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Supporting Information

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Total Synthesis of (+)-Aquaticol via Biomimetic Phenol Dearomatization. A Case of Double Diastereofacial Differentiation in Diels-Alder Dimerization of Orthoquinols Involving a C_2-Symmetric Transition State**

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Experimental Section

General. All moisture and oxygen sensitive reactions were carried out in flame-dried glassware under N_2. Tetrahydrofuran (THF) was purified by filtration through alumina under N_2 immediately

before use. Acetic anhydride (Ac_2O), acetic acid (AcOH), nitric acid 100% (HNO_3) and MeOH were used as received. SIBX was furnished by SIMAFEX and was used as received. (±)-Cuparene (**4**) was prepared according to the procedure of Krief and Barbeaux.[1] Evaporations were conducted under reduced pressure at temperatures less than 30°C unless otherwise noted. Further drying of the residues was accomplished under high vacuum. Reactions were monitored by thin-layer chromatography (TLC) carried out on 0.25 silica gel plates (60F-254) using UV as a visualizing agent and a solution of phosphomolybdic acid (12 g) in EtOH (200 mL). Column chromatography was carried out under positive pressure using 40-63 μm silica gel (Merck) and the indicated solvents. Melting points were measured in open capillary tubes and are uncorrected. NMR spectra of samples in the indicated solvent were run at 250, 300 or 400 MHz and calibrated using residual solvent as an internal standard. Low resolution electron impact mass spectrometry data (EIMS) were recorded at 70 eV. High resolution mass spectrometry data (HRMS) and elemental analysis were obtained from the mass spectrometry laboratory at the Centre Régional de Mesures Physiques de l'Ouest (CRMPO), Rennes, France.

(±)-Nitrocuparene 6. To a solution of (±)-cuparene **4** (202 mg, 1 mmol)[1] in Ac_2O (0.4 mL) was added dropwise a solution of HNO_3 (110 μL, 2.48 mmol) in AcOH (475 μL, 7.9 mmol). The resulting mixture was stirred at room temperature and additional HNO_3 (1 equiv.) was added dropwise every hour. After 3 h, TLC monitoring, eluting with hexanes indicated total consumption of **4**. The reaction mixture was then diluted with H_2O and extracted with Et_2O (2 × 5 mL). The combinated organic phases were washed with 20% aqueous NaOH (3 × 10 mL), brine (4 × 10 mL), dried on anhydrous Na_2SO_4, filtered and concentrated at room temperature. Purification by flash chromatography eluting with pentane gave (±)-nitrocuparene **6** as a yellow oil (140 mg, 57%): R_f = 0.75 (hexanes/Et_2O, 4:1); IR (NaCl) ν_{max} 2960, 2873, 1526, 1345 cm^{-1}; ^1H NMR ($CDCl_3$, 300 MHz) δ 0.56 (s, 3H), 1.06 (s, 3H), 1.28 (s, 3H), 1.50-1.90 (m, 5H), 2.35-2.50 (m, 1H), 2.56 (s, 3H), 7.23 (d, *J* = 8.3 Hz, 1H), 7.48 (dd, *J* = 1.9 Hz, 8.3 Hz, 1H), 7.95 (d, *J* = 1.9 Hz, 1H); ^{13}C NMR ($CDCl_3$, 75 MHz) δ 148.7, 147.2, 131.8, 130.5, 123.0, 50.5, 44.3, 39.5, 36.8, 26.2, 24.1, 19.9, 19.6; EIMS m/z (rel intensity) 247 (M^+, 14), 232 (16), 217 (10), 177 (61), 160 (100); HRMS (EIMS) calcd for $C_{15}H_{21}NO_2$ 247.1572, found 247.1572.

(±)-Acetoxycuparene 7. Hydrogenation of nitrocuparene **6** (247 mg, 1 mmol) in a mixture of Ac_2O/AcOH (2:1) (10 mL) was carried out under H_2 for 12 h at room temperature in the presence of 10% Pd/C as a catalyst (197 mg) using an autoclave (4.5 bars) with mechanical stirring. The reaction mixture was filtered through Celite, and the solid was washed with Et_2O (50 mL). Et_2O was removed by evaporation and $NaNO_2$ (274.6 mg, 4 mmol) was added at 0°C as a solid in one portion. After 10 min, all solid was dissolved, the solution turned slowly green apple and some brownish gas formed. The solution was maintained at 0°C for 1 h, after which time it was allowed to warm up to room temperature and was stirred for 24 h. The reaction mixture was then diluted with H_2O and CH_2Cl_2. After decantation, the two layers were separated, and the aqueous phase was further extracted with CH_2Cl_2 (3 × 5 mL). The combined organic phases were washed with saturated aqueous $NaHCO_3$ (3 × 10 mL), brine (10 mL), dried over Na_2SO_4, filtered and evaporated to give quantitatively the (±)-acetoxycuparene **7** (260 mg, 100%) as a brown oily residue. If necessary, the product can be further purified by flash chromatography eluting with hexanes/Et_2O (95:5). R_f = 0.60 (hexanes/Et_2O, 4:1); IR (NaCl) ν_{max} 2964, 1768, 1211 cm^{-1}; ^1H NMR ($CDCl_3$, 400 MHz) δ 0.62 (s, 3H), 1.08 (s, 3H), 1.29 (s, 3H), 1.50-1.90 (m, 5H), 2.18 (s, 3H), 2.34 (s, 3H), 2.40-2.60 (m, 1H), 7.01 (s, 1H), 7.16 (s, 2H); ^{13}C NMR ($CDCl_3$, 100 MHz) δ 169.1, 148.6, 146.7, 129.9, 126.7, 124.6, 120.5, 50.2, 44.2, 39.5, 36.7, 26.3, 24.1, 24.1, 20.8, 19.6, 15.6; EIMS m/z (rel intensity) 260 (M^+, 78), 218 (76), 190 (32), 148 (100), 136 (93), 91 (47); Anal. Calcd for $C_{17}H_{24}O_2$: C, 78.42; H, 9.29; O, 12.29 Found: C, 78.46; H, 9.27; O, 12.27.

(±)-Hydroxycuparene 3. To a solution of (±)-acetoxycuparene **7** (92 mg, 0.35 mmol) in aqueous MeOH (3 mL) was added powdered KOH (39 mg, 0.7 mmol) in one portion. The solution slowly turned dark brown and the reaction was stopped after 30 min. The resulting mixture was then concentrated and diluted with H_2O (5 mL) and Et_2O (5 mL). The aqueous phase was acidified by adding dropwise aqueous 1M HCl and extracted with Et_2O (3 × 5 mL). The combined organic layers were washed with brine (10 mL), dried over $MgSO_4$, filtered and evaporated at room temperature to give quantitatively (±)-hydroxycuparene **3** (76 mg, 100%) as a pale brown oil, which was used without further purification: R_f = 0.40 (hexanes/Et_2O, 4:1); IR (NaCl) ν_{max} 3395, 2926, 1591 cm^{-1}; ^1H NMR ($CDCl_3$, 250 MHz) δ 0.62 (s, 3H), 1.09 (s, 3H), 1.27 (s, 3H), 1.55-1.90 (m, 5H), 2.27 (s, 3H), 2.40-2.60 (m, 1H), 5.15 (bs, 1H), 6.84 (d, *J* = 1.8 Hz, 1H), 6.90 (dd, *J* = 1.8, 7.9

Hz, 1H), 7.07 (d, J = 7.9 Hz, 1H); ^{13}C NMR ($CDCl_3$, 62.9 MHz) δ 152.8, 147.1, 129.9, 120.4, 119.6, 114.0, 50.2, 44.1, 39.6, 36.7, 26.4, 24.3, 24.2, 19.6, 15.2; EIMS m/z (rel intensity) 218 (M+, 100); HRMS (EIMS) calcd for $C_{15}H_{22}O$ 218.1668, found 218.1671.

Separation of the two enantiomers of (±)-hydroxycuparene **3** was accomplished by chiral semi-preparative HPLC, which was performed on a Varian ProStar system equipped with a Daicel Chiracel OJ-H column (20 × 200 mm), and eluting with *n*-hexane/*i*-PrOH (9:1) at a flow rate of 18 mL/min. Column effluent was monitored by UV detection at 218 nm using a ProStar 320 UV-visible detector [rt = 22.3 min for (7*R*)-**3** and 28.1 min for (7*S*)-**3**].

(7*R*)-Hydroxycuparene (+)-3. Pale brown oil; R_f = 0.40 (hexanes/Et_2O, 4:1); IR (NaCl) ν_{max} 3424, 1654 cm^{-1}; ^{1}H NMR ($CDCl_3$, 250 MHz) δ 0.60 (s, 3H), 1.07 (s, 3H), 1.25 (s, 3H), 1.50-1.90 (m, 5H), 2.25 (s, 3H), 2.40-2.60 (m, 1H), 5.01 (bs, 1H), 6.82 (d, J = 1.8 Hz, 1H), 6.87 (dd, J = 1.8, 7.9 Hz, 1H), 7.05 (d, J = 7.9 Hz, 1H); ^{13}C NMR ($CDCl_3$, 62.9 MHz) δ 152.8, 147.1, 129.9, 120.4, 119.5, 113.9, 50.2, 44.1, 39.6, 36.7, 26.4, 24.3, 24.2, 19.6, 15.2; EIMS m/z (rel intensity) 218 (M^+, 52), 203 (8), 161 (39), 148 (100), 136 (90); $[\alpha]_D^{23}$ = +56° (c = 0.6, $CHCl_3$). [lit.[2] $[\alpha]_D$ = +63° (c = 1.35, $CHCl_3$)]. CAS = [52554-81-1].

(7*S*)-Hydroxycuparene (–)-3. Pale brown oil, R_f = 0.40 (hexanes/Et_2O, 4:1); IR (NaCl) ν_{max} 3420, 1653 cm^{-1}; ^{1}H NMR ($CDCl_3$, 250 MHz) δ 0.59 (s, 3H), 1.07 (s, 3H), 1.24 (s, 3H), 1.50-1.90 (m, 5H), 2.24 (s, 3H), 2.40-2.55 (m, 1H), 4.91 (bs, 1H), 6.81 (d, J = 1.8 Hz, 1H), 6.87 (dd, J = 1.8, 7.9 Hz, 1H), 7.04 (d, J = 7.9 Hz, 1H); ^{13}C NMR ($CDCl_3$, 62.9 MHz) δ 152.9, 147.1, 129.9, 120.3, 119.5, 113.9, 50.2, 44.1, 39.6, 36.7, 26.4, 24.3, 24.2, 19.6, 15.2; EIMS m/z (rel intensity) 218 (M^+, 45), 203 (5), 161 (39), 148 (100), 136 (92); $[\alpha]_D^{23}$ = -60° (c = 0.4, $CHCl_3$). [lit.[2] $[\alpha]_D$ = -65° (c = 1.2, $CHCl_3$)]. CAS = [38412-84-9].

Typical procedure for SIBX oxidation. To a solution of hydroxycuparene (–)-**3** (85 mg, 0.39 mmol) in THF (4 mL) was added SIBX (365 mg, 0.58 mmol) as a solid in one portion. The resulting suspension was stirred at room temperature for 24 h, after which time TFA (30 μL, 0.39

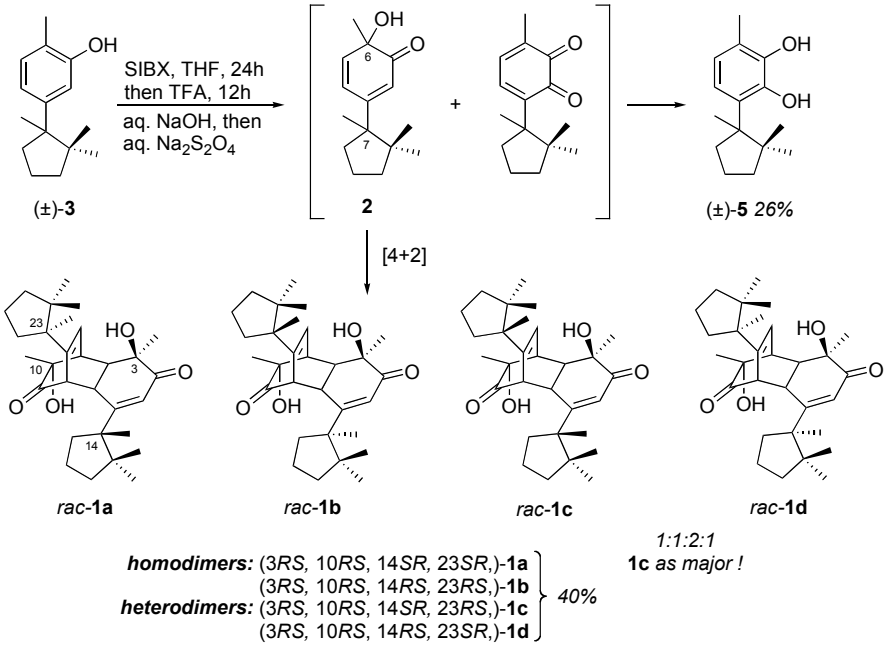
mmol) was added and the mixture was further stirred for 12 h. The reaction mixture was then diluted with CH_2Cl_2 (10 mL) and H_2O (10 mL). An aqueous 1M solution of NaOH (5 mL) was added dropwise until pH = 8. The aqueous phase was extracted with CH_2Cl_2 (3 × 10 mL). The combined organic phases were washed with aqueous 1M NaOH (15 mL) and brine (2 × 15 mL), then shaken vigorously with a saturated aqueous solution of $Na_2S_2O_4$ (40 mL), washed again with brine (40 mL), dried on Na_2SO_4, filtered and evaporated at room temperature to give a crude pale brown oily residue (95 mg). This residue was purified by flash chromatography, eluting first with CH_2Cl_2 then with CH_2Cl_2/MeOH (100:1), to give two residues, which were again purified separately by flash chromatography, eluting with hexanes/acetone (6:1), to furnish respectively (7*S*)-1,2-dihydroxycuparene (–)-**5** (20 mg, 22%), and a 1:1 mixture of (3*R,*10*R,*14*S,*23*S*)-aquaticol (+)-**1a** and the all *S* dimer (–)-**1b** (45 mg, 49%) as white powdery solids. This diastereoisomeric mixture was separated by semi-preparative reverse phase HPLC, which was performed on a Thermo Spectra system equipped with a Deltapak C-18 column (7.8 × 300 mm, 15 μm), using a gradient elution at a flow rate of 3 mL/min with the following mobile phases: solvent A [H_2O–TFA (99:1)] and solvent B [CH_3CN–TFA (99:1)] (0-55 min: 30% to 100% solvent B). Column effluent was monitored by UV detection at 240 nm using a Spectra UV6000LP detector [rt = 49.9 min for (–)-**1b** and 51.8 min for (+)-**1a**] **.**

Oxidation of hydroxycuparene (+)-**3** (74 mg, 0.34 mmol) was carried out as described for (–)-**3** and gave rise to 1,2-dihydroxycuparene (+)-**5** (23 mg, 29%) and a 1:1 mixture of (3*S,*10*S,*14*R,*23*R*)-aquaticol (–)-**1a** and the all *R* dimer (+)-**1b** (40 mg, 50%). This mixture was separated as described above for (+)-**1a** and (–)-**1b**. *Ent*-aquaticol (–)-**1a** was recrystallized for X-ray analysis (*vide infra*).

Oxidation of hydroxycuparene (±)-**3** (200 mg, 0.92 mmol) was carried out as described for (–)-**3** and gave rise to *rac*-1,2-dihydroxycuparene (±)-**5** (56 mg, 26%) and an inseparable 2:1:1:1 racemic mixture of **1a**-**d** (86 mg, 40%), from which the major diastereoisomer *rac*-**1c** could be crystallized for X-ray analysis (*vide infra*). Thus, out of 32 possible *endo*-stereodimers, only eight are produced, four resulting from a combination of two identical orthoquinols **2** (i.e., (±)-**1a**/**b**) and four from two orthoquinols **2** with opposite configuration at the cyclopentanyl stereogenic C7 center (i.e., (±)-

1c/d) (see Scheme 4). Crystallization of this mixture furnished a sample of the major dimer, which turned out to be the heterodimer *rac*-**1c**.

Scheme 4. SIBX-mediated oxidation of (±)-hydroxycuparene (**3**).



1,2-Dihydroxycuparene (±)-5. Colorless plates from slow evaporation of hexanes; R_f = 0.65 (CH_2Cl_2/MeOH, 40:1); mp 45.5°C (hexanes); IR (NaCl) ν_{max} 3518, 2957, 1462 cm^{-1}; ^1H NMR ($CDCl_3$, 250 MHz) δ 0.78 (s, 3H), 1.20 (s, 3H), 1.43 (s, 3H), 1.45-1.90 (m, 5H), 2.23 (s, 3H), 2.50-2.70 (m, 1H), 4.99 (bs, 1H), 5.61 (s, 1H), 6.61 (d, *J* = 8.2 Hz, 1H), 6.81 (d, *J* = 8.2 Hz, 1H); ^{13}C NMR ($CDCl_3$, 62.9 MHz) δ 143.1, 141.9, 131.1, 121.1, 120.7, 120.5, 50.9, 44.8, 40.7, 39.1, 26.7, 25.3, 22.8, 20.2, 15.3; EIMS m/z (rel intensity) 234 (M^+, 45), 164 (8), 151 (100); HRMS (EIMS) calcd for $C_{15}H_{22}O_2$ 234.1616, found 234.1620.

(7*R*)-1,2-Dihydroxycuparene (+)-5. White solid; mp 69.8°C (hexanes); R_f = 0.65 (CH_2Cl_2/MeOH, 40:1); IR (NaCl) ν_{max} 3505, 2957, 1461 cm^{-1}; ^1H NMR ($CDCl_3$, 250 MHz) δ 0.77 (s, 3H), 1.19 (s, 3H), 1.42 (s, 3H), 1.45-1.90 (m, 5H), 2.23 (s, 3H), 2.50-2.70 (m, 1H), 4.98 (bs, 1H), 5.60 (s, 1H), 6.61 (d, *J* = 8.2 Hz, 1H), 6.80 (d, *J* = 8.2 Hz, 1H); ^{13}C NMR ($CDCl_3$, 62.9 MHz) δ 143.1, 141.9, 131.1, 121.1, 120.7, 120.5, 50.9, 44.8, 40.7, 39.1, 26.7, 25.3, 22.8, 20.2, 15.3; EIMS m/z (rel

intensity) 234 (M^+, 100), 219 (8), 164 (95), 151 (98); Anal. Calcd for $C_{15}H_{22}O_2$: C, 76.80; H, 9.46; O, 13.66 Found: C, 76.52; H, 9.51; O, 13.98; $[\alpha]_D^{23}$ = +56° (*c* = 0.23, $CHCl_3$).

(7*S*)-1,2-Dihydroxycuparene (–)-5. Colorless prisms from slow evaporation of hexanes; mp 133-134°C (hexanes) (lit.[3] mp 72.0-73.0°C); R_f = 0.65 (CH_2Cl_2/MeOH, 40:1); IR (NaCl) ν_{max} 3518, 2957, 1462 cm^{-1}; ^1H NMR ($CDCl_3$, 250 MHz) δ 0.77 (s, 3H), 1.19 (s, 3H), 1.42 (s, 3H), 1.45-1.90 (m, 5H), 2.23 (s, 3H), 2.50-2.70 (m, 1H), 4.96 (bs, 1H), 5.59 (s, 1H), 6.61 (d, *J* = 8.2 Hz, 1H), 6.80 (d, *J* = 8.2 Hz, 1H); ^{13}C NMR ($CDCl_3$, 62.9 MHz) δ 143.1, 141.9, 131.1, 121.1, 120.7, 120.5, 50.9, 44.8, 40.7, 39.1, 26.7, 25.3, 22.8, 20.2, 15.3; EIMS m/z (rel intensity) 234 (M^+, 54), 164 (54), 151 (100); $[\alpha]_D^{23}$ = -60.0° (*c* = 0.21, $CHCl_3$) [lit.[3] $[\alpha]_D$ = -57.4° ($CHCl_3$)]. CAS = [85526-56-3].

Aquaticol (+)-1a. Colorless prisms from slow evaporation of EtOH and a trace of $CHCl_3$; mp 170-171°C (EtOH) (lit.[4] mp 194-196°C ($CHCl_3$)); R_f = 0.19 (CH_2Cl_2/MeOH, 40:1); IR (NaCl) ν_{max} 3373, 3229, 2973, 1675 (broad), 1204, 1139 cm^{-1}; ^1H NMR ($CDCl_3$, 400 MHz) δ 0.52 (s, 3H), 0.77 (s, 3H), 0.88 (s, 3H), 0.90 (s, 3H), 0.93 (s, 3H), 1.13 (s, 3H), 1.20-2.10 (m, 11 H), 1.29 (s, 3H), 1.35 (s, 3H), 2.25-2.40 (m, 1H), 3.02 (dd, *J* = 3.2, 9.0 Hz, 1H), 3.35-3.50 (m, 3H), 6.10 (dd, *J* = 1.5, 6.8 Hz, 1H), 6.17 (s, 1H); ^{13}C NMR ($CDCl_3$, 100 MHz) δ 211.1, 201.7, 164.8, 141.8, 131.3, 124.9, 73.2, 72.2, 54.0, 52.4, 49.7, 47.9, 45.8, 44.7, 41.4, 40.0, 40.0, 39.0, 35.4, 34.3, 33.5, 26.5, 26.4, 26.3, 24.1, 22.2, 21.9, 21.6, 19.7, 18.9; EIMS m/z (rel intensity) 468 (M^+, 9), 450 (4), 358 (77), 343 (41), 234 (61), 191 (55), 165 (62), 111 (100); $[\alpha]_D^{23}$ = +27.5° (*c* = 0.1, $CHCl_3$). [lit.[4] $[\alpha]_D$ = +28.3° (*c* = 0.6, $CHCl_3$)]. CAS = [221012-52-8].

(3*S*,10*S*,14*S*,23*S*)-6,12-(1,2,2-trimethylcyclopentyl)-3,10-dihydroxy-3,10-dimethyltricyclo[6.2.2.0^{2,7}]dodeca-5,11-diene-4,9-dione (–)1b. Yellow solid; R_f = 0.19 (CH_2Cl_2/MeOH, 40:1); IR (NaCl) ν_{max} 3064, 2962, 2877, 1728, 1673, 1462 cm^{-1}; ^1H NMR ($CDCl_3$, 400 MHz) δ 0.58 (s, 3H), 0.77 (s, 3H), 0.85 (s, 3H), 0.93 (s, 3H), 1.03 (s, 3H), 1.15-1.45 (m, 2H), 1.28 (s, 3H), 1.33 (s, 6H), 1.50-1.85 (m, 9H), 2.00-2.20 (m, 1H), 2.98 (dd, *J* = 2.9, 8.6 Hz, 1H), 3.35 (d, *J* = 8.6 Hz, 1H), 3.48 (dd, *J* = 2.9, 6.7 Hz, 1H), 3.63 (s, 1H), 6.12 (s, 1H), 6.21 (d, *J* = 7.1 Hz, 1H); ^{13}C NMR ($CDCl_3$, 100 MHz) δ 212.1, 201.6, 165.8, 141.6, 133.6, 124.2, 73.3, 72.0, 55.3, 53.5, 50.4, 46.3, 46.2, 46.0, 41.8, 40.3, 39.7, 39.4, 37.4, 35.2, 33.2, 26.6, 26.0, 25.7, 25.5, 23.4, 21.5,

21.3, 19.9, 19.6; EIMS m/z (rel intensity) 468 (M^+, 24), 450 (6), 425 (11), 234 (62), 191 (69), 165 (100); HRMS (ESIMS) calcd for $C_{30}H_{44}O_4Na^+$ [MNa^+] 491.3137, found 491.3151; $[\alpha]_D^{23}$ = -90.1° (*c* = 0.044, $CHCl_3$); CCDC 607012.

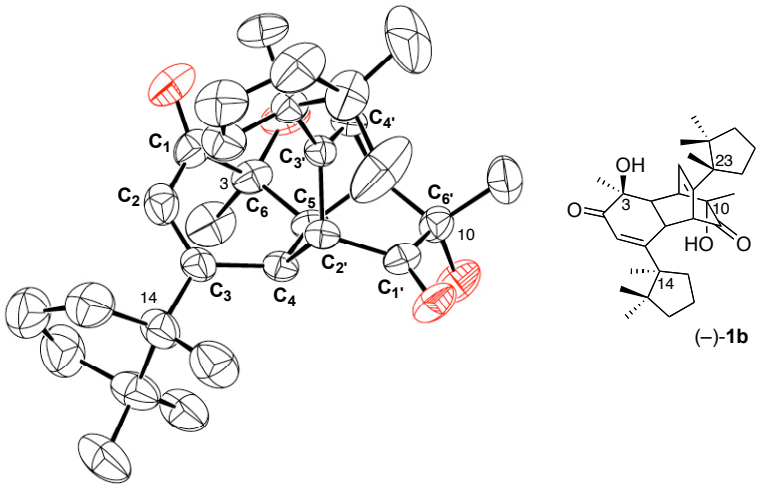


Figure 1. ORTEP diagram of the X-ray crystal structure of the all S dimer (–)-**1b**.

***Ent*-Aquaticol (–)-1a.** Colorless prisms from slow evaporation of EtOH and a trace of $CHCl_3$, and colorless needles from $CHCl_3$ evaporation; mp 168.6°C (EtOH) and 195.0°C ($CHCl_3$); R_f = 0.19 (CH_2Cl_2/MeOH, 40:1); IR (NaCl) ν_{max} 3439, 2973, 1727, 1673 cm^{-1}; ^1H NMR ($CDCl_3$, 400 MHz) δ 0.53 (s, 3H), 0.78 (s, 3H), 0.89 (s, 3H), 0.91 (s, 3H), 0.93 (s, 3H), 1.14 (s, 3H), 1.20-2.08 (m, 11 H), 1.29 (s, 3H), 1.35 (s, 3H), 2.27-2.40 (m, 1H), 3.02 (dd, *J* = 3.1, 8.9 Hz, 1H), 3.38-3.47 (m, 3H), 6.10 (d, *J* = 6.8 Hz, 1H), 6.18 (s, 1H); ^{13}C NMR ($CDCl_3$, 100 MHz) δ 211.1, 201.7, 164.8, 141.8, 131.3, 124.9, 73.2, 72.2, 54.0, 52.4, 49.7, 47.9, 45.8, 44.7, 41.4, 40.0, 40.0, 39.0, 35.4, 34.3, 33.5, 26.5, 26.4, 26.3, 24.1, 22.2, 21.9, 21.6, 19.6, 18.9; EIMS m/z (rel intensity) 468 (M^+, 8), 450 (3), 425 (8), 381 (11), 234 (22), 165 (58), 111 (100); HRMS (ESIMS) calcd for $C_{30}H_{44}O_4Na^+$ [MNa^+] 491.3137, found 491.3142; $[\alpha]_D^{23}$ = -26.3° (*c* = 0.038, $CHCl_3$); CCDC 295794.

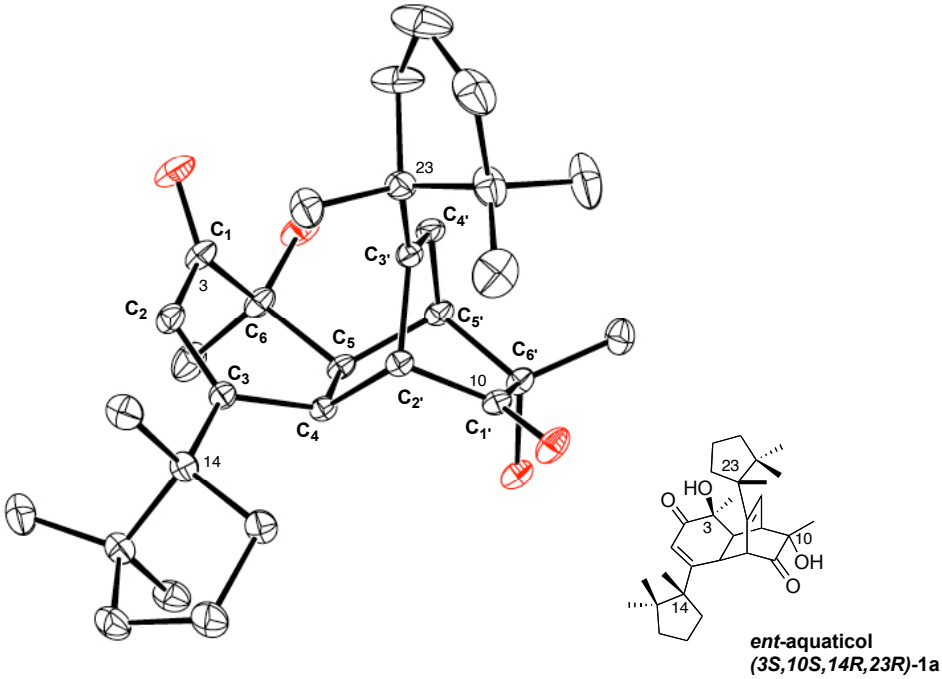


Figure 2. ORTEP diagram of the X-ray crystal structure of *ent*-aquaticol (–)-**1a**.

