# SUPPORTING INFORMATION

## Catalysis-Based and Protecting Group-Free Total Syntheses of the Marine Oxylipins Hybridalactone and the Ecklonialactones A, B and C

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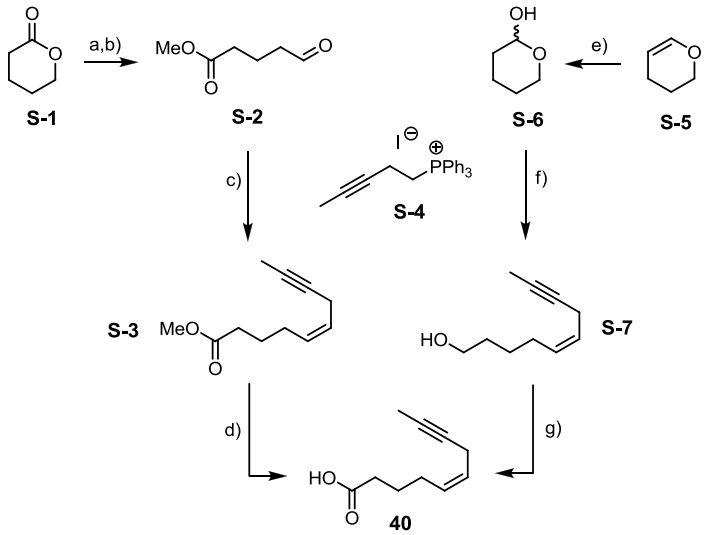
**X-ray Crystal Structure Analysis of Compound 20**: $C_{16}H_{17}ClN_2O_6$, $M_r$ = 368.77 g · mol$^{-1}$, colorless block, crystal size 0.24 x 0.13 x 0.08 mm, monoclinic, space group *C2*, *a* = 16.4887(6) Å, *b* = 7.1507(3) Å, *c* = 14.5744(6) Å, β = 101.3360(10)°, *V* = 1684.88(12) Å$^3$, *T* = 100 K, *Z* = 4, $D_{calc}$ = 1.454 g · cm$^3$, $\lambda$ = 1.54178 Å, $\mu$(*Cu-K*$_\alpha$) = 2.341 mm$^{-1}$, Gaussian absorption correction ($T_{min}$ = 0.60, $T_{max}$ = 0.83), Nonius KappaCCD diffractometer, 3.09° < θ < 66.60°, 19135 measured reflections, 2577 independent reflections, 2469 reflections with $I > 2\sigma(I)$, Structure solved by direct methods and refined by full-matrix least-squares against $F^2$ to $R_1$ = 0.027 [$I > 2\sigma(I)$], $wR_2$ = 0.060, 288 parameters, H atoms riding, *S* = 1.083, absolute structure parameter *0.025(12),* residual electron density +0.2 / –0.2 e Å$^{-3}$. **CCDC 821651** contains the supplementary crystallographic data, which can be obtained free of charge via www.ccdc.cam.uk/data_request/cif.

**General.** All reactions were carried out under Ar in flame-dried glassware. The solvents used were purified by distillation over the drying agents indicated and were transferred under Ar: THF, $Et_2O$, 1,4-dioxane (Mg/anthracene), $CH_2Cl_2$, DME, MeCN ($CaH_2$), hexane, toluene (Na/K), MeOH (Mg). Flash chromatography: Merck silica gel 60 (230–400 mesh). NMR: Spectra were recorded on Bruker DPX 300, AMX 300, AV 400, or AVIII 600 spectrometer in the solvents indicated; chemical shifts ($\delta$) are given in ppm relative to TMS, coupling constants (*J*) in Hz. The solvent signals were used as references and the chemical shifts converted to the TMS scale ($CDCl_3$: $\delta_C \equiv$ 77.0 ppm; residual $CHCl_3$ in $CDCl_3$: $\delta_H \equiv$ 7.24 ppm; $CD_2Cl_2$: $\delta_C \equiv$ 53.8 ppm; residual $^1$H: $\delta_H \equiv$ 5.32 ppm; [$D_8$]-toluene: $\delta_C \equiv$ 20.4 ppm; residual $D_5C_6CD_2H$: $\delta_H \equiv$ 2.09 ppm; $C_6D_6$: $\delta_C \equiv$ 128.0 ppm; residual $C_6D_5H$: $\delta_H \equiv$ 7.15 ppm). IR: Spectrum One (Perkin-Elmer) spectrometer, wavenumbers ($\tilde{\nu}$) in cm$^{-1}$. MS (EI): Finnigan MAT 8200 (70 eV), ESI-MS: ESQ3000 (Bruker), accurate mass determinations: Bruker APEX III FT-MS (7 T magnet) or Mat 95 (Finnigan). Unless stated otherwise, all commercially available compounds (Fluka, Lancaster, Aldrich) were used as received.

**Preparation of the Unsaturated Acid 40**




**Scheme S1**. Reagents and conditions: a) MeOH, Dowex 50W-X8, reflux; b) PCC, MS 5Å, $CH_2Cl_2$, 82% (over both steps); c) **S-4**, NaHMDS, toluene/THF (1:4), –90°C → RT, 81%; d) KOH, MeOH, reflux, 93%; e) aq. HCl, 64%; f) **S-4**, NaH, DMF, 45%; g) (i) Dess-Martin periodinane, $NaHCO_3$, $CH_2Cl_2$; (ii) $NaClO_2$, $NaH_2PO_4$, 2-methyl-2-butene, *t*BuOH/$H_2O$, 91%.

**5-Iodopent-2-yne.** $PPh_3$ (7.0 g, 26.8 mmol), imidazole (1.8 g, 26.8 mmol) and iodine (6.8 g, 26.8 mmol) were successively added to a solution of 3-pentyn-1-ol (1.5 g, 17.8 mmol) in MeCN (22 mL) and $Et_2O$ (68 mL). The resulting mixture was stirred for 2 h before the reaction was quenched with aq. sat. $NaHCO_3$ (50 mL). The organic phase was washed with aq. sat. $Na_2S_2O_3$ (40 mL), dried over $Na_2SO_4$ and evaporated, and the residue passed through a short plug of silica (pentanes) to give, after careful evaporation, the title compound as a volatile liquid which was immediately used in the next step (3.45 g, quant.). $^1$H NMR (400 MHz, $CDCl_3$): $\delta$ = 3.19 (t, *J* = 7.3 Hz, 2H), 2.71 (tq, *J* = 7.5, 2.5 Hz, 2H), 1.77 ppm (t, *J* = 2.5 Hz, 3 Hz); $^{13}$C NMR (100 MHz, $CDCl_3$): $\delta$ = 77.9, 77.8, 24.1, 3.5, 2.6 ppm.

**But-2-ynyl-5-triphenylphosphonium iodide (S-4).** $PPh_3$ (4.67 g, 17.8 mmol) was added to a solution of 5-iodo-2-pentyne (3.45 g, 17.8 mmol) in toluene (15 mL) and the resulting mixture stirred at 80°C overnight. After reaching ambient temperature, the precipitate was filtered off, washed with toluene and dried in vacuo to give the title salt as a colorless solid (4.05 g, 50%). $^1$H NMR (400 MHz, [$D_6$]-DMSO): $\delta$ = 7.92-7.75 (m, 15H), 3.84 (dt, *J* = 13.1, 7.2 Hz, 2H), 3.33 (s, 3H), 1.52 ppm (t, *J* = 2.3 Hz, 2H); $^{13}$C NMR (100 MHz, [$D_6$]-DMSO): $\delta$ = 135.0 (d, *J* = 3 Hz), 133.7 (d, *J* = 10 Hz), 130.2 (d, *J* = 12 Hz), 118.1 (d, *J* = 87 Hz), 79.6, 76.3 (d, *J* = 14 Hz), 20.1 (d, *J* = 51 Hz), 12.3 (d, *J* = 4 Hz), 2.9 ppm; IR (film): $\tilde{\nu}$ = 3017 (w), 2903 (w), 1585 (w), 1434 (m), 1384 (w), 1341 (w), 1136 (w), 1110 (s), 995 (m), 843 (s), 733 (s), 719 (s), 685 (s) cm$^{-1}$; MS (ESI$^-$): *m/z*: 329.2 [456-I]; HRMS (ESI): *m/z*: calcd. for $C_{23}H_{22}P$: 329.1454 [M-I]$^+$; found: 329.1452.

**Methyl 5-Hydroxy-pentanoate**.[1] Dowex 50W-X8 resin (100 mg) was added to a solution of δ-valerolactone (7.0 g, 70 mmol) in MeOH (365 mL) and the resulting suspension was stirred at reflux temperature for 4 h and at ambient temperature overnight. The resin was then filtered off and the solvent evaporated to give the title compound as a colorless liquid, which was used in the next step without further purification (8 g, quant.). $^1$H NMR (400 MHz, $CDCl_3$): $\delta$ = 3.67 (s, 3H), 3.65 (t, *J* = 6.3 Hz, 2H), 2.36 (t, *J* = 7.2 Hz, 2H), 1.76-1.68 (m, 2H), 1.63-1.56 (m, 2H) ppm; $^{13}$C NMR (100 MHz, $CDCl_3$): δ = 174.2, 66.1, 51.5, 33.6, 31.9, 21.0 ppm. HRMS (CI, *i*-butane): *m/z*: calcd. for $C_6H_{13}O_3$ 133.0865 [M+H]$^+$, found: 133.0865.

**Aldehyde S-2**.[1] Powdered MS 5 Å (100 mg) and PCC (6.5 g, 30 mmol) were added to a solution of methyl 5-hydroxy-pentanoate (2.0 g, 15 mmol) in $CH_2Cl_2$ (20 mL) and the resulting mixture was stirred overnight. For work-up, the mixture was diluted with $Et_2O$ (50 mL), causing the formation of a black precipitate, which was filtered off through a pad of silica. After careful rising of the silica with ether, the combined filtrates were evaporated and the solvent removed in vacuo to give the desired aldehyde as a colorless oil, which was used in the next step without further purification (1.6 g, 82%). $^1$H NMR (400 MHz, $CDCl_3$): $\delta$ = 9.76 (t, *J* = 1.3 Hz, 1H), 3.66 (s, 3H), 2.52 (dt, *J* = 7.2, 1.3 Hz, 2H), 2.36 (t, *J* = 7.2 Hz, 2H), 1.94 (qi, *J* = 7.2 Hz, 2H) ppm; $^{13}$C NMR (100 MHz, $CDCl_3$): $\delta$ = 201.5, 173.3, 51.6, 42.8, 32.9, 17.3 ppm; IR (film): $\tilde{\nu}$ = 2951, 1729, 1706, 1436, 1418, 1370, 1317, 1201, 1150, 1059, 1016, 993, 900, 864, 844, 799, 783, 703 cm$^{-1}$; MS (EI): *m/z* (%): 131 (< 1) [M]$^+$, 111 (< 1), 102 (17), 99 (43), 87 (9), 74 (100), 71 (33), 59 (47), 55 (46), 43 (97), 39 (24), 39 (27); HRMS (CI, *i*-butane): *m/z*: calcd. for $C_6H_{11}O_3$ 131.0708 [M+H]$^+$, found: 131.0708.

[1] Enholm, E.; Joshi, A.; Wright, D. L. *Bioorg. Med. Chem. Lett.* **2005**, *15*, 5262.

**Compound S-3**. A solution of NaHMDS (0.39 g, 2.1 mmol) in THF (2 mL) was added to a suspension of phosphonium iodide **S-4** (0.91 g, 2.0 mmol) in THF (20 mL) and toluene (5 mL) at –30°C. The mixture was then stirred at ambient temperature for 1 h before it was cooled to –90°C. A solution of compound **S-2** (0.29 g, 2.2 mmol) in THF (2 mL) was added and the mixture allowed to slowly reach ambient temperature overnight. The reaction was quenched with aq. sat. $NH_4Cl$ (4 mL) and water (1 mL), the aqueous phase was extracted with $Et_2O$, the combined organic layers were dried and evaporated, and the residue purified by flash chromatography (pentanes/$Et_2O$, 2:1) to give the title compound as a colorless oil (0.29 g, 81%). $^1$H NMR (400 MHz, $CDCl_3$): $\delta$ = 5.50-5.37 (m, 2H), 3.66 (s, 3H), 2.88-2.85 (m, 2H), 2.32 (t, *J* = 7.6 Hz, 2H), 2.08 (q, *J* = 7.2 Hz, 2H), 1.77 (t, *J* = 2.7 Hz, 3H), 1.70 (qi, *J* = 7.4 Hz, 2H) ppm; $^{13}$C NMR (100 MHz, $CDCl_3$): $\delta$ = 174.0, 129.9, 126.0, 77.2, 75.4, 51.5, 33.4, 26.4, 24.5, 17.1, 3.5 ppm; IR (film): $\tilde{\nu}$ = 3020, 2950, 1736, 1436, 1367, 1293, 1201, 1155, 1088, 1027, 861, 799, 689 cm$^{-1}$; MS (EI): *m/z* (%): 180 (1) $[M]^+$, 165 (2), 149 (24), 140 (9), 120 (24), 106 (72), 91 (100), 77 (49), 66 (22), 53 (22), 39 (30), 27 (23); HRMS (EI): *m/z*: calcd. for $C_{11}H_{16}O_2$ 180.1150 $[M]^+$, found: 180.1150.

**Compound S-6**. 3,4-Dihydro-2*H*-pyran (4.6 g, 55 mmol) was added dropwise to aq. HCl (0.2 M, 20 mL) at 0 °C and the resulting mixture was stirred at that temperature for 20 min before it was warmed to ambient temperature and stirred for additional 90 min. For work up, the mixture was carefully neutralized with aq. sat. $NaHCO_3$ and the product was extracted with $CH_2Cl_2$. The combined extracts were dried over $Na_2SO_4$, the solvent was evaporated, and the crude product purified by Kugelrohr distillation (ca. 130 $^o$C, 5 mbar) to give tetrahydro-2*H*-pyran-2-ol as a colorless oil (3.6 g, 35 mmol, 64%). The spectral data were identical with those of a commercial sample.

**Compound S-7**. Phosphonium iodide **S-4** (0.18 g, 0.40 mmol) was added to a suspension of NaH (9.6 mg, 0.40 mmol) in DMF (2 mL) and the resulting mixture was stirred at ambient temperature for 30 min. A solution of compound **S-6** (0.020 g, 0.20 mmol) in DMF (1 mL) was introduced and the resulting mixture stirred overnight. The reaction was quenched with aq. sat. $NH_4Cl$ and the product extracted with a mixture of pentane and $Et_2O$. The combined organic layers were dried over $Na_2SO_4$ and evaporated, and the residue was purified by flash chromatography (pentane/$Et_2O$, 3 : 2) to give product **S-7** as a colorless oil (13.7 mg, 45%). $^1$H NMR (400 MHz, $CDCl_3$): δ = 5.50-5.39 (m, 2H), 3.65 (t, *J* = 6.5 Hz, 2H), 2.93-2.83 (m, 2H), 2.08 (dt, *J* = 5.7, 7.2 Hz, 2H), 1.78 (t, *J* = 2.7 Hz, 3H), 1.63-1.54 (m, 2H), 1.50-1.40 (m, 2H), 1.26 (brs, 1H) ppm; $^{13}$C NMR (100 MHz, $CDCl_3$): δ = 130.9, 125.3, 77.4, 75.4, 62.8, 32.3, 26.8, 25.5, 17.1, 3.5 ppm; IR (film): $\tilde{\nu}$ = 3351, 3020, 2932, 2860, 1435, 1063, 689 cm$^{-1}$.

**Acid 40**. ***Method 1***: KOH (0.13 g, 2.3 mmol) was added to a solution of compound **S-3** (0.27 g, 1.5 mmol) in MeOH (3 mL) and the resulting mixture stirred at reflux temperature for 2 h. For work-up, the mixture was diluted with water, acidified by aq. HCl until pH ≈ 2 was reached, and the aqueous layer extracted with $Et_2O$. The combined pentane phases were evaporated and the residue dried in vacuo. Colorless syrup (0.23 g, 93%).

***Method 2***: A solution of (*Z*)-5-decen-8-ynol **S-7** (13.7 mg, 0.090 mmol) in $CH_2Cl_2$ (1.5 mL) was added to a mixture of Dess-Martin periodinane (0.051 g, 0.12 mmol) and $NaHCO_3$ (0.038 g, 0.45 mmol) in $CH_2Cl_2$ (1.5 mL), and the resulting mixture was stirred at room temperature for 2 h. The reaction was quenched with aq. sat. $Na_2S_2O_3$ and the product extracted with $Et_2O$. The combined organic layer was dried over $Na_2SO_4$ and evaporated, and the resulting crude product used in the next step without further purification. 2-Methyl-2-butene (0.070 g, 1.0 mmol), $NaH_2PO_4$ (0.061 g, 0.51 mmol) and $NaClO_2$ were sequentially added to a solution of the crude aldehyde in a mixture of *t*BuOH (2 mL) and $H_2O$ (2 mL). The resulting mixture was stirred for 20 min before the reaction was quenched with aq.

sat. $NH_4Cl$ and the product extracted with a mixture of pentane and $Et_2O$. The combined extracts were dried over $Na_2SO_4$ and evaporated, and the residue was purified by flash chromatography (pentane/$Et_2O$, 3:2) to furnish acid **40** as a colorless oil (13.6 mg, 91%). $^1$H NMR (400 MHz, $CDCl_3$): $\delta$ = 5.52-5.37 (m, 2H), 2.89-2.85 (m, 2H), 2.37 (t, *J* = 7.5 Hz, 2H), 2.12 (q, *J* = 7.2 Hz, 2H), 1.77 (t, *J* = 2.6 Hz, 3H), 1.72 (qi, *J* = 7.4 Hz, 2H) ppm; $^{13}$C NMR (100 MHz, $CDCl_3$): $\delta$ = 179.4, 129.7, 126.2, 77.2, 75.5, 33.2, 26.3, 24.2, 17.1, 3.5 ppm; IR (film): $\tilde{\nu}$ = 3020, 2920, 2861, 2667, 1705, 1413, 1292, 1239, 1156, 1086, 910, 798, 677 cm$^{-1}$; MS (EI): *m/z* (%): 166 (1) $[M]^+$, 147 (1), 137 (6), 126 (15), 106 (66), 91 (100), 77 (63), 66 (38), 53 (24), 45 (13), 39 (35), 27 (29); HRMS (EI): *m/z*: calcd. for $C_{10}H_{14}O_2$ 166.0994 $[M]^+$, found: 166.0994.

**Preparation of the Common Intermediate 22 – Auxiliary Based Route**

**Compound 13.** Vinylmagnesium bromide (1 M in THF, 19.5 mL, 19.5 mmol) was added over 15 min to a suspension of CuI (3.71 g, 19.5 mmol) in THF (116 mL) at –78°C and the resulting mixture stirred for 30 min before a solution of compound **12** (2.9 g, 12 mmol)[2] in THF (30 mL) was added over the course of 1 h. Once the addition was complete, allyl iodide (4.08 g, 24.4 mmol) was introduced and the mixture warmed to –60°C, causing a color change to black and finally pale brown. After stirring for 30 min at –60°C, the mixture was allowed to reach ambient temperature. The reaction was quenched with aq. sat. $NaHCO_3$, the aqueous layer extracted with *tert*-butyl methyl ether, the combined organic phases were dried and evaporated, and the residue purified by flash chromatography (hexanes/EtOAc, 10:1) to give product **13** as a pale yellow syrup (3.12 g, 86%). $[\alpha]_D^{20}$ = –148 (c = 0.28, $CH_2Cl_2$); $^1$H NMR (400 MHz, $CDCl_3$): $\delta$ = 5.85-5.69 (m, 2H), 5.34 (d, *J* = 5.3 Hz, 1H), 5.24-5.23 (m, 1H), 5.20 (dt, *J* = 7.7, 1.1 Hz, 1H), 5.14-5.12 (m, 1H), 5.10-5.08 (m, 1H), 3.49 (td, *J* = 10.7, 4.2 Hz, 1H), 2.76-2.70 (m, 1H), 2.57-2.48 (m, 3H), 2.14 (dsept., *J* = 7.0, 2.7 Hz, 1H), 2.04-1.99 (m, 1H), 1.69-1.62 (m, 2H), 1.42-1.29 (m, 1H), 1.24 (ddt, *J* = 12.4, 10.5, 3.0 Hz, 1H), 1.08-0.94 (m, 1H), 0.92 (d, *J* = 6.6 Hz, 3H), 0.89 (d, *J* = 7.1 Hz, 3H), 0.87-0.81 (m, 2H), 0.79 (d, *J* = 6.8 Hz, 3H) ppm; $^{13}$C NMR (100 MHz, $CDCl_3$): $\delta$ = 175.8, 134.4, 134.1, 118.7, 118.1, 103.6, 78.6, 50.6, 47.6, 45.6, 40.1, 34.3, 33.3, 31.4, 25.3, 23.0, 22.2, 20.9, 15.6 ppm; IR (film): $\tilde{\nu}$ = 2951, 2921, 2856, 1775, 1453, 1413, 1370, 1317, 1239, 1165, 1102, 988, 915, 677 cm$^{-1}$; MS (EI): *m/z* (%): 307 (<1) $[M+H]^+$, 291 (< 1), 260 (< 1), 221 (1), 168 (6), 151 (6), 139 (40), 122 (14), 109 (10), 94 (100), 83 (68), 79 (57), 69 (22), 55 (36), 41 (27); HRMS (ESI): *m/z*: calcd. for $C_{19}H_{30}O_3Na$ 329.2087 $[M+Na]^+$, found: 329.2085; elemental analysis calcd. (%) for: $C_{19}H_{30}O_3$ (306.44): C 74.47, H 9.87; found: C 74.35, H 9.78.

**Compound 14**. A solution of compound **13** (0.96 g, 3.1 mmol) in trifluoroacidic acid (80% in water, 10 mL) was stirred overnight before all volatile materials were pumped off in vacuo at 40-50°C bath temperature. The residue was purified by flash chromatography (hexanes/EtOAc, 3:1) to give product **14** as a pale bown oil (502 mg, 95%). $^1$H NMR (400 MHz, $CDCl_3$): $\delta$ = 5.91-5.69 (m, 4H), 5.71 (d, *J* = 5.1 Hz, 1H), 5.55 (d, *J* = 5.8 Hz, 1H), 5.27-5.09 (m, 8H), 2.93-2.87 (m, 1H), 2.82-2.73 (m, 2H), 2.64-2.43 (m, 4H), 2.39-2.31 (m, 1H) ppm; $^{13}$C NMR (100 MHz, $CDCl_3$): $\delta$ = 177.8, 176.0, 133.9, 133.7, 133.4, 132.9, 119.8, 119.3, 118.8, 118.5, 101.2, 97.5, 51.9, 49.2, 45.6, 41.7, 32.7, 31.2 ppm; IR (film): $\tilde{\nu}$ = 3378, 3082, 2984, 1749, 1643, 1437, 1359, 1316, 1167, 1113, 993, 917, 816, 730, 671 cm$^{-1}$; MS (EI): *m/z* (%): 168 (2) $[M]^+$, 150 (7), 139 (1), 127 (2), 122 (7), 105 (2), 99 (18), 94 (51), 79 (100), 70 (35),

[2] Moradai, O. M.; Paquette, L. A. *Org. Synth*. **2003**, *80*, 66.

66 (24), 53 (18), 41 (23), 27 (17); HRMS (ESI): *m/z*: calcd. for $C_9H_{12}O_3Na$ 191.0679 $[M+Na]^+$, found: 191.0679.

**Compound 15**. $NaBH_4$ (1.21 g, 31.8 mmol) was added in portions to a solution of compound **14** (2.13 g, 12.7 mmol) in MeOH (53 mL). After stirring for 1 h at ambient temperature, additional $NaBH_4$ (242 mg, 6.40 mmol) was introduced and stirring continued for another 45 min. Next, the mixture was acidified upon addition of HCl in $Et_2O$ (16 mL, 40 mmol, 2.5 M) and the resulting mixture stirred at reflux temperature for 1 h. After reaching ambient temperature, the mixture was carefully diluted with aq. sat. $NaHCO_3$ (75 mL), the aqueous phase was extracted with $CH_2Cl_2$, the combined organic layers were dried and evaporated, and the residue purified by flash chromatography (pentanes/$Et_2O$, 8:1) to give the title compound as a colorless oil (1.45 g, 75%). $[\alpha]_D^{20}$ = –1.2 (c = 0.37, $CH_2Cl_2$); $^1$H NMR (400 MHz, $CDCl_3$): $\delta$ = 5.83-5.65 (m, 2H), 5.21-5.08 (m, 4H), 4.34 (dd, *J* = 9.1, 8.1 Hz, 1H), 3.89 (dd, *J* = 9.2, 9.8 Hz, 1H), 3.02-2.93 (m, 1H), 2.49-2.41 (m, 3H) ppm; $^{13}$C NMR (100 MHz, $CDCl_3$): $\delta$ = 177.5, 135.1, 133.8, 118.7, 118.4, 70.0, 44.9, 44.6, 32.1 ppm; IR (film): $\tilde{\nu}$ = 3081, 2985, 2907, 1771, 1642, 1479, 1437, 1347, 1322, 1235, 1197, 1162, 1096, 1065, 1014, 917, 741, 679 $cm^{-1}$; MS (EI): *m/z* (%): 152 (19) $[M]^+$, 137 (1), 123 (3), 111 (11), 107 (24), 93 (31), 79 (96), 67 (24), 54 (100), 39 (33), 27 (21); HRMS (CI, *i*-butane): *m/z*: calcd. for $C_9H_{13}O_2$ 153.0916 $[M+H]^+$, found: 153.0914.

