Supplementary Material

Stereospecific cyclization of a pseudo-C_2-symmetric unsaturated diol

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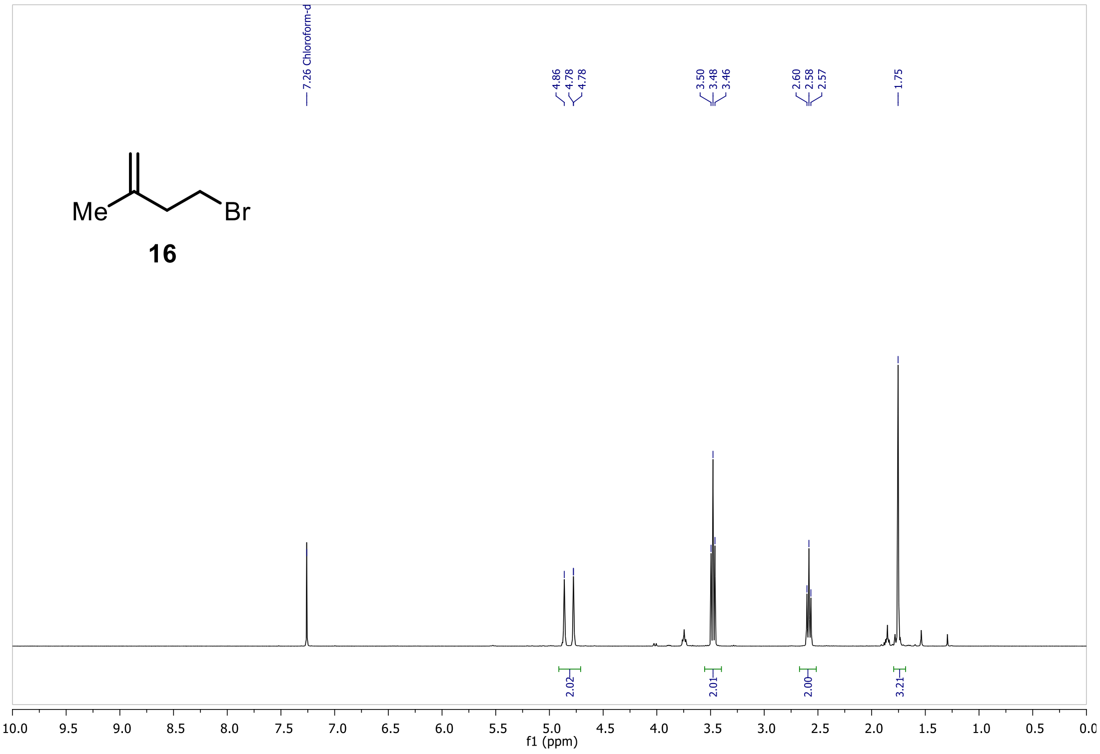
Table of Contents

