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Direct oxidative functionalization of saturated dispiro-cyclopropanated bicyclo[3.3.1]nonanes

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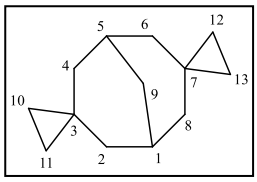
Experimental details

^{1}H and ^{13}C NMR spectra were recorded on a 400 MHz spectrometer Agilent 400-MR (400.0 and 100.6 MHz for ^{1}H and ^{13}C, respectively) at room temperature; chemical shifts δ were measured with reference to the solvent ($CDCl_3$, δ_H = 7.26 ppm, δ_C = 77.16 ppm). When necessary, assignments of signals in NMR spectra were made using 2D techniques. Accurate mass measurements (HRMS) were obtained on Jeol GCMate II mass spectrometer with electrospray ionization (ESI). GC-MS data were obtained on MS Finnigan MAT ITD-700 mass spectrometer with electron impact ionization (EI). Analytical thin layer chromatography was carried out with silica gel plates (supported on aluminum); the detection was done by UV lamp (254 and 365 nm). Column chromatography was performed on silica gel (Merck, 230–400 mesh). Starting compounds **1a**,[S1] **1b,**[S2] **2a**[S3] and **2b**[S2] were obtained *via* described methods. All other starting materials were commercially available. All reagents except commercial products of satisfactory quality were purified according to literature procedures prior to use.

*Synthesis of hydrocarbons **3a,b*** via *reduction of compounds **2a,b** (general method).*[S4]

To the solution of **2a,b** (5 mmol) in the mixture of *tert*-butanol (16 ml) and absolute ether (65 ml) lithium (1.12 g, 0.16 mol) was added in portions in 4 days under vigorous stirring and reflux under argon. The resulting mixture was cooled down to r.t., quenched with water (50 ml) and extracted with ether (3 × 20 ml). Combined organic layers were washed with water (3 × 20 mL), and dried over $MgSO_4$. The solvent was evaporated under reduced pressure.

*Dispiro[cyclopropane-1,3'-bicyclo[3.3.1]nonane-7',1''-cyclopropane] (**3a**)*. Yield 0.87 g (99%). Colorless liquid, R_f = 0.81 (petroleum ether).

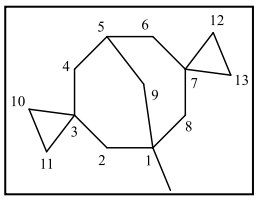


^{1}H NMR ($CDCl_3$, δ, ppm): 0.07-0.11 (m, 4H, $C^{10}H_2$, $C^{12}H_2$), 0.54-0.58 (m, 4H, $C^{11}H_2$, $C^{13}H_2$), 1.08 (br.d, ^2J = 13.0 Hz, 4H, H^2_e, H^4_e, H^6_e, H^8_e), 1.57-1.60 (m, 2H, C^9H_2), 1.95-2.00 (m, 2H, H^1, H^5), 1.97-2.03 (m, 4H, H^2_a, H^4_a, H^6_a, H^8_a).

^{13}C NMR ($CDCl_3$, δ, ppm): 12.2 (2C, C^{10}, C^{12}), 13.3 (2C, C^3, C^7), 21.6 (2C, C^{11}, C^{13}), 28.9 (2C, C^1, C^5), 33.0 (C^9), 41.8 (4C, C^2, C^4, C^6, C^8).

GC-MS (EI) *m/z* (*I*, %): 176 (1) $[M]^+$, 161 (3) $[M-15]^+$, 148 (12) $[M-28]^+$, 147 (8) $[M-29]^+$, 133 (8) $[M-43]^+$, 120 (17) $[M-56]^+$, 106 (44) $[M-70]^+$, 92 (100) $[M-84]^+$.

*1'-Methyldispiro[cyclopropane-1,3'-bicyclo[3.3.1]nonane-7',1''-cyclopropane] (**3b**)*. Yield 0.90 g (95%). Colorless liquid, R_f = 0.89 (petroleum ether).



^{1}H NMR ($CDCl_3$, δ, ppm): 0.04-0.11 (m, 4H $C^{10}H_2$, $C^{12}H_2$), 0.52-0.60 (m, 4H, $C^{11}H_2$, $C^{13}H_2$), 0.81 (s, 3H, CH_3), 0.94 (br.d, ^2J = 13.6 Hz, 2H, H^2_e, H^8_e), 1.03 (br.d, ^2J = 13.5 Hz, 2H, H^4_e, H^6_e), 1.34-1.36 (m, 2H, C^9H_2), 1.63 (d, ^2J = 13.6 Hz, 2H, H^2_a, H^8_a), 1.93 (dd, ^2J = 13.5 Hz, ^3J = 5.6 Hz, 2H, H^4_a, H^6_a), 2.00-2.07 (m, 1H, H^5).

^{13}C NMR ($CDCl_3$, δ, ppm): 12.1 (2C, C^{10}, C^{12}), 14.0 (2C, C^3, C^7), 21.8 (2C, C^{11}, C^{13}), 30.4 (C^5), 31.1 (C^1), 33.4 (CH_3), 40.7 (C^9), 41.1 (2C, C^4, C^6), 49.0 (2C, C^2, C^8).

GC-MS (EI) *m/z* (*I*, %): 190 (2) $[M]^+$, 175 (6) $[M-15]^+$, 162 (9) $[M-28]^+$, 161 (16) $[M-29]^+$, 147 (7) $[M-43]^+$, 134 (21) $[M-56]^+$, 121 (56) $[M-69]^+$, 106 (100) $[M-84]^+$.

*Synthesis of hydrocarbon **3a** by the Simmons-Smith cyclopropanation.*[S5]

To the mixture of diene **1a** (0.74 g, 5 mmol) and diethylzinc (1 M hexane solution, 10 ml, 10 mmol) in absolute benzene (30 ml), CH_2I_2 (1.21 ml, 4.02 g, 15 mmol) was added *via* dropping funnel under argon. The resulting mixture was heated up to 60 °C and stirred for 4 h. Then it was cooled down to r.t. and poured into 1% HCl (25 ml) under stirring. Organic layer was separated, washed with water (20 ml) and 5% aqueous $NaHCO_3$ (20 ml), and dried over $MgSO_4$. The solvent was evaporated under reduced pressure. Yield 0.83 g (94%).

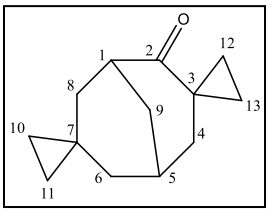
Oxidation of hydrocarbons 3a,b

Oxidation via "dry" ozonation (method A).[S6] Hydrocarbon **3a,b** (1 mmol), silica gel (1:100 mass ratio) and pentane (60 ml) were stirred for 1 h. The solvent was evaporated under reduced pressure. Silica gel containing adsorbed hydrocarbon was placed into "U"-tube, cooled down to -45 °C and ozonated at this temperature for 5-40 min (ozone concentration 100 $g \cdot m^{-3}$, flow rate 6 $sm^3 \cdot s^{-1}$). Then the system was allowed to warm up to r.t., silica gel washed with CH_2Cl_2 (200 ml), the solvent was evaporated under reduced pressure. The products were isolated via preparative column chromatography (SiO_2).

Oxidation with TFDO (method B).[S7] To the solution of $NaHCO_3$ (18.9 g, 0.25 mol) and 1,1,1-trifluoroacetone (25 ml, 31.3 g, 0.33 mol) in water (35 ml) Oxone (40 g, 0.065 mol) was added carefully in portions at 0-3 °C, 200 torr, under vigorous stirring. The reaction mixture was stirred until the end of foam generation. The solution of TFDO in trifluoroacetone (ca. 0.33 M, 24 ml, 8 mmol) was collected at -78 °C into the flack containing hydrocarbon **3a,b** (1 mmol), allowed to warm up to -20 °C and stirred at this temperature for 2 h. The solvent was condensed at 25 °C into the flack cooled down to -78 °C. The products were isolated *via* preparative column chromatography (SiO_2).

Oxidation with ruthenium tetroxide (method C).[S8] To the solution of hydrocarbon **3a,b** (1 mmol) in CCl_4 (1 ml), CH_3CN (1 ml) and phosphate buffer (1.5 ml, pH = 7) $NaIO_4$ (3 mmol, 0.64 g) and $RuCl_3 \cdot xH_2O$ (ca. 0.2 mmol, 58 mg, ω(Ru) 35-40%) were quickly added in the atmosphere of argon. The reaction mixture was stirred at 25-60 °C for 0.5-16 h, diluted with H_2O (3 ml), and extracted with CH_2Cl_2 (5 × 15 ml). The combined organic layers were washed with a mixture (6 ml) of saturated $Na_2S_2O_3$, $NaHCO_3$, and NaCl (1:1:1) and dried over anhydrous $MgSO_4$. The solvent was evaporated under reduced pressure. The products were isolated *via* preparative column chromatography (SiO_2).

Dispiro[cyclopropane-1,3'-bicyclo[3.3.1]nonane-7',1''-cyclopropane]-2'-one (**4a**). Yield 34 mg (18%), method A, 40 min; 40 mg (21%), method B; 59 mg (38%), method C, 25 °C, 4 h; 44 mg (23%), method C, 25 °C, 6 h. Yellowish oil, R_f = 0.27 (petroleum ether : DCM = 1:1).

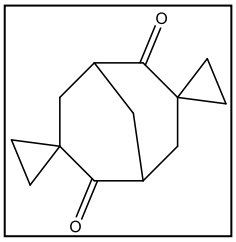


^{1}H NMR ($CDCl_3$, δ, ppm): 0.11-0.17 (m, 2H, $C^{10}H_2$), 0.26-0.32 (m, 1H, $H^{11'}$), 0.46-0.52 (m, 1H, $H^{11''}$), 0.63-0.71 (m, 1H, $H^{12''}$), 0.78-0.86 (m, 1H, $H^{13''}$). 0.99 (ddd, ^2J = 13.0 Hz, ^4J = 2.0 Hz, ^4J = 2.0 Hz, 1H, $H^6{}_e$), 1.14 (dddd, ^2J = 13.2 Hz, ^3J = 3.3 Hz, ^4J = 2.1 Hz, ^4J = 2.0 Hz, 1H, $H^8{}_e$), 1.45-1.51 (m, 2H, $H^{12'}$, $H^{13'}$), 1.70 (dd, ^2J = 13.2 Hz, ^3J = 2.3 Hz, 1H, $H^4{}_e$), 1.82 (dddd, ^2J = 13.1 Hz, ^3J = 2.3 Hz, ^3J = 3.2 Hz, ^4J = 2.3 Hz, 1H, $H^{9''}$), 2.06 (ddd, ^2J = 13.2 Hz, ^3J = 4.2 Hz, ^4J = 1.7 Hz, 1H, $H^8{}_a$), 2.16 (ddddd, ^2J = 13.1 Hz, ^3J = 3.3 Hz, ^3J = 3.0 Hz, ^4J = 2.0 Hz, ^4J = 2.0 Hz, 1H, $H^{9'}$), 2.20-2.29 (m, 3H, H^5, $H^4{}_a$, $H^6{}_a$), 2.52-2.56 (m, 1H, H^1).

^{13}C NMR ($CDCl_3$, δ, ppm): 10.1 (CH_2, C^{10}), 13.8 (C^7), 17.1 (CH_2, C^{11}), 25.1 (CH_2, C^{12}), 26.2 (CH_2, C^{13}), 26.7 (C^3), 28.8 (C^5), 30.7 (C^9), 39.6 (C^4), 40.9 (C^8), 42.4 (C^6), 44.4 (C^1), 217.7 (C=O).

HRMS (ESI, m/z): calcd. for $C_{13}H_{18}O$ $[M+H]^+$ 191.1430, found 191.1450.

Dispiro[cyclopropane-1,3'-bicyclo[3.3.1]nonane-7',1''-cyclopropane]-2',6'-dione (**5a**). Yield 33 mg (16%), method A, 40 min; 12 mg (6%), method B; 16 mg (8%), method C, 25 °C, 4 h; 27 mg (13%), method C, 25 °C, 6 h; 51 mg (25%), method C, 60 °C, 16 h. Brown crystals, m.p. 127–129 °C (from $CDCl_3$), R_f = 0.28 (petroleum ether : DCM = 1:3).

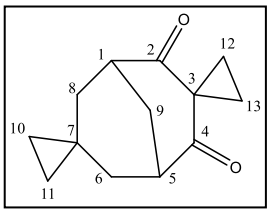


^{1}H NMR ($CDCl_3$, δ, ppm): 0.61 (ddd, ^2J = 3.6 ^3J = 7.2 Hz, ^3J = 9.1 Hz, 2H, $2CH_2$, *cy*-Pr), 0.77 (ddd, ^2J = 3.2, ^3J = 6.9 Hz, ^3J = 9.1 Hz, 2H, 2C*H*H in both *cy*-Pr), 1.08 (ddd, ^2J = 3.2, ^3J = 7.2 Hz, ^3J = 9.9 Hz, 2H, 2C*H*H in both *cy*-Pr), 1.57 (br.d, ^2J = 13.8 Hz, 2H, 2 C*H*H), 1.74 (ddd, ^2J = 3.6, ^3J = 6.9 Hz, ^3J = 9.9 Hz, 2H, 2C*H*H in both *cy*-Pr), 2.37-2.42 (m, 2H, CH_2, bridge), 2.42 (dd, ^2J = 13.8 Hz, ^3J = 5.4 Hz, 2H, 2 C*H*H), 2.78-2.84 (m, 2H, 2CH).

^{13}C NMR ($CDCl_3$, δ, ppm): 17.1 ($2CH_2$, *cy*-Pr), 26.5 ($2C_{spiro}$), 28.1 ($2CH_2$, *cy*-Pr), 31.4 (CH_2, bridge), 39.6 ($2CH_2$), 44.3 (2CH), 214.0 (2C=O).

HRMS (ESI, m/z): calcd. for $C_{13}H_{16}O_2$ $[M+H]^+$ 205.1223, found 205.1227.

Dispiro[cyclopropane-1,3'-bicyclo[3.3.1]nonane-7',1''-cyclopropane]-2',4'-dione (**6a**). Yield 17 mg (8%), method A, 40 min; 8 mg (4%), method B; 12 mg (6%), method C, 25 °C, 4 h; 6 mg (3%), method C, 25 °C, 6 h. Yellowish oil, R_f = 0.18 (petroleum ether : DCM = 1:2).

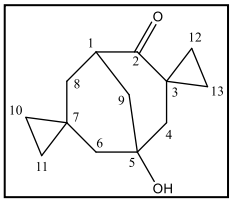


^{1}H NMR ($CDCl_3$, δ, ppm): 0.25 (br.s, 4H, $C^{10}H_2$, $C^{11}H_2$), 1.21-1.33 (m, 2H, $H^6{}_e$, $H^8{}_e$), 1.72-1.79 (m, 2H, $C^{12}H_2$), 1.81-1.88 (m, 2H, $C^{13}H_2$), 1.97 (dt, ^2J = 13.8 Hz, ^3J = 2.7 Hz, 1H, $H^{9'}$), 2.27 (dd, ^2J = 13.5 Hz, ^3J = 3.9 Hz, 2H, $H^6{}_a$, $H^8{}_e$), 2.41-2.49 (m, 1H, $H^{9''}$), 2.78-2.84 (m, 2H, H^1, H^5).

^{13}C NMR ($CDCl_3$, δ, ppm): 10.8 ($^1J_{CH}$ = 160 Hz, C^{10}), 14.2 (C^7), 16.4 ($^1J_{CH}$ = 161 Hz, C^{11}), 27.4 ($^1J_{CH}$ = 169 Hz, C^{13}), 27.7 ($^1J_{CH}$ = 131 Hz, C^9), 31.2 ($^1J_{CH}$ = 169 Hz, C^{12}), 39.7 ($^1J_{CH}$ = 130 Hz, 2C, C^6, C^8), 41.7 (C^3), 44.0 ($^1J_{CH}$ = 137 Hz, 2C, C^1, C^5), 212.1 (2C=O).

HRMS (ESI, m/z): calcd. for $C_{13}H_{16}O_2$ $[M+Na]^+$ 227.1043, found 227.1042.

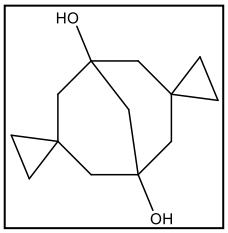
5-Hydroxydispiro[cyclopropane-1,3'-bicyclo[3.3.1]nonane-7',1''-cyclopropane]-2'-one (**7**). Yield 25 mg (12%), method B. Yellowish oil, R_f = 0.10 (DCM : MeOH = 100:1).



^{1}H NMR ($CDCl_3$, δ, ppm): 0.22-0.29 (m, 2H, $C^{10}H_2$), 0.30-0.36 (m, 1H, $H^{11'}$), 0.51-0.57 (m, 1H, $H^{11''}$), 0.70-0.89 (m, 2H, $H^{12'}$ $H^{13'}$), 1.14 (dddd, ^2J = 13.4 Hz, ^3J = 3.1 Hz, ^4J = 2.0 Hz, ^4J = 1.8 Hz, 1H, $H^8{}_e$), 1.22 (ddd, ^2J = 13.0 Hz, ^4J = 2.0 Hz, ^4J = 2.4 Hz, 1H, $H^6{}_e$), 1.44-1.52 (m, 2H, $H^{12''}$ $H^{13''}$), 1.79 (ddd, ^2J = 12.4 Hz, ^3J = 2.5 Hz, ^4J = 2.7 Hz, 1H, $H^{9''}$), 1.93 (dd, ^2J = 13.6 Hz, ^3J = 2.7 Hz, 1H, $H^4{}_e$), 2.03 (ddd, ^2J = 13.3 Hz, ^3J = 4.4 Hz, ^4J = 1.7 Hz, 1H, $H^8{}_a$), 2.17-2.23 (m, 2H, $H^4{}_a$, $H^6{}_a$), (dddd, ^2J = 12.4 Hz, ^3J = 3.9 Hz, ^3J = 3.0 Hz, ^4J = 2.4 Hz, ^4J = 1.8 Hz, 1H, $H^{9'}$), 2.67-2.72 (m, 1H, H^1), 3.53 (br.s., 1H, OH).

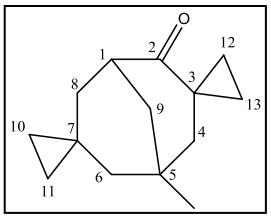
^{13}C NMR ($CDCl_3$, δ, ppm): 9.8 (C^{10}), 15.0 (C^{7}), 17.1 (C^{11}), 25.3 (C^{12}), 26.1 (C^{13}), 26.4 (C^{3}), 39.4 (C^{9}), 39.8 (C^{8}), 46.3 (C^{1}), 47.4 (C^{4}), 50.4 (C^{6}), 70.0 (C^{5}), 215.7 (C^{2}=O).
HRMS (ESI, m/z): calcd. for $C_{13}H_{18}O_2$ $[M+H]^+$ 207.1380, found 207.1375.

Dispiro[cyclopropane-1,3'-bicyclo[3.3.1]nonane-7',1''-cyclopropane]-1',5'-diol (**8**). Yield 8 mg (4%), method B. White crystals, m.p. 144–145 °C (from $CDCl_3$), R_f = 0.42 (petroleum ether : DCM : MeOH = 3:1:0.5).



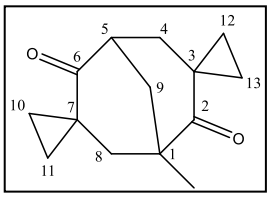
^{1}H NMR ($CDCl_3$, δ, ppm): 0.23-0.23 (m, 4H, $2CH_2$, *cy*-Pr), 0.65-0.71 (m, 4H, $2CH_2$, *cy*-Pr), 1.24 (d, ^{2}J = 13.0 Hz, 4H, $4CH_2$), 1.72 (m, 2H, CH_2, bridge), 1.97 (d, ^{2}J = 13.0 Hz, 4H, $4CH_2$), 3.49 (br.s, 2H, 2OH).
^{13}C NMR ($CDCl_3$, δ, ppm): 11.3 ($2CH_2$, *cy*-Pr), 13.9 ($2C_{spiro}$), 21.7 ($2CH_2$, *cy*-Pr), 48.9 ($4CH_2$), 50.9 (CH_2, bridge), 73.0 (2COH).
HRMS (ESI, m/z): calcd. for $C_{13}H_{20}O_2$ $[M+NH_4]^+$ 226.1802, found 226.1801.

5-Methyldispiro[cyclopropane-1,3'-bicyclo[3.3.1]nonane-7',1''-cyclopropane]-2'-one (**4b**). Yield 51 mg (25%), method A, 30 min; 61 mg (30%), method B; 86 mg (42%), method C, 25 °C, 30 min; 43 mg (21%), method C, 25 °C, 3 h. Colorless oil, R_f = 0.25 (petroleum ether : DCM = 1:2).



^{1}H NMR ($CDCl_3$, δ, ppm): 0.09-0.17 (m, 2H, $C^{10}H_2$), 0.28 (dddd, ^{2}J = 4.4 Hz, ^{3}J = 9.2 Hz, ^{3}J = 5.6 Hz, ^{4}J = 1.7 Hz, 1H, $H^{11''}$), 0.47 (dddd, ^{2}J = 4.4 Hz, ^{3}J = 9.1 Hz, ^{3}J = 5.6 Hz, ^{4}J = 1.7 Hz, 1H, $H^{11'}$), 0.59-0.68 (m, 1H, $H^{12''}$), 0.73-0.82 (m, 1H, $H^{13''}$), 0.87 (ddd, ^{2}J = 13.5 Hz, ^{4}J = 2.2 Hz, ^{4}J = 2.4 Hz, 1H, H^{6}_{e}), 0.96 (s, 3H, CH_3), 1.11 (dddd, ^{2}J = 13.1 Hz, ^{3}J = 3.4 Hz, ^{4}J = 2.2 Hz, ^{4}J = 2.0 Hz, H^{8}_{e}), 1.41-1.48 (m, 2H, $H^{12'}$, $H^{13'}$), 1.54 (ddd, ^{2}J = 13.0 Hz, ^{3}J = 2.4 Hz, ^{4}J = 2.4 Hz, 1H, $H^{9''}$), 1.60 (dd, ^{2}J = 13.9 Hz, ^{4}J = 2.4 Hz, 1H, H^{4}_{e}), 1.85 (dd, ^{2}J = 13.9 Hz, ^{4}J = 1.9 Hz, 1H, H^{4}_{a}), 1.92 (ddd, ^{2}J = 13.5 Hz, ^{4}J = 1.9 Hz, ^{4}J = 1.7 Hz, 1H, H^{6}_{a}), 1.97 (ddd, ^{2}J = 13.1 Hz, ^{3}J = 4.2 Hz, ^{4}J = 1.7 Hz, 1H, H^{8}_{a}), 2.00 (dddd, ^{2}J = 13.0 Hz, ^{3}J = 3.7 Hz, ^{4}J = 2.4 Hz, ^{4}J = 2.0 Hz, 1H, $H^{9'}$), 2.54 (dddd, ^{3}J = 4.2 Hz, ^{3}J = 3.4 Hz, ^{3}J = 3.7 Hz, ^{3}J = 2.4 Hz, 1H, H^{1}).
^{13}C NMR ($CDCl_3$, δ, ppm): 10.1 (C^{10}), 14.5 (C^{7}), 17.2 (C^{11}), 25.3 (C^{13}), 26.51 (C^{3}), 26.58 (C^{12}), 31.9 (C^{5}), 32.5 (CH_3), 38.2 (C^{9}), 40.4 (C^{8}), 45.3 (C^{1}), 46.7 (C^{4}), 49.7 (C^{6}), 217.5 (C=O).
HRMS (ESI, m/z): calcd. for $C_{14}H_{20}O$ $[M+H]^+$ 205.1587, found 205.1595.

1-Methyldispiro[cyclopropane-1,3'-bicyclo[3.3.1]nonane-7',1''-cyclopropane]-2',6'-dione (**5b**). Yield 28 mg (13%), method A, 30 min; 9 mg (4%), method B; 7 mg (3%), method C, 25 °C, 30 min; 33 mg (15%), method C, 60 °C, 6 h. White crystals, m.p. 83–84 °C (from $CDCl_3$), R_f = 0.25 (petroleum ether : DCM : MeOH = 3:1:0.5).

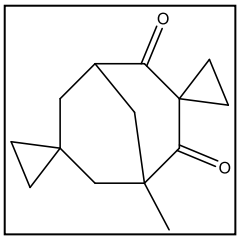


^{1}H NMR ($CDCl_3$, δ, ppm): 0.57 (ddd, ^2J = 3.7 Hz, ^3J = 9.1 Hz, ^3J = 7.2 Hz, 1H, $H^{10'}$), 0.60 (ddd, ^2J = 3.7 Hz, ^3J = 9.1 Hz, ^3J = 7.2 Hz, 1H, $H^{12'}$), 0.741 (ddd, ^2J = 3.2 Hz, ^3J = 9.1 Hz, ^3J = 7.0 Hz, 2H, $H^{11'}$, $H^{13'}$), 1.07 (dddd, ^2J = 3.2 Hz, ^3J = 9.8 Hz, ^3J = 7.2 Hz, ^4J = 1.2 Hz, 1H, $H^{13''}$), 1.11 (dddd, ^2J = 3.2 Hz, ^3J = 9.8 Hz, ^3J = 7.2 Hz, ^4J = 1.2 Hz, 1H, $H^{11''}$), 1.17 (s, 3H, CH_3), 1.40 (dd, ^2J = 13.7 Hz, ^4J = 3.1 Hz, 1H, H^8_e), 1.56 (ddd, ^2J = 13.7 Hz, ^4J = 2.7 Hz, ^3J = 2.9 Hz, 1H, H^4_e), 1.67 (ddd, ^2J = 3.7 Hz, ^3J = 9.8 Hz, ^3J = 7.0 Hz, 1H, $H^{12''}$), 1.70 (ddd, ^2J = 3.7 Hz, ^3J = 9.8 Hz, ^3J = 7.0 Hz, 1H, $H^{10''}$), 2.15 (br.d, ^2J = 13.7 Hz, 1H, H^8_a), 2.24 (ddd, ^2J = 13.5 Hz, ^3J = 2.3 Hz, ^4J = 3.1 Hz, 1H, $H^{9'}$), 2.29 (ddd, ^2J = 13.5 Hz, ^3J = 3.7 Hz, ^4J = 2.7 Hz, 1H, $H^{9''}$), 2.43 (br.dd, ^2J = 13.7 Hz, ^3J = 5.1 Hz, 1H, H^4_a), 2.77 (dddd, ^3J = 2.3 Hz, ^3J = 3.7 Hz, ^3J = 2.9 Hz, ^3J = 5.1 Hz, 1H, H^5).

^{13}C NMR ($CDCl_3$, δ, ppm): 17.1 (C^{10}), 17.9 (C^{12}), 24.8 (CH_3), 26.3 (C^3), 26.4 (C^7), 28.26 (C^{13}), 28.30 (C^{11}), 39.0 (C^9), 40.2 (C^4), 44.5 (C^5), 45.1 (C^1), 47.8 (C^8), 214.1 (C^6=O), 215.5 (C^2=O).

HRMS (ESI, m/z): calcd. for $C_{14}H_{18}O_2$ $[M+H]^+$ 219.1380, found 219.1380.

1-Methyldispiro[cyclopropane-1,3'-bicyclo[3.3.1]nonane-7',1''-cyclopropane]-2',4'-dione (**6b**). Yield 11 mg (5%), method A, 30 min; 9 mg (4%), method B; 20 mg (9%), method C, 60 °C, 6 h. Yellowish oil, R_f = 0.22 (petroleum ether : DCM : MeOH = 3:1:0.5).



^{1}H NMR ($CDCl_3$, δ, ppm): 0.19-0.27 (m, 4H, $2CH_2$, *cy*-Pr), 1.09-1.16 (m, 1H, CH_2), 1.13 (s, 3H, CH_3), 1.27-1.30 (m, 1H, CH_2), 1.66-1.73 (m, 2H, CH_2, *cy*-Pr), 1.78-1.86 (m, 2H, CH_2, *cy*-Pr + 1H, CH_2, bridge), 1.95 (d, ^2J = 13.4 Hz, 1H, CH_2), 2.18 (dd, ^2J = 13.5 Hz, ^3J = 4.5 Hz, 1H, CH_2), 2.30 (dm, ^2J = 13.7 Hz, 1H, CH_2, bridge), 2.84 (1H, CH).