**Compound 18**. $Me_3Al$ (8.2 mL, 16 mmol, 2 M in heptane) was added at 0°C to a suspension of *N,O*-dimethylhydroxylamine hydrochloride (1.6 g, 16 mmol) in $CH_2Cl_2$ (16 mL) and the resulting mixture was stirred for 2 h at that temperature. Next, a solution of compound **15** (1.0 g, 6.6 mmol) in $CH_2Cl_2$ (16 mL) was introduced and stirring continued for 2 h. The reaction was quenched by careful, dropwise addition of aq. $H_2SO_4$ (10% *w/w*) and stirring continued until all precipitates had dissolved. The aqueous layer was extracted with $CH_2Cl_2$, the combined organic layers were dried and evaporated, and the residue quickly passed through a pad of silica, eluting with hexanes/EtOAc (1:2). Evaporation of the filtrate gave Weinreb amide **16**, which had to be used in the next step without delay. Characteristic data: $^1$H NMR (400 MHz, $CDCl_3$): $\delta$ = 5.78-5.64 (m, 2H), 5.22-5.16 (m, 2H), 5.07-5.01 (m, 1H), 4.99-4.96 (m, 1H), 3.68 (s, 3H), 3.60-3.49 (m, 2H), 3.18 (s, 3H), 2.53-2.41 (m, 2H), 2.39-2.26 (m, 2H) ppm.

A solution of Weinreb amide **16** (1.3 g, 6.2 mmol) and complex **17** (228 mg, 0.25 mmol)[3] in $CH_2Cl_2$ (36 mL) was stirred overnight before all volatile materials were evaporated. The residue was purified by flash chromatography (hexanes/EtOAc, 1:2) to give product **18** as a syrup (0.85 g, 74% over both steps). $[\alpha]_D^{20}$ = –169 (c = 0.7, $CH_2Cl_2$); $^1$H NMR (400 MHz, $CDCl_3$): $\delta$ = 5.57-5.53 (m, 1H), 5.57-5.54 (m, 1H), 3.71 (s, 3H), 3.69-3.65 (m, 1H), 5.38-3.54 (m, 1H), 3.28 (br t, *J* = 6.1 Hz, 2H), 3.20 (s, 3H), 2.74-2.66 (m, 1H), 2.59-2.51 (m, 1H), 2.02 ppm (br s, 1H); $^{13}$C NMR (100 MHz, $CDCl_3$): $\delta$ = 176.6, 130.9, 129.9, 65.5, 61.3, 52.6, 42.4, 37.1, 32.5 ppm; IR (film): $\tilde{\nu}$ = 3417 (br, m), 3051 (w), 2934 (m), 1636 (s), 1444 (m), 1386 (s), 1324 (m), 1177 (m), 1116 (w), 1074 (m), 1030 (s), 1006 (s), 967 (m), 949 (w), 890 (w), 852 (w), 710 (s) $cm^{-1}$; MS (EI): *m/z* (%): 185 (6) $[M]^+$, 167 (9), 154 (1), 136 (1), 125 (30), 108 (11), 97 (12), 79 (100), 67 (46), 61 (29), 55 (5), 41 (18), 31 (9); HRMS (ESI): *m/z*: calcd. for $C_9H_{15}NO_3Na$: 208.0944 $[M+Na]^+$; found: 208.0944.

**Compound 19**. $NaHCO_3$ (908 mg, 10.81 mmol) and Dess-Martin periodinane (688 mg, 1.61 mmol) were successively added to a solution of compound **18** (200 mg, 1.08 mmol) in $CH_2Cl_2$ (12 mL) and the resulting mixture was stirred for 1.5 h. The reaction was quenched at 0°C with aq. sat. $Na_2S_2O_3$,

[3] Fürstner, A.; Guth, O.; Düffels, A.; Seidel, G.; Liebl, M.; Gabor, B.; Mynott, R. *Chem. Eur. J.* **2001**, *7*, 4811.

the aqueous phase was extracted with $CH_2Cl_2$, and the combined organic layers were washed with brine, dried over $Na_2SO_4$ and evaporated. The residue was purified by flash chromatography (pentanes/$Et_2O$, 1:1) to give aldehyde **19** as a pale yellow oil, which turned out to be rather unstable and was therefore used without delay in the next step (144 mg, 73%). $[\alpha]_D^{20}$ = –189.6 (c = 0.43, $CH_2Cl_2$); $^1$H NMR (400 MHz, $CDCl_3$): $\delta$ = 9.69 (s, 1H), 5.84-5.81-5.84 (m, 1H), 5.73-5.70 (m, 1H), 4.01 (br s, 1H), 3.81 (q, *J* = 7.3 Hz, 1H), 3.72 (br s, 3H), 3.20 (s, 3H), 2.78-2.62 ppm (m, 2H); $^{13}$C NMR (100 MHz, $CDCl_3$): $\delta$ = 199.7, 174.8, 132.7, 124.6, 62.7, 61.3, 38.4, 35.5, 32.5 ppm; IR (film): $\tilde{\nu}$ = 2939 (m), 2718 (w), 1720 (s), 1652 (s), 1443 (m), 1386 (s), 1342 (w), 1316 (w), 1176 (m), 1113 (m), 1003 (s), 964 (m), 948 (m), 843 (w), 704 (s) cm$^{-1}$; MS (EI): *m/z* (%): 183 (16) $[M]^+$, 166 (1), 154 (6), 134 (1), 123 (27), 105 (3), 95 (12), 79 (8), 67 (100), 61 (32), 46 (4), 39 (20), 29 (4); HRMS (EI): *m/z*: calcd. for $C_9H_{13}NO_3$: 183.0895 $[M]^+$; found: 183.0893.

**Compound 20.** 2-Chloro-4-nitrobenzoyl chloride (50 mg, 0.23 mmol, 1.05 eq.) and catalytic amounts of DMAP were added to a solution of compound **18** (40 mg, 0.22 mmol) in $CH_2Cl_2$ (1 mL) and $Et_3N$ (34 µL, 0.24 mmol). The mixture was stirred overnight before the reaction was quenched with aq. sat. $NaHCO_3$. A standard extractive work-up followed by purification of the crude product by flash chromatography (hexanes/EtOAc, 2:1) furnished product **20** as a white crystalline powder (53 mg, 65%). Crystals suitable for X-ray diffraction were grown by slowly diffusing pentane into a solution of **20** in $Et_2O$. $[\alpha]_D^{20}$ = –53 (c = 0.01, $CH_2Cl_2$); $^1$H NMR (400 MHz, $CDCl_3$): $\delta$ = 8.30 (d, *J* = 2.2 Hz, 1H), 8.14 (dd, *J* = 8.6, 2.2 Hz, 1H), 7.94 (d, *J* = 8.6 Hz, 1H), 5.77 (dq, *J* = 5.6, 2.3 Hz, 1H), 5.66 (dq, *J* = 5.9, 2.0 Hz, 1H), 4.43 (dd, *J* = 10.9, 6.3 Hz, 1H), 4.40 (dd, *J* = 10.8, 5.8 Hz, 1H), 3.67 (s, 3H), 3.66-3.61 (m, 1H), 3.36-3.30 (m, 1H), 3.18 (s, 3H), 2.77 (ddq, *J* = 16.6, 9.5, 2.4 Hz, 1H), 2.57 (ddq, *J* = 16.6, 7.0, 2.3 Hz, 1H) ppm; $^{13}$C NMR (100 MHz, $CDCl_3$): $\delta$ = 175.7 (br), 164.1, 149.4, 135.9, 134.7, 132.1, 130.9, 129.6, 126.0, 121.4, 68.6, 61.3, 48.8, 42.8, 37.2, 32.5 (br) ppm; IR (film): $\tilde{\nu}$ = 3096, 3000, 2959, 2893, 1734, 1655, 1523, 1354, 1262, 1246, 1108, 1048, 1011, 773, 709 cm$^{-1}$; MS (EI): *m/z* (%): 368 (3) $[M]^+$, 308 (14), 280 (3), 184 (26), 167 (15), 138 (13), 107 (29), 79 (100); HRMS (ESI): *m/z*: calcd. for $C_{16}H_{17}N_2O_6NaCl$ 391.0667 $[M+Na]^+$, found: 391.0670.

**Compound 22**. Compound **21** (227 mg, 1.18 mmol) and $K_2CO_3$ (217 mg, 1.57 mmol) were added to a solution of aldehyde **19** (144 mg, 0.79 mmol) in MeOH (10 mL) and the resulting mixture was stirred overnight. For work up, the mixture was partitioned between $CH_2Cl_2$ and brine, the combined organic layers were dried ($Na_2SO_4$) and evaporated, and the residue was purified by flash chromatography (pentanes/$Et_2O$, 4:1) to give the corresponding terminal alkyne as a colorless oil (106 mg, 75%), which analyzed as follows: $[\alpha]_D^{20}$ = –165 (c = 0.22, $CH_2Cl_2$); $^1$H NMR (400 MHz, $CDCl_3$): $\delta$ = 5.71-5.68 (m, 1H), 5.64-5.61 (m, 1H), 3.99-3.94 (m, 1H), 3.74 (s, 3H), 3.58 (br q, *J* = 7.4 Hz, 1H), 3.22 (s, 3H), 2.77 (ddq, *J* = 16.4, 9.5, 2.3 Hz, 1H), 2.49 (ddq, *J* = 16.3, 7.4, 2.4 Hz, 1H), 2.14 ppm (d, *J* = 2.5 Hz, 1H); $^{13}$C NMR (100 MHz, $CDCl_3$): $\delta$ = 175.2, 130.1, 129.6, 85.9, 69.3, 61.7, 47.0, 39.5, 36.9, 32.4 ppm; IR (film): $\tilde{\nu}$ = 3292 (m), 2939 (m), 1652 (s), 1445 (m), 1423 (m), 1386 (s) 1340 (m), 1311 (w), 1163 (s), 1101 (m), 1008 (s), 975 (m), 937 (m), 814 (w), 767 (w) cm$^{-1}$; MS (EI): *m/z* (%): 179 (5) $[M]^+$, 164 (< 1), 148 (16), 133 (< 1), 119 (25), 106 (2), 91 (100), 77 (2), 65 (29), 61 (8), 51 (5), 39 (12), 27 (2); HRMS (EI): *m/z*: calcd. for $C_{10}H_{13}NO_2$: 179.0946 $[M]^+$; found: 179.0946.

LiHMDS (177 mg, 1.06 mmol) was added to a solution of the terminal alkyne (150 mg, 0.84 mmol) in THF (5 mL) at –78°C. After stirring for 1.5 h, MeOTf (147 µL 1.3 mmol) was introduced and stirring continued at that temperature for 1 h. The reaction was quenched with aq. sat. $NaHCO_3$ while cold before the mixture was allowed to reach ambient temperature. A standard extractive work up

followed by flash chromatography of the crude material (pentanes/$Et_2O$, 4:1) gave product **22** as a colorless oil (130 mg, 80%). $[\alpha]_D^{20}$ = –307 (c = 0.4, $CH_2Cl_2$); $^1$H NMR (400 MHz, $CDCl_3$): $\delta$ = 5.66-5.63 (m, 1H), 5.60-5.57 (m, 1H), 3.91-3.86 (m, 1H), 3.73 (s, 3H), 3.53-3.48 (m, 1H), 2.21 (s, 3H), 2.78-2.69 (m, 1H), 2.49-2.43 (m, 1H), 1.76 ppm (d, *J* = 2.5 Hz, 3H); $^{13}$C NMR (100 MHz, $CDCl_3$): $\delta$ = 175.5, 131.0, 128.8, 80.8, 76.8, 61.6, 47.2, 39.9, 36.8, 32.3, 3.5 ppm; IR (film): $\tilde{\nu}$ = 2941 (w), 2919 (w), 1656 (s), 1443 (m), 1416 (m), 1384 (s), 1342 (m), 1310 (m), 1176 (m), 1102 (m), 1005 (s), 945 (m), 809 (w) cm$^{-1}$; MS (EI): *m/z* (%): 193 (7) $[M]^+$, 178 (<1), 162 (23), 147 (1), 133 (30), 121 (3), 105 (100), 91 (2), 79 (41), 65 (6), 58 (6), 51 (10), 39 (11), 27 (9); HRMS (EI): *m/z*: calcd. for $C_{11}H_{15}NO_2$: 193.1102 $[M]^+$; found: 193.1103.

**Preparation of the Common Intermediate 22 – Catalytic Route**

**Pinacol Boronate 30c**. Pinacol borane (16 mL, 110 mmol) was slowly added to phenylacetylene (12.8 mL, 122 mmol) and the resulting mixture was stirred at 140°C for 5 d. After reaching ambient temperature, the product was purified by distillation (72-74°C, $10^{-3}$ mbar) to give boronate **30c** as a colorless oil, which crystallized upon storage in the freezer (22.6 g, 89%). $^1$H NMR (400 MHz, $CDCl_3$): $\delta$ = 7.48-7.50 (m, 2H), 7.40 (d, *J* = 18.4 Hz, 1H), 7.27-7.36 (m, 3H), 6.18 (d, *J* = 18.4 Hz, 1H), 1.32 ppm (s, 12H); $^{13}$C NMR (100 MHz, $CDCl_3$): $\delta$ = 149.5, 137.4, 128.9, 128.5, 127.0, 83.3, 24.8 ppm; $^{11}$B NMR (128 MHz, $CDCl_3$): $\delta$ = 31.0 ppm; IR (film): $\tilde{\nu}$ = 3022 (w), 2977 (m), 2931 (w), 1620 (s), 1575 (m), 1494 (m), 1448 (m), 1385 (m), 1347 (s), 1319 (s), 1269 (w), 1208 (s), 1163 (w), 1140 (s), 1107 (w), 1072 (w), 996 (m), 968 (m), 849 (m), 746 (s), 690 (s) cm$^{-1}$; MS (EI): *m/z* (%): 230 (89) $[M]^+$, 215 (31), 202 (1), 187 (10), 172 (10), 157 (11), 144 (100), 130 (91), 118 (14), 105 (22), 85 (8), 77 (13), 71 (2), 59 (6), 43 (16), 29 (3); HRMS (EI): *m/z*: calcd. for $C_{14}H_{19}O_2B$: 230.1478 $[M]^+$; found: 230.1480.

**Compound 31c**. Diene **35** (15 mg, 57 µmol)[4] and aq. KOH (1.5 M, 570 µL) were successively added to a solution of $[Rh(C_2H_4)Cl]_2$ (10 mg, 26 µmol) in 1,4-dioxane (10 mL) and the resulting mixture was stirred for 15 min before pinacol boronate **30c** (790 mg, 3.4 mmol) and 2[5*H*]-furanone **29** (140 mg, 1.7 mmol) and a catalytic amount of $SiO_2$ were introduced. The mixture was stirred for 3 d at ambient temperature before all volatile materials were evaporated. The residue was purified by flash chromatography (pentanes/$Et_2O$, 1:1) to give compound **31c** as a colorless syrup, which solidified upon standing (170 mg, 52%, 80% *ee,* $[\alpha]_D^{20}$ = +19 (c = 0.1, $CH_2Cl_2$)). Recrystallization from pentanes/$CH_2Cl_2$ increased the *ee* to 93% (140 mg) (GC: 25 m Hydrodex-B column, ∅ 0.25 mm, 230/200 50 min iso 8/min 230 5 min iso/350; 0.5 bar $H_2$, FID detector, $R_t$ = 43.9 min, $R_t$ (enantiomer) = 45.2 min). $^1$H NMR (400 MHz, $CDCl_3$): $\delta$ = 7.24-7.37 (m, 5H), 6.53 (d, *J* = 15.9 Hz, 1H), 6.11 (dd, *J* = 15.7, 8.1 Hz, 1H), 4.51 (dd, *J* = 8.8, 7.8 Hz, 1H), 4.10 (dd, *J* = 9.0, 8.2 Hz, 1H), 3.35-3.46 (m, 1H), 2.76 (dd, *J* = 17.4, 8.3 Hz, 1H), 2.48 ppm (dd, *J* = 17.4, 9.1 Hz, 1H); $^{13}$C NMR (100 MHz, $CDCl_3$): $\delta$ = 176.4, 136.1, 132.7, 128.7, 128.0, 126.9, 126.3, 72.5, 39.5, 34.7 ppm; IR (film): $\tilde{\nu}$ = 1773 (s), 1760 (s), 1493 (w), 1478 (w), 1450 (w), 1417 (w), 1356 (w), 1273 (w), 1221 (w), 1178 (s), 1163 (m), 1042 (w), 1004 (m), 976 (m), 889 (w), 838 (w) cm$^{-1}$; MS (EI): *m/z* (%): 188 (50) $[M]^+$, 141 (1), 130 (100), 115 (27), 104 (6), 91 (7), 77 (6), 71 (3), 64 (12), 51 (9), 39 (5), 27 (2); HRMS (EI): *m/z*: calcd. for $C_{12}H_{12}O_2$: 188.0837

[4] Defieber, C.; Paquin, J.-F.; Serna, S.; Carreira, E. M. *Org. Lett*. **2004**, *6*, 3873.

$[M]^+$; found: 188.0838. The enantiomer of this compound is known in the literature [*ent*-**31c**, *ee* = 91%, $[\alpha]_D^{23}$ = –33.9 (c = 1.0, $CHCl_3$)].[5]

**Compound 32.** *n*BuLi (1.6 M in heptanes, 200 µL, 0.32 mmol) was added to a solution of *i*$Pr_2NH$ (49 µL, 0.35 mmol) in THF (8 mL) at –78°C and the resulting mixture was stirred at 0°C for 30 min. After cooling to –78°C, a solution of compound **31c** (60 mg, 0.32 mmol) in THF (6 mL) was introduced and stirring continued at this temperature for 30 min prior to the addition of allyl iodide (35 µL, 0.38 mmol). After an additional 45 min, the reaction was quenched with aq. sat. $NaHCO_3$ (5 mL), the aqueous phase was extracted with $Et_2O$, the combined organic layers were dried over $Na_2SO_4$ and evaporated, and the residue was purified by flash chromatography (pentanes/$Et_2O$, 10:1) to give product **32** as a colorless oil (63 mg, 87%). $[\alpha]_D^{20}$ = + 56 (c = 0.05, $CH_2Cl_2$); $^1$H NMR (400 MHz, $CDCl_3$): $\delta$ = 7.38-7.25 (m, 5H), 6.52 (d, *J* = 15.7 Hz, 1H), 6.03 (dd, *J* = 15.9, 8.6 Hz, 1H), 5.87-5.77 (m, 1H), 5.19-5.12 (m, 2H), 4.42 (dd, *J* = 9.1, 8.1 Hz, 1H), 3.99 (dd, *J* = 9.9, 9.1 Hz, 1H), 3.21-3.11 (m, 1H), 2.58-2.47 ppm (m, 3H); $^{13}$C NMR (100 MHz, $CDCl_3$): $\delta$ = 177.5, 136.1, 133.9, 133.8, 128.7, 128.1, 126.3, 126.2, 118.5, 70.2, 45.1, 44.6, 32.1 ppm; IR (film): $\tilde{\nu}$ = 3078 (w), 3027 (w), 2984 (w), 2907 (w), 1769 (s), 1641 (w), 1495 (w), 1352 (w), 1160 (m), 1013 (s), 966 (m), 748 (m) $cm^{-1}$; MS (EI): *m/z* (%): 228 (56) $[M]^+$, 186 (85), 170 (28), 155 (28), 141 (99), 129 (100), 115 (54), 104 (57), 91 (62), 79 (42), 66 (14), 51 (15), 39 (23); HRMS (EI): *m/z*: calcd. for $C_{15}H_{16}O_2$ $[M]^+$ 228.1150, found: 228.1152.

**Compound 18.** $Me_3Al$ (2 M in heptanes, 329 µL, 0.66 mmol) was added to a solution of *N,O*-dimethylhydroxylamine hydrochloride (64 mg, 0.66 mmol) in $CH_2Cl_2$ (2 mL) at 0°C and the resulting mixture was warmed to ambient temperature and stirred for 2 h. A solution of compound **32** (60 mg, 0.26 mmol) in $CH_2Cl_2$ (2 mL) was introduced at 0°C and stirring continued at this temperature for 2 h before the reaction was quenched by careful addition of aq. $H_2SO_4$ (3 mL, 10% *v/v*). The aqueous phase was washed with $CH_2Cl_2$ (3 x 4 mL), the combined organic layers were dried over $Na_2SO_4$ and evaporated. The residue was rapidly passed through a short pad of silica, eluting with hexanes/EtOAc (1:2). Product **33** thus obtained was immediately dissolved in $CH_2Cl_2$ (10 mL), the indenylidene metathesis catalyst **17** (19 mg, 0.02 mmol, 8 mol%) was added and the resulting mixture stirred overnight at ambient temperature. For work up, the solvent was evaporated and the residue purified by flash chromatography (hexanes/EtOAc, 1:2) to give product **18** as a yellow syrup (36 mg, 75% for two steps). The analytical and spectral data were identical to those reported above for the material derived from the auxiliary-based route.

## Total Synthesis of Hybridalactone

**2,3-Dibromopentanoic acid.**[6] Bromine (16.5 g, 103 mmol) was added at 0°C to a solution of 2*E*-pentenoic acid (10 g, 100 mmol) in $CH_2Cl_2$ (200 mL). Once the addition was complete, the mixture was stirred at ambient temperature for 3 h before all volatile materials were evaporated. The resulting product was used in the next step without further purification (25.5 g, 98%). $^1$H NMR (400 MHz, $CDCl_3$): $\delta$ = 10.61 (br s, 1H), 4.45 (d, *J* = 11.1 Hz, 1H), 4.36 (ddd, *J* = 11.1, 8.2, 2.7 Hz, 1H), 2.31 (ddq, *J* = 14.6, 7.4, 2.6 Hz, 1H), 1.90 (ddq, *J* = 15.2, 7.4, 7.3 Hz, 1H), 1.11 (t, *J* = 7.2 Hz, 3H) ppm;

[5] Kim, S.-G. *Tetrahedron Lett*. **2008**, *49*, 6148.

[6] Mori, K.; Brevet, J.-L. *Synthesis*, **1991**, 1125.

$^{13}$C NMR (100 MHz, $CDCl_3$): $\delta$ = 173.4, 53.3, 46.8, 28.3, 10.5 ppm; IR (film): $\tilde{\nu}$ = 3019, 2919, 1704, 1434, 1291, 1238, 1154, 909, 744, 694 cm$^{-1}$; HRMS (CI, *i*-butane): *m/z*: calcd. for $C_5H_9O_2Br_2$ 258.8969 $[M+H]^+$, found: 258.8966.

**Bromide 25**.[6] A solution of dibromopentanoic acid (18 g, 70 mmol) in DMF (15 mL) was added over the course of 1 h to a suspension of $NaHCO_3$ (10 g, 118 mmol, 1.7 eq.) in DMF (30 mL), which was stirred at 70°C under vacuum (ca. 130 mbar). Under these conditions, the volatile bromide **25** distilled off and was collected in a cold trap (–78°C). The collected material was washed with a minimum amount of water (ca. 150 µL/1 mL of product) and dried over $Na_2SO_4$ to give product **25** as a colorless liquid (8.2 g, 87%, *Z:E* > 96:4, GC). $^1$H NMR (400 MHz, $CDCl_3$): $\delta$ = 6.13-6.06 (m, 2H), 2.25-2.17 (m, 2H), 1.02 (t, *J* = 7.6 Hz, 3H) ppm; $^{13}$C NMR (100 MHz, $CDCl_3$): $\delta$ = 136.4, 107.0, 23.2, 12.6 ppm; IR (film): $\tilde{\nu}$ = 2970, 2936, 1686, 1623, 1460, 1333, 1284, 1071, 886 cm$^{-1}$.

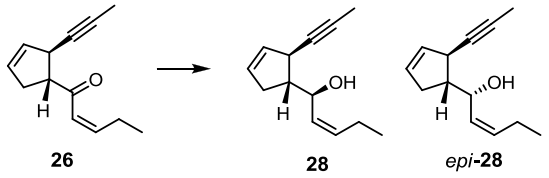
**Compound 26**. A solution of (*Z*)-1-bromo-1-butene (**25**, 1.35 g, 10 mmol) in $Et_2O$ (4 mL) was added dropwise over 10 min to a suspension of lithium sand (0.31 g, 45 mmol) in $Et_2O$ (8 mL) at –50°C. The resulting mixture was stirred at this temperature for 20 min before it was warmed to –40°C and stirred for additional 1 h. The mixture was then allowed to reach ambient temperature, before unreacted lithium was filtered off through a short pad of dried Celite and the resulting filtrate was immediately used in the next step.

A solution of (*Z*)-1-butenyllithium (ca. 0.8 M in $Et_2O$, 1.5 mL, 1.2 mmol) prepared as described above was slowly added to a solution of Weinreb amide **22** (0.19 g, 4.0 mmol) in $Et_2O$ (4 mL) at 0°C and the resulting mixture stirred at 0°C for 1 h. The reaction was quenched with aq. sat. $NH_4Cl$ and the product extracted with $Et_2O$. The combined organic layers were dried over $Na_2SO_4$ and evaporated. Purification of the residue by flash chromatography (hexane/EtOAc, 40:1) provided product **26** as a pale yellow oil (0.16 g, 83%). $[\alpha]_D^{20}$ = –366 (c = 0.10, $CH_2Cl_2$); $^1$H NMR (400 MHz, $C_6D_6$): δ = 6.02 (dt, *J* = 11.3, 1.7 Hz, 1H), 5.75 (dt, *J* = 11.4, 7.5 Hz, 1H), 5.54 (dq, *J* = 5.6, 2.3 Hz, 1H), 5.36 (dq, *J* = 5.5, 2.5 Hz, 1H), 4.03 (dqi, *J* = 9.5, 2.4 Hz, 1H), 3.29 (dt, *J* = 9.6, 6.9 Hz, 1H), 2.66 (dtd, *J* = 7.5, 7.5, 1.7 Hz, 2H), 2.59 (ddq, *J* = 16.7, 7.1, 2.4 Hz, 1H), 2.37 (ddq, *J* = 16.7, 9.8, 2.3 Hz, 1H), 1.51 (d, *J* = 2.3 Hz, 3H), 0.84 (t, *J* = 7.6 Hz, 3H) ppm; $^{13}$C NMR (100 MHz, $C_6D_6$): δ = 199.3, 150.8, 131.2, 129.0, 125.8, 81.5, 76.8, 58.8, 39.0, 34.9, 23.4, 13.7, 3.5 ppm; IR (film): $\tilde{\nu}$ = 3063, 3018, 2966, 2919, 2855, 1689, 1614, 1460, 1445, 1417, 1322, 1270, 1204, 1099, 1048, 1004, 943, 833, 811, 710 cm$^{-1}$; MS (EI): *m/z* (%): 188 (13) $[M]^+$, 173 (21), 159 (27), 145 (17), 131 (47), 117 (13), 105 (21), 91 (16), 83 (100), 77 (20), 65 (6), 55 (29), 39 (12), 29 (11); HRMS (EI): *m/z*: calcd. for $C_{13}H_{16}O$: 188.1201 $[M]^+$; found: 188.1202.