1. General Information

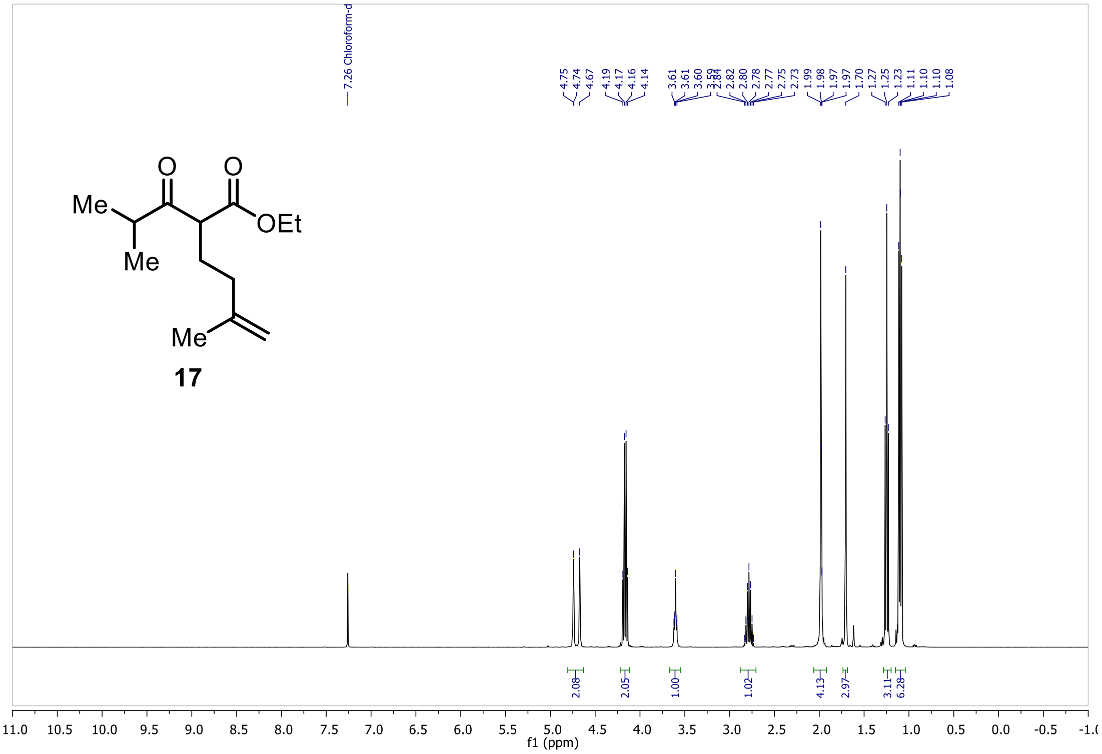
Unless otherwise stated, all glassware was flame-dried before use and all reactions were performed under an atmosphere of argon. All solvents were distilled from appropriate drying agents prior to use. All reagents were used as received from commercial suppliers unless otherwise stated. Trifluoromethanesulfonic anhydride (Tf_2O) was distilled over P_4O_{10} prior to use and stored under inert atmosphere in the fridge for a maximum of roughly 3 weeks.[1] Reaction progress was monitored by thin layer chromatography (TLC) performed on aluminum plates coated with silica gel F254 with 0.2 mm thickness. Chromatograms were visualized by fluorescence quenching with UV light at 254 nm or by staining using potassium permanganate. Flash column chromatography was performed using silica gel 60 (230-400 mesh, Merck and co.). Neat infrared spectra were recorded using a Perkin-Elmer Spectrum 100 FT-IR spectrometer. Wavenumbers (ν_{max}) are reported in cm^{-1}. Mass spectra were obtained using a Finnigan MAT 8200 or (70 eV) or an Agilent 5973 (70 eV) spectrometer, using electrospray ionization (ESI). Optical rotations were measured on a Perkin Elmer 341 polarimeter using a 100 mm path-length cell at 589 nm (c given in g/100 ml). Chiral HPLC was performed using AGILENT Infinity 1260 with Chiralpak I, Chiralpak IC, or Lux-3 Cellulose-3 columns. Details on chromatographic conditions are indicated under each compound. All ^1H NMR and ^{13}C NMR spectra were recorded using a Bruker AV-400 or AV-600 spectrometer at 300K. Chemical shifts are given in parts per million (ppm, δ), referenced to the solvent peak of $CDCl_3$, defined at δ = 7.26 ppm (^1H-NMR) and δ = 77.16 (^{13}C-NMR). Coupling constants are quoted in Hz (J). ^1H NMR splitting patterns are designated as singlet (s), doublet (d), triplet (t), quartet (q) as they appeared in the spectrum. If the appearance of a signal differs from the expected splitting pattern, the observed pattern is designated as apparent (app). Splitting patterns that could not be interpreted or easily visualized are designated as multiplet (m) or broad (br).

