Supporting Information

Concise Formal Synthesis of the Pseudopterosins via Anionic Oxy-Cope/Transannular Michael Addition Cascade

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I. Experimental Information

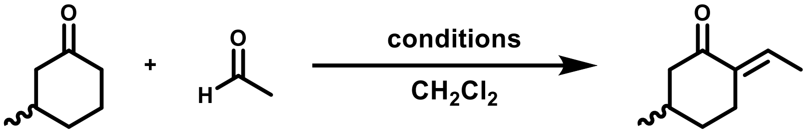
Materials and Methods

All reactions were conducted in flame-or oven-dried glassware under an inert atmosphere of argon (Ar) unless otherwise noted. Reaction solvents including dichloromethane (CH_2Cl_2, Fisher, HPLC Grade), hexanes (Fisher, HPLC Grade), diethyl ether (Et_2O, Fisher, BHT stabilized, HPLC Grade), benzene (C_6H_6, Fisher, HPLC Grade), tetrahydrofuran (THF, Fisher, HPLC Grade), and toluene ($PhCH_3$, Fisher, HPLC Grade) were dried by percolation through a column packed with neutral alumina and a column packed with Q5 reactant (a supported copper catalyst for scavenging oxygen) under a positive pressure of argon. Argon gas (5.0 grade, AR 5.0UH-T, Praxair) was dispensed from size T cylinders. Gases were dispensed into 12" helium quality latex balloons (CTI Industries or Sigma-Aldrich). All other commercially available solvents and/or reagents were used as received, unless otherwise noted.

Solvents for workup and chromatography were: acetone (Fisher, ACS grade), hexanes (Fisher or EMD, ACS Grade), ethyl acetate (EtOAc, Fisher, ACS Grade), dichloromethane (CH_2Cl_2, Fisher, ACS Grade), and methanol (MeOH, Fisher, ACS Grade). Reactions that were performed open to air utilized solvent dispensed from a wash bottle or solvent bottle, and no precautions were taken to exclude water. Column chromatography was performed using EMD Millipore 60 Å (0.040–0.063 mm) mesh silica gel (SiO_2). Analytical thin-layer chromatography was performed on Merck silica gel 60 F254 TLC plates. Visualization was accomplished with UV (254 or 210 nm), and potassium permanganate ($KMnO_4$), *p*-anisaldehyde, vanillin, cerium ammonium molybdate (CAM), or phosphomolybdic acid (PMA) staining solutions.

^1H NMR and ^{13}C NMR spectra were recorded at 298 K on Bruker GN500 (500 MHz, ^1H; 126 MHz, ^{13}C), Bruker CRYO500 (500 MHz, ^1H; 126 MHz, ^{13}C), and Bruker AVANCE600 (600 MHz, ^1H; 151 MHz, ^{13}C) spectrometers. ^1H and ^{13}C spectra were referenced to residual chloroform (7.26 ppm, ^1H; 77.00 ppm, ^{13}C). Chemical shifts are reported in ppm and multiplicities are indicated by: s (singlet),d (doublet), t (triplet), q (quartet), m (multiplet), and br s (broad singlet). Coupling constants, J, are reported in Hertz. Infrared (IR) spectra were recorded on a Perkin-Elmer spectrum RX1 FT-IR instrument. Mass spectrometry data was obtained from the University of California, Irvine Mass Spectrometry Facility. High-resolution mass spectra (HRMS) were recorded on a Waters LCT Premier spectrometer using ESI-TOF (electrospray ionization-time of flight) and data are reported in the form of (m/z). Melting points (mp) were recorded on a Laboratory Devices MelTemp II melting point apparatus and are uncorrected. Optical rotations were measured using Jasco P-1010 polarimeter. Chloroform-d ($CDCl_3$, D 99.8%, DLM-7) was purchased from Cambridge Isotope Laboratories. (*R*)-3-methylcyclohexan-1-one was synthesized according to a literature procedure.[1]

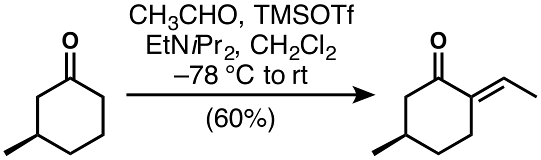
Optimization of Aldol Condensation



Entry	Aldehyde [eq.]	Reagents [eq.]	yield
1	1.0	1.1 $TiCl_4$, 1.2 $EtNiPr_2$	44%
2	1.1	1.2 $TiCl_4$, 1.3 $EtNiPr_2$	58%
3 (10 mmol)	1.1	1.2 $TiCl_4$, 1.3 $EtNiPr_2$	22-35%
4	2.0	1.5 TMSOTf, 1.5 $EtNiPr_2$ then $TiCl_4$ 0.1	27%
5	2.0	1.5 TMSOTf, 1.5 $EtNiPr_2$, then 0.05 TMSOTf	60%

To a solution of (±)-3-methylcyclohexanone (**12**) (1.0 equiv.) in anhydrous CH_2Cl_2, the Lewis acid and base were added sequentially. The resulting solution was stirred for 15 min, at which time freshly distilled acetaldehyde was added and stirring was continued for 10 min. The reaction mixture was allowed to warm to room temperature and stirring was continued for 3 h. The reaction mixture was poured into $NaHCO_3$ (sat. aq.) and extracted with Et_2O (3×50 mL). The combined organic layers were washed with brine and dried over $MgSO_4$. The volatiles were removed under reduced pressure and purification by flash chromatography (hexanes/Et_2O = 20/1) afforded the desired product **13** as a colorless oil.

Experimental Procedures and Characterization Data



12 **13**

Enone 13: To a solution of (*R*)-3-methylcyclohexanone (**12**) (9.8 g, 87 mmol, 1.0 equiv.) and *N*,*N*-diisopropylethylamine (31 mL, 0.18 mol, 2.0 equiv.) in anhydrous CH_2Cl_2 (220 mL) at –78 °C was added TMSOTf (32 mL, 0.18 mol, 2.0 equiv.) dropwise over 40 min. The resulting solution was stirred for 15 min, at which time freshly distilled acetaldehyde (15 mL, 0.26 mol, 3.0 equiv.) was added and stirring was continued for 10 min. Following the addition of more TMSOTf (1.5 mL, 8.7 mmol, 0.10 equiv.), the reaction mixture was allowed to warm to room temperature and stirring was continued for 3 h. The reaction mixture was poured into $NaHCO_3$ (sat. aq.) and extracted with Et_2O (3×50 mL). The combined organic extracts were washed with brine and dried over $MgSO_4$. The volatiles were removed under reduced pressure and purification by flash chromatography (hexanes/Et_2O = 20/1) afforded the desired product **13** as a colorless oil (7.2 g, 60%). The spectral data for this compound are consistent with those reported in the literature.[2]

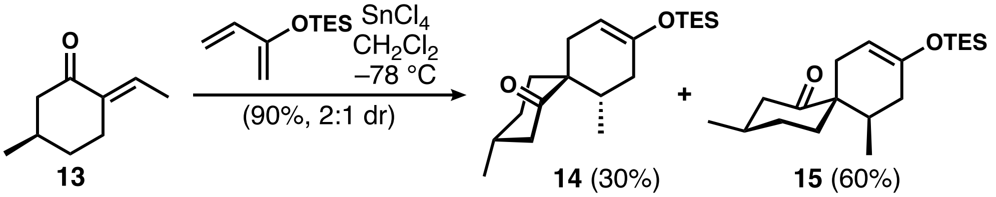
^{1}H NMR (600 MHz, CDCl$_3$) δ 6.76 – 6.66 (m, 1H), 2.71 (d, *J* = 16.7 Hz, 1H), 2.54 (d, *J* = 13.8 Hz, 1H), 2.27 (t, *J* = 13.0 Hz, 1H), 2.05 – 1.92 (m, 2H), 1.90 (d, *J* = 13.2 Hz, 1H), 1.74 (d, *J* = 7.2 Hz, 3H), 1.39 – 1.27 (m, 1H), 1.02 (d, *J* = 6.0 Hz, 3H).

^{13}C NMR (151 MHz, CDCl$_3$) δ 201.1, 136.6, 134.3, 48.5, 31.7, 30.2, 25.4, 21.9, 13.78.

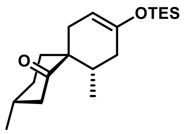
IR (film) 2952, 2927, 2871, 1687, 1617 cm^{-1}.

HRMS (ESI) m/z calculated for $C_9H_{14}OH$ $[M+H]^+$ 139.1118, found 139.1123.

$[\alpha]^{22}_D$ = +85.7 (*c* = 1.0, CHCl$_3$).



Spirocyclic ketones 14 and 15: To a solution of ketone (1.4 g, 9.8 mmol, 1.0 equiv.) and silyl enol ether (1.8 g, 9.8 mmol, 1.0 equiv.) at –78°C in anhydrous CH_2Cl_2 (20 mL) was added a solution of $SnCl_4$ (1.0 M in CH_2Cl_2, 0.49 mL, 0.49 mmol, 0.05 equiv.) and the resulting solution was stirred for 1 h at –78 °C. Pyridine (1.0 mL) was added and the reaction was allowed to warm to room temperature. The resulting suspension was filtered over SiO_2 with ethyl acetate. The volatiles were removed under reduced pressure and purification by flash chromatography (hexanes/Et_2O = 40/1) afforded product **14** (1.9 g, 60%) and product **15** (0.95 g, 30%) each as colorless oils.



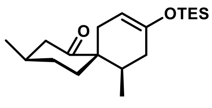
^{1}H NMR (500 MHz, CDCl$_3$) δ 4.82 – 4.71 (m, 1H), 2.45 – 2.36 (m, 1H), 2.34 – 2.26 (m, 2H), 2.24 – 2.12 (m, 1H), 2.01 – 1.88 (m, 2H), 1.88 – 1.81 (m, 1H), 1.81 – 1.65 (m, 3H), 1.58 – 1.34 (m, 2H), 1.04 – 0.99 (m, 3H), 0.99 – 0.91 (m, 12H), 0.63 (q, *J* = 7.8 Hz, 6H).

^{13}C NMR (126 MHz, CDCl$_3$) δ 214.6, 147.3, 101.5, 50.2, 46.2, 34.9, 34.9, 32.2, 31.1, 29.5, 28.7, 21.8, 14.9, 6.9, 5.1.

HRMS (ESI) m/z calculated for $C_{19}H_{34}O_2SiNa$ $[M+Na]^+$ 345.2220, found 345.2235.

IR (film) 2952, 2914, 2874, 1706, 1676 cm^{-1}.

$[\alpha]^{22}_D$ = +17.9 (*c* = 1.0, CHCl$_3$).



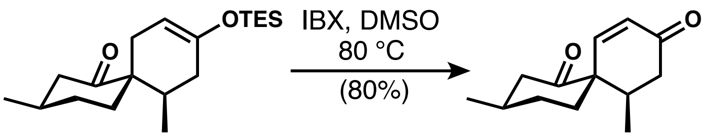
^{1}H NMR (500 MHz, CDCl$_3$) δ 4.76 – 4.55 (m, 1H), 2.45 – 2.27 (m, 2H), 2.23 (dd, *J* = 16.5, 5.2 Hz, 1H), 2.11 – 2.02 (m, 2H), 1.98 (d, *J* = 16.1 Hz, 1H), 1.81 (dt, *J* = 12.9, 3.3 Hz, 2H), 1.75 – 1.63 (m, 2H), 1.56 – 1.33 (m, 2H), 1.03 – 0.89 (m, 12H), 0.85 (d, *J* = 6.7 Hz, 3H), 0.64 (q, *J* = 7.9 Hz, 6H).

^{13}C NMR (126 MHz, CDCl$_3$) δ 215.4, 150.0, 99.9, 49.2, 47.8, 35.2, 33.4, 32.2, 32.1, 29.5, 26.5, 22.3, 16.3, 6.8, 5.2.

HRMS (ESI) m/z calculated for $C_{19}H_{34}O_2SiNa$ $[M+Na]^+$ 345.2220, found 345.2226.

IR (film) 2953, 2875, 1704, 1675 cm^{-1}.

$[\alpha]^{22}_D$ = −30.2 (*c* = 1.0, CHCl$_3$).



15 16

Spirocyclic ketoenone 16: Silyl enol ether **15** (0.39 g, 1.2 mmol, 1.0 equiv.) and IBX (0.68 g, 2.4 mmol, 2.0 equiv.) were dissolved in DMSO (12 ml) under an argon atmosphere and the mixture was heated to 80 °C for 1 h. NaHCO$_3$ (sat. aq.) was added and the resulting mixture was extracted with EtOAc (5×20 mL). The combined organic extracts were washed with brine (10 mL) and dried over MgSO$_4$. The volatiles were removed under reduced pressure and purification by flash chromatography (hexanes/EtOAc = 10/1) afforded the desired product **16** as a colorless oil (0.20 g, 80%).

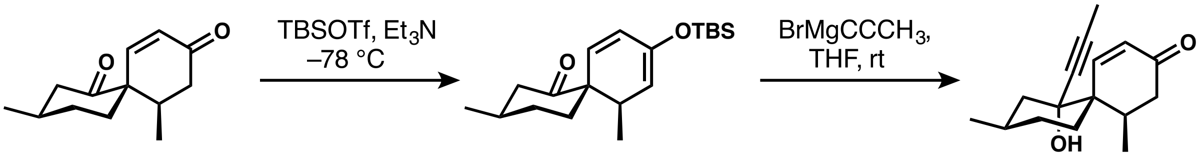
^{1}H NMR (500 MHz, CDCl$_3$) δ 6.95 (d, *J* = 10.3 Hz, 1H), 6.01 (d, *J* = 10.3 Hz, 1H), 2.84 – 2.77 (m, 1H), 2.74 (dd, *J* = 17.0, 4.6 Hz, 1H), 2.44 (ddd, *J* = 13.8, 4.3, 1.9 Hz, 1H), 2.36 – 2.27 (m, 1H), 2.22 (dd, *J* = 16.9, 8.0 Hz, 1H), 2.03 (dt, *J* = 13.5, 3.5 Hz, 1H), 2.00 – 1.90 (m, *J* = 11.8, 6.6 Hz, 1H), 1.89 – 1.81 (m, 1H), 1.80 – 1.72 (m, 1H), 1.65 – 1.54 (m, 1H), 1.08 (d, *J* = 6.5 Hz, 3H), 0.94 (d, *J* = 6.9 Hz, 3H).

^{13}C NMR (126 MHz, CDCl$_3$) δ 209.2, 198.9, 148.4, 129.6, 54.0, 47.8, 42.7, 35.2, 33.7, 33.1, 29.5, 22.3, 16.1.

HRMS (ESI) m/z calculated for $C_{13}H_{18}O_2Na$ $[M+Na]^+$ 229.1199, found 229.1207.

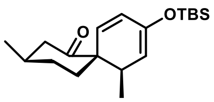
IR (film) 2926, 2869, 1705, 1678 cm^{-1}.

$[\alpha]^{22}_D$ = +13.9 (*c* = 1.0, CHCl$_3$).



16 S1 **11** (91%, 2 steps
5.8:1 dr)

Propargylic alcohols 11: To a solution of ketone (0.56 g, 2.7 mmol, 1.0 equiv.) in anhydrous CH$_2$Cl$_2$ (27 mL) at −78 °C was added Et$_3$N (1.3 mL, 9.5 mmol, 3.5 equiv.) followed by TBSOTf (0.68 mL, 3.0 mmol, 1.1 equiv.). The resulting mixture was stirred at −78 °C for 3 h, at which time it was poured into NaHCO$_3$ (sat. aq., 20 mL) and extracted with hexanes (3×20 mL). The combined organic extracts were washed with brine and dried over $MgSO_4$. The volatiles were removed under reduced pressure and purification by flash chromatography (hexanes/EtOAc = 40/1→20/1→4/1) afforded the desired product **S1** as a colorless oil (0.87 g, 98%).



^{1}H NMR (500 MHz, $CDCl_3$) δ 5.82 – 5.60 (m, 2H), 4.83 (d, J = 3.9 Hz, 1H), 3.05 – 2.87 (m, 1H), 2.41 (t, J = 13.1 Hz, 1H), 2.24 (ddd, J = 13.3, 4.0, 2.0 Hz, 1H), 2.06 – 1.95 (m, 1H), 1.88 – 1.73 (m, 1H), 1.73 – 1.65 (m, 1H), 1.59 – 1.43 (m, 2H), 1.02 (d, J = 6.5 Hz, 3H), 0.92 – 0.87 (m, 12H), 0.11 (s, 3H), 0.10 (s, 3H).

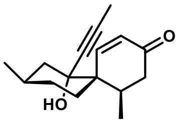
^{13}C NMR (126 MHz, $CDCl_3$) δ 210.1, 145.4, 128.8, 127.3, 111.7, 51.9, 47.0, 35.6, 32.0, 31.8, 29.7, 25.8, 22.5, 18.2, 14.5, −4.4, −4.5.

HRMS (ESI) m/z calculated for $C_{19}H_{32}O_2SiNa$ $[M+Na]^+$ 343.2064, found 343.2075.

IR (film) 2954, 2928, 2856, 1709, 1650 cm^{-1}.

$[\alpha]^{22}_D$ = −226.4 (*c* = 1.0, $CHCl_3$).

To a solution of silyl enol ether **S1** (0.83 g, 2.6 mmol, 1.0 equiv.) in anhydrous THF (26 mL) at room temperature was added a solution of propynylmagnesium bromide (0.5 M in THF, 20 mL, 4.0 equiv.). The resulting mixture was stirred for 15 h at room temperature, at which time HCl (aq., 1.0 M) was added until the reaction mixture was acidified. After stirring for 1 h the reaction was extracted with EtOAc (3×20 mL). The combined organic extracts were washed with brine (20 mL) and dried over $MgSO_4$. The volatiles were removed under reduced pressure and purification by flash chromatography (hexanes/EtOAc = 10/1→4/1→2/1) afforded product **11** as a colorless oil (0.52 g, 80%) and product **11'** as a colorless solid (90 mg, 14%). Compound **11'** was characterized by X-ray crystallography; the structure and associated data can be found in Section II of this Supporting Information.



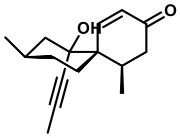
^{1}H NMR (500 MHz, $CDCl_3$) δ 6.93 (d, *J* = 10.6 Hz, 1H), 6.01 (d, *J* = 10.6 Hz, 1H), 2.87 – 2.70 (m, 2H), 2.22 (dd, *J* = 16.7, 8.6 Hz, 1H), 2.10 – 1.95 (m, 1H), 1.91 – 1.78 (m, 3H), 1.78 – 1.68 (m, 4H), 1.64 – 1.50 (m, 2H), 1.20 – 1.06 (m, 4H), 0.92 (d, *J* = 6.3 Hz, 3H).

^{13}C NMR (126 MHz, $CDCl_3$) δ 200.2, 153.6, 128.9, 82.8, 82.4, 73.5, 47.0, 46.0, 44.0, 34.4, 29.6, 27.0, 26.8, 21.8, 19.1, 3.6.

IR (film) 3400 (br), 2948, 2920, 2867, 1664 cm^{-1}.

HRMS (ESI) m/z calculated for $C_{16}H_{22}O_2Na$ $[M+Na]^+$ 269.1512, found 269.1518.

$[\alpha]^{22}_D$ = −41.2 (*c* = 1.0, $CHCl_3$).



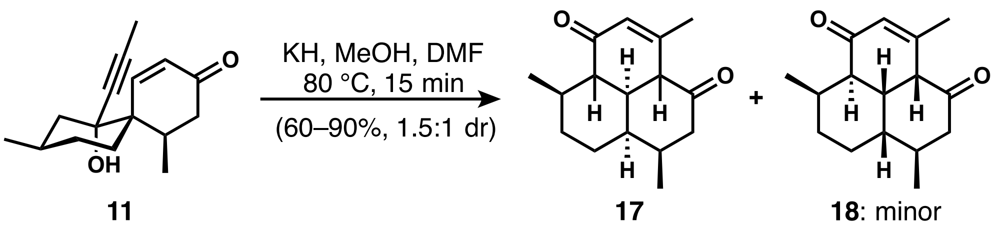
^{1}H NMR (500 MHz, $CDCl_3$) δ 6.77 (dd, *J* = 10.5, 1.6 Hz, 1H), 6.13 (d, *J* = 10.5 Hz, 1H), 3.41 (dd, *J* = 17.3, 5.6 Hz, 1H), 2.87 – 2.68 (m, 1H), 2.11 (dd, *J* = 17.3, 2.8 Hz, 1H), 1.90 (s, 3H), 1.82 – 1.74 (m, 1H), 1.73 – 1.66 (m, 1H), 1.66 – 1.52 (m, 3H), 1.33 (t, *J* = 12.5 Hz, 1H), 1.27 – 1.16 (m, 2H), 0.98 (d, *J* = 7.1 Hz, 3H), 0.96 (d, *J* = 6.6 Hz, 3H).

^{13}C NMR (126 MHz, CDCl$_3$) δ 200.6, 147.3, 131.5, 83.9, 81.2, 76.1, 48.0, 46.1, 44.7, 36.5, 32.1, 30.4, 29.6, 21.7, 18.2, 3.9.

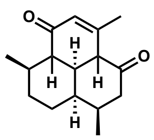
IR (film) 3393 (br), 2948, 2920, 2855, 1663 cm^{-1}.

HRMS (ESI) m/z calculated for $C_{16}H_{22}O_2Na$ $[M+Na]^+$ 269.1512, found 269.1517.

$[\alpha]^{22}_D$ = +104.6 (*c* = 1.0, CHCl$_3$).



Tricyclic enones 17 and 18: To a suspension of KH (50 mg, 1.2 mmol, 4.0 equiv.) in carefully degassed anhydrous DMF (1.5 mL) and methanol (1.5 mL) at 80 °C was added a solution of the alcohol **11** (76 mg, 0.31 mmol, 1.0 equiv.) in anhydrous DMF (1.5 mL). The color immediately turned a dark red and after less than 15 min the color changed to a yellow/brown color. After the color change the reaction mixture was poured quickly into an ice-cold solution NH$_4$Cl (sat. aq., 10 mL) and the resulting mixture was extracted with EtOAc (3×10 mL). The combined organic extracts were washed with brine (10 mL) and dried over MgSO$_4$. The volatiles were removed under reduced pressure and purification by flash chromatography (benzene/Et$_2$O = 20/1) afforded the desired product **18** as a white solid (21 mg, 28%) and the undesired product **17** as a white solid (32 mg, 42%). The yield of this reaction varies owing to decomposition of the product under the reaction conditions. Compound **18** was characterized by X-ray crystallography; the structure and associated data can be found in Section II of this Supporting Information.



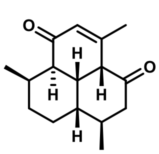
^{1}H NMR (500 MHz, CDCl$_3$) δ 5.91 (s, 1H), 3.39 (d, *J* = 6.5 Hz, 1H), 2.72 (dd, *J* = 14.4, 5.8 Hz, 1H), 2.65 (dt, *J* = 13.7, 7.0 Hz, 1H), 2.57 (dt, *J* = 13.3, 6.5 Hz, 1H), 2.40 – 2.34 (m, 1H), 2.23 (dd, *J* = 14.5, 6.4 Hz, 1H), 1.94 (d, *J* = 0.5 Hz, 3H), 1.87 – 1.78 (m, 2H), 1.68 – 1.57 (m, 3H), 1.45 – 1.36 (m, 1H), 1.15 – 1.10 (m, 6H).

^{13}C NMR (126 MHz, CDCl$_3$) δ 209.9, 200.6, 155.9, 128.8, 55.7, 49.6, 48.4, 44.1, 37.2, 36.5, 30.6, 29.0, 24.5, 24.0, 22.9, 19.6.

HRMS (ESI) m/z calculated for $C_{16}H_{22}O_2Na$ $[M+Na]^+$ 269.1512, found 269.1520.

IR (film) 2920, 2866, 1711, 1667, 1377 cm^{-1}.

$[\alpha]^{22}_D$ = −100.0 (*c* = 1.0, CHCl$_3$).



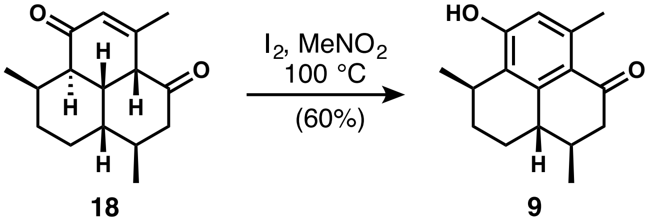
^{1}H NMR (500 MHz, CDCl$_3$) δ 5.97 (d, *J* = 1.1 Hz, 1H), 3.22 (d, *J* = 5.8 Hz, 1H), 2.90 – 2.83 (m, 1H), 2.66 – 2.61 (m, 1H), 2.43 (dd, *J* = 12.1, 3.2 Hz, 1H), 2.30 – 2.22 (m, 2H), 2.14 (dd, *J* = 14.0, 4.2 Hz, 1H), 1.97 – 1.85 (m, 5H), 1.77 – 1.72 (m, 2H), 1.41 – 1.35 (m, 1H), 1.05 (d, *J* = 6.1 Hz, 3H), 0.86 (d, *J* = 7.0 Hz, 3H).

^{13}C NMR (126 MHz, CDCl$_3$) δ 208.5, 198.9, 158.0, 128.7, 56.7, 49.8, 45.3, 42.8, 40.8, 31.0, 27.2, 26.8, 24.6, 20.5, 20.0, 13.0.

HRMS (ESI) m/z calculated for $C_{16}H_{22}O_2Na$ $[M+Na]^+$ 269.1512, found 269.1512.

IR (film) 2923, 1712, 1663, 1378 cm^{-1}.

$[\alpha]^{22}_D$ = +20.9 (*c* = 0.65, CHCl$_3$).



Phenol 9: Enone **18** (14 mg, 0.057 mmol, 1.0 equiv.) and iodine (87 mg, 0.34 mmol, 6.0 equiv.) were dissolved in anhydrous MeNO$_2$ (0.50 mL) under an argon atmosphere and the resulting mixture was heated to 100 °C for 6 h. Na$_2$S$_2$O$_3$ (sat. aq., 2.0 mL) was added and stirring was continued for 30 min. The resulting mixture was extracted with EtOAc (5×5 mL). The combined organic extracts were washed with brine (5.0 mL) and dried over MgSO$_4$. The volatiles were removed under reduced pressure and purification by flash chromatography (hexanes/acetone = 10/1) afforded the desired product **9** as a red solid (8.4 mg, 60%).

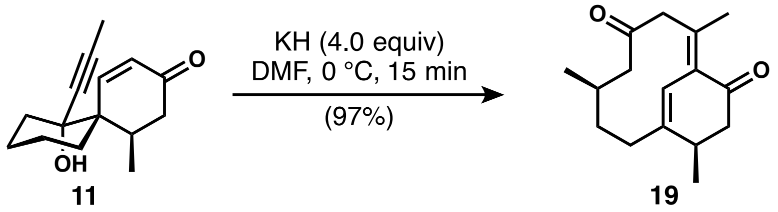
^{1}H NMR (500 MHz, CDCl$_3$) δ 6.52 (s, 1H), 5.37 (s, 1H), 3.16 (dd, *J* = 14.7, 7.4 Hz, 1H), 2.68 – 2.47 (m, 4H), 2.39 – 2.17 (m, 4H), 1.85 – 1.64 (m, 1H), 1.40 (tdd, *J* = 12.8, 8.4, 4.1 Hz, 1H), 1.27 (d, *J* = 6.8 Hz, 3H), 1.16 – 1.06 (m, 4H).

^{13}C NMR (126 MHz, CDCl$_3$) δ 199.7, 157.2, 148.4, 141.3, 125.9, 124.7, 117.7, 48.9, 44.6, 35.3, 31.7, 28.1, 27.3, 23.5, 22.7, 19.6.

HRMS (ESI) m/z calculated for $C_{16}H_{20}O_2Na$ $[M+Na]^+$ 267.1356, found 267.1360.

$[\alpha]^{22}_D$ = −23.6 (*c* = 0.20, CHCl$_3$), Lit: **$[\alpha]^{25}_D$** = 62.4 (*c* = 0.5, CHCl$_3$) for enantiomer.

The spectral data for this compound are consistent with those reported in the literature.[3]



Bicyclic dienedione 19: To a suspension of KH (80 mg, 0.20 mmol, 4.0 equiv.) in carefully degassed anhydrous DMF (5.0 mL) at 0 °C was added a solution of the alcohol **11** (123 mg, 0.50 mmol, 1.0 equiv.)

in anhydrous DMF (5.0°mL). The color immediately turned into a dark red and after 15 min the color changed to a yellow/brown color. After the color change, acetic acid (0.5 mL) was added. The resulting mixture was poured into water (15 mL) and extracted with EtOAc (3×20 mL). The combined organic extracts were washed with brine (20 mL) and dried over $MgSO_4$. The volatiles were removed under reduced pressure and purification by flash chromatography (hexanes/EtOAc = 4/1) afforded the desired product **19** as a colorless oil (120 mg, 97%,).

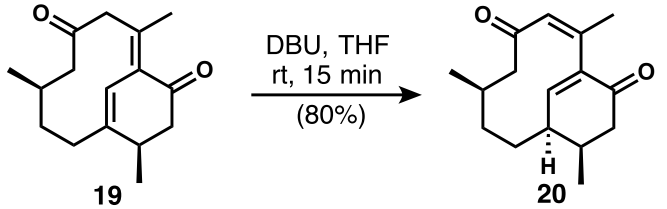
^{1}H NMR (600 MHz, $CDCl_3$) δ 6.03 (s, 1H), 3.24 (s, 2H), 2.73 (dd, *J* = 15.6, 9.1 Hz, 1H), 2.58 (dd, *J* = 16.5, 5.3 Hz, 1H), 2.45 – 2.33 (m, 1H), 2.34 – 2.22 (m, 6H), 2.21 – 2.13 (m, 1H), 2.10 (dd, *J* = 15.7, 4.1 Hz, 1H), 1.96 – 1.88 (m, 1H), 1.66 – 1.55 (m, 1H), 1.08 – 1.00 (m, 6H).

^{13}C NMR (151 MHz, $CDCl_3$) δ 208.6, 201.3, 145.8, 140.3, 129.2, 124.4, 53.4, 51.4, 47.7, 33.4, 31.6, 30.0 (2×C), 22.6, 22.3, 16.9.

HRMS (ESI) m/z calculated for $C_{16}H_{22}O_2Na$ $[M+Na]^+$ 269.1512, found 269.1514.

IR (film) 2955, 2926, 2872, 1686, 1586 cm^{-1}.

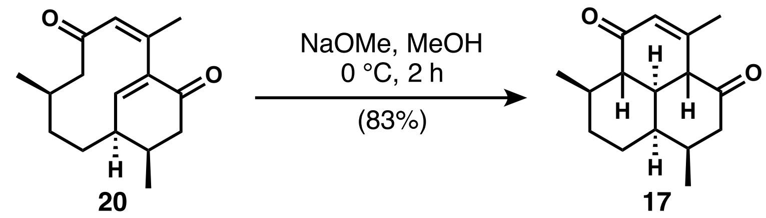
$[\alpha]^{22}_D$ = +100.6 (*c* = 1.0, $CHCl_3$).



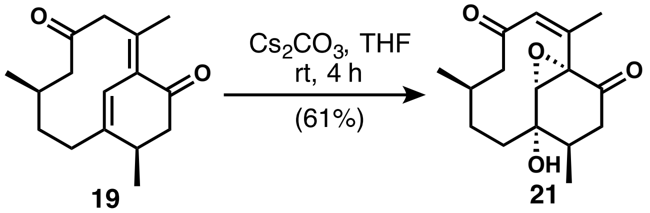
Bicyclic dienedione 20: To a solution of **19** (18 mg, 0.073 mmol, 1.0 equiv.) in carefully degassed anhydrous THF (1.0 mL) at rt was added DBU (33 µL, 0.22 mmol, 3.0 equiv.). After 15 min a solution of NH_4Cl (sat. aq., 1 mL) and HCl (1.0 M, 0.20 mL) was added. The resulting mixture was extracted with EtOAc (3×5 mL). The combined organic extracts were washed with brine (5 mL) and dried over $MgSO_4$. The volatiles were removed under reduced pressure and purification by flash chromatography (hexanes/EtOAc = 9/1) afforded the desired product **20** as a colorless solid (14 mg, 80%,). This compound was characterized by X-ray crystallography; the structure and associated data can be found in Section II of this Supporting Information.

^{1}H NMR (600 MHz, $CDCl_3$) δ 7.06 (d, *J* = 6.5 Hz, 1H), 5.94 (s, 1H), 2.52 – 2.37 (m, 6H), 2.07 (s, 3H), 1.86 (d, *J* = 13.1 Hz, 1H), 1.78 (ddd, *J* = 14.0, 9.8, 4.7 Hz, 1H), 1.62 – 1.52 (m, 2H), 1.30 – 1.26 (m, 1H), 1.03 (d, *J* = 6.4 Hz, 3H), 0.87 (d, *J* = 6.6 Hz, 3H).

^{13}C NMR (151 MHz, $CDCl_3$) δ 205.3, 197.1, 158.4, 148.6, 139.4, 134.1, 46.9, 41.7, 39.1, 32.1, 28.6, 26.6, 22.1, 20.3, 20.0, 18.3.



