

A convenient synthetic route to useful monobranched polyetoxyated halogen terminated [3,3-Co(1,2-C₂B₉H₁₁)₂]⁻ synthons

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SUPPORTING INFORMATION

	Page
Experimental	S2
Spectral Data	S8
Crystal Structure Information for [N(CH ₃) ₄][5]	S32
Crystal Structure Information for [N(CH ₃) ₄][6]	S32

Experimental Section

Instrumentation. Elemental analyses were performed using a Carlo Erba EA1108 microanalyzer. IR spectra were recorded from KBr pellets on a Shimadzu FTIR-8300 spectrophotometer. The magnetic resonance spectra were recorded with a Bruker ARX 300 and Bruker AdvancedII instruments equipped with the appropriate decoupling accessories. Chemical shifts are reported in units of parts per million downfield from the reference, and all coupling constants are reported in Hertz. The mass spectra were recorded in the negative ion mode using a Bruker Biflex MALDI-TOF-MS (N₂ laser; λ_{exc} 337 nm (0.5 ns pulses); voltage ion source 20.00 kV (Uis1) and 17.50 kV (Uis2)).

Materials. Experiments were carried out, except when noted, under air with some subsequent manipulation in the open laboratory. Tetrahydrofuran (THF) and ethanol (EtOH) were used as received. Other solvents were reagent grade. All organic and inorganic salts were Fluka or Aldrich analytical reagent grade and were used as received. [3,3'-Co(8-(OCH₂CH₂)₂-1,2-C₂B₉H₁₀)(1',2'-C₂B₉H₁₁)] [2] was prepared according to the literature.¹

Synthesis of Na[3,3'-Co(8-(OCH₂CH₂)₂F-1,2-C₂B₉H₁₀)(1',2'-C₂B₉H₁₁)]·2Et₂O, Na[3]. Hydrofluoric acid (7.6 μ L, 0.488 mmol) (48% in water) was added dropwise to a stirred solution of [2] (200 mg, 0.49 mmol) in 10 mL of THF at 0 °C. The resulting solution was stirred overnight. The solvent was removed and acidic water (10 mL) (1 M HCl) was added to the orange residue. This was extracted with diethyl ether (3x10 mL). The organic phase was then extracted by NaHCO₃(aq) (3x10mL) and NaCl(aq) (3x10mL). The solvent was removed and the resulting orange precipitate was washed with water and petroleum ether, and dried in vacuo, giving the desired compound Na[3]·2Et₂O (0.23 g, 80%). (Found: C, 32.1; H, 8.1%. Calcd for C₁₆H₄₉B₁₈CoFNaO₄: C, 31.9; H, 8.2%); $\mu_{\text{max}}/\text{cm}^{-1}$ 3043 (C_c-H), 2926 and 2870 (C_{alkyl}-H), 2568 and 2517 (B-H), 1453 and 1352 (CH₂), 1148, 1133, 1120 and 1099 (C-O-C) and 1056 (C-F); δ_{H} (300 MHz; CD₃COCD₃; (CH₃)₄Si) 4.16 (2H, br s, C_c-H), 4.13 (2H, br s, C_c-H), 3.67 (2H, m, OCH₂CH₂), 3.55 (2H, t, *J* 5, OCH₂CH₂), 3.39 (8H, q, *J* 7, Et₂O), 3.27 (4H, m, OCH₂CH₂), 2.88-1.43 (17H, m, B-H), 1.09 (12H, t, *J* 7, Et₂O); $\delta_{\text{H}\{\text{B}\}}$ (300 MHz; CD₃COCD₃; (CH₃)₄Si) 4.16 (2H, br s, C_c-H), 4.13 (2H, br s, C_c-H), 3.67 (2H, m, OCH₂CH₂), 3.55 (2H, t, *J* 5, OCH₂CH₂), 3.39 (8H, q, *J* 7, Et₂O), 3.27 (4H, m,

OCH₂CH₂), 2.88 (4H, s, B-H), 2.68 (4H, s, B-H), 2.00 (2H, s, B-H), 1.80 (2H, s, B-H), 1.66 (1H, s, B-H), 1.61 (2H, s, B-H), 1.52 (1H, s, B-H), 1.43 (1H, s, B-H), 1.09 (12H, t, *J* 7, Et₂O); δ_C(75 MHz; CD₃COCD₃; (CH₃)₄Si) 72.0 (1C, s, OCH₂), 71.6 (1C, s, OCH₂), 68.3 (1C, s, OCH₂), 62.9 (4C, s, Et₂O), 60.8 (1C, s, CH₂F), 53.3 (2C, s, C_c-H), 46.6 (2C, s, C_c-H), 14.7 (4C, s, Et₂O); δ_B(96 MHz; CD₃COCD₃; BF₃·OEt₂) 24.5 (1B, s, B(8)), 5.9 (1B, d, *J* 134), 1.3 (1B, d, *J* 140), -1.6 (1B, d, *J* 170), -3.7 (2B, d, *J* 160), -6.3 (4B, d, *J* 132), -7.4 (2B, d, *J* 133), -16.4 (2B, d, *J* 154), -19.5 (2B, d, *J* 155), -21.2 (1B, d, *J* 158), -27.7 (1B, d, *J* 156); *m/z* (MALDI-TOF-MS) 456.2 (M+2(CH₂), 13.7%), 442.2 (M+CH₂, 8.4), 428.2 (M, 67.9), 338.6 (M-C₄H₈OF, 5.3) and 323.5 (M-C₄H₈O₂F, 4.7).

Synthesis of Cs[3,3'-Co(8-(OCH₂CH₂)₂Cl-(1,2-C₂B₉H₁₀)(1',2'-C₂B₉H₁₁)], Cs[4]. This compound was prepared using the same procedure as for Na[3], but using hydrochloric acid (0.101 mL, 1.22 mmol) instead of hydrofluoric acid and CsCl to isolate the Cs⁺ salt of [4]⁻ (0.42 g, 88 %). (Found: C, 16.4; H, 5.1%. Calcd for C₈H₂₉B₁₈CoCsO₂: C, 16.5; H, 5.0%); μ_{max}/cm⁻¹ 3041 (C_c-H), 2923 and 2880 (C_{alkyl}-H), 2565 and 2521 (B-H), 1448 and 1356 (CH₂) and 1151, 1138, 1117 and 1095 (C-O-C); δ_H(300 MHz; CD₃COCD₃; (CH₃)₄Si) 4.24 (4H, br s, C_c-H), 3.72 (2H, m, OCH₂CH₂), 3.68 (2H, m, OCH₂CH₂), 3.60 (4H, m, OCH₂CH₂), 2.90-1.46 (17H, m, B-H); δ_{H{B}}(300 MHz; CD₃COCD₃; (CH₃)₄Si) 4.24 (4H, br s, C_c-H), 3.72 (2H, m, OCH₂CH₂), 3.68 (2H, m, OCH₂CH₂), 3.60 (4H, m, OCH₂CH₂), 2.90 (3H, s, B-H), 2.74 (2H, s, B-H), 2.68 (1H, s, B-H), 2.47 (1H, s, B-H), 1.98 (2H, s, B-H), 1.78 (2H, s, B-H), 1.68 (1H, s, B-H), 1.64 (2H, s, B-H), 1.55 (2H, s, B-H), 1.46 (1H, s, B-H); δ_C(75 MHz; CD₃COCD₃; (CH₃)₄Si) 71.9 (1C, s, OCH₂), 71.0 (1C, s, OCH₂), 68.4 (1C, s, OCH₂), 54.0 (2C, s, C_c-H), 46.5 (2C, s, C_c-H), 43.1 (1C, s, CH₂Cl); δ_B(96 MHz; CD₃COCD₃; BF₃·OEt₂) 25.4 (1B, s, B(8)), 6.6 (1B, d, *J* 137), 2.7 (1B, d, *J* 140), -0.2 (1B, d, *J* 157), -2.0 (2B, d, *J* 162), -5.0 (2B, d, *J* 128), -5.9 (4B, d, *J* 115), -15.0 (2B, d, *J* 154), -18.1 (2B, d, *J* 154), -19.7 (1B, d, *J* 158), -26.2 (1B, d, *J* 158); *m/z* (MALDI-TOF-MS) 446.2 (M, 100).

Synthesis of N(CH₃)₄[3,3'-Co(8-(OCH₂CH₂O)₂Br-1,2-C₂B₉H₁₀)(1',2'-C₂B₉H₁₁)], [N(CH₃)₄][5]. This compound was prepared using the same procedure as for Na[3], but using hydrobromic acid (0.17 mL, 1.22 mmol) instead of hydrofluoric acid and [N(CH₃)₄]Cl to isolate the [N(CH₃)₄]⁺ salt of [5]⁻ (0.56 g, 81%). (Found: C, 25.8; H, 7.8; N, 2.5%. Calcd for C₁₂H₄₁B₁₈CoNO₂: C, 25.5; H, 7.4; N, 2.5 %); μ_{max}/cm⁻¹ 3045 (C_c-H),

2875 (C_{alkyl}-H), 2561 and 2523 (B-H), 1455 and 1364 (CH₂), 1151, 1128, 1116 and 1094 (C-O-C) and 944 (C-N); δ_{H} (300 MHz; CD₃COCD₃; (CH₃)₄Si) 4.25 (4H, br s, C_c-H), 3.79 (2H, t, *J* 5, OCH₂CH₂), 3.56 (4H, m, OCH₂CH₂), 3.53 (2H, m, OCH₂CH₂), 3.44 (12H, s, N(CH₃)₄), 2.89-1.45 (17H, m, B-H); $\delta_{\text{H}\{\text{B}\}}$ (300 MHz; CD₃COCD₃; (CH₃)₄Si) 4.25 (4H, br s, C_c-H), 3.79 (2H, t, *J* 5, OCH₂CH₂), 3.56 (4H, m, OCH₂CH₂), 3.53 (2H, m, OCH₂CH₂), 3.44 (12H, s, N(CH₃)₄), 2.89 (3H, s, B-H), 2.75 (2H, s, B-H), 2.68 (1H, s, B-H), 2.43 (1H, s, B-H), 1.97 (2H, s, B-H), 1.77 (2H, s, B-H), 1.70 (1H, s, B-H), 1.65 (2H, s, B-H), 1.55 (2H, s, B-H), 1.45 (1H, s, B-H); δ_{C} (75 MHz; CD₃COCD₃; (CH₃)₄Si) 71.6 (1C, s, OCH₂), 70.9 (1C, s, OCH₂), 68.5 (1C, s, OCH₂), 55.3 (4C, s, N(CH₃)₄), 54.3 (2C, s, C_c-H), 46.4 (2C, s, C_c-H), 31.0 (1C, s, CH₂Br); δ_{B} (96 MHz; CD₃COCD₃; BF₃·OEt₂) 23.7 (1B, s, B(8)), 4.8 (1B, d, *J* 136), 1.3 (1B, d, *J* 141), -1.6 (1B, d, *J* 155), -3.4 (2B, d, *J* 160), -6.6 (2B, d, *J* 96), -7.5 (4B, d, *J* 126), -16.4 (2B, d, *J* 153), -19.6 (2B, d, *J* 192), -21.1 (1B, d, *J* 155), -27.6 (1B, d, *J* 162); *m/z* (MALDI-TOF-MS) 491.2 (M, 63.6%), 428.0 (M-Br+OH, 9.6), 410.9 (M-Br, 12.6), 382.8 (M-Br-C₂H₄, 3.2), 365.7 (M-Br-C₂H₄O, 5.1), 337.6 (M-C₄H₈OBr, 4.3) and 323.5 (M-C₄H₈O₂Br, 1.5).

Synthesis of [N(CH₃)₄][3,3'-Co(8-(OCH₂CH₂)₂I-1,2-C₂B₉H₁₀)(1',2'-C₂B₉H₁₁)], N(CH₃)₄[6]. This compound was prepared using the same procedure as for Na[3], but using hydroiodic acid (0.07 mL, 0.49 mmol) instead of hydrofluoric acid and N(CH₃)₄Cl to isolate the [N(CH₃)₄]⁺ salt of [6]⁻ (0.24 g, 80%). (Found: C, 23.6; H, 6.8; N, 2.4%. Calcd for C₁₂H₄₁B₁₈CoNO₂: C, 23.6; H, 6.8; N, 2.3%); $\mu_{\text{max}}/\text{cm}^{-1}$ 3043 (C_c-H), 2890 (C_{alkyl}-H), 2555 and 2531 (B-H), 1448 and 1376 (CH₂), 1149, 1125, 1121 and 1099 (C-O-C) and 945 (C-N); δ_{H} (300 MHz; CD₃COCD₃; (CH₃)₄Si) 4.26 (4H, br s, C_c-H), 3.71 (2H, t, *J* 6, OCH₂CH₂), 3.54 (4H, m, OCH₂CH₂), 3.45 (12H, s, N(CH₃)₄), 3.30 (2H, t, *J* 6, OCH₂CH₂I), 2.89-1.46 (17H, m, B-H); $\delta_{\text{H}\{\text{B}\}}$ (300 MHz; CD₃COCD₃; (CH₃)₄Si) 4.26 (4H, br s, C_c-H), 3.71 (2H, t, *J* 6, OCH₂CH₂), 3.54 (4H, m, OCH₂CH₂), 3.45 (12H, s, N(CH₃)₄), 3.30 (2H, t, *J* 6, OCH₂CH₂I), 2.89 (3H, s, B-H), 2.74 (2H, s, B-H), 2.69 (1H, s, B-H), 2.42 (1H, s, B-H), 1.97 (2H, s, B-H), 1.77 (2H, s, B-H), 1.70 (1H, s, B-H), 1.65 (2H, s, B-H), 1.55 (2H, s, B-H), 1.46 (1H, s, B-H); δ_{C} (75 MHz; CD₃COCD₃; (CH₃)₄Si) 71.6 (1C, s, OCH₂), 71.5 (1C, s, OCH₂), 68.4 (1C, s, OCH₂), 55.2 (4C, s, N(CH₃)₄), 54.5 (2C, s, C_c-H), 46.4 (2C, s, C_c-H), 3.6 (1C, s, CH₂I); δ_{B} (96 MHz; CD₃COCD₃; BF₃·OEt₂) 23.7 (1B, s, B(8)), 4.7 (1B, d, *J* 135), 1.3 (1B, d, *J* 139), -1.6 (1B, d, *J* 157), -3.4 (2B, d, *J* 158), -6.6 (2B, d, *J* 100), -7.5 (4B, d, *J* 122), -16.4 (2B,

d, *J* 153), -19.6 (2B, d, *J* 154), -21.1 (1B, d, *J* 152), -27.6 (1B, d, *J* 166); *m/z* (MALDI-TOF-MS) 664.9 (M+I, 8.0%), 538.4 (M, 24.8), 410.9 (M-I, 21.5), 382.8 (M-I-C₂H₄, 10.8), 365.7 (M-I-C₂H₄O, 14.2) and 337.6 (M-C₄H₈OI, 20.6).

Synthesis of [N(CH₃)₄][3,3'-Co(8-(OCH₂CH₂)₂Br-1,2-C₂B₉H₁₀)(8'-I-1',2'-C₂B₉H₁₀)], [N(CH₃)₄][7].

Iodine (26 mg, 0.103 mmol) was added to a stirred solution of N(CH₃)₄[5] (29 mg, 0.05 mmol) in 5 mL of EtOH. The reaction mixture was left to stand overnight at room temperature and was then heated under reflux 1.5h. The excess iodine was decomposed by the addition of a solution of Na₂SO₃ in water and the resulting mixture was evaporated. This was washed with water and the product was redissolved in the minimum volume of ethanol and an aqueous solution containing an excess of N(CH₃)₄Cl was added, resulting in the formation of an orange precipitate. This was filtered off, washed with water and petroleum ether, and dried in vacuo, giving the desired compound N(CH₃)₄[7] (0.03 g, 81%). (Found: C, 21.2; H, 5.6; N, 2.1%. Calcd for C₁₂H₄₀B₁₈CoNO₂BrI: C, 20.9; H, 5.8; N, 2.0%); $\mu_{\max}/\text{cm}^{-1}$ 3042 (C_c-H), 2885 (C_{alkyl}-H), 2559 and 2529 (B-H), 1445 and 1371 (CH₂), 1145, 1129, 1118 and 1096 (C-O-C) and 946 (C-N); δ_{H} (300 MHz; CD₃COCD₃; (CH₃)₄Si) 4.49 (2H, br s, C_c-H), 4.19 (2H, br s, C_c-H), 3.73 (2H, t, *J* 8, OCH₂CH₂), 3.56 (4H, t, *J* 6, OCH₂CH₂), 3.53 (2H, m, OCH₂CH₂), 3.45 (12H, s, N(CH₃)₄), 3.16-1.66 (16H, m, B-H); $\delta_{\text{H}\{\text{B}\}}$ (300 MHz; CD₃COCD₃; (CH₃)₄Si) 4.49 (2H, br s, C_c-H), 4.19 (2H, br s, C_c-H), 3.73 (2H, t, *J* 8, OCH₂CH₂), 3.56 (4H, t, *J* 6, OCH₂CH₂), 3.53 (2H, m, OCH₂CH₂), 3.45 (12H, s, N(CH₃)₄), 3.16 (2H, s, B-H), 3.01 (2H, s, B-H), 2.85 (1H, s, B-H), 2.81 (1H, s, B-H), 2.40 (2H, s, B-H), 1.95 (1H, s, B-H), 1.72 (2H, s, B-H), 1.66 (3H, s, B-H); δ_{C} (75 MHz; CD₃COCD₃; (CH₃)₄Si) 71.6 (1C, s, OCH₂), 70.8 (1C, s, OCH₂), 68.1 (1C, s, OCH₂), 56.5 (2C, s, C_c-H), 55.3 (4C, s, N(CH₃)₄), 54.6 (2C, s, C_c-H), 30.6 (1C, s, CH₂Br); δ_{B} (96 MHz; CD₃COCD₃; BF₃·OEt₂) 22.4 (1B, s, B(8)), 0.3 (2B, d, *J* 136), -3.8 (2B, d, *J* 105), -4.9 (4B, d, *J* 145), -6.5 (2B, d, *J* 127), -6.5 (1B, s, B(8')), -17.1 (2B, d, *J* 180), -19.2 (2B, d, *J* 177), -22.4 (1B, d, *J* 180), -26.6 (1B, d, *J* 175); *m/z* (MALDI-TOF-MS) 617.6 (M, 70.5%), 570.4 (M-I+2Br, 6.8), 537.4 (M-I, 13.7), 492.2 (M-I-Br, 8.9).

