Electronic supplementary materials *Mendeleev Commun.*, 2019, **29**, 628–630

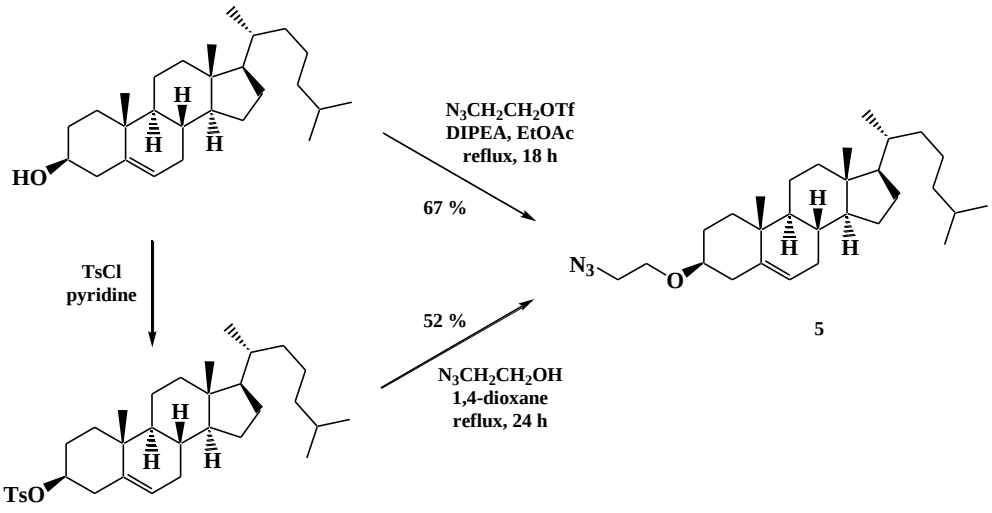
‘Click’ synthesis of cobalt bis(dicarbollide)–cholesterol conjugates

Anna A. Druzina, Akim V. Shmal’ko, Ekaterina P. Andreichuk, Olga B. Zhidkova, Irina D. Kosenko, Andrey Semioshkin, Igor B. Sivaev, Swadhin Mandal, Zheyu Shen and Vladimir I. Bregadze

Experimental

General. Compounds **1a** [S1], **1b** [S2], **2a** [S3], **3a** [S4], **3b** [S4], **9** [S5], 4-$HOC_6H_4OCH_2C{\equiv}CH$ [S6] and 2-azidoethyl triflate [S7] were prepared according to the literature procedures. Other chemicals were commercial reagent grade. The reaction progress was monitored by TLC (Merck F254 silica gel on aluminum plates). Acros Organics silica gel (0.060–0.200 mm) was used for column chromatography. NMR spectra were recorded on a Bruker Avance-400 spectrometer at 400.1 MHz (^{1}H), 128.4 MHz (^{11}B) and 100.0 MHz (^{13}C). The residual signal of the NMR solvent relative to TMS was taken as the internal reference for ^{1}H and ^{13}C NMR spectra. The assignment of signals in the cholesterol fragment was performed using standard atom numeration. ^{11}B NMR spectra were referenced to $BF_3{\cdot}Et_2O$ as external standard. Infrared spectra were recorded on an IR Prestige-21 (SHIMADZU) instrument. High resolution mass spectra (HRMS) were measured on a Bruker micrOTOF II instrument using electrospray ionization (ESI). The measurements were done in a negative ion mode (3200 V); mass range from *m*/*z* 50 to *m*/*z* 3000; external or internal calibration was done with ESI Tuning Mix, Agilent.

Synthesis of 3β-(2-azidoethoxy)cholest-5-ene (5).



Scheme S1

2-Azidoethyl triflate (4.50 g, 21 mmol) and DIPEA (5 ml) were added to a solution of cholesterol (2.65 g, 6.85 mmol) in ethyl acetate (15 ml), and the mixture was refluxed for 18 h. After cooling to room temperature, the mixture was washed with HCl (1*N*, 3 x 30 ml). The organic phase was dried over Na_2SO_4, filtered and concentrated to dryness. The residue was purified by column chromatography on silica gel using a gradient of hexane-ethyl acetate eluent (the product was eluted by 3:1 v/v mixture) to obtain 2.00 g (67%) of the title product. The spectral characteristics of the product are in good agreement with the literature data [S8].

Synthesis of 2b. A mixture of the tetrahydropyran onium derivative of cobalt bis(dicarbollide) **1b** (100 mg, 0.24 mmol), propargyl alcohol (19 μl, 0.29 mmol) and sodium metal (13 mg, 0.56 mmol) in acetonitrile (25 ml) was reflux for 3 h. The reaction mixture was cooled to room temperature and concentrated to dryness under reduced pressure. The crude product was purified by column chromatography on silica using mixture of dichloromethane and acetone (3:2) to obtain 110 mg (94%) of the orange product. ^{1}H NMR (acetone-d_6, ppm): 4.27 (2H, s, CH_{carb}), 4.20 (2H, s, CH_{carb}), 4.10 (2H, d, J = 2.4 Hz, CH_2C≡CH), 3.46 (2H, t, J = 6.6 Hz, CH_2OCH$_2$C≡CH), 3.41 (2H, t, J = 6.3 Hz, BOCH_2CH$_2$), 2.88 (1H, t, J = 2.4 Hz, OCH$_2$C≡CH), 1.57-1.50 (2H, m, CH_2CH$_2$OCH$_2$C≡CH), 1.48-1.43 (2H, m, BOCH$_2$CH_2CH$_2$), 1.39-1.33 (2H, m, CH$_2$CH_2CH$_2$).^{13}C NMP(acetone-d_6, ppm): 80.3 (C≡CH), 74.6 (C≡CH), 69.6 (CH$_2$OCH$_2$C≡CH), 68.6 (BOCH$_2$), 57.4 (OCH$_2$C≡CH), 54.3 (CH$_{carb}$), 46.3 (CH$_{carb}$), 31.6 (CH$_2$CH$_2$OCH$_2$C≡CH), 30.0 (BOCH$_2$$CH_2$), 22.6 (CH$_2$$CH_2CH_2$).^{11}B NMR (acetone-$d_6$, ppm): 22.9 (1B, s), 3.6 (1B, d, J = 141 Hz), 0.1 (1B, d, J = 156 Hz), -2.5 (1B, d, J = 142 Hz), -4.3 (2B, d, , J = 138 Hz), -7.6 (2B, d, J = 120 Hz), -8.3 (4B, d, J = 120 Hz), -17.4 (2B, d, J = 144 Hz), -20.4 (2B, d, J = 153 Hz), -22.1 (1B, d), -28.5 (1B, d, J = 161 Hz).

Synthesis of 4a [S9]**.** A mixture the 1,4-dioxane onium derivative of cobalt bis(dicarbollide) **1a** (250 mg, 0.61 mmol), 4-HOC$_6$H$_4$OCH$_2$C≡CH (90 mg, 0.61 mmol) and K_2CO_3 (800 mg, 6.10 mmol) in acetonitrile (30 ml) was refluxed for 5 h. The mixture was cooled to room temperature, filtered and concentrated to dryness under reduced pressure. The residue was dissolved in dichloromethane (25 ml) and treated with 2.5% solution of KOH (25 ml). The organic layer was separated, washed with water (3 × 30 ml), dried over anhydrous Na_2SO_4 and evaporated *in vacuo*. The crude product was purified by column chromatography on silica using mixture of dichloromethane and acetone (3:2) to obtain 320 mg (87%) of orange product. ^{1}H NMR (acetone-d_6, ppm): 6.93 (4H, m, C$_6$$H_4$), 4.72 (2H, d, J = 2.4 Hz, OCH_2C≡CH), 4.29 (4H, s, CH_{carb}), 4.09 (2H, t, J = 5.0 Hz, C$_6$H$_4$OCH_2CH$_2$O), 3.80 (2H, t, J = 5.0 Hz, C$_6$H$_4$OCH$_2$CH_2O), 3.67-3.55 (4H, m, OCH_2CH_2O) 3.04 (1H, t, J = 2.4 Hz, OCH$_2$C≡CH). ^{13}C NMR (acetone-d_6, ppm): 153.8, 151.9, 115.9, 115.4, 79.2, 75.9, 71.9, 69.4, 68.4, 68.0, 56.0, 54.4, 46.4. ^{11}B NMR (acetone-d_6, ppm): 22.9 (1B, s), 3.9 (1B, d), 0.4 (1B, d), -2.4 (1B, d), -4.2 (2B, d,), -7.8 (6B, d,), -17.2 (2B, d), -20.4 (2B, d), -21.9 (1B, d), -28.3 (1B, d). ESI-MS *m*/*z* for $C_{17}H_{36}B_{18}O_4Co$: calcd. 558.3747, found 558.3743 $[M]^-$.

Synthesis of 4b. A mixture of compound **1b** (100 mg, 0.24 mmol), 4-HOC$_6$H$_4$OCH$_2$C≡CH (40 mg, 0.24 mmol) and K_2CO_3 (300 mg, 2.17 mmol) in acetonitrile (30 ml) was refluxed for 5 h. The mixture was cooled to room temperature, filtered and concentrated

to dryness under reduced pressure. The residue was purified by column chromatography on silica using mixture of dichloromethane and acetone (3:2) to obtain 121 mg (89%) of orange product. ^{1}H NMR (acetone-d_6, ppm):6.92-6.85 (4H, m, C_6H_4), 4.69 (2H, d, J = 2.4 Hz, $OCH_2C{\equiv}CH$), 4.27 (2H, s, CH_{carb}),4.21 (2H, s, CH_{carb}), 3.91 (2H, t, J = 6.6 Hz, $C_6H_4OCH_2CH_2$), 3.45 (2H, t, J = 5.8 Hz, $BOCH_2CH_2$),3.02 (1H, t, J = 2.4 Hz, $OCH_2C{\equiv}CH$), 1.76-1.69 (2H, m, $CH_2CH_2CH_2$), 1.53-1.46 (4H, m, $CH_2CH_2CH_2$).^{11}B NMR (acetone-d_6, ppm): 23.0 (1B, s), 3.7 (1B, d, J = 128 Hz), 0.2 (1B, d, J = 143 Hz), -2.4 (1B, d, J = 143 Hz), -4.3 (2B, d, , J = 155 Hz), -7.5 (2B, d, J = 134 Hz), -8.3 (4B, d), -17.3 (2B, d, J = 151 Hz), -20.4 (2B, d, J = 155Hz), -22.0 (1B, d), -28.5 (1B, d, J = 146Hz).

Synthesis of 6a. Copper(I) iodide (5 mg, 0.03 mmol) and Et_3N (3 drops) were added to a solution of alkyne **2a** (114 mg, 0.23 mmol) and azide **5 (**117 mg, 0.26 mmol) in acetonitrile (25 ml). The mixture was refluxed for 18 h, cooled to room temperature, and concentrated to dryness under reduced pressure. The residue was purified by column chromatography on silica using a mixture of dichloromethane and acetone (3:2) as a eluent to obtain 220 mg (99%) of the product. ^{1}H NMR (acetone-d_6, ppm): 7.96 (1H, s, CH_{C2N3}), 5.32 (1H, d, J= 5.0 Hz, CH(6)), 4.62 (2H, s, $OCH_2C_2N_3$), 4.54 (2H, t, J=5.2 Hz, NCH_2CH_2O), 4.21 (4H, s, CH_{carb}), 3.88 (2H, t, J=5.2 Hz, NCH_2CH_2O), 3.61 (6H, m, OCH_2), 3.52 (2H, t, J=5.0 Hz, OCH_2), 3.12 (1H, m, CH(3)), 2.33-1.11 (28H, br.m), 0.98 (3H, s, CH_3(19)), 0.93 (3H, d, J=6.5Hz, CH_3(21)), 0.852 (3H, d, J= 6.7Hz, CH_3(26)), 0.848 (3H, d, J = 6.7 Hz, CH_3(27)), 0.69 (3H, s, CH_3(18)). ^{11}B NMR (acetone-d_6, ppm): 23.2 (1B, s), 4.4 (1B, d, J = 136 Hz), 0.4 (1B, d, J = 151 Hz), -2.4 (1B, d, J = 142 Hz), -4.4 (2B, d, J = 153 Hz), -7.2 (2B, d, J = 128 Hz), -8.0 (4B, d, J = 118 Hz), -17.3 (2B, d, J = 151 Hz), -20.4 (2B, d, J = 160 Hz), -22.1 (1B, d), -28.5 (1B, d, J=173 Hz). ^{13}C NMR (acetone-d_6, ppm): 140.6, 121.4, 79.2, 71.7, 70.0, 69.1, 68.3, 66.1, 64.2, 56.7, 56.1, 54.0, 50.5, 50.2, 46.5, 42.2, 39.7, 39.4, 38.9, 37.0, 36.6, 36.1, 35.7, 31.7, 28.2, 28.1, 27.8, 24.1, 23.6, 22.2, 22.0, 20.9, 18.9, 18.3, 11.4. ESI-MS, m/z для $C_{40}H_{81}B_{18}CoN_3O_4$: calcd. 921.7375 $[M]^-$, found 921.7362 $[M]^-$.

Synthesis of 6b. Copper(I) iodide (15 mg, 0.08 mmol) and Pr^i_2EtN (1.0 ml) were added to a solution of alkyne **2b** (360 mg, 0.70 mmol) and azide **5 (**475 mg, 0.83 mmol) in ethanol (15 ml) and refluxed for 7 h. The mixture was cooled to room temperature and filtered through ca. 2–3 cm layer of silica. The filtrate was concentrated, the residue was dissolved in dichloromethane (50 ml) and washed with HCl (1N, 3 x 30 ml). The organic layer was dried over Na_2SO_4, filtered and concentrated. The residue was dissolved in acetone (5 ml) and treated with an excess of aqueous solution of CsCl and stored in a fridge for a few hours. The precipitate formed was filtered off and purified by column chromatography on silica with a mixture of dichloromethane and acetonitrile (3:1, v/v) as eluent. The main fraction was collected and vacuum dried to give 460 mg (62%) of prodict **6b** as an orange foam. ^{1}H NMR (acetone-d_6, ppm): 8.13 (1H, s, CH_{C2N3}), 5.35 (1H, m, CH(6)), 4.66 (2H, t, J = 5.3 Hz, NCH_2CH_2O), 4.21 (4H, s, CH_{carb}), 3.96 (2H, m, NCH_2CH_2O), 3.80 (2H, m, OCH_2), 3.72 (2H, m, OCH_2), 3.66 (4H, m, OCH_2), 3.61 (2H, m, OCH_2), 3.17 (1H, m, CH(3)), 3.07 (2H, m, $CH_2C_2N_3$), 2.33-1.13 (28H, br. m), 1.02 (3H, s, CH_3(19)), 0.96 (3H, d, J = 5.3 Hz, CH_3(21)), 0.89 (3H, s, CH_3(26)), 0.88 (3H, s, CH_3(27)), 0.73

(3H, s, C*H*$_3$(18)). ^{13}C NMR (acetone-*d*$_6$, ppm): 143.6 (*C*CHN$_3$), 140.5 (*C*(5)), 124.7 (C*C*HN$_3$), 121.5 (*C*(6)), 79.2 (*C*(3)), 72.0 (O*C*H$_2$), 70.1 (O*C*H$_2$), 69.7 (O*C*H$_2$), 69.1 (O*C*H$_2$), 68.4 (O*C*H$_2$), 65.7 (NCH$_2$*C*H$_2$O), 56.7 (*C*(14)), 56.2 (*C*(17)), 53.1 (*C*H$_{carb}$), 51.7 (N*C*H$_2$CH$_2$O), 50.2 (*C*(9)), 46.6 (*C*H$_{carb}$), 42.2 (*C*(4)), 39.8 (*C*(13)), 39.4 (*C*(12)), 38.9 (*C*(24)), 37.0 (*C*(1)), 36.6 (*C*(10)), 36.1 (*C*(22)), 35.8 (*C*(20)), 31.9 (*C*(8)), 31.8 (*C*(2)), 28.1 (*C*(7)+*C*(13)), 27.8 (*C*(25)), 25.4 (*C*H$_2$), 24.1 (*C*(15)), 23.7 (*C*(23)), 22.3 (*C*(26)), 22.0 (*C*(27)), 20.9 (*C*(11)), 19.0 (*C*(19)), 18.3 (*C*(21)), 11.4 (*C*(18)). ^{11}B NMR (acetone-*d*$_6$, ppm): 23.2 (1B, s), 4.4 (1B, d, *J* = 137 Hz), 0.5 (1B, d, *J* = 141 Hz), -2.4 (1B, d, *J* = 147 Hz), -4.4 (1B, d, *J* = 143 Hz), -7.2 (3B, d, *J* = 124 Hz), -8.0 (4B, d, *J* = 141 Hz), -17.2 (2B, d, *J* = 120 Hz), -20.3 (2B, d, *J*= 161 Hz), -22.0 (1B, d), -28.3 (1B, d, *J* = 184 Hz). IR (ν/cm^{-1}): 2535 (BH), 1617 (triazole). ESI-MS, *m*/z for C$_{41}$H$_{83}$B$_{18}$CoN$_3$O$_4$: calcd. 935.7532 [M]$^-$, found 935.7521 [M]$^-$.

Synthesis of 7a was performed similarly to **6b** using alkyne **3a** (450 mg, 0.90 mmol) and azide **5 (**490 mg, 0.90 mmol). Yield 550 mg (59%). ^{1}H NMR (acetone-*d*$_6$, ppm):7.98 (1H, s, C*H*$_{C2N3}$), 5.35 (1H, m, C*H*(6)), 4.58 (4H, m, NC*H*$_2$CH$_2$O+C*H*$_2$C$_2$N$_3$), 4.29 (2H, s, C*H*$_{carb}$), 4.23 (2H, s, C*H*$_{carb}$), 3.92 (2H, t, *J* = 5.3 Hz, NCH$_2$C*H*$_2$O), 3.46 (4H, m, OCH$_2$), 3.15 (2H, m, C*H*(3)), 2.32-1.07 (34H, br. m), 0.97 (3H, s, CH$_3$(*19*)), 0.96 (3H, d, *J* = 6.5 Hz, C*H*$_3$(21)), 0.89 (3H, s, C*H*$_3$(26)), 0.88 (3H, s, C*H*$_3$(27)), 0.73 (3H, s, C*H*$_3$(18)). ^{13}C NMR (acetone-*d*$_6$, ppm):144.6 (*C*CHN$_3$), 140.5 (*C*(5)), 122.6 (C*C*HN$_3$), 121.7 (*C*(6)), 79.2 (*C*(3)), 70.0 (O*C*H$_2$),68.6 (O*C*H$_2$),66.1 (NCH$_2$*C*H$_2$O), 63.8 (*C*H$_2$CCHN$_3$), 56.7 (*C*(14)), 56.1 (*C*(17)), 54.4 (*C*H$_{carb}$), 50.4 (N*C*H$_2$CH$_2$O), 50.2 (*C*(9)), 46.4 (*C*H$_{carb}$), 42.2 (*C*(4)), 39.7 (*C*(13)), 39.4 (*C*(12)), 38.9 (*C*(24)), 37.0 (*C*(1)), 36.6 (*C*(10)), 36.1 (*C*(22)), 35.7 (*C*(20)), 31.8 (*C*(8)), 31.7 (*C*(2)), 29.5 (*C*H$_2$), 28.2 (*C*(7)), 28.1 (*C*(16)), 27.8 (*C*(25)), 24.1 (*C*(15)), 23.6 (*C*(23)), 22.8 (*C*H$_2$), 22.2 (*C*(26)), 22.0 (*C*(27)), 20.9 (*C*(11)), 18.9 (C(19)), 18.3 (*C*(21)), 11.4 (*C*(18)).^{11}B NMR (acetone-*d*$_6$, ppm):22.9 (1B, s), 3.6 (1B, d, *J* =123 Hz), 0.2 (1B, d, *J* = 156 Hz), -2.3 (1B, d, *J* = 140 Hz), -4.4 (1B, d, *J* = 153 Hz), -7.6 (3B, d, *J* = 118 Hz), -8.4 (4B, d, *J* = 113 Hz), -17.5 (2B, d, *J* = 165 Hz), -20.4 (2B, d, *J* = 156 Hz), -22.2 (1B, d, *J* = 156 Hz), -28.2 (1B, d, *J* = 173 Hz). IR (ν/cm^{-1}): 2539 (BH), 1616 (triazole).ESI-MS, *m*/z для C$_{41}$H$_{83}$B$_{18}$CoN$_3$O$_3$: calcd. 919.7583 [M]$^-$, found 919.7575 [M]$^-$.

Synthesis of 7b was similarly to **6b** using alkyne **3b** (400 mg, 0.77 mmol) and azide **5 (**430 mg, 0.93 mmol). Yield 520 mg (63%). ^{1}H NMR (acetone-*d*$_6$, ppm):8.69 (1H, s, C*H*$_{C2N3}$),5.35 (1H, m, C*H*(6)), 4.95 (2H, t, *J* = 4.9 Hz, NC*H*$_2$CH$_2$O), 4.23 (2H, s, *C*H$_{carb}$), 4.16 (2H, s, *C*H$_{carb}$), 4.08 (2H, t, *J* = 4.9 Hz, NCH$_2$C*H*$_2$O), 3.79 (2H, m, OC*H*$_2$), 3.50 (4H, m, OC*H*$_2$), 3.29 (2H, t, *J* = 5.8 Hz, C*H*$_2$C$_2$N$_3$), 3.23 (2H, m, C*H*(3)), 2.31-1.17 (34H, br. m), 1.01 (3H, s, C*H*$_3$(19)), 0.96 (3H, d, *J* = 6.4 Hz, CH$_3$(21)), 0.89 (3H, s, C*H*$_3$(26)), 0.87 (3H, s, C*H*$_3$(27)), 0.72 (3H, s, C*H*$_3$(18)).^{13}C NMR (acetone-*d*$_6$, ppm): 142.0 (*C*CHN$_3$), 140.3 (*C*(5)), 128.3 (C*C*HN$_3$), 121.7 (*C*(6)), 79.3 (*C*(3)), 71.00 (O*C*H$_2$), 69.0 (O*C*H$_2$), 68.5 (O*C*H$_2$), 64.9 (NCH$_2$*C*H$_2$O), 56.7 (*C*(14)), 56.1 (*C*(17)), 54.2 (N*C*H$_2$CH$_2$O), 53.8 (*C*H$_{carb}$), 50.2 (*C*(9)), 46.6 (*C*H$_{carb}$), 42.2 (*C*(4)), 39.7 (*C*(13)), 39.4 (*C*(12)), 38.8 (*C*(24)), 37.0 (*C*(1)), 36.6 (*C*(10)), 36.1 (C(22)), 35.7 (*C*(20)), 31.8 (*C*(8)), 31.8 (*C*(2)), 29.5 (CH$_2$), 29.1 (CH$_2$), 28.1 (*C*(7)+*C*(16)), 27.8 (*C*(25)), 24.1 (*C*(15)), 23.7 (*C*(23)), 22.6 (*C*H$_2$), 22.3 (*C*(26)), 22.1 (*C*(27)), 21.0 (*C*(11)), 19.0 (*C*(19)), 18.4 (*C*(21)), 11.5 (*C*(18)).^{11}B NMR (acetone-*d*$_6$, ppm):23.0 (1B, s), 4.8 (1B, d, *J* = 133 Hz), 0.5 (1B, d, *J* = 138

Hz), -2.4 (1B, d, *J* = 147 Hz), -4.5 (1B, d, *J* = 150 Hz), -7.0 (3B, d, *J* = 134 Hz), -8.0 (4B, d, *J* = 128 Hz), -17.1 (2B, d, *J* = 149 Hz), -20.2 (2B, d, J = 166 Hz), -22.0 (1B, d), -28.3 (1B, d). IR (ν/cm^{-1}): 2544 (BH), 1617 (triazole). ESI-MS, *m*/z для $C_{42}H_{85}B_{18}CoN_3O_3$: calcd. 933.7740 $[M]^-$, found 933.7727 $[M]^-$.