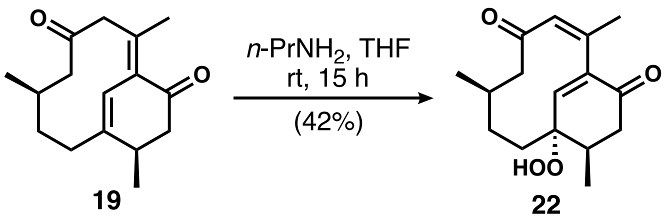
Tricyclic enone 17: To a solution of **20** (12 mg, 0.049 mmol, 1.0 equiv.) in carefully degassed anhydrous MeOH (1.0 mL) at 0 °C was added a solution of NaOMe in MeOH (0.05 M, 0.0049 mmol, 0.10 equiv.). After 2 h the volatiles were removed under reduced pressure and purification by flash chromatography (hexanes/EtOAc = 20/1) afforded the product **17** as a colorless solid (10 mg, 83%). Characterization data for **17** can be found above.



Epoxide 21: To a solution of **19** (24 mg, 0.10 mmol, 1.0 equiv.) in anhydrous THF (1.0 mL) at rt was added Cs_2CO_3 (98 mg, 0.30 mmol, 3.0 equiv.). After 4 h water (2 mL) was added. The resulting mixture was extracted with EtOAc (3×5 mL). The combined organic extracts were washed with brine (5 mL) and dried over $MgSO_4$. the volatiles were removed under reduced pressure and purification by flash chromatography (hexanes/EtOAc = 10/1) afforded the product **21** as a colorless solid (17 mg, 61%, *ca.* 75% pure). In addition to the NMR data provided below, this compound was characterized by X-ray crystallography; the structure and associated data can be found in Section II of this Supporting Information.

^{1}H NMR (600 MHz, CDCl$_3$) δ 6.01 (s, 1H), 3.70 (s, 1H), 2.70 (dd, J = 20.2, 7.0 Hz, 1H), 2.63 – 2.56 (m, 1H), 2.56 – 2.46 (m, 2H), 1.96 – 1.82 (m, 5H), 1.81 – 1.74 (m, 1H), 1.19 – 1.11 (m, 2H), 0.96 (d, J = 8.0 Hz, 3H), 0.89 (d, J = 7.1 Hz, 3H).

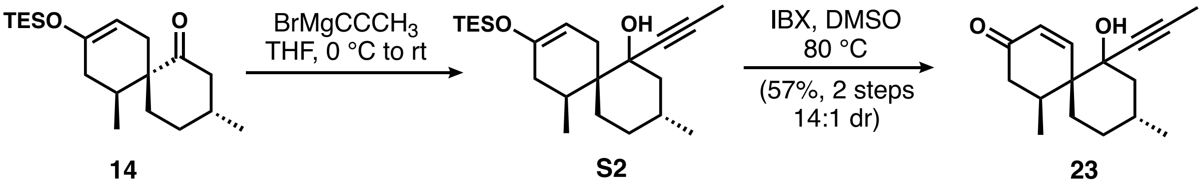
^{13}C NMR (151 MHz, CDCl$_3$) δ 204.2, 203.7, 140.2, 133.4, 73.3, 68.8, 65.8, 46.9, 42.8, 33.8, 27.2, 24.3, 24.1, 20.6, 20.0, 14.3.



Hydroperoxide 22: To a solution of **19** (24 mg, 0.10 mmol, 1.0 equiv.) in anhydrous THF (1.0 mL) at rt was added *n*-propylamine (25 µL, 0.30 mmol, 3.0 equiv.). After 15 h a solution of HCl (1.0 M, 1 mL) was added. The resulting mixture was extracted with EtOAc (3×5 mL). The combined organic extracts were washed with brine (5 mL) and dried over $MgSO_4$. the volatiles were removed under reduced pressure and purification by flash chromatography (hexanes/EtOAc = 10/1) afforded the product **21** as a colorless solid (12 mg, 42%). In addition to the NMR data provided below, this compound was characterized by X-ray crystallography; the structure and associated data can be found in Section II of this Supporting Information.

^{1}H NMR (500 MHz, CDCl$_3$) δ 8.21 (s, 1H), 7.06 (s, 1H), 6.00 (s, 1H), 3.04 (td, *J* = 13.0, 6.6 Hz, 1H), 2.74 (dd, *J* = 18.8, 5.7 Hz, 1H), 2.57 – 2.44 (m, 1H), 2.44 – 2.26 (m, 2H), 2.10 (d, *J* = 0.8 Hz, 3H), 1.94 (dd, *J* = 16.2, 3.4 Hz, 1H), 1.83 – 1.63 (m, 3H), 1.49 – 1.43 (m, 1H), 1.03 (d, *J* = 6.8 Hz, 3H), 0.86 (d, *J* = 7.0 Hz, 3H).

^{13}C NMR (126 MHz, CDCl$_3$) δ 205.2, 195.7, 157.5, 147.9, 140.7, 134.7, 86.5, 47.4, 43.6, 33.1, 28.1, 23.8, 23.8, 21.8, 19.4, 13.9.



Propargylic alcohols 23: To a solution of silyl enol ether (1.1 g, 3.3 mmol, 1.0 equiv.) in anhydrous THF (7.0 mL) at 0 °C was added a solution of propynylmagnesium bromide (0.5 M in THF, 27 mL, 4.0 equiv.). The resulting mixture was stirred for 15 h at room temperature, at which time $NaHCO_3$ (sat. aq., 10 mL) was added and the resulting mixture was extracted with EtOAc (3×10 mL). The combined organic extracts were washed with brine (10 mL) and dried over $MgSO_4$. The volatiles were removed under reduced pressure and the crude reaction product was used as is for the next step.

The crude alcohol **S2**, K_2CO_3 (0.46 g, 3.3 mmol, 1.0 equiv.) and IBX (1.9 g, 6.6 mmol, 2.0 equiv.) were dissolved in DMSO (33 mL) under an argon atmosphere and heated to 80 °C for 2 h. $NaHCO_3$ (sat. aq., 50 mL) was added and the resulting mixture was extracted with EtOAc (5×40 mL). The combined organic extracts were washed with brine (20 mL) and dried over $MgSO_4$. The volatiles were removed under reduced pressure and purification by flash chromatography (hexanes/EtOAc = 4/1) afforded the desired product **23** as a mixture of diastereomers (0.46, 57%, dr 14:1) that were separated by careful chromatography in one instance for characterization.

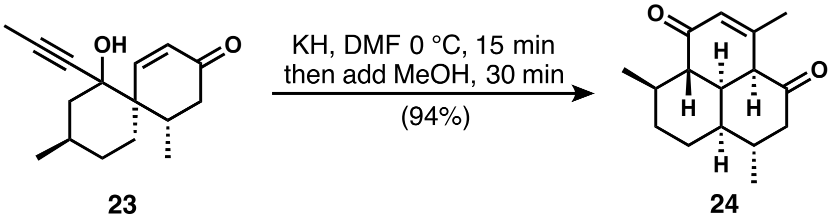
Major diastereomer: **^{1}H NMR (500 MHz, CDCl$_3$)** δ 6.56 (dd, *J* = 10.4, 2.0 Hz, 1H), 6.10 (d, *J* = 10.3 Hz, 1H), 3.49 (dd, *J* = 17.3, 5.9 Hz, 1H), 2.63 – 2.50 (m, 1H), 2.16 (s, 1H), 2.06 (d, *J* = 17.3 Hz, 1H), 1.96 – 1.89 (m, 1H), 1.88 – 1.82 (m, 4H), 1.79 – 1.66 (m, 3H), 1.55 – 1.49 (m, 1H), 0.98 (d, *J* = 2.0 Hz, 3H), 0.96 (d, *J* = 2.8 Hz, 3H).

^{13}C NMR (126 MHz, CDCl$_3$) δ 200.7, 153.5, 130.0, 83.0, 81.5, 76.0, 45.7, 44.5, 44.5, 33.0, 30.6, 29.6, 28.7, 21.9, 18.4, 3.7.

HRMS (ESI) m/z calculated for $C_{16}H_{22}O_2Na$ $[M+Na]^+$ 269.1512, found 269.1512

IR (film) 3386, 2922, 2869, 1665 cm^{-1}.

$[\alpha]^{22}_{D}$ = +130.6 (*c* = 1.0, CHCl$_3$).



Tricyclic enone 24: To a suspension of KH (32.0 mg, 0.80 mmol, 4.0 equiv.) in anhydrous DMF (1.0 mL) at 0 °C was added a solution of the alcohol **23** (50 mg, 0.20 mmol, 1.0 equiv.) in anhydrous DMF (1.0 mL). The color immediately turned into a dark red and after 15 min the color changed to a yellow/brown color. After the color change, methanol (1 mL) was added and stirring was continued for 30 min, at which time water (5 mL) was added and the resulting mixture was extracted with EtOAc (3×10 mL). The combined organic extracts were washed with brine (10 mL) and dried over MgSO$_4$. The volatiles were removed under reduced pressure and purification by flash chromatography (hexanes/EtOAc = 4/1) afforded the desired product **24** as a yellow solid (48 mg, 94%). This compound was characterized by X-ray crystallography; the structure and associated data can be found in Section II.

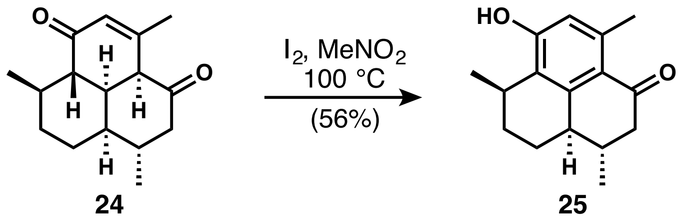
^{1}H NMR (500 MHz, CDCl$_3$) δ 5.89 (d, *J* = 1.2 Hz, 1H), 3.22 (d, *J* = 5.7 Hz, 1H), 2.63 – 2.51 (m, 1H), 2.45 (dd, *J* = 11.9, 3.2 Hz, 1H), 2.31 – 2.13 (m, 2H), 1.92 (d, *J* = 1.0 Hz, 3H), 1.91 – 1.87 (m, 1H), 1.87 – 1.79 (m, 2H), 1.77 – 1.62 (m, 1H), 1.59 – 1.49 (m, 1H), 1.45 (tt, *J* = 14.0, 3.7 Hz, 1H), 1.18 – 1.09 (m, 4H), 1.03 (d, *J* = 6.1 Hz, 3H).

^{13}C NMR (126 MHz, CDCl$_3$) δ 208.8, 200.9, 156.0, 128.6, 57.8, 50.1, 48.4, 47.7, 42.8, 31.4, 31.2, 28.9, 26.1, 23.9, 22.6, 19.7.

IR (film) 2931, 2862, 1708, 1661 cm^{-1}.

HRMS (ESI) m/z calculated for $C_{16}H_{22}O_2Na$ $[M+Na]^+$ 269.1512, found 269.1520.

$[\alpha]^{22}_{D}$ = −100.3 (*c* = 1.0, CHCl$_3$).



Phenol 25: Enone **24** (0.10 g, 0.41 mmol, 1.0 equiv.) and iodine (0.62 g, 2.4 mmol, 6.0 equiv.) were dissolved in anhydrous $MeNO_2$ (4.0 mL) under an argon atmosphere and heated to 100 °C for 6 h. $Na_2S_2O_3$ (sat. aq., 4 mL) was added and stirring was continued for 30 min. The resulting mixture was extracted with EtOAc (5×5 mL). The combined organic extracts were washed with brine (10 mL) and dried over $MgSO_4$. The volatiles were removed under reduced pressure and purification by flash chromatography (hexanes/acetone = 10/1) afforded the desired product as a red solid (56 mg, 56%).

^{1}H NMR (500 MHz, CDCl$_3$) δ 6.55 (s, 1H), 5.81 (s, 1H), 3.25 – 3.05 (m, 1H), 2.71 (dd, J = 17.7, 4.3 Hz, 1H), 2.57 (s, 3H), 2.39 – 2.30 (m, 1H), 2.30 – 2.14 (m, 1H), 2.11 – 1.99 (m, 1H), 1.96 – 1.85 (m, 1H), 1.85 – 1.78 (m, 2H), 1.58 – 1.45 (m, 1H), 1.24 (d, J = 7.0 Hz, 3H), 1.11 (d, J = 6.5 Hz, 3H).

^{13}C NMR (126 MHz, CDCl$_3$) δ 199.8, 157.1, 146.4, 142.0, 125.7, 125.1, 117.5, 49.5, 44.1, 35.7, 29.1, 26.9, 23.7, 22.2, 21.1, 19.4.

IR (film) 3137 (br), 2922, 2865, 1628, 1574 cm^{-1}.

HRMS (ESI) m/z calculated for $C_{16}H_{19}O_2$ [M-H]$^-$ 243.1385, found 243.1376.

$[\alpha]^{22}_D$ = +11.0 (c = 1.0, $CHCl_3$).

II. Data from X-ray Crystal Structures

Definitions:

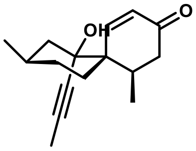
$wR2 = [\Sigma[w(F_o^2-F_c^2)^2] / \Sigma[w(F_o^2)^2]]^{1/2}$

$R1 = \Sigma||F_o|-|F_c|| / \Sigma|F_o|$

$Goof = S = [\Sigma[w(F_o^2-F_c^2)^2] / (n-p)]^{1/2}$ where n is the number of reflections and p is the total number of parameters refined.

The thermal ellipsoid plot is shown at the 50% probability level.

X-ray Data Collection, Structure Solution and Refinement for alcohol 11' (cdv62)



11'

A colorless crystal of approximate dimensions 0.160 x 0.183 x 0.200 mm was mounted in a cryoloop and transferred to a Bruker SMART APEX II diffractometer. The APEX2[4] program package was used to determine the unit-cell parameters and for data collection (45 sec/frame scan time for a sphere of diffraction data). The raw frame data was processed using SAINT[5] and SADABS[6] to yield the reflection data file. Subsequent calculations were carried out using the SHELXTL[7] program. The diffraction symmetry was *mmm* and the systematic absences were consistent with the orthorhombic space group $P2_12_12_1$ that was later determined to be correct.

The structure was solved by dual space methods and refined on F^2 by full-matrix least-squares techniques. The analytical scattering factors[8] for neutral atoms were used throughout the analysis. Hydrogen atom H(1) was located from a difference-Fourier map and refined (x,y,z and U_{iso}). The remaining hydrogen atoms were included using a riding model.

Least squares analysis yielded wR2 = 0.0889 and Goof = 1.040 for 170 variables refined against 3419 data (0.73 Å), R1 = 0.0391 for those 3113 data with $I > 2.0\sigma(I)$. Due to the absence of any atom heavier than oxygen, the absolute structure could not be assigned by refinement of the Flack parameter[6].

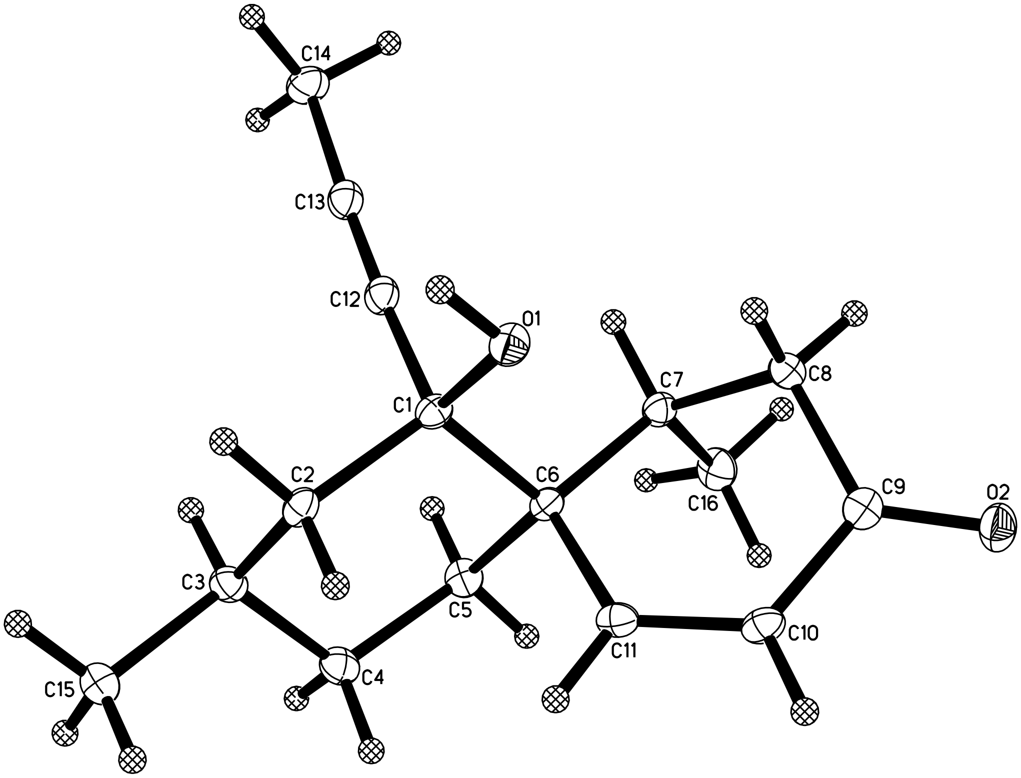

C14
C13
C12
O1
C1
C7
C8
C2
C6
C16
C9
O2
C3
C5
C11
C10
C15
C4

Table 1. Crystal data and structure refinement for cdv62.

Identification code	cdv62 (Vincenzo Ramella)	
Empirical formula	$C_{16} H_{22} O_2$	
Formula weight	246.33	
Temperature	88(2) K	
Wavelength	0.71073 Å	
Crystal system	Orthorhombic	
Space group	$P2_12_12_1$	
Unit cell dimensions	a = 8.2997(8) Å	α = 90°.
	b = 12.6503(12) Å	β = 90°.
	c = 12.9757(12) Å	γ = 90°.
Volume	1362.4(2) Å^3	
Z	4	
Density (calculated)	1.201 Mg/m^3	
Absorption coefficient	0.077 mm^{-1}	
F(000)	536	
Crystal color	colorless	
Crystal size	0.200 x 0.183 x 0.160 mm^3	
Theta range for data collection	2.248 to 29.131°	
Index ranges	$-11 \leq h \leq 10$, $-17 \leq k \leq 17$, $-17 \leq l \leq 17$	
Reflections collected	12526	
Independent reflections	3419 [R(int) = 0.0378]	
Completeness to theta = 25.500°	100.0 %	
Absorption correction	Semi-empirical from equivalents	
Max. and min. transmission	0.8621 and 0.8205	
Refinement method	Full-matrix least-squares on F^2	
Data / restraints / parameters	3419 / 0 / 170	
Goodness-of-fit on F^2	1.040	
Final R indices [I>2sigma(I) = 3113 data]	R1 = 0.0391, wR2 = 0.0846	
R indices (all data, 0.73 Å)	R1 = 0.0458, wR2 = 0.0889	
Largest diff. peak and hole	0.291 and -0.169 e.Å^{-3}	

Table 2. Atomic coordinates (x 10^4) and equivalent isotropic displacement parameters (Å^2 x 10^3) for cdv62. U(eq) is defined as one third of the trace of the orthogonalized U^{ij} tensor.

	x	y	z	U(eq)
O(1)	3128(2)	5375(1)	4807(1)	13(1)
O(2)	2233(2)	3430(1)	1673(1)	17(1)
C(1)	4712(2)	4980(1)	5043(1)	11(1)
C(2)	5866(2)	5925(1)	5164(1)	12(1)
C(3)	7624(2)	5610(2)	5342(1)	13(1)
C(4)	8174(2)	4870(2)	4483(2)	15(1)
C(5)	7034(2)	3934(2)	4329(2)	14(1)
C(6)	5243(2)	4233(1)	4133(1)	11(1)
C(7)	4180(2)	3217(2)	4088(1)	12(1)
C(8)	2574(2)	3413(2)	3514(1)	13(1)
C(9)	2909(2)	3790(1)	2436(1)	13(1)
C(10)	4115(2)	4631(2)	2358(1)	13(1)
C(11)	5138(2)	4838(2)	3125(1)	12(1)
C(12)	4633(2)	4373(2)	6022(1)	13(1)
C(13)	4436(2)	3916(2)	6816(2)	14(1)
C(14)	4135(2)	3337(2)	7781(1)	17(1)
C(15)	8682(2)	6598(2)	5407(2)	16(1)
C(16)	4999(2)	2255(2)	3595(2)	17(1)

Table 3. Bond lengths [Å] and angles [°] for cdv62.

O(1)-C(1)	1.439(2)
O(2)-C(9)	1.226(2)
C(1)-C(12)	1.485(2)
C(1)-C(2)	1.540(3)
C(1)-C(6)	1.575(2)
C(2)-C(3)	1.530(2)
C(3)-C(4)	1.526(3)
C(3)-C(15)	1.530(3)
C(4)-C(5)	1.529(3)
C(5)-C(6)	1.555(2)
C(6)-C(11)	1.518(3)
C(6)-C(7)	1.560(3)
C(7)-C(16)	1.534(3)
C(7)-C(8)	1.547(3)
C(8)-C(9)	1.504(2)
C(9)-C(10)	1.464(3)
C(10)-C(11)	1.334(3)
C(12)-C(13)	1.193(3)
C(13)-C(14)	1.472(3)
O(1)-C(1)-C(12)	108.70(15)
O(1)-C(1)-C(2)	108.67(14)
C(12)-C(1)-C(2)	109.92(15)
O(1)-C(1)-C(6)	107.74(14)
C(12)-C(1)-C(6)	110.10(15)
C(2)-C(1)-C(6)	111.62(14)
C(3)-C(2)-C(1)	114.00(15)
C(4)-C(3)-C(15)	111.71(15)
C(4)-C(3)-C(2)	109.56(15)
C(15)-C(3)-C(2)	110.08(15)
C(3)-C(4)-C(5)	112.66(15)
C(4)-C(5)-C(6)	115.18(15)
C(11)-C(6)-C(5)	108.57(15)
C(11)-C(6)-C(7)	110.56(15)

C(5)-C(6)-C(7)	110.31(14)
C(11)-C(6)-C(1)	109.08(14)
C(5)-C(6)-C(1)	106.87(14)
C(7)-C(6)-C(1)	111.33(15)
C(16)-C(7)-C(8)	107.97(15)
C(16)-C(7)-C(6)	114.73(15)
C(8)-C(7)-C(6)	111.92(15)
C(9)-C(8)-C(7)	109.84(15)
O(2)-C(9)-C(10)	121.86(17)
O(2)-C(9)-C(8)	123.28(16)
C(10)-C(9)-C(8)	114.85(16)
C(11)-C(10)-C(9)	121.78(17)
C(10)-C(11)-C(6)	125.44(17)
C(13)-C(12)-C(1)	174.4(2)
C(12)-C(13)-C(14)	177.8(2)

Table 4. Anisotropic displacement parameters ($Å^2 \times 10^3$) for cdv62. The anisotropic displacement factor exponent takes the form: $-2p^2[h^2 a^{*2}U^{11} + ... + 2 h k a^* b^* U^{12}]$

	U^{11}	U^{22}	U^{33}	U^{23}	U^{13}	U^{12}
O(1)	12(1)	15(1)	13(1)	-2(1)	-1(1)	4(1)
O(2)	19(1)	17(1)	14(1)	1(1)	-5(1)	-1(1)
C(1)	11(1)	12(1)	10(1)	0(1)	1(1)	2(1)
C(2)	15(1)	10(1)	10(1)	-1(1)	0(1)	1(1)
C(3)	13(1)	13(1)	12(1)	2(1)	-1(1)	-1(1)
C(4)	11(1)	16(1)	16(1)	0(1)	0(1)	1(1)
C(5)	13(1)	12(1)	16(1)	-2(1)	1(1)	3(1)
C(6)	12(1)	11(1)	9(1)	0(1)	1(1)	0(1)
C(7)	15(1)	12(1)	10(1)	1(1)	0(1)	-2(1)
C(8)	13(1)	14(1)	14(1)	0(1)	1(1)	-3(1)
C(9)	13(1)	12(1)	14(1)	1(1)	-1(1)	3(1)
C(10)	17(1)	11(1)	11(1)	2(1)	2(1)	0(1)
C(11)	15(1)	9(1)	13(1)	0(1)	4(1)	0(1)
C(12)	13(1)	13(1)	13(1)	-3(1)	0(1)	1(1)
C(13)	13(1)	14(1)	14(1)	-2(1)	-1(1)	1(1)
C(14)	19(1)	20(1)	13(1)	4(1)	1(1)	0(1)
C(15)	14(1)	17(1)	16(1)	-1(1)	-1(1)	-3(1)
C(16)	20(1)	12(1)	19(1)	-1(1)	0(1)	-1(1)

Table 5. Hydrogen coordinates (x 10^4) and isotropic displacement parameters (Å^2 x 10^3) for cdv62.

	x	y	z	U(eq)
H(2A)	5803	6367	4536	14
H(2B)	5500	6362	5753	14
H(3A)	7698	5223	6013	15
H(4A)	9264	4600	4648	18
H(4B)	8249	5273	3831	18
H(5A)	7087	3479	4949	16
H(5B)	7424	3511	3738	16
H(7A)	3906	3022	4814	15
H(8A)	1940	2751	3490	16
H(8B)	1934	3951	3888	16
H(10A)	4171	5041	1746	16
H(11A)	5861	5413	3033	15
H(14A)	3436	2730	7641	26
H(14B)	3608	3807	8277	26
H(14C)	5160	3089	8066	26
H(15A)	9815	6388	5468	24
H(15B)	8373	7015	6012	24
H(15C)	8537	7024	4783	24
H(16A)	4243	1660	3581	26
H(16B)	5951	2060	4000	26
H(16C)	5327	2430	2890	26
H(1)	2900(30)	5760(20)	5320(20)	32(7)

Table 6. Torsion angles [°] for cdv62.

O(1)-C(1)-C(2)-C(3)	-175.91(14)
C(12)-C(1)-C(2)-C(3)	65.24(19)
C(6)-C(1)-C(2)-C(3)	-57.2(2)
C(1)-C(2)-C(3)-C(4)	54.4(2)
C(1)-C(2)-C(3)-C(15)	177.60(15)
C(15)-C(3)-C(4)-C(5)	-174.05(16)
C(2)-C(3)-C(4)-C(5)	-51.8(2)
C(3)-C(4)-C(5)-C(6)	55.0(2)
C(4)-C(5)-C(6)-C(11)	63.8(2)
C(4)-C(5)-C(6)-C(7)	-174.89(15)
C(4)-C(5)-C(6)-C(1)	-53.7(2)
O(1)-C(1)-C(6)-C(11)	55.47(18)
C(12)-C(1)-C(6)-C(11)	173.87(15)
C(2)-C(1)-C(6)-C(11)	-63.76(19)
O(1)-C(1)-C(6)-C(5)	172.67(14)
C(12)-C(1)-C(6)-C(5)	-68.93(18)
C(2)-C(1)-C(6)-C(5)	53.44(18)
O(1)-C(1)-C(6)-C(7)	-66.80(18)
C(12)-C(1)-C(6)-C(7)	51.6(2)
C(2)-C(1)-C(6)-C(7)	173.96(15)
C(11)-C(6)-C(7)-C(16)	84.59(19)
C(5)-C(6)-C(7)-C(16)	-35.5(2)
C(1)-C(6)-C(7)-C(16)	-154.00(15)
C(11)-C(6)-C(7)-C(8)	-38.9(2)
C(5)-C(6)-C(7)-C(8)	-158.99(15)
C(1)-C(6)-C(7)-C(8)	82.53(18)
C(16)-C(7)-C(8)-C(9)	-68.83(18)
C(6)-C(7)-C(8)-C(9)	58.37(19)
C(7)-C(8)-C(9)-O(2)	133.14(18)
C(7)-C(8)-C(9)-C(10)	-47.0(2)
O(2)-C(9)-C(10)-C(11)	-162.57(18)
C(8)-C(9)-C(10)-C(11)	17.6(3)
C(9)-C(10)-C(11)-C(6)	2.3(3)
C(5)-C(6)-C(11)-C(10)	130.20(19)

C(7)-C(6)-C(11)-C(10)	9.1(3)
C(1)-C(6)-C(11)-C(10)	-113.7(2)

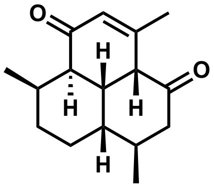
Table 7. Hydrogen bonds for cdv62 [Å and °].

D-H...A	d(D-H)	d(H...A)	d(D...A)	<(DHA)
O(1)-H(1)...O(2)#1	0.84(3)	2.04(3)	2.869(2)	168(3)

Symmetry transformations used to generate equivalent atoms:

#1 -x+1/2,-y+1,z+1/2

X-ray Data Collection, Structure Solution and Refinement for tricyclic enone 18 (cdv53).



18

A colorless crystal of approximate dimensions 0.142 x 0.161 x 0.326 mm was mounted on a glass fiber and transferred to a Bruker SMART APEX II diffractometer. The APEX2[4] program package was used to determine the unit-cell parameters and for data collection (30 sec/frame scan time for a sphere of diffraction data). The raw frame data was processed using SAINT[5] and SADABS[6] to yield the reflection data file. Subsequent calculations were carried out using the SHELXTL[7] program. The diffraction symmetry was 2/*m* and the systematic absences were consistent with the monoclinic space groups *Cc* and *C*2/*c*. It was later determined that space group *C*2/*c* was correct.

The structure was solved by direct methods and refined on F^2 by full-matrix least-squares techniques. The analytical scattering factors[8] for neutral atoms were used throughout the analysis. Hydrogen atoms were located from a difference-Fourier map and refined (x,y,z and U_{iso}).

Least-squares analysis yielded wR2 = 0.1067 and Goof = 1.046 for 251 variables refined against 2937 data (0.78 Å), R1 = 0.0388 for those 2474 data with $I > 2.0\sigma(I)$.

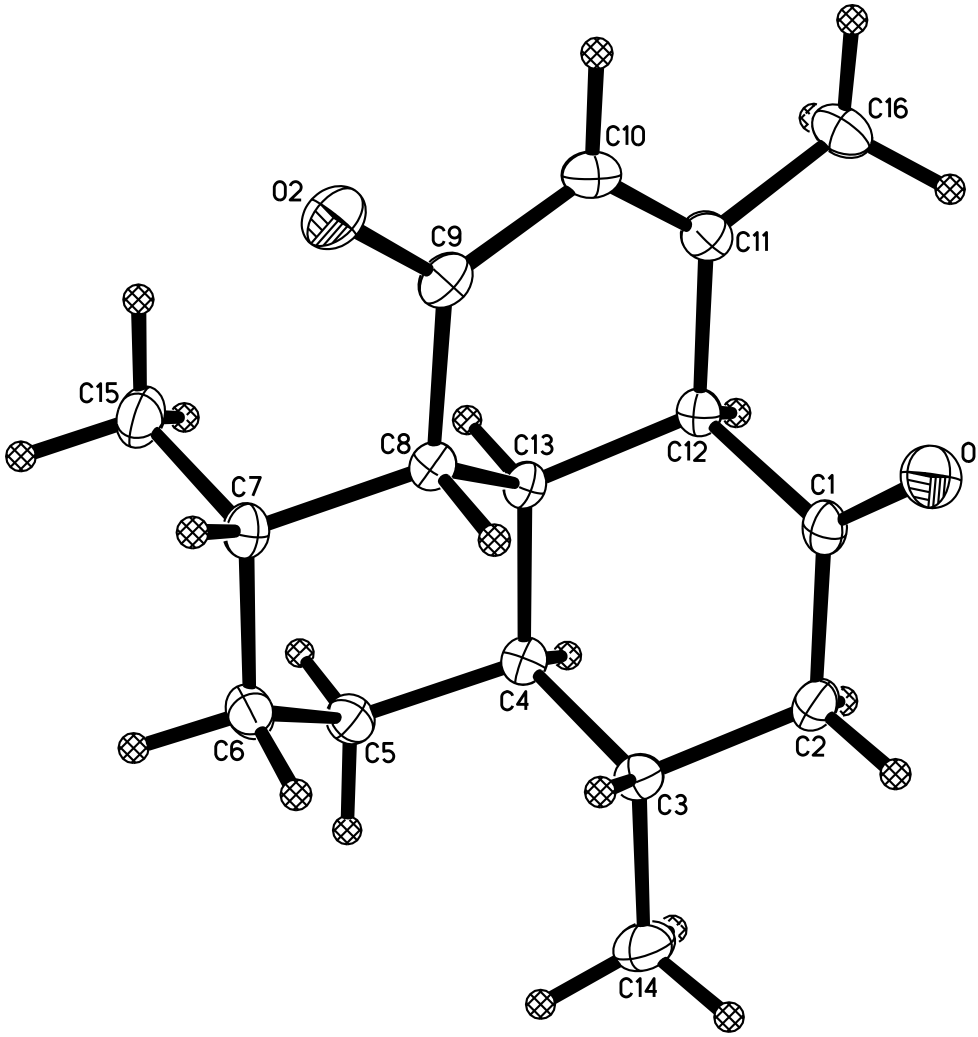

C16
C10
O2
C9
C11
C15
C8
C13
C12
O1
C7
C1
C4
C6
C5
C2
C3
C14

Table 1. Crystal data and structure refinement for cdv53.