(3*R*,10*R*,14*R*,23*R*)-6,12-(1,2,2-trimethylcyclopentyl)-3,10-dihydroxy-3,10-dimethyltricyclo[6.2.2.0^{2,7}]dodeca-5,11-diene-4,9-dione (+)-1b. yellow solid; R_f = 0.19 (CH_2Cl_2/MeOH, 40:1); IR (NaCl) ν_{max} 3426, 2961, 1726, 1672 cm^{-1}; ^{1}H NMR ($CDCl_3$, 400 MHz) δ 0.58 (s, 3H), 0.77 (s, 3H), 0.85 (s, 3H), 0.92 (s, 3H), 1.03 (s, 3H), 1.15-1.45 (m, 2H), 1.28 (s, 3H), 1.32 (s, 3H), 1.33 (s, 3H), 1.50-1.85 (m, 9H), 2.00-2.20 (m, 1H), 2.98 (dd, *J* = 3.1, 8.6 Hz, 1H), 3.36 (d, *J* = 8.8 Hz, 1H), 3.48 (dd, *J* = 2.8, 6.7 Hz, 1H), 3.63 (s, 1H), 6.12 (s, 1H), 6.20 (d, *J* = 6.1 Hz, 1H); ^{13}C NMR ($CDCl_3$, 62.9 MHz) δ 212.1, 201.6, 165.7, 141.5, 133.6, 124.3, 73.2, 72.0, 55.3, 53.5, 50.4, 46.2, 46.0, 41.8, 40.3, 39.7, 39.4, 37.4, 35.2, 33.2, 26.6, 26.0, 25.6, 25.5, 23.4, 21.5, 21.3, 19.9, 19.6; EIMS m/z (rel intensity) 468 (M^+, 15), 425 (8), 381 (10), 234 (40), 191 (49), 165 (100); HRMS (ESIMS) calcd for $C_{30}H_{44}O_4Na^+$ [MNa^+] 491.3137, found 491.3134; $[\alpha]_D^{23}$ = +93.0° (*c* = 0.043, $CHCl_3$).

(3*RS*,10*RS*,14*SR*,23*S*)-6,12-(1,2,2-trimethylcyclopentyl)-3,10-dihydroxy-3,10-dimethyltricyclo[6.2.2.0^{2,7}]dodeca-5,11-diene-4,9-dione (±)-1c. A single crystal of this compound was obtained from the inseparable 1:1:2:1 racemic mixture of **1a-d**, which resulted from the SIBX-

mediated oxidation of hydroxycuparene (±)-**3** (*vide supra*), via slow evaporation of EtOH and a trace of $CHCl_3$; CCDC 295795.

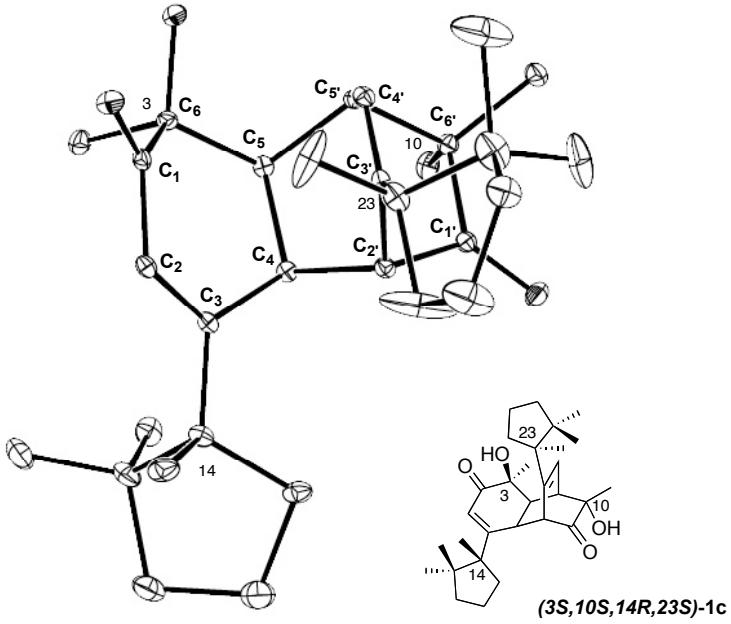
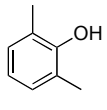
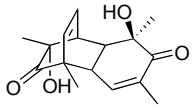
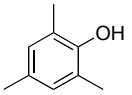
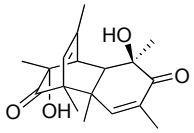
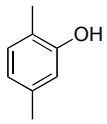
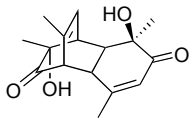
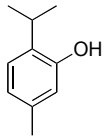
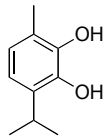
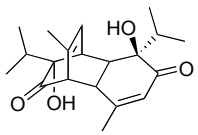
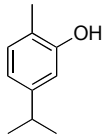
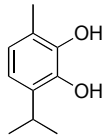
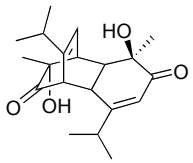
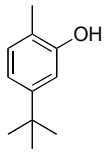
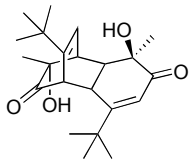
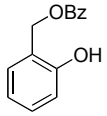
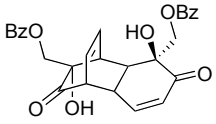


Figure 3. ORTEP diagram of the X-ray crystal structure of *rac*-**1c**.

Modified procedure for SIBX oxidation of a series of 2-alkylphenols on 10 mmol scale. To a solution of phenol (10 mmol) in THF (25 mL) was added SIBX (6.875 g, 11 mmol) as a solid in one portion. The resulting suspension was stirred at room temperature for 24 h, after which time TFA (780 μL, 10 mmol) was added and the mixture was further stirred for 12 h. The reaction mixture was then diluted with CH_2Cl_2 (100 mL) and H_2O (50 mL). An aqueous 1M solution of NaOH was added slowly and continuously with vigorous shaking until all solid material dissolved. The aqueous phase was extracted with CH_2Cl_2 (3 × 20 mL). The combined organic phases were washed with aqueous 1M NaOH (40 mL), H_2O (50 mL) and brine (2 × 50 mL), then shaken vigorously with a saturated aqueous solution of $Na_2S_2O_4$ (100 mL), washed again with brine (50 mL), dried on Na_2SO_4, filtered and evaporated at room temperature to give a residue, which was then purified by column chromatography (see Table 1 below).

Table 1. SIBX-mediated dearomatizing hydroxylation of a series of 2-alkylphenols.[a]

entry	phenols	products
1	 **8**	 **9** (96%)[b]
2	 **10**	 **11** (94%)[b]
3	 **12**	 **13** (49%)[c,d]
4	 **14**	 **15** (14%)[b]  **16** (50%)[c]
5	 **17**	 **15** (24%)[b]  **18** (48%)[c]
6	 **19**	 **20** (39%)[b,d]
7	 **21**	 **(±)-grandifloracin** (**22**) (30%)[c,d,e]

[a]Reactions were performed on 10 mmol scale in THF (0.4 M) with SIBX (1.1 equiv.) following the general procedure described below. [b]Isolated yields after column chromatography. [c]Isolated yields after column chromatography, followed by two recrystallizations from a cold mixture of CH_2Cl_2/hexanes. [d]The catechol was not isolated after purification. [e]During workup, a saturated aqueous solution of Na_2CO_3 was used instead of an aqueous 1M solution of NaOH.

3,10-Dihydroxy-3,5,8,12-tetramethyl-tricyclo[6.2.2.0^{2,7}]dodeca-5,11-diene-4,9-dione 9. 2,6-Dimethylphenol **8** (1.22 g, 10 mmol) was oxidized with SIBX according to the modified 10 mmol

scale procedure to give after purification by flash chromatography, eluting with hexanes/acetone (3:1), the dimer **9** as a white solid (1.32 g, 96%). Colorless prisms were obtained by slow evaporation of $CHCl_3$. Rf = 0.24 (hexanes/acetone, 3:1); mp 172.0°C ($CHCl_3$) (lit.[5] mp 194-196°C); IR (neat): ν_{max} 3416, 1713, 1670 (cm^{-1}); ^1H NMR ($CDCl_3$, 300 MHz): δ 1.24 (s, 3H), 1.32 (s, 3H), 1.43 (s, 3H), 1.85 (s, 3H), 2.33 (s, 1H), 2.80-2.95 (m, 1H), 3.25 (dd, *J* = 1.7, 8.3 Hz, 1H), 3.38 (d, *J* = 6.8 Hz, 1H), 4.00 (s, 1H), 5.51 (d, *J* = 8.1 Hz, 1H), 6.20-6.35 (m, 2H); ^{13}C NMR ($CDCl_3$, 100MHz): δ 214.8, 203.0, 139.3, 135.7, 135.3, 133.2, 73.6, 72.9, 53.7, 44.2, 43.6, 42.7, 31.7, 26.2, 16.3, 15.6; EIMS m/z (rel intensity) 276 (M^+, 12), 242 (7), 216 (7), 138 (100), 122 (36), 121 (78); CAS [5520-77-4], [35018-89-4], [54832-05-2], [146076-45-1].

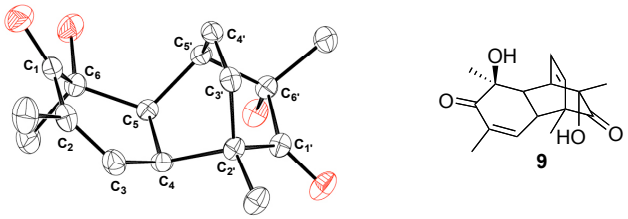


Figure 4. ORTEP diagram of the X-ray crystal structure of dimer **9**.

3,10-Dihydroxy-3,5,7,8,10,11-hexamethyl-tricyclo[6.2.2.0^{2,7}]dodeca-5,11-diene-4,9-dione 11. 2,4,6-Trimethylphenol **10** (1.36 g, 10 mmol) was oxidized with SIBX according to the modified 10 mmol scale procedure to give after purification by flash chromatography, eluting with hexanes/acetone (3:1), the dimer **11** as a white solid (1.42 g, 94%). Colorless prisms were obtained by slow evaporation of $CHCl_3$. R_f = 0.44 (hexanes/acetone, 3:1); mp 159-162°C ($CHCl_3$) (lit.[6] mp 181-182°C); IR (neat): ν_{max} 3481, 2972, 2927, 1719, 1681, 1448, 1361 (cm^{-1}); ^1H NMR ($CDCl_3$, 300 MHz): δ 1.16 (s, 3H), 1.24 (s, 6H), 1.36 (s, 3H), 1.70 (d, *J* = 1.7 Hz, 3H), 1.83 (d, *J* = 1.5 Hz, 3H), 2.23 (bs, 1H), 2.80 (d, *J* = 2.1 Hz, 1H), 3.14 (t, *J* = 2.1 Hz, 1H), 3.92 (s, 1H), , 5.04 (s, 1H), 6.03 (s, 1H); ^{13}C NMR ($CDCl_3$, 100 MHz): δ 214.0, 202.3, 145.1, 144.9, 132.8, 127.3, 73.6, 71.9, 57.6, 48.6, 48.5, 45.1, 32.3, 25.0, 23.0, 21.3, 16.1, 12.3; EIMS m/z (rel intensity) 304 (M^+, 10), 153 (26), 152 (42), 135 (100), 110 (40), 109 (52); CAS [35018-92-9], [40525-14-2].

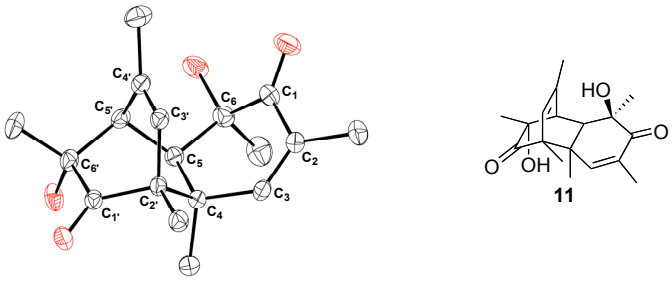


Figure 5. ORTEP diagram of the X-ray crystal structure of **11**.

3,10-Dihydroxy-3,6,10,12-tetramethyltricyclo[6.2.2.0^{2,7}]dodeca-5,11-diene-4,9-dione 13. 2,5-Dimethylphenol **12** (1.22 g, 10 mmol) was oxidized with SIBX according to the general 10 mmol scale procedure to give after purification by flash chromatography, eluting with hexanes/acetone (30:1), the dimer **13** as a brown solid (730 mg). Two recrystallizations from a mixture of CH_2Cl_2/hexanes in freezer gave pure **13** as colorless prisms (676 mg, 49%). R_f = 0.10 (hexanes/acetone, 3:1); mp 189°C (CH_2Cl_2/hexanes) (lit.[7] mp 200°C); IR (neat): ν_{max} 3435, 1729, 1671, 1379, 1159 (cm^{-1}); ^{1}H NMR ($CDCl_3$, 300 MHz): δ 1.25 (s, 3H), 1.30 (s, 3H), 1.61 (d, *J* = 1.3 Hz, 3H), 2.00 (d, *J* = 1.0 Hz, 3H), 2.28 (bs, 1H), 3.10-3.20 (m, 3H), 3.32 (dd, *J* = 1.3, 6.8 Hz, 1H), 4.00 (bs, 1H), 5.87 (d, *J* = 6.8 Hz, 1H), 6.02 (s, 1H); ^{13}C NMR ($CDCl_3$, 100 MHz) : δ 212.7, 201.4, 156.3, 136.5, 128.3, 124.9, 73.1, 72.9, 56.9, 44.7, 44.2, 41.1, 32.0, 25.9, 22.4, 21.5; EIMS m/z (rel intensity) 276 (M$^+$, 69), 216 (13), 215 (52), 188 (35), 187 (100), 159 (65), 122 (43); CAS [35018-90-7].

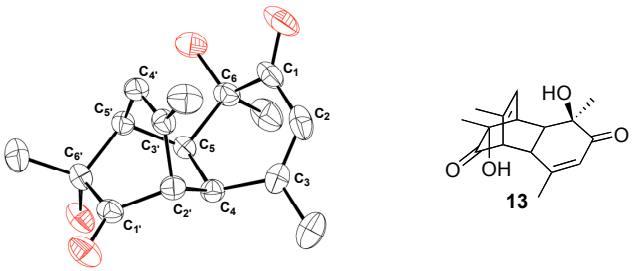


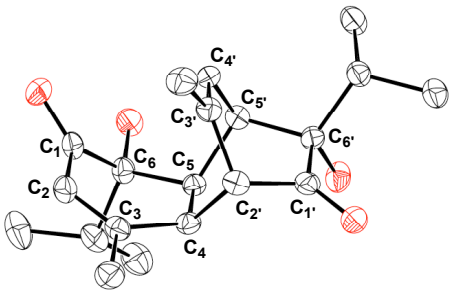
Figure 6. ORTEP diagram of the X-ray crystal structure of **13**.

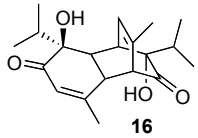
Thymol **(14**, 1.5 g, 10 mmol) was oxidized with SIBX according to the general 10 mmol scale procedure to give after purification by flash chromatography, eluting with hexanes/Et_2O (1:1), 3-*iso*propyl-1,2-dihydroxy-6-methylbenzene (**15**) as a brown oil (229 mg, 14%) and dimer **16** as a

yellow solid (970 mg), which was recrystallized twice from a mixture of CH_2Cl_2/hexanes in freezer to give pure **16** as white needles (830 mg, 50%).

3-*Iso*propyl-1,2-dihydroxy-6-methylbenzene 15. Brown oil; R_f = 0.4 (hexanes/Et_2O, 1:1); IR (neat): ν_{max} 3453, 2963, 1467 (cm^{-1}); ^1H NMR ($CDCl_3$, 300 MHz): δ 1.26 (d, *J* = 6.8 Hz, 6H), 2.24 (s, 3H), 3.17 *(*sept., *J* = 6.8 Hz, 1H), 5.31 (bs, 2H), 6.69 (d, *J* = 7.9 Hz, 1H), 6.73 (d, *J* = 8.1 Hz, 1H); ^{13}C NMR ($CDCl_3$, 75 MHz): δ 141.5, 141.0, 132.5, 121.9, 121.3, 117.4, 27.1, 22.6, 15.3; EIMS m/z (rel intensity) 166 (M^+, 92), 151 (100), 133 (56), 105 (60); CAS [490-06-2].

3,10-Dihydroxy-3,10-di-*iso*propyl-6,12-dimethyl-tricyclo[6.2.2.0^{2,7}]dodeca-5,11-diene-4,9-dione 16. White needles (hexanes/CH_2Cl_2), colorless prisms also obtained from slow evaporation of $CHCl_3$; R_f = 0.27 (hexanes/Et_2O, 1:1); mp 159.5°C ($CHCl_3$) (lit.[8] mp 168-170°C (hexanes)); IR (neat): ν_{max} 3481, 2972, 2927, 1719, 1681, 1448, 1361 (cm^{-1}); ^1H NMR ($CDCl_3$, 400 MHz): δ 0.56 (d, *J* = 6.6 Hz, 3H), 0.81 (d, *J* = 6.8 Hz, 3H), 0.84 (d, *J* = 7.1 Hz, 3H), 0.95 (d, *J* = 6.6 Hz, 3H), 1.50-1.65 (m, 1H), 1.60 (s, 3H), 1.76 (sept., *J* = 6.8 Hz, 1H), 1.95 (s, 3H), 2.36 (bs, 1H), 3.08 (d, *J* = 7.3 Hz, 1H), 3.16 (s, 1H), 3.26 (d, *J* = 8.3 Hz, 1H), 3.29 (d, *J* = 6.6 Hz, 1H), 3.79 (s, 1H), 5.82 (d, *J* = 6.1 Hz, 1H), 5.97 (s, 1H); ^{13}C NMR ($CDCl_3$, 100 MHz) : δ 214.8, 201.8, 155.9, 135.7, 126.6, 125.3, 78.1, 77.8, 57.2, 47.1, 41.8, 37.2, 37.2, 32.5, 22.1, 21.3, 16.7, 16.6, 16.3, 16.0; ESIMS (MeOH) m/z 333.0 ([M + H^+]); CAS [90334-19-3].





16

Figure 7. ORTEP diagram of the X-ray crystal structure of **16**.

Carcavrol (**17**, 1.5 g, 10 mmol) was oxidized with SIBX according to the general 10 mmol scale procedure to give after purification by flash chromatography, eluting with hexanes/Et_2O (1:1), 3-*iso*propyl-1,2-dihydroxy-6-methylbenzene (**15**) as a brown oil (398 mg, 24%) and dimer **18** as a

yellow solid (930 mg), which was recristallized twice from a mixture of CH_2Cl_2/hexanes in freezer to give pure **18** as white needles (795 mg, 47.9%).

3,10-Dihydroxy-6,12-di-*iso*propyl-3,10-dimethyl-tricyclo[6.2.2.0^{2,7}]dodeca-5,11-diene-4,9-dione (18). White needles (hexanes/CH_2Cl_2), colorless prisms also obtained from slow evaporation of $CHCl_3$. R_f = 0.15 (hexanes/Et_2O, 1:1); mp 136°C (hexanes/CH_2Cl_2) (lit.[9] 138-139°C (hexane)); IR (neat): ν_{max} 3451, 2967, 1724, 1676, 1157 cm^{-1}; ^{1}H NMR ($CDCl_3$, 300 MHz): δ 0.84 (d, *J* = 6.8 Hz, 3H), 0.88 (d, *J* = 6.6 Hz, 3H), 1.11 (d, *J* = 7.0 Hz, 3H), 1.12 (d, *J* = 6.6 Hz, 3H), 1.22 (s, 3H), 1.24 (s, 3H), 1.83 (sept., *J* = 6.8 Hz, 1H), 2.48 (sept., *J* = 6.8 Hz, 1H), 3.12 (dd, *J* = 2.5, 8.7 Hz, 1H), 3.13-3.17 (m, 1H), 3.23 (dd, *J* = 1.9, 8.7 Hz, 1H), 3.35 (dq, *J* = 1.0, 2.4, 6.8 Hz, 1H), 5.84 (d, *J* = 6.8 Hz, 1H), 5.96 (s, 1H); ^{13}C NMR ($CDCl_3$, 100 MHz) : δ 212.3, 201.9, 166.5, 145.6, 126.1, 119.9, 73.4, 72.8, 55.8, 44.6, 41.9, 40.8, 33.2, 32.8, 32.2, 25.8, 22.9, 20.7, 20.0, 19.2; EIMS m/z (rel intensity) 332 (M^+, 31), 315 (16), 289 (18), 271 (40), 243 (48), 166 (42), 149 (61), 125 (100); CAS [113159-72-1].

6,12-Di-*tert*-butyl-3,10-dihydroxy-3,10-dimethyl-tricyclo[6.2.2.0^{2,7}]dodeca-5,11-diene-4,9-dione 20. Oxidation of 5-*tert*-butyl-2-methylphenol (**19**, 70 mg, 0.43 mmol) with SIBX according to the general procedure gave after purification by flash chromatography, eluting with hexanes/EtOAc (4:1) to (1:1), dimer **20** as white crystals (30 mg, 39% not in Table). R_f = 0.11 (hexanes/acetone, 10:1); mp 178-180 °C ($CHCl_3$); IR (neat) ν_{max} 3451, 1727, 1677 cm^{-1}; ^{1}H NMR ($CDCl_3$, 400 MHz) δ 0.86 (s, 9H), 1.23 (m, 15H), 3.01 (d, *J* = 8.8 Hz, 1H), 3.25-3.50 (m, 3H), 6.01 (s, 1H), 6.05 (s, 1H); ^{13}C NMR ($CDCl_3$, 100 MHz) δ 211.1, 202.4, 166.9, 145.8, 128.5, 121.2, 73.8, 72.1, 53.6, 45.2, 40.7, 38.5, 37.8, 34.4, 32.7, 29.2, 28.2, 26.1; LSIMS m/z (rel intensity) 383 (MNa^+, 100), 361 (MH^+, 43), 360 (13), 343 (7), 303 (12); HRMS (LSIMS) calcd for $C_{22}H_{33}O_4$ 361.2379, found 361.2382.

(±)-Grandifloracin (22). Oxidation of 2-hydroxybenzyl benzoate (**21**, 456 mg, 2 mmol) with SIBX according to the general procedure gave after purification by flash chromatography, eluting with hexanes/acetone (3:1), a residue that was recrystallized twice from a mixture of CH_2Cl_2/hexanes in freezer to give pure (±)-grandifloracin **(22)** as white fines crystals (146.4 mg, 30%). R_f = 0.20

(hexanes/acetone, 3:1); mp 188-188.5°C (MeOH) (lit.[10] 161-163°); IR ν_{max} 3450, 1720, 1711, 1683, 1620 (cm^{-1}); ^1H NMR ($CDCl_3$, 300 MHz): δ 3.20-3.35 (m, 3H), 3.69 (d, *J* = 6.8 Hz, 1H), 4.23 (d, *J* = 12.0 Hz, 1H), 4.40-4.43 (m, 2H), 4.46 (d, *J* = 12.0 Hz, 1H), 6.00 (t, *J* = 6.7 Hz, 1H), 6.20 (d, *J* = 9.8 Hz, 1H), 6.43 (t, *J* = 7.2 Hz, 1H), 6.58 (dd, *J* = 3.6, 10.0 Hz, 1H), 7.92 (d, *J* = 7.3 Hz, 2H), 8.05 (d, *J* = 7.3 Hz, 2H); ^{13}C NMR ($CDCl_3$, 75 MHz): δ 208.1, 198.1, 166.6, 165.8, 146.7, 135.1, 133.4, 133.3, 129.8, 129.7, 129.3, 129.2, 128.5, 128.5, 128.4, 128.0, 75.4, 74.4, 71.8, 68.1, 52.1, 41.0, 39.9, 37.3; ESIMS (MeOH) m/z 511.5 ([M + Na^+]); HRMS (ESIMS) calcd for $C_{28}H_{24}O_8Na$ 511.1369, found 511.1365.

Modelisation. All calculations were performed using Gaussian03.[11] Every TS was characterized by the existence of a single imaginary frequency, associated to the normal mode corresponding to the formation of the C_5-$C_{5'}$ bond. The four TS's leading to the observed cyclodimers **1a-d** were thus determined (see Figure 8) and first examined here to address the role of the cyclopentyl unit in the slight preference observed in favor of the heterodimer **1c** when starting from (±)-**3** (see Scheme 4). The relative populations of **1a**:**1b**:**1c**:**1d** were estimated to be, respectively, 0.97:1.15:2.12:0.76 from Maxwell-Boltzmann statistics using the relative ΔG's of their corresponding TS's (see Table 2). These theoretical estimations agree remarkably well with the experimental results (Scheme 4). An examination of the major NBO interactions between the two monomers indicates that the slightly lower energy of **TS-c** could originate from higher $\sigma\#\rightarrow p_\pi^*{}_{C4}$ and $\sigma\#\rightarrow p_{\pi\ C4'}$ interactions (where σ# is the incipient first-formed C_5–$C_{5'}$ bond, see Table 5). As said in the main text, The **TS-a**' structure (Figure 8), which is analogous to **TS-a**, but with opposite configurations at the two C_6 centers, was also calculated to examine any perturbation brought by this stereochemical change. Changing this configuration at either of the two C_6 centers exactly leads to the same TS structure. The coordinates of the **TS-a**' geometry given below are those of the TS that would lead to the non-observed (3*R*,10*S*,14*S*,23*S*)-cyclodimer.

Table 2. B3LYP/6-31G* absolute energies (E_{tot}, a.u.), energies corrected to 0 K (E_0, a.u.), enthalpies (H_{298}, a.u.) and Gibb's free energies at 298 K (G_{298}, a.u.) for all transition states described in the text. The last column report the relative free energies ΔG in kcal/mol.

	E_{tot}	E_0	H_{298}	G_{298}	ΔG
TS-a	-1470.497723	-1469.808551	-1469.773500	-1469.870253	0.46
TS-b	-1470.49788	-1469.808541	-1469.773531	-1469.870413	0.36
TS-c	-1470.497633	-1469.808595	-1469.773449	-1469.870989	0.00
TS-d	-1470.497533	-1469.808594	-1469.773555	-1469.870025	0.60
TS-a'	-1470.481136	-1469.792794	-1469.757333	-1469.855192	9.92

Table 3. Interatomic distances (Å) calculated at the B3LYP/6-31G* level. Atom labels refer to Scheme 3.

	C_5-C_5,	C_2-C_4,	C_4-C_2,
TS-a	1.928	3.345	3.344
TS-b	1.925	3.293	3.456
TS-c	1.951	3.435	3.232
TS-d	1.922	3.369	3.492
TS-a'	1.991	3.269	3.377

Table 4. Dihedral angles calculated at the B3LYP/6-31G* level. Atom labels refer to Scheme 3.

	∠C_{Me}-C_6-C_5-$C_{5'}$	∠O-C_6-C_5-$C_{5'}$	∠C_{Me}-$C_{6'}$-$C_{5'}$-C_5	∠O-$C_{6'}$-$C_{5'}$-C_5
TS-a	–160.43	–40.37	–160.45	–40.39
TS-b	–162.19	–42.07	–157.06	–37.24
TS-c	–158.46	–38.47	–162.77	–42.75
TS-d	–160.22	–40.31	–156.93	–37.05
TS-a'	–162.34	–42.31	–49.61	–170.73

Table 5. Main orbital interactions between the σ orbital of the incipient bond (σ#) and singly occupied hybrid orbitals of the two orthoquinol units (E(2), kcal/mol) calculated at the B3LYP/6-31G* level. Natural orbitals occupancies are given in parentheses. Atom labels refer to Scheme 3.

	$D_{NBO} \rightarrow A_{NBO}$	E(2)	$D_{NBO} \rightarrow A_{NBO}$	E(2)
TS-a	σ# (1.696) → $p_{\pi}^{*}{}_{C4'}$ (0.954)	23.78	σ# (1.696) → $p_{\pi\,C4}$ (0.954)	23.78
TS-b	σ# (1.681) → $p_{\pi}^{*}{}_{C4}$ (0.954)	23.57	σ# (1.681) → $p_{\pi\,C4'}$ (0.964)	22.13
TS-c	σ# (1.625) → $p_{\pi}^{*}{}_{C4}$ (0.961)	25.37	σ# (1.625) → $p_{\pi\,C4'}$ (0.970)	25.39
TS-d	σ# (1.696) → $p_{\pi}^{*}{}_{C4'}$ (0.954)	22.29	σ# (1.696) → $p_{\pi\,C4}$ (0.954)	23.04
TS-a'	σ# (1.628) → $p_{\pi}^{*}{}_{C4}$ (0.936)	27.62	σ# (1.628)→ $p_{\pi\,C4'}$ (0.991)	26.84

Table 6. Cieplak σ→σ#* orbital interactions (kcal/mol) calculated at the B3LYP/6-31G* level. Atom labels refer to Scheme 3.

