Supporting Information

Spiro-Fused Six-Membered N-Heterocyclic Carbene: New Scaffold toward Unique Properties and Activities

Bin-Miao Yang, Kai Xiang, Yong-Qiang Tu,* Shi-Heng Zhang, Deng-Tao Yang, Shao-Hua Wang and Fu-Ming Zhang

State Key Laboratory of Applied Organic Chemistry & Department of Chemistry,
Lanzhou University, Lanzhou 730000, P. R. China
E-mail: tuyq@lzu.edu.cn

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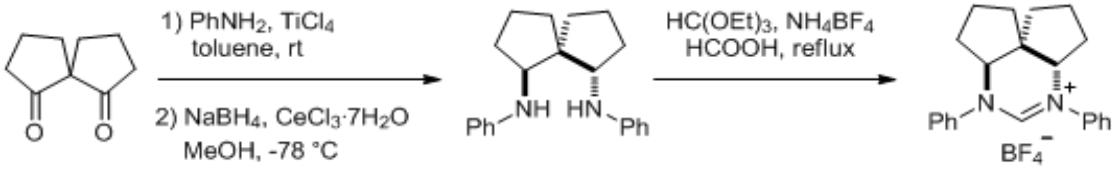
Experimental procedures:

All experiments except for preparation of compound **3** and **1 HBF$_4$** were performed in MBRAUN glove box (H_2O < 0.5 ppm, O_2 < 0.5 ppm). Solvents were dried by standard methods and distilled under argon. ^{1}H, ^{13}C and ^{19}F NMR spectra were recorded on Bruker AX-400 MHz or Varian Mercury-600 MHz instruments and spectral data were reported in ppm. NMR multiplicities are abbreviated as follows: s = singlet, d = doublet, t = triplet, sept = septet, m = multiplet, br = broad signal. 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.

Tetrafluoroborate salt **7 HBF$_4$** [1] was prepared according to literature procedures, other reagents were purchased from commercial sources.

Preparation of *cis,cis*-diamine compound 3 and tetrafluoroborate salt 1 HBF$_4$:[2]



Aniline (2 mL, 22 mmol) was added to a solution of spiro[4,4]nonane-1,6-dione **2** (1.5200 g, 10 mmol) in dry toluene (100 mL) under argon at room temperature, then $TiCl_4$ (2M in dichloromethane, 20 mL, 40 mmol) was added dropwise to the solution. The reaction mixture was stirred at room temperature for 6 hours, then triethylamine (42 ml, 300 mmol) was added slowly. The reaction mixture was stirred for 10 min then cooled to 0 ℃, and saturated aqueous solution of Na_2CO_3 (20 ml) was added. The organic layer was separated and aqueous layer was extracted with dichloromethane (3 × 50 mL). The combined organic layer was washed with brine (100 ml), dried over Na_2SO_4 and concentrated under vacuum to get residue. $CeCl_3·7H_2O$ was added to a solution of the residue in methanol (15 mL) under argon at -78 ℃. Ten min later, $NaBH_4$ (0.8360 g, 22 mmol) was added. The reaction mixture was stirred at -78 ℃ for 10 min and then water (1 mL) was added. The mixture was allowed to warm to room temperature and concentrated under vacuum. The residue was dissolved in water (15 mL) and then extracted with ethyl ethanoate (3 × 30 mL). The combined organic layer was washed with brine (30 mL), dried over Na_2SO_4 and concentrated under vacuum. Purification of the residue by column chromatography on silica gel (eluting with petroleum ether/ethyl acetate 100:1) provided *cis, cis*-N^1,N^6-diphenylspiro[4.4]nonane-1,6-diamine **3** (*cis, cis*-**3** : *cis, trans*-**3** = 5.3 : 1 determined by ^{1}H NMR) as yellow oil (1.4669 g, two steps, 48% yield). **3** (1.4669 g, 4.8 mmol) was dissolved in triethoxymethane (10 ml) and ammonium fluoroborate (2.0160 g, 19.2 mmol). Then catalytic amount of formic acid was added under argon at room temperature and the reaction system was refluxed for 12 hours. The reaction mixture was cooled to room temperature and concentrated under vacuum. Purification of the residue by column chromatography on silica gel (eluting with dichloromethane /methanol 50:1-30:1) provided tetrafluoroborate salt **1 HBF$_4$** (1.8431 g, 95% yield).

***Cis,cis*-diamine compound 3:**

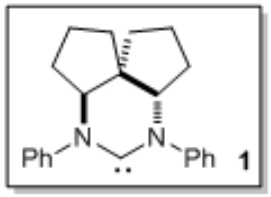
^{1}H NMR (400 MHz, $CDCl_3$, ppm): δ 7.20 (dd, *J* = 8.4, 7.2 Hz, 4H), 6.75 (t, *J* = 7.2 Hz, 2H), 6.65 (d, *J* = 7.6 Hz, 4H), 4.26 (s, 2H), 3.74 (dd, *J* = 4.8, 2.0 Hz, 2H), 2.09-1.98 (m, 2H), 1.90-1.72 (m, 8H), 1.66-1.63 (m, 2H); **^{13}C NMR** (100 MHz, $CDCl_3$, ppm): δ 147.6 (C), 129.1 (CH), 117.4 (CH), 113.8 (CH), 60.5 (CH), 56.5 (C), 35.7 (CH_2),

31.2 (CH_2), 20.2 (CH_2); **MS** (EI) *m/z* (%) 306 (M^+, 23）, 214 (57), 132 (70), 119 (70), 93 (100), 77 (31), 65 (11); **IR** *v* (cm^{-1}): 3386, 2927, 2868, 1601, 1501, 1265, 739, 703; **HRMS** (ESI) calcd for $C_{22}H_{24}BF_3N_2$ $[M+H]^+$: 307.2169, found 307.2165, Error 1.3 ppm.

1 HBF_4:

m.p. 167-168 ℃; **^{1}H NMR** (400 MHz, $CDCl_3$, ppm): δ 7.88 (s, 1H), 7.52-7.49 (m, 4H), 7.45-7.36 (m, 6H), 4.13 (t, *J* = 5.6 Hz, 2H), 2.13-1.99 (m, 4H), 1.98-1.68 (m, 8H); **^{13}C NMR** (100 MHz, $CDCl_3$, ppm): δ 151.5 (CH), 140.0 (C), 130.2 (CH), 129.5 (CH), 125.0 (CH), 62.9 (CH), 50.1 (C), 35.5 (CH_2), 29.7 (CH_2), 19.9 (CH_2); **MS** (EI) *m/z* (%) 317 ($[M-BF_4]^+$, 57), 316 (100), 224 (46), 194 (36), 119 (39), 93 (43), 77 (88), 51 (14); **IR** *v* (cm^{-1}): 2961, 2880, 1642, 1591, 1496, 1064, 765, 699; **HRMS** (ESI) calcd for $C_{22}H_{25}BF_4N_2$ $[M-BF_4]^+$:317.2012, found 317.2008, Error 1.3 ppm.

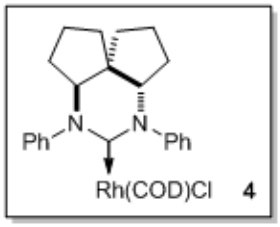
NHC 1:



The synthetic reaction was performed in a glove box. To a reaction flask containing LiHMDS (0.0200g, 0.12 mmol) at room temperature, was added a solution of tetrafluoroborate salt **1 HBF_4** (0.0404 g, 0.1 mmol) in benzene (1.5 mL). The resulting mixture was stirred for 50 min, after which the mixture was filtered off by a PTFF filter. The filtrate was condensed under reduced pressure to afford NHC **1** as a white solid (0.0311 g, 98%). Colorless crystals of **1** suitable for X-ray structure determination were obtained via evaporation of a petroleum ether/toluene (1:2) solution at -40 ℃.

^{1}H NMR (600 MHz, C_6D_6, ppm): δ 7.71 (dd, *J* = 8.4, 1.2 Hz, 4H), 7.18-7.15 (m, 4H), 6.96-6.94 (m, 2H), 3.36 (t, *J* = 6.0 Hz, 2H), 1.69-1.63 (m, 2H), 1.42-1.37 (m, 4H), 1.36-1.28 (m, 2H), 1.23-1.17 (m, 2H), 1.08-1.03 (m, 2H); **^{13}C NMR** (150 MHz, C_6D_6, ppm): δ 244.4 (NCN), 149.6 (C), 128.6 (CH), 123.9 (CH), 122.0 (CH), 56.6 (CH), 50.6 (C), 36.1 (CH_2), 31.2 (CH_2), 21.0 (CH_2).

RhCl(COD)(NHC) 4:

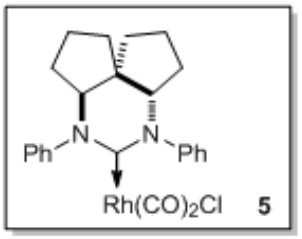


In glove box**,** tetrafluoroborate salt **1 HBF_4** (0.0404 g, 0.1 mmol) was dissolved in benzene (2 mL) then LiHMDS (0.0200 g, 0.12 mmol) was added to the solution. The reaction mixture was stirred at room temperature for 50 min, and then chloro(1,5-cyclooctadiene)rhodium(I) dimer (0.0247 g, 0.05 mmol) was added. Three hours later, the reaction system was removed from the glove box and purified by column chromatography on neutral alumina (eluting with petroleum ether/ethyl acetate 20:1-10:1) provided RhCl(COD)(NHC) **4** as yellow powder (0.0440 g, 74% yield).

m.p. 199-200 ℃ (dec); **^{1}H NMR** (400 MHz, $CDCl_3$, ppm): δ 8.00 (d, *J* = 7.6 Hz, 4H), 7.46 (dd, *J* =15.2, 7.2 Hz, 2H), 7.37-7.32(m, 2H), 4.52-4.43 (m, 2H), 3.62-3.58 (m, 2H), 2.55-2.52 (m, 1H), 2.47-2.43 (m, 1H), 2.40-2.33 (m,

1H), 2.12-1.99 (m, 2H), 1.95-1.84 (m, 1H), 1.83-1.65 (m, 5H), 1.64-1.47 (m, 5H), 1.33-1.17 (m, 5H), 1.15-1.09 (m, 1H); **^{13}C NMR** (100 MHz, $CDCl_3$, ppm): 209.0 (d, NCN, J_{CRh} = 46.0 Hz), 147.1 (C), 145.3 (CH), 129.4 (CH), 128.3 (CH), 128.2 (CH), 127.8 (CH), 126.9 (CH), 126.6 (CH), 95.5 (d, CH, J_{CRh} = 7.0 Hz), 95.2 (d, CH, J_{CRh} = 7.0 Hz), 67.8 (d, CH, J_{CRh} = 16.0 Hz), 67.2 (d, CH, J_{CRh} = 16.0 Hz), 64.9 (CH), 64.1 (CH), 51,8 (C), 37.4 (CH_2), 34.2 (CH_2), 32.6 (CH_2), 31.4 (CH_2), 31.3 (CH_2), 31.1 (CH_2), 27.6 (CH_2), 27.5 (CH_2), 21.8 (CH_2), 20.0 (CH_2); **MS** (EI) *m/z* (%) 562 (M+, <1%), 419 (22), 418(100), 317(19), 132(7), 77(17), 67(19), 54(19); **IR** *v* (cm^{-1}): 2935, 2869, 1594, 1468, 1278, 759, 703; **HRMS** (ESI) calcd for $C_{30}H_{36}ClN_2Rh$ [M-Cl]$^+$: 527.1928, found 527.1952, Error 4.6 ppm.

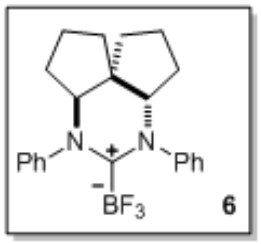
RhCl(CO)$_2$(NHC) 5:



Compound **4** (0.0208 g, 0.037 mmol) was dissolved in dichloromethane (2 mL), and carbon monoxide was bubbled through the solution for 1.5 hours at room temperature. The reaction mixture was concentrated and purified by column chromatography on neutral alumina (eluting with petroleum ether/ethyl acetate 20:1-10:1) provided light yellow powder **5** (0.0180 g, 95% yield).

^{1}H NMR (400 MHz, $CDCl_3$, ppm): δ 7.53-7.51 (m, 2H), 7.45-7.41 (m, 4H), 7.38-7.33 (m, 4H), 3.72-3.68 (m, 2H), 2.18-2.08 (m, 2H), 1.96-1.90 (m, 3H), 1.87-1.79 (m, 2H), 1.77-1.69 (m, 5H); **^{13}C NMR** (150 MHz, $CDCl_3$, ppm): 189.9 (d, NCN, J_{CRh} = 38.1 Hz), 186.6 (d, CO, J_{CRh} = 54.0 Hz), 183.3 (d, CO, J_{CRh} = 78.0 Hz), 145.0 (C), 144.5 (C), 129.3 (CH), 129.2 (CH), 129.1 (CH), 128.9 (CH), 128.0 (CH), 127.8 (CH), 64.4 (CH), 63.7 (CH), 50.2 (C), 36.3 (CH_2), 35.1 (CH_2), 31.3 (CH_2), 30.4 (CH_2), 20.3 (CH_2), 20.0 (CH_2); **MS** (EI) *m/z* (%) 510 (M+, <1%), 419 (8), 418 (30), 366 (48), 317 (100), 194 (10), 93 (66), 77 (90), 67 (53), 55 (41); **IR** *v* (cm^{-1}): 2070.76 (CO Ⅰ), 1990.55 (CO Ⅱ) (DCM) or 2059.1 (CO Ⅰ), 1983.2(CO Ⅱ) (KBr disk); **HRMS** (ESI) calcd for $C_{24}H_{24}ClN_2O_2Rh$ [M-Cl]+: 475.0887, found 475.0900, Error 2.7 ppm.

NHC-BF$_3$ 6:

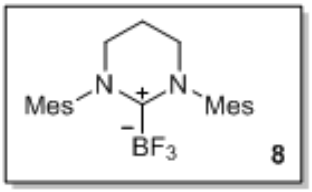


In glove box, a solution of tetrafluoroborate salt **1 HBF$_4$** (0.0404 g, 0.1 mmol) in benzene/tetrahydrofuran (20/1) mixture (1.5 mL) was added to LiHMDS (0.0200 g, 0.12 mmol) at room temperature. The reaction mixture was stirred for 12 hours, then the reaction system was removed from the glove box and purified by column chromatography on neutral alumina (eluting with petroleum ether/ethyl acetate c 20:1-10:1) provided **6** as white solid (0.0365 g, 95% yield).

m.p. 171-172 ℃; **^{1}H NMR** (400 MHz, $CDCl_3$, ppm): δ 7.44-7.32 (m, 10H), 3.60 (t, *J* = 6.4 Hz, 2H), 2.15-2.08 (m, 2H), 1.95-1.81 (m, 6H), 1.77-1.69 (m, 4H); **^{13}C NMR** (150 MHz, $CDCl_3$, ppm): 176.2 (C), 144.0 (C), 130.1 (CH), 128.9 (CH), 128.1 (CH), 127.0 (CH), 65.5 (CH), 50.4 (C), 35.9 (CH_2), 31.1 (CH_2), 20.4 (CH_2); **^{19}F NMR** (376

MHz, $CDCl_3$, ppm): δ 133.33 (q, 3F, J_{BF} = 36.8 Hz); **MS** (EI) *m/z* (%) 384 (M+, <1%), 315 (100), 224 (26), 194 (28), 118 (25), 77 (84), 51 (14); **IR** *v* (cm^{-1}): 2930, 2869, 1596, 1515, 1070, 945, 767, 701; **HRMS** (ESI) calcd for $C_{22}H_{24}BF_3N_2$ $[M+Na]^+$: 406.1913, found 406.1917, Error 1.0 ppm.

