Supplementary Information

Hyperstable Alkenes: Are they Remarkably Unreactive?

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Contents

A. Experimental

General Experimental

^{1}H and ^{13}C NMR spectra were recorded on either a Bruker AVANCE or Bruker ASCEND 500 MHz spectrometer, measured in ppm and are referenced to their solvent residual peaks ($CDCl_3$: δ_H 7.26 ppm, δ_C 77.0 ppm; C_6D_6: 7.16 ppm, 128.06 ppm; *d*$_6$-DMSO: 2.50 ppm, 49.52 ppm; MeOD: 3.31 ppm, 49.0 ppm). ^{11}B NMR spectra were recorded on a Bruker AVANCE 300 MHz spectrometer, at 96 MHz using 5 mm borosilicate glass NMR tubes and are quoted relative to a boron trifluoride diethyl etherate external standard. Coupling constants (*J*) are reported in Hertz (Hz) and are quoted to the nearest 0.1Hz. Multiplicities are abbreviated: s = singlet, d = doublet, t = triplet, q = quartet, p = pentet, dd = doublet of doublets, dt = doublet of triplets, m = multiplet, br = broad.

HRESIMS spectra were recorded with a Bruker MicrOTOF-Q spectrometer, using a Bruker ESI source. GCMS spectra were recorded using a Shimadzu GCMS-QP5000 spectrometer. The GC ramp rate was as follows: 70°C for 2 min; increased to 250°C at 10°C/min and held for 5 min. LRESIMS spectra were recorded on a Bruker HCT 3D Ion Trap spectrometer. Melting points were determined using either an SRS DigiMelt MPA161 melting point apparatus or an Electrothermal melting point apparatus and have been reported uncorrected. HR-GCMS analyses were conducted on a Thermo Scientific Q Exactive GC Orbitrap GC-MS/MS in splitless injection mode on a Restek Rxi-5Sil MS w/Integra-Guard column (30 m x 0.25 mm x 0.25 µm). Ions were generated via Electron Ionisation (EI) at 70 eV and were scanned from 50 to 750 m/z at 60,000 resolution in positive ion mode. The inlet, transfer line and source were held at 250°C, 280°C and 280°C respectively and the flow rate was maintained at 1.0 mL/min. The GC ramp rate was as follows: 80°C for 2 min; increased to 180°C at 20°C/min and held for 0.5 min; increased to 330°C at 10°C/min and held for 10 min.

Single crystal X-ray diffraction data were acquired on an Oxford Diffraction Gemini Ultra or a Bruker D8 Venture diffractometer. Relevant experimental, crystal and refinement data are included in Table S-E3. Structures were solved and refined with SHELX[1] and all calculations were carried out within the WinGX interface[2]. Structure diagrams were produced with Mercury (CCDC, vers. 2023.3).

Thin layer chromatography (TLC) was performed using pre-coated aluminium-backed silica gel 60 F_{254} sheets. TLC plates were either visualised under UV light (254 nm) or chemically developed using one of the following solutions; potassium permanganate stain: prepared by combining $KMnO_4$ (1.5 g), K_2CO_3 (10 g) and, 10% NaOH (1.25 mL) in water (200 mL); vanillin stain: prepared by dissolving vanillin (15 g) and conc. H_2SO_4 in EtOH (250 mL); phosphomolybdic acid stain: prepared by dissolving phosphomolybdic acid (10 g) in ethanol (100 mL). Column chromatography was performed using silica gel 60 (230-400 mesh), solvents were distilled before use and solvent mixtures have been reported as v/v ratios.

Tetrahydrofuran (THF) was freshly distilled from a blue or purple sodium-benzophenone ketyl still. Dichloromethane (DCM) was freshly distilled from a calcium hydride still before use. Methanol was distilled from calcium hydride and stored over freshly activated 4 Å molecular sieves. *N,N*-Diisopropylamine and triethylamine were distilled from calcium hydride and

stored over oven-dried potassium hydroxide pellets. Dibromomethane was fractionally distilled and stored over freshly activated 4 Å molecular sieves, in the dark. Cyclooctadiene and methanesulfonic acid were purchased from Sigma-Aldrich and used without further purification.

n-Butyllithium was titrated against *N*-pivaloyl-*o*-toluidine in anhydrous THF, to a yellow endpoint. 9-BBN was titrated against a solution of anhydrous methanol in anhydrous THF under argon, according to published procedures.[3] Boron dimethyl sulfide complex (BMS) was titrated against a solution of glycerol, methanol, and water, measuring the volume of hydrogen produced with a gas burette, according to published procedures.[3]

Organoborane reactions were performed under strictly maintained inert atmospheres. Before use, glassware and Teflon-coated stirrer bars were washed with strongly basic solutions of sodium hydroxide (20 g) in water (25 mL) and isopropanol (75 mL). Glassware was dried using an electric heat gun under high vacuum and purged with argon before use. Ground-glass joints were carefully greased with Apiezon M vacuum grease.

Experimental Setup for Iterative Organoborane Homologation Reactions

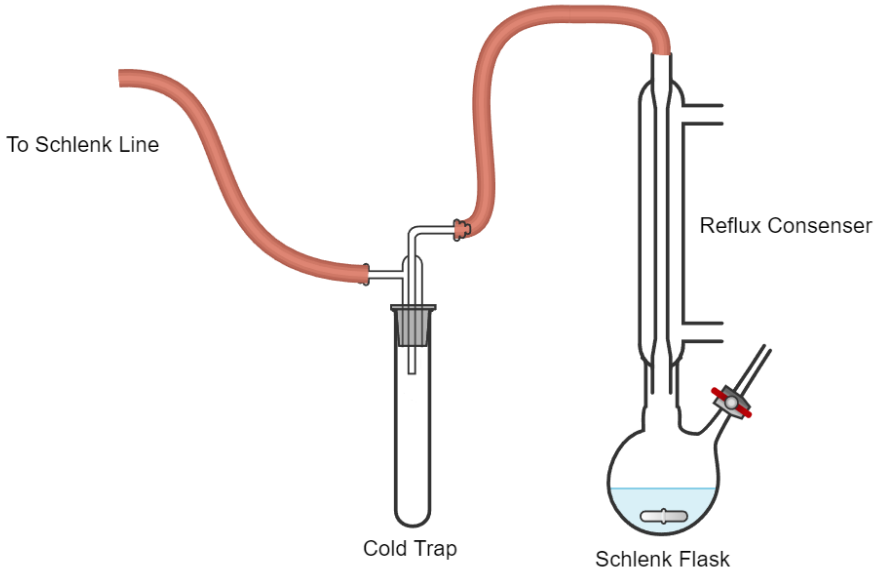
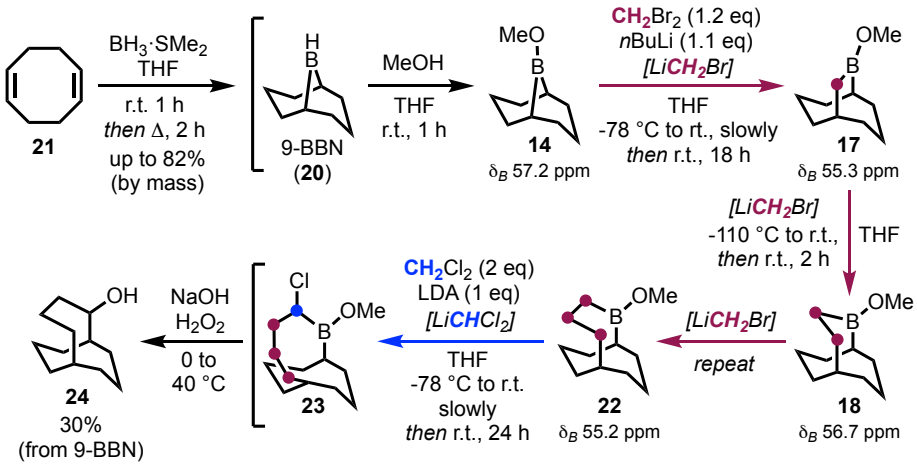


Figure S1. Homologation Apparatus. Image generated utilising the drawing tool available at chemix.org.

Synthesis of hyperstable alkenes **13** and **25**.



Adapting the procedure of Brown[4]: a freshly base-bathed 100 mL Schlenk flask was connected to a large-cold-trap via a reflux condenser using clear rubber tubing, a bean-shaped Teflon-coated stirrer bar (*ca.* 1 cm in length) was added to the flask (as per Figure S1). The entire apparatus was placed under vacuum (1 Torr) and the glass components were dried using an electric heat-gun. Vacuum was maintained until the glassware cooled and then the apparatus was purged with argon 3 to 5 times. The Schlenk flask was lowered into a room-temperature water bath and then charged with anhydrous THF (4.4 mL), and neat borane-dimethyl sulfide complex (1.65 mL, 16.5 mmol) was added under an argon atmosphere. Cyclooctadiene (**21**, 2.0 mL, 16.3 mmol) was added dropwise to the solution with gentle stirring, forming a cloudy suspension within 5 minutes of addition. The mixture was stirred at room temperature for 1 hour and then heated to reflux (*ca.* 90 °C silicone oil bath) for 2 hours. The solution was slowly cooled overnight, generating a large quantity of white precipitate. The suspension was cooled to -10 °C (water ice/acetone) and the solvent was carefully removed with a syringe (this is most conveniently discarded into a large beaker containing a cold 4.0 M NaOH solution, leading to some foaming). The remaining white solid was dried under vacuum (1 Torr) to give **20** as a free-flowing white powder (1.68 g, *ca.* 82%), which was used immediately without further purification. **NOTE:** to prevent exposure to the atmosphere, mass was recorded by quickly and carefully detaching the pre-weighed Schlenk flask from the apparatus, attaching a greased stopper, and recording the mass of the product. The apparatus was then reassembled, placed under vacuum and purged with argon 3 to 5 times, as before.

Adapting the procedure of Brown[5]: 9-BBN (**20**, 1.21 g, *ca.* 9.93 mmol) was suspended in freshly distilled anhydrous THF (5 mL) and stirred until a thick slurry was generated. Methanol (800 µL, 19.8 mmol) was added dropwise at room temperature leading to vigorous evolution of hydrogen gas. After visible gas evolution had ceased and a clear solution had formed, the solvents were cautiously removed under high vacuum, leaving **14** as a colourless oil that was resuspended in anhydrous THF (to a concentration of approximately 1 M) under an argon atmosphere, and used without further purification. Yields were assumed to be quantitative from 9-BBN for the purpose of determining stoichiometry. **NOTE:** B-methoxy-9-borabicyclo[3.3.1]nonane (**14**) is pyrophoric when concentrated,[6] necessitating caution when handling the above solution. [^{11}**B NMR** ($CDCl_3$, 96 MHz): δ (ppm) 57.2.]

First Homologation: Continuing the one-pot procedure described above, B-MeO-9-BBN **14** (*ca.* 5 mmol) was suspended in anhydrous THF (5 mL) and cooled to -78 °C (dry ice/acetone) with vigorous stirring under an argon atmosphere. Freshly distilled dibromomethane (420 μL, 6.0 mmol) was added, followed by dropwise addition of *n*-butyllithium (1.42 M in hexanes, 3.85 mL, 5.5 mmol) onto the cold wall of the Schlenk flask over 20 minutes. The mixture was then allowed to warm to room temperature slowly overnight, a white precipitate typically formed and was present until the cooling bath reached -25 °C. After 20 hours at room temperature, ^{11}B NMR showed a single peak at 55.3 ppm, indicating the successful formation of **17**.

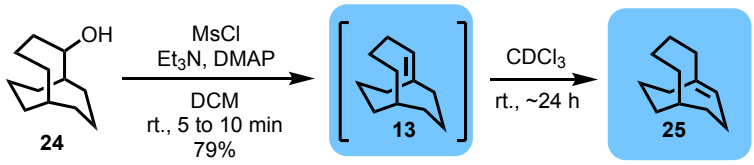
Second Homologation: Continuing the one-pot procedure described above (reaction scale based on *ca.* 11.4 mmol of **14**), the reaction mixture was carefully concentrated to approximately half its initial volume using high vacuum and an inline cold trap (as per Figure S1). The clear solution was diluted with freshly distilled anhydrous THF (30 mL) and cooled to -100 °C (EtOH/liquid nitrogen). Dibromomethane (950 μL, 13.7 mmol) was added, followed by dropwise addition of *n*-butyllithium (1.42 M in hexanes, 8.8 mL, 12.5 mmol) over 10 minutes against the cold wall of the Schlenk flask. The temperature was maintained below -95 °C for 10 minutes and then allowed to warm to -75 °C over 30 minutes. The mixture was removed from the cooling bath and stirred at room temperature for 2 hours. ^{11}B NMR gave a single peak at 56.7 ppm, indicating the completion of the second homologation to give intermediate **18**.

Third Homologation: Continuing the one-pot procedure outline above (reaction scale based on *ca.*12.2 mmol of **18**), the reaction mixture was carefully concentrated at room temperature, using high vacuum and an inline cold trap (as per Figure S1), to remove the hexanes introduced during the previous homologation step. The mixture was then diluted with freshly distilled anhydrous THF (40 mL, total volume was *ca*. 60 mL) and cooled to -85 °C (EtOH/liquid nitrogen) [Note: attempting to reach temperatures below -85 °C would typically lead to the generation of a thick white precipitate]. Dibromomethane (1.0 mL, 14.4 mmol) was then added, followed by the dropwise addition of *n*-butyllithium (1.42 M in hexanes, 9.5 mL, 13.5 mmol) against the cold wall of the flask over approximately 30 minutes. The mixture was maintained at -80 °C for 20 minutes and then allowed to warm to -20 °C with the cooling bath, whereupon it was removed from the cooling bath and stirred at room temperature for 72 hours. ^{11}B NMR gave a single peak at 55.4 ppm, indicating the completion of the third homologation to give intermediate **22.**

Final Homologation: Continuing the one-pot procedure outlined above (reaction scale based upon *ca. 12.2* mol of **22**), the reaction mixture was cooled to -78 °C (dry ice/acetone), freshly distilled anhydrous dichloromethane (2.4 mL, 37.6 mmol) was added, followed by the dropwise addition of a freshly prepared solution of lithium *N,N*-diisopropylamide (0.85 M in THF/hexanes, 11.0 mL, 9.4 mmol) against the cold wall of the flask over 20 minutes. The dark coloured solution was then removed from the cooling bath and allowed to warm to room temperature slowly. After 2 hours at room temperature, the mixture was cooled to 0 °C, and an aqueous solution of sodium hydroxide (7.5 M, 5.0 mL, 37.5 mmol) was added, after which the argon atmosphere was no longer required. The reflux condenser was removed and an internal thermometer was added. Hydrogen peroxide (30% in water, 2.5 mL, *ca.* 22.1 mmol) was then added dropwise, maintaining an internal temperature below 20 °C. The mixture was

warmed to room temperature, stirred for 1 hour, then heated to 40 °C for 1 hour. The aqueous phase was saturated with sodium chloride such that the organic phase separated and was then collected. The aqueous phase was extracted with distilled petroleum spirits (2 x 30 mL), the organic fractions were combined and dried over anhydrous sodium sulfate and concentrated *in vacuo*. The crude residue was suspended in petroleum spirits with vigorous shaking and washed with a saturated solution of ammonium chloride (10 mL), forming a triphasic system. The petroleum spirit layer was collected, dried over anhydrous sodium sulfate and concentrated *in vacuo*. The resulting yellow waxy residue was purified by column chromatography (5 to 10% EtOAc in petroleum spirits, R_f = 0.35 at 20%) to give **24** as a colourless solid (650 mg, 30%).

24: m.p. 175-178 °C; ^{1}H NMR (500 MHz, $CDCl_3$): δ 3.85 (ddd, *J* = 8.7, 5.5, 3.4 Hz, 1H), 2.44 – 2.34 (m, 2H), 2.05 – 1.93 (m, 3H), 1.88 – 1.55 (m, 15H), 1.34 – 1.29 (m, 1H); ^{13}C NMR (125 MHz, $CDCl_3$): δ 76.4, 41.1, 35.5, 34.3, 33.1, 31.6, 31.5, 29.5, 26.2, 23.4, 23.3, 20.4; HRMS (ESI): *m/z* calcd for $C_{12}H_{22}O+H^+$: 183.1743 [*M*+H]$^+$; found: 183.1741.

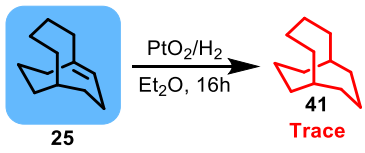


Methanesulfonyl chloride (20 μL, 0.26 mmol) was added to a solution of **24** (44 mg, 0.24 mmol) and triethylamine (100 μL, 0.72 mmol) in anhydrous DCM (5 mL), at room temperature, under a nitrogen atmosphere. After 5 minutes the reaction mixture was partially concentrated under a stream of nitrogen and then passed through a short silica plug, eluting with a small quantity of DCM. The eluent was concentrated under a stream of nitrogen to give a mixture of bridgehead alkenes (predominantly **13** with a small trace of **25**) as a colourless wax (31 mg, 79%). The complete isomerisation of several milligrams of **13** into **25** was observed after standing in $CDCl_3$ (0.7 mL) for 24 hours at room temperature.

13: ^{1}H NMR (500 MHz, $CDCl_3$): δ 5.33 (ddt, *J* = 10.2, 6.3, 1.1 Hz, 1H), 2.49 – 2.41 (m, 2H), 2.40 – 2.31 (m, 1H), 2.06 – 1.91 (m, 3H), 1.83 – 1.46 (m, 12H), 1.39 – 1.31 (m, 1H); ^{13}C NMR (125 MHz, $CDCl_3$): δ 137.2, 125.8, 37.2, 31.5, 31.1, 30.1, 28.6, 28.1, 25.7, 24.4, 24.1, 22.8.

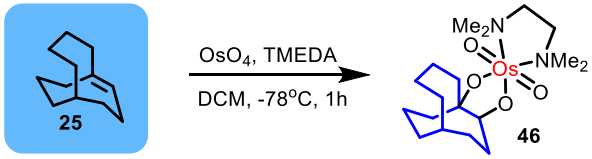
25: ^{1}H NMR (500 MHz, $CDCl_3$): δ 5.36 (dd, *J* = 11.3, 5.5 Hz, 1H), 2.47 – 2.38 (m, 1H), 2.34 – 2.22 (m, 2H), 2.20 – 2.16 (m, 1H), 1.96 – 1.89 (m, 3H), 1.86 – 1.63 (m, 6H), 1.60 – 1.46 (m, 3H), 1.45 – 1.27 (m, 3H); ^{13}C NMR (125 MHz, $CDCl_3$): δ 137.4, 127.1, 39.4, 35.4, 34.9, 34.6, 32.8, 31.4, 29.0, 28.2, 24.8, 21.9; HR-GCMS: *m/z* calcd for $C_{12}H_{20}$: 164.1560 [$M^{\bullet+}$]; found: 164.1559.

Reactions with alkene **25**.



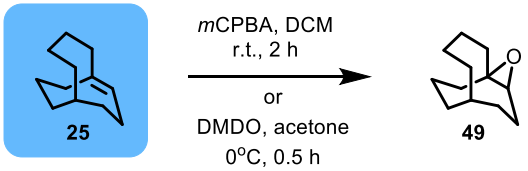
Hydrogenation with transition metal catalysts. Alkene **25** (4.2 mg, 26 µmol) were dissolved in diethyl ether (4.0 mL) and platinum(IV) oxide monohydrate (0.25 mg, 1.0 µmol). The reaction was purged with argon by gentle exposure to house vacuum, then purged with hydrogen gas via a hydrogen filled balloon. The catalyst changed from brown to black after exposure to hydrogen. The reaction was left to stir for 16 hours with the hydrogen balloon attached, after which the hydrogen gas was slowly vacuumed off via house vacuum. The mixture was filtered through a celite plug. The solvent was evaporated under a gentle stream of nitrogen gas. GCMS analysis showed a trace of **41** and vast majority the starting alkene **25**. No sign of alkane was observed by GCMS when the reaction was repeated using palladium on carbon as the catalyst.

Hydrogenation with diimide. Following the procedure of Reese, [7] 2,4,6-triisopropylbenzenesulphonyl hydrazide (17 mg, 57 µmol) was added to a solution of alkene **25** (4.2 mg, 26 µmol) in anhydrous methanol (0.4 mL) under argon. The reaction was left to stir at room temperature for 17 h after which was extracted with pentane. The pentane layer was analysed by GCMS to find no sign of alkane but only **25**.



Osmate formation. Adapting the procedure of Rychnovsky,[8] alkene **25** (4.2 mg, 25.6 µmol) in anhydrous DCM (0.5 mL) and TMEDA (5.0 µL, 33.4 µmol) was cooled to -78°C (dry ice/acetone). OsO_4 (6.6 mg, 25.9 µmol) was added in one-portion and the reaction allowed to stir until no starting material could be detected by TLC (1 h). The solvent and excess amine were removed by vacuum, followed by column purification (Si gel, 3% MeOH/DCM) to give the desired osmate **46** as a brown solid (9.0 mg, 65.7%). For X-ray crystallography, the osmate was crystalised from THF via vapour diffusion (pentane as the anti-solvent).

46: ^{1}H NMR (500 MHz, $CDCl_3$): δ 4.23 (dd, *J* = 8.1, 4.1 Hz, 1H), 3.02 (s, 3H), 2.81 (s, 3H), 2.79 (s, 3H), 2.78 (s, 3H), 2.74 (s, 3H), 2.47 (dddd, *J* = 14.0, 9.9, 4.2, 2.2 Hz, 1H), 2.34 – 2.12 (m, 5H), 2.09 – 2.00 (m, 2H), 1.98 – 1.68 (m, 11H), 1.37 (dd, *J* = 15.6, 6.6 Hz, 1H); ^{13}C NMR (125 MHz, $CDCl_3$): δ 93.8, 92.4, 63.9, 63.6, 53.4, 51.5, 51.1, 50.8, 50.7, 35.5, 34.1, 33.1, 32.7, 31.6, 28.3, 27.7, 23.6, 23.4; HRMS (ESI): *m/z* calcd for $C_{18}H_{36}N_2O_4{}^{192}Os+H^+$: 537.2363 $[M+H]^+$; found: 537.2372.

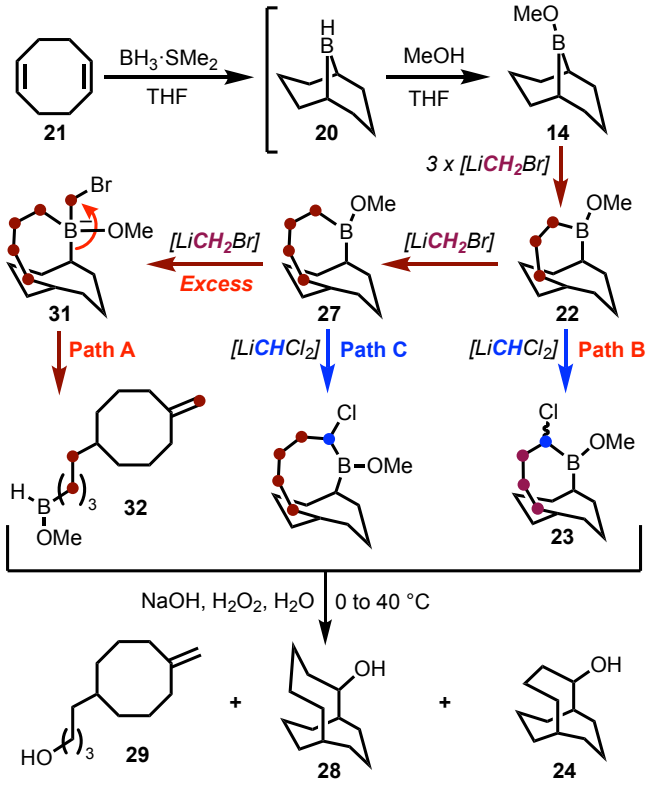


Epoxidation with mCPBA. *m*CPBA (3.00 mg, 77%, 13.4 μmol) was added to a solution of alkene **25** (1.50 mg, 9.15 μmol) in DCM (0.5 mL). After 2 h of stirring, the solvent was removed under a gentle stream of nitrogen gas. Purification by Si gel chromatography or base treatment (1M NaOH) of the crude residue both led to the decomposition of the epoxide.