Synthesis of 8a. Copper(I) iodide (3 mg, 0.02 mmol) and Et_3N (3 drops) were added to a solution of alkyne **4a** (100 mg, 0.17 mmol) and azide **5** (90 mg, 0.20 mmol) in acetonitrile (25 ml). The mixture was refluxed for 18 h, allowed to cool to room temperature, and concentrated to dryness under reduced pressure. The residue was purified by column chromatography on silica using a mixture of dichloromethane and acetone (3:2) as the eluent to obtain 143 mg (81%) of the product. ^{1}H NMR (acetone-d_6, ppm): 8.10 (1H, s, CH_{C2N3}), 6.91-6.84 (4H, m, C_6H_4), 5.30 (1H, d, *J*= 5.0Hz, C*H*(6)), 5.16 (2H, s, OC$H_2C_2N_3$), 4.56 (2H, t, *J*=5.2 Hz, NCH_2CH_2O), 4.25 (4H, s, CH_{carb}), 4.04 (2H, t, *J*=4.9 Hz, $OCH_2CH_2OCH_2CH_2$), 3.84 (2H, t, *J*= 5.2Hz, NCH_2CH_2O), 3.77 (2H, t, *J*=4.9 Hz, $OCH_2CH_2OCH_2CH_2$), 3.61-3.57 (4H, m, $BOCH_2CH_2O$), 3.09 (1H, m, C*H*(3)),2.33-1.17 (28H, br. m.),1.01 (3H, s, CH_3(19)), 0.96 (3H, s, CH_3(19)), 0.94 (3H, d, *J*=6.4 Hz, CH_3(21)), 0.86 (3H, s, CH_3(26)), 0.85 (3H, s, CH_3(27)), 0.70 (3H, s, CH_3(18)). ^{13}C NMR (acetone-d_6, ppm): 153.4, 152.5, 144.3, 140.5, 124.8, 121.5, 115.6, 115.5, 79.2, 72.0, 69.5, 68.4, 68.0, 66.0, 62.0, 56.7, 56.2, 54.5, 54.1, 50.8, 50.2, 46.4, 42.2, 39.8, 39.4, 38.9, 37.0, 36.6, 36.1, 35.8, 31.9, 31.8, 28.1, 27.8, 24.1, 23.7, 22.3, 22.0, 20.9, 18.9, 18.4, 11.5. ^{11}B NMR (acetone-d_6, ppm):22.9 (1B, s), 4.0 (1B, d, *J*=128 Hz), 0.4 (1B, d, *J*=143 Hz), -2.4 (1B, d, *J*=143 Hz), -4.3 (2B, d, *J*=155 Hz), -7.4 (2B, d, *J*=134 Hz), -8.1 (4B, d), -17.2 (2B, d, *J*=151 Hz), -20.4 (2B, d, *J*=155 Hz), -21.7 (1B, d), -28.4 (1B, d, *J*=146 Hz). ESI-MS, *m*/z для $C_{46}H_{85}B_{18}CoN_3O_5$: calcd. 1013.7641 $[M]^-$, found 1013.7630 $[M]^-$.

Synthesis of 8b was similarly to **6b** using CuI (5 mg, 0.03 mmol), alkyne **4b** (120 mg, 0.20 mmol) and azide **5 (**110 mg, (0.24 mmol). Yield 170 mg (74%). ^{1}H NMR (acetone-d_6, ppm): 8.01 (1H, s, CH_{C2N3}), 6.95 (2H, d, *J* = 8.9 Hz, C_6H_4), 6.87 (2H, d, *J* = 8.9 Hz, C_6H_4), 5.33 (1H, m, C*H*(6)), 5.12 (2H, s, OC$H_2C_2N_3$), 4.56 (2H, m, NCH_2CH_2O), 4.29 (2H, s, CH_{carb}), 4.24 (2H, s, CH_{carb}), 3.90 (m, 4H, OCH_2), 3.47 (2H, m, NCH_2CH_2O), 3.13 (1H, m, C*H*(3)), 2.29-1.17 (34H, br. m), 1.00 (3H, s, CH_3(19)), 0.96 (3H, d, *J* = 6.3 Hz, CH_3(21)), 0.89 (3H, s, CH_3(26)), 0.88 (3H, s, CH_3(27)), 0.73 (3H, s, CH_3(18)).^{13}C NMR (acetone-d_6, ppm): 153.7 (C_{ar}-O), 152.4 (C_{ar}-O), 143.5 (*C*CHN_3), 140.5 (*C*(5)), 124.2 (C*C*HN_3), 121.5 (*C*(6)), 115.7 (*C*H_{ar}), 115.3 (*C*H_{ar}), 79.2 (C(3)), 68.6 (O*C*H_2), 68.2 (NCH_2CH_2O), 66.2 (O*C*H_2), 62.1 (O*C*H_2), 56.7 (*C*(14)), 56.2 (*C*(17)), 54.5 (*C*H_{carb}), 50.4 (NCH_2CH_2O), 50.2 (*C*(9)), 46.4 (*C*H_{carb}), 42.2 (*C*(4)), 39.8 (*C*(13)), 39.4 (*C*(12)), 38.9 (*C*(24)), 37.0 (*C*(1)), 36.6 (*C*(10)), 36.1 (*C*(28)), 35.8 (*C*(20)), 31.9 (C(8)), 31.8 (*C*(2)), 29.6 (CH_2), 29.2 (*C*H_2), 28.2 (*C*(7)), 28.1 (*C*(16)), 27.8 (*C*(25)), 24.1 (*C*(15)), 23.8 (*C*(23)), 22.7 (*C*H_2), 22.4 (*C*(26)), 22.1 (*C*(27)), 21.0 (*C*(11)), 19.0 (*C*(19)), 18.4 (*C*(21)), 11.5 (*C*(18)). ^{11}B NMR (acetone-d_6, ppm): 22.9 (1B, s), 3.6 (1B, d, *J* = 142 Hz), 0.3 (1B, d, *J* = 166 Hz), -2.5 (1B, d, *J* = 156 Hz), -4.2 (1B, d, *J* = 140 Hz), -7.5 (3B, d, *J* = 132 Hz), -8.3 (4B, d, *J* = 118 Hz), -17.4 (2B, d, *J* = 132 Hz), -20.4 (2B, d, *J* = 154 Hz), -22.1 (1B, d, *J* = 128 Hz), -28.6 (1B, d, *J* = 155 Hz). IR (ν/cm^{-1}): 2532 (BH), 1616 (triazole). ESI-MS, *m*/z for $C_{46}H_{85}B_{18}CoN_3O_5$: calcd. 1011.7849 $[M]^-$, found 1011.7827 $[M]^-$.

Compound 10 was prepared similarly to **6b** using alkyne **9** (220 mg, 0.35 mmol) and azide **5** (200 mg, 0.42 mmol). Yield 200 mg (54%). ^{1}H NMR (acetone-d_6, ppm):7.78 (1H, s, CH_{C2N3}), 5.36 (1H, m, CH(6)), 4.55 (4H, m, m, NCH_2CH$_2$O+CH_2C$_2$N$_3$), 4.41 (2H, s, CH_{carb}), 4.22 (2H, s, CH_{carb}), 3.87 (2H, t, J=5.1, NCH$_2$CH_2O), 3.17 (1H, CH(3)), 2.34-1.15 (34H, br. m), 1.03 (3H, s, CH$_3$(19)), 0.97 (3H, d, J = 6.3 Hz, CH_3(21)), 0.89 (3H, d, J =7.78 Hz, CH$_3$(26)), 0.88 (3H, d, J =7.78 Hz, CH$_3$(27)), 0.73 (3H, s, CH$_3$(18)).^{13}C NMR (acetone-d_6, ppm): 147.4 (CCHN$_3$), 140.6 (C(5)), 122.5 (CCHN$_3$), 121.5 (C(6)), 79.3 (C(3)), 66.3 (NCH$_2$$CH_2$O), 63.4 ($CH_2$CCHN$_3$), 56.7 ($C$(14)), 56.6 ($CH_{carb}$), 56.2 ($C$(17)), 54.5 ($CH_{carb}$), 50.4 (N$CH_2CH_2$O),50.2 ($C$(9)), 42.2 ($C$(4)), 39.8 ($C$(13)), 39.4 ($C$(12)), 38.9 ($C$(24)), 37.1 ($C$(1)), 36.7 ($C$(10)), 36.1 ($C$(22)), 35.8 ($C$(20)), 31.9 ($C$(8)), 31.8 ($C$(2)), 28.2 ($C$(7)), 28.1 ($C$(16)), 27.8 ($C$(25)), 24.1 ($C$(15)), 23.7 ($C$(23)), 22.3 ($C$(26)), 22.1 ($C$(27)), 21.0 (C(11)), 19.0 (C(19)), 18.4 (C(21)), 11.5 (C(18)).^{11}B NMR (acetone-d_6, ppm):21.7 (1B, s), -0.22 (1B, d, J = 180 Hz), -5.5 (6B, s+d, J = 141 Hz), -7.2 (4B, d, J = 124 Hz), -17.7 (2B, d, J = 155 Hz), -19.8 (2B, d, J = 161), -23.0 (1B, d), -26.9 (1B, d). IR (ν/cm^{-1}): 2546 (BH), 1608 (triazole).ESI-MS, m/z for C$_{36}$H$_{72}$B$_{18}$CoIN$_3$O$_2$: calcd. 959.5804 [M]$^-$, found 959.5796 [M]$^-$.

References

[S1] F. Teixidor, J. Pedrajas, I. Rojo, C. Viñas, R. Kivekäs, R. Sillanpää, I. Sivaev, V. Bregadze and S. Sjöberg, *Organometallics*, 2003, **22**, 3414.

[S2] J. Llop, C. Masalles, C. Viñas, F. Teixidor, R. Sillanpää and R. Kivekäs, *Dalton Trans.*, 2003, 556.

[S3] B.A. Wojtczak, A. Andrysiak, B. Grüner and Z.J. Lesnikowski, *Chem. Eur. J.*, 2008, **14**, 10675.

[S4] I. D. Kosenko, I. A. Lobanova, L. A. Chekulaeva, I. A. Godovikov and V. I. Bregadze, *Russ. Chem. Bull*., 2013, **62**, 497.

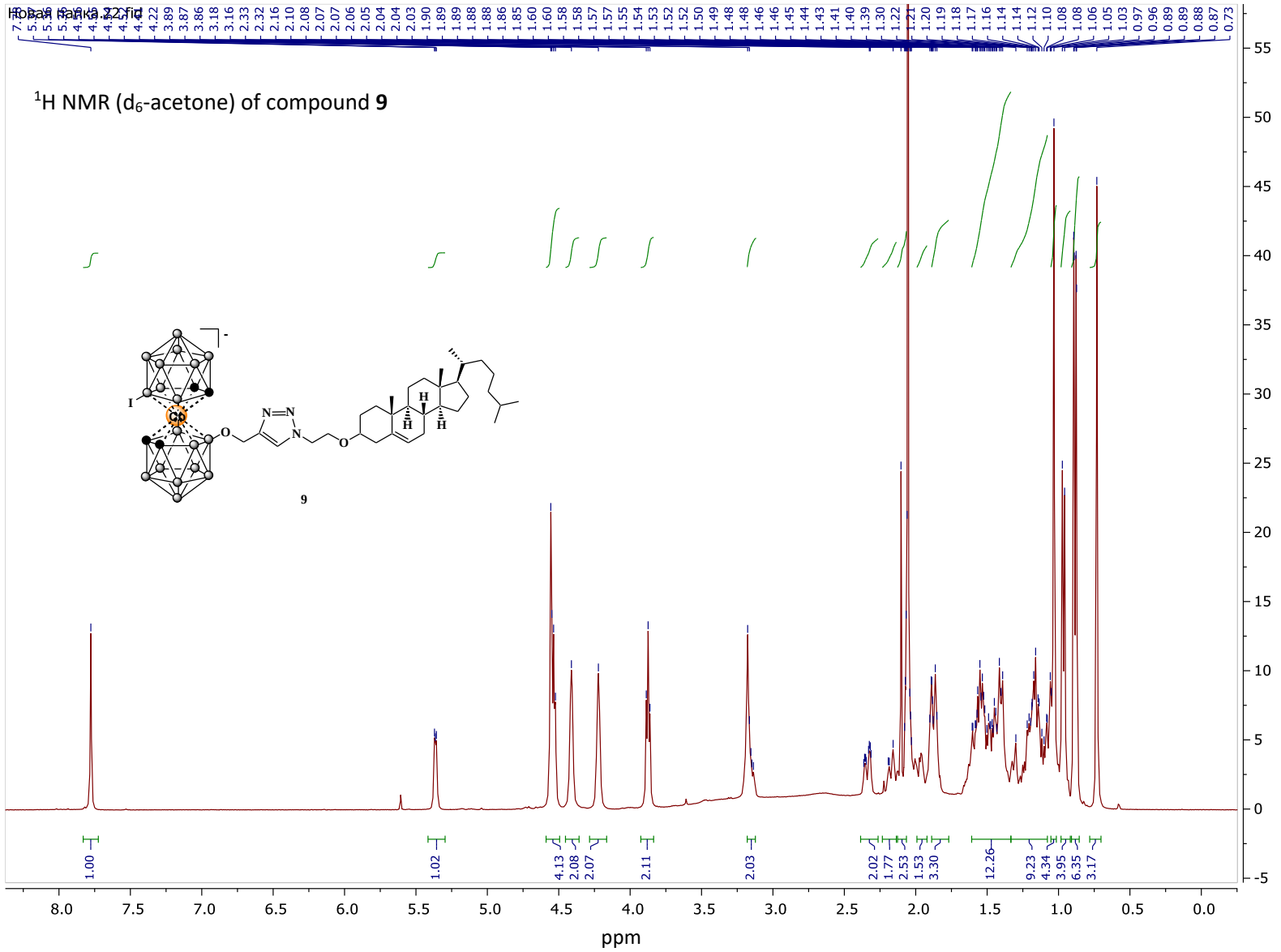
[S5] I. D. Kosenko, I. A. Lobanova, I. V. Ananyev, I. A. Godovikov, L. A. Chekulaeva, Z. A. Starikova, S. Qi and V. I. Bregadze, *J. Organomet. Chem.*, 2014, **769**, 72.

[S6] M. Srinivasan, S. Sankararaman, H. Hopf, I. Dix and P.G. Jones, *J. Org. Chem.,* 2001, **66**, 4299.

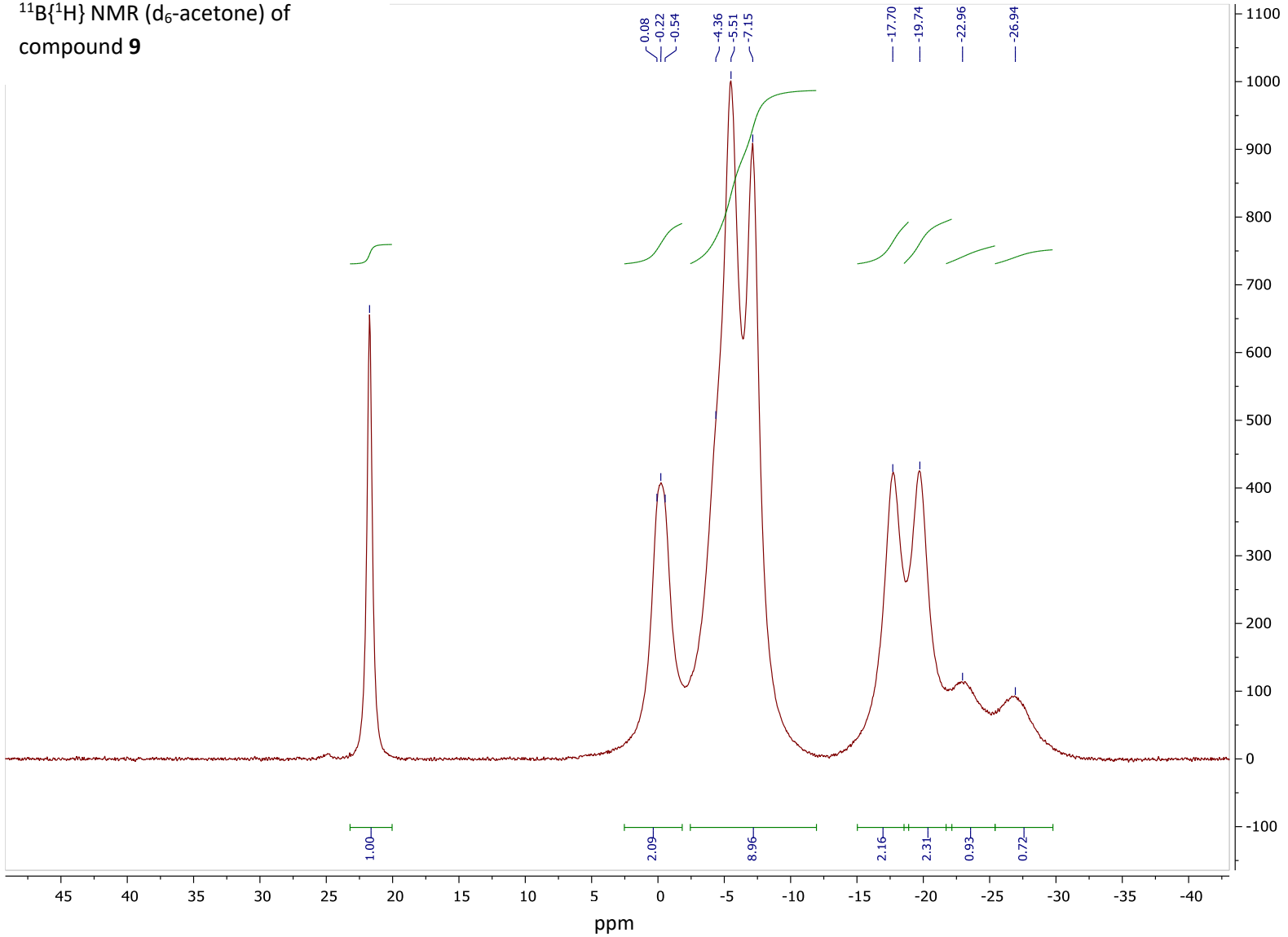
[S7] T. Maruyama, Y. Yamamoto, Y. Kano, M. Kurazono, E. Matsuhisa, H. Takata, T. Takata, K. Atsumi, K. Iwamatsu and E. Shitara, *Bioorg. Med. Chem.*, 2007, **15**, 6379.

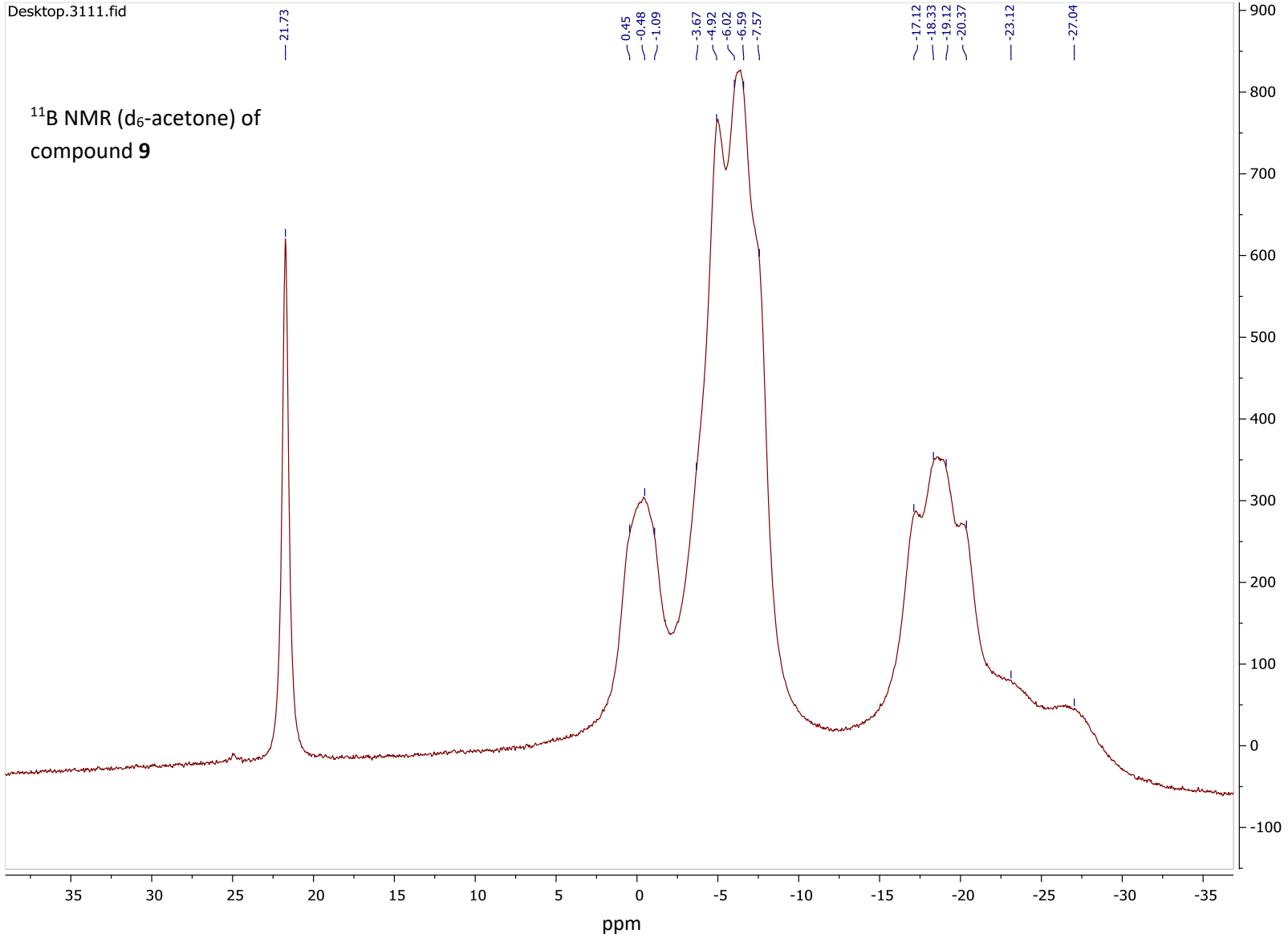
[S8] X. Zhang, X. Yang and S. Zhang, *Synth. Commun.*, 2009, **39**, 830.

