Electronic Supplementary Material (ESI) for Chemical Communications

An expedient approach to the total synthesis of (+)-5-*epi*-eudesma-4(15)-ene-1*β*,6*β*-diol

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Supplementary Information

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1. General

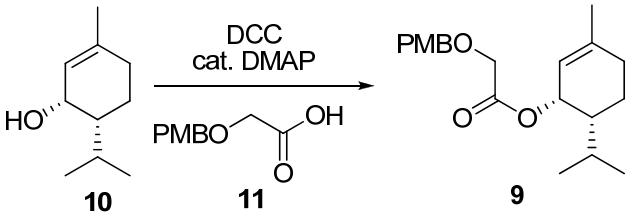
Unless otherwise indicated, all reactions were carried out under a positive pressure of nitrogen and with oven-dried glassware using standard Schlenk techniques. Infrared spectra (IR) were recorded on a Perkin-Elmer FT-IR spectrometer (diamond ATR Golden Gate sampling). ^{1}H NMR and 13C NMR spectra were recorded on Bruker AMX 300 (^{1}H, 300 MHz; ^{13}C, 75 MHz), 400 (^{1}H, 400 MHz; ^{13}C, 100 MHz) or 500 (^{1}H, 500 MHz; ^{13}C, 125 MHz) spectrometers in the solvent indicated. Chemical shifts are reported in parts per million (ppm) relative to internal standard (tetramethylsilane, δ_H = 0.00; $CDCl_3$, δ_H = 7.26). Data are presented as follows: chemical shift (δ, ppm), integration, multiplicity (s = singlet, d = doublet, t = triplet, q = quadruplet, m = multiplet, br = broad), coupling constant (reported in Hz), assignment. ^{13}C NMR chemical shifts are reported in parts per million (ppm) relative to internal standard (tetramethylsilane, δ_C = 0.00; $CDCl_3$, δ_C = 77.00). Electron impact (EI) mass spectra were obtained using Varian CH–4 or SM–1 instruments operating at 40–70eV and for Electrospray ionization (ESI) HRMS analyses were measured on a VG analytical 7070E instrument. Melting points were determined on a Büchi 540 spectrometer and are uncorrected. Electron impact (EI) mass spectra were obtained using Varian CH-4 or SM-1 instruments operating at 40 eV and electrospray (ESI) spectra using an Applied Biosystems API 150EX LC/MS system. Optical rotations were measured at 20 ◦C on a Perkin Elmer 241 polarimeter using a quartz cell (l = 10 cm) with a Na high-pressure lamp (λ = 589).

Product purification by flash column chromatography was performed using Brunschwig silica gel 60 Å (32-63 mesh). Analytical thin layer chromatography (TLC) was carried out using Merck commercial aluminium sheets coated (0.2 mm layer thickness) with Kieselgel 60 F_{254}, with visualization by ultraviolet.

Solvents (Toluene, THF, CH_2Cl_2, and Et3N) were purified by filtration on Al_2O_3 drying columns (Solvtek® system). Reactions and manipulations involving organometallic or moisture sensitive compounds were carried out under dry nitrogen and glassware was heated under vacuum prior use.

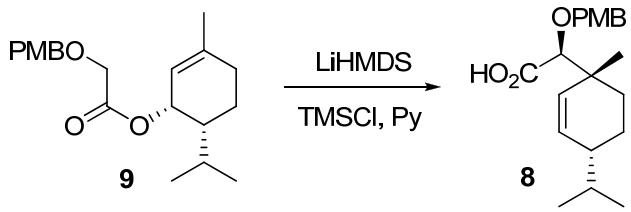
2. Experimental procedures

Glycolate (-)-**9**



To a solution of (–)-*cis*-piperitol **10** (2.8 g, 17.95 mmol) a in anhydrous CH_2Cl_2 (50 mL) was added acid **11**[1] (6.0 g, 30.61 mmol) followed by dicyclohexylcarbodiimide (9.24 g, 44.9 mmol) and N-N-dimethylamino pyridine (440 mg, 3.59 mmol) at 0 ^{o}C under nitrogen. The slurry was stirred at room temperature for 12 h. The resulting white solids were filtered off and washed with 100 mL of ether. The ether layer was washed with 25 mL of 1 N HC1, 25 mL of saturated $NaHCO_3$, and 25 mL of brine, dried (Na_2SO_4), and evaporated. The crude residue was purified by flash chromatography (ethylacete/pentane, 3/10) to give the title compound **8** (4.53 g, 76%) as colorless oil. $\mathbf{R}_f$ = 0.55 (20% ethyl acetate/pentane); **^{1}H NMR (400 MHz, $CDCl_3$) δ** 7.30 (d, *J* = 8.7 Hz, 2H), 6.89 (d, *J* = 8.7 Hz, 2H), 5.70 – 5.65 (m, 1H), 5.38 – 5.33 (m, 1H), 4.57 (s, 2H), 4.03 (s, 2H), 3.81 (s, 3H), 2.09 – 1.95 (m, 2H), 1.83 – 1.75 (m, 1H), 1.71 (s, 3H), 1.61 – 1.40 (m, 2H), 1.18 (ddt, *J* = 12.4, 9.1, 3.1 Hz, 1H), 0.95 (d, *J* = 6.7 Hz, 3H), 0.91 (d, *J* = 6.7 Hz, 3H); **^{13}C NMR (100 MHz, $CDCl_3$) δ** 170.24, 159.44, 141.99, 129.69, 129.40, 119.53, 113.83, 72.84, 69.35, 67.00, 55.26, 44.47, 31.24, 28.38, 23.32, 21.39, 20.82, 20.72.; **IR (ATR, neat) ν_{max}** 2960, 2873, 1743, 1512, 1115, 1035, 896 cm^{-1}.; **HRMS (ESI):** calcd. for $C_{20}H_{32}O_4N_1$ $(M+NH_4)^+$ *m/z* 350.2325 found *m/z* 350.2322.; **$[\alpha]^{25}_D$** –120.9 (*c* 2.40, $CHCl_3$).

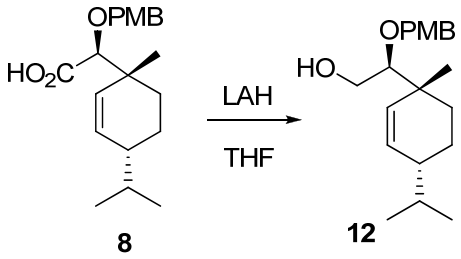
Carboxylic acid (-)-**8**



[1] *Prepared as mentioned in the literature* : Stockley, M.; Clegg, W.; Fontana, G.; Golding, B. T.; Martin, N.; Rigoreau, L. J. M.; Smith, G. C. M.; Griffina, R. J. *Bioorg. Med. Chem. Lett.* **2001**, *11*, 2837–2841.

To a solution of compound **9** (4.5 g, 13.55 mmol) in THF (200 mL) was added TMSCl (15.5 mL, 122.0 mmol) and pyridine (4.8 mL, 59.5 mmol) at –78 °C and stirred for 5 min. Then, a freshly prepared LiHMDS in THF [Prepared by adding *n*-BuLi (1.6 M in hexanes, 42.4 mL, 67.8 mmol) into a solution of HMDS (15 mL, 71.9 mmol) in THF (65.0 mL) at –20 °C, and stirring at –10 °C for 30 min, then to rt for 1 h] was added into the reaction mixture via cannula at –78 °C. After 30 min at –78 °C, the reaction mixture was warmed slowly to room temperature for 1 h. The reaction was quenched at 0 °C with 1 N HC1 (15 mL) and the solvent was removed under reduced pressure. The resulting residue was acidified to pH=2 with conc. HCl and extracted with 2X 30 mL of ether. The combined organic layers were washed with brine and the solvent was removed under reduced pressure. The crude product was purified over short silica gel chromotography (ethylacetate/pentane, 8:10) to yield acid **8** (4.3 g, 95 %) as viscous oil. $\mathbf{R}_f$ = 0.32 (50% ethyl acetate/pentane); **^{1}H NMR (400 MHz, $CDCl_3$) δ** 7.28 (d, *J* = 8.2 Hz, 2H), 6.89 (d, *J* = 8.3 Hz, 2H), 5.67 – 5.63 (m, 1H), 5.51 – 5.44 (m, 1H), 4.65 (d, *J* = 11.2 Hz, 1H), 4.34 (d, *J* = 11.4 Hz, 1H), 3.81 (s, 3H), 3.77 (bs, 1H), 2.06 – 1.98 (m, 1H), 1.84 (qd, *J* = 6.0, 3.1 Hz, 1H), 1.61 – 1.51 (m, 1H), 1.50 – 1.41 (m, 1H), 1.29 – 1.06 (m, 2H), 1.05 (s, 3H), 0.87 (d, *J* = 6.8 Hz, 3H), 0.83 (d, *J* = 6.8 Hz, 3H); **^{13}C NMR (100 MHz, $CDCl_3$) δ** 180.22, 159.59, 132.24, 131.71, 130.01, 128.97, 113.86, 82.81, 72.82, 55.27, 41.47, 38.20, 31.84, 31.38, 23.87, 21.35, 19.83, 19.38.; **IR (ATR, neat)** ν_{max} 2955, 2871, 1711, 1512, 1246, 1089, 1035, 819 cm^{-1}.; **HRMS (ESI):** calcd. for $C_{20}H_{32}O_4N_1$ $(M+NH_4)^+$ *m/z* 350.2325 found *m/z* 350.2317.; **$[\alpha]^{25}_D$** –27.4 (*c* 2.0, $CHCl_3$).

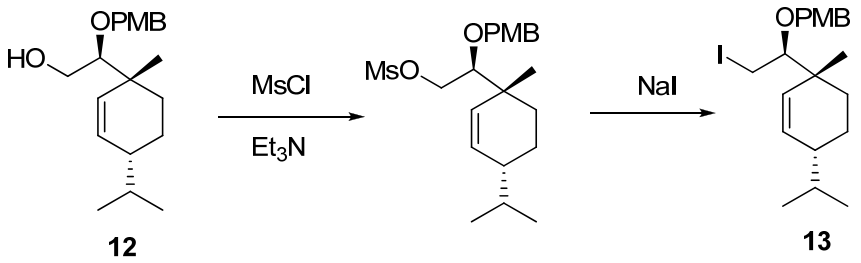
Alcohol (-)-**12**



A stirred suspension of LAH (1.73 g, 45.33 mmol) in THF (80 mL) was coo at 0 °C and then treated drop wise with a solution of carboxylic acid **8** (4.3 g, 12.95 mmol) in THF (40 mL). The resulting suspension was allowed to stire at room temperature for 12 h, and then further refluxed it for 2h. The resultant mixture was warmed to room temperature and stirred for 2 h. The reaction

was quenched by adding 60 g of $Na_2SO_4 \cdot 10H_2O$/Celite mixture (1:1) at 0 °C and the solution was stirred for 3 h. The mixture was then filtered through a pad of Celite and concentrated under reduced pressure. The residue was then purified by flash chromatography (ethylacetate/pentane, 4:10) to afford the alcohol **12** (3.8 g, 92%) as colorless oil. $\mathbf{R}_f$ = 0.40 (40 % ethyl acetate/pentane).; **^{1}H NMR (400 MHz, $CDCl_3$) δ** 7.30 (d, *J* = 6.5 Hz, 2H), 6.90 (d, *J* = 8.6 Hz, 2H), 5.66 (ddd, *J* = 10.3, 2.8, 0.9 Hz, 1H), 5.47 (ddd, *J* = 10.3, 2.3, 1.2 Hz, 1H), 4.67 (d, *J* = 11.2 Hz, 1H), 4.60 (d, *J* = 11.1 Hz, 1H), 3.81 (s, 3H), 3.77 (ddd, *J* = 10.9, 7.1, 3.6 Hz, 1H), 3.65 (ddd, *J* = 11.3, 7.2, 3.5 Hz, 1H), 3.39 (dd, *J* = 7.2, 3.6 Hz, 1H), 1.98 (dddd, *J* = 13.5, 5.9, 3.0, 1.2 Hz, 1H), 1.87 (ddq, *J* = 8.6, 5.7, 2.9 Hz, 1H), 1.84 – 1.80 (m, 1H), 1.65 – 1.57 (m, 1H), 1.57 – 1.52 (m, 1H), 1.40 (dddd, *J* = 13.3, 11.9, 8.9, 3.1 Hz, 1H), 1.20 (ddd, *J* = 13.3, 11.7, 3.3 Hz, 1H), 1.01 (s, 3H), 0.92 (d, *J* = 6.8 Hz, 3H), 0.89 (d, *J* = 6.8 Hz, 3H); **^{13}C NMR (101 MHz, $CDCl_3$) δ** 159.26, 133.79, 131.47, 130.88, 129.35, 113.87, 84.78, 74.36, 62.24, 55.24, 41.62, 38.61, 31.91, 31.82, 24.13, 21.68, 19.88, 19.56.; **IR (ATR, neat)** ν_{max} 2955, 2870, 1711, 1612, 1512, 1245, 1089, 1033, 818 cm^{-1}.; **HRMS (ESI):** calcd. for $C_{20}H_{30}O_3Na$ $(M+Na)^+$ *m/z* 341.2087 found *m/z* 347.2095.; **$[\alpha]^{25}_D$** –20.1 (*c* 2.0, $CHCl_3$).

Iodide (-)-**13**



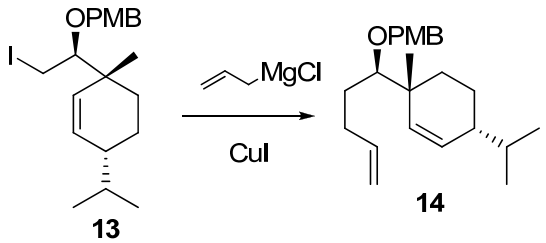
12 **13**

To a stirred solution of alcohol **12** (3.8 g, 11.95 mmol) and Et_3N (4.2 mL, 29.87 mmol) in CH_2Cl_2 was added methane sulfonylchloride (1.9 mL, 23.9 mmol) at 0 °C under nitrogen atmosphere and stirred it for 4 h. The reaction was quenched with ice water (20 mL), and the organic layer was washed with sat. $NaHCO_3$, brine and dried over Na_2SO_4. The solvent was removed under reduced pressure to yield methanesulfonate (4.7 g, 92%) as a coloress viscous oil and was carried forward without purification. $\mathbf{R}_f$ = 0.45 (40% ethyl acetate/pentane); **^{1}H NMR (400 MHz, $CDCl_3$) δ** 7.34 (d, *J* = 6.6 Hz, 2H), 6.93 (d, *J* = 6.7 Hz, 2H), 5.72 (ddd, *J* = 10.2, 2.8, 1.0 Hz, 1H), 5.46 (ddd, *J* = 10.3, 2.4, 1.3 Hz, 1H), 4.75 (d, *J* = 10.9 Hz, 1H), 4.61 (d, *J* = 11.0 Hz, 1H), 4.54 (dd, *J* = 10.6, 2.5 Hz, 1H), 4.30 (dd, *J* = 10.6, 7.6 Hz, 1H), 3.86 (s, 3H), 3.59 (dd, *J*

= 7.6, 2.5 Hz, 1H), 3.01 (s, 3H), 2.01 (ddd, *J* = 13.5, 5.7, 3.0 Hz, 1H), 1.93 (dt, *J* = 5.9, 2.7 Hz, 1H), 1.67 – 1.58 (m, 1H), 1.59 – 1.51 (m, 1H), 1.35 – 1.27 (m, 1H), 1.26 – 1.17 (m, 1H), 1.04 (s, 3H), 0.94 (d, *J* = 6.8 Hz, 3H), 0.90 (d, *J* = 6.8 Hz, 3H); **^{13}C NMR (101 MHz, $CDCl_3$) δ** 159.29, 132.65, 132.61, 130.41, 129.61, 113.76, 81.35, 74.27, 71.59, 55.32, 41.62, 38.69, 37.39, 31.88, 31.75, 23.57, 21.34, 19.89, 19.47.; **IR (ATR, neat)** ν_{max} 2958, 2871, 1611, 1512, 1461, 1355, 1174, 956, 823 cm^{-1}; **LRMS (ESI):** $C_{21}H_{32}O_5NaS$ $(M+Na)^+$ *m/z* 419.19; **$[\alpha]^{25}_D$** –12.6 (*c* 2.1, $CHCl_3$).

A mixture of the above methanesulfonate (4.56 g, 10.65 mmol) and NaI (9.6 g, 63.93 mmol) in methylethylketone (100 mL) was heated under reflux for 24 h. After cooling, the mixture was diluted with diethylether (50 mL) and poured into water (50 mL). The organic layer was washed with aq. Sodium thiosulfate, aq. $NaHCO_3$, and brine and evaporated to dryness. The resulting residue was purified by flash chromotograpy (diethylether/pentane, 2:10) to afford the iodo compound **13** (4.1 g, 84%) as pale yellow oil. R_f = 0.60 (5% ethyl acetate/pentane); **^{1}H NMR (400 MHz, $CDCl_3$) δ** 7.37 (d, *J* = 2.0 Hz, 2H), 6.89 (d, *J* = 2.1 Hz, 2H), 5.70 (dd, *J* = 10.2, 2.8 Hz, 1H), 5.47 (d, *J* = 7.7 Hz, 1H), 4.89 (d, *J* = 10.2 Hz, 1H), 4.61 (d, *J* = 10.2 Hz, 1H), 3.82 (s, 3H), 3.61 (dd, *J* = 9.1, 2.5 Hz, 1H), 3.46 (dd, *J* = 10.5, 2.5 Hz, 1H), 3.30 (dd, *J* = 10.5, 9.1 Hz, 1H), 2.02 – 1.94 (m, 1H), 1.88 – 1.84 (m, 1H), 1.67 – 1.51 (m, 2H), 1.45 – 1.37 (m, 1H), 1.29 – 1.18 (m, 1H), 1.00 (s, 3H), 0.92 (d, *J* = 6.7 Hz, 3H), 0.89 (d, *J* = 6.8 Hz, 3H); **^{13}C NMR (100 MHz, $CDCl_3$) δ** 159.18, 133.41, 132.00, 130.54, 129.54, 113.65, 85.12, 75.02, 55.27, 41.61, 41.28, 31.89, 31.54, 23.34, 21.60, 20.01, 19.68, 7.24; **IR (ATR, neat)** ν_{max} 2954, 2868, 1612, 1512, 1460, 1246, 1173, 1077, 1034, 820 cm^{-1}; **HRMS (ESI):** calcd. for $C_{20}H_{33}N_1O_2I$ $(M+NH_4)^+$ *m/z* 446.1550 found *m/z* 446.1542; **$[\alpha]^{25}_D$** –5.1 (*c* 1.04, $CHCl_3$).