^{13}C NMR ($CDCl_3$, δ, ppm): 10.6 (CH_2, *cy*-Pr), 14.5 (C_{spiro}), 16.3 (CH_2, *cy*-Pr), 24.8 (CH_3), 27.2 (CH_2, *cy*-Pr), 31.4 (CH_2, *cy*-Pr), 35.3 (CH_2, bridge), 39.0 (CH_2), 41.2 (C_{spiro}), 44.4 (C), 44.8 (CH), 47.7 (CH_2), 212.3 (C=O), 213.0 (C=O).

HRMS (ESI, m/z): calcd. for $C_{14}H_{18}O_2$ $[M+H]^+$ 219.1380, found 219.1380.

Calculation details

The geometries of molecules were fully optimized by means of density functional theory (DFT) calculations. The PBE functional for full electron 3z basis sets (triple set size). All calculations were performed using the MBC100k cluster at the Joint Supercomputer Center (Moscow, Russia) with the use of the PRIRODA04 program written by Laikov.[S9]

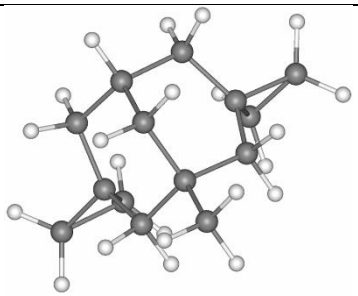
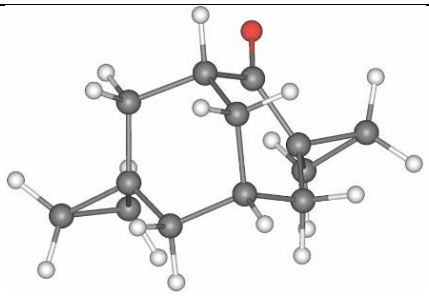
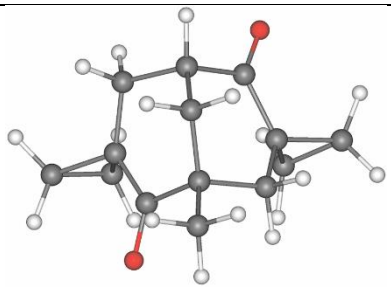
		
(**3b**)	(**4a**)	(**5b**)
E = -546.085312 au	E = -580.797692 au	E = -694.045010 au

Figure S1. DFT-calculations of total energy

Table S1. XYZ coordinates for **3b** (Å)

C	1.38810299	0.55250875	-0.78155587
C	1.63294378	-0.24151092	0.49996943
C	1.07114545	-1.66122391	0.48767749
C	-0.30387891	-1.80677546	-0.19652296
C	-1.51225203	-1.23628189	0.57442316
C	-1.58785874	0.28833937	0.60839745
C	-1.18596980	0.97614294	-0.69475146
C	0.00897834	0.35275117	-1.46061616
H	-0.48579636	-2.88828852	-0.31609013
C	-0.24444134	-1.16101168	-1.58874204
C	0.06835404	0.99899611	-2.85382084
C	1.74261900	0.49786164	1.81702729
C	-1.36899600	1.00923247	1.92205617
C	2.98467780	-0.05308034	1.15850772
C	-2.76219349	0.89230147	1.35173709
H	0.55886892	-1.62210120	-2.18866462
H	-1.19051818	-1.33425152	-2.12980281
H	-0.87673939	0.85167767	-3.39766702
H	0.24938056	2.08288827	-2.78106064
H	0.87852076	0.56251024	-3.45696846
H	1.38167702	0.00090577	2.71731648
H	1.60248510	1.57862247	1.81203712
H	3.67852846	0.65376991	0.70156405
H	3.45704548	-0.92793175	1.60724102
H	-3.45965349	0.20985380	1.83924865
H	-3.22117152	1.78928797	0.93387729
H	-0.89100287	1.98831267	1.89686311
H	-1.12830459	0.41288542	2.80195038
H	-1.53621986	-1.63443530	1.60193408
H	-2.42073259	-1.61756413	0.07361360
H	2.14773264	0.24370557	-1.52307050
H	1.56220365	1.62556129	-0.59471513
H	-0.99477996	2.04635868	-0.50835001
H	-2.05128178	0.93482748	-1.38162189
H	1.03348334	-2.05691505	1.51572532
H	1.77504357	-2.30792946	-0.06714636

Table S2. XYZ coordinates for **4a** (Å)

C	1.23858617	0.85504972	-0.84082406
C	1.66853753	-0.11479125	0.22308672
C	1.01996039	-1.50331488	0.30025377
C	-0.28286562	-1.67420757	-0.50711329
C	-1.55948905	-1.10964391	0.15310780
C	-1.62955517	0.41160119	0.18253125
C	-1.25215522	1.06184480	-1.13999259
C	0.05546090	0.47686457	-1.73219408
H	-0.43950860	-2.75904058	-0.62644154
C	-0.08504530	-1.04267302	-1.89214398
C	2.11926720	0.56581194	1.52337899
C	-1.30011633	1.14188912	1.47006902
C	3.14706023	-0.00486035	0.61186932
C	-2.73267569	1.05273242	0.99161760
H	0.80862621	-1.46578098	-2.37903996
H	-0.94271187	-1.26553204	-2.54818204
H	1.87798266	0.03303409	2.44294733
H	2.02204375	1.65023512	1.55090758
H	3.74050812	0.69624336	0.02647346
H	3.62988733	-0.94181178	0.88963136
H	-3.41205434	0.39590731	1.53586427
H	-3.19471290	1.95799263	0.59659872
H	-0.79832490	2.10666100	1.39846534
H	-1.01764958	0.54786978	2.33921218
H	-1.66708183	-1.51159758	1.17365862
H	-2.42342962	-1.48747855	-0.42385997
H	-1.15379321	2.15118738	-1.02227420
H	-2.05561907	0.88616060	-1.87765157
H	0.84559313	-1.77574100	1.35360953
H	1.73860182	-2.24205864	-0.09212142
O	1.79355428	1.94264441	-0.98081214
H	0.24111857	0.96480269	-2.70063203

Table S3. XYZ coordinates for **5b** (Å)

C	1.21779222	0.65719707	-0.56983682
C	1.64788581	-0.34158766	0.46815475
C	1.06971130	-1.75222248	0.43779725
C	-0.34114887	-1.81054961	-0.18586450
C	-1.35489350	-1.14304394	0.74937853
C	-1.65718308	0.31217255	0.53974175
C	-1.25756702	0.96506917	-0.77944674
C	-0.01019637	0.34018132	-1.45887464
H	1.05222568	-2.18021890	1.45083111
H	-1.09459920	2.04371859	-0.63420988
H	-0.64107604	-2.86696630	-0.24834016
O	-1.84268710	-1.78072309	1.67839408
C	-0.27252240	-1.17043273	-1.57413923
C	0.18657293	0.97290966	-2.84262926
C	1.94801761	0.30080422	1.83581830
C	-1.56986333	1.14076193	1.83571905
C	3.07378265	-0.17273757	0.98334914
H	1.71939616	-2.40238451	-0.17227569
H	-2.08825032	0.86308963	-1.49948182
C	-2.90262944	0.83618744	1.24185752
H	0.52274781	-1.65837400	-2.16215479
H	-1.21234929	-1.32487911	-2.12950532
H	-0.70431208	0.80213926	-3.46444229
H	0.36101112	2.05209031	-2.75903486
H	1.05204400	0.53090814	-3.35643892
O	1.78322106	1.74200950	-0.67307228
H	1.66125927	-0.28622625	2.70783033
H	1.79018592	1.37602770	1.90306512
H	3.67173056	0.58585342	0.48055059
H	3.58601438	-1.09349977	1.26219925
H	-3.51250602	0.08623121	1.74356746
H	-3.43620808	1.63465127	0.72649124
H	-1.15976760	2.14471229	1.72953440
H	-1.28583874	0.59713123	2.73546733

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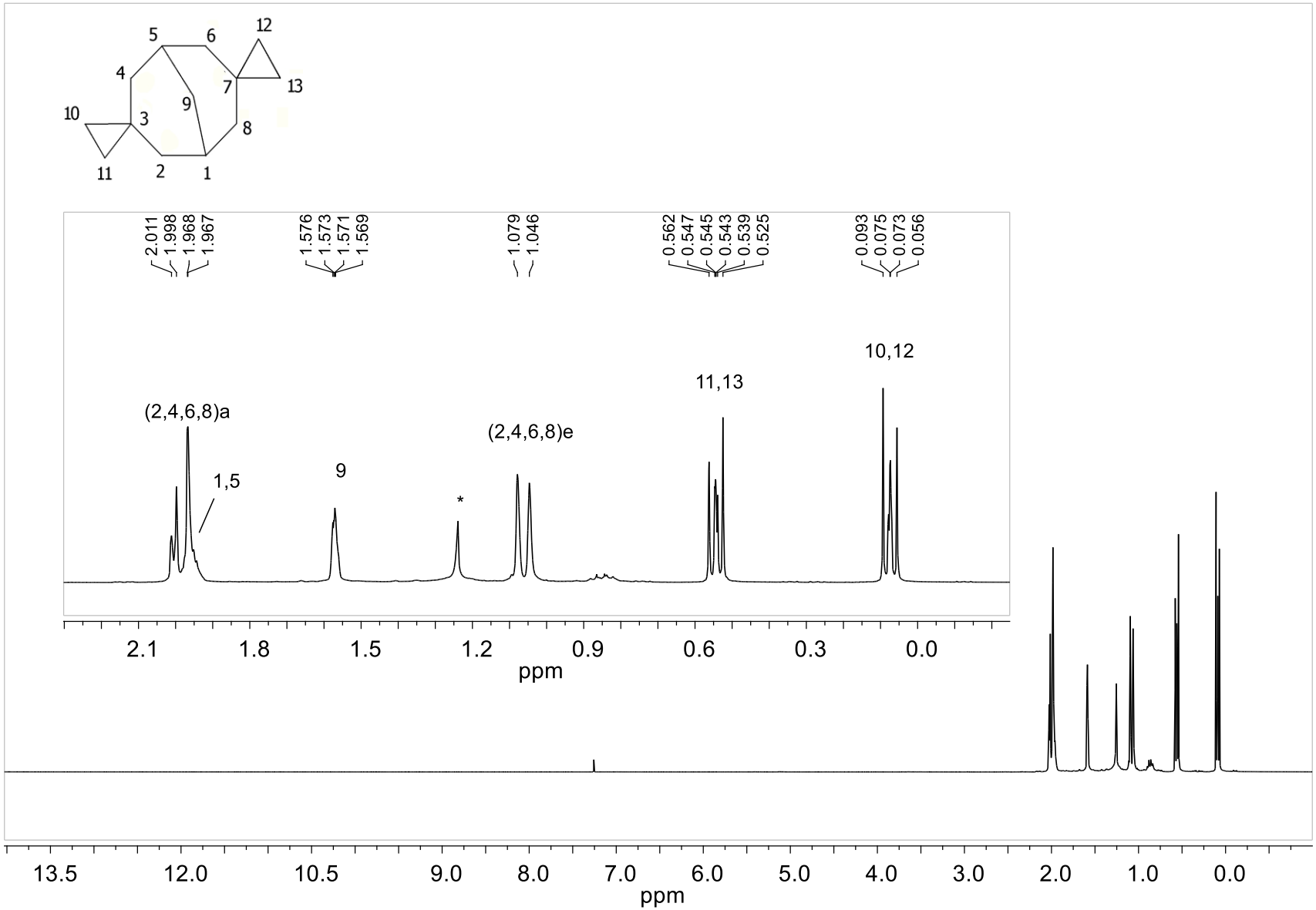
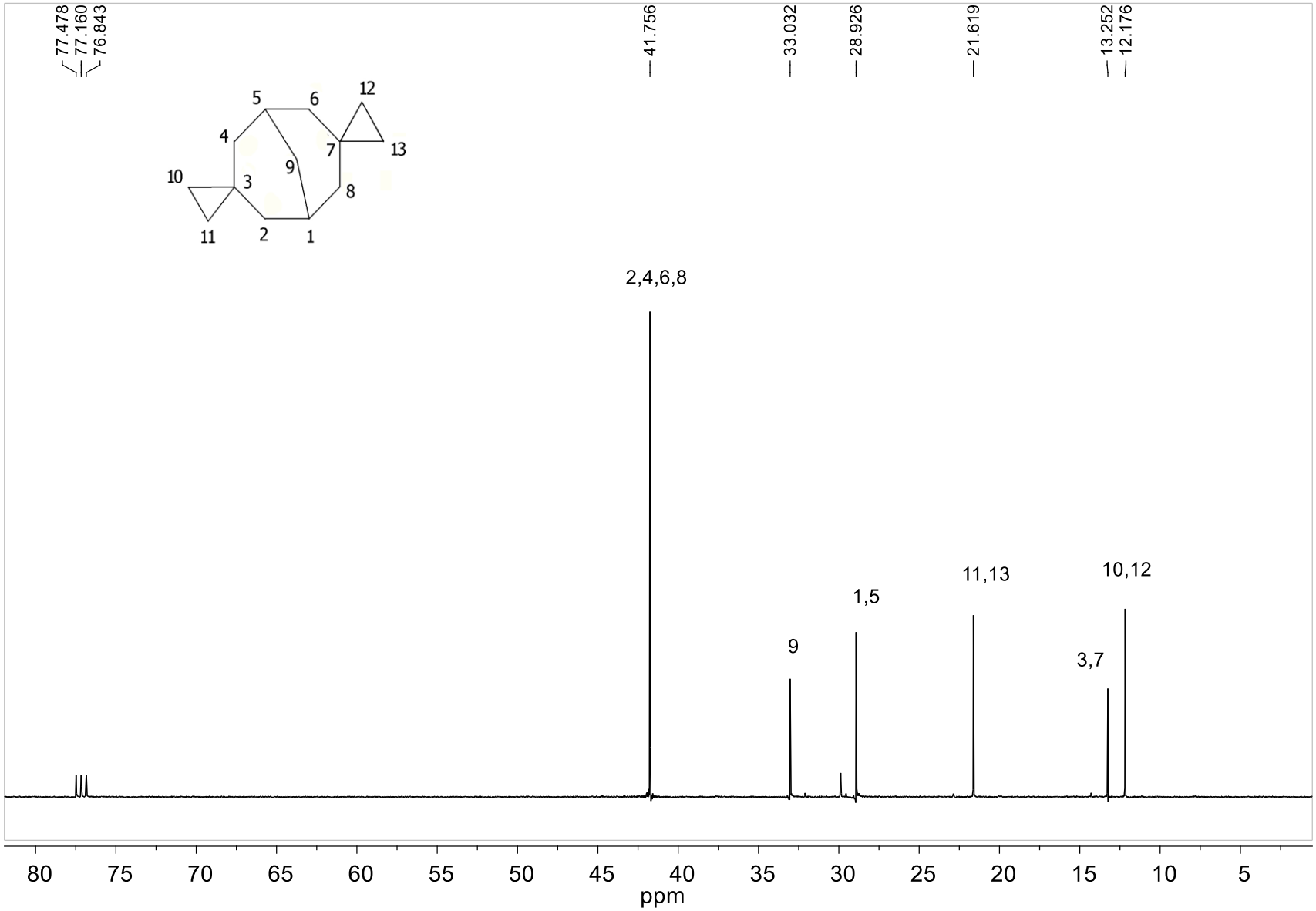
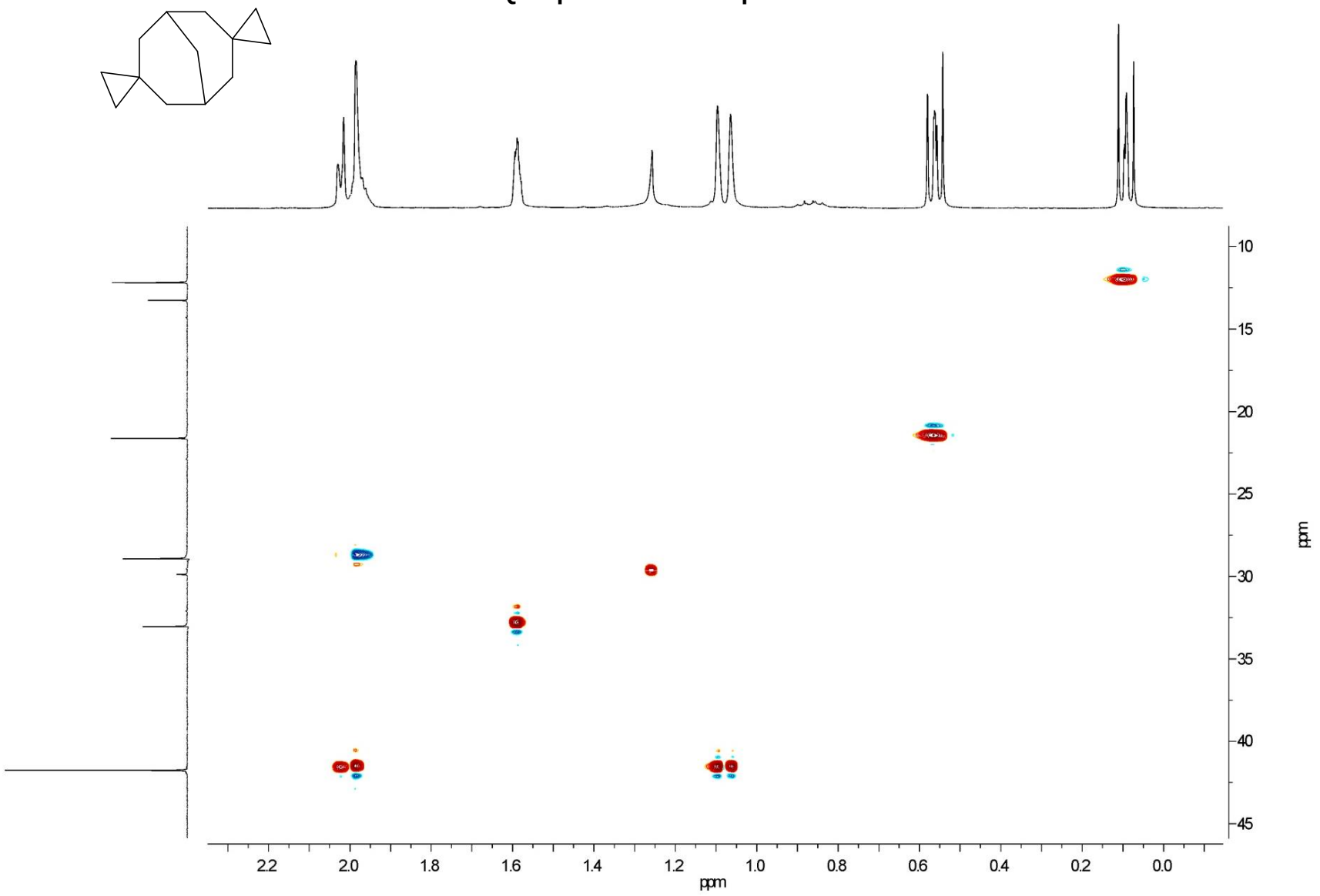
^{1}H NMR (400 MHz, $CDCl_3$) spectrum of compound 3a



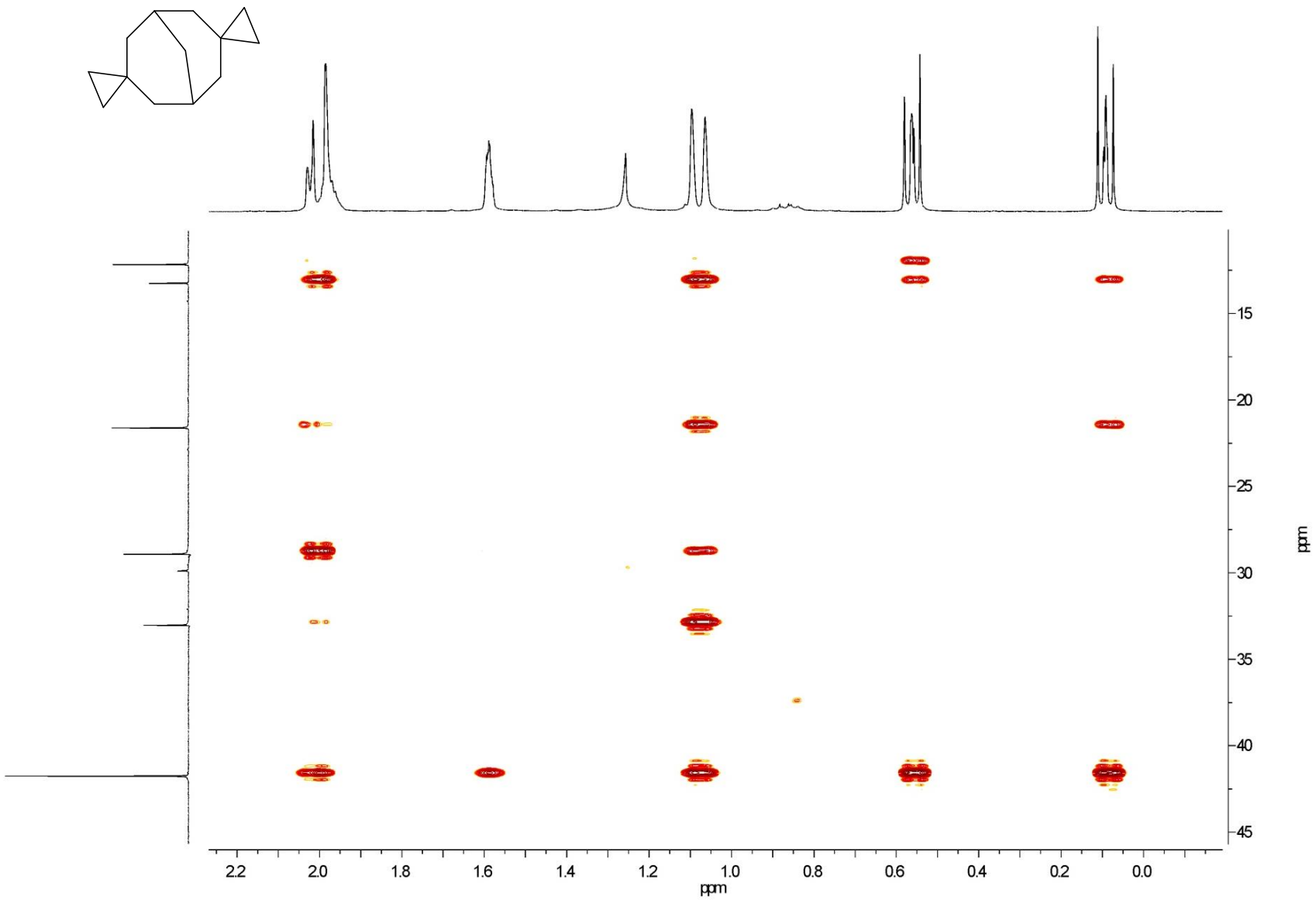
^{13}C NMR (101 MHz, $CDCl_3$) spectrum of compound 3a



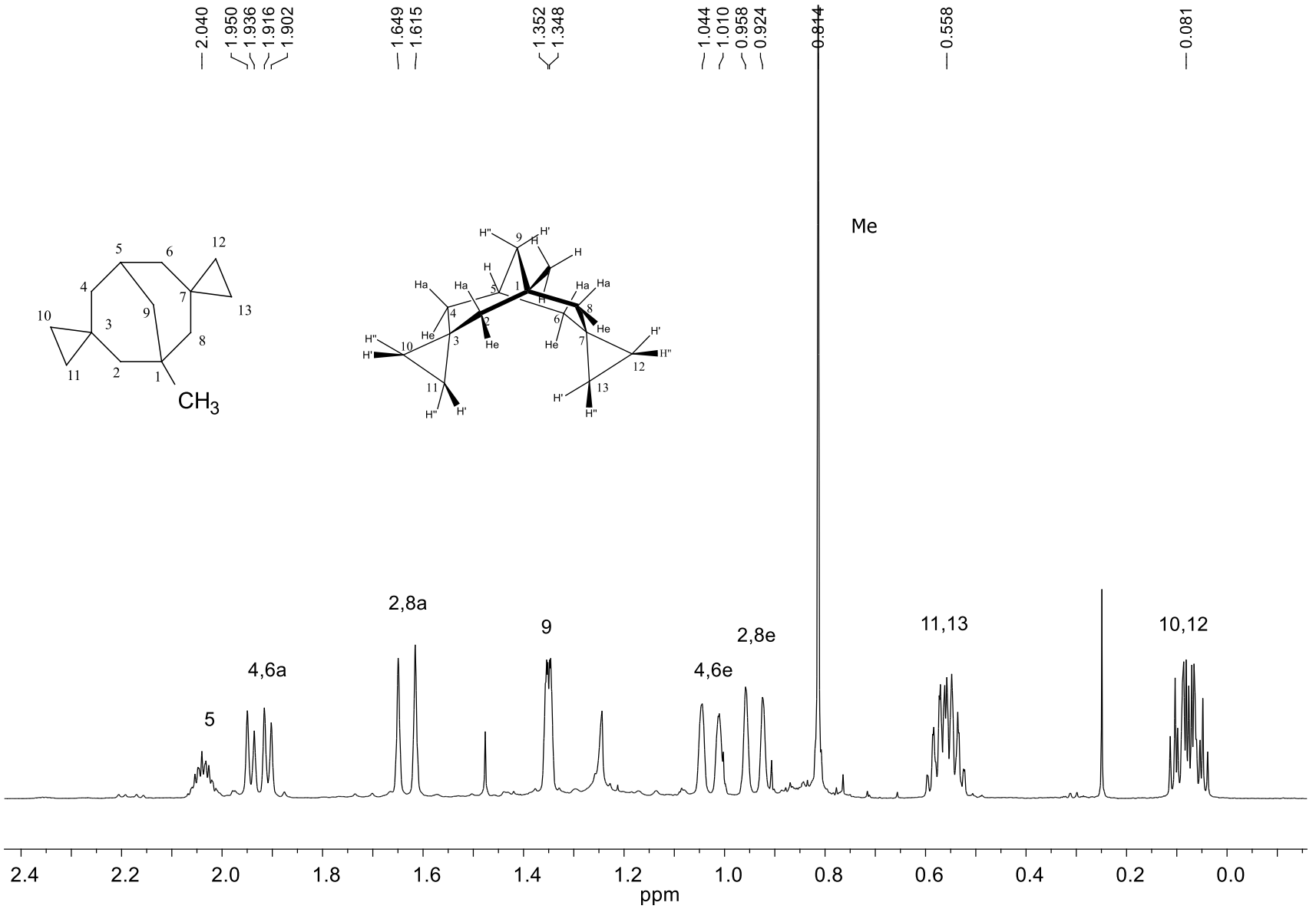
HSQC spectrum of compound 3a



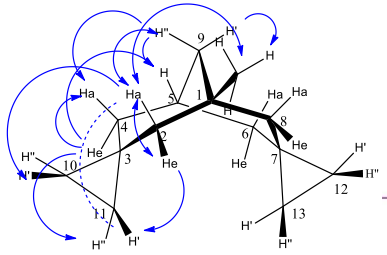
HMBC spectrum of compound 3a



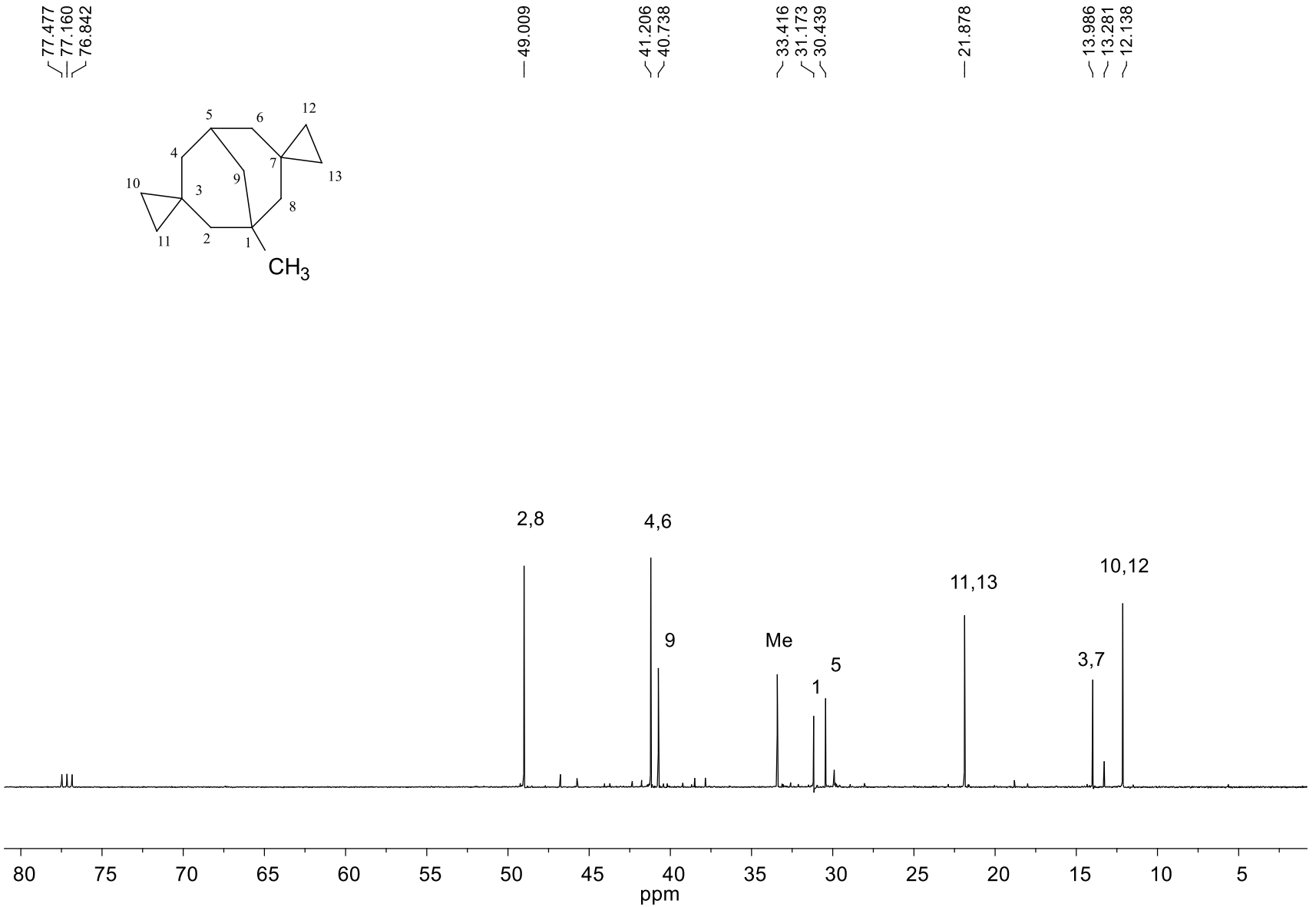
^{1}H NMR (400 MHz, $CDCl_3$) spectrum of compound 3b



