

Supporting Information

Skeletal Diversification by C–C Cleavage to Access Bicyclic Frameworks from a Common Tricyclooctane Intermediate

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1 General Considerations

Unless otherwise noted, all reactions were performed in flame or oven-dried glassware fitted with rubber septa under a positive pressure of nitrogen using standard Schlenk techniques. Air- and moisture-sensitive liquids were transferred via syringe or stainless steel cannula through rubber septa. Solids were added under inert gas or were dissolved in appropriate solvents. Low temperature reactions were carried out in a Dewar vessel filled with a cooling agent: acetone/dry ice ($-78\text{ }^{\circ}\text{C}$), $\text{H}_2\text{O}/\text{ice}$ ($0\text{--}5\text{ }^{\circ}\text{C}$). Reaction temperatures above $23\text{ }^{\circ}\text{C}$ were conducted in an oil bath or in a heated metal block (reactions conducted in vials). The reaction mixtures were magnetically stirred and monitored by NMR spectroscopy or analytical thin-layer chromatography (TLC), using glass plates precoated with silica gel (Silicycle Siliaplates, glass-backed, extra hard layer, 60 \AA , $250\text{ }\mu\text{m}$ thickness, F254 indicator). TLC plates were visualized by exposure to ultraviolet light (254 nm), were stained by submersion in aqueous potassium permanganate solution (KMnO_4), *p*-anisaldehyde, or ceric ammonium molybdate solution (CAM), and were developed by heating with a heat gun. Flash-column chromatography on silica gel was performed as described by Still et al.,¹ employing silica gel (Silicycle silica gel, $40\text{--}63\text{ }\mu\text{m}$ particle size). Organic solutions were concentrated under reduced pressure on a temperature-controlled rotary evaporator equipped with a dry ice/isopropanol condenser. Yields refer to chromatographically and spectroscopically (^1H and ^{13}C NMR) pure material.

1.1 Materials

Unless noted below, commercial reagents were purchased from Sigma Aldrich, Acros Organics, ChemImpex, Oakwood Chemical, Combi-blocks, TCI, and/or Alfa Aesar, and used without additional purification. Solvents were purchased from Fisher Scientific, Acros Organics, Alfa Aesar, and Sigma Aldrich. Tetrahydrofuran (THF), diethyl ether (Et_2O), acetonitrile (CH_3CN), benzene, toluene (PhMe), methanol (MeOH), and triethylamine (Et_3N) were sparged with argon and dried by passing through alumina columns using argon in a Glass Contour solvent purification system. Dichloromethane (CH_2Cl_2 , DCM) was freshly distilled over calcium hydride under a N_2 atmosphere prior to each use.

1.2 NMR spectroscopy

NMR spectral data were obtained using deuterated solvents, obtained from Cambridge Isotope Laboratories, Inc. ^1H NMR and ^{13}C NMR data were recorded on Bruker AVB-400, AVQ-400, AV-500, NEO-500, AV-600 or AV-700 spectrometers operating at 400 MHz , 400 MHz , 500 MHz , 500 MHz , 600 MHz , 700 MHz for proton nuclei (100 MHz , 100 MHz , 125 MHz , 125 MHz , 150 MHz , 175 MHz for carbon nuclei), respectively. Proton chemical shifts are expressed in parts per million (ppm, δ scale) and are referenced to residual protium in the NMR solvent (CHCl_3 : δ 7.26). Carbon chemical shifts are expressed in parts per million (δ scale, assigned carbon atom) and are referenced to the carbon resonance of the NMR solvent (CDCl_3 : δ 77.16). ^1H NMR spectroscopic data are reported as follows: Chemical shift in ppm (multiplicity, coupling constants J (Hz), integration) (e.g., “5.21 (t, 3 J = 7.3 Hz, ^1H)”). The multiplicities are abbreviated with s (singlet),

br s (broad singlet), d (doublet), t (triplet), q (quartet), p (pentet), se (sextet), h (heptet), m (multiplet) and app (apparent multiplicity). In case of combined multiplicities, the multiplicity with the larger coupling constant is stated first. Except for multiplets, the chemical shift of all signals, as well for centrosymmetric multiplets, is reported as the center of the resonance range. Data for ^{13}C spectroscopy are reported in terms of chemical shift (δ ppm). In addition to 1D NMR experiments, 2D NMR techniques such as homonuclear correlation spectroscopy (COSY), heteronuclear single quantum coherence (HSQC), heteronuclear multiple bond coherence (HMBC) and nuclear Overhauser enhancement spectroscopy (NOESY) were used in structure elucidation. All raw FID files were processed and the spectra analyzed using the program MestReNOVA 11.0 from Mestrelab Research S. L.

Note: The AVB-400, AVQ-400, AV-500, DRX-500 and AV-600 instruments were partially supported by NIH grants SRR023679A, RR02424A-01, S10RR03353-01 and 1S10RR016634-01, and NSF grants CHE-9633007, CHE-8208992, CHE-0130862, and CHE-8703048. The AV-700 instrument was supported by the Berkeley College of Chemistry NMR facility.

1.3 Mass spectrometry

Mass spectral data were obtained from the Mass Spectral Facility at the University of California, Berkeley, on a Finnigan/Thermo LTQ-FT instrument (ESI). Data acquisition and processing were performed using the XcaliburTM software.

1.4 IR spectroscopy

IR spectroscopic data were recorded on a Bruker ALPHA FT-IR spectrophotometer using a diamond attenuated total reflectance (ATR) accessory. When required, substances were dissolved in dichloromethane prior to direct application on the ATR unit. Data are represented as follows: frequency of absorption (cm^{-1}), and intensity of absorption (s = strong, m = medium, w = weak, br = broad).

1.5 X-ray analysis

Single-crystal X-ray diffraction experiments were performed at the UC Berkeley CHEXRAY crystallographic facility. Measurements of all compounds were performed on a Rigaku XtaLAB P200 rotating anode equipped with a Pilatus 200K hybrid pixel array detector. Data were collected using Cu $K\alpha$ radiation ($\lambda = 1.54184 \text{ \AA}$). Crystals were kept at 100(2) K throughout collection. Data collection was performed with CrysAlisPro. 2 Data processing was done using CrysAlisPro and included either a multi-scan absorption or face-indexed absorption correction applied using the SCALE3 ABSPACK scaling algorithm within CrysAlisPro. All structures were solved with SHELXT.3 Structures were refined with SHELXL.4 All non-hydrogen atoms were refined anisotropically, and hydrogen atoms were either included at the geometrically calculated positions and refined using a riding model or located as Q peaks in the Fourier difference map.

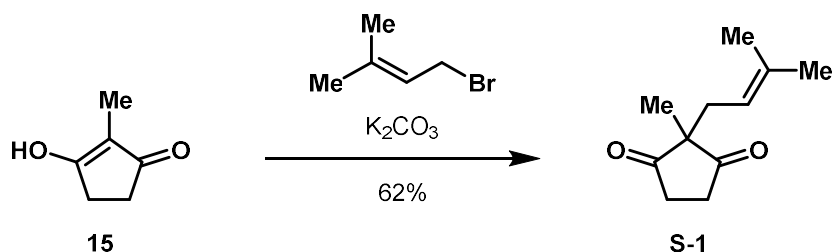
Note: The instruments are supported by an NIH Shared Instrumentation Grant S10-RR027172.

1.6 UV-Vis spectroscopy

UV-Vis spectroscopy was performed on a Varian 5000 UV-Vis-NIR spectrometer using quartz cuvettes with a path length of 1 cm. Data were collected using DCM as a solvent with an absorbance window between 200 and 650 nm.

2 Synthetic Procedures and Analytical Data

2.1 Synthesis of prenylated 2-methylcyclopentane-1,3-dione **S-1**



A flame-dried flask was charged with 2-methylcyclopentane-1,3-dione (**15**, 5.0 g, 45 mmol, 1 equiv) followed by acetone (200 mL). To this orange stirring suspension was added potassium carbonate (9.2 g, 67 mmol, 1.5 equiv) as a single portion followed by the stream-wise addition of 1-bromo-3-methylbut-2-ene (10 mL, 89 mmol, 2 equiv). The cloudy light-brown reaction mixture was stirred under an atmosphere of nitrogen for 24 h. The reaction mixture was then concentrated *in vacuo*, resuspended in ether, and mixed with a solution of sat. aq. NaCl. The aqueous layer was extracted two times with ether. The combined organic fractions were dried over Na_2SO_4 , filtered, and concentrated *in vacuo*. The crude reaction mixture was purified by silica gel flash chromatography (gradient 5:1 pentane: diethyl ether to 1:1 pentane: diethyl ether) to yield **S-1** as a pale-yellow oil (5.1 g, 62%).

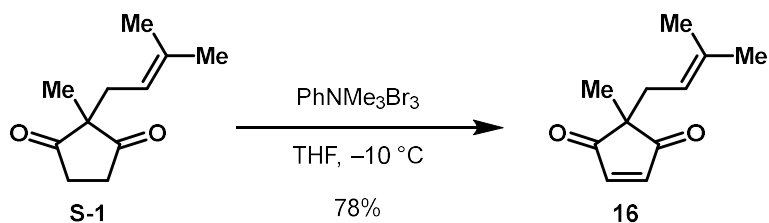
R_f = 0.55 (hexane:EtOAc = 10:1), UV-active, blue spot (*p*-anisaldehyde)

1H NMR (500 MHz, $CDCl_3$) δ 4.91 (tt, J = 7.8, 1.6 Hz, 1H), 2.75 – 2.61 (m, 4H), 2.31 (d, J = 7.9 Hz, 2H), 1.64 (s, 3H), 1.55 (s, 3H), 1.08 (s, 3H) ppm.

^{13}C NMR (126 MHz, $CDCl_3$) δ 217.1, 136.8, 117.2, 57.1, 35.7, 35.5, 26.0, 18.5, 17.9 ppm.

Spectral data were consistent with those reported in the literature.¹

2.2 Synthesis of enedione **16**



A solution of **S-1** (3.0 g, 17 mmol, 1 equiv) in THF (170 mL) was cooled to $-10\text{ }^\circ\text{C}$. To this cooled solution was added phenyltrimethylammonium tribromide (6.3 g, 17 mmol, 1 equiv) in four portions, after which the solution turned bright and cloudy yellow-orange. Portions were added in 30 min intervals. Completion of the reaction was judged by TLC (usually within 3 h). Upon completion, the reaction mixture was diluted with diethyl ether and quenched with sat. aq. NaHCO_3 and sat. aq. $\text{Na}_2\text{S}_2\text{O}_3$ (4:1). The layers were separated and the aqueous layer was extracted twice with diethyl ether. The combined organic layers were dried over Na_2SO_4 , filtered, and concentrated *in vacuo*. The crude reaction mixture was purified by silica gel flash chromatography (gradient 5:1 pentane: diethyl ether to 1:1 pentane: diethyl ether) to yield **16** as a bright yellow oil (2.3 g, 78%).

At temperatures above $0\text{ }^\circ\text{C}$, bromo-enedione **33** was isolated in 15% yield (0.44 g) as a yellow solid. Lowering the temperature completely suppressed formation of this product (see page S19 for analytical data).

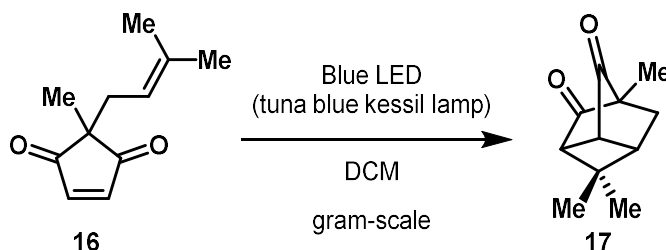
$R_f = 0.55$ (hexane:EtOAc = 10:1), UV-active, blue-green spot (*p*-anisaldehyde)

$^1\text{H NMR}$ (500 MHz, CDCl_3) δ 7.21 (s, 2H), 4.83 – 4.75 (m, 1H), 2.36 (d, $J = 7.8\text{ Hz}$, 2H), 1.58 (s, 3H), 1.54 (s, 3H) 1.13 (s, 3H) ppm.

$^{13}\text{C NMR}$ (126 MHz, CDCl_3) δ 208.0, 148.6, 136.4, 117.5, 51.0, 33.5, 25.9, 18.7, 17.7 ppm.

Spectral data was consistent with those found in the literature.²

2.3 Preparative-scale Synthesis of [3.2.1.0^{3,6}] tricyclooctane **17**



Enedione **16** (1.0 g, 5.6 mmol) was dissolved in DCM (100 mL) under air in a round-bottomed flask. The resulting pale-yellow solution was then moved to a photoreactor containing two tuna blue Kessil lamps (see below). The pale-yellow reaction mixture was irradiated at maximum intensity under a constant stream of air to maintain the temperature at 23 °C. After complete consumption of the starting material (as judged by NMR), the now clear reaction mixture was concentrated *in vacuo* to yield title compound **17**.

Note: reaction time was heavily dependent on reaction scale. Reaction time was optimized for a given scale through careful monitoring of reaction progress by NMR. Prolonged exposure increased the presence of baseline impurities and decreased yield of desired tricycle.

Slight impurities could be washed away with heptanes and filtration (for impurities that are not soluble in heptanes) yielding pure **17** as a pale-yellow amorphous solid. The resulting tricycle was not stable to silica gel chromatography but was of sufficient purity to be used directly in the subsequent reactions without purification.

Optimization scale: Reaction at 0.1 mmol was performed in a Penn1A-photoreactor (see below) Irradiation at 420 nm for 10 h led to complete conversion at this scale and set-up. Reaction efficiency was determined by NMR yield (95%, average of 3 trials).

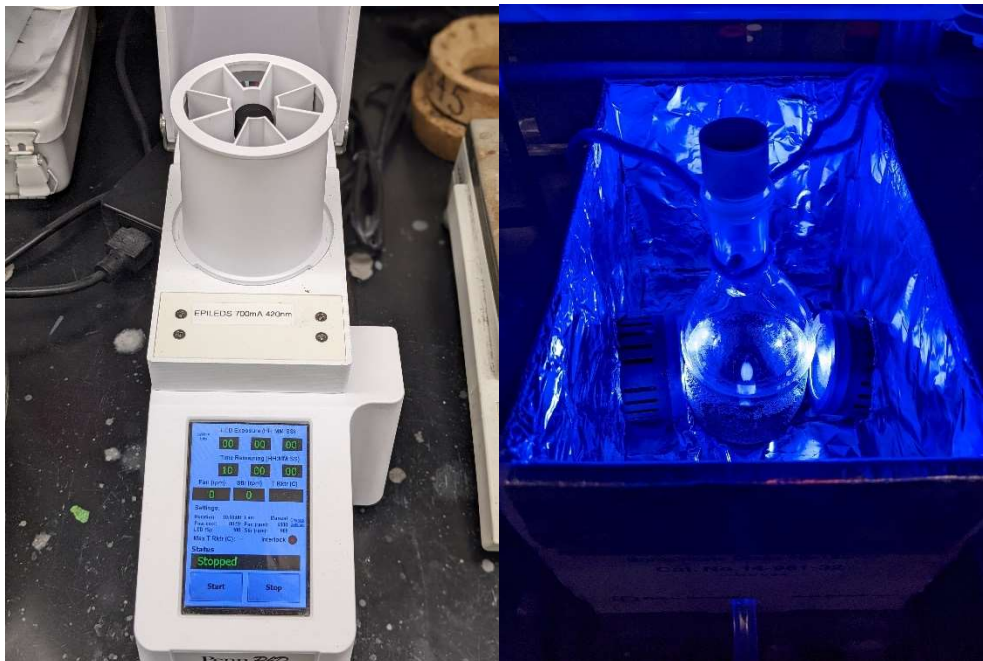
R_f = 0.4 (hexane:EtOAc = 10:1), green streak (*p*-anisaldehyde)

¹H NMR (500 MHz, CDCl₃) δ 3.25 (t, *J* = 4.4 Hz, 1H), 3.00 (t, *J* = 4.8 Hz, 1H), 2.61 (dd, *J* = 5.2, 4.7 Hz, 1H), 2.23 – 2.15 (m, 2H), 1.47 (s, 3H), 1.13 (s, 3H), 0.98 (s, 3H) ppm.

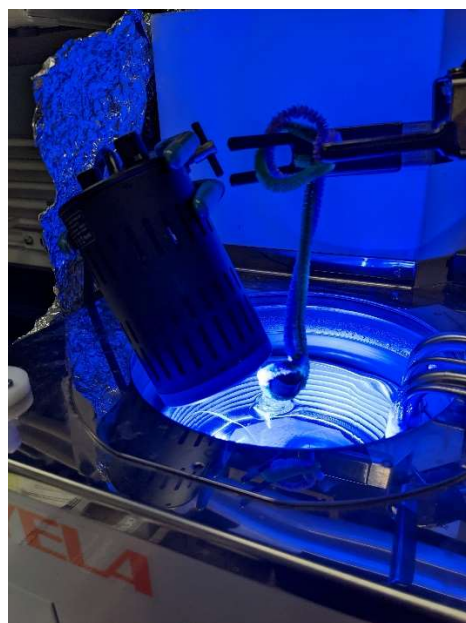
¹³C NMR (151 MHz, CDCl₃) δ 208.8, 207.1, 61.4, 59.4, 46.7, 45.6, 41.5, 35.2, 28.6, 21.9, 7.0 ppm.

IR (neat): ν = 2970, 2880, 1737, 1726, 1453, 1367, 1229, 1217, 1145, 118, 1099, and 527.

HRMS (EI, *m/z*): for [M]⁺ calcd. for C₁₁H₁₄O₂ 178.0994; found 178.0993.

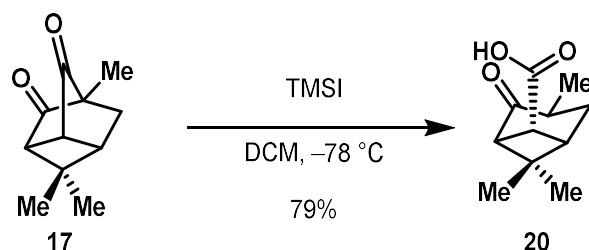


Left: Standard Penn photoreactor setup for optimization scale. Fan 68000 rpm, Stir 909 rpm, LED% 100. Right: preparative-scale reaction full intensity irradiation with two tuna blue Kessil lamps and constant stream of air



Low temperature LED setup. Cooling bath set to $-30\text{ }^{\circ}\text{C}$ and irradiated at full intensity with tuna blue Kessil lamp

2.4 Synthesis of bicyclo [3.1.1]heptane 20



A solution of tricycle **17** (50 mg, 0.28 mmol, 1 equiv) in DCM (2.8 mL) was cooled to $-78\text{ }^{\circ}\text{C}$. TMSI (40 μL , 0.28 mmol, 1 equiv) was added to the cooled solution. The orange reaction mixture was stirred for 1 h and then quenched by the addition of sat. aq. NaCl and diluted with EtOAc. The layers were separated, and the aqueous layer was extracted twice with EtOAc. The combined organic layers were dried over Na_2SO_4 , filtered, and concentrated *in vacuo*. The crude residue was purified by silica gel flash chromatography (hexanes: EtOAc 1:2) to afford **20** as an orange oil (43 mg, 0.22 mmol, 79%).

$R_f = 0.4$ (hexane:EtOAc = 1:1), yellow streak (*p*-anisaldehyde)

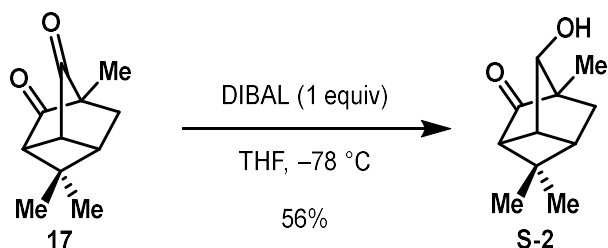
$^1\text{H NMR}$ (500 MHz, CDCl_3) δ 3.58 (t, $J = 5.8$ Hz, 1H), 2.92 (t, $J = 5.2$ Hz, 1H), 2.64 – 2.51 (m, 2H), 2.34 (dt, $J = 10.0, 6.9$ Hz, 1H), 1.59 – 1.45 (m, 1H), 1.34 (s, 3H), 1.16 (d, $J = 6.8$ Hz, 3H), 0.77 (s, 3H) ppm.

$^{13}\text{C NMR}$ (126 MHz, CDCl_3) δ 214.6, 179.1, 60.4, 45.1, 40.5, 39.3, 37.8, 28.8, 26.1, 21.3, 14.9 ppm.

IR (neat): $\nu = 3454, 2962, 2937, 2877, 1711, 1455, 1378, 1253, 1230, 1216, 1146, 1119, 1099, 1056, 1013, 987, 953, 913, 864, 841, \text{ and } 723$.

HRMS (ESI, m/z): for $[\text{M}-\text{H}]^-$ calcd. for $\text{C}_{11}\text{H}_{15}\text{O}_3$ 195.1027; found 195.1027.

2.5 Synthesis of ketoalcohol S-2



A flame-dried flask was charged with tricyclic **17** (400 mg, 2.24 mmol, 1 equiv) and THF (22 mL). The clear solution was cooled to $-78\text{ }^{\circ}\text{C}$. DIBAL (2.24 mL, 1M in hexanes, 1 equiv) was added dropwise to the cooled solution. The reaction mixture was stirred for 1 h then quenched by the addition of sat. aq. NaCl and diluted with EtOAc. The layers were separated and the aqueous layer was extracted twice with EtOAc. The combined organic layers were dried over Na_2SO_4 , filtered, and concentrated *in vacuo*. The crude compound was purified by silica gel flash chromatography (hexanes: EtOAc 1:1) to afford **S-2** as a white solid (230 mg, 1.3 mmol, 56%).

The doubly reduced diol (**25**) was also isolated in ca. 20% yield. However, a more selective synthesis was later developed using 2 equiv of DIBAL (*vide infra*). Starting material was also observed and recovered in ca. 10% yield.

$R_f = 0.25$ (hexane:EtOAc = 4:1), purple spot (*p*-anisaldehyde)

$^1\text{H NMR}$ (400 MHz, CDCl_3) δ 3.57 (d, $J = 1.9$ Hz, 1H), 3.12 (td, $J = 4.4, 1.9$ Hz, 1H), 2.37 (m, 2H), 2.18 (dd, $J = 12.5, 6.6$ Hz, 1H), 1.57 (d, $J = 12.5$ Hz, 1H), 1.29 (s, 3H), 1.08 (s, 3H), 0.75 (s, 3H) ppm.

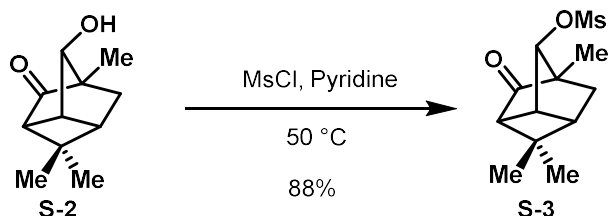
$^{13}\text{C NMR}$ (101 MHz, CDCl_3) δ 215.6, 77.7, 57.9, 56.5, 44.4, 43.4, 43.2, 32.6, 28.4, 20.9, 10.1 ppm.

IR (neat): $\nu = 3418, 2958, 2870, 1720, 1454, 1277, 1124, 1094, 1061, 877, \text{ and } 564$.

HRMS (ESI, m/z): for $[\text{M}+\text{H}]^+$ calcd. for $\text{C}_{11}\text{H}_{17}\text{O}_2$ 181.1223; found 181.1223.

M.p. = $68\text{ }^{\circ}\text{C}$

2.6 Synthesis of mesylate S-3



A flame-dried vial was charged with ketoalcohol **S-2** (160 mg, 0.89 mmol, 1 equiv) and pyridine (1.79 mL, 22.2 mmol, 25 equiv). Mesityl chloride (0.14 mL, 1.8 mmol, 2 equiv) was added to the resulting solution. The vial was moved to a pre-heated vial block at 50 °C. After stirring 3 h at this temperature, the reaction mixture was cooled back to room temperature then quenched by the addition of sat. aq. NH₄Cl and diluted with EtOAc. The layers were separated and the aqueous layer was extracted twice with EtOAc. The combined organic layers were dried over Na₂SO₄, filtered, and concentrated *in vacuo*. The crude residue was purified by silica gel flash chromatography (hexanes: EtOAc 2:1) to afford **S-3** as a pale amorphous solid (200 mg, 0.78 mmol, 88%). Notably, the elevated temperature and choice of pyridine as solvent were crucial for reproducibility.

R_f = 0.30 (hexane:EtOAc = 4:1), blue spot (*p*-anisaldehyde)

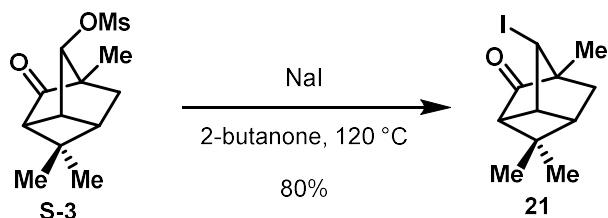
¹H NMR (400 MHz, CDCl₃) δ 4.42 (d, *J* = 1.9 Hz, 1H), 3.46 (td, *J* = 4.4, 1.9 Hz, 1H), 3.04 (s, 3H), 2.56 – 2.46 (m, 2H), 2.20 (dd, *J* = 13.0, 6.3 Hz, 1H), 1.72 (d, *J* = 12.9 Hz, 1H), 1.33 (s, 3H), 1.18 (s, 3H), 0.80 (s, 3H) ppm.

¹³C NMR (101 MHz, CDCl₃) δ 210.8, 85.0, 57.2, 57.1, 43.8, 43.3, 38.7, 33.5, 28.2, 20.8, 10.1 ppm.

IR (neat): ν = 3022, 2958, 2872, 1742, 1457, 1354, 1174, 1064, 959, 884, 856, 812, 770, 693, 595, 561, 520, and 491.

HRMS (ESI, *m/z*): for [M+Na]⁺ calcd. for C₁₂H₁₈NaO₄S₁ 281.0818; found 281.0818.

2.7 Synthesis of iodide **21**



A flame-dried vial was charged with keto-mesylate **S-3** (50 mg, 0.19 mmol, 1 equiv) and 2-butanone (2 mL). Sodium iodide (87 mg, 0.58 mmol, 3 equiv) was added to the solution resulting in a slightly orange heterogeneous reaction mixture. The vial was sealed and moved to a preheated vial block at 120 °C. After 14 h at this temperature, the reaction mixture was cooled to room temperature then quenched by the addition of sat. aq. NaHCO₃ and sat. aq. Na₂S₂O₃ (4:1) and diluted with EtOAc. The layers were separated and the aqueous layer was extracted twice with EtOAc. The combined organic layers were dried over Na₂SO₄, filtered, and concentrated *in vacuo*. The crude residue was purified by silica gel flash chromatography (hexanes: EtOAc 4:1) to afford **21** as a pale orange solid (45 mg, 0.15 mmol, 80%).

R_f = 0.75 (hexane:EtOAc = 4:1), UV-active, purple spot (*p*-anisaldehyde)

¹H NMR (500 MHz, CDCl₃) δ 3.98 (d, *J* = 2.3 Hz, 1H), 3.42 (td, *J* = 4.3, 2.3 Hz, 1H), 2.45 (t, *J* = 4.6 Hz, 1H), 2.30 (q, *J* = 4.6 Hz, 1H), 1.78 – 1.72 (m, 2H), 1.31 (s, 3H), 1.16 (s, 3H), 0.80 (s, 3H) ppm.

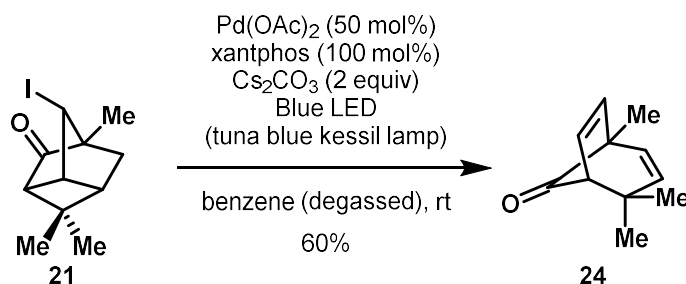
¹³C NMR (126 MHz, CDCl₃) δ 213.2, 58.2, 55.9, 46.8, 43.3, 41.2, 40.2, 35.2, 28.1, 19.6, 13.4 ppm.

IR (neat): ν = 2958, 2927, 2868, 1746, 1461, 1381, 1296, 1278, 1252, 1203, 1149, 1074, 1054, 1019, 905, 856, 836, 735, and 703.

HRMS (EI, *m/z*): for [M]⁺ calcd. for C₁₁H₁₆OI 291.0240; found 291.0240.

M.p = 40 °C

2.8 Synthesis of bicyclo[3.2.1]octane **24**



Ketoiodide **21** (8 mg, 0.028 mmol, 1 equiv), Pd(OAc)₂ (3.1 mg, 0.014 mmol, 0.5 equiv), and xantphos (16 mg, 0.028 mmol, 1 equiv) were added to a flame-dried vial. The reaction vessel was moved into the glove box, after which Cs₂CO₃ (18 mg, 0.055 mmol, 2 equiv) and degassed benzene (0.11 mL, free-pump-thaw) were added. The vial was sealed and removed from the glove box then placed in a photoreactor equipped with two tuna blue Kessil lamps (see above). The light orange reaction mixture was irradiated at maximum intensity under a constant stream of air to maintain the temperature at 23 °C. The reaction mixture immediately began to darken in color becoming brown-black after 30 min. After 3 h, the crude reaction mixture was removed from the photoreactor and loaded directly onto a pipette silica gel column and purified (pentane:ether 10:1) to afford **24** (3 mg, 0.017 mmol, 60% adjusted for BHT impurity (from Et₂O stabilizer) in NMR) as a clear oil.

Note: **24** is sensitive to temperature and prolonged LED exposure. Concentration on the rotovap at elevated temperatures (>35 °C) led to complete decomposition.

R_f = 0.77 (hexane:EtOAc = 4:1), UV-active, purple spot (*p*-anisaldehyde)

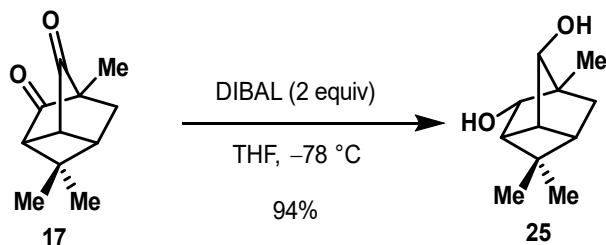
¹H NMR (500 MHz, C₆D₆) δ 6.17 (d, *J* = 6.8 Hz, 1H), 5.75 (dd, *J* = 6.8, 3.2 Hz, 1H), 5.43 (d, *J* = 9.4 Hz, 1H), 4.90 (dd, *J* = 9.4, 1.9 Hz, 1H), 2.44 (dd, *J* = 3.4, 1.9 Hz, 1H), 1.07 (s, 3H), 1.04 (s, 3H), 0.72 (s, 3H) ppm.

¹³C NMR (151 MHz, C₆D₆) δ 210.2, 145.5, 137.2, 135.4, 129.4, 59.4, 47.8, 41.4, 27.3, 24.7, 14.2 ppm.

IR (neat): ν = 2901, 1777, 1324, 1244, 1151, 859, 726, and 588.

HRMS (EI, *m/z*): for [M]⁺ calcd. for C₁₁H₁₅O 163.1117; found 163.1117.

2.9 Synthesis of diol **25**



A flame-dried flask was charged with tricycle **17** (500 mg, 2.81 mmol, 1 equiv) and THF (44 mL). The clear solution was cooled to $-78\text{ }^{\circ}\text{C}$. DIBAL (5.62 mL, 1M in hexanes, 2 equiv) was added dropwise to the cooled solution. The reaction mixture was stirred for 1 h then quenched by the addition of sat. aq. NaCl and diluted with EtOAc. The layers were separated and the aqueous layer was extracted twice with EtOAc. The combined organic layers were dried over Na_2SO_4 , filtered, and concentrated *in vacuo*. The crude compound was purified by silica gel flash chromatography (hexanes: EtOAc 1:1) to afford diol **25** as a white solid (480 mg, 2.6 mmol, 94%).

Suitable crystals for X-ray analysis could be grown through slow diffusion from a pentane EtOAc solution.

$R_f = 0.55$ (hexane:EtOAc = 1:1), blue spot (*p*-anisaldehyde)

$^1\text{H NMR}$ (400 MHz, CDCl_3) δ 3.76 (dd, $J = 6.9, 2.2$ Hz, 1H), 3.48 (d, $J = 1.9$ Hz, 1H), 2.81 (td, $J = 4.4, 1.9$ Hz, 1H), 2.14 (ddd, $J = 11.4, 6.9, 4.4$ Hz, 2H), 1.98 (d, $J = 12.8$ Hz, 1H), 1.71 – 1.64 (m, 1H), 1.14 (s, 3H), 1.13 (s, 3H) 1.04 (s, 3H) ppm.

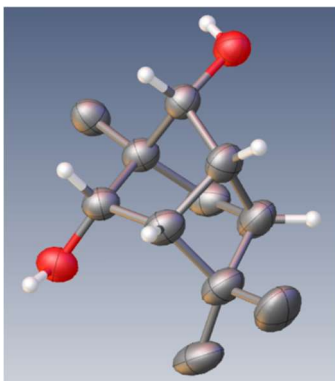
$^{13}\text{C NMR}$ (101 MHz, CDCl_3) δ 79.5, 78.3, 49.6, 47.0, 45.8, 43.9, 39.0, 30.2, 30.1, 22.7, 14.3 ppm.

IR (neat): $\nu = 3370, 2995, 2946, 2924, 2867, 1461, 1366, 1281, 1217, 1108, 1095, 179, 1032,$ and 666.

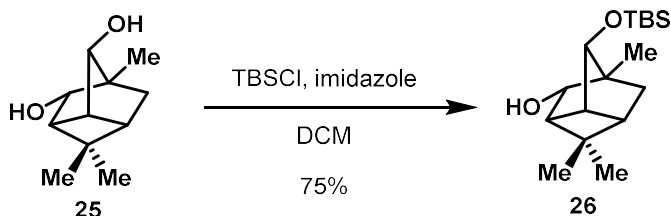
HRMS (ESI, m/z): for $[\text{M}+\text{H}]^+$ calcd. for $\text{C}_{12}\text{H}_{17}\text{O}_2$ 181.1234; found 181.1235.

M.p. = $89\text{ }^{\circ}\text{C}$

X-ray structure:



2.10 Synthesis of silyl ether **26**



A flame-dried flask was charged with diol **25** (60 mg, 0.33 mmol, 1 equiv), DCM (3.3 mL) and imidazole (67 mg, 0.99 mmol, 3 equiv). To the stirring suspension was added TBSCl (60 mg, 0.40 mmol, 1.2 equiv) and a white precipitate formed. The reaction mixture was stirred for 14 h at 23 °C then quenched by the addition of sat. aq. NaCl and diluted with EtOAc. The layers were separated and the aqueous layer was extracted twice with EtOAc. The combined organic layers were dried over Na₂SO₄, filtered, and concentrated *in vacuo*. The crude compound was purified by silica gel flash chromatography (hexanes: EtOAc 4:1) to afford **26** as a clear oil (73 mg, 0.25 mmol, 75%).

R_f = 0.7 (hexane:EtOAc = 4:1), UV-active, blue spot (*p*-anisaldehyde)

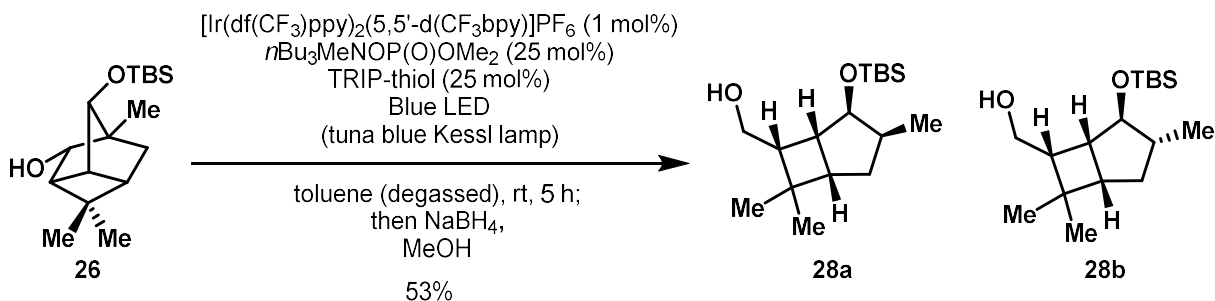
¹H NMR (500 MHz, CDCl₃) δ 3.74 (dd, *J* = 6.6, 2.2 Hz, 1H), 3.40 (d, *J* = 2.0 Hz, 1H), 2.67 (td, *J* = 4.4, 1.8 Hz, 1H), 2.13 – 2.04 (m, 2H), 1.86 (d, *J* = 12.2 Hz, 1H), 1.75 (ddd, *J* = 12.2, 7.3, 2.3 Hz, 1H), 1.13 (s, 3H), 1.12 (s, 3H), 0.98 (s, 3H), 0.87 (s, 9H), 0.03 (s, 3H), 0.02 (s, 3H) ppm.

¹³C NMR (101 MHz, CDCl₃) δ 79.5, 78.4, 49.9, 47.7, 45.8, 44.3, 38.9, 30.6, 30.3, 25.9, 22.8, 18.2, 14.6, -4.3, -4.7 ppm.

IR (neat): ν = 3436, 2927, 2998, 2895, 2859, 1739, 1462, 1366, 1256, 1137, 1118, 1084, 1061, 867, 836, and 775.

HRMS (ESI, *m/z*): for [M+Na]⁺ calcd. for C₁₇H₃₂NaO₂Si 319.2064; found 319.2063.

2.11 Synthesis of [3.2.0] bicycloheptane **28**



A flame-dried vial was charged with alcohol **26** (20 mg, 0.067 mmol, 1 equiv), [Ir(df(CF₃)ppy)₂(5,5'-d(CF₃bpy))]PF₆ (0.07 mg, 0.00067 mmol, 0.01 equiv), and TRIP-thiol (4.0 mg, 0.017 mmol, 0.25 equiv) then moved into a glovebox. In the glovebox, *n*Bu₃MeNOP(O)OMe₂ (5.5 mg, 0.017 mmol, 0.25 equiv) and degassed toluene (0.67 mL, freeze-pump-thaw) were added. The vial was moved from the glovebox to a photoreactor equipped with two tuna blue Kessil lamps (see above). The orange reaction mixture was irradiated at maximum intensity under a constant stream of air to maintain the temperature at 23 °C. After 5 h, the vial was removed from the photoreactor and placed under nitrogen.

To the crude reaction mixture under an atmosphere of nitrogen was added a solution of NaBH₄ (5.1 mg, 0.13 mmol, 2 equiv) in methanol (0.13 mL). The bubbling reaction mixture was stirred for 30 min after which it was quenched with sat. aq. NH₄Cl and diluted with EtOAc. The layers were separated and the aqueous layer was extracted twice with EtOAc. The combined organic layers were washed with sat. aq. NaCl, dried over Na₂SO₄, filtered, and concentrated *in vacuo*. The crude residue was purified by preparative thin layer chromatography (hexanes:EtOAc 1:1) to yield **28a** and **28b** as clear oils (11 mg, 0.036 mmol, 53% 1:1 *dr*).

Diastereomer **28a**

R_f = 0.65 (hexane:EtOAc = 4:1), blue spot (*p*-anisaldehyde)

¹H NMR (500 MHz, CDCl₃) δ 3.95 (d, *J* = 4.3 Hz, 1H), 3.69 – 3.58 (m, 2H), 2.63 (dd, *J* = 10.3, 8.0 Hz, 1H), 2.36 (t, *J* = 8.2 Hz, 1H), 2.25 (q, *J* = 8.8 Hz, 1H), 2.07 (dt, *J* = 12.0, 5.9 Hz, 1H), 1.64 – 1.60 (m, 1H), 1.39 (td, *J* = 12.6, 8.4 Hz, 1H), 1.16 (s, 3H), 0.97 (d, *J* = 6.5 Hz, 3H), 0.93 – 0.84 (m, 12H), 0.02 (s, 6H) ppm.

