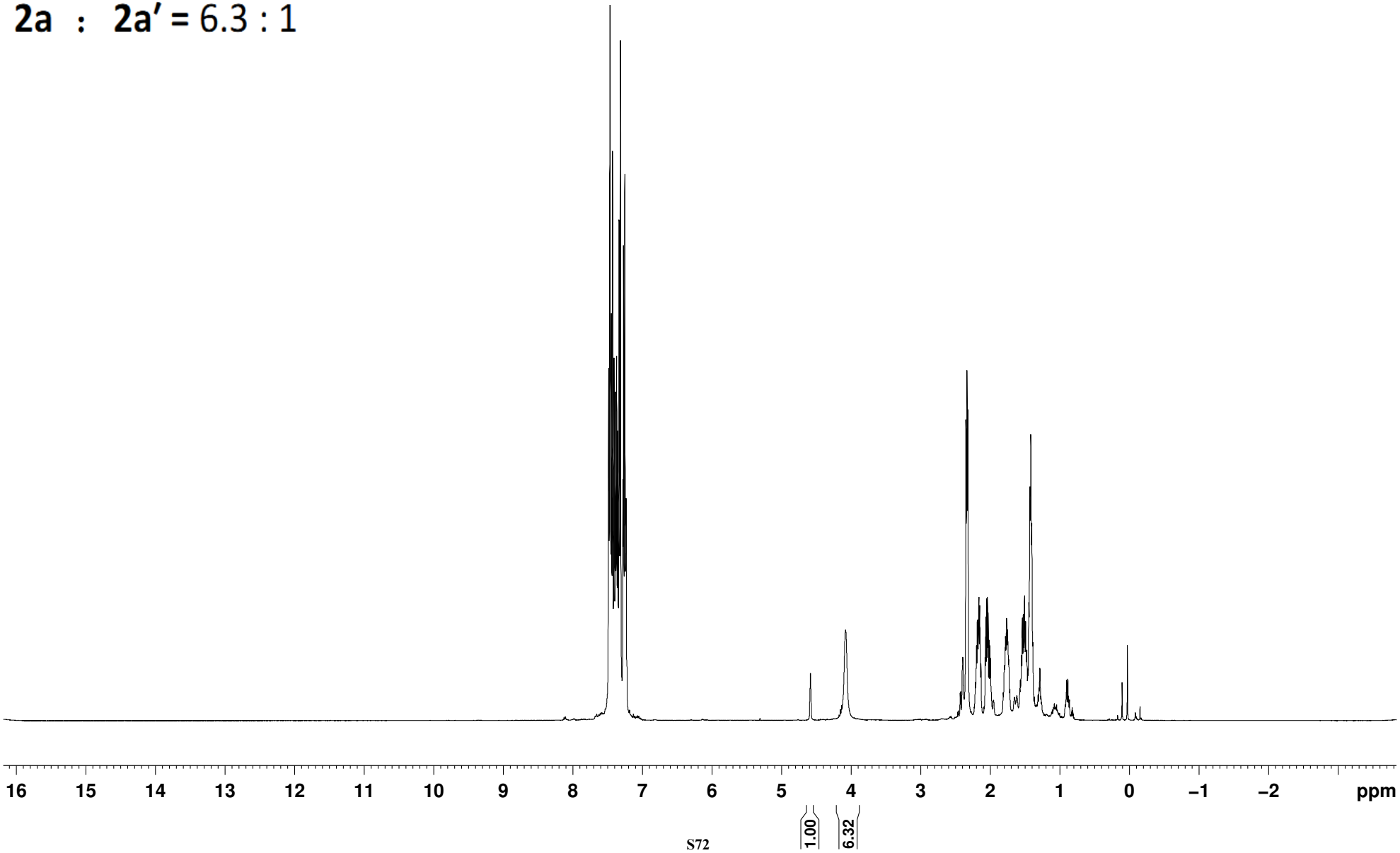


czm7p8a3


202.73
138.81
137.87
131.03
128.77
128.35
127.81
127.78
127.45
77.32
77.00
76.68
65.25
58.22
31.56
26.78
22.27
21.17
Ph
O
Ph
N3
2a
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
ppm

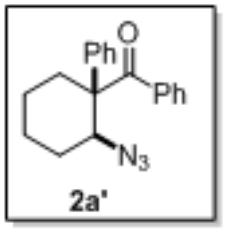
zz2p54b–4

2a : 2a′ = 6.3 : 1

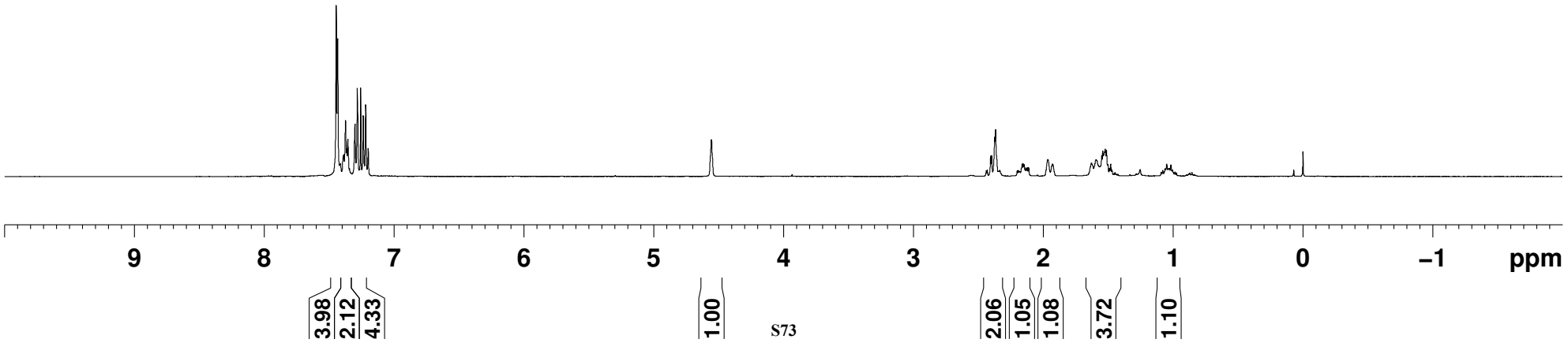


czm7p8b

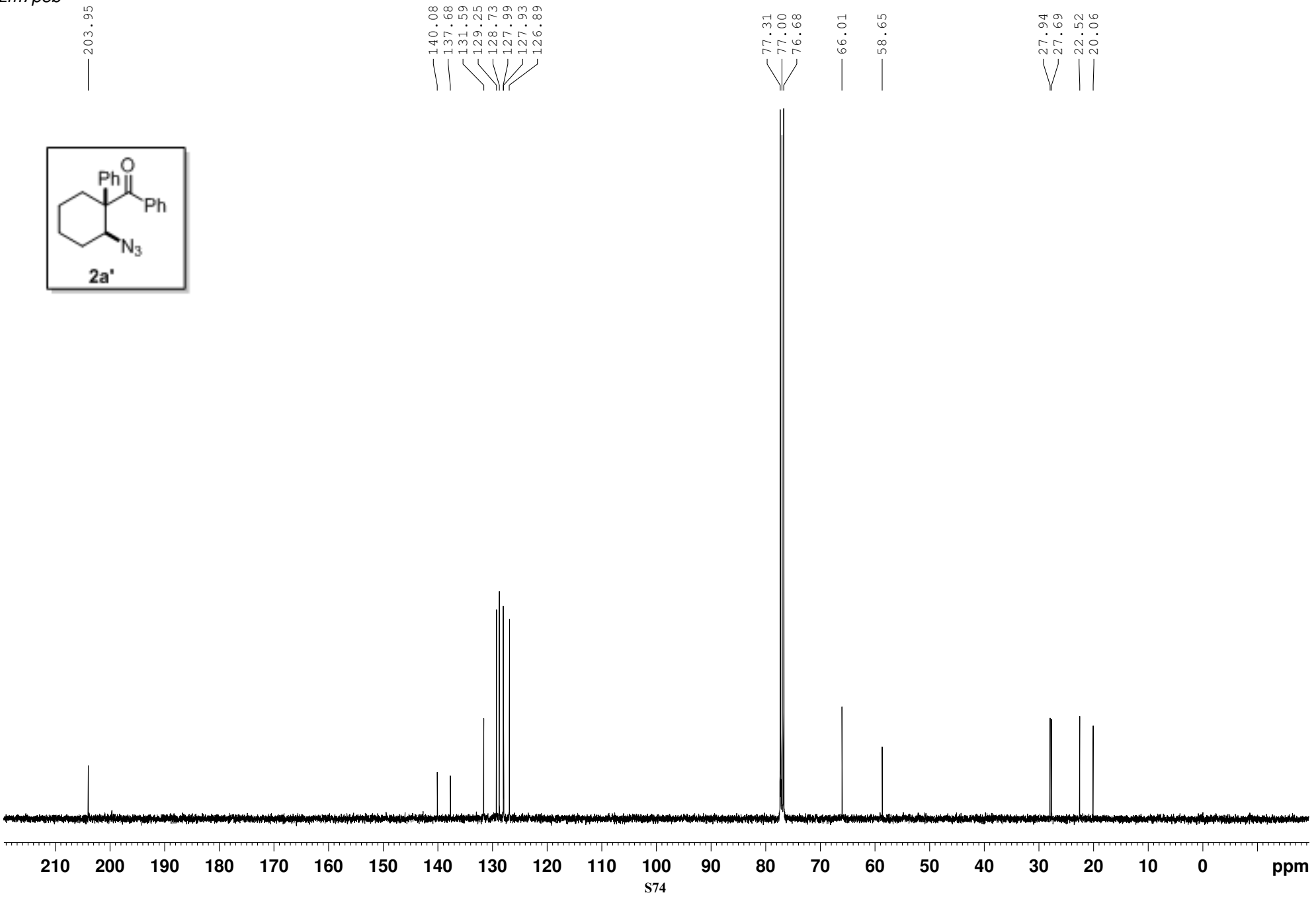
7.447 7.436 7.414 7.397 7.393 7.390 7.387 7.375 7.365 7.357 7.303 7.285 7.282 7.259 7.239 7.221 7.201 4.558 2.440 2.432 2.406 2.398 2.375 2.367 2.335 2.201 2.194 2.164 2.157 2.148 2.134 2.128 2.119 2.112 1.965 1.930 1.631 1.593 1.562 1.551 1.542 1.536 1.529 1.523 1.513 1.504 1.491 1.481 1.471 1.081 1.062 1.050 1.039 1.029 1.017 1.006 0.071 0.000



2a'

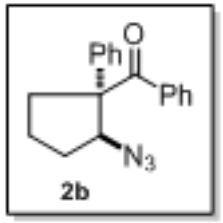


czm7p8b


203.95
140.08
137.68
131.59
129.25
128.73
127.99
127.93
126.89
77.31
77.00
76.68
66.01
58.65
27.94
27.69
22.52
20.06
Ph
O
Ph
N3
2a'
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
ppm

czm7p8a6

7.578 7.575 7.392 7.376 7.360 7.339 7.293 7.287 7.279 7.259 7.252 7.240 4.595 4.582 2.535 2.511 2.501 2.488 2.477 2.454 2.336 2.330 2.316 2.309 2.297 2.281 2.277 2.148 2.143 2.135 2.127 2.122 2.114 2.101 2.010 2.005 1.999 1.994 1.987 1.983 1.964 1.959 1.948 1.926 1.918 1.910 1.903 1.894 1.887 1.879 1.871 1.721 1.712 1.701 1.697 1.689 1.686

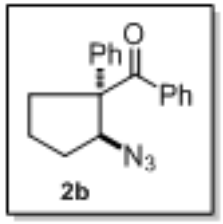


2b

15 14 13 12 11 10 9 8 7 6 5 4 3 2 1 0 –1 –2 ppm

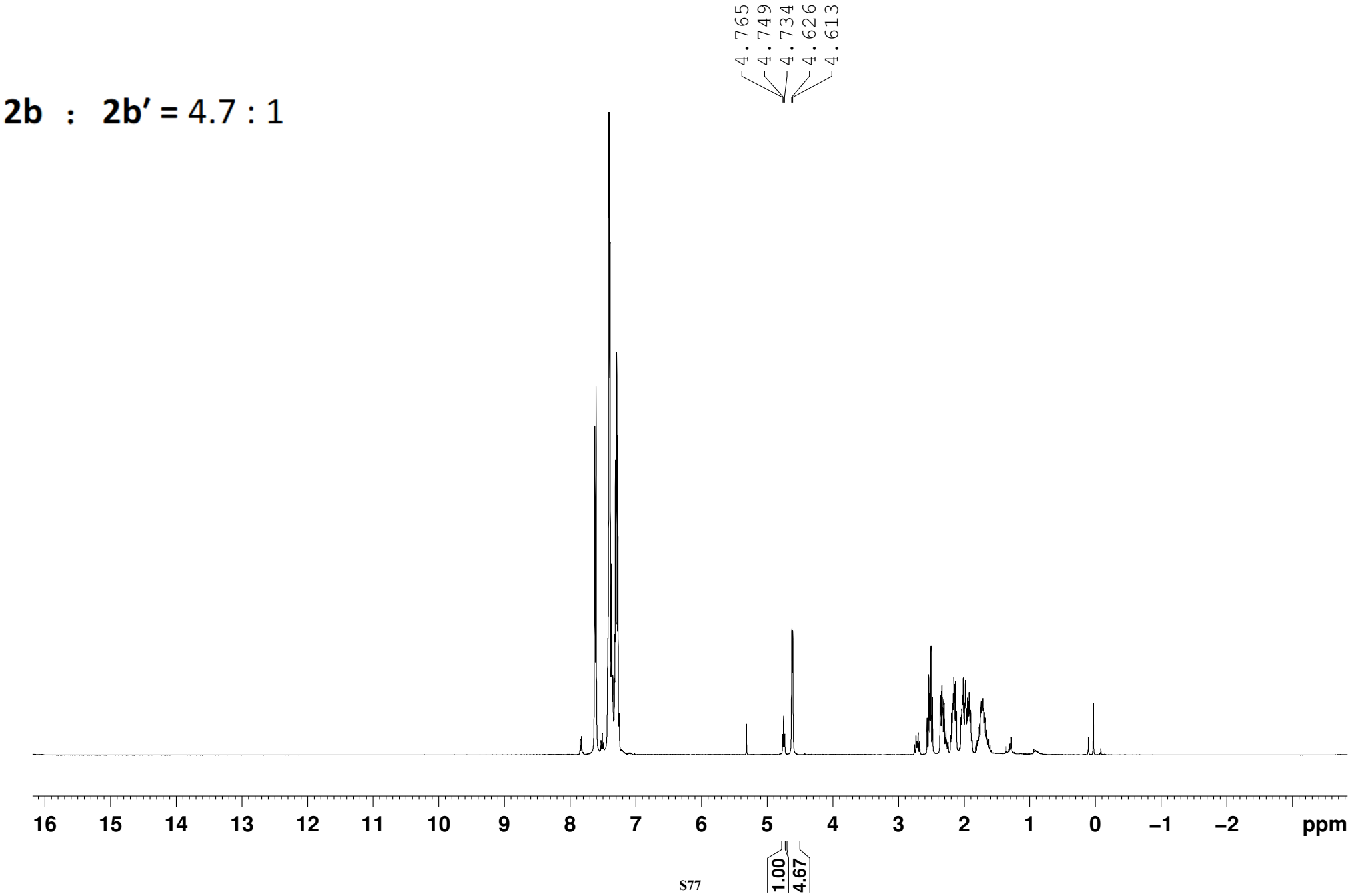
2.05 5.03 3.14 1.00 1.02 1.04 1.05 2.08 1.05

czm7p8a6

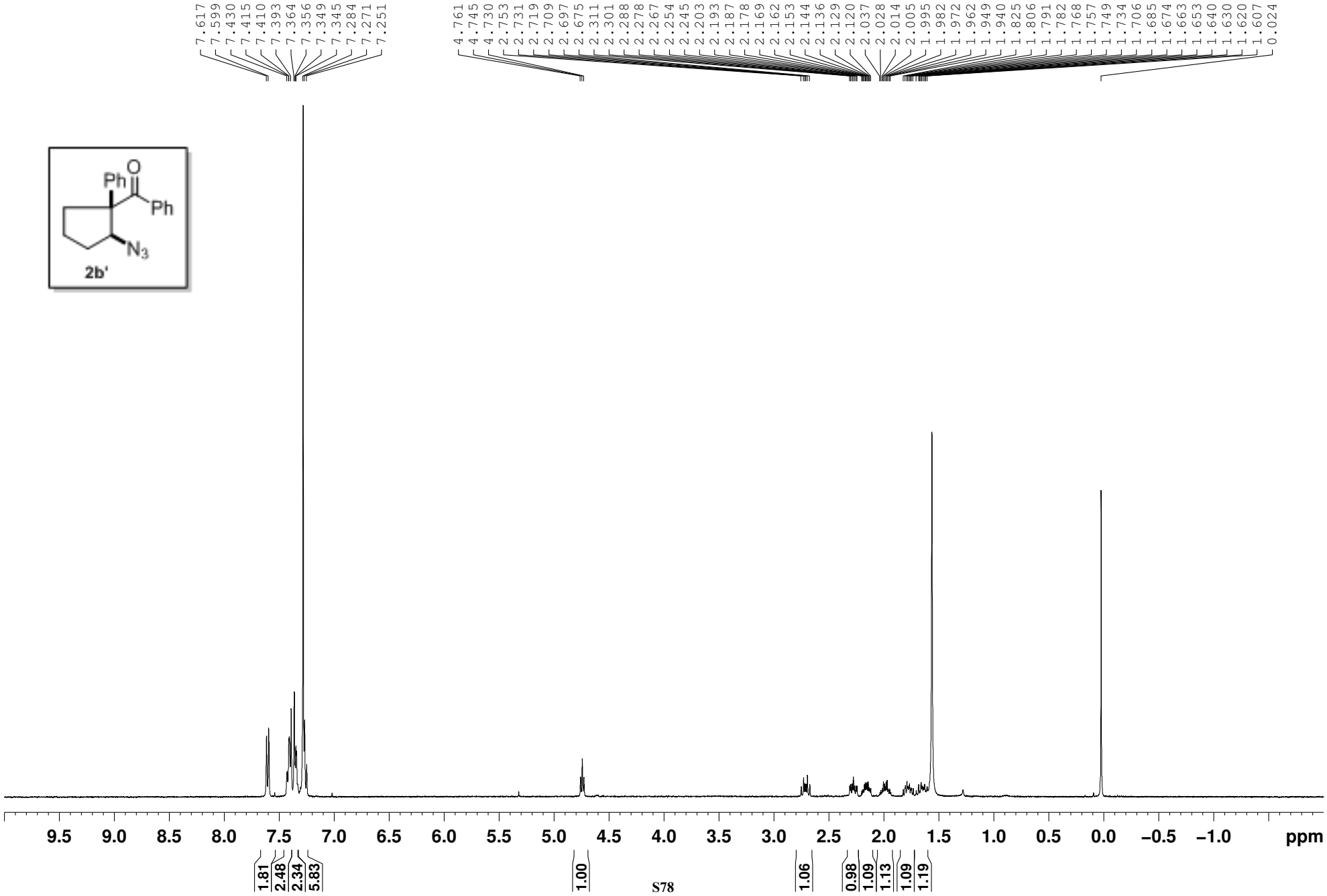

O
Ph
Ph
N3
2b

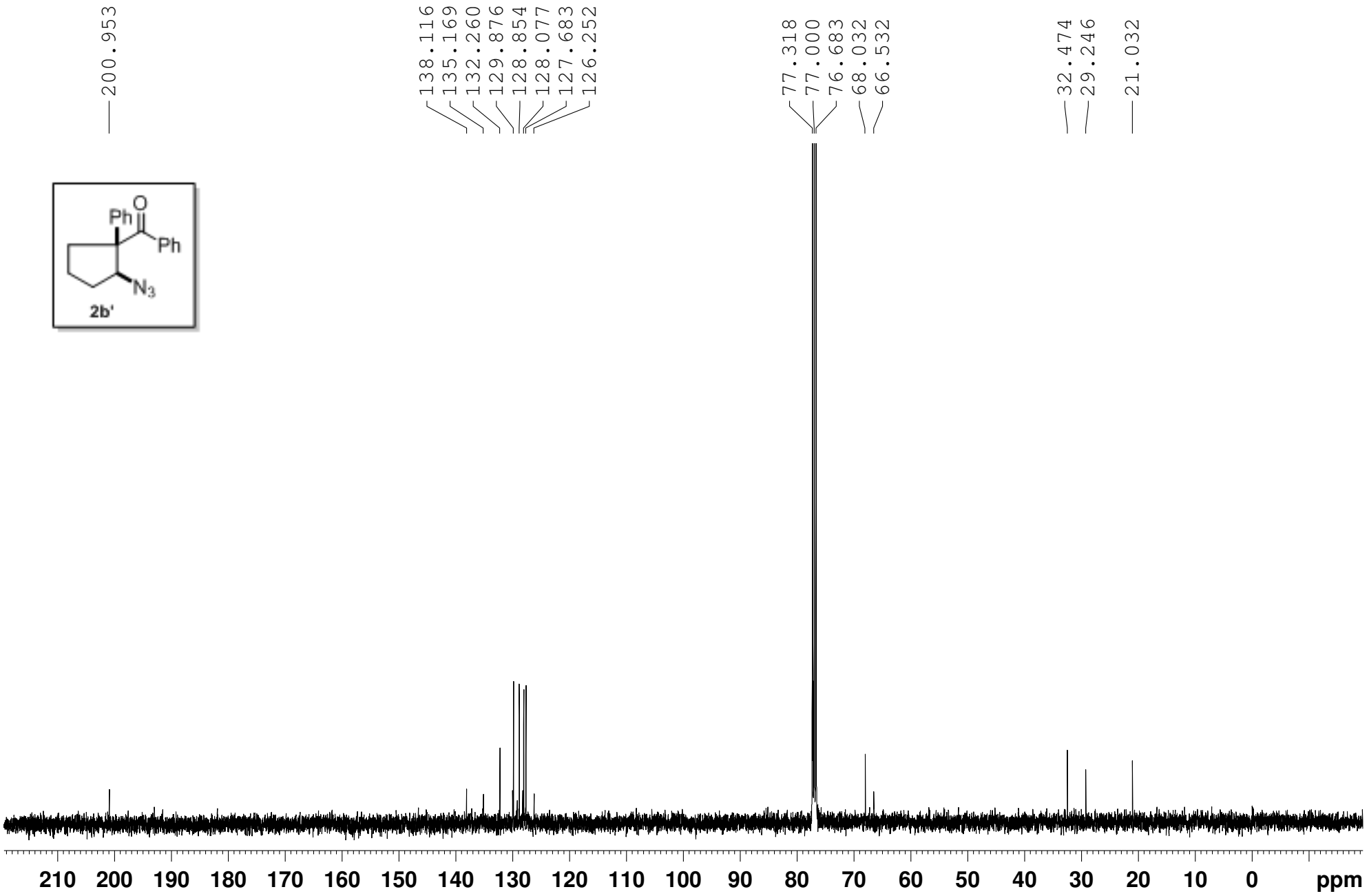
199.78
139.98
137.75
131.84
129.19
128.84
128.09
127.45
126.22
77.32
77.00
76.68
69.79
67.42
34.00
30.01
20.62
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 ppm

czm7p19a1


4.765
4.749
4.734
4.626
4.613
2b : 2b′ = 4.7 : 1
16 15 14 13 12 11 10 9 8 7 6 5 4 3 2 1 0 –1 –2 ppm
1.00
4.67

zz2p85b3

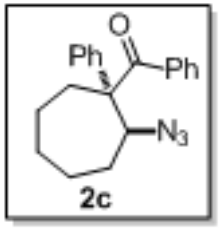

7.617
7.599
7.430
7.415
7.410
7.393
7.364
7.356
7.349
7.345
7.284
7.271
7.251
4.761
4.745
4.730
2.753
2.731
2.719
2.709
2.697
2.675
2.311
2.301
2.288
2.278
2.267
2.254
2.245
2.203
2.193
2.187
2.178
2.169
2.162
2.153
2.144
2.136
2.129
2.120
2.037
2.028
2.014
2.005
1.995
1.982
1.972
1.962
1.949
1.940
1.825
1.806
1.791
1.782
1.768
1.757
1.749
1.734
1.706
1.685
1.674
1.663
1.653
1.640
1.630
1.620
1.607
0.024
Ph
O
Ph
N3
2b'
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
−0.5
−1.0
ppm
1.81
2.48
2.34
5.83
1.00
1.06
0.98
1.09
1.13
1.09
1.19


200.953
138.116
135.169
132.260
129.876
128.854
128.077
127.683
126.252
77.318
77.000
76.683
68.032
66.532
32.474
29.246
21.032
Ph
O
Ph
N3
2b'
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 ppm

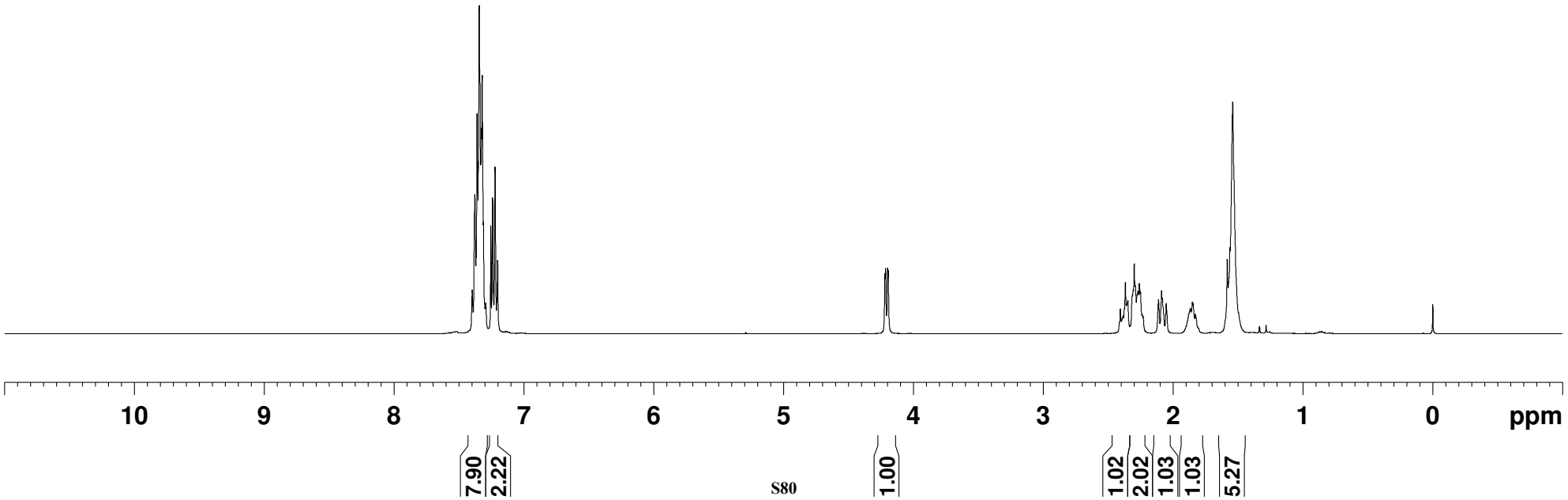
zz2p59b5

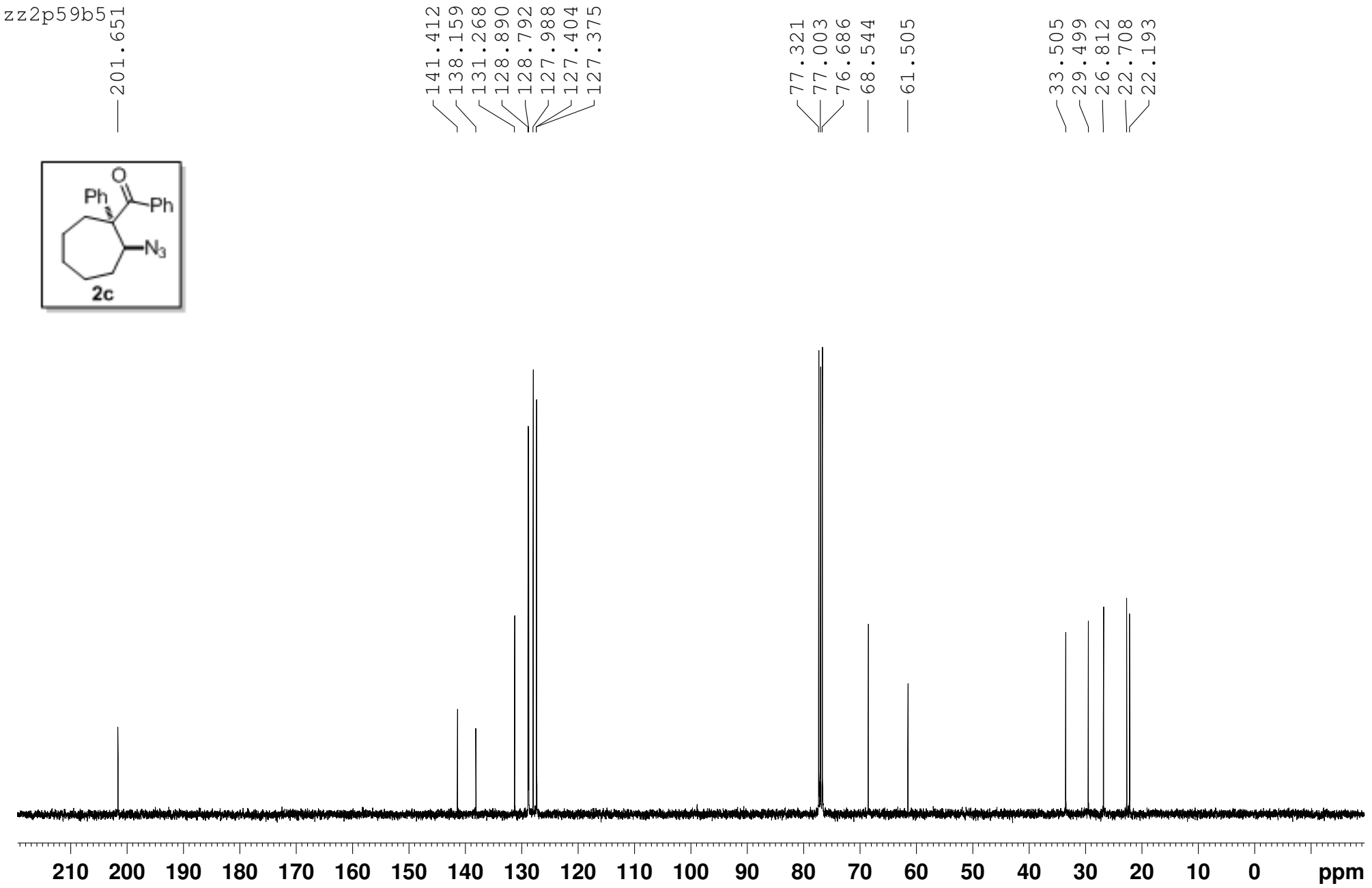
7.400
7.380
7.363
7.346
7.341
7.333
7.328
7.323
7.313
7.300
7.296
7.256
7.243
7.224
7.204

4.221
4.215
4.200
4.195
2.406
2.385
2.368
2.349
2.314
2.308
2.300
2.291
2.278
2.272
2.261
2.252
2.237
2.231
2.113
2.089
2.084
2.053
1.868
1.852
1.846
1.828
1.583
1.562
1.542
0.000

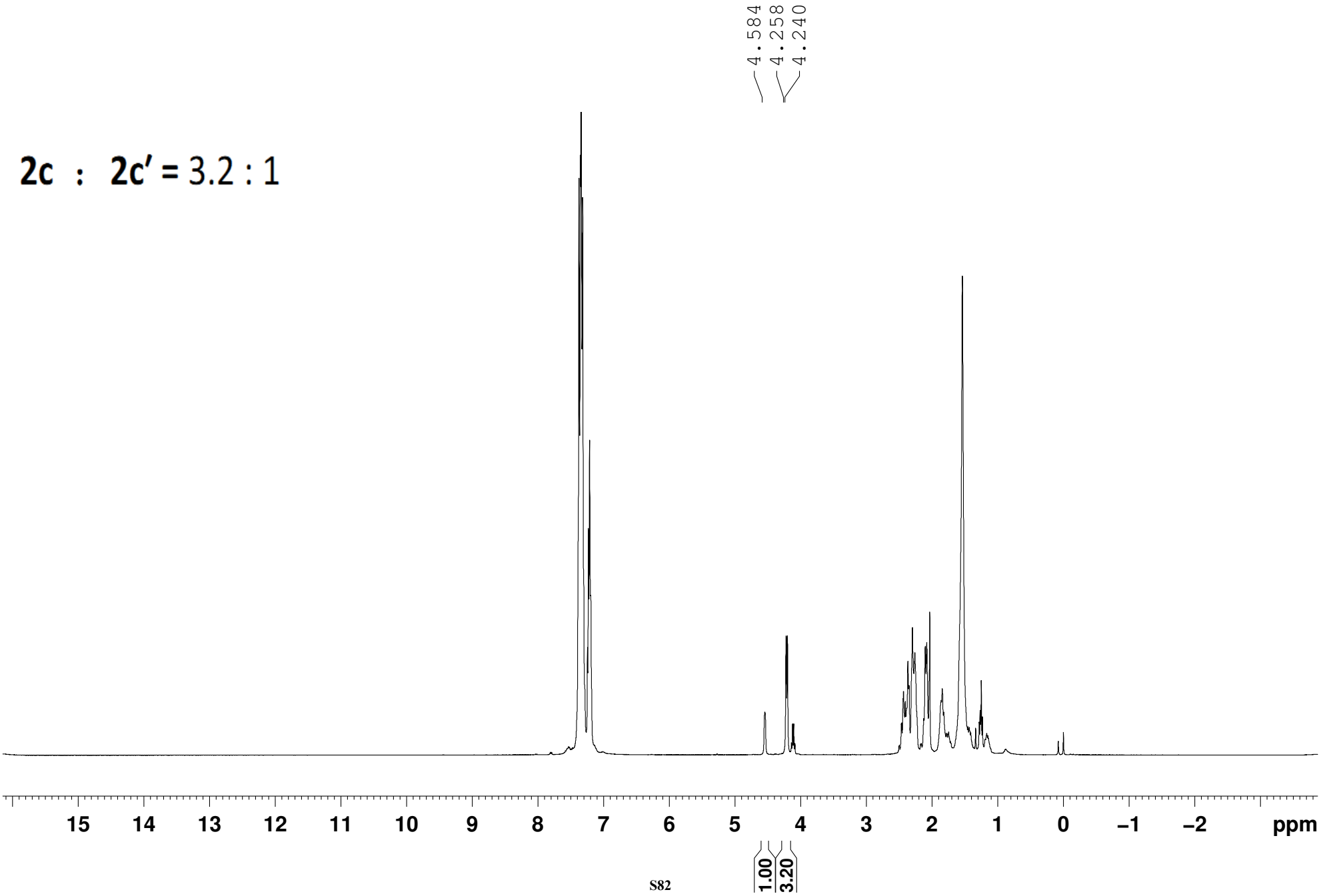


2c



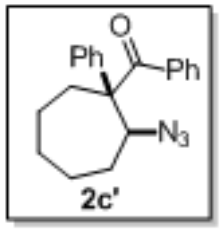

zz2p59b5
201.651
141.412
138.159
131.268
128.890
128.792
127.988
127.404
127.375
77.321
77.003
76.686
68.544
61.505
33.505
29.499
26.812
22.708
22.193
O
Ph
Ph
N3
2c
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 ppm

zz2p61a1

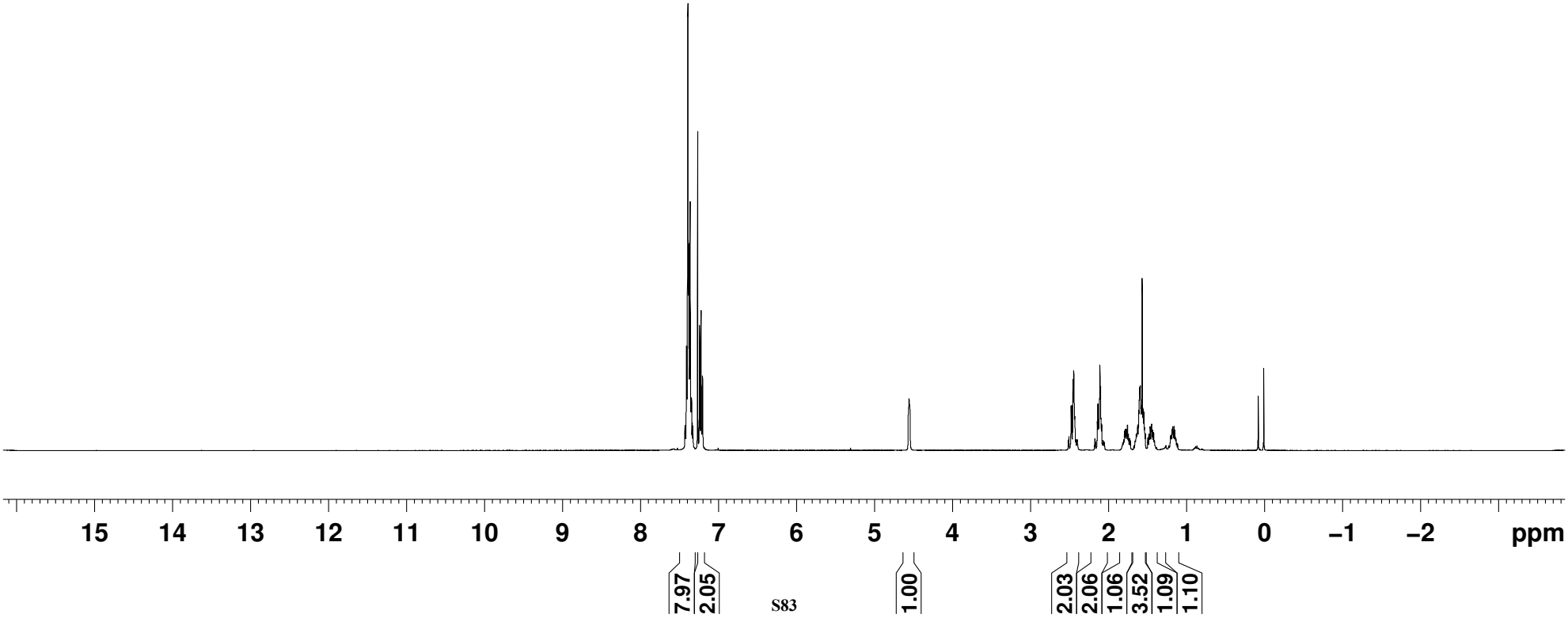

4.584
4.258
4.240
2c : 2c′ = 3.2 : 1
15
14
13
12
11
10
9
8
7
6
5
4
3
2
1
0
–1
–2
ppm
1.00
3.20