Identification code	cdv53 (Vincenzo Ramella)	
Empirical formula	$C_{16} H_{22} O_2$	
Formula weight	246.33	
Temperature	133(2) K	
Wavelength	0.71073 Å	
Crystal system	Monoclinic	
Space group	*C*2/*c*	
Unit cell dimensions	a = 17.6844(13) Å	α = 90°.
	b = 14.2786(10) Å	β = 107.4578(9)°.
	c = 11.0138(8) Å	γ = 90°.
Volume	2653.0(3) $Å^3$	
Z	8	
Density (calculated)	1.233 Mg/m^3	
Absorption coefficient	0.079 mm^{-1}	
F(000)	1072	
Crystal color	colorless	
Crystal size	0.326 x 0.161 x 0.142 mm^3	
Theta range for data collection	1.869 to 27.100°	
Index ranges	$-22 \le h \le 22$, $-18 \le k \le 18$, $-14 \le l \le 14$	
Reflections collected	15111	
Independent reflections	2937 [R(int) = 0.0254]	
Completeness to theta = 25.500°	100.0 %	
Absorption correction	Semi-empirical from equivalents	
Max. and min. transmission	0.8621 and 0.8151	
Refinement method	Full-matrix least-squares on F^2	
Data / restraints / parameters	2937 / 0 / 251	
Goodness-of-fit on F^2	1.046	
Final R indices [I>2sigma(I) = 2474 data]	R1 = 0.0388, wR2 = 0.0994	
R indices (all data, 0.78 Å)	R1 = 0.0485, wR2 = 0.1067	
Largest diff. peak and hole	0.380 and -0.180 $e.Å^{-3}$	

Table 2. Atomic coordinates (x 10^4) and equivalent isotropic displacement parameters (Å^2 x 10^3) for cdv53. U(eq) is defined as one third of the trace of the orthogonalized U^{ij} tensor.

	x	y	z	U(eq)
O(1)	1500(1)	4081(1)	4448(1)	25(1)
O(2)	1784(1)	1329(1)	1792(1)	23(1)
C(1)	2091(1)	4239(1)	4139(1)	16(1)
C(2)	2857(1)	4555(1)	5066(1)	18(1)
C(3)	3567(1)	3949(1)	5015(1)	16(1)
C(4)	3610(1)	3914(1)	3638(1)	15(1)
C(5)	4298(1)	3321(1)	3478(1)	18(1)
C(6)	4176(1)	2272(1)	3647(1)	19(1)
C(7)	3396(1)	1909(1)	2732(1)	17(1)
C(8)	2703(1)	2508(1)	2881(1)	14(1)
C(9)	1899(1)	2163(1)	2055(1)	16(1)
C(10)	1257(1)	2846(1)	1615(1)	18(1)
C(11)	1335(1)	3756(1)	1916(1)	16(1)
C(12)	2107(1)	4137(1)	2763(1)	14(1)
C(13)	2830(1)	3558(1)	2697(1)	13(1)
C(14)	4319(1)	4346(1)	5951(1)	28(1)
C(15)	3429(1)	1868(1)	1357(1)	23(1)
C(16)	675(1)	4445(1)	1442(1)	23(1)

Table 3. Bond lengths [Å] and angles [°] for cdv53.

O(1)-C(1)	1.2131(14)
O(2)-C(9)	1.2276(14)
C(1)-C(2)	1.5006(16)
C(1)-C(12)	1.5309(15)
C(2)-C(3)	1.5393(16)
C(3)-C(14)	1.5261(17)
C(3)-C(4)	1.5422(15)
C(4)-C(5)	1.5347(16)
C(4)-C(13)	1.5429(15)
C(5)-C(6)	1.5315(17)
C(6)-C(7)	1.5352(16)
C(7)-C(15)	1.5343(16)
C(7)-C(8)	1.5429(16)
C(8)-C(9)	1.5226(16)
C(8)-C(13)	1.5378(15)
C(9)-C(10)	1.4641(16)
C(10)-C(11)	1.3377(17)
C(11)-C(16)	1.4972(16)
C(11)-C(12)	1.5050(16)
C(12)-C(13)	1.5414(15)
O(1)-C(1)-C(2)	122.84(10)
O(1)-C(1)-C(12)	122.22(10)
C(2)-C(1)-C(12)	114.94(9)
C(1)-C(2)-C(3)	112.66(9)
C(14)-C(3)-C(2)	108.77(10)
C(14)-C(3)-C(4)	112.67(10)
C(2)-C(3)-C(4)	109.62(9)
C(5)-C(4)-C(3)	113.94(9)
C(5)-C(4)-C(13)	108.69(9)
C(3)-C(4)-C(13)	111.88(9)
C(6)-C(5)-C(4)	112.42(9)
C(5)-C(6)-C(7)	112.45(10)
C(15)-C(7)-C(6)	111.58(10)

C(15)-C(7)-C(8)	113.10(10)
C(6)-C(7)-C(8)	109.18(9)
C(9)-C(8)-C(13)	112.55(9)
C(9)-C(8)-C(7)	112.71(9)
C(13)-C(8)-C(7)	112.06(9)
O(2)-C(9)-C(10)	120.73(11)
O(2)-C(9)-C(8)	120.87(11)
C(10)-C(9)-C(8)	118.37(10)
C(11)-C(10)-C(9)	123.48(11)
C(10)-C(11)-C(16)	122.67(11)
C(10)-C(11)-C(12)	120.82(10)
C(16)-C(11)-C(12)	116.51(10)
C(11)-C(12)-C(1)	111.44(9)
C(11)-C(12)-C(13)	112.79(9)
C(1)-C(12)-C(13)	111.06(9)
C(8)-C(13)-C(12)	111.16(9)
C(8)-C(13)-C(4)	111.67(9)
C(12)-C(13)-C(4)	112.27(9)

Table 4. Anisotropic displacement parameters ($Å^2$ x 10^3) for cdv53. The anisotropic displacement factor exponent takes the form: $-2\pi^2[h^2 a^{*2}U^{11} + ... + 2 h k a^* b^* U^{12}]$

	U^{11}	U^{22}	U^{33}	U^{23}	U^{13}	U^{12}
O(1)	20(1)	37(1)	21(1)	1(1)	10(1)	-1(1)
O(2)	26(1)	16(1)	27(1)	-5(1)	6(1)	-5(1)
C(1)	20(1)	12(1)	17(1)	2(1)	7(1)	4(1)
C(2)	22(1)	18(1)	14(1)	-2(1)	7(1)	1(1)
C(3)	17(1)	16(1)	15(1)	-1(1)	4(1)	-1(1)
C(4)	16(1)	13(1)	16(1)	0(1)	6(1)	-2(1)
C(5)	15(1)	20(1)	20(1)	-1(1)	6(1)	-1(1)
C(6)	17(1)	18(1)	22(1)	0(1)	6(1)	3(1)
C(7)	19(1)	13(1)	19(1)	-1(1)	6(1)	2(1)
C(8)	16(1)	12(1)	13(1)	1(1)	5(1)	-1(1)
C(9)	21(1)	16(1)	14(1)	0(1)	7(1)	-2(1)
C(10)	16(1)	21(1)	16(1)	0(1)	2(1)	-3(1)
C(11)	16(1)	19(1)	13(1)	4(1)	5(1)	1(1)
C(12)	16(1)	12(1)	14(1)	2(1)	5(1)	1(1)
C(13)	16(1)	12(1)	12(1)	1(1)	6(1)	0(1)
C(14)	21(1)	38(1)	21(1)	-9(1)	2(1)	-4(1)
C(15)	25(1)	23(1)	23(1)	-5(1)	11(1)	1(1)
C(16)	18(1)	23(1)	26(1)	4(1)	2(1)	3(1)

Table 5. Hydrogen coordinates (x 10^4) and isotropic displacement parameters (Å^2 x 10^3) for cdv53.

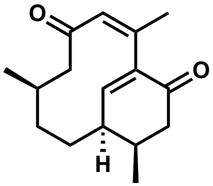
	x	y	z	U(eq)
H(2A)	2796(9)	4546(11)	5910(15)	27(4)
H(2B)	2966(8)	5188(11)	4822(14)	24(4)
H(3A)	3493(8)	3306(10)	5306(13)	18(3)
H(4A)	3684(8)	4561(10)	3401(13)	17(3)
H(5A)	4341(8)	3433(10)	2626(14)	21(3)
H(5B)	4815(9)	3520(10)	4093(14)	21(4)
H(6A)	4190(8)	2150(10)	4534(14)	21(4)
H(6B)	4621(9)	1916(11)	3505(14)	25(4)
H(7A)	3308(9)	1277(10)	2992(14)	20(3)
H(8A)	2679(8)	2414(10)	3770(13)	17(3)
H(10A)	759(9)	2604(11)	1087(14)	26(4)
H(12A)	2178(8)	4787(10)	2502(12)	16(3)
H(13A)	2865(7)	3661(9)	1819(12)	10(3)
H(14A)	4784(11)	3952(12)	6043(16)	38(4)
H(14B)	4244(9)	4419(11)	6788(16)	33(4)
H(14C)	4425(10)	4974(13)	5652(17)	42(5)
H(15A)	3857(10)	1423(12)	1288(16)	39(4)
H(15B)	3542(9)	2493(12)	1037(15)	32(4)
H(15C)	2924(10)	1639(12)	778(16)	31(4)
H(16A)	177(11)	4134(12)	1014(17)	41(5)
H(16B)	816(9)	4866(11)	834(15)	31(4)
H(16C)	617(9)	4837(11)	2150(15)	29(4)

Table 6. Torsion angles [°] for cdv53.

O(1)-C(1)-C(2)-C(3)	127.98(12)
C(12)-C(1)-C(2)-C(3)	-52.48(13)
C(1)-C(2)-C(3)-C(14)	177.88(10)
C(1)-C(2)-C(3)-C(4)	54.29(12)
C(14)-C(3)-C(4)-C(5)	59.06(13)
C(2)-C(3)-C(4)-C(5)	-179.67(9)
C(14)-C(3)-C(4)-C(13)	-177.16(10)
C(2)-C(3)-C(4)-C(13)	-55.89(12)
C(3)-C(4)-C(5)-C(6)	69.72(13)
C(13)-C(4)-C(5)-C(6)	-55.78(12)
C(4)-C(5)-C(6)-C(7)	56.59(13)
C(5)-C(6)-C(7)-C(15)	71.56(12)
C(5)-C(6)-C(7)-C(8)	-54.20(13)
C(15)-C(7)-C(8)-C(9)	58.12(13)
C(6)-C(7)-C(8)-C(9)	-177.00(9)
C(15)-C(7)-C(8)-C(13)	-70.06(12)
C(6)-C(7)-C(8)-C(13)	54.82(12)
C(13)-C(8)-C(9)-O(2)	158.55(10)
C(7)-C(8)-C(9)-O(2)	30.62(14)
C(13)-C(8)-C(9)-C(10)	-23.43(13)
C(7)-C(8)-C(9)-C(10)	-151.35(10)
O(2)-C(9)-C(10)-C(11)	177.00(11)
C(8)-C(9)-C(10)-C(11)	-1.02(17)
C(9)-C(10)-C(11)-C(16)	179.12(11)
C(9)-C(10)-C(11)-C(12)	-0.92(17)
C(10)-C(11)-C(12)-C(1)	-98.57(12)
C(16)-C(11)-C(12)-C(1)	81.38(12)
C(10)-C(11)-C(12)-C(13)	27.15(14)
C(16)-C(11)-C(12)-C(13)	-152.89(10)
O(1)-C(1)-C(12)-C(11)	-4.32(15)
C(2)-C(1)-C(12)-C(11)	176.15(10)
O(1)-C(1)-C(12)-C(13)	-130.99(11)
C(2)-C(1)-C(12)-C(13)	49.47(12)
C(9)-C(8)-C(13)-C(12)	48.03(12)

C(7)-C(8)-C(13)-C(12)	176.29(9)
C(9)-C(8)-C(13)-C(4)	174.25(9)
C(7)-C(8)-C(13)-C(4)	-57.48(12)
C(11)-C(12)-C(13)-C(8)	-50.12(12)
C(1)-C(12)-C(13)-C(8)	75.81(11)
C(11)-C(12)-C(13)-C(4)	-176.01(9)
C(1)-C(12)-C(13)-C(4)	-50.08(12)
C(5)-C(4)-C(13)-C(8)	56.17(11)
C(3)-C(4)-C(13)-C(8)	-70.52(12)
C(5)-C(4)-C(13)-C(12)	-178.21(9)
C(3)-C(4)-C(13)-C(12)	55.10(12)

X-ray Data Collection, Structure Solution and Refinement for bicyclic dienedione 20 (cdv 50).



20

A colorless crystal of approximate dimensions 0.238 x 0.287 x 0.299 mm was mounted on a glass fiber and transferred to a Bruker SMART APEX II diffractometer. The APEX2[4] program package was used to determine the unit-cell parameters and for data collection (20 sec/frame scan time for a sphere of diffraction data). The raw frame data was processed using SAINT[5] and SADABS[6] to yield the reflection data file. Subsequent calculations were carried out using the SHELXTL[7] program. The diffraction symmetry was 2/*m* and the systematic absences were consistent with the monoclinic space group $P2_1/n$ that was later determined to be correct.

The structure was solved by direct methods and refined on F^2 by full-matrix least-squares techniques. The analytical scattering factors[8] for neutral atoms were used throughout the analysis. Hydrogen atoms were located from a difference-Fourier map and refined (x,y,z and U_{iso}).

Least-squares analysis yielded wR2 = 0.0959 and Goof = 1.049 for 251 variables refined against 3450 data (0.73 Å), R1 = 0.0364 for those 3066 data with $I > 2.0\sigma(I)$.

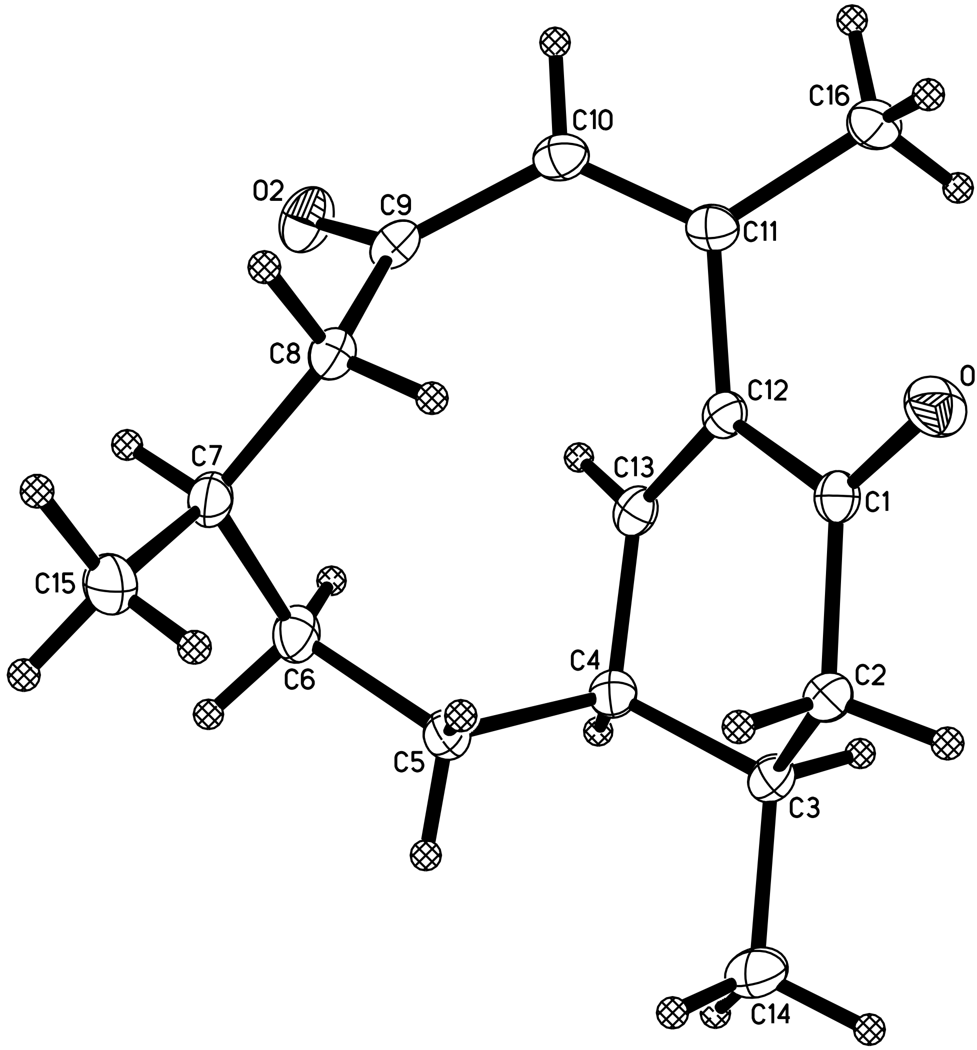

O2
C9
C10
C16
C11
C8
C12
O1
C7
C13
C1
C15
C6
C4
C2
C5
C3
C14

Table 1. Crystal data and structure refinement for cdv50.

Identification code	cdv50 (Vincenzo Ramella)	
Empirical formula	$C_{16} H_{22} O_2$	
Formula weight	246.33	
Temperature	88(2) K	
Wavelength	0.71073 Å	
Crystal system	Monoclinic	
Space group	$P2_1/n$	
Unit cell dimensions	a = 14.1975(5) Å	α = 90°.
	b = 6.6489(2) Å	β = 109.0023(4)°.
	c = 15.1788(6) Å	γ = 90°.
Volume	1354.76(8) $Å^3$	
Z	4	
Density (calculated)	1.208 Mg/m^3	
Absorption coefficient	0.078 mm^{-1}	
F(000)	536	
Crystal color	colorless	
Crystal size	0.299 x 0.287 x 0.238 mm^3	
Theta range for data collection	1.707 to 29.157°	
Index ranges	$-18 \le h \le 19$, $-8\ k \le 9$, $-20 \le l \le 19$	
Reflections collected	16200	
Independent reflections	3450 [R(int) = 0.0163]	
Completeness to theta = 25.500°	100.0 %	
Absorption correction	Semi-empirical from equivalents	
Max. and min. transmission	0.8621 and 0.8470	
Refinement method	Full-matrix least-squares on F^2	
Data / restraints / parameters	3450 / 0 / 251	
Goodness-of-fit on F^2	1.049	
Final R indices [I>2sigma(I) = 3066 data]	R1 = 0.0364, wR2 = 0.0912	
R indices (all data, 0.73 Å)	R1 = 0.0419, wR2 = 0.0959	
Largest diff. peak and hole	0.362 and -0.174 $e.Å^{-3}$	

Table 2. Atomic coordinates (x 10^4) and equivalent isotropic displacement parameters (Å^2 x 10^3) for cdv50. U(eq) is defined as one third of the trace of the orthogonalized U^{ij} tensor.

	x	y	z	U(eq)
O(1)	6207(1)	306(1)	974(1)	21(1)
O(2)	6131(1)	7183(1)	3496(1)	24(1)
C(1)	5532(1)	832(1)	1258(1)	14(1)
C(2)	4777(1)	-660(1)	1371(1)	15(1)
C(3)	3780(1)	256(2)	1346(1)	16(1)
C(4)	3952(1)	2045(2)	2023(1)	15(1)
C(5)	4343(1)	1435(2)	3068(1)	17(1)
C(6)	4646(1)	3227(2)	3754(1)	19(1)
C(7)	5766(1)	3435(2)	4312(1)	18(1)
C(8)	6447(1)	3663(2)	3715(1)	15(1)
C(9)	6335(1)	5617(2)	3174(1)	16(1)
C(10)	6579(1)	5680(2)	2288(1)	17(1)
C(11)	6213(1)	4464(1)	1548(1)	15(1)
C(12)	5444(1)	2949(1)	1544(1)	13(1)
C(13)	4678(1)	3480(1)	1837(1)	15(1)
C(14)	3087(1)	-1345(2)	1520(1)	25(1)
C(15)	6124(1)	1682(2)	4995(1)	24(1)
C(16)	6512(1)	4704(2)	686(1)	20(1)

Table 3. Bond lengths [Å] and angles [°] for cdv50.

O(1)-C(1)	1.2225(12)
O(2)-C(9)	1.2248(12)
C(1)-C(12)	1.4908(13)
C(1)-C(2)	1.5114(13)
C(2)-C(3)	1.5306(13)
C(2)-H(2A)	0.989(13)
C(2)-H(2B)	0.983(14)
C(3)-C(14)	1.5298(14)
C(3)-C(4)	1.5387(13)
C(3)-H(3A)	0.987(13)
C(4)-C(13)	1.4977(13)
C(4)-C(5)	1.5538(13)
C(4)-H(4A)	0.999(13)
C(5)-C(6)	1.5486(14)
C(5)-H(5A)	0.977(13)
C(5)-H(5B)	0.984(13)
C(6)-C(7)	1.5452(14)
C(6)-H(6A)	1.006(13)
C(6)-H(6B)	0.997(13)
C(7)-C(15)	1.5321(15)
C(7)-C(8)	1.5334(13)
C(7)-H(7A)	0.987(13)
C(8)-C(9)	1.5174(13)
C(8)-H(8A)	0.995(13)
C(8)-H(8B)	0.984(12)
C(9)-C(10)	1.4939(14)
C(10)-C(11)	1.3434(14)
C(10)-H(10A)	0.959(14)
C(11)-C(12)	1.4844(13)
C(11)-C(16)	1.5090(13)
C(12)-C(13)	1.3484(13)
C(13)-H(13A)	0.966(13)
C(14)-H(14A)	0.987(15)
C(14)-H(14B)	0.989(15)

C(14)-H(14C)	1.001(15)
C(15)-H(15A)	1.002(15)
C(15)-H(15B)	0.988(15)
C(15)-H(15C)	0.994(15)
C(16)-H(16A)	0.981(16)
C(16)-H(16B)	0.968(18)
C(16)-H(16C)	0.967(18)
O(1)-C(1)-C(12)	121.53(9)
O(1)-C(1)-C(2)	121.26(9)
C(12)-C(1)-C(2)	117.16(8)
C(1)-C(2)-C(3)	114.87(8)
C(1)-C(2)-H(2A)	105.3(8)
C(3)-C(2)-H(2A)	109.7(7)
C(1)-C(2)-H(2B)	107.8(8)
C(3)-C(2)-H(2B)	111.0(8)
H(2A)-C(2)-H(2B)	107.9(11)
C(14)-C(3)-C(2)	111.12(9)
C(14)-C(3)-C(4)	113.15(8)
C(2)-C(3)-C(4)	110.26(8)
C(14)-C(3)-H(3A)	107.9(7)
C(2)-C(3)-H(3A)	107.2(7)
C(4)-C(3)-H(3A)	107.0(7)
C(13)-C(4)-C(3)	109.62(8)
C(13)-C(4)-C(5)	108.60(7)
C(3)-C(4)-C(5)	113.98(8)
C(13)-C(4)-H(4A)	108.1(7)
C(3)-C(4)-H(4A)	109.0(7)
C(5)-C(4)-H(4A)	107.3(7)
C(6)-C(5)-C(4)	114.51(8)
C(6)-C(5)-H(5A)	109.1(8)
C(4)-C(5)-H(5A)	106.9(8)
C(6)-C(5)-H(5B)	109.7(8)
C(4)-C(5)-H(5B)	108.7(7)
H(5A)-C(5)-H(5B)	107.6(11)
C(7)-C(6)-C(5)	116.65(8)

C(7)-C(6)-H(6A)	109.4(7)
C(5)-C(6)-H(6A)	109.6(7)
C(7)-C(6)-H(6B)	106.7(8)
C(5)-C(6)-H(6B)	108.2(8)
H(6A)-C(6)-H(6B)	105.8(11)
C(15)-C(7)-C(8)	109.91(8)
C(15)-C(7)-C(6)	111.03(9)
C(8)-C(7)-C(6)	114.75(8)
C(15)-C(7)-H(7A)	109.0(7)
C(8)-C(7)-H(7A)	106.1(8)
C(6)-C(7)-H(7A)	105.7(8)
C(9)-C(8)-C(7)	115.49(8)
C(9)-C(8)-H(8A)	102.6(8)
C(7)-C(8)-H(8A)	108.5(7)
C(9)-C(8)-H(8B)	111.1(7)
C(7)-C(8)-H(8B)	111.6(7)
H(8A)-C(8)-H(8B)	106.7(10)
O(2)-C(9)-C(10)	119.29(9)
O(2)-C(9)-C(8)	120.57(9)
C(10)-C(9)-C(8)	119.85(8)
C(11)-C(10)-C(9)	126.61(9)
C(11)-C(10)-H(10A)	119.7(8)
C(9)-C(10)-H(10A)	113.5(8)
C(10)-C(11)-C(12)	119.64(9)
C(10)-C(11)-C(16)	121.36(9)
C(12)-C(11)-C(16)	118.84(8)
C(13)-C(12)-C(11)	119.51(8)
C(13)-C(12)-C(1)	119.76(8)
C(11)-C(12)-C(1)	120.68(8)
C(12)-C(13)-C(4)	125.05(9)
C(12)-C(13)-H(13A)	117.8(8)
C(4)-C(13)-H(13A)	117.0(7)
C(3)-C(14)-H(14A)	110.7(9)
C(3)-C(14)-H(14B)	111.4(8)
H(14A)-C(14)-H(14B)	107.6(12)
C(3)-C(14)-H(14C)	111.5(9)

H(14A)-C(14)-H(14C)	107.7(12)
H(14B)-C(14)-H(14C)	107.9(12)
C(7)-C(15)-H(15A)	109.9(9)
C(7)-C(15)-H(15B)	111.8(8)
H(15A)-C(15)-H(15B)	108.2(12)
C(7)-C(15)-H(15C)	111.0(9)
H(15A)-C(15)-H(15C)	107.9(12)
H(15B)-C(15)-H(15C)	108.0(12)
C(11)-C(16)-H(16A)	111.0(9)
C(11)-C(16)-H(16B)	111.0(10)
H(16A)-C(16)-H(16B)	109.2(13)
C(11)-C(16)-H(16C)	111.7(10)
H(16A)-C(16)-H(16C)	106.1(13)
H(16B)-C(16)-H(16C)	107.7(14)

Table 4. Anisotropic displacement parameters ($Å^2 \times 10^3$) for cdv50. The anisotropic displacement factor exponent takes the form: $-2\pi^2[h^2 a^{*2}U^{11} + ... + 2 h k a^* b^* U^{12}]$

	U^{11}	U^{22}	U^{33}	U^{23}	U^{13}	U^{12}
O(1)	20(1)	21(1)	25(1)	-1(1)	12(1)	2(1)
O(2)	29(1)	17(1)	23(1)	-5(1)	5(1)	2(1)
C(1)	14(1)	16(1)	11(1)	1(1)	2(1)	1(1)
C(2)	17(1)	14(1)	16(1)	-2(1)	6(1)	-1(1)
C(3)	14(1)	19(1)	14(1)	-2(1)	3(1)	-3(1)
C(4)	12(1)	18(1)	15(1)	0(1)	3(1)	1(1)
C(5)	15(1)	21(1)	15(1)	-1(1)	5(1)	-2(1)
C(6)	16(1)	25(1)	17(1)	-5(1)	7(1)	1(1)
C(7)	18(1)	21(1)	14(1)	-4(1)	5(1)	-1(1)
C(8)	14(1)	16(1)	14(1)	-1(1)	3(1)	0(1)
C(9)	14(1)	16(1)	16(1)	-2(1)	1(1)	-2(1)
C(10)	17(1)	15(1)	19(1)	2(1)	4(1)	-2(1)
C(11)	15(1)	14(1)	17(1)	3(1)	4(1)	0(1)
C(12)	14(1)	13(1)	11(1)	1(1)	2(1)	0(1)
C(13)	15(1)	14(1)	12(1)	0(1)	1(1)	1(1)
C(14)	20(1)	28(1)	29(1)	-6(1)	9(1)	-10(1)
C(15)	22(1)	32(1)	15(1)	3(1)	4(1)	-5(1)
C(16)	23(1)	22(1)	18(1)	2(1)	7(1)	-5(1)

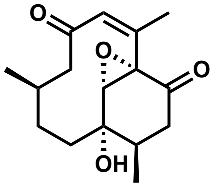
Table 5. Hydrogen coordinates (x 10^4) and isotropic displacement parameters (Å^2 x 10^3) for cdv50.

	x	y	z	U(eq)
H(2A)	5099(10)	-1300(20)	1983(9)	21(3)
H(2B)	4682(10)	-1700(20)	888(9)	23(3)
H(3A)	3462(9)	796(19)	712(9)	18(3)
H(4A)	3308(10)	2771(19)	1915(9)	19(3)
H(5A)	3810(10)	680(20)	3193(9)	23(3)
H(5B)	4913(10)	521(19)	3167(9)	21(3)
H(6A)	4398(10)	4520(20)	3412(9)	20(3)
H(6B)	4291(10)	3090(20)	4220(9)	25(3)
H(7A)	5829(10)	4700(20)	4669(9)	21(3)
H(8A)	7149(10)	3720(20)	4135(9)	22(3)
H(8B)	6398(9)	2495(19)	3305(8)	15(3)
H(10A)	7001(10)	6780(20)	2256(9)	22(3)
H(13A)	4617(9)	4880(20)	1979(9)	19(3)
H(14A)	2465(11)	-730(20)	1548(10)	34(4)
H(14B)	2903(11)	-2360(20)	1017(10)	33(4)
H(14C)	3406(11)	-2060(20)	2124(10)	33(4)
H(15A)	5707(11)	1590(20)	5415(11)	34(4)
H(15B)	6079(11)	380(20)	4667(10)	28(4)
H(15C)	6828(11)	1880(20)	5393(10)	33(4)
H(16A)	5935(12)	4550(20)	119(11)	37(4)
H(16B)	6813(12)	6010(30)	676(11)	46(4)
H(16C)	6986(13)	3690(30)	651(12)	51(5)

Table 6. Torsion angles [°] for cdv50.

O(1)-C(1)-C(2)-C(3)	-156.55(9)
C(12)-C(1)-C(2)-C(3)	26.02(11)
C(1)-C(2)-C(3)-C(14)	-176.82(8)
C(1)-C(2)-C(3)-C(4)	-50.53(11)
C(14)-C(3)-C(4)-C(13)	176.94(8)
C(2)-C(3)-C(4)-C(13)	51.80(10)
C(14)-C(3)-C(4)-C(5)	54.99(11)
C(2)-C(3)-C(4)-C(5)	-70.15(10)
C(13)-C(4)-C(5)-C(6)	50.13(10)
C(3)-C(4)-C(5)-C(6)	172.64(8)
C(4)-C(5)-C(6)-C(7)	-112.60(10)
C(5)-C(6)-C(7)-C(15)	-66.50(11)
C(5)-C(6)-C(7)-C(8)	58.88(12)
C(15)-C(7)-C(8)-C(9)	-166.07(8)
C(6)-C(7)-C(8)-C(9)	67.97(11)
C(7)-C(8)-C(9)-O(2)	33.59(13)
C(7)-C(8)-C(9)-C(10)	-152.75(8)
O(2)-C(9)-C(10)-C(11)	-132.90(11)
C(8)-C(9)-C(10)-C(11)	53.36(14)
C(9)-C(10)-C(11)-C(12)	3.84(15)
C(9)-C(10)-C(11)-C(16)	179.26(9)
C(10)-C(11)-C(12)-C(13)	44.09(13)
C(16)-C(11)-C(12)-C(13)	-131.44(10)
C(10)-C(11)-C(12)-C(1)	-133.41(10)
C(16)-C(11)-C(12)-C(1)	51.06(12)
O(1)-C(1)-C(12)-C(13)	178.77(9)
C(2)-C(1)-C(12)-C(13)	-3.81(12)
O(1)-C(1)-C(12)-C(11)	-3.75(13)
C(2)-C(1)-C(12)-C(11)	173.67(8)
C(11)-C(12)-C(13)-C(4)	-169.13(8)
C(1)-C(12)-C(13)-C(4)	8.39(13)
C(3)-C(4)-C(13)-C(12)	-33.18(12)
C(5)-C(4)-C(13)-C(12)	91.94(11)

X-ray Data Collection, Structure Solution and Refinement for hydroperoxide 21 (cdv52).



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A colorless crystal of approximate dimensions 0.081 x 0.117 x 0.174 mm was mounted in a cryoloop and transferred to a Bruker SMART APEX II diffractometer. The APEX2[4] program package was used to determine the unit-cell parameters and for data collection (120 sec/frame scan time for a sphere of diffraction data). The raw frame data was processed using SAINT[5] and SADABS[6] to yield the reflection data file. Subsequent calculations were carried out using the SHELXTL[7] program. The diffraction symmetry was *mmm* and the systematic absences were consistent with the orthorhombic space group $P2_12_12_1$ that was later determined to be correct.

The structure was solved by dual space methods and refined on F^2 by full-matrix least-squares techniques. The analytical scattering factors[8] for neutral atoms were used throughout the analysis. Hydrogen atom H(2) was located from a difference-Fourier map and refined (x,y,z and U_{iso}). The remaining hydrogen atoms were included using a riding model.

Least squares analysis yielded wR2 = 0.0828 and Goof = 1.036 for 188 variables refined against 2940 data (0.80 Å), R1 = 0.0405 for those 2420 data with $I > 2.0\sigma(I)$. Due to the lack of any atom heavier than oxygen, the absolute structure could not be assigned by refinement of the Flack parameter[6].