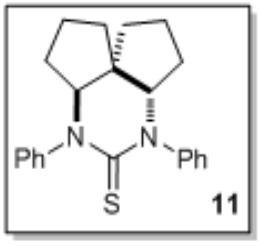
NHC-BF_3 8:



In glove box, a solution of tetrafluoroborate salt **7 HBF_4** (0.0204 g, 0.1 mmol) in benzene/tetrahydrofuran (20/1) mixture (1.5 mL) was added to LiHMDS (0.0200 g, 0.12 mmol) at room temperature. The reaction mixture was stirred for 12 hours, and then removed from the glove box and purified by column chromatography on neutral alumina (eluting with dichloromethane/methanol 100:1) provided **8** as white solid (0.0191g, 99% yield).

m.p. 251-253 ℃; **^{1}H NMR** (400 MHz, CD_2Cl_2, ppm): δ 6.92 (s, 4H), 3.46 (t, *J* = 5.6 Hz, 4H), 2.36-2.31 (m, 2H), 2.29 (s, 6H), 2.28 (s, 12H); **^{13}C NMR** (150 MHz, CD_2Cl_2, ppm): δ 177.9 (C), 141.3 (C), 138.0 (C), 134.6 (C) 129.3 (CH), 48.7 (CH_2), 21.1 (CH_3), 21.0 (CH_2), 17.8 (CH_3); **^{19}F NMR** (376 MHz, CD_2Cl_2, ppm): δ -138.28 (q, 3F, J_{FB} = 31.2 Hz); **MS** (EI) *m/z* (%) 388 (M+, <1%), 369 (5), 320 (48), 159 (100), 146 (32), 131 (22), 91 (33), 77 (15), 65 (6); **IR** *v* (cm^{-1}): 2930, 2865, 1611, 1531, 1109, 1066, 940, 853; **HRMS** (ESI) calcd for $C_{22}H_{24}BF_3N_2$ $[M+NH_4]^+$: 405.2672, found 405.2683, Error 2.7 ppm.

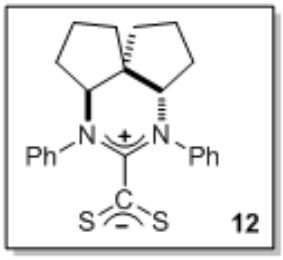
Thiourea 11:



In glove box**,** tetrafluoroborate salt **1 HBF_4** (0.0202 g, 0.05 mmol) was dissolved in benzene (1 mL) then LiHMDS (0.0100 g, 0.06 mmol) was added to the solution. The reaction mixture was stirred at room temperature for 50 min, then S_8 (0.0256 g, 0.1 mmol) was added. Twelve hours later, the reaction system was removed from the glove box and purified by column chromatography on neutral alumina (eluting with petroleum ether/ethyl acetate 20:1-10:1) provided thiourea **11** as white solid (0.0167 g , 96 % yield).

m.p. 169-171 ℃; **^{1}H NMR** (400 MHz, $CDCl_3$, ppm): δ 7.41-7.37 (m, 4H), 7.30-7.25 (m, 6H), 3.76 (t, *J* = 6.8 Hz, 2H), 2.21-2.12 (m, 2H), 2.04-1.87 (m, 6H), 1.77-1.67 (m, 4H); **^{13}C NMR** (100 MHz, $CDCl_3$, ppm): 182.0 (C), 146.4 (C), 129.0 (CH), 127.9 (CH), 126.8 (CH), 68.6 (CH), 54.2 (C), 37.4 (CH_2), 32.5 (CH_2), 22.2 (CH_2); **MS** (EI) *m/z* (%) 348 (M^+, 62), 347 (100), 227 (11), 93 (16), 77 (26), 67 (7), 51 (8); **IR** *v* (cm^{-1}): 2925, 2854, 1593, 1493, 1267, 752, 692; **HRMS** (ESI) calcd for $C_{22}H_{24}N_2S$ $[M+H]^+$: 349.1733, found 349.1730, Error 0.9 ppm.

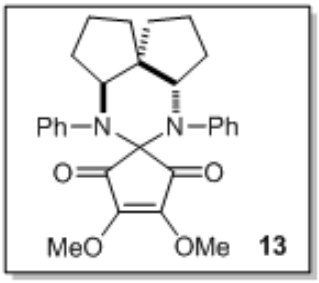
Compound 12:



In glove box**,** tetrafluoroborate salt **1 HBF$_4$** (0.0202 g, 0.05 mmol) was dissolved in benzene (1 mL) then LiHMDS (0.0100 g, 0.06 mmol) was added to the solution. The reaction mixture was stirred at room temperature for 50 min, then CS_2 (0.003 ml, 0.05 mmol) was added. Twelve hours later, the reaction system was removed from the glove box and purified by column chromatography on neutral alumina (eluting with petroleum ether/EtOAc 20:1-10:1) provided **12** as red solid (0.0173 g , 88% yield).

^{1}H NMR (400 MHz, $CDCl_3$, ppm): δ 7.50 (d, *J* = 6.4 Hz, 4H), 7.33-7.28 (m, 6H), 3.82 (t, *J* = 5.6 Hz, 2H), 2.17-2.10 (m, 4H), 2.09-1.93 (m, 4H), 1.86-1.75 (m, 4H); **^{13}C NMR** (100 MHz, $CDCl_3$, ppm): 229.0 (NCN),163.9 (SCS), 140.6 (C), 129.2 (CH), 128.7 (CH), 128.6 (CH), 65.7 (CH), 50.5 (C), 35.9 (CH_2), 30.4 (CH_2), 20.2 (CH_2); **MS** (EI) *m/z* (%) 392 (M^+, 40), 347 (22), 315 (100), 224 (26), 93 (45), 77 (99), 67 (19), 51 (15); **IR** *v* (cm^{-1}): 2960, 2870, 1548, 1487, 1058, 773, 697; **HRMS** (ESI) calcd for $C_{23}H_{24}N_2S_2$ $[M+H]^+$: 393.1454, found 393.1451, Error 0.8 ppm.

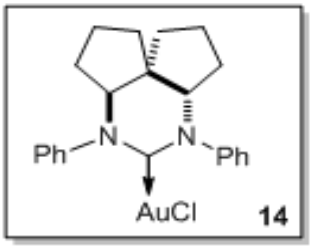
Compound 13:



In glove box**,** tetrafluoroborate salt **1 HBF$_4$** (0.0202 g, 0.05 mmol) was dissolved in benzene (1 mL) then LiHMDS (0.0100 g, 0.06 mmol) was added to the solution. The reaction mixture was stirred at room temperature for 50 min, then 3,4-dimethoxycyclobut-3-ene-1,2-dione (0.0118 g, 0.06 mmol) was added. Twelve hours later, the reaction system was removed from the glove box and purified by column chromatography on silica gel (eluting with petroleum ether/ethyl acetate 20:1-15:1) provided **13** as rufous solid (0.0132 g , 58% yield).

^{1}H NMR (400 MHz, $CDCl_3$, ppm): δ 7.20-7.16 (m, 4H), 7.11-7.05 (m, 4H), 6.97-6.95 (m, 2H), 4.37 (dd, *J* = 6.0, 3.6 Hz, 1H), 4.15 (dd, *J* = 5.2, 2.0 Hz, 1H), 4.09 (s, 3H), 3.28 (s, 3H), 2.20-2.13 (m, 1H), 1.82-1.72 (m, 1H), 1.71-1.57 (m, 4H), 1.56-1.41 (m, 5H), 1.34-1.26 (m, 1H); **^{13}C NMR** (100 MHz, $CDCl_3$, ppm): δ 204.0 (C), 180.4 (C), 170.1 (C), 149.2 (C), 145.6 (C), 144.7 (C),129.6 (CH), 128.8 (CH), 128.5 (CH), 128.3 (CH), 126.4 (CH), 125.4 (CH), 81.2 (C), 64.2 (CH), 63.5 (CH), 60.1 (CH_3), 59.1 (CH_3), 57.1 (C), 38.3 (CH_2), 37.6 (CH_2), 32.4 (CH_2), 31.2 (CH_2), 23.0 (CH_2), 22.3 (CH_2); **MS** (EI) *m/z* (%) 458 (M^+, 4), 401 (100), 387 (61), 371 (37), 328 (11), 77 (39), 67 (9), 55 (6); **IR** *v* (cm^{-1}): 2953, 2870, 1707, 1593, 1492, 737, 704; **HRMS** (ESI) calcd for $C_{28}H_{30}N_2O_4$ $[M+H]^+$: 459.2278, found 459.2271, Error 1.5 ppm.

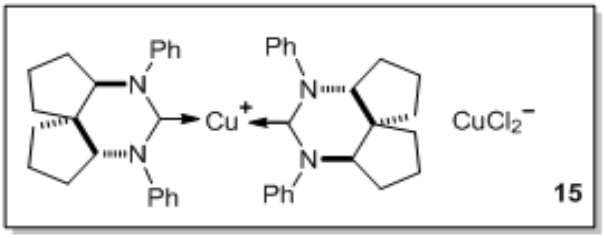
Au(NHC)Cl 14:



In glove box**,** tetrafluoroborate salt **1 HBF$_4$** (0.0607 g, 0.15 mmol) was dissolved in benzene (2 mL) then LiHMDS (0.0301 g,0.18 mmol) was added to the solution. The reaction mixture was stirred at room temperature for 50 min, and then Au(Me_2S)Cl (0.0531 mg, 0.18 mmol) was added. Twelve hours later, the reaction system was removed from the glove box and purified by column chromatography on neutral alumina (eluting with petroleum ether/ethyl acetate 20:1-10:1) provided Au(NHC)Cl **14** as white powder (0.0821 g , 99%).

m.p. 204-206 ℃; **^{1}H NMR** (400 MHz, $CDCl_3$, ppm): δ 7.42-7.39 (m, 4H), 7.36-7.32(m, 6H), 3.72 (t, *J* = 6.0 Hz, 2H), 2.08,-2.01 (m, 2H), 2.00-1.89 (m, 2H), 1.88-1.80 (m, 2H), 1.78-1.69 (m, 6H); **^{13}C NMR** (100 MHz, $CDCl_3$, ppm): δ 189.4 (NCN), 146.2 (C), 129.6 (CH), 128.2 (CH), 127.6 (CH), 63.6 (CH), 49.9 (C), 35.8 (CH_2), 30.9 (CH_2), 20.2 (CH_2); **MS** (EI) *m/z* (%) 548 (M+, 100), 513 (22), 315 (42), 194 (12), 93 (17), 77 (46), 67 (9), 51 (8); **IR** *v* (cm^{-1}): 2952, 2871, 1595, 1494, 1275, 767, 699; **HRMS** (ESI) calcd for $C_{22}H_{24}AuClN_2$ $[2M\text{-}Cl]^+$: 1061.2893, found 1061.2957, Error 6.0 ppm.

Cu(NHC)$_2$ CuCl$_2$ 15:



In glove box**,** tetrafluoroborate salt **1 HBF$_4$** (0.0404 g, 0.1 mmol) and copper (I) chloride (0.0106 g, 0.105 mmol) were dissolved in benzene (1.5 ml) then LiHMDS (0.0200 g, 0.12 mmol) was added to the solution. The reaction mixture was stirred at room temperature for 12 hours, then the mixture was filtered off by PTFF filter. The filtrate was evaporated under reduced pressure to get crude product **15**. **15** was grown from a toluene/tetrahydrofuran (20:1) solution at -40 ℃ as colorless crystals (0.0294 g, 71 % yield).

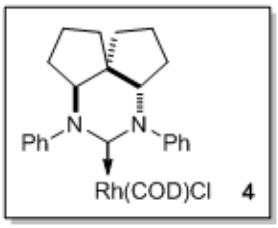
m.p. 99-101 ℃; **^{1}H NMR** (600 MHz, C_6D_6, ppm): δ 7.20-7.15 (m, 16H), 7.07-7.04 (m, 4H), 3.12 (t, *J* = 4.0 Hz, 4H), 1.47-1.41 (m, 4H), 1.41-1.36 (m, 8H), 1.36-1.27 (m, 4H), 1.26-1.16 (m, 4H), 1.12-1.09 (m, 4H); **^{13}C NMR** (150 MHz, C_6D_6, ppm): 198.5 (C), 146.8 (C), 129.7 (CH), 128.3 (CH), 126.2 (CH), 61.4 (CH), 49.7 (C), 35.5 (CH_2), 30.7 (CH_2), 20.2 (CH_2); **MS** (EI) *m/z* (%) 695 ($[M\text{-}CuCl_2]^+$, <1%), 414 (88), 379 (15), 315 (100), 224 (32), 195 (24), 132 (12), 93 (31), 77 (60), 67 (11), 51 (11); **IR** *v* (cm^{-1}): 2959, 2866, 1593, 1490, 1351, 1275, 766, 702; **HRMS** (ESI) calcd for $C_{44}H_{48}N_4Cu_2Cl_2$ $[M\text{-}CuCl_2]^+$: 695.3170, found 695.3185 Error 2.2 ppm.

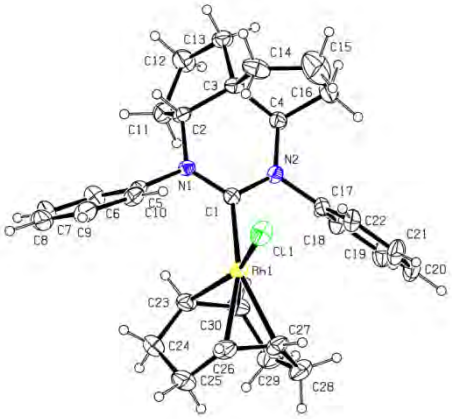
Reference

1 M. Mayr, K. Wurst, K.-H, Ongania, M. R. Buchmeiser, *Chem. Eur. J.* **2004**, *10*, 1256.

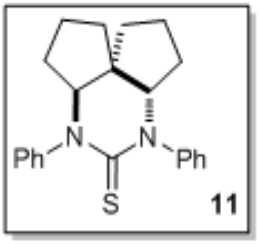
2 a) A. R. Katritzky, A. Denisenko, S. N. Denisenko, M. Arend, *J. Heterocycl. Chem.* **2000**, *37*, 1309; b) S. Saba, A. Brescia, M. K. Kaloustian, *Tetrahedron Lett.* **1991**, *32*, 5031.

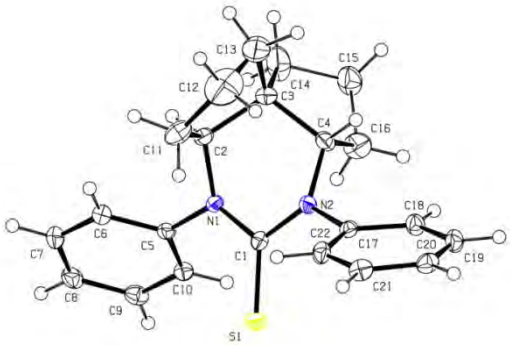
2. X-Ray ellipsoid plots of 4, 11, 14, and 15



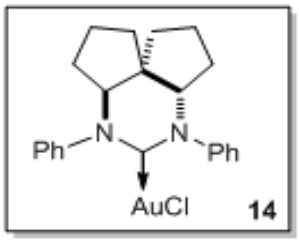


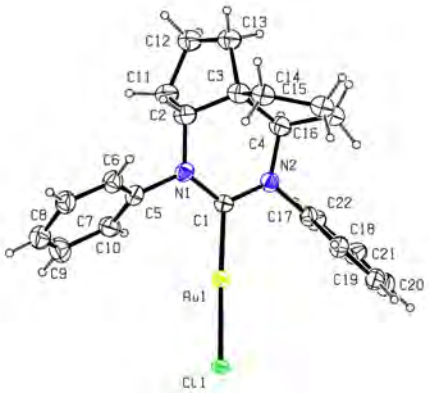
X-ray structures of **4** with thermal ellipsoids was drawn at 30% probability level. The crystal structure has been deposited at the Cambridge Crystallographic Data Centre and allocated the deposition number: 973602.



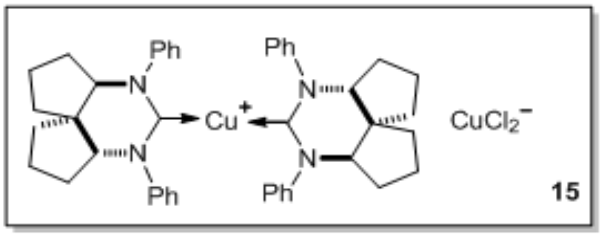


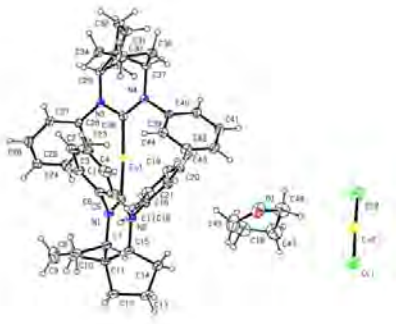
X-ray structures of **11** with thermal ellipsoids was drawn at 30% probability level. The crystal structure has been deposited at the Cambridge Crystallographic Data Centre and allocated the deposition number: 973596.