Synthesis of [N(CH₃)₄][3,3'-Co(8-(OCH₂CH₂)₂I-1,2-C₂B₉H₁₀)(8'-I-1',2'-C₂B₉H₁₀)], [N(CH₃)₄][8]. This compound was prepared using the same procedure as for

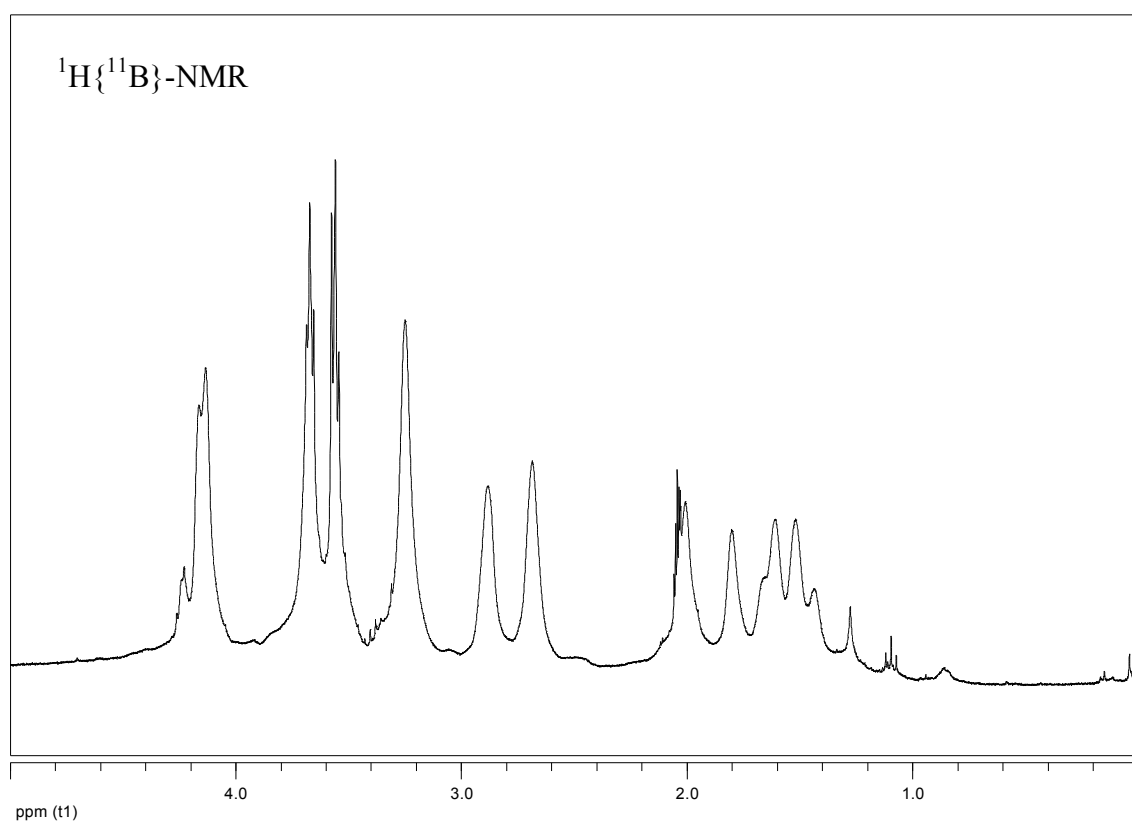
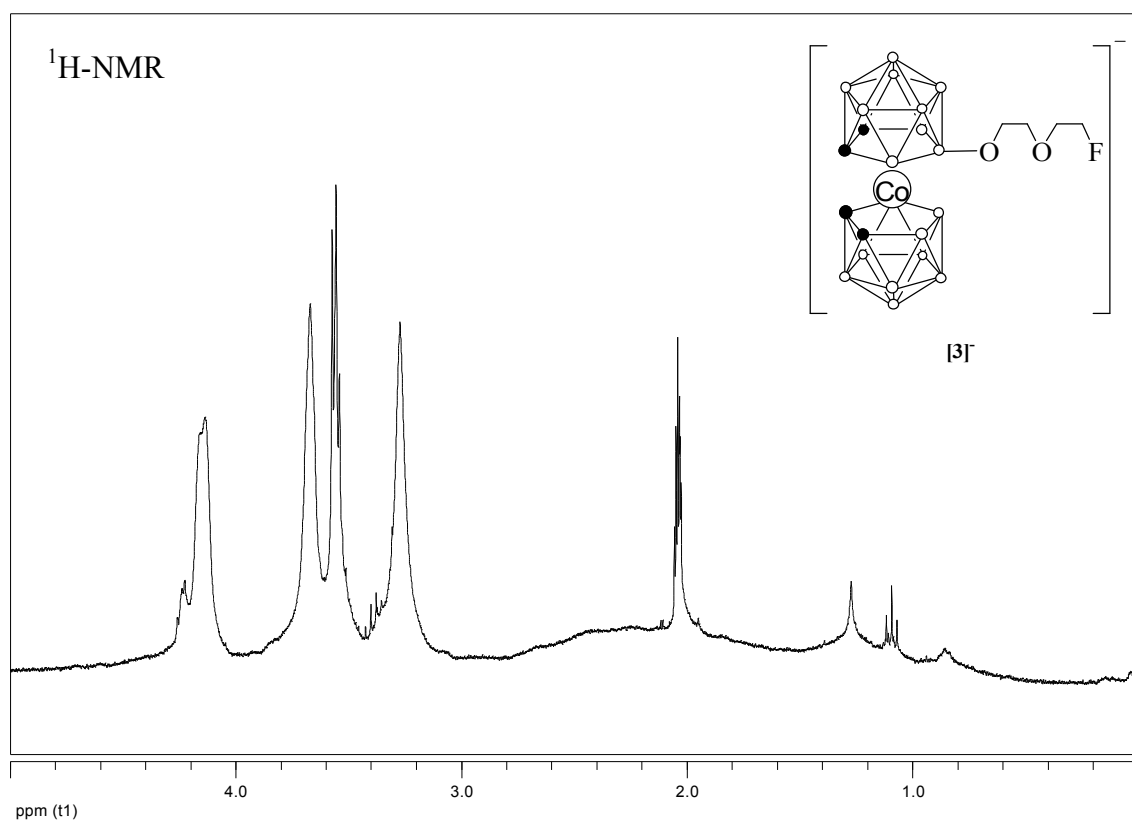
[N(CH₃)₄][7], but using [6]⁻ (29 mg, 0.047 mmol) instead of [5]⁻, giving the desired compound N(CH₃)₄[8] (0.03 g, 83%). (Found: C, 19.6; H, 5.4; N, 2.0%. Calcd for C₁₂H₄₀B₁₈CoNO₂I₂: C, 19.5; H, 5.5; N, 1.9%); $\mu_{\max}/\text{cm}^{-1}$ 3039 (C_c-H), 2895 (C_{alkyl}-H), 2560 and 2538 (B-H), 1442 and 1380 (CH₂), 1152, 1129, 1118 and 1097 (C-O-C) and 943 (C-N); δ_{H} (300 MHz; CD₃COCD₃; (CH₃)₄Si) 4.49 (2H, br s, C_c-H), 4.19 (2H, br s, C_c-H), 3.68 (2H, t, *J* 6, OCH₂CH₂), 3.60 (4H, m, OCH₂CH₂), 3.45 (12H, s, N(CH₃)₄), 3.30 (2H, t, *J* 6, OCH₂CH₂), 3.16-1.66 (16H, m, B-H); $\delta_{\text{H}\{\text{B}\}}$ (300 MHz; CD₃COCD₃; (CH₃)₄Si) 4.49 (2H, br s, C_c-H), 4.19 (2H, br s, C_c-H), 3.68 (2H, t, *J* 6, OCH₂CH₂), 3.60 (4H, m, OCH₂CH₂), 3.45 (12H, s, N(CH₃)₄), 3.30 (2H, t, *J* 6, OCH₂CH₂), 3.16 (2H, s, B-H), 3.00 (2H, s, B-H), 2.85 (1H, s, B-H), 2.77 (1H, s, B-H), 2.36 (2H, s, B-H), 1.95 (1H, s, B-H), 1.72 (2H, s, B-H), 1.66 (3H, s, B-H); δ_{C} (75 MHz; CD₃COCD₃; (CH₃)₄Si) 71.6 (1C, s, OCH₂), 71.3 (1C, s, OCH₂), 68.2 (1C, s, OCH₂), 56.4 (2C, s, C_c-H), 55.2 (4C, s, N(CH₃)₄), 54.6 (2C, s, C_c-H), 3.11 (1C, s, CH₂I); δ_{B} (96 MHz; CD₃COCD₃; BF₃·OEt₂) 22.4 (1B, s, B(8)), 0.4 (2B, d, *J* 147), -3.9 (2B, d, *J* 109), -4.9 (4B, d, *J* 140), -6.4 (2B, d, *J* 127), -6.4 (1B, s, B(8')), -17.1 (2B, d, *J* 180), -19.2 (2B, d, *J* 177), -22.4 (1B, d, *J* 177), -26.5 (1B, d, *J* 165); *m/z* (MALDI-TOF-MS) 664.2 (M, 100.0%).

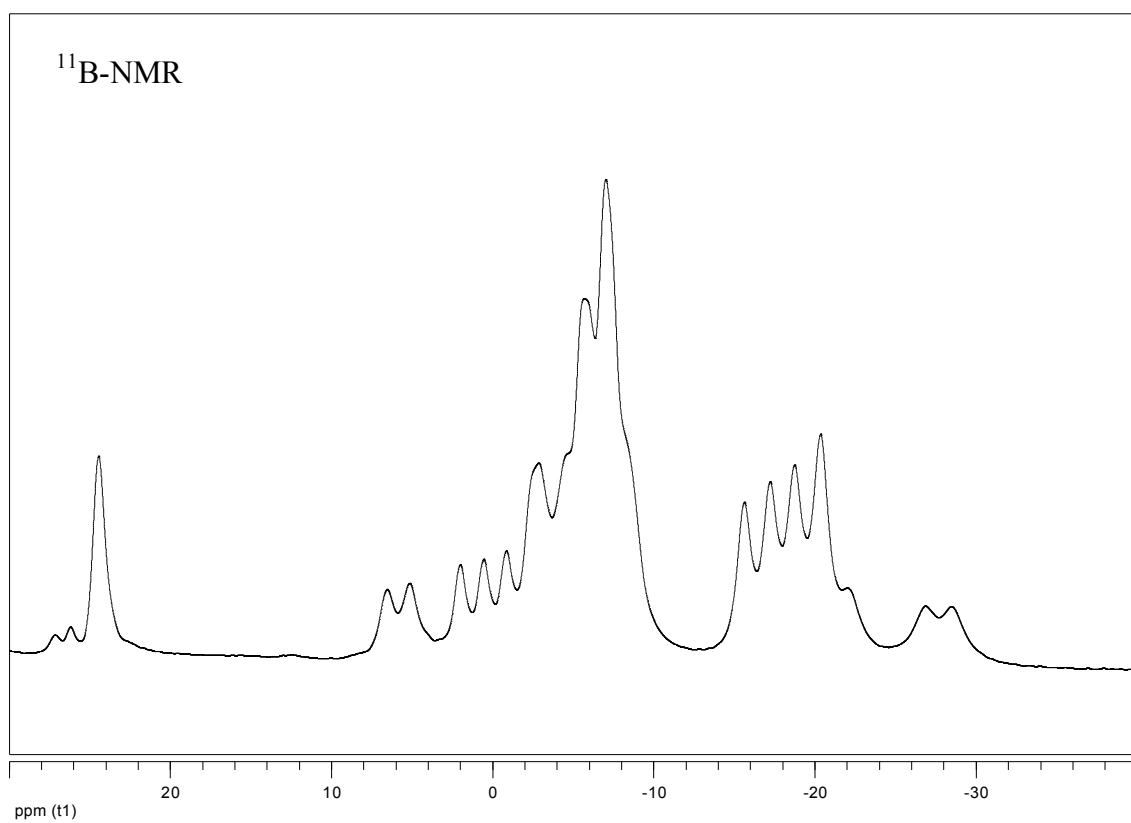
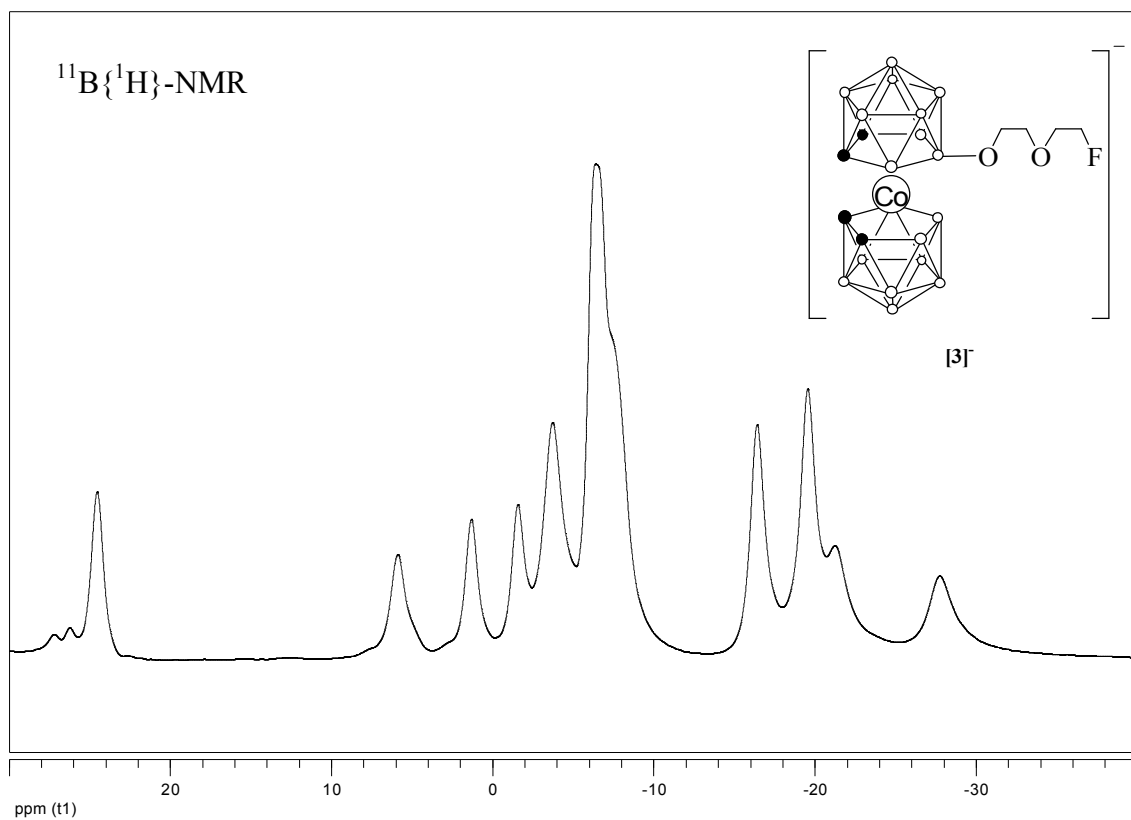
Synthesis of [N(CH₃)₄][3,3'-Co(8-(OCH₂CH₂)₂SH-1,2-C₂B₉H₁₀)(1',2'-C₂B₉H₁₁)], [N(CH₃)₄][9]. This compound was prepared using the same procedure as for Na[3], but using sodium hydrosulfide (15 mg, 0.244 mmol) instead of hydrofluoric acid, and the reaction mixture was heated under reflux for 6h after overnight stirring. After the work-up procedure, the desired [N(CH₃)₄][9] was obtained (0.11 g, 85%). (Found: C, 27.8; H, 8.1; N, 2.6; S, 6.4%. Calcd for C₁₂H₄₂B₁₈CoNO₂S: C, 27.8; H, 8.2; N, 2.7; S, 6.2%); $\mu_{\max}/\text{cm}^{-1}$ 3042 (C_c-H), 2889 (C_{alkyl}-H), 2556 and 2533 (B-H), 1437 and 1376 (CH₂), 1149, 1125, 1122 and 1101 (C-O-C) and 946 (C-N); δ_{H} (300 MHz; CD₃COCD₃; (CH₃)₄Si) 4.27 (4H, br s, C_c-H), 3.70 (2H, t, *J* 6, OCH₂CH₂), 3.58 (2H, m, OCH₂CH₂), 3.50 (2H, m, OCH₂CH₂), 3.44 (12H, s, N(CH₃)₄), 2.91 (2H, t, *J* 6, CH₂SH), 2.92-1.46 (17H, m, B-H), 1.39 (1H, s, S-H); $\delta_{\text{H}\{\text{B}\}}$ (300 MHz; CD₃COCD₃; (CH₃)₄Si) 4.27 (4H, br s, C_c-H), 3.70 (2H, t, *J* 6, OCH₂CH₂), 3.58 (2H, m, OCH₂CH₂), 3.50 (2H, m, OCH₂CH₂), 3.44 (12H, s, N(CH₃)₄), 2.91 (2H, t, *J* 6, CH₂SH), 2.92 (3H, s, B-H), 2.76 (2H, s, B-H), 2.69 (1H, s, B-H), 2.39 (1H, s, B-H), 1.97 (2H, s, B-H), 1.77 (2H, s, B-H), 1.71 (1H, s, B-H), 1.65 (2H, s, B-H), 1.55 (2H, s, B-H), 1.46 (1H, s, B-H), 1.39 (1H, s, S-H); δ_{C} (75 MHz; CD₃COCD₃; (CH₃)₄Si) 72.6 (1C, s, OCH₂), 69.2 (1C, s, OCH₂), 68.3

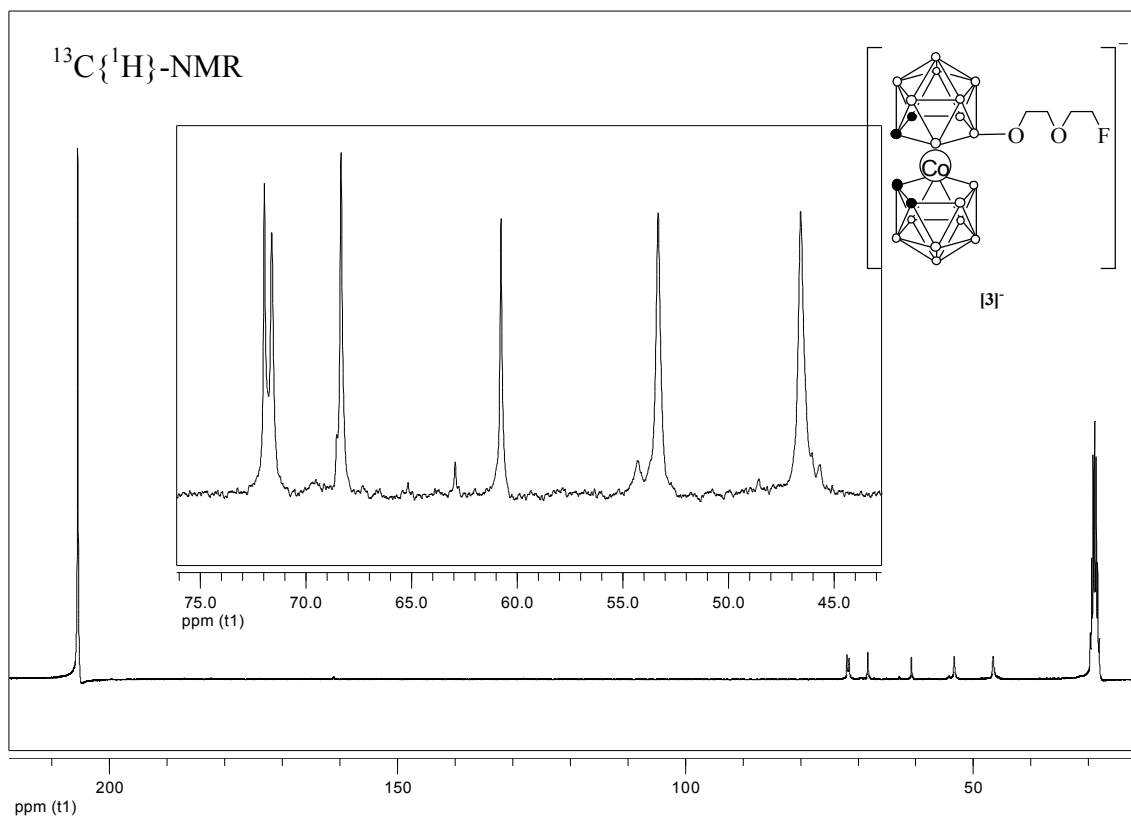
(1C, s, OCH₂), 55.3 (4C, s, N(CH₃)₄), 54.7 (2C, s, C_c-H), 46.4 (2C, s, C_c-H), 38.7 (1C, s, CH₂SH); δ_B(96 MHz; CD₃COCD₃; BF₃·OEt₂) 22.8 (1B, s, B(8)), 3.7 (1B, d, *J* 135), 0.5 (1B, d, *J* 143), -2.4 (1B, d, *J* 147), -4.1 (2B, d, *J* 159), -7.5 (2B, d, *J* 89), -8.2 (4B, d, *J* 121), -17.2 (2B, d, *J* 153), -20.4 (2B, d, *J* 149), -21.8 (1B, d), -28.4 (1B, d, *J* 149); *m/z* (MALDI-TOF-MS) 458.7 (M+CH₂, 6.6%), 444.7 (M, 27.5), 410.6 (M-SH, 10.1), 382.6 (M-C₂H₄SH, 19.8), 366.5 (M-OC₂H₄SH, 15.3), 337.5 (M-OC₄H₈SH, 18.1), 324.5 (M-O₂C₄H₈SH, 2.5).