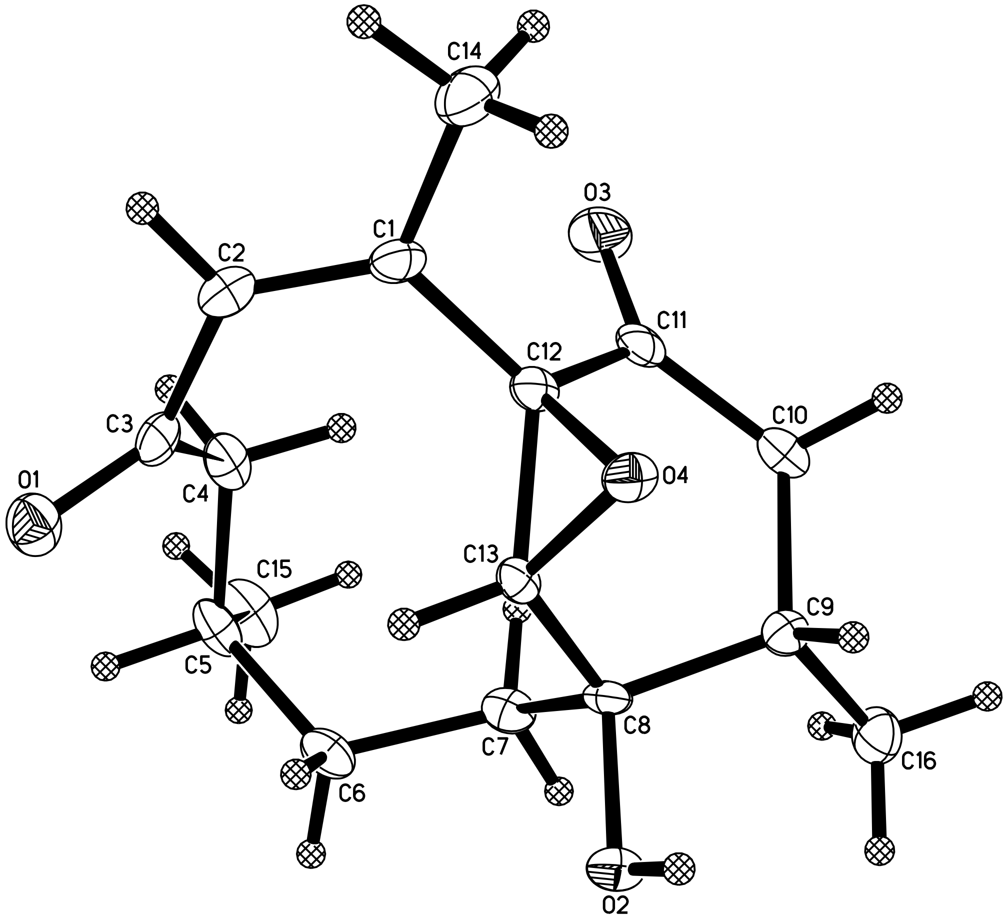

C14
O3
C1
C2
C11
C12
C10
C3
C4
O4
O1
C13
C15
C9
C5
C8
C7
C16
C6
O2

Table 1. Crystal data and structure refinement for cdv52.

Identification code	cdv52 (Vincenzo Ramella)	
Empirical formula	$C_{16} H_{22} O_4$	
Formula weight	278.33	
Temperature	88(2) K	
Wavelength	0.71073 Å	
Crystal system	Orthorhombic	
Space group	$P2_12_12_1$	
Unit cell dimensions	a = 8.3509(9) Å	a = 90°.
	b = 11.8006(13) Å	b = 90°.
	c = 14.6529(16) Å	g = 90°.
Volume	1444.0(3) $Å^3$	
Z	4	
Density (calculated)	1.280 Mg/m^3	
Absorption coefficient	0.091 mm^{-1}	
F(000)	600	
Crystal color	colorless	
Crystal size	0.174 x 0.117 x 0.081 mm^3	
Theta range for data collection	2.216 to 26.307°	
Index ranges	$-10 \leq h \leq 10$, $-14 \leq k \leq 14$, $-18 \leq l \leq 18$	
Reflections collected	15903	
Independent reflections	2940 [R(int) = 0.0634]	
Completeness to theta = 25.500°	100.0 %	
Absorption correction	Semi-empirical from equivalents	
Max. and min. transmission	0.8620 and 0.8307	
Refinement method	Full-matrix least-squares on F^2	
Data / restraints / parameters	2940 / 0 / 188	
Goodness-of-fit on F^2	1.036	
Final R indices [I>2sigma(I) = 2420 data]	R1 = 0.0405, wR2 = 0.0765	
R indices (all data, 0.80 Å)	R1 = 0.0582, wR2 = 0.0828	
Largest diff. peak and hole	0.204 and -0.177 $e.Å^{-3}$	

Table 2. Atomic coordinates (x 10^4) and equivalent isotropic displacement parameters (Å^2 x 10^3) for cdv52. U(eq) is defined as one third of the trace of the orthogonalized U^{ij} tensor.

	x	y	z	U(eq)
O(1)	70(2)	3750(1)	1426(1)	22(1)
O(2)	3625(2)	3486(2)	-1507(1)	18(1)
O(3)	6247(2)	5014(2)	1602(1)	26(1)
O(4)	5102(2)	2531(1)	393(1)	15(1)
C(1)	4084(3)	3154(2)	1886(2)	16(1)
C(2)	2570(3)	3391(2)	2110(2)	20(1)
C(3)	1428(3)	4096(2)	1571(2)	18(1)
C(4)	1937(3)	5277(2)	1306(2)	19(1)
C(5)	1146(3)	5777(2)	451(2)	19(1)
C(6)	1636(3)	5177(2)	-438(2)	18(1)
C(7)	3455(3)	5198(2)	-655(2)	17(1)
C(8)	4283(3)	4046(2)	-718(2)	13(1)
C(9)	6118(3)	4134(2)	-817(2)	14(1)
C(10)	6924(3)	4578(2)	61(2)	17(1)
C(11)	6042(3)	4404(2)	945(2)	16(1)
C(12)	4789(3)	3496(2)	983(2)	14(1)
C(13)	3901(3)	3334(2)	109(2)	12(1)
C(14)	5171(4)	2456(2)	2474(2)	24(1)
C(15)	1469(4)	7055(2)	404(2)	28(1)
C(16)	6667(3)	4821(2)	-1639(2)	22(1)

Table 3. Bond lengths [Å] and angles [°] for cdv52.

O(1)-C(3)	1.224(3)
O(2)-C(8)	1.441(3)
O(3)-C(11)	1.215(3)
O(4)-C(13)	1.442(3)
O(4)-C(12)	1.454(3)
C(1)-C(2)	1.335(4)
C(1)-C(14)	1.499(4)
C(1)-C(12)	1.503(4)
C(2)-C(3)	1.492(4)
C(3)-C(4)	1.508(4)
C(4)-C(5)	1.535(4)
C(5)-C(15)	1.533(4)
C(5)-C(6)	1.538(4)
C(6)-C(7)	1.552(3)
C(7)-C(8)	1.528(4)
C(8)-C(13)	1.508(3)
C(8)-C(9)	1.543(3)
C(9)-C(16)	1.521(3)
C(9)-C(10)	1.544(4)
C(10)-C(11)	1.504(4)
C(11)-C(12)	1.498(4)
C(12)-C(13)	1.492(3)
C(13)-O(4)-C(12)	62.04(15)
C(2)-C(1)-C(14)	123.2(3)
C(2)-C(1)-C(12)	122.1(3)
C(14)-C(1)-C(12)	114.6(2)
C(1)-C(2)-C(3)	126.3(3)
O(1)-C(3)-C(2)	119.9(2)
O(1)-C(3)-C(4)	121.6(2)
C(2)-C(3)-C(4)	118.1(2)
C(3)-C(4)-C(5)	116.4(2)
C(15)-C(5)-C(4)	109.8(2)
C(15)-C(5)-C(6)	111.6(2)

C(4)-C(5)-C(6)	113.6(2)
C(5)-C(6)-C(7)	115.2(2)
C(8)-C(7)-C(6)	116.2(2)
O(2)-C(8)-C(13)	108.03(19)
O(2)-C(8)-C(7)	106.5(2)
C(13)-C(8)-C(7)	110.6(2)
O(2)-C(8)-C(9)	109.5(2)
C(13)-C(8)-C(9)	108.9(2)
C(7)-C(8)-C(9)	113.3(2)
C(16)-C(9)-C(8)	114.2(2)
C(16)-C(9)-C(10)	110.4(2)
C(8)-C(9)-C(10)	112.2(2)
C(11)-C(10)-C(9)	117.2(2)
O(3)-C(11)-C(12)	119.5(2)
O(3)-C(11)-C(10)	122.2(2)
C(12)-C(11)-C(10)	118.2(2)
O(4)-C(12)-C(13)	58.57(15)
O(4)-C(12)-C(11)	114.4(2)
C(13)-C(12)-C(11)	113.9(2)
O(4)-C(12)-C(1)	112.6(2)
C(13)-C(12)-C(1)	121.7(2)
C(11)-C(12)-C(1)	119.9(2)
O(4)-C(13)-C(12)	59.39(15)
O(4)-C(13)-C(8)	116.8(2)
C(12)-C(13)-C(8)	120.9(2)

Table 4. Anisotropic displacement parameters ($Å^2$ x 10^3) for cdv52. The anisotropic displacement factor exponent takes the form: $-2p^2[h^2 a^{*2}U^{11} + ... + 2 h k a^* b^* U^{12}]$

	U^{11}	U^{22}	U^{33}	U^{23}	U^{13}	U^{12}
O(1)	19(1)	22(1)	25(1)	-5(1)	2(1)	2(1)
O(2)	19(1)	19(1)	15(1)	-2(1)	-4(1)	-1(1)
O(3)	26(1)	29(1)	24(1)	-11(1)	-5(1)	-2(1)
O(4)	19(1)	13(1)	14(1)	-2(1)	-1(1)	4(1)
C(1)	20(1)	18(1)	11(1)	-3(1)	-2(1)	1(1)
C(2)	23(2)	24(2)	13(1)	-1(1)	2(1)	0(1)
C(3)	17(1)	23(1)	14(1)	-7(1)	5(1)	3(1)
C(4)	14(1)	18(1)	26(2)	-11(1)	0(1)	2(1)
C(5)	12(1)	13(1)	32(2)	-4(1)	-4(1)	1(1)
C(6)	16(1)	14(1)	23(1)	3(1)	-5(1)	1(1)
C(7)	19(1)	14(1)	18(1)	4(1)	-4(1)	-2(1)
C(8)	14(1)	16(1)	10(1)	0(1)	-4(1)	-2(1)
C(9)	16(1)	13(1)	14(1)	1(1)	0(1)	1(1)
C(10)	14(1)	14(1)	23(2)	0(1)	-5(1)	1(1)
C(11)	14(1)	17(1)	18(1)	-1(1)	-5(1)	6(1)
C(12)	15(1)	13(1)	14(1)	-3(1)	-2(1)	6(1)
C(13)	11(1)	10(1)	15(1)	-2(1)	-1(1)	2(1)
C(14)	29(2)	25(2)	18(1)	4(1)	3(1)	7(1)
C(15)	24(2)	16(1)	45(2)	-4(1)	-3(2)	4(1)
C(16)	18(2)	25(2)	22(2)	5(1)	3(1)	-2(1)

Table 5. Hydrogen coordinates (x 10^4) and isotropic displacement parameters (Å^2 x 10^3) for cdv52.

	x	y	z	U(eq)
H(2)	4090(40)	2830(30)	-1560(20)	32(9)
H(2A)	2183	3080	2666	24
H(4A)	3111	5274	1210	23
H(4B)	1713	5789	1826	23
H(5A)	-37	5676	521	23
H(6A)	1056	5537	-952	21
H(6B)	1282	4378	-405	21
H(7A)	3610	5598	-1242	20
H(7B)	3999	5648	-177	20
H(9A)	6522	3345	-912	17
H(10A)	7985	4210	116	21
H(10B)	7113	5401	-15	21
H(13A)	2764	3079	167	14
H(14A)	5596	1821	2118	36
H(14B)	4570	2164	2998	36
H(14C)	6059	2927	2691	36
H(15A)	932	7374	-132	42
H(15B)	2625	7187	357	42
H(15C)	1058	7419	957	42
H(16A)	6158	4523	-2192	33
H(16B)	7833	4765	-1698	33
H(16C)	6362	5616	-1556	33

Table 6. Torsion angles [°] for cdv52.

C(14)-C(1)-C(2)-C(3)	178.7(3)
C(12)-C(1)-C(2)-C(3)	-6.2(4)
C(1)-C(2)-C(3)-O(1)	132.2(3)
C(1)-C(2)-C(3)-C(4)	-54.2(4)
O(1)-C(3)-C(4)-C(5)	-32.1(4)
C(2)-C(3)-C(4)-C(5)	154.4(2)
C(3)-C(4)-C(5)-C(15)	166.4(2)
C(3)-C(4)-C(5)-C(6)	-67.9(3)
C(15)-C(5)-C(6)-C(7)	65.1(3)
C(4)-C(5)-C(6)-C(7)	-59.6(3)
C(5)-C(6)-C(7)-C(8)	118.9(2)
C(6)-C(7)-C(8)-O(2)	66.6(3)
C(6)-C(7)-C(8)-C(13)	-50.5(3)
C(6)-C(7)-C(8)-C(9)	-173.0(2)
O(2)-C(8)-C(9)-C(16)	61.2(3)
C(13)-C(8)-C(9)-C(16)	179.2(2)
C(7)-C(8)-C(9)-C(16)	-57.4(3)
O(2)-C(8)-C(9)-C(10)	-172.27(19)
C(13)-C(8)-C(9)-C(10)	-54.3(3)
C(7)-C(8)-C(9)-C(10)	69.1(3)
C(16)-C(9)-C(10)-C(11)	152.9(2)
C(8)-C(9)-C(10)-C(11)	24.4(3)
C(9)-C(10)-C(11)-O(3)	-154.6(2)
C(9)-C(10)-C(11)-C(12)	21.0(3)
C(13)-O(4)-C(12)-C(11)	-104.2(2)
C(13)-O(4)-C(12)-C(1)	114.4(2)
O(3)-C(11)-C(12)-O(4)	-153.2(2)
C(10)-C(11)-C(12)-O(4)	31.0(3)
O(3)-C(11)-C(12)-C(13)	141.9(2)
C(10)-C(11)-C(12)-C(13)	-33.8(3)
O(3)-C(11)-C(12)-C(1)	-14.9(4)
C(10)-C(11)-C(12)-C(1)	169.4(2)
C(2)-C(1)-C(12)-O(4)	-110.7(3)
C(14)-C(1)-C(12)-O(4)	64.8(3)

C(2)-C(1)-C(12)-C(13)	-44.7(4)
C(14)-C(1)-C(12)-C(13)	130.8(3)
C(2)-C(1)-C(12)-C(11)	110.4(3)
C(14)-C(1)-C(12)-C(11)	-74.1(3)
C(12)-O(4)-C(13)-C(8)	111.7(2)
C(11)-C(12)-C(13)-O(4)	104.9(2)
C(1)-C(12)-C(13)-O(4)	-98.7(2)
O(4)-C(12)-C(13)-C(8)	-104.9(2)
C(11)-C(12)-C(13)-C(8)	0.1(3)
C(1)-C(12)-C(13)-C(8)	156.5(2)
O(2)-C(8)-C(13)-O(4)	93.8(2)
C(7)-C(8)-C(13)-O(4)	-150.10(19)
C(9)-C(8)-C(13)-O(4)	-25.1(3)
O(2)-C(8)-C(13)-C(12)	162.5(2)
C(7)-C(8)-C(13)-C(12)	-81.4(3)
C(9)-C(8)-C(13)-C(12)	43.7(3)

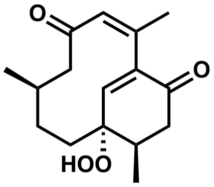
Table 7. Hydrogen bonds for cdv52 [Å and °].

D-H...A	d(D-H)	d(H...A)	d(D...A)	<(DHA)
O(2)-H(2)...O(1)#1	0.86(3)	2.05(3)	2.905(3)	169(3)

Symmetry transformations used to generate equivalent atoms:

#1 x+1/2,-y+1/2,-z

X-ray Data Collection, Structure Solution and Refinement for hydroperoxide 22 (cdv49).



22

A colorless crystal of approximate dimensions 0.262 x 0.290 x 0.454 mm was mounted in on a glass fiber and transferred to a Bruker SMART APEX II diffractometer. The APEX2[4] program package was used to determine the unit-cell parameters and for data collection (10 sec/frame scan time for a sphere of diffraction data). The raw frame data was processed using SAINT[5] and SADABS[6] to yield the reflection data file. Subsequent calculations were carried out using the SHELXTL[7] program. There were no systematic absences nor any diffraction symmetry other than the Friedel condition. The centrosymmetric triclinic space group $P\bar{1}$ was assigned and later determined to be correct.

The structure was solved by direct methods and refined on F^2 by full-matrix least-squares techniques. The analytical scattering factors[8] for neutral atoms were used throughout the analysis. Hydrogen atoms were located from a difference-Fourier map and refined (x,y,z and U_{iso}).

Least-squares analysis yielded wR2 = 0.0997 and Goof = 1.036 for 269 variables refined against 3509 data (0.74 Å), R1 = 0.0375 for those 3162 data with $I > 2.0\sigma(I)$.

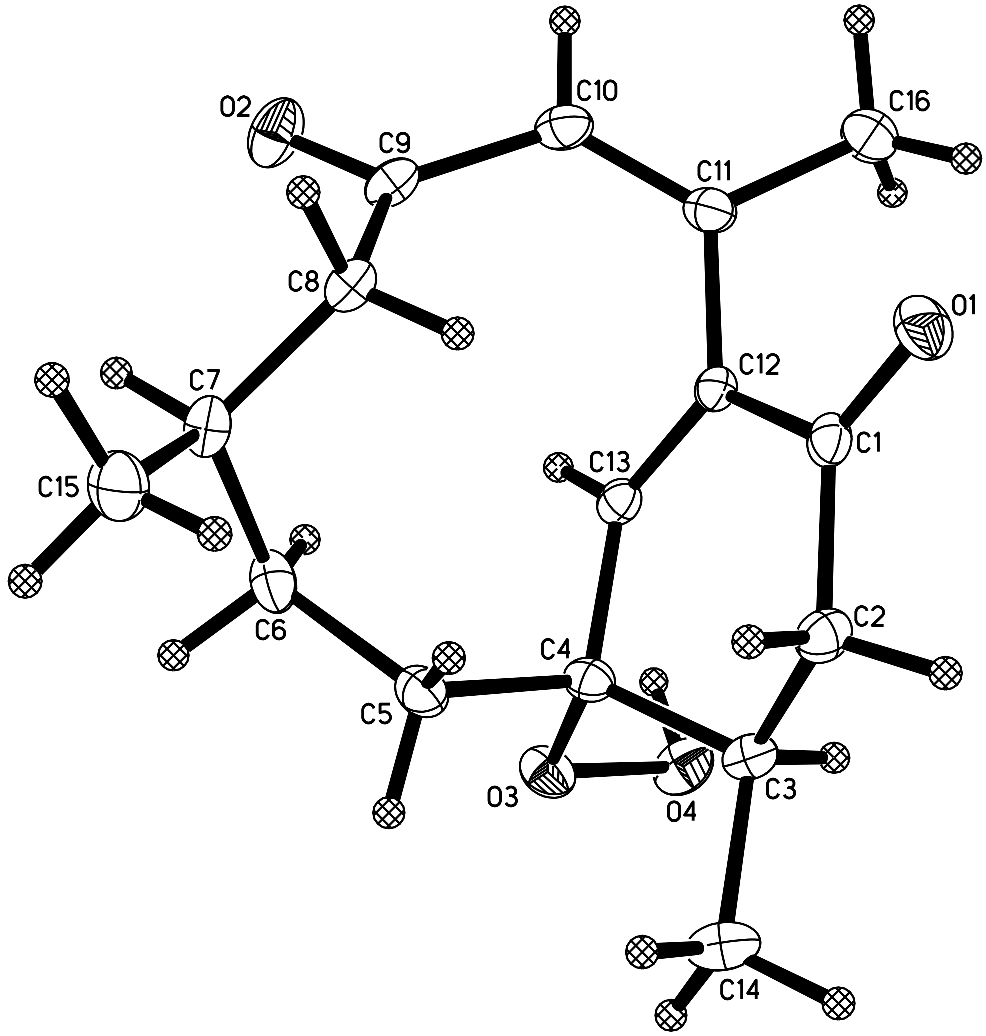

O2
C9
C10
C11
C16
C8
O1
C7
C12
C1
C15
C13
C6
C2
C4
C5
O3
O4
C3
C14

Table 1. Crystal data and structure refinement for cdv49.

Identification code	cdv49 (Vincenzo Ramella)	
Empirical formula	$C_{16} H_{22} O_4$	
Formula weight	278.33	
Temperature	133(2) K	
Wavelength	0.71073 Å	
Crystal system	Triclinic	
Space group	$P\bar{1}$	
Unit cell dimensions	a = 9.3233(7) Å	α = 81.7916(9)°.
	b = 9.3480(7) Å	β = 66.0140(8)°.
	c = 9.6872(7) Å	γ = 73.6845(9)°.
Volume	739.92(10) $Å^3$	
Z	2	
Density (calculated)	1.249 Mg/m^3	
Absorption coefficient	0.089 mm^{-1}	
F(000)	300	
Crystal color	colorless	
Crystal size	0.454 x 0.290 x 0.262 mm^3	
Theta range for data collection	2.271 to 28.782°	
Index ranges	$-12 \leq h \leq 12$, $-12 \leq k \leq 12$, $-12 \leq l \leq 12$	
Reflections collected	8940	
Independent reflections	3509 [R(int) = 0.0158]	
Completeness to theta = 25.500°	99.7 %	
Absorption correction	Semi-empirical from equivalents	
Max. and min. transmission	0.8621 and 0.8220	
Refinement method	Full-matrix least-squares on F^2	
Data / restraints / parameters	3509 / 0 / 269	
Goodness-of-fit on F^2	1.036	
Final R indices [I>2sigma(I) = 3162 data]	R1 = 0.0375, wR2 = 0.0959	
R indices (all data, 0.74 Å)	R1 = 0.0414, wR2 = 0.0997	
Largest diff. peak and hole	0.409 and -0.183 $e.Å^{-3}$	

Table 2. Atomic coordinates (x 10^4) and equivalent isotropic displacement parameters (Å^2 x 10^3) for cdv49. U(eq) is defined as one third of the trace of the orthogonalized U^{ij} tensor.

	x	y	z	U(eq)
O(1)	9844(1)	1070(1)	6278(1)	22(1)
O(2)	3901(1)	2607(1)	5194(1)	24(1)
O(3)	9142(1)	5280(1)	1877(1)	19(1)
O(4)	9252(1)	6387(1)	2737(1)	23(1)
C(1)	9744(1)	1947(1)	5241(1)	15(1)
C(2)	11189(1)	1984(1)	3779(1)	18(1)
C(3)	11040(1)	3390(1)	2767(1)	17(1)
C(4)	9378(1)	3838(1)	2638(1)	15(1)
C(5)	9201(1)	2811(1)	1635(1)	18(1)
C(6)	7455(1)	2979(1)	1759(1)	20(1)
C(7)	6748(1)	1613(1)	2442(1)	18(1)
C(8)	6608(1)	1204(1)	4079(1)	16(1)
C(9)	5245(1)	2222(1)	5265(1)	17(1)
C(10)	5399(1)	2619(1)	6617(1)	18(1)
C(11)	6689(1)	2899(1)	6714(1)	17(1)
C(12)	8162(1)	2968(1)	5341(1)	14(1)
C(13)	8046(1)	3879(1)	4172(1)	14(1)
C(14)	12455(1)	3181(1)	1232(1)	25(1)
C(15)	7717(2)	248(1)	1460(1)	24(1)
C(16)	6665(2)	3264(2)	8182(1)	28(1)

Table 3. Bond lengths [Å] and angles [°] for cdv49.

O(1)-C(1)	1.2199(13)
O(2)-C(9)	1.2308(13)
O(3)-C(4)	1.4458(12)
O(3)-O(4)	1.4663(11)
O(4)-H(4)	0.921(18)
C(1)-C(12)	1.4881(14)
C(1)-C(2)	1.5107(14)
C(2)-C(3)	1.5327(14)
C(2)-H(2A)	0.987(14)
C(2)-H(2B)	0.962(15)
C(3)-C(14)	1.5273(15)
C(3)-C(4)	1.5384(14)
C(3)-H(3A)	0.993(13)
C(4)-C(13)	1.4971(14)
C(4)-C(5)	1.5433(14)
C(5)-C(6)	1.5465(15)
C(5)-H(5A)	0.981(14)
C(5)-H(5B)	0.962(15)
C(6)-C(7)	1.5420(15)
C(6)-H(6A)	1.002(14)
C(6)-H(6B)	0.985(16)
C(7)-C(15)	1.5333(15)
C(7)-C(8)	1.5374(15)
C(7)-H(7A)	0.973(14)
C(8)-C(9)	1.5126(14)
C(8)-H(8A)	0.974(15)
C(8)-H(8B)	0.970(13)
C(9)-C(10)	1.4810(15)
C(10)-C(11)	1.3415(15)
C(10)-H(10A)	0.965(15)
C(11)-C(12)	1.4831(14)
C(11)-C(16)	1.5000(15)
C(12)-C(13)	1.3388(14)
C(13)-H(13A)	0.984(14)

C(14)-H(14A)	0.979(16)
C(14)-H(14B)	0.984(16)
C(14)-H(14C)	0.984(16)
C(15)-H(15A)	0.978(16)
C(15)-H(15B)	0.999(16)
C(15)-H(15C)	0.981(17)
C(16)-H(16A)	0.94(2)
C(16)-H(16B)	0.99(2)
C(16)-H(16C)	0.95(2)

C(4)-O(3)-O(4)	108.66(7)
O(3)-O(4)-H(4)	99.6(11)
O(1)-C(1)-C(12)	120.82(9)
O(1)-C(1)-C(2)	121.67(9)
C(12)-C(1)-C(2)	117.42(9)
C(1)-C(2)-C(3)	116.00(8)
C(1)-C(2)-H(2A)	104.9(8)
C(3)-C(2)-H(2A)	111.3(8)
C(1)-C(2)-H(2B)	108.0(9)
C(3)-C(2)-H(2B)	110.7(9)
H(2A)-C(2)-H(2B)	105.1(12)
C(14)-C(3)-C(2)	110.48(9)
C(14)-C(3)-C(4)	112.96(9)
C(2)-C(3)-C(4)	110.96(8)
C(14)-C(3)-H(3A)	109.5(7)
C(2)-C(3)-H(3A)	108.2(7)
C(4)-C(3)-H(3A)	104.5(7)
O(3)-C(4)-C(13)	109.49(8)
O(3)-C(4)-C(3)	110.90(8)
C(13)-C(4)-C(3)	110.56(8)
O(3)-C(4)-C(5)	102.77(8)
C(13)-C(4)-C(5)	109.17(8)
C(3)-C(4)-C(5)	113.65(8)
C(4)-C(5)-C(6)	115.60(9)
C(4)-C(5)-H(5A)	106.9(8)
C(6)-C(5)-H(5A)	110.3(8)

C(4)-C(5)-H(5B)	106.5(9)
C(6)-C(5)-H(5B)	110.1(9)
H(5A)-C(5)-H(5B)	106.9(12)
C(7)-C(6)-C(5)	115.57(9)
C(7)-C(6)-H(6A)	109.2(8)
C(5)-C(6)-H(6A)	111.2(8)
C(7)-C(6)-H(6B)	106.2(9)
C(5)-C(6)-H(6B)	108.9(9)
H(6A)-C(6)-H(6B)	105.2(11)
C(15)-C(7)-C(8)	109.64(9)
C(15)-C(7)-C(6)	111.54(9)
C(8)-C(7)-C(6)	113.80(8)
C(15)-C(7)-H(7A)	107.2(8)
C(8)-C(7)-H(7A)	107.7(8)
C(6)-C(7)-H(7A)	106.7(8)
C(9)-C(8)-C(7)	115.40(9)
C(9)-C(8)-H(8A)	102.3(8)
C(7)-C(8)-H(8A)	108.0(8)
C(9)-C(8)-H(8B)	112.3(8)
C(7)-C(8)-H(8B)	111.9(8)
H(8A)-C(8)-H(8B)	105.9(11)
O(2)-C(9)-C(10)	118.15(9)
O(2)-C(9)-C(8)	118.64(9)
C(10)-C(9)-C(8)	122.72(9)
C(11)-C(10)-C(9)	128.17(10)
C(11)-C(10)-H(10A)	118.4(9)
C(9)-C(10)-H(10A)	113.4(9)
C(10)-C(11)-C(12)	120.85(9)
C(10)-C(11)-C(16)	121.87(10)
C(12)-C(11)-C(16)	117.13(9)
C(13)-C(12)-C(11)	119.99(9)
C(13)-C(12)-C(1)	120.57(9)
C(11)-C(12)-C(1)	119.33(9)
C(12)-C(13)-C(4)	124.41(9)
C(12)-C(13)-H(13A)	119.7(8)
C(4)-C(13)-H(13A)	115.7(8)

C(3)-C(14)-H(14A)	111.4(9)
C(3)-C(14)-H(14B)	110.6(9)
H(14A)-C(14)-H(14B)	107.9(13)
C(3)-C(14)-H(14C)	110.7(9)
H(14A)-C(14)-H(14C)	108.3(13)
H(14B)-C(14)-H(14C)	107.8(13)
C(7)-C(15)-H(15A)	110.9(10)
C(7)-C(15)-H(15B)	111.3(9)
H(15A)-C(15)-H(15B)	109.9(13)
C(7)-C(15)-H(15C)	110.6(10)
H(15A)-C(15)-H(15C)	106.9(13)
H(15B)-C(15)-H(15C)	107.1(13)
C(11)-C(16)-H(16A)	112.7(12)
C(11)-C(16)-H(16B)	107.6(12)
H(16A)-C(16)-H(16B)	103.8(17)
C(11)-C(16)-H(16C)	111.8(12)
H(16A)-C(16)-H(16C)	111.4(17)
H(16B)-C(16)-H(16C)	109.2(17)

Table 4. Anisotropic displacement parameters ($Å^2 \times 10^3$) for cdv49. The anisotropic displacement factor exponent takes the form: $-2\pi^2[h^2 a^{*2}U^{11} + ... + 2 h k a^* b^* U^{12}]$

	U^{11}	U^{22}	U^{33}	U^{23}	U^{13}	U^{12}
O(1)	26(1)	20(1)	21(1)	4(1)	-13(1)	-5(1)
O(2)	15(1)	25(1)	34(1)	-9(1)	-10(1)	-1(1)
O(3)	28(1)	14(1)	17(1)	2(1)	-8(1)	-7(1)
O(4)	22(1)	16(1)	30(1)	-5(1)	-7(1)	-6(1)
C(1)	17(1)	15(1)	17(1)	0(1)	-9(1)	-6(1)
C(2)	13(1)	18(1)	21(1)	0(1)	-6(1)	-3(1)
C(3)	14(1)	17(1)	17(1)	0(1)	-3(1)	-6(1)
C(4)	17(1)	12(1)	14(1)	1(1)	-5(1)	-5(1)
C(5)	22(1)	18(1)	14(1)	-1(1)	-6(1)	-7(1)
C(6)	26(1)	19(1)	20(1)	0(1)	-14(1)	-5(1)
C(7)	18(1)	19(1)	21(1)	-3(1)	-11(1)	-4(1)
C(8)	13(1)	14(1)	20(1)	-2(1)	-6(1)	-4(1)
C(9)	14(1)	14(1)	22(1)	0(1)	-6(1)	-6(1)
C(10)	15(1)	20(1)	17(1)	-2(1)	-1(1)	-6(1)
C(11)	18(1)	18(1)	14(1)	0(1)	-4(1)	-6(1)
C(12)	14(1)	16(1)	13(1)	-2(1)	-5(1)	-6(1)
C(13)	14(1)	14(1)	16(1)	-2(1)	-5(1)	-4(1)
C(14)	18(1)	27(1)	23(1)	0(1)	0(1)	-7(1)
C(15)	30(1)	22(1)	23(1)	-6(1)	-10(1)	-8(1)
C(16)	26(1)	44(1)	14(1)	-4(1)	-4(1)	-15(1)

Table 5. Hydrogen coordinates (x 10^4) and isotropic displacement parameters (Å^2 x 10^3) for cdv49.

	x	y	z	U(eq)
H(4)	8170(20)	6730(19)	3330(20)	42(5)
H(2A)	11358(17)	1084(16)	3255(15)	21(3)
H(2B)	12128(18)	1819(16)	4021(16)	26(4)
H(3A)	11049(15)	4235(15)	3277(15)	16(3)
H(5A)	9667(16)	1783(16)	1897(15)	20(3)
H(5B)	9880(18)	3015(16)	611(17)	25(3)
H(6A)	6695(17)	3884(16)	2333(16)	21(3)
H(6B)	7435(18)	3157(16)	739(18)	29(4)
H(7A)	5660(17)	1870(16)	2445(16)	23(3)
H(8A)	6308(17)	254(16)	4362(16)	24(3)
H(8B)	7638(16)	1044(14)	4175(15)	16(3)
H(10A)	4417(18)	2707(16)	7513(17)	25(3)
H(13A)	7004(17)	4582(15)	4271(15)	19(3)
H(14A)	12335(19)	4042(18)	548(18)	35(4)
H(14B)	13490(20)	3053(17)	1348(18)	33(4)
H(14C)	12530(18)	2288(18)	753(17)	30(4)
H(15A)	7837(19)	491(18)	408(19)	35(4)
H(15B)	8806(19)	-155(17)	1513(17)	31(4)
H(15C)	7150(20)	-557(19)	1809(18)	37(4)
H(16A)	7650(30)	2820(20)	8300(20)	58(6)
H(16B)	6590(30)	4340(30)	8150(20)	64(6)
H(16C)	5770(20)	3040(20)	9020(20)	55(5)

Table 6. Torsion angles [°] for cdv49.