Epoxidation with DMDO. DMDO in acetone (prepared according to the procedure reported by Taber[9], approx. 40mM, 0.3 mL) was added to a solution of **25** (2.0 mg, 12 μmol) in pentane (0.3 mL) at 0°C. This was stirred until no starting alkene was observed (0.5 h). The acetone was removed by a gentle stream of nitrogen gas. The residue was taken up in pentane, dried over Na_2SO_4 and concentrated under a gentle stream of nitrogen gas to give the epoxide **49** as a white paste (2.0 mg, 91%).

49: ^{1}H NMR (500 MHz, $CDCl_3$): δ 3.00 (dd, *J* = 11.5, 3.8 Hz, 1H), 2.65 (q, *J* = 9.4 Hz, 1H), 2.17 (dddd, *J* = 12.6, 5.6, 2.4, 1.1 Hz, 1H), 2.14 – 2.09 (m, 1H), 2.04 (dqd, *J* = 13.2, 3.7, 1.0 Hz, 1H), 2.01 – 1.92 (m, 2H), 1.88 – 1.80 (m, 2H), 1.78 – 1.59 (m, 6H), 1.55 – 1.36 (m, 4H), 1.09 (tdd, *J* = 13.3, 7.4, 2.8 Hz, 1H); ^{13}C NMR (125 MHz, $CDCl_3$): δ 64.1, 60.9, 38.6, 35.3, 34.9, 34.1, 30.6, 27.5, 26.3, 24.3, 23.5, 21.8; HRMS (ESI): *m/z* calcd for $C_{12}H_{20}O+H^+$: 181.1587 $[M+H]^+$; found: 181.1578.

Synthesis of hyperstable alkenes **10** and **6**.



Adapting the procedure of Brown[4]: a freshly base-bathed 100 mL Schlenk flask was connected to a large-cold-trap via a reflux condenser using clear rubber tubing, a bean-shaped Teflon-coated stirrer bar (*ca.* 1 cm in length) was added to the flask (as per Figure S1). The entire apparatus was placed under vacuum (1 Torr) and the glass components were dried using an electric heat-gun. Vacuum was maintained until the glassware cooled and then the apparatus

was purged with argon 3 to 5 times. The Schlenk flask was lowered into a room-temperature water bath and then charged with anhydrous THF (2.2 mL) and neat borane-dimethyl sulfide complex (850 µL, 8.5 mmol) was added under an argon atmosphere. Cyclooctadiene (**21**, 1.0 mL, 8.15 mmol) was added to the solution with gentle stirring, forming a cloudy suspension within 5 minutes of addition. The mixture was stirred at room temperature for 1 hour and then heated to reflux (*ca.* 90 °C water bath) for 2 hours. The solution was slowly cooled overnight, generating a thick white precipitate. The suspension was cooled to -10 °C and the solvent was removed using a syringe and discarded (this is most conveniently discarded into a large beaker containing a cold 4.0 M sodium hydroxide solution, leading to some foaming). The remaining white solid was dried under high vacuum to give **20** as a free-flowing white powder (860 mg, *ca.* 86%), which was used immediately without further purification.

Adapting the procedure of Brown[5]: The 9-BBN (**20**, 860 mg, *ca.* 7.0 mmol) obtained above was suspended in freshly distilled anhydrous THF (20 mL) under an argon atmosphere and stirred vigorously. Methanol (300 µL, 7.4 mmol) was added dropwise at room temperature leading to vigorous evolution of hydrogen gas. The mixture was stirred for 1 hour at room temperature, whereupon ^{11}B NMR returned a single peak at 57.2 ppm, indicating the successful formation of **14**. Yields are assumed to be quantitative from 9-BBN (**20**) for the purpose of determining stoichiometry.

First Homologation: The above solution was cooled to -78 °C (dry ice/acetone), with vigorous stirring under an argon atmosphere. Freshly distilled dibromomethane (600 µL, 8.6 mmol) was added, followed by the dropwise addition of *n*-butyllithium (2.0 M in hexanes, 3.85 mL, 7.7 mmol) to the cold wall of the Schlenk flask over 30 minutes. The mixture and the cooling bath were then allowed to warm to room temperature and stirred for approximately 60 hours, after which ^{11}B NMR showed a single peak at 55.3 ppm, indicating the successful formation of **17**.

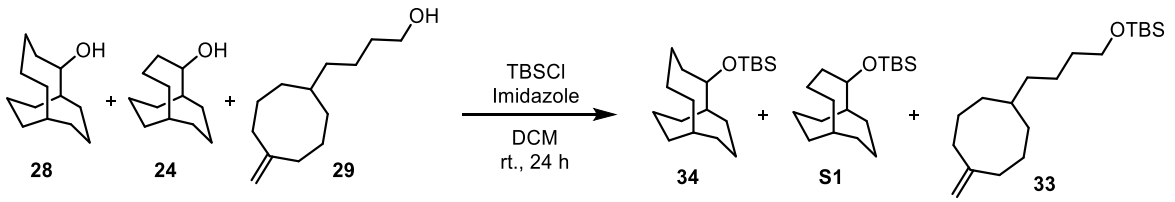
Second Homologation: The above solution was cooled to -100 °C (EtOH/liquid nitrogen) with vigorous stirring. Dibromomethane (600 µL, 8.6 mmol) was added, followed by the dropwise addition of *n*-butyllithium (2.0 M in hexanes, 3.85 mL, 7.7 mmol) to the cold wall of the Schlenk Flask over 25 minutes. The reaction mixture and the cooling bath were then allowed to warm to room temperature slowly overnight, whereupon ^{11}B NMR gave a single peak at 56.7 ppm, indicating the successful formation of **18.**

Third Homologation: The mixture obtained above was diluted with freshly distilled anhydrous THF (25 mL), and cooled to -85 °C (EtOH/liquid nitrogen) with vigorous stirring, under an argon atmosphere. Dibromomethane (600 µL, 8.6 mmol) was added, followed by the dropwise addition of *n*-butyllithium (2.0 M in hexanes, 3.85 mL, 7.7 mmol) to the cold wall of the Schlenk flask over 30 minutes. The reaction mixture was maintained at -85 °C for 10 minutes and then removed from the cooling bath and allowed to warm to room temperature over 2 hours, whereupon ^{11}B NMR gave a single peak at 55.2 ppm, indicating the successful formation of **22**.

Fourth Homologation: The mixture obtained above was cooled to -85 °C (EtOH/liquid nitrogen) with vigorous stirring, under an argon atmosphere. Dibromomethane (600 uL, 8.6

mmol) was added, followed by the dropwise addition of *n*-butyllithium (2.0 M in hexanes, 3.85 mL, 7.7 mmol) to the cold wall of the Schlenk flask over 30 minutes. The reaction mixture was maintained at -85 °C for 10 minutes and then the cooling bath was allowed to warm to room temperature slowly overnight, after which ^{11}B NMR gave a single peak at 52.3 ppm, indicating the successful formation of **27**.

Final Homologation: The mixture obtained above was cooled to -78 °C (dry ice/acetone) with vigorous stirring, under an argon atmosphere. Freshly distilled anhydrous dichloromethane (1.35 mL, 21.1 mmol) was added, followed by the dropwise addition of a freshly prepared solution of lithium *N,N*-diisopropylamide (0.63 M in THF/hexanes, 13.5 mL, 8.5 mmol) to the cold wall of the Schlenk flask, over 20 minutes. The reaction mixture was then allowed to warm to room temperature overnight, together with the cooling bath. As the mixture warmed, it darkened in colour, transitioning from a light tan at -70 °C to a darker amber by -40 °C. After 16 hours at room temperature, the mixture was cooled to 0 °C and an aqueous solution of sodium hydroxide (4.2 M, 5.0 mL, 21.0 mmol) was added, following which the argon atmosphere was no longer required. An internal thermometer was attached in place of the reflux condenser and hydrogen peroxide (30% in water, 1.6 mL, *ca.* 14.1 mmol) was added dropwise, ensuring that the internal temperature did not exceed 20 °C during addition. The mixture was then warmed to room temperature, stirred for 1 hour, and then heated to 40 °C for 1 hour in a water bath. Sodium chloride was added to saturate the aqueous phase. The organic layer was collected, dried over sodium sulfate and concentrated *in vacuo*. Column chromatography (5 to 20% EtOAc in petroleum spirits) was used to fractionate the complex mixture obtained, the compounds obtained with R_f values between 0.25 and 0.35 (measured at 20% EtOAc in petroleum spirits) were combined and concentrated *in vacuo*, yielding a pale-yellow oil containing **24**, **28**, and **29**, in a ratio of approximately 1:2:3 (**24**:**28**:**29**, by ^1H NMR), which was used without further purification.
28: HRMS (ESI): *m/z* calcd for $C_{13}H_{24}O+H^+$: 197.1900 $[M+H]^+$; found: 197.1898; *m/z* calcd for $C_{12}H_{24}O\text{-}OH^+$: 179.1794 $[M\text{-}OH]^+$; found: 179.1792.

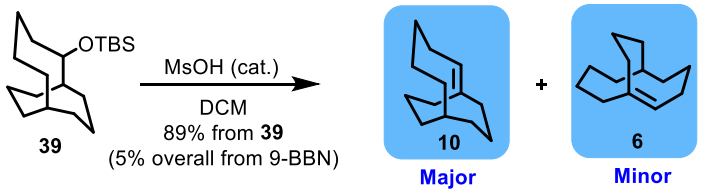


approximately 1:2:3

The alcohol mixture obtained above (535 mg) and imidazole (400 mg, 5.90 mmol) were suspended in freshly distilled anhydrous DCM (30 mL) under an argon atmosphere. *tert*-Butyldimethylsilyl chloride (600 mg, 4.0 mmol) was added in a single portion, which quickly generated a white suspension. The mixture was stirred at room temperature for 18 hours and then quenched with a saturated solution of ammonium chloride (5 mL), diluted with water (20 mL), and extracted with DCM (3 x 20 ml). The combined organic extracts were dried over anhydrous sodium sulfate and concentrated *in vacuo*. The crude residue was partially purified by column chromatography (petroleum spirits) to afford the desired product **34** as a colourless oil (198 mg; containing minor unidentified by-products), in addition to **S1** and **33**.

34: R_f = 0.41 (petroleum spirits); ^{1}H NMR (500 MHz, C_6D_6): δ 4.24 (ddd, J = 9.0, 4.7, 2.8 Hz, 1H), 2.44 – 2.33 (m, 1H), 2.22 – 2.05 (m, 2H), 1.98 – 1.71 (m, 6H), 1.70 – 1.40 (m, 16H), 1.01 (s, 9H), 0.13 (s, 3H), 0.12 (s, 3H); ^{13}C NMR **(**125 MHz, C_6D_6): δ 75.9, 43.7, 35.8, 31.4, 31.0, 29.5, 28.9, 28.6, 26.5, 26.2, 26.0, 24.3, 22.1, 21.3, 18.2, -4.0, -4.3; HRMS (ESI): *m/z* calcd for $C_{19}H_{38}OSi$-H^+: 309.2608 $[M-H]^+$; found: 309.2612; *m/z* calcd for $C_{19}H_{38}OSi$-$C_6H_{15}OSi^+$: 179.1794 $[M-OTBS]^+$; found: 179.1795.

33: ^{1}H NMR (500 MHz, $CDCl_3$): δ 4.76 – 4.72 (m, 2H), 3.58 (t, J = 6.7 Hz, 2H), 2.25 (ddd, J = 14.0, 8.1, 3.9 Hz, 2H), 2.12 (ddd, J = 13.8, 8.9, 4.0 Hz, 2H), 1.89 – 1.78 (m, 2H), 1.60 – 1.41 (m, 7H), 1.33 – 1.18 (m, 4H), 1.17 – 1.08 (m, 2H), 0.89 (s, 9H), 0.04 (s, 6H); ^{13}C NMR (125 MHz, $CDCl_3$): δ 152.4, 110.9, 63.3, 38.6, 36.2, 35.7, 33.4, 33.2, 26.9, 26.0, 23.5, 18.4, -5.2; HR-GCMS: *m/z* calcd for $C_{19}H_{38}OSi$-$C_4H_9^+$: 253.1988 $[M - C_4H_9]^{\bullet+}$; found: 253.1986.



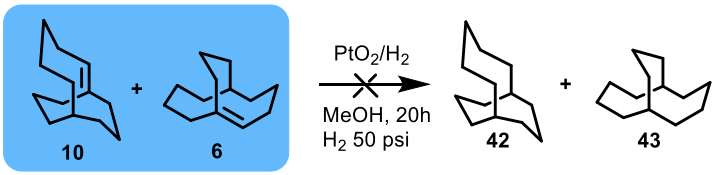
A 1% solution of methanesulfonic acid in DCM was prepared from methanesulfonic acid (10 uL) and freshly distilled anhydrous DCM (1.0 mL) under an argon atmosphere. Three drops of this mixture were then added to a solution of the silyl ether **34** (6.0 mg, *ca.* 0.02 mmol) in DCM (0.5 mL) in a 4 mL glass vial. The mixture was stirred at room temperature for 5 minutes, and then loaded directly onto a silica gel pipette column, eluting with distilled *n*-pentane to return an inseparable mixture of the isomeric title compounds as a clear oil (3 mg, 89%). [Note: The ratio of major and minor isomers differed depending on the reaction temperature. A mixture of ~9:1 was obtained when conducted at –78 °C, whereas at room temperature it varied between ~4:1 to 6:1.]

10 (major): ^{1}H NMR (500 MHz, C_6D_6): δ 5.34 (ddt, *J* = 11.2, 5.0, 1.8 Hz, 1H), 2.42 (td, *J* = 13.6, 3.4 Hz, 1H), 2.36 – 2.25 (m, 1H), 2.24 – 2.15 (m, 2H), 2.09 – 2.02 (m, 1H), 1.92 – 1.79 (m, 2H), 1.78 – 1.71 (m, 2H), 1.71 – 1.50 (m, 6H), 1.49 – 1.39 (m, 4H), 1.28 – 1.17 (m, 2H); ^{13}C NMR (125 MHz, C_6D_6): δ 137.9, 126.6, 32.6, 31.0, 30.9, 30.2, 30.0, 30.0, 29.1, 28.7, 25.8, 23.7, 22.6; ^{1}H NMR (700 MHz, $CDCl_3$): δ 5.38 – 5.33 (m, 1H), 2.50 (td, *J* = 13.7, 3.5 Hz, 1H), 2.32 (ddd, *J* = 24.8, 11.8, 4.0 Hz, 1H), 2.26 – 2.15 (m, 2H), 2.06 (dq, *J* = 13.0, 3.8 Hz, 1H), 1.97 – 1.83 (m, 2H), 1.81 – 1.76 (m, 2H), 1.75 – 1.57 (m, 6H), 1.54 (ddd, *J* = 13.1, 3.6, 1.5 Hz, 1H), 1.50 – 1.44 (m, 2H), 1.41 (dtd, *J* = 14.5, 7.7, 2.0 Hz, 1H), 1.32 – 1.20 (m, 2H); ^{13}C NMR (175 MHz, $CDCl_3$): δ 138.0, 126.1, 32.3, 30.54, 30.49, 29.8, 29.6, 28.7, 28.3, 25.4, 23.3, 22.2.

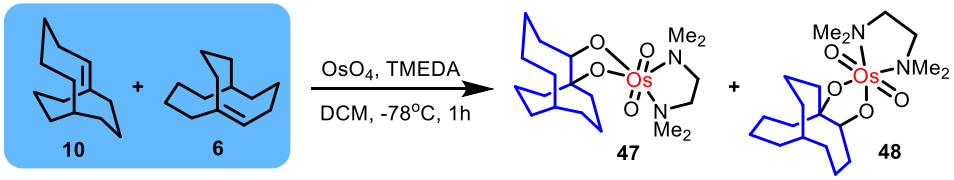
6 (minor): Chemical shifts were extracted from the data set of the alkene mixture. Due to peaks overlapping, some signals were unidentifiable. ^{1}H NMR (700 MHz, $CDCl_3$): δ 5.67 (dd, *J* = 11.1, 6.1, 1H), 2.48 – 2.41 (m, 1H), 2.42 – 2.38 (m, 1H), 2.34 – 2.32 (m, 1H), 2.17 – 2.12 (m, 1H), 2.02 – 1.97 (m, 1), 1.93 – 1.90 (m, 1H). Signals mainly extracted from HSQC. ^{13}C NMR (175 MHz, $CDCl_3$): δ 139.1, 126.3, 37.6, 33.6, 31.2, 31.1, 25.1, 24.2, 22.0.

HR-GCMS (alkene mixture): *m/z* calcd for $C_{13}H_{22}$: 178.1717 $[M^{\bullet+}]$; found: 178.1715.

Reactions with alkenes **10** and **6.**



Hydrogenation. Following the procedure of McMurry[10]: A 5:1 mixture (^{1}H NMR) of alkenes **10** and **6** (2.5 mg, 14 µmol) were dissolved in methanol (0.5 mL). The solution was transferred to a Parr Shaker bottle and the volume was made up to 1 mL, followed by the addition of platinum(IV) oxide (0.3 mg, 1.3 µmol). The reaction was purged with hydrogen gas by gentle exposure to house vacuum and backfilled with hydrogen. This process was repeated three times before charging the reaction vessel with hydrogen gas to a pressure of 50 psi. The reaction was left shaking for 20 hours, after which the pressure was slowly released, and the hydrogen atmosphere, together with adsorbed hydrogen, were removed under vacuum. The mixture was filtered through a celite plug, prewashed with methanol and the ^{1}H NMR spectrum was directly recorded. The ^{1}H NMR spectrum matched well with the starting alkene mixture (see below), revealing no hydrogenation had taken place. The NMR sample was then extracted with pentane, and GCMS analysis performed using the pentane layer, which showed only the starting alkene peaks.



Osmate formation. Adapting the procedure of Rychnovsky,[8] a mixture of alkenes **10** and **6** (5.4:1 by ^{1}H NMR, 10.5 mg, 58.9 µmol) in anhydrous DCM (1.5 mL) was added TMEDA (11.5 µL, 76.8 µmol). After cooling to -78°C (dry ice/acetone), OsO_4 (16.8 mg, 66.1 µmol) was added in one-portion and the reaction allowed to react until no starting material could be detected by TLC (1 h). The solvent and excess amine were removed by vacuum, followed by column purification (Si gel, 3% MeOH/DCM) to give the desired osmates as a brown solid (ratio 5.7:1 ^{1}H NMR, 31.6 mg, 97.5%).

Recrystallisation via vapour diffusion. The brown osmates in a 4 mL glass vial was dissolved in a small amount of distilled acetone. The vial was then placed inside a 20 mL scintillation vial containing pentane, the anti-solvent. This was left in the dark undisturbed. The level of pentane in the scintillation vial was checked daily to ensure it was above the solvent level in the 4 mL glass vial. Crystals were collected for X-ray crystallography.

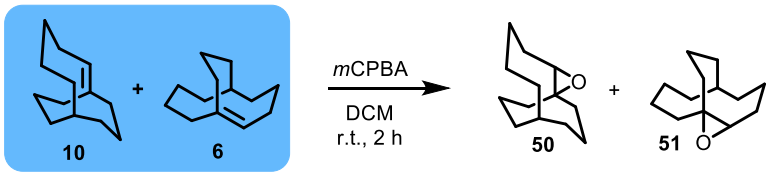
Enhancement of the minor osmate. Vapour diffusion recrystallisation was performed as described above. Once crystals were formed, the lightly coloured mother liquor was carefully pipetted out leaving the crystals in the 4 mL glass vial. The crystals remained in the vial were subjected to another round of vapour diffusion recrystallisation. After five cycles of recrystallisation, the osmates ratio had improved to 1.6:1 (crystals) and 17.7:1 (mother liquor).

47: ^{1}H NMR (700 MHz, CD_2Cl_2): δ 4.31 (dd, *J* = 6.7, 4.9 Hz, 1H), 3.06 – 2.93 (m, 4H), 2.72 (s, 3H), 2.71 (s, 3H), 2.70 (s, 3H), 2.69 (s, 3H), 2.45 – 2.38 (m, 1H), 2.17 (t, *J* = 11.4 Hz, 1H), 2.14 – 2.08 (m, 1H), 2.03 – 1.99 (m, 1H), 1.94 – 1.86 (m, 3H), 1.83 – 1.60 (m, 14H); ^{13}C NMR (176 MHz, CD_2Cl_2): δ 92.8, 91.0, 64.4, 64.1, 51.7, 51.4, 51.3, 50.9, 37.4, 37.3, 32.0, 31.4, 30.9, 30.4, 28.0,

26.9, 25.3, 23.2, 22.3; (176 MHz, C_6D_6): δ 93.1, 90.4, 63.4, 63.08, 50.9, 50.59, 50.57, 50.31, 38.1, 37.3, 31.8, 31.03, 30.6, 30.5, 27.6, 27.2, 25.2, 23.4, 22.3.

48: ^{1}H NMR (700 MHz, CD_2Cl_2): δ 4.14 (dd, *J* = 11.2, 5.0 Hz, 1H), 3.06 – 2.93 (m, 4H), 2.75 (s, 3H), 2.74 (s, 3H), 2.70 (s, 6H), 2.39 – 2.35 (m, 1H), 2.22 – 2.18 (m, 1H), 2.12 – 2.06 (m, 2H), 2.01 – 1.87 (m, 6H), 1.85 – 1.57 (m, 9H), 1.40 – 1.34 (m, 1H), 1.15 (dt, *J* = 14.8, 3.8 Hz, 1H); ^{13}C NMR (176 MHz, CD_2Cl_2): δ 91.8, 90.4, 64.4, 63.97, 51.9, 51.23, 51.1, 50.7, 35.9, 34.8, 32.4, 31.1, 30.83, 30.81, 29.0, 24.9, 23.8, 22.3, 22.1; (176 MHz, C_6D_6): δ 92.2, 90.9, 63.5, 63.12, 51.0, 50.59, 50.57, 50.34, 36.4, 35.2, 32.3, 31.00 (2C), 30.9, 29.4, 24.9, 24.3, 22.8. [1C overlapped with another signal.]

HRMS (ESI) of mixture **47** and **48**: *m/z* calcd for $C_{19}H_{38}N_2O_4{}^{192}Os+H^+$: 551.2519 $[M+H]^+$; found: 551.2514.



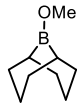
Epoxidation. To a mixture of alkenes **10** and **6** (1.3 mg, 7.3 μmol) in DCM (0.5 mL) was added *m*CPBA (2.38 mg, 10.6 μmol). The homogeneous solution was stirred for 2 h at room temperature. The reaction was concentrated under a gentle stream of nitrogen gas and the residue passed through a pipette column (Si gel, 10% diethyl ether/pentane) to give epoxides **50** and **51** as an inseparable mixture.

[5.3.3]-epoxide **50**: ^{1}H NMR (700 MHz, $CDCl_3$): δ 3.13 (ddd, *J* = 10.2, 3.1, 1.1 Hz, 1H), 2.21 – 2.11 (m, 3H), 1.89 – 1.78 (m, 4H), 1.78 – 1.68 (m, 2H), 1.67 – 1.62 (m, 3H), 1.61 – 1.49 (m, 5H), 1.40 – 1.34 (m, 4H); ^{13}C NMR (176 MHz, $CDCl_3$): δ 65.3, 64.3, 35.2, 29.9, 29.5, 29.3, 29.2, 28.6, 27.1, 26.4, 22.3, 21.8, 21.2.

