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Supporting Information

Bridgehead epoxide *iso*-euphoranin E from β-caryophyllene oxide via sequential cationic formation and scission of [4.3.2]propellane

Georgijs Stakanovs, Dace Rasina, Sergey Belyakov, Artis Kinens, Aigars Jirgensons**

Corresponding Authors

Georgijs Stakanovs – *Latvian Institute of Organic Synthesis, Aizkraukles Str. 21, LV-1006, Riga, Latvia*; e-mail: georgijs.stakanovs@osi.lv

Aigars Jirgensons – *Latvian Institute of Organic Synthesis, Aizkraukles Str. 21, LV-1006, Riga, Latvia*; e-mail: aigars@osi.lv

CONTENTS

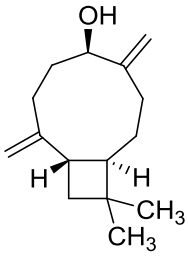
General information, synthetic procedures and characterization

General. Melting points were detected with an OptiMelt MPA100 melting point apparatus, with a heating rate of 3 °C/min. Specific optical rotations were measured at specified temperature on a Rudolph Research Analytical Autopol VI polarimeter, cell length 100 mm, using the solvent and concentration stated, at 589 nm. Infrared spectra (IR) were obtained using a Shimadzu IR Prestige-21 Fourier-transform IR spectrometer. ^{1}H, ^{13}C, and 2D NMR spectra were recorded on 400 MHz Bruker spectrometer using the residual solvent peak as an internal reference. High-resolution molecular masses (HRMS) were determined on a Waters Synapt G2-Si hybrid quadrupole time-of-flight (TOF) mass spectrometer equipped with an electron spray ion source (ESI). Gas chromatographic (GC) analysis was performed on Agilent Technologies gas chromatographer with triple-axis detector, heating range 40–280 ^{o}C, column 30 m x 0.25 mm, 0.25 μm, 7 inch cage. Reagents were purchased from commercial sources and used as received. Commercial (–)-β-caryophyllene oxide (CAS 1139-30-6, 95%) was obtained from Sigma-Aldrich. Flash chromatography was carried out using Kieselgel (35−70 μm) silica gel. Thin layer chromatography was performed on TLC silica gel 60 F254 aluminium sheets (Merck) and was visualized by staining with $KMnO_4$ or cerium ammonium molybdate stain systems.

Crystal Structure Analysis. A suitable crystal was selected, and the X-ray crystal data were acquired on an XtaLAB Synergy-S, Dualflex, HyPix diffractometer (Rigaku) with Cu Kα radiation (λ = 1.54184 Å). The crystal was kept at 150 K (for compounds **13**, **10**, **7**, **11**) or 160 K (for compound **2**) during data collection. The CrysAlis PRO 1.171.40.35a software package was used for intensity data acquisition. Crystal structures were solved and refined by the SHELXT 2014/4 program. Non-hydrogen atoms were refined anisotropically with the full least-squares approximation. Hydrogen-atom positions were calculated geometrically and refined using the riding-model approximation. The absolute configuration of the compounds has been determined both by the anomalous dispersion method and known chiral centers from the parent compound. Single-crystal X-Ray crystallography data, ORTEP drawings and the refinement model description are

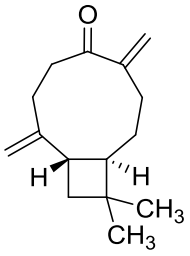
available in SI. Crystallographic data for the structures have been deposited in the Cambridge Crystallographic Data Center with deposition numbers 2346928–2346932.

(1*S*,5*R*,9*R*)-10,10-Dimethyl-2,6-dimethylenebicyclo[7.2.0]undecan-5-ol (6)



Synthesis and full characterization can be found in previous publications (*Org. Biomol. Chem.* **2022**, *20*, 2455 and *J. Nat. Prod.* **2023**, *86*, 2368). Diisopropylamine (3.85 ml; 27.5 mmol) was dissolved in anhydrous tetrahydrofuran (THF, 70 mL) and the solution was cooled to 0 ^{o}C. A solution (2.0 M) of *n*BuLi in hexanes (13.7 ml, 27.5 mmol) was added dropwise to the mixture. The reaction mixture was stirred for 15 min at 0 ^{o}C and a solution of (–)-β-caryophyllene oxide (5.50 g; 25.0 mmol) in anhydrous THF (25 mL) was added dropwise. Reaction mixture was refluxed for 4 h. Then it was allowed to cool down to rt and quenched with saturated aqueous NH_4Cl solution (100 mL). THF was evaporated under reduced pressure, and the mixture was extracted with Et_2O (3×100 mL). The organic layer was washed with brine, dried with anhydrous Na_2SO_4, filtered, and concentrated under reduced pressure. The residue was purified by column chromatography using EtOAc-hexane (1:4) elution to obtain the title product (5.07 g, 92%) as a light yellow oil. $[\boldsymbol{\alpha}]_{\boldsymbol{D}}^{\boldsymbol{20}}$ +10 (*c* 0.93, $CHCl_3$). **^{1}H NMR** (400 MHz, $CDCl_3$) δ (ppm): 5.04 (s, 1H), 4.95 (s, 1H), 4.78 (d, *J* = 1.4 Hz, 1H), 4.76 (d, *J* = 1.4 Hz, 1H), 4.09 (ddd, *J* = 8.9, 3.9, 1.0 Hz, 1H), 2.57 – 2.47 (m, 1H), 2.31 (ddd, *J* = 18.2, 9.5, 5.7 Hz, 2H), 2.09 – 1.89 (m, 2H), 1.89 – 1.68 (m, 4H), 1.68 – 1.49 (m, 4H), 0.98 (s, 6H). **^{13}C NMR** (101 MHz, $CDCl_3$) δ (ppm): 152.6, 151.4, 113.6, 109.3, 75.3, 54.4, 44.0, 37.1, 33.6, 33.0, 32.7, 32.6, 30.8, 30.2, 22.1. **HRMS** *m/z*: 221.1908 $[M + H]^+$ (calcd for $C_{15}H_{25}O$ 221.1905).

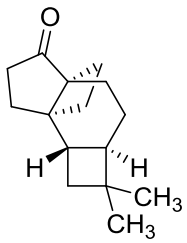
(1*S*,9*R*)-10,10-Dimethyl-2,6-dimethylenebicyclo[7.2.0]undecan-5-one (8)



To the solution of allylic alcohol **6** (3.79 g; 17.2 mmol) in dichloromethane (DCM, 40 mL), TEMPO (403 mg; 2.58 mmol) and $PhI(OAc)_2$ (6.37 g; 19.8 mmol) were subsequently added. Reaction mixture was stirred for 6 h at rt and then was washed by saturated $NaHCO_3$ aqueous solution and with 20% $Na_2S_2O_3$ aqueous solution. Organic layer was dried with anhydrous Na_2SO_4, filtered and

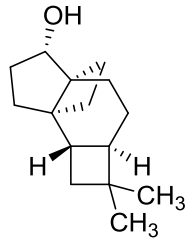
concentrated under reduced pressure. The residue was purified by column chromatography using hexanes/Et_2O (4:1) elution to obtain title product as a colorless oil (2.85 g, 76%). $[\boldsymbol{\alpha}]_{\boldsymbol{D}}^{\boldsymbol{20}}$ +20 (*c* 0.98, $CHCl_3$). **^{1}H NMR** (400 MHz, $CDCl_3$) δ (ppm): 5.59 (s, 1H), 5.53 (d, *J* = 1.1 Hz, 1H), 4.96 (d, *J* = 1.2 Hz, 1H), 4.90 (s, 1H), 2.82 (ddd, *J* = 11.6, 6.0, 4.7 Hz, 1H), 2.67 (td, *J* = 11.3, 4.9 Hz, 1H), 2.59 – 2.49 (m, 1H), 2.46 – 2.29 (m, 2H), 2.27 – 2.13 (m, 2H), 1.67 – 1.51 (m, 3H), 1.47 – 1.36 (m, 2H), 0.94 (s, 3H), 0.92 (s, 3H). **^{13}C NMR** (101 MHz, $CDCl_3$) δ (ppm): 206.3, 151.7, 150.9, 122.5, 112.4, 52.2, 46.6, 41.8, 39.2, 34.7, 33.4, 31.5, 31.0, 29.9, 22.0. **HRMS** *m/z*: 219.1754 $[M + H]^+$ (calcd for $C_{15}H_{23}O$ 219.1749). **FT-IR** (thin film): 3078, 2946, 2863, 1681, 1636, 1452, 1364, 1347, 1300, 1282, 1176, 1111, 1074, 917, 888 cm^{-1}. Spectral data correspond to the literature (*Chem. Nat. Compd.* **2017**, *53*, 66).

(2a*R*,4a*R*,7a*R*,7b*S*)-2,2-Dimethyloctahydro-5*H*-4a,7a-ethanocyclobuta[*e*]inden-5-one (12)



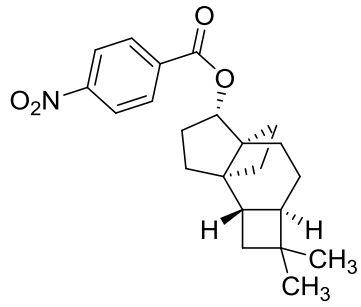
To the solution of enone **8** (2.71 g; 12.4 mmol) in dry MeCN (125 mL) was added $AlCl_3$ (248 mg; 1.86 mmol) at 0 ^{o}C. Reaction mixture was warmed up to rt and was stirred for 1 h. Then saturated $NaHCO_3$ aqueous solution was added to the mixture and MeCN was evaporated under reduced pressure. Mixture was extracted with Et_2O and washed with brine. Organic layer was dried with anhydrous Na_2SO_4, filtered and concentrated under reduced pressure. The residue was purified by column chromatography using hexanes/Et_2O (4:1) elution to obtain title product (2.34 g, 87%) as a white crystalline solid (Et_2O). **mp** 46–48 ^{o}C. $[\boldsymbol{\alpha}]_{\boldsymbol{D}}^{\boldsymbol{20}}$ –129 (*c* 1.00, $CHCl_3$). **^{1}H NMR** (400 MHz, $CDCl_3$) δ (ppm): 2.76 (ddd, *J* = 18.2, 10.5, 9.3 Hz, 1H), 2.41 – 2.27 (m, 2H), 1.97 – 1.82 (m, 4H), 1.78 – 1.69 (m, 2H), 1.66 – 1.52 (m, 5H), 1.49 – 1.40 (m, 1H), 1.30 – 1.20 (m, 1H), 1.09 (s, 3H), 1.04 (s, 3H). **^{13}C NMR** (101 MHz, $CDCl_3$) δ (ppm): 223.7, 50.6, 47.5, 43.7, 40.7, 39.0, 38.0, 36.0, 33.2, 30.6, 26.7, 24.8, 22.0, 20.9, 19.7. **HRMS** *m/z*: 219.1752 $[M + H]^+$ (calcd for $C_{15}H_{23}O$ 219.1749). **FT-IR** (thin film): 2944, 2862, 1735, 1455, 1364, 1284, 1065 cm^{-1}.

(2a*R*,4a*R*,5*S*,7a*R*,7b*S*)-2,2-Dimethyloctahydro-5*H*-4a,7a-ethanocyclobuta[*e*]inden-5-ol (9)



To the solution of ketone **12** (1.90 g; 8.71 mmol) in dry MeOH (90 mL) was added $NaBH_4$ (330 mg; 8.71 mmol) at rt. Reaction mixture was stirred at rt for 2 h and then was quenched by addition of 1 M HCl aqueous solution. MeOH was evaporated under reduced pressure; the mixture was extracted with Et_2O and washed with brine. Organic layer was dried with anhydrous Na_2SO_4, filtered and concentrated under reduced pressure. The residue was purified by column chromatography using hexanes/EtOAc (4:1) elution to obtain title product (1.77 g, 92%, >10:1 *dr*) as white crystalline solid (EtOAc). **mp** 69–71 °C. $[\boldsymbol{\alpha}]_{\boldsymbol{D}}^{\boldsymbol{20}}$ –66.9 (*c* 1.00, $CHCl_3$). **^{1}H NMR** (400 MHz, $CDCl_3$) δ (ppm): 3.71 (dd, *J* = 10.5, 6.4 Hz, 1H), 2.16 (ddd, *J* = 12.8, 11.2, 5.4 Hz, 1H), 2.04 – 1.96 (m, 2H), 1.95 – 1.88 (m, 1H), 1.88 – 1.79 (m, 1H), 1.71 – 1.62 (m, 2H), 1.61 – 1.54 (m, 2H), 1.53 – 1.45 (m, 3H), 1.45 – 1.34 (m, 4H), 1.21 (tdd, *J* = 12.7, 6.1, 0.7 Hz, 1H), 1.09 (s, 3H), 1.06 (s, 3H). **^{13}C NMR** (101 MHz, $CDCl_3$) δ (ppm): 82.5, 48.6, 48.0, 42.9, 40.0, 38.8, 35.8, 34.6, 33.2, 30.6, 30.4, 21.8, 21.1, 19.9, 18.7. **HRMS** *m/z*: 203.1801 $[M - OH]^+$ (calcd for $C_{15}H_{23}$ 203.1800). **FT-IR** (thin film): 3308, 2952, 2944, 2929, 2862, 2725, 1459, 1363, 1071, 1033 cm^{-1}.

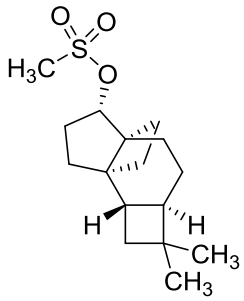
(2a*R*,4a*R*,5*S*,7a*R*,7b*S*)-2,2-dimethyloctahydro-5*H*-4a,7a-ethanocyclobuta[*e*]inden-5-yl 4-nitrobenzoate (13)



4-Nitrobenzoyl chloride (126 mg; 0.68 mmol) was dissolved in DCM (7 mL). DIPEA (0.24 mL; 1.36 mmol), DMAP (8 mg, 0.06 mmol) and alcohol **9** (100 mg, 0.45 mmol) were subsequently added to the solution at rt. Reaction mixture was stirred for 4 h at rt, quenched with saturated $NaHCO_3$ aqueous solution. Organic layer was dried with anhydrous Na_2SO_4, filtered and concentrated under reduced pressure. The residue was purified by column chromatography using hexanes/EtOAc (20:1) elution to obtain title product (107 mg, 64%) as white crystalline solid (EtOAc). **mp** 168–170 °C. $[\boldsymbol{\alpha}]_{\boldsymbol{D}}^{\boldsymbol{20}}$ –41.1 (*c* 1.02, $CHCl_3$). **^{1}H NMR** (400 MHz, $CDCl_3$) δ (ppm): 8.30 – 8.25 (m, 2H), 8.21 – 8.17 (m, 2H), 4.97 (dd, *J* = 10.2, 6.5 Hz, 1H), 2.33 – 2.20 (m, 2H), 2.19 – 1.95 (m,

3H), 1.80 – 1.61 (m, 4H), 1.62 – 1.49 (m, 4H), 1.48 – 1.32 (m, 3H), 1.10 (s, 3H), 1.08 (s, 3H). **^{13}C NMR** (101 MHz, $CDCl_3$) δ (ppm): 164.8, 150.6, 136.3, 130.8, 123.6, 85.2, 48.5, 48.0, 42.8, 39.6, 39.0, 35.7, 34.9, 30.6, 30.2, 30.1, 22.0, 21.03, 20.98, 18.5. **HRMS** *m/z*: 203.1804 $[M - C_6H_4NO_4]^+$ (calcd for $C_{15}H_{23}$ 203.1800). **FT-IR** (thin film): 2955, 2855, 1716, 1715, 1608, 1531, 1461, 1351, 1286, 1125, 1016, 874, 760, 720 cm^{-1}. The structure was confirmed by single-crystal X-ray analysis. Suitable crystals were prepared by dissolving 10 mg of ester in warm (60 ^oC) EtOH (1 mL) in a screw-cap 10 mL vial. The cap was set on the top to avoid airborne dust and sealed loosely for the slow evaporation of solvent. After standing for 48 h appropriate crystals for single-crystal X-ray analysis were formed. Crystal data for ester: $C_{22}H_{27}NO_4$ (M = 369.46 g/mol): orthorhombic, space group $P2_12_12_1$ (no. 19), a = 6.06579(5) Å, b = 16.68048(13) Å, c = 18.97466(18) Å, V = 1919.86(3) $Å^3$, Z = 4, T = 150.0(2) K, μ(Cu Kα) = 0.705 mm^{-1}, *Dcalc* = 1.2781 g/cm^3, 12058 reflections measured ($2\Theta \leq 155.0°$), 3897 unique (R_{int} = 0.0278, R_{sigma} = 0.0288) which were used in all calculations. The final R_1 was 0.0313 ($I \geq 2\sigma(I)$) and wR_2 was 0.0814 (all data).

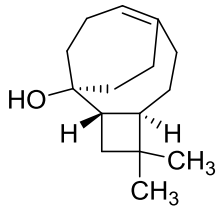
(2a*R*,4a*R*,5*S*,7a*R*,7b*S*)-2,2-Dimethyloctahydro-5*H*-4a,7a-ethanocyclobuta[*e*]inden-5-yl methanesulfonate (14)



Alcohol **9** (1.58 g; 7.18 mmol) was dissolved in DCM (100 mL). To the solution Et_3N (7 mL; 50.3 mmol) was added and the mixture was cooled to 0 ^oC. MsCl (2.23 mL; 28.7 mmol) was added to the mixture dropwise and then mixture was allowed to warm up to rt. Reaction mixture was stirred for 4 h at rt and then was quenched with saturated $NaHCO_3$ aqueous solution. Organic layer was dried with anhydrous Na_2SO_4, filtered and concentrated under reduced pressure. The residue was purified by column chromatography using hexanes/Et_2O (2:1) mixture elution to obtain title product (1.93 g, 90%) as a colorless oil. $[\boldsymbol{\alpha}]_{\boldsymbol{D}}^{\boldsymbol{20}}$ –69.3 (*c* 1.00, $CHCl_3$). **^{1}H NMR** (400 MHz, C_6D_6) δ (ppm): 4.41 (dd, J = 10.3, 6.8 Hz, 1H), 2.23 (s, 3H), 2.10 – 1.96 (m, 4H), 1.93 – 1.81 (m, 1H), 1.72 – 1.57 (m, 1H), 1.55 – 1.40 (m, 4H), 1.39 – 1.22 (m, 5H), 1.07 (s, 3H), 1.03 (s, 3H), 1.00 – 0.89 (m, 1H). **^{13}C NMR** (101 MHz, C_6D_6) δ (ppm): 89.7, 47.9, 47.4, 42.9, 39.8, 38.8, 37.7, 35.6, 34.3, 30.9, 30.5, 29.9, 21.8, 21.0,

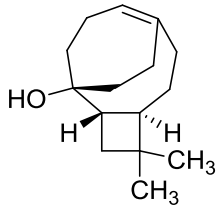
20.8, 18.5. **HRMS** *m/z*: 203.1804 $[M - CH_3SO_3]^+$ (calcd for $C_{15}H_{23}$ 203.1800). **FT-IR** (thin film): 3032, 2944, 2862, 1459, 1357, 1257, 1176, 962, 887, 854, 756, 530 cm^{-1}.

(1*R*,2*S*,5*R*)-4,4-Dimethyltricyclo[6.3.2.$0^{2,5}$]tridec-8-en-1-ol (10)



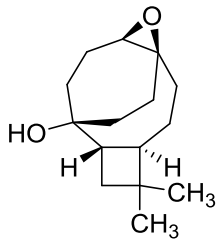
Mesylate **14** (1.88 g; 6.30 mmol) was dissolved in 1,4-dioxane/H_2O (1:1, 60 mL). The solution was refluxed for 16 h and then cooled down to rt. Reaction mixture was quenched with saturated $NaHCO_3$ aqueous solution and extracted with Et_2O. Organic layer was washed with brine, dried with anhydrous Na_2SO_4, filtered and concentrated under reduced pressure. The residue was purified by column chromatography using hexanes/Et_2O (2:1) elution to obtain title product (618 mg, 45%) as white crystalline solid (Et_2O). **mp** 105 °C. $[\boldsymbol{\alpha}]_{\boldsymbol{D}}^{\boldsymbol{20}}$ +24.3 (*c* 1.00, $CHCl_3$). **H NMR** (400 MHz, $CDCl_3$) δ (ppm): 5.48 (tt, *J* = 7.3, 1.2 Hz, 1H), 2.65 (tdd, *J* = 14.4, 5.7, 2.4 Hz, 1H), 2.44 (ddd, *J* = 12.5, 7.5, 1.1 Hz, 1H), 2.32 (ddt, *J* = 13.9, 12.0, 8.1 Hz, 1H), 2.14 – 1.97 (m, 3H), 1.93 (dddd, *J* = 12.6, 11.5, 2.5, 1.1 Hz, 1H), 1.86 – 1.65 (m, 5H), 1.64 – 1.56 (m, 3H), 1.26 (qd, *J* = 12.2, 7.5 Hz, 1H), 1.12 (br. s, 1H), 0.96 (s, 3H), 0.92 (s, 3H). **^{13}C NMR** (101 MHz, $CDCl_3$) δ (ppm): 141.9, 122.8, 74.3, 52.8, 49.1, 44.0, 36.8, 36.2, 33.3, 32.5, 31.7, 30.3, 29.2, 23.7, 21.5. **HRMS** *m/z*: 203.1810 $[M - OH]^+$ (calcd for $C_{15}H_{23}$ 203.1800). **FT-IR** (thin film): 3366, 2942, 2855, 1655, 1456, 1442, 1399, 1361, 1330, 1271, 1236, 1217, 1191, 1142, 1114, 1064, 1033, 993, 927, 896, 843, 835, 761, 666 cm^{-1}. The structure was confirmed by single-crystal X-ray analysis. Suitable crystals were prepared by dissolving 10 mg of alcohol in hexane (1 mL) in a screw-cap 10 mL vial. The cap was set on the top to avoid airborne dust and sealed loosely for the slow evaporation of solvent. After standing for 48 h appropriate crystals for single-crystal X-ray analysis were formed. Crystal data for alcohol: $C_{15}H_{24}O$ (*M* = 220.36 g/mol): trigonal, space group $P3_1$ (no. 144), *a* = 13.3360(4) Å, *c* = 6.2105(2) Å, *V* = 956.56(5) $Å^3$, *Z* = 3, *T* = 150.0(1) K, μ(Cu Kα) = 0.523 mm^{-1}, *Dcalc* = 1.1475 g/cm^3, 5016 reflections measured ($2\Theta \leq 155.0°$), 2221 unique (R_{int} = 0.0256, R_{sigma} = 0.0311) which were used in all calculations. The final R_1 was 0.0302 ($I \geq 2\sigma(I)$) and wR_2 was 0.0765 (all data).

(1*S*,2*S*,5*R*)-4,4-Dimethyltricyclo[6.3.2.0^{2,5}]tridec-8-en-1-ol (7)



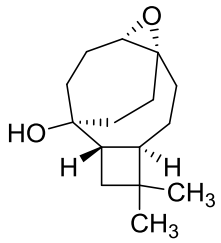
To the mixture of allylic alcohol **6** (1.50 g; 6.81 mmol) and Et_3N in 40 mL of dry THF, MsCl (0.63 mL; 8.17 mmol) was added dropwise at –20 °C. Reaction mixture was stirred for 2 h at −20 °C and then filtered. The filtrate was concentrated under reduced pressure, giving a crude allylic mesylate **8**, to which water (30 mL) and THF (30 mL) were added. Mixture was stirred at rt for 12 h and then reaction was quenched with saturated $NaHCO_3$ aqueous solution. THF was evaporated under reduced pressure and the mixture was extracted with Et_2O and washed with brine. Organic layer was dried with anhydrous Na_2SO_4, filtered and concentrated under reduced pressure. The residue was purified by column chromatography using hexanes/EtOAc (4:1) elution to obtain starting allylic alcohol **6** (224 mg, 15%) and the title product (552 mg, 37%) as white crystalline solid (EtOAc). **mp** 147–148 °C. $[\boldsymbol{\alpha}]_{\boldsymbol{D}}^{\mathbf{26}}$ +170 (*c* 0.98, $CHCl_3$). **^{1}H NMR** (400 MHz, $CDCl_3$) δ (ppm): 5.40 (td, *J* = 8.0, 2.9 Hz, 1H), 2.50 – 2.34 (m, 2H), 2.31 – 2.24 (m, 1H), 2.18 (tdd, *J* = 13.5, 4.4, 1.1 Hz, 1H), 2.09 (dd, *J* = 11.7, 7.4 Hz, 1H), 2.03 – 1.95 (m, 1H), 1.94 – 1.85 (m, 2H), 1.77 (td, *J* = 11.3, 7.8 Hz, 1H), 1.67 – 1.48 (m, 4H), 1.47 – 1.35 (m, 3H), 1.12 (br. s, 1H), 0.98 (s, 6H). **^{13}C NMR** (101 MHz, $CDCl_3$) δ (ppm): 138.2, 126.2, 75.3, 52.1, 47.9, 37.7, 36.6, 35.5, 33.6, 33.5, 30.1, 26.3, 24.7, 23.8, 22.0. **HRMS** *m/z*: 203.1801 $[M-OH]^+$ (calcd for $C_{15}H_{23}$ 203.1800). **FT-IR** (thin film): 3369, 2952, 2854, 1661, 1457, 1430, 1360, 1277, 1238, 1193, 1115, 1089, 1048, 991, 924, 886, 854, 799, 668, 636, 600, 582, 526 cm^{-1}. The structure was confirmed by single-crystal X-ray analysis. Suitable crystals were prepared by dissolving 10 mg of alcohol in hexane (1 mL) in a screw-cap 10 mL vial. The cap was set on the top to avoid airborne dust and sealed loosely for the slow evaporation of solvent. After standing for 48 h appropriate crystals for single-crystal X-ray analysis were formed. Crystal data for alcohol: $C_{15}H_{24}O$ (*M* = 220.34 g/mol): trigonal, space group $P3_2$ (no. 145), *a* = 13.0367(2) Å, *c* = 6.6998(1) Å, *V* = 986.12(3) Å^3, *Z* = 3, *T* = 160.0(1) K, μ(CuKα) = 0.508 mm^{-1}, *Dcalc* = 1.113 g/cm^3, 9553 reflections measured (2Θ ≤ 160.0°), 2086 unique (R_{int} = 0.0306, R_{sigma} = 0.0240) which were used in all calculations. The final R_1 was 0.0306 ($I > 2\sigma(I)$) and wR_2 was 0.0824 (all data).

Euphoranin E (2)



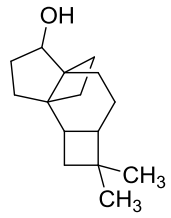
To the solution of alcohol **7** (200 mg; 0.91 mmol) in (DCM, 15 mL) *m*CPBA (70%, 336 mg; 1.36 mmol) was added portionwise. After 2 h, reaction mixture was sequentially washed with saturated Na_2SO_3 and $NaHCO_3$ aqueous solutions. Organic phase was dried with anhyrous Na_2SO_4, filtered, concentrated under reduced pressure. The residue was purified via column chromatography using 1:1 hexane/Et_2O to pure Et_2O gradient elution to obtain title product (139 mg, 65%) as white crystalline solid (Et_2O). **mp** 199–201 ^oC. $[\boldsymbol{\alpha}]_{\boldsymbol{D}}^{\boldsymbol{20}}$ +70.5 (*c* 1.00, $CHCl_3$). **^{1}H NMR** (400 MHz, $CDCl_3$) δ (ppm): 2.76 (dd, *J* = 8.9, 6.0 Hz, 1H), 2.40 – 2.27 (m, 1H), 2.26 – 2.12 (m, 3H), 2.05 (dt, *J* = 13.0, 6.5 Hz, 1H), 2.01 – 1.89 (m, 2H), 1.80 – 1.66 (m, 2H), 1.65 – 1.54 (m, 3H), 1.53 – 1.36 (m, 3H), 1.25 (br. s, 1H), 1.02 (s, 6H), 0.92 – 0.77 (m, 1H). **^{1}H NMR** (400 MHz, C_6D_6) δ (ppm): 2.43 (dd, *J* = 9.0, 6.0 Hz, 1H), 2.07 – 1.94 (m, 2H), 1.94 – 1.77 (m, 4H), 1.65 (dddd, *J* = 16.0, 10.9, 9.6, 1.1 Hz, 1H), 1.57 – 1.44 (m, 3H), 1.41 – 1.24 (m, 3H), 1.19 – 1.01 (m, 2H), 0.92 (s, 3H), 0.89 (s, 3H), 0.75 (dddd, *J* = 12.6, 11.4, 8.1, 1.0 Hz, 1H), 0.52 (br. s, 1H). **^{13}C NMR** (101 MHz, $CDCl_3$) δ (ppm): 74.8, 64.9, 59.4, 50.5, 45.8, 36.1, 34.9, 33.7, 33.5, 31.9, 30.1, 26.8, 25.8, 24.3, 21.5. **HRMS** *m/z*: 219.1748 $[M - OH]^+$ (calcd for $C_{15}H_{23}O$ 219.1749). **FT-IR** (thin film): 3355, 2953, 2859, 1730, 1457, 1362, 1348, 1286, 1238, 1201, 1093, 1052, 1039, 1024, 997, 987, 951, 931, 922, 892, 821, 753, 683, 629, 576 cm^{-1}. The structure was confirmed by single-crystal X-ray analysis. Suitable crystals were prepared by dissolving 10 mg of alcohol in *n*-pentane (1 mL) in a screw-cap 10 mL vial. The cap was set on the top to avoid airborne dust and sealed loosely for the slow evaporation of solvent. After standing for 48 h appropriate crystals for single-crystal X-ray analysis were formed. Crystal data for epoxyalcohol: $C_{15}H_{24}O_2$ (*M* = 236.36 g/mol): trigonal, space group $P3_2$ (no. 145), *a* = 13.0332(1) Å, *c* = 6.70964(7) Å, *V* = 987.04(2) $Å^3$, *Z* = 3, *T* = 150.0(1) K, μ(Cu Kα) = 0.599 mm^{-1}, *Dcalc* = 1.1928 g/cm^3, 9171 reflections measured (2Θ ≤ 160.0°), 2601 unique (R_{int} = 0.0177, R_{sigma} = 0.0156) which were used in all calculations. The final R_1 was 0.0297 ($I > 2\sigma(I)$) and wR_2 was 0.0770 (all data).

***iso*-Euphoranin E (11)**



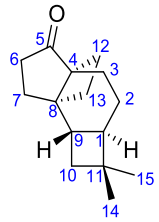
To the solution of alcohol **10** (511 mg; 2.32 mmol) in DCM (25 mL) *m*CPBA (70%, 858 mg; 3.48 mmol) was added portionwise. After 2 h, reaction mixture was sequentially washed with saturated Na_2SO_3 and $NaHCO_3$ aqueous solutions. Organic phase was dried with anhyrous Na_2SO_4, filtered, concentrated under reduced pressure. The residue was purified via column chromatography using 1:1 hexanes/Et_2O to pure Et_2O gradient elution. The collected fraction was triturated with *n*-pentane, filtered and dried to yield the first crop of white crystalline solid (285 mg, 52%). The filtrate was evaporated, triturated with *n*-pentane, centrifuged and dried to yield the second crop (67 mg, 12%). **mp** 109 °C. $[\boldsymbol{\alpha}]_{\boldsymbol{D}}^{\boldsymbol{20}}$ +75.8 (*c* 1.00, $CHCl_3$). **^{1}H NMR** (400 MHz, $CDCl_3$) δ (ppm): 3.02 (dd, *J* = 8.2, 5.9 Hz, 1H), 2.28 – 2.17 (m, 2H), 2.12 (dddd, *J* = 12.7, 9.2, 7.3, 1.7 Hz, 1H), 2.06 – 1.84 (m, 5H), 1.84 – 1.74 (m, 1H), 1.73 – 1.57 (m, 4H), 1.57 – 1.46 (m, 2H), 1.36 – 1.24 (m, 1H), 1.20 (s, 1H), 1.00 (s, 3H), 0.99 (s, 3H). **^{13}C NMR** (101 MHz, $CDCl_3$) δ (ppm): 73.3, 60.7, 57.7, 49.3, 48.2, 42.1, 37.1, 36.0, 32.6, 32.1, 31.0, 30.3, 26.0, 25.9, 21.6. **HRMS** *m/z*: 219.1751 $[M - OH]^+$ (calcd for $C_{15}H_{23}O$ 219.1749). **FT-IR** (thin film): 3434, 2952, 2929, 2866, 1719, 1477, 1456, 1405, 1366, 1335, 1289, 1201, 1133, 1077, 1038, 979, 938, 916, 860, 834, 760, 572 cm^{-1}. The structure was confirmed by single-crystal X-ray analysis. Suitable crystals were prepared by dissolving 10 mg of epoxyalcohol in *n*-pentane (1 mL) in a screw-cap 10 mL vial. The cap was set on the top to avoid airborne dust and sealed loosely for the slow evaporation of solvent. After standing for 48 h appropriate crystals for single-crystal X-ray analysis were formed. Crystal data for epoxyalcohol: $C_{60}H_{96}O_8$ (*M* = 945.43 g/mol): monoclinic, space group $P2_1$ (no. 4), *a* = 9.3483(1) Å, *b* = 17.5247(3) Å, *c* = 16.1772(2) Å, β = 90.546(1)°, *V* = 2650.13(6) $Å^3$, *Z* = 2, *T* = 170.0(1) K, μ(Cu Kα) = 0.595 mm^{-1}, *Dcalc* = 1.1847 g/cm^3, 47326 reflections measured ($2\Theta \leq 160.0°$), 11054 unique (R_{int} = 0.0522, R_{sigma} = 0.0330) which were used in all calculations. The final R_1 was 0.0536 ($I > 2\sigma(I)$) and wR_2 was 0.1474 (all data).

Table S1. Occurrence of 4,4-dimethyltetracyclo[6.3.0^{2,5}.0^{1,8}]tridecan-9-ol in plant extracts



Plant species	Percentage, %	Reference
Ageratum conyzoides	0.04	*C. R. Chim*. **2004**, *7* (10–11), 1019
Patrinia scabra	0.24–13.42	*Chem. Biodivers.* **2005**, *2* (10), 1351
Artemisia scoparia	1.98	*Food Chem.* **2009**, *114* (2), 642
Polygonum minus	0.122	*Molecules* **2010**, *15* (10), 7006
Salvia elegans	4.02	*Pharm. Biol.* **2010**, *49* (5), 456
Solanum erianthum	2.8	*J. Essent. Oil. Bear. Pl.* **2012**, *15* (3), 387
Carthamus tinctorius	2.15	*Acta Chromatogr.* **2012**, *24* (4), 653
Pricasma quassioides	3.08	*Chin. Herb. Med.* **2013**, *5* (1), 73
Murraya koenigii	3.6	*Food Res. Int.* **2013**, *52* (1), 8
Wedelia biflora	0.17	*Asian J. Chem.* **2013**, *25* (9), 5051
Blumea balsamifera	0.83	*Asian J. Chem.* **2013**, *25* (11), 6361
Psidium guajava	12.975	*J. Essent. Oil. Bear. Pl.* **2014**, *17* (6), 1293
Feronia elephantum	0.91	*Int. J. Pharm. Pharm. Sci.* **2014**, *6* (7), 2010
Broussonetia papyrifera	0.66	*Int. J. Pharm. Sci. Res.* **2015**, *6* (9), 3954
Plectranthus amboinicus	0.2	*Int. J. Pharm. Pharm. Sci.* **2016**, *8* (8), 223
Debregeasia longifolia	0.93	*Int. J. Pharm.* **2016**, *6* (1), 124
Cullen plicata	1.68	*Ind. Crops Prod.* **2016**, *8*, 36
Syzygium aromaticum	0.13	*J. Biol. Act. Prod. Nat.* **2017**, *7* (6), 452
	not reported	*Arch. Microbiol.* **2022**, *204* (11), 674
Sideritis clandestine ssp *peloponnesiaca*	0.2–1.36	*J. Chromatogr. A* **2017**, *1524*, 290
Humulus lupus	0.07	*J. Chromatogr. A* **2018**, *1536*, 110
Achillea wilhelmsii	not reported	*J. Chem.* **2019**, *2019*, 5734257
Myrtus communis	0.67	*J. Anal. Chem.* **2019**, *74* (8), 756
Artemisia nilagirica	1.99	*Molecules* **2021**, *26* (16), 4905
Lavandula latifolia	0.0177	*Int. J. Pharm. Sci. Res.* **2021**, *12* (1), 668
Tagetes lucida	5.3	*Nat. Prod. Res.* **2021**, *36* (18), 4745
Cornus macrophylla	1.52	*Molecules* **2022**, *27* (13), 4081

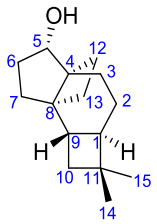
Table S2. NMR spectroscopic data of compound **12**



Position	δ_H, (*J*, Hz)	δ_C, type	^{1}H-^{1}H NOESY	HMBC (C→H)
1	1.88, m*	43.7, CH	H-2β, -3β, -15	H-14, -15
2β	1.30 – 1.20, m	19.7, CH_2	H-1, -2α	H-3
2α	1.59, m*		H-2β	
3β	1.60, m*	24.8, CH_2	H-1, -2β, -3α	H-1
3α	1.75, m*		H-3β	
4	–	50.6, C	–	H-2β, -2α, -7, -9, -12
5	–	223.7, C	–	H-3β, -3α, -6β, -6α, -12, -13
6β	2.37, m*	38.0, CH_2	H-6α, -7β	H-12, -13
6α	2.76, ddd (18.2, 10.5, 9.3)		H-6β, -7α, -9	
7β	1.66, m*	33.2, CH_2	H-6β, -7α	H-6β, -6α, -12
7α	1.95, m*		H-6α, -7β	
8	–	47.5, C	–	H-6β, -6α, -9, -10β, -10α, -12
9	1.62, m*	40.7, CH	H-6α, -14	H-10β, -10α, -12
10β	1.49 – 1.40, m	36.0, CH_2	H-10α, -15	H-1, -9, -14, -15
10α	1.60, m*		H-10β, -14	
11	–	39.0, C	–	H-14, -15
12	2.37, m* 1.75, m*	22.0, CH_2	H-13	H-13
13	1.93, m*	26.7, CH_2	H-12	H-12
14	1.04, s	20.9, CH_3	H-9, -10α	H-10β, -15
15	1.09, s	30.6, CH_3	H-1, -10β	H-1, -10α, -15

* proton signal partly overlaps with other signal; approximate position was assigned by HSQC spectrum

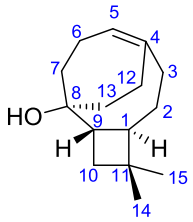
Table S3. NMR spectroscopic data of compound **9**



Position	δ_H, (*J*, Hz)	δ_C, type	^{1}H-^{1}H NOESY	HMBC (C→H)
1	1.98, m*	42.9, CH	H-10, -15	H-2, -3, -9, -10, -14, -15
2	1.55, m* 1.39, m*	18.7, CH_2	H-13	H-9, -10
3	1.95 – 1.88, m 1.39, m*	19.9, CH_2	H-13	H-5, -13
4	–	48.6, C	–	H-3, -7, -9, -13
5	3.71, dd (10.5, 6.4)	82.5, CH	H-6, -7	H-3, -6, -7, -12
6	2.00, m* 1.88 – 1.79, m	33.2, CH_2	H-5, -7	H-5, -13
7	1.50, m* 1.21, tdd (12.7, 6.1, 0.7)	34.6, CH_2	H-5, -6	H-6, -9
8	–	48.0, C	–	H-1, -7, -10 -13
9	1.67, m*	40.0, CH	H-10, -14	H-1, -6, -7, -10, -13
10	1.50, m* 1.38, m*	35.8, CH_2	H-1, -9	H-1, -2, -7
11	–	38.8, C	–	H-1, -10, -14, -15
12	1.67, m* 1.48, m*	30.4, CH_2	H-13	H-5
13	2.16, ddd (12.8, 11.2, 5.4) 1.40, m*	21.8, CH_2	H-2, -3, -12	H-1, -3, -7 -9, -12
14	1.06, s	21.1, CH_3	H-9, -15	H-1, -10, -15
15	1.09, s	30.6, CH_3	H-1, -14	H-10, -14

* proton signal partly overlaps with other signal; approximate position assigned by HSQC spectrum

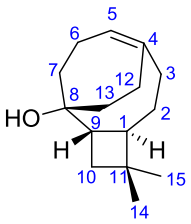
Table S4. NMR spectroscopic data of compound **10**



Position	δ_H, (*J*, Hz)	δ_C, type	^{1}H-^{1}H NOESY	HMBC (C→H)
1	1.77, m	49.1, CH	H-15	H-2α, -3α, -9, -10, -14, -15
2β	1.69, m*	32.5, CH_2	H-3β	H-3α
2α	1.26, qd (12.2, 7.5)		H-3α, -5, -9, -14	
3β	1.61, m*	36.8, CH_2	H-2β	H-2α, -12
3α	2.44, ddd (12.5, 7.5, 1.1)		H-2α, -5	
4	–	141.9, C	–	H-3β, -3α, -6, -12
5	5.48, tt (7.3, 1.2)	122.8, CH	H-2α, -3α, -6, -12	H-3β, -3α, -6, -12
6	2.32, ddt (13.9, 12.0, 8.1) 2.08, m*	23.7, CH_2	H-5, -7	H-7
7	1.78, m*	44.0	H-6	H-6
8	–	74.3, C	–	H-6, -10, -12
9	2.02, m*	52.8, CH	H-2α, -14	H-1, -2, -6, -7, -10
10	1.61, m*	36.2, CH_2	H-14, -15	H-1, -9, -14, -15
11	–	31.7, C	–	H-10, -14, -15
12	2.65, tdd (14.4, 5.7, 2.4) 1.93, dddd (12.6, 11.5, 2.5, 1.1)	29.2, CH_2	H-5, -13	H-3, -13
13	2.08, m* 1.72, m*	33.3, CH_2	H-12	H-9, -12
14	0.92, s	21.5, CH_3	H-2α, -9, -10, -15	H-10, -15
15	0.96, s	30.3, CH_3	H-1, -10, -14	H-10, -14

* proton signal partly overlaps with other signal; approximate position was assigned by HSQC spectrum

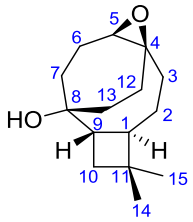
Table S5. NMR spectroscopic data of compound **7**