**Compound 28**. EtOH (0.12 mL, 2.0 mmol) was added dropwise to a solution of $LiAlH_4$ (2.0 M in THF, 1.0 mL, 2.0 mmol) in THF (1 mL) and the resulting mixture was stirred for 10 min before a solution of (*R*)-1,1'-bi-2-naphthol (0.57 g, 2.0 mmol) in THF (3 mL) was added dropwise at 0°C. Stirring was continued for 30 min at room temperature before the solution was cooled to –78°C. This cold mixture was then added via canula to a cold (–78°C) solution of enone **26** (0.11 g, 0.60 mmol) in THF (4 mL). After stirring at –78°C for 72 h, MeOH was added and the mixture allowed to reach ambient temperature. Aq. sat. $NH_4Cl$ and aq. HCl (1 M) were then added, the product was extracted with $Et_2O$, the combined organic layers were dried over $Na_2SO_4$ and evaporated. Purification of the residue by flash chromatography (hexane/EtOAc, 10:1) afforded product **28** as a pale yellow oil (0.10 g, 90%, dr >10 : 1). $[\alpha]_D^{20}$ = –175 (c = 0.05, $CH_2Cl_2$); $^1$H NMR (400 MHz, $C_6D_6$): δ = 5.68 (dq, *J* = 5.6, 2.1 Hz, 1H), 5.51 (dq, *J* = 5.5, 2.5 Hz, 1H), 5.37-5.29 (m, 2H), 4.33-4.28 (m, 1H), 3.65-3.59 (m, 1H), 2.64-2.54 (m, 1H), 2.36 (ddq, *J* = 16.5, 8.9, 2.3 Hz, 1H), 2.01 (ddq, *J* = 16.5, 6.8, 2.3 Hz, 1H), 1.96-1.83 (m, 2H), 1.54

(d, *J* = 2.4 Hz, 3H), 1.24 (br s, 1H), 0.81 (t, *J* = 7.4 Hz, 3H) ppm; $^{13}$C NMR (100 MHz, $C_6D_6$): δ = 134.7, 134.6, 132.2, 131.2, 82.5, 76.8, 70.3, 53.2, 39.3, 35.1, 21.7, 14.7, 3.8 ppm; IR (film): $\tilde{\nu}$ = 3363, 3060, 3007, 2963, 2919, 2856, 1445, 1287, 1068, 1032, 937, 752, 716 cm$^{-1}$; MS (EI): *m/z* (%): 189 (< 1), 172 (11), 157 (26), 143 (40), 128 (24), 115 (12), 104 (100), 91 (43), 85 (25), 77 (25), 67 (14), 57 (22), 41 (25), 19 (16); HRMS (CI, *i*-butane): calcd for $C_{13}H_{19}O$: 191.1436 $[M+H]^+$; found: 191.1437.

**Table S1**. Reduction of ketone **26** with various reducing agents.[a]




**26** **28** *epi*-**28**

| Entry | Conditions | Yield | 28 : *epi*-28 |
|---|---|---|---|
| 1 | L-selectride, THF, –78°C | 31% | 1:0 |
| 2 | K-selectride, THF, –78°C | [b] | |
| 3 | $LiHBEt_3$, THF, –78°C | 65% | 5:1 |
| 4 | $BH_3$·THF, (*R*)-Me-CBS[c] | 67% | 1:7 |
| 5 | $BH_3$·THF, (*S*)-Me-CBS[c] | n.d. | 1:2.5 |
| 6 | Dibal-H, THF, –78°C | n.d. | 1:1 |
| 7 | Dibal-H, *n*-BuLi, THF/hexane, –78°C[d] | 77% | 4:1 |
| 8 | Dibal-H, *sec*-BuLi, THF/hexane, –78°C | 65% | 5:1 |
| 9 | Dibal-H, *tert*-BuLi, THF/hexane, –78°C | 61% | 5:1 |
| 10 | Dibal-H, *tert*-BuOLi, THF, –78°C | n.d. | 2:1 |
| 11 | Red-Al, THF, –78°C | n.d. | 3:1 |
| 12 | $LiAlH_4$, THF, –78°C | n.d. | 2:1 |
| 13 | $LiAlH_4$, *S*-BINOL, EtOH, THF, –78°C | n.d. | 2:1 |
| **14** | **$LiAlH_4$, *R*-BINOL, EtOH, THF, –78°C** | **90%** | **>10:1** |

[a] The use of *S*-Alpine hydride, *S*-Alpine borane, $KHB(OiPr)_3$, Luche conditions ($NaBH_4$, $CeCl_3$) afforded only complex mixtures; [b] 1,4-reduction only; [c] Me-CBS refers to *B*-methyl oxazaborolidine derived from 1,1-diphenylpyrrolidinomethanol, cf. ref. 7; [d] see ref. 8

**Compound 36**. $CH_2I_2$ (32 µL, 0.40 mmol) was added dropwise to a solution of $Et_2Zn$ (1.0 M in hexane, 0.20 mL, 0.20 mmol) in $CH_2Cl_2$ (1 mL) at –10°C. After stirring for 15 min, the mixture was cooled to -30°C and a solution of alcohol **28** (19.0 mg, 0.10 mmol) in $CH_2Cl_2$ (1 mL) was introduced. The resulting mixture was stirred at –20°C for 16 h before the reaction was quenched with aq. sat. $NH_4Cl$

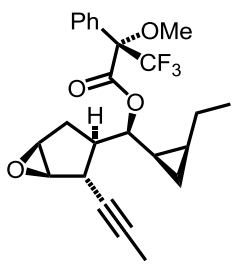
[7] Corey, E. J.; Helal, C. J. *Angew. Chem., Int. Ed*. **1998**, *37*, 1986.

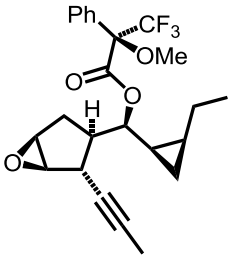
[8] Kim, S.; Ahn, K. H. *J. Org. Chem*. **1984**, *49*, 1717.

and the product extracted with $Et_2O$. The combined organic layers were dried over $Na_2SO_4$. Evaporation of the solvent followed by purification of the residue by flash chromatography (hexane/EtOAc, 10:1) provided product **36** as a colorless oil (13.3 mg, 65%). $[\alpha]_D^{20}$ = –141 (c = 0.27, $CH_2Cl_2$); $^1$H NMR (400 MHz, $C_6D_6$): δ = 5.73 (dq, *J* = 5.7, 2.2 Hz, 1H), 5.59 (dq, *J* = 5.7, 2.4 Hz, 1H), 3.80 (m, 1H), 3.15 (dd, *J* = 9.0, 4.9 Hz, 1H), 2.69 (dtd, *J* = 8.9, 7.5, 4.9 Hz, 1H), 2.41 (ddq, *J* = 16.3, 7.4, 2.5 Hz, 1H), 2.31 (ddq, *J* = 16.3, 7.5, 2.4 Hz, 1H), 1.56 (d, *J* = 2.4 Hz, 3H), 1.48-1.38 (m, 1H), 1.15 (br s, 1H), 1.00 (tdd, *J* = 8.7, 8.7, 5.6 Hz, 1H), 0.94 (t, *J* = 6.7 Hz, 3H), 0.93-0.83 (m, 1H), 0.70-0.60 (m, 1H), 0.47 (td, *J* = 8.4, 4.4 Hz, 1H), –0.18 (dtd, *J* = 5.5, 5.4, 1.3 Hz, 1H) ppm; $^{13}$C NMR (100 MHz, $C_6D_6$): δ = 132.2, 130.2, 82.9, 76.1, 73.0, 53.3, 37.5, 35.3, 22.7, 22.3, 19.4, 14.5, 9.0, 3.5 ppm; IR (film): $\tilde{\nu}$ = 3404, 2960, 2920, 2205, 2162, 2153, 2019, 1963, 1455, 1031, 714 cm$^{-1}$; MS (EI): *m/z* (%): 203 (2), 186 (12), 171 (21), 157 (31), 143 (38), 129 (45), 117 (99.7), 104 (71), 99 (23), 91 (58), 77 (32), 65 (13), 57 (100), 41 (24), 29 (13); HRMS (CI, *i*-butane): calcd for $C_{14}H_{21}O$: 205.1592 $[M+H]^+$; found: 205.1590.

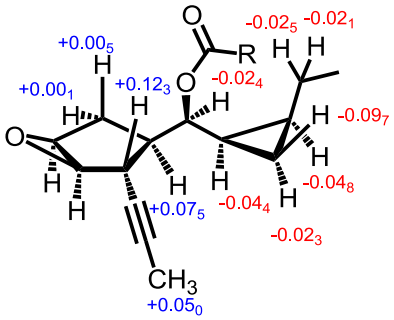
**Compound 38**. A solution of compound **36** (9.9 mg, 0.048 mmol) in $CH_2Cl_2$ (2 mL) was added to a reaction flask containing powdered activated MS 3Å. After stirring for 10 min, a stock solution of $VO(acac)_2$ (0.02 M in $CH_2Cl_2$, 0.24 mL, 4.8 μmol) was introduced and the resulting mixture stirred for 5 min before it was cooled to 0°C. A solution of *t*BuOOH (ca. 5.5 M in decane, 27 μL, 0.15 mmol) in $CH_2Cl_2$ (1 mL) was added dropwise and the resulting mixture stirred at ambient temperature for 2.5 h. At this point, a second portion of the stock solution of $VO(acac)_2$ (0.02 M in $CH_2Cl_2$, 0.12 mL, 2.4 μmol) was added and stirring continued at room temperature for another 2.5 h before the reaction was quenched with aq. sat. $Na_2S_2O_3$. Extraction with $CH_2Cl_2$, evaporation of the solvent and purification of the residue by flash chromatography (hexane/EtOAc, 5:1) furnished product **38** (7.4 mg, 69%) as a colorless oil. $[\alpha]_D^{20}$ = –97 (c = 0.16, $CH_2Cl_2$); $^1$H NMR (600 MHz, $C_6D_6$): δ = 3.53 (dq, *J* = Σ 4.4 Hz, 1H), 3.38 (d, *J* = 2.6 Hz, 1H), 3.15 (dd, *J* = 8.3, 5.9 Hz, 1H), 3.06 (m, 1H), 2.57 (br s, 1H), 2.46 (dddd, *J* = 9.0, 5.8, 3.1, 1.7 Hz, 1H), 1.85 (ddd, *J* = 14.8, 9.0, 1.4, 1H), 1.82 (ddd, *J* = 14.8, 3.1, –0.6, 1H), 1.54 (m, 1H), 1.48 (d, *J* = 2.6 Hz, 3H), 1.02 (m, 1H), 0.95 (t, *J* = 7.1 Hz, 3H), 0.69 (qd, *J* = 8.5, 5.5 Hz, 1H), 0.57 (m, 1H), 0.52 (tdd, *J* = 8.4, 4.2, 0.9 Hz, 1H), 0.01 (td, *J* = 5.5, 4.2 Hz, 1H) ppm; $^{13}$C NMR (150 MHz, $C_6D_6$): δ = 79.1 (s), 78.3 (s), 73.6 (d, $^1J_{CH}$ = 144 Hz), 61.2 (d, $^1J_{CH}$ = 188 Hz), 58.3 (d, $^1J_{CH}$ = 185 Hz), 52.1 (d, $^1J_{CH}$ = 134 Hz), 33.0 (d, $^1J_{CH}$ = 138 Hz), 30.8 (t, $^1J_{CH}$ = 130 Hz), 23.1 (d, $^1J_{CH}$ = 156 Hz), 22.8 (t, $^1J_{CH}$ = 126 Hz), 18.9 (d, $^1J_{CH}$ = 157 Hz), 14.6 (q, $^1J_{CH}$ = 126 Hz), 8.7 (t, $^1J_{CH}$ = 159 Hz), 3.4 ppm (q, $^1J_{CH}$ = 131 Hz); IR (film): $\tilde{\nu}$ = 3452, 2960, 2921, 2366, 2140, 2036, 1983, 1029, 840 cm$^{-1}$; MS (EI): *m/z* (%): 220 (< 1) $[M]^+$, 203 (3), 191 (2), 173 (2), 164 (10), 147 (4), 121 (13), 99 (57), 91 (27), 79 (40), 66 (10), 57 (100), 41 (23), 29 (12); HRMS (ESI): calcd for $C_{14}H_{20}O_2Na$: 243.1355 $[M+Na]^+$; found: 243.1354.

**(*S*)-Mosher ester derived from 38.** $^1$H NMR (600 MHz, $C_6D_6$): δ = 7.89 (d, *J* = 7.8 Hz, 2H), 7.19 (m, 2H), 7.10 (t, *J* = 7.4 Hz, 1H), 5.05 (t, *J* = 10.0 Hz, 1H), 3.62 (q, $J_{HF}$ = 1.0 Hz, 3H), 3.29 (d, *J* = 2.5 Hz, 1H), 3.03 (m, 1H), 3.02 (m, 1H), 2.52 (t, *J* = 10.0 Hz, 1H), 1.95 (d, *J* = 15.0 Hz, 1H), 1.69 (ddd, *J* = 14.9, 10.0, 1.2 Hz, 1H), 1.66 (m, 1H), 1.45 (d, *J* = 2.5 Hz, 3H), 1.15 (m, 1H), 0.92 (t, *J* = 7.3 Hz, 3H), 0.55 (m, 1H), 0.54 (m, 1H), 0.42 (tdd, *J* = 8.4, 4.6, 0.7 Hz, 1H), 0.19 (td, *J* = 5.8, 4.6 Hz, 1H) ppm; $^{13}$C NMR (150 MHz, $C_6D_6$): δ = 166.5, 133.2, 129.5, 128.5, 128.1, 124.4 (q, $J_{CF}$ = 288.5 Hz), 85.2 (q, $J_{CF}$ = 27.5 Hz), 82.9, 78.9, 77.8, 60.0, 57.1, 55.5 (q, $J_{CF}$ = 1.1 Hz), 49.5, 34.9, 28.8, 23.6, 21.0, 20.6, 14.3, 9.6, 3.3 ppm.





**(*R*)-Mosher ester derived from 38.** $^{1}$H NMR (600 MHz, $C_6D_6$): δ = 7.85 (d, *J* = 7.7 Hz, 2H), 7.14 (m, 2H), 7.08 (t, *J* = 7.4 Hz, 1H), 5.08 (t, *J* = 10.1 Hz, 1H), 3.56 (q, $J_{HF}$ = 1.0 Hz, 3H), 3.33 (d, *J* = 2.5 Hz, 1H), 3.05 (d, *J* = 2.2 Hz, 1H), 2.90 (m, 1H), 2.44 (t, *J* = 10.0 Hz, 1H), 1.95 (d, *J* = 14.9 Hz, 1H), 1.69 (ddd, *J* = 14.9, 10.0, 1.1 Hz, 1H), 1.68 (m, 1H), 1.40 (d, *J* = 2.5 Hz, 3H), 1.17 (m, 1H), 0.91 (t, *J* = 7.3 Hz, 3H), 0.60 (m, 1H), 0.59 (m, 1H), 0.44 (tdd, *J* = 8.4, 4.4, 0.7 Hz, 1H), 0.29 (td, *J* = 5.8, 4.4 Hz, 1H) ppm; $^{13}$C NMR (150 MHz, $C_6D_6$): δ = 166.6, 133.4, 129.4, 128.5, 127.8, 124.4 (q, $J_{CF}$ = 288.5 Hz), 84.9 (q, $J_{CF}$ = 27.5 Hz), 82.4, 78.5, 77.6, 59.9, 57.1, 55.5 (q, $J_{CF}$ = 1.2 Hz), 49.5, 34.5, 28.6, 23.6, 21.3, 20.9, 14.2, 9.7, 3.3 ppm.



**Scheme S2.** Analysis [$\Delta\delta_{(S)-(R)}$] of the Mosher Esters derived from **38**.

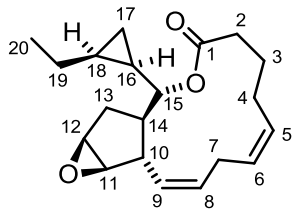
**Compound 41**. Carbodiimide *p*-toluenesulfonate **39** (72.0 mg, 0.17 mmol) was added to a solution of (*Z*)-5-decen-8-ynoic acid **40** (23.3 mg, 0.14 mmol) in $CH_2Cl_2$ (0.5 mL) and the resulting mixture stirred for 1.5 h before a solution of compound **38** (9.8 mg, 0.044 mmol) in $CH_2Cl_2$ (0.5 mL) and a catalytic amount of DMAP were added. After stirring for 7 d, the precipitate was filtered off through a pad of silica, the filtrate was evaporated and the residue purified by flash chromatography (hexane/EtOAc, 10:1) to give product **41** (12.6 mg, 77%) as a colorless oil. $[\alpha]_D^{20}$ = –68 (c = 0.43, $CH_2Cl_2$); $^{1}$H NMR (600 MHz, $CDCl_3$): δ = 5.47-5.36 (m, 2H), 4.57 (t, *J* = 9.8 Hz, 1H), 3.48 (m, 1H), 3.45 (d, *J* = 2.5 Hz, 1H), 2.87 (m, 2H), 2.75 (dq, *J* = Σ 4.5 Hz, 1H), 2.40 (tt, *J* = 9.7, 1.9 Hz, 1H), 2.32 (t, *J* = 7.5 Hz, 2H), 2.15 (dd, *J* = 14.9, 2.0 Hz, 1H), 2.09 (q, *J* = 7.1 Hz, 2H), 2.05 (ddd, *J* = 14.9, 9.8, 1.4 Hz, 1H), 1.77 (d, *J* = 2.5 Hz, 3H), 1.76 (t, *J* = 2.6 Hz, 3H), 1.70 (qi, *J* = 7.5 Hz, 2H), 1.66 (m, 1H), 1.09 (m, 1H), 0.99 (t, *J* = 7.2 Hz, 3H), 0.86 (m, 1H), 0.80 (dtd, *J* = 10.0, 8.6, 5.6 Hz, 1H), 0.56 (tdd, *J* = 8.5, 4.5, 0.6 Hz, 1H), 0.05 (td, *J* = 5.7, 4.7 Hz, 1H) ppm; $^{13}$C NMR (150 MHz, $CDCl_3$): δ = 173.5 (s), 130.1 (d, $^{1}J_{CH}$ = 154 Hz), 125.8 (d, $^{1}J_{CH}$ = 155 Hz), 78.5 (s), 78.0 (d, $^{1}J_{CH}$ = 152 Hz), 77.9 (s), 77.4 (s), 75.4 (s), 60.5 (d, $^{1}J_{CH}$ = 189 Hz), 57.8 (d, $^{1}J_{CH}$ = 185 Hz), 50.0 (d, $^{1}J_{CH}$ = 135 Hz), 34.1 (t, $^{1}J_{CH}$ = 128 Hz), 33.8 (d, $^{1}J_{CH}$ = 138 Hz), 28.7 (t, $^{1}J_{CH}$ = 130 Hz), 26.5 (t, $^{1}J_{CH}$ = 126 Hz), 24.8 (t, $^{1}J_{CH}$ = 129 Hz), 23.1 (t, $^{1}J_{CH}$ = 125 Hz), 21.1 (d, $^{1}J_{CH}$ = 158 Hz), 20.2 (d, $^{1}J_{CH}$ = 157 Hz), 17.1 (t, $^{1}J_{CH}$ = 130 Hz), 14.2 (q, $^{1}J_{CH}$ = 125 Hz), 8.7 (t, $^{1}J_{CH}$ = 160 Hz), 3.6 (q, $^{1}J_{CH}$ = 131 Hz), 3.5 ppm (q, $^{1}J_{CH}$ = 131 Hz); IR (film): $\tilde{\nu}$ = 2923, 2358, 2337, 2178, 1728, 1155, 1035, 844 cm$^{-1}$; MS (EI): *m/z* (%): 368 (< 1) $[M]^+$, 339 (< 1), 229 (1), 225 (< 1), 203 (15), 159 (6), 149 (18), 105 (100), 91 (22), 79 (26), 55 (19), 41 (12); HRMS (ESI): calcd for $C_{24}H_{32}O_3Na$: 391.2244 $[M+Na]^+$; found: 391.2246.

**Compound 42**. Diyne **41** (9.6 mg, 0.026 mmol) was dissolved in toluene (13 mL) and powdered, activated MS 5Å (0.15 g) was added. The suspension was stirred for 15 min before a stock solution of complex **43b** (0.01 M in toluene, 0.39 mL, 3.9 µmol) was added and the resulting mixture stirred at

70°C for 24 h. After reaching ambient temperature, the suspension was filtered through a pad of silica, the filtrate was evaporated, and the residue purified by flash chromatography (hexanes/EtOAc, 10:1) to afford product **42** as a colorless oil (6.5 mg, 79%). $[\alpha]_D^{20}$ = –29 (c = 0.32, $CH_2Cl_2$); $^1$H NMR (600 MHz, $C_6D_6$): δ = 5.29 (dddt, *J* = 10.9, 6.0, 5.4, 1.4 Hz, 1H), 5.24 (dddt, *J* = 10.9, 7.9, 7.0, 1.4 Hz, 1H), 4.42 (t, *J* = 10.0 Hz, 1H), 3.38 (d, *J* = 2.5 Hz, 1H), 3.23 (ddd, *J* = 6.4, 2.8, 2.0 Hz, 1H), 3.05 (t, *J* = 2.4 Hz, 1H), 3.03 (tt, *J* = 10.3, 7.3 Hz, 1H), 2.72 (ddd, *J* = 18.7, 6.0, 3.1 Hz, 1H), 2.64 (m, 1H), 2.62 (m, 1H), 2.36 (m, 1H), 2.30 (ddd, *J* = 15.8, 8.8, 2.8 Hz, 1H), 2.25 (ddd, *J* = 15.8, 8.2, 2.8 Hz, 1H), 1.71 (m, 1H), 1.65 (ddd, *J* = 14.7, 10.2, 2.3 Hz, 1H), 1.62 (dd, *J* = 14.7, 7.7 Hz, 1H), 1.61 (m, 1H), 1.45 (m, 1H), 0.90-0.82 (m, 5H), 0.57-0.49 (m, 2H), –0.04 (m, 1H) ppm; $^{13}$C NMR (150 MHz, $C_6D_6$): δ = 172.4 (s), 133.9 (d, $^1J_{CH}$ = 152 Hz), 123.6 (d, $^1J_{CH}$ = 159 Hz), 81.11 (s), 81.10 (s), 80.1 (d, $^1J_{CH}$ = 148 Hz), 63.1 (d, $^1J_{CH}$ = 187 Hz), 59.7 (d, $^1J_{CH}$ = 184 Hz), 55.7 (d, $^1J_{CH}$ = 133 Hz), 38.1 (d, $^1J_{CH}$ = 135 Hz), 33.2 (d, $^1J_{CH}$ = 128 Hz), 30.4 (t, $^1J_{CH}$ = 130 Hz), 26.5 (t, $^1J_{CH}$ = 127 Hz), 24.4 (t, $^1J_{CH}$ = 129 Hz), 23.4 (t, $^1J_{CH}$ = 126 Hz), 20.9 (d, $^1J_{CH}$ = 159 Hz), 20.6 (d, $^1J_{CH}$ = 158 Hz), 17.6 (t, $^1J_{CH}$ = 130 Hz), 14.2 (q, $^1J_{CH}$ = 126 Hz), 9.1 ppm (t, $^1J_{CH}$ = 160 Hz); IR (film): $\tilde{\nu}$ = 2958, 2928, 2339, 2157, 2020, 1725, 1443, 1373, 1247, 1207, 1154, 1086, 1038, 938, 839, 798, 700 cm$^{-1}$; MS (EI): *m/z* (%): 314 (29) $[M]^+$, 299 (10), 285 (5), 267 (5), 245 (22), 227 (11), 216 (21), 198 (20), 155 (36), 143 (100), 129 (93), 105 (53), 91 (88), 79 (71), 67 (37), 55 (67), 41 (45); HRMS (ESI): calcd for $C_{20}H_{26}O_3Na$: 337.1774 $[M+Na]^+$; found: 337.1771.

**Hybridalactone ((–)-1)**. $Ni(OAc)_2{\cdot}4H_2O$ (84.6 mg, 0.34 mmol) was dissolved to EtOH (10 mL). $NaBH_4$ (12.7 mg, 0.34 mmol) and ethylenediamine (33 µL, 0.50 mmol) were sequentially added, and $H_2$ was bubbled through the resulting black suspension for 15 min. An aliquot of the suspension (0.12 mL, ca. 4.1 µmol) was added to a solution of cycloalkyne **42** (4.5 mg, 0.014 mmol) in EtOH (3 mL) and the resulting mixture was stirred under $H_2$ (1 atm) for 3 h. The catalyst was filtered off and the filtrate was evaporated. Purification of the residue by flash chromatography (hexane/EtOAc, 10:1) provided the title compound as colorless oil (3.8 mg, 84%). $[\alpha]_D^{20}$ = –52 (c = 0.19, MeOH); IR (film): $\tilde{\nu}$ = 2962, 2352, 1724, 1260, 1214, 1022, 840, 800 cm$^{-1}$; MS (EI): m/z (%) = 316 (9) $[M]^+$, 247 (10), 234 (8), 218 (30), 178 (13), 161 (11), 145 (19), 131 (56), 117 (99), 105 (54), 91 (83), 79 (100), 67 (64), 55 (87), 41 (76); HRMS ($ESI^+$): calcd for $C_{20}H_{28}O_3Na$: 339.1931 $[M+Na]^+$, found: 339.1929.