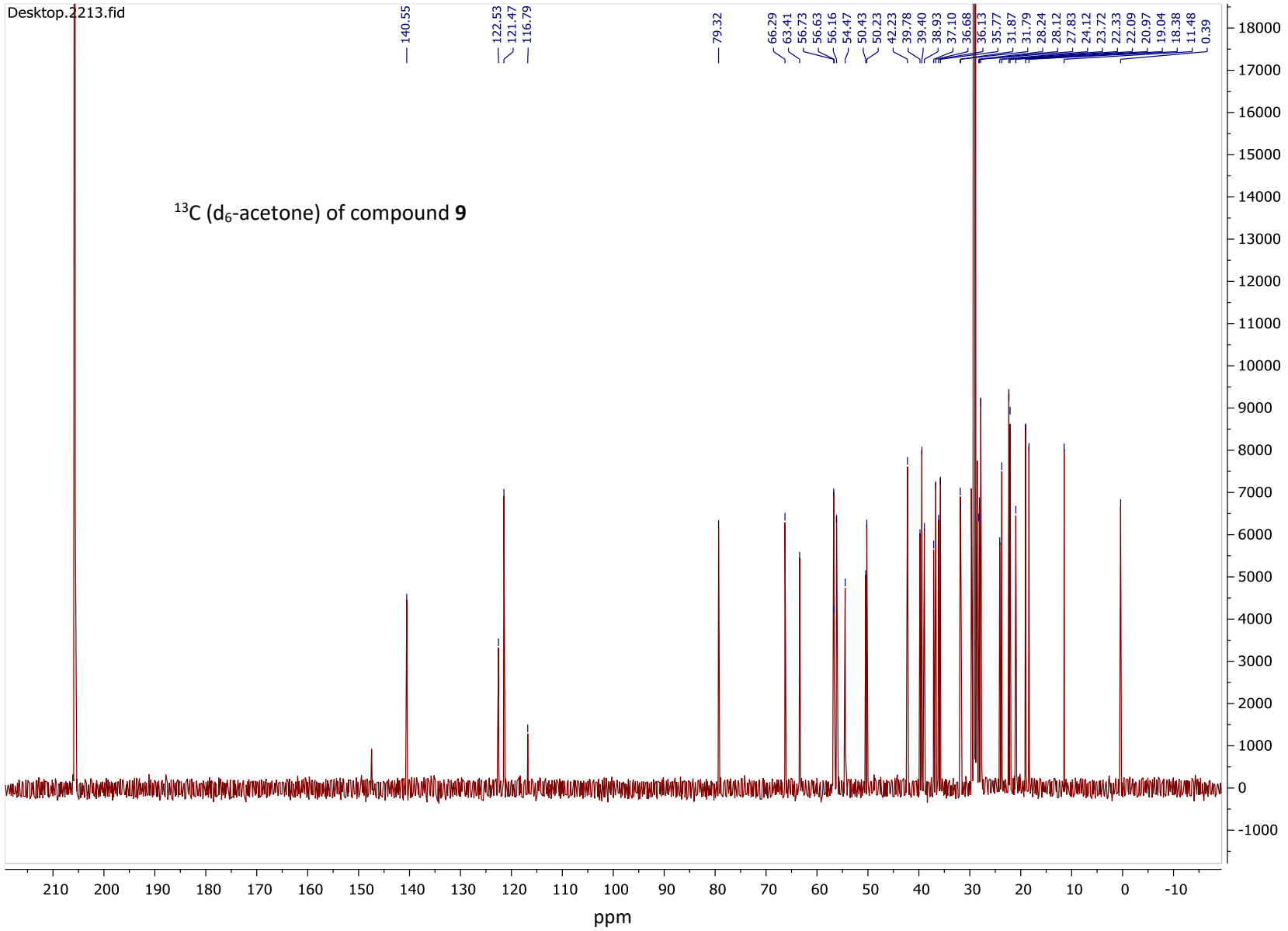
[S9] A. V. Shmal'ko, I. B. Sivaev, V. I. Bregadze and L. V. Kovalenko, *Inorg. Lett.*, 2015, **2**, 1.

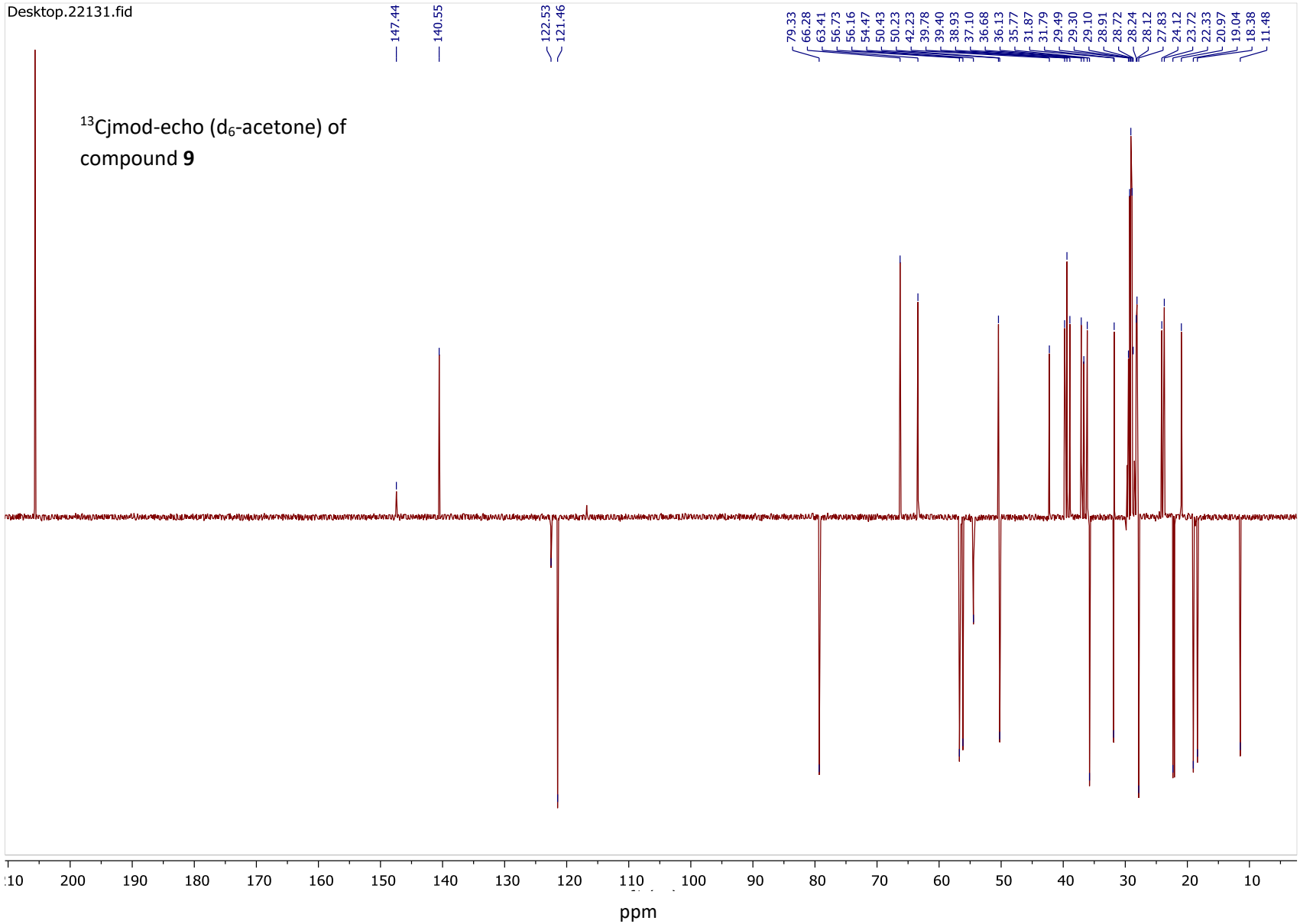

Roba3 Hanka 22.fid
^{1}H NMR (d$_6$-acetone) of compound **9**
9
ppm

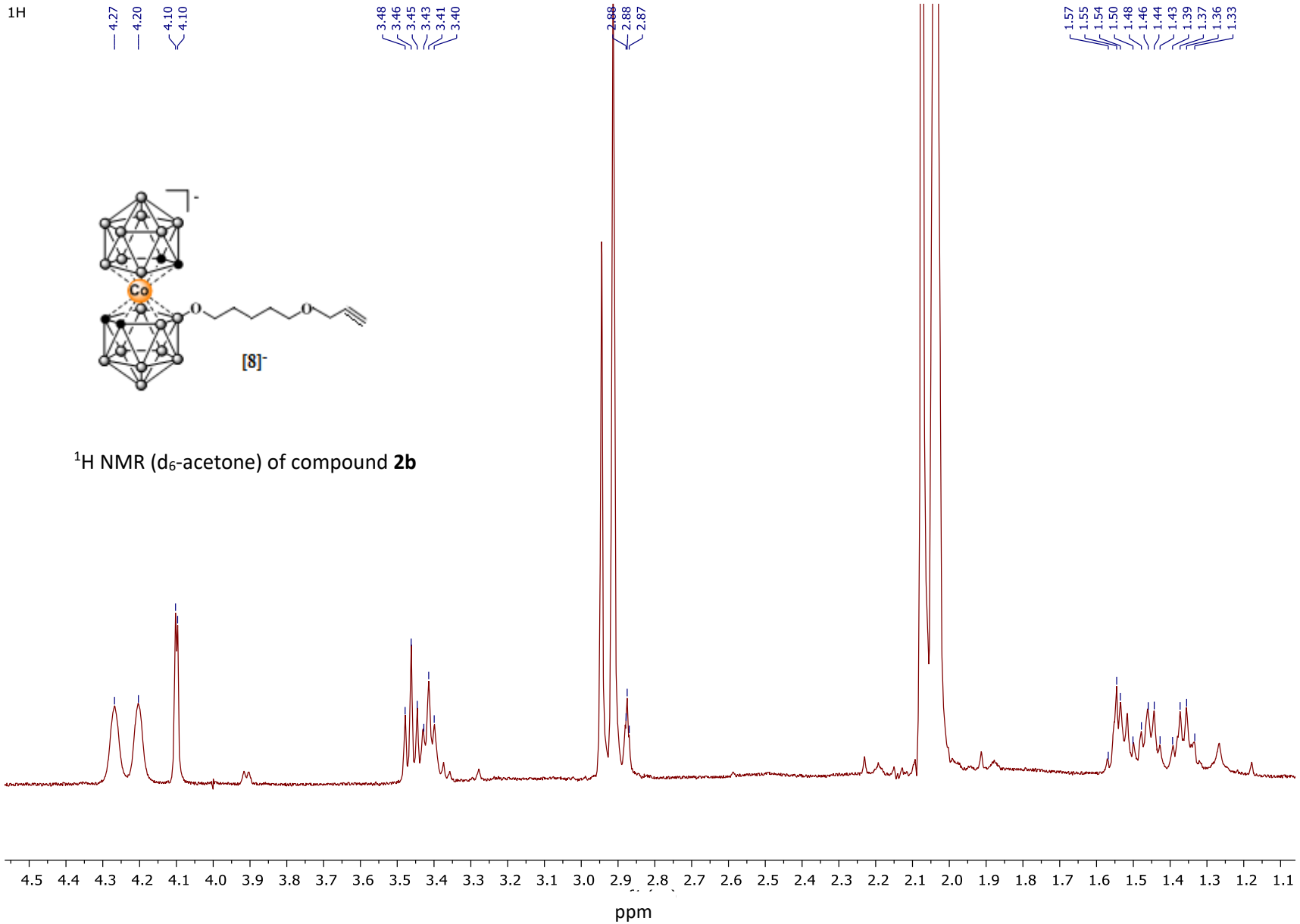
$^{11}B\{^{1}H\}$ NMR (d_6-acetone) of compound **9**



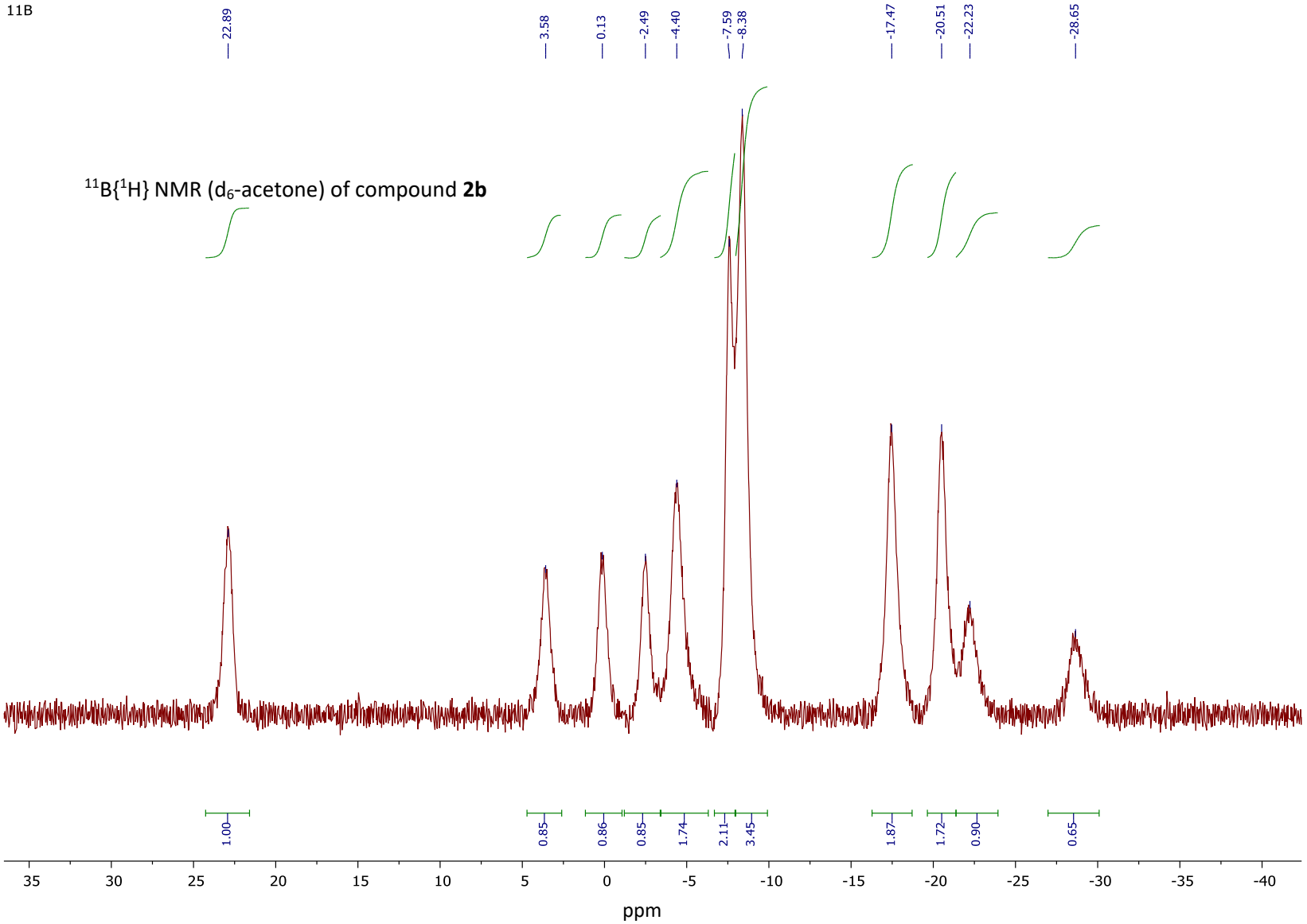

Desktop.3111.fid
^{11}B NMR (d_6-acetone) of compound **9**
21.73
0.45
-0.48
-1.09
-3.67
-4.92
-6.02
-6.59
-7.57
-17.12
-18.33
-19.12
-20.37
-23.12
-27.04
900
800
700
600
500
400
300
200
100
0
-100
35
30
25
20
15
10
5
0
-5
-10
-15
-20
-25
-30
-35
ppm


Desktop.2213.fid
140.55
122.53
121.47
116.79
79.32
66.29
63.41
56.73
56.63
56.16
54.47
50.43
50.23
42.23
39.78
39.40
38.93
37.10
36.68
36.13
35.77
31.87
31.79
28.24
28.12
27.83
24.12
23.72
22.33
22.09
20.97
19.04
18.38
11.48
0.39
^{13}C (d_6-acetone) of compound **9**
ppm

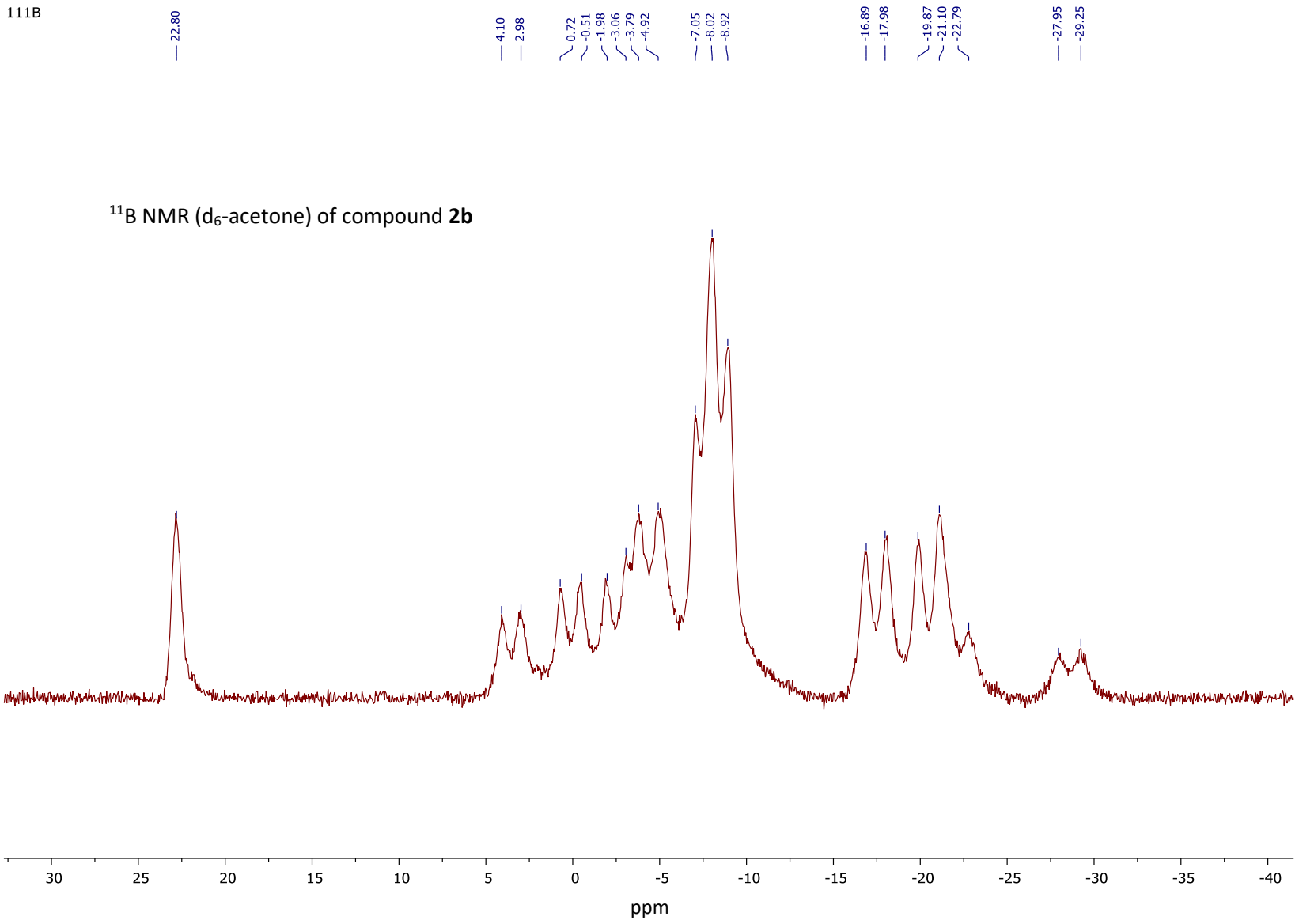

Desktop.22131.fid
147.44
140.55
122.53
121.46
79.33
66.28
63.41
56.73
56.16
54.47
50.43
50.23
42.23
39.78
39.40
38.93
37.10
36.68
36.13
35.77
31.87
31.79
29.49
29.30
29.10
28.91
28.72
28.24
28.12
27.83
24.12
23.72
22.33
20.97
19.04
18.38
11.48
^{13}Cjmod-echo (d_6-acetone) of compound **9**
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
ppm



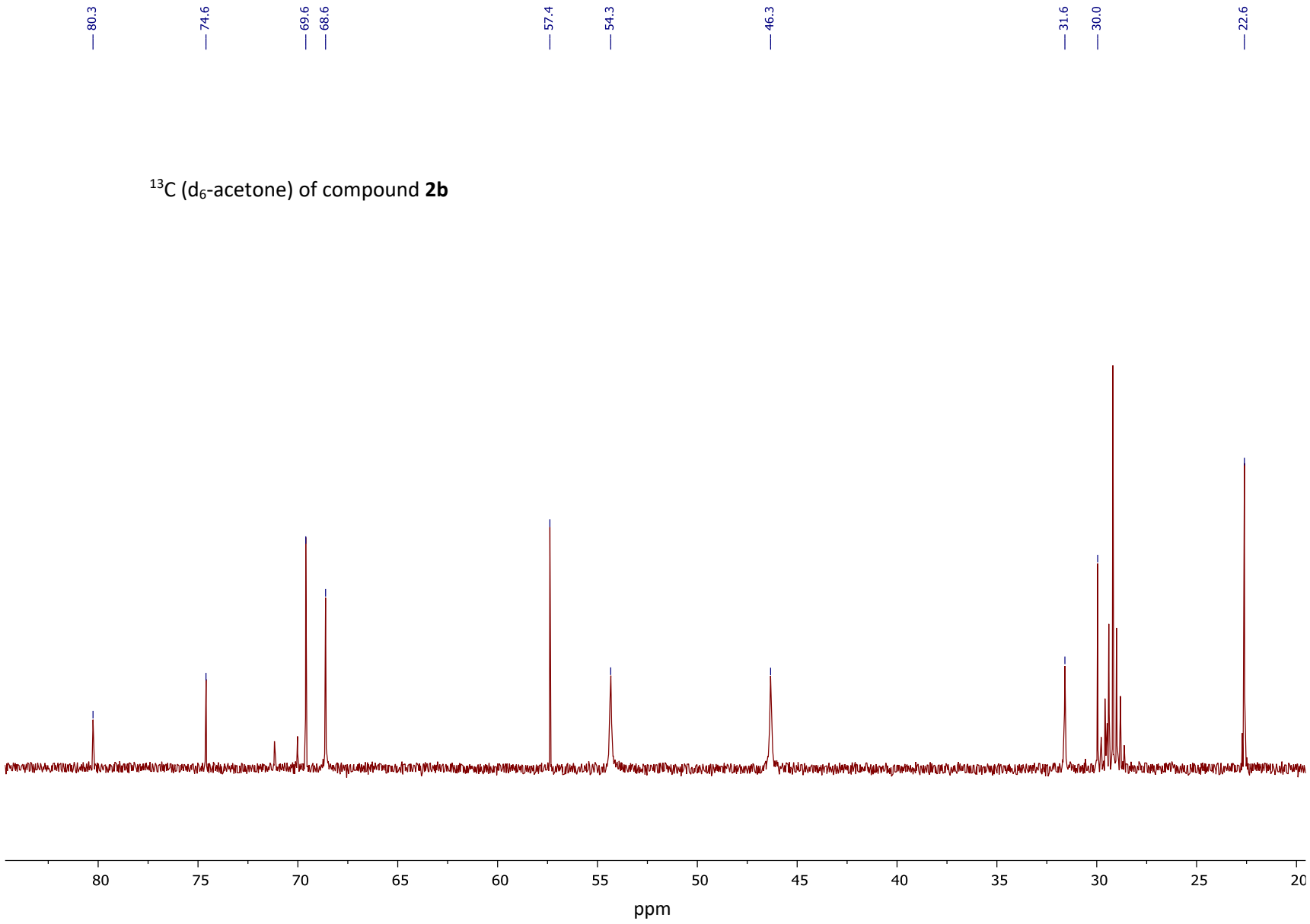
^{1}H NMR (d_6-acetone) of compound **2b**