Position	δ_H, (*J*, Hz)	δ_C, type	^1H-^1H NOESY	HMBC (C→H)
1	1.64, m*	47.9, CH	H-15	H-2, -3, -10, -14, -15
2	1.58, m* 1.41, m*	26.3, CH_2	H-3, -12	H-1, -3, -9
3	2.09, dd (11.7, 7.4) 1.77, td (11.3, 7.8)	36.5, CH_2	H-2, -5	H-1, -2, -5, -12
4	–	138.2, C	–	H-2, -3 -6, -12, -13
5	5.40, td (8.0, 2.9)	126.2, CH	H-3, -6	H-2, -3, -6, -7, -12
6	2.41, m* 1.89, m*	23.8, CH_2	H-5, -7, -12	H-7
7	2.18, tdd (13.5, 4.4, 1.1) 1.41, m*	35.5, CH_2	H-7	H-6
8	–	75.2, C	–	H-1, -6, -7, -10, -12
9	1.88, m*	52.1, CH	H-13, -14	H-2, -7, -10, -13
10	1.52, m* 1.43, m*	33.6, CH_2	H-14, -15	H -14, -15
11	–	33.5, C	–	H-9, -14, -15
12	2.41, m* 1.99, m	24.7, CH_2	H-2, -6, -13	H-3, -5, -13
13	2.27, m 1.49, m*	37.7, CH_2	H-9, -12	H-7, -9, -12
14, 15	0.98, s	30.1, 22.0 2×CH_3	H-1, -9, -10	H-1, -10

* proton signal partly overlaps with other signal; approximate position was assigned by HSQC spectrum

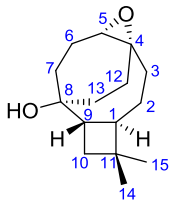
Table S6. NMR spectroscopic data of euphoranin E (**2**)



Position	δ_H, (*J*, Hz)	δ_C, type	^{1}H-^{1}H NOESY	HMBC (C→H)
1	1.73, m*	45.8, CH	H-3, -5, -7, -10, -15	H-3, -9, -13, -14, -15
2	1.97, m	24.3, CH_2	H-3, -12	H-3, -9
3	2.05, dt 0.86, m	36.1, CH_2	H-1, -2, -5, -13	H-1, -5
4	–	59.4, C	–	H-2, -3, -6, -13
5	2.76, dd (8.9, 6.0)	64.9, CH	H-1, -3, -6	H-2, -3, -6, -7
6	2.21, m* 1.55, m*	26.8, CH_2	H-5	H-3, -5
7	2.34, m 1.56, m*	31.9, CH_2	H-1, -13	H-6
8	–	74.8, C	–	H-1, -2, -7
9	2.17, m*	50.5, CH	H-14	H-1, -7
10	1.62, m* 1.49, m*	33.5, CH_2	H-1, -14, -15	H-1, -9, -14, -15
11	–	33.7, C	–	H-1, -9, -14, -15
12	2.18, m* 1.39, m*	34.9, CH_2	H-2	H-2, -7
13	1.71, m* 1.46, m*	25.8, CH_2	H-3, -7	H-13
14, 15	1.02, s	30.1, 21.5, 2×CH_3	H-1, -9, -10	H-1, -10

* proton signal partly overlaps with other signal; approximate position was assigned by HSQC spectrum

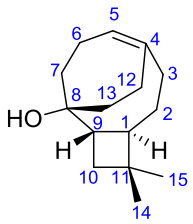
Table S7. NMR spectroscopic data of *iso*-euphoranin E (**11**)



Position	δ_H, (*J*, Hz)	δ_C, type	^{1}H-^{1}H NOESY	HMBC (C→H)
1	1.88, m*	48.2, CH	H-15	H-2, -9, -14, -15
2	1.52, m* 1.31, m	26.0, CH_2	H-14, -15	H-9
3	1.91, m* 1.61, m*	37.1, CH_2	H-5	H-2
4	–	60.7, C	–	H-2, -5, -6, -13
5	3.02, dd (8.2, 5.9)	57.7, CH	H-3, -6, -12	H-3, -6, -12
6	2.23, m* 1.53, m*	25.9, CH_2	H-5, -7	H-5, -7
7	1.96, m*	42.1, CH_2	H-6	H-5, -6, -9
8	–	73.3, C	–	H-7, -9, -10, -13
9	2.22, m*	49.3, CH	H-13, -14	H-1, -7, -10
10	1.68, m*	36.0, CH_2	H-14, -15	H-1, -9, -14, -15
11	–	32.1, C	–	H-1, -14, -15
12	2.02, m* 1.79, m*	31.0, CH_2	H-5	H-13
13	2.12, dddd (12.7, 9.2, 7.3, 1.7) 1.71, m*	32.6, CH_2	H-9	H-7
14	0.99, s	21.6, CH_3	H-2, -9, -10, -15	H-1, -10, -15
15	1.00, s	30.3, CH_3	H-1, -2 -10, -14	H-14

* proton signal partly overlaps with other signal; approximate position was assigned by HSQC spectrum

Table S8. Comparison of NMR data between synthesized and isolated bridgehead olefin **7**



Position	this work	isolated*	this work	isolated*
	δ_H, type	δ_H, type	δ_C	δ_C
1	1.64, m†	1.61, ddd	47.9	47.8
2‡	1.58, m† 1.41, m†	1.51, m 1.37, m	26.3	26.2
3	2.09, dd 1.77, td	2.08, dd 1.76, ddd	36.5	36.4
4	–	–	138.2	138.1
5	5.40, td	5.39, ddd	126.2	126.1
6	2.41, m† 1.89, m†	2.40, m 1.90, m	23.8	23.6
7	2.18, tdd 1.41, m†	2.21, ddd 1.43, m	35.5	35.4
8	–	–	75.2	75.1
9	1.88, m†	1.89, m	52.1	52.0
10‡	1.52, m† 1.43, m†	1.54, m 1.39, m	33.6	33.5
11	–	–	33.5	33.3
12	2.41, m† 1.99, m	2.41, m 1.96, m	24.7	24.5
13	2.27, m 1.49, m†	2.27, ddd 1.44§	37.7	37.6
14/15	0.98, s	0.98, s	30.1, 22.0	30.0, 21.8

* from *Euphorbia wangii* (*Phytochemistry* **1997**, *45* (2), 343); † proton signal partly overlaps with other signal; approximate position was assigned by HSQC spectrum; ‡^{13}C signals were given vice versa in isolation paper (*Phytochemistry* **1997**, *45* (2), 343), assignment was corrected here; § multiplicity not reported

Table S9. Comparison of ^{13}C NMR chemical shifts ($CDCl_3$) of euphoranin E and synthetic epoxyalcohol **2**

Euphoranin E (isolated)* (101 MHz)	74.6	64.7	59.2	50.3	45.6		34.7	34.1	33.6	33.4		29.9	26.6	25.7	25.7	24.2	21.3
Epoxyalcohol **2** (synthetsized)† (50 MHz)	74.7	64.8	59.2	50.4	45.8	36.1	34.8		33.6	33.5	31.8	30.0	26.7	25.8		24.3	21.4
Epoxyalcohol **2** (synthesized) (101 MHz) *This work*	74.8	64.9	59.4	50.5	45.8	36.1	34.9		33.7	33.5	31.9	30.1	26.8	25.8		24.3	21.5
Position	**8**	**5**	**4**	**9**	**1**	**3**	**12**		**11**	**10**	**7**	**14/15**	**6**	**13**		**2**	**14/15**

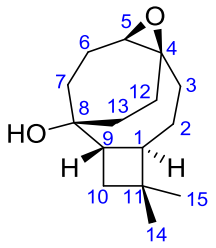
Green cells indicate deviation ≤ 0.2 ppm comparing to our product, red cells indicate presence/absence of ^{13}C signals comparing with isolated material

* from *Euphorbia wangii* (*Ind. J. Chem.* **1996**, *35B*, 1308)

†*Agric. Biol. Chem.* **1989**, *53* (11), 3011; the assignment of ^{13}C signals was corrected

Table S10. Comparison of characteristic ^{1}H NMR signals of euphoranin E and synthetic epoxyalcohol **2** in $CDCl_3$ or C_6D_6 solutions

Position	**H-5**		**H-14 or H-15**		**H-14 or H-15**	
Euphoranin E (isolated)* (400 MHz)	2.41, m (reported in $CDCl_3$)		0.91, s (reported in $CDCl_3$)		0.88, s (reported in $CDCl_3$)	
Epoxyalcohol **2** (synthesized)† (200 MHz)	2.76, dd (reported in $CDCl_3$)		1.03, s (reported in $CDCl_3$)		1.03, s (reported in $CDCl_3$)	
Epoxyalcohol **2** (synthesized) (400 MHz) *This work*	2.76, dd ($CDCl_3$)	2.43, dd (C_6D_6)	1.02, s ($CDCl_3$)	0.92, s (C_6D_6),	1.02, s ($CDCl_3$)	0.89, s (C_6D_6),



* from *Euphorbia wangii* (*Ind. J. Chem.* **1996**, *35B*, 1308)

† *Agric. Biol. Chem.* **1989**, *53* (11), 3011

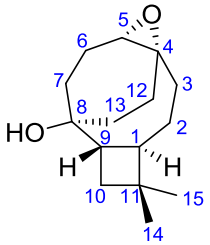
Table S11. Comparison of ^{13}C NMR chemical shifts ($CDCl_3$) of euphoranin E and synthetic epoxyalcohol **11**

Euphoranin E (isolated)* (101 MHz)	74.6	64.7	59.2	50.3	45.6	34.7	34.1	33.6	33.4	29.9	26.6	25.7	25.7	24.2	21.3
Epoxyalcohol **11** (synthesized) (101 MHz) *This work*	73.3	60.7	57.7	49.3	48.2	42.1	37.1	36.0	32.6	32.1	31.0	30.3	26.0	25.9	21.6
Position	**8**	**4**	**5**	**9**	**1**	**7**	**3**	**10**	**13**	**11**	**12**	**15**	**2**	**6**	**14**

* from *Euphorbia wangii* (*Ind. J. Chem.* **1996**, *35B*, 1308)

Table S12. Comparison of characteristic ^{1}H NMR ($CDCl_3$) signals of euphoranin E and synthetic epoxyalcohol **11**

Position	**H-5**	**H-14**	**H-15**
Euphoranin E (isolated)* (400 MHz)	2.41, m	0.91, s	0.88, s
Epoxyalcohol **11** (synthetic) (400 MHz) *This work*	3.02, dd	0.99, s	1.00, s

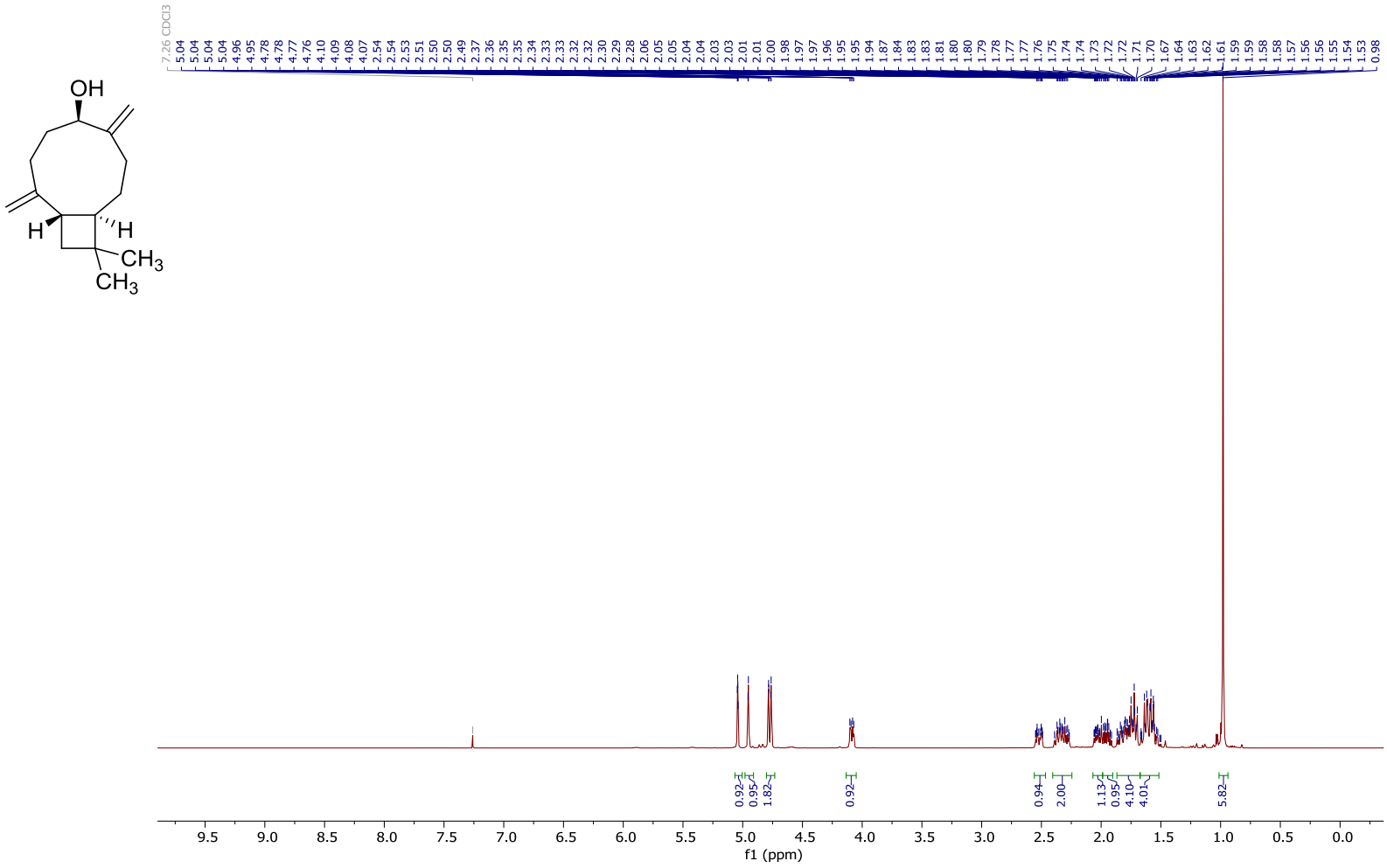


* from *Euphorbia wangii* (*Ind. J. Chem.* **1996**, *35B*, 1308)

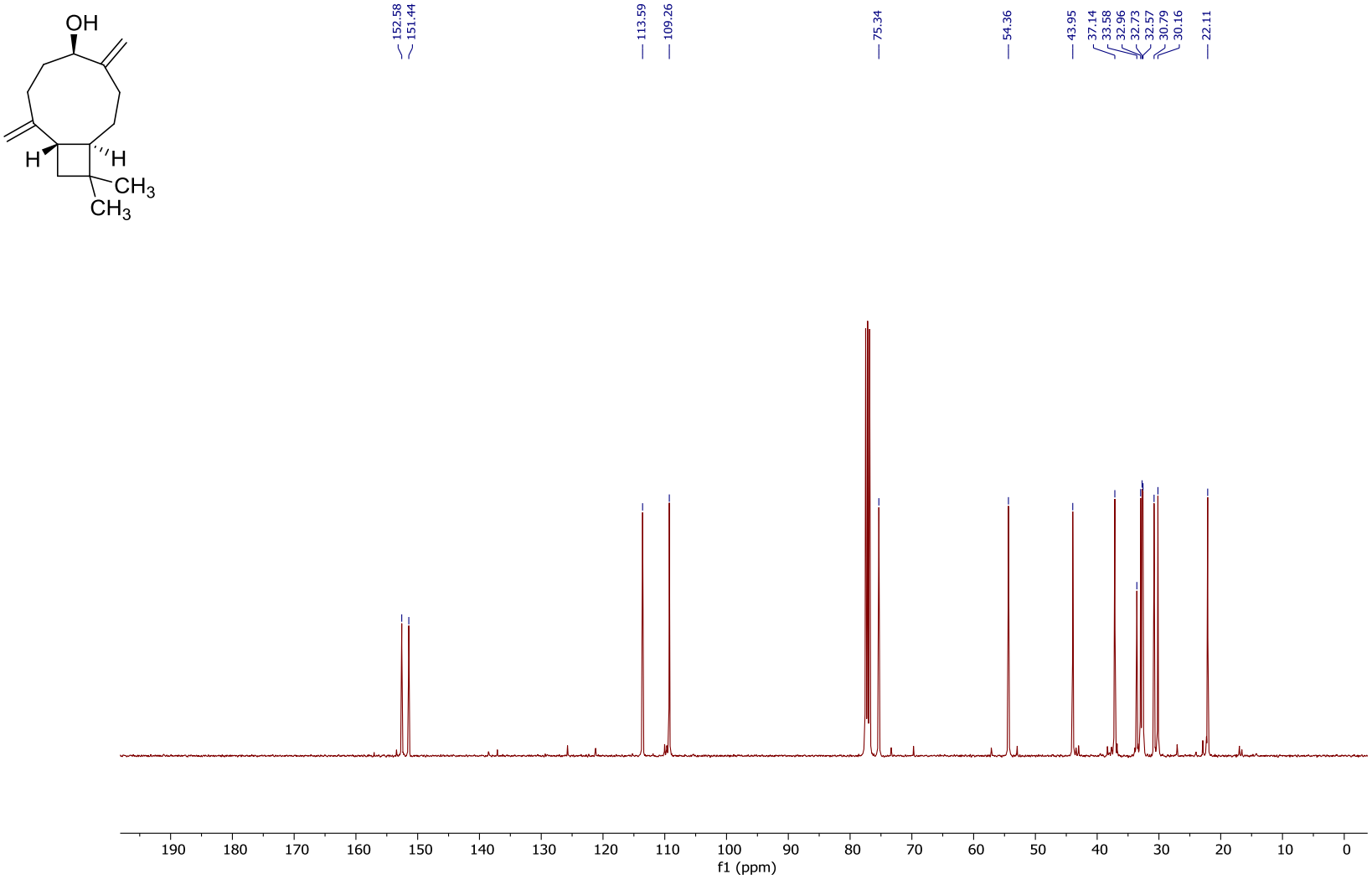
NMR spectra of synthesized compounds

S1. NMR of (1*S*,5*R*,9*R*)-10,10-dimethyl-2,6-dimethylenebicyclo[7.2.0]undecan-5-ol (**6**)

^{1}H NMR (400 MHz, $CDCl_3$) of (1*S*,5*R*,9*R*)-10,10-dimethyl-2,6-dimethylenebicyclo[7.2.0]undecan-5-ol (**6**)

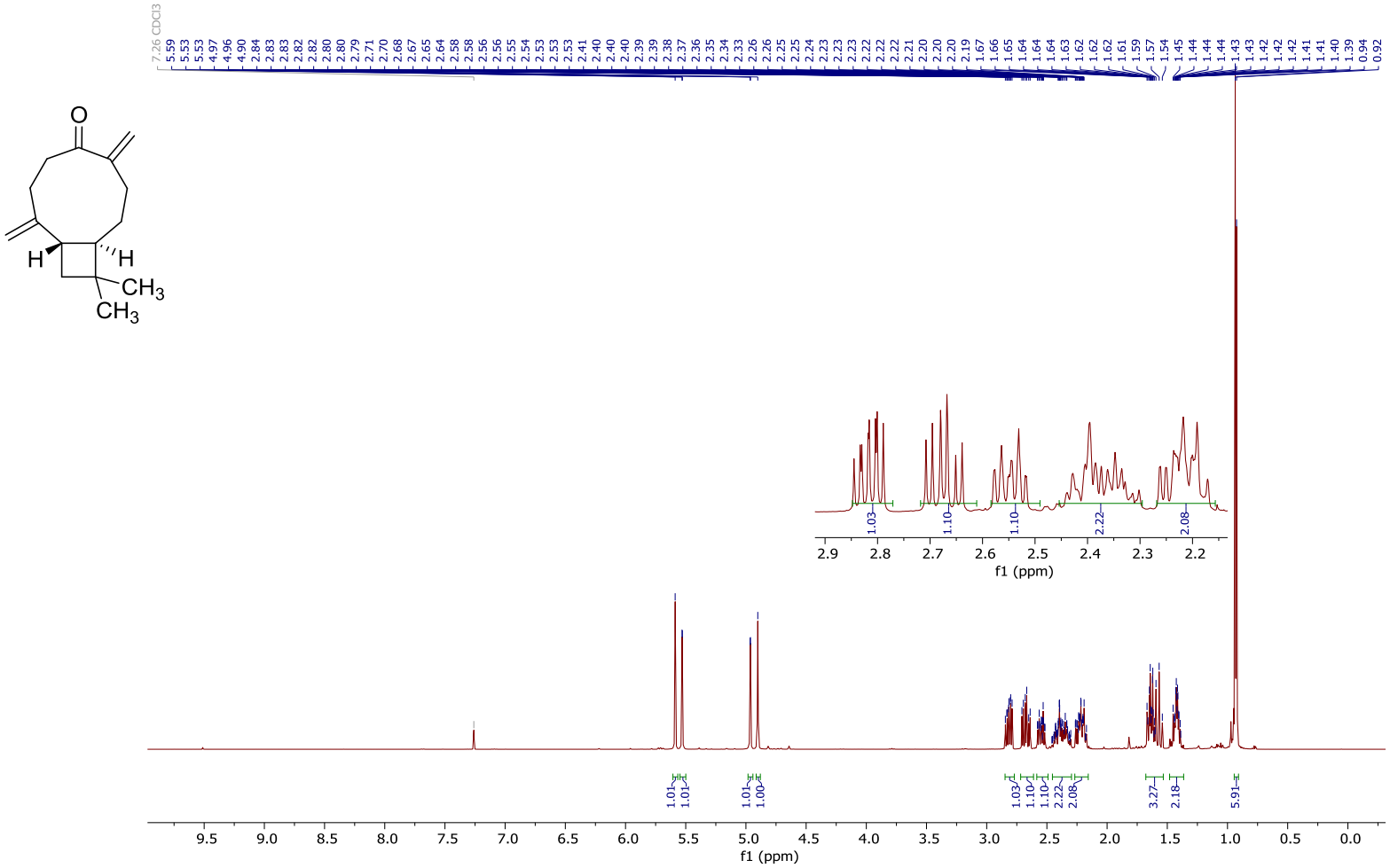


^{13}C NMR (101 MHz, $CDCl_3$) of (1*S*,5*R*,9*R*)-10,10-dimethyl-2,6-dimethylenebicyclo[7.2.0]undecan-5-ol (**6**)

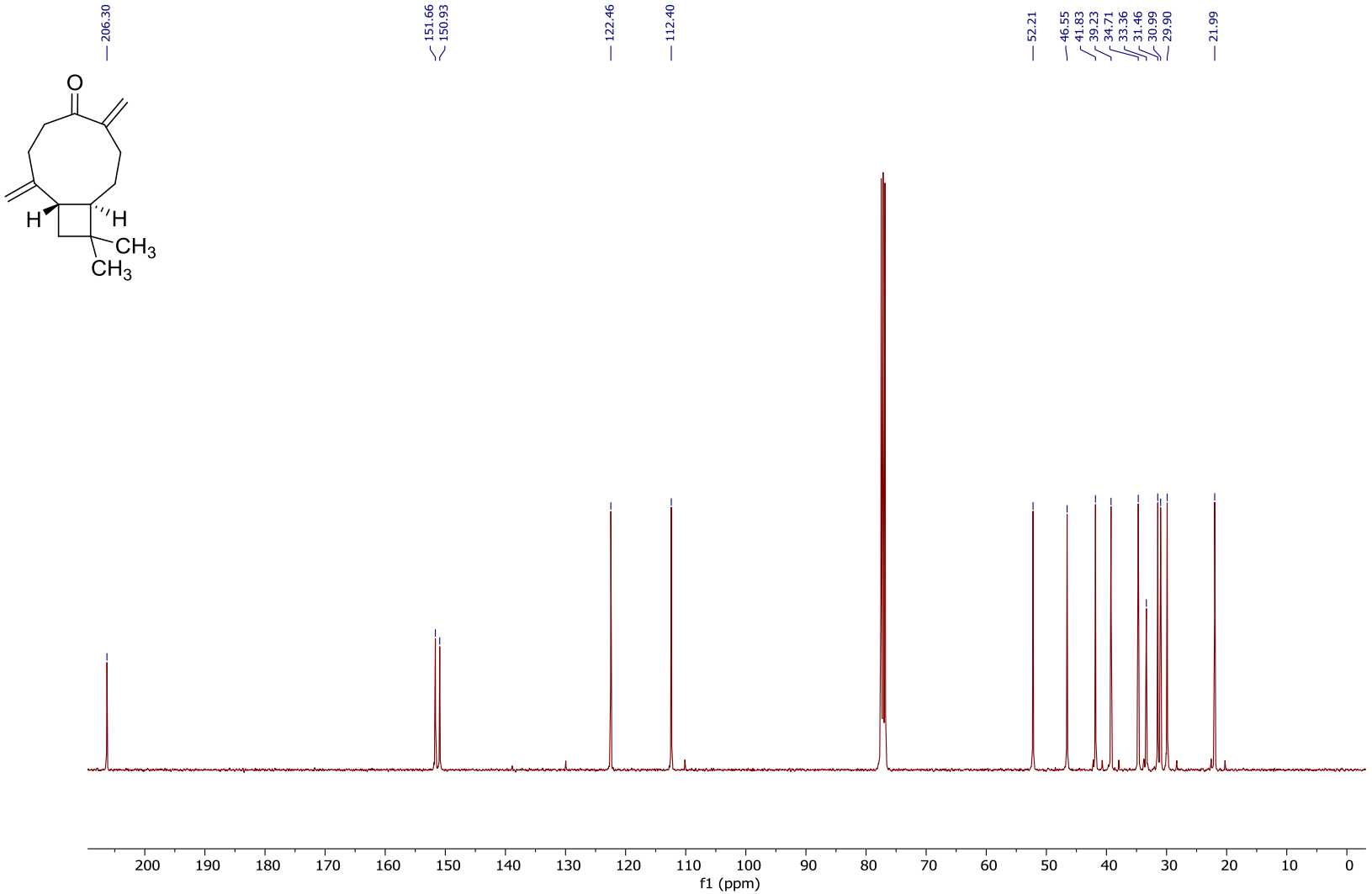


S2. NMR of (1*S*,9*R*)-10,10-dimethyl-2,6-dimethylenebicyclo[7.2.0]undecan-5-one (**8**)

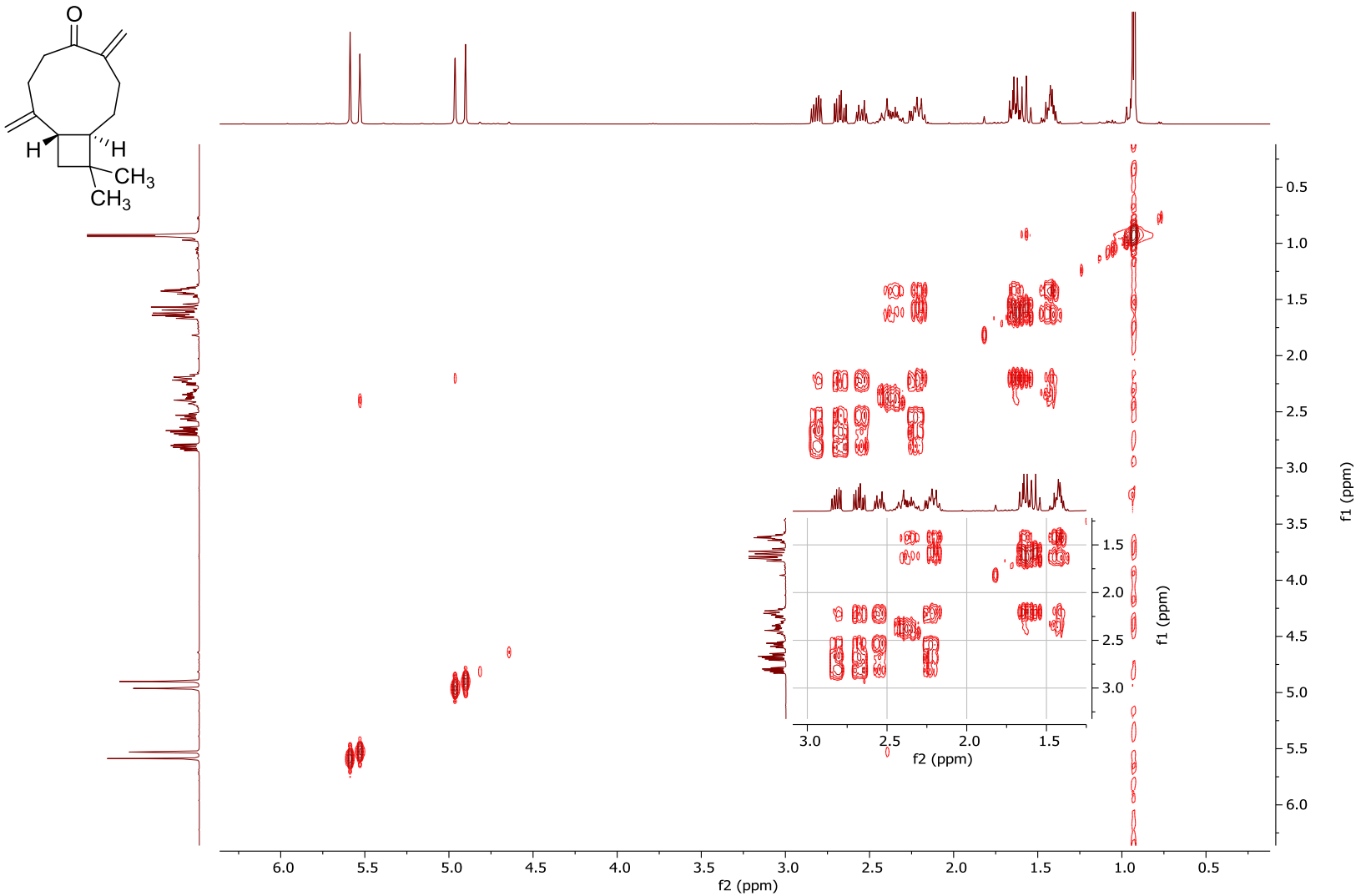
^{1}H NMR (400 MHz, $CDCl_3$) of (1*S*,5*R*,9*R*)-10,10-dimethyl-2,6-dimethylenebicyclo[7.2.0]undecan-5-one (**8**)



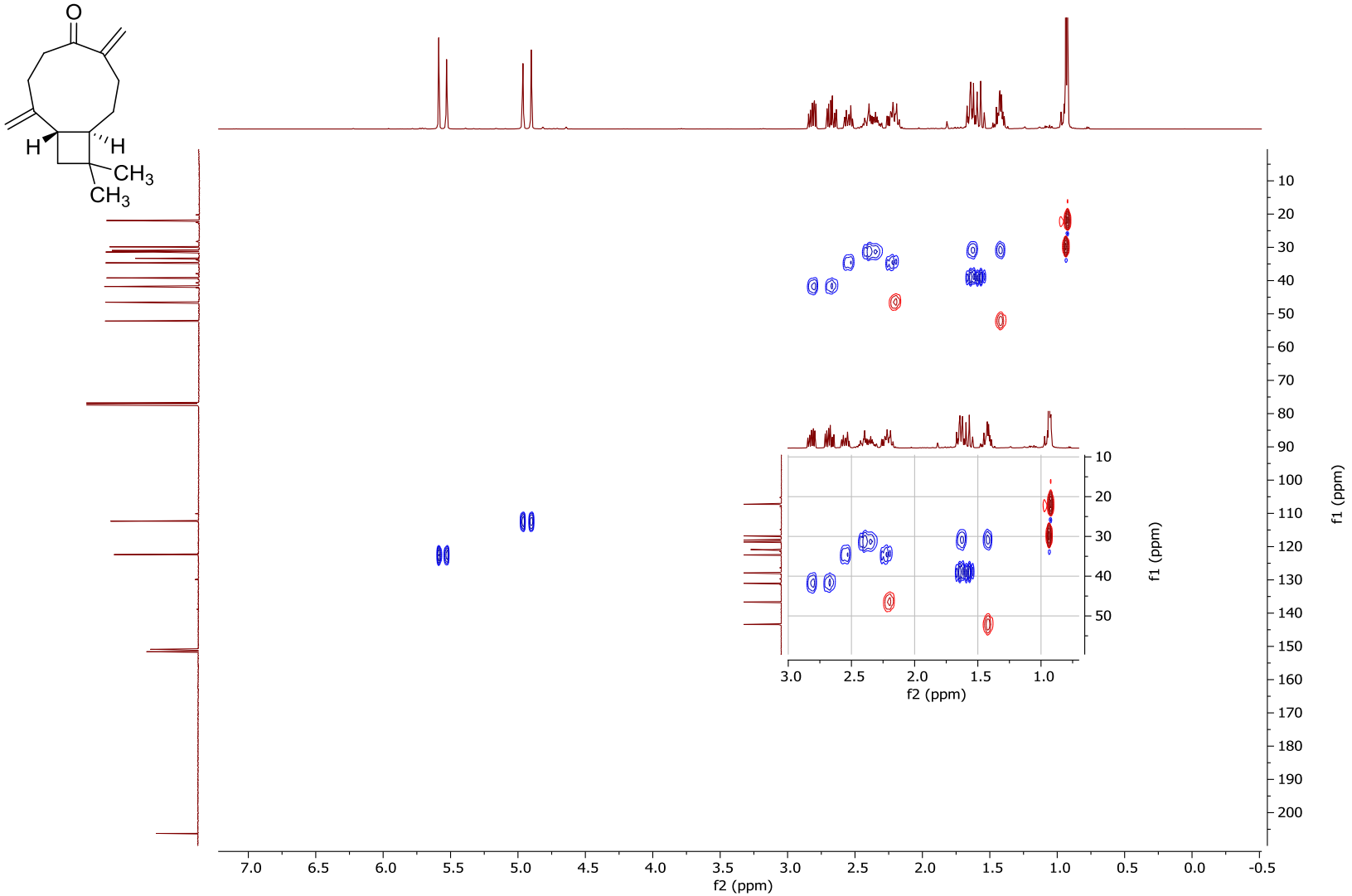
^{13}C NMR (101 MHz, $CDCl_3$) of (1*S*,9*R*)-10,10-dimethyl-2,6-dimethylenebicyclo[7.2.0]undecan-5-one (**8**)



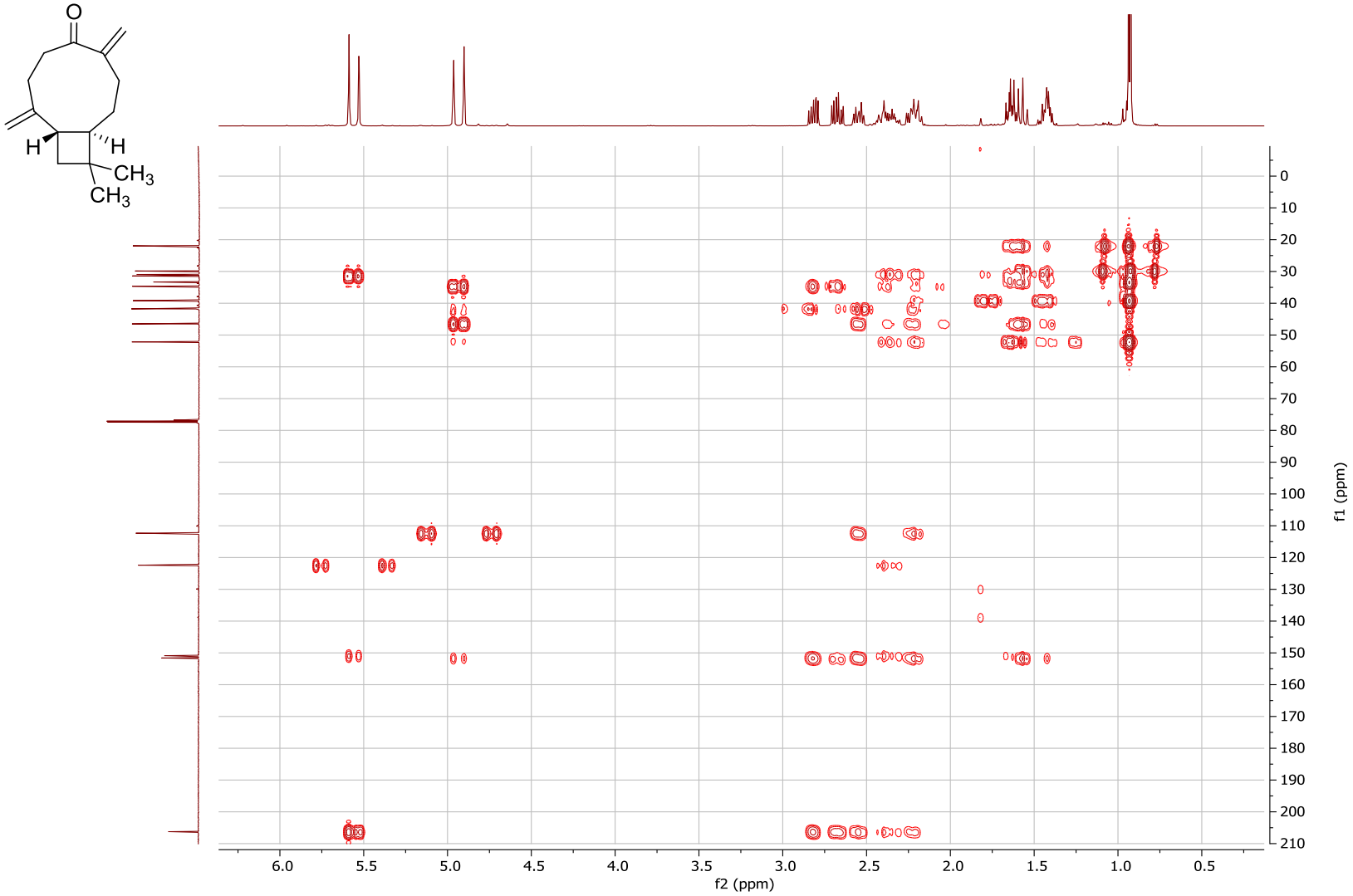
COSY of (1*S*,9*R*)-10,10-dimethyl-2,6-dimethylenebicyclo[7.2.0]undecan-5-one (**8**)



HSQC of (1*S*,9*R*)-10,10-dimethyl-2,6-dimethylenebicyclo[7.2.0]undecan-5-one (**8**)

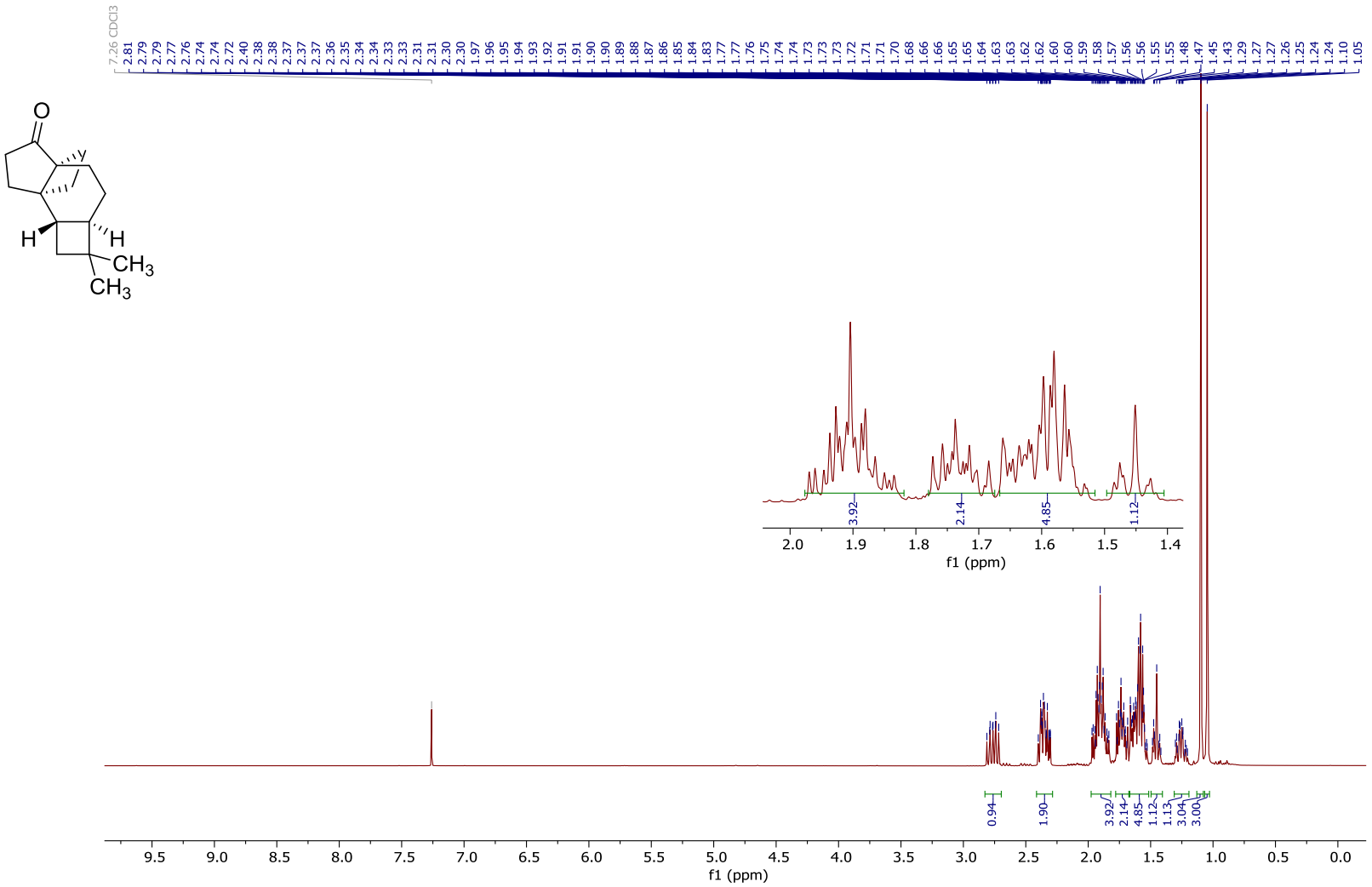


HMBC of (1*S*,9*R*)-10,10-dimethyl-2,6-dimethylenebicyclo[7.2.0]undecan-5-one (**8**)