**Table S2.** Comparison of the recorded $^{1}$H NMR data ($CDCl_3$) of hybridalactone (**1**) with those reported in the literature.[9]




| position | $\delta_H$ (lit., 360 MHz) (mult., *J* in Hz) | $\delta_H$ (exp., 600 MHz) (mult., *J* in Hz) | Δδ |
|---|---|---|---|
| 2 | 2.38 (m) | 2.343 | 0.04 |
| | 2.27 (ddd, 3, 7, 15) | 2.24 (ddd, 15.5, 7.1, 2.9) | 0.03 |
| 3 | 2.00 (m) | 1.92 (m) | 0.08 |
| | 1.51 (m) | 1.47 (m) | 0.04 |
| 4 | 2.37 (ddd, 3, 7.5, 15) | 2.340 | 0.03 |
| | 2.00 (m) | 1.97 | 0.03 |
| 5 | 5.27 (dd, 2, 4, 11, 11) | 5.23 (tddd, 10.8, 3.8, 2.3, 1.0) | 0.04 |
| 6 | 5.48 (tdd, 0.7, 4, 11, 11) | 5.46 (tddd, 10.9, 4.3, 1.9, 0.8) | 0.02 |
| 7 | 3.38 (td, 11, 11, 14) | 3.35 (dt, 14.6, 11.2) | 0.03 |
| 8 | 5.53 (tdd, 0.7, 4, 5, 11, 11) | 5.50 (dddd, 11.4, 10.8, 4.5, 1.0) | 0.03 |
| 9 | 5.07 (td, 2, 11, 11) | 5.05 (tdd, 10.7, 2.2, 0.7) | 0.02 |
| 10 | 2.97 (d, 11) | 2.93 (d, 10.7) | 0.04 |
| 11 | 3.19 (d, 2.5) | 3.15 (d, 2.5) | 0.04 |
| 12 | 3.51 (dd, 1, 2.5) | 3.49 (m) | 0.02 |
| 13 | 2.25 (d, 14) | 2.22 (d, 13.7) | 0.03 |
| | 2.00 (m) | 1.97 (ddd, 13.8, 10.2, 1.4) | 0.03 |
| 14 | 2.00 (m) | 2.02 (t, 10.1) | -0.02 |
| 15 | 4.72 (t, 10) | 4.70 (t, 10.1) | 0.02 |
| 16 | 0.76 (tdd, 5.5, 8, 8, 10) | 0.73 (dtd, 10.1, 8.5, 5.6) | 0.03 |
| 17 | 0.57 (td, 5.5, 8, 8) | 0.54 (tdd, 8.5, 4.6, 0.8) | 0.03 |
| | 0.05 (q, 5.5, 5.5, 5.5) | 0.02 (dt, 4.7, 5.7) | 0.03 |
| 18 | 0.91 (m, 2.5, 4. 5.5, 8, 8) | 0.87 (m) | 0.04 |
| 19 | 1.75 (ddq, 4, 7, 13) | 1.71 (ddq, 13.9, 4.1, 7.0) | 0.04 |
| | 1.17 (ddq, 2.5, 7, 13) | 1.13 (ddq, 13.9, 10.2, 7.2) | 0.04 |
| 20 | 1.03 (t, 7) | 1.01 (t, 7.3) | 0.02 |

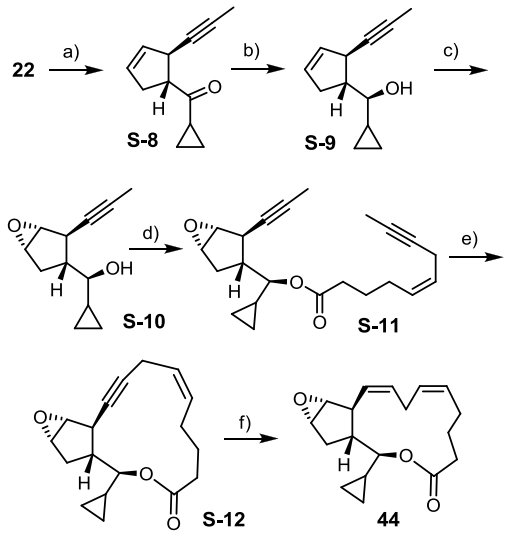
[9] Higgs, M. D.; Mulheirn, L. J. *Tetrahedron* **1981**, *37*, 4259.

**Table S3.** Comparison of the recorded $^{13}C$ NMR data ($CDCl_3$) of hybridalactone (**1**) with those reported in the literature.[9]

| position | $\delta_C$ (lit., 90 MHz) (mult.) | $\delta_C$ (exp., 150 MHz) (mult., $^1J_{CH}$ in Hz) | Δδ |
|---|---|---|---|
| 1 | 176.1 (s) | 173.2 (s) | 2.9 |
| 2 | 32.7 (t) | 32.7 (t, 128.5) | 0.0 |
| 3 | 24.0 (t) | 24.0 (t, 130) | 0.0 |
| 4 | 25.7 (t) | 25.7 (t, 126) | 0.0 |
| 5 | 128.4 (d) | 128.5 (d, 151) | -0.1 |
| 6 | 128.0 (d) | 128.1 (d. 156) | -0.1 |
| 7 | 26.3 (t) | 26.3 (t, 126.3) | 0.0 |
| 8 | 128.9 (d) | 129.0 (d, 154) | -0.1 |
| 9 | 126.9 (d) | 127.0 (d, 153.5) | -0.1 |
| 10 | 41.6 (d) | 41.5 (d, 132) | 0.1 |
| 11 | 60.8 (d) | 60.9 (d, 186) | -0.1 |
| 12 | 58.0 (d) | 58.2 (d, 183.6) | -0.2 |
| 13 | 27.6 (t) | 28.6 (dd, 133, 127) | -1.0 |
| 14 | 49.0 (d) | 48.9 (d, 134) | 0.1 |
| 15 | 78.8 (d) | 78.9 (d, 152) | -0.1 |
| 16 | 21.1 (d) | 21.2 (d, 156) | -0.1 |
| 17 | 8.4 (t) | 8.5 (t, 156) | -0.1 |
| 18 | 20.4 (d) | 20.4 (d, 156) | 0.0 |
| 19 | 23.0 (t) | 23.2 (t, 124) | -0.2 |
| 20 | 14.0 (q) | 14.2 (q, 125) | -0.2 |

## Synthesis of Des-Ethyl-Hybridalactone

**Des-Ethyl-Hybridalactone**. As an initial foray into the preparation of analogues, we targeted compound **44** differing from (–)-**1** only in the absence of the lateral ethyl substituent on the cyclopropyl unit. Whereas this formal deletion is thought to be a minor change in functional regard, it greatly simplifies the synthesis by avoiding the delicate stereoselective cyclopropanation (Scheme S3). Rather, it sufficed to react Weinreb amide **22** with cyclopropylmagnesium bromide and to reduce the resulting ketone **S-8** with L-selectride at low temperature to give the corresponding alcohol **S-9** as a single isomer. The rest of the synthesis follows the steps as outlined in the publication for hybridalactone itself. Although the steps were not optimized, the targeted compound **44** was obtained in respectable overall yield. Once again, the RCAM reaction was best performed with the modified catalyst **43b** endowed with tris-(*p*-methoxyphenyl)silanolate ligands.




**Scheme S3**. Reagents and conditions: a) cyclopropylmagnesium bromide, $Et_2O$/THF, 0°C, 90%; b) LiBH(*sec*-Bu)$_3$, THF, –78°C, 75%; c) *t*BuOOH, VO(acac)$_2$ (8 mol%), $CH_2Cl_2$, 0°C, 65%; d) acid **40**, **39**, DMAP cat., $CH_2Cl_2$, 68%; e) **43b** (4 mol%), MS 5Å, toluene, 72%; e) P2-Ni cat. [Ni(OAc)$_2$·4H$_2$O, $NaBH_4$, ethylenediamine], $H_2$ (1 atm), MeOH, 67%.

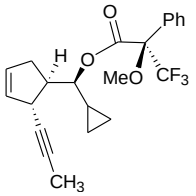
**Compound S-8**. Mg-turnings (530 mg, 22 mmol) were activated with a crystal of iodine before they were suspended in THF (35 mL). Cyclopropyl bromide (2.0 g, 17 mmol) was added at such a rate as to maintain gentle reflux. Once the reaction had ceased, the resulting solution of the Grignard reagent was syphoned off unreacted magnesium via canula.

An aliquot of this solution (~ 0.28 M in THF, 2 mL, 0.56 mmol) was then slowly added to a solution of compound **22** (108 mg, 0.56 mmol) in $Et_2O$ (2 mL) at 0°C. After stirring for 1 h at this temperature, more of the Grignard solution was introduced (0.5 mL, 0.14 mmol) and stirring continued for another 30 min. The reaction was quenched with aq. sat. $NaHCO_3$, the resulting mixture was extracted with $Et_2O$, the combined ether layers were dried and evaporated, and the residue purified by flash chromatography (pentanes/$Et_2O$, 7:1) to give the title compound as a colorless oil (88 mg, 90%). $[\alpha]_D^{20}$ = –156 ($CH_2Cl_2$, c = 1.4); $^1$H NMR (400 MHz, $CDCl_3$): $\delta$ = 5.67 (dq, *J* = 5.5, 2.4 Hz, 1H), 5.57 (dq, *J* = 5.6, 2.2 Hz, 1H), 3.83-3.78 (m, 1H), 3.41 (dt, *J* = 9.6, 6.9 Hz, 1H), 2.73 (ddq, *J* = 16.7, 9.5, 2.4 Hz, 1H), 2.64 (ddq, *J* = 16.7, 7.1, 2.4 Hz, 1H), 2.07 (tt, *J* = 7.8, 4.6 Hz, 1H), 1.80 (d, *J* = 2.3 Hz, 3H), 1.08-1.04 (m, 2H), 0.94-0.89 (m, 2H) ppm; $^{13}$C NMR (100 MHz, $CDCl_3$): $\delta$ = 210.4, 130.6, 129.1, 80.8, 76.8, 58.0, 38.5, 34.7, 19.6, 11.1, 11.0, 3.6 ppm; IR (film): $\tilde{\nu}$ = 3062, 3009, 2919, 2857, 1694, 1444, 1385, 1200, 1112, 1087, 1049, 937, 816, 713 cm$^{-1}$; MS (EI): *m/z* (%): 174 (7) [M]$^+$, 159 (18), 146 (6), 131 (19), 117 (11), 105 (21), 91 (11), 77 (20), 69 (100), 51 (8), 41 (35), 39 (16); HRMS (EI): *m/z*: calcd. for $C_{12}H_{14}O$ 174.1045 [M]$^+$, found: 174.1046.

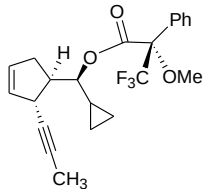
**Compound S-9**. L-Selectride (1 M in THF, 510 µL, 0.51 mmol) was slowly added to a solution of ketone **S-8** (80 mg, 0.46 mmol, 1.0 eq.) in THF (8 mL) at –78°C. After stirring for 1 h, more L-Selectride (230 µL, 0.5 eq.) was introduced and stirring continued for 30 min. The reaction was quenched with sat. aq. $NH_4Cl$ while cold, the mixture allowed to reach ambient temperature, the aqueous layer was extracted with $Et_2O$, the combined ether layers were dried and evaporated, and the residue purified by flash chromatography (pentanes/$Et_2O$, 7:1) to give product **S-9** as a colorless oil (61 mg, 75%).

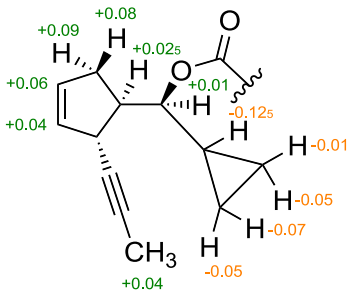
$[\alpha]_D^{20}$ = –124 ($CH_2Cl_2$, c = 0.8); $^1$H NMR (400 MHz, $CDCl_3$): δ = 5.73 (dddd, *J* = 5.5, 2.6, 2.5 Hz, 1H), 5.61 (dddd, *J* = 3.9, 1.8 Hz, 1H), 3.51-3.46 (m, 1H), 2.96 (dd, *J* = 8.5, 6.4 Hz, 1H), 2.59-2.49 (m, 2H), 2.30-2.20 (m, 1H), 1.80 (d, *J* = 2.3 Hz, 3H), 1.01 (dtt, *J* = 8.3, 8.2, 5.0 Hz, 1H), 0.60-0.48 (m, 2H), 0.32-0.30 (m, 2H) ppm; $^{13}$C NMR (100 MHz, $CDCl_3$): δ = 131.6, 130.3, 81.8, 79.3, 77.2, 53.0, 38.5, 35.0, 16.5, 3.7, 3.4, 2.0 ppm; IR (film): $\tilde{\nu}$ = 3418, 3064, 3004, 2918, 2856, 1620, 1429, 1348, 1303, 1264, 1086, 1026, 944, 824, 720 cm$^{-1}$; MS (ESI$^+$): 199 $[M+Na]^+$.

**(*R*)-Mosher-Ester Derived from S-9.** $^1$H NMR (600 MHz, $C_6D_6$): δ = 7.77 (d, *J* = 7.7 Hz, 2H), 7.08 (m, 2H), 7.03 (m, 1H), 5.55 (dq, *J* = 5.7, 2.2 Hz, 1H), 5.35 (dq, *J* = 5.7, 2.4 Hz, 1H), 4.60 (dd, *J* = 9.9, 4.9 Hz, 1H), 3.61 (m, 1H), 3.50 (s, 3H), 2.78 (ddt, *J* = 9.2, 4.9, 7.7 Hz, 1H), 2.21 (dddt, *J* = 16.6, 9.2, 2.0, 2.5 Hz, 1H), 1.97 (ddq, *J* = 16.6, 7.7, 2.4 Hz, 1H), 1.45 (d, *J* = 2.5 Hz, 3H), 1.00 (m, 1H), 0.43 (m, 1H), 0.29 (m, 1H), 0.28 (m, 1H), 0.10 (m, 1H) ppm; $^{13}$C NMR (150 MHz, $C_6D_6$): δ = 166.5, 133.2, 131.7, 129.6, 129.5, 128.5, 127.8, 124.3 ($J_{CF}$ = 288.4 Hz), 85.0 ($J_{CF}$ = 27.3 Hz), 83.2, 81.5, 76.7, 55.4 ($J_{CF}$ = 1.2 Hz), 50.5, 38.4, 35.0, 14.1, 4.3, 4.0, 3.4 ppm.




**(*S*)-Mosher-Ester Derived from S-9.** $^1$H NMR (600 MHz, $C_6D_6$): δ = 7.77 (d, *J* = 7.7 Hz, 2H), 7.10 (m, 2H), 7.05 (m, 1H), 5.59 (dq, *J* = 5.7, 2.2 Hz, 1H), 5.41 (dq, *J* = 5.7, 2.3 Hz, 1H), 4.61 (dd, *J* = 9.7, 5.0 Hz, 1H), 3.66 (m, 1H), 3.46 (s, 3H), 2.81 (ddt, *J* = 9.3, 5.0, 7.4 Hz, 1H), 2.30 (dddt, *J* = 16.8, 9.4, 2.0, 2.5 Hz, 1H), 2.05 (ddq, *J* = 16.8, 7.4, 2.4 Hz, 1H), 1.49 (d, *J* = 2.5 Hz, 3H), 0.88 (m, 1H), 0.42 (m, 1H), 0.23 (m, 2H), 0.05 (m, 1H) ppm; $^{13}$C NMR (150 MHz, $C_6D_6$): δ = 166.5, 133.1, 131.9, 129.6 (2 C), 128.5, 128.0 ($J_{CF}$ = 0.6 Hz), 124.3 ($J_{CF}$ = 288.4 Hz), 85.3 ($J_{CF}$ = 27.4 Hz), 83.3, 81.5, 76.9, 55.4 ($J_{CF}$ = 1.1 Hz), 50.4, 38.6, 35.3, 14.0, 3.92, 3.88, 3.4 ppm.




**Scheme S4.** Analysis [$\Delta\delta_{(S)-(R)}$] of the Mosher Esters derived from **S-9**.

**Compound S-10**. $VO(acac)_2$ (13.2 mg, 50 µmol) and *t*BuOOH (5.5 M in decane, 224 µL, 1.24 mmol) were added to a solution of alcohol **S-9** (55 mg, 0.31 mmol) in $CH_2Cl_2$ (6 mL) at 0°C and the mixture stirred at this temperature for 2 h. The reaction was quenched with aq. sat. $Na_2S_2O_3$, the aqueous phase extracted with $CH_2Cl_2$, the combined extracts were dried over $Na_2SO_4$ and evaporated, and the residue was purified by flash chromatography ($Et_2O$/pentanes, 4:1) to give product **S-10** as a colorless oil (38.4 mg, 65%). $[\alpha]_D^{20}$ = –80 (c = 0.26, $CH_2Cl_2$); $^1$H NMR (600 MHz, $C_6D_6$): δ = 3.48 (dq, Σ *J* = 4.6, 1H), 3.36 (d, *J* = 2.7 Hz, 1H), 3.04 (m, 1H), 2.84 (s, O*H*), 2.83 (m, 1H), 2.45 (m, 1H), 1.81 (ddd, *J* = 15.0, 10.8, 1.8 Hz, 1H), 1.79 (ddd, *J* = 15.0, 1.3, -0.5 Hz, 1H), 1.48 (d, *J* = 2.6 Hz, 3H), 0.65 (m, 1H), 0.30 (m, 2H),

0.27 (m, 1H), 0.19 (m, 1H) ppm; $^{13}$C NMR (150 MHz, $C_6D_6$): δ = 79.0 (s), 78.3 (s), 77.3 (d, $^1J_{CH}$ = 144 Hz), 61.4 (d, $^1J_{CH}$ = 189 Hz), 58.5 (d, $^1J_{CH}$ = 185 Hz), 51.4 (d, $^1J_{CH}$ = 134 Hz), 32.9 (d, $^1J_{CH}$ = 138 Hz), 31.1 (t, $^1J_{CH}$ = 130 Hz), 17.2 (d, $^1J_{CH}$ = 158 Hz), 3.4 (q, $^1J_{CH}$ = 131 Hz), 2.7 (t, $^1J_{CH}$ = 162 Hz), 2.4 (t, $^1J_{CH}$ = 162 Hz) ppm; IR (film): $\tilde{\nu}$ = 3422, 3002, 2921, 2855, 1439, 1405, 1362, 1262, 1233, 1196, 1024, 984, 944, 914, 842, 693 cm$^{-1}$; MS (EI): *m/z* (%): 192 (< 1) $[M]^+$, 175 (1), 159 (2), 145 (2), 131 (4), 121 (25), 104 (73), 91 (48), 79 (80), 71 (93), 53 (24), 43 (100); HRMS (CI, *i*-butane): *m/z*: calcd. for $C_{12}H_{17}O_2$ 193.1229 $[M+H]^+$, found: 193.1229.

**Compound S-11**. A solution of acid **40** and carbodiimide **39** in $CH_2Cl_2$ (1 mL) was stirred for 30 min before a solution of compound **S-10** (10 mg, 52 µmol) in $CH_2Cl_2$ (0.5 mL) and catalytic DMAP were introduced. Stirring was continued for 3 d before the precipitate was filtered off through a pad of silica and the filtrate was evaporated. The residue was purified by flash chromatography (hexanes/EtOAc, 15:1) to give the title compound as a colorless syrup (12 mg, 68%). $[\alpha]_D^{20}$ = –83 (c = 0.3, $CH_2Cl_2$); $^1$H NMR (400 MHz, $CDCl_3$): δ = 5.54 (dddt, *J* = 7.1, 10.4, 7.1, 1.6 Hz, 1H), 5.23 (dddt, *J* = 10.8, 7.2, 7.2, 1.7 Hz, 1H), 4.60 (t, *J* = 9.3 Hz, 1H), 3.40 (d, *J* = 2.5 Hz, 1H), 3.11-3.09 (m, 2H), 2.89-2.84 (m, 2H), 2.55 (tt, *J* = 9.7, 1.8 Hz, 1H), 2.16 (t, *J* = 7.5 Hz, 2H), 2.10 (dd, *J* = 14.9, 2.0 Hz, 1H), 1.89 (dd, *J* = 14.7, 7.3 Hz, 2H), 1.77 (ddd, *J* = 14.8, 9.8, 1.4 Hz, 1H), 1.62 (dd, *J* = 14.6, 7.3 Hz, 2H), 1.54 (t, *J* = 2.7 Hz, 3H), 1.48 (d, *J* = 2.5 Hz, 3H), 0.69-0.60 (m, 1H), 0.56-0.50 (m, 1H), 0.36-0.21 (m, 3H) ppm; $^{13}$C NMR (100 MHz, $CDCl_3$): δ = 172.9, 130.2, 126.5, 81.6, 78.8, 78.6, 77.9, 75.6, 60.8, 57.6, 50.5, 34.6, 34.1, 29.4, 26.7, 25.1, 17.6, 15.4, 5.3, 3.4, 2.5 ppm; IR (film): $\tilde{\nu}$ = 3018, 2920, 2858, 1725, 1439, 1405, 1370, 1288, 1259, 1240, 1193, 1154, 1085, 1051, 1027, 991, 968, 929, 842, 800, 693 cm$^{-1}$; MS (EI): *m/z* (%): 340 (<1) $[M]^+$, 294 (1), 175 (9), 149 (8), 105 (100), 91 (19), 79 (18), 55 (12), 41 (10); HRMS (ESI): *m/z*: calcd. for $C_{22}H_{28}O_3Na$ 363.1931 $[M+Na]^+$, found: 363.1933.

**Compound S-12**. Molecular sieves (powder, 5 Å) were added to a solution of diyne **S-11** (5 mg, 15 µmol) in toluene (5 mL) and the suspension stirred for 20 min before a complex **43b** (1 mg, 4 mol%) was introduced. The mixture was stirred overnight before it was filtered through a plug of silica and the filtrate was evaporated. Purification of the residue by flash chromatography (hexanes/EtOAc, 15:1) gave cycloalkyne **S-12** as a colorless oil (3 mg, 72%). $[\alpha]_D^{20}$ = –16 (c = 0.18, $CH_2Cl_2$); $^1$H NMR (600 MHz, $C_6D_6$): δ = 5.29 (dddt, *J* = 10.8, 6.5, 5.5, 1.5 Hz, 1H), 5.20 (dddt, *J* = 10.8, 8.3, 6.9, 1.3 Hz, 1H), 3.95 (dd, Σ *J* = 19.9 Hz, 1H), 3.39 (m, 1H), 3.16 (ddd, *J* = 7.5, 3.0, 1.9 Hz, 1H), 3.03 (t, *J* = 2.6 Hz, 1H), 2.98 (tdd, *J* = 10.4, Σ 15.9 Hz, 1H), 2.70 (ddd, *J* = 18.6, 6.5, 3.1 Hz, 1H), 2.64 (ddd, *J* = 18.6, 5.4, 1.6 Hz, 1H), 2.63 (m, 1H), 2.30 (m, 1H), 2.29 (ddd, *J* = 16.3, 9.4, 2.4 Hz, 1H), 2.23 (ddd, *J* = 16.3, 8.8, 2.4 Hz, 1H), 1.74 (m, 1H), 1.60 (ddd, *J* = 14.6, 10.3, 2.7 Hz, 1H), 1.55 (m, 1H), 1.54 (dd, *J* = 14.7, 8.4 Hz, 1H), 0.78 (m, 1H), 0.19 (m, 2H), 0.18 (m, 1H), - 0.07 (m, 1H) ppm; $^{13}$C NMR (150 MHz, $C_6D_6$): δ = 172.4 (s), 133.9 (d, $^1J_{CH}$ = 153 Hz), 123.8 (d, $^1J_{CH}$ = 159 Hz), 83.9 (d, $^1J_{CH}$ = 148 Hz), 80.96 (s), 80.93 (s), 63.5 (d, $^1J_{CH}$ = 188 Hz), 59.6 (d, 183 Hz), 56.2 (d, $^1J_{CH}$ = 133 Hz), 38.1 (d, $^1J_{CH}$ = 135 Hz), 32.6 (t, $^1J_{CH}$ = 128 Hz), 30.9 (t, $^1J_{CH}$ = 131 Hz), 26.3 (t, $^1J_{CH}$ = 127 Hz), 24.1 (t, $^1J_{CH}$ = 129 Hz), 17.6 (t, $^1J_{CH}$ = 130 Hz), 14.9 (d, $^1J_{CH}$ = 162 Hz), 5.3 (dd, $^1J_{CH}$ = 161, 163 Hz), 2.2 (dd, $^1J_{CH}$ = 161, 162 Hz) ppm; IR (film): $\tilde{\nu}$ = 3083, 3012, 2926, 2855, 1724, 1436, 1373, 1244, 1206, 1155, 1100, 1024, 988, 943, 837, 718, 698 cm$^{-1}$; MS (EI): *m/z* (%): 286 (< 1) $[M]^+$, 257 (2), 216 (13), 198 (14), 157 (32), 143 (91), 129 (79), 115 (47), 103 (26), 91 (100), 77 (59), 65 (41), 55 (61), 41 (77); HRMS (ESI): *m/z*: calcd. for $C_{18}H_{22}O_3Na$ 309.1461 $[M+Na]^+$, found: 309.1460.

**Des-Ethyl-Hydridalactone (44)**. $NaBH_4 \cdot 4H_2O$ (9.6 mg, 0.25 mmol) und ethylendiamine (17 µL, 0.25 mmol) were added to a solution of $Ni(OAc)_2 \cdot 4H_2O$ (84 mg, 0.34 mmol) in MeOH (10 mL). Hydrogen gas was then bubbled through the stirred suspension for 15 min.