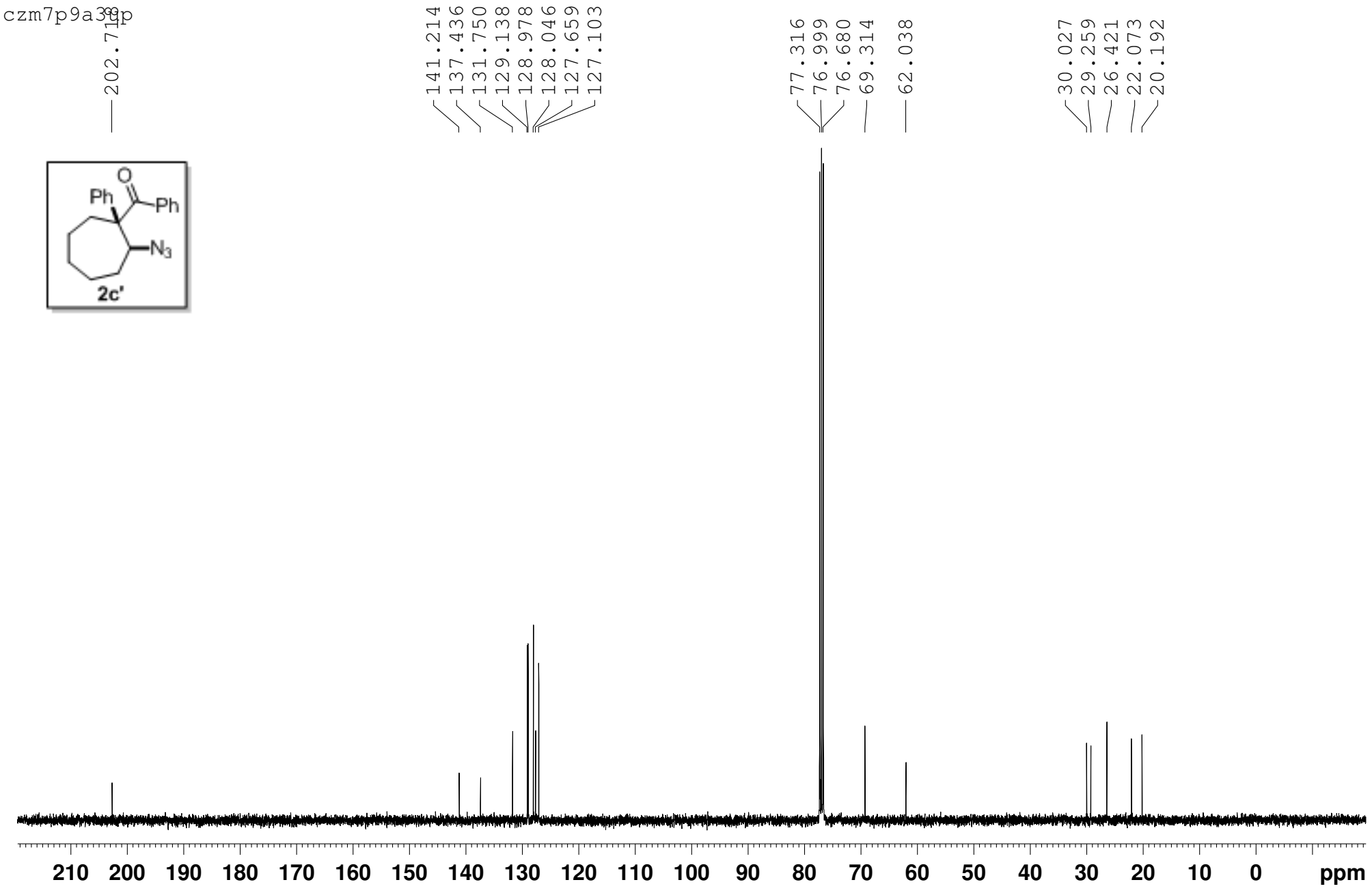
czm7p9a3up

7.431 7.412 7.409 7.395 7.387 7.383 7.378 7.367 7.356 7.353 7.348 7.339 7.333 7.270 7.245 7.237 7.226 7.206 4.566 4.562 4.559 4.555 4.549 2.480 2.472 2.455 2.447 2.434 2.144 2.137 2.131 2.126 2.112 2.104 2.096 2.089 1.785 1.769 1.758 1.627 1.614 1.600 1.593 1.585 1.577 1.569 1.555 1.547 1.539 1.468 1.454 1.448 1.436 1.186 1.177 1.161 0.082 0.011



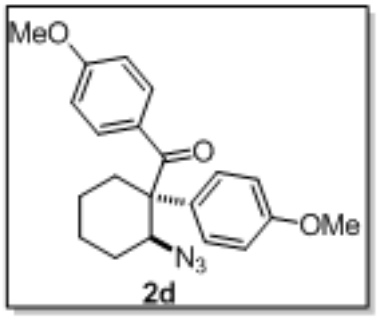
2c'



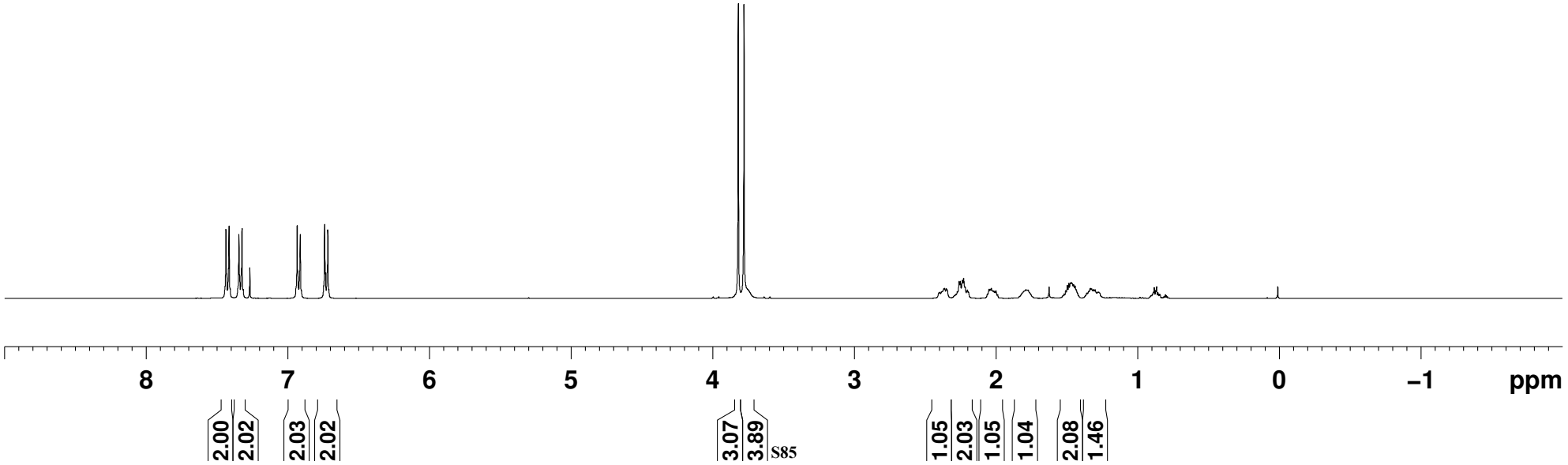

czm7p9a3sp
202.711
141.214
137.436
131.750
129.138
128.978
128.046
127.659
127.103
77.316
76.999
76.680
69.314
62.038
30.027
29.259
26.421
22.073
20.192
O
Ph
Ph
N3
2c'
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 ppm

zz2p80a3xia

7.439 7.434 7.421 7.416 7.409 7.347 7.342 7.325 7.317 7.270 6.943 6.936 6.931 6.914 6.748 6.742 6.737 6.724 6.719 3.821 3.780 2.386 2.379 2.370 2.364 2.351 2.274 2.261 2.253 2.239 2.229 2.219 2.203 2.195 2.051 2.043 2.034 2.024 2.018 2.010 2.001 1.790 1.774 1.509 1.498 1.487 1.477 1.467 1.452 1.443 1.435 1.345 1.336 1.326 1.313 1.302 1.278 0.011

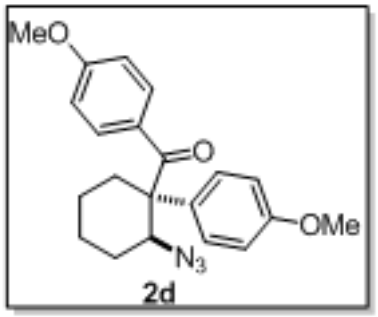


2d

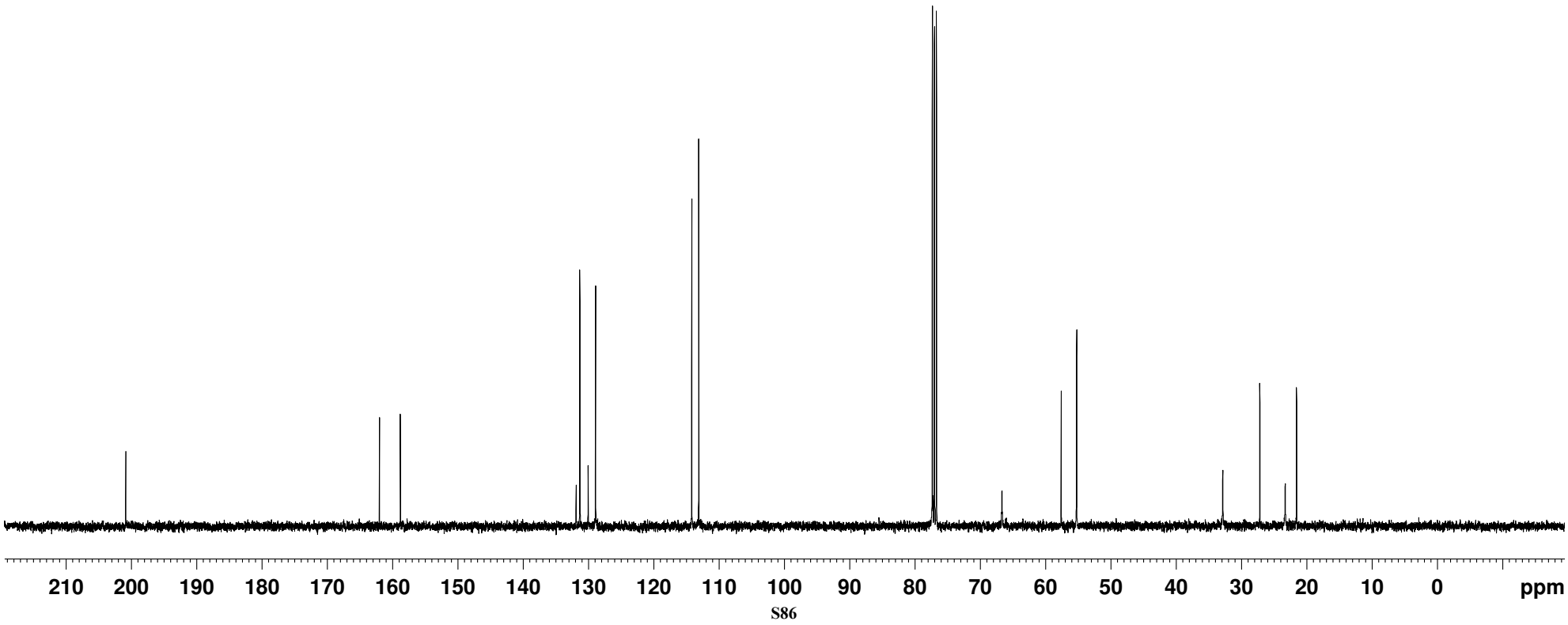


zz2p80a3xia

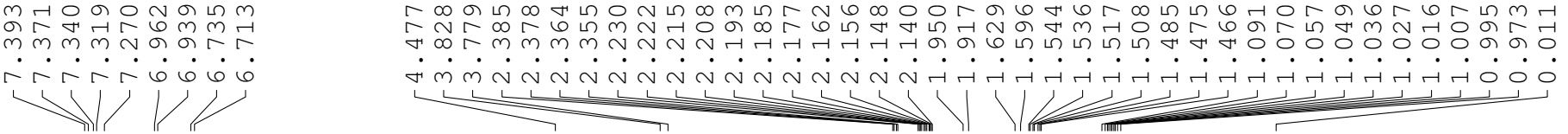
200.85
161.99
158.79
131.86
131.31
130.04
128.90
114.17
113.11
77.32
77.00
76.69
66.65
57.58
55.25
55.19
32.85
27.16
23.27
21.54

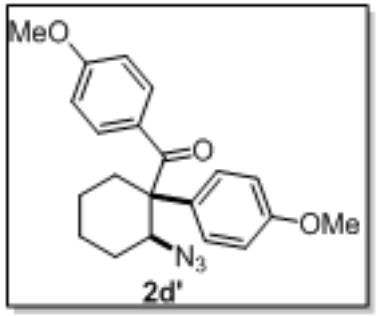


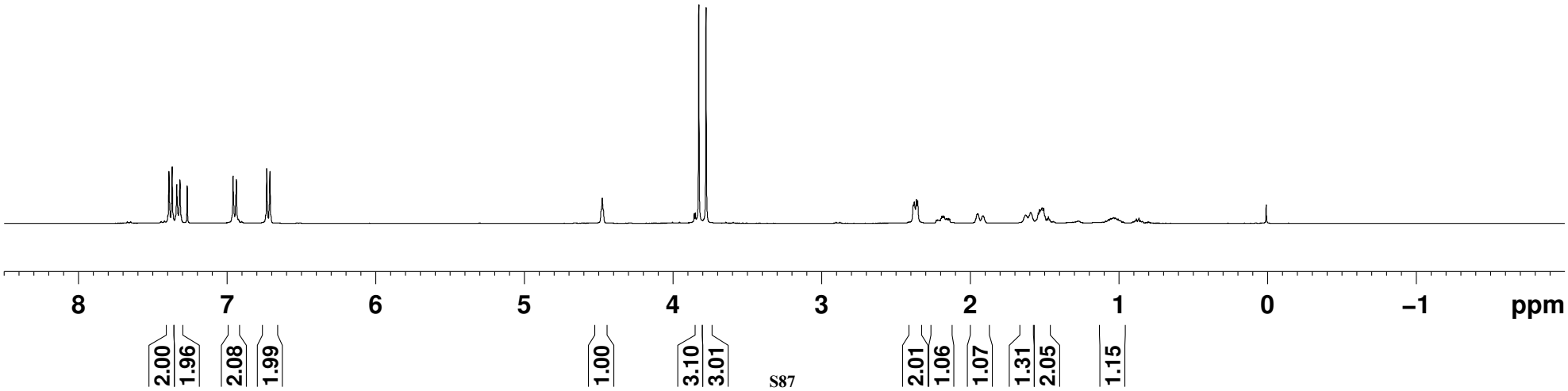
2d



zz2p79b3-H

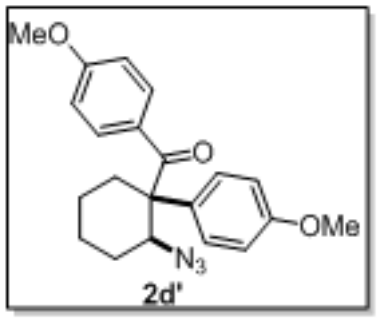

7.393
7.371
7.340
7.319
7.270
6.962
6.939
6.735
6.713
4.477
3.828
3.779
2.385
2.378
2.364
2.355
2.230
2.222
2.215
2.208
2.193
2.185
2.177
2.162
2.156
2.148
2.140
1.950
1.917
1.629
1.596
1.544
1.536
1.517
1.508
1.485
1.475
1.466
1.091
1.070
1.057
1.049
1.036
1.027
1.016
1.007
0.995
0.973
0.011


MeO
O
OMe
N3
2d'

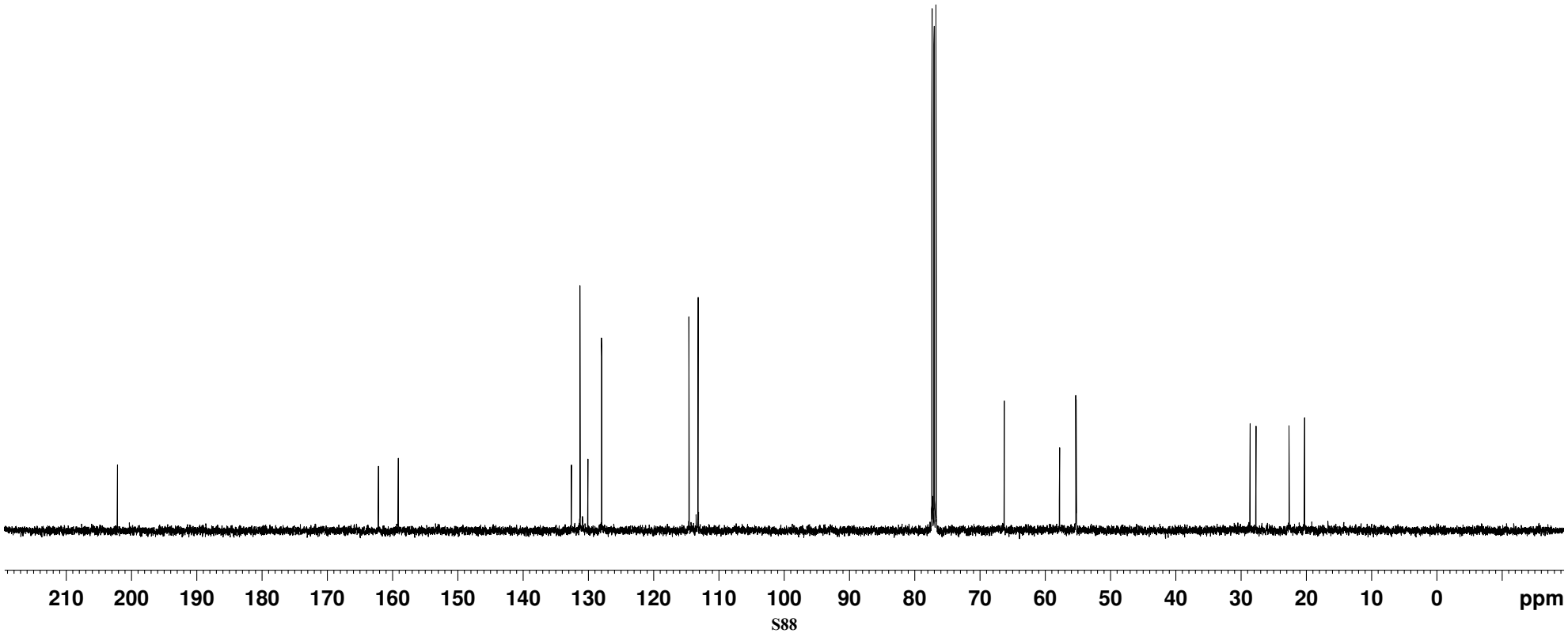

8
7
6
5
4
3
2
1
0
−1
ppm
2.00
1.96
2.08
1.99
1.00
3.10
3.01
2.01
1.06
1.07
1.31
2.05
1.15

202.13
162.14
159.09
132.56
131.26
130.04
127.93
114.55
113.16
77.32
77.00
76.69
66.24
57.78
55.28
55.22
28.58
27.67
22.59
20.22

zz2p79b2shang



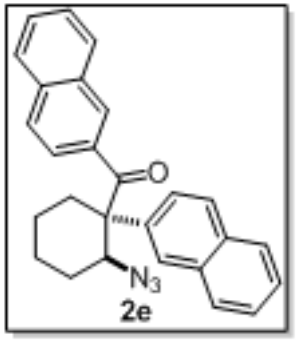
2d'



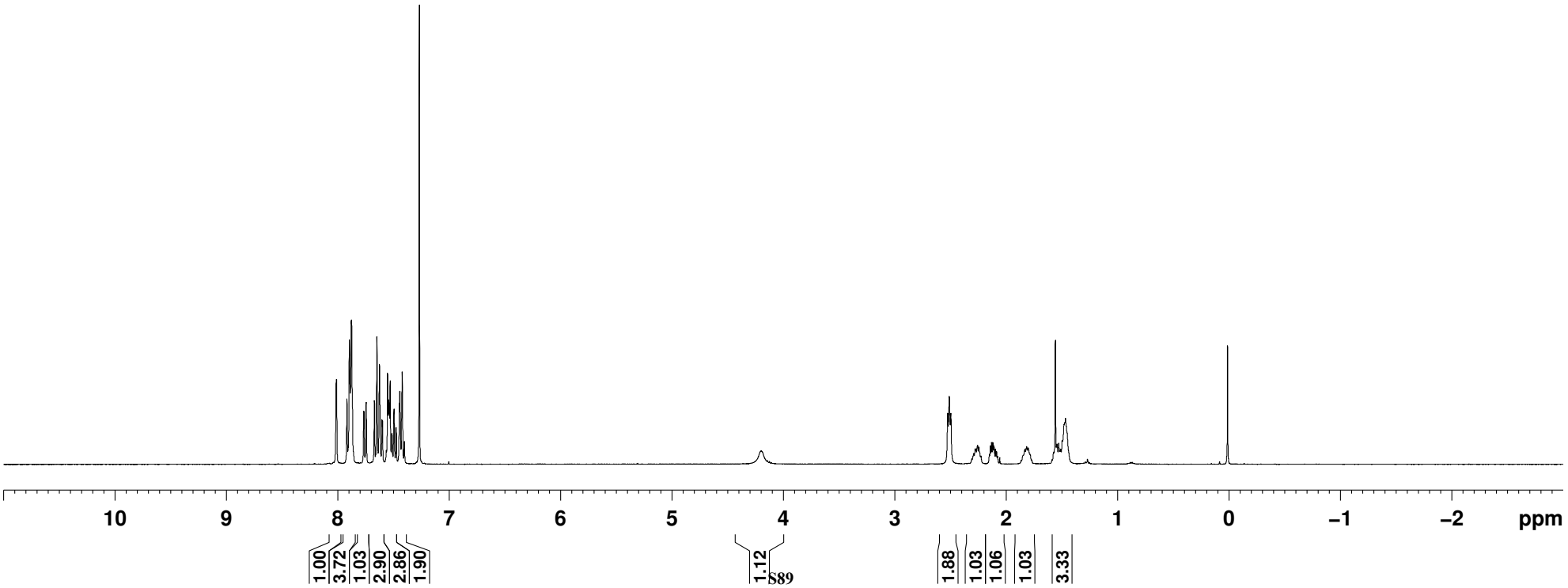
czm–2014422

8.016
8.014
7.920
7.898
7.879
7.768
7.747
7.673
7.651
7.628
7.605
7.601
7.567
7.555
7.550
7.545
7.542
7.537
7.532
7.514
7.497
7.479
7.450
7.445
7.424
7.405
7.270

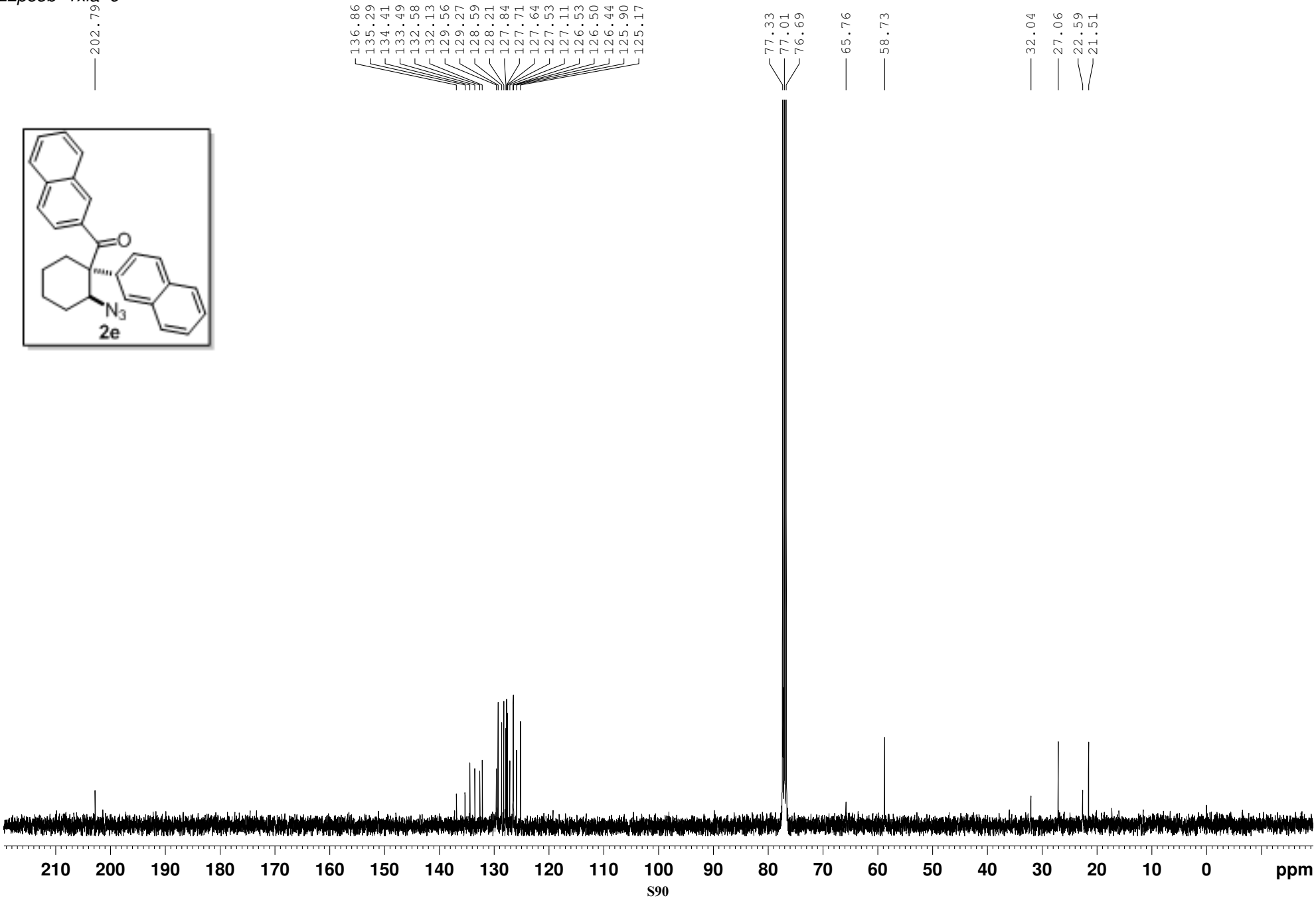
4.202
2.526
2.511
2.497
2.309
2.291
2.278
2.257
2.246
2.227
2.152
2.142
2.132
2.121
2.111
2.098
2.088
2.077
2.058
1.834
1.817
1.804
1.787
1.575
1.559
1.544
1.529
1.517
1.510
1.497
1.482
1.468
0.013