	$\sigma_{C6\text{-}Me} \rightarrow \sigma\#^*$	$\sigma_{C6'\text{-}Me} \rightarrow \sigma\#^*$	$\sigma_{C6\text{-}O} \rightarrow \sigma\#^*$	$\sigma_{C6'\text{-}O} \rightarrow \sigma\#^*$
TS-a	3.01	3.01	-	-
TS-b	3.07	2.88	-	-
TS-c	3.02	3.05	-	-
TS-d	3.10	2.89	-	-
TS-a'	-	3.16	2.29	-

Table 7: Felkin-Anh σ# → σ* orbital interactions (kcal/mol) calculated at the B3LYP/6-31G* level. Atom labels refer to Scheme 3.

	$\sigma\# \rightarrow \sigma^*_{C6\text{-}Me}$	$\sigma\# \rightarrow \sigma^*_{C6'\text{-}Me}$	$\sigma\# \rightarrow \sigma^*_{C6\text{-}O}$	$\sigma\# \rightarrow \sigma^*_{C6'\text{-}O}$
TS-a	2.66	2.66	1.11	1.11
TS-b	2.76	2.55	1.19	1.04
TS-c	2.61	2.83	1.09	1.24
TS-d	2.60	2.51	1.18	1.07
TS-a'	-	2.85	1.15	4.44

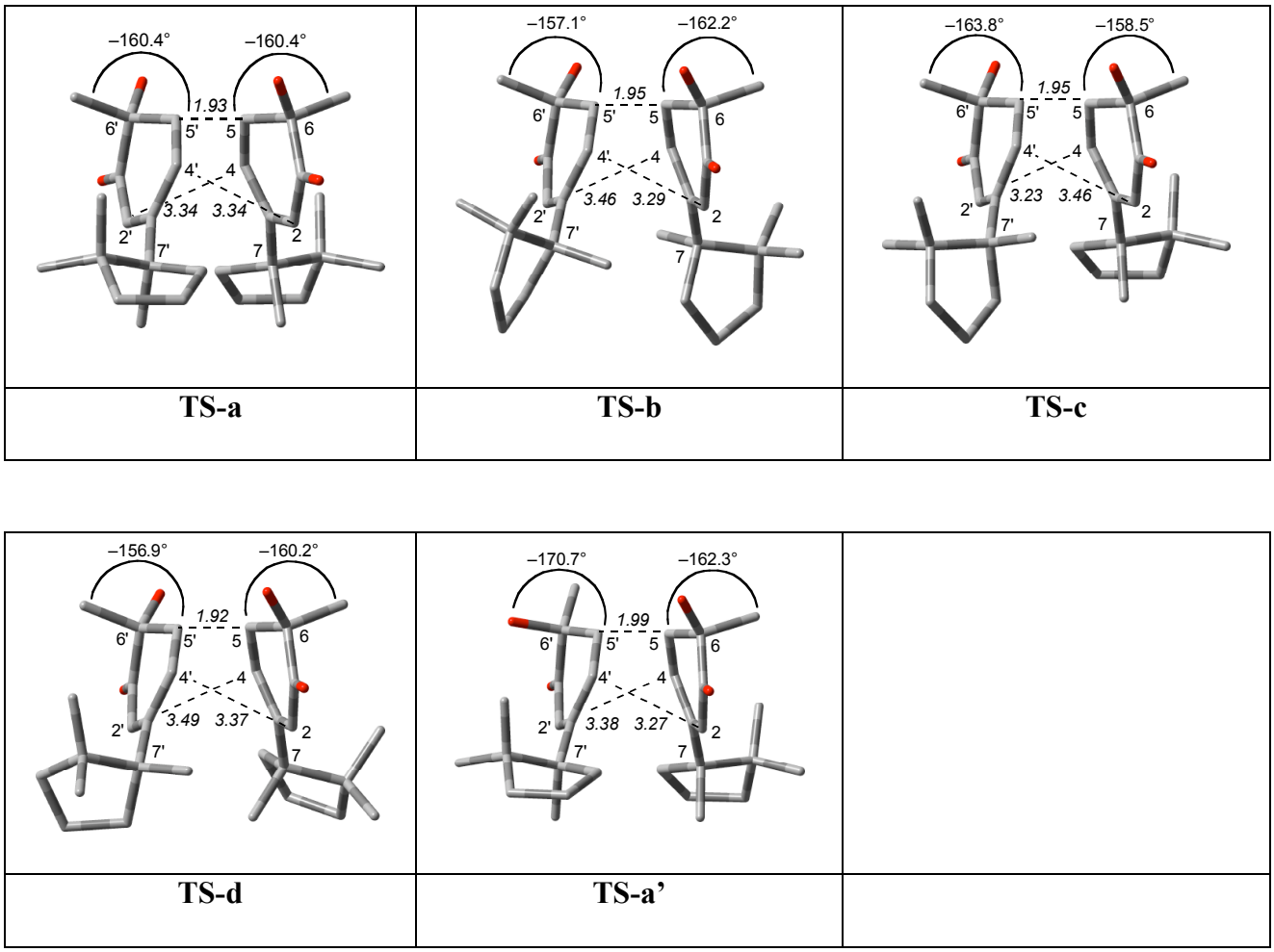


Figure 8. Structures of transition states calculated at the B3LYP/6-31G(d) level.

Geometries of transition states optimized at the B3LYP/6-31G(d) level

TS-a [3R,10R,14S,23S]

C	0.90174900	2.17122600	0.33974500
C	-0.90197200	2.17132300	-0.33989500
C	-1.59716700	1.07106700	0.20939300
C	1.06489600	-0.31177900	1.68901900
H	-5.64926600	-1.16232700	-1.68205100
C	-0.75313900	2.20702000	-1.85368000
C	-0.46244300	0.80134400	-2.38904700
O	0.20095600	0.70184600	-3.42966200
H	2.26955500	3.73000700	2.15295100
C	-1.71642900	-0.17703700	-0.46858700
H	1.04624600	-2.83500400	0.29829300
C	-1.06461000	-0.31182600	-1.68884200
H	-4.41376000	-2.40302500	-1.88645100
C	-4.13020300	-1.10885900	-0.12948700
H	2.29214300	-2.77117100	1.54983400
H	2.03384000	1.19987800	-1.18997600
H	1.14194100	3.12597200	-0.12382800
H	-1.14216400	3.12612000	0.12356500
H	2.93599700	2.07670100	2.19288100
H	5.77542500	-1.86079800	-1.11774100
H	-2.03419700	1.20009400	1.18977400
H	2.64457200	-3.50724400	-0.00975700
H	1.98572200	2.69225200	3.56771000
H	4.78908400	-3.12283800	-0.40344700
H	-5.70163700	0.34722900	0.18952000
C	4.74360000	-2.12977100	-0.86448900
H	-4.20122200	1.08155100	-0.38127900
H	1.60824900	-2.04834200	-1.95626900
H	4.26208400	-1.59883900	-2.94190500
C	4.13031300	-1.10853300	0.12924900
C	2.48692600	-1.46374900	-1.66588400
C	2.11557800	-2.68267700	0.47537100
H	3.64681100	-3.16541300	-2.45774200
H	-4.04864300	-0.71453400	-2.28361800
C	4.57738700	-1.36519400	1.57653800
C	4.60911100	0.30345800	-0.27204100
C	3.81458800	-2.14290700	-2.10384000
H	2.37402600	-0.50091300	-2.16577000
C	0.46257100	0.80137100	2.38910600
C	1.71649500	-0.17701900	0.46865900
C	-2.56119300	-1.32344900	0.11597500
C	1.59694300	1.07095400	-0.20952300
C	0.75302500	2.20703500	1.85354600
H	1.00165100	-1.26552200	2.19835600
C	2.56126500	-1.32346600	-0.11571700
H	-1.00103400	-1.26561000	-2.19804700
O	-0.20076500	0.70190500	3.42976200
O	-0.28532000	3.07409000	2.27475500
C	2.08424500	2.70138400	2.47735300

H	-0.64070000	2.62712800	3.07280100
H	4.41342700	-2.40149400	1.88715100
C	-2.48715400	-1.46313900	1.66623200
C	-2.11531000	-2.68286400	-0.47450900
H	-1.04613200	-2.83537800	-0.29666400
H	-2.29121200	-2.77154700	-1.54906300
H	-2.64480800	-3.50722400	0.01041700
H	-1.60862800	-2.04778400	1.95697100
C	-3.81503100	-2.14181300	2.10429900
H	-2.37413900	-0.50013700	2.16576400
C	-4.60927300	0.30327200	0.27097700
C	-4.74359700	-2.12966800	0.86462400
C	-4.57684000	-1.36629500	-1.57677900
H	-3.64749500	-3.16401000	2.45920100
H	-4.78862400	-3.12302200	0.40416000
H	-5.77559500	-1.86084800	1.11734200
H	-4.26278500	-1.59692100	2.94169100
H	-4.35158000	0.56191800	1.30356700
H	4.35128300	0.56146400	-1.30475600
H	5.70147900	0.34762000	-0.19071700
H	4.20101000	1.08203500	0.37982300
H	4.05018200	-0.71231900	2.28308600
H	5.65007300	-1.16221200	1.68110100
O	0.28513700	3.07418700	-2.27483900
H	0.64060600	2.62727100	-3.07286900
C	-2.08436500	2.70110600	-2.47767700
H	-2.27007200	3.72961500	-2.15313800
H	-1.98558400	2.69219400	-3.56801100
H	-2.93599200	2.07611000	-2.19352000

TS-b [3R,10R,14R,23R]

C	0.88615900	-2.33623400	-0.23798900
C	-0.97562700	-2.21970100	0.23531500
C	-1.25346000	0.21415900	1.67622700
C	1.58777400	-1.30089300	0.42215500
H	-5.80698400	0.28641800	0.42456800
C	-1.00840300	-2.31967600	1.75619000
C	-0.75438200	-0.94386300	2.38412600
O	-0.20861600	-0.90337500	3.49439900
C	1.28422700	0.18219600	-1.44432300
C	-1.55733700	-1.06633600	-0.34351100
H	3.11110100	-2.27680200	-1.84568900
C	-1.75203500	0.14738100	0.38438400
H	-1.57281100	0.94875200	-2.25290500
H	-4.60282900	0.90804300	1.55673100
C	-4.03147300	1.03992400	-0.57623800
C	-1.74664200	1.76821600	-1.55280200
H	-1.21454400	-3.14191800	-0.29153600
H	1.90925400	-1.48971300	1.43710200
H	1.30628200	1.15704000	-1.91470500
H	2.29520200	-2.78507800	-3.34726600
H	4.95180700	2.40920400	1.63291500
H	1.01839400	-3.31980500	0.20746300

H	-0.76974800	2.18448700	-1.28985200
H	2.37009200	-3.89336600	-1.95987100
H	5.39195300	2.95899000	0.02696800
H	-5.39335900	0.19755500	-2.03315500
C	4.57048100	2.53271500	0.61349700
C	-2.40957000	-2.81227700	2.20128700
H	-4.01575900	-0.84872500	-1.70750400
H	1.75578700	2.64467700	-0.69440700
H	3.20063800	3.95880600	1.56417700
C	4.13315100	1.15821000	0.03681100
C	2.10422900	2.50128500	0.33078700
H	1.58335800	0.75600700	2.47065900
H	3.37844900	4.21549100	-0.15989000
H	-4.35829000	-0.66013700	0.77479500
C	4.22794800	1.22433500	-1.50250400
C	5.04159400	0.01533700	0.51661200
C	3.31090500	3.43766300	0.60771400
H	1.24893800	2.71324800	0.98197800
C	0.72740500	-0.87390700	-2.25764400
C	1.81262400	-0.02982900	-0.17555800
C	-2.48743600	1.33254200	-0.26524600
C	0.89983500	-2.31053800	-1.75787300
H	-1.24127300	1.14281200	2.23473600
C	2.62303900	1.05273000	0.56232200
H	-1.86756000	-1.12615600	-1.37860700
O	0.18420300	-0.70162500	-3.35802800
O	-0.12304200	-3.11098400	-2.32317600
C	2.26962700	-2.84418700	-2.25436500
H	-0.37463100	-2.61578600	-3.13213400
O	-0.04361200	-3.22719500	2.26096500
H	0.22752200	-2.81707900	3.11018500
H	-2.57092200	-3.82202400	1.81125400
H	-3.21489900	-2.16067700	1.85202900
H	-2.43619000	-2.85323300	3.29502800
C	-2.60252500	2.57031300	0.66455900
H	5.27091300	1.40242600	-1.79014800
H	3.63205700	2.03789200	-1.92976400
H	3.90975200	0.29266700	-1.97981000
H	-2.30442800	2.54575600	-2.08379200
H	-2.89754700	2.26388500	1.67268600
C	-3.71455500	3.44836300	0.05512600
H	-1.64801700	3.10042900	0.76112000
C	-4.31479800	0.19725100	-1.83163100
C	-4.60988000	2.47749400	-0.75742000
C	-4.73018100	0.35748900	0.61903400
H	-4.27374700	3.97485100	0.83529200
H	-5.65604200	2.50688900	-0.43326300
H	-4.61062200	2.75194500	-1.81820300
H	-3.29135000	4.22043700	-0.59610000
H	-3.81800400	0.59388000	-2.72233500
H	5.14329100	-0.00908600	1.60555800
H	6.04878100	0.13423200	0.09953600
H	4.66642100	-0.96228500	0.18882800
H	3.10159300	1.63783400	2.61575800

C	2.60742500	0.81419100	2.09317500
H	3.11779400	-0.10347200	2.39499200

TS-c [3R,10R,14S,23R]

C	-1.02938100	2.21686200	0.04120700
C	0.85023500	2.26474100	0.56180400
C	1.18189300	-0.41876400	1.36364600
C	-1.58231000	0.98499100	0.44846000
H	5.28315800	-1.41867200	1.62399700
C	0.82501200	2.00259100	2.05838100
C	0.62687200	0.50610400	2.32613900
O	0.07291200	0.17534000	3.38340600
C	-1.23138100	0.00664700	-1.72539000
C	1.56023000	1.34010200	-0.23302300
H	-3.24432300	2.33065500	-1.58770000
C	1.76338600	-0.01087600	0.16722800
H	3.05566400	0.43234000	-2.38109000
H	3.68801900	-2.16877100	1.66186600
C	4.14079000	-1.02023900	-0.17364900
C	2.58631200	-0.53438800	-2.18552500
H	0.97584400	3.30518800	0.27101400
H	-1.91495800	0.90660100	1.47399800
H	-1.19123700	-0.83019600	-2.41223800
H	-2.47452700	3.23951000	-2.91180200
H	-5.51683300	-2.36536500	1.10595100
H	-1.27125000	3.05281600	0.69445500
H	1.55599800	-0.47214500	-2.54503200
H	-2.64709200	3.98716500	-1.30859900
H	-4.51199600	-3.41493000	0.12376200
H	5.98713600	0.12048600	-0.09082900
C	-4.49295500	-2.51116600	0.74322300
C	2.18315500	2.43902000	2.66793900
H	4.53957700	1.13205300	-0.05103700
H	-1.29646200	-2.33906100	1.64973800
H	-3.89211100	-2.31327100	2.84920200
C	-4.02508600	-1.29793100	-0.10162700
C	-2.23755400	-1.79852400	1.50929200
H	-3.19901800	-3.70852300	2.04933600
H	3.85137000	-0.43078800	1.93265900
C	-4.55958700	-1.35244700	-1.54052100
C	-4.56288600	-0.01024700	0.55946500
C	-3.47158700	-2.65871000	1.89926500
H	-2.17060800	-0.92358900	2.15696100
C	-0.75834200	1.26409100	-2.26070200
C	-1.72332800	-0.12978800	-0.43617700
C	2.62614200	-0.95260400	-0.69349800
C	-1.04389400	2.53018400	-1.44717600
H	1.17582100	-1.45794500	1.67019500
C	-2.43219900	-1.42032400	0.01057500
H	1.90843900	1.67806500	-1.19954900
O	-0.20878900	1.39193400	-3.36215600
O	-0.09450100	3.51994700	-1.80265400
C	-2.45481800	3.04669400	-1.83424300

H	0.19202500	3.24459900	-2.69970000
O	-0.20735200	2.71702900	2.71586400
H	-0.47159500	2.11188800	3.44164300
H	2.29646700	3.52066500	2.54570700
H	3.03367100	1.93627800	2.19818700
H	2.17773300	2.20798400	3.73812400
C	2.20842800	-2.44963500	-0.63988900
H	-5.65002900	-1.23583500	-1.54086500
H	-4.33591200	-2.30398200	-2.03261300
H	-4.14325200	-0.54569200	-2.15588200
H	3.10595900	-1.26996100	-2.80589800
H	1.87248300	-2.74105500	0.35754600
C	3.47562500	-3.26209800	-1.02051100
H	1.37168700	-2.64177200	-1.31967500
C	4.97438000	0.22909600	-0.49729100
C	4.66997600	-2.27903300	-0.91204000
C	4.23247600	-1.27235700	1.34685000
H	3.59802600	-4.11892500	-0.35006500
H	5.52202800	-2.71599000	-0.37936900
H	5.03611000	-2.00529400	-1.90764800
H	3.39808100	-3.67218600	-2.03263700
H	5.07482700	0.39746000	-1.57360700
H	-4.24461900	0.09223200	1.60208000
H	-5.65902000	-0.03383200	0.55548400
H	-4.25330100	0.89286700	0.02418300
H	-2.35119700	-3.56196000	-0.43767700
C	-1.92496200	-2.62827600	-0.81496000
H	-0.83713800	-2.70727500	-0.72409400
H	-2.16965400	-2.56813600	-1.87767200

TS-d [3R,10R,14R,23S]

C	-0.88644700	2.29694300	0.32770300
C	0.98165200	2.06809700	0.71807500
C	1.56586000	1.16341300	-0.19840200
C	-1.37760800	0.23613500	-1.54946600
H	5.73803200	0.45824000	-0.43767500
C	1.04252200	1.69204000	2.19431200
C	0.82663900	0.18362400	2.36668900
O	0.29704300	-0.21366600	3.41262900
H	-2.36830000	4.31649900	-0.82238700
C	1.79587400	-0.21276400	0.10662300
H	-0.79707800	-2.37787900	0.45484800
C	1.34753200	-0.68400600	1.33210900
H	4.23221800	0.97082400	0.32725800
C	4.12781800	-0.96702200	-0.71127200
H	-1.41449100	-2.47638000	-1.19773700
H	-1.84761000	0.99518000	1.72302200
H	-1.00375200	3.11033600	1.04058100
H	1.20396700	3.11110300	0.49944200
H	-3.15892800	2.75005000	-1.13062600
H	-5.80321500	-2.22779500	0.45504000
H	1.85896900	1.55651600	-1.16297600
H	-2.22078800	-3.36211000	0.09660900

H	-2.38158000	3.63966300	-2.46614200
H	-4.60440500	-3.41029200	-0.02912600
H	5.95745400	-1.61939000	-1.67904100
C	-4.72404200	-2.41061300	0.40397300
H	4.75714900	-1.01079000	-2.82128500
H	-2.08885600	-1.43448200	2.31125900
H	-4.76177400	-2.09565700	2.59367500
C	-4.03745800	-1.34671800	-0.50708600
C	-2.96281100	-1.24838600	1.67778700
C	-1.70939100	-2.42561900	-0.14652500
H	-3.60652000	-3.30309100	2.06613300
H	4.42024300	1.08490200	-1.42977100
C	-4.03416700	-1.81627200	-1.97087200
C	-4.83041400	-0.02337900	-0.43943700
C	-4.04863500	-2.33741200	1.79914400
H	-3.38553100	-0.29184700	1.99950200
C	-0.82987500	1.47989000	-2.04304900
C	-1.84600400	0.07892500	-0.24935800
C	2.54292200	-1.11749400	-0.90290000
C	-1.57487900	1.11492700	0.68385900
C	-0.94617400	2.70984000	-1.13461800
H	-1.43152400	-0.57100300	-2.27140500
C	-2.59796300	-1.19672400	0.16921600
H	1.38494400	-1.73605400	1.58910500
O	-0.34000900	1.63553300	-3.16923600
O	0.08108000	3.62262900	-1.48130000
C	-2.31451800	3.38994600	-1.40228600
H	0.28344400	3.38831300	-2.41249700
H	-3.49003000	-2.75656000	-2.10444100
C	2.34392600	-2.63056400	-0.57940800
H	1.33437400	-2.84434700	-0.21987100
C	3.45037800	-3.04788700	0.42813000
H	2.45254700	-3.19790900	-1.50889600
C	4.88475400	-1.59570700	-1.90473000
C	4.37997300	-1.81954100	0.55459900
C	4.64705000	0.46908000	-0.55094400
H	3.03886900	-3.33666900	1.40117800
H	4.11773200	-1.23835100	1.44639100
H	5.43668600	-2.09328400	0.65399700
H	3.99671900	-3.92046000	0.05451300
H	4.57344300	-2.62367100	-2.11626900
H	-4.91841000	0.36689400	0.57982900
H	-5.84784300	-0.18360800	-0.81568500
H	-4.37006200	0.75274300	-1.05971900
H	-3.60119900	-1.06819400	-2.64369100
H	-5.06567000	-1.98803100	-2.30279600
O	0.07717600	2.37782000	2.97239300
H	-0.17282700	1.71671500	3.65328400
C	2.44646400	2.04837400	2.74857800
H	2.58802200	3.13186600	2.68750200
H	2.49475200	1.75000400	3.80084800
H	3.25282700	1.55088100	2.20284700
H	2.33490700	0.18771000	-2.68404200
C	2.07702600	-0.81896000	-2.34179000

H	0.99209900	-0.91610100	-2.42640200
H	2.52866200	-1.52600600	-3.04221000

TS-a' [3R,10S,14S,23S]

C	0.94067500	2.12518100	0.39291900
C	-0.94397300	2.20001900	-0.24592300
C	-1.63710500	1.08643800	0.26775100
C	1.06621300	-0.39705500	1.64408300
H	-5.67641400	-1.12515100	-1.67510500
C	-0.80388300	2.29691800	-1.75586200
C	-0.50697900	0.91433000	-2.34623400
O	0.14646400	0.86539100	-3.39765000
C	-1.74328400	-0.13750300	-0.45424900
H	1.03646200	-2.91264500	0.14425500
C	-1.09257100	-0.22543900	-1.68122700
H	-4.42022200	-2.33399100	-1.93768600
C	-4.14609100	-1.10826900	-0.13229300
H	2.26042100	-2.86206800	1.41813200
H	1.95018100	1.17231300	-1.22352700
H	1.16996800	3.08784400	-0.06228600
H	-1.15760700	3.15298600	0.23406000
H	5.77546900	-1.78523100	-1.17062800
H	-2.07483400	1.16548600	1.25364400
H	2.65184000	-3.54802700	-0.15506800
H	4.79263100	-3.09672600	-0.54407200
H	-5.73447100	0.31330600	0.25253800
C	4.74265200	-2.08147000	-0.95384900
H	-4.24508700	1.09040100	-0.29066000
H	1.63277200	-2.08145500	-2.07013200
H	4.28125600	-1.41672100	-2.99365000
C	4.09230200	-1.12463500	0.07717400
C	2.47489300	-1.45560400	-1.75667200
C	2.09995200	-2.74659300	0.34390100
H	3.72747900	-3.04178300	-2.64627600
H	-4.08802800	-0.62483500	-2.26895200
C	4.52380200	-1.43499400	1.51840300
C	4.53353600	0.32151200	-0.23824900
C	3.84083800	-2.04337900	-2.21118100
H	2.30738800	-0.48599700	-2.22764100
C	0.52335700	0.70865700	2.42565400
C	1.68247400	-0.24410600	0.41794100
C	-2.57279200	-1.31297000	0.09367500
C	1.55421800	1.02684900	-0.22810300
C	0.88710100	2.12342500	1.92345800
H	1.01183600	-1.35971500	2.13806900
C	2.53113000	-1.36429700	-0.20125900
H	-1.02058000	-1.16185200	-2.22025000
O	-0.09799300	0.54601600	3.47164100
H	4.37816500	-2.48679300	1.78368900
C	-2.48667400	-1.50974700	1.63709300
C	-2.11618000	-2.64532500	-0.54822800
H	-1.04398100	-2.79035800	-0.38443700
H	-2.29976800	-2.69815200	-1.62377700

H	-2.63160800	-3.49284300	-0.08878900
H	-1.59487900	-2.08605500	1.90186200
C	-3.79868100	-2.23084700	2.05411300
H	-2.39126300	-0.56438100	2.17314400
C	-4.64132500	0.27985500	0.32876300
C	-4.73934900	-2.17628800	0.82415800
C	-4.59972100	-1.31375400	-1.58568300
H	-3.61025200	-3.26565600	2.35824900
H	-4.77927200	-3.14972900	0.32251200
H	-5.77146000	-1.92902300	1.09745800
H	-4.24753200	-1.73473600	2.92071400
H	-4.38380700	0.49659000	1.37108400
H	4.27940100	0.63085900	-1.25815900
H	5.62370100	0.39128100	-0.14242400
H	4.09313600	1.04145200	0.45877800
H	3.97562800	-0.81782700	2.24018400
H	5.59095700	-1.21534000	1.64439000
O	0.22512800	3.18798200	-2.14908900
H	0.58183200	2.76906500	-2.96240800
C	-2.14223500	2.80578700	-2.35252500
H	-2.33434000	3.82039500	-1.98937300
H	-2.04798300	2.83925000	-3.44270300
H	-2.98769900	2.16390400	-2.08888000
C	0.01865800	3.19835100	2.57101900
H	0.29010400	4.19165200	2.18979500
H	-1.04983400	3.04338100	2.40110100
H	0.18534700	3.17292300	3.64948700
O	2.25205700	2.29338300	2.38221500
H	2.54394700	3.17155600	2.08538900

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^{13}C and ^{1}H NMR Spectra

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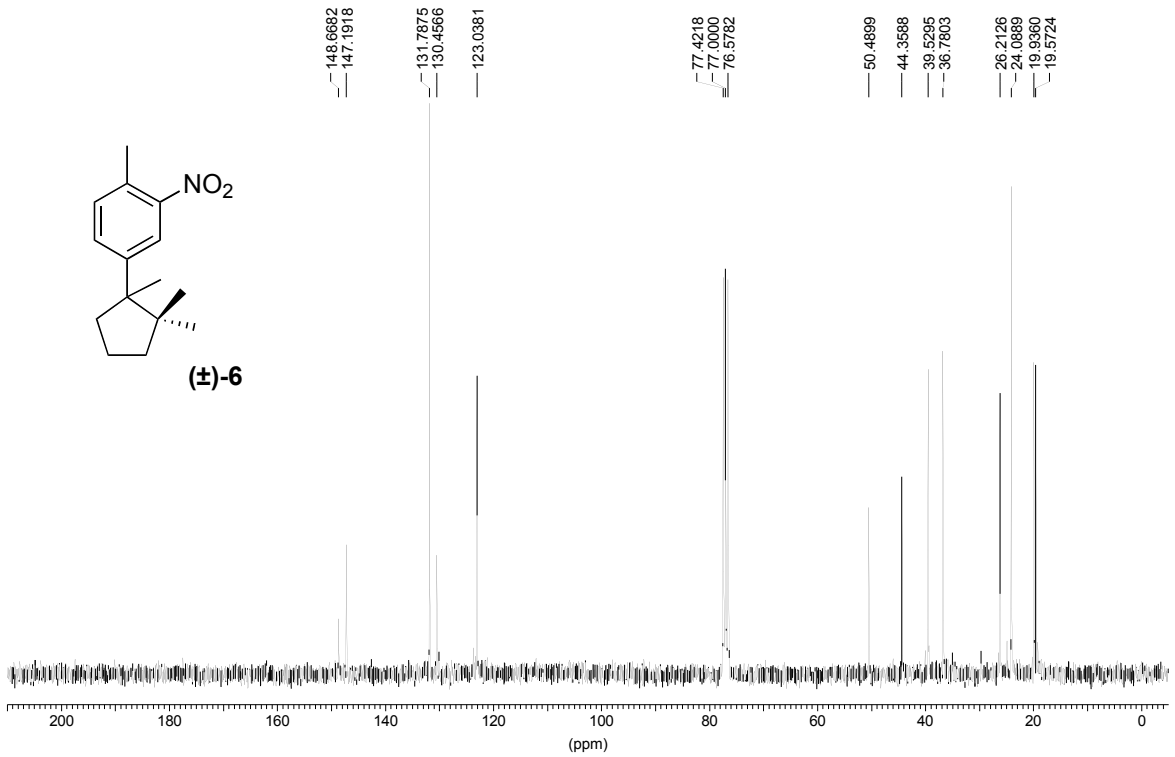