An aliquot of the resulting P2-Ni suspension (60 µL) was added to a solution of cycloalkyne **S-12** (3.0 mg, 10.5 µmol) in MeOH (2 mL) and the resulting mixture was stirred under an atmosphere of $H_2$ for 3 h. For work-up, the mixture was diluted with $Et_2O$ (5 mL) and filtered through a pad of silica, the filtrate was evaporated, and the residue purified by HPLC [150 mm YMC-ODS-A 5 µm, Ø 20 mm, eluent: MeCN/$H_2O$ (80:20), 10 mL/min, 308 K, $R_t$ = 8.0] to give product **44** as a colorless oil (2 mg, 67%). $[\alpha]_D^{20}$ = –23 (c = 0.1, $CH_2Cl_2$); $^1$H NMR (600 MHz, $C_6D_6$): $\delta$ = 5.38 (m, 1H), 5.36 (dddd, *J* = 11.2, 10.8, 4.5, 0.9 Hz, 1H), 5.10 (tddd, *J* = 10.9, 4.0, 2.4, 0.9 Hz, 1H), 4.88 (tdd, *J* = 10.8, 2.3, 0.7 Hz, 1H), 4.76 (dd, *J* = 10.5, 9.2 Hz, 1H), 3.26 (dt, *J* = 14.8, 11.2 Hz, 1H), 3.11 (d, *J* = 10.7 Hz, 1H), 3.11 (dd, Σ *J* = 3.7 Hz, 1H), 3.03 (d, *J* = 2.5 Hz, 1H), 2.44 (m, 1H), 2.30 (ddd, *J* = 15.7, 11.3, 2.6 Hz, 1H), 2.15 (dd, *J* = 15.0, 1.7 Hz, 1H), 2.09(0) (m, 1H), 2.08(6) (m, 1H), 1.94 (m, 1H), 1.88 (m, 1H), 1.82 (m, 1H), 1.49 (ddd, *J* = 15.0, 10.0, 1.4 Hz, 1H), 1.23 (m, 1H), 0.55 (m, 1H), 0.54 (m, 1H), 0.41 (m, 1H), 0.35 (m, 1H), 0.23 (m, 1H) ppm; $^1$H NMR (600 MHz, $CDCl_3$): $\delta$ = 5.50 (td, *J* = 11.0, 4.5 Hz, 1H), 5.46 (td, *J* = 10.9, 4.0 Hz, 1H), 5.24 (tdd, *J* = 10.9, Σ 5.6 Hz, 1H), 5.05 (td, *J* = 10.6, 1.9 Hz, 1H), 4.36 (dd, Σ *J* = 19.6 Hz, 1H), 3.50 (m, 1H), 3.34 (dt, *J* = 14.7, 11.1 Hz, 1H), 3.17 (d, *J* =2.5 Hz, 1H), 2.93 (d, *J* = 10.7 Hz, 1H), 2.25 (ddd, *J* = 15.7, 7.1, 2.8 Hz, 1H), 2.38-2.30 (m, 2H), 2.35 (d, *J* = 14.6 Hz, 1H), 2.34 (ddd, *J* = 15.7, 11.3, 2.6 Hz, 1H), 2.25 (ddd, *J* = 15.7, 7.1, 2.8 Hz, 1H), 2.04 (t, *J* = 10.2 Hz, 1H), 1.99 (ddd, *J* = 14.6, 10.1, 1.2 Hz, 1H), 1.99-1.90 (m, 2H), 1.47 (m, 1H), 0.73 (m, 1H), 0.63 (m, 1H), 0.45 (m, 1H), 0.34 (m, 2H) ppm; $^{13}$C NMR (150 MHz, $C_6D_6$): $\delta$ = 172.5 (s), 128.9 (d, $^1J_{CH}$ = 153 Hz), 128.6 (d, $^1J_{CH}$ = 153 Hz), 128.4 (d, $^1J_{CH}$ = 153 Hz), 127.6 (d, $^1J_{CH}$ = 153 Hz), 82.6 (d, $^1J_{CH}$ = 151 Hz), 61.0 (d, $^1J_{CH}$ = 185 Hz), 57.9 (d, $^1J_{CH}$ = 183 Hz), 49.3 (d, $^1J_{CH}$ = 132 Hz), 42.1 (d, $^1J_{CH}$ = 132 Hz), 32.7 (t, $^1J_{CH}$ = 128 Hz), 29.0 (dd, $^1J_{CH}$ = 132, 126 Hz), 26.5 (t, $^1J_{CH}$ = 126 Hz), 26.0 (t, $^1J_{CH}$ = 127 Hz), 24.1 (t, $^1J_{CH}$ = 129 Hz), 15.4 (d, $^1J_{CH}$ = 158 Hz), 5.6 (t, $^1J_{CH}$ = 161 Hz), 2.2 (t, $^1J_{CH}$ = 161 Hz) ppm; $^{13}$C NMR (150 MHz, $CDCl_3$): $\delta$ = 173.1 (C), 129.1 (CH), 128.5 (CH), 127.2 (CH), 127.1 (CH), 82.4 (CH), 61.3 (CH), 58.4 (CH), 48.9 (CH), 41.6 (CH), 32.6 ($CH_2$), 28.9 ($CH_2$), 26.4 ($CH_2$), 25.7 ($CH_2$), 23.9 ($CH_2$), 14.9 (CH), 5.3 ($CH_2$), 1.7 ($CH_2$) ppm; IR (film): $\tilde{\nu}$ = 3017, 2956, 2931, 2911, 2855, 1716, 1443, 1421, 1400, 1375, 1213, 1163, 1026, 933, 842, 703 cm$^{-1}$; HRMS (EI): *m/z*: calcd. for $C_{18}H_{24}O_3Na$ 311.1618 $[M+Na]^+$, found: 311.1618.

## Total Synthesis of the Ecklonialactones

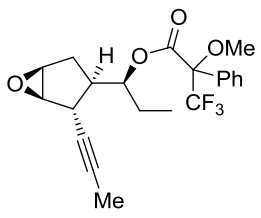
**Ketone 23**. EtMgBr (3 M in THF, 95 µL, 0.28 mmol) was added to a solution of Weinreb amide **22** (50 mg, 0.26 mmol) in THF (2 mL) at 0°C and the resulting mixture was stirred at that temperature for 30 min before the reaction was quenched with aq. sat. $NH_4Cl$ (2 mL). The aqueous layer was extracted with $Et_2O$ (3 x 2 mL), the combined organic phases were dried over $Na_2SO_4$ and evaporated, and the residue was purified by flash chromatography (pentanes/$Et_2O$, 7:1) to give ketone **23** as a colorless oil (39 mg, 93%). $[\alpha]_D^{20}$ = –394 (c = 0.25, $CH_2Cl_2$); $^1$H NMR (300 MHz, $CDCl_3$): $\delta$ = 5.53-5.49 (m, 1H), 5.43-5.39 (m, 1H), 3.59-3.52 (m, 1H), 3.13 (dt, *J* = 9.2, 7.6 Hz, 1H), 2.57-2.33 (m, 4H), 1.65 (d, *J* = 2.6 Hz, 3H), 0.95 ppm (t, *J* = 7.3 Hz, 3H); $^{13}$C NMR (75 MHz, $CDCl_3$): $\delta$ = 211.1, 130.6, 128.9, 80.6, 76.9, 57.3, 38.8, 35.4, 34.9, 7.8, 3.6 ppm; IR (film): $\tilde{\nu}$ = 3064 (w), 2977 (w), 2920 (w), 2857 (w), 1711 (s), 1446 (w), 1411 (w), 1362 (w), 1205 (w), 1118 (m), 1029 (w), 940 (w), 902 (w), 715 (m) cm$^{-1}$; MS (EI): *m/z* (%): 161 (3) $[M-H]^+$, 147 (7), 133 (100), 119 (5), 105 (72), 91 (19), 79 (45), 65 (8), 57 (61), 51

(13), 39 (15), 29 (47); HRMS (CI, *iso*-butane): *m/z*: calcd. for $C_{11}H_{15}O$: 163.1123 $[M+H]^+$; found: 163.1122.

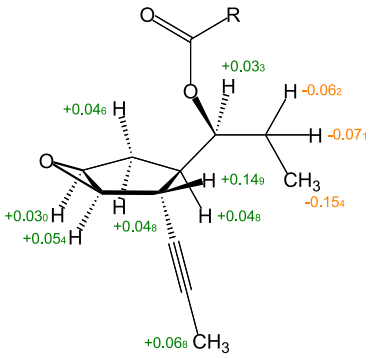
**Alcohol 24**. L-Selectride (1 M in THF, 660 µL, 0.66 mmol) was added dropwise to a solution of ketone **23** (97 mg, 0.6 mmol) in THF (10 mL) at –78°C and the resulting mixture stirred at that temperature for 2 h before the reaction was quenched by careful addition of aq. sat. $NH_4Cl$ (1 mL) to the cold mixture. After reaching ambient temperature, the mixture was diluted with aq. sat. $NH_4Cl$ (6 mL), the aqueous layer was extracted with $CH_2Cl_2$ (3 x 5 mL), the combined organic phases were dried ($Na_2SO_4$) and evaporated, and the residue was purified by flash chromatography (pentanes/$Et_2O$, 7:1) to give alcohol **24** as a colorless oil (68 mg, 69%). $[\alpha]_D^{20}$ = –232 (c = 0.2, $CH_2Cl_2$); $^1$H NMR (400 MHz, $CDCl_3$): $\delta$ = 5.71-5.68 (m, 1H), 5.59-5.56 (m, 1H), 3.58-3.53 (m, 1H), 3.43-3.38 (m, 1H), 2.51-2.44 (m, 1H), 2.37 (dq, *J* = 8.3, 7.6 Hz, 1H), 2.12-2.04 (m, 1H), 1.79 (d, *J* = 2.3 Hz, 3H), 1.67-1.57 (m, 1H), 1.52-1.40 (m, 1H), 0.99 ppm (t, *J* = 7.5 Hz, 3H); $^{13}$C NMR (100 MHz, $CDCl_3$): $\delta$ = 131.7, 130.2, 81.8, 76.9, 76.8, 52.3, 38.5, 35.4, 28.6, 9.9, 3.6 ppm; IR (film): $\tilde{\nu}$ = 3419 (m, br), 3057 (w), 2961 (m), 2920 (s), 2855 (m), 1458 (m), 1378 (m), 1304 (m), 1123 (m), 1060 (m), 1029 (m), 970 (s), 943 (s), 892 (m), 718 (s), 679 (m) $cm^{-1}$; MS (EI): *m/z* (%): 164 (< 1) $[M]^+$, 146 (28), 135 (27), 131 (14), 117 (100), 104 (19), 91 (64), 79 (24), 65 (10), 59 (9), 51 (9), 39 (13), 31 (10); HRMS (CI, *iso*-butane): *m/z*: calcd. for $C_{11}H_{17}O$: 165.1279 $[M+H]^+$; found: 165.1277.

**Compound 45**. $VO(acac)_2$ (7.8 mg, 0.03 mmol) was added to a solution of alcohol **24** (85 mg, 0.52 mmol) in $CH_2Cl_2$ (10 mL) prior to the slow addition of *t*BuOOH (5.5 M in decane, 133 µL, 0.73 mmol). After stirring for 2 h, additional $VO(acac)_2$ (7.8 mg, 0.03 mmol) was introduced and stirring continued for 1 h. For work up, the mixture was poured into aq. sat. $Na_2S_2O_3$ (10 mL), the aqueous layer was extracted with $CH_2Cl_2$ (3 x 5 mL), the combined organic phases were dried ($Na_2SO_4$) and evaporated, and the residue was purified by flash chromatography (pentanes/$Et_2O$, 4:1) to give epoxide **45** as a colorless oil (90 mg, 94%). $[\alpha]_D^{20}$ = –97 (c = 0.14, $CH_2Cl_2$); $^1$H NMR (600 MHz, $CDCl_3$): $\delta$ = 3.57 (dd, Σ *J* = 4.2 Hz, 1H), 3.53 (d, *J* = 2.7 Hz, 1H), 3.38 (d, *J* = 2.7 Hz, O*H*), 3.32 (ddt, *J* = 7.6, 5.5, 3.0 Hz, 1H), 3.16 (dq, Σ *J* = 4.7 Hz, 1H), 2.39 (ddt, *J* = 10.7, 3.2, 1.7 Hz, 1H), 2.31 (ddd, *J* = 14.9, 10.8, 1.6 Hz, 1H), 1.96 (dd, *J* = 14.9, 1.7 Hz, 1H), 1.78 (d, *J* = 2.6 Hz, 3H), 1.46 (dqi, *J* = 13.7, 7.5 Hz, 1H), 1.41 (ddq, *J* = 13.8, 7.4, 5.6 Hz, 1H), 0.91 ppm (t, *J* = 7.4 Hz, 3H); $^{13}$C NMR (150 MHz, $CDCl_3$): $\delta$ = 78.6 (s), 77.9 (s), 75.2 (d, *J* = 143 Hz), 61.9 (d, $J_{CH}$ = 190 Hz), 59.2 (d, $J_{CH}$ = 186 Hz), 49.1 (d, $J_{CH}$ = 134 Hz), 32.4 (t, $J_{CH}$ = 131 Hz), 31.3 (d, $J_{CH}$ = 138 Hz), 29.4 (t, $J_{CH}$ = 125 Hz), 10.3 (q, $J_{CH}$ = 125 Hz), 3.6 ppm (q, $J_{CH}$ = 131 Hz) ; IR (film): $\tilde{\nu}$ = 3434 (br), 2961 (m), 2922 (m), 2876 (m), 1439 (m), 1404 (m), 1263 (m), 1104 (m), 1054 (m), 975 (s), 940 (m), 840 (s), 693 (m) $cm^{-1}$; MS (EI): *m/z* (%): 180 (< 1) $[M]^+$, 161 (< 1), 151 (22), 133 (7), 121 (18), 105 (100), 91 (29), 79 (64), 66 (15), 57 (15), 39 (22), 29 (18); HRMS (EI): *m/z*: calcd. for $C_{11}H_{16}O_2$: 180.1150 $[M]^+$; found: 180.1152.

**(*R*)-Mosher-Ester derived from 45**: $^1$H NMR (600 MHz, $CDCl_3$): $\delta$ = 7.56 (m, 2H), 7.40 (m, 3H), 4.96 (ddd, *J* = 9.9, 6.2, 3.4 Hz, 1H), 3.59 (q, $J_{HF}$ = 1.0 Hz, 3H), 3.48 (m, 1H), 3.43 (d, *J* = 2.5 Hz, 1H), 2.66 (dq, *J* = 4.6 Hz, 1H), 2.36 (tt, *J* = 9.9, 1.9 Hz, 1H), 2.03 (ddd, *J* = 15.0, 9.9, 1.4 Hz, 1H), 1.83 (dd, *J* = 15.0, 2.0 Hz, 1H), 1.77 (ddq, *J* = 15.1, 3.4, 7.5 Hz, 1H), 1.57 (ddq, *J* = 15.0, 6.3, 7.5 Hz, 1H), 1.70 (d, *J* = 2.5 Hz, 3H), 0.84 ppm (t, *J* = 7.5 Hz, 3H); $^{13}$C NMR (150 MHz, $CDCl_3$): $\delta$ = 166.1, 132.1, 129.5, 128.4, 127.4, 123.4 (q, $J_{CF}$ = 288.5 Hz), 84.5 (q, $J_{CF}$ = 27.5 Hz), 81.3, 78.5, 77.2, 60.8, 57.8, 55.4 (q, $J_{CF}$ = 1.2 Hz), 46.7, 33.8, 28.7, 24.5, 8.4, 3.5 ppm.



**(*S*)-Mosher-Ester derived from 45:** $^{1}$H NMR (600 MHz, $CDCl_3$): $\delta$ = 7.59 (m, 2H), 7.39 (m, 3H), 4.99 (ddd, *J* = 10.2, 6.4, 3.4, 1H), 3.59 (q, $J_{HF}$ = 1.1 Hz, 3H), 3.51 (m, 1H), 3.49 (d, *J* = 2.5 Hz, 1H), 2.81 (dq, Σ *J* = 4.4 Hz, 1H), 2.41 (tt, *J* = 9.9, 1.8 Hz, 1H), 2.08 (ddd, *J* = 15.0, 9.9, 1.3, 1H), 1.88 (dd, *J* = 15.0, 1.9 Hz, 1H), 1.77 (d, *J* = 2.5 Hz, 3H), 1.70 (ddq, *J* = 15.0, 3.4, 7.5 Hz, 1H), 1.50 (ddq, *J* = 15.0, 6.4, 7.4 Hz, 1H), 0.68 ppm (t, *J* = 7.4 Hz, 3H); $^{13}$C NMR (150 MHz, $CDCl_3$): $\delta$ = 166.1, 132.3, 129.5, 128.4, 127.3, 123.9 (q, $J_{CF}$ = 288.7 Hz), 84.4 (q, $J_{CF}$ = 27.5 Hz), 81.5, 79.9, 77.3, 60.8, 57.9, 55.6 (q, $J_{CF}$ = 1.3 Hz), 46.8, 34.3, 28.9, 24.4, 8.0, 3.6 ppm.




**Scheme S5.** Analysis [$\Delta\delta_{(S)-(R)}$] of the Mosher Esters derived from **45**.

**Compound 46**. Carbodiimide *p*-toluenesulfonate **39** (85 mg, 0.2 mmol) was added to a solution of 9-undecynoic acid (30 mg, 0.17 mmol) in $CH_2Cl_2$ (1.5 mL) and the resulting mixture was stirred for 1.5 h before a solution of alcohol **45** (20 mg, 0.11 mmol) in $CH_2Cl_2$ (1.5 mL) was introduced. DMAP (0.67 mg, 5.6 µmol) was then added and the resulting mixture stirred at ambient temperature overnight. For work up, all volatile materials were evaporated and the residue purified by flash chromatography (hexanes/EtOAc, 15:1) to give ester **46** as a colorless oil (23 mg, 61%). $[\alpha]_D^{20}$ = –101 (c = 0.78, $CH_2Cl_2$); $^{1}$H NMR (400 MHz, $CDCl_3$): $\delta$ = 4.77 (ddd, *J* = 9.2, 7.5, 3.6 Hz, 1H), 3.49 (t, *J* = 1.9 Hz, 1H), 3.48 (t, *J* = 2.9 Hz, 1H), 2.83 (dt, *J* = 5.0, 2.5 Hz, 1H), 2.39 (tt, *J* = 2.9, 2.5 Hz, 1H), 2.32 (td, *J* = 7.5, 1.7 Hz, 2H), 2.14-2.06 (m, 3H), 1.87 (dd, *J* = 14.8, 2.7 Hz, 1H), 1.79 (d, *J* = 2.6 Hz, 3H), 1.78 (t, *J* = 2.6 Hz, 3H), 1.72-1.61 (m, 3H), 1.50-1.20 (m, 9H), 0.83 ppm (t, *J* = 7.5 Hz, 3H); $^{13}$C NMR (100 MHz, $CDCl_3$): $\delta$ = 173.5, 79.3, 78.4, 78.2, 77.5, 75.4, 61.3, 58.2, 48.6, 34.6, 33.7, 29.3, 29.1, 29.0, 28.8, 28.7, 25.3, 25.1, 18.7, 9.0, 3.6, 3.5 ppm; IR (film): $\tilde{\nu}$ = 3017 (w), 2967 (m), 2932 (s), 2857 (m), 1731 (s), 1463 (m), 1441 (m), 1380 (m), 1244 (m), 1179 (m), 1091 (m), 1029 (w), 908 (s), 845 (s), 730 (s) cm$^{-1}$; MS (EI): *m/z* (%): 344 (1) [M]$^+$, 329 (1), 315 (4), 222 (3), 197 (2), 179 (2), 162 (52), 147 (16), 119 (14), 105 (100), 91 (16), 81 (26), 67 (18), 55 (25), 41 (19); HRMS (ESI): *m/z*: calcd. for $C_{22}H_{32}O_3Na$: 367.2244 [M+Na]$^+$; found: 367.2247.

**Compound 47**. MS 5Å (powder, ca. 10 mg) was added to a solution of compound **46** (5.0 mg, 14.5 µmol) in toluene (1 mL) and the resulting mixture stirred for 20 min. In a second flask, complex **43a** (17.6 mg, 16.2 µmol) was dissolved in toluene (1 mL) and 45 µL (0.72 µmol, 4 mol%) of this stock solution were added to the suspension containing the diyne **46**. The mixture was stirred for 3 h at ambient temperature before it was filtered through a short plug of silica and evaporated. The residue was purified by flash chromatography (hexanes/EtOAc, 15:1) to give product **47** as a colorless oil (3.4 mg, 80%). $[\alpha]_D^{20}$ = –52 (c = 0.05, $CH_2Cl_2$); $^{1}$H NMR (600 MHz, $CDCl_3$): $\delta$ = 4.66 (ddd, *J* = 10.9, 7.8, 3.0 Hz, 1H), 3.51 (dd, Σ *J* = 4.7 Hz, 1H), 3.48 (d, *J* = 2.5 Hz, 1H), 2.89 (tt, *J* = 4.6, 2.1 Hz, 1H), 2.57 (tt, *J* = 10.8,

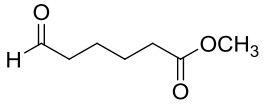
4.8 Hz, 1H), 2.29 (t, *J* = 7.2 Hz, 2H), 2.17 (m, 2H), 2.10 (ddd, *J* = 14.9, 10.9, 2.2 Hz, 1H), 1.76 (m, 1H), 1.71 (dd, *J* = 14.8, 5.1 Hz, 1H), 1.70 (m, 1H), 1.66 (ddq, *J* = 14.5, 7.4, 3.1 Hz, 1H), 1.51-1.42 (m, 8H), 1.41 (dqi., *J* = 14.5, 7.4 Hz, 1H), 0.82 ppm (t, *J* = 7.4 Hz, 3H); $^{13}$C NMR (150 MHz, $CDCl_3$): $\delta$ = 173.8 (s), 83.3 (s), 80.5 (s), 79.6 (d), 62.6 (d), 60.0 (d), 52.1 (d), 36.5 (d), 33.9 (t), 30.0 (t), 26.7 (t), 26.1 (t), 25.6 (t), 25.50 (t), 25.49 (t), 23.9 (t), 18.2 (t), 8.9 (q) ppm; IR (film): $\tilde{\nu}$ = 3017 (w), 2962 (m), 2926 (m), 2855 (m), 1726 (s), 1456 (m), 1378 (m), 1266 (m), 1226 (m), 1089 (m), 1031 (w), 842 (m) cm$^{-1}$; HRMS (ESI): *m/z*: calcd. for $C_{18}H_{26}O_3Na$: 313.1774 $[M+Na]^+$; found: 313.1751.

**Ecklonialactone B (3).** A mixture containing compound **47** (2.0 mg, 6.9 µmol) and commercial Lindlar catalyst (2.8 mg) in $CH_2Cl_2$ (4 mL) was stirred under an atmosphere of hydrogen (1 atm) for 2.5 h. The catalyst was filtered off and the filtrate evaporated to give product **3** as a colorless oil (1.8 mg, 90%). $[\alpha]_D^{20}$ = –19 (c = 0.07, $CH_2Cl_2$); $^1$H NMR (600 MHz, $CDCl_3$): $\delta$ = 5.47 (4d, *J* = 10.6, 8.4, 7.0, 1.2 Hz, 1H), 5.10 (ddt, *J* = 10.7, 9.6, 1.2 Hz, 1H), 4.95 (3d, *J* = 10.3, 7.6, 3.0 Hz, 1H), 3.49 (d, *J* = 2.6 Hz, 1H), 3.23 (d, *J* = 2.6 Hz, 1H), 3.00 (d, *J* = 9.7 Hz, 1H), 2.40 (3d, *J* = 15.2, 6.9, 3.8 Hz, 1H), 2.35 (3d, *J* = 15.2, 10.3, 3.2 Hz, 1H), 2.05 (m, 2H), 1.92 (m, 1H), 1.90 (m, 1H), 1.87 (m, 1H), 1.85 (m, 1H), 1.70 (ddq, *J* = 14.6, 3.1, 7.4 Hz, 1H), 1.55 (m, 1H), 1.42 (m, 2H), 1.38 (m, 2H), 1.37 (m, 1H), 1.35 (m, 3H), 1.29 (m, 1H), 0.79 ppm (t, *J* = 7.4 Hz, 3H); $^{13}$C NMR (150 MHz, $CDCl_3$): $\delta$ = 174.1 (s), 131.9 (d, $J_{CH}$ = 153 Hz), 128.3 (d, $J_{CH}$ = 153), 78.7 (d, $J_{CH}$ = 152 Hz), 61.1 (d, $J_{CH}$ = 186 Hz), 57.2 (d, $J_{CH}$ = 184 Hz), 46.4 (d, $J_{CH}$ = 134 Hz), 40.0 (d, $J_{CH}$ = 133 Hz), 33.5 (t, $J_{CH}$ = 128 Hz), 28.8 (t, $J_{CH}$ = 130 Hz), 26.79 (t), 26.75 (t), 26.3 (t), 25.4 (t), 25.3 (t), 25.2 (t), 24.2 (t, $J_{CH}$ = 128 Hz), 8.8 (q, $J_{CH}$ = 126 Hz) ppm; IR (film): $\tilde{\nu}$ = 2961 (m), 2931 (m), 2855 (w), 1732 (m), 1456 (w), 1260 (s), 1216 (w), 1175 (w), 1087 (s), 1018 (s), 862 (m), 799 (s) cm$^{-1}$; HRMS (ESI): *m/z*: calcd. for $C_{18}H_{28}O_3Na$: 315.1931 $[M+Na]^+$; found: 315.1929.