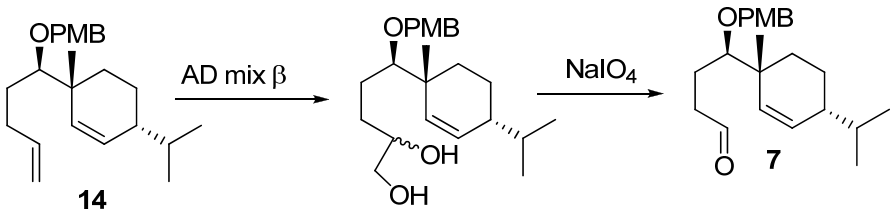
Diene (-)-**14**



Allylmagnesium chloride (10.8 mL, 17.2 mmol, 1.7 M in THF) was added to a mixture of CuI (140 mg, 0.74 mmol, 15 mol%) and iodide **13** (2.1 g, 4.91 mmol) in THF–HMPA (6:1, 30 mL) at

–40 °C over a period of 10 min. The mixture was allowed to warm to 0 °C over a period of 2 h then at room temperature for 16 h. The reaction was quenched by aq. NH_3 and NH_4Cl solution at 0 °C. The organic layer was separated and the aqueous layer was extracted with diethyl ether and the combined organic phase was washed with brine. After drying over Na_2SO_4, the solvent was removed under vacuo. The residue was purified with gel column chromatography (ether/pentane, 1:10) to give 1.22 g (73%) of **14** as colorless oil. $\mathbf{R}_f$ = 0.42 (10% diethylether/pentane); **^{1}H NMR (400 MHz, $CDCl_3$) δ** 7.29 (d, *J* = 1.7 Hz, 2H), 6.87 (d, *J* = 2.1 Hz, 2H), 5.86 – 5.79 (m, 1H), 5.63 (dd, *J* = 10.3, 2.7 Hz, 1H), 5.48 (d, *J* = 8.8 Hz, 1H), 5.03 (d, *J* = 16.7 Hz, 1H), 4.96 (d, *J* = 1.8 Hz, 1H), 4.56 (d, *J* = 10.8 Hz, 1H), 4.52 (d, *J* = 10.8 Hz, 1H), 3.81 (s, 3H), 3.26 (dd, *J* = 8.2, 3.8 Hz, 1H), 2.35 – 2.25 (m, 1H), 2.17 – 2.04 (m, 1H), 2.01 – 1.97 (m, 1H), 1.90 – 1.87 (m, 1H), 1.68 – 1.58 (m, 3H), 1.54 – 1.42 (m, 2H), 1.28 – 1.15 (m, 1H), 0.97 (s, 3H), 0.92 (d, *J* = 6.7 Hz, 3H), 0.88 (d, *J* = 6.8 Hz, 3H); **^{13}C NMR (101 MHz, $CDCl_3$) δ** 158.99, 139.01, 135.00, 131.31, 130.70, 129.16, 114.50, 113.65, 83.90, 74.36, 55.28, 41.72, 39.82, 31.93, 31.49, 31.33, 30.34, 23.65, 21.69, 19.96, 19.63; **IR (ATR, neat)** ν_{max} 2953, 2868, 1613, 1512, 1460, 1245, 1173, 1078, 1037, 906, 820 cm^{-1};**HRMS (ESI):** Not ionized; **$[\alpha]^{25}_D$** –5.4 (*c* 1.62, $CHCl_3$).

Aldehyde (-)-**7**

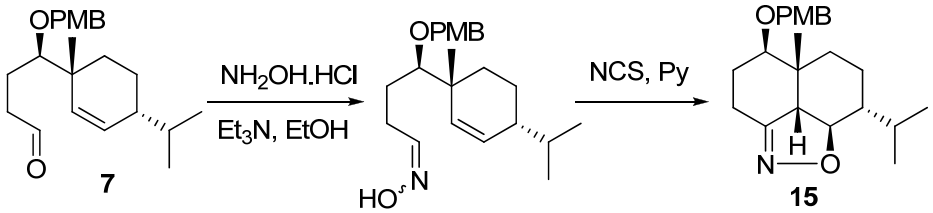


A solution of diene **14** (1.2 g, 3.51mmol) in 18 mL of *tert*-BuOH was treated with a solution of 6 g of AD-mix- β in 18 mL of distilled water at 0 °C. After 15 min, the solution was warm to 5 °C and was stirred for 36 h. The mixture was quenched with a saturated solution of Na_2SO_3 and stirred for 1 h. The aqueous layer was extracted with EtOAc (5X 20 mL) and the combined organic extracts were dried over Na_2SO_4, filtered and concentrated under reduced pressure. The residue was purified by flash chromatography on silica gel (EtOAc/pentane, 8:10) to give 1.2 g (91%) of diol as a viscous liquid. $\mathbf{R}_f$ = 0.25 (60% ethyl acetate/pentane); **^{1}H NMR (400 MHz, $CDCl_3$) δ** 7.28 (d, *J* = 8.1 Hz, 2H), 6.87 (d, *J* = 7.9 Hz, 2H), 5.65 (dd, *J* = 10.2, 2.7 Hz, 1H), 5.47 (dd, *J* = 10.4, 2.3 Hz, 1H), 4.58 (dd, *J* = 10.8, 2.6 Hz, 1H), 4.48 (d, *J* = 10.8 Hz, 1H), 3.80 (s, 3H), 3.65 – 3.55 (m, 2H), 3.42 – 3.35 (m, 1H), 3.23 (t, *J* = 6.0 Hz, 1H), 2.75 (bs, 1H), 2.48 (bs,

1H), 2.00 – 1.96 (m, 1H), 1.89 – 1.85 (m, 1H), 1.80 – 1.56 (m, 5H), 1.51 – 1.41 (m, 2H), 1.29 – 1.17 (m, 1H), 0.98 (s, 3H), 0.92 (d, *J* = 6.7 Hz, 3H), 0.88 (d, *J* = 6.8 Hz, 3H); **^{13}C NMR (100 MHz, $CDCl_3$) δ** 159.06, 134.81, 130.88, 130.84, 129.28, 113.65, 84.64, 74.59, 72.29, 66.73, 55.24, 41.69, 39.88, 31.89, 31.17, 30.56, 26.65, 23.75, 21.74, 19.98, 19.68; **IR (ATR, neat)** ν_{max} 3375, 2932, 2868, 1612, 1512, 1460, 1246, 1068, 1035, 818 cm^{-1}; **HRMS (ESI):** calcd. for $C_{23}H_{37}O_4$ $(M+H)^+$ *m/z* 377.2686 found *m/z* 377.2703; **$[\alpha]^{25}_D$** –0.29 (*c* 1.15, $CHCl_3$).

$NaIO_4$ was added to the solution of above diol in a mixture of 16 mL of *tert*-BuOH and 16 mL of distilled water at 0 °C in portion over 5 mint and mixture was stirred at room temperature for 1 h. The reaction mixture was quenched with water and extracted with EtOAc (3 x 10 mL). The combined organic layers were washed with brine, dried (Na_2SO_4) and concentrated. Flash column chromatography (2:10 ethyl acetate/pentane) of the crude product gave aldehyde **7** (1.05 g, 95%) as a colorless. **R*f*** = 0.61 (30% ethyl acetate/pentane); **^{1}H NMR (400 MHz, $CDCl_3$)** δ 9.70 (t, *J* = 1.8 Hz, 1H), 7.27 (d, *J* = 8.6 Hz, 2H), 6.88 (d, *J* = 8.7 Hz, 2H), 5.67 (dd, *J* = 7.4, 0.8 Hz, 1H), 5.49 (ddd, *J* = 10.3, 2.3, 1.1 Hz, 1H), 4.57 (d, *J* = 10.8 Hz, 1H), 4.42 (d, *J* = 10.8 Hz, 1H), 3.81 (s, 3H), 3.24 (dd, *J* = 9.4, 3.3 Hz, 1H), 2.53 (ddd, *J* = 8.1, 6.6, 1.9 Hz, 1H), 2.44 (dddd, *J* = 17.3, 8.0, 6.5, 1.6 Hz, 1H), 1.98 (dddd, *J* = 13.5, 6.3, 3.2, 1.1 Hz, 1H), 1.94 – 1.85 (m, 2H), 1.85 – 1.76 (m, 1H), 1.63 – 1.55 (m, 2H), 1.53 – 1.42 (m, 1H), 1.28 – 1.19 (m, 1H), 1.00 (s, 3H), 0.92 (d, *J* = 6.8 Hz, 3H), 0.89 (d, *J* = 6.8 Hz, 3H); **^{13}C NMR (101 MHz, $CDCl_3$) δ** 202.63, 159.10, 134.54, 131.11, 130.81, 129.30, 113.69, 83.79, 74.32, 55.25, 41.66, 41.60, 39.94, 31.89, 31.12, 23.84, 23.47, 21.73, 19.98, 19.68; **IR (ATR, neat)** ν_{max} 2955, 2869, 1612, 1722, 1612, 1512, 1461, 1246, 1077, 1034, 817 cm^{-1}; **HRMS (ESI):** calcd. for $C_{22}H_{33}O_3$ $(M+H)^+$ *m/z* 345.2424 found *m/z* 345.2422; **$[\alpha]^{25}_D$** –5.9 (*c* 1.17, $CHCl_3$).

Isoxazole (-)-**15**

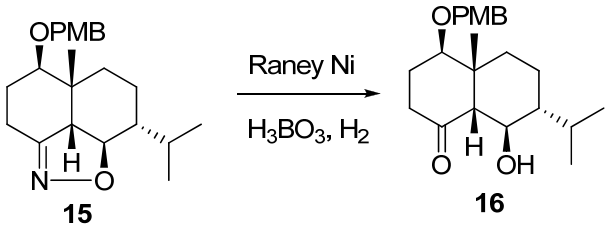


To a solution of the above aldehyde **7** (1.05 g, 3.05 mmol) in EtOH (23 ml) were added NH_2OH-HCl (2.2 g, 32.0 mmol) and Et_3N (4.6 mL, 33.0 mmol) at 0 °C and the mixture was stirred at rt

for 16 h. The reaction was diluted with water and extracted with AcOEt. The combined extracts were dried with Na_2SO_4 and concentrated to afford a diastereomeric mixture of oxime as viscous oil (1.04g, 95%).

To a solution of above oxime (970 mg, 2.70 mmol) and N-chlorosucinimde (380 mg, 2.85 mmol) in chloroform (43 mL) was added pyridine (156 µL) at room temperature and stirred it for 2 h. Then, it was further stirred at 60 ^oC for another 6 h. The solvent was removed under reduced pressure and diluted with water (15 mL). The mixture was extracted with CH_2Cl_2 (3 X 20 mL) and the combined extracts were dried over Na_2SO_4 and concentrated in vacuo. The residue was purified by flash chromatography (3:10 ethyl acetate/pentane) to give isoxazoline **15** (800 mg, 83%). $\mathbf{R}_f$ = 0.45 (30% ethyl acetate/pentane); **^{1}H NMR (500 MHz, $CDCl_3$) δ** 7.28 (d, *J* = 8.3 Hz, 2H), 6.90 (d, *J* = 8.6 Hz, 2H), 4.85 (ddd, *J* = 11.2, 1.1, 2.6 Hz, 1H), 4.58 (d, *J* = 11.2 Hz, 1H), 4.36 (d, *J* = 11.2 Hz, 1H), 3.82 (s, 3H), 3.32 (dt, *J* = 11.8, 1.5 Hz, 1H), 3.11 (dd, *J* = 2.8, 0.8 Hz, 1H), 2.52 (ddd, *J* = 13.4, 5.3, 2.0 Hz, 1H), 1.76 – 1.67 (m, 3H), 1.50 – 1.43 (m, 1H), 1.40 – 1.31 (m, 2H), 1.21 (s, 3H), 1.24 – 1.17 (m, 1H), 1.03 (d, *J* = 6.6 Hz, 3H), 0.93 (d, *J* = 6.7 Hz, 3H); **^{13}C NMR (101 MHz, $CDCl_3$) δ** 159.12, 130.63, 129.12, 113.70, 99.92, 81.91, 77.91, 71.03, 55.26, 52.59, 41.27, 37.82, 30.14, 29.00, 26.57, 24.36, 21.27, 21.03, 20.46, 19.48; **IR (ATR, neat) ν_{max}** 2952, 2870, 1611, 1512, 1461, 1276, 1247, 1172, 1072, 1032, 820 cm^{-1}; **HRMS (ESI):** calcd. for $C_{22}H_{32}N_1O_3$ $(M+H)^+$ *m/z* 358.2376 found *m/z* 358.2375; **$[\alpha]^{25}_D$** –37.2 (*c* 1.04, $CHCl_3$).

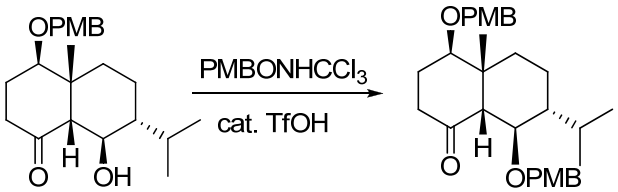
Hydroxy ketone (+)-**16**



To a solution of isoxazoline **15** (570 mg, 1.6 mmol) in methanol/water (10:1, 80 mL) was added boric acid (890 mg, 14.4 mmol) and a Raney nickel (20-30 mg, 50% in water). The reaction was placed under hydrogen atmosphere for 6 at room temperature. The reaction mixture was filtered through Celite and the solvent was removed under reduced pressure. The obtained residue was dissolved in CH_2Cl_2 (15 mL) and washed with saturated aq. $NaHCO_3$. The aqueous layer was extracted with CH_2Cl_2 (2 X 15 mL) and the combined organic layers were washed with brine,

dried over Na_2SO_4, and concentrated in vacuo to yield 430 mg (75%) of pure hydroxy ketone **16** after chromatography (5:10, ethyl acetate/pentane). **R_f** = 0.32 (50% ethyl acetate/pentane); **^{1}H NMR (400 MHz, $CDCl_3$) δ** 7.27 (d, *J* = 8.1, 2H), 6.90 (d, *J* = 8.2 Hz, 2H), 4.64 (d, *J* = 11.6 Hz, 1H), 4.38 (d, *J* = 11.6 Hz, 1H), 3.85 – 3.81 (m, 1H), 3.82 (s, 3H), 3.72 – 3.65 (m, 1H), 2.62 (td, *J* = 14.7, 7.1 Hz, 1H), 2.41 – 2.27 (m, 2H), 2.18 – 2.07 (m, 2H), 1.95 (dd, *J* = 10.7, 1.9 Hz, 1H), 1.89 – 1.76 (m, 1H), 1.44 – 1.37 (m, 1H), 1.35 – 1.28 (m, 1H), 1.14 – 1.07 (m, 1H), 0.93 (s, 3H), 0.90 (d, *J* = 7.0 Hz, 3H), 0.88 – 0.78 (m, 2H), 0.74 (d, *J* = 6.9 Hz, 3H); **^{13}C NMR (100 MHz, $CDCl_3$) δ** 212.52, 159.29, 130.32, 129.59, 113.78, 72.09, 70.74, 70.18, 68.10, 55.28, 49.99, 42.56, 36.33, 33.91, 25.82, 25.60, 22.21, 20.81, 18.13, 15.95; **IR (ATR, neat) ν_{max}** 3440, 2951, 2873, 1694, 1611, 1511, 1252, 1247, 1171, 1051, 1034, 810 cm^{-1}; **HRMS (ESI):** calcd. for $C_{22}H_{36}N_1O_4$ $(M+NH_4)^+$ *m/z* 378.2638 found *m/z* 378.2653; **$[\alpha]^{25}_D$** +13.3 (*c* 1.0, $CHCl_3$).

Ketone (-)-**17**

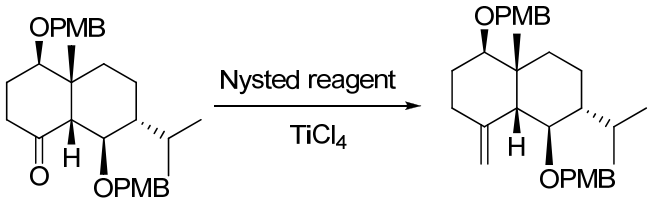


16 **17**

To a solution of β-hydroxy ketone **16** (100 mg, 0.28 mmol) and p-methoxybenzyl-2,2,2-trichloroacetimidate (118 mg, 0.42 mmol) in anhydrous diethylether (3 mL) was added a solution of triflic acid in diethyl ether (0.2 M in ethere, 40 µL, 0.008 mmol) at 0 ^oC. After 10 min, the reaction mixture was allowed to stir at room temperature for 24 h. The reaction mixture was cooled back to 0 ^oC and treated with a aliquot of triflic acid (20 µL, 0.004 mmol) and stirred at rt for another 3 h. The mixture was quenched with sat. solution of $NaHCO_3$ and extracted with ether (3 X 10 mL). The combined organic layers were dried over Na_2SO_4, concentrated in vacuo and purified by flash chromatography (ethylacetate/pentane, 1:4) to give PMB ether **17** as pale yellow oil (110 mg, 82%). **R*f*** = 0.45 (40% ethyl acetate/pentane); **^{1}H NMR (300 MHz, $CDCl_3$) δ** 7.27 (d, *J* = 8.4 Hz, 2H), 7.19 (d, *J* = 8.2 Hz, 2H), 6.90 (d, *J* = 8.3 Hz, 2H), 6.84 (d, *J* = 8.5 Hz, 2H), 4.65 (d, *J* = 11.6 Hz, 1H), 4.39 (d, *J* = 11.4, 1H), 4.38 (d, *J* = 9.7 Hz, 1H), 4.18 (d, *J* = 9.6 Hz, 1H), 3.89 – 3.75 (m, 2H), 3.82 (s, 3H), 3.79 (s, 3H), 2.73 – 2.61 (m, 1H), 2.37 – 2.27 (m, 3H), 2.24 – 2.05 (m, 2H), 1.93 – 1.75 (m, 1H), 1.49 – 1.27 (m, 2H), 0.94 (s, 3H), 0.91 (d, *J* = 7.2

Hz, 3H), 0.90 – 0.87 (m, 2H), 0.77 (d, *J* = 6.9 Hz, 3H); **^{13}C NMR (75 MHz, $CDCl_3$) δ** 211.60, 159.28, 159.20, 130.36, 130.09, 129.81, 129.56, 113.77, 113.75, 76.78, 72.13, 70.70, 68.38, 64.69, 55.26, 55.24, 46.88, 43.08, 36.83, 33.92, 26.28, 25.10, 22.02, 21.07, 18.05, 15.82; **IR (ATR, neat)** ν_{max} 2954, 2872, 1711, 1611, 1511, 1461, 1244, 1247, 1174, 1061, 1032, 820 cm^{-1}; **HRMS (ESI):** calcd. for $C_{30}H_{44}N_1O_5$ $(M+NH_4)^+$ *m/z* 498.3214 found *m/z* 498.3213; **$[\alpha]^{25}_D$** –6.2 (*c* 1.9, $CHCl_3$).