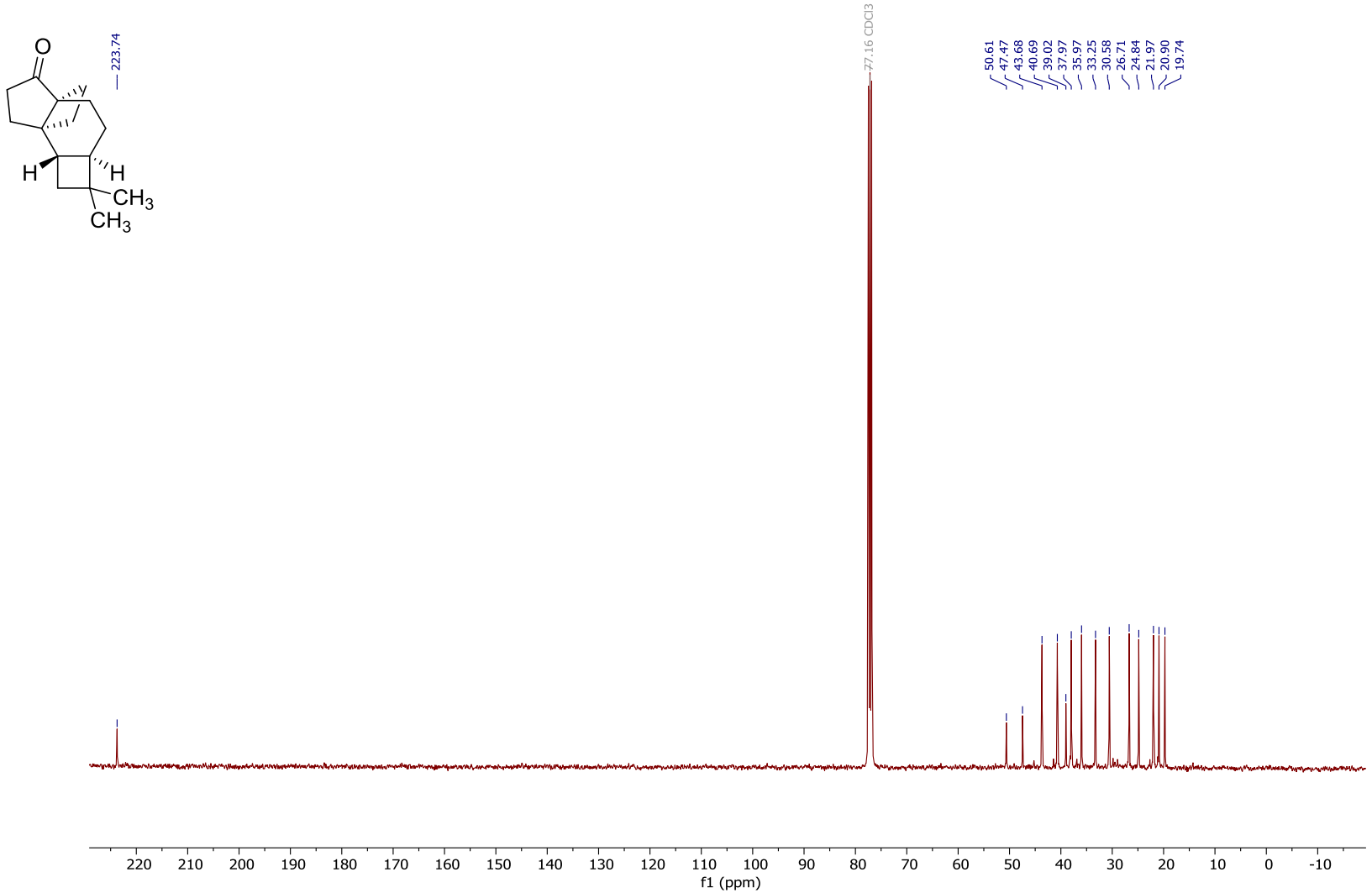


S3. NMR of (2a*R*,4a*R*,7a*R*,7b*S*)-2,2-dimethyloctahydro-5*H*-4a,7a-ethanocyclobuta[*e*]inden-5-one (**12**)

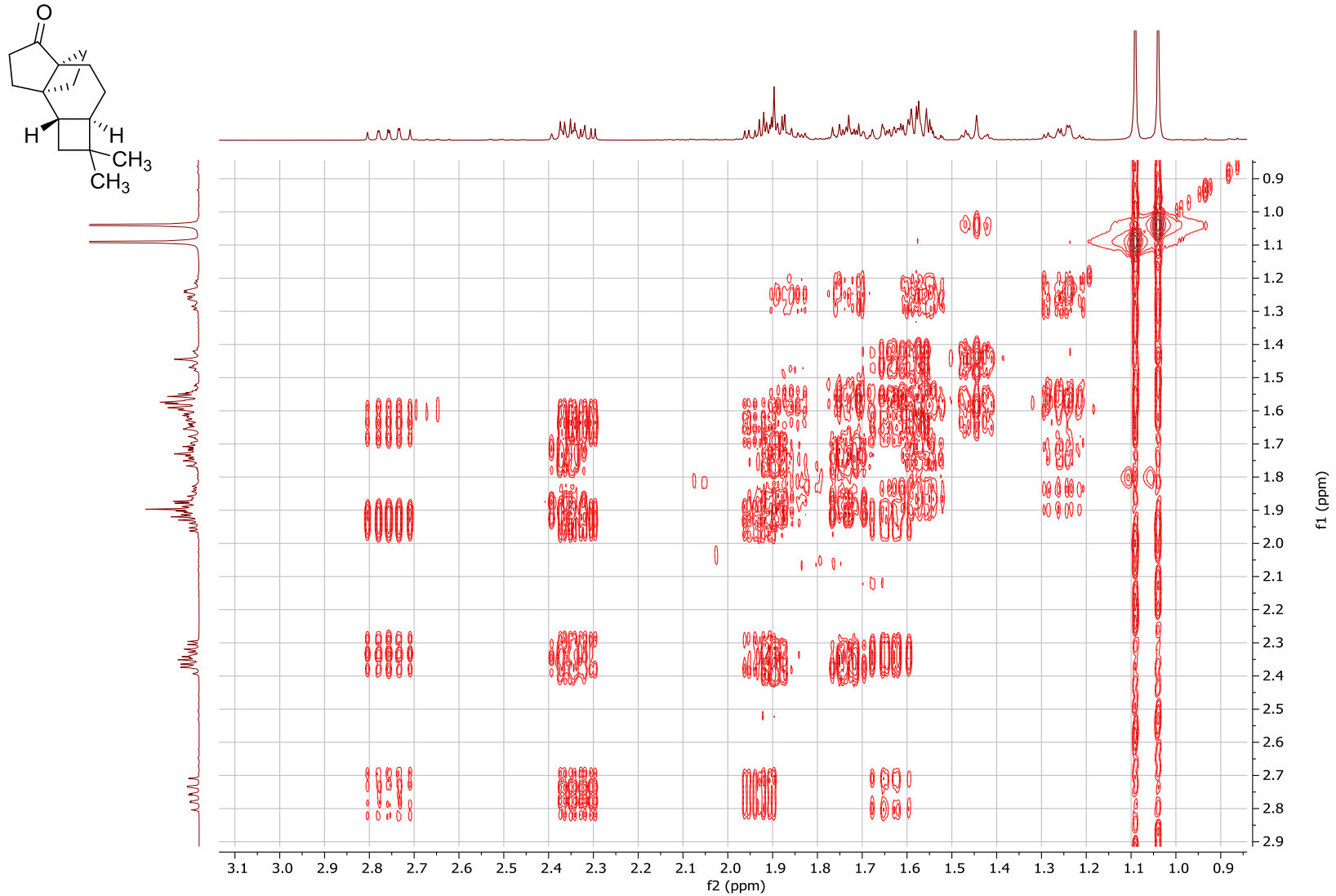
^{1}H NMR (400 MHz, $CDCl_3$) of (2a*R*,4a*R*,7a*R*,7b*S*)-2,2-dimethyloctahydro-5*H*-4a,7a-ethanocyclobuta[*e*]inden-5-one (**12**)



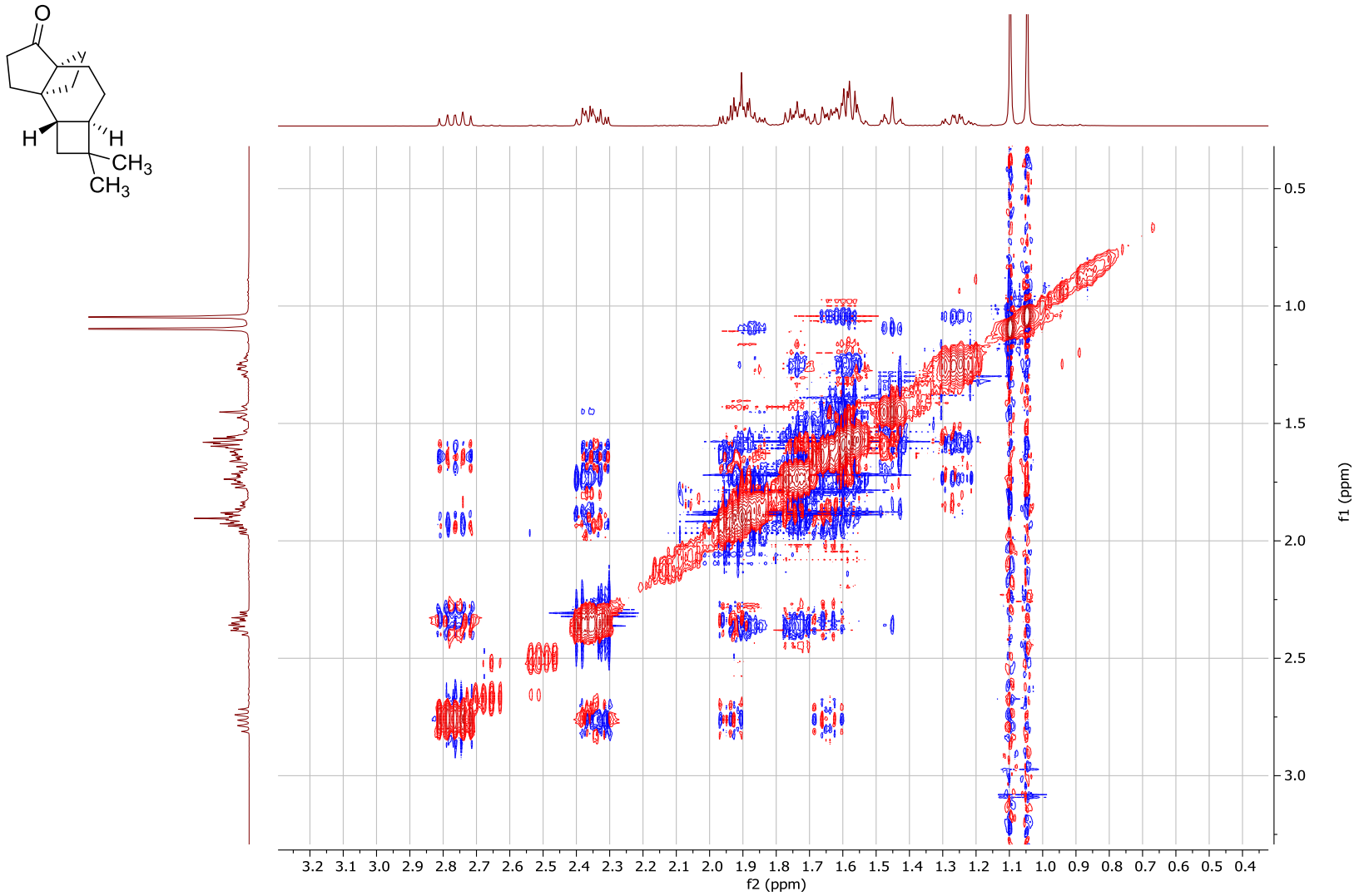
^{13}C NMR (101 MHz, $CDCl_3$) of (2a*R*,4a*R*,7a*R*,7b*S*)-2,2-dimethyloctahydro-5*H*-4a,7a-ethanocyclobuta[*e*]inden-5-one (**12**)



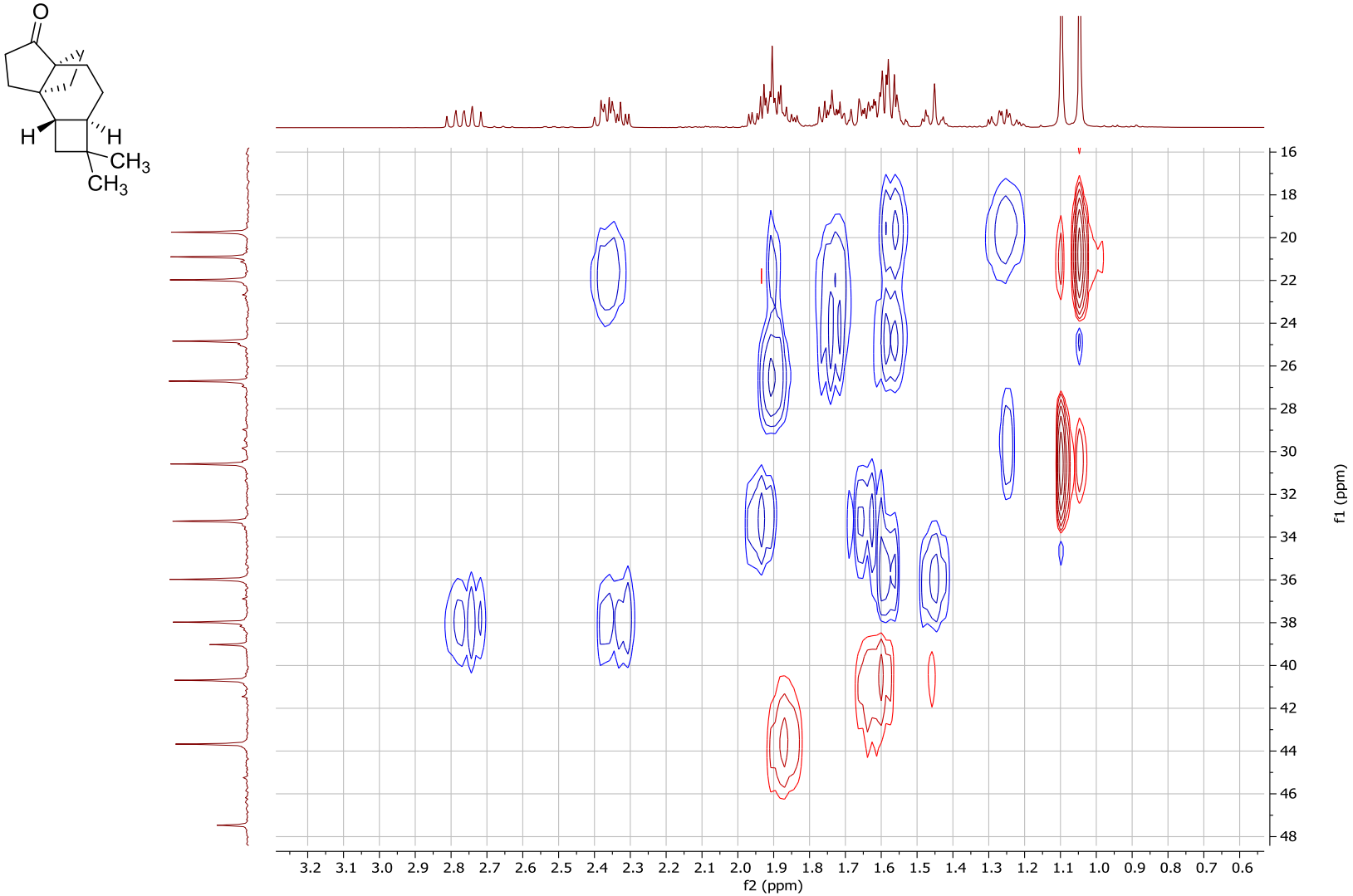
COSY of (2a*R*,4a*R*,7a*R*,7b*S*)-2,2-dimethyloctahydro-5*H*-4a,7a-ethanocyclobuta[*e*]inden-5-one (**12**)



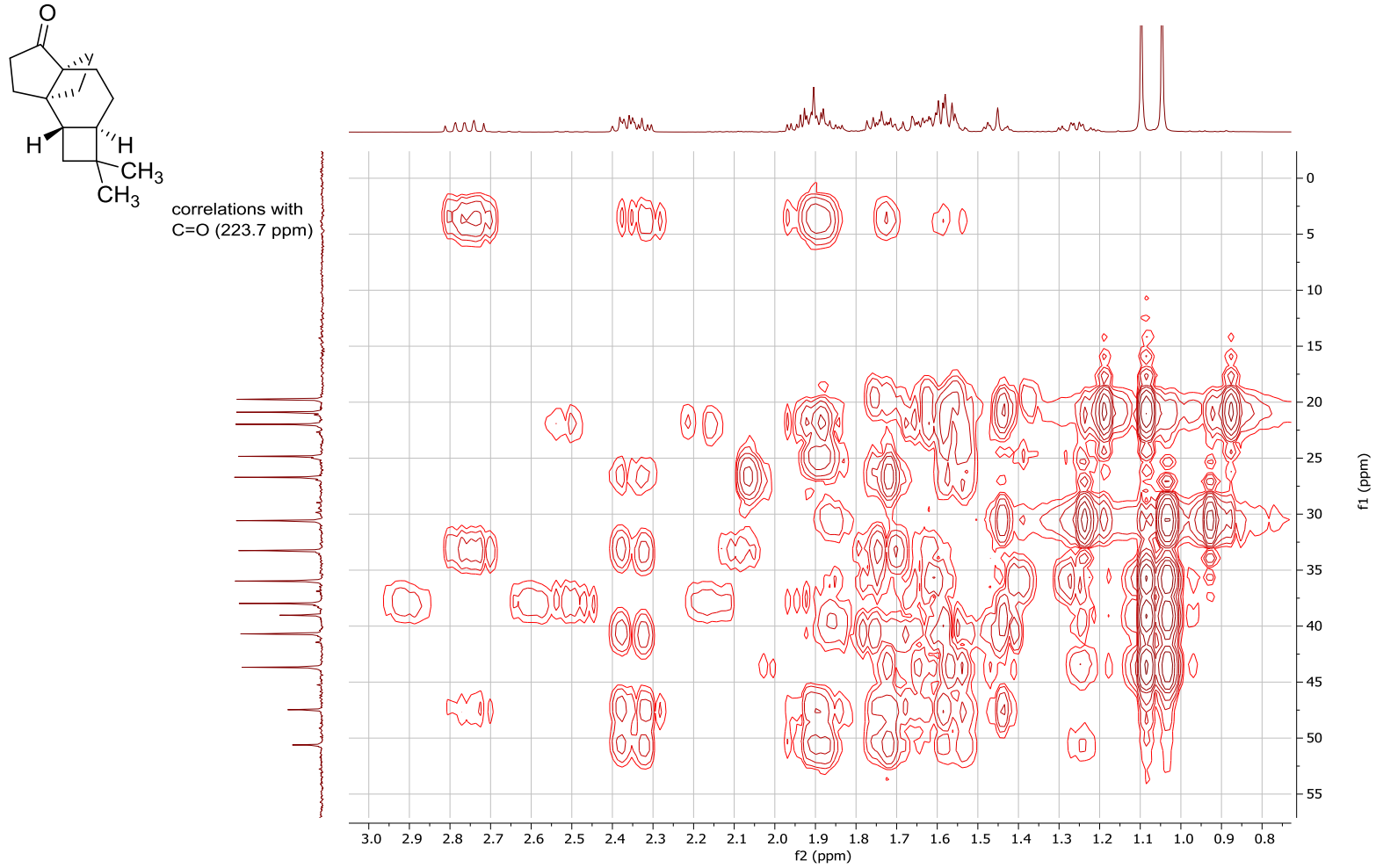
NOESY of (2a*R*,4a*R*,7a*R*,7b*S*)-2,2-dimethyloctahydro-5*H*-4a,7a-ethanocyclobuta[*e*]inden-5-one (**12**)



HSQC of (2a*R*,4a*R*,7a*R*,7b*S*)-2,2-dimethyloctahydro-5*H*-4a,7a-ethanocyclobuta[*e*]inden-5-one (**12**)



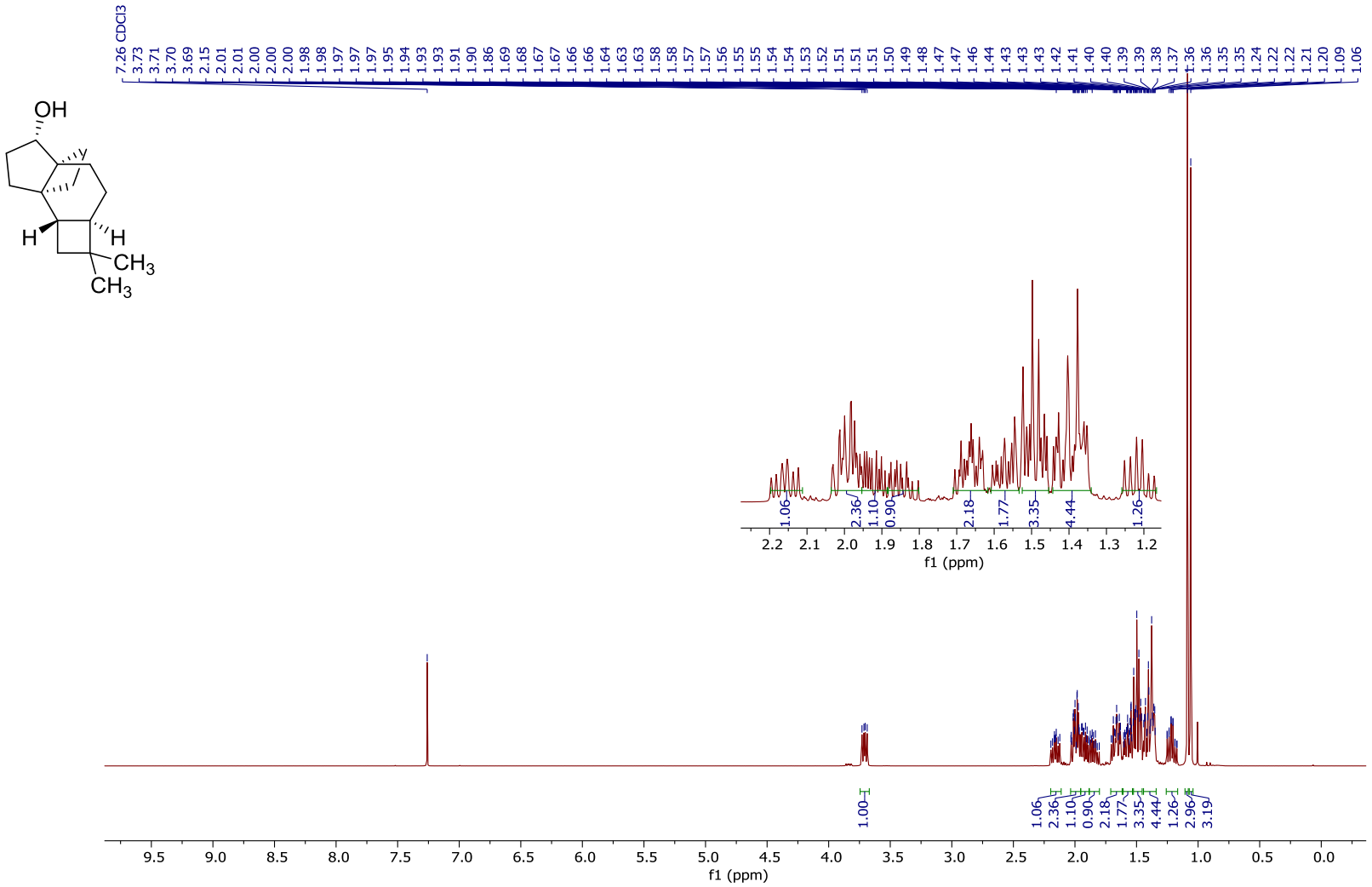
HMBC of (2a*R*,4a*R*,7a*R*,7b*S*)-2,2-dimethyloctahydro-5*H*-4a,7a-ethanocyclobuta[*e*]inden-5-one (**12**)



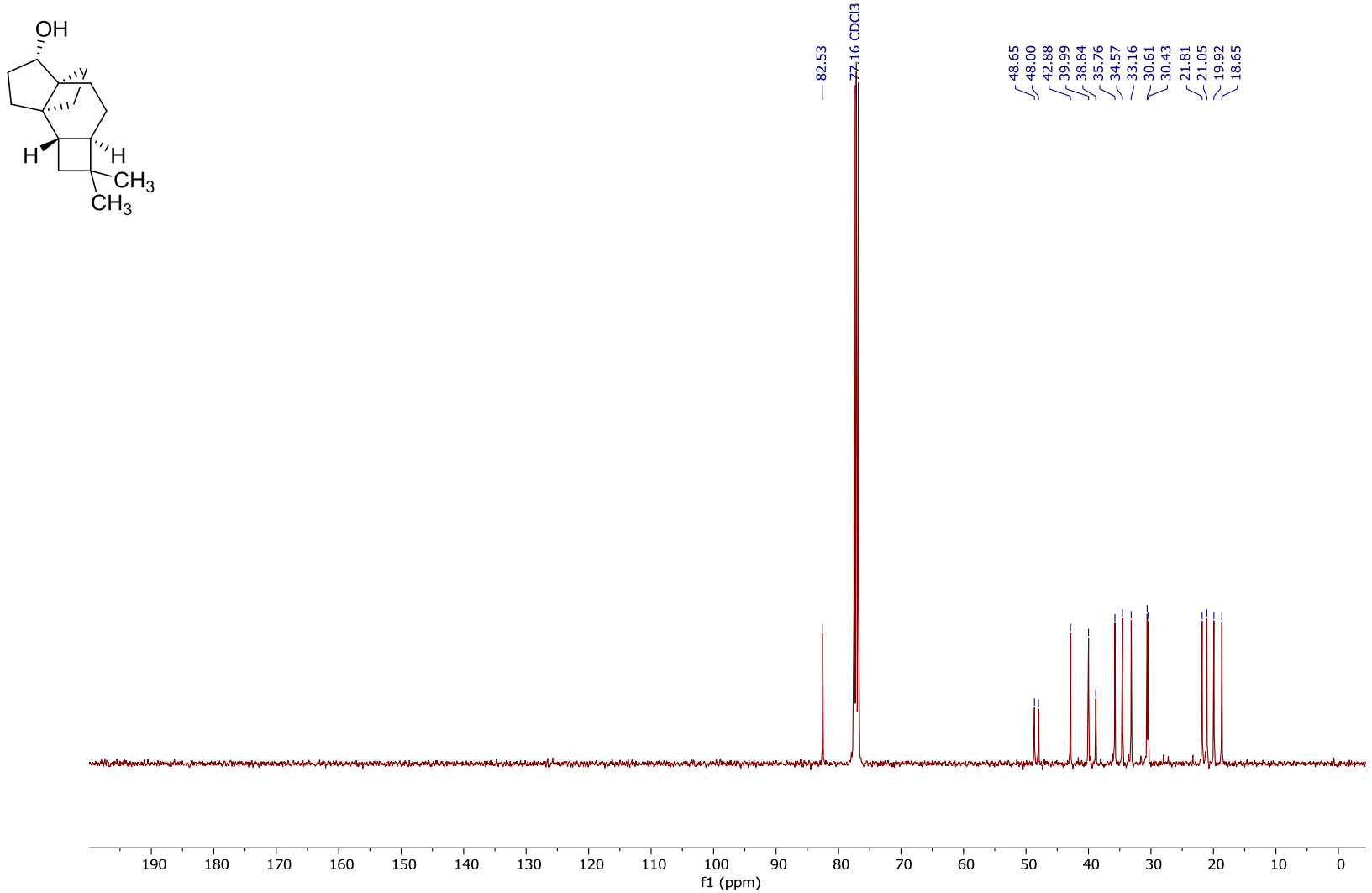
Due to the location of carbonyl carbon in strong downfield region (223.7 ppm), its HMBC correlations with protons are out of margins and appear in the upper side of the spectrum.

S4. NMR of (2a*R*,4a*R*,5*S*,7a*R*,7b*S*)-2,2-dimethyloctahydro-5*H*-4a,7a-ethanocyclobuta[*e*]inden-5-ol (**9**)

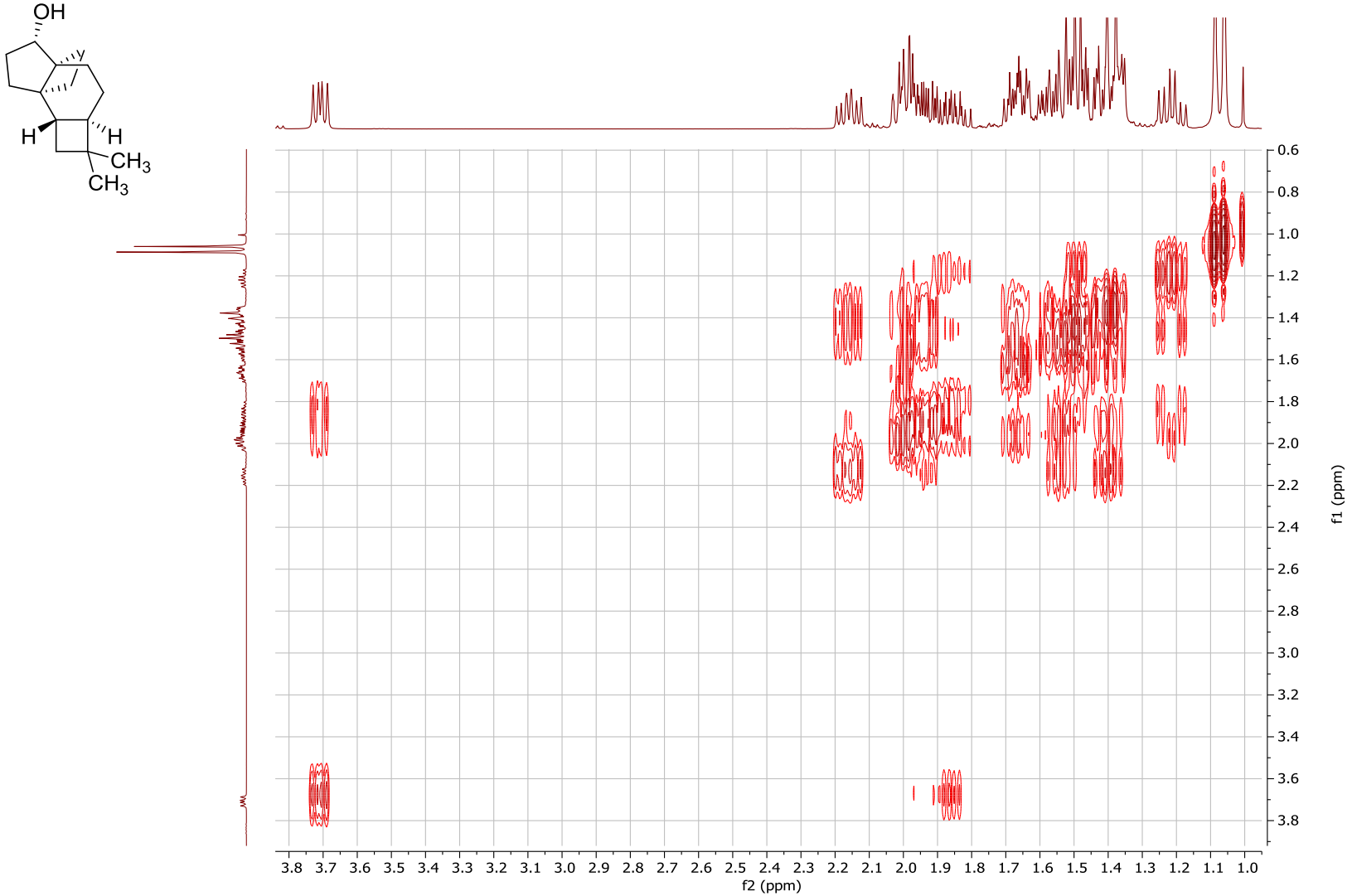
^{1}H NMR (400 MHz, $CDCl_3$) of (2a*R*,4a*R*,5*S*,7a*R*,7b*S*)-2,2-dimethyloctahydro-5*H*-4a,7a-ethanocyclobuta[*e*]inden-5-ol (**9**)



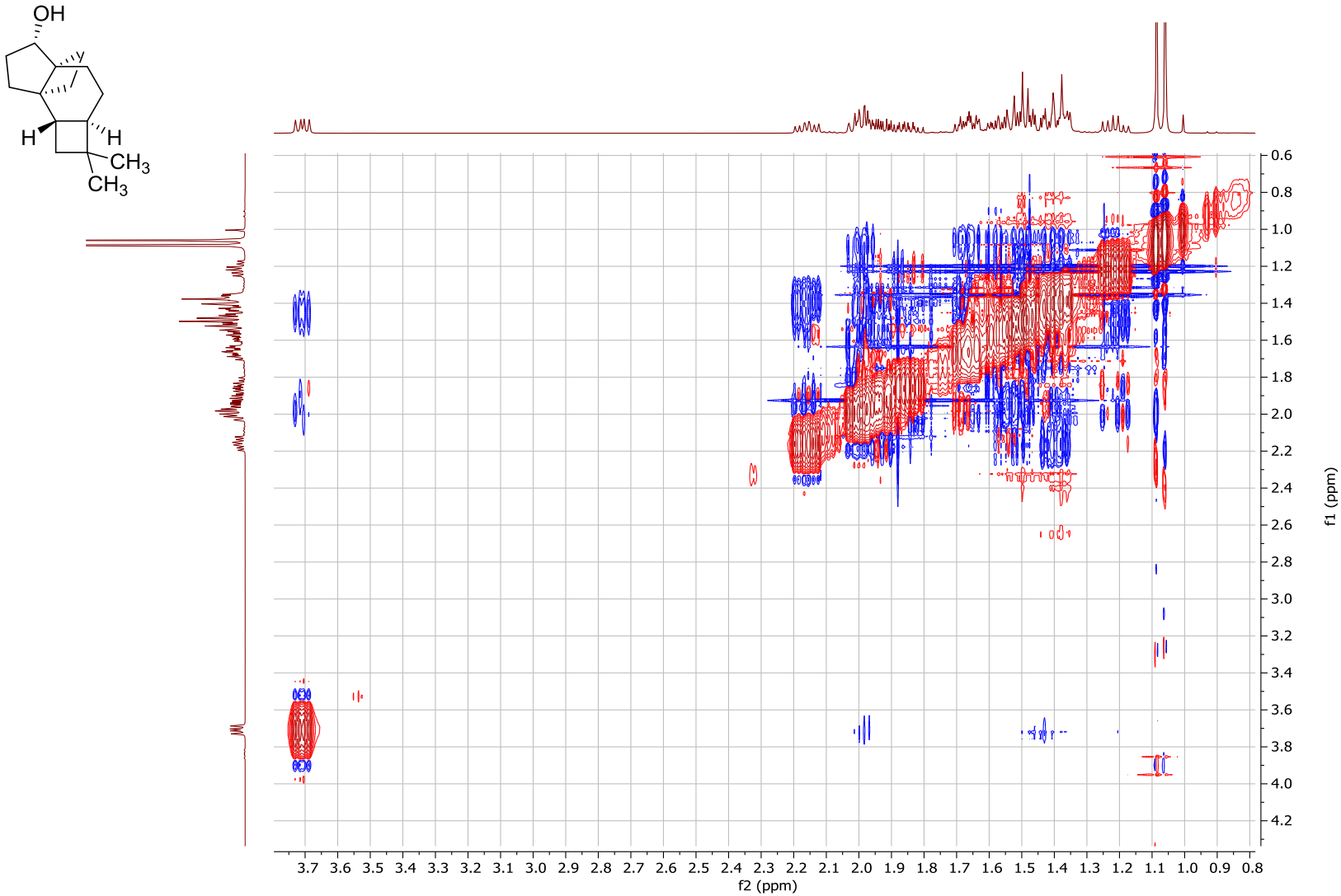
^{13}C NMR (101 MHz, $CDCl_3$) of (2a*R*,4a*R*,5*S*,7a*R*,7b*S*)-2,2-dimethyloctahydro-5*H*-4a,7a-ethanocyclobuta[*e*]inden-5-ol (**9**)



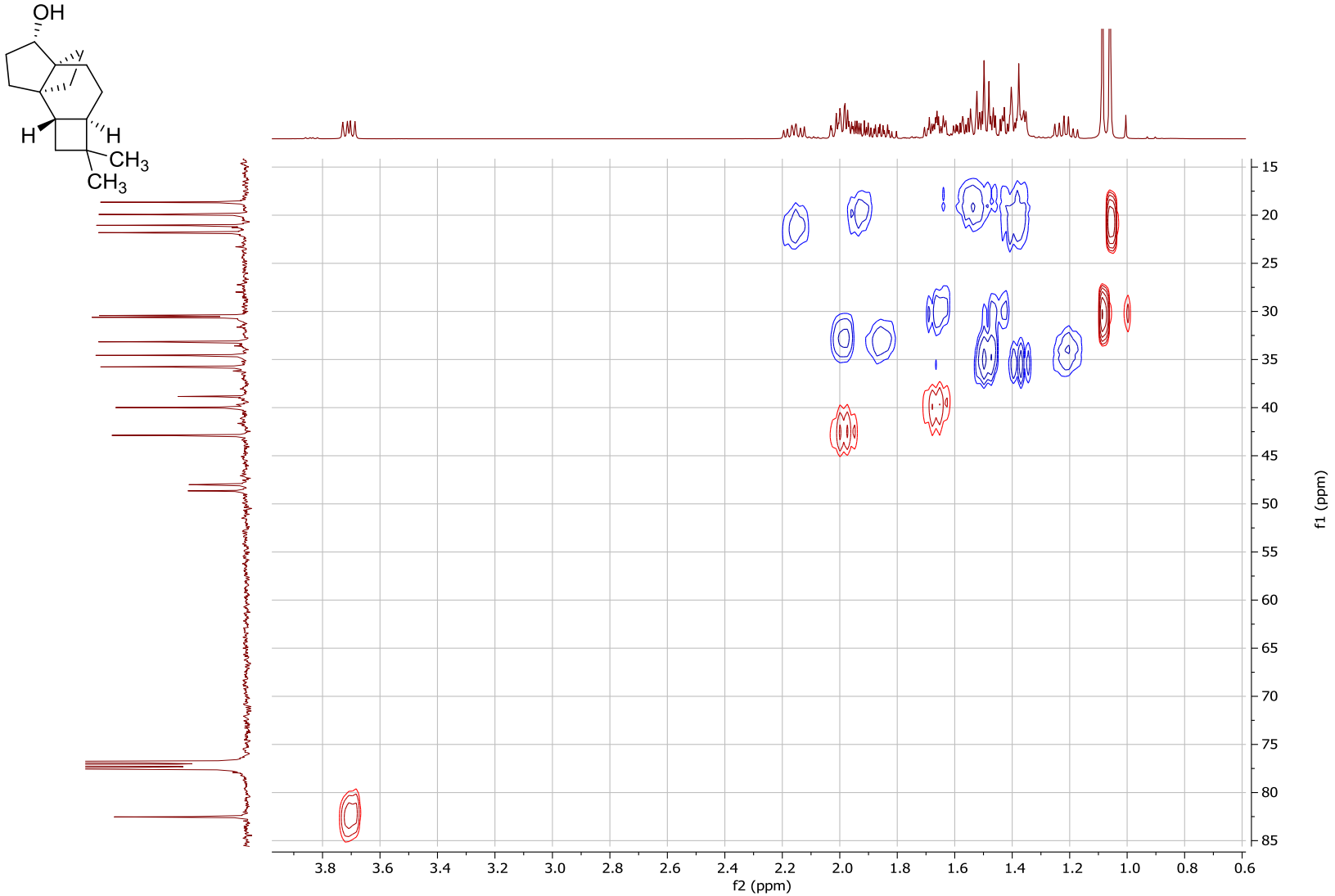
COSY of (2a*R*,4a*R*,5*S*,7a*R*,7b*S*)-2,2-dimethyloctahydro-5*H*-4a,7a-ethanocyclobuta[*e*]inden-5-ol (**9**)



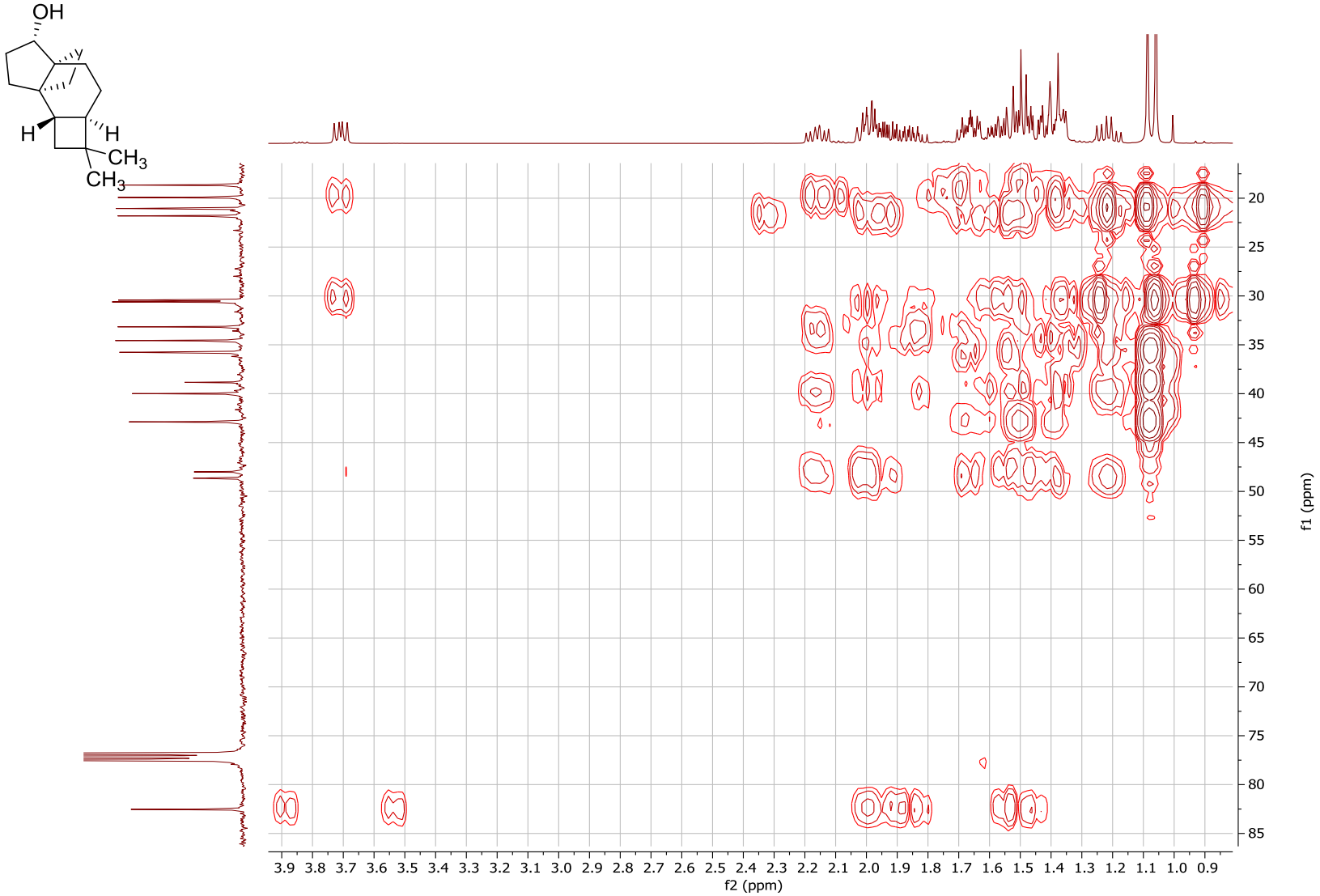
NOESY of (2a*R*,4a*R*,5*S*,7a*R*,7b*S*)-2,2-dimethyloctahydro-5*H*-4a,7a-ethanocyclobuta[*e*]inden-5-ol (**9**)



HSQC of (2a*R*,4a*R*,5*S*,7a*R*,7b*S*)-2,2-dimethyloctahydro-5*H*-4a,7a-ethanocyclobuta[*e*]inden-5-ol (**9**)