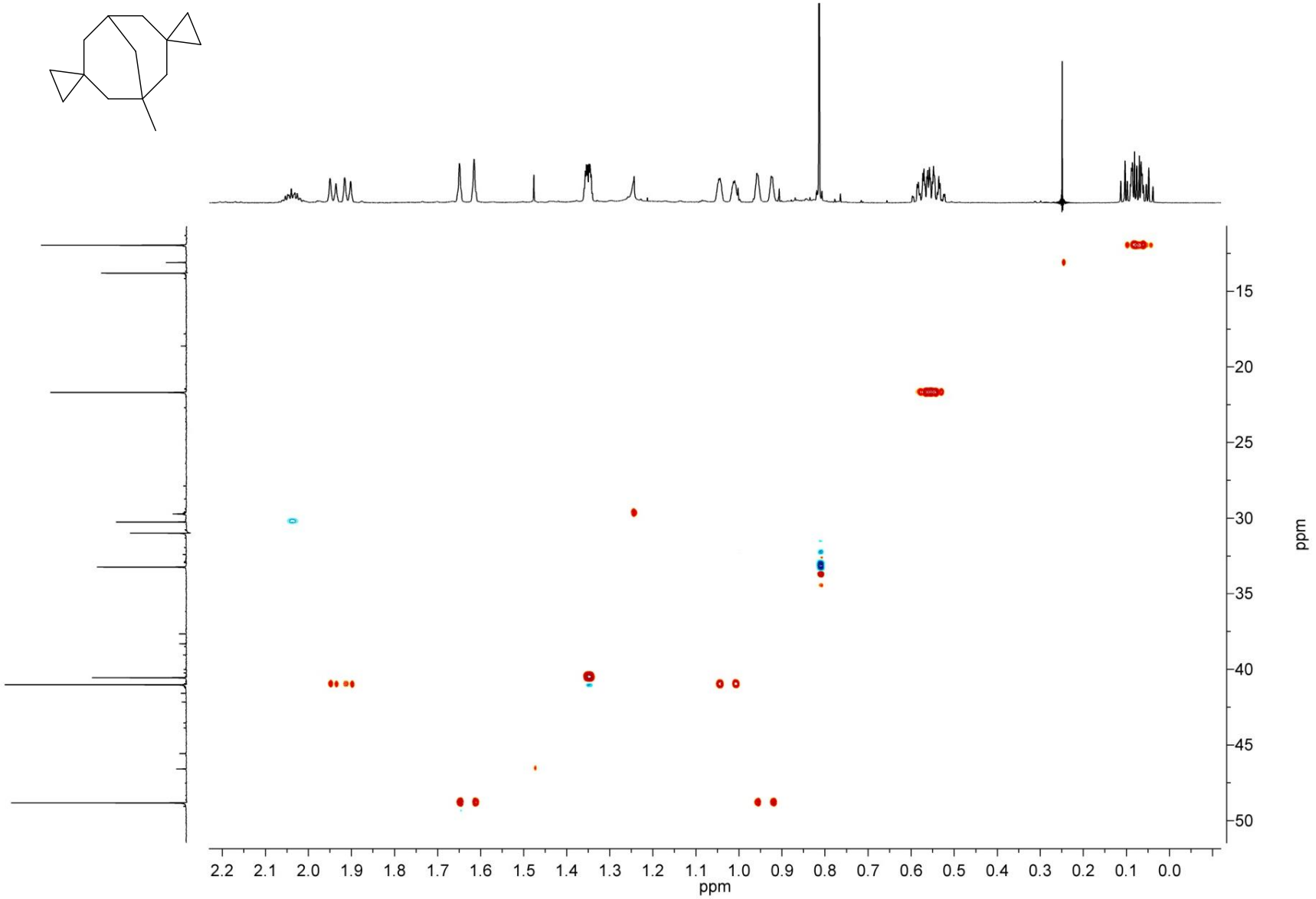
NOESY-1D spectra of compound 3b



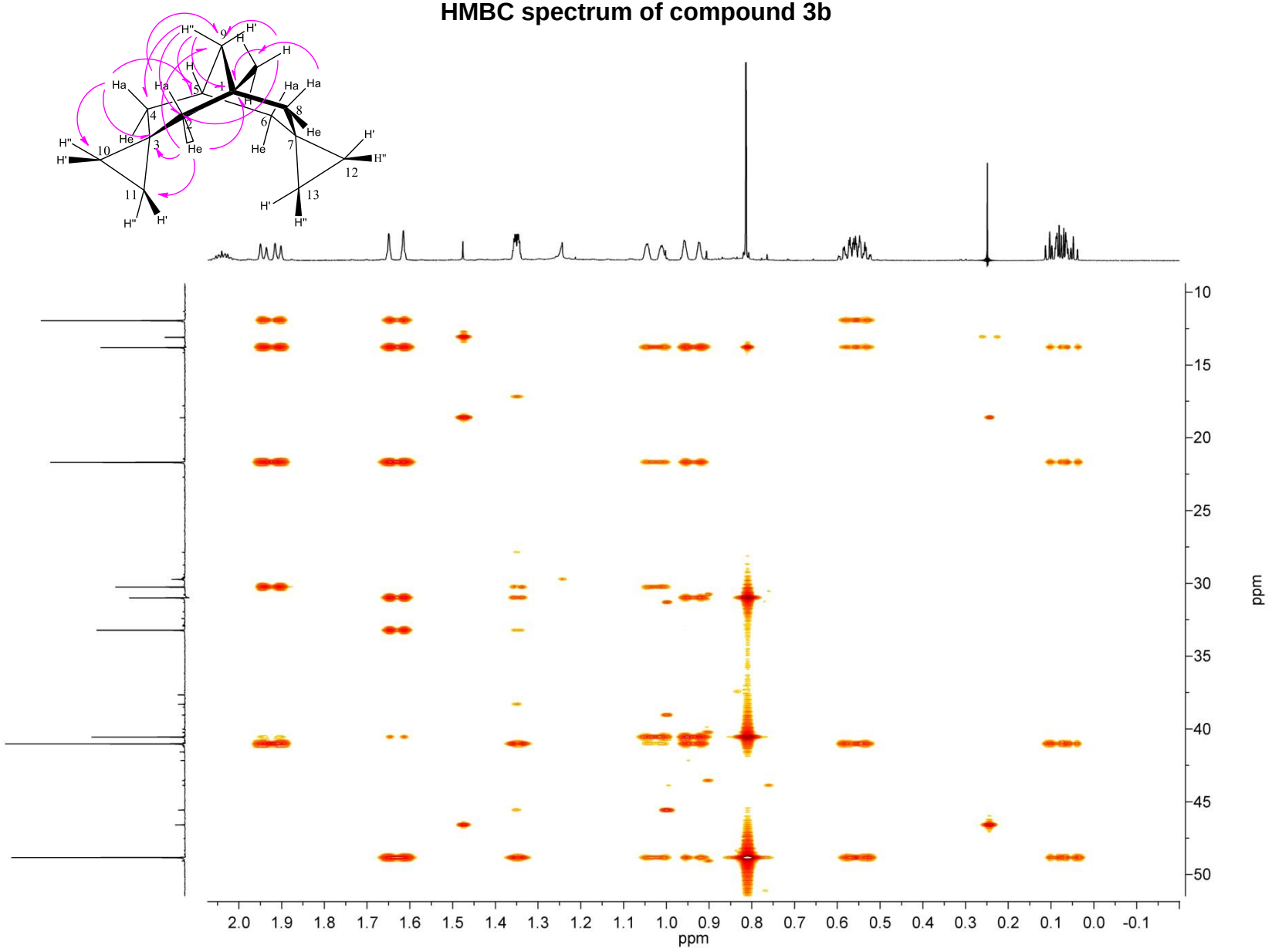
^{13}C NMR (101 MHz, $CDCl_3$) spectrum of compound 3b



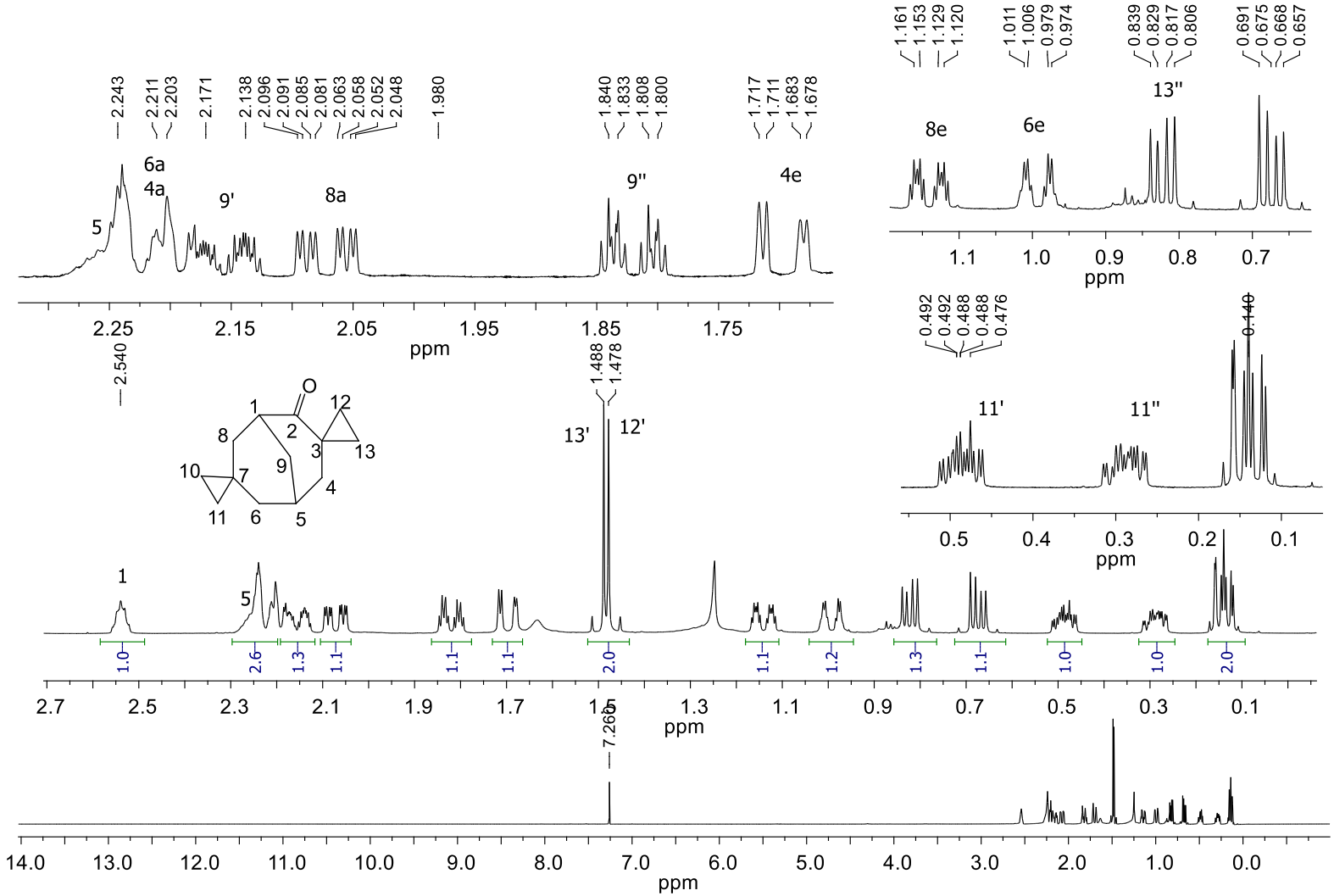
HSQC spectrum of compound 3b



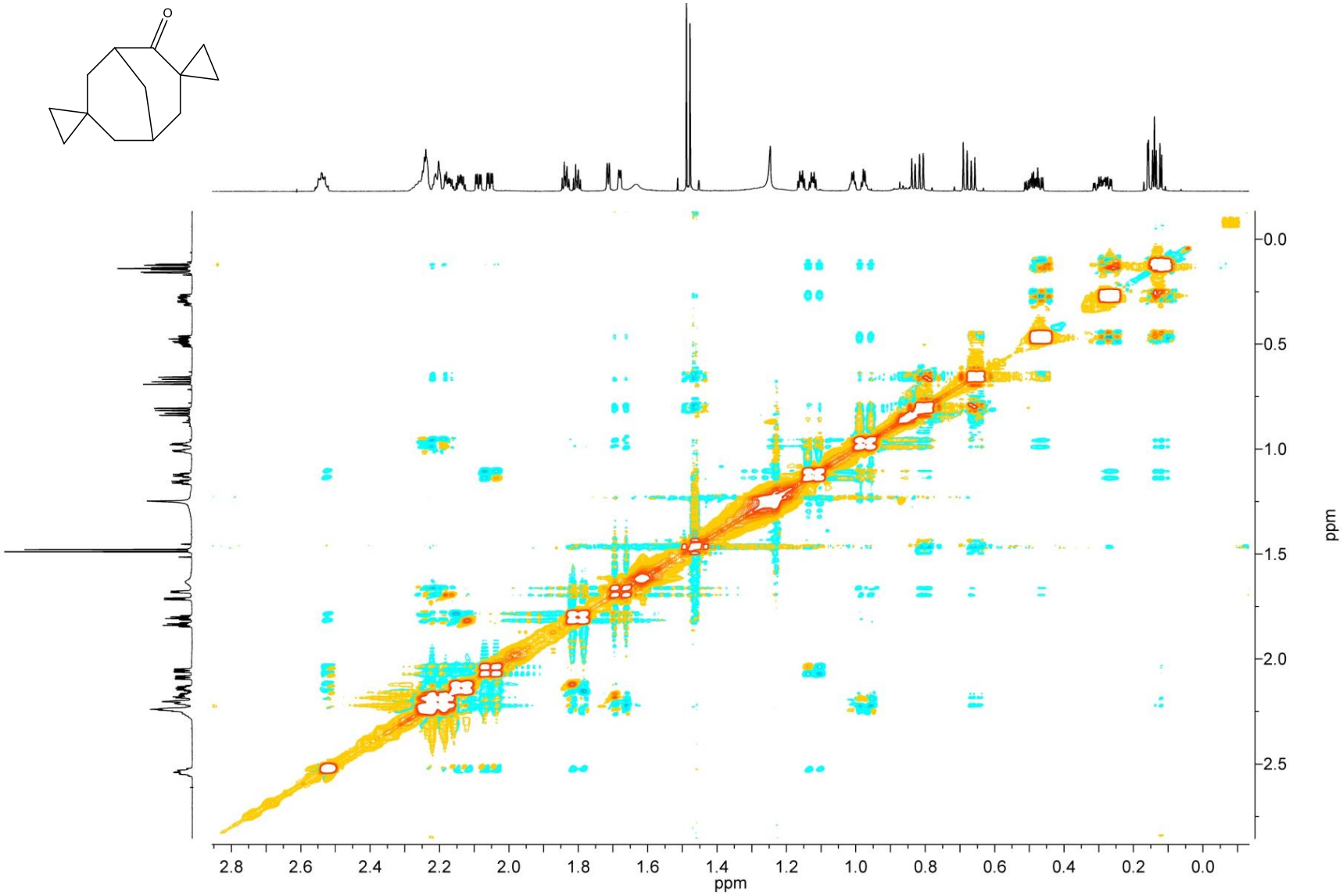
HMBC spectrum of compound 3b



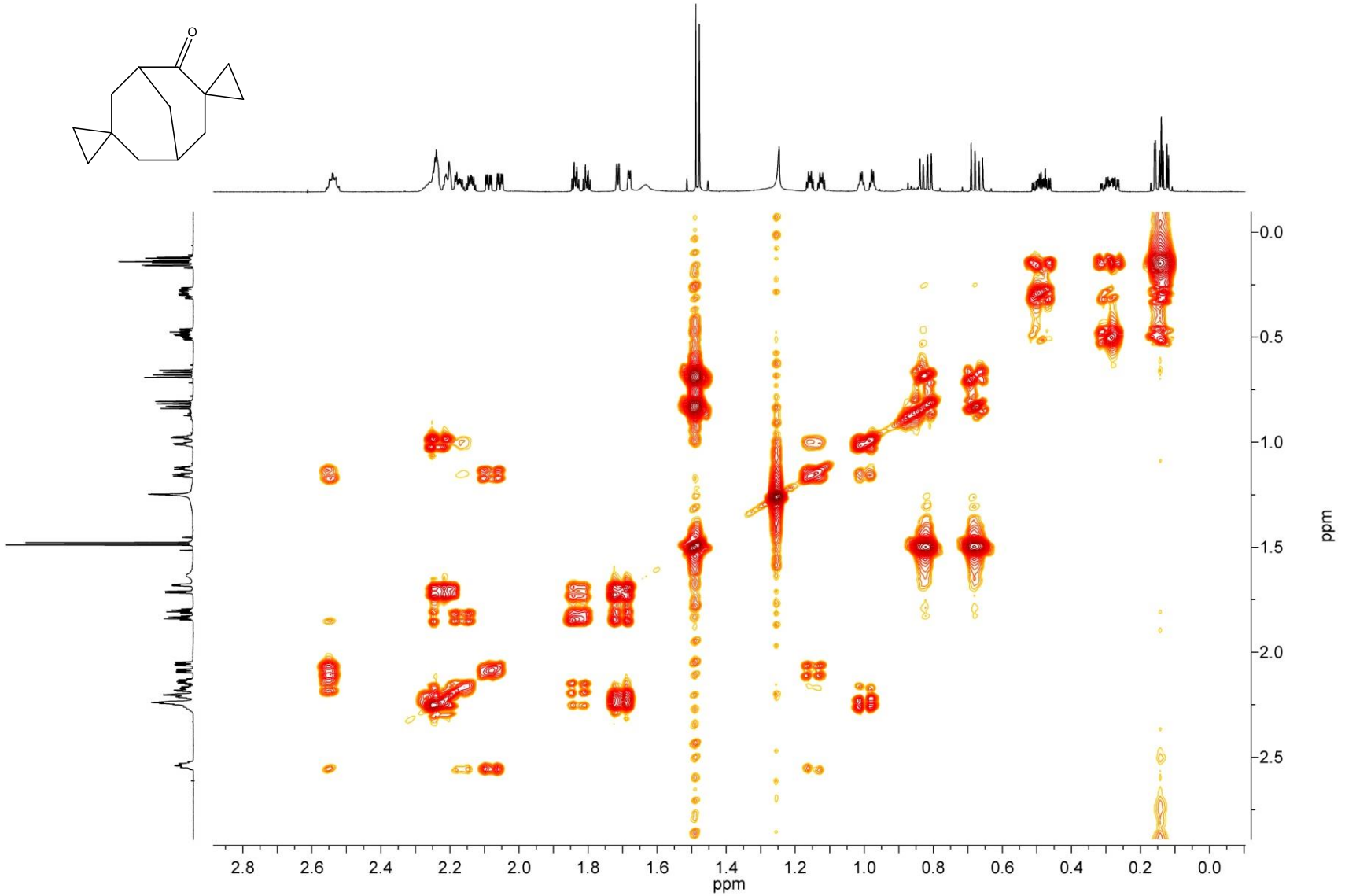
^{1}H NMR (400 MHz, $CDCl_3$) spectrum of compound 4a