Olefin (+)-**18**

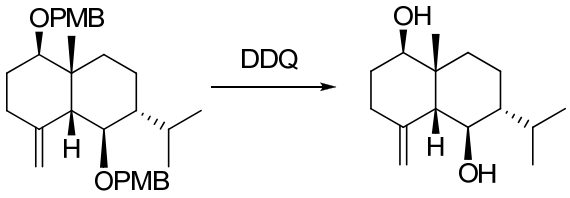


17 **18**

Neat $TiCl_4$ (90 µL, 0.83 mmol) was added to a solution of freshly shaken Nysted's reagent (nominally 20%w/w in THF, 1.7 mL, 0.88 mmol) in THF (2.5 mL) at 0°C, followed by a solution of ketone **17** (120 mg, 0.25 mmol) in THF (3 mL). The cooling bath was removed and the mixture was stirred at room temperature for 2 h, then at 50 °C for 6 h. The dark brown slurry was diluted with diethyl ether (5 mL) and poured into a 1N solution of aq. HCl (5 mL) at 0 °C. The organic layer was separated and the aqueous layer was extracted with diethyl ether (3 X 5 mL). The combined extracts were washed once with brine, dried over anhydrous Na_2SO_4 and concentrated under reduced pressure. The crude material was purified by flash chromatography (ethylacetate/pentane, 1:10) to yield the olefin **18** (31 mg, 25%, 44% brsm) as a pale oil, further elution (ethylacetate/pentane, 4:10) gave recovered starting material **17** (52 mg, 43%). **R*f*** = 0.70 (20% ethyl acetate/pentane); **^{1}H NMR (300 MHz, $CDCl_3$) δ** 7.29 (d, *J* = 8.4 Hz, 2H), 7.23 (d, *J* = 8.6 Hz, 2H), 6.91 (d, *J* = 2.0 Hz, 2H), 6.83 (d, *J* = 8.7 Hz, 2H), 4.95 (d, *J* = 3.0 Hz, 1H), 4.89 (d, *J* = 2.6 Hz, 1H), 4.61 (d, *J* = 11.6 Hz, 1H), 4.43 (d, *J* = 9.4 Hz, 1H), 4.36 (d, *J* = 11.6 Hz, 1H), 4.26 (d, *J* = 9.4 Hz, 1H), 3.82 (s, 3H), 3.79 (s, 3H), 3.57 (dd, *J* = 11.5, 4.7 Hz, 1H), 3.40 (t, *J* = 10.4 Hz, 1H), 2.39 (dd, *J* = 9.4, 3.7 Hz, 2H), 2.26 – 2.16 (m, 1H), 2.13 – 2.03 (m, 3H), 1.63 – 1.54 (m, 1H), 1.34 – 1.26 (m, 4H), 0.91 (s, 3H), 0.87 (d, *J* = 7.0 Hz, 3H), 0.75 (d, *J* = 6.9 Hz, 3H); **^{13}C NMR (75 MHz, $CDCl_3$) δ** 159.10, 159.08, 145.54, 131.04, 130.94, 129.78, 129.40, 113.67, 113.06, 76.16, 74.05, 72.58, 70.39, 60.14, 55.26, 49.03, 40.89, 34.26, 30.66, 27.17,

25.62, 22.27, 21.33, 17.94, 16.10; **IR (ATR, neat)** ν_{max} 2931, 2875, 1612, 1511, 1245, 1172, 1063, 1035, 890, 820 cm^{-1}; **HRMS (ESI):** calcd. for $C_{31}H_{46}N_1O_4$ $(M+NH_4)^+$ *m/z* 496.34221 found *m/z* 496.3414; $[\alpha]^{25}_D$ +6.9 (*c* 1.34, $CHCl_3$).

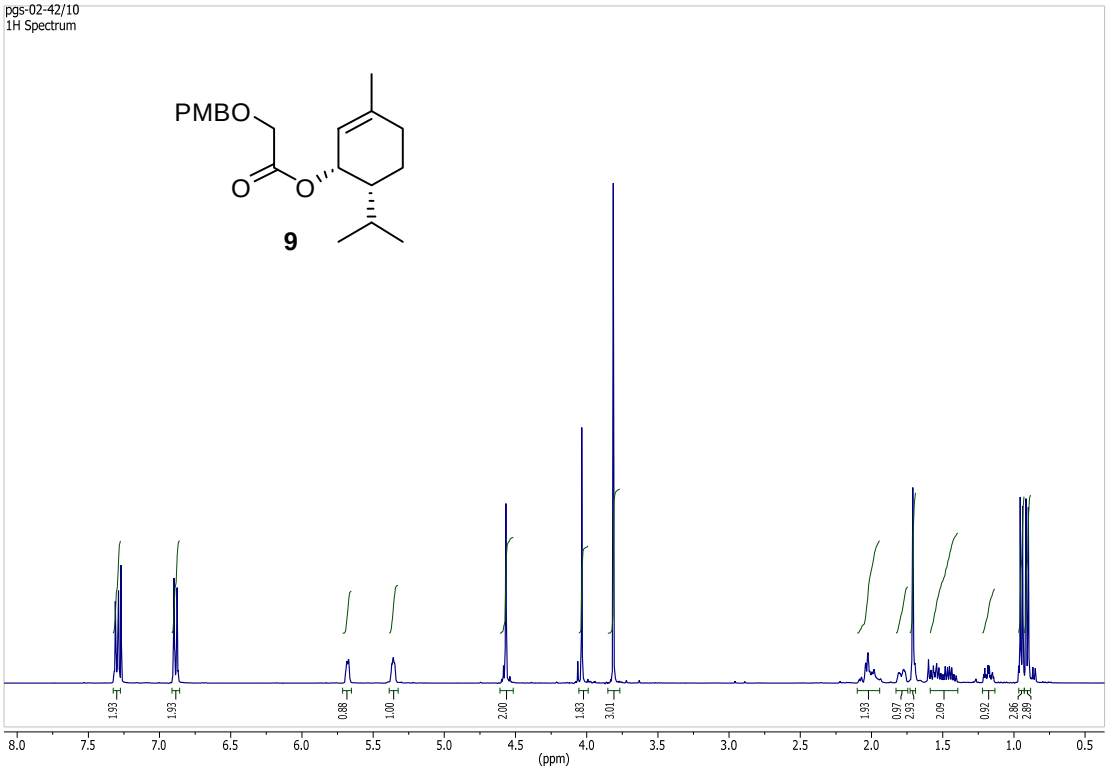
(+)-5-*epi*-eudesma-4(15)-ene-1*β*,6*β*-diol (**2**)

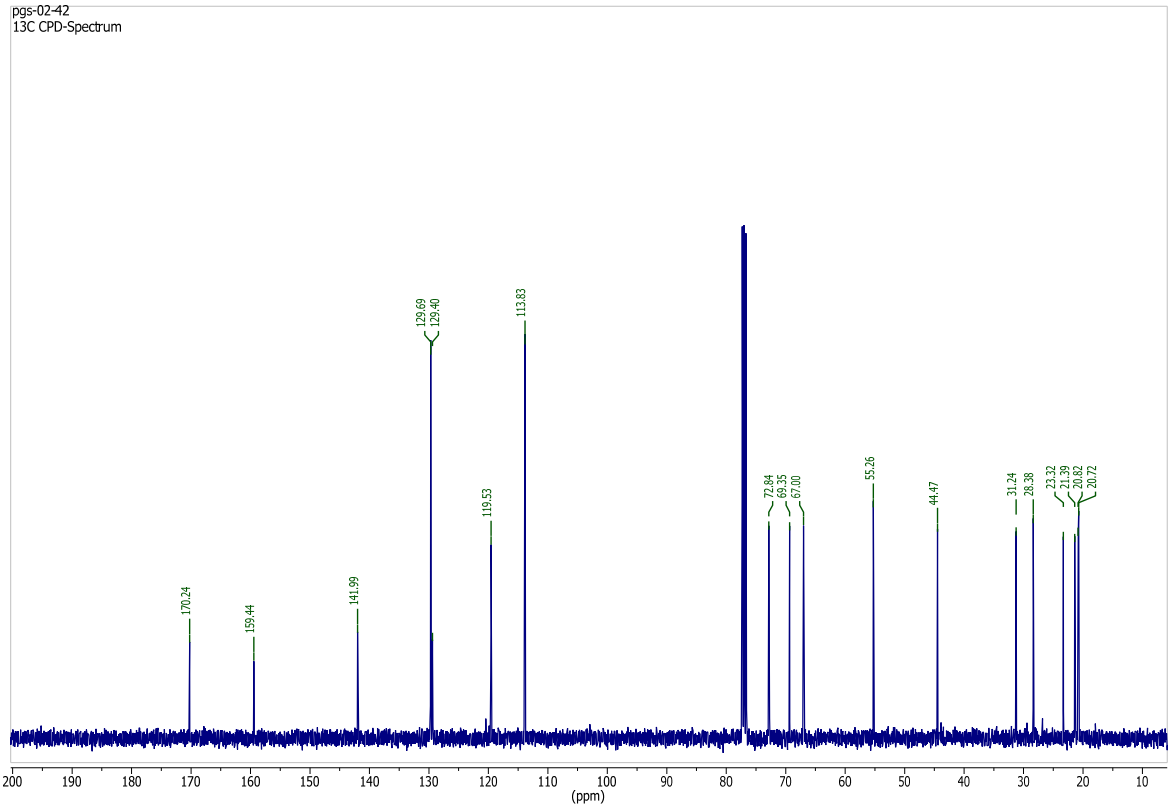


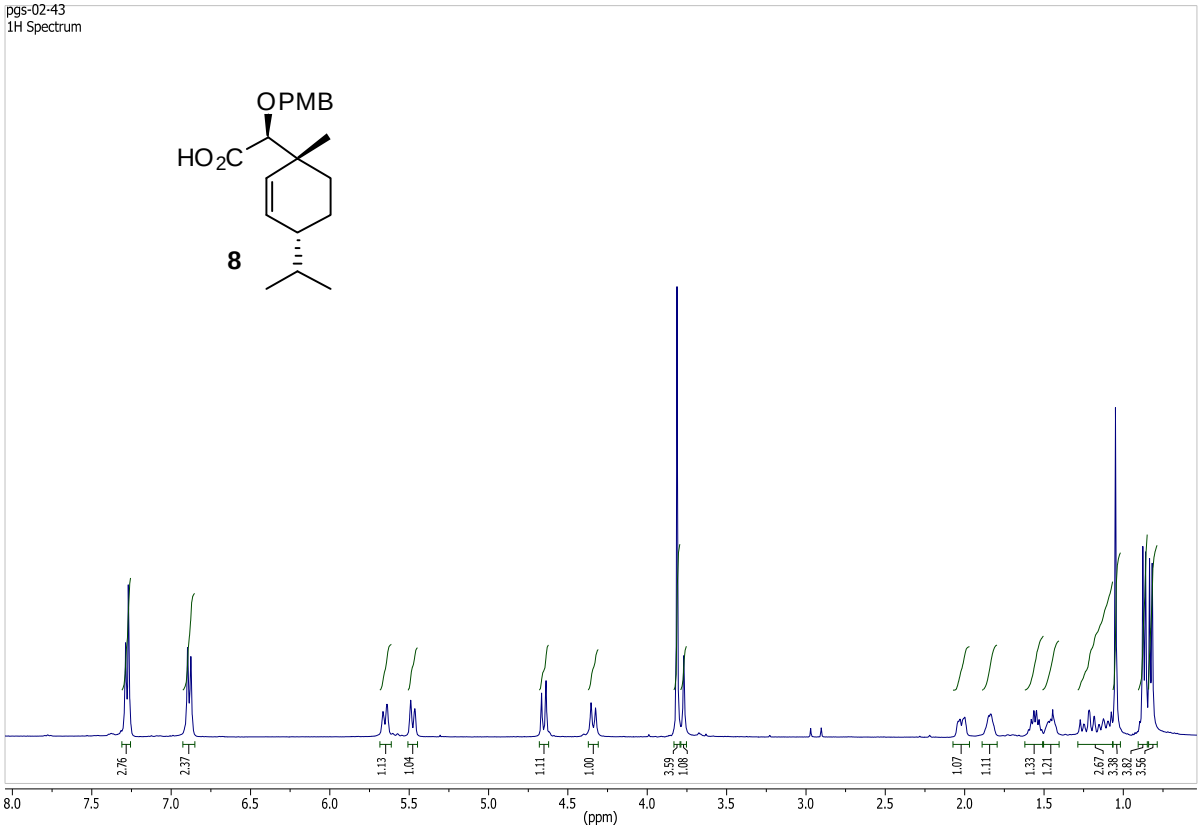
18 **2**

The compound **18** (24.5 mg, 0.103 mmol) was dissolved in CH_2Cl_2 and pH 8 phosphate buffer mixture (1.6 mL, 5:1). The solution was cooled to 0 °C and was added DDQ (137 mg, 0.606 mmol) at once with vigorous stirring. After 2 h, the reaction was diluted with CH_2Cl_2 and the organic layer was washed with half-saturated $NaHCO_3$ solution (3 X 5 mL), brine, dried over Na_2SO_4 and concentrated. Flash chromatography (ethylacetate/pentate, 1:1) to give the target molecule **2** in 73% yield (9.2 mg) as viscous oil. **R***f* = 0.45 (40% ethyl acetate/pentane); **^{1}H NMR (500 MHz, $CDCl_3$) δ** 4.99 (brt, *J* = 2.2 Hz, 1H), 4.85 (t, *J* = 2.0 Hz, 1H), 3.95 (dd, *J* = 11.7, 4.8 Hz, 1H), 3.53 (t, *J* = 10.0 Hz, 1H), 2.36 – 2.32 (m, 1H), 2.31 – 2.28 (m, 1H), 2.23 (pd, *J* = 7.0, 2.5 Hz, 1H), 2.08 (dt, *J* = 14.0, 3.1 Hz, 1H), 1.90 (dtd, *J* = 12.6, 5.1, 2.5 Hz, 1H), 1.85 (d, *J* = 10.1 Hz, 1H), 1.65 – 1.59 (m, 1H), 1.48 (dq, *J* = 12.5, 3.2 Hz, 1H), 1.36 – 1.28 (m, 1H), 1.27 – 1.24 (m, 1H), 1.06 (td, *J* = 13.6, 4.1 Hz, 1H), 0.95 (d, *J* = 7.1 Hz, 3H), 0.88 (s, 3H), 0.86 (d, *J* = 6.9 Hz, 3H); **^{13}C NMR (125 MHz, $CDCl_3$) δ** 145.44, 114.17, 68.15, 67.14, 61.62, 49.09, 40.09, 34.38, 31.08, 29.74, 26.43, 21.32, 20.91, 18.05, 16.22; **IR (ATR, neat)** ν_{max} 3379, 2954, 2869, 1724, 1647, 1460, 1244, 1247, 1173, 1031, 878 cm^{-1}; **HRMS (ESI):** calcd. for $C_{15}H_{25}O$ $(M-H_2O+H)^+$ *m/z* 221.1899 found *m/z* 221.1899; $[\alpha]^{25}_D$ +33.2 (*c* 0.41, $CHCl_3$).