O(1)-C(1)-C(2)-C(3)	-163.35(10)
C(12)-C(1)-C(2)-C(3)	20.02(13)
C(1)-C(2)-C(3)-C(14)	-171.10(9)
C(1)-C(2)-C(3)-C(4)	-45.01(12)
O(4)-O(3)-C(4)-C(13)	63.08(10)
O(4)-O(3)-C(4)-C(3)	-59.19(10)
O(4)-O(3)-C(4)-C(5)	179.01(7)
C(14)-C(3)-C(4)-O(3)	-63.98(11)
C(2)-C(3)-C(4)-O(3)	171.32(8)
C(14)-C(3)-C(4)-C(13)	174.37(9)
C(2)-C(3)-C(4)-C(13)	49.68(11)
C(14)-C(3)-C(4)-C(5)	51.20(12)
C(2)-C(3)-C(4)-C(5)	-73.50(11)
O(3)-C(4)-C(5)-C(6)	-73.66(10)
C(13)-C(4)-C(5)-C(6)	42.50(12)
C(3)-C(4)-C(5)-C(6)	166.43(9)
C(4)-C(5)-C(6)-C(7)	-114.00(10)
C(5)-C(6)-C(7)-C(15)	-62.92(12)
C(5)-C(6)-C(7)-C(8)	61.77(12)
C(15)-C(7)-C(8)-C(9)	-159.68(9)
C(6)-C(7)-C(8)-C(9)	74.62(11)
C(7)-C(8)-C(9)-O(2)	44.51(13)
C(7)-C(8)-C(9)-C(10)	-143.63(10)
O(2)-C(9)-C(10)-C(11)	-149.71(11)
C(8)-C(9)-C(10)-C(11)	38.39(17)
C(9)-C(10)-C(11)-C(12)	5.58(17)
C(9)-C(10)-C(11)-C(16)	-178.98(11)
C(10)-C(11)-C(12)-C(13)	54.08(14)
C(16)-C(11)-C(12)-C(13)	-121.56(12)
C(10)-C(11)-C(12)-C(1)	-122.05(11)
C(16)-C(11)-C(12)-C(1)	62.31(13)
O(1)-C(1)-C(12)-C(13)	-176.85(9)
C(2)-C(1)-C(12)-C(13)	-0.18(14)
O(1)-C(1)-C(12)-C(11)	-0.74(15)

C(2)-C(1)-C(12)-C(11)	175.93(9)
C(11)-C(12)-C(13)-C(4)	-168.20(9)
C(1)-C(12)-C(13)-C(4)	7.88(15)
O(3)-C(4)-C(13)-C(12)	-155.96(9)
C(3)-C(4)-C(13)-C(12)	-33.48(13)
C(5)-C(4)-C(13)-C(12)	92.25(12)

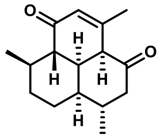
Table 7. Hydrogen bonds for cdv49 [Å and °].

D-H...A	d(D-H)	d(H...A)	d(D...A)	<(DHA)
O(4)-H(4)...O(2)#1	0.921(18)	1.871(19)	2.7817(12)	169.8(16)

Symmetry transformations used to generate equivalent atoms:

#1 -x+1,-y+1,-z+1

X-ray Data Collection, Structure Solution and Refinement for tricyclic enone 24 (cdv48).



24

A colorless crystal of approximate dimensions 0.106 x 0.146 x 0.332 mm was mounted on a glass fiber and transferred to a Bruker SMART APEX II diffractometer. The APEX2[4] program package was used to determine the unit-cell parameters and for data collection (90 sec/frame scan time for a sphere of diffraction data). The raw frame data was processed using SAINT[5] and SADABS[6] to yield the reflection data file. Subsequent calculations were carried out using the SHELXTL[7] program. The diffraction symmetry was *mmm* and the systematic absences were consistent with the orthorhombic space group *Pbcn* that was later determined to be correct.

The structure was solved by direct methods and refined on F^2 by full-matrix least-squares techniques. The analytical scattering factors[8] for neutral atoms were used throughout the analysis. Hydrogen atoms were located from a difference-Fourier map and refined (x,y,z and U_{iso}).

Least-squares analysis yielded wR2 = 0.1080 and Goof = 1.023 for 251 variables refined against 3421 data (0.75 Å), R1 = 0.0420 for those 2835 data with I > 2.0σ(I).

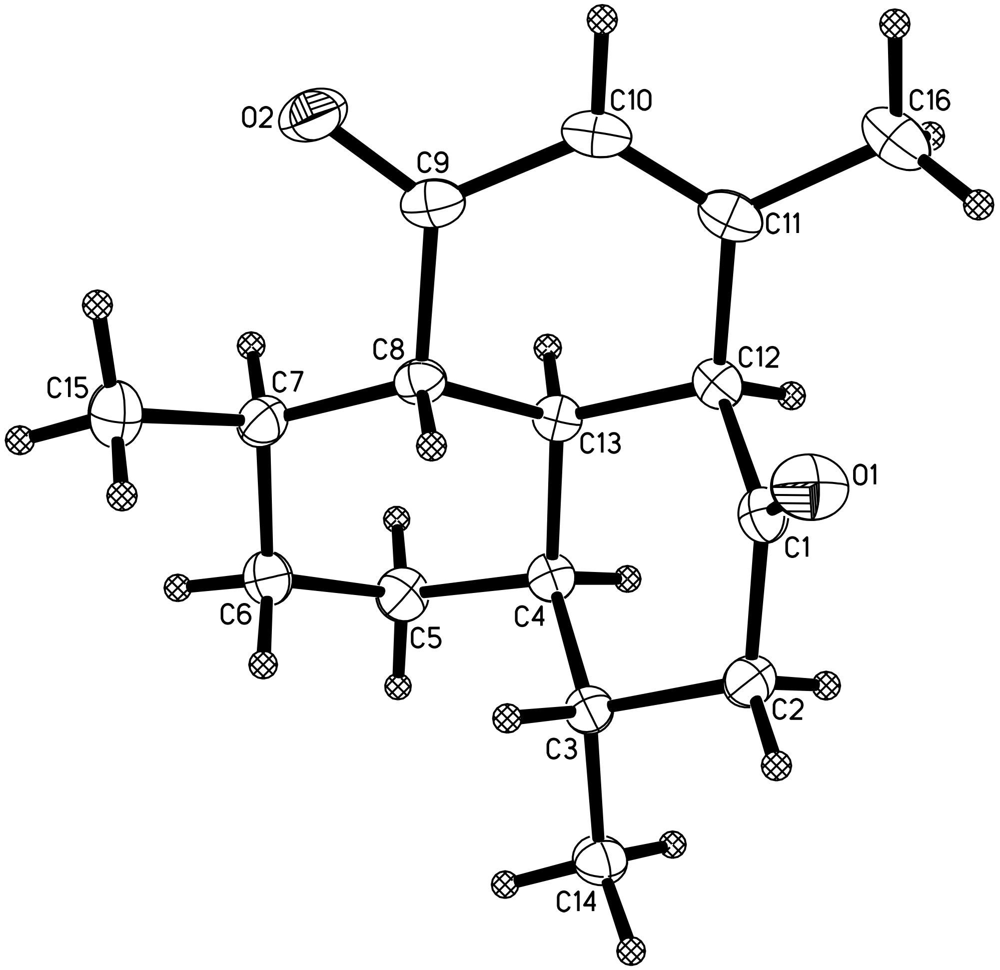

O2
C10
C16
C9
C11
C15
C7
C8
C12
C13
O1
C1
C6
C5
C4
C2
C3
C14

Table 1. Crystal data and structure refinement for cdv48.

Identification code	cdv48 (Vincenzo Ramella)	
Empirical formula	$C_{16} H_{22} O_2$	
Formula weight	246.33	
Temperature	133(2) K	
Wavelength	0.71073 Å	
Crystal system	Orthorhombic	
Space group	*Pbcn*	
Unit cell dimensions	a = 23.1932(11) Å	α= 90°.
	b = 11.6587(6) Å	β= 90°.
	c = 10.2797(5) Å	γ = 90°.
Volume	2779.7(2) $Å^3$	
Z	8	
Density (calculated)	1.177 Mg/m^3	
Absorption coefficient	0.076 mm^{-1}	
F(000)	1072	
Crystal color	colorless	
Crystal size	0.332 x 0.146 x 0.106 mm^3	
Theta range for data collection	1.756 to 28.286°	
Index ranges	$-30 \leq h \leq 30$, $-14 \leq k \leq 15$, $-13 \leq l \leq 13$	
Reflections collected	31333	
Independent reflections	3421 [R(int) = 0.0330]	
Completeness to theta = 25.500°	100.0 %	
Absorption correction	Semi-empirical from equivalents	
Max. and min. transmission	0.8621 and 0.8097	
Refinement method	Full-matrix least-squares on F^2	
Data / restraints / parameters	3421 / 0 / 251	
Goodness-of-fit on F^2	1.023	
Final R indices [I>2sigma(I) = 2835 data]	R1 = 0.0420, wR2 = 0.1010	
R indices (all data, 0.75 Å)	R1 = 0.0542, wR2 = 0.1080	
Largest diff. peak and hole	0.372 and -0.163 $e.Å^{-3}$	

Table 2. Atomic coordinates (x 10^4) and equivalent isotropic displacement parameters (Å^{2}x 10^3) for cdv48. U(eq) is defined as one third of the trace of the orthogonalized U^{ij} tensor.

	x	y	z	U(eq)
O(1)	2865(1)	10319(1)	1678(1)	29(1)
O(2)	4775(1)	8282(1)	611(1)	30(1)
C(1)	3007(1)	9802(1)	2651(1)	19(1)
C(2)	2589(1)	9115(1)	3449(1)	20(1)
C(3)	2790(1)	7875(1)	3688(1)	17(1)
C(4)	3414(1)	7859(1)	4198(1)	18(1)
C(5)	3657(1)	6647(1)	4363(1)	23(1)
C(6)	3732(1)	6052(1)	3055(1)	24(1)
C(7)	4129(1)	6710(1)	2124(1)	22(1)
C(8)	3950(1)	7977(1)	2004(1)	17(1)
C(9)	4400(1)	8705(1)	1293(1)	21(1)
C(10)	4375(1)	9956(1)	1460(1)	23(1)
C(11)	4029(1)	10480(1)	2311(1)	21(1)
C(12)	3626(1)	9793(1)	3158(1)	18(1)
C(13)	3831(1)	8544(1)	3338(1)	17(1)
C(14)	2374(1)	7308(1)	4648(1)	23(1)
C(15)	4142(1)	6084(1)	814(1)	32(1)
C(16)	4035(1)	11755(1)	2494(1)	28(1)

Table 3. Bond lengths [Å] and angles [°] for cdv48.

O(1)-C(1)	1.2132(14)
O(2)-C(9)	1.2225(15)
C(1)-C(2)	1.5016(16)
C(1)-C(12)	1.5278(16)
C(2)-C(3)	1.5394(16)
C(3)-C(14)	1.5311(16)
C(3)-C(4)	1.5379(16)
C(4)-C(5)	1.5304(16)
C(4)-C(13)	1.5355(15)
C(5)-C(6)	1.5240(17)
C(6)-C(7)	1.5338(17)
C(7)-C(15)	1.5324(17)
C(7)-C(8)	1.5397(16)
C(8)-C(9)	1.5310(16)
C(8)-C(13)	1.5466(15)
C(9)-C(10)	1.4689(18)
C(10)-C(11)	1.3341(18)
C(11)-C(16)	1.4993(17)
C(11)-C(12)	1.5069(16)
C(12)-C(13)	1.5423(15)
O(1)-C(1)-C(2)	122.67(11)
O(1)-C(1)-C(12)	122.65(11)
C(2)-C(1)-C(12)	114.68(9)
C(1)-C(2)-C(3)	113.09(9)
C(14)-C(3)-C(4)	111.63(9)
C(14)-C(3)-C(2)	108.49(9)
C(4)-C(3)-C(2)	110.58(9)
C(5)-C(4)-C(13)	108.17(9)
C(5)-C(4)-C(3)	113.29(10)
C(13)-C(4)-C(3)	112.97(9)
C(6)-C(5)-C(4)	111.41(10)
C(5)-C(6)-C(7)	113.01(10)
C(15)-C(7)-C(6)	108.70(10)

C(15)-C(7)-C(8)	113.05(10)
C(6)-C(7)-C(8)	111.58(9)
C(9)-C(8)-C(7)	112.70(9)
C(9)-C(8)-C(13)	107.90(9)
C(7)-C(8)-C(13)	112.77(9)
O(2)-C(9)-C(10)	119.76(11)
O(2)-C(9)-C(8)	122.37(11)
C(10)-C(9)-C(8)	117.86(10)
C(11)-C(10)-C(9)	123.70(11)
C(10)-C(11)-C(16)	122.09(11)
C(10)-C(11)-C(12)	120.49(11)
C(16)-C(11)-C(12)	117.40(11)
C(11)-C(12)-C(1)	112.45(9)
C(11)-C(12)-C(13)	112.34(10)
C(1)-C(12)-C(13)	109.72(9)
C(4)-C(13)-C(12)	111.47(9)
C(4)-C(13)-C(8)	113.58(9)
C(12)-C(13)-C(8)	110.58(9)

Table 4. Anisotropic displacement parameters ($Å^2$x 10^3) for cdv48. The anisotropic displacement factor exponent takes the form: $-2\pi^2$[h^2 $a^{*2}U^{11}$ + ... + 2 h k a* b* U^{12}]

	U^{11}	U^{22}	U^{33}	U^{23}	U^{13}	U^{12}
O(1)	28(1)	32(1)	25(1)	12(1)	-5(1)	0(1)
O(2)	23(1)	38(1)	28(1)	-4(1)	8(1)	-5(1)
C(1)	22(1)	17(1)	18(1)	0(1)	0(1)	1(1)
C(2)	19(1)	21(1)	21(1)	2(1)	1(1)	2(1)
C(3)	19(1)	18(1)	14(1)	1(1)	2(1)	0(1)
C(4)	21(1)	18(1)	13(1)	2(1)	0(1)	0(1)
C(5)	26(1)	21(1)	22(1)	6(1)	0(1)	3(1)
C(6)	24(1)	18(1)	30(1)	1(1)	2(1)	2(1)
C(7)	18(1)	24(1)	24(1)	-3(1)	1(1)	1(1)
C(8)	15(1)	21(1)	16(1)	-1(1)	-1(1)	-2(1)
C(9)	17(1)	30(1)	15(1)	0(1)	-2(1)	-5(1)
C(10)	21(1)	28(1)	19(1)	4(1)	-2(1)	-9(1)
C(11)	22(1)	23(1)	18(1)	3(1)	-6(1)	-7(1)
C(12)	22(1)	18(1)	13(1)	0(1)	-1(1)	-2(1)
C(13)	17(1)	19(1)	14(1)	1(1)	-2(1)	-1(1)
C(14)	25(1)	22(1)	23(1)	1(1)	5(1)	-4(1)
C(15)	37(1)	28(1)	31(1)	-9(1)	7(1)	-1(1)
C(16)	40(1)	22(1)	22(1)	3(1)	-4(1)	-10(1)

Table 5. Hydrogen coordinates (x 10^4) and isotropic displacement parameters ($Å^2$x 10 ^{3}) for cdv48.

	x	y	z	U(eq)
H(2A)	2210(6)	9139(12)	3031(14)	22(3)
H(2B)	2562(6)	9483(12)	4274(14)	22(3)
H(3A)	2777(5)	7475(11)	2863(13)	14(3)
H(4A)	3410(6)	8236(11)	5053(13)	17(3)
H(5A)	4040(7)	6701(12)	4805(15)	27(4)
H(5B)	3414(6)	6189(13)	4942(15)	27(4)
H(6A)	3347(6)	5930(12)	2616(14)	24(4)
H(6B)	3896(7)	5287(14)	3195(15)	30(4)
H(7A)	4522(6)	6710(12)	2526(15)	26(4)
H(8A)	3595(6)	8018(11)	1461(13)	19(3)
H(10A)	4638(6)	10388(13)	939(15)	27(4)
H(12A)	3610(6)	10135(11)	4030(14)	18(3)
H(13A)	4205(6)	8583(11)	3812(13)	16(3)
H(14A)	2464(7)	6498(14)	4784(15)	34(4)
H(14B)	1965(6)	7368(13)	4294(14)	25(4)
H(14C)	2412(6)	7690(13)	5502(15)	29(4)
H(15A)	4261(8)	5276(16)	942(17)	45(5)
H(15B)	4410(7)	6435(15)	187(17)	39(4)
H(15C)	3749(8)	6087(16)	380(18)	48(5)
H(16A)	4299(7)	12124(15)	1869(17)	39(4)
H(16B)	4163(7)	11921(13)	3364(17)	36(4)
H(16C)	3639(8)	12083(14)	2374(17)	40(4)

Table 6. Torsion angles [°] for cdv48.

O(1)-C(1)-C(2)-C(3)	127.26(12)
C(12)-C(1)-C(2)-C(3)	-52.35(13)
C(1)-C(2)-C(3)-C(14)	172.82(10)
C(1)-C(2)-C(3)-C(4)	50.08(13)
C(14)-C(3)-C(4)-C(5)	63.31(13)
C(2)-C(3)-C(4)-C(5)	-175.81(9)
C(14)-C(3)-C(4)-C(13)	-173.24(9)
C(2)-C(3)-C(4)-C(13)	-52.36(12)
C(13)-C(4)-C(5)-C(6)	-58.87(13)
C(3)-C(4)-C(5)-C(6)	67.17(13)
C(4)-C(5)-C(6)-C(7)	58.10(14)
C(5)-C(6)-C(7)-C(15)	-176.11(11)
C(5)-C(6)-C(7)-C(8)	-50.76(14)
C(15)-C(7)-C(8)-C(9)	-67.90(13)
C(6)-C(7)-C(8)-C(9)	169.20(10)
C(15)-C(7)-C(8)-C(13)	169.63(10)
C(6)-C(7)-C(8)-C(13)	46.73(13)
C(7)-C(8)-C(9)-O(2)	17.99(15)
C(13)-C(8)-C(9)-O(2)	143.16(11)
C(7)-C(8)-C(9)-C(10)	-161.39(10)
C(13)-C(8)-C(9)-C(10)	-36.22(13)
O(2)-C(9)-C(10)-C(11)	-171.14(11)
C(8)-C(9)-C(10)-C(11)	8.25(17)
C(9)-C(10)-C(11)-C(16)	177.22(11)
C(9)-C(10)-C(11)-C(12)	-0.94(18)
C(10)-C(11)-C(12)-C(1)	-100.96(13)
C(16)-C(11)-C(12)-C(1)	80.79(13)
C(10)-C(11)-C(12)-C(13)	23.41(15)
C(16)-C(11)-C(12)-C(13)	-154.83(10)
O(1)-C(1)-C(12)-C(11)	-0.48(16)
C(2)-C(1)-C(12)-C(11)	179.12(10)
O(1)-C(1)-C(12)-C(13)	-126.29(11)
C(2)-C(1)-C(12)-C(13)	53.32(12)
C(5)-C(4)-C(13)-C(12)	-178.24(9)

C(3)-C(4)-C(13)-C(12)	55.53(12)
C(5)-C(4)-C(13)-C(8)	56.05(12)
C(3)-C(4)-C(13)-C(8)	-70.19(12)
C(11)-C(12)-C(13)-C(4)	-179.74(9)
C(1)-C(12)-C(13)-C(4)	-53.87(12)
C(11)-C(12)-C(13)-C(8)	-52.38(12)
C(1)-C(12)-C(13)-C(8)	73.49(11)
C(9)-C(8)-C(13)-C(4)	-176.32(9)
C(7)-C(8)-C(13)-C(4)	-51.20(13)
C(9)-C(8)-C(13)-C(12)	57.49(12)
C(7)-C(8)-C(13)-C(12)	-177.38(9)

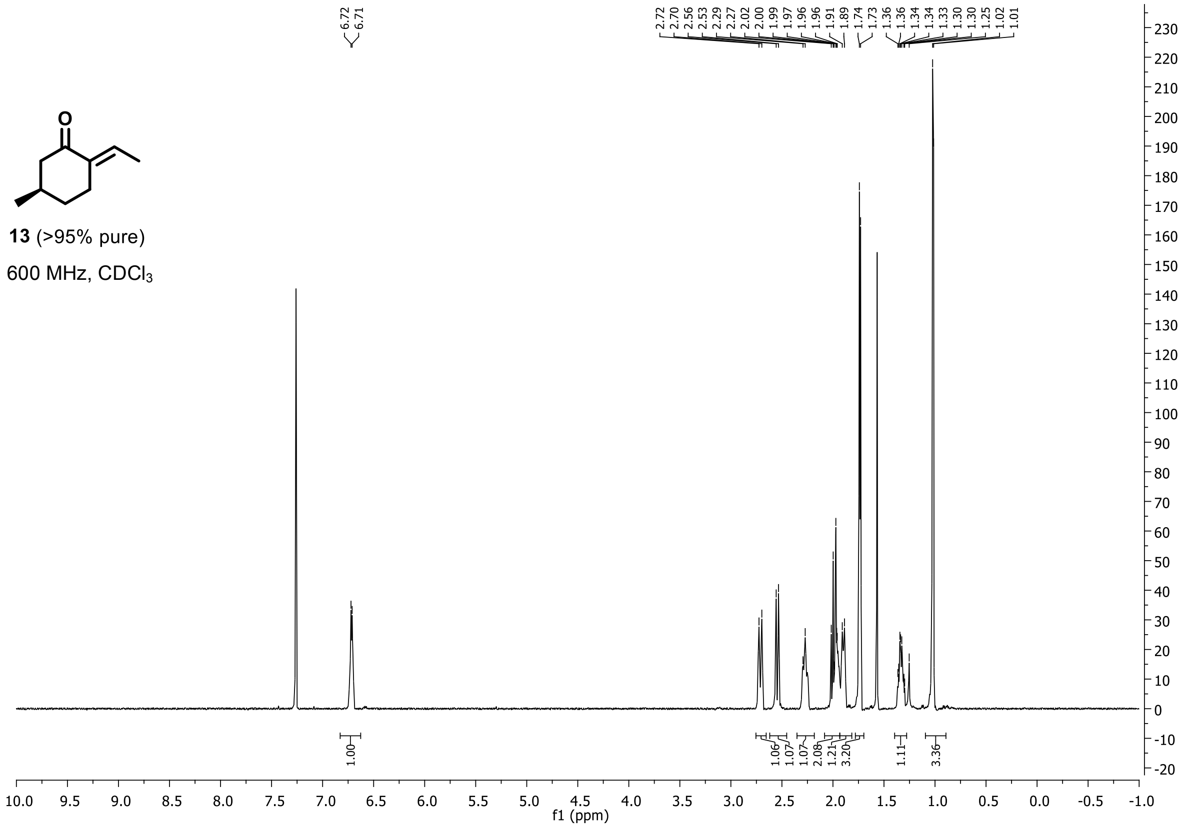
Table 7. Hydrogen bonds for cdv48 [Å and °].

D-H...A	d(D-H)	d(H...A)	d(D...A)	<(DHA)
C(2)-H(2B)...O(1)#1	0.953(15)	2.579(15)	3.4446(15)	151.1(11)
C(10)-H(10A)...O(2)#2	0.956(15)	2.607(16)	3.5559(15)	171.8(12)

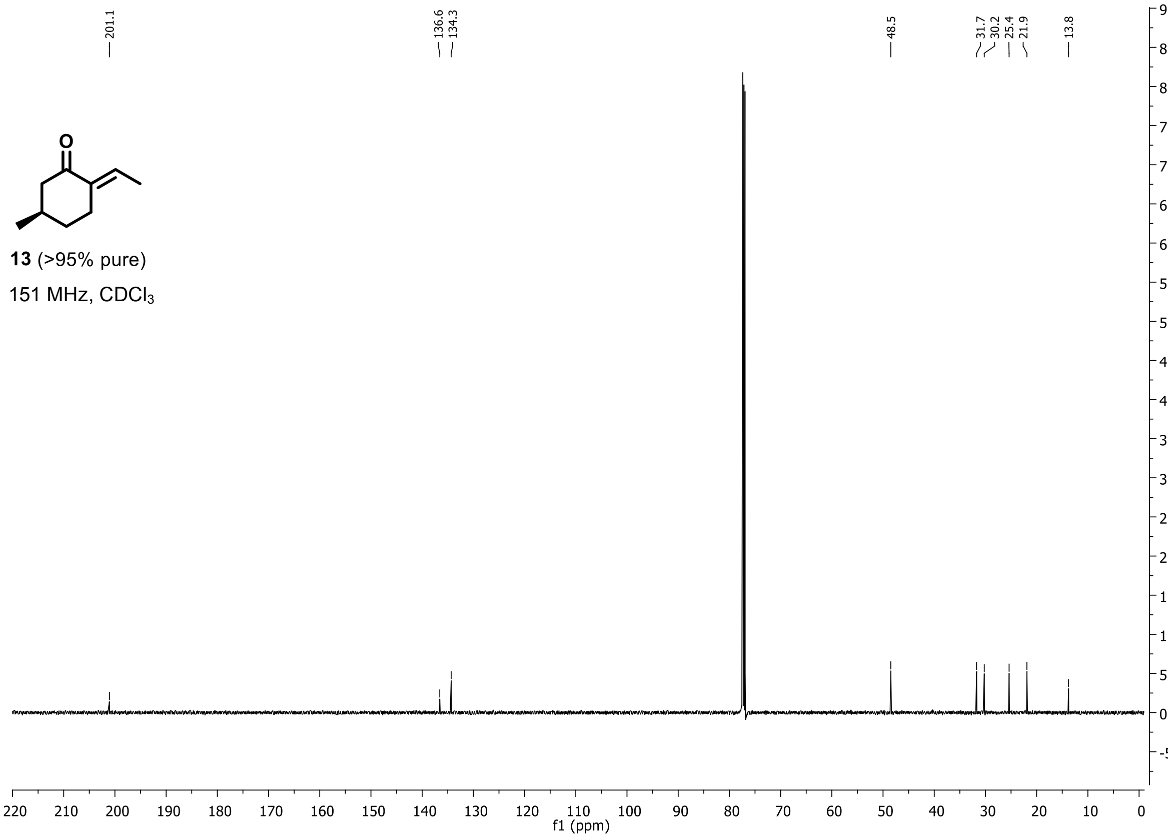
Symmetry transformations used to generate equivalent atoms:

#1 x,-y+2,z+1/2 #2 -x+1,-y+2,-z

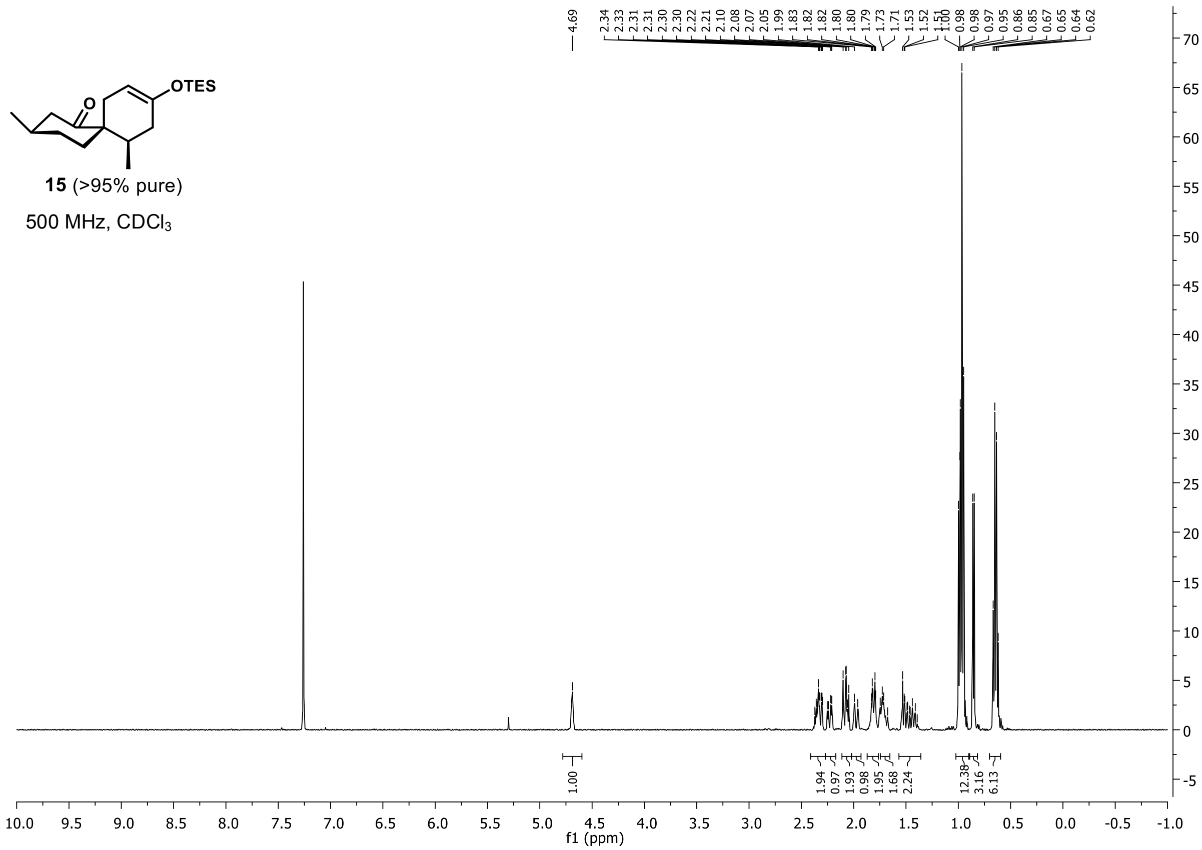
III. NMR Spectra

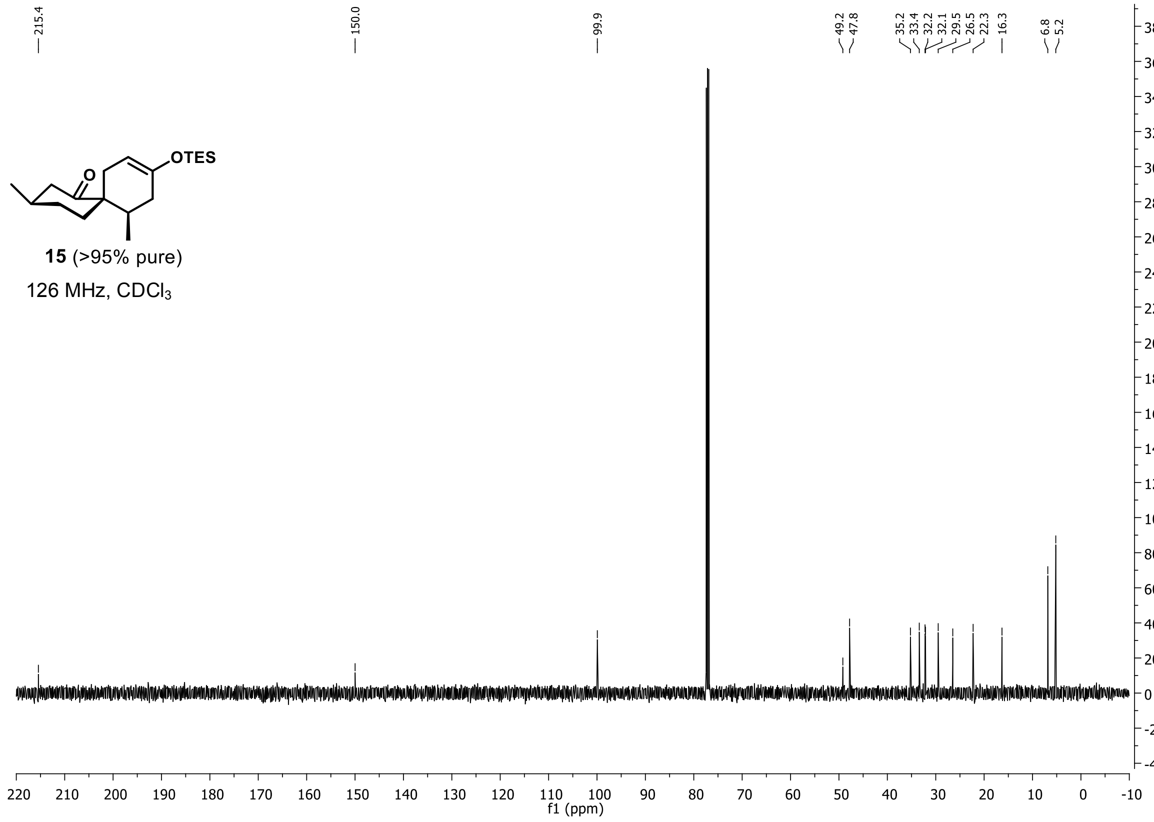

13 (>95% pure)

