Supporting Information

Rhodium-Catalyzed Amidation of the Cage B(4)−H Bond in *o*-Carboranes with Dioxazolones by Carboxylic Acid-Assisted B(4)−H Bond Activation

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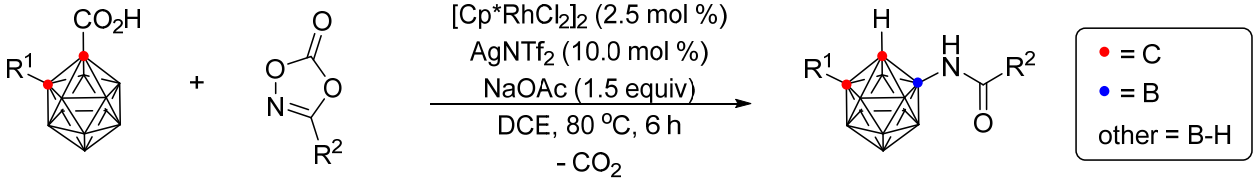
Contents

1. Experimental Section

General:

Commercial available reagents were used without purification. All reaction mixtures were stirred magnetically and were monitored by thin-layer chromatography using silica gel pre-coated glass plates, which were visualized with UV light and then, developed using a solution of $KMnO_4$. Flash column chromatography was carried out using silica gel (230-400 mesh). ^{1}H NMR (400 MHz), $^{13}C\{^{1}H\}$ NMR (100 MHz), ^{11}B NMR (128 MHz), $^{11}B\{^{1}H\}$ NMR (128 MHz), and ^{19}F NMR (377 MHz) spectra were recorded on NMR spectrometer. Deuterated chloroform was used as the solvent and chemical shift values (δ) are reported in parts per million relative to the residual signals of this solvent [δ 7.26 for ^{1}H (chloroform-*d*), and δ 77.2 for $^{13}C\{^{1}H\}$ (chloroform-*d*)]. Infrared spectra were recorded on FT-IR spectrometer as either a thin film pressed between two sodium chloride plates or as a solid suspended in a potassium bromide disk. High resolution mass spectra (HRMS) were obtained by fast atom bombardment (FAB) using a double focusing magnetic sector mass spectrometer and electron impact (EI) ionization technique (magnetic sector-electric sector double focusing mass analyzer) from the KBSI (Korea Basic Science Institute). Melting points were determined in open capillary tube.

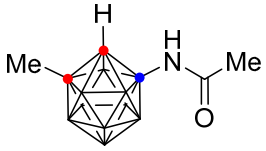
2. Procedure of the Rh-Catalyzed B(4)−H Amidation of *o*-Carborane



1 **2** **3**

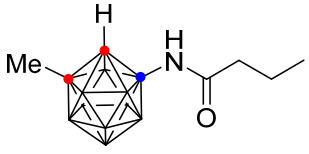
A dried test tube equipped with a magnetic stirrer was charged with carboxylated *o*-carborane **1** (0.2 mmol), 1,4,2-dioxazol-5-one **2** (0.24 mmol), $[Cp^*RhCl_2]_2$ (2.5 mol %, 3.1 mg), $AgSbF_6$ (10.0 mol %, 6.9 mg), NaOAc (0.3 mmol, 24.6 mg), and DCE (2.0 mL) under a nitrogen atmosphere. After being stirred at 80 °C for 6 h, the reaction mixture was cooled to room temperature, filtered through a pad of Celite and concentrated under reduced pressure. The crude product was purified by column chromatography on silica gel.

3a: Yield: 40.9 mg (95%); R_f = 0.3 (EtOAc:CH_2Cl_2:Hexane = 2:1:1); White solid; Melting point: 110-113 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 5.30 (s, 1H), 4.95 (s, 1H), 2.05 (s, 3H), 2.03 (s, 3H); $^{13}C\{^1H\}$ NMR (100 MHz, $CDCl_3$) δ 173.6, 69.3, 61.1, 26.0, 25.1; $^{11}B\{^1H\}$ NMR (128 MHz, $CDCl_3$) δ -3.58 - -4.50 (m, 2B), -7.36 (s, 1B), -10.00 - -12.05 (m, 6B), -15.58 (s, 1B); IR (film): 3415, 3085, 2616, 2579, 1643, 1465, 1370 cm^{-1}; HRMS (FAB) *m/z*: $[M + H]^+$ Calcd for $C_5H_{17}B_{10}NO$ 218.2319; Found 218.2321.



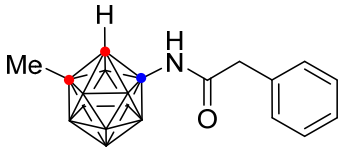
3a

3b: Yield: 48.4 mg (97%); R_f = 0.3 (EtOAc: Hexane = 1:5); White solid; Melting point: 84-87 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 5.19 (s, 1H), 4.99 (s, 1H), 2.20 (t, J = 7.4 Hz, 2H), 2.04 (s, 3H), 1.70-1.60 (m, 2H), 0.96 (t, J = 7.4 Hz, 3H); $^{13}C\{^1H\}$ NMR (100 MHz, $CDCl_3$) δ 176.5, 69.3, 61.2, 40.0, 26.0, 19.0, 13.8; $^{11}B\{^1H\}$ NMR (128 MHz, $CDCl_3$) δ -3.46 - -4.53 (m, 2B), -7.39 (s, 1B), -9.92 - -12.01 (m, 6B), -15.61 (s, 1B); IR (film): 3418, 2961, 2928, 2585, 1659, 1379 cm^{-1}; HRMS (FAB) *m/z*: $[M + H]^+$ Calcd for $C_7H_{21}B_{10}NO$ 246.2632; Found 246.2636.



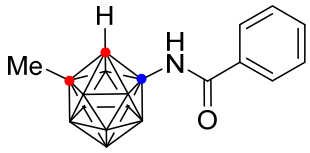
3b

3c: Yield: 57.4 mg (98%); R_f = 0.3 (EtOAc:Hexane = 1:5); White solid; Melting point: 149-151 ºC; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.39-7.35 (m, 2H), 7.32-7.28 (m, 1H), 7.25-7.23 (m, 2H), 5.20 (s, 1H), 4.96 (s, 1H), 3.58 (s, 2H), 2.03 (s, 3H); ^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$) δ 174.4, 134.8, 129.5, 129.1, 127.5, 69.3, 61.1, 45.0, 26.0; ^{11}B{^{1}H} NMR (128 MHz, $CDCl_3$) δ -3.46 - -4.42 (m, 2B), -7.41 (s, 1B), -9.98 - -12.02 (m, 6B), -15.49 (s, 1B); IR (film): 3297, 3044, 2588, 2570, 1472, 1321, 932, 803, 707 cm^{-1}; HRMS (FAB) *m/z*: $[M + H]^+$ Calcd for $C_{11}H_{21}B_{10}NO$ 294.2632; Found 294.2631.



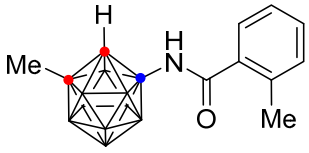
3c

3d: Yield: 52.7 mg (94%); R_f = 0.5 (EtOAc:Hexane = 1:5); White solid; Melting point: 148-150 ºC; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.80-7.78 (m, 2H), 7.55-7.50 (m, 1H), 7.47-7.43 (m, 2H), 5.97 (s, 1H), 5.11 (s, 1H), 2.08 (s, 3H); ^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$) δ 170.1, 134.6, 132.0, 128.8, 127.3, 69.4, 61.3, 26.1; ^{11}B{^{1}H} NMR (128 MHz, $CDCl_3$) δ -3.08 - -4.33 (m, 2B), -7.19 (s, 1B), -9.76 - -11.91 (m, 6B), -15.35 (s, 1B); IR (film): 3237, 3124, 2554, 2530, 1647, 1471, 961, 833, 653 cm^{-1}; HRMS (FAB) *m/z*: $[M + H]^+$ Calcd for $C_{10}H_{19}B_{10}NO$ 280.2475; Found 280.2474.



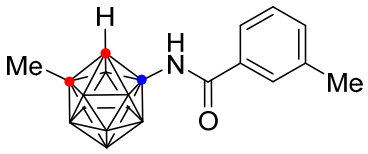
3d

3e: Yield: 56.7 mg (97%); R_f = 0.3 (EtOAc:Hexane = 1:5); White solid; Melting point: 138-140 ºC; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.40-7.38 (m, 1H), 7.34-7.30 (m, 1H), 7.23-7.20 (m, *2*H), 5.55 (s, 1H), 5.12 (s, 1H), 2.45 (s, 3H), 2.10 (s, 3H); ^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$) δ 173.1, 137.0, 136.0, 131.3, 130.3, 126.7, 126.0, 69.5, 61.2, 26.1, 20.0; ^{11}B{^{1}H} NMR (128 MHz, $CDCl_3$) δ -3.36 - -4.36 (m, 2B), -7.20 (s, 1B), -9.84 - -11.91 (m, 6B), -15.42 (s, 1B); IR (film): 3258, 2918, 2586, 1665, 1426, 1245, 1157, 1024, 794, 752, 691 cm^{-1}; HRMS (FAB) *m/z*: $[M + H]^+$ Calcd for $C_{11}H_{21}B_{10}NO$ 294.2632; Found 294.2635.



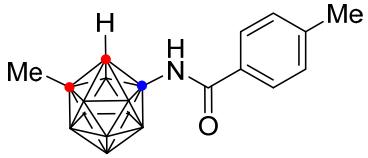
3e

3f: Yield: 58.7 mg (99%); R_f = 0.3 (EtOAc:Hexane = 1:5); White solid; Melting point: 173-175 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.60 (s, 1H), 7.59-7.56 (m, 1H), 7.34-7.33 (m, 2H), 5.93 (s, 1H), 5.12 (s, 1H), 2.41 (s, 3H), 2.09 (s, 3H); ^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$) δ 170.3, 138.6, 134.6, 132.8, 128.7, 128.0, 124.3, 69.4, 61.3, 26.1, 21.5; ^{11}B{^{1}H} NMR (128 MHz, $CDCl_3$) δ -3.08 - -4.37 (m, 2B), -7.23 (s, 1B), -9.75 - -11.93 (m, 6B), -15.46 (s, 1B); IR (film): 3327, 2924, 2585, 1643, 1474, 928, 882, 741, 633 cm^{-1}; HRMS (FAB) *m/z*: $[M + H]^+$ Calcd for $C_{11}H_{21}B_{10}NO$ 294.2632; Found 294.2631.



3f

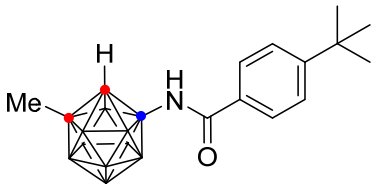
3g: Yield: 57.1 mg (98%); R_f = 0.5 (EtOAc:Hexane = 1:5); White solid; Melting point: 143-145 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.68 (d, J = 8.2 Hz, 2H), 7.25 (d, J = 8.6 Hz, 2H), 5.92 (s, 1H), 5.12 (s, 1H), 2.41 (s, 3H), 2.08 (s, 3H); ^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$) δ 170.0, 142.5, 131.8, 129.4, 127.3, 69.4, 61.3, 26.0, 21.6; ^{11}B{^{1}H} NMR (128 MHz, $CDCl_3$) δ -3.00 - -4.37 (m, 2B), -7.23 (s, 1B), -9.77 - -11.95 (m, 6B), -15.47 (s, 1B); IR (film): 3216, 3090, 2587, 1638, 1472, 1278, 935, 751, 684 cm^{-1}; HRMS (FAB) *m/z*: $[M + H]^+$ Calcd for $C_{11}H_{21}B_{10}NO$ 294.2632; Found 294.2631.



3g

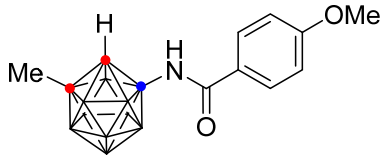
3h: Yield: 62.8 mg (98%); R_f = 0.4 (EtOAc:CH_2Cl_2:Hexane = 1:1:5); White solid; Melting point: 64-68 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.73 (d, J = 8.5 Hz, 2H), 7.46 (d, J = 8.4, 2H), 5.93 (s, 1H), 5.13 (s, 1H), 2.08 (s, 3H), 1.34 (s, 9H); ^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$) δ 170.0, 155.6, 131.7, 127.1, 125.7, 69.4, 61.3, 35.1, 31.3, 26.1; ^{11}B{^{1}H} NMR (128 MHz, $CDCl_3$) δ -3.02 - -4.41 (m, 2B), -7.25 (s, 1B), -

9.78 - -11.94 (m, 6B), -15.43 (s, 1B); IR (film): 8428, 3217, 2964, 2588, 1639, 1474, 1272, 903, 851, 773 cm^{-1} HRMS (FAB) *m/z*: $[M + H]^+$ Calcd for $C_{14}H_{27}B_{10}NO$ 336.3101; Found 336.3097.



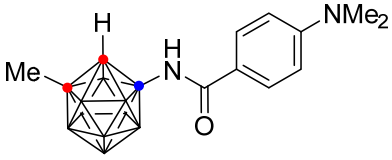
3h

3i: Yield: 58.4 mg (94%); R_f = 0.2 (EtOAc:Hexane = 1:5); White solid; Melting point: 159-161 °C; ^1H NMR (400 MHz, $CDCl_3$) δ 7.76 (d, J = 8.9, 2H), 6.93 (d, J = 8.8 Hz, 2H), 5.90 (s, 1H), 5.11 (s, 1H), 3.86 (s, 3H), 2.07 (s, 3H); $^{13}C\{^1H\}$ NMR (100 MHz, $CDCl_3$) δ 169.6, 162.7, 129.2, 126.8, 113.9, 69.3, 61.3, 55.6, 26.1; $^{11}B\{^1H\}$ NMR (128 MHz, $CDCl_3$) δ -3.00 - -4.43 (m, 2B), -7.28 (s, 1B), -9.80 - -11.96 (m, 6B), -15.50 (s, 1B); IR (film): 3425, 3273, 2966, 1581, 1637, 1440, 1253, 903, 844, 767 cm^{-1}; HRMS (FAB) *m/z*: $[M + H]^+$ Calcd for $C_{11}H_{21}B_{10}NO$ 310.2581; Found 310.2578.



3i

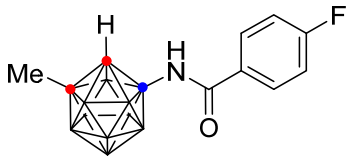
3j: Yield: 44.9 mg (71%); R_f = 0.2 (EtOAc:CH_2Cl_2:Hexane = 1:1:5); Ivory solid; Melting point: 158-160 °C; ^1H NMR (400 MHz, $CDCl_3$) δ 7.68 (d, J = 9.0 Hz, 2H), 6.67 (d, J = 9.0 Hz, 2H), 5.82 (s, 1H), 5.15 (s, 1H), 3.03 (s, 6H), 2.07 (s, 3H); $^{13}C\{^1H\}$ NMR (100 MHz, $CDCl_3$) δ 169.9, 152.8, 128.9, 121.0, 111.1, 69.2, 61.4, 40.2, 26.1; $^{11}B\{^1H\}$ NMR (128 MHz, $CDCl_3$) δ -2.66 (s, 1B), -4.58 (s, 1B), -7.27 (s, 1B), -9.83 - -11.99 (m, 6B), -15.75 (s, 1B); IR (film): 3212, 2577, 2259, 1607, 1195, 945, 883, 763, 639 cm^{-1}; HRMS (FAB) *m/z*: $[M + H]^+$ Calcd for $C_{12}H_{24}B_{10}N_2O$ 323.2897; Found 323.2899.



3j

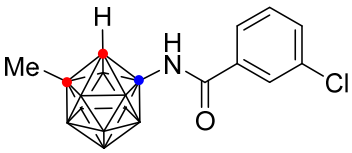
3k: Yield: 58.5 mg (99%); R_f = 0.6 (EtOAc:CH_2Cl_2:Hexane = 1:1:5); White solid; Melting point: 146-148 °C; ^1H NMR (400 MHz, $CDCl_3$) δ 7.82-7.79 (m, 2H), 7.15-7.10 (m, 2H), 5.89 (s, 1H), 5.08 (s, 1H),

2.09 (s, 3H); $^{13}C\{^{1}H\}$ NMR (100 MHz, $CDCl_3$) δ 169.1, 165.1 (d, J = 252.6 Hz), 130.8 (d, J = 2.8 Hz), 129.7 (d, J = 9.5 Hz), 115.8 (d, J = 22.0 Hz), 69.5, 61.3, 26.0; $^{11}B\{^{1}H\}$ NMR (128 MHz, $CDCl_3$) δ -3.17 - -4.25 (m, 2B), -7.20 (s, 1B), -9.80 - -11.92 (m, 6B), -15.35 (s, 1B); ^{19}F NMR (376 MHz, $CDCl_3$) δ -63.02; IR (film): 3290, 3090, 2639, 2604, 1638, 1475, 1306, 905, 822, 720 cm^{-1}; HRMS (FAB) *m/z*: $[M + H]^+$ Calcd for $C_{10}H_{18}B_{10}NOF$ 298.2381; Found 298.2383.



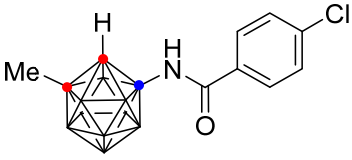
3k

3l: Yield: 69.1 mg (99%); R_f = 0.4 (EtOAc:Hexane = 1:5); White solid; Melting point: 149-152 ºC; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.77 (t, J = 1.9 Hz, 1H), 7.65 (dt, J = 7.7 Hz, J = 1.4 Hz, 1H), 7.50 (tq, J = 8.0 Hz, J = 1.0 Hz, 1H), 7.39 (t, J = 7.9 Hz, 1H), 5.90 (s, 1H), 5.06 (s, 1H), 2.09 (s, 3H); $^{13}C\{^{1}H\}$ NMR (100 MHz, $CDCl_3$) δ 168.8, 136.5, 135.0, 132.0, 130.1, 127.7, 125.3, 69.5, 61.2, 26.1; $^{11}B\{^{1}H\}$ NMR (128 MHz, $CDCl_3$) δ -3.29 - -4.20 (m, 2B), -7.21 (s, 1B), -9.83 - -11.89 (m, 6B), -15.25 (s, 1B); IR (film): 3270, 3087, 2573, 1641, 1289, 908, 807, 734, 680 cm^{-1}; HRMS (FAB) *m/z*: $[M + H]^+$ Calcd for $C_{10}H_{18}B_{10}NOCl$ 314.2085; Found 314.2085.



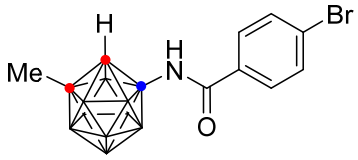
3l

3m: Yield: 69.4 mg (99%); R_f = 0.4 (EtOAc:Hexane = 1:5); White solid; Melting point: 136-138 ºC; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.73 (d, J = 8.7 Hz, 2H), 7.42 (d, J = 8.6 Hz, 2H), 5.92 (s, 1H), 5.07 (s, 1H), 2.08 (s, 3H); $^{13}C\{^{1}H\}$ NMR (100 MHz, $CDCl_3$) δ 169.1, 138.3, 133.0, 129.0, 128.7, 69.5, 61.2, 26.0; $^{11}B\{^{1}H\}$ NMR (128 MHz, $CDCl_3$) δ -3.23 - -4.22 (m, 2B), -7.20 (s, 1B), -9.82 - -11.94 (m, 6B), -15.31 (s, 1B); IR (film): 3288, 2941, 2584, 1639, 1270, 903, 846, 756 cm^{-1}; HRMS (FAB) *m/z*: $[M + H]^+$ Calcd for $C_{10}H_{18}B_{10}NOCl$ 314.2085; Found 314.2089.



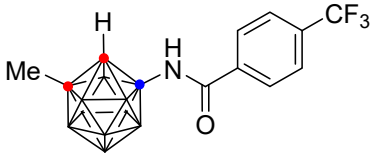
3m

3n: Yield: 65.9 mg (93%); R_f = 0.4 (EtOAc: Hexane = 1:5); White solid; Melting point: 115-117 ºC; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.65 (d, J = 8.5 Hz, 2H), 7.57 (d, J = 8.5 Hz, 2H), 5.97 (s, 1H), 5.06 (s, 1H), 2.08 (s, 3H); ^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$) δ 169.2, 133.5, 132.0, 128.9, 126.8, 69.5, 61.2, 26.1; ^{11}B{^{1}H} NMR (128 MHz, $CDCl_3$) δ -3.25 - -4.26 (m, 2B), -7.22 (s, 1B), -9.81 - -11.93 (m, 6B), -15.26 (s, 1B); IR (film): 3423, 3080, 2941, 2588, 1648, 1265, 901, 843, 754 cm^{-1}; HRMS (FAB) *m/z*: $[M + H]^+$ Calcd for $C_{10}H_{18}B_{10}NOBr$ 358.1580; Found 358.1584.



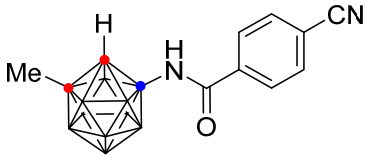
3n

3o: Yield: 69.8 mg (98%); R_f = 0.5 (EtOAc:CH_2Cl_2:Hexane = 1:1:5); White solid; Melting point: 117-120 ºC; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.89 (d, J = 8.1 Hz, 2H), 7.70 (d, J = 8.3 Hz, *2*H), 6.02 (s, 1H), 5.07 (s, 1H), 2.09 (s, 3H); ^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$) δ 168.9, 138.0, 133.7 (q, J = 32.8 Hz), 127.8, 125.8 (q, J = 3.7 Hz), 123.6 (q, J = 263.2 Hz), 69.6, 61.2, 26.1; ^{11}B{^{1}H} NMR (128 MHz, $CDCl_3$) δ -3.36 - -4.10 (m, 2B), -7.17 (s, 1B), -9.77 - -11.89 (m, 6B), -15.20 (s, 1B); IR (film): 3216, 2589, 1644, 1234, 1066, 904, 884, 772 cm^{-1}; HRMS (FAB) *m/z*: $[M]^+$ Calcd for $C_{11}H_{18}B_{10}NOF_3$ 347.2271; Found 347.2272.



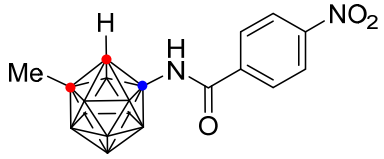
3o

3p: Yield: 76.3 mg (98%); R_f = 0.3 (EtOAc:CH_2Cl_2:Hexane = 1:1:5); White solid; Melting point: 170-172 ºC; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.90 (d, J = 8.5 Hz, 2H), 7.76 (d, J = 8.6 Hz, 2H), 5.99 (s, 1H), 5.04 (s, 1H), 2.10 (s, 3H); ^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$) δ 168.4, 138.6, 132.6, 128.0, 118.0, 115.4, 69.6, 61.2, 26.0; ^{11}B{^{1}H} NMR (128 MHz, $CDCl_3$) δ -3.43 - -4.01 (m, 2B), -7.16 (s, 1B), -9.79 - -11.91 (m, 6B), -15.13 (s, 1B); IR (film): 3401, 3262, 2942, 2588, 1667, 1268, 905, 867, 781 cm^{-1}; HRMS (FAB) *m/z*: $[M + H]^+$ Calcd for $C_{11}H_{18}B_{10}N_2O$ 305.2428; Found 305.2431.



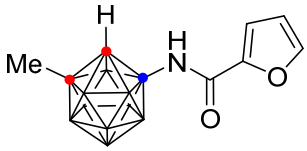
3p

3q: Yield: 34.2 mg (53%); R_f = 0.4 (EtOAc:CH_2Cl_2:Hexane = 1:1:5); White solid; Melting point: 168-170 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.31 (d, J = 8.7 Hz, 2H), 7.96 (d, J = 8.7 Hz, 2H), 5.98 (s, 1H), 5.04 (s, 1H), 2.11 (s, 3H); ^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$) δ 168.1, 149.9, 140.3, 128.5, 124.0, 69.7, 61.2, 26.1; ^{11}B{^{1}H} NMR (128 MHz, $CDCl_3$) δ -3.53 - -3.95 (m, 2B), -7.19 (s, 1B), -9.78 - -11.89 (m, 6B), -15.12 (s, 1B); IR (film): 3310, 3074, 2943, 2577, 1654, 1523, 1482, 1195, 960, 841, 735 cm^{-1}; HRMS (FAB) *m/z*: $[M + H]^+$ Calcd for $C_{10}H_{18}B_{10}N_2O_3$ 325.2326; Found 325.2330.



3q

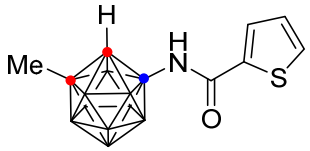
3r: Yield: 39.0 mg (79%); R_f = 0.3 (EtOAc:Hexane = 1:5); Yellow liquid; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.48 (d, J = 1.0 Hz, 1H), 7.11 (d, J = 3.5 Hz, 1H), 6.52 (dd, J = 3.5 Hz, J = 1.7 Hz, 1H), 6.16 (s, 1H), 5.02 (s, 1H), 2.07 (s, 3H); ^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$) δ 160.9, 148.0, 144.5, 115.0, 112.6, 69.4, 61.2, 26.0; ^{11}B{^{1}H} NMR (128 MHz, $CDCl_3$) δ -3.40 - -4.21 (m, 2B), -7.20 (s, 1B), -9.78 - -11.89 (m, 6B), -15.37 (s, 1B); IR (film): 3407, 3287, 2943, 2594, 1650, 1389, 1225, 935, 869, 757 cm^{-1}; HRMS (FAB) *m/z*: $[M + H]^+$ Calcd for $C_8H_{17}B_{10}NO_2$ 270.2268; Found 270.2269.



3r

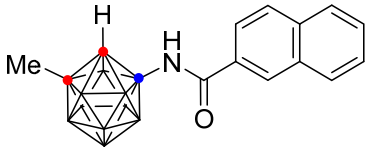
3s: Yield: 54.4 mg (96%); R_f = 0.5 (EtOAc:CH_2Cl_2:Hexane = 1:1:5); Purple solid; Melting point: 113-116 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.52 (dd, J = 5.0 Hz, J = 1.0 Hz, 1H), 7.50 (dd, J = 3.8 Hz, J = 1.0 Hz, 1H), 7.09 (dd, J = 4.9 Hz, J = 3.8 Hz, 1H), 5.77 (s, 1H), 5.05 (s, 1H), 2.07 (s, 3H); ^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$) δ 164.5, 139.7, 131.3, 128.8, 128.0, 69.4, 61.3, 26.0; ^{11}B{^{1}H} NMR (128 MHz,

$CDCl_3$) δ -3.34 - -4.29 (m, 2B), -7.27 (s, 1B), -9.80 - -11.91 (m, 6B), -15.34 (s, 1B); IR (film): 3219, 3084, 2587, 1627, 1478, 1243, 917, 883, 781 cm^{-1}; HRMS (FAB) *m/z*: $[M + H]^+$ Calcd for $C_8H_{17}B_{10}NOS$ 286.2039; Found 286.2040.



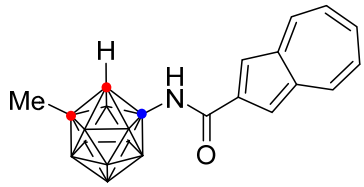
3s

3t: Yield: 63.5 mg (97%); R_f = 0.4 (EtOAc:CH_2Cl_2:Hexane = 1:1:5); White solid; Melting point: 183-185 °C; ^1H NMR (400 MHz, $CDCl_3$) δ 8.29 (s, 1H), 7.95-7.83 (m, 4H), 7.60-7.53 (m, 2H), 6.10 (s, 1H), 5.16 (s, 1H), 2.10 (s, 3H); $^{13}C\{^1H\}$ NMR (100 MHz, $CDCl_3$) δ 170.2, 135.0, 132.7, 131.9, 129.1, 128.7, 128.0, 127.9, 127.86, 127.0, 123.7, 69.4, 61.4, 26.1; $^{11}B\{^1H\}$ NMR (128 MHz, $CDCl_3$) δ -2.97 - -4.24 (m, 2B), -7.13 (s, 1B), -9.70 - -11.87 (m, 6B), -15.40 (s, 1B); IR (film): 3211, 2572, 1640, 1469, 1277, 949, 883, 754 cm^{-1}; HRMS (FAB) *m/z*: $[M + H]^+$ Calcd for $C_{14}H_{21}B_{10}NO$ 330.2634; Found 330.2635.



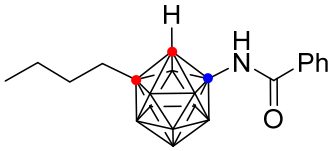
3t

3u: Yield: 60.6 mg (95%); R_f = 0.3 (EtOAc:CH_2Cl_2:Hexane = 1:1:5); Blue solid; Melting point: 204-206 °C; ^1H NMR (400 MHz, $CDCl_3$) δ 8.41 (d, J = 9.1 Hz, 2H), 7.68 (t, J = 9.9 Hz, 1H), 7.64 (s, 2H), 7.23 (t, J = 9.8 Hz, 2H), 6.17 (s, 1H), 5.19 (s, 1H), 2.09 (s, 3H); $^{13}C\{^1H\}$ NMR (100 MHz, $CDCl_3$) δ 168.4, 142.6, 140.4, 140.2, 140.0, 124.3, 116.6, 69.4, 61.4, 26.1; $^{11}B\{^1H\}$ NMR (128 MHz, $CDCl_3$) δ -3.06 - -4.39 (m, 2B), -7.20 (s, 1B), -9.73 - -11.88 (m, 6B), -15.45 (s, 1B); IR (film): 8209, 2560, 1644, 1455, 951, 883, 735 cm^{-1}; HRMS (FAB) *m/z*: $[M + H]^+$ Calcd for $C_{14}H_{21}B_{10}NO$ 330.2634; Found 330.2629.



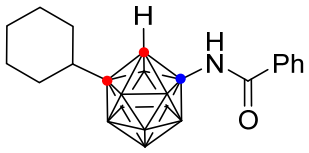
3u

5a: Yield: 65.1 mg (98%); R_f = 0.3 (EtOAc:CH_2Cl_2:Hexane = 1:1:15); White solid; Melting point: 160-162 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.80-7.78 (m, 2H), 7.55-7.51 (m, 1H), 7.45 (t, J = 7.4 Hz, 2H), 5.94 (s, 1H), 5.11 (s, 1H), 2.28-2.24 (m, 2H), 1.52-1.44 (m, 2H), 1.35-1.26 (m, 2H), 0.91 (t, J = 7.3 Hz, 3H); ^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$) δ 170.2, 134.7, 132.0, 128.8, 127.3, 74.6, 60.7, 38.0, 31.3, 22.2, 13.7; ^{11}B{^{1}H} NMR (128 MHz, $CDCl_3$) δ -3.48 - -6.38 (m, 3B), -9.97 - -12.48 (m, 6B), -16.06 (s, 1B); IR (film): 3428, 3309, 2959, 2567, 1637, 1470, 998, 805, 672 cm^{-1}; HRMS (FAB) *m/z*: $[M + H]^+$ Calcd for $C_{13}H_{25}B_{10}NO$ 322.2947; Found 322.2948.



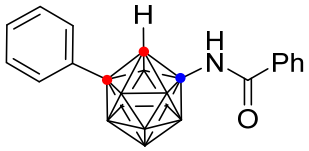
5a

5b: Yield: 65.0 mg (94%); R_f = 0.6 (EtOAc:CH_2Cl_2:Hexane = 1:1:5); White solid; Melting point: 180-182 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.80-7.78 (m, 2H), 7.55-7.50 (m, 1H), 7.45 (t, J = 7.4 Hz, 2H), 5.94 (s, 1H), 5.24 (s, 1H), 2.17-2.09 (m, 1H), 2.00-1.93 (m, 2H), 1.85-1.82 (m, 2H), 1.68-1.65 (m, 1H), 1.28-1.03 (m, 5H); ^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$) δ 170.2, 134.8, 132.0, 128.8, 127.3, 80.4, 59.2, 43.6, 33.2, 33.1, 26.5, 26.4, 25.2; ^{11}B{^{1}H} NMR (128 MHz, $CDCl_3$) δ -3.90 - -5.63 (m, 3B), -9.90 - -14.31 (m, 6B), -16.31 (s, 1B); IR (film): 3211, 2935, 2580, 1635, 1477, 931, 792, 639 cm^{-1}; HRMS (FAB) *m/z*: $[M + H]^+$ Calcd for $C_{15}H_{27}B_{10}NO$ 348.3103; Found 348.3099.



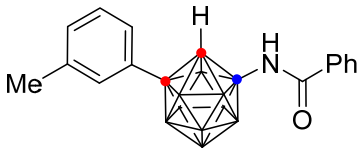
5b

5c: Yield: 61.1 mg (90%); R_f = 0.4 (EtOAc:CH_2Cl_2:Hexane = 1:1:15); White solid; Melting point: 206-208 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.82-7.80 (m, 2H), 7.55-7.51 (m, 3H), 7.48-7.44 (m, 2H), 7.42-7.32 (m, 3H), 6.02 (s, 1H), 5.56 (s, 1H); ^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$) δ 170.2, 134.7, 133.5, 132.1, 130.0, 129.0, 128.8, 127.7, 127.3, 75.6, 59.8; ^{11}B{^{1}H} NMR (128 MHz, $CDCl_3$) δ -3.19 - -4.87 (m, 3B), -9.43 - -12.05 (m, 6B), -15.77 (s, 1B); IR (film): 3432, 2559, 1636, 1472, 1209, 988, 762, 701 cm^{-1}; HRMS (FAB) *m/z*: $[M + H]^+$ Calcd for $C_{15}H_{21}B_{10}NO$ 342.2634; Found 342.2631.



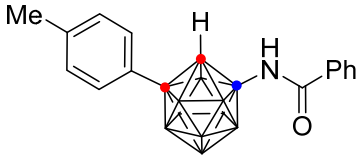
5c

5d: Yield: 56.6 mg (80%); R_f = 0.5 (Acetone:Hexane = 1:2); White solid; Melting point: 163-165 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.82-7.80 (m, 2H), 7.56-7.51 (m, 1H), 7.48-7.44 (m, 2H), 7.35-7.31 (m, 2H), 7.24-7.18 (m, 2H), 5.99 (s, 1H), 5.54 (s, 1H), 2.36 (s, 3H); ^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$) δ 170.2, 138.9, 134.7, 133.4, 132.1, 130.8, 128.81, 128.80, 128.2, 127.3, 124.8, 75.7, 59.7, 21.5; ^{11}B{^{1}H} NMR (128 MHz, $CDCl_3$) δ -3.20 - -4.89 (m, 3B), -9.59 - -12.08 (m, 6B), -15.70 (s, 1B); IR (film): 3429, 2576, 1643, 1442, 1207, 999, 707, 689 cm^{-1}; HRMS (FAB) *m/z*: $[M + H]^+$ Calcd for $C_{16}H_{23}B_{10}NO$ 356.2790; Found 356.2785.



5d

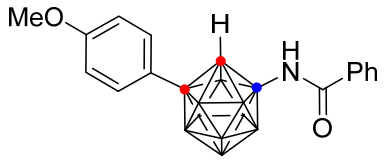
5e: Yield: 53.7 mg (76%); R_f = 0.6 (EtOAc:CH_2Cl_2:Hexane = 1:1:5); White solid; Melting point: 172-174 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.82-7.79 (m, 2H), 7.55-7.51 (m, 1H), 7.48-7.41 (m, 4H), 7.13 (d, J = 8.0 Hz, 2H), 6.00 (s, 1H), 5.51 (s, 1H), 2.34 (s, 3H); ^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$) δ 170.2, 140.3, 134.7, 132.1, 130.6, 129.6, 128.8, 127.6, 127.3, 75.8, 60.0, 21.1; ^{11}B{^{1}H} NMR (128 MHz, $CDCl_3$) δ -3.24 - -4.87 (m, 3B), -9.54 - -12.03 (m, 6B), -15.70 (s, 1B); IR (film): 3215, 2923, 2576, 1642, 1443, 900, 883, 710 cm^{-1}; HRMS (FAB) *m/z*: $[M + H]^+$ Calcd for $C_{16}H_{23}B_{10}NO$ 356.2790; Found 356.2785.



5e

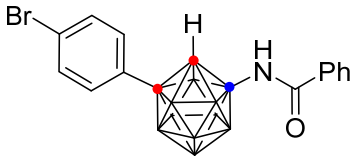
5f: Yield: 53.9 mg (73%); R_f = 0.4 (EtOAc:CH_2Cl_2:Hexane = 1:1:5); White solid; Melting point: 151-154 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.80 (d, J = 7.3 Hz, 2H), 7.53 (t, J = 7.3 Hz, 1H), 7.48-7.44 (m, 4H), 6.83 (d, J = 8.9 Hz, 2H), 6.02 (s, 1H), 5.45 (s, 1H), 3.81 (s, 3H); ^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$)

δ 170.2, 160.9, 134.6, 132.0, 129.4, 128.8, 127.3, 125.5, 114.1, 75.9, 60.6, 55.6; $^{11}B\{^{1}H\}$ NMR (128 MHz, $CDCl_3$) δ -3.17 - -4.74 (m, 3B), -9.63 - -11.93 (m, 6B), -15.62 (s, 1B); IR (film): 3214, 2935, 2578, 1644, 1259, 998, 867, 736 cm^{-1}; HRMS (FAB) *m/z*: $[M + H]^+$ Calcd for $C_{16}H_{23}B_{10}NO_2$ 372.2737; Found 372.2741.



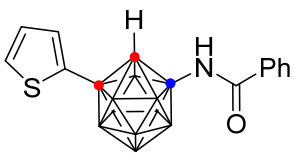
5f

5g: Yield: 71.1 mg (85%); R_f = 0.6 (EtOAc:CH_2Cl_2:Hexane = 1:1:5); White solid; Melting point: 184-186 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.82-7.79 (m, 2H), 7.56-7.52 (m, 1H), 7.49-7.44 (m, 4H), 7.43-7.40 (m, 2H), 6.01 (s, 1H), 5.53 (s, 1H); $^{13}C\{^{1}H\}$ NMR (100 MHz, $CDCl_3$) δ 170.3, 134.6, 132.6, 132.2, 129.3, 128.8, 127.3, 124.8, 74.6, 59.7; $^{11}B\{^{1}H\}$ NMR (128 MHz, $CDCl_3$) δ -3.96 - -5.70 (m, 3B), -10.00 - -14.30 (m, 6B), -16.32 (s, 1B); IR (film): 3210, 2578, 1644, 1469, 1011, 883, 833, 709, 639 cm^{-1}; HRMS (FAB) *m/z*: $[M + H]^+$ Calcd for $C_{15}H_{20}B_{10}BrNO$ 420.1739; Found 420.1735.



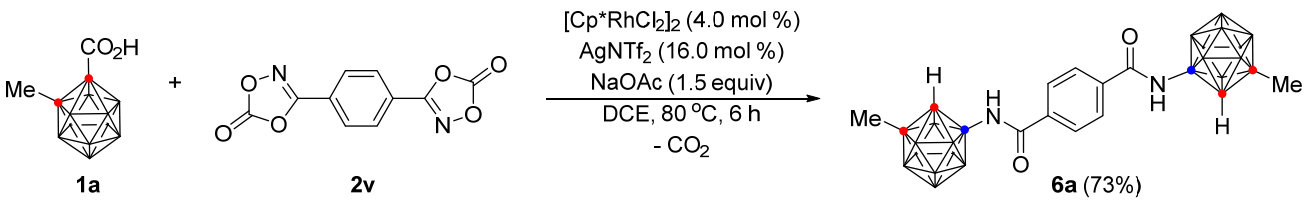
5g

5h: Yield: 53.9 mg (78%); R_f = 0.5 (EtOAc:CH_2Cl_2:Hexane = 1:1:5); White solid; Melting point: 153-155 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.81-7.78 (m, 2H), 7.55-7.51 (m, 1H), 7.46 (t, J = 7.4 Hz, 2H), 7.27-7.22 (m, 2H), 6.91 (dd, J = 5.2 Hz, J = 3.8 Hz, 1H), 5.99 (s, 1H), 5.37 (s, 1H); $^{13}C\{^{1}H\}$ NMR (100 MHz, $CDCl_3$) δ 170.1, 136.7, 134.6, 132.1, 130.2, 128.8, 128.2, 127.33, 127.30, 71.0, 63.0; $^{11}B\{^{1}H\}$ NMR (128 MHz, $CDCl_3$) δ -2.94 - -5.17 (m, 3B), -10.10 - -11.44 (m, 6B), -14.84 (s, 1B); IR (film): 3209, 2575, 1644, 1469, 1256, 946, 884, 708 cm^{-1}; HRMS (FAB) *m/z*: $[M + H]^+$ Calcd for $C_{13}H_{19}B_{10}NOS$ 348.2198; Found 348.2199.



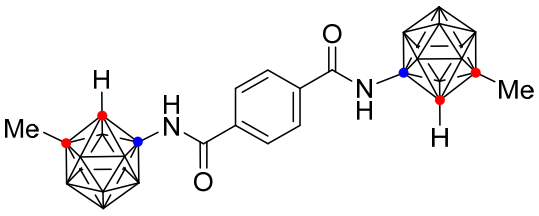
5h

3. Two-Fold Selective B(4)−H Amidation Reaction

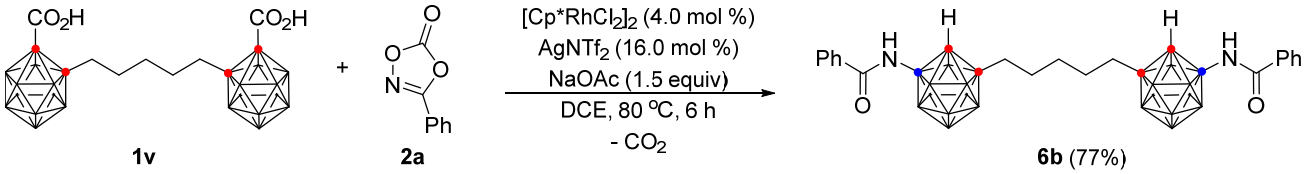


A dried test tube equipped with a magnetic stirrer was charged with *o*-carborane **1a** (0.48 mmol, 97.1 mg), 1,4,2-dioxazol-5-one **2v** (0.2 mmol, 49.6 mg), $[Cp^*RhCl_2]_2$ (4.0 mol %, 4.9 mg), $AgSbF_6$ (16.0 mol %, 11.0 mg), NaOAc (1.5 equiv, 24.6 mg), and DCE (2.0 mL) under a nitrogen atmosphere. After being stirred at 80 °C for 6 h, the reaction mixture was cooled to room temperature, filtered through a pad of Celite and concentrated under reduced pressure. The crude product was purified by column chromatography on silica gel to afford the amidation product **6a** (73%, 69.6 mg) as white solid.

6a: Yield: 69.1 mg (73%); R_f = 0.3 (Acetone:Hexane = 1:4); White solid; Melting point: 309-312 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.86 (s, 4H), 5.98 (s, 2H), 5.07 (s, 2H), 2.10 (s, 6H); $^{13}C\{^1H\}$ NMR (100 MHz, $CDCl_3$) δ 169.1, 133.7, 127.7, 69.6, 61.3, 26.1; $^{11}B\{^1H\}$ NMR (128 MHz, $CDCl_3$) δ -3.26 - -4.12 (m, 2B), -7.17 (s, 1B), -9.80 - -11.87 (m, 6B), 15.13 (s, 1H); IR (film): 3423, 3097, 2570, 1637, 1273, 987, 893, 725 cm^{-1}; HRMS (FAB) *m/z*: $[M + H]^+$ Calcd for $C_{14}H_{32}B_{20}N_2O_2$ 481.4405; Found 481.4406.



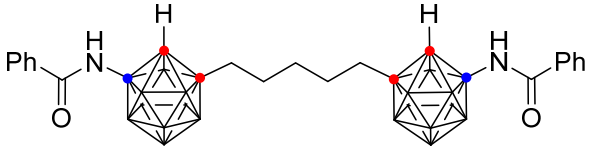
6a



A dried test tube equipped with a magnetic stirrer was charged with *o*-carborane **1a** (0.2 mmol, 88.9 mg), 1,4,2-dioxazol-5-one **2v** (0.48 mmol, 78.3 mg), $[Cp^*RhCl_2]_2$ (4.0 mol %, 4.9 mg), $AgSbF_6$ (16.0 mol %, 11.0 mg), NaOAc (1.5 equiv, 24.6 mg), and DCE (2.0 mL) under a nitrogen atmosphere. After being stirred at 80 °C for 6 h, the reaction mixture was cooled to room temperature, filtered through a pad of

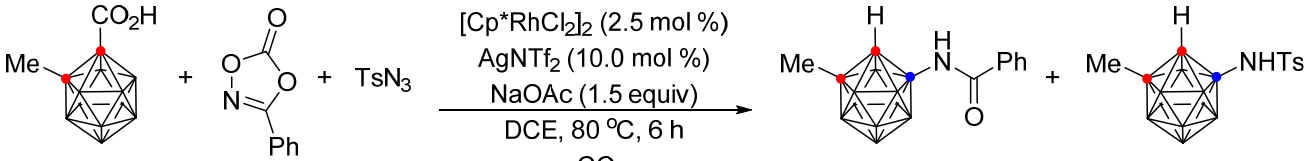
Celite and concentrated under reduced pressure. The crude product was purified by column chromatography on silica gel to afford the amidation product **6b** (77%, 91.6 mg) as white solid.

6b: Yield: 92.1 mg (77%); R_f = 0.3 (EtOAc:CH_2Cl_2:Hexane = 1:1:5); White solid; Melting point: 97-99 ^oC; ^1H NMR (400 MHz, $CDCl_3$) δ 7.80-7.78 (m, 4H), 7.55-7.50 (m, 2H), 7.47-7.43 (m, 4H), 5.96 (s, 2H), 5.11 (s, 2H), 2.27-2.22 (m, 4H), 1.55-1.47 (m, 4H), 1.28-1.21 (m, 2H); $^{13}C\{^1H\}$ NMR (100 MHz, $CDCl_3$) δ 170.2, 134.6, 132.0, 128.8, 127.3, 74.0, 60.9, 38.0, 28.9, 28.4; $^{11}B\{^1H\}$ NMR (128 MHz, $CDCl_3$) δ -3.41 - -6.13 (m, 3B), -9.97 - -12.44 (m, 6B), -15.68 (s, 1B); IR (film): 3428, 2956, 2581, 1644, 1276, 1073, 709 cm^{-1}; HRMS (FAB) *m/z*: $[M + H]^+$ Calcd for $C_{23}H_{42}B_{20}N_2O_2$ 599.5187; Found 599.5187.



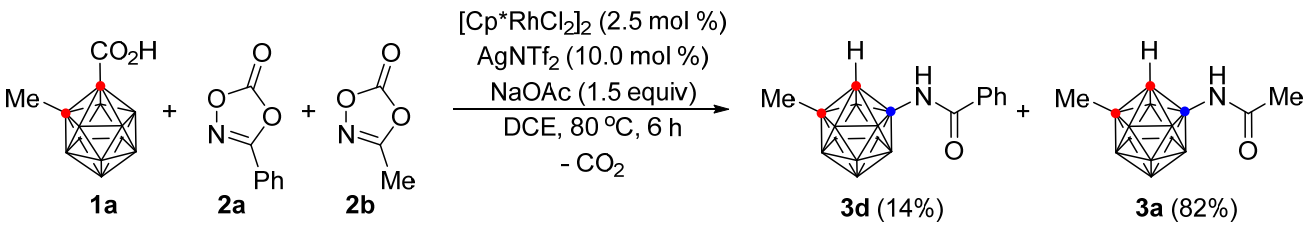
6b

4. Comparison of TsN_3 and dioxazolone in B-H activation

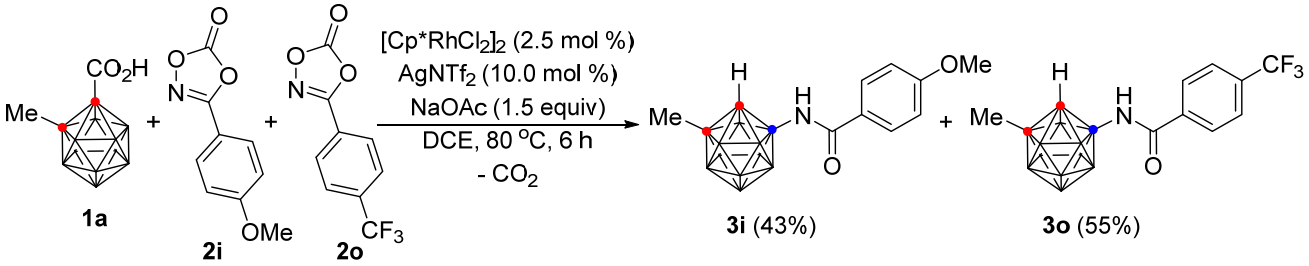


1a **2a** **7** **3d** (90%) trace

A dried test tube equipped with a magnetic stirrer was charged with amidated *o*-carborane **1a** (0.2 mmol, 40.5 mg), 1,4,2-dioxazol-5-one **2a** (0.2 mmol, 32.6 mg), TsN_3 **7** (0.2 mmol, 39.4 mg), $[Cp^*RhCl_2]_2$ (2.5 mol %, 3.1 mg), $AgSbF_6$ (10.0 mol %, 6.9 mg), NaOAc (1.5 equiv, 24.6 mg), and DCE (2.0 mL) under a nitrogen atmosphere. After being stirred at 80 °C for 6 h, the reaction mixture was cooled to room temperature, filtered through a pad of Celite and concentrated under reduced pressure. The crude product was purified by column chromatography on silica gel to afford the amidation product **3d** (90%, 56.0 mg) as white solid.

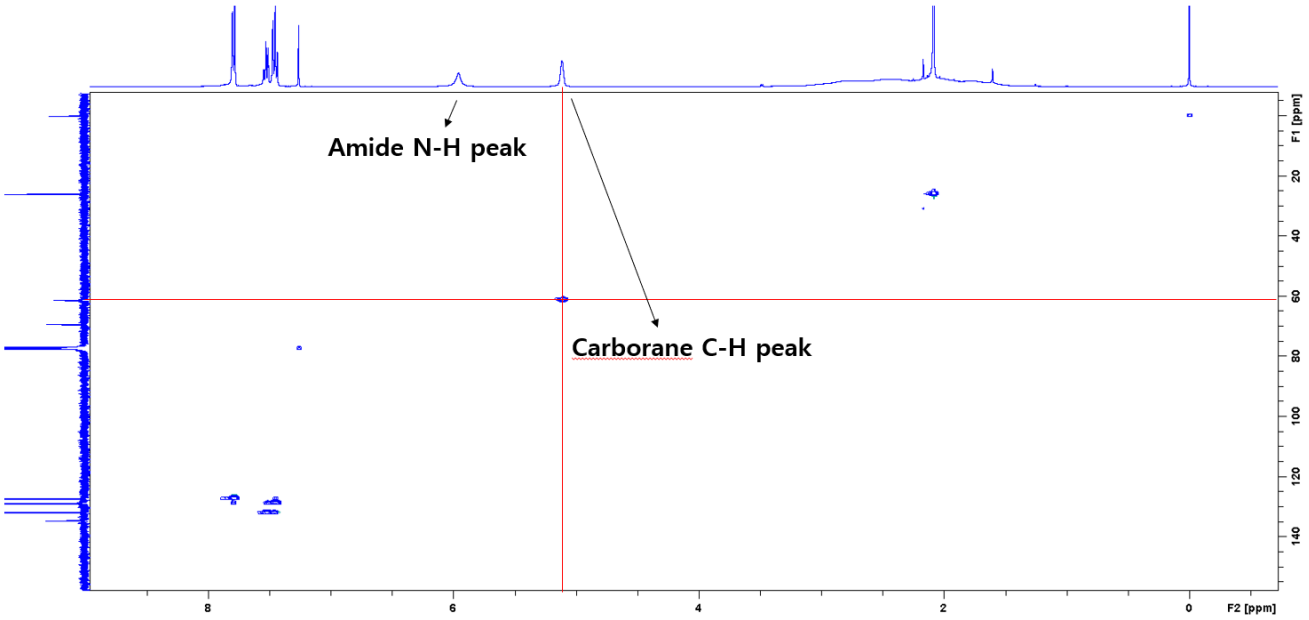


A dried test tube equipped with a magnetic stirrer was charged with amidated *o*-carborane **1a** (0.2 mmol, 40.5 mg), 1,4,2-dioxazol-5-one **2a** (0.2 mmol, 32.6 mg), **2b** (0.2 mmol, 20.2 mg), $[Cp^*RhCl_2]_2$ (2.5 mol %, 3.1 mg), $AgSbF_6$ (10.0 mol %, 6.9 mg), NaOAc (1.5 equiv, 24.6 mg), and DCE (2.0 mL) under a nitrogen atmosphere. After being stirred at 80 °C for 6 h, the reaction mixture was cooled to room temperature, filtered through a pad of Celite and concentrated under reduced pressure. The crude product was purified by column chromatography on silica gel to afford the amidation product **3a** (82%, 35.3 mg) and **3d** (14%, 7.8 mg) as white solid.



A dried test tube equipped with a magnetic stirrer was charged with amidated *o*-carborane **1a** (0.2 mmol, 40.5 mg), 1,4,2-dioxazol-5-one **2i** (0.2 mmol, 38.6 mg), **2o** (0.2 mmol, 46.2 mg), $[Cp^*RhCl_2]_2$ (2.5 mol %, 3.1 mg), $AgSbF_6$ (10.0 mol %, 6.9 mg), NaOAc (1.5 equiv, 24.6 mg), and DCE (2.0 mL) under a nitrogen atmosphere. After being stirred at 80 °C for 6 h, the reaction mixture was cooled to room temperature, filtered through a pad of Celite and concentrated under reduced pressure. The crude product was purified by column chromatography on silica gel to afford the amidation product **3i** (43%, 25.1 mg) and **3o** (55%, 38.0 mg) as white solid.