[4.4.3]-epoxide **51**: Chemical shifts were extracted from the data set of the epoxide mixture. Due to peaks overlapping, some signals were unidentifiable. ^{1}H NMR (700 MHz, $CDCl_3$): δ 3.30 (dd, *J* = 11.5, 3.9 Hz, 1H), 2.05 – 1.99 (m, 2H), 1.49 – 1.41 (m, 2H); ^{13}C NMR (176 MHz, $CDCl_3$): δ 63.9(HSQC), 62.7 (HMBC), 34.2, 30.6, 30.25, 30.15, 29.7, 24.6, 23.2, 21.2.

HRMS (ESI) of mixture **50** and **51**: *m/z* calcd for $C_{13}H_{22}O+H^+$: 195.1743 $[M+H]^+$; found: 195.1734; *m/z* calcd for $C_{13}H_{22}O+Na)^+$: 217.1563 $[M+Na]^+$; found: 217.1552.

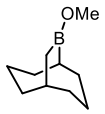
B. NMR Spectra



14

^{11}B NMR

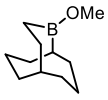
$CDCl_3$, 96 MHz



17

^{11}B NMR

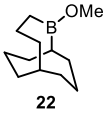
$CDCl_3$, 96 MHz



18

^{11}B NMR

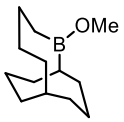
$CDCl_3$, 96 MHz



22

^{11}B NMR

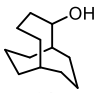
$CDCl_3$, 96 MHz



27

^{11}B NMR

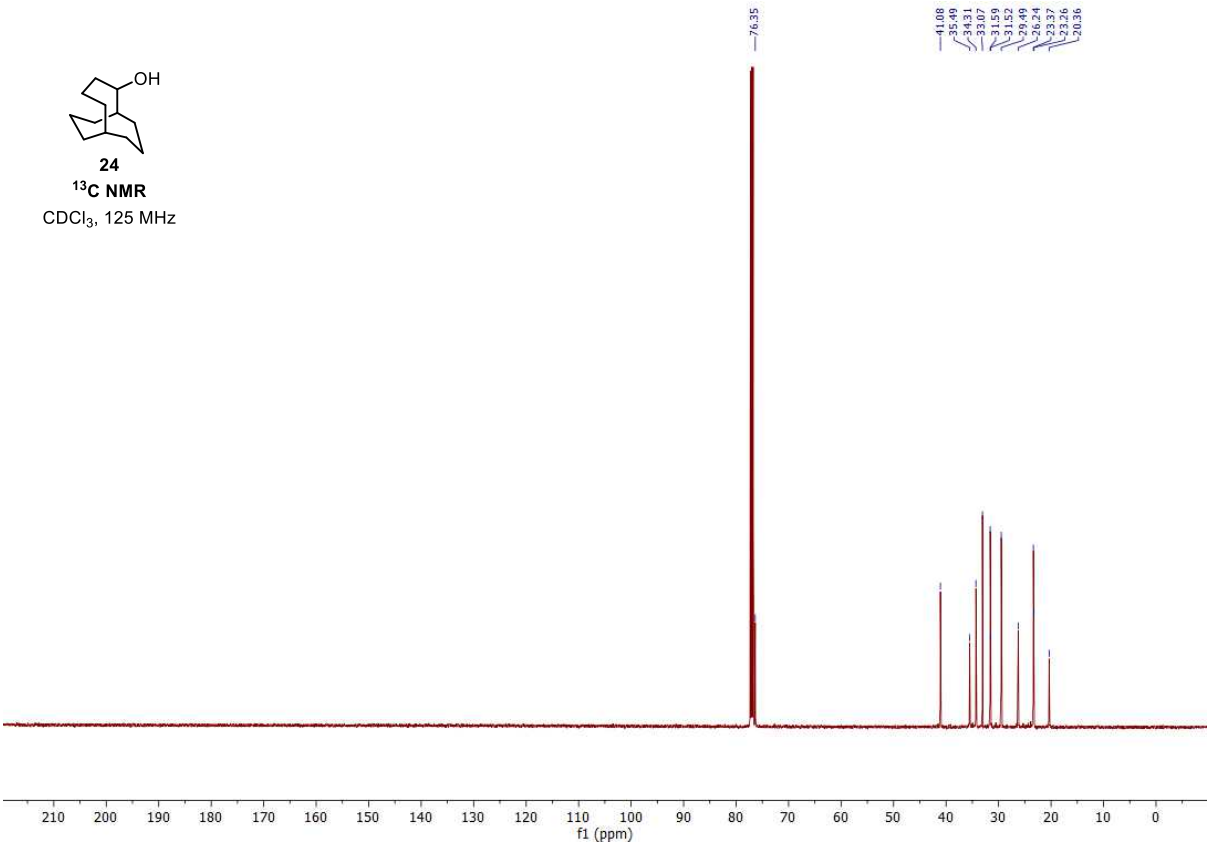
$CDCl_3$, 96 MHz

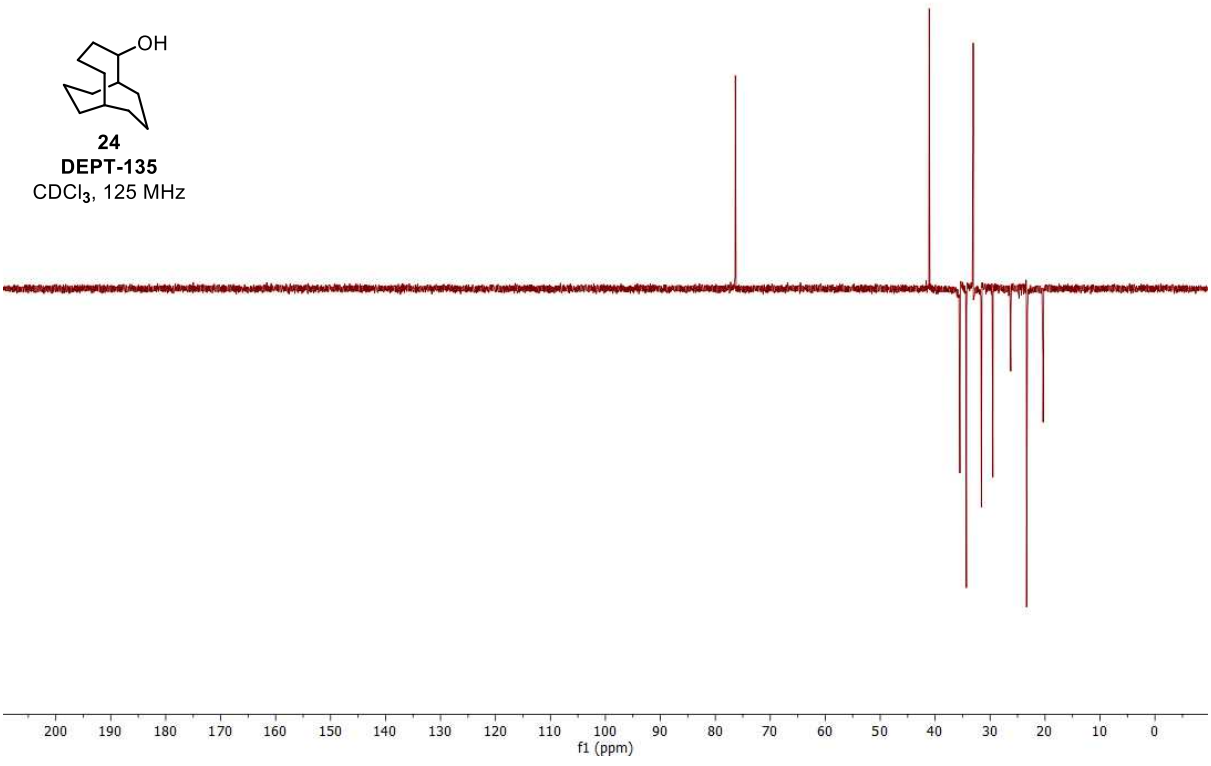


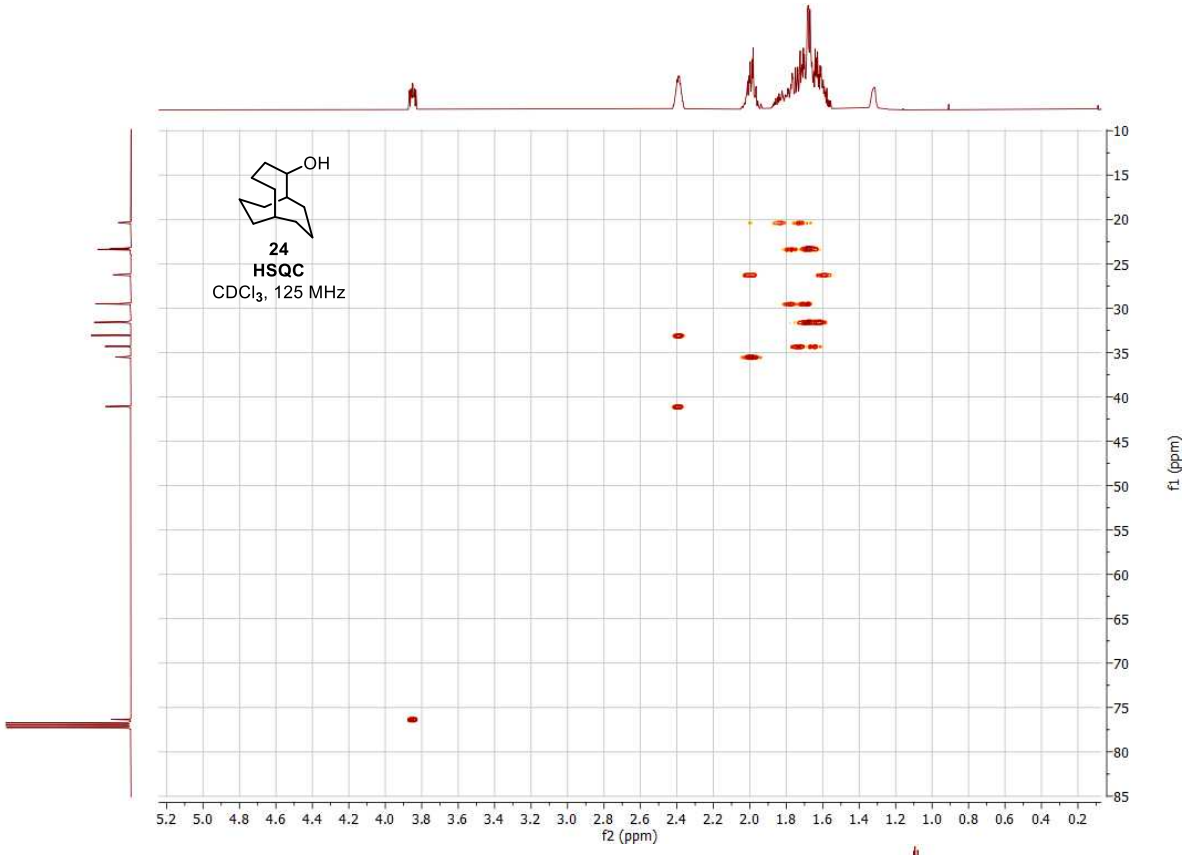
24

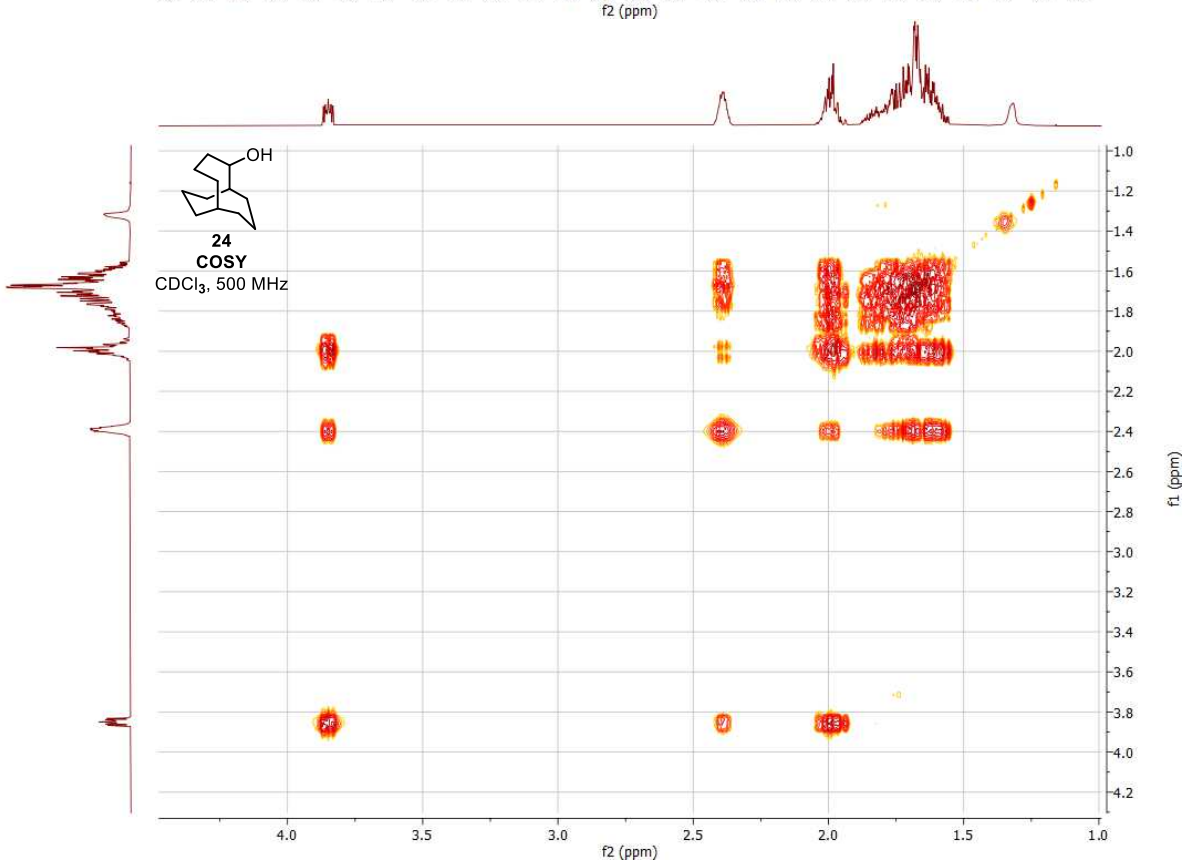
^{1}H NMR

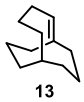
$CDCl_3$, 500 MHz


OH
24
13C NMR
CDCl3, 125 MHz
76.35
41.08
35.49
34.31
33.07
31.59
31.52
29.49
26.24
23.37
23.26
20.36
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
f1 (ppm)


OH
24
DEPT-135
CDCl3, 125 MHz
200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
f1 (ppm)


OH
24
HSQC
CDCl3, 125 MHz
f2 (ppm)
f1 (ppm)

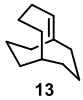

OH
24
COSY
CDCl3, 500 MHz
f2 (ppm)
f1 (ppm)