¹³C NMR (151 MHz, CDCl₃) δ 76.7, 60.6, 46.2, 45.6, 44.3, 42.0, 35.4, 34.9, 33.5, 29.9, 26.0, 18.35, 18.2, 14.5, -4.6, -4.7 ppm.

IR (neat): ν = 3322, 2953, 2930, 2857, 1462, 1385, 1362, 1253, 1117, 1095, 1057, 1018, 864, 833, 773, and 670.

HRMS (ESI, m/z): for $[M+Na]^+$ calcd. for $C_{17}H_{34}NaO_2Si$ 321.3220; found 321.3219.

Diastereomer **28b**

R_f = 0.63 (hexane:EtOAc = 4:1), blue spot (*p*-anisaldehyde)

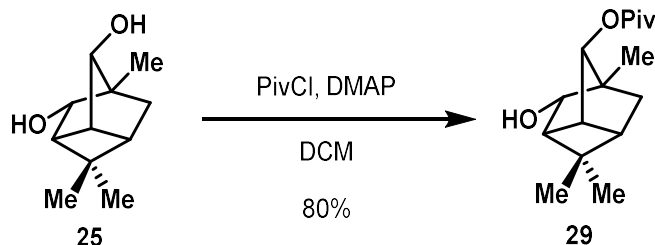
1H NMR (500 MHz, $CDCl_3$) δ 3.82 – 3.74 (m, 2H), 3.71 (dt, J = 8.3, 4.3 Hz, 1H), 2.50 (td, J = 9.3, 5.0 Hz, 1H), 2.31 – 2.17 (m, 2H), 1.82 – 1.71 (m, 2H), 1.18 (s, 3H), 1.15 – 1.08 (m, 1H), 1.03 (d, J = 6.1 Hz, 3H), 0.90 (s, 3H), 0.87 (s, 9H), 0.06 (s, 3H), 0.04 (s, 3H) ppm.

^{13}C NMR (126 MHz, $CDCl_3$) δ 81.09, 62.84, 46.70, 45.41, 44.01, 36.00, 33.35, 33.08, 26.04, 19.58, 18.24, 17.12, –4.00, –4.16 ppm.

IR (neat) ν : 3346, 2970, 2951, 2929, 2857, 1738, 1462, 1365, 1252, 1229, 1217, 1206, 1117, 1094, 1058, 1018, 864, 833, 800, 773, 670, 610, and 539.

HRMS (ESI, m/z): for $[M+Na]^+$ calcd. for $C_{17}H_{34}NaO_2Si$ 321.3220; found 321.3220.

2.12 Synthesis of Pivalate alcohol 29



A flame-dried flask was charged with diol **25** (90 mg, 0.49 mmol, 1 equiv), DCM (5 mL) and DMAP (72 mg, 0.59 mmol, 1.2 equiv), followed by PivCl (60 mg, 0.40 mmol, 1 equiv). The reaction mixture was stirred until consumption of starting material was noted by TLC (~3 h). The reaction mixture was quenched by the addition of sat. aq. NH_4Cl and diluted with EtOAc. The layers were separated and the aqueous layer was extracted twice with EtOAc. The combined organic layers were washed with sat. aq. NaCl, dried over Na_2SO_4 , filtered, and concentrated *in vacuo*. The crude compound was purified by silica gel flash chromatography (hexanes: EtOAc 2:1) to afford **29** as a yellow solid (110 mg, 0.40 mmol, 80%).

R_f = 0.50 (hexane:EtOAc = 2:1), blue spot (*p*-anisaldehyde)

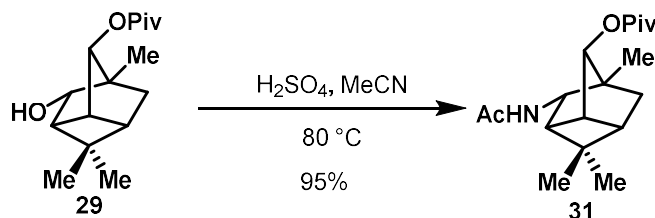
$^1\text{H NMR}$ (500 MHz, CDCl_3) δ 4.46 (d, J = 1.9 Hz, 1H), 3.87 (dd, J = 7.2, 2.2 Hz, 1H), 2.91 (td, J = 4.4, 1.9 Hz, 1H), 2.16 (td, J = 6.6, 4.8 Hz, 1H), 2.13 – 2.03 (m, 2H), 1.72 (ddd, J = 12.7, 7.8, 2.3 Hz, 1H), 1.17 (d, J = 1.3 Hz, 9H), 1.12 (s, 6H), 1.00 (s, 3H) ppm.

$^{13}\text{C NMR}$ (126 MHz, CDCl_3) δ 178.5, 79.7, 78.7, 49.0, 46.0, 44.8, 43.8, 39.3, 39.1, 31.3, 30.0, 27.3, 22.7, 14.51 ppm.

IR (neat): ν = 3462, 3008, 2970, 2873, 1712, 1480, 1461, 1420, 1359, 1285, 1220, 1160, 1096, 1031, 989, 905, 962, and 529.

HRMS (ESI, m/z): for $[\text{M}+\text{Na}]^+$ calcd. for $\text{C}_{16}\text{H}_{26}\text{NaO}_3$ 289.1774; found 289.1174.

2.13 Synthesis of pivalate amide **31**



A vial was charged with pivalate **29** (4 mg, 0.015 mmol, 1 equiv) and acetonitrile (0.3 mL). No effort was made to exclude moisture. To the stirring yellow solution was added conc. H_2SO_4 (5 μL). The reaction mixture was moved to a preheated vial block at $80\text{ }^\circ\text{C}$. The reaction mixture stirred at this temperature until complete consumption of starting material (as determined by TLC, ~ 30 min). The reaction mixture was cooled to $23\text{ }^\circ\text{C}$ then quenched by the addition of sat. aq. NaHCO_3 and diluted with EtOAc. The layers were separated and the aqueous layer was extracted three times with EtOAc. The combined organic layers were washed with sat. aq. NaCl , dried over Na_2SO_4 , filtered, and concentrated *in vacuo* to give amide **31** (4.4 mg, 0.014 mmol, 95%) as a white amorphous solid of suitable purity.

$R_f = 0.1$ (hexane:EtOAc = 1:3), purple spot (*p*-anisaldehyde)

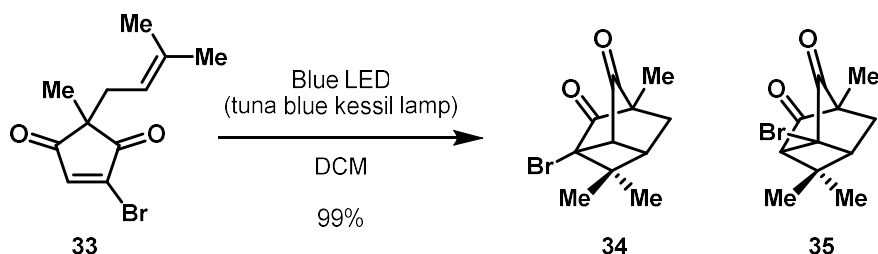
$^1\text{H NMR}$ (500 MHz, MeOD) δ 4.52 (d, $J = 1.9$ Hz, 1H), 4.40 (dd, $J = 7.2, 2.1$ Hz, 1H), 2.93 (d, $J = 2.1$ Hz, 1H), 2.43 – 2.36 (m, 1H), 2.14 – 2.06 (m, 2H), 1.93 (s, 3H), 1.76 (ddd, $J = 12.7, 7.9, 2.2$ Hz, 1H), 1.16 (m, 15H), 1.05 (s, 3H) ppm.

$^{13}\text{C NMR}$ (151 MHz, MeOD) δ 179.8, 176.4, 84.0, 80.6, 49.7, 46.1, 45.6, 45.0, 40.5, 40.0, 32.6, 30.2, 27.6, 22.8, 22.1, 14.9 ppm.

IR (neat): $\nu = 3452, 3010, 2960, 2930, 2871, 1730, 1670, 1480, 1462, 1289, 1217, 1166, 1030, 992, 872, 847, 668, 587$.

HRMS (ESI, m/z): for $[\text{M}+\text{Na}]^+$ calcd. for $\text{C}_{18}\text{H}_{29}\text{NaO}_3\text{N}$ 330.2040; found 330.2039.

2.14 Synthesis of bromo tricyclo[3.2.1.0^{3,6}]octane **34** and **35**



Enedione **33** (50 mg, 0.14 mmol) was dissolved in DCM (2.8 mL) under air in a 1 dram vial. The resulting pale-yellow solution was then moved to a photoreactor containing two tuna blue Kessil lamps (see above). The light orange reaction mixture was irradiated at maximum intensity under a constant stream of air to maintain room temperature. After complete consumption of the starting material (monitored by NMR), the clear reaction mixture was concentrated *in vacuo* to yield title compounds **34** and **35** (50 mg, 0.14 mmol, 99%, 1.3:1).

33 R_f = 0.75 (hexane:EtOAc = 4:1), UV-active blue spot (*p*-anisaldehyde)

¹H NMR (500 MHz, CDCl₃) δ 7.44 (s, 2H), 4.78 (t, J = 7.9 Hz, 2H), 2.41 (dd, J = 7.8, 5.6 Hz, 4H), 1.60 (s, 6H), 1.53 (s, 6H), 1.20 (s, 6H).

¹³C NMR (126 MHz, CDCl₃) δ 203.2, 200.3, 148.3, 148.1, 137.2, 116.9, 52.8, 34.0, 25.9, 18.7, 17.7.

IR (neat): ν = 2971, 2931, 2873, 1753, 1709, 1562, 1452, 1377, 1315, 1229, 1118, 1078, 833, 790, and 413.

HRMS (EI, m/z): for [M]⁺ calcd. for C₁₁H₁₃O₂Br 256.0099; found 256.0103.

M.p: 85 °C

34 & 35 R_f = 0.75 (hexane:EtOAc = 4:1), UV-active blue streak (*p*-anisaldehyde)

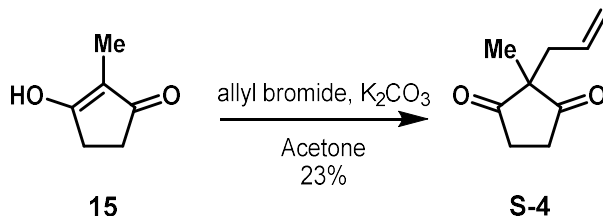
¹H NMR (500 MHz, CDCl₃) δ 3.47 – 3.39 (m, 1H), 3.13 (d, J = 5.7 Hz, 1H), 2.94 (td, J = 5.0, 2.4 Hz, 1H), 2.80 (t, J = 6.0 Hz, 1H), 2.33 (dd, J = 12.4, 6.5 Hz, 1H), 2.24 (d, J = 12.5 Hz, 1H), 2.19 – 2.11 (m, 2H), 1.85 (d, J = 1.6 Hz, 3H), 1.49 (d, J = 1.6 Hz, 3H), 1.24 – 1.15 (m, 6H), 1.04 – 0.93 (m, 6H) ppm.

¹³C NMR (126 MHz, CDCl₃) δ 205.7, 203.3, 201.9, 201.0, 70.4, 68.1, 60.0, 58.2, 56.9, 54.9, 51.3, 49.4, 46.5, 40.5, 35.5, 33.6, 28.1, 28.1, 23.4, 20.0, 7.5, 7.4 ppm.

IR (neat): ν = 2966, 2938, 2878, 1717, 1457, 1391, 1250, 1222, 1147, 1097, 1059, 1018, 999, 056, 913, 866, 921, 768, 660, and 597.

HRMS (EI, m/z): for [M]⁺ calcd. for C₁₁H₁₃O₂Br 256.0099; found 256.0099.

2.15 Synthesis of methyl allyl 1,3-cyclopentanedione **S-4**



To a solution of 2-methylcyclopentane-1,3-dione **15** (5.0 g, 45 mmol, 1 equiv) in acetone (200 ml) was added potassium carbonate (9.2 g, 67 mmol, 1.5 equiv) in a single portion followed by allyl bromide (10 ml, 89 mmol, 2 equiv) dropwise via syringe. The mixture turned turbid during the addition of bromide. The reaction mixture was stirred under nitrogen for 24 h then concentrated by rotary evaporation and resuspended in Et_2O . The suspension was then quenched by addition of sat. aq. NaCl. The layers were separated and the aqueous layer was extracted twice with Et_2O . The combined organic layers were dried over Na_2SO_4 , filtered, and concentrated in *vacuo*. The crude residue was purified by silica gel flash chromatography (hexanes: EtOAc 4:1) to afford **S-4** as a colorless to pale yellow oil (1.54 g, 10 mmol, 23%).

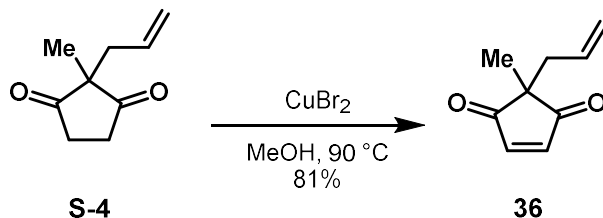
R_f = 0.38 (hexane:EtOAc = 4:1), UV-active blue spot (*p*-anisaldehyde)

1H NMR (500 MHz, $CDCl_3$) δ 5.63 – 5.54 (m, 1H), 5.09 – 5.03 (m, 2H), 2.80 – 2.64 (m, 4H), 2.35 (d, J = 7.5 Hz, 2H), 1.12 (s, 3H) ppm.

^{13}C NMR (126 MHz, $CDCl_3$) δ 216.4, 131.6, 120.0, 56.9, 40.2, 35.5, 19.0 ppm.

Spectral data were consistent with those found in the literature²

2.16 Synthesis of enedione **36**



To a solution of 2-allyl-2-methylcyclopentane-1,3-dione **S-4** (1.0 g, 1 equiv, 6.6 mmol) in MeOH (45 mL) was added copper(II) bromide (3.2 g, 2.2 equiv, 14 mmol). The resulting brown solution was moved to a preheated oil bath and stirred at $90\text{ }^\circ\text{C}$ under an argon atmosphere. After 1 h the reaction mixture was cooled to room temperature, quenched with 15 mL of distilled water followed by 15 mL of 1 M aq. HCl solution, and diluted with Et_2O . The layers were separated, and the aqueous layer was extracted twice with Et_2O . The combined organic layers were dried over Na_2SO_4 , filtered, and concentrated in *vacuo*. The crude residue was purified by silica-gel flash column chromatography (Pentane: diethyl ether = 10:1 to 4:1) to afford **36** as a yellow oil (0.80 g, 5.3 mmol, 81%).

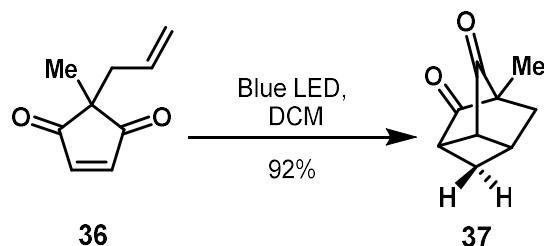
$R_f = 0.48$ (hexane:EtOAc = 4:1), UV-active KMnO_4

$^1\text{H NMR}$ (400 MHz, CDCl_3) δ 7.23 (s, 2H), 5.48 (ddt, $J = 17.6, 10.1, 7.5$ Hz, 1H), 5.07 – 4.92 (m, 2H), 2.38 (dt, $J = 7.5, 1.1$ Hz, 2H), 1.15 (s, 3H) ppm.

$^{13}\text{C NMR}$ (126 MHz, CDCl_3) δ 207.6, 148.7, 131.8, 120.0, 51.0, 39.1, 19.0 ppm.

Spectral data were consistent with those found in the literature²

2.17 Synthesis of tricycle 37



Enedione **36** (16 mg, 0.1 mmol) was dissolved in DCM (1 mL) under air in a 1 dram vial. The resulting pale-yellow solution was then moved to a Penn1a photoreactor affixed with a 420 nm plate (see above). The reaction mixture was irradiated at this wavelength for 12 h after which it was removed from the photoreactor, and concentrated *in vacuo* to yield tricycle **37**. The compound was unstable to silica gel chromatography, so the yield was assessed by ^1H NMR to be 92%.

R_f = 0.30 (hexane:EtOAc = 4:1), streak KMnO_4

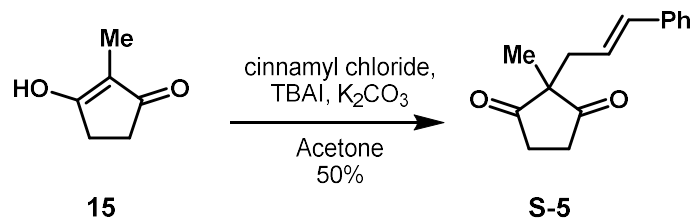
^1H NMR (500 MHz, CDCl_3) δ 3.29 – 3.21 (m, 2H), 3.16 (dddd, J = 10.4, 6.3, 4.6, 2.0 Hz, 1H), 2.97 (ddd, J = 11.4, 6.6, 4.9 Hz, 1H), 2.40 (ddd, J = 12.1, 6.7, 3.0 Hz, 1H), 2.06 (dd, J = 25.5, 11.1 Hz, 2H), 1.17 (s, 3H) ppm.

^{13}C NMR (126 MHz, CDCl_3) δ 209.7, 208.2, 60.0, 51.4, 48.0, 40.8, 38.0, 32.7, 7.3.

IR (neat): ν = 3453, 2971, 2933, 2871, 1780, 1727, 1451, 1347, 1140, 1063, 1019, 897, 821, 779, 703, 608, 504, and 473 ppm.

HRMS (EI, m/z): for $[\text{M}]^+$ calcd. for $\text{C}_9\text{H}_{10}\text{O}_2$ 150.0681; found 150.0679.

2.18 Synthesis of dione S-5



A solution of 2-methylcyclopentane-1,3-dione **15** (1.0 g, 8.9 mmol, 1 equiv) and tetra-*n*-butylammonium iodide (33 mg, 8.9 μmol, 1 mol%) in dry acetone (40 ml) was added cinnamyl chloride (2.7 g, 18 mmol, 2 equiv) in one portion. The mixture turned turbid during the addition of cinnamyl chloride. After stirring for 5 min, potassium carbonate (1.8 g, 13 mmol, 1.5 equiv) was added to the mixture and it was stirred under nitrogen for 24 h then concentrated by rotary evaporation and resuspended in ether. The mixture was then quenched by addition of sat. aq. NaCl. The aqueous layer was further extracted twice with Et₂O. The combined organic layers were dried over Na₂SO₄, filtered, and concentrated in *vacuo*. The crude residue was purified by silica gel flash chromatography (hexanes: EtOAc 10:1 to 2:1) to afford **S-5** as a white to pale-yellow solid (1.0 g, 4.4 mmol, 50%).

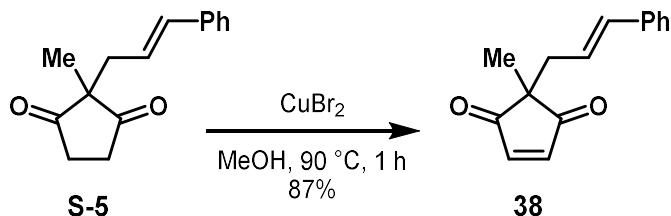
R_f = 0.50 (hexane:EtOAc = 2:1), UV-active KMnO₄

¹H NMR (600 MHz, CDCl₃) δ 7.32 – 7.27 (m, 4H), 7.24 – 7.20 (m, 1H), 6.41 (dt, *J* = 15.8, 1.3 Hz, 1H), 5.98 (dt, *J* = 15.6, 7.7 Hz, 1H), 2.82 – 2.72 (m, 2H), 2.72 – 2.64 (m, 2H), 2.51 (dd, *J* = 7.7, 1.3 Hz, 2H), 1.17 (s, 3H) ppm.

¹³C NMR (151 MHz, CDCl₃) δ 216.5, 136.8, 134.9, 128.7, 127.9, 126.4, 122.8, 57.2, 39.4, 35.6, 19.2 ppm.

Spectral data were consistent with those found in the literature²

2.19 Synthesis of enedione **38**



To a solution of 2-cinnamyl-2-methylcyclopentane-1,3-dione (**S-5** 0.5 g, 1 equiv, 2.2 mmol) in MeOH (45 mL) was added copper(II) bromide (1.1 g, 2.2 equiv, 4.8 mmol). The resulting brown solution was moved to a preheated oil bath and stirred at $90\text{ }^\circ\text{C}$ under an argon atmosphere. After 1 h, the reaction mixture was cooled to room temperature, quenched with 15 mL of distilled water followed by 15 mL of 1 M aq. HCl solution, and diluted with Et_2O . The layers were separated, and the aqueous layer was extracted twice with Et_2O . The combined organic layers were dried over Na_2SO_4 , filtered, and concentrated in *vacuo*. The crude residue was purified by silica-gel flash column chromatography (pentane: diethyl ether = 10:1 to 4:1) to afford **38** as a yellow solid (0.43 g, 1.9 mmol, 87%).

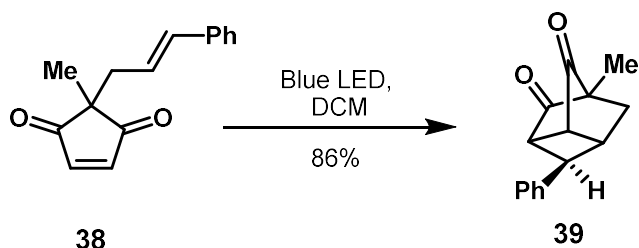
$R_f = 0.22$ (hexane:EtOAc = 10:1), UV-active KMnO_4

$^1\text{H NMR}$ (500 MHz, CDCl_3) δ 7.30 (dd, $J = 4.6, 2.0$ Hz, 7H), 7.24 (d, $J = 3.0$ Hz, 2H), 6.44 – 6.35 (m, 1H), 5.91 (dt, $J = 15.6, 7.7$ Hz, 1H), 2.59 (d, $J = 7.8$ Hz, 2H), 1.24 (s, 3H) ppm.

$^{13}\text{C NMR}$ (126 MHz, CDCl_3) δ 207.4, 148.6, 136.8, 134.7, 128.6, 127.7, 126.4, 122.9, 51.2, 38.1, 18.9 ppm.

Spectral data were consistent with those found in the literature²

2.20 Synthesis of tricycle 39



Enedione **38** (22 mg, 0.1 mmol) was dissolved in DCM (1 mL) under air in a 1 dram vial. The resulting pale-yellow solution was then moved to a Penn1a photoreactor affixed with a 420 nm plate (see above). The reaction mixture was irradiated at this wavelength for 12 h after which it was removed from the photoreactor and concentrated *in vacuo* to yield tricycle **39**. The compound was unstable to silica gel chromatography, so the yield was assessed by $^1\text{H NMR}$ to be 86%.

R_f = 0.15 (hexane:EtOAc = 10:1), streak KMnO_4

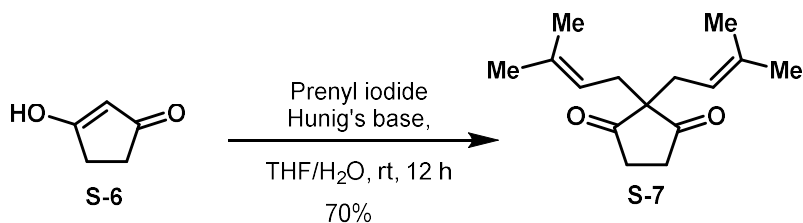
$^1\text{H NMR}$ (600 MHz, CDCl_3) δ 7.45 – 7.38 (m, 2H), 7.36 – 7.33 (m, 2H), 7.33 – 7.29 (m, 1H), 3.48 (s, 1H), 3.43 (dt, J = 13.3, 4.7 Hz, 2H), 3.17 (dt, J = 6.8, 5.2 Hz, 1H), 2.52 – 2.45 (m, 1H), 2.22 (d, J = 12.2 Hz, 1H), 1.25 (s, 3H) ppm.

$^{13}\text{C NMR}$ (151 MHz, CDCl_3) δ 209.2, 206.7, 140.6, 129.1, 127.4, 126.7, 59.4, 56.2, 55.1, 46.55, 39.5, 37.9, 7.2 ppm.

IR (neat): ν = 2965, 2931, 2870, 1762, 1732, 1602, 1498, 1450, 1261, 1181, 1097, 1044, 802, 749, 699, 660, 597, 561.

HRMS (ESI, m/z): for $[\text{M}+\text{H}]^+$ calcd. for $\text{C}_{15}\text{H}_{15}\text{O}_2$ 227.1067; found 227.1067.

2.21 Synthesis of bisprenyl dione S-7



Synthesis of prenyl iodide:

To a solution of prenyl bromide (20 g, 134 mmol, 2.8 equiv) in acetone (200 mL) was added sodium iodide (24.1 g, 161 mmol, 3.0 equiv). The reaction mixture was stirred for 5 min during which a white precipitate formed. The mixture was filtered through a plug of silica and the solvent was evaporated carefully *in vacuo*. The brown crude residue was dissolved in Et₂O (100 mL) and the solution was washed with sat. aq. NaHCO₃ (50 mL) and sat. aq. Na₂S₂O₃ (10 %, 50 mL), which decolorized the solution from brown to pale yellow. The organic layer was dried over Na₂SO₄ and concentrated *in vacuo*. Crude prenyl iodide was directly used in the subsequent reaction without further purification.

Notes: Prenyl bromide and iodide decompose under moisture and air. Using freshly opened or synthesized prenyl bromide ensures reproducibility of experiments. Prenyl iodide is light-sensitive and needs to be used rapidly after synthesis. Blocking light and ensuring a N₂ atmosphere significantly reduces decomposition.

To a solution of 1,3-cyclopentanedione (**S-6** 4.99 g, 50.9 mmol, 1 equiv) in a THF/water mixture (4:1, 400 mL) at 0 °C was slowly added DIPEA (18.2 mL, 104 mmol, 2.1 equiv) and prenyl iodide (crude prepared as above, 134 mmol, 2.6 equiv). The reaction mixture was allowed to warm to room temperature and stirred for 18 h. THF was then removed by rotary evaporation. To the remaining mixture was added DCM and saturated sodium bicarbonate solution. The aqueous phase was extracted with DCM two times. The combined organic phases were washed with brine, dried over Na₂SO₄ and concentrated *in vacuo*. The crude residue was purified by flash chromatography (Hex/EtOAc = 9/1) to give diketone **S-7** (8.34 g, 70%).

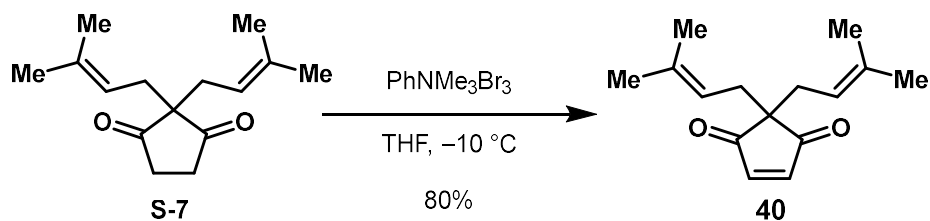
R_f = 0.50 (hexane:EtOAc = 10:1), UV-active spot (*p*-anisaldehyde)

¹H NMR (500 MHz, CDCl₃) δ 4.87 (tt, J = 7.7, 1.5 Hz, 1H), 2.55 (s, 2H), 2.34 (d, J = 7.9 Hz, 2H), 1.62 (s, 3H), 1.56 (s, 3H) ppm.

¹³C NMR (126 MHz, CDCl₃) δ 218.0, 136.5, 117.4, 61.6, 36.8, 34.5, 26.0, 17.9 ppm.

Spectral data consistent with those found in the literature³

2.22 Synthesis of enedione **40**



A solution of **S-7** (3.00 g, 12.8 mmol, 1 equiv) in THF (130 mL) was cooled to $-10\text{ }^\circ\text{C}$. To this cooled solution was added phenyltrimethylammonium tribromide (4.7 g, 17 mmol, 1 equiv) in four portions after which the solution turned bright yellow. Portions were added in 30 min intervals. Completion of the reaction was determined by TLC; ~ 3 h. Upon completion, the reaction mixture was diluted with diethyl ether and quenched with sat. aq. NaHCO_3 and sat. aq. $\text{Na}_2\text{S}_2\text{O}_3$ (4:1). The layers were separated and the aqueous layer was extracted two further times with diethyl ether. The combined organic layers were dried over Na_2SO_4 , filtered, and concentrated *in vacuo*. The crude reaction mixture was purified by silica gel flash chromatography (gradient 5:1 pentane: diethyl ether to 1:1 pentane: diethyl ether) to yield **40** as a bright yellow solid (2.38 g, 80%).

$R_f = 0.50$ (hexane:EtOAc = 10:1), UV-active blue spot (*p*-anisaldehyde)

$^1\text{H NMR}$ (400 MHz, CDCl_3) δ 7.23 (s, 1H), 4.76 (tt, $J = 7.8, 1.5$ Hz, 1H), 2.37 (d, $J = 7.8$ Hz, 2H), 1.55 (dd, $J = 11.9, 1.4$ Hz, 6H) ppm.

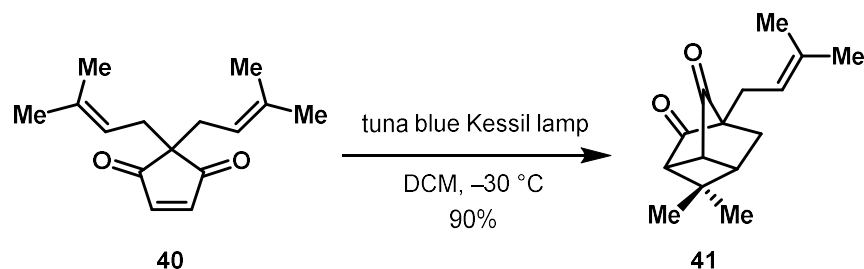
$^{13}\text{C NMR}$ (101 MHz, CDCl_3) δ 208.0, 150.0, 136.2, 117.3, 55.6, 32.8, 25.9, 17.7 ppm.

IR (neat): $\nu = 2972, 2914, 2859, 1700, 1441, 1378, 1324, 1231, 1057, 1030, 985, 836, 700,$ and 577.

HRMS (ESI, m/z): for $[\text{M}+\text{Na}]^+$ calcd. for $\text{C}_{15}\text{H}_{20}\text{NaO}_2$ 255.1356; found 255.1357.

M.p: $70\text{ }^\circ\text{C}$

2.23 Synthesis of prenylated tricyclo[3.2.1.0^{3,6}]octane **41**



Enedione **40** (50 mg, 0.28 mmol) was dissolved in DCM (2.8 mL) under air in a 1 dram vial. The resulting pale-yellow solution was cooled to $-30\text{ }^{\circ}\text{C}$. A tuna blue Kessil lamp was affixed, and the solution was irradiated for 3 h (see above). After complete consumption of the starting material (monitored by NMR), the clear reaction mixture was concentrated *in vacuo* and washed with heptanes to yield title compound **41** (45 mg, 0.25 mmol).

$R_f = 0.5$ (hexane:EtOAc = 10:1), green streak (*p*-anisaldehyde)

$^1\text{H NMR}$ (700 MHz, CDCl_3) δ 5.22 (tt, $J = 7.5, 1.5$ Hz, 1H), 3.22 (t, $J = 4.4$ Hz, 1H), 2.98 (t, $J = 4.9$ Hz, 1H), 2.59 (dt, $J = 6.7, 5.0$ Hz, 1H), 2.42 – 2.37 (m, 1H), 2.30 (dd, $J = 15.5, 7.5$ Hz, 1H), 2.24 (dd, $J = 12.6, 6.7$ Hz, 1H), 2.09 (d, $J = 12.7$ Hz, 1H), 1.70 (d, $J = 1.5$ Hz, 3H), 1.65 (s, 3H), 1.45 (s, 3H), 0.97 (s, 3H) ppm.

$^{13}\text{C NMR}$ (176 MHz, CDCl_3) δ 208.6, 207.0, 134.4, 118.5, 62.9, 61.5, 46.7, 45.7, 41.4, 32.3, 28.5, 26.0, 21.9, 21.5, 17.9 ppm.

IR (neat): $\nu = 2966, 2934, 1776, 1715, 1452, 1386, 1375, 1246, 1222, 1169, 1110, 1058, 983, 910, 720, 647$.

HRMS (ESI, m/z): for $[\text{M}+\text{Na}]^+$ calcd. for $\text{C}_{15}\text{H}_{20}\text{NaO}_2$ 255.1356; found 255.1357.

3 Optimization Table of Key [2+2] Photocycloaddition

entry	conditions	conversion (yield)
1	254 nm ^[a]	0%
2	310 nm ^[a]	0%
3	350 nm ^[a]	0%
4	365 nm ^[b]	100% (58%)
5	385 nm ^[b]	100% (85%)
6	420 nm ^[b]	100% (95% ^[c])
7	450 nm ^[b]	82% (80%)
8	470 nm ^[b]	56% (54%)
9	520 nm ^[b]	0%
10	420 nm, benzene ^[b]	56% (53%)
11	420 nm, MeOH ^[b]	100% (<10%)
12	tuna blue kessil lamp, 5 mmol scale	100% ^[d]
13	420 nm, 50 h ^[b]	100% (<10%)

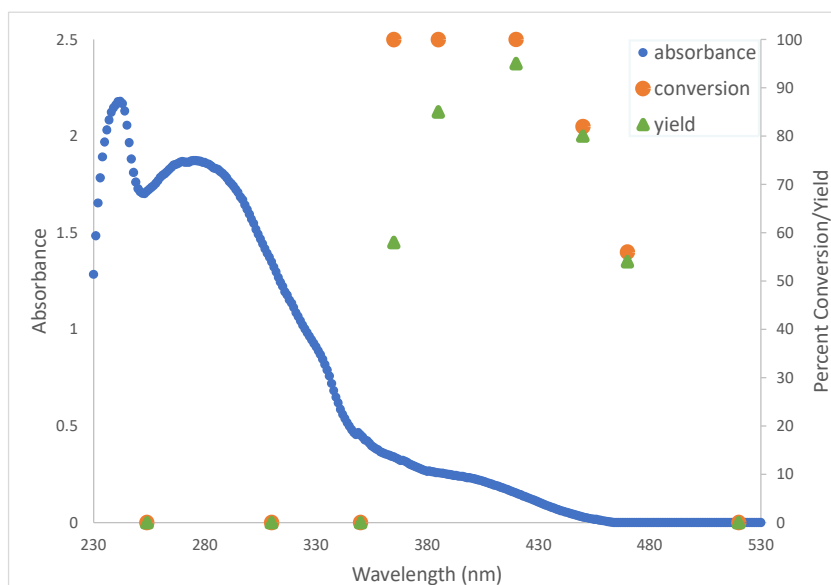
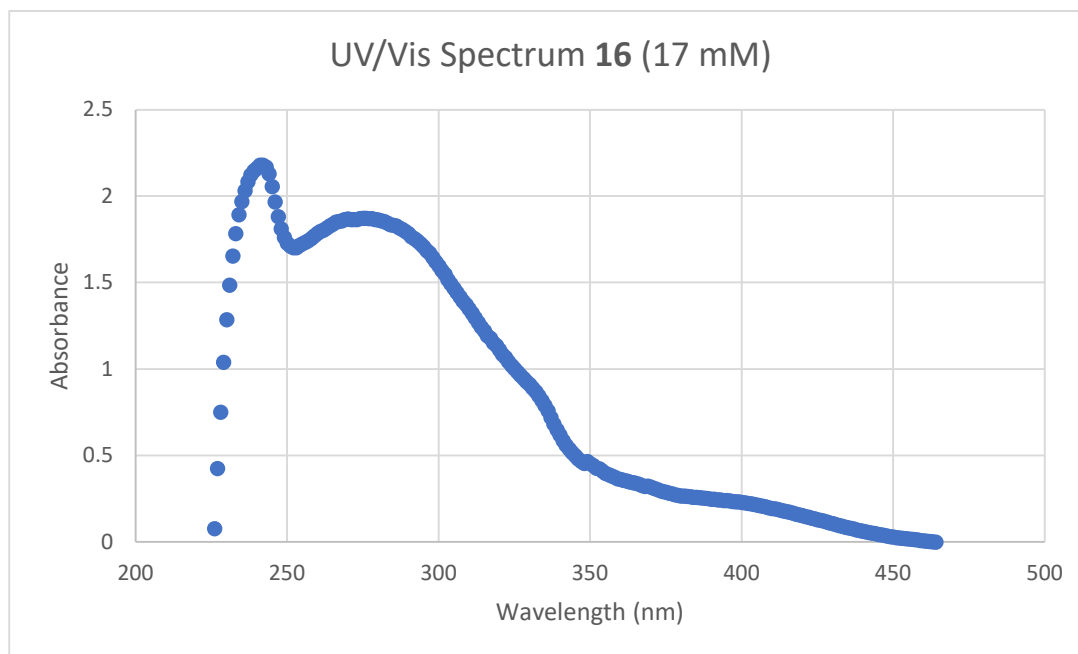


Table 1. a. Optimization of the key [2+2] cycloaddition. Percent conversion noted after 10 h of irradiation on 0.05 mmol scale in DCM (0.1 M). Percent yield determined by NMR. [a]Irradiated in a Luzchem photobox with UVA, UVB, or UVC lamps.[b] Penn1a photoreactor was used and maintained at 23 °C. [c] Average of 3 runs, 0.1 mmol scale. [d]Reaction time extended to 90 h. b. UV/Vis absorbance spectrum of **16** plotted against yield and conversion at varying wavelengths.

4 UV/Vis spectrum of 16



5 References

- (1) Qin, X.-L., Li, A., Han, F.-S. *J. Am. Chem. Soc.* 2021, **143**, 2994–3002.
- (2) Manna, M. S., Mukherjee, S. *Chem. Sci.* 2014, **5**, 1627–1633.
- (3) Narender, T., Sarkar, S., Venkateswarlu, K., Kumar, J. K. *Tetrahedron Lett.*, 2010, **51**, 6576–6579.

6 X-ray crystallographic data

Crystal structure of diol 25

A colorless block 0.12 x 0.07 x 0.04 mm in size was mounted on a Cryolop with Paratone oil. Data were collected in a nitrogen gas stream at 100(2) K using omega scans. Crystal-to-detector distance was 33.00 mm and exposure time was 3.00 seconds per frame at low angles and 13.00 seconds at high angles, using a scan width of 0.5°. Data collection was 100% complete to 74.000° in θ . A total of 32348 reflections were collected covering the indices $-29 \leq h \leq 27$, $-29 \leq k \leq 24$, $-7 \leq l \leq 7$. 3522 reflections were found to be symmetry independent, with an R_{int} of 0.0438. Indexing and unit cell refinement indicated a primitive, tetragonal lattice. The space group was found to be $P 4_2/nm$ (No. 102). The data were integrated using the CrysAlis^{Pro} 1.172.42.72a software program and scaled using the SCALE3 ABSPACK scaling algorithm. Solution by intrinsic phasing (SHELXT-2015) produced a heavy-atom phasing model consistent with the proposed structure. All non-hydrogen atoms were refined anisotropically by full-matrix least-squares (SHELXL-2014). All hydrogen atoms were placed using a riding model. Their positions were constrained relative to their parent atom using the appropriate HFIX command in SHELXL-2014. A solvent mask was applied to remove electron density related to an unidentifiable, disordered outer sphere solvent molecule.

Note: Hydroxyl hydrogens found in the difference map were not stable in the refinement, thus HFIX147 was used to place these hydrogens. Their position in space may not be completely accurate, resulting in H2A not having an acceptor due to an incorrect position.