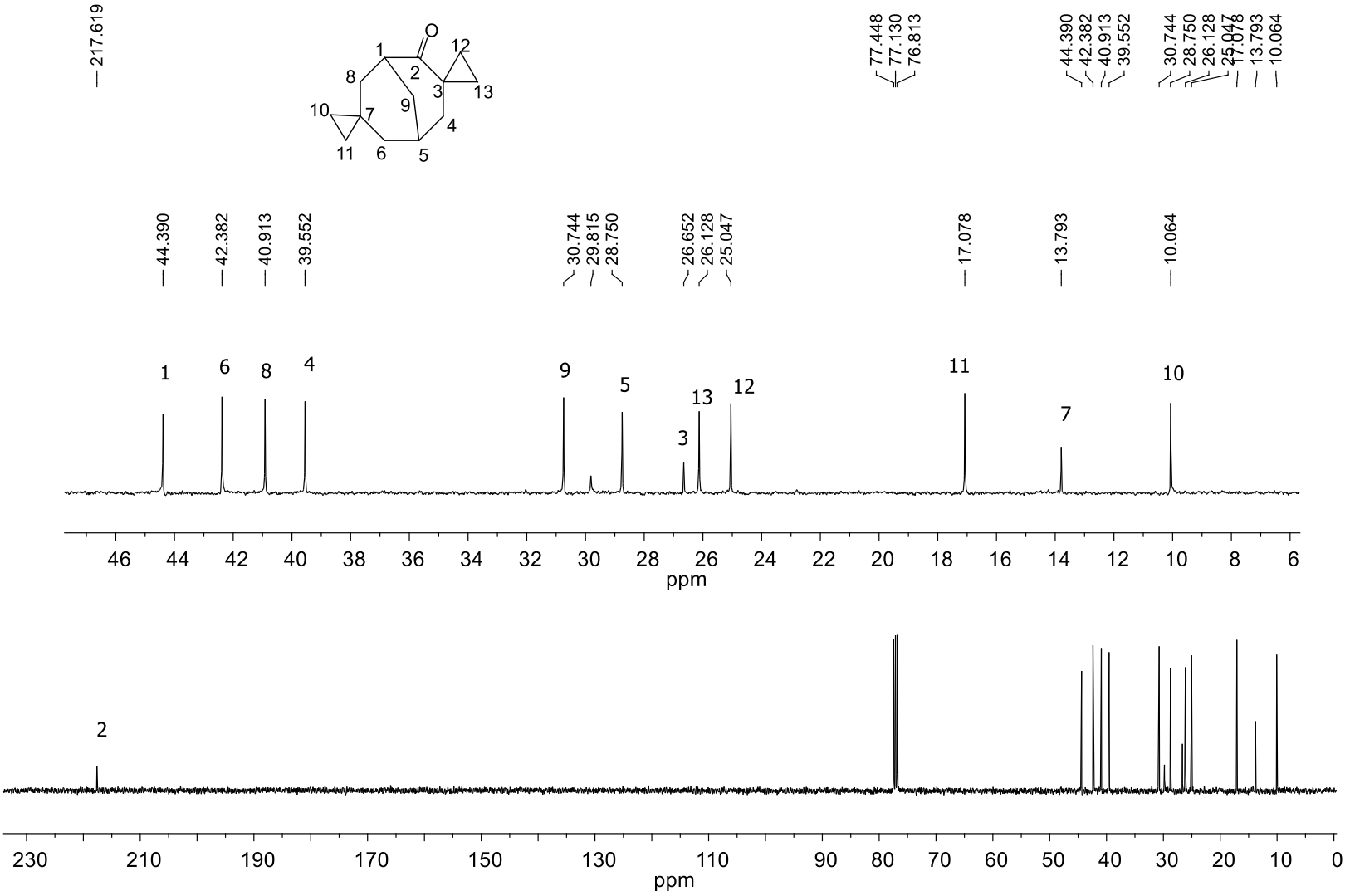
NOESY-2D spectrum of compound 4a



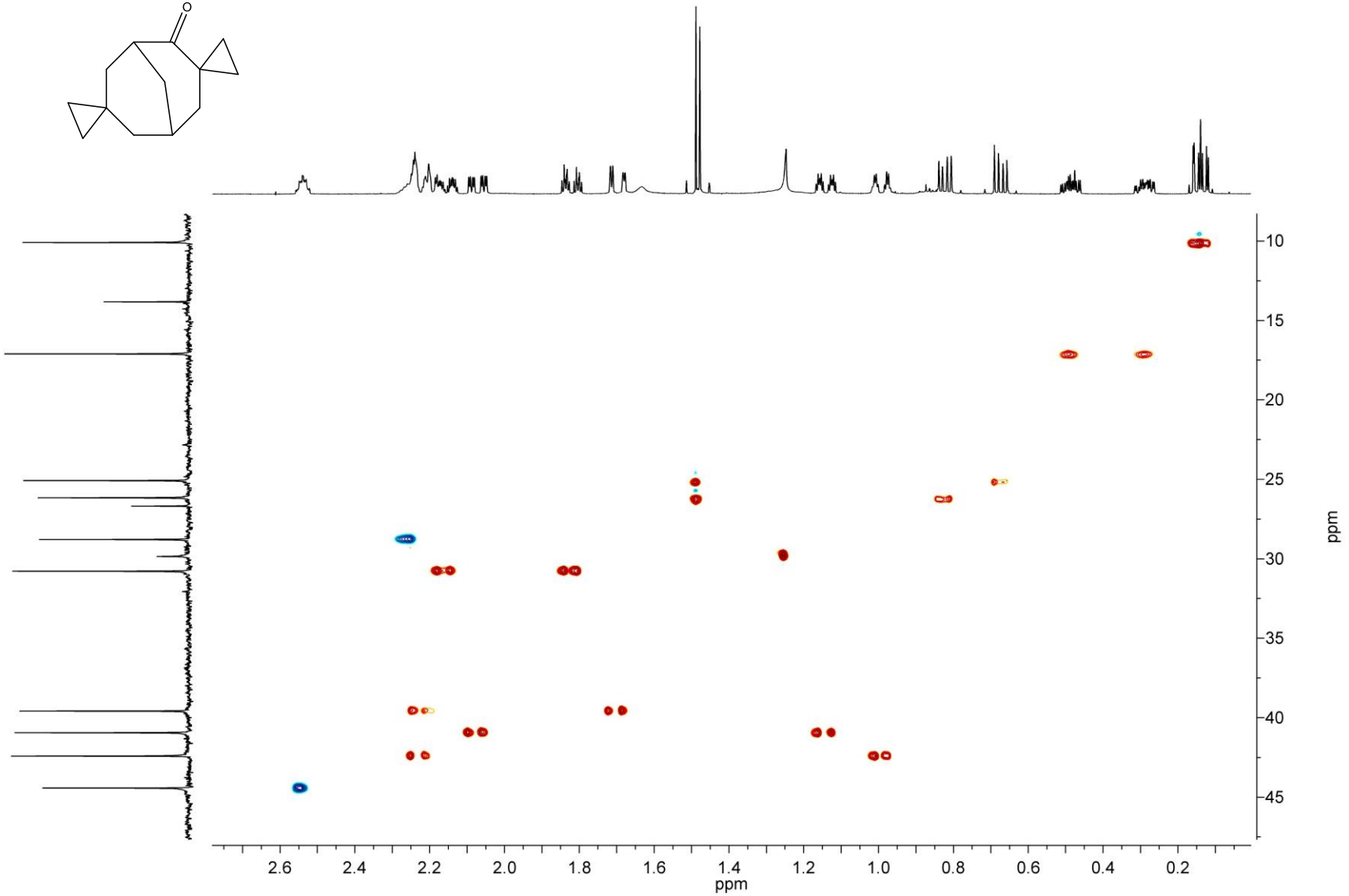
gCOSY spectrum of compound 4a



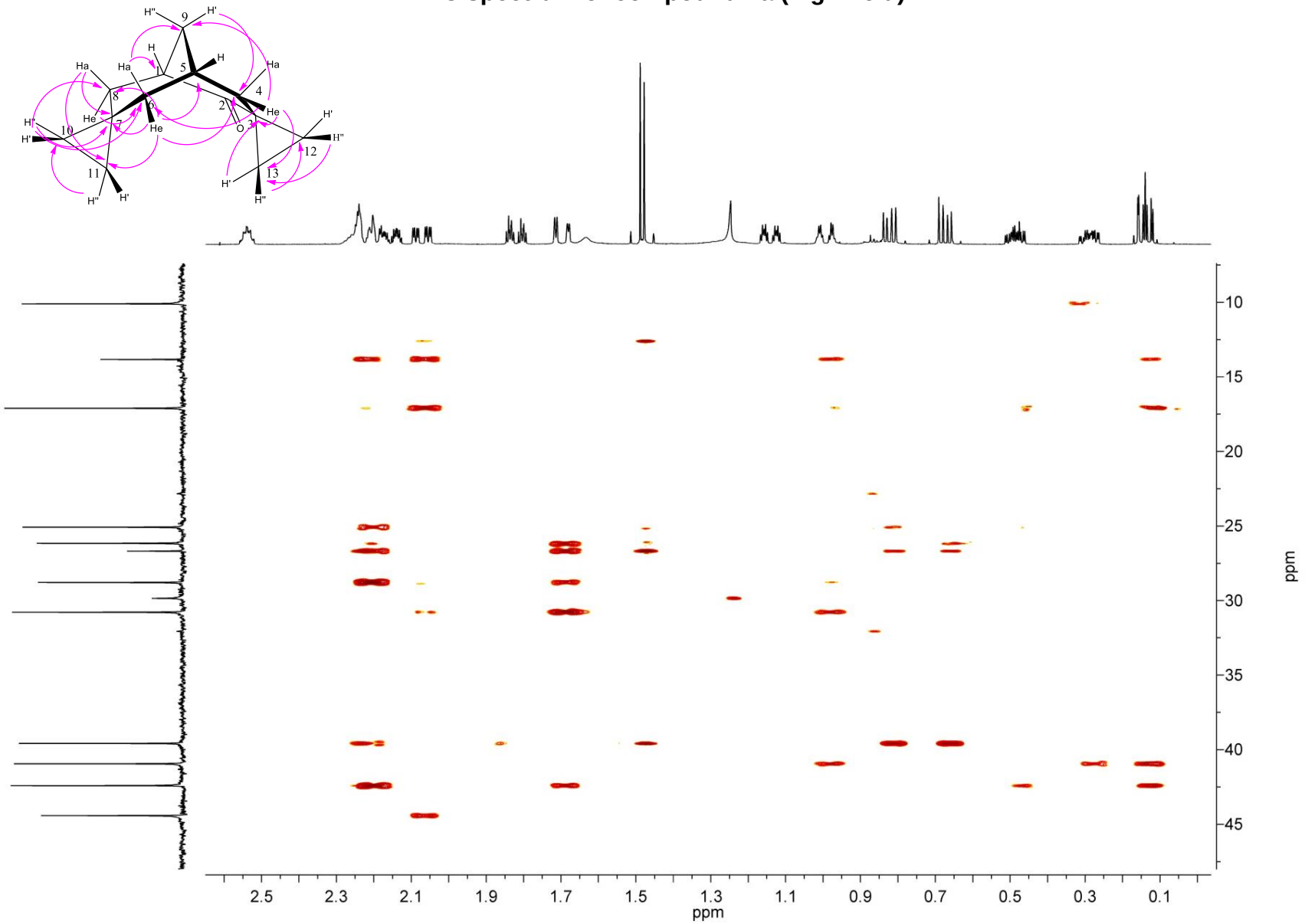
^{13}C NMR (101 MHz, $CDCl_3$) spectrum of compound 4a



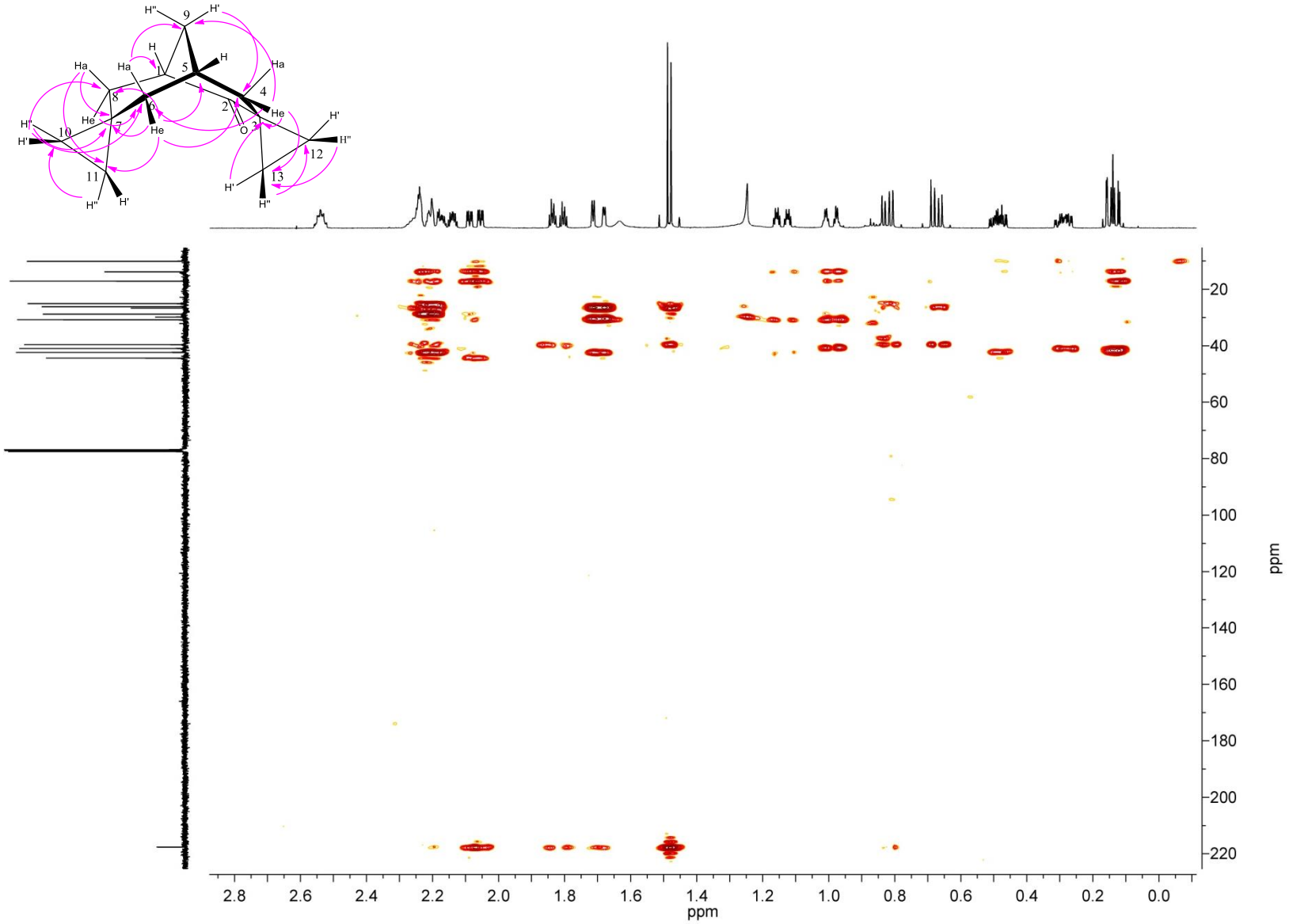
HSQC spectrum of compound 4a



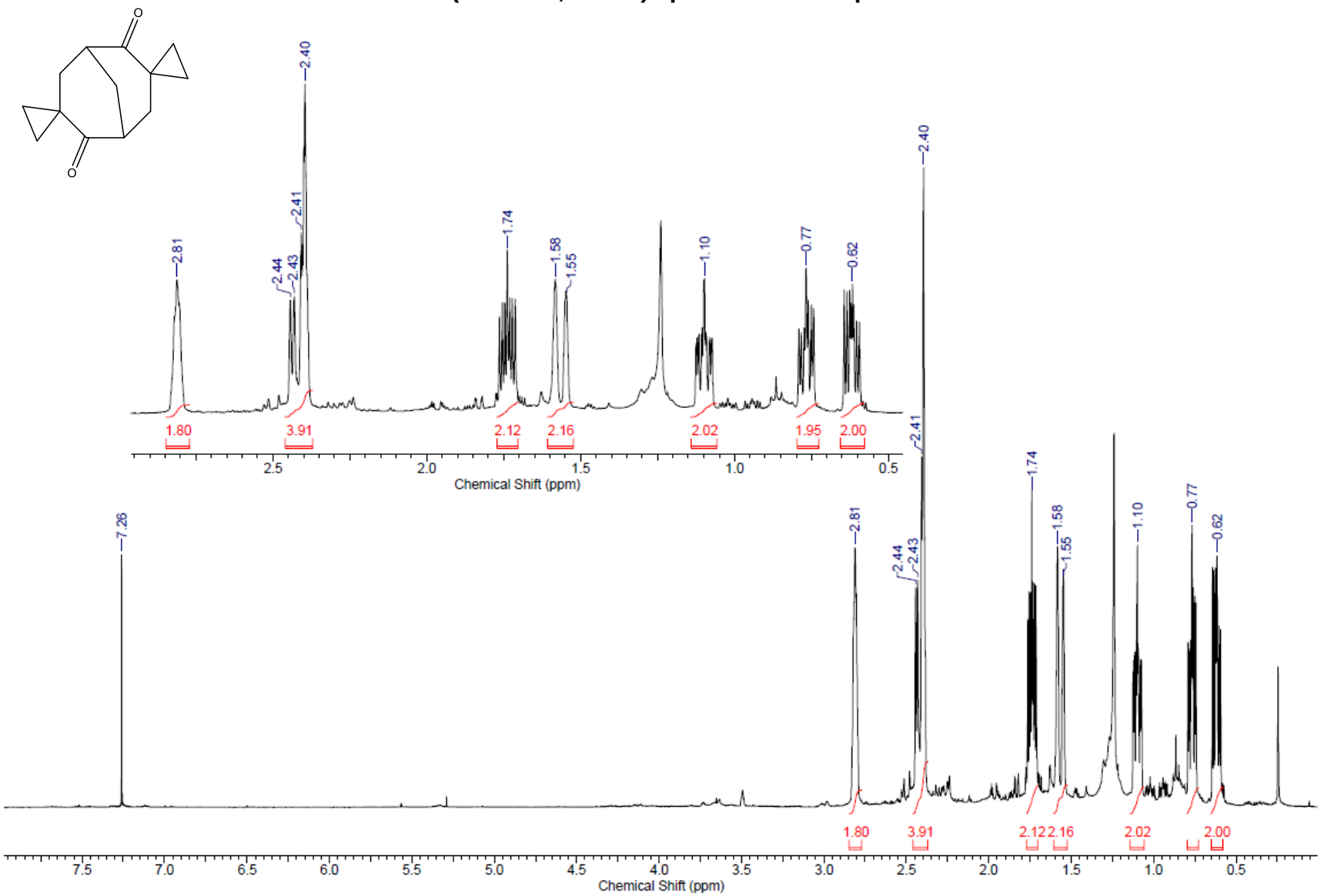
HMBC spectrum of compound 4a (high field)



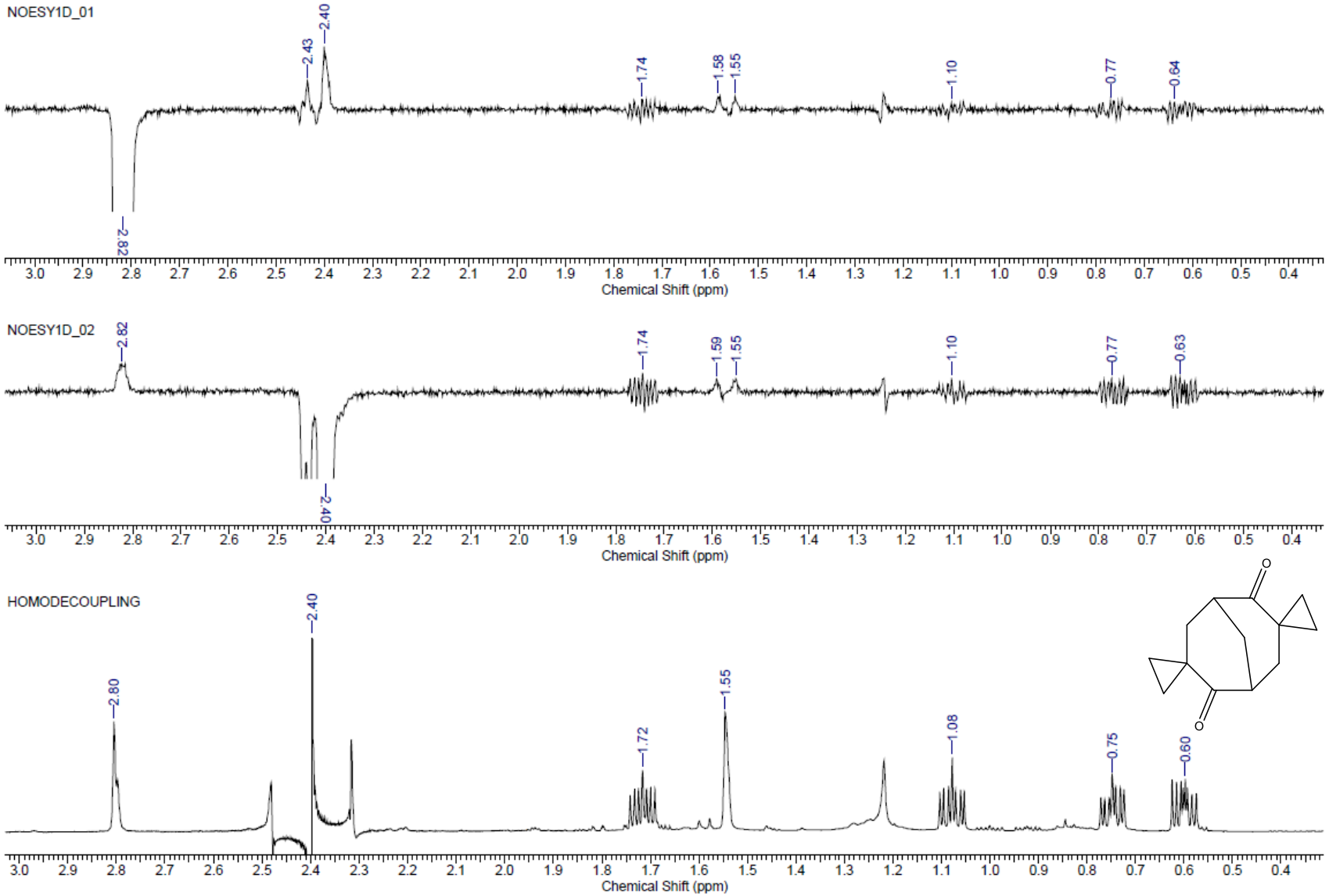
HMBC spectrum of compound 4a



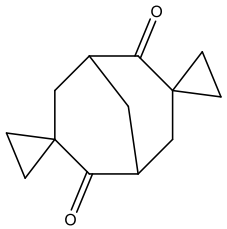
^{1}H NMR (400 MHz, $CDCl_3$) spectrum of compound 5a



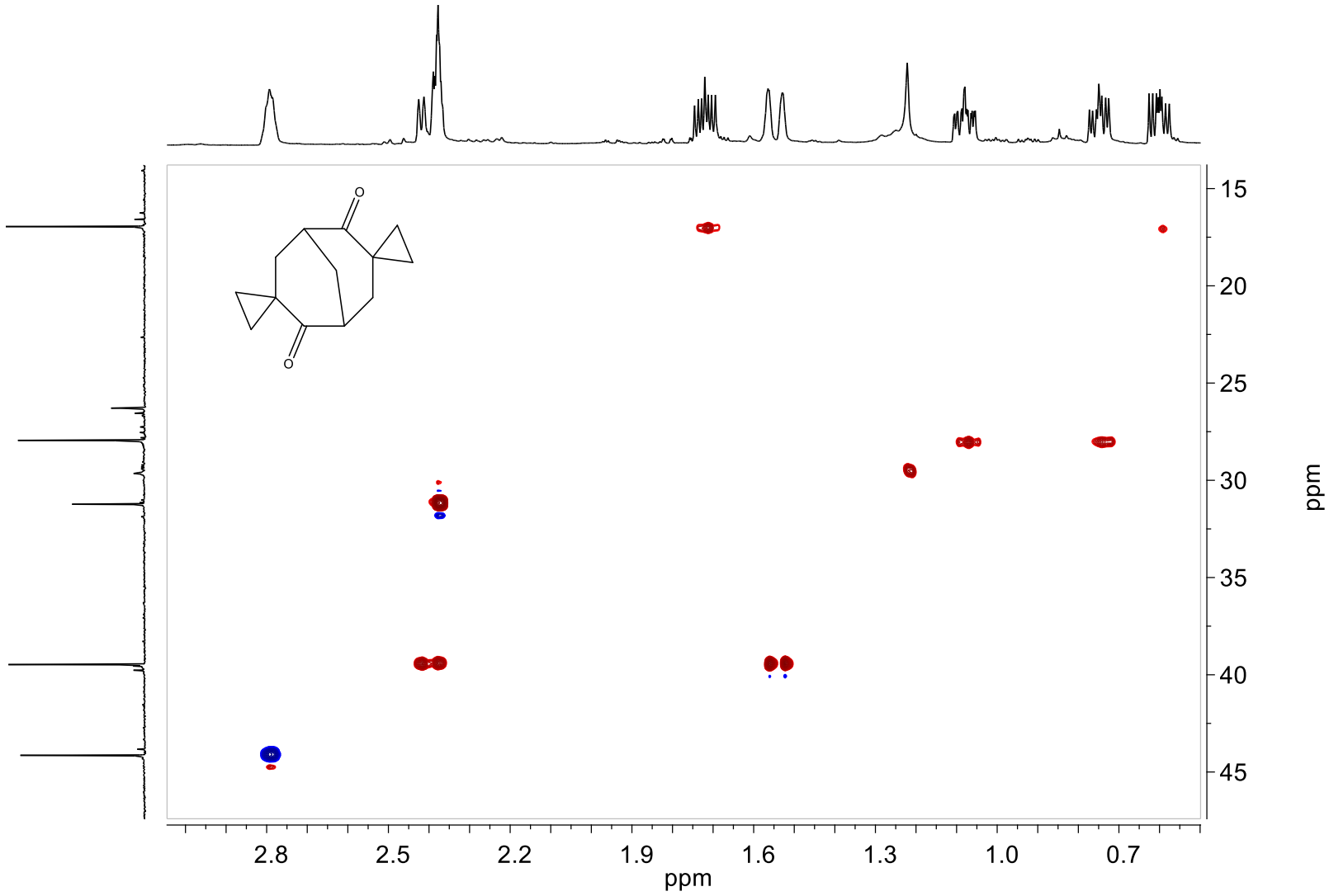
NOESY and Homodecoupling spectra of compound 5a



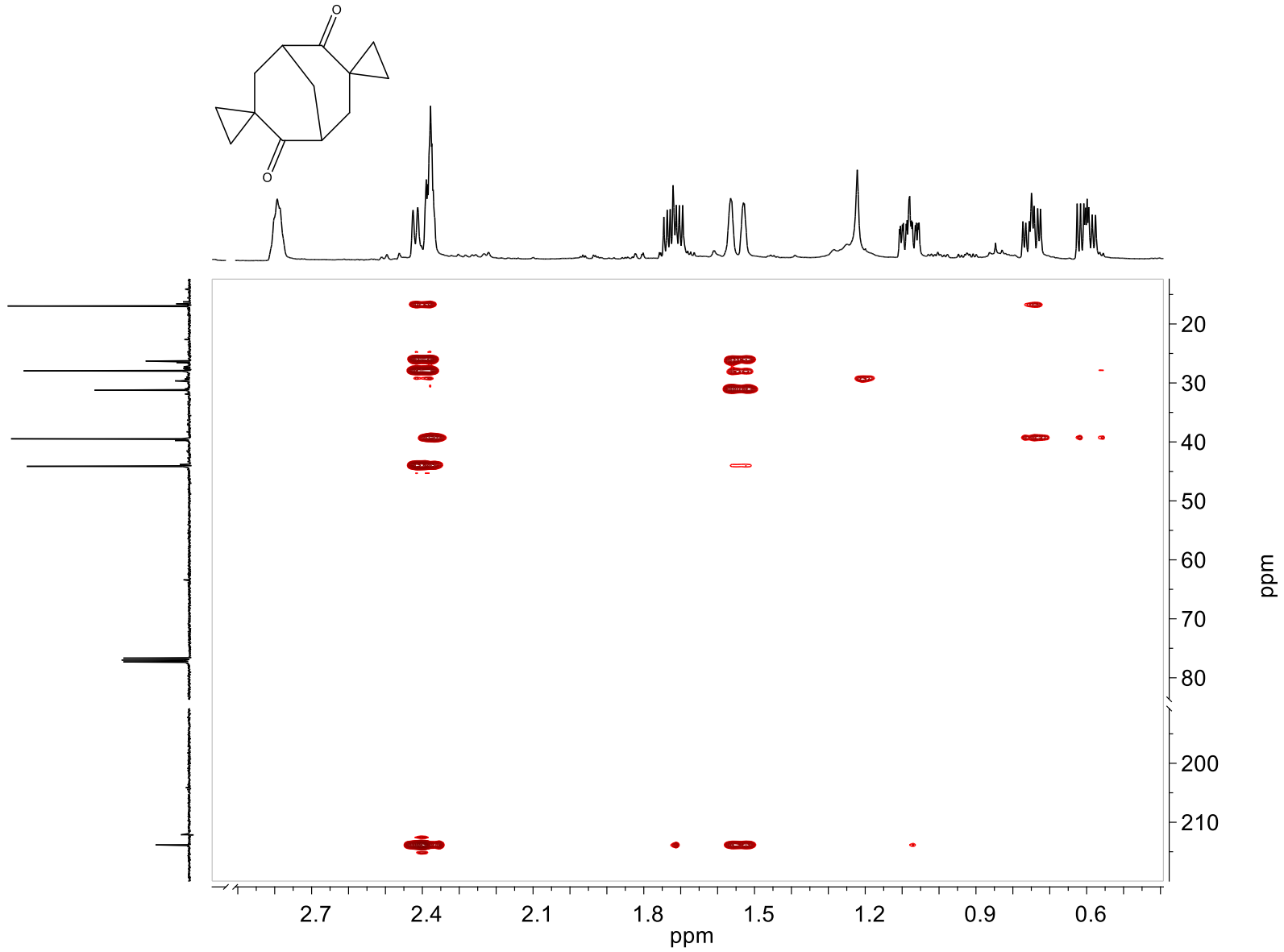
^{13}C NMR (101 MHz, $CDCl_3$) spectrum of compound 5a