Synthesis of [N(CH₃)₄][3,3'-Co(8-OCH₂CH₂OH-1,2-C₂B₉H₁₀)(1',2'-C₂B₉H₁₁)], [N(CH₃)₄][10]. To a 25 mL round-bottom flask were added Mg metal (45 mg, 1.85 mmol) and 2 mL of anhydrous THF. Then, a solution of [N(CH₃)₄][5] (50 mg, 0.09 mmol) in THF and dibromoethane (0.05 mL, 0.12 mmol) were added dropwise, at the same time, to the Mg suspension. Once the addition was completed the reaction mixture was left refluxing. When it returns to room temperature, water is added to destroy the excess of magnesium. The solution is evaporated. The resulting residue is dissolved in Et₂O and extracted 3x HCl (1M). The product was redissolved in the minimum volume of ethanol and an aqueous solution containing an excess of [N(CH₃)₄]Cl was added, resulting in the formation of an orange precipitate. This was filtered off, washed with water and petroleum ether, and dried in vacuo. The desired compound was obtained as N(CH₃)₄[10] (0.03 g, 76%). (Found: C, 26.2; H, 8.3; N, 3.1%. Calcd for C₁₀H₃₈B₁₈CoNO₂: C, 26.2; H, 8.4; N, 3.1%); μ_{max}/cm⁻¹ 3524 (O-H), 3038 (C-H)_c, 2956, 2925 and 2857 (C-H)_{aryl/alkyl}, 2556 (B-H), 1482 δ(CH₃), 1167 δ(CH) and 946 (C-N); δ_H(300 MHz; CD₃COCD₃; (CH₃)₄Si) 4.18 (4H, br s, C_c-H), 3.55 (4H, m, OCH₂CH₂), 3.44 (12H, s, N(CH₃)₄), 2.94 (1H, br s, O-H), 2.88-1.44 (17H, m, B-H); δ_{H(B)}}(300 MHz; CD₃COCD₃; (CH₃)₄Si) 4.18 (4H, br s, C_c-H), 3.55 (4H, m, OCH₂CH₂), 3.44 (12H, s, N(CH₃)₄), 2.94 (1H, br s, O-H), 2.88 (3H, s, B-H), 2.71 (2H, s, B-H), 2.69 (1H, s, B-H), 2.67 (1H, s, B-H), 2.00 (2H, s, B-H), 1.78 (2H, s, B-H), 1.68 (1H, s, B-H), 1.61 (2H, s, B-H), 1.54 (2H, s, B-H), 1.44 (1H, s, B-H); δ_C(75 MHz; CD₃COCD₃; (CH₃)₄Si) 70.36 (1C, s, OCH₂), 62.66 (1C, s, CH₂OH), 55.22 (4C, s, N(CH₃)₄), 53.67 (2C, s, C_c-H), 46.36 (2C, s, C_c-H); δ_B(96 MHz; CD₃COCD₃; BF₃·OEt₂) 24.31 (1B, s, B(8)), 5.45 (1B, d, *J* 137), 1.07 (1B, d, *J* 142), -1.84 (1B, d, *J* 162), -3.69 (2B, d, *J* 164), -6.57 (2B, d, *J* 125), -7.30 (4B, d, *J* 123), -16.57 (2B, d, *J* 155), -19.57 (2B, d, *J* 159), -21.40 (1B, d, *J* 179), -27.94 (1B, d, *J* 166); *m/z* (MALDI-TOF-MS) 384.31 (M, 100%).

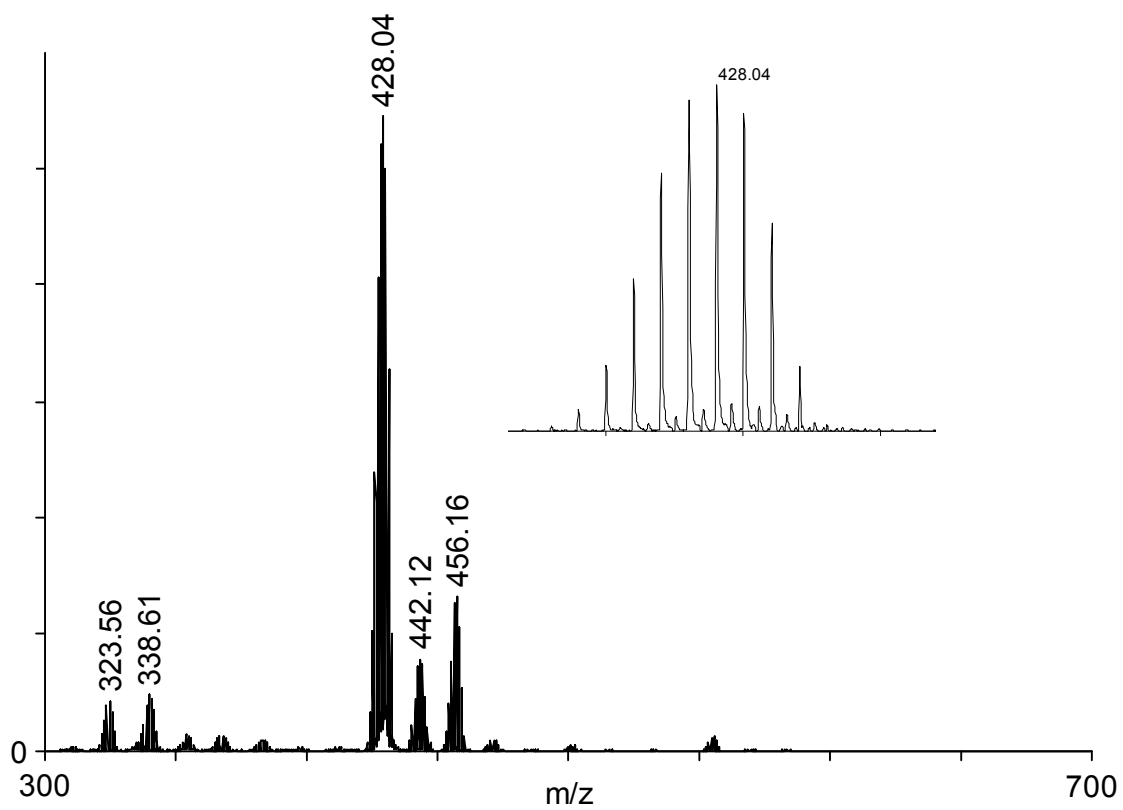
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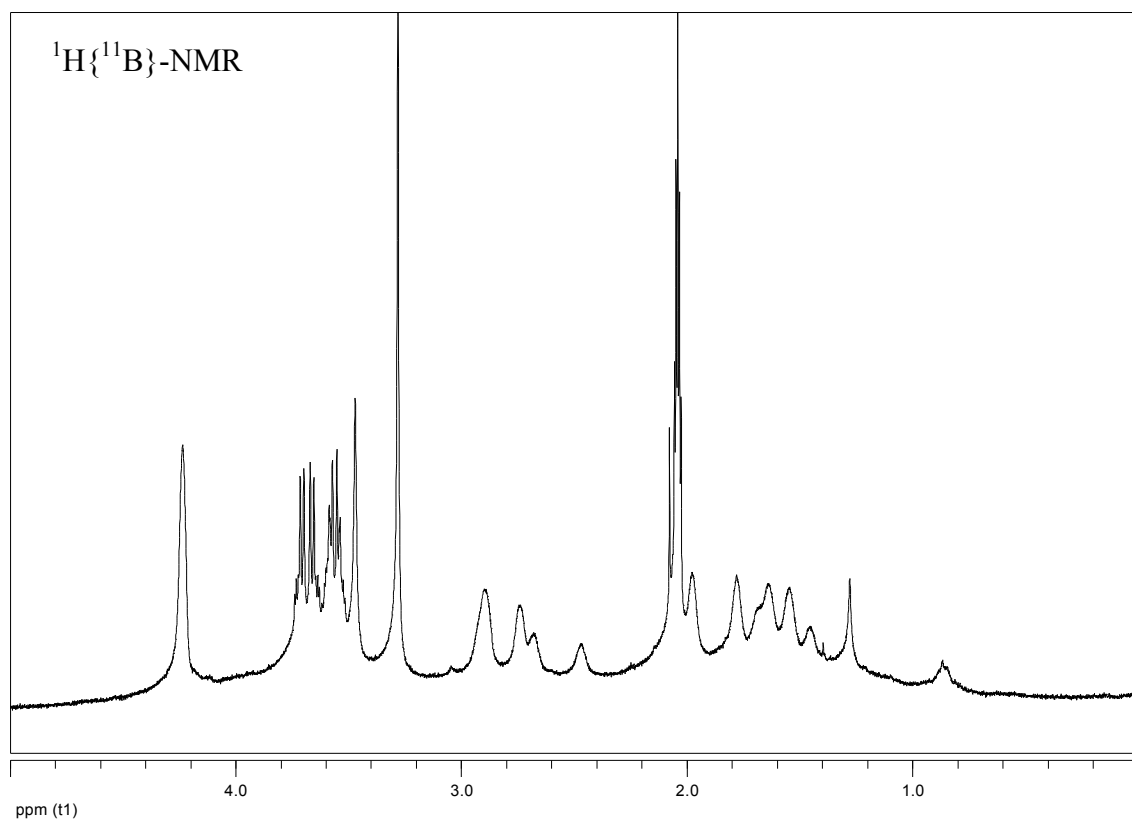
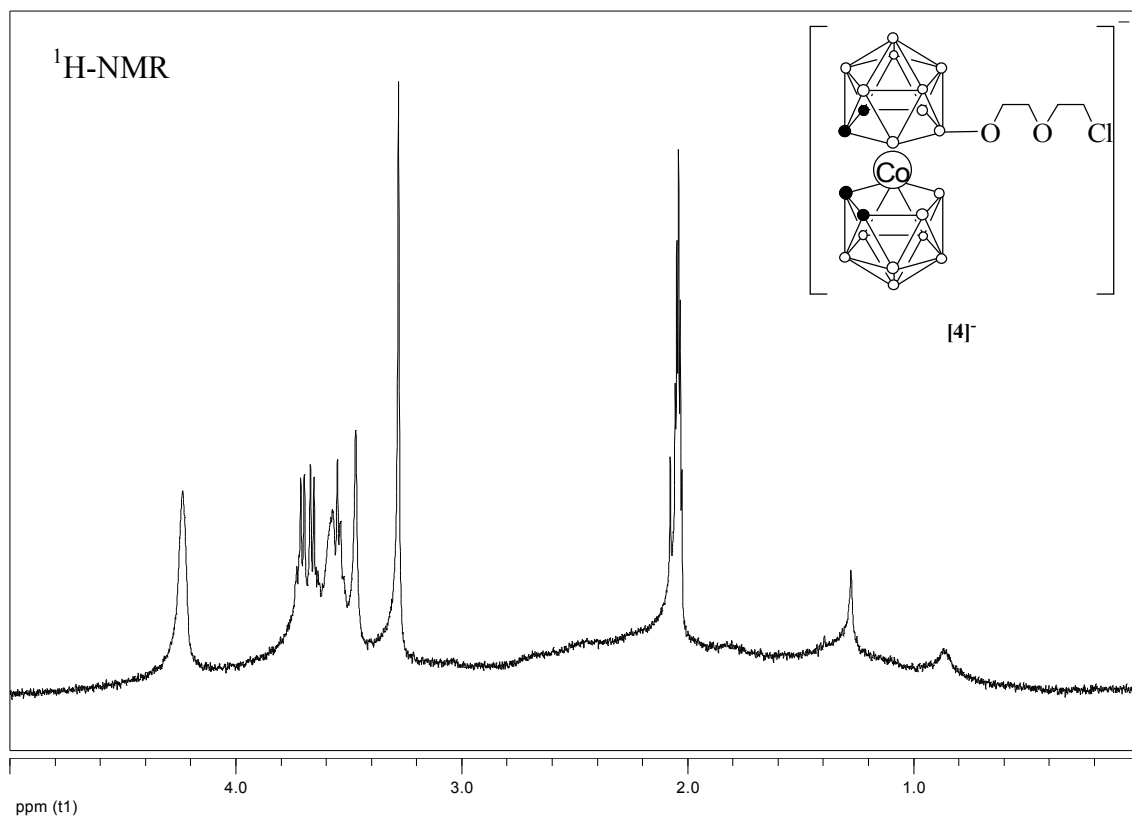


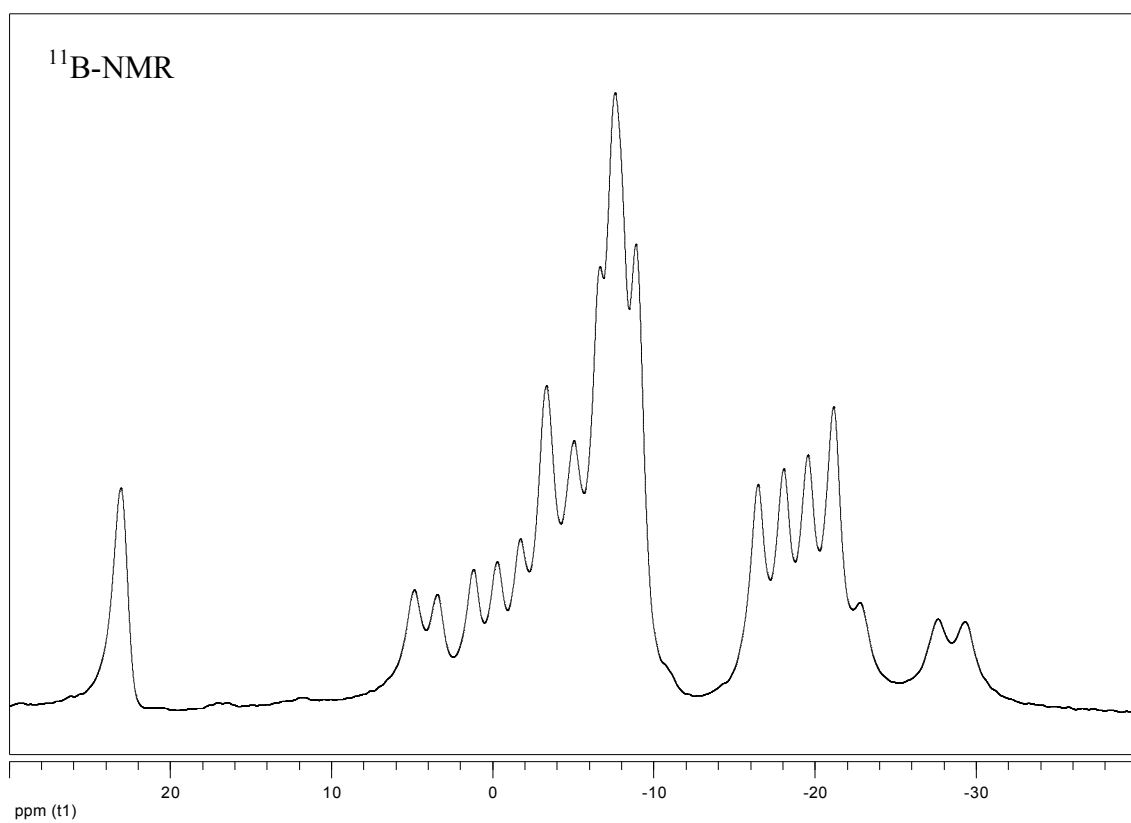
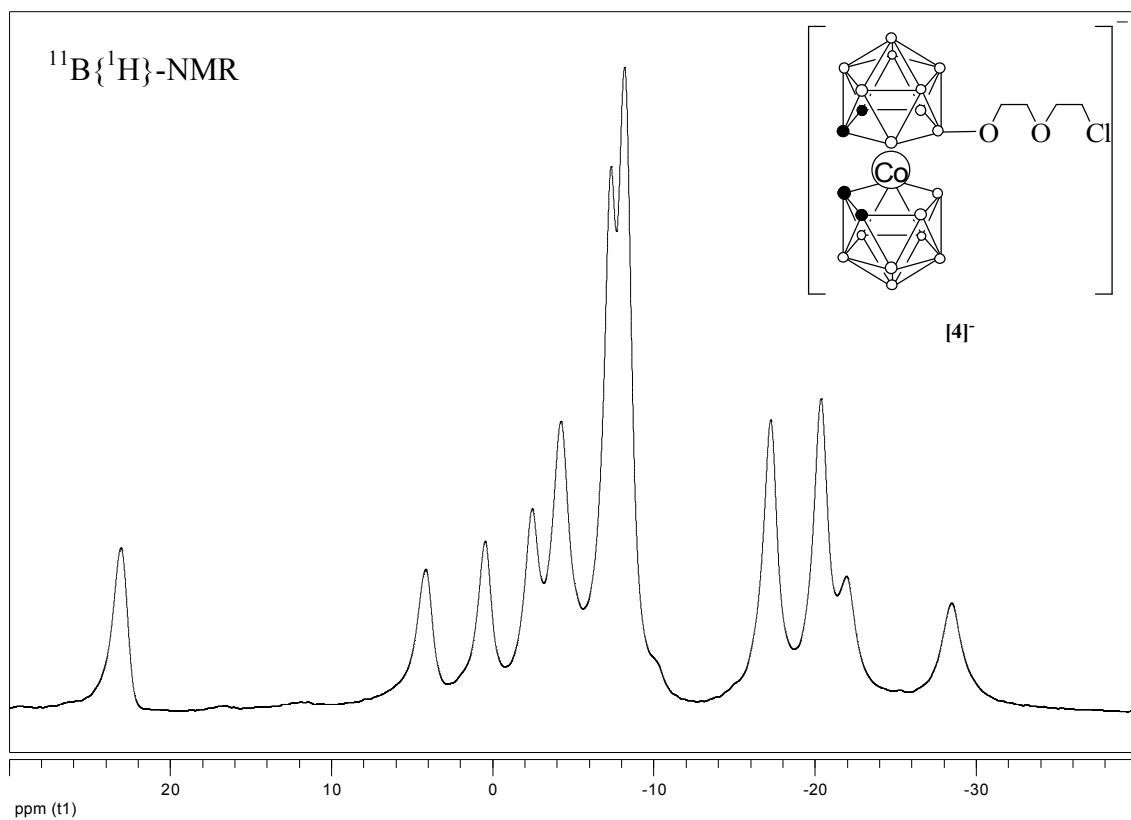


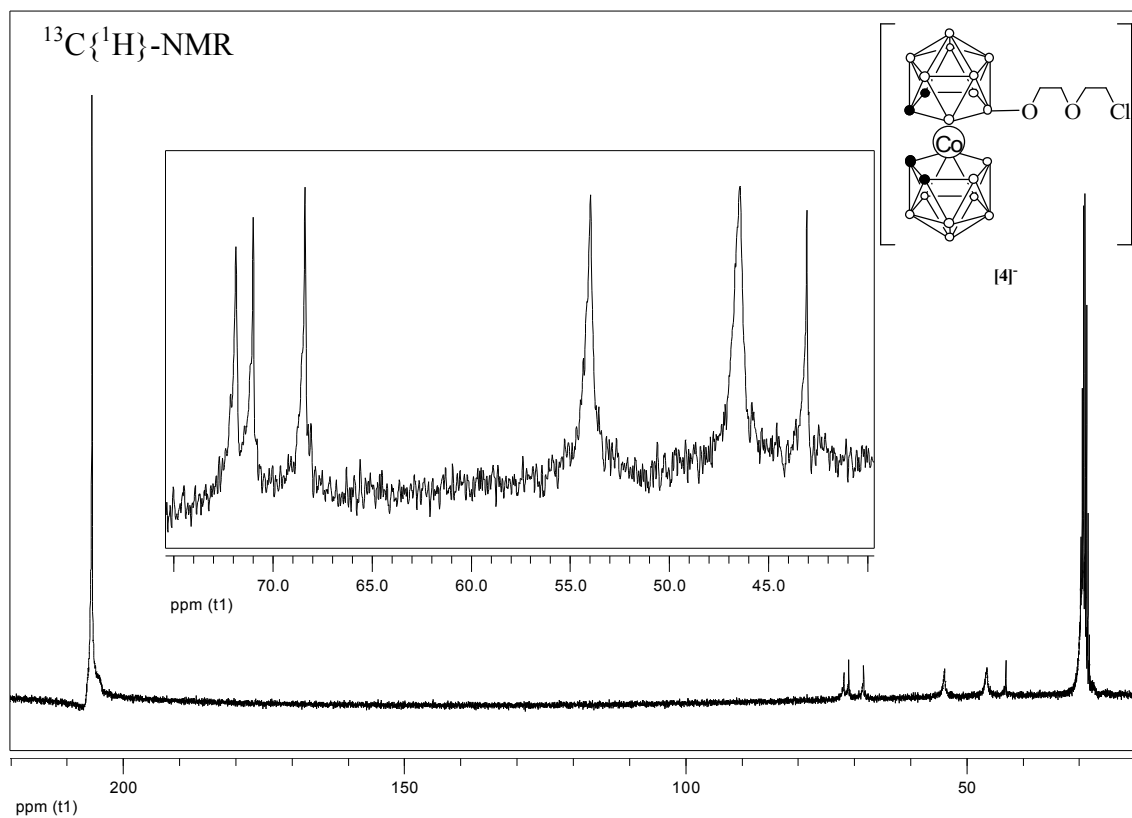


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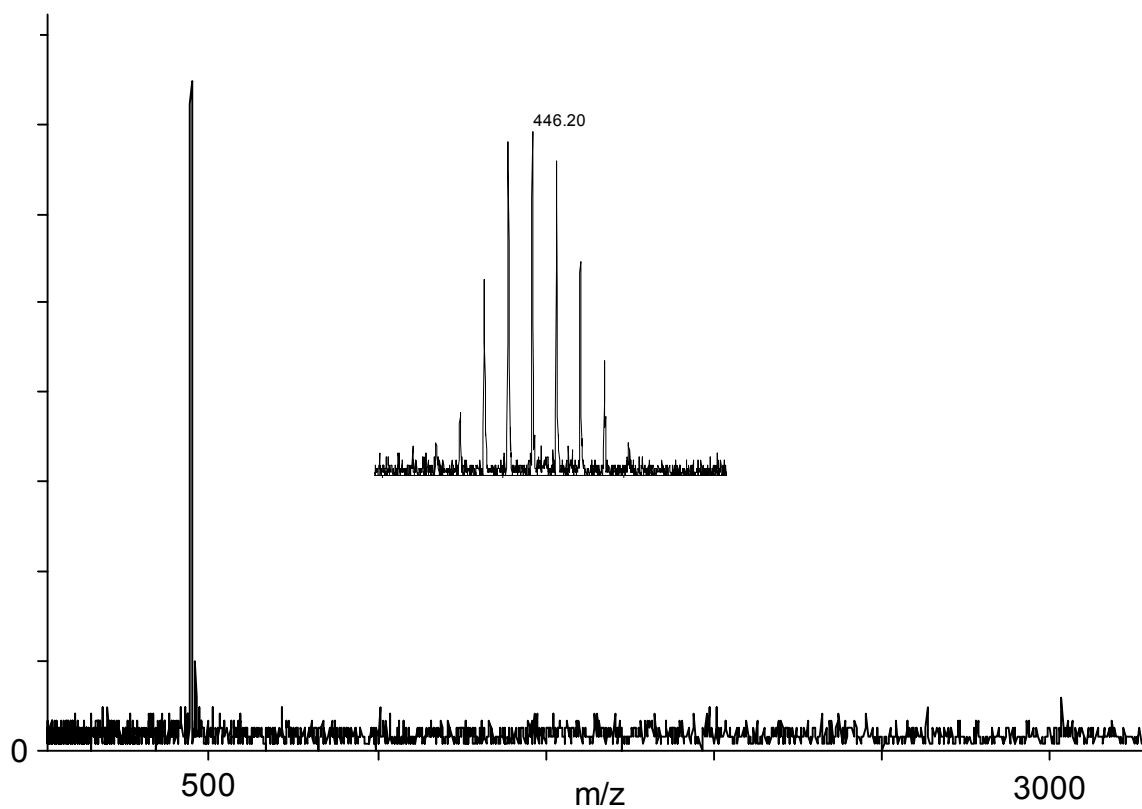