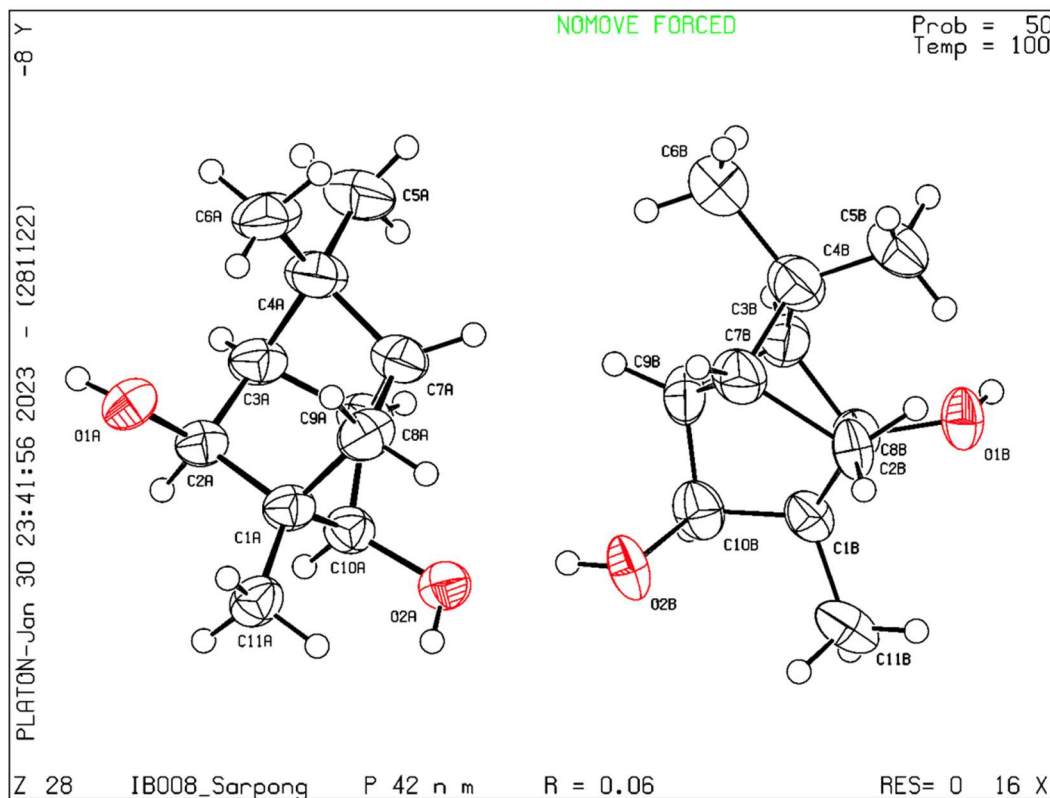


Table 1. Crystal data and structure refinement for IB008_Sarpong.

Identification code	IB008_Sarpong	
Empirical formula	C ₁₁ H ₁₈ O ₂	
Formula weight	182.25	
Temperature	100(2) K	
Wavelength	1.54184 Å	
Crystal system	Tetragonal	
Space group	P 42 n m	
Unit cell dimensions	a = 23.5301(3) Å	a = 90°.
	b = 23.5301(3) Å	b = 90°.
	c = 5.98071(11) Å	g = 90°.
Volume	3311.31(10) Å ³	
Z	12	
Density (calculated)	1.097 Mg/m ³	
Absorption coefficient	0.583 mm ⁻¹	
F(000)	1200	
Crystal size	0.120 x 0.070 x 0.040 mm ³	
Theta range for data collection	2.656 to 75.283°.	
Index ranges	-29<=h<=27, -29<=k<=24, -7<=l<=7	
Reflections collected	32348	
Independent reflections	3522 [R(int) = 0.0438]	
Completeness to theta = 74.000°	99.9 %	
Absorption correction	Semi-empirical from equivalents	
Max. and min. transmission	1.00000 and 0.79637	
Refinement method	Full-matrix least-squares on F ²	
Data / restraints / parameters	3522 / 32 / 246	
Goodness-of-fit on F ²	1.086	
Final R indices [I>2sigma(I)]	R1 = 0.0597, wR2 = 0.1670	
R indices (all data)	R1 = 0.0646, wR2 = 0.1725	
Absolute structure parameter	0.0(4)	
Extinction coefficient	n/a	
Largest diff. peak and hole	0.384 and -0.296 e.Å ⁻³	

Table 2. Atomic coordinates ($\times 10^4$) and equivalent isotropic displacement parameters ($\text{\AA}^2 \times 10^3$)

for ib008_sarpong. $U(\text{eq})$ is defined as one third of the trace of the orthogonalized U^{ij} tensor.

	x	y	z	$U(\text{eq})$
O(1A)	3776(1)	1465(1)	3551(4)	48(1)
O(2A)	5827(1)	1493(1)	2226(4)	47(1)
C(1A)	4822(1)	1381(1)	3436(6)	42(1)
C(2A)	4277(1)	1554(1)	2229(6)	41(1)
C(3A)	4388(2)	2168(1)	1466(6)	48(1)
C(4A)	4398(2)	2626(2)	3355(8)	59(1)
C(5A)	4460(2)	3215(2)	2285(11)	83(2)
C(6A)	3945(2)	2657(2)	5163(8)	70(1)
C(7A)	4994(2)	2385(2)	3948(8)	60(1)
C(8A)	4961(2)	1823(2)	5239(6)	52(1)
C(9A)	5056(2)	2174(1)	1475(8)	51(1)
C(10A)	5243(1)	1562(1)	1595(6)	42(1)
C(11A)	4858(2)	771(2)	4203(7)	48(1)
O(1B)	7883(3)	3492(3)	5332(12)	46(2)
O(2B)	6600(3)	1886(3)	4886(13)	50(2)
C(1B)	7358(15)	2596(14)	5293(10)	43(3)
C(2B)	7435(6)	3198(9)	4250(40)	43(3)
C(3B)	6841(4)	3463(4)	4537(16)	51(2)
C(4B)	6671(4)	3609(3)	6974(16)	60(2)
C(5B)	7037(4)	3945(3)	8478(16)	61(2)
C(6B)	6050(20)	3890(20)	6950(20)	88(7)
C(7B)	6598(3)	2961(3)	7382(15)	55(2)
C(8B)	7326(3)	2878(3)	7689(12)	45(2)
C(9B)	6465(4)	2902(4)	4809(19)	57(2)
C(10B)	6839(10)	2416(6)	4100(40)	49(3)
C(11B)	7823(8)	2166(6)	4995(11)	60(2)

Table 3. Bond lengths [Å] and angles [°] for ib008_sarpong.

O(1A)-C(2A)	1.437(4)
O(1A)-H(1A)	0.8400
O(2A)-C(10A)	1.435(4)
O(2A)-H(2A)	0.8400
C(1A)-C(11A)	1.509(4)
C(1A)-C(2A)	1.528(4)
C(1A)-C(8A)	1.534(5)
C(1A)-C(10A)	1.540(5)
C(2A)-C(3A)	1.535(5)
C(2A)-H(2AA)	1.0000
C(3A)-C(4A)	1.561(5)
C(3A)-C(9A)	1.573(5)
C(3A)-H(3A)	1.0000
C(4A)-C(6A)	1.520(6)
C(4A)-C(5A)	1.535(6)
C(4A)-C(7A)	1.554(5)
C(5A)-H(5AA)	0.9800
C(5A)-H(5AB)	0.9800
C(5A)-H(5AC)	0.9800
C(6A)-H(6AA)	0.9800
C(6A)-H(6AB)	0.9800
C(6A)-H(6AC)	0.9800
C(7A)-C(8A)	1.532(6)
C(7A)-C(9A)	1.567(6)
C(7A)-H(7A)	1.0000
C(8A)-H(8AA)	0.9900
C(8A)-H(8AB)	0.9900
C(9A)-C(10A)	1.507(4)
C(9A)-H(9A)	1.0000
C(10A)-H(10A)	1.0000
C(11A)-H(11A)	0.9800
C(11A)-H(11B)	0.9800
C(11A)-H(11C)	0.9800
O(1B)-C(2B)	1.42(2)

O(1B)-H(1B)	0.8400
O(2B)-C(10B)	1.45(2)
O(2B)-H(2B)	0.8400
C(1B)-C(10B)	1.48(4)
C(1B)-C(11B)	1.501(9)
C(1B)-C(2B)	1.56(4)
C(1B)-C(8B)	1.581(15)
C(2B)-C(3B)	1.540(15)
C(2B)-H(2BA)	1.0000
C(3B)-C(4B)	1.550(13)
C(3B)-C(9B)	1.598(16)
C(3B)-H(3B)	1.0000
C(4B)-C(5B)	1.474(12)
C(4B)-C(7B)	1.553(10)
C(4B)-C(6B)	1.61(3)
C(5B)-H(5BA)	0.9800
C(5B)-H(5BB)	0.9800
C(5B)-H(5BC)	0.9800
C(6B)-H(6BA)	0.9800
C(6B)-H(6BB)	0.9800
C(6B)-H(6BC)	0.9800
C(7B)-C(9B)	1.577(14)
C(7B)-C(8B)	1.732(8)
C(7B)-H(7B)	1.0000
C(8B)-H(8BA)	0.9900
C(8B)-H(8BB)	0.9900
C(9B)-C(10B)	1.503(18)
C(9B)-H(9B)	1.0000
C(10B)-H(10B)	1.0000
C(11B)-H(11D)	0.9800
C(11B)-H(11E)	0.9800
C(11B)-H(11F)	0.9800
C(2A)-O(1A)-H(1A)	109.5
C(10A)-O(2A)-H(2A)	109.5
C(11A)-C(1A)-C(2A)	116.4(3)

C(11A)-C(1A)-C(8A)	114.8(3)
C(2A)-C(1A)-C(8A)	109.3(2)
C(11A)-C(1A)-C(10A)	116.4(3)
C(2A)-C(1A)-C(10A)	97.3(3)
C(8A)-C(1A)-C(10A)	100.2(3)
O(1A)-C(2A)-C(1A)	113.0(3)
O(1A)-C(2A)-C(3A)	116.1(3)
C(1A)-C(2A)-C(3A)	104.4(3)
O(1A)-C(2A)-H(2AA)	107.6
C(1A)-C(2A)-H(2AA)	107.6
C(3A)-C(2A)-H(2AA)	107.6
C(2A)-C(3A)-C(4A)	115.9(3)
C(2A)-C(3A)-C(9A)	100.2(2)
C(4A)-C(3A)-C(9A)	88.6(3)
C(2A)-C(3A)-H(3A)	116.0
C(4A)-C(3A)-H(3A)	116.0
C(9A)-C(3A)-H(3A)	116.0
C(6A)-C(4A)-C(5A)	108.7(4)
C(6A)-C(4A)-C(7A)	119.2(4)
C(5A)-C(4A)-C(7A)	109.8(4)
C(6A)-C(4A)-C(3A)	122.5(3)
C(5A)-C(4A)-C(3A)	108.9(4)
C(7A)-C(4A)-C(3A)	85.8(3)
C(4A)-C(5A)-H(5AA)	109.5
C(4A)-C(5A)-H(5AB)	109.5
H(5AA)-C(5A)-H(5AB)	109.5
C(4A)-C(5A)-H(5AC)	109.5
H(5AA)-C(5A)-H(5AC)	109.5
H(5AB)-C(5A)-H(5AC)	109.5
C(4A)-C(6A)-H(6AA)	109.5
C(4A)-C(6A)-H(6AB)	109.5
H(6AA)-C(6A)-H(6AB)	109.5
C(4A)-C(6A)-H(6AC)	109.5
H(6AA)-C(6A)-H(6AC)	109.5
H(6AB)-C(6A)-H(6AC)	109.5
C(8A)-C(7A)-C(4A)	112.6(3)

C(8A)-C(7A)-C(9A)	102.0(3)
C(4A)-C(7A)-C(9A)	89.1(3)
C(8A)-C(7A)-H(7A)	116.4
C(4A)-C(7A)-H(7A)	116.4
C(9A)-C(7A)-H(7A)	116.4
C(7A)-C(8A)-C(1A)	104.0(3)
C(7A)-C(8A)-H(8AA)	111.0
C(1A)-C(8A)-H(8AA)	111.0
C(7A)-C(8A)-H(8AB)	111.0
C(1A)-C(8A)-H(8AB)	111.0
H(8AA)-C(8A)-H(8AB)	109.0
C(10A)-C(9A)-C(7A)	106.5(3)
C(10A)-C(9A)-C(3A)	106.4(3)
C(7A)-C(9A)-C(3A)	85.0(3)
C(10A)-C(9A)-H(9A)	117.9
C(7A)-C(9A)-H(9A)	117.9
C(3A)-C(9A)-H(9A)	117.9
O(2A)-C(10A)-C(9A)	113.6(3)
O(2A)-C(10A)-C(1A)	113.4(3)
C(9A)-C(10A)-C(1A)	96.4(3)
O(2A)-C(10A)-H(10A)	110.9
C(9A)-C(10A)-H(10A)	110.9
C(1A)-C(10A)-H(10A)	110.9
C(1A)-C(11A)-H(11A)	109.5
C(1A)-C(11A)-H(11B)	109.5
H(11A)-C(11A)-H(11B)	109.5
C(1A)-C(11A)-H(11C)	109.5
H(11A)-C(11A)-H(11C)	109.5
H(11B)-C(11A)-H(11C)	109.5
C(2B)-O(1B)-H(1B)	109.5
C(10B)-O(2B)-H(2B)	109.5
C(10B)-C(1B)-C(11B)	111(2)
C(10B)-C(1B)-C(2B)	99.5(6)
C(11B)-C(1B)-C(2B)	119(3)
C(10B)-C(1B)-C(8B)	121.1(19)
C(11B)-C(1B)-C(8B)	115.2(11)

C(2B)-C(1B)-C(8B)	89.2(19)
O(1B)-C(2B)-C(3B)	115.2(15)
O(1B)-C(2B)-C(1B)	110.3(19)
C(3B)-C(2B)-C(1B)	102.7(13)
O(1B)-C(2B)-H(2BA)	109.5
C(3B)-C(2B)-H(2BA)	109.5
C(1B)-C(2B)-H(2BA)	109.5
C(2B)-C(3B)-C(4B)	115.4(11)
C(2B)-C(3B)-C(9B)	100.3(10)
C(4B)-C(3B)-C(9B)	86.8(8)
C(2B)-C(3B)-H(3B)	116.5
C(4B)-C(3B)-H(3B)	116.5
C(9B)-C(3B)-H(3B)	116.5
C(5B)-C(4B)-C(3B)	122.8(7)
C(5B)-C(4B)-C(7B)	119.6(8)
C(3B)-C(4B)-C(7B)	87.7(6)
C(5B)-C(4B)-C(6B)	108.6(18)
C(3B)-C(4B)-C(6B)	108.6(8)
C(7B)-C(4B)-C(6B)	108(2)
C(4B)-C(5B)-H(5BA)	109.5
C(4B)-C(5B)-H(5BB)	109.5
H(5BA)-C(5B)-H(5BB)	109.5
C(4B)-C(5B)-H(5BC)	109.5
H(5BA)-C(5B)-H(5BC)	109.5
H(5BB)-C(5B)-H(5BC)	109.5
C(4B)-C(6B)-H(6BA)	109.5
C(4B)-C(6B)-H(6BB)	109.5
H(6BA)-C(6B)-H(6BB)	109.5
C(4B)-C(6B)-H(6BC)	109.5
H(6BA)-C(6B)-H(6BC)	109.5
H(6BB)-C(6B)-H(6BC)	109.5
C(4B)-C(7B)-C(9B)	87.4(7)
C(4B)-C(7B)-C(8B)	91.1(5)
C(9B)-C(7B)-C(8B)	106.9(6)
C(4B)-C(7B)-H(7B)	121.1
C(9B)-C(7B)-H(7B)	121.1

C(8B)-C(7B)-H(7B)	121.1
C(1B)-C(8B)-C(7B)	90.0(12)
C(1B)-C(8B)-H(8BA)	113.6
C(7B)-C(8B)-H(8BA)	113.6
C(1B)-C(8B)-H(8BB)	113.6
C(7B)-C(8B)-H(8BB)	113.6
H(8BA)-C(8B)-H(8BB)	110.9
C(10B)-C(9B)-C(7B)	103.0(11)
C(10B)-C(9B)-C(3B)	106.0(11)
C(7B)-C(9B)-C(3B)	85.2(7)
C(10B)-C(9B)-H(9B)	119.0
C(7B)-C(9B)-H(9B)	119.0
C(3B)-C(9B)-H(9B)	119.0
O(2B)-C(10B)-C(1B)	114(2)
O(2B)-C(10B)-C(9B)	109.8(16)
C(1B)-C(10B)-C(9B)	97.5(11)
O(2B)-C(10B)-H(10B)	111.4
C(1B)-C(10B)-H(10B)	111.4
C(9B)-C(10B)-H(10B)	111.4
C(1B)-C(11B)-H(11D)	109.5
C(1B)-C(11B)-H(11E)	109.5
H(11D)-C(11B)-H(11E)	109.5
C(1B)-C(11B)-H(11F)	109.5
H(11D)-C(11B)-H(11F)	109.5
H(11E)-C(11B)-H(11F)	109.5

Symmetry transformations used to generate equivalent atoms:

Table 4. Anisotropic displacement parameters ($\text{\AA}^2 \times 10^3$) for ib008_sarpong. The anisotropic displacement factor exponent takes the form: $-2p^2[h^2 a^* 2U_{11} + \dots + 2 h k a^* b^* U_{12}]$

	U11	U22	U33	U23	U13	U12
O(1A)	43(1)	54(1)	46(1)	5(1)	-2(1)	10(1)
O(2A)	46(1)	44(1)	50(1)	-2(1)	-4(1)	5(1)
C(1A)	46(2)	39(2)	41(2)	2(1)	-2(1)	7(1)
C(2A)	45(2)	41(2)	38(1)	1(1)	0(1)	7(1)
C(3A)	57(2)	42(2)	46(2)	1(1)	-4(2)	12(1)
C(4A)	69(2)	44(2)	64(2)	-11(2)	-6(2)	13(2)
C(5A)	92(3)	42(2)	114(4)	-5(2)	-10(3)	14(2)
C(6A)	72(3)	69(3)	68(2)	-26(2)	-12(2)	31(2)
C(7A)	63(2)	44(2)	72(3)	-16(2)	-11(2)	7(2)
C(8A)	50(2)	64(2)	42(2)	-11(2)	-7(2)	14(2)
C(9A)	60(2)	36(2)	59(2)	2(2)	-3(2)	3(1)
C(10A)	46(2)	38(2)	41(2)	1(1)	-4(1)	3(1)
C(11A)	43(2)	47(2)	55(2)	11(1)	-2(2)	6(1)
O(1B)	40(3)	52(3)	45(3)	11(3)	-2(3)	-18(3)
O(2B)	55(4)	47(4)	46(4)	5(3)	-9(3)	-25(3)
C(1B)	52(9)	35(5)	42(2)	2(4)	-5(5)	-6(4)
C(2B)	44(6)	44(5)	41(5)	6(3)	-6(5)	-4(5)
C(3B)	43(4)	42(4)	67(5)	9(3)	-6(3)	-1(3)
C(4B)	63(4)	47(3)	70(5)	-5(3)	6(4)	-7(3)
C(5B)	77(5)	41(3)	64(4)	-3(3)	8(4)	-12(3)
C(6B)	71(15)	61(10)	132(8)	-24(13)	-8(14)	-4(9)
C(7B)	53(4)	46(4)	66(4)	0(4)	12(4)	-8(3)
C(8B)	42(3)	48(3)	46(3)	2(2)	-2(2)	-19(3)
C(9B)	39(4)	50(4)	81(6)	1(4)	-14(4)	-11(4)
C(10B)	56(6)	43(7)	49(6)	12(5)	0(4)	-13(5)
C(11B)	88(11)	33(7)	58(3)	-6(7)	-5(10)	-4(2)

Table 5. Hydrogen coordinates ($\times 10^4$) and isotropic displacement parameters ($\text{\AA}^2 \times 10^3$) for ib008_sarpong.

	x	y	z	U(eq)
H(1A)	3486	1510	2749	71
H(2A)	5885	1154	2606	70
H(2AA)	4243	1313	858	50
H(3A)	4202	2284	34	58
H(5AA)	4777	3210	1219	124
H(5AB)	4536	3497	3453	124
H(5AC)	4108	3314	1501	124
H(6AA)	3585	2781	4500	105
H(6AB)	4062	2929	6314	105
H(6AC)	3895	2281	5840	105
H(7A)	5283	2666	4476	72
H(8AA)	4659	1838	6390	62
H(8AB)	5328	1737	5973	62
H(9A)	5254	2428	386	62
H(10A)	5160	1360	161	50
H(11A)	4611	717	5507	72
H(11B)	5251	681	4609	72
H(11C)	4733	519	2992	72
H(1B)	7992	3762	4520	68
H(2B)	6314	1803	4111	75
H(2BA)	7523	3160	2622	52
H(3B)	6718	3738	3357	61
H(5BA)	7410	3761	8602	91
H(5BB)	6861	3967	9960	91
H(5BC)	7084	4329	7871	91
H(6BA)	6054	4239	6064	132
H(6BB)	5931	3977	8487	132
H(6BC)	5776	3621	6292	132

H(7B)	6328	2815	8537	66
H(8BA)	7535	3242	7802	55
H(8BB)	7433	2618	8918	55
H(9B)	6060	2909	4302	68
H(10B)	6897	2412	2449	59
H(11D)	7952	2169	3437	89
H(11E)	7679	1787	5373	89
H(11F)	8142	2260	5981	89

Table 6. Torsion angles [°] for ib008_sarpong.

C(11A)-C(1A)-C(2A)-O(1A)	58.2(4)
C(8A)-C(1A)-C(2A)-O(1A)	-73.9(3)
C(10A)-C(1A)-C(2A)-O(1A)	-177.5(2)
C(11A)-C(1A)-C(2A)-C(3A)	-174.7(3)
C(8A)-C(1A)-C(2A)-C(3A)	53.2(3)
C(10A)-C(1A)-C(2A)-C(3A)	-50.4(3)
O(1A)-C(2A)-C(3A)-C(4A)	53.8(4)
C(1A)-C(2A)-C(3A)-C(4A)	-71.3(3)
O(1A)-C(2A)-C(3A)-C(9A)	147.3(3)
C(1A)-C(2A)-C(3A)-C(9A)	22.1(3)
C(2A)-C(3A)-C(4A)-C(6A)	-46.9(5)
C(9A)-C(3A)-C(4A)-C(6A)	-147.5(4)
C(2A)-C(3A)-C(4A)-C(5A)	-175.1(3)
C(9A)-C(3A)-C(4A)-C(5A)	84.3(4)
C(2A)-C(3A)-C(4A)-C(7A)	75.4(3)
C(9A)-C(3A)-C(4A)-C(7A)	-25.2(3)
C(6A)-C(4A)-C(7A)-C(8A)	47.9(5)
C(5A)-C(4A)-C(7A)-C(8A)	174.1(4)
C(3A)-C(4A)-C(7A)-C(8A)	-77.3(4)
C(6A)-C(4A)-C(7A)-C(9A)	150.5(4)
C(5A)-C(4A)-C(7A)-C(9A)	-83.3(4)
C(3A)-C(4A)-C(7A)-C(9A)	25.3(3)
C(4A)-C(7A)-C(8A)-C(1A)	77.2(4)
C(9A)-C(7A)-C(8A)-C(1A)	-16.8(4)
C(11A)-C(1A)-C(8A)-C(7A)	170.7(3)
C(2A)-C(1A)-C(8A)-C(7A)	-56.4(3)
C(10A)-C(1A)-C(8A)-C(7A)	45.1(3)
C(8A)-C(7A)-C(9A)-C(10A)	-17.9(4)
C(4A)-C(7A)-C(9A)-C(10A)	-130.9(3)
C(8A)-C(7A)-C(9A)-C(3A)	87.7(3)
C(4A)-C(7A)-C(9A)-C(3A)	-25.2(3)
C(2A)-C(3A)-C(9A)-C(10A)	14.8(4)
C(4A)-C(3A)-C(9A)-C(10A)	130.9(3)
C(2A)-C(3A)-C(9A)-C(7A)	-91.0(3)

C(4A)-C(3A)-C(9A)-C(7A)	25.1(3)
C(7A)-C(9A)-C(10A)-O(2A)	-74.3(4)
C(3A)-C(9A)-C(10A)-O(2A)	-164.0(3)
C(7A)-C(9A)-C(10A)-C(1A)	44.6(3)
C(3A)-C(9A)-C(10A)-C(1A)	-45.0(4)
C(11A)-C(1A)-C(10A)-O(2A)	-59.6(4)
C(2A)-C(1A)-C(10A)-O(2A)	176.1(2)
C(8A)-C(1A)-C(10A)-O(2A)	64.9(3)
C(11A)-C(1A)-C(10A)-C(9A)	-178.7(3)
C(2A)-C(1A)-C(10A)-C(9A)	57.0(3)
C(8A)-C(1A)-C(10A)-C(9A)	-54.2(3)
C(10B)-C(1B)-C(2B)-O(1B)	173.4(17)
C(11B)-C(1B)-C(2B)-O(1B)	-67(2)
C(8B)-C(1B)-C(2B)-O(1B)	51.9(17)
C(10B)-C(1B)-C(2B)-C(3B)	50.1(8)
C(11B)-C(1B)-C(2B)-C(3B)	170.1(18)
C(8B)-C(1B)-C(2B)-C(3B)	-71.3(17)
O(1B)-C(2B)-C(3B)-C(4B)	-49.8(16)
C(1B)-C(2B)-C(3B)-C(4B)	70.2(16)
O(1B)-C(2B)-C(3B)-C(9B)	-141.1(13)
C(1B)-C(2B)-C(3B)-C(9B)	-21.2(16)
C(2B)-C(3B)-C(4B)-C(5B)	51.1(13)
C(9B)-C(3B)-C(4B)-C(5B)	151.0(8)
C(2B)-C(3B)-C(4B)-C(7B)	-73.1(10)
C(9B)-C(3B)-C(4B)-C(7B)	26.8(6)
C(2B)-C(3B)-C(4B)-C(6B)	179(3)
C(9B)-C(3B)-C(4B)-C(6B)	-81(2)
C(5B)-C(4B)-C(7B)-C(9B)	-154.1(8)
C(3B)-C(4B)-C(7B)-C(9B)	-27.2(6)
C(6B)-C(4B)-C(7B)-C(9B)	81.5(9)
C(5B)-C(4B)-C(7B)-C(8B)	-47.2(9)
C(3B)-C(4B)-C(7B)-C(8B)	79.6(6)
C(6B)-C(4B)-C(7B)-C(8B)	-171.6(8)
C(10B)-C(1B)-C(8B)-C(7B)	-12(2)
C(11B)-C(1B)-C(8B)-C(7B)	-150(3)
C(2B)-C(1B)-C(8B)-C(7B)	88.2(13)

C(4B)-C(7B)-C(8B)-C(1B)	-105.3(14)
C(9B)-C(7B)-C(8B)-C(1B)	-17.7(15)
C(4B)-C(7B)-C(9B)-C(10B)	131.8(10)
C(8B)-C(7B)-C(9B)-C(10B)	41.4(11)
C(4B)-C(7B)-C(9B)-C(3B)	26.4(6)
C(8B)-C(7B)-C(9B)-C(3B)	-63.9(7)
C(2B)-C(3B)-C(9B)-C(10B)	-13.3(19)
C(4B)-C(3B)-C(9B)-C(10B)	-128.6(12)
C(2B)-C(3B)-C(9B)-C(7B)	88.8(11)
C(4B)-C(3B)-C(9B)-C(7B)	-26.5(6)
C(11B)-C(1B)-C(10B)-O(2B)	61(2)
C(2B)-C(1B)-C(10B)-O(2B)	-172.8(18)
C(8B)-C(1B)-C(10B)-O(2B)	-78(2)
C(11B)-C(1B)-C(10B)-C(9B)	177.3(17)
C(2B)-C(1B)-C(10B)-C(9B)	-56.9(11)
C(8B)-C(1B)-C(10B)-C(9B)	38(2)
C(7B)-C(9B)-C(10B)-O(2B)	74.9(15)
C(3B)-C(9B)-C(10B)-O(2B)	163.6(13)
C(7B)-C(9B)-C(10B)-C(1B)	-44.5(17)
C(3B)-C(9B)-C(10B)-C(1B)	44.2(18)

Symmetry transformations used to generate equivalent atoms:

Crystal Structure of Bromoenedione 33

A yellow block 0.23 x 0.13 x 0.09 mm in size was mounted on a Cryoloop with Paratone oil. Data were collected in a nitrogen gas stream at 100(2) K using omega scans. Crystal-to-detector distance was 33.00 mm and exposure time was 0.50 seconds per frame using a scan width of 0.5°. Data collection was 100% complete to 74.000° in θ . A total of 12788 reflections were collected covering the indices $-8 \leq h \leq 8$, $-24 \leq k \leq 24$, $-10 \leq l \leq 10$. 2325 reflections were found to be symmetry independent, with an R_{int} of 0.0382. Indexing and unit cell refinement indicated a primitive, monoclinic lattice. The space group was found to be P 21/n (No. 14). The data were integrated using the CrysAlis^{Pro} 1.172.42.72a software program and scaled using the SCALE3 ABSPACK scaling algorithm. Solution by intrinsic phasing (SHELXT-2015) produced a heavy-atom phasing model consistent with the proposed structure. All non-hydrogen atoms were refined anisotropically by full-matrix least-squares (SHELXL-2014). All hydrogen atoms were placed using a riding model. Their positions were constrained relative to their parent atom using the appropriate HFIX command in SHELXL-2014.

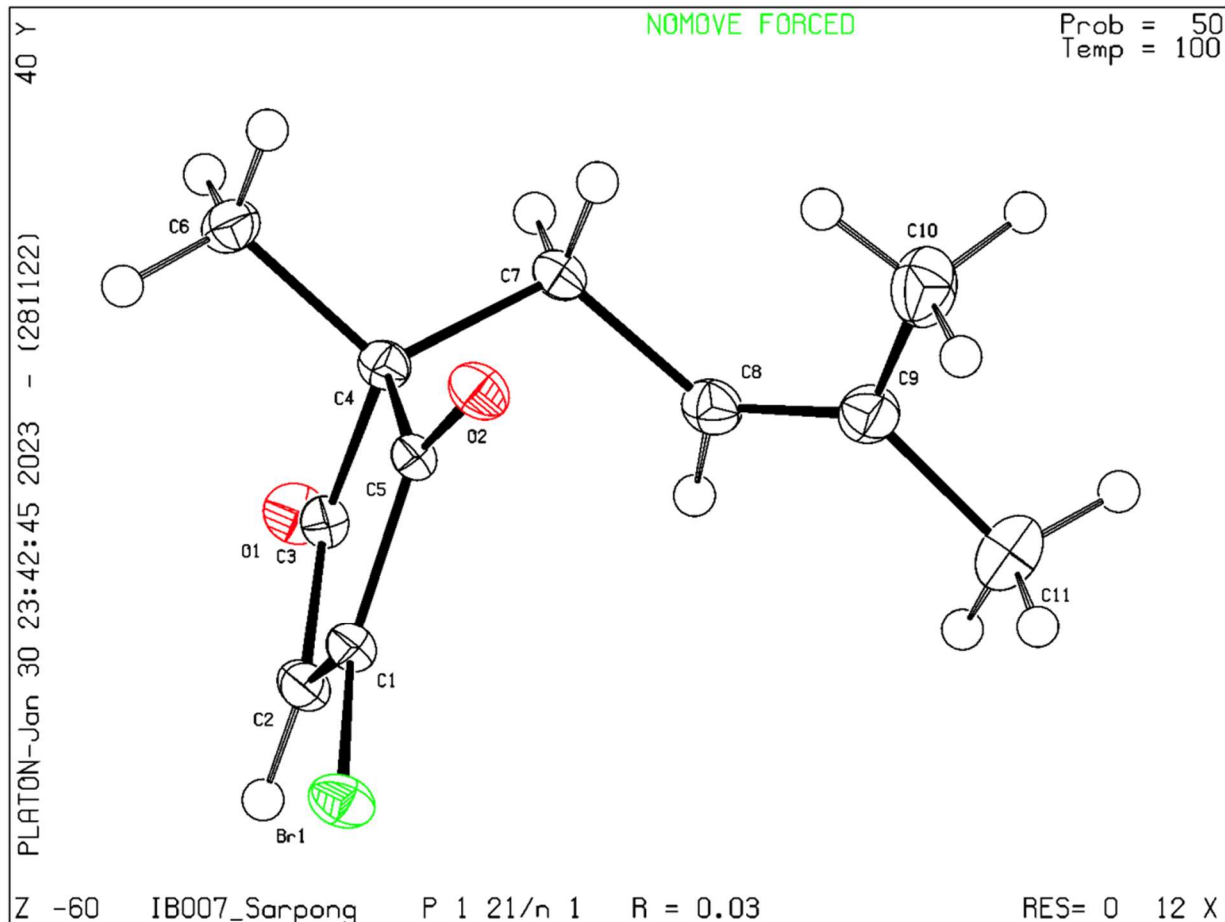


Table 1. Crystal data and structure refinement for IB007_Sarpong.

Identification code	IB007_Sarpong	
Empirical formula	C ₁₁ H ₁₃ Br O ₂	
Formula weight	257.12	
Temperature	100(2) K	
Wavelength	1.54184 Å	
Crystal system	Monoclinic	
Space group	P 2 ₁ /n	
Unit cell dimensions	a = 6.69110(10) Å	a = 90°.
	b = 19.8327(3) Å	b = 99.3160(10)°.
	c = 8.71150(10) Å	g = 90°.
Volume	1140.79(3) Å ³	
Z	4	
Density (calculated)	1.497 Mg/m ³	
Absorption coefficient	4.700 mm ⁻¹	
F(000)	520	
Crystal size	0.230 x 0.130 x 0.090 mm ³	
Theta range for data collection	4.459 to 74.440°.	
Index ranges	-8<=h<=8, -24<=k<=24, -10<=l<=10	
Reflections collected	12788	
Independent reflections	2325 [R(int) = 0.0382]	
Completeness to theta = 74.000°	99.5 %	
Absorption correction	Semi-empirical from equivalents	
Max. and min. transmission	1.00000 and 0.75728	
Refinement method	Full-matrix least-squares on F ²	
Data / restraints / parameters	2325 / 0 / 130	
Goodness-of-fit on F ²	1.088	
Final R indices [I>2sigma(I)]	R1 = 0.0294, wR2 = 0.0806	
R indices (all data)	R1 = 0.0297, wR2 = 0.0808	
Extinction coefficient	n/a	
Largest diff. peak and hole	0.452 and -0.679 e.Å ⁻³	

Table 2. Atomic coordinates ($\times 10^4$) and equivalent isotropic displacement parameters ($\text{\AA}^2 \times 10^3$)

for ib007_sarpong. $U(\text{eq})$ is defined as one third of the trace of the orthogonalized U^{ij} tensor.

	x	y	z	$U(\text{eq})$
Br(1)	7462(1)	6067(1)	8900(1)	20(1)
O(1)	3697(2)	7239(1)	3871(2)	21(1)
O(2)	10182(2)	6625(1)	6437(2)	19(1)
C(1)	6793(3)	6506(1)	6997(2)	16(1)
C(2)	4940(3)	6660(1)	6257(2)	17(1)
C(3)	5115(3)	7039(1)	4815(2)	16(1)
C(4)	7350(3)	7149(1)	4722(2)	15(1)
C(5)	8398(3)	6745(1)	6112(2)	14(1)
C(6)	7894(3)	7900(1)	4963(2)	19(1)
C(7)	7935(3)	6883(1)	3191(2)	17(1)
C(8)	7348(3)	6158(1)	2864(2)	19(1)
C(9)	8572(3)	5631(1)	2783(2)	22(1)
C(10)	10839(4)	5669(1)	3006(3)	31(1)
C(11)	7703(4)	4939(1)	2387(3)	34(1)

Table 3. Bond lengths [Å] and angles [°] for ib007_sarpong.

Br(1)-C(1)	1.8620(19)
O(1)-C(3)	1.217(2)
O(2)-C(5)	1.205(2)
C(1)-C(2)	1.337(3)
C(1)-C(5)	1.497(2)
C(2)-C(3)	1.484(3)
C(2)-H(2)	0.9500
C(3)-C(4)	1.526(3)
C(4)-C(5)	1.525(3)
C(4)-C(6)	1.540(3)
C(4)-C(7)	1.542(3)
C(6)-H(6A)	0.9800
C(6)-H(6B)	0.9800
C(6)-H(6C)	0.9800
C(7)-C(8)	1.506(3)
C(7)-H(7A)	0.9900
C(7)-H(7B)	0.9900
C(8)-C(9)	1.336(3)
C(8)-H(8)	0.9500
C(9)-C(10)	1.499(3)
C(9)-C(11)	1.509(3)
C(10)-H(10A)	0.9800
C(10)-H(10B)	0.9800
C(10)-H(10C)	0.9800
C(11)-H(11A)	0.9800
C(11)-H(11B)	0.9800
C(11)-H(11C)	0.9800
C(2)-C(1)-C(5)	111.46(17)
C(2)-C(1)-Br(1)	127.37(15)
C(5)-C(1)-Br(1)	121.16(14)
C(1)-C(2)-C(3)	109.26(17)
C(1)-C(2)-H(2)	125.4
C(3)-C(2)-H(2)	125.4

O(1)-C(3)-C(2)	125.24(18)
O(1)-C(3)-C(4)	125.52(17)
C(2)-C(3)-C(4)	109.23(16)
C(5)-C(4)-C(3)	102.20(15)
C(5)-C(4)-C(6)	109.35(15)
C(3)-C(4)-C(6)	110.04(16)
C(5)-C(4)-C(7)	111.03(16)
C(3)-C(4)-C(7)	112.66(16)
C(6)-C(4)-C(7)	111.19(16)
O(2)-C(5)-C(1)	125.62(17)
O(2)-C(5)-C(4)	126.95(17)
C(1)-C(5)-C(4)	107.42(15)
C(4)-C(6)-H(6A)	109.5
C(4)-C(6)-H(6B)	109.5
H(6A)-C(6)-H(6B)	109.5
C(4)-C(6)-H(6C)	109.5
H(6A)-C(6)-H(6C)	109.5
H(6B)-C(6)-H(6C)	109.5
C(8)-C(7)-C(4)	113.27(16)
C(8)-C(7)-H(7A)	108.9
C(4)-C(7)-H(7A)	108.9
C(8)-C(7)-H(7B)	108.9
C(4)-C(7)-H(7B)	108.9
H(7A)-C(7)-H(7B)	107.7
C(9)-C(8)-C(7)	127.8(2)
C(9)-C(8)-H(8)	116.1
C(7)-C(8)-H(8)	116.1
C(8)-C(9)-C(10)	124.8(2)
C(8)-C(9)-C(11)	120.4(2)
C(10)-C(9)-C(11)	114.8(2)
C(9)-C(10)-H(10A)	109.5
C(9)-C(10)-H(10B)	109.5
H(10A)-C(10)-H(10B)	109.5
C(9)-C(10)-H(10C)	109.5
H(10A)-C(10)-H(10C)	109.5
H(10B)-C(10)-H(10C)	109.5

C(9)-C(11)-H(11A)	109.5
C(9)-C(11)-H(11B)	109.5
H(11A)-C(11)-H(11B)	109.5
C(9)-C(11)-H(11C)	109.5
H(11A)-C(11)-H(11C)	109.5
H(11B)-C(11)-H(11C)	109.5

Symmetry transformations used to generate equivalent atoms:

Table 4. Anisotropic displacement parameters ($\text{\AA}^2 \times 10^3$) for ib007_sarpong. The anisotropic displacement factor exponent takes the form: $-2p^2 [h^2 a^2 U_{11} + \dots + 2 h k a^* b^* U_{12}]$

	U11	U22	U33	U23	U13	U12
Br(1)	20(1)	25(1)	16(1)	6(1)	5(1)	1(1)
O(1)	18(1)	25(1)	20(1)	3(1)	1(1)	2(1)
O(2)	13(1)	24(1)	19(1)	0(1)	3(1)	1(1)
C(1)	17(1)	16(1)	15(1)	-1(1)	6(1)	-1(1)
C(2)	16(1)	19(1)	16(1)	0(1)	6(1)	1(1)
C(3)	16(1)	15(1)	16(1)	-2(1)	4(1)	0(1)
C(4)	14(1)	17(1)	15(1)	0(1)	3(1)	-1(1)
C(5)	16(1)	14(1)	13(1)	-1(1)	6(1)	-1(1)
C(6)	23(1)	16(1)	17(1)	1(1)	3(1)	-3(1)
C(7)	20(1)	19(1)	14(1)	0(1)	7(1)	-1(1)
C(8)	20(1)	23(1)	15(1)	-1(1)	3(1)	-3(1)
C(9)	29(1)	20(1)	17(1)	1(1)	5(1)	-2(1)
C(10)	28(1)	27(1)	39(1)	-4(1)	4(1)	5(1)
C(11)	40(1)	21(1)	40(1)	-3(1)	8(1)	-2(1)

Table 5. Hydrogen coordinates ($\times 10^4$) and isotropic displacement parameters ($\text{\AA}^2 \times 10^3$) for ib007_sarpong.