5. NMR Study for HSQCGP(2D NMR spectrum)



6. X-ray Crystallography

3d (50 mg) was dissolved in ACN (2.0 mL) in a 10 mL glass vial to give a clear solution. The 10 mL vial was sealed with a screw cap. Vapor diffusion afforded crystals of the composition **3d** suitable for X-ray diffraction within 2 day at room temperature. A block-like specimen of $C_{10}H_{19}B_{10}NO$, approximate dimensions 0.100 mm x 0.100 mm x 0.150 mm, was used for the X-ray crystallographic analysis. The X-ray intensity data were measured. (ellipsoid = 40%, CCDC = 1896569)

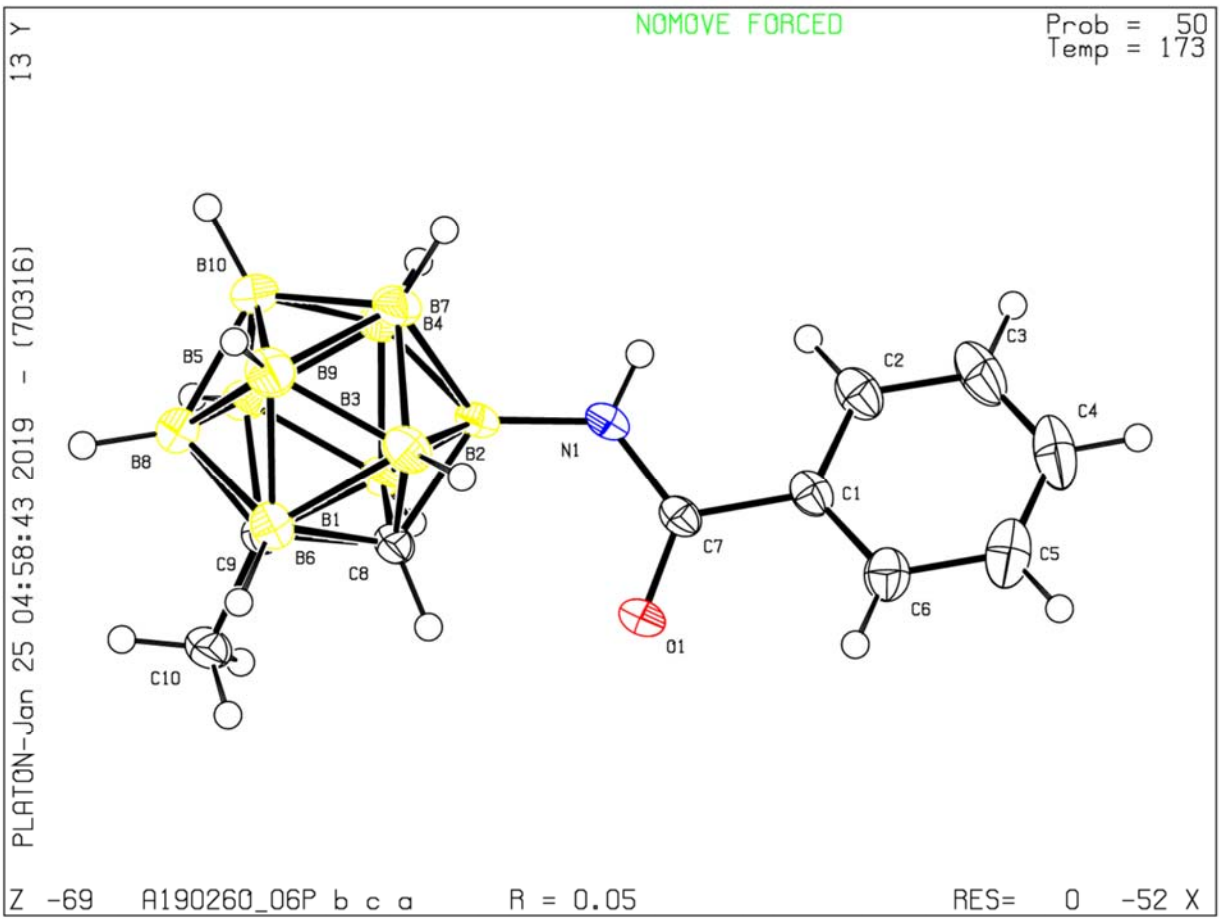


Table 1. Crystal data and structure refinement for **3d**.

Empirical formula	$C_{10}H_{19}B_{10}NO$
Formula weight	277.36
Temperature	173(2) K
Wavelength	0.71073 Å
Crystal system	Orthorhombic
Space group	*Pbca*

Unit cell dimensions	a = 9.4145(6) Å	α = 90°
	b = 16.7722(10) Å	β = 90°
	c = 20.1088(11) Å	γ = 90°
Volume	3175.2(3) $Å^3$	
Z	8	
Density (calculated)	1.160 Mg/m^3	
Absorption coefficient	0.062 mm^{-1}	
F(000)	1152	
Crystal size	0.368 x 0.123 x 0.115 mm^3	
Theta range for data collection	3.163 to 28.297°.	
Index ranges	–12<=h<=12, –22<=k<=22, –22<=l<=26	
Reflections collected	51187	
Independent reflections	3946 [R(int) = 0.0917]	
Completeness to theta = 25.242°	99.7 %	
Absorption correction	Semi-empirical from equivalents	
Max. and min. transmission	0.7457 and 0.6875	
Refinement method	Full-matrix least-squares on F^2	
Data / restraints / parameters	3946 / 0 / 233	
Goodness-of-fit on F^2	1.066	
Final R indices [I>2sigma(I)]	R1 = 0.0540, wR2 = 0.1225	
R indices (all data)	R1 = 0.0979, wR2 = 0.1445	
Largest diff. peak and hole	0.322 and –0.285 $e \cdot Å^{-3}$	

Table 2. Atomic coordinates (x 10^4) and equivalent isotropic displacement parameters ($Å^2$ x 10^3) for **3d**. U(eq) is defined as one third of the trace of the orthogonalized U^{ij} tensor.

	x	y	z	U(eq)
C(1)	7420(2)	5688(1)	8211(1)	24(1)
C(2)	8563(2)	5240(1)	7985(1)	30(1)
C(3)	9286(2)	4743(1)	8419(1)	42(1)
C(4)	8880(2)	4693(1)	9078(1)	47(1)
C(5)	7723(2)	5126(1)	9302(1)	43(1)
C(6)	6988(2)	5619(1)	8870(1)	32(1)
C(7)	6648(2)	6274(1)	7778(1)	23(1)
O(1)	5429(1)	6486(1)	7914(1)	33(1)
N(1)	7365(2)	6575(1)	7252(1)	25(1)
C(8)	5249(2)	7635(1)	6832(1)	24(1)
C(9)	4644(2)	7884(1)	6089(1)	23(1)
C(10)	3058(2)	7811(1)	5969(1)	31(1)
B(1)	5577(2)	7010(1)	6171(1)	24(1)
B(2)	6887(2)	7206(1)	6793(1)	23(1)
B(3)	6645(2)	8216(1)	7062(1)	28(1)
B(4)	7329(2)	7230(1)	5931(1)	26(1)
B(5)	5868(2)	7650(1)	5489(1)	28(1)
B(6)	5188(2)	8631(1)	6625(1)	27(1)
B(7)	7996(2)	7981(1)	6481(1)	29(1)
B(8)	5625(2)	8646(1)	5766(1)	30(1)
B(9)	6936(2)	8859(1)	6376(1)	32(1)
B(10)	7369(2)	8248(1)	5679(1)	31(1)

—

Table 3. Bond lengths [Å] and angles [°] for **3d**.

C(1)-C(2)	1.388(2)	B(2)-B(4)	1.784(3)
C(1)-C(6)	1.392(2)	B(2)-B(3)	1.793(3)
C(1)-C(7)	1.501(2)	B(3)-B(6)	1.771(3)
C(2)-C(3)	1.386(3)	B(3)-B(7)	1.771(3)
C(2)-H(2)	0.9500	B(3)-B(9)	1.773(3)
C(3)-C(4)	1.382(3)	B(3)-H(3B)	1.08(2)
C(3)-H(3)	0.9500	B(4)-B(10)	1.782(3)
C(4)-C(5)	1.384(3)	B(4)-B(5)	1.783(3)
C(4)-H(4)	0.9500	B(4)-B(7)	1.790(3)
C(5)-C(6)	1.385(3)	B(4)-H(4B)	1.10(2)
C(5)-H(5)	0.9500	B(5)-B(10)	1.775(3)
C(6)-H(6)	0.9500	B(5)-B(8)	1.776(3)
C(7)-O(1)	1.2318(19)	B(5)-H(5B)	1.09(2)
C(7)-N(1)	1.353(2)	B(6)-B(9)	1.763(3)
N(1)-B(2)	1.475(2)	B(6)-B(8)	1.776(3)
N(1)-H(1N)	0.84(2)	B(6)-H(6B)	1.08(2)
C(8)-C(9)	1.652(2)	B(7)-B(10)	1.775(3)
C(8)-B(3)	1.700(3)	B(7)-B(9)	1.792(3)
C(8)-B(2)	1.703(2)	B(7)-H(7B)	1.10(2)
C(8)-B(1)	1.720(2)	B(8)-B(9)	1.775(3)
C(8)-B(6)	1.721(3)	B(8)-B(10)	1.781(3)
C(8)-H(8)	1.01(2)	B(8)-H(8B)	1.08(2)
C(9)-C(10)	1.518(2)	B(9)-B(10)	1.782(3)
C(9)-B(8)	1.706(3)	B(9)-H(9B)	1.10(2)
C(9)-B(5)	1.714(2)	B(10)-H(10B)	1.12(2)
C(9)-B(1)	1.717(2)		
C(9)-B(6)	1.730(2)	C(2)-C(1)-C(6)	119.54(16)
C(10)-H(10A)	0.9800	C(2)-C(1)-C(7)	122.70(15)
C(10)-H(10D)	0.9800	C(6)-C(1)-C(7)	117.72(15)
C(10)-H(10C)	0.9800	C(3)-C(2)-C(1)	120.03(18)
B(1)-B(4)	1.759(3)	C(3)-C(2)-H(2)	120.0
B(1)-B(5)	1.764(3)	C(1)-C(2)-H(2)	120.0
B(1)-B(2)	1.787(3)	C(4)-C(3)-C(2)	120.29(19)
B(1)-H(1B)	1.05(2)	C(4)-C(3)-H(3)	119.9
B(2)-B(7)	1.782(3)	C(2)-C(3)-H(3)	119.9

C(3)-C(4)-C(5) 119.90(18)
C(3)-C(4)-H(4) 120.0
C(5)-C(4)-H(4) 120.0
C(4)-C(5)-C(6) 120.10(19)
C(4)-C(5)-H(5) 119.9
C(6)-C(5)-H(5) 119.9
C(5)-C(6)-C(1) 120.10(18)
C(5)-C(6)-H(6) 120.0
C(1)-C(6)-H(6) 120.0
O(1)-C(7)-N(1) 122.09(15)
O(1)-C(7)-C(1) 120.75(15)
N(1)-C(7)-C(1) 117.12(14)
C(7)-N(1)-B(2) 127.19(14)
C(7)-N(1)-H(1N) 117.2(13)
B(2)-N(1)-H(1N) 115.1(13)
C(9)-C(8)-B(3) 111.57(13)
C(9)-C(8)-B(2) 112.19(12)
B(3)-C(8)-B(2) 63.58(11)
C(9)-C(8)-B(1) 61.17(10)
B(3)-C(8)-B(1) 114.90(13)
B(2)-C(8)-B(1) 62.92(10)
C(9)-C(8)-B(6) 61.67(10)
B(3)-C(8)-B(6) 62.33(11)
B(2)-C(8)-B(6) 115.42(13)
B(1)-C(8)-B(6) 114.28(13)
C(9)-C(8)-H(8) 113.2(11)
B(3)-C(8)-H(8) 124.3(11)
B(2)-C(8)-H(8) 123.1(11)
B(1)-C(8)-H(8) 114.9(11)
B(6)-C(8)-H(8) 115.3(11)
C(10)-C(9)-C(8) 117.56(13)
C(10)-C(9)-B(8) 122.21(14)
C(8)-C(9)-B(8) 110.30(13)
C(10)-C(9)-B(5) 122.03(13)
C(8)-C(9)-B(5) 110.31(12)
B(8)-C(9)-B(5) 62.59(11)
C(10)-C(9)-B(1) 116.67(14)
C(8)-C(9)-B(1) 61.37(10)
B(8)-C(9)-B(1) 113.58(13)
B(5)-C(9)-B(1) 61.87(11)
C(10)-C(9)-B(6) 116.71(14)
C(8)-C(9)-B(6) 61.14(10)
B(8)-C(9)-B(6) 62.26(11)
B(5)-C(9)-B(6) 113.94(13)
B(1)-C(9)-B(6) 114.00(12)
C(9)-C(10)-H(10A) 109.5
C(9)-C(10)-H(10D) 109.5
H(10A)-C(10)-H(10D) 109.5
C(9)-C(10)-H(10C) 109.5
H(10A)-C(10)-H(10C) 109.5
H(10D)-C(10)-H(10C) 109.5
C(9)-B(1)-C(8) 57.46(9)
C(9)-B(1)-B(4) 105.90(13)
C(8)-B(1)-B(4) 104.62(13)
C(9)-B(1)-B(5) 58.97(10)
C(8)-B(1)-B(5) 104.91(14)
B(4)-B(1)-B(5) 60.84(11)
C(9)-B(1)-B(2) 105.26(13)
C(8)-B(1)-B(2) 58.08(10)
B(4)-B(1)-B(2) 60.40(10)
B(5)-B(1)-B(2) 108.98(14)
C(9)-B(1)-H(1B) 117.5(11)
C(8)-B(1)-H(1B) 118.1(10)
B(4)-B(1)-H(1B) 130.4(10)
B(5)-B(1)-H(1B) 123.9(10)
B(2)-B(1)-H(1B) 123.5(10)
N(1)-B(2)-C(8) 123.46(14)
N(1)-B(2)-B(7) 124.39(14)
C(8)-B(2)-B(7) 103.79(13)
N(1)-B(2)-B(4) 123.59(14)
C(8)-B(2)-B(4) 104.25(12)
B(7)-B(2)-B(4) 60.27(11)
N(1)-B(2)-B(1) 121.13(14)
C(8)-B(2)-B(1) 59.00(10)
B(7)-B(2)-B(1) 107.00(13)
B(4)-B(2)-B(1) 59.01(10)

N(1)-B(2)-B(3)	121.89(14)	C(9)-B(5)-B(8)	58.49(10)
C(8)-B(2)-B(3)	58.12(10)	B(1)-B(5)-B(8)	107.99(13)
B(7)-B(2)-B(3)	59.41(11)	B(10)-B(5)-B(8)	60.19(12)
B(4)-B(2)-B(3)	107.53(13)	C(9)-B(5)-B(4)	104.97(12)
B(1)-B(2)-B(3)	107.29(13)	B(1)-B(5)-B(4)	59.44(10)
C(8)-B(3)-B(6)	59.43(10)	B(10)-B(5)-B(4)	60.09(11)
C(8)-B(3)-B(7)	104.37(13)	B(8)-B(5)-B(4)	108.33(14)
B(6)-B(3)-B(7)	108.47(14)	C(9)-B(5)-H(5B)	117.7(11)
C(8)-B(3)-B(9)	104.84(13)	B(1)-B(5)-H(5B)	117.0(11)
B(6)-B(3)-B(9)	59.66(11)	B(10)-B(5)-H(5B)	129.5(11)
B(7)-B(3)-B(9)	60.74(12)	B(8)-B(5)-H(5B)	121.3(11)
C(8)-B(3)-B(2)	58.30(10)	B(4)-B(5)-H(5B)	126.0(11)
B(6)-B(3)-B(2)	108.67(13)	C(8)-B(6)-C(9)	57.19(9)
B(7)-B(3)-B(2)	59.98(11)	C(8)-B(6)-B(9)	104.38(14)
B(9)-B(3)-B(2)	108.70(14)	C(9)-B(6)-B(9)	104.83(14)
C(8)-B(3)-H(3B)	117.7(11)	C(8)-B(6)-B(3)	58.24(10)
B(6)-B(3)-H(3B)	118.3(11)	C(9)-B(6)-B(3)	104.71(13)
B(7)-B(3)-H(3B)	128.1(11)	B(9)-B(6)-B(3)	60.24(12)
B(9)-B(3)-H(3B)	127.6(11)	C(8)-B(6)-B(8)	103.96(13)
B(2)-B(3)-H(3B)	118.9(10)	C(9)-B(6)-B(8)	58.20(10)
B(1)-B(4)-B(10)	107.39(13)	B(9)-B(6)-B(8)	60.21(12)
B(1)-B(4)-B(5)	59.72(10)	B(3)-B(6)-B(8)	107.98(14)
B(10)-B(4)-B(5)	59.71(11)	C(8)-B(6)-H(6B)	118.4(11)
B(1)-B(4)-B(2)	60.58(10)	C(9)-B(6)-H(6B)	115.0(11)
B(10)-B(4)-B(2)	107.63(14)	B(9)-B(6)-H(6B)	132.5(11)
B(5)-B(4)-B(2)	108.24(13)	B(3)-B(6)-H(6B)	127.1(10)
B(1)-B(4)-B(7)	107.88(13)	B(8)-B(6)-H(6B)	122.0(10)
B(10)-B(4)-B(7)	59.60(11)	B(3)-B(7)-B(10)	107.68(14)
B(5)-B(4)-B(7)	107.50(14)	B(3)-B(7)-B(2)	60.60(11)
B(2)-B(4)-B(7)	59.82(10)	B(10)-B(7)-B(2)	108.00(13)
B(1)-B(4)-H(4B)	118.7(10)	B(3)-B(7)-B(4)	108.19(13)
B(10)-B(4)-H(4B)	125.0(10)	B(10)-B(7)-B(4)	59.97(11)
B(5)-B(4)-H(4B)	121.4(10)	B(2)-B(7)-B(4)	59.92(10)
B(2)-B(4)-H(4B)	120.0(10)	B(3)-B(7)-B(9)	59.67(11)
B(7)-B(4)-H(4B)	124.2(10)	B(10)-B(7)-B(9)	59.96(12)
C(9)-B(5)-B(1)	59.16(10)	B(2)-B(7)-B(9)	108.35(13)
C(9)-B(5)-B(10)	104.72(13)	B(4)-B(7)-B(9)	108.04(14)
B(1)-B(5)-B(10)	107.47(13)	B(3)-B(7)-H(7B)	121.8(10)

B(10)-B(7)-H(7B)	122.9(10)	B(6)-B(9)-B(7)	107.92(14)
B(2)-B(7)-H(7B)	119.7(11)	B(3)-B(9)-B(7)	59.59(11)
B(4)-B(7)-H(7B)	120.5(10)	B(8)-B(9)-B(7)	107.69(14)
B(9)-B(7)-H(7B)	123.5(11)	B(10)-B(9)-B(7)	59.55(12)
C(9)-B(8)-B(9)	105.32(13)	B(6)-B(9)-H(9B)	119.3(11)
C(9)-B(8)-B(5)	58.92(11)	B(3)-B(9)-H(9B)	120.1(10)
B(9)-B(8)-B(5)	108.44(14)	B(8)-B(9)-H(9B)	122.3(11)
C(9)-B(8)-B(6)	59.54(10)	B(10)-B(9)-H(9B)	124.5(11)
B(9)-B(8)-B(6)	59.51(12)	B(7)-B(9)-H(9B)	122.9(11)
B(5)-B(8)-B(6)	108.72(14)	B(5)-B(10)-B(7)	108.55(14)
C(9)-B(8)-B(10)	104.79(14)	B(5)-B(10)-B(8)	59.95(11)
B(9)-B(8)-B(10)	60.16(12)	B(7)-B(10)-B(8)	108.20(14)
B(5)-B(8)-B(10)	59.86(12)	B(5)-B(10)-B(4)	60.19(11)
B(6)-B(8)-B(10)	107.67(14)	B(7)-B(10)-B(4)	60.44(11)
C(9)-B(8)-H(8B)	117.1(11)	B(8)-B(10)-B(4)	108.21(13)
B(9)-B(8)-H(8B)	128.0(11)	B(5)-B(10)-B(9)	108.19(14)
B(5)-B(8)-H(8B)	118.4(11)	B(7)-B(10)-B(9)	60.50(12)
B(6)-B(8)-H(8B)	119.1(11)	B(8)-B(10)-B(9)	59.77(12)
B(10)-B(8)-H(8B)	128.1(11)	B(4)-B(10)-B(9)	108.85(14)
B(6)-B(9)-B(3)	60.11(11)	B(5)-B(10)-H(10B)	121.3(11)
B(6)-B(9)-B(8)	60.28(11)	B(7)-B(10)-H(10B)	121.3(11)
B(3)-B(9)-B(8)	107.93(14)	B(8)-B(10)-H(10B)	122.1(11)
B(6)-B(9)-B(10)	108.21(14)	B(4)-B(10)-H(10B)	120.9(11)
B(3)-B(9)-B(10)	107.29(14)	B(9)-B(10)-H(10B)	121.8(11)
B(8)-B(9)-B(10)	60.07(12)		

Symmetry transformations used to generate equivalent atoms:

Table 4. Anisotropic displacement parameters ($Å^2$ x 10^3) for **3d**. The anisotropic displacement factor exponent takes the form: $-2\pi^2[h^2a^{*2}U^{11} + ... + 2 h k a^* b^* U^{12}]$

U^{11}	U^{22}	U^{33}	U^{23}	U^{13}	U^{12}	
C(1)21(1)	20(1)	31(1)	-2(1)	-7(1)	-2(1)	
C(2)28(1)	23(1)	41(1)	-4(1)	-7(1)	3(1)	
C(3)38(1)	25(1)	64(1)	-2(1)	-16(1)	9(1)	
C(4)55(1)	30(1)	56(1)	8(1)	-27(1)	2(1)	
C(5)59(1)	33(1)	36(1)	7(1)	-13(1)	-5(1)	
C(6)36(1)	27(1)	32(1)	2(1)	-4(1)	-1(1)	
C(7)17(1)	24(1)	27(1)	-1(1)	-4(1)	0(1)	
O(1)17(1)	44(1)	37(1)	9(1)	3(1)	6(1)	
N(1)15(1)	29(1)	31(1)	2(1)	1(1)	5(1)	
C(8)19(1)	30(1)	22(1)	2(1)	-2(1)	3(1)	
C(9)20(1)	30(1)	19(1)	1(1)	-1(1)	2(1)	
C(10)	20(1)	43(1)	28(1)	3(1)	-2(1)	2(1)
B(1)19(1)	29(1)	24(1)	1(1)	-1(1)	0(1)	
B(2)14(1)	28(1)	27(1)	0(1)	0(1)	0(1)	
B(3)24(1)	28(1)	30(1)	-5(1)	-6(1)	0(1)	
B(4)19(1)	33(1)	26(1)	-1(1)	4(1)	2(1)	
B(5)25(1)	39(1)	20(1)	0(1)	4(1)	1(1)	
B(6)27(1)	27(1)	27(1)	0(1)	-3(1)	3(1)	
B(7)18(1)	32(1)	36(1)	2(1)	-1(1)	-3(1)	
B(8)27(1)	32(1)	29(1)	7(1)	1(1)	0(1)	
B(9)28(1)	27(1)	42(1)	2(1)	-4(1)	-5(1)	
B(10)	22(1)	37(1)	34(1)	8(1)	5(1)	-2(1)

Table 5. Hydrogen coordinates (x 10^4) and isotropic displacement parameters ($Å^2$ x 10^2) for **3d**.

	x	y	z	U(eq)
H(2)	8849	5275	7533	36
H(3)	10065	4435	8263	51
H(4)	9394	4363	9377	56
H(5)	7433	5085	9754	51
H(6)	6187	5910	9024	38
H(1N)	8220(20)	6434(11)	7206(9)	30
H(8)	4480(20)	7448(12)	7145(9)	35
H(10A)	2825	7257	5859	46
H(10D)	2782	8158	5599	46
H(10C)	2543	7970	6371	46
H(1B)	5000(20)	6475(12)	6142(9)	36
H(3B)	6760(20)	8354(12)	7584(10)	41
H(4B)	7980(20)	6753(12)	5714(9)	39
H(5B)	5470(20)	7453(12)	5005(10)	42
H(6B)	4340(20)	8990(12)	6828(10)	40
H(7B)	9120(20)	7994(12)	6616(10)	43
H(8B)	5080(20)	9061(12)	5442(10)	44
H(9B)	7350(20)	9466(13)	6457(10)	49
H(10B)	8110(20)	8454(12)	5282(10)	47

Table 6. Hydrogen bonds for **3d** [Å and °].

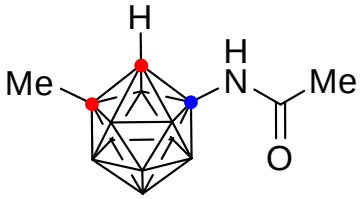
D-H...A	d(D-H)	d(H...A)	d(D...A)	<(DHA)
N(1)-H(1N)...O(1)#1	0.84(2)	2.10(2)	2.9080(18)	161.3(18)

Symmetry transformations used to generate equivalent atoms: #1 x+1/2,y,-z+3/2

7. References

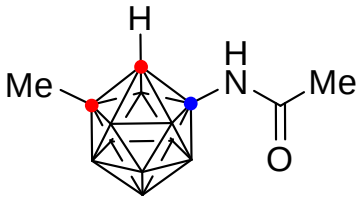
1) (a) Lyu, H.; Quan Y.; Xie, Z. Transition Metal Catalyzed Direct Amination of Cage B(4)−H Bond in *o*-Carboranes: Synthesis of Tertiary, Secondary and Primary *o*-Carboranyl Amines. *J. Am. Chem. Soc.* **2016**, *138*, 39, 12727-12730. (b) Lyu, H.; Quan, Y.; Xie, Z. Palladium-Catalyzed Direct Dialkenylation of Cage B−H Bonds in *o*-Carboranes through Cross-Coupling Reactions. *Angew. Chem. Int. Ed.* **2015**, *54*, 10623-10626. (c) Quan, Y.; Tang, C.; Xie, Z. Palladium Catalyzed Regioselective B-C(sp) Coupling via Direct Cage B−H Activation: Synthesis of B(4)-Alkynylated *o*-Carboranes. *Chem. Sci*. **2016**, *7*, 5838-5845. (d) Lyu, H.; Quan, Y.; Xie, Z. Rhodium-Catalyzed Regioselective Hydroxylation of Cage B−H Bonds of *o*-Carboranes with O_2 or Air. *Angew. Chem., Int. Ed.* **2016**, *55*, 11840-11844.
2) Hong, S. Y.; Park, Y.; Hwang, Y.; Kim, Y. B.; Baik, M.-H.; Chang, S. Selective formation of γ-lactams via C–H amidation enabled by tailored iridium catalysts *Science* **2018**, *359*, 1016.

^{1}H NMR



3a

$^{13}C\{^{1}H\}$ NMR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H
N
Me
Me
O

3a

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77.5
77.2
76.8
69.3
61.1
26.0
25.1
200
190
180
170
160
150
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80
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60
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40
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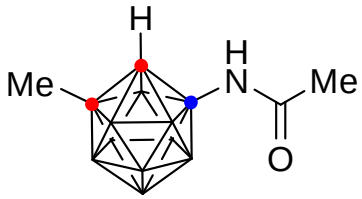
ppm

$^{11}B\{^{1}H\}$ NMR


H
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N
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Me
O

3a

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-15.58
2.071
1.000
6.065
1.021
5
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-5
-10
-15
-20
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ppm

^{11}B NMR

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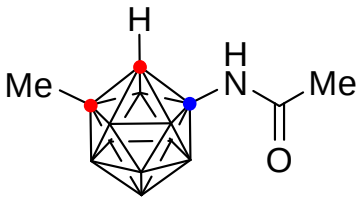

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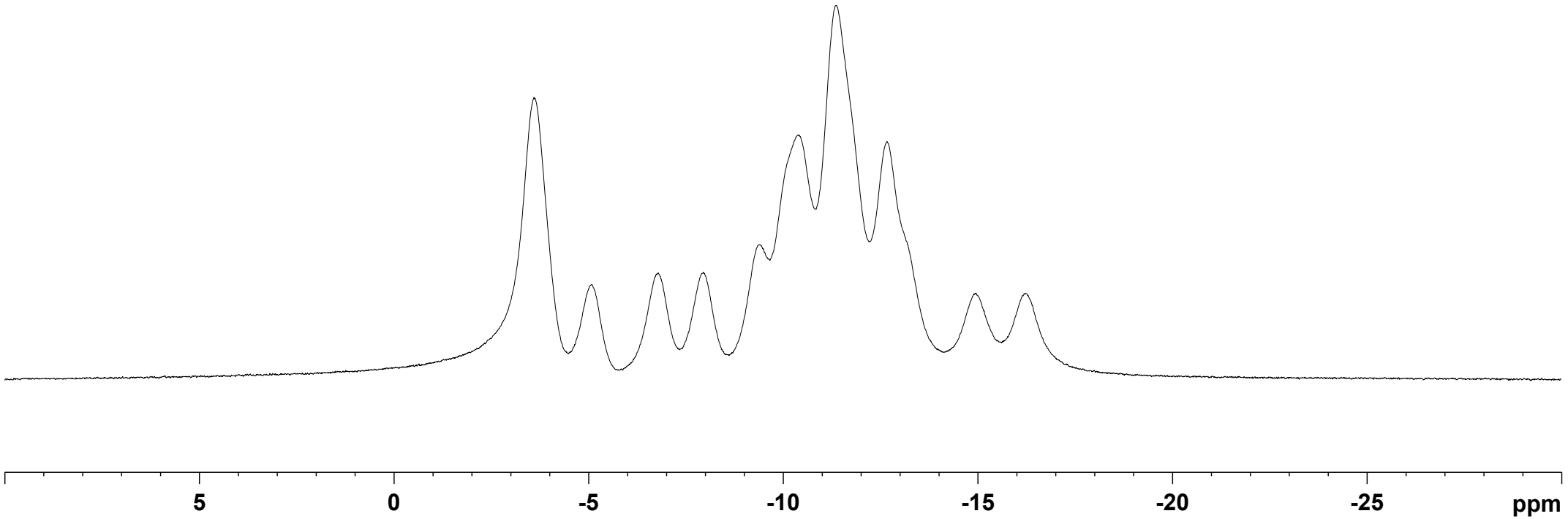
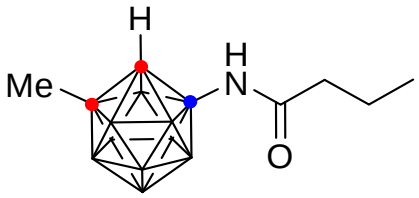
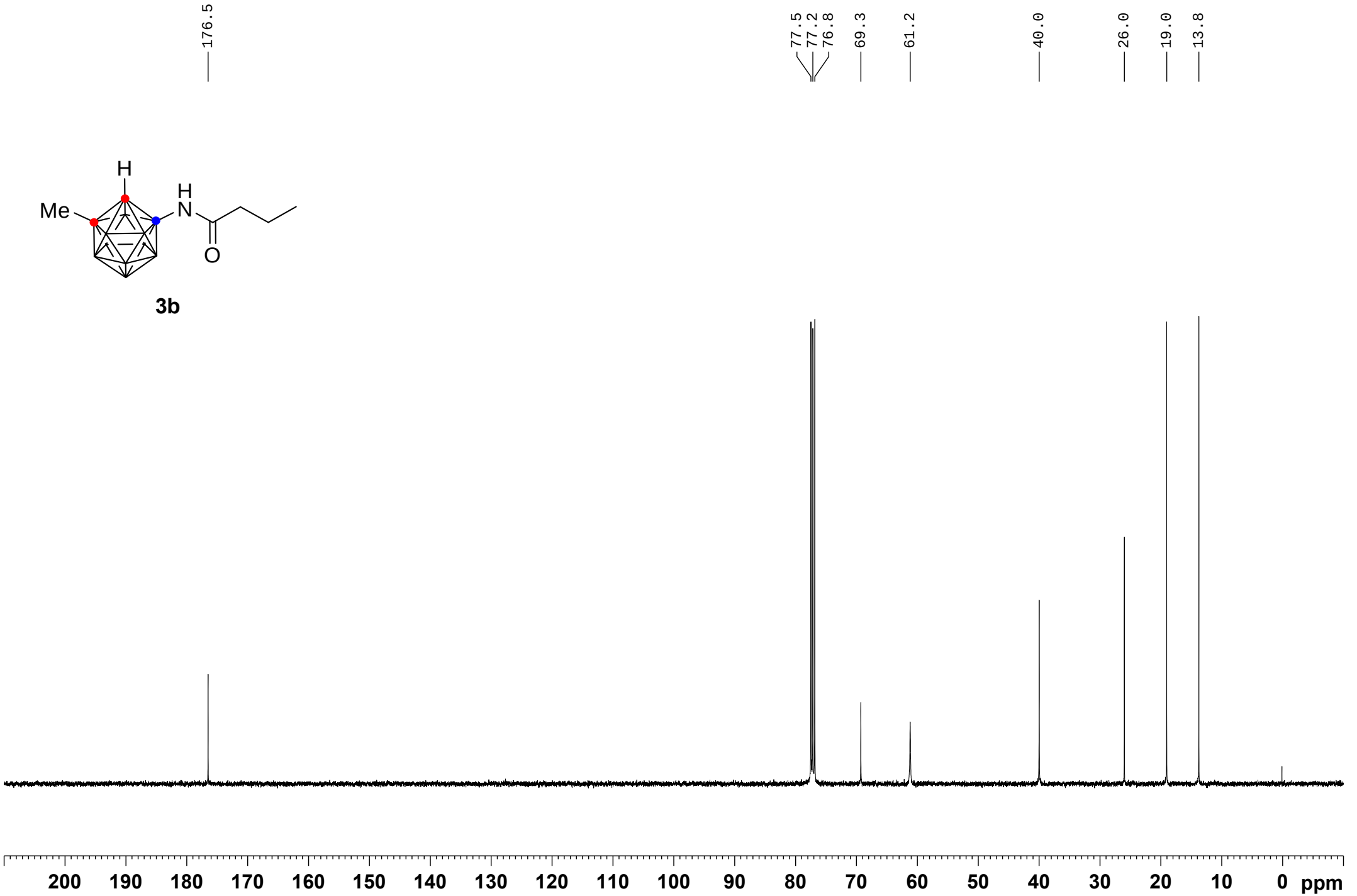


^{1}H NMR



3b

$^{13}C\{^{1}H\}$ NMR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H
N
O
3b
200
190
180
170
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150
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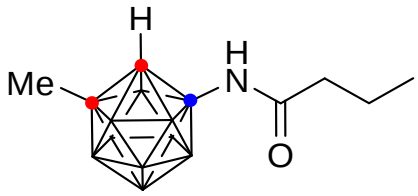
0
ppm

$^{11}B\{^{1}H\}$ NMR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Me
H
N
O

3b

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6.004
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^{11}B NMR

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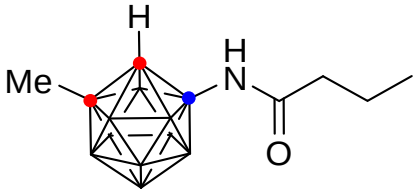
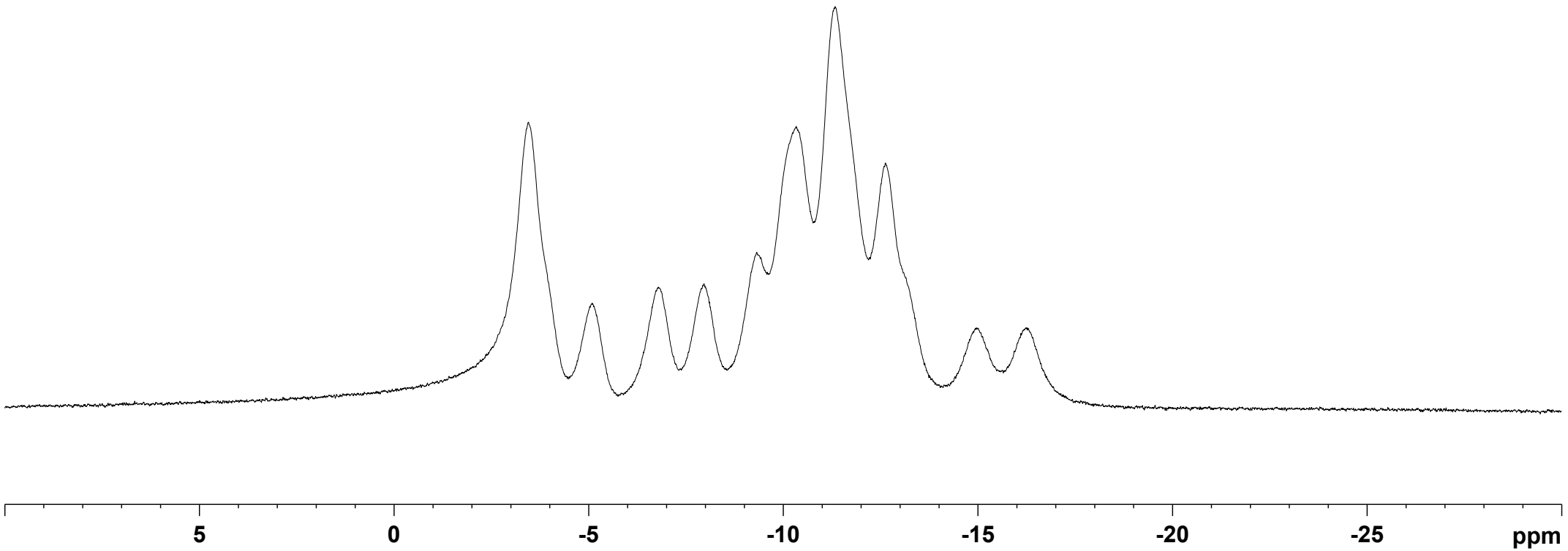


3b



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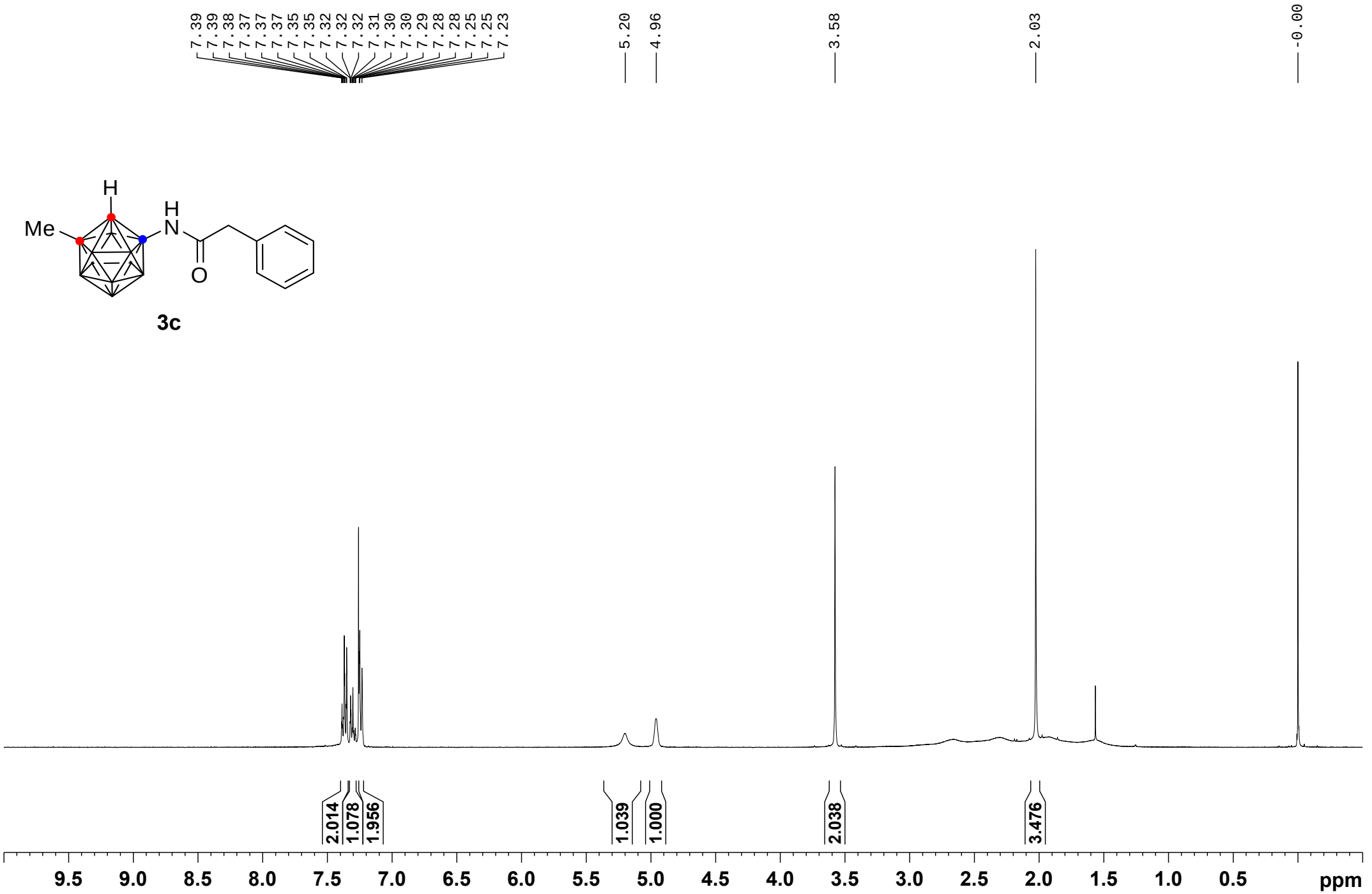
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7.29
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5.0
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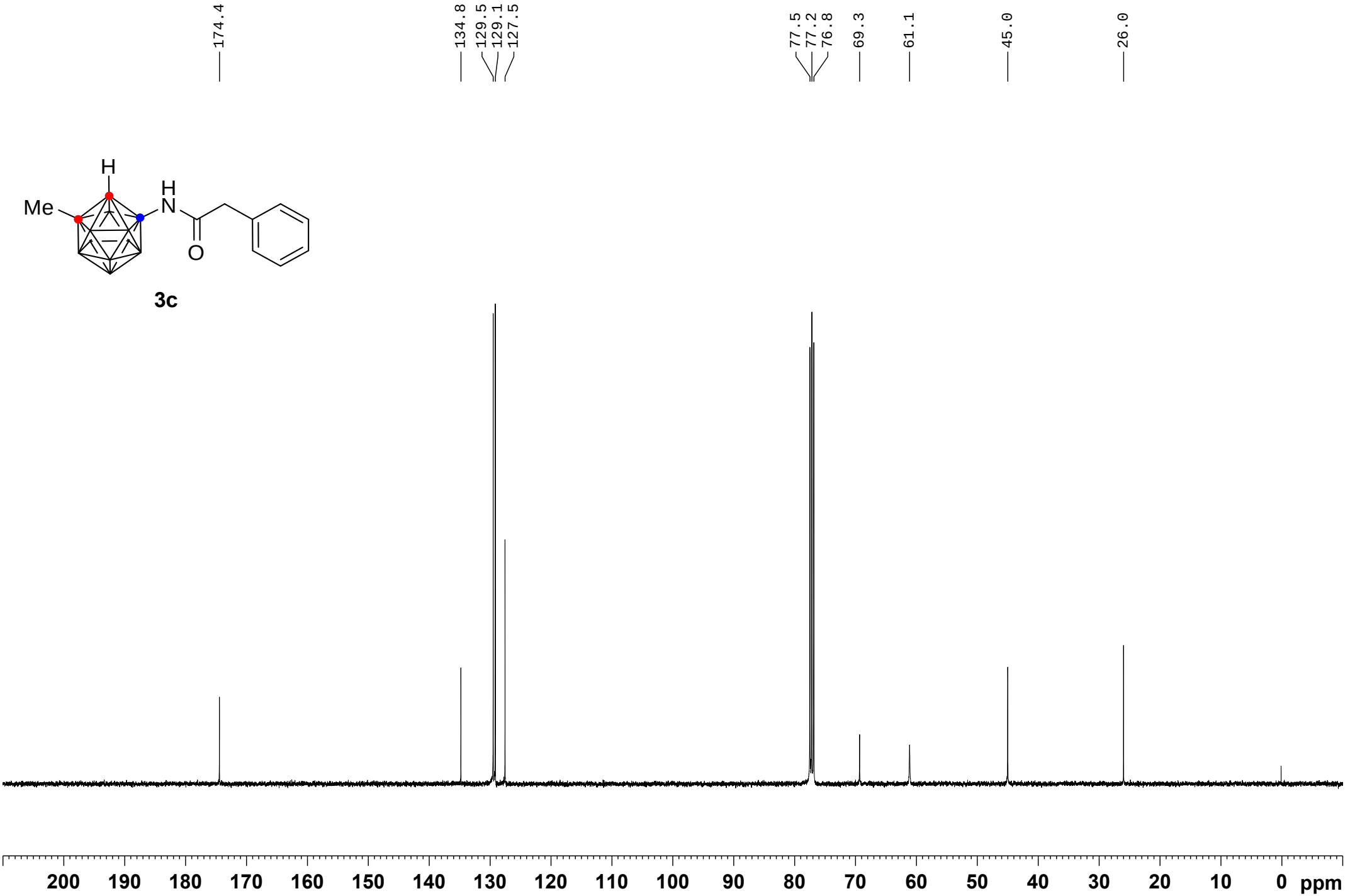
3c

$^{13}C\{^{1}H\}$ NMR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Me
H
N
O
3c
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180
170
160
150
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20
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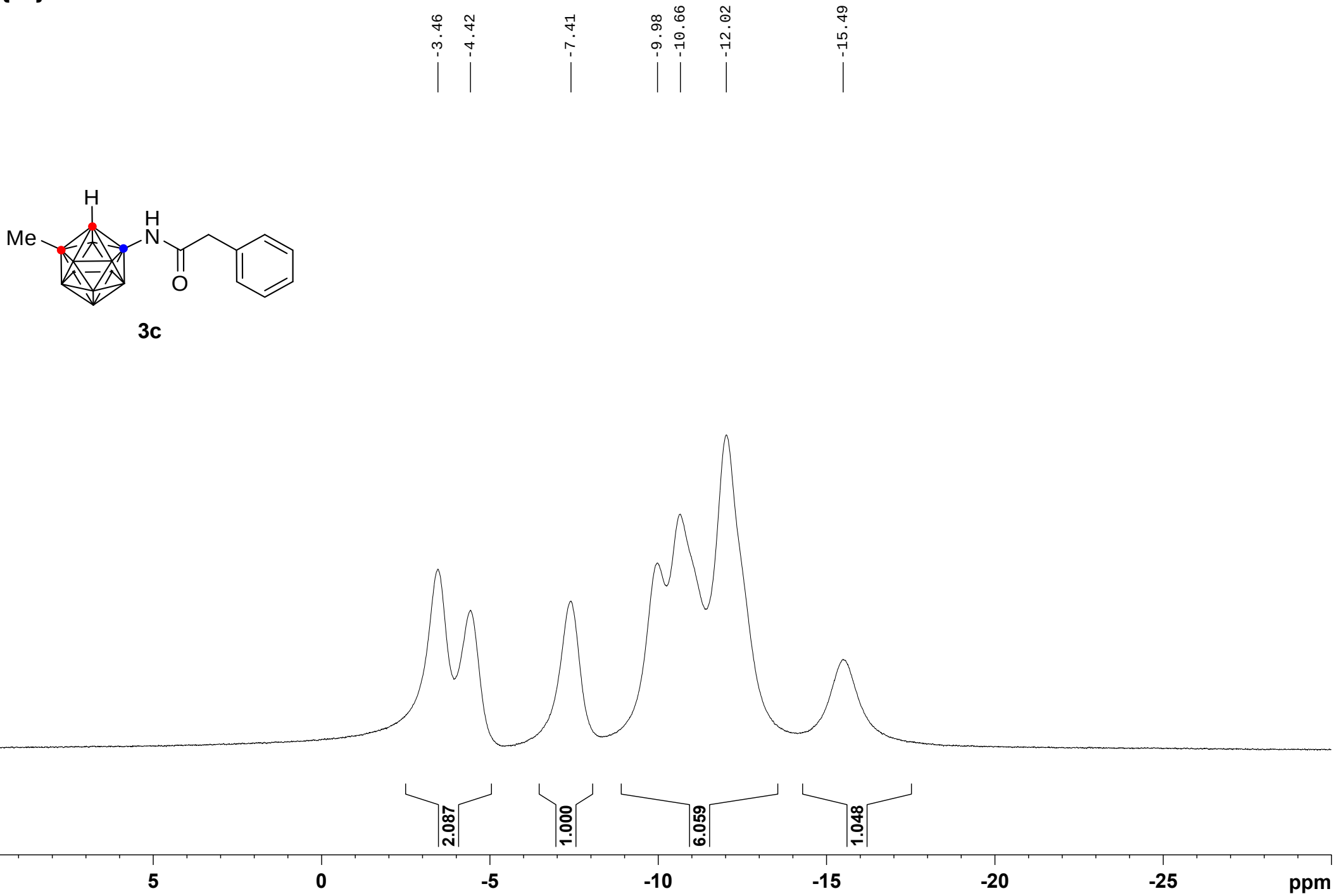
0
ppm

$^{11}B\{^{1}H\}$ NMR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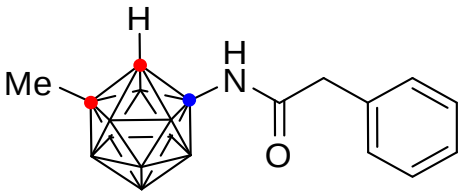
3c

^{11}B NMR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O

3c

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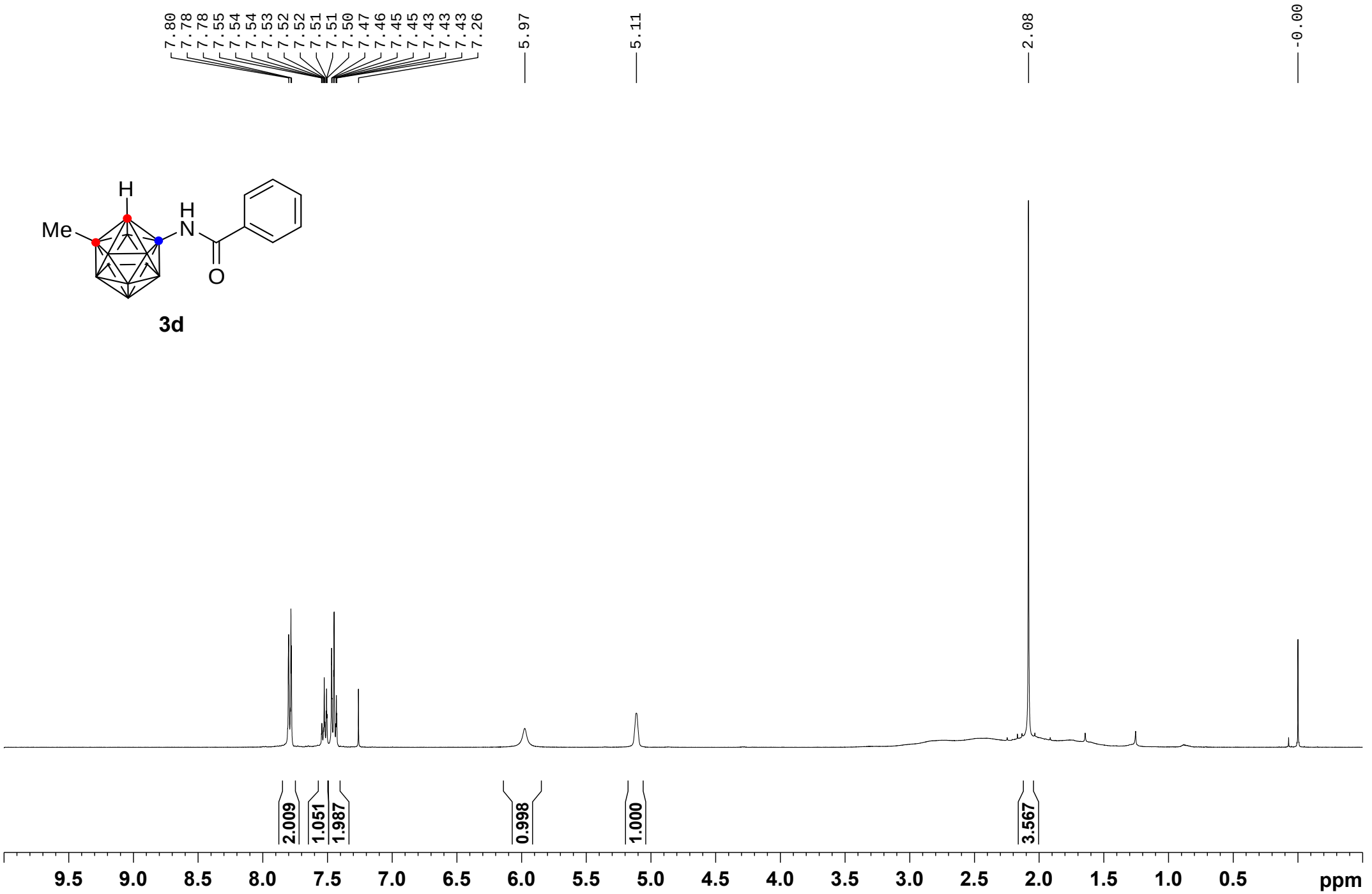
^{1}H NMR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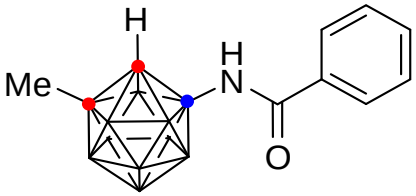
3d

$^{13}C\{^{1}H\}$ NMR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Me
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3d

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69.4
61.3
26.1
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160
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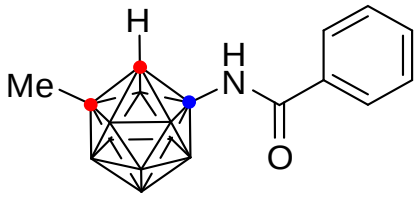
0
ppm