X-ray structures of **14** with thermal ellipsoids was drawn at 30% probability level. The crystal structure has been deposited at the Cambridge Crystallographic Data Centre and allocated the deposition number: 973598.





X-ray structures of **15** with thermal ellipsoids was drawn at 30% probability level. The crystal structure has been deposited at the Cambridge Crystallographic Data Centre and allocated the deposition number: 973600.

3. Selected Bond Lengths and Angles of NHC 1 , Bis-(*p*-nitrobenaoate) of Diol 2′ and 6-Mes

Table 1. Selected Bond Lengths (Å) and Angles (deg) of NHC **1** and Bis-(*p*-nitrobenaoate) of Diol **2′**.

	1	**2′**
C3-C4	1.528	1.520
C3-C2	1.530	1.520
C4-C16	1.544	1.514
C2-C11	1.533	1.514
C16-C15	1.526	1.521
C11-C12	1.539	1.521
C15-C14	1.504	1.486
C13-C12	1.546	1.486
C14-C3	1.532	1.524
C13-C3	1.534	1.524
C2-C3-C4	110.65	117.55
C2-C3-C13	100.28	103.31
C4-C3-C14	105.46	103.31
C3-C4-N(O)2	110.10	105.23
C16-C4-N(O)2	111.05	108.94
C3-C2-N(O)1	109.08	105.23
C11-C2-N(O)1	115.20	108.94

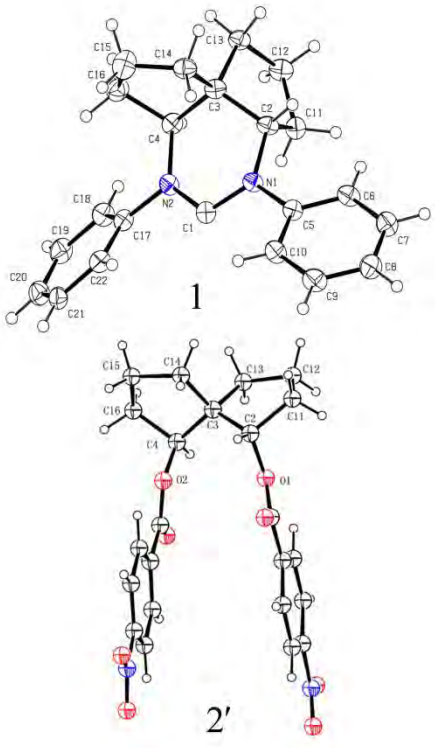
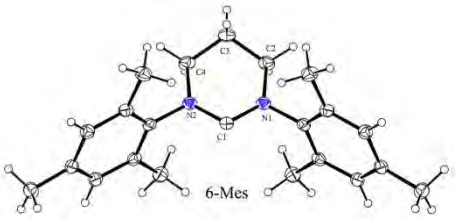
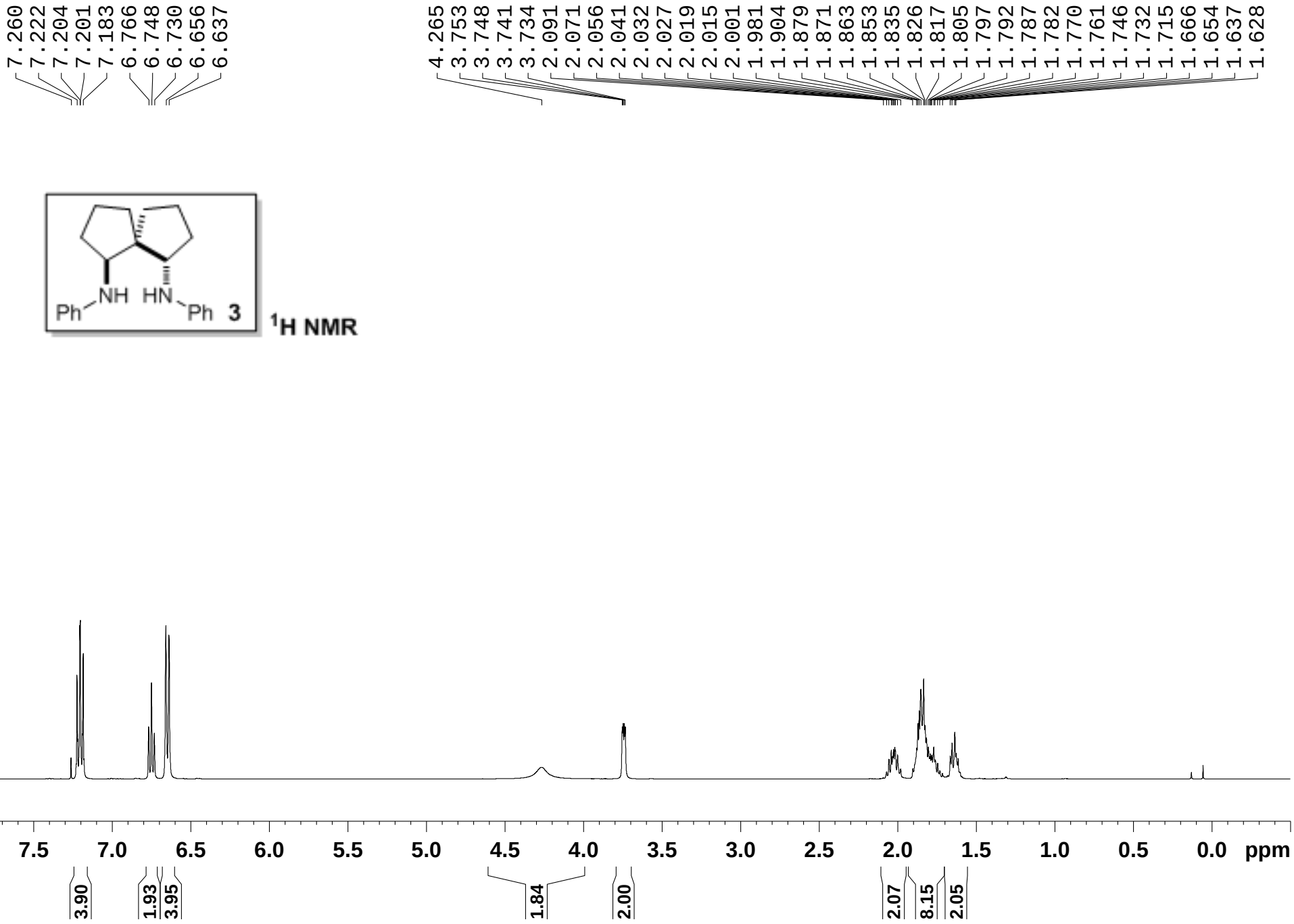


Table 2. Selected Angles (deg) of NHC **1** and **6-Mes**.

	1	**6-Mes**
C2-C3-C4	110.65	108.39
C3-C4-N2	110.10	108.88
C3-C2-N1	110.20	108.88
C4-N2-C1	127.78	126.27
C2-N1-C1	124.61	126.27
N1-C1-N2	115.56	114.65