**Table S4.** Comparison of the recorded $^{13}C$ NMR data of ecklonialactone B (**3**) with those reported in the literature.[10]

| Position | $\delta_C$ (lit.) | multiplicity | $\delta_C$ (exp.) | multiplicity, $^1J_{CH}$ | Δδ |
|---|---|---|---|---|---|
| 1 | 173.8 | s | 174.1 | s | -0.3 |
| 2 | 33.5 | t | 33.5 | t, 128 Hz | 0 |
| 3 | 24.1 | t | 24.2 | t, 128 Hz | -0.1 |
| 4 | 26.8 | t | 26.8 | t | 0 |
| 5 | 25.3 | t | 25.2 | t | 0.1 |
| 6 | 26.2 | t | 26.3 | t | -0.1 |
| 7 | 26.8 | t | 26.8 | t | 0 |
| 8 | 25.3 | t | 25.3 | t | 0 |
| 9 | 131.8 | d | 131.9 | d, 153 Hz | -0.1 |
| 10 | 128.2 | d | 128.3 | d, 153 Hz | -0.1 |
| 11 | 40.0 | d | 40.0 | d, 133 Hz | 0 |
| 12 | 61.0 | d | 61.1 | d, 186 Hz | -0.1 |
| 13 | 57.0 | d | 57.2 | d, 184 Hz | -0.2 |
| 14 | 28.8 | t | 28.8 | t, 130 Hz | 0 |
| 15 | 46.3 | d | 46.4 | d, 134 Hz | -0.1 |
| 16 | 78.6 | d | 78.7 | d, 152 Hz | -0.1 |
| 17 | 25.3 | t | 25.4 | t | -0.1 |
| 18 | 8.7 | q | 8.8 | q, 126 Hz | -0.1 |

**Methyl 6-Oxohexanoate.**[11] Ozone (ca. 40-50 mg/cm$^3$) was bubbled through a mixture of cyclohexene (6.1 g, 74 mmol) and $NaHCO_3$ (2.0 g, 23.8 mmol) in $CH_2Cl_2$ (250 mL) and MeOH (50 mL) at –78°C until a pale blue color persisted. The mixture was then purged with Ar before it is allowed to reach ambient temperature. The mixture was filtered and the filtrate reduced to a volume of ca 50 mL. After dilution with $CH_2Cl_2$ (250 mL), $NEt_3$ (16 mL, 115 mmol) and $Ac_2O$ (21.5 mL, 227 mmol) were introduced at 0°C and the resulting solution stirred overnight at ambient temperature. For work up, the mixture was successively washed with HCl (0.1 M, 150 mL), NaOH (10% *w/w*, 150 mL) and $H_2O$ (150 mL), the organic layer (peroxide test must be negative at this point) was dried over $Na_2SO_4$ and evaporated. Distillation of the residue afforded the title compound as a colorless oil (5.7 g, 53%). $^1H$ NMR (400 MHz, $CDCl_3$): $\delta$ = 9.74 (t, $J$ = 1.6 Hz, 1H), 3.64 (s, 3H), 2.46-2.41 (m, 2H), 2.34-2.29 (m, 2H), 1.68-1.59 ppm (m, 4H); $^{13}C$ NMR (100 MHz, $CDCl_3$): $\delta$ = 202.0, 173.6, 51.5, 43.4, 33.6, 24.3, 21.4 ppm; IR (film): $\tilde{\nu}$ = 2951 (m), 2871 (w), 2723 (w), 1719 (s), 1436 (m), 1365 (m), 1196 (s), 1155 (s), 1093 (m), 1009 (m), 988 (m), 881 (w), 849 (w) 754 (w) cm$^{-1}$;




[10] (a) Kurata, K.; Taniguchi, K.; Shiraishi, K.; Hayama, N.; Tanaka, I.; Suzuki, M. *Chem. Lett*. **1989**, 267; (b) Kurata, K.; Taniguchi, K.; Shiraishi, K.; Suzuki, M. *Phytochemistry* **1993**, *33*, 155; (c) Todd, J. S.; Proteau, P. J.; Gerwick, W. H. *J. Nat. Prod*. **1994**, *57*, 171.

[11] Claus, R. E.; Schreiber, S. L. *Org. Synth*. **1990**, *Coll. Vol. 7*, 168.

MS (EI): *m/z* (%): 144 (1) $[M-H]^+$, 126 (1), 116 (28), 113 (54), 101 (48), 95 (8), 87 (95), 84 (21), 74 (59), 70 (14), 67 (45), 59 (100), 55 (68), 43 (59), 39 (20), 29 (54), 27 (28); HRMS (CI, *iso*-butane): *m/z*: calcd. for $C_7H_{13}O_3$: 145.0865 $[M]^+$; found: 145.0863.

**Undec-6*Z*-en-9-ynoic acid methyl ester.** A solution of NaHMDS (210 mg, 1.15 mmol) in THF (2 mL) was added at –30°C to a solution of but-2-ynyl-5-triphenylphosphonium iodide in THF (13 mL) and toluene (3 mL). The resulting mixture was allowed to reach ambient temperature and stirred until a clear yellow solution had formed (ca. 1 h). At this point, the solution was cooled to –90°C before a solution of methyl 6-oxohexanoate (183 mg, 1.20 mmol) in THF (1 mL) was introduced. The resulting mixture was stirred overnight while reaching ambient temperature. Quenching of the reaction with aq. $NH_4Cl$ (4 mL) followed by a standard extractive work up ($Et_2O$) and flash chromatography of the crude material (pentanes/$Et_2O$, 1:1) furnished the title compound as a colorless oil (228 mg, 98%). $^1$H NMR (400 MHz, $CDCl_3$): $\delta$ = 5.45-5.36 (m, 2H), 3.63 (s, 3H), 2.87-2.84 (m, 2H), 2.31 (t, *J* = 7.5 Hz, 2H), 2.07-2.02 (m, 2H), 1.76 (t, *J* = 2.6 Hz, 3H), 1.67-1.59 (m, 2H), 1.42-1.35 ppm (m, 2H); $^{13}$C NMR (100 MHz, $CDCl_3$): $\delta$ = 174.0, 130.6, 125.3, 75.3, 51.4, 33.9, 28.8, 26.7, 24.5, 17.1, 3.5 ppm; IR (film): $\tilde{\nu}$ = 3019 (w), 2922 (w), 2869 (w), 1734 (s), 1435 (m), 1361 (w), 1198 (m), 1171 (m), 1149 (m), 1095 (w), 1019 (w), 826 (w), 798 (w), 693 (w) $cm^{-1}$; MS (EI): *m/z* (%): 194 (1) $[M]^+$, 179 (2), 163 (40), 147 (13), 134 (12), 120 (100), 105 (56), 91 (90), 74 (41), 66 (37), 59 (32), 41 (47), 27 (25); HRMS (EI): *m/z*: calcd. for $C_{12}H_{18}O_2$: 194.1307 $[M]^+$; found: 194.1307.

**Undec-6*Z*-en-9-ynoic acid**. KOH (100 mg, 1.78 mmol) was added to a solution of undec-6*Z*-en-9-ynoic acid methyl ester (228 mg, 1.18 mmol) in EtOH (2 mL) and the resulting mixture was stirred at reflux temperature for 1.5 h. After reaching ambient temperature, the solvent was evaporated, and the residue suspended in $H_2O$ (5 mL). HCl (1 M) was added until a pH ≈ 2 was reached. The aqueous phase was extracted with pentanes (3 x 5 mL), the organic layer was evaporated and the residue dried in vacuo to give the title compound as a colorless syrup (155 mg, 73%). $^1$H NMR (400 MHz, $CDCl_3$): $\delta$ = 1.45-1.38 (m, 2H), 1.69-1.61 (m, 2H), 1.77 (t, *J* = 2.5 Hz, 3H), 2.09-2.04 (m, 2H), 2.36 (t, *J* = 7.4 Hz, 2H), 2.88-2.85 (m, 2H), 5.47-5.38 ppm (m, 2H); $^{13}$C NMR (100 MHz, $CDCl_3$): $\delta$ = 180.0, 130.5, 125.4, 75.4, 33.9, 28.7, 26.6, 24.2, 17.1, 3.5 ppm; IR (film): $\tilde{\nu}$ = 3019 (m), 2921 (br m), 2861 (m), 1706 (s), 1413 (m), 1289 (m), 1233 (m), 909 (m), 799 (w), 732 (m) $cm^{-1}$; MS (EI): *m/z* (%): 180 (4) $[M]^+$, 163 (2), 151 (16), 140 (17), 133 (3), 120 (38), 107 (41), 93 (100), 79 (83), 66 (47), 53 (27), 41 (43), 27 (27); HRMS (EI): *m/z*: calcd. for $C_{11}H_{16}O_2$: 180.1150 $[M]^+$; found: 180.1149.

**Compound 51**. Carbodiimide *p*-toluenesulfonate **39** (30 mg, 70 µmol) was added to a solution of undec-6*Z*-en-9-ynoic acid (11 mg, 58 µmol) in $CH_2Cl_2$ (0.5 mL) and the resulting mixture stirred for 1.5 h before a solution of alcohol **45** (7.0 mg, 39 µmol) in $CH_2Cl_2$ (0.5 mL) and DMAP (0.2 mg) were introduced. After stirring overnight, all volatile materials were evaporated and the residue purified by flash chromatography (hexanes/EtOAc, 15:1) to give product **51** as a colorless oil (8.6 mg, 65%). $[\alpha]_D^{20}$ = –86 ($CH_2Cl_2$, c = 0.43); $^1$H NMR (400 MHz, $CDCl_3$): $\delta$ = 5.47-5.39 (m, 2H), 4.76 (ddd, *J* = 9.2, 7.4, 3.5 Hz, 1H), 3.50-3.47 (m, 2H), 2.88 (dq, *J* = 4.9, 2.5 Hz, 2H), 2.83 (dq, *J* = 2.4, 2.1 Hz, 1H), 2.40-2.31 (m, 3H), 2.40-2.11 (m, 3H), 1.85 (dd, *J* = 14.9, 2.5 Hz, 1H), 1.80 (d, *J* = 2.5 Hz, 3H), 1.78 (t, *J* = 2.5 Hz, 3H), 1.73-1.62 (m, 3H), 1.49-1.38 (m, 3H), 0.83 ppm (t, *J* = 7.4 Hz, 3H); $^{13}$C NMR (100 MHz, $CDCl_3$): $\delta$ = 173.3, 130.7, 125.3, 78.4, 78.2, 77.6, 77.4, 75.3, 61.3, 58.2, 48.5, 34.5, 33.7, 29.3, 28.9, 26.8, 25.3, 24.7, 17.1, 8.9, 3.6, 3.5 ppm; IR (film): $\tilde{\nu}$ = 3020 (w), 2967 (m), 2921 (m), 2859 (w), 1729 (s), 1456

(m), 1441 (m), 1380 (m), 1256 (m), 1173 (s), 1144 (s), 1090 (s), 1030 (m), 953 (m), 928 (m); MS (EI): *m/z* (%): 342 (1) $[M]^+$, 313 (1), 289 (1), 274 (<1), 255 (<1), 235 (3), 197 (<1), 179 (1), 163 (15), 105 (100), 91 (21), 79 (18), 55 (9), 41 (12); HRMS (ESI): *m/z*: calcd. for $C_{22}H_{30}O_3Na$: 365.2078 $[M+Na]^+$; found: 365.2090.

**Compound 52**. Diyne **51** (3.9 mg, 11.4 µmol) was dissolved in toluene (1 mL) and MS 5Å (powder, 10 mg) were added. After stirring for 20 min, 86 µL of a stock solution of complex **43b** [7.2 mg (6.6 µmol) in toluene (1 mL)] were added and the mixture stirred at ambient temperature for 7 h. For work up, the suspension was filtered through a cotton plug, the filtrate was evaporated and the residue purified by flash chromatography (hexanes/EtOAc, 15:1) to give compound **52** as a colorless liquid (3.5 mg, 90%). $[\alpha]_D^{20}$ = –84 ($CH_2Cl_2$, c = 0.05); $^1$H NMR (600 MHz, $CDCl_3$): $\delta$ = 5.56 (dt, *J* = 10.6, 7.0 Hz, 1H), 5.51 (ddd, *J* = 10.6, 8.3, 6.8 Hz, 1H), 4.75 (ddd, *J* = 10.7, 8.4, 2.9, 1H), 3.50 (t, *J* = 2.5 Hz, 1H), 3.46 (d, *J* = 2.5 Hz, 1H), 2.92 (ddd, *J* = 17.2, 6.8, 2.0 Hz, 1H), 2.83 (dt, *J* = 5.4, 2.0 Hz, 1H), 2.75 (ddd, *J* = 17.1, 7.1, 2.6 Hz, 1H), 2.54 (tt, *J* = 10.6, 5.8 Hz, 1H), 2.41 (dt, *J* = 15.2, 7.2 Hz, 1H), 2.27 (dt, *J* = 15.2, 7.4 Hz, 2H), 2.21 (ddt, *J* = 12.9, 8.3, 7.7 Hz, 1H), 2.07 (ddd, *J* = 14.8, 10.6, 2.4 Hz, 1H), 1.99 (dq, *J* = 13.0, 6.8 Hz, 2H), 1.71 (m, 1H), 1.66 (dd, *J* = 14.8, 6.0, 1H), 1.61 (ddq, *J* = 14.4, 2.8, 7.4 Hz, 1H), 1.48 (qi., *J* = 7.4 Hz, 1H), 1.37 (ddq, *J* = 14.4, 8.4, 7.4 Hz, 1H), 0.82 ppm (t, *J* = 7.4 Hz, 3H); $^{13}$C NMR (150 MHz, $CDCl_3$): $\delta$ = 173.2 (s), 133.0 (d, $J_{CH}$ = 154 Hz), 123.8 (d, $J_{CH}$ = 161 Hz), 81.4 (s), 79.6 (s), 78.9 (d, $J_{CH}$ = 148 Hz), 62.8 (d, $J_{CH}$ = 189 Hz), 59.8 (d, $J_{CH}$ = 185 Hz), 53.11 (d, $J_{CH}$ = 134 Hz), 36.7 (d, $J_{CH}$ = 136 Hz), 34.3 (t, $J_{CH}$ = 128 Hz), 30.2 (t, $J_{CH}$ = 130 Hz), 27.5 (t, $J_{CH}$ = 127 Hz), 27.4 (t, $J_{CH}$ = 126 Hz), 25.7 (t), 24.9 (t, $J_{CH}$ = 128 Hz), 16.4 (t, $J_{CH}$ = 131 Hz), 9.0 (q, $J_{CH}$ = 126 Hz) ppm; IR (film): $\tilde{\nu}$ = 3021 (w), 2962 (m), 2930 (m), 2855 (w), 1726 (s), 1459 (m), 1441 (w), 1380 (w), 1350 (w) 1330 (w), 1266 (m), 1251 (m), 1228 (m), 1211 (m), 1185 (m), 1165 (m), 1153 (m), 1091 (m), 1059 (w), 1032 (w), 1011 (w), 942 (w), 842 (s), 799 (w) $cm^{-1}$; MS (EI): *m/z* (%): 288 (2) $[M]^+$, 270 (2), 259 (10), 241 (10), 213 (11), 201 (20), 187 (32), 157 (31), 143 (100), 129 (73), 115 (40), 103 (18), 91 (76), 79 (35), 65 (22), 55 (30), 41 (36); HRMS (ESI): *m/z*: calcd. for $C_{18}H_{24}O_3Na$: 311.1617 $[M+Na]^+$; found: 311.1618.

**Ecklonialactone A (2)**. $NaBH_4$ (9.6 mg, 0.25 mmol) and ethylenediamine (17 µL, 0.25 mmol) were successively added to a solution of $Ni(OAc)_2{\cdot}4H_2O$ (84 mg, 0.34 mmol) in EtOH (10 mL). $H_2$ was bubbled through the resulting black suspension for 15 min. An aliquot (200 µL, ca. 7 µmol) of this suspension was then added to a solution of cycloalkyne **52** (8.0 mg, 17 µmol) in EtOH (2 mL) and the resulting mixture was stirred under $H_2$ (1 atm) for 2 h. The catalyst was filtered off, the filtrate was evaporated and the residue purified by preparative HPLC (150 mm YMC-ODS-A 5 µm, MeCN/water 80:20, flow rate 15 mL/min, $t_r$ = 6.68 min) to give ecklonialactone A (**2**) as a colorless solid (5.5 mg, 69%). $[\alpha]_D^{20}$ = - 59 ($CH_2Cl_2$, c = 0.025); $^1$H NMR (600 MHz, $CDCl_3$): $\delta$ = 5.49 (tdd, *J* = 10.5, 5.0, 1.3 Hz, 1H), 5.48 (dtt, *J* = 10.6, 7.5, 1.5 Hz, 1H), 5.40 (m, 1H), 5.07 (dddd, *J* = 10.7, 9.8, 2.3, 0.9 Hz, 1H), 4.89 (dddd, *J* = 8.9, 7.3, 3.1, 1.5 Hz, 1H), 3.49 (d, *J* = 2.6 Hz, 1H), 3.21 (dd, *J* = 2.6, 0.5 Hz, 1H), 3.08 (ddd, *J* = 15.5, 10.5, 8.0 Hz, 1H), 3.06 (d, *J* = 9.6 Hz, 1H), 2.63 (ddd, *J* = 15.5, 5.9, 5.0 Hz, 1H), 2.41 (ddd, *J* = 15.5, 7.3, 5.2 Hz, 1H), 2.35 (ddd, *J* = 15.0, 8.9, 5.1 Hz, 1H), 2.04 (m, 1H), 1.99 (m, 1H), 1.93 (m, 2H), 1.87 (m, 1H), 1.75 (m, 1H), 1.72 (m, 1H), 1.69 (m, 1H), 1.43 (m, 2H), 1.39 (dqi, *J* = 14.6, 7.3 Hz, 1H), 0.79 ppm (t, *J* = 7.4 Hz, 3H); $^1$H NMR (600 MHz, $C_6D_6$): $\delta$ = 5.42 (m, 1H), 5.39 (m, 1H), 5.37 (tdd, *J* = 10.5, 5.0, 1.3 Hz, 1H), 5.27 (ddd, *J* = 10.9, 7.4, 3.2 Hz, 1H), 4.87 (4d, *J* = 10.6, 10.0, 3.2, 1.0 Hz, 1H), 3.19 (d, *J* = 9.9 Hz, 1H), 3.05 (m, 1H), 3.04 (ddt, *J* = 2.6, 0.5 Hz, 1H), 2.96 (m, 1H), 2.48 (m, 1H), 2.21 (ddd, *J* = 14.9, 6.9, 5.5 Hz, 1H), 2.17 (ddd, *J* = 14.9, 8.8, 5.1 Hz, 1H), 1.90 (m, 1H), 1.84 (m, 1H), 1.80 (t, *J* = 10.0 Hz, 1H), 1.68 (m, 1H), 1.62 (ddq, *J* = 14.5, 3.2, 7.4, 1H), 1.50 (ddt, *J* = 14.9, 1.2 Hz, 1H), 1.41 (m,

1H), 1.37 (ddd, *J* = 15.0, 9.4, 1.3 Hz, 1H), 1.30 (m, 2H), 1.24 (dqi., *J* = 14.5, 7.4 Hz, 1H), 0.77 ppm (t, *J* = 7.4 Hz, 3H); $^{13}$C NMR (150 MHz, $CDCl_3$): $\delta$ = 173.7 (s), 129.8 (d), 129.5 (d), 128.0 (d), 127.4 (d), 78.5 (d), 61.0 (d), 57.2 (d), 45.9 (d), 40.0 (d), 33.6 (t), 28.8 (t), 28.1 (t), 26.3 (t), 26.0 (t), 25.2 (t), 24.3 (t), 8.7 (q) ppm; IR (film): $\tilde{\nu}$ = 3007 (m), 2962 (m), 2931 (m), 2855 (m), 1726 (s), 1456 (w), 1441 (w), 1398 (w), 1380 (w), 1342 (w), 1254 (m), 1218 (m), 1145 (m), 1105 (w), 1087 (w), 1051 (w), 1019 (w), 971 (w), 953 (w), 930 (w), 912 (w), 842 (m), 804 (w), 749 (w), 741 (w), 718 (w), 695 (w) cm$^{-1}$; MS (ESI$^+$): 313 [M+Na]$^+$, 329 [M+K]$^+$, 603 [2M+Na]$^+$; HRMS (ESI): *m/z*: calcd. for $C_{18}H_{26}O_3Na$: 313.1774 [M+Na]$^+$; found: 313.1771.

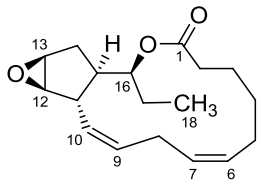



**Table S5.** Comparison of the recorded $^{13}$C NMR data ($CDCl_3$) of ecklonialactone A (**2**) with those reported in the literature.[10] Assignments marked * may be interchanged.

| Position | $\delta_C$ (lit., 67.9 MHz), ppm | $\delta_C$ (exp., 150 MHz), ppm | Δδ |
|---|---|---|---|
| 1 | 173.6 | 173.7 | 0.1 |
| 2 | 33.6 | 33.6 | 0 |
| 3 | 24.3 | 24.3 | 0 |
| 4 | 28.1 | 28.1 | 0 |
| 5 | 26.0 | 26.0 | 0 |
| 6* | 129.5 | 129.5 | 0 |
| 7 | 128.0 | 128.0 | 0 |
| 8 | 26.3 | 26.3 | 0 |
| 9* | 129.8 | 129.8 | 0 |
| 10 | 127.5 | 127.4 | -0.1 |
| 11 | 40.1 | 40.0 | -0.1 |
| 12 | 61.0 | 61.0 | 0 |
| 13 | 57.2 | 57.2 | 0 |
| 14 | 28.8 | 28.8 | 0 |
| 15 | 46.0 | 45.9 | -0.1 |
| 16 | 78.6 | 78.5 | -0.1 |
| 17 | 25.3 | 25.2 | -0.1 |
| 18 | 8.7 | 8.7 | 0 |

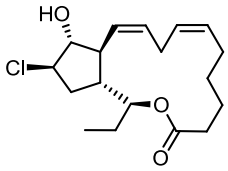



**Table S6**. Comparison of the recorded $^{13}C$ NMR data (ppm, $CDCl_3$) of eiseniachloride A (**7**) with those reported in the literature.[12]

| Position | $\delta_C$ (lit., 125 MHz) | $\delta_C$ (exp., 150 MHz), multiplicity [$^1J_{CH}$] | | Δδ |
|---|---|---|---|---|
| 1 | 173.8 | 173.8 | s | 0.0 |
| 2 | 32.8 | 32.8 | t | 0.0 |
| 3 | 24.5 | 24.6 | t | -0.1 |
| 4 | 27.7 | 27.7 | t | 0.0 |
| 5 | 25.6 | 25.6 | t | 0.0 |
| 6 | 130.0* | 130.0 | d | 0.0 |
| 7 | 126.9* | 126.7 | d | 0.2 |
| 8 | 26.7 | 26.7 | t | 0.0 |
| 9 | 130.9 | 131.0 | d | -0.1 |
| 10 | 130.2 | 130.0 | d | 0.2 |
| 11 | 45.4 | 45.2 | d [129.3] | 0.2 |
| 12 | 85.5 | 85.4 | d [147.9] | 0.1 |
| 13 | 62.7 | 62.6 | d [155.3] | 0.1 |
| 14 | 36.5 | 36.4 | t | 0.1 |
| 15 | 41.8 | 41.5 | d [129.3] | 0.3 |
| 16 | 77.4 | 77.4 | d [146.4] | 0.0 |
| 17 | 25.6 | 25.5 | t | 0.1 |
| 18 | 9.9 | 9.9 | q [126.4] | 0.0 |

* The assignment of these two signals had to be interchanged relative to the assignment made in the original publication.

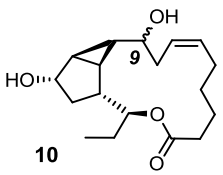
[12] Kousaka, K.; Ogi, N.; Akazawa, Y.; Fujieda, M.; Yamamoto, Y.; Takada, Y.; Kimura, J. *J. Nat. Prod*. **2003**, *66*, 1318.

**Table S7**. Comparison of the recorded $^{1}$H NMR data (ppm, $CDCl_3$) of eiseniachloride A (**7**) with those reported in the literature.[12]

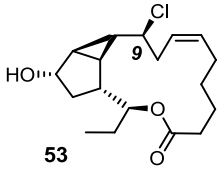
| **$\delta_H$ (lit., 500 MHz)** | | | **$\delta_H$ (exp., 600 MHz)** | | |
|---|---|---|---|---|---|
| $H_3$-18 | 0.82 | t | $H_3$-18 | 0.81 | t, *J* = 7.4 Hz |
| H-3 | 1.25 | m | H-3 | (1.71) | m |
| H-4<br>$H_2$-17 | 1.58* | m | H-4<br>$H_2$-17 | (1.22)<br>(1.57) | m<br>m |
| H'-4 | 1.75* | m | H'-4 | (1.57) | m |
| H'-3<br>H-5 | 1.80 | m | H'-3<br>H-5 | (1.77)<br>(1.79) | m<br>m |
| H-14 | 2.05 | ddd | H-14 | (2.04) | m |
| H'-14 | 2.13 | ddd | H'-14 | (2.10) | m |
| H-15 | 2.32 | m | H-15 | (2.31) | m |
| H-2 | 2.35 | m | H-2 | (2.31) | m |
| H'-5 | 2.45 | m | H'-5 | (2.40) | m |
| H-8 | 2.48 | m | H-8 | (2.47) | m |
| H'-2 | 2.50 | m | H'-2 | (2.47) | m |
| H-11 | 2.97 | ddd | H-11 | 2.96 | q, *J* = 9.4 Hz |
| H'-8 | 3.41 | m | H'-8 | 3.40 | ddd, *J* = 15.1, 10.7, 8.6 Hz |
| H-12 | 3.83 | dd | H-12 | 3.81 | dd, *J* = 8.7, 6.7 Hz |
| H-13 | 4.04 | ddd | H-13 | 4.03 | dt, *J* = 9.0, 6.4 |
| H-16 | 4.73 | dt | H-16 | 4.70 | ddd, *J* = 7.2, 6.4, 3.7 Hz |
| H-10 | 5.35 | dd | H-10 | 5.34 | m |
| H-6 | 5.40 | m | H-6 | (5.38) | m |
| H-7 | 5.45 | m | H-7 | (5.40) | m |
| H-9 | 5.58 | dt | H-9 | 5.57 | tdd, *J* = 10.9, 3.7, 0.8 Hz |

* supposedly erroneous assignment in the literature

**Table S8**. Comparison of the $^{13}C$ NMR spectra (ppm, $CDCl_3$) of oxylipin **10**[12] with its chlorinated analogue **53** derived from opening of **2** in non-purified $CDCl_3$.