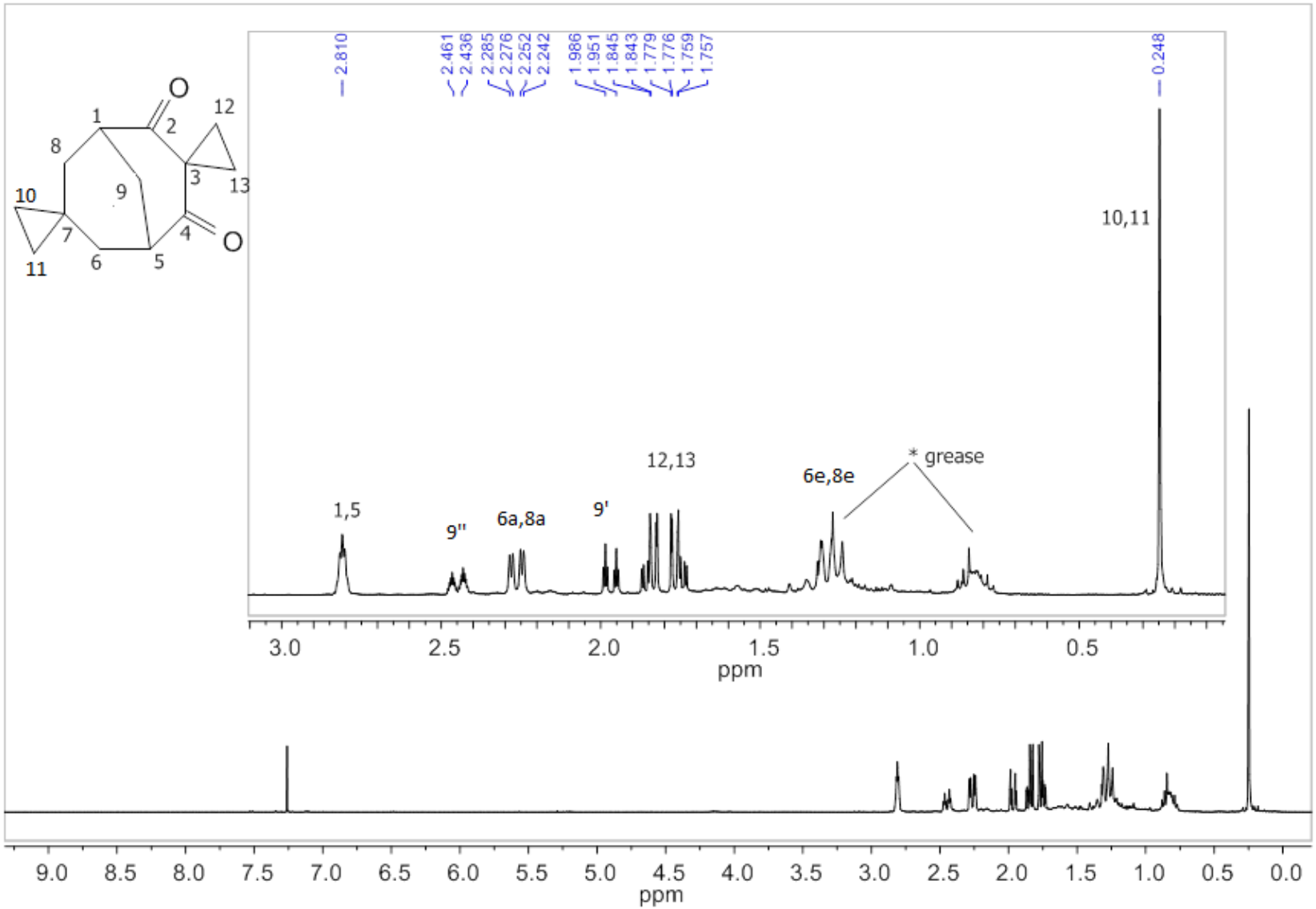
HSQC spectrum of compound 5a



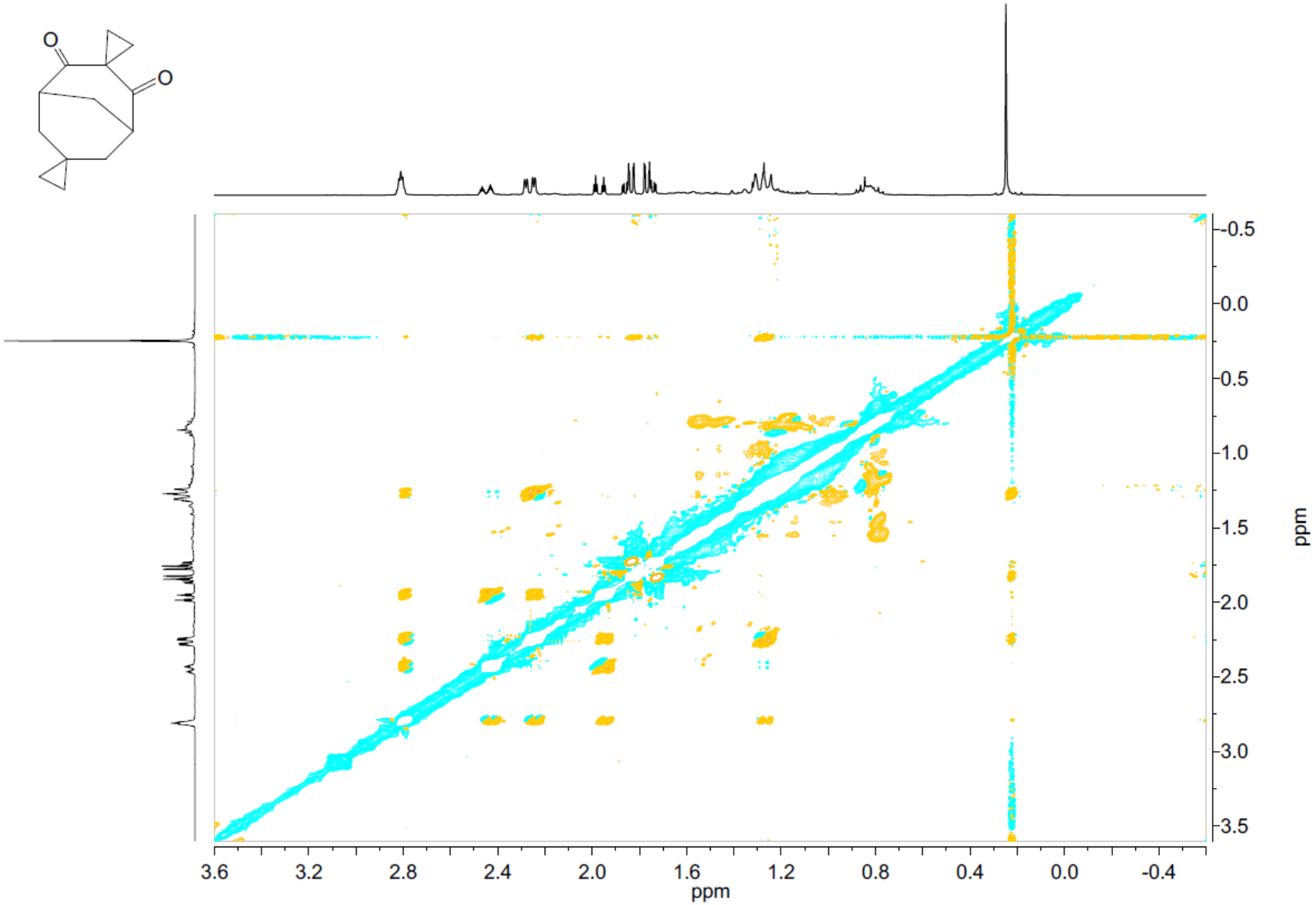
HMBC spectrum of compound 5a



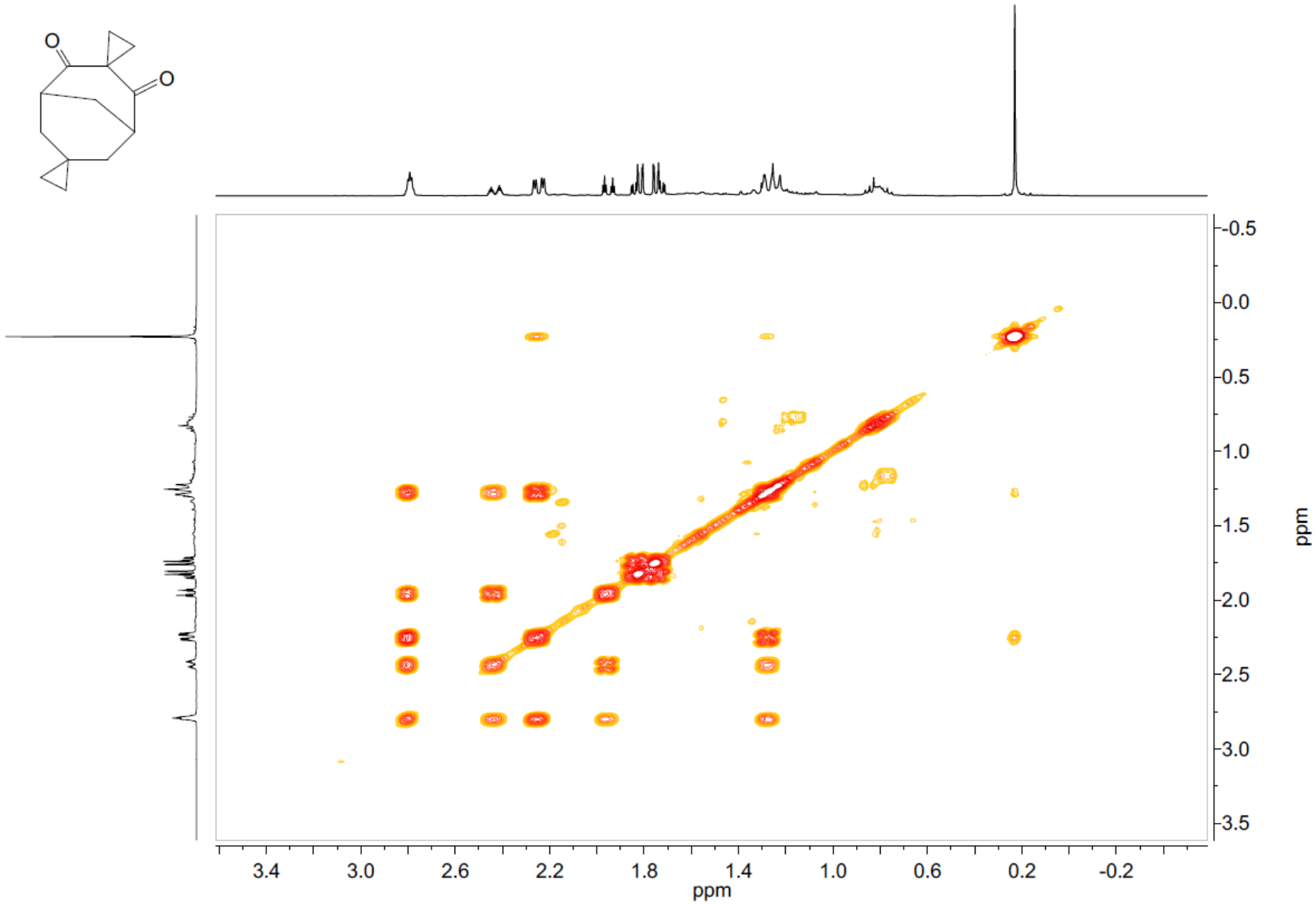
^{1}H NMR (400 MHz, $CDCl_3$) spectrum of compound 6a



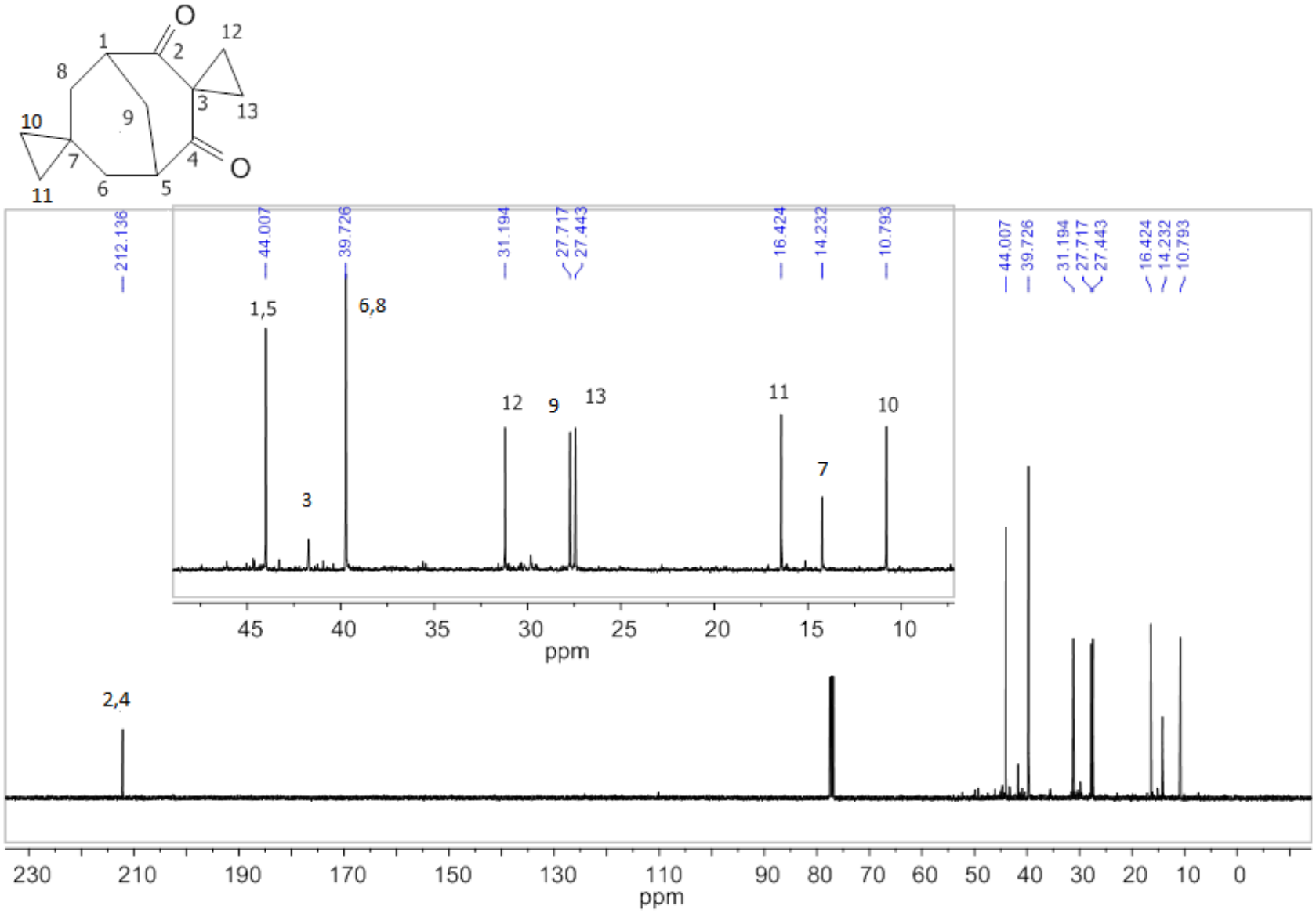
NOESY-2D spectrum of compound 6a



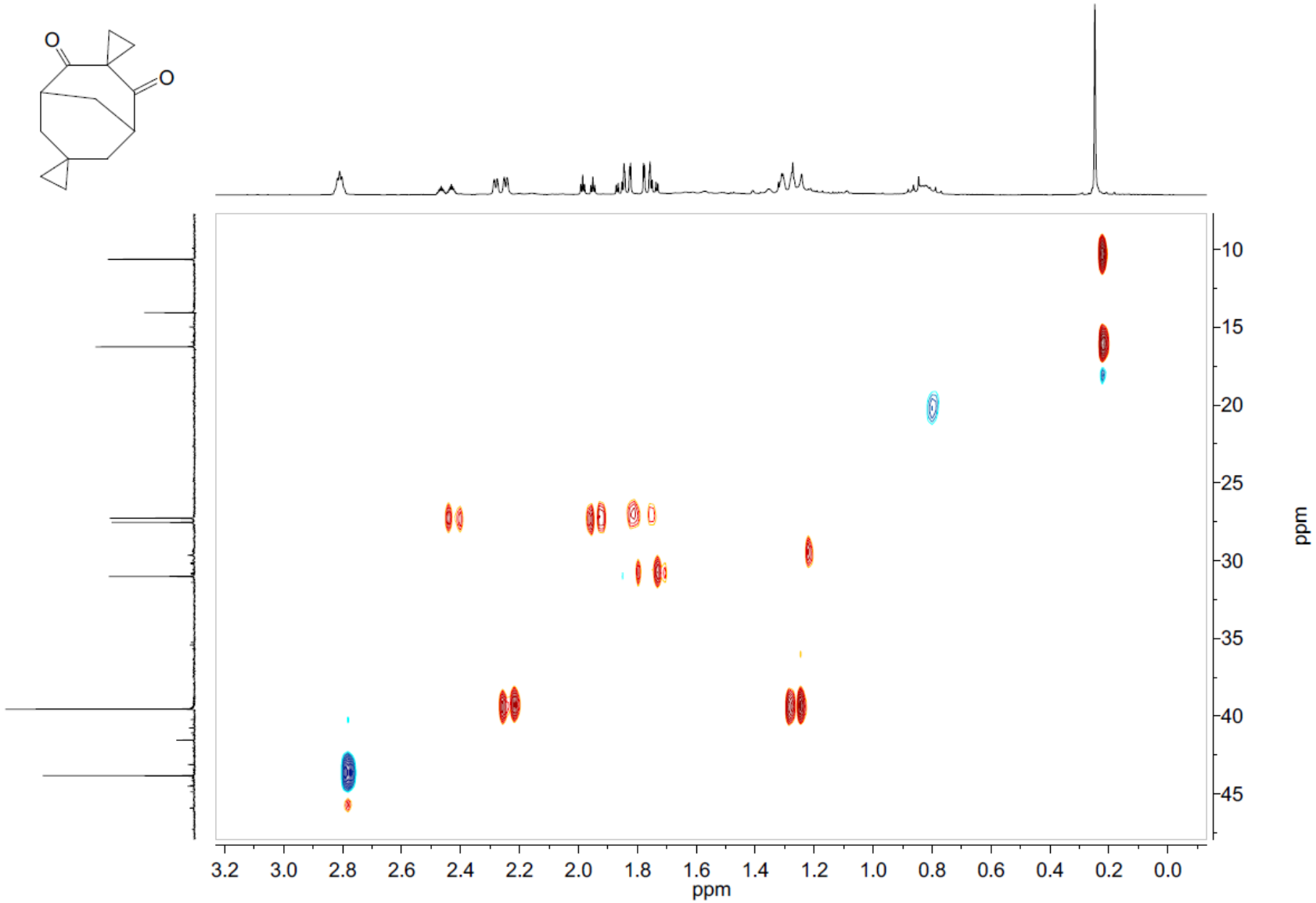
COSY spectrum of compound 6a



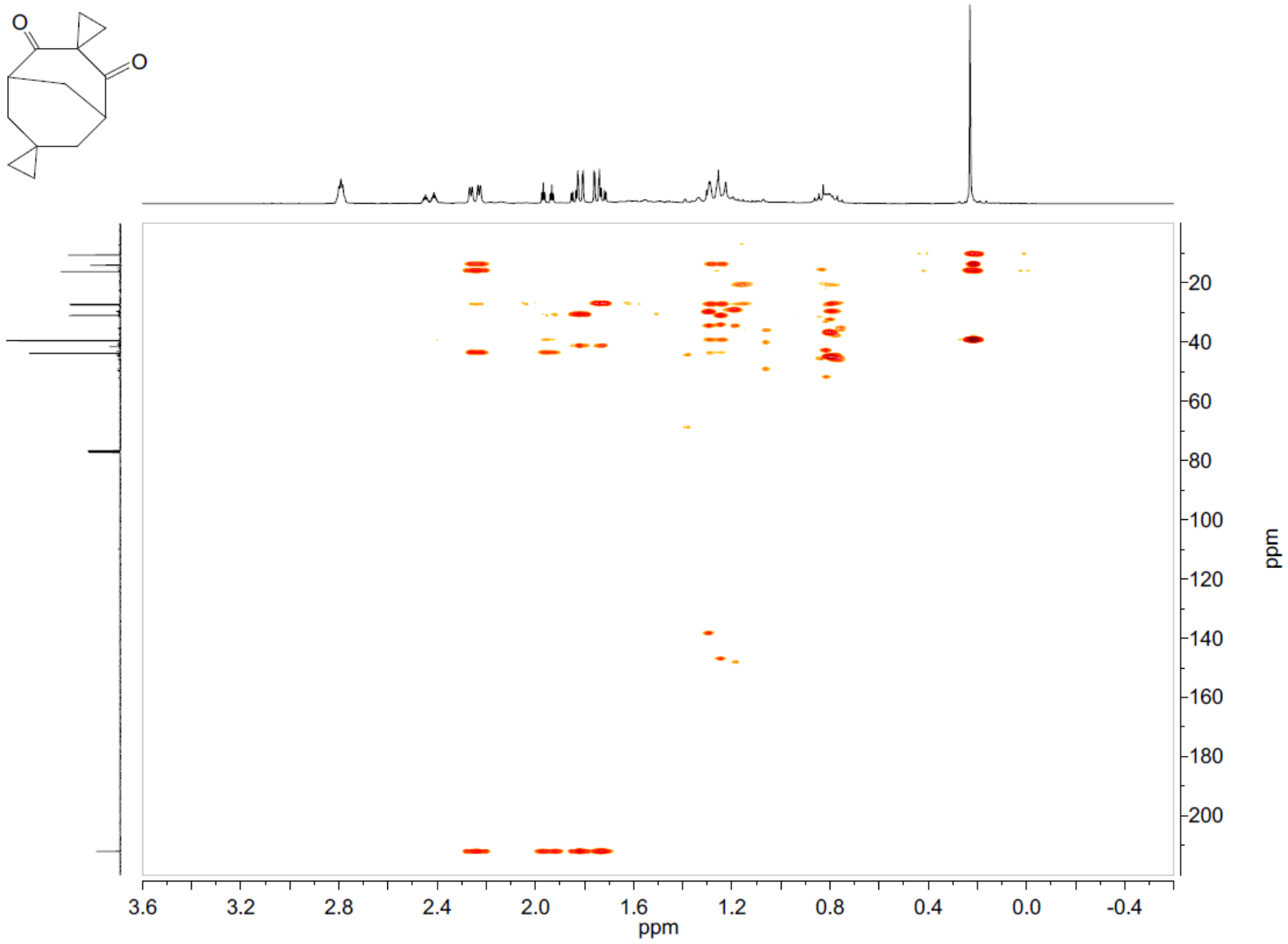
^{13}C NMR (101 MHz, $CDCl_3$) spectrum of compound 6a



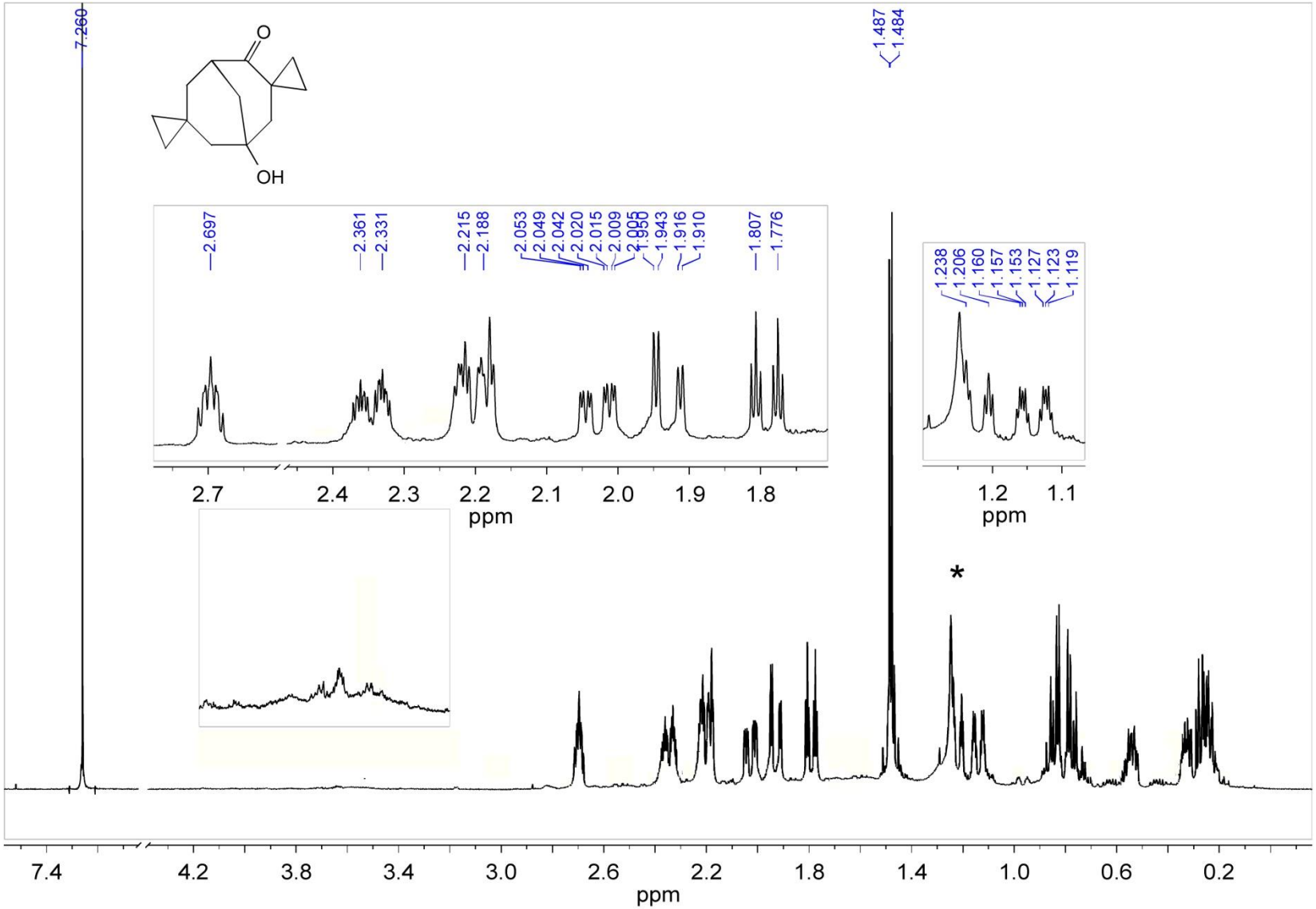
HSQC spectrum of compound 6a



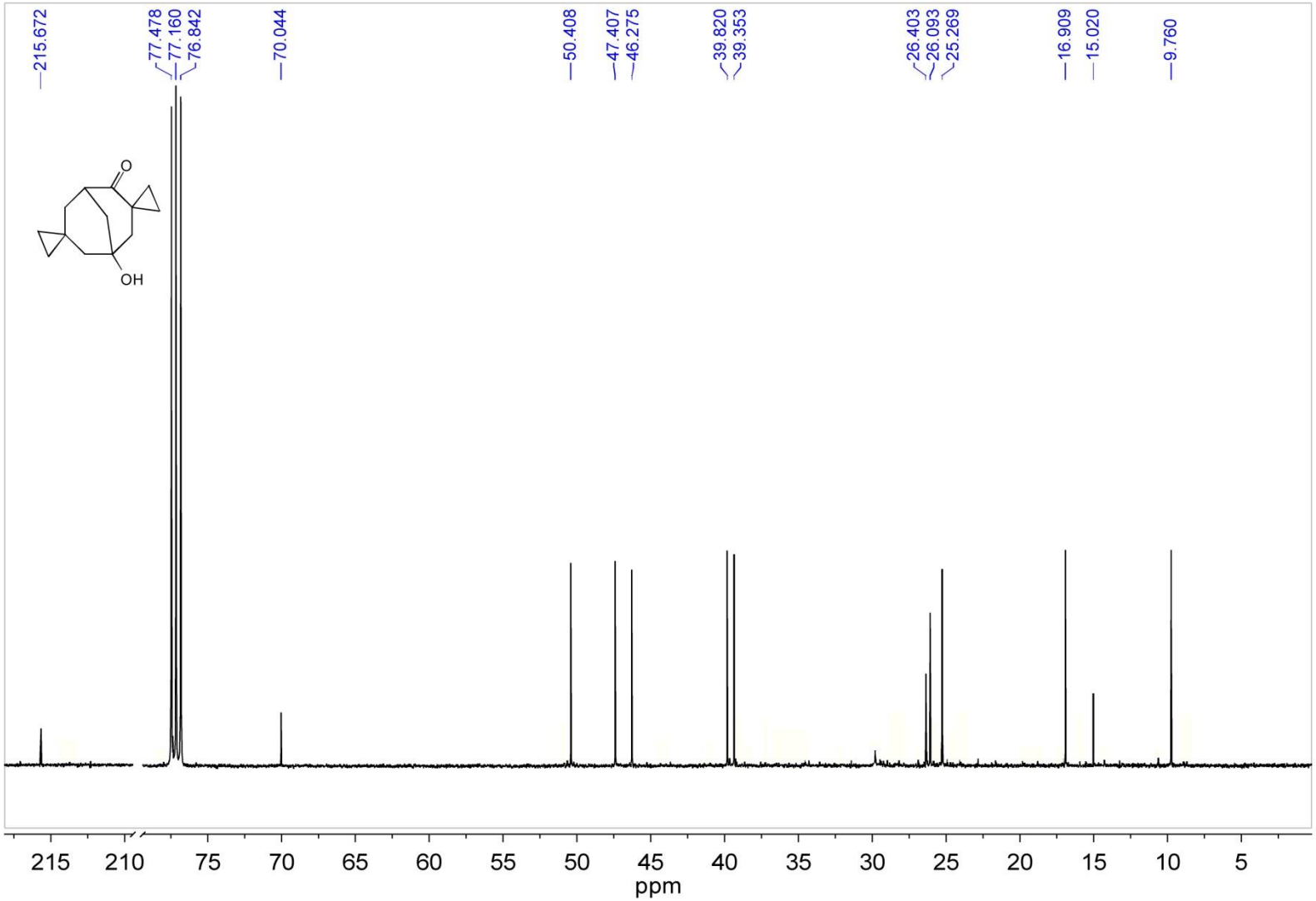
HMBC spectrum of compound 6a



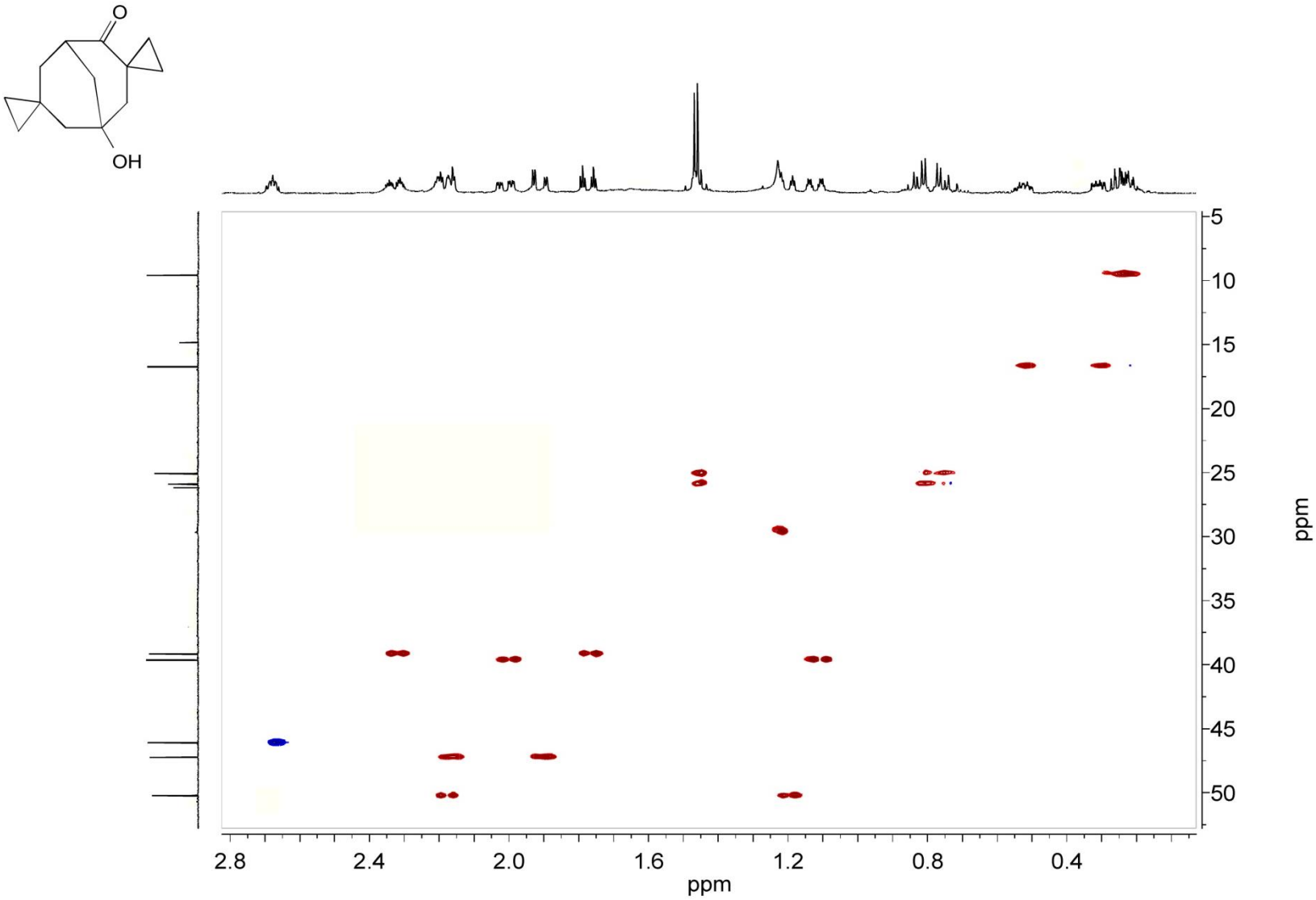
^{1}H NMR (400 MHz, $CDCl_3$) spectrum of compound 7