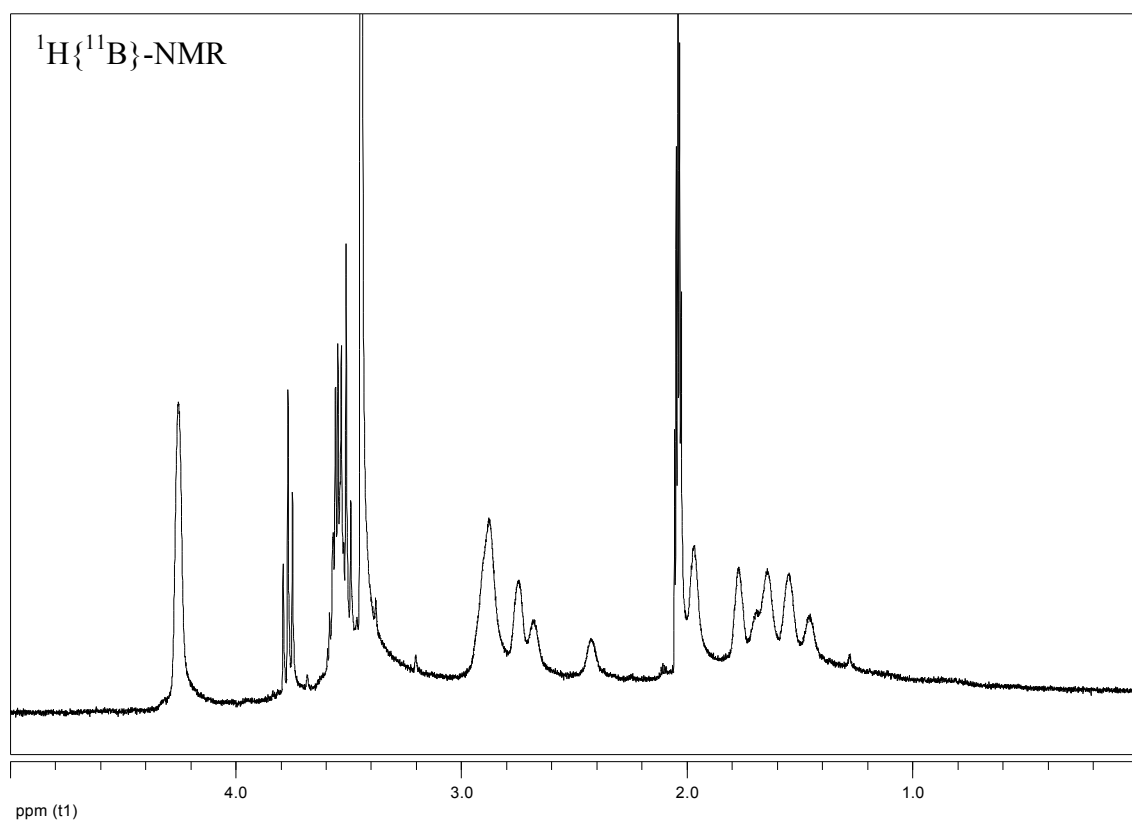
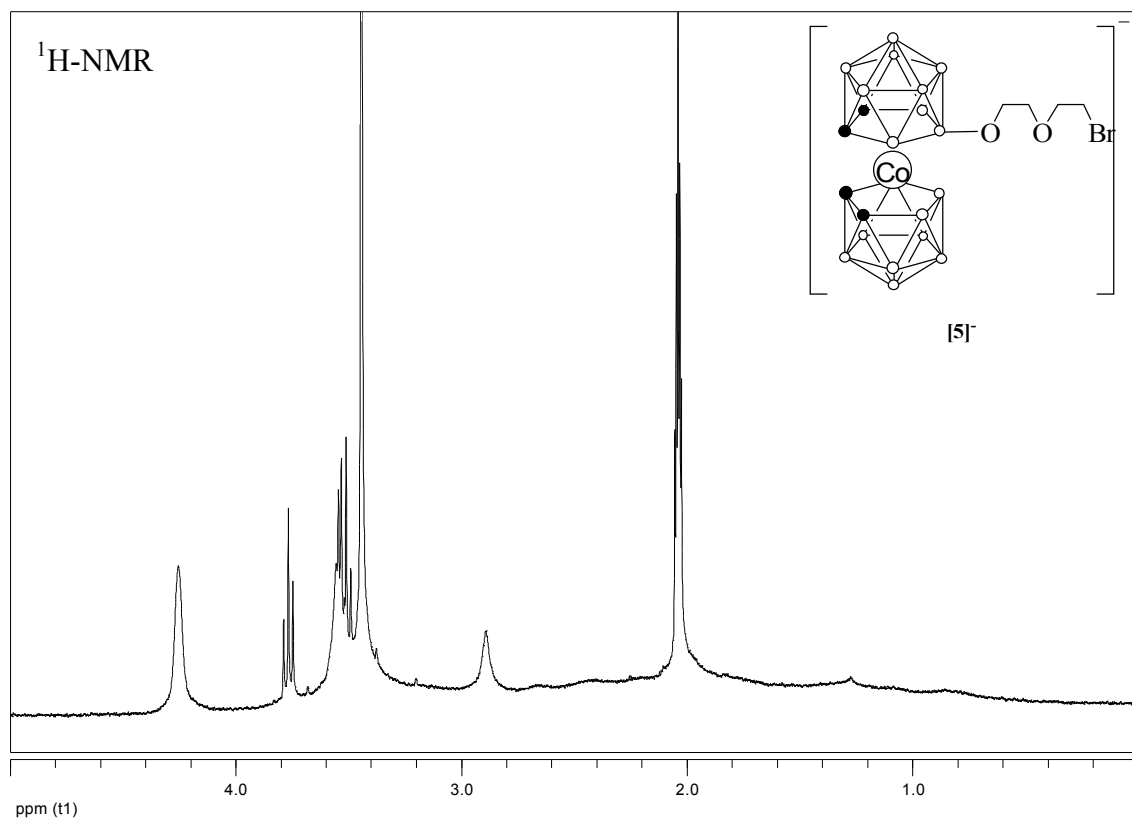


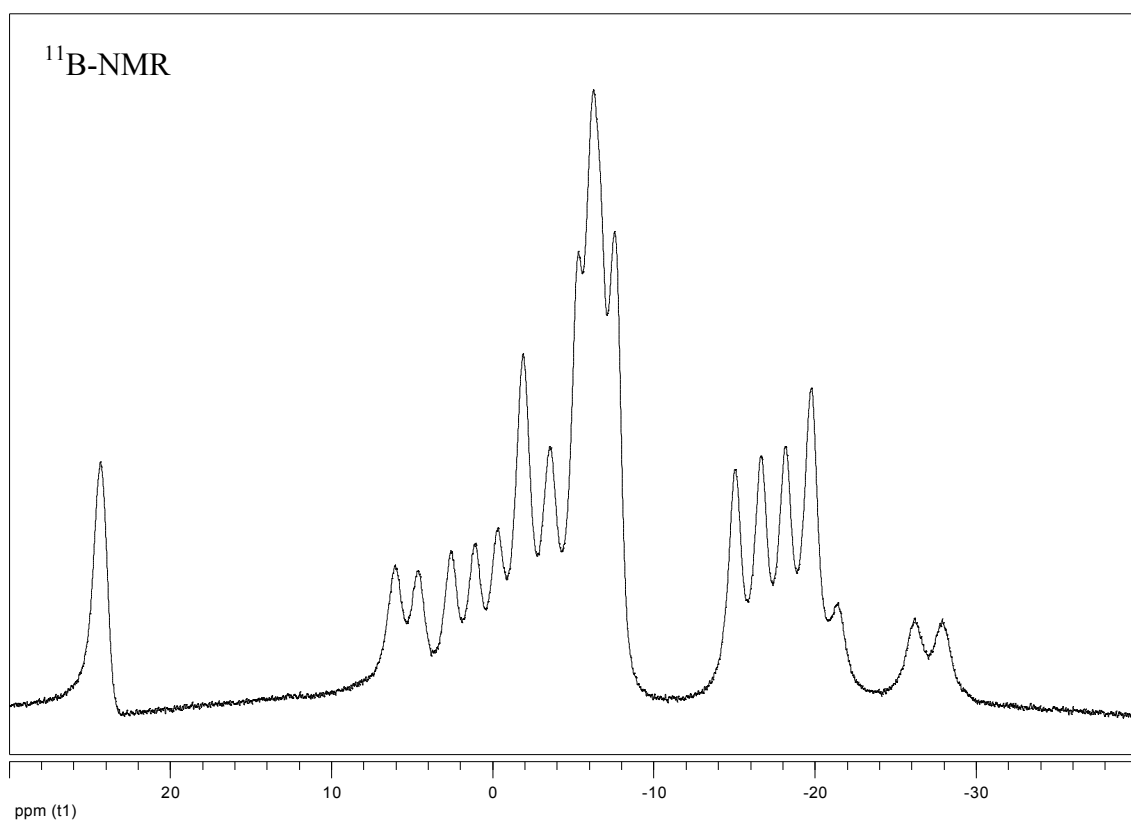
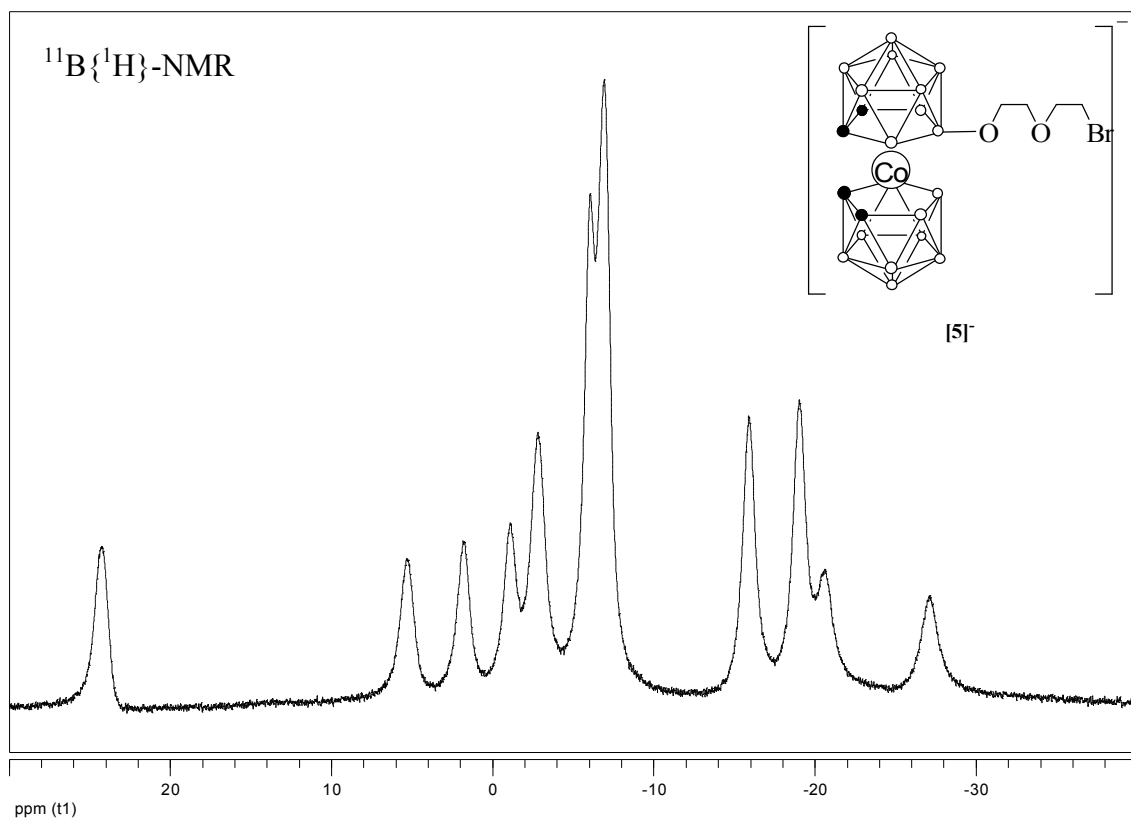


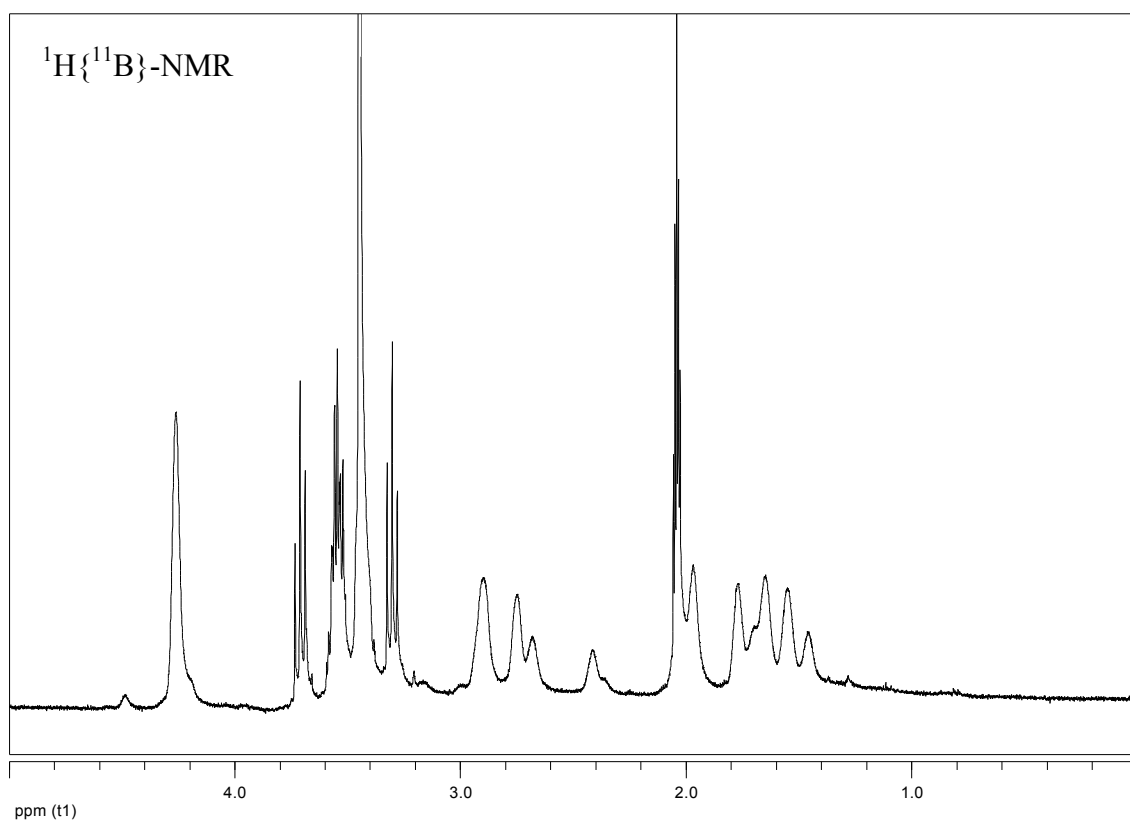
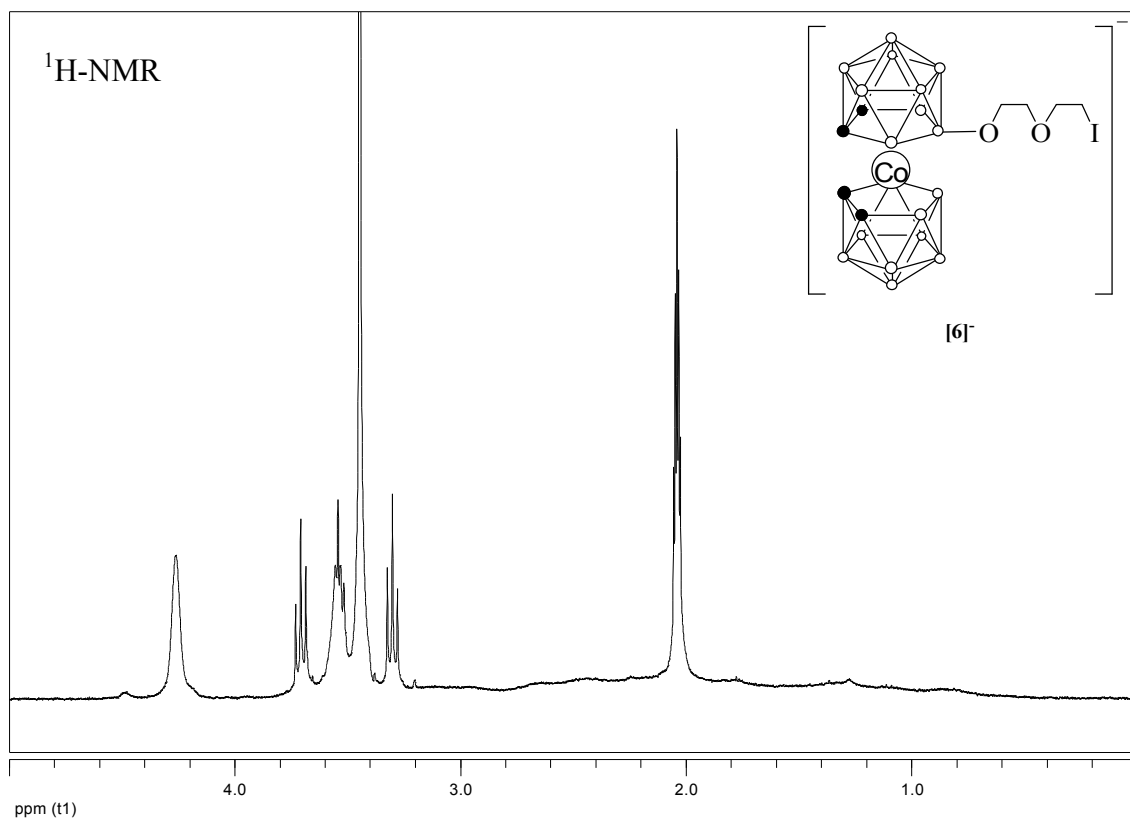