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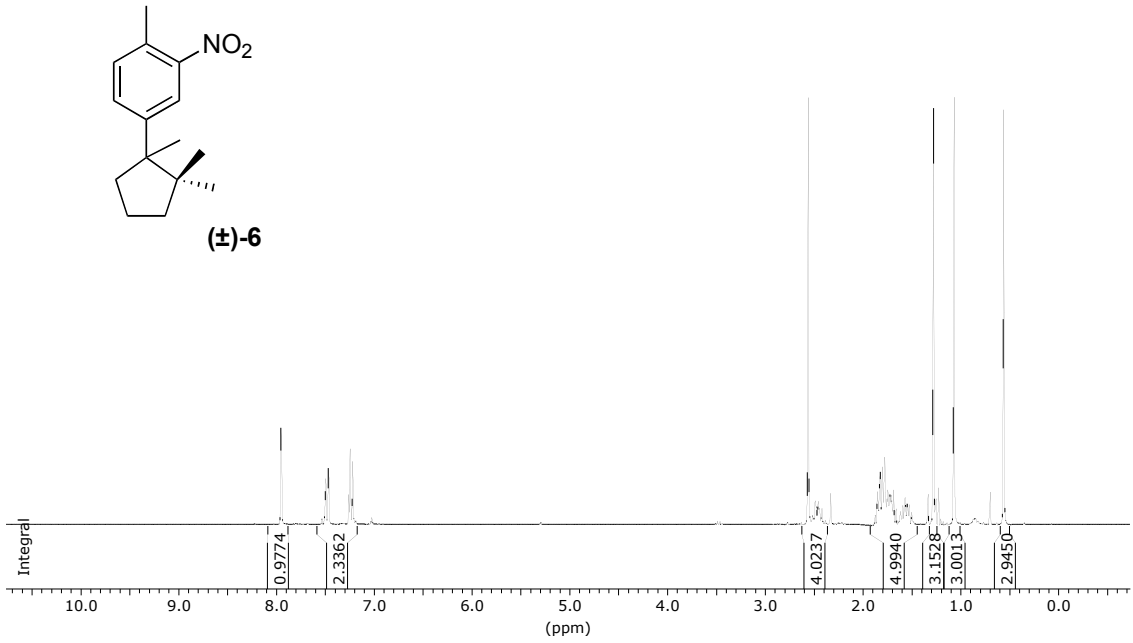

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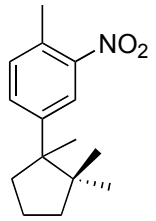


(±)-6

Peak Picking Parameter

Peak constant PC = 0.00
Noise = 214
Sens. level = 0

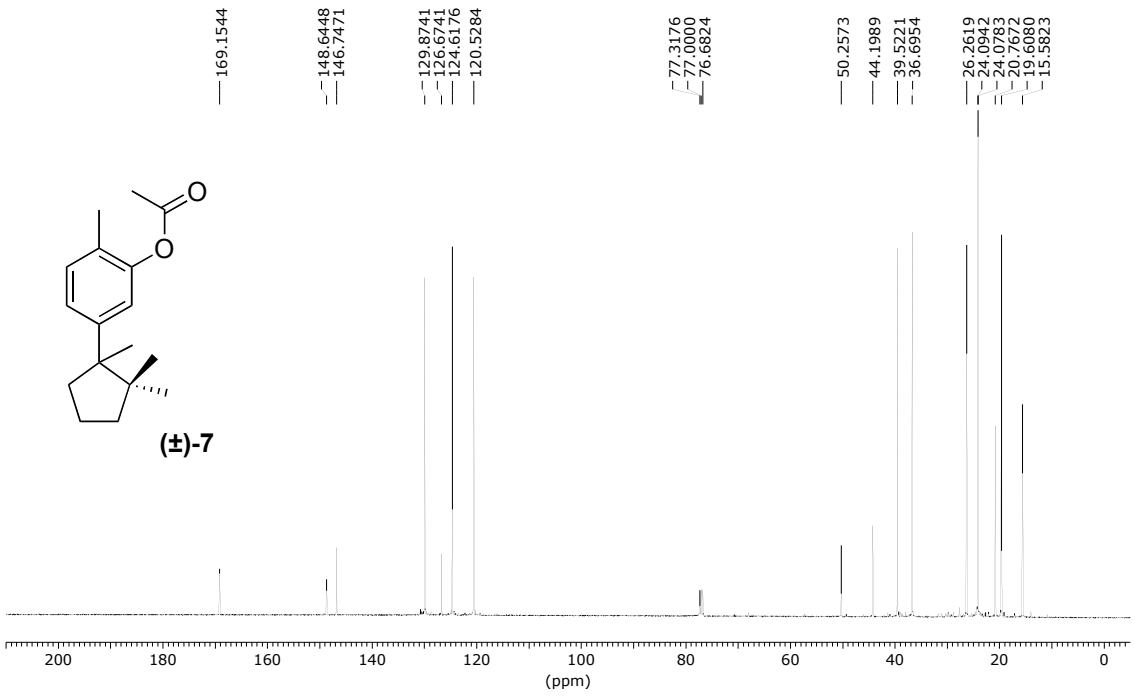
Peak Picking region

Start(ppm/Hz)	End(ppm/Hz)	MI(%)	MAXI(%)
9.05/ 2715.8	6.83/ 2049.3	10.11	28.05
7.55/ 2267.1	7.38/ 2215.1	7.01	16.51
3.07/ 921.7	0.09/ 28.4	90.94	118.47
7.30/ 2189.9	7.21/ 2163.5	5.65	8.62

Peak Picking results

Peak Nr.	Data Point	Frequency	PPM	Intensity	%Int.
1	9412	2386.92	7.9529	39594	22.5
2	9417	2385.03	7.9467	33896	19.3
3	9777	2249.40	7.4947	18730	10.6
4	9782	2247.51	7.4885	15680	8.9
5	9799	2241.11	7.4671	23009	13.1
6	9803	2239.60	7.4621	18906	10.7
7	9964	2178.94	7.2600	12182	6.9
8	9975	2174.80	7.2462	30997	17.6
9	9997	2166.51	7.2186	25835	14.7
10	13710	767.60	2.5576	175331	99.6
11	14730	383.30	1.2771	173298	98.5
12	14898	320.01	1.0662	175968	100.0
13	15302	167.80	0.5591	170569	96.9

JGB176-1 - 190104 - DPX400 -



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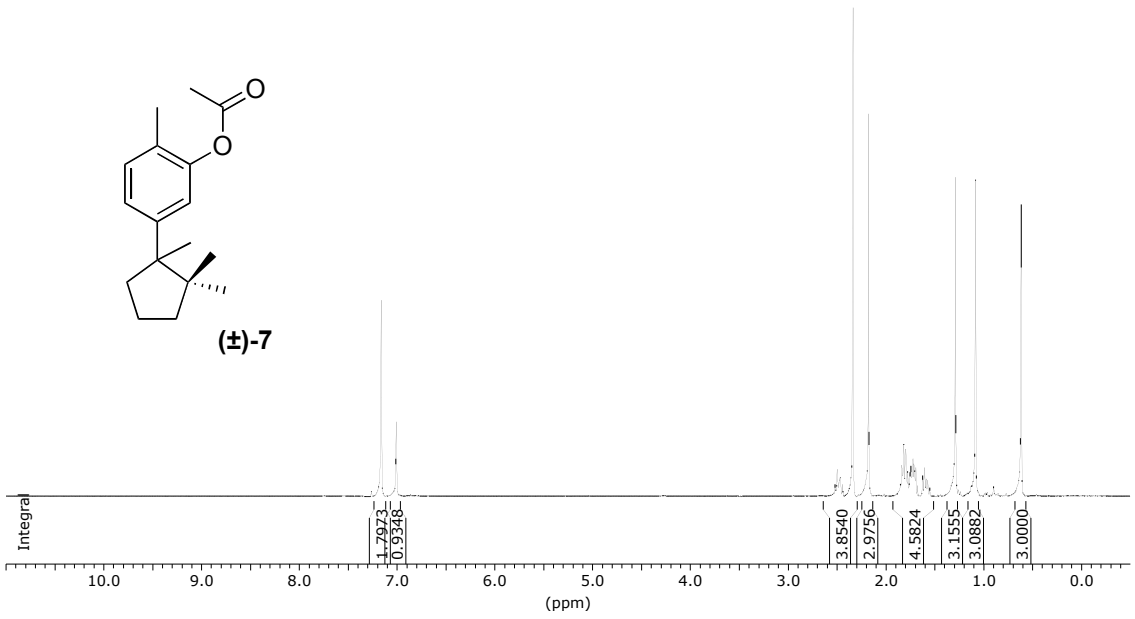

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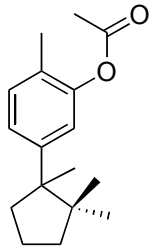

(±)-7

Peak Picking Parameter

Peak constant PC = 1.00
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Sens. level = 148

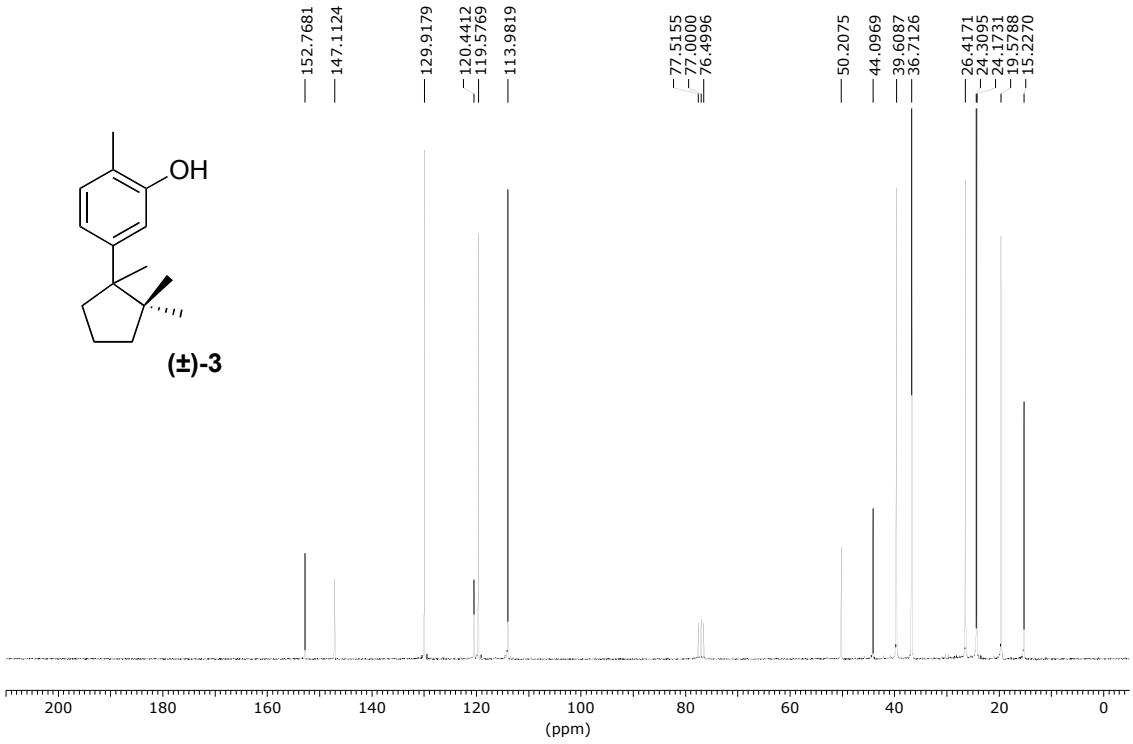
Peak Picking region

Start(ppm/Hz)	End(ppm/Hz)	MI(%)	MAXI(%)
7.29/ 2918.1	7.24/ 2898.3	0.83	3.72
7.20/ 2881.0	6.94/ 2777.3	14.12	41.64
3.50/ 1400.6	0.07/ 26.6	54.73	118.48

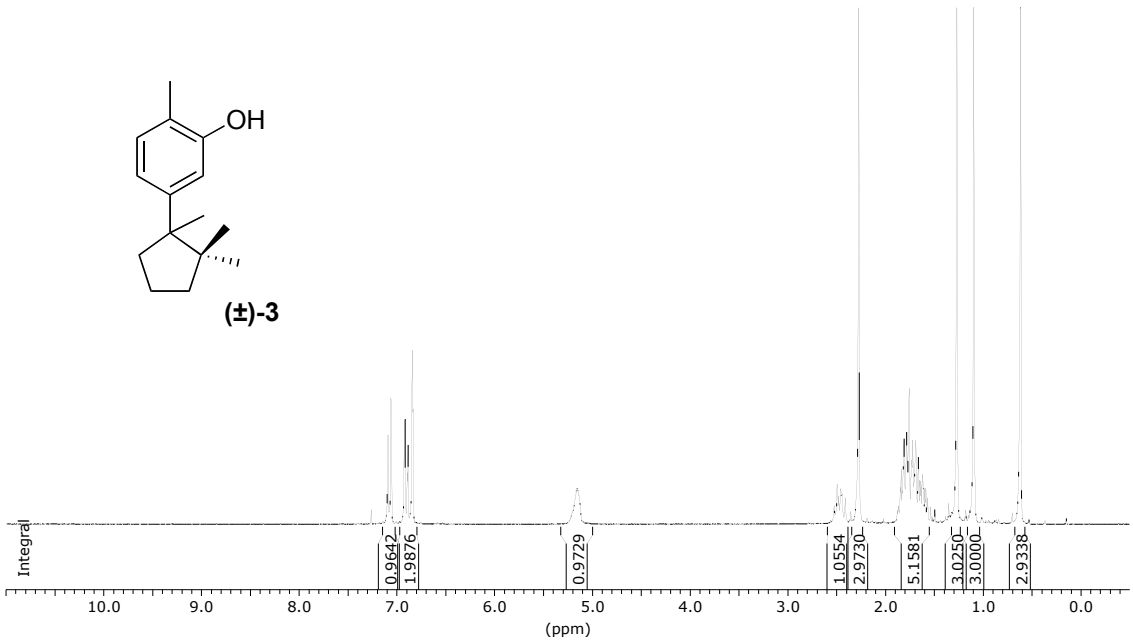
Peak Picking results

Peak Nr.	Data Point	Frequency	PPM	Intensity	%Int.
1	12750	2904.94	7.2600	3149	1.1
2	12910	2865.82	7.1622	112999	40.1
3	13162	2804.20	7.0082	42381	15.0
4	20806	935.00	2.3367	281632	100.0
5	21067	871.17	2.1772	219521	77.9
6	22522	515.38	1.2880	183863	65.3
7	22860	432.73	1.0815	181562	64.5
8	23622	246.39	0.6158	166815	59.2

JGB222-2 - HPLC hydroxycuparene - dc141f.101 - AC250 -



JGB222-2 - dc140f.101 - AC250 -



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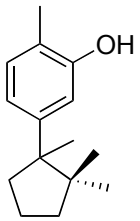


(±)-3

Peak Picking Parameter

Peak constant PC = 1.00
Noise = 12
Sens. level = 47

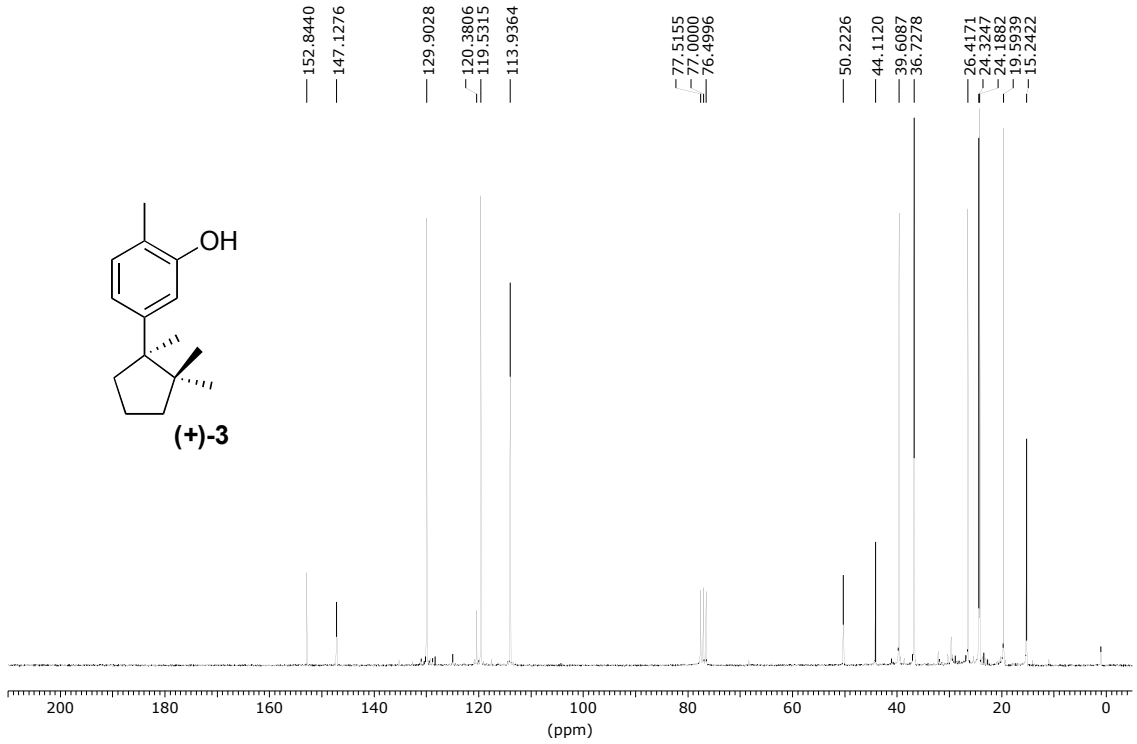
Peak Picking region

Start(ppm/Hz)	End(ppm/Hz)	MI(%)	MAXI(%)
8.61/ 2153.5	6.23/ 1557.8	1.83	29.93
5.52/ 1379.6	4.60/ 1151.3	2.52	12.75
3.38/ 845.2	-0.34/ -84.7	81.36	111.54
7.34/ 1835.5	7.10/ 1774.8	1.46	3.69

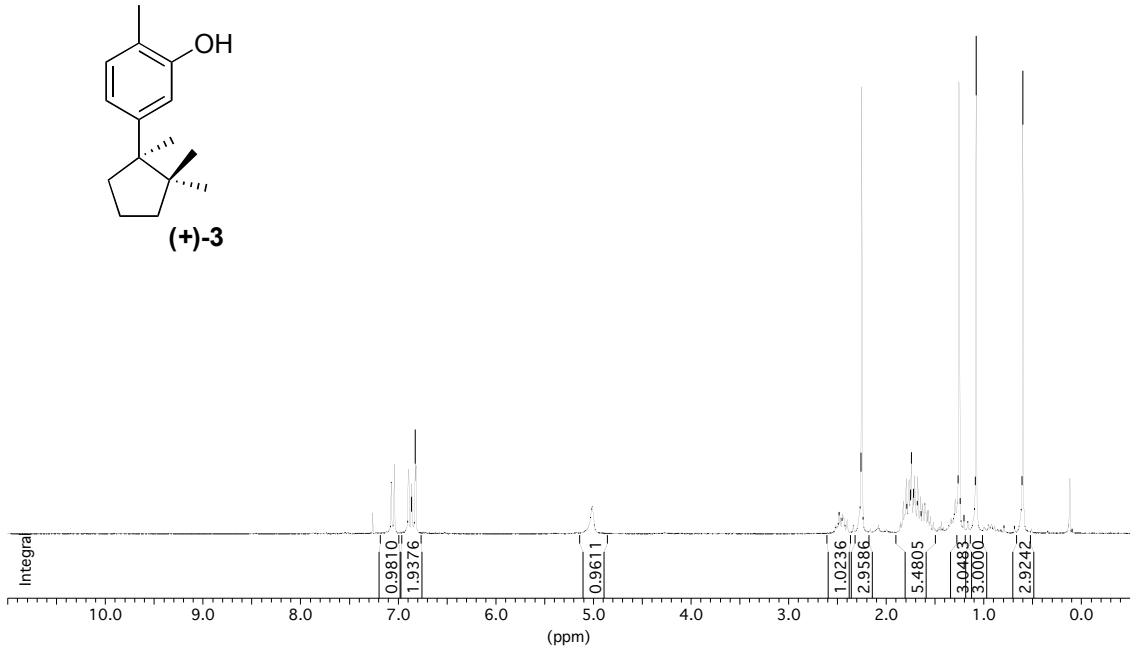
Peak Picking results

Peak Nr.	Data Point	Frequency	PPM	Intensity	%Int.
1	6981	1815.96	7.2600	665	1.8
2	7120	1773.55	7.0904	4170	11.0
3	7146	1765.61	7.0587	5890	15.6
4	7257	1731.74	6.9233	4543	12.0
5	7263	1729.91	6.9159	4904	13.0
6	7283	1723.80	6.8915	2913	7.7
7	7289	1721.97	6.8842	3691	9.8
8	7324	1711.29	6.8415	8131	21.5
9	7330	1709.46	6.8342	6364	16.9
10	8708	1288.93	5.1530	1671	4.4
11	11069	568.41	2.2724	35327	93.6
12	11893	316.94	1.2671	35911	95.1
13	12035	273.61	1.0938	37760	100.0
14	12425	154.59	0.6180	36227	95.9

JGC222-1 - (R)-Hydroxycuparene - dc250f.101 - AC250

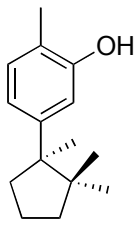


(R)-Hydroxycuparene - dc251f.101 - AC250 -



Peak List

File Name :
c:\docume~1\julien\mesdoc~1\chimie\rmn\dec04~1\dc251f\101001.1R
Peak Results saved in File : C:\RMN\EDIT.ASC
Nucleus : 1H
SF : 250.132854 MHz
OFFSET : 15.7748 ppm
SW_p : 5000.00 Hz
SI : 16384



(+)-3

Peak Picking Parameter

Peak constant PC = 1.00
Noise = 2
Sens. level = 7

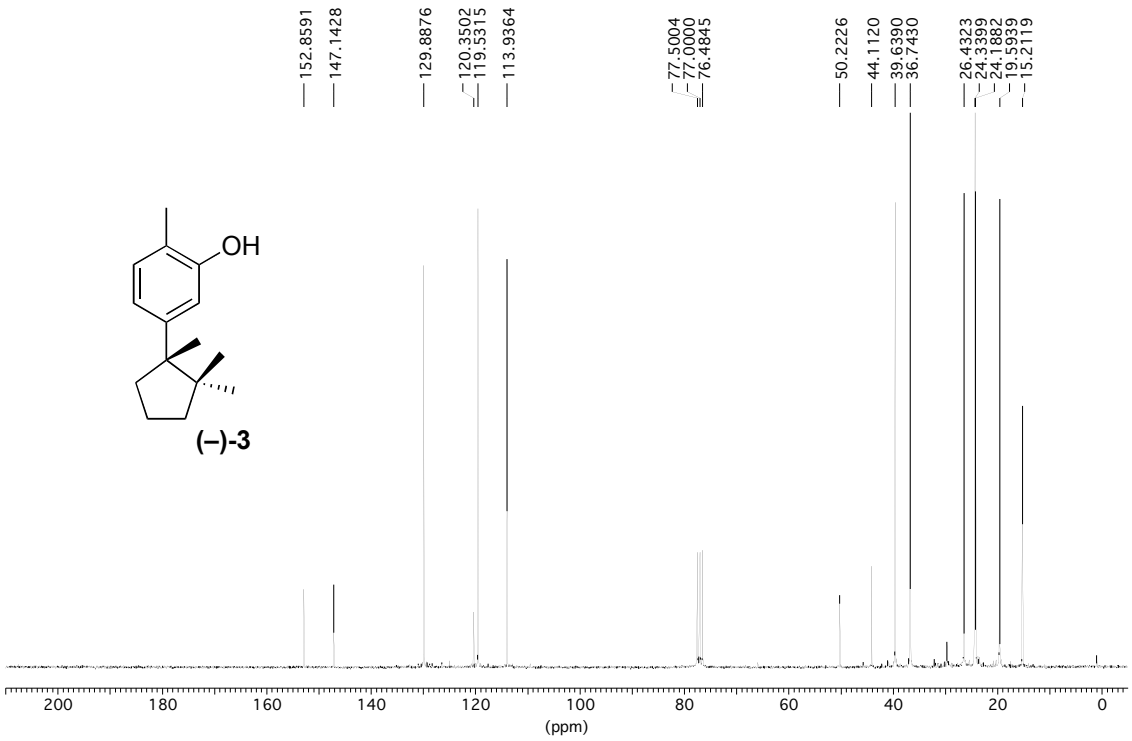
Peak Picking region

Start(ppm/Hz)	End(ppm/Hz)	MI(%)	MAXI(%)
7.46/ 1866.6	6.42/ 1606.0	2.87	23.38
5.22/ 1305.1	4.87/ 1217.5	5.79	9.43
5.27/ 1318.2	4.89/ 1222.1	4.61	9.49
3.95/ 989.2	-0.28/ -68.8	68.76	121.12

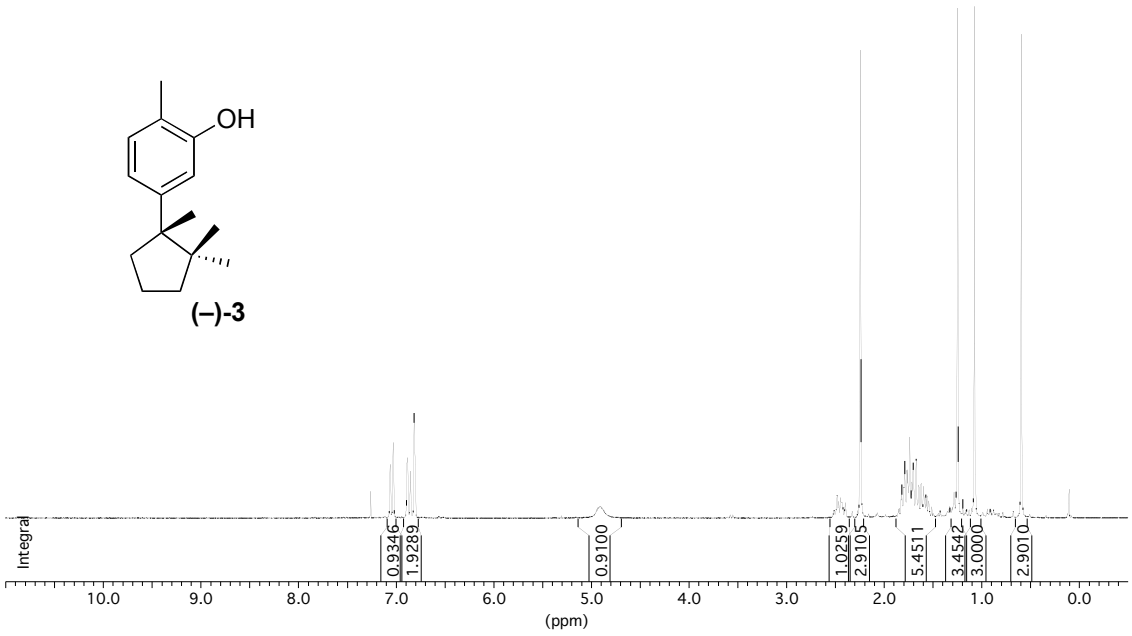
Peak Picking results

Peak Nr.	Data Point	Frequency	PPM	Intensity	%Int.
1	6979	1815.96	7.2600	265	4.2
2	7136	1768.05	7.0685	648	10.4
3	7162	1760.12	7.0355	876	14.0
4	7278	1724.72	6.8952	714	11.4
5	7284	1722.89	6.8879	811	13.0
6	7304	1716.78	6.8635	462	7.4
7	7310	1714.95	6.8562	632	10.1
8	7338	1706.41	6.8220	1307	20.9
9	7344	1704.58	6.8147	980	15.7
10	8822	1253.53	5.0114	344	5.5
11	11086	562.61	2.2492	5619	89.7
12	11904	312.97	1.2512	5683	90.7
13	12048	269.03	1.0755	6263	100.0
14	12440	149.40	0.5973	5824	93.0

(S)-Hydroxycuparene - jv021f.101 - AC250 -

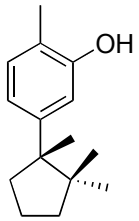


(S)-Hydroxycuparene - jv020f.101 - AC250 -



Peak List

File Name :
c:\docume~1\julien\mesdoc~1\chimie\rmn\janv05~1\jv020f\101001.1R
Peak Results saved in File : C:\RMN\EDIT.ASC
Nucleus : 1H
SF : 250.132854 MHz
OFFSET : 15.7748 ppm
SW_p : 5000.00 Hz
SI : 16384