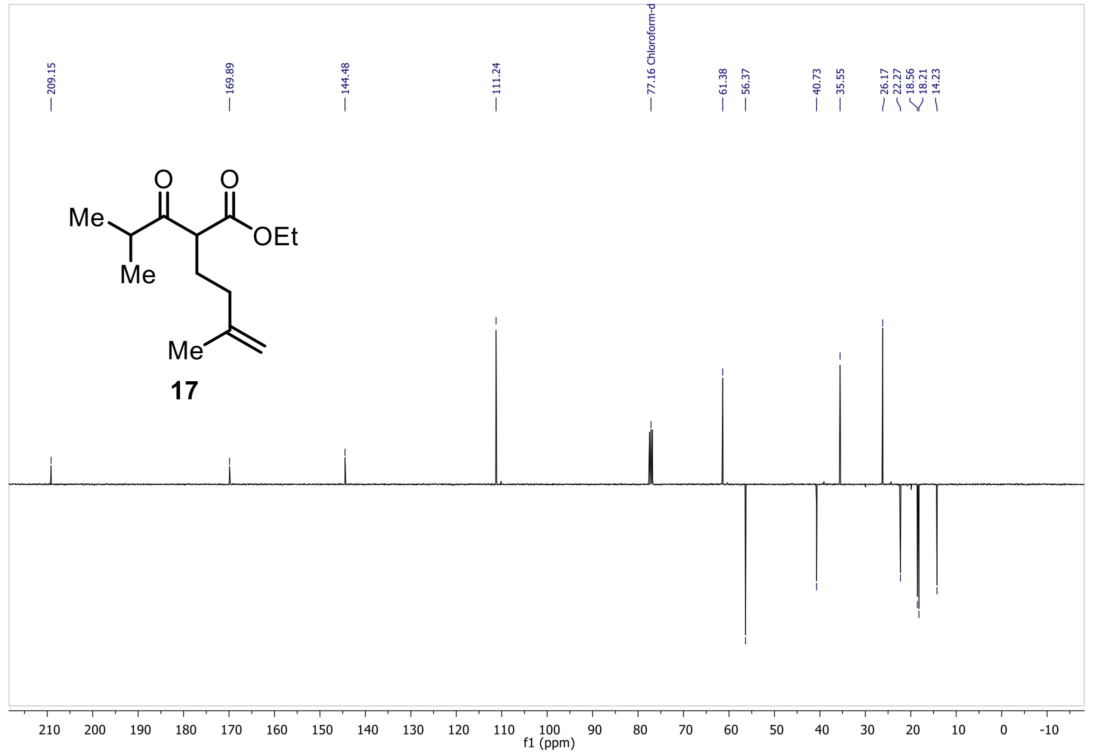
2. NMR Spectra

4-Bromo-2-methylbut-1-ene (16)

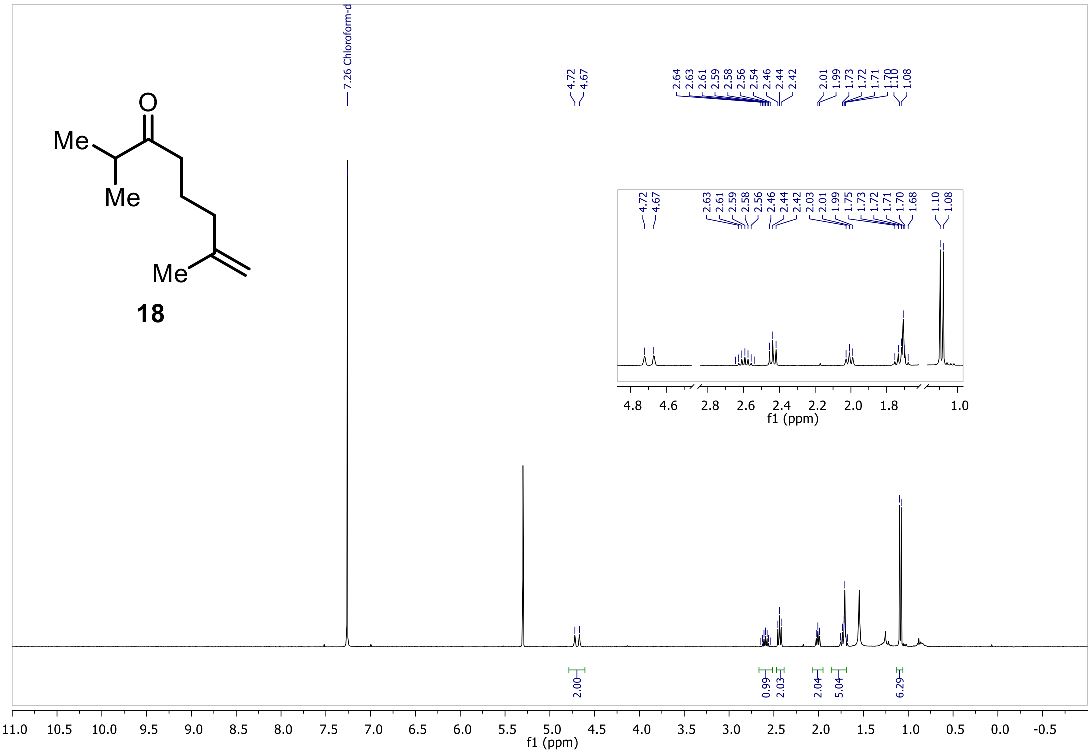


Ethyl 2-isobutyryl-5-methylhex-5-enoate (17)