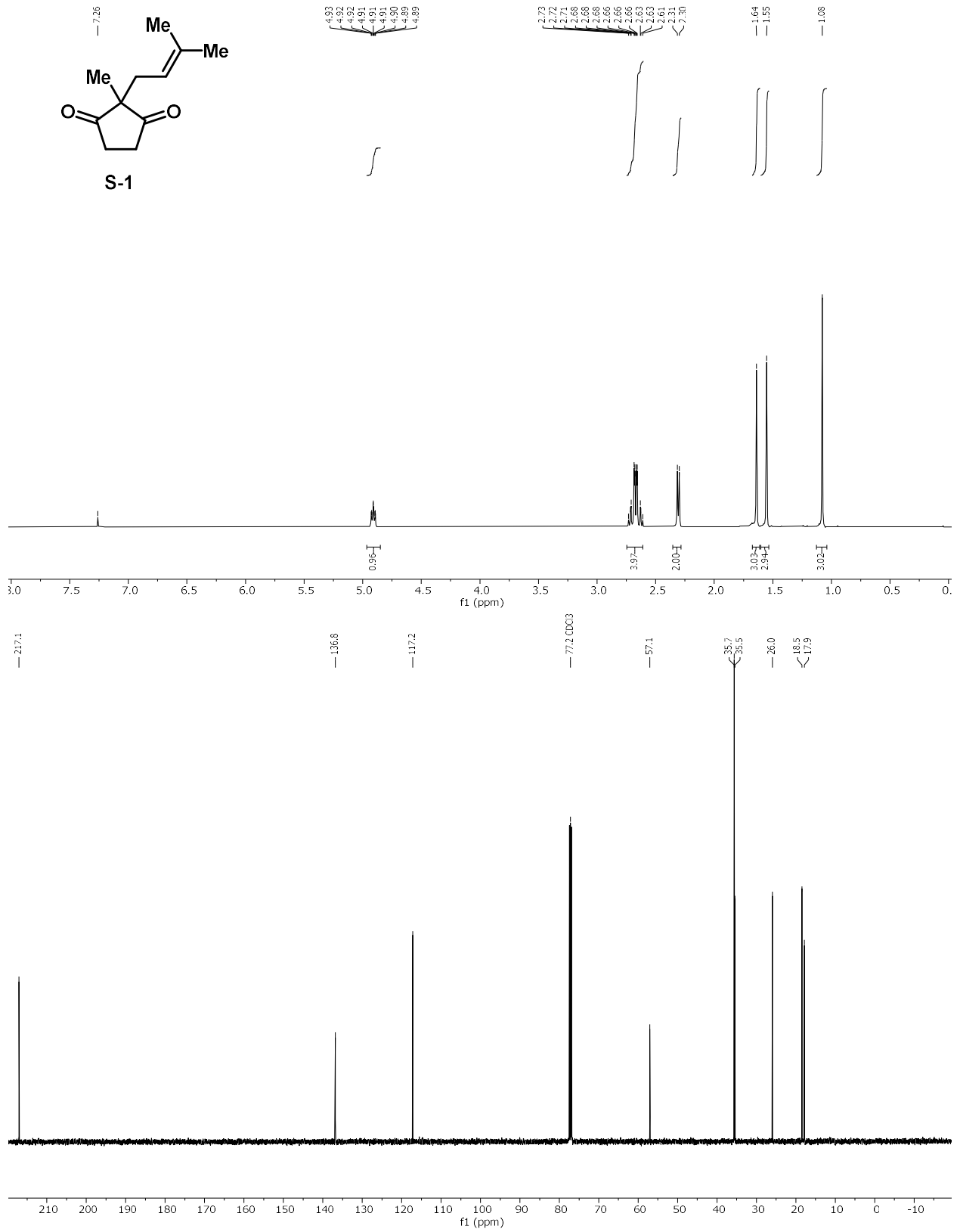
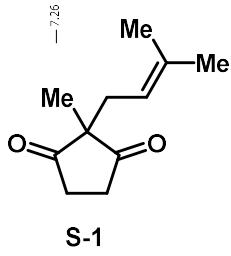
	x	y	z	U(eq)
H(2)	3706	6546	6599	20
H(6A)	7549	8051	5959	28
H(6B)	7130	8165	4116	28
H(6C)	9348	7961	4969	28
H(7A)	7269	7166	2319	21
H(7B)	9417	6929	3240	21
H(8)	5937	6063	2694	23
H(10A)	11303	5569	2020	47
H(10B)	11416	5341	3795	47
H(10C)	11278	6124	3350	47
H(11A)	6222	4959	2263	50
H(11B)	8215	4624	3226	50
H(11C)	8108	4784	1414	50

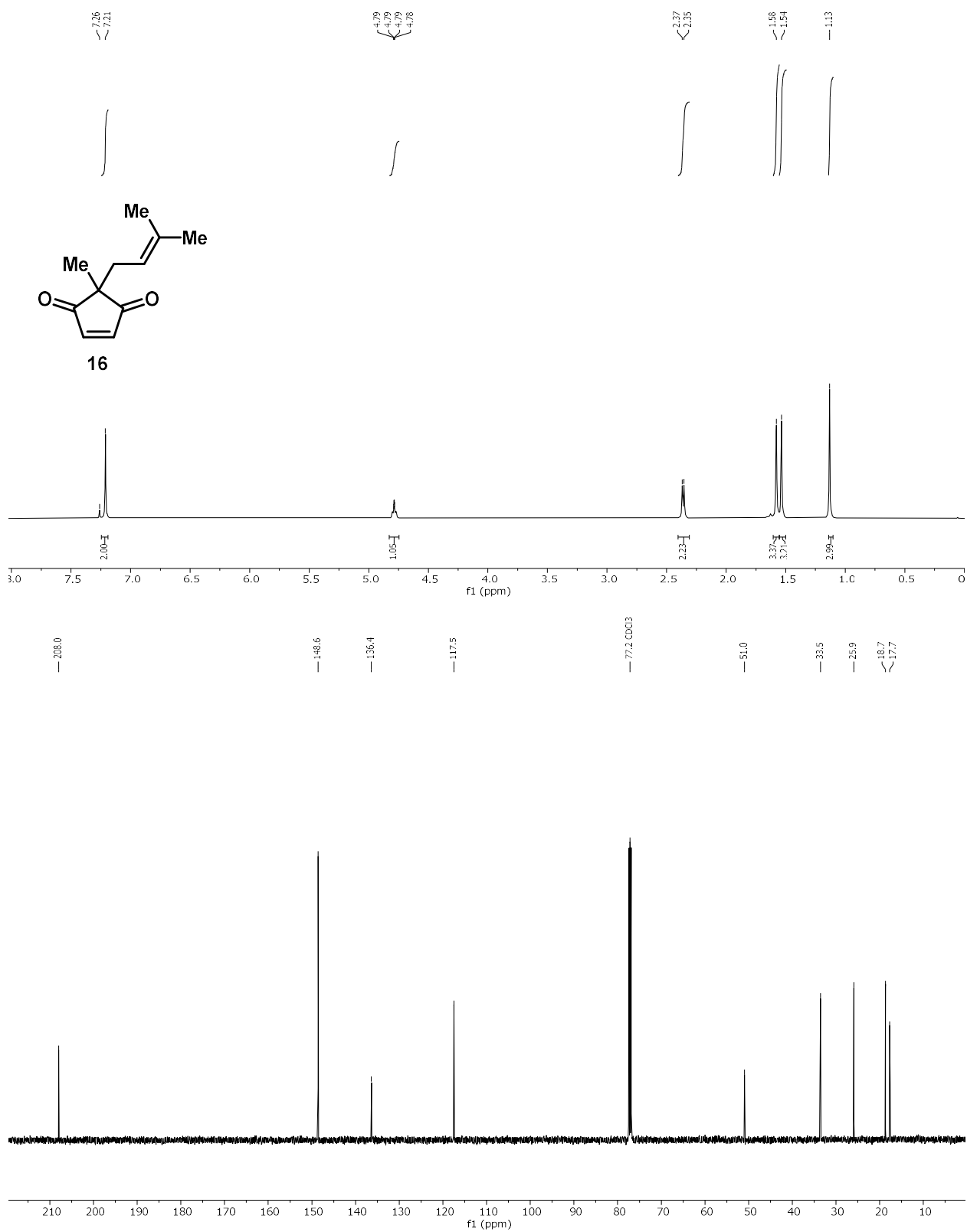
Table 6. Torsion angles [°] for ib007_sarpong.

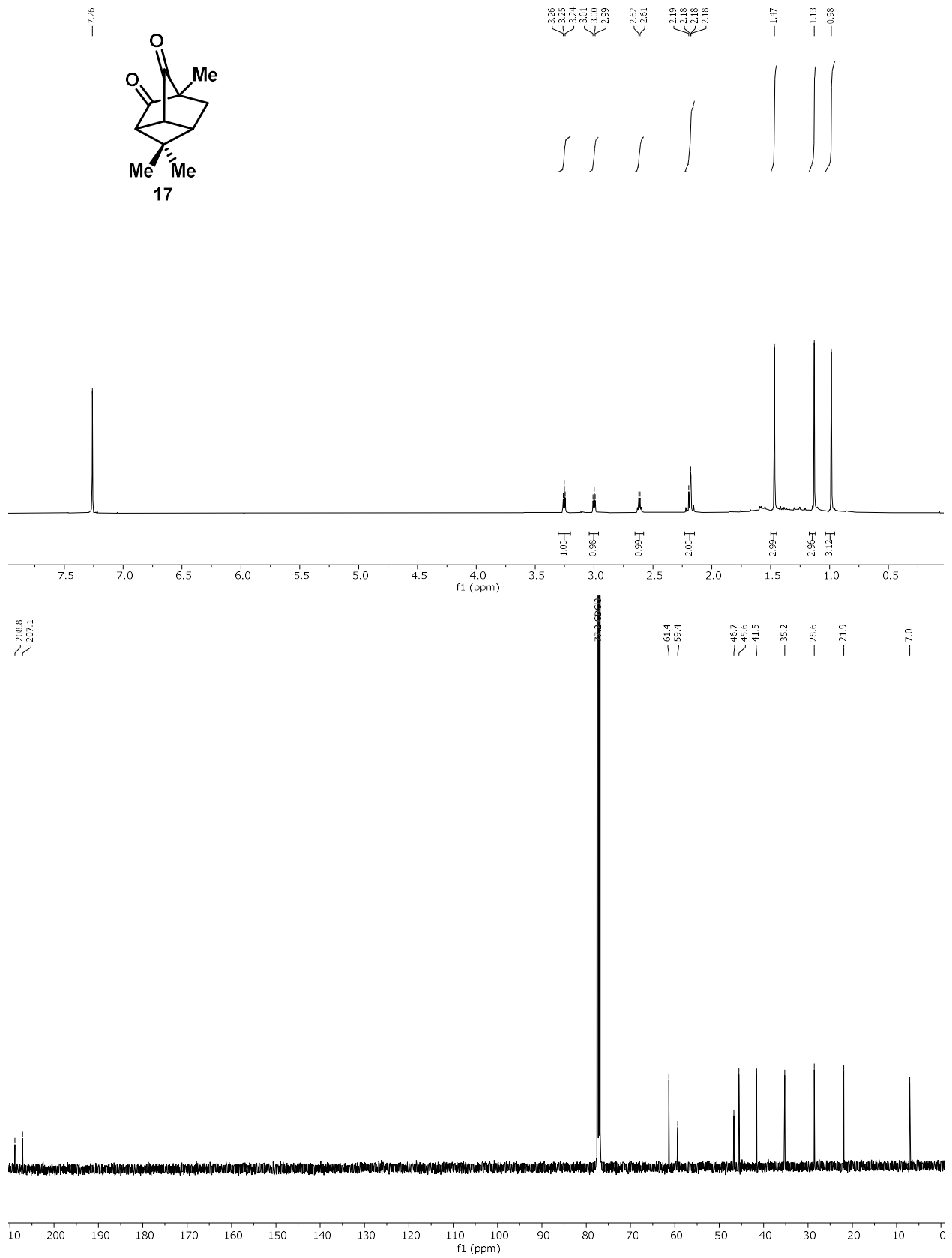
C(5)-C(1)-C(2)-C(3)	-1.7(2)
Br(1)-C(1)-C(2)-C(3)	177.19(14)
C(1)-C(2)-C(3)-O(1)	178.35(19)
C(1)-C(2)-C(3)-C(4)	-2.7(2)
O(1)-C(3)-C(4)-C(5)	-175.42(18)
C(2)-C(3)-C(4)-C(5)	5.61(19)
O(1)-C(3)-C(4)-C(6)	68.5(2)
C(2)-C(3)-C(4)-C(6)	-110.47(18)
O(1)-C(3)-C(4)-C(7)	-56.2(3)
C(2)-C(3)-C(4)-C(7)	124.83(17)
C(2)-C(1)-C(5)-O(2)	-173.30(19)
Br(1)-C(1)-C(5)-O(2)	7.7(3)
C(2)-C(1)-C(5)-C(4)	5.4(2)
Br(1)-C(1)-C(5)-C(4)	-173.57(13)
C(3)-C(4)-C(5)-O(2)	172.25(19)
C(6)-C(4)-C(5)-O(2)	-71.2(2)
C(7)-C(4)-C(5)-O(2)	51.9(3)
C(3)-C(4)-C(5)-C(1)	-6.42(19)
C(6)-C(4)-C(5)-C(1)	110.16(17)
C(7)-C(4)-C(5)-C(1)	-126.78(16)
C(5)-C(4)-C(7)-C(8)	60.6(2)
C(3)-C(4)-C(7)-C(8)	-53.3(2)
C(6)-C(4)-C(7)-C(8)	-177.40(17)
C(4)-C(7)-C(8)-C(9)	-115.6(2)
C(7)-C(8)-C(9)-C(10)	-0.3(4)
C(7)-C(8)-C(9)-C(11)	-177.9(2)

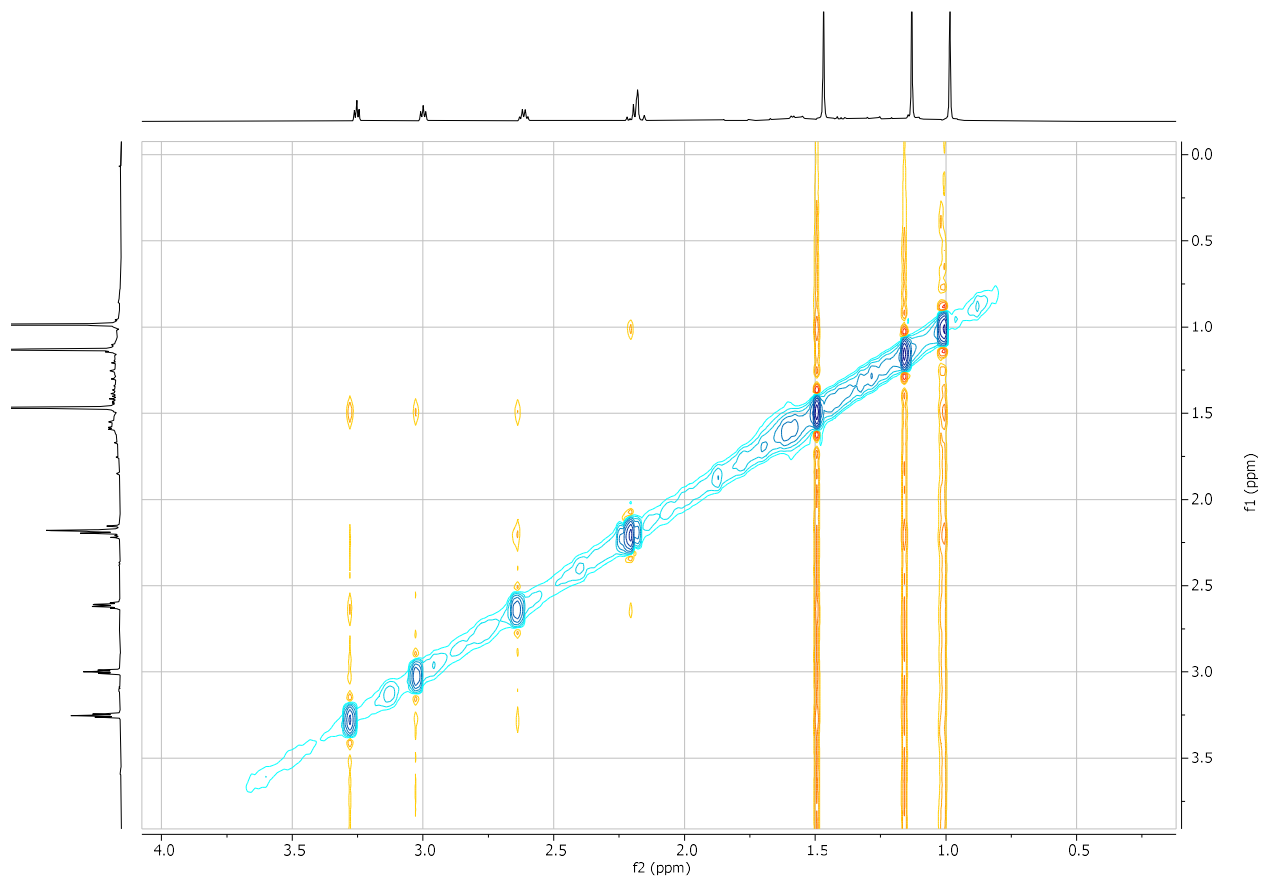
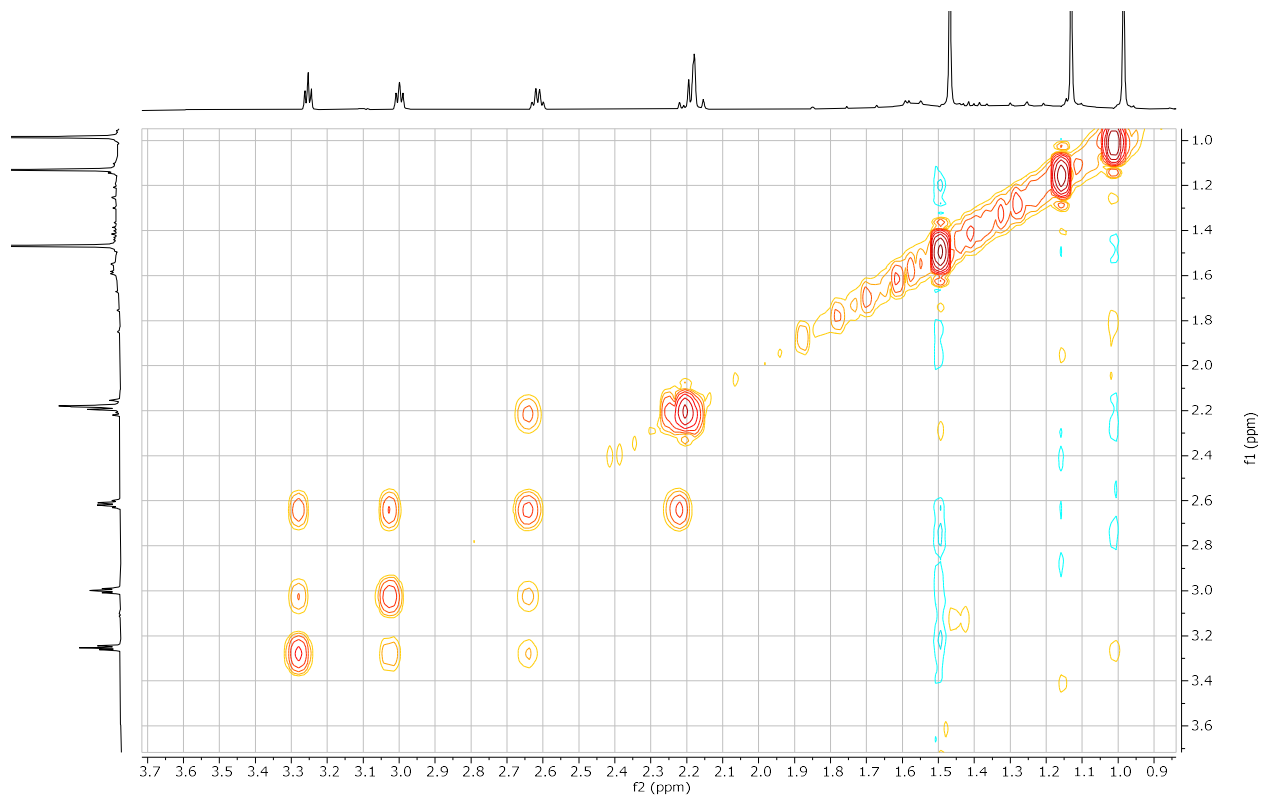
Symmetry transformations used to generate equivalent atoms:

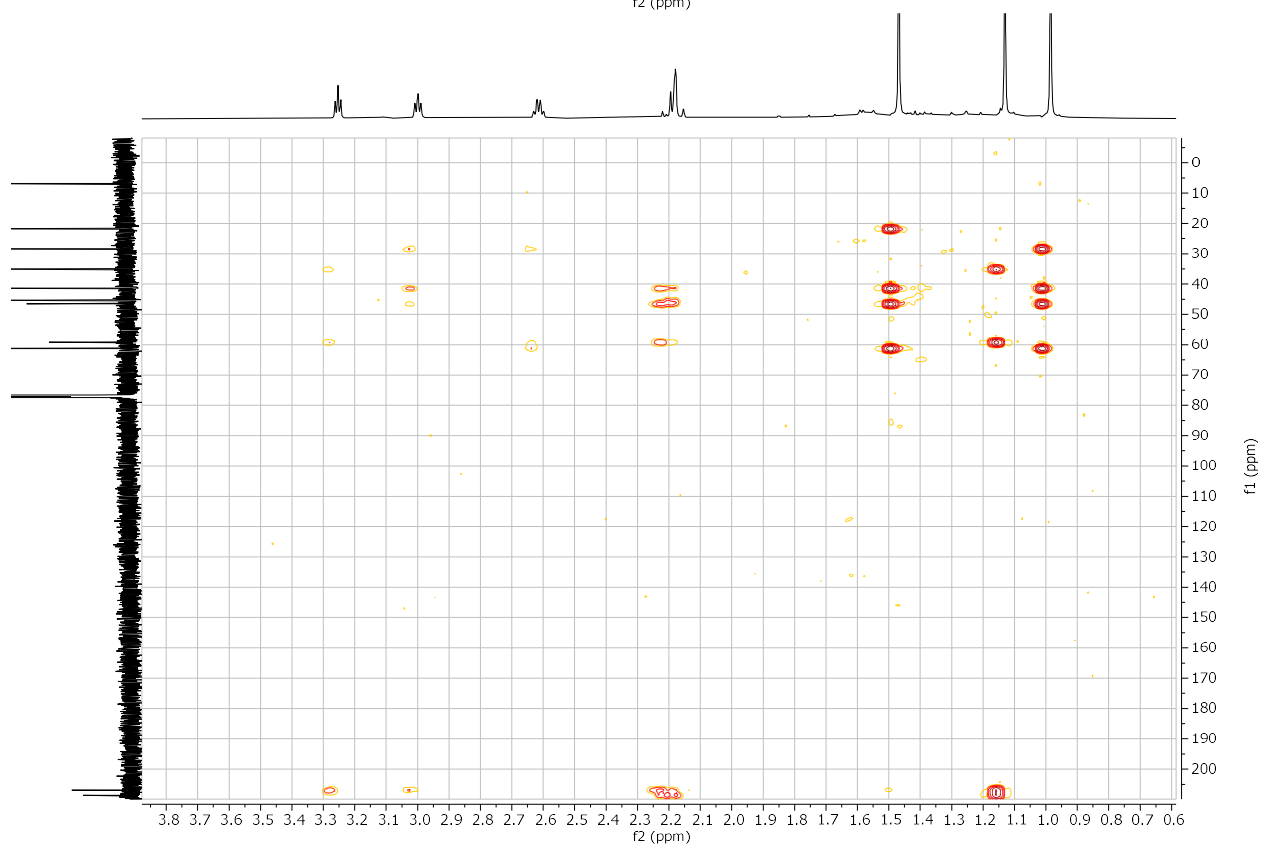
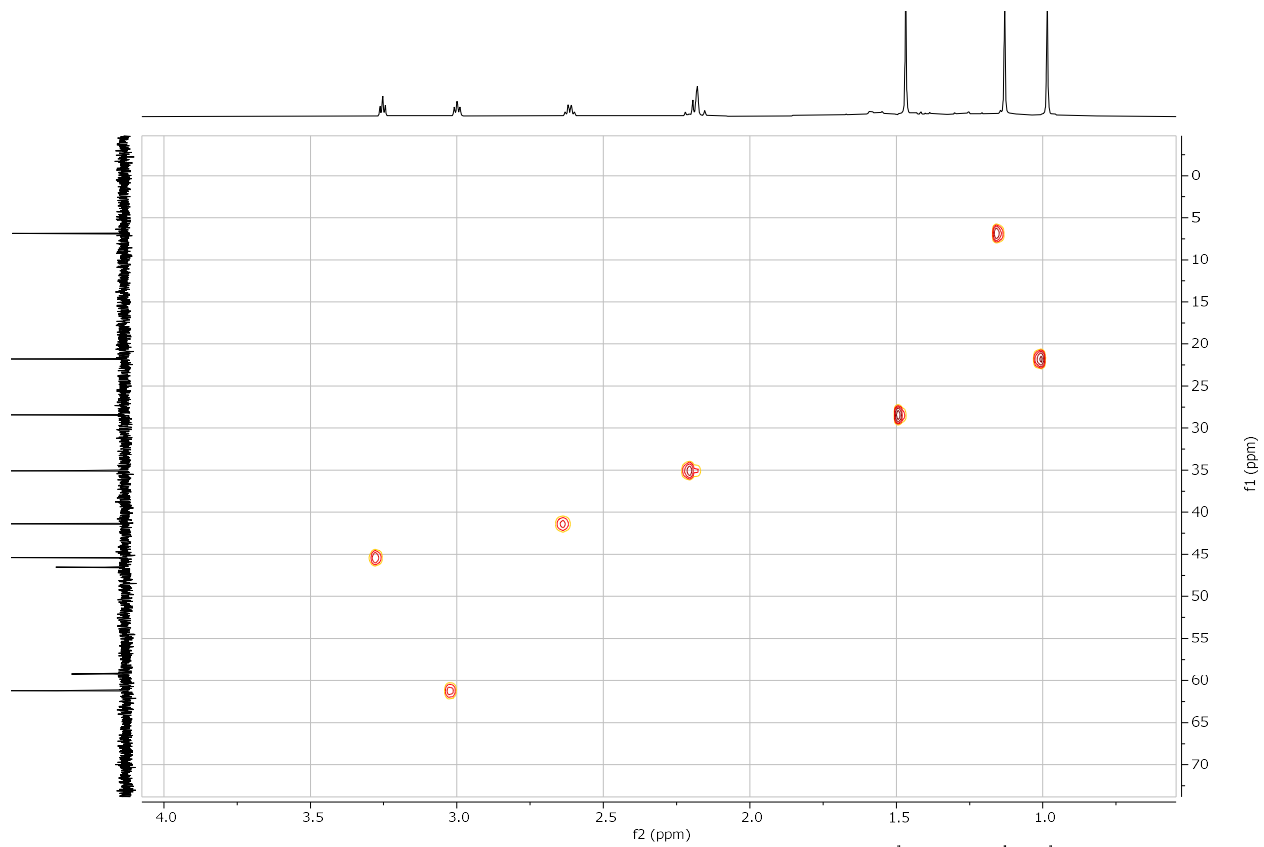
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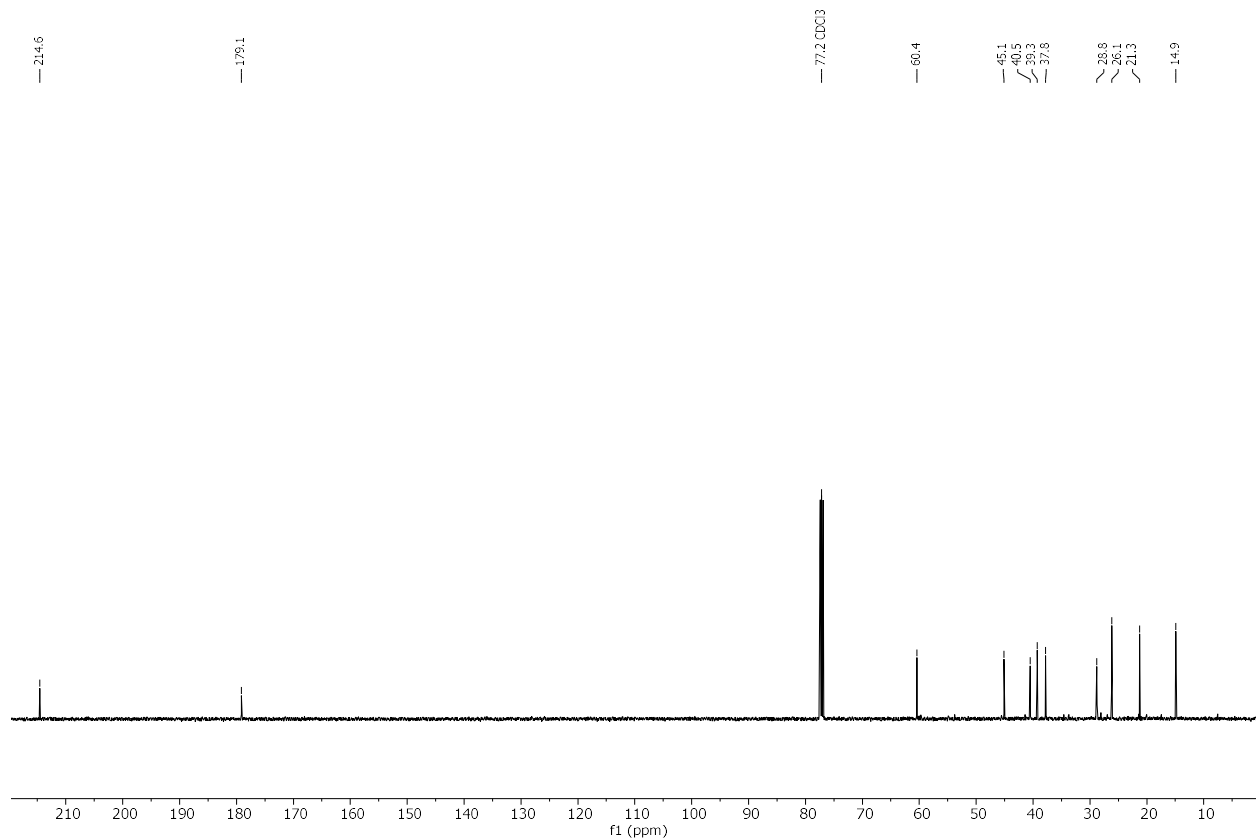
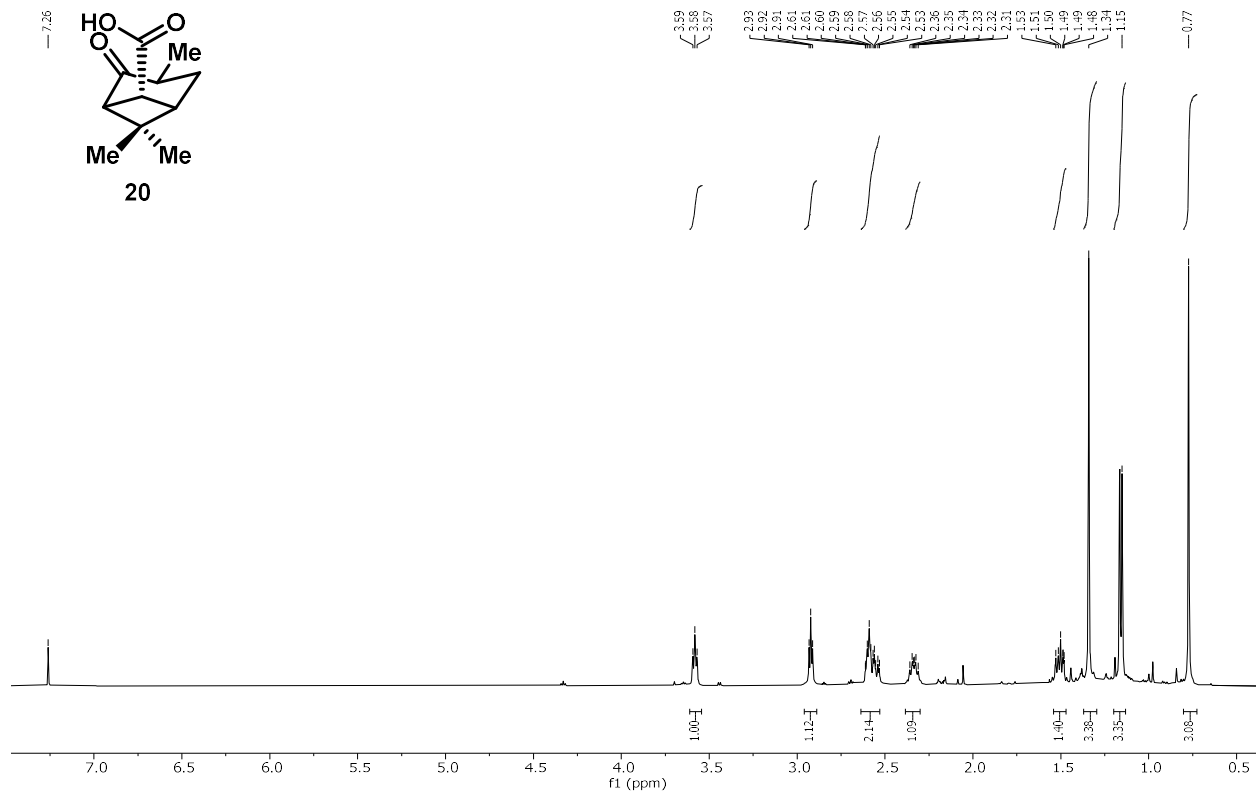
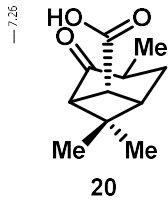


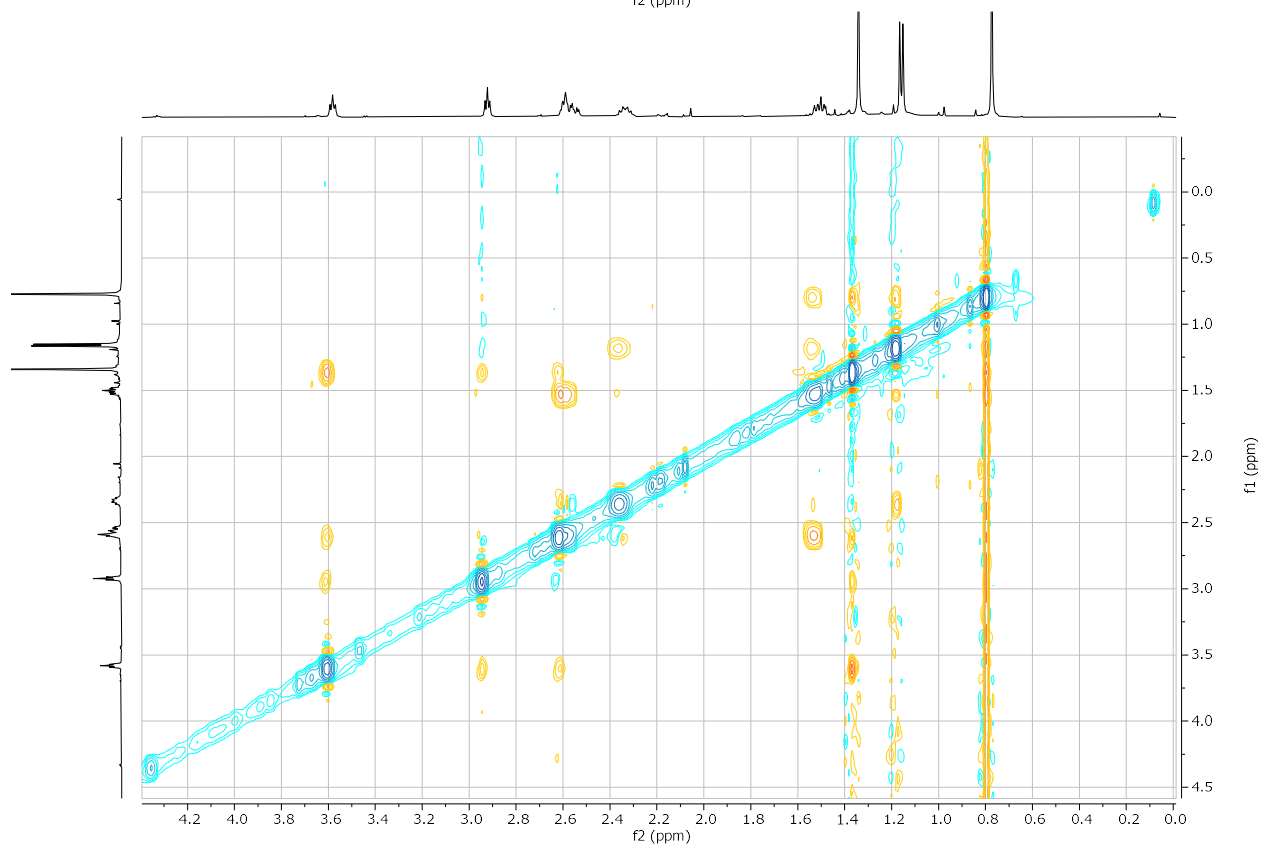
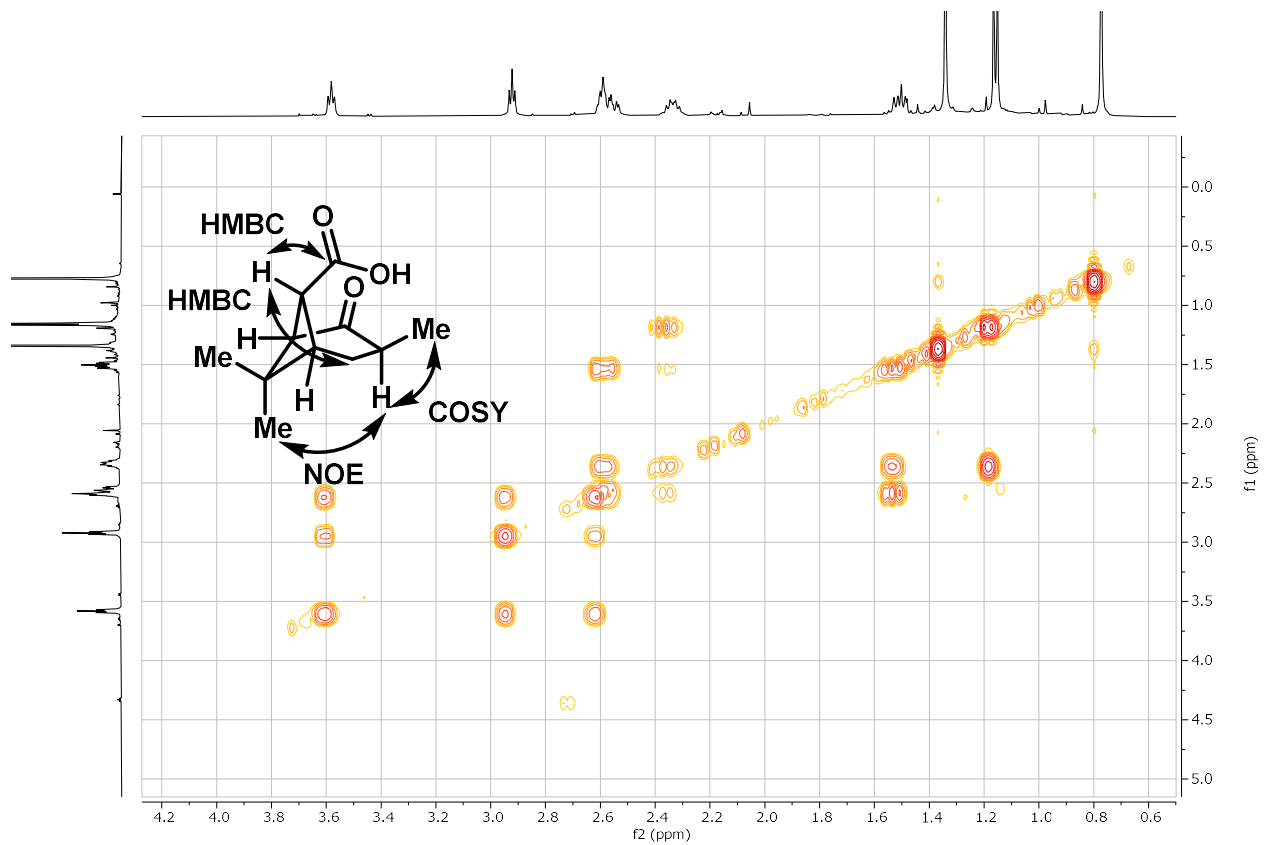