2e



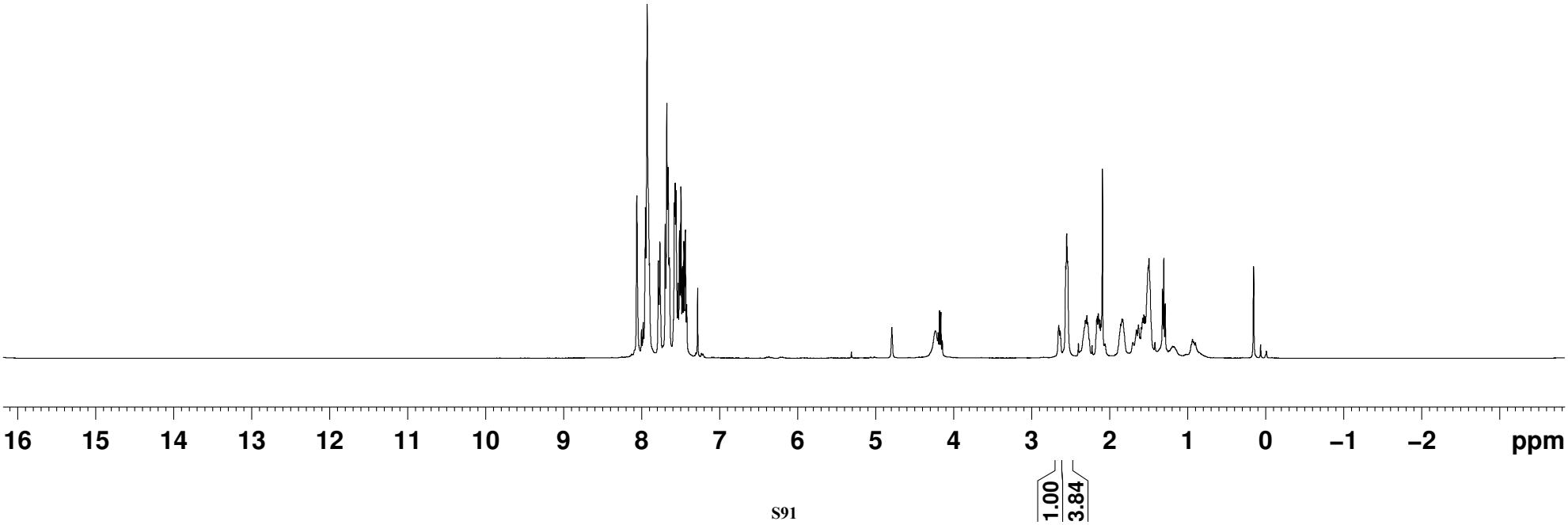
zz2p83b–1xia–c



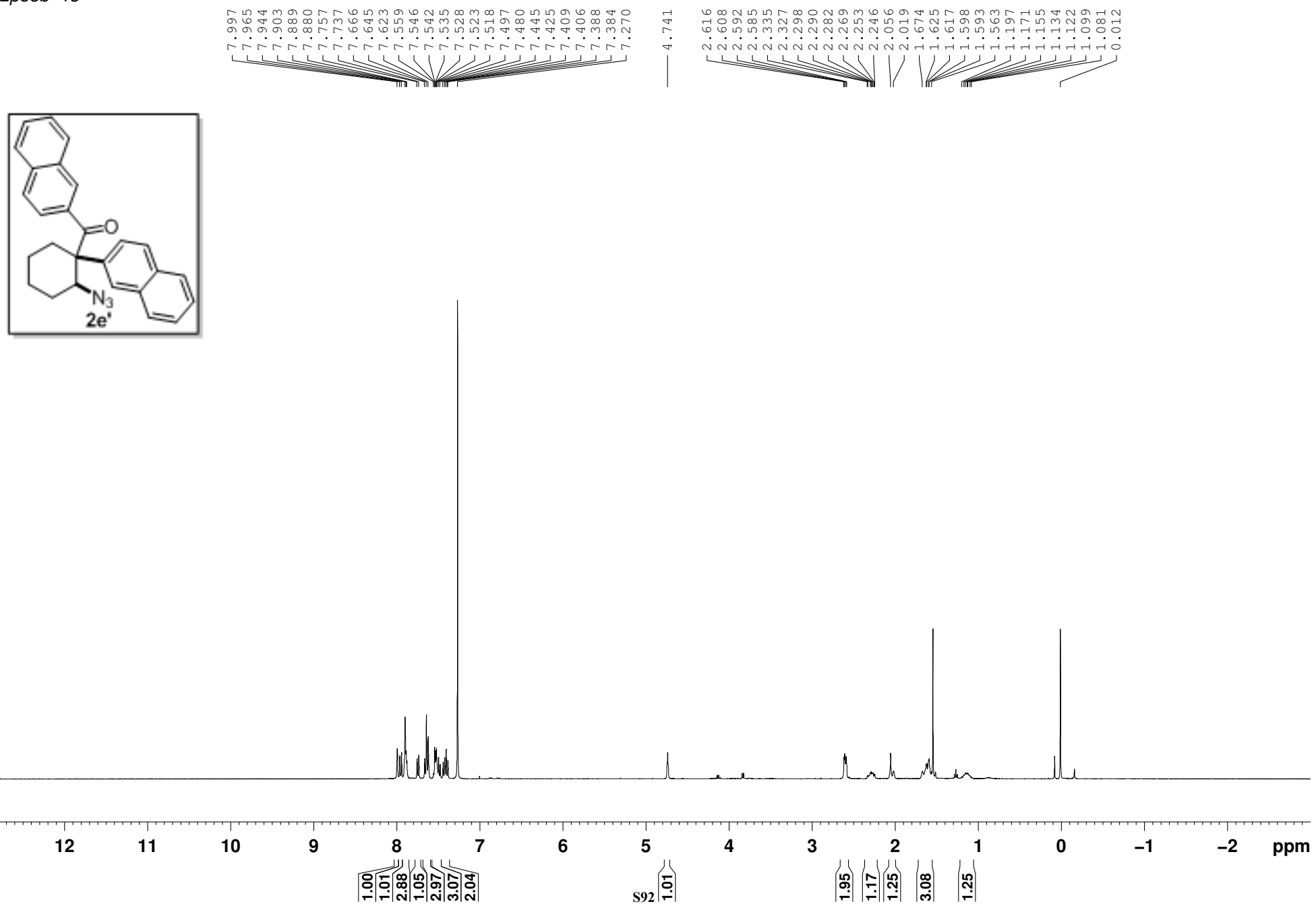
zz2p83b1-H

2.652
2.636
2.564
2.551
2.538

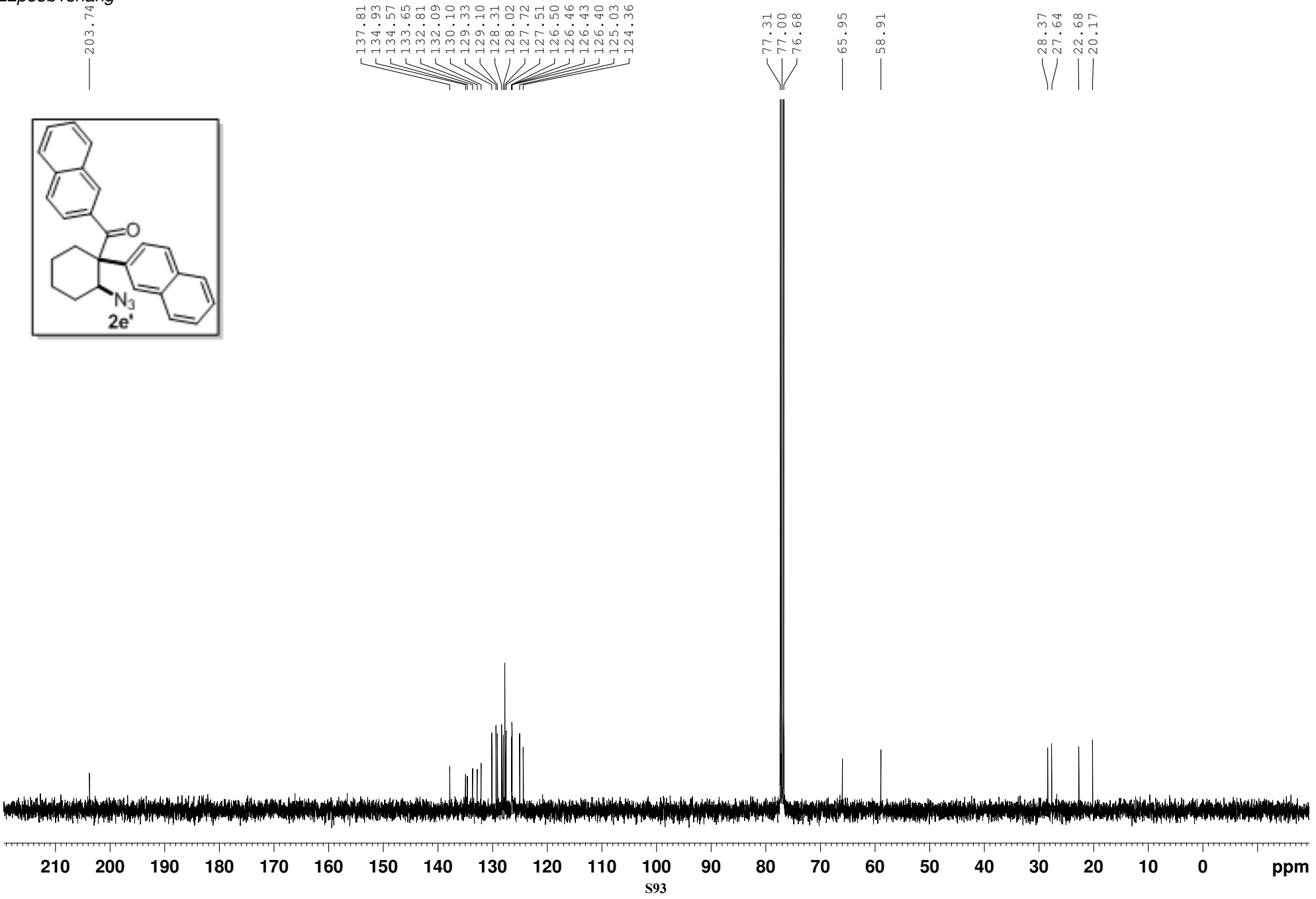
2e : 2e′ = 3.8 : 1



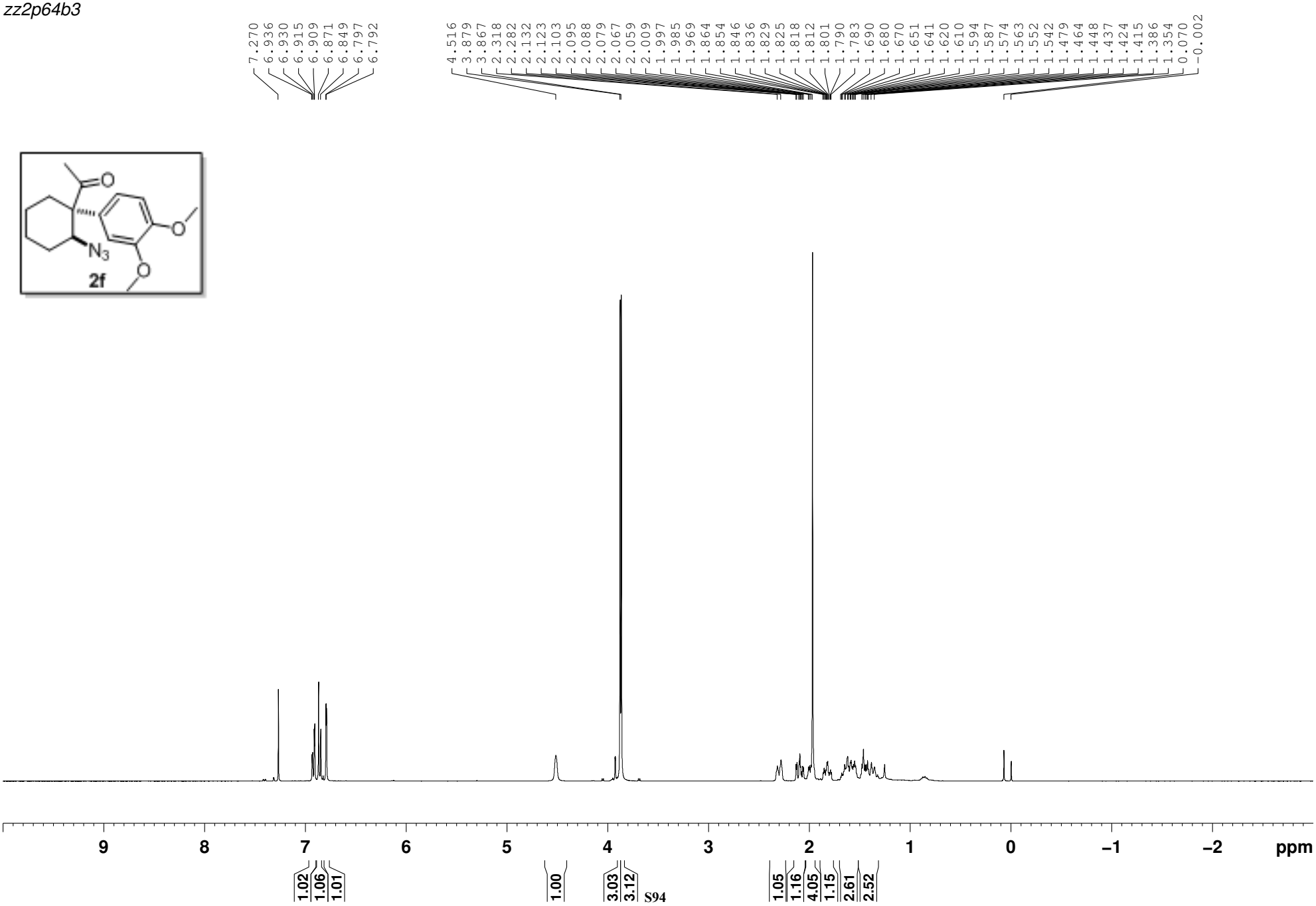
zz2p83b–1s


7.997
7.965
7.944
7.903
7.889
7.880
7.757
7.737
7.666
7.645
7.623
7.559
7.546
7.542
7.535
7.528
7.523
7.518
7.497
7.480
7.445
7.425
7.409
7.406
7.388
7.384
7.270
4.741
2.616
2.608
2.592
2.585
2.335
2.327
2.298
2.290
2.282
2.269
2.253
2.246
2.056
2.019
1.674
1.625
1.617
1.598
1.593
1.563
1.197
1.171
1.155
1.134
1.122
1.099
1.081
0.012
O
N3
2e'
12
11
10
9
8
7
6
5
4
3
2
1
0
–1
–2
ppm
1.00
1.01
2.88
1.05
2.97
3.07
2.04
1.01
1.95
1.17
1.25
3.08
1.25

zz2p83b1shang

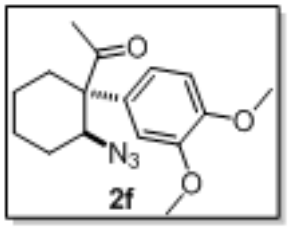


zz2p64b3


7.270
6.936
6.930
6.915
6.909
6.871
6.849
6.797
6.792
4.516
3.879
3.867
2.318
2.282
2.132
2.123
2.103
2.095
2.088
2.079
2.067
2.059
2.009
1.997
1.985
1.969
1.864
1.854
1.846
1.836
1.829
1.825
1.818
1.812
1.801
1.790
1.783
1.690
1.680
1.670
1.651
1.641
1.620
1.610
1.594
1.587
1.574
1.563
1.552
1.542
1.479
1.464
1.448
1.437
1.424
1.415
1.386
1.354
0.070
-0.002
O
O
O
N3
2f
9
8
7
6
5
4
3
2
1
0
–1
–2
ppm
1.02
1.06
1.01
1.00
3.03
3.12
1.05
1.16
4.05
1.15
2.61
2.52

zz2p64b3

208.03
149.24
148.30
130.02
120.01
111.26
110.73
77.32
77.00
76.68
62.75
58.31
56.01
55.80
27.89
26.05
25.02
21.13
20.87



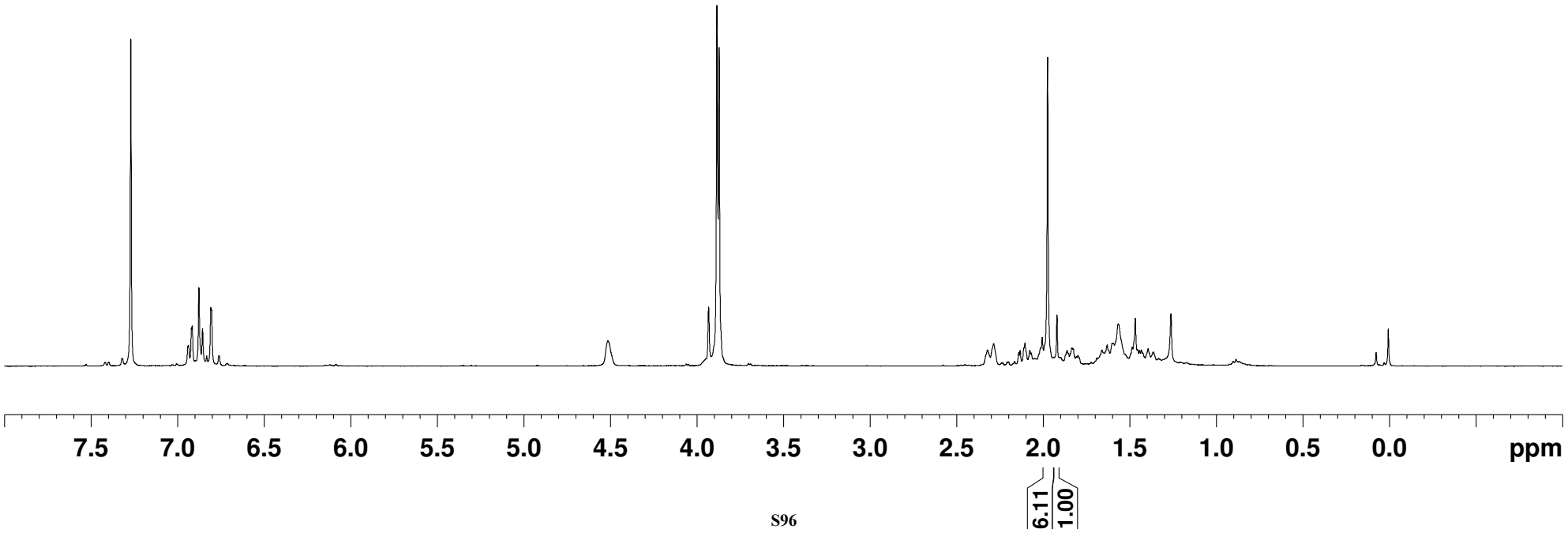
2f

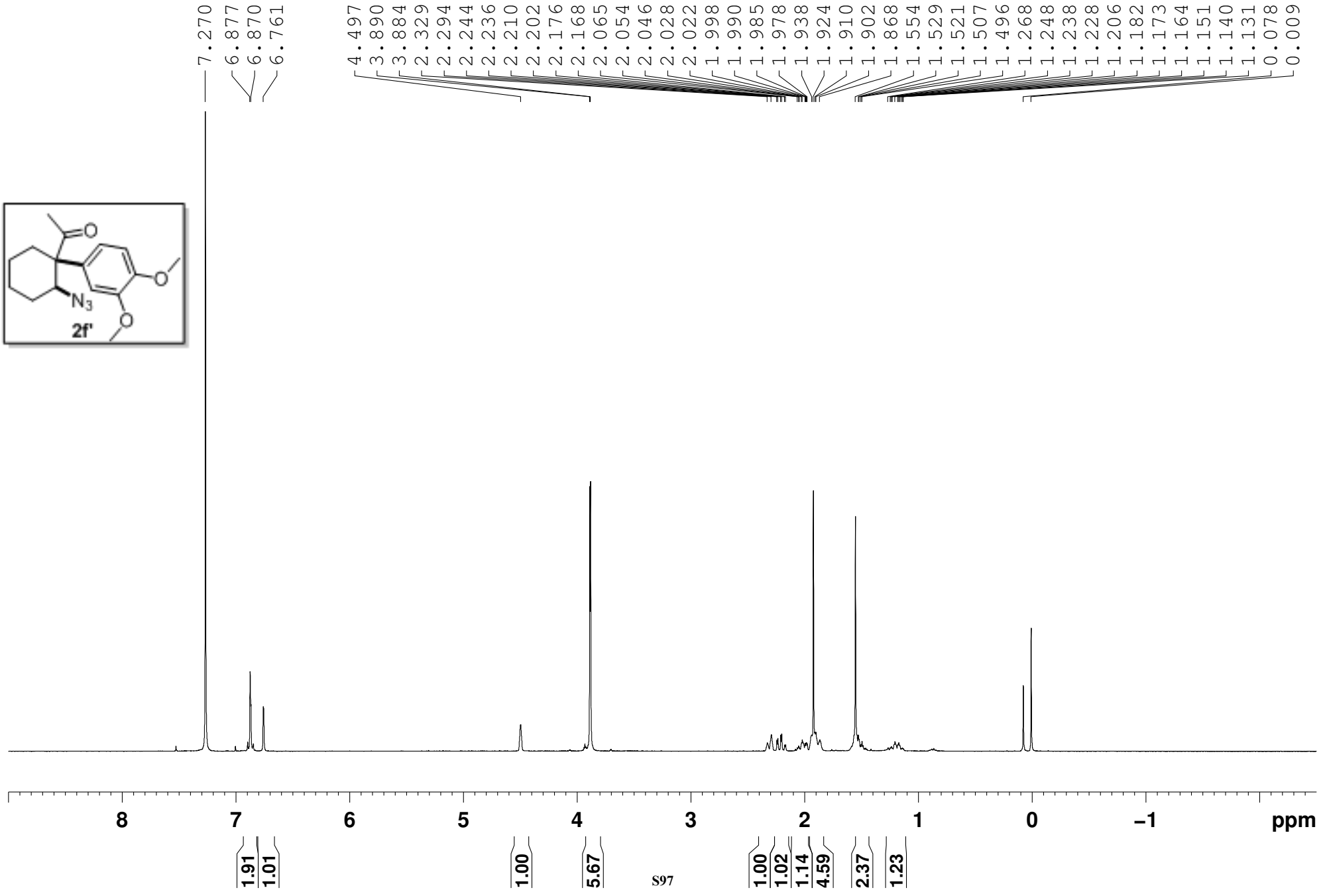
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 ppm

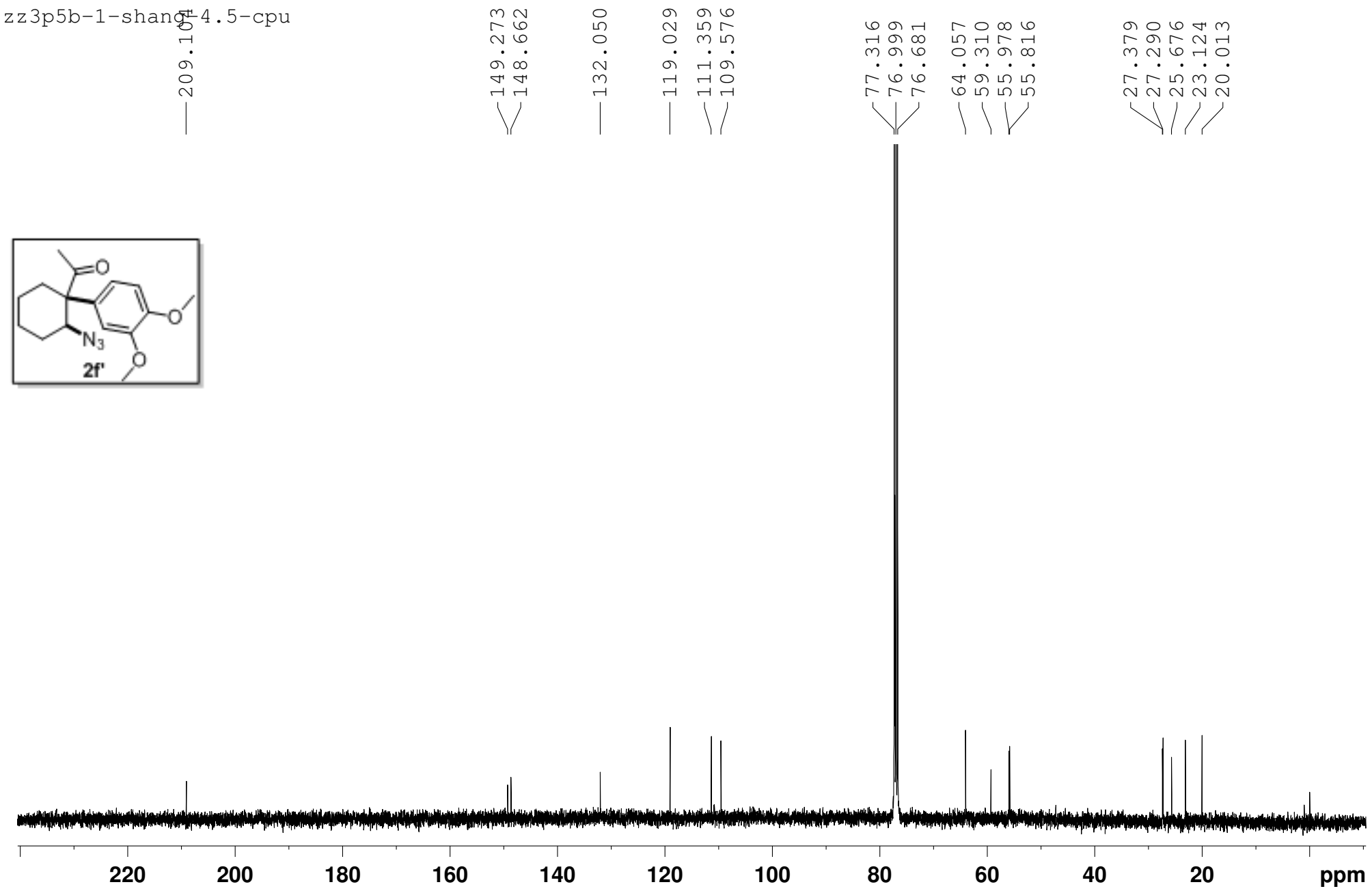
czm7p21a3

1.990
1.936

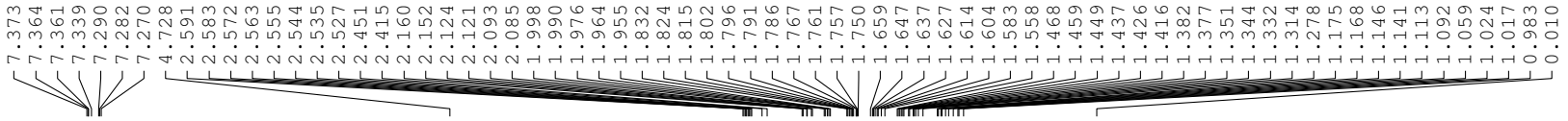
2f : 2f′ = 6.1 : 1

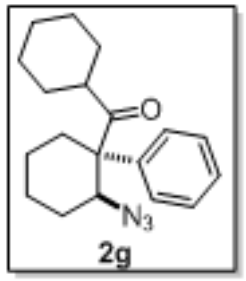



zz3p5b-1-shang-4,5
7.270
6.877
6.870
6.761
4.497
3.890
3.884
2.329
2.294
2.244
2.236
2.210
2.202
2.176
2.168
2.065
2.054
2.046
2.028
2.022
1.998
1.990
1.985
1.978
1.938
1.924
1.910
1.902
1.868
1.554
1.529
1.521
1.507
1.496
1.268
1.248
1.238
1.228
1.206
1.182
1.173
1.164
1.151
1.140
1.131
0.078
0.009
O
O
O
N3
2f'
8
7
6
5
4
3
2
1
0
−1
ppm
1.91
1.01
1.00
5.67
1.00
1.02
1.14
4.59
2.37
1.23

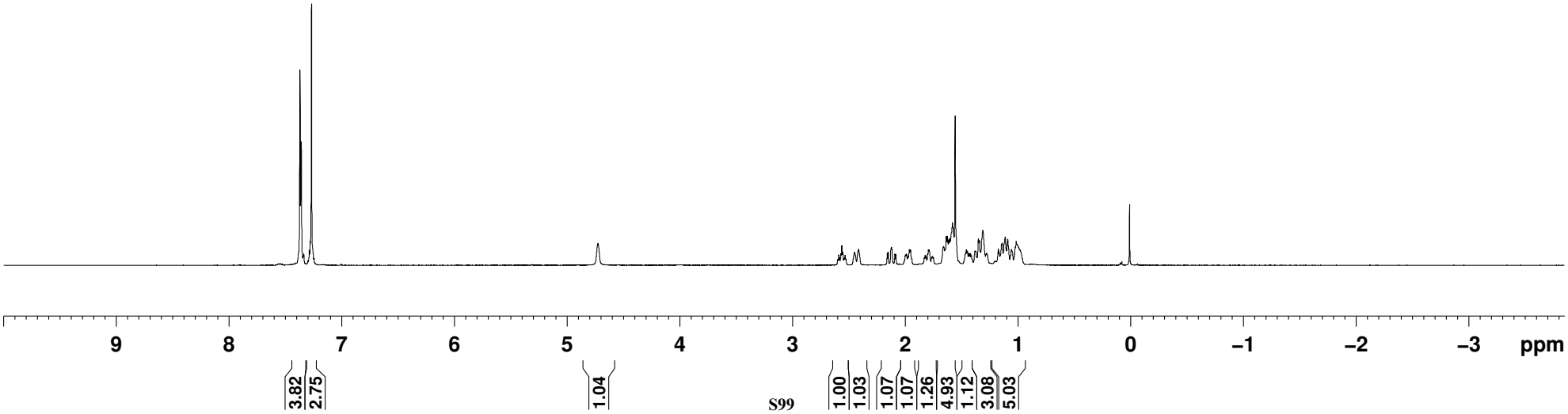

zz3p5b-1-shang-4.5-cpu
209.104
149.273
148.662
132.050
119.029
111.359
109.576
77.316
76.999
76.681
64.057
59.310
55.978
55.816
27.379
27.290
25.676
23.124
20.013
O
O
O
N3
2f'
220
200
180
160
140
120
100
80
60
40
20
ppm

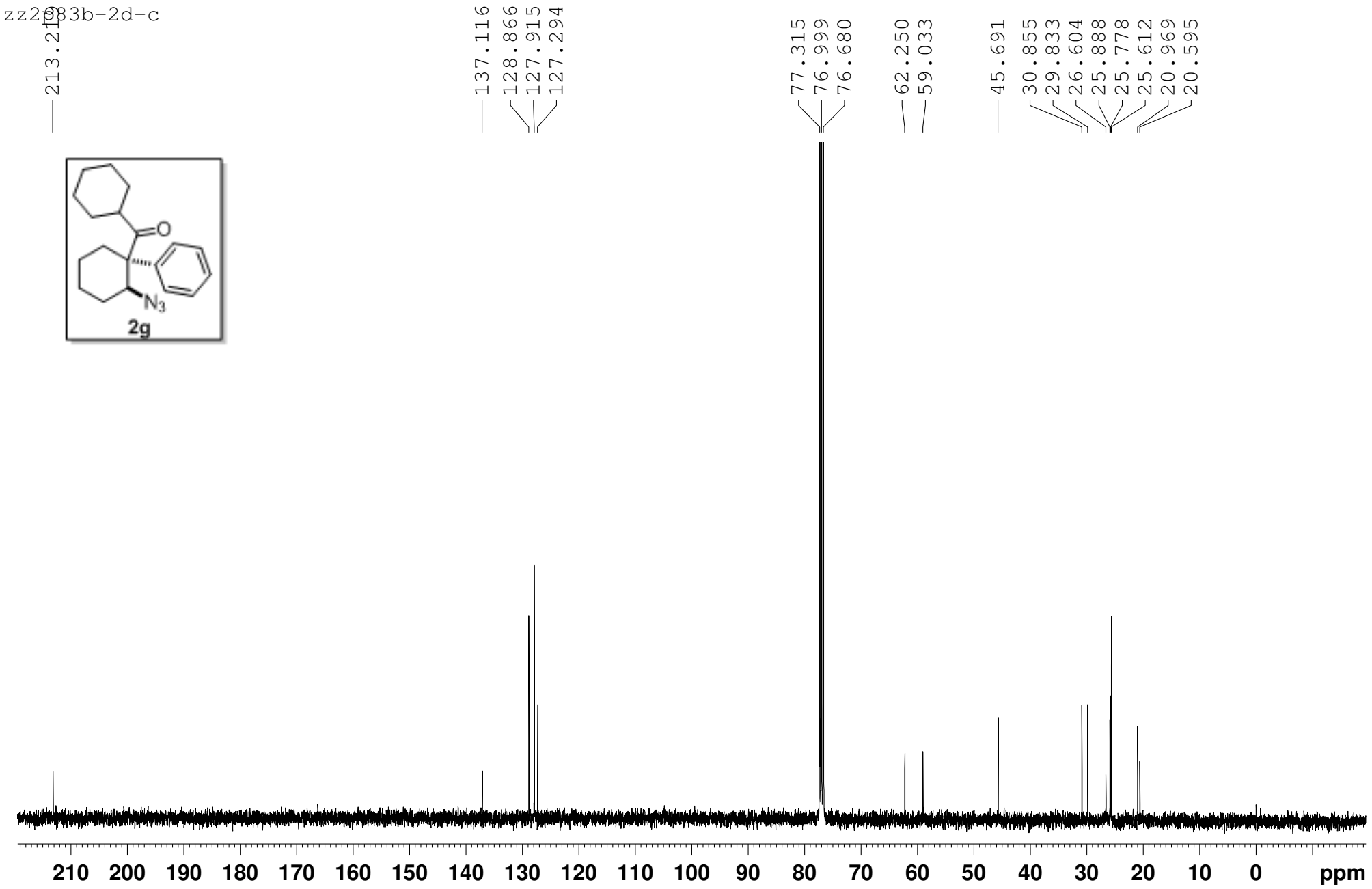
zz2p83b2-1x



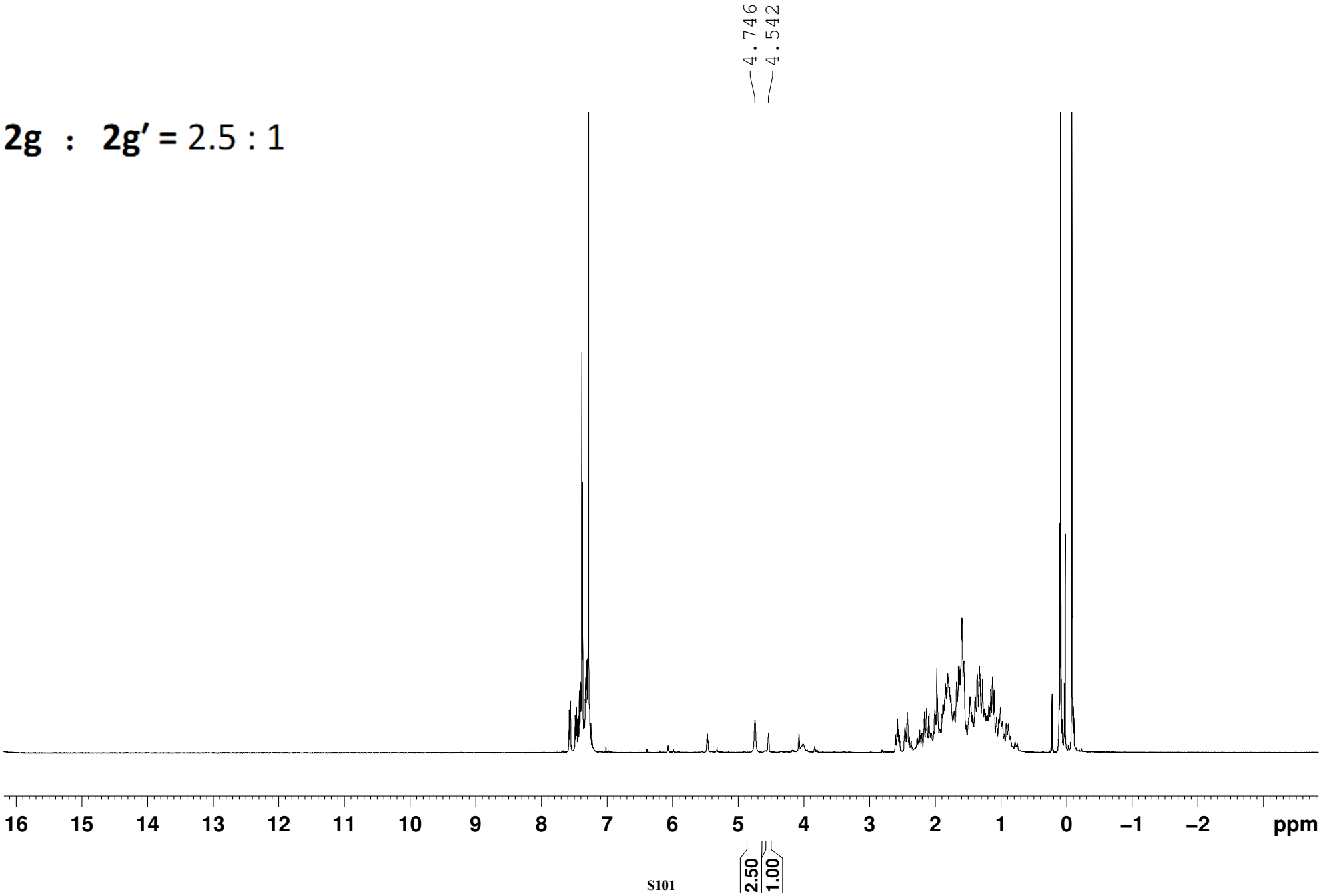



```
NAME          zz2p83b2-1x
EXPNO                  10
PROCNO                  1
Date_           20140408
Time               18.15
INSTRUM            spect
PROBHD   5 mm PABBO BB/
PULPROG             zg30
TD                 65536
SOLVENT            CDCl3
NS                    16
DS                     2
SWH             8012.820 Hz
FIDRES          0.122266 Hz
AQ              4.0894966 sec
RG                   256
DW                62.400 usec
DE                 6.50 usec
TE                296.9 K
D1             1.00000000 sec
TD0                    1

======== CHANNEL f1 ========
SFO1         400.1324710 MHz
NUC1                   1H
P1                  14.10 usec
SI                 65536
SF           400.1300055 MHz
WDW                   EM
SSB                    0
LB                  0.30 Hz
GB                     0
PC                  1.00
```



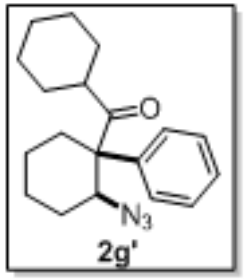

zz2p83b-2d-c
213.211
137.116
128.866
127.915
127.294
77.315
76.999
76.680
62.250
59.033
45.691
30.855
29.833
26.604
25.888
25.778
25.612
20.969
20.595
O
N3
2g
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 ppm

zz2p83b2-H

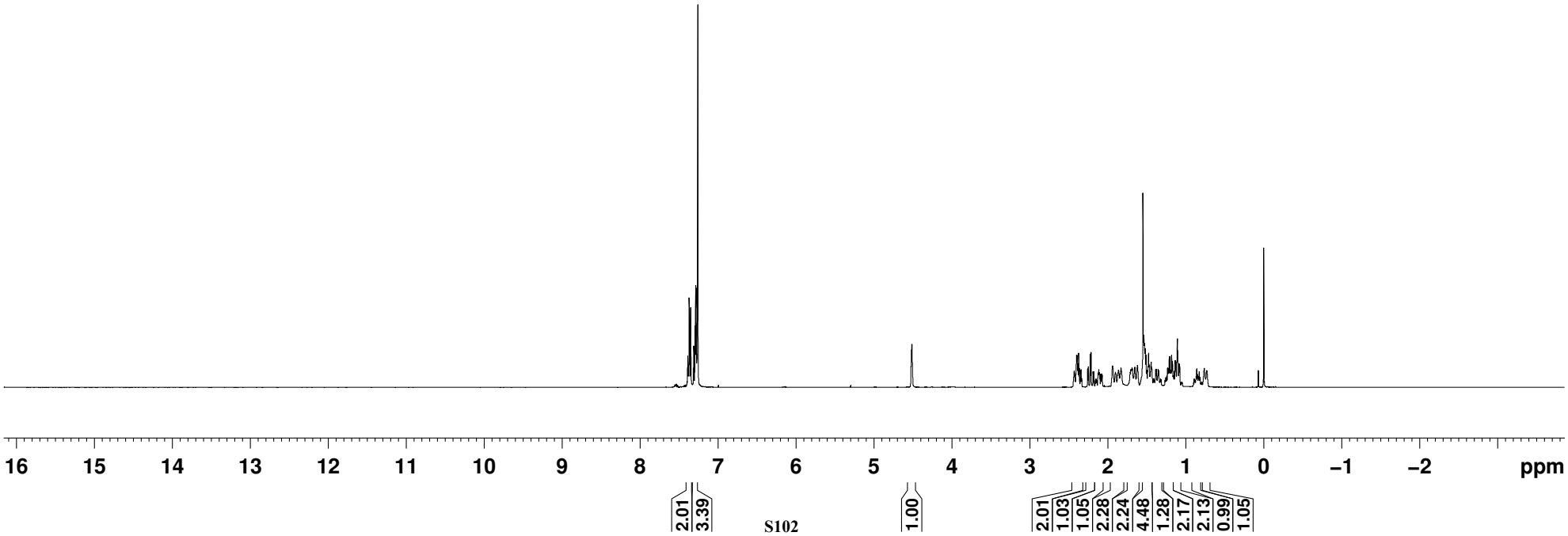

4.746
4.542
2g : 2g′ = 2.5 : 1
16 15 14 13 12 11 10 9 8 7 6 5 4 3 2 1 0 –1 –2 ppm
2.50
1.00

zz2p83b2shang

7.390 7.372 7.353 7.314 7.311 7.296 7.289 7.285 7.278 7.267 7.261 4.518 4.514 2.432 2.403 2.395 2.383 2.374 2.366 2.345 2.259 2.250 2.225 2.216 2.190 2.182 2.124 2.122 2.116 2.109 2.092 2.086 2.079 2.072 1.940 1.904 1.897 1.867 1.863 1.842 1.833 1.829 1.714 1.706 1.702 1.694 1.690 1.686 1.657 1.653 1.621 1.550 1.540 1.531 1.520 1.510 1.501 1.487 1.478 1.469 1.444 1.436 1.386 1.378 1.356 1.348 1.234 1.225 1.212 1.202 1.195 1.191 1.183 1.173 1.150 1.140 1.131 1.108 1.085 1.079 0.860 0.851 0.828 0.767 0.763 0.731 0.000

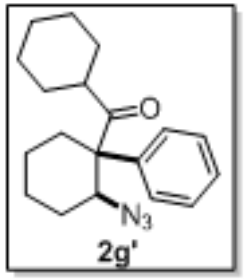



```
NAME          zz2p83b2shang
EXPNO                    10
PROCNO                    1
Date_              20140405
Time                  17.04
INSTRUM               spect
PROBHD   5 mm PABBO BB/
PULPROG                zg30
TD                    65536
SOLVENT               CDCl3
NS                       16
DS                        2
SWH                8012.820 Hz
FIDRES                0.122266 Hz
AQ                 4.0894966 sec
RG                      287
DW                    62.400 usec
DE                     6.50 usec
TE                    294.3 K
D1                 1.00000000 sec
TD0                       1

======== CHANNEL f1 ========
SFO1             400.1324710 MHz
NUC1                      1H
P1                    11.60 usec
SI                    65536
SF               400.1300094 MHz
WDW                      EM
SSB                       0
LB                     0.30 Hz
GB                        0
PC                     1.00
```