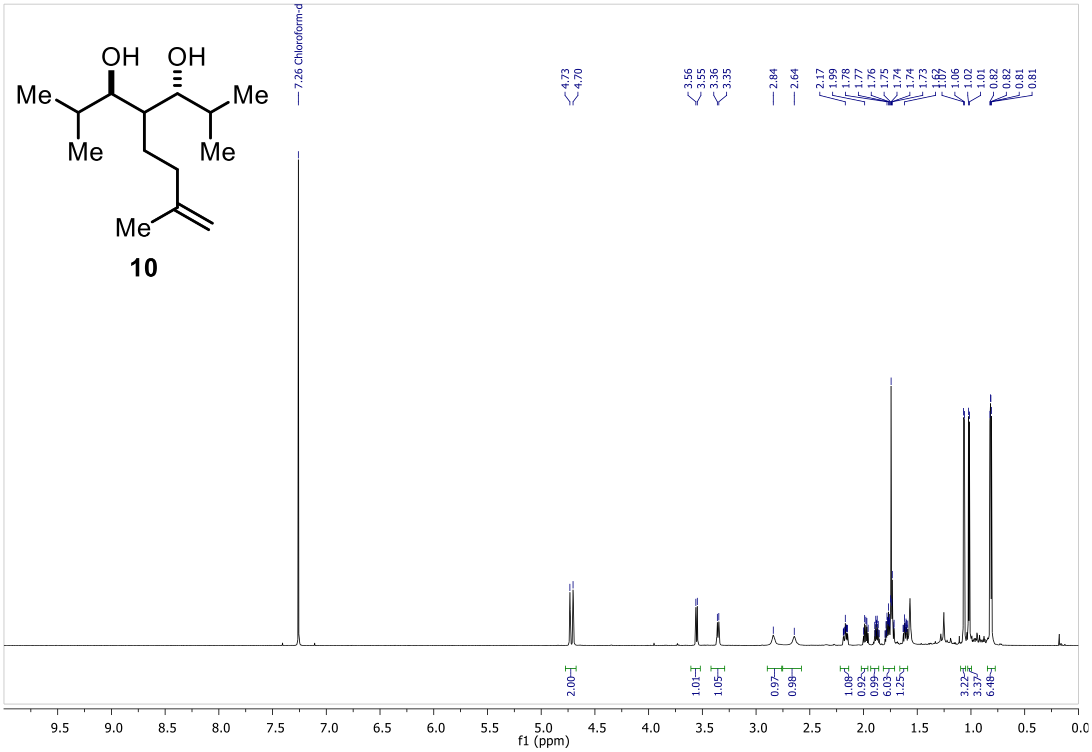


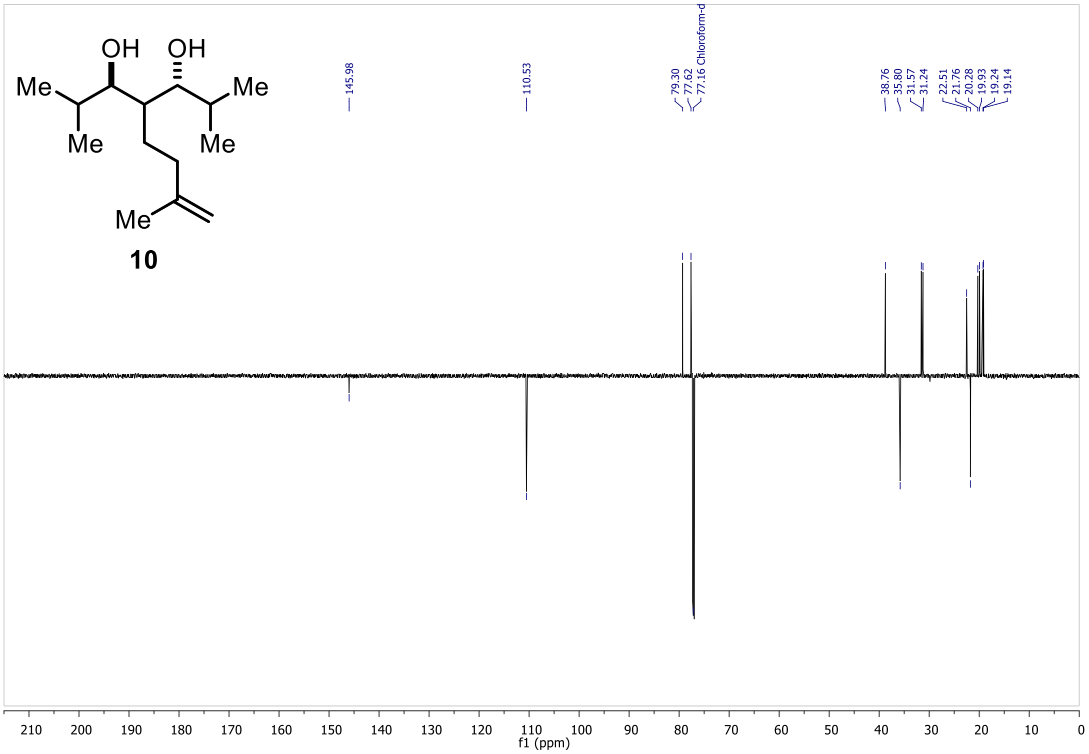


2,7-Dimethyloct-7-en-3-one (18)