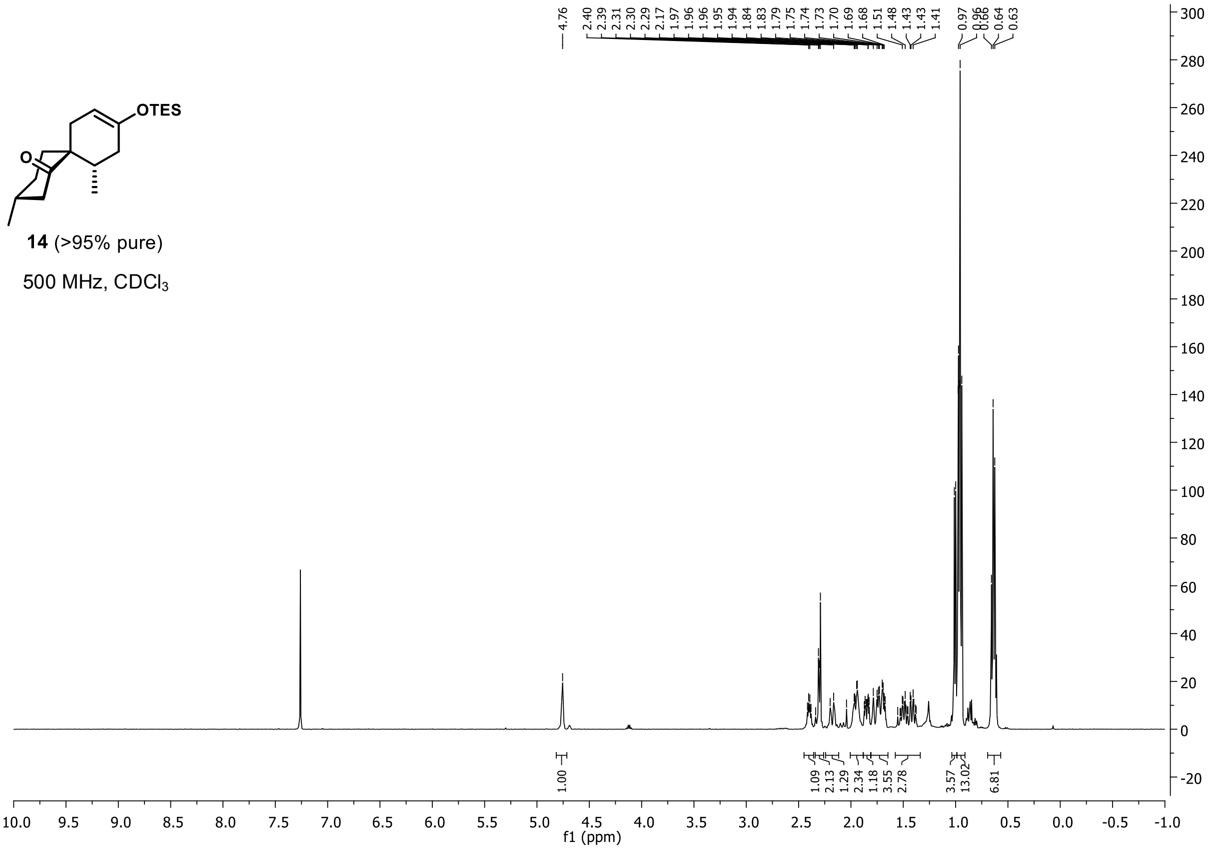
600 MHz, CDCl$_3$


13 (>95% pure)

151 MHz, CDCl$_3$

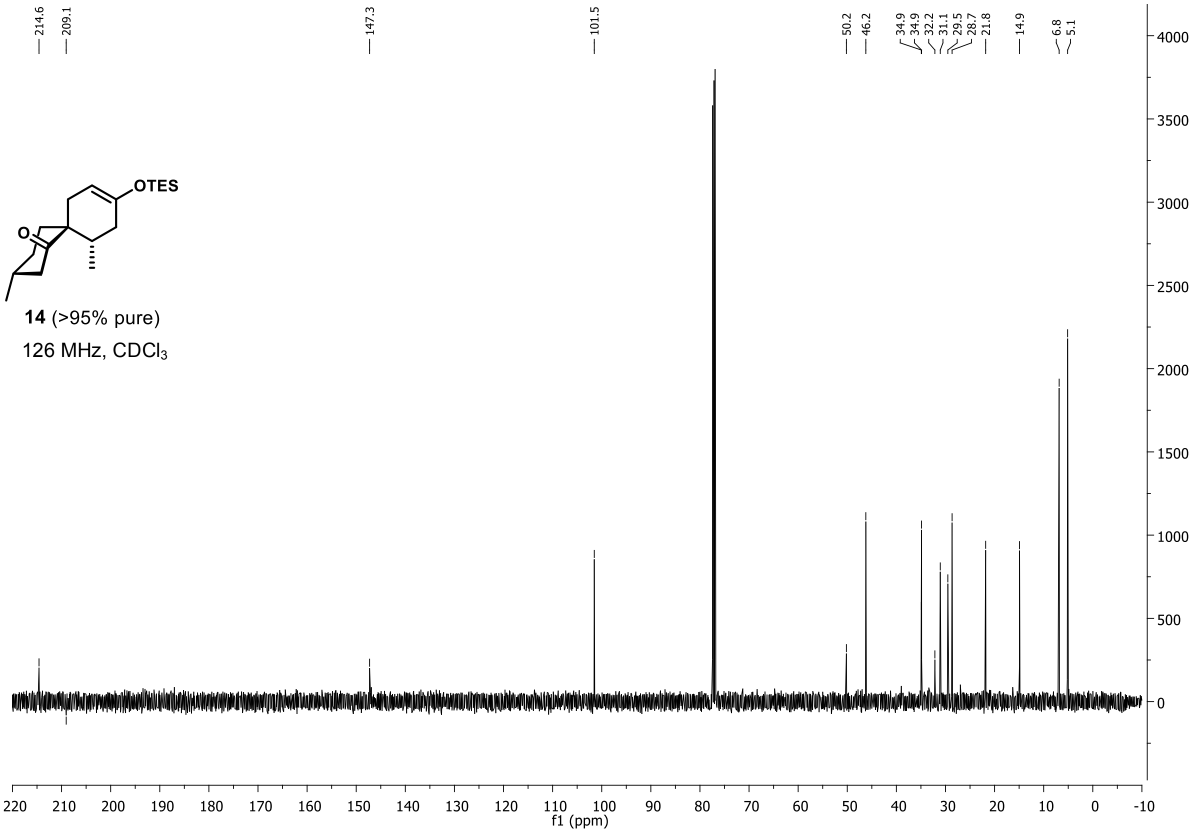

OTES
O
15 (>95% pure)
500 MHz, CDCl3
4.69
2.34
2.33
2.31
2.31
2.30
2.30
2.22
2.21
2.10
2.08
2.07
2.05
1.99
1.83
1.82
1.82
1.80
1.80
1.79
1.73
1.71
1.53
1.52
1.51
1.00
0.98
0.98
0.97
0.95
0.86
0.85
0.67
0.65
0.64
0.62
1.00
1.94
0.97
1.93
0.98
1.95
1.68
2.24
12.38
3.16
6.13
f1 (ppm)


OTES
O
15 (>95% pure)
126 MHz, CDCl3
215.4
150.0
99.9
49.2
47.8
35.2
33.4
32.2
32.1
29.5
26.5
22.3
16.3
6.8
5.2
f1 (ppm)



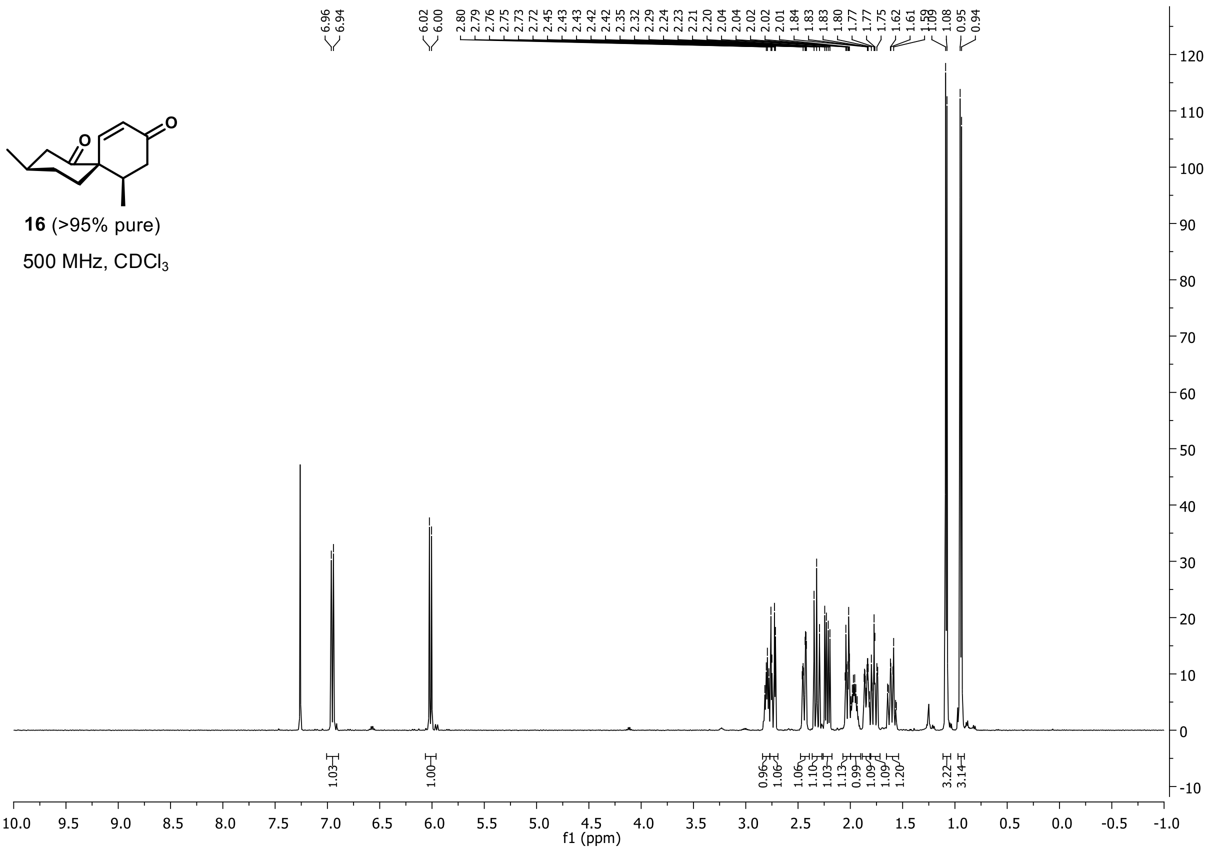
14 (>95% pure)

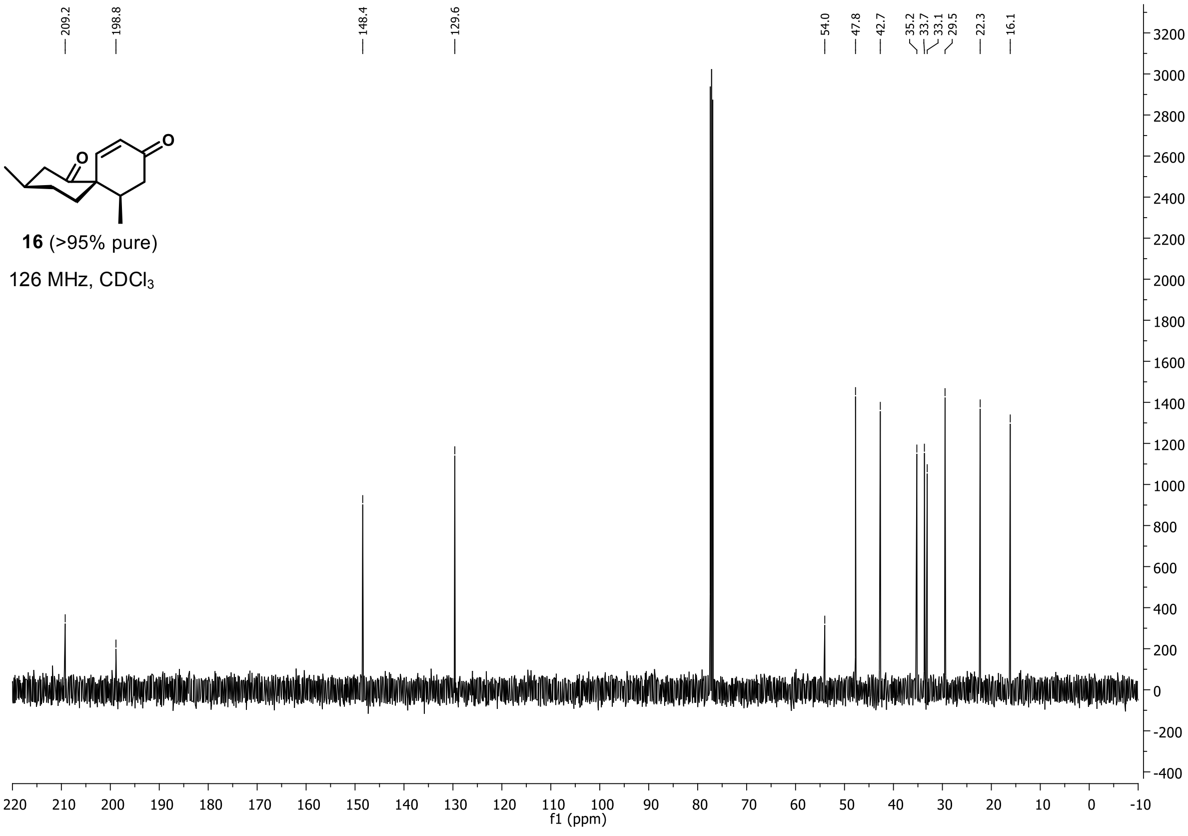
500 MHz, $CDCl_3$

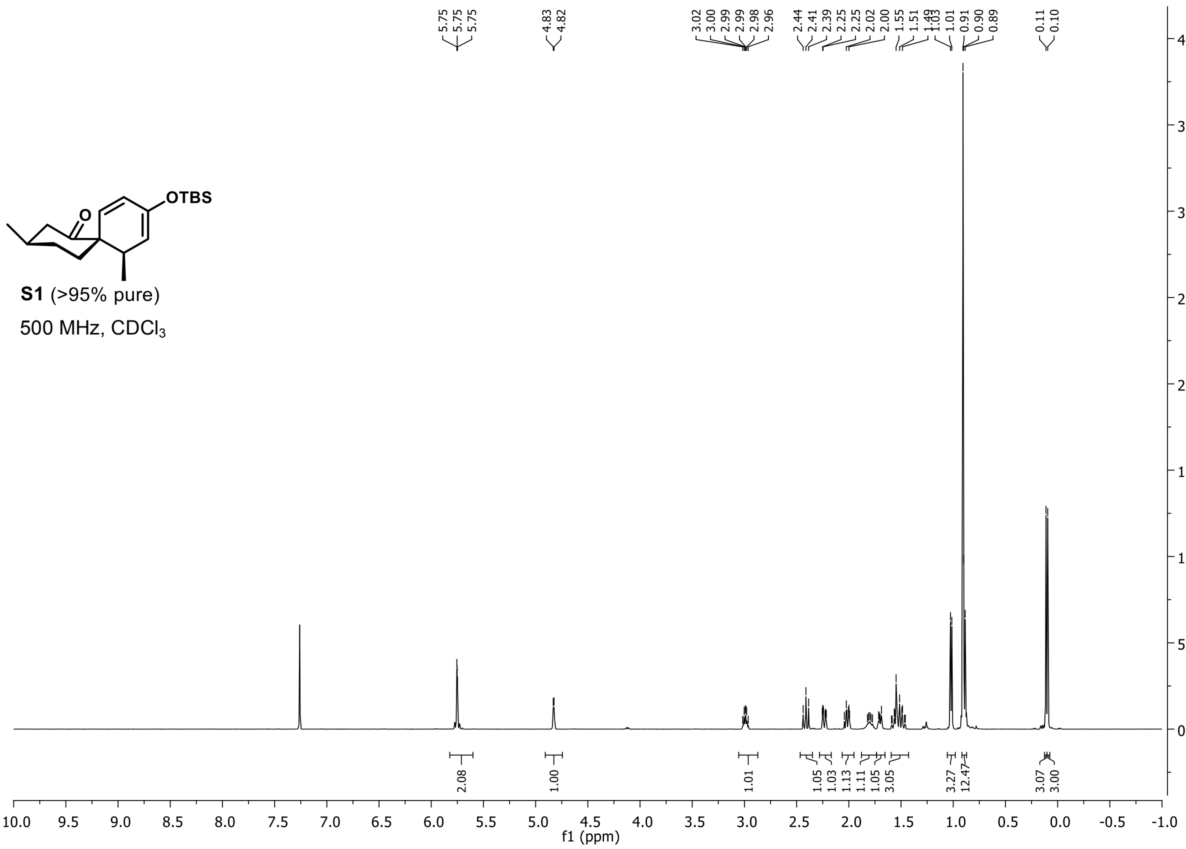


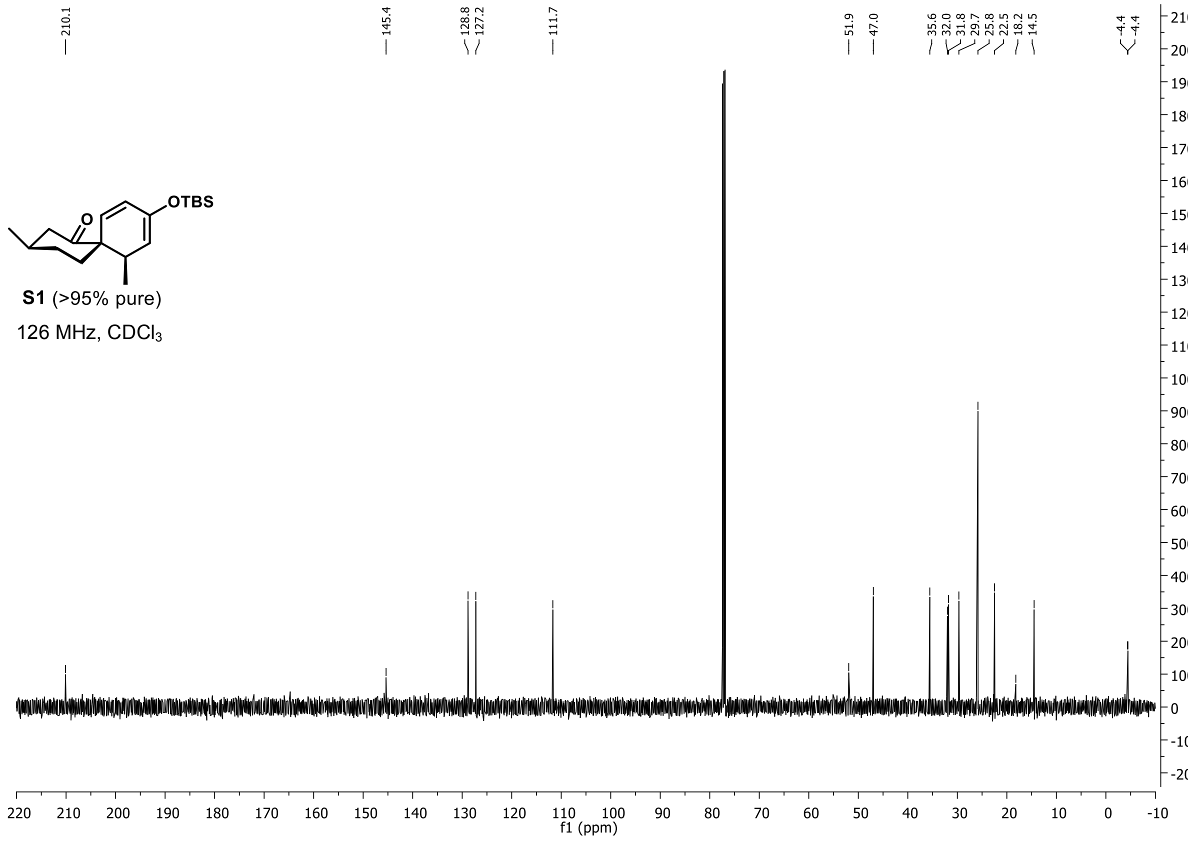
14 (>95% pure)

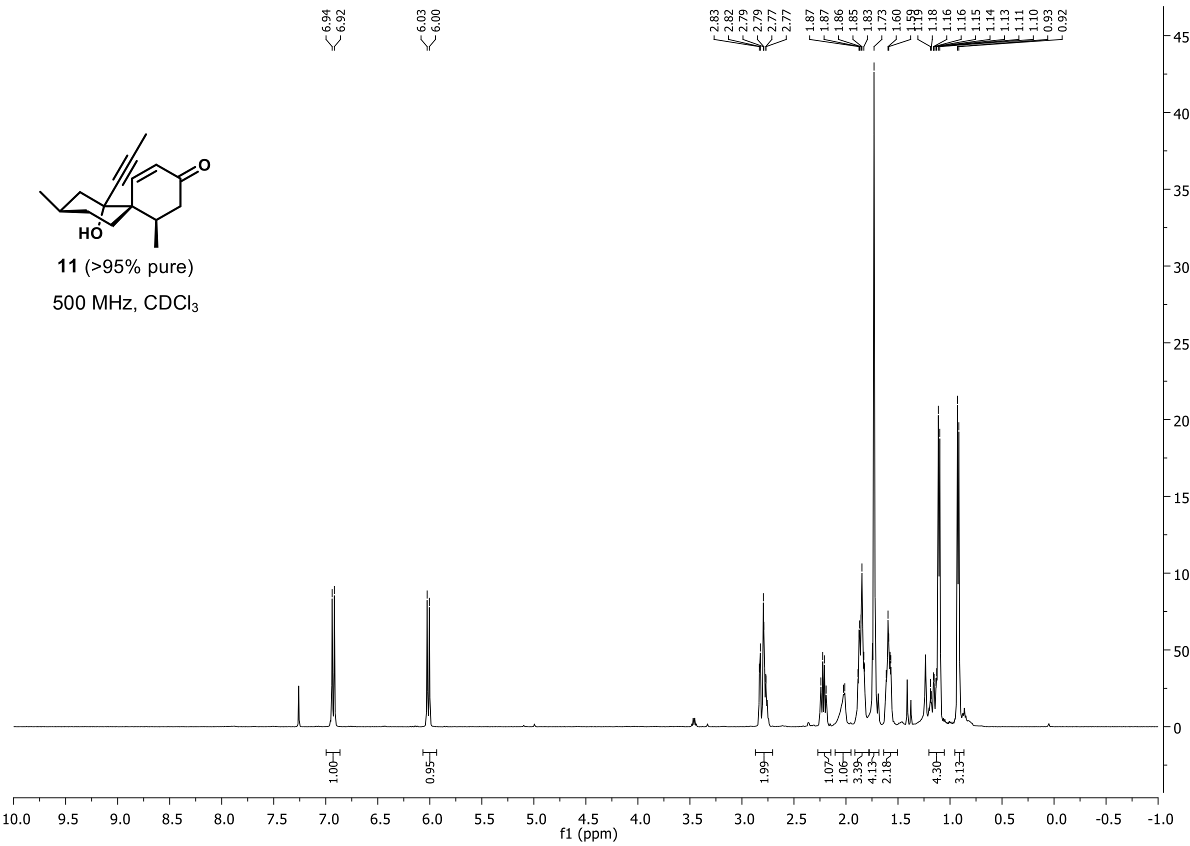
126 MHz, $CDCl_3$


6.96
6.94
6.02
6.00
2.80
2.79
2.76
2.75
2.73
2.72
2.45
2.43
2.43
2.42
2.42
2.35
2.32
2.29
2.24
2.23
2.21
2.20
2.04
2.04
2.02
2.02
2.01
1.84
1.83
1.83
1.80
1.77
1.77
1.75
1.62
1.61
1.59
1.09
1.08
0.95
0.94
O
O
16 (>95% pure)
500 MHz, CDCl$_3$
1.03
1.00
0.96
1.06
1.06
1.10
1.03
1.13
0.99
1.09
1.09
1.20
3.22
3.14
120
110
100
90
80
70
60
50
40
30
20
10
0
-10
10.0
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
-0.5
-1.0
f1 (ppm)


209.2
198.8
148.4
129.6
54.0
47.8
42.7
35.2
33.7
33.1
29.5
22.3
16.1
O
O
16 (>95% pure)
126 MHz, CDCl$_3$
3200
3000
2800
2600
2400
2200
2000
1800
1600
1400
1200
1000
800
600
400
200
0
-200
-400
220
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
-10
f1 (ppm)

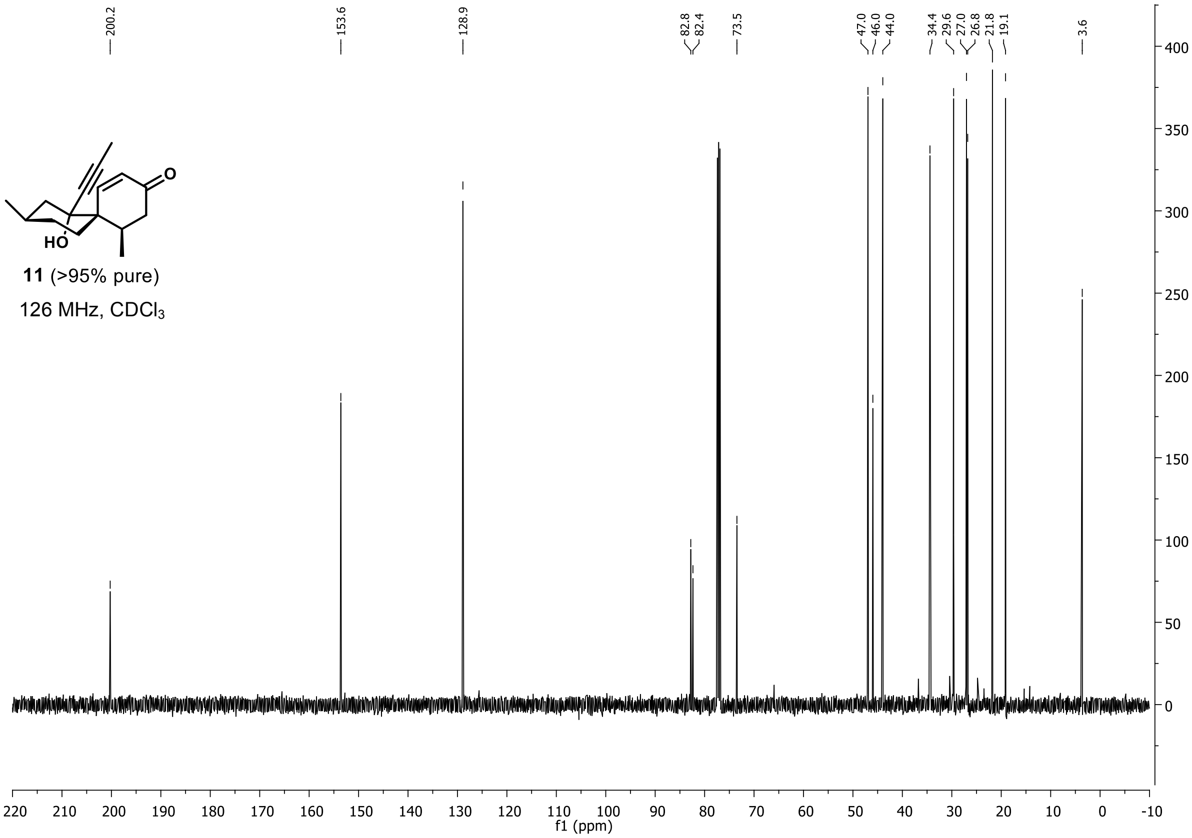

OTBS
O
S1 (>95% pure)
500 MHz, CDCl3
5.75 5.75 5.75
4.83 4.82
3.02 3.00 2.99 2.99 2.98 2.96
2.44 2.41 2.39 2.25 2.25 2.02 2.00 1.55 1.51 1.49 1.03 1.01 0.91 0.90 0.89
0.11 0.10
2.08
1.00
1.01
1.05 1.03 1.13 1.11 1.05 3.05
3.27 12.47
3.07 3.00
10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0 -0.5 -1.0
f1 (ppm)
400 350 300 250 200 150 100 50 0


OTBS
O
S1 (>95% pure)
126 MHz, CDCl3
210.1
145.4
128.8 127.2
111.7
51.9
47.0
35.6 32.0 31.8 29.7 25.8 22.5 18.2 14.5
-4.4 -4.4
220 210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10
f1 (ppm)
2100 2000 1900 1800 1700 1600 1500 1400 1300 1200 1100 1000 900 800 700 600 500 400 300 200 100 0 -100 -200



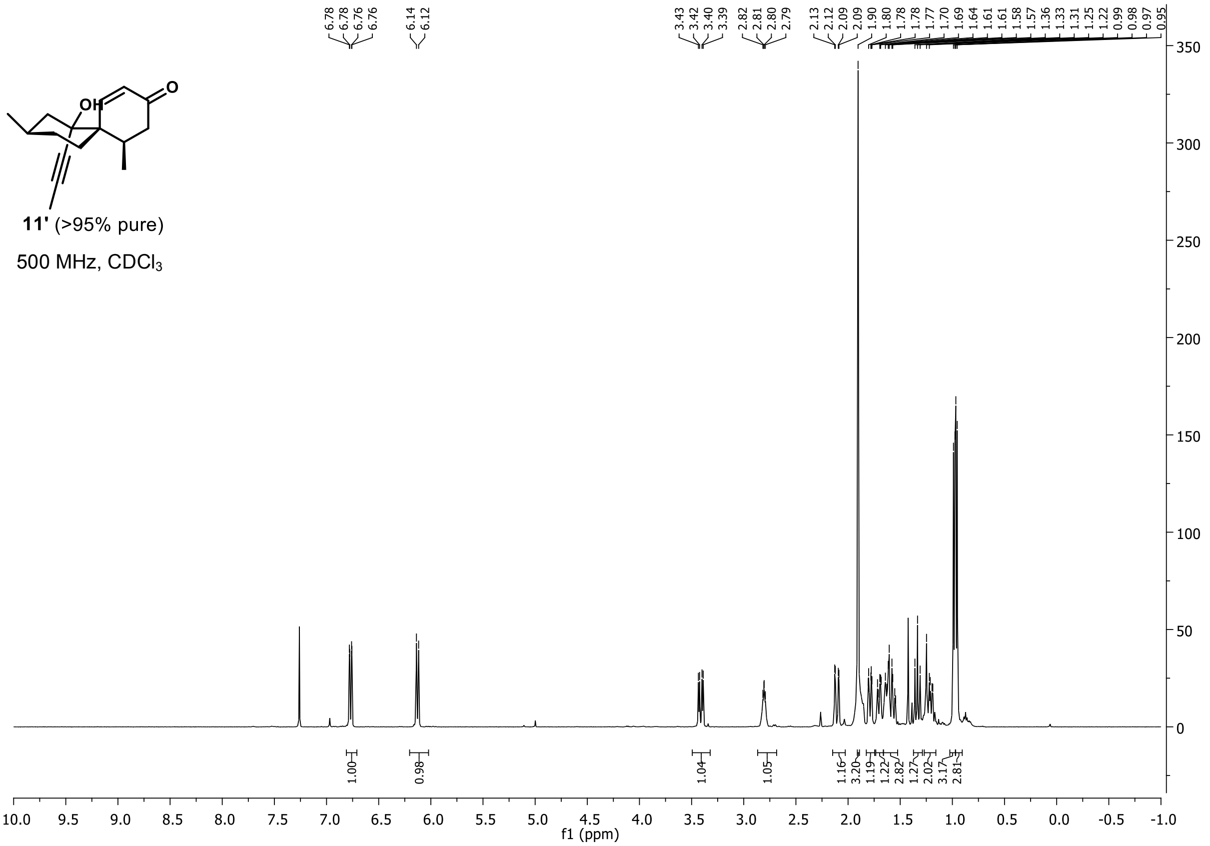
11 (>95% pure)