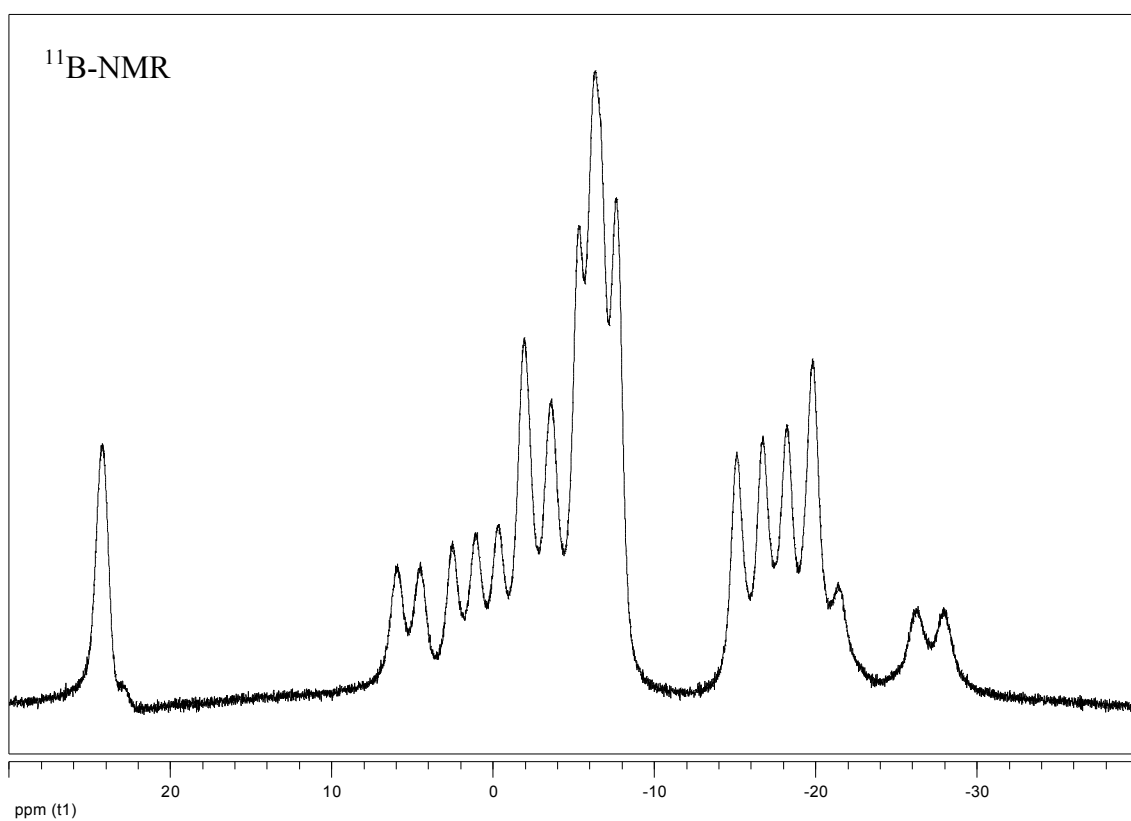
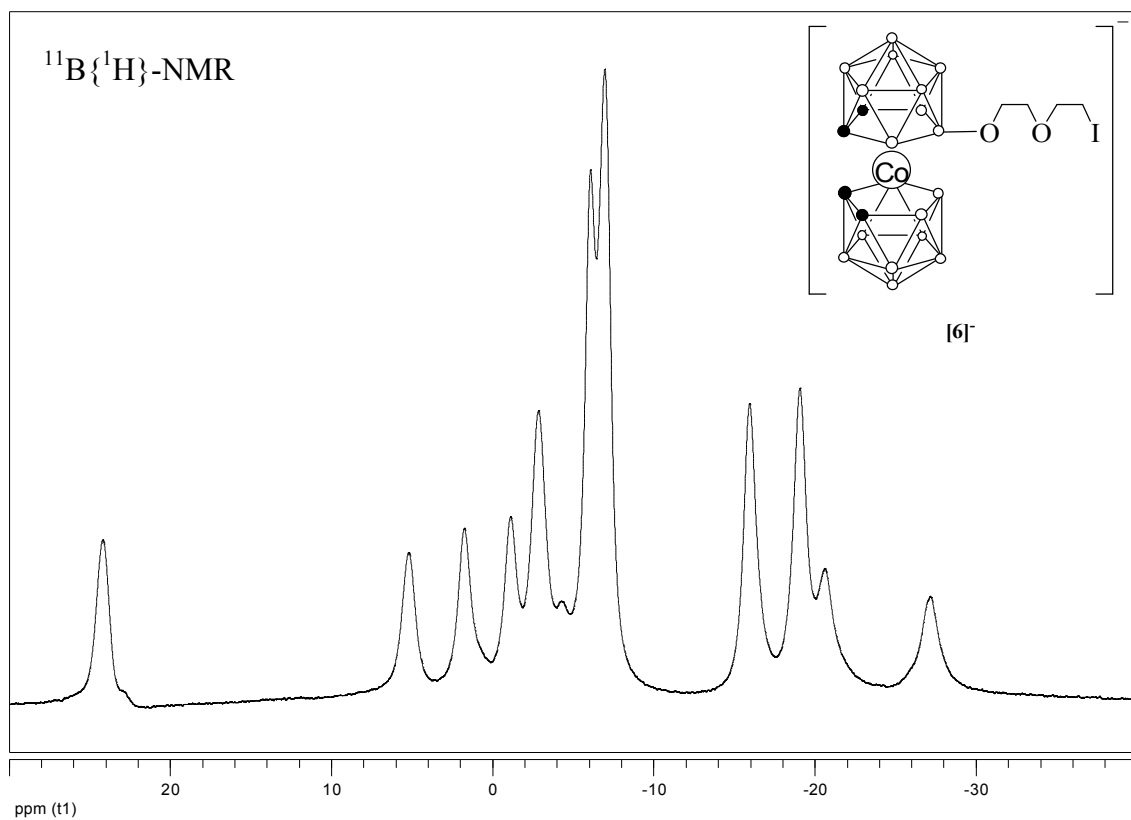
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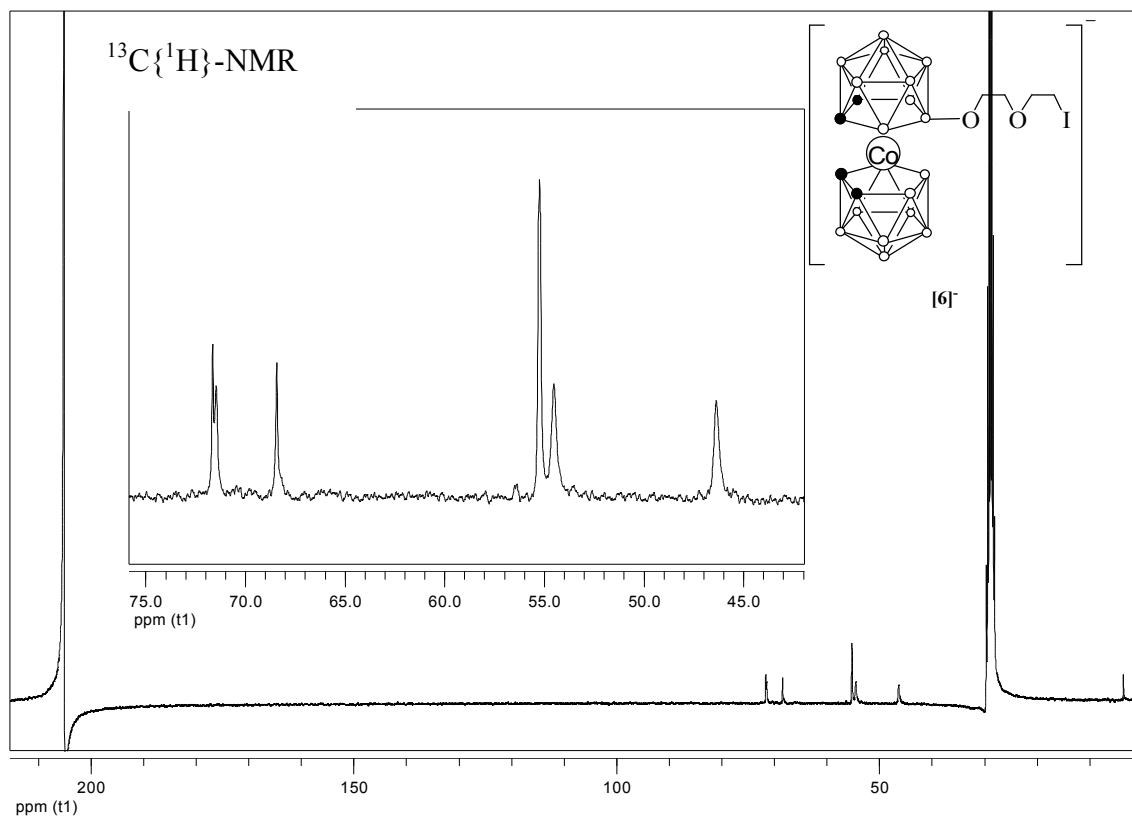




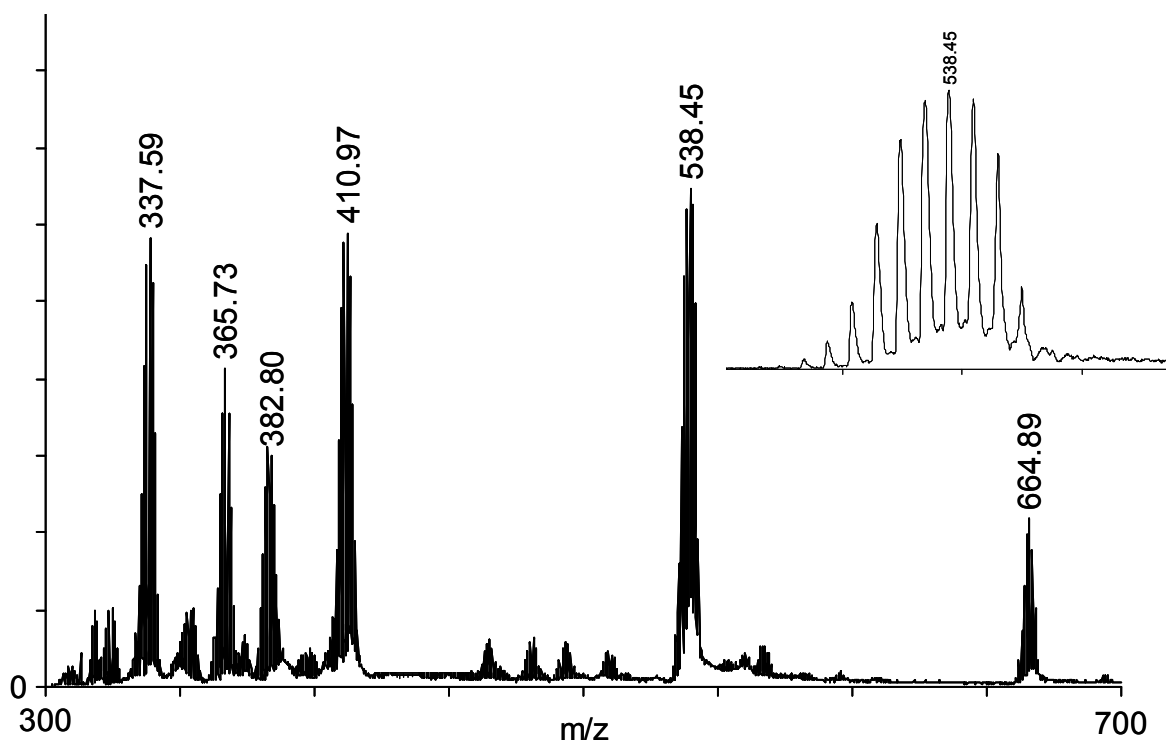


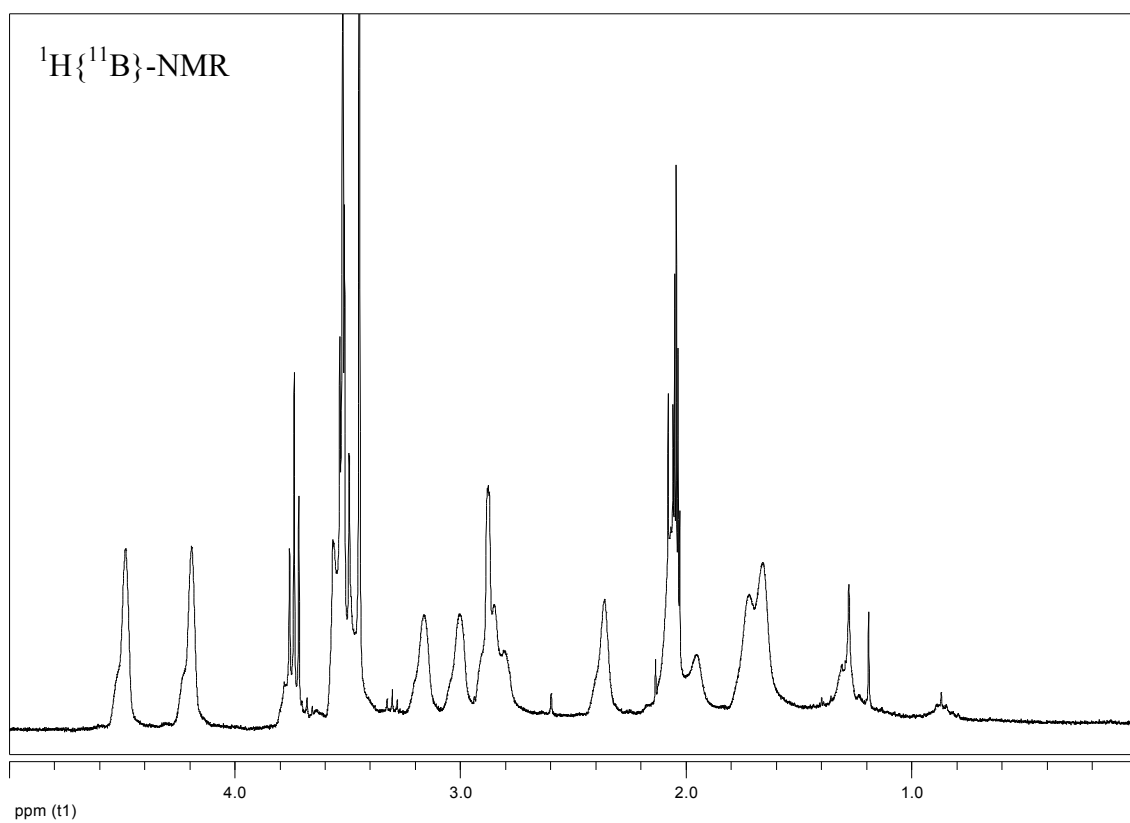
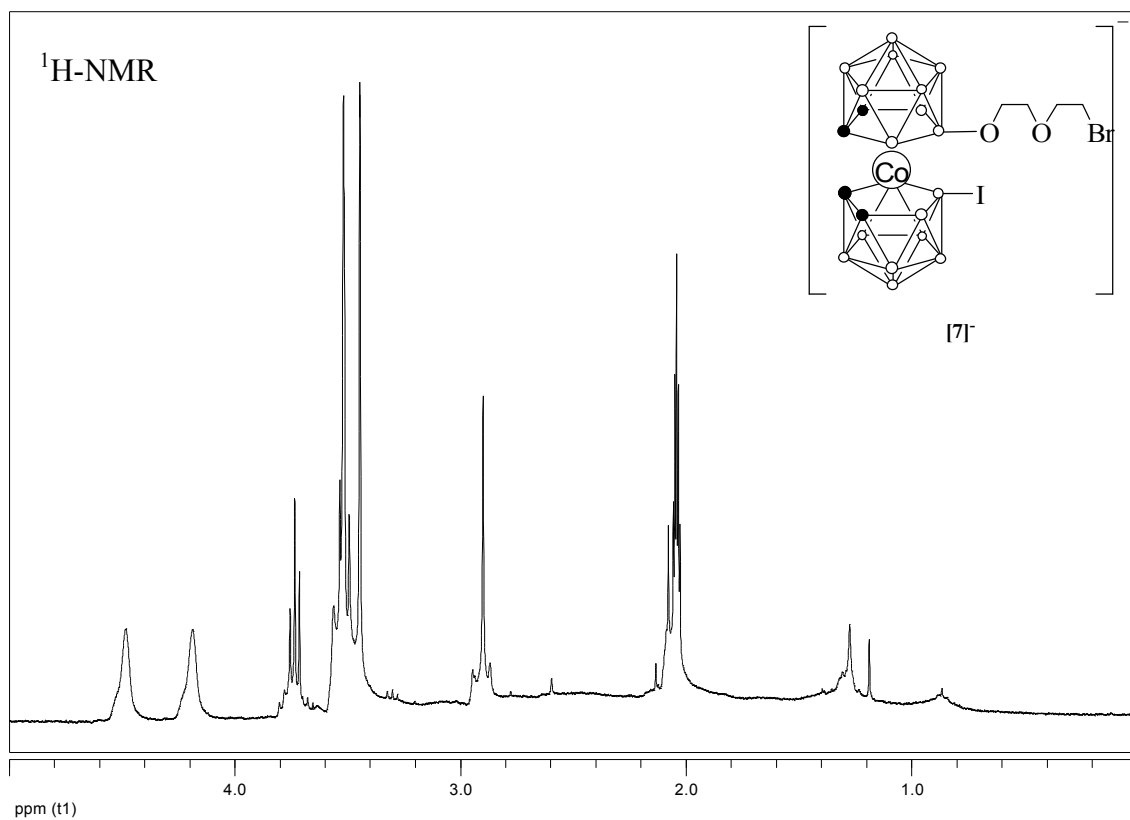


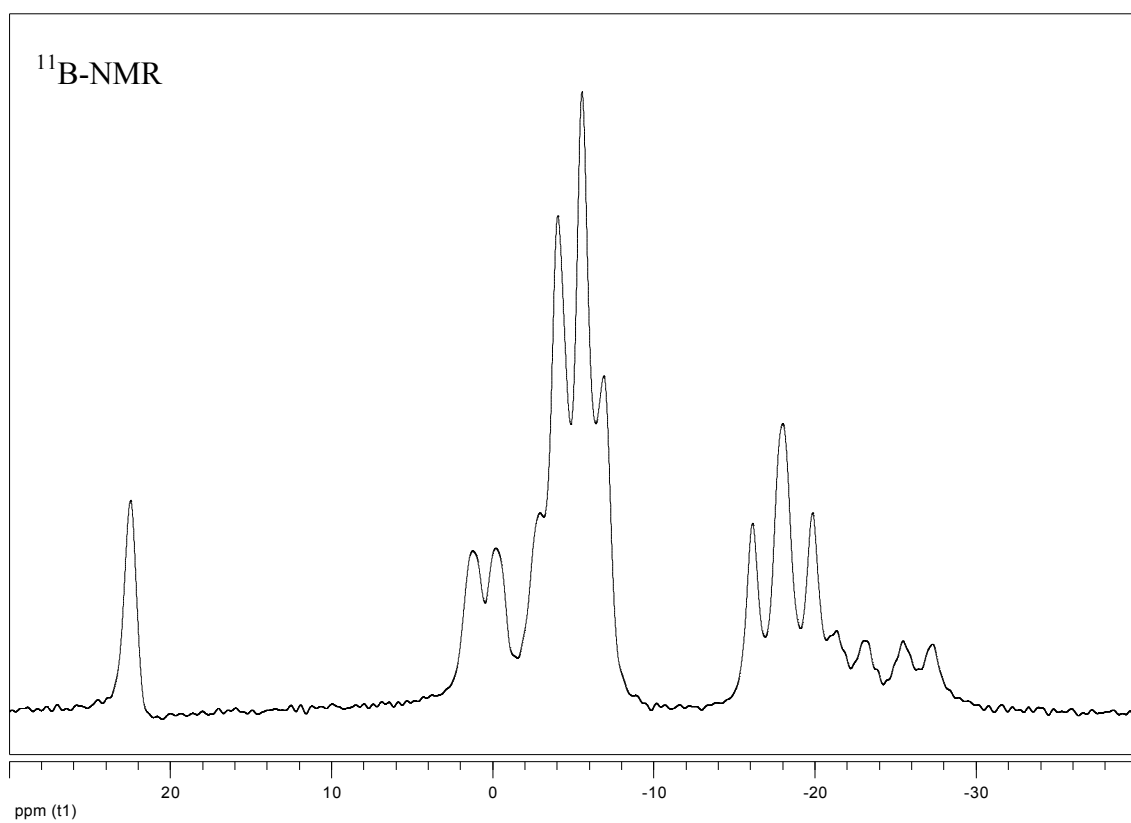
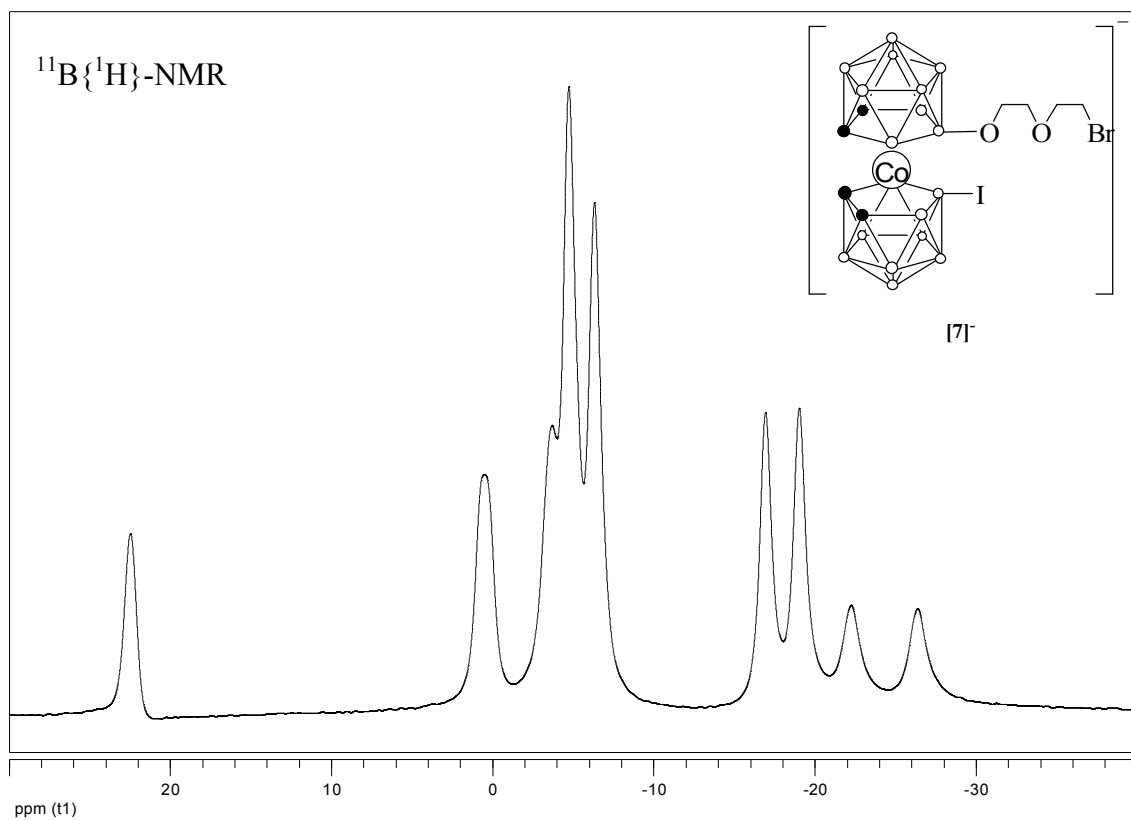