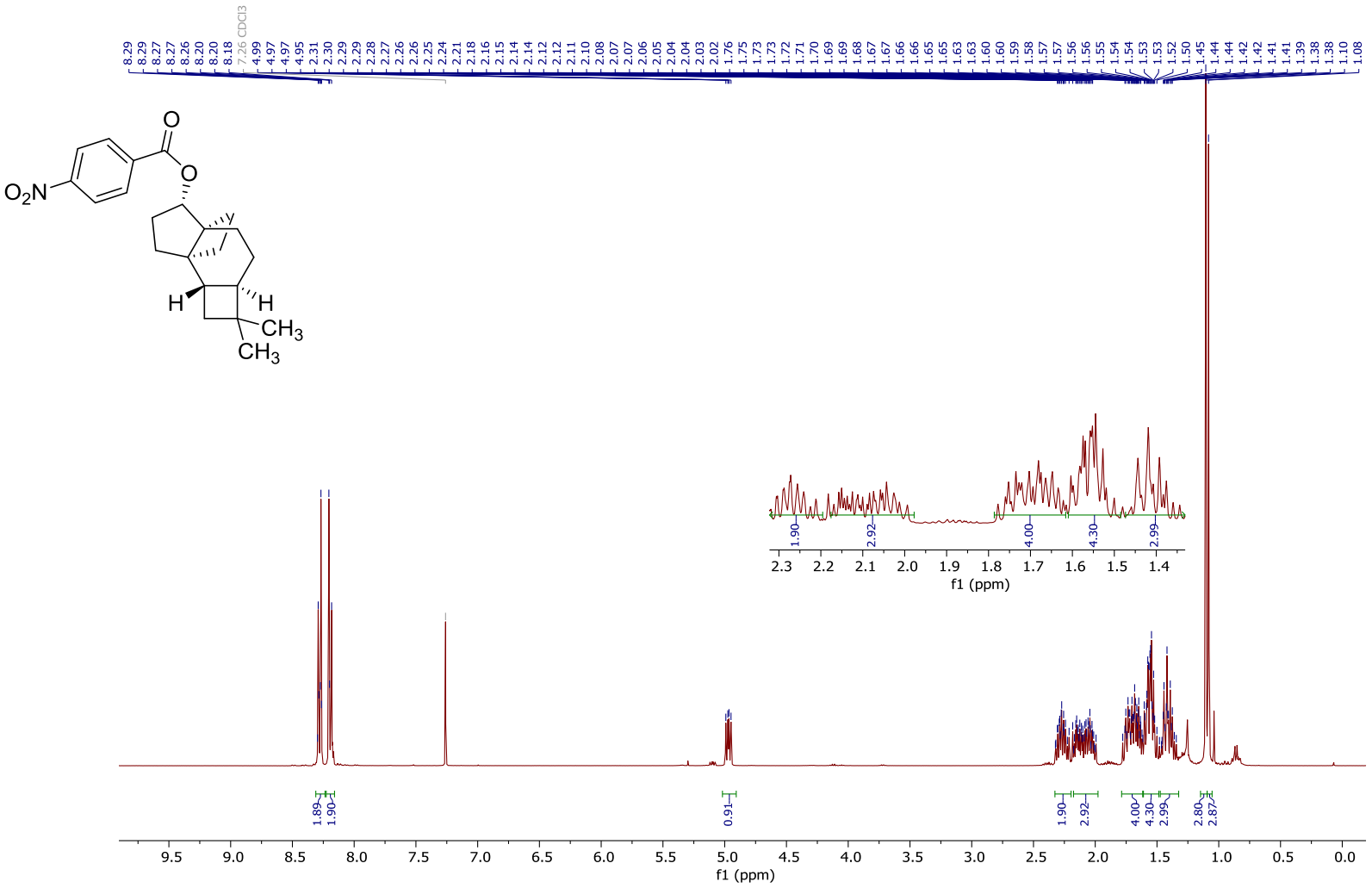


HMBC of (2a*R*,4a*R*,5*S*,7a*R*,7b*S*)-2,2-dimethyloctahydro-5*H*-4a,7a-ethanocyclobuta[*e*]inden-5-ol (**9**)

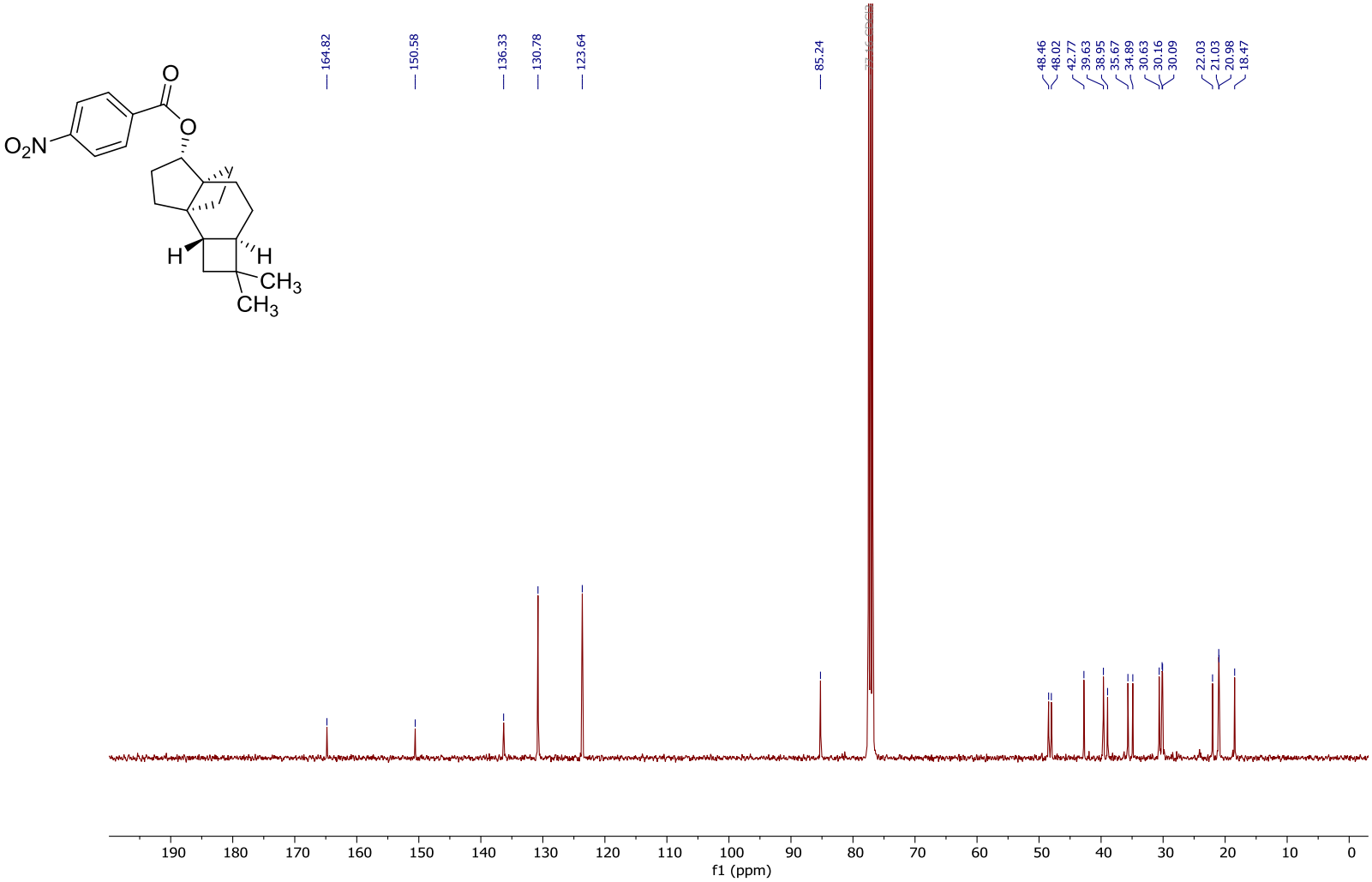


S5. NMR of (2a*R*,4a*R*,5*S*,7a*R*,7b*S*)-2,2-dimethyloctahydro-5*H*-4a,7a-ethanocyclobuta[*e*]inden-5-yl 4-nitrobenzoate (**13**)

^{1}H NMR (400 MHz, $CDCl_3$) of (2a*R*,4a*R*,5*S*,7a*R*,7b*S*)-2,2-dimethyloctahydro-5*H*-4a,7a-ethanocyclobuta[*e*]inden-5-yl 4-nitrobenzoate (**13**)

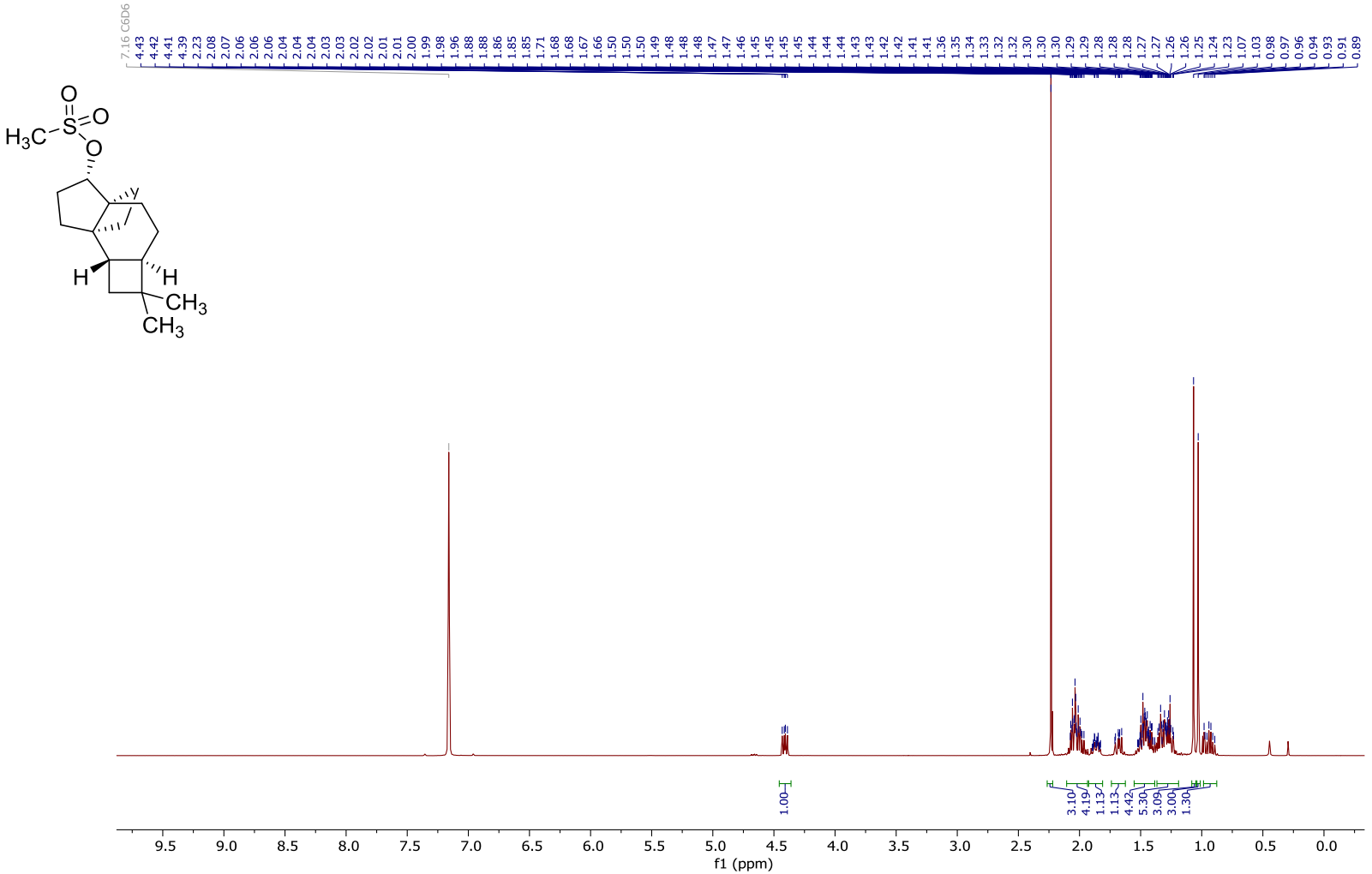


^{13}C NMR (101 MHz, $CDCl_3$) of (2a*R*,4a*R*,5*S*,7a*R*,7b*S*)-2,2-dimethyloctahydro-5*H*-4a,7a-ethanocyclobuta[*e*]inden-5-yl 4-nitrobenzoate (**13**)

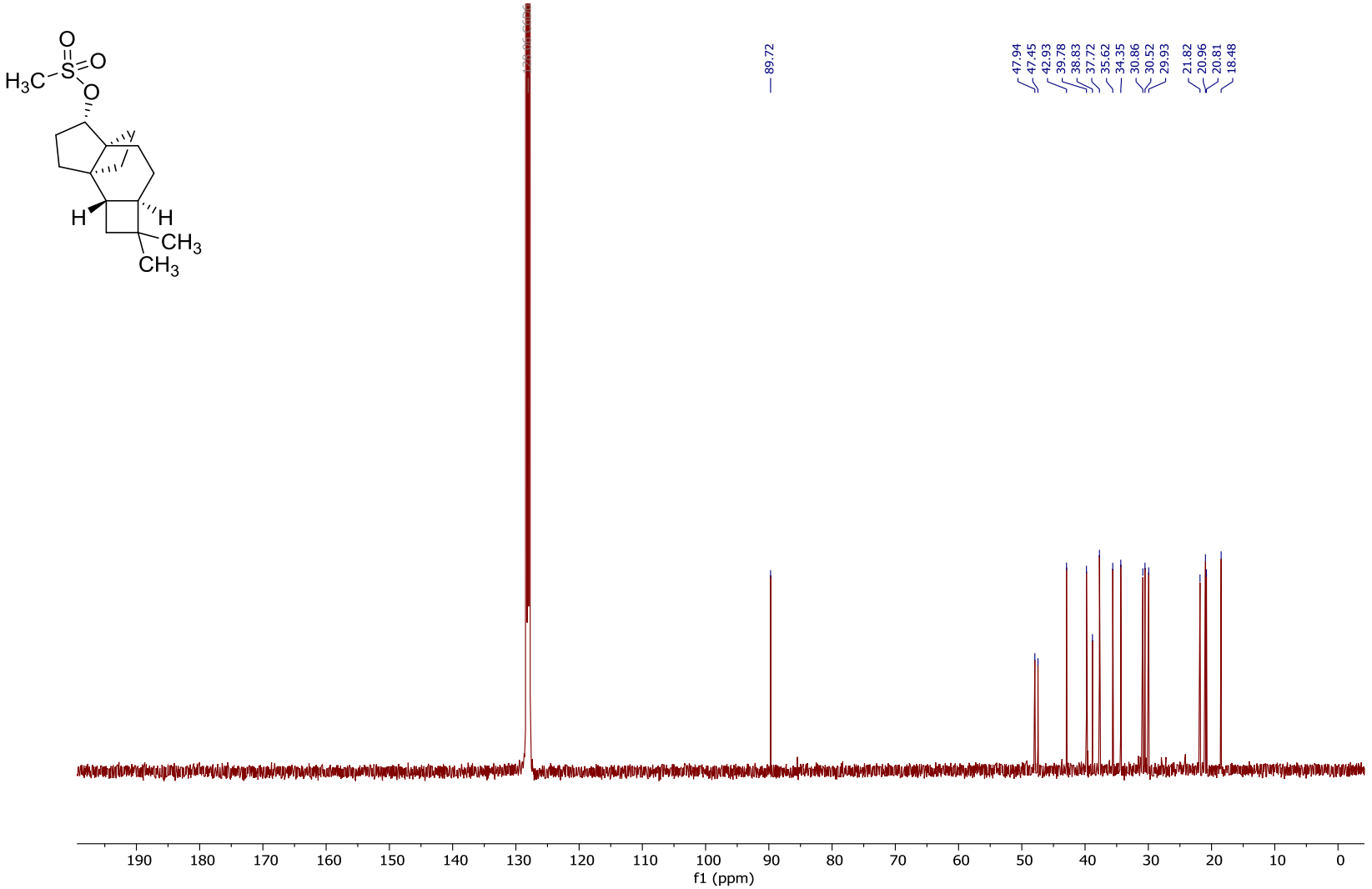


S6. NMR of (2a*R*,4a*R*,5*S*,7a*R*,7b*S*)-2,2-dimethyloctahydro-5*H*-4a,7a-ethanocyclobuta[*e*]inden-5-yl methanesulfonate (**14**)

^{1}H NMR (400 MHz, C_6D_6) of (2a*R*,4a*R*,5*S*,7a*R*,7b*S*)-2,2-dimethyloctahydro-5*H*-4a,7a-ethanocyclobuta[*e*]inden-5-yl methanesulfonate (**14**)

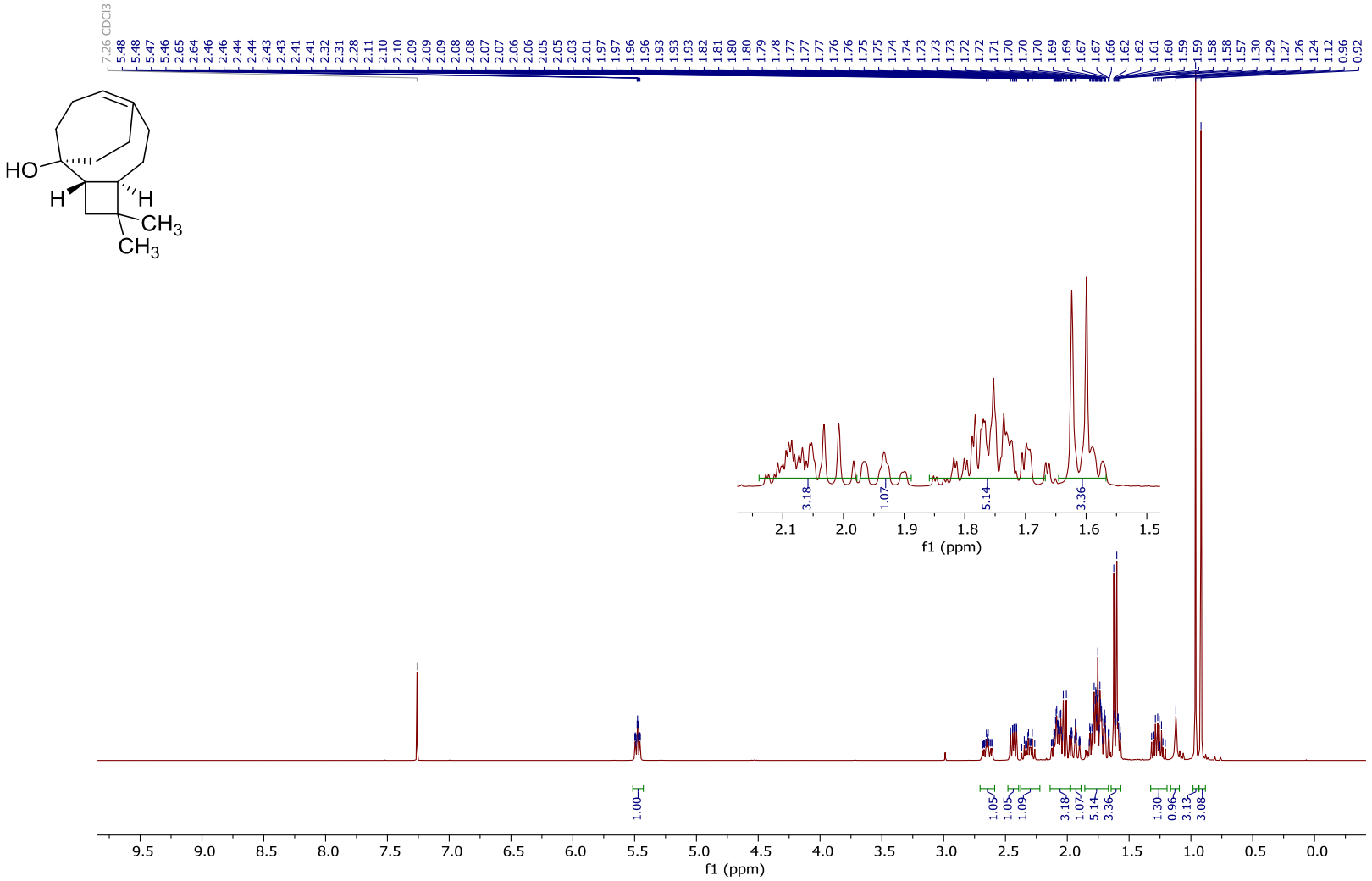


^{13}C NMR (101 MHz, C_6D_6) of (2a*R*,4a*R*,5*S*,7a*R*,7b*S*)-2,2-dimethyloctahydro-5*H*-4a,7a-ethanocyclobuta[*e*]inden-5-yl methanesulfonate (**14**)

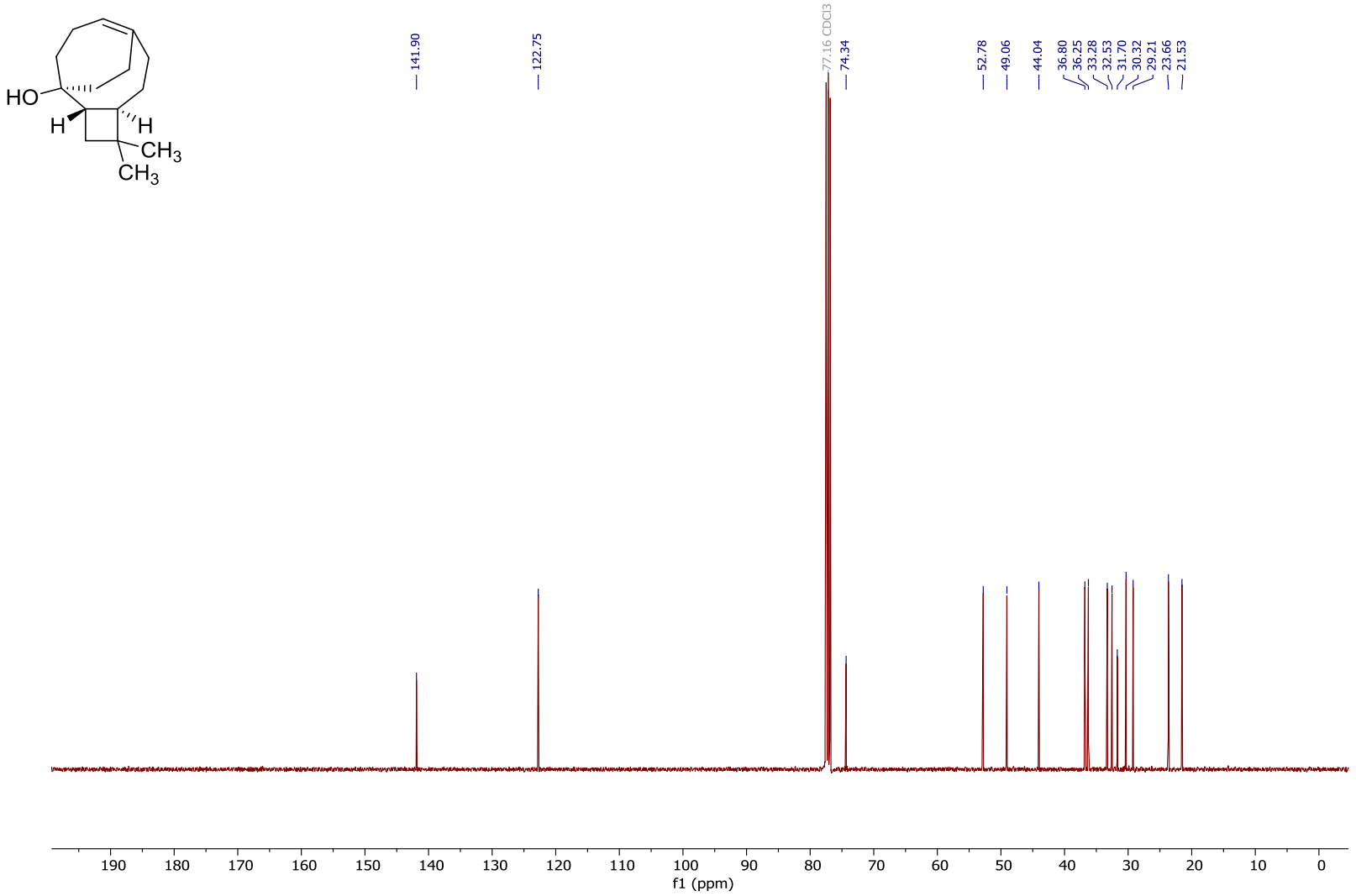


S7. NMR of (1*R*,2*S*,5*R*)-4,4-dimethyltricyclo[6.3.2.$0^{2,5}$]tridec-8-en-1-ol (**10**)

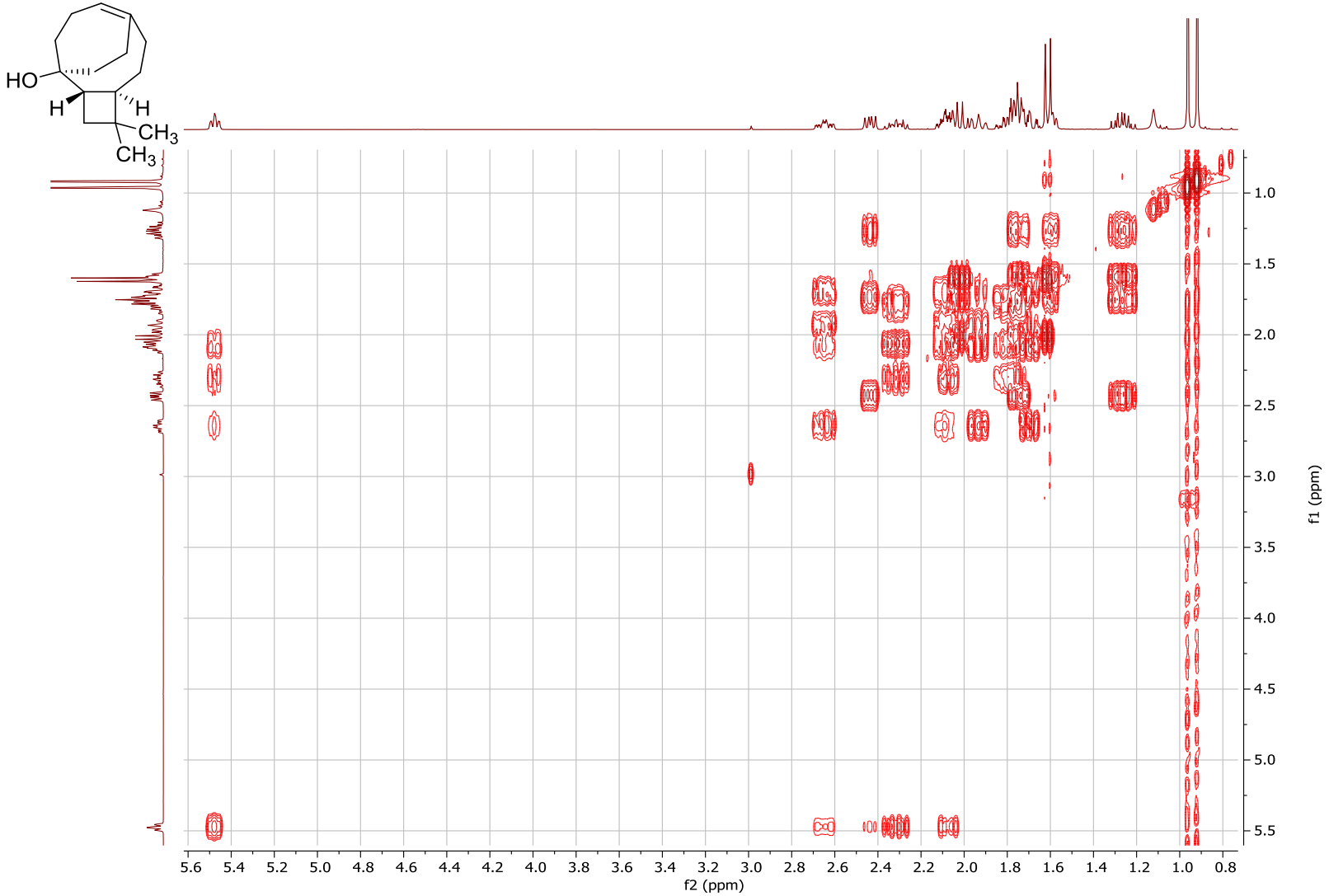
^{1}H NMR (400 MHz, $CDCl_3$) of (1*R*,2*S*,5*R*)-4,4-dimethyltricyclo[6.3.2.$0^{2,5}$]tridec-8-en-1-ol (**10**)



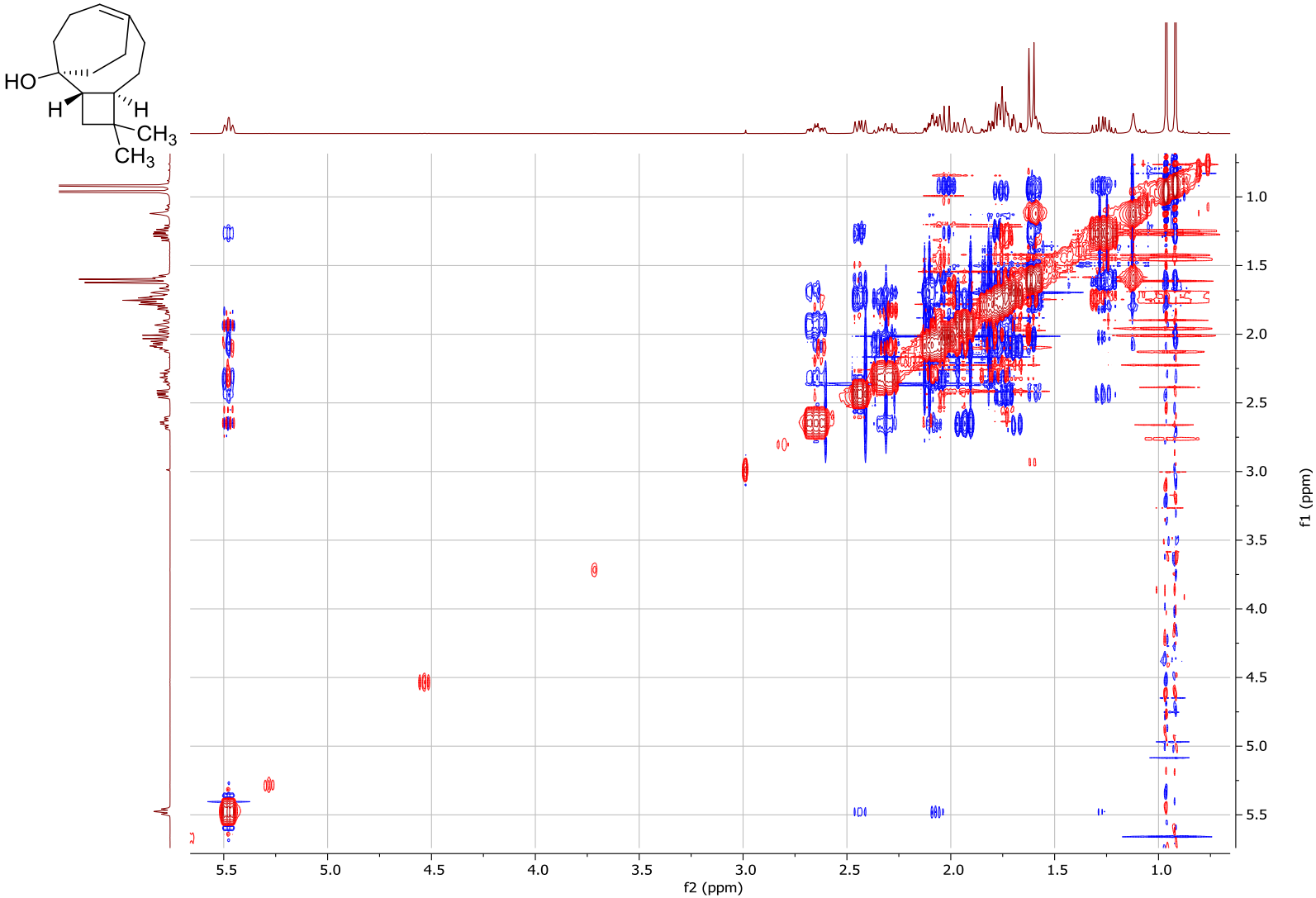
^{13}C NMR (400 MHz, $CDCl_3$) of (1*R*,2*S*,5*R*)-4,4-dimethyltricyclo[6.3.2.0^{2,5}]tridec-8-en-1-ol (**10**)



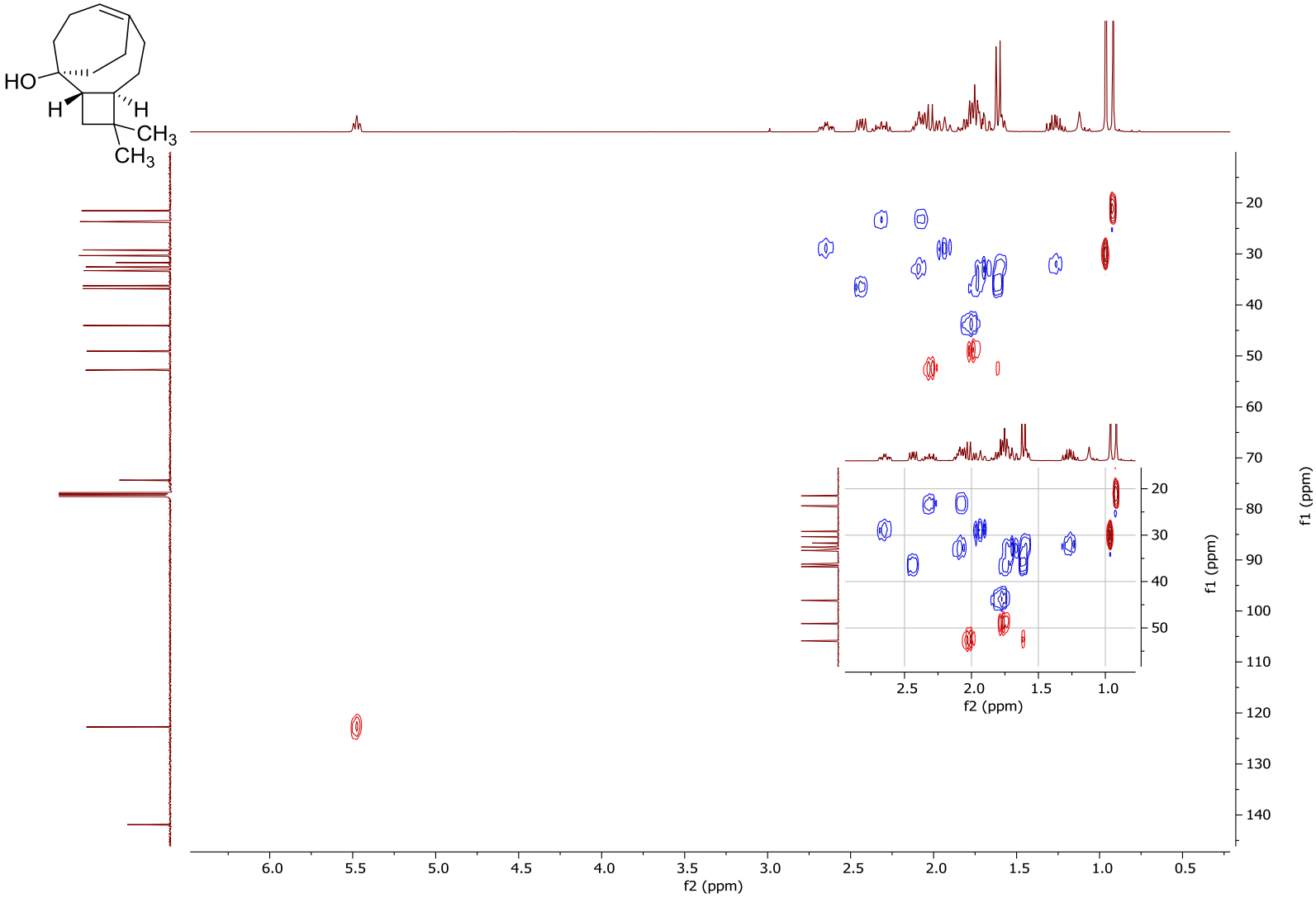
COSY of (1*R*,2*S*,5*R*)-4,4-dimethyltricyclo[6.3.2.0^{2,5}]tridec-8-en-1-ol (**10**)



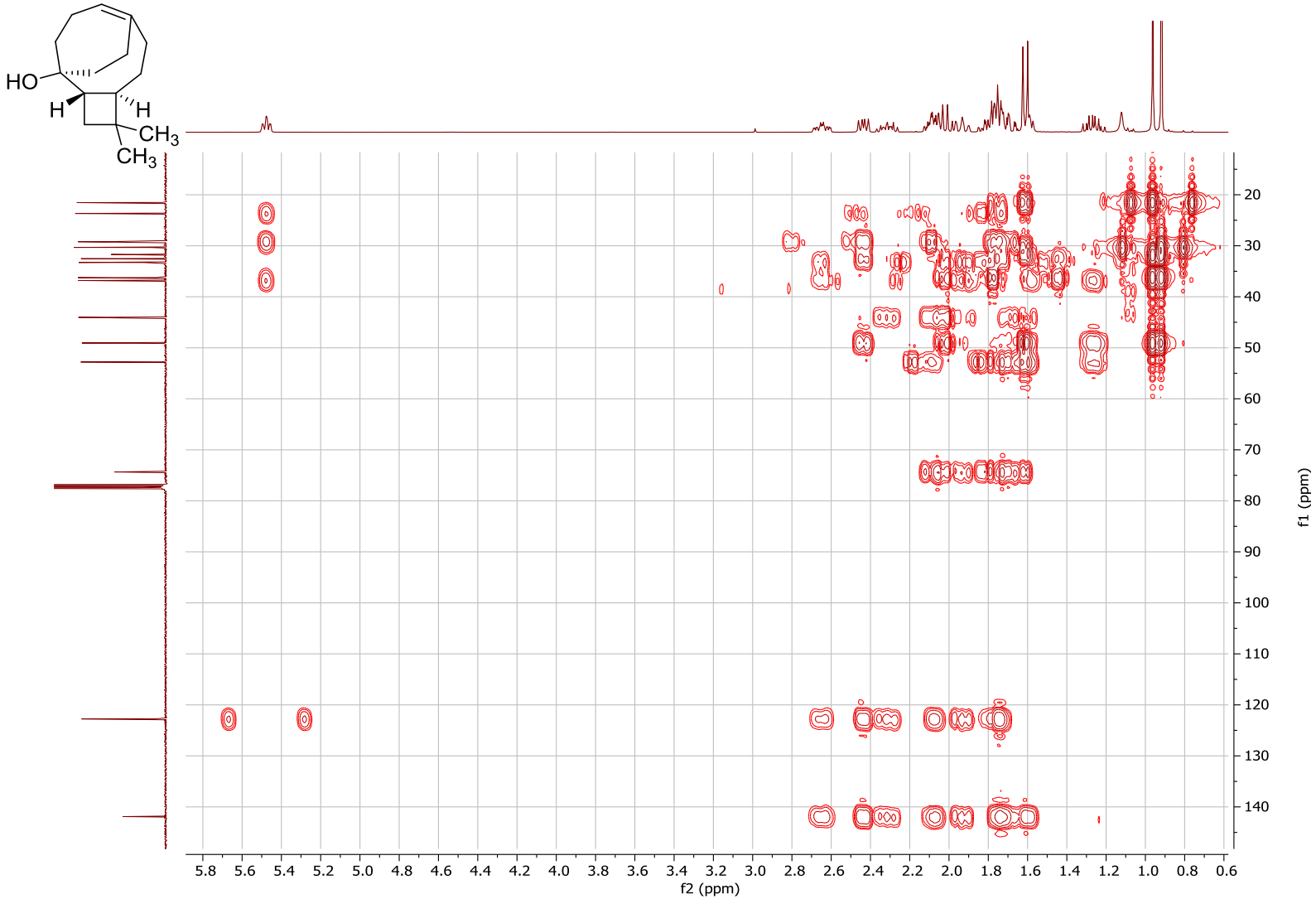
NOESY of (1*R*,2*S*,5*R*)-4,4-dimethyltricyclo[6.3.2.0^{2,5}]tridec-8-en-1-ol (**10**)



HSQC of (1*R*,2*S*,5*R*)-4,4-dimethyltricyclo[6.3.2.$0^{2,5}$]tridec-8-en-1-ol (**10**)

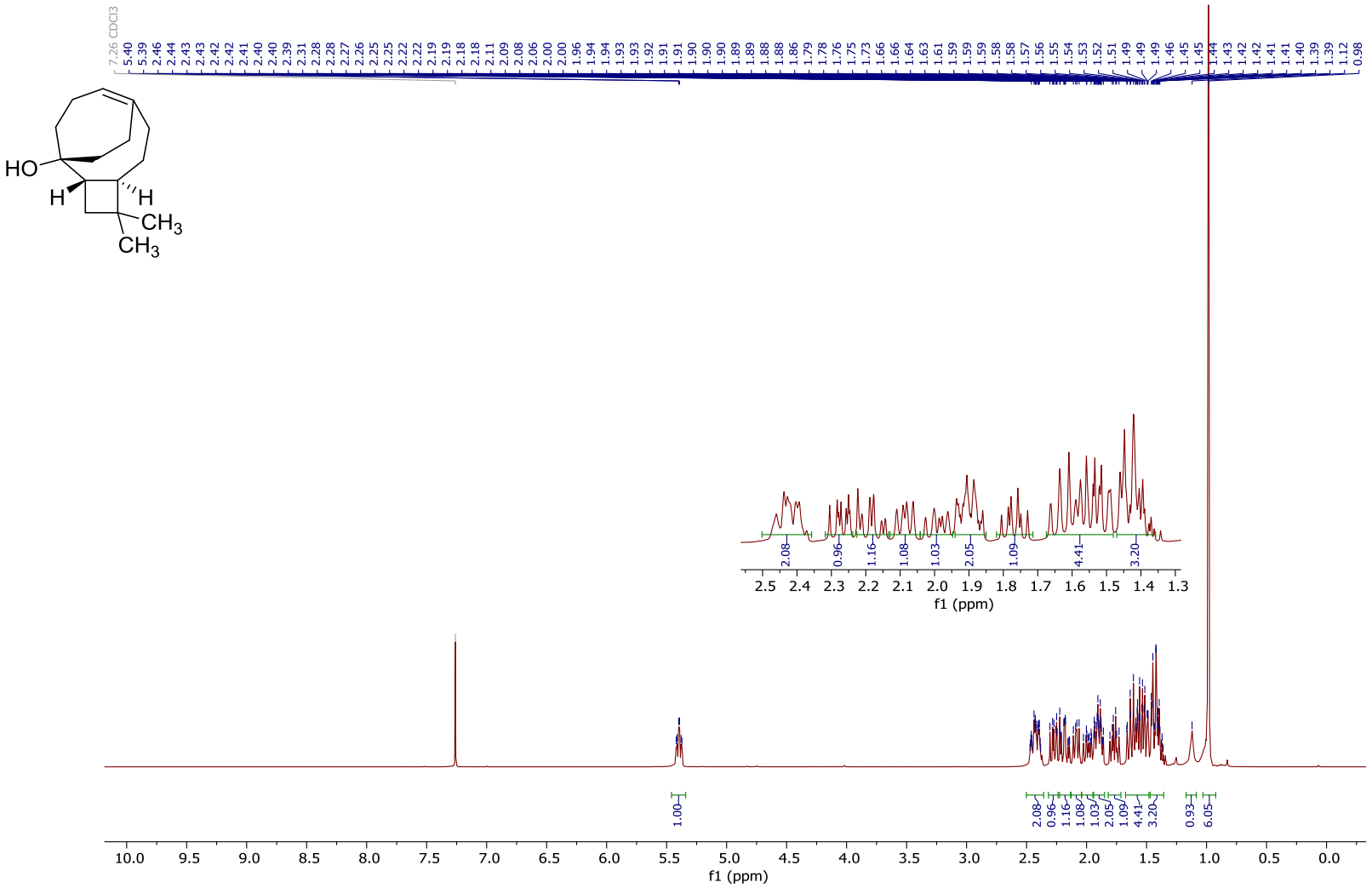


HMBC of (1*R*,2*S*,5*R*)-4,4-dimethyltricyclo[6.3.2.$0^{2,5}$]tridec-8-en-1-ol (**10**)