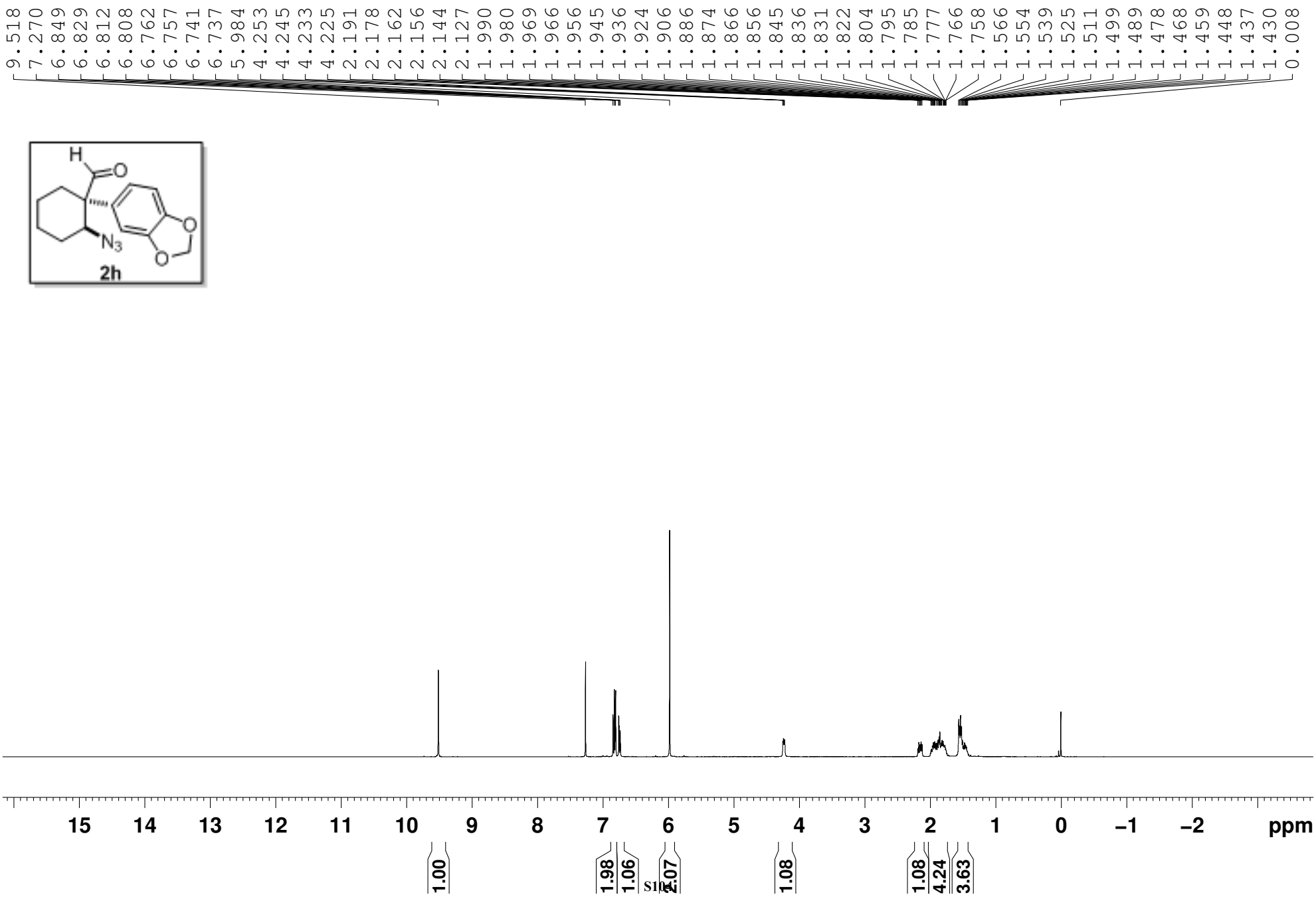
zz2p83b2shang

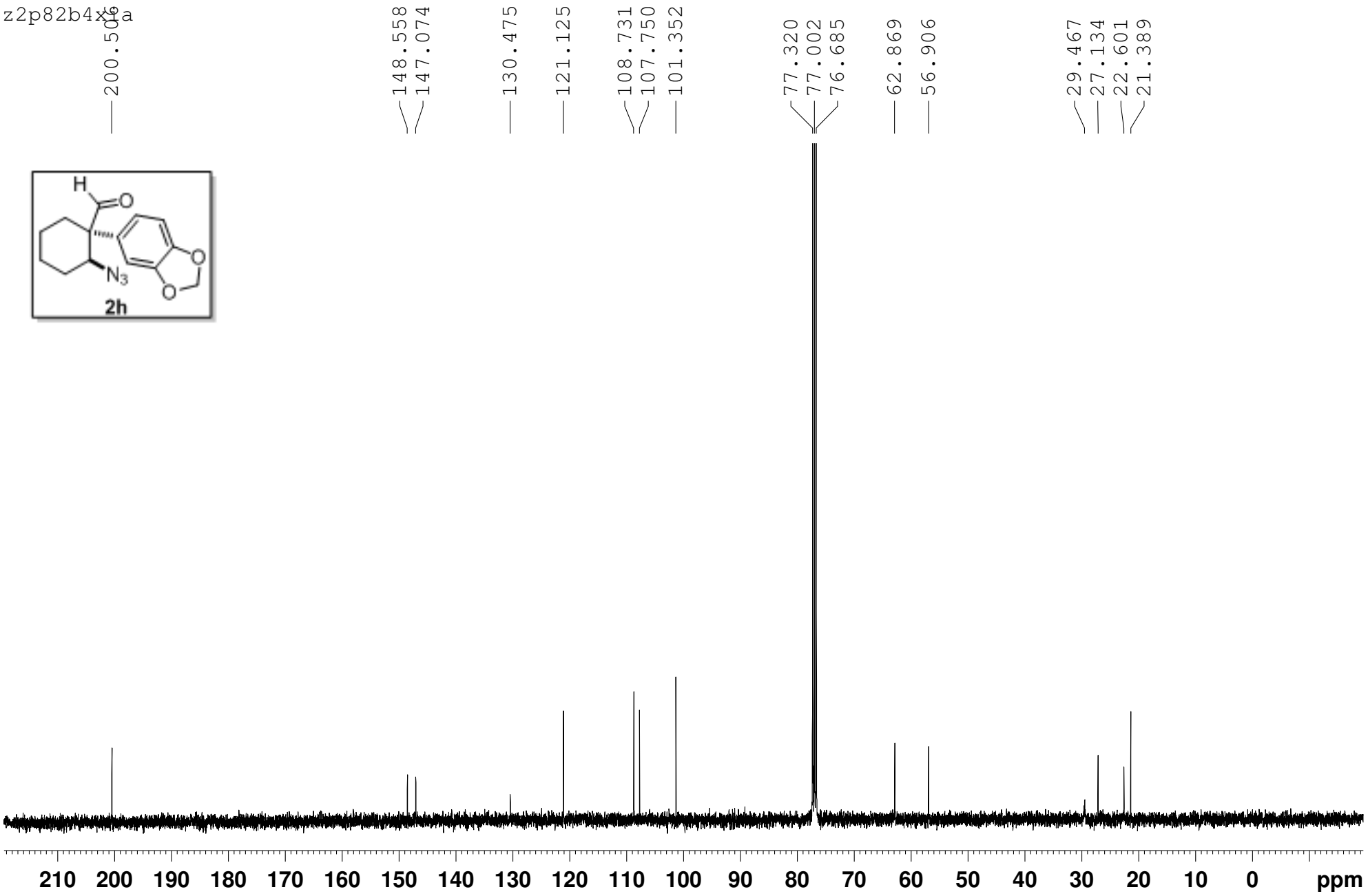
214.47
139.29
128.74
127.69
126.94
77.32
77.00
76.68
64.17
59.96
46.57
31.63
29.90
27.55
26.59
25.61
25.56
25.52
23.69
20.20



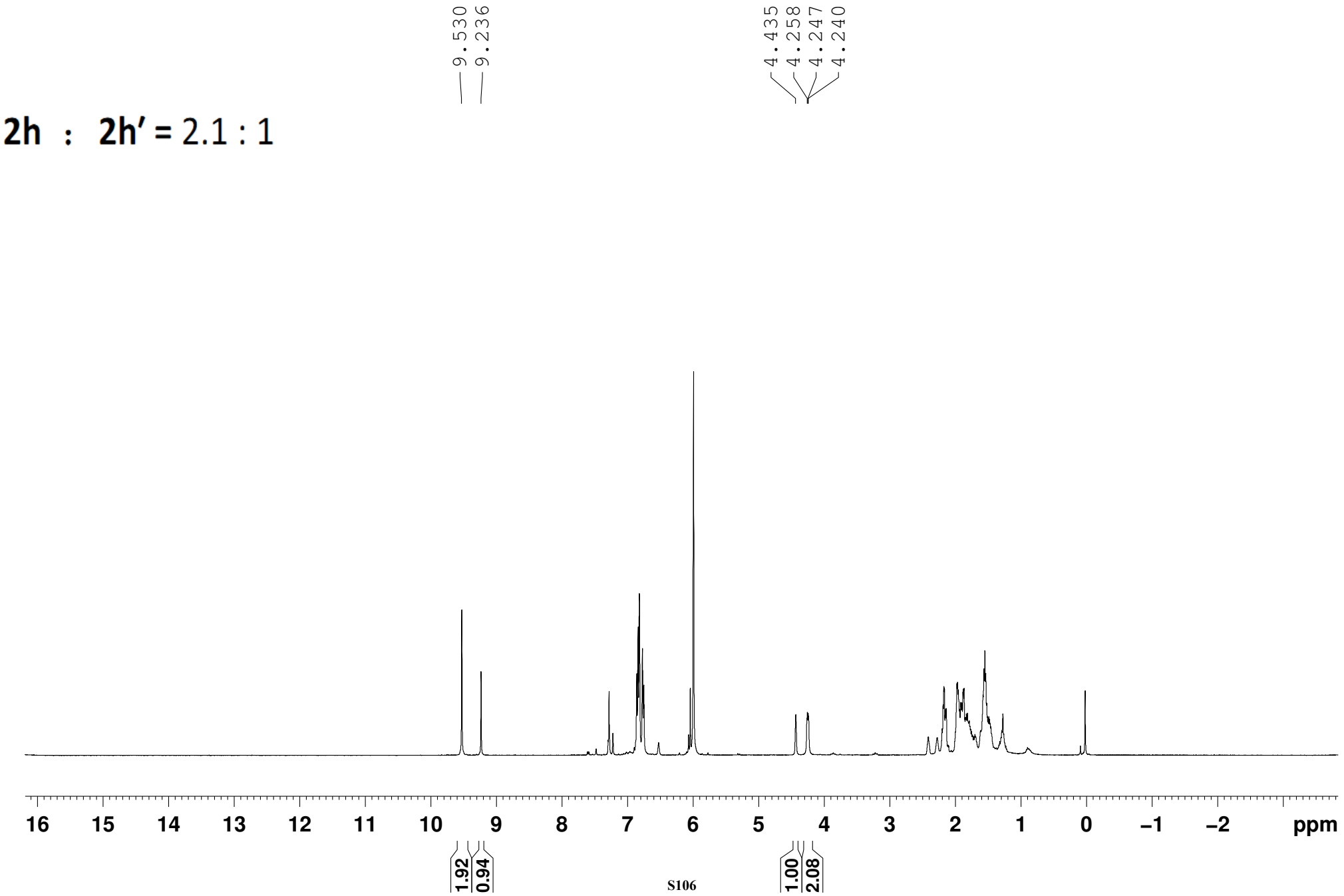
2g'

210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 ppm


9.518
7.270
6.849
6.829
6.812
6.808
6.762
6.757
6.741
6.737
5.984
4.253
4.245
4.233
4.225
2.191
2.178
2.162
2.156
2.144
2.127
1.990
1.980
1.969
1.966
1.956
1.945
1.936
1.924
1.906
1.886
1.874
1.866
1.856
1.845
1.836
1.831
1.822
1.804
1.795
1.785
1.777
1.766
1.758
1.566
1.554
1.539
1.525
1.511
1.499
1.489
1.478
1.468
1.459
1.448
1.437
1.430
0.008
H
O
O
O
N3
2h
15
14
13
12
11
10
9
8
7
6
5
4
3
2
1
0
–1
–2
ppm
1.00
1.98
1.06
2.07
1.08
1.08
4.24
3.63

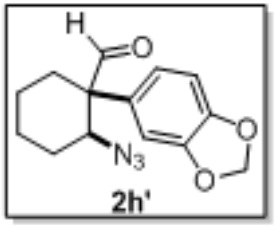

zz2p82b4xda
200.504
148.558
147.074
130.475
121.125
108.731
107.750
101.352
77.320
77.002
76.685
62.869
56.906
29.467
27.134
22.601
21.389
H
O
N3
O
O
2h
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 ppm

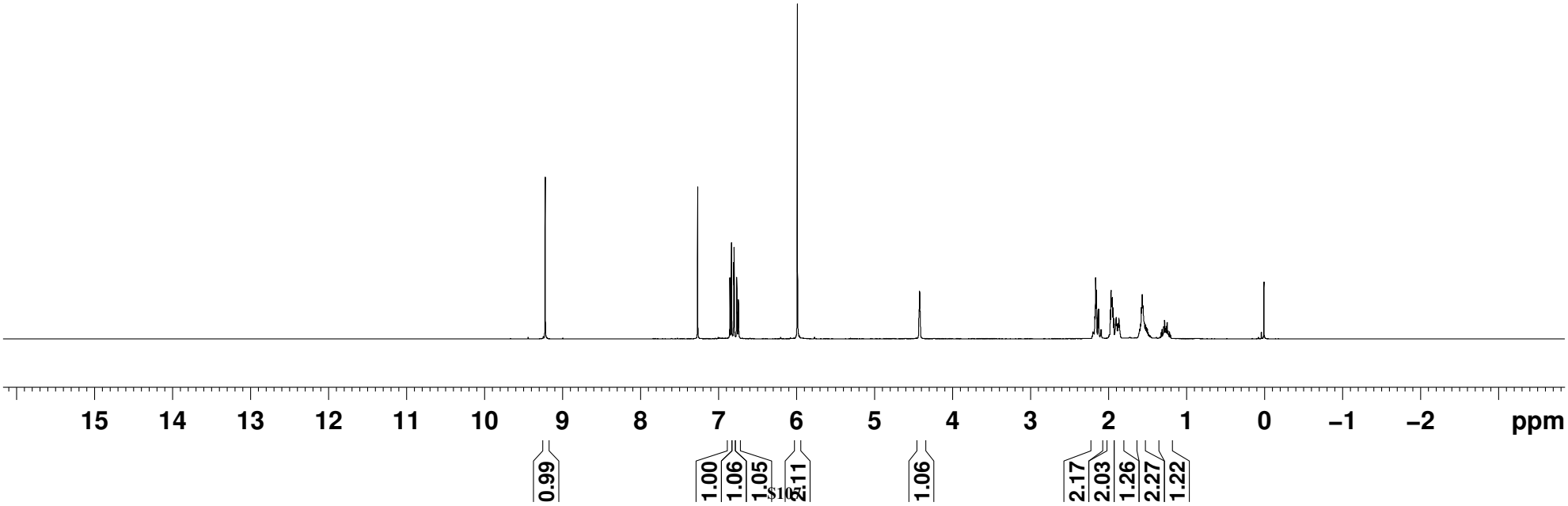
zz2p84b2

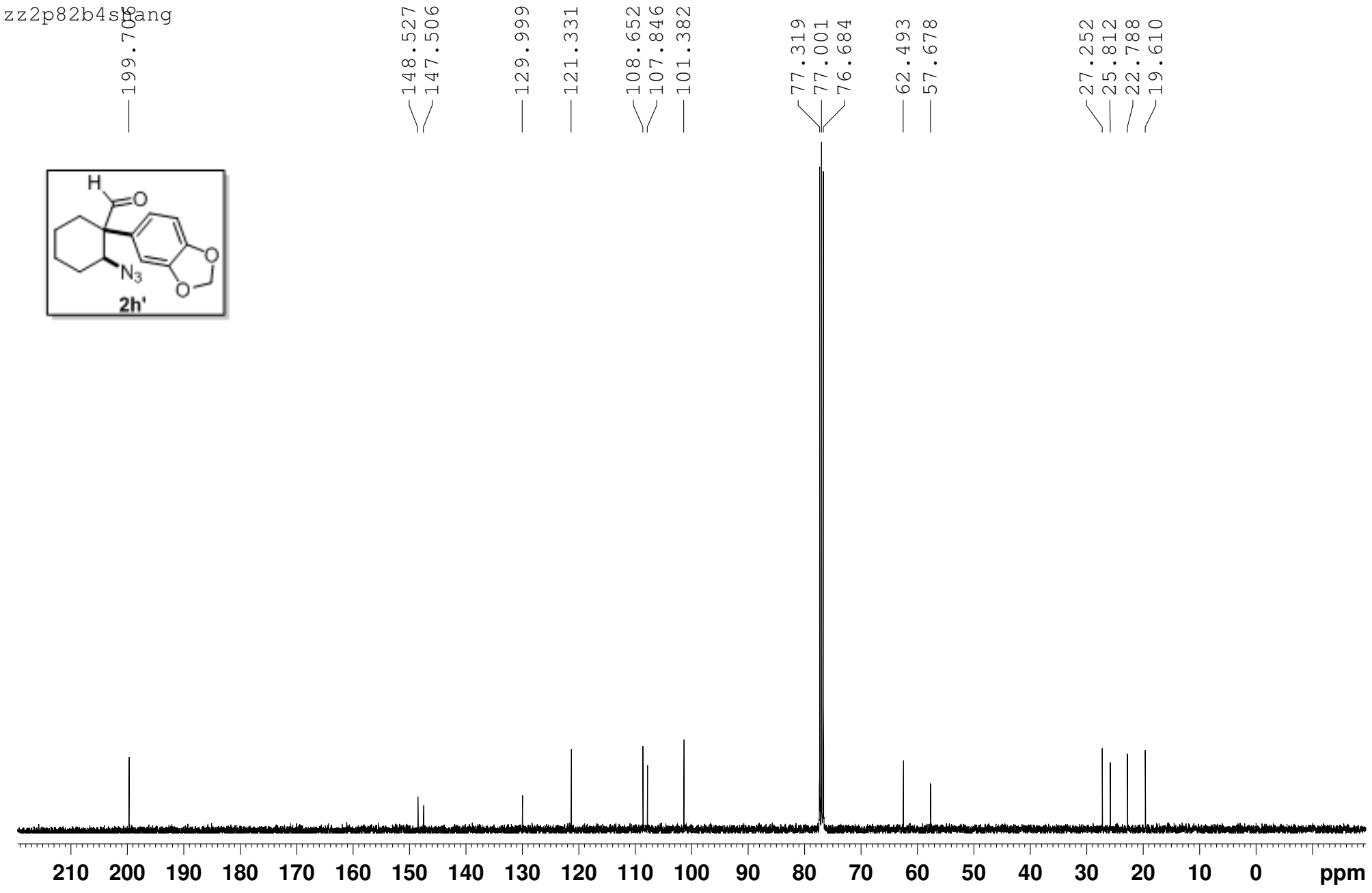

9.530
9.236
4.435
4.258
4.247
4.240
2h : 2h′ = 2.1 : 1
16 15 14 13 12 11 10 9 8 7 6 5 4 3 2 1 0 –1 –2 ppm
1.92
0.94
1.00
2.08

zz2p82b4shang

9.225
7.270
6.856
6.836
6.806
6.802
6.769
6.764
6.748
6.744
5.991
4.424
2.176
2.167
2.158
2.136
2.127
2.102
2.093
1.977
1.969
1.960
1.952
1.945
1.941
1.933
1.911
1.903
1.896
1.886
1.877
1.869
1.860
1.603
1.591
1.581
1.569
1.560
1.548
1.543
1.532
1.527
1.518
1.511
1.502
1.493
1.325
1.314
1.301
1.294
1.283
1.271
1.261
1.249
1.237
1.230
1.219
0.009

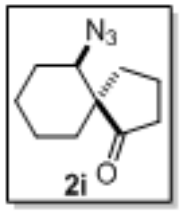


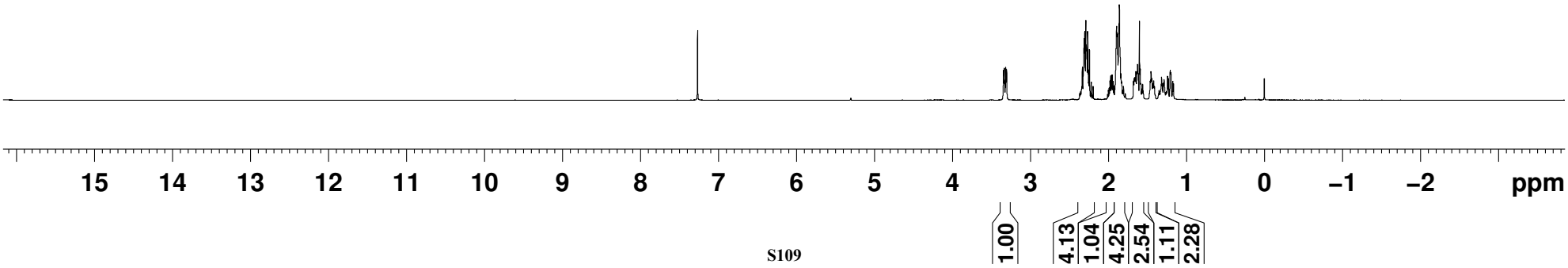



zz2p82b4sh2ang
199.700
148.527
147.506
129.999
121.331
108.652
107.846
101.382
77.319
77.001
76.684
62.493
57.678
27.252
25.812
22.788
19.610
H
O
N3
O
O
2h'
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 ppm

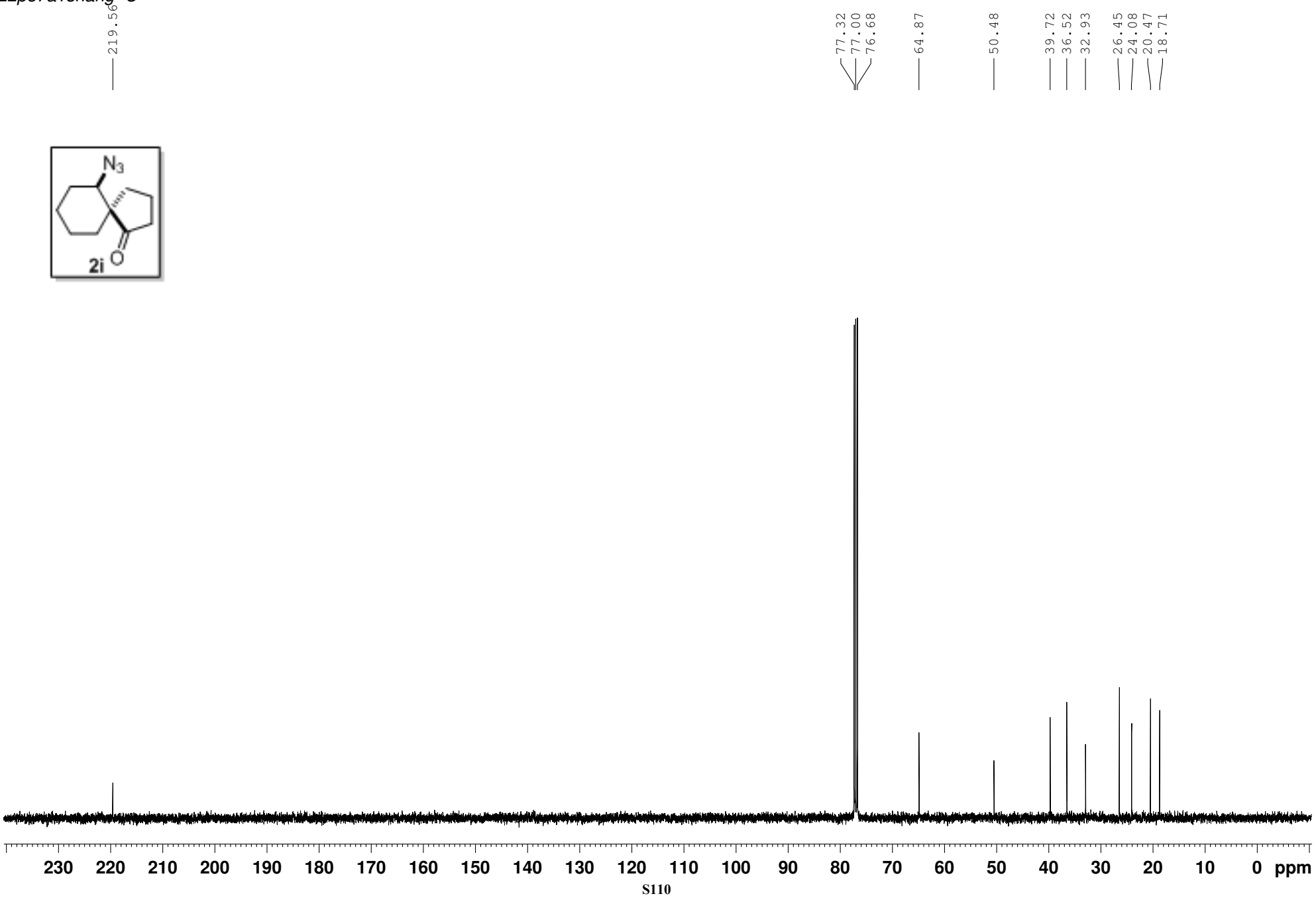
zz2p87a1-shang

7.270 3.347 3.336 3.318 3.308 3.336 2.312 2.304 2.291 2.285 2.268 2.261 2.254 2.245 2.222 2.199 1.993 1.982 1.972 1.962 1.952 1.941 1.931 1.921 1.896 1.889 1.863 1.842 1.835 1.810 1.679 1.669 1.660 1.650 1.637 1.628 1.620 1.603 1.594 1.586 1.563 1.466 1.457 1.446 1.434 1.423 1.413 1.321 1.312 1.297 1.288 1.244 1.234 1.208 1.203 1.177 1.168 0.003