(–)-3

Peak Picking Parameter

Peak constant PC = 1.00
Noise = 1
Sens. level = 6

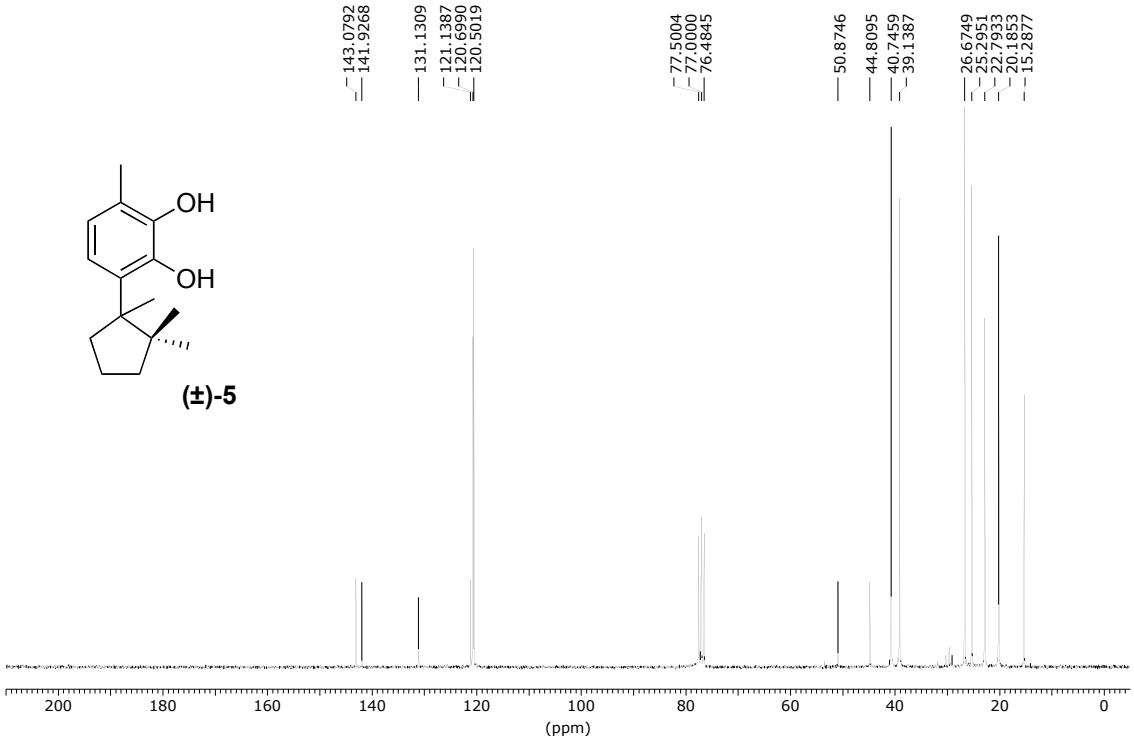
Peak Picking region

Start(ppm/Hz)	End(ppm/Hz)	MI(%)	MAXI(%)
8.32/ 2080.6	6.11/ 1529.4	4.76	29.74
5.25/ 1312.1	4.71/ 1178.5	1.84	10.62
3.75/ 939.2	0.30/ 76.2	85.65	124.57

Peak Picking results

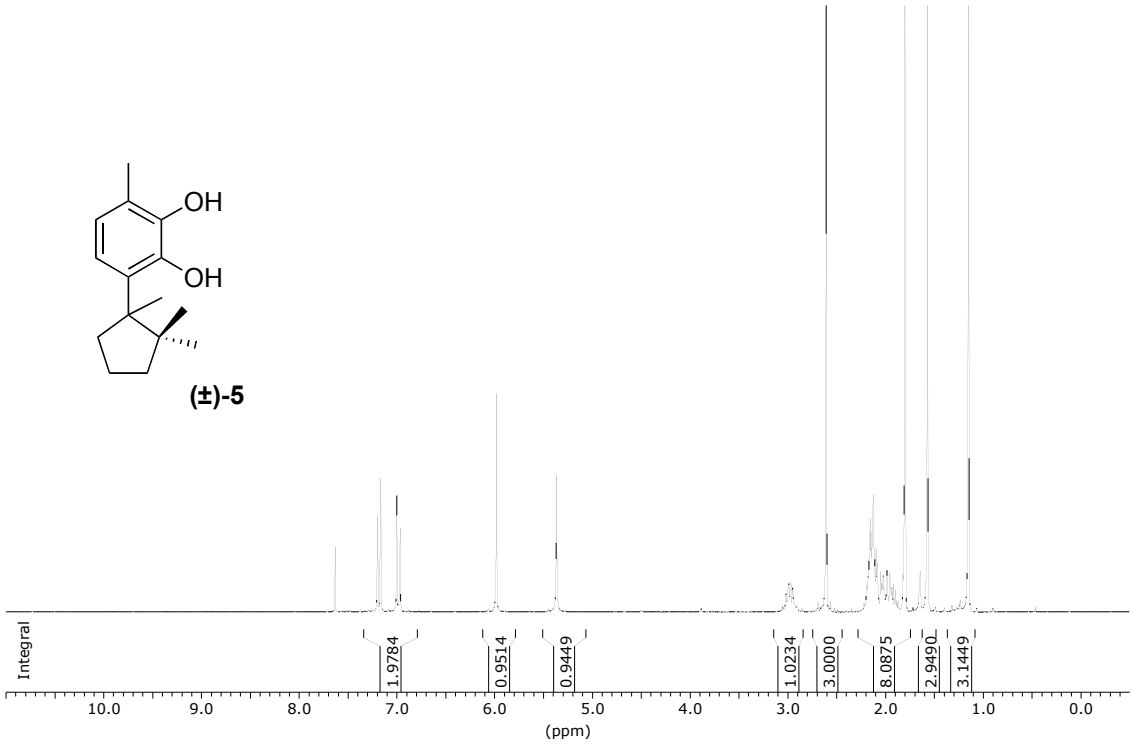
Peak Nr.	Data Point	Frequency	PPM	Intensity	%Int.
1	6979	1815.96	7.2600	277	5.2
2	7144	1765.61	7.0587	558	10.5
3	7170	1757.68	7.0282	784	14.8
4	7285	1722.58	6.8867	568	10.7
5	7291	1720.75	6.8793	625	11.8
6	7311	1714.65	6.8549	364	6.8
7	7317	1712.82	6.8476	485	9.1
8	7345	1704.27	6.8135	1089	20.5
9	7351	1702.44	6.8061	811	15.3
10	8903	1228.81	4.9126	121	2.3
11	11092	560.78	2.2419	4852	91.4
12	11908	311.75	1.2463	5288	99.6
13	12052	267.81	1.0707	5309	100.0
14	12444	148.18	0.5924	5019	94.5

JGC221-1 - jv300f.101 - AC250 -



(±)-5

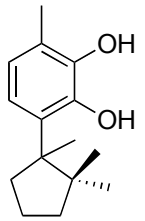
JGC221-1 - jv302f.101 - AC250 -



(±)-5

Peak List

File Name :
c:\docume~1\julien\mesdoc~1\chimie\rmn\janv05~1\jv302f\101001.1R
Peak Results saved in File : C:\RMN\EDIT.ASC
Nucleus : 1H
SF : 250.132854 MHz
OFFSET : 15.7748 ppm
SW_p : 5000.00 Hz
SI : 16384



(±)-5

Peak Picking Parameter

Peak constant PC = 1.00
Noise = 9
Sens. level = 35

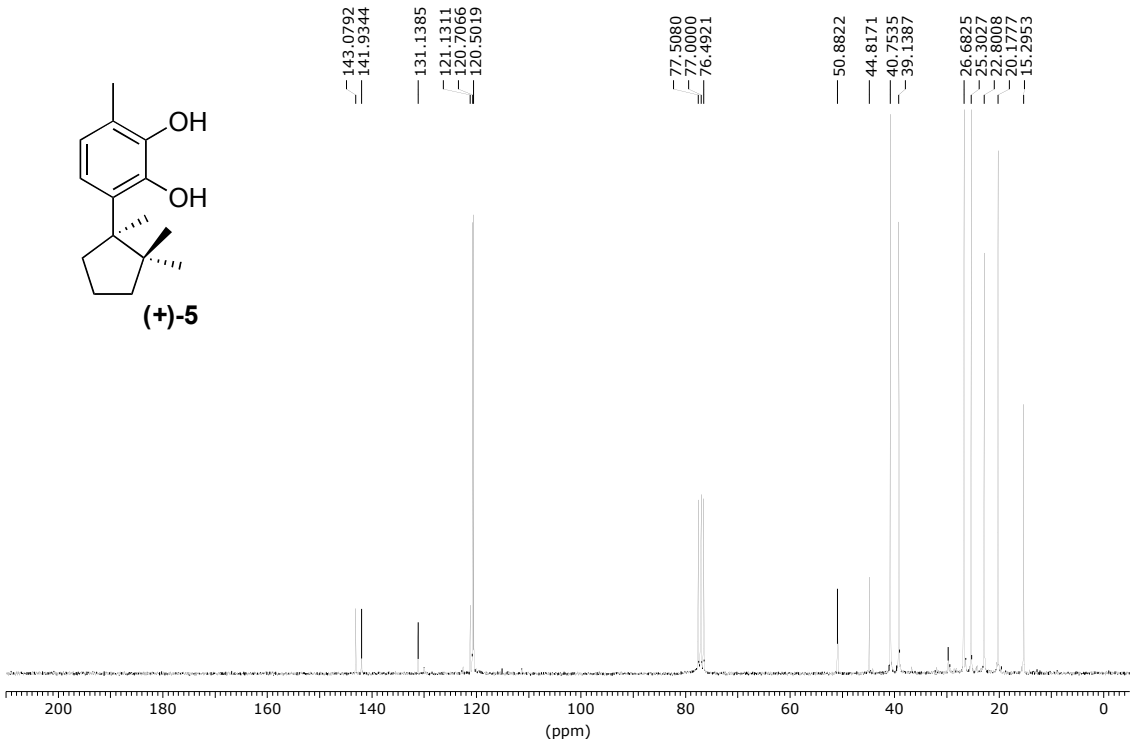
Peak Picking region

Start(ppm/Hz)	End(ppm/Hz)	MI(%)	MAXI(%)
15.77/ 3945.8	-4.21/-1054.2	-0.12	100.00

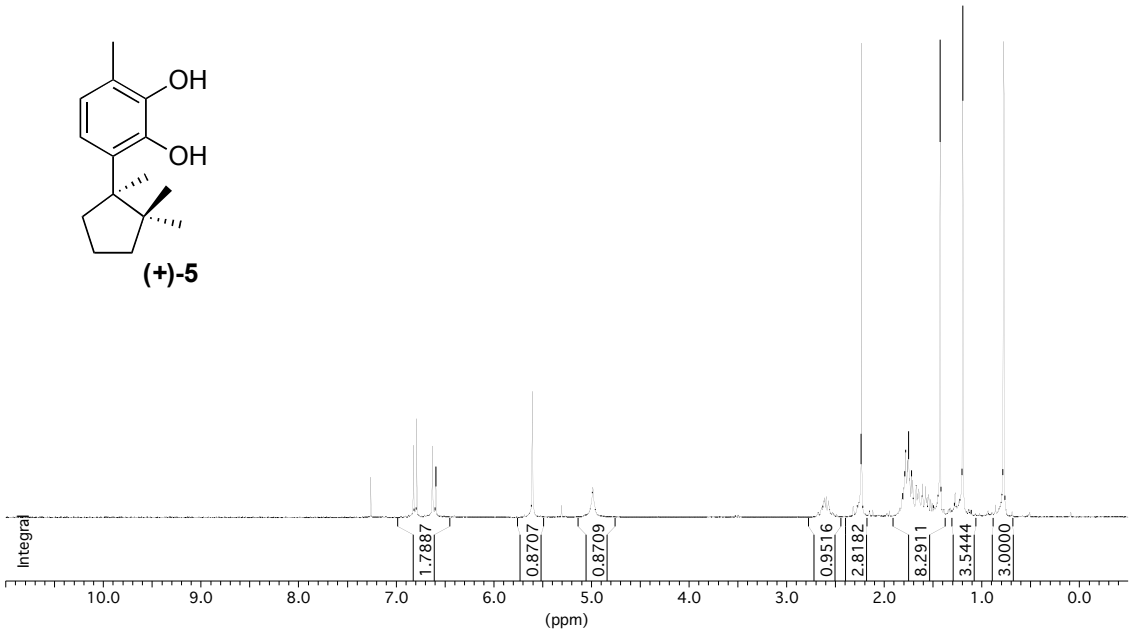
Peak Picking results

Peak Nr.	Data Point	Frequency	PPM	Intensity	%Int.
1	6979	1815.96	7.2600	5375	9.1
2	7335	1707.32	6.8257	8044	13.6
3	7362	1699.08	6.7927	11309	19.1
4	7496	1658.19	6.6292	9771	16.5
5	7521	1650.56	6.5987	5683	9.6
6	7523	1649.95	6.5963	7051	11.9
7	8332	1403.06	5.6093	18282	30.9
8	8837	1248.95	4.9931	11524	19.5
9	11099	558.64	2.2334	59089	99.8
10	11758	357.53	1.4294	59201	100.0
11	11947	299.85	1.1988	58272	98.4
12	12292	194.57	0.7778	55333	93.5

JGC224-1 - (R)-Catechol - AC250 - jv01.101

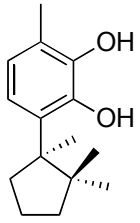


JGC224-1 - (R)-Catechol - AC250 - jv010f.101



Peak List

File Name :
c:\docume~1\julien\mesdoc~1\chimie\rmn\janv05~1\jv010f\101001.1R
Peak Results saved in File : C:\RMN\EDIT.ASC
Nucleus : 1H
SF : 250.132855 MHz
OFFSET : 15.7735 ppm
SW_p : 5000.00 Hz
SI : 16384



(+)-5

Peak Picking Parameter

Peak constant PC = 1.00
Noise = 9
Sens. level = 36

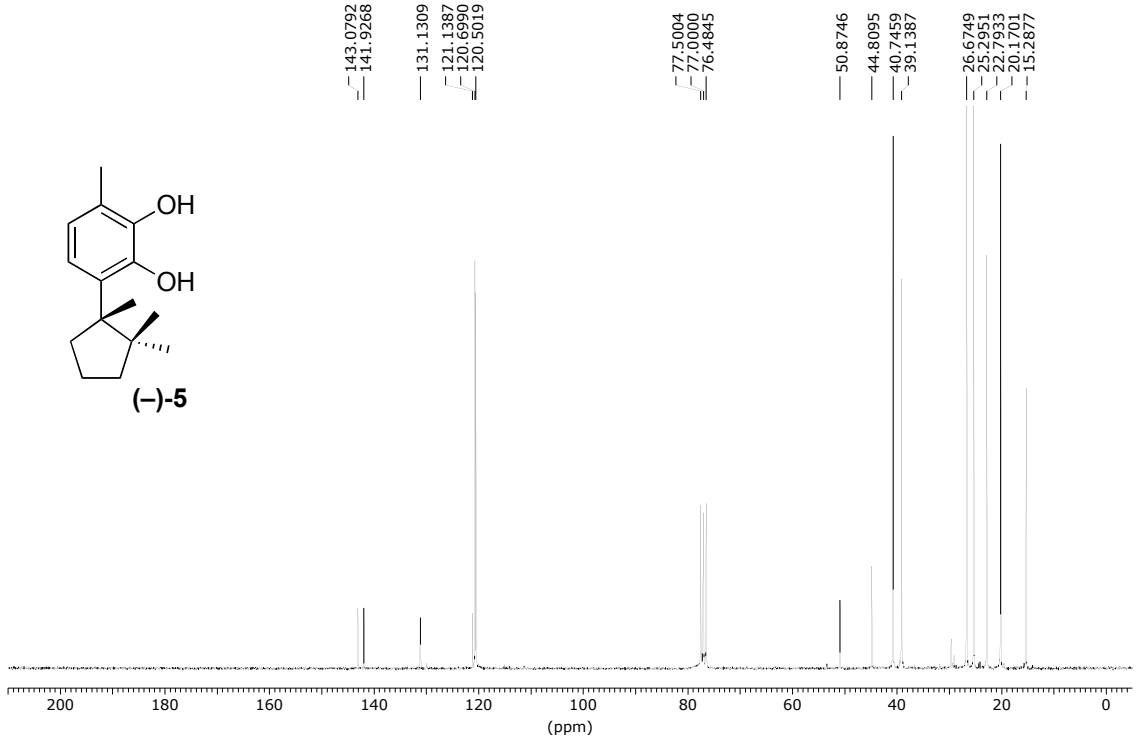
Peak Picking region

Start(ppm/Hz)	End(ppm/Hz)	MI(%)	MAXI(%)
8.29/ 2074.8	5.53/ 1384.1	3.65	33.29
5.13/ 1284.0	4.67/ 1167.2	4.51	10.20
3.42/ 855.3	-0.28/ -69.1	79.69	134.50

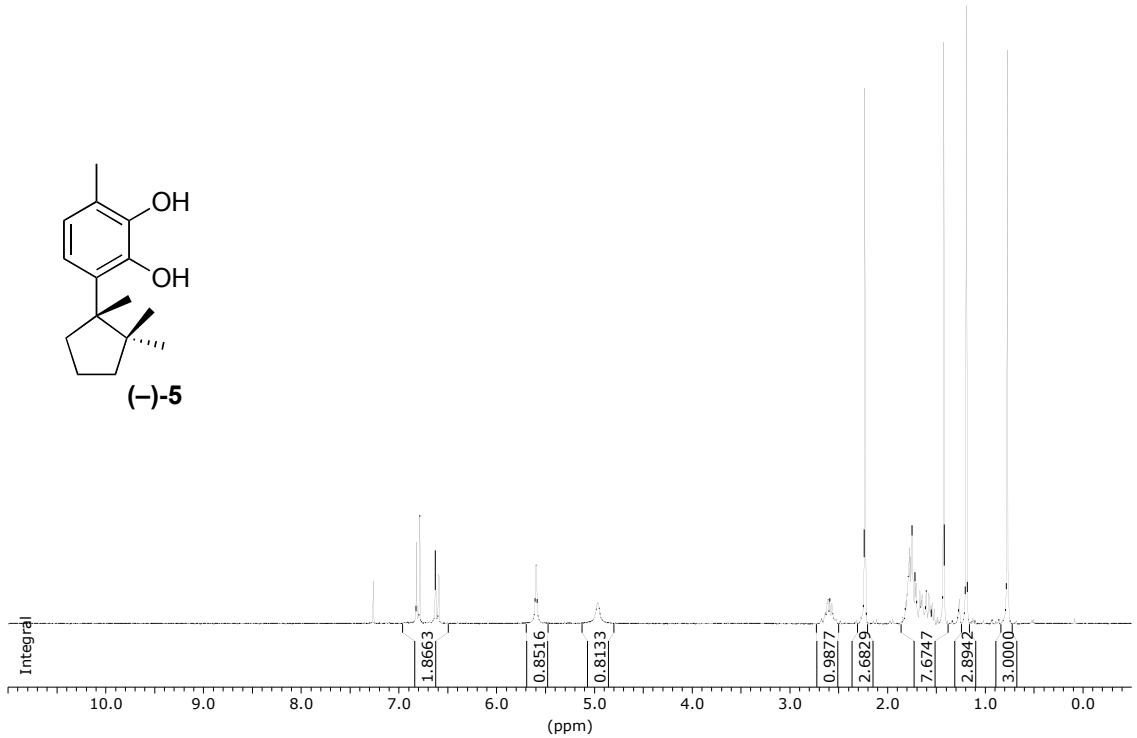
Peak Picking results

Peak Nr.	Data Point	Frequency	PPM	Intensity	%Int.
1	6978	1815.96	7.2600	3798	7.8
2	7338	1706.10	6.8208	6836	14.0
3	7365	1697.86	6.7878	9376	19.2
4	7498	1657.27	6.6256	6780	13.9
5	7525	1649.03	6.5926	4793	9.8
6	8337	1401.23	5.6019	11991	24.6
7	8845	1246.20	4.9822	2816	5.8
8	11100	558.03	2.2309	45188	92.6
9	11761	356.31	1.4245	45524	93.3
10	11951	298.33	1.1927	48798	100.0
11	12295	193.34	0.7730	45360	93.0

JGC225-1 - (S)-catechol - AC250 - jv080f.101

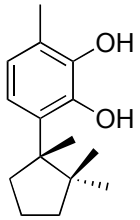


JGC225-1 - ja10.102 - AC250 -



Peak List

File Name : c:\docume~1\julien\bureau\ja10\102001.1R
Peak Results saved in File : C:\RMN\EDIT.ASC
Nucleus : 1H
SF : 250.133708 MHz
OFFSET : 15.7760 ppm
SW_p : 5000.00 Hz
SI : 16384



(–)-5

Peak Picking Parameter

Peak constant PC = 1.00
Noise = 1
Sens. level = 4

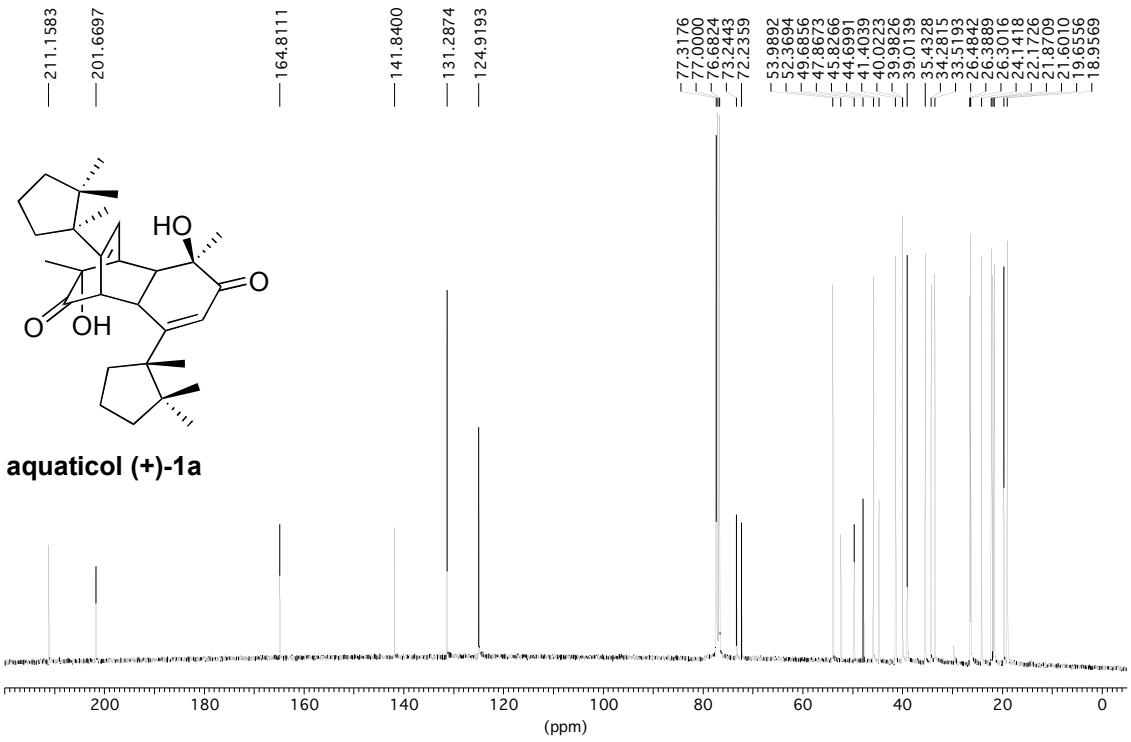
Peak Picking region

Start(ppm/Hz)	End(ppm/Hz)	MI(%)	MAXI(%)
6.96/ 1740.6	6.47/ 1619.1	7.22	18.94
7.36/ 1841.3	7.17/ 1792.8	6.50	11.71
5.75/ 1439.4	4.92/ 1229.4	3.05	12.19
3.82/ 956.0	0.55/ 137.5	81.11	115.58

Peak Picking results

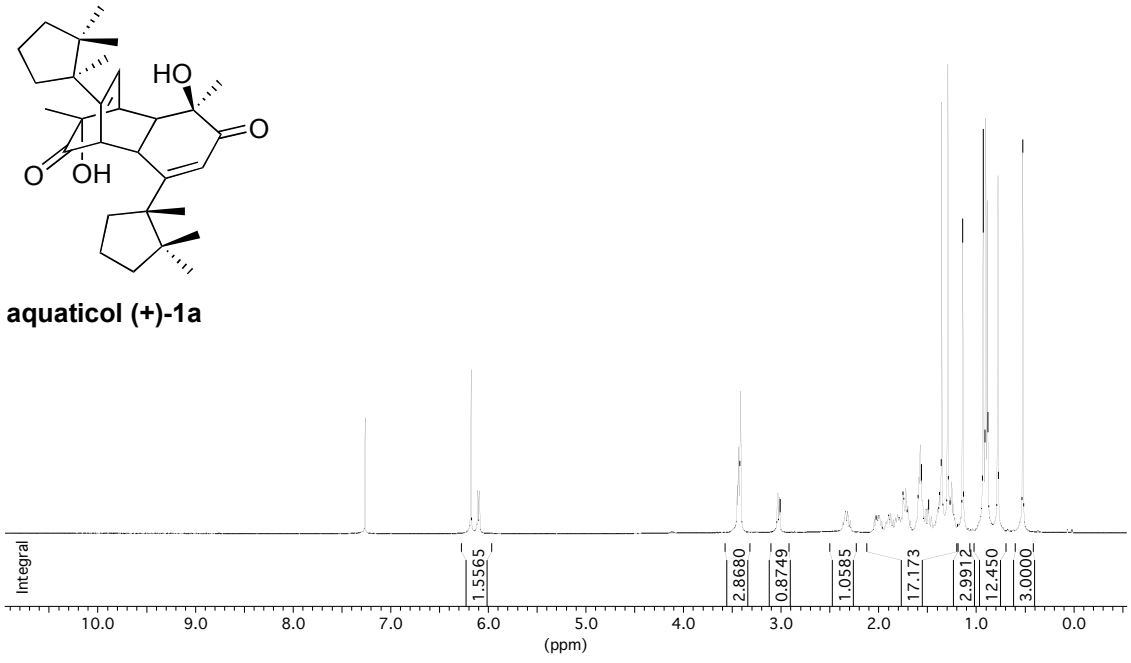
Peak Nr.	Data Point	Frequency	PPM	Intensity	%Int.
1	6980	1815.97	7.2600	284	6.8
2	7343	1705.19	6.8171	537	12.9
3	7370	1696.95	6.7842	728	17.5
4	7501	1656.97	6.6244	480	11.6
5	7528	1648.73	6.5914	327	7.9
6	8346	1399.10	5.5934	388	9.3
7	8863	1241.32	4.9626	141	3.4
8	11102	558.04	2.2310	3579	86.2
9	11765	355.70	1.4221	3904	94.0
10	11955	297.72	1.1902	4151	100.0
11	12299	192.74	0.7706	3835	92.4