13

^{1}H NMR

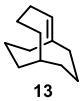
$CDCl_3$, 500 MHz



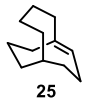
13

^{13}C NMR

$CDCl_3$, 125 MHz



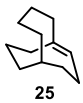
13
DEPT-135
$CDCl_3$, 125 MHz



25

^{1}H NMR

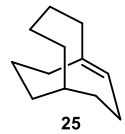
$CDCl_3$, 500 MHz



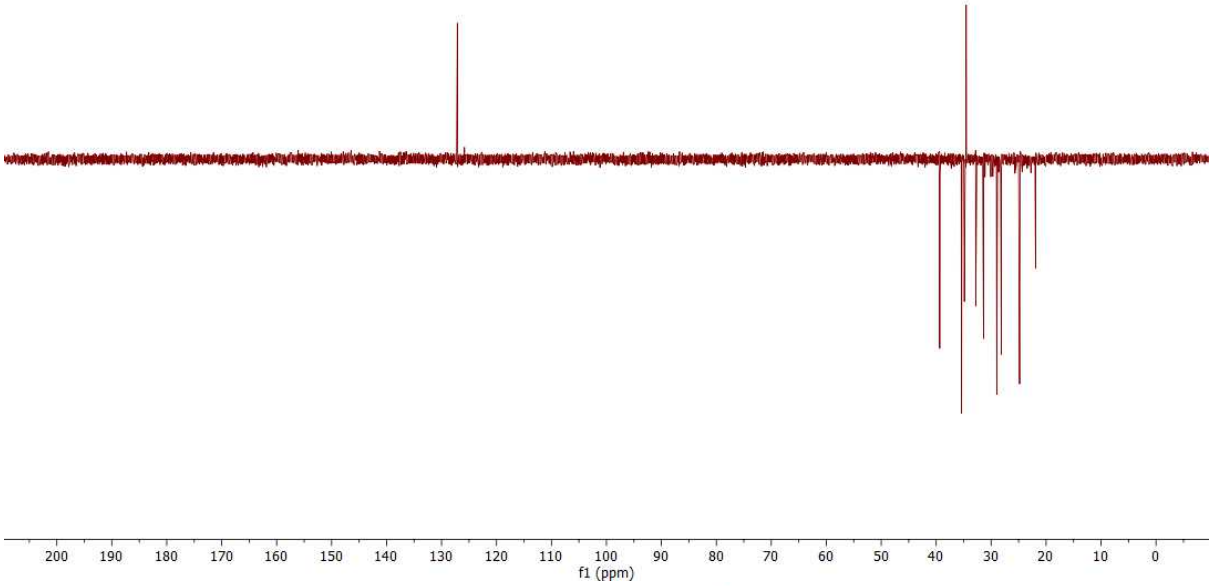
25

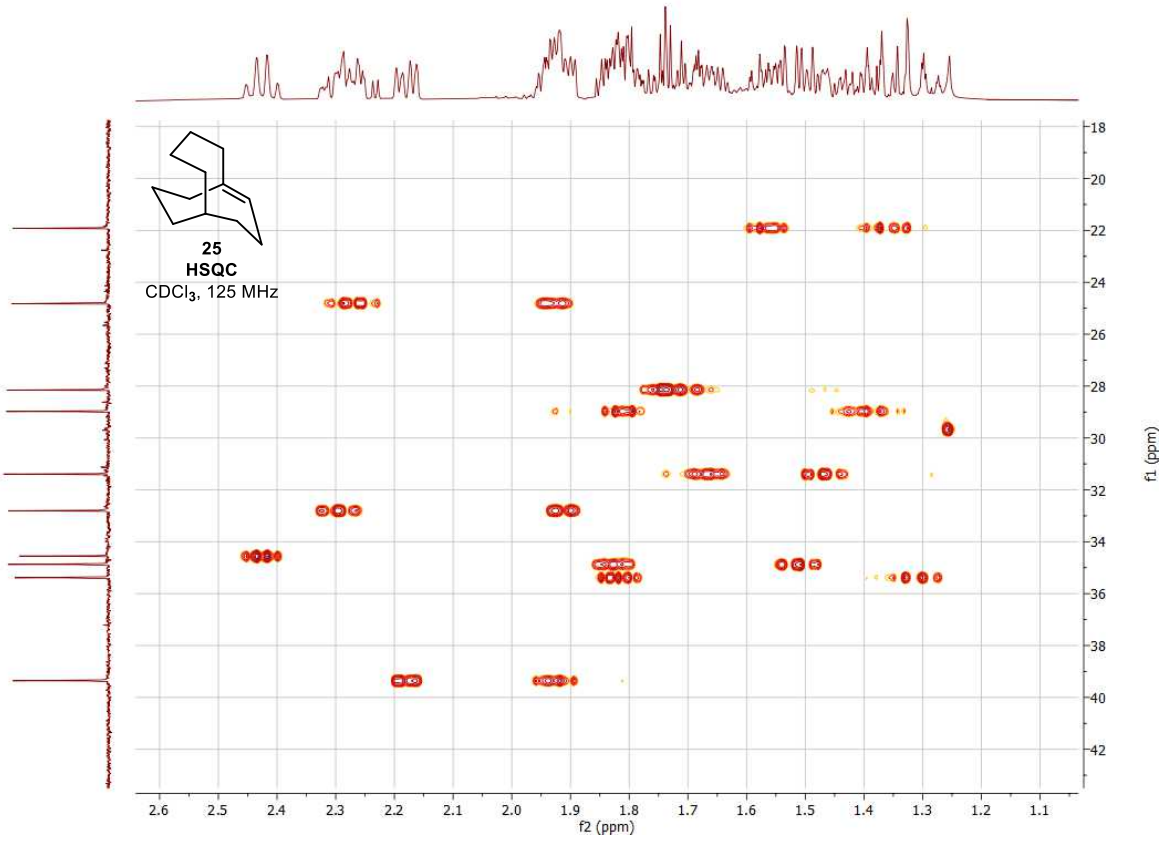
^{13}C NMR

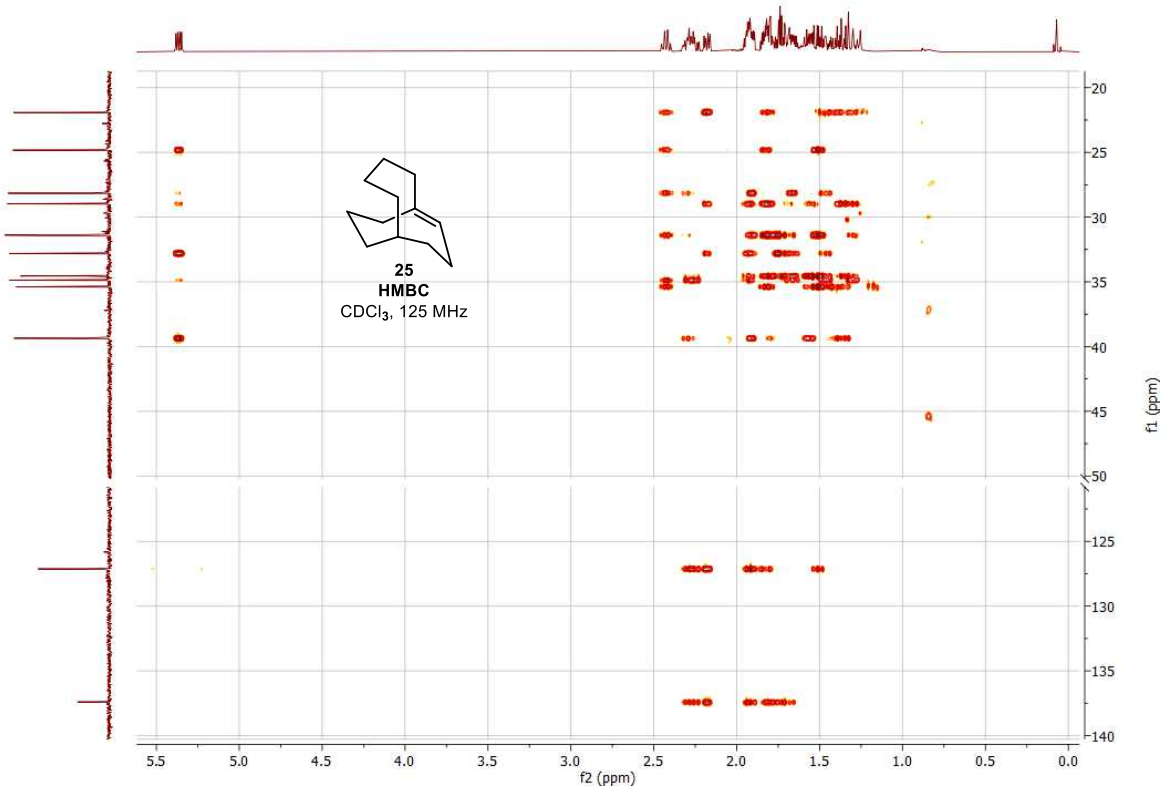
$CDCl_3$, 125 MHz



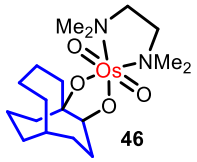
25
DEPT-135
$CDCl_3$, 125 MHz






25
HMBC
CDCl3, 125 MHz
f2 (ppm)
f1 (ppm)

scR112.1.fid
as500, 433 osmate, CDCl3

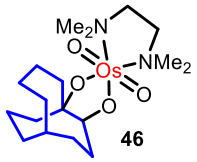


46

^{1}H NMR

$CDCl_3$, 500 MHz

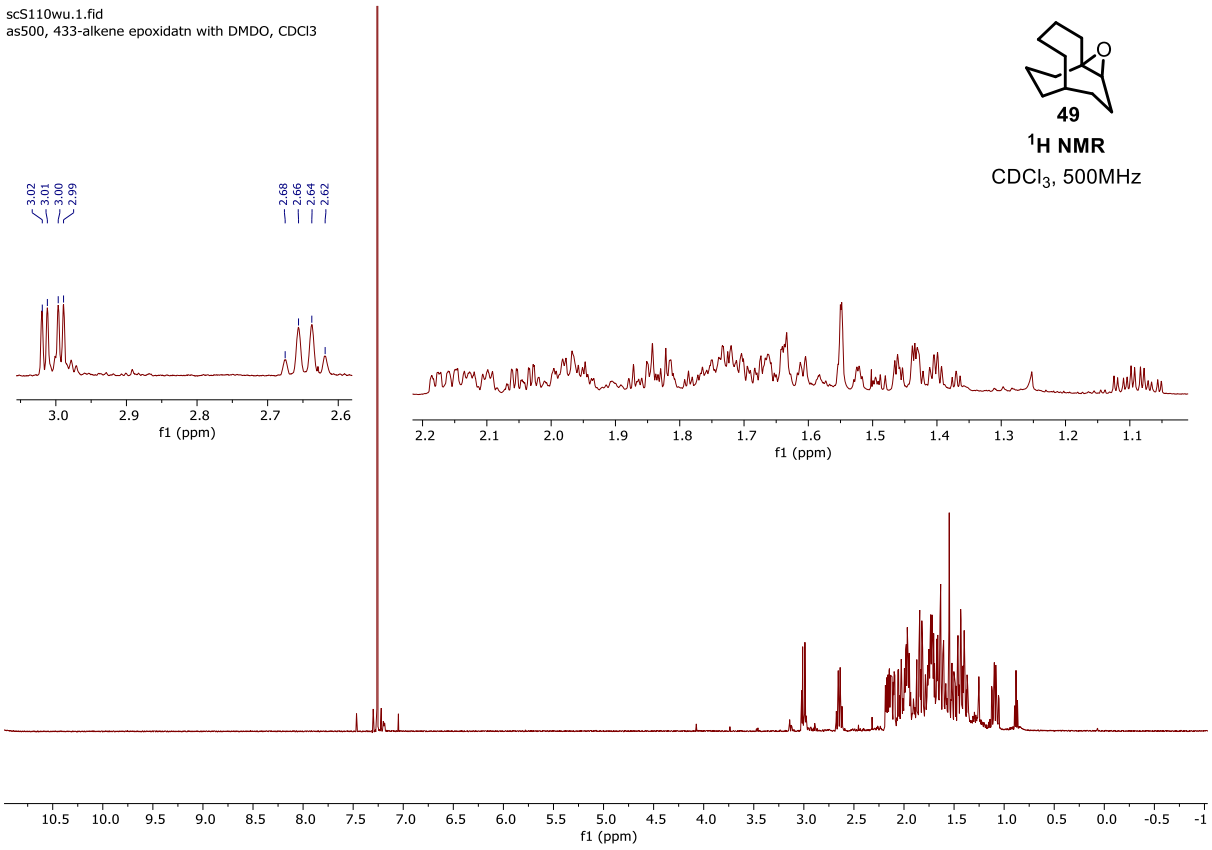
scR112.2.fid
as500, 433 osmate, CDCl3

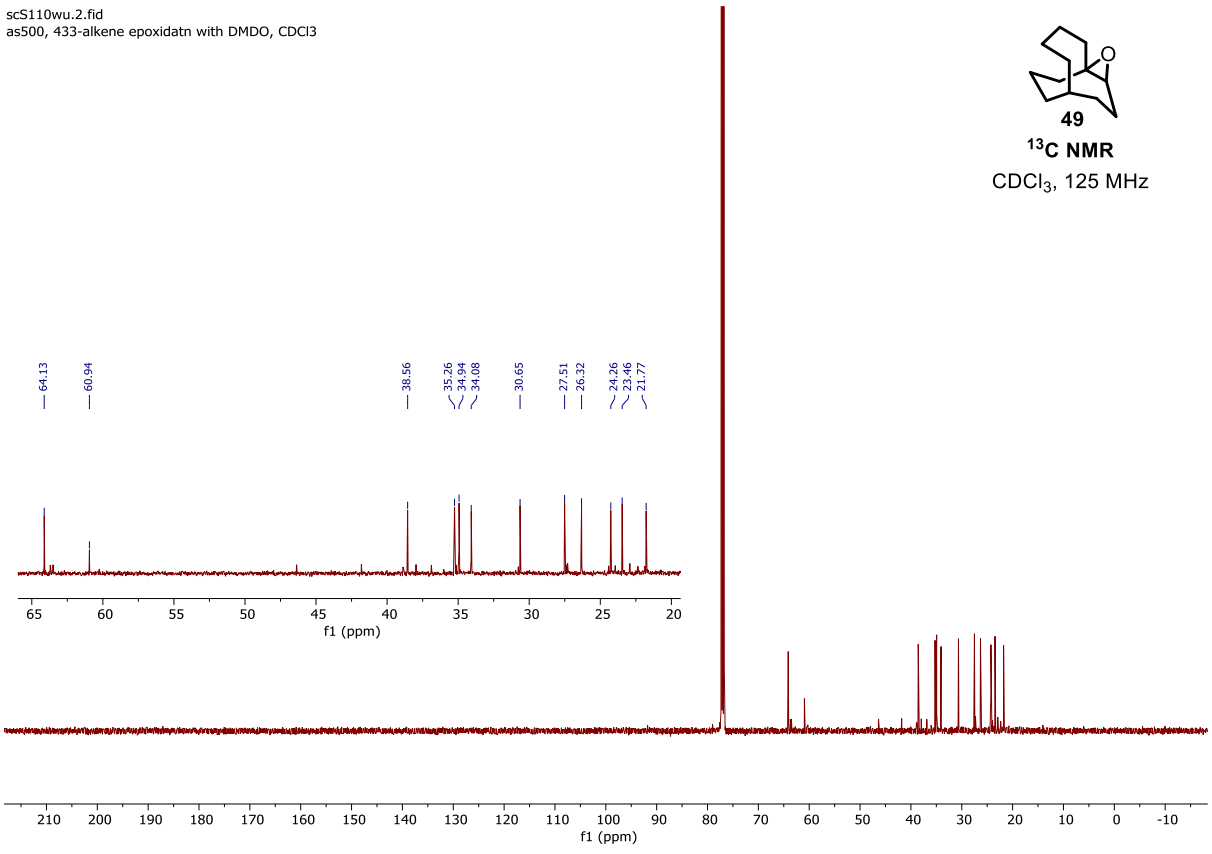


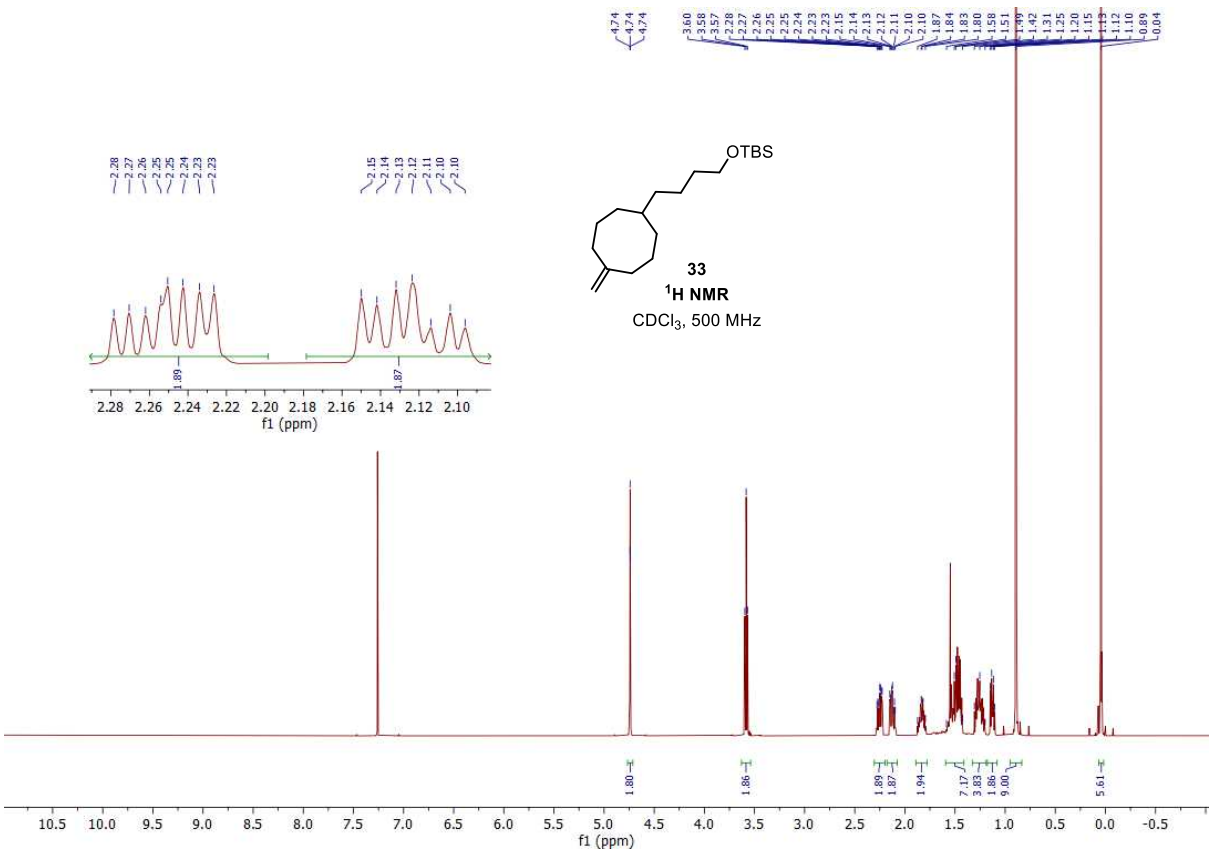
46

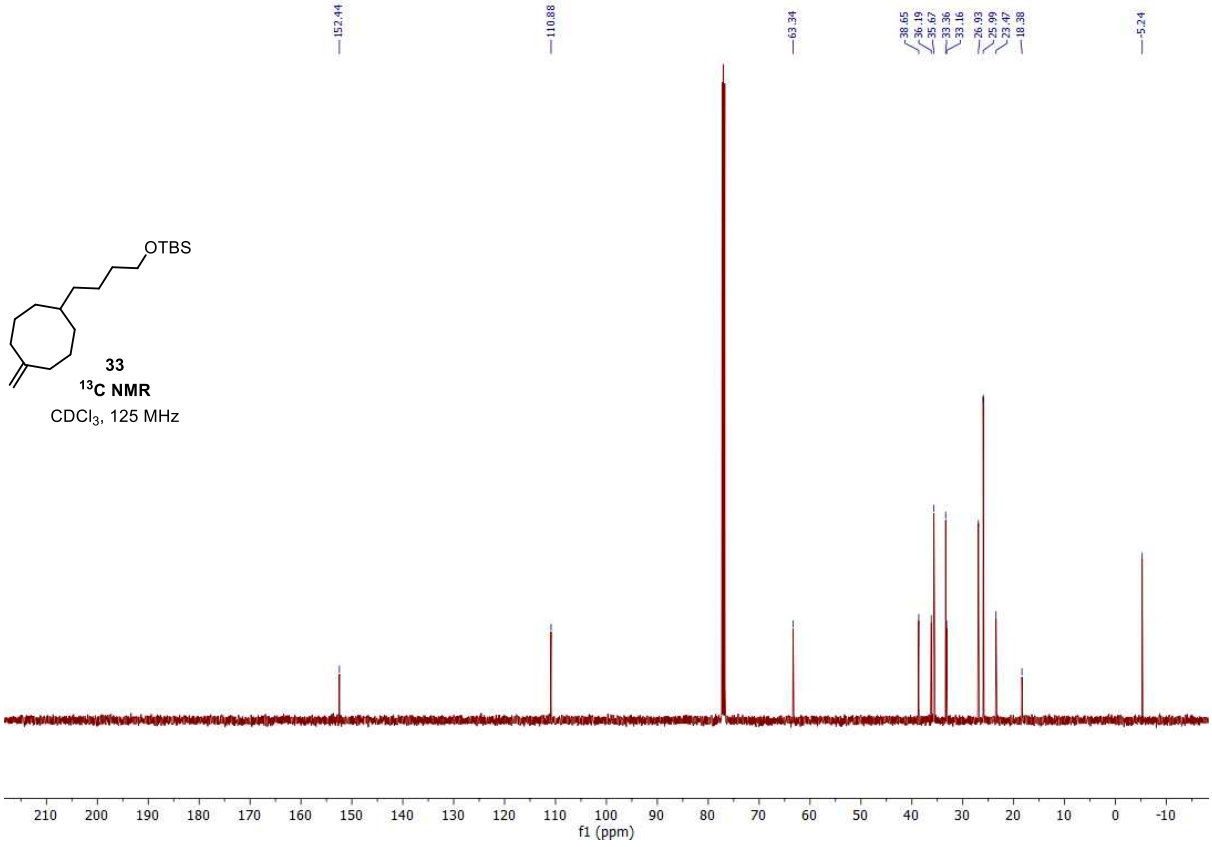
^{13}C NMR

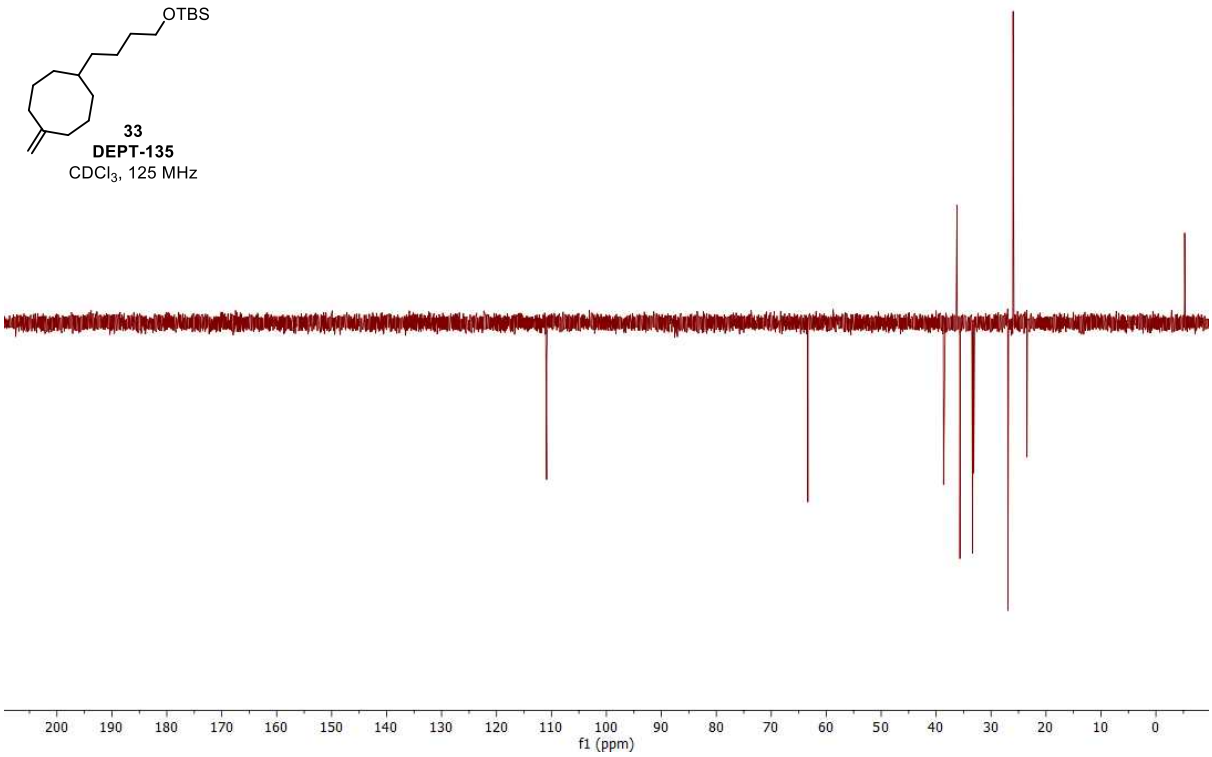
$CDCl_3$, 125 MHz

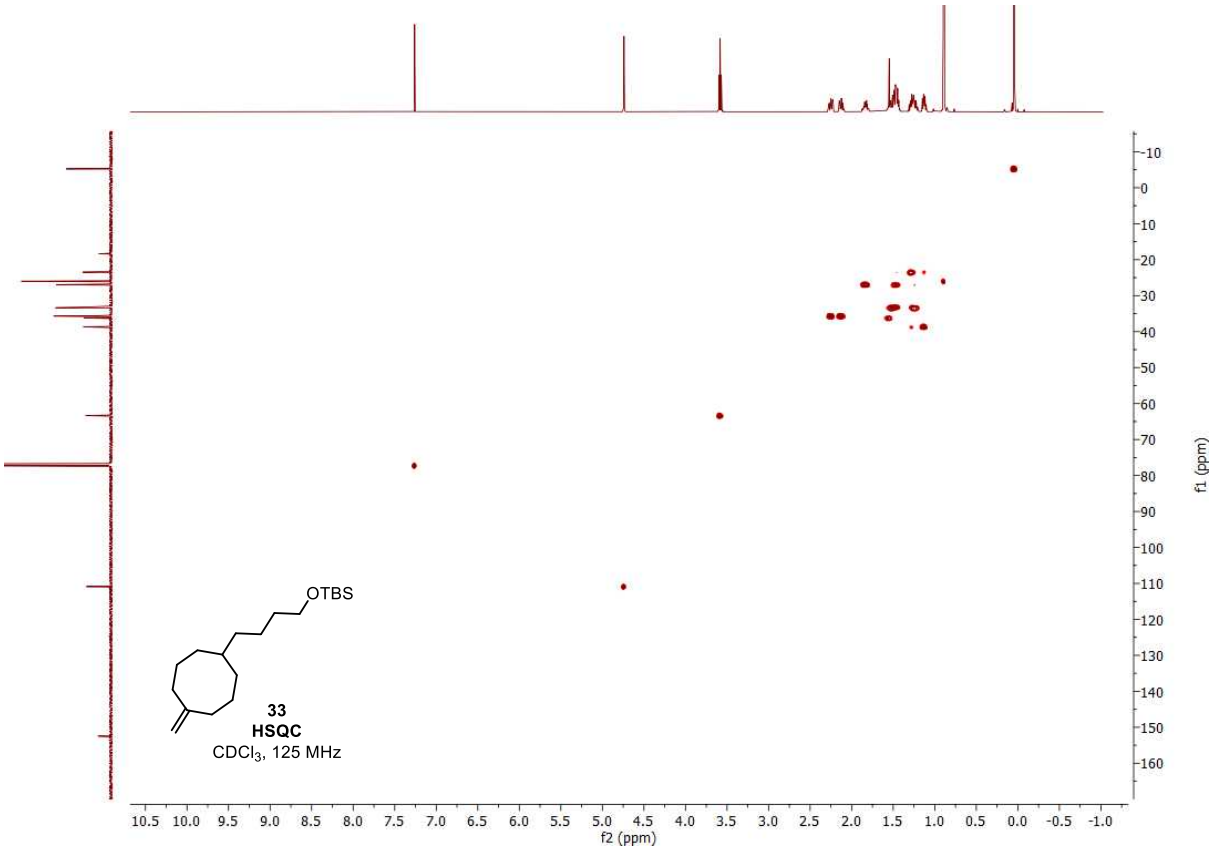

scS110wu.1.fid
as500, 433-alkene epoxidatn with DMDO, CDCl3
49
1H NMR
CDCl3, 500MHz
3.02
3.01
3.00
2.99
2.68
2.66
2.64
2.62
f1 (ppm)

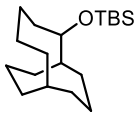

scS110wu.2.fid
as500, 433-alkene epoxidatn with DMDO, CDCl3
49
13C NMR
CDCl3, 125 MHz
64.13
60.94
38.56
35.26
34.94
34.08
30.65
27.51
26.32
24.26
23.46
21.77
f1 (ppm)


OTBS
33
^{1}H NMR
$CDCl_3$, 500 MHz
f1 (ppm)


OTBS
33
^{13}C NMR
$CDCl_3$, 125 MHz
f1 (ppm)


OTBS
33
DEPT-135
CDCl3, 125 MHz
200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
f1 (ppm)

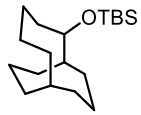

OTBS
33
HSQC
CDCl3, 125 MHz
10.5 10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0 -0.5 -1.0
f2 (ppm)
-10 0 10 20 30 40 50 60 70 80 90 100 110 120 130 140 150 160
f1 (ppm)