$^{11}B\{^{1}H\}$ NMR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3d

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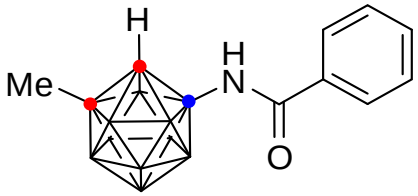
^{11}B NMR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3d

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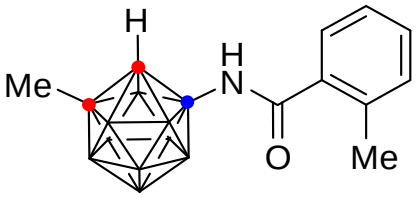
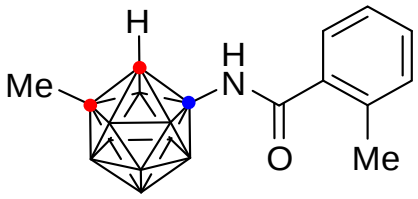
^{1}H NMR



3e

$^{13}C\{^{1}H\}$ NMR


H
Me
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N
O
Me

3e

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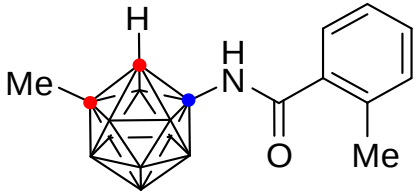
77.2
76.8
69.5
61.2
26.1
20.0
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
ppm

$^{11}B\{^{1}H\}$ NMR

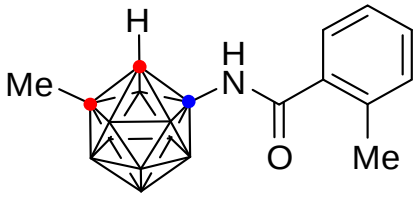

H
H
N
Me
O
Me

3e

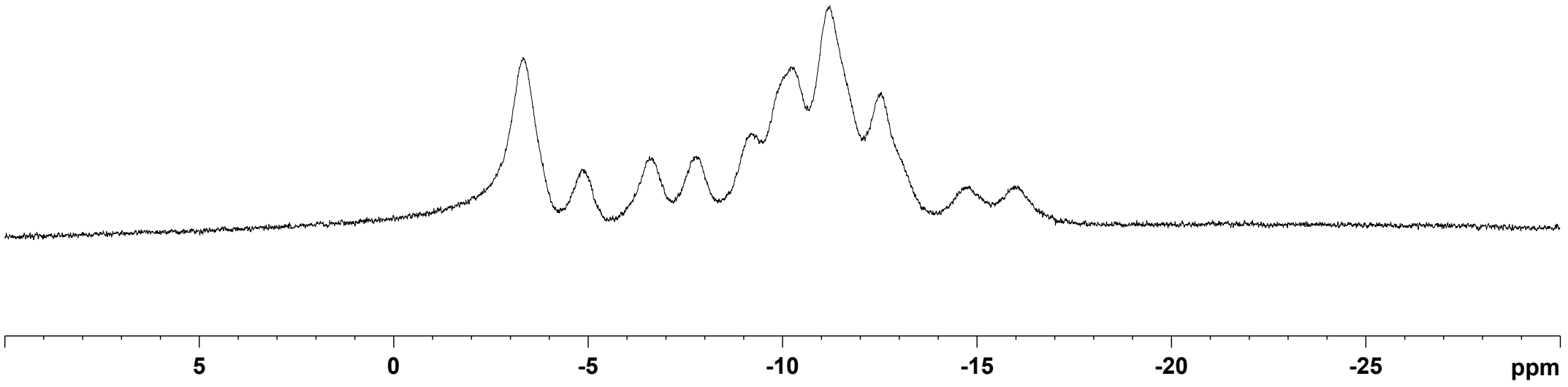
-3.36
-4.36
-7.20
-9.84
-10.56
-11.91
-15.42
2.078
1.000
6.061
1.078
5
0
-5
-10
-15
-20
-25
ppm

^{11}B NMR

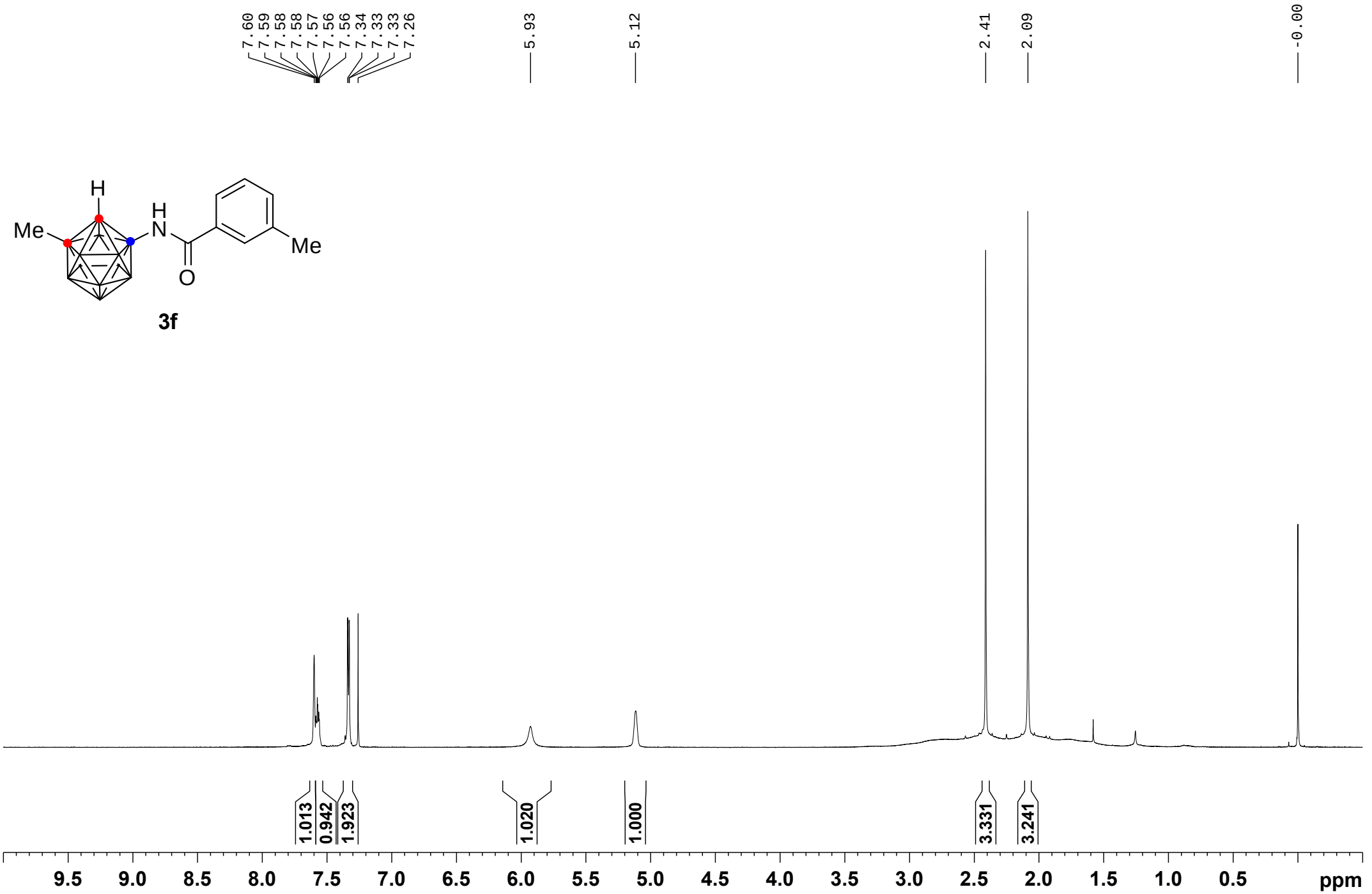
-3.33 -4.84 -6.58 -7.79 -9.20 -10.20 -11.21 -12.54 -14.80 -16.05



3e

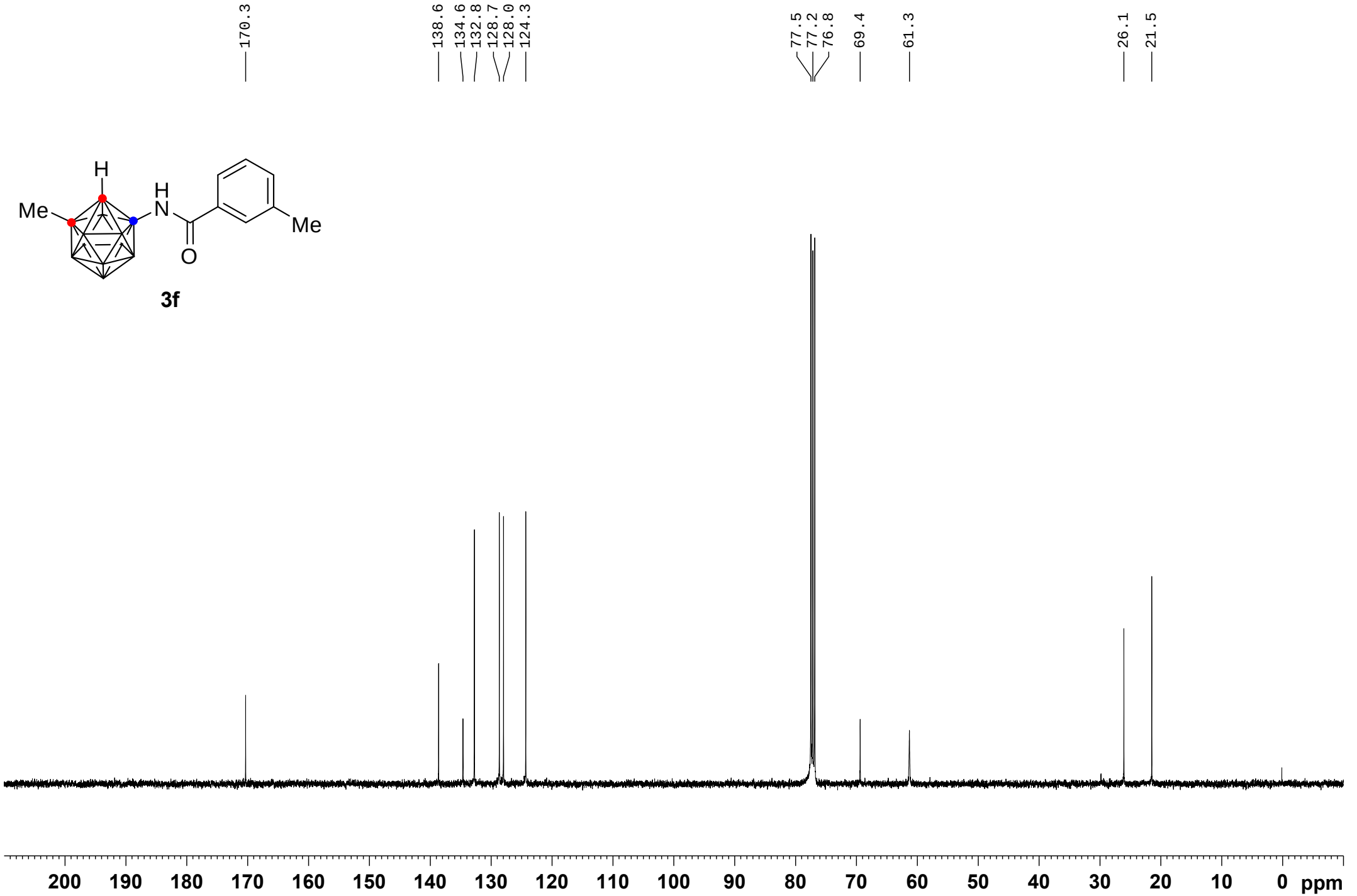


^{1}H NMR

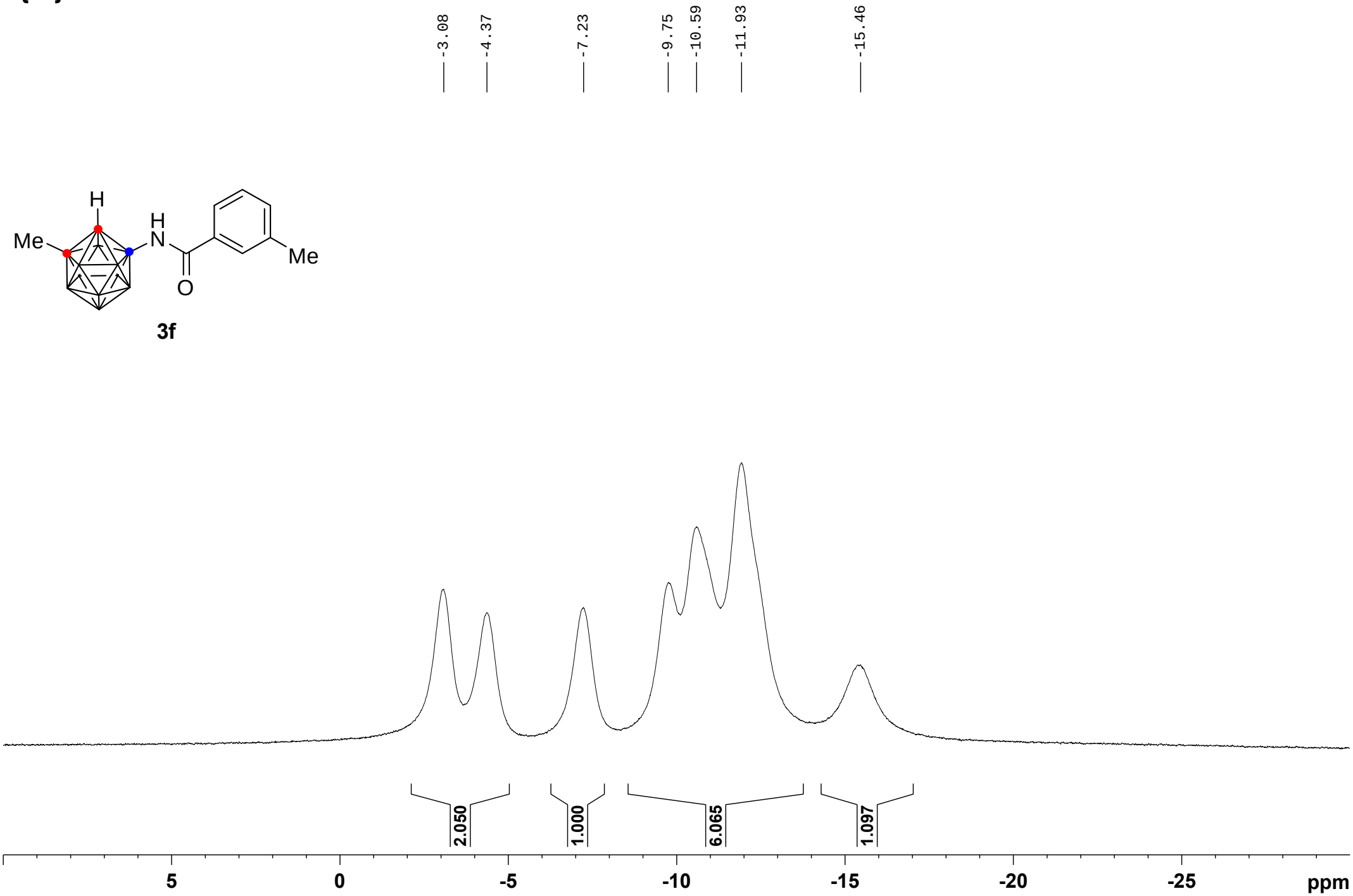

7.60
7.59
7.58
7.58
7.57
7.56
7.56
7.34
7.33
7.33
7.26
5.93
5.12
2.41
2.09
0.00
H
H
N
Me
Me
O
1.013
0.942
1.923
1.020
1.000
3.331
3.241
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
ppm

3f

$^{13}C\{^{1}H\}$ NMR


170.3
138.6
134.6
132.8
128.7
128.0
124.3
77.5
77.2
76.8
69.4
61.3
26.1
21.5
H
H
N
Me
Me
O
3f
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
ppm

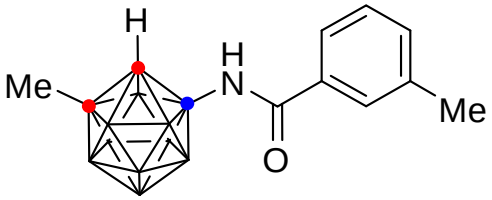
$^{11}B\{^{1}H\}$ NMR


-3.08
-4.37
-7.23
-9.75
-10.59
-11.93
-15.46
H
Me
H
N
O
Me
2.050
1.000
6.065
1.097
5
0
-5
-10
-15
-20
-25
ppm

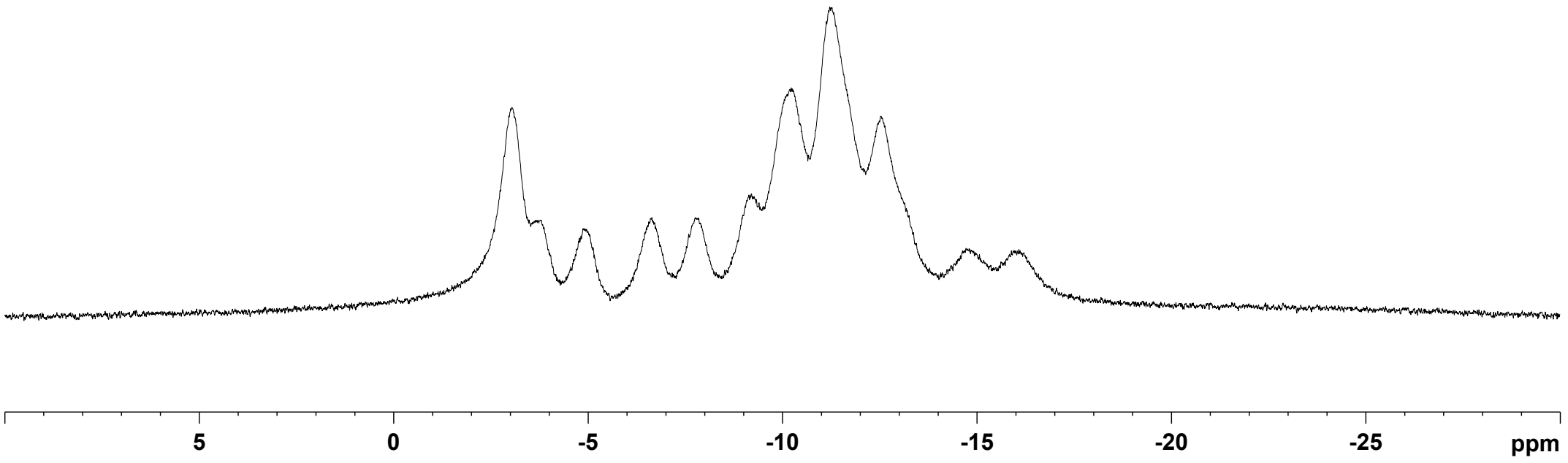
3f

^{11}B NMR

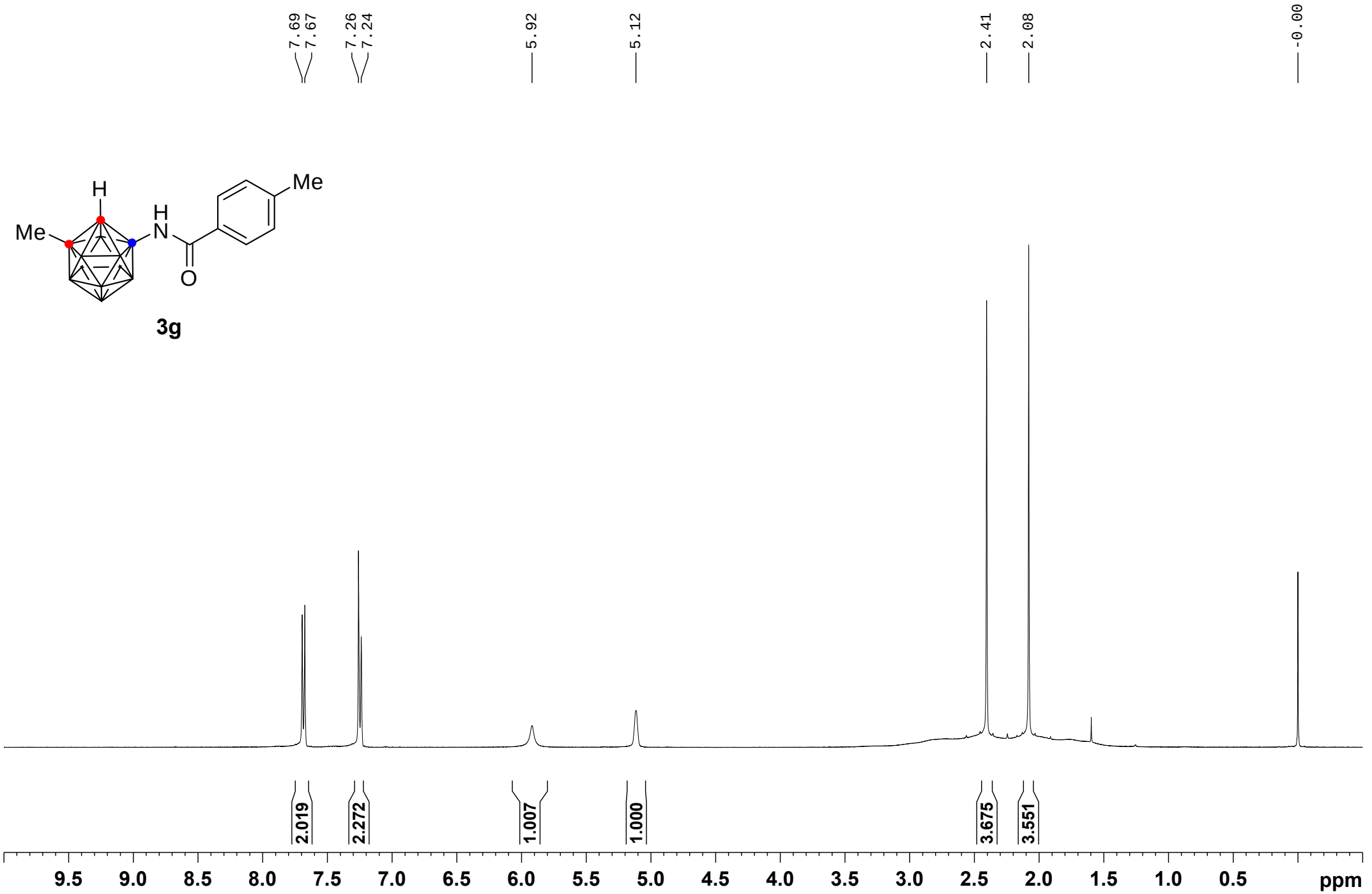
-3.04 -3.77 -4.89 -6.64 -7.77 -9.20 -10.22 -11.21 -12.53 -14.72 -16.08



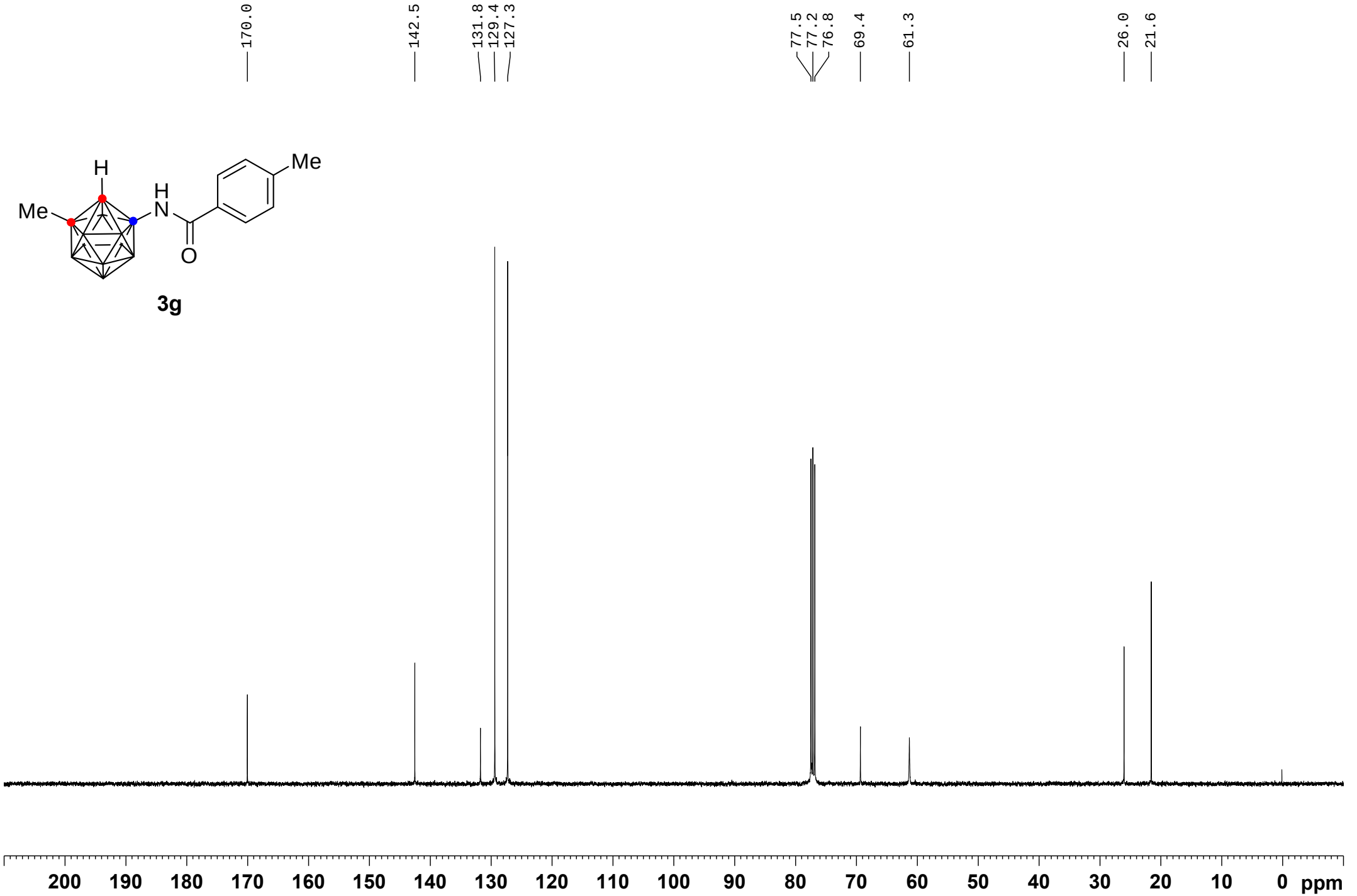
3f



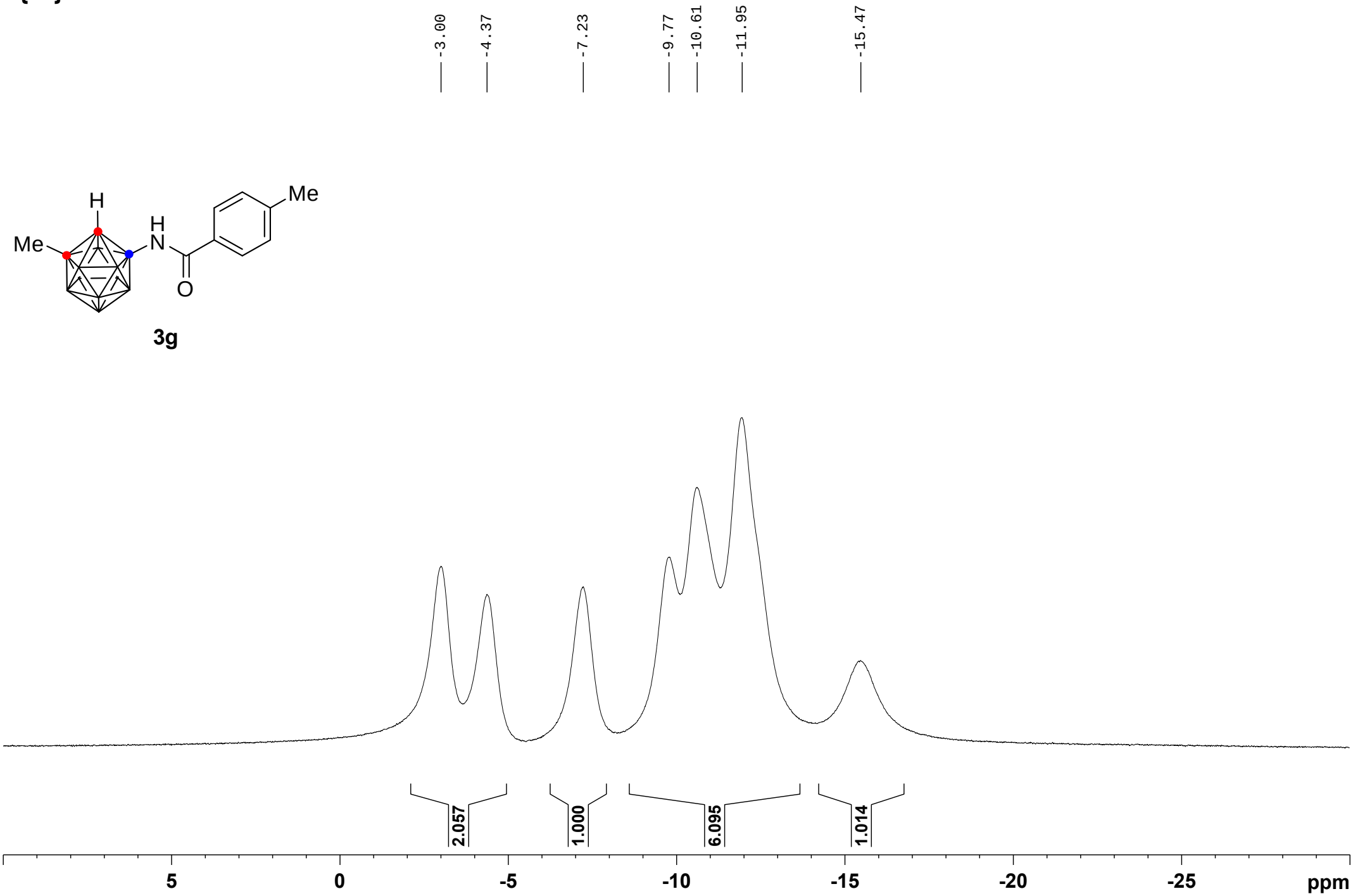
^{1}H NMR


7.69
7.67
7.26
7.24
5.92
5.12
2.41
2.08
-0.00
H
Me
H
N
O
Me
3g
2.019
2.272
1.007
1.000
3.675
3.551
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
ppm

$^{13}C\{^{1}H\}$ NMR

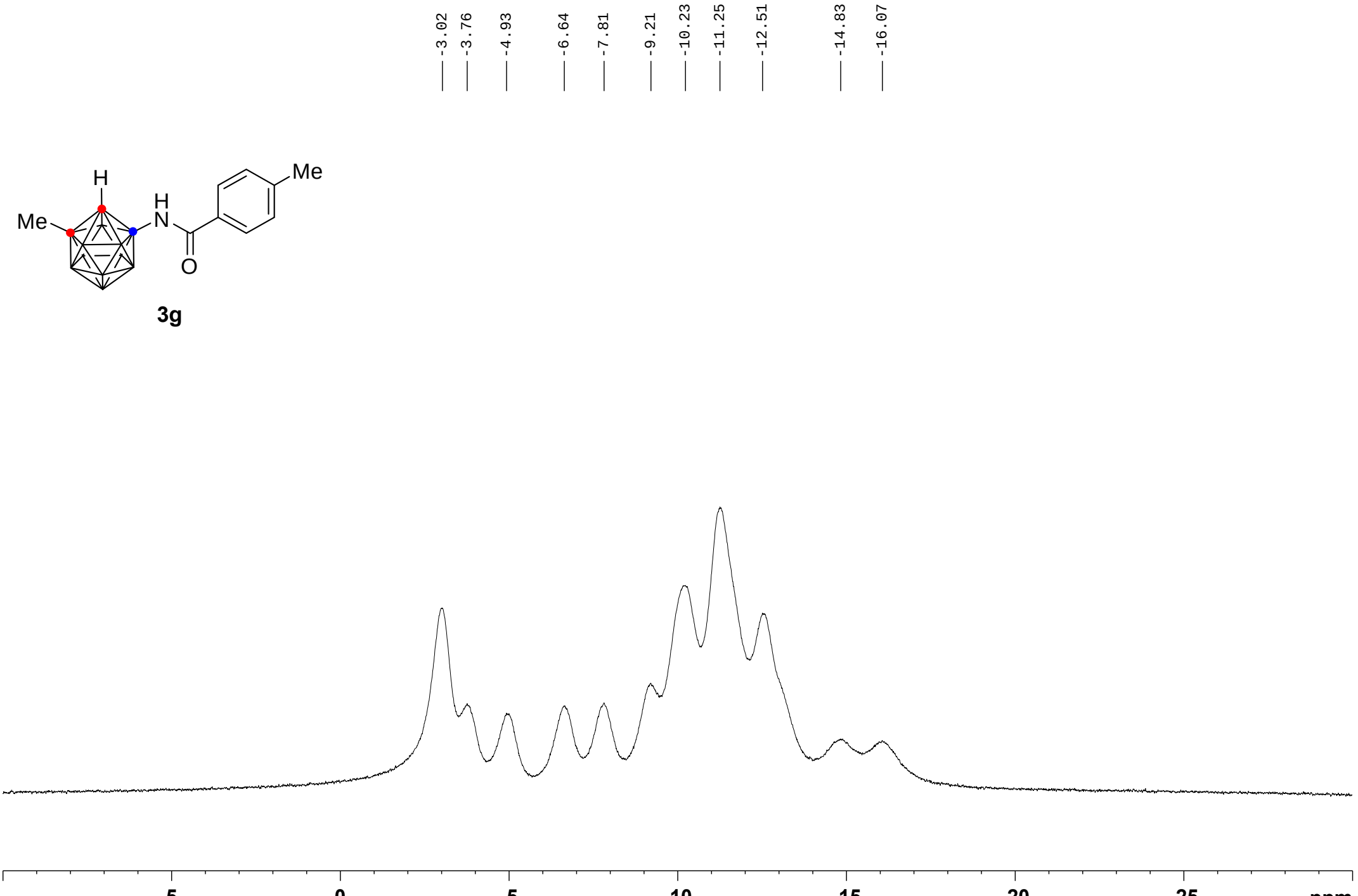

170.0
142.5
131.8
129.4
127.3
77.5
77.2
76.8
69.4
61.3
26.0
21.6
H
Me
H
N
O
Me
3g
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
ppm

$^{11}B\{^{1}H\}$ NMR


-3.00
-4.37
-7.23
-9.77
-10.61
-11.95
-15.47
H
Me
H
N
O
Me
2.057
1.000
6.095
1.014
5
0
-5
-10
-15
-20
-25
ppm

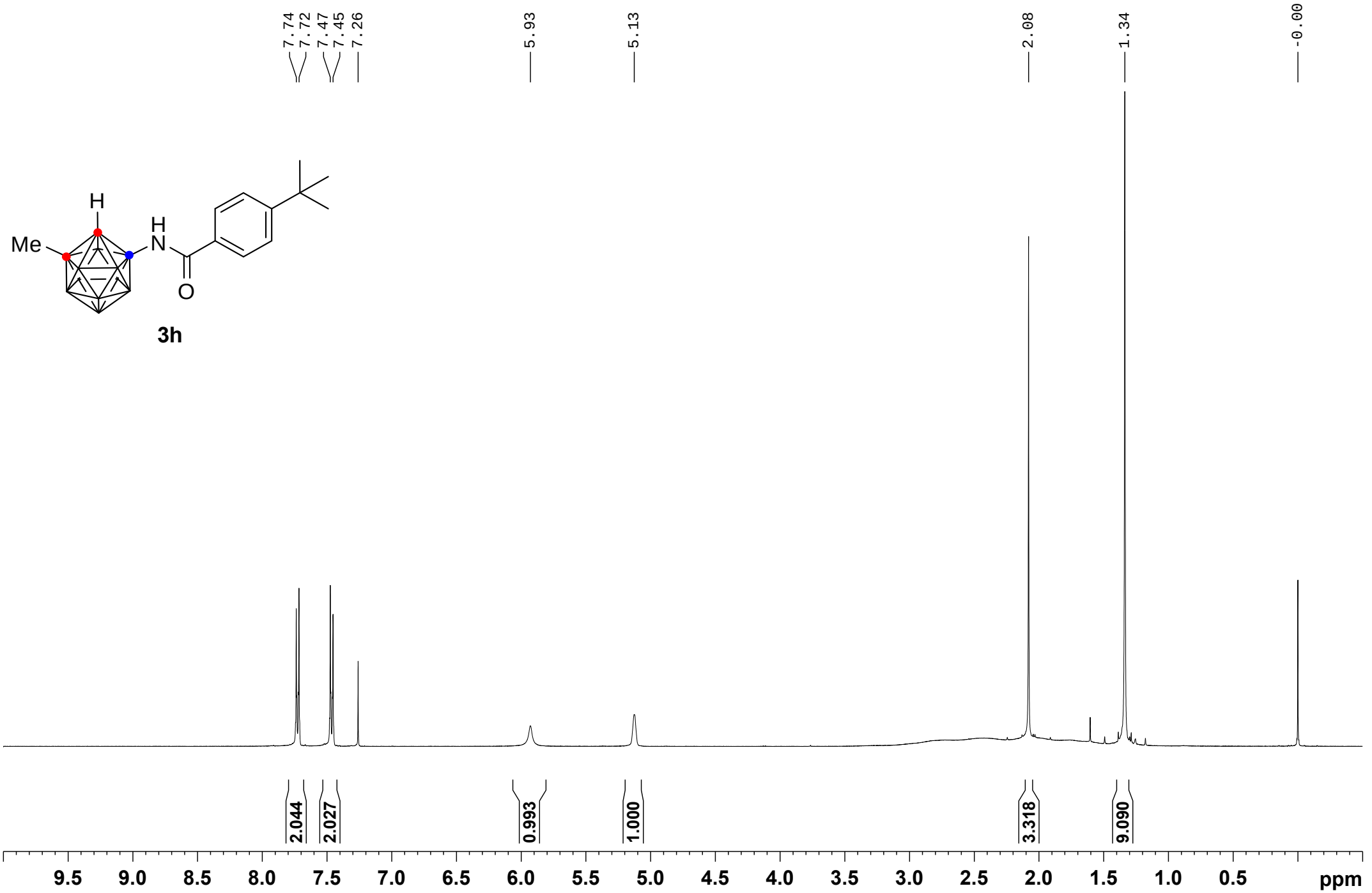
3g

^{11}B NMR

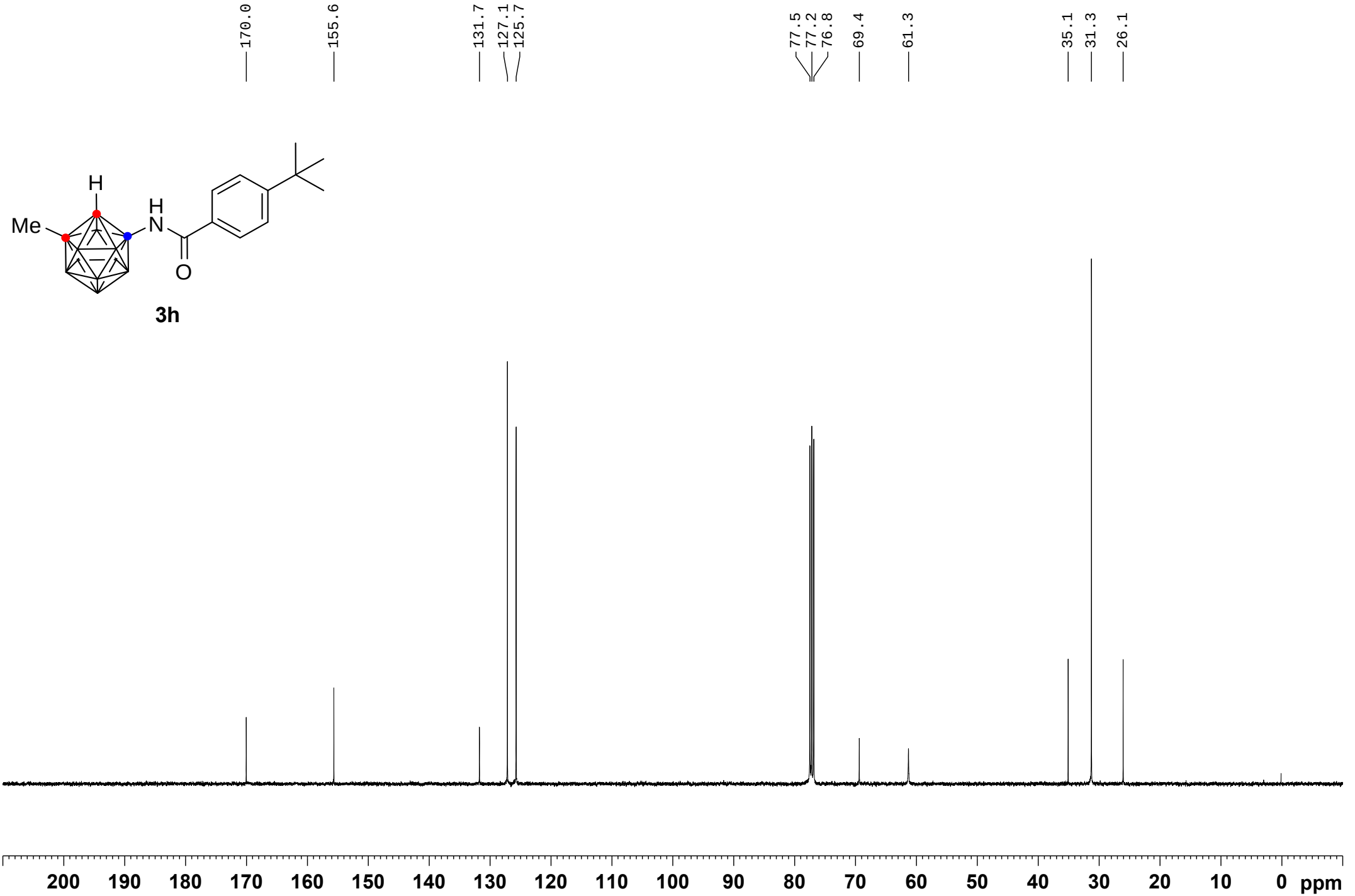

-3.02
-3.76
-4.93
-6.64
-7.81
-9.21
-10.23
-11.25
-12.51
-14.83
-16.07
H
Me
H
N
O
Me
5
0
-5
-10
-15
-20
-25
ppm

3g

^{1}H NMR

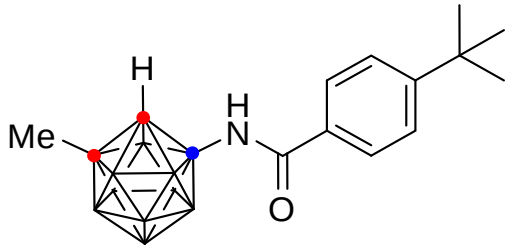

7.74
7.72
7.47
7.45
7.26
5.93
5.13
2.08
1.34
-0.00
H
Me
H
N
O
3h
2.044
2.027
0.993
1.000
3.318
9.090
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
ppm

$^{13}C\{^{1}H\}$ NMR


170.0
155.6
131.7
127.1
125.7
77.5
77.2
76.8
69.4
61.3
35.1
31.3
26.1
H
Me
H
N
O
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
ppm

3h

$^{11}B\{^{1}H\}$ NMR

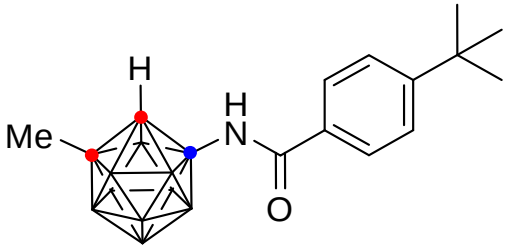

H
Me
H
N
O

3h

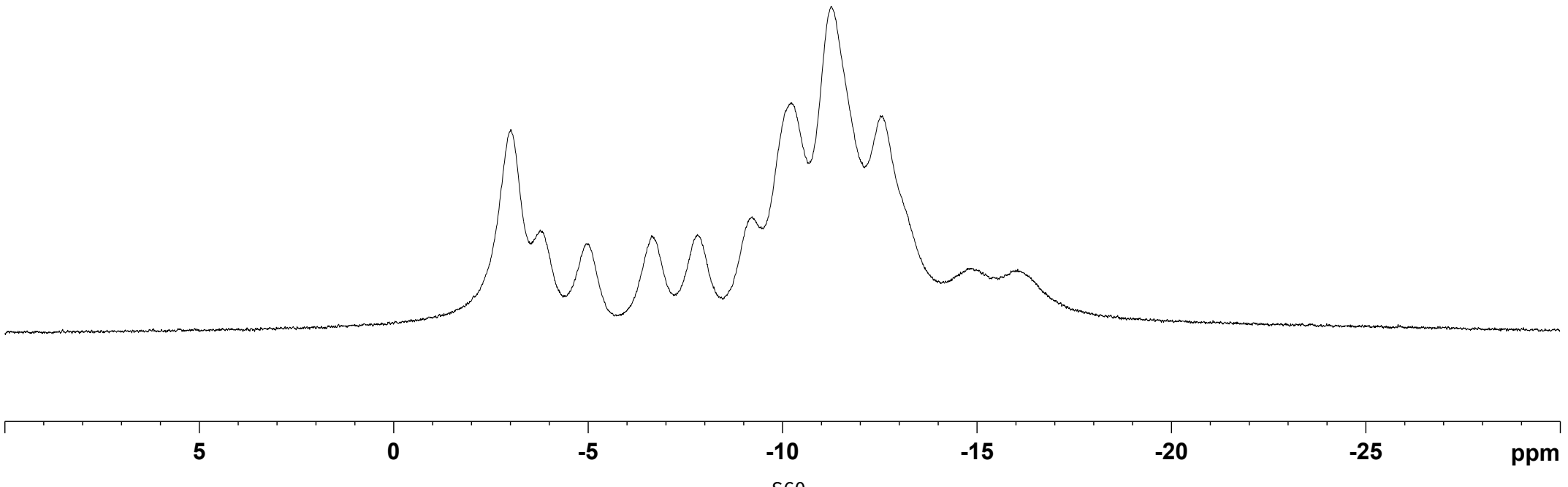
-3.02
-4.41
-7.25
-9.78
-10.61
-11.94
-15.43
2.088
1.000
6.010
1.073
5
0
-5
-10
-15
-20
-25
ppm

^{11}B NMR

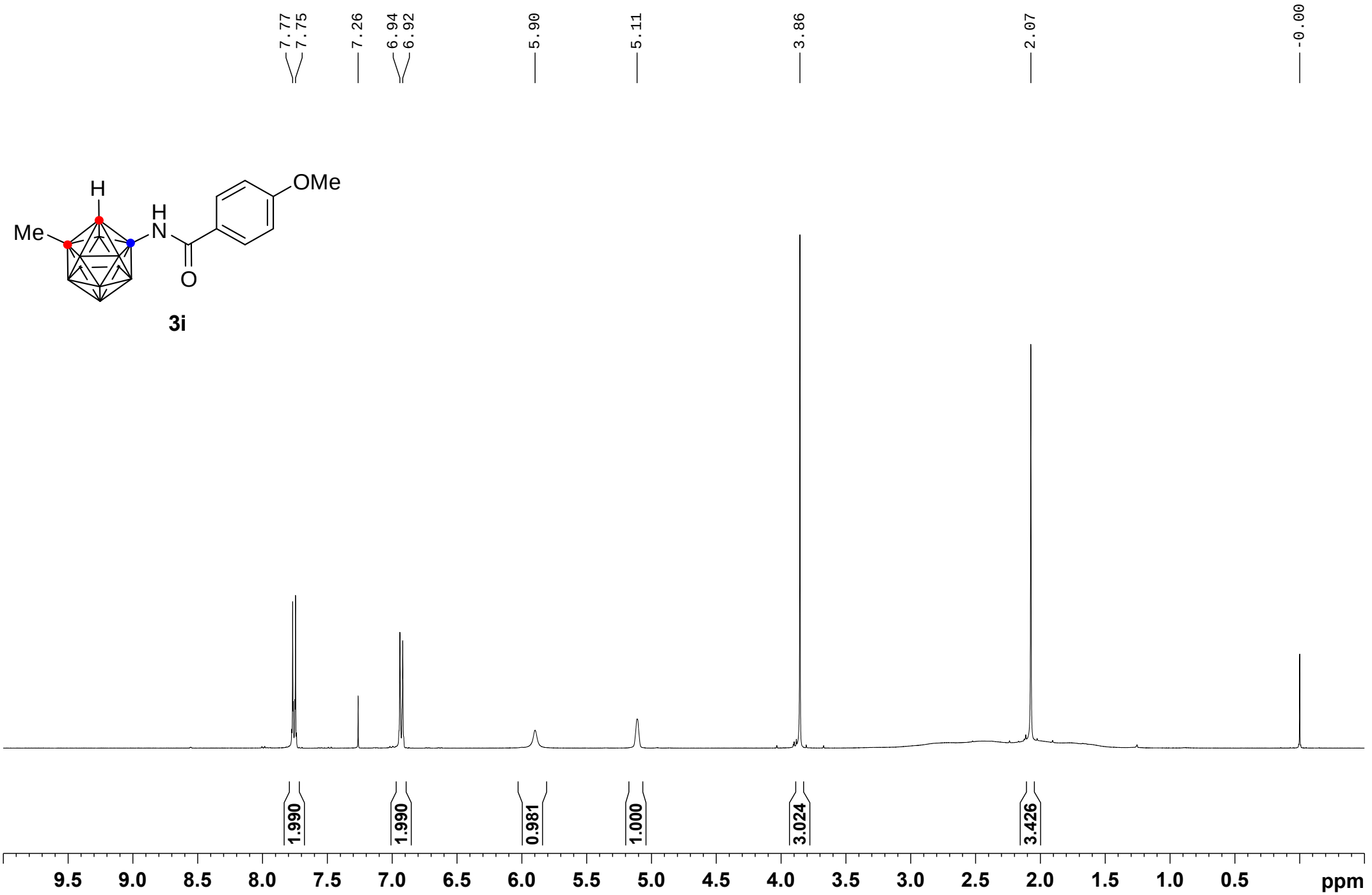
-3.01 -3.77 -5.00 -6.64 -7.81 -9.22 -10.24 -11.25 -12.57 -14.85 -16.05



3h

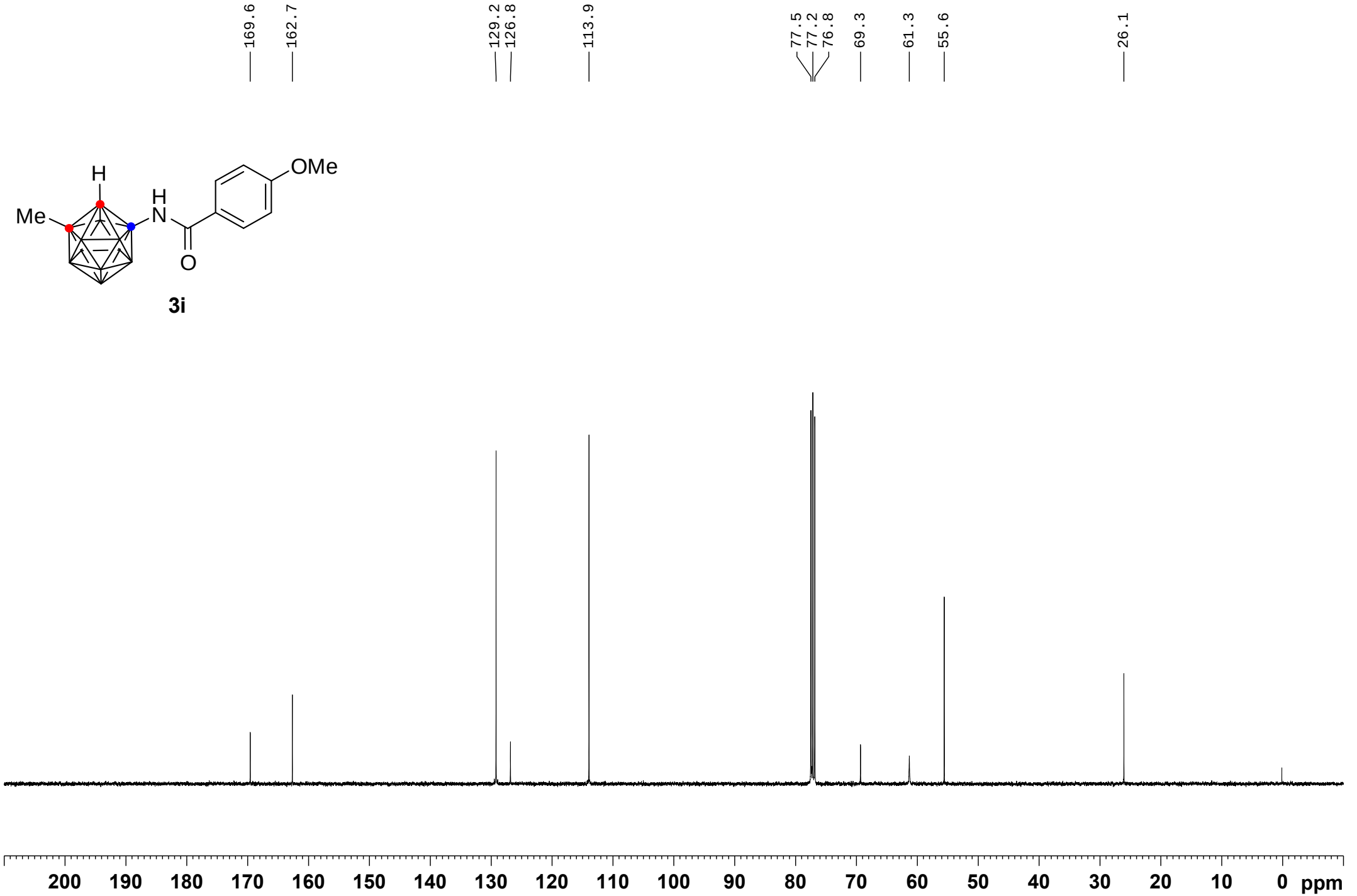


^{1}H NMR


7.77
7.75
7.26
6.94
6.92
5.90
5.11
3.86
2.07
-0.00
H
Me
H
N
O
OMe
1.990
1.990
0.981
1.000
3.024
3.426
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
ppm