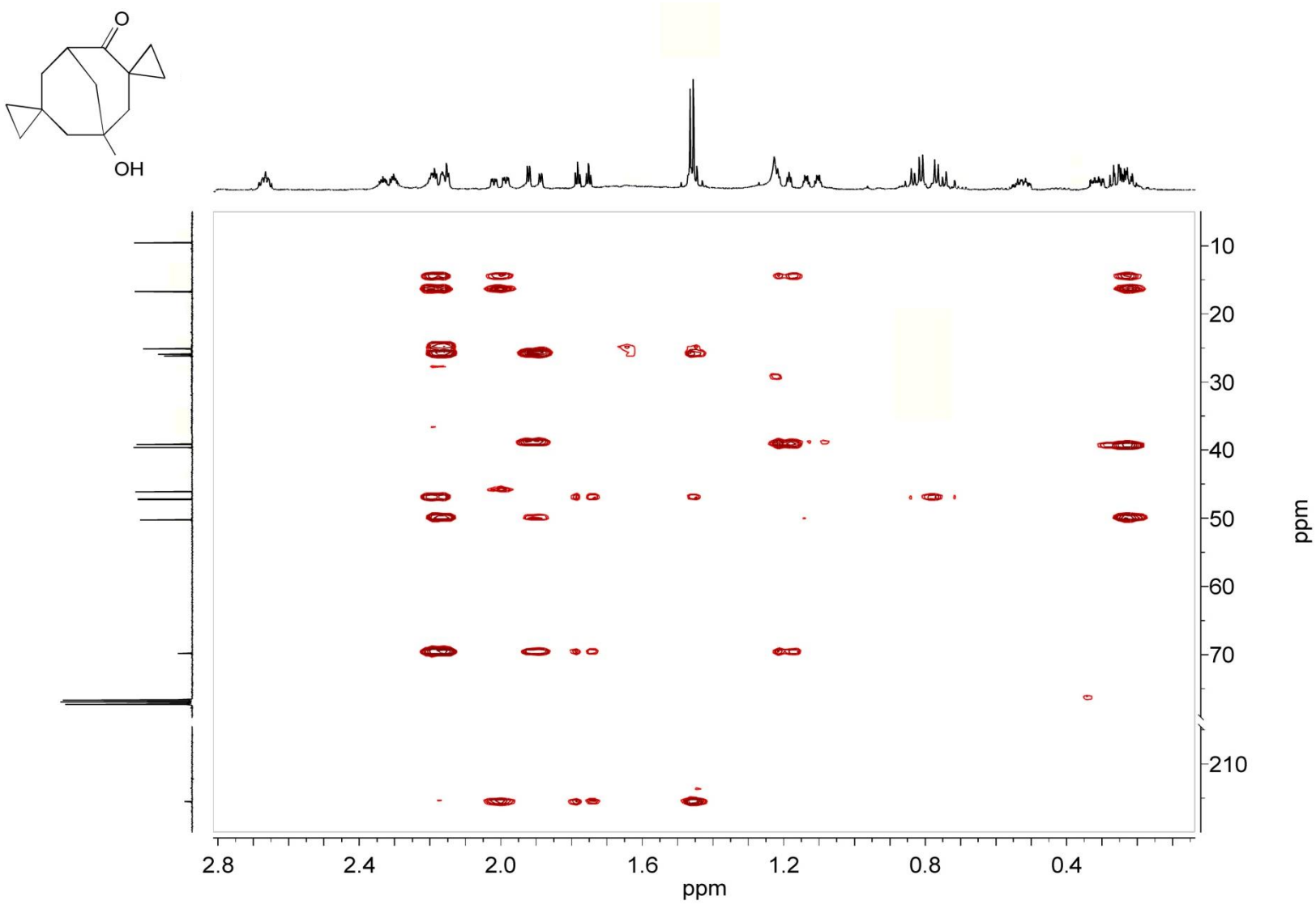
^{13}C NMR (101 MHz, $CDCl_3$) spectrum of compound 7



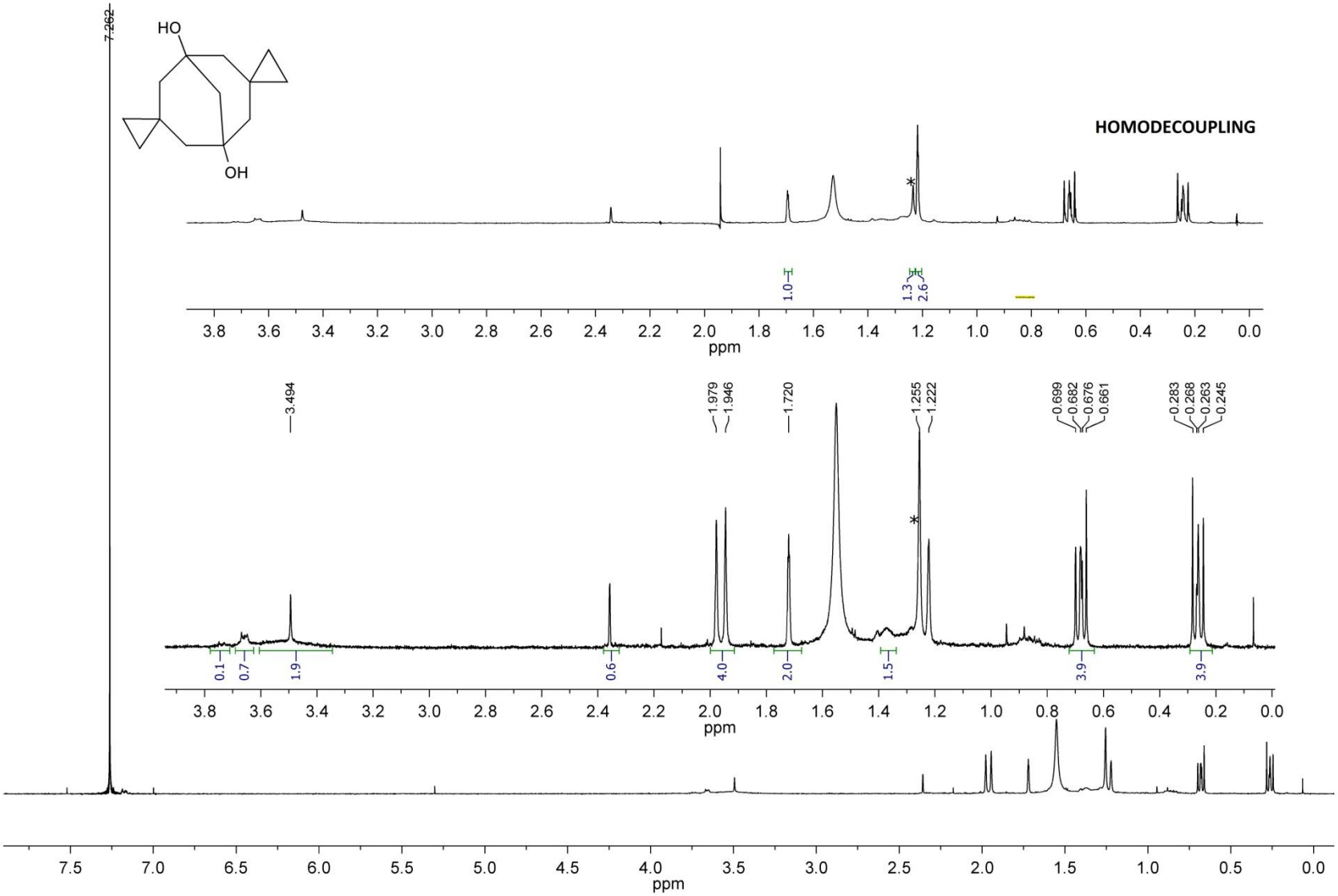
HSQC spectrum of compound 7



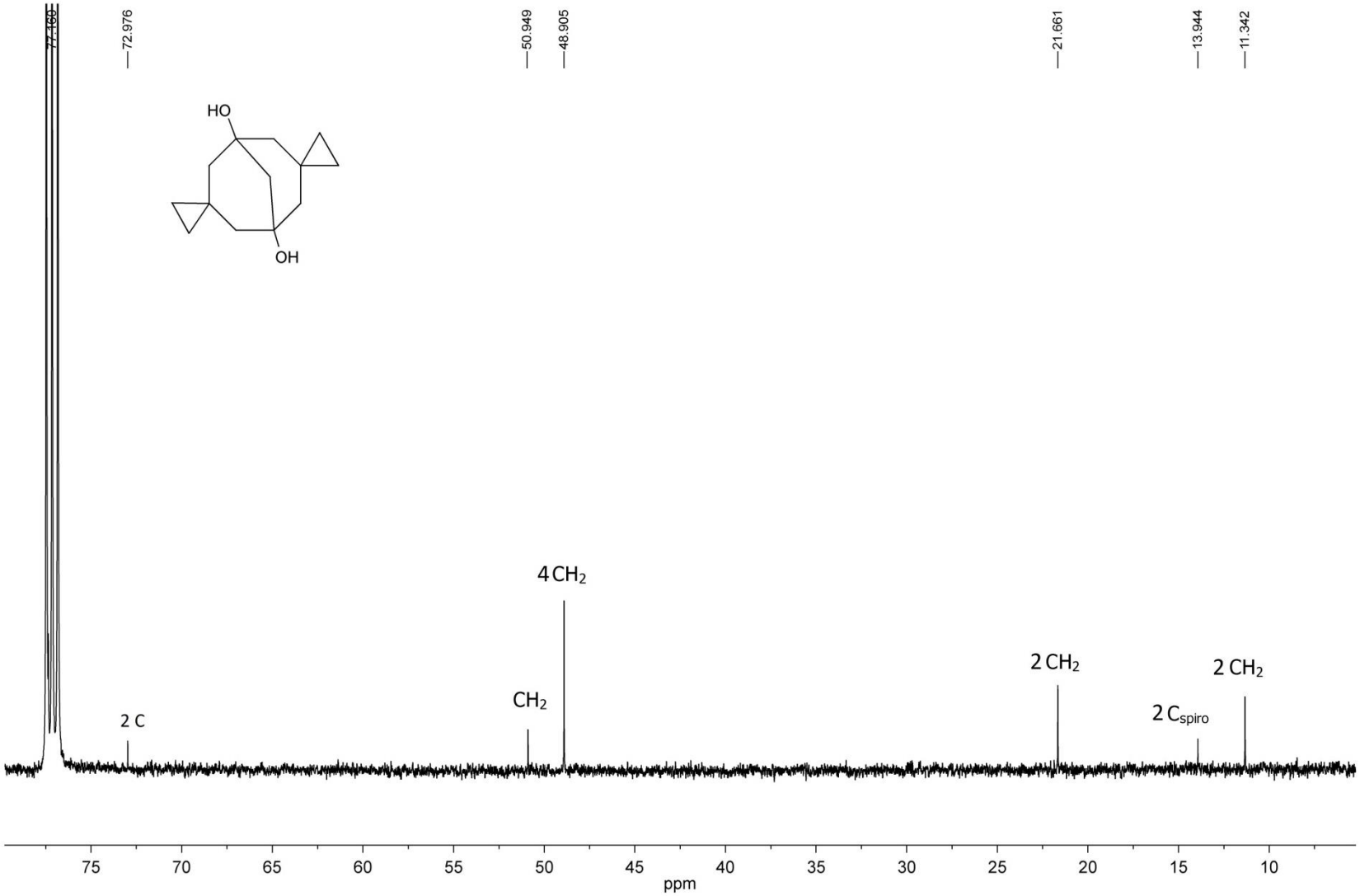
HMBC spectrum of compound 7



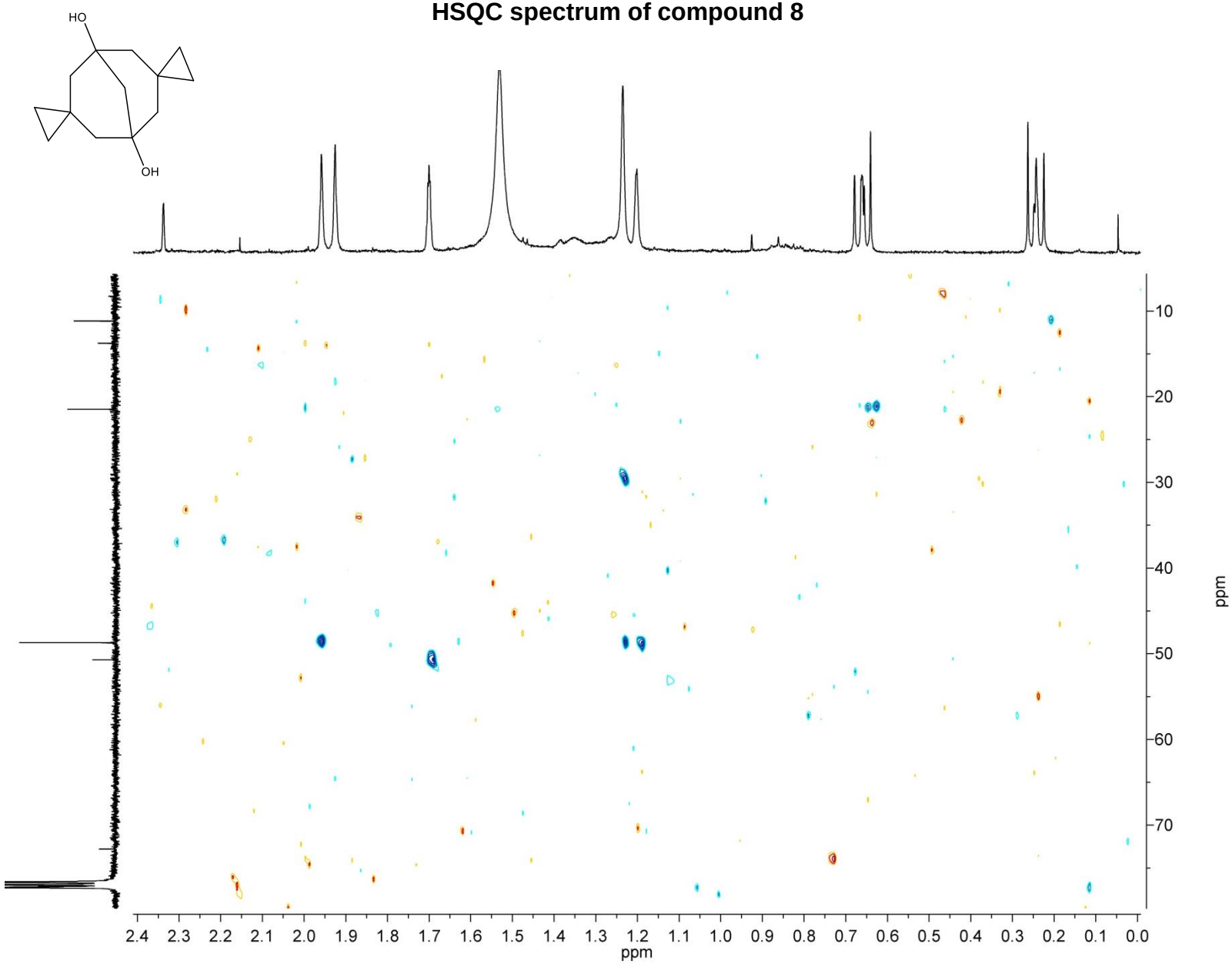
^{1}H NMR (400 MHz, $CDCl_3$) and homodecoupling spectra of compound 8



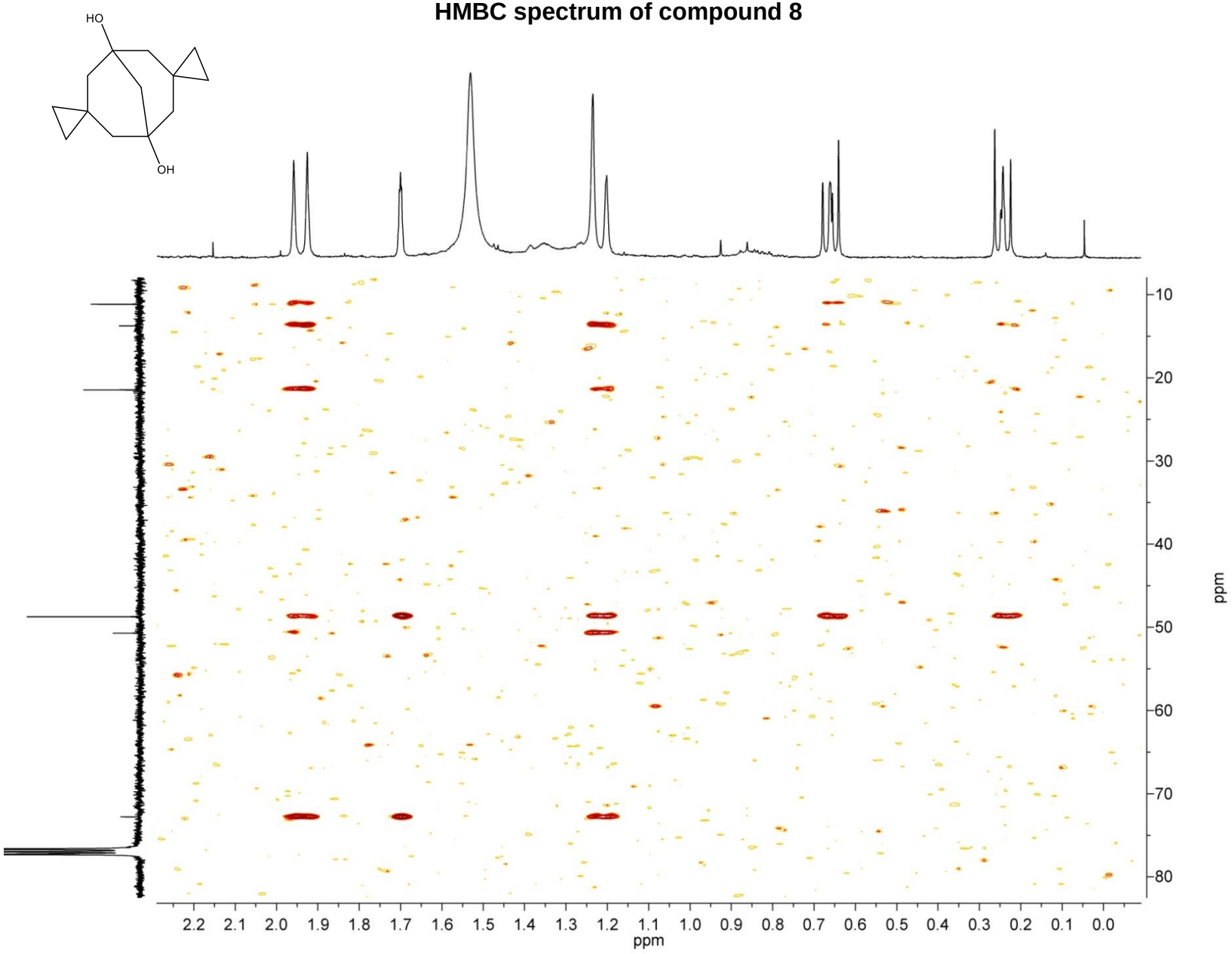
^{13}C NMR (101 MHz, $CDCl_3$) spectrum of compound 8