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7.204
7.201
7.183
6.766
6.748
6.730
6.656
6.637
4.265
3.753
3.748
3.741
3.734
2.091
2.071
2.056
2.041
2.032
2.027
2.019
2.015
2.001
1.981
1.904
1.879
1.871
1.863
1.853
1.835
1.826
1.817
1.805
1.797
1.792
1.787
1.782
1.770
1.761
1.746
1.732
1.715
1.666
1.654
1.637
1.628
Ph
NH
HN
Ph
3
1H NMR
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
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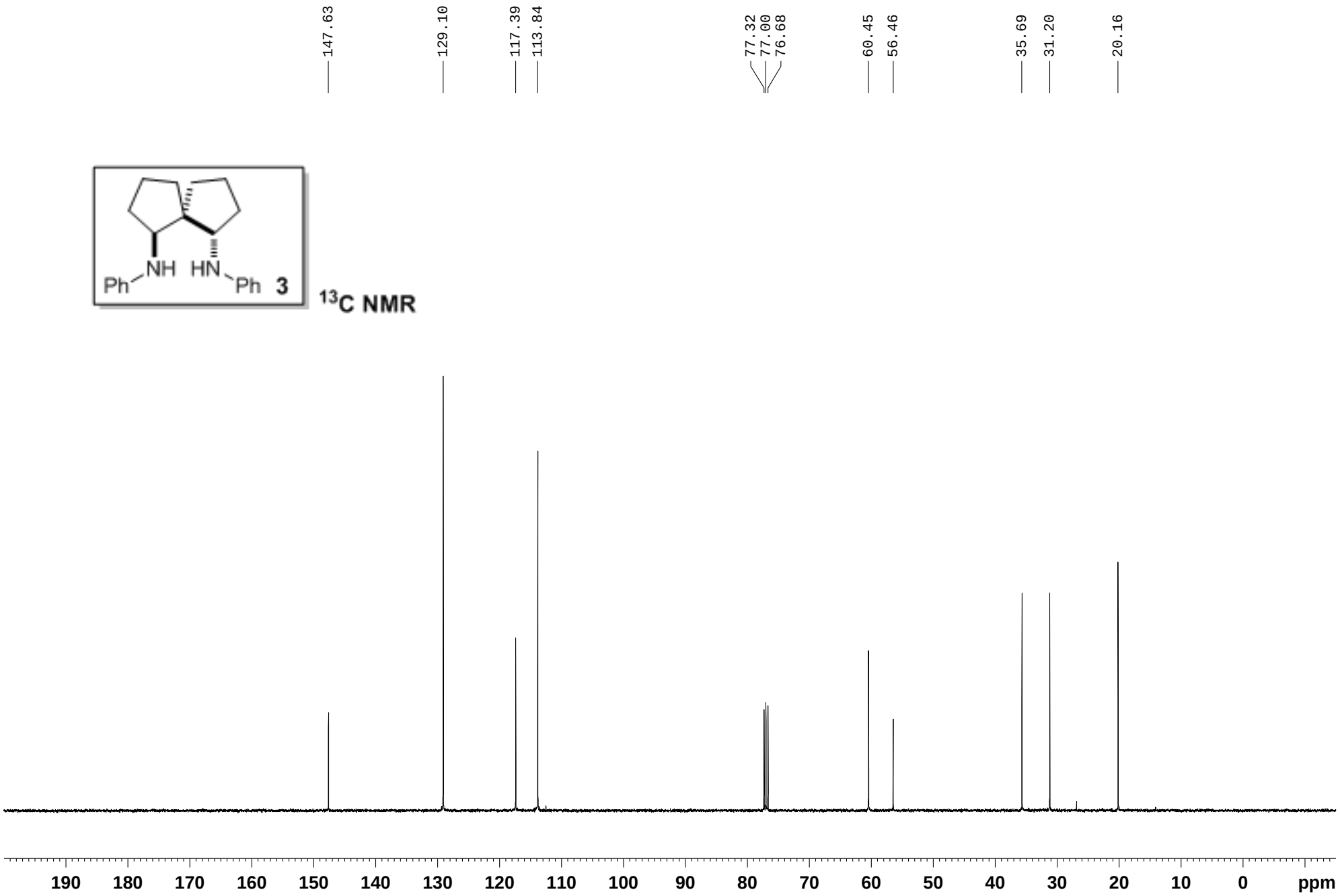
1.93
3.95
1.84
2.00
2.07
8.15
2.05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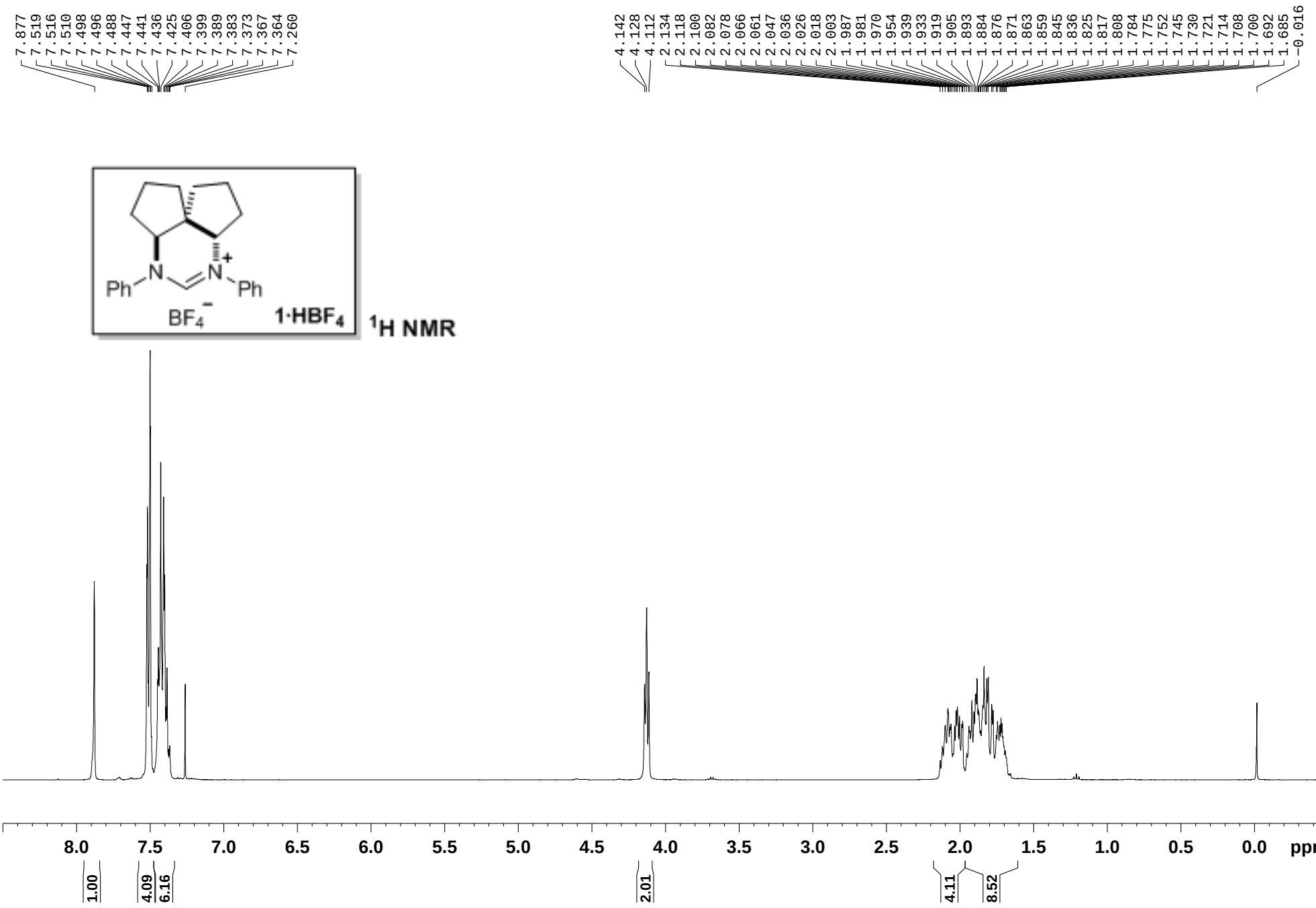
129.10
117.39
113.84
77.32
77.00
76.68
60.45
56.46
35.69
31.20
20.16
Ph NH HN Ph 3
13C NMR
190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 ppm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7.436
7.425
7.406
7.399
7.389
7.383
7.373
7.367
7.364
7.260
4.142
4.128
4.112
2.134
2.118
2.100
2.082
2.078
2.066
2.061
2.047
2.036
2.026
2.018
2.003
1.987
1.981
1.970
1.954
1.939
1.933
1.919
1.905
1.893
1.884
1.876
1.871
1.863
1.859
1.845
1.836
1.825
1.817
1.808
1.784
1.775
1.752
1.745
1.730
1.721
1.714
1.708
1.700
1.692
1.685
-0.016
Ph
N
N+
Ph
BF4−
1·HBF4
1H NMR
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7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
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1.0
0.5
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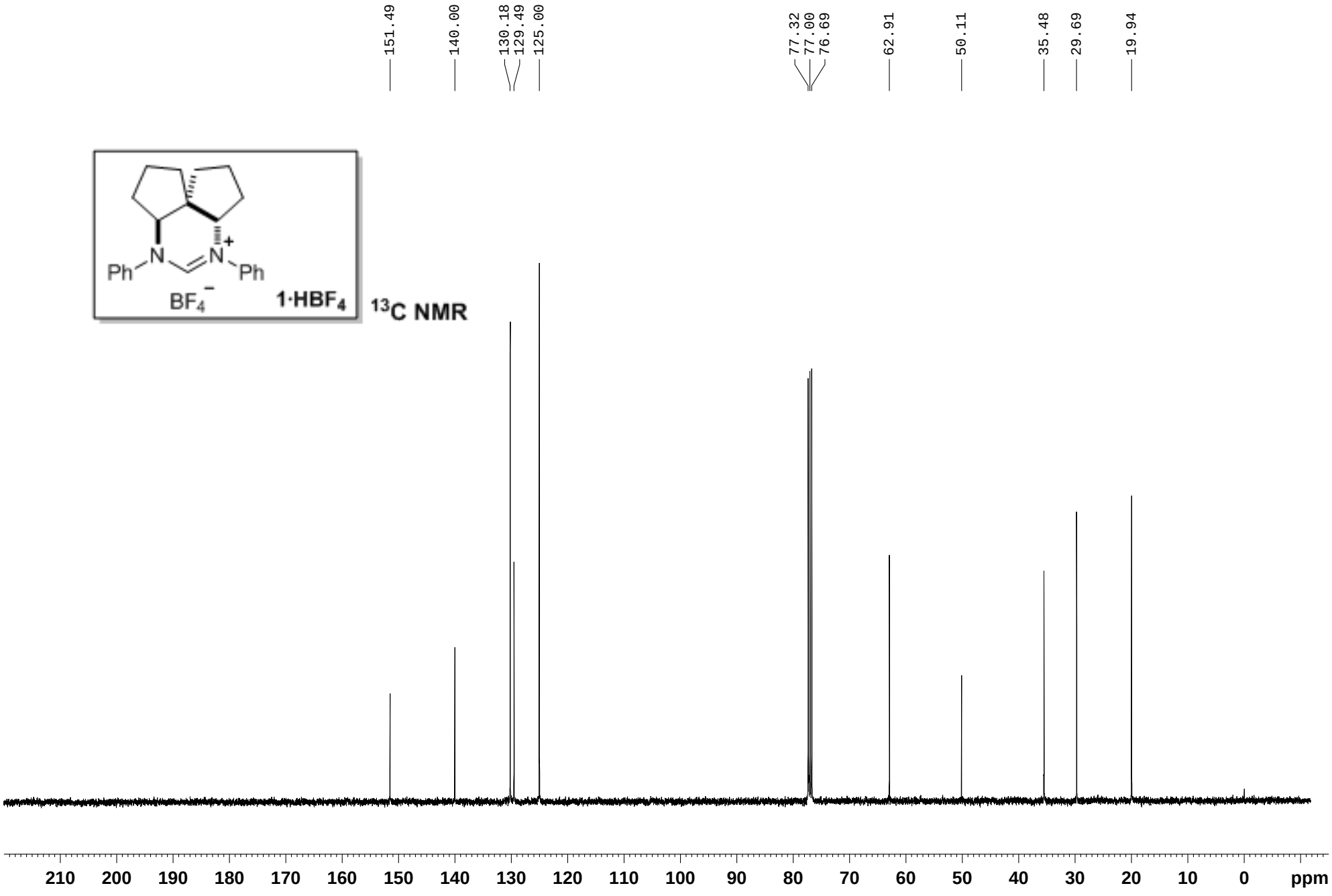
4.09
6.16
2.01
4.11
8.52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129.49
125.00
77.32
77.00
76.69
62.91
50.11
35.48
29.69
19.94
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N+
Ph
BF4−
1·HBF4
13C NMR
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200
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180
170
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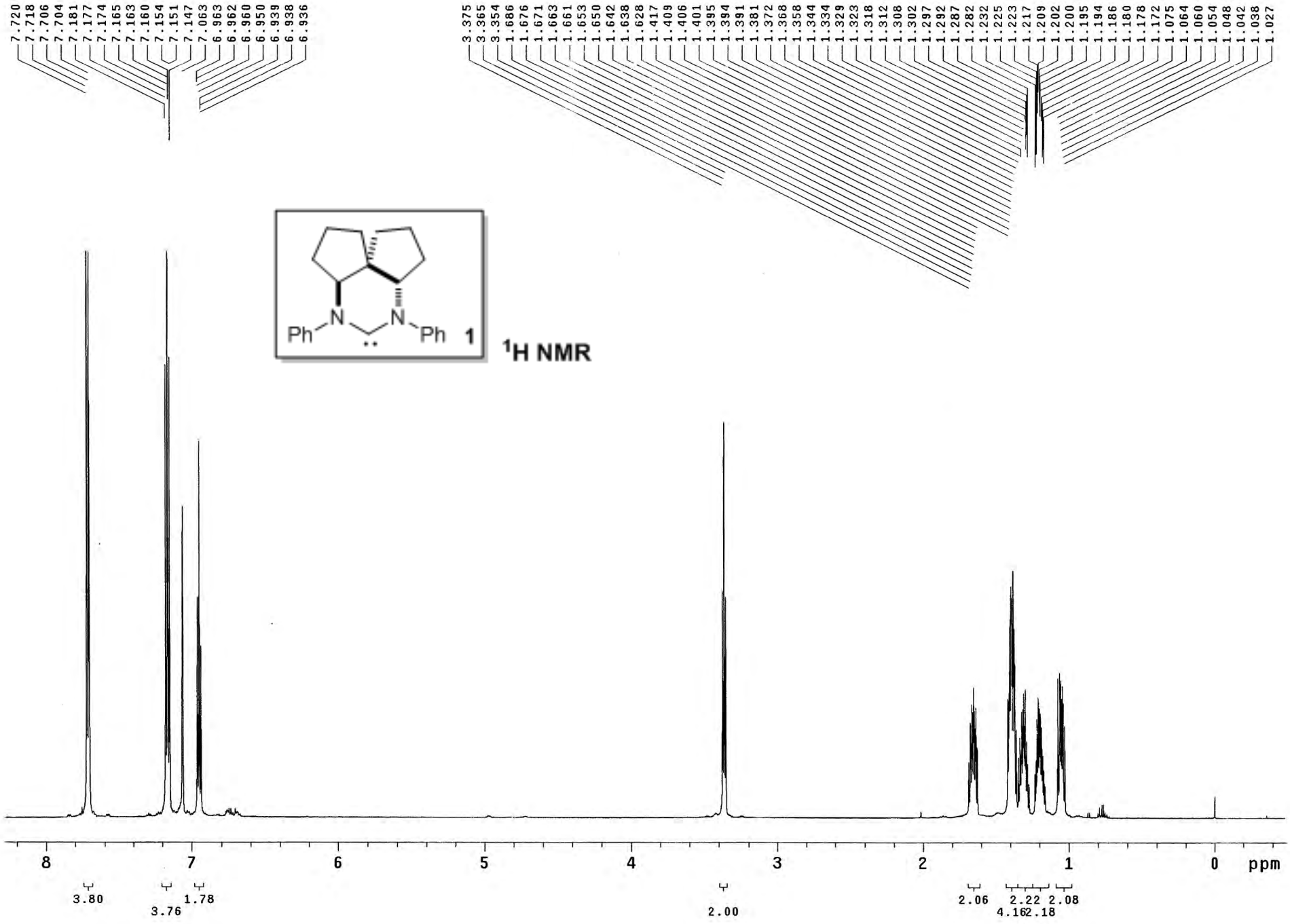
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
ppm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7.160
7.154
7.151
7.147
7.063
6.963
6.962
6.960
6.950
6.939
6.938
6.936
3.375
3.365
3.354
1.686
1.676
1.671
1.663
1.661
1.653
1.650
1.642
1.638
1.628
1.417
1.409
1.406
1.401
1.395
1.394
1.391
1.381
1.372
1.368
1.358
1.344
1.334
1.329
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1.308
1.302
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1.292
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1.282
1.232
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1.217
1.209
1.202
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1.194
1.186
1.180
1.178
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1.075
1.064
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1.048
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1.038
1.027
Ph
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N
Ph
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7
6
5
4
3
2
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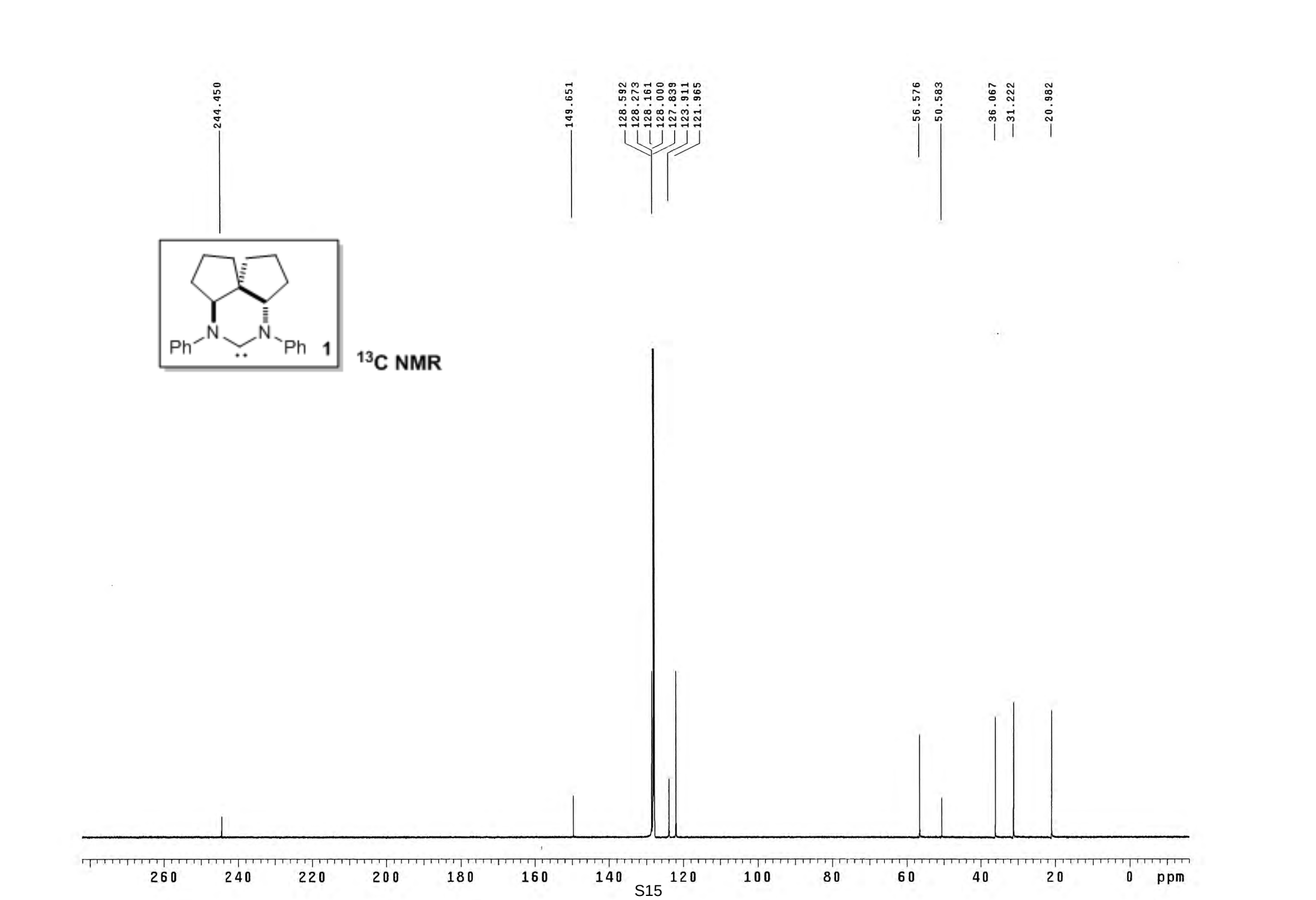
2.22
2.18
2.08

^{1}H NMR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128.000
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123.911
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Ph
N
N
Ph
1
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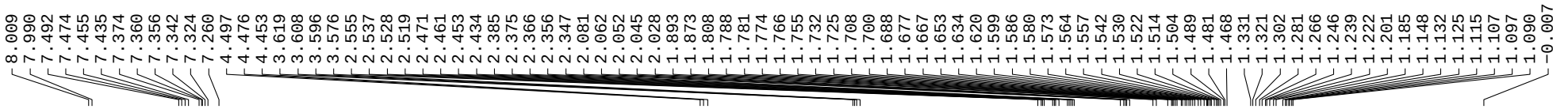
220
200
180
160
140
120
100
80
60
40
20
0
ppm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7.360
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7.342
7.324
7.260
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4.476
4.453
3.619
3.608
3.596
3.576
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2.537
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2.453
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1.522
1.514
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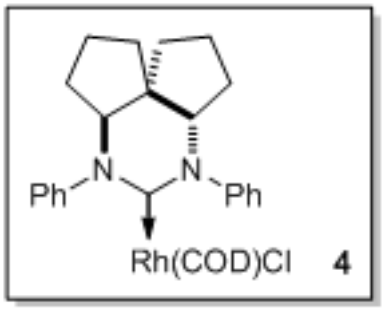
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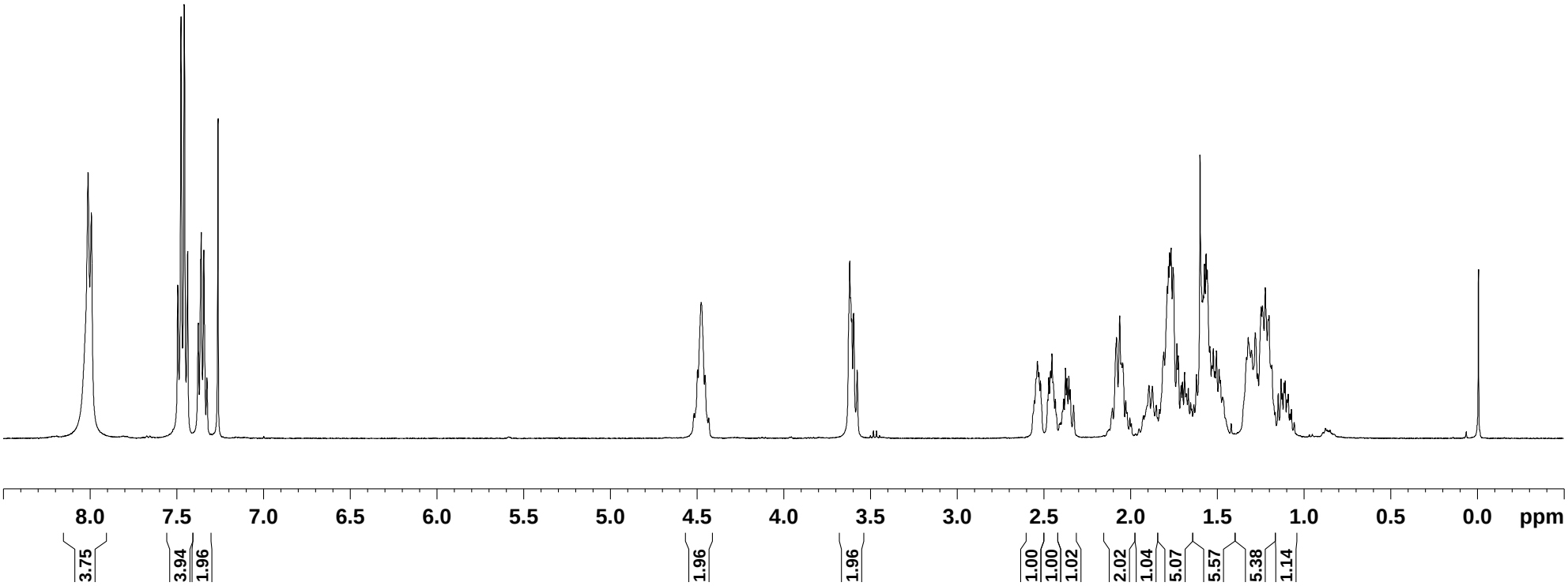
N
Ph
Rh(COD)Cl