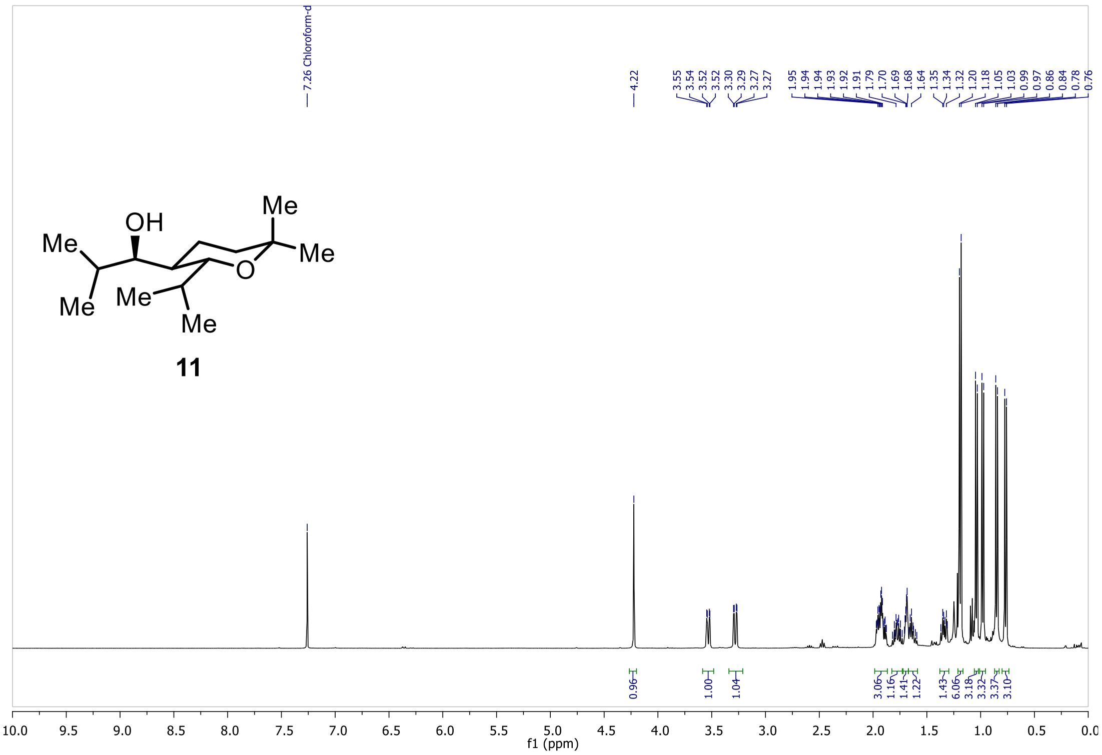


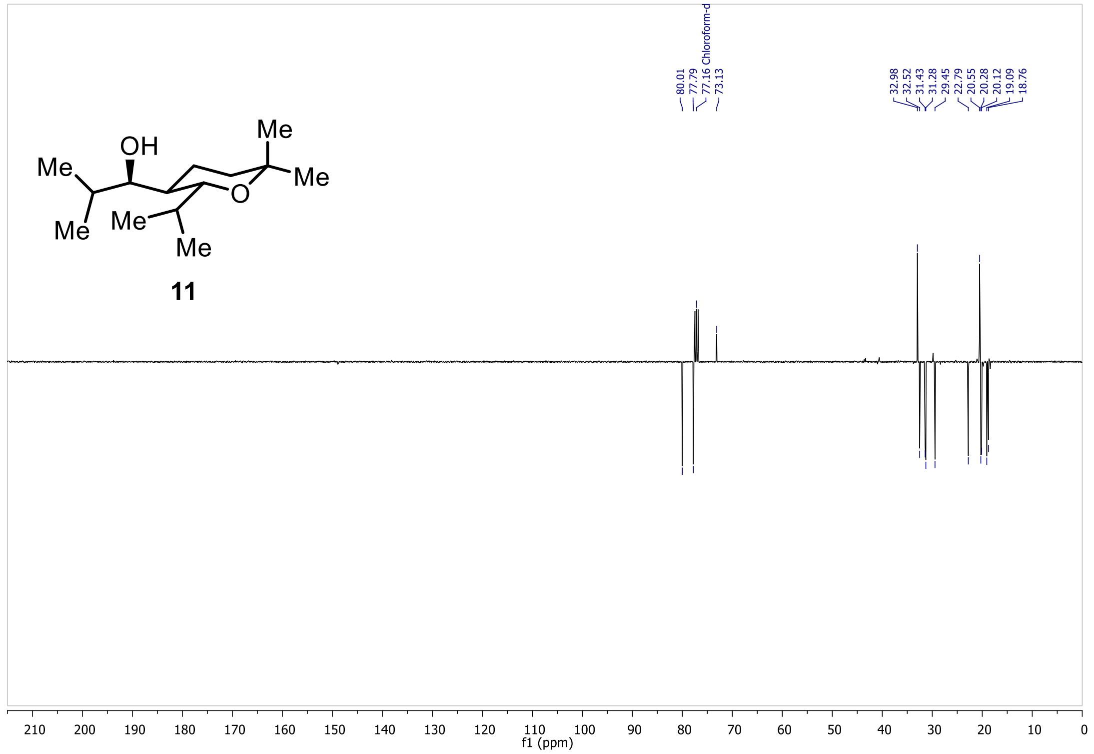
rac-(3*R**,5*R**)-**2,6-Dimethyl-4-(3-methylbut-3-en-1-yl)heptane-3,5-diol (10)**