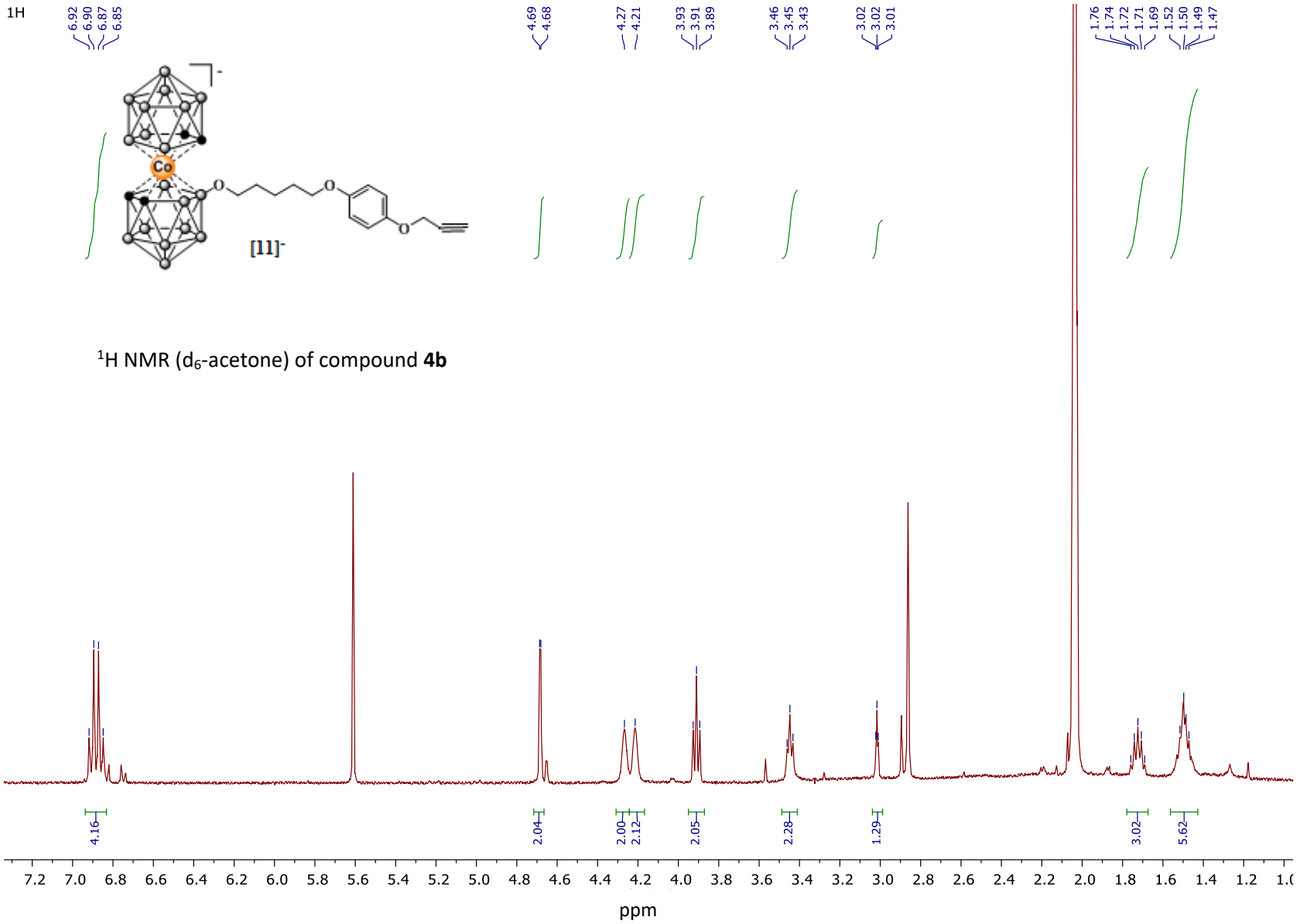
$^{11}B\{^{1}H\}$ NMR (d_6-acetone) of compound **2b**



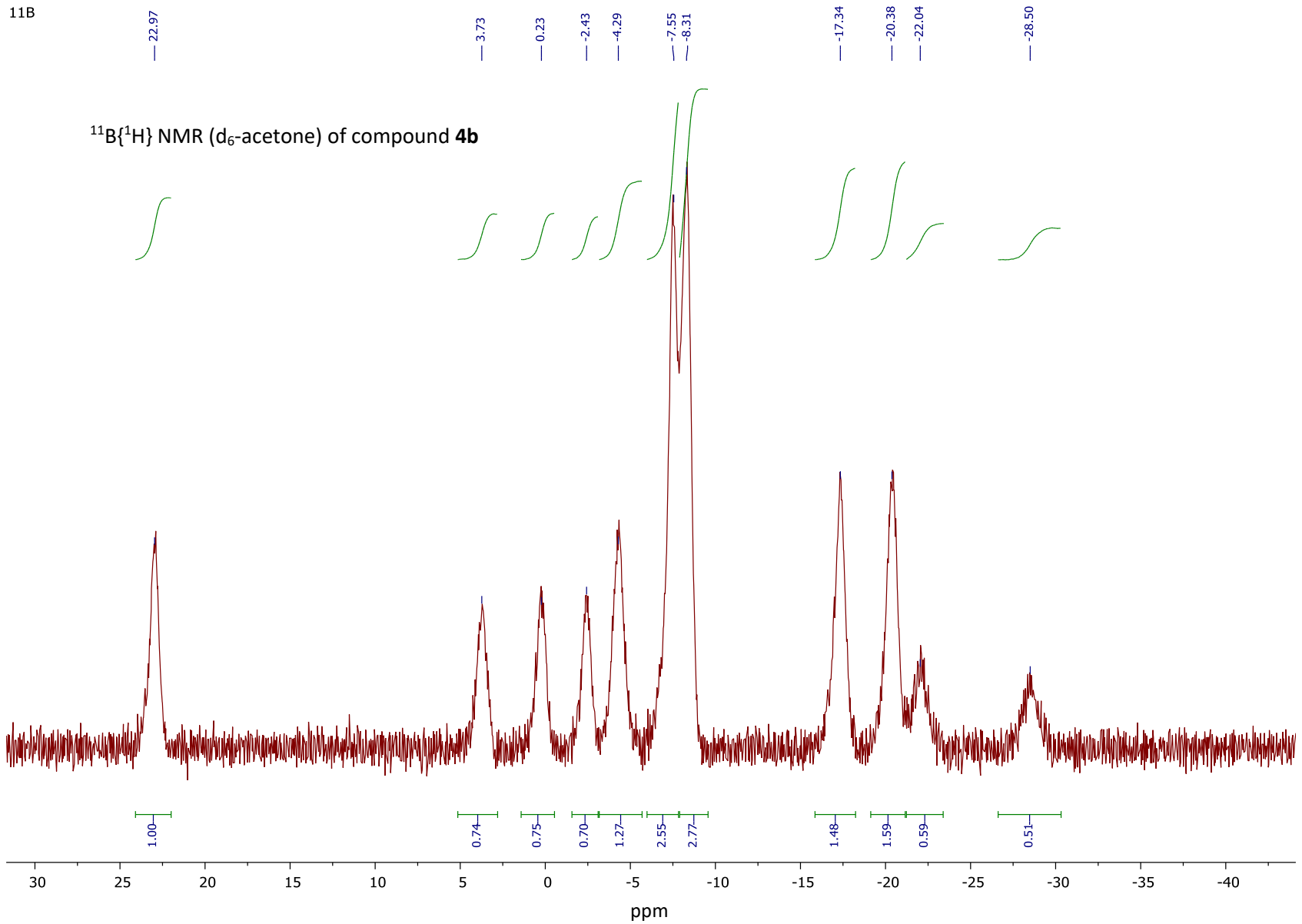
^{11}B NMR (d_6-acetone) of compound **2b**



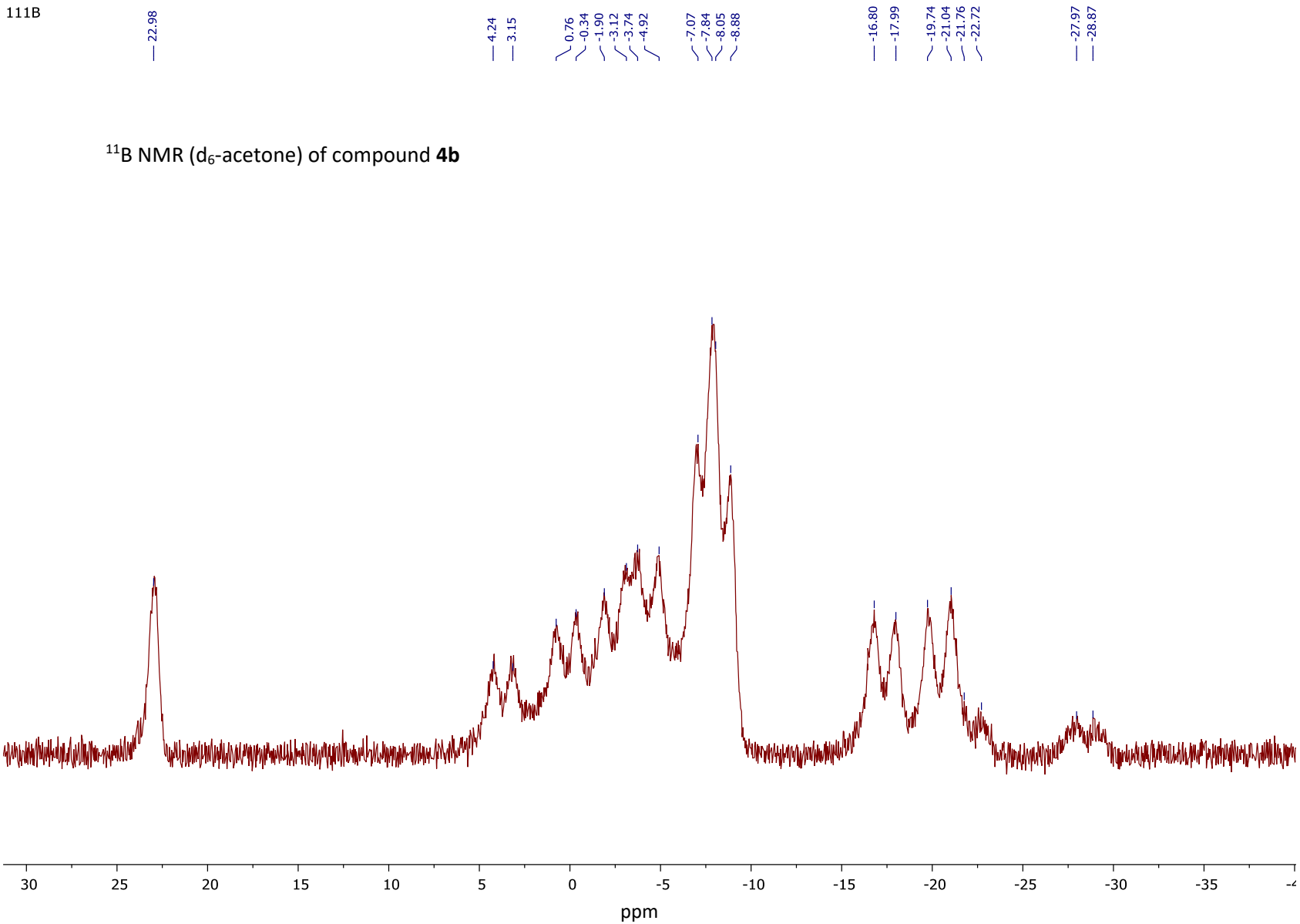
^{13}C (d_6-acetone) of compound **2b**



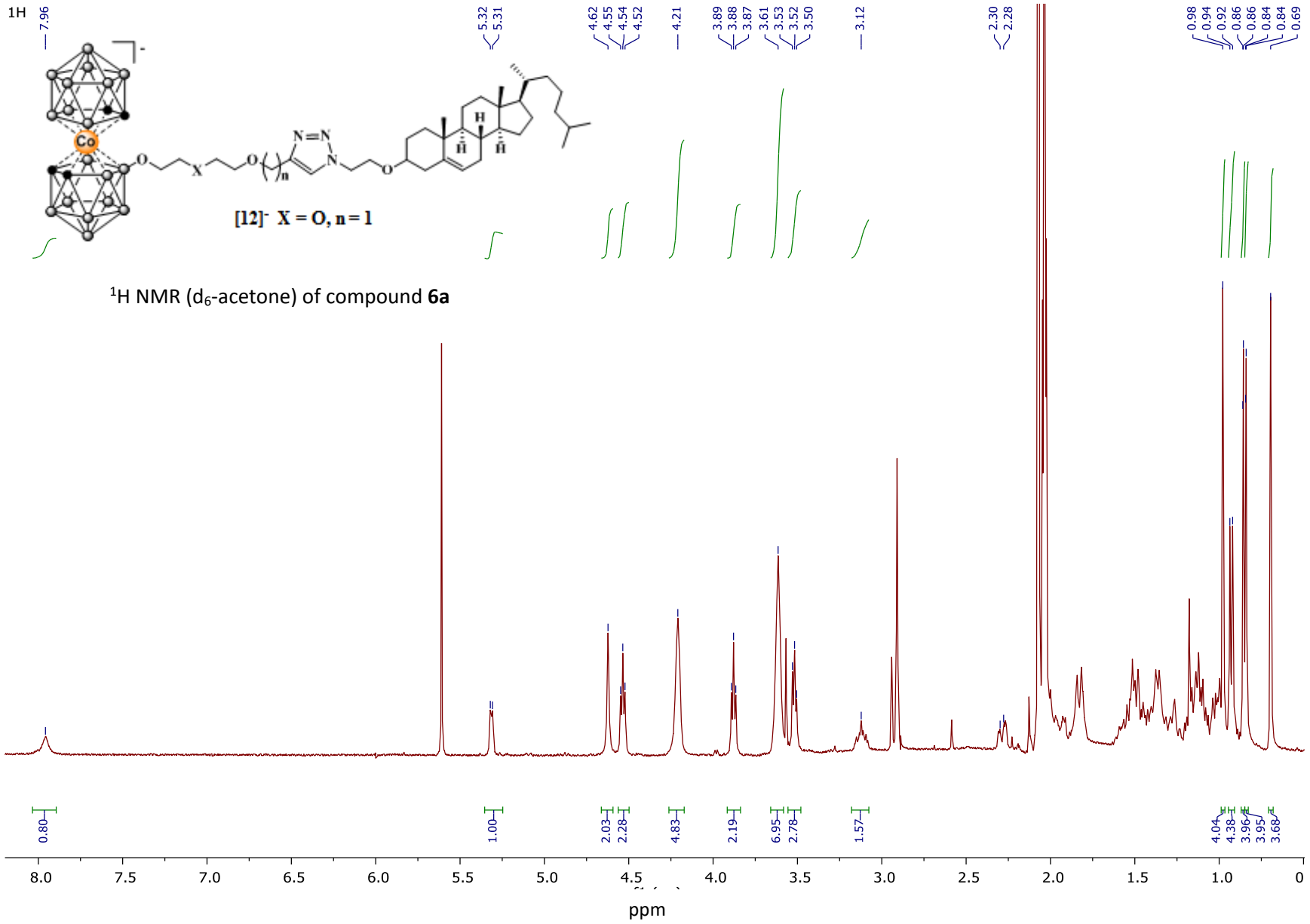
^{1}H NMR (d_6-acetone) of compound **4b**



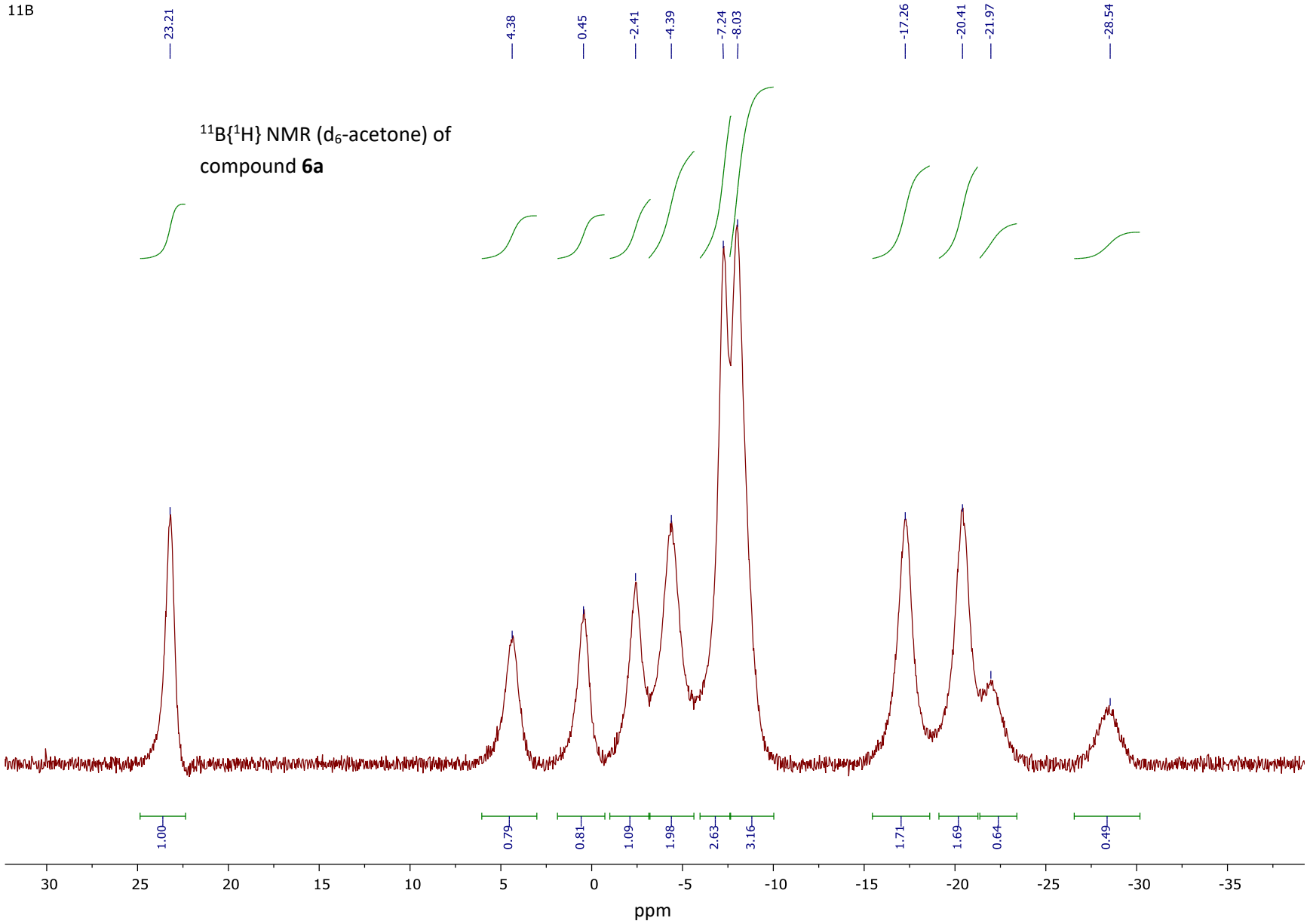
$^{11}B\{^{1}H\}$ NMR (d_6-acetone) of compound **4b**



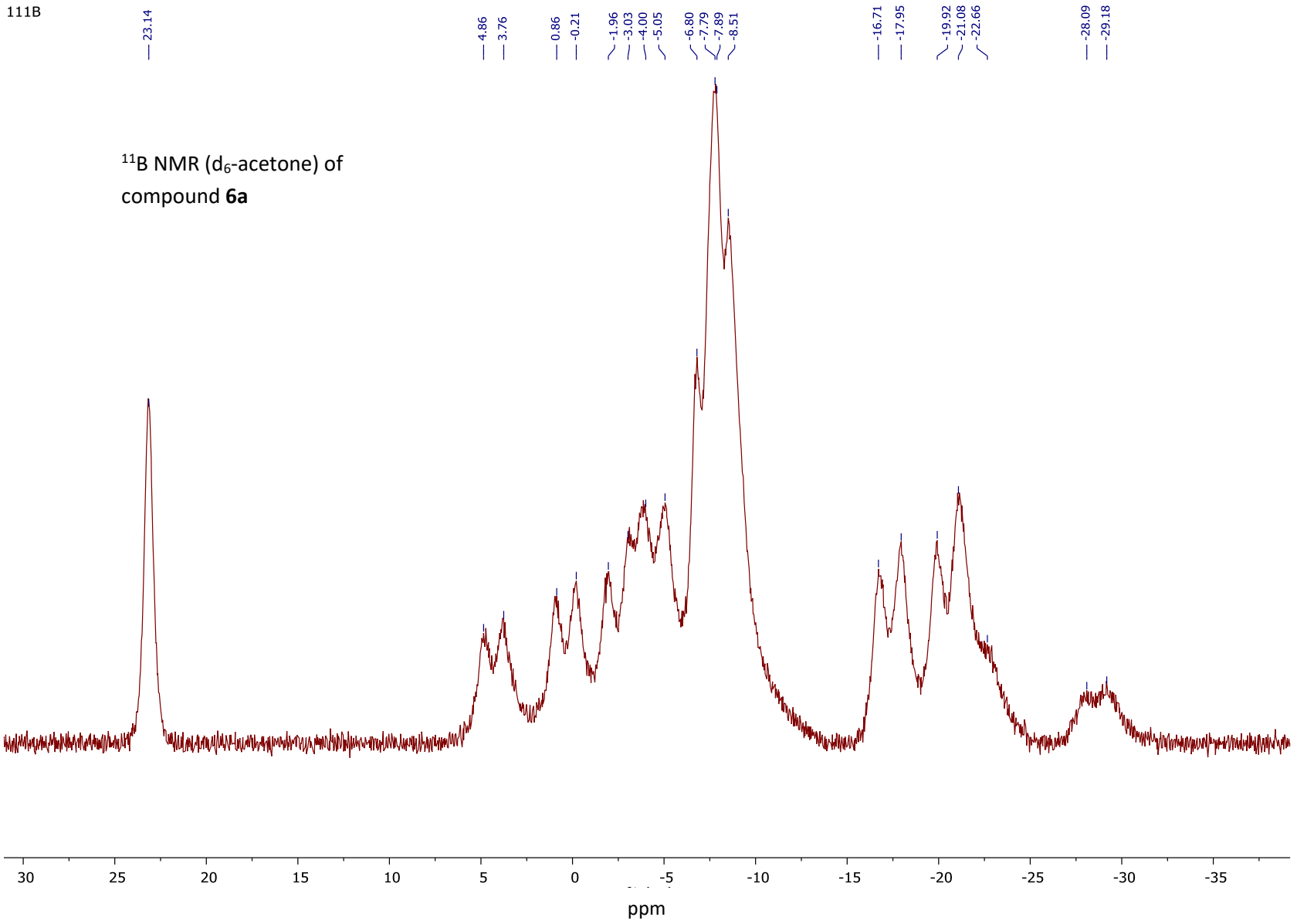
^{11}B NMR (d_6-acetone) of compound **4b**