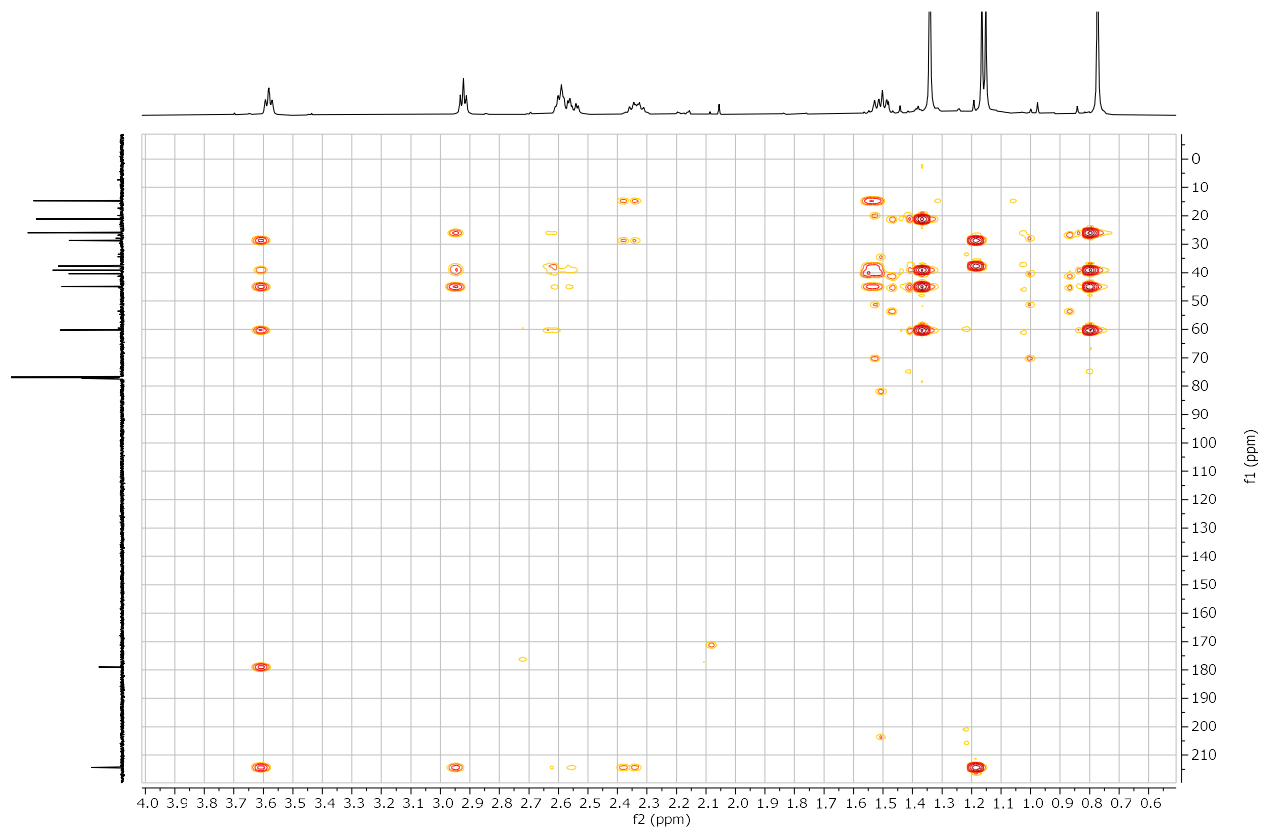
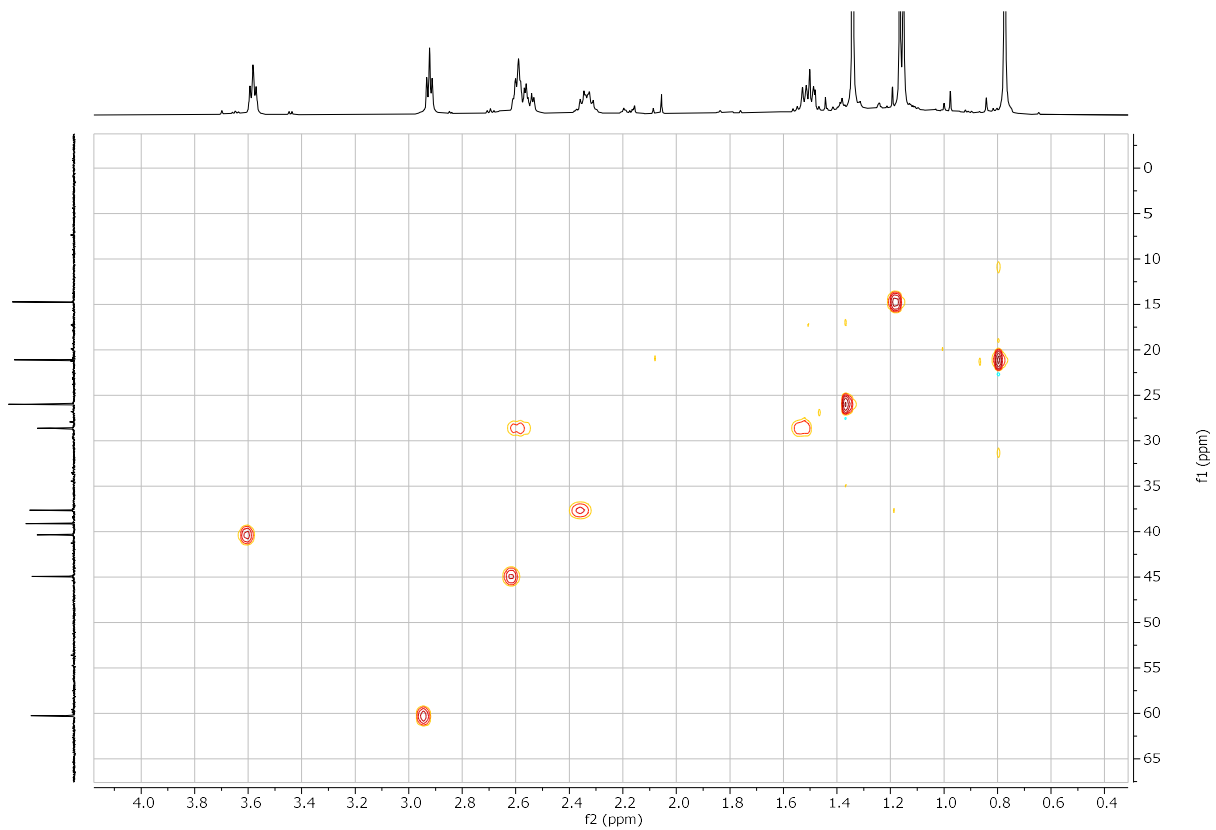




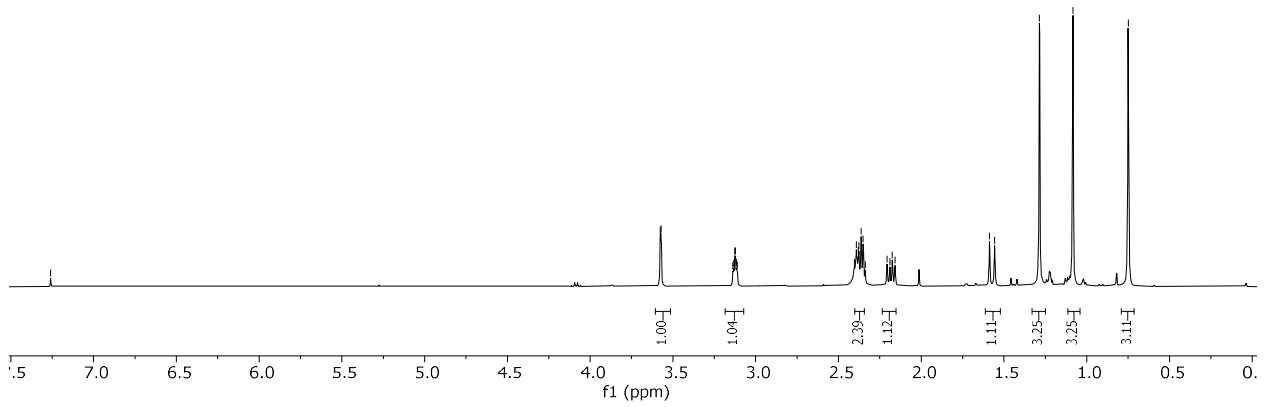
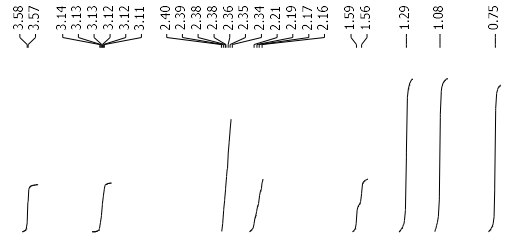
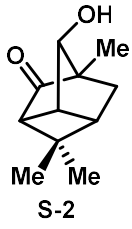




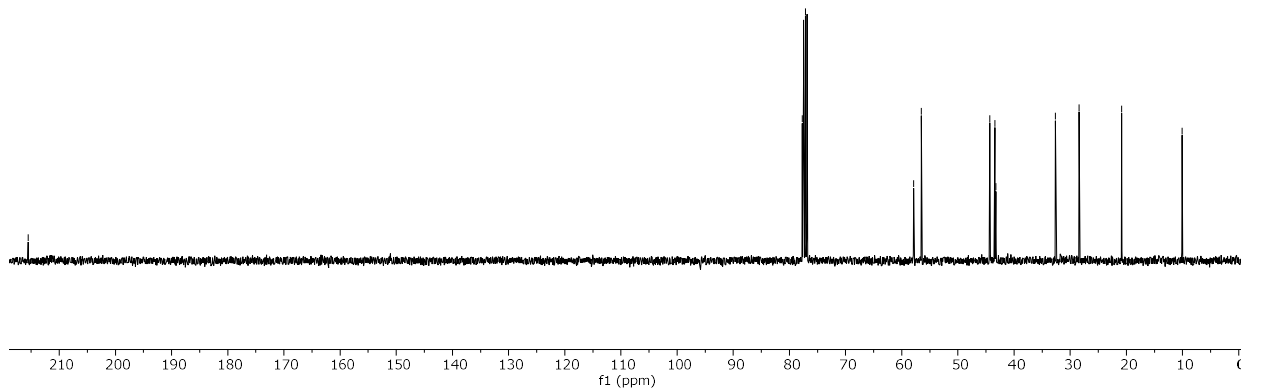
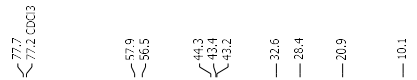


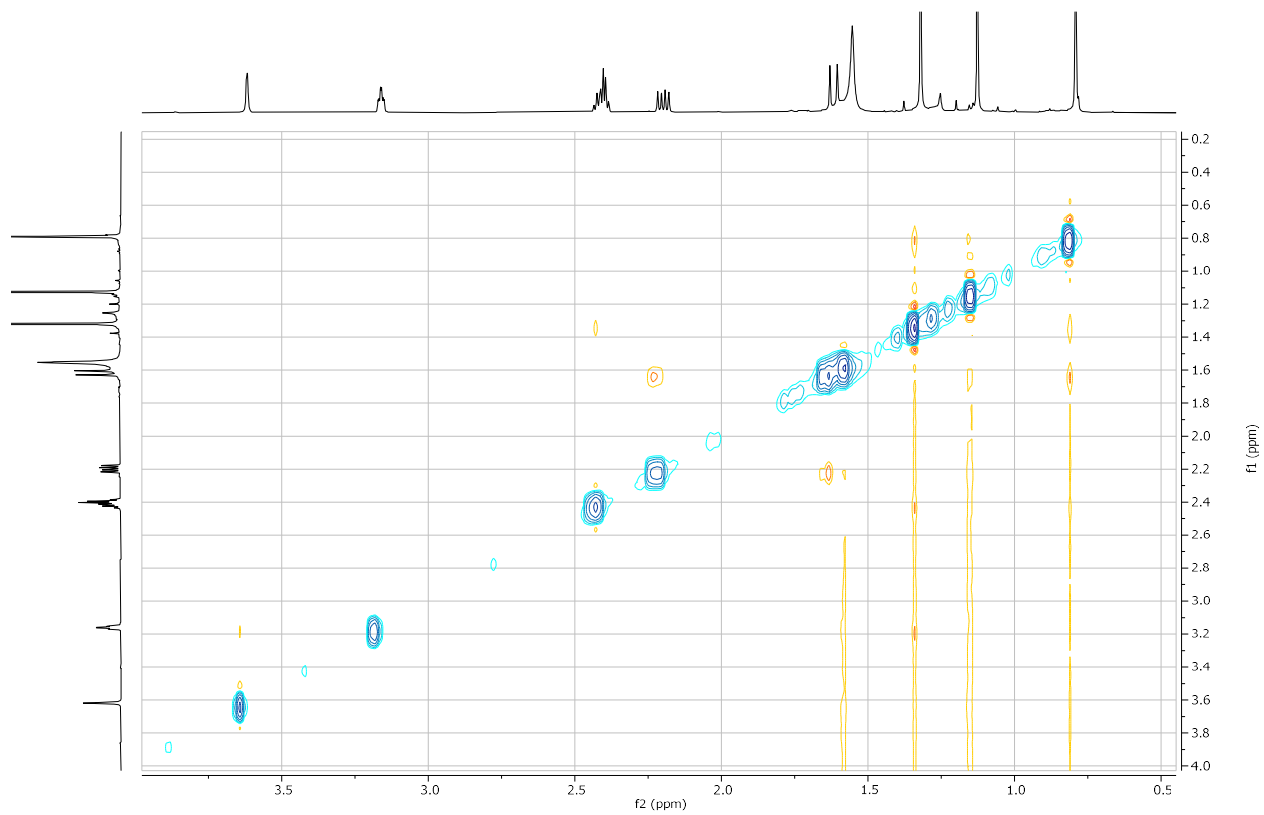
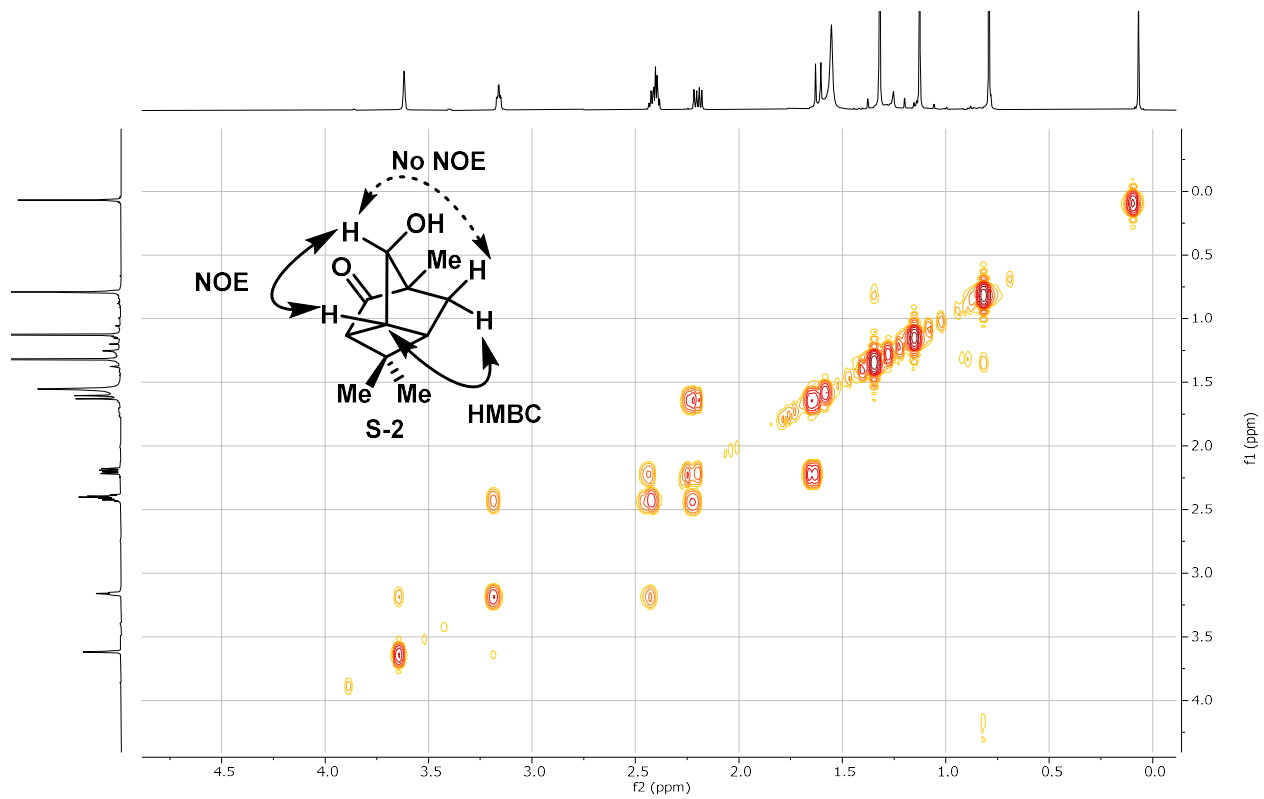


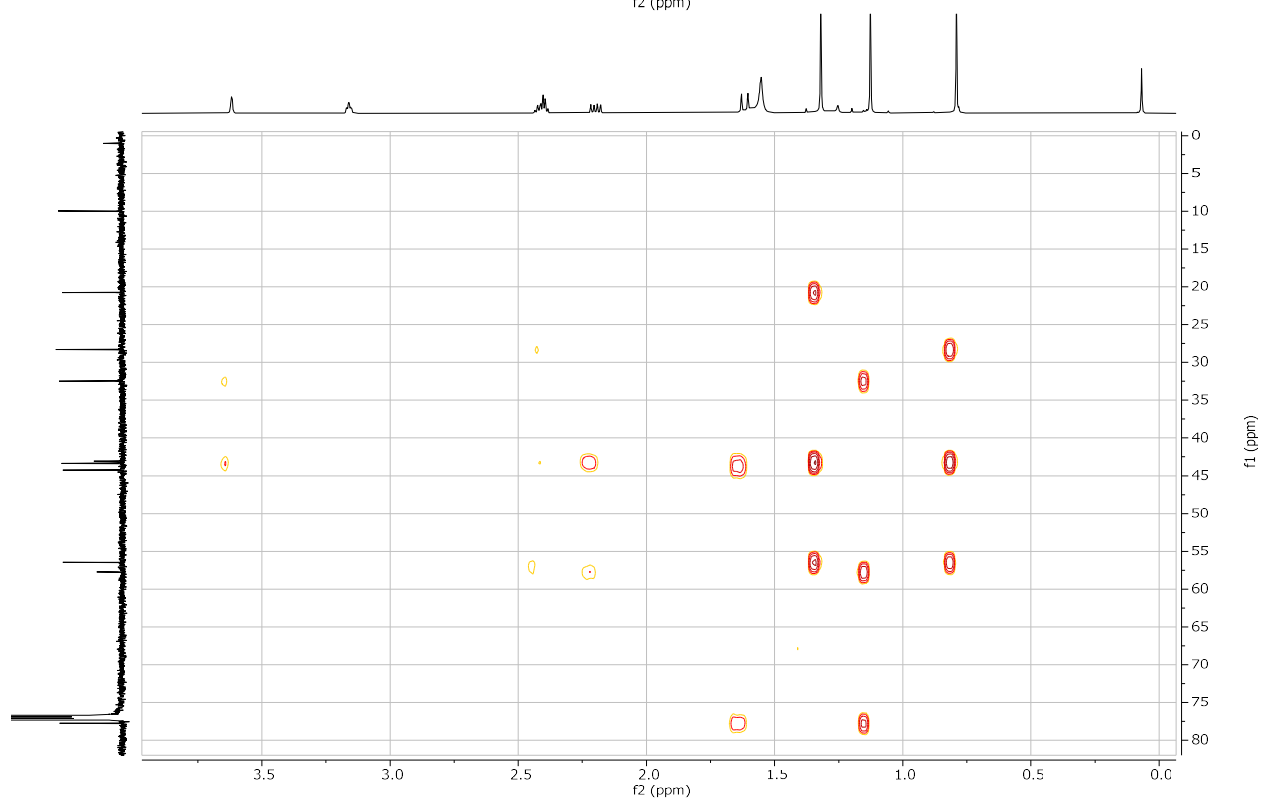
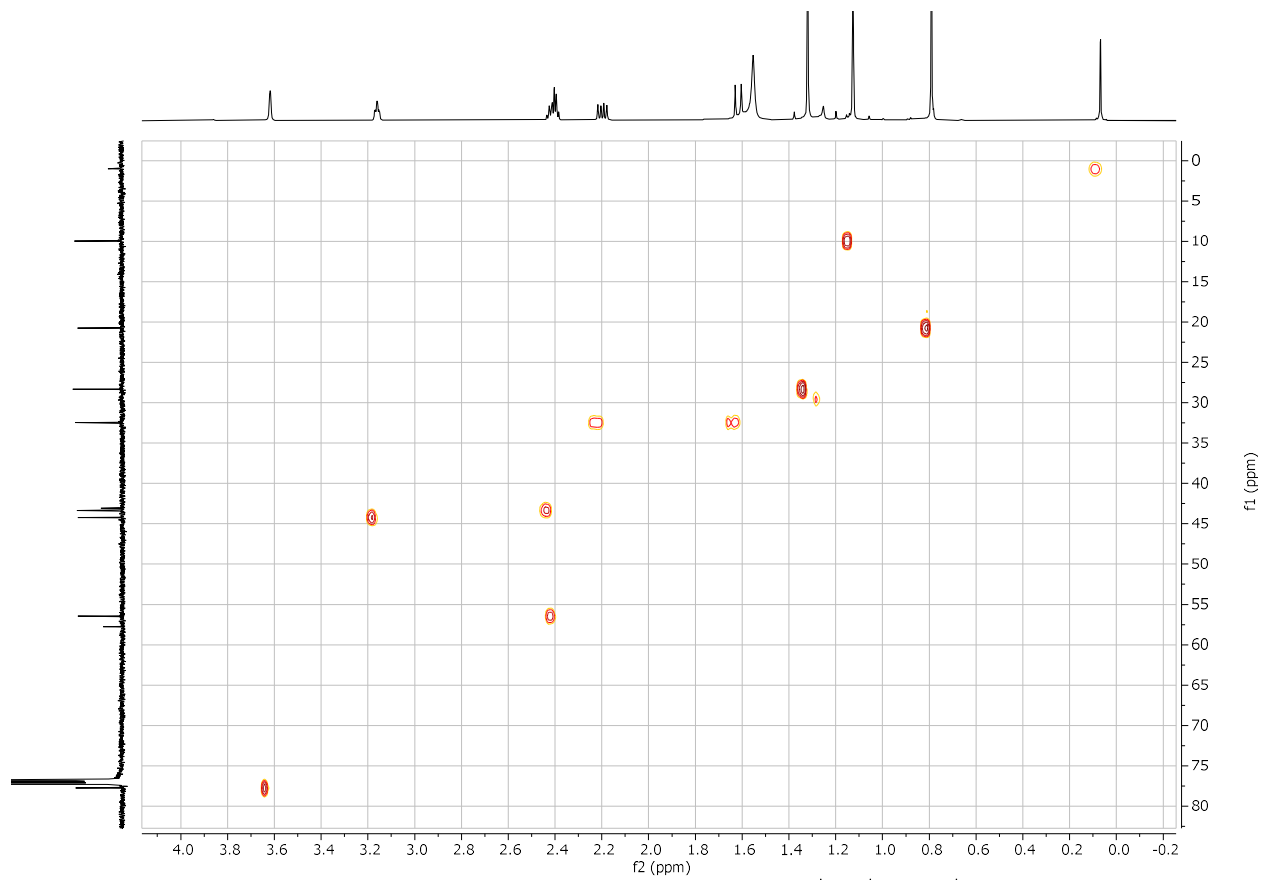
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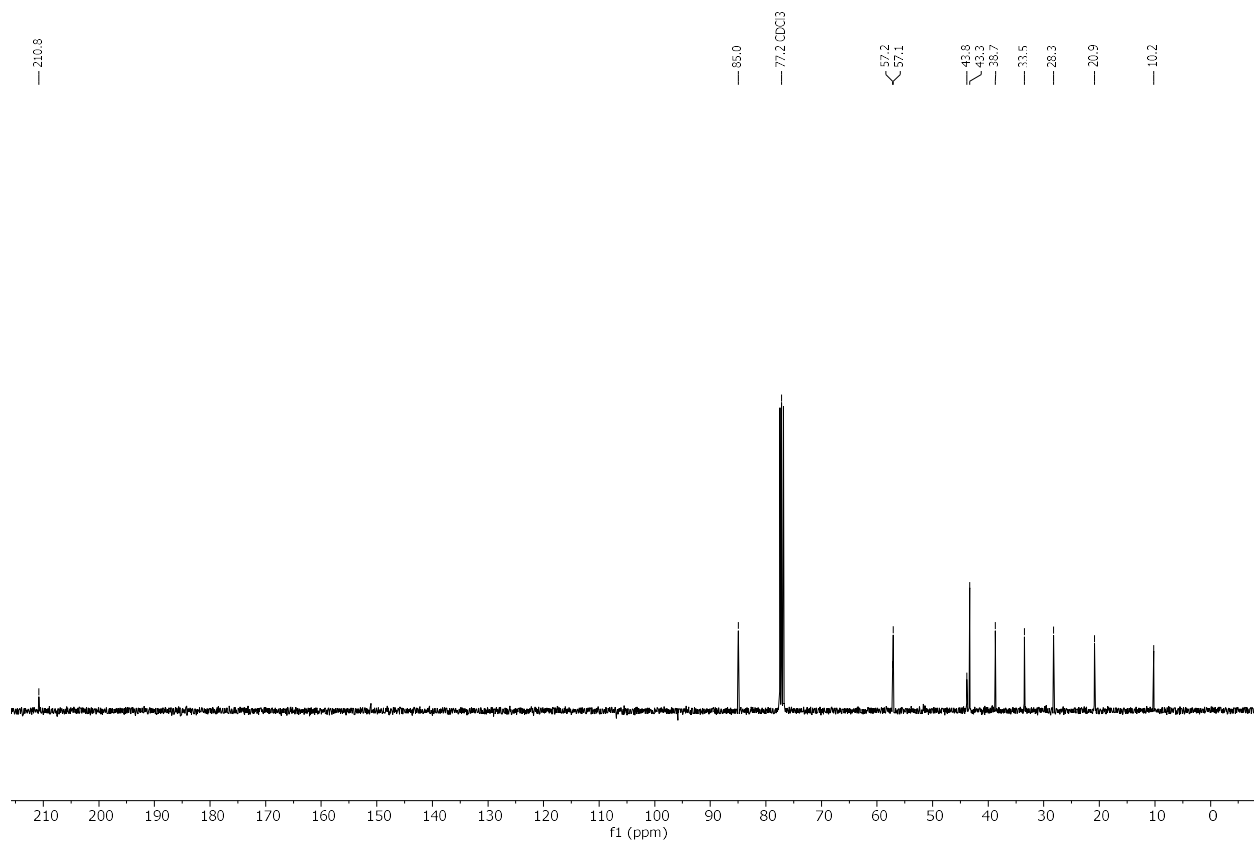
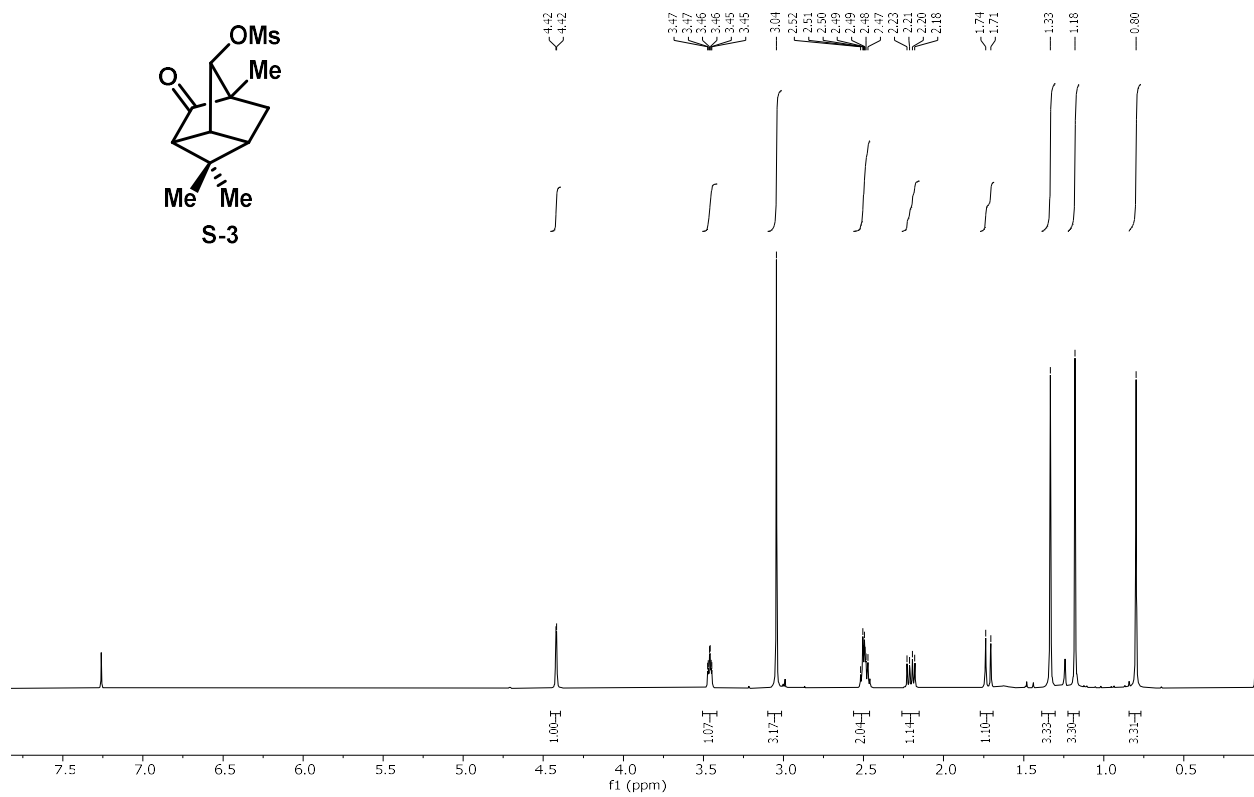
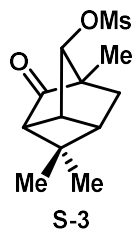


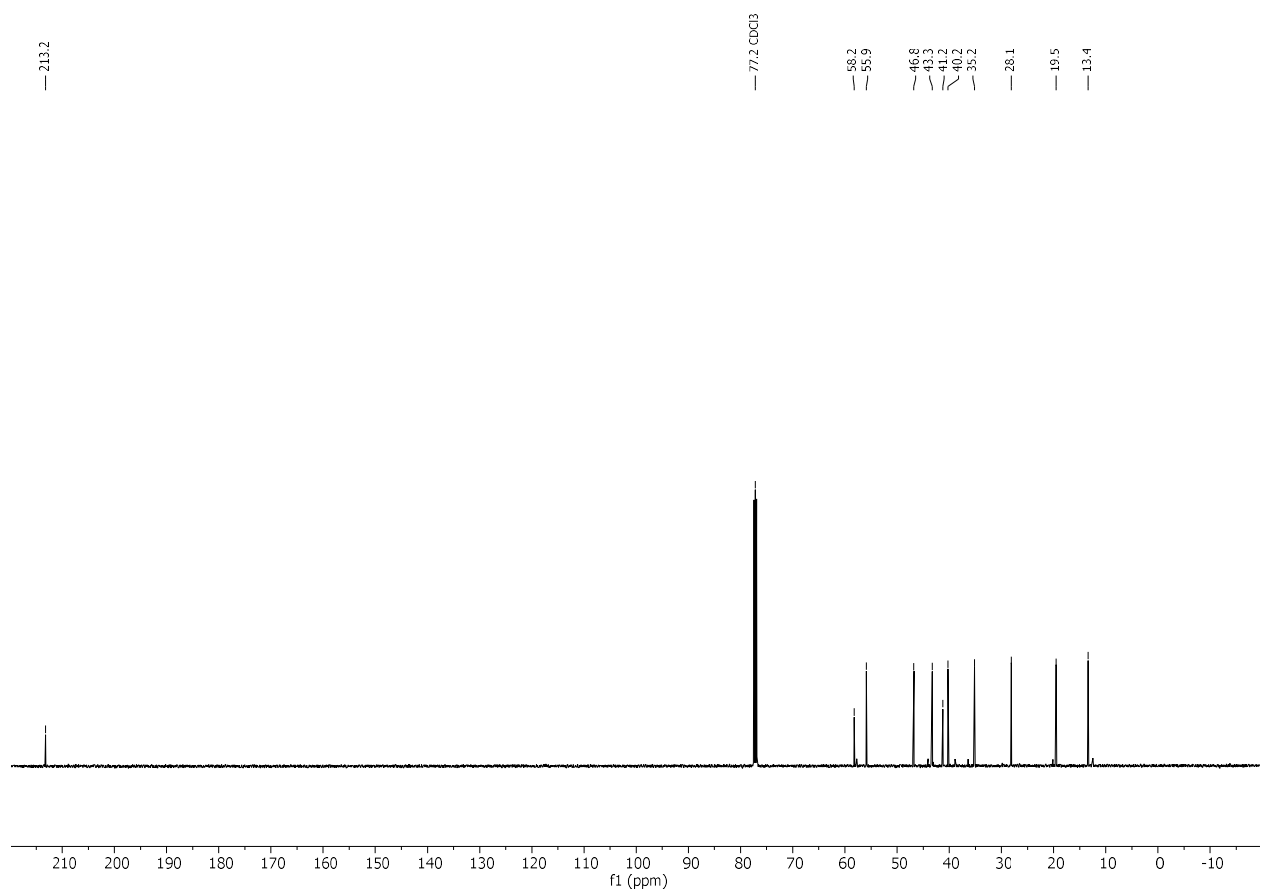
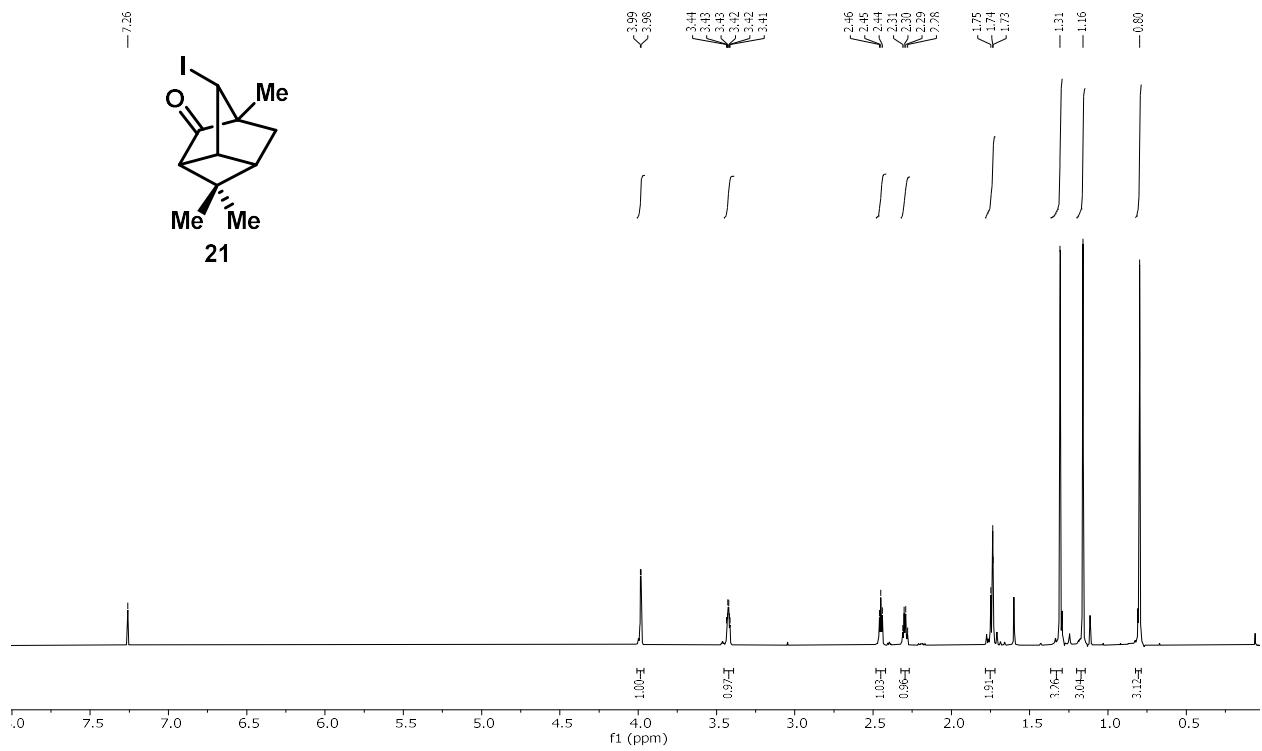
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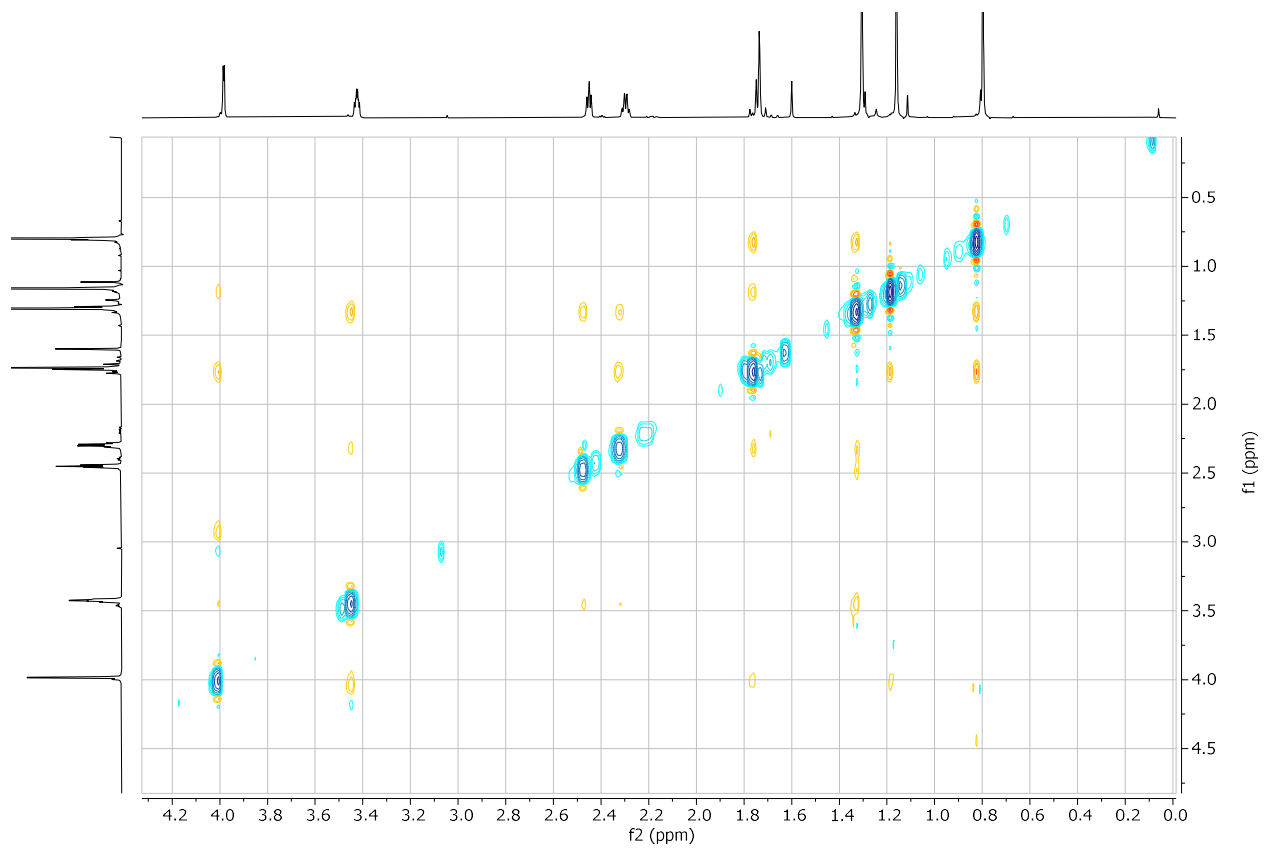
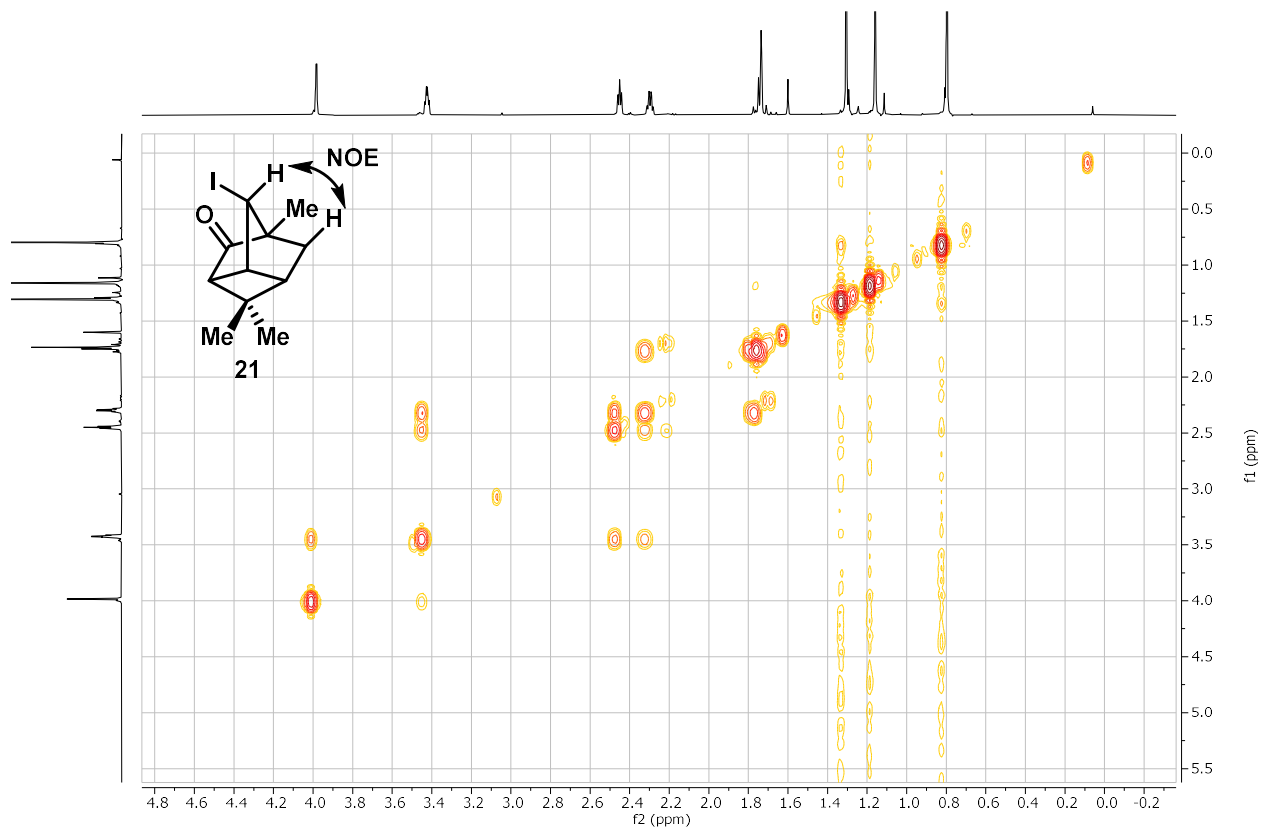