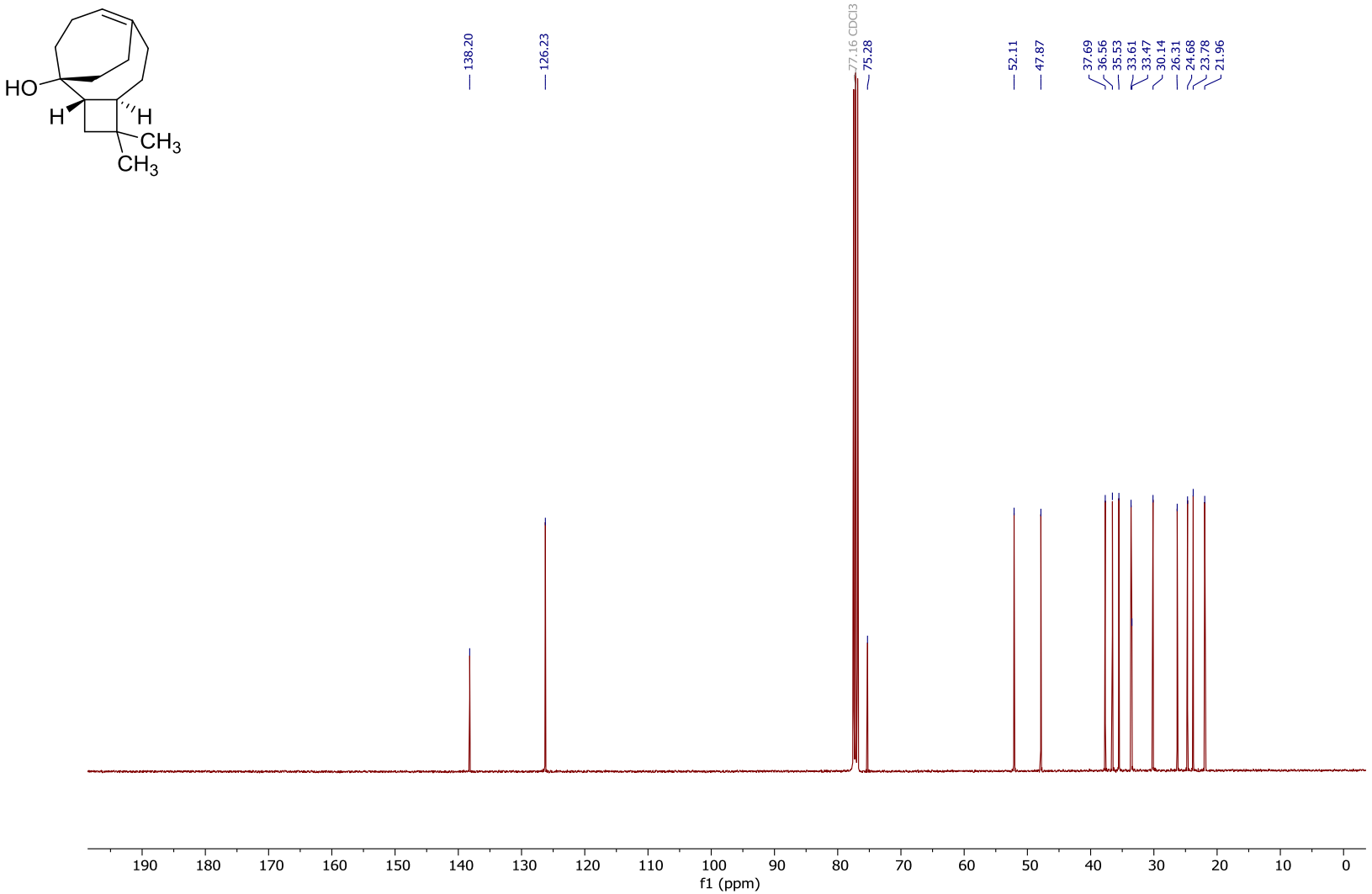


S8. NMR of (1*S*,2*S*,5*R*)-4,4-dimethyltricyclo[6.3.2.0^{2,5}]tridec-8-en-1-ol (**7**)

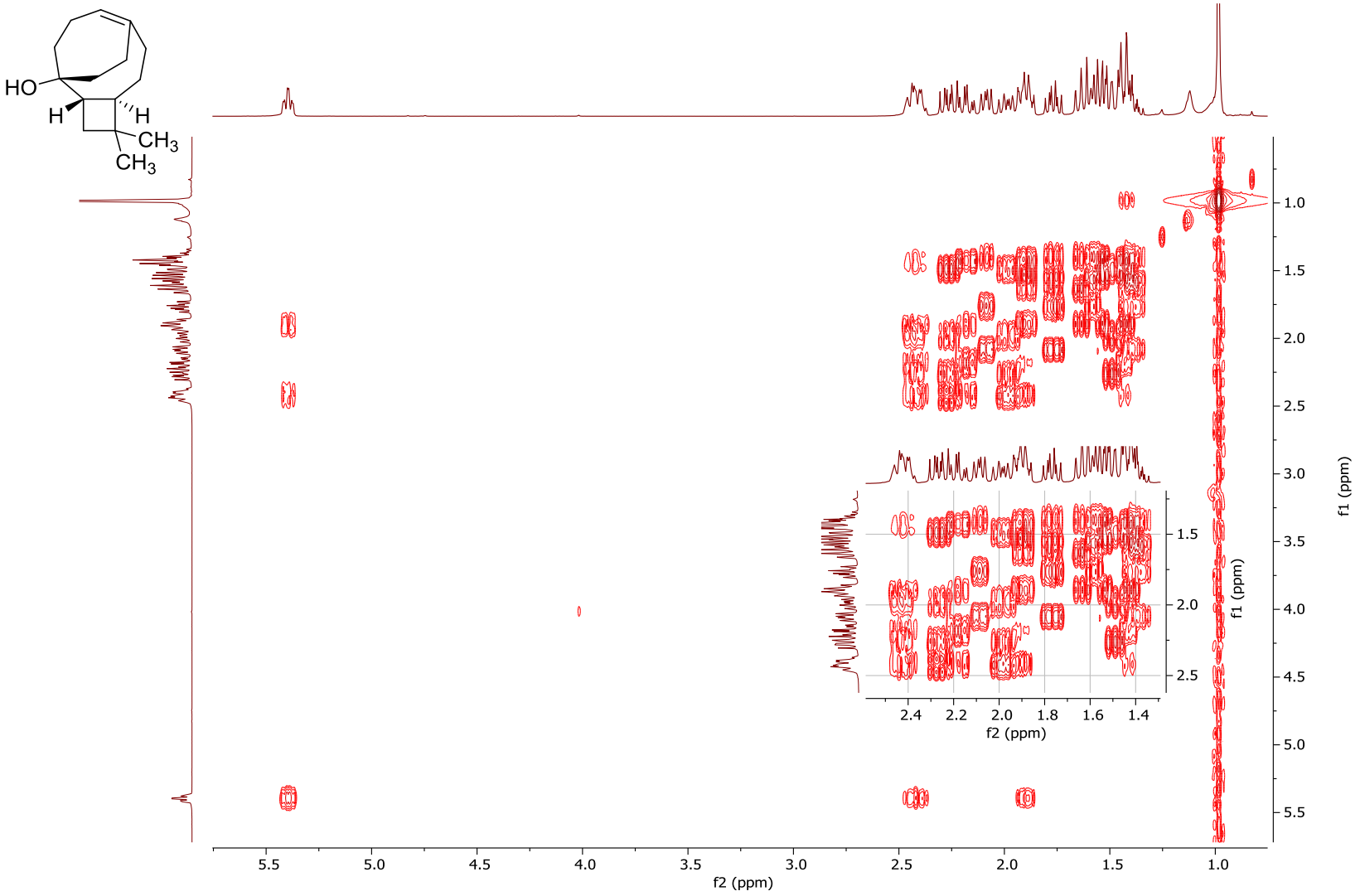
^{1}H NMR (400 MHz, $CDCl_3$) of (1*S*,2*S*,5*R*)-4,4-dimethyltricyclo[6.3.2.0^{2,5}]tridec-8-en-1-ol (**7**)



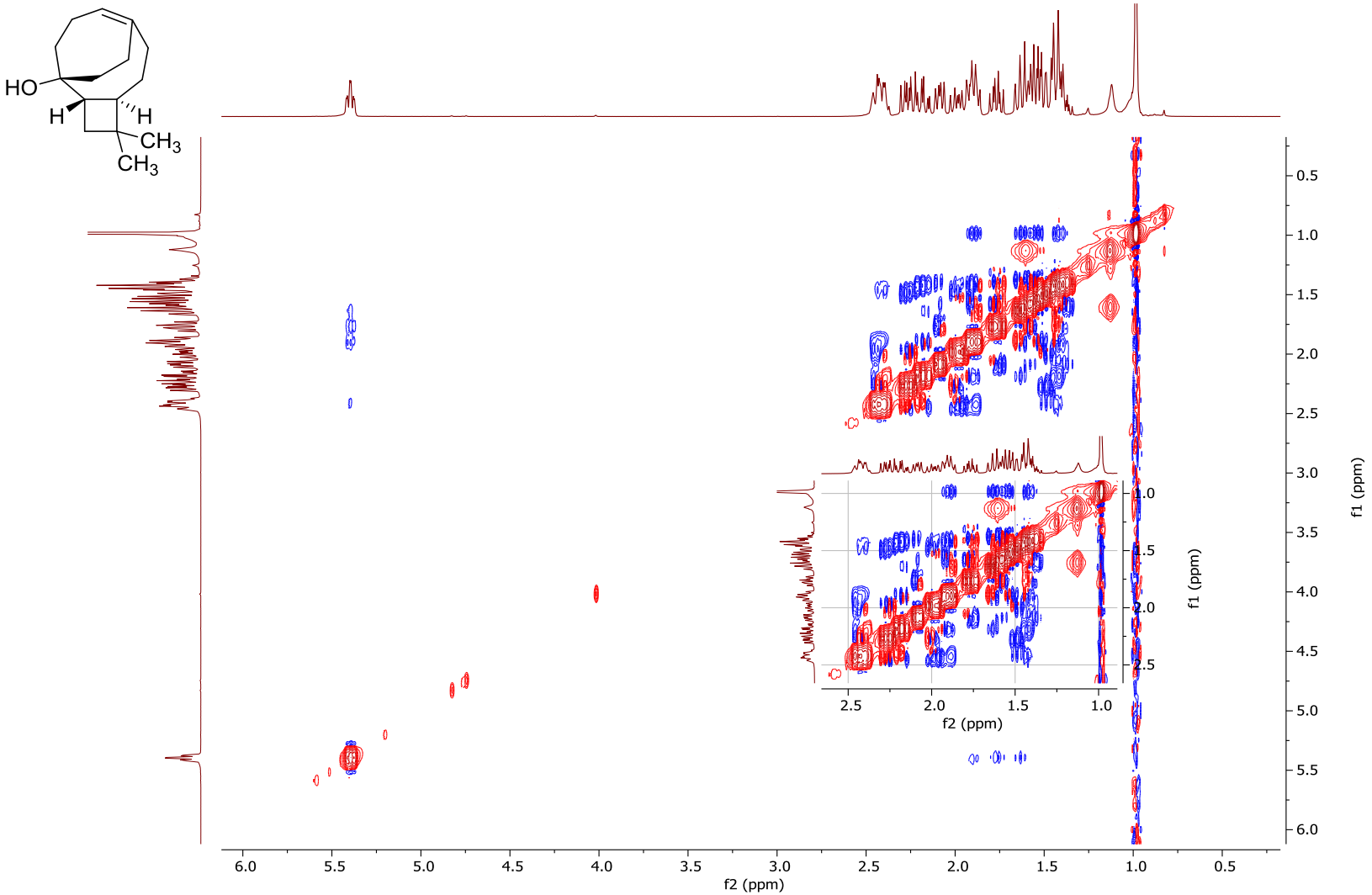
^{13}C NMR (101 MHz, $CDCl_3$) of (1*S*,2*S*,5*R*)-4,4-dimethyltricyclo[6.3.2.0^{2,5}]tridec-8-en-1-ol (**7**)



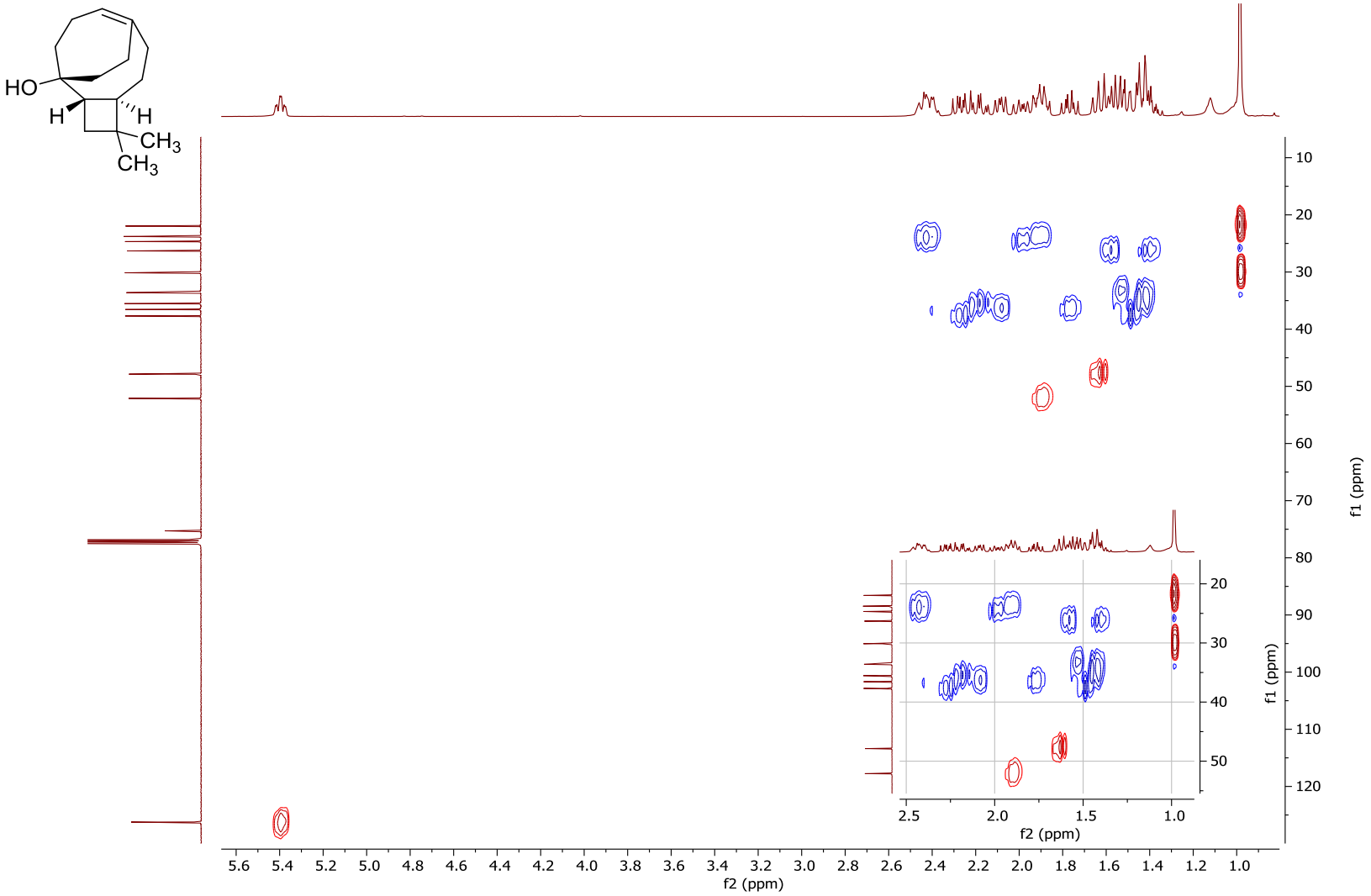
COSY of (1*S*,2*S*,5*R*)-4,4-dimethyltricyclo[6.3.2.0^{2,5}]tridec-8-en-1-ol (**7**)



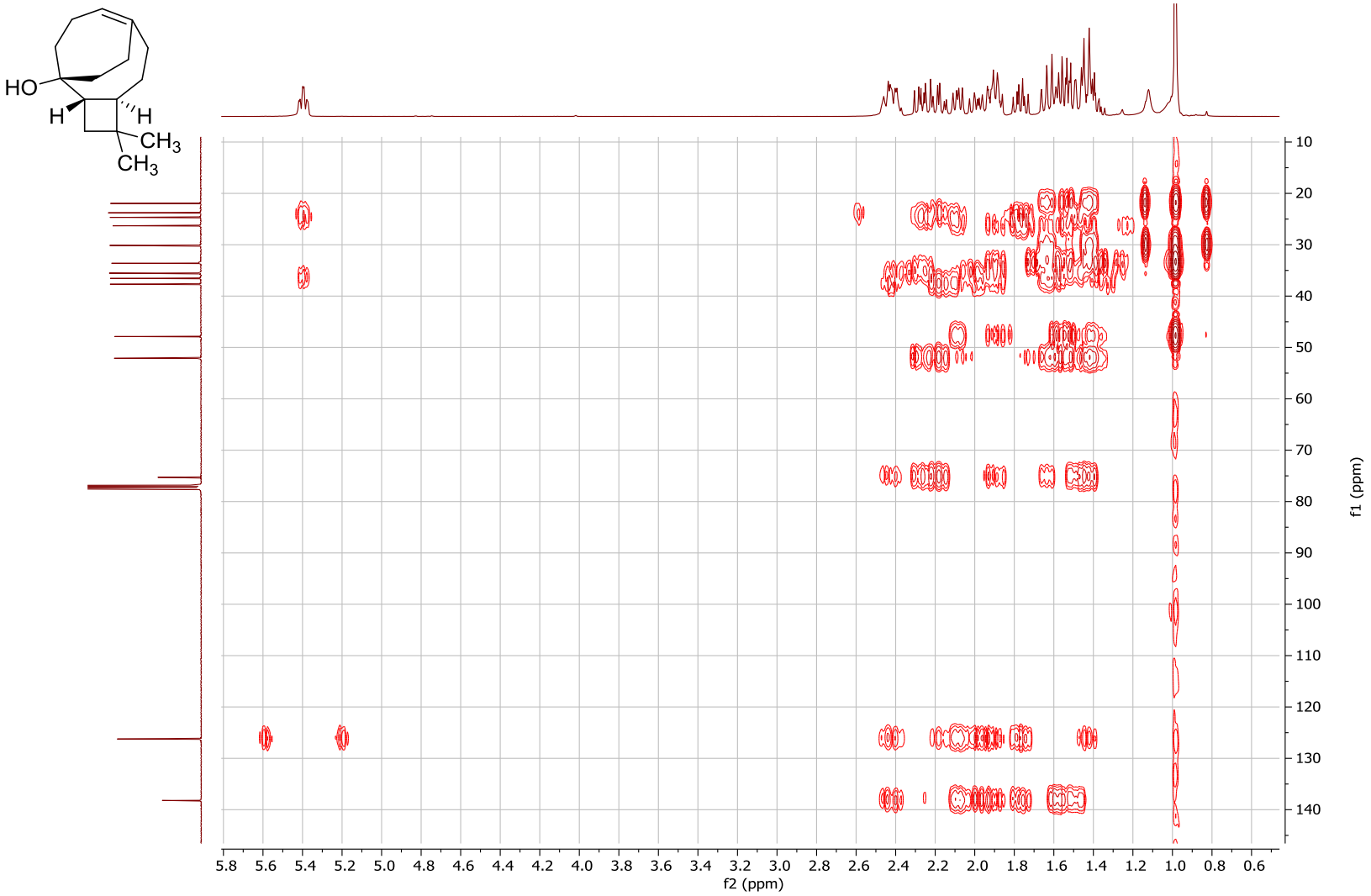
NOESY of (1*S*,2*S*,5*R*)-4,4-dimethyltricyclo[6.3.2.0^{2,5}]tridec-8-en-1-ol (**7**)



HSQC of (1*S*,2*S*,5*R*)-4,4-dimethyltricyclo[6.3.2.0^{2,5}]tridec-8-en-1-ol (**7**)

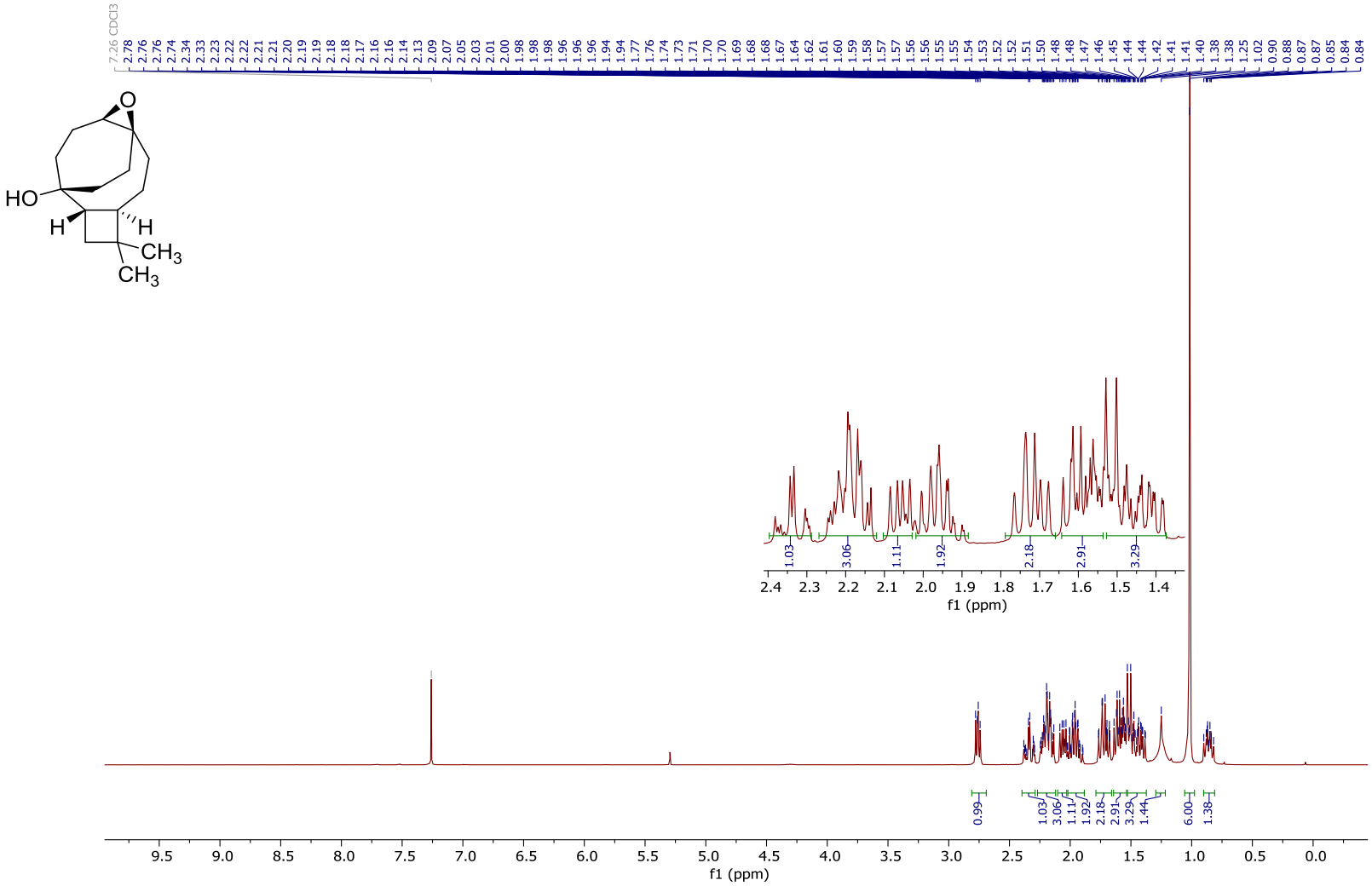


HMBC of (1*S*,2*S*,5*R*)-4,4-dimethyltricyclo[6.3.2.$0^{2,5}$]tridec-8-en-1-ol (**7**)

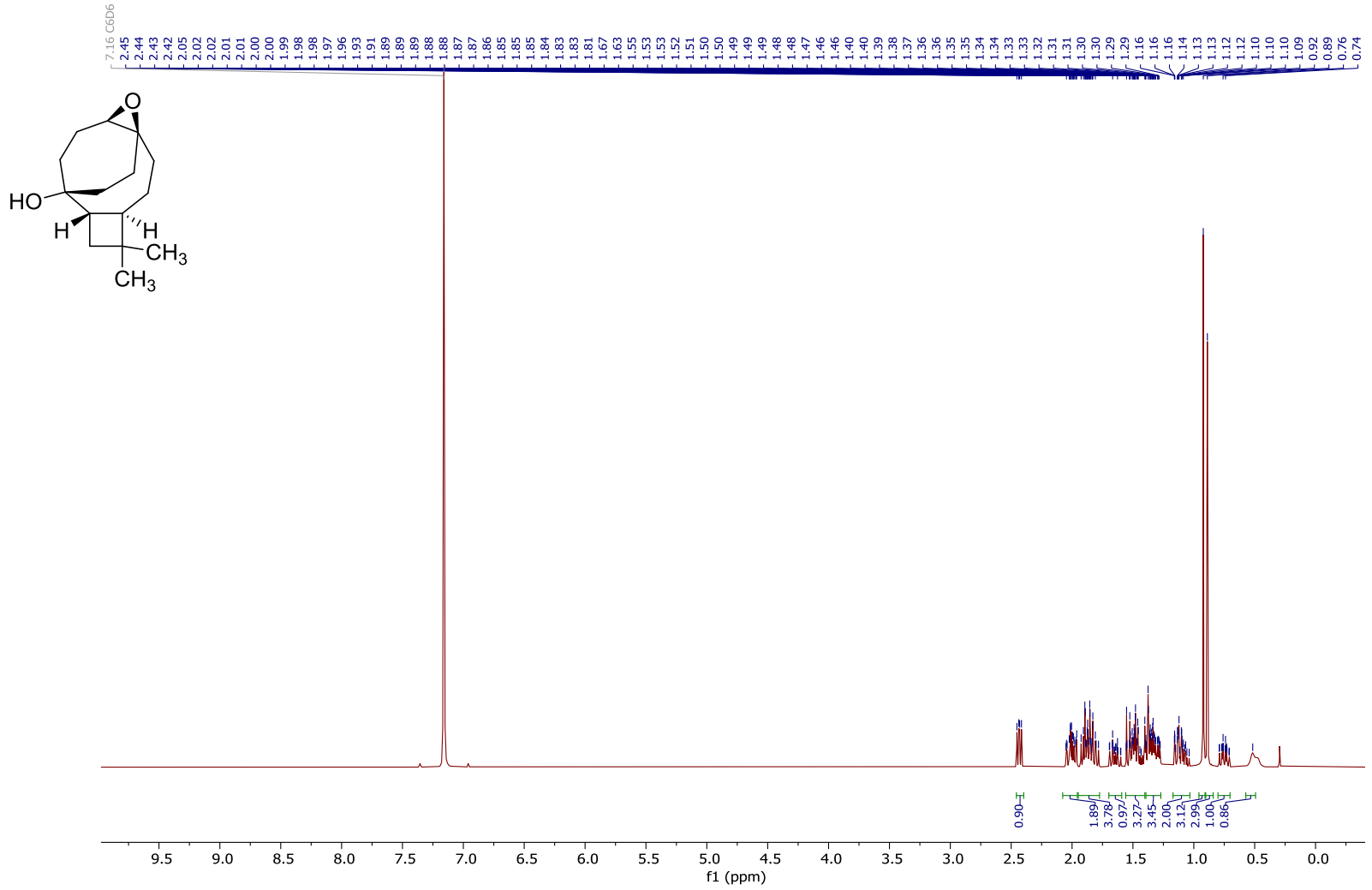


S9. NMR of euphoranin E (**2**)

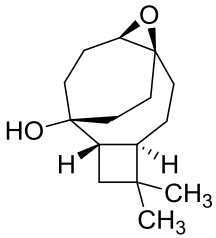
^{1}H NMR (400 MHz, $CDCl_3$) of euphoranin E (**2**)



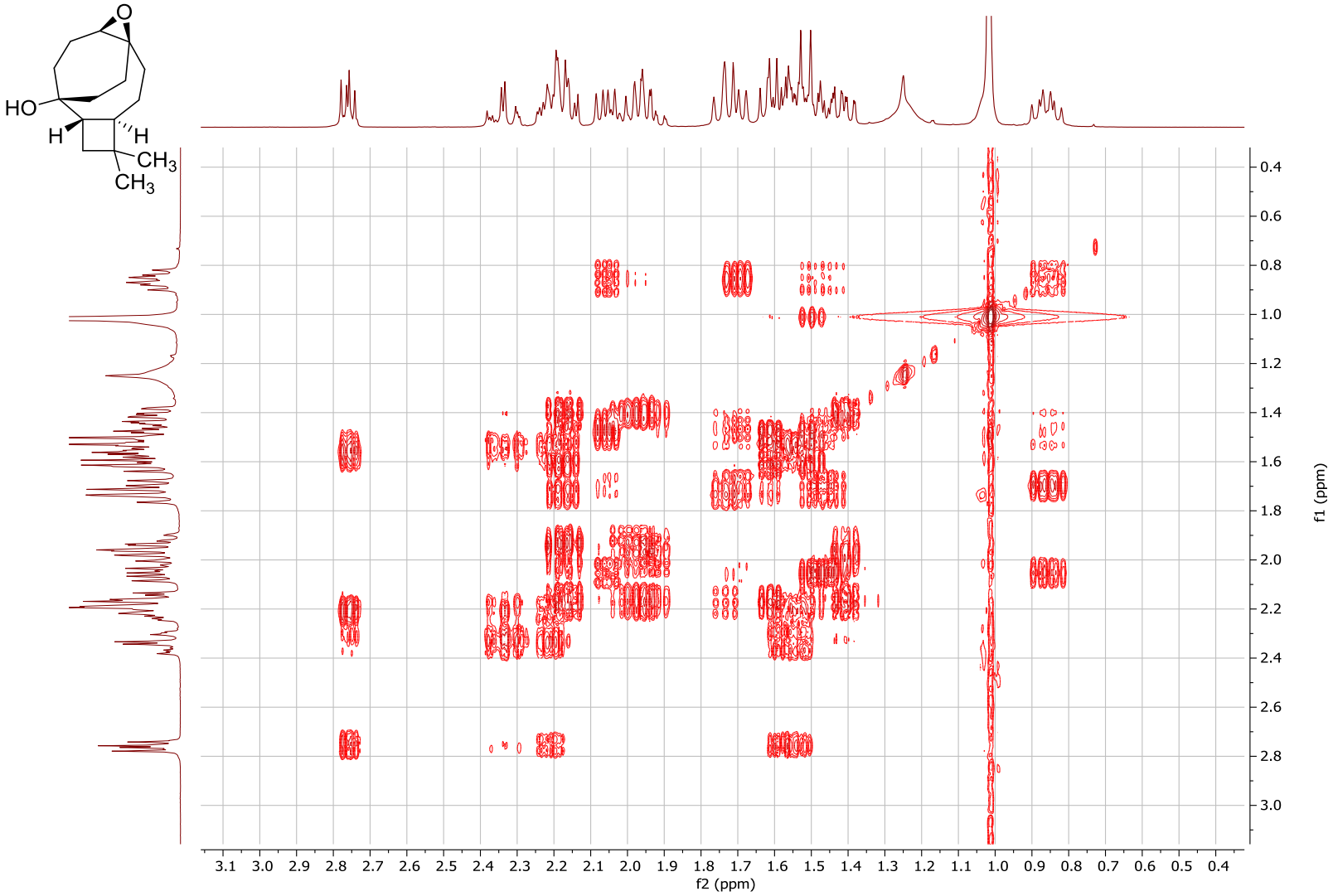
^{1}H NMR (400 MHz, C_6D_6) of euphoranin E (**2**)



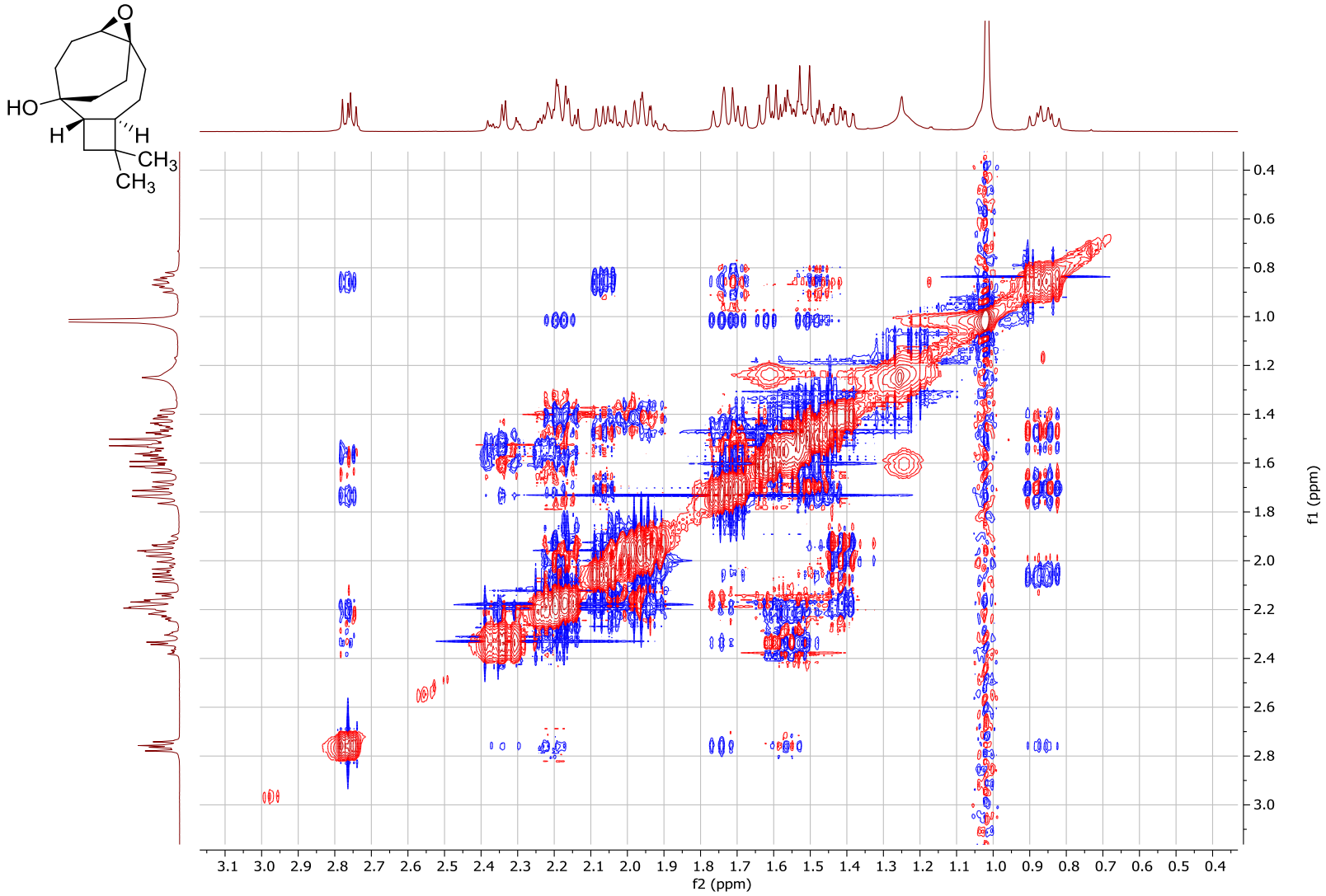
^{13}C NMR (101 MHz, $CDCl_3$) of euphoranin E (**2**)



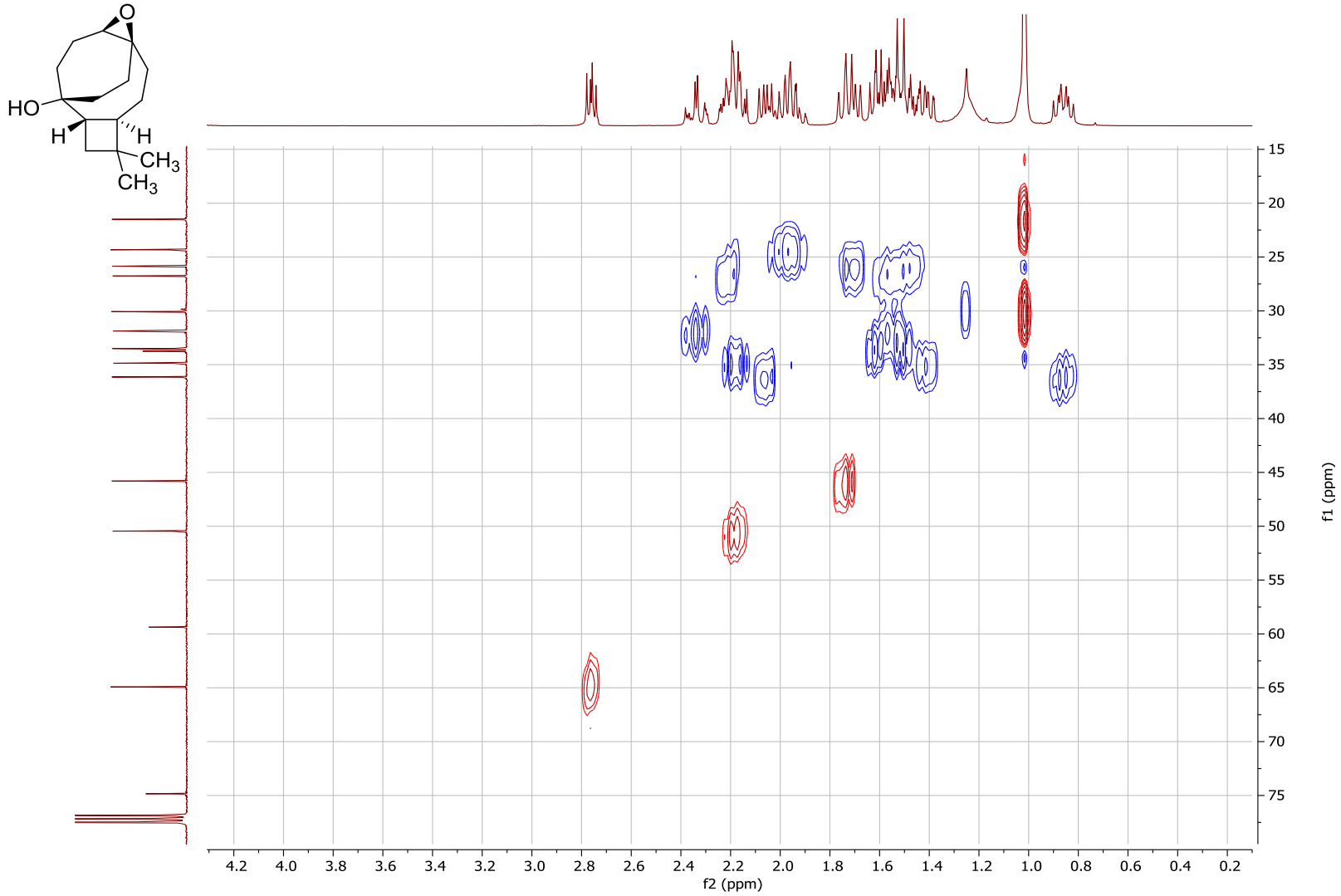
COSY of euphoranin E (**2**)



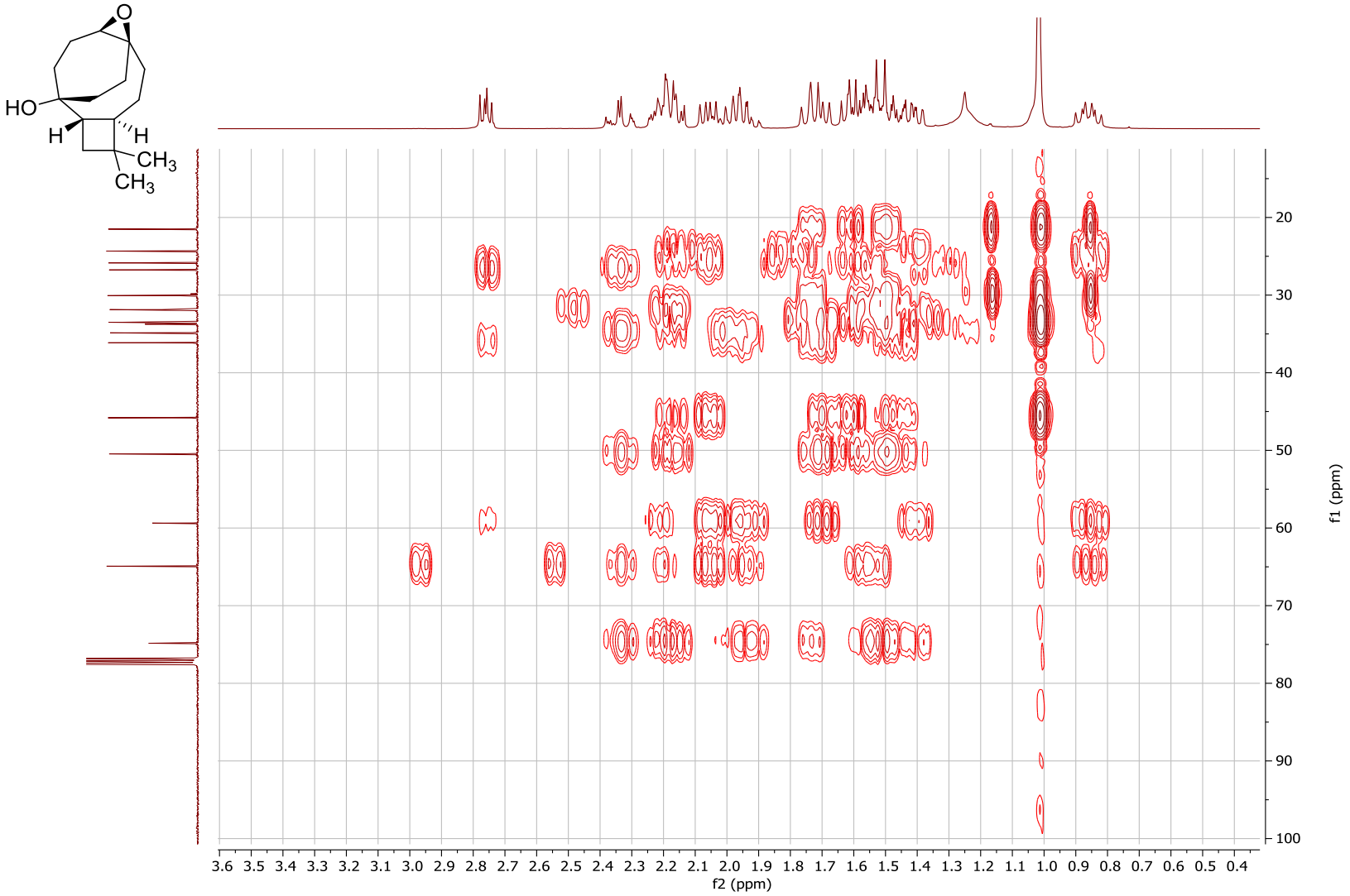
NOESY of euphoranin E (**2**)