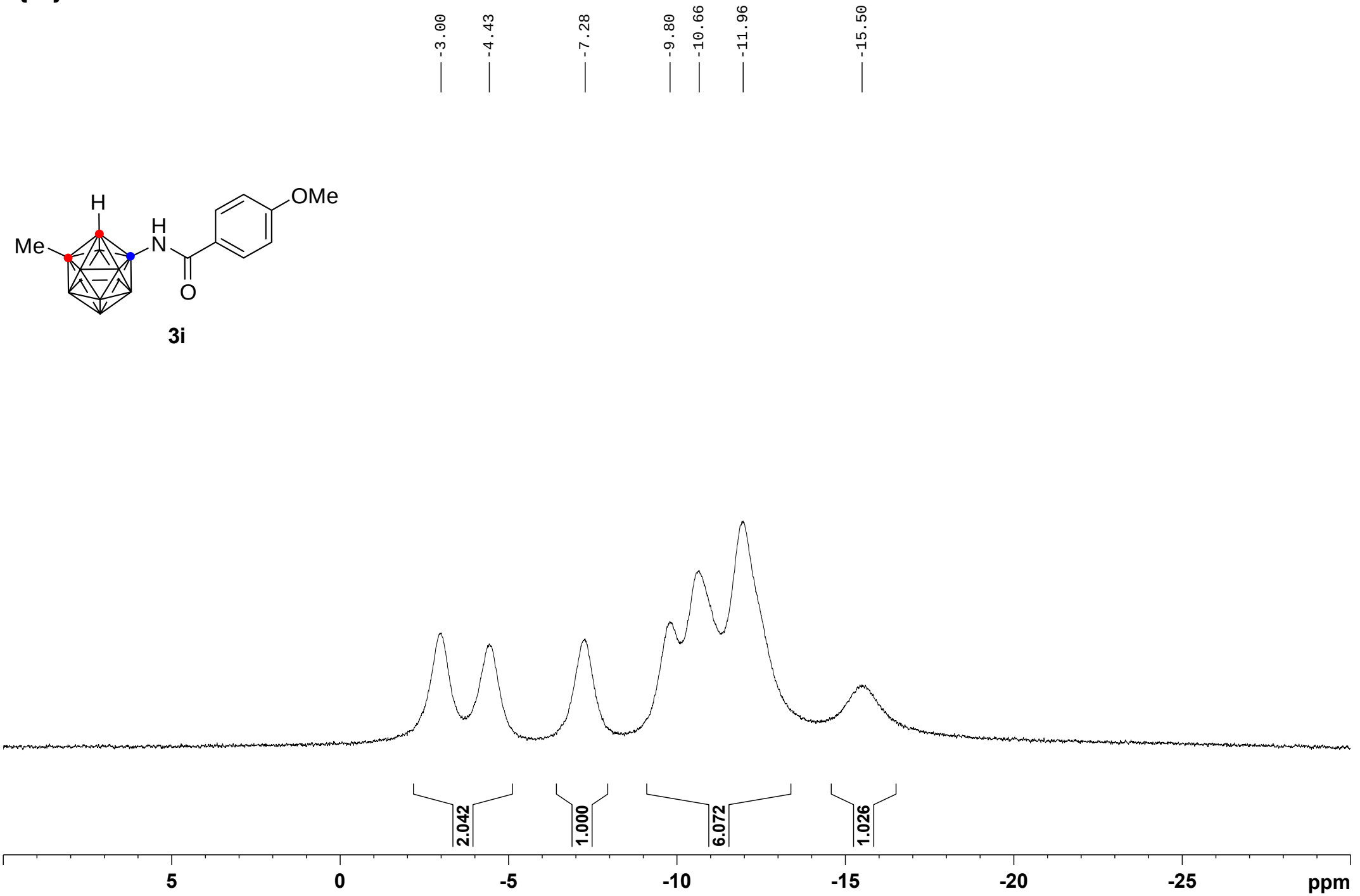
3i

$^{13}C\{^{1}H\}$ NMR


169.6
162.7
129.2
126.8
113.9
77.5
77.2
76.8
69.3
61.3
55.6
26.1
H
Me
H
N
O
OMe
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
ppm

3i

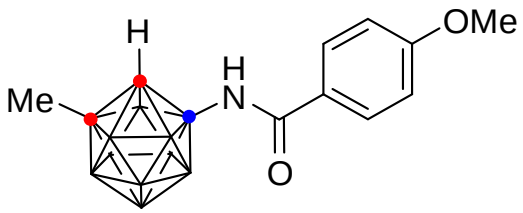
$^{11}B\{^{1}H\}$ NMR


-3.00
-4.43
-7.28
-9.80
-10.66
-11.96
-15.50
H
Me
H
N
O
OMe
2.042
1.000
6.072
1.026
5
0
-5
-10
-15
-20
-25
ppm

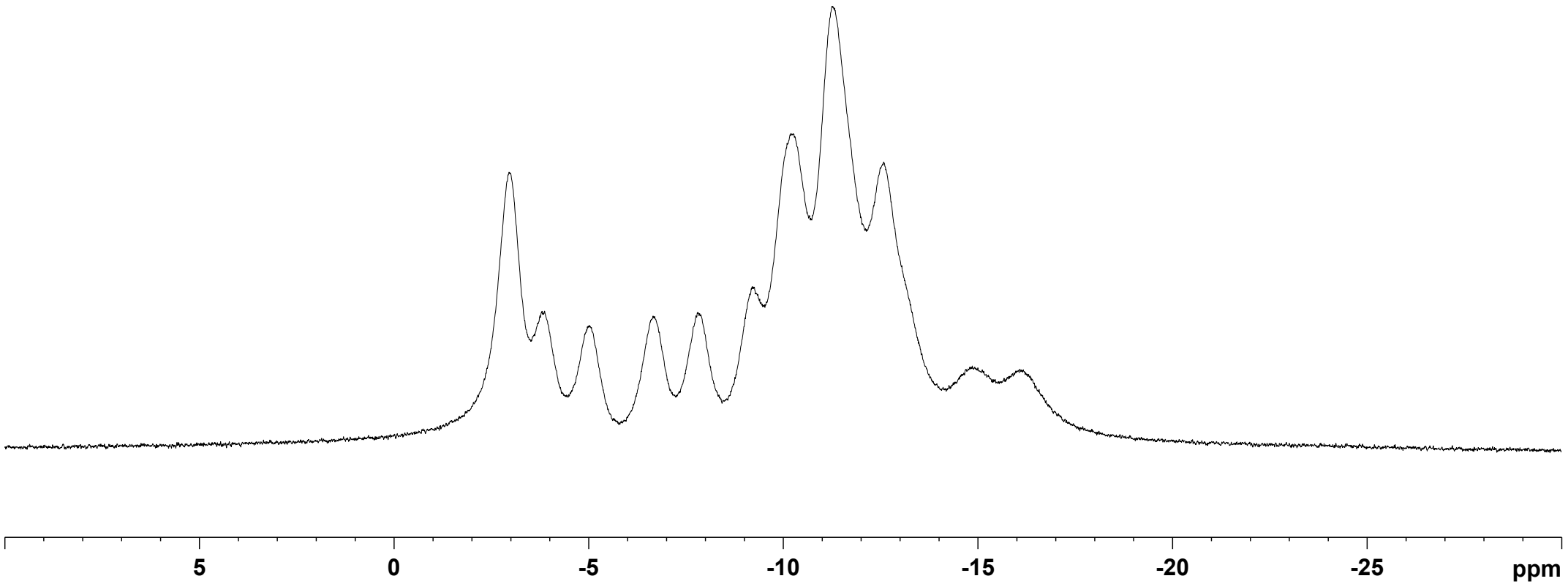
3i

^{11}B NMR

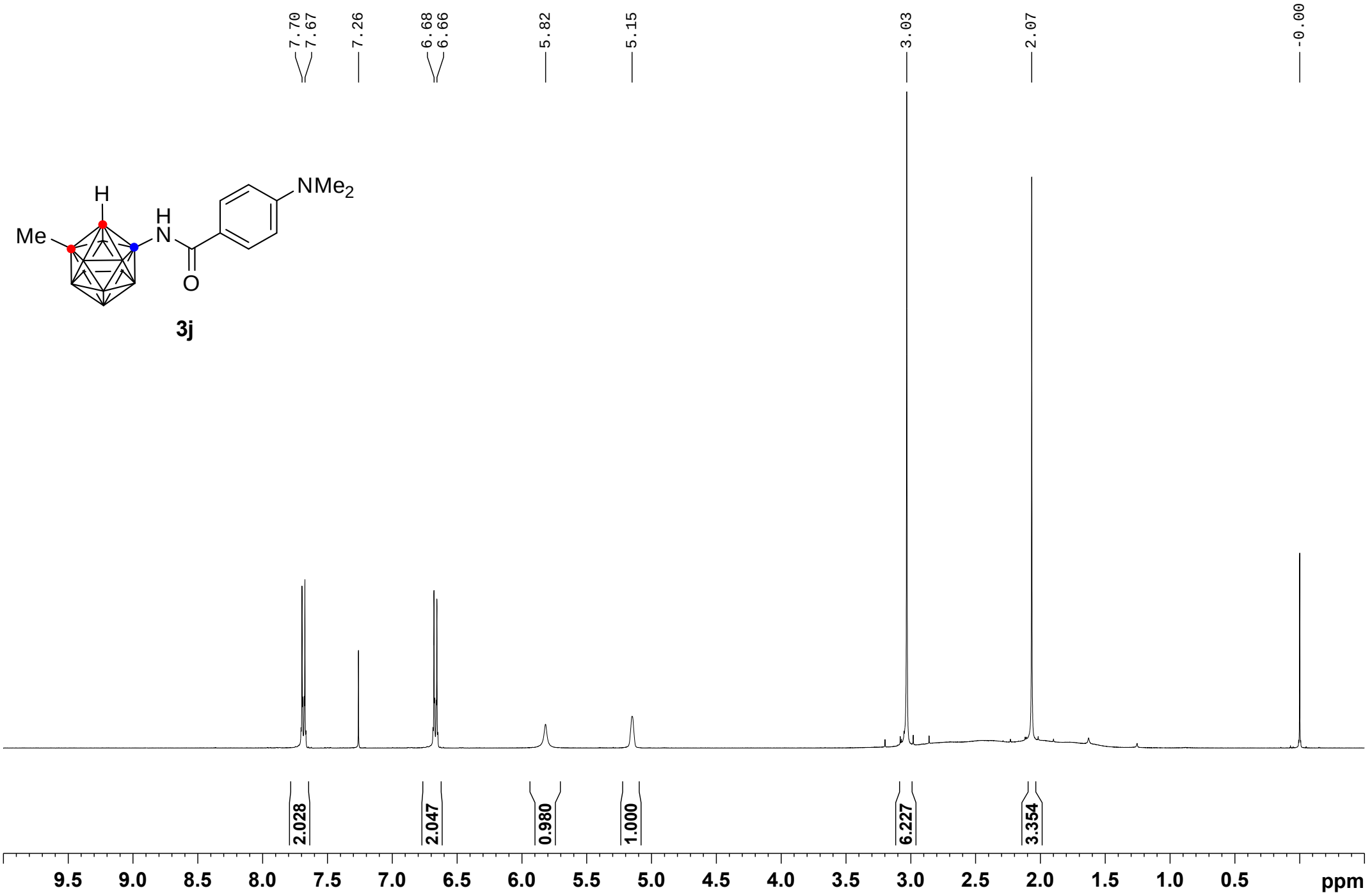
-3.01 -3.87 -5.07 -6.70 -7.89 -9.26 -10.27 -11.32 -12.60 -14.86 -16.17



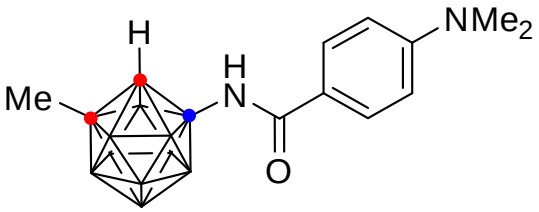
3i



^{1}H NMR


7.70
7.67
7.26
6.68
6.66
5.82
5.15
3.03
2.07
-0.00
H
Me
H
N
O
NMe2
3j
2.028
2.047
0.980
1.000
6.227
3.354
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
ppm

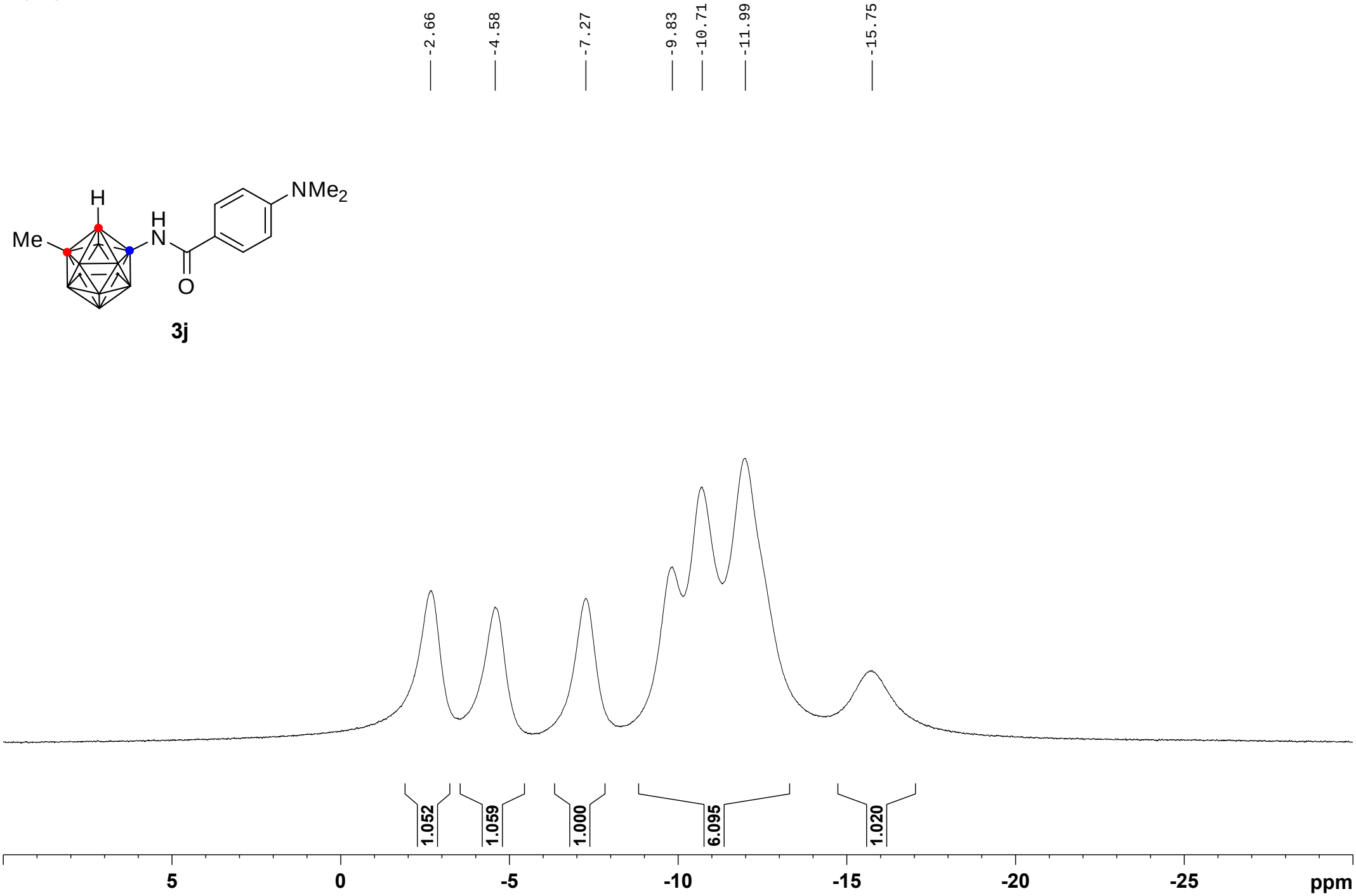
$^{13}C\{^{1}H\}$ NMR


H
Me
H
N
O
NMe2

3j

169.9
152.8
128.9
121.0
111.1
77.5
77.2
76.8
69.2
61.4
40.2
26.1
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
ppm

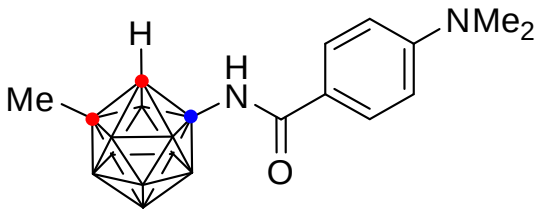
$^{11}B\{^{1}H\}$ NMR


-2.66
-4.58
-7.27
-9.83
-10.71
-11.99
-15.75
H
Me
H
N
O
NMe2
1.052
1.059
1.000
6.095
1.020
5
0
-5
-10
-15
-20
-25
ppm

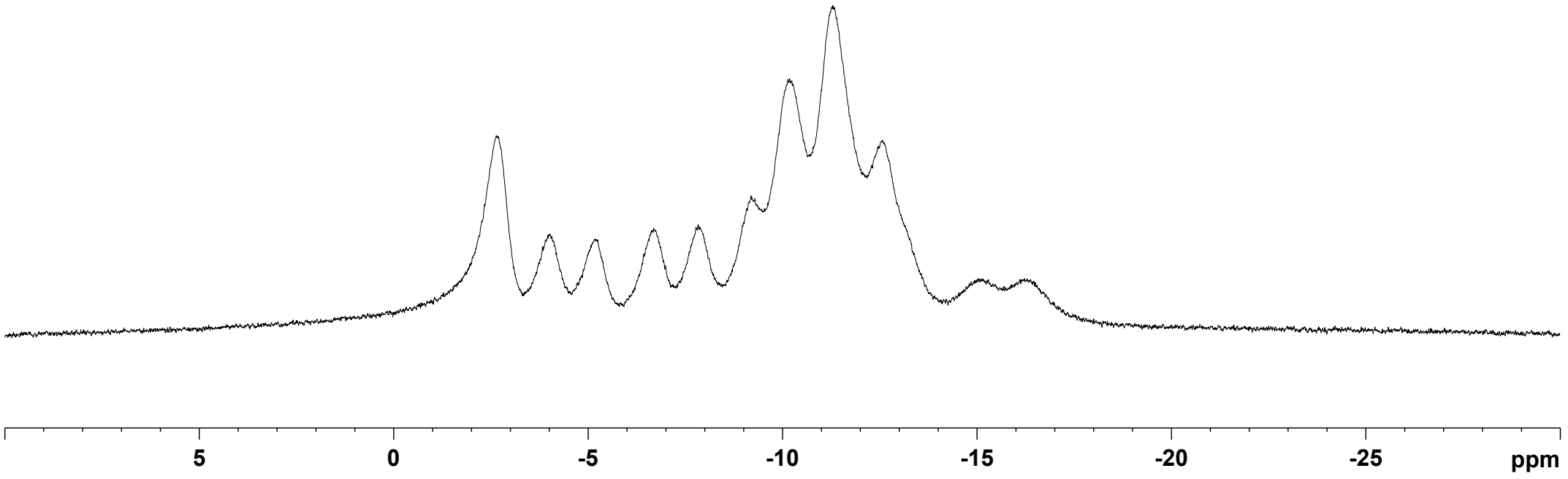
3j

^{11}B NMR

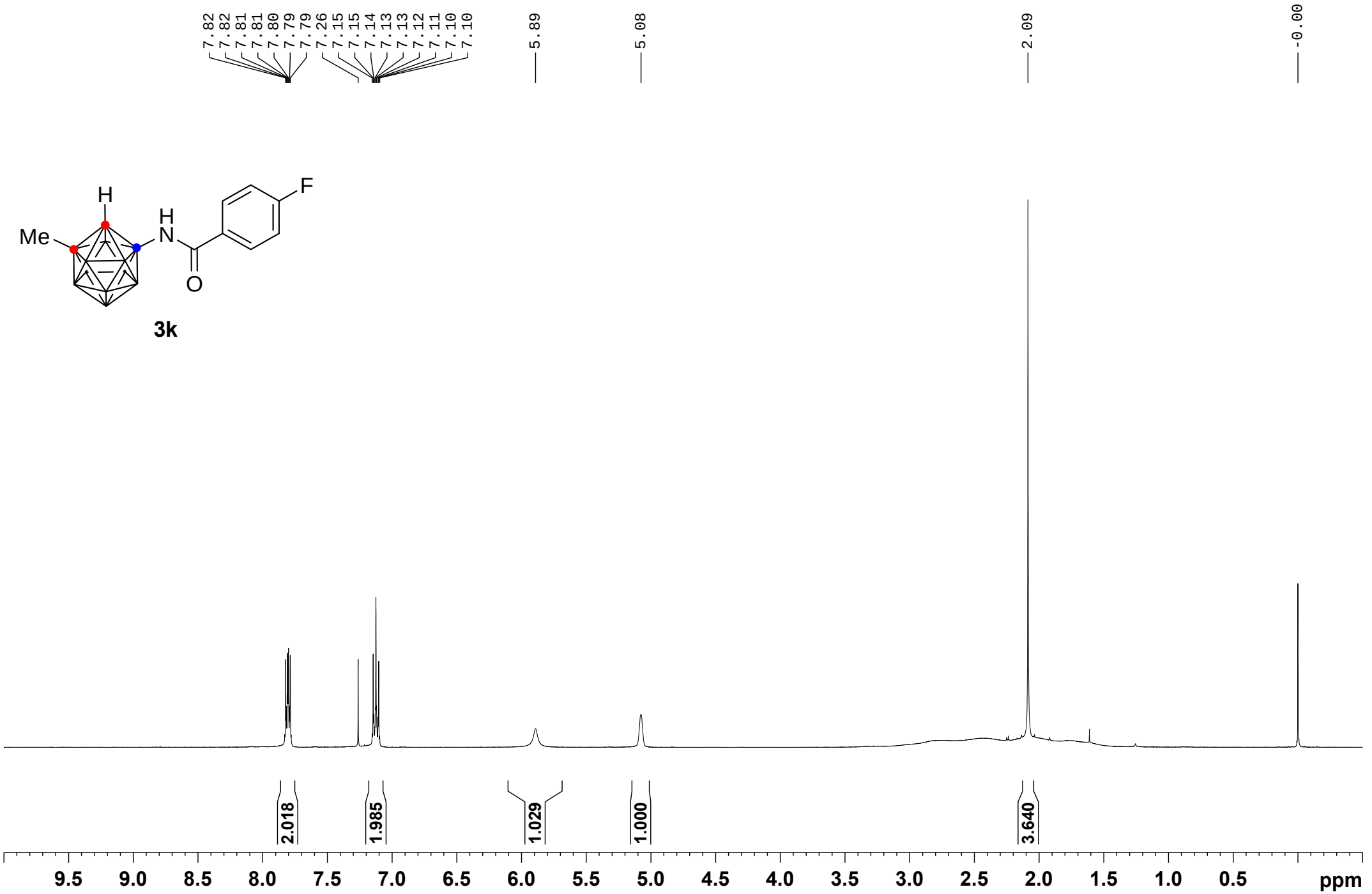
-2.64 -4.01 -5.18 -6.69 -7.84 -9.19 -10.18 -11.30 -12.57 -15.03 -16.22



3j

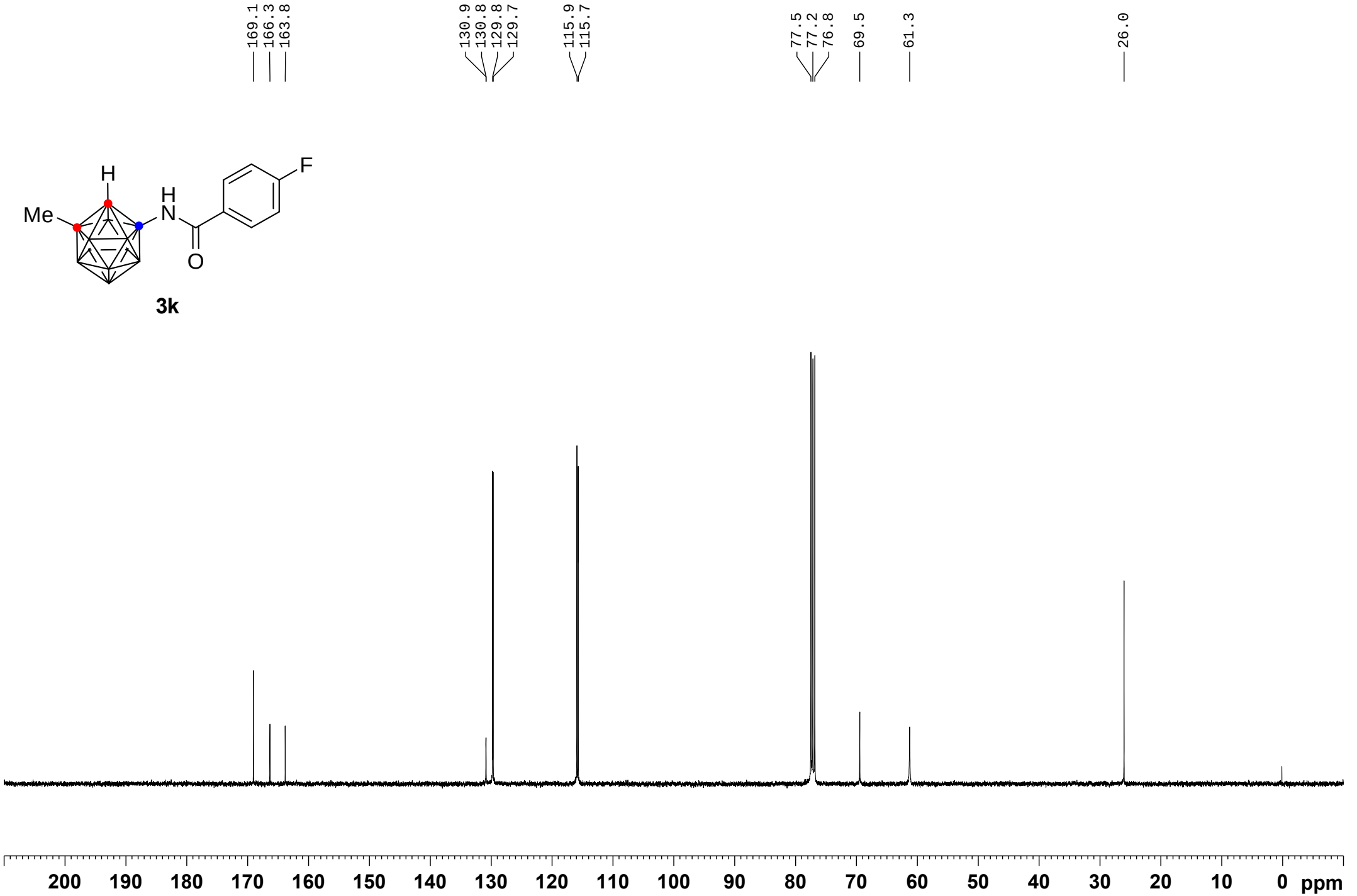


^{1}H NMR

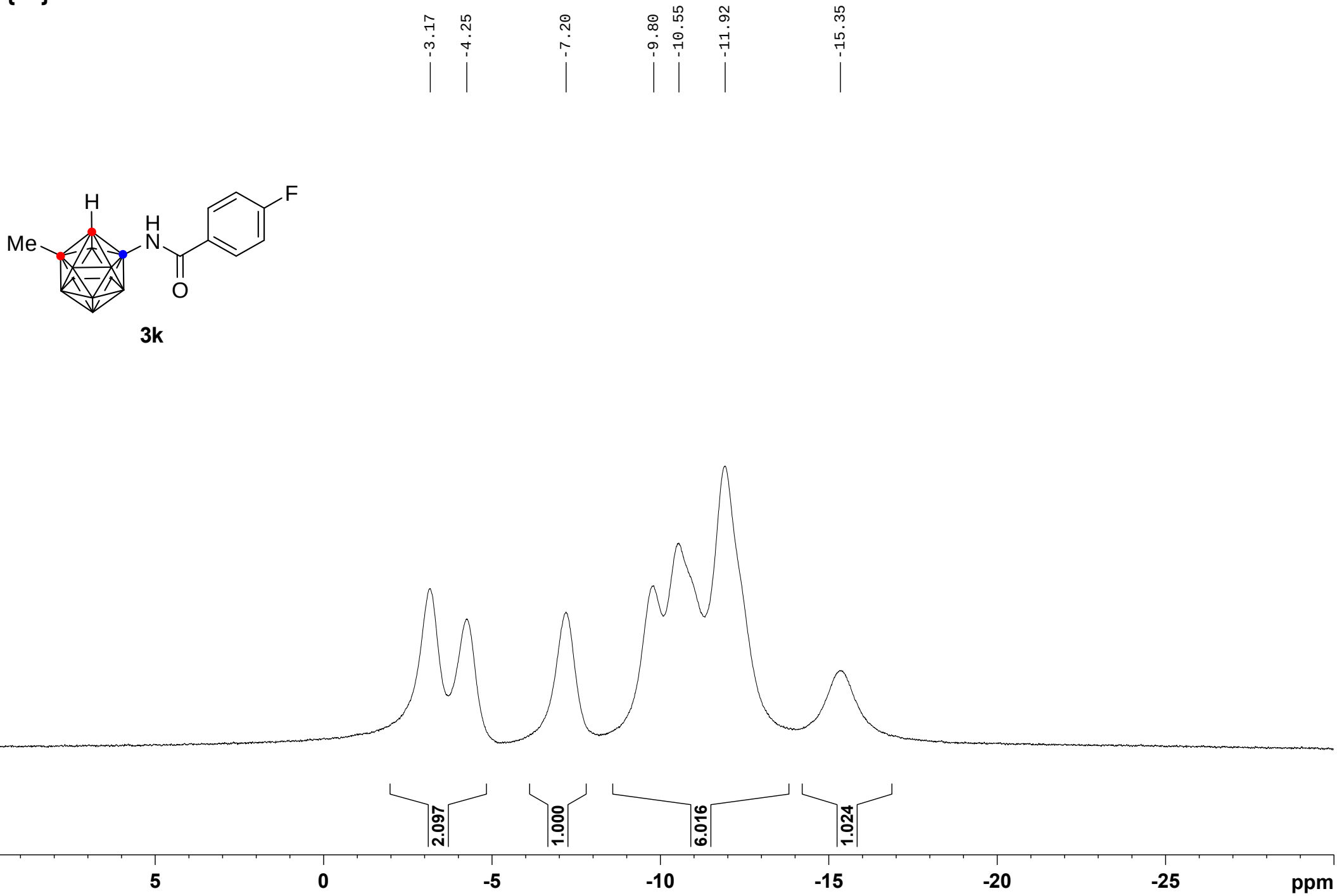

7.82
7.82
7.81
7.80
7.79
7.79
7.26
7.15
7.15
7.14
7.13
7.13
7.12
7.11
7.10
7.10
5.89
5.08
2.09
-0.00
H
Me
H
N
O
F
2.018
1.985
1.029
1.000
3.640
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
ppm

3k

$^{13}C\{^{1}H\}$ NMR


169.1
166.3
163.8
130.9
130.8
129.8
129.7
115.9
115.7
77.5
77.2
76.8
69.5
61.3
26.0
H
Me
H
N
O
F
3k
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
ppm

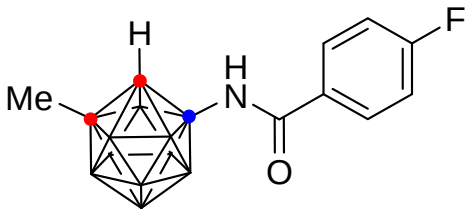
$^{11}B\{^{1}H\}$ NMR


-3.17
-4.25
-7.20
-9.80
-10.55
-11.92
-15.35
H
Me
H
N
O
F
2.097
1.000
6.016
1.024
5
0
-5
-10
-15
-20
-25
ppm

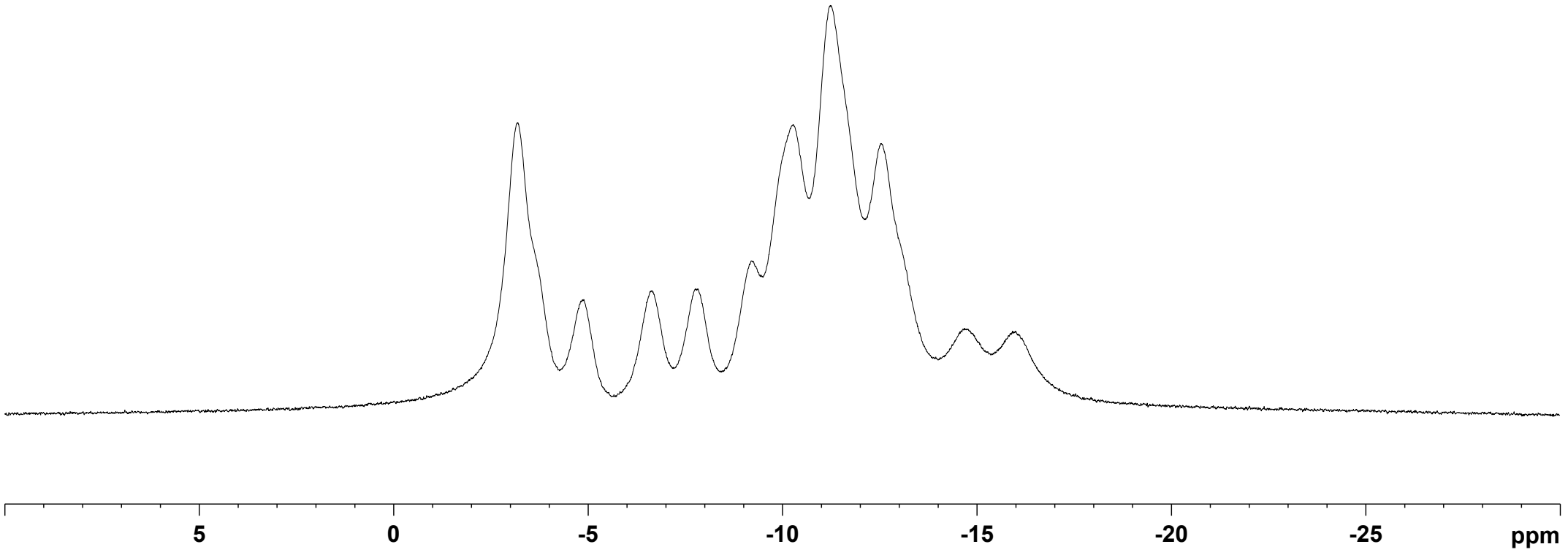
3k

^{11}B NMR

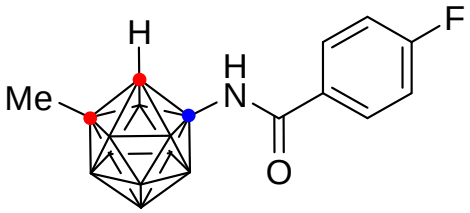
-3.19 -4.89 -6.64 -7.77 -9.21 -10.27 -11.23 -12.53 -14.68 -15.92



3k

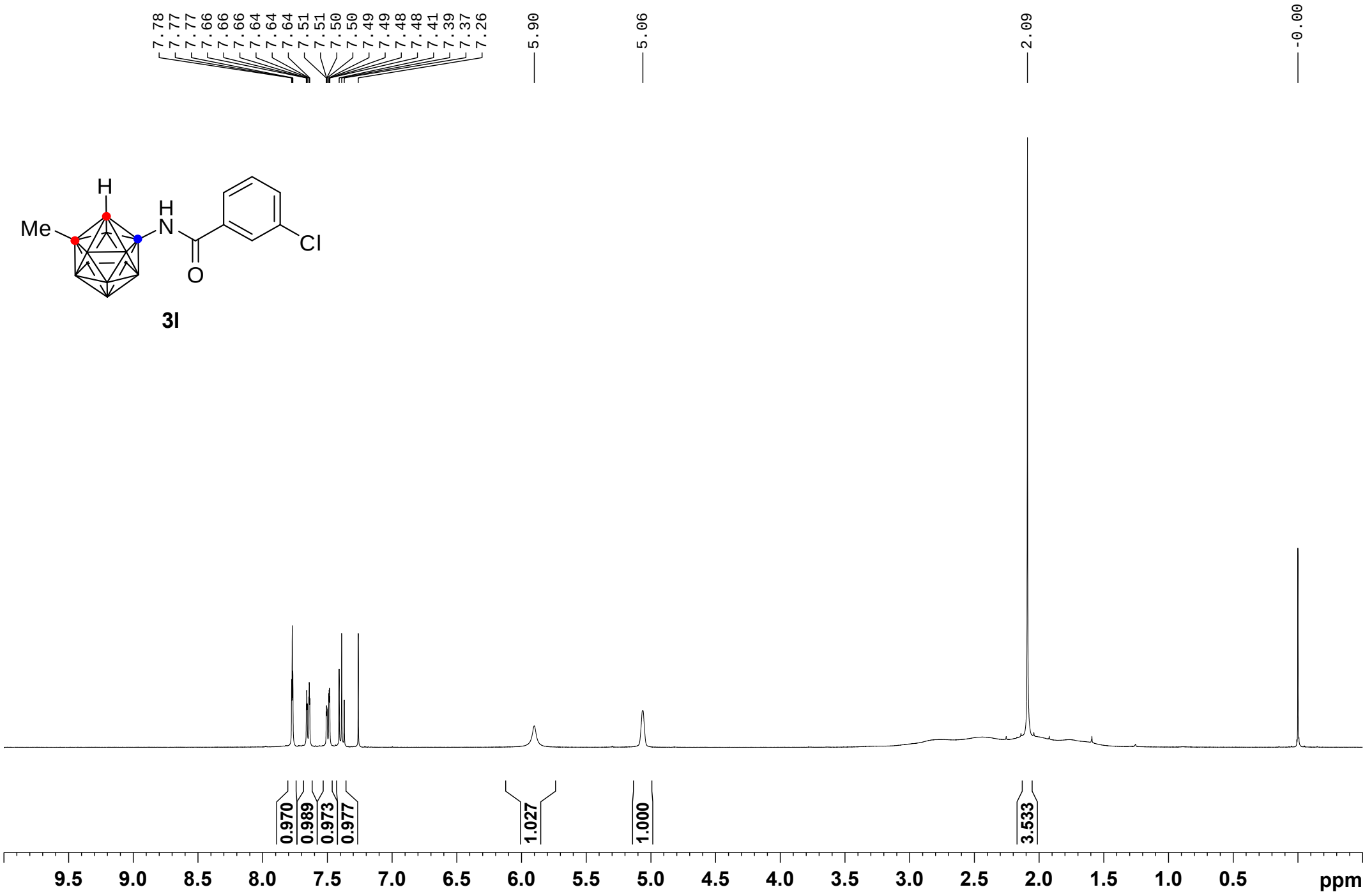


^{19}F NMR



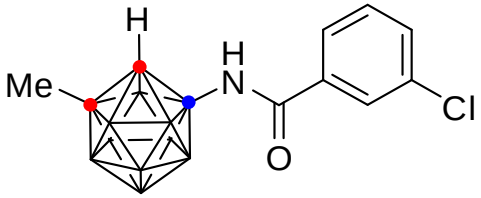
3k

^{1}H NMR


7.78
7.77
7.77
7.66
7.66
7.64
7.64
7.64
7.51
7.51
7.50
7.50
7.49
7.49
7.48
7.48
7.41
7.39
7.37
7.26
5.90
5.06
2.09
-0.00
H
H
N
Me
O
Cl
0.970
0.989
0.973
0.977
1.027
1.000
3.533
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
ppm

3l

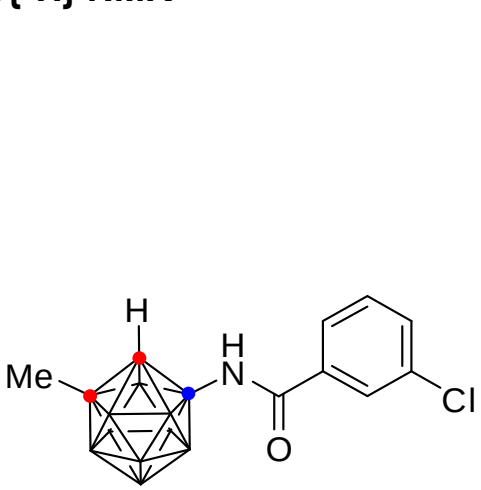
$^{13}C\{^{1}H\}$ NMR


H
H
N
Me
Cl
O

3l

168.8
136.5
135.0
132.0
130.1
127.7
125.3
77.5
77.2
76.8
69.5
61.2
26.1
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
ppm

$^{11}B\{^{1}H\}$ NMR

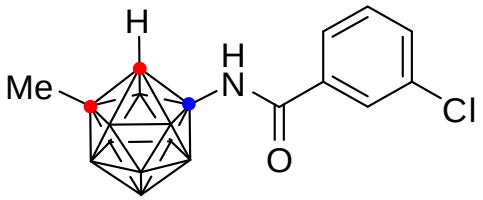

H
H
N
Me
Cl
O

3l

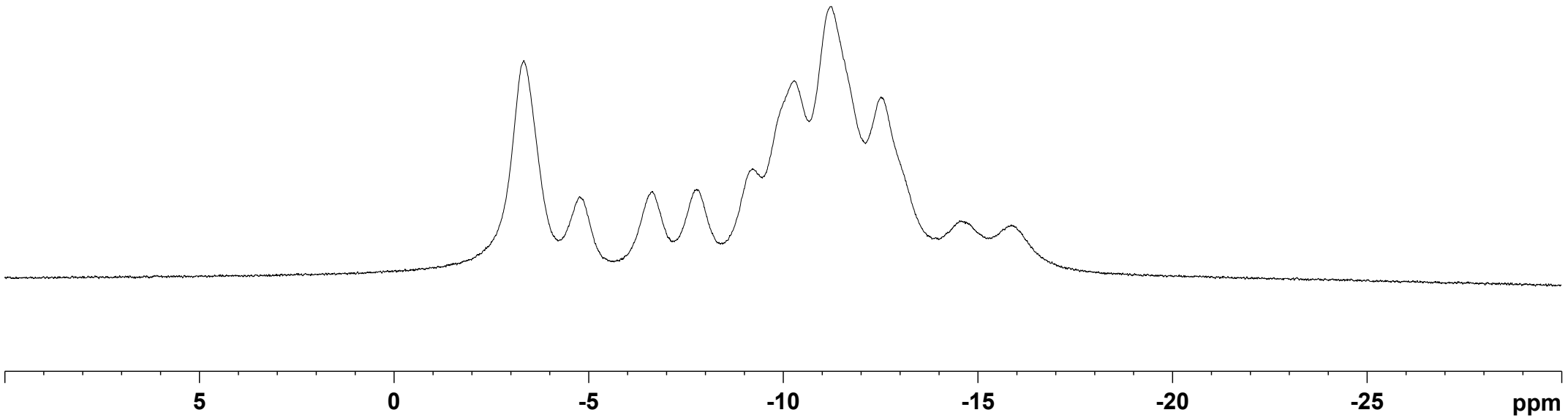
-3.29
-4.20
-7.21
-9.83
-10.48
-11.89
-15.25
2.090
1.000
6.146
1.040
5
0
-5
-10
-15
-20
-25
ppm

^{11}B NMR

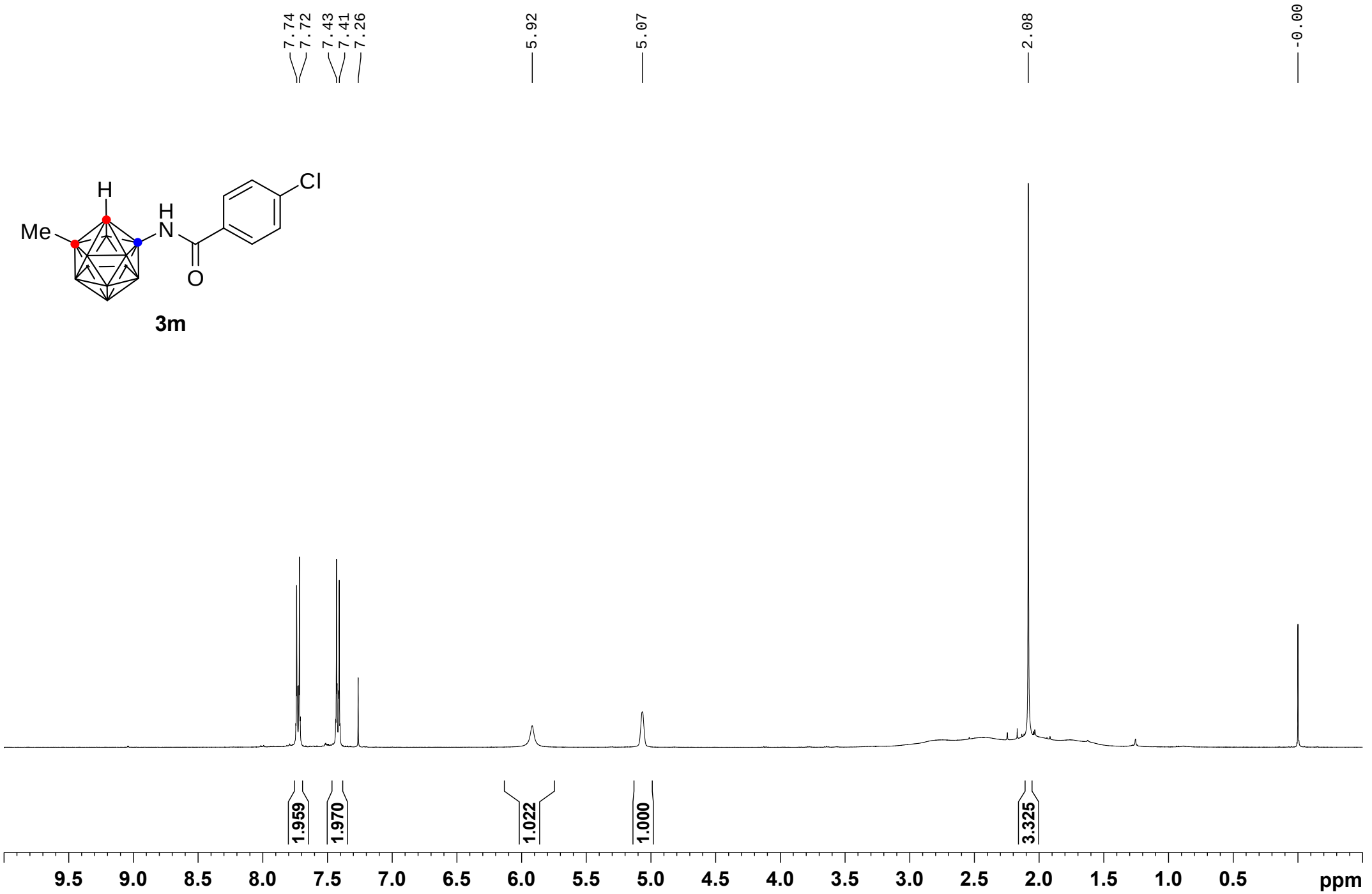
-3.34 -4.77 -6.65 -7.82 -9.22 -10.29 -11.25 -12.55 -14.53 -15.86



3l

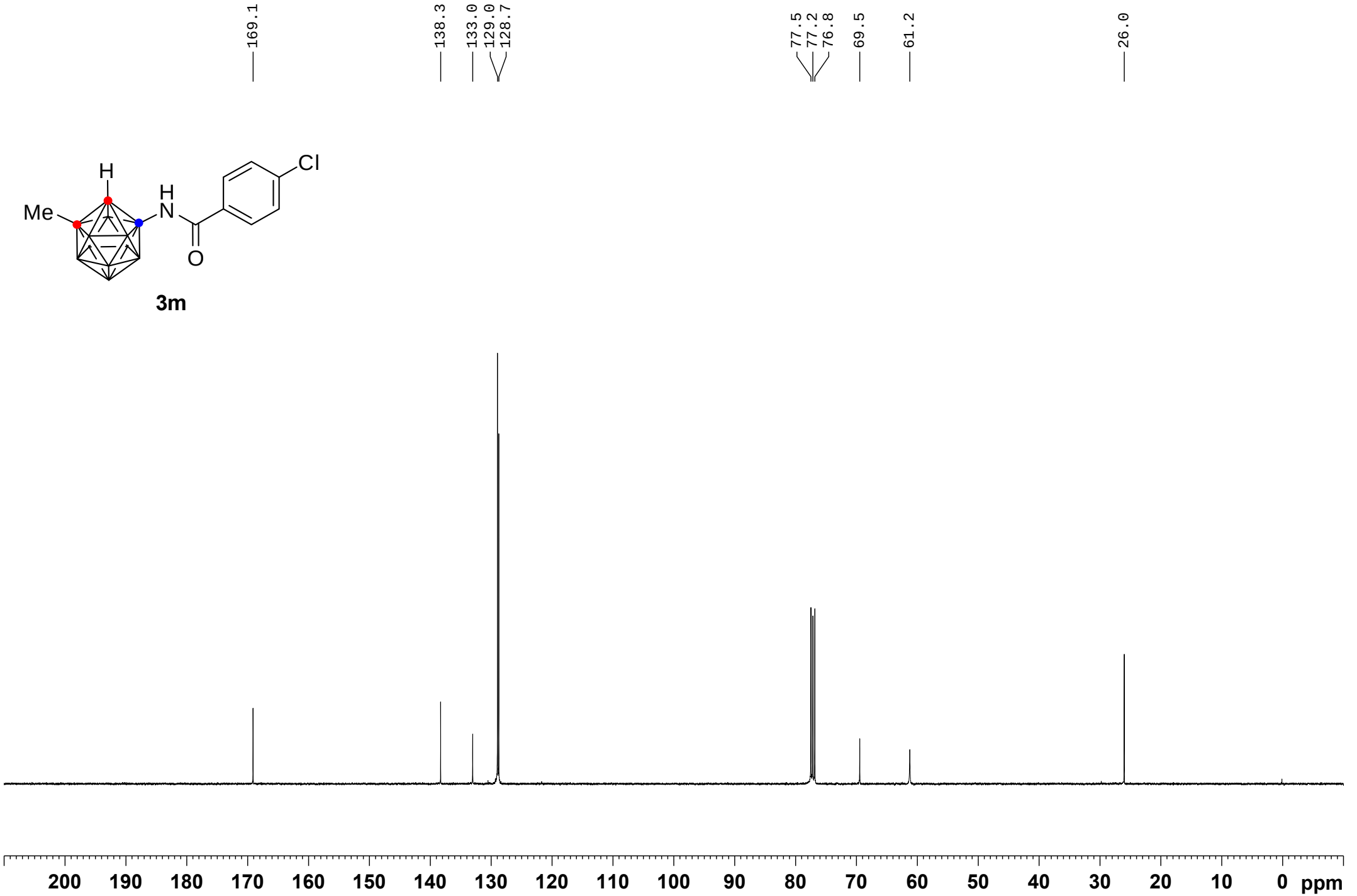


^{1}H NMR

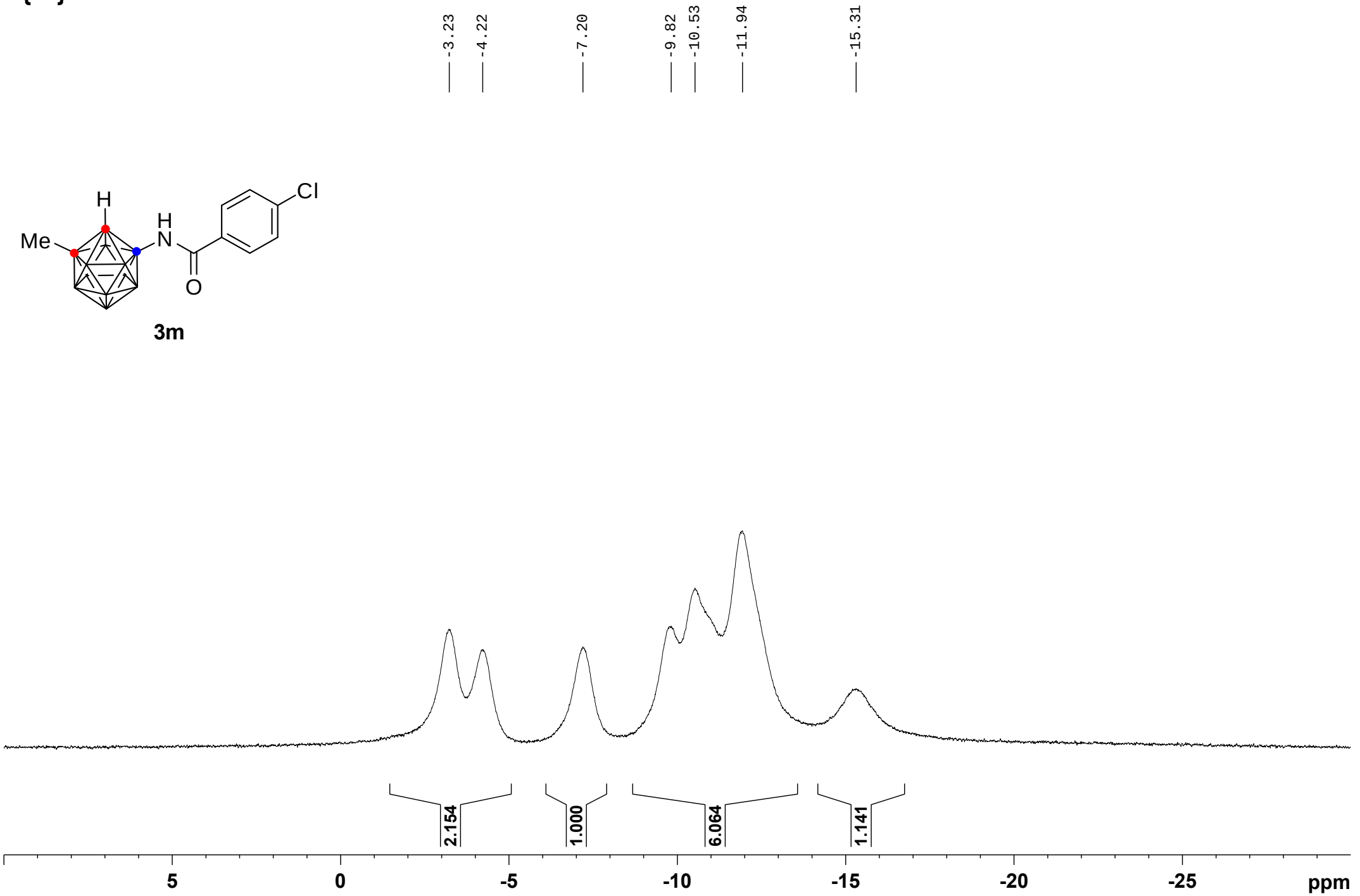

7.74
7.72
7.43
7.41
7.26
5.92
5.07
2.08
-0.00
H
Me
H
N
O
Cl
1.959
1.970
1.022
1.000
3.325
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
ppm