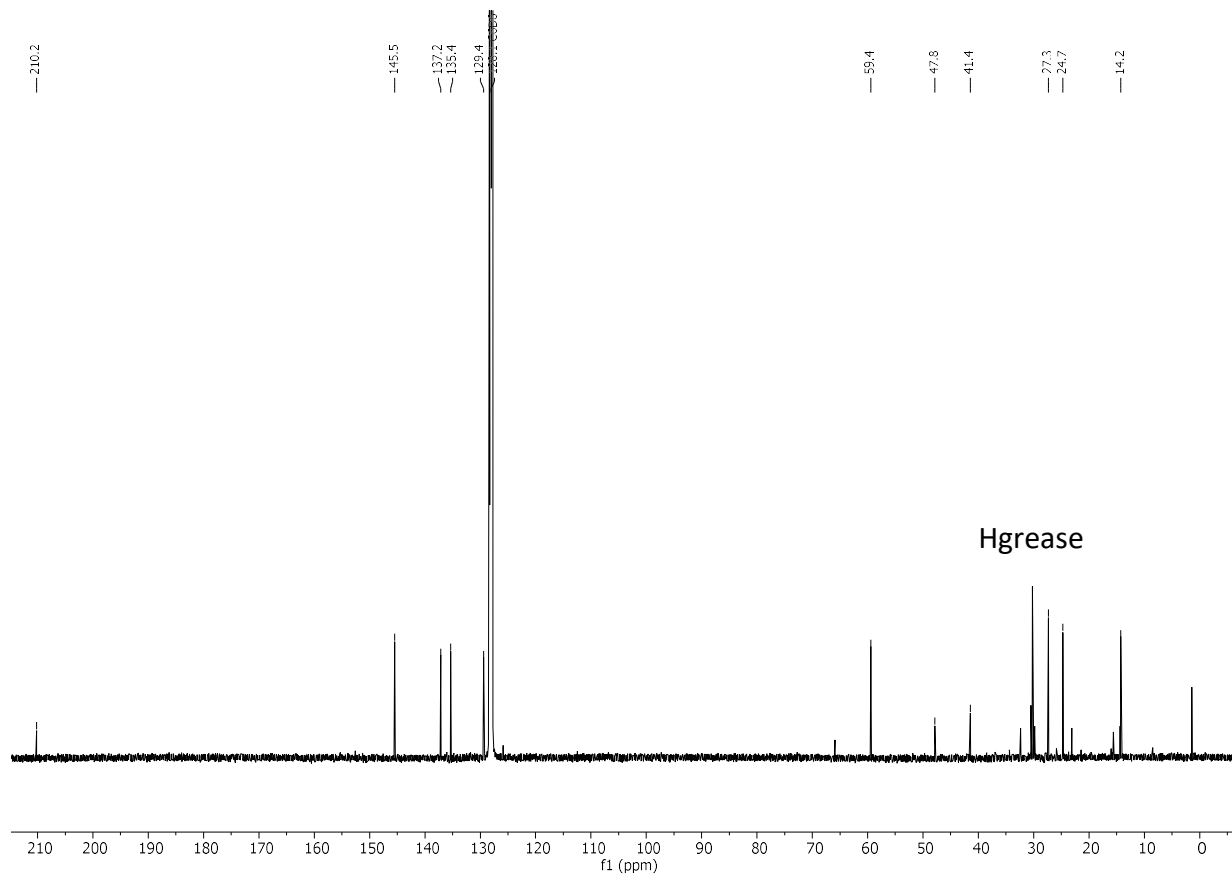
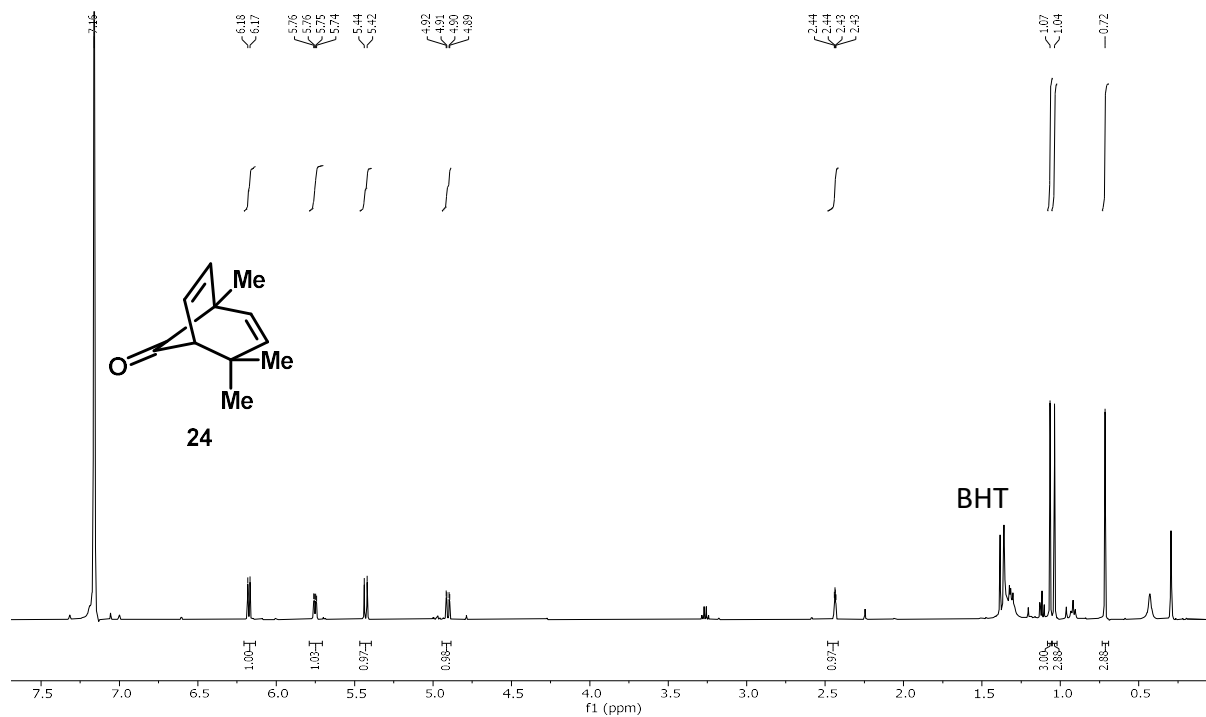


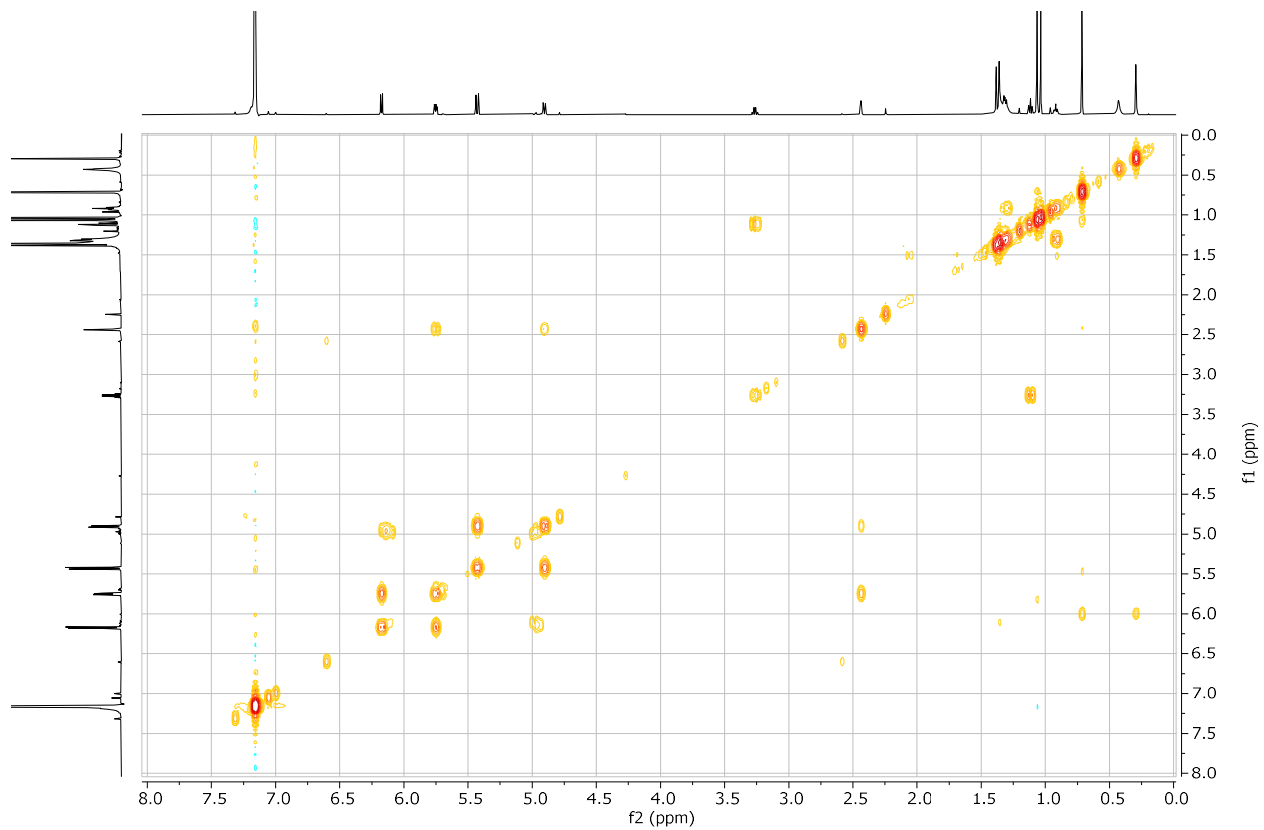




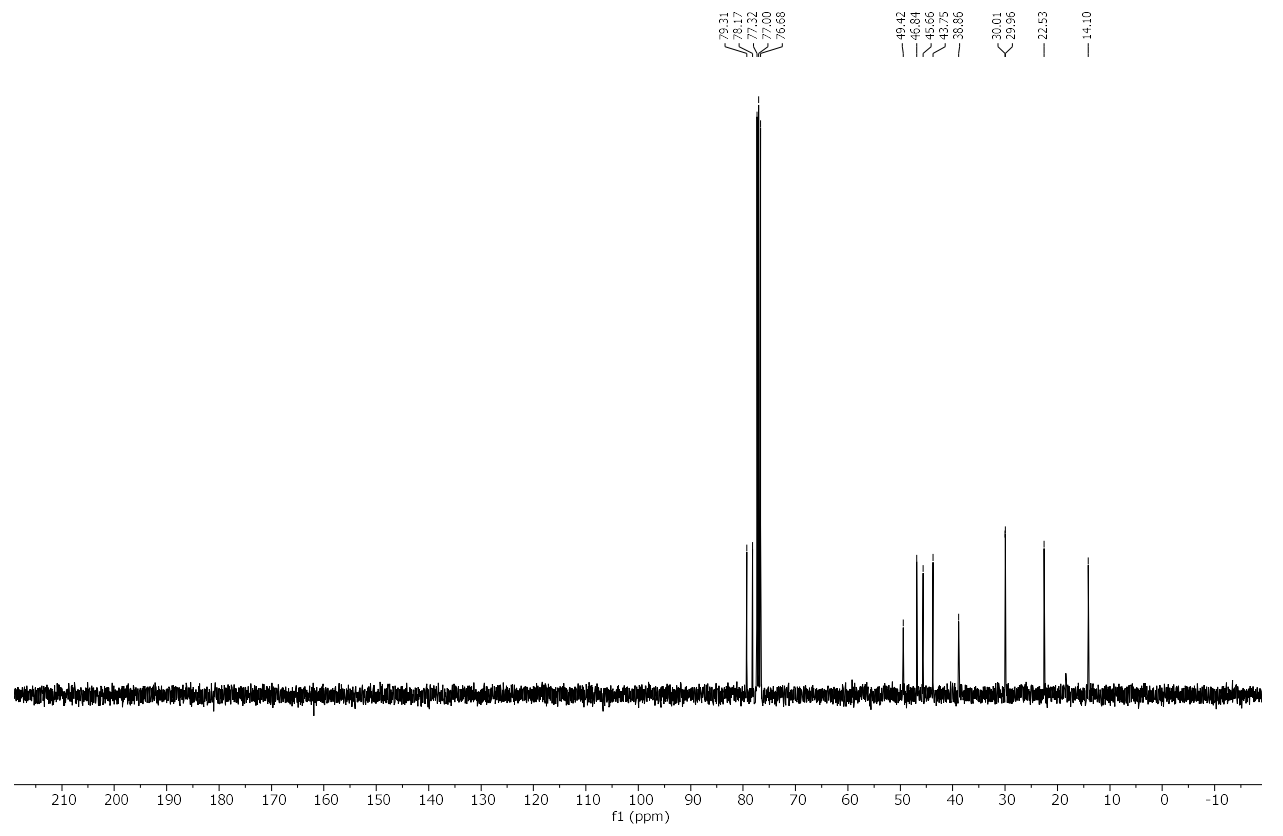
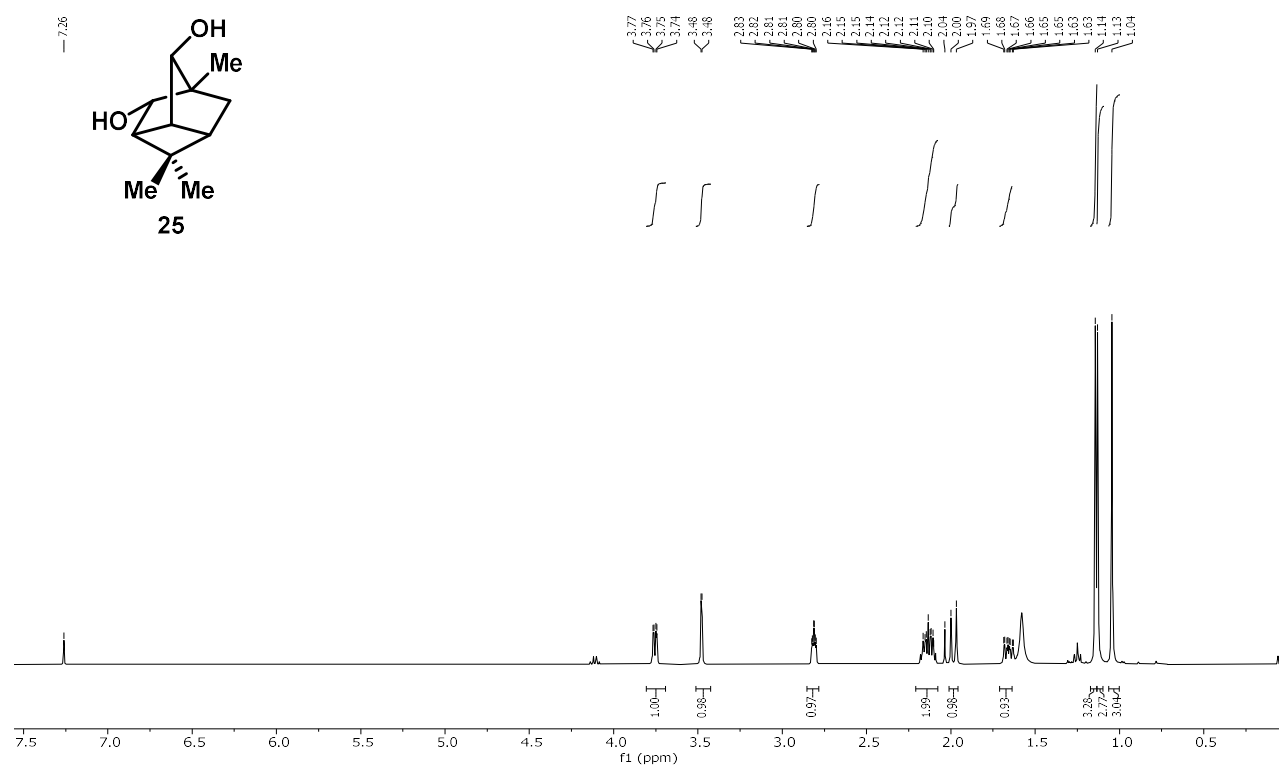
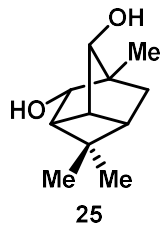


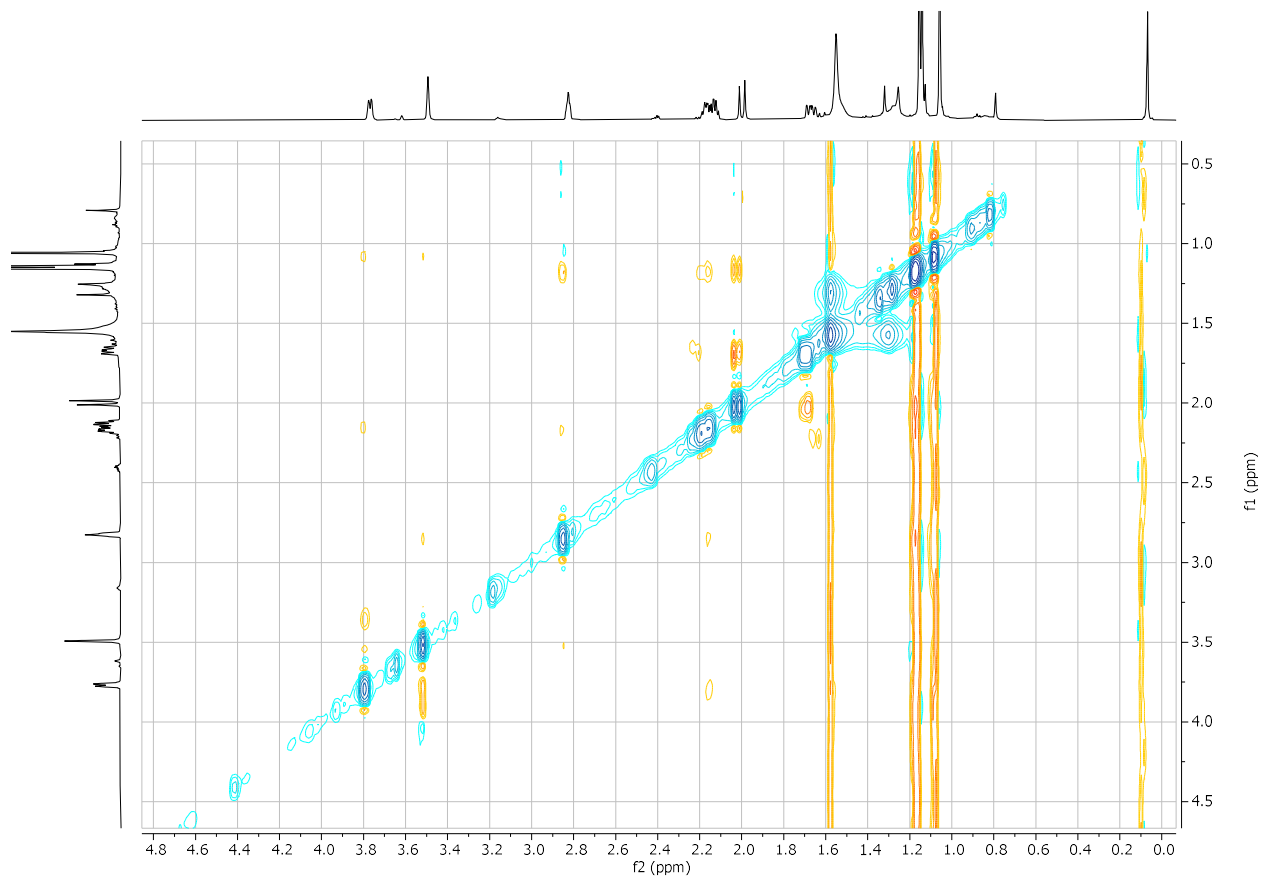
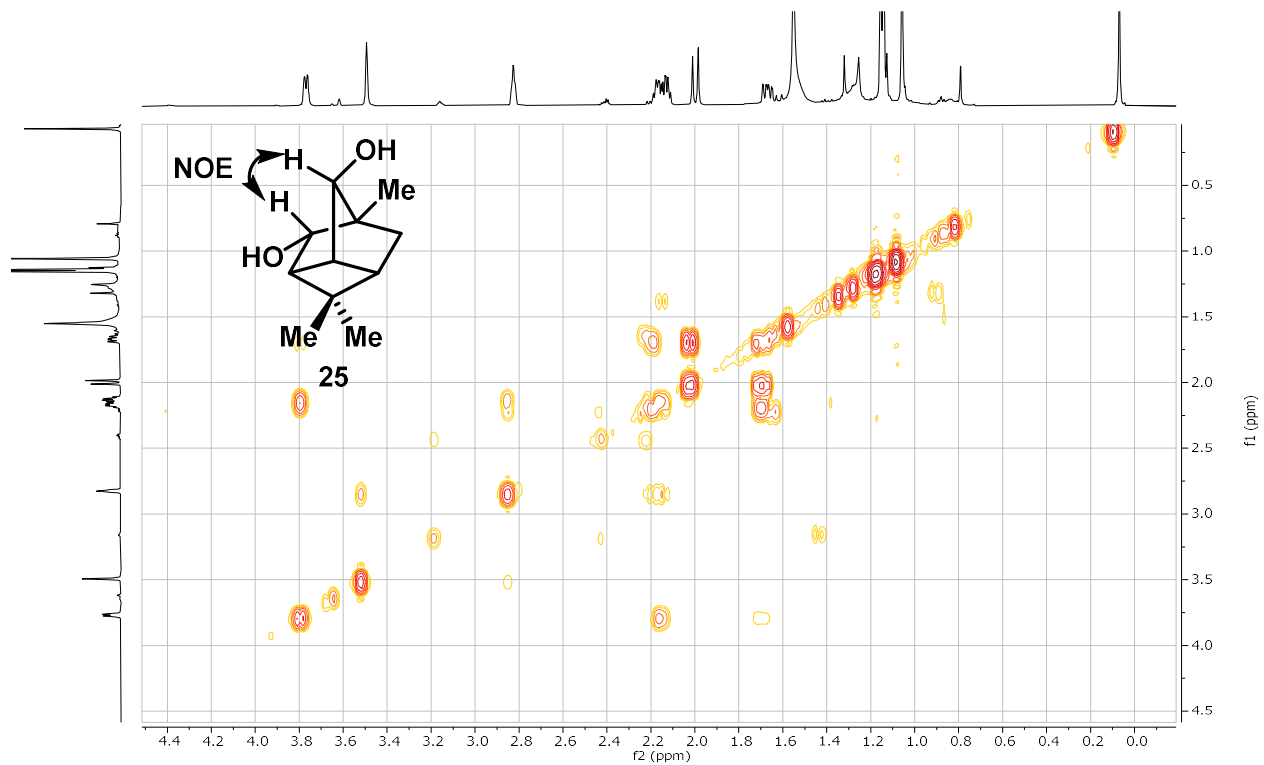


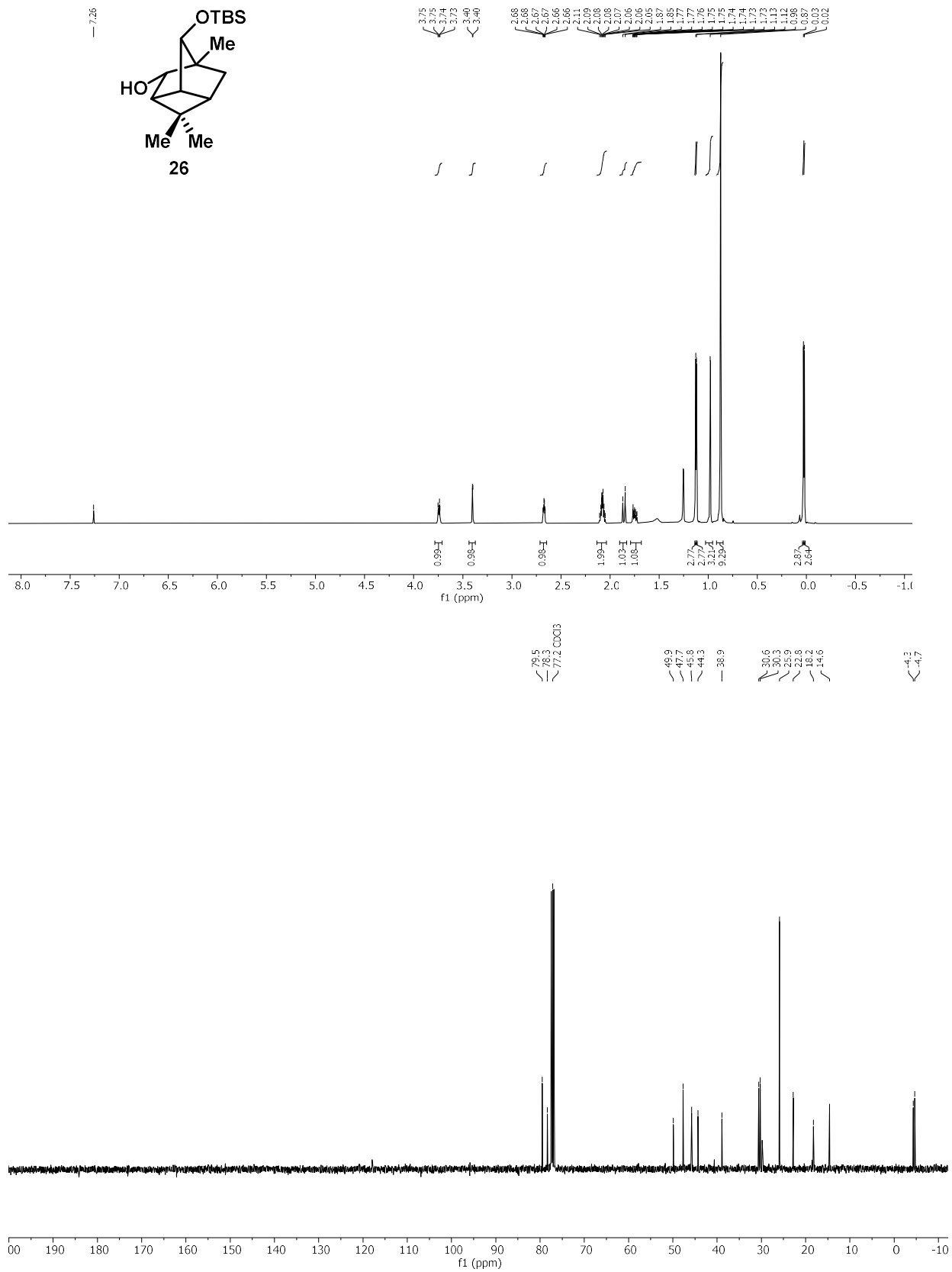


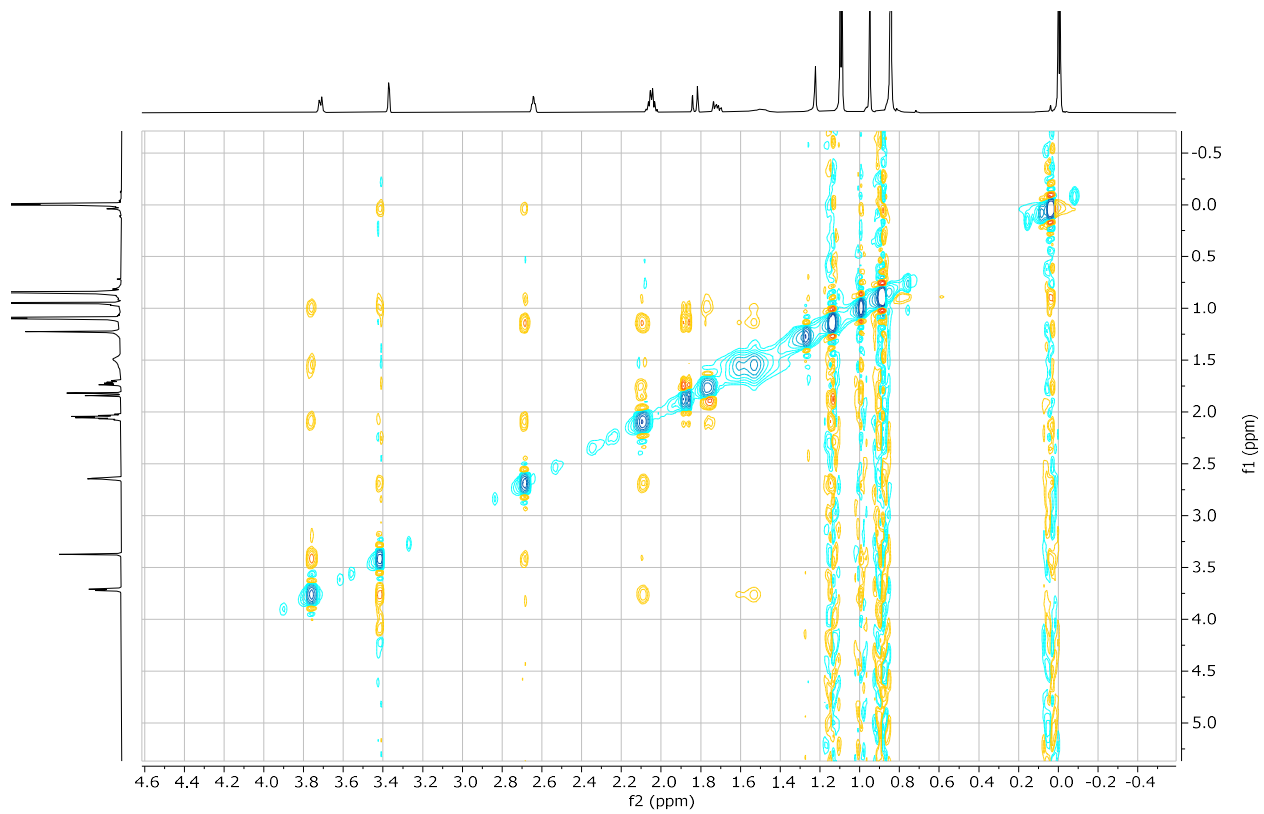
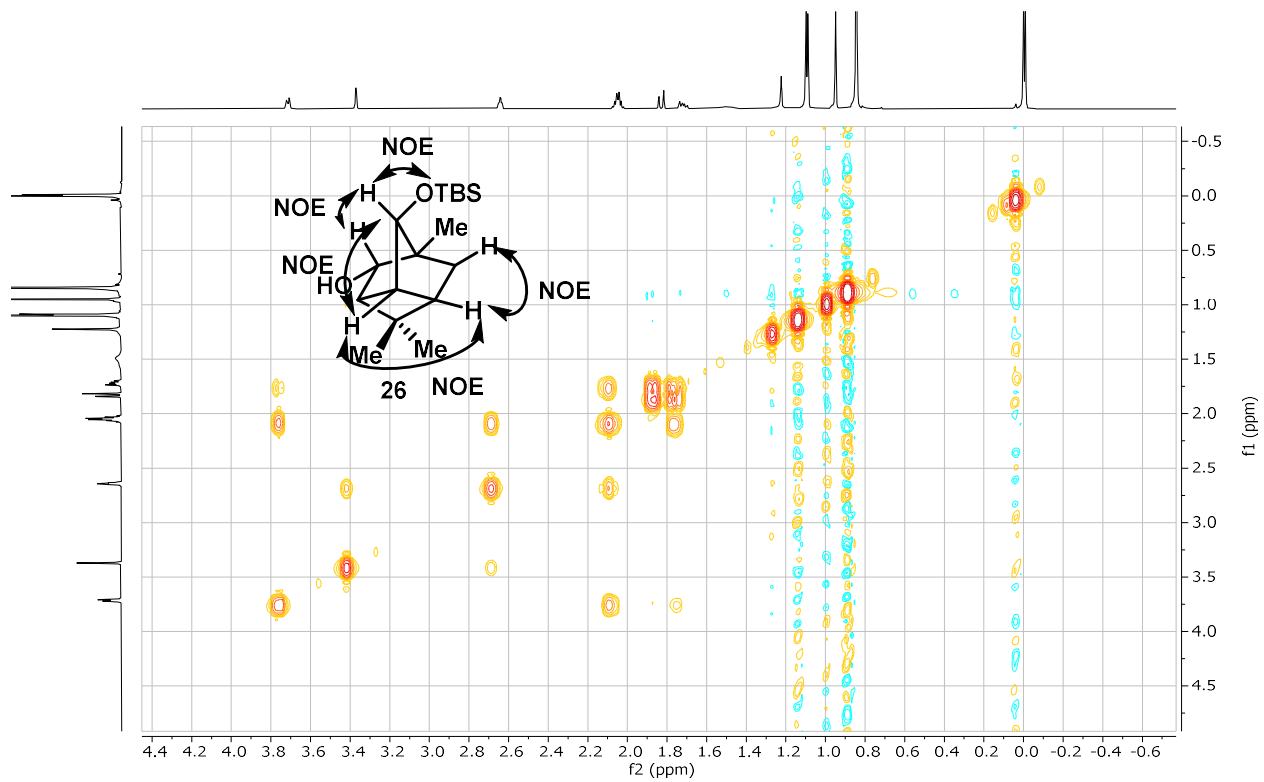