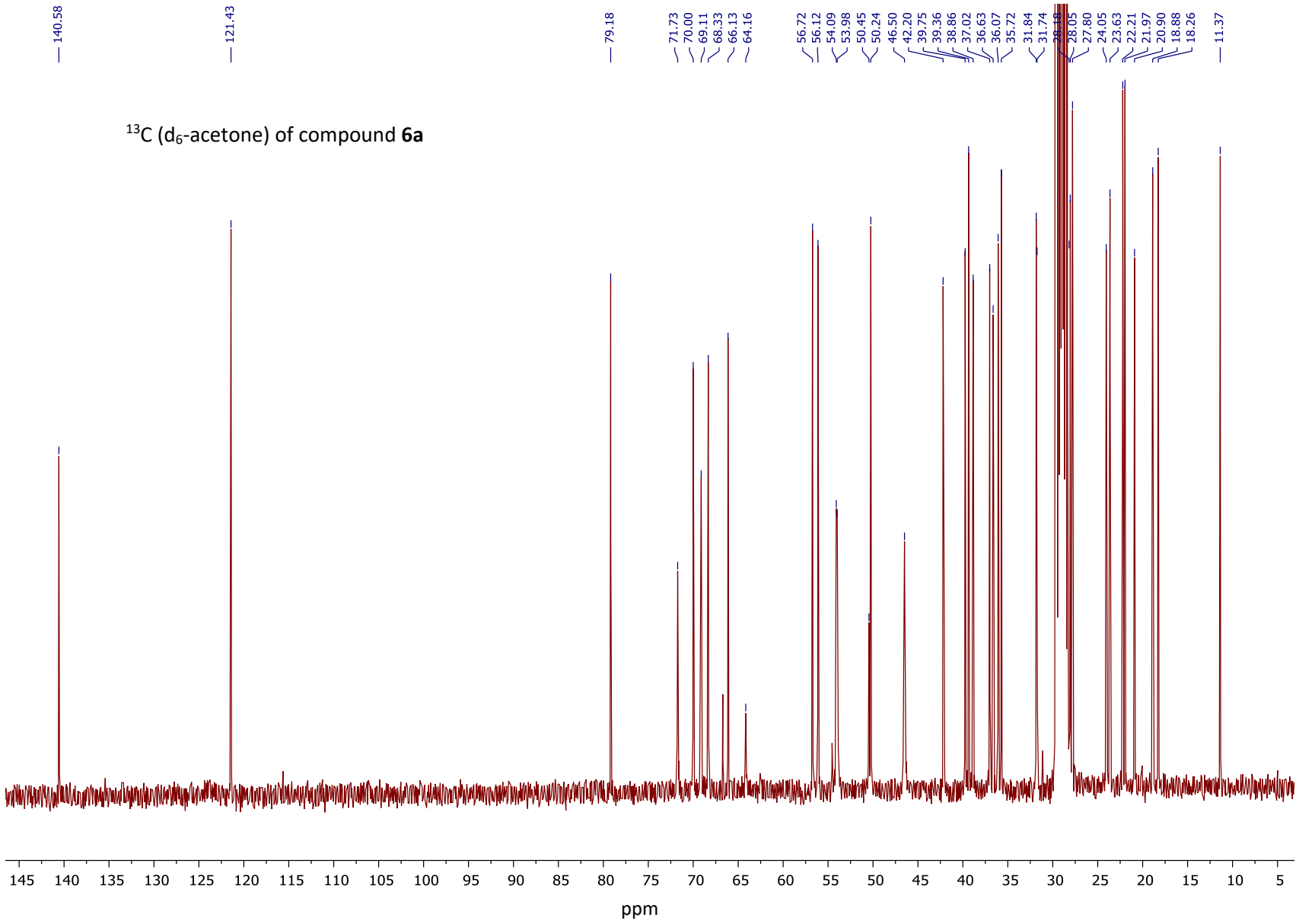
^{1}H NMR (d_6-acetone) of compound **6a**



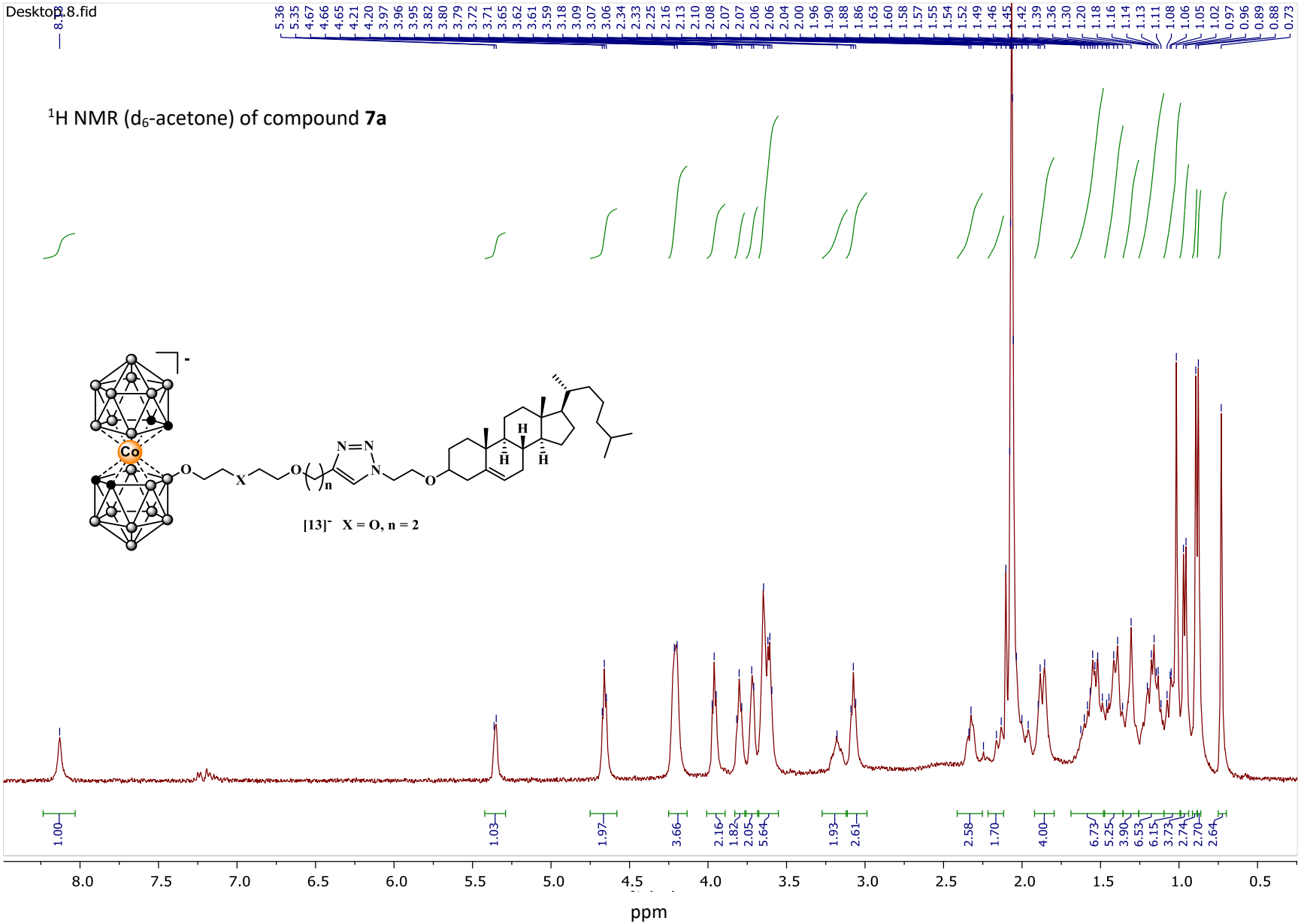
$^{11}B\{^{1}H\}$ NMR (d_6-acetone) of compound **6a**

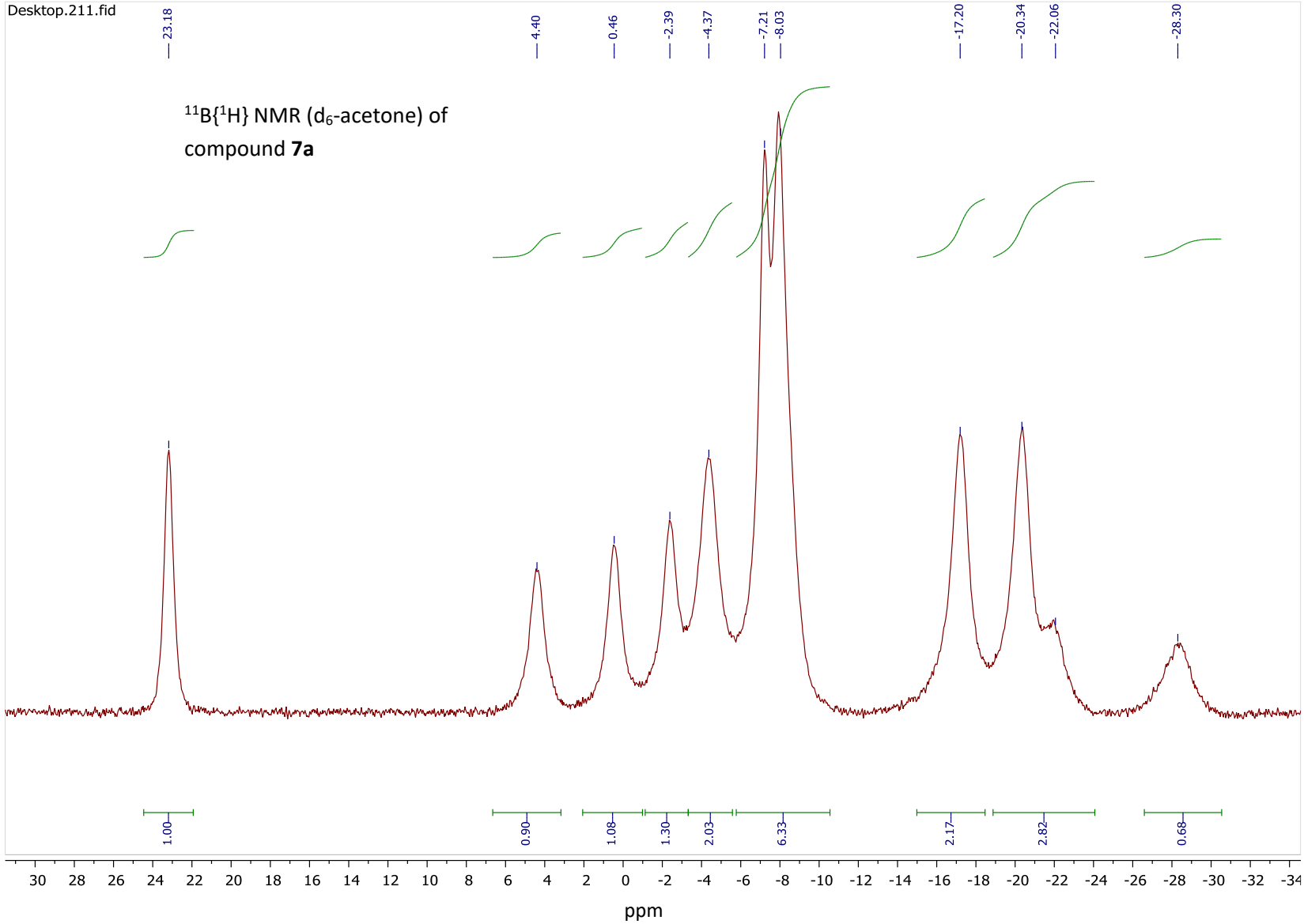


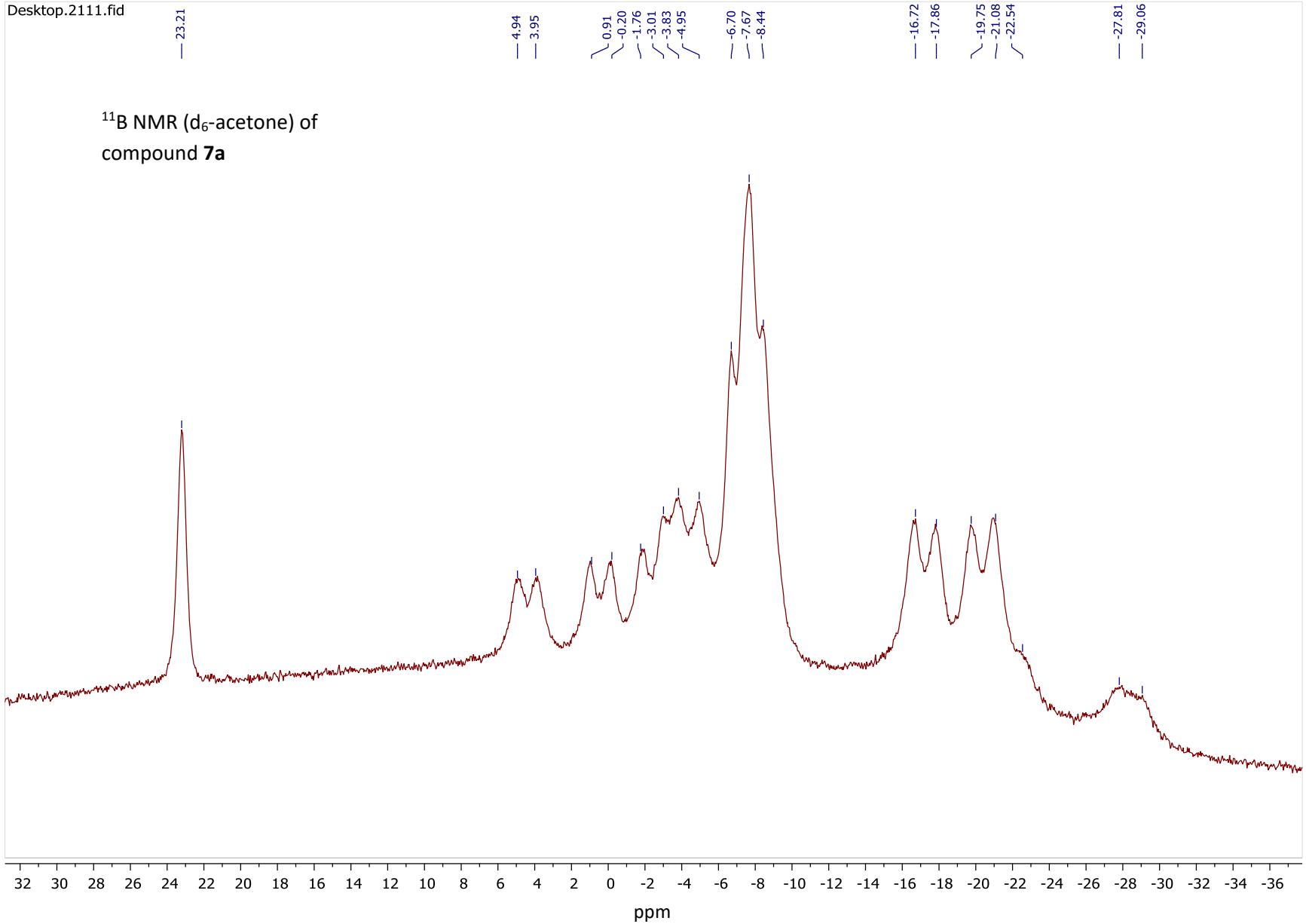
^{11}B NMR (d_6-acetone) of compound **6a**