3. Spectroscopic data



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1.11
1.00
3.59
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1.07
1.11
1.33
1.21
2.67
3.38
3.82
3.56
8.0
7.5
7.0
6.5
6.0
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3.0
2.5
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1.5
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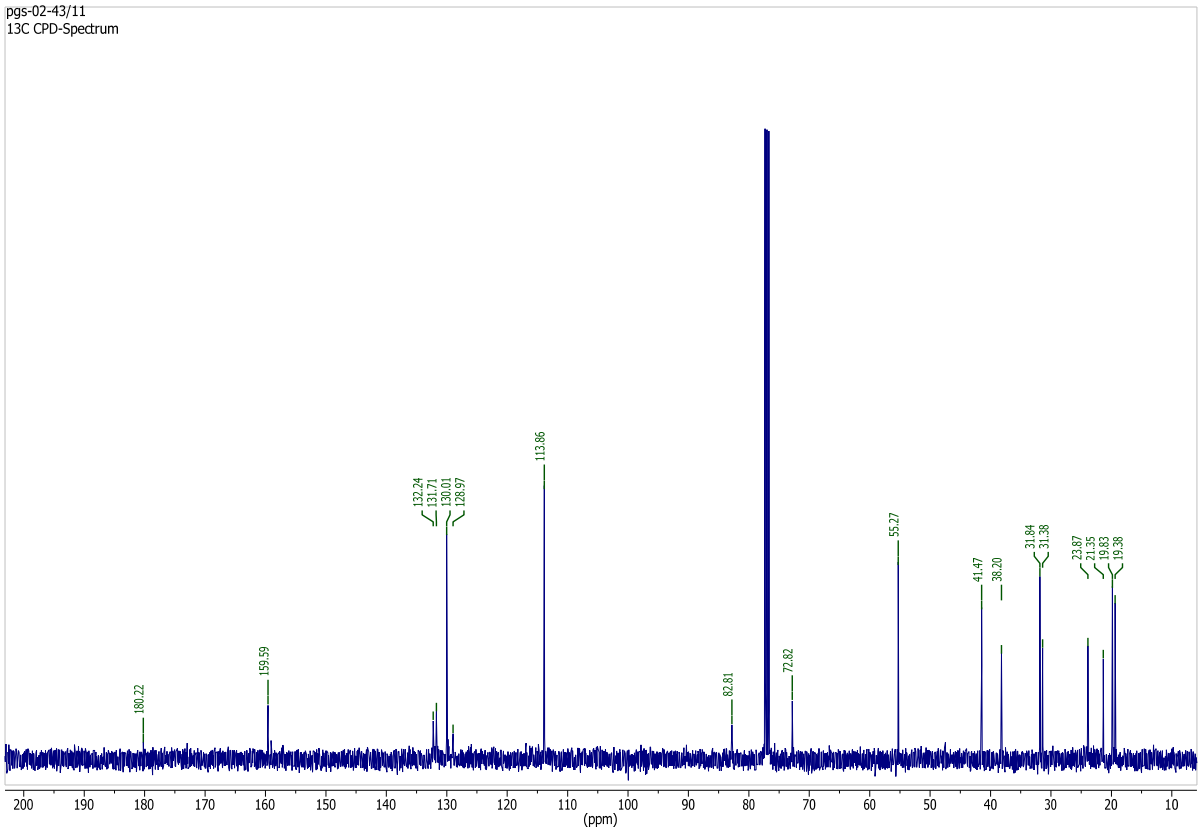
(ppm)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41.47
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31.84
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21.35
19.83
19.38
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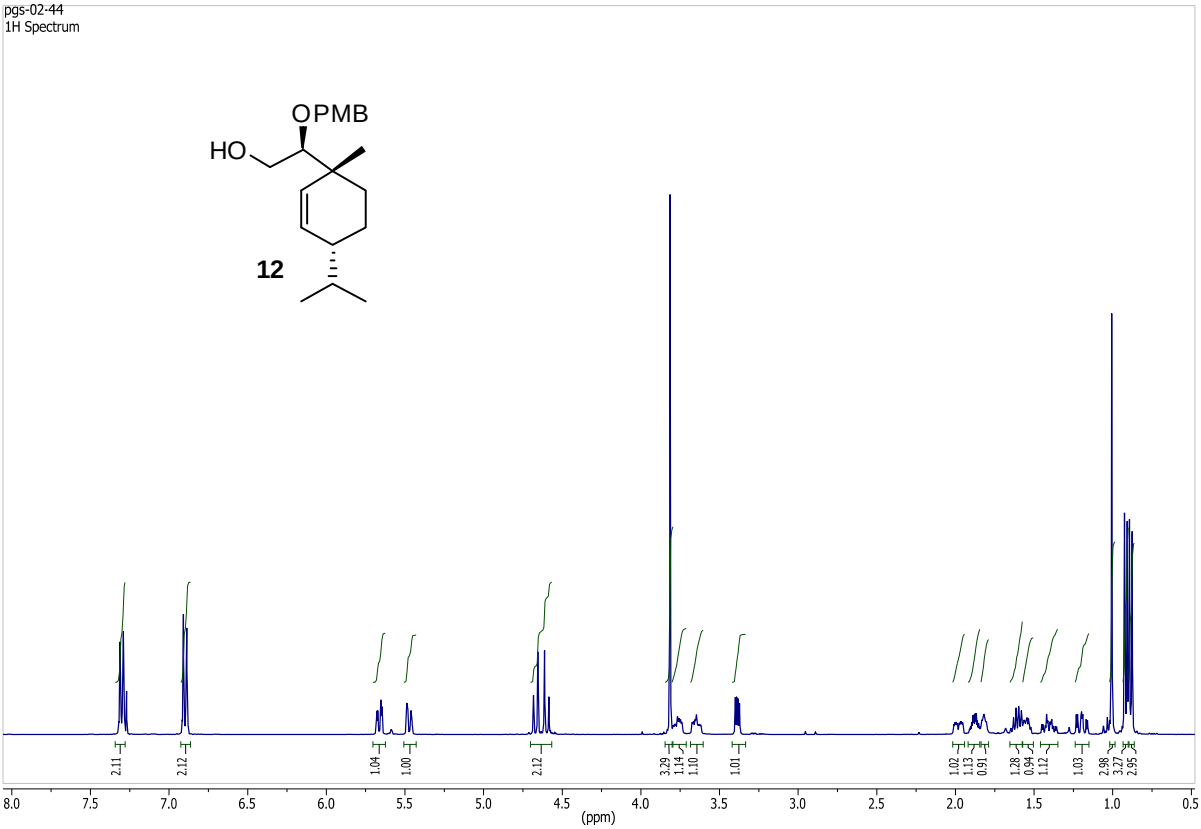
20
10
(ppm)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2.12
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1.00
2.12
3.29
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1.10
1.01
1.02
1.13
0.91
1.28
0.94
1.12
1.03
2.98
3.27
2.95
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7.5
7.0
6.5
6.0
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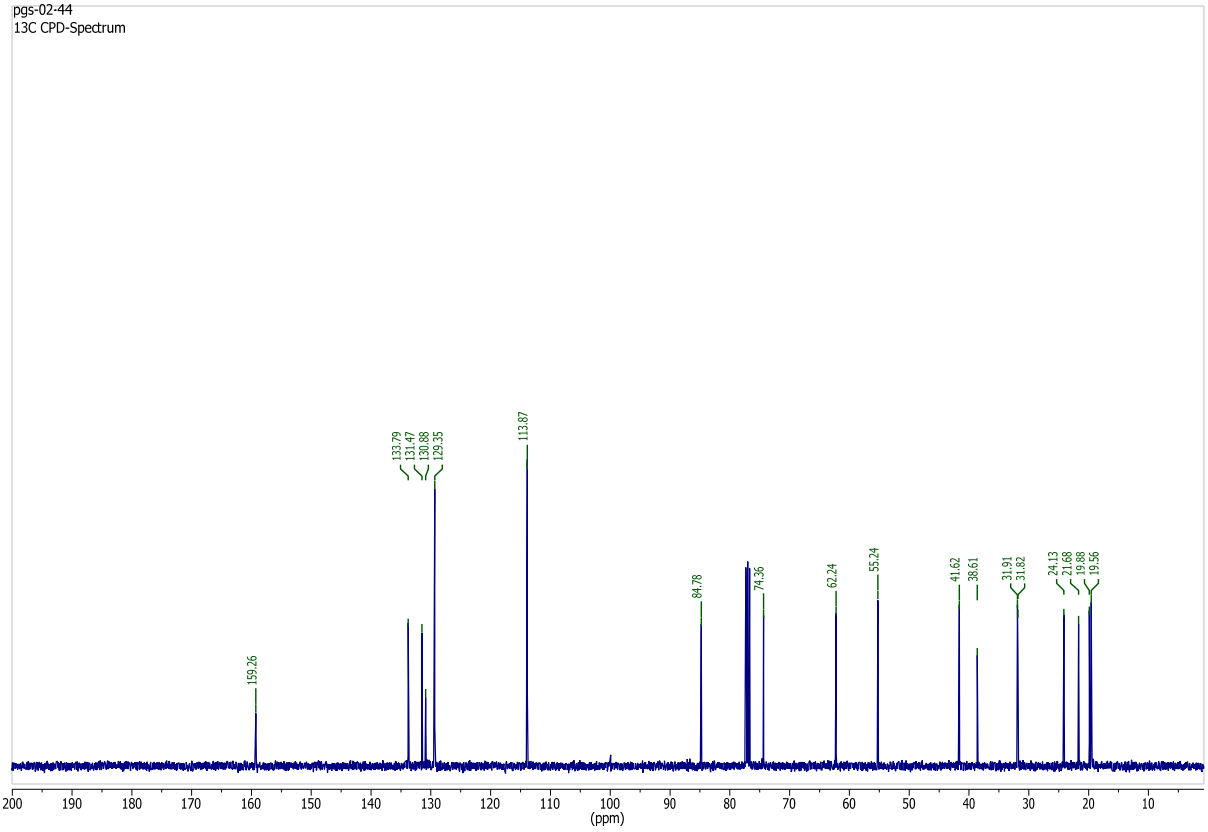
(ppm)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19.56
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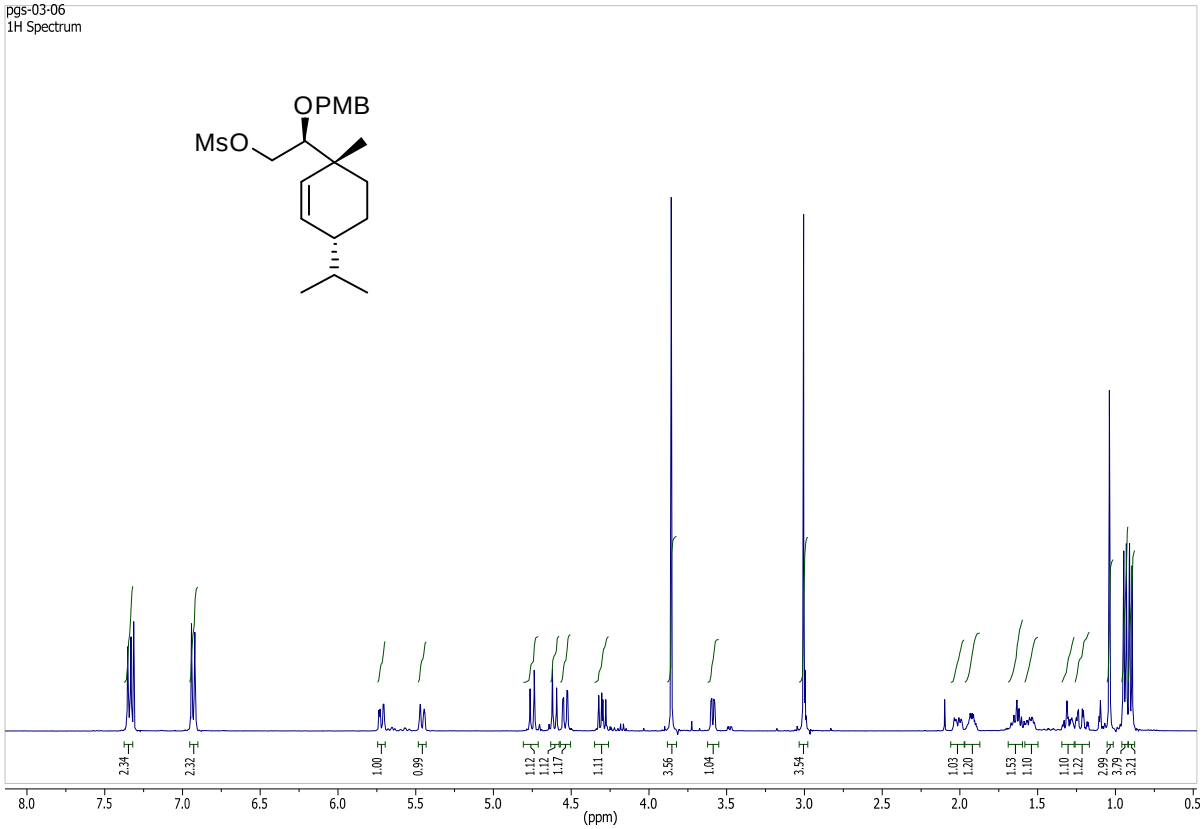
20
10
(ppm)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1.12
1.17
1.11
3.56
1.04
3.54
1.03
1.20
1.53
1.10
1.10
1.22
2.99
3.79
3.21
8.0
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7.0
6.5
6.0