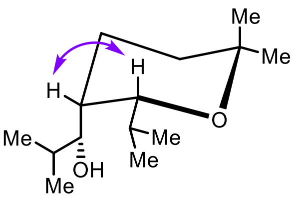
rac-(*R**)-1-((2*R**,3*R**)-**2-Isopropyl-6,6-dimethyltetrahydro-2H-pyran-3-yl)-2-methylpropan-1-ol (11)**



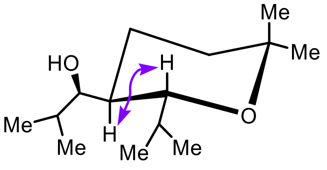


3. 2D NMR analysis

Selected NOESY interactions:

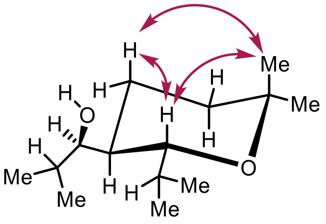


Karplus value: J = 2-5 Hz



Karplus value: J = 8-15 Hz

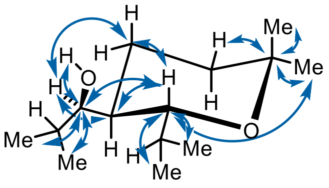
is J = 10.1 Hz



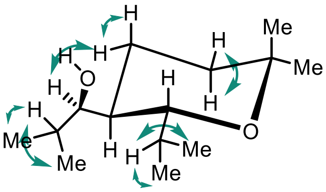
most relevant NOESY

All observed interactions according to 2D NMR data:

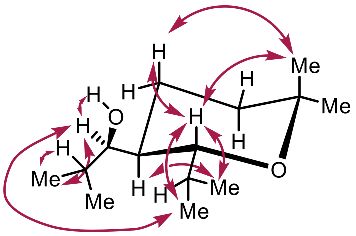
HMBC



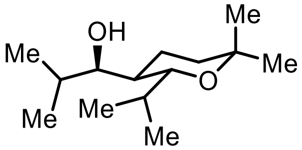
COSY



NOESY



700 MHz ^{1}H-^{1}H COSY Spectra of 11



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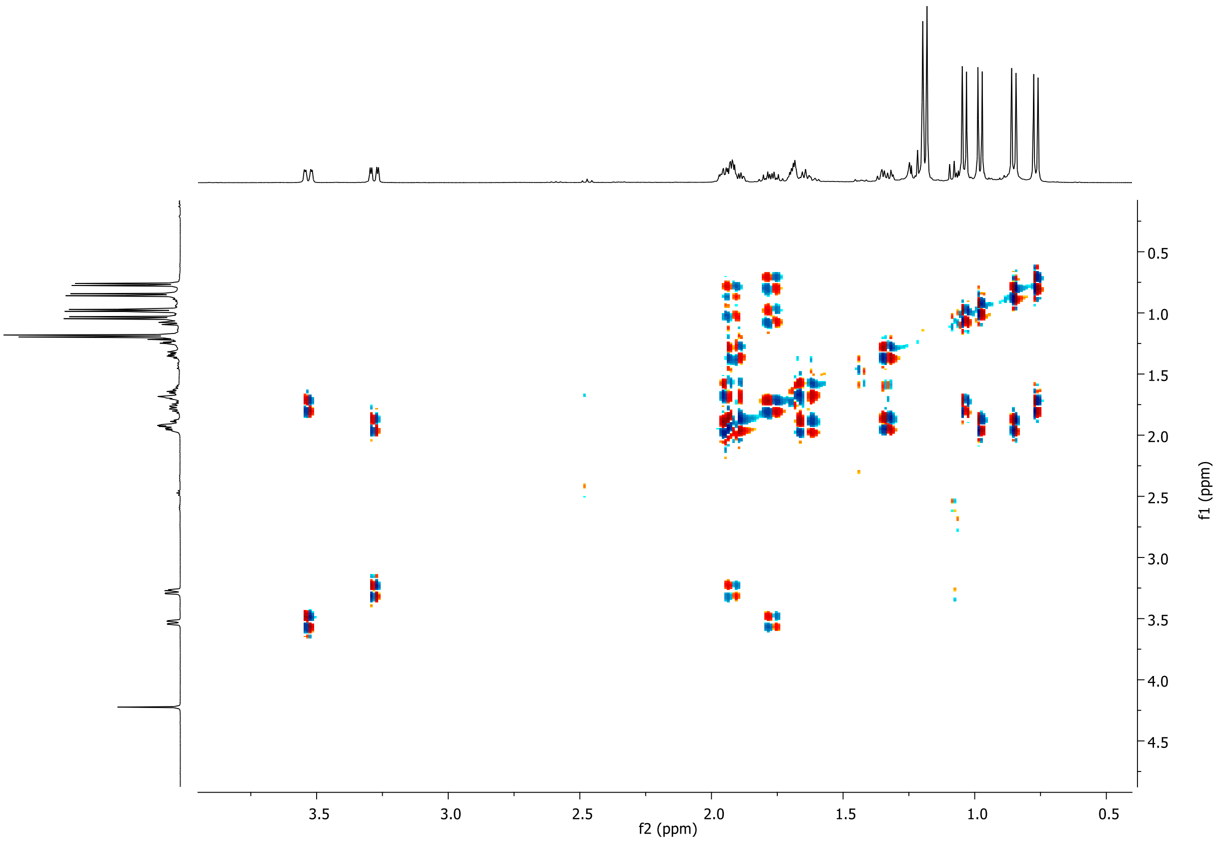
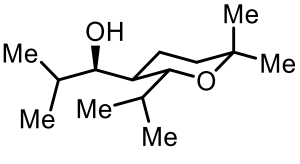


700 MHz NOESY Spectra of 11



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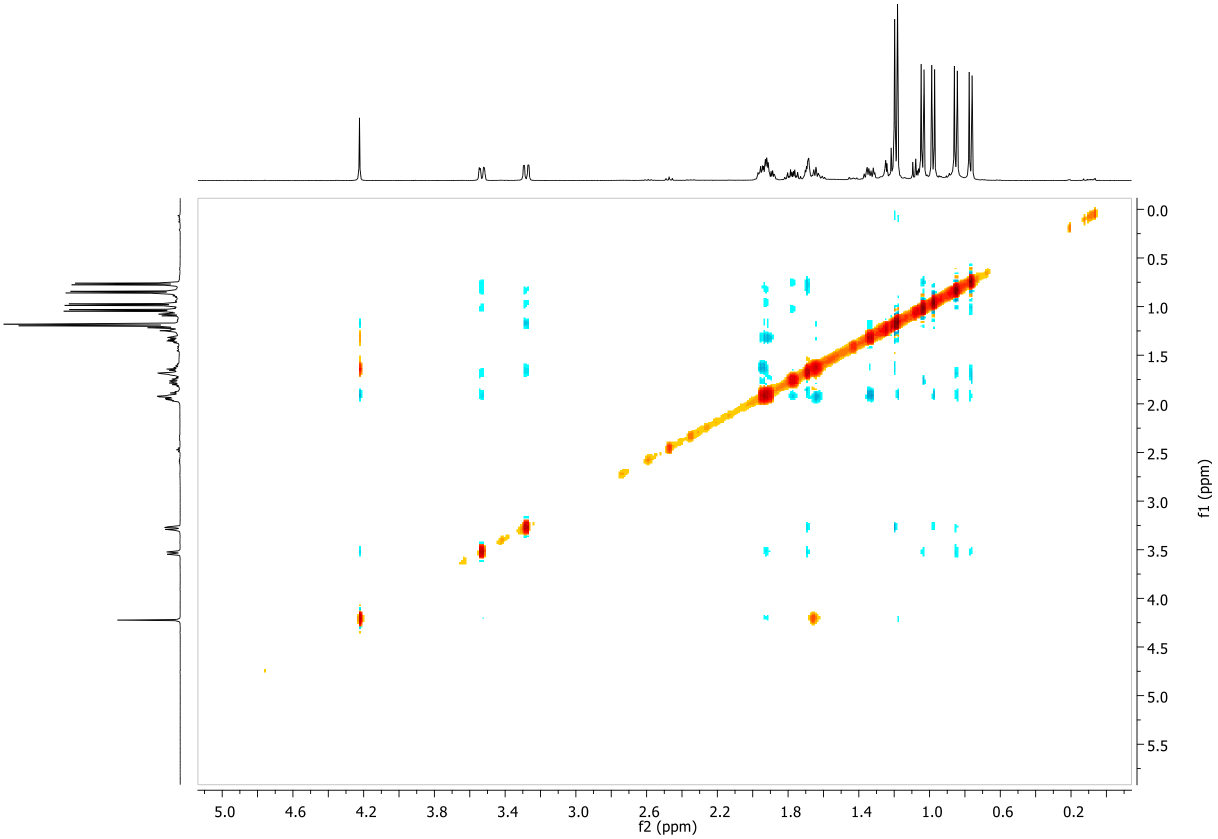
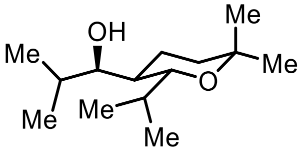