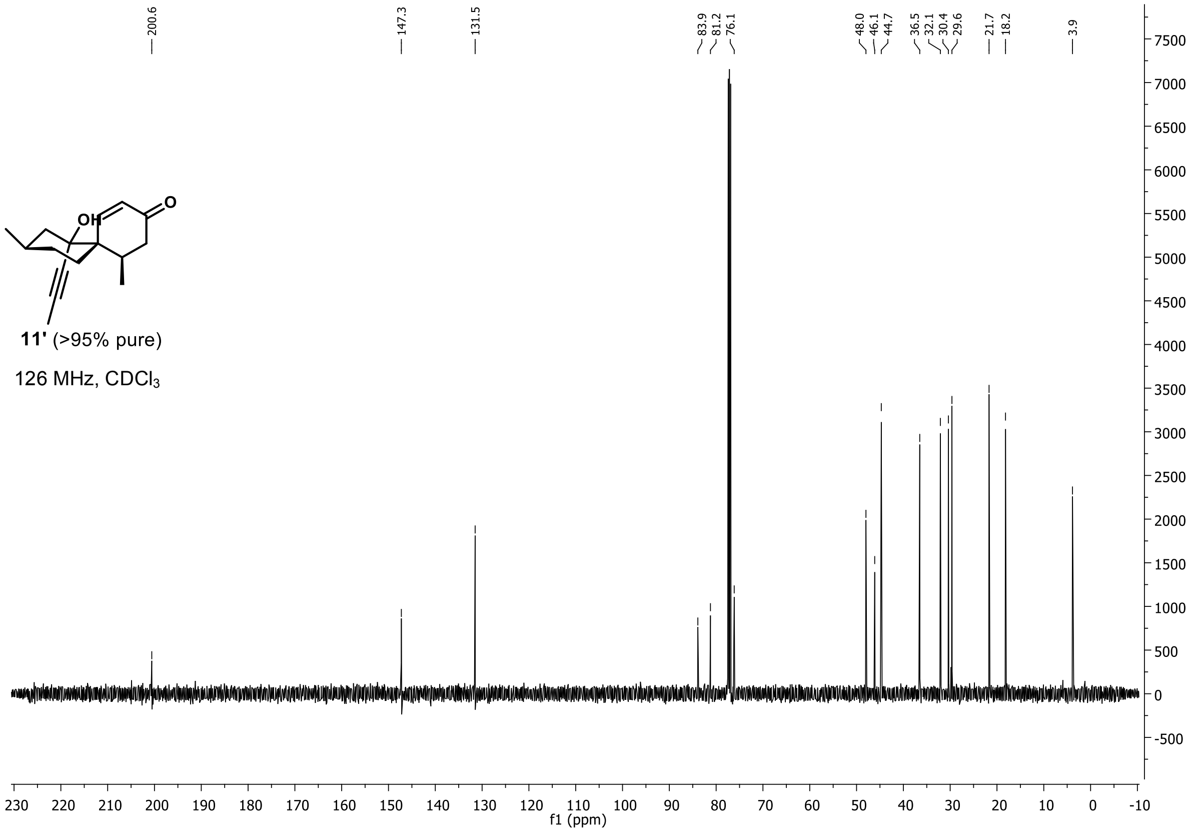
500 MHz, $CDCl_3$

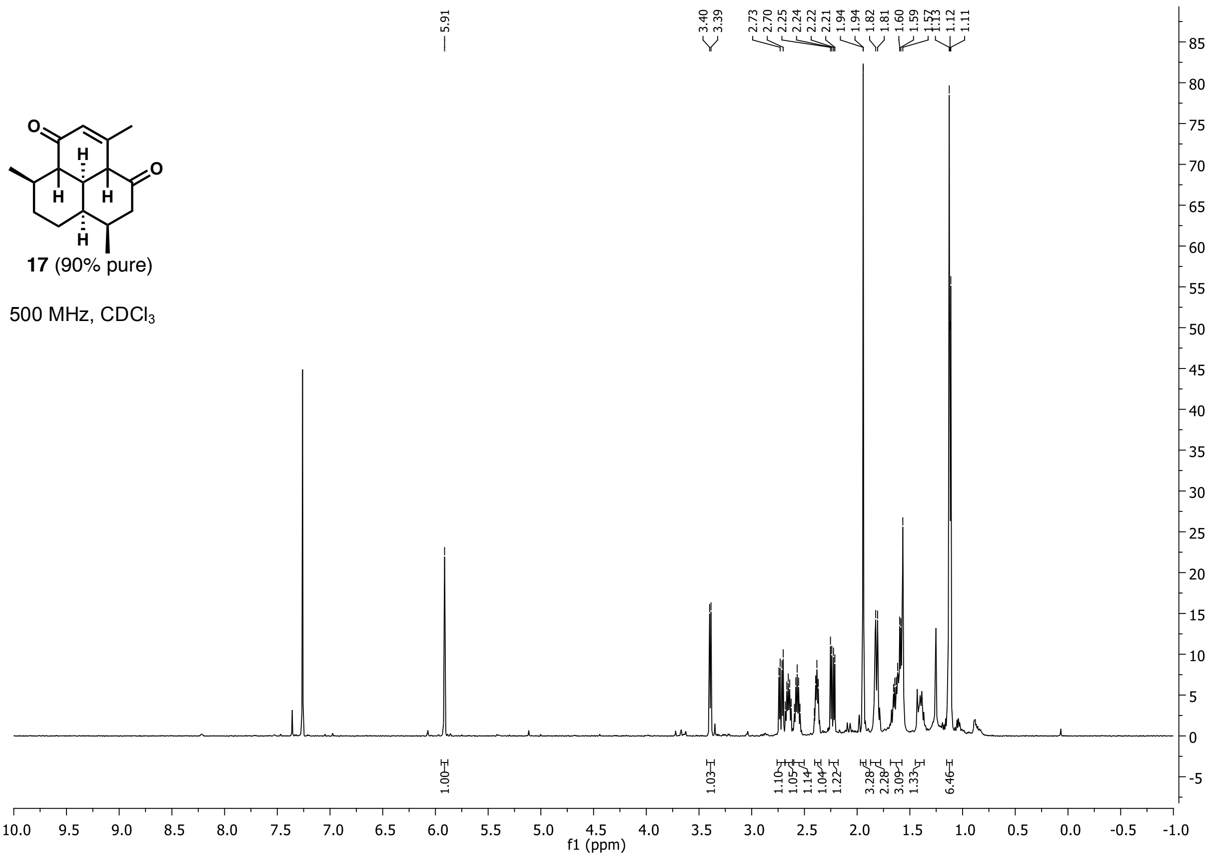


11 (>95% pure)

126 MHz, $CDCl_3$

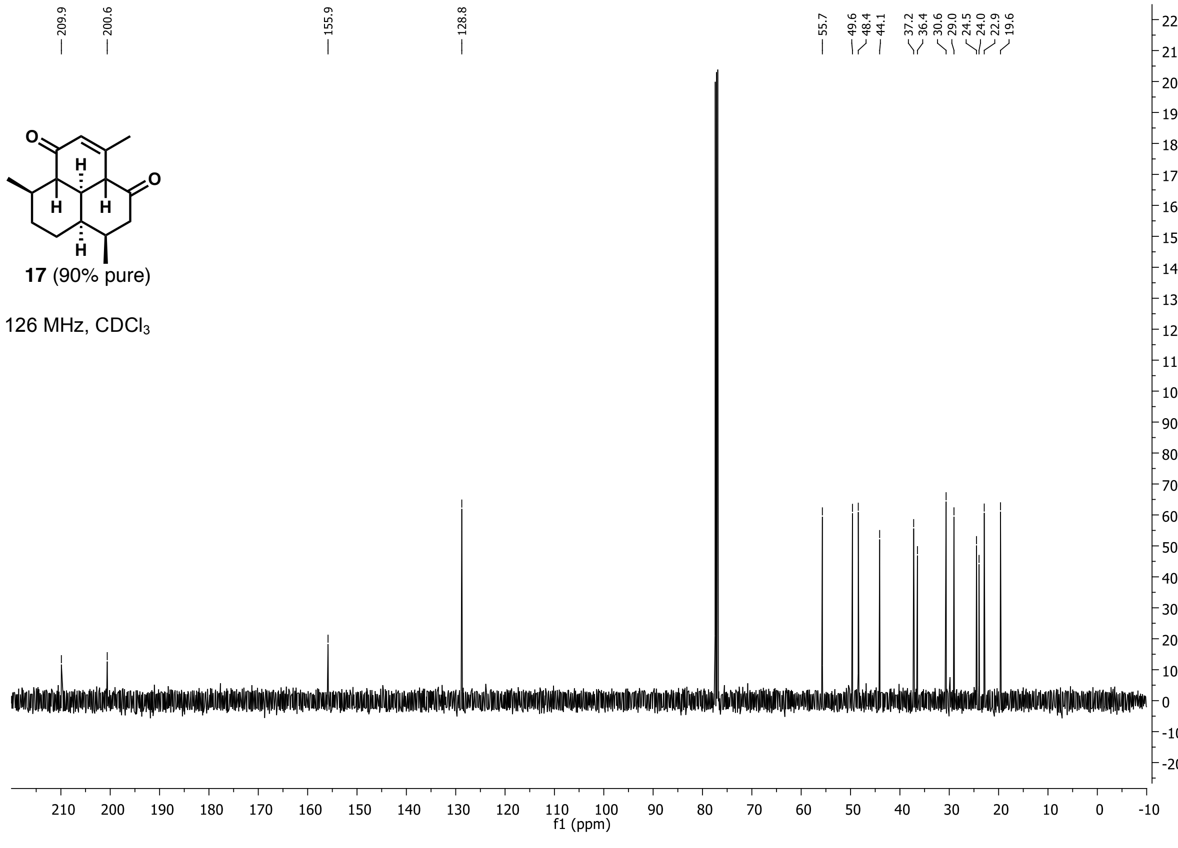

6.78
6.78
6.76
6.76
6.14
6.12
3.43
3.42
3.40
3.39
2.82
2.81
2.80
2.79
2.13
2.12
2.09
2.09
1.90
1.80
1.78
1.78
1.77
1.70
1.69
1.64
1.61
1.61
1.58
1.57
1.36
1.33
1.31
1.25
1.22
0.99
0.98
0.97
0.95
OH
O
11' (>95% pure)
500 MHz, CDCl$_3$
1.00
0.98
1.04
1.05
1.16
3.20
1.19
1.22
2.82
1.27
2.02
3.17
2.81
350
300
250
200
150
100
50
0
10.0
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
-0.5
-1.0
f1 (ppm)


200.6
147.3
131.5
83.9
81.2
76.1
48.0
46.1
44.7
36.5
32.1
30.4
29.6
21.7
18.2
3.9
OH
O
11' (>95% pure)
126 MHz, CDCl$_3$
7500
7000
6500
6000
5500
5000
4500
4000
3500
3000
2500
2000
1500
1000
500
0
-500
230
220
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
-10
f1 (ppm)



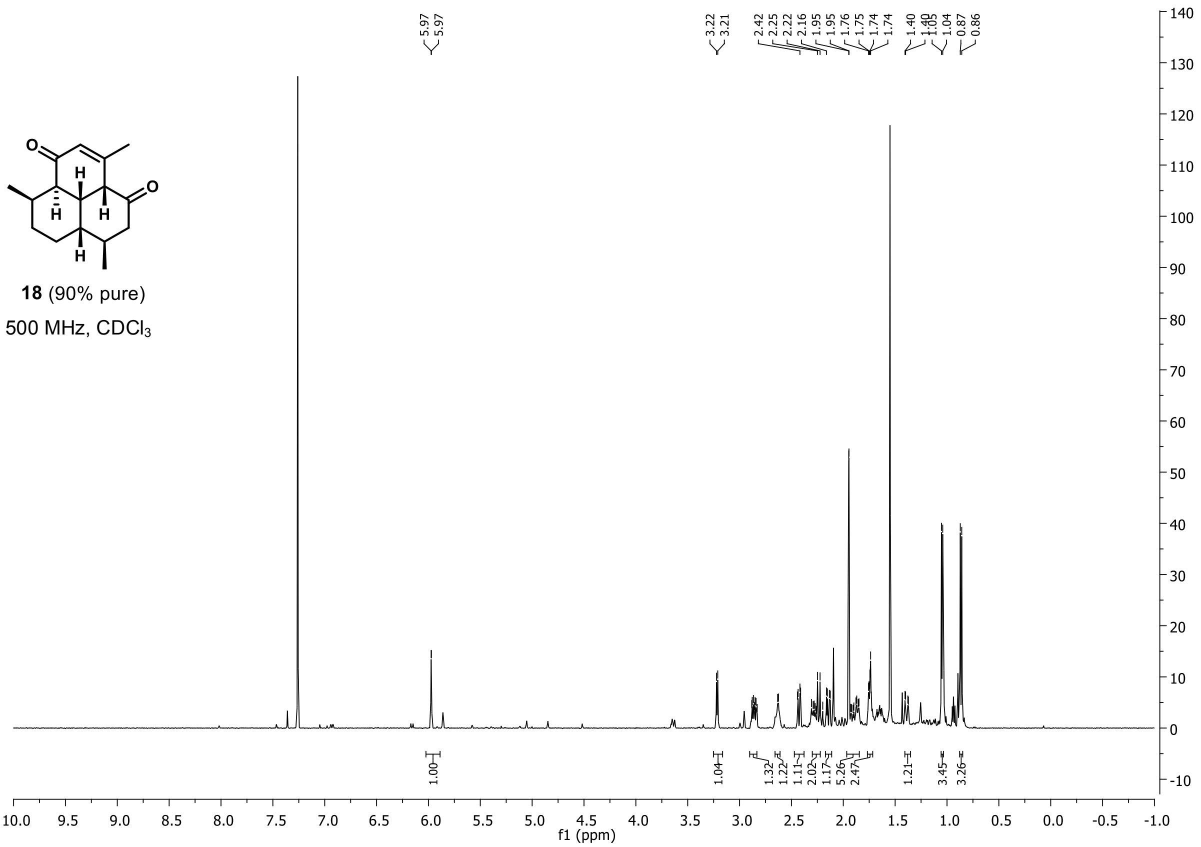
17 (90% pure)

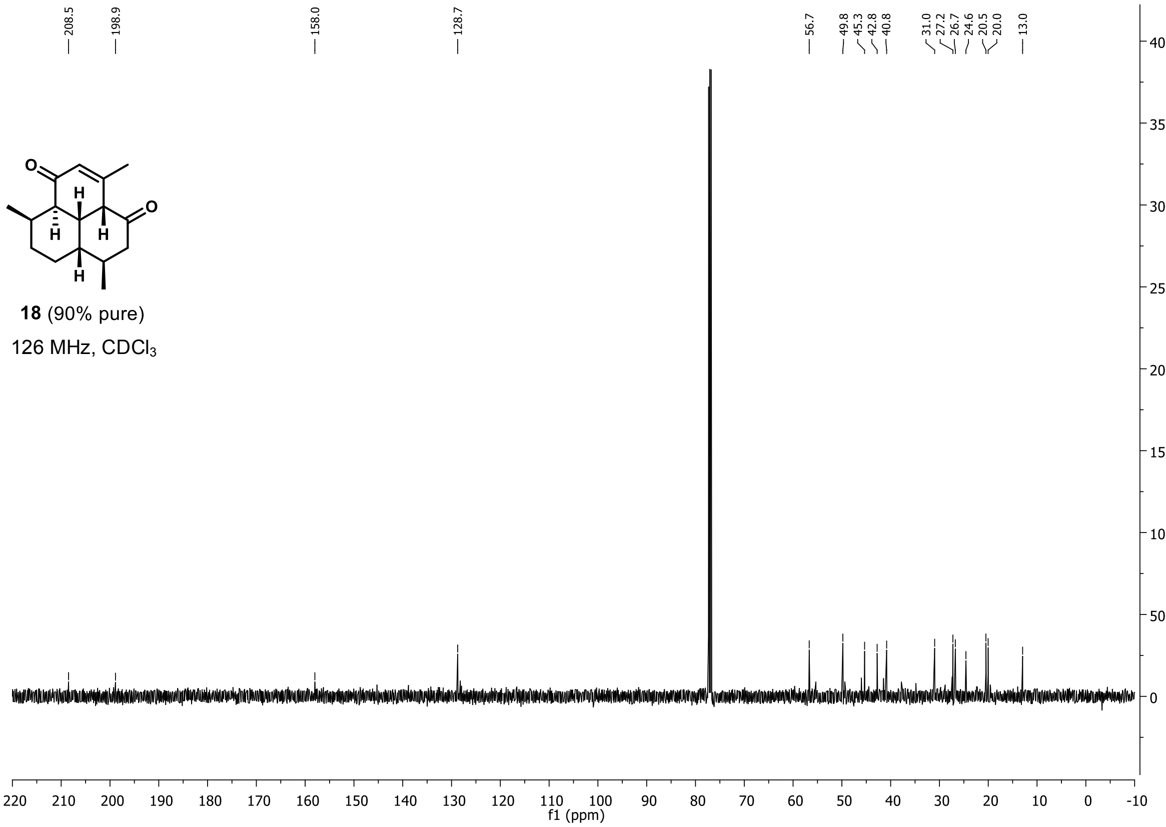
500 MHz, $CDCl_3$

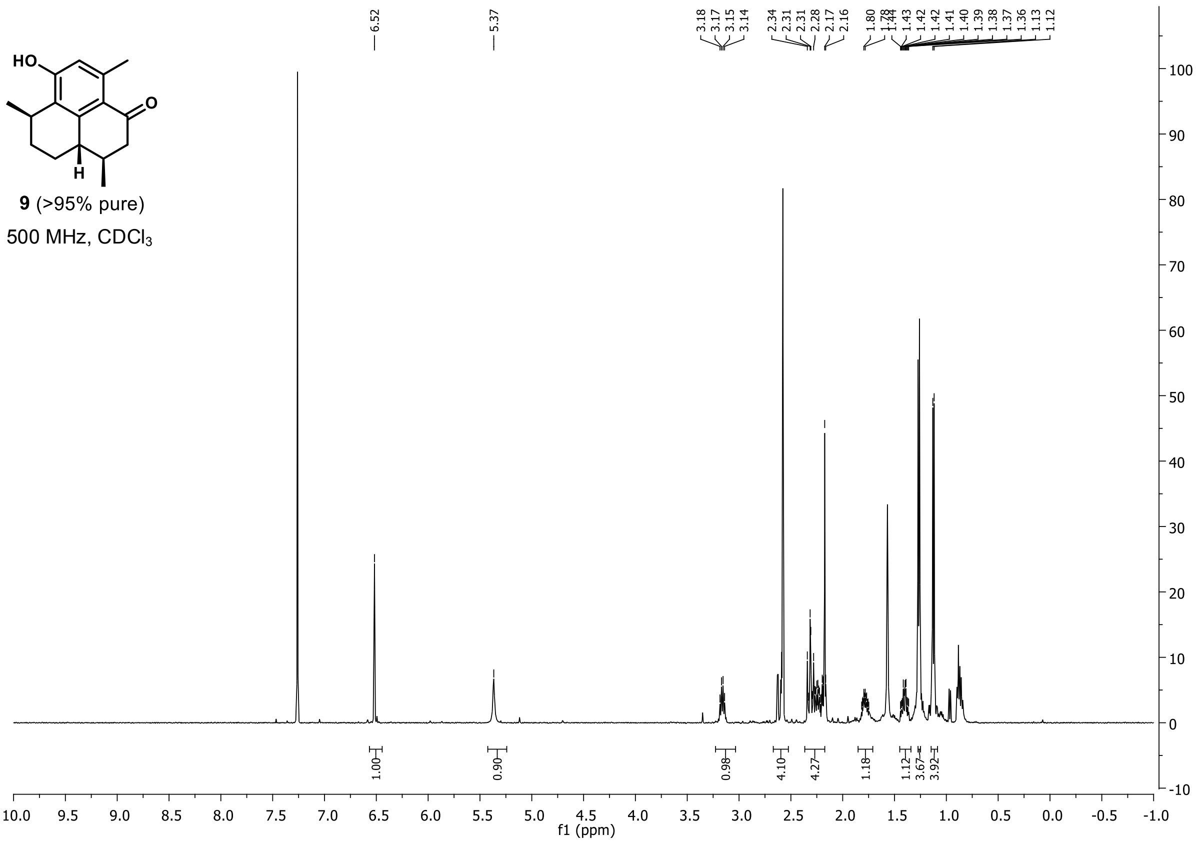


17 (90% pure)

126 MHz, $CDCl_3$

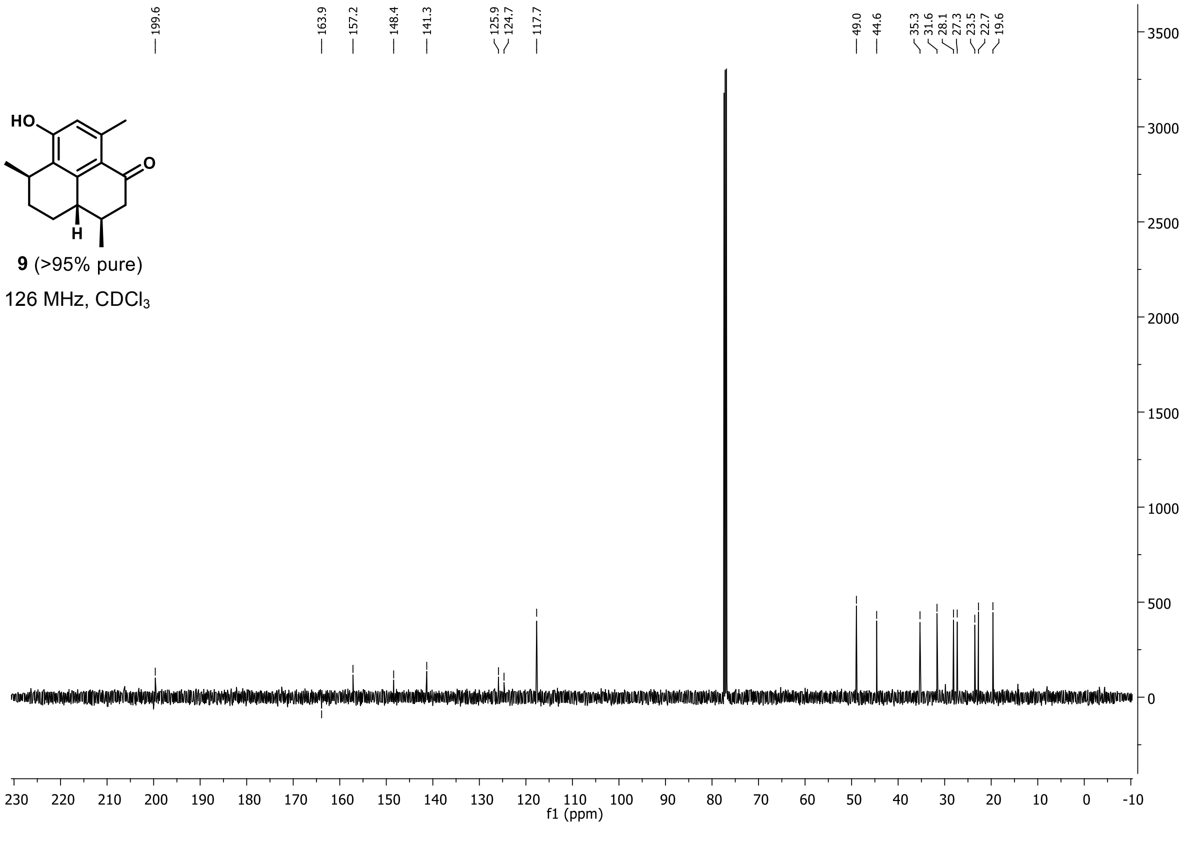

5.97
5.97
3.22
3.21
2.42
2.25
2.22
2.16
1.95
1.95
1.76
1.75
1.74
1.74
1.40
1.40
1.05
1.04
0.87
0.86
O
O
H
H
H
H
18 (90% pure)
500 MHz, CDCl3
1.00
1.04
1.32
1.22
1.11
2.02
1.17
5.26
2.47
1.21
3.45
3.26
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
-10
10.0
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
-0.5
-1.0
f1 (ppm)


208.5
198.9
158.0
128.7
56.7
49.8
45.3
42.8
40.8
31.0
27.2
26.7
24.6
20.5
20.0
13.0
O
O
H
H
H
H
18 (90% pure)
126 MHz, CDCl3
4000
3500
3000
2500
2000
1500
1000
500
0
220
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
-10
f1 (ppm)



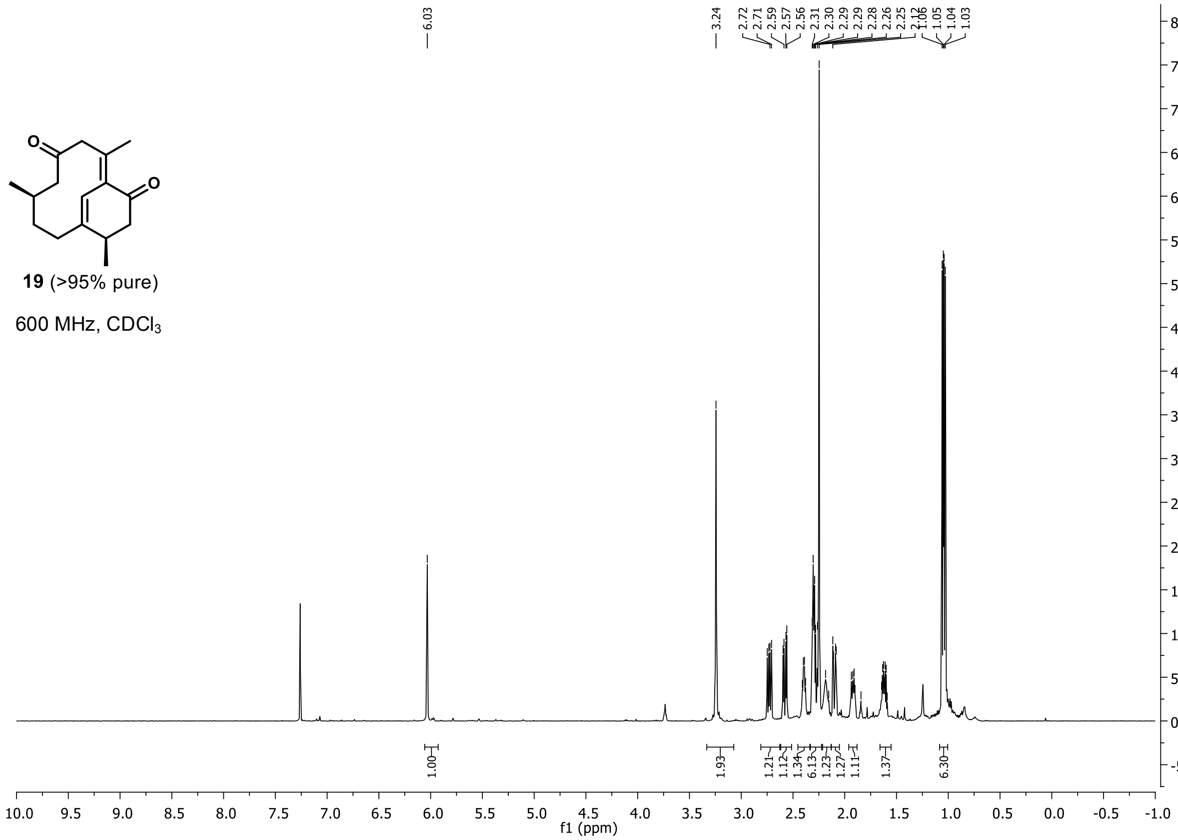
9 (>95% pure)

500 MHz, $CDCl_3$



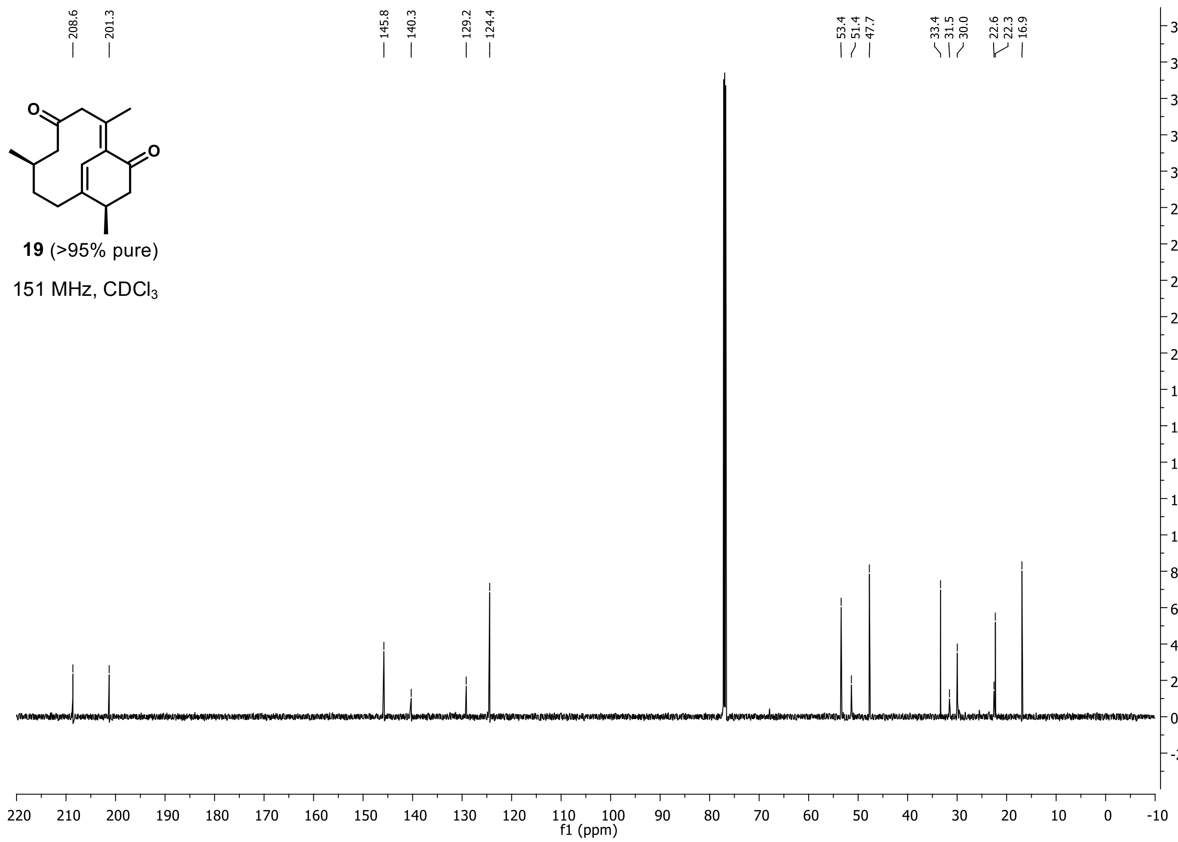
9 (>95% pure)

126 MHz, $CDCl_3$



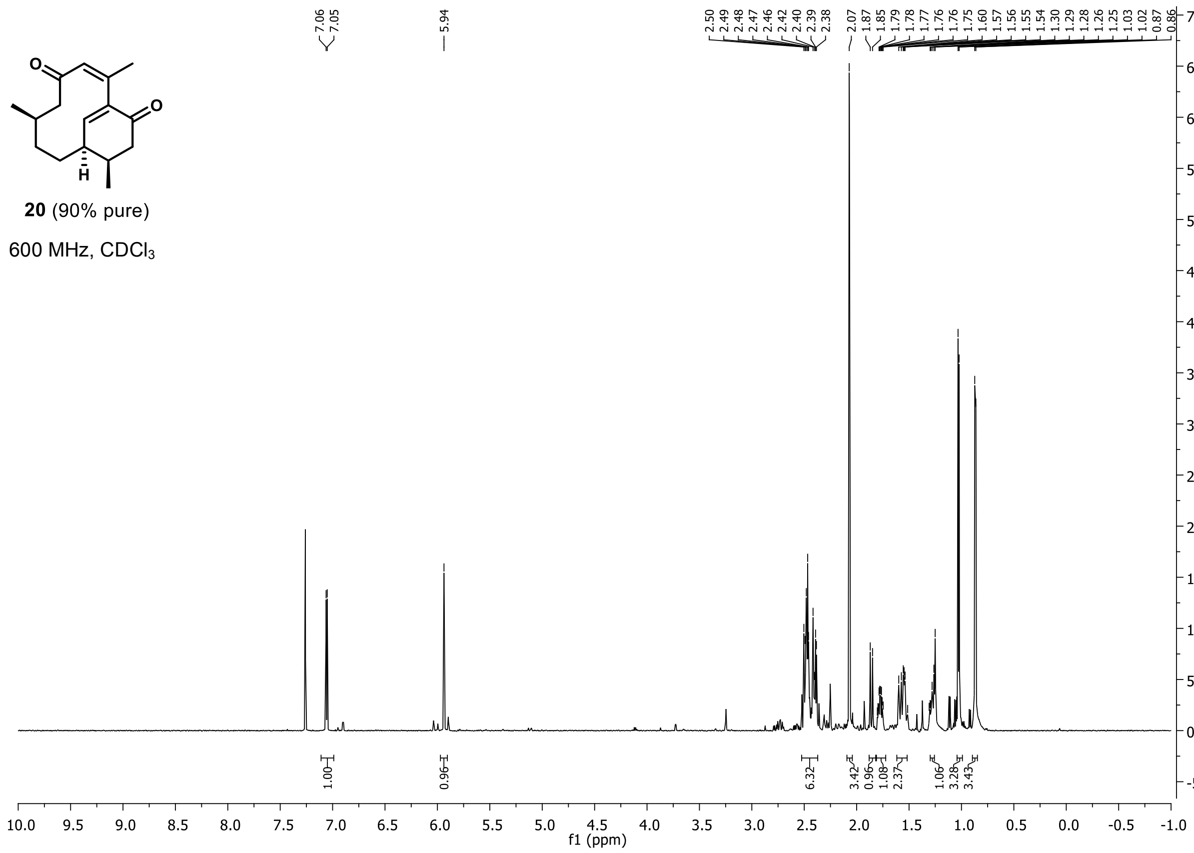
19 (>95% pure)

600 MHz, CDCl$_3$



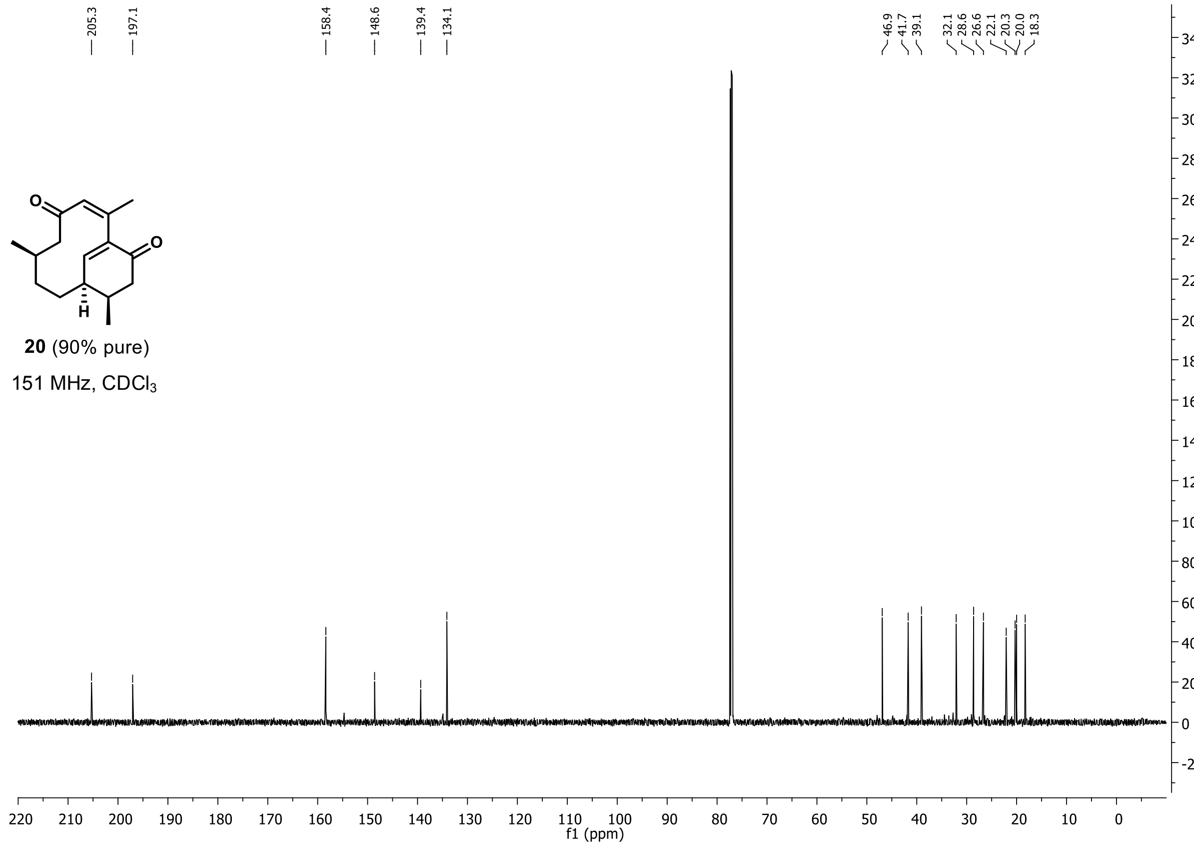
19 (>95% pure)