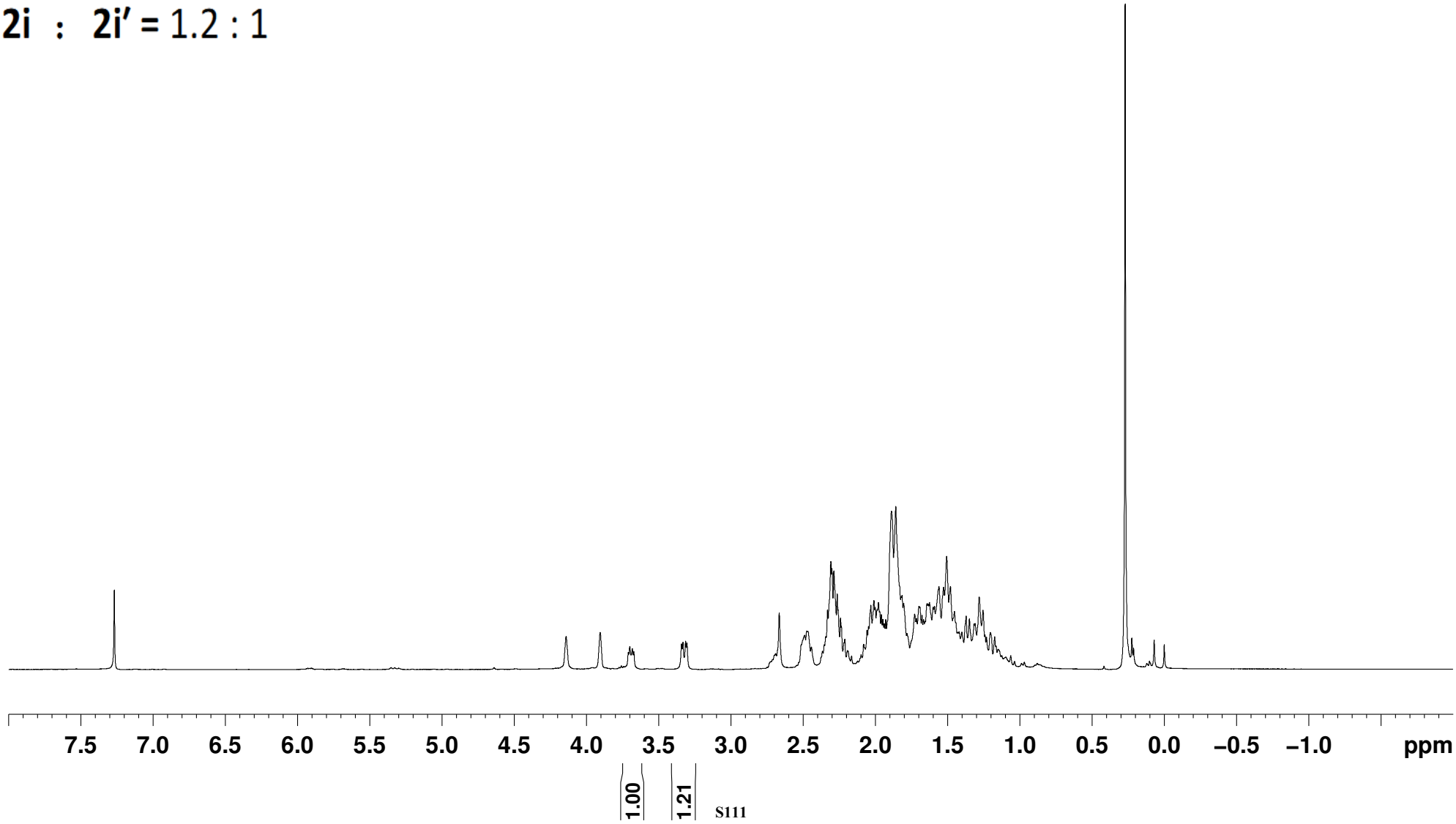
zz2p87a1shang-C



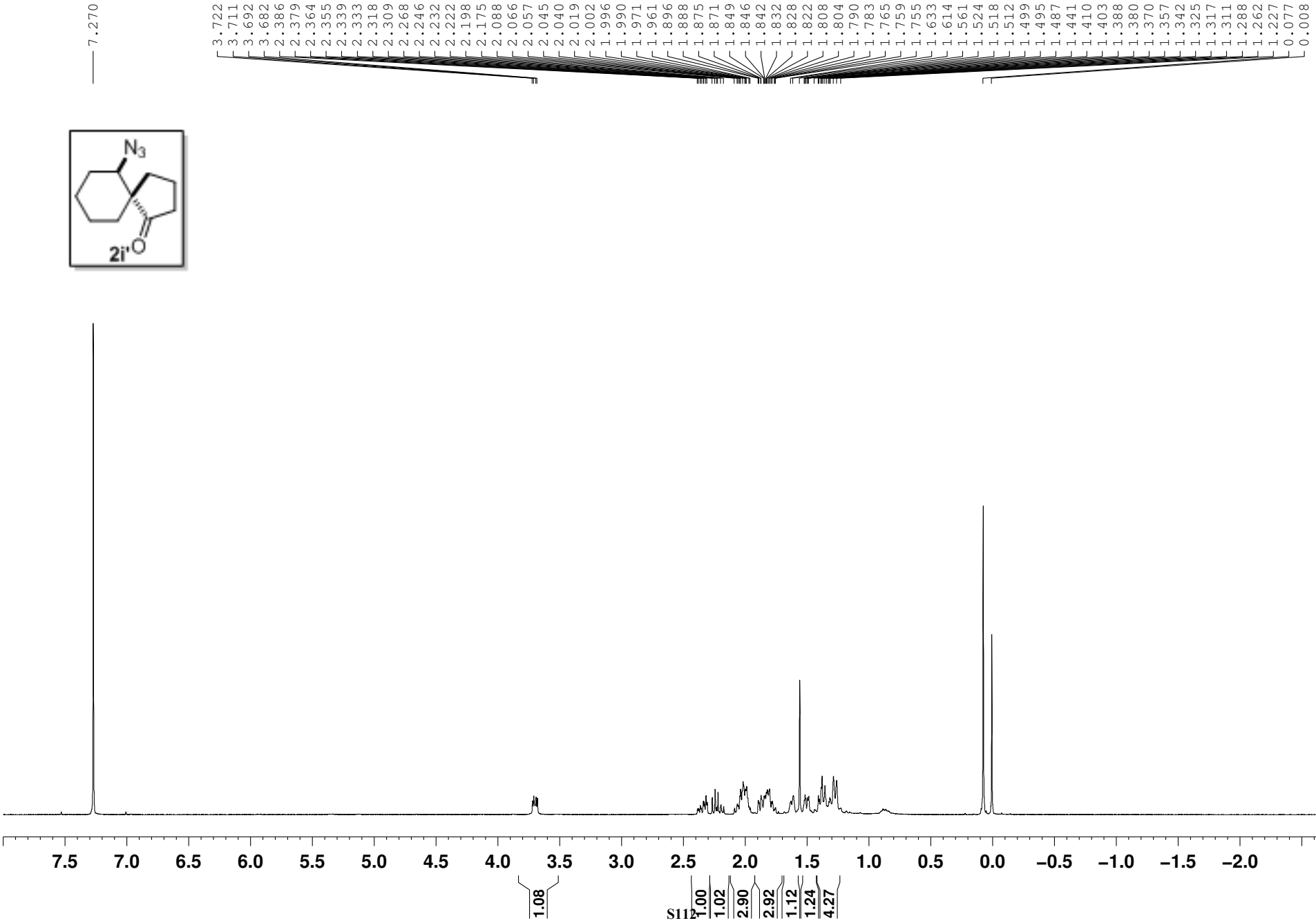
zz2p87a2

3.711
3.701
3.683
3.673
3.343
3.333
3.315
3.305

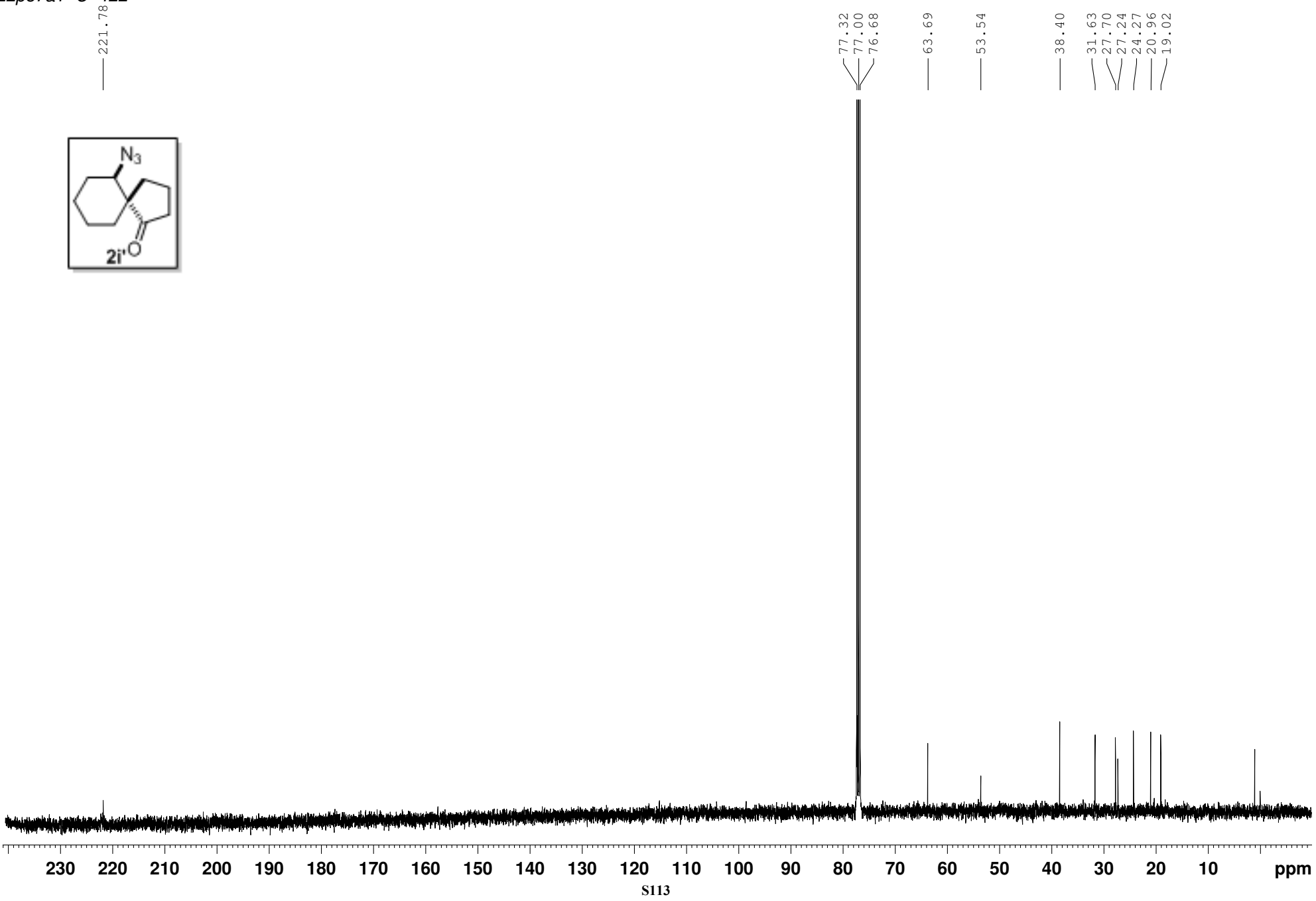
2i : 2i′ = 1.2 : 1



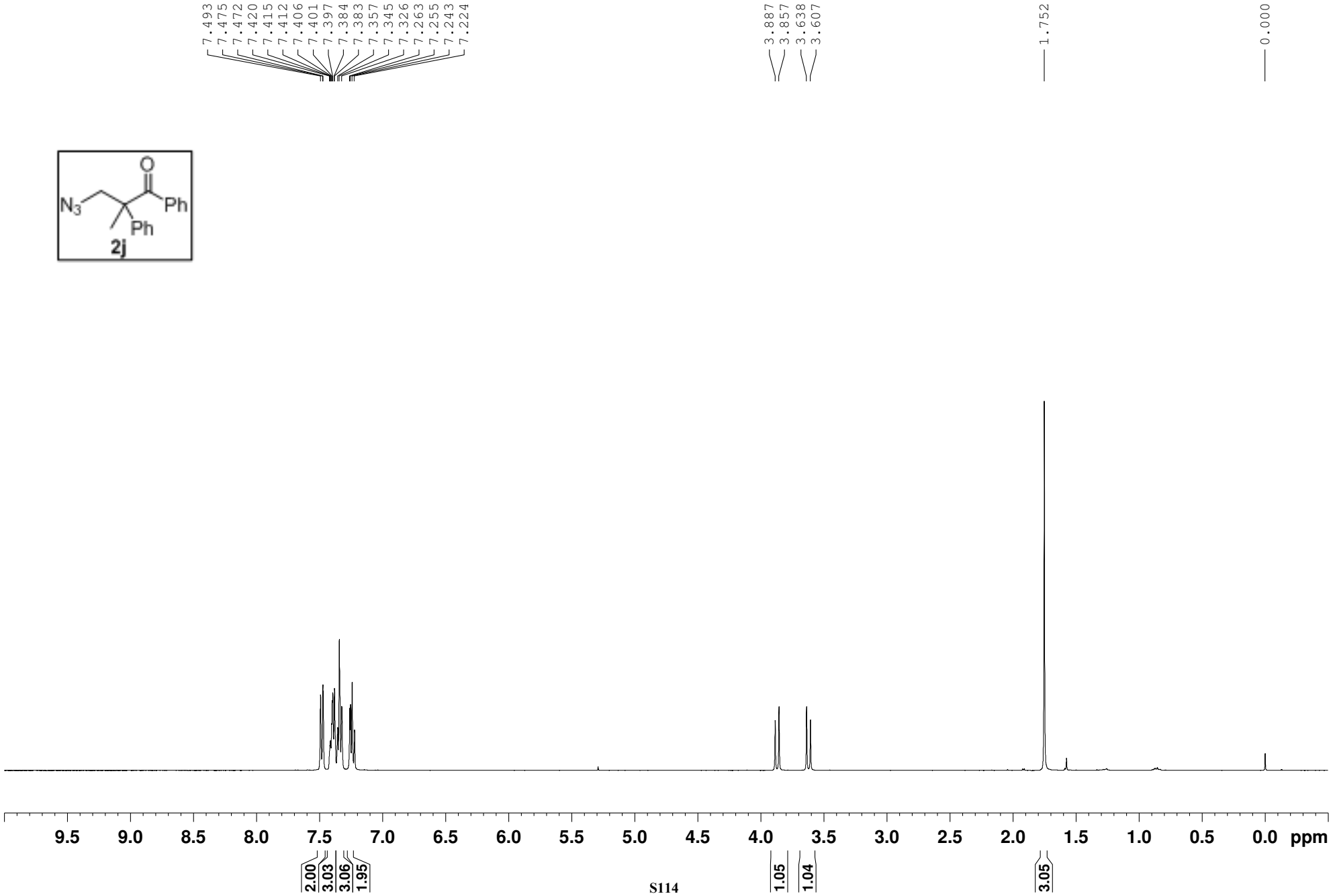
zz2p87axia−1



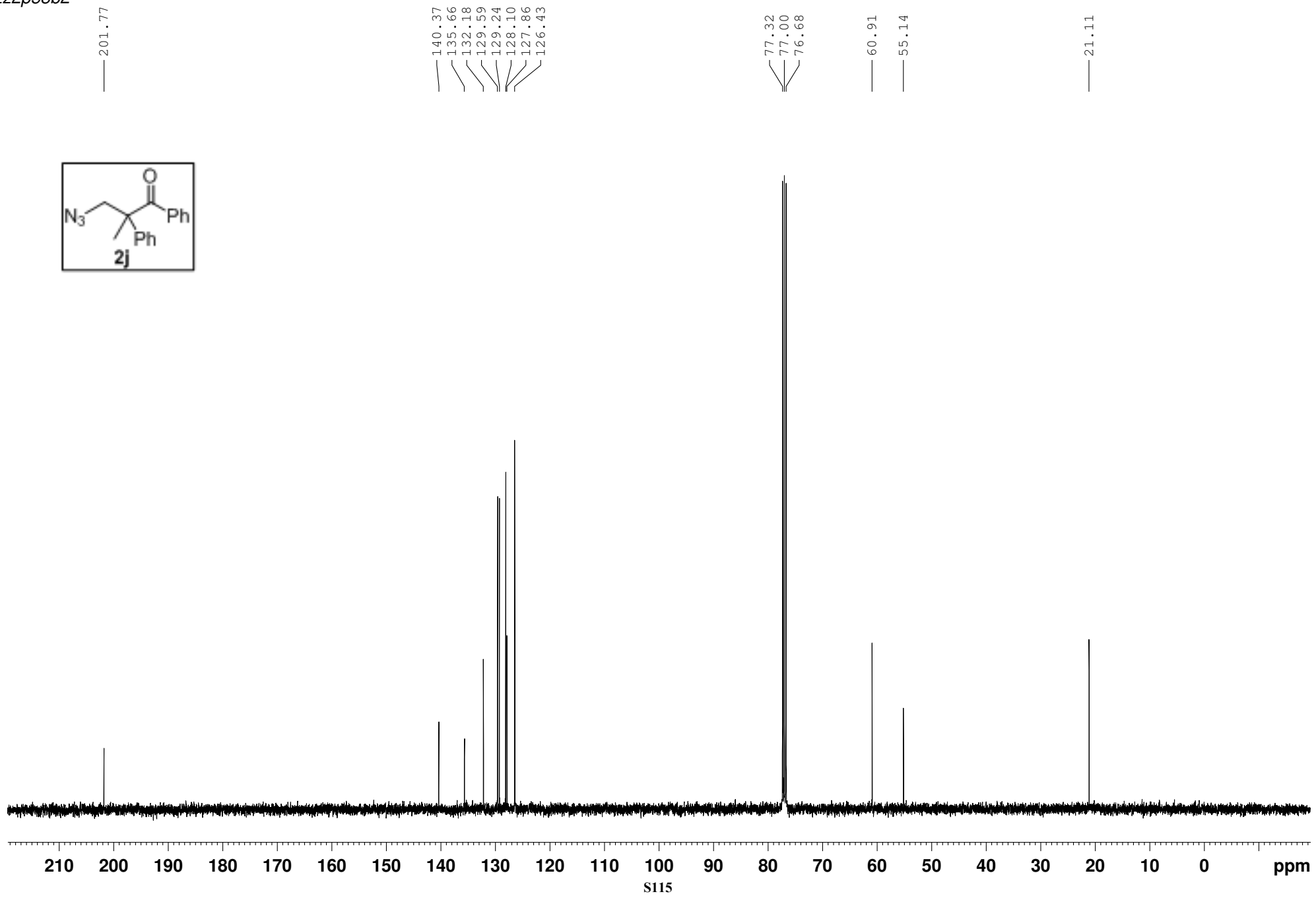
zz2p87a1-C-422



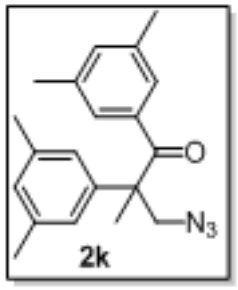
zz2p58b2


7.493
7.475
7.472
7.420
7.415
7.412
7.406
7.401
7.397
7.384
7.383
7.357
7.345
7.326
7.263
7.255
7.243
7.224
3.887
3.857
3.638
3.607
1.752
0.000
O
N3
Ph
Ph
2j
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
ppm
2.00
3.03
3.06
1.95
1.05
1.04
3.05

zz2p58b2


201.77
140.37
135.66
132.18
129.59
129.24
128.10
127.86
126.43
77.32
77.00
76.68
60.91
55.14
21.11
O
N3
Ph
Ph
2j
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
ppm

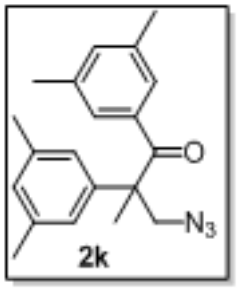
zz2p72a3

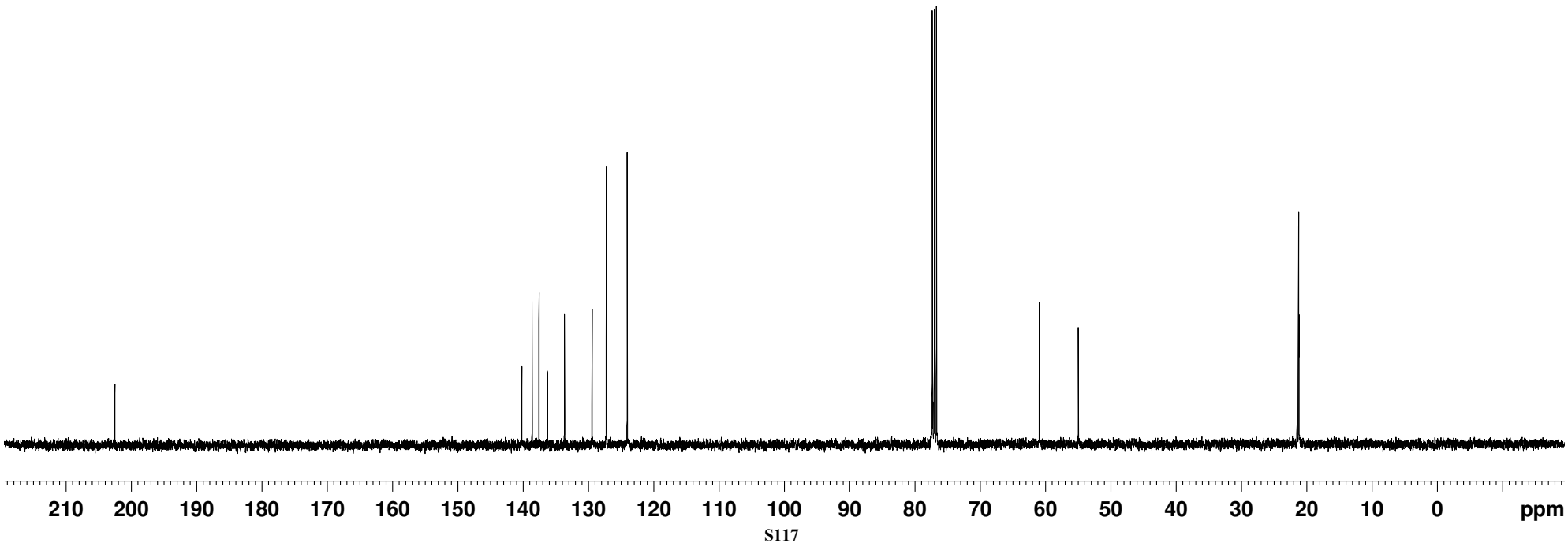

O
N3
2k

7.270
7.096
7.050
6.978
6.947
3.931
3.901
3.561
3.531
2.324
2.214
1.708
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
−0.5
−1.0
ppm
2.93
2.98
1.00
1.02
6.08
6.10
3.00

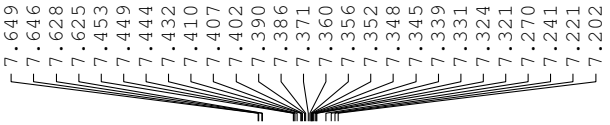
zz2p72a3

202.52
140.19
138.61
137.55
136.27
133.65
129.42
127.23
124.05
77.32
77.00
76.68
60.91
54.95
21.44
21.20
21.16



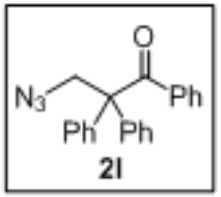


zz2p84a3

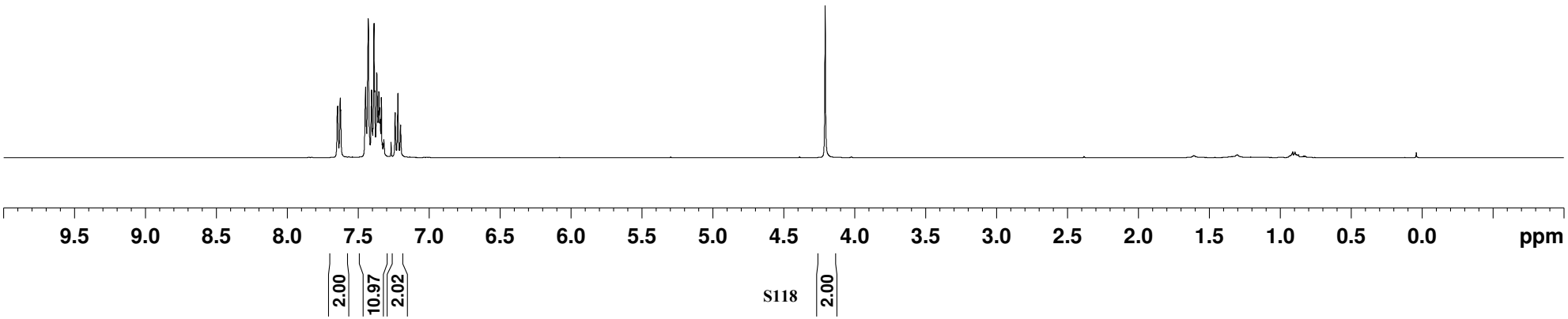

7.649
7.646
7.628
7.625
7.453
7.449
7.444
7.432
7.410
7.407
7.402
7.390
7.386
7.371
7.360
7.356
7.352
7.348
7.345
7.339
7.331
7.324
7.321
7.270
7.241
7.221
7.202

4.209

0.041

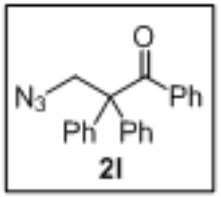

O
N3
Ph
Ph
Ph

2l

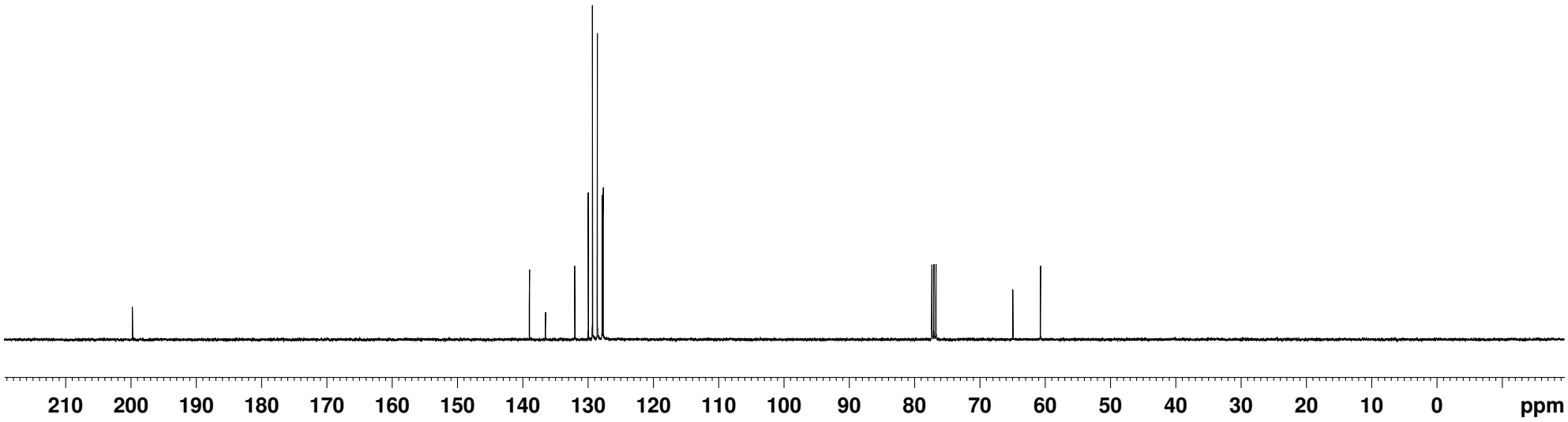

9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
ppm
2.00
10.97
2.02
2.00

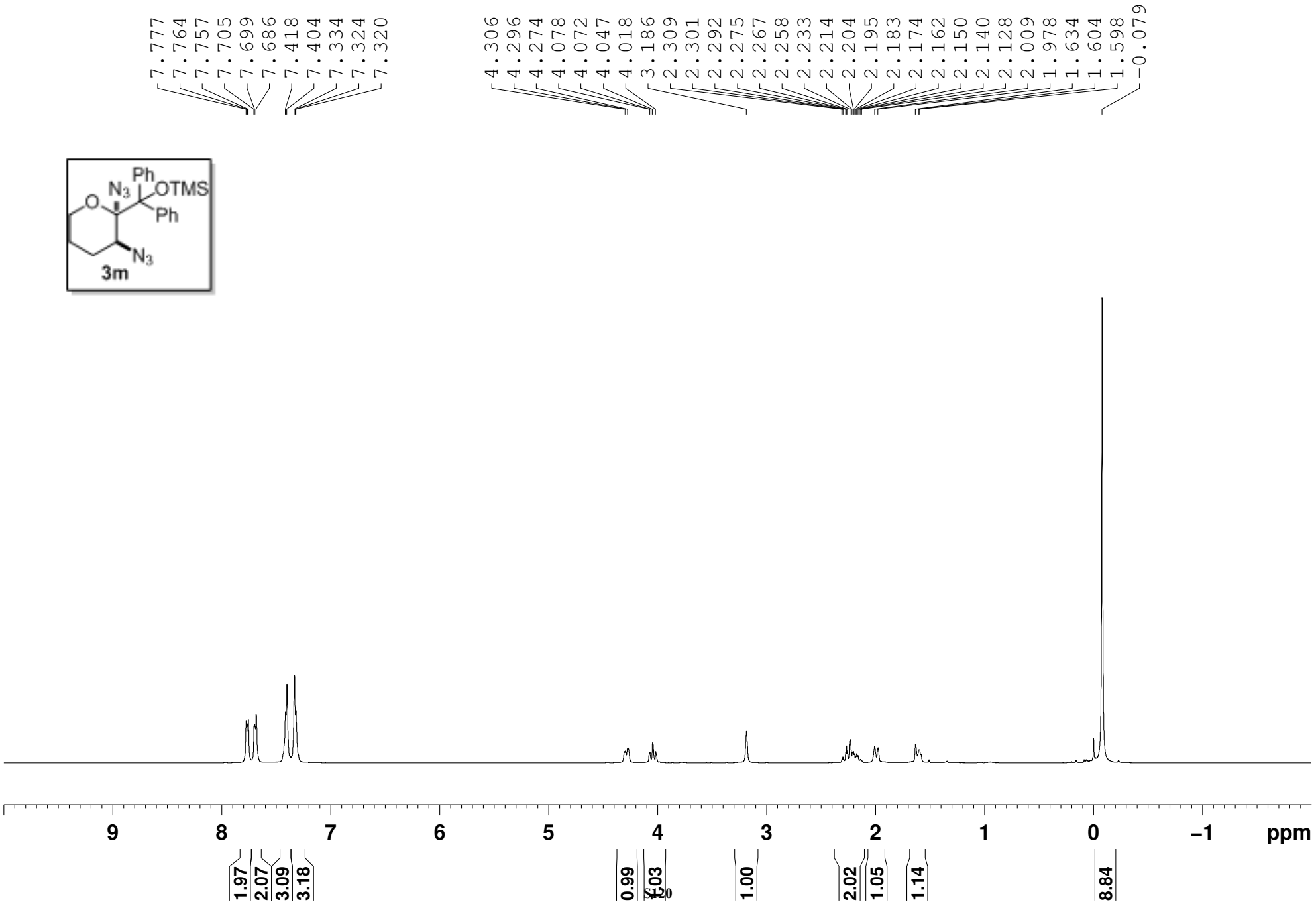
zz2p84a3

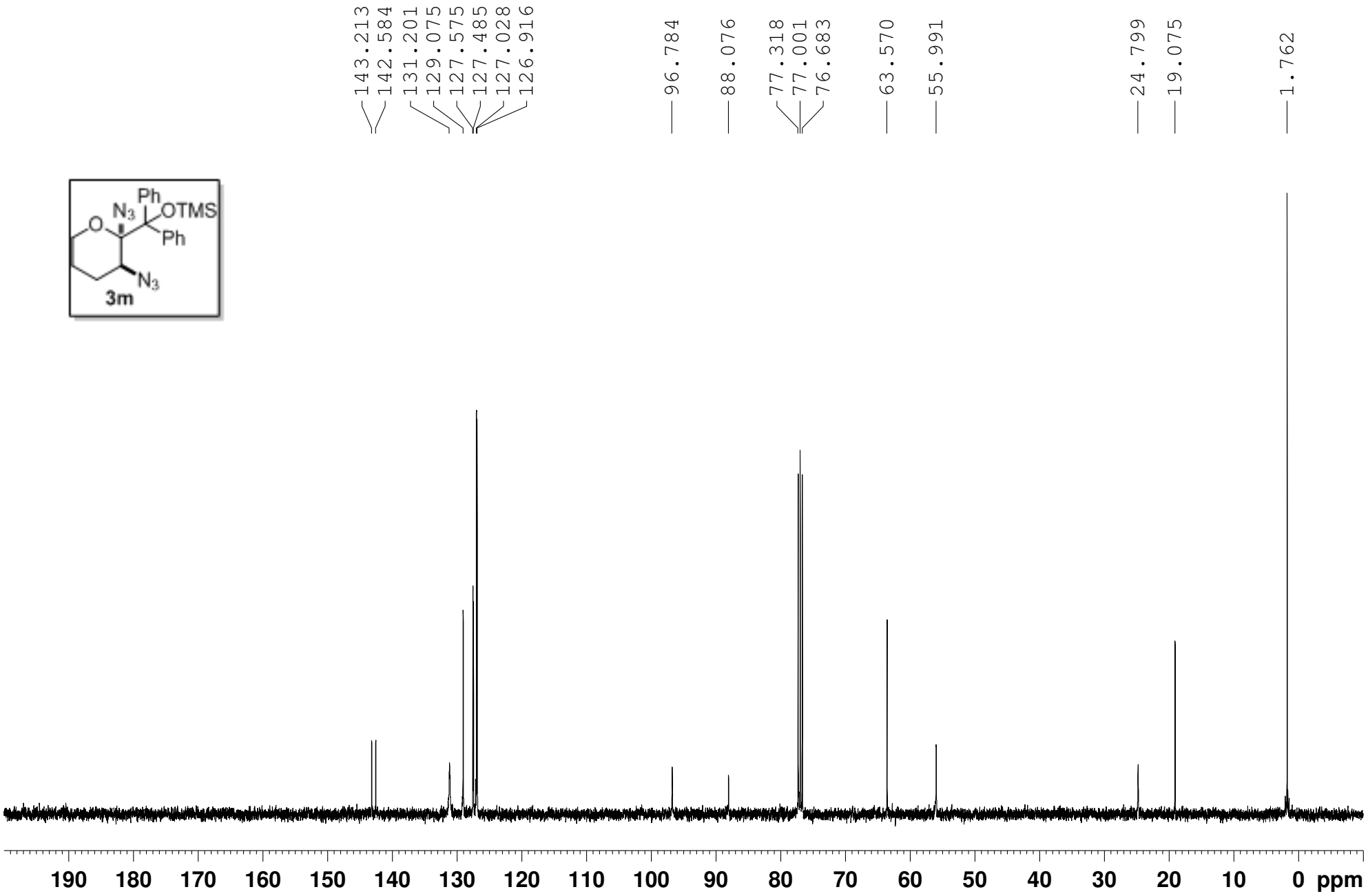
199.76
138.95
136.49
132.02
129.96
129.31
128.55
127.82
127.66
77.32
77.00
76.68
64.92
60.68



2l

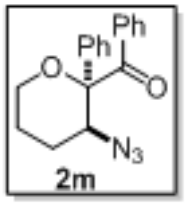


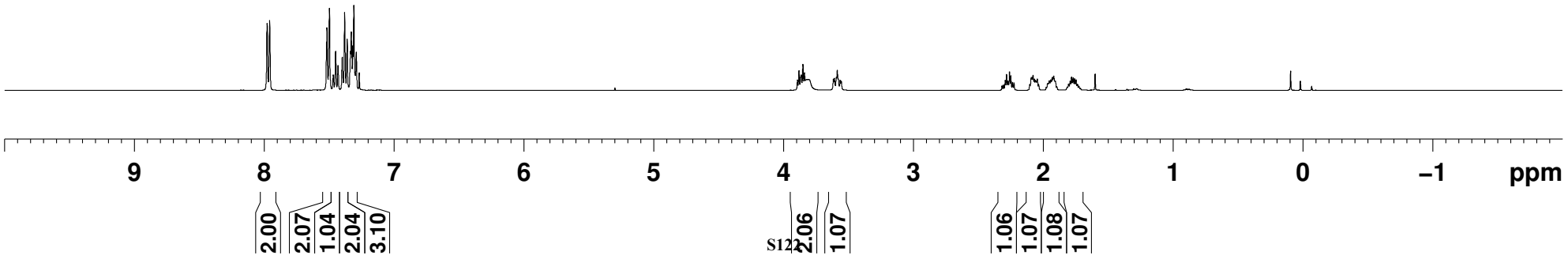

7.777
7.764
7.757
7.705
7.699
7.686
7.418
7.404
7.334
7.324
7.320
4.306
4.296
4.274
4.078
4.072
4.047
4.018
3.186
2.309
2.301
2.292
2.275
2.267
2.258
2.233
2.214
2.204
2.195
2.183
2.174
2.162
2.150
2.140
2.128
2.009
1.978
1.634
1.604
1.598
-0.079
Ph
N3
OTMS
O
Ph
N3
3m
9
8
7
6
5
4
3
2
1
0
−1
ppm
1.97
2.07
3.09
3.18
0.99
2.03
1.20
1.00
2.02
1.05
1.14
8.84


143.213
142.584
131.201
129.075
127.575
127.485
127.028
126.916
96.784
88.076
77.318
77.001
76.683
63.570
55.991
24.799
19.075
1.762
Ph
N3
OTMS
O
Ph
N3
3m
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
ppm

czm7p7b

7.980 7.961 7.519 7.500 7.470 7.452 7.433 7.400 7.383 7.363 7.338 7.331 7.320 7.312 7.292 7.270 3.894 3.882 3.870 3.865 3.852 3.840 3.822 3.807 3.617 3.609 3.595 3.587 3.580 3.565 3.557 2.294 2.284 2.273 2.261 2.250 2.237 2.226 2.094 2.079 2.070 2.061 2.046 1.966 1.954 1.943 1.930 1.920 1.909 1.806 1.794 1.782 1.771 1.760 1.748 1.737 0.095 0.020





czm7p7b

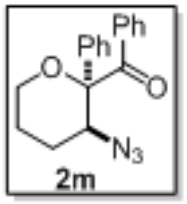
199.543

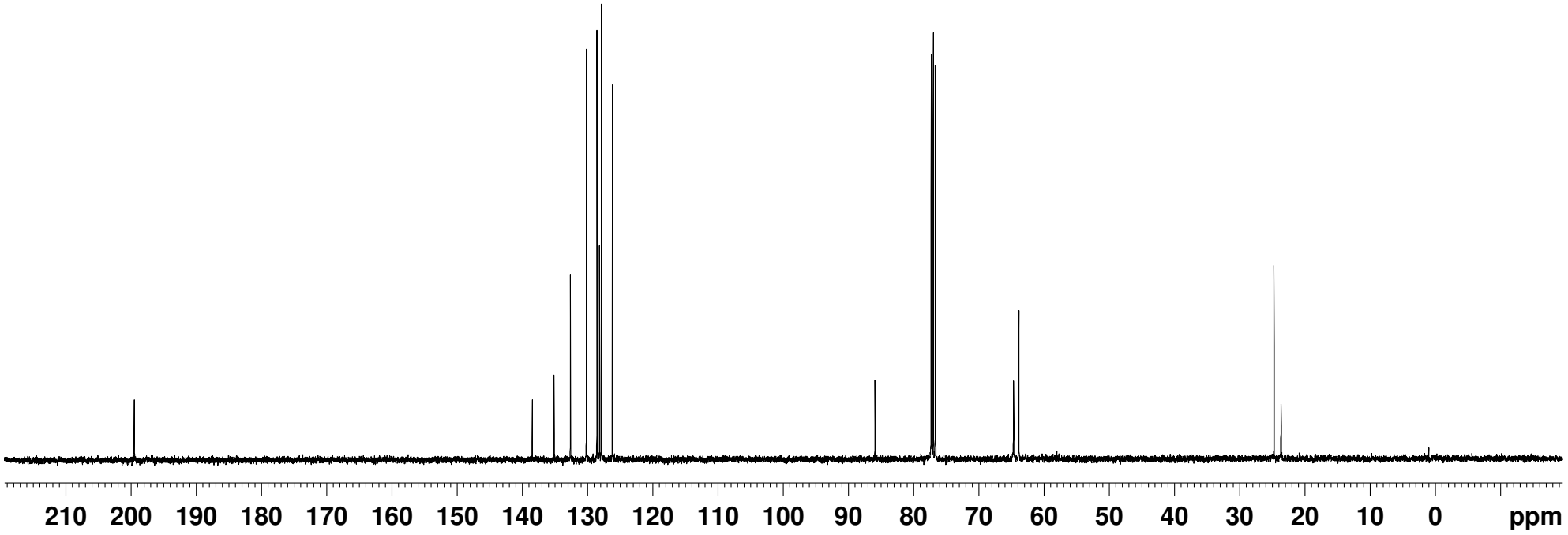
138.496
135.163
132.659
130.200
128.592
128.183
127.899
126.215

85.941
77.319
77.001
76.683

64.680
63.880

24.737
23.653



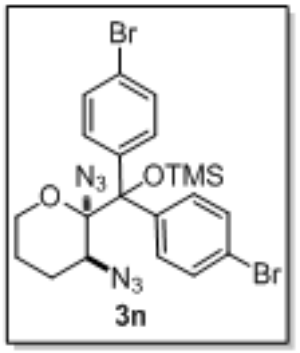


zz2p64a2

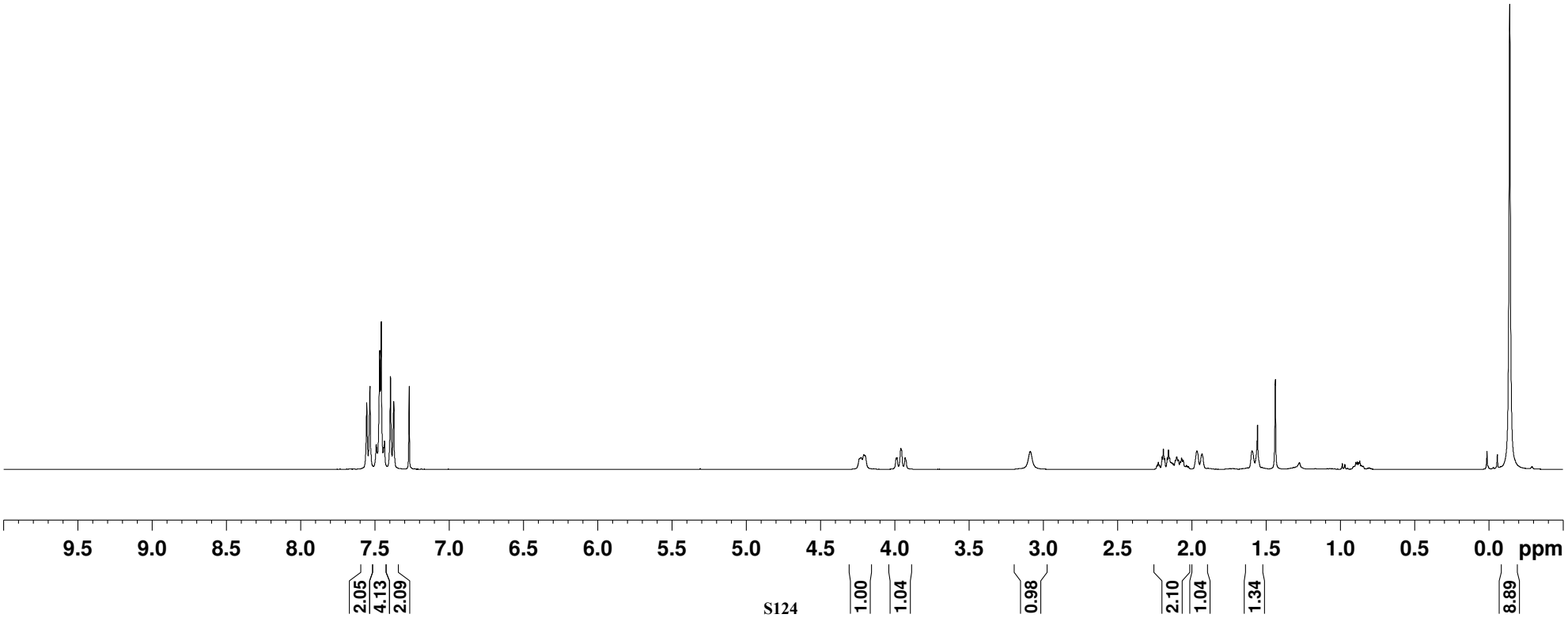
7.557
7.535
7.492
7.470
7.459
7.437
7.397
7.375
7.270

4.237
4.227
4.209
3.991
3.985
3.960
3.931
3.088
2.235
2.226
2.217
2.200
2.192
2.183
2.165
2.157
2.150
2.142
2.136
2.131
2.124
2.111
2.102
2.091
2.079
2.070
2.059
2.046
2.036
2.023
1.966
1.931
1.595
1.558

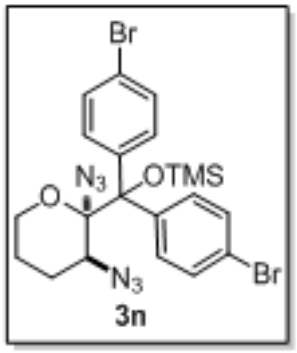
-0.141



3n



zz2p64a2-c

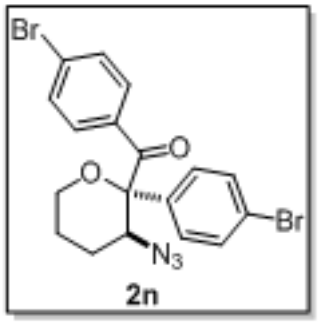


142.016
141.398
132.953
130.664
130.327
130.133
122.154
121.975
96.436
87.450
77.318
77.000
76.683
63.736
55.839
26.914
24.487
18.990
1.869