JGC236-5 - 400 MHz - 090305 -



aquaticol (+)-1a

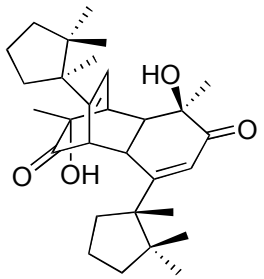
JGC236-5 - 100305 - 400 MHz



aquaticol (+)-1a

Peak List

File Name : c:\docume~1\julien\mesdoc~1\chimie\rmn\400mhz~1\aquati~1\100305~1\1\pdata\1\1R.1R
Peak Results saved in File : C:\RMN\EDIT.ASC
Nucleus : off
SF : 400.130018 MHz
OFFSET : 17.9670 ppm
SW_p : 8012.82 Hz
SI : 32768



aquaticol (+)-1a

Peak Picking Parameter

Peak constant PC = 1.00
Noise = 395129
Sens. level = 1580514

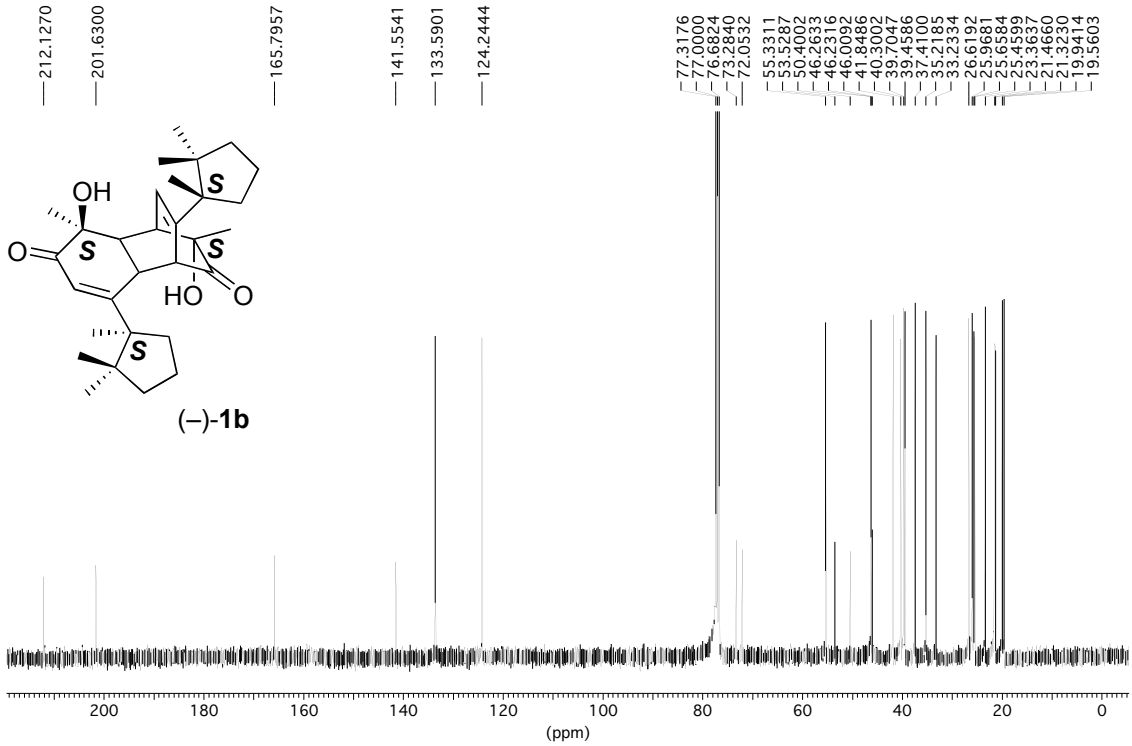
Peak Picking region

Start(ppm/Hz)	End(ppm/Hz)	MI(%)	MAXI(%)
3.04/ 1216.9	3.01/ 1203.2	6.63	9.81
8.31/ 3325.5	5.21/ 2085.3	6.66	42.51
2.69/ 1076.8	0.02/ 6.3	55.93	120.00

Peak Picking results

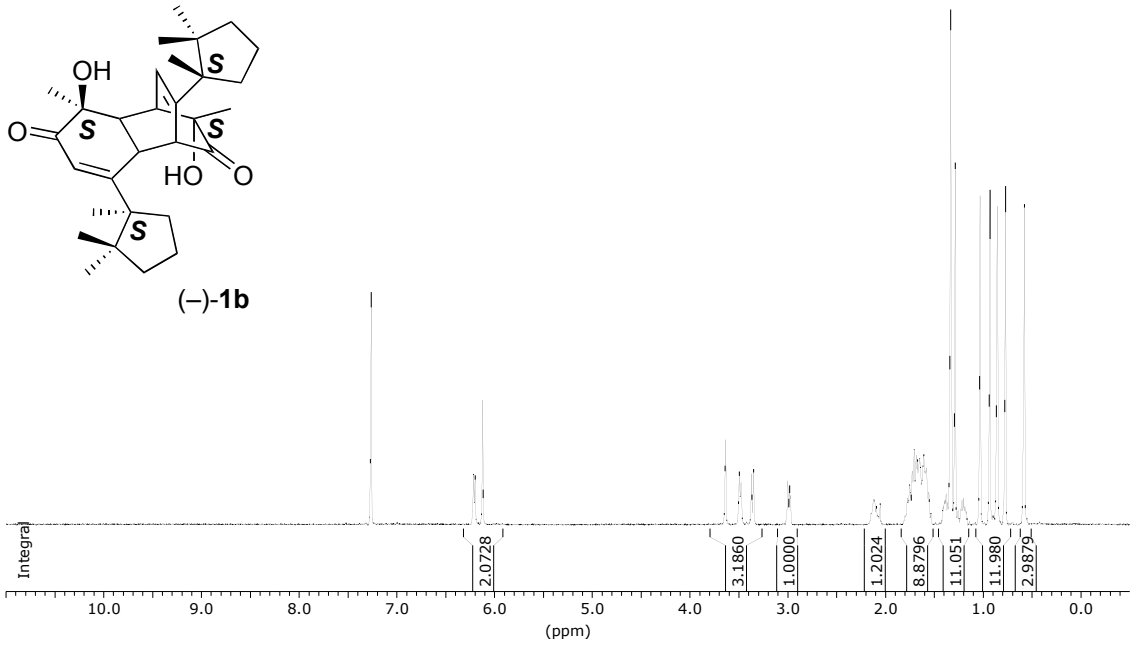
Peak Nr.	Data Point	Frequency	PPM	Intensity	%Int.
1	17520	2904.94	7.2600	105466784	24.4
2	19296	2470.66	6.1746	150062496	34.7
3	19406	2443.76	6.1074	36964896	8.5
4	19412	2442.29	6.1037	38443592	8.9
5	19434	2436.91	6.0903	37561148	8.7
6	19440	2435.44	6.0866	36761280	8.5
7	24427	1215.96	3.0389	35920704	8.3
8	24440	1212.78	3.0310	35359064	8.2
9	24463	1207.16	3.0169	32201516	7.4
10	24477	1203.74	3.0084	30163188	7.0
11	27189	540.57	1.3510	397587680	91.9
12	27288	516.36	1.2905	432846336	100.0
13	27541	454.49	1.1359	289850400	67.0
14	27882	371.10	0.9275	372819488	86.1
15	27923	361.08	0.9024	382923328	88.5
16	27952	353.99	0.8847	306628928	70.8
17	28129	310.71	0.7765	329792256	76.2
18	28544	209.22	0.5229	363255456	83.9

JGC236-1 - 100305 - DPX400 -



(–)-**1b**

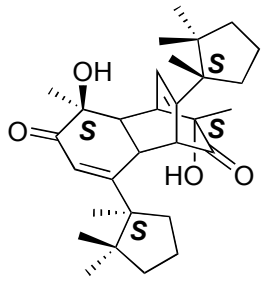
JGC236-1 - DPX400 - 210305 -



(–)-**1b**

Peak List

File Name : c:\docume~1\julien\mesdoc~1\chimie\rmn\400mhz~1\aquati~1\210305~2\1\pdata\1\1R.1R
Peak Results saved in File : C:\RMN\EDIT.ASC
Nucleus : off
SF : 400.130018 MHz
OFFSET : 15.0122 ppm
SW_p : 8012.82 Hz
SI : 32768



(–)-**1b**

Peak Picking Parameter

Peak constant PC = 0.00
Noise = 234429
Sens. level = 0

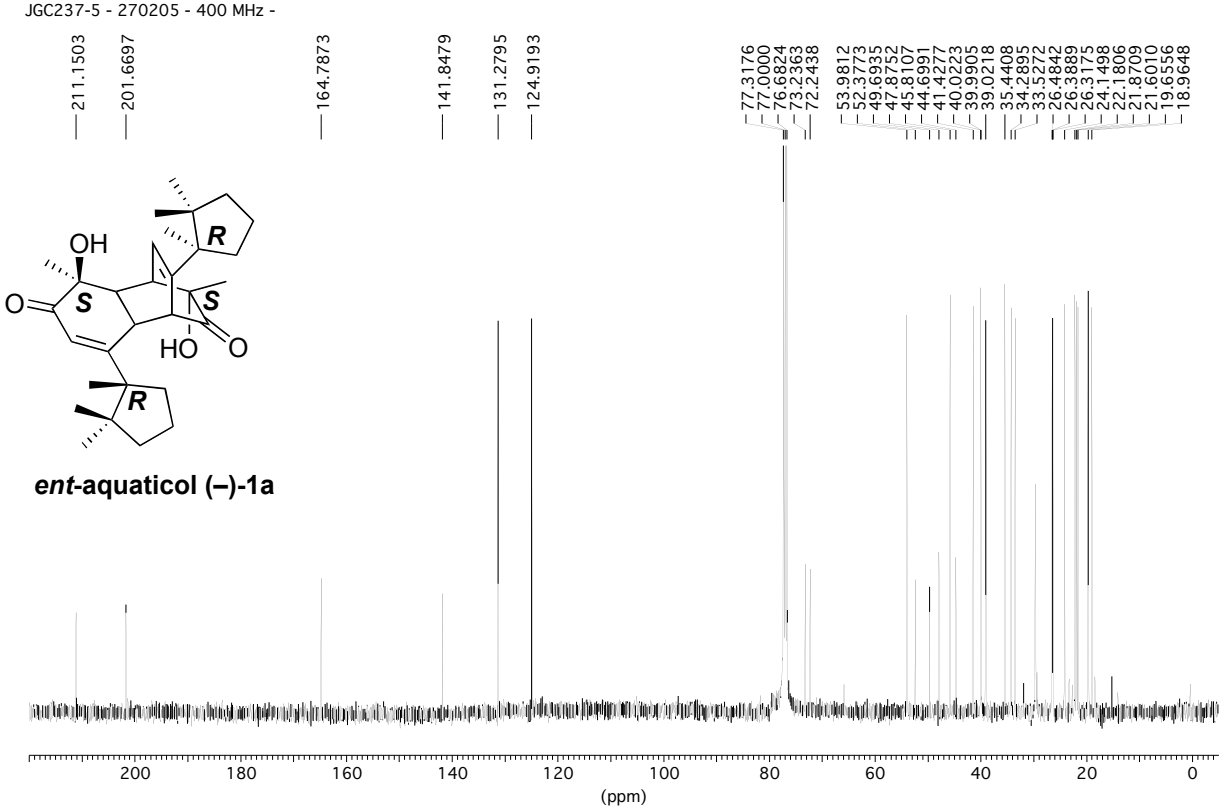
Peak Picking region

Start(ppm/Hz)	End(ppm/Hz)	MI(%)	MAXI(%)
7.57/ 3027.9	7.08/ 2833.3	39.68	49.77
6.63/ 2653.8	5.72/ 2290.2	5.95	39.37
3.77/ 1507.7	2.90/ 1160.2	3.97	17.98
3.49/ 1396.2	3.49/ 1395.0	8.33	8.89
2.57/ 1027.9	-0.22/ -87.6	37.74	118.87

Peak Picking results

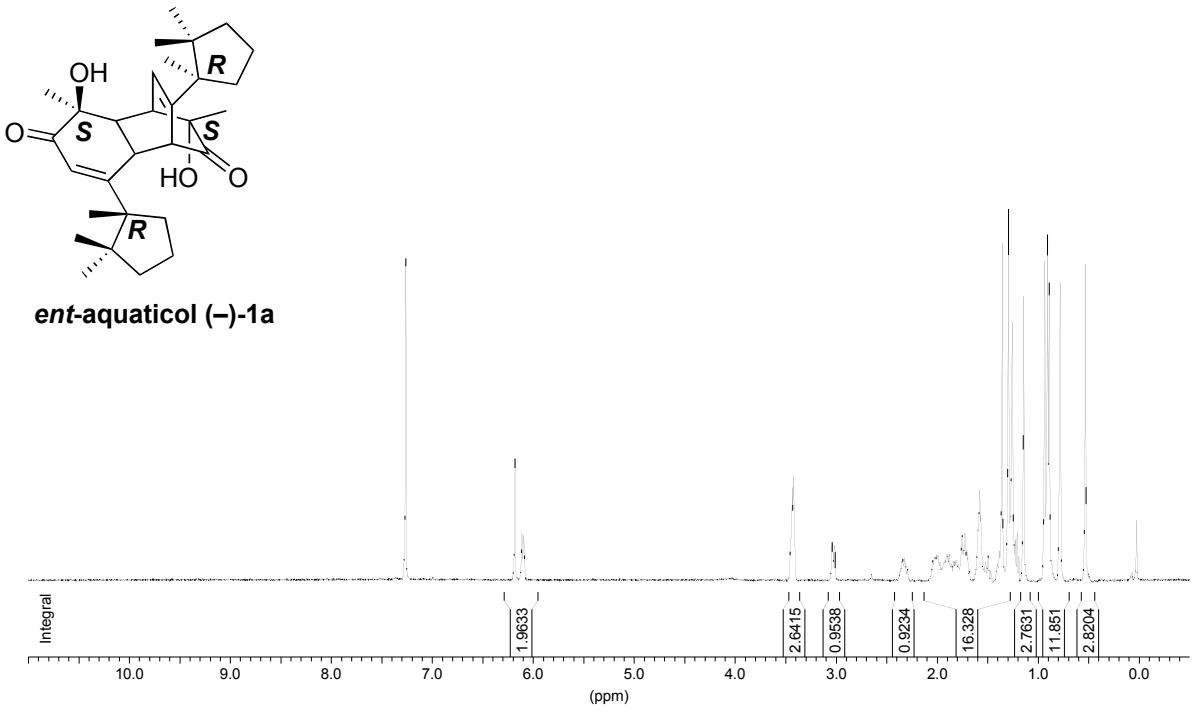
Peak Nr.	Data Point	Frequency	PPM	Intensity	%Int.
1	12685	2904.94	7.2600	225668576	44.7
2	14394	2487.04	6.2156	49270128	9.8
3	14423	2479.95	6.1979	48148456	9.5
4	14553	2448.16	6.1184	121710056	24.1
5	18618	1454.14	3.6342	82746304	16.4
6	18846	1398.38	3.4948	51381892	10.2
7	18857	1395.69	3.4881	42859828	8.5
8	18873	1391.78	3.4783	41150580	8.2
9	18885	1388.85	3.4710	31719620	6.3
10	19053	1347.77	3.3683	49243156	9.8
11	19088	1339.21	3.3469	53982944	10.7
12	19657	1200.07	2.9992	41959656	8.3
13	19670	1196.89	2.9913	35341820	7.0
14	19693	1191.26	2.9772	38017160	7.5
15	19705	1188.33	2.9699	28544820	5.7
16	22389	532.01	1.3296	504604992	100.0
17	22465	513.42	1.2831	359725664	71.3
18	22881	411.70	1.0289	324893888	64.4
19	23048	370.86	0.9268	329101792	65.2
20	23168	341.52	0.8535	313791488	62.2
21	23303	308.50	0.7710	334809408	66.4
22	23619	231.23	0.5779	315032704	62.4

JGC237-5 - 270205 - 400 MHz -



***ent*-aquaticol (–)-1a**

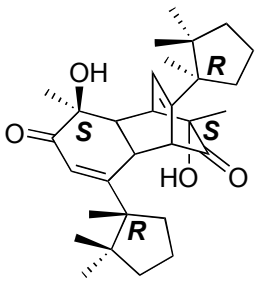
JGD237-5 - DPX400 - 270205 -



***ent*-aquaticol (–)-1a**

Peak List

File Name : d:\nmr2(j~1\nmr\270205~3\1\FID.1R
Peak Results saved in File : C:\WIN1D\TMP\EDIT.ASC
Nucleus : off
SF : 400.130018 MHz
OFFSET : 15.0122 ppm
SW_p : 8012.82 Hz
SI : 32768



***ent*-aquaticol (–)-1a**

Peak Picking Parameter

Peak constant PC = 1.00
Noise = 32
Sens. level = 128

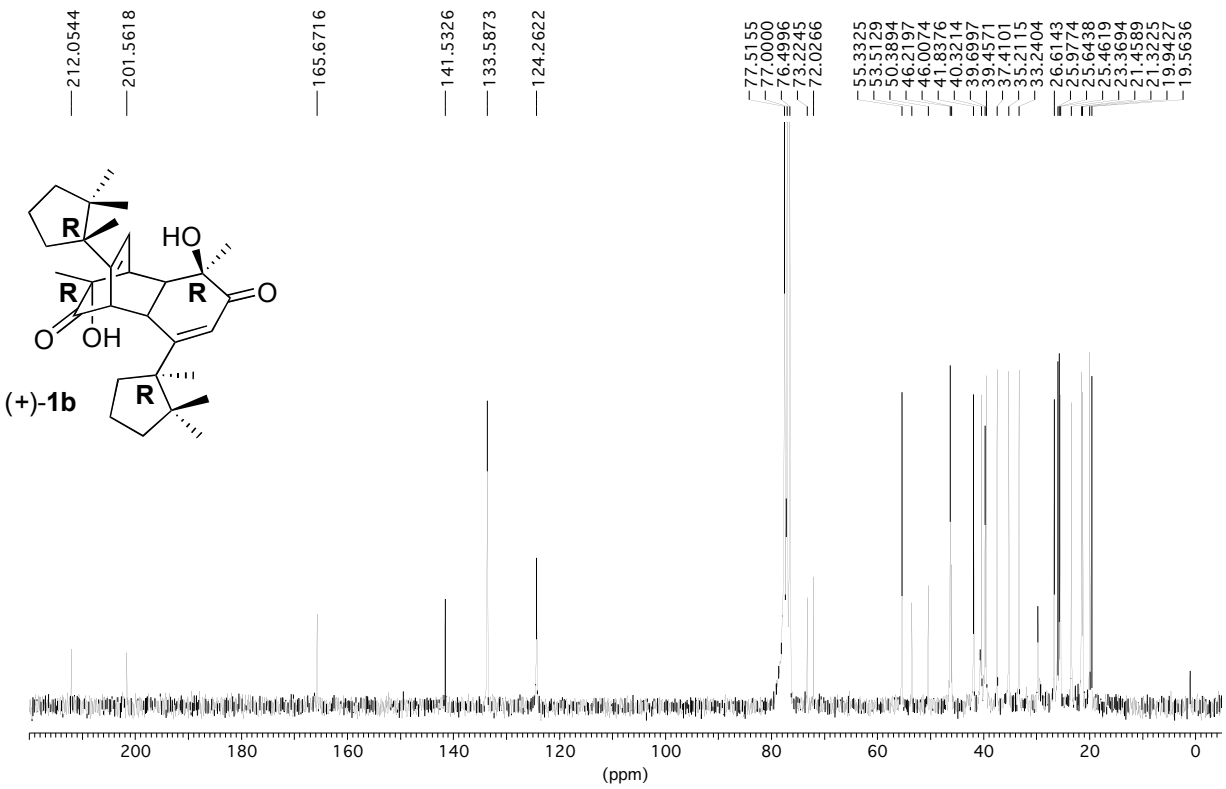
Peak Picking region

Start(ppm/Hz)	End(ppm/Hz)	MI(%)	MAXI(%)
7.72/ 3089.8	5.72/ 2290.4	6.75	101.94
3.05/ 1220.6	3.01/ 1203.2	9.07	11.87
3.01/ 1205.4	3.01/ 1203.2	7.15	8.34
1.82/ 727.6	1.14/ 456.0	83.93	109.49
1.15/ 461.8	0.49/ 195.8	68.18	105.02

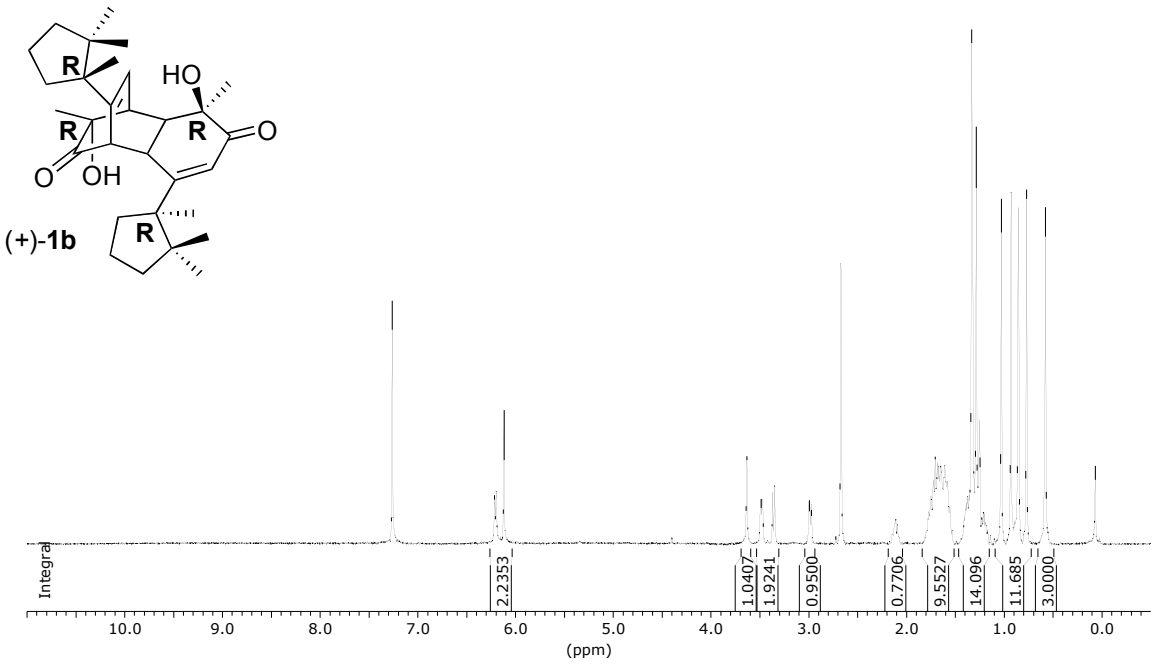
Peak Picking results

Peak Nr.	Data Point	Frequency	PPM	Intensity	%Int.
1	12685	2904.94	7.2600	30772	85.9
2	14456	2471.88	6.1777	11645	32.5
3	14566	2444.98	6.1105	4463	12.5
4	14594	2438.13	6.0934	4276	11.9
5	19589	1216.70	3.0408	3662	10.2
6	19601	1213.76	3.0334	3419	9.5
7	19625	1207.89	3.0188	3295	9.2
8	19638	1204.71	3.0108	2589	7.2
9	22349	541.79	1.3540	32724	91.3
10	22448	517.58	1.2935	35837	100.0
11	22698	456.45	1.1407	27257	76.1
12	23039	373.06	0.9323	30700	85.7
13	23081	362.79	0.9067	32994	92.1
14	23111	355.45	0.8883	28027	78.2
15	23286	312.66	0.7814	28385	79.2
16	23701	211.18	0.5278	30298	84.5

JGC237-1 - ms120f.101 - AC250 -

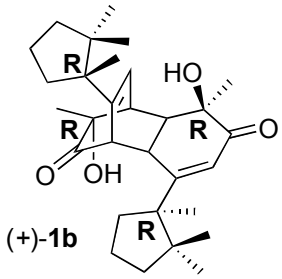


JGC237-1 - 220305 - DPX400 -



Peak List

File Name : d:\nmr2(j~1\nmr\220305~2\1\FID.1R
Peak Results saved in File : C:\WIN1D\TMP\EDIT.ASC
Nucleus : off
SF : 400.130019 MHz
OFFSET : 15.0110 ppm
SW_p : 8012.82 Hz
SI : 32768



(+)-1b

Peak Picking Parameter

Peak constant PC = 1.00
Noise = 21
Sens. level = 82

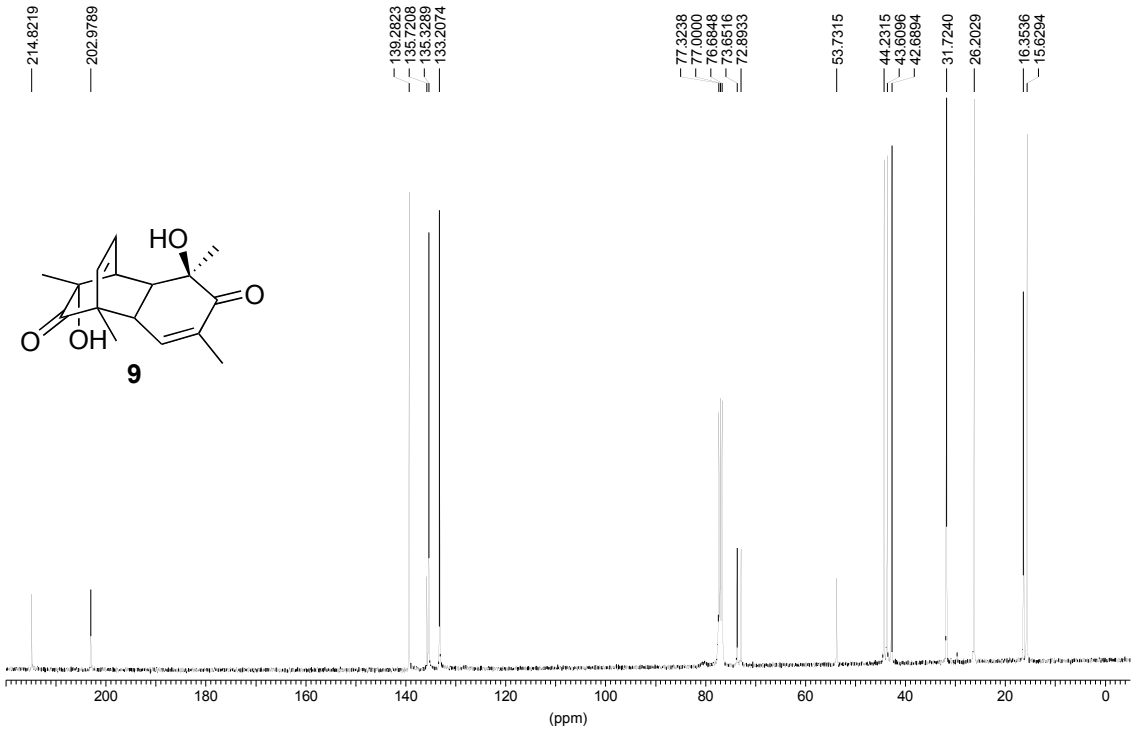
Peak Picking region

Start(ppm/Hz)	End(ppm/Hz)	MI(%)	MAXI(%)
7.96/ 3186.6	7.01/ 2803.0	44.46	53.02
6.15/ 2460.6	6.11/ 2445.5	25.07	26.57
6.25/ 2500.2	6.18/ 2472.9	9.47	13.93
6.21/ 2486.1	6.21/ 2484.8	8.67	9.87
6.21/ 2486.1	6.21/ 2484.6	8.55	9.99
1.14/ 456.2	0.42/ 169.9	63.73	77.38
1.47/ 589.5	1.12/ 447.4	79.26	102.83
3.67/ 1466.6	3.46/ 1383.5	7.32	19.82
2.97/ 1188.8	2.96/ 1183.2	6.82	7.86

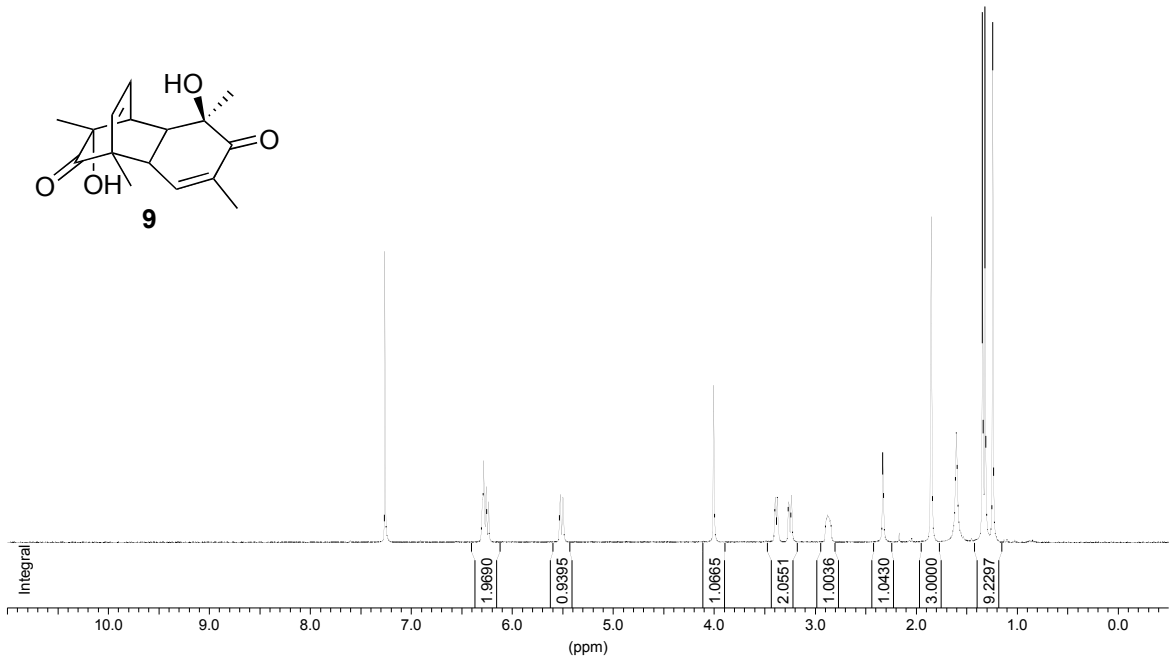
Peak Picking results

Peak Nr.	Data Point	Frequency	PPM	Intensity	%Int.
1	12683	2904.94	7.2600	13363	47.0
2	14398	2485.57	6.2119	2558	9.0
3	14423	2479.46	6.1966	2742	9.6
4	14554	2447.42	6.1166	7174	25.2
5	18620	1453.16	3.6317	4842	17.0
6	18846	1397.89	3.4936	2435	8.6
7	18858	1394.96	3.4863	2520	8.9
8	18874	1391.05	3.4765	2522	8.9
9	18885	1388.36	3.4698	2222	7.8
10	19052	1347.52	3.3677	2914	10.2
11	19088	1338.72	3.3457	3281	11.5
12	19658	1199.33	2.9974	2378	8.4
13	19671	1196.16	2.9894	2472	8.7
14	19693	1190.78	2.9760	2264	8.0
15	19705	1187.84	2.9686	1961	6.9
16	22388	531.76	1.3290	28449	100.0
17	22397	529.56	1.3235	24559	86.3
18	22465	512.93	1.2819	23944	84.2
19	22881	411.21	1.0277	19836	69.7
20	23048	370.37	0.9256	20325	71.4
21	23168	341.03	0.8523	19503	68.6
22	23304	307.77	0.7692	20441	71.9
23	23620	230.50	0.5761	19066	67.0