34

^{1}H NMR

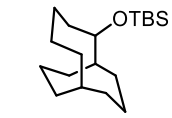
C_6D_6, 500 MHz



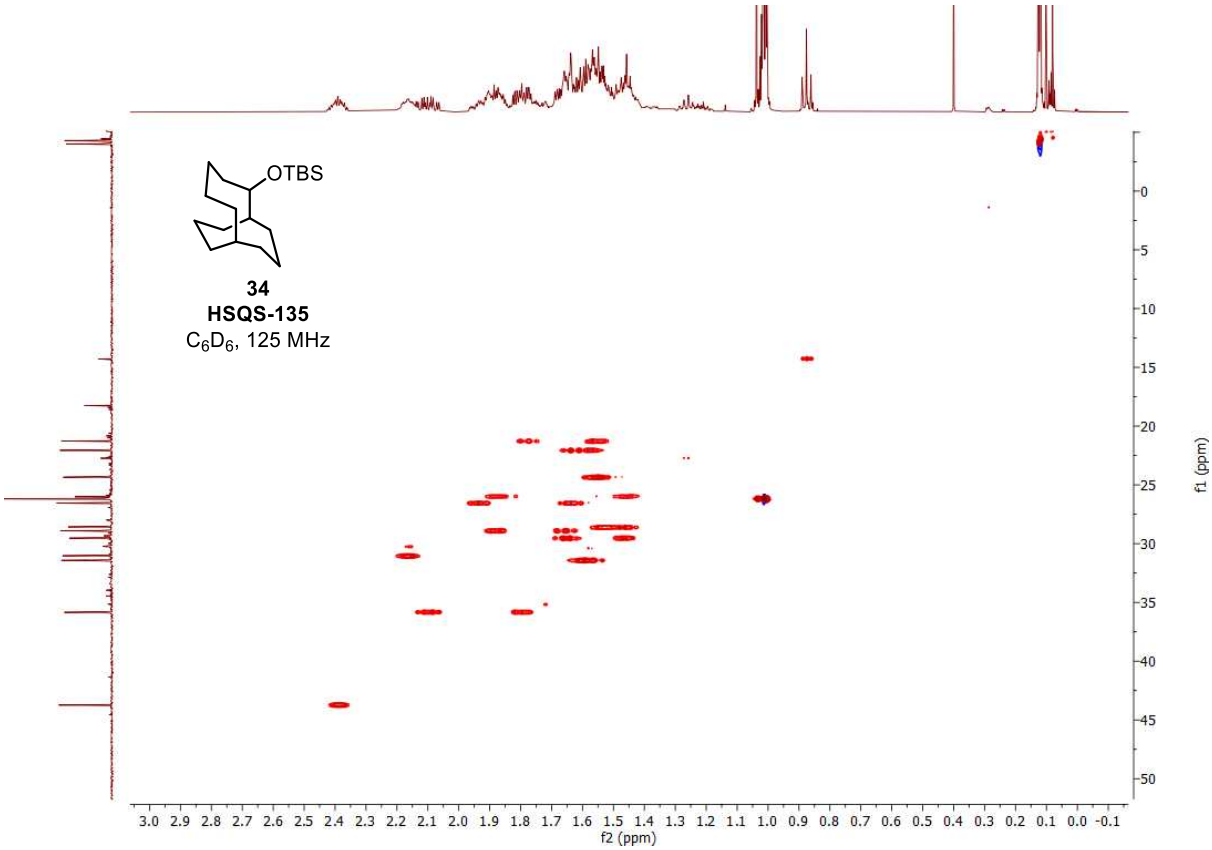
34

^{13}C NMR

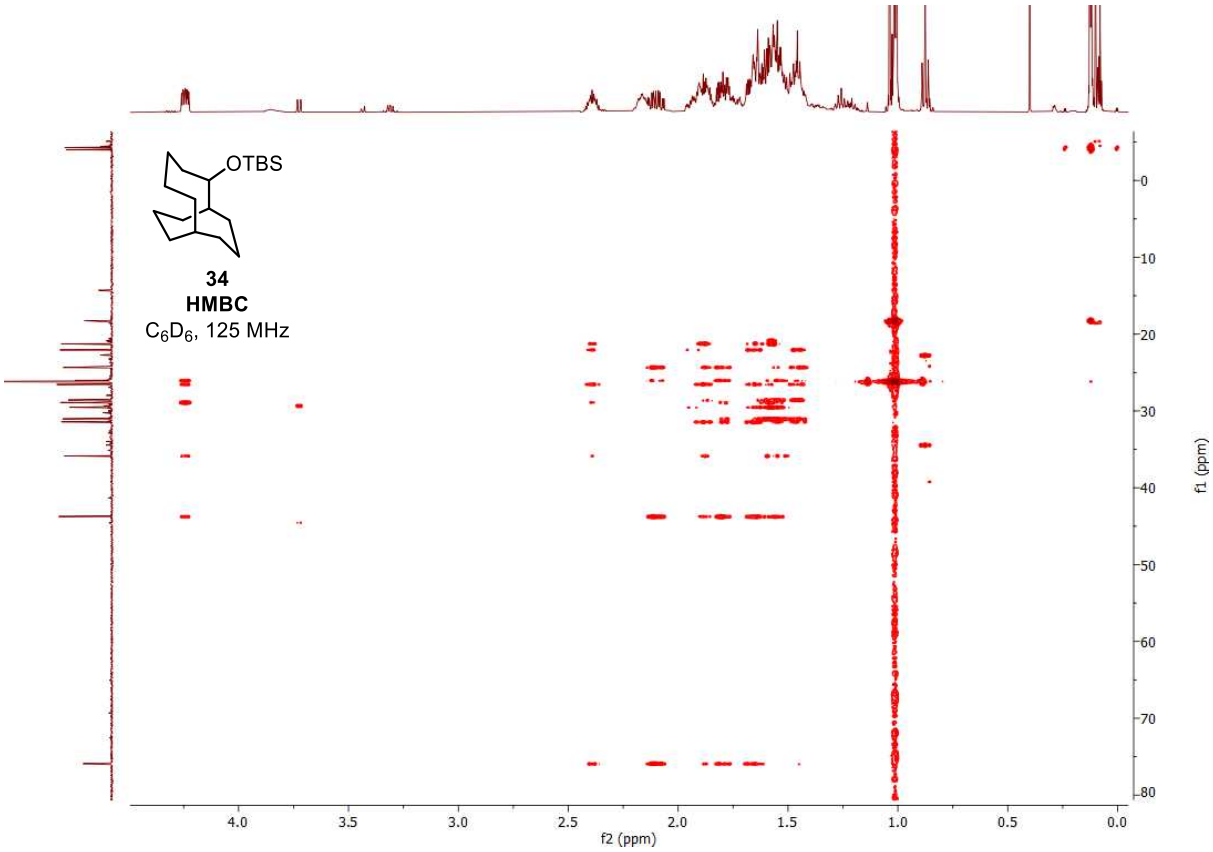
C_6D_6, 125 MHz

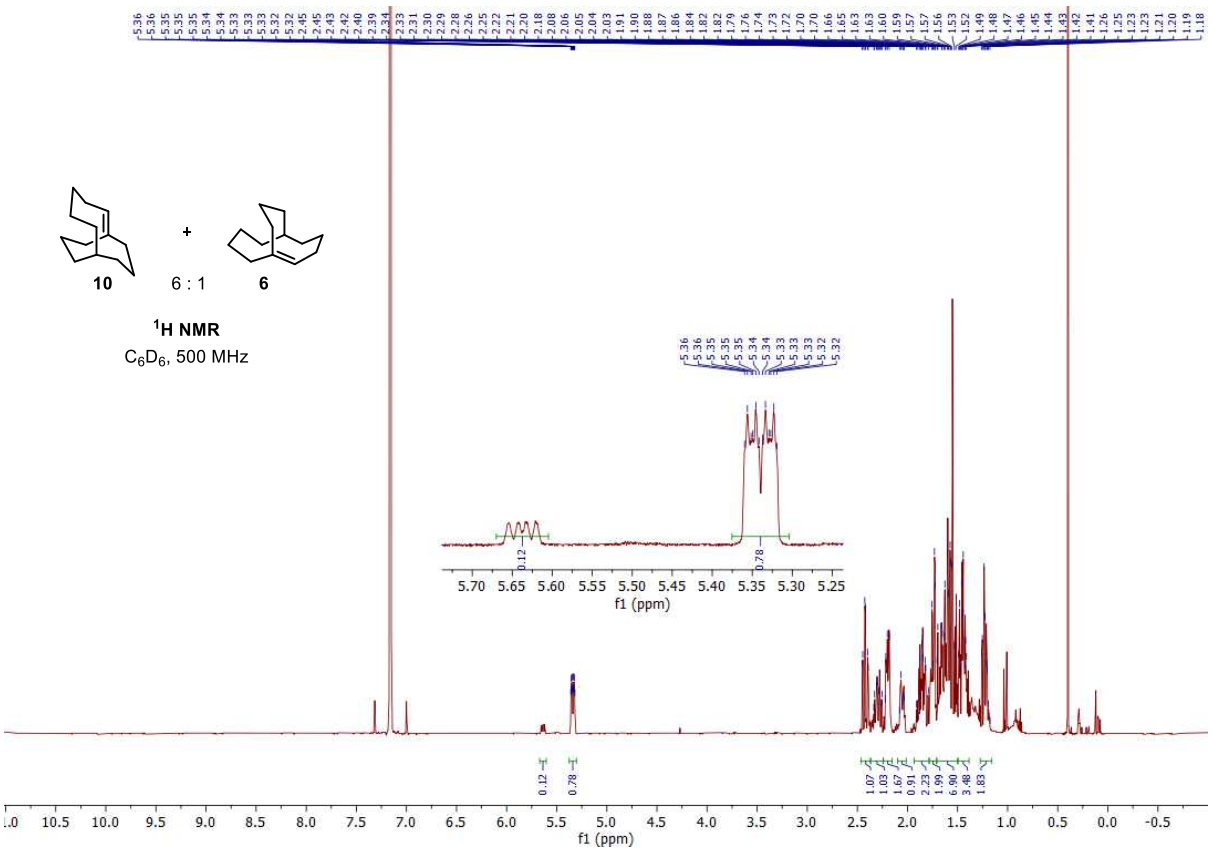


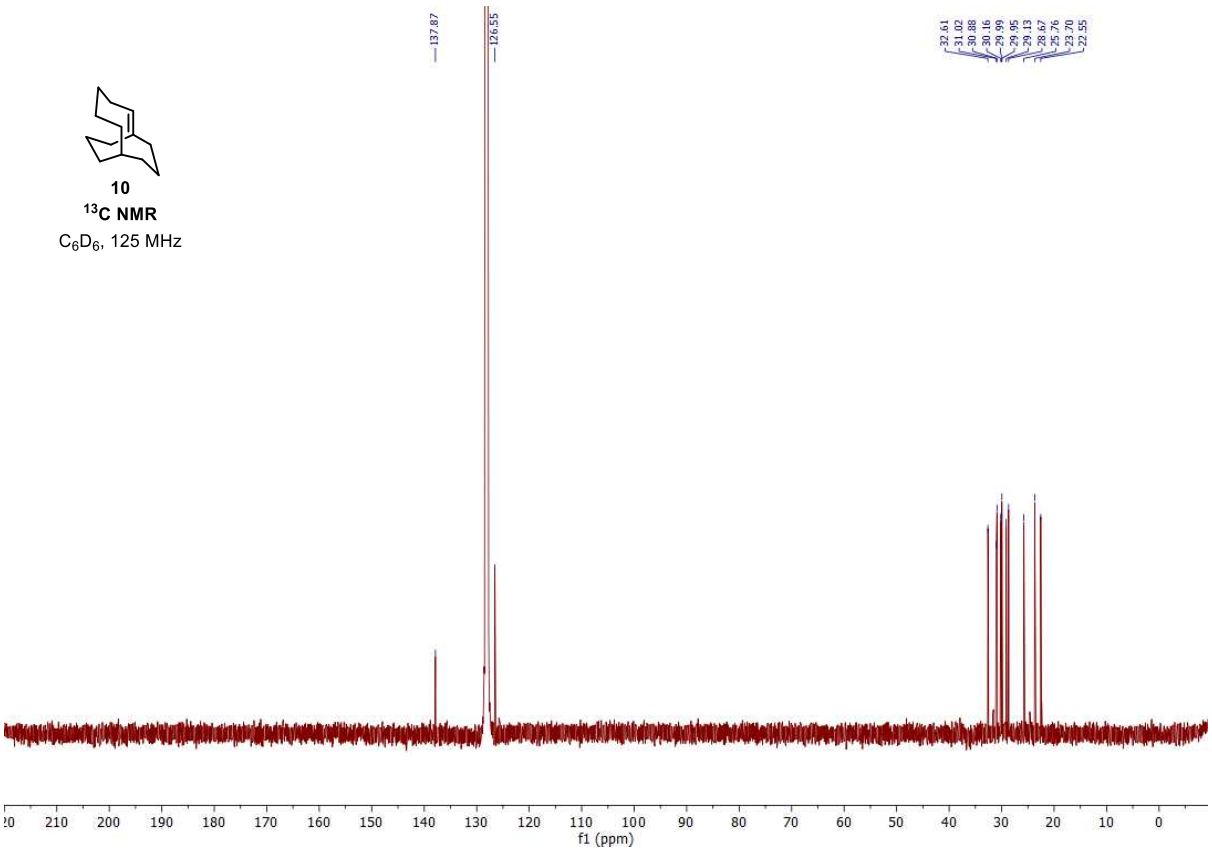
34
DEPT-135
C_6D_6, 125 MHz

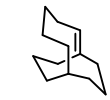


34
HSQS-135
C_6D_6, 125 MHz

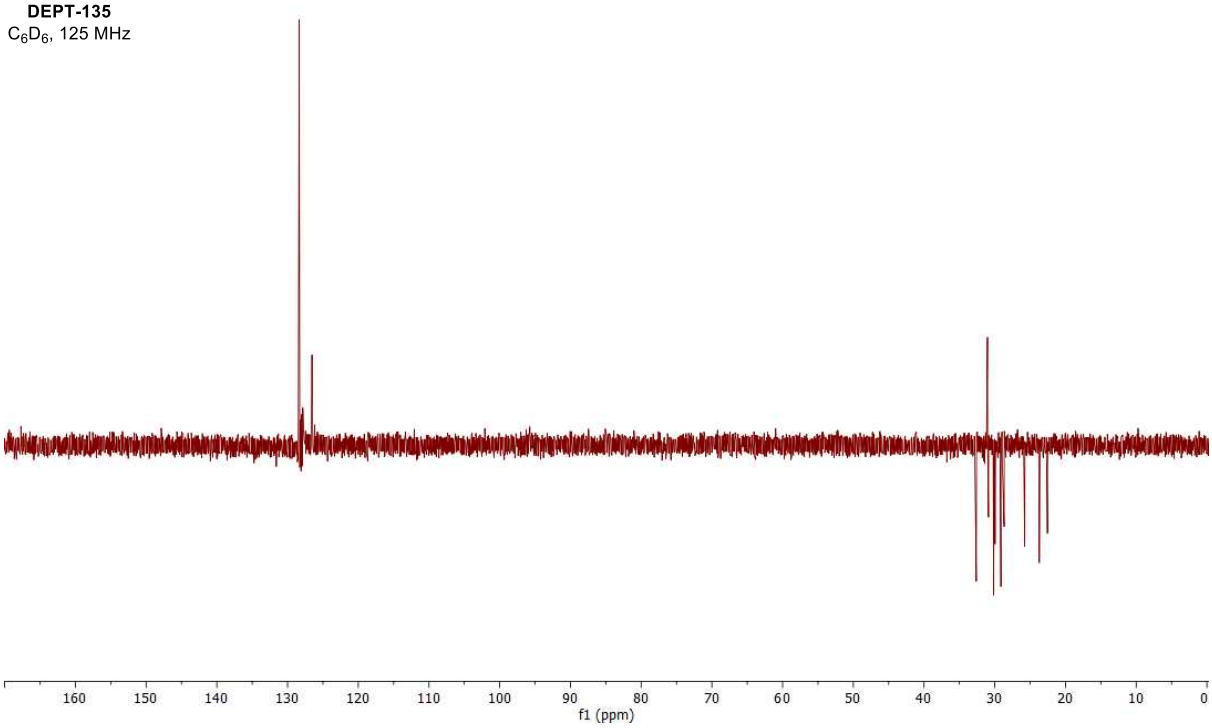

OTBS
34
HMBC
C6D6, 125 MHz
f2 (ppm)
f1 (ppm)

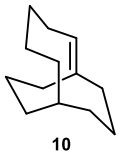

10
6 : 1
6
^{1}H NMR
C_6D_6, 500 MHz
f1 (ppm)


10
^{13}C NMR
C_6D_6, 125 MHz
137.87
126.55
f1 (ppm)

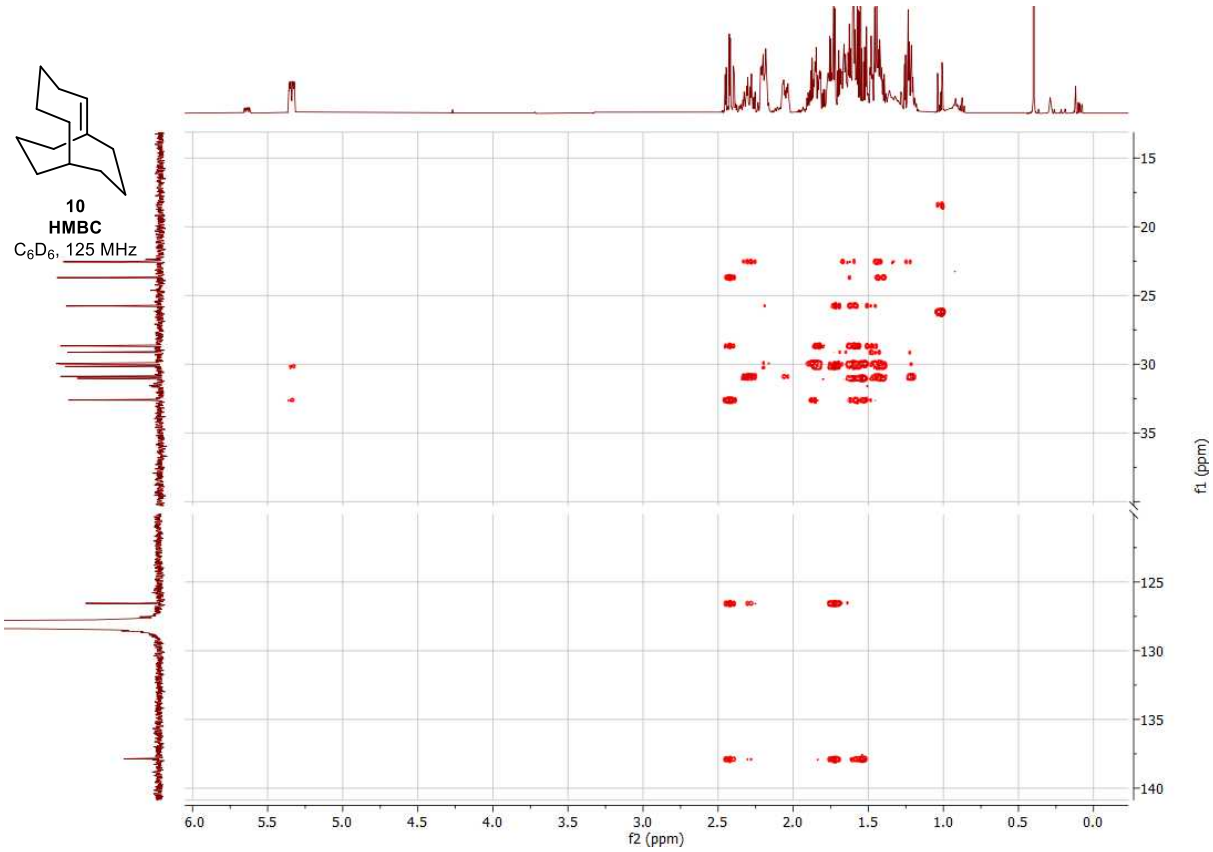


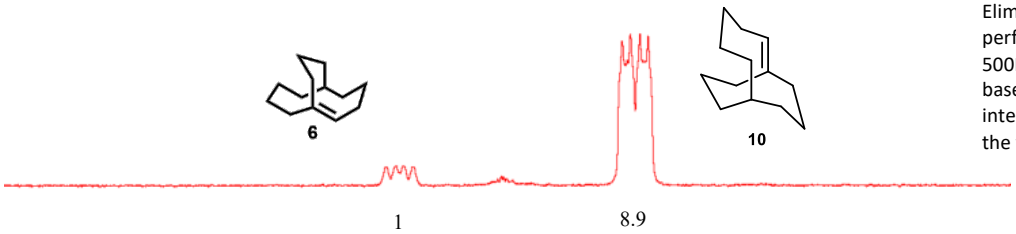
10
DEPT-135
C_6D_6, 125 MHz



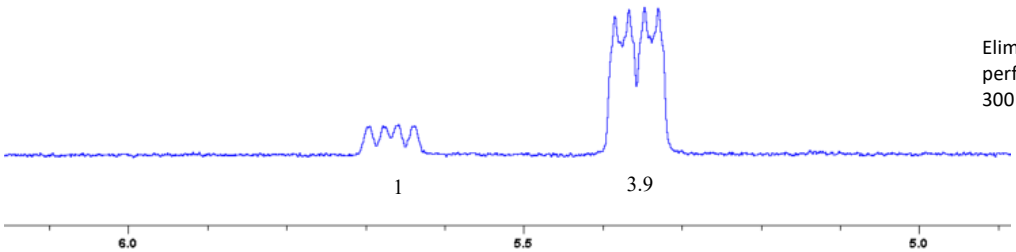


10
HSQC
C_6D_6, 125 MHz



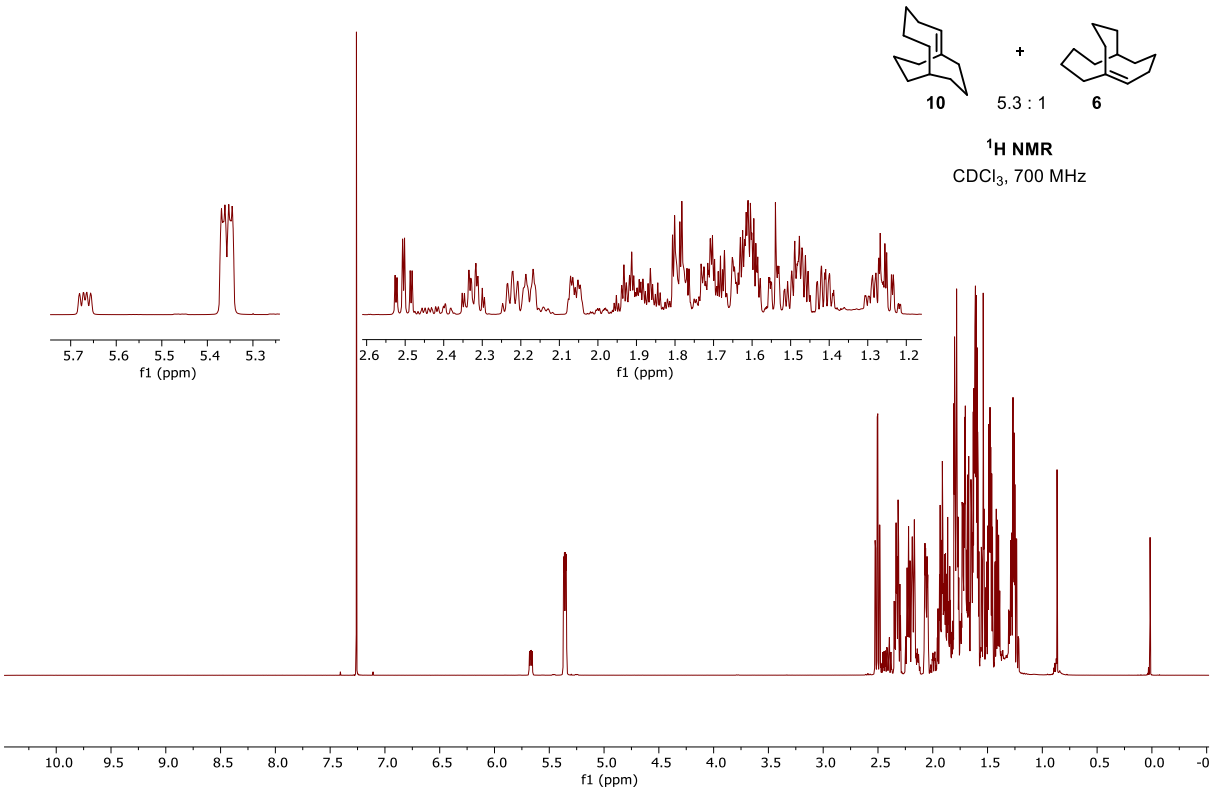


Elimination reaction performed at -78°C, 500MHz. All ratios were based on ^{1}H NMR integration (TopSpin) of the vinyl proton signal.