4

^{1}H MNR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2.0
1.5
1.0
0.5
0.0
ppm
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3.94
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1.96
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1.00
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2.02
1.04
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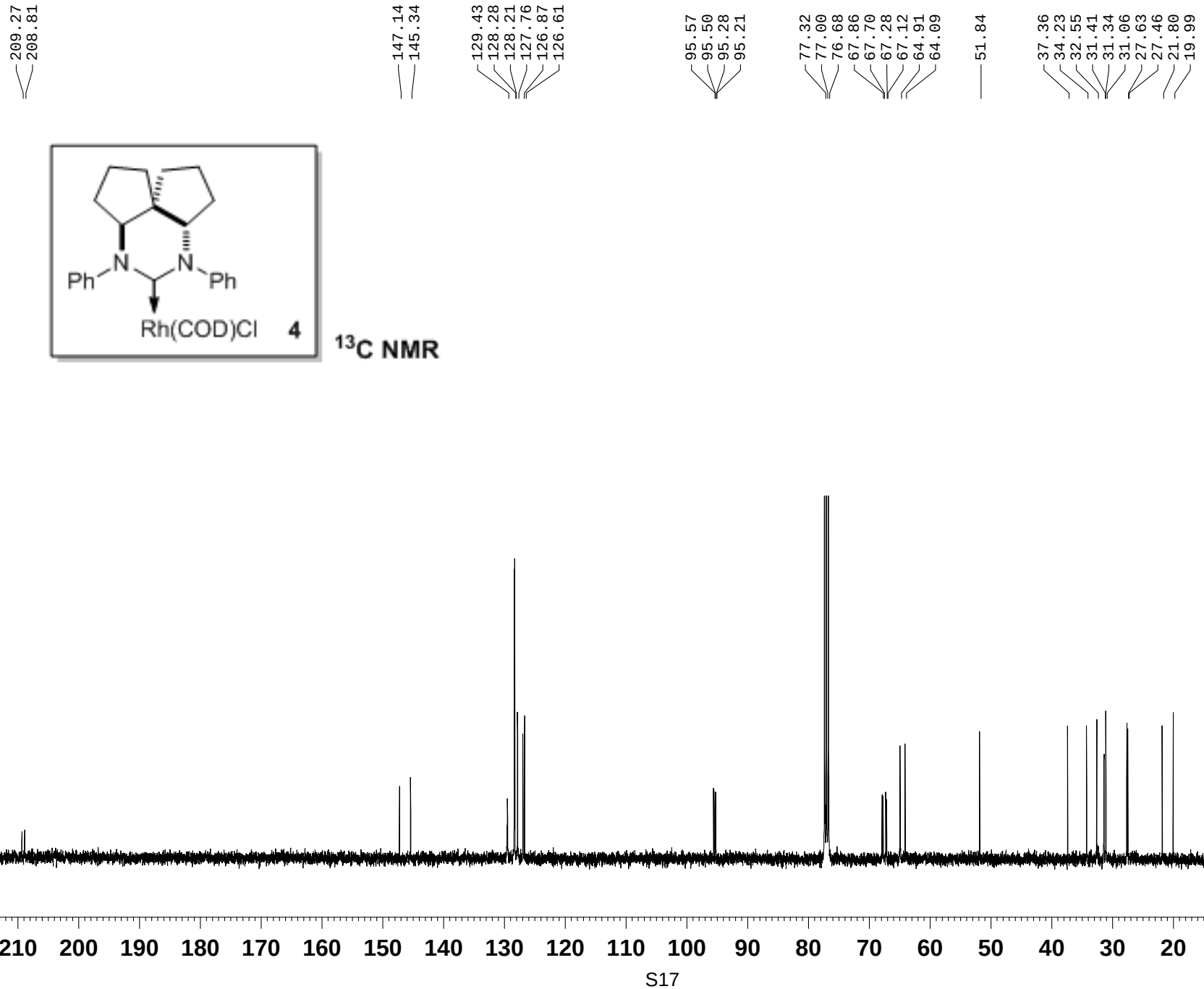
1.14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128.28
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126.61
95.57
95.50
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95.21
77.32
77.00
76.68
67.86
67.70
67.28
67.12
64.91
64.09
51.84
37.36
34.23
32.55
31.41
31.34
31.06
27.63
27.46
21.80
19.99
Ph
N
N
Ph
Rh(COD)Cl
4
210
200
190
180
170
160
150
140
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120
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100
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80
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60
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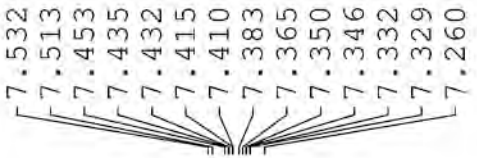
40
30
20
10
0
ppm

^{13}C NMR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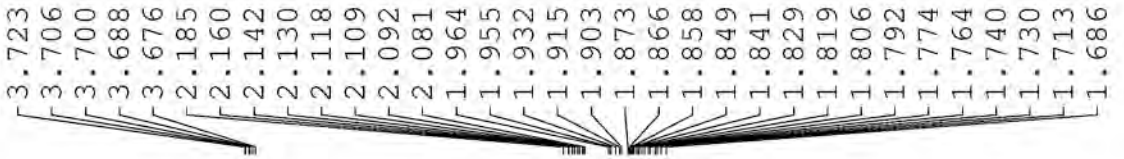
7.260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3.676
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2.142
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2.118
2.109
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2.081
1.964
1.955
1.932
1.915
1.903
1.873
1.866
1.858
1.849
1.841
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1.774
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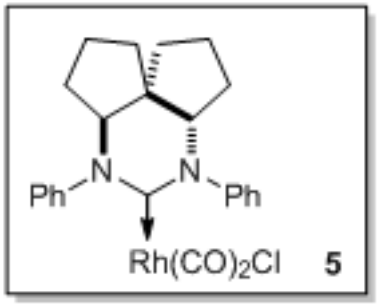
1.730
1.713
1.686


Ph
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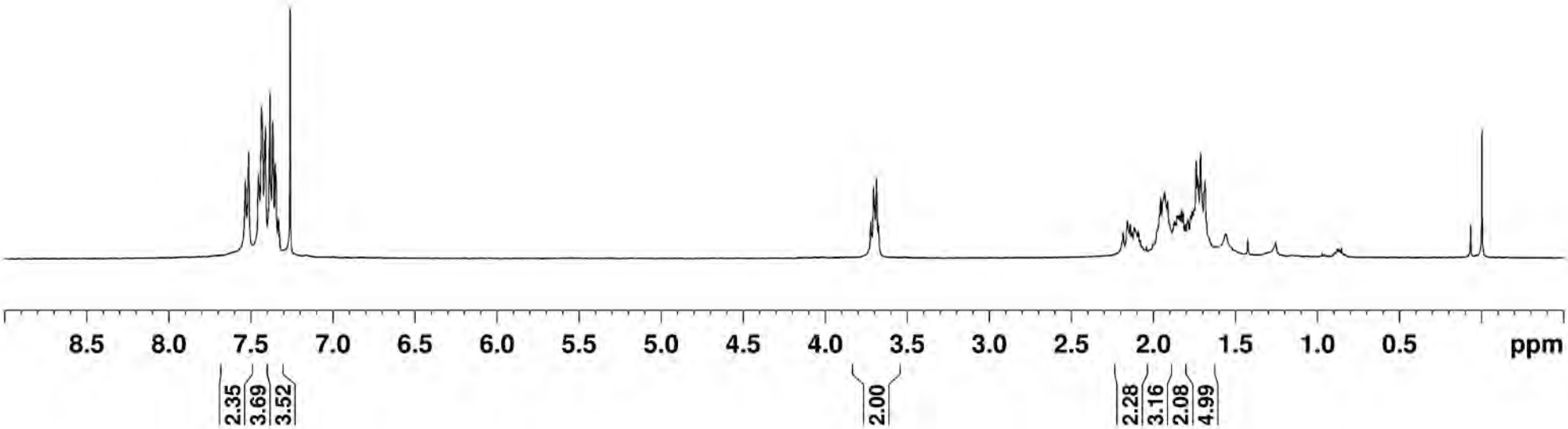
N
Ph
Rh(CO)2Cl
5

^{1}H NMR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8.0
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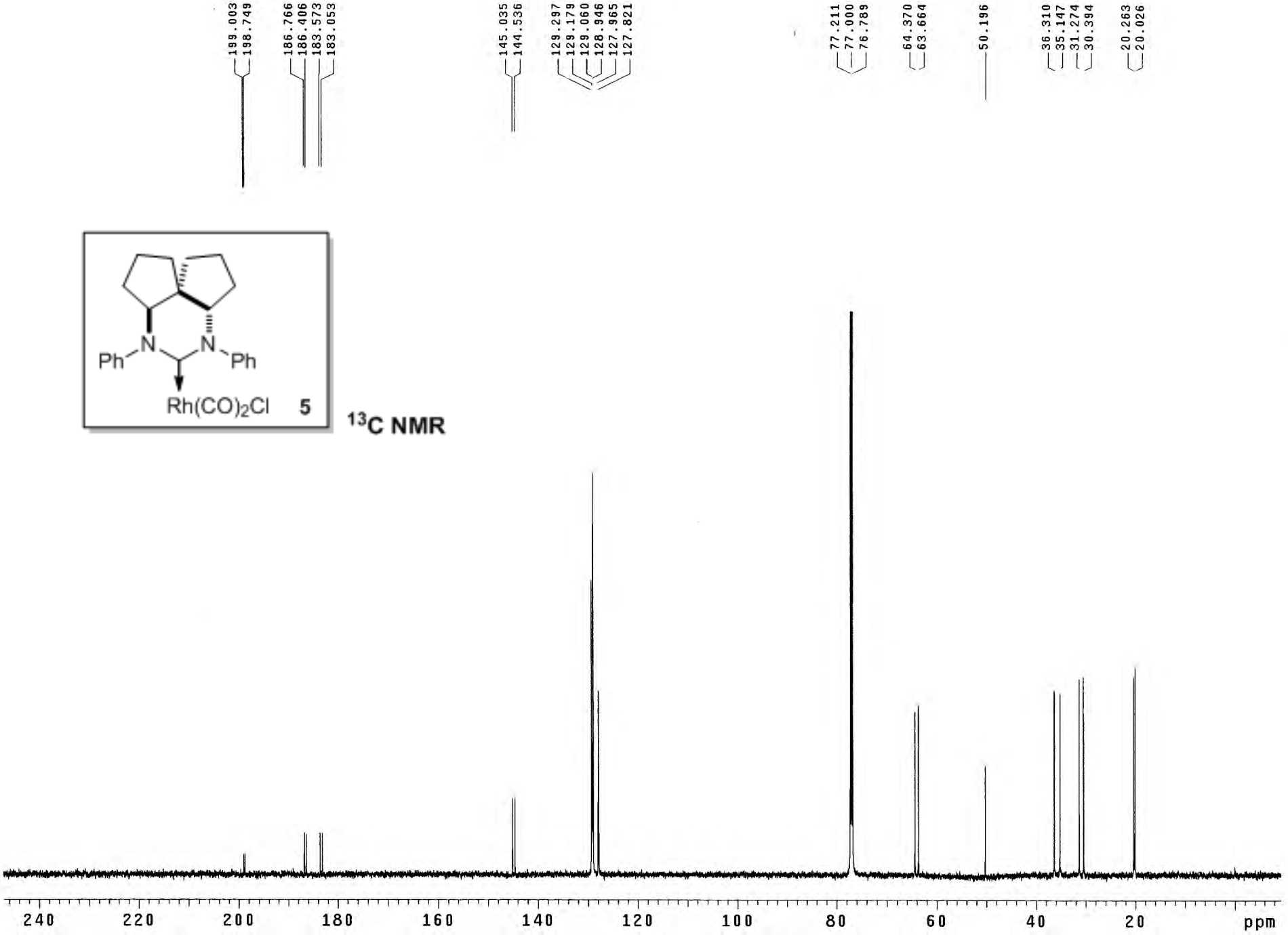
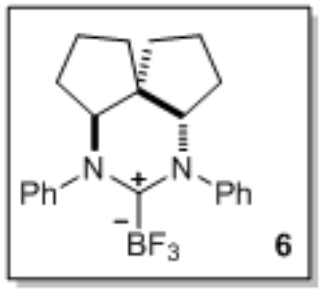
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
ppm
2.35
3.69
3.52
2.00
2.28
3.16
2.08
4.99


199.003
198.749
186.766
186.406
183.573
183.053
145.035
144.536
129.297
129.179
129.060
128.946
127.965
127.821
77.211
77.000
76.789
64.370
63.664
50.196
36.310
35.147
31.274
30.394
20.263
20.026
Ph
N
N
Ph
Rh(CO)2Cl
5
13C NMR
240
220
200
180
160
140
120
100
80
60
40
20
ppm

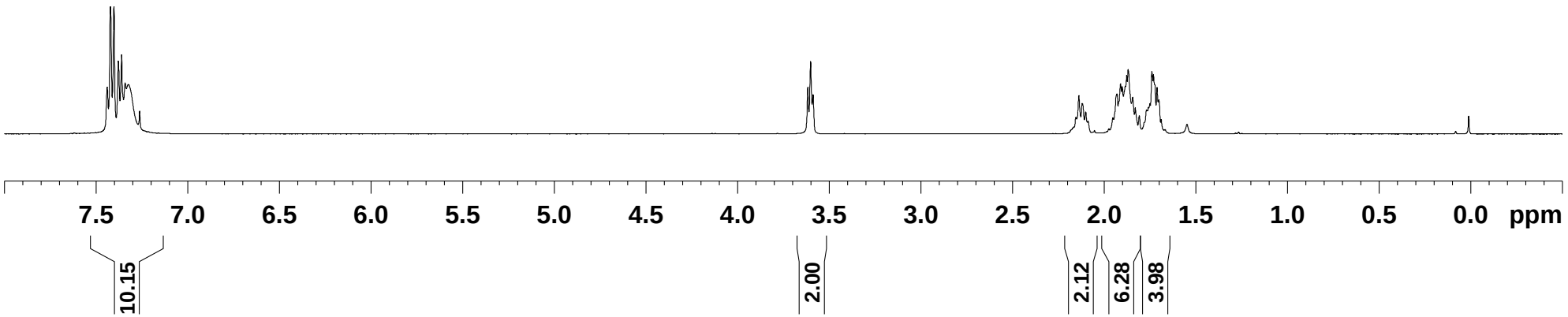
ybm3p89a1-3rd

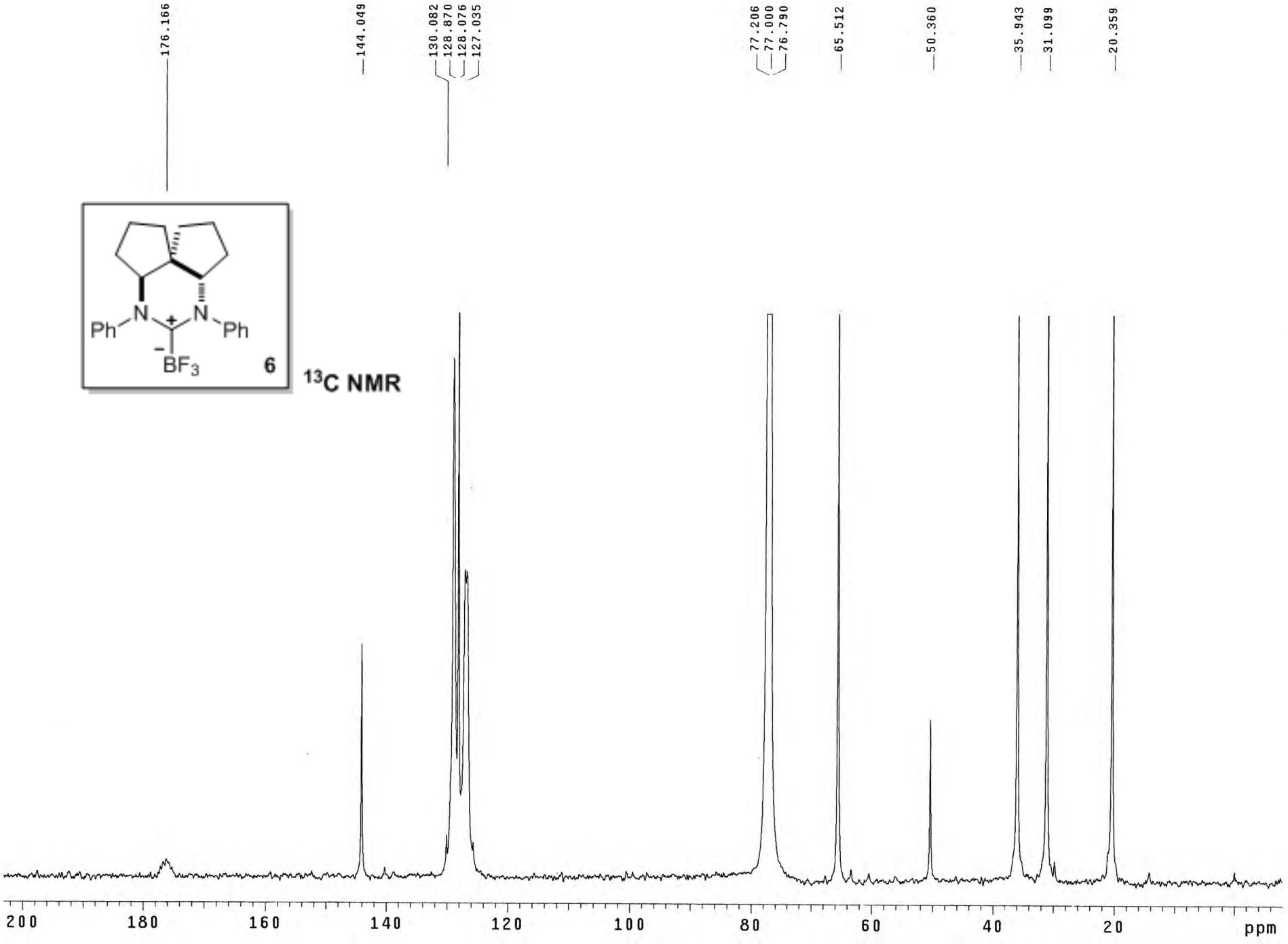
7.437
7.420
7.400
7.376
7.359
7.340
7.322
7.260