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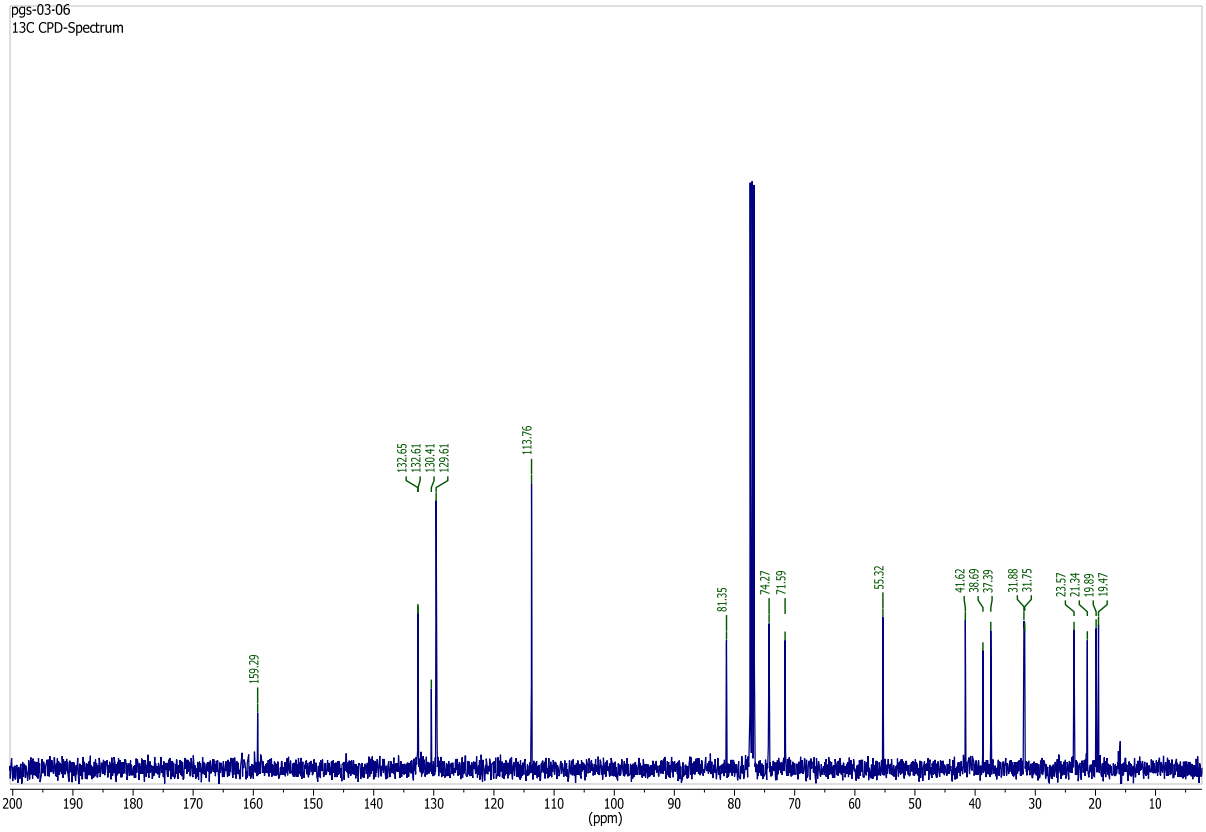
(ppm)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50
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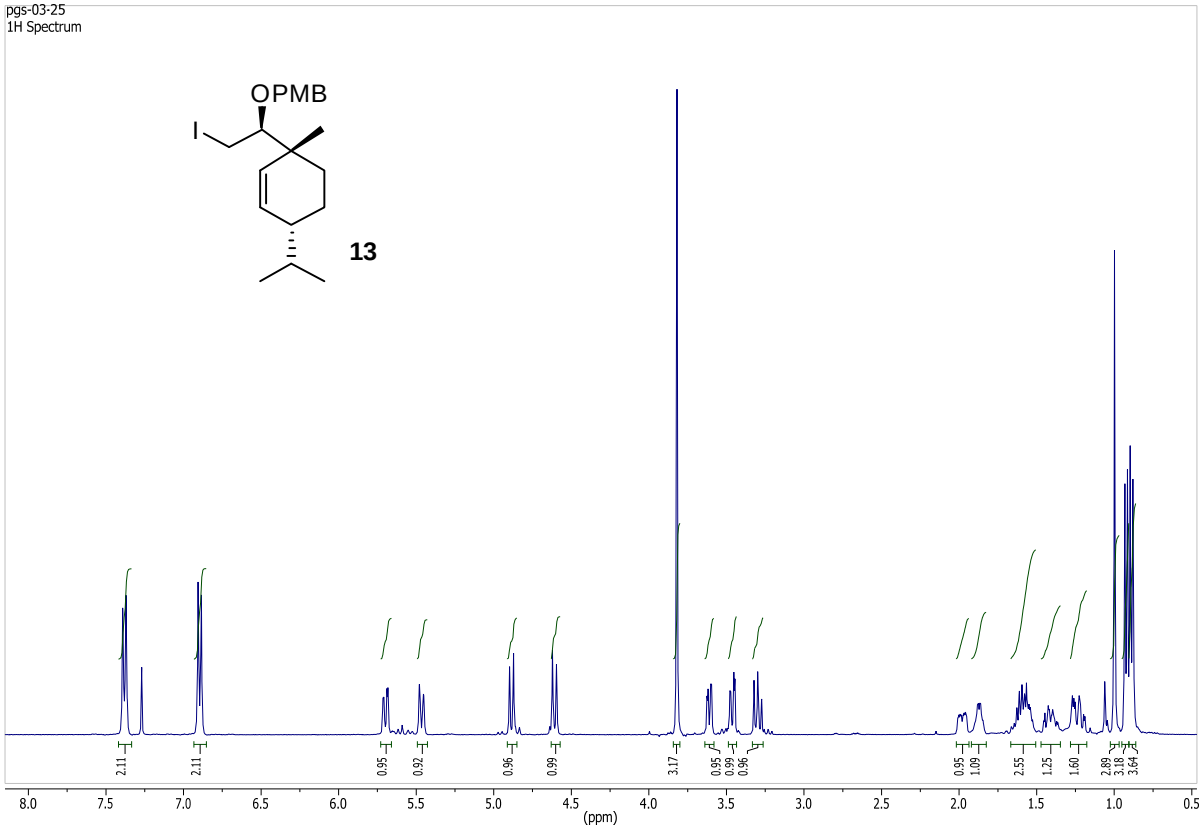
20
10
(ppm)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OPMB
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2.11
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0.96
0.99
3.17
0.95
0.99
0.96
0.95
1.09
2.55
1.25
1.60
2.89
3.18
3.64
8.0
7.5
7.0
6.5
6.0
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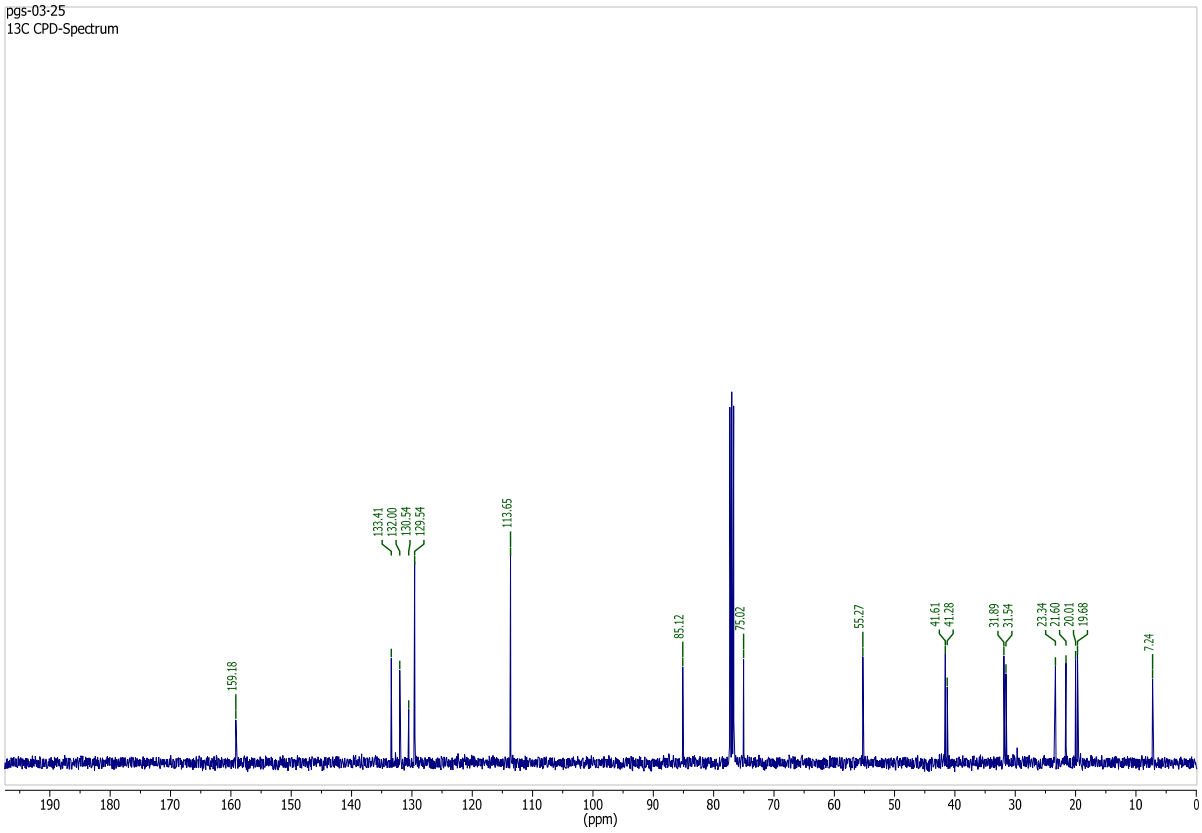
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
(ppm)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7.24
190
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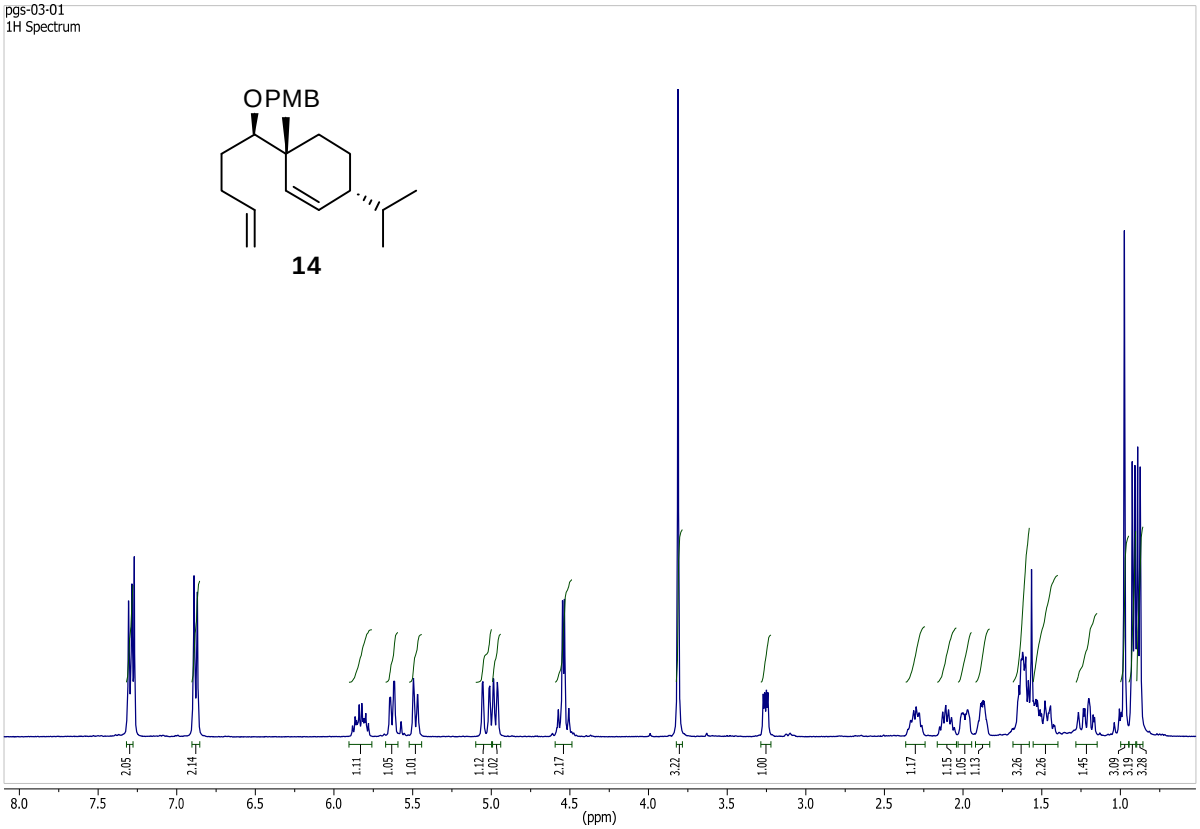
(ppm)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1.02
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2.5
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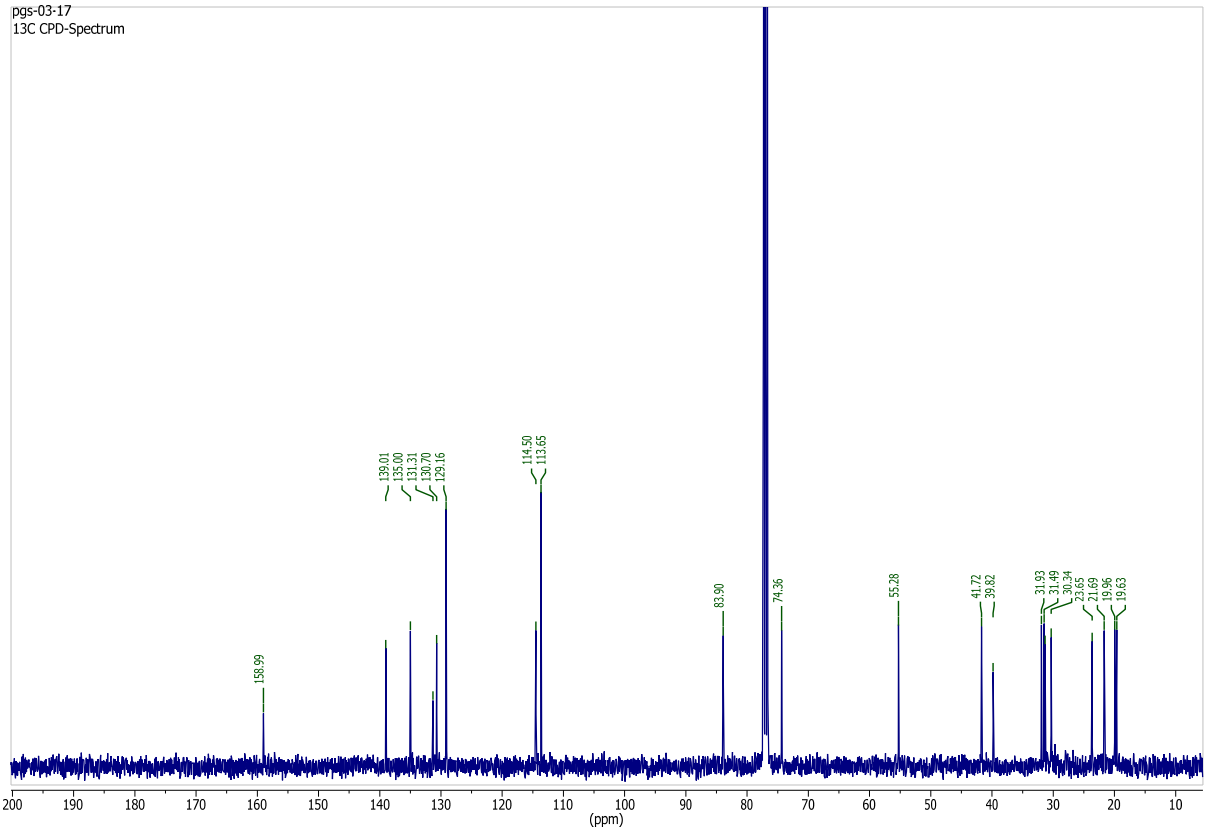
1.5
1.0
(ppm)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113.65
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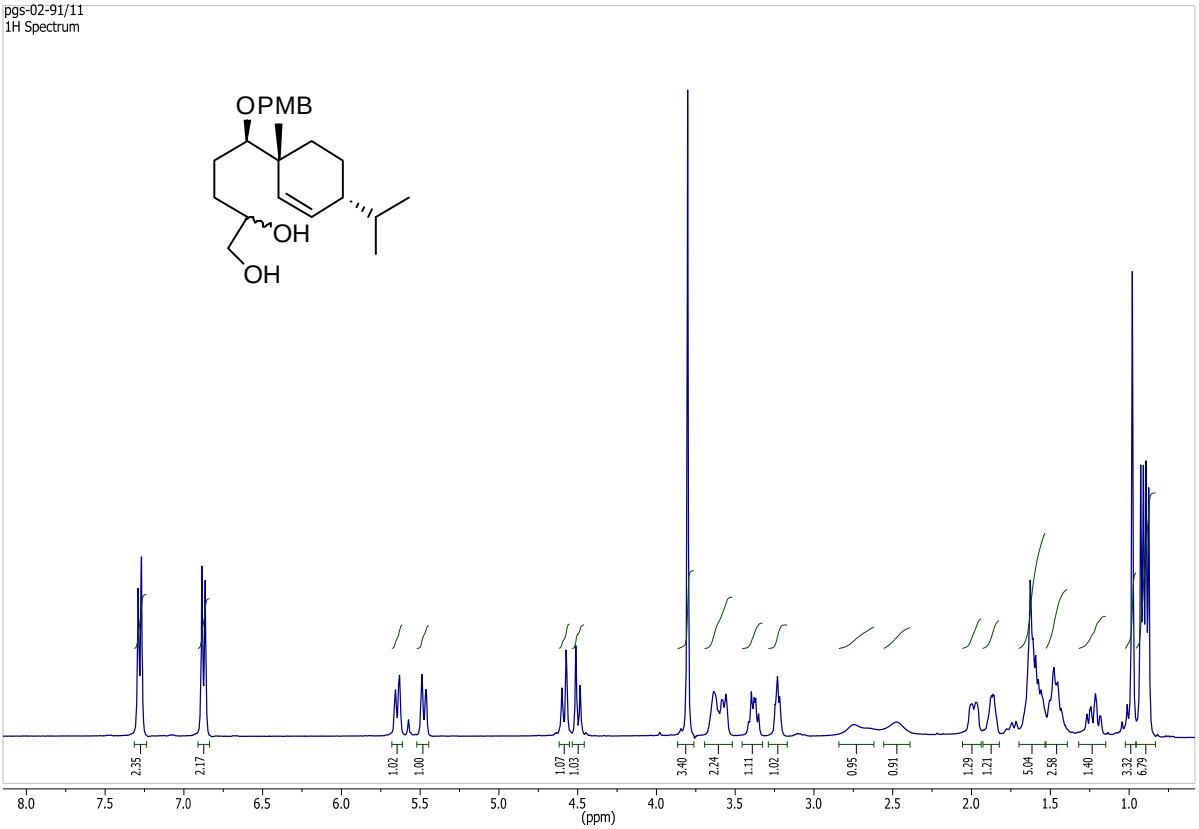
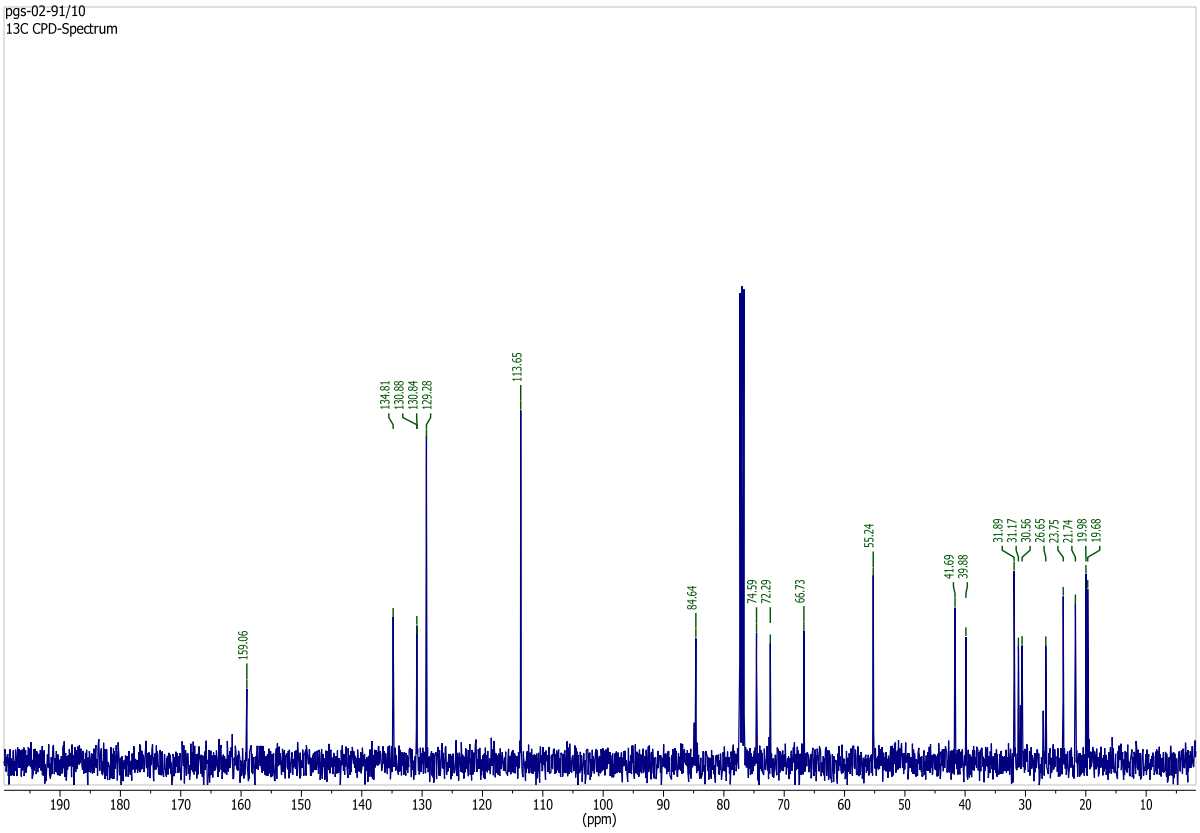
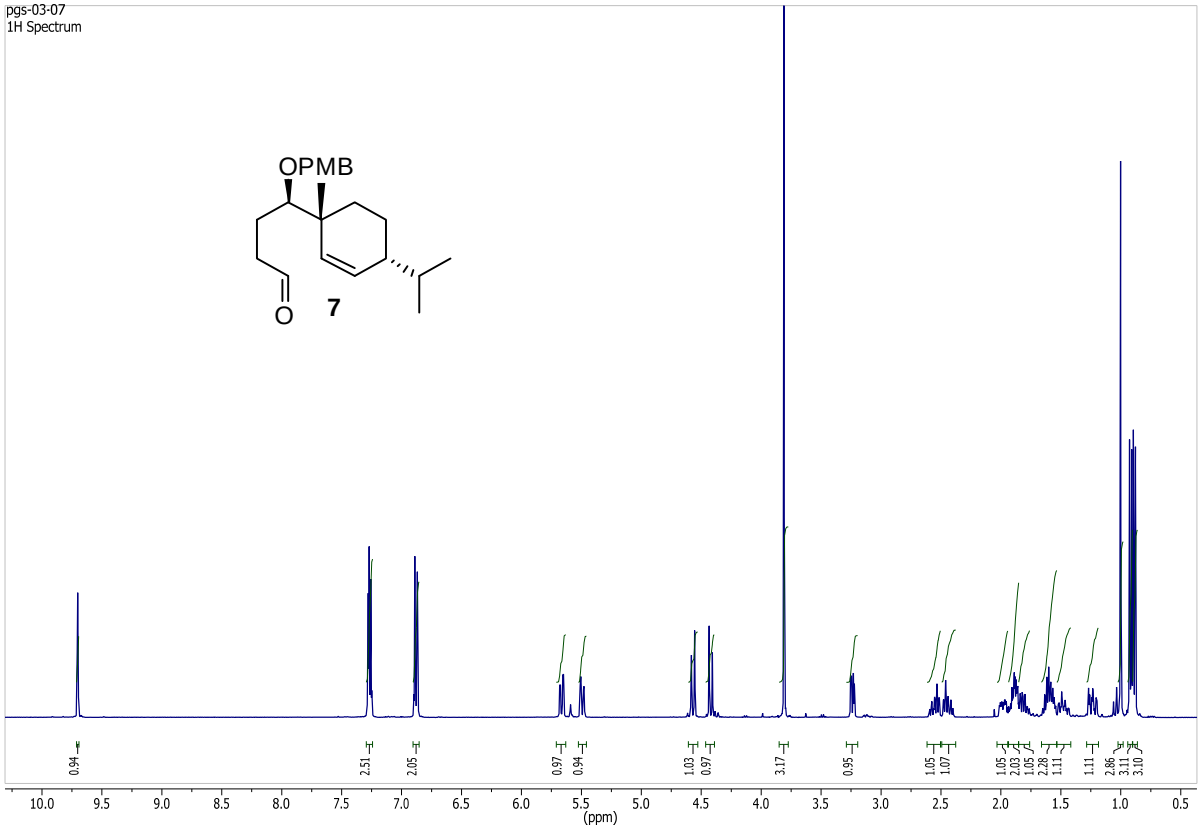
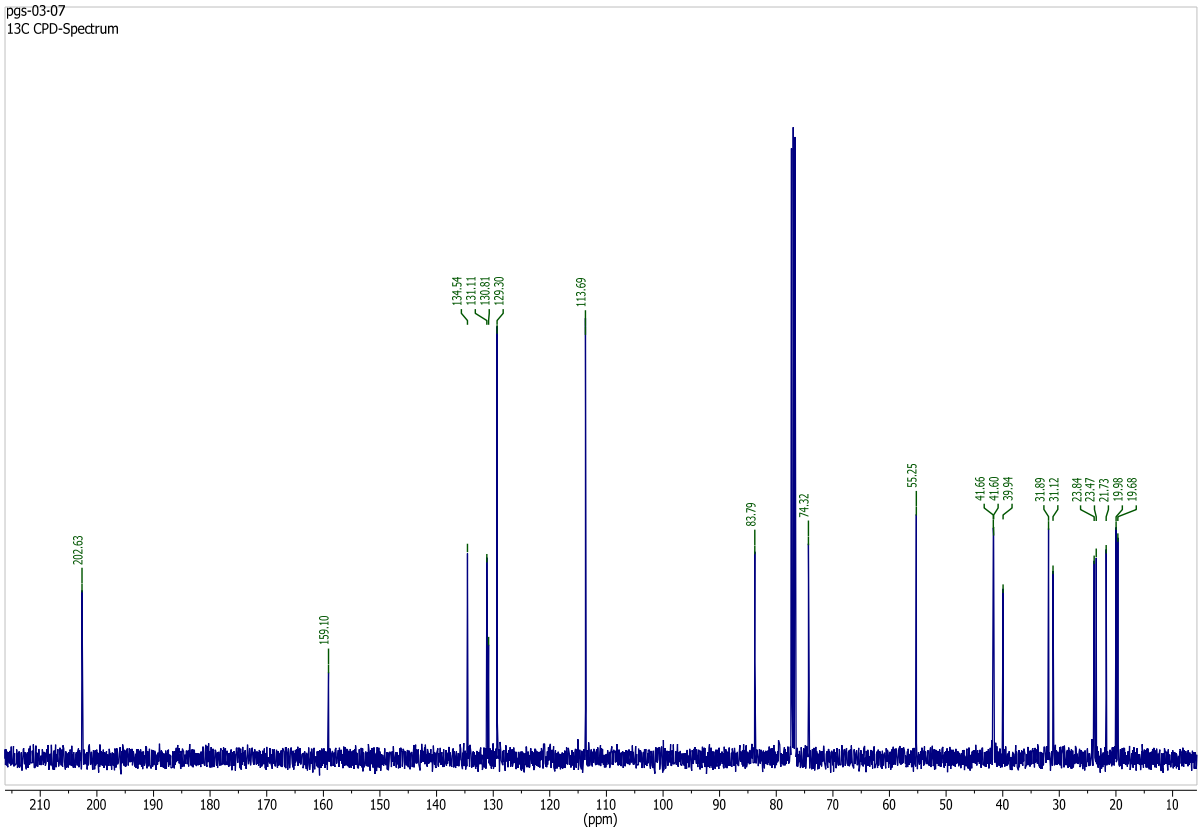
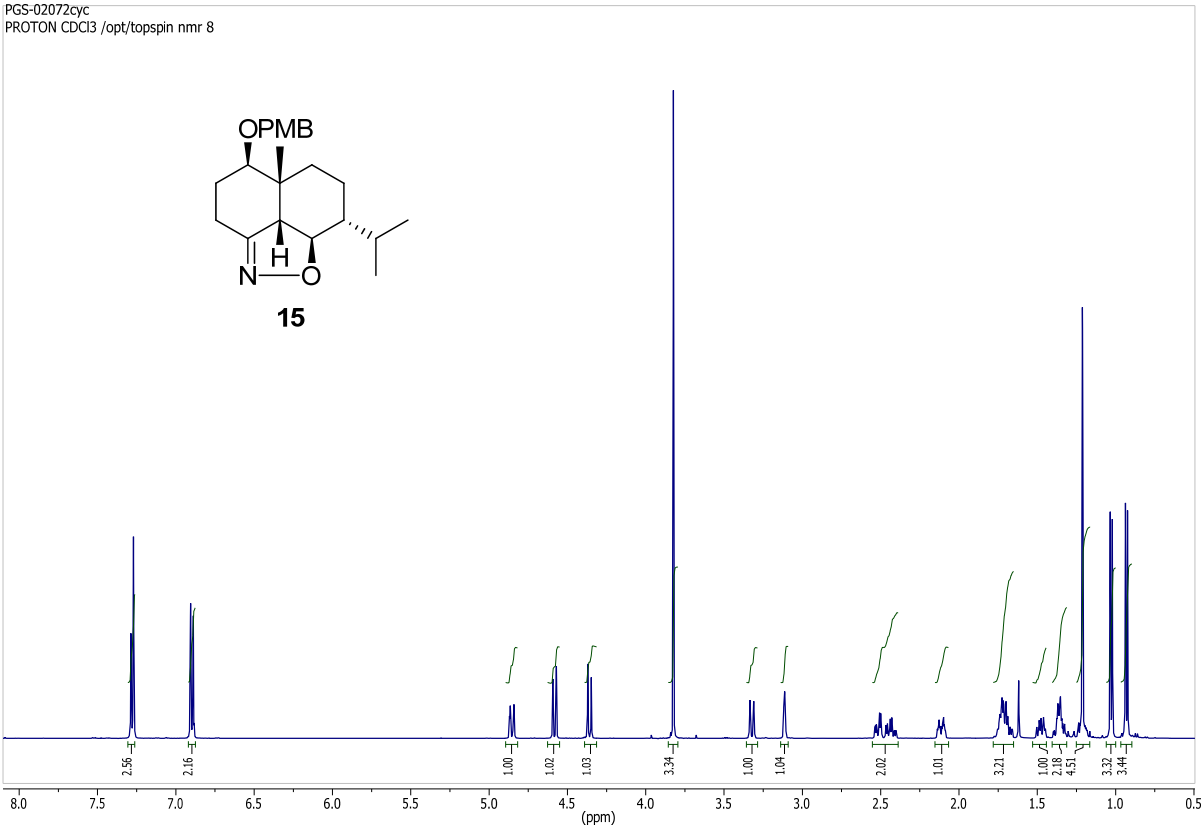
39.82
31.93
31.49
30.34
23.65
21.69
19.96
19.63
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
(ppm)