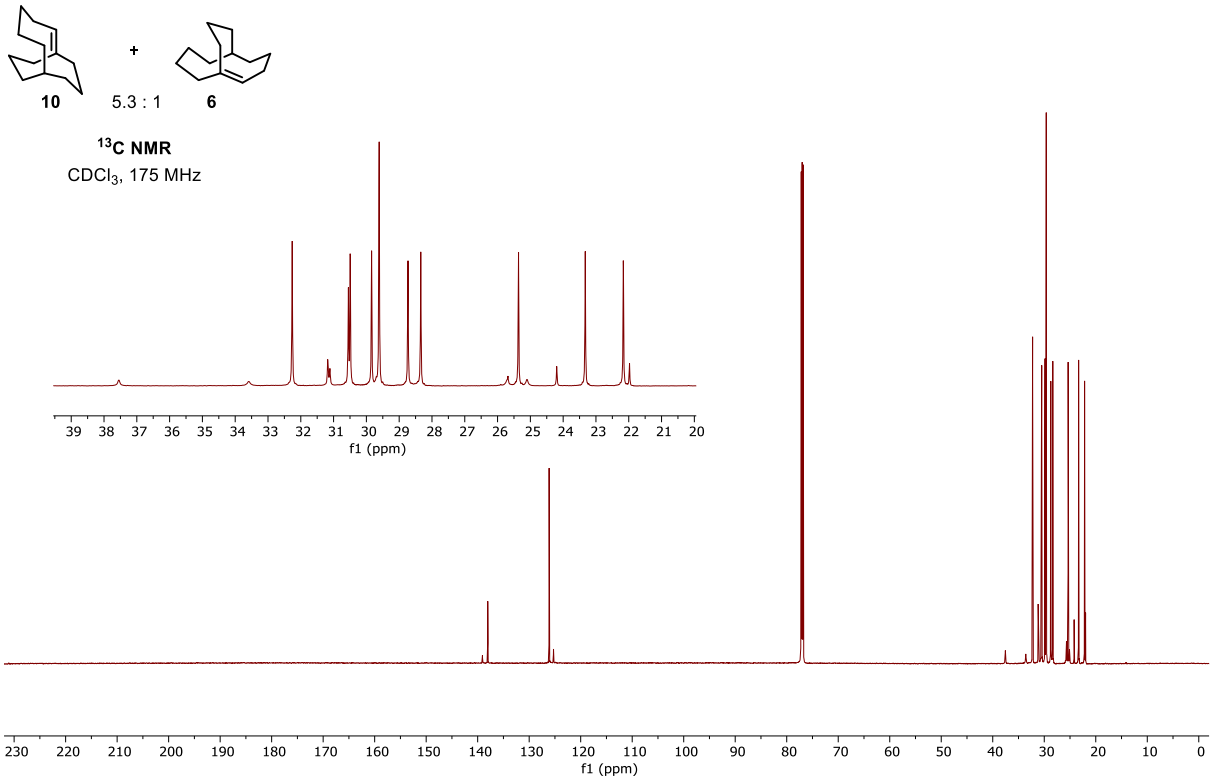


Elimination reaction performed at r.t., 300 MHz

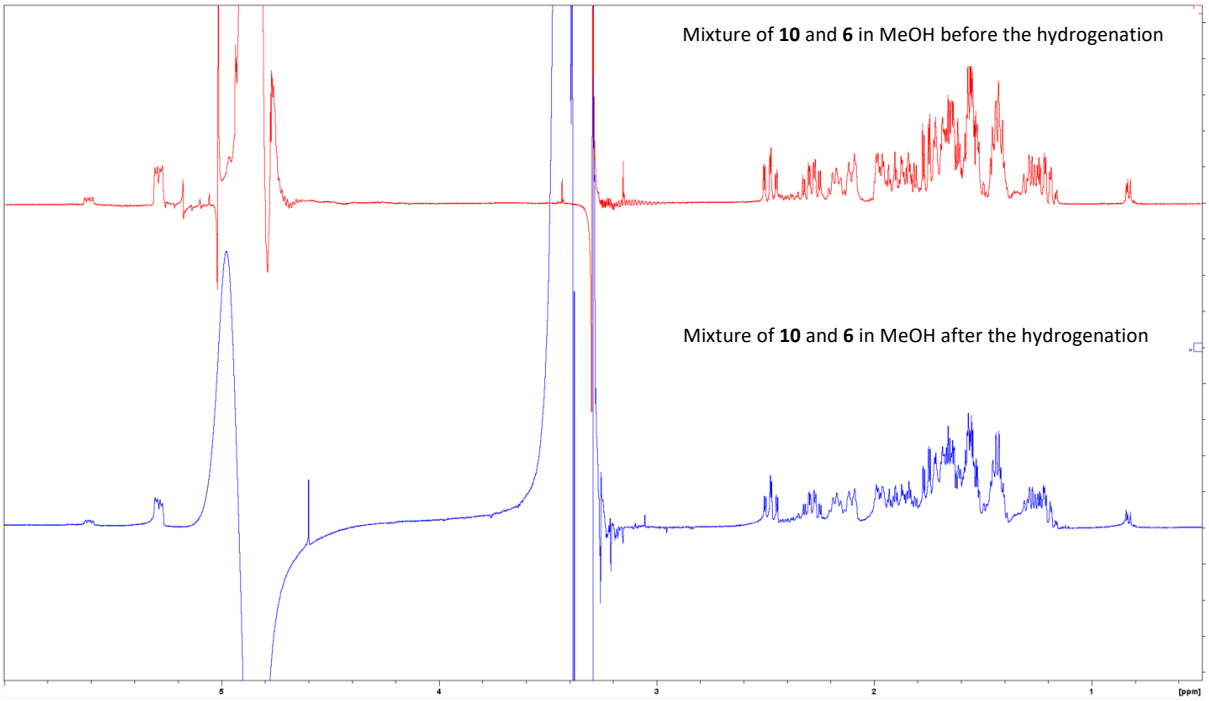
CW_scR104_20240208.1.fid
CW_scR104_20240208



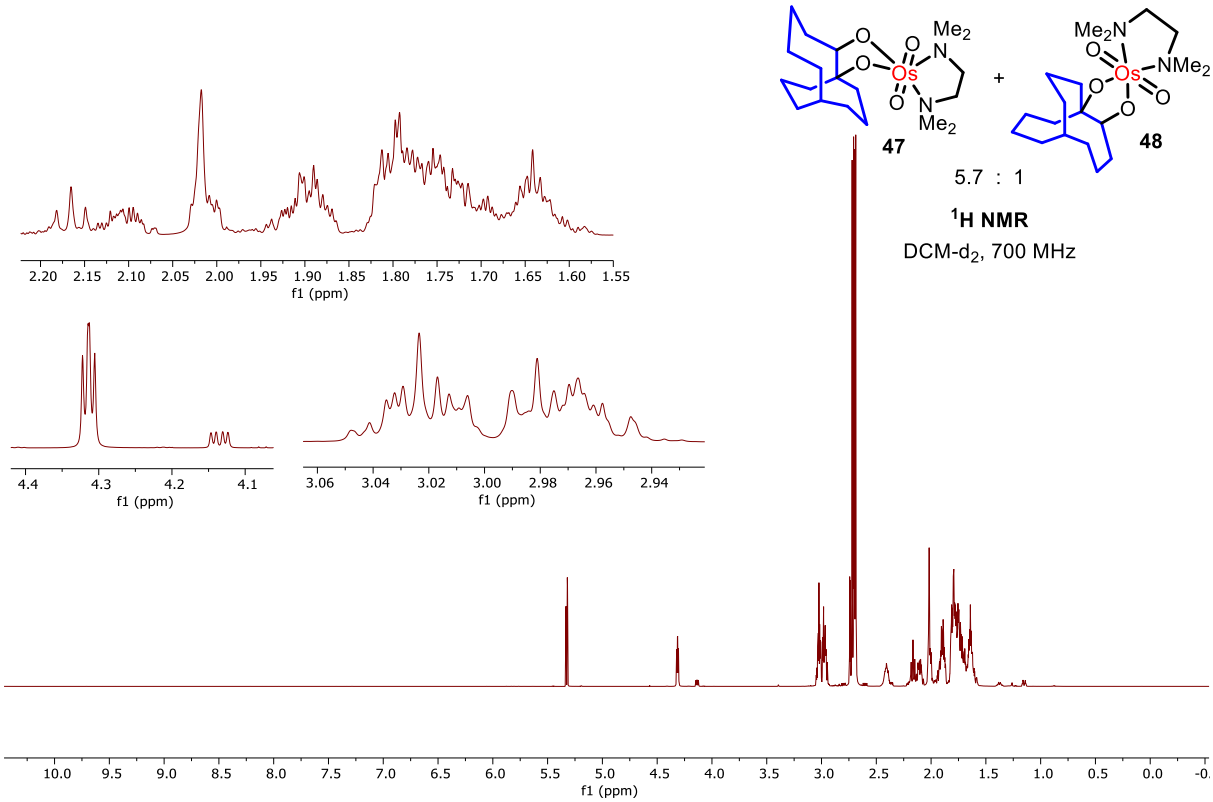
CW_scR104_20240208.7.fid
CW_scR104_20240208



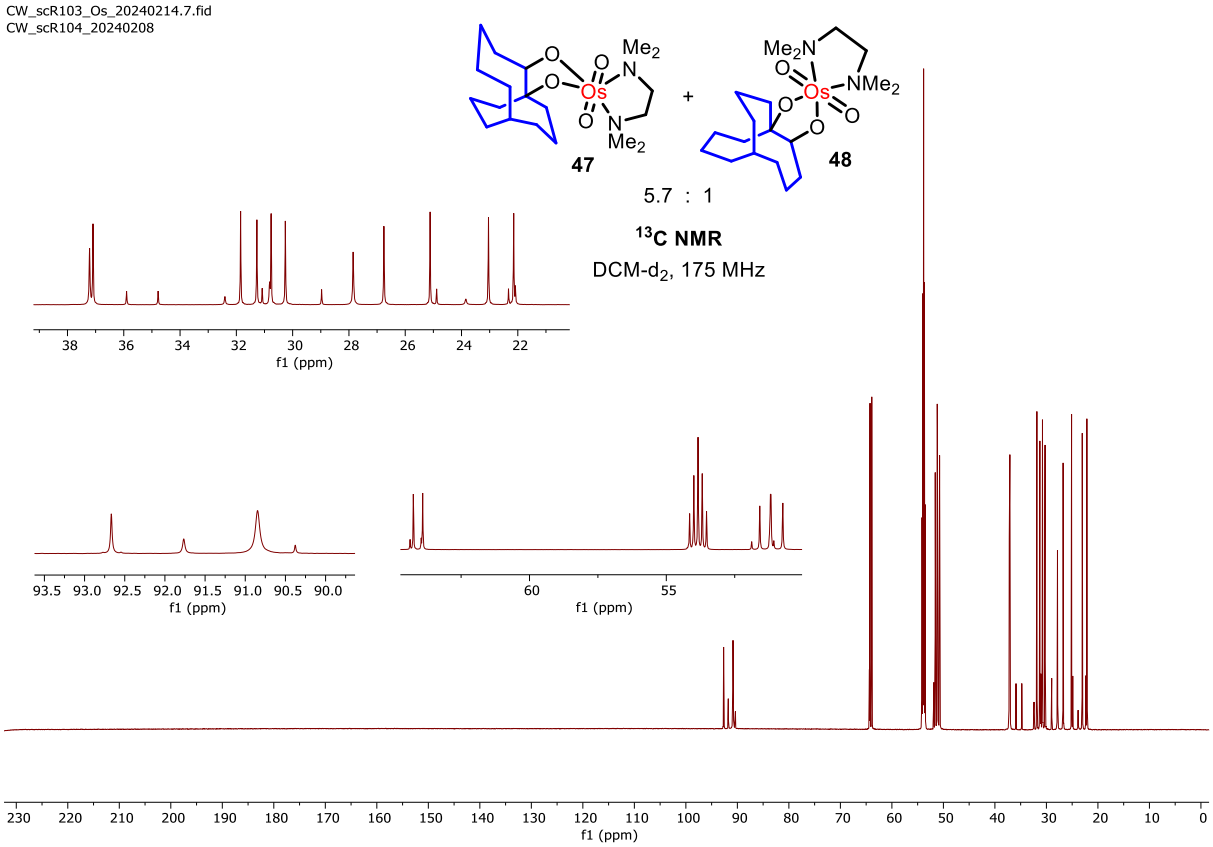
^{1}H NMR (500 MHz) spectra with solvent suppression were recorded using the WET experiment (multiple solvent suppression, enhanced through T1 effects) in TopSpin4.0 with shimming at δ4.7 (water signal) to suppress signals from non-deuterated methanol.

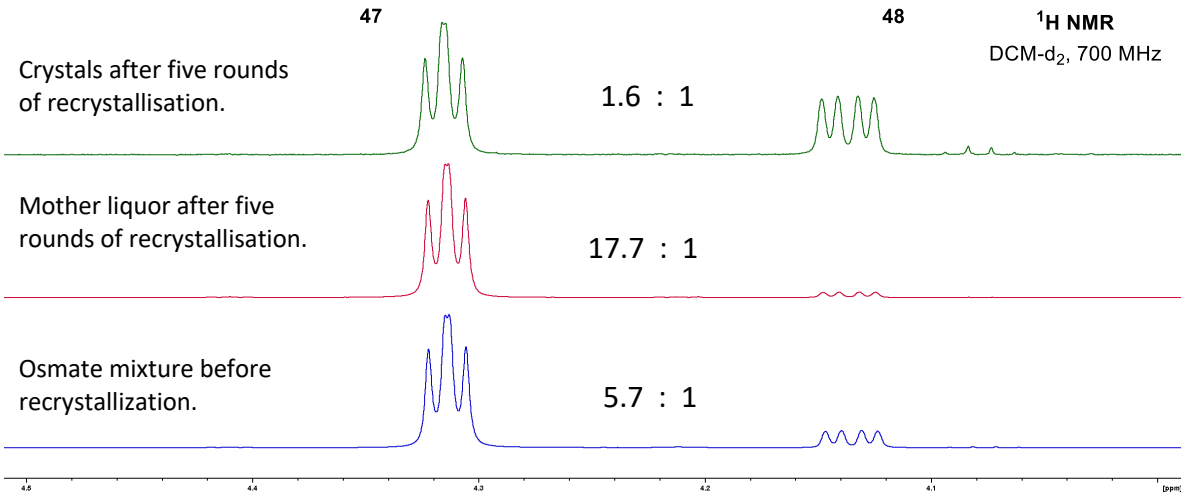


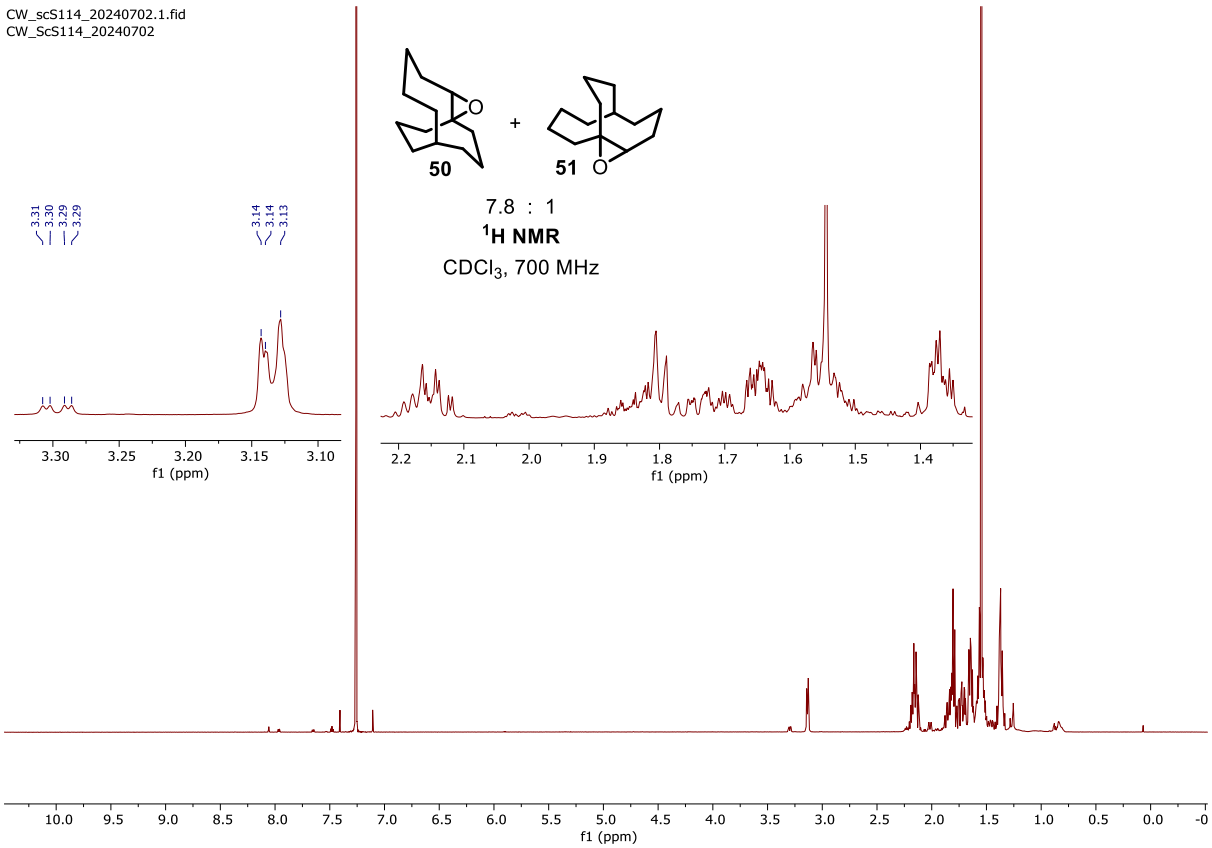
CW_scR103_Os_20240214.1.fid
CW_scR104_20240208

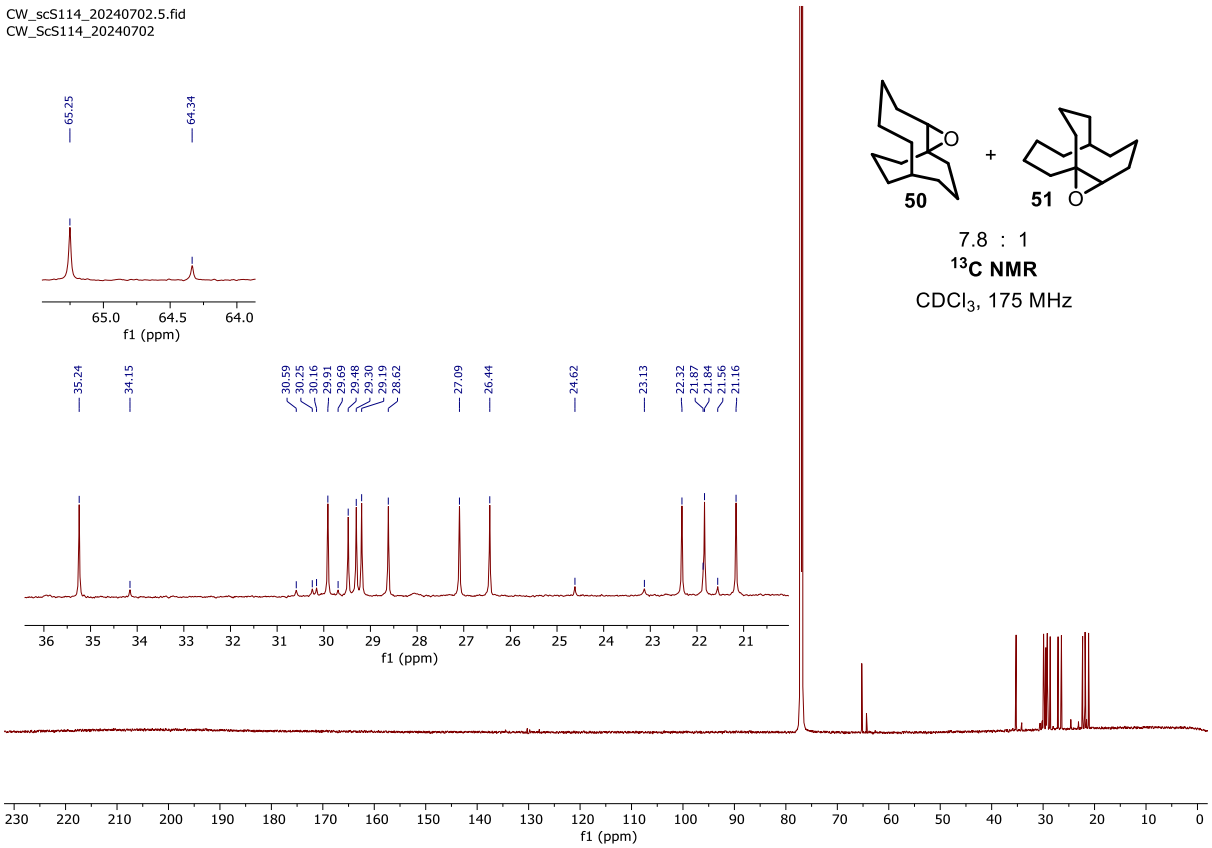


CW_scR103_Os_20240214.7.fid
CW_scR104_20240208



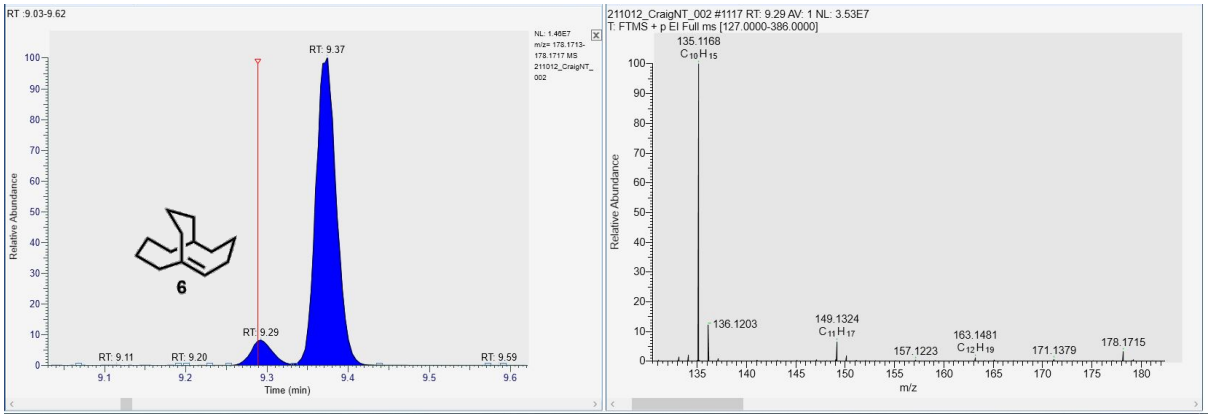

47
48
^{1}H NMR
DCM-d$_2$, 700 MHz
Crystals after five rounds of recrystallisation.
1.6 : 1
Mother liquor after five rounds of recrystallisation.
17.7 : 1
Osmate mixture before recrystallization.
5.7 : 1

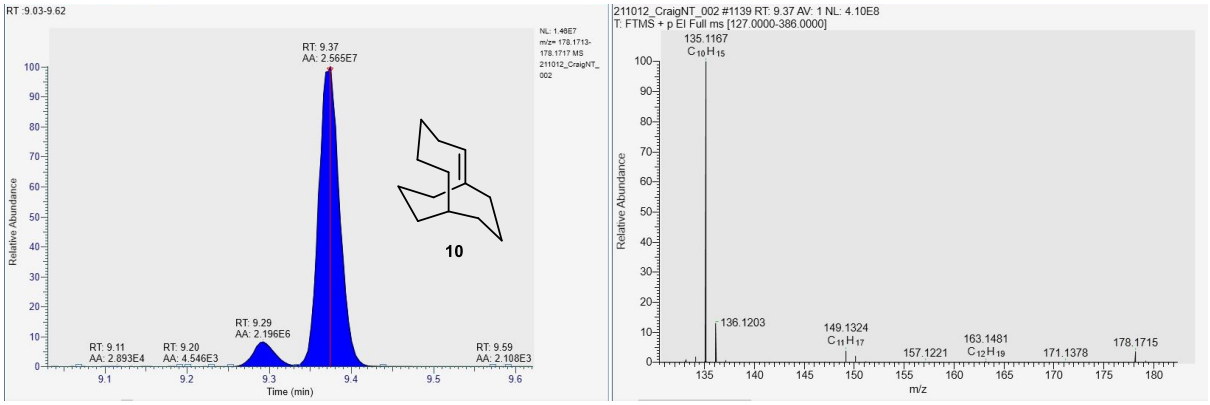

CW_scS114_20240702.1.fid
CW_ScS114_20240702
50
51
7.8 : 1
1H NMR
CDCl3, 700 MHz
3.31
3.30
3.29
3.29
3.14
3.14
3.13
f1 (ppm)