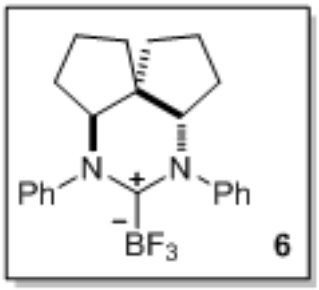
3.615
3.599
3.586
2.152
2.136
2.118
2.098
2.085
1.952
1.930
1.920
1.910
1.901
1.885
1.877
1.869
1.844
1.830
1.808
1.770
1.765
1.758
1.750
1.740
1.731
1.723
1.711
1.701
1.688
0.011



^{1}H NMR

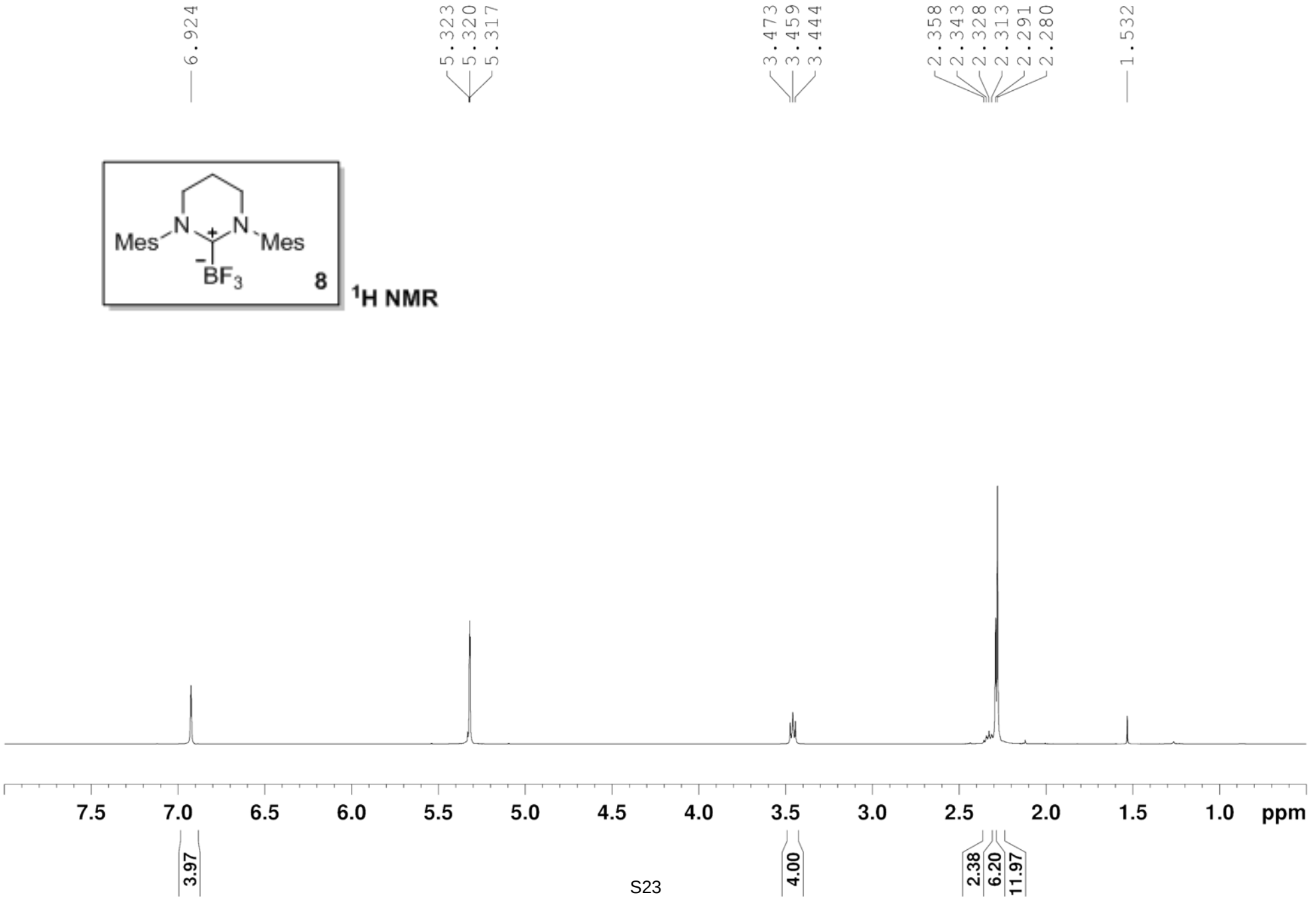


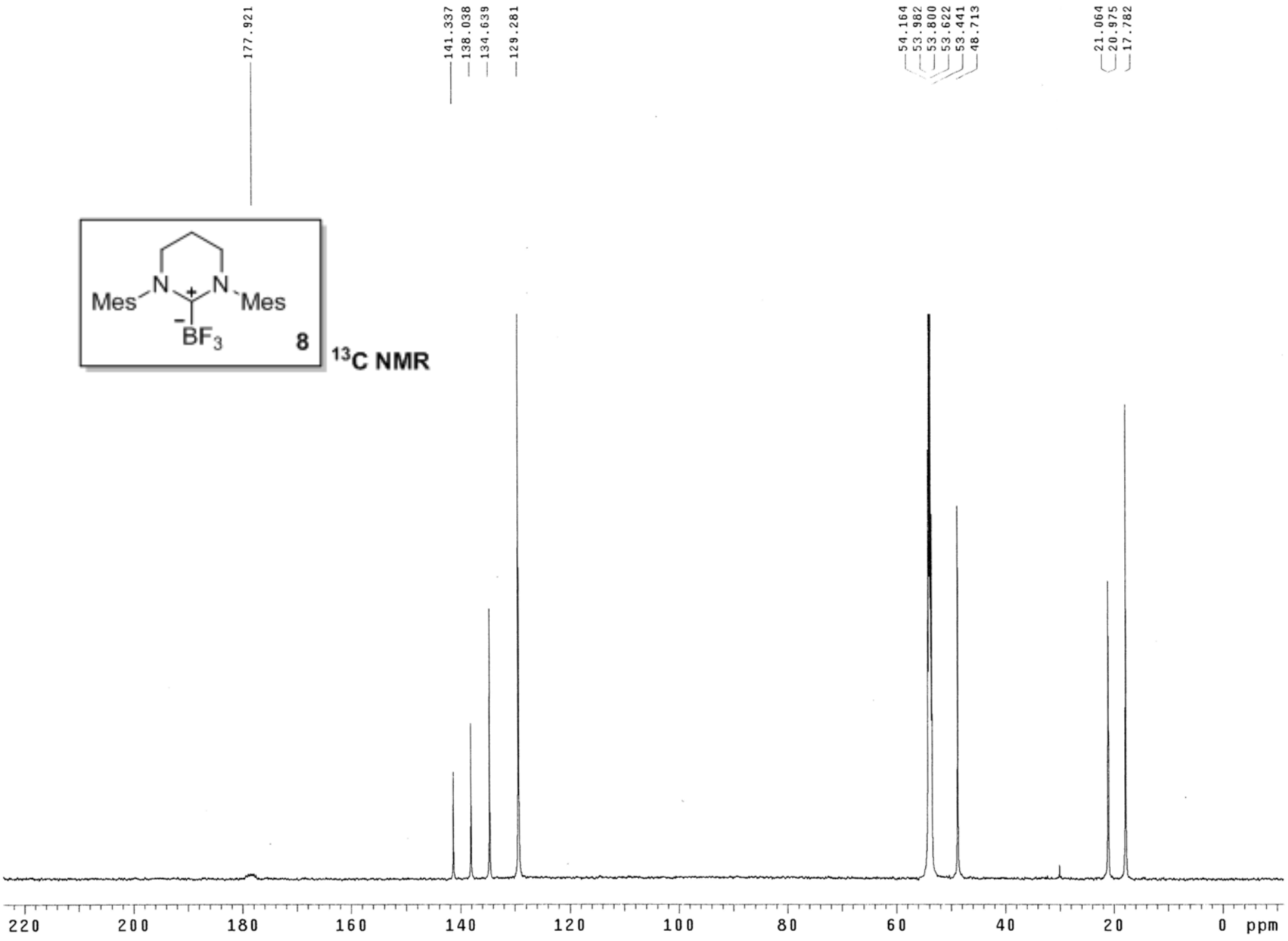

176.166
144.049
130.082
128.870
128.076
127.035
77.206
77.000
76.790
65.512
50.360
35.943
31.099
20.359
Ph
N
+
N
Ph
-
BF3
6
13C NMR
200
180
160
140
120
100
80
60
40
20
ppm


Ph
N
+
N
Ph
-
BF3

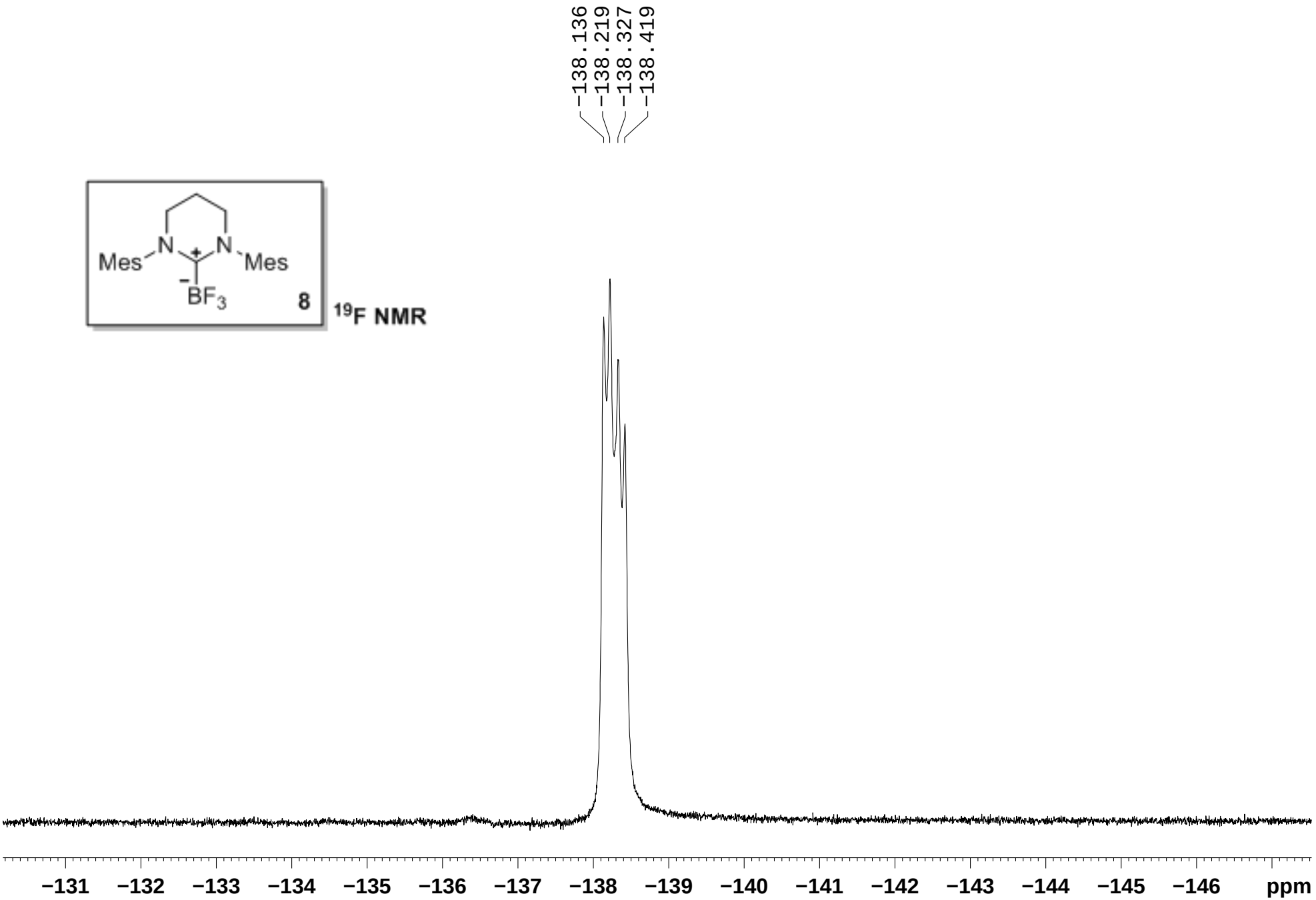
6 ^{19}**F NMR**

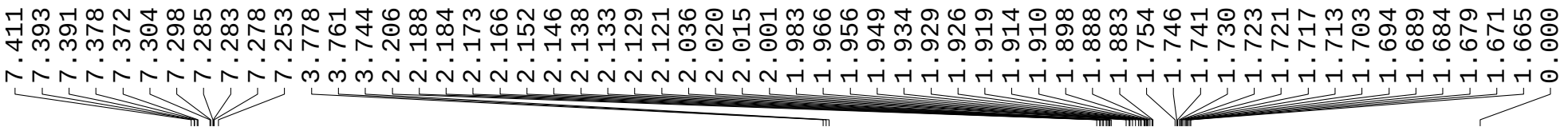
-133.184
-133.282
-133.382
-133.480
−128
−129
−130
−131
−132
−133
−134
−135
−136
−137
ppm

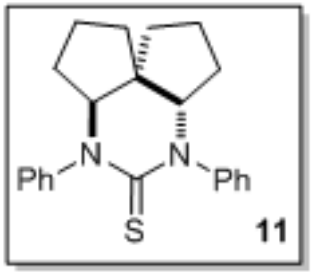

6.924
5.323
5.320
5.317
3.473
3.459
3.444
2.358
2.343
2.328
2.313
2.291
2.280
1.532
Mes
N
+
N
Mes
BF3
-
8
1H NMR
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
ppm
3.97
4.00
2.38
6.20
11.97


177.921
141.337
138.038
134.639
129.281
54.164
53.982
53.800
53.622
53.441
48.713
21.064
20.975
17.782
Mes
N
+
N
Mes
BF3
8
220
200
180
160
140
120
100
80
60
40
20
0
ppm

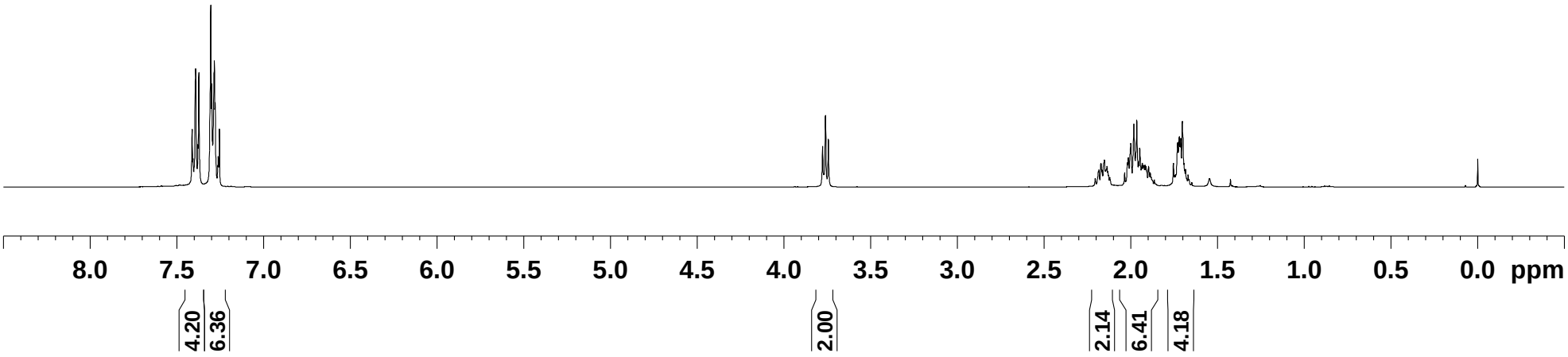
^{13}C NMR

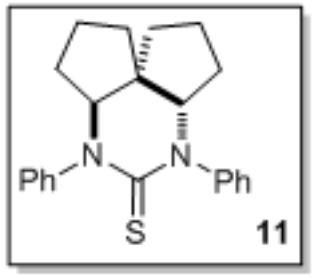

−138.136
−138.219
−138.327
−138.419
Mes
N
N
Mes
BF3
8
19F NMR
−131
−132
−133
−134
−135
−136
−137
−138
−139
−140
−141
−142
−143
−144
−145
−146
ppm