3m

$^{13}C\{^{1}H\}$ NMR

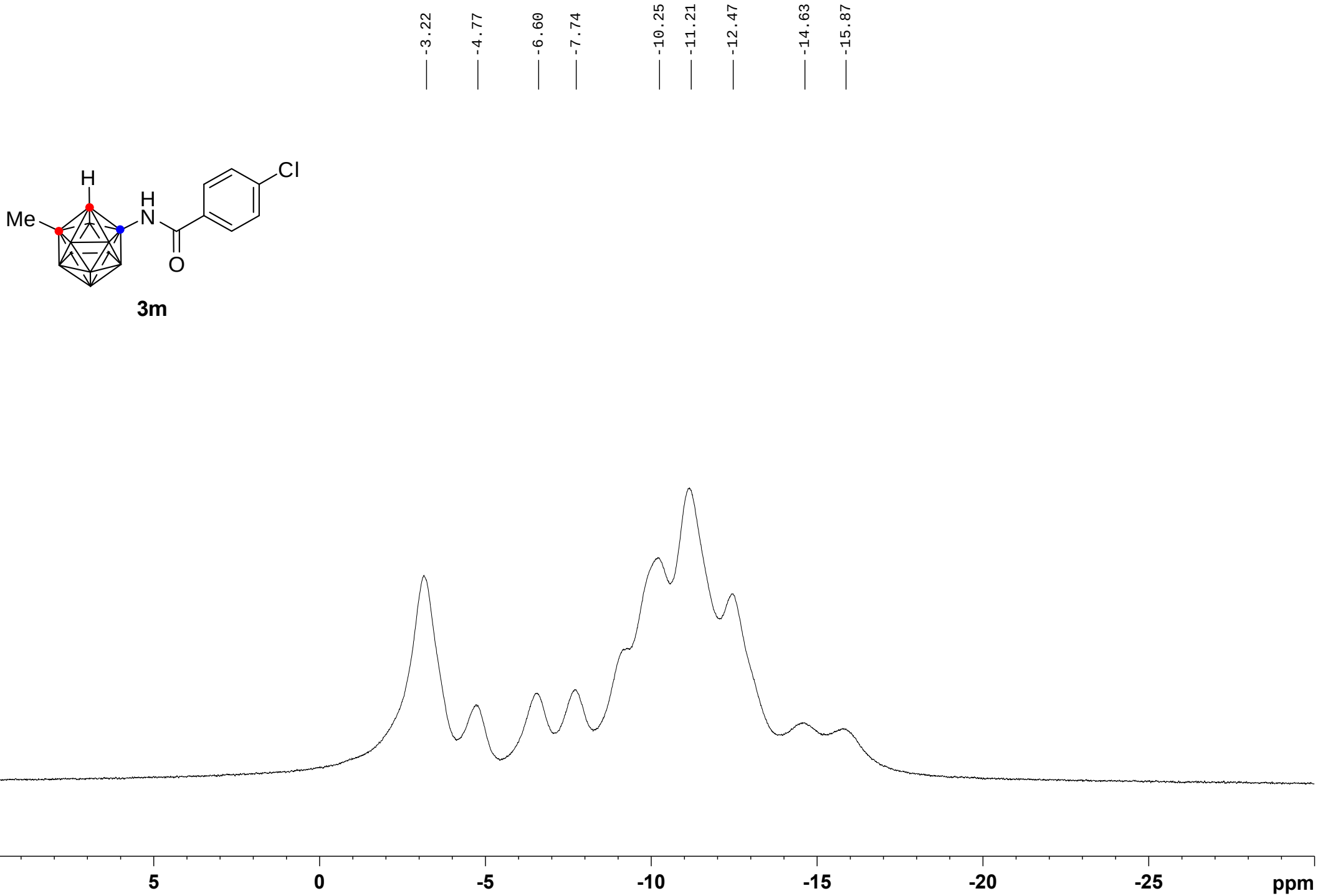

169.1
138.3
133.0
129.0
128.7
77.5
77.2
76.8
69.5
61.2
26.0
H
Me
N
H
O
Cl
3m
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
ppm

$^{11}B\{^{1}H\}$ NMR

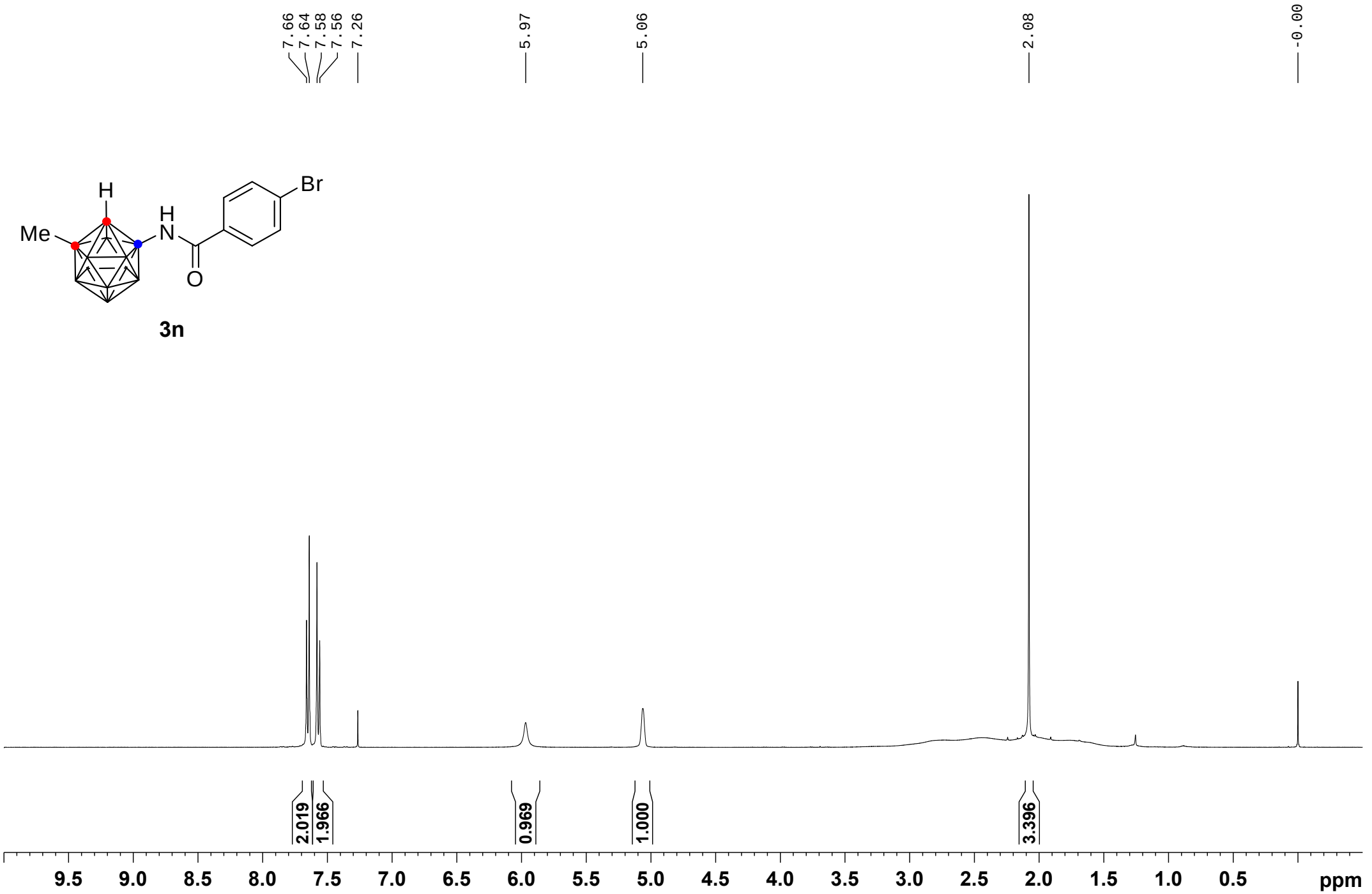

-3.23
-4.22
-7.20
-9.82
-10.53
-11.94
-15.31
H
Me
H
N
O
Cl
2.154
1.000
6.064
1.141
5
0
-5
-10
-15
-20
-25
ppm

3m

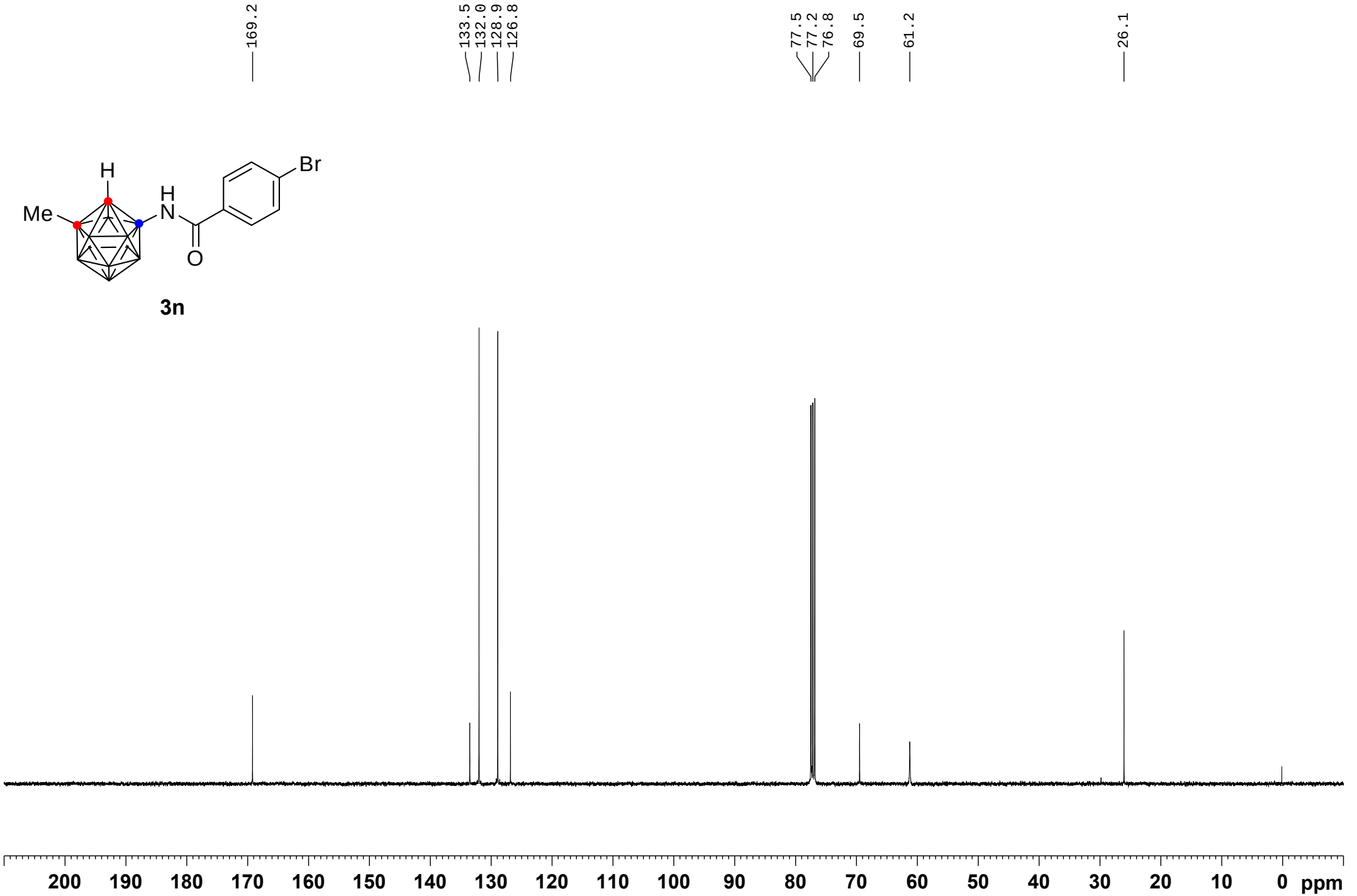
^{11}B NMR


-3.22
-4.77
-6.60
-7.74
-10.25
-11.21
-12.47
-14.63
-15.87
H
H
N
Me
O
Cl
3m
5
0
-5
-10
-15
-20
-25
ppm

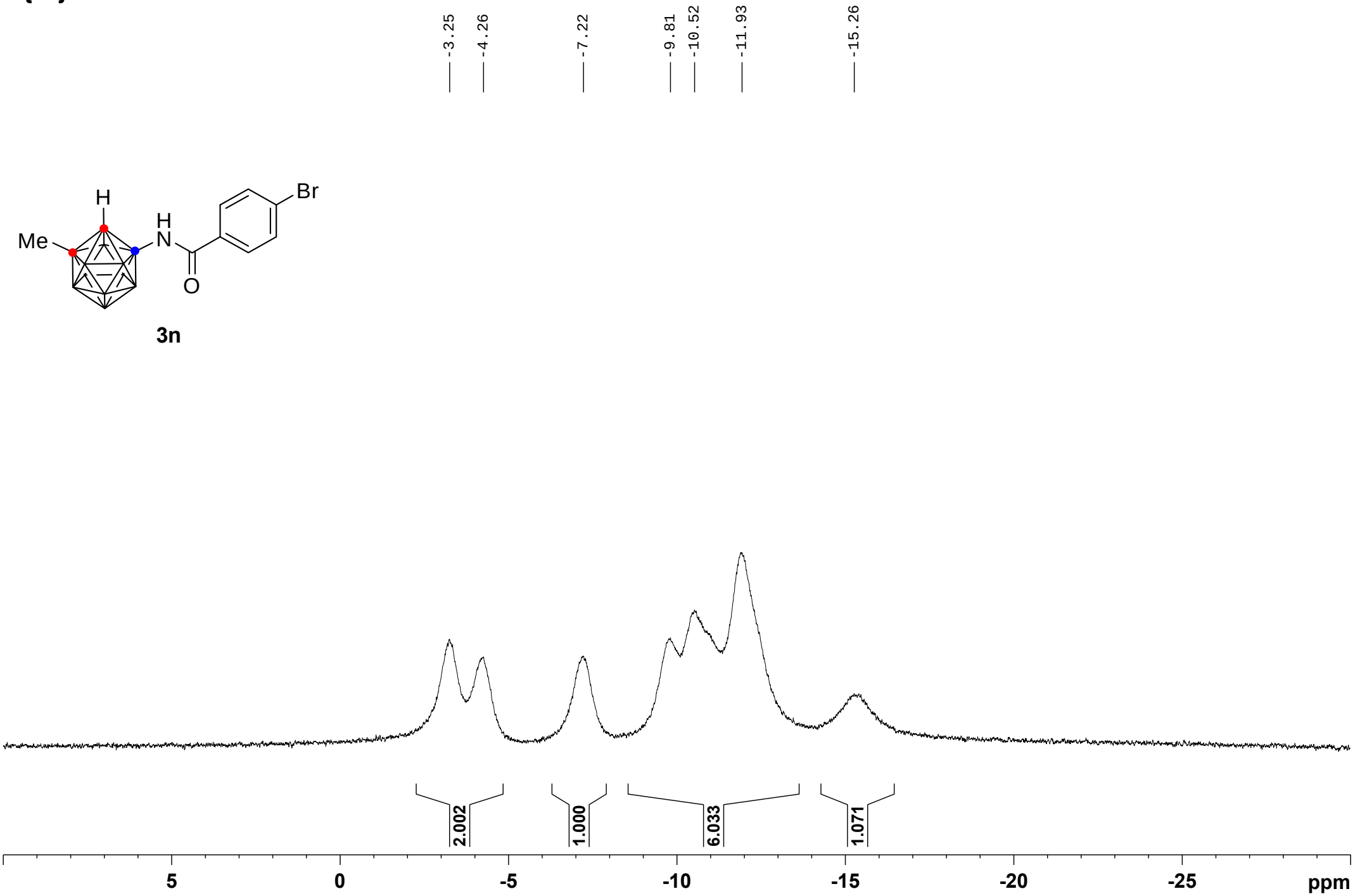
^{1}H NMR


7.66
7.64
7.58
7.56
7.26
5.97
5.06
2.08
0.00
H
Me
H
N
O
Br
3n
2.019
1.966
0.969
1.000
3.396
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
ppm

$^{13}C\{^{1}H\}$ NMR


169.2
133.5
132.0
128.9
126.8
77.5
77.2
76.8
69.5
61.2
26.1
H
Me
H
N
O
Br
3n
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
ppm

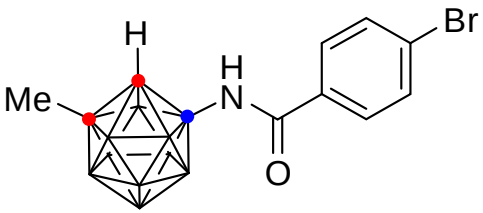
$^{11}B\{^{1}H\}$ NMR


-3.25
-4.26
-7.22
-9.81
-10.52
-11.93
-15.26
H
Me
H
N
O
Br
2.002
1.000
6.033
1.071
5
0
-5
-10
-15
-20
-25
ppm

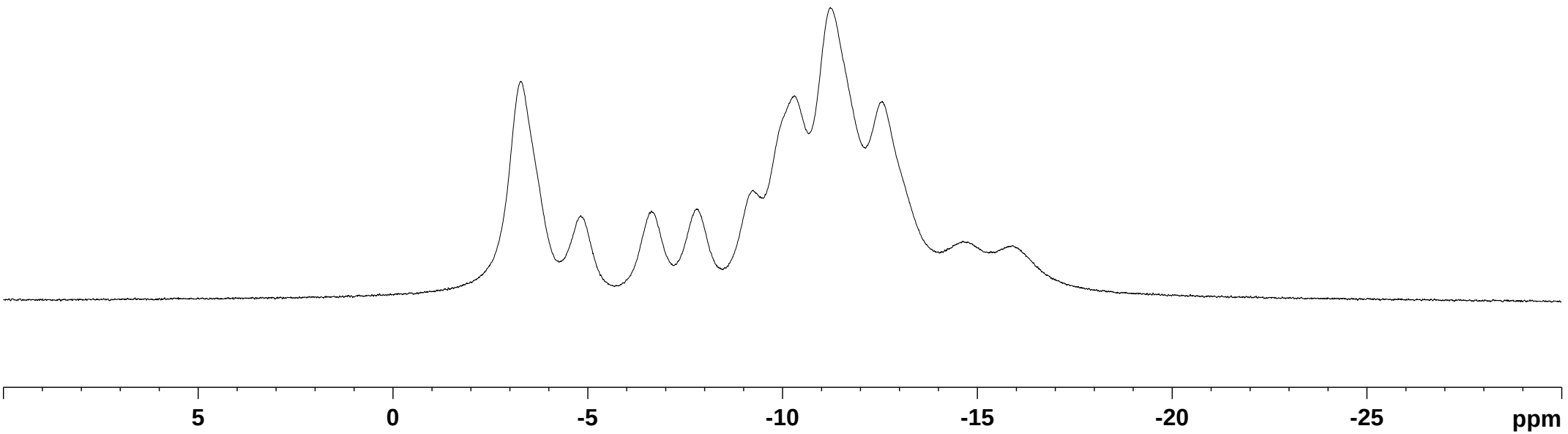
3n

^{11}B NMR

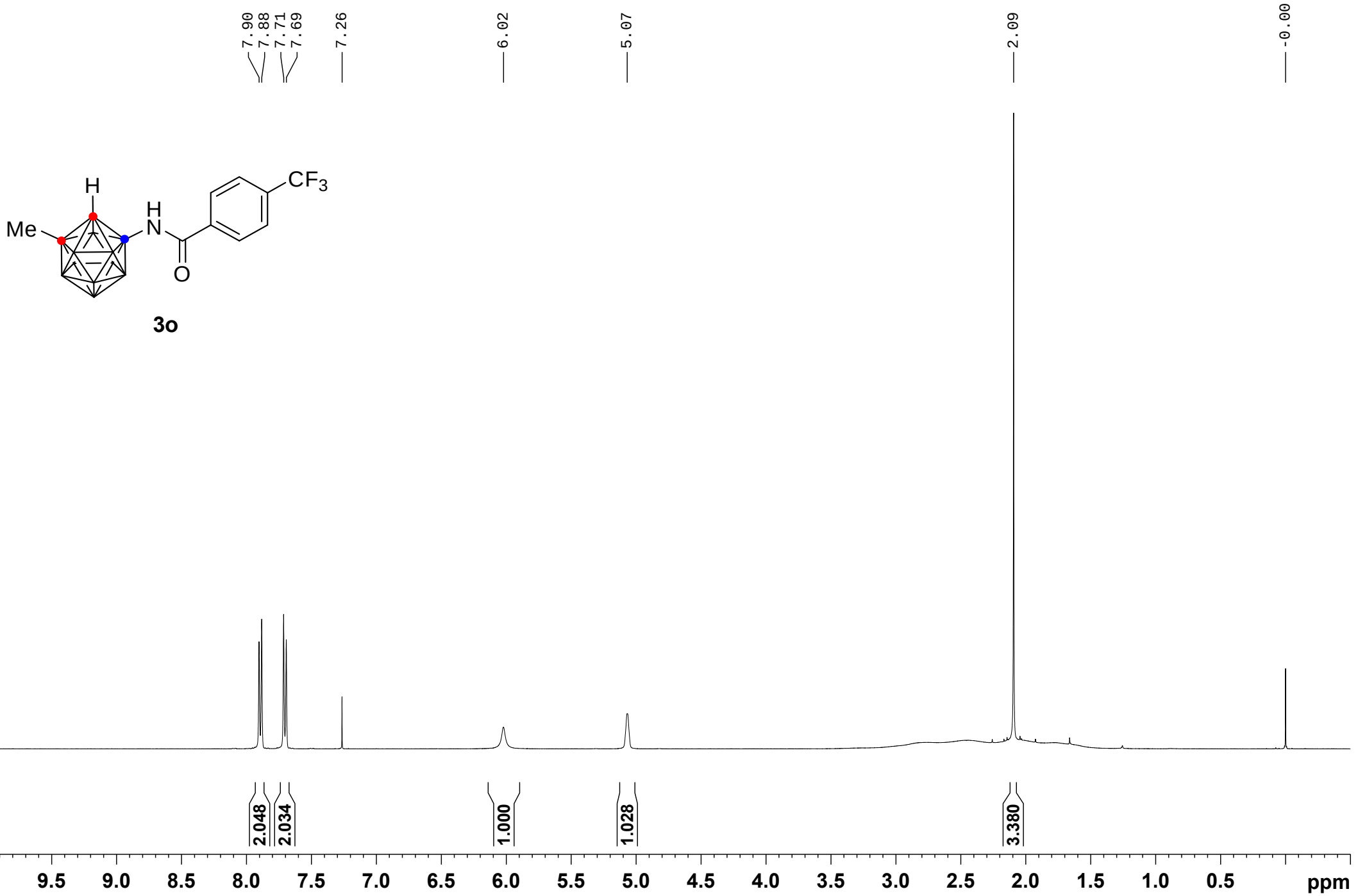
-3.32 -4.82 -6.64 -7.84 -9.25 -10.32 -11.27 -12.56 -14.62 -15.91



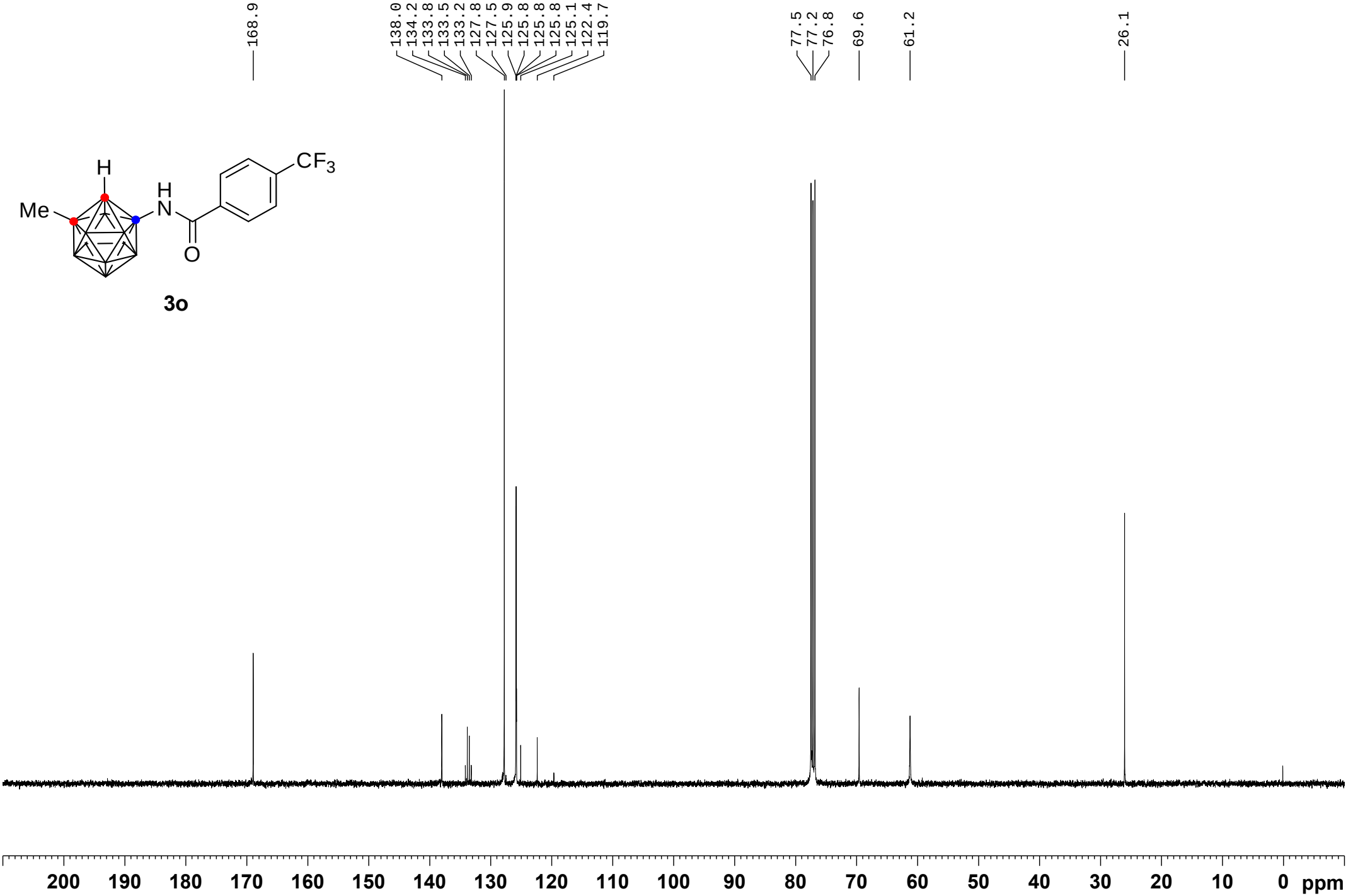
3n



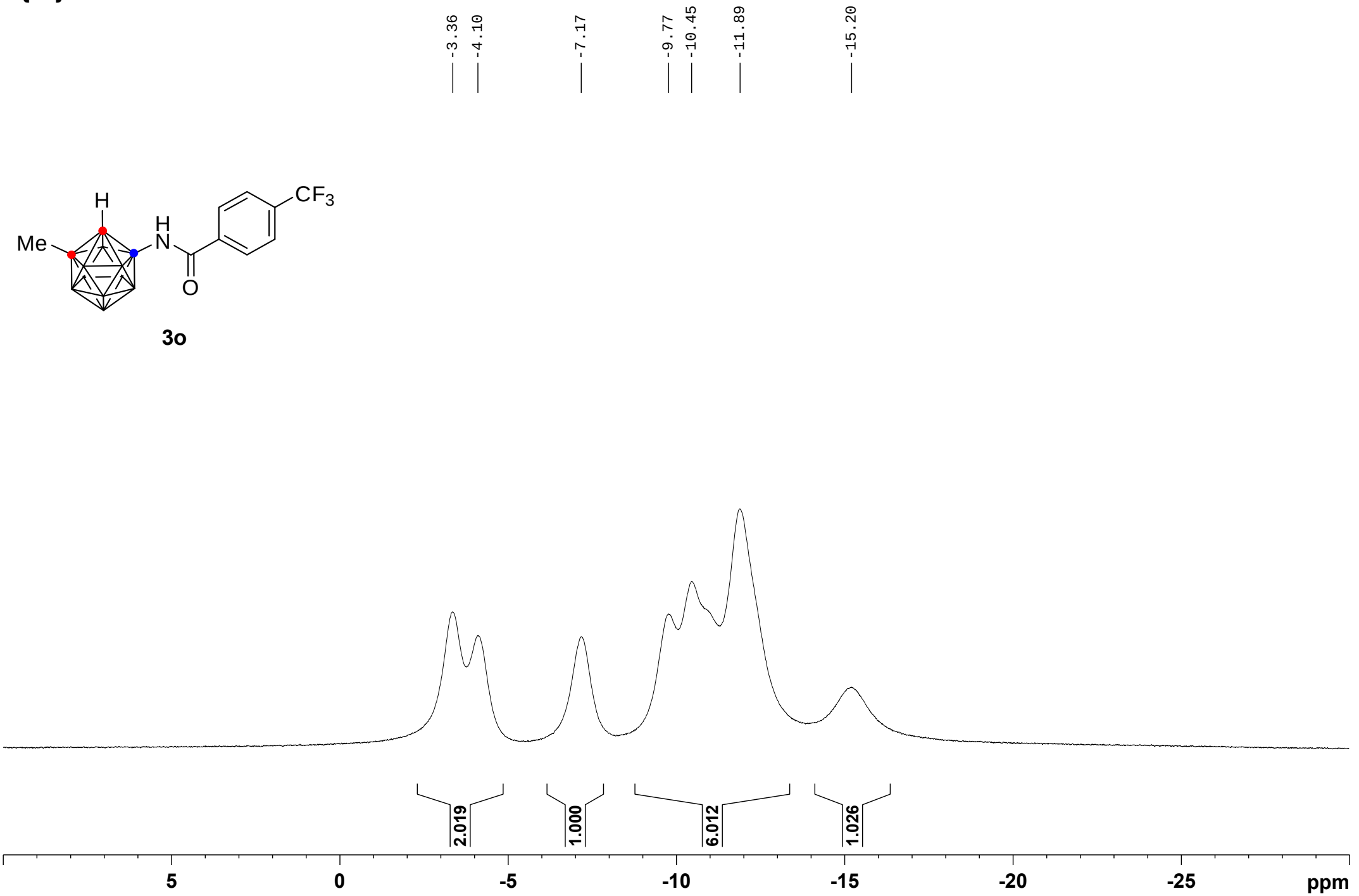
^{1}H NMR


7.90
7.88
7.71
7.69
7.26
6.02
5.07
2.09
0.00
H
Me
N
H
O
CF3
3o
2.048
2.034
1.000
1.028
3.380
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
ppm

$^{13}C\{^{1}H\}$ NMR

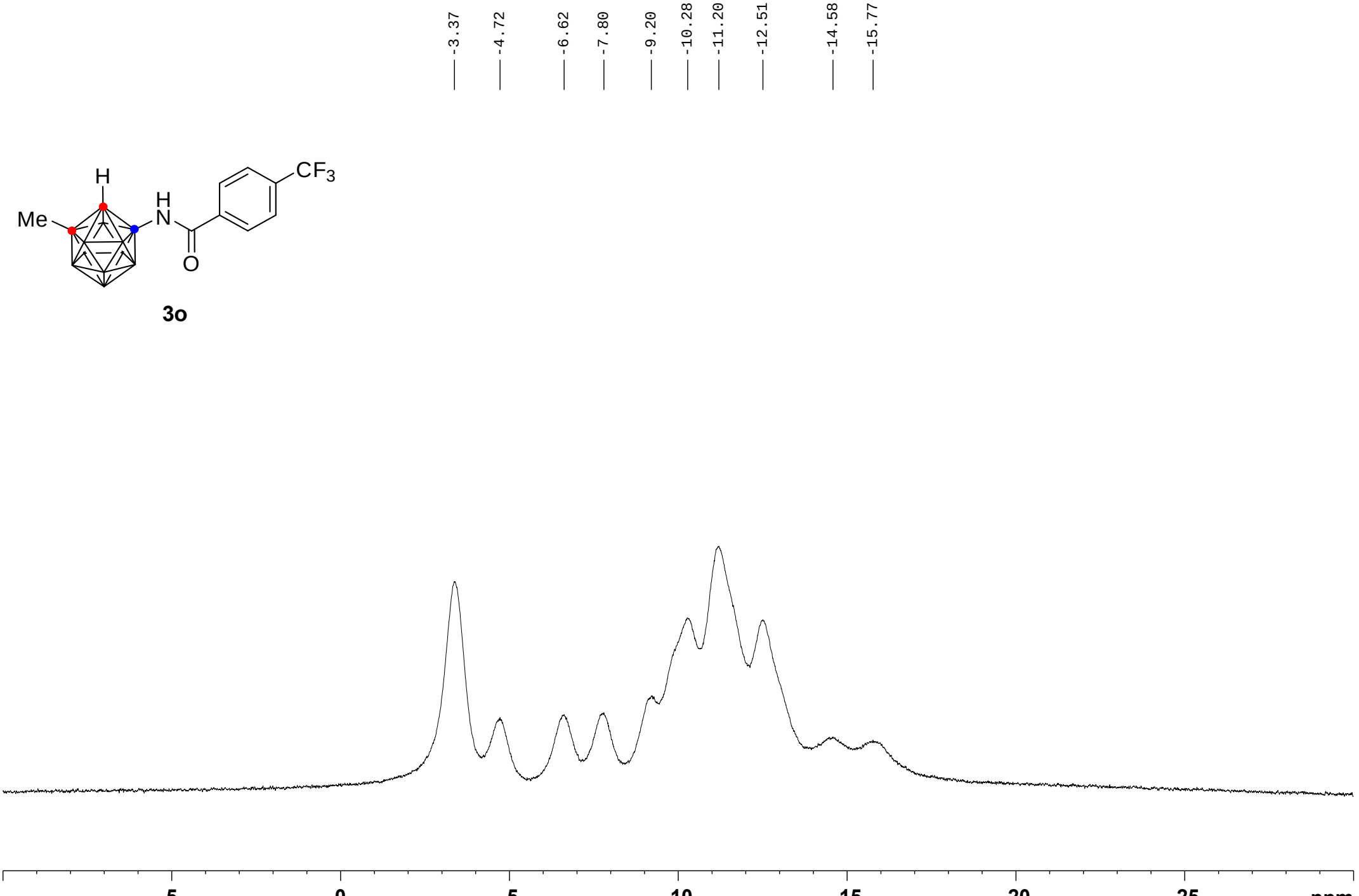

168.9
138.0
134.2
133.8
133.5
133.2
127.8
127.5
125.9
125.8
125.8
125.1
122.4
119.7
77.5
77.2
76.8
69.6
61.2
26.1
H
Me
N
H
O
CF3
3o
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
ppm

$^{11}B\{^{1}H\}$ NMR


-3.36
-4.10
-7.17
-9.77
-10.45
-11.89
-15.20
H
Me
H
N
O
CF3
2.019
1.000
6.012
1.026
5
0
-5
-10
-15
-20
-25
ppm

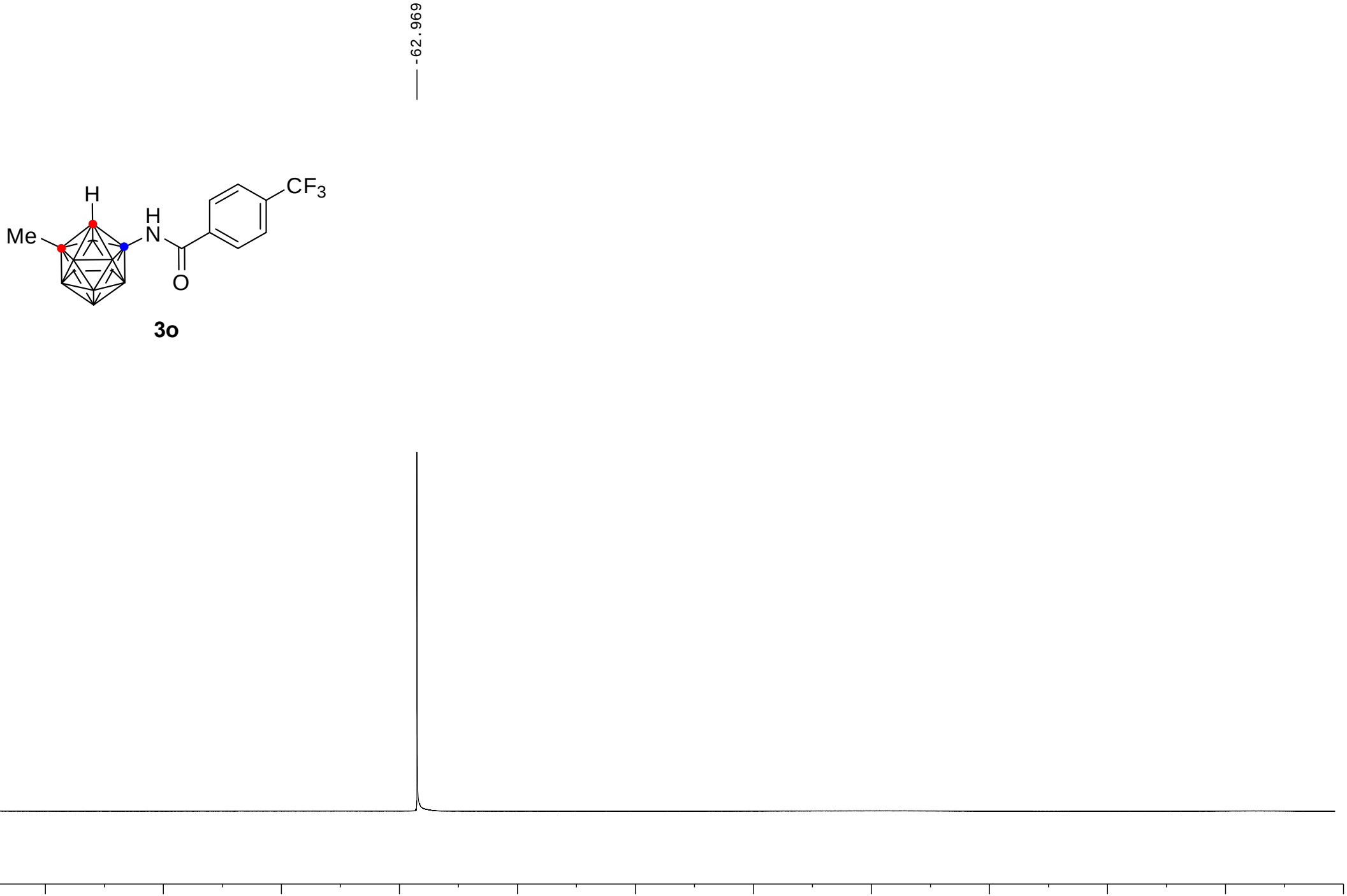
3o

^{11}B NMR


-3.37
-4.72
-6.62
-7.80
-9.20
-10.28
-11.20
-12.51
-14.58
-15.77
H
Me
H
N
O
CF3
5
0
-5
-10
-15
-20
-25
ppm

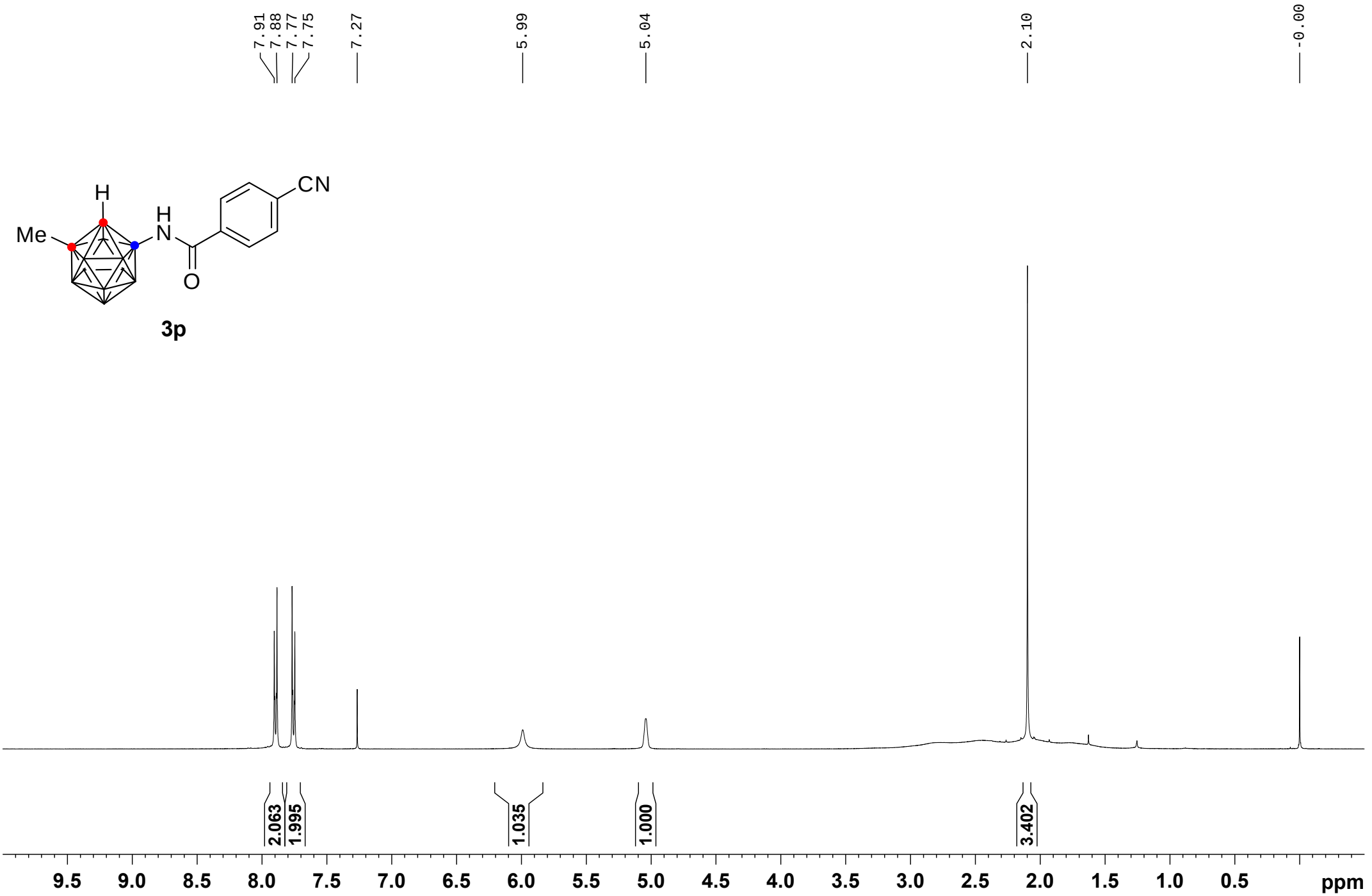
3o

^{19}F NMR

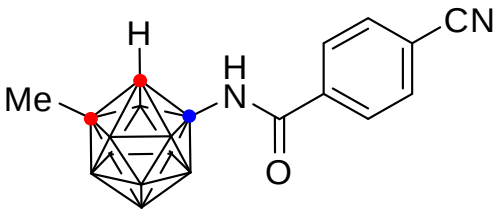


3o

^{1}H NMR


7.91
7.88
7.77
7.75
7.27
5.99
5.04
2.10
0.00
H
Me
H
N
O
CN
3p
2.063
1.995
1.035
1.000
3.402
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
ppm

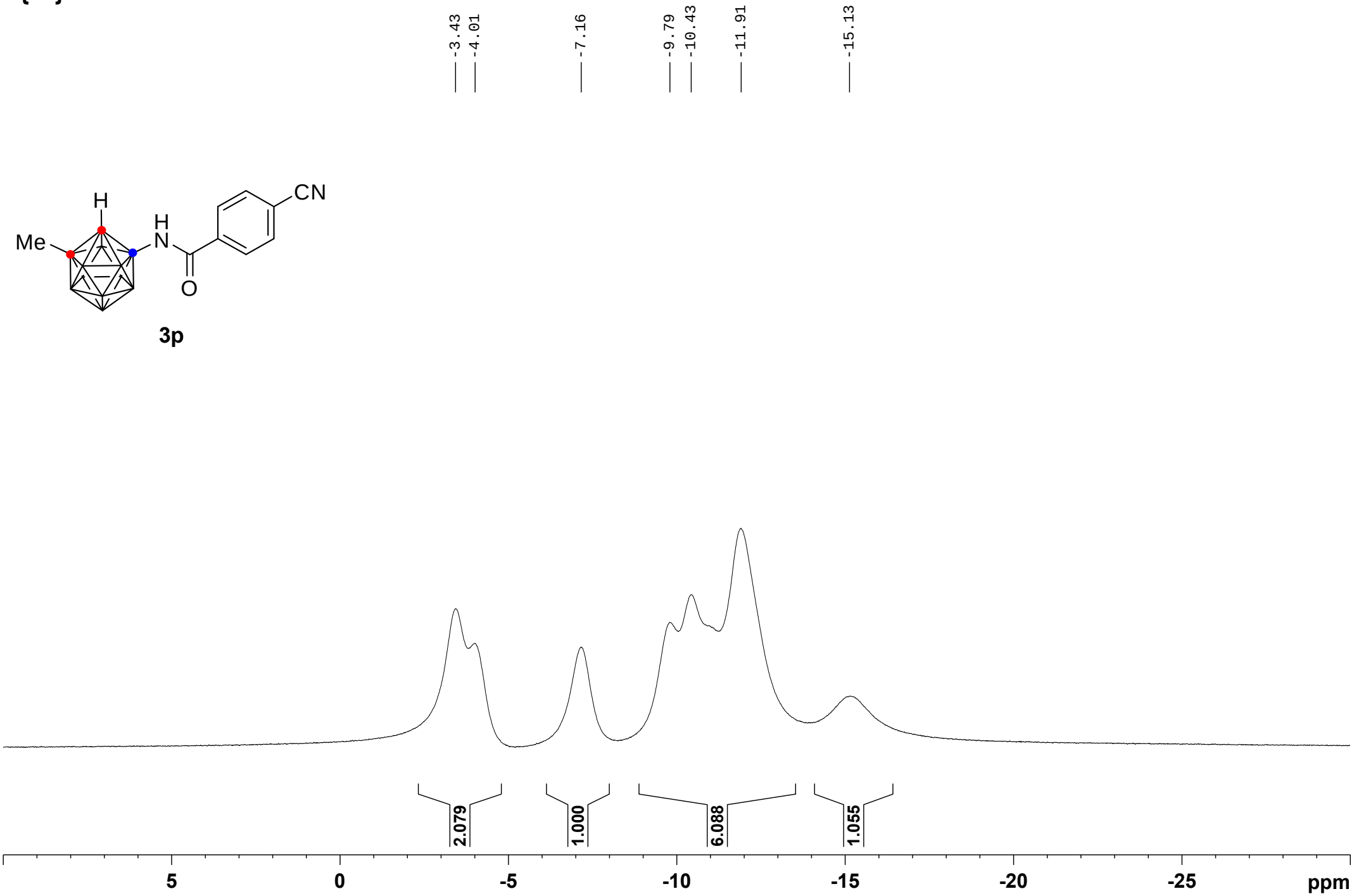
$^{13}C\{^{1}H\}$ NMR


H
Me
H
N
O
CN

3p

168.4
138.6
132.6
128.0
118.0
115.4
77.5
77.2
76.8
69.6
61.2
26.0
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
ppm

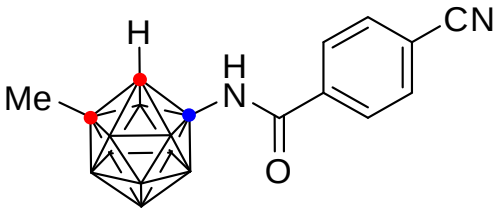
$^{11}B\{^{1}H\}$ NMR


-3.43
-4.01
-7.16
-9.79
-10.43
-11.91
-15.13
H
H
N
Me
O
CN
2.079
1.000
6.088
1.055
5
0
-5
-10
-15
-20
-25
ppm

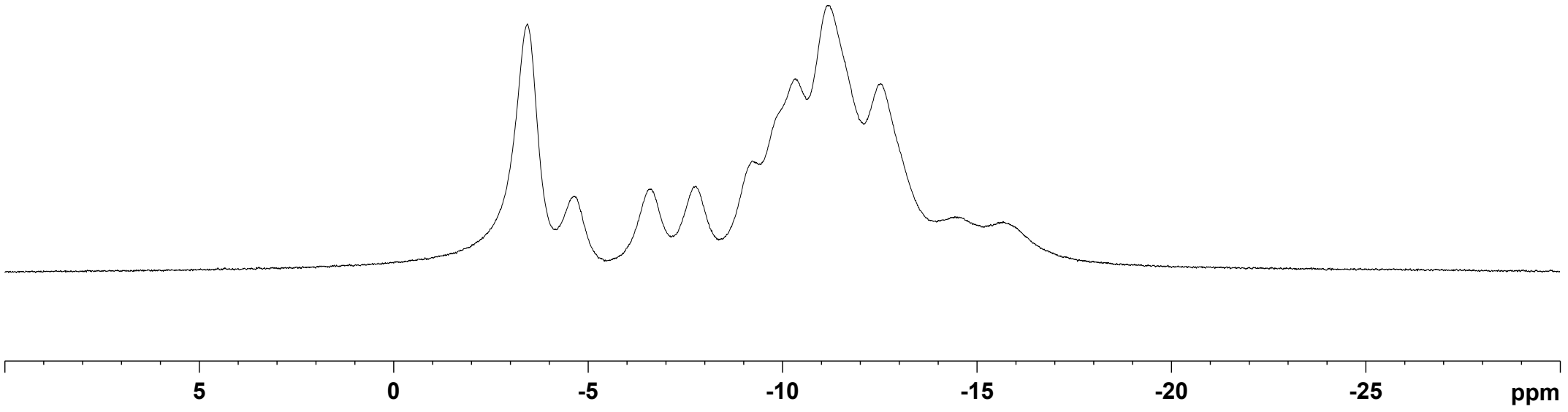
3p

^{11}B NMR

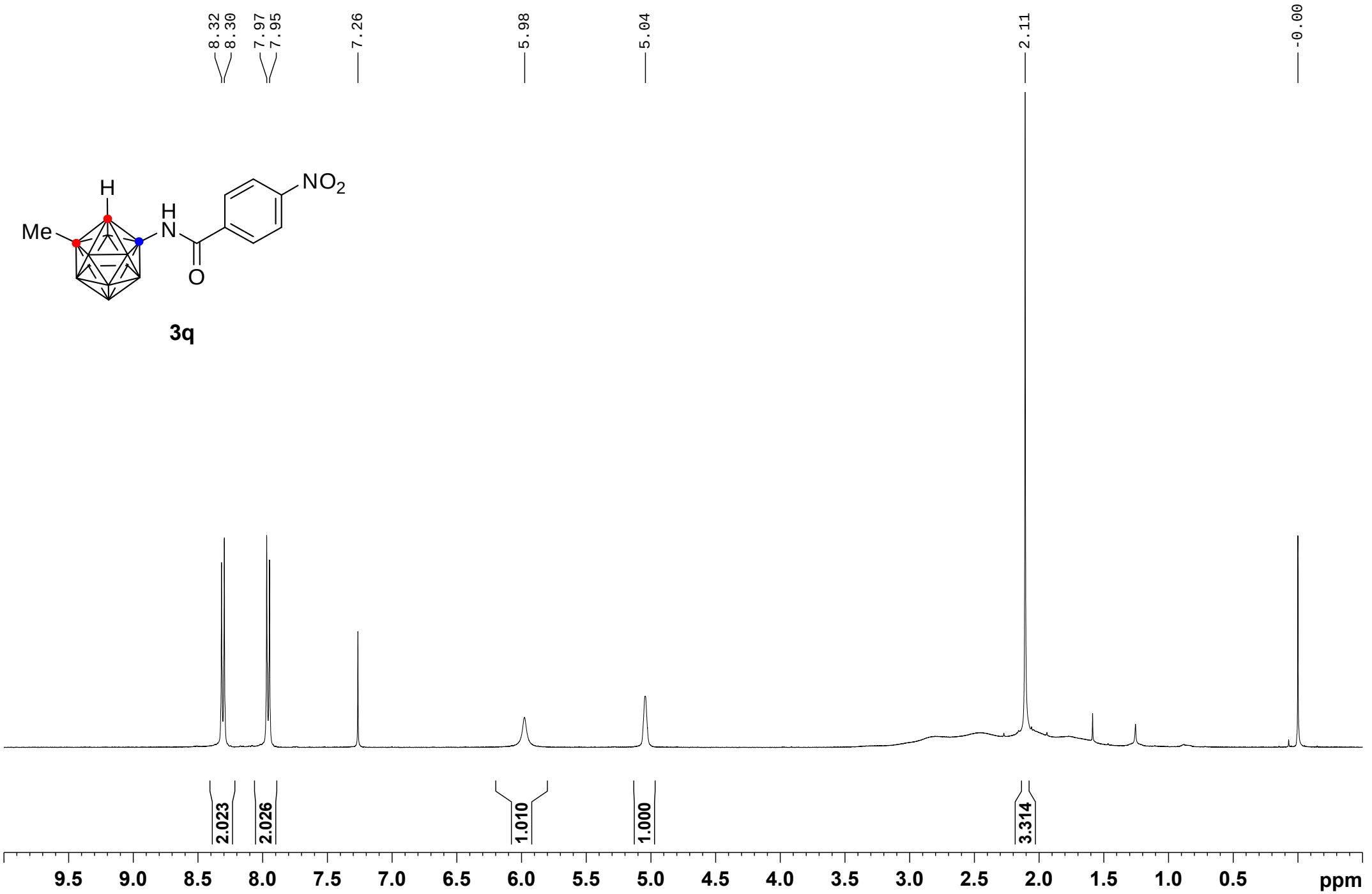
-3.44
-4.64
-6.59
-7.77
-9.22
-10.34
-11.19
-12.53
-14.43
-15.67