700 MHz HMBC Spectra of 11



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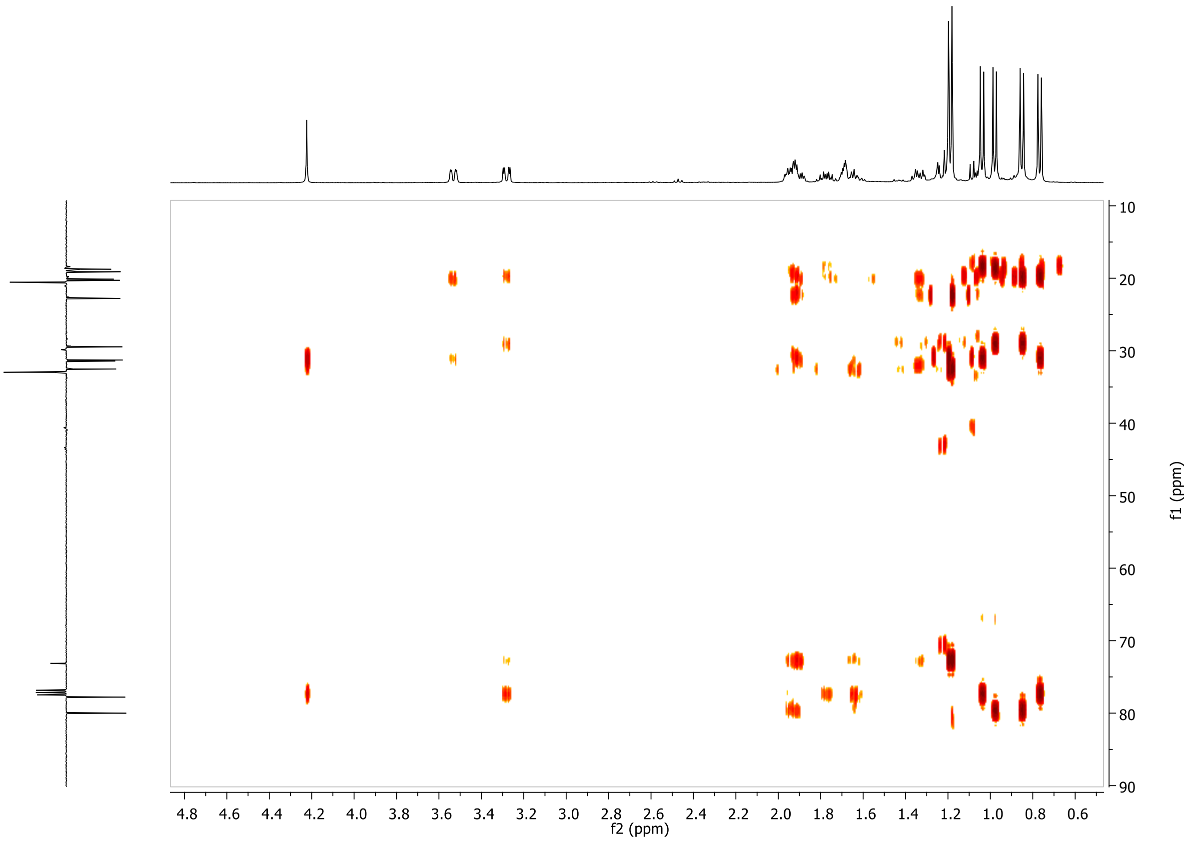

4. References

1. Fulmer, G. R. *et al.*, *Organometallics* **2010**, *29*, 2176–2179.