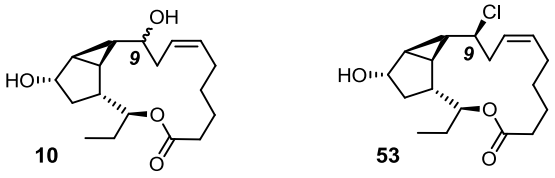

**10**



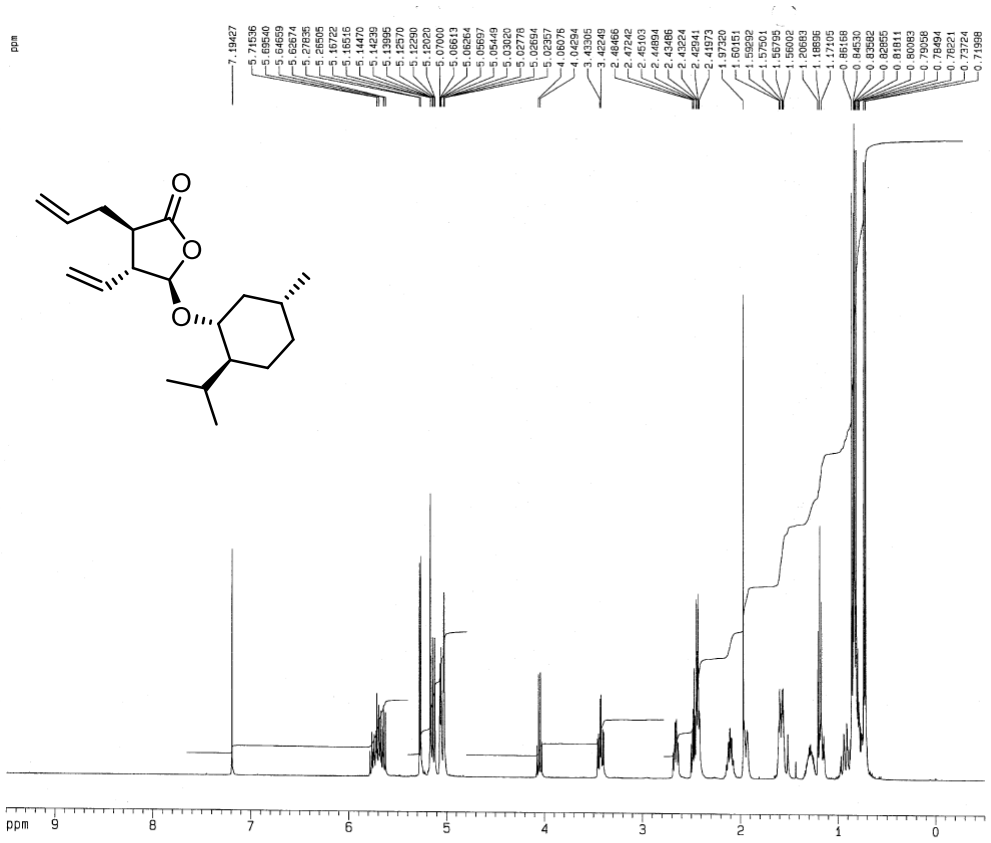

**53**

| Position | $\delta_C$ (lit., 125 MHz) | $\delta_C$ (exp., 150 MHz); multiplicity [$^1J_{CH}$] | | Δδ |
|---|---|---|---|---|
| 1 | 174.3 | 174.4 | s | -0.1 |
| 2 | 34.5 | 34.4 | t | 0.1 |
| 3 | 24.0 | 23.7 | t | 0.3 |
| 4 | 27.4 | 27.2 | t | 0.2 |
| 5 | 26.1 | 25.9 | t | 0.2 |
| 6 | 130.3 | 129.6 | d | 0.7 |
| 7 | 126.6 | 127.0 | d | -0.4 |
| 8 | 32.2 | 32.5 | t | -0.3 |
| **9** | **68.3** | **60.8** | **d [152.1]** | **7.5** |
| 10 | 26.1 | 26.5 | d [161.9] | -0.4 |
| 11 | 24.4 | 27.7 | d [168.6] | -3.3 |
| 12 | 27.2 | 29.5 | d [168.5] | -2.3 |
| 13 | 74.8 | 74.7 | d [151.2] | 0.1 |
| 14 | 37.1 | 36.7 | t | 0.4 |
| 15 | 43.8 | 43.6 | d [134.1] | 0.2 |
| 16 | 78.2 | 77.8 | d [149.9] | 0.4 |
| 17 | 26.6 | 26.8 | t | -0.2 |
| 18 | 9.6 | 9.7 | q [126.1] | -0.1 |

**Table S8**. Comparison of the $^{1}$H NMR spectra (ppm, $CDCl_3$) of oxylipin **10**[12] with its chlorinated analogue **53** derived from opening of **2** in non-purified $CDCl_3$.




| **$\delta_H$ (lit., 500 MHz)** | | | **$\delta_H$ (exp., 600 MHz)** | | |
|---|---|---|---|---|---|
| H-10 | 0.79 | dt, *J* = 4.7, 3.6 Hz | H-10 | 0.93 | dt, *J* = 5.6, 3.5 Hz |
| $H_3$-18 | 0.86 | t, *J* = 7.3 Hz | $H_3$-18 | 0.85 | t, *J* = 7.4 Hz |
| H-17 | 1.48 | m | H-17 | (1.48) | m |
| H-14 | 1.50 | m | H-14 | (1.47) | m |
| H-11 | 1.53 | dd, *J* = 6.0, 3.6 Hz | H-11 | (1.71) | m |
| H-12<br>$H_2$-4 | 1.60 | m | H-12 | (1.70) | m |
| | | | H-4 | (1.57) | m |
| | | | H'-4 | (1.46) | m |
| H'-14 | 1.64 | dd, *J* = 7.8, 5.0 Hz | H'-14 | (1.57) | m |
| H-3 | 1.72 | ddd, *J* = 14.7, 7.8, 3.7 Hz | H-3 | (1.74) | m |
| H'-17 | 1.73 | ddq, *J* = 14.2, 7.3, 3.2 Hz | H'-17 | (1.69) | m |
| H'-3 | 1.80 | m | H'-3 | (1.78) | m |
| H-5 | 1.95 | ddd, *J* = 13.5, 8.2, 8.2 Hz | H-5 | (1.94) | m |
| H-15 | 2.05 | m | H-15 | (2.08) | m |
| H'-5 | 2.08 | m | H'-5 | (2.11) | m |
| $H_2$-8 | 2.15 | m | H-8 | (2.41) | m |
| | | | H'-8 | (2.36) | m |
| H-2 | 2.33 | dd, *J* = 14.4, 10.1, 4.1 Hz | H-2 | (2.31) | m |
| H'-2 | 2.58 | ddd, *J* = 14.4, 7.8, 3.7 Hz | H'-2 | 2.56 | ddd, *J* = 14.5, 7.6, 3.7 Hz |
| **H-9** | **4.18** | **ddd, *J* = 8.2, 4.8, 4.7 Hz** | **H-9** | **4.57** | **ddd, *J* = 9.3, 5.6, 3.0 Hz** |
| H-13 | 4.22 | d, *J* = 5.0 Hz | H-13 | 4.24 | d, *J* = 5.2 Hz |
| H-16 | 4.85 | ddd, *J* = 9.9, 8.5, 3.2 Hz | H-16 | 4.80 | ddd, *J* = 9.8, 8.2, 3.4 Hz |
| H-7 | 5.32 | dt, *J* = 10.5, 6.8 Hz | H-7 | (5.34) | m |
| H-6 | 5.55 | m | H-6 | (5.49) | m |




hiv-ha-063-02

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EXPNO                      10
PROCNO                      1

F2 - Acquisition Parameters
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PROBHD   5 mm BBO BB-1H
PULPROG                zg30
TD                    65536
SOLVENT               CDCl3
NS                       32
DS                        8
SWH                8278.146 Hz
FIDRES            0.126314 Hz
AQ                3.9584243 sec
RG                      114
DW                 60.400 usec
DE                  6.50 usec
TE                 303.0 K
D1                0.00300000 sec

======== CHANNEL f1 ========
NUC1                      1H
P1                     9.25 usec
PL1                    0.00 dB
SFO1           400.1324710 MHz

F2 - Processing parameters
SI                     32768
SF                400.1300357 MHz
WDW                       EM
SSB                        0
LB                      0.30 Hz
GB                         0
PC                      2.00

1D NMR plot parameters
CX                     22.00 cm
CY                     15.00 cm
F1P                   9.500 ppm
F1                  3801.24 Hz
F2P                  -0.500 ppm
F2                  -200.07 Hz
PPMCM              0.45455 ppm/cm
HZCM             181.87729 Hz/cm
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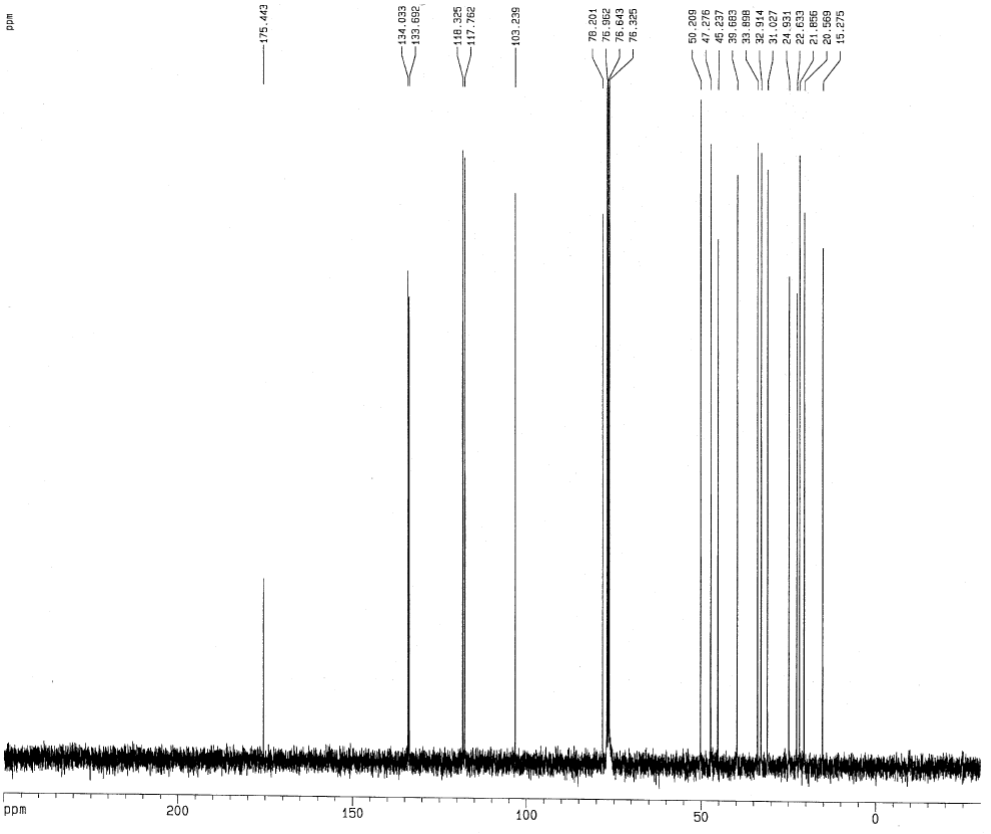


hiv-ha-063-02

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EXPNO                      11
PROCNO                      1

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Time                   19.02
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PULPROG             zgdc30
TD                    65536
SOLVENT               CDCl3
NS                     1500
DS                        2
SWH               33112.582 Hz
FIDRES            0.505258 Hz
AQ                0.9896436 sec
RG                     16384
DW                 15.100 usec
DE                  6.00 usec
TE                 303.0 K
D1                0.03000000 sec
d11               0.03000000 sec

======== CHANNEL f1 ========
NUC1                      13C
P1                    10.94 usec
PL1                    5.00 dB
SFO1           100.6242789 MHz

======== CHANNEL f2 ========
CPDPRG2                waltz16
NUC2                      1H
PCPD2                 90.00 usec
PL2                    0.00 dB
PL12                  19.75 dB
SFO2           400.1324710 MHz

F2 - Processing parameters
SI                     32768
SF                100.6128045 MHz
WDW                       EM
SSB                        0
LB                      1.00 Hz
GB                         0
PC                      2.00

1D NMR plot parameters
CX                     22.00 cm
CY                     15.00 cm
F1P                   250.000 ppm
F1                  25153.20 Hz
F2P                  -30.000 ppm
F2                  -3018.38 Hz
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HZCM            1280.52661 Hz/cm
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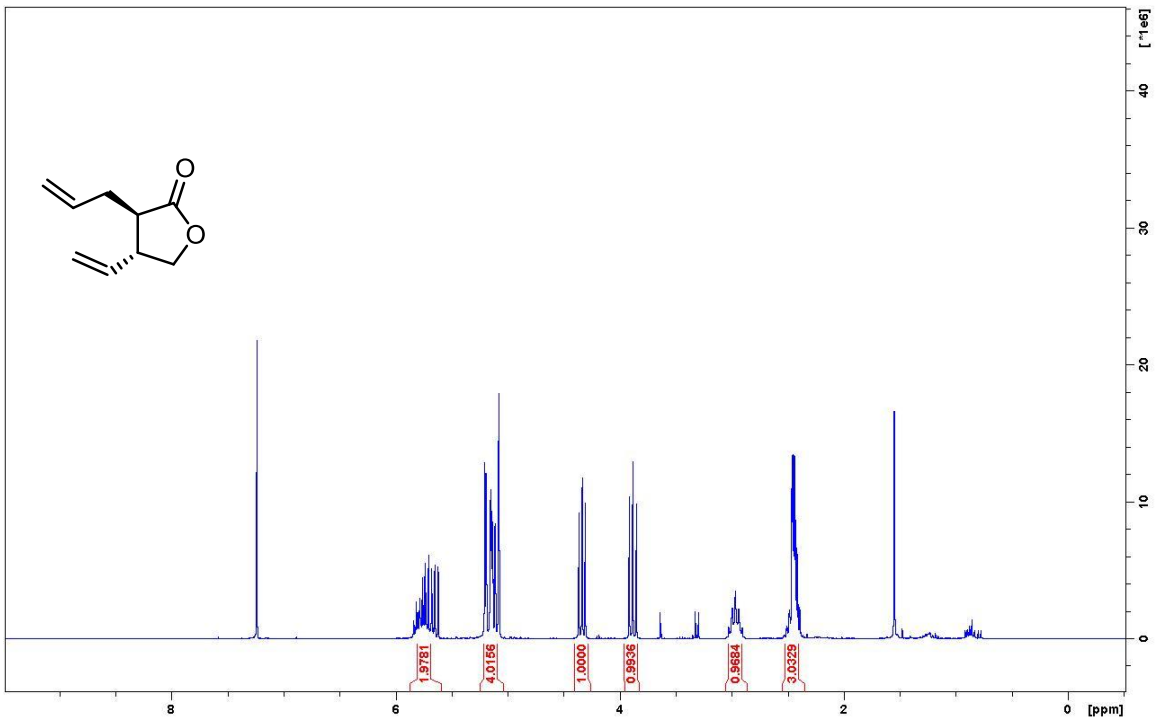


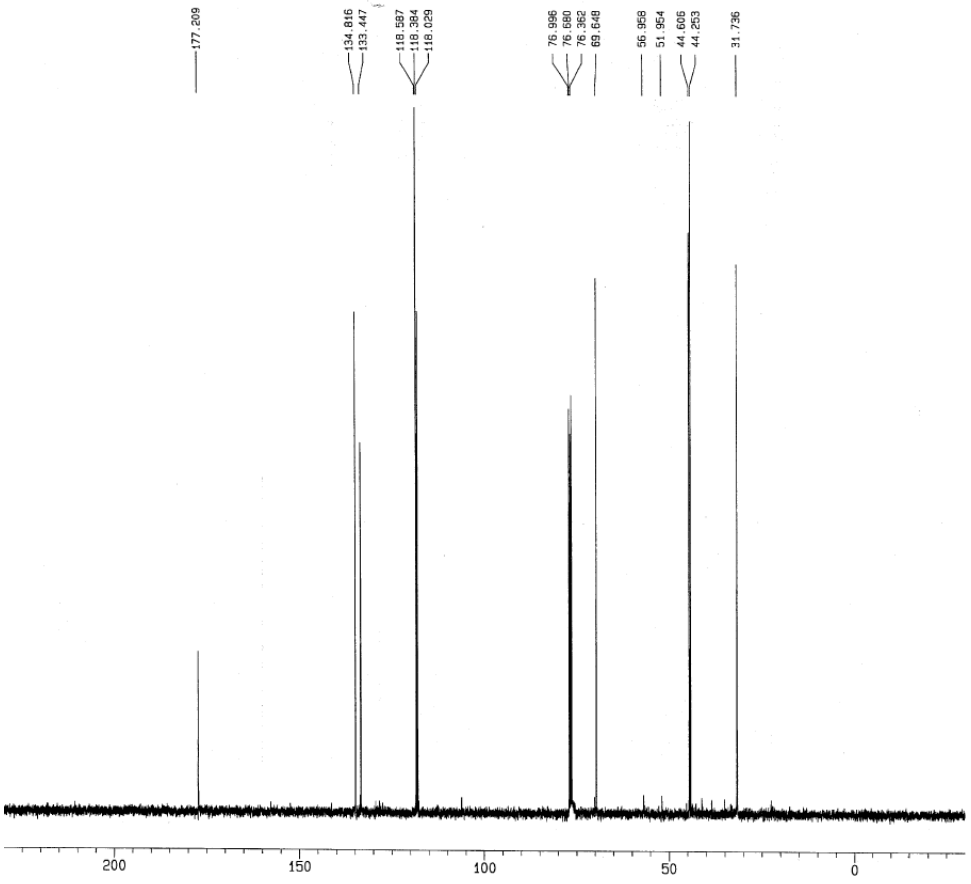


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EXPNO                      11
PROCNO                      1

F2 - Acquisition Parameters
Date_              20070414
Time                   20.15
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PULPROG             zgdc30
TD                      65536
SOLVENT                CDCl3
NS                       1500
DS                          2
SWH               33112.582 Hz
FIDRES             0.505258 Hz
AQ                 0.9896436 sec
RG                   18390.4
DW                  15.100 usec
DE                   6.00 usec
TE                   303.0 K
D1              0.03000000 sec
d11             0.03000000 sec

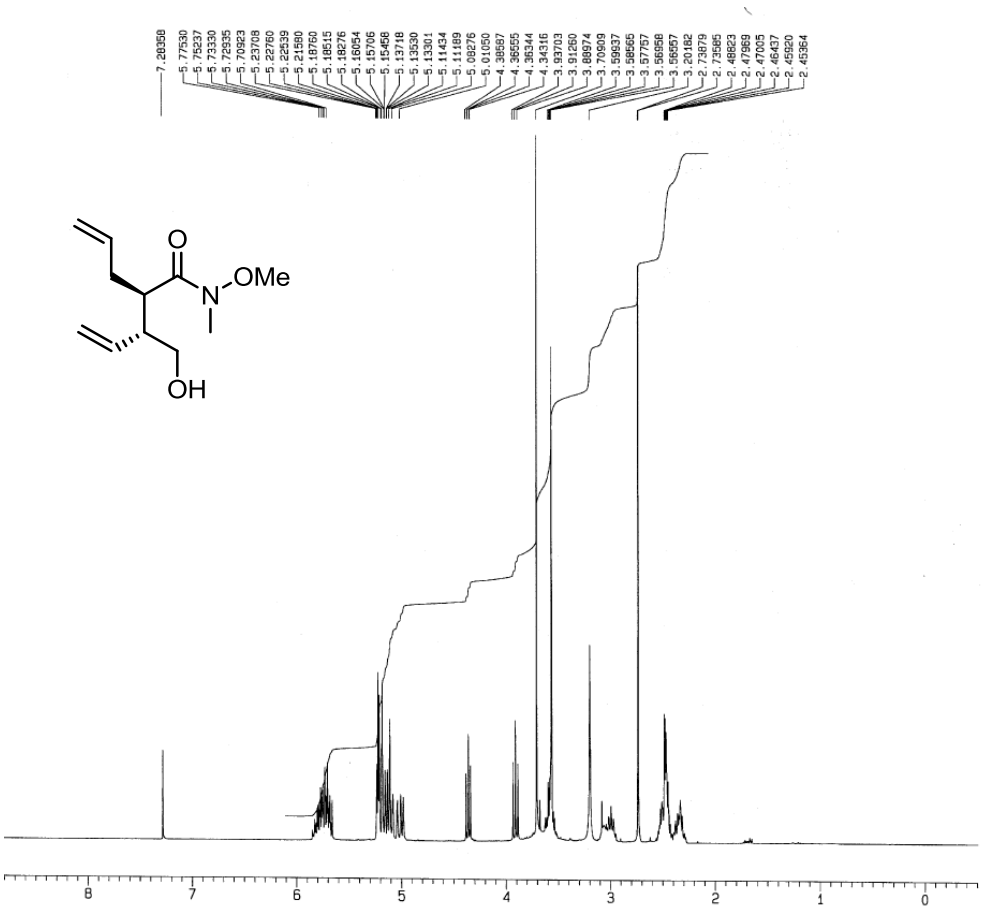
======== CHANNEL f1 ========
NUC1                    13C
P1                   10.94 usec
PL1                   5.00 dB
SFO1           100.6242789 MHz

======== CHANNEL f2 ========
CPDPRG2             waltz16
NUC2                    1H
PCPD2                90.00 usec
PL2                   0.00 dB
PL12                 19.76 dB
SFO2           400.1324710 MHz

F2 - Processing parameters
SI                       32768
SF             100.6128045 MHz
WDW                         EM
SSB                          0
LB                    1.00 Hz
GB                           0
PC                    2.00

1D NMR plot parameters
CX                   22.00 cm
CY                   15.00 cm
F1P                 250.000 ppm
F1                25153.20 Hz
F2P                 -30.000 ppm
F2                -3018.38 Hz
PPMCM              12.72727 ppm/cm
HZCM             1280.52661 Hz/cm
```

avm-aa-385-02

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EXPNO                     10
PROCNO                     1

F2 - Acquisition Parameters
Date_               20070418
Time                    1.09
INSTRUM                av400
PROBHD   5 mm BBO BB-1H
PULPROG                zg30
TD                    65536
SOLVENT               CDCl3
NS                       32
DS                        8
SWH                8278.146 Hz
FIDRES            0.126314 Hz
AQ                3.9584243 sec
RG                      114
DW                   60.400 usec
DE                    6.50 usec
TE                   303.0 K
D1                0.00300000 sec

======== CHANNEL f1 ========
NUC1                      1H
P1                     9.25 usec
PL1                    0.00 dB
SFO1           400.1324710 MHz

F2 - Processing parameters
SI                      32768
SF                400.1300000 MHz
WDW                        EM
SSB                         0
LB                       0.30 Hz
GB                          0
PC                       2.00

1D NMR plot parameters
CX                      22.00 cm
CY                      15.00 cm
F1P                     9.500 ppm
F1                    3801.24 Hz
F2P                    -0.500 ppm
F2                    -200.07 Hz
PPMCM                 0.45455 ppm/cm
HZCM                181.87727 Hz/cm
```
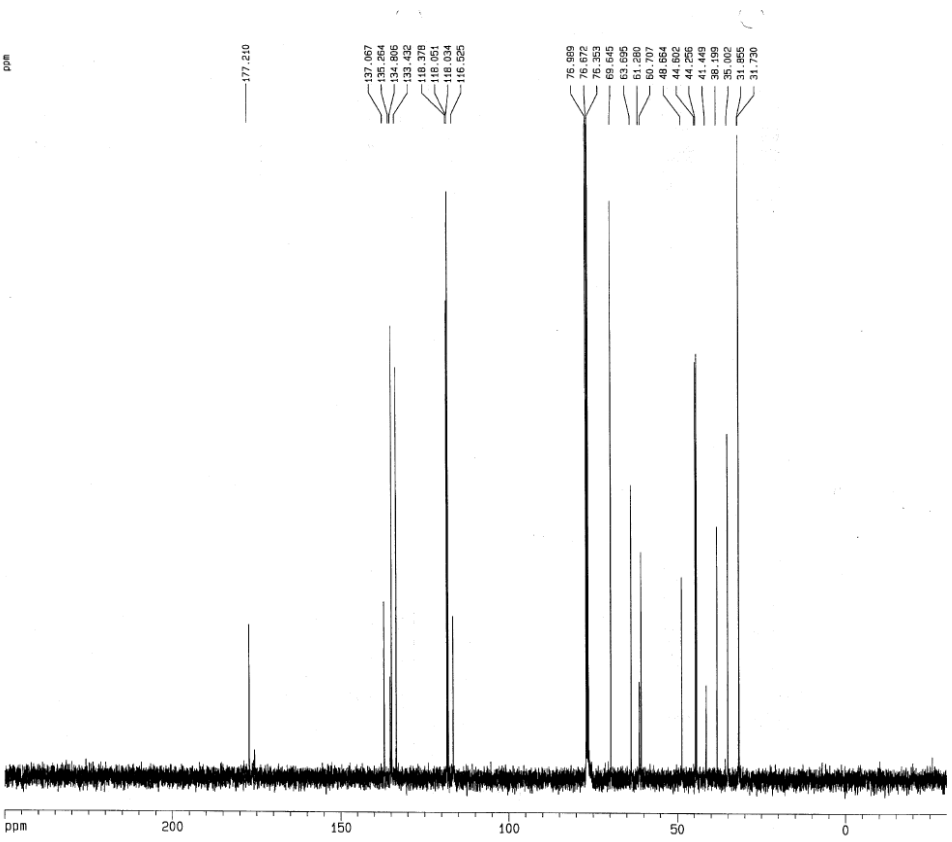