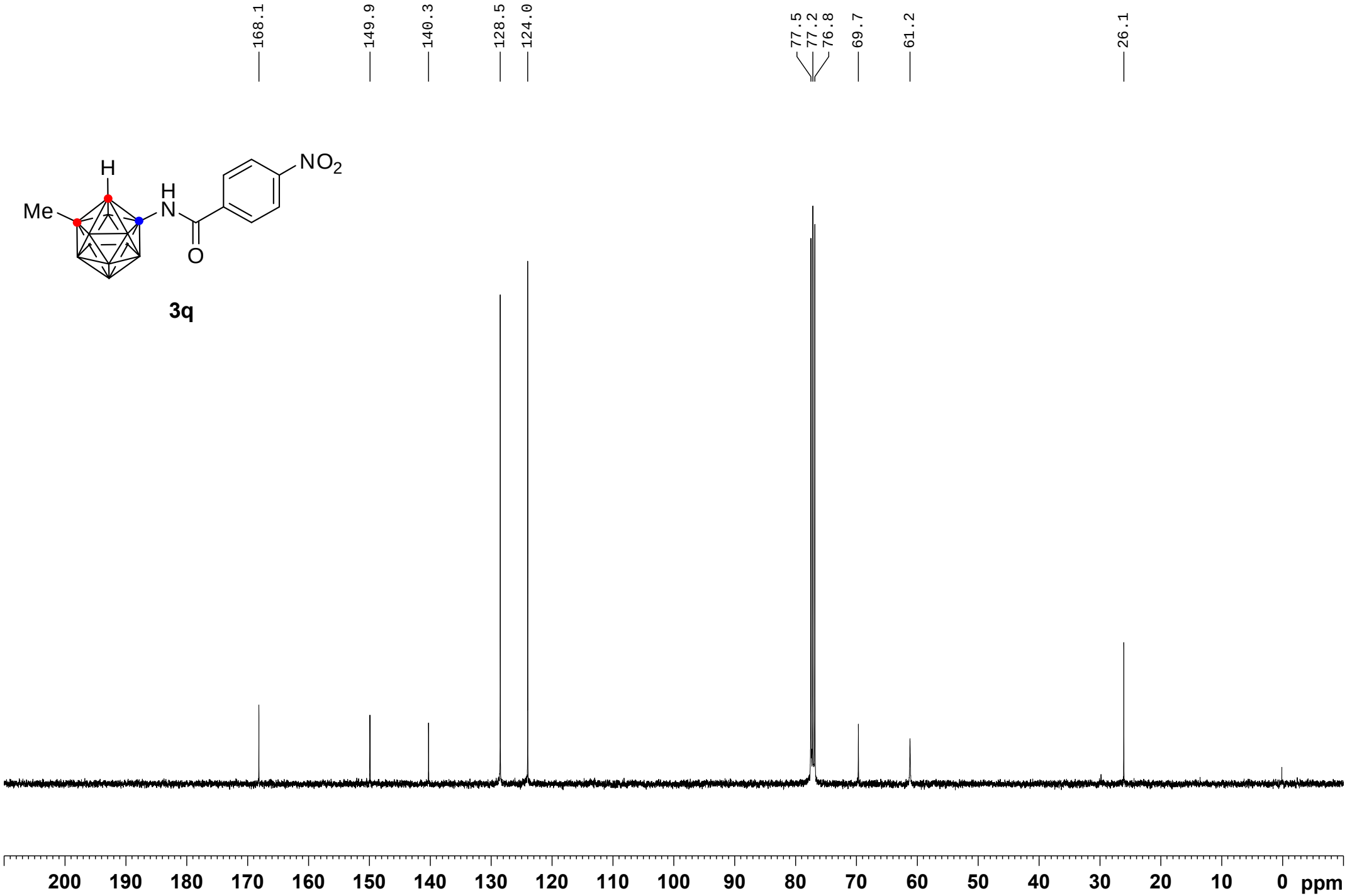
3p



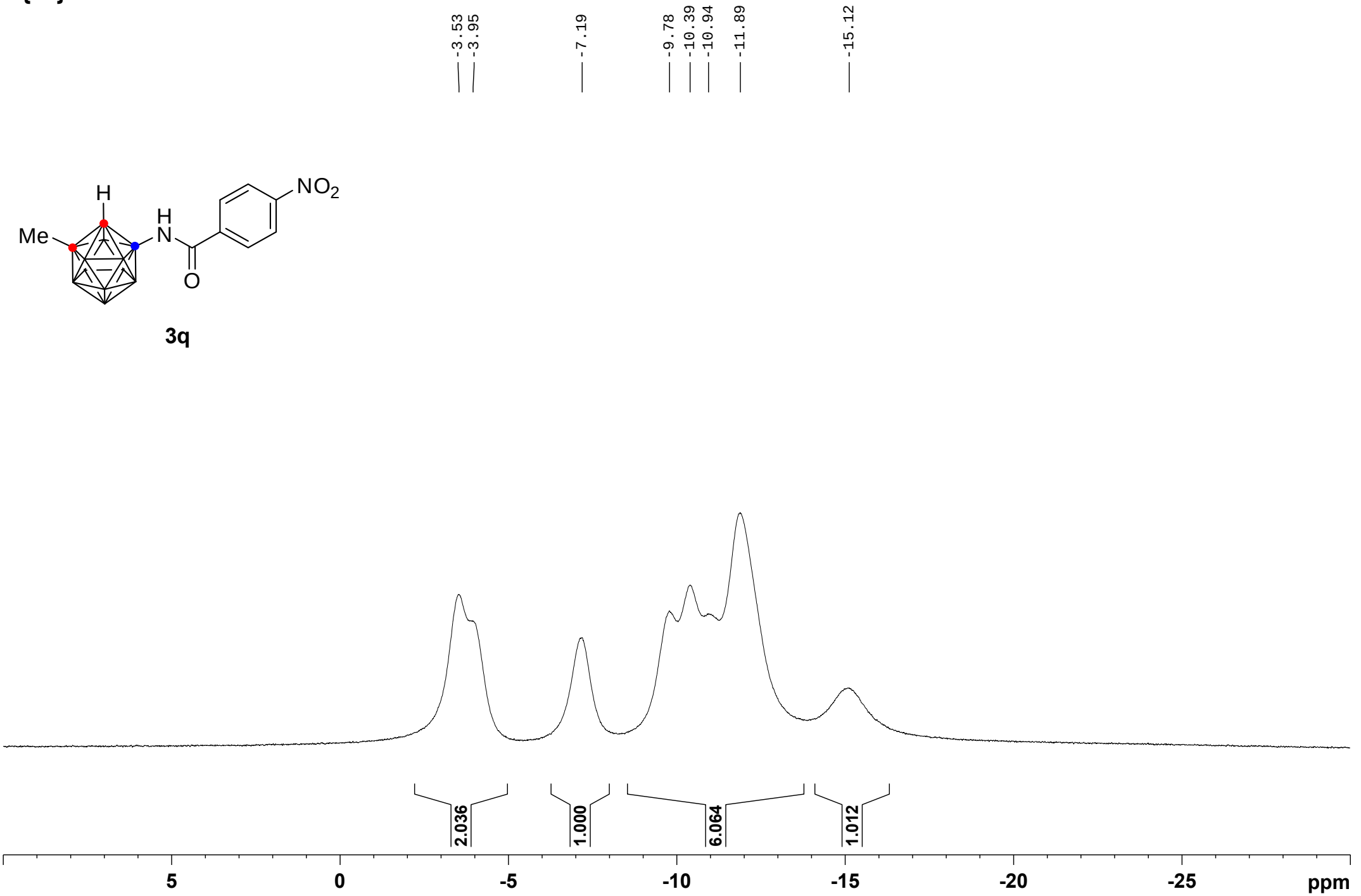
^{1}H NMR


8.32
8.30
7.97
7.95
7.26
5.98
5.04
2.11
0.00
H
Me
H
N
O
NO2
3q
2.023
2.026
1.010
1.000
3.314
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
ppm

$^{13}C\{^{1}H\}$ NMR


168.1
149.9
140.3
128.5
124.0
77.5
77.2
76.8
69.7
61.2
26.1
H
Me
H
N
O
NO2
3q
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
ppm

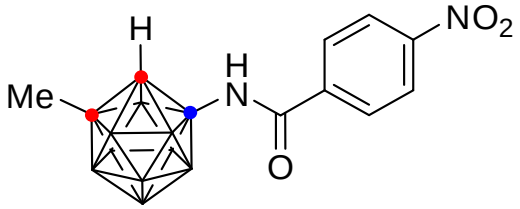
$^{11}B\{^{1}H\}$ NMR


-3.53
-3.95
-7.19
-9.78
-10.39
-10.94
-11.89
-15.12
H
Me
H
N
O
NO2
2.036
1.000
6.064
1.012
5
0
-5
-10
-15
-20
-25
ppm

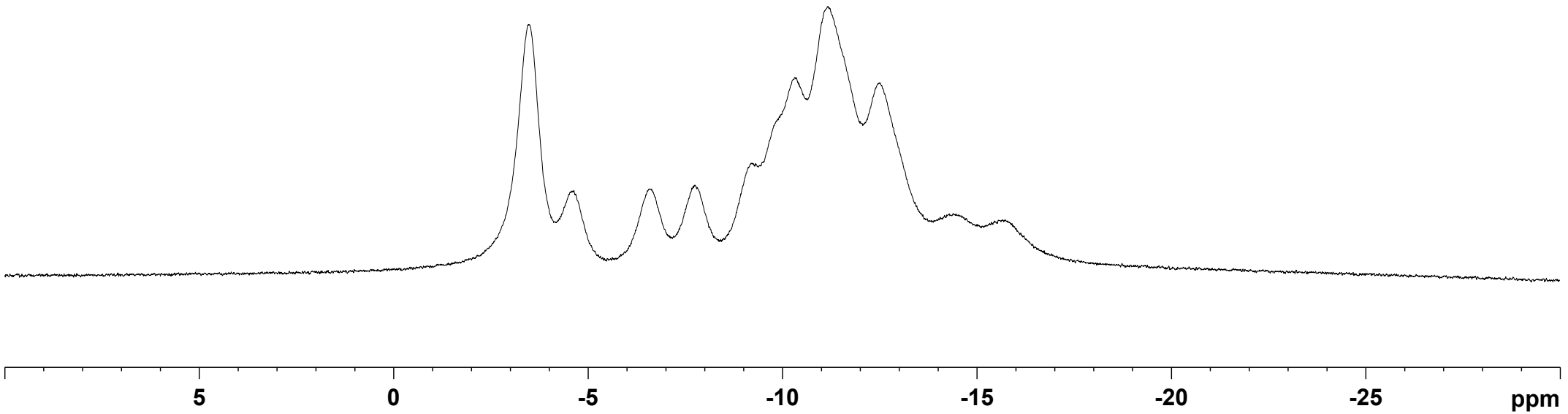
3q

^{11}B NMR

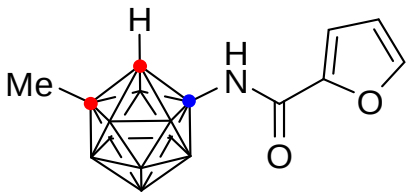
-3.46
-4.63
-6.58
-7.75
-9.22
-10.31
-11.16
-12.50
-14.40
-15.73



3q

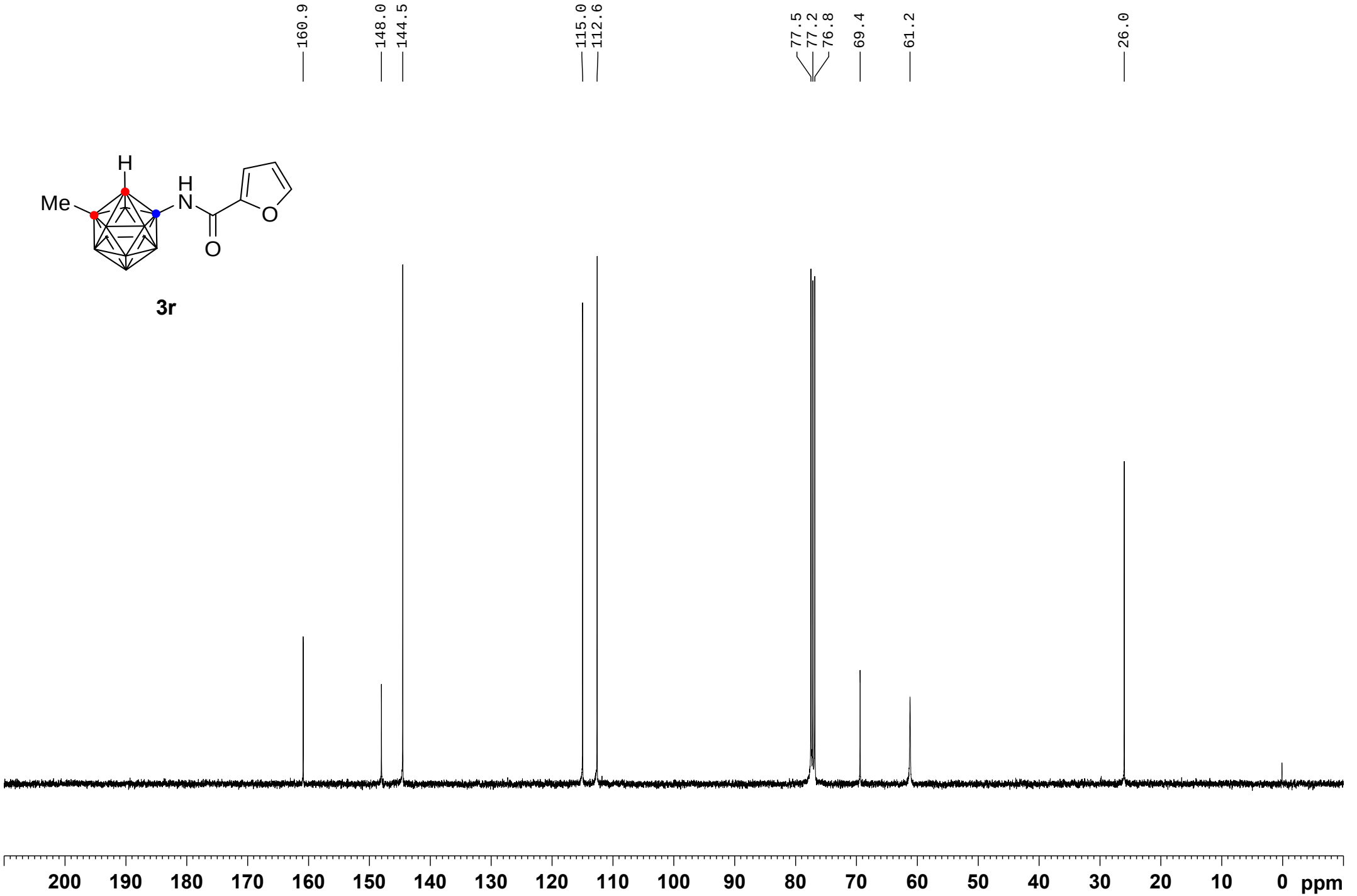


^{1}H NMR

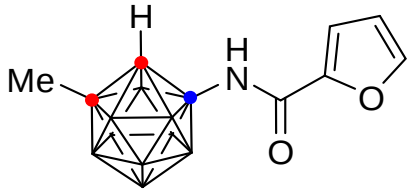


3r

$^{13}C\{^{1}H\}$ NMR


160.9
148.0
144.5
115.0
112.6
77.5
77.2
76.8
69.4
61.2
26.0
H
Me
H
N
O
O
3r
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
ppm

$^{11}B\{^{1}H\}$ NMR

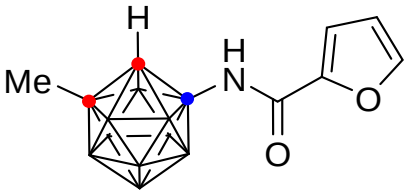

H
Me
H
N
O
O

3r

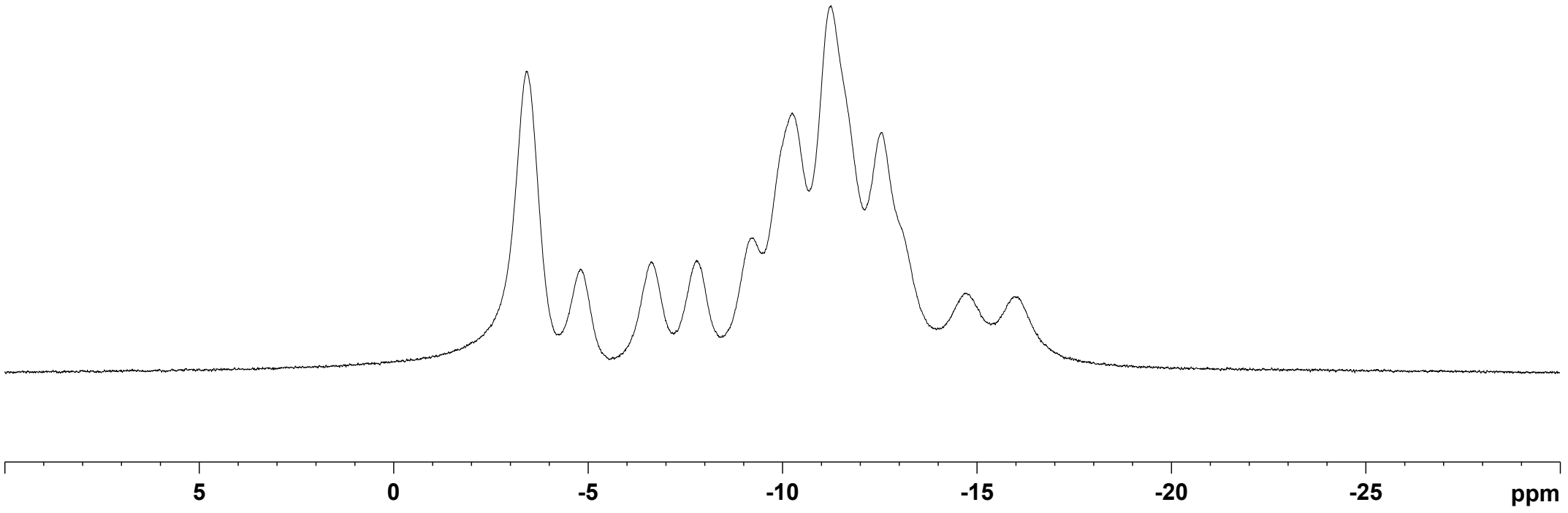
-3.40
-4.21
-7.20
-9.78
-10.55
-11.89
-15.37
2.092
1.000
6.099
1.058
5
0
-5
-10
-15
-20
-25
ppm

^{11}B NMR

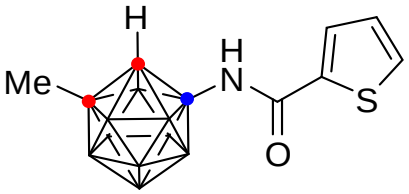
-3.41 -4.80 -6.63 -7.79 -9.24 -10.25 -11.25 -12.56 -14.70 -16.05



3r

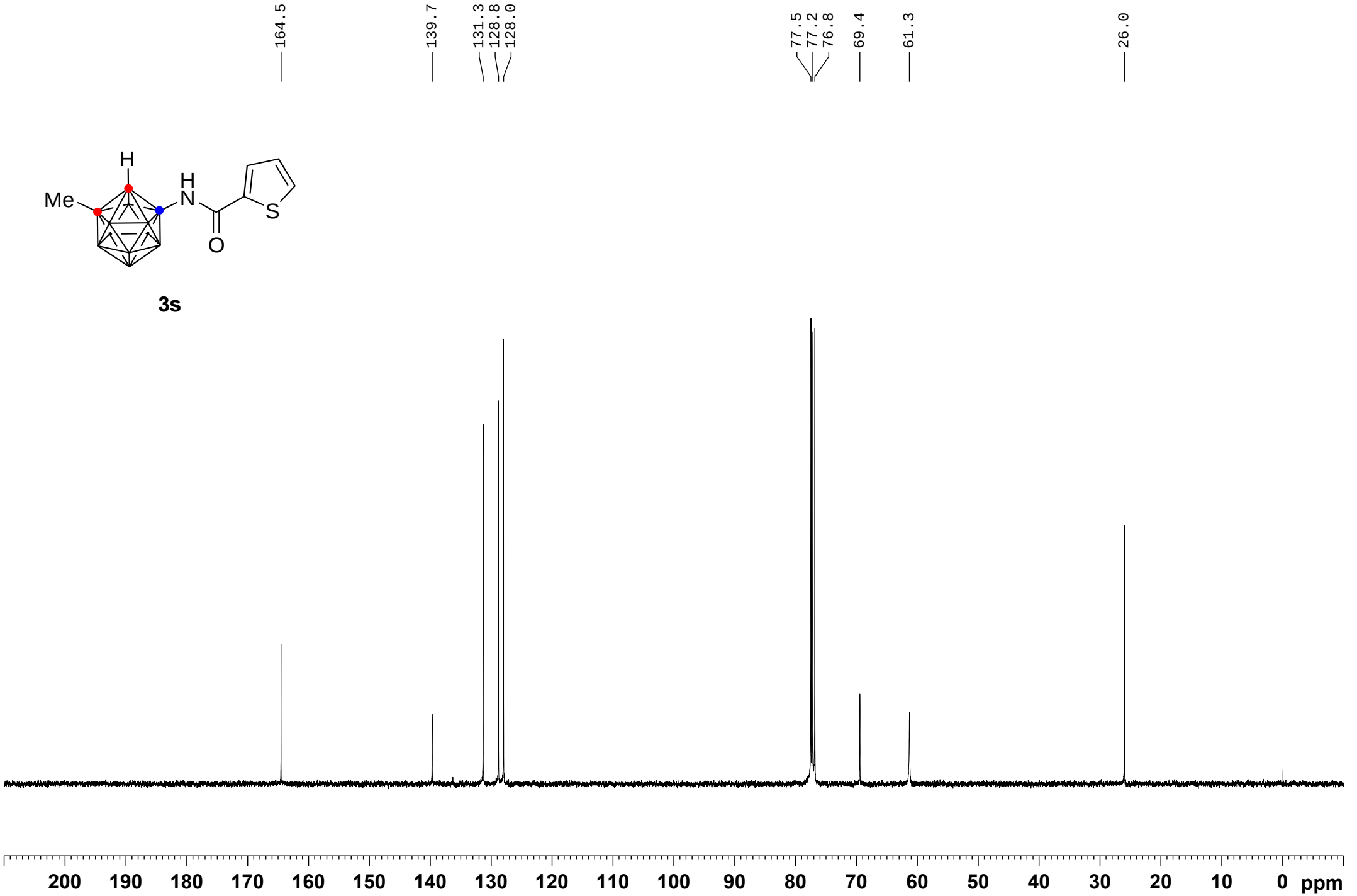


^{1}H NMR



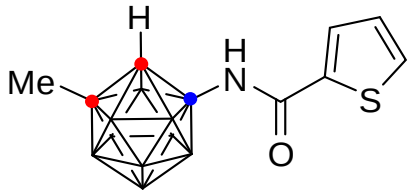
3s

$^{13}C\{^{1}H\}$ NMR


164.5
139.7
131.3
128.8
128.0
77.5
77.2
76.8
69.4
61.3
26.0
H
Me
H
N
S
O
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
ppm

3s

$^{11}B\{^{1}H\}$ NMR

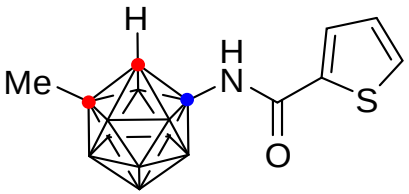

H
H
N
Me
S
O

3s

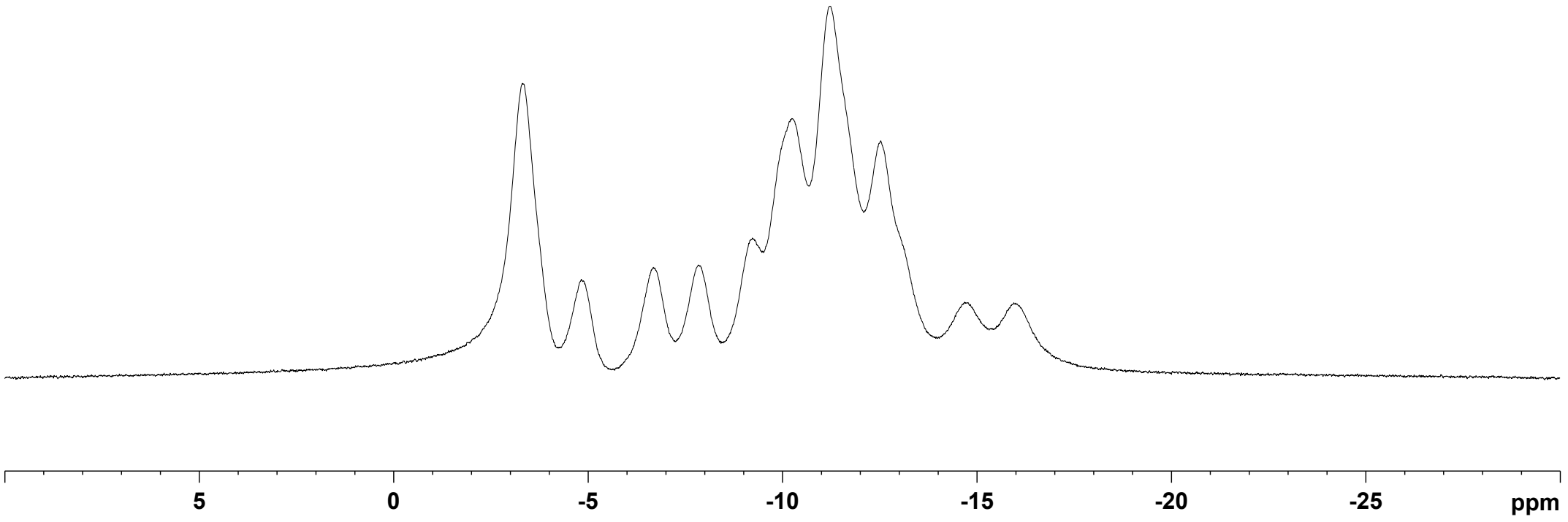
-3.34
-4.29
-7.27
-9.80
-10.57
-11.91
-15.34
2.074
1.000
6.027
1.021
5
0
-5
-10
-15
-20
-25
ppm

^{11}B NMR

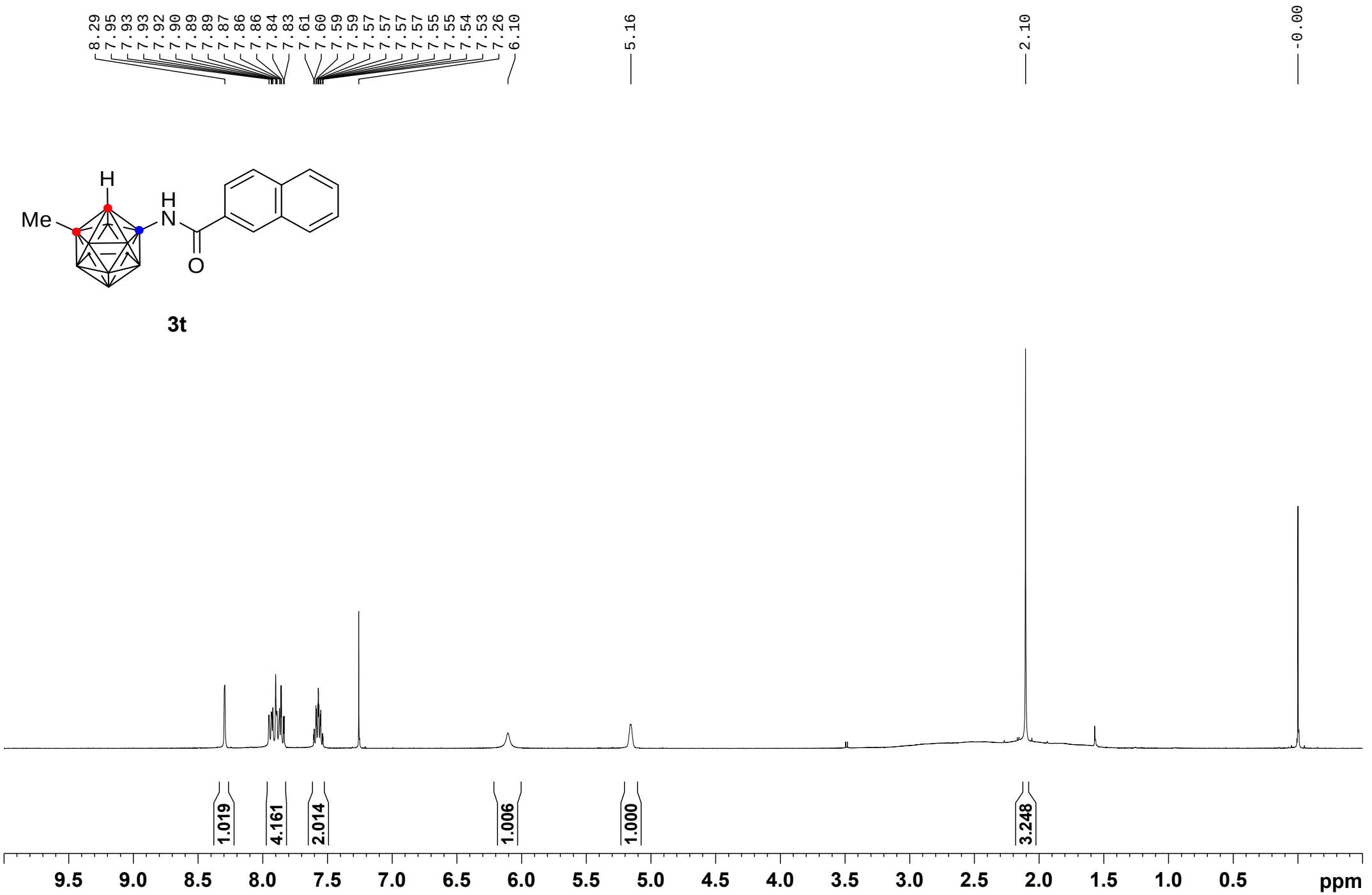
-3.31 -4.82 -6.68 -7.84 -9.23 -10.24 -11.22 -12.53 -14.68 -15.95



3s

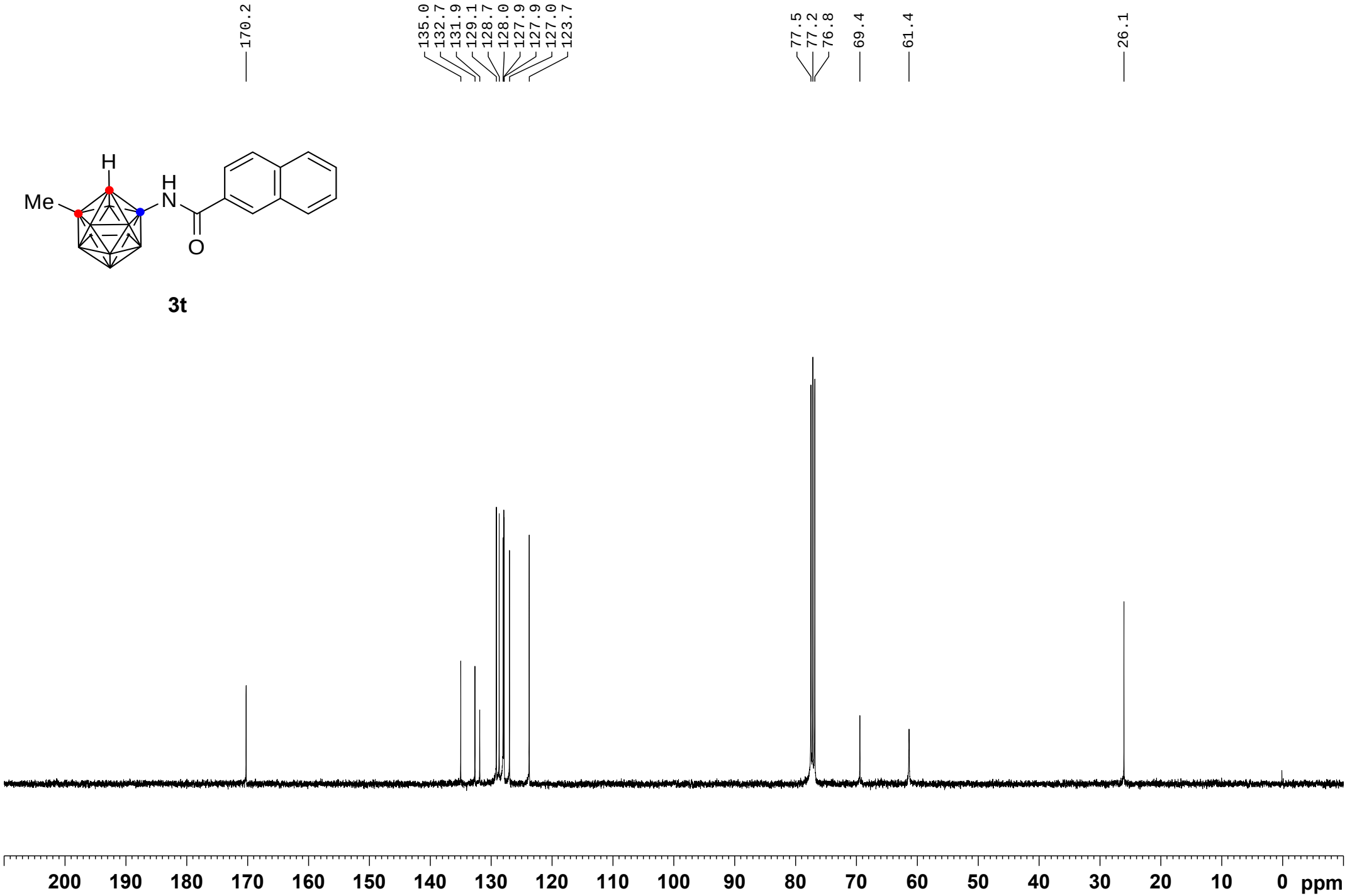


^{1}H NMR


8.29
7.95
7.93
7.93
7.92
7.90
7.89
7.89
7.87
7.86
7.86
7.84
7.83
7.61
7.60
7.59
7.59
7.57
7.57
7.57
7.55
7.55
7.54
7.53
7.26
6.10
5.16
2.10
-0.00
H
H
N
Me
O
1.019
4.161
2.014
1.006
1.000
3.248
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
ppm

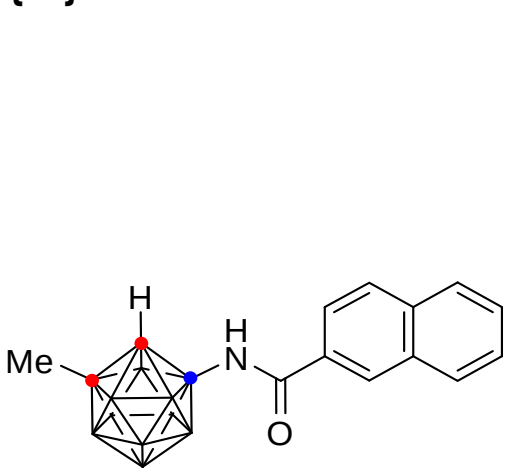
3t

$^{13}C\{^{1}H\}$ NMR


170.2
135.0
132.7
131.9
129.1
128.7
128.0
127.9
127.9
127.0
123.7
77.5
77.2
76.8
69.4
61.4
26.1
H
Me
H
N
O
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
ppm

3t

$^{11}B\{^{1}H\}$ NMR

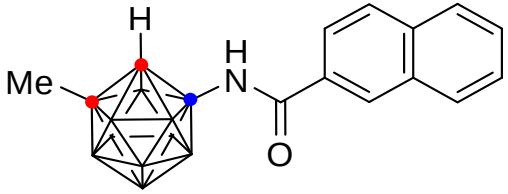

H
Me
H
N
O

3t

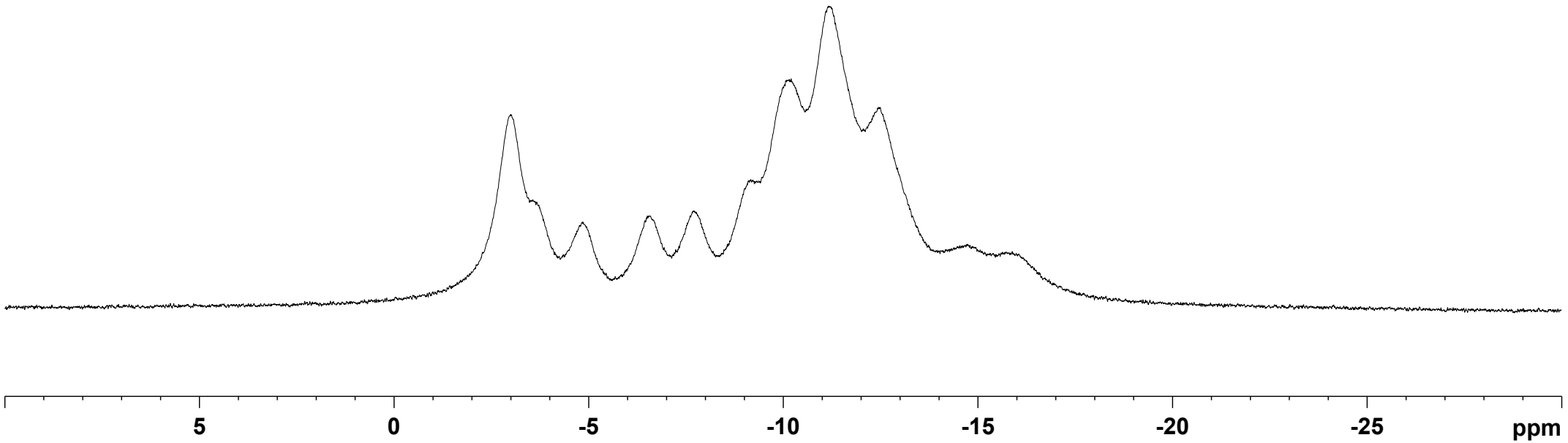
-2.97
-4.24
-7.13
-9.70
-10.54
-11.87
-15.40
2.093
1.000
6.034
1.034
5
0
-5
-10
-15
-20
-25
ppm

^{11}B NMR

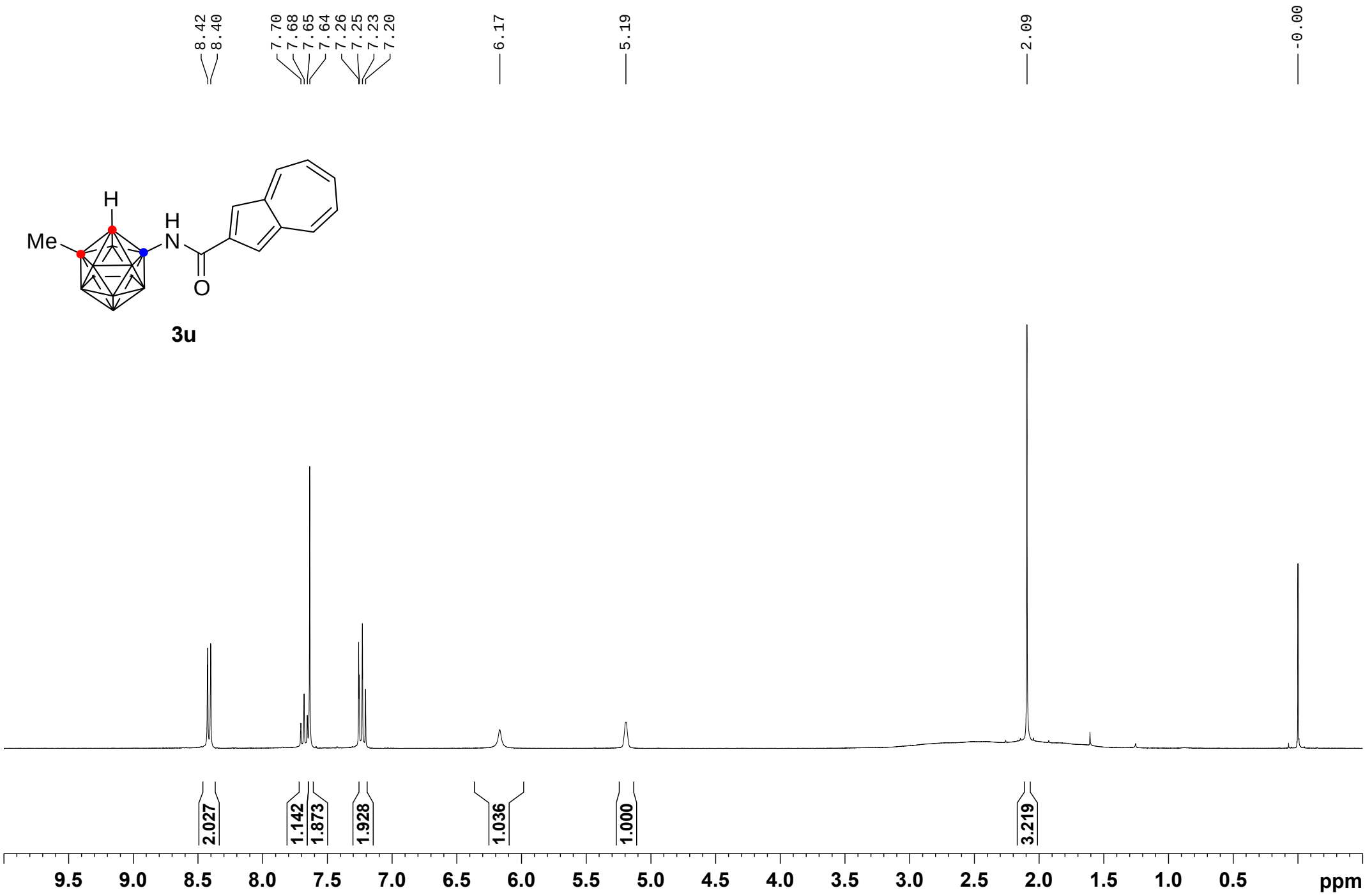
-3.00 -3.62 -4.85 -6.56 -7.69 -9.15 -10.20 -11.17 -12.46 -14.74 -15.88



3t

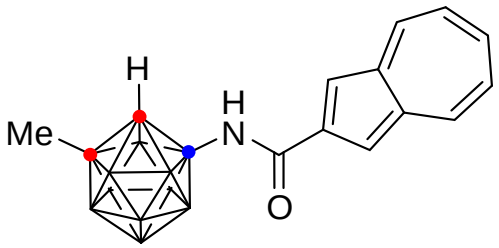


^{1}H NMR


8.42
8.40
7.70
7.68
7.65
7.64
7.26
7.25
7.23
7.20
6.17
5.19
2.09
-0.00
H
Me
H
N
O
2.027
1.142
1.873
1.928
1.036
1.000
3.219
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
ppm

3u

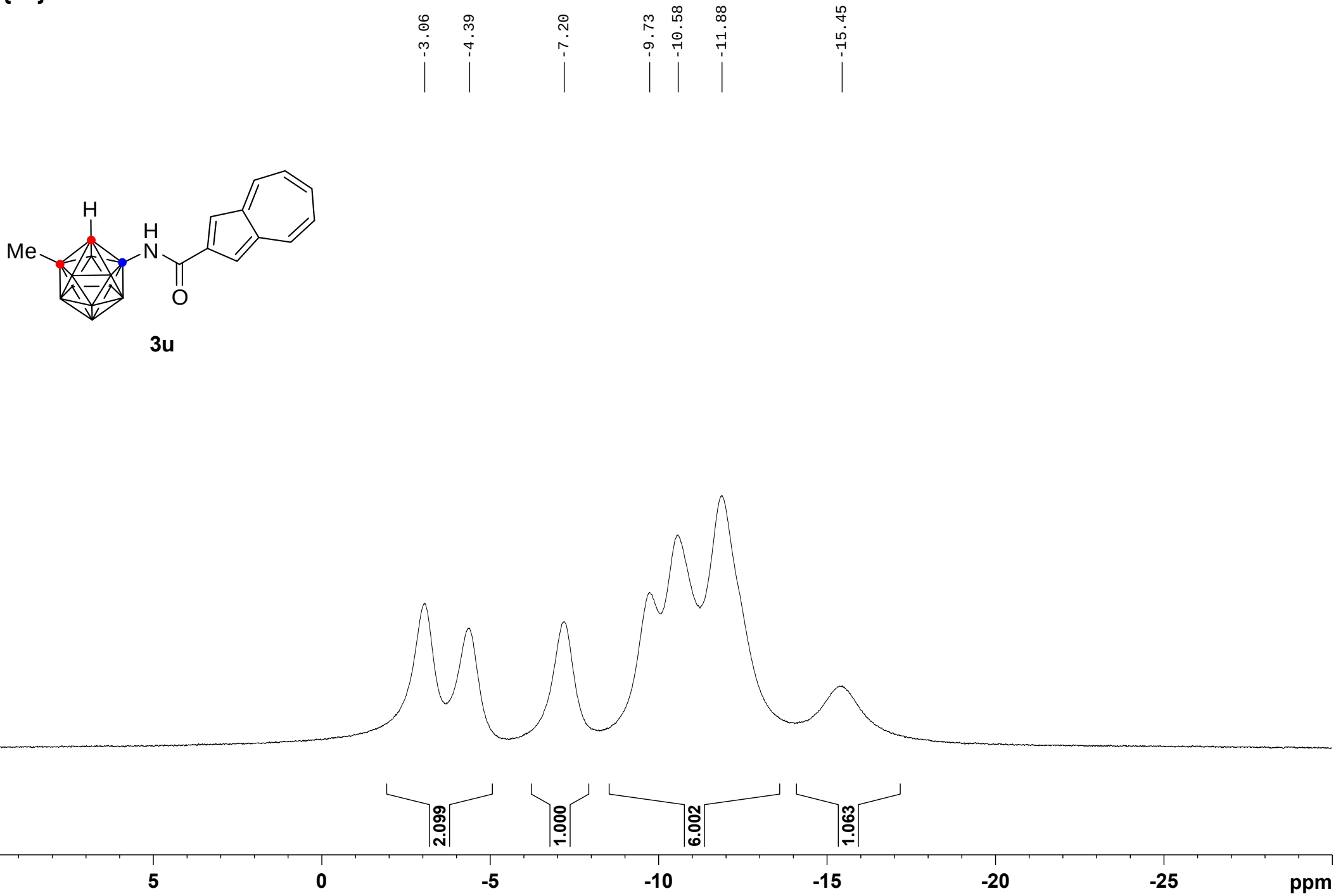
$^{13}C\{^{1}H\}$ NMR


H
Me
H
N
O

3u

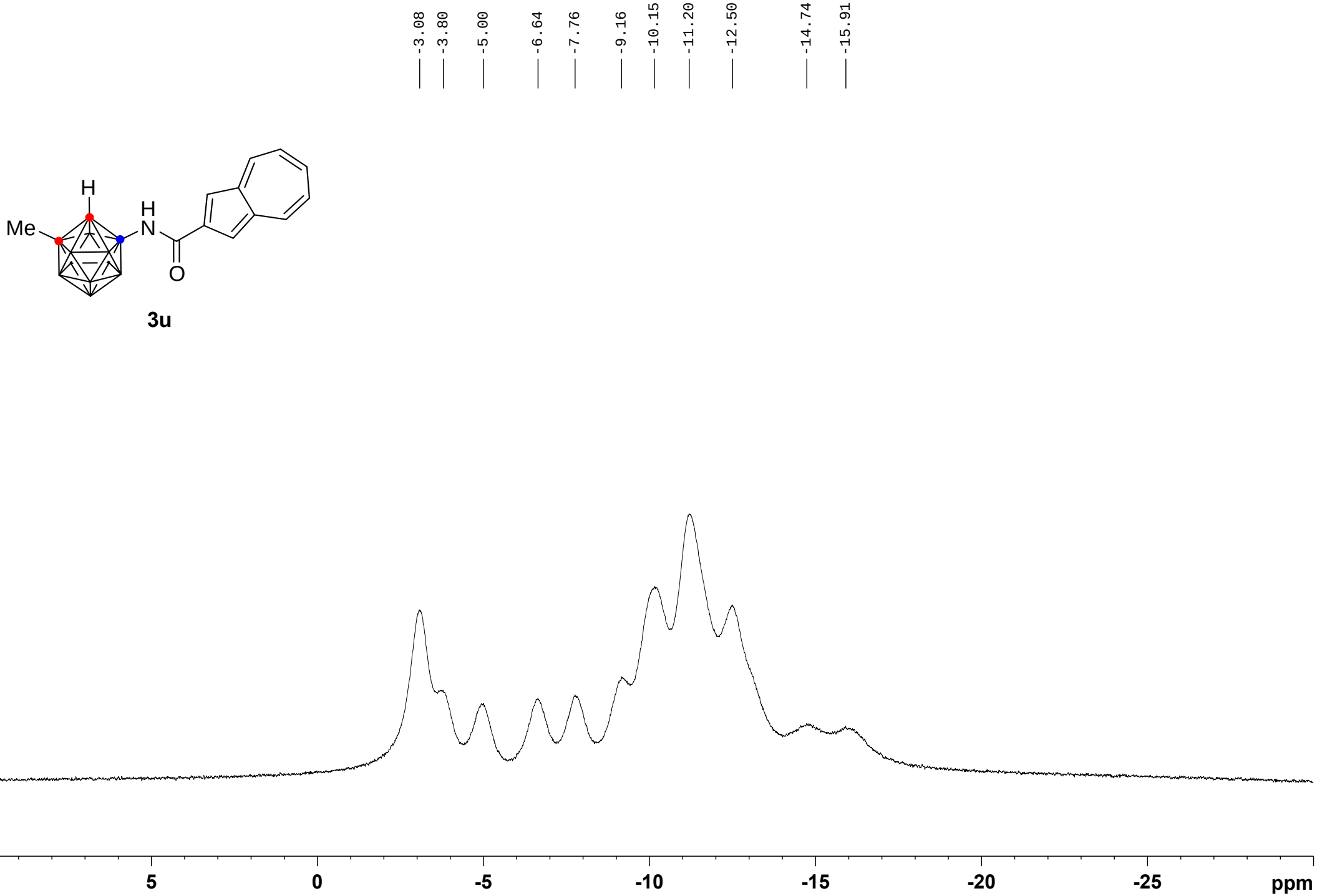
168.4
142.6
140.4
140.2
140.0
124.3
116.6
77.5
77.2
76.8
69.4
61.4
26.1
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
ppm

$^{11}B\{^{1}H\}$ NMR


-3.06
-4.39
-7.20
-9.73
-10.58
-11.88
-15.45
H
Me
H
N
O
2.099
1.000
6.002
1.063
5
0
-5
-10
-15
-20
-25
ppm

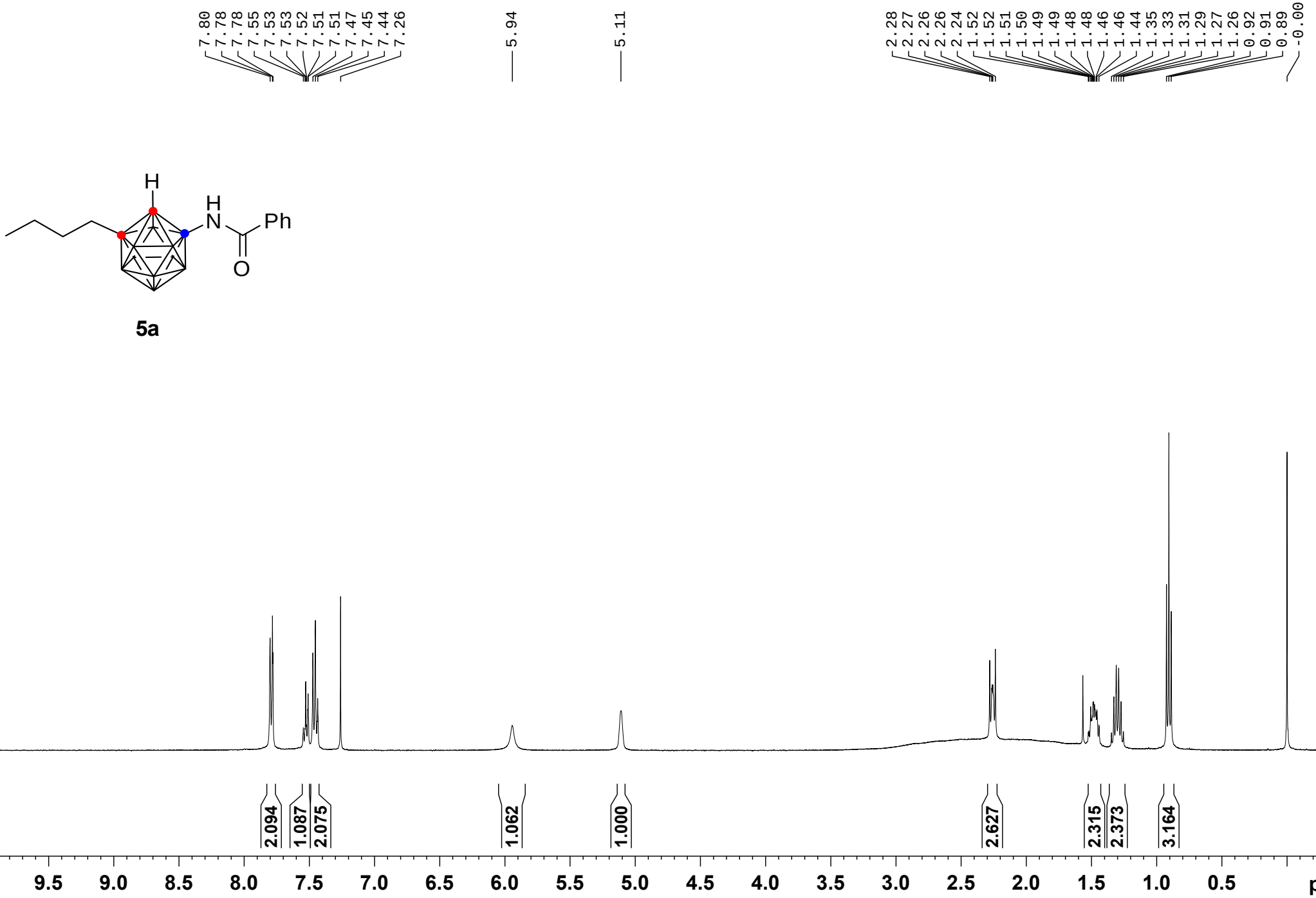
3u

^{11}B NMR


-3.08
-3.80
-5.00
-6.64
-7.76
-9.16
-10.15
-11.20
-12.50
-14.74
-15.91
H
Me
H
N
O
5
0
-5
-10
-15
-20
-25
ppm