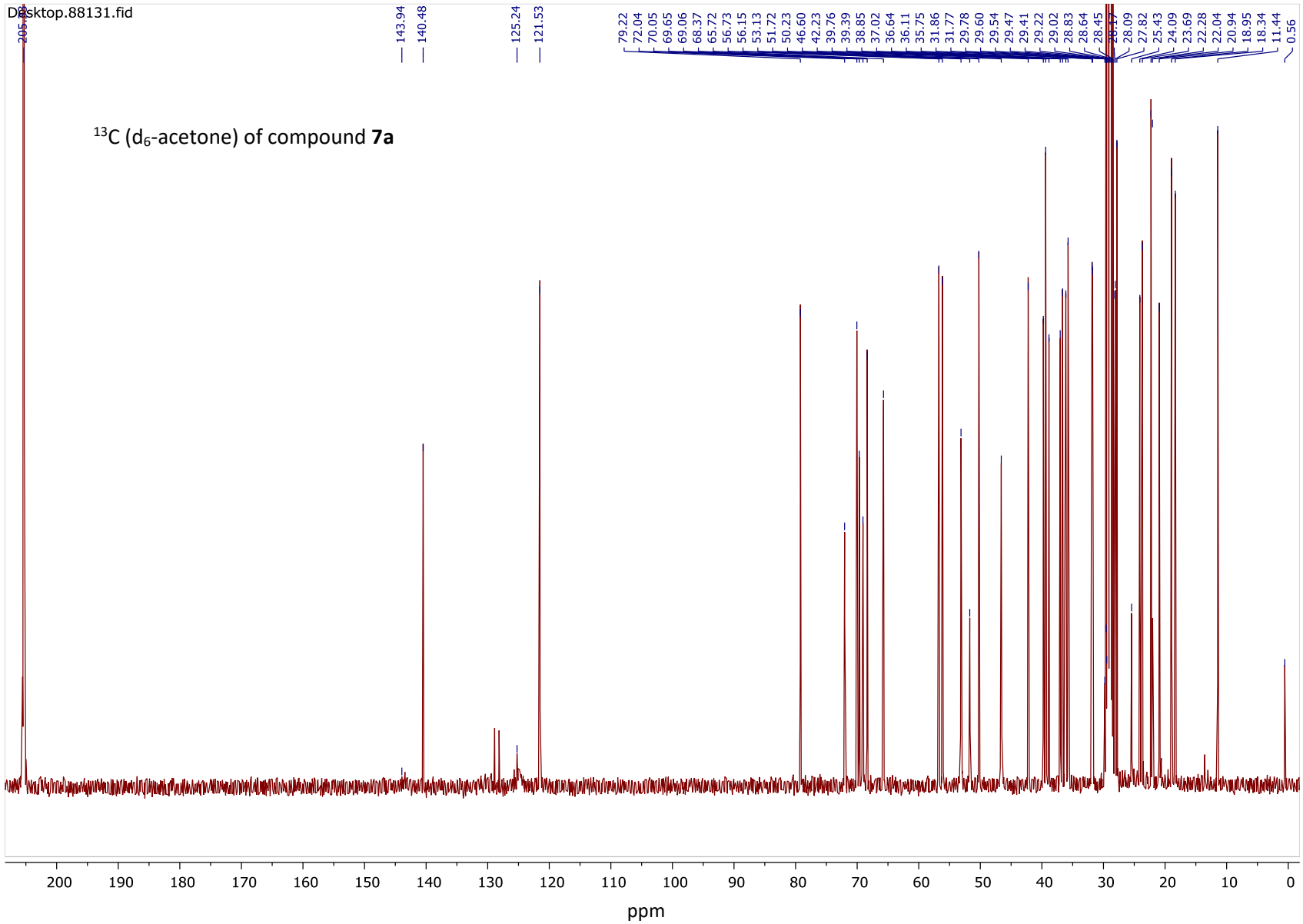


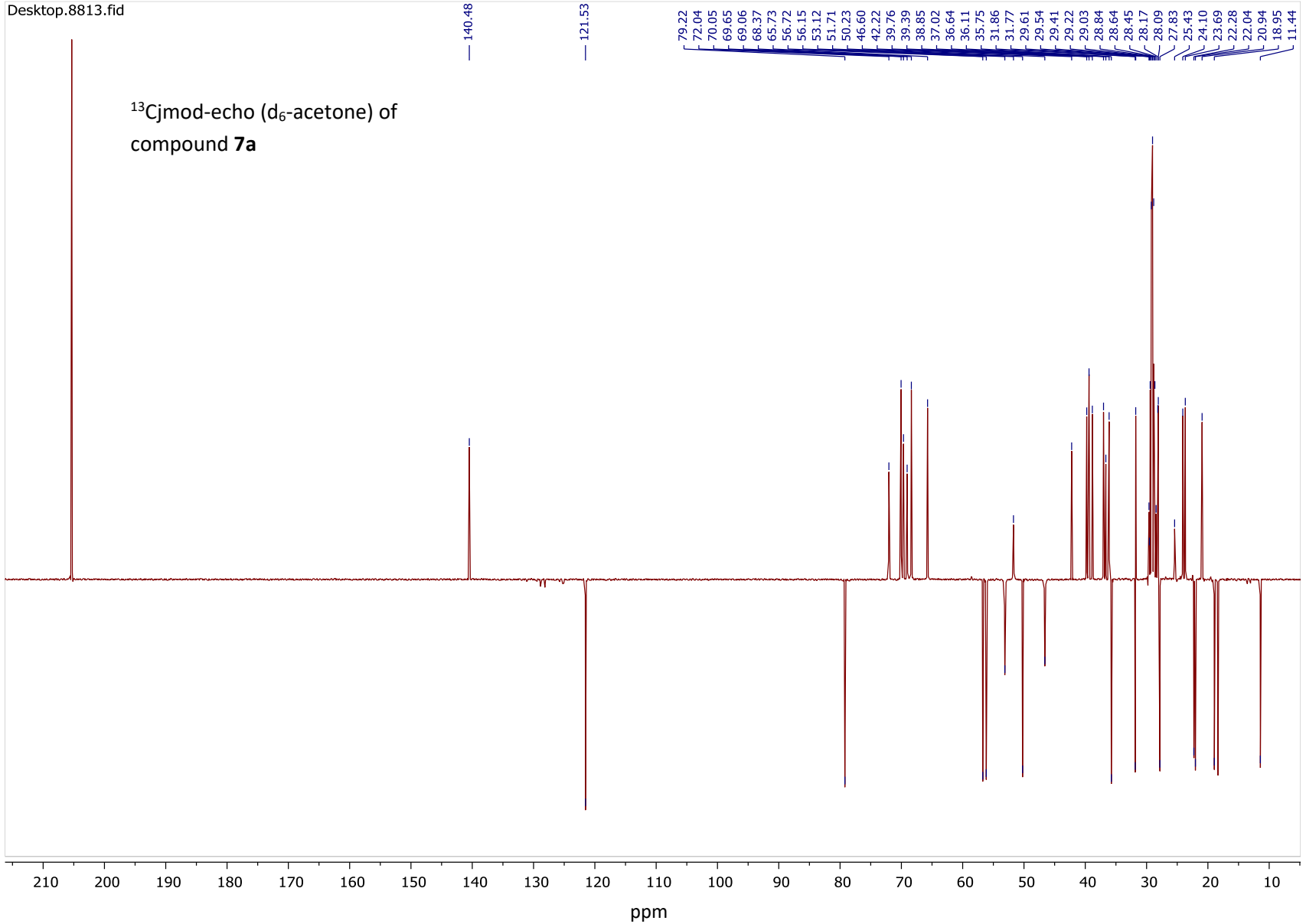
^{13}C (d_6-acetone) of compound **6a**

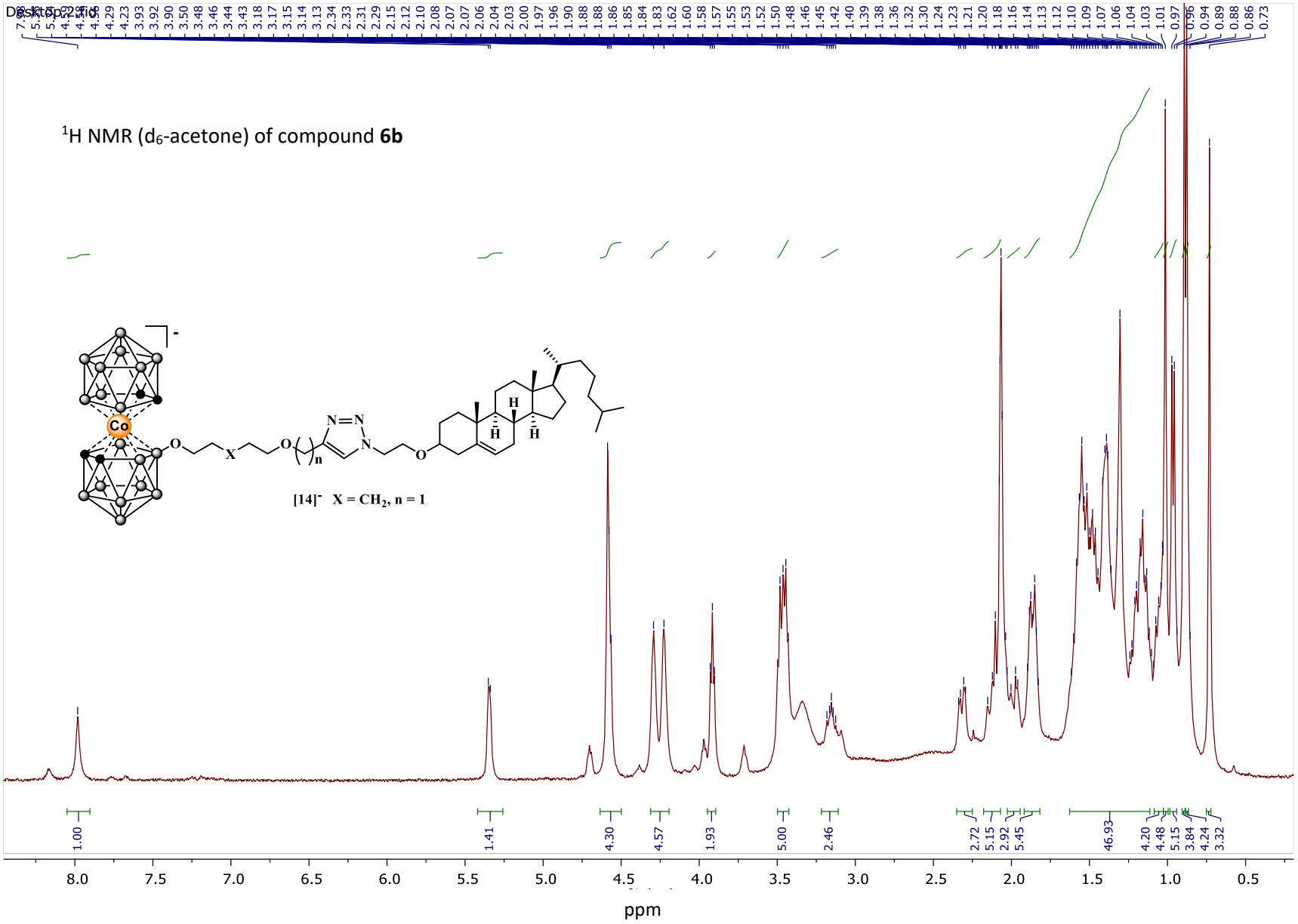

Desktop2.8.fid
^{1}H NMR (d$_6$-acetone) of compound **7a**
[13]$^-$ X = O, n = 2
ppm

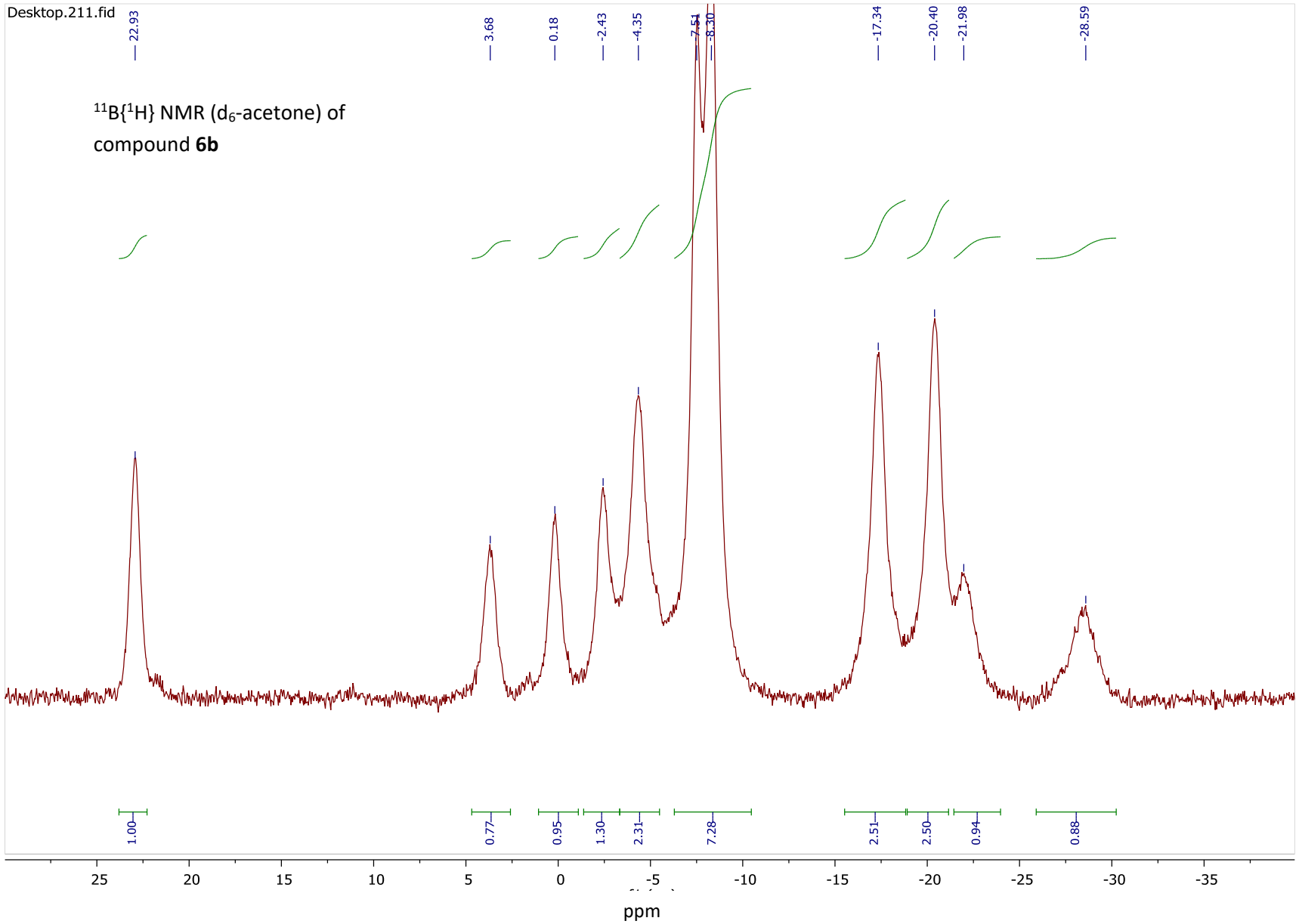

Desktop.211.fid
23.18
4.40
0.46
-2.39
-4.37
-7.21
-8.03
-17.20
-20.34
-22.06
-28.30
$^{11}B\{^{1}H\}$ NMR (d_6-acetone) of compound **7a**
1.00
0.90
1.08
1.30
2.03
6.33
2.17
2.82
0.68
30 28 26 24 22 20 18 16 14 12 10 8 6 4 2 0 -2 -4 -6 -8 -10 -12 -14 -16 -18 -20 -22 -24 -26 -28 -30 -32 -34
ppm

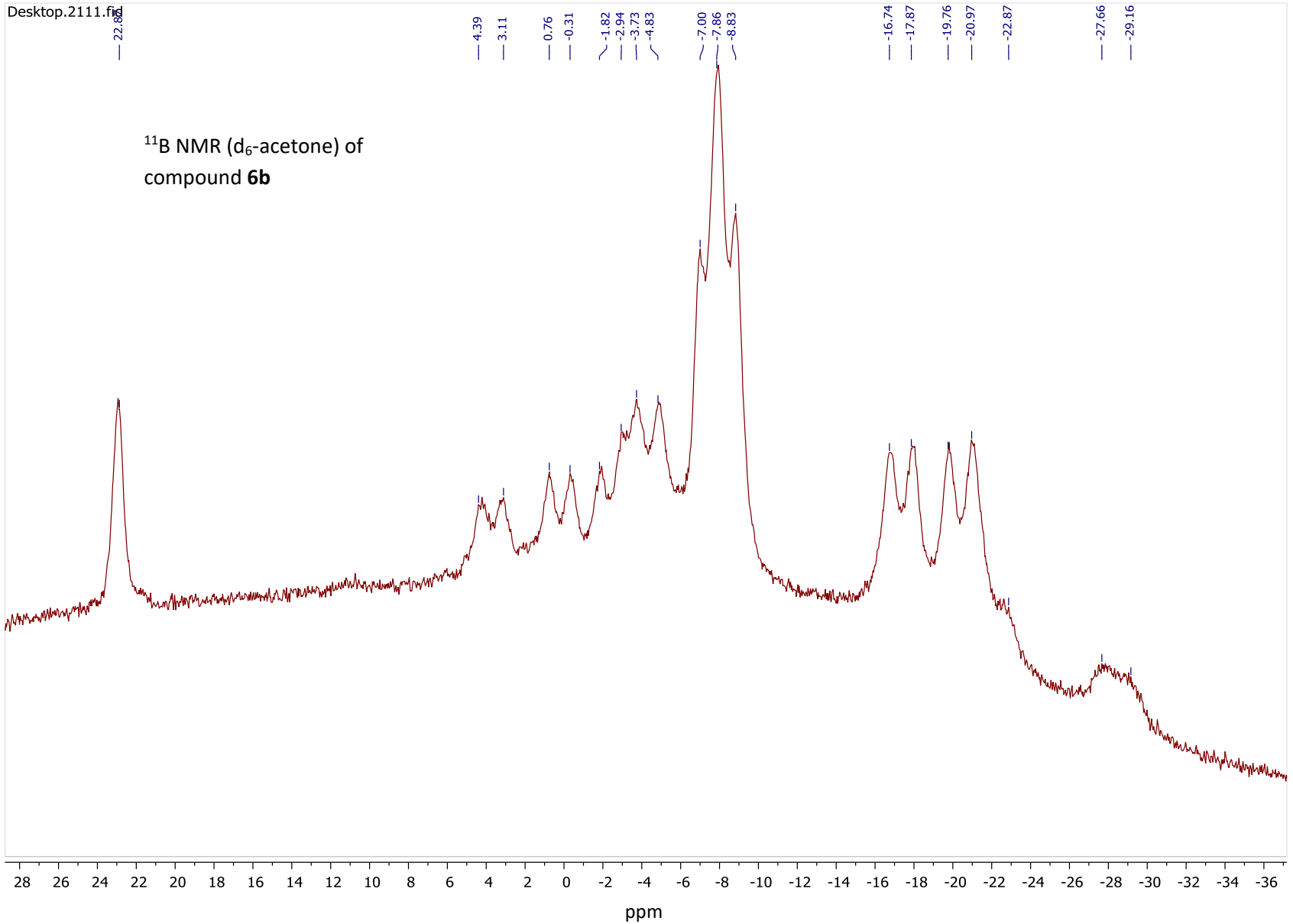

Desktop.2111.fid
23.21
4.94
3.95
0.91
-0.20
-1.76
-3.01
-3.83
-4.95
-6.70
-7.67
-8.44
-16.72
-17.86
-19.75
-21.08
-22.54
-27.81
-29.06
^{11}B NMR (d_6-acetone) of compound **7a**
32 30 28 26 24 22 20 18 16 14 12 10 8 6 4 2 0 -2 -4 -6 -8 -10 -12 -14 -16 -18 -20 -22 -24 -26 -28 -30 -32 -34 -36
ppm

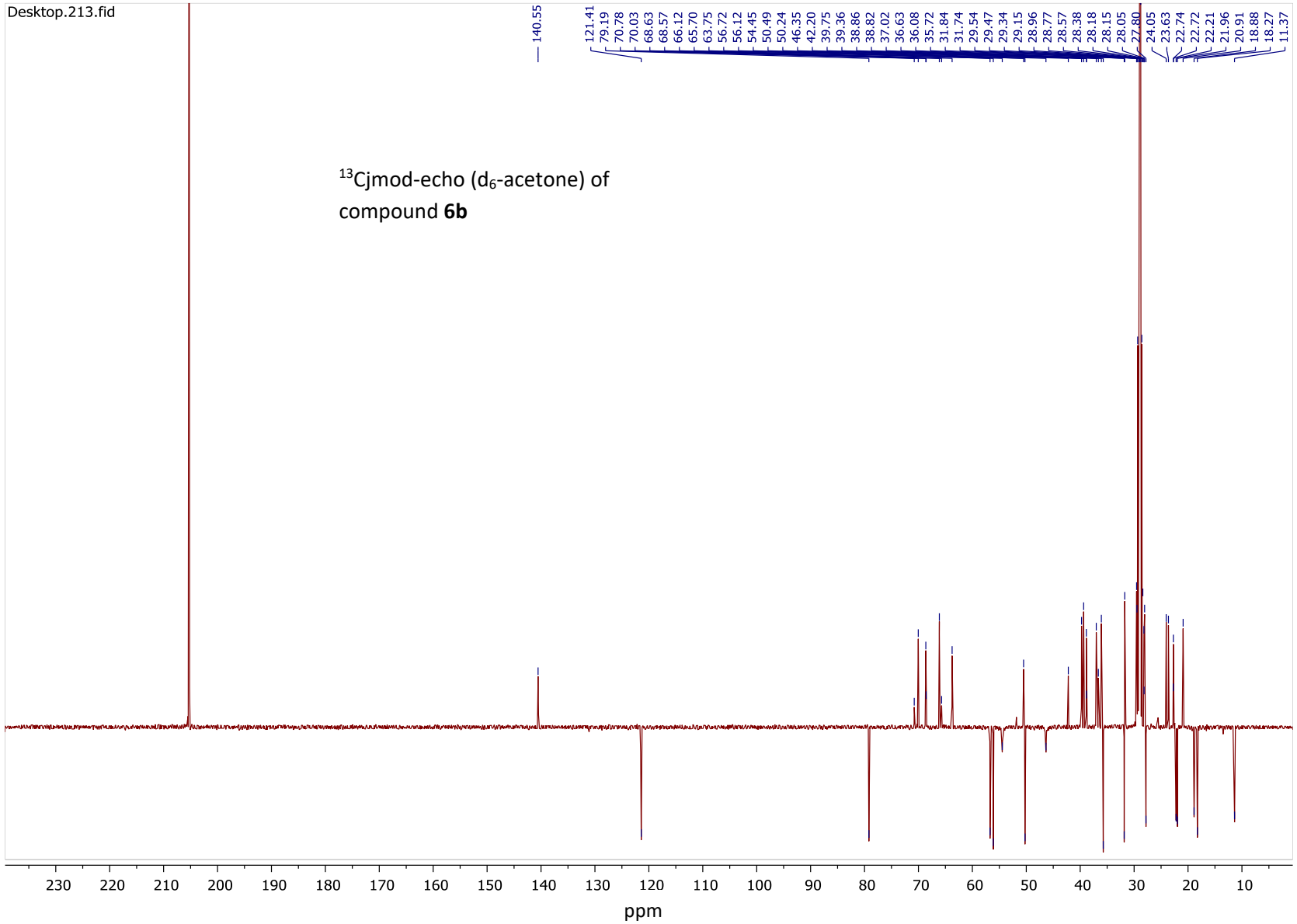

Desktop.88131.fid
205.93
143.94
140.48
125.24
121.53
79.22
72.04
70.05
69.65
69.06
68.37
65.72
56.73
56.15
53.13
51.72
50.23
46.60
42.23
39.76
39.39
38.85
37.02
36.64
36.11
35.75
31.86
31.77
29.78
29.60
29.54
29.47
29.41
29.22
29.02
28.83
28.64
28.45
28.17
28.09
27.82
25.43
24.09
23.69
22.28
22.04
20.94
18.95
18.34
11.44
0.56
^{13}C (d_6-acetone) of compound **7a**
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
ppm


Desktop.8813.fid
140.48
121.53
79.22
72.04
70.05
69.65
69.06
68.37
65.73
56.72
56.15
53.12
51.71
50.23
46.60
42.22
39.76
39.39
38.85
37.02
36.64
36.11
35.75
31.86
31.77
29.61
29.54
29.41
29.22
29.03
28.84
28.64
28.45
28.17
28.09
27.83
25.43
24.10
23.69
22.28
22.04
20.94
18.95
11.44
^{13}Cjmod-echo (d_6-acetone) of compound **7a**
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
ppm

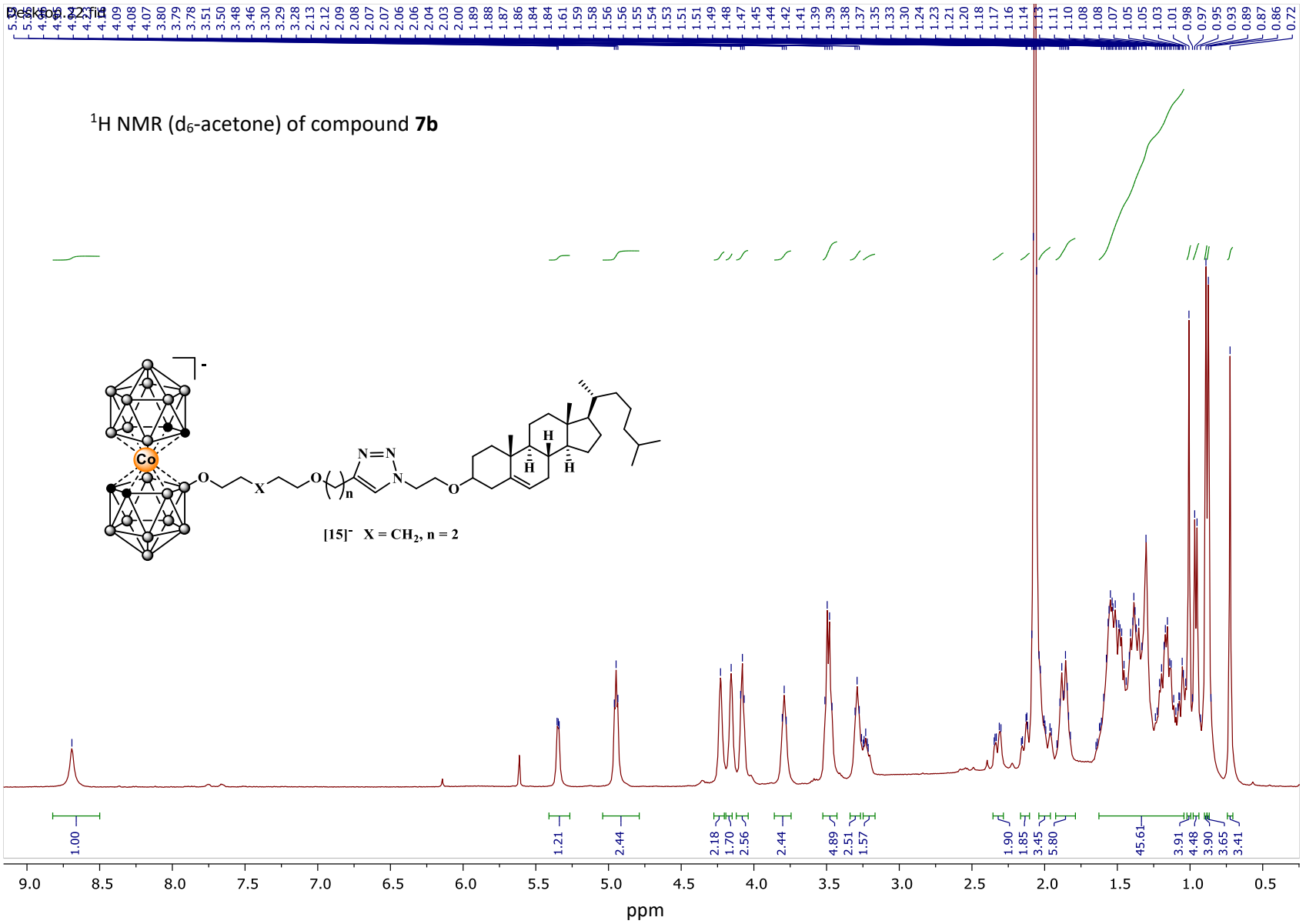

Desktop 22.fid
^{1}H NMR (d_6-acetone) of compound **6b**
Co
O
X
O
n
N=N
N
O
H
H
H
[14]$^-$ X = CH$_2$, n = 1
1.00
1.41
4.30
4.57
1.93
5.00
2.46
2.72
5.15
2.92
5.45
46.93
4.20
4.48
5.15
3.84
4.24
3.32
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
ppm