HSQC of euphoranin E (**2**)

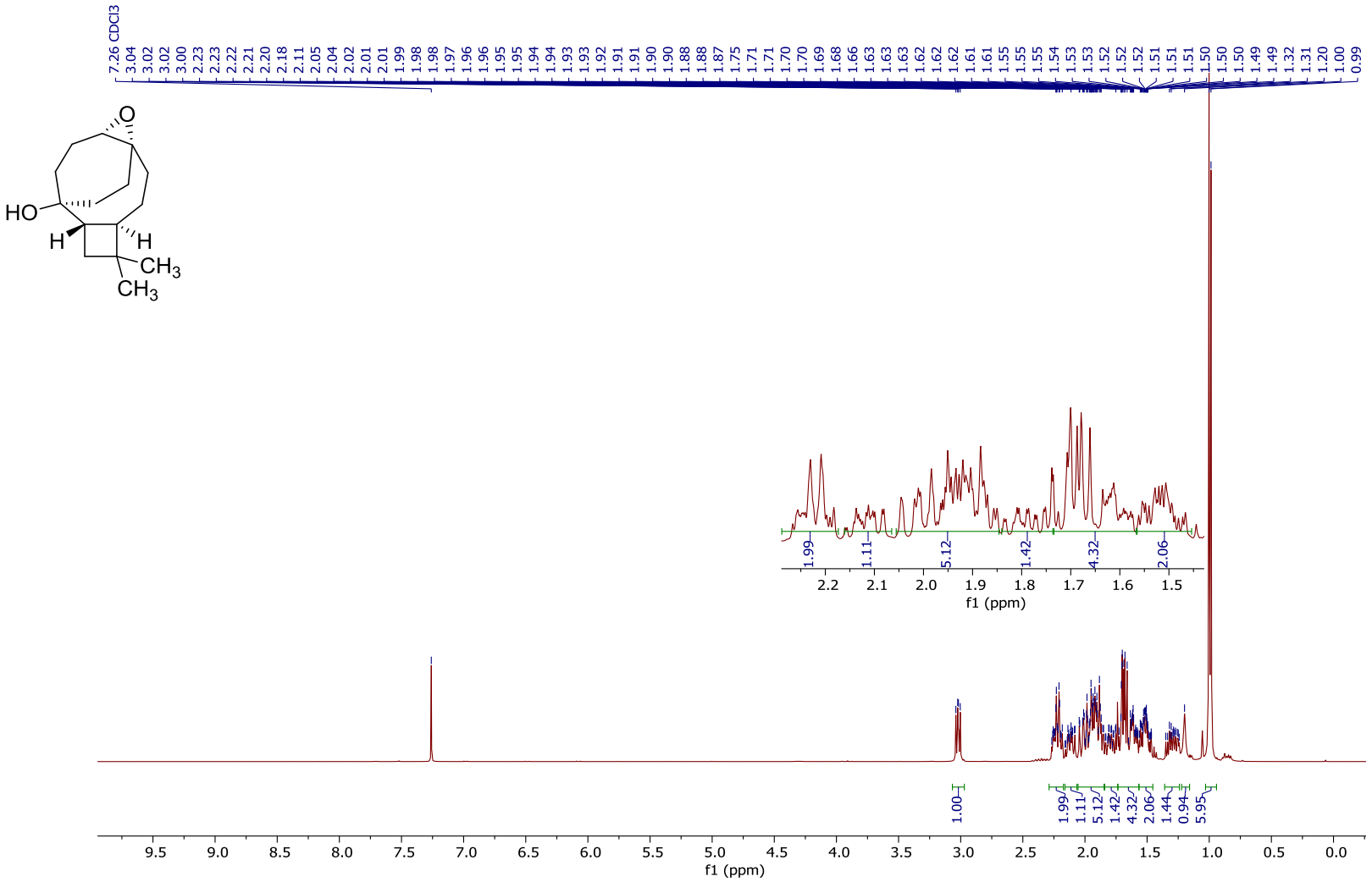


HMBC of euphoranin E (**2**)

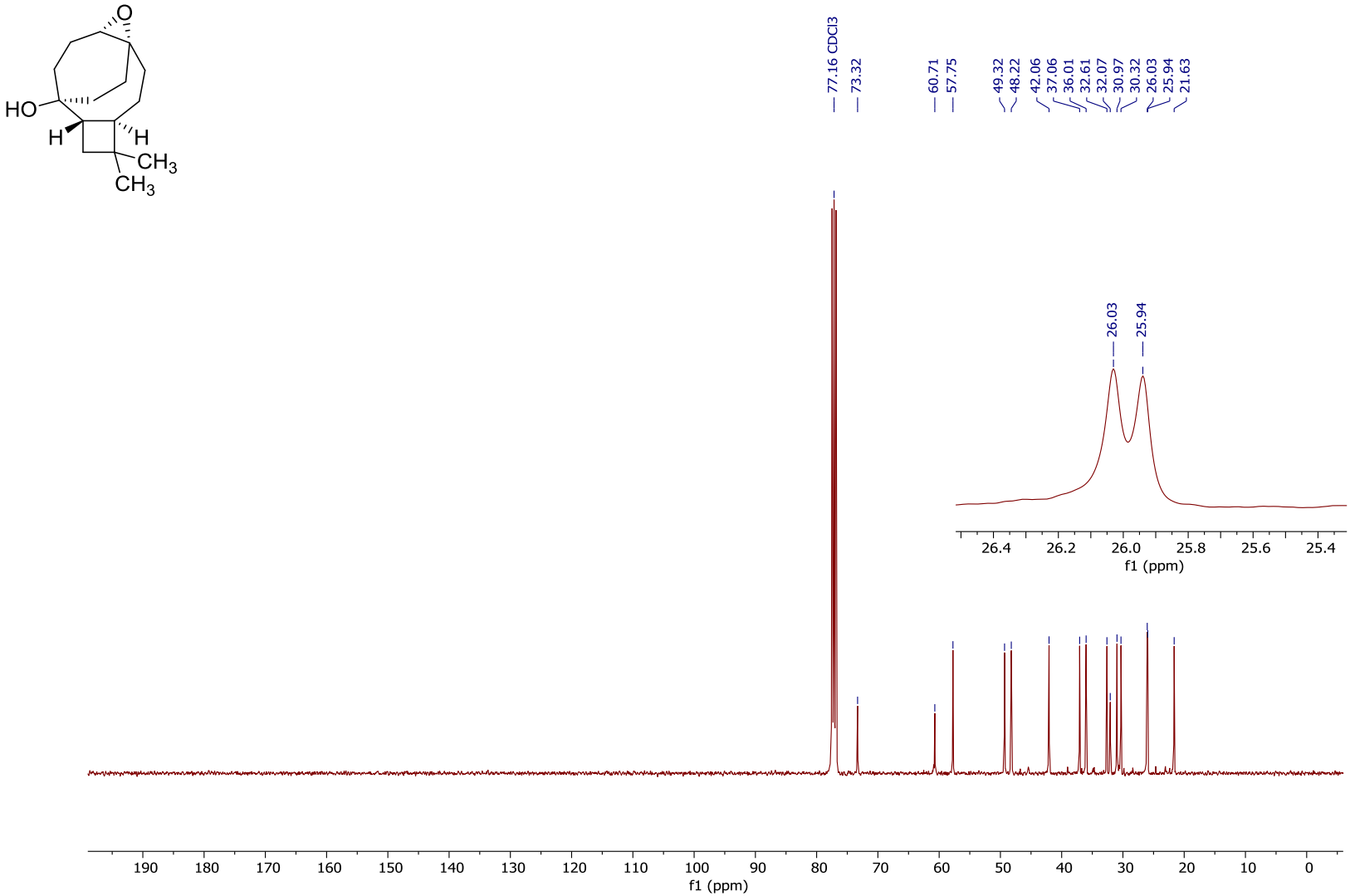


S10. NMR of *iso*-euphoranin E (**11**)

^{1}H NMR (400 MHz, $CDCl_3$) of *iso*-euphoranin E (**11**)

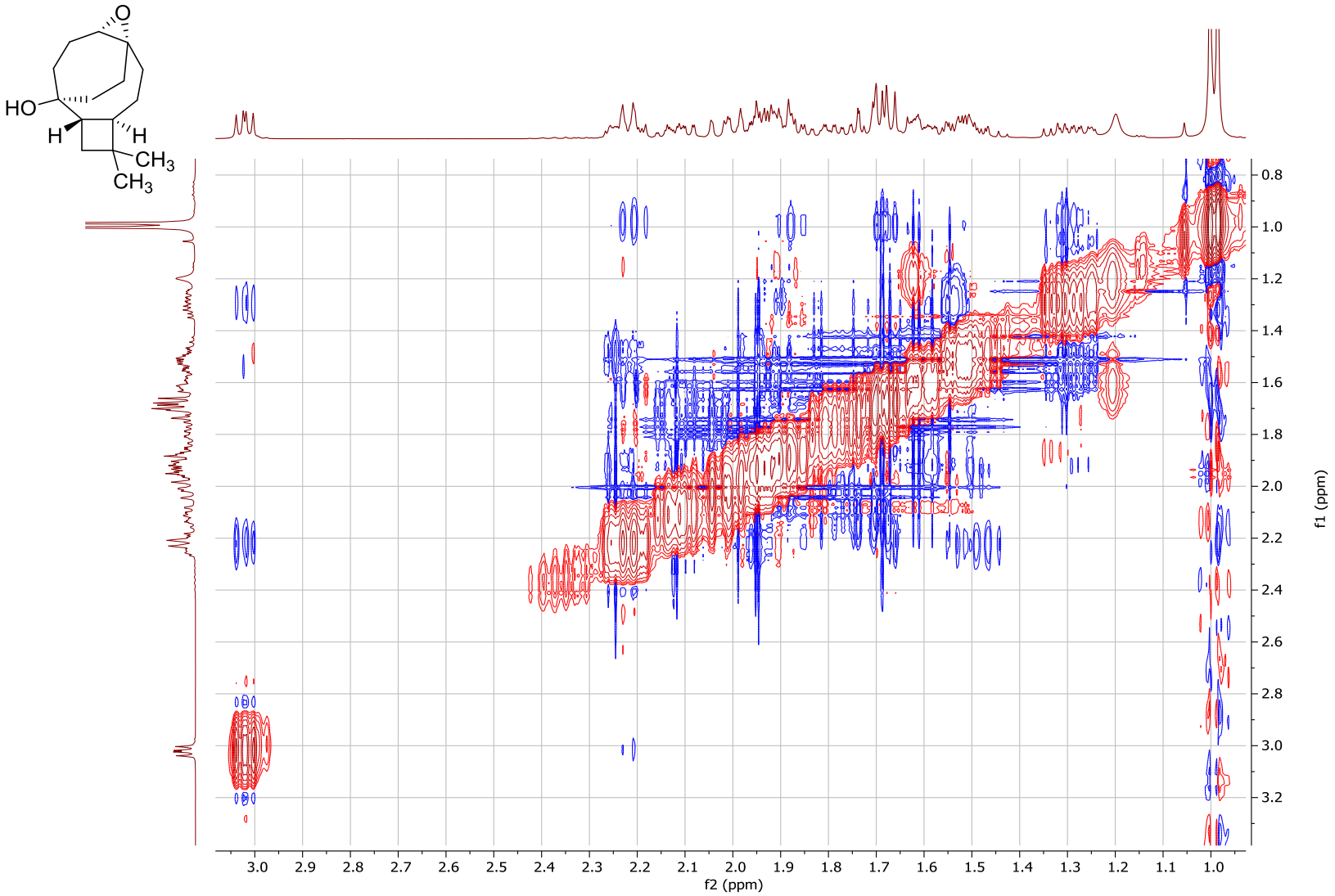


^{13}C NMR (101 MHz, $CDCl_3$) of *iso*-euphoranin E (**11**)



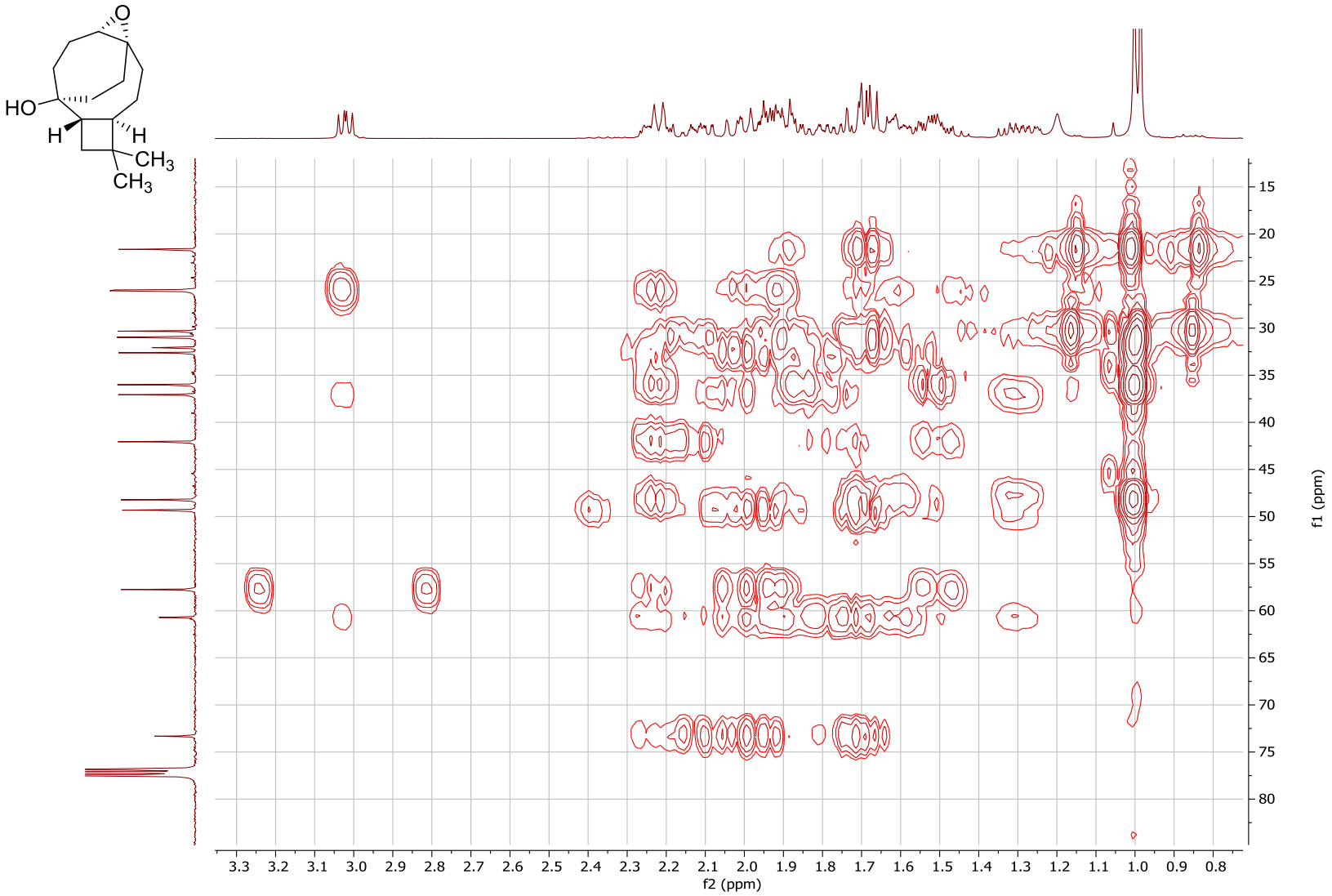
COSY of *iso*-euphoranin E (**11**)

NOESY of *iso*-euphoranin E (**11**)



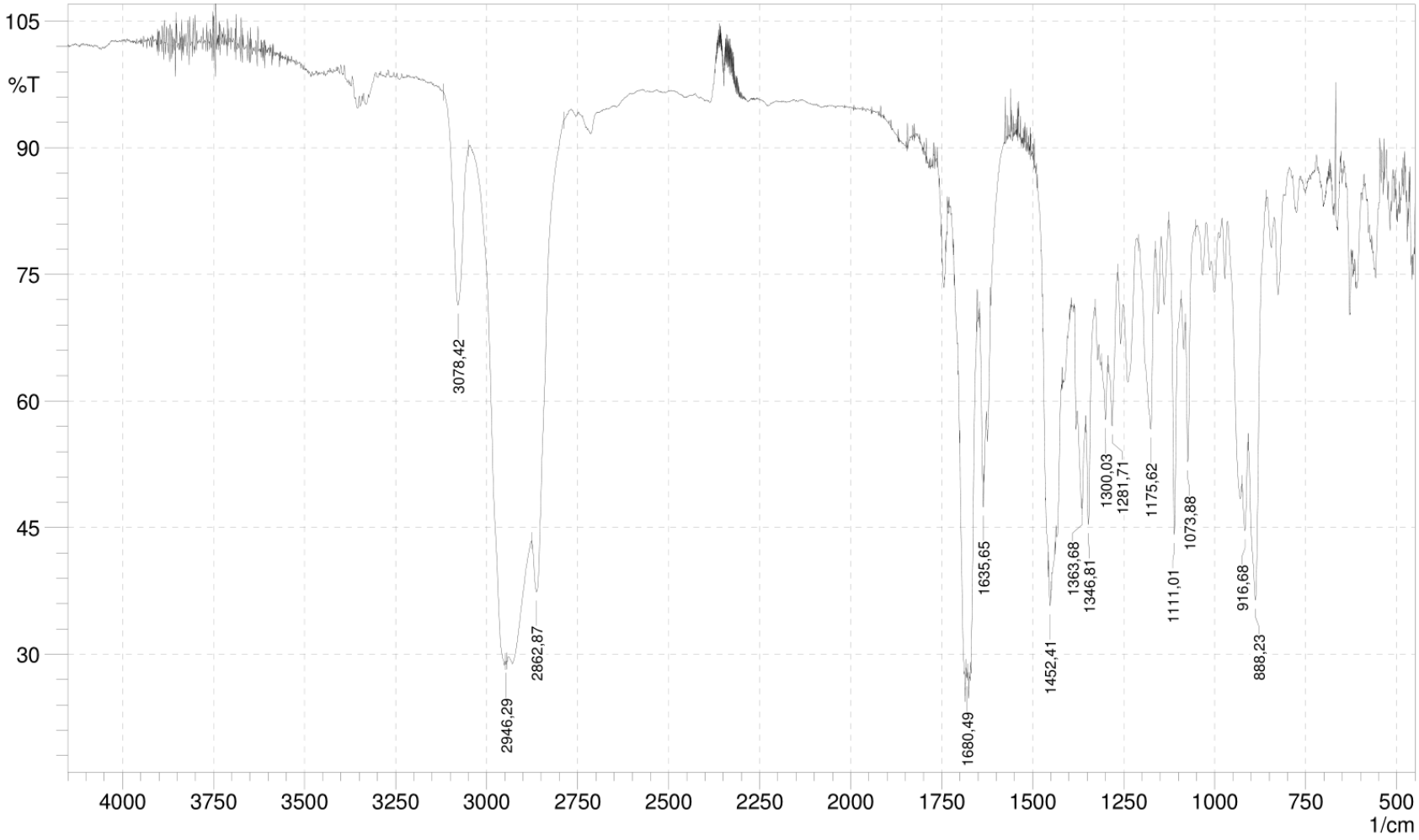
HSQC of *iso*-euphoranin E (**11**)

HMBC of *iso*-euphoranin E (**11**)

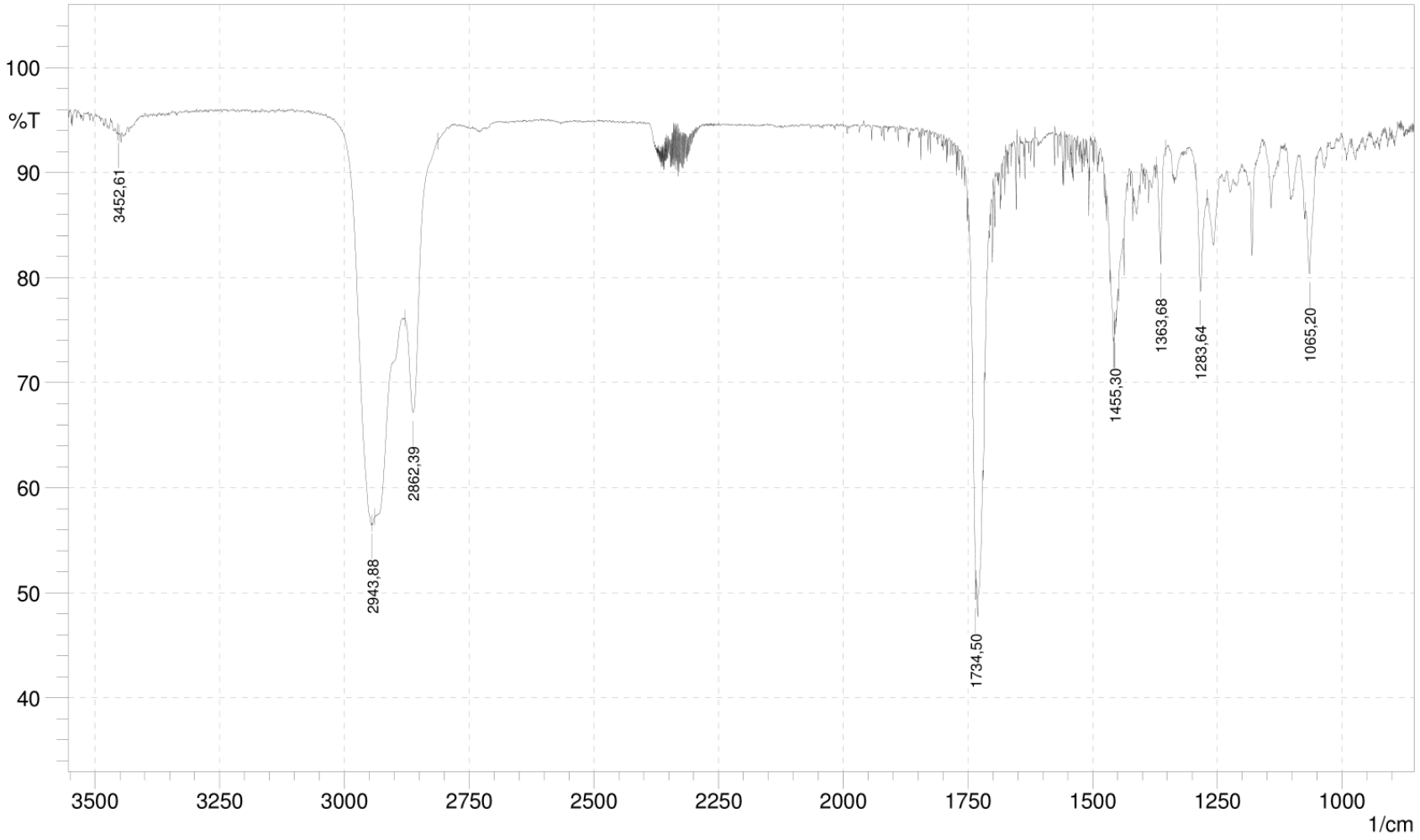


IR spectra

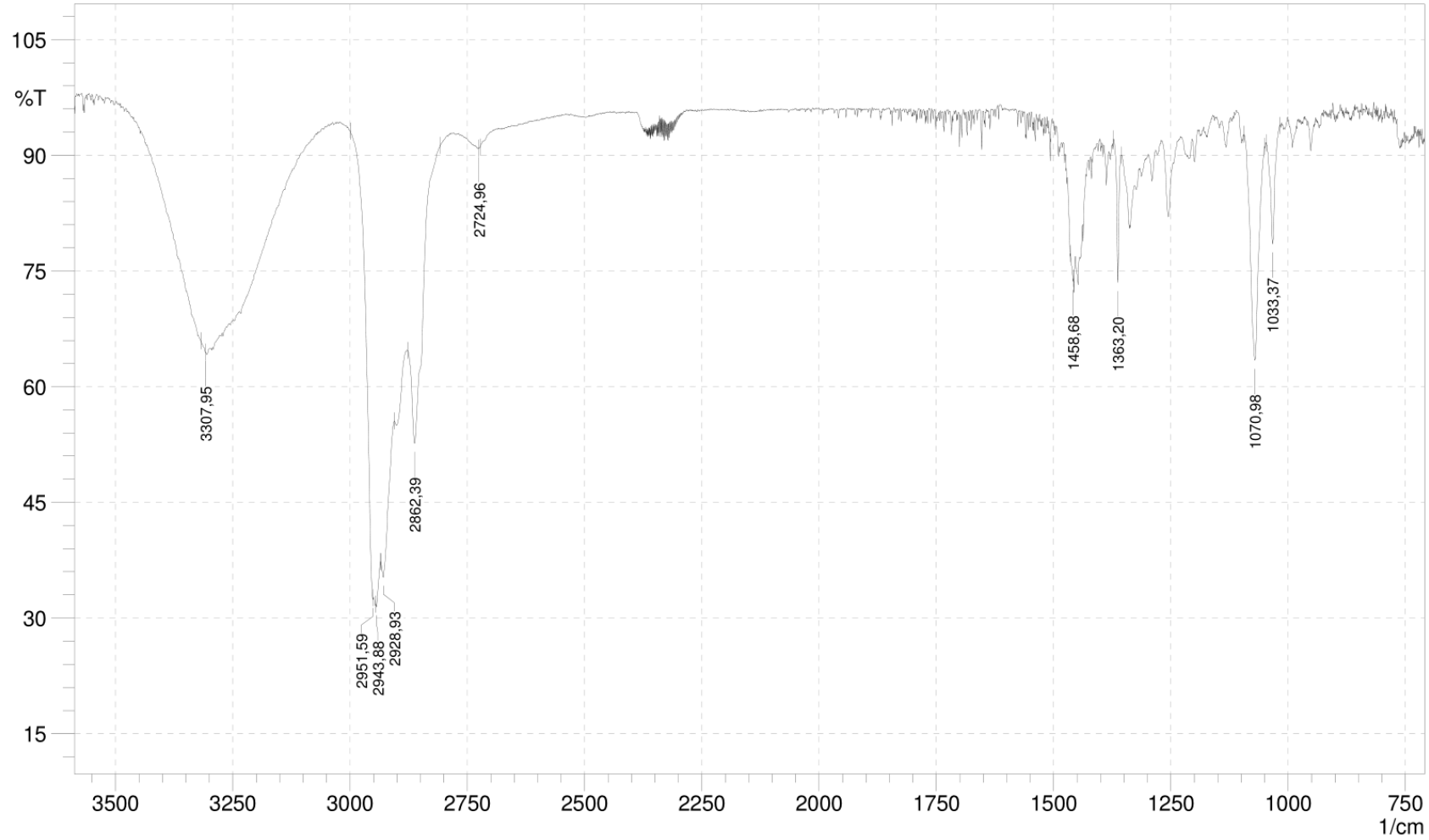
IR (thin film) of (1*S*,5*R*,9*R*)-10,10-dimethyl-2,6-dimethylenebicyclo[7.2.0]undecan-5-one (**8**)



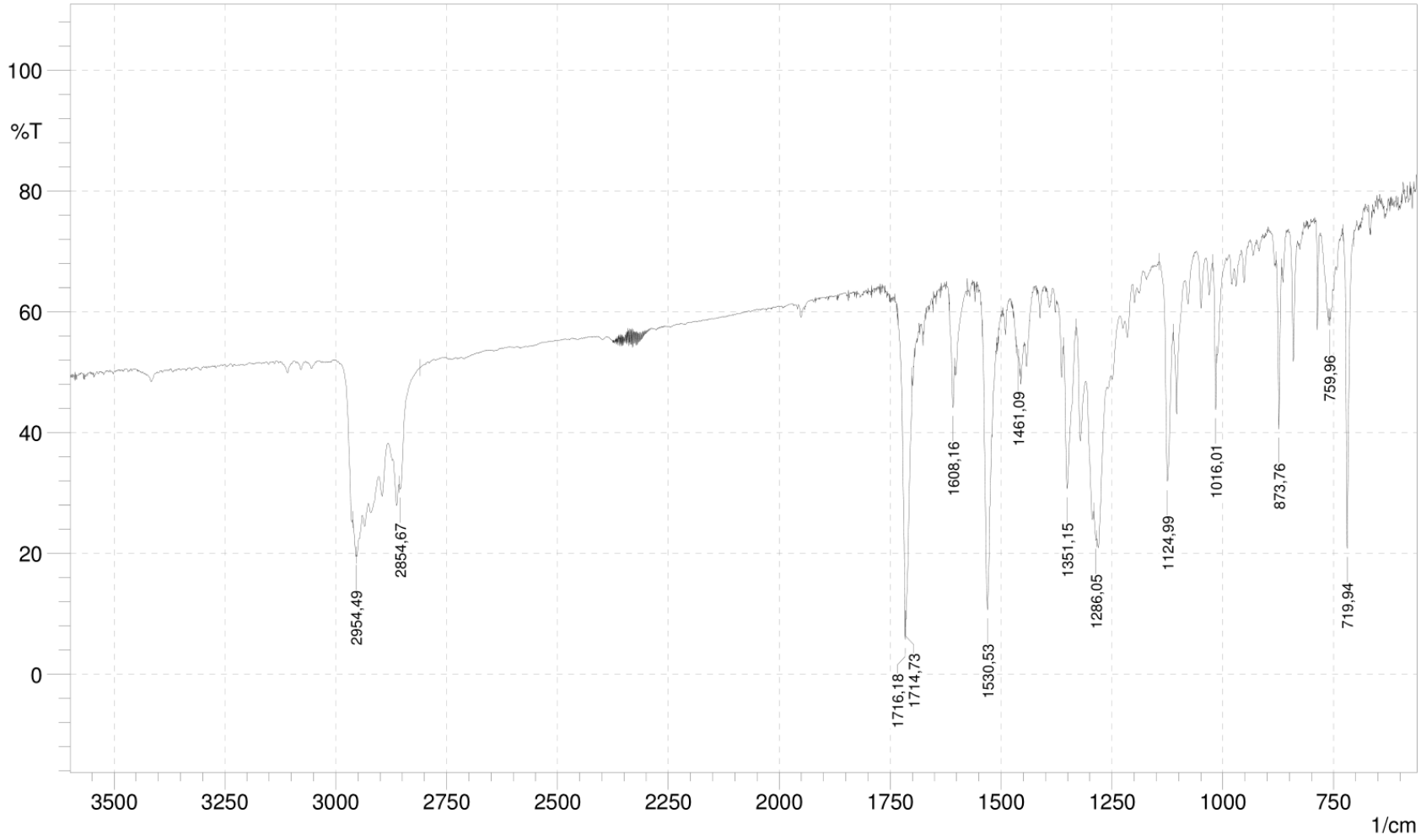
IR (thin film) of (2a*R*,4a*R*,7a*R*,7b*S*)-2,2-dimethyloctahydro-5*H*-4a,7a-ethanocyclobuta[*e*]inden-5-one (**12**)



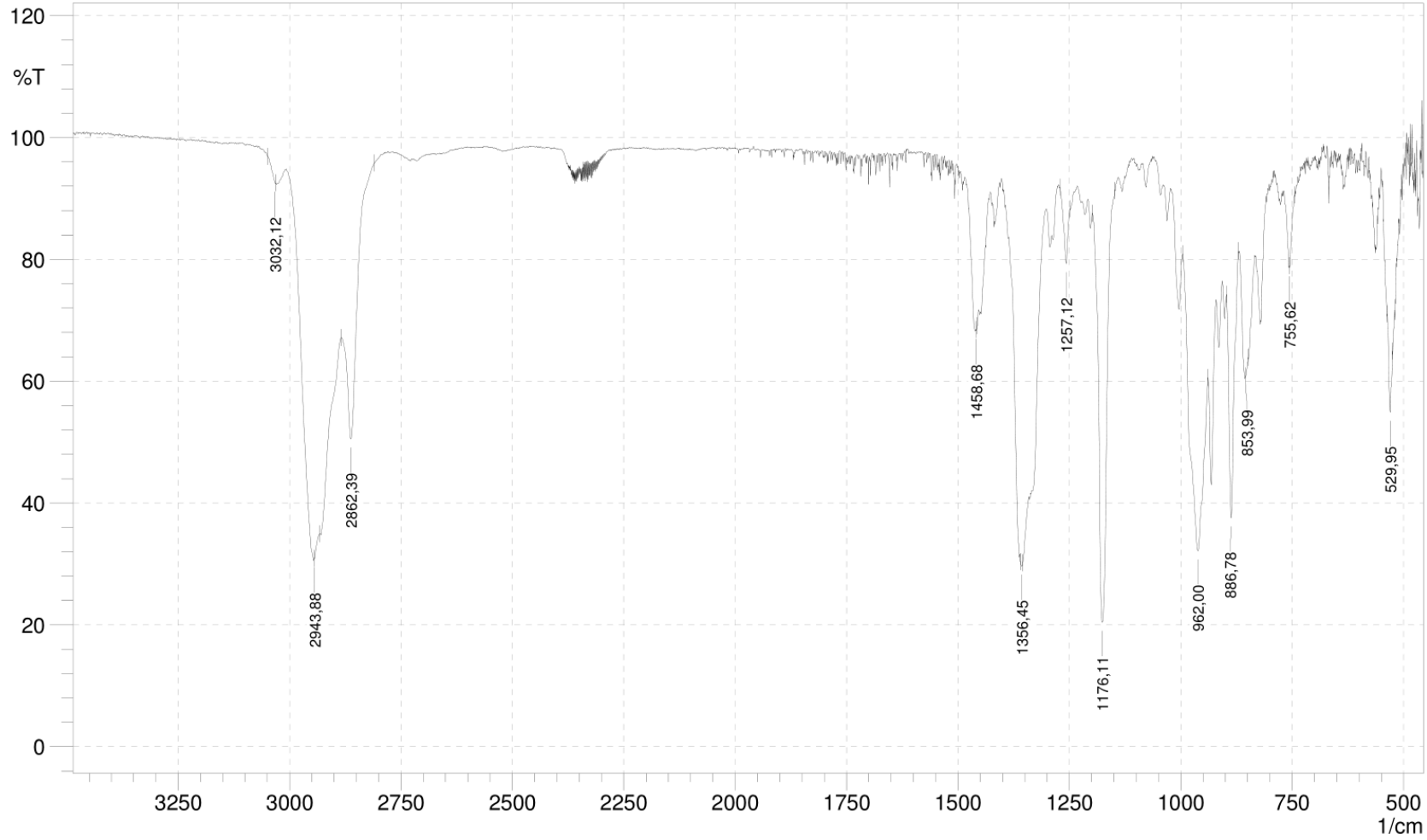
IR (thin film) of (2a*R*,4a*R*,7a*R*,7b*S*)-2,2-dimethyloctahydro-5*H*-4a,7a-ethanocyclobuta[*e*]inden-5-ol (**9**)



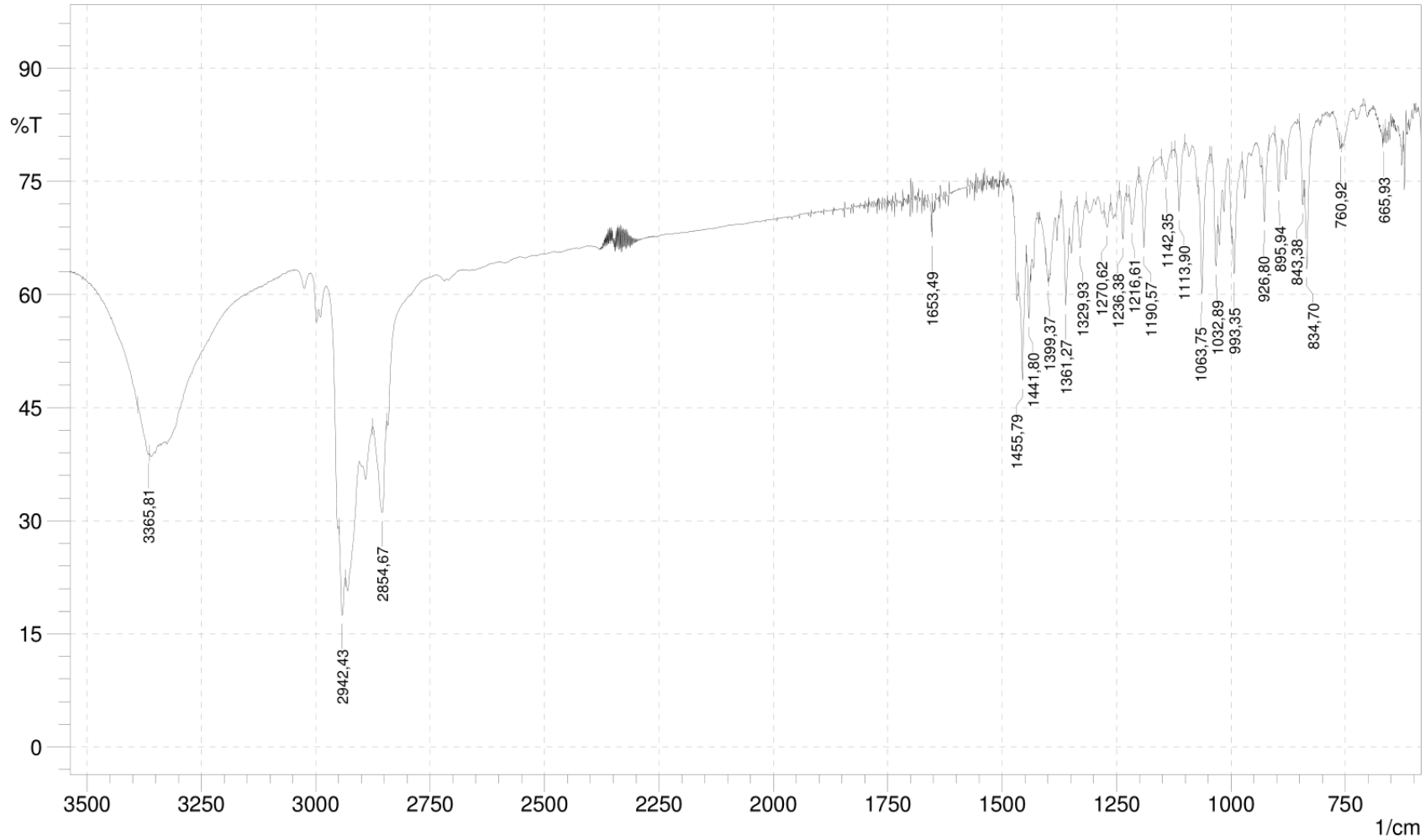
IR (thin film) of (2a*R*,4a*R*,5*S*,7a*R*,7b*S*)-2,2-dimethyloctahydro-5*H*-4a,7a-ethanocyclobuta[*e*]inden-5-yl 4-nitrobenzoate (**13**)



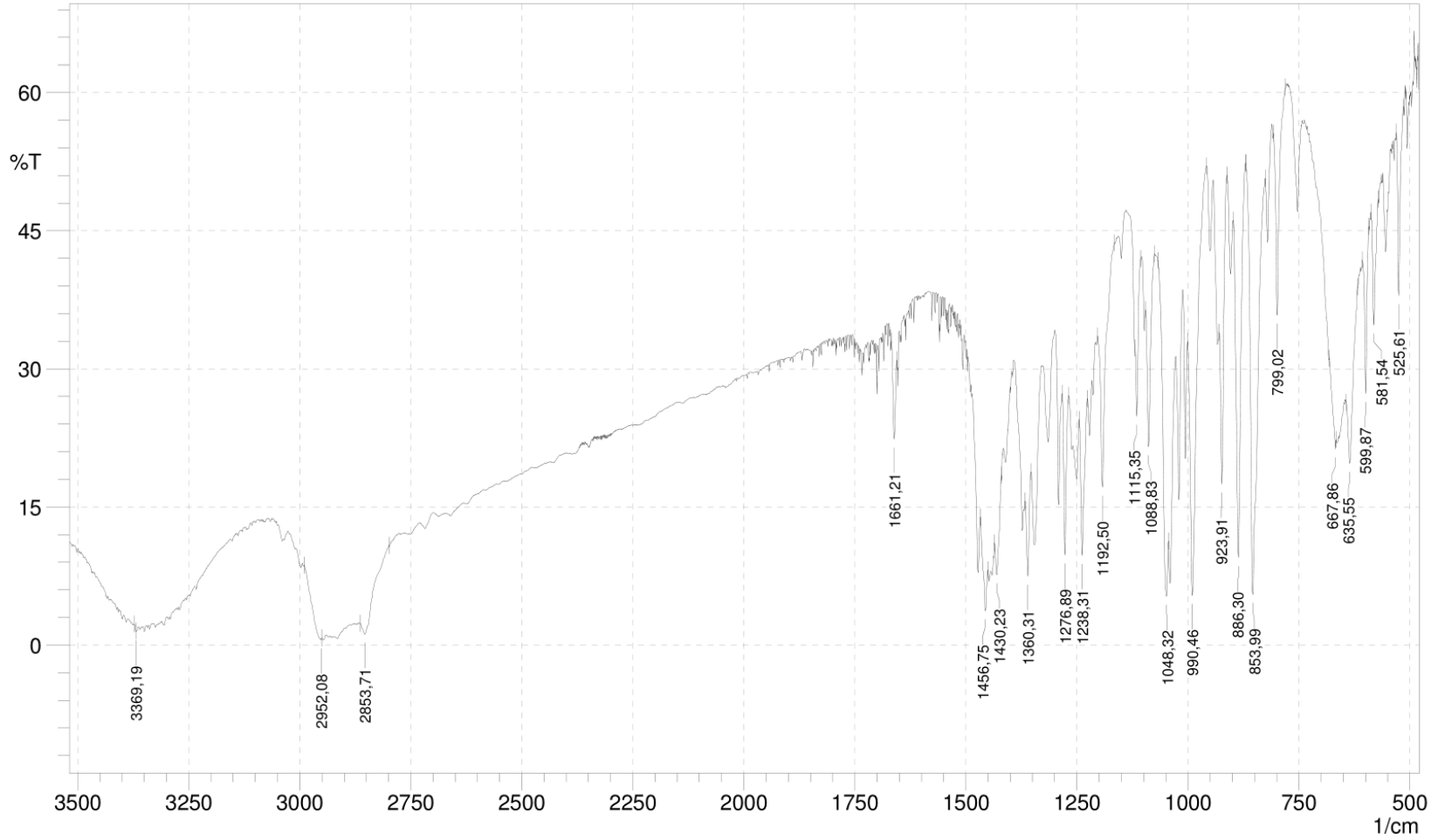
IR (thin film) of (2a*R*,4a*R*,5*S*,7a*R*,7b*S*)-2,2-dimethyloctahydro-5*H*-4a,7a-ethanocyclobuta[*e*]inden-5-yl 4-methanesulfonate (**14**)