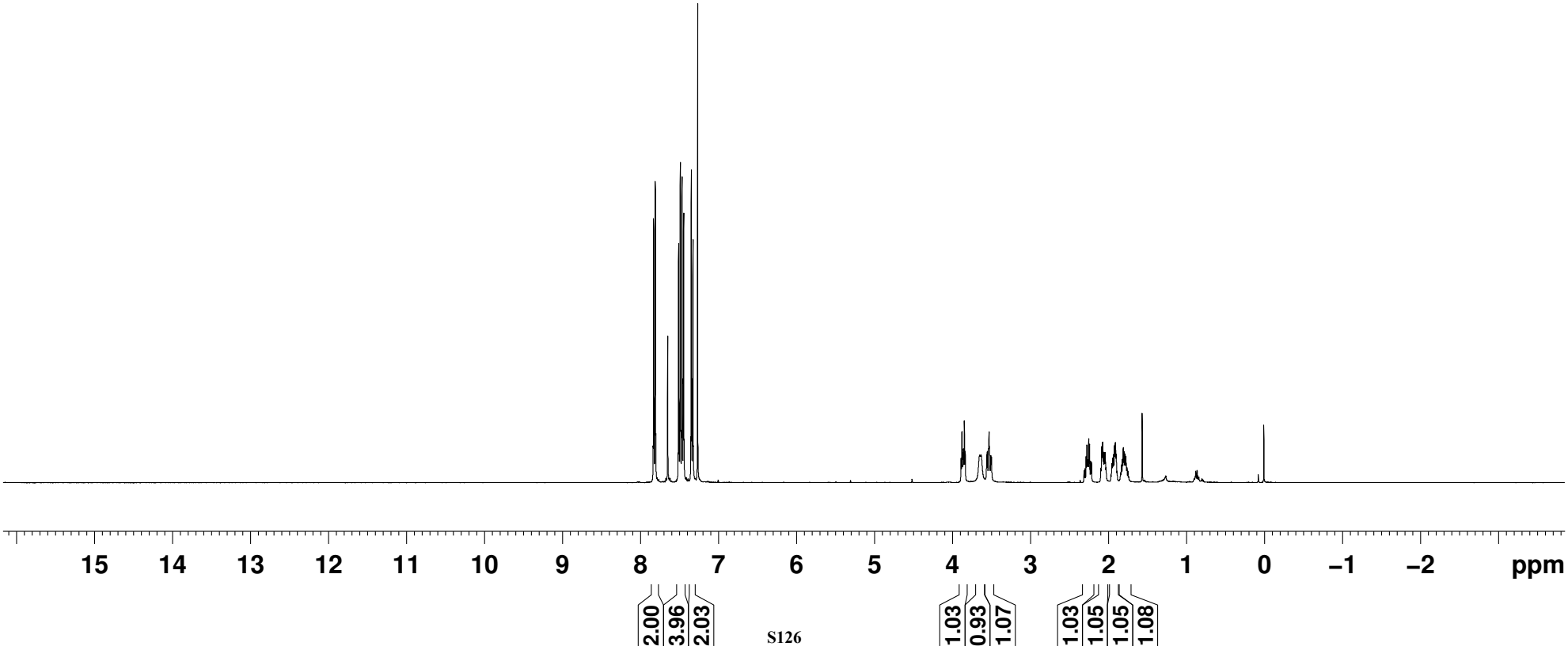
220 200 180 160 140 120 100 80 60 40 20 0 ppm

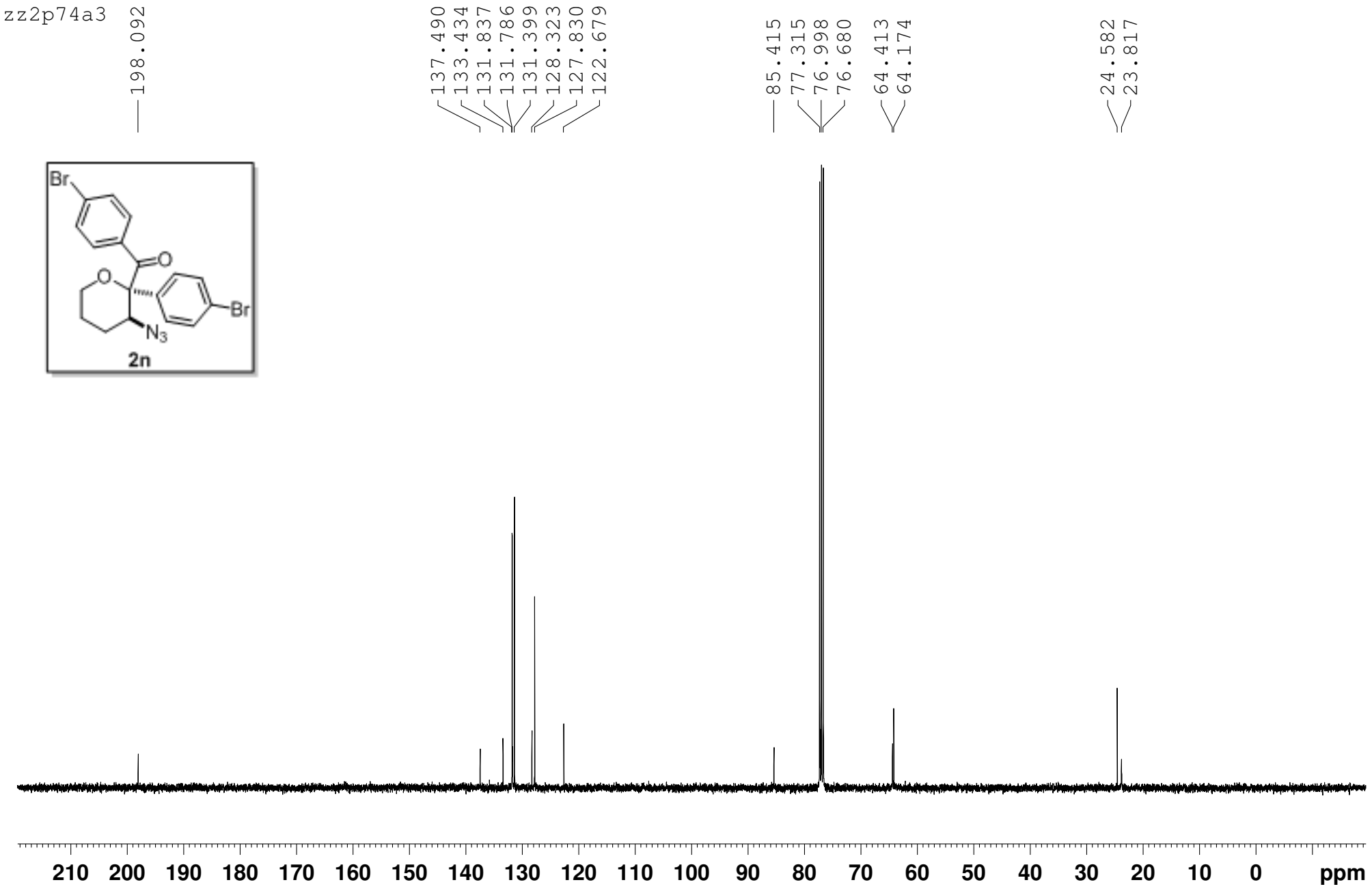
zz2p74a3

7.840 7.835 7.830 7.817 7.813 7.807 7.654 7.520 7.514 7.510 7.497 7.492 7.487 7.477 7.471 7.466 7.454 7.449 7.443 7.358 7.352 7.347 7.335 7.330 7.324 7.270 3.880 3.869 3.862 3.850 3.839 3.654 3.636 3.563 3.555 3.539 3.532 3.509 3.502 2.289 2.278 2.255 2.245 2.088 2.077 2.066 2.055 2.043 1.948 1.936 1.925 1.913 1.902 1.812 1.801 1.788 1.777 0.009

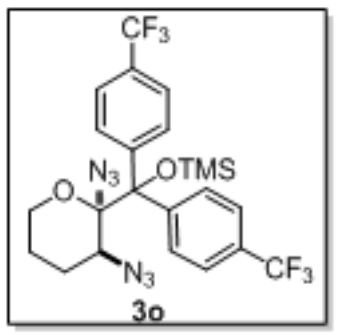


2n

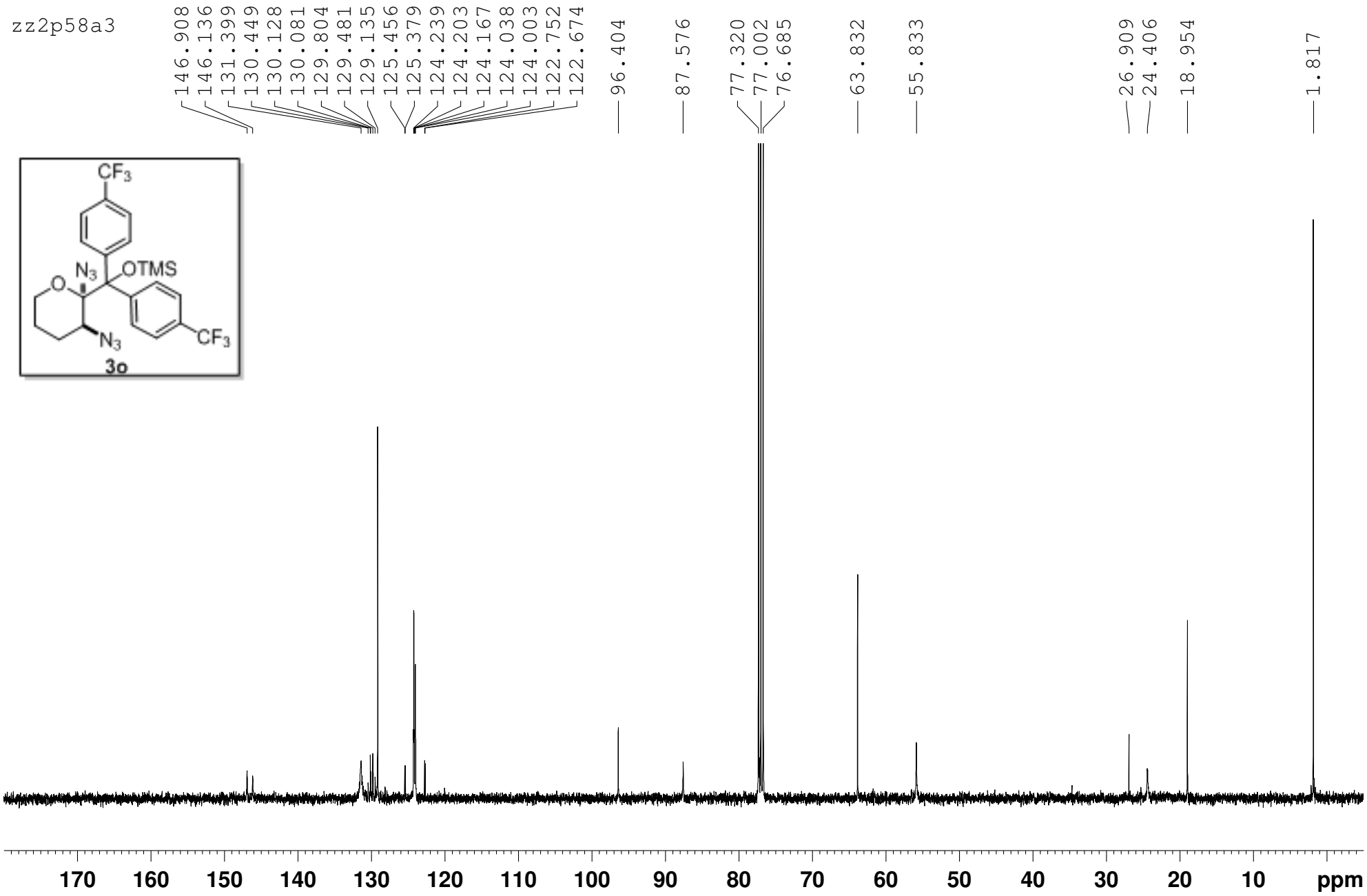



zz2p74a3
198.092
137.490
133.434
131.837
131.786
131.399
128.323
127.830
122.679
85.415
77.315
76.998
76.680
64.413
64.174
24.582
23.817
Br
O
O
Br
N3
2n
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 ppm

zz2p58a3

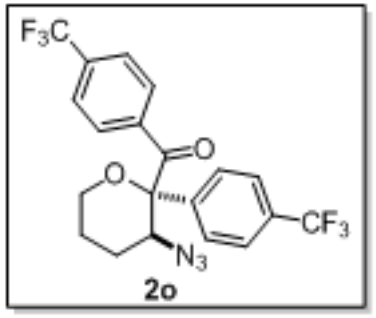

CF3
N3
OTMS
O
N3
CF3
3o

7.801
7.781
7.735
7.714
7.639
7.619
7.549
7.528
7.270
4.274
4.264
4.245
4.038
4.031
4.007
4.001
3.977
3.972
3.154
2.257
2.249
2.240
2.223
2.215
2.206
2.189
2.181
2.173
2.158
2.151
2.139
2.130
2.118
2.106
2.097
2.085
2.073
2.064
2.051
2.001
1.966
1.629
1.595
0.126
9
8
7
6
5
4
3
2
1
0
ppm
1.87
1.99
1.92
2.00
0.93
0.98
0.93
1.95
0.96
1.01
8.72

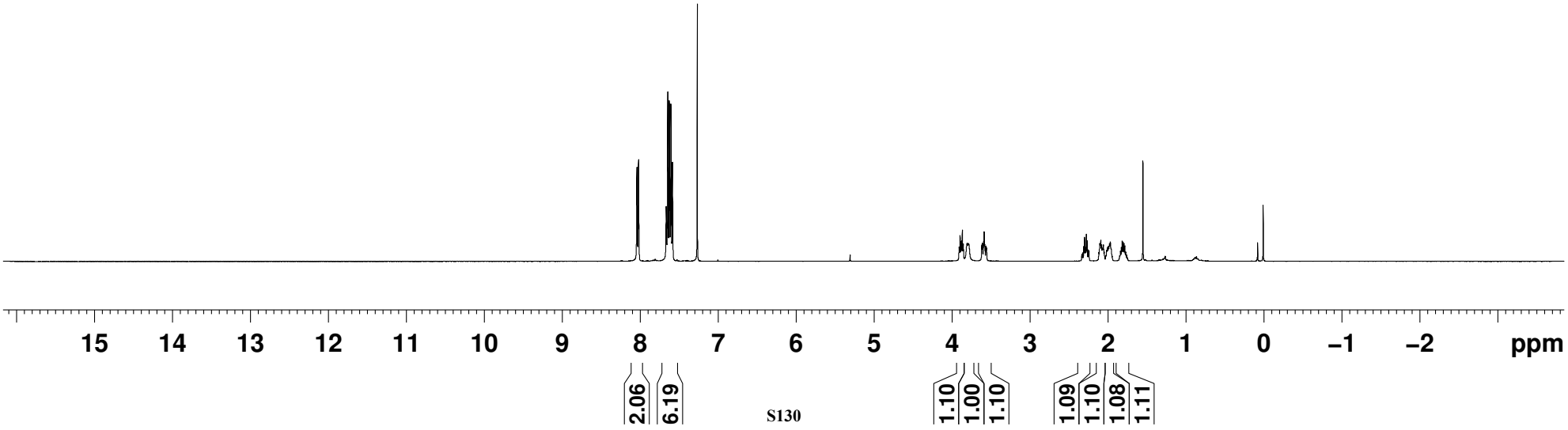

zz2p58a3
146.908
146.136
131.399
130.449
130.128
130.081
129.804
129.481
129.135
125.456
125.379
124.239
124.203
124.167
124.038
124.003
122.752
122.674
96.404
87.576
77.320
77.002
76.685
63.832
55.833
26.909
24.406
18.954
1.817
CF3
N3
OTMS
O
N3
CF3
3o
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
ppm

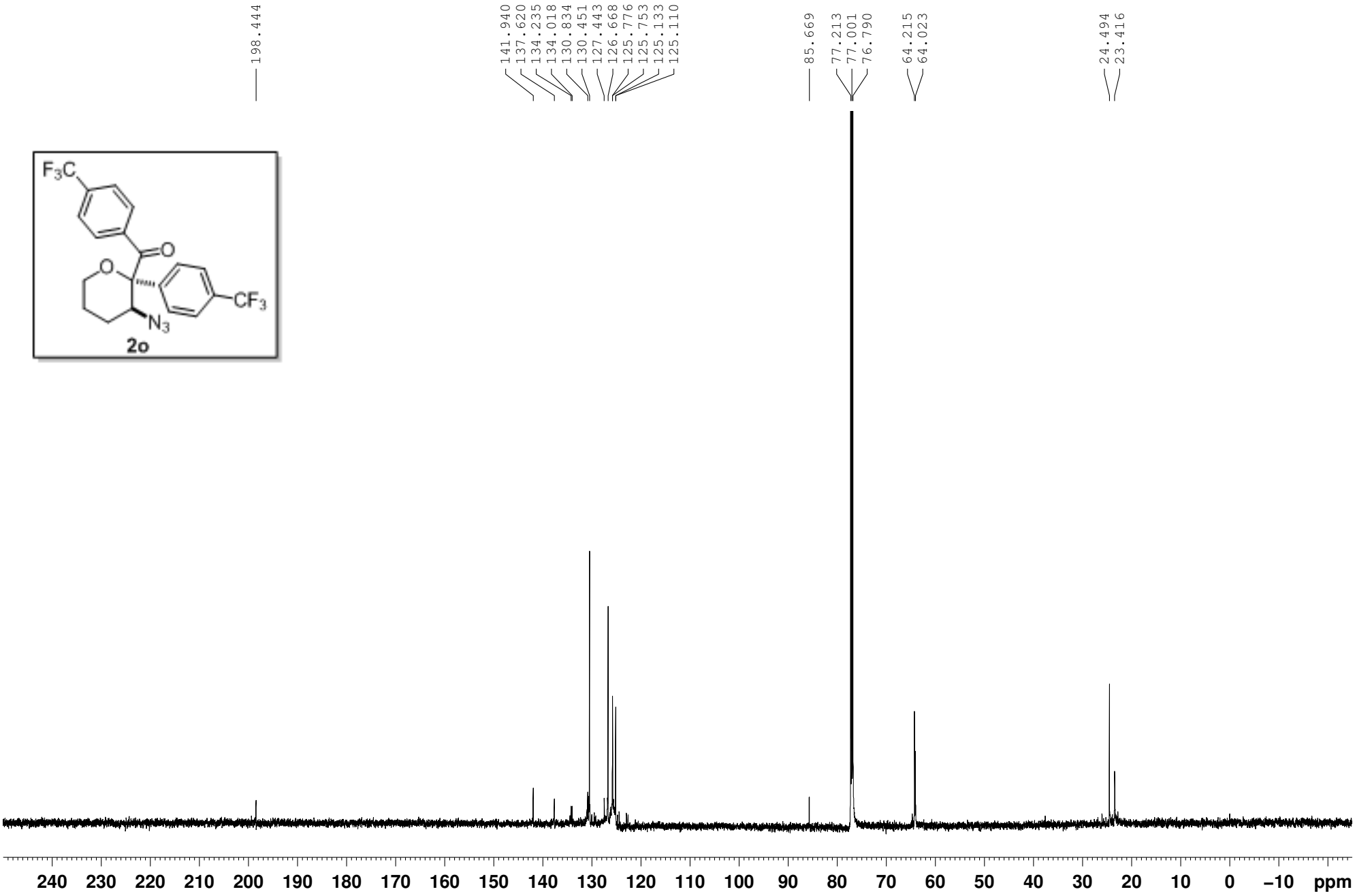
czm7p8a7down

8.044 8.023 7.670 7.648 7.629 7.609 7.588 7.270 3.911 3.899 3.886 3.881 3.869 3.857 3.807 3.789 3.619 3.611 3.597 3.589 3.581 3.567 3.559 2.336 2.325 2.312 2.302 2.291 2.279 2.268 2.255 2.245 2.118 2.107 2.092 2.083 2.075 2.069 2.059 2.050 2.028 2.018 2.005 1.994 1.981 1.971 1.947 1.852 1.841 1.830 1.818 1.807 1.795 1.784 1.773 1.761 0.082 0.010

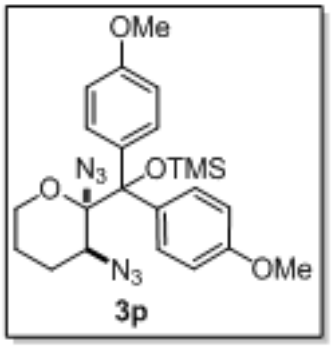


2o

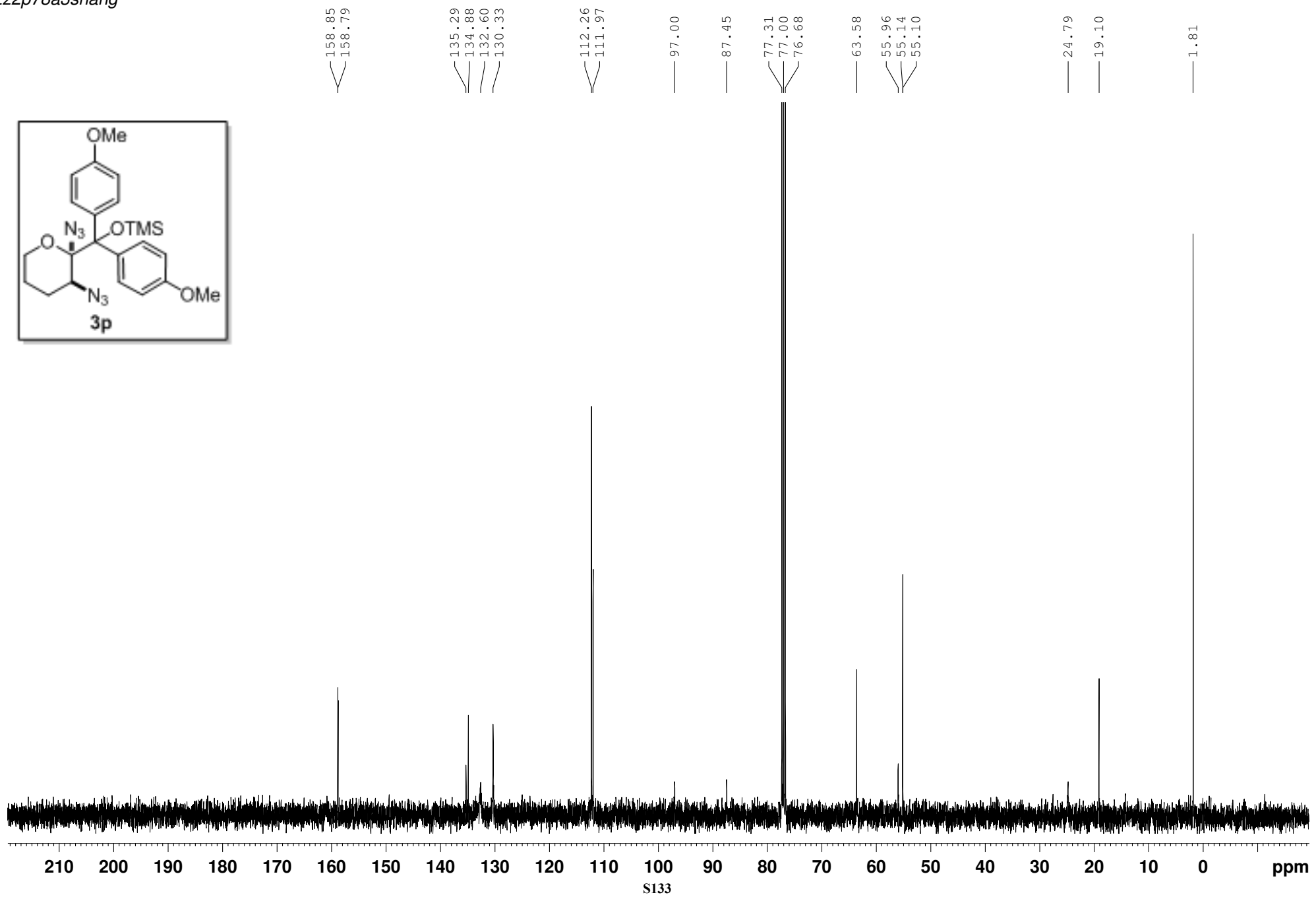



198.444
141.940
137.620
134.235
134.018
130.834
130.451
127.443
126.668
125.776
125.753
125.133
125.110
85.669
77.213
77.001
76.790
64.215
64.023
24.494
23.416
F3C
O
O
CF3
N3
2o
240 230 220 210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 −10 ppm

zz2p78a3shang

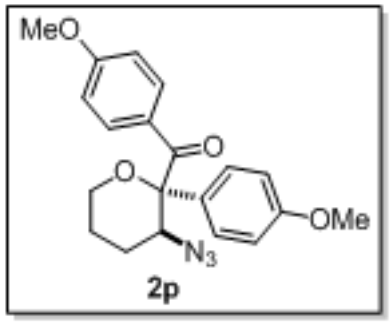


zz2p78a3shang

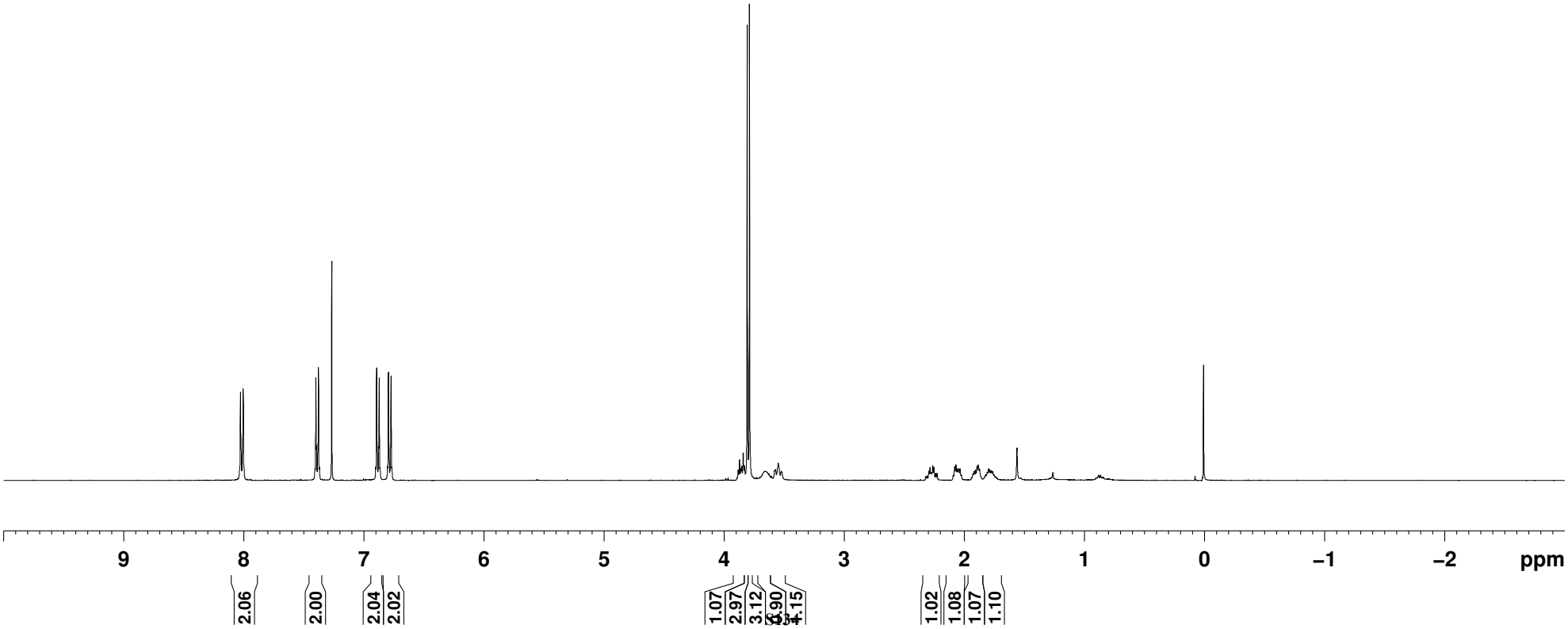


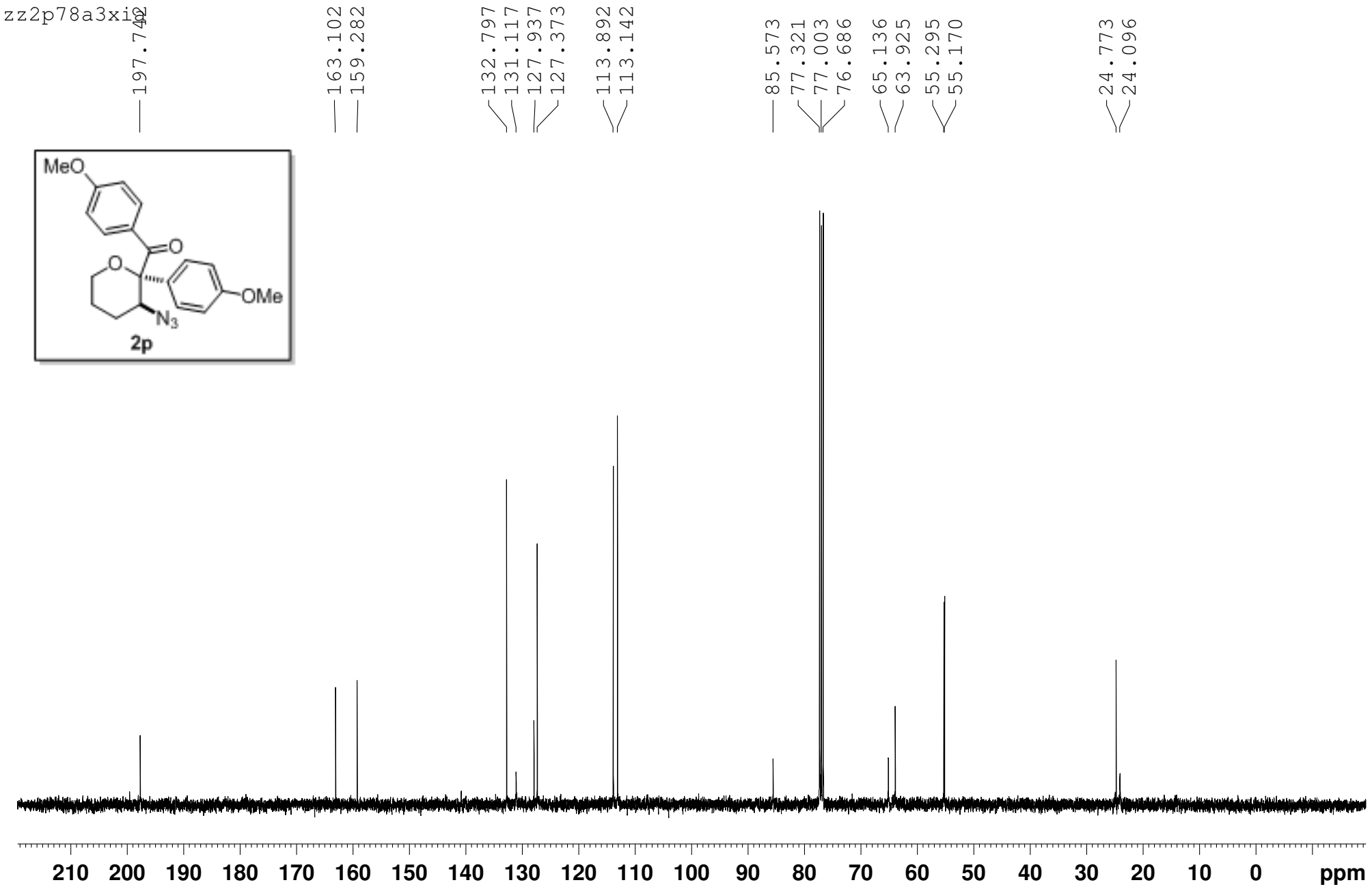
czm2p13a2

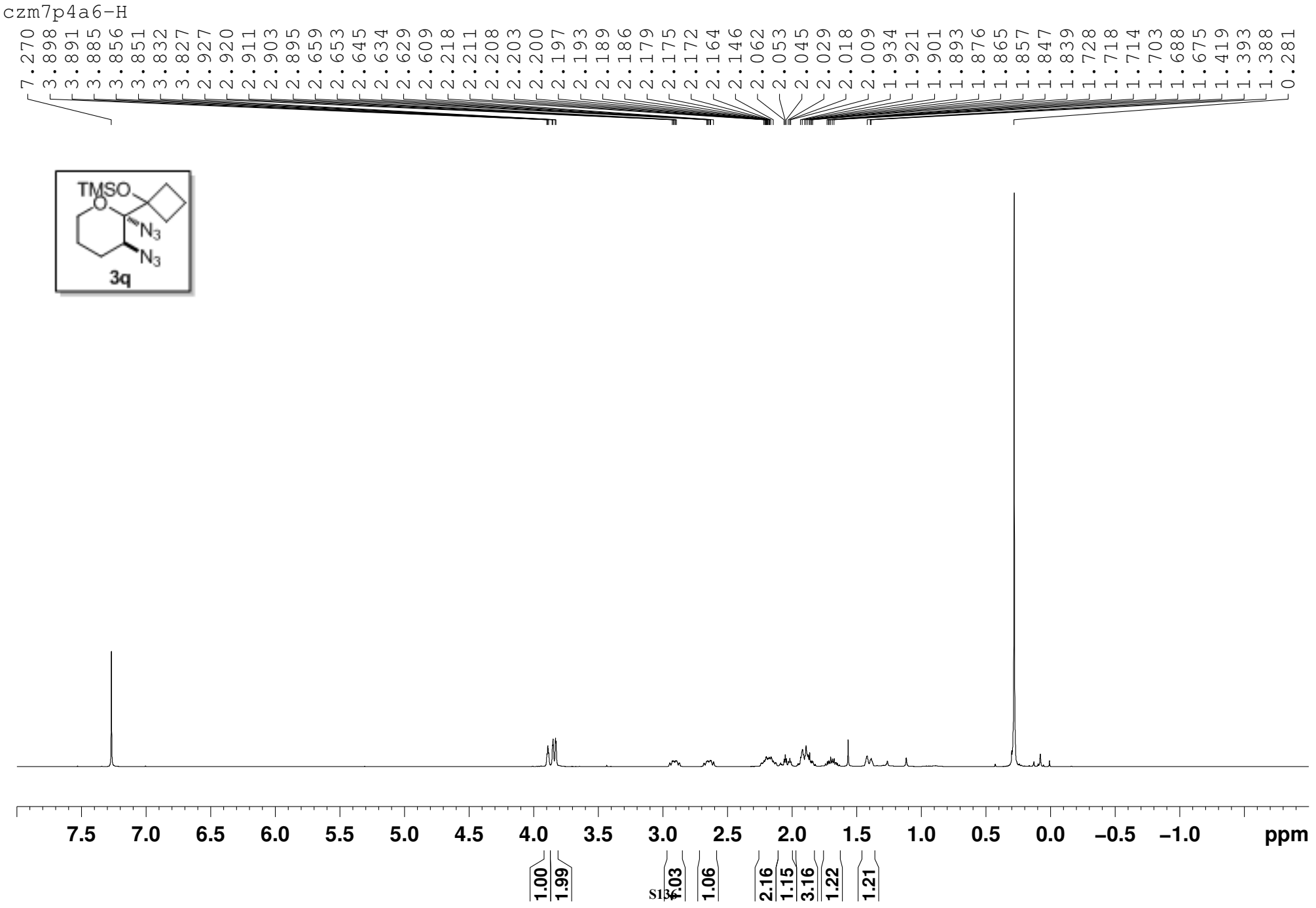
8.030 8.007 8.001 7.410 7.402 7.397 7.386 7.380 7.373 7.270 6.904 6.896 6.891 6.879 6.874 6.867 6.805 6.798 6.793 6.781 6.776 6.769 3.885 3.874 3.863 3.855 3.843 3.810 3.792 3.663 3.627 3.610 3.582 3.574 3.551 3.528 3.520 2.323 2.312 2.298 2.288 2.280 2.273 2.265 2.255 2.240 2.229 2.094 2.082 2.071 2.060 2.054 2.050 2.038 2.027 1.941 1.931 1.919 1.908 1.897 1.885 1.875 1.864 1.824 1.811 1.800 1.788 1.776 1.765 1.754 1.741 0.010