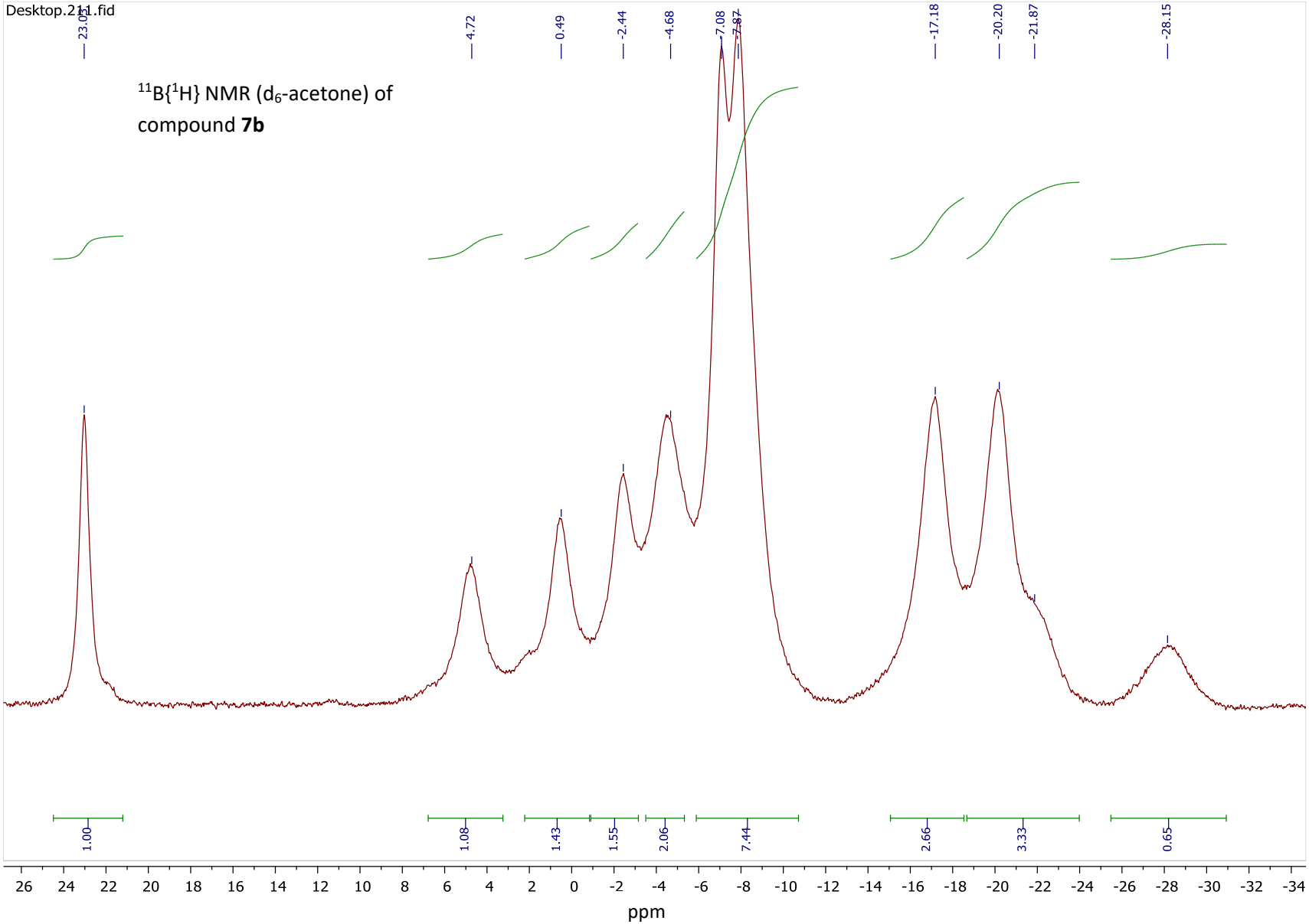

Desktop.211.fid
22.93
3.68
0.18
-2.43
-4.35
7.54
8.30
-17.34
-20.40
-21.98
-28.59
$^{11}B\{^{1}H\}$ NMR (d_6-acetone) of compound **6b**
1.00
0.77
0.95
1.30
2.31
7.28
2.51
2.50
0.94
0.88
25
20
15
10
5
0
-5
-10
-15
-20
-25
-30
-35
ppm

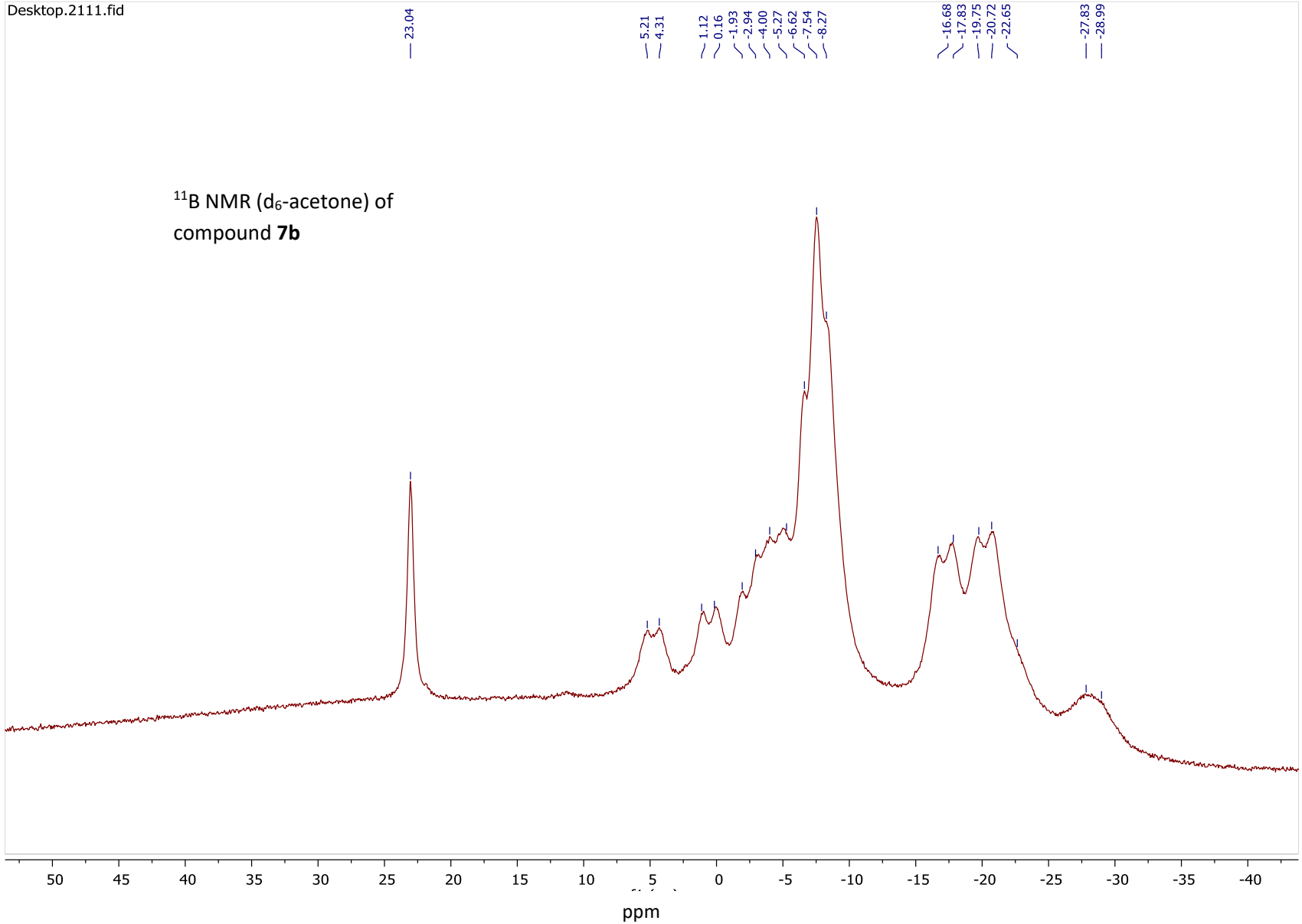

Desktop.2111.fid
22.82
4.39
3.11
0.76
-0.31
-1.82
-2.94
-3.73
-4.83
-7.00
-7.86
-8.83
-16.74
-17.87
-19.76
-20.97
-22.87
-27.66
-29.16
^{11}B NMR (d_6-acetone) of compound **6b**
28 26 24 22 20 18 16 14 12 10 8 6 4 2 0 -2 -4 -6 -8 -10 -12 -14 -16 -18 -20 -22 -24 -26 -28 -30 -32 -34 -36
ppm



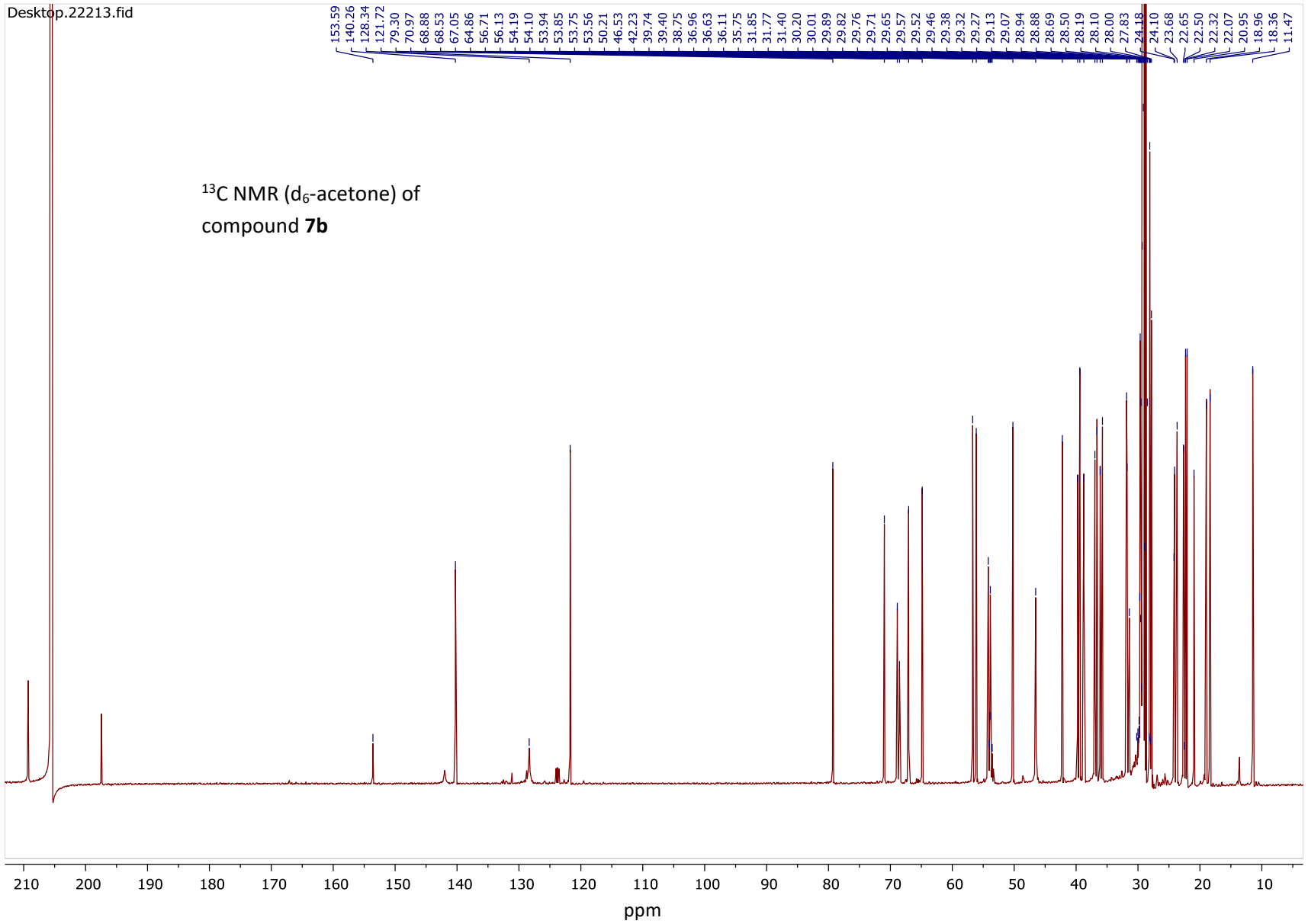
^{13}Cjmod-echo (d_6-acetone) of compound **6b**


Desktop2.22.fid
^{1}H NMR (d_6-acetone) of compound **7b**
Co
O
X
O
n
N=N
N
O
H
H
H
[15]$^-$ X = CH$_2$, n = 2
1.00
1.21
2.44
2.18
1.70
2.56
2.44
4.89
2.51
1.57
1.90
1.85
3.45
5.80
45.61
3.91
4.48
3.90
3.65
3.41
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

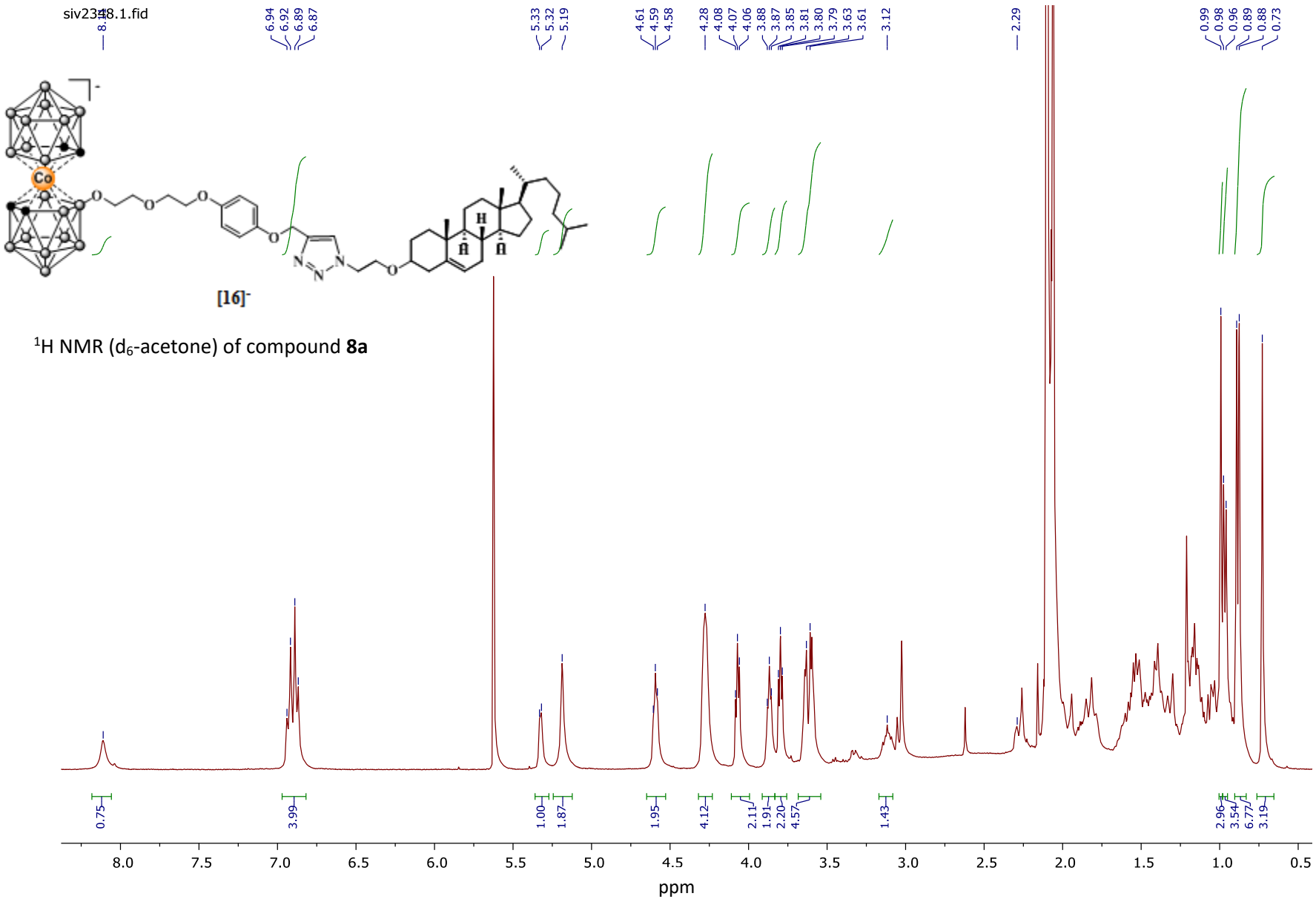

Desktop.211.fid
$^{11}B\{^{1}H\}$ NMR (d_6-acetone) of compound **7b**
23.02
4.72
0.49
-2.44
-4.68
7.08
7.07
-17.18
-20.20
-21.87
-28.15
1.00
1.08
1.43
1.55
2.06
7.44
2.66
3.33
0.65
26 24 22 20 18 16 14 12 10 8 6 4 2 0 -2 -4 -6 -8 -10 -12 -14 -16 -18 -20 -22 -24 -26 -28 -30 -32 -34
ppm



^{11}B NMR (d_6-acetone) of compound **7b**

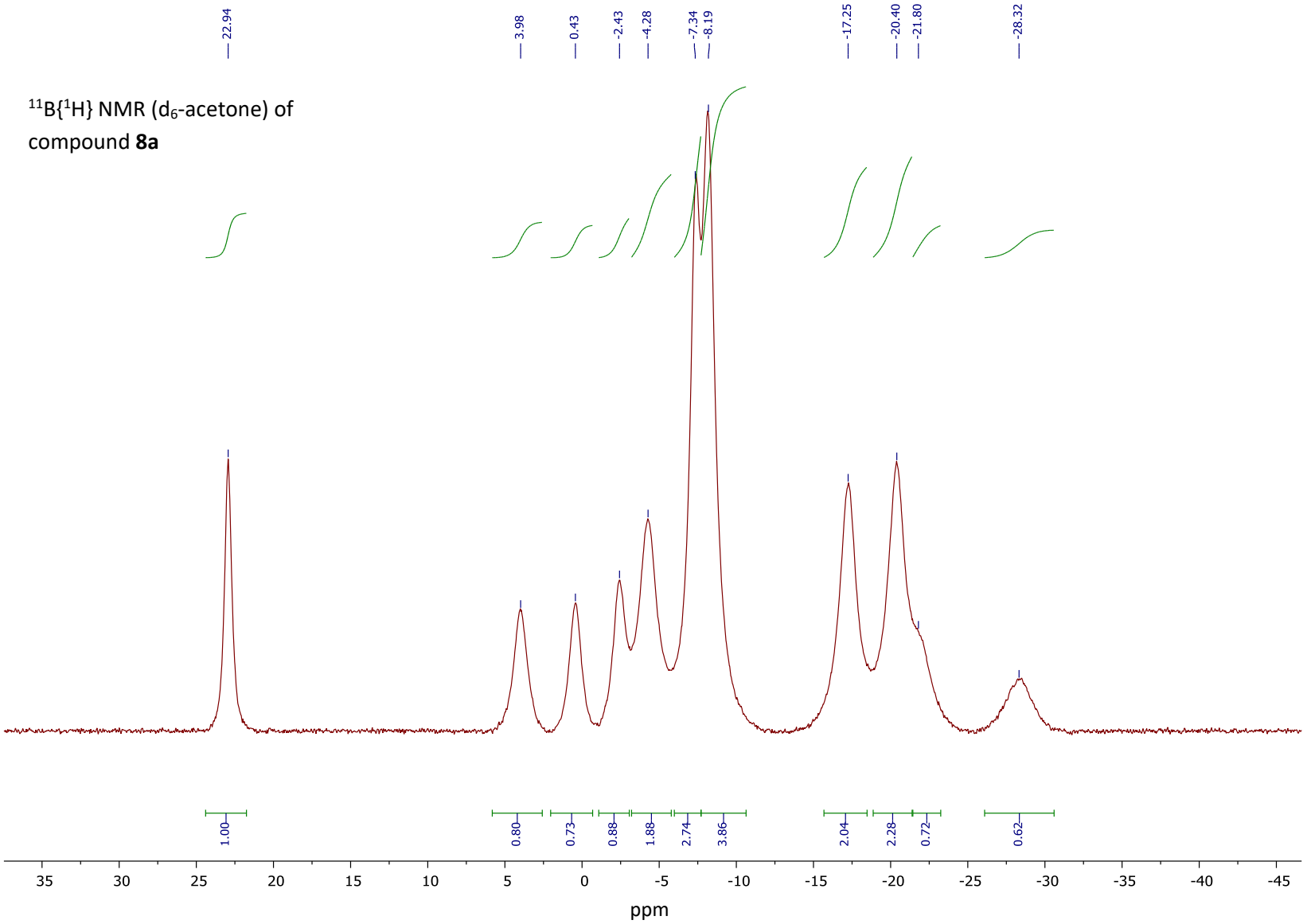


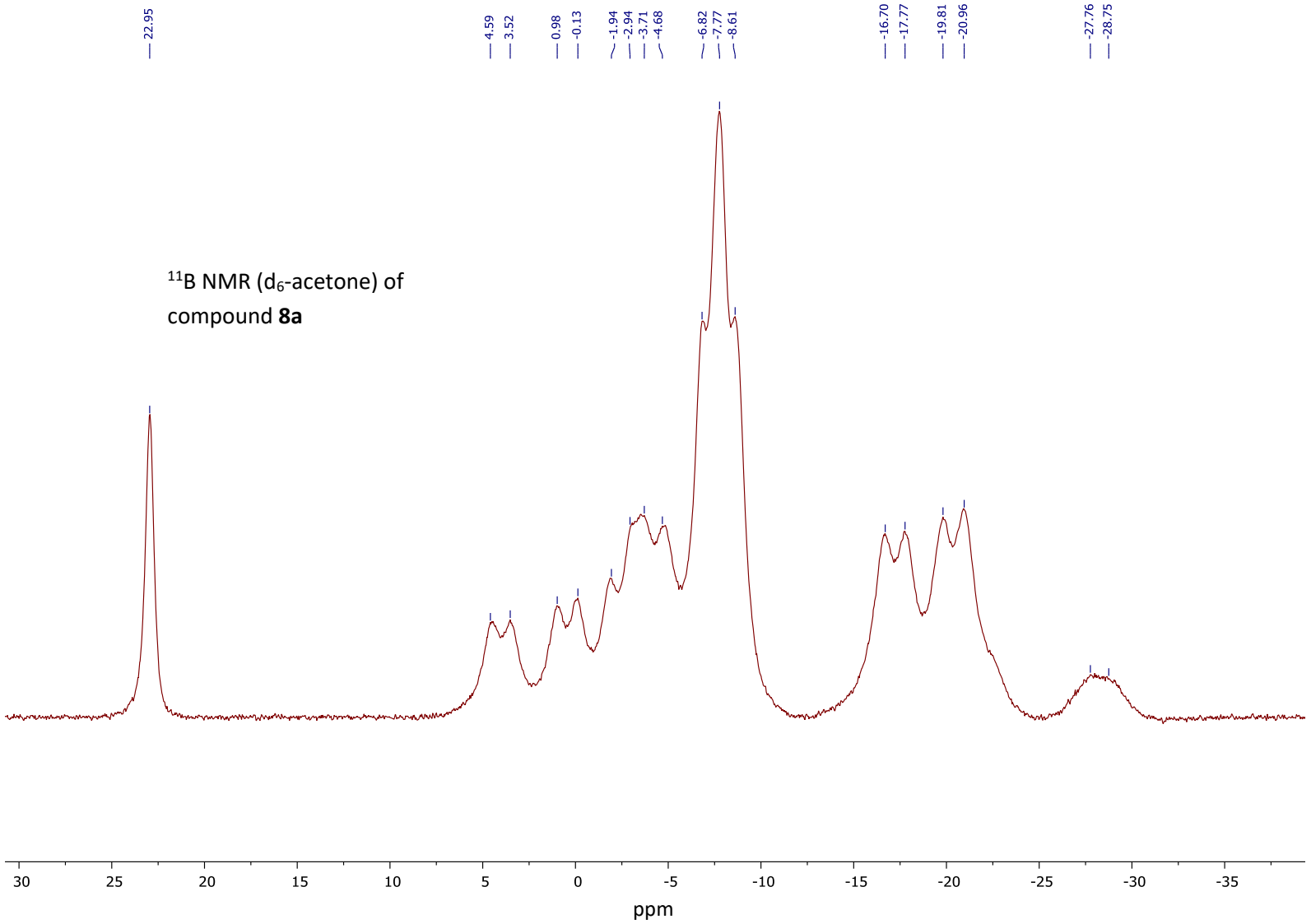
^{13}C NMR (d_6-acetone) of compound **7b**