7.411
7.393
7.391
7.378
7.372
7.304
7.298
7.285
7.283
7.278
7.253
3.778
3.761
3.744
2.206
2.188
2.184
2.173
2.166
2.152
2.146
2.138
2.133
2.129
2.121
2.036
2.020
2.015
2.001
1.983
1.966
1.956
1.949
1.934
1.929
1.926
1.919
1.914
1.910
1.898
1.888
1.883
1.754
1.746
1.741
1.730
1.723
1.721
1.717
1.713
1.703
1.694
1.689
1.684
1.679
1.671
1.665
0.000


Ph
N
N
Ph
S
11

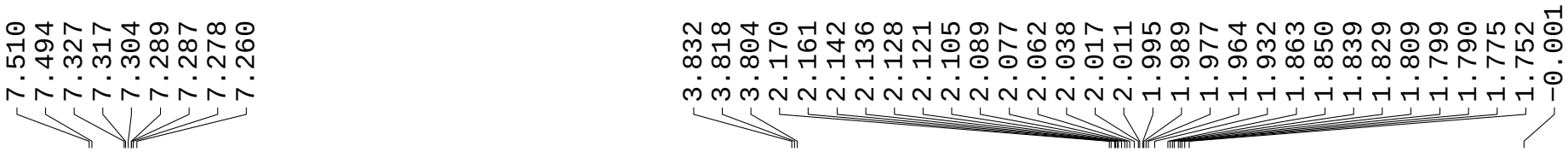
^{1}H NMR

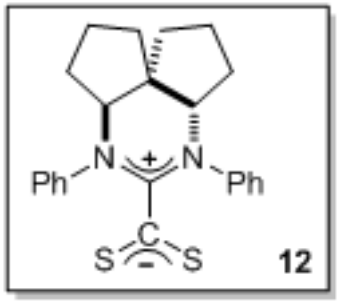

8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
ppm
4.20
6.36
2.00
2.14
6.41
4.18


Ph
N
N
Ph
S
11

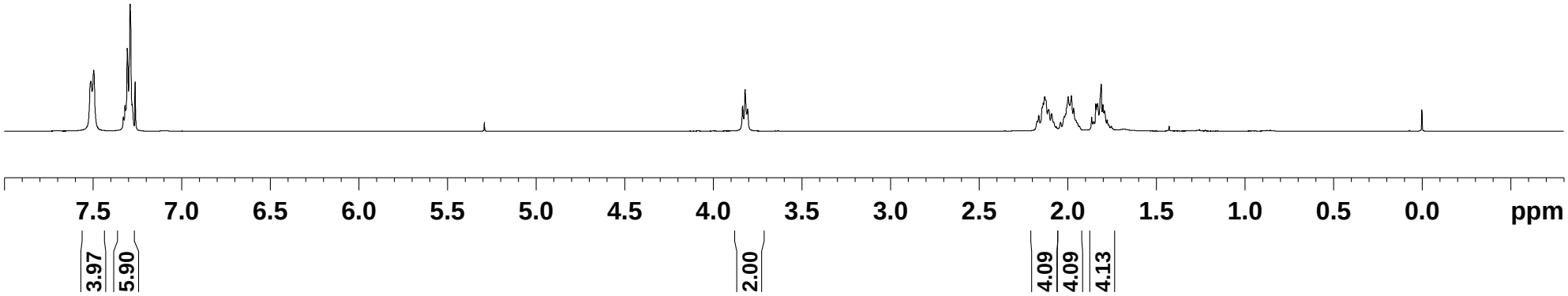
^{13}C NMR

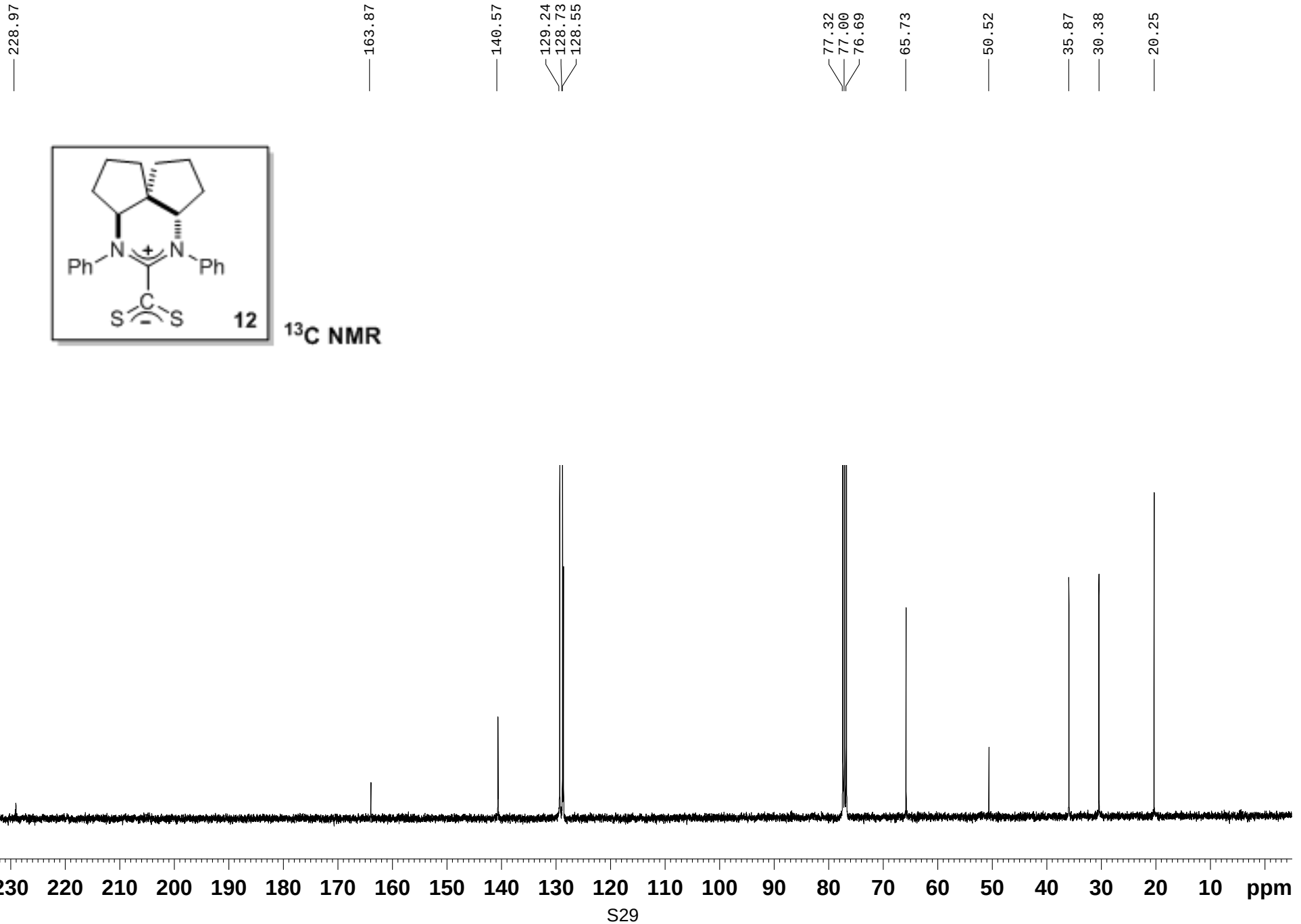
182.00
146.45
128.96
127.89
126.82
77.32
77.00
76.68
68.57
54.22
37.44
32.54
22.16
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
ppm


7.510
7.494
7.327
7.317
7.304
7.289
7.287
7.278
7.260
3.832
3.818
3.804
2.170
2.161
2.142
2.136
2.128
2.121
2.105
2.089
2.077
2.062
2.038
2.017
2.011
1.995
1.989
1.977
1.964
1.932
1.863
1.850
1.839
1.829
1.809
1.799
1.790
1.775
1.752
-0.001

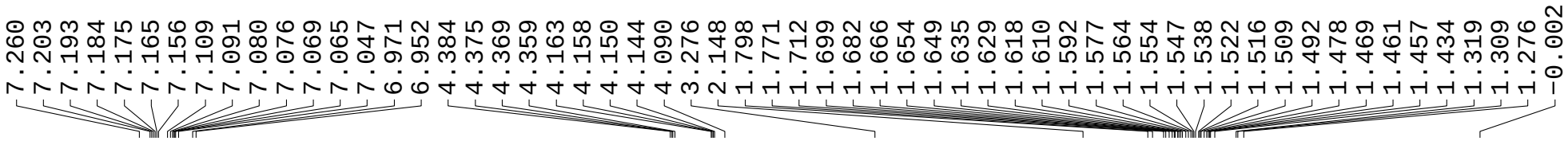

Ph
N
+
N
Ph
C
S
S
12

^{1}H NMR


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
3.97
5.90
2.00
4.09
4.09
4.13


228.97
163.87
140.57
129.24
128.73
128.55
77.32
77.00
76.69
65.73
50.52
35.87
30.38
20.25
Ph
N
+
N
Ph
C
S
S
12
230 220 210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 ppm

^{13}C NMR


7.260
7.203
7.193
7.184
7.175
7.165
7.156
7.109
7.091
7.080
7.076
7.069
7.065
7.047
6.971
6.952
4.384
4.375
4.369
4.359
4.163
4.158
4.150
4.144
4.090
3.276
2.148
1.798
1.771
1.712
1.699
1.682
1.666
1.654
1.649
1.635
1.629
1.618
1.610
1.592
1.577
1.564
1.554
1.547
1.538
1.522
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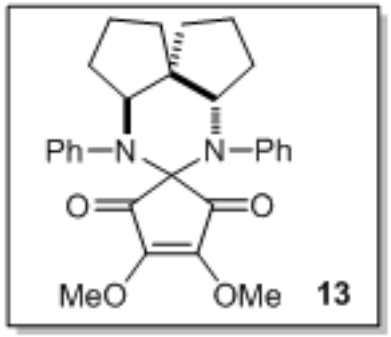
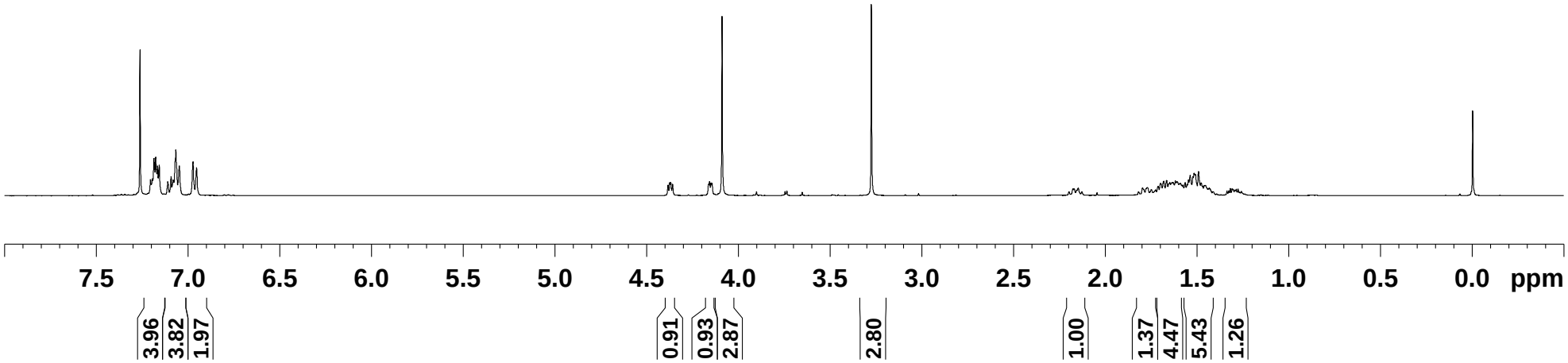
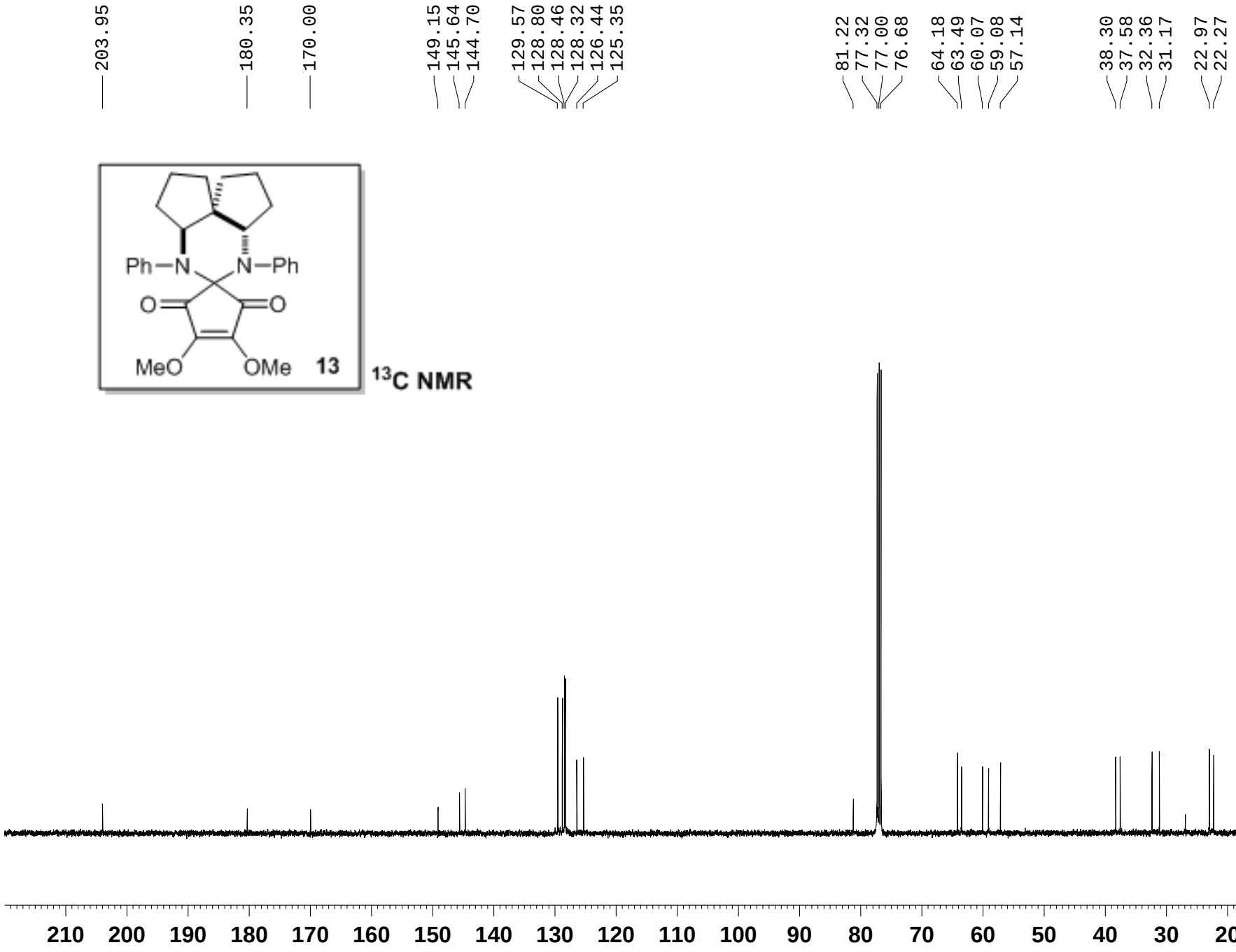
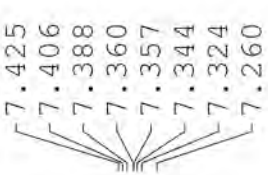
1.457
1.434
1.319
1.309
1.276
-0.002