JGD48-1 - DPX400 - 091005 -

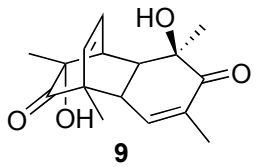


JGD48-1 - 300MHz - 260406 -



Peak List

File Name : c:\docume~1\julien\bureau\jge048~1\1\pdata\1\1R.1R
Peak Results saved in File : C:\WIN1D\TMP\EDIT.ASC
Nucleus : off
SF : 300.130006 MHz
OFFSET : 16.4635 ppm
SW_p : 6188.12 Hz
SI : 32768



9

Peak Picking Parameter

Peak constant PC = 1.00
Noise = 105885
Sens. level = 423542

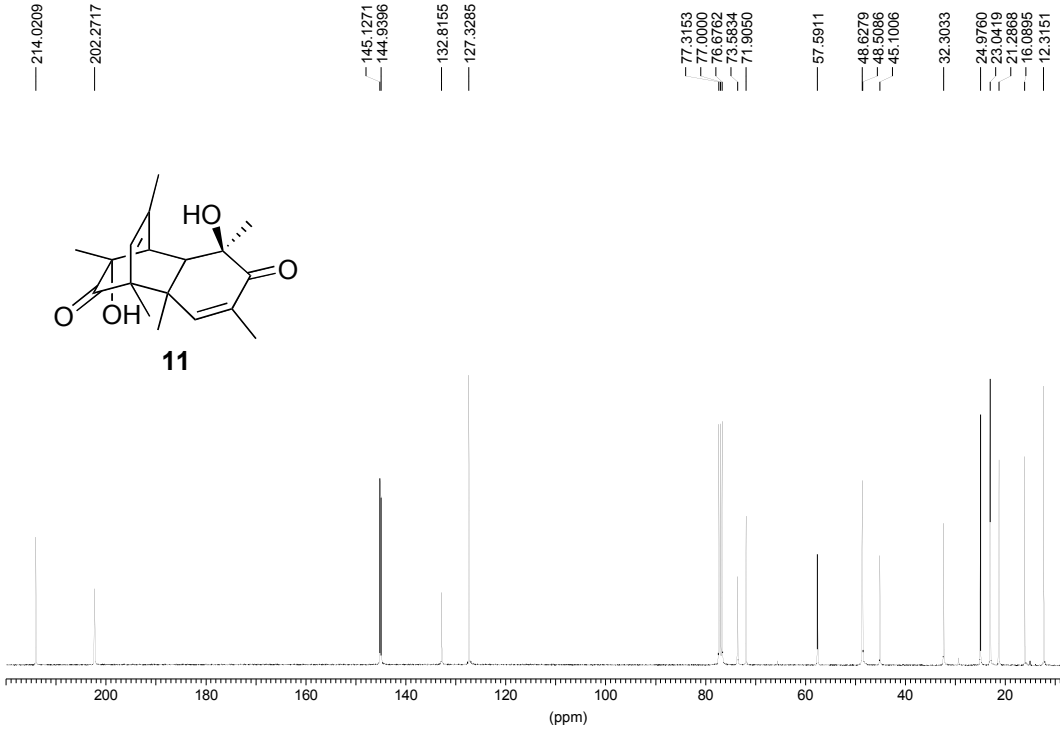
Peak Picking region

Start(ppm/Hz)	End(ppm/Hz)	MI(%)	MAXI(%)
5.86/ 1758.8	5.32/ 1597.7	6.09	23.96
4.43/ 1330.5	3.86/ 1159.6	27.17	50.86
3.48/ 1045.7	3.15/ 945.4	4.28	24.56
2.39/ 717.7	2.14/ 642.9	16.12	25.56
1.99/ 595.8	1.80/ 538.8	60.10	67.73
1.57/ 472.0	1.16/ 348.3	97.04	102.86
1.67/ 501.4	1.57/ 472.0	19.54	26.97
8.38/ 2515.7	6.61/ 1985.0	48.42	83.45

Peak Picking results

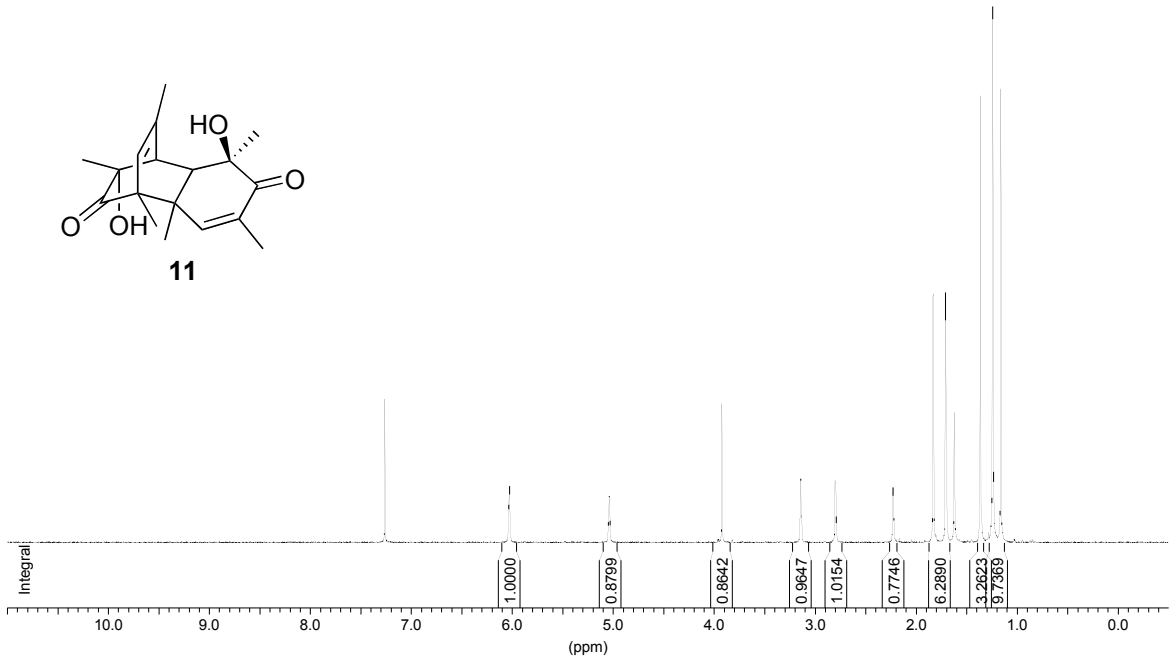
Peak Nr.	Data Point	Frequency	PPM	Intensity	%Int.
1	14627	2178.94	7.2600	167867168	54.3
2	17387	1657.73	5.5234	27754644	9.0
3	17430	1649.61	5.4963	26035728	8.4
4	19800	1202.04	4.0051	90750840	29.3
5	20770	1018.86	3.3947	26100242	8.4
6	20806	1012.06	3.3721	26257764	8.5
7	20978	979.58	3.2639	23403428	7.6
8	20987	977.88	3.2582	23146184	7.5
9	21022	971.27	3.2362	27259416	8.8
10	21031	969.57	3.2305	26779684	8.7
11	22463	699.14	2.3295	51884976	16.8
12	23224	555.43	1.8506	187980608	60.8
13	23622	480.27	1.6002	63490100	20.5
14	24031	403.03	1.3429	305954624	98.9
15	24072	395.29	1.3171	309223520	100.0
16	24196	371.87	1.2390	300153600	97.1

JGD47-1 - DPX400 - 251005 -



11

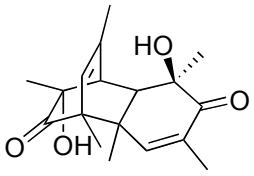
JGD47-1 - 300MHz - 260406 -



11

Peak List

File Name : c:\docume~1\julien\mesdoc~1\b\jgd47-1\1\pdata\1\1R.1R
Peak Results saved in File : C:\WIN1D\TMP\EDIT.ASC
Nucleus : off
SF : 300.130006 MHz
OFFSET : 16.4635 ppm
SW_p : 6188.12 Hz
SI : 32768



11

Peak Picking Parameter

Peak constant PC = 1.00
Noise = 77493
Sens. level = 309974

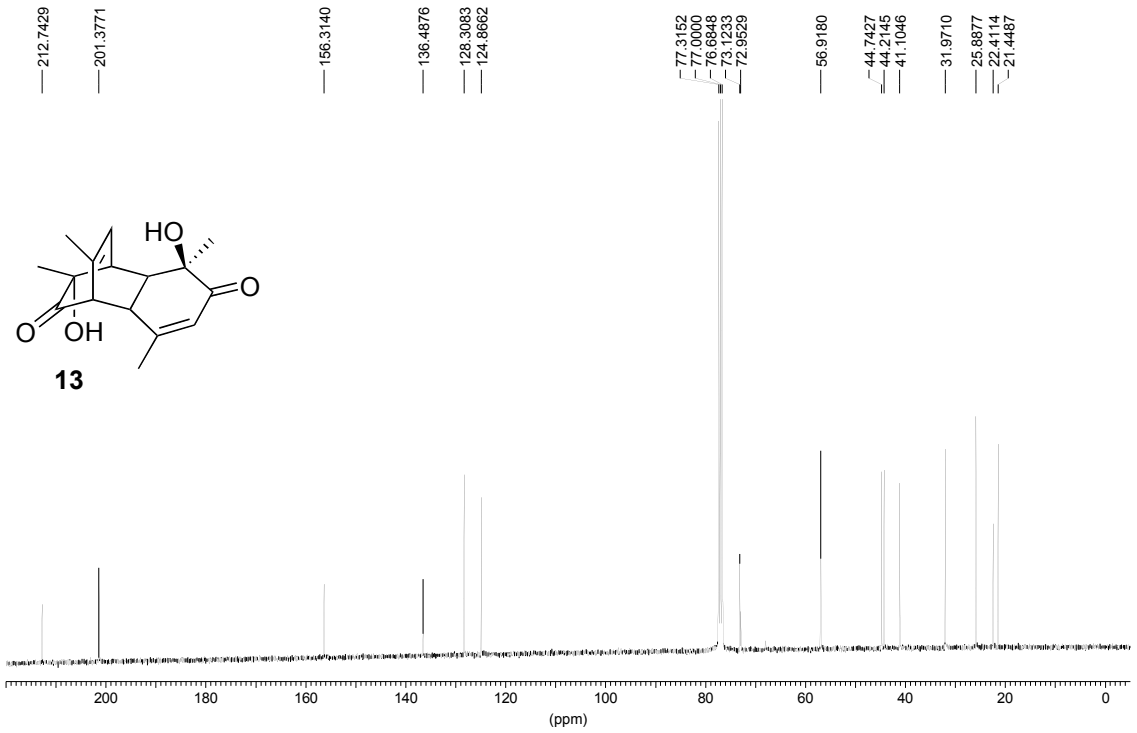
Peak Picking region

Start(ppm/Hz)	End(ppm/Hz)	MI(%)	MAXI(%)
1.84/ 552.6	1.80/ 539.8	45.64	53.12
1.72/ 516.7	1.66/ 497.3	45.13	55.33
1.63/ 489.3	1.61/ 483.3	31.86	33.56
1.38/ 415.5	1.12/ 334.7	80.00	91.40
1.33/ 400.0	1.21/ 361.7	98.42	119.85
2.25/ 675.9	2.20/ 659.5	9.28	24.93
3.45/ 1034.9	2.76/ 828.3	4.66	18.73
6.16/ 1849.6	5.87/ 1760.5	10.27	15.60
7.63/ 2291.1	7.09/ 2129.1	26.46	31.97

Peak Picking results

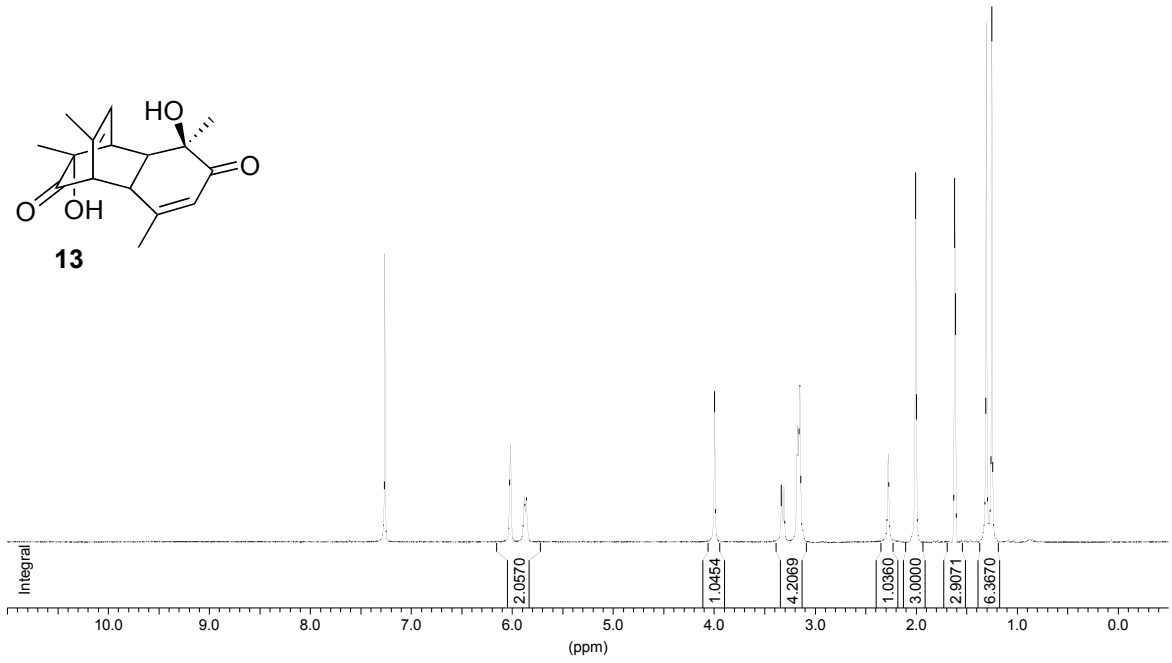
Peak Nr.	Data Point	Frequency	PPM	Intensity	%Int.
1	14627	2178.94	7.2600	92131568	26.7
2	16587	1808.81	6.0267	36251212	10.5
3	18161	1511.56	5.0364	29690160	8.6
4	19933	1176.93	3.9214	89203896	25.9
5	21160	945.21	3.1493	22372652	6.5
6	21171	943.13	3.1424	40809868	11.8
7	21182	941.06	3.1355	22326620	6.5
8	21713	840.78	2.8014	39722180	11.5
9	21724	838.70	2.7945	37706848	10.9
10	22625	668.55	2.2275	35303276	10.2
11	23252	550.14	1.8330	157818704	45.8
12	23260	548.63	1.8280	159965696	46.4
13	23453	512.19	1.7065	160686480	46.6
14	23462	510.49	1.7009	157186112	45.6
15	24002	408.51	1.3611	287281632	83.3
16	24196	371.87	1.2390	344749408	100.0
17	24318	348.83	1.1623	291640384	84.6

JGD52-2 - DPX400 - 050306 -



13

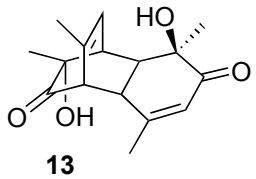
JGD52-2 - 300MHz - 240406 -



13

Peak List

File Name : d:\rmn\avril2~1\jgd52-2\2\pdata\1\1R.1R
Peak Results saved in File : C:\WIN1D\TMP\EDIT.ASC
Nucleus : off
SF : 300.130006 MHz
OFFSET : 16.4642 ppm
SW_p : 6188.12 Hz
SI : 32768



13

Peak Picking Parameter

Peak constant PC = 1.00
Noise = 115425
Sens. level = 461701

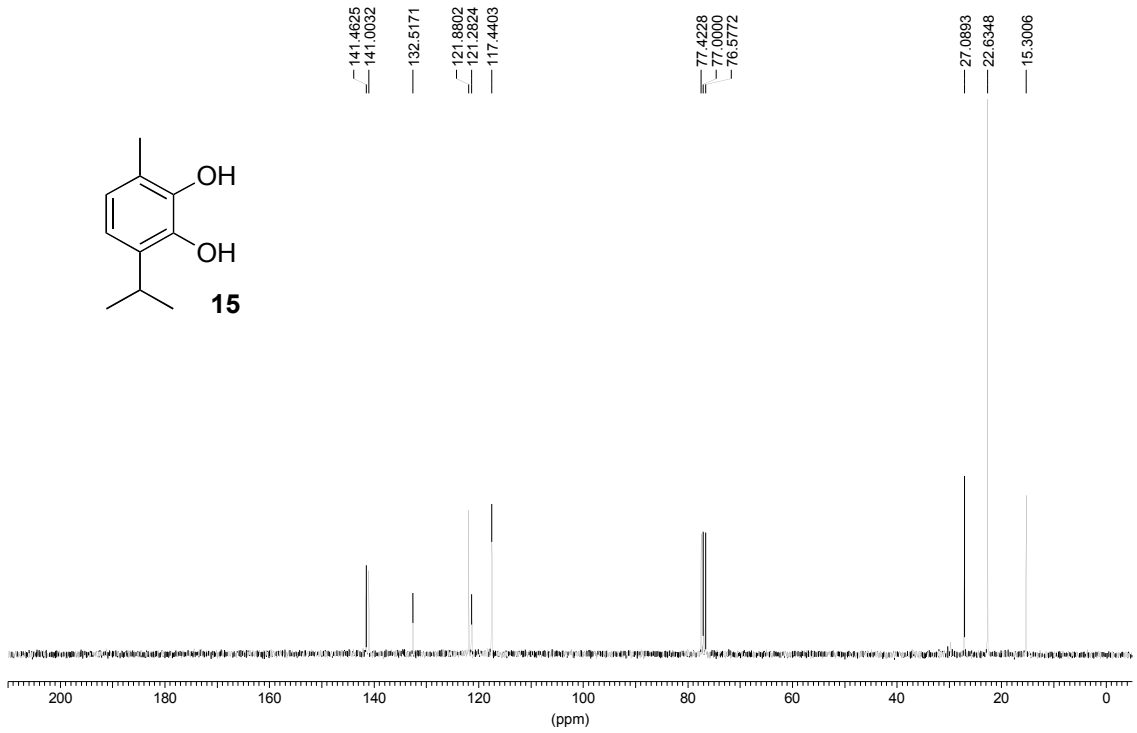
Peak Picking region

Start(ppm/Hz)	End(ppm/Hz)	MI(%)	MAXI(%)
3.40/ 1021.7	3.29/ 987.5	8.91	12.16
7.82/ 2348.3	5.56/ 1667.9	6.60	64.41
2.56/ 768.6	2.06/ 618.7	15.63	24.83
2.32/ 695.6	1.45/ 434.2	66.15	76.04
1.72/ 515.0	0.55/ 165.3	92.02	103.83
4.80/ 1441.3	3.79/ 1137.6	28.48	61.12
4.70/ 1410.5	3.78/ 1133.9	27.09	60.77

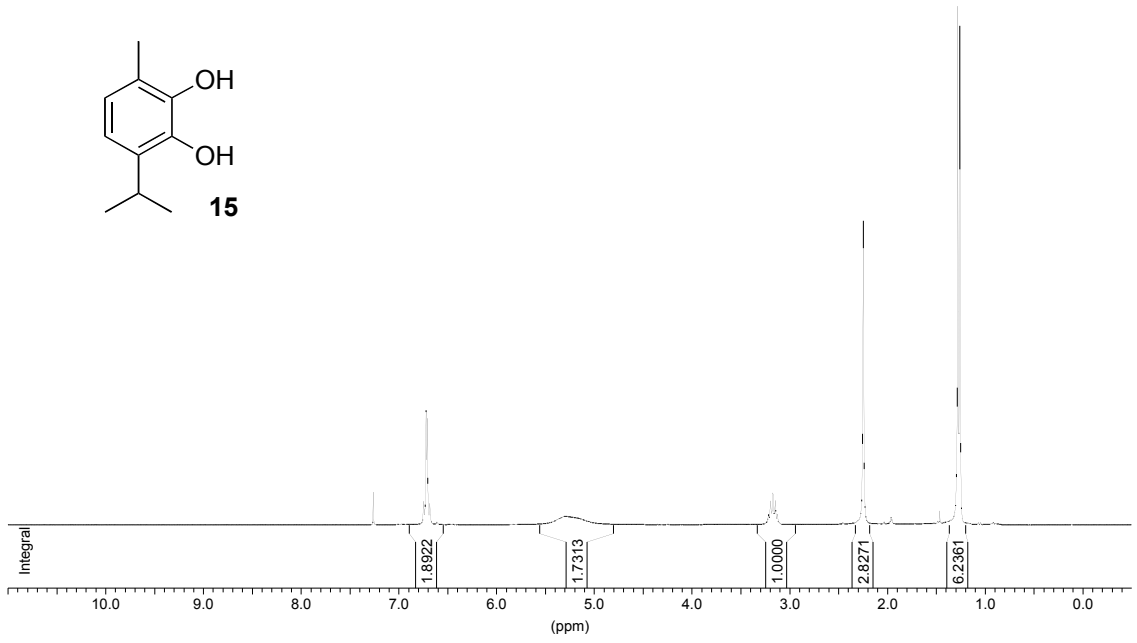
Peak Picking results

Peak Nr.	Data Point	Frequency	PPM	Intensity	%Int.
1	14628	2178.94	7.2600	154825552	53.8
2	16603	1805.97	6.0173	52506044	18.2
3	16822	1764.62	5.8795	24401028	8.5
4	16858	1757.82	5.8569	23834774	8.3
5	19815	1199.40	3.9963	80981936	28.1
6	20868	1000.54	3.3337	30579236	10.6
7	20875	999.22	3.3293	30421046	10.6
8	20904	993.74	3.3110	29702136	10.3
9	20911	992.42	3.3066	28719682	10.0
10	22548	683.28	2.2766	47104736	16.4
11	22979	601.89	2.0054	198407904	68.9
12	22984	600.94	2.0023	196714720	68.3
13	23596	485.37	1.6172	195402176	67.9
14	23603	484.05	1.6128	192196544	66.8
15	24093	391.51	1.3045	278892128	96.9
16	24182	374.71	1.2485	287810528	100.0

JGE15-1-1 - 260406 - 300MHz -

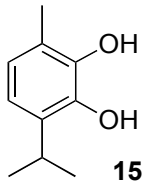


JGE15-1-1 - 260406 - 300MHz -



Peak List

File Name : d:\rmn\avril2~1\jge015~1\1\pdata\1\1R.1R
Peak Results saved in File : C:\WIN1D\TMP\EDIT.ASC
Nucleus : off
SF : 300.130006 MHz
OFFSET : 16.4642 ppm
SW_p : 6188.12 Hz
SI : 32768



15

Peak Picking Parameter

Peak constant PC = 1.00
Noise = 60060
Sens. level = 240242

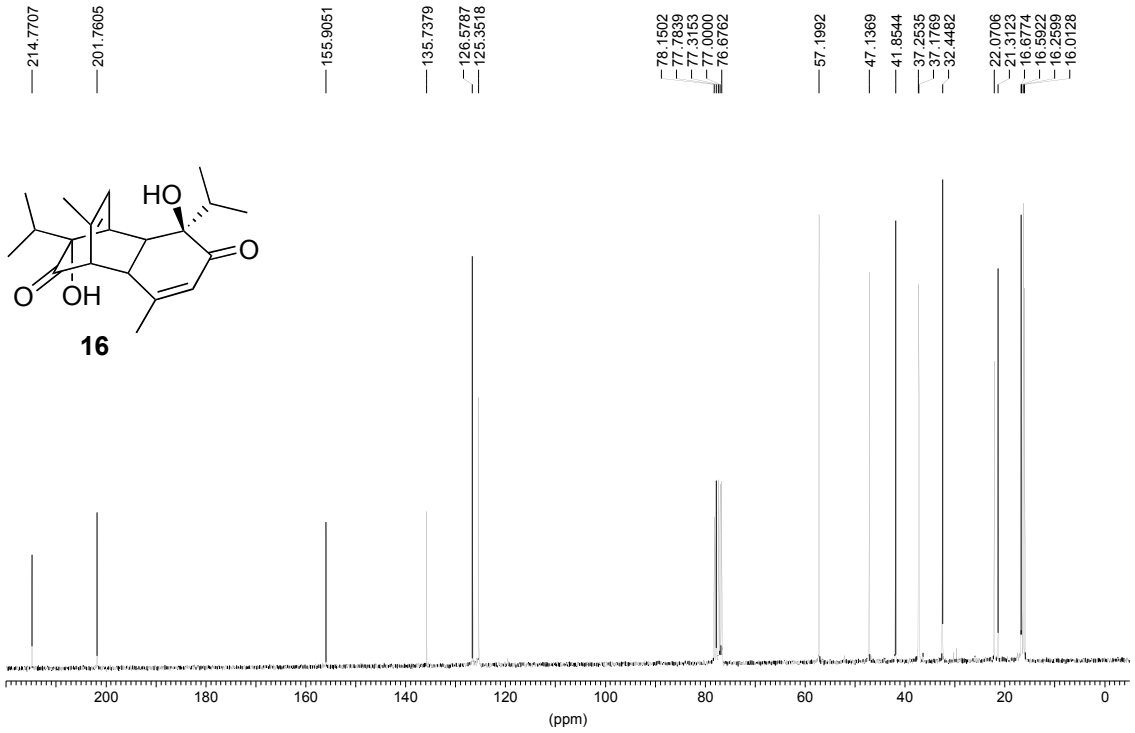
Peak Picking region

Start(ppm/Hz)	End(ppm/Hz)	MI(%)	MAXI(%)
8.84/ 2653.5	6.38/ 1916.3	2.53	31.67
5.70/ 1709.5	4.92/ 1475.3	1.32	5.83
3.35/ 1006.0	3.07/ 921.2	0.28	7.86
3.33/ 998.8	3.00/ 901.4	-0.07	7.56
3.25/ 976.4	3.23/ 969.2	0.39	1.95
3.11/ 934.4	3.10/ 930.1	0.22	0.90
3.11/ 932.0	3.10/ 929.7	0.14	1.25
2.39/ 716.7	2.09/ 627.9	52.57	70.27
1.39/ 416.6	1.14/ 341.3	94.70	107.78

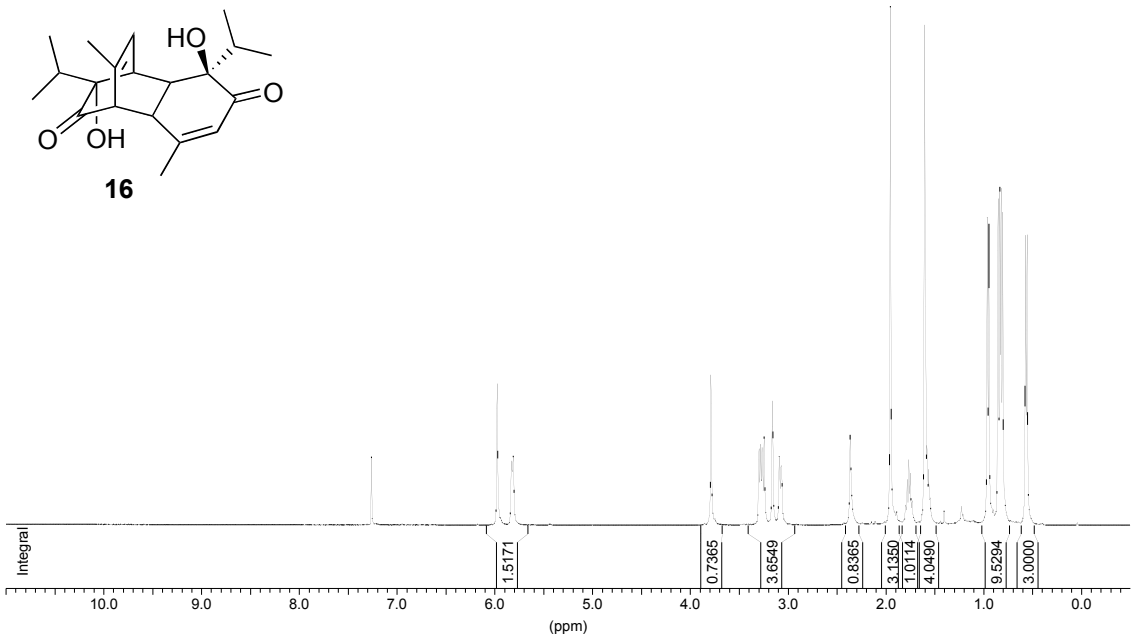
Peak Picking results

Peak Nr.	Data Point	Frequency	PPM	Intensity	%Int.
1	14628	2178.94	7.2600	18604374	6.3
2	15445	2024.66	6.7459	13122386	4.4
3	15488	2016.54	6.7189	65008652	22.0
4	15507	2012.95	6.7069	60433952	20.5
5	15549	2005.02	6.6805	11988676	4.1
6	17730	1593.14	5.3082	4671816	1.6
7	21020	971.84	3.2381	1480282	0.5
8	21055	965.23	3.2160	5847721	2.0
9	21091	958.43	3.1934	13519367	4.6
10	21128	951.44	3.1701	17922724	6.1
11	21164	944.64	3.1474	13720642	4.6
12	21200	937.85	3.1248	5821022	2.0
13	21235	931.24	3.1028	1234400	0.4
14	22598	673.84	2.2452	172747296	58.5
15	24134	383.77	1.2787	295080352	100.0
16	24170	376.97	1.2560	283679264	96.1