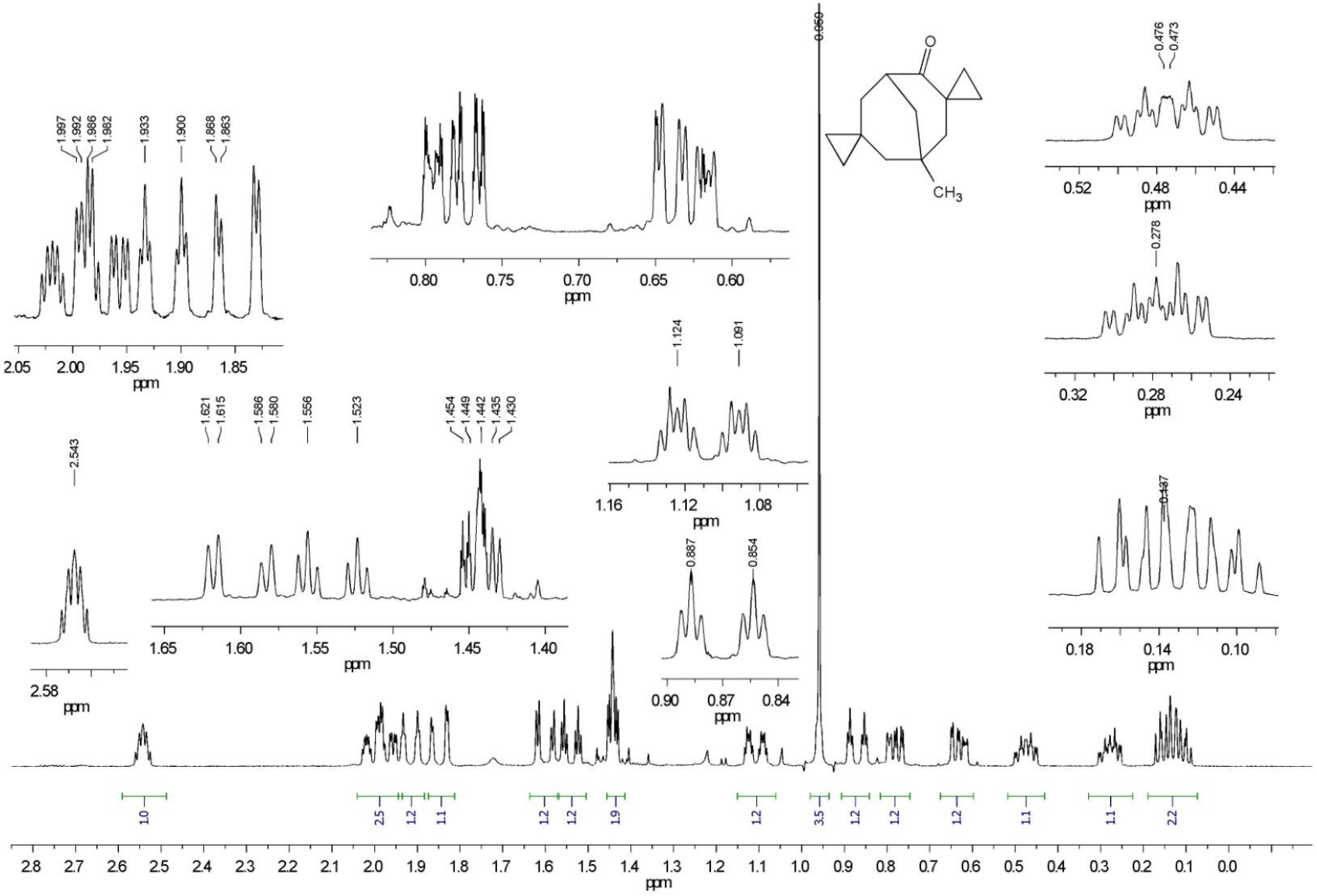
HSQC spectrum of compound 8



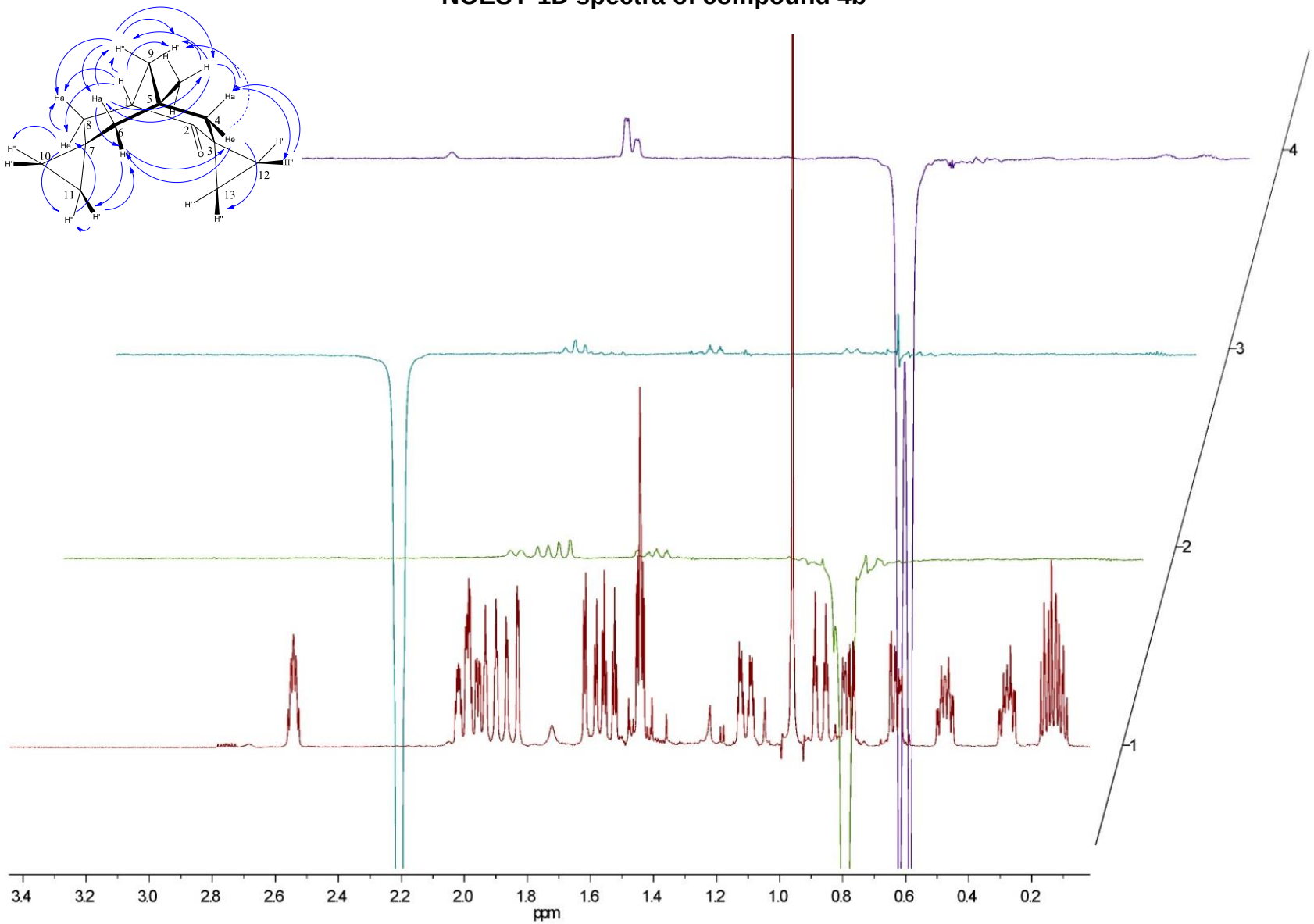
HMBC spectrum of compound 8



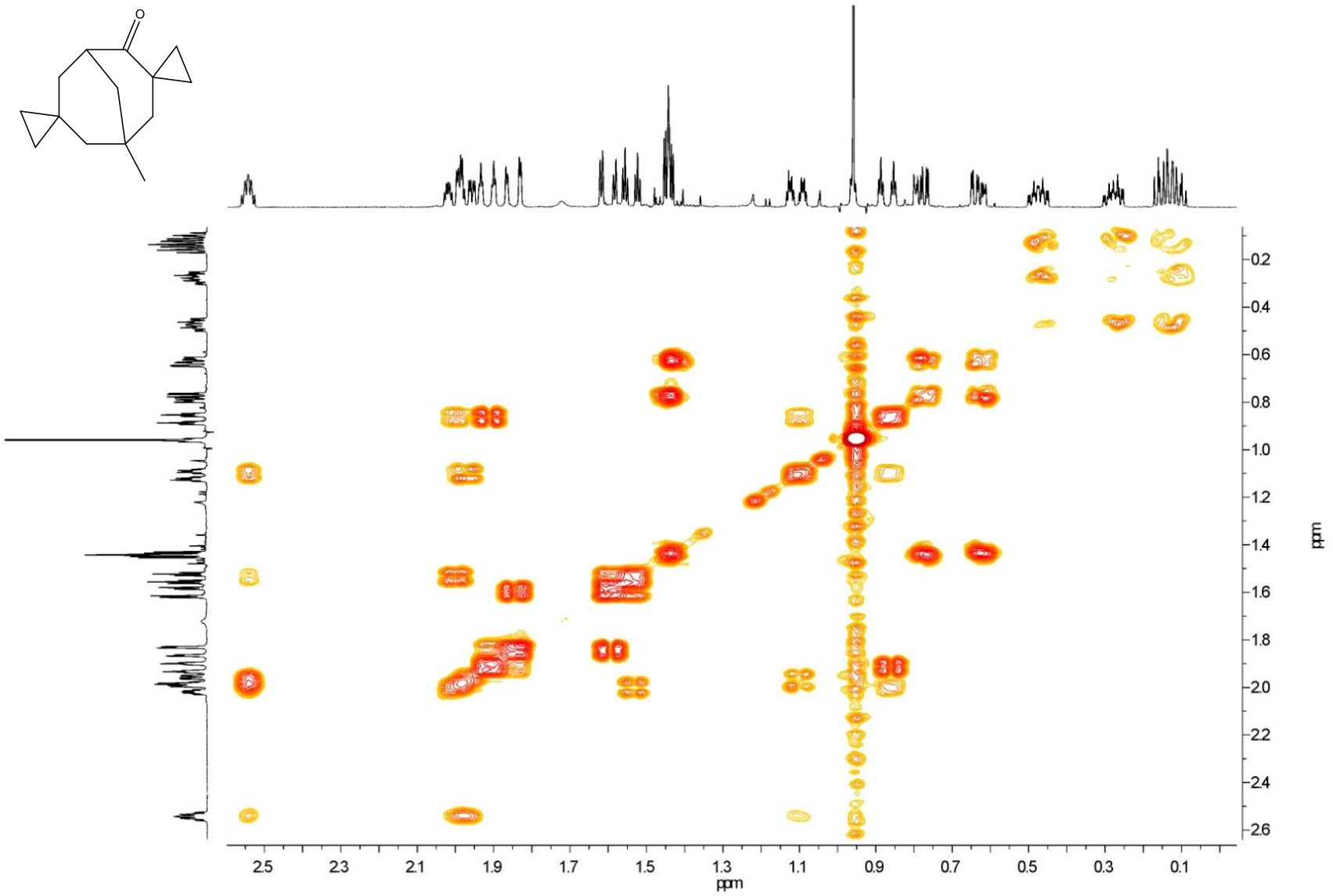
^{1}H NMR (400 MHz, $CDCl_3$) spectrum of compound 4b



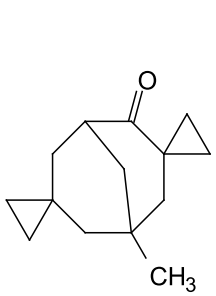
NOESY-1D spectra of compound 4b

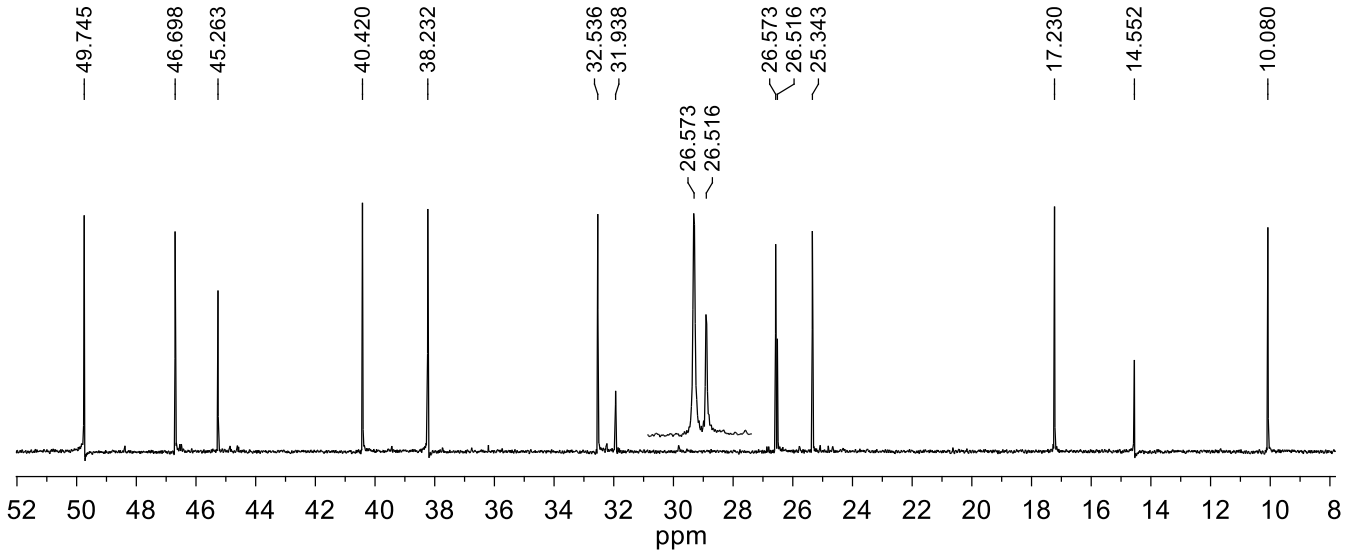


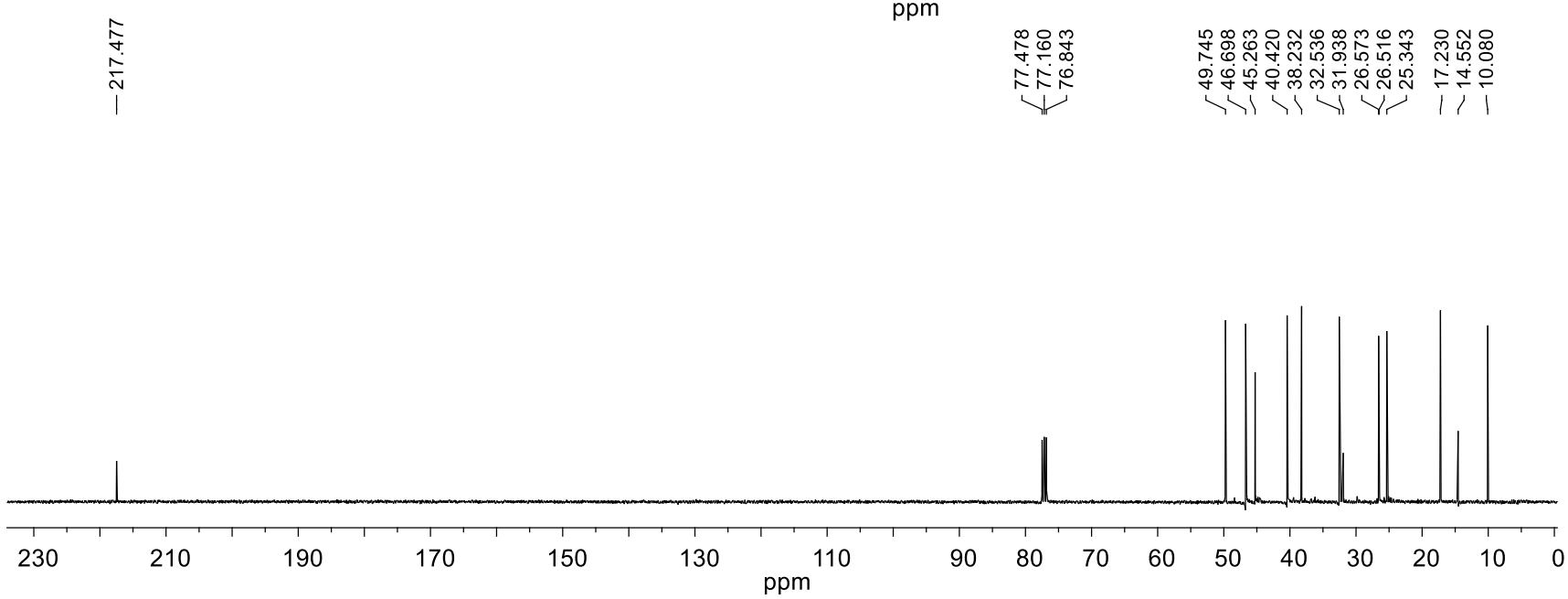
gCOSY spectrum of compound 4b



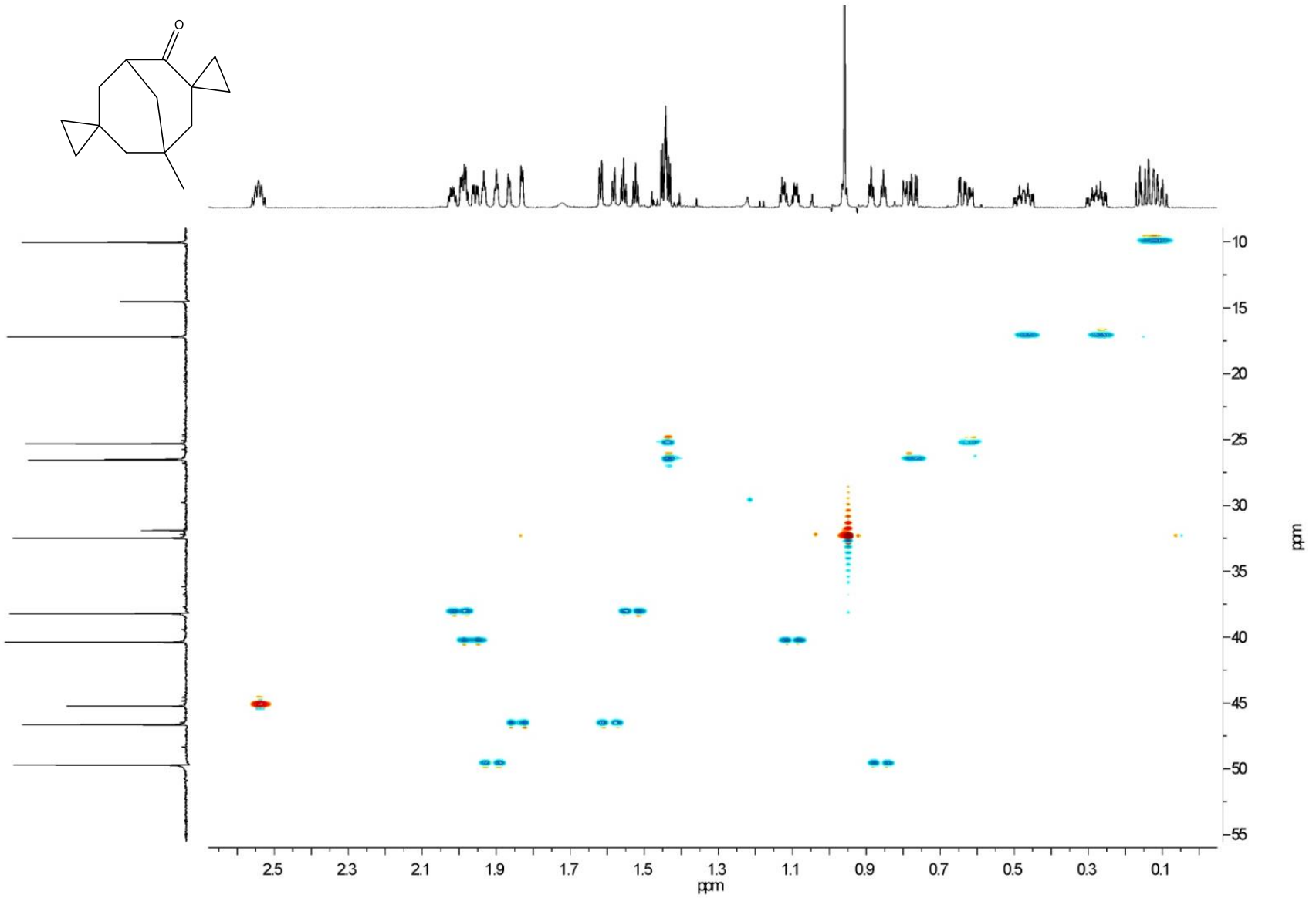
^{13}C NMR (101 MHz, $CDCl_3$) spectrum of compound 4b



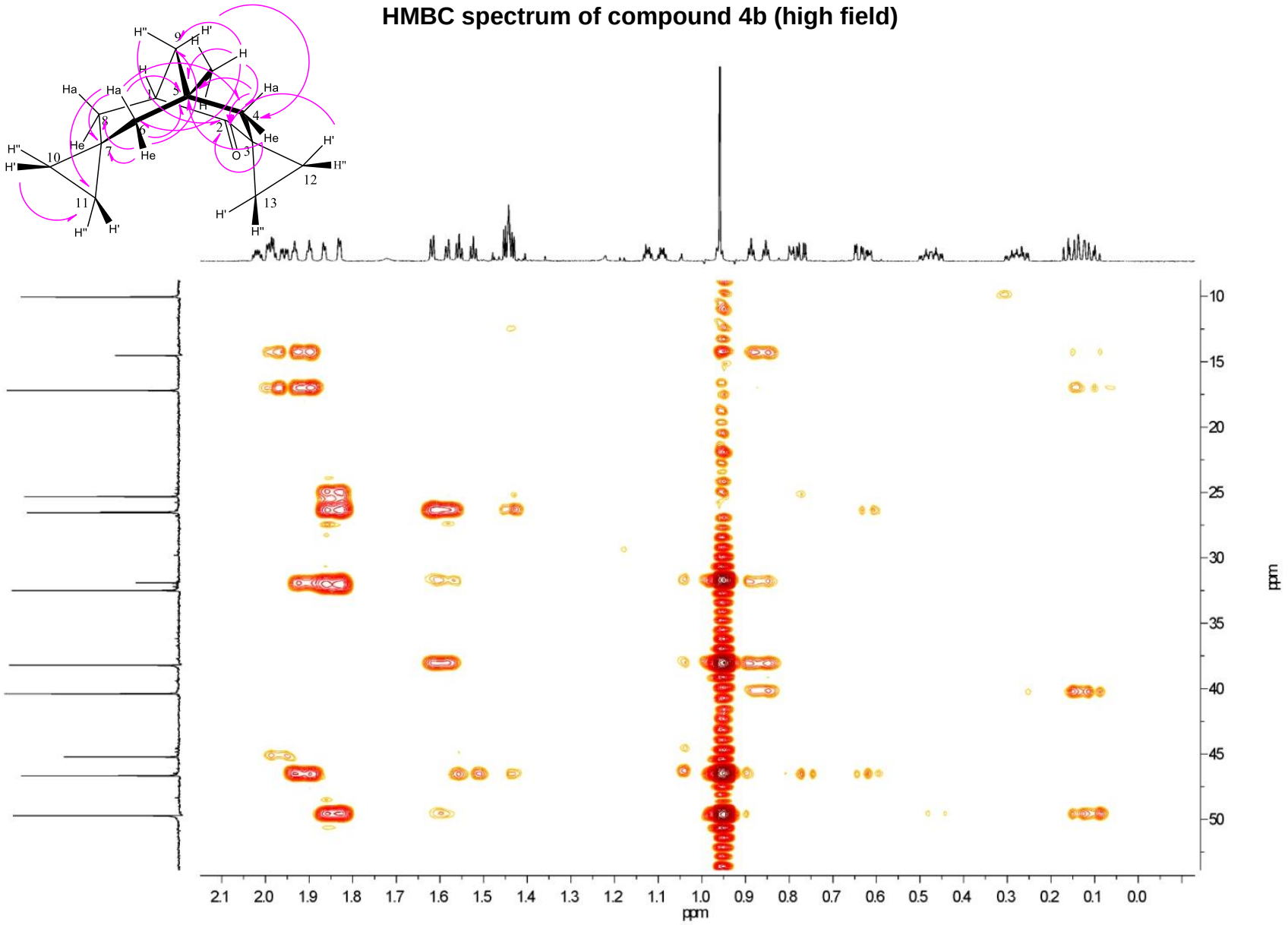




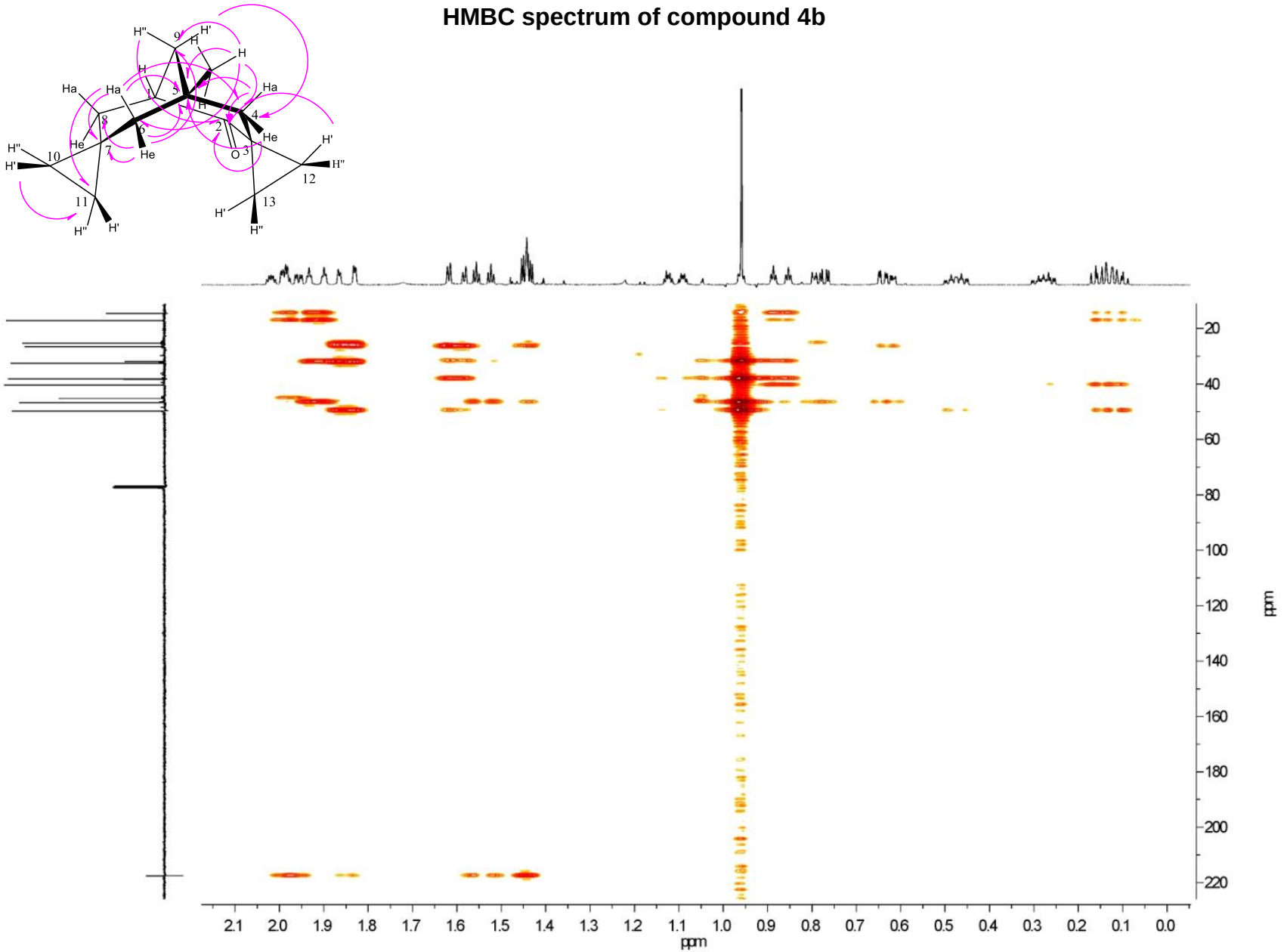
HSQC spectrum of compound 4b



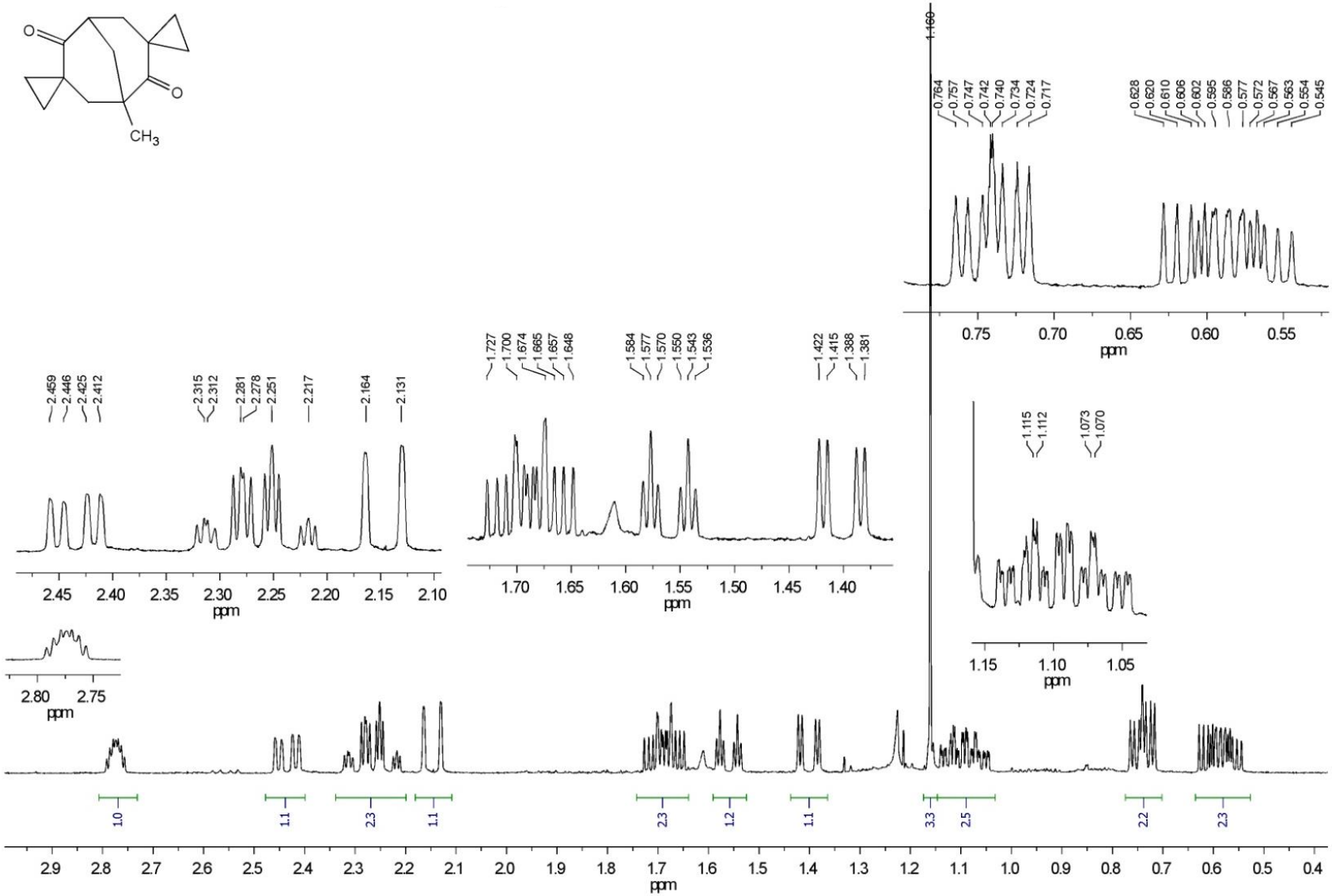
HMBC spectrum of compound 4b (high field)