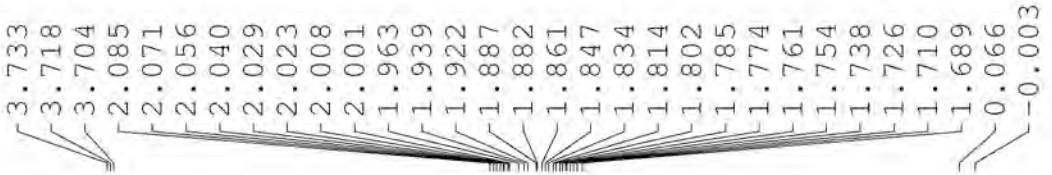

Ph—N
N—Ph
O
O
MeO
OMe
13

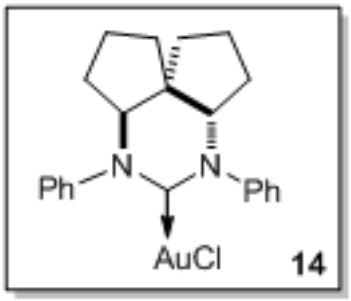
^{1}H NMR


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
3.96
3.82
1.97
0.91
0.93
2.87
2.80
1.00
1.37
4.47
5.43
1.26

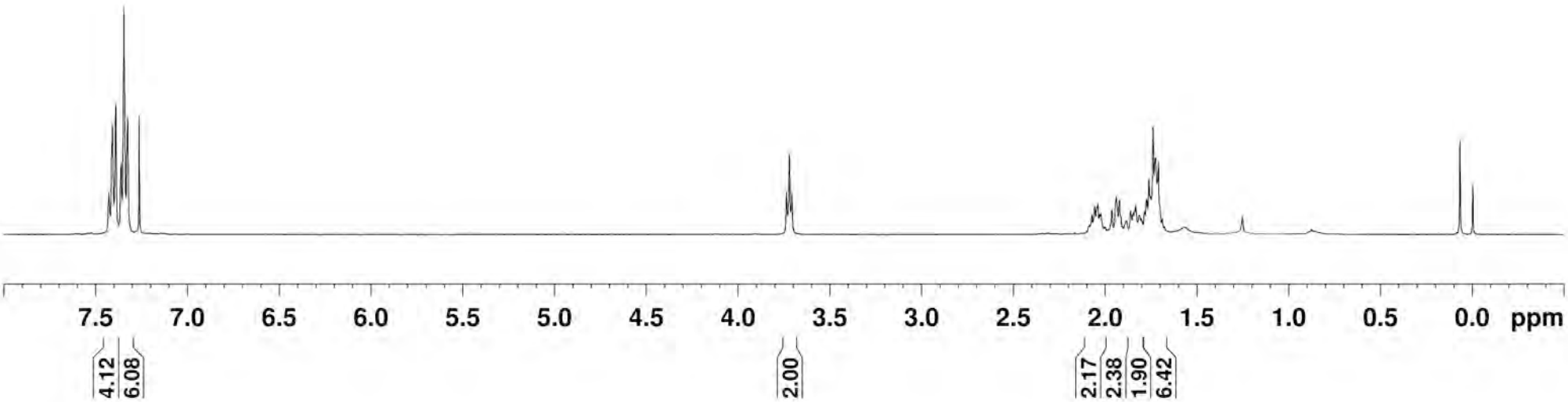

203.95
180.35
170.00
149.15
145.64
144.70
129.57
128.80
128.46
128.32
126.44
125.35
81.22
77.32
77.00
76.68
64.18
63.49
60.07
59.08
57.14
38.30
37.58
32.36
31.17
22.97
22.27
Ph—N
N—Ph
O
O
MeO
OMe
13
13C NMR
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
ppm

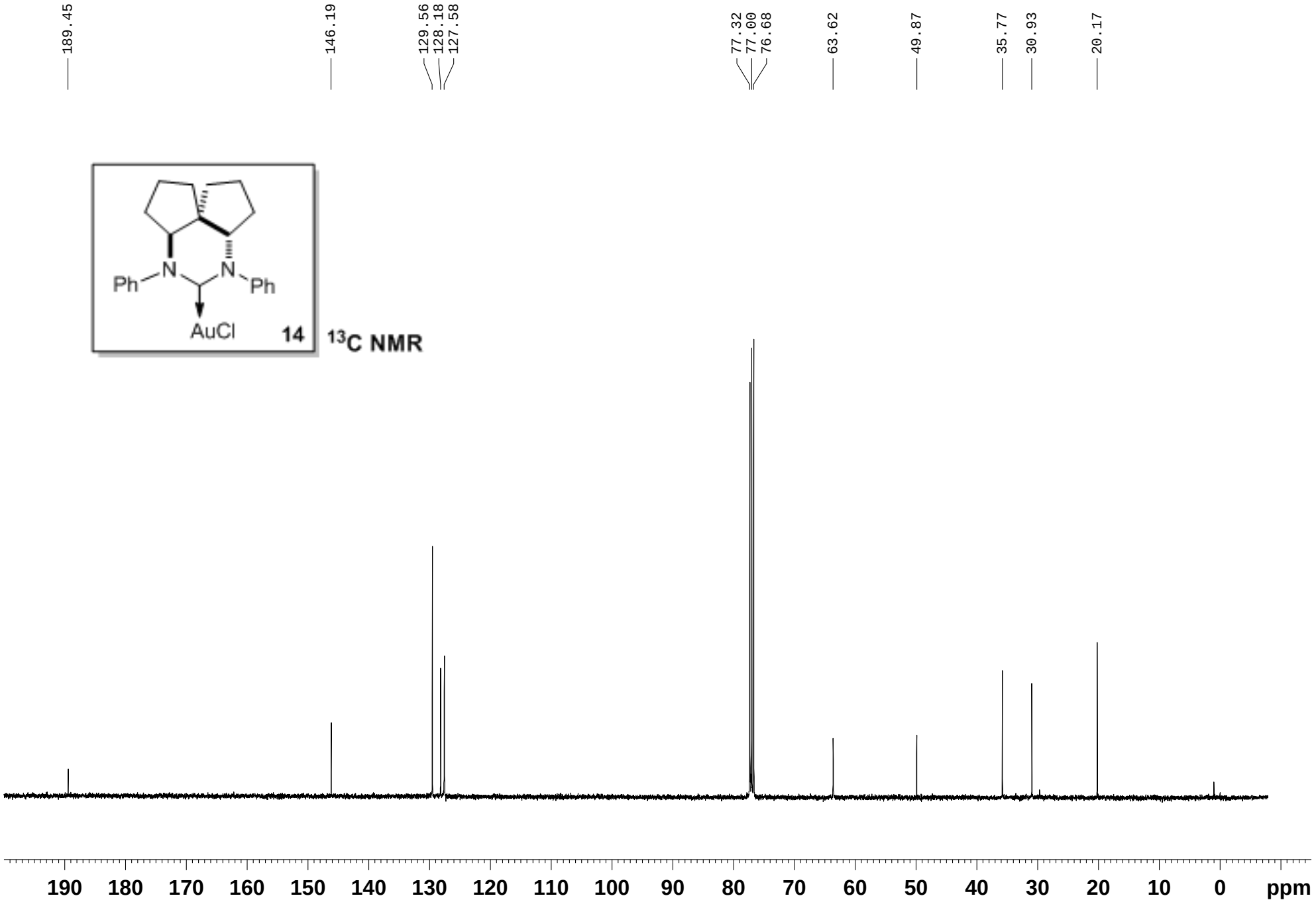

7.425
7.406
7.388
7.360
7.357
7.344
7.324
7.260

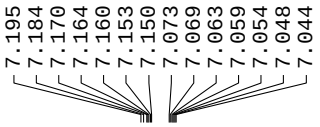

3.733
3.718
3.704
2.085
2.071
2.056
2.040
2.029
2.023
2.008
2.001
1.963
1.939
1.922
1.887
1.882
1.861
1.847
1.834
1.814
1.802
1.785
1.774
1.761
1.754
1.738
1.726
1.710
1.689
0.066
-0.003

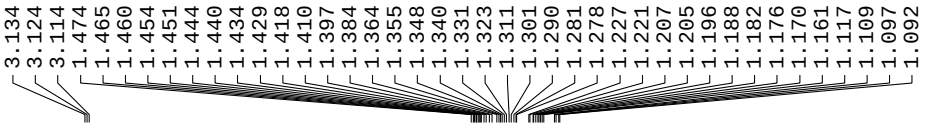

Ph
N
N
Ph
AuCl
14

^{1}H NMR


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
4.12
6.08
2.00
2.17
2.38
1.90
6.42


189.45
146.19
129.56
128.18
127.58
77.32
77.00
76.68
63.62
49.87
35.77
30.93
20.17
Ph
N
N
Ph
AuCl
14
13C NMR
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
ppm


7.195
7.184
7.170
7.164
7.160
7.153
7.150
7.073
7.069
7.063
7.059
7.054
7.048
7.044


3.134
3.124
3.114
1.474
1.465
1.460
1.454
1.451
1.444
1.440
1.434
1.429
1.418
1.410
1.397
1.384
1.364
1.355
1.348
1.340
1.331
1.323
1.311
1.301
1.290
1.281
1.278
1.227
1.221
1.207
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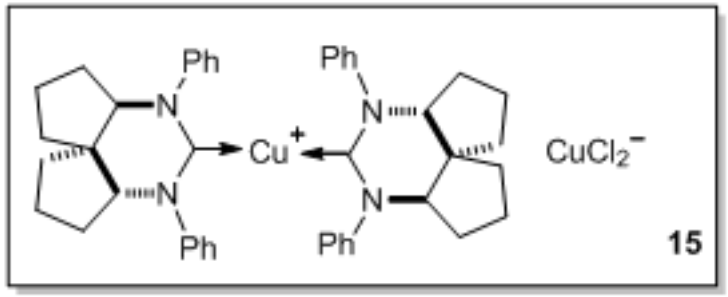
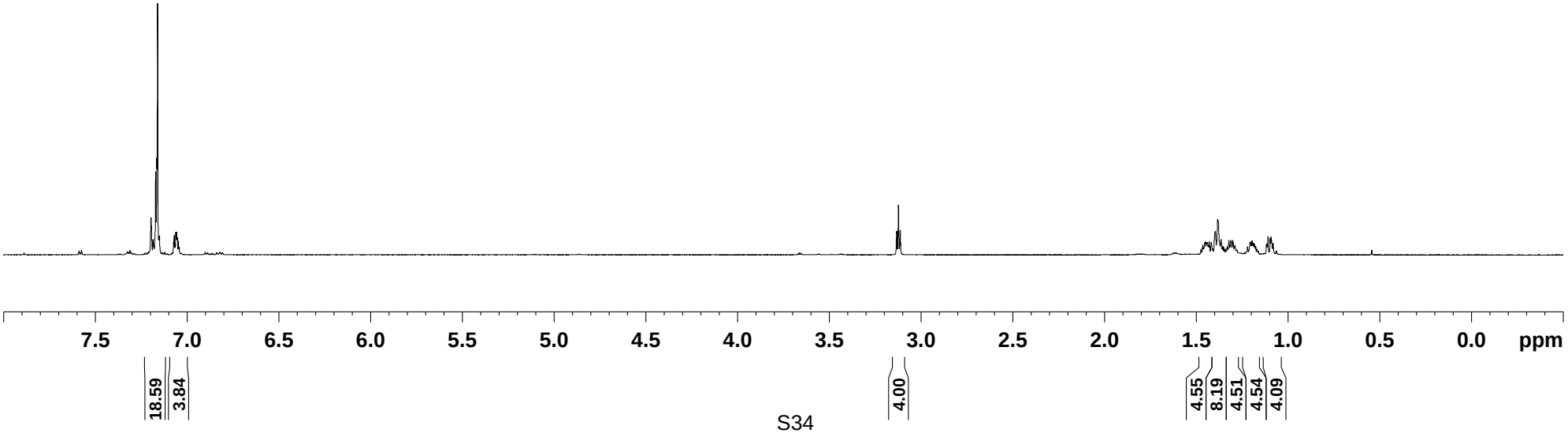
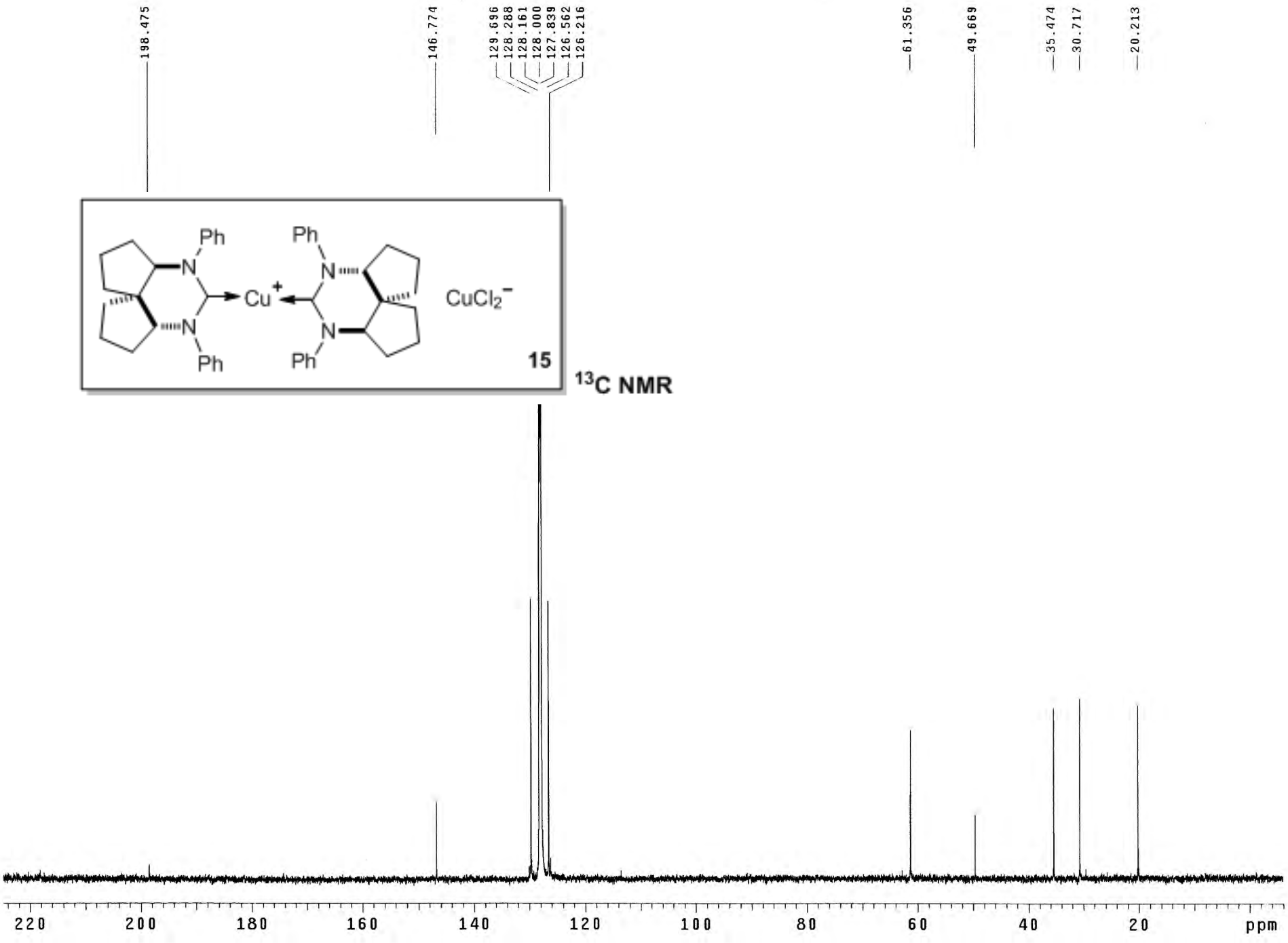
1.170
1.161
1.117
1.109
1.097
1.092


Ph
Ph
N
N
Cu+
N
N
Ph
Ph
CuCl2−
15

^{1}H NMR


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
18.59
3.84
4.00
4.55
8.19
4.51
4.54
4.09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146.774
129.696
128.288
128.161
128.000
127.839
126.562
126.216
61.356
49.669
35.474
30.717
20.213
Ph
N
Cu+
N
Ph
Ph
N
N
Ph
CuCl2−
15
13C NMR
220
200
180
160
140
120
100
80
60
40
20
ppm