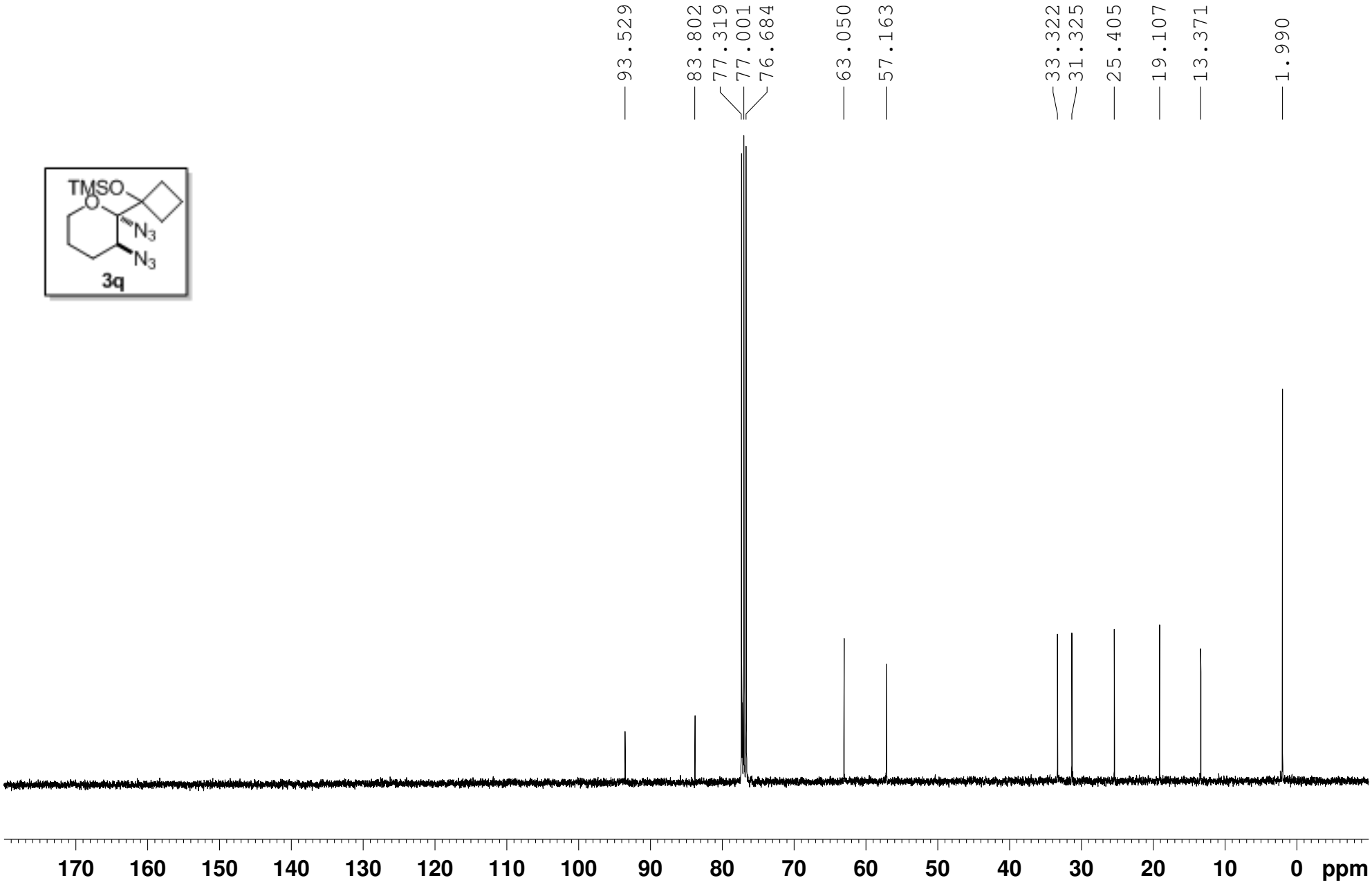


2p

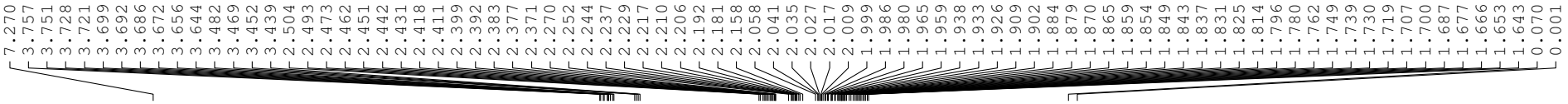


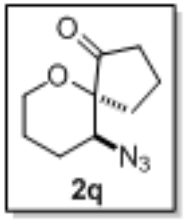

zz2p78a3xi2
197.742
163.102
159.282
132.797
131.117
127.937
127.373
113.892
113.142
85.573
77.321
77.003
76.686
65.136
63.925
55.295
55.170
24.773
24.096
MeO
O
O
OMe
N3
2p
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 ppm


czm7p4a6-H
7.270
3.898
3.891
3.885
3.856
3.851
3.832
3.827
2.927
2.920
2.911
2.903
2.895
2.659
2.653
2.645
2.634
2.629
2.609
2.218
2.211
2.208
2.203
2.200
2.197
2.193
2.189
2.186
2.179
2.175
2.172
2.164
2.146
2.062
2.053
2.045
2.029
2.018
2.009
1.934
1.921
1.901
1.893
1.876
1.865
1.857
1.847
1.839
1.728
1.718
1.714
1.703
1.688
1.675
1.419
1.393
1.388
0.281
TMSO
O
N3
N3
3q
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
1.99
4.03
1.06
2.16
1.15
3.16
1.22
1.21


93.529
83.802
77.319
77.001
76.684
63.050
57.163
33.322
31.325
25.405
19.107
13.371
1.990
TMSO
O
N3
N3
3q
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
ppm

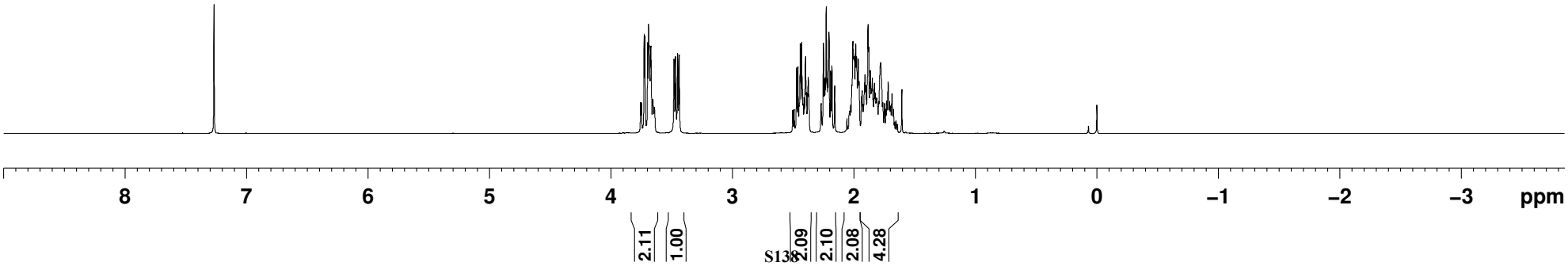
czm7p17b1



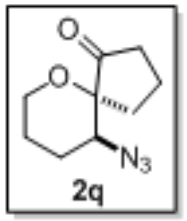


2q

```
NAME           czm7p17b1
EXPNO                 10
PROCNO                 1
Date_           20140408
Time               18.09
INSTRUM            spect
PROBHD   5 mm PABBO BB/
PULPROG             zg30
TD                 65536
SOLVENT            CDCl3
NS                    16
DS                     2
SWH             8012.820 Hz
FIDRES          0.122266 Hz
AQ              4.0894966 sec
RG                   144
DW                62.400 usec
DE                 6.50 usec
TE                297.0 K
D1             1.00000000 sec
TD0                    1

======== CHANNEL f1 ========
SFO1         400.1324710 MHz
NUC1                   1H
P1                14.10 usec
SI                 65536
SF           400.1300059 MHz
WDW                   EM
SSB                    0
LB                0.30 Hz
GB                     0
PC                  1.00
```

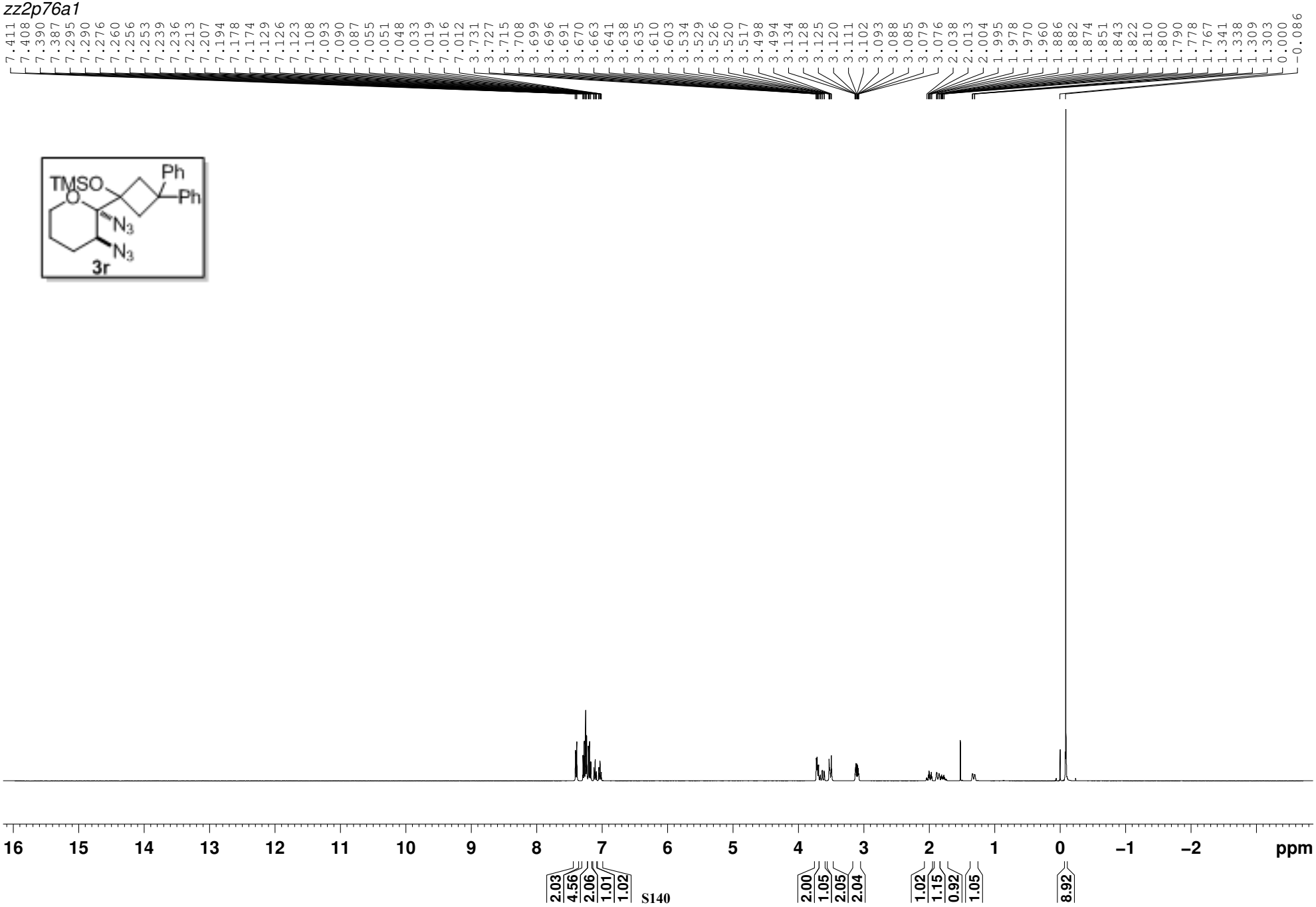


czm7p7a


O
O
N3
2q

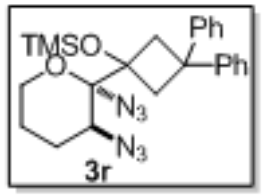
214.57
77.91
77.32
77.00
76.69
62.64
59.77
38.38
35.84
24.74
23.55
18.00
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
ppm

zz2p76a1

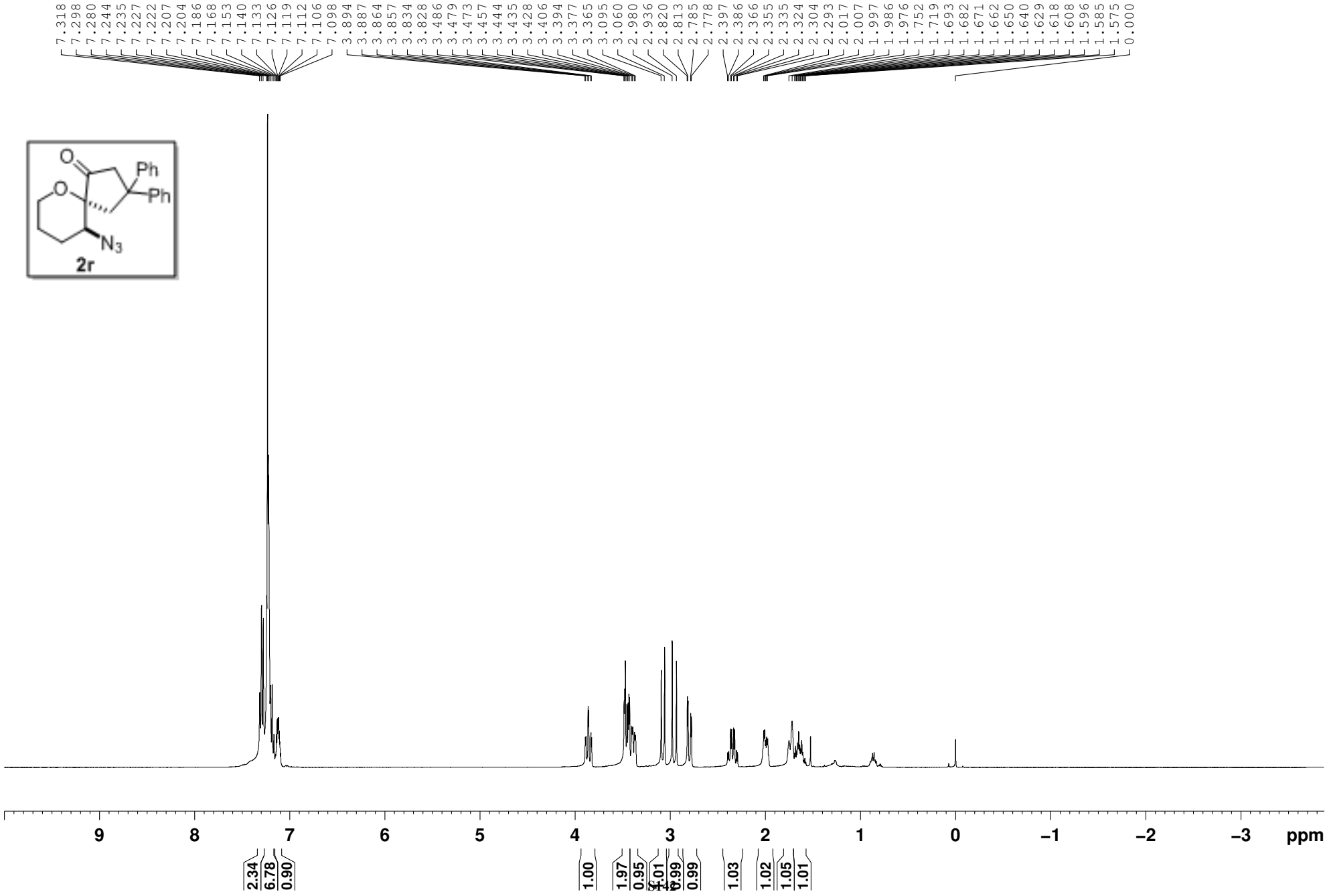

7.411
7.408
7.390
7.387
7.295
7.290
7.276
7.260
7.256
7.253
7.239
7.236
7.213
7.207
7.194
7.178
7.174
7.129
7.126
7.123
7.108
7.093
7.090
7.087
7.055
7.051
7.048
7.033
7.019
7.016
7.012
3.731
3.727
3.715
3.708
3.699
3.696
3.691
3.670
3.663
3.641
3.638
3.635
3.610
3.603
3.534
3.529
3.526
3.520
3.517
3.498
3.494
3.134
3.128
3.125
3.120
3.111
3.102
3.093
3.088
3.085
3.079
3.076
2.038
2.013
2.004
1.995
1.978
1.970
1.960
1.886
1.882
1.874
1.851
1.843
1.822
1.810
1.800
1.790
1.778
1.767
1.341
1.338
1.309
1.303
0.000
-0.086
TMSO
Ph
Ph
N3
N3
3r
16
15
14
13
12
11
10
9
8
7
6
5
4
3
2
1
0
–1
–2
ppm
2.03
4.56
2.06
1.01
1.02
2.00
1.05
2.05
2.04
1.02
1.15
0.92
1.05
8.92

zz2p75a5

150.35
150.02
128.34
127.90
126.40
125.73
125.41
124.89
93.19
79.96
77.31
77.00
76.68
62.93
57.36
47.05
44.06
43.49
25.08
18.94
1.70

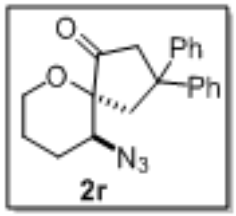


czm7p11b


7.318
7.298
7.280
7.244
7.235
7.227
7.222
7.207
7.204
7.186
7.168
7.153
7.140
7.133
7.126
7.119
7.112
7.106
7.098
3.894
3.887
3.864
3.857
3.834
3.828
3.486
3.479
3.473
3.457
3.444
3.435
3.428
3.406
3.394
3.377
3.365
3.095
3.060
2.980
2.936
2.820
2.813
2.785
2.778
2.397
2.386
2.366
2.355
2.335
2.324
2.304
2.293
2.017
2.007
1.997
1.986
1.976
1.752
1.719
1.693
1.682
1.671
1.662
1.650
1.640
1.629
1.618
1.608
1.596
1.585
1.575
0.000
O
Ph
Ph
O
N3
2r
9
8
7
6
5
4
3
2
1
0
–1
–2
–3
ppm
2.34
6.78
0.90
1.00
1.97
0.95
1.01
0.99
0.99
1.03
1.02
1.05
1.01

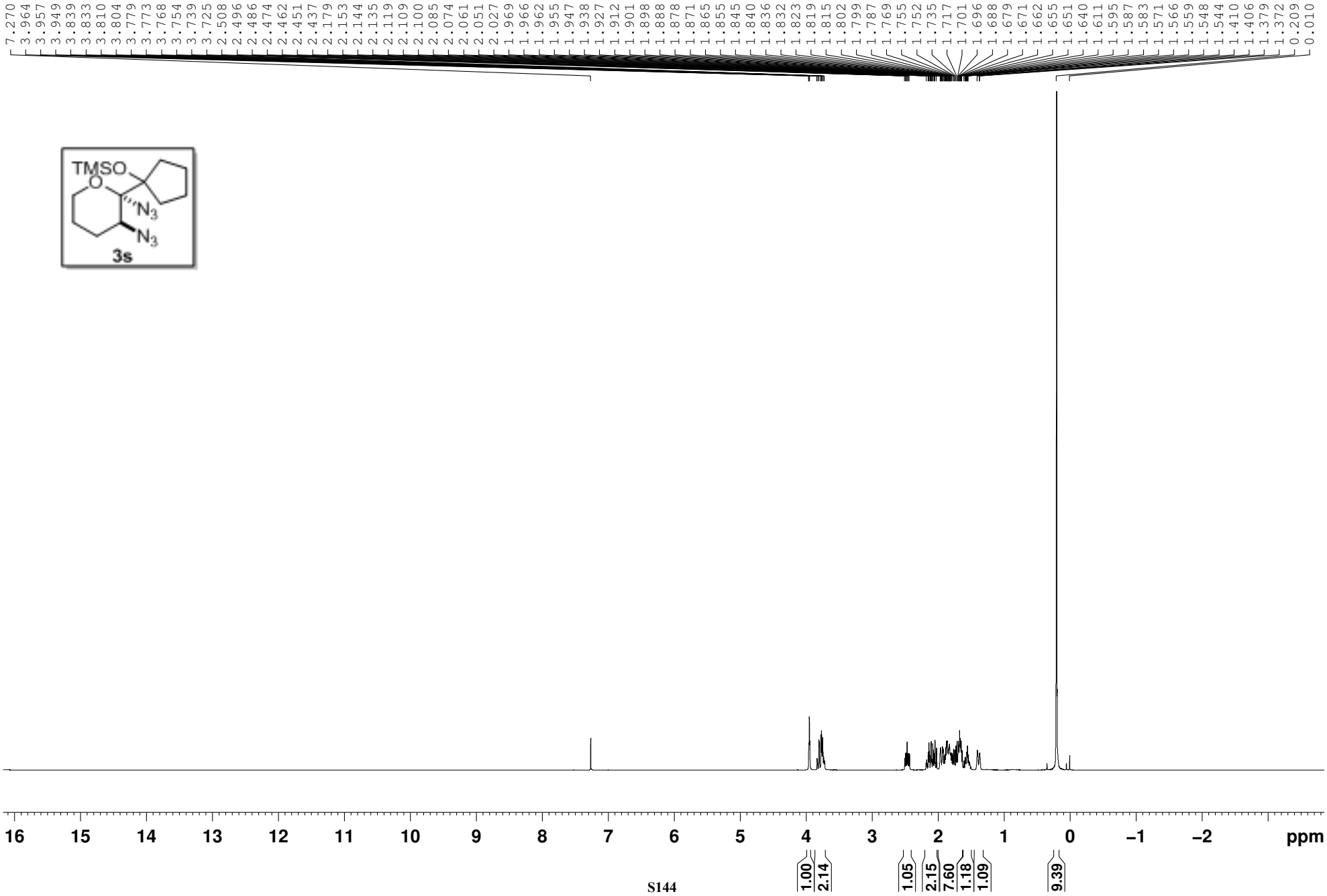
czm7p11b

213.63
148.62
146.70
128.55
128.08
127.04
126.41
126.32
125.98
78.40
77.32
77.00
76.68
62.18
60.53
53.23
48.45
48.05
24.29
23.58

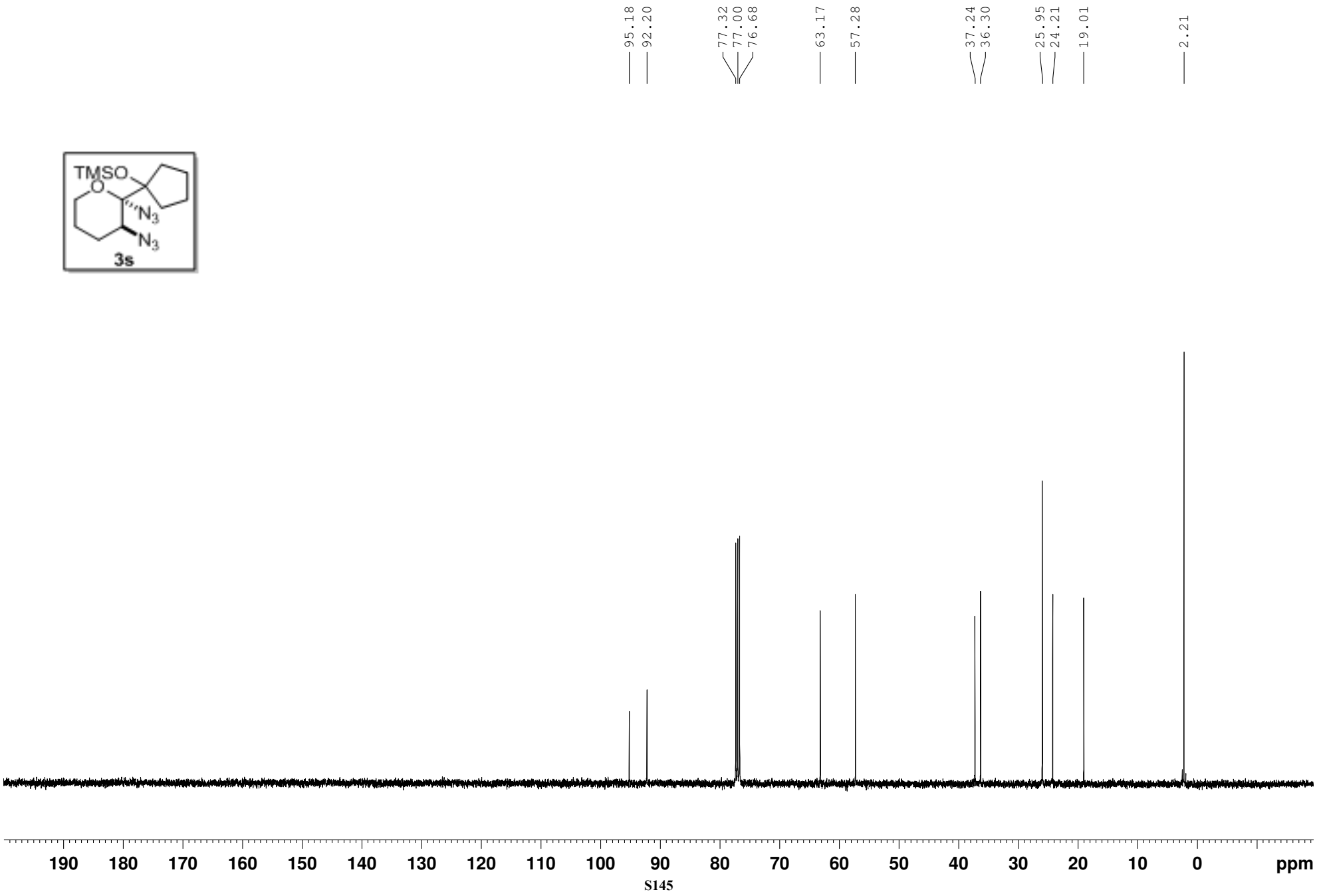


2r

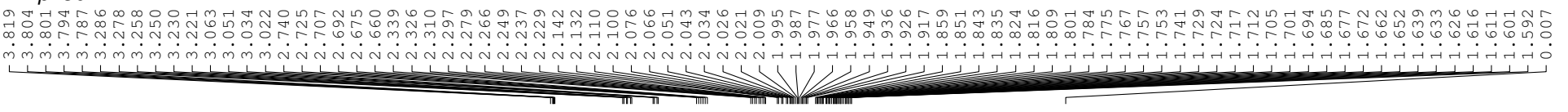
zz2p78b5

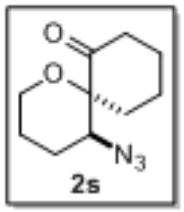

7.270
3.964
3.957
3.949
3.839
3.833
3.810
3.804
3.779
3.773
3.768
3.754
3.739
3.725
2.508
2.496
2.486
2.474
2.462
2.451
2.437
2.179
2.153
2.144
2.135
2.119
2.109
2.100
2.085
2.074
2.061
2.051
2.027
1.969
1.966
1.962
1.955
1.947
1.938
1.927
1.912
1.901
1.898
1.888
1.878
1.871
1.865
1.855
1.845
1.840
1.836
1.832
1.823
1.819
1.815
1.802
1.799
1.787
1.769
1.755
1.752
1.735
1.717
1.701
1.696
1.688
1.679
1.671
1.662
1.655
1.651
1.640
1.611
1.595
1.587
1.583
1.571
1.566
1.559
1.548
1.544
1.410
1.406
1.379
1.372
0.209
0.010
TMSO
O
N3
N3
3s
16
15
14
13
12
11
10
9
8
7
6
5
4
3
2
1
0
–1
–2
ppm
1.00
2.14
1.05
2.15
7.60
1.18
1.09
9.39

zz2p78b5-C

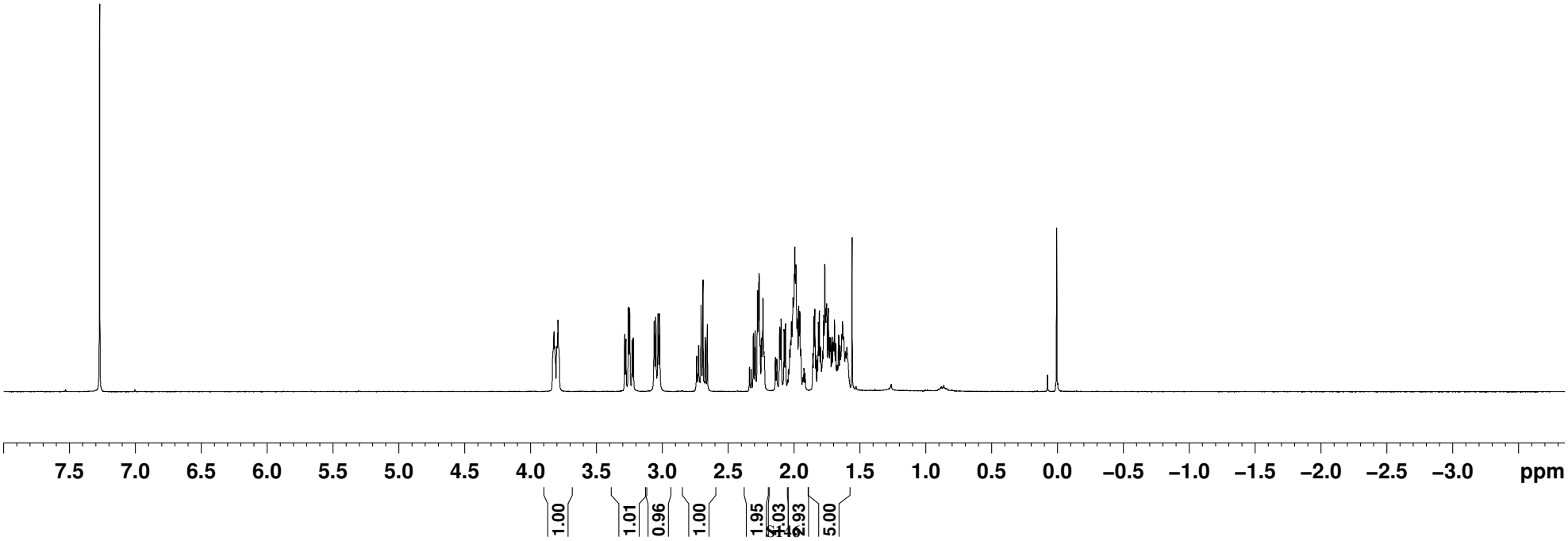

95.18
92.20
77.32
77.00
76.68
63.17
57.28
37.24
36.30
25.95
24.21
19.01
2.21
TMSO
O
N3
N3
3s
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
ppm

czm7p13b2

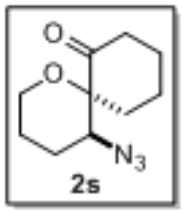




2s



czm7p13b2

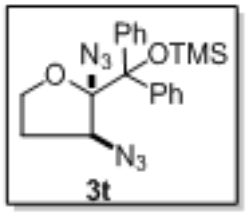


2s

211.08
80.14
77.32
77.00
76.68
63.34
62.26
39.86
37.84
27.53
24.91
23.84
20.00

210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 ppm

czm7p8a-2

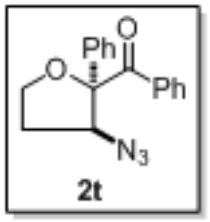

Ph
OTMS
N_3
O
Ph
N_3
3t

7.704
7.684
7.673
7.654
7.354
7.337
7.317
7.303
7.286
7.270
4.446
4.425
4.403
4.351
3.581
2.511
2.119
2.102
0.012
9
8
7
6
5
4
3
2
1
0
ppm
4.00
5.92
2.02
0.90
1.00
0.99
8.98

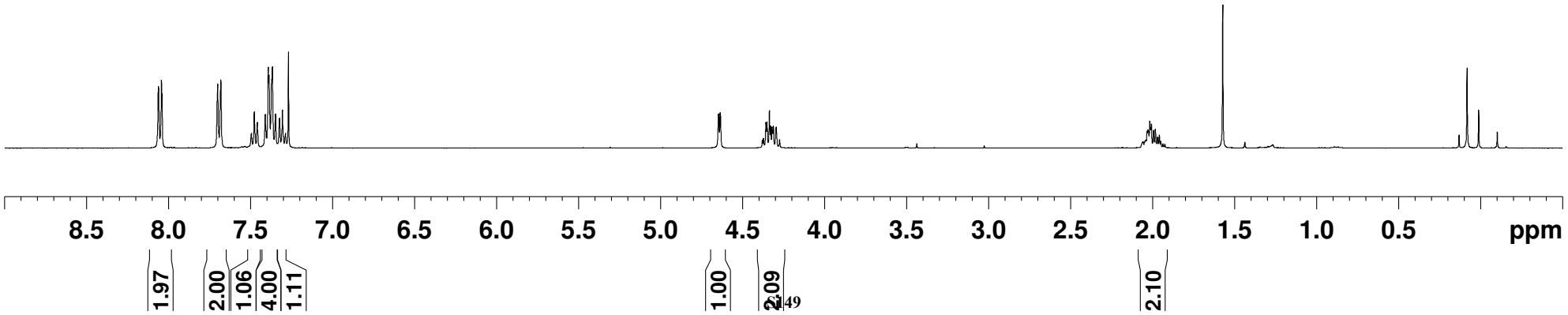
czmweizhi

8.045 8.041 7.705 7.702 7.683 7.497 7.479 7.460 7.412 7.407 7.393 7.389 7.372 7.368 7.349 7.325 7.307 7.288 7.270

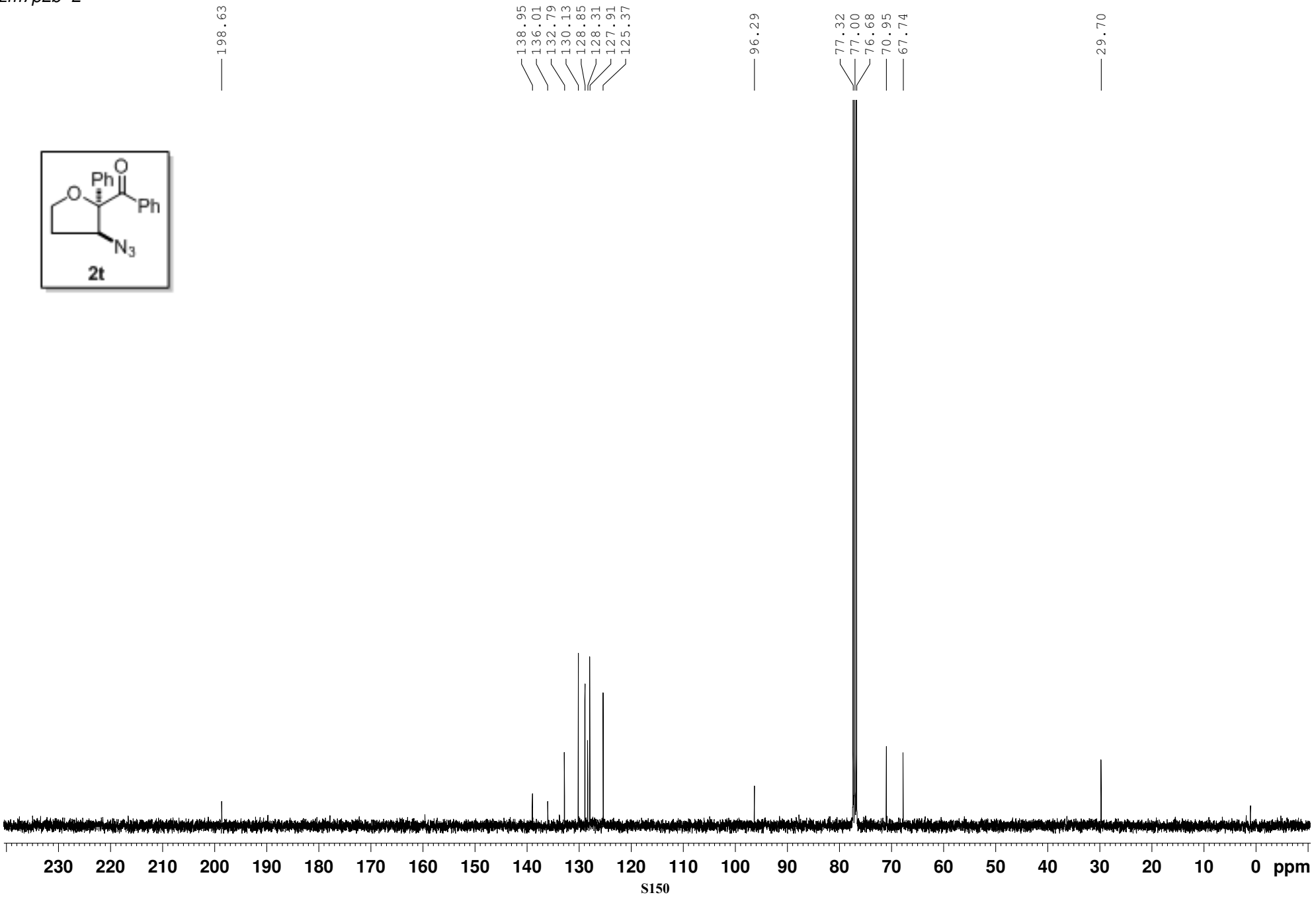
4.648 4.638 4.380 4.373 4.359 4.352 4.337 4.329 4.321 4.313 4.296 4.275 2.064 2.060 2.057 2.047 2.043 2.040 2.034 2.031 2.027 2.024 2.018 2.014 2.007 1.994 1.984 1.970 1.959 1.950 1.937 1.926 0.082