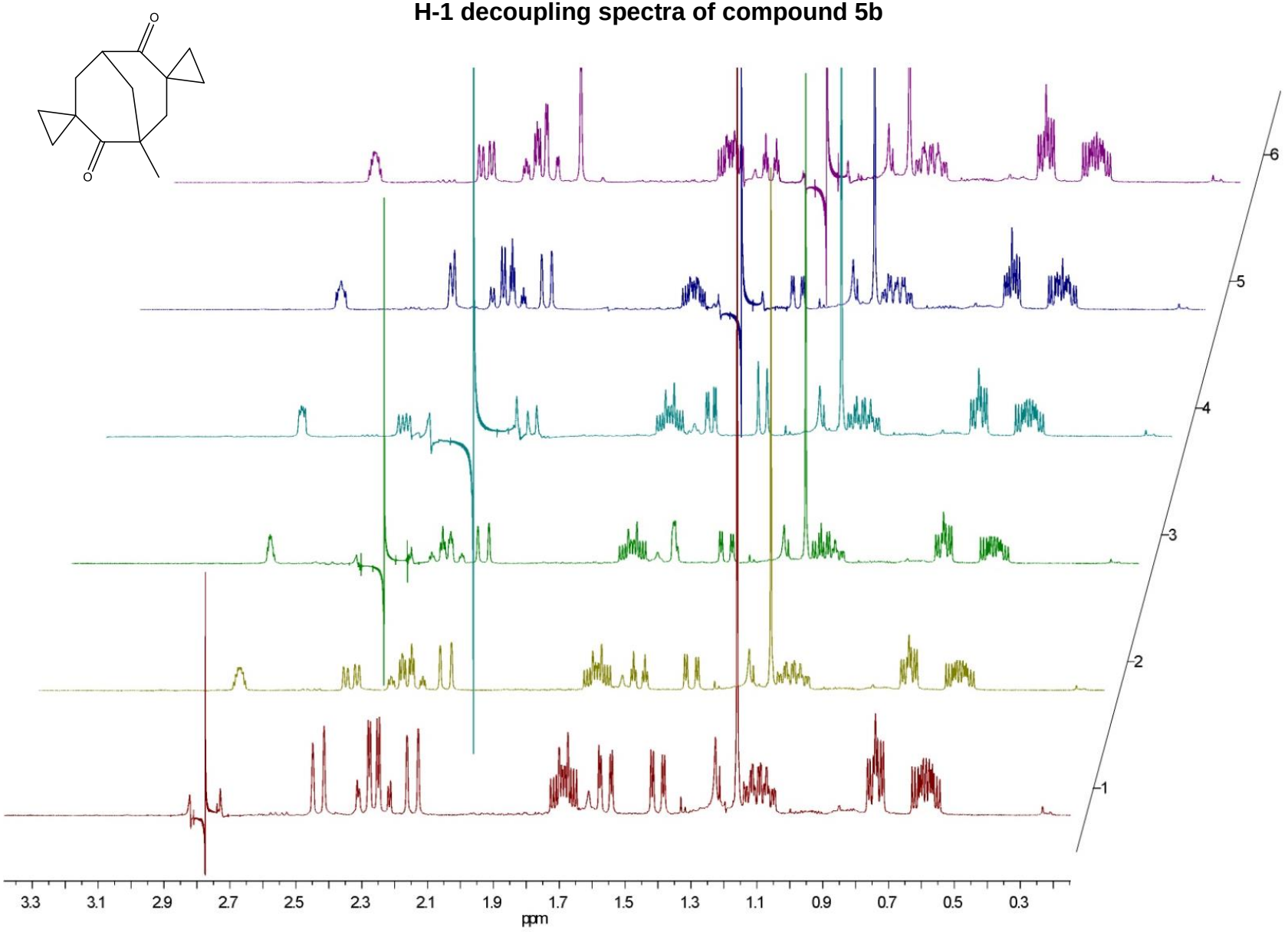
HMBC spectrum of compound 4b



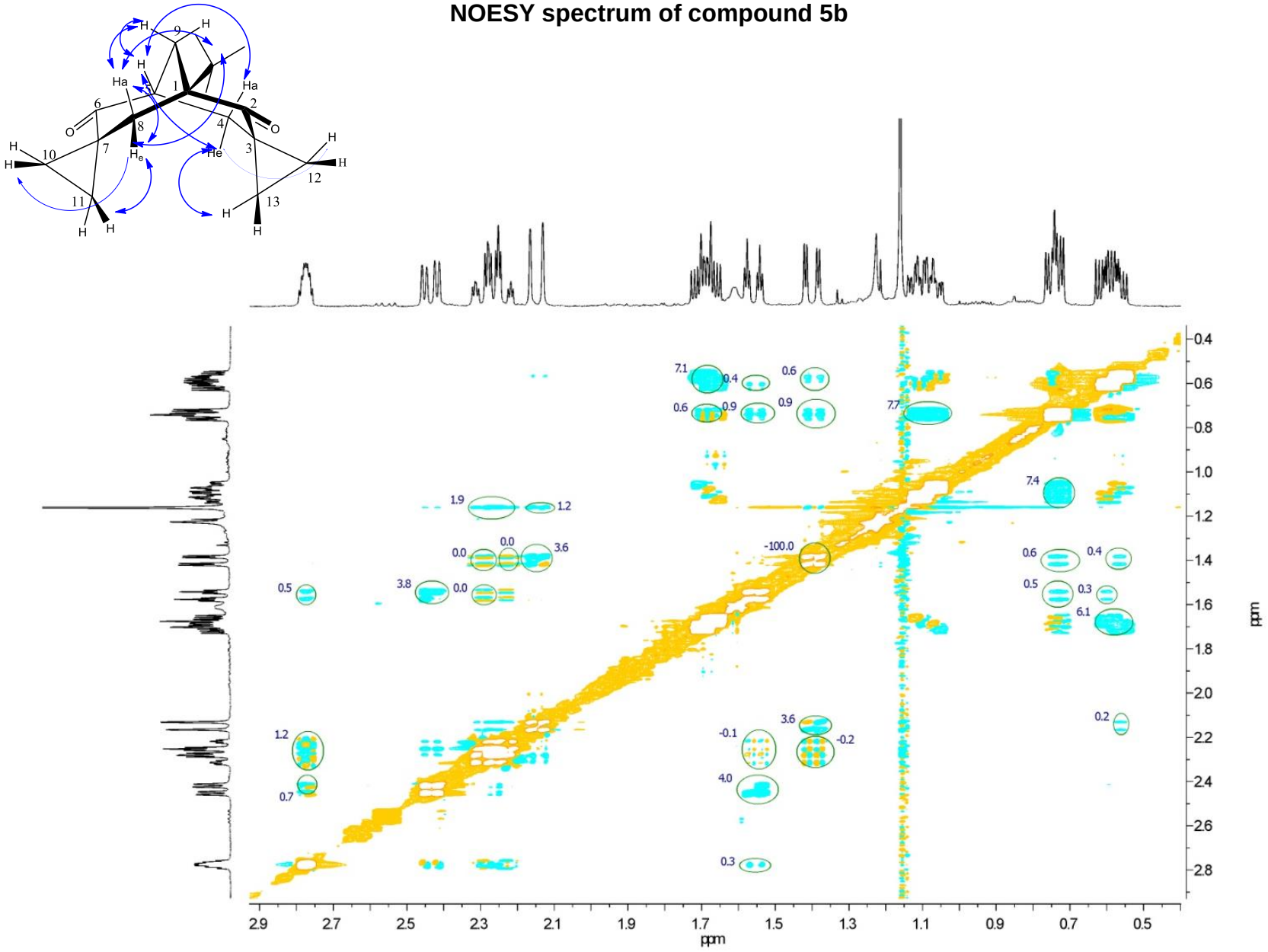
^{1}H NMR (400 MHz, $CDCl_3$) spectrum of compound 5b



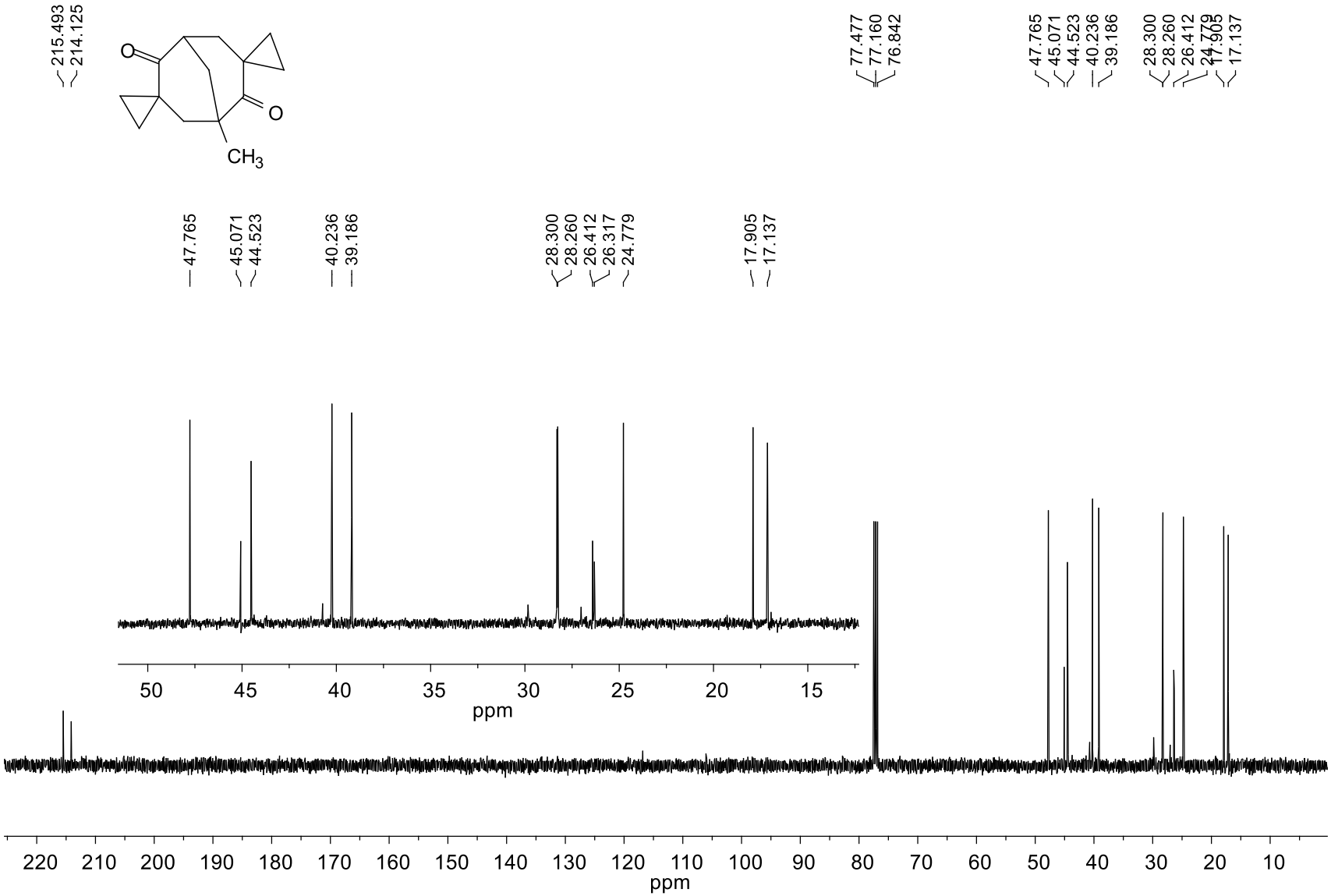
H-1 decoupling spectra of compound 5b



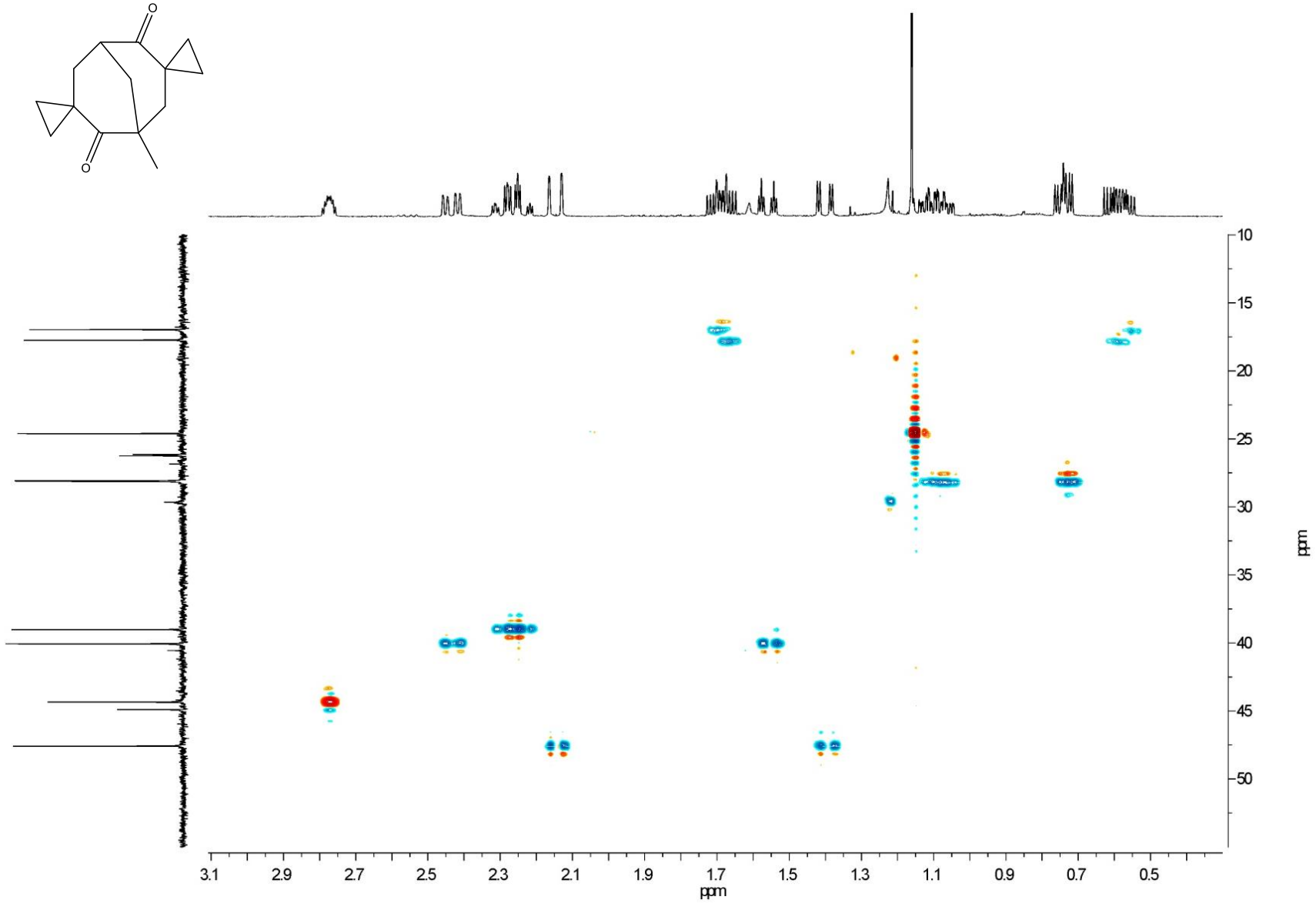
NOESY spectrum of compound 5b



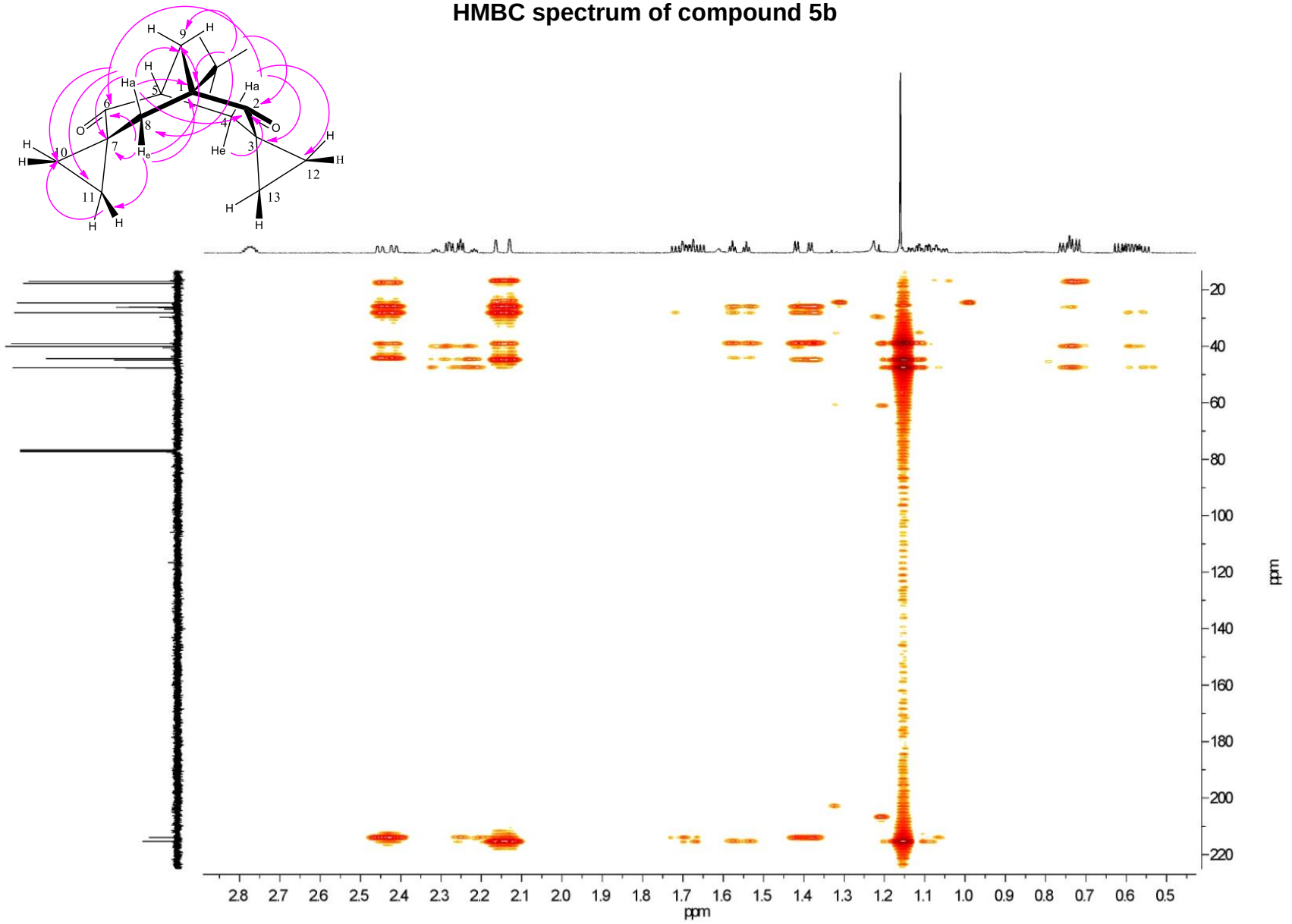
^{13}C NMR (101 MHz, $CDCl_3$) spectrum of compound 5b



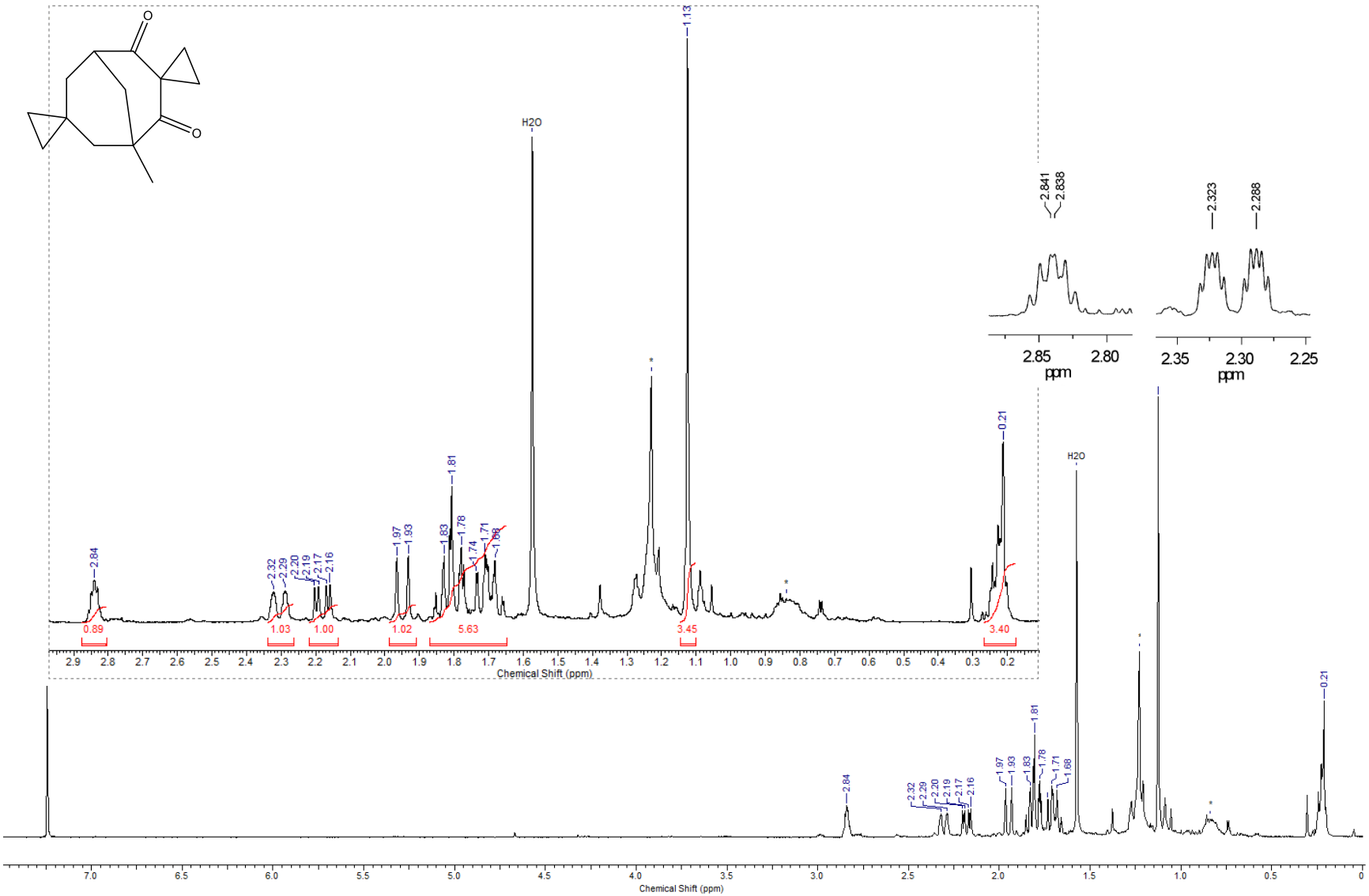
HSQC spectrum of compound 5b



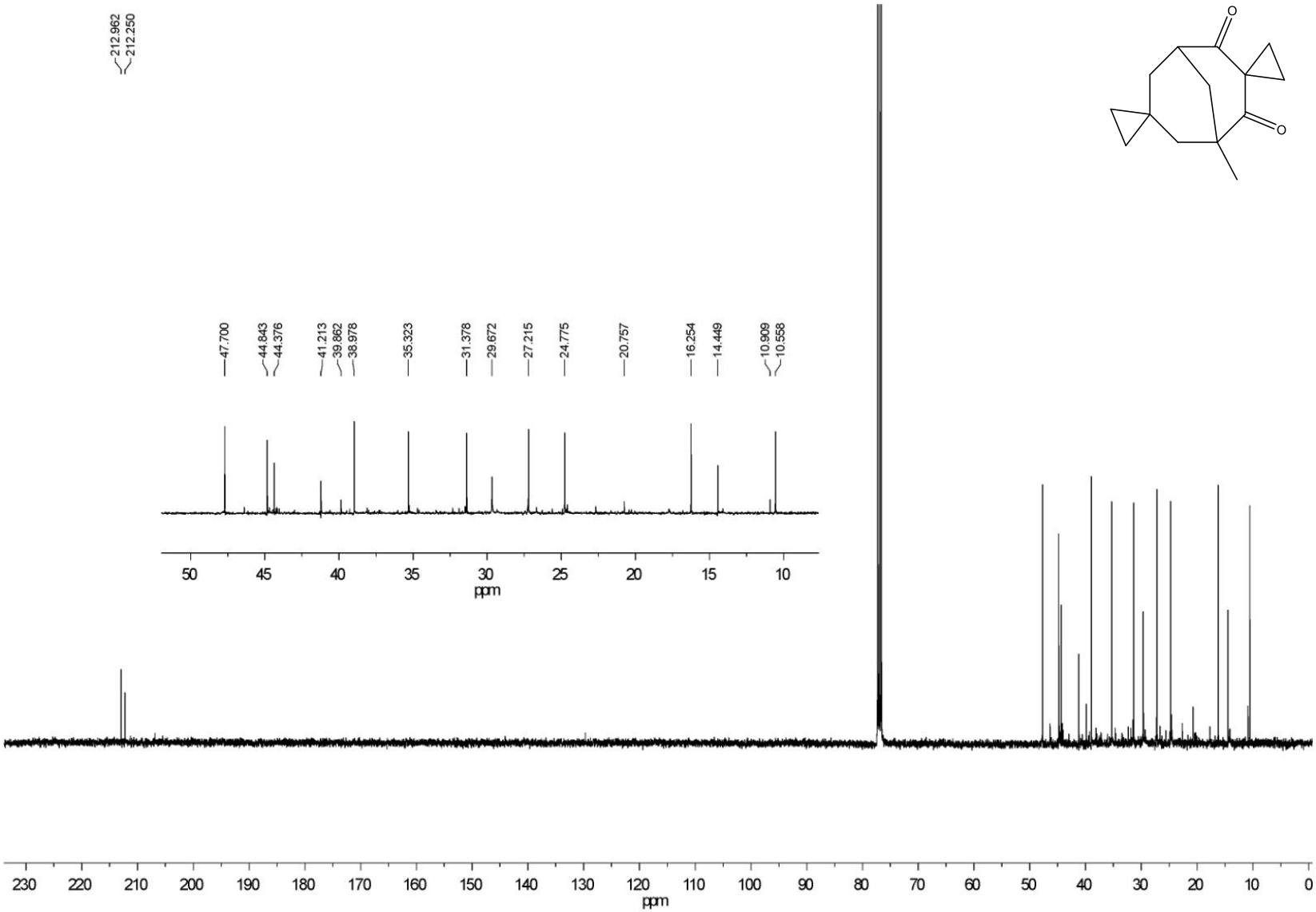
HMBC spectrum of compound 5b



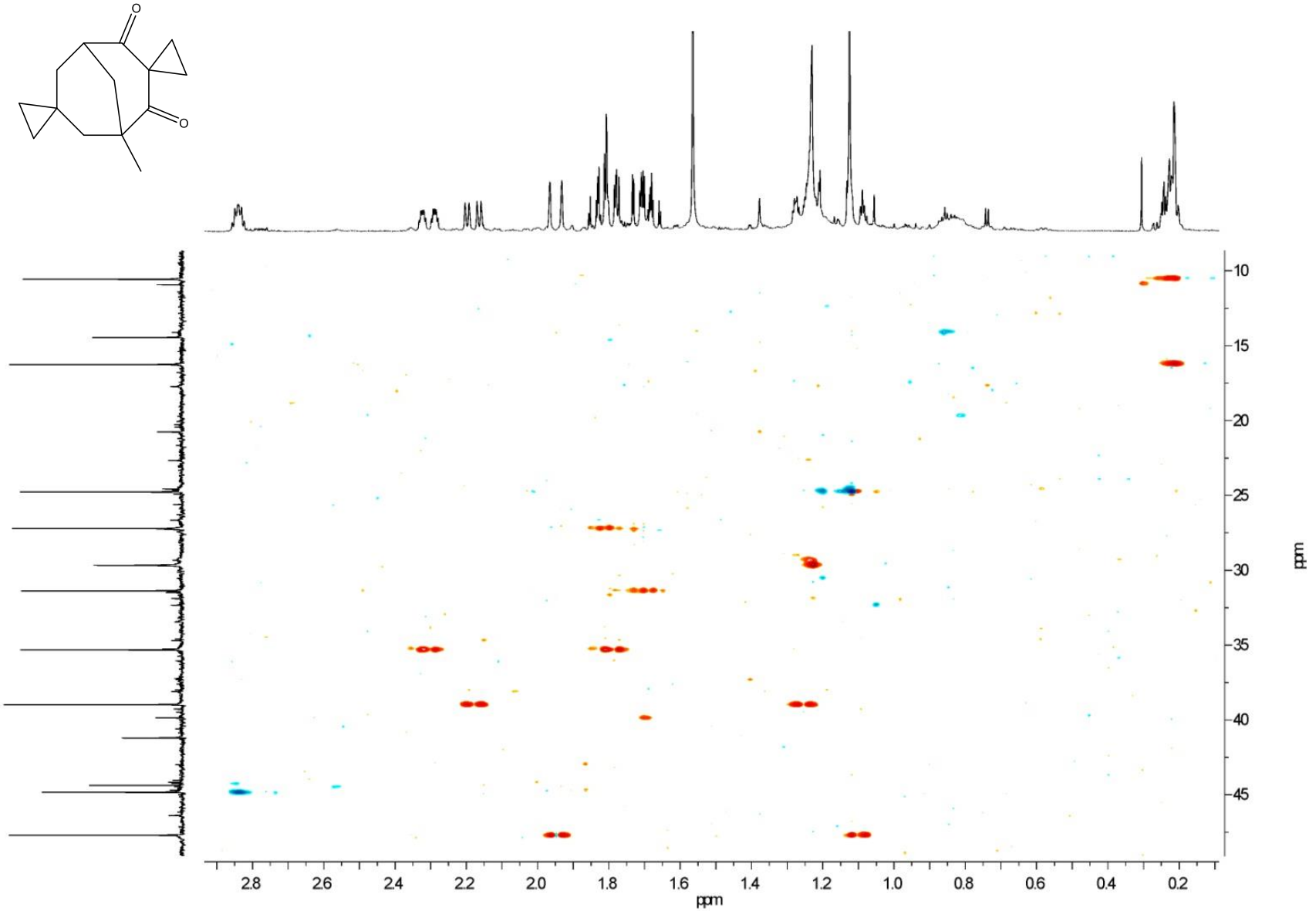
^{1}H NMR (400 MHz, $CDCl_3$) spectrum of compound 6b



^{13}C NMR (101 MHz, $CDCl_3$) spectrum of compound 6b



HSQC spectrum of compound 6b



HMBC spectrum of compound 6b