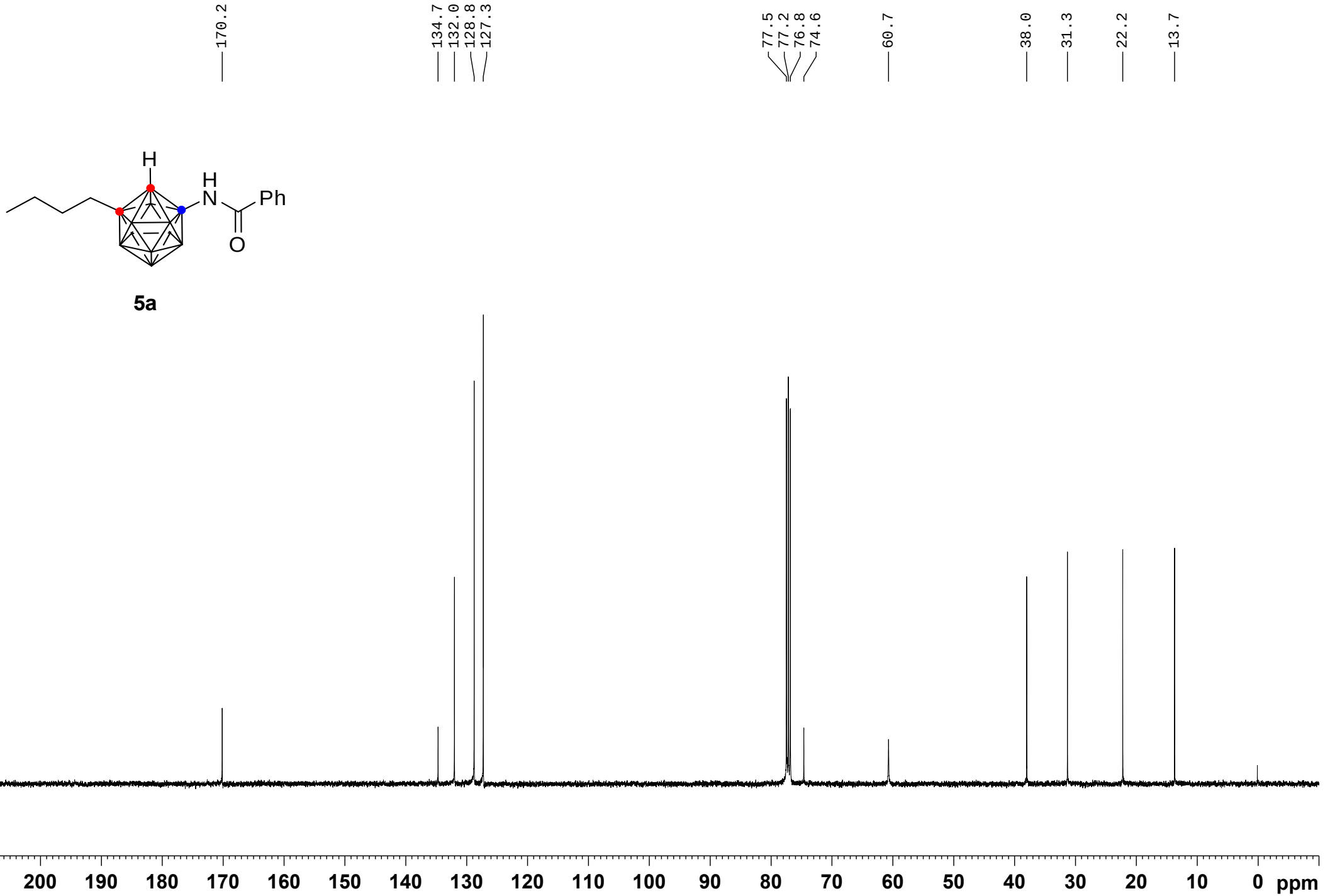
3u

^{1}H NMR


7.80
7.78
7.78
7.55
7.53
7.53
7.52
7.51
7.51
7.47
7.45
7.44
7.26
5.94
5.11
2.28
2.27
2.26
2.26
2.24
1.52
1.52
1.51
1.50
1.49
1.49
1.48
1.48
1.46
1.46
1.44
1.35
1.33
1.31
1.29
1.27
1.26
0.92
0.91
0.89
-0.00
H
H
N
Ph
O
2.094
1.087
2.075
1.062
1.000
2.627
2.315
2.373
3.164
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
ppm

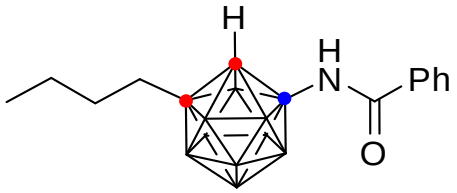
5a

$^{13}C\{^{1}H\}$ NMR


170.2
134.7
132.0
128.8
127.3
77.5
77.2
76.8
74.6
60.7
38.0
31.3
22.2
13.7
H
H
N
Ph
O
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
ppm

5a

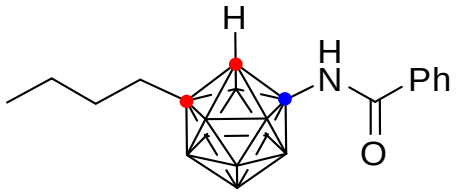
$^{11}B\{^{1}H\}$ NMR


H
H
N
Ph
O

5a

-3.48
-4.99
-6.38
-9.97
-10.71
-12.48
-16.06
3.086
6.058
1.000
5
0
-5
-10
-15
-20
-25
ppm

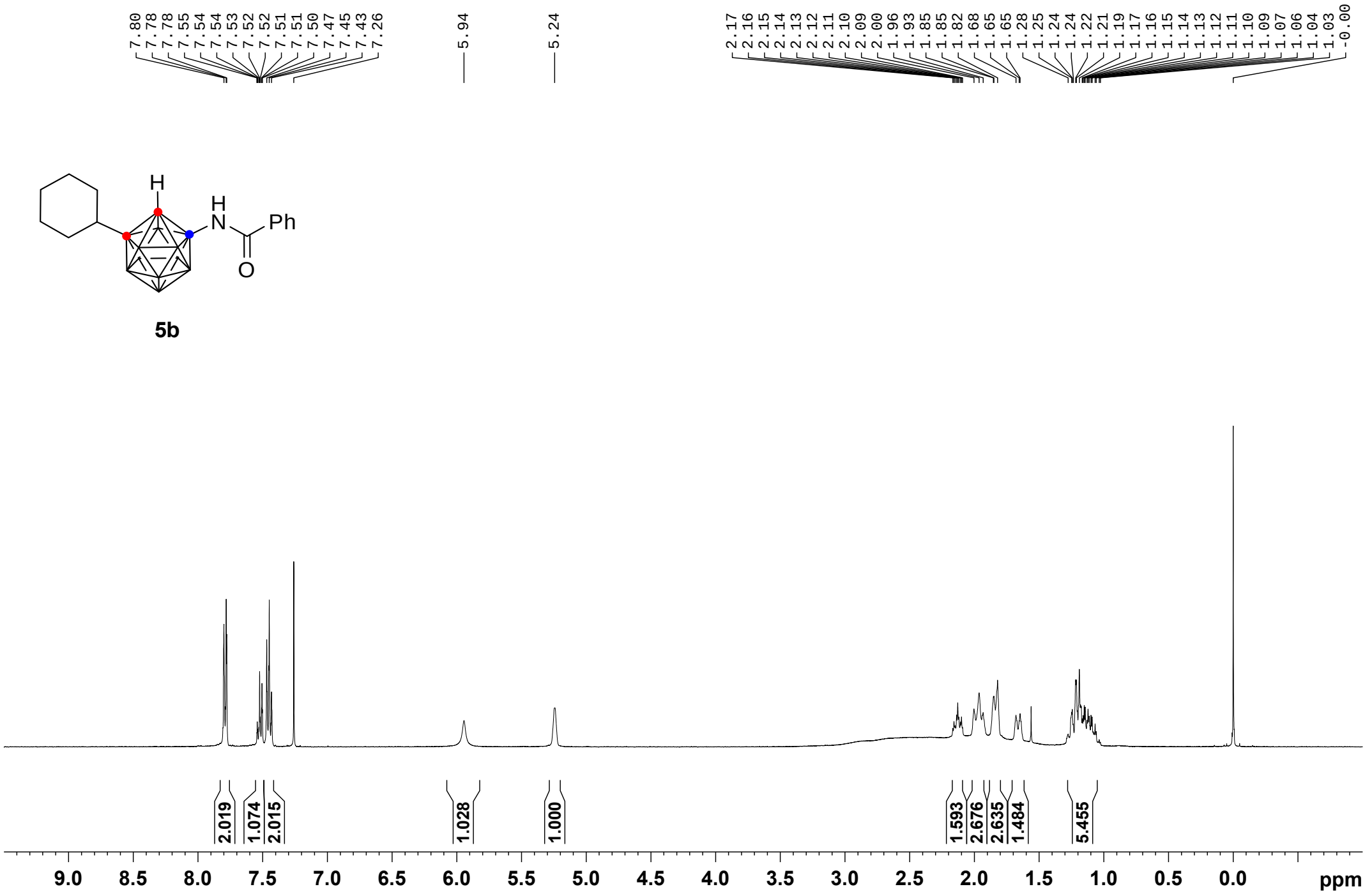
^{11}B NMR


H
H
N
Ph
O

5a

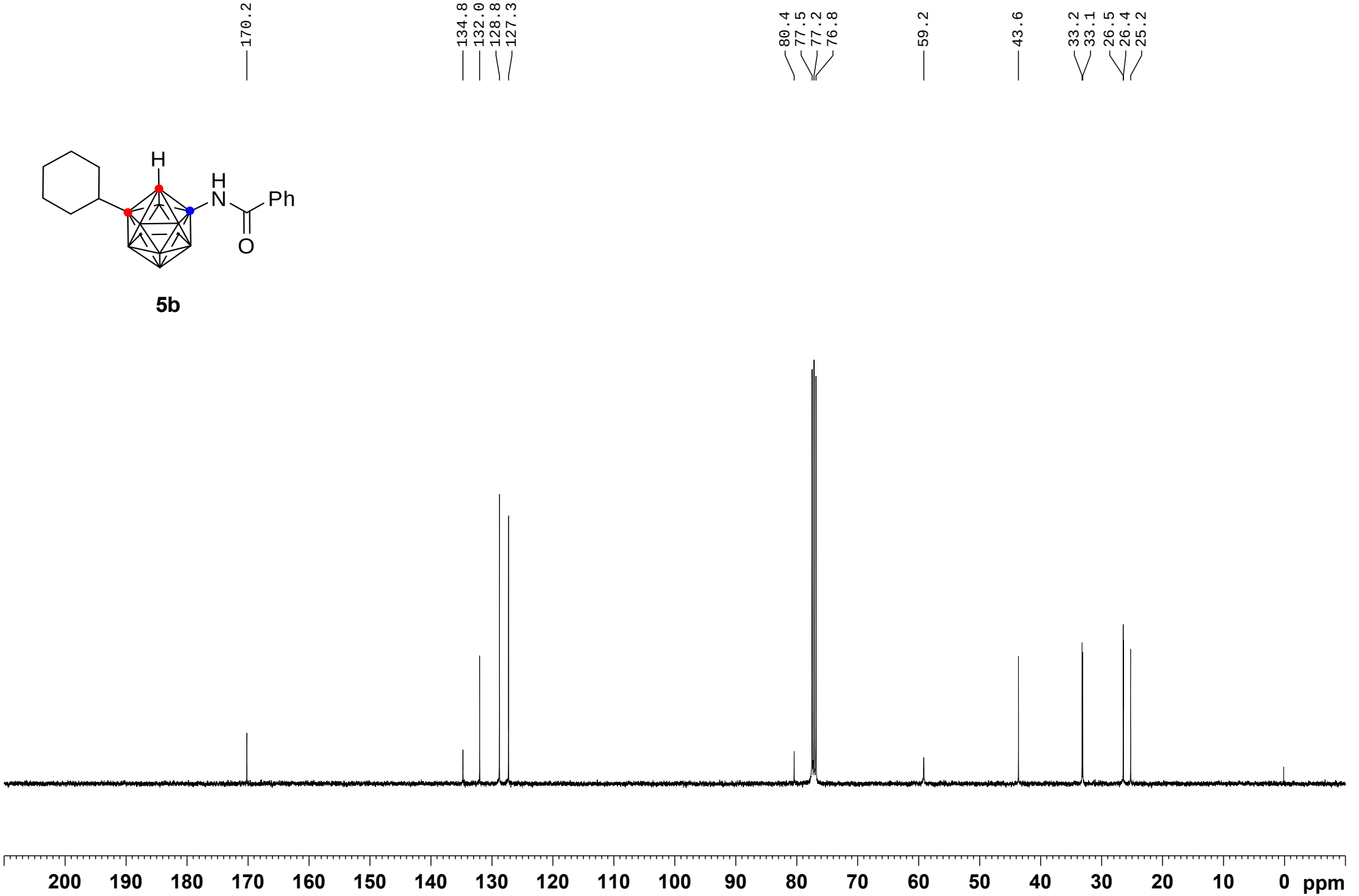
-3.46
-4.36
-5.65
-6.98
-9.43
-10.46
-11.35
-12.47
-15.60
-16.73
5
0
-5
-10
-15
-20
-25
ppm

^{1}H NMR


7.80
7.78
7.78
7.55
7.54
7.54
7.53
7.52
7.52
7.51
7.51
7.50
7.47
7.45
7.43
7.26
5.94
5.24
2.17
2.16
2.15
2.14
2.13
2.12
2.11
2.10
2.09
2.00
1.96
1.93
1.85
1.85
1.82
1.68
1.65
1.65
1.28
1.25
1.24
1.24
1.22
1.21
1.19
1.17
1.16
1.15
1.14
1.13
1.12
1.11
1.10
1.09
1.07
1.06
1.04
1.03
-0.00
H
H
N
Ph
O
2.019
1.074
2.015
1.028
1.000
1.593
2.676
2.635
1.484
5.455
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

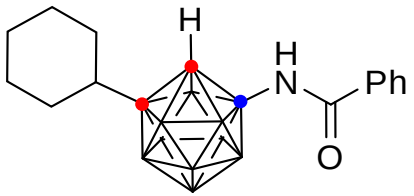
5b

$^{13}C\{^{1}H\}$ NMR


170.2
134.8
132.0
128.8
127.3
80.4
77.5
77.2
76.8
59.2
43.6
33.2
33.1
26.5
26.4
25.2
H
H
N
Ph
O
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
ppm

5b

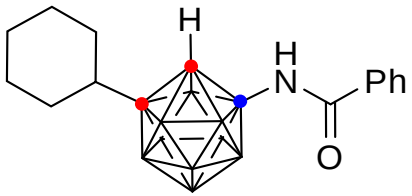
$^{11}B\{^{1}H\}$ NMR


H
H
N
Ph
O

5b

-3.90
-5.63
-9.90
-10.77
-12.85
-14.31
-16.31
3.123
6.009
1.000
5
0
-5
-10
-15
-20
-25
ppm

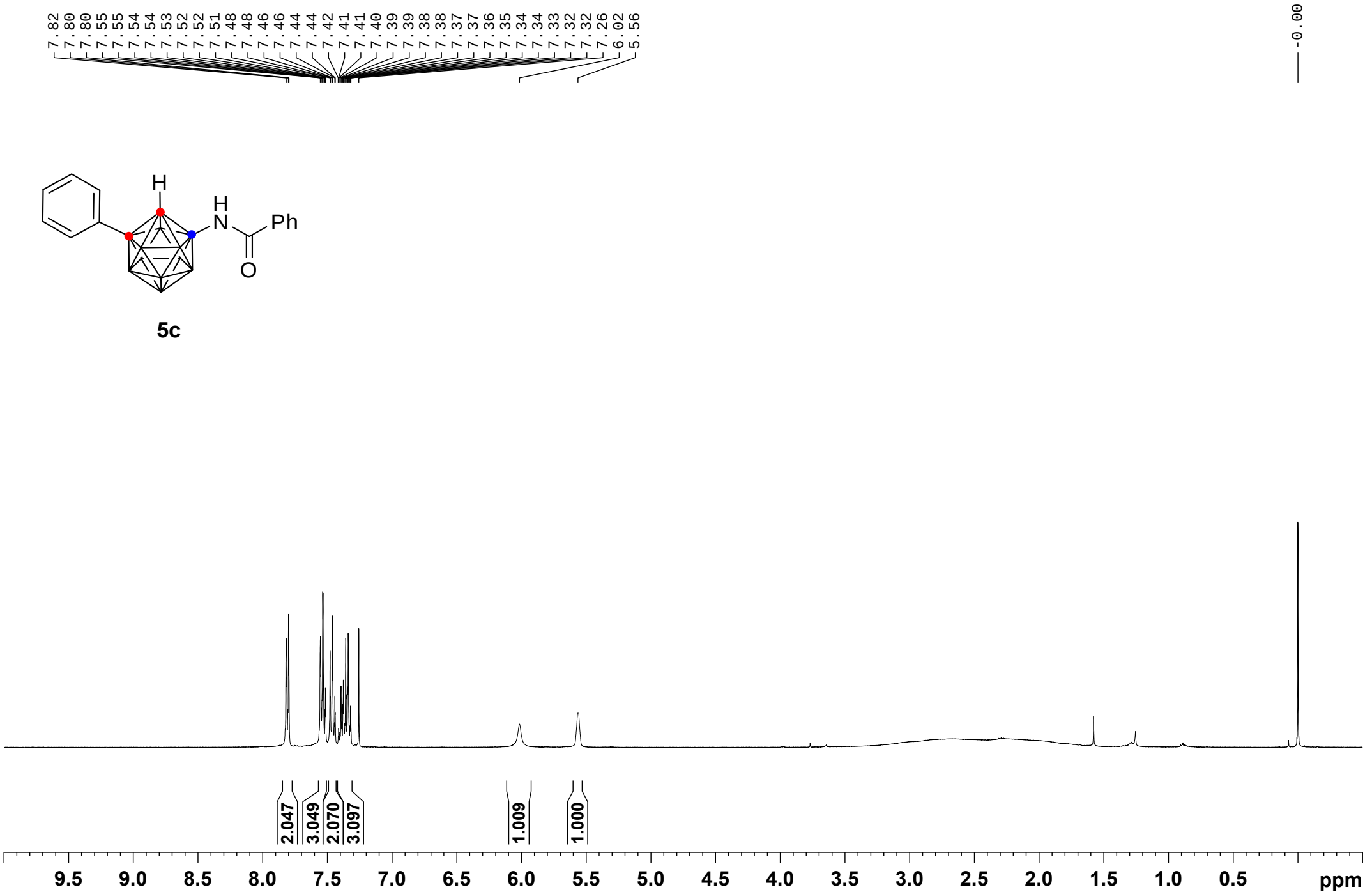
^{11}B NMR


H
H
N
Ph
O

5b

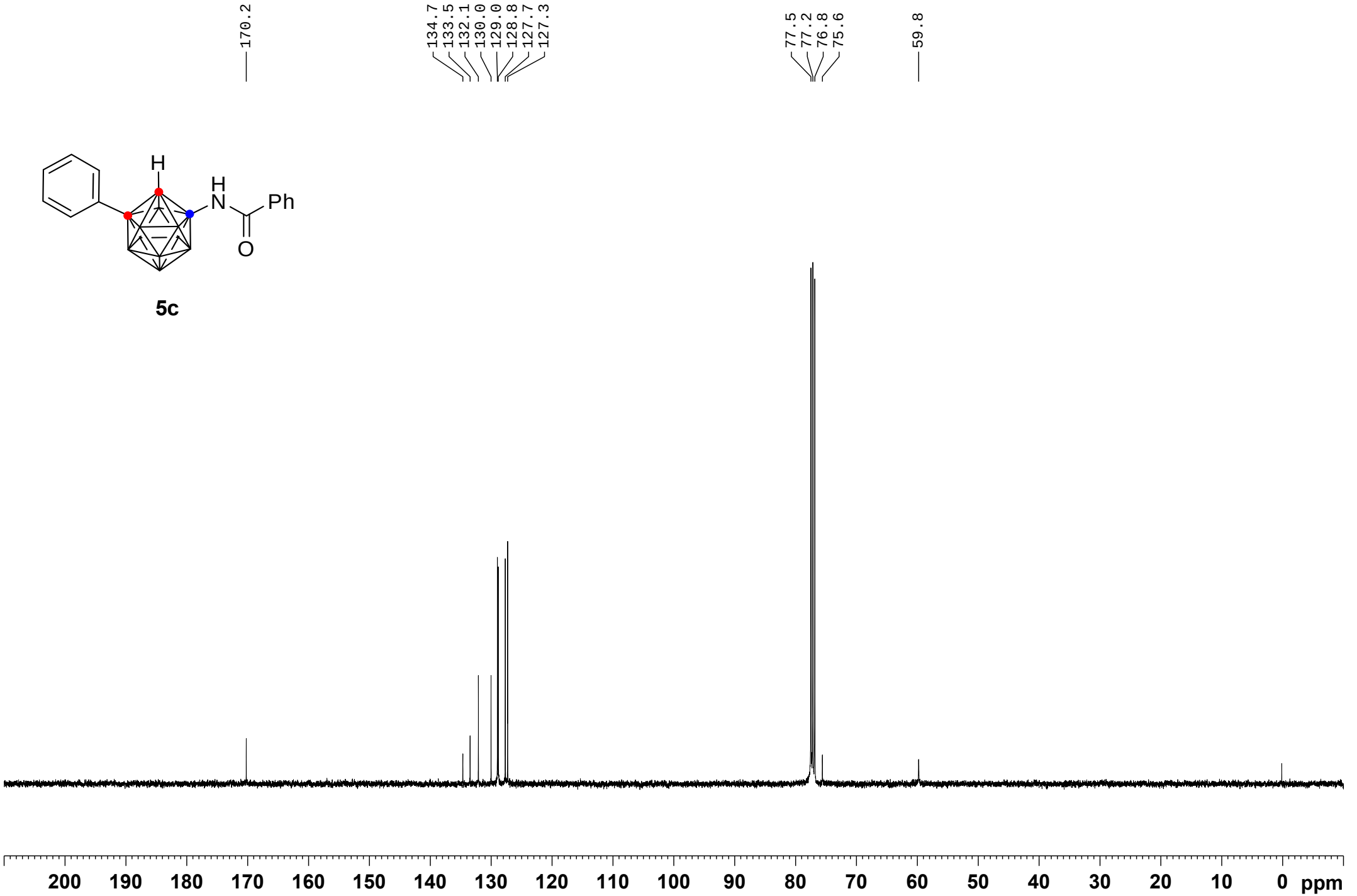
-4.01
-5.17
-6.30
-9.36
-10.38
-11.49
-12.26
-13.50
-15.08
-16.92
5
0
-5
-10
-15
-20
-25
ppm

^{1}H NMR


7.82
7.80
7.80
7.55
7.55
7.54
7.54
7.53
7.52
7.52
7.51
7.48
7.48
7.46
7.46
7.44
7.44
7.42
7.41
7.41
7.40
7.39
7.39
7.38
7.38
7.37
7.37
7.36
7.35
7.34
7.34
7.33
7.32
7.32
7.26
6.02
5.56
-0.00
H
H
N
Ph
O
2.047
3.049
2.070
3.097
1.009
1.000
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
ppm

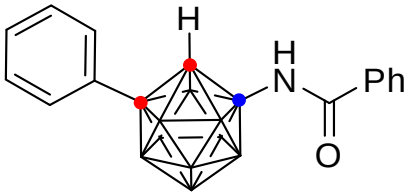
5c

$^{13}C\{^{1}H\}$ NMR


170.2
134.7
133.5
132.1
130.0
129.0
128.8
127.7
127.3
77.5
77.2
76.8
75.6
59.8
H
H
N
Ph
O
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
ppm

5c

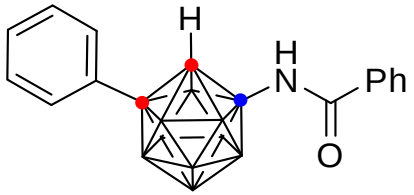
$^{11}B\{^{1}H\}$ NMR


H
H
N
Ph
O

5c

-3.19
-4.87
-9.43
-10.41
-12.05
-15.77
3.008
6.009
1.000
5
0
-5
-10
-15
-20
-25
ppm

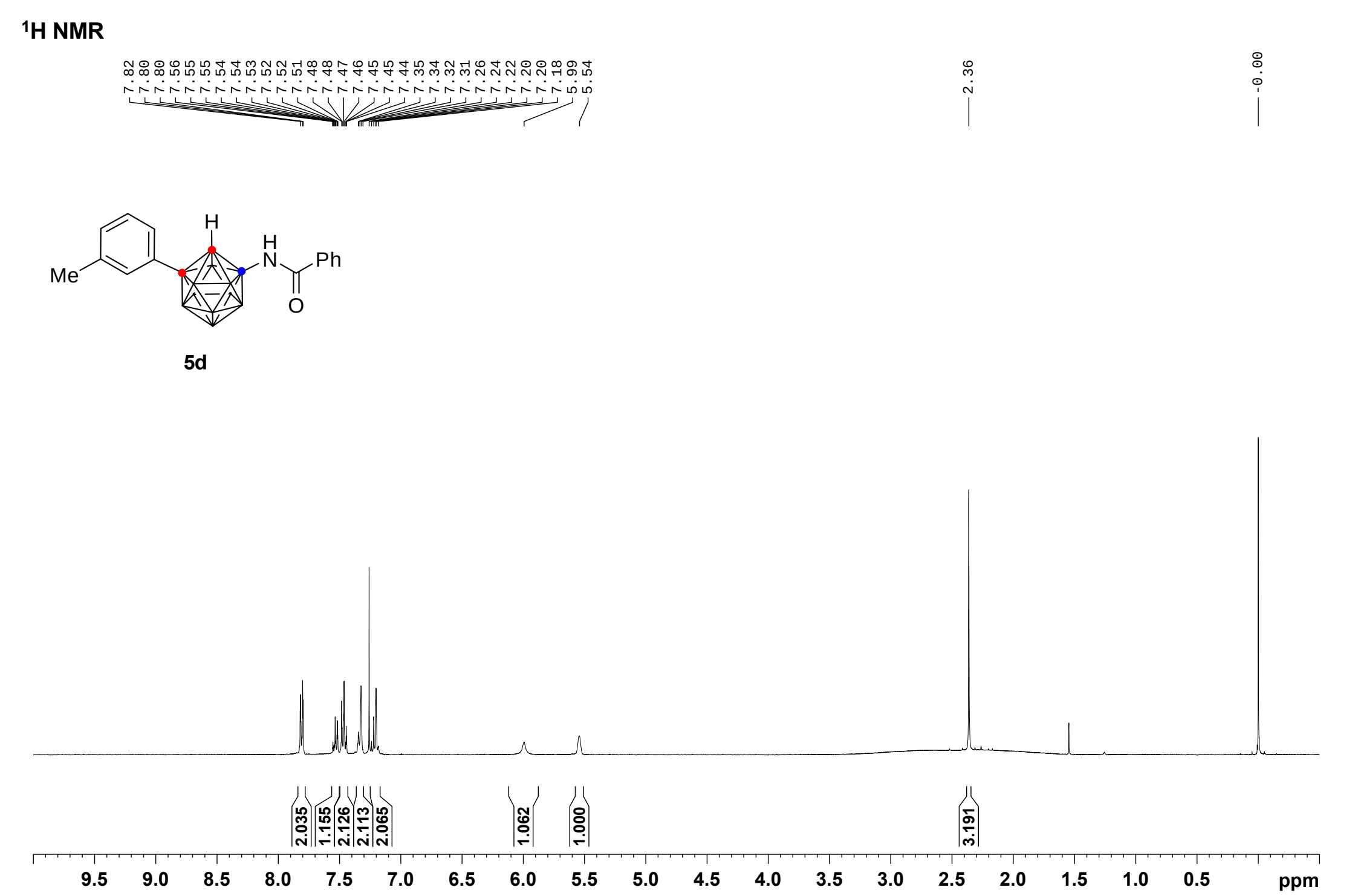
^{11}B NMR


H
H
N
Ph
O

5c

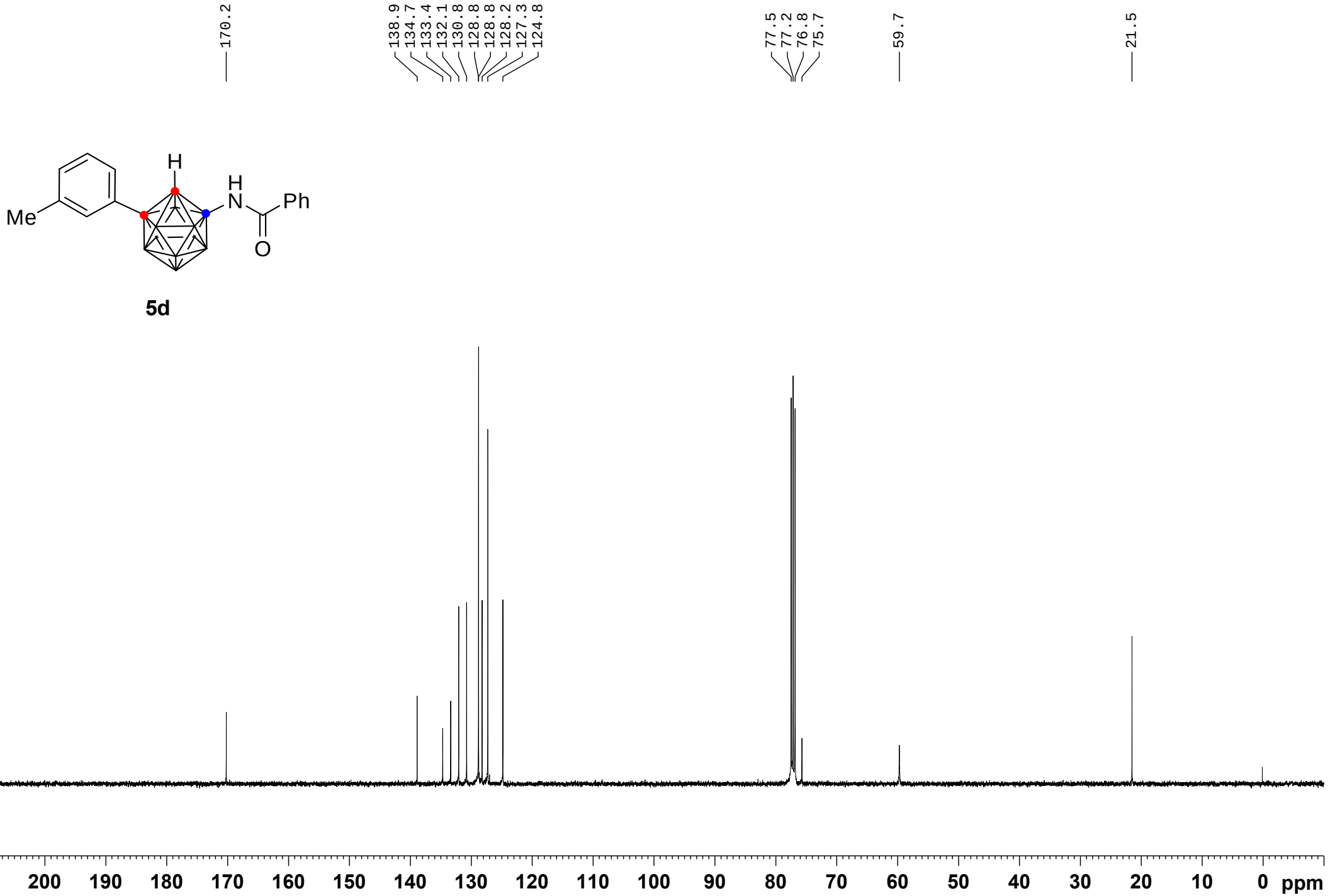
-3.24
-4.30
-5.46
-8.86
-9.91
-11.20
-12.62
-15.12
-16.19
5
0
-5
-10
-15
-20
-25
ppm

^{1}H NMR


7.82
7.80
7.80
7.56
7.55
7.54
7.54
7.53
7.52
7.52
7.51
7.48
7.48
7.47
7.46
7.45
7.45
7.44
7.35
7.34
7.32
7.31
7.26
7.24
7.22
7.20
7.20
7.18
5.99
5.54
2.36
-0.00
H
H
N
Ph
Me
O
2.035
1.155
2.126
2.113
2.065
1.062
1.000
3.191
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
ppm

5d

$^{13}C\{^{1}H\}$ NMR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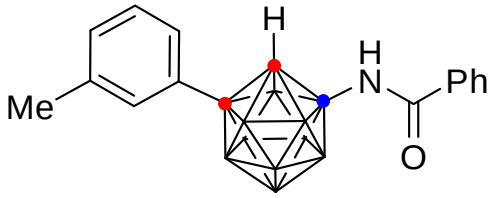
138.9
134.7
133.4
132.1
130.8
128.8
128.8
128.2
127.3
124.8
77.5
77.2
76.8
75.7
59.7
21.5
H
H
N
Ph
O
Me
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
ppm

5d

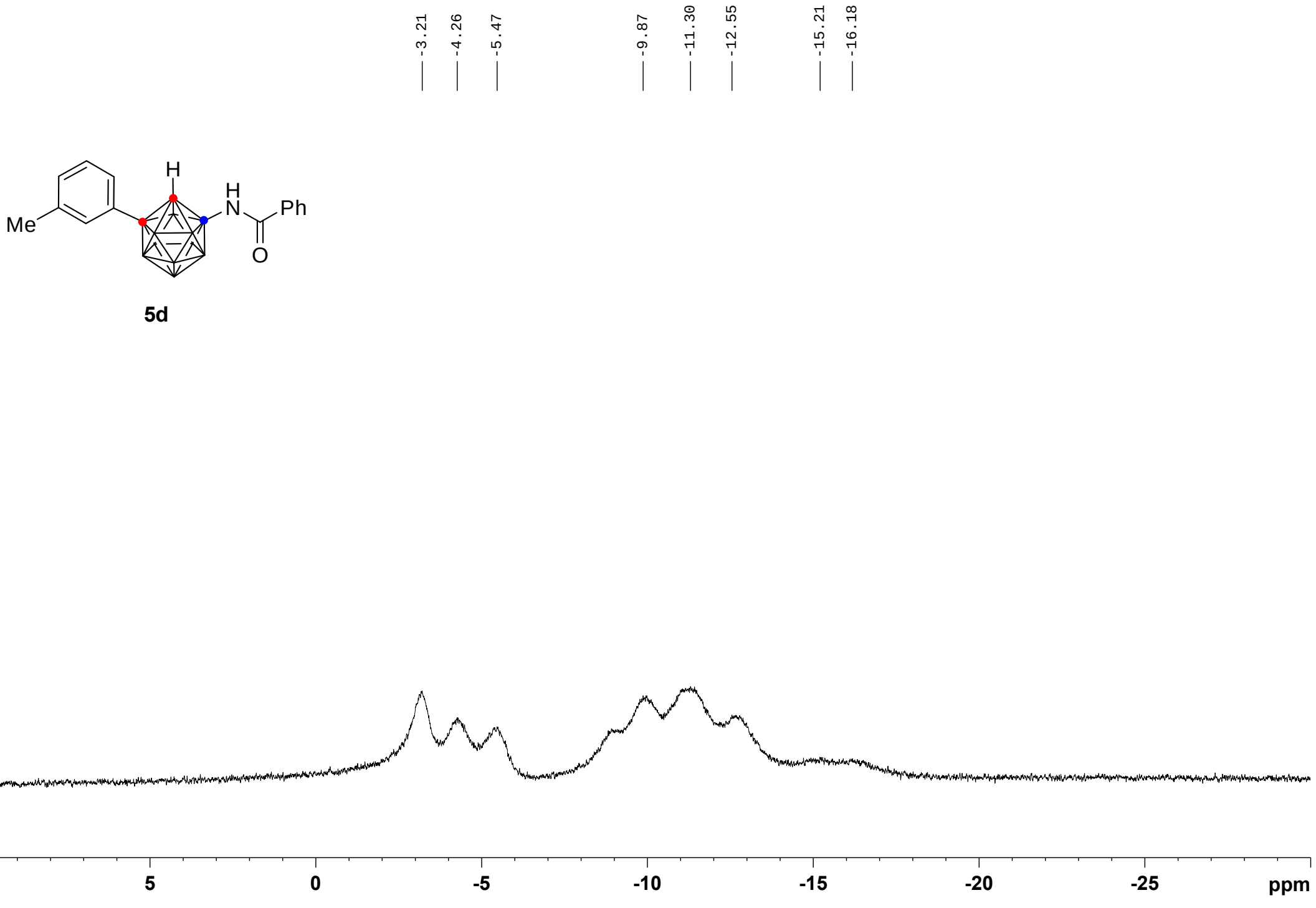
$^{11}B\{^{1}H\}$ NMR


H
H
N
Ph
O
Me

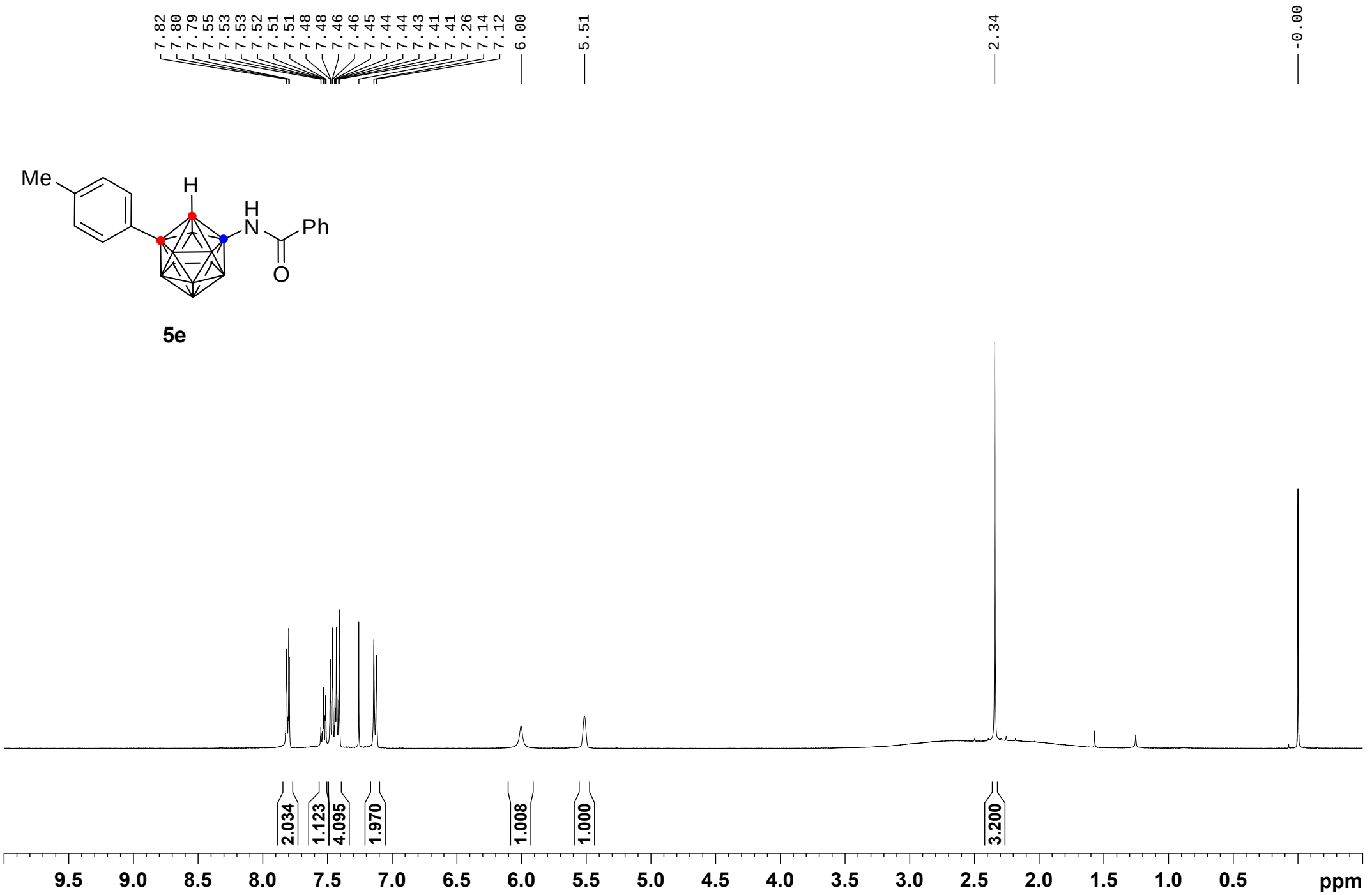
5d

-3.20
-4.89
-9.59
-10.40
-12.08
-15.70
3.028
6.044
1.000
5
0
-5
-10
-15
-20
-25
ppm

^{11}B NMR

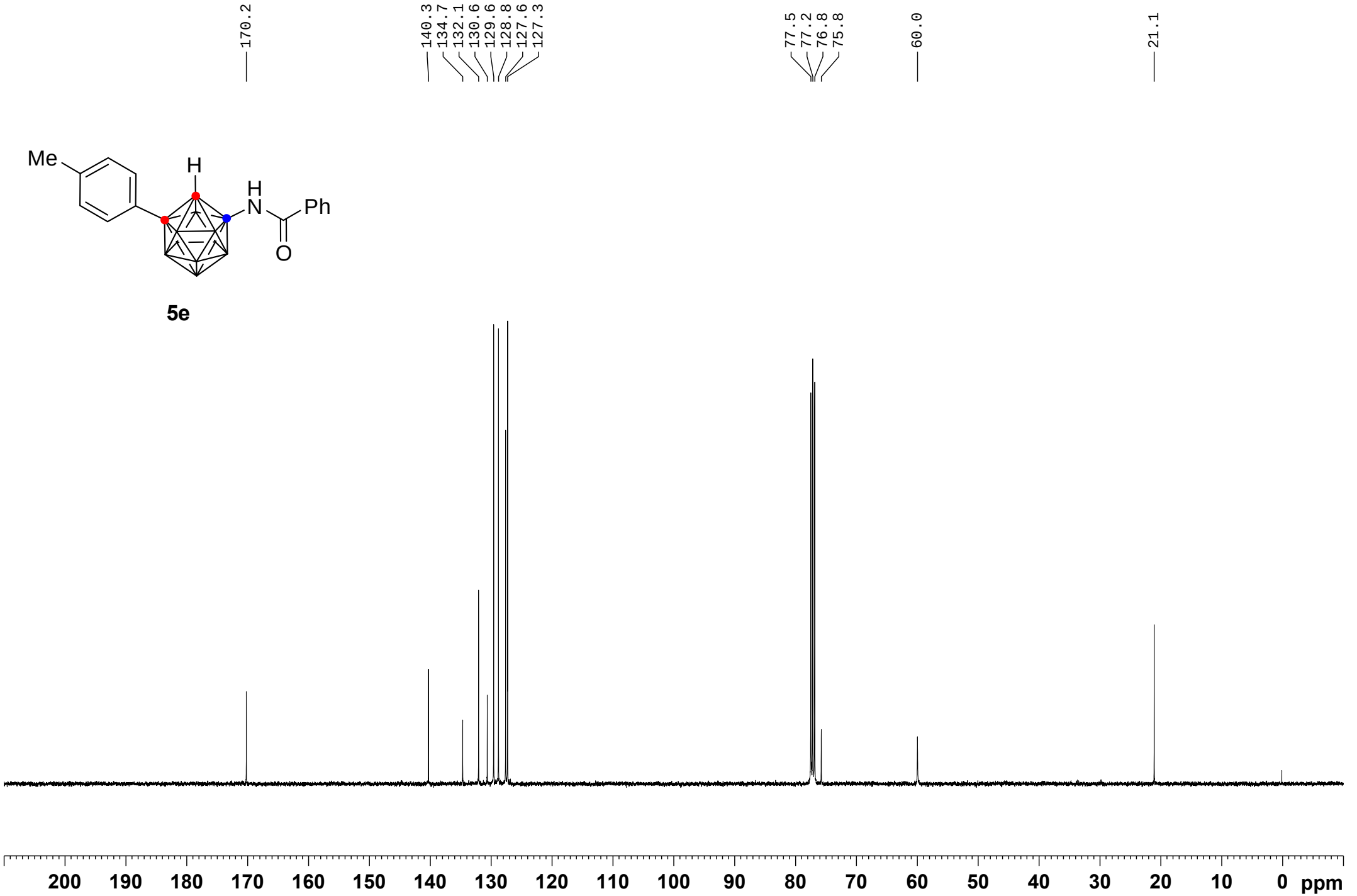

-3.21
-4.26
-5.47
-9.87
-11.30
-12.55
-15.21
-16.18
H
H
N
Ph
Me
O
5d
5
0
-5
-10
-15
-20
-25
ppm

^{1}H NMR


7.82
7.80
7.79
7.55
7.53
7.53
7.52
7.51
7.51
7.48
7.48
7.46
7.46
7.45
7.44
7.44
7.43
7.41
7.41
7.26
7.14
7.12
6.00
5.51
2.34
-0.00
Me
H
H
N
Ph
O
2.034
1.123
4.095
1.970
1.008
1.000
3.200
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
ppm

5e

$^{13}C\{^{1}H\}$ NMR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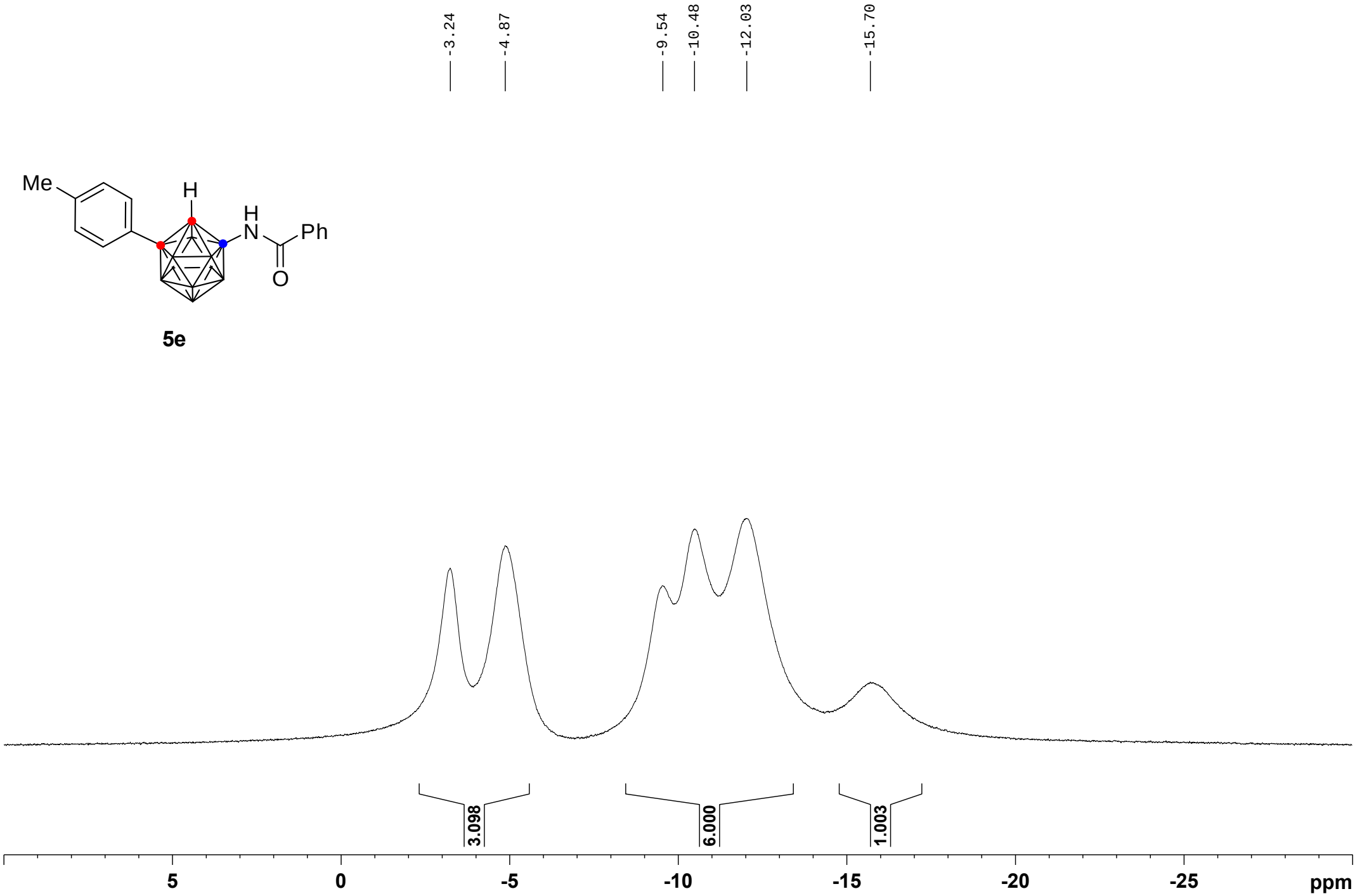
140.3
134.7
132.1
130.6
129.6
128.8
127.6
127.3
77.5
77.2
76.8
75.8
60.0
21.1
Me
H
H
N
Ph
O
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
ppm

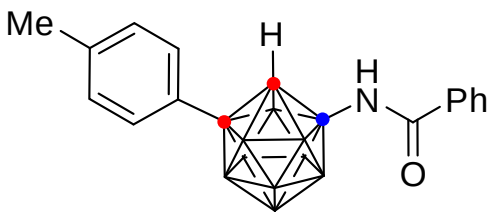
5e

$^{11}B\{^{1}H\}$ NMR


-3.24
-4.87
-9.54
-10.48
-12.03
-15.70
Me
H
H
N
Ph
O
3.098
6.000
1.003
5
0
-5
-10
-15
-20
-25
ppm