151 MHz, CDCl$_3$



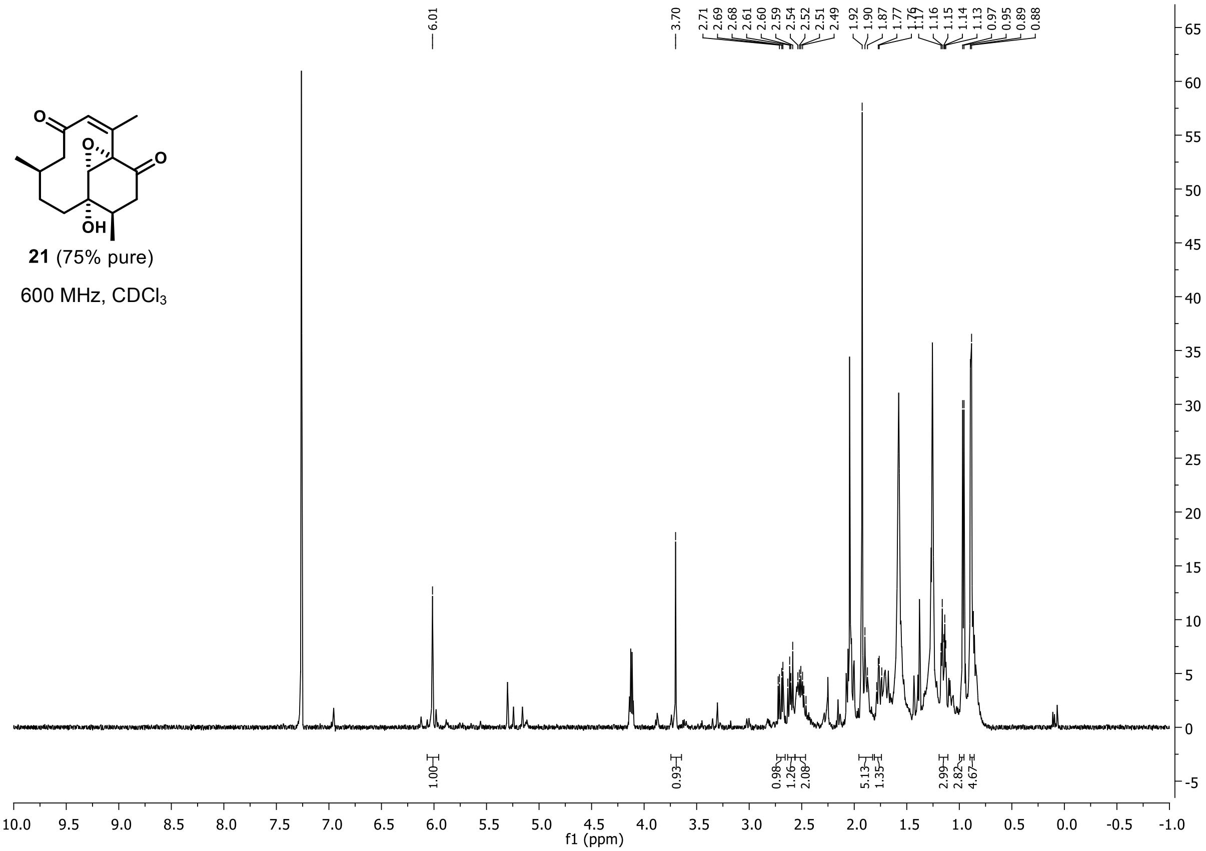
20 (90% pure)

600 MHz, CDCl$_3$

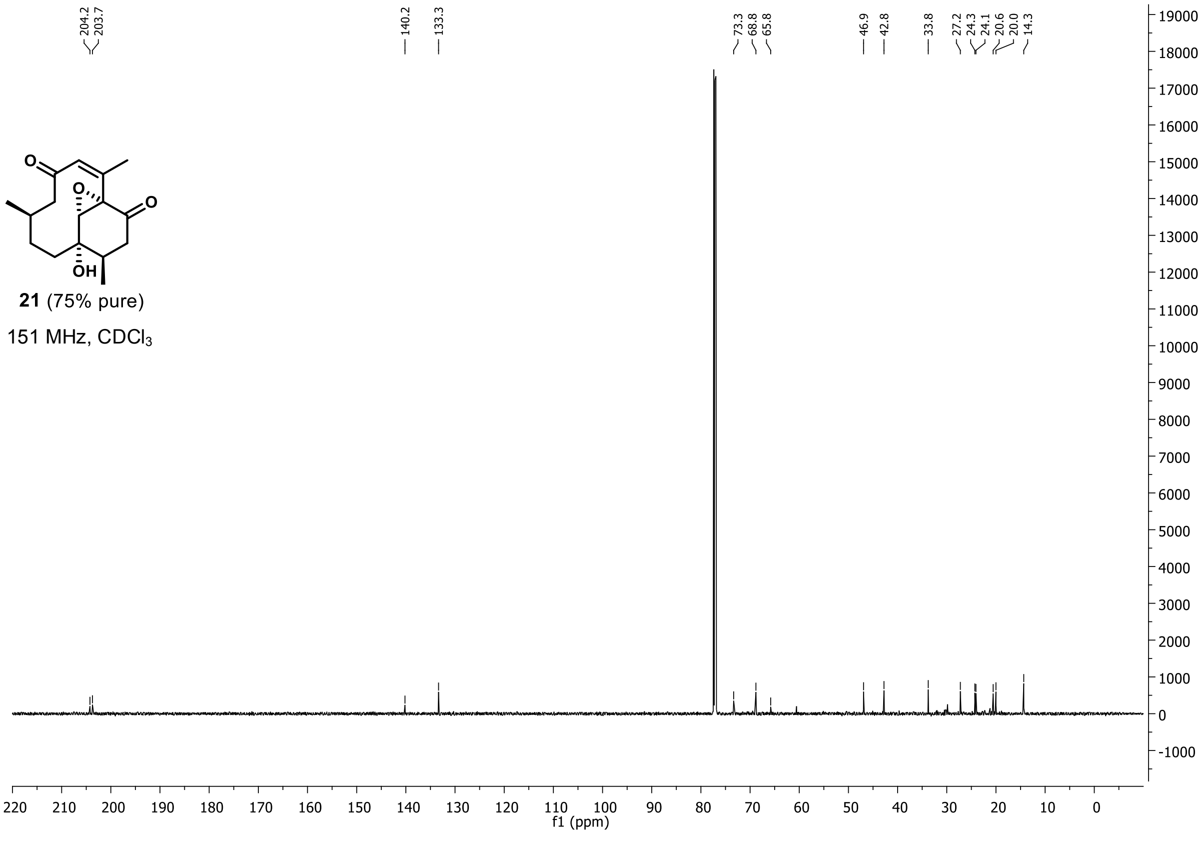


20 (90% pure)

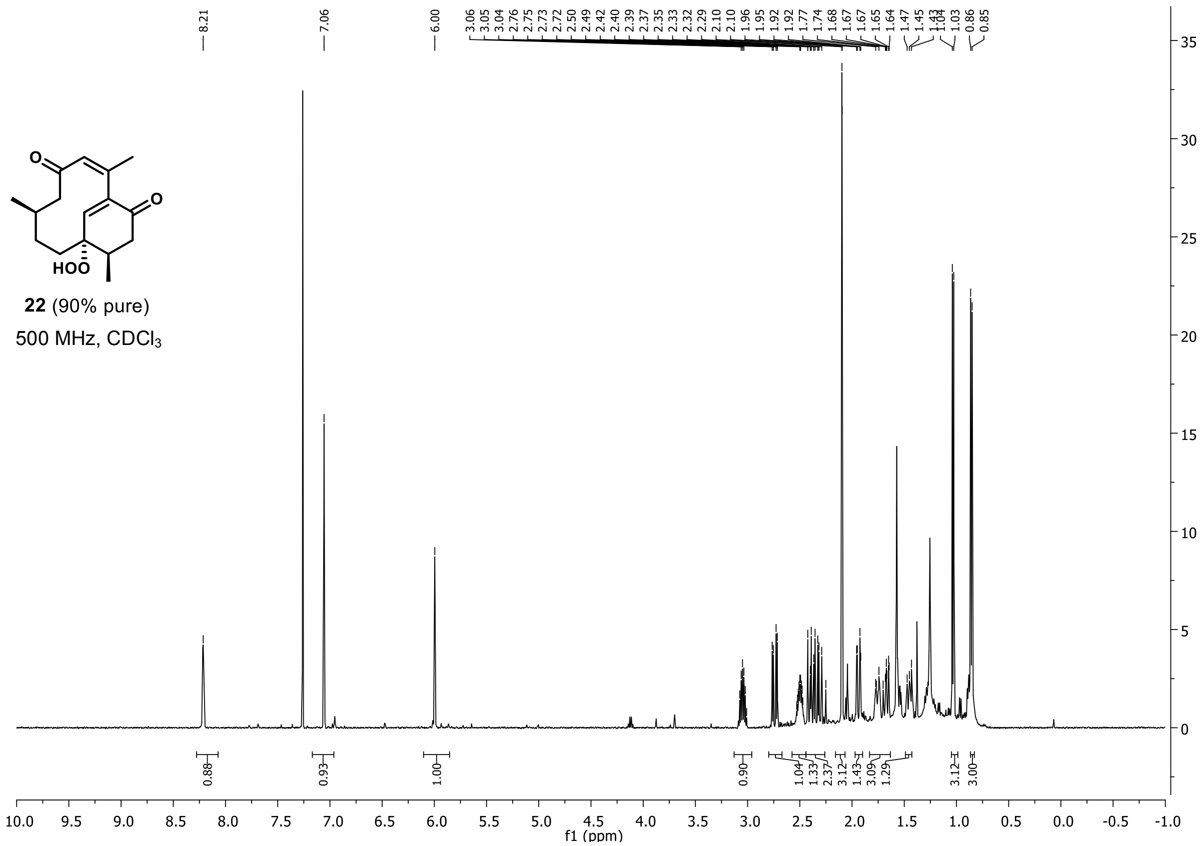
151 MHz, CDCl$_3$


21 (75% pure)

600 MHz, CDCl$_3$

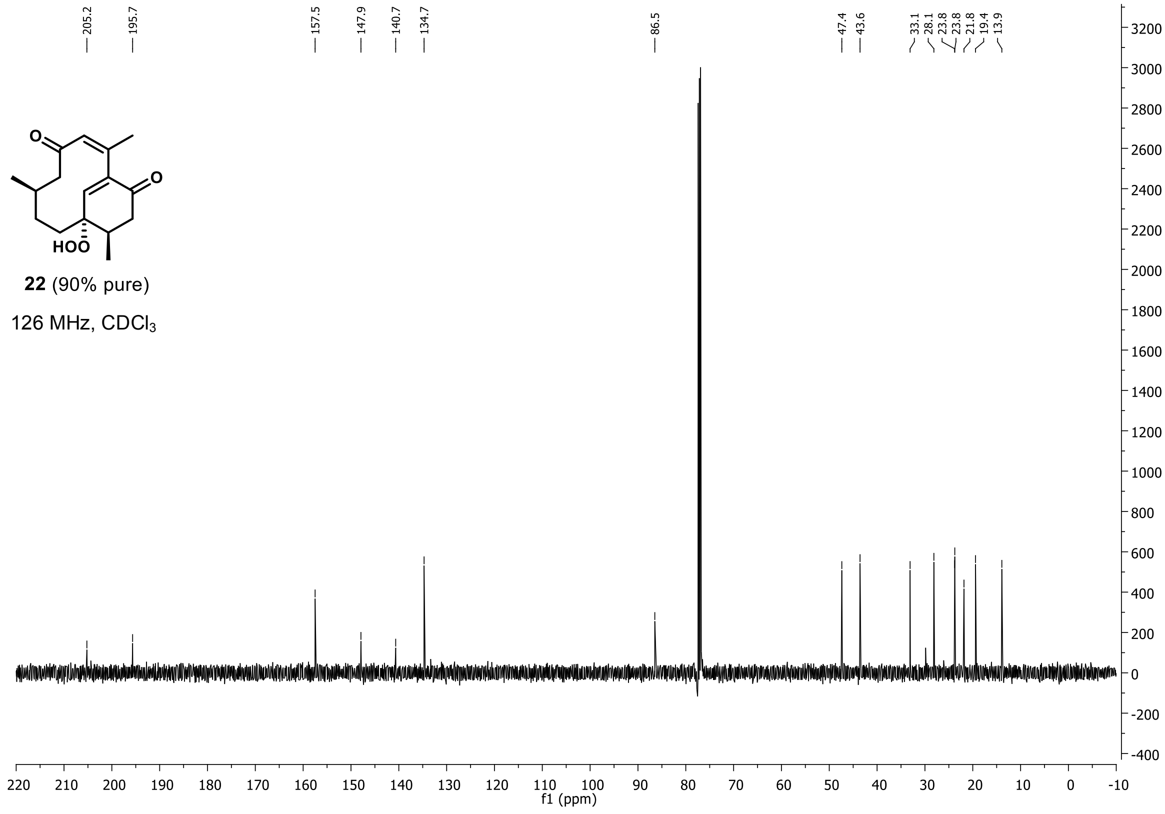

21 (75% pure)

151 MHz, CDCl$_3$



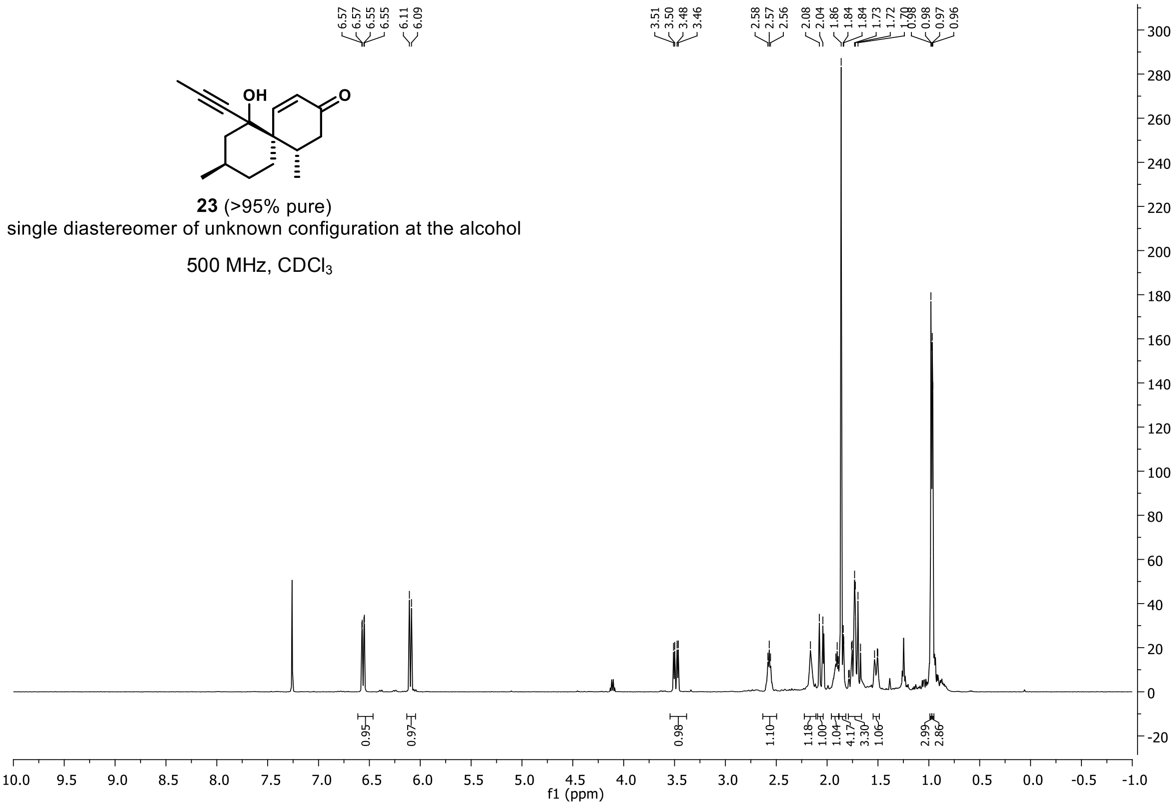
22 (90% pure)

500 MHz, CDCl$_3$



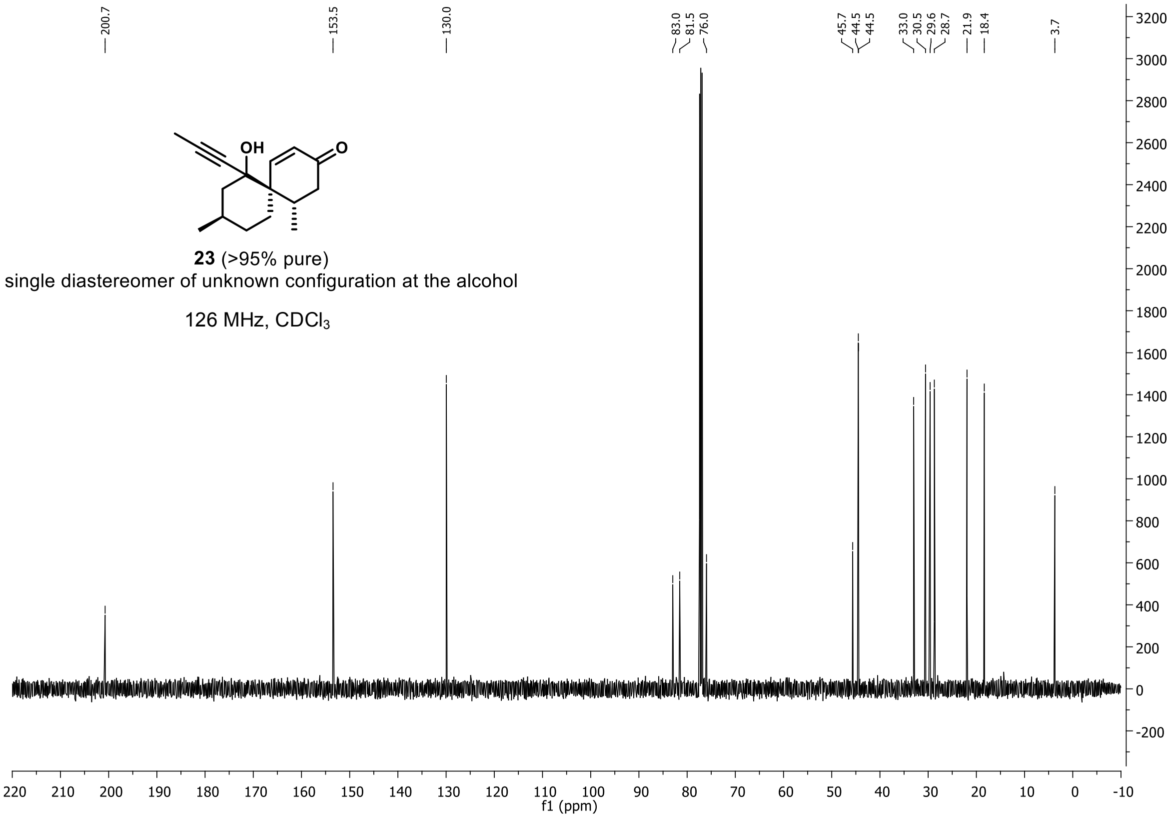
22 (90% pure)

126 MHz, CDCl$_3$



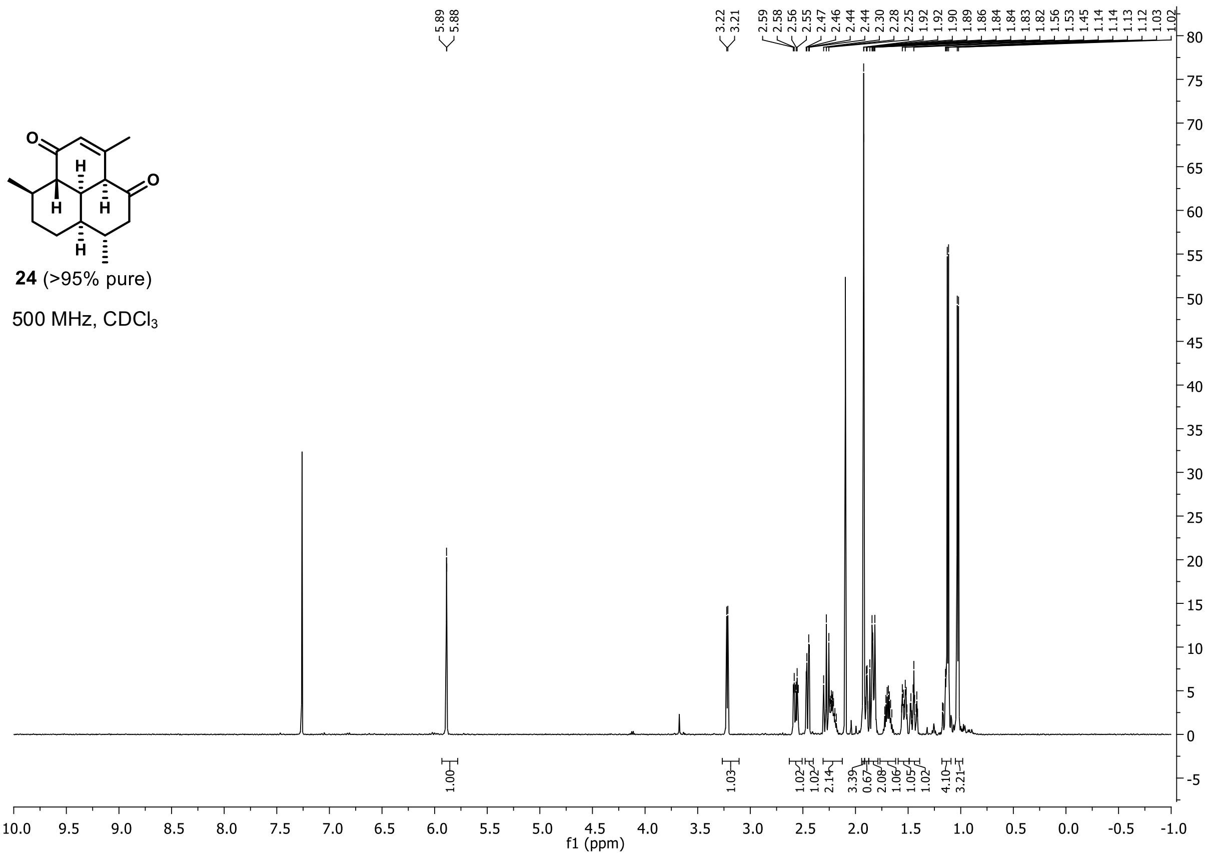
23 (>95% pure)
single diastereomer of unknown configuration at the alcohol

500 MHz, $CDCl_3$



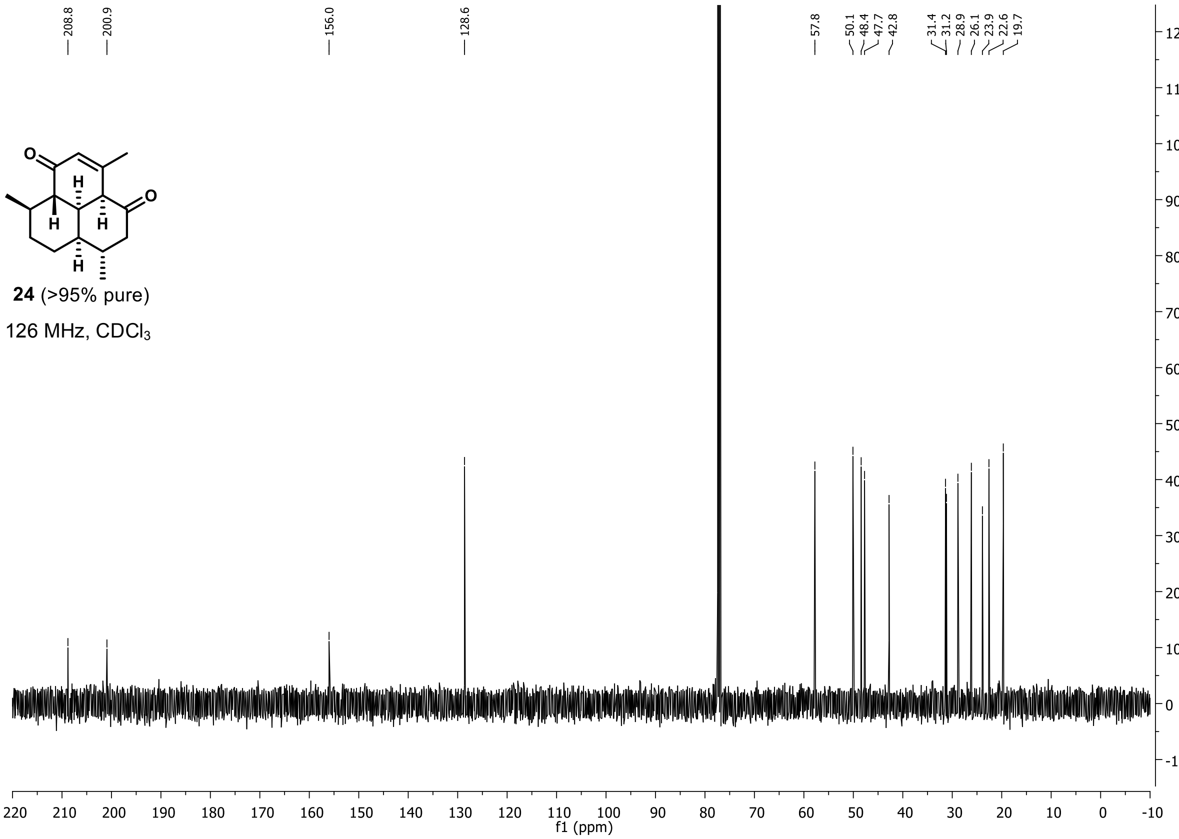
23 (>95% pure)
single diastereomer of unknown configuration at the alcohol

126 MHz, $CDCl_3$



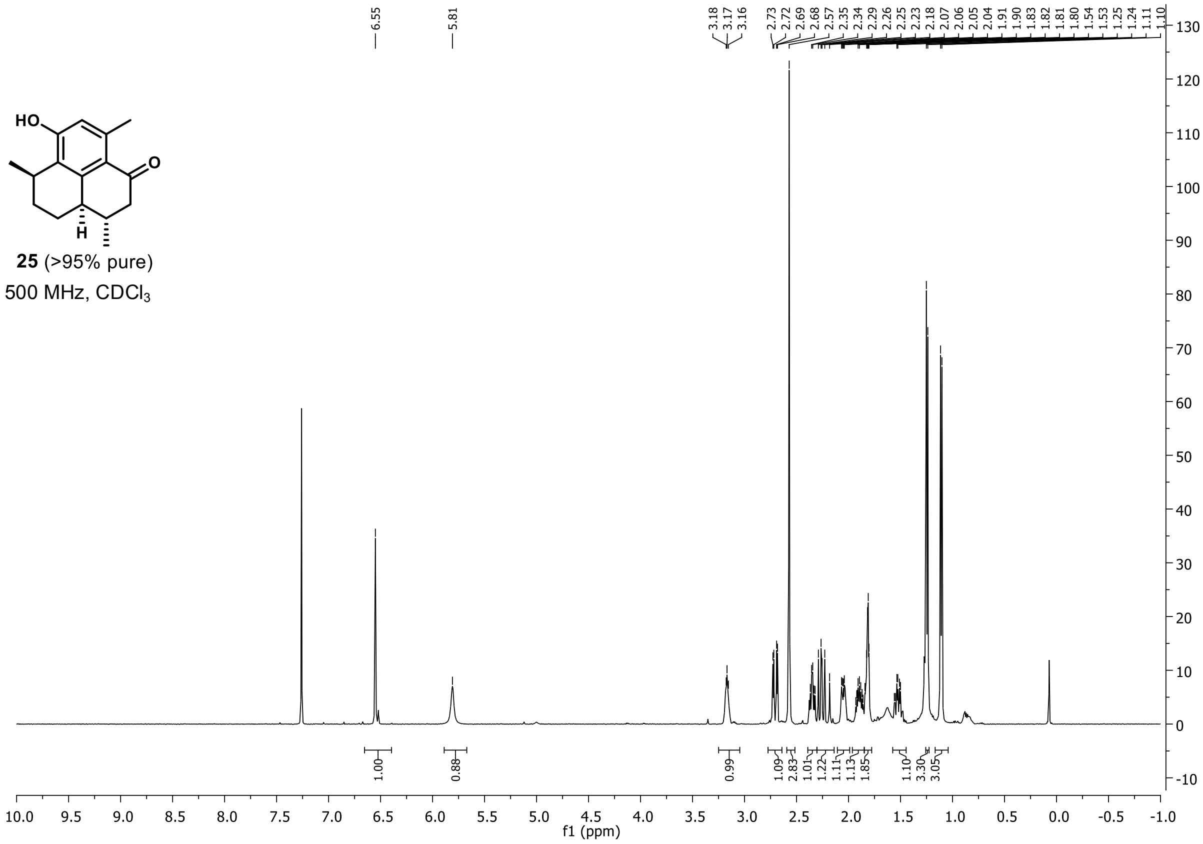
24 (>95% pure)

500 MHz, CDCl$_3$



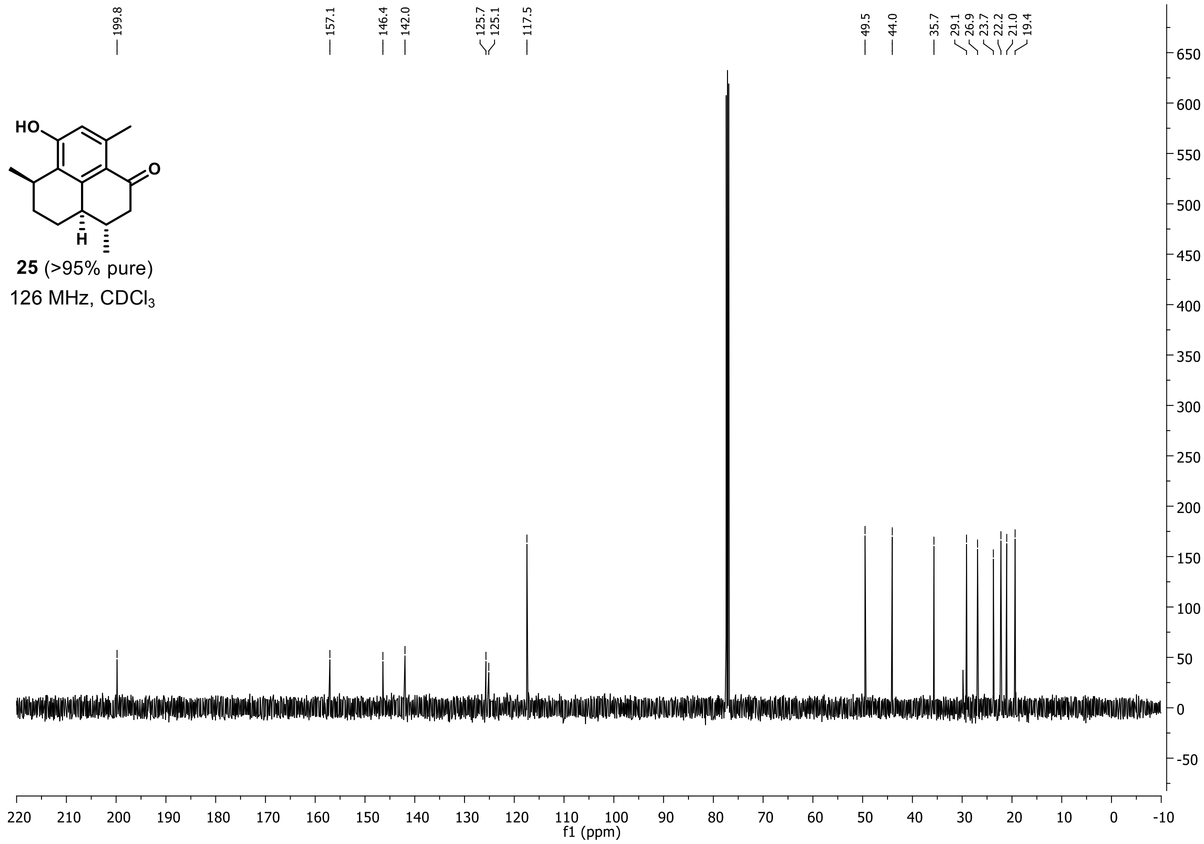
24 (>95% pure)

126 MHz, CDCl$_3$



25 (>95% pure)

500 MHz, $CDCl_3$



25 (>95% pure)

126 MHz, $CDCl_3$

IV. References.

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