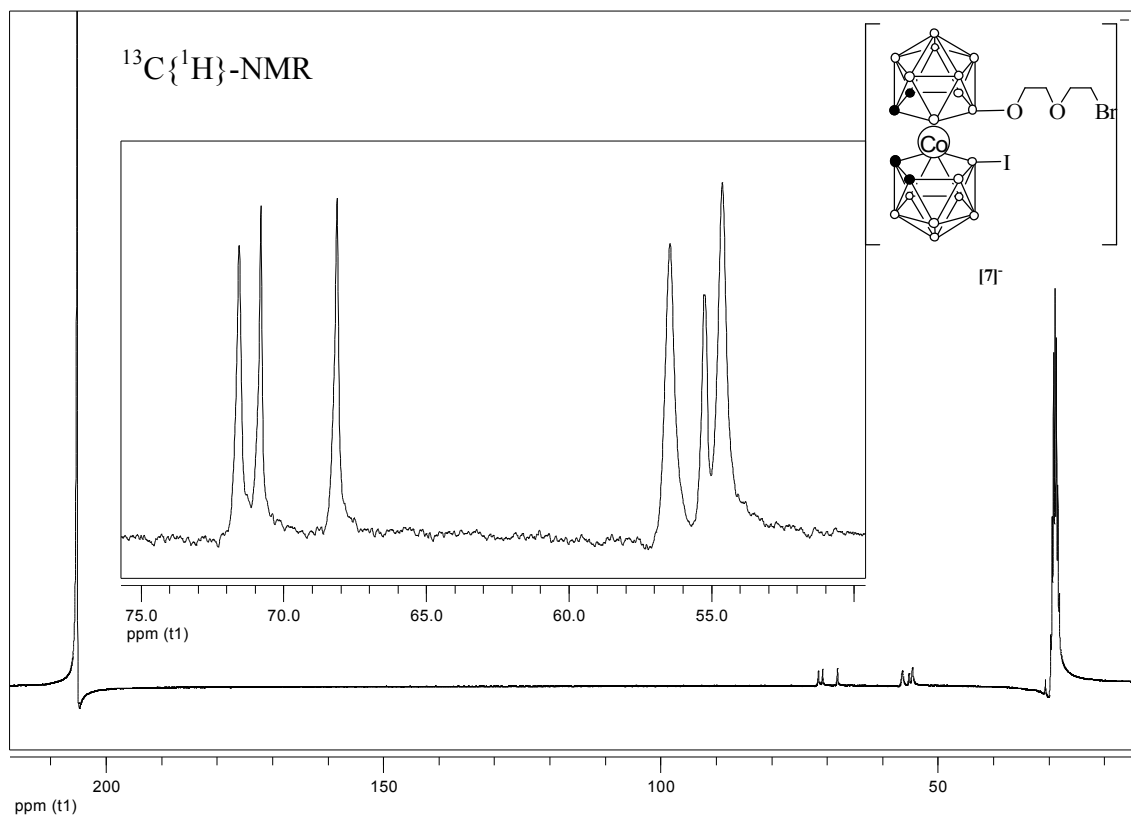


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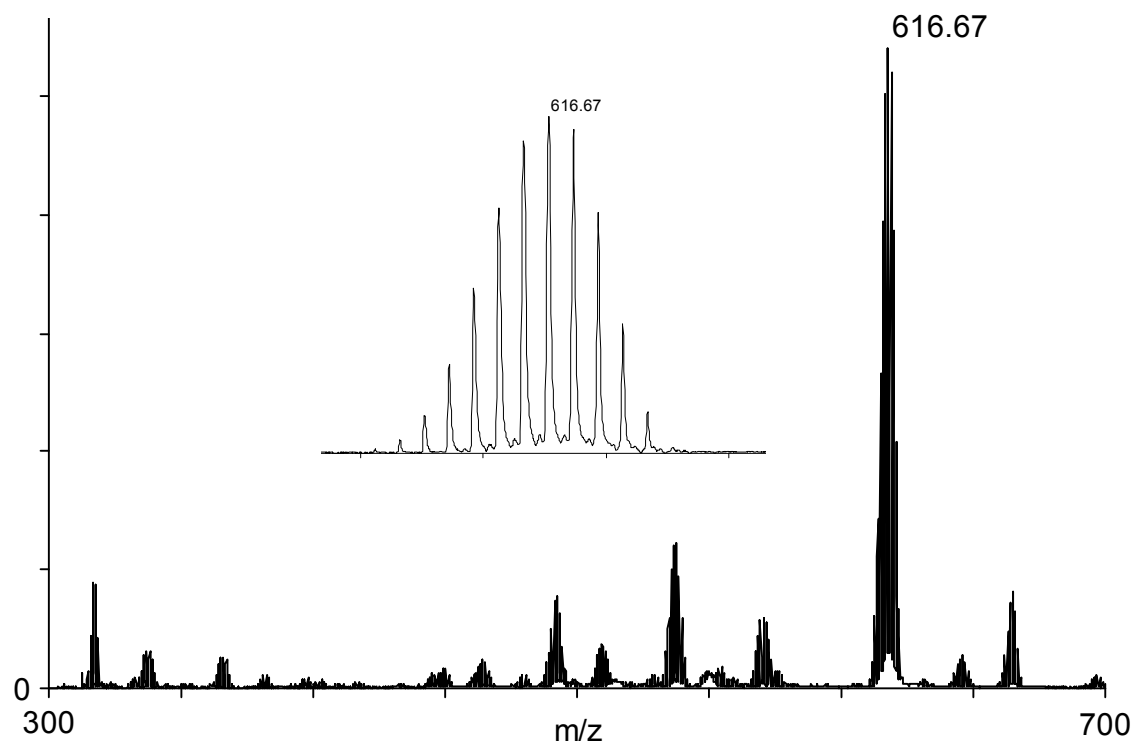


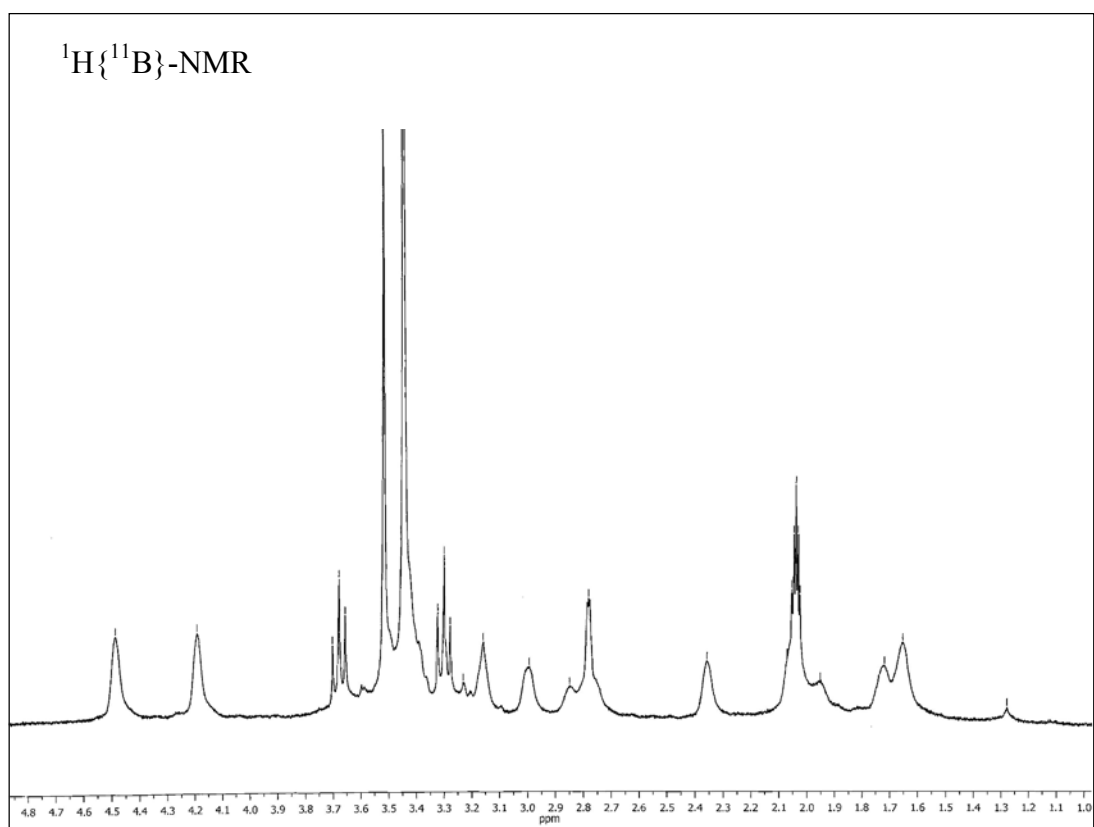
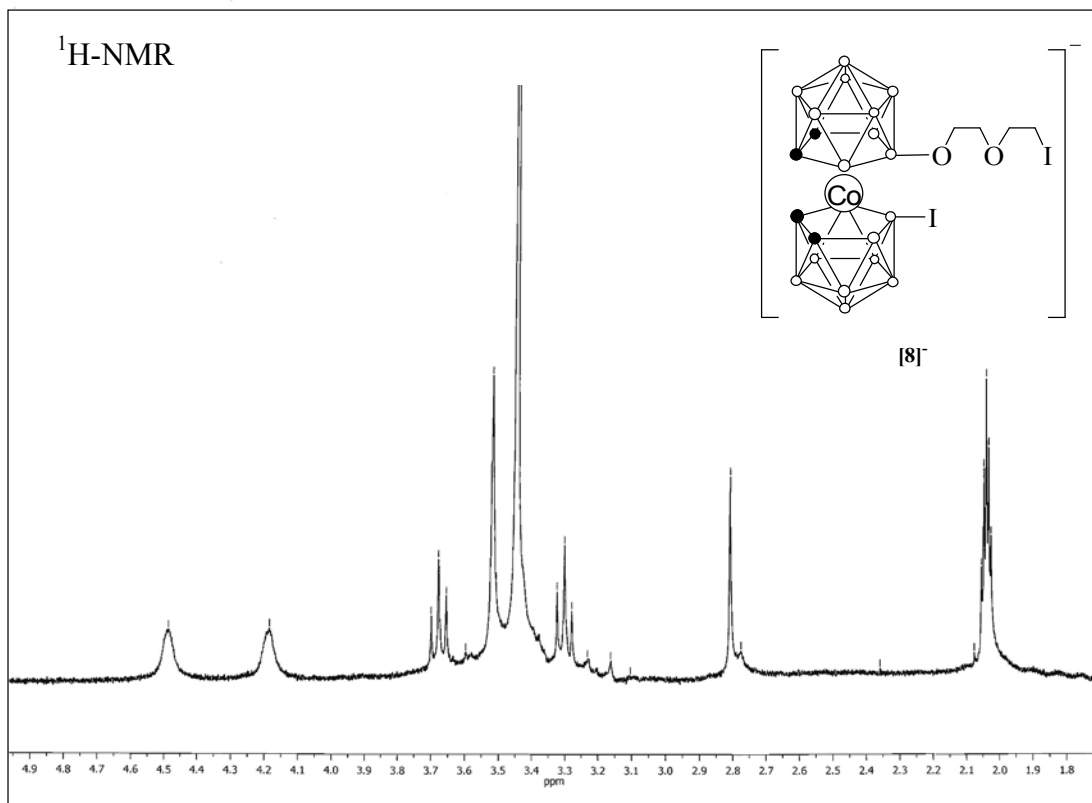


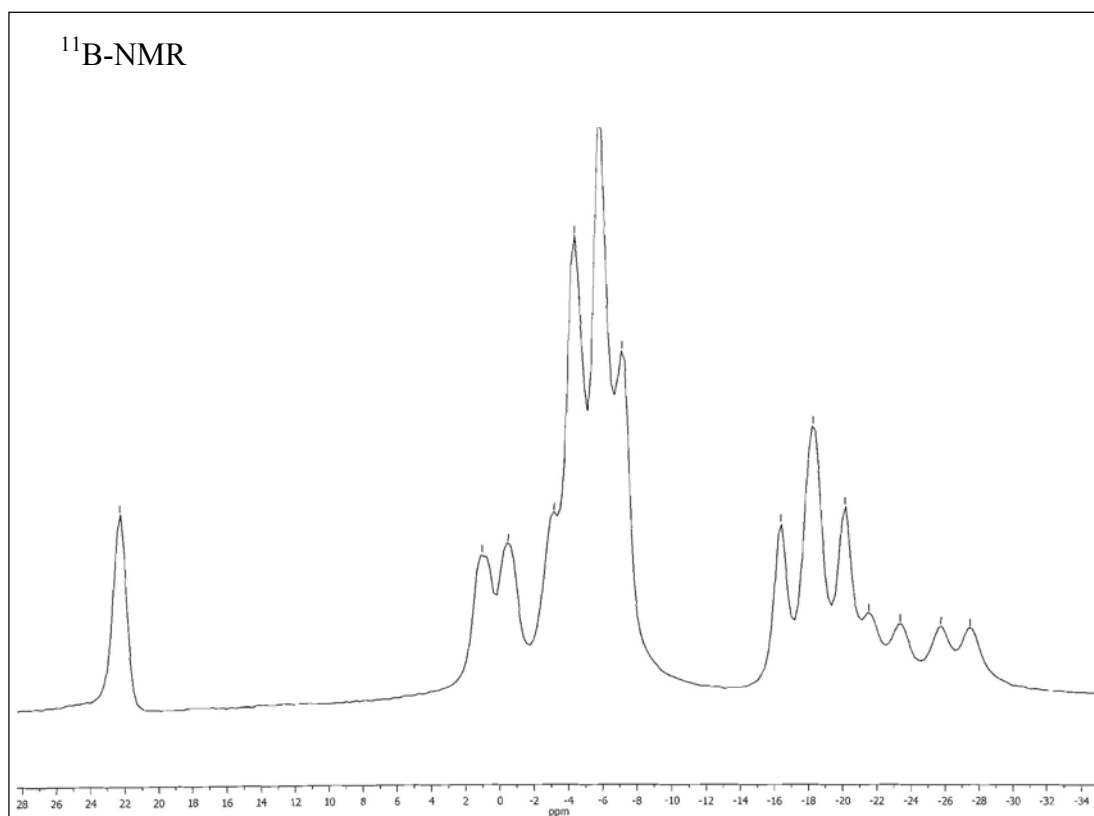
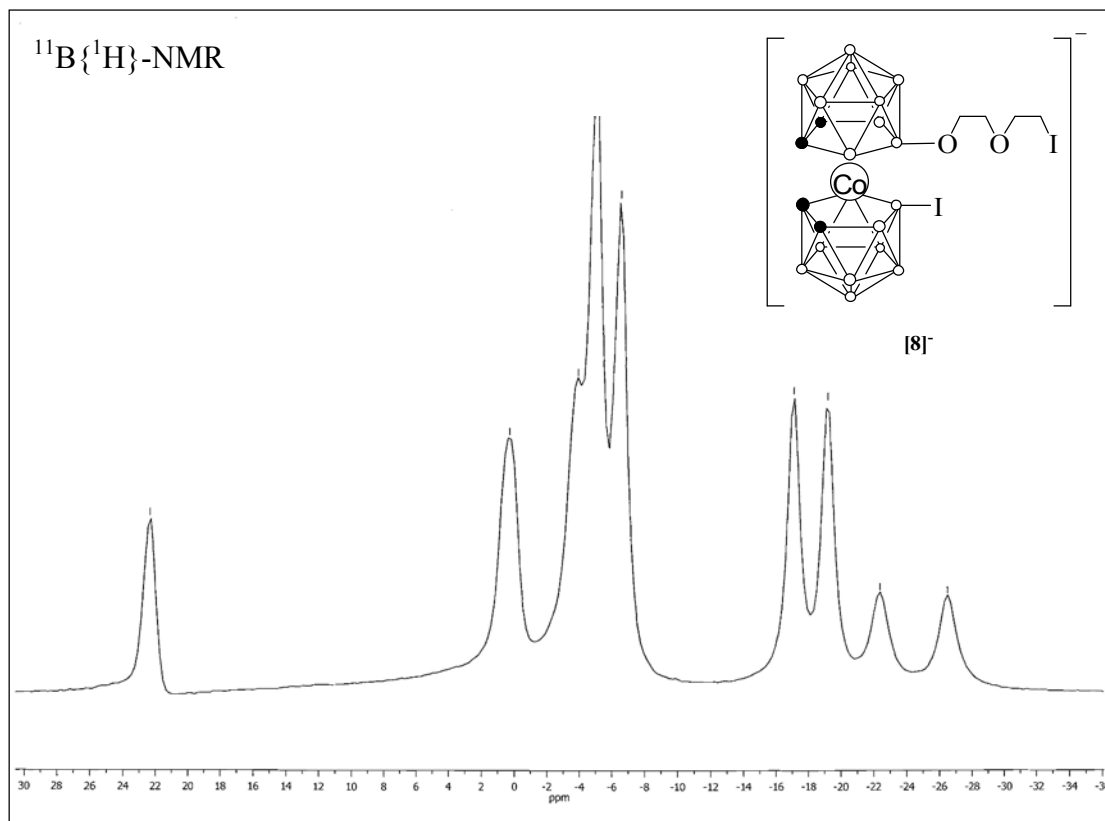