5e

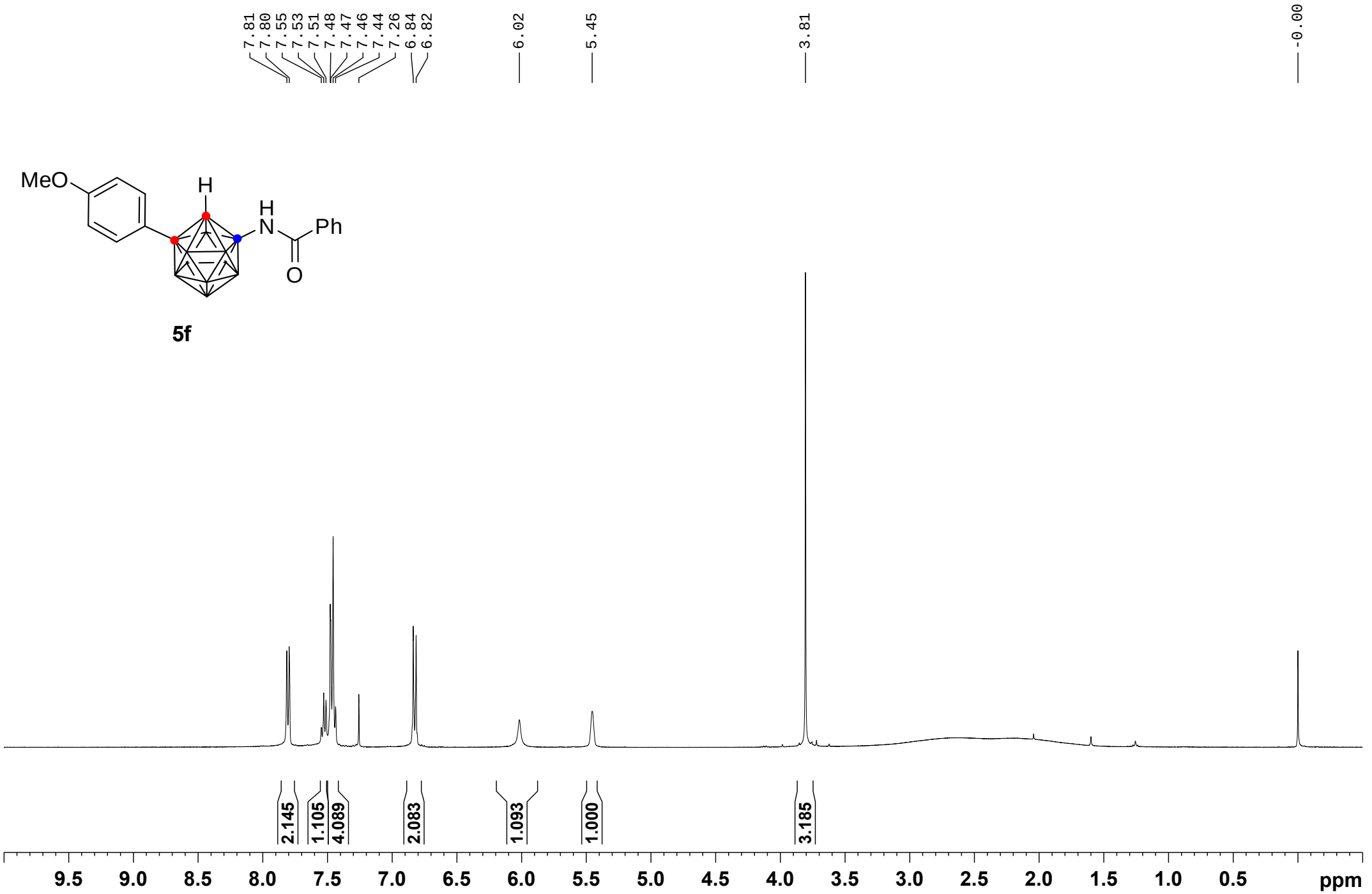
^{11}B NMR


Me
H
H
N
Ph
O

5e

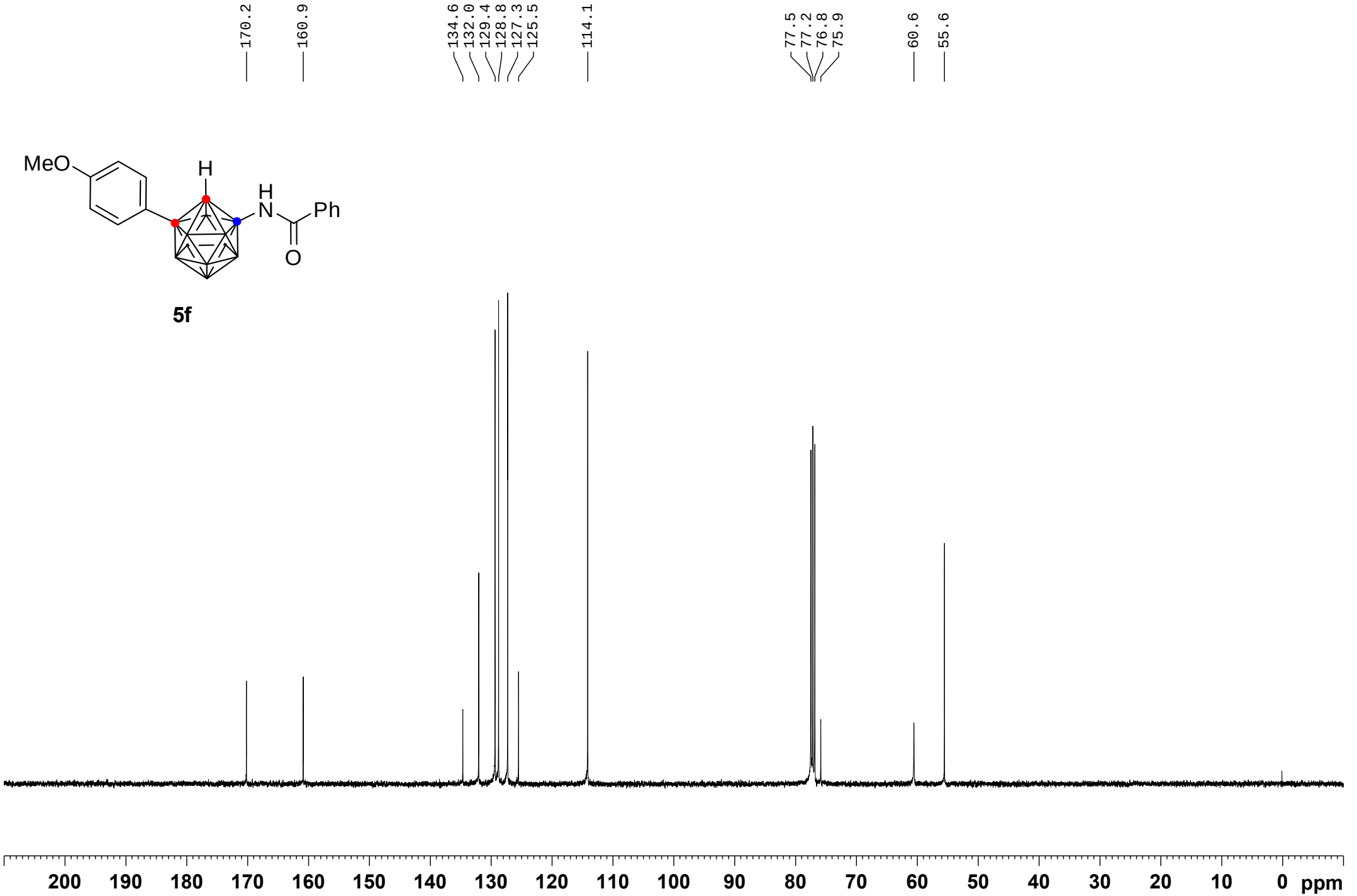
-3.22
-4.28
-5.42
-9.02
-10.01
-11.18
-12.50
-15.12
-16.20
5
0
-5
-10
-15
-20
-25
ppm

^{1}H NMR


7.81
7.80
7.55
7.53
7.51
7.48
7.47
7.46
7.44
7.26
6.84
6.82
6.02
5.45
3.81
-0.00
MeO
H
H
N
Ph
O
2.145
1.105
4.089
2.083
1.093
1.000
3.185
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
ppm

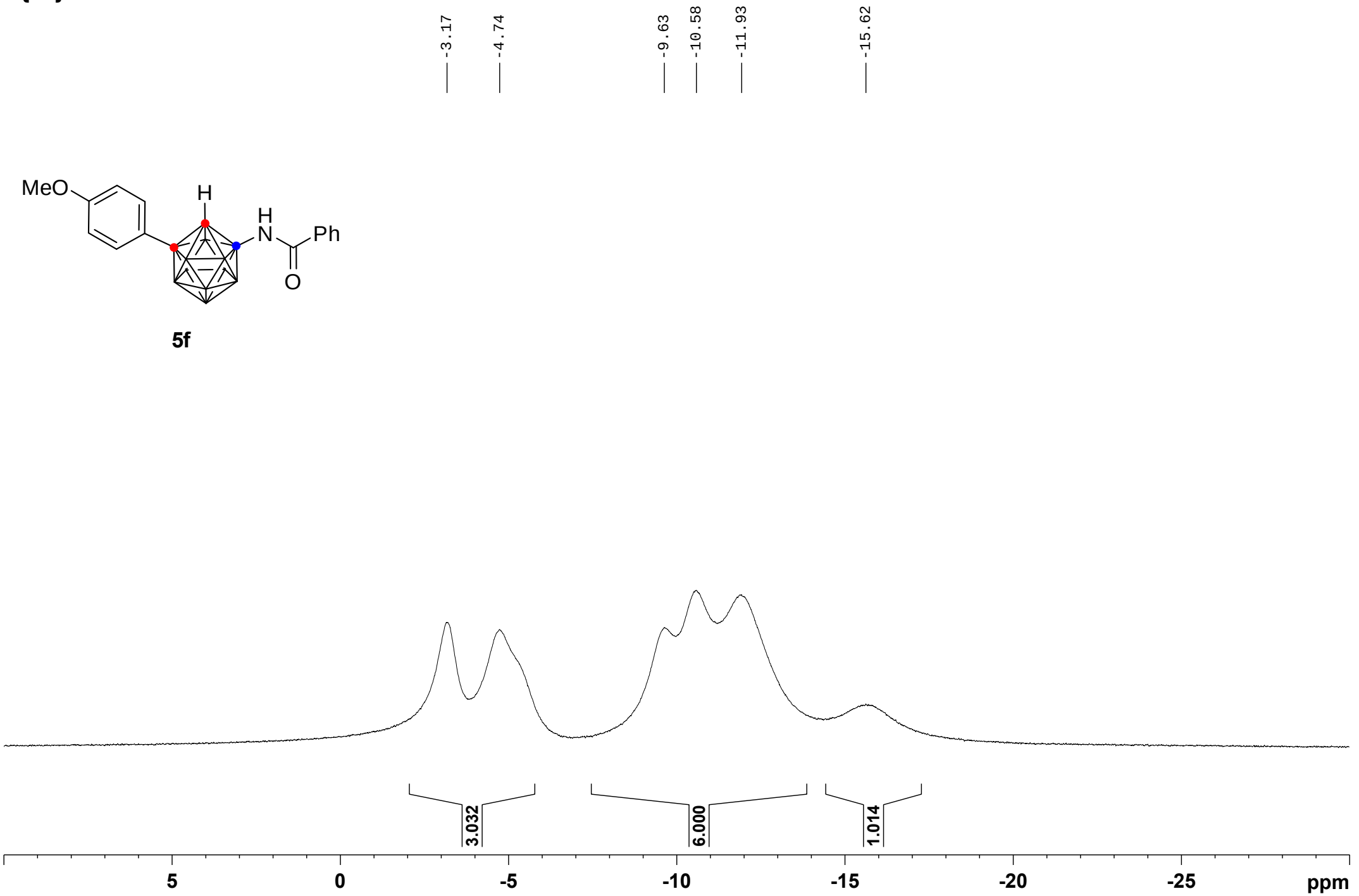
5f

$^{13}C\{^{1}H\}$ NMR


170.2
160.9
134.6
132.0
129.4
128.8
127.3
125.5
114.1
77.5
77.2
76.8
75.9
60.6
55.6
MeO
H
H
N
Ph
O
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
ppm

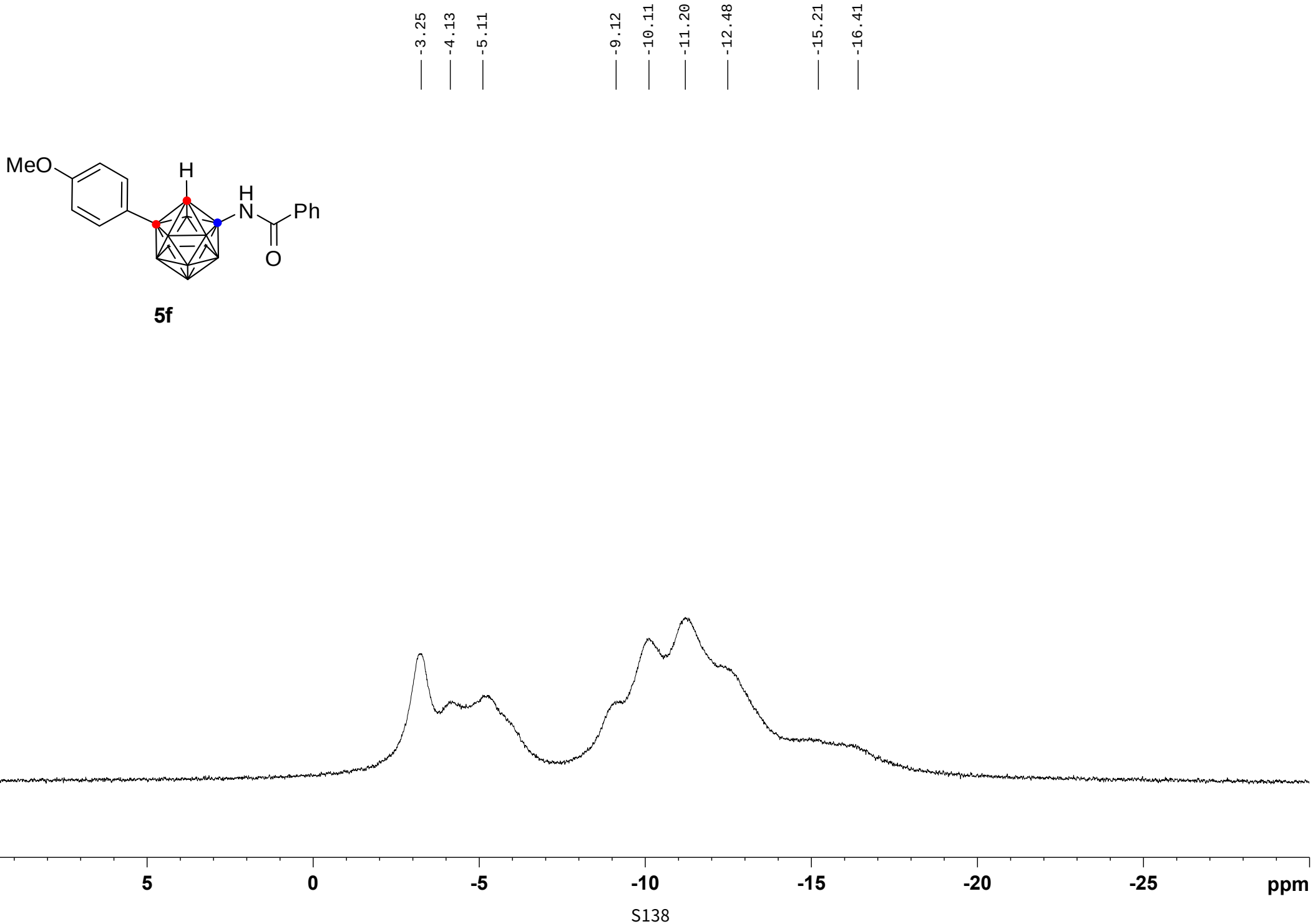
5f

$^{11}B\{^{1}H\}$ NMR

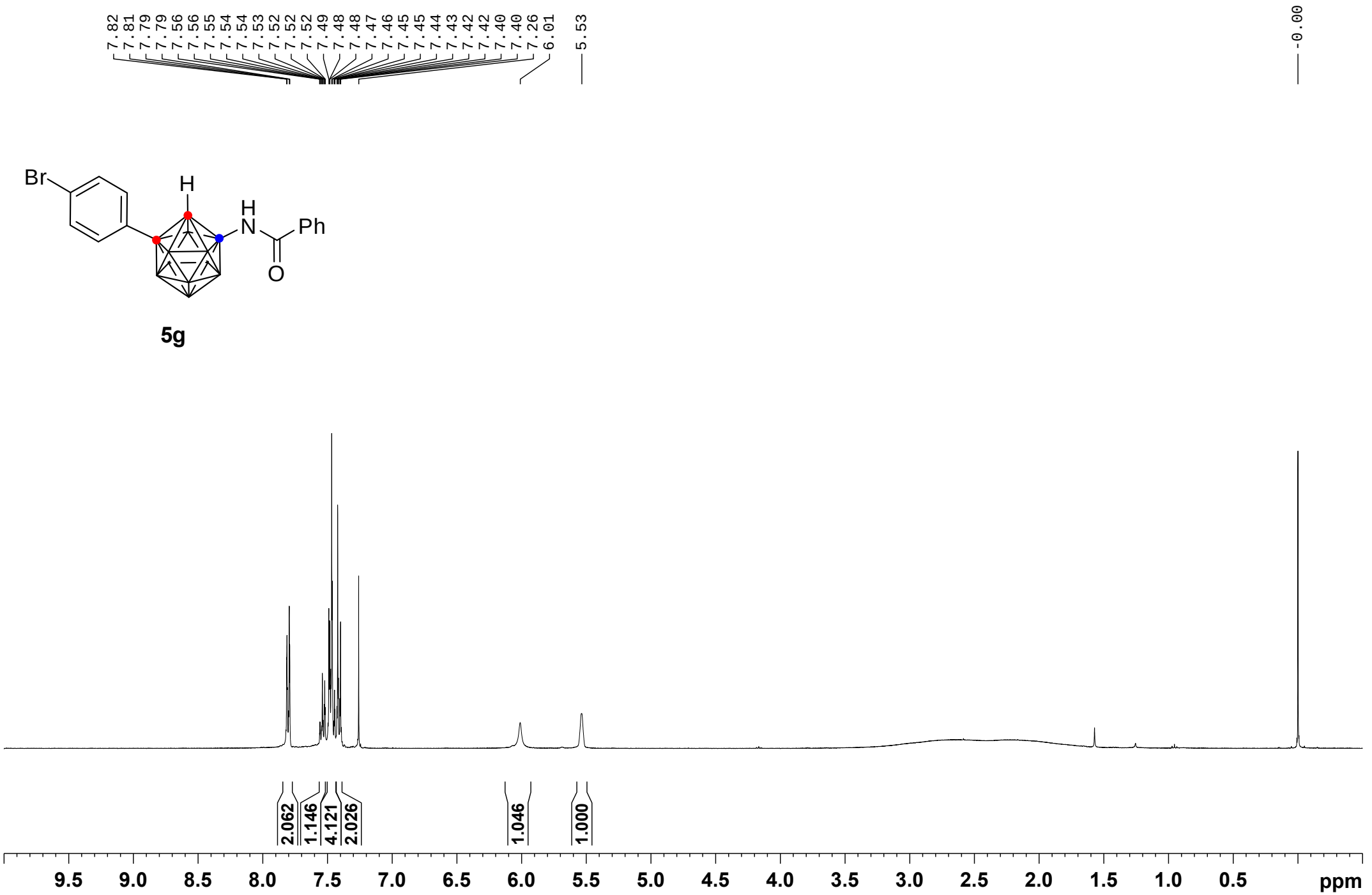

-3.17
-4.74
-9.63
-10.58
-11.93
-15.62
MeO
H
H
N
Ph
O
3.032
6.000
1.014
5
0
-5
-10
-15
-20
-25
ppm

5f

^{11}B NMR

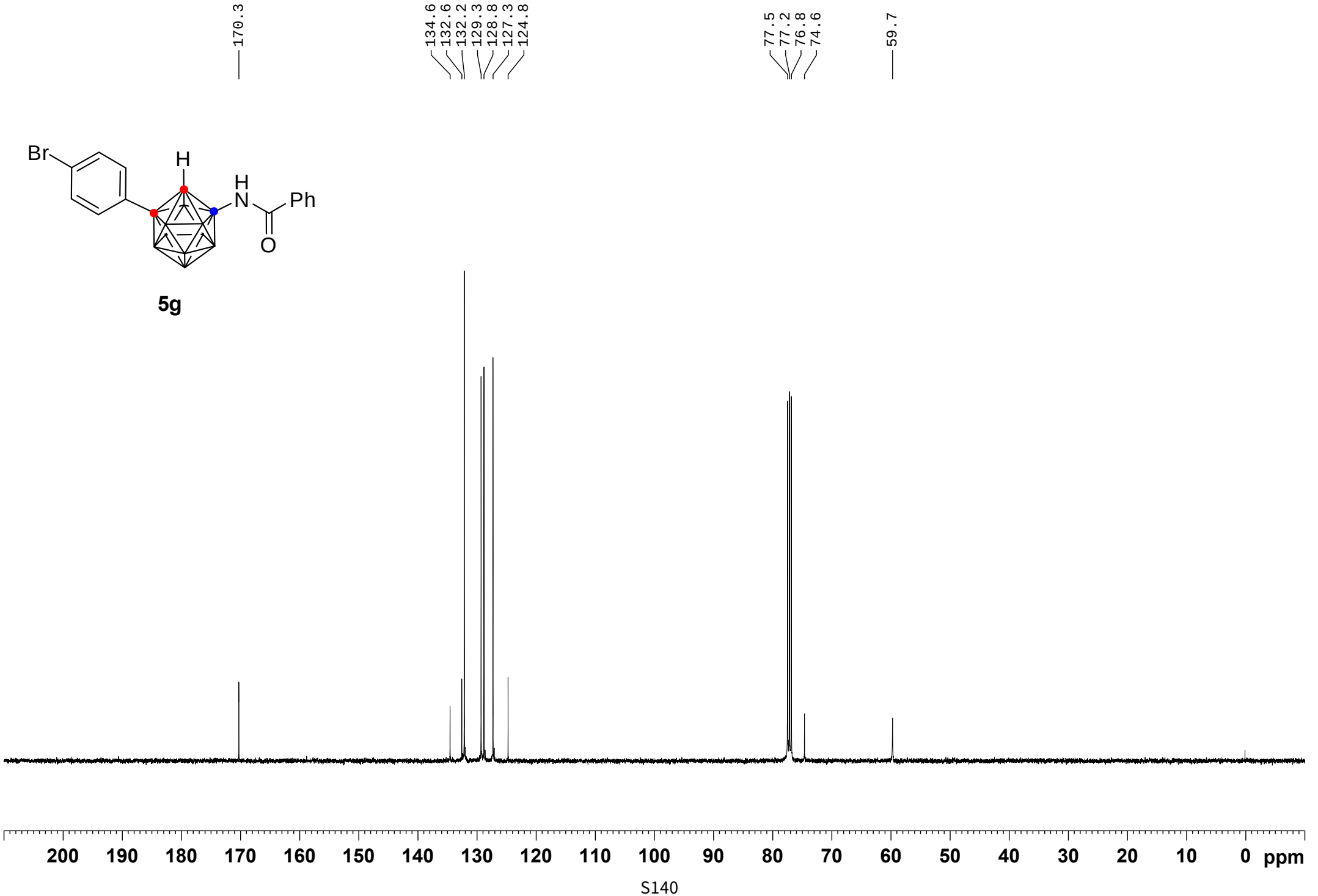

-3.25
-4.13
-5.11
-9.12
-10.11
-11.20
-12.48
-15.21
-16.41
MeO
H
H
N
Ph
O
5f
5
0
-5
-10
-15
-20
-25
ppm

^{1}H NMR

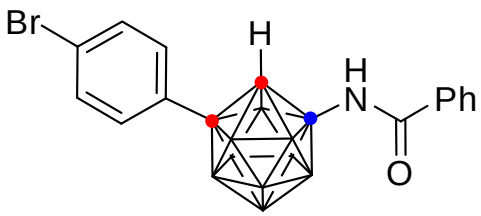

7.82
7.81
7.79
7.79
7.56
7.56
7.55
7.54
7.54
7.53
7.52
7.52
7.52
7.49
7.48
7.48
7.47
7.46
7.45
7.45
7.44
7.43
7.42
7.42
7.40
7.40
7.26
6.01
5.53
0.00
Br
H
H
N
Ph
O
2.062
1.146
4.121
2.026
1.046
1.000
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
ppm

5g

$^{13}C\{^{1}H\}$ NMR


170.3
134.6
132.6
132.2
129.3
128.8
127.3
124.8
77.5
77.2
76.8
74.6
59.7
Br
H
H
N
Ph
O
5g
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
ppm

$^{11}B\{^{1}H\}$ NMR

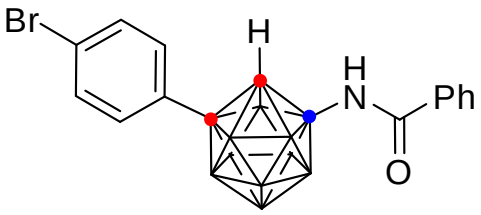

Br
H
H
N
Ph
O

5g

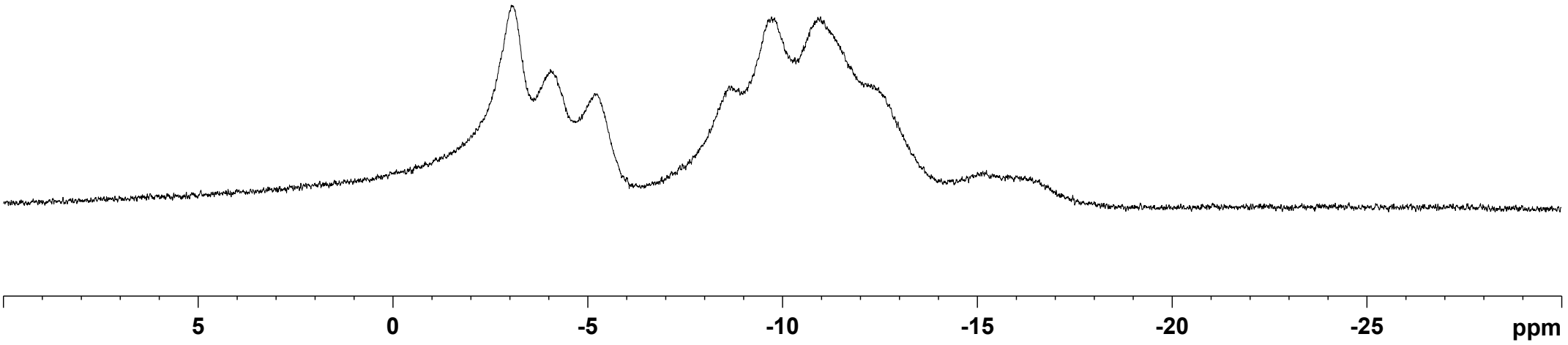
-3.96
-5.70
-10.00
-10.78
-12.88
-14.30
-16.32
3.040
6.057
1.000
5
0
-5
-10
-15
-20
-25
ppm

^{11}B NMR

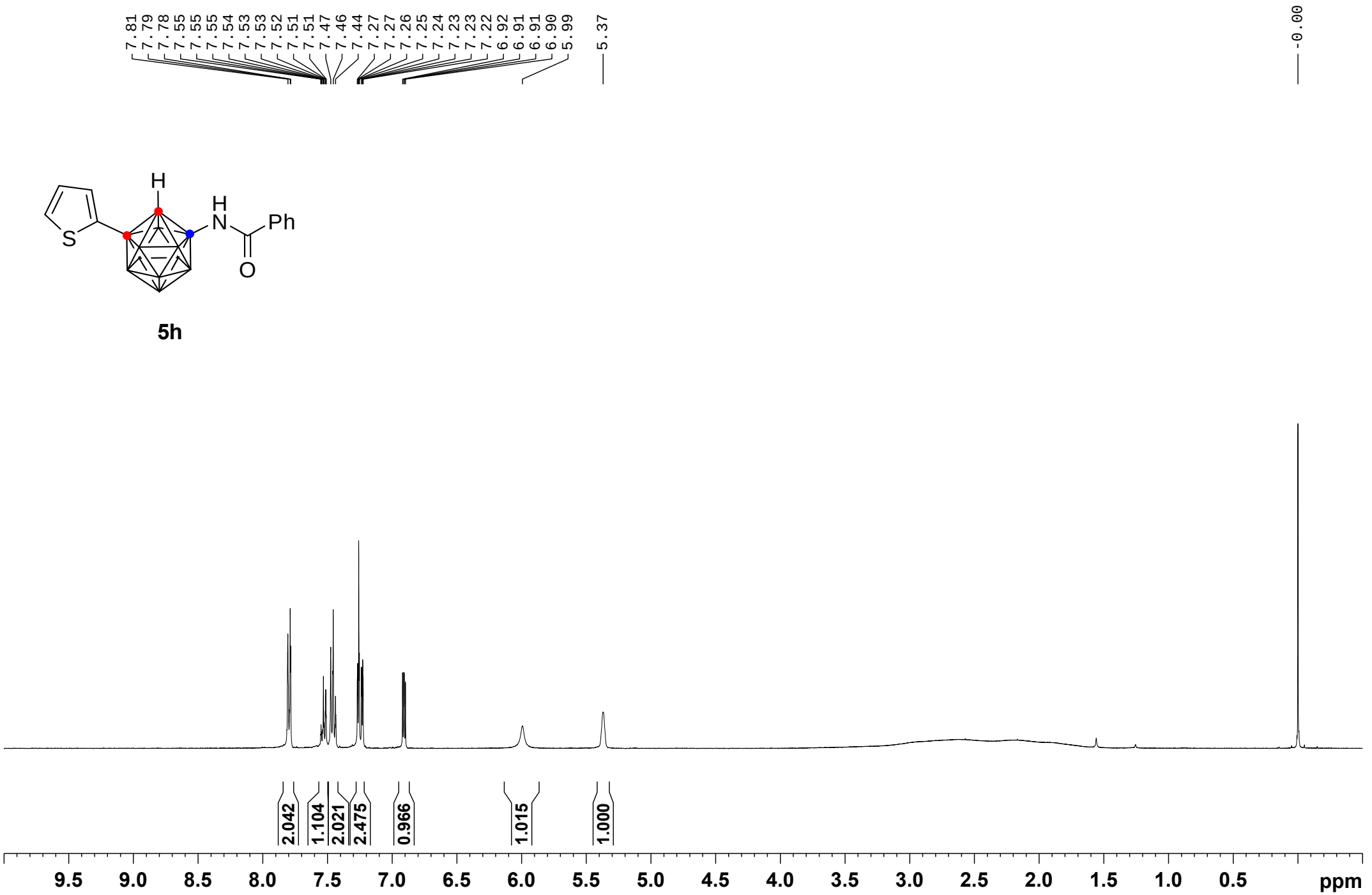
-3.04
-4.04
-5.17
-8.68
-9.72
-10.98
-12.31
-15.23
-16.18



5g

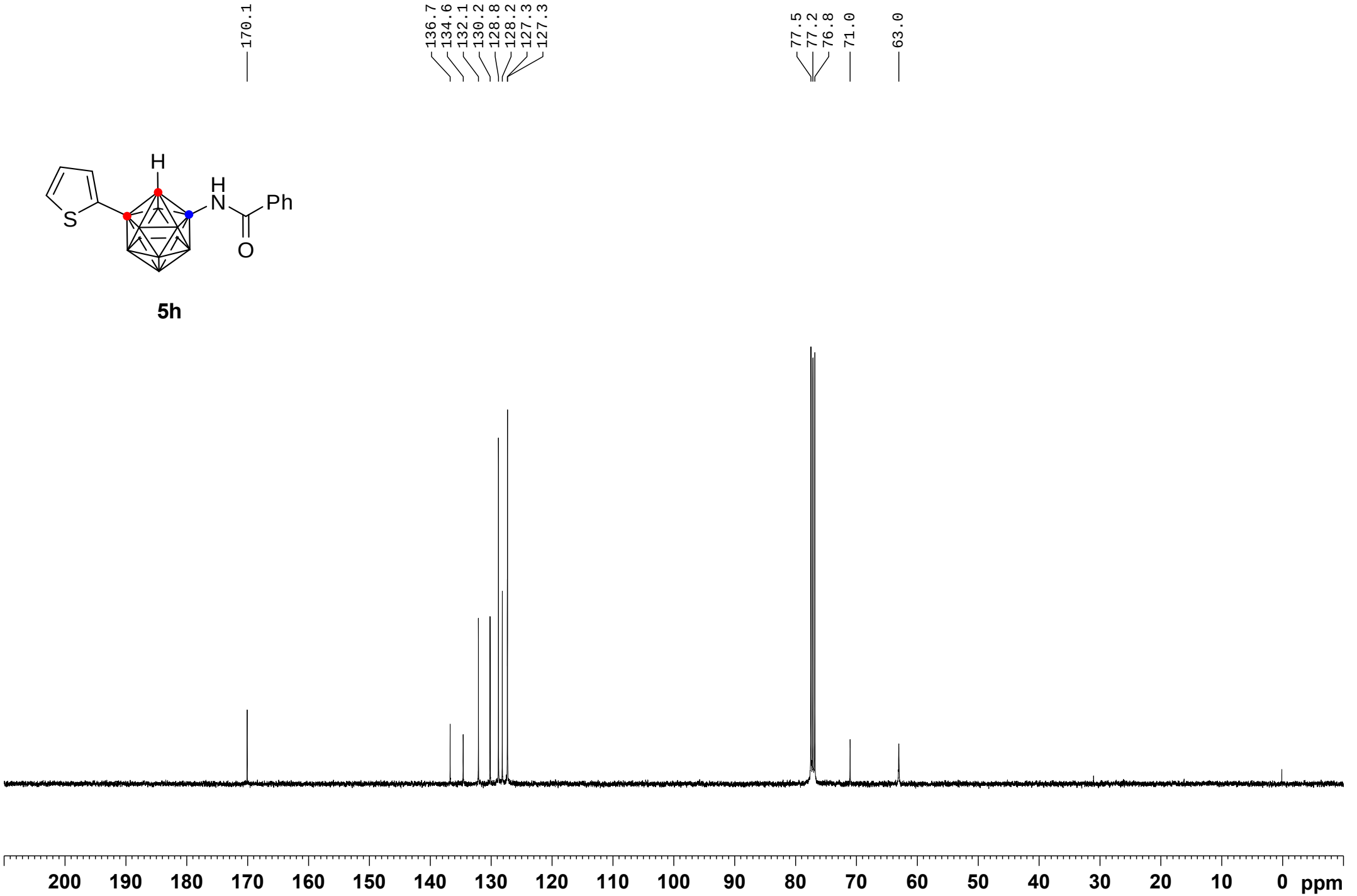


^{1}H NMR


7.81
7.79
7.78
7.55
7.55
7.55
7.54
7.53
7.53
7.52
7.51
7.51
7.47
7.46
7.44
7.27
7.27
7.26
7.25
7.24
7.23
7.23
7.22
6.92
6.91
6.91
6.90
5.99
5.37
-0.00
H
H
N
Ph
S
O
2.042
1.104
2.021
2.475
0.966
1.015
1.000
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
ppm

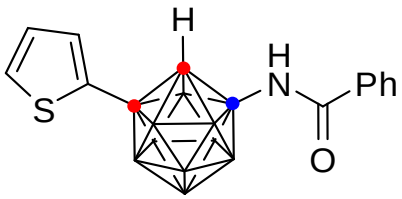
5h

$^{13}C\{^{1}H\}$ NMR


170.1
136.7
134.6
132.1
130.2
128.8
128.2
127.3
127.3
77.5
77.2
76.8
71.0
63.0
H
H
N
Ph
S
O
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
ppm

5h

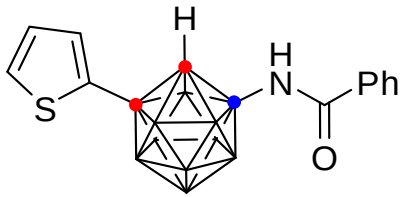
$^{11}B\{^{1}H\}$ NMR


H
H
N
Ph
S
O

5h

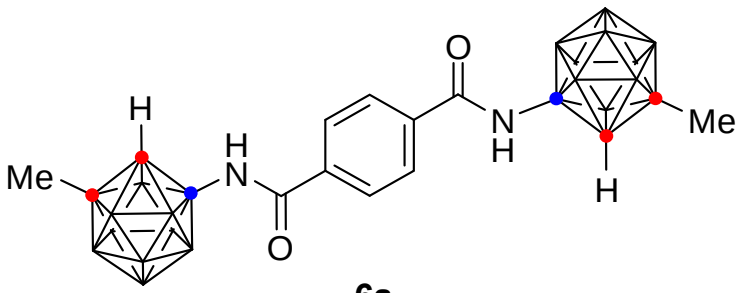
-2.94
-4.17
-5.17
-10.10
-10.66
-11.44
-14.84
3.168
6.025
1.000
5
0
-5
-10
-15
-20
-25
ppm

^{11}B NMR



5h

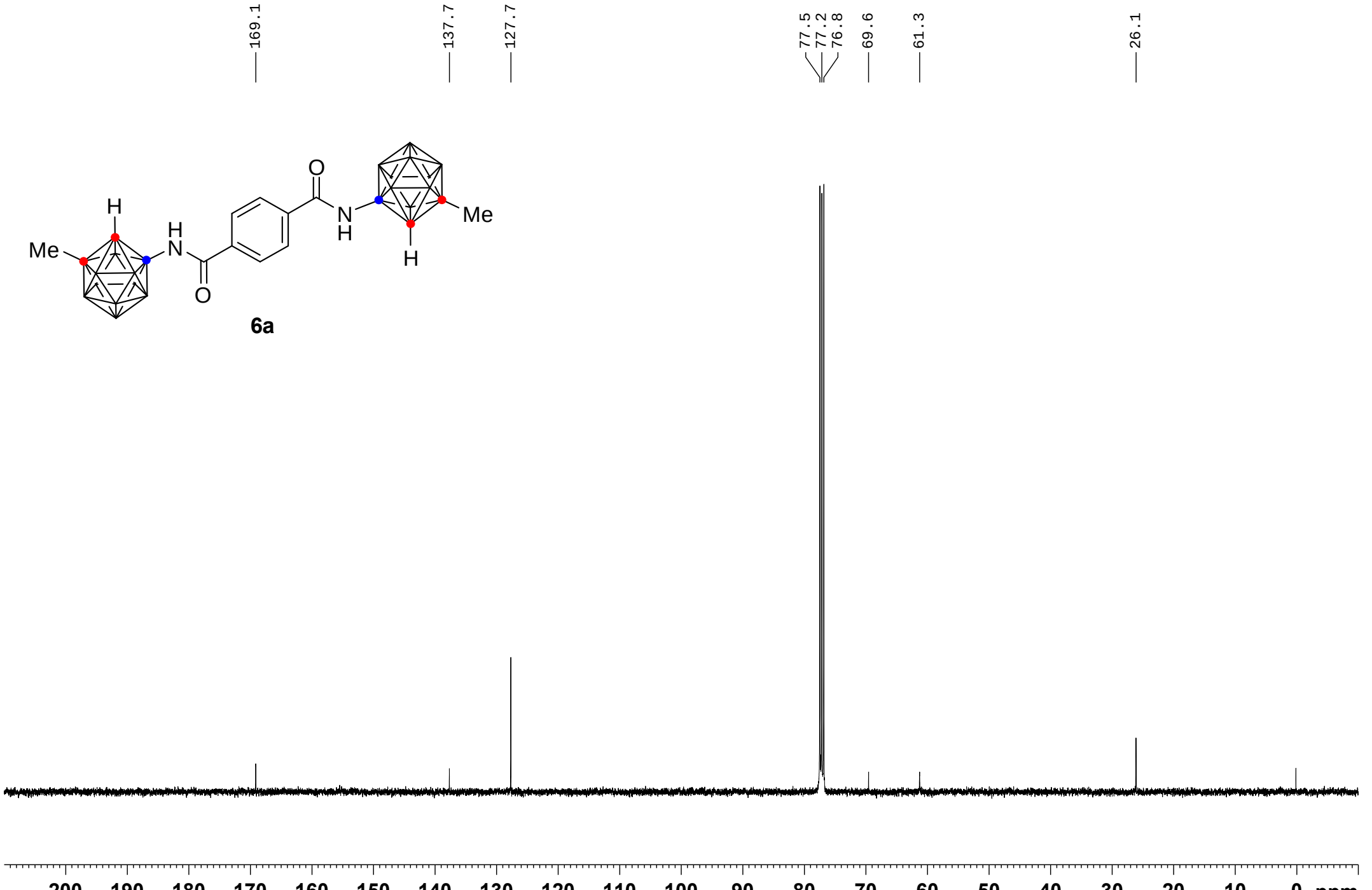
^{1}H NMR


H
Me
H
N
O
O
N
H
Me
H

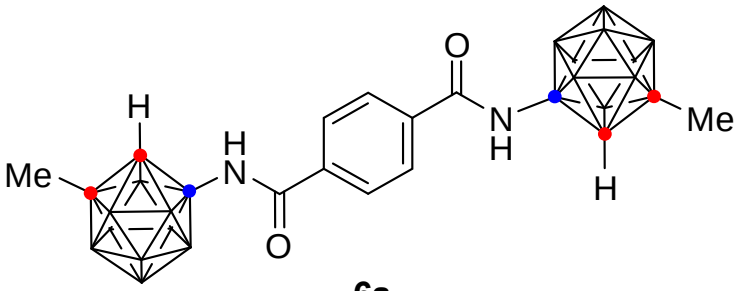
6a

7.86
7.26
5.98
5.07
2.10
-0.00
4.034
2.007
2.000
6.286
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
ppm

$^{13}C\{^{1}H\}$ NMR


169.1
137.7
127.7
77.5
77.2
76.8
69.6
61.3
26.1
Me
H
N
H
O
O
N
H
Me
H
6a
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
ppm

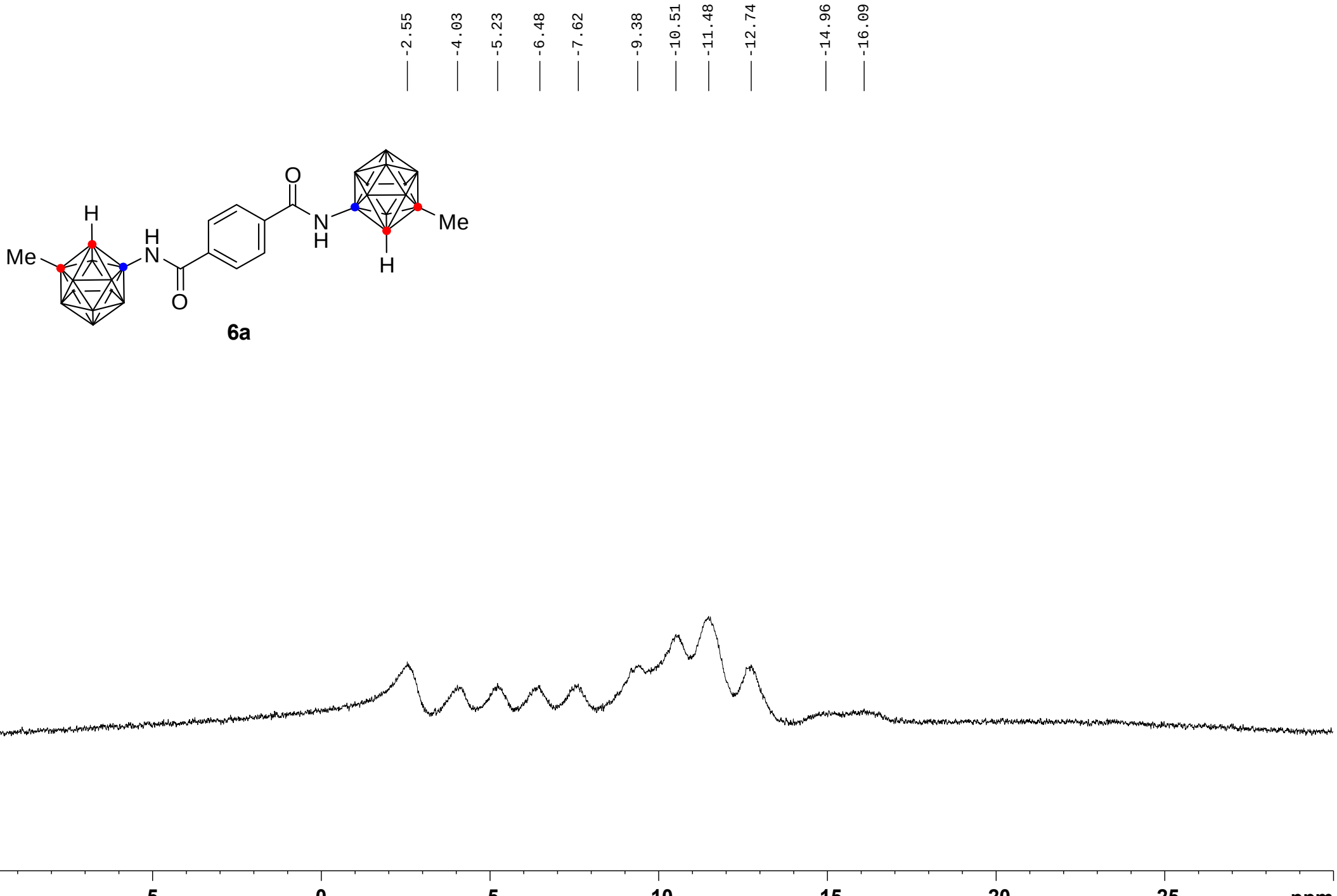
$^{11}B\{^{1}H\}$ NMR


H
Me
N
H
O
O
N
H
Me
H

6a

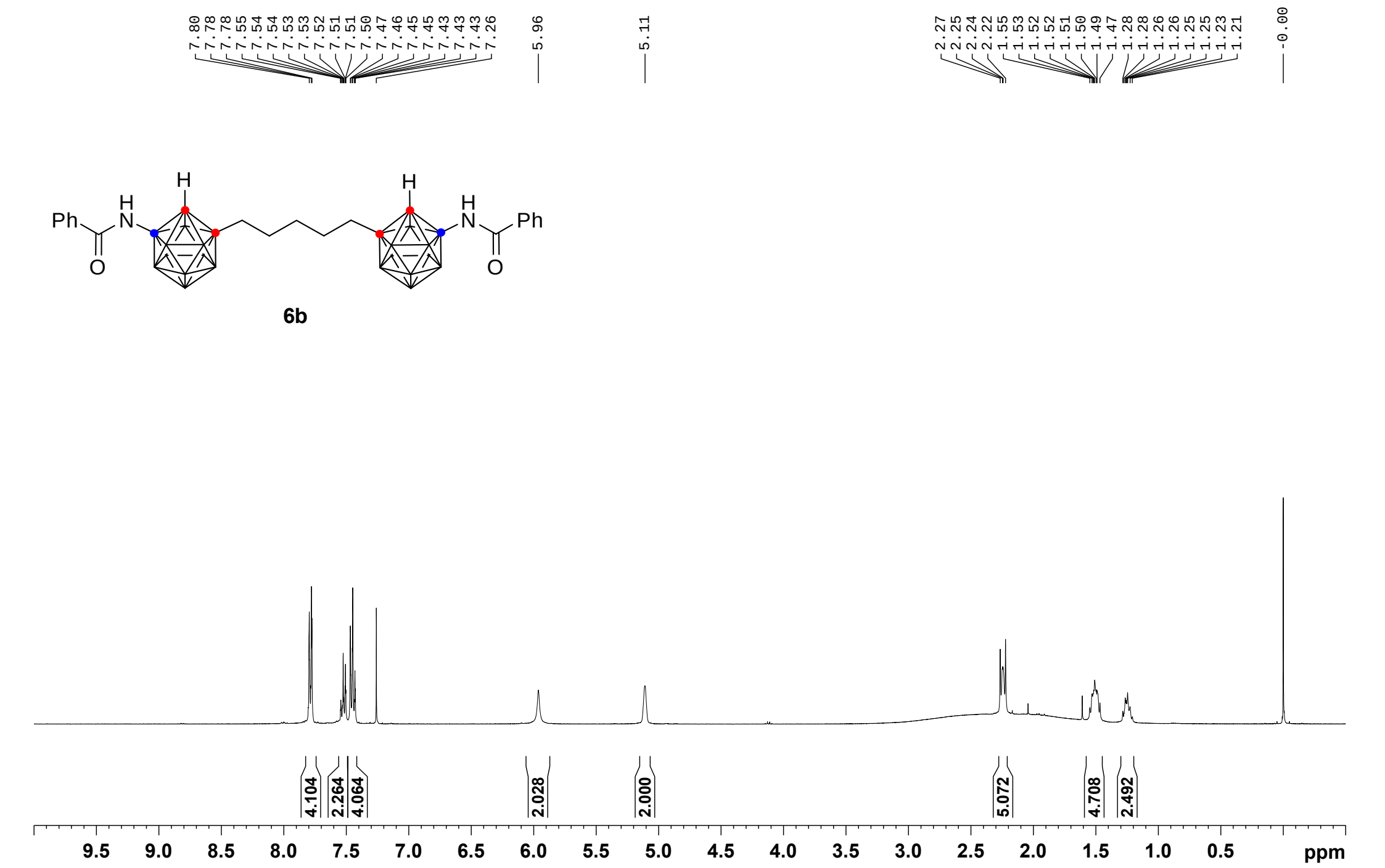
-3.26
-4.12
-7.17
-9.80
-10.49
-11.87
-15.13
2.078
1.000
6.011
1.019
5
0
-5
-10
-15
-20
-25
ppm

^{11}B NMR

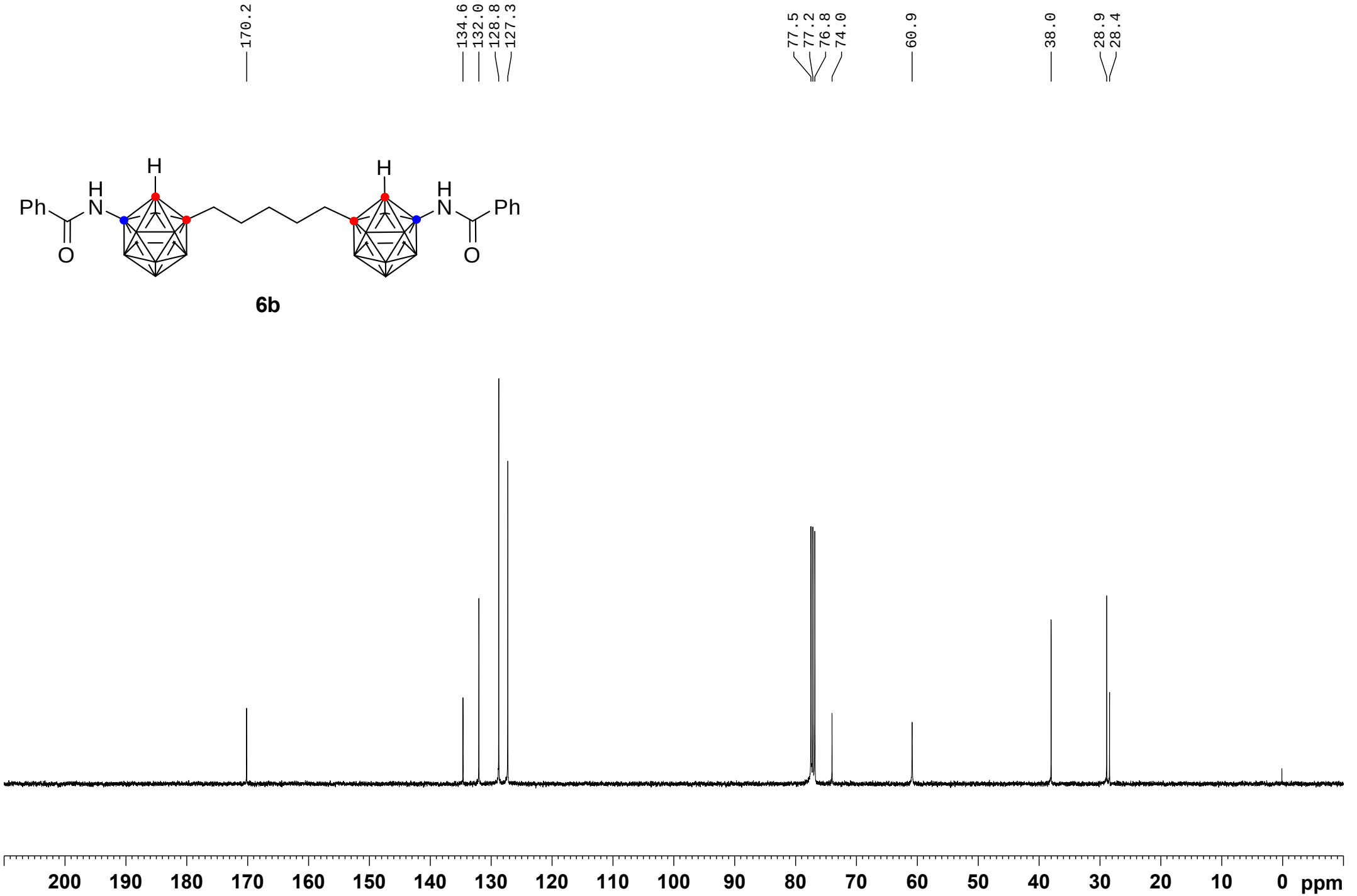

-2.55
-4.03
-5.23
-6.48
-7.62
-9.38
-10.51
-11.48
-12.74
-14.96
-16.09
H
Me
H
N
O
O
N
H
Me
H
5
0
-5
-10
-15
-20
-25
ppm

6a

^{1}H NMR

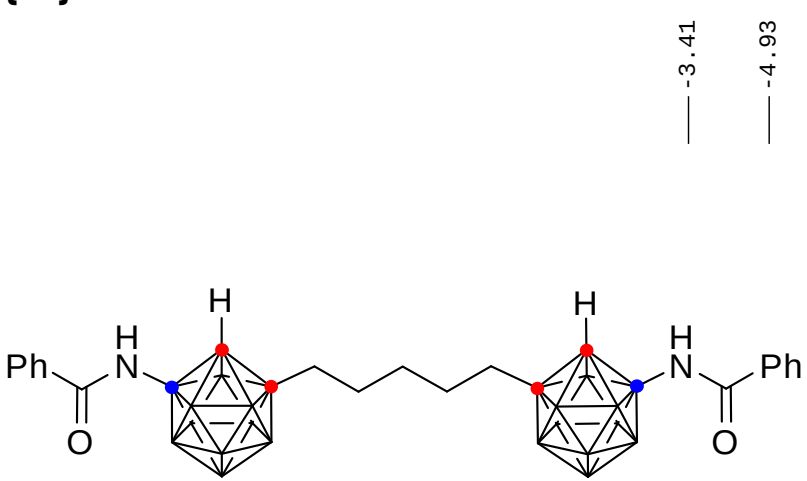

7.80
7.78
7.78
7.55
7.54
7.54
7.53
7.53
7.52
7.51
7.51
7.50
7.47
7.46
7.45
7.45
7.43
7.43
7.43
7.26
5.96
5.11
2.27
2.25
2.24
2.22
1.55
1.53
1.52
1.52
1.51
1.50
1.49
1.47
1.28
1.28
1.26
1.26
1.25
1.25
1.23
1.21
-0.00
H
H
N
Ph
O
H
H
N
Ph
O
6b
4.104
2.264
4.064
2.028
2.000
5.072
4.708
2.492
9.5
9.0
8.5
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
ppm

$^{13}C\{^{1}H\}$ NMR


170.2
134.6
132.0
128.8
127.3
77.5
77.2
76.8
74.0
60.9
38.0
28.9
28.4
Ph
N
H
O
H
H
N
Ph
O
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
ppm

6b

$^{11}B\{^{1}H\}$ NMR

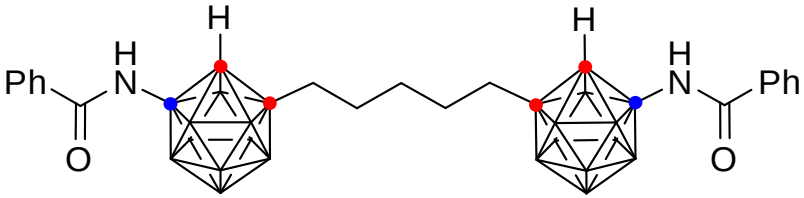

H
H
Ph
N
O
H
H
N
Ph
O

6b

-3.41
-4.93
-6.13
-9.97
-10.67
-12.44
-15.68
3.069
6.044
1.000
5
0
-5
-10
-15
-20
-25
ppm

^{11}B NMR

-3.29 -4.25 -5.35 -6.68 -9.15 -10.22 -11.20 -12.71 -16.48



6b