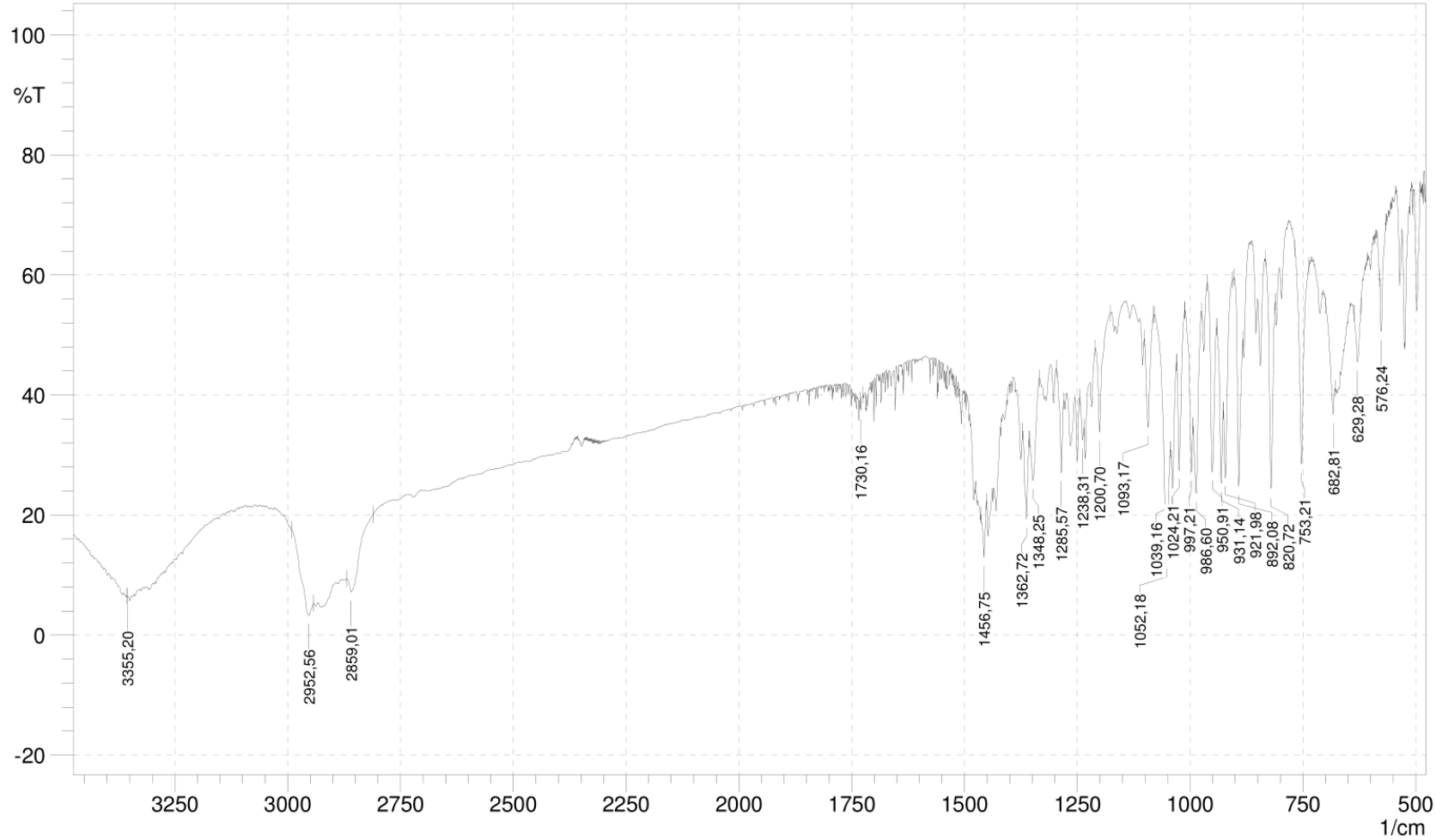
IR (thin film) of (1*R*,2*S*,5*R*)-4,4-dimethyltricyclo[6.3.2.$0^{2,5}$]tridec-8-en-1-ol (**10**)



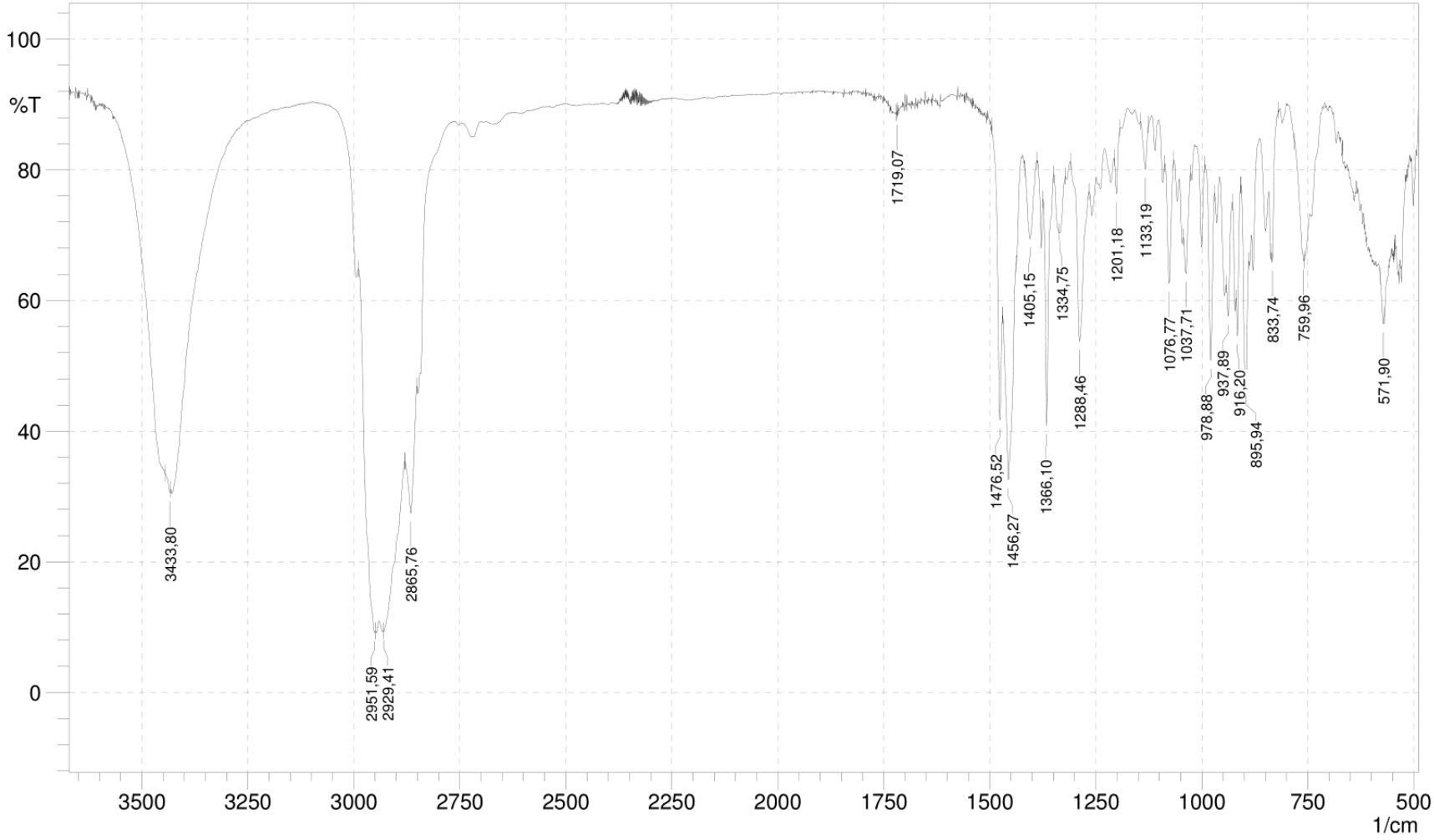
IR (thin film) of (1*S*,2*S*,5*R*)-4,4-dimethyltricyclo[6.3.2.$0^{2,5}$]tridec-8-en-1-ol (**7**)



IR (thin film) of euphoranin E (**2**)

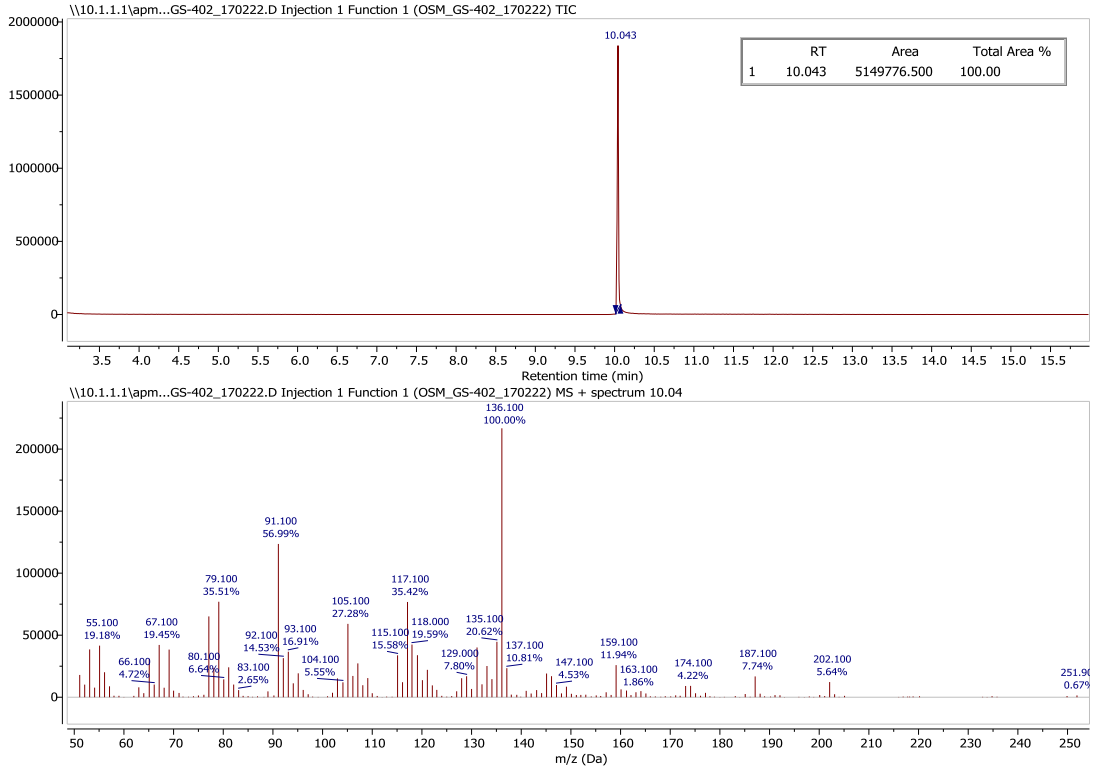


IR (thin film) of *iso*-euphoranin E (**11**)

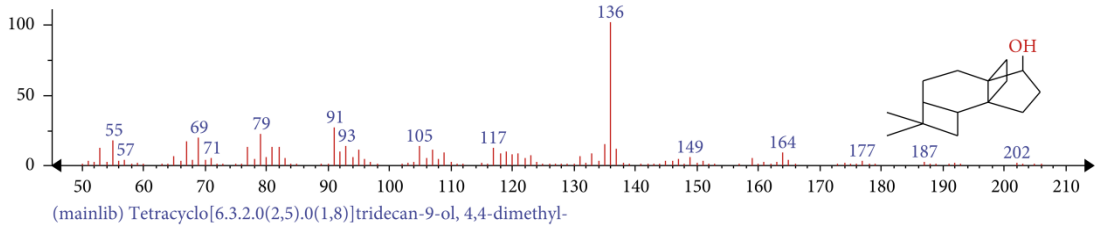


Mass spectra of synthetic and isolated from nature propellane-containing alcohol 9

Mass spectrum (GC-MS) of synthesized alcohol **9**



Mass spectrum (GC-MS) of isolated 4,4-dimethyltetracyclo[6.3.0^{2,5}.0^{1,8}]tridecan-9-ol from *Achillea wilhelmsii*



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X-Ray crystallographic supplementary data for compound 13

Computing details

Data collection: *CrysAlis PRO* 1.171.40.35a (Rigaku OD, 2018); cell refinement: *CrysAlis PRO* 1.171.40.35a (Rigaku OD, 2018); data reduction: *CrysAlis PRO* 1.171.40.35a (Rigaku OD, 2018); program(s) used to solve structure: SHELXT 2014/4 (Sheldrick, 2014); program(s) used to refine structure: *SHELXL2017*/1 (Sheldrick, 2017).

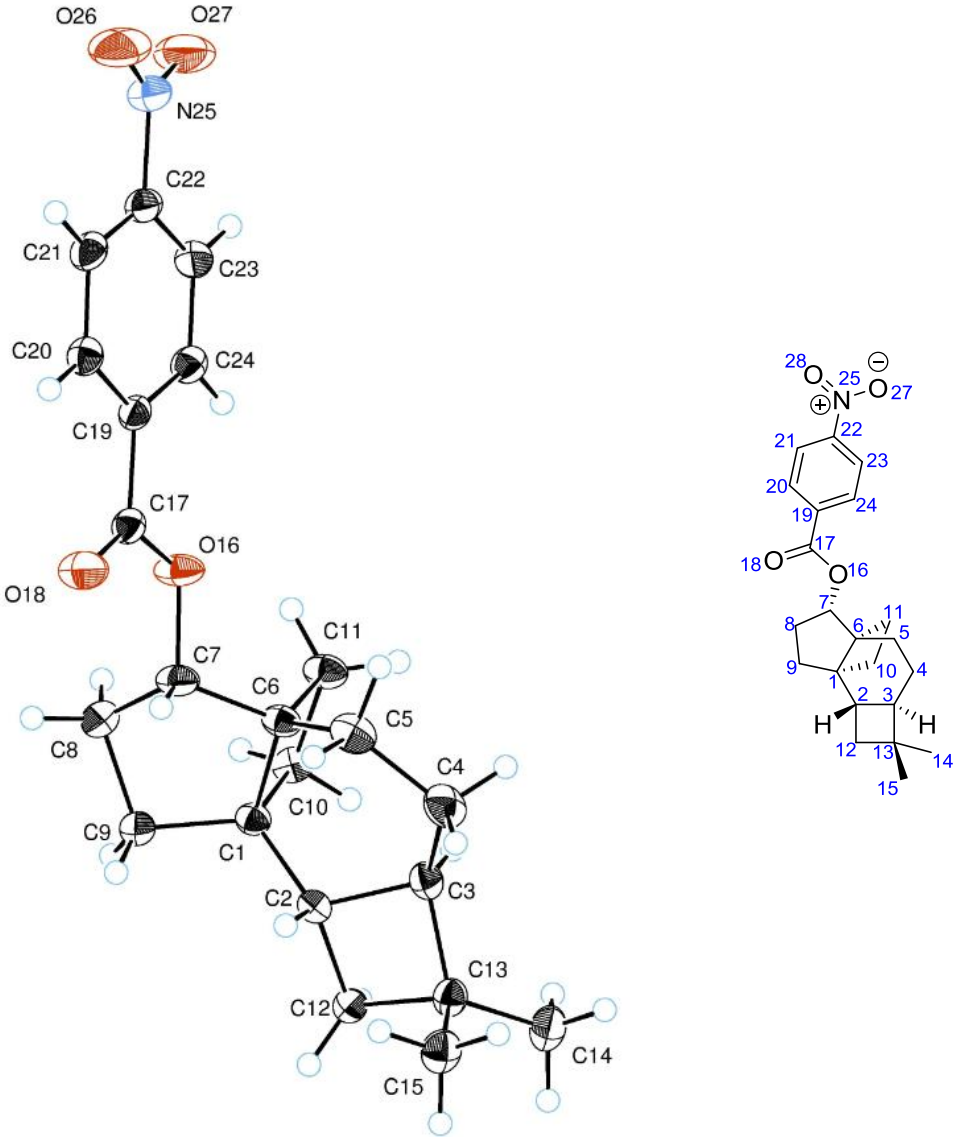


Fig S1. The asymmetric unit of the compound **13** drawn with displacement ellipsoids at the 50% probability level

Crystal data and structure refinement

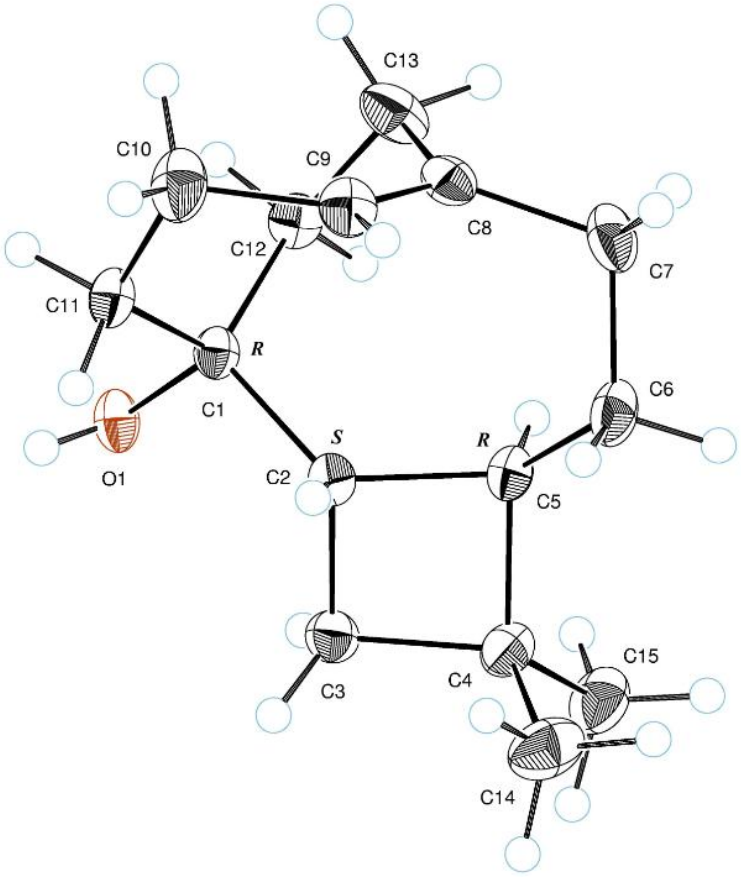
Empirical formula	$C_{22}H_{27}NO_4$
Formula weight	369.46
Temperature/K	150.0(2)
Crystal system	orthorhombic
Space group	$P2_12_12_1$
a/Å	6.06579(5)
b/Å	16.68048(13)
c/Å	18.97466(18)
α/°	90
β/°	90
γ/°	90
Volume/Å^3	1919.86(3)
Z	4
ρ_{calc}g/cm^3	1.2781
μ/mm^{-1}	0.705
F(000)	792
Crystal size/mm^3	0.19 × 0.11 × 0.08
Radiation	Cu Kα (λ = 1.54184)
2Θ max. for data collection/°	155.0
Index ranges	$-7 \leq h \leq 6$, $-21 \leq k \leq 19$, $-23 \leq l \leq 24$
Reflections collected	12058
Independent reflections	3897 [R_{int} = 0.0278, R_{sigma} = 0.0288]
Data/restraints/parameters	3897/0/246
Goodness-of-fit on F^2	1.058
Final R indexes [$I > 2\sigma(I)$]	R_1 = 0.0313, wR_2 = 0.0806
Final R indexes [all data]	R_1 = 0.0323, wR_2 = 0.0814
Largest diff. peak/hole / e Å^{-3}	0.16/-0.17
Flack's x parameter	0.02(3)

Crystallographic data have been deposited at the Cambridge Crystallographic Data Center with the deposition number 2346928.

X-Ray crystallographic supplementary data for compound 10

Computing details

Data collection: *CrysAlis PRO* 1.171.40.35a (Rigaku OD, 2018); cell refinement: *CrysAlis PRO* 1.171.40.35a (Rigaku OD, 2018); data reduction: *CrysAlis PRO* 1.171.40.35a (Rigaku OD, 2018); program(s) used to solve structure: SHELXT 2014/4 (Sheldrick, 2014); program(s) used to refine structure: *SHELXL2017*/1 (Sheldrick, 2017).



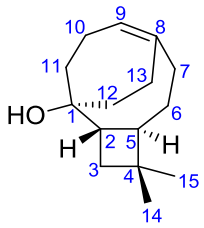


Fig S2. The asymmetric unit of the compound **10** drawn with displacement ellipsoids at the 50% probability level

Crystal data and structure refinement

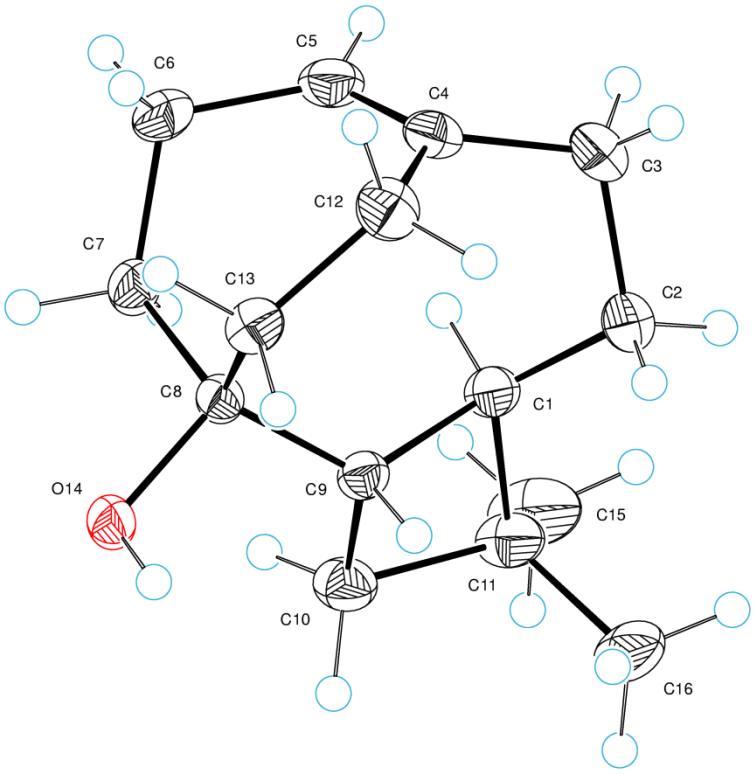
Empirical formula	$C_{15}H_{24}O$
Formula weight	220.36
Temperature/K	150.0(1)
Crystal system	trigonal
Space group	$P3_1$
a/Å	13.3360(4)
b/Å	13.3360(4)
c/Å	6.2105(2)
α/°	90
β/°	90
γ/°	120
Volume/Å^3	956.56(5)
Z	3
ρ_{calc}g/cm^3	1.1475
μ/mm^{-1}	0.523
F(000)	366
Crystal size/mm^3	0.17 × 0.02 × 0.01
Radiation	CuKα (λ = 1.54184 Å)
2Θ max. for data collection/°	155.0
Index ranges	$-16 \leq h \leq 16$, $-16 \leq k \leq 14$, $-7 \leq l \leq 7$
Reflections collected	5016
Independent reflections	2221 [R_{int} = 0.0256, R_{sigma} = 0.0311]
Data/restraints/parameters	2221/1/151
Goodness-of-fit on F^2	1.062
Final R indexes [$I > 2\sigma(I)$]	R_1 = 0.0302, wR_2 = 0.0761
Final R indexes [all data]	R_1 = 0.0311, wR_2 = 0.0765
Largest diff. peak/hole / e Å^{-3}	0.13/-0.12
Flack's x parameter	0.1(2)

Crystallographic data have been deposited at the Cambridge Crystallographic Data Center with the deposition number 2346929.

X-Ray crystallographic supplementary data for compound 7

Computing details

Data collection: *CrysAlis PRO* 1.171.40.35a (Rigaku OD, 2018); cell refinement: *CrysAlis PRO* 1.171.40.35a (Rigaku OD, 2018); data reduction: *CrysAlis PRO* 1.171.40.35a (Rigaku OD, 2018); program(s) used to solve structure: SHELXT 2014/4 (Sheldrick, 2014); program(s) used to refine structure: *SHELXL2017*/1 (Sheldrick, 2017).



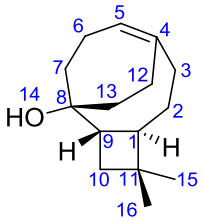


Fig S3. The asymmetric unit of the compound **7** drawn with displacement ellipsoids at the 50% probability level

Crystal data and structure refinement

Empirical formula	$C_{15}H_{24}O$
Formula weight	220.34
Temperature/K	160.0(1)
Crystal system	trigonal
Space group	$P3_2$
a/Å	13.0367(2)
b/Å	13.0367(2)
c/Å	6.6998(1)
α/°	90
β/°	90
γ/°	120
Volume/Å^3	986.12(3)
Z	3
ρ_{calc}g/cm^3	1.113
μ/mm^{-1}	0.508
F(000)	366.0
Crystal size/mm^3	0.24 × 0.03 × 0.02
Radiation	CuKα (λ = 1.54184 Å)
2Θ max. for data collection/°	160.0
Index ranges	$-16 \leq h \leq 16$, $-16 \leq k \leq 16$, $-8 \leq l \leq 5$
Reflections collected	9553
Independent reflections	2086 [R_{int} = 0.0306, R_{sigma} = 0.0240]
Data/restraints/parameters	2086/1/152
Goodness-of-fit on F^2	1.056
Final R indexes [$I > 2\sigma(I)$]	R_1 = 0.0306, wR_2 = 0.0820
Final R indexes [all data]	R_1 = 0.0312, wR_2 = 0.0824
Largest diff. peak/hole / e Å^{-3}	0.18/-0.15
Flack's x parameter	0.1(2)

Crystallographic data have been deposited at the Cambridge Crystallographic Data Center with the deposition number 2346931.

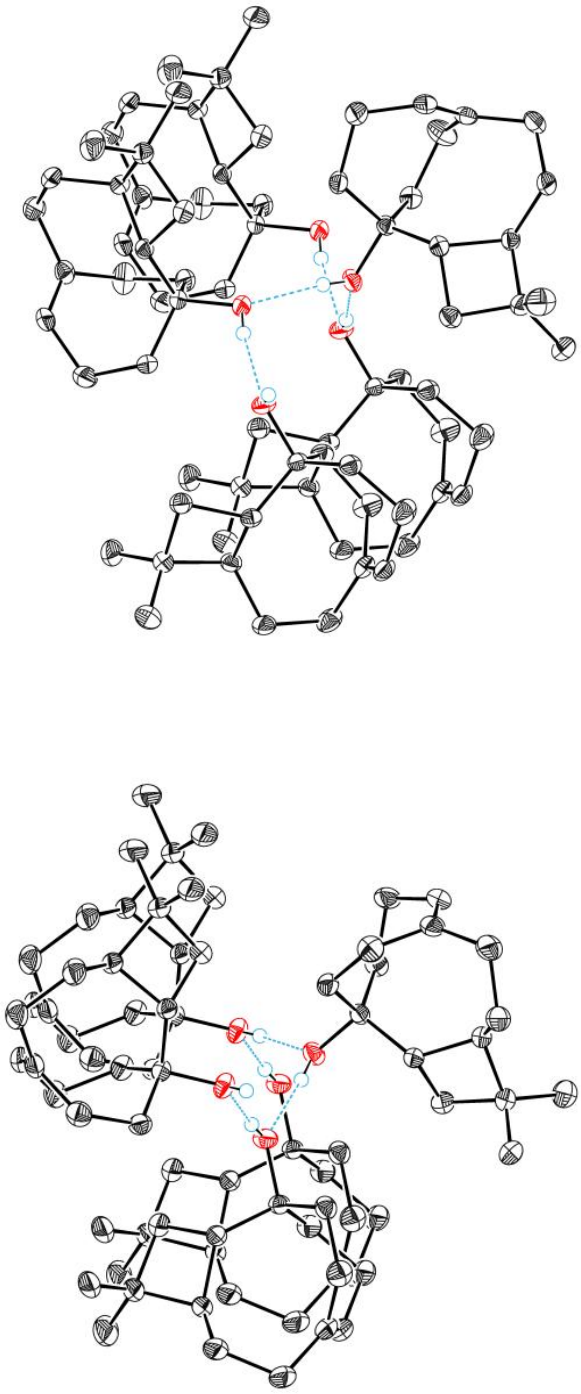
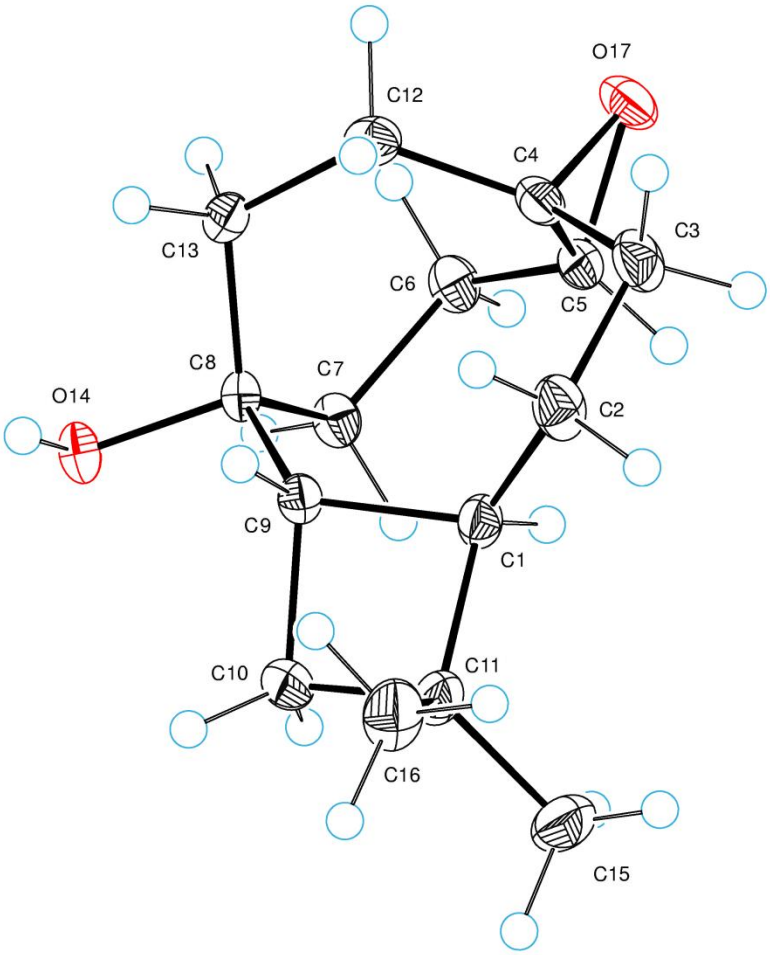


Fig. S4. Formation of the molecular chains in the crystal structures of **10** (top) and **7** (bottom). For the sake of clarity, hydrogen atoms not involved in the H-bonds shown have been omitted.

X-Ray crystallographic supplementary data for compound 2

Computing details

Data collection: *CrysAlis PRO* 1.171.40.35a (Rigaku OD, 2018); cell refinement: *CrysAlis PRO* 1.171.40.35a (Rigaku OD, 2018); data reduction: *CrysAlis PRO* 1.171.40.35a (Rigaku OD, 2018); program(s) used to solve structure: SHELXT 2014/4 (Sheldrick, 2014); program(s) used to refine structure: *SHELXL2017*/1 (Sheldrick, 2017).



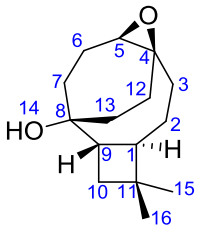


Fig S5. The asymmetric unit of the compound **2** drawn with displacement ellipsoids at the 50% probability level

Crystal data and structure refinement

Empirical formula	$C_{15}H_{24}O_2$
Formula weight	236.36
Temperature/K	150.0(1)
Crystal system	trigonal
Space group	$P3_2$
a/Å	13.03323(11)
b/Å	13.03323(11)
c/Å	6.70964(7)
α/°	90
β/°	90
γ/°	120
Volume/Å^3	987.039(15)
Z	3
ρ_{calc}g/cm^3	1.1928
μ/mm^{-1}	0.599
F(000)	391.1
Crystal size/mm^3	0.22 × 0.07 × 0.06
Radiation	Cu Kα (λ = 1.54184 Å)
2Θ max. for data collection/°	160.0
Index ranges	$-16 \leq h \leq 16$, $-16 \leq k \leq 16$, $-8 \leq l \leq 8$
Reflections collected	9171
Independent reflections	2601 [R_{int} = 0.0177, R_{sigma} = 0.0156]
Data/restraints/parameters	2601/1/160
Goodness-of-fit on F^2	1.084
Final R indexes [$I > 2\sigma(I)$]	R_1 = 0.0297, wR_2 = 0.0770
Final R indexes [all data]	R_1 = 0.0298, wR_2 = 0.0770
Largest diff. peak/hole / e Å^{-3}	0.16/-0.17
Flack's x parameter	0.1(2)

Crystallographic data have been deposited at the Cambridge Crystallographic Data Center with the deposition number 2346932.

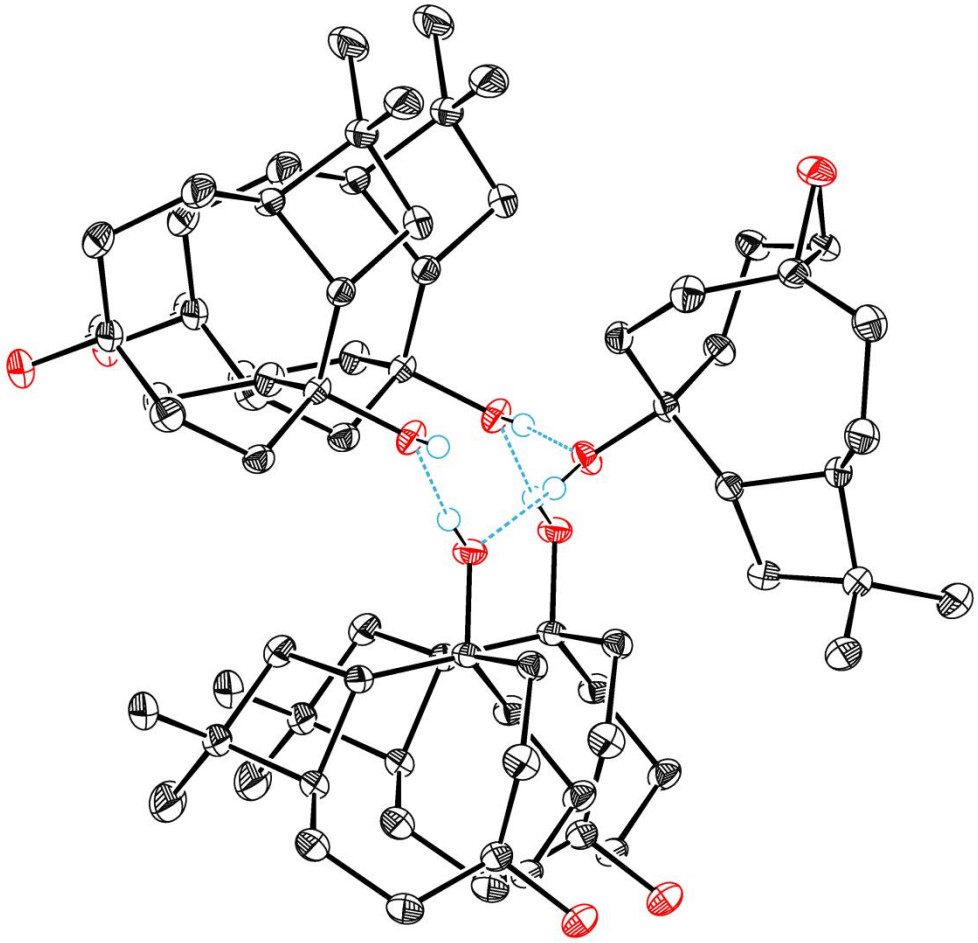


Fig. S6. Formation of the molecular chains in the crystal structure of **2**. For the sake of clarity, hydrogen atoms not involved in the H-bonds shown have been omitted.

X-Ray crystallographic supplementary data for compound 11

Computing details

Data collection: *CrysAlis PRO* 1.171.40.35a (Rigaku OD, 2018); cell refinement: *CrysAlis PRO* 1.171.40.35a (Rigaku OD, 2018); data reduction: *CrysAlis PRO* 1.171.40.35a (Rigaku OD, 2018); program(s) used to solve structure: SHELXT 2014/4 (Sheldrick, 2014); program(s) used to refine structure: *SHELXL2017*/1 (Sheldrick, 2017).

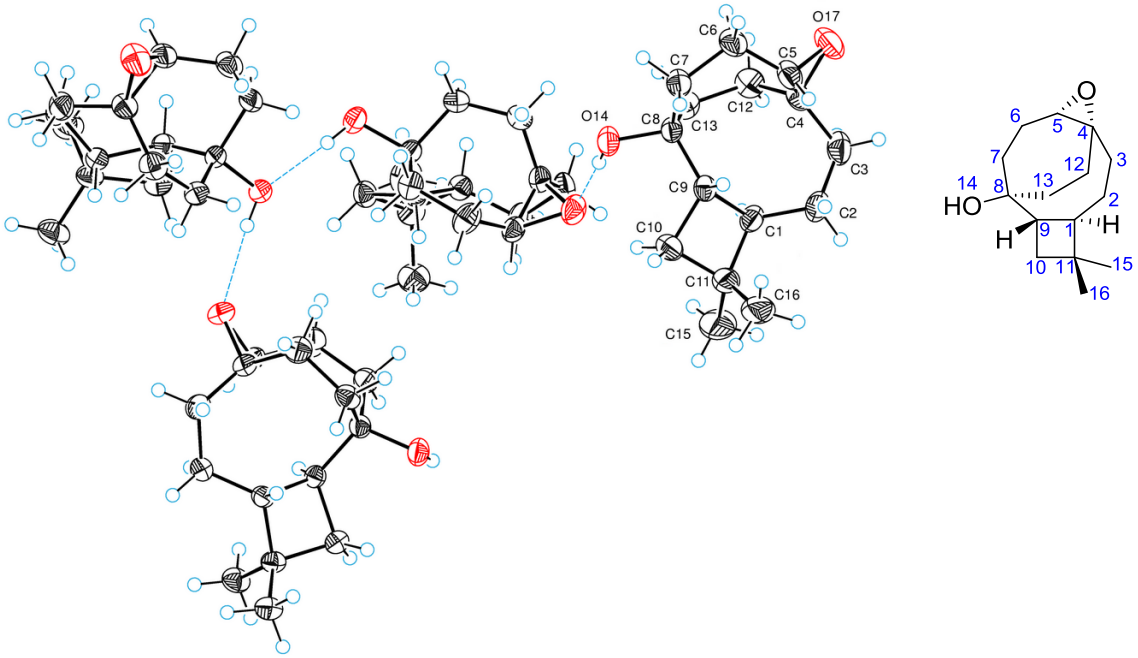


Fig S7. The asymmetric unit of the compound **11** drawn with displacement ellipsoids at the 50% probability level. The unit consists of 4 independent molecules forming hydrogen bonds. All 4 molecules represent the same stereoisomer.

Crystal data and structure refinement

Empirical formula	$C_{60}H_{96}O_8$
Formula weight	945.43
Temperature/K	170.0(1)
Crystal system	monoclinic
Space group	$P2_1$
a/Å	9.3483(1)
b/Å	17.5247(3)
c/Å	16.1772(2)
α/°	90
β/°	90.546(1)
γ/°	90
Volume/Å^3	2650.13(6)
Z	2
ρ_{calc}g/cm^3	1.1847
μ/mm^{-1}	0.595
F(000)	1040
Crystal size/mm^3	0.19 × 0.02 × 0.01
Radiation	Cu Kα (λ = 1.54184 Å)
2Θ max. for data collection/°	160.0
Index ranges	$-9 \leq h \leq 11$, $-22 \leq k \leq 21$, $-20 \leq l \leq 20$
Reflections collected	47326
Independent reflections	11054 [R_{int} = 0.0522, R_{sigma} = 0.0330]
Data/restraints/parameters	11054/1/637
Goodness-of-fit on F^2	1.034
Final R indexes [$I > 2\sigma(I)$]	R_1 = 0.0536, wR_2 = 0.1468
Final R indexes [all data]	R_1 = 0.0543, wR_2 = 0.1474
Largest diff. peak/hole / e Å^{-3}	0.29/-0.26
Flack's x parameter	0.02(7)

Crystallographic data have been deposited at the Cambridge Crystallographic Data Center with the deposition number 2346930.