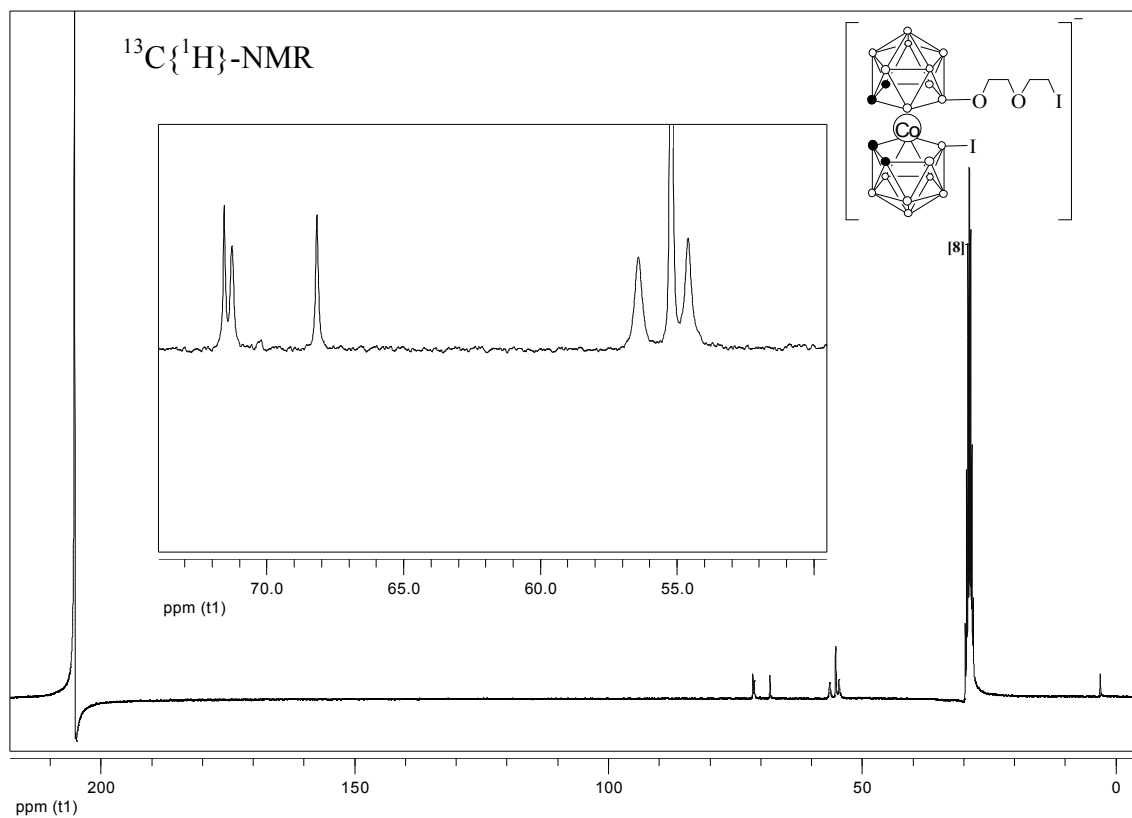


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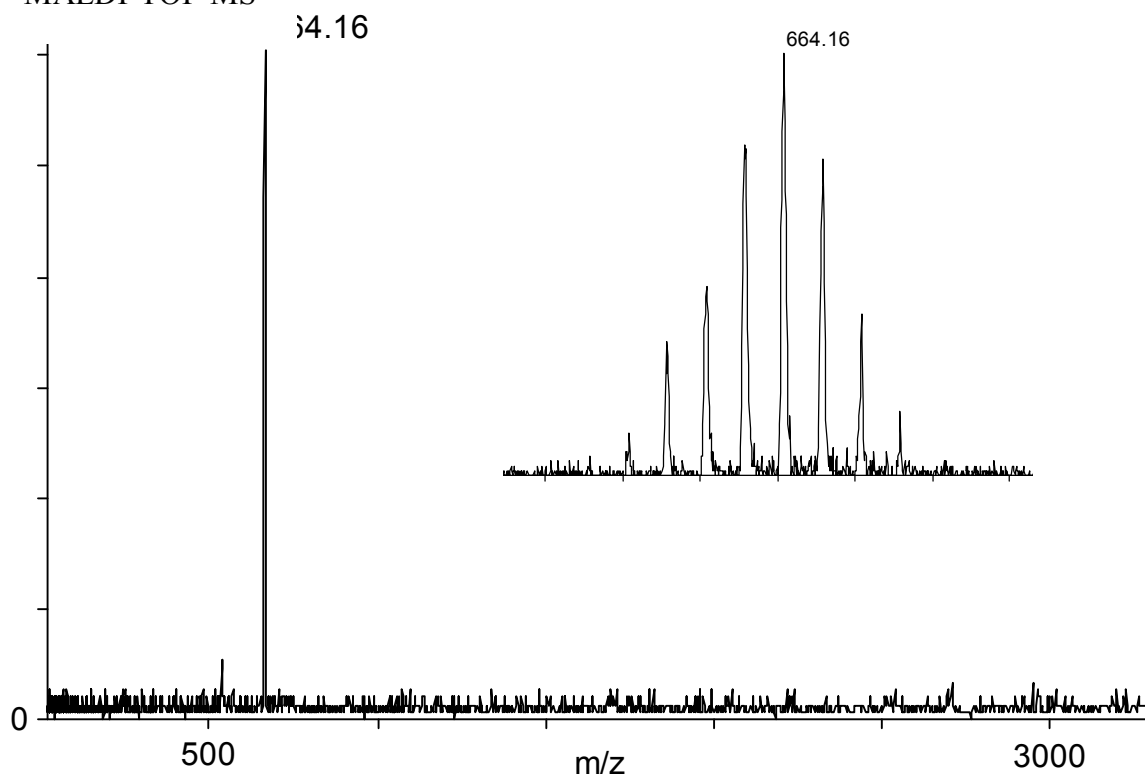


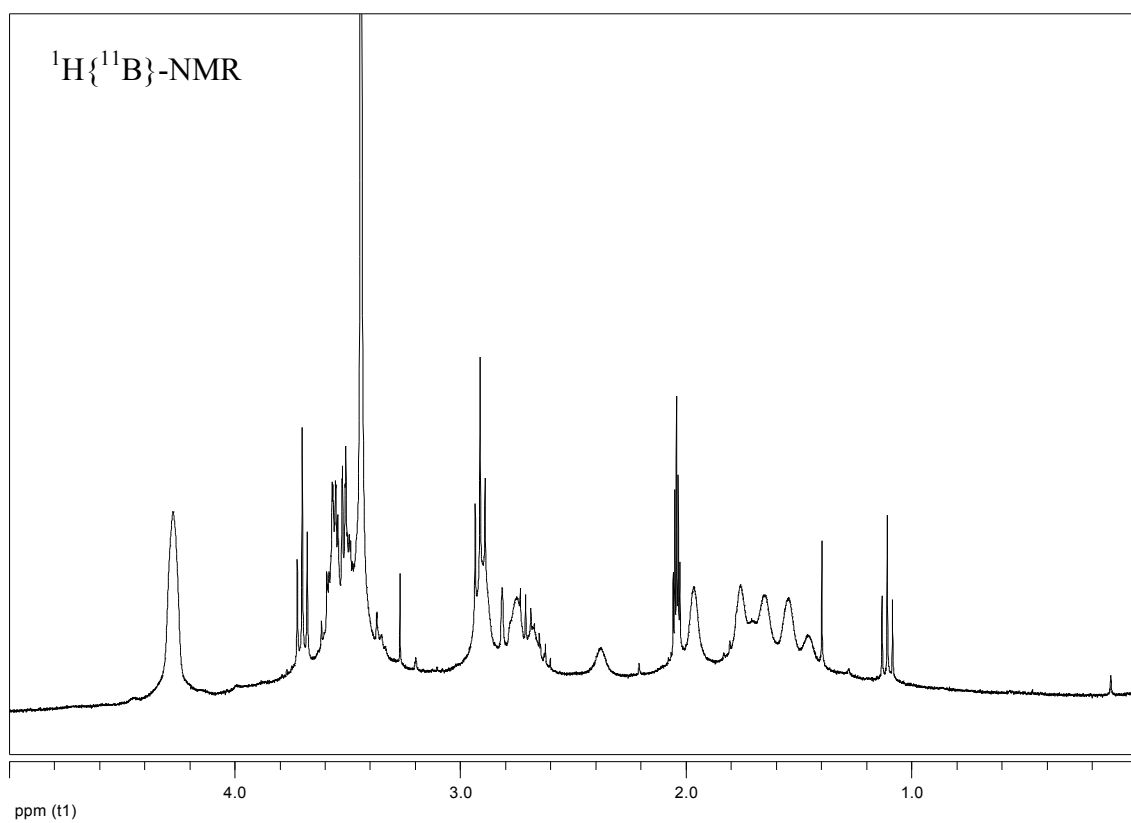
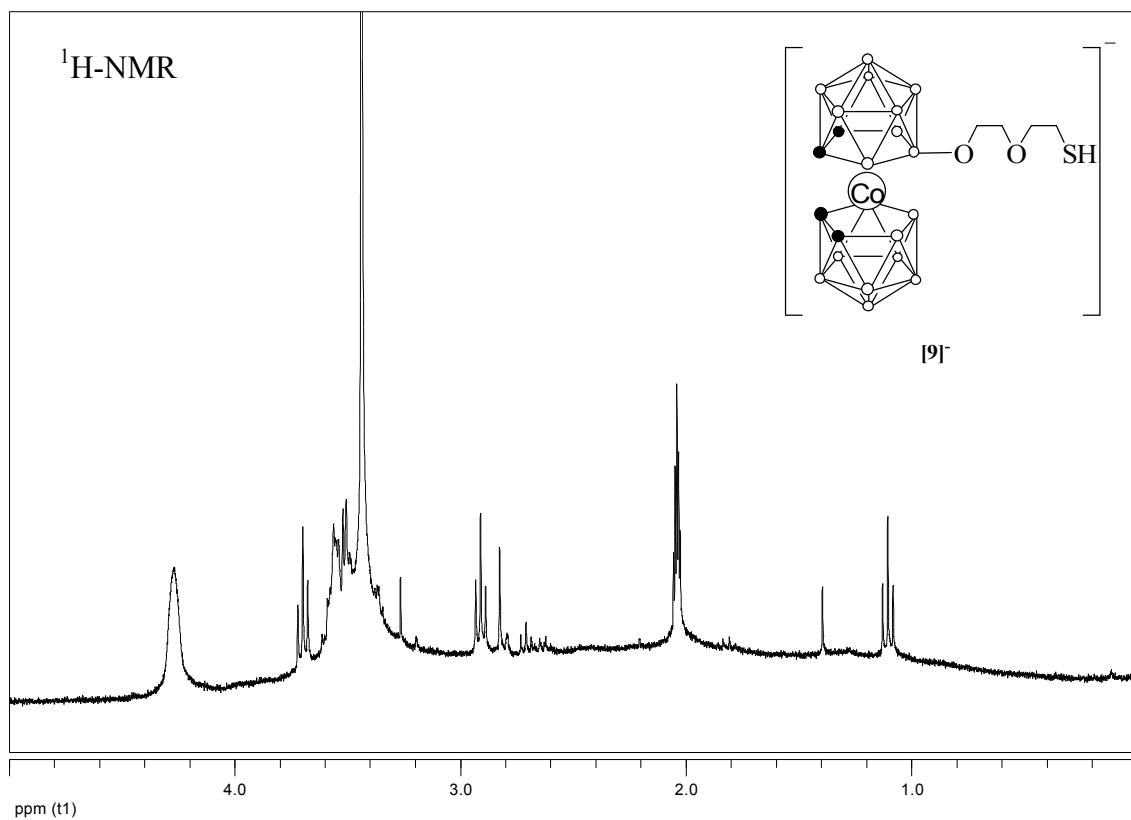


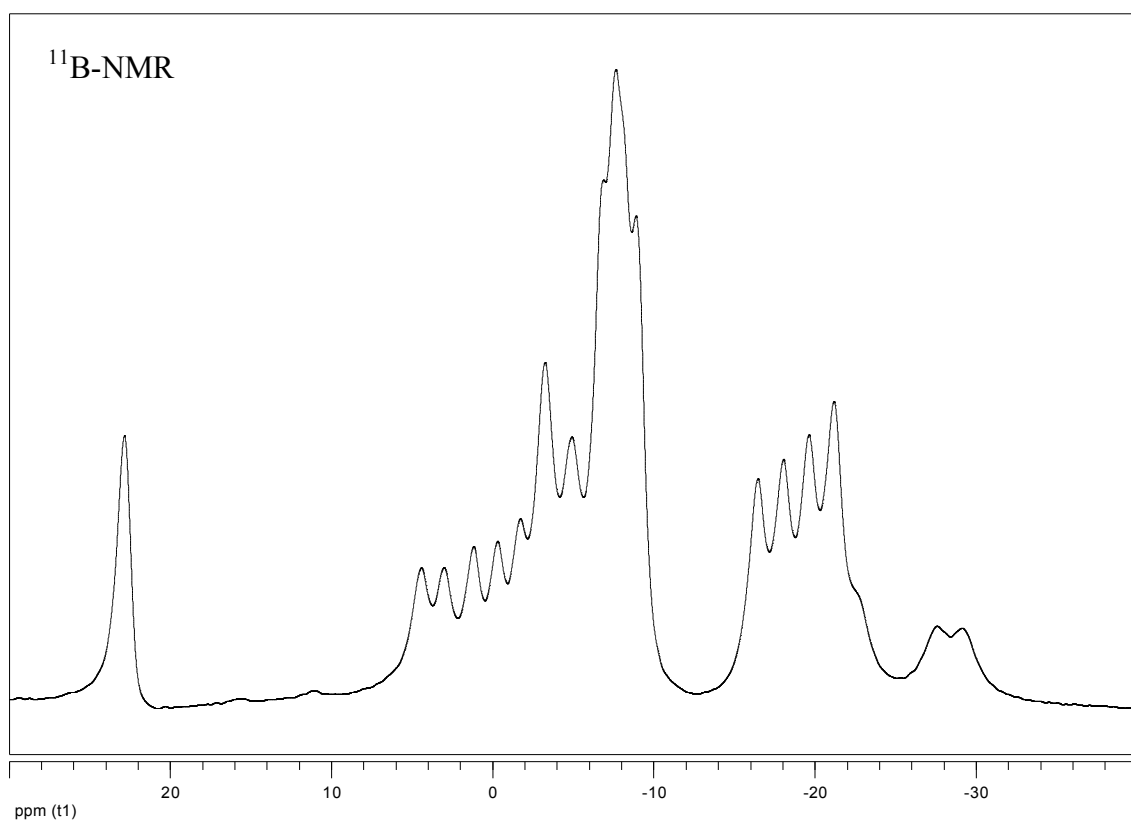
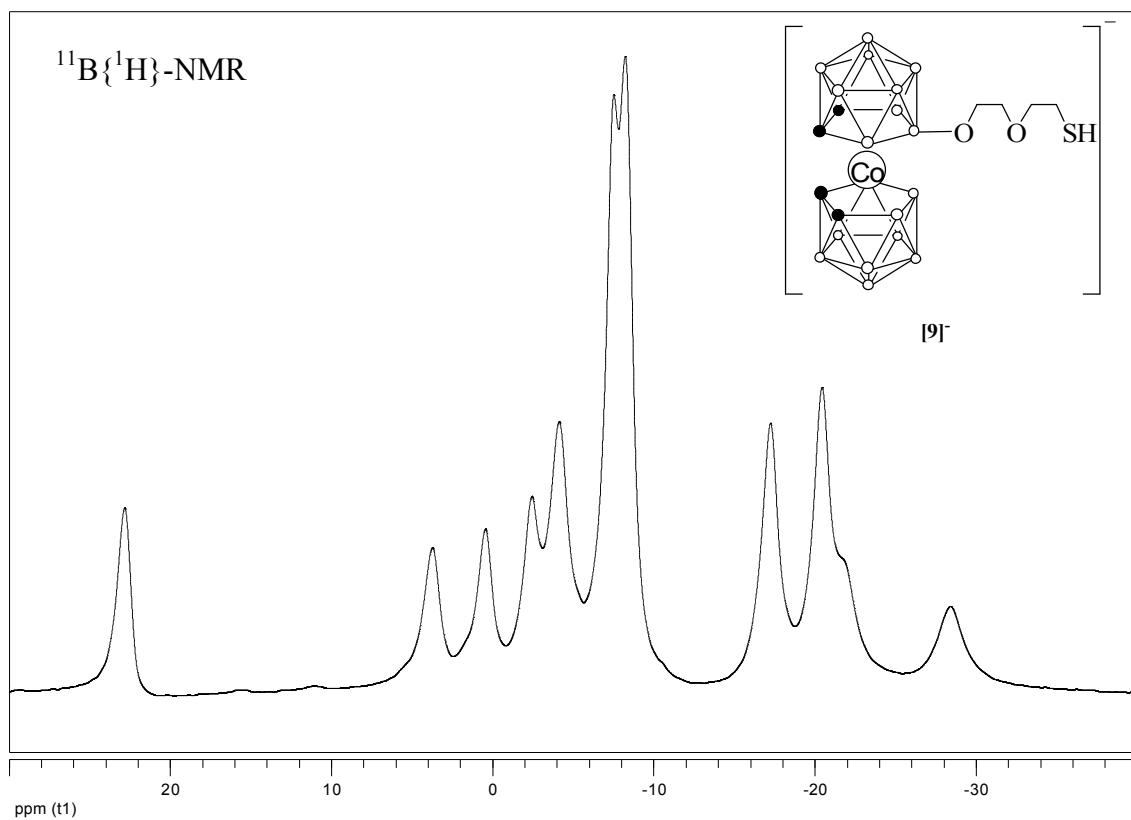


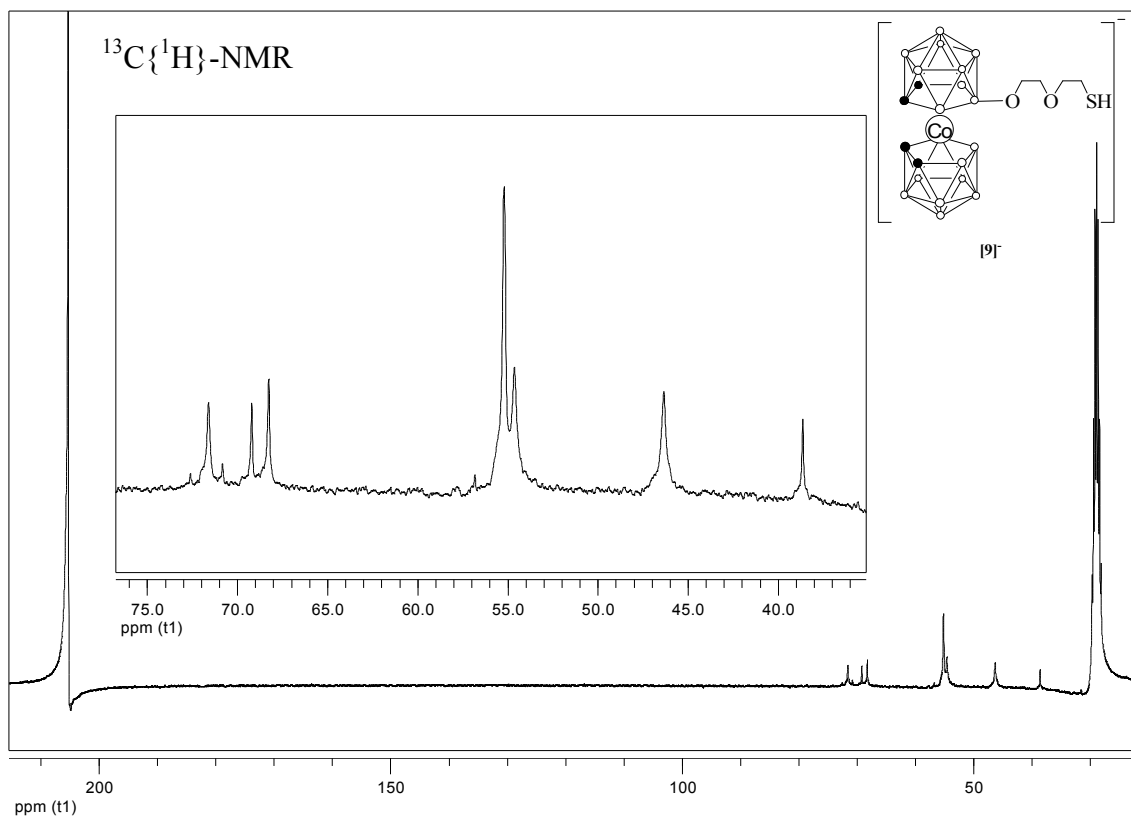


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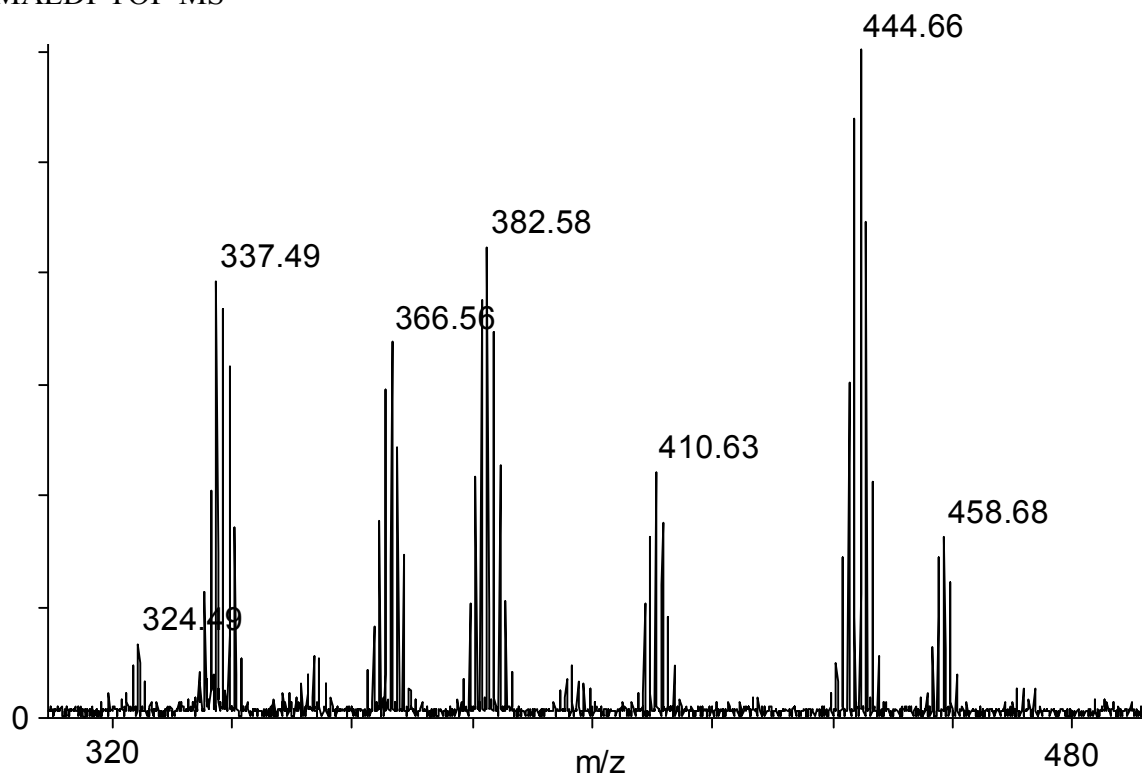