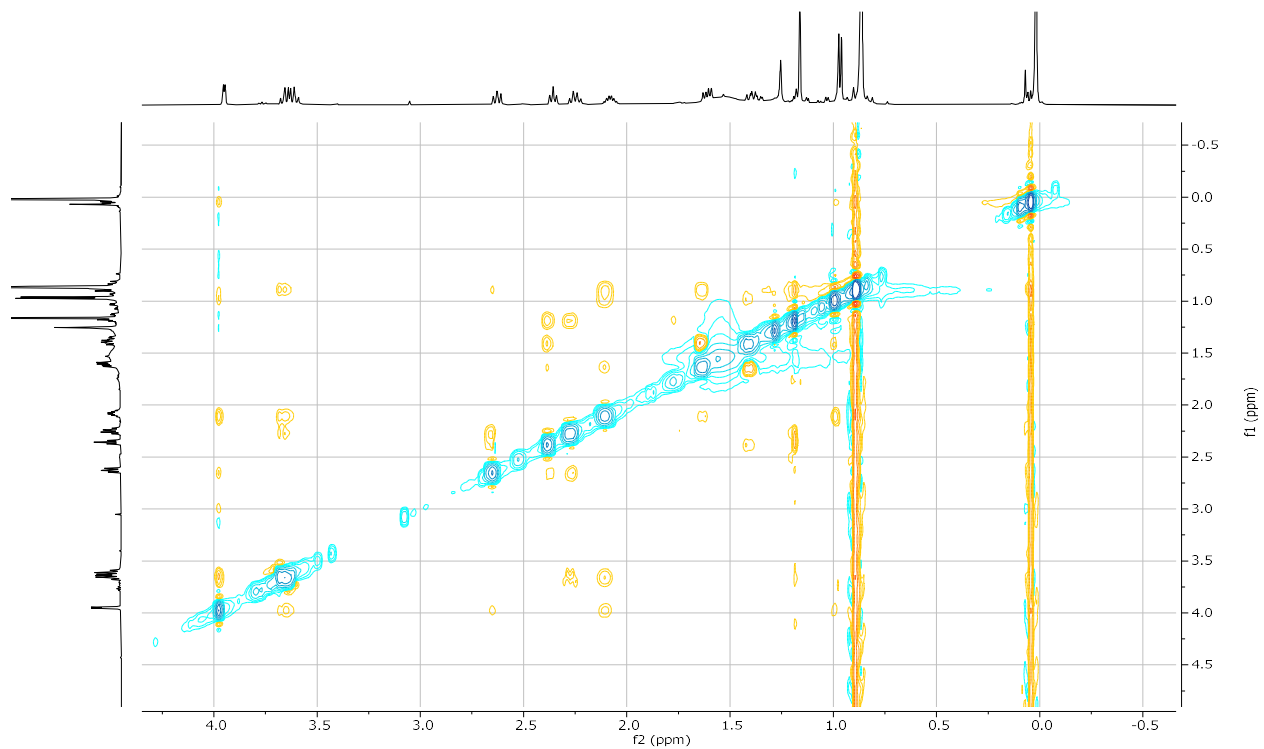
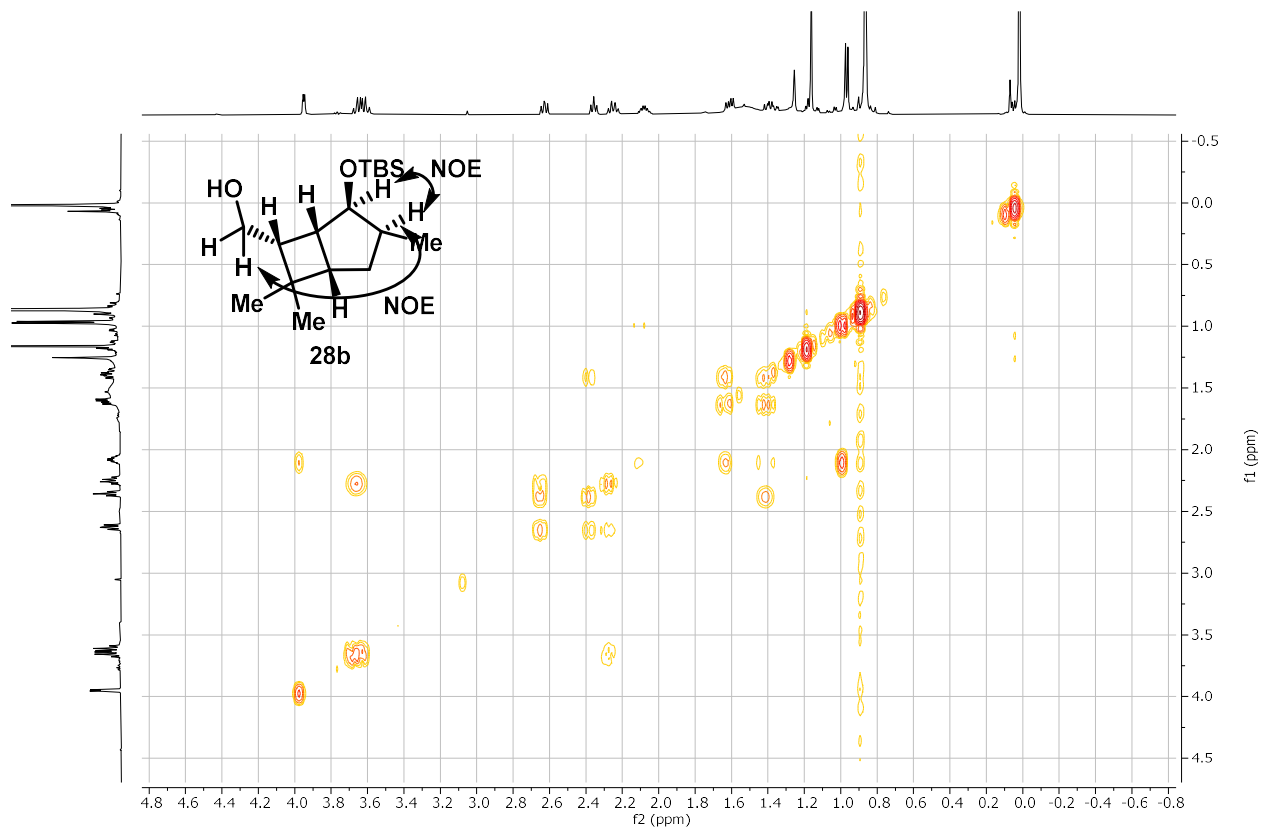
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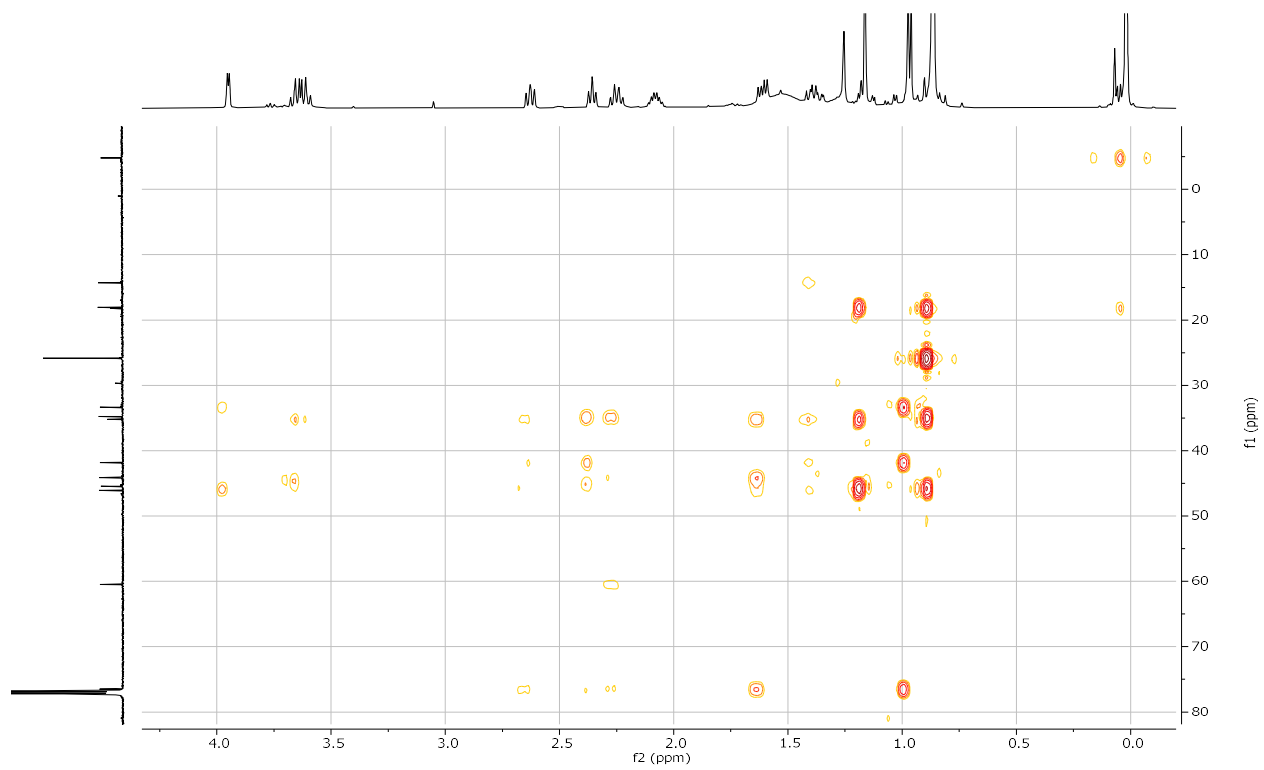
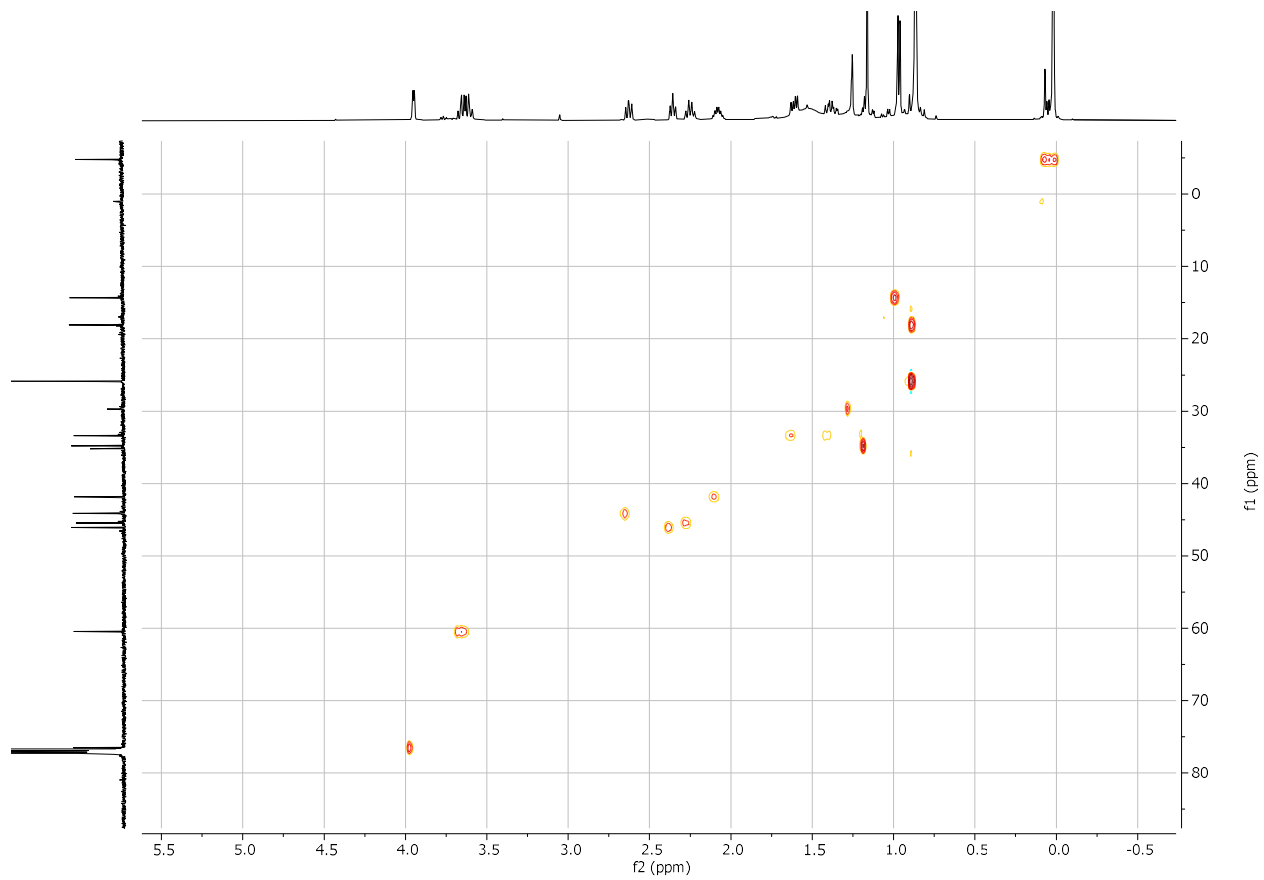


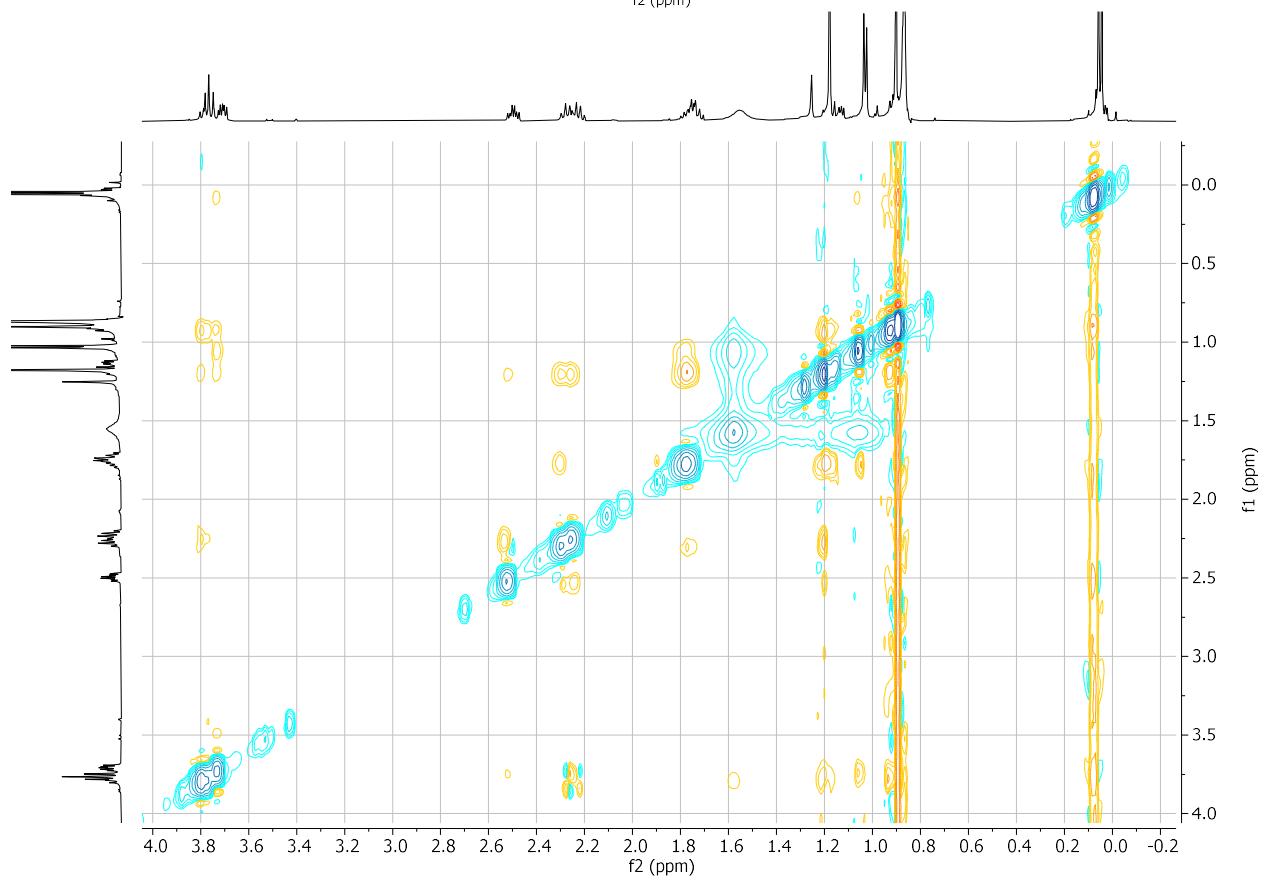
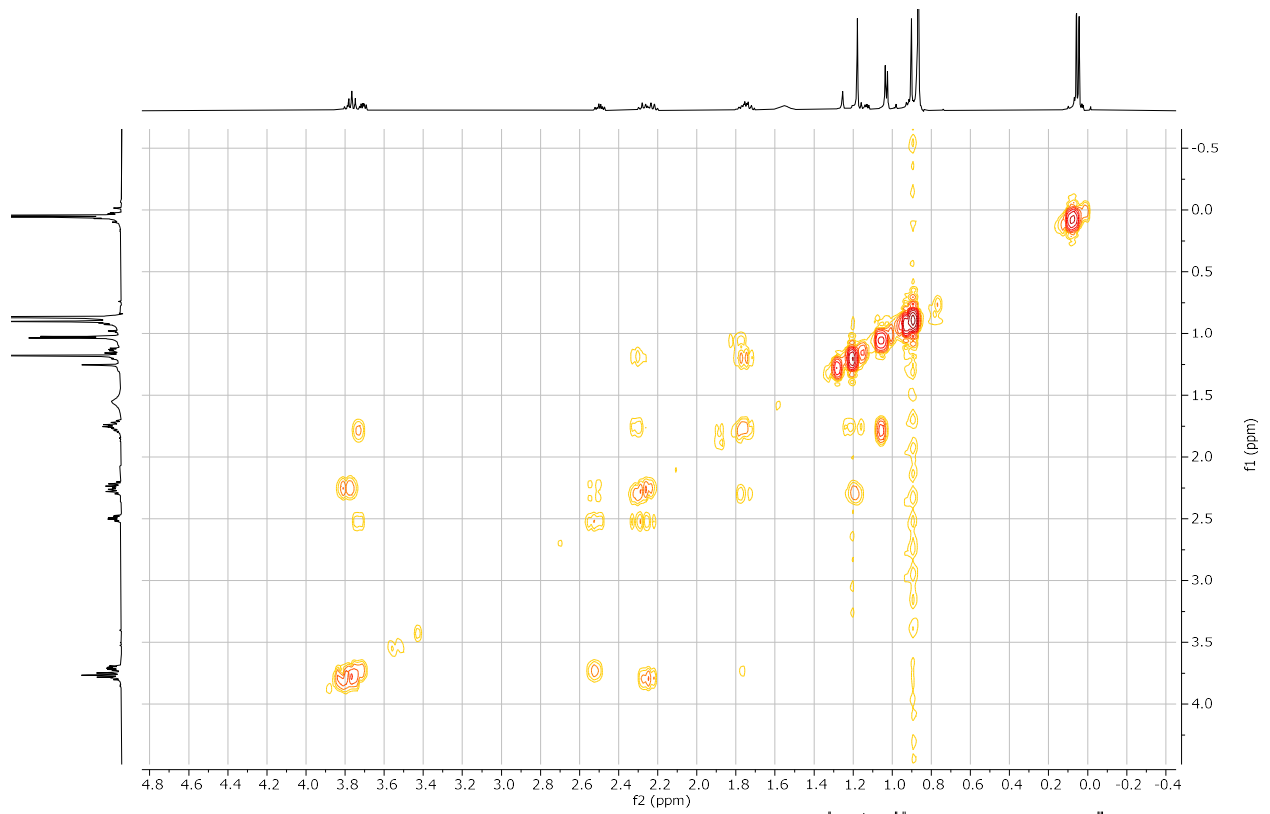


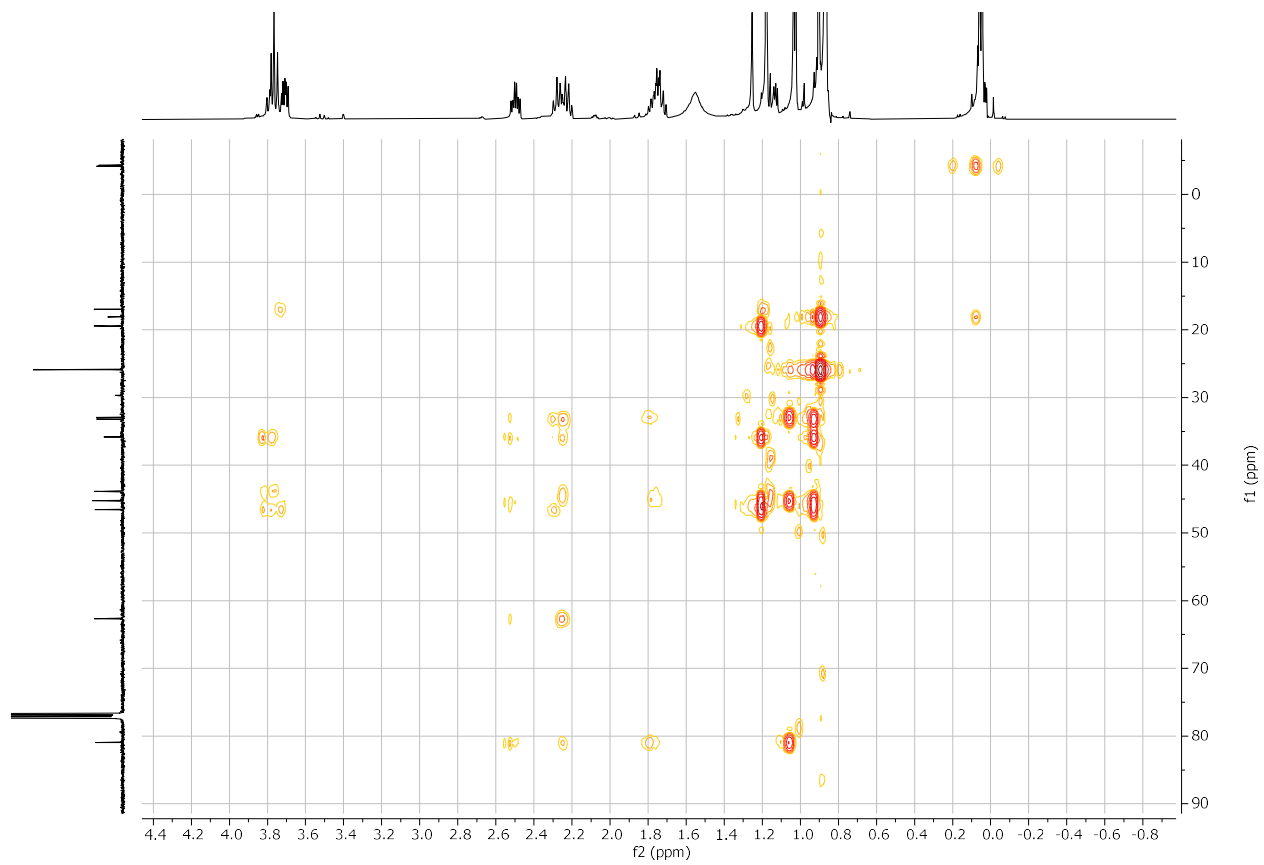
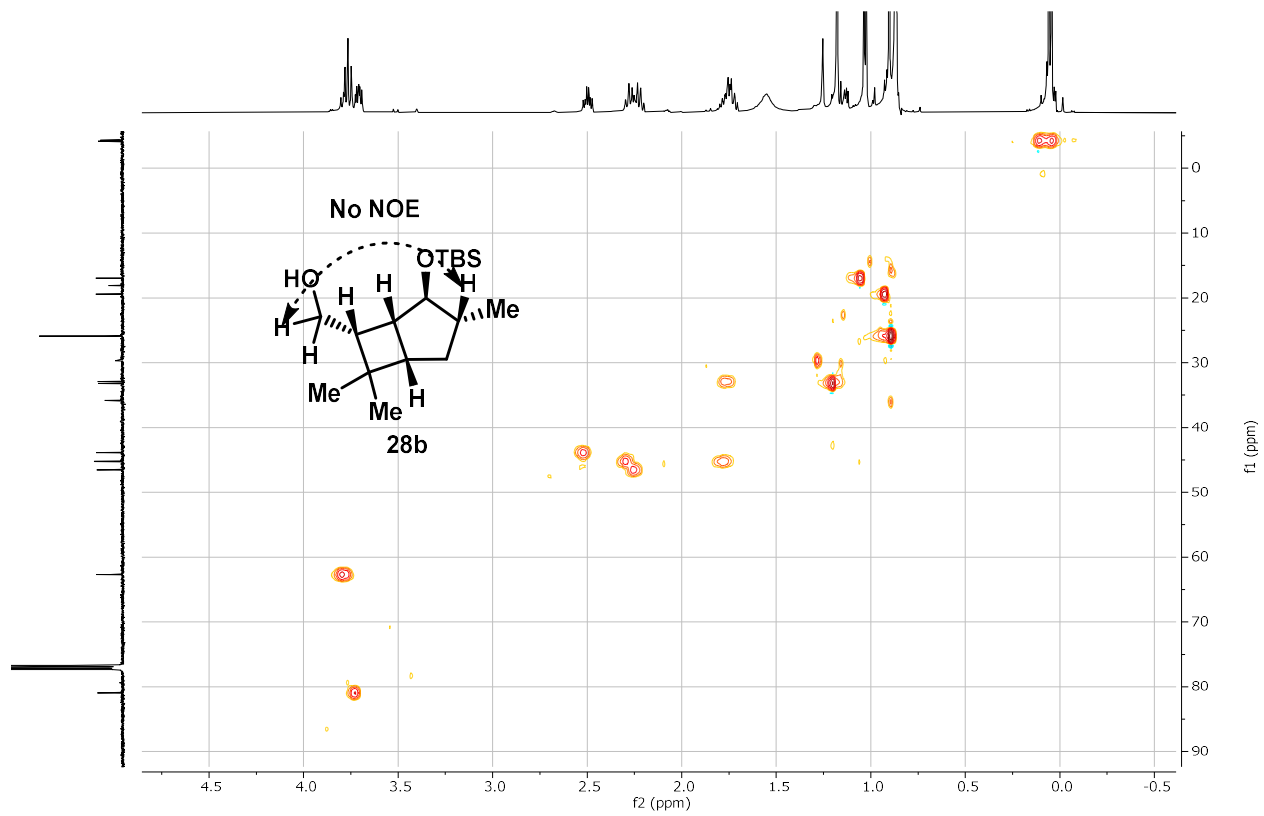


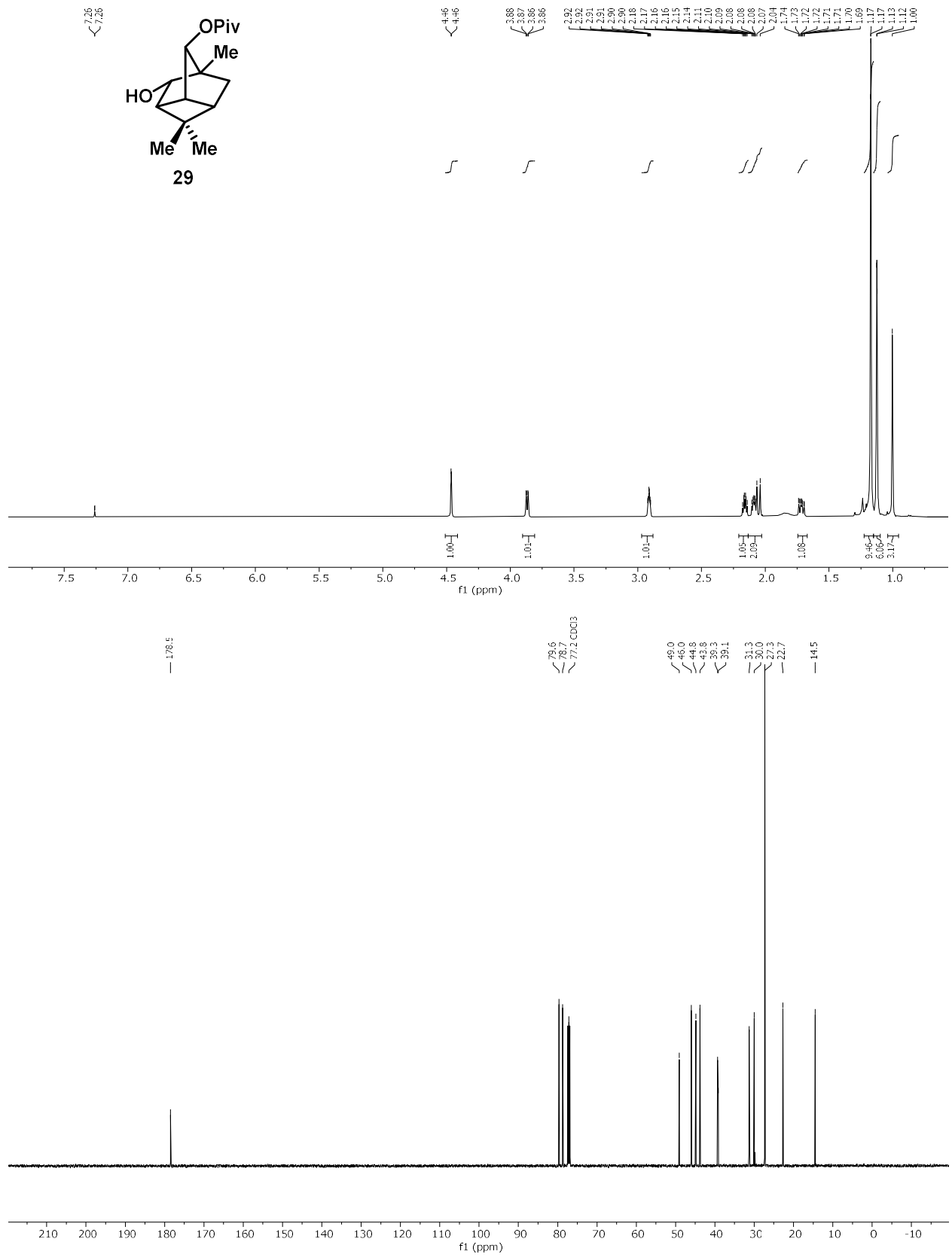


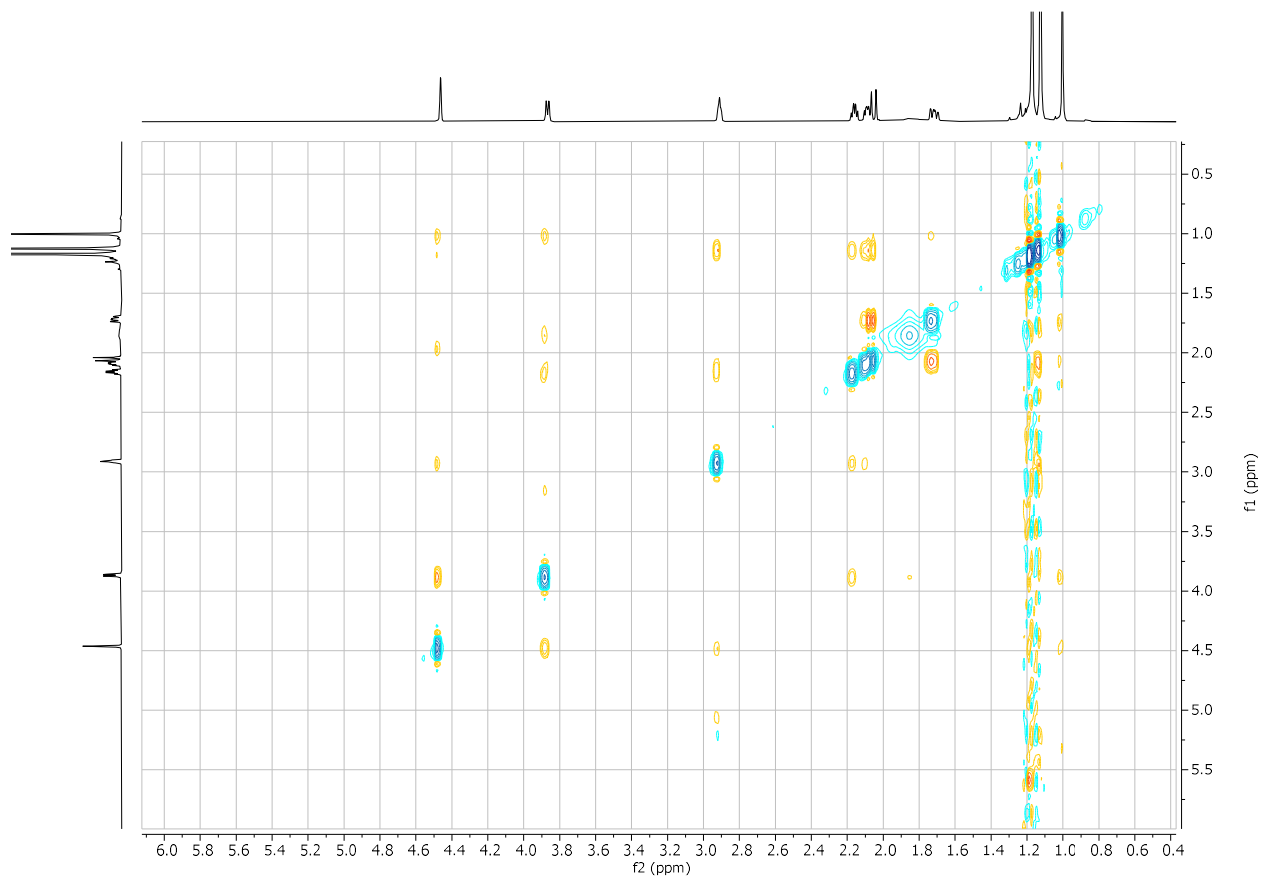
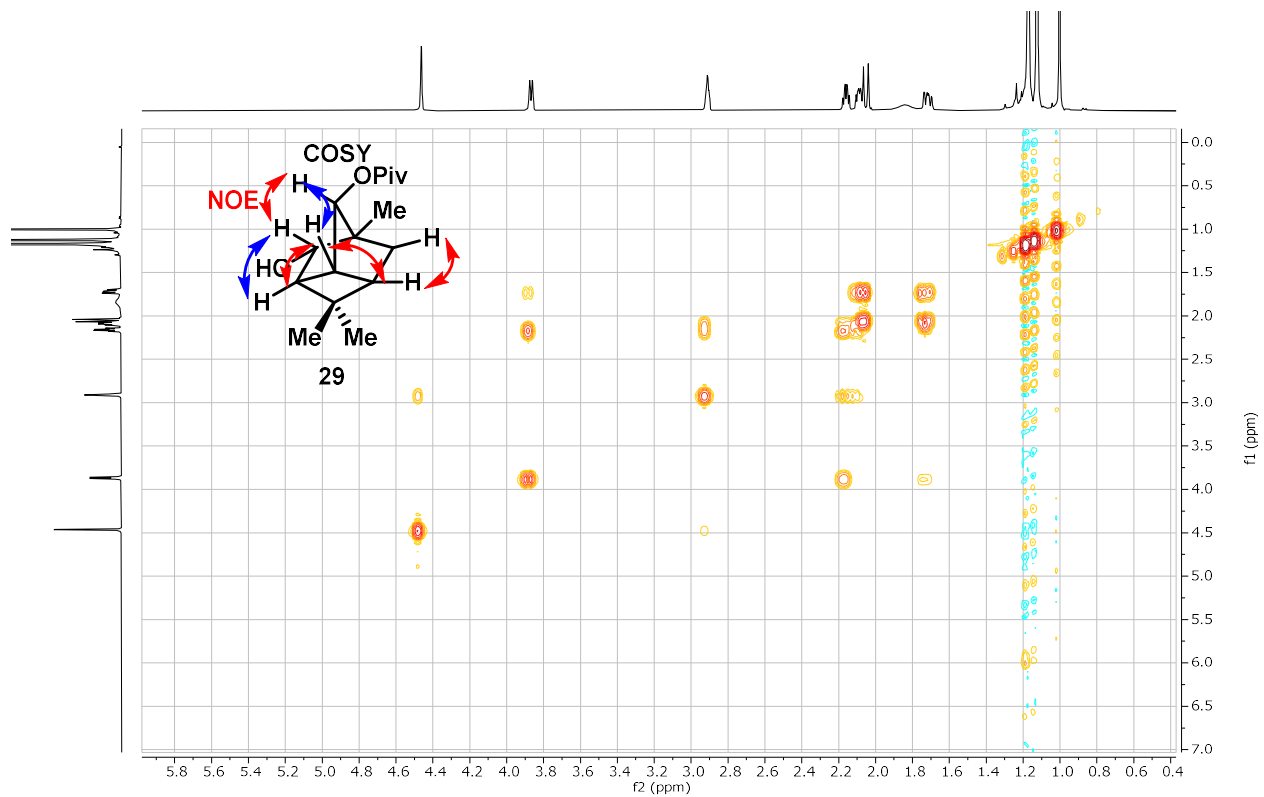


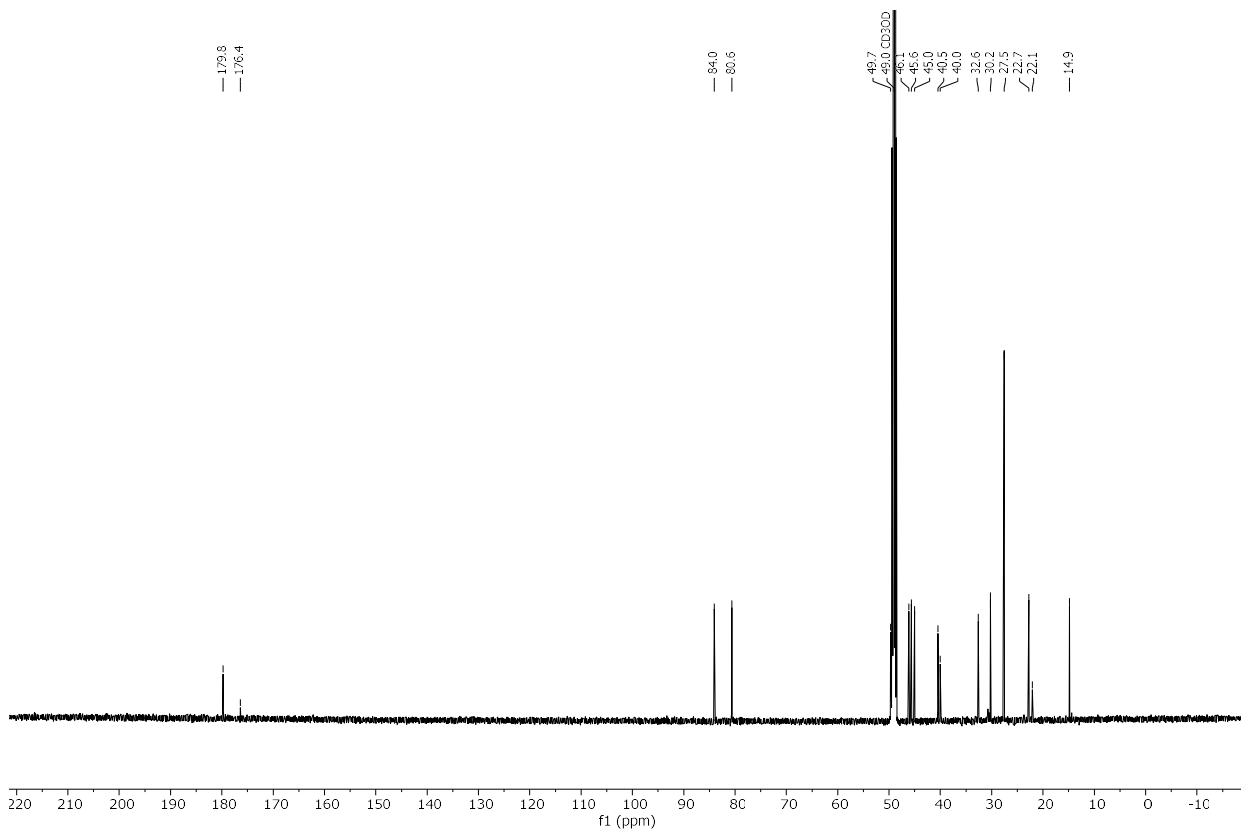
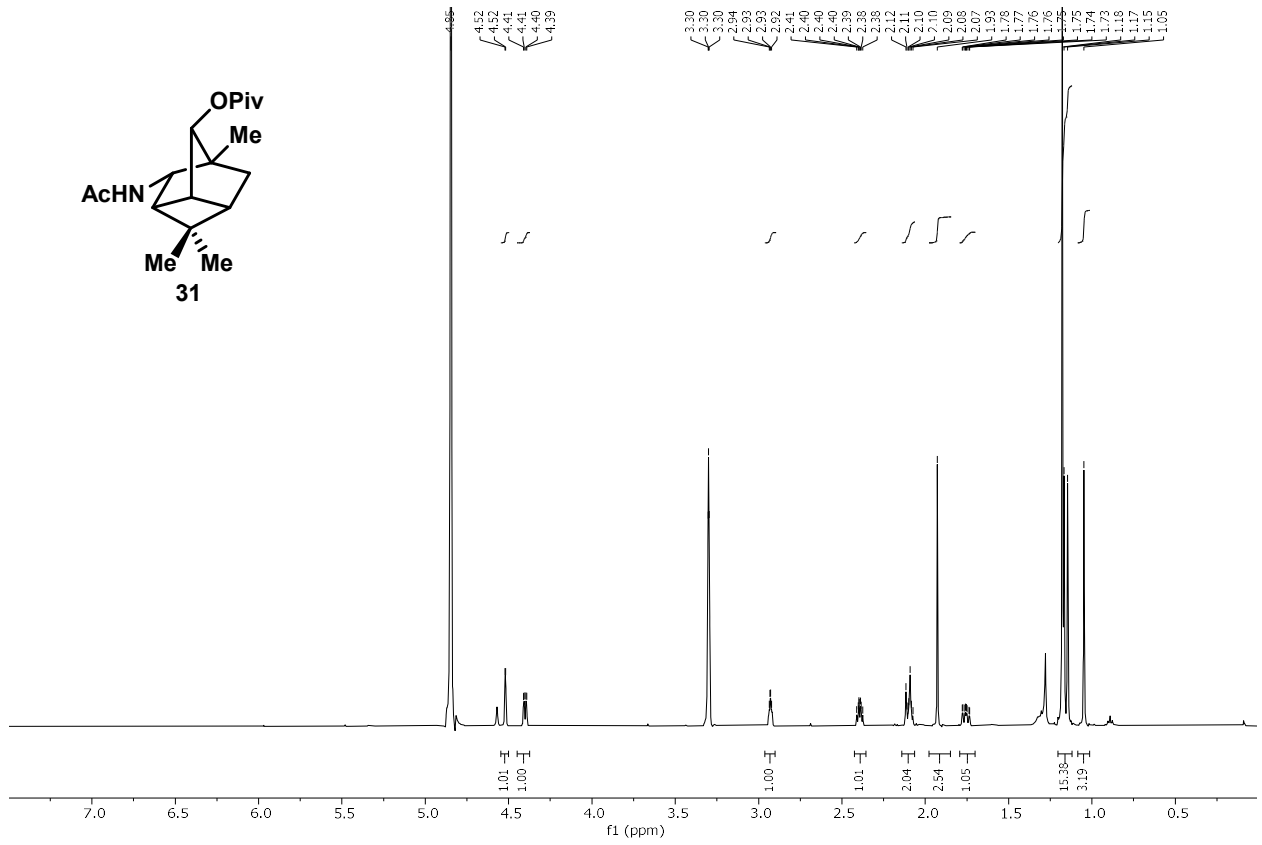
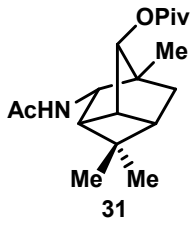