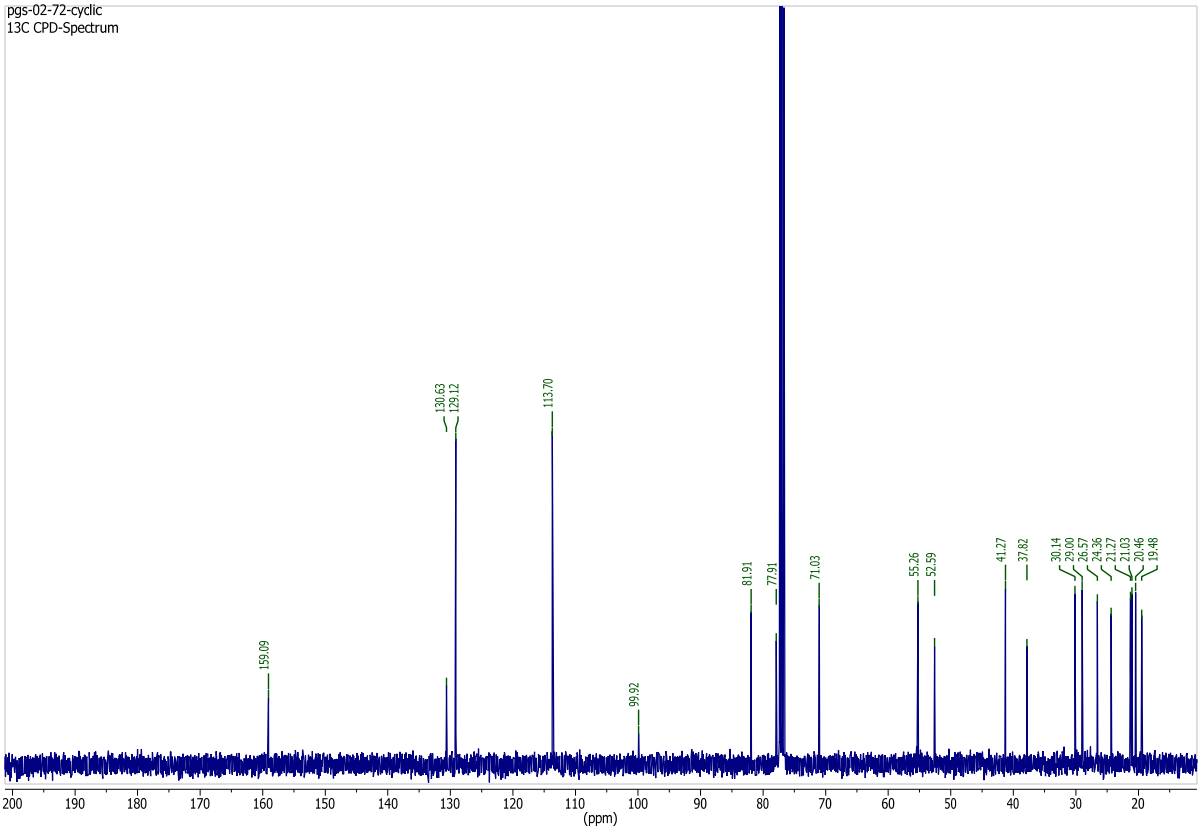

pgs-02-91/11
1H Spectrum
OPMB
OH
OH
2.35
2.17
1.02
1.00
1.07
1.03
3.40
2.24
1.11
1.02
0.95
0.91
1.29
1.21
5.04
2.58
1.40
3.32
6.79
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
(ppm)

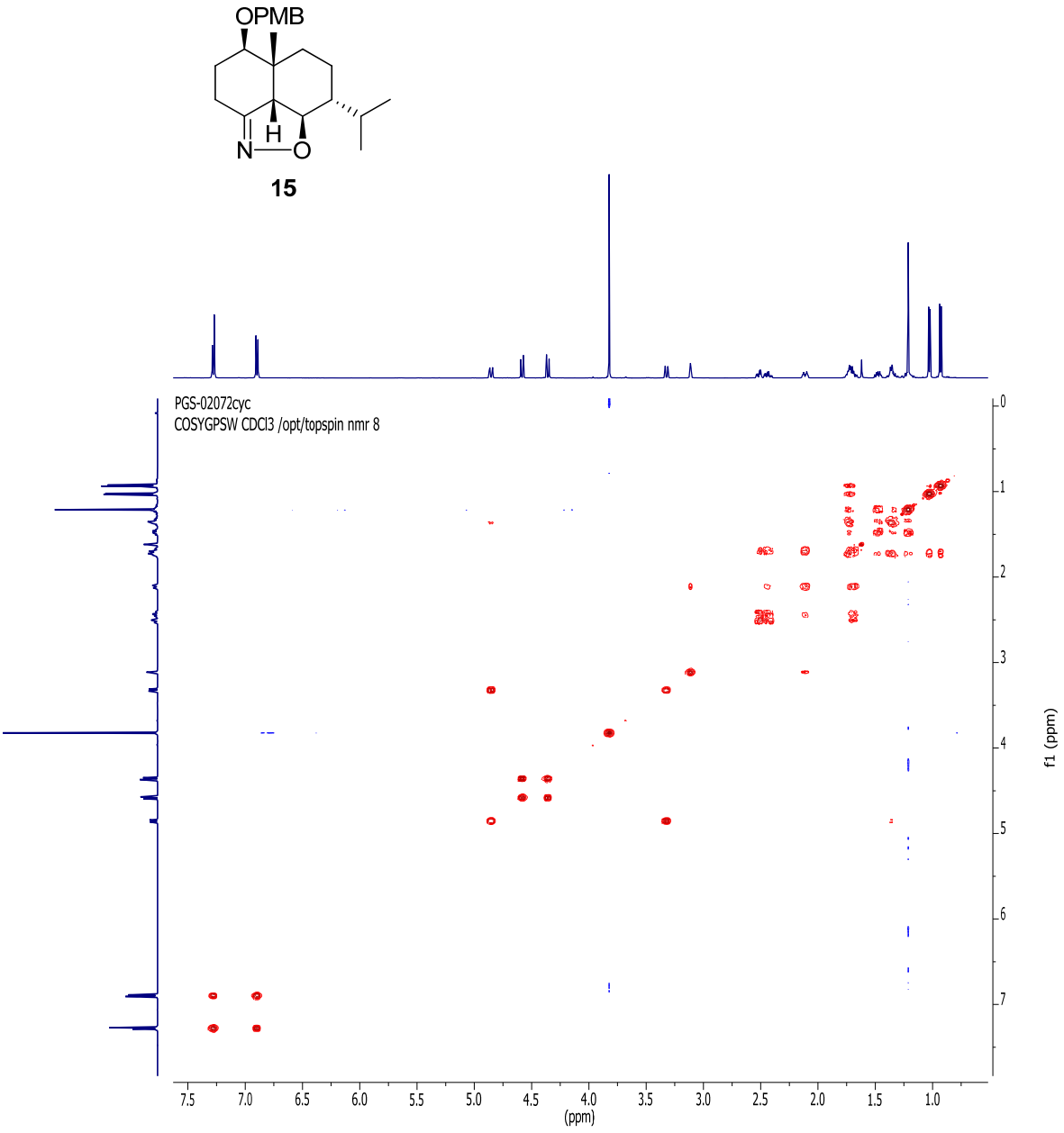

pgs-02-91/10
13C CPD-Spectrum
159.06
134.81
130.88
130.84
129.28
113.65
84.64
74.59
72.29
66.73
55.24
41.69
39.88
31.89
31.17
30.56
26.65
23.75
21.74
19.98
19.68
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
(ppm)

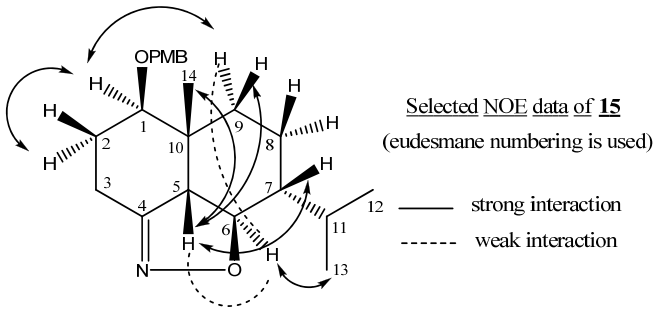

pgs-03-07
1H Spectrum
OPMB
O
7
0.94
2.51
2.05
0.97
0.94
1.03
0.97
3.17
0.95
1.05
1.07
1.05
2.03
1.05
2.28
1.11
1.11
2.86
3.11
3.10
10.0
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
(ppm)

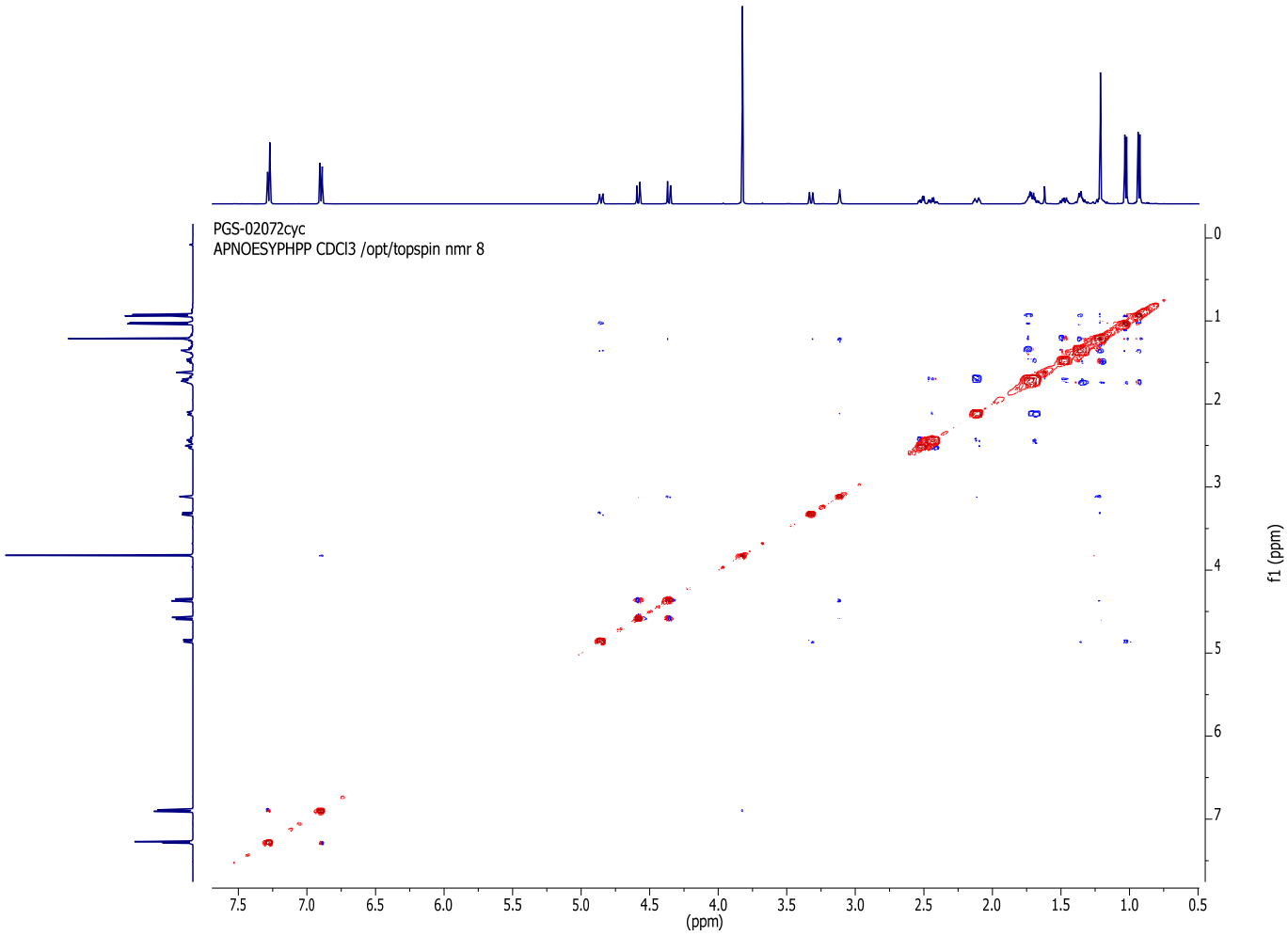

pgs-03-07
13C CPD-Spectrum
202.63
159.10
134.54
131.11
130.81
129.30
113.69
83.79
74.32
55.25
41.66
41.60
39.94
31.89
31.12
23.84
23.47
21.73
19.98
19.68
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
(ppm)

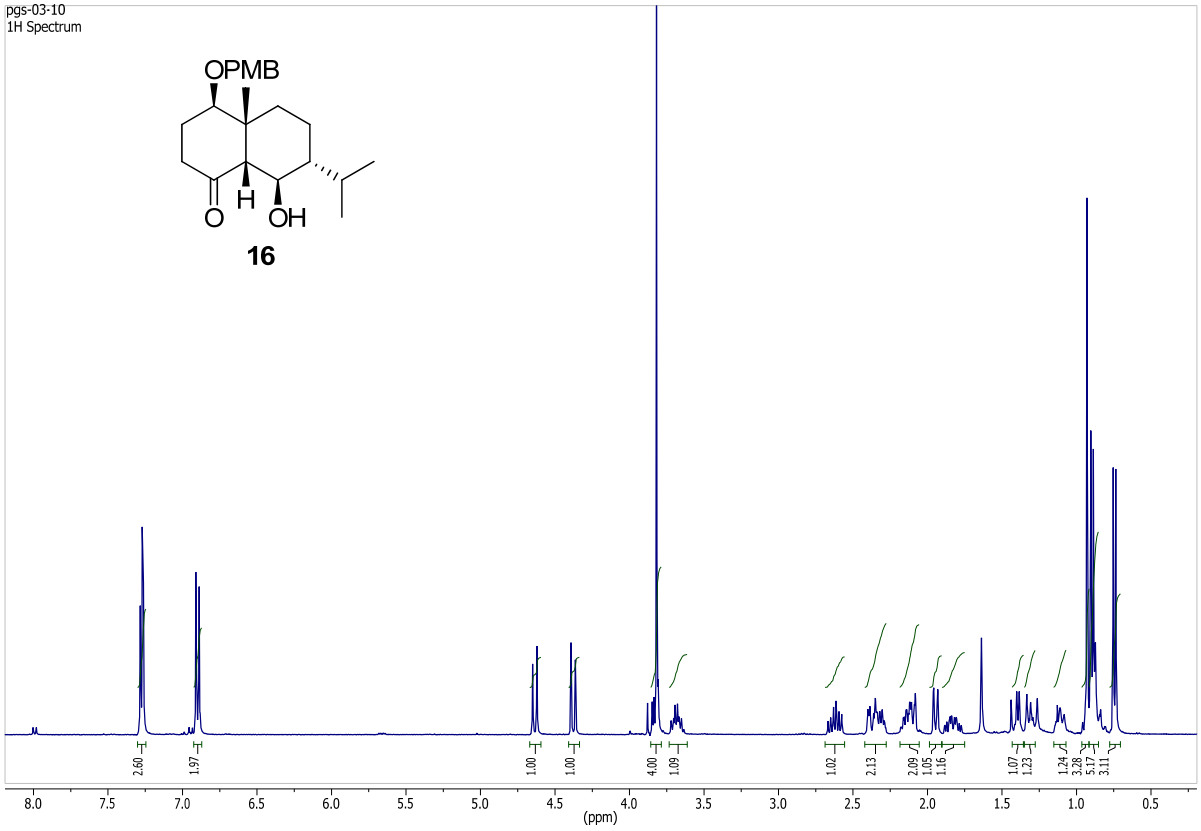

PGS-02072cyc
PROTON CDCl3 /opt/topspin nmr 8
OPMB
H
N
O
15
2.56
2.16
1.00
1.02
1.03
3.34
1.00
1.04
2.02
1.01
3.21
1.00
2.18
4.51
3.22
3.44
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
(ppm)