CW_scS114_20240702.5.fid
CW_ScS114_20240702
50
51
7.8 : 1
13C NMR
CDCl3, 175 MHz
65.25
64.34
35.24
34.15
30.59
30.25
30.16
29.91
29.69
29.48
29.30
29.19
28.62
27.09
26.44
24.62
23.13
22.32
21.87
21.84
21.56
21.16
f1 (ppm)

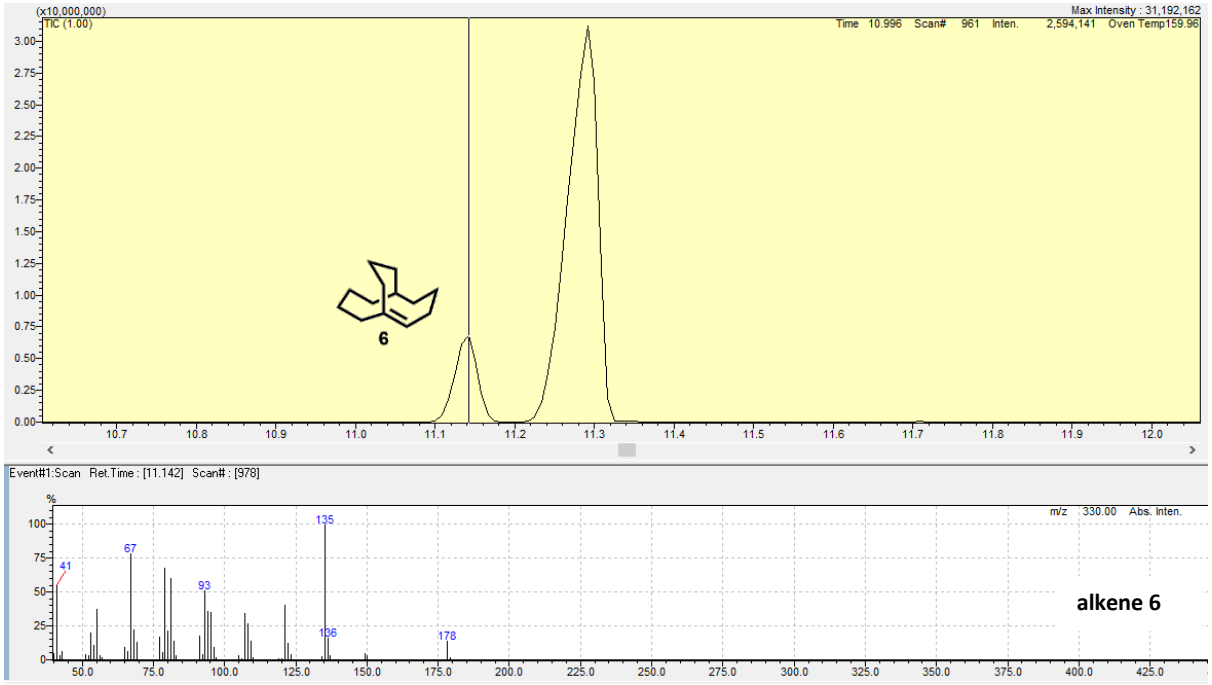
C. GCMS Data

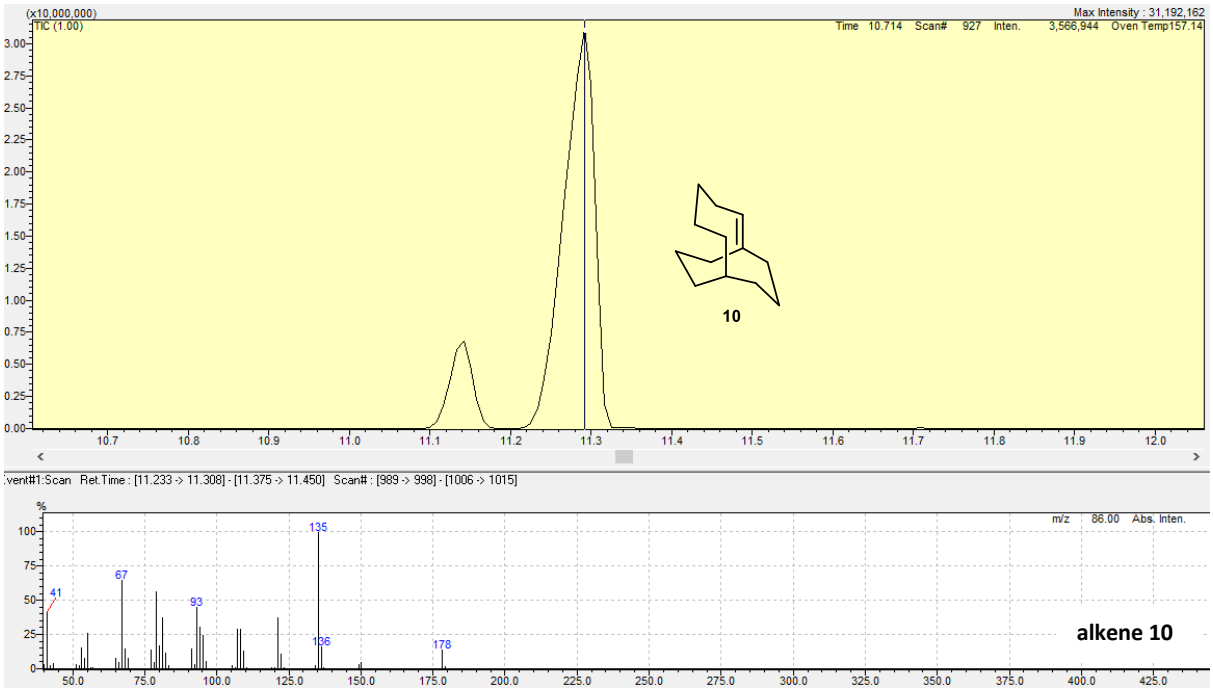
Mixture of alkenes **10** and **6** from the elimination of bicyclo[5.3.3]tridecan-2-ol (**28**)





Pentane extract from the methanolic solution after hydrogenation of **10** and **6**.





D. Olefin Strain Energy Calculations

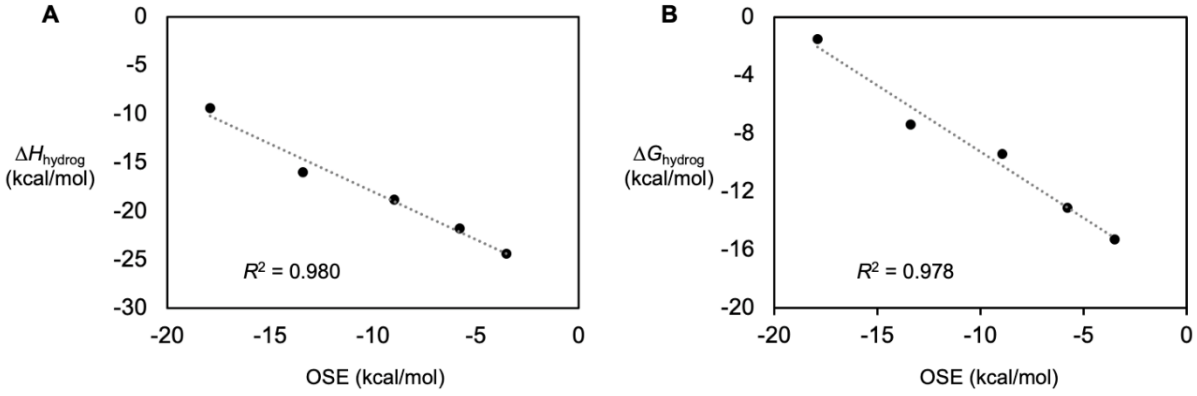
To obtain accurate estimates of olefin strain energies, we applied Rablen's group increment method.[11] This method estimates the strain energy of a hydrocarbon based on the difference between the molecule's computed enthalpy and the sum of a set of group increments, where the group increments represent "strain-free" reference energy contributions for different carbon bonding environments. The strain energies of an alkene and its corresponding alkane allow calculation of the alkene's OSE. The method has been defined for a number of computational model chemistries; in our case we utilised the CBS-QB3 model chemistry.[12, 13] Separately, we calculated the more readily computed enthalpies and free energies of hydrogenation of the alkenes with density functional theory (M06-2X/def2-TZVPP).[14] The values of OSE, DH_{hydrog} and DG_{hydrog} for five alkenes are listed in Table S1. Graphs plotting DH_{hydrog} and DG_{hydrog} against OSE are shown in Figure S2. Raw data for both sets of calculations are provided on the following pages.

Table S1. Olefin strain energies calculated by the group increment method, and enthalpies and free energies of hydrogenation calculated with M06-2X/def2-TZVPP (kcal/mol).

Alkene	**OSE** by CBS-QB3 group increments[a]	**ΔH_{hydrog}** by M06-2X[b]	**ΔG_{hydrog}** by M06-2X[c]
2	–3.5	–24.4	–15.3
4	–9.0	–18.8	–9.4
8	–13.4	–16.0	–7.4
10	–17.9	–9.4	–1.5
13	–5.8	–21.8	–13.1

[a] 0 K. [b] 298.15 K. [c] 298.15 K, 1 atm.

Figure S2. Plots of (**A**) ΔH_{hydrog} against OSE and (**B**) ΔG_{hydrog} against OSE for the alkenes listed in Table S-D1.

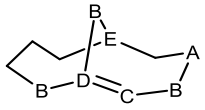


Olefin Strain Data

The method of calculating OSE based on CBS-QB3 group increment values is illustrated below for the case of alkene **2** (Table S2). The group increments and enthalpies are given in Hartree; OSE is given in kcal/mol. Data for all five alkenes and their corresponding alkanes are provided in Table S3.

Table S2. OSE of alkene **2**.

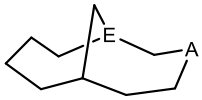
Bicyclo[4.4.1]undec-1-ene (2)



5 x A = C - $(C)_2(H)_2$
3 x B = C - $(C_d)(C)(H)_2$
1 x C = C_d - (H)(C)
1 x D = C_d - $(C)_2$
1 x E =C - $(H)(C)_3$

Groups	Number	Group Increments
C - (C)2(H)2	5	-39.22572
C - (Cd)(C)(H)2	3	-39.22506
Cd - (H)(C)	1	-38.62273
Cd - (C)2	1	-38.03924
C - (H)(C)3	1	-38.63907
	Total:	-429.10482
CBS-QB3 enthalpy	-429.087575	
OSE	-3.5 kcal/mol	

Bicyclo[4.4.1]undecane ($2H_2$)



9 x A = C - $(C)_2(H)_2$
2 x E = C - $(H)(C)_3$

Groups	Number	Group Increments
C - (C)2(H)2	9	-39.22572
C - (H)(C)3	2	-38.63907
	Total:	-430.30962
CBS-QB3 enthalpy	-430.286777	

Table S3. Group increments and enthalpies.[a]

	Alkene		**Corresponding alkane**	
	Sum of group increments	Enthalpy	Sum of group increments	Enthalpy
2	-429.10482	-429.087575	-430.30962	-430.286777
4	-468.33054	-468.298156	-469.53534	-469.488681
8	-546.78198	-546.739438	-547.98678	-547.922938
10	-507.55626	-507.517622	-508.76106	-508.693869
13	-468.33054	-468.284569	-469.53534	-469.480160

[a] CBS-QB3, 0 K, in Hartree.

M06-2X Computed Geometries and Energies

Prior to the quantum mechanical calculations, conformer sampling was undertaken with the OPLS4 forcefield[15] using the mixed torsional/low-mode sampling algorithm in MacroModel.[16] Geometry optimizations on the stable conformers were undertaken with M06-2X/def2-TZVPP in Gaussian 16;[17] the optimized coordinates are listed below. Underneath each set of coordinates are reported the number of imaginary frequencies, electronic potential energy ("E"), enthalpy at 298.15 K ("H"), and Gibbs free energy at 298.15 K and 1 atm ("G"). All energies are given in Hartree.

The hydrogenation energies reported in the paper represent the conversion of the most stable conformer of the alkene into that of the corresponding alkane. To estimate the degree to which other conformers may contribute to the overall hydrogenation energies, Boltzmann analyses were performed using the OPLS4 conformer energies. The results are summarized in Table S4. The results showed that upon inclusion of the additional conformers, the hydrogenation energies become more negative by 0–1 kcal/mol. Because the differences are consistent across the series, the hydrogenation energies display the same trends regardless of whether they are calculated with or without the inclusion of Boltzmann averaging.

Table S4. Effects of conformational averaging on the alkene hydrogenation energies.

Alkene	**Number of conformers with $0 \leq E_{rel} \leq 3$ kcal/mol**		**Effect of Boltzmann averaging on ΔG_{hydrog} (kcal/mol)**	**ΔG_{hydrog} (kcal/mol)**	
	Alkene	Alkane		Without Boltzmann averaging	With Boltzmann averaging
2	2	2	–0.5	–15.3	–15.8
4	5	4	–0.5	–9.4	–9.9
6	5	14	–0.9	–3.6	–4.5
8	2	4	–0.7	–7.4	–8.1
10	1	1	0.0	–1.5	–1.5
13	1	4	–0.8	–13.1	–13.9
25	2	4	–0.9	–8.8	–9.7

H_2
H 0.000000 0.000000 0.369670
H 0.000000 0.000000 -0.369670
0 imaginary frequencies
E = -1.168869
H = -1.155396
G = -1.170179

2
C -0.283990 1.136910 0.458755
C 0.019057 -0.004022 1.394092

C 0.683552 1.704762 -0.253782
C 2.113172 1.229132 -0.219286
C 2.271238 -0.195158 -0.775446
C 1.799568 -1.321553 0.153685
C 0.337590 -1.293980 0.623605
H 0.224986 -2.122006 1.330418
C -0.646236 -1.536880 -0.532537
C -2.099846 -1.107213 -0.274905
C -2.401593 0.355126 -0.632168
C -1.742191 1.428197 0.251581
H -0.835470 -0.169996 2.050947
H 0.865263 0.243287 2.040596
H 0.429297 2.493475 -0.955522
H 2.500898 1.256748 0.804938
H 2.736799 1.907404 -0.801630
H 3.327756 -0.374200 -0.988253
H 1.754476 -0.252893 -1.736259
H 2.436749 -1.312357 1.043750
H 1.986365 -2.276858 -0.345763
H -0.618479 -2.601172 -0.775832
H -0.295483 -1.013042 -1.425311
H -2.378402 -1.311935 0.763413
H -2.755184 -1.729045 -0.887438
H -3.482715 0.510179 -0.619434
H -2.072908 0.518337 -1.662599
H -2.249157 1.458229 1.220372
H -1.876708 2.403928 -0.217953
0 imaginary frequencies
E = -429.955185
H = -429.673281
G = -429.717225

Alkane 2H_2 derived from 2

C 1.990382 -1.260290 -0.357109
C 2.339463 0.187751 -0.710259
C 1.880106 1.255453 0.284127
C 0.393879 1.261436 0.666291
C -0.506504 1.596839 -0.531408
C -1.990382 1.260290 -0.357110
C -2.339463 -0.187751 -0.710259
C -1.880106 -1.255453 0.284127
C -0.393879 -1.261436 0.666290
C 0.506504 -1.596839 -0.531408
C -0.000000 -0.000000 1.447875
H 2.572665 -1.912273 -1.011208

H 2.312576 -1.488565 0.664072
H 3.423937 0.276219 -0.808536
H 1.934422 0.402336 -1.703304
H 2.460645 1.141973 1.204749
H 2.141798 2.236566 -0.123422
H -0.147668 1.088660 -1.429478
H -2.312576 1.488565 0.664071
H -2.572665 1.912273 -1.011208
H -3.423937 -0.276219 -0.808537
H -1.934421 -0.402336 -1.703305
H -2.460646 -1.141973 1.204749
H -2.141798 -2.236566 -0.123423
H -0.277617 -2.085835 1.377772
H 0.147669 -1.088659 -1.429478
H 0.396154 -2.664649 -0.735162
H 0.835256 -0.239695 2.111048
H -0.835256 0.239695 2.111047
H 0.277617 2.085835 1.377773
H -0.396154 2.664649 -0.735162
0 imaginary frequencies
E = -431.174002
H = -430.867494
G = -430.911778

4

C 0.411953 -1.291790 0.431178
C -0.407061 -1.655290 -0.550434
C -1.895282 -1.439623 -0.551911
C -2.278353 -0.000884 -0.939476
C -1.947271 1.136791 0.044906
C -0.481072 1.515736 0.389495
C 0.024460 0.831517 1.670571
C -0.109175 -0.691539 1.701750
C 0.452001 1.476673 -0.851198
C 1.953322 1.199209 -0.648023
C 2.377951 -0.264605 -0.820196
C 1.913897 -1.260903 0.251556
H 0.026130 -2.017638 -1.480011
H -2.333284 -1.678480 0.418796
H -2.360040 -2.117149 -1.270010
H -3.361781 0.027005 -1.083285
H -1.850126 0.224005 -1.918771
H -2.476402 0.947702 0.985036
H -2.418611 2.027836 -0.378278
H -0.536192 1.243509 2.513639

H 1.064558 1.112126 1.843326
H -1.153468 -0.956846 1.855626
H 0.447292 -1.084350 2.556704
H 0.349256 2.445876 -1.344569
H 0.091468 0.745160 -1.570900
H 2.304126 1.584318 0.312098
H 2.498037 1.769401 -1.403256
H 3.468850 -0.305588 -0.871504
H 2.011865 -0.608675 -1.791793
H 2.386078 -1.007097 1.204364
H 2.280177 -2.253182 -0.021313
H -0.530157 2.570313 0.674802
0 imaginary frequencies
E = -469.248855
H = -468.936405
G = -468.982410

Alkane 4H_2 derived from 4

C 0.828663 1.397680 0.483980
H 1.573388 2.103385 0.862518
C -0.426580 2.254393 0.200540
C -1.464999 1.799987 -0.837757
C -2.261075 0.502366 -0.647726
C -1.464999 -0.800857 -0.793853
C -0.828663 -1.397680 0.483980
C 0.426580 -2.254393 0.200540
C 1.464999 -1.799987 -0.837757
C 2.261075 -0.502366 -0.647726
C 1.464999 0.800857 -0.793853
C -0.619689 -0.439287 1.661245
C 0.619689 0.439287 1.661245
H -0.087108 3.236061 -0.141013
H -0.933824 2.436901 1.153474
H -0.991796 1.759886 -1.822553
H -2.191241 2.614321 -0.905897
H -3.028844 0.505862 -1.424786
H -2.808023 0.524018 0.297410
H -0.716235 -0.644547 -1.566487
H -2.128708 -1.566199 -1.202215
H 0.933824 -2.436901 1.153474
H 0.087108 -3.236061 -0.141013
H 0.991796 -1.759886 -1.822553
H 2.191241 -2.614321 -0.905897
H 3.028844 -0.505862 -1.424786
H 2.808023 -0.524018 0.297410

H 0.716235 0.644547 -1.566487
H 2.128708 1.566199 -1.202215
H -0.572080 -1.054984 2.564003
H -1.504621 0.185673 1.786975
H 1.504621 -0.185673 1.786975
H 0.572080 1.054984 2.564003
H -1.573388 -2.103385 0.862518
0 imaginary frequencies
E = -470.458961
H = -470.121686
G = -470.167528

6

C -0.468446 -1.445457 -1.072215
C 0.570493 -1.436256 -0.246121
C -1.919359 -1.346462 -0.721885
C -2.399931 0.102064 -0.950800
C -2.014784 1.215608 0.044915
C -0.538031 1.576241 0.360824
C 1.896192 1.476731 -0.674768
C 1.956149 -1.143642 -0.766548
C 0.443587 -1.604761 1.250353
C -0.344215 -0.522349 1.999746
C -0.043021 0.941854 1.684199
C 0.377600 1.552712 -0.884891
C 2.525952 0.158989 -0.183042
H -0.263936 -1.322352 -2.133985
H -2.503745 -1.993042 -1.380894
H -2.122730 -1.674393 0.296423
H -2.081120 0.399745 -1.954006
H -3.492211 0.095364 -0.983112
H -2.487297 2.116555 -0.355678
H -2.523717 1.026702 0.994981
H -0.575194 2.636685 0.628199
H 2.348667 1.711998 -1.641842
H 2.212766 2.278077 0.000461
H 2.635373 -1.957869 -0.495061
H 1.939151 -1.088882 -1.857702
H -0.028150 -2.568440 1.459290
H 1.446343 -1.666617 1.678335
H -1.412702 -0.684499 1.863213
H -0.165039 -0.672919 3.067505
H 1.019279 1.153506 1.814807
H -0.542286 1.511660 2.473243
H 0.089808 0.765171 -1.570757

H 0.184251 2.484787 -1.424658
H 3.591105 0.202185 -0.421018
H 2.478275 0.094937 0.903649
0 imaginary frequencies
E = -508.547187
H = -508.204264
G = -508.252092

Alkane 6H_2 derived from 6

C 0.455569 1.888070 -0.904960
C -0.817209 1.693386 -0.018087
C 1.868777 1.418255 -0.498599
C 2.357343 0.015957 -0.903398
C 2.095030 -1.221367 -0.030612
C 0.640429 -1.685156 0.190686
C -1.716957 -1.608697 -0.893747
C -2.020801 0.953785 -0.688710
C -0.603717 1.356612 1.471824
C 0.263894 0.202289 2.003788
C 0.091160 -1.249476 1.559455
C -0.216643 -1.399935 -1.044130
C -2.445582 -0.443035 -0.218906
H 0.251775 1.516345 -1.912997
H 0.554352 2.967653 -1.031812
H -1.203926 2.711480 0.048984
H 2.541957 2.105060 -1.017293
H 2.048653 1.608317 0.559114
H 2.009818 -0.182891 -1.921022
H 3.445248 0.083406 -0.984100
H 2.637365 -2.037431 -0.515274
H 2.581330 -1.086224 0.940144
H 0.673994 -2.777010 0.267117
H -2.142243 -1.728547 -1.893513
H -1.925357 -2.540893 -0.359913
H -2.887413 1.598075 -0.528313
H -1.870547 0.939052 -1.772739
H -0.177265 2.253446 1.932016
H -1.601171 1.266873 1.913037
H 1.315670 0.453886 1.886448
H 0.100858 0.213802 3.085334
H -0.941928 -1.579798 1.668357
H 0.652851 -1.837820 2.291749
H -0.058967 -0.383883 -1.390456
H 0.160600 -2.038441 -1.848798
H -3.511885 -0.553747 -0.428434
H -2.361527 -0.494846 0.864740