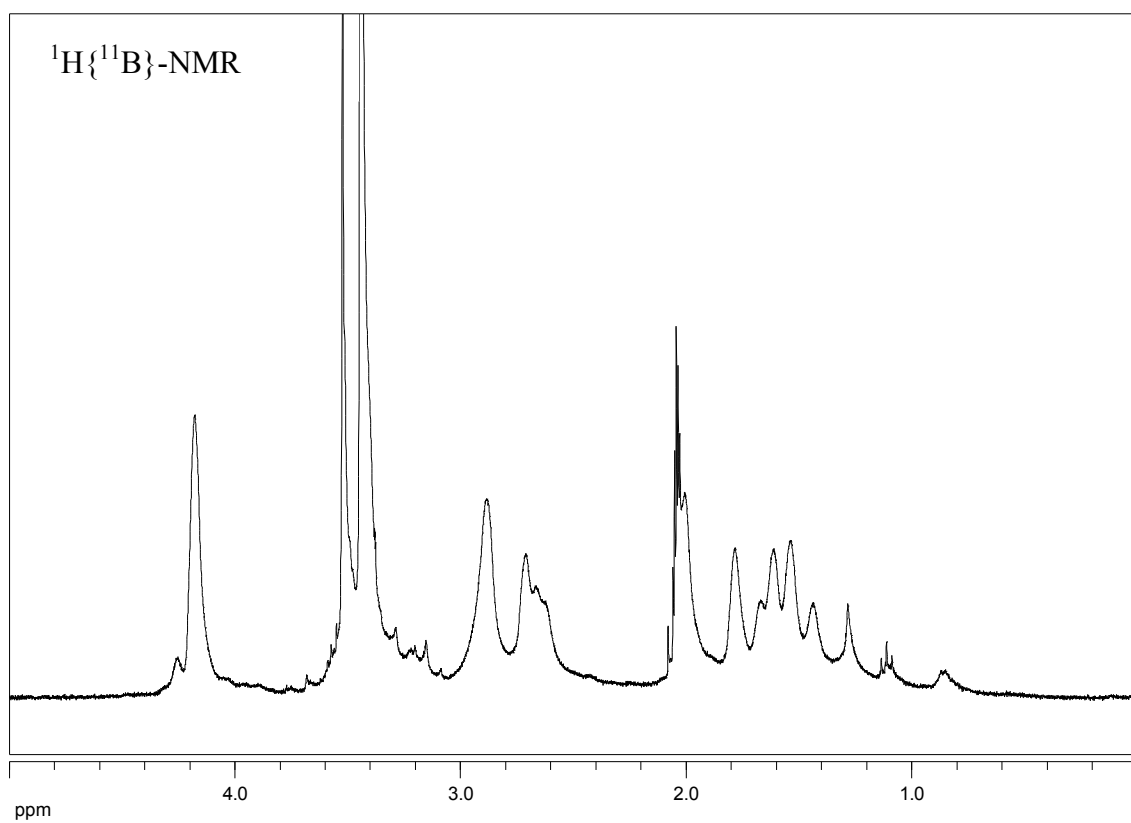
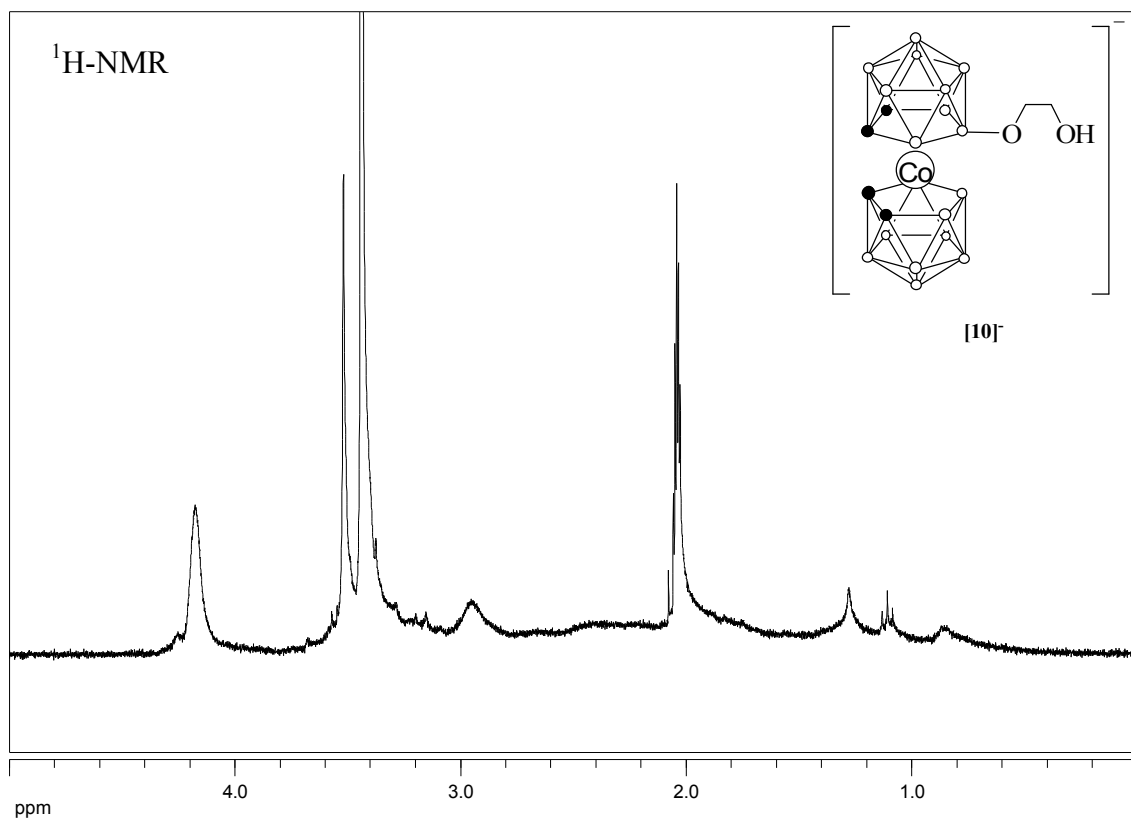


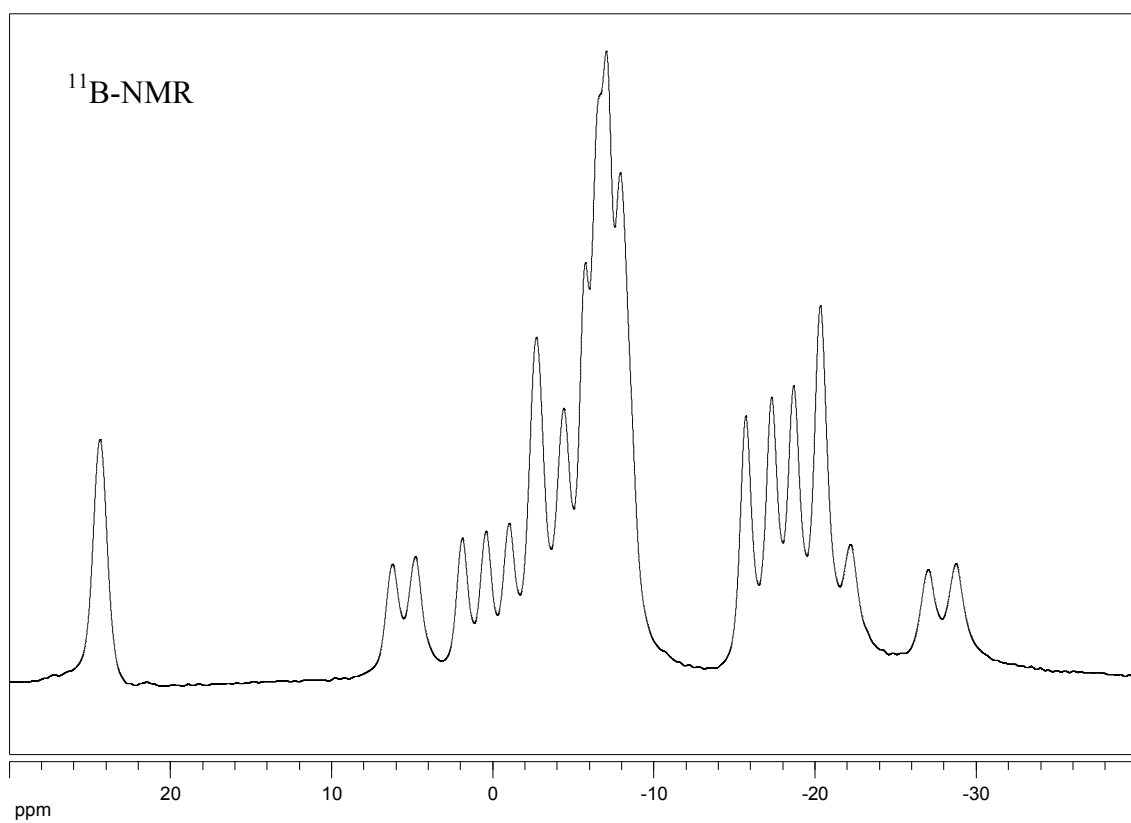
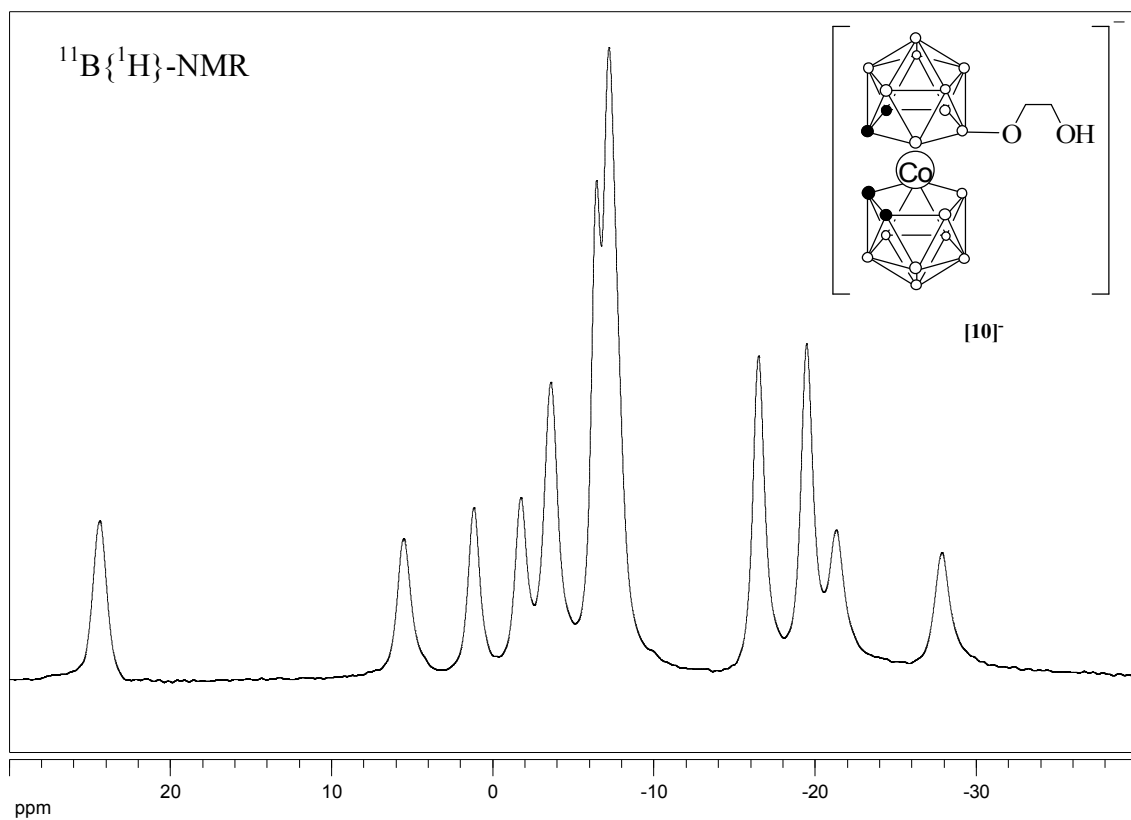


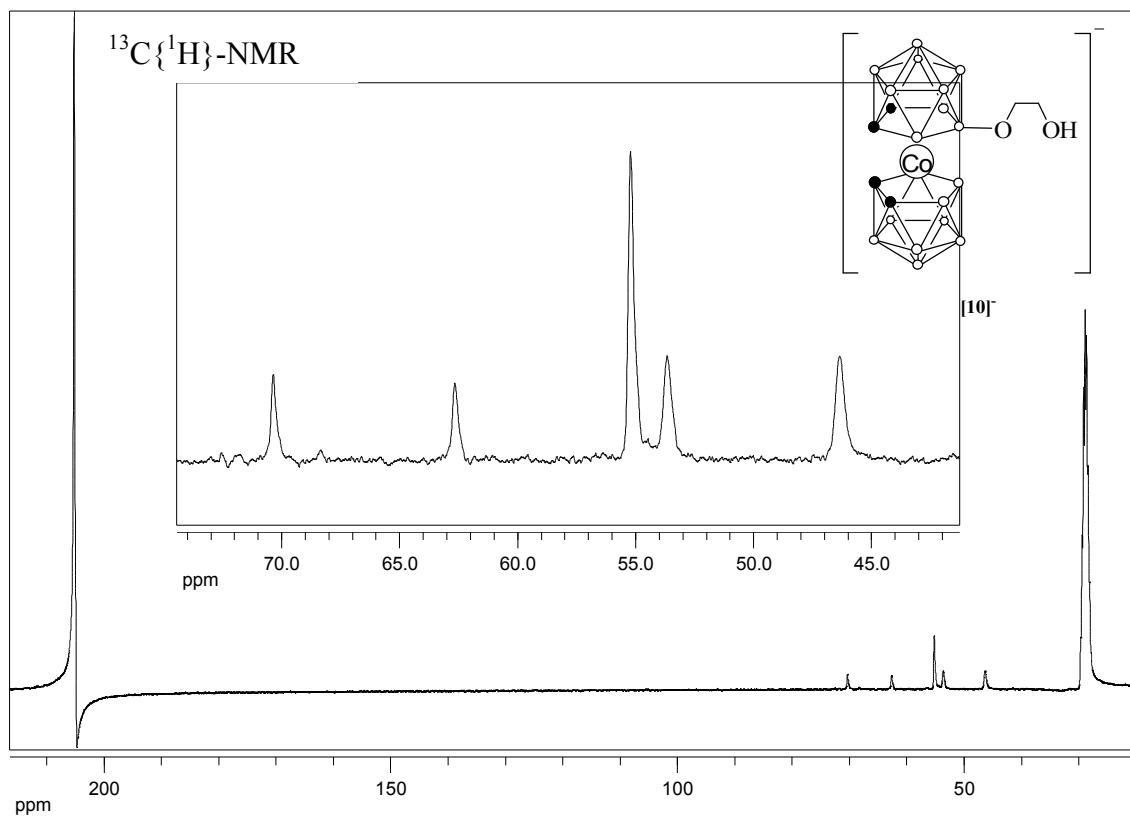


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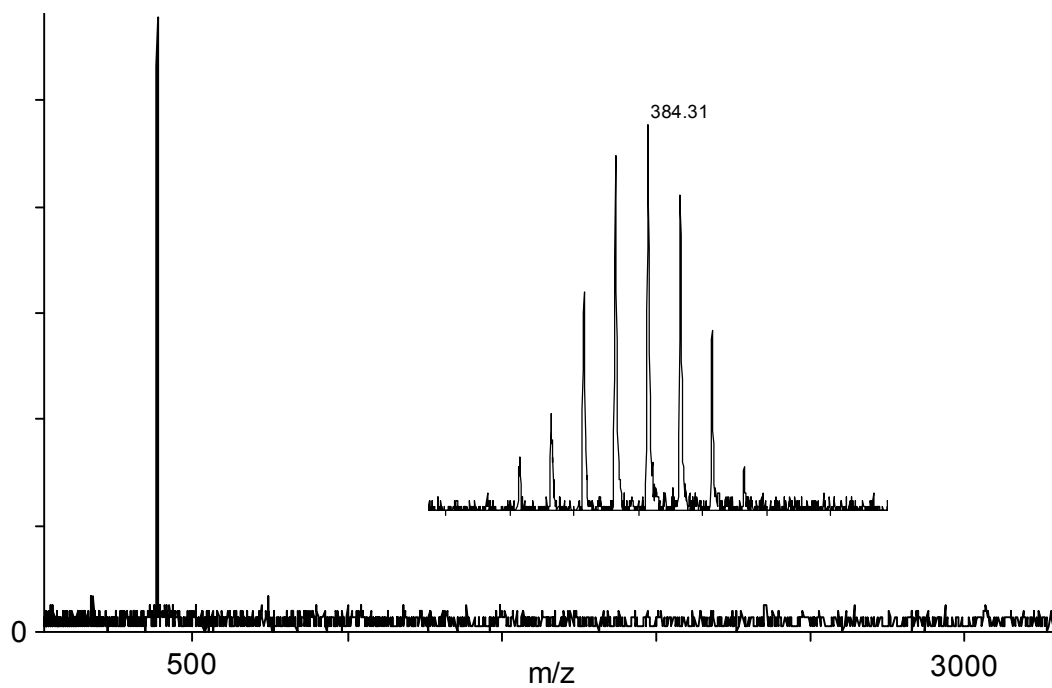








MALDI-TOF-MS



X-ray Structure Determinations of N(CH₃)₄[5] and N(CH₃)₄[6]:

Single-crystal data collections for N(CH₃)₄[5] and N(CH₃)₄[6] were performed at –100° with an Enraf Nonius KappaCCD diffractometer using graphite monochromatized Mo K_α radiation. The structures were solved by direct methods and refined on F² by the SHELXL97 program.² The non-hydrogen atoms were refined with anisotropic displacement parameters. The hydrogen atoms were treated as riding atoms using the SHELXL97 default parameters. The crystallographic, structure refinement and bond parameters for N(CH₃)₄[5] and N(CH₃)₄[6] are reported in CIF-files deposited at CCDC with the reference numbers 738981 and 738982. These data can be obtained free of charge via www.ccdc.cam.ac.uk/conts/retrieving.html (or from the Cambridge Crystallographic Data Centre, 12 Union Road, Cambridge CB2 1EZ, U.K.; fax: (+44) 1223-336033; or e-mail: deposit@ccdc.cam.ac.uk).

References

¹ I. Rojo, J. Pedrajas, F. Teixidor, C. Viñas, R. Kivekas, R. Sillanpää, I. Sivaev, V. Bregadze, S. Sjöberg. *Organometallics* **2003**, *22*, 3414.

² Sheldrick, G.M. *Acta Cryst.* **2008**, A64, 112.