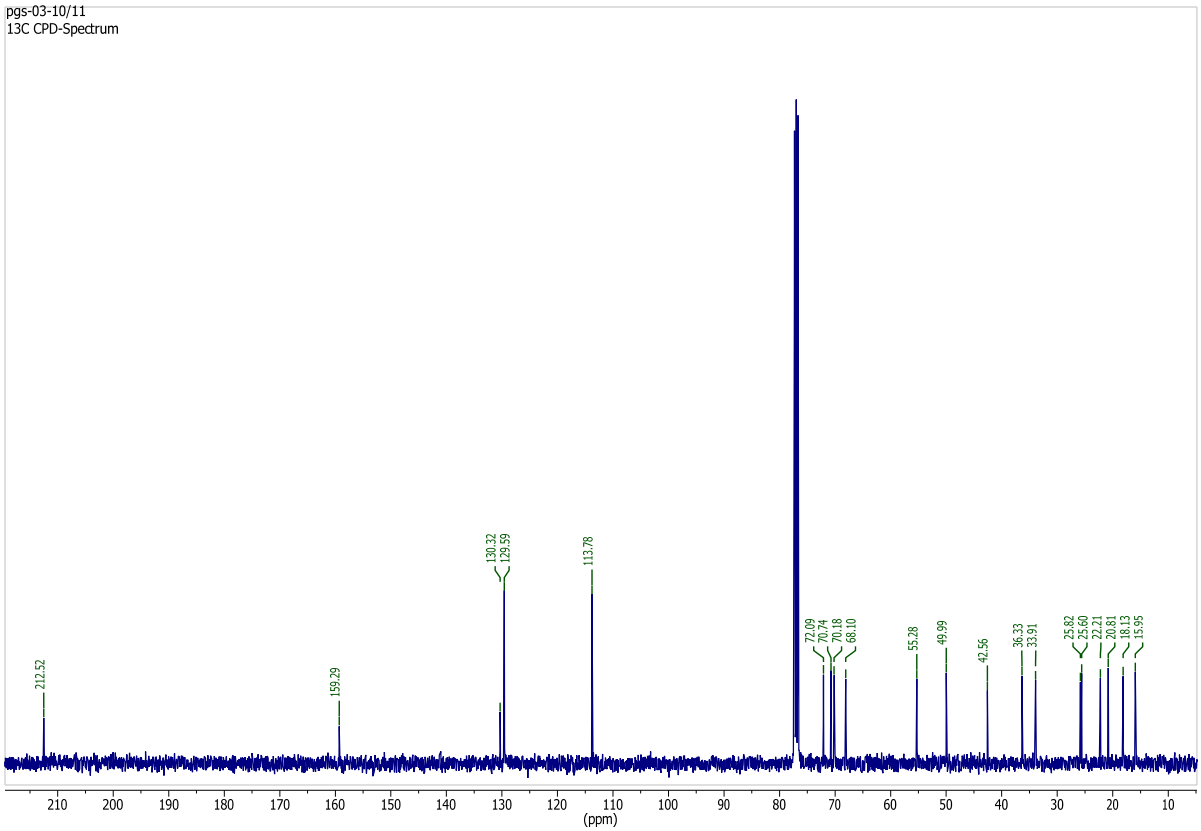

pgs-02-72-cyclic
13C CPD-Spectrum
159.09
130.63
129.12
113.70
99.92
81.91
77.91
71.03
55.26
52.59
41.27
37.82
30.14
29.00
26.57
24.36
21.27
21.03
20.46
19.48
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
(ppm)

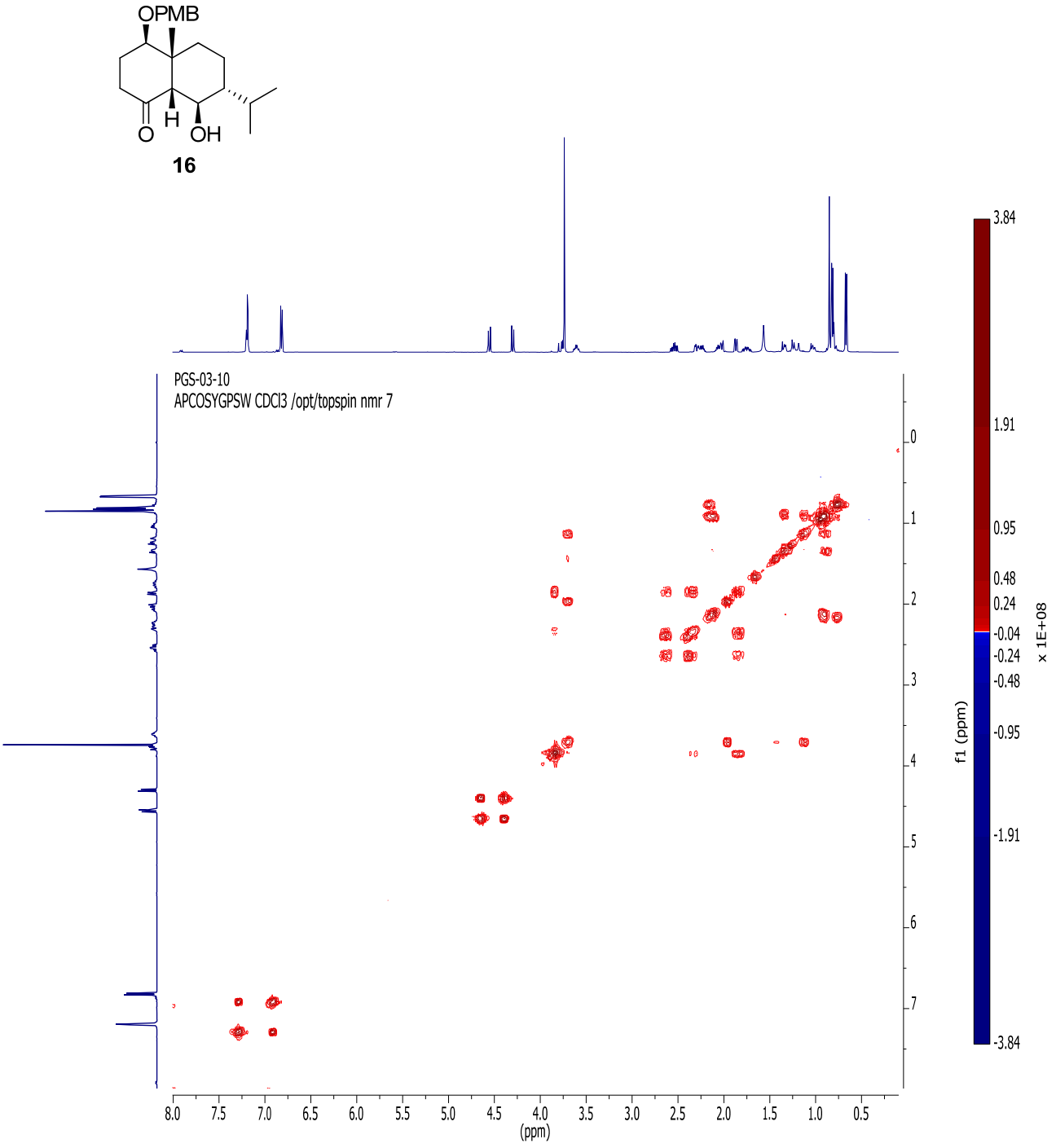

OPMB
H
N
O
15
PGS-02072cyc
COSYGPSW CDCl3 /opt/topspin nmr 8
f1 (ppm)
(ppm)

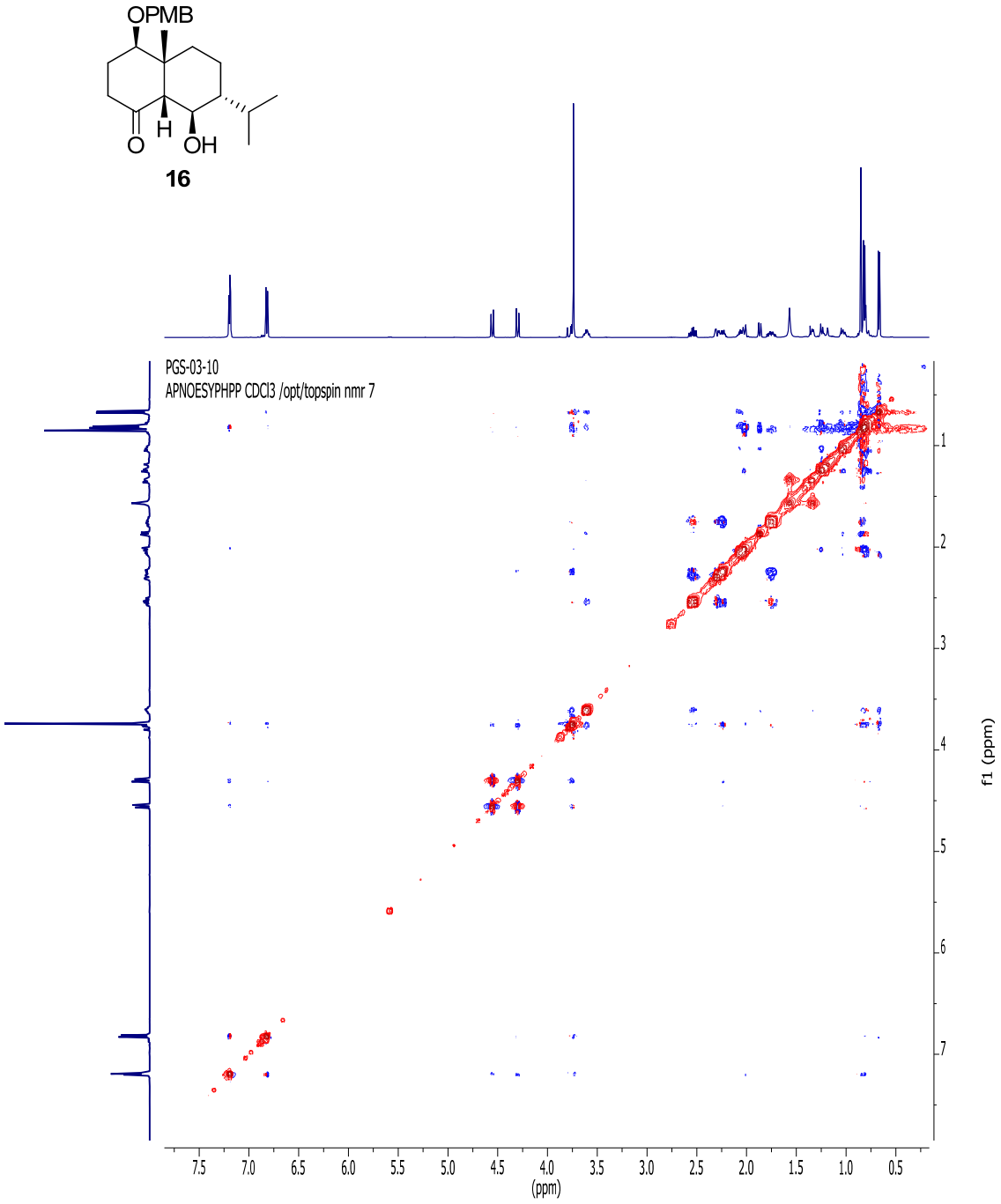


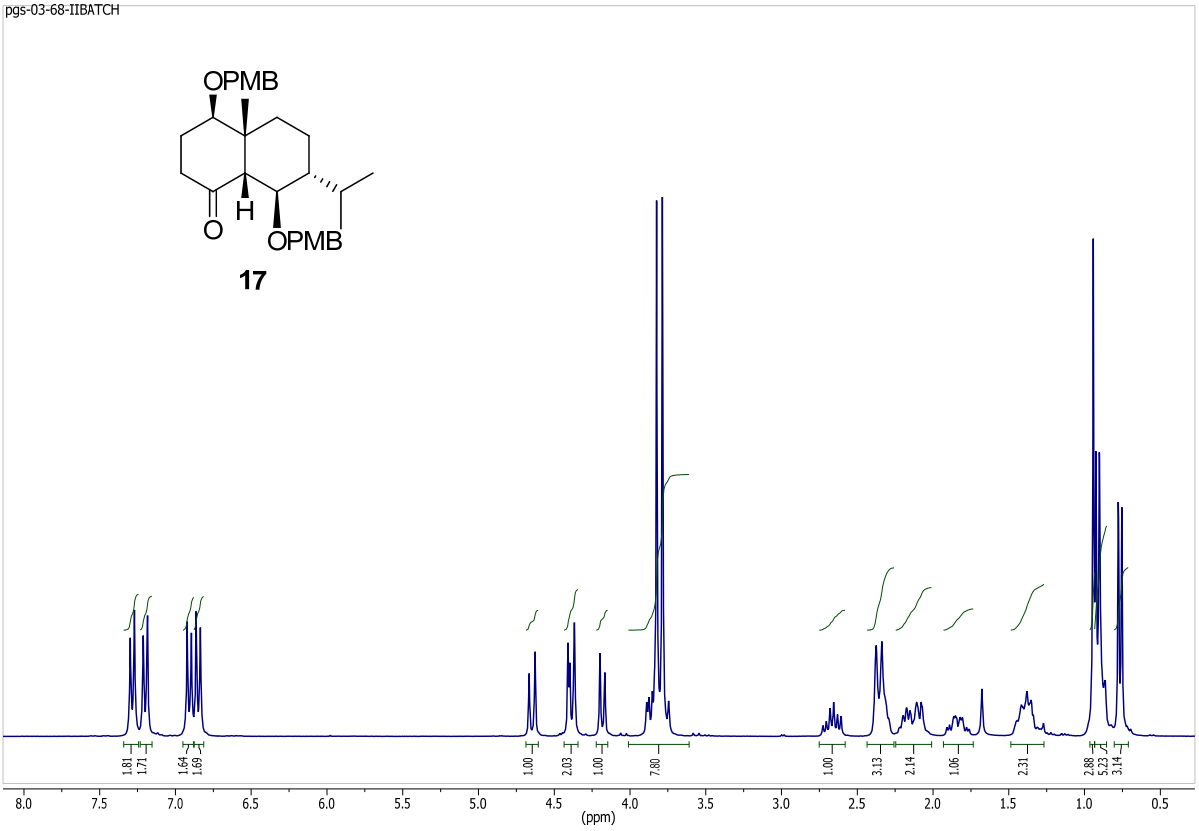


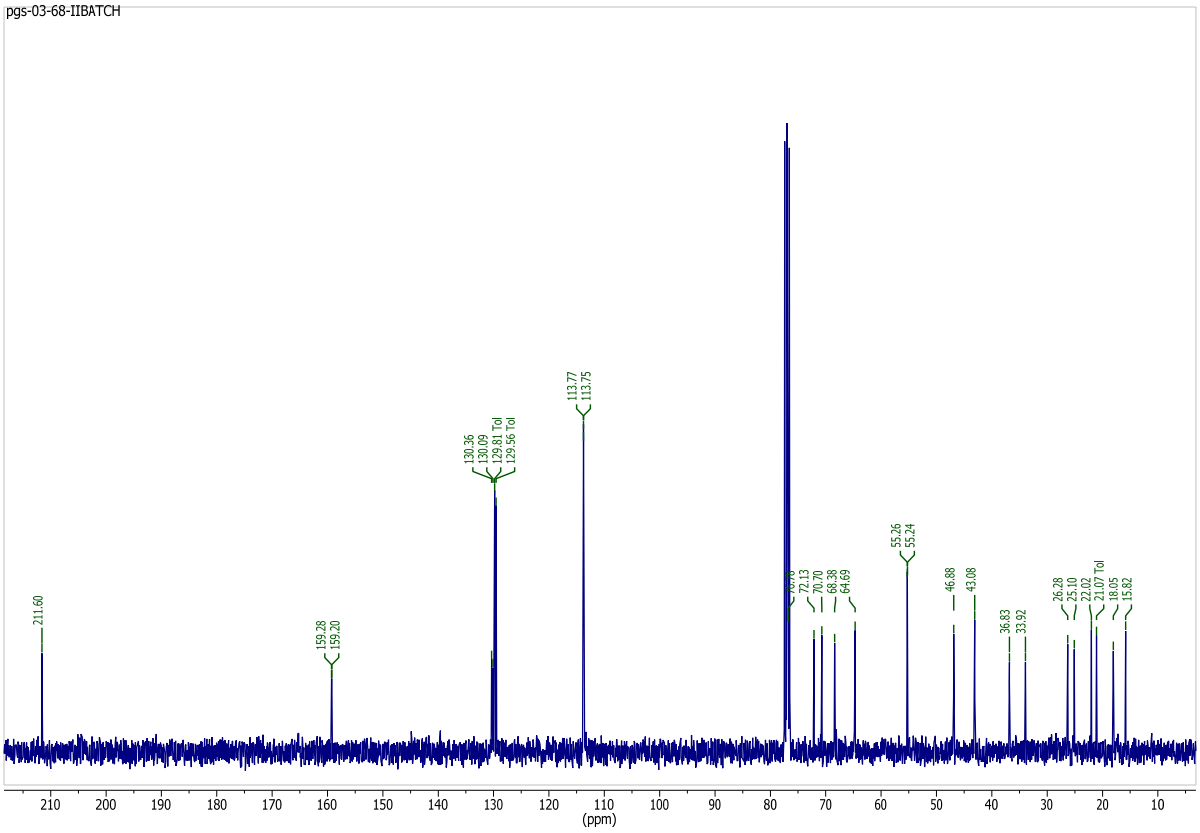

pgs-03-10
1H Spectrum
OPMB
H
O
OH
16
2.60
1.97
1.00
1.00
4.00
1.09
1.02
2.13
2.09
1.05
1.16
1.07
1.23
1.24
3.28
5.17
3.11
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
(ppm)