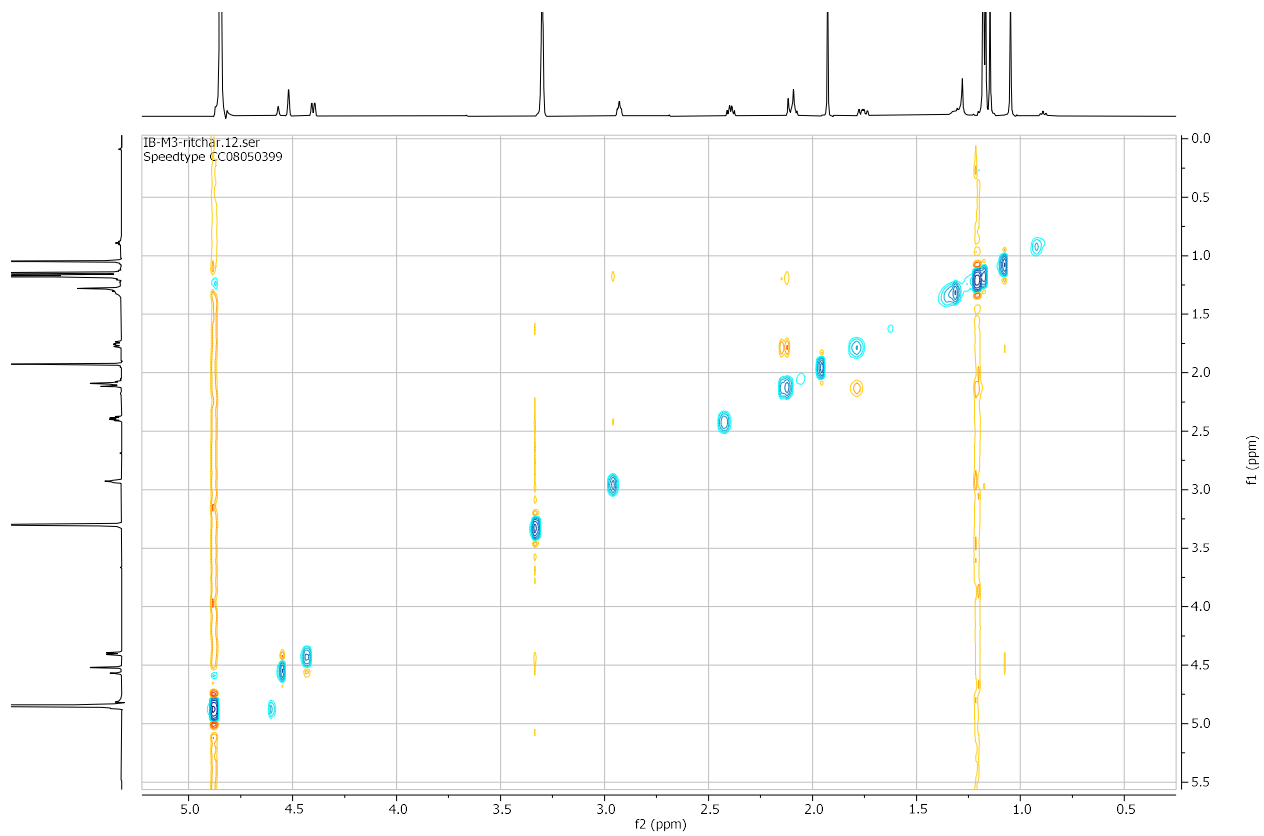
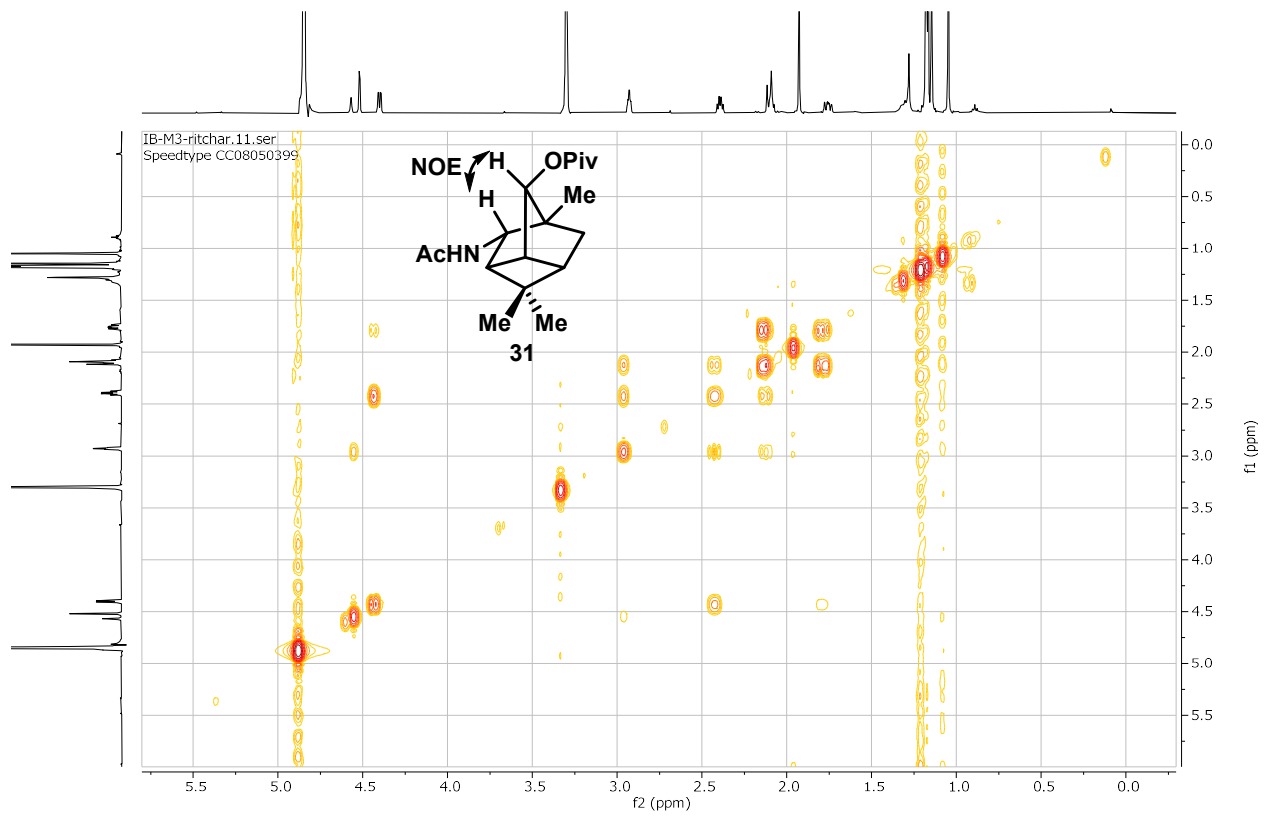


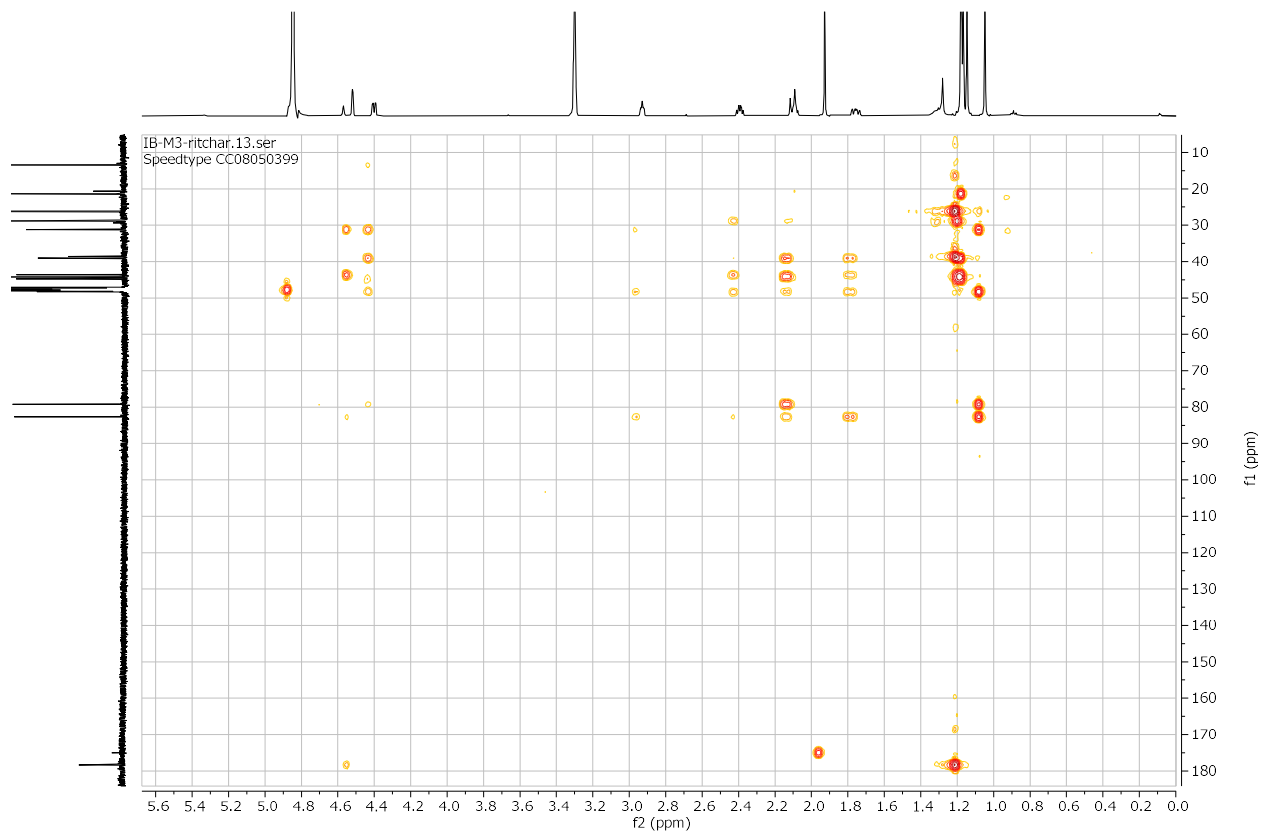
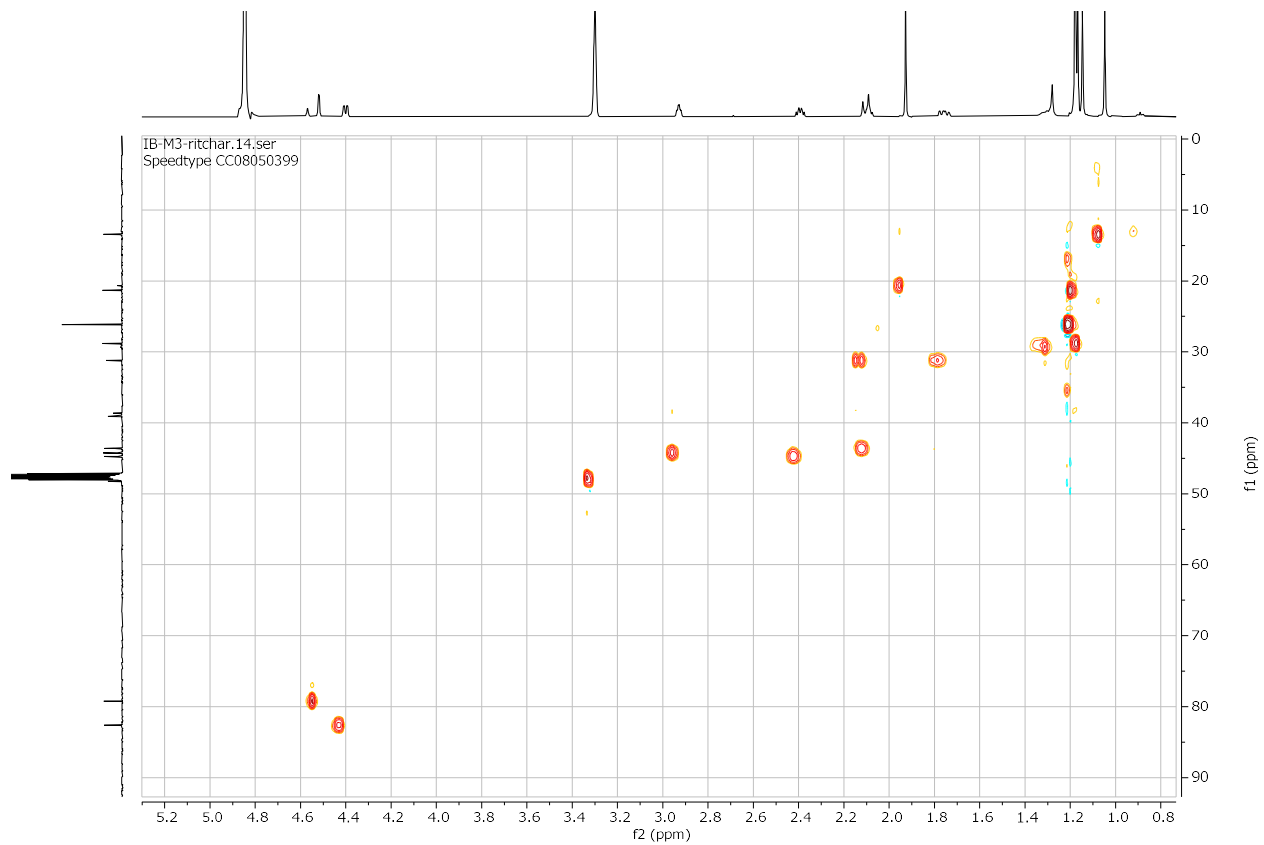


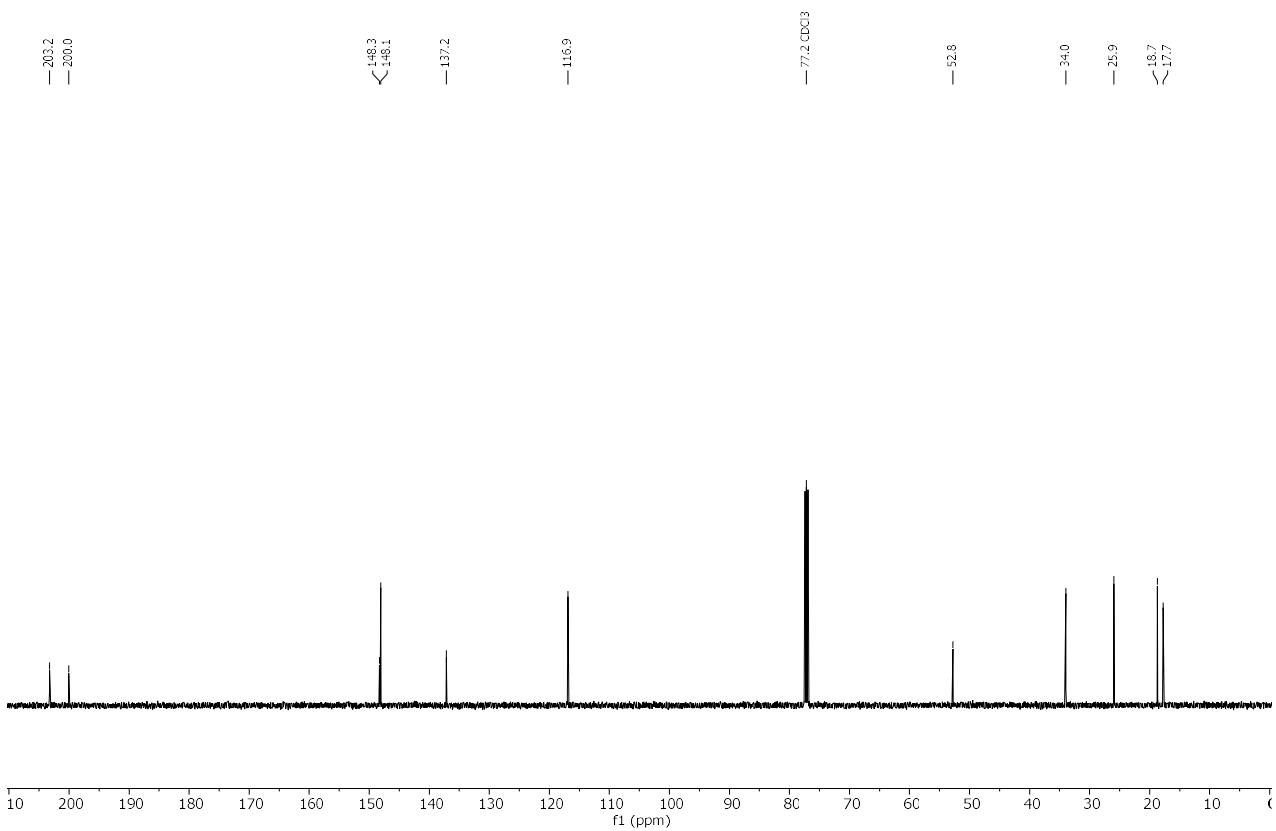
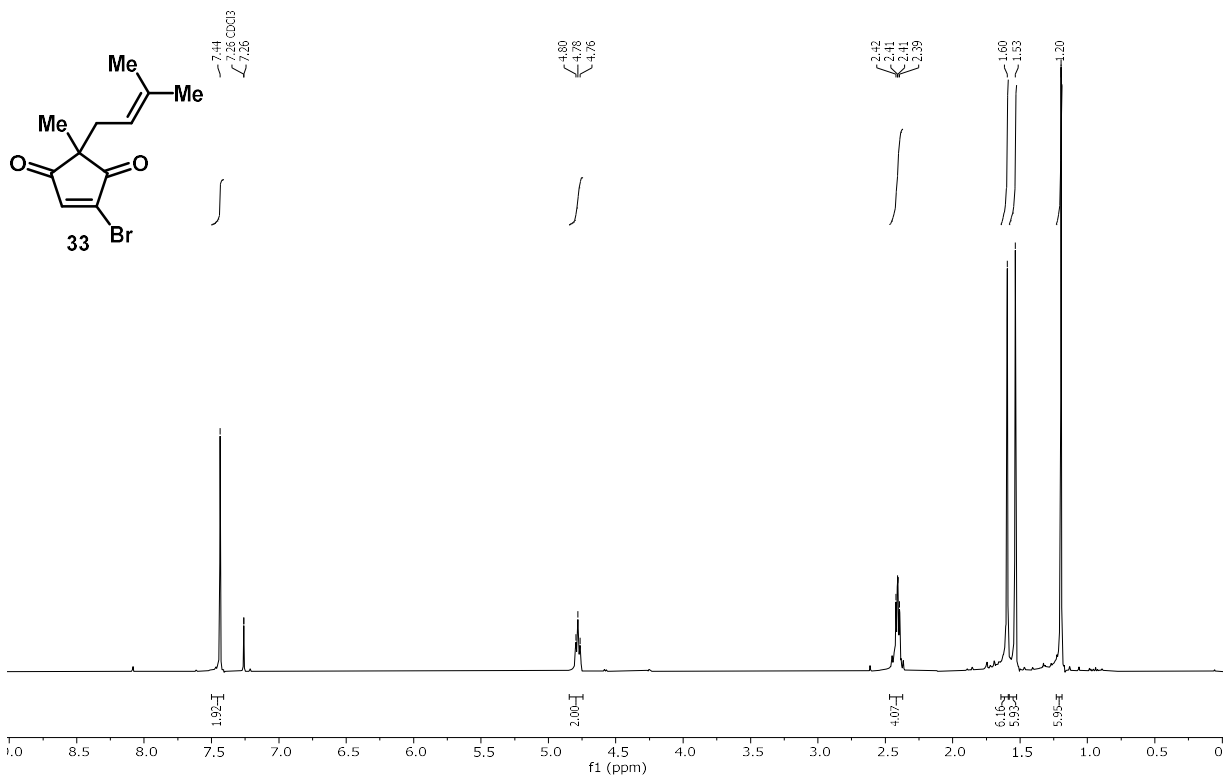


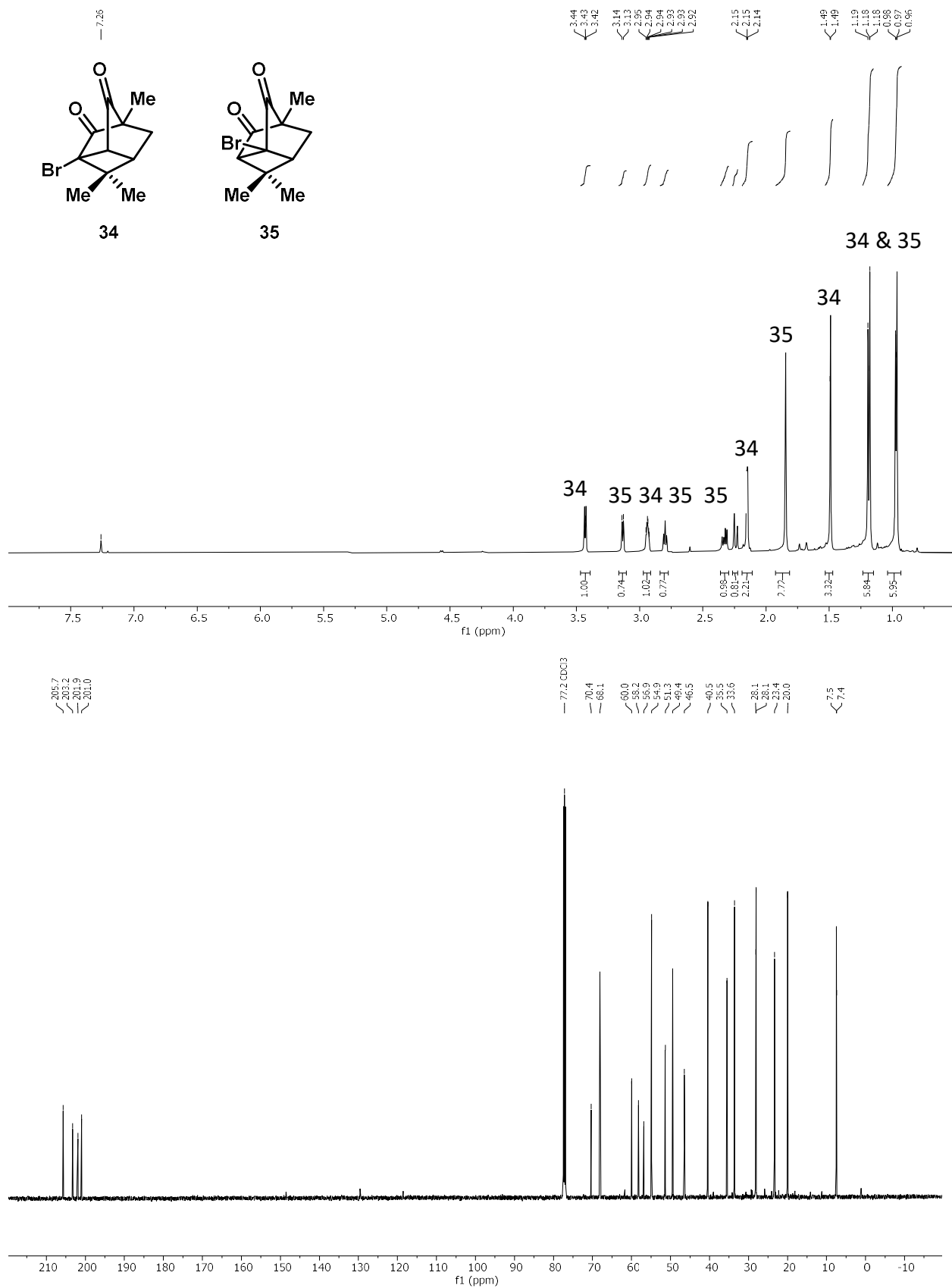


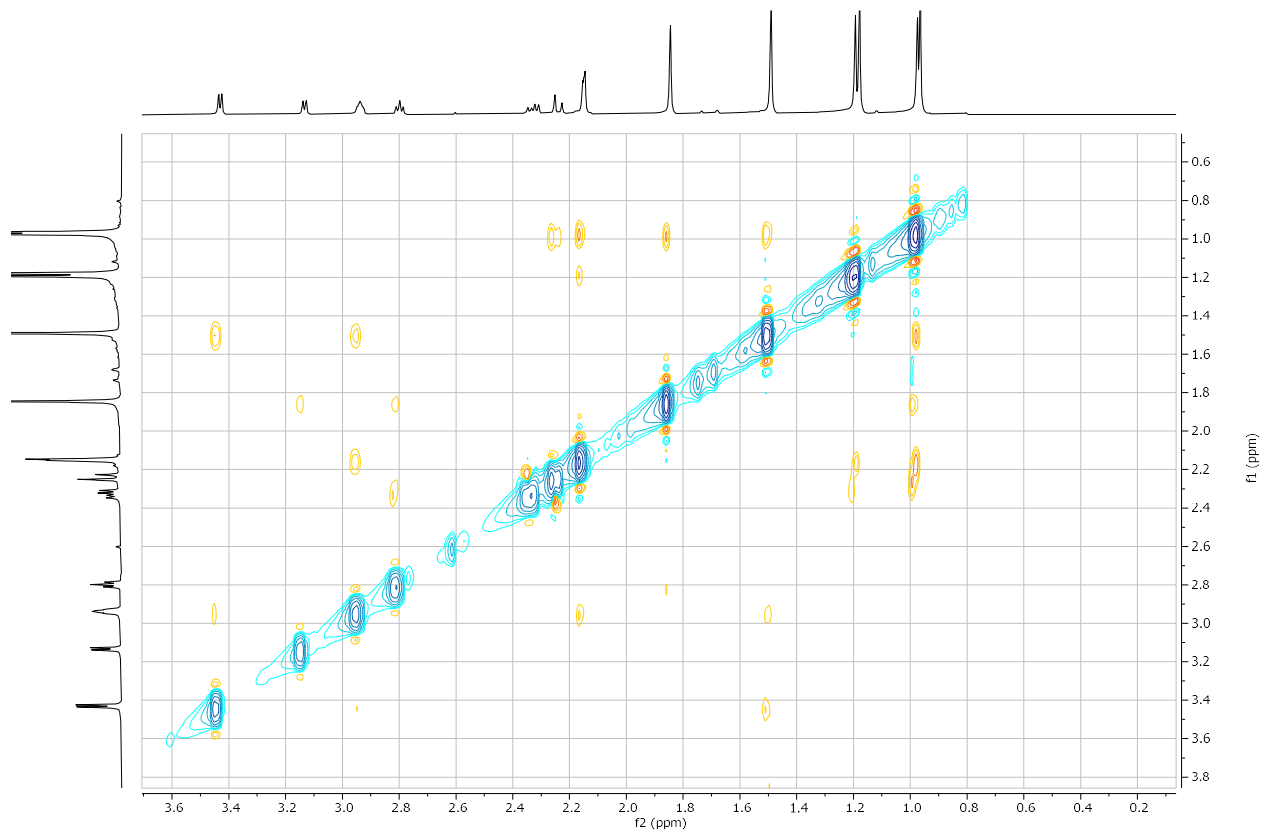
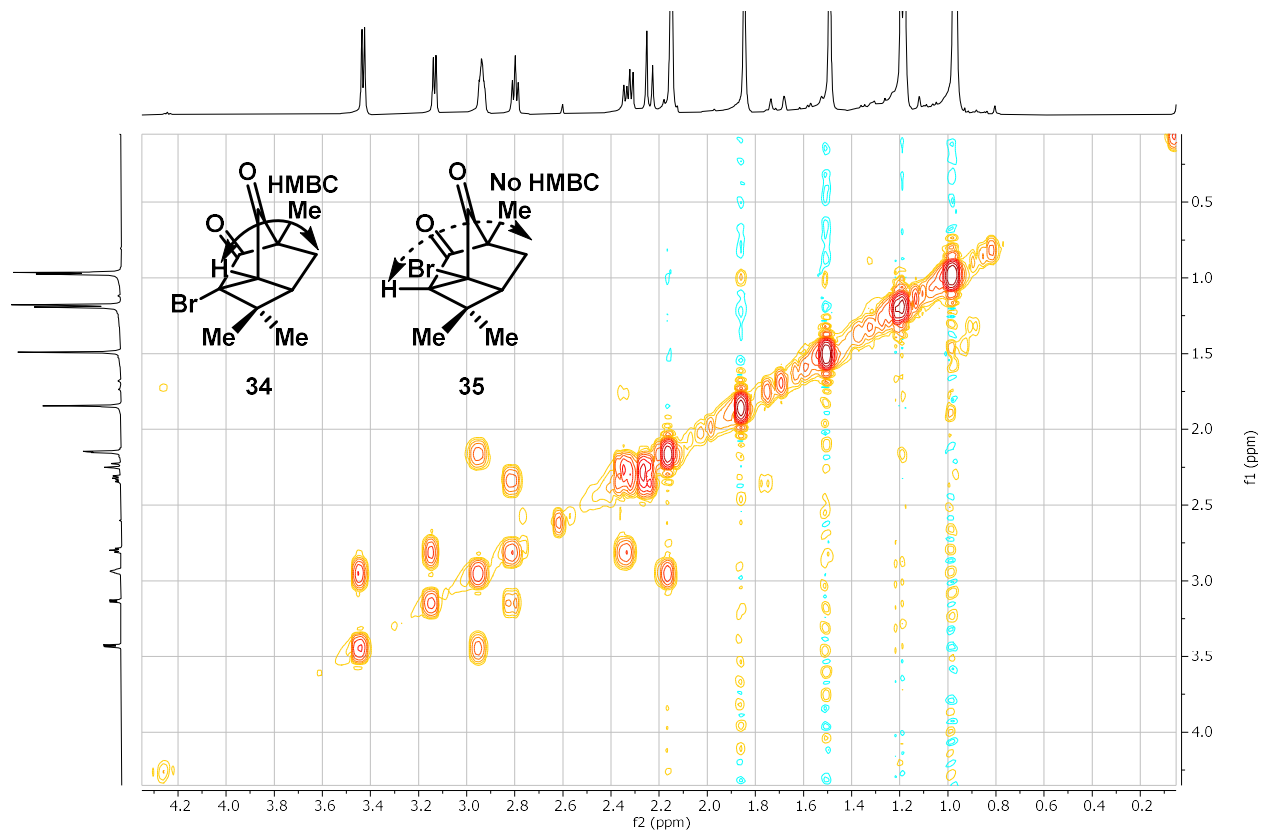


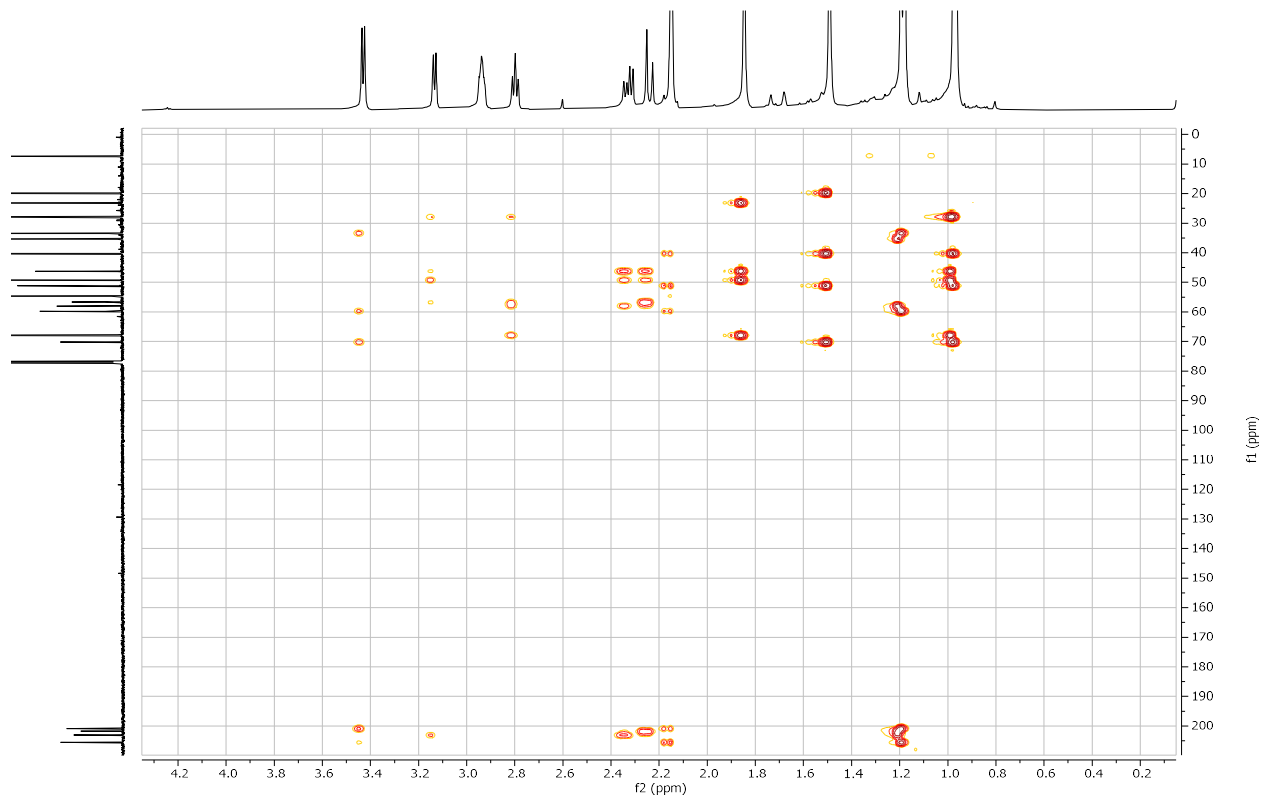
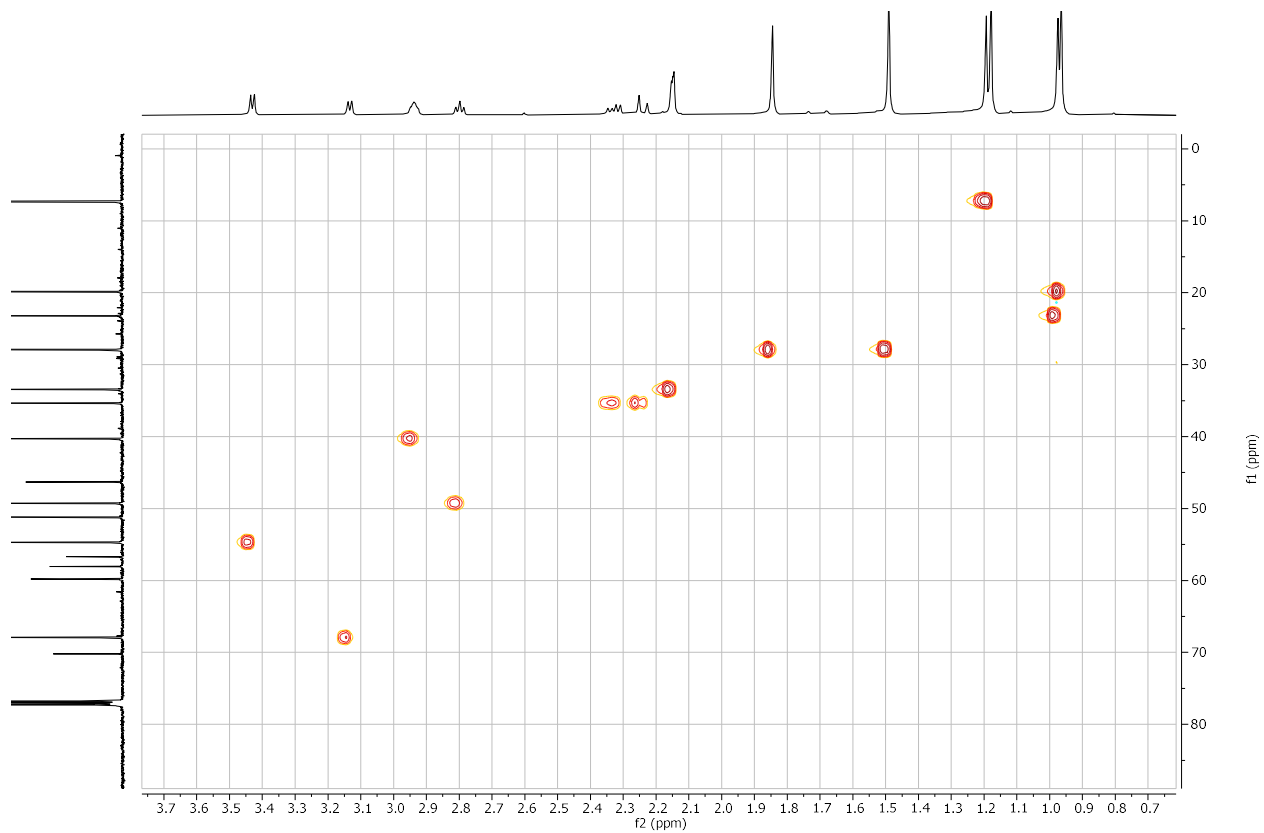


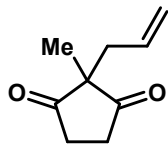












S-4