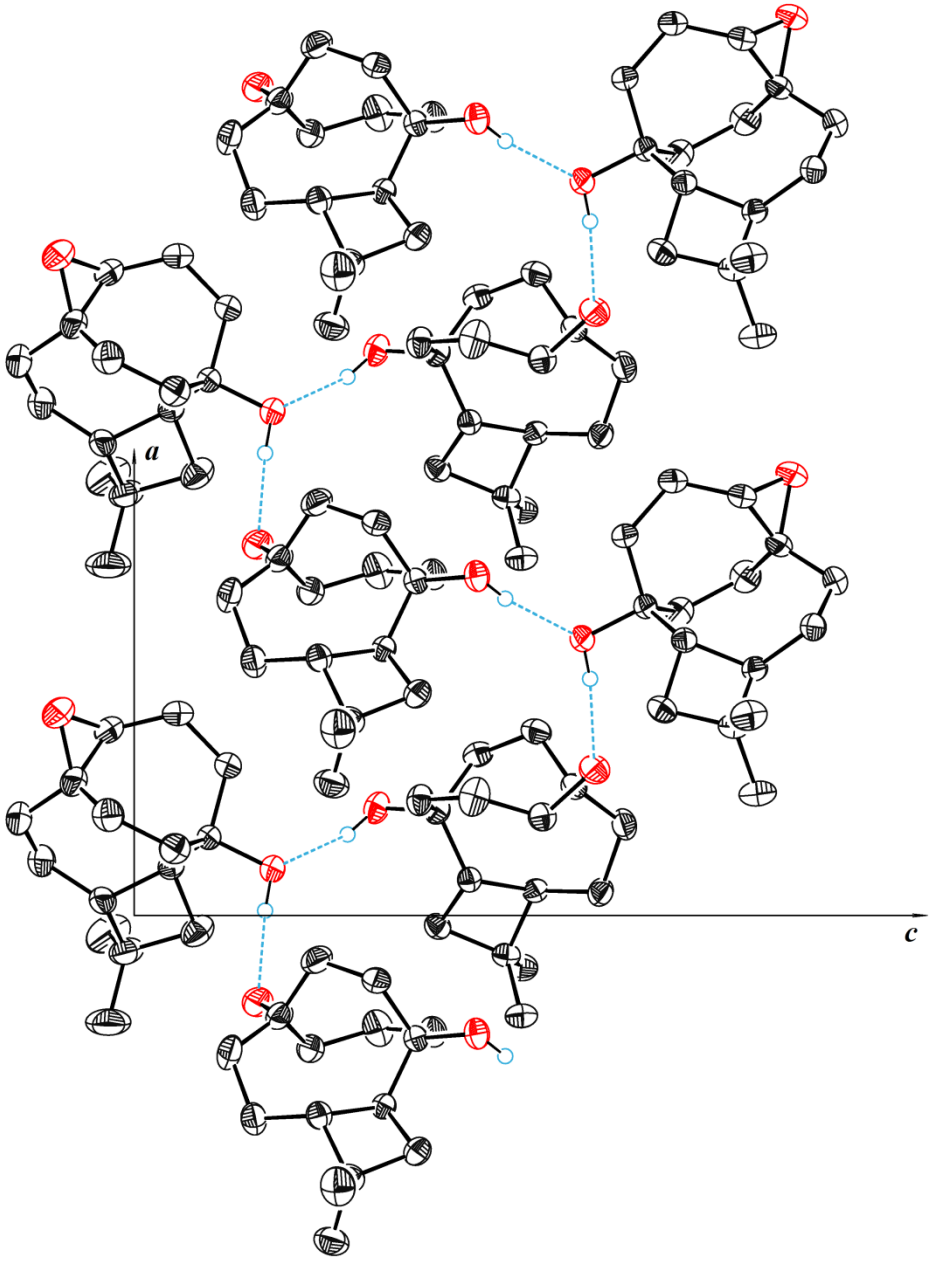


Fig S8. A projection of the crystal structure of **11** along monoclinic axis. For the sake of clarity, hydrogen atoms not involved in the H-bonds shown have been omitted.

Procedure for the DFT calculations

All calculations were performed using the Gaussian 09 software package.[1] All geometry optimizations were performed without any restrictions using the B3LYP method and 6-31+G(d) basis set for all atoms. The transition state (TS) geometries were located by performing a coordinate scan for corresponding bond formation or dissociation. The obtained transition state like structure was then optimized to the TS using the Berny algorithm without any restrictions. The stationary point was verified to be real minima (zero imaginary frequency) or TS (one imaginary frequency) by performing frequency calculations at the same level of theory. Intrinsic reaction coordinates (IRC) were calculated for all TS to confirm that the first-order saddle points connect the correct stationary points of a starting material and a product on the potential energy surface. Single-point energy (SPE) calculations were performed on the stationary points using the 6-311++G(3df,2p) basis set for all atoms. SPE calculations were carried out in THF (ε = 7.4257) or MeCN (ε = 35.688) using implicit solvent modeling with the IEFPCM method. All calculations were performed using superfine integral grid (integral=grid=superfine).[2]

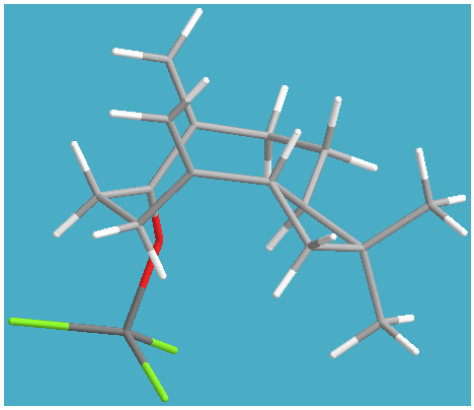
References

(1) Frisch, M. J.; Trucks, G. W.; Schlegel, H. B.; Scuseria, G. E.; Robb, M. A.; Cheeseman, J. R.; Scalmani, G.; Barone, V.; Mennucci, B.; Petersson, G. A.; Nakatsuji, H.; Caricato, M.; Li, X.; Hratchian, H. P.; Izmaylov, A. F.; Bloino, J.; Zheng, G.; Sonnenberg, J. L.; Hada, M.; Ehara, M.; Toyota, K.; Fukuda, R.; Hasegawa, J.; Ishida, M.; Nakajima, T.; Honda, Y.; Kitao, O.; Nakai, H.; Vreven, T.; Jr., J. A. M.; Peralta, J. E.; Ogliaro, F.; Bearpark, M.; Heyd, J. J.; Brothers, E.; Kudin, K. N.; Staroverov, V. N.; Keith, T.; Kobayashi, R.; Normand, J.; Raghavachari, K.; Rendell, A.; Burant, J. C.; Iyengar, S. S.; Tomasi, J.; Cossi, M.; Rega, N.; Millam, J. M.; Klene, M.; Knox, J. E.; Cross, J. B.; Bakken, V.; Adamo, C.; Jaramillo, J.; Gomperts, R.; Stratmann, R. E.; Yazyev, O.; Austin, A. J.; Cammi, R.; Pomelli, C.; Ochterski, J. W.; Martin, R. L.; Morokuma, K.; Zakrzewski, V. G.; Voth, G. A.; Salvador, P.; Dannenberg, J. J.; Dapprich, S.; Daniels, A. D.; Farkas, O.; Foresman, J. B.; Ortiz, J. V.; Cioslowski, J.; Fox, D. J. Gaussian 09, Revision D.01, 2013.

(2) Bootsma, A. N.; Wheeler, S. *Popular Integration Grids Can Result in Large Errors in DFT-Computed Free Energies*; preprint; 2019. https://doi.org/10.26434/chemrxiv.8864204.v4.

Optimized geometries

SM-A



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Sum of electronic and thermal Energies= -2282.950091
Sum of electronic and thermal Enthalpies= -2282.949147
Sum of electronic and thermal Free Energies= -2283.026220

E(RB3LYP) = -2283.65418504 (MeCN)

0 1

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H	-4.95211400	-2.59226200	-0.17300800
H	-4.16904300	-2.47477100	1.40820800
H	-4.86491600	-1.03091600	0.65286700
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H	-3.77147500	2.92568500	-1.02925700
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C	0.42312700	2.13922100	-0.63901600
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H	-0.35819800	0.49633600	-1.84922600
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Al	2.72839700	-0.48456400	-0.13191500
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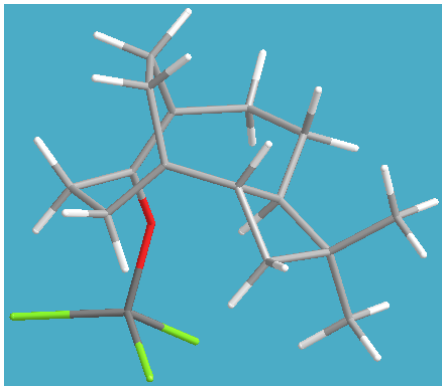
TS-A



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Thermal correction to Energy= 0.366540
Thermal correction to Enthalpy= 0.367484
Thermal correction to Gibbs Free Energy= 0.294738
Sum of electronic and zero-point Energies= -2282.934141
Sum of electronic and thermal Energies= -2282.912728
Sum of electronic and thermal Enthalpies= -2282.911784
Sum of electronic and thermal Free Energies= -2282.984529

E(RB3LYP) = -2283.62753599 (MeCN)

0 1

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C	-1.93147000	-0.65605500	0.42110100
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H	-1.56816100	-1.27579900	-2.14459800
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H	-4.30607400	-3.12574200	-0.42649800
H	-3.89354500	-2.70050900	1.23997400
H	-4.62308400	-1.49277400	0.17158500
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H	-0.54966700	-2.89384000	-0.52199200
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H	-2.28305300	-1.08689200	2.47218700
H	-3.25239900	0.24416200	1.88044100
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H	-0.30526400	0.23326300	2.72468800
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C	-2.48722300	2.62649100	-0.45462300
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H	-3.56488200	2.54805600	-0.29097100
C	-0.75390000	1.79519800	1.34269300
C	-1.73163800	2.87703100	0.94368100
H	-1.24585100	3.85578100	0.86831800
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C	0.32765500	1.54055600	0.55461100
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C	0.42110800	2.20775900	-0.80702300
H	1.41261800	2.08879500	-1.24974700
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H	-0.75822600	2.11863100	-2.65608800
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Cl	3.22931100	-1.73434400	1.53635100
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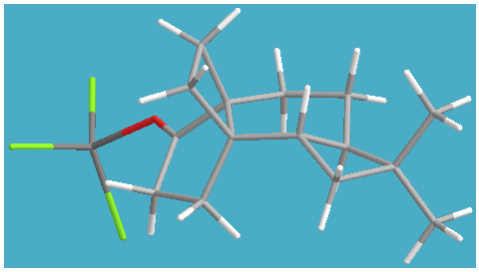
INT-A



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Sum of electronic and thermal Energies=	-2282.958837
Sum of electronic and thermal Enthalpies=	-2282.957892
Sum of electronic and thermal Free Energies=	-2283.032047

E(RB3LYP) = -2283.65836511 (MeCN)

0 1

C	-3.02388400	0.74248300	0.03873000
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C	-4.65122500	-0.63345000	-0.36035300
C	-3.15050000	-0.78479200	0.08184200
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H	-3.92634600	0.69098200	-1.99001300
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H	-2.61731100	-1.21301600	-0.78278900
C	-5.64353000	-0.51598700	0.80380100
H	-6.63129400	-0.21251600	0.43409700
H	-5.76258500	-1.47972300	1.31513400
H	-5.33356600	0.22128800	1.55326800
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H	-5.26634700	-2.64904100	-0.92039800
H	-6.12844200	-1.36519300	-1.78510200
H	-4.45591200	-1.75734900	-2.22213300
C	-2.53701500	-1.36374100	1.34950100
H	-2.66760300	-2.44929000	1.44453300
H	-2.99366600	-0.90609400	2.23741900
C	-1.01278800	-1.06147500	1.29171400
H	-0.53862700	-1.22945300	2.26619700
H	-0.56165800	-1.79273900	0.60852900
C	-1.59337400	1.23721800	-0.12676400
C	-1.24343800	2.48859900	0.74525400
H	-0.48506800	3.13486300	0.28900200
H	-2.09063900	3.11593900	1.03958100
C	-0.64143400	0.37615200	0.81085100
C	-0.65191000	1.56031100	1.83892100
H	0.30840500	1.83543600	2.28635600
H	-1.36094500	1.34646600	2.64503700
C	0.65082200	0.35358000	0.04515900
O	1.69289100	-0.13431400	0.52535800
C	0.53047400	0.97496700	-1.32076800
H	1.01606600	0.34045600	-2.07180500
H	1.12001600	1.90471500	-1.30291300
C	-0.97927600	1.21122300	-1.53895000
H	-1.40114300	0.38684600	-2.12656700
H	-1.17819400	2.13694100	-2.08939400
Al	3.48555700	-0.34215800	-0.07124900
Cl	4.45083500	-1.26622800	1.57621700
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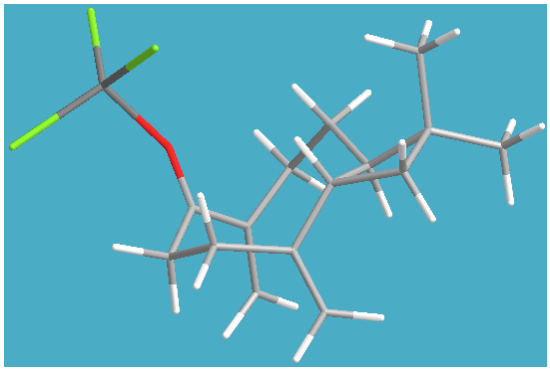
SM-B



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Sum of electronic and thermal Energies=	-2282.950324
Sum of electronic and thermal Enthalpies=	-2282.949379
Sum of electronic and thermal Free Energies=	-2283.026979

E(RB3LYP) = -2283.65444420 (MeCN)

0 1

C	-0.59573200	1.25235300	0.81449800
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C	0.39784300	1.27439400	1.90314300
C	1.70662500	1.67444100	-1.13531400
C	0.84491300	2.45315300	2.38006300
C	2.60363700	2.67142700	-1.09858000
H	1.53940900	2.48117200	3.21567300
H	0.51853700	3.41461300	2.00002700
H	3.65579400	2.50199000	-0.88485000
H	2.31659800	3.70345800	-1.29095700
C	0.85471200	-0.05360600	2.46880500
H	1.57399100	0.15891300	3.26824900
C	2.07968500	0.21958400	-0.91056800
H	1.26087300	-0.40778700	-1.28110200
C	2.52831700	-0.35158300	0.49241600
H	3.08838000	0.42934100	1.02686400
C	1.50480600	-1.00161500	1.43118300
H	0.72385100	-1.49548000	0.84277000
C	-0.66306500	2.32538000	-0.22301300
H	-0.33193300	3.28095000	0.18639100
H	-1.69429200	2.42270000	-0.57446900
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C	3.56347800	-1.26836400	-0.25749800
C	3.41980500	-0.32263100	-1.48520100
H	3.36932500	-0.78726700	-2.47679300
H	4.20081700	0.44493400	-1.49949600
H	0.00353100	-0.56878600	2.93082600
H	1.99795700	-1.79942600	2.00290900
C	4.95108600	-1.34670400	0.38066300
H	4.92047800	-1.89497000	1.33241300
H	5.65865700	-1.86904200	-0.27703400
H	5.35696400	-0.34722100	0.58197000
C	3.03984300	-2.67845500	-0.56783700
H	3.72315000	-3.18386800	-1.26225500
H	2.97465300	-3.29563600	0.33682300
H	2.04843900	-2.66471100	-1.03458100
H	0.18587500	2.85174800	-2.11432300
O	-1.32551000	0.23042300	0.73800100
Al	-2.75499000	-0.56508900	-0.19256400
Cl	-4.09702500	1.03669400	-0.66395400
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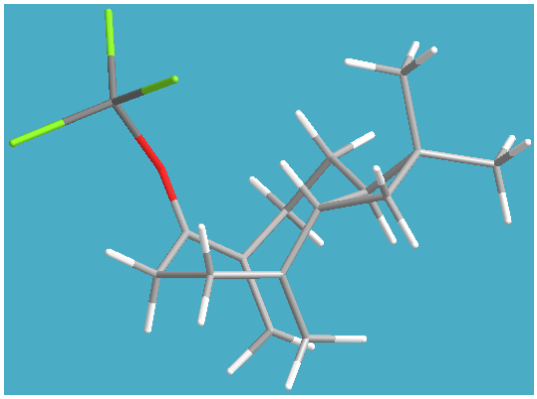
Cl	-3.50462600	-1.97071100	1.21584200

TS-B



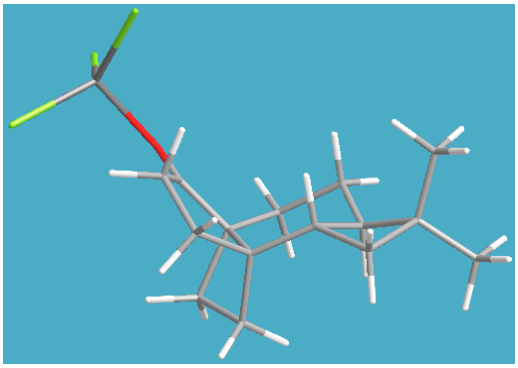
Zero-point correction= 0.345372
(Hartree/Particle)
Thermal correction to Energy= 0.366664
Thermal correction to Enthalpy= 0.367608
Thermal correction to Gibbs Free Energy= 0.294717
Sum of electronic and zero-point Energies= -2282.933221
Sum of electronic and thermal Energies= -2282.911930
Sum of electronic and thermal Enthalpies= -2282.910986
Sum of electronic and thermal Free Energies= -2282.983877

E(RB3LYP) = -2283.62621007 (MeCN)

0 1

C	-0.54009900	1.42926800	0.74838200
C	0.31420800	1.97060200	-1.63288100
C	0.58811500	1.55915100	1.50149800
C	1.55281300	1.54769900	-0.95238200
C	1.56231400	2.67507600	1.18426500
C	2.35038500	2.55106800	-0.24837000
H	2.34876000	2.72505700	1.94151900
H	1.07060100	3.65222700	1.15353700
H	3.37621000	2.22408400	-0.06909300
H	2.34429500	3.52541900	-0.74211100
C	1.02416300	0.45431500	2.44563100
H	1.79860900	0.83679700	3.12463900
C	1.81544400	0.12946300	-0.76451200
H	0.91563400	-0.44455600	-1.00228200
C	2.50498100	-0.42030000	0.53386400
H	3.25610100	0.30013200	0.88515600
C	1.57578000	-0.79097600	1.69236600
H	0.73733300	-1.38529200	1.31563400
C	-0.73394000	2.32890600	-0.46391400
H	-0.59381800	3.38268900	-0.20489100
H	-1.73139700	2.21293100	-0.89316800
H	-0.10476100	1.16350500	-2.23781900
C	3.25820900	-1.47724600	-0.34865900
C	3.02720500	-0.52960700	-1.56842100
H	2.73986500	-0.96838400	-2.52804100
H	3.85309100	0.17488800	-1.71086000
H	0.18418800	0.13235900	3.07023500
H	2.12462200	-1.42790500	2.40112100
C	4.71992000	-1.72682800	0.02078700
H	4.79440600	-2.26875200	0.97225800
H	5.22123200	-2.33412000	-0.74385300
H	5.27815800	-0.78765500	0.12424700
C	2.50459700	-2.80461800	-0.50933700
H	2.98714400	-3.42005700	-1.27876700
H	2.51698800	-3.37345900	0.42767000
H	1.45754200	-2.66879500	-0.80015100
H	0.46425000	2.87326600	-2.23423100
O	-1.39933400	0.43926000	0.94266400
Al	-2.61260800	-0.48988600	0.02320900
Cl	-4.14619900	0.84759300	-0.70662800
Cl	-1.51926400	-1.31702000	-1.69729300
Cl	-3.33601200	-2.03914800	1.30723400

INT-B



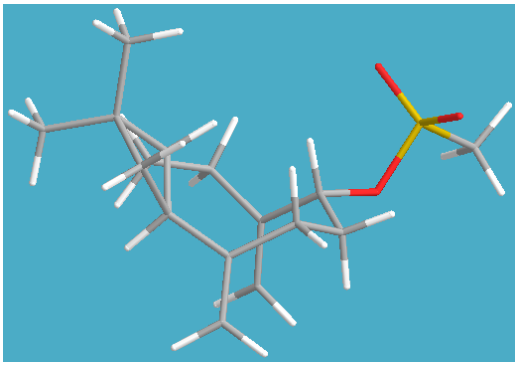
Zero-point correction= 0.347136
(Hartree/Particle)
Thermal correction to Energy= 0.368472
Thermal correction to Enthalpy= 0.369416
Thermal correction to Gibbs Free Energy= 0.295369
Sum of electronic and zero-point Energies= -2282.979411
Sum of electronic and thermal Energies= -2282.958076
Sum of electronic and thermal Enthalpies= -2282.957132
Sum of electronic and thermal Free Energies= -2283.031178

E(RB3LYP) = -2283.65835264 (MeCN)

0 1

C	-0.62849700	0.60764200	0.05033900
C	0.79462800	1.83661800	-1.48531700
C	0.63117800	0.87827400	0.79764900
C	1.67993300	1.39179300	-0.27930600
C	0.68016000	2.35348300	1.39303800
C	2.02782100	2.57850400	0.66024900
H	0.66852200	2.38830500	2.48578600
H	-0.12187900	2.99759700	1.01924900
H	2.88140400	2.36755000	1.31194400
H	2.18351000	3.55333900	0.18688900
C	1.04477800	-0.21821400	1.81958600
H	1.51069900	0.27954700	2.67864700
C	2.66982900	0.28899300	-0.60487500
H	2.12353400	-0.42389100	-1.24275800
C	3.17271000	-0.49276600	0.61372100
H	3.57397700	0.22195900	1.34962400
C	2.05622100	-1.27560900	1.29269400
H	1.57394200	-1.96252100	0.58380600
C	-0.52820600	1.04850200	-1.38193700
H	-1.42638100	1.59161600	-1.69734700
H	-0.51824200	0.12464700	-1.98181000
H	1.30229800	1.65057700	-2.43670100
C	4.40810200	-0.95125100	-0.24297300
C	4.13031600	0.32934300	-1.12652100
H	4.29077800	0.24390900	-2.20741500
H	4.68780100	1.19563700	-0.74976800
H	0.13621300	-0.69940800	2.19960800
H	2.39964100	-1.87913500	2.14268600
C	5.74991800	-0.98465300	0.48927500
H	5.79171500	-1.81984300	1.20117900
H	6.58100300	-1.11042000	-0.21721900
H	5.92465700	-0.05711200	1.04861800
C	4.19454000	-2.25860400	-1.01683600
H	5.00248500	-2.40847100	-1.74433200
H	4.19725100	-3.11947000	-0.33630200
H	3.24823500	-2.27718700	-1.56924700
H	0.58944900	2.91172200	-1.44099700
O	-1.62115800	0.05741500	0.57062500
Al	-3.34716800	-0.44955200	-0.03256900
Cl	-4.20765300	1.41162900	-0.65263600
Cl	-2.89860600	-1.78215900	-1.65023200
Cl	-4.22425600	-1.34573000	1.67943000

SM-C



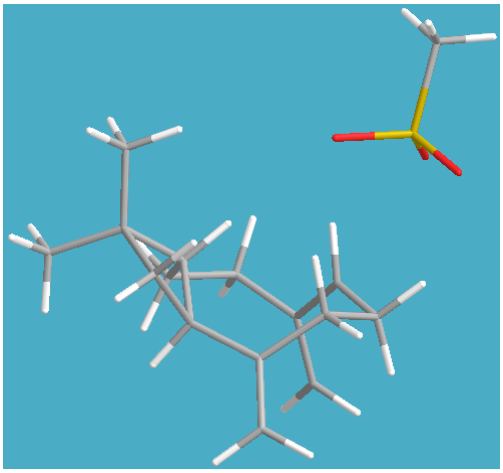
Zero-point correction= 0.398893
(Hartree/Particle)
Thermal correction to Energy= 0.420288
Thermal correction to Enthalpy= 0.421232
Thermal correction to Gibbs Free Energy= 0.348186
Sum of electronic and zero-point Energies= -1248.724241
Sum of electronic and thermal Energies= -1248.702846
Sum of electronic and thermal Enthalpies= -1248.701902
Sum of electronic and thermal Free Energies= -1248.774948

E(RB3LYP) = -1249.47307640 (THF)

0 1

C	1.13762300	0.47497000	0.15945000
C	-0.49504100	1.74208200	-1.41066200
C	0.46897500	0.40742700	1.52559200
C	-1.69033500	1.98077000	-0.50083300
C	0.48333400	1.45499200	2.35760000
C	-1.98841000	3.22545800	-0.09768100
H	0.05794400	1.38501700	3.35661000
H	0.91502800	2.41394900	2.08595000
H	-2.82238200	3.42677600	0.57152700
H	-1.40914500	4.08894100	-0.42070400
C	-0.15308000	-0.92245800	1.91074500
H	0.38538300	-1.73030300	1.39793400
C	-2.57952900	0.82558800	-0.10566200
H	-3.18122700	1.14618500	0.75333300
C	-2.07356200	-0.62843400	0.17320400
H	-1.26803600	-0.88004500	-0.52914800
C	-1.66537800	-1.04119000	1.59228400
H	-2.23023800	-0.44174200	2.31907700
C	-3.40280500	-1.17132500	-0.47233100
C	-3.53902700	0.21429300	-1.17283700
H	-4.53992100	0.65644500	-1.24578600
H	-3.08532000	0.20737500	-2.17154400
H	-0.01662600	-1.09267400	2.98587500
H	-1.95469300	-2.08766500	1.76601400
C	-3.24416000	-2.38726300	-1.38606300
H	-2.97691600	-3.28440500	-0.81074000
H	-4.17865700	-2.60443000	-1.92102400
H	-2.45963000	-2.22520600	-2.13564200
C	-4.53444400	-1.41273900	0.53699400
H	-5.48000700	-1.58615900	0.00689100
H	-4.33798400	-2.29607900	1.15769900
H	-4.68562500	-0.56022900	1.20935300
H	-0.44960400	2.55151400	-2.14904400
O	2.60219100	0.39363800	0.43911000
S	3.47296900	-0.65905800	-0.46248900
O	2.98499200	-2.02137700	-0.22335300
O	3.57037500	-0.17745600	-1.84406200
C	5.04171300	-0.41516100	0.37762100
H	5.33065700	0.63219600	0.27912500
H	4.92531700	-0.70108100	1.42381800
H	5.76198500	-1.06446100	-0.12558800
C	0.88904500	1.70604800	-0.71366200
H	1.65552400	1.69980800	-1.49613200
H	1.03051100	2.62069600	-0.12729000
H	-0.62513900	0.81672900	-1.98732300
H	0.88132000	-0.42301200	-0.40953300

TS-C



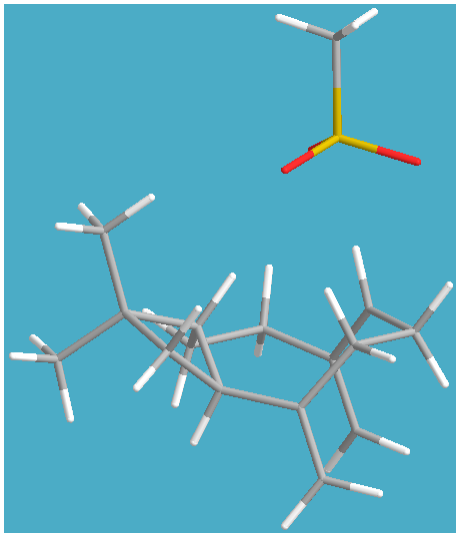
Zero-point correction= 0.395879
(Hartree/Particle)
Thermal correction to Energy= 0.417505
Thermal correction to Enthalpy= 0.418449
Thermal correction to Gibbs Free Energy= 0.344812
Sum of electronic and zero-point Energies= -1248.670121
Sum of electronic and thermal Energies= -1248.648495
Sum of electronic and thermal Enthalpies= -1248.647550
Sum of electronic and thermal Free Energies= -1248.721187

E(RB3LYP) = -1249.43318236 (THF)

0 1

C	0.57031700	1.40849800	0.55493100
C	-0.01766400	1.09846000	-1.78444400
C	-0.37391700	1.87663300	1.52537900
C	-1.50719000	1.24337300	-1.60139500
C	-0.72163800	3.19054900	1.55656500
C	-2.14419200	2.30417700	-2.13026900
H	-1.40144900	3.57449500	2.31375900
H	-0.29752400	3.91756300	0.87159400
H	-3.21585900	2.44663800	-2.00932000
H	-1.62037400	3.05192100	-2.72316100
C	-0.94273400	0.84083000	2.47412800
H	-0.13078600	0.16688400	2.77317500
C	-2.27711800	0.18071500	-0.85442900
H	-3.27547800	0.58059000	-0.63955300
C	-1.75987800	-0.55672500	0.43322000
H	-0.68570300	-0.76100400	0.34720700
C	-2.08089100	0.00865900	1.82513200
H	-2.99110400	0.62218700	1.77597100
C	-2.47239400	-1.86390200	-0.08609100
C	-2.43893900	-1.22543000	-1.50774000
H	-3.31370900	-1.36607000	-2.15354600
H	-1.53971200	-1.52419600	-2.05812000
H	-1.31591000	1.32363700	3.38446300
H	-2.30542800	-0.81706600	2.51309400
C	-1.67667300	-3.15646200	0.09746000
H	-1.63673200	-3.44853500	1.15595800
H	-2.14363200	-3.98348900	-0.45449500
H	-0.64562400	-3.04532000	-0.25645300
C	-3.90940500	-2.03915200	0.42493900
H	-4.40823000	-2.84159900	-0.13362200
H	-3.92798600	-2.31898100	1.48579700
H	-4.51456200	-1.13205300	0.30749800
H	0.29772100	1.49025300	-2.75638700
O	3.22739300	0.31963300	1.14584700
S	3.18157500	-0.56934600	-0.06684000
O	1.86675200	-1.30150200	-0.14526700
O	3.52522900	0.14661400	-1.33000300
C	4.45158400	-1.83102600	0.17463200
H	5.41877200	-1.32964800	0.25155100
H	4.22673200	-2.37817200	1.09253600
H	4.43455700	-2.50112900	-0.68780900
C	0.85102600	1.97791000	-0.74296300
H	1.89372800	1.78530700	-1.02722200
H	0.56719400	3.02517700	-0.86481200
H	0.33460900	0.06746900	-1.70401800
H	1.03454600	0.44408000	0.74641400

INT-C



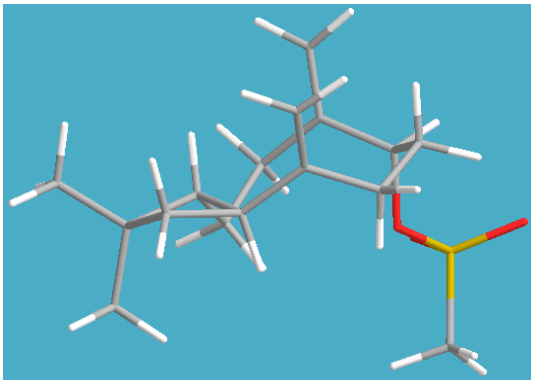
Zero-point correction= 0.396231
(Hartree/Particle)
Thermal correction to Energy= 0.418491
Thermal correction to Enthalpy= 0.419435
Thermal correction to Gibbs Free Energy= 0.344953
Sum of electronic and zero-point Energies= -1248.673526
Sum of electronic and thermal Energies= -1248.651266
Sum of electronic and thermal Enthalpies= -1248.650322
Sum of electronic and thermal Free Energies= -1248.724804

E(RB3LYP) = -1249.43452361 (THF)

0 1

C	-0.18418700	-1.93647200	0.71617100
C	0.11490200	-1.38455500	-1.65868500
C	1.03157600	-1.91935700	1.46264100
C	1.57091900	-1.03678300	-1.54366800
C	2.00024300	-2.84818500	1.21260300
C	2.50145800	-1.88004100	-2.04063300
H	2.93914700	-2.84132000	1.76198300
H	1.85460400	-3.66730500	0.51738100
H	3.56446100	-1.65765200	-1.97944000
H	2.22750000	-2.79709100	-2.55983500
C	1.22553100	-0.78462200	2.45235700
H	0.24257000	-0.47357600	2.82195700
C	1.98423000	0.25492200	-0.88748000
H	3.07121000	0.22041400	-0.74392100
C	1.33839300	0.82699700	0.42602000
H	0.25384700	0.66547600	0.42509500
C	1.92193800	0.43366400	1.78841100
H	2.99710500	0.22702700	1.68994100
C	1.55636500	2.27473800	-0.15727400
C	1.61952200	1.61019500	-1.56737200
H	2.34634300	2.00313600	-2.28851200
H	0.62800500	1.57892900	-2.03037500
H	1.81319200	-1.12190500	3.31412400
H	1.83358100	1.27828700	2.48448500
C	0.40958900	3.25752400	0.07810900
H	0.35012800	3.54427800	1.13746300
H	0.56411000	4.17724000	-0.50326800
H	-0.55106000	2.81990000	-0.21173800
C	2.89887500	2.90834200	0.23631600
H	3.07257300	3.81285300	-0.36079700
H	2.90568300	3.20763300	1.29220400
H	3.75253200	2.23886400	0.07310700
H	-0.09964900	-1.87244400	-2.61504600
O	-2.26434300	0.18034800	1.34545200
S	-2.90532700	0.20085200	-0.01854400
O	-2.13932400	1.04183200	-0.99050600
O	-3.18692300	-1.17819600	-0.52703600
C	-4.50996800	1.00273100	0.20234900
H	-5.09354500	0.41382900	0.91303400
H	-4.34156800	2.01167800	0.58479800
H	-5.00832900	1.03784800	-0.76879800
C	-0.37131100	-2.52323000	-0.58983700
H	-1.43544700	-2.66311800	-0.80061100
H	0.23133900	-3.41095200	-0.79336400
H	-0.55119800	-0.52449600	-1.55462100
H	-1.00565000	-1.30824000	1.08801700

SM-D



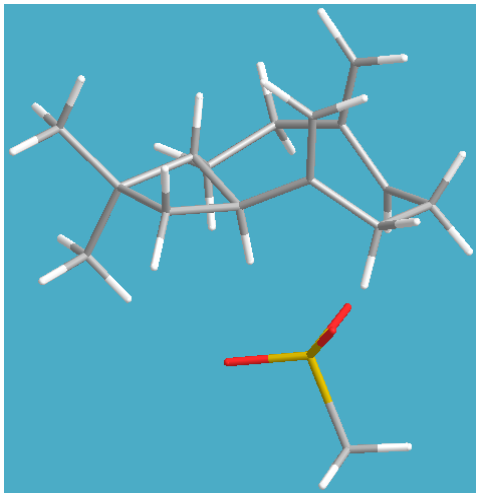
Zero-point correction= 0.398853
(Hartree/Particle)
Thermal correction to Energy= 0.420207
Thermal correction to Enthalpy= 0.421152
Thermal correction to Gibbs Free Energy= 0.347498
Sum of electronic and zero-point Energies= -1248.720946
Sum of electronic and thermal Energies= -1248.699591
Sum of electronic and thermal Enthalpies= -1248.698647
Sum of electronic and thermal Free Energies= -1248.772301

E(RB3LYP) = -1249.47015126 (THF)

0 1

C	-1.47636100	0.99342200	0.64836300
C	0.05099200	2.01015400	-1.26235900
C	-0.48672100	0.45825200	1.68405400
C	1.50504700	1.87759200	-0.80955100
C	-0.08147400	1.28092900	2.66074300
C	2.18619500	2.96198400	-0.41200000
H	0.59107800	0.93879500	3.44286400
H	-0.40336700	2.31796300	2.72688400
H	3.22698900	2.91847300	-0.10423600
H	1.71893200	3.94473300	-0.37577200
C	-0.05600800	-0.99313800	1.65636400
H	0.45529500	-1.19486700	2.60573600
C	2.12912000	0.50575900	-0.90555500
H	1.67946400	-0.00337200	-1.76928300
C	2.09440600	-0.50008500	0.29882800
H	2.27952100	0.07424600	1.21637400
C	0.88529400	-1.41913800	0.50200300
H	0.31690600	-1.49916600	-0.43196700
C	-1.03526000	2.21132600	-0.18125500
H	-0.71966800	2.99469600	0.51746500
H	-1.93808300	2.58142700	-0.68317200
H	-0.22618300	1.14796200	-1.88004300
C	3.48137200	-1.05596200	-0.18877500
C	3.66295500	0.28720000	-0.96178500
H	4.12097000	0.24428300	-1.95751900
H	4.21161300	1.01675500	-0.35635600
H	-0.94574400	-1.63491800	1.63660900
H	1.22779500	-2.43690600	0.73708700
C	4.50001500	-1.35100400	0.91325400
H	4.19358600	-2.21756900	1.51561000
H	5.48825400	-1.57694200	0.48967200
H	4.61339100	-0.49554700	1.59066000
C	3.37465700	-2.25383200	-1.14331600
H	4.34719800	-2.44878200	-1.61411500
H	3.07749100	-3.16686800	-0.61191800
H	2.64778200	-2.08551100	-1.94675900
H	-0.01700700	2.88519800	-1.92138800
O	-1.85052200	-0.06730700	-0.30426400
H	-2.39039200	1.28781700	1.17498200
S	-3.38713800	-0.63688100	-0.23760600
O	-3.50658400	-1.61099000	0.84885700
O	-4.32157400	0.49073800	-0.29419300
C	-3.36781400	-1.49812200	-1.81369400
H	-3.20990400	-0.77027300	-2.61054200
H	-2.57516600	-2.24762300	-1.79247700
H	-4.34561400	-1.97545100	-1.91180800

TS-D



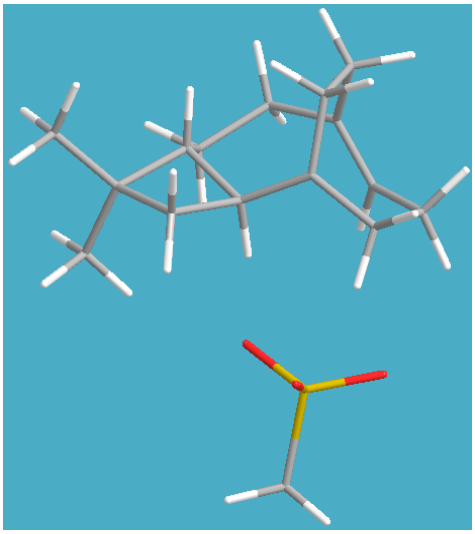
Zero-point correction= 0.396576
(Hartree/Particle)
Thermal correction to Energy= 0.417785
Thermal correction to Enthalpy= 0.418729
Thermal correction to Gibbs Free Energy= 0.347270
Sum of electronic and zero-point Energies= -1248.670710
Sum of electronic and thermal Energies= -1248.649502
Sum of electronic and thermal Enthalpies= -1248.648557
Sum of electronic and thermal Free Energies= -1248.720017

E(RB3LYP) = -1249.43011842 (THF)

0 1

C	-0.82220000	1.98011300	0.66190400
C	0.20944400	2.14132600	-1.68563900
C	0.27110600	1.71916600	1.53277600
C	1.47250900	1.45442300	-1.23045500
C	1.33687600	2.58225300	1.54862600
C	2.63175300	2.14517400	-1.15776400
H	2.17990300	2.40972400	2.21290200
H	1.33874800	3.52431900	1.01526100
H	3.56669100	1.67528200	-0.86231800
H	2.68839700	3.19665200	-1.43260900
C	0.28733400	0.46772800	2.39128800
H	0.99296200	0.62312000	3.21606600
C	1.37662300	-0.01552500	-0.88298900
H	0.36555600	-0.36028800	-1.11031300
C	1.78097100	-0.58311000	0.53234200
H	2.60562000	0.02067200	0.94134100
C	0.69114900	-0.79946000	1.58763300
H	-0.19741400	-1.22443700	1.11365200
C	-0.68449700	2.82027700	-0.53475000
H	-0.18436100	3.76464000	-0.28796300
H	-1.66083600	3.03606100	-0.97167300
H	-0.45255100	1.42568200	-2.17515500
C	2.40484000	-1.83617700	-0.18631700
C	2.41693400	-1.00235200	-1.50076300
H	2.10634600	-1.51139000	-2.42052800
H	3.38740800	-0.52290400	-1.67370000
H	-0.70486200	0.30730800	2.82761500
H	1.03662700	-1.54820500	2.31430300
C	3.77104200	-2.27842500	0.34031500
H	3.68709200	-2.70534500	1.34913600
H	4.21173500	-3.04857600	-0.30700600
H	4.47665300	-1.43859200	0.38827700
C	1.45277900	-3.03724800	-0.28266500
H	1.86538400	-3.78049200	-0.97772300
H	1.32833600	-3.52794100	0.69053500
H	0.45412300	-2.76130500	-0.63679300
H	0.44145100	2.95658000	-2.37905900
O	-1.90489500	0.11295600	-0.96142800
H	-1.77376100	1.49541500	0.87971100
S	-2.79977000	-0.74850400	-0.08782900
O	-2.27252100	-2.12323800	0.08911100
O	-3.13611300	-0.02935400	1.18163800
C	-4.34992900	-0.90663400	-1.00777300
H	-4.76612300	0.08985300	-1.16978300
H	-4.13722300	-1.39774700	-1.95971200
H	-5.03176100	-1.51411500	-0.40839100

INT-D



Zero-point correction= 0.399132
(Hartree/Particle)
Thermal correction to Energy= 0.420340
Thermal correction to Enthalpy= 0.421285
Thermal correction to Gibbs Free Energy= 0.348991
Sum of electronic and zero-point Energies= -1248.685749
Sum of electronic and thermal Energies= -1248.664541
Sum of electronic and thermal Enthalpies= -1248.663597
Sum of electronic and thermal Free Energies= -1248.735890

E(RB3LYP) = -1249.44858342 (THF)

0 1

C	0.04836600	-2.14460800	0.94036700
C	0.28670300	-1.74334600	-1.67021400
C	-1.27106400	-1.97384300	1.16047500
C	-0.94650200	-1.04585400	-1.33855900
C	-2.25991900	-2.49661300	0.13631700
C	-2.21310400	-1.78715400	-1.32953400
H	-3.28800900	-2.39725900	0.49248100
H	-2.07169500	-3.55747100	-0.05401400
H	-3.07718300	-1.12637900	-1.42346700
H	-2.25602800	-2.56456500	-2.09542200
C	-1.78239900	-1.03688900	2.24087800
H	-2.84480200	-1.23304800	2.43775700
C	-0.87995700	0.25173600	-0.68684700
H	0.13647200	0.44934500	-0.33294000
C	-1.93358300	0.73017300	0.36420800
H	-2.92770100	0.32195100	0.13466600
C	-1.58565600	0.45384400	1.83268600
H	-0.54050900	0.73083500	2.00448800
C	0.57717300	-2.69805400	-0.35047300
H	0.13591000	-3.67110800	-0.59253000
H	1.66633500	-2.76328700	-0.32294900
H	1.13721600	-1.06099800	-1.77824200
C	-1.86266500	2.17052100	-0.26187300
C	-1.29553500	1.52190400	-1.56474200
H	-0.44513600	1.99575300	-2.06091500
H	-2.08014700	1.28669700	-2.29196900
H	-1.24828700	-1.21143600	3.18234500
H	-2.20583600	1.08816900	2.48219100
C	-3.20675800	2.88125900	-0.42218300
H	-3.61294900	3.17203400	0.55555000
H	-3.09831800	3.79632300	-1.01885900
H	-3.94922600	2.24255800	-0.91837700
C	-0.83202600	3.09070500	0.40573800
H	-0.69505300	3.99551700	-0.20047400
H	-1.18209600	3.40627400	1.39678800
H	0.14466300	2.61159600	0.52970200
H	0.18386300	-2.42661500	-2.51767600
O	3.18235700	-1.06390100	0.38497200
H	0.78258800	-1.71384300	1.61706500
S	2.86014200	0.35973900	0.06597500
O	2.45456100	0.56321700	-1.36633900
O	1.86893400	0.96764200	1.01659200
C	4.39881300	1.28562000	0.28598400
H	4.72300100	1.16913800	1.32244800
H	5.14536500	0.87526900	-0.39750200
H	4.20714100	2.33664000	0.05908700