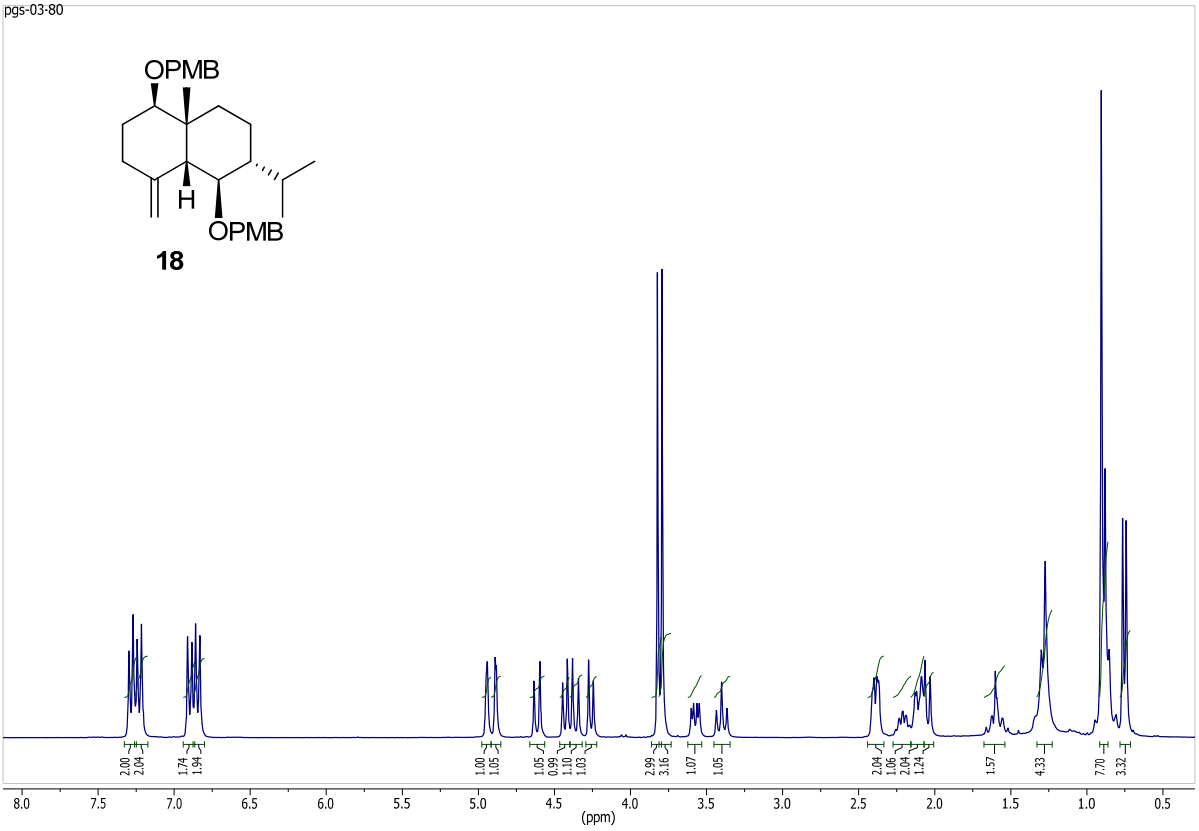

pgs-03-10/11
13C CPD-Spectrum
212.52
159.29
130.32
129.59
113.78
72.09
70.74
70.18
68.10
55.28
49.99
42.56
36.33
33.91
25.82
25.60
22.21
20.81
18.13
15.95
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
(ppm)

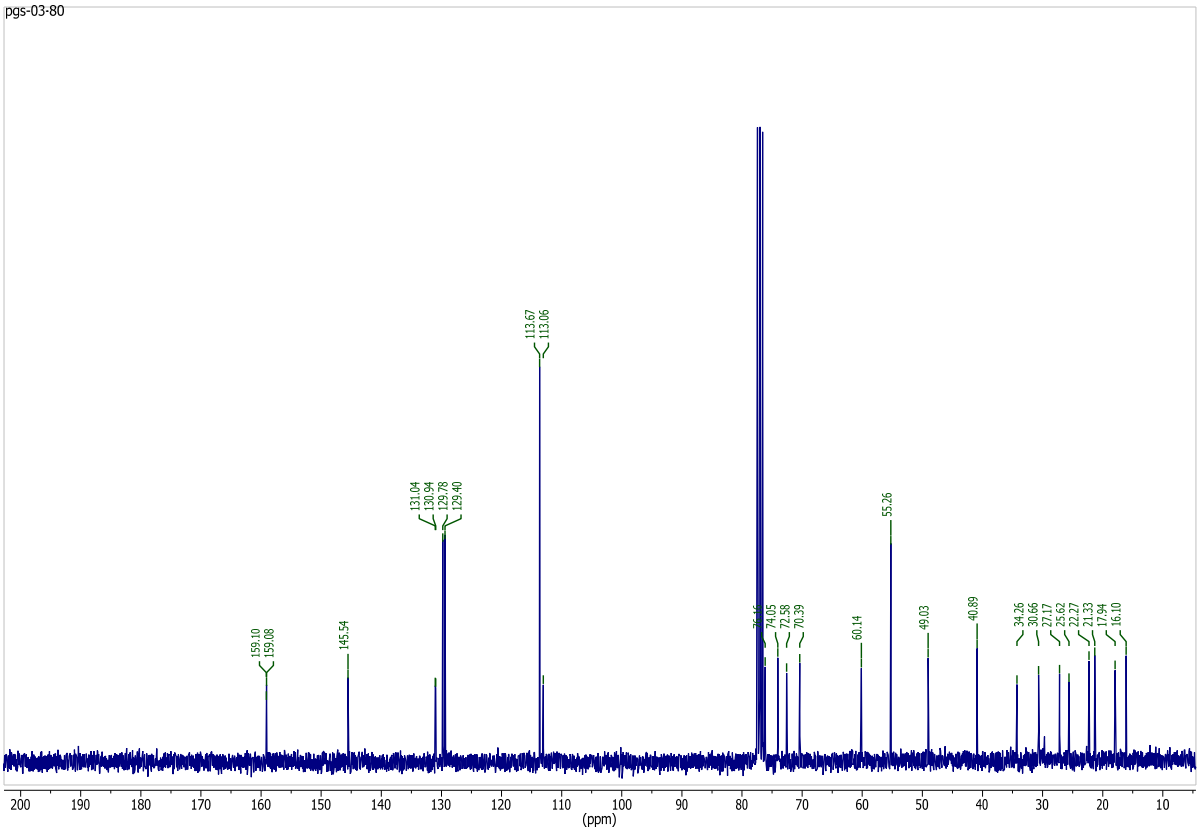

OPMB
H
O
OH
16
PGS-03-10
APCOSYGPSW CDCl3 /opt/topspin nmr 7
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
(ppm)
0
1
2
3
4
5
6
7
f1 (ppm)
3.84
1.91
0.95
0.48
0.24
-0.04
-0.24
-0.48
-0.95
-1.91
-3.84
x 1E+08

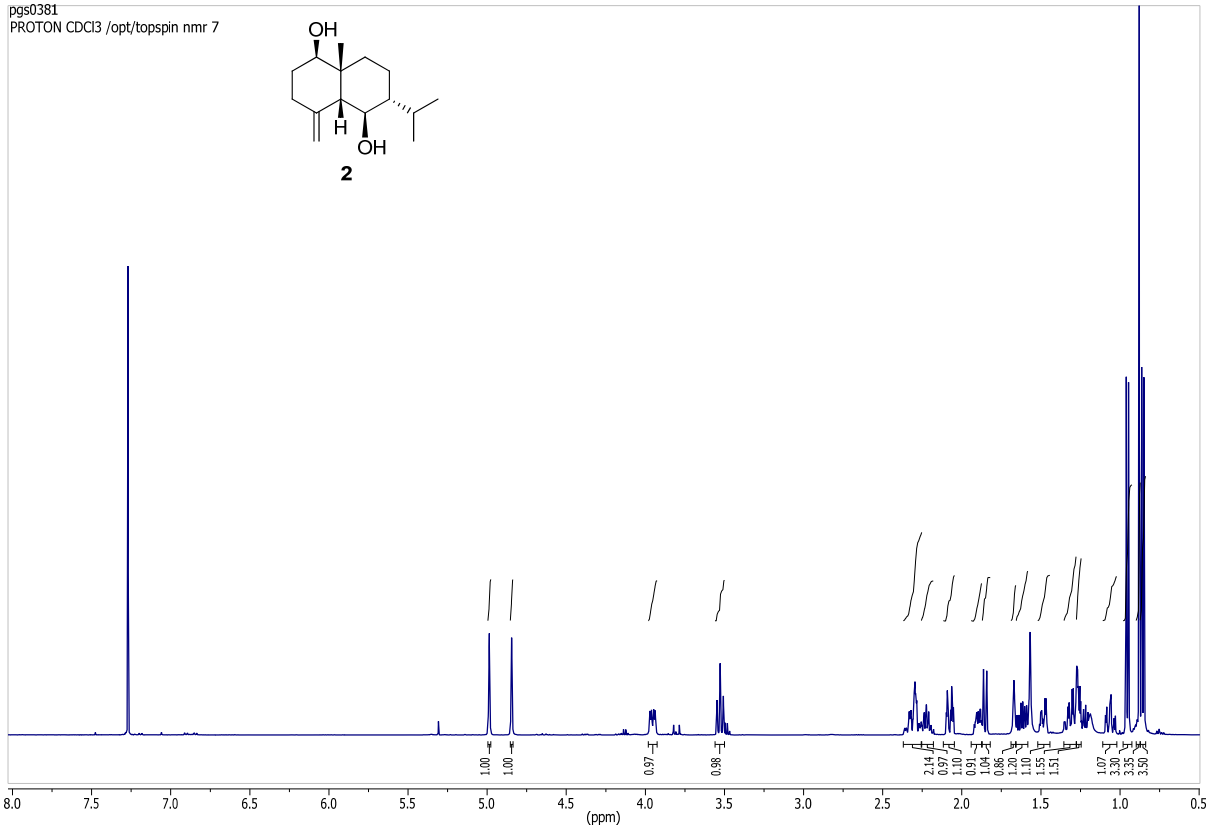

OPMB
H
O
OH
16
PGS-03-10
APNOESYPHPP CDCl3 /opt/topspin nmr 7
f1 (ppm)
(ppm)

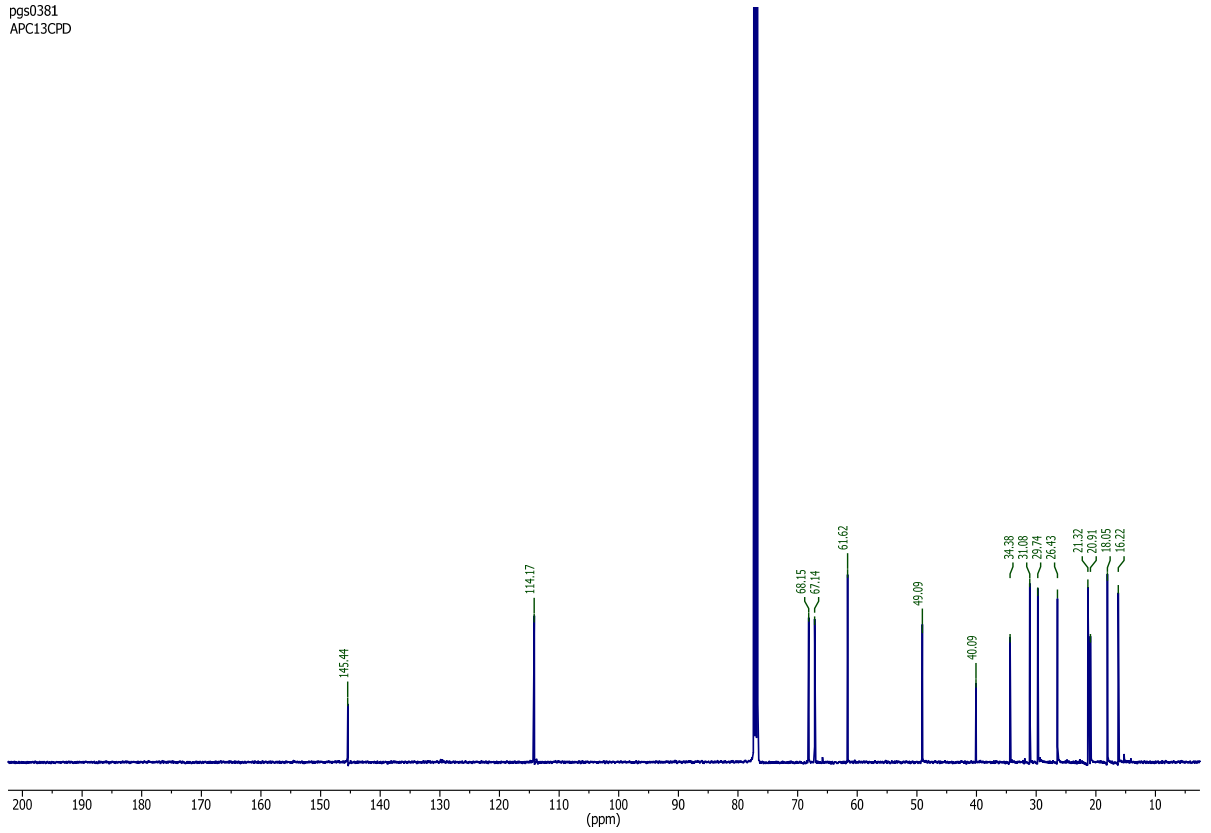

pgs-03-68-IIBATCH
OPMB
H
O
OPMB
17
1.81
1.71
1.64
1.69
1.00
2.03
1.00
7.80
1.00
3.13
2.14
1.06
2.31
2.88
5.23
3.14
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
(ppm)


pgs-03-68-IIBATCH
211.60
159.28
159.20
130.36
130.09
129.81 Tol
129.56 Tol
113.77
113.75
76.76
72.13
70.70
68.38
64.69
55.26
55.24
46.88
43.08
36.83
33.92
26.28
25.10
22.02
21.07 Tol
18.05
15.82
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
(ppm)


pgs-03-80
OPMB
H
OPMB
18
(ppm)


pgs-03-80
159.10
159.08
145.54
131.04
130.94
129.78
129.40
113.67
113.06
77.46
74.05
72.58
70.39
60.14
55.26
49.03
40.89
34.26
30.66
27.17
25.62
22.27
21.33
17.94
16.10
(ppm)


pgs0381
PROTON CDCl3 /opt/topspin nmr 7
OH
H
OH
2
1.00
1.00
0.97
0.98
2.14
0.97
1.10
0.91
1.04
0.86
1.20
1.10
1.55
1.51
1.07
3.30
3.35
3.50
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
(ppm)


pgs0381
APC13CPD
145.44
114.17
68.15
67.14
61.62
49.09
40.09
34.38
31.08
29.74
26.43
21.32
20.91
18.05
16.22
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
(ppm)

Comparison table of characterization data

^{1}H NMR

Synthetic (500 MHz, $CDCl_3$)	**Isolated1**[i] (500 MHz, $CDCl_3$)	**Isolated**[ii] (500 MHz, $CDCl_3$)
4.99 (brt, *J* = 2.2 Hz, 1H)	4.95 (brt, *J* = 2.1 Hz, 1H)	4.97 (s, 1H)
4.85 (t, *J* = 2.0 Hz, 1H)	4.81 (brt, *J* = 2.0 Hz, 1H)	4.83 (s, 1H)
3.95 (dd, *J* = 11.7, 4.8 Hz, 1H)	3.92 (dd, *J* = 11.6, 4.8 Hz, 1H)	3.94 (dd, J = 11.7, 4.9 Hz, 1H)
3.53 (t, *J* = 10.0 Hz, 1H)	3.49 (t, *J* = 10.0 Hz, 1H)	3.51 (t, J = 10.2 Hz, 1H)
2.36 – 2.32 (m, 1H)	2.27 (m, 1H)	2.28 (m, 1H)
2.31 – 2.28 (m, 1H)	2.27 (m, 1H)	2.28 (m, 1H)
2.23 (sed, *J* = 7.0, 2.5 Hz, 1H)	2.19 (sed, *J* = 7.1, 2.5 Hz, 1H)	2.26 (sed, J = 7.1, 2.1 Hz, 1H)
2.08 (dt, *J* = 14.0, 3.1 Hz, 1H)	2.04 (dt, J = 14.0, 3.2 Hz, 1H)	2.06 (dt, J = 13.8, 3.0 Hz, 1H)
1.90 (dtd, *J* = 12.6, 5.1, 2.5 Hz, 1H)	1.86 (dtd, J = 12.5, 5.2, 2.7 Hz, 1H)	1.86 (m, 1H)
1.85 (d, *J* = 10.1 Hz, 1H)	1.82 (d, J = 10.2 Hz, 1H)	1.84 (d, J = 10.2 Hz, 1H)
1.65 – 1.59 (m, 1H)	1.58 (qd, J = 12.2, 5.7 Hz, 1H)	1.60 (qd, J = 11.7, 5.8 Hz, 1H)
1.48 (dq, *J* = 12.5, 3.2 Hz, 1H)	1.45 (dq, J = 13.4, 3.4 Hz, 1H)	1.45 (dq, J = 13.5, 3.4 Hz, 1H)
1.36 – 1.28 (m, 1H)	1.26 (qd, J = 12.9, 3.2 Hz, 1H)	1.26 (qd, J = 12.9, 2.8 Hz, 1H)
1.27 – 1.24 (m, 1H)	1.22 (tt, J = 12.5, 2.6 Hz, 1H)	1.22 (tt, J = 12.6, 2.8 Hz, 1H)
1.06 (td, *J* = 13.6, 4.1 Hz, 1H)	1.02 (td, J = 13.7, 3.9 Hz, 1H)	1.04 (td, J = 13.3, 3.4 Hz, 1H)
0.95 (d, *J* = 7.1 Hz, 3H)	0.92 (d, J = 7.1 Hz, 3H)	0.94 (d, J = 7.1 Hz, 3H)
0.88 (s, 3H)	0.84 (s, 3H)	0.85 (s, 3H)
0.86 (d, *J* = 6.9 Hz, 3H)	0.82 (d, J = 7.0 Hz, 1H)	0.85 (d, J = 7.1 Hz, 3H)

^{13}C NMR

Synthetic (125 MHz, $CDCl_3$)	**Isolated**[i] (125 MHz, $CDCl_3$)	**Isolated**[ii] (125 MHz, $CDCl_3$)
145.4	145.5	145.4
114.2	114.2	114.2
68.2	68.1	68.1
67.1	67.1	67.1
61.6	61.7	61.6
49.1	49.1	49.0
40.1	40.1	40.1
34.4	34.4	34.3
31.1	31.1	31.0
29.7	29.8	29.7
26.4	26.5	26.4
21.3		

20.9 18.1 16.2	21.3 20.9 18.1 16.3	21.3 20.9 18.0 16.2

Optical rotation

Synthetic	Isolated[i]	Isolated[ii]
$[\alpha]_D^{25}$ +33.2° (*c* 0.41, $CHCl_3$)	$[\alpha]_D^{20}$ +36.5° (*c* 0.32, $CHCl_3$)	$[\alpha]_D^{20}$ – 88.0° (*c* 0.6, $CHCl_3$)

i. Zhang, H.-J.; Tan, G. T.; Santarsiero, B. D.; Mesecar, A. D.; Hung, N. V.; Cuong, N. M.; Soejarto, D. D.; Pezzuto, J. M.; Fong, H. H. S. *J. Nat. Prod.* **2003**, *66*, 609–615.

ii. Sun, Z.; Chen, B.; Zhang, Z.; Hu, C. *J. Nat. Prod.* **2004**, *67*, 1975–1979.