0 imaginary frequencies
E = -509.747093
H = -509.379386
G = -509.428075

8

H	0.273729	0.123253	0.101744
C	0.873315	0.312579	0.963710
C	1.048392	1.830516	0.948382
C	0.916356	2.342394	-0.489836
C	-0.459215	2.062213	-1.136119
C	-0.630468	0.765724	-1.972132
C	2.176033	-0.448085	0.696406
C	1.985127	-1.784619	-0.038530
C	1.250350	-1.685849	-1.399846
C	-0.234506	-1.596520	-1.183037
C	-1.014976	-0.519902	-1.267531
C	-2.336034	-0.502985	-0.518343
C	-2.250737	-0.883383	0.975780
C	-1.475682	0.036509	1.946760
C	0.031740	-0.227667	2.119455
H	2.011938	2.124521	1.374785
H	0.278267	2.309968	1.559755
H	1.701341	1.895330	-1.109539
H	1.094525	3.419367	-0.508086
H	-0.674818	2.887233	-1.816385
H	-1.232921	2.109447	-0.363906
H	0.265803	0.616013	-2.574574
H	-1.439253	0.958318	-2.684779
H	2.718230	-0.618795	1.632548
H	2.825635	0.181047	0.078821
H	1.442090	-2.489802	0.597899
H	2.969874	-2.225462	-0.205873
H	1.494268	-2.572879	-1.988363
H	1.631883	-0.823908	-1.950710
H	-0.648807	-2.469973	-0.683023
H	-2.789685	0.487530	-0.603992
H	-3.036775	-1.193983	-0.994992
H	-1.854464	-1.898019	1.064067
H	-3.281460	-0.937709	1.334349
H	-1.944383	-0.075581	2.926597
H	-1.636157	1.082185	1.664653
H	0.182781	-1.307639	2.216241
H	0.370190	0.213987	3.062030

0 imaginary frequencies
E = -547.852308

H = -547.480379
G = -547.531395

Alkane 8H_2 derived from 8

C	1.757328	-1.453474	-0.478945
C	2.051891	0.003617	-0.000905
C	0.585430	-2.301218	0.059056
C	-0.753731	-2.311108	-0.706827
C	-1.820927	-1.473063	-0.010674
C	-1.411916	-0.002219	0.000657
C	-0.762053	1.766112	-1.646928
C	1.751683	1.145475	-1.022971
C	-1.824591	0.721717	1.279896
C	-1.826302	0.742193	-1.266240
C	0.577602	1.100029	-2.023515
C	1.754650	0.316945	1.499731
C	0.579741	1.203698	1.963278
C	-0.757557	0.541325	2.354495
H	1.729698	-1.464327	-1.572251
H	2.655770	-2.015946	-0.218524
H	3.142315	0.005819	-0.001502
H	0.951491	-3.328322	0.089039
H	0.392537	-2.037720	1.102970
H	-0.603746	-1.946543	-1.727963
H	-1.104245	-3.339937	-0.802766
H	-2.795250	-1.587120	-0.494556
H	-1.934682	-1.842616	1.013073
H	-0.323030	0.000072	-0.000164
H	-1.115473	2.362260	-2.489688
H	-0.611766	2.469113	-0.821495
H	1.722579	2.097599	-0.485576
H	2.648571	1.203794	-1.642295
H	-1.942060	1.792719	1.088220
H	-2.797895	0.356077	1.619634
H	-1.941264	0.040166	-2.097797
H	-2.801030	1.216461	-1.119982
H	0.385849	0.063473	-2.315315
H	0.940697	1.587037	-2.929502
H	1.728284	-0.624628	2.055522
H	2.651376	0.825647	1.858150
H	0.943415	1.745457	2.837384
H	0.384660	1.974336	1.211979
H	-1.109928	0.971764	3.293166
H	-0.604366	-0.524804	2.549595

0 imaginary frequencies

E = -549.058257
H = -548.661254
G = -548.713420

10

C	-0.438909	1.488529	-0.864024
C	0.992758	1.532719	-0.252792
C	-1.651138	1.476851	0.087886
C	-2.523457	-0.918368	0.097339
C	-1.216016	-1.448557	-0.411324
C	-0.032623	-1.448228	0.198547
C	1.332088	-0.062527	1.847949
C	1.152768	1.342073	1.272222
C	2.012487	0.684845	-1.056654
C	1.631239	-0.707958	-1.584932
C	1.206481	-1.805800	-0.596472
C	0.197270	-1.067169	1.636629
C	-2.771347	0.531276	-0.363549
H	-0.537960	2.348833	-1.530087
H	-0.520887	0.621946	-1.510151
H	1.328193	2.562416	-0.397616
H	-1.356015	1.167994	1.089418
H	-2.043743	2.489313	0.195468
H	-3.339949	-1.551505	-0.256366
H	-2.559039	-0.943551	1.187040
H	-1.228849	-1.758079	-1.456135
H	2.259439	-0.484879	1.456032
H	1.493248	0.040995	2.923500
H	2.060378	1.888472	1.544394
H	0.345703	1.857287	1.795756
H	2.294147	1.261896	-1.941589
H	2.927396	0.603241	-0.461227
H	0.834451	-0.603603	-2.324509
H	2.495783	-1.077739	-2.142518
H	2.034770	-2.048717	0.071737
H	1.009131	-2.707507	-1.179727
H	-0.716469	-0.697056	2.099770
H	0.469080	-1.980395	2.178593
H	-3.728541	0.860417	0.045779
H	-2.869878	0.564101	-1.452508

0 imaginary frequencies
E = -508.551398
H = -508.208478
G = -508.256426

Alkane 10H$_2$ derived from 10

C -2.358564 -0.704932 0.110883
C -1.112226 -1.564671 -0.242666
C -2.451452 0.764608 -0.328944
C -0.222896 2.229631 -0.360930
C 1.131530 1.946468 0.319797
C 1.951957 0.632645 0.178211
C 1.174706 -1.249779 -1.520531
C -0.334830 -0.997096 -1.446067
C -0.303397 -1.913954 1.013446
C 0.376603 -0.787738 1.787812
C 1.774737 -0.353774 1.344126
C 2.015469 -0.004575 -1.230090
C -1.545724 1.821381 0.333475
H -3.236446 -1.196091 -0.315313
H -2.507958 -0.738361 1.194628
H -1.503682 -2.532555 -0.566651
H -2.362031 0.842086 -1.415501
H -3.481307 1.056329 -0.110497
H -0.254441 3.317225 -0.447048
H -0.206711 1.885526 -1.395955
H 1.793837 2.730173 -0.055457
H 1.023852 2.154431 1.390081
H 2.971823 0.994867 0.331751
H 1.478113 -2.061290 -0.858847
H 1.436774 -1.583740 -2.526068
H -0.815782 -1.373992 -2.351157
H -0.472784 0.074905 -1.486160
H -1.012836 -2.399436 1.689192
H 0.437789 -2.682241 0.780154
H -0.278806 0.081845 1.835933
H 0.477192 -1.129751 2.820489
H 2.381258 -1.244773 1.149476
H 2.234737 0.128076 2.211017
H 1.772803 0.759539 -1.975662
H 3.058289 -0.274076 -1.414545
H -2.147400 2.729726 0.390350
H -1.361756 1.552301 1.374658

0 imaginary frequencies
E = -509.746146
H = -509.378781
G = -509.428977

13

C -0.946918 1.212617 -1.142921
C 0.459179 1.523206 -0.519264

C -2.122925 0.777039 -0.236733
C -2.388024 -0.746889 -0.166227
C -1.105822 -1.504682 -0.351473
C -0.028725 -1.376604 0.414783
C 0.882951 0.488801 1.879069
C 0.533528 1.697050 1.013699
C 1.665501 0.718483 -1.084418
C 1.624742 -0.796962 -1.340795
C 1.317272 -1.737060 -0.164740
C -0.044216 -0.721211 1.767110
H -0.826722 0.479072 -1.942705
H -1.264740 2.129843 -1.640208
H 0.671336 2.533219 -0.876610
H -1.969534 1.157197 0.771435
H -3.032033 1.264645 -0.592283
H -2.884778 -0.988420 0.775751
H -3.082542 -1.029246 -0.957497
H -0.985209 -2.014562 -1.303504
H 1.903469 0.174716 1.649021
H 0.904238 0.814588 2.921354
H 1.314827 2.438919 1.200315
H -0.387226 2.158137 1.376541
H 1.908803 1.159513 -2.054737
H 2.526224 0.944205 -0.445911
H 0.886735 -0.999105 -2.119815
H 2.593624 -1.068043 -1.769341
H 2.103242 -1.682444 0.590592
H 1.312163 -2.762894 -0.539163
H -1.060725 -0.445878 2.050382
H 0.289582 -1.466192 2.497846
0 imaginary frequencies
E = -469.235278
H = -468.922860
G = -468.968843

Alkane 13H_2 derived from 13 (and 25)

C 2.249508 0.316311 -0.201354
C 1.498722 -1.025485 -0.142938
C 1.561578 1.666796 0.032934
C 0.269808 1.967023 -0.740408
C -1.064685 1.851161 0.011086
C -1.800578 0.500998 0.155243
C -0.068993 -0.435447 1.944700
C 0.901334 -1.378295 1.227993
C 0.614600 -1.322481 -1.387867
C -0.884508 -1.564236 -1.221676

C -1.815183 -0.357781 -1.124950
C -1.505520 -0.278555 1.448139
H 3.080281 0.255357 0.508873
H 2.715520 0.356174 -1.191232
H 2.317934 -1.743941 -0.236132
H 1.392214 1.838655 1.095331
H 2.302809 2.417390 -0.251589
H 0.328896 3.006749 -1.067880
H 0.231768 1.383965 -1.661225
H -0.948992 2.297663 1.004782
H -1.759336 2.505625 -0.521266
H -2.843045 0.804444 0.281936
H -0.146244 -0.814548 2.967570
H 0.379049 0.551070 2.045738
H 0.447097 -2.372063 1.167006
H 1.755399 -1.495189 1.901943
H 0.768240 -0.549636 -2.143776
H 1.013608 -2.234653 -1.836244
H -1.209570 -2.130923 -2.097754
H -1.059364 -2.228809 -0.373356
H -2.828460 -0.752765 -1.232055
H -1.659667 0.285059 -1.996891
H -2.036530 0.244012 2.248578
H -1.978110 -1.263700 1.382234
0 imaginary frequencies
E = -470.450166
H = -470.112963
G = -470.159916

25

C -0.184824 1.933681 0.397655
C -1.426136 0.996482 0.331725
C 1.152892 1.735825 -0.349676
C 2.215449 0.774260 0.209884
C 2.215832 -0.636413 -0.421127
C 0.821739 -1.186265 -0.463829
C -0.253910 -0.856460 1.838856
C -1.503622 -0.070800 1.446323
C -1.872945 0.510791 -1.069101
C -1.426395 -0.895008 -1.510932
C 0.062653 -0.922424 -1.523977
C 0.286418 -1.830145 0.788555
H -0.550522 2.900473 0.041252
H 0.041531 2.091972 1.458367
H -2.227500 1.687474 0.607342
H 0.959454 1.501542 -1.398319

H 1.606171 2.729676 -0.355769
H 3.201730 1.208294 0.033328
H 2.117048 0.705364 1.293857
H 2.600424 -0.550472 -1.439502
H 2.897711 -1.284219 0.134144
H 0.528183 -0.158561 2.137657
H -0.496176 -1.431411 2.736481
H -1.830001 0.446844 2.352165
H -2.308917 -0.772672 1.206267
H -2.965623 0.532611 -1.095602
H -1.536889 1.238267 -1.814958
H -1.837666 -1.638383 -0.827299
H -1.843054 -1.102260 -2.497898
H 0.533775 -0.471202 -2.393306
H -0.503353 -2.539361 0.533489
H 1.090761 -2.415120 1.242168
0 imaginary frequencies
E = -469.242297
H = -468.929878
G = -468.975667

44

C -2.101736 -0.074910 0.000023
H -2.664387 -0.405012 -0.875679
H -2.091766 1.012002 -0.000569
H -2.663988 -0.404064 0.876345
C -0.729429 -0.673440 0.000017
H -0.705371 -1.759782 0.000065
C 0.443593 -0.043743 -0.000009
C 0.621477 1.447385 -0.000047
H 1.196756 1.756963 0.875955
H 1.196707 1.756937 -0.876090
H -0.316224 1.995325 -0.000018
C 1.734873 -0.813205 0.000008
H 2.335601 -0.558326 -0.876724
H 2.335596 -0.558298 0.876735
H 1.564413 -1.888270 0.000024
0 imaginary frequencies
E = -196.508962
H = -196.364300
G = -196.402032

Alkane 44H_2 derived from 44

C 0.742124 -0.696258 0.260079
H 0.751525 -1.736657 -0.075233

H 0.624688 -0.725948 1.348575
C -0.481738 -0.003480 -0.341781
H -0.363141 -0.005604 -1.431043
C 2.071152 -0.040799 -0.095415
H 2.159740 0.952737 0.343406
H 2.910974 -0.634366 0.264912
H 2.175160 0.062449 -1.177382
C -1.749917 -0.777507 0.003695
H -1.904742 -0.786126 1.085505
H -2.629404 -0.323929 -0.454756
H -1.687259 -1.813239 -0.332740
C -0.601901 1.445460 0.121653
H -0.651760 1.489974 1.212983
H 0.244684 2.050389 -0.201340
H -1.508781 1.905825 -0.272268
0 imaginary frequencies
E = -197.731835
H = -197.562907
G = -197.600611

45
C 1.829976 -0.022441 -0.360315
C 1.145937 -1.205955 0.314544
C 1.198358 1.285978 0.106182
H 1.710810 -0.113452 -1.443776
H 2.900652 -0.021752 -0.153016
C -0.327490 -1.259694 -0.076376
H 1.226748 -1.091253 1.399271
H 1.639777 -2.142784 0.053815
C -0.303695 1.216685 0.095258
H 1.528805 2.113147 -0.525957
H 1.545456 1.525651 1.117325
C -1.000893 0.087881 -0.003351
H -0.867226 -1.960953 0.566300
H -0.433666 -1.650201 -1.095174
H -0.840908 2.157499 0.165616
C -2.498968 0.069366 -0.054889
H -2.909104 -0.488332 0.790594
H -2.915025 1.075470 -0.040092
H -2.845663 -0.433966 -0.961227
0 imaginary frequencies
E = -273.931023
H = -273.747847
G = -273.786272

Alkane 45H_2 derived from 45

C	-0.090338	0.325052	1.253149
C	0.575238	0.894333	-0.000000
C	-0.090338	-1.201750	1.257895
H	-1.124799	0.686195	1.290703
H	0.409121	0.709653	2.145543
C	-0.090338	0.325052	-1.253149
H	1.621426	0.564916	-0.000000
C	-0.754986	-1.755509	0.000000
H	-0.592997	-1.577519	2.150725
H	0.943309	-1.559313	1.302893
C	-0.090338	-1.201750	-1.257895
H	0.409121	0.709653	-2.145543
H	-1.124799	0.686195	-1.290703
H	-1.812322	-1.471690	0.000000
H	-0.719982	-2.846214	0.000000
H	0.943309	-1.559313	-1.302893
H	-0.592997	-1.577519	-2.150725
C	0.547627	2.416658	-0.000000
H	1.042956	2.822485	0.883244
H	1.042956	2.822485	-0.883244
H	-0.483469	2.777468	-0.000000

0 imaginary frequencies

E = -275.154021

H = -274.946640

G = -274.985141

E. X-ray Crystallography

Table S5. Crystal and Refinement Data

	46	**47/48**·H_2O
CCDC	2378473	2378474
Formula	$C_{18}H_{36}N_2O_4Os$	$C_{19}H_{40}N_2O_5Os$
M.W	534.69	566.73
Crystal system	orthorhombic	orthorhombic
Space group	$P2_12_12_1$	*Pbca*
a (Å)	11.4540(2)	14.241(3)
b (Å)	11.5998(2)	13.816(2)
c (Å)	15.4489(3)	22.522(4)
V (Å^3)	2052.60(6)	4431(1)
T (K)	190(2)	190(2)
Z	4	8
R1 (obsd data)	0.0384	0.0474
wR_2	0.0965	0.1382
GOF	1.048	1.057

The crystal structures of the Os(VI) complexes **46** and **47**/**48**·H_2O were determined. In each case disorder of the hydrocarbon component of the bicyclic ring system was a feature. In the structure of **46**, the 6 donor atoms and the metal are perfectly ordered but all other atoms are disordered between two positions where they were refined with complementary occupancies and isotropic thermal parameters (ratio 54:46%). The tetramethylethylenediamine (TMEDA) ligand is disordered between its λ and δ conformers and this is correlated with disorder of the [4.3.3] hydrocarbon moiety with the two contributors (shown in orange and purple in Figure S3) related by an approximate mirror plane symmetry element passing through Os1, O1 and O2. The absence of any classical H-bonding donors facilitates this disorder. The disordered C-atoms were refined with restraints on the geometries of the two bicyclic hydrocarbon contributors using the SAME command in SHELXL and a common refined C−C bond length (DFIX). The refined thermal parameters of all disordered atoms were consistent.

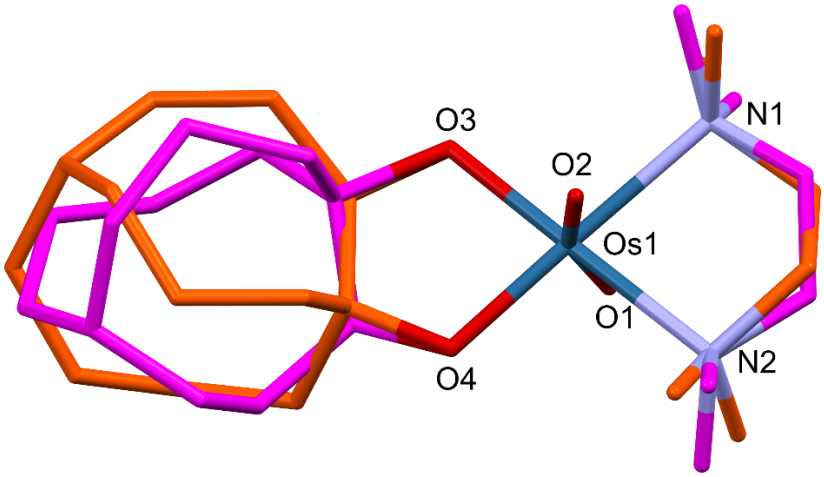


Figure S3. Disorder in the structure of **46**.

The crystal structure of **47**/**48**·H_2O was more complicated and comprised a non-stoichiometric co-crystal of **47** ([5.3.3] isomer, 36%) and **48** ([4.4.3] isomer, 64%). The metal, six donor atoms and the TMEDA ligand are at 100% occupancy while the bicyclic hydrocarbon moieties are disordered (Figure S4). Isotropic refinement of the C-atoms within the bicyclic ring systems was necessary to resolve their positional parameters and restraints on the C–C bonds and 1-3 positions were applied during refinement which resulted in acceptable thermal parameters.

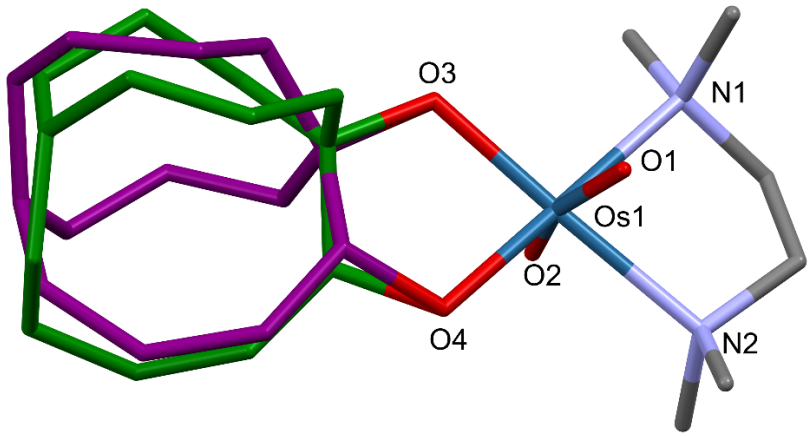


Figure S4. Disorder in the structure of the co-crystal **47**/**48**·H_2O with **47** ([5.3.3] isomer) shown in green and **48** ([4.4.3] isomer) in purple.

F. References

1 G. M. Sheldrick, *Acta Crystallogr. C Struct. Chem.*, 2015, **71**, 3.

2 L. J. Farrugia, *J. Appl. Crystallogr.*, 1999, **32**, 837.

3 H. C. Brown, *Organic Synthesis via Boranes*, John Wiley & Sons, 1975.

4 H. C. Brown, A. K. Mandal and S. U. Kulkarni, *J. Org. Chem.*, 1977, **42**, 1392.

5 G. W. Kramer and H. C. Brown, *J. Organomet. Chem.*, 1974, **73**, 1.

6 R. S. Dhillon, *Preparation and Properties. In Hydroboration and Organic Synthesis: 9-Borabicyclo[3.3.1]nonane (9-BBN)*, Springer Berlin Heidelberg, 2007, pp 5-15.

7 N. J. Cusack, C. B. Reese, A. C. Risius and B. Roozpeikar, *Tetrahedron*, 1976, **32**, 2157.

8 A. S. Burns, C. Dooley, P. R. Carlson, J. W. Ziller and S. D. Rychnovsky, *Org. Lett.*, 2019, **21**, 10125.

9 D. T. Taber, P. W. DeMatteo and R. A. Hassan, *Org. Synth.*, 2013, 350.

10 J. E. McMurry, T. Lectka and C. N. Hodge, *J. Am. Chem. Soc.*, 1989, **111**, 8867.

11 P. R. Rablen, *Chemistry* 2020, **2**, 347-360.

12 J. A. Montgomery Jr., M. J. Frisch, J. W. Ochterski and G. A. Petersson, *J. Chem. Phys.*, 1999, **110**, 2822.

13 J. A. Montgomery Jr., M. J. Frisch, J. W. Ochterski and G. A. Petersson, *J. Chem. Phys.*, 2000, **112**, 6532.

14 Y. Zhao and D. G. Truhlar, *Theor. Chem. Acc.*, 2008, **120**, 215.

15 C. Lu, C. Wu, D. Ghoreishi, W. Chen, L. Wang, W. Damm, G. A. Ross, M. K. Dahlgren, E. Russell, C. D. Von Bargen, R. Abel, R. A. Friesner and E. D. Harder, *J. Chem. Theory Comput.*, 2021, **17**, 4291.

16 MacroModel, Schrödinger, LLC, New York, NY, 2021.

17 Gaussian 16, Revision C.01, M. J. Frisch, G. W. Trucks, H. B. Schlegel, G. E. Scuseria, M. A. Robb, J. R. Cheeseman, G. Scalmani, V. Barone, G. A. Petersson, H. Nakatsuji, X. Li, M. Caricato, A. V. Marenich, J. Bloino, B. G. Janesko, R. Gomperts, B. Mennucci, H. P. Hratchian, J. V. Ortiz, A. F. Izmaylov, J. L. Sonnenberg, D. Williams-Young, F. Ding, F. Lipparini, F. Egidi, J. Goings, B. Peng, A. Petrone, T. Henderson, D. Ranasinghe, V. G. Zakrzewski, J. Gao, N. Rega, G. Zheng, W. Liang, M. Hada, M. Ehara, K. Toyota, R. Fukuda, J. Hasegawa, M. Ishida, T. Nakajima, Y. Honda, O. Kitao, H. Nakai, T. Vreven, K. Throssell, J. A. Montgomery, Jr., J. E. Peralta, F. Ogliaro, M. J. Bearpark, J. J. Heyd, E. N. Brothers, K. N. Kudin, V. N. Staroverov, T. A. Keith, R. Kobayashi, J. Normand, K. Raghavachari, A. P. Rendell, J. C. Burant, S. S. Iyengar, J. Tomasi, M. Cossi, J. M. Millam, M. Klene, C. Adamo, R. Cammi, J. W. Ochterski, R. L. Martin, K. Morokuma, O. Farkas, J. B. Foresman and D. J. Fox, Gaussian, Inc., Wallingford CT, 2016.