JGC266-2 - DPX400 - 200306 -

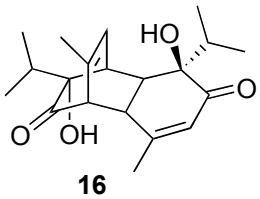


JGC266-2 - DPX400 - 200306 -



Peak List

File Name : d:\rmn\mars20~1\jgc266-2\1\pdata\1\1R.1R
Peak Results saved in File : C:\WIN1D\TMP\EDIT.ASC
Nucleus : off
SF : 400.130018 MHz
OFFSET : 17.9688 ppm
SW_p : 8012.82 Hz
SI : 32768



16

Peak Picking Parameter

Peak constant PC = 1.00
Noise = 466561
Sens. level = 1866243

Peak Picking region

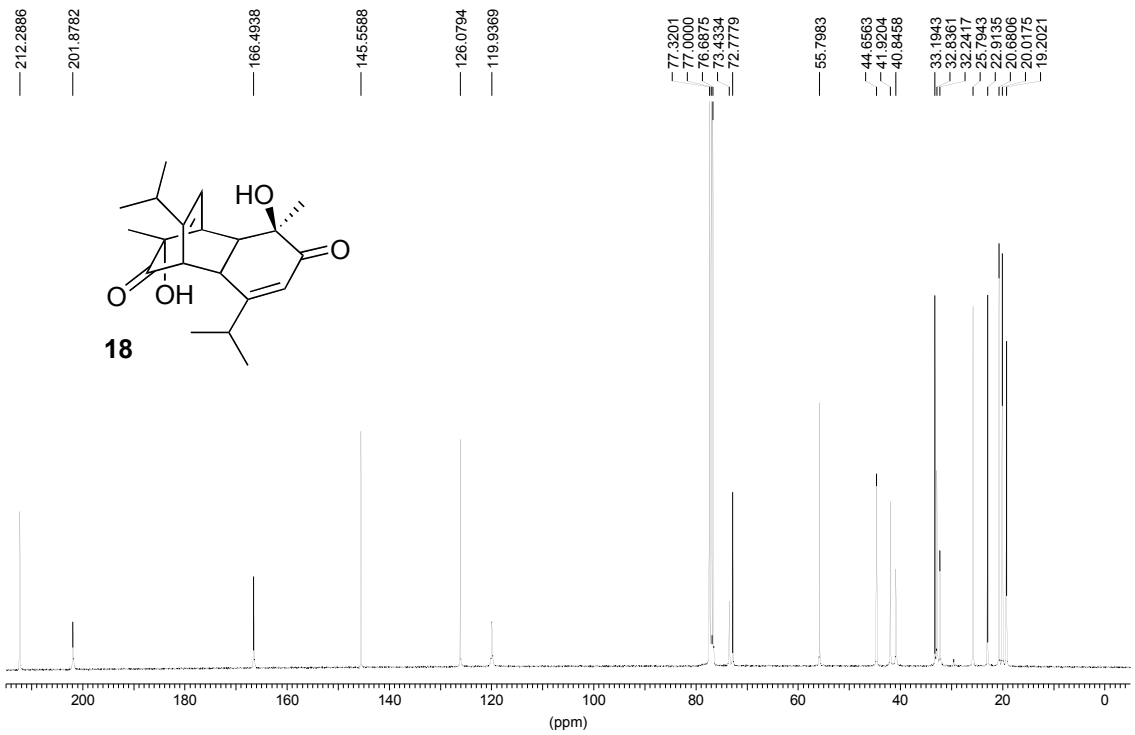
Start(ppm/Hz)	End(ppm/Hz)	MI(%)	MAXI(%)
1.82/ 726.4	1.81/ 725.4	-0.04	1.40
1.72/ 686.8	1.71/ 685.6	-0.37	2.31
1.72/ 687.5	1.71/ 685.1	0.41	2.43
1.72/ 687.5	1.71/ 683.4	-0.94	2.43
1.72/ 686.3	1.71/ 683.4	0.09	2.59
1.80/ 719.8	1.73/ 691.0	2.27	12.71
2.16/ 864.6	1.49/ 595.3	87.71	102.30
1.05/ 421.0	0.41/ 163.3	42.73	81.53
8.71/ 3486.9	5.55/ 2219.8	8.45	41.24

Peak Picking results

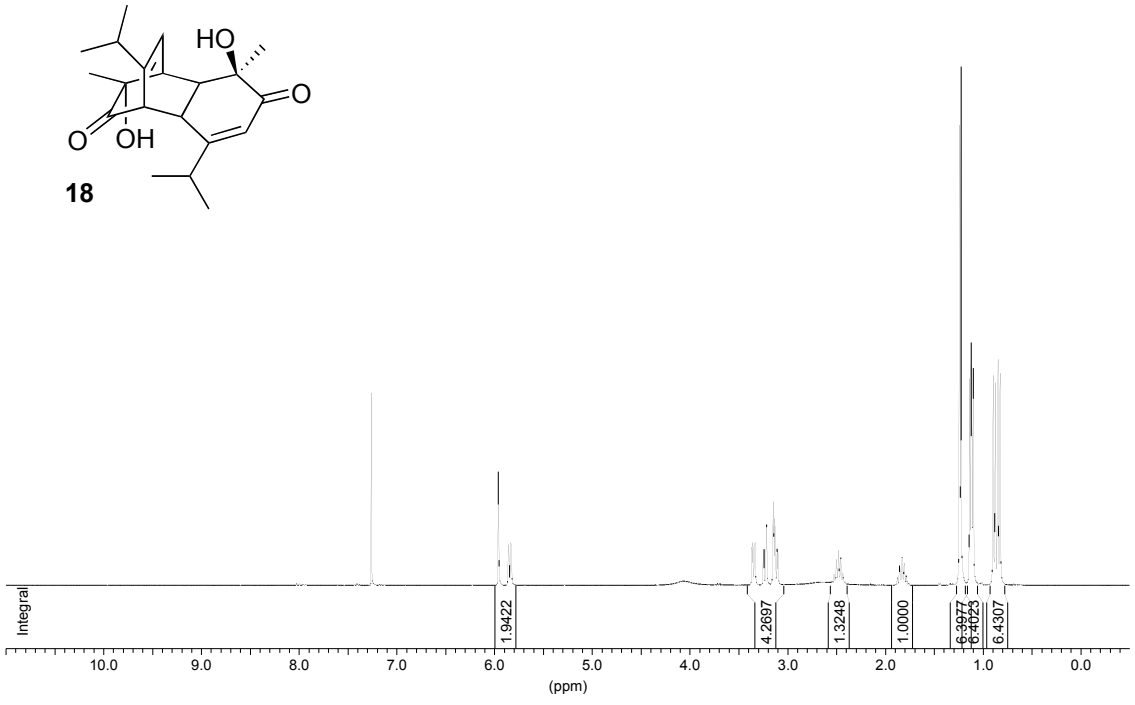
Peak Nr.	Data Point	Frequency	PPM	Intensity	%Int.
1	17523	2904.94	7.2600	41002096	11.2
2	19626	2390.69	5.9748	100410904	27.4
3	19867	2331.76	5.8275	46729700	12.8
4	19892	2325.65	5.8122	48710092	13.3
5	23204	1515.76	3.7882	106926824	29.2
6	24006	1319.64	3.2980	55805432	15.2
7	24034	1312.80	3.2809	59639316	16.3
8	24060	1306.44	3.2650	55540808	15.2
9	24094	1298.12	3.2443	62196256	17.0
10	24232	1264.38	3.1599	88022480	24.0
11	24348	1236.01	3.0890	49771492	13.6
12	24379	1228.43	3.0701	42685428	11.7
13	25544	943.55	2.3581	62504548	17.1
14	26207	781.43	1.9529	366314944	100.0
15	26434	725.92	1.8142	1978485	0.5
16	26461	719.32	1.7977	12396355	3.4
17	26488	712.72	1.7812	30681066	8.4
18	26516	705.87	1.7641	44556748	12.2
19	26544	699.02	1.7470	34509840	9.4
20	26571	692.42	1.7305	15366506	4.2
21	26597	686.06	1.7146	2954734	0.8
22	26781	641.07	1.6021	360734976	98.5
23	27827	385.29	0.9629	210710624	57.5
24	27854	378.69	0.9464	206983168	56.5
25	28009	340.78	0.8517	220006896	60.1
26	28038	333.69	0.8340	237691472	64.9
27	28058	328.80	0.8217	238469120	65.1

28	28086	321.95	0.8046	215654816	58.9
29	28465	229.28	0.5730	199410304	54.4
30	28492	222.67	0.5565	201934272	55.1

JGC266-4 - DPX400 - 050805 -

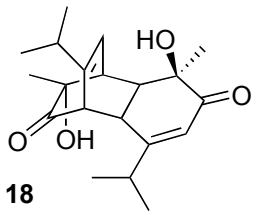


JGE13A-2-recrist - 300MHz - 220406 -



Peak List

File Name : d:\rmn\jge013~1\2\pdata\1\1R.1R
Peak Results saved in File : C:\WIN1D\TMP\EDIT.ASC
Nucleus : off
SF : 300.130006 MHz
OFFSET : 16.4635 ppm
SW_p : 6188.12 Hz
SI : 32768



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Peak Picking Parameter

Peak constant PC = 1.00
Noise = 99902
Sens. level = 399608

Peak Picking region

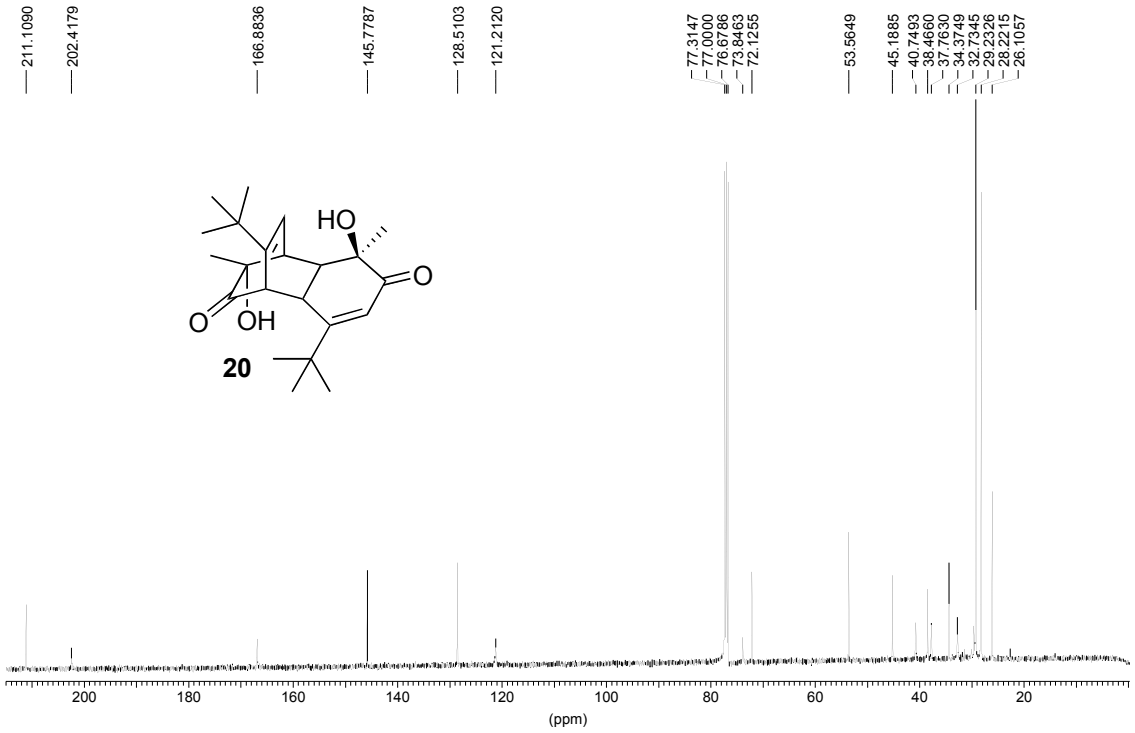
Start(ppm/Hz)	End(ppm/Hz)	MI(%)	MAXI(%)
2.59/ 776.0	2.35/ 706.7	0.61	7.54
1.90/ 570.9	1.87/ 560.2	0.16	2.21
1.78/ 533.3	1.75/ 526.5	0.22	1.08
1.79/ 537.3	1.77/ 532.6	1.81	2.82
1.82/ 545.6	1.81/ 541.8	4.07	4.48
1.84/ 551.5	1.83/ 547.9	5.31	5.88
1.86/ 557.1	1.85/ 555.2	3.48	5.04
1.77/ 530.9	1.76/ 526.9	0.17	0.98
3.11/ 934.6	3.09/ 927.3	5.94	10.41

Peak Picking results

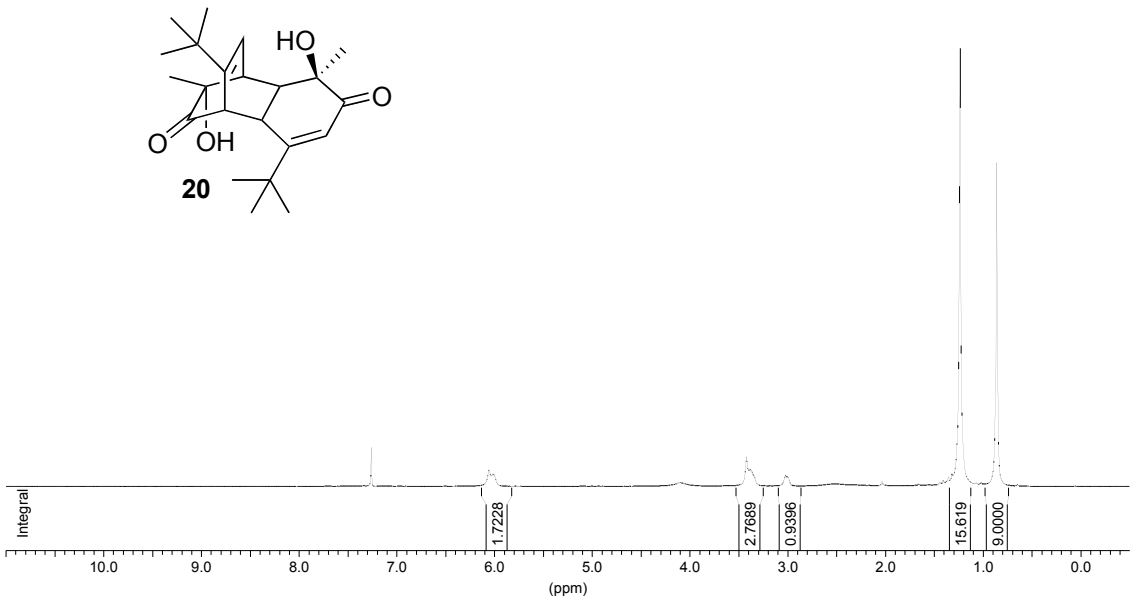
Peak Nr.	Data Point	Frequency	PPM	Intensity	%Int.
1	14627	2178.94	7.2600	118798960	37.1
2	16695	1788.41	5.9588	69934056	21.8
3	16862	1756.87	5.8537	25119614	7.8
4	16898	1750.07	5.8311	26192540	8.2
5	20816	1010.17	3.3658	18879232	5.9
6	20821	1009.23	3.3626	25221260	7.9
7	20828	1007.91	3.3582	22982432	7.2
8	20834	1006.77	3.3545	26291602	8.2
9	20852	1003.38	3.3431	20041456	6.3
10	20857	1002.43	3.3400	25194152	7.9
11	20865	1000.92	3.3350	23107572	7.2
12	20870	999.98	3.3318	26338258	8.2
13	21002	975.05	3.2488	18611726	5.8
14	21012	973.16	3.2425	22176124	6.9
15	21048	966.36	3.2198	30863660	9.6
16	21058	964.47	3.2135	37362020	11.7
17	21181	941.24	3.1361	41119756	12.8
18	21194	938.79	3.1279	36483872	11.4
19	21227	932.56	3.1072	22358040	7.0
20	21240	930.10	3.0990	22000848	6.9
21	22119	764.11	2.5459	2412906	0.8
22	22154	757.50	2.5239	6916284	2.2
23	22190	750.70	2.5012	15946376	5.0
24	22226	743.90	2.4786	21626308	6.8
25	22261	737.29	2.4566	16956178	5.3
26	22297	730.49	2.4339	7522006	2.3
27	22333	723.69	2.4113	1976065	0.6

28	23149	569.60	1.8978	683631	0.2
29	23185	562.80	1.8752	4528644	1.4
30	23221	556.00	1.8525	12173032	3.8
31	23257	549.20	1.8299	17320846	5.4
32	23293	542.40	1.8072	13733128	4.3
33	23329	535.60	1.7846	5845228	1.8
34	23365	528.80	1.7619	1077140	0.3
35	24197	371.68	1.2384	284078656	88.7
36	24218	367.72	1.2252	320151872	100.0
37	24359	341.09	1.1365	127368280	39.8
38	24381	336.94	1.1226	149856192	46.8
39	24394	334.48	1.1145	135602400	42.4
40	24418	329.95	1.0994	134062128	41.9
41	24743	268.57	0.8949	129483536	40.4
42	24778	261.96	0.8728	125000136	39.0
43	24819	254.22	0.8470	139360176	43.5
44	24855	247.42	0.8244	130770768	40.8

JGE16-2-1 - DPX400 -

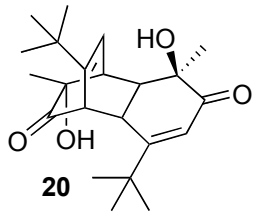


JGE16-2-1 - DPX400 -



Peak List

File Name : d:\rmn\mai200~1\jge16-~1\2\pdata\1\1R.1R
Peak Results saved in File : C:\WIN1D\TMP\EDIT.ASC
Nucleus : off
SF : 300.130006 MHz
OFFSET : 16.4642 ppm
SW_p : 6188.12 Hz
SI : 32768



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Peak Picking Parameter

Peak constant PC = 0.00
Noise = 69205
Sens. level = 0

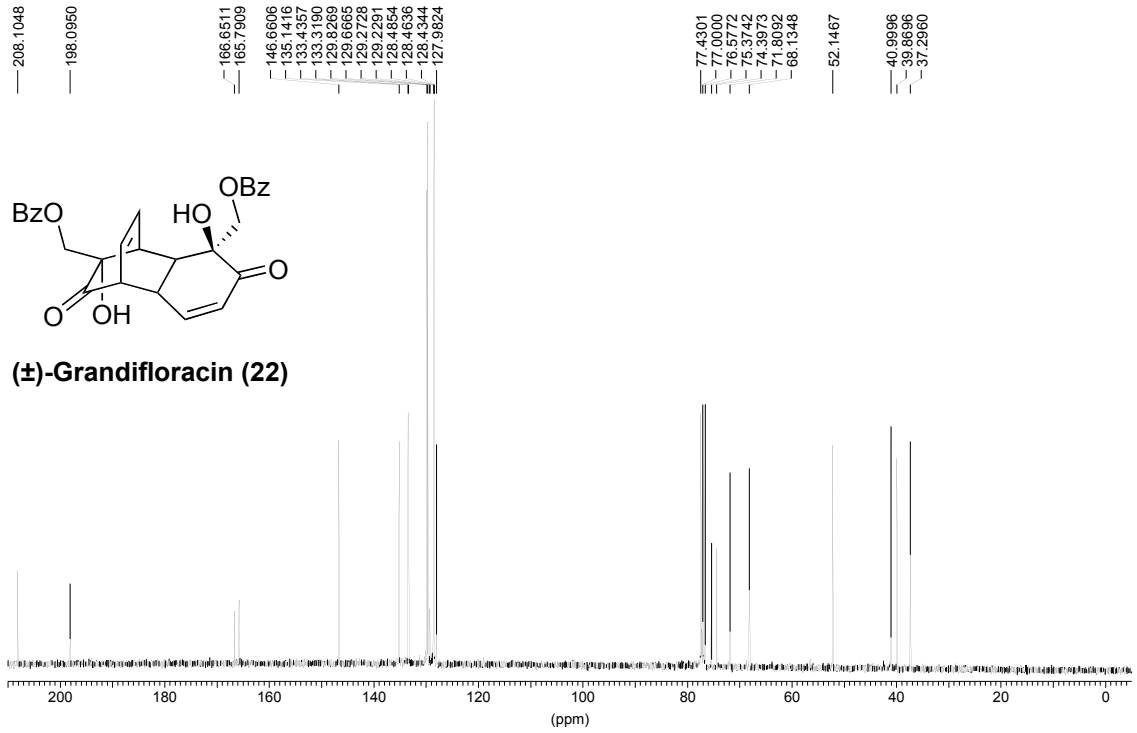
Peak Picking region

Start(ppm/Hz)	End(ppm/Hz)	MI(%)	MAXI(%)
2.22/ 665.0	0.59/ 176.8	70.13	105.45
6.56/ 1967.8	5.72/ 1718.0	1.68	15.33
7.58/ 2275.3	6.88/ 2063.9	8.39	15.11
3.16/ 946.9	2.95/ 886.9	2.05	4.04
3.07/ 921.6	2.97/ 890.1	2.00	3.67
3.01/ 902.7	2.97/ 891.2	2.08	3.41

Peak Picking results

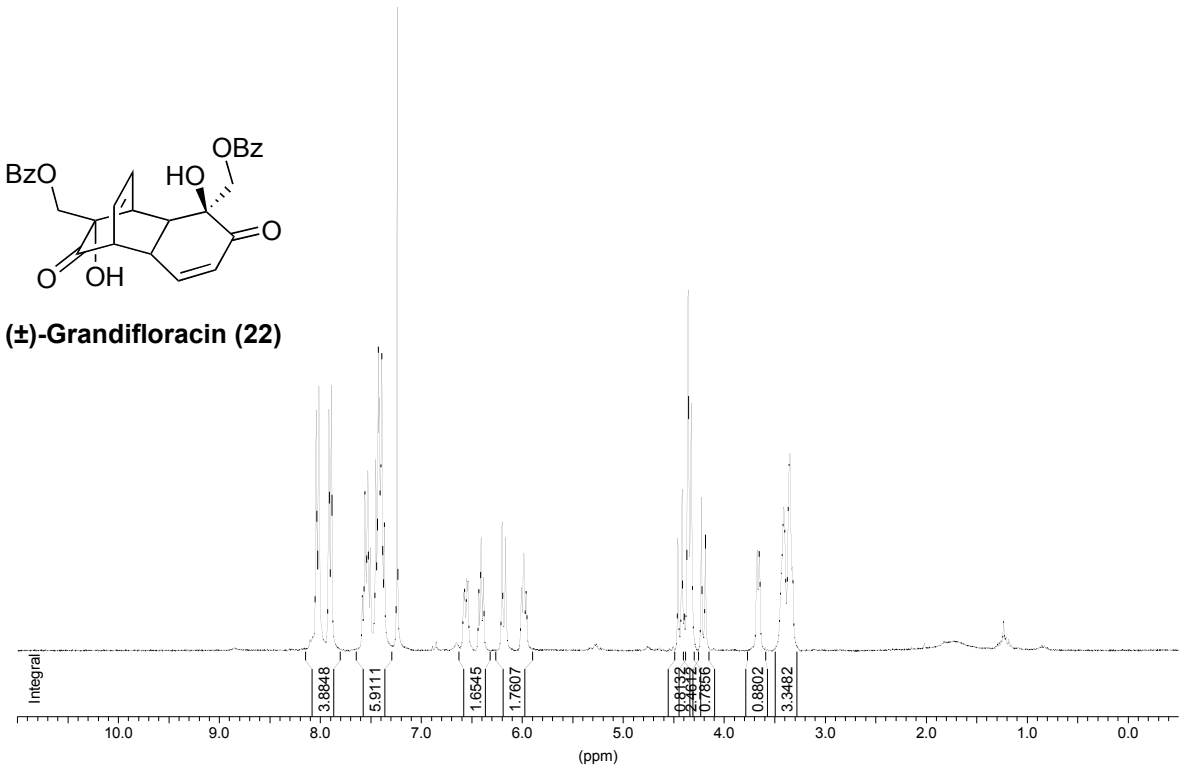
Peak Nr.	Data Point	Frequency	PPM	Intensity	%Int.
1	14628	2178.94	7.2600	35684356	8.9
2	16545	1816.93	6.0538	15467625	3.8
3	16610	1804.65	6.0129	11053498	2.7
4	21366	906.50	3.0203	9859828	2.4
5	21401	899.89	2.9983	8825004	2.2
6	24206	370.17	1.2334	402628736	100.0
7	24800	258.00	0.8596	297444192	73.9

JGE07B-2-R - 300MHz - 230406 -



(±)-Grandifloracin (22)

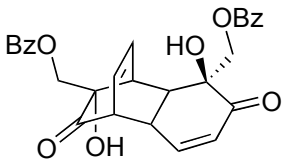
JGE007B-2-R - 300MHz -



(±)-Grandifloracin (22)

Peak List

File Name : d:\rmn\mai200~1\jge007~1\1\pdata\1\1R.1R
Peak Results saved in File : C:\WIN1D\TMP\EDIT.ASC
Nucleus : off
SF : 300.130006 MHz
OFFSET : 16.4635 ppm
SW_p : 6188.12 Hz
SI : 32768



(±)-Grandifloracin (22)

Peak Picking Parameter

Peak constant PC = 1.00
Noise = 206160
Sens. level = 824639

Peak Picking region

Start(ppm/Hz)	End(ppm/Hz)	MI(%)	MAXI(%)
9.12/ 2736.0	6.61/ 1985.0	93.38	140.61
8.32/ 2497.2	7.84/ 2353.6	35.12	45.71
6.84/ 2051.7	5.82/ 1745.5	7.50	28.06
3.82/ 1146.1	3.63/ 1088.4	14.15	25.36
3.81/ 1143.9	3.61/ 1084.0	9.79	25.77
4.33/ 1298.2	4.08/ 1223.2	16.43	30.14
4.67/ 1403.0	4.43/ 1330.3	16.22	32.21

Peak Picking results

Peak Nr.	Data Point	Frequency	PPM	Intensity	%Int.
1	13354	2419.35	8.0610	136513184	37.5
2	13393	2411.98	8.0365	150018096	41.2
3	13552	2381.95	7.9364	137095568	37.7
4	13591	2374.59	7.9119	150595264	41.4
5	14627	2178.94	7.2600	364004160	100.0
6	15671	1981.79	6.6031	34103332	9.4
7	15690	1978.20	6.5911	36090004	9.9
8	15724	1971.78	6.5698	42200328	11.6
9	15743	1968.19	6.5578	40524284	11.1
10	15910	1936.65	6.4527	36298164	10.0
11	15948	1929.48	6.4288	65546816	18.0
12	15986	1922.30	6.4049	42864020	11.8
13	16278	1867.16	6.2212	73585480	20.2
14	16330	1857.34	6.1884	64611316	17.8
15	16585	1809.18	6.0280	35948484	9.9
16	16621	1802.38	6.0053	55562332	15.3
17	16656	1795.77	5.9833	34015588	9.3
18	19045	1344.62	4.4801	66509288	18.3
19	19108	1332.72	4.4405	94347032	25.9
20	19416	1274.56	4.2467	90293968	24.8
21	19479	1262.66	4.2070	68090912	18.7
22	20291	1109.32	3.6961	58567752	16.1
23	20325	1102.90	3.6747	58082472	16.0