2t



czm7p2b–2


198.63
138.95
136.01
132.79
130.13
128.85
128.31
127.91
125.37
96.29
77.32
77.00
76.68
70.95
67.74
29.70
Ph
O
Ph
O
N3
2t
230 220 210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 ppm

zz2p78b4

7.115
7.068
7.061
7.053
7.048
7.032
7.028
7.020
7.012
6.757
6.736
6.721

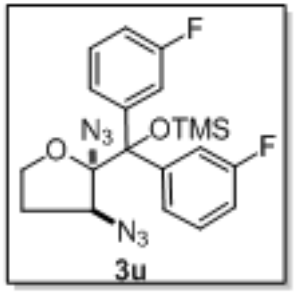
4.207
4.186
4.164
4.072
4.057

3.436

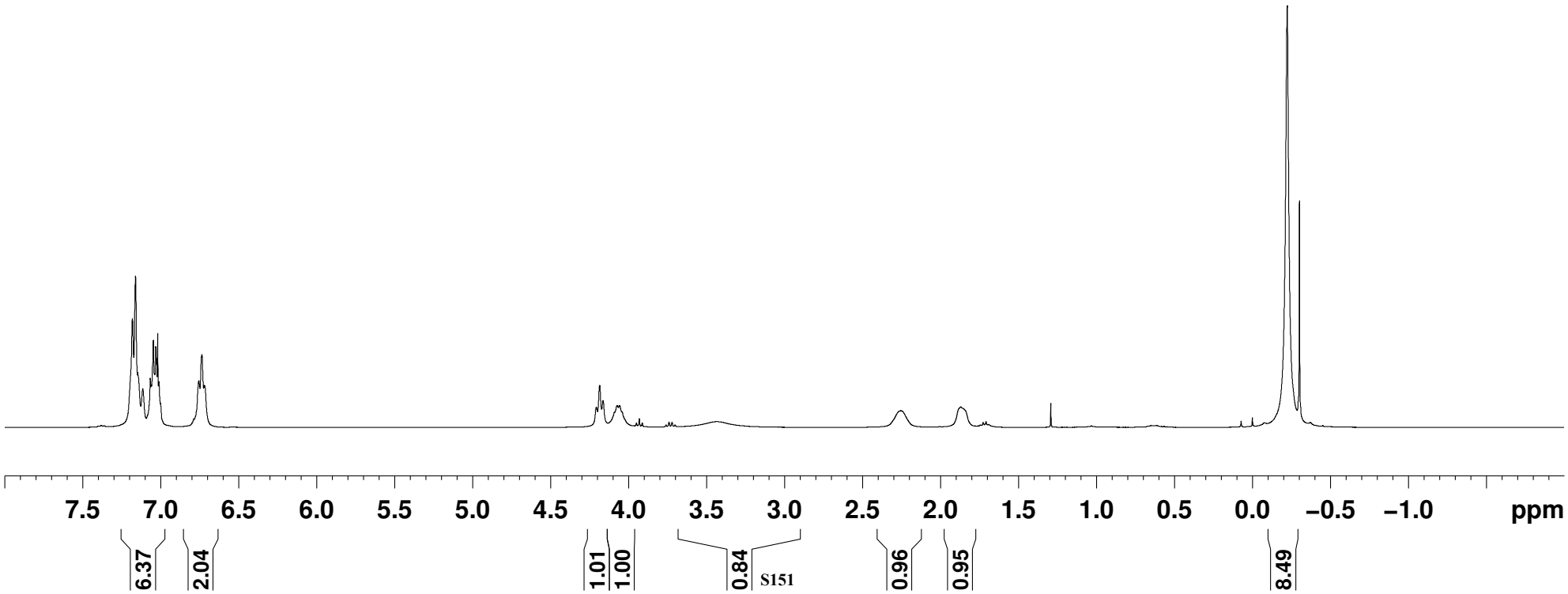
2.256

1.870

0.073
0.000
-0.224
-0.302

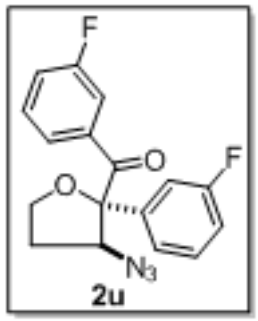


3u



czm7p13a1

7.852 7.849 7.835 7.832 7.829 7.791 7.785 7.781 7.767 7.762 7.760 7.757 7.463 7.460 7.447 7.443 7.441 7.414 7.409 7.404 7.395 7.389 7.383 7.380 7.375 7.369 7.360 7.355 7.349 7.340 7.335 7.270 7.227 7.225 7.220 7.218 7.206 7.204 7.200 7.197 7.186 7.183 7.179 7.177 7.041 7.039 7.035 7.033 7.021 7.019 7.014 7.012 7.000 6.998 6.994 6.992 4.618 4.609 4.380 4.365 4.359 4.348 4.342 4.335 4.332 4.327 4.322 4.306 4.302 4.285 2.076 2.062 2.059 2.056 2.053 2.046 2.043 2.040 2.037 2.021 2.010 1.996 1.986 1.972 1.961 1.952 0.011



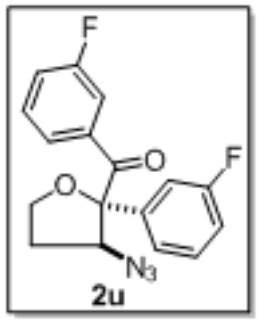
2u

16 15 14 13 12 11 10 9 8 7 6 5 4 3 2 1 0 –1 –2 ppm

1.00 1.02 1.03 3.15 1.06 1.06 1.07 2.14 1.04 1.10

czm7p13a1–C

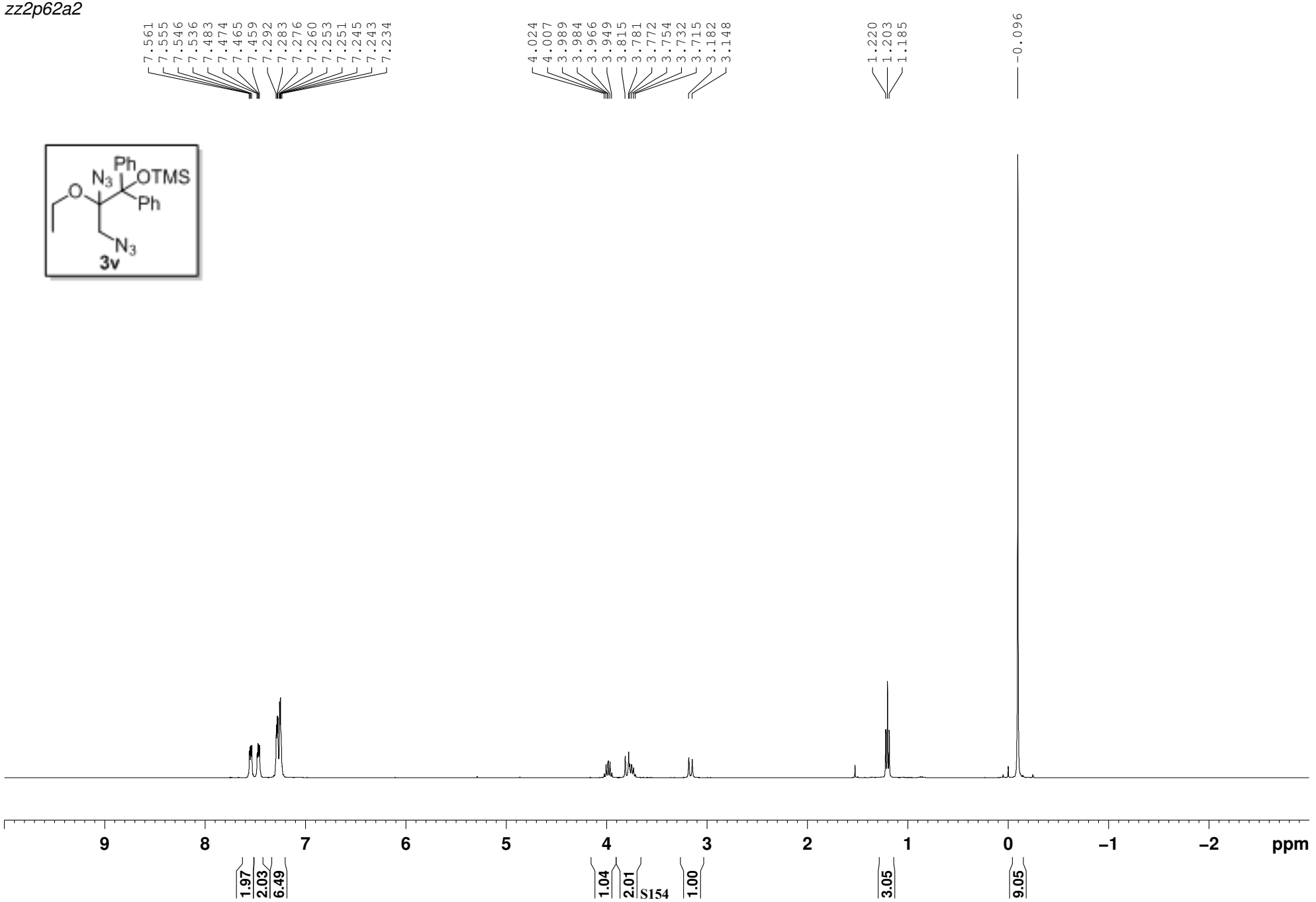
197.22
164.35
163.39
161.89
160.93
141.52
141.45
137.63
137.56
130.62
130.54
129.64
129.57
125.90
125.87
121.11
121.08
120.11
119.90
117.15
116.92
115.63
115.42
112.85
112.62
95.87
77.32
77.00
76.68
71.03
68.02
29.70



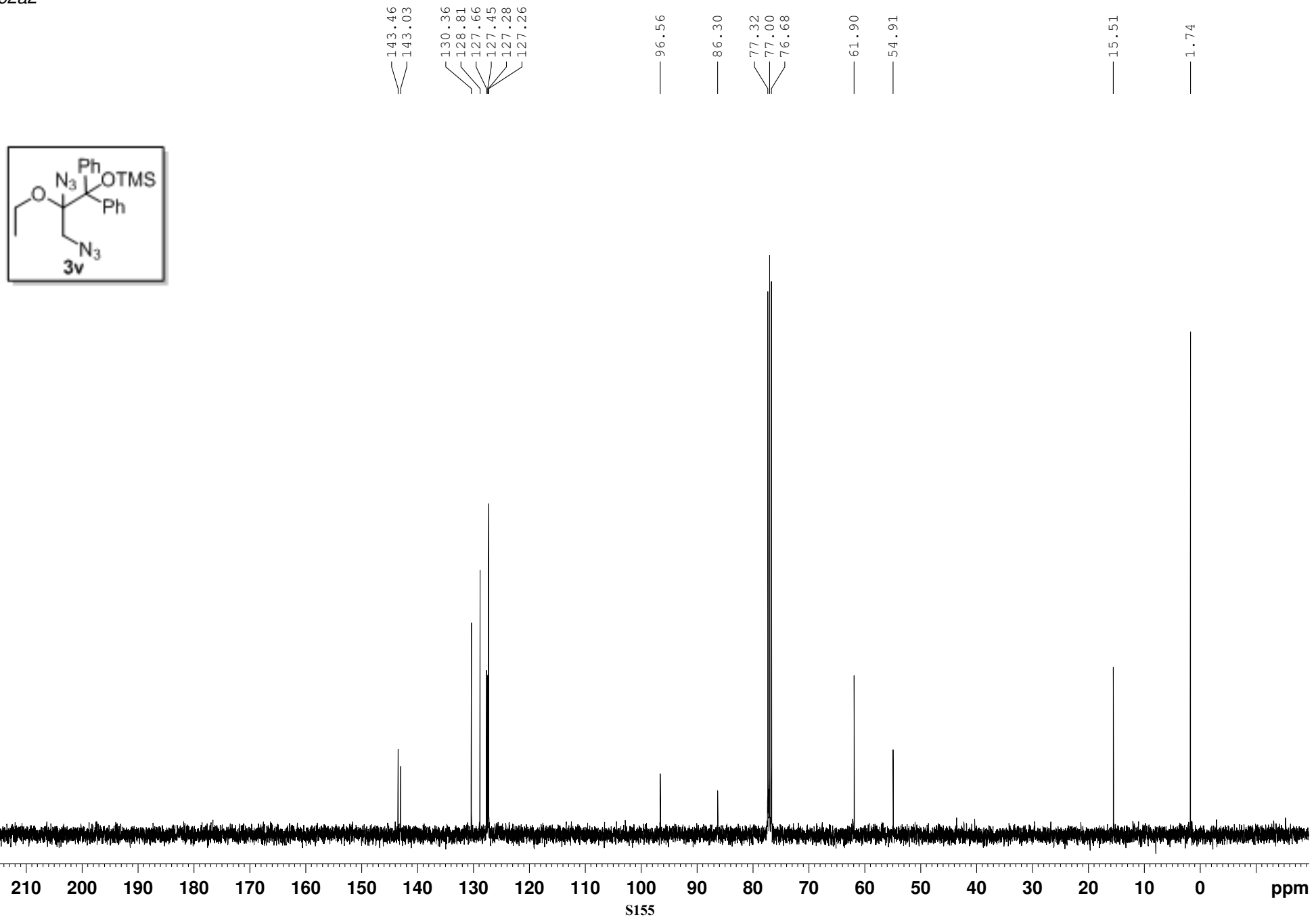
2u

210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 ppm

zz2p62a2


7.561
7.555
7.546
7.536
7.483
7.474
7.465
7.459
7.292
7.283
7.276
7.260
7.253
7.251
7.245
7.243
7.234
4.024
4.007
3.989
3.984
3.966
3.949
3.815
3.781
3.772
3.754
3.732
3.715
3.182
3.148
1.220
1.203
1.185
-0.096
Ph
N3
OTMS
O
Ph
N3
3v
9
8
7
6
5
4
3
2
1
0
–1
–2
ppm
1.97
2.03
6.49
1.04
2.01
1.00
3.05
9.05

zz2p62a2


143.46
143.03
130.36
128.81
127.66
127.45
127.28
127.26
96.56
86.30
77.32
77.00
76.68
61.90
54.91
15.51
1.74
Ph
N3
OTMS
O
Ph
N3
3v
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
ppm

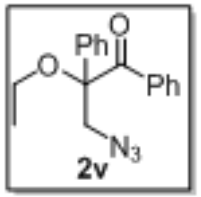
zz2p66a2

8.005
7.986
7.558
7.540
7.475
7.457
7.438
7.406
7.388
7.369
7.335
7.329
7.317
7.309
7.299
7.290
7.270

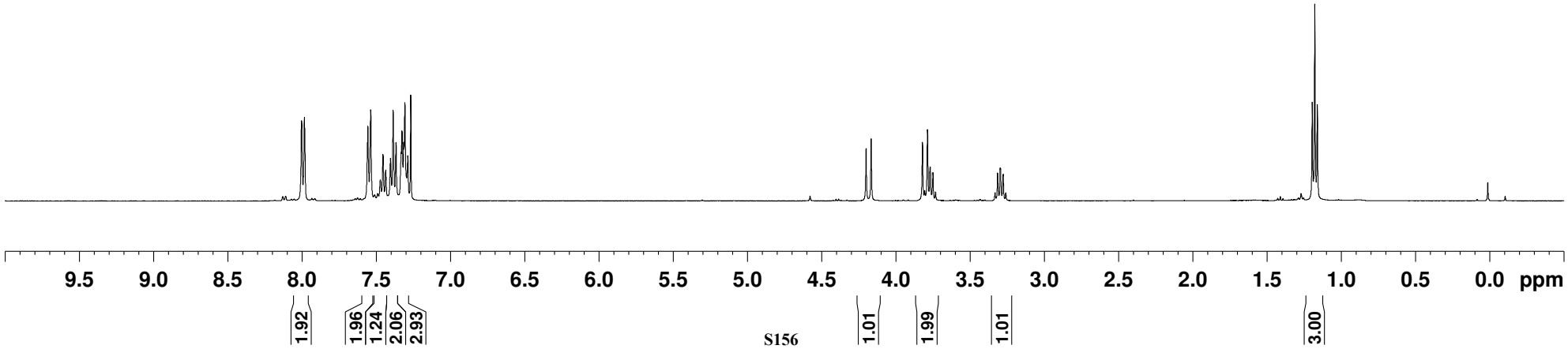
4.202
4.168
3.822
3.807
3.789
3.772
3.769
3.752
3.734
3.334
3.316
3.299
3.296
3.278
3.261

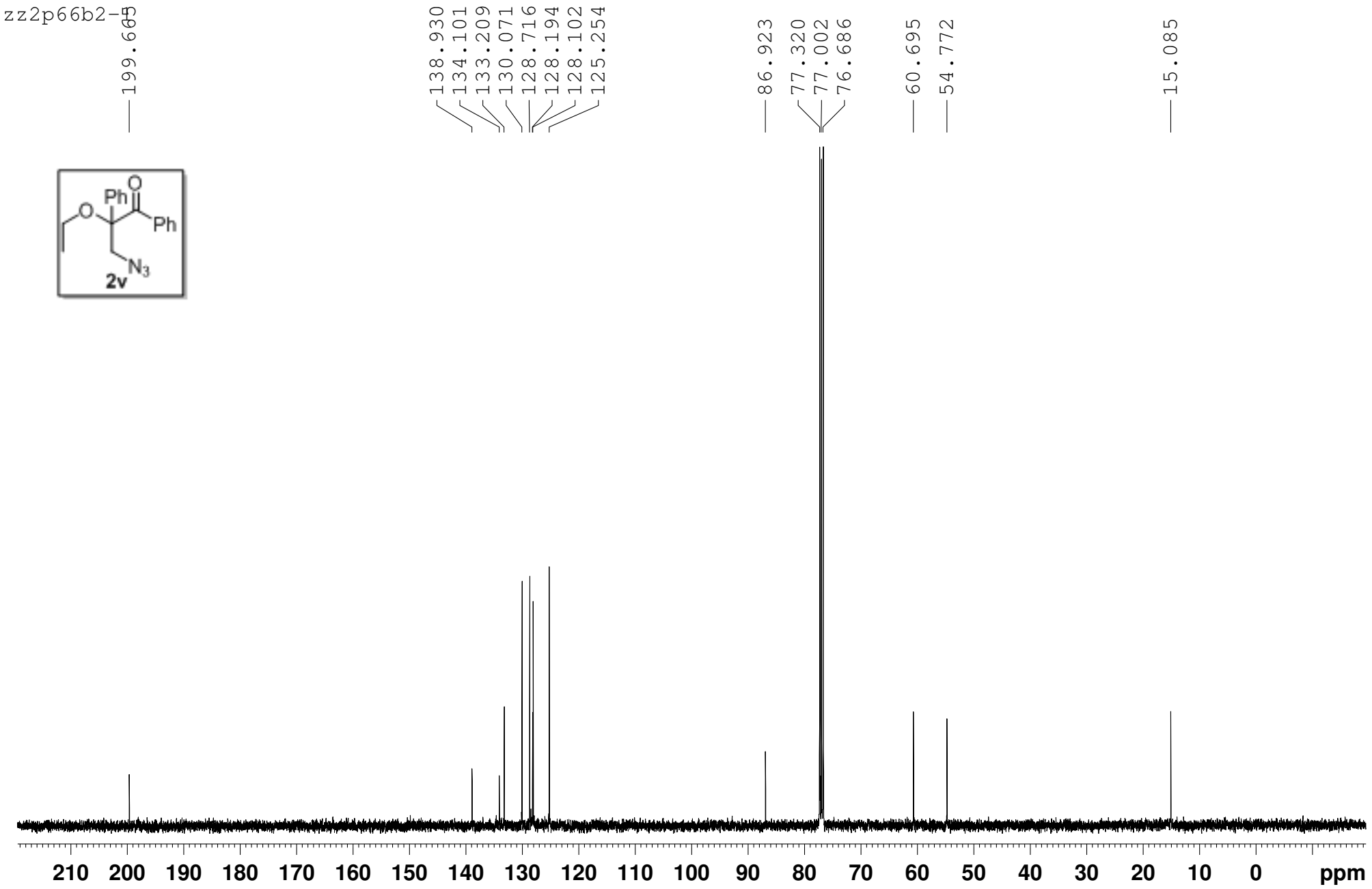
1.196
1.179
1.162

0.014

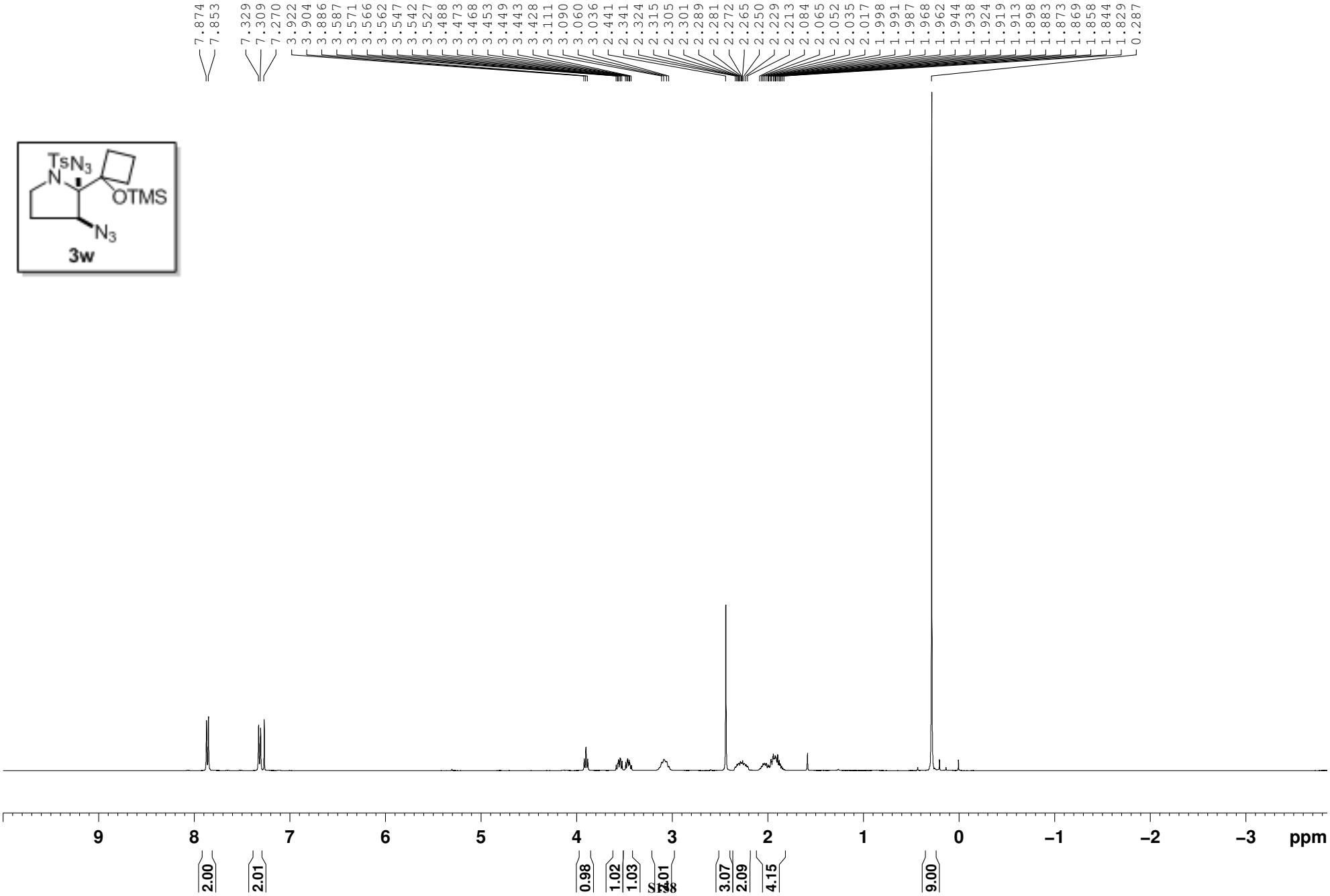


2v

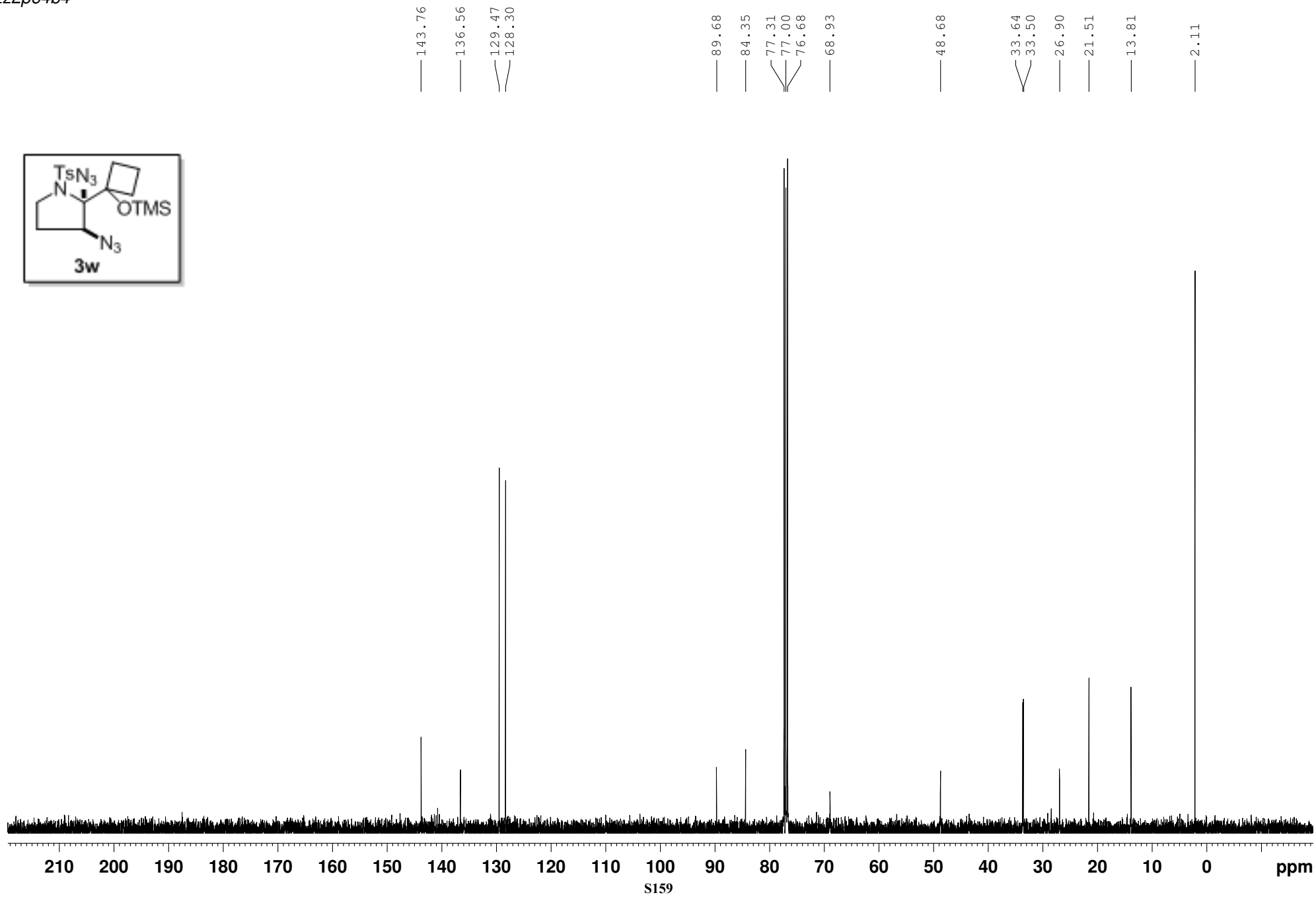



zz2p66b2-13
199.665
138.930
134.101
133.209
130.071
128.716
128.194
128.102
125.254
86.923
77.320
77.002
76.686
60.695
54.772
15.085
Ph
O
O
Ph
N3
2v
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 ppm

zz2p64b4

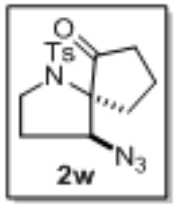

7.874
7.853
7.329
7.309
7.270
3.922
3.904
3.886
3.587
3.571
3.566
3.562
3.547
3.542
3.527
3.488
3.473
3.468
3.453
3.449
3.443
3.428
3.111
3.090
3.060
3.036
2.441
2.341
2.324
2.315
2.305
2.301
2.289
2.281
2.272
2.265
2.250
2.229
2.213
2.084
2.065
2.052
2.035
2.017
1.998
1.991
1.987
1.968
1.962
1.944
1.938
1.924
1.919
1.913
1.898
1.883
1.873
1.869
1.858
1.844
1.829
0.287
TsN3
N
OTMS
N3
3w
9
8
7
6
5
4
3
2
1
0
−1
−2
−3
ppm
2.00
2.01
0.98
1.02
1.03
2.01
3.07
2.09
4.15
9.00

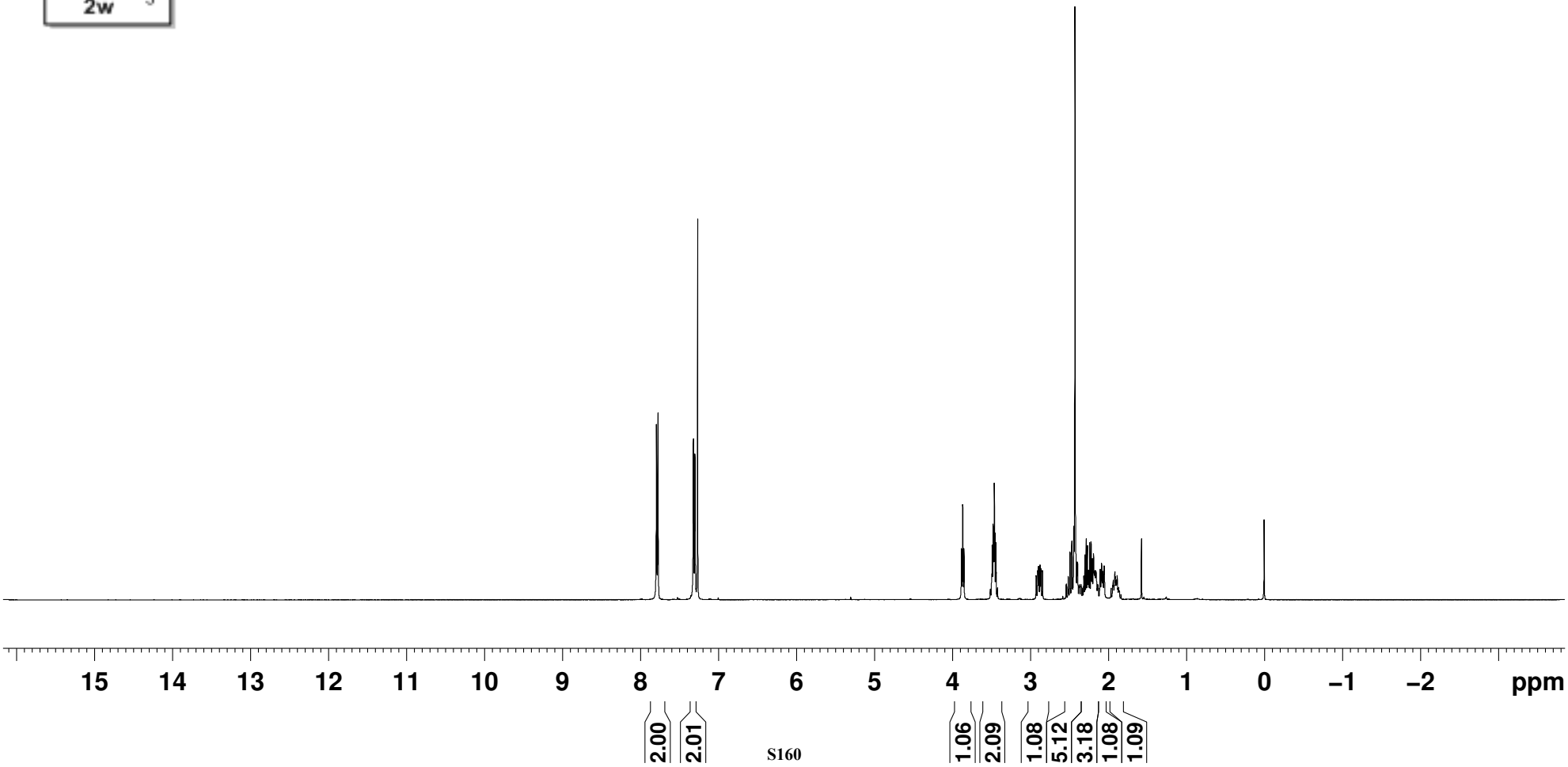
zz2p64b4


143.76
136.56
129.47
128.30
89.68
84.35
77.31
77.00
76.68
68.93
48.68
33.64
33.50
26.90
21.51
13.81
2.11
Ts
N3
N
OTMS
N3
3w
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
ppm

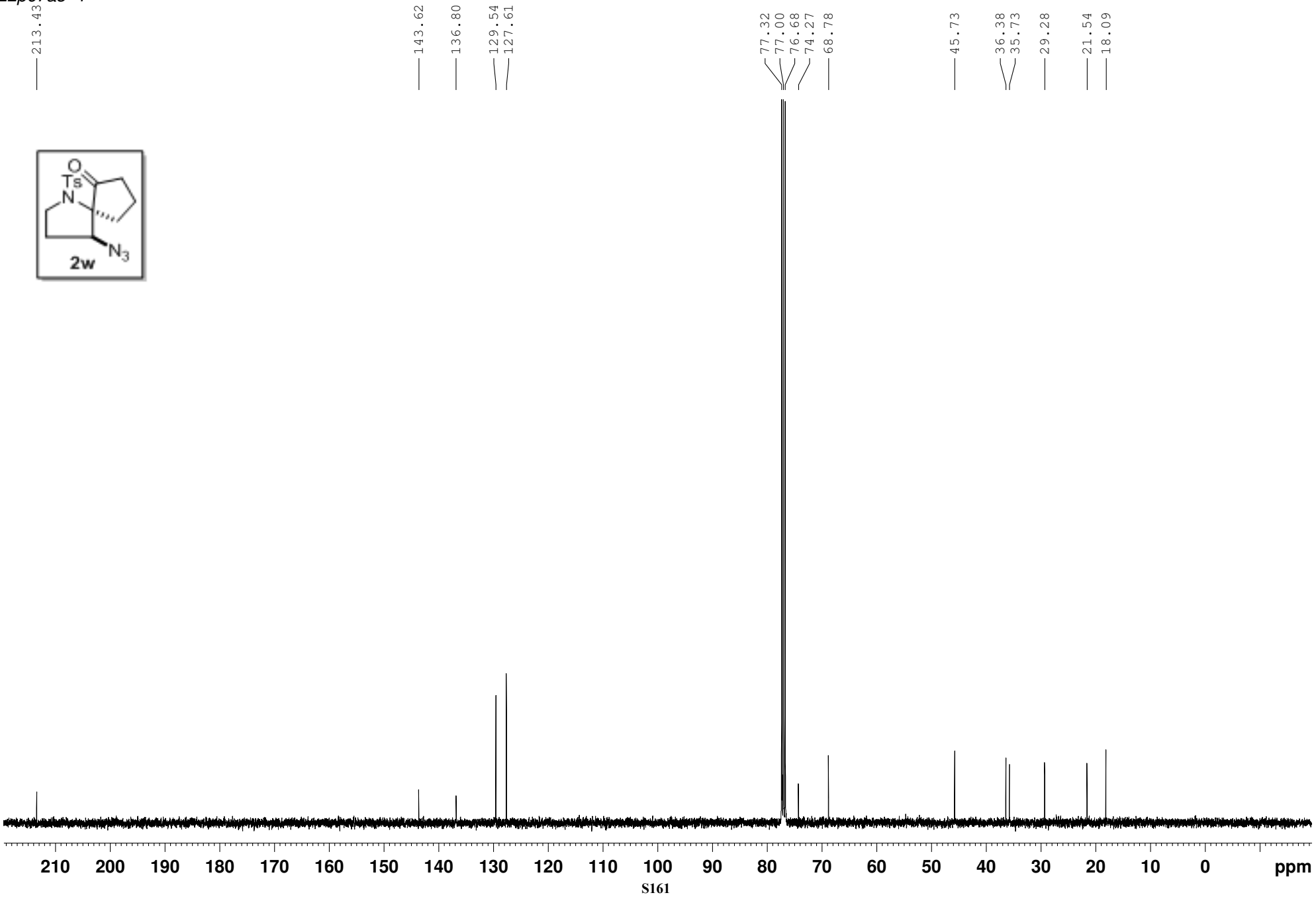
zz2p67a3

7.799 7.778 7.325 7.305 7.270 3.887 3.871 3.855 3.493 3.483 3.478 3.474 3.465 3.459 3.448 3.442 2.929 2.909 2.900 2.896 2.881 2.877 2.867 2.848 2.520 2.517 2.495 2.472 2.470 2.446 2.432 2.403 2.399 2.320 2.303 2.288 2.271 2.261 2.256 2.243 2.225 2.212 2.208 2.193 2.182 2.175 2.164 2.108 2.090 2.075 2.057 1.941 1.919 1.914 1.909 1.896 1.892 0.007





zz2p67a3–1


213.43
143.62
136.80
129.54
127.61
77.32
77.00
76.68
74.27
68.78
45.73
36.38
35.73
29.28
21.54
18.09
O
Ts
N
N3
2w
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
ppm