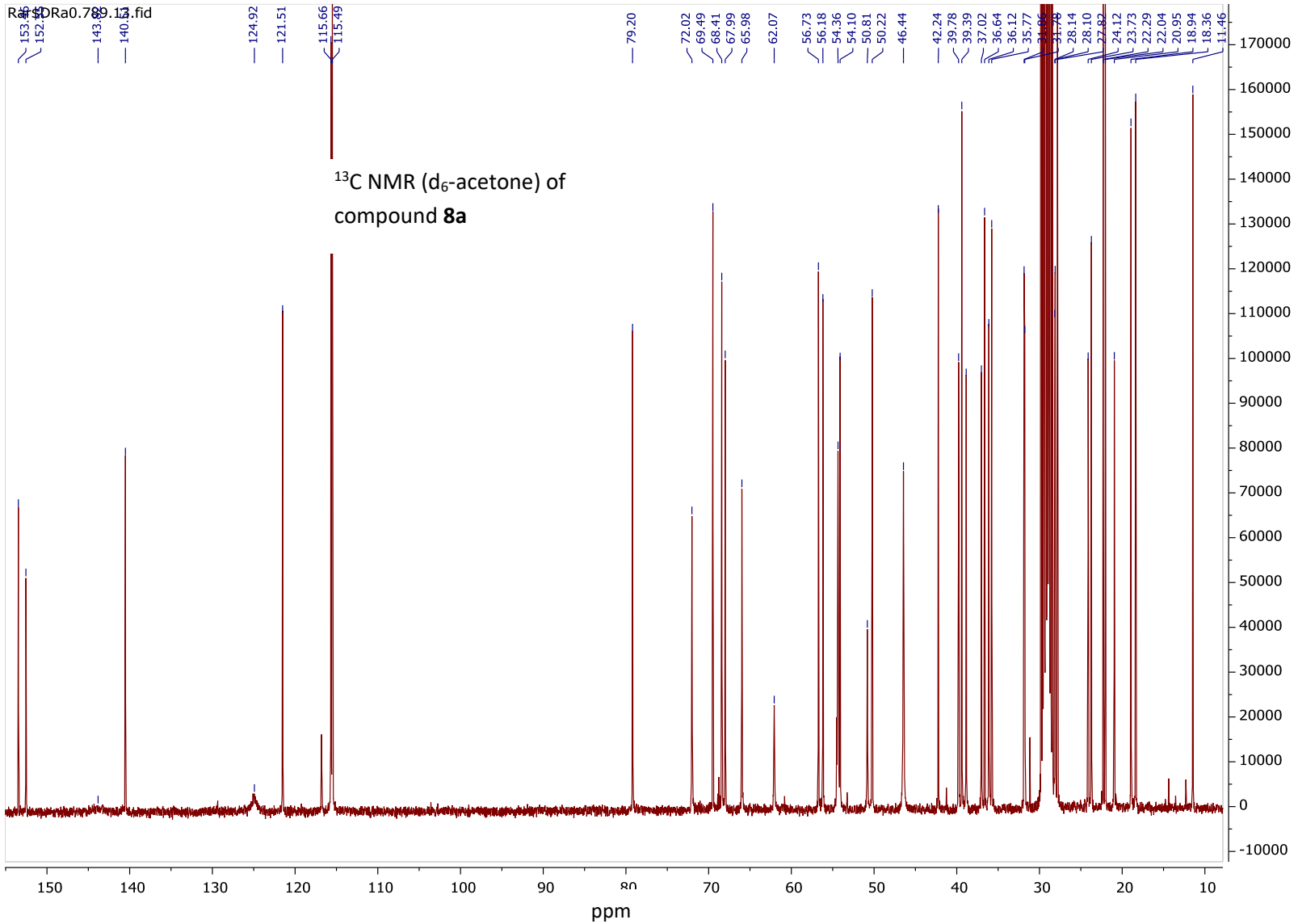
^{1}H NMR (d_6-acetone) of compound **8a**

$^{11}B\{^{1}H\}$ NMR (d_6-acetone) of compound **8a**

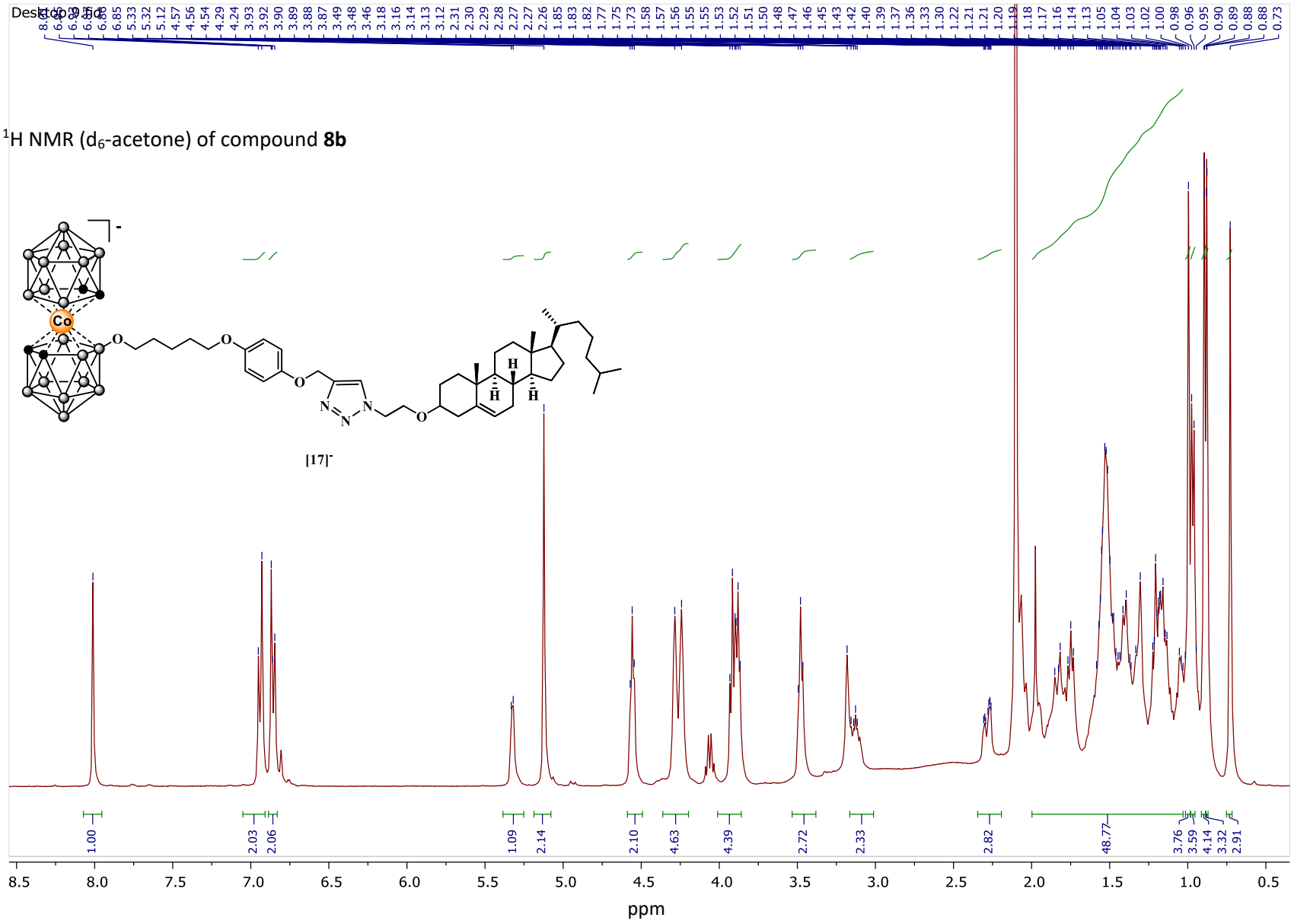


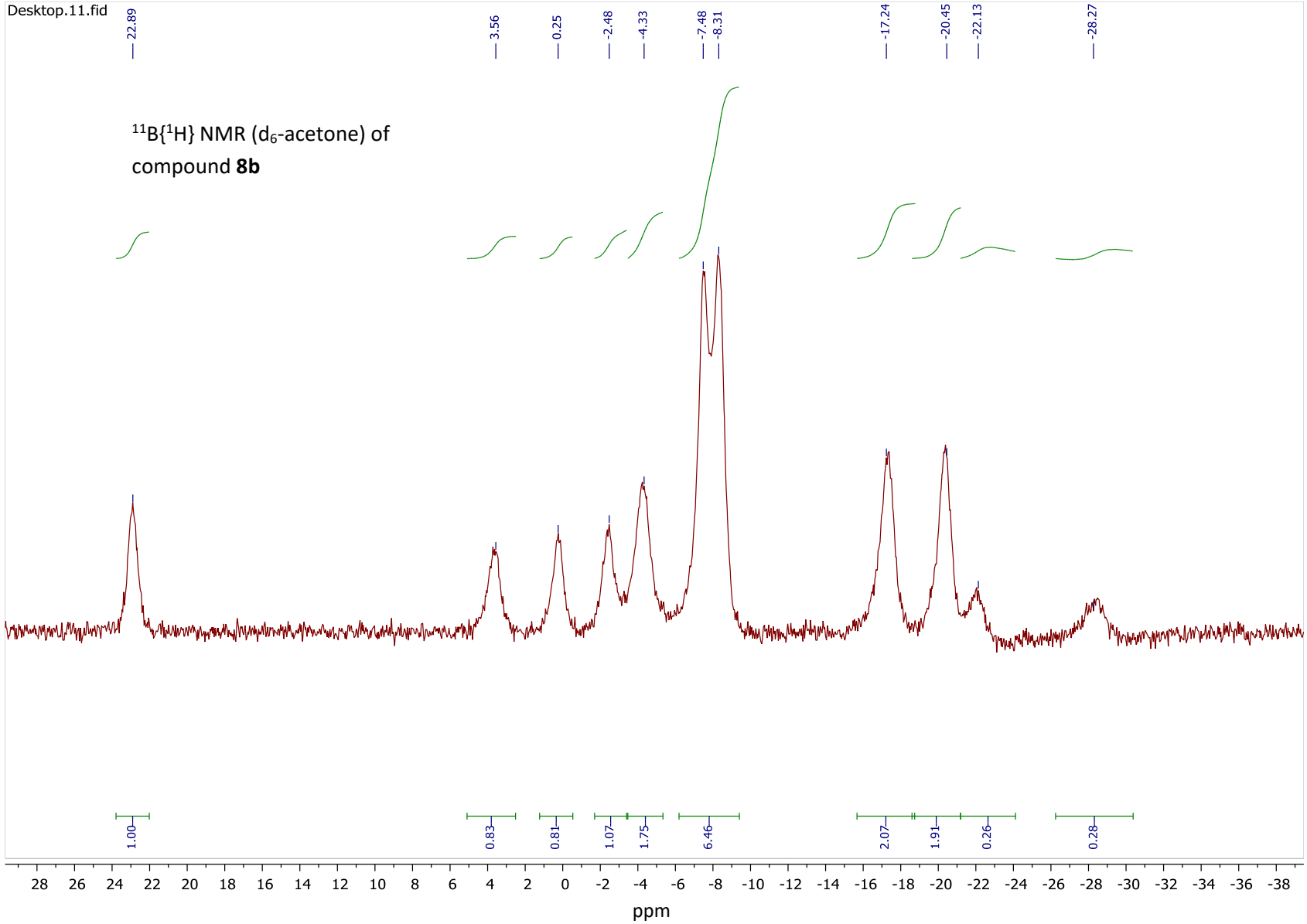


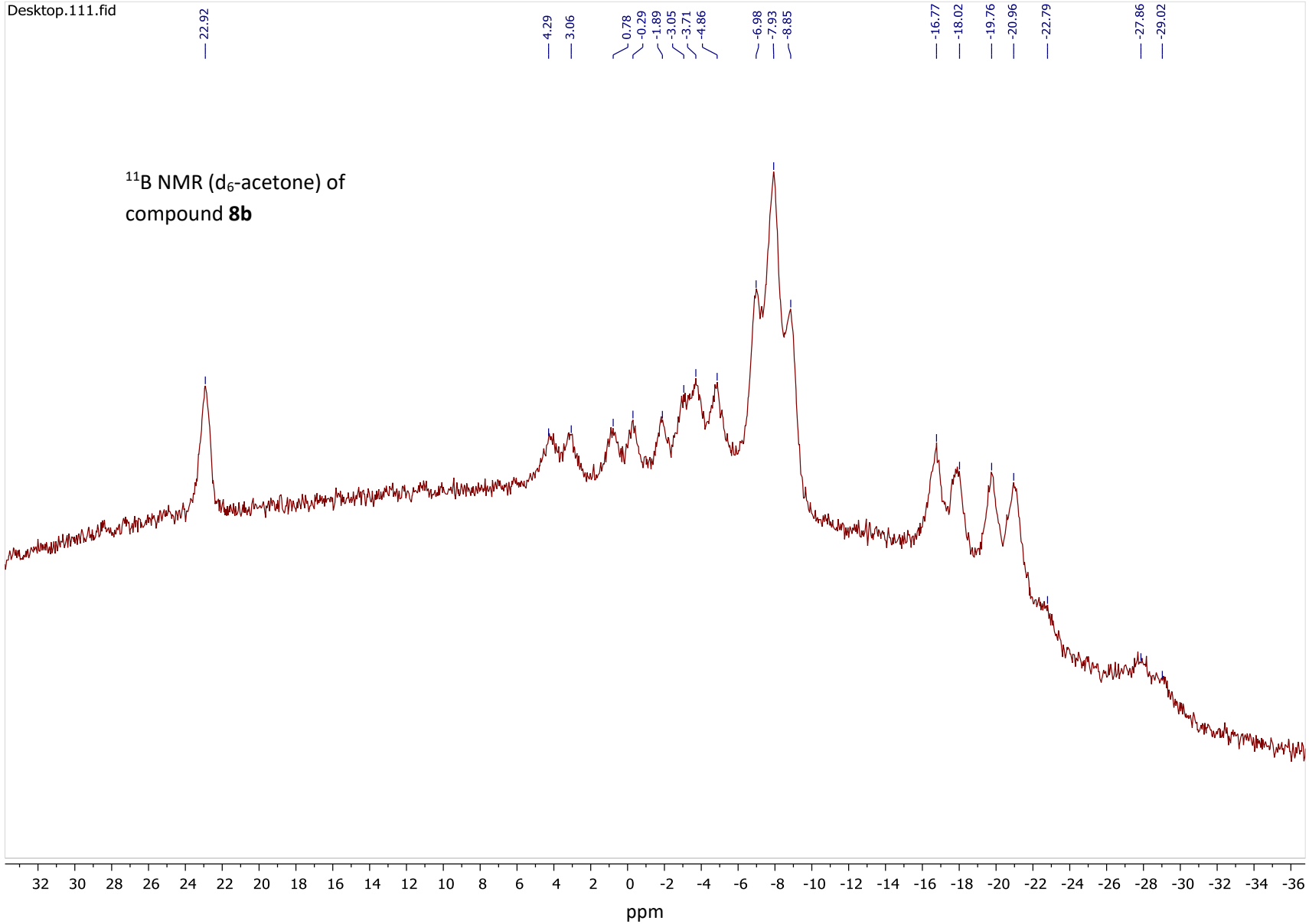
^{11}B NMR (d_6-acetone) of compound **8a**

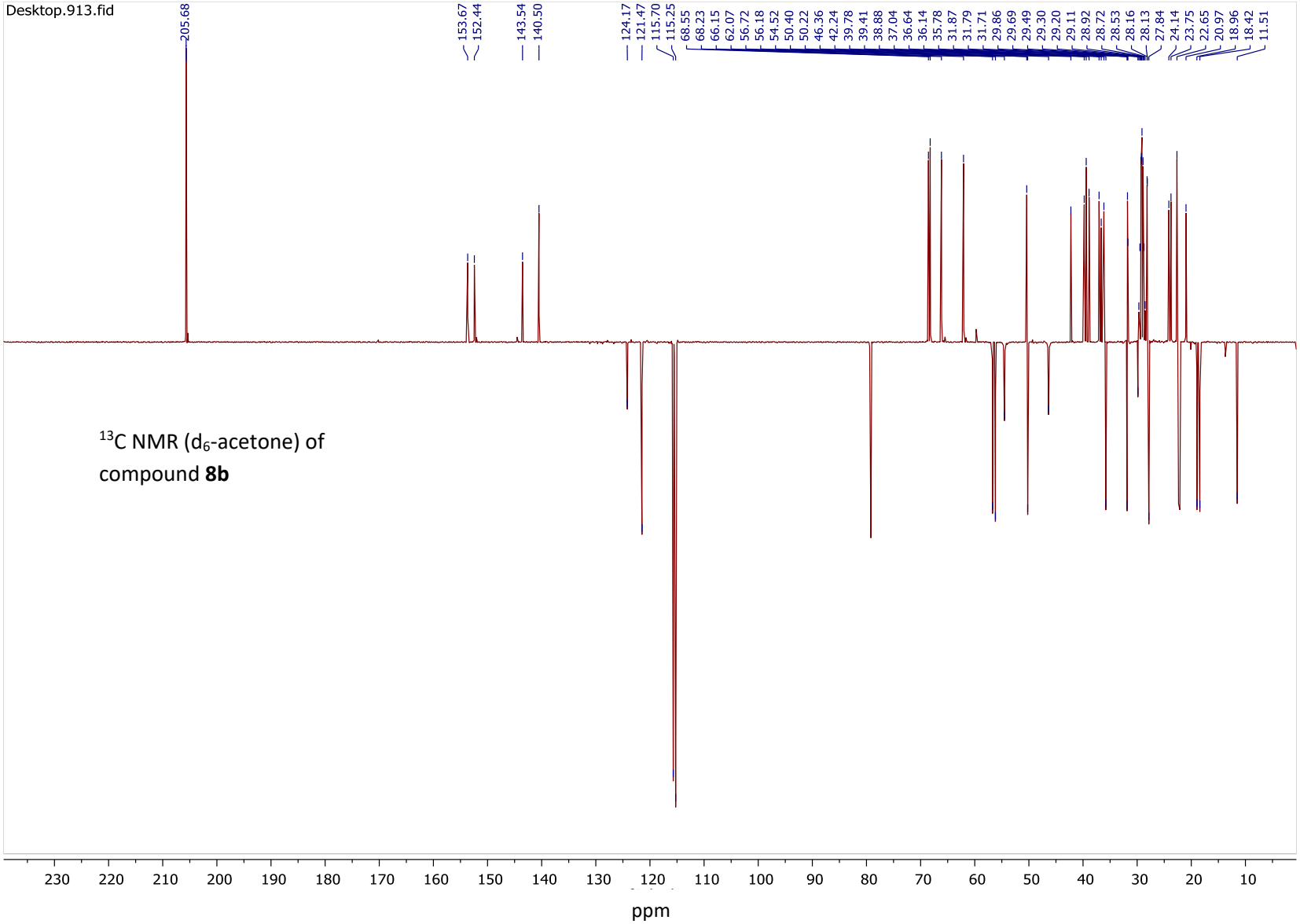

Rafa DRa0.789.13.fid
153.46
152.44
143.82
140.13
124.92
121.51
115.66
115.49
79.20
72.02
69.49
68.41
67.99
65.98
62.07
56.73
56.18
54.36
54.10
50.81
50.22
46.44
42.24
39.78
39.39
37.02
36.64
36.12
35.77
31.78
28.14
28.10
27.82
24.12
23.73
22.29
22.04
20.95
18.94
18.36
11.46
^{13}C NMR (d_6-acetone) of compound **8a**
170000
160000
150000
140000
130000
120000
110000
100000
90000
80000
70000
60000
50000
40000
30000
20000
10000
0
-10000
150
140
130
120
110
100
90
70
60
50
40
30
20
10
ppm

^{1}H NMR (d_6-acetone) of compound **8b**




Desktop.11.fid
22.89
3.56
0.25
-2.48
-4.33
-7.48
-8.31
-17.24
-20.45
-22.13
-28.27
$^{11}B\{^{1}H\}$ NMR (d_6-acetone) of compound **8b**
1.00
0.83
0.81
1.07
1.75
6.46
2.07
1.91
0.26
0.28
28 26 24 22 20 18 16 14 12 10 8 6 4 2 0 -2 -4 -6 -8 -10 -12 -14 -16 -18 -20 -22 -24 -26 -28 -30 -32 -34 -36 -38
ppm


Desktop.111.fid
22.92
4.29
3.06
0.78
-0.29
-1.89
-3.05
-3.71
-4.86
-6.98
-7.93
-8.85
-16.77
-18.02
-19.76
-20.96
-22.79
-27.86
-29.02
^{11}B NMR (d_6-acetone) of compound **8b**
32 30 28 26 24 22 20 18 16 14 12 10 8 6 4 2 0 -2 -4 -6 -8 -10 -12 -14 -16 -18 -20 -22 -24 -26 -28 -30 -32 -34 -36
ppm



^{13}C NMR (d_6-acetone) of compound **8b**