avm-aa-386-02




```
Current Data Parameters
NAME                 a117046
EXPNO                     11
PROCNO                     1

F2 - Acquisition Parameters
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Time                    1.37
INSTRUM                av400
PROBHD   5 mm BBO BB-1H
PULPROG             zgdc30
TD                    65536
SOLVENT               CDCl3
NS                     1500
DS                        2
SWH               33112.582 Hz
FIDRES            0.505258 Hz
AQ                0.9896436 sec
RG                    16384
DW                   15.100 usec
DE                    8.00 usec
TE                   303.0 K
D1                0.03000000 sec
d11               0.03000000 sec

======== CHANNEL f1 ========
NUC1                      13C
P1                    10.94 usec
PL1                    5.00 dB
SFO1           100.6242769 MHz

======== CHANNEL f2 ========
CPDPRG2             waltz16
NUC2                      1H
PCPD2                 90.00 usec
PL2                    0.00 dB
PL12                  19.76 dB
SFO2           400.1324710 MHz

F2 - Processing parameters
SI                      32768
SF                100.6128045 MHz
WDW                        EM
SSB                         0
LB                       1.00 Hz
GB                          0
PC                       2.00

1D NMR plot parameters
CX                      22.00 cm
CY                      15.00 cm
F1P                   250.000 ppm
F1                  25153.20 Hz
F2P                   -30.000 ppm
F2                   -3018.38 Hz
PPMCM                12.72727 ppm/cm
HZCM                1280.52661 Hz/cm
```
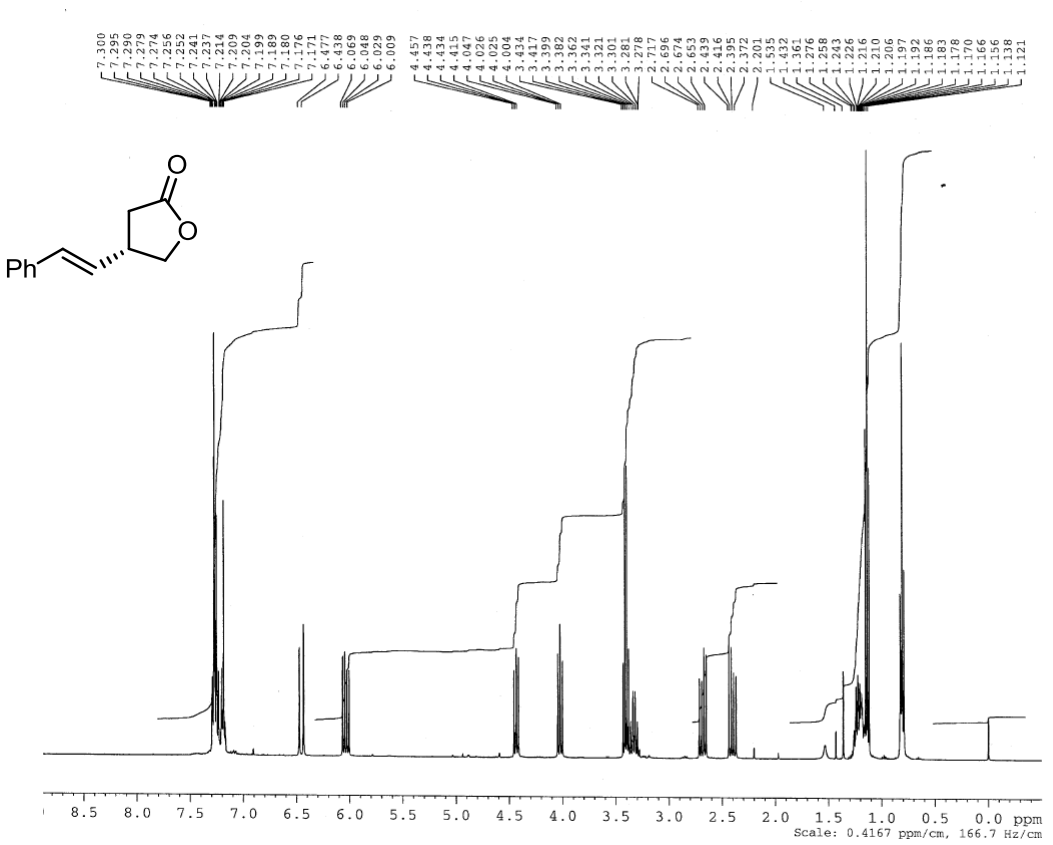

avm-aa-386-02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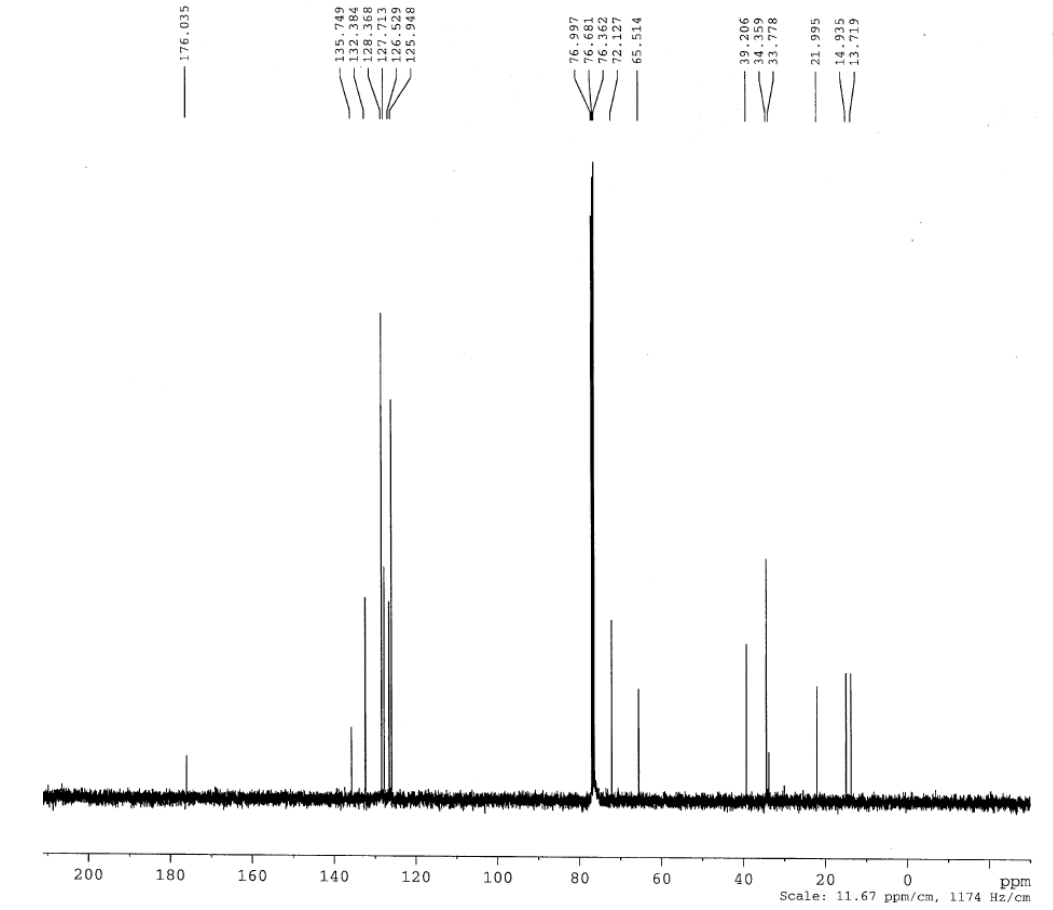
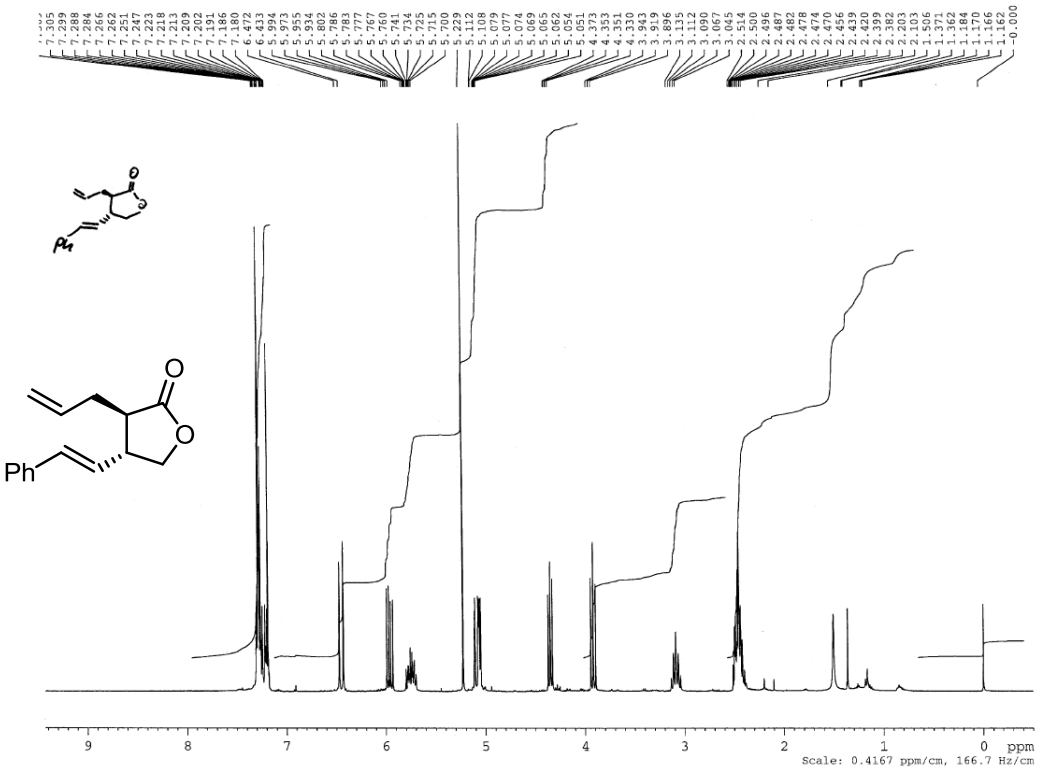
7.279
7.274
7.256
7.252
7.241
7.237
7.214
7.209
7.204
7.194
7.189
7.180
7.176
7.171
6.477
6.438
6.069
6.048
6.029
6.009
4.457
4.438
4.434
4.415
4.047
4.026
4.025
4.004
3.434
3.417
3.399
3.382
3.362
3.341
3.321
3.301
3.281
3.278
3.177
2.696
2.676
2.653
2.439
2.416
2.395
2.372
2.201
1.535
1.432
1.361
1.276
1.258
1.243
1.226
1.216
1.206
1.197
1.192
1.186
1.183
1.178
1.170
1.166
1.156
1.138
1.121
O
O
Ph
Current Data Parameters
NAME mz31050
EXPNO 10
PROCNO 1
F2 - Acquisition Parameters
Date_ 20090331
Time 21.37
INSTRUM av400
PROBHD 5 mm BBO BB-1H
PULPROG zg30
TD 65536
SOLVENT CDCl3
NS 32
DS 8
SWH 8278.146 Hz
FIDRES 0.126314 Hz
AQ 3.9584243 sec
RG 181
DW 60.400 usec
DE 6.50 usec
TE 303.0 K
D1 0.00300000 sec
TD0 1
======== CHANNEL f1 ========
NUC1 1H
P1 9.25 usec
PL1 0.00 dB
SFO1 400.1324710 MHz
F2 - Processing parameters
SI 32768
SF 400.1300376 MHz
WDW EM
SSB 0
LB 0.30 Hz
GB 0
PC 2.00
SR 37.60 Hz
HIV-HB-168-02
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 ppm
Scale: 0.4167 ppm/cm, 166.7 Hz/cm


176.035
135.749
132.384
128.368
127.713
126.529
125.948
76.997
76.681
76.362
72.127
65.514
39.206
34.359
33.778
21.995
14.935
13.719
Current Data Parameters
NAME mz31050
EXPNO 11
PROCNO 1
F2 - Acquisition Parameters
Date_ 20090331
Time 22.06
INSTRUM av400
PROBHD 5 mm BBO BB-1H
PULPROG zgdc30
TD 65536
SOLVENT CDCl3
NS 1500
DS 2
SWH 33112.582 Hz
FIDRES 0.505258 Hz
AQ 0.9896436 sec
RG 18390.4
DW 15.100 use
DE 8.00 use
TE 303.0 K
D1 0.03000000 sec
d11 0.03000000 sec
TD0 1
======== CHANNEL f1 ========
NUC1 13C
P1 10.94 use
PL1 5.00 dB
SFO1 100.6242789 MHz
======== CHANNEL f2 ========
CPDPRG2 waltz16
NUC2 1H
PCPD2 90.00 use
PL2 0.00 dB
PL12 19.76 dB
SFO2 400.1324710 MHz
F2 - Processing parameters
SI 32768
SF 100.6128045 MHz
WDW EM
SSB 0
LB 1.00 Hz
GB 0
PC 2.00
SR 75.46 Hz
HIV-HB-168-02
200 180 160 140 120 100 80 60 40 20 0 ppm
Scale: 11.67 ppm/cm, 1174 Hz/cm

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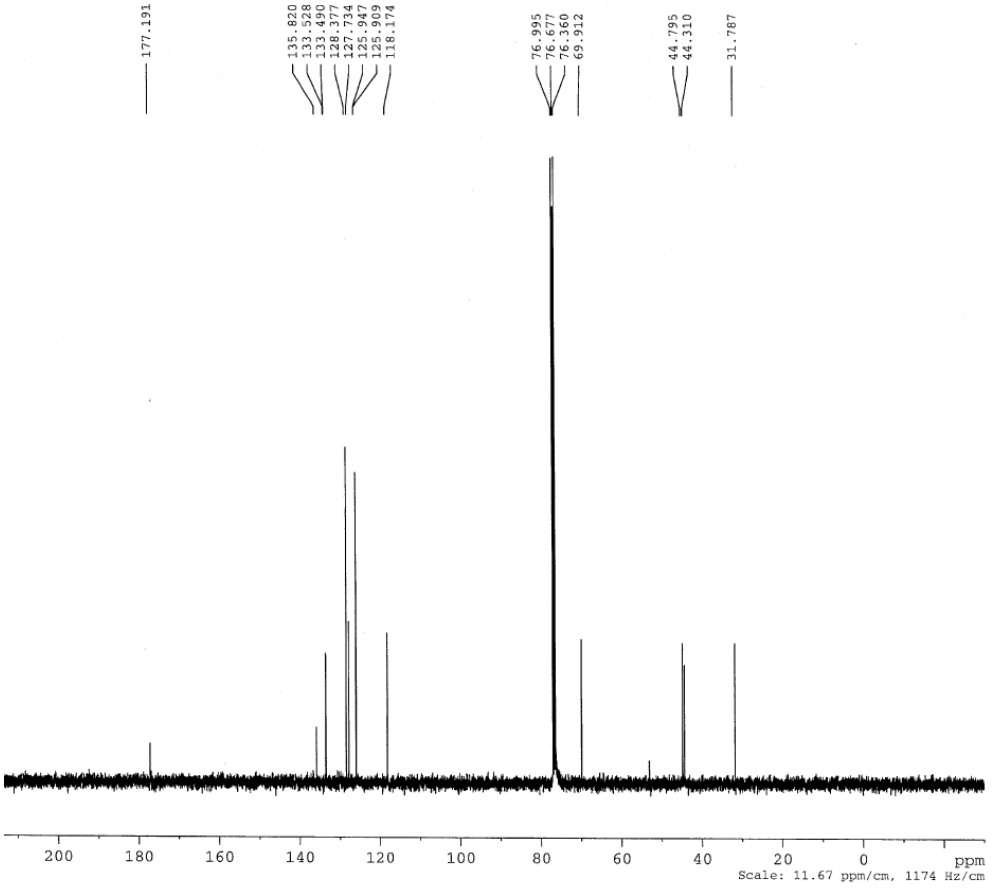
NAME                a103026
EXPNO                    10
PROCNO                    1

F2 - Acquisition Parameters
Date_              20090403
Time                  22.39
INSTRUM                av400
PROBHD   5 mm BBO BB-1H
PULPROG                zg30
TD                    65536
SOLVENT               CDCl3
NS                       32
DS                        8
SWH                8278.146 Hz
FIDRES            0.126314 Hz
AQ                3.9584243 sec
RG                      256
DW                   60.400 usec
DE                    6.50 usec
TE                   303.0 K
D1                0.00300000 sec
TD0                       1

======== CHANNEL f1 ========
NUC1                      1H
P1                     9.25 usec
PL1                    0.00 dB
SFO1          400.1324710 MHz

F2 - Processing parameters
SI                    32768
SF                400.1300372 MHz
WDW                       EM
SSB                        0
LB                      0.30 Hz
GB                         0
PC                      2.00
SR                     37.19 Hz
```

HIV-HB-172-01

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Current Data Parameters
NAME                a103026
EXPNO                    11
PROCNO                    1

F2 - Acquisition Parameters
Date_              20090403
Time                  23.08
INSTRUM                av400
PROBHD   5 mm BBO BB-1H
PULPROG             zgdc30
TD                    65536
SOLVENT               CDCl3
NS                     1500
DS                        2
SWH               33112.582 Hz
FIDRES            0.505258 Hz
AQ                0.9896436 sec
RG                    16384
DW                   15.100 usec
DE                    8.00 usec
TE                   303.0 K
D1                0.03000000 sec
d11               0.03000000 sec
TD0                       1

======== CHANNEL f1 ========
NUC1                     13C
P1                    10.94 usec
PL1                    5.00 dB
SFO1          100.6242789 MHz

======== CHANNEL f2 ========
CPDPRG2             waltz16
NUC2                      1H
PCPD2                 90.00 usec
PL2                    0.00 dB
PL12                  19.76 dB
SFO2          400.1324710 MHz

F2 - Processing parameters
SI                    32768
SF                100.6128045 MHz
WDW                       EM
SSB                        0
LB                      1.00 Hz
GB                         0
PC                      2.00
SR                     75.46 Hz
```
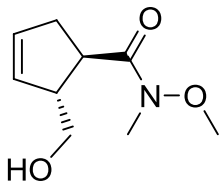
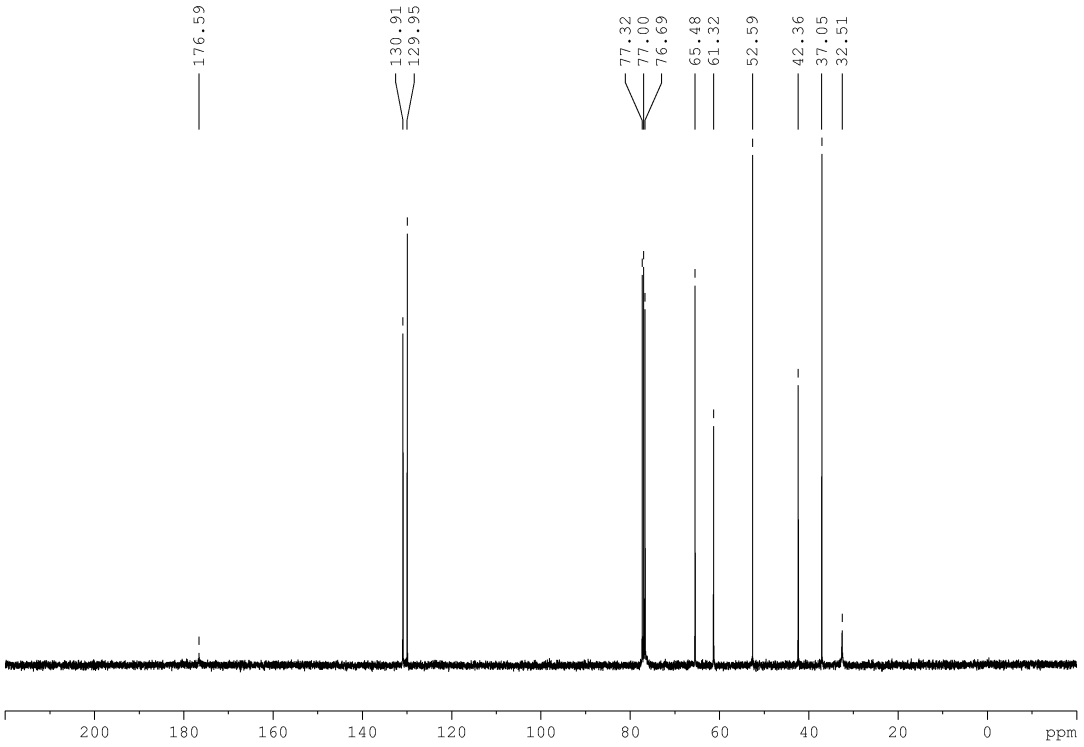
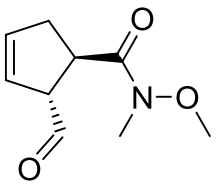

HIV-HB-172-01

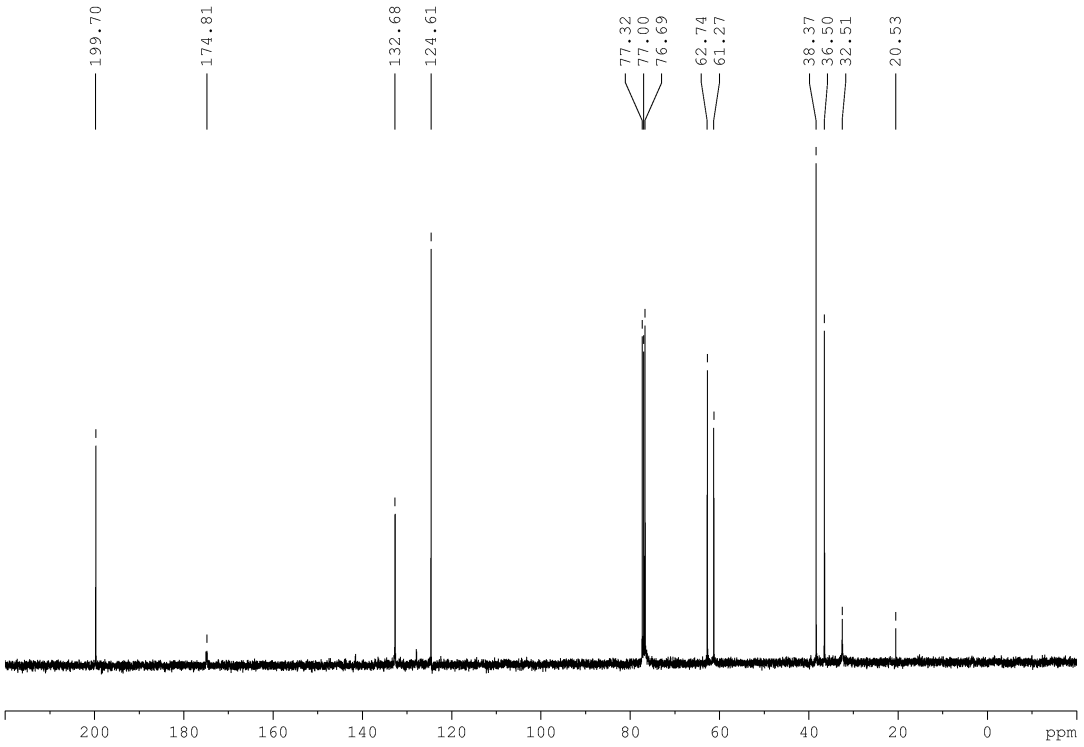

O
N–O
HO

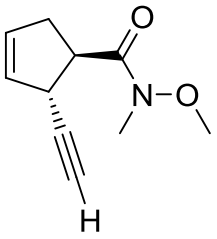

1.00
1.00
2.95
1.17
1.06
2.05
3.10
1.05
1.03
1.30
9
8
7
6
5
4
3
2
1
0
ppm


176.59
130.91
129.95
77.32
77.00
76.69
65.48
61.32
52.59
42.36
37.05
32.51
200
180
160
140
120
100
80
60
40
20
0
ppm

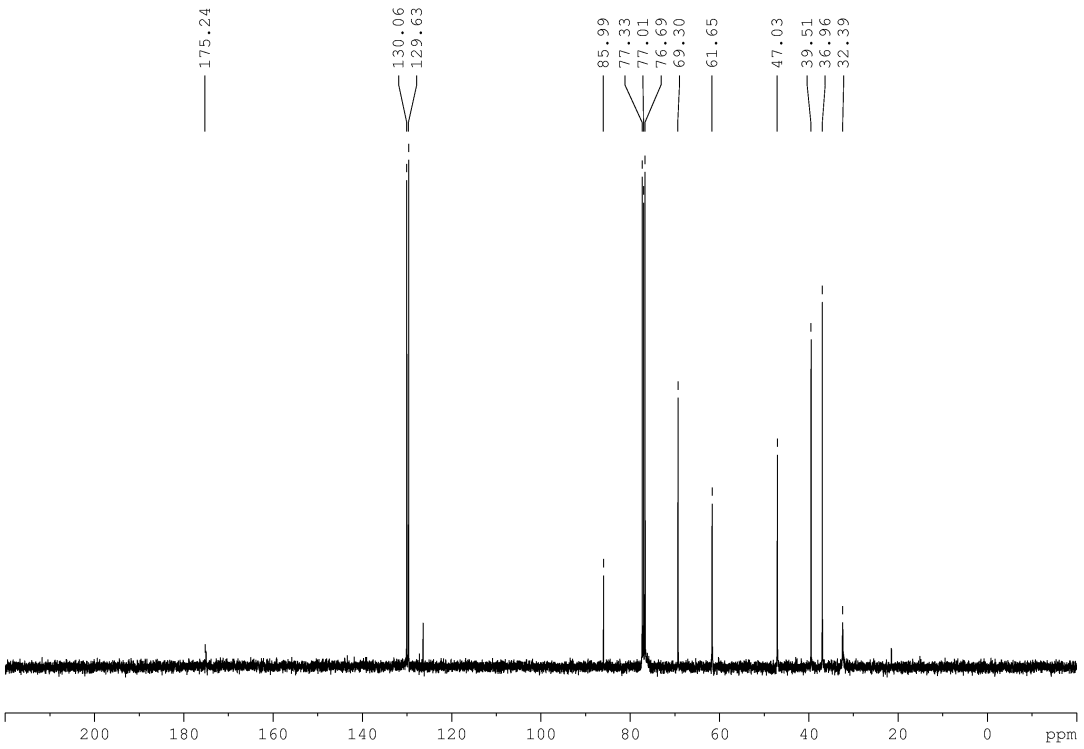

O
N
O
O

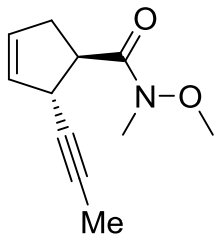

1.00
1.08
1.07
1.07
1.14
3.52
3.51
2.36
9
8
7
6
5
4
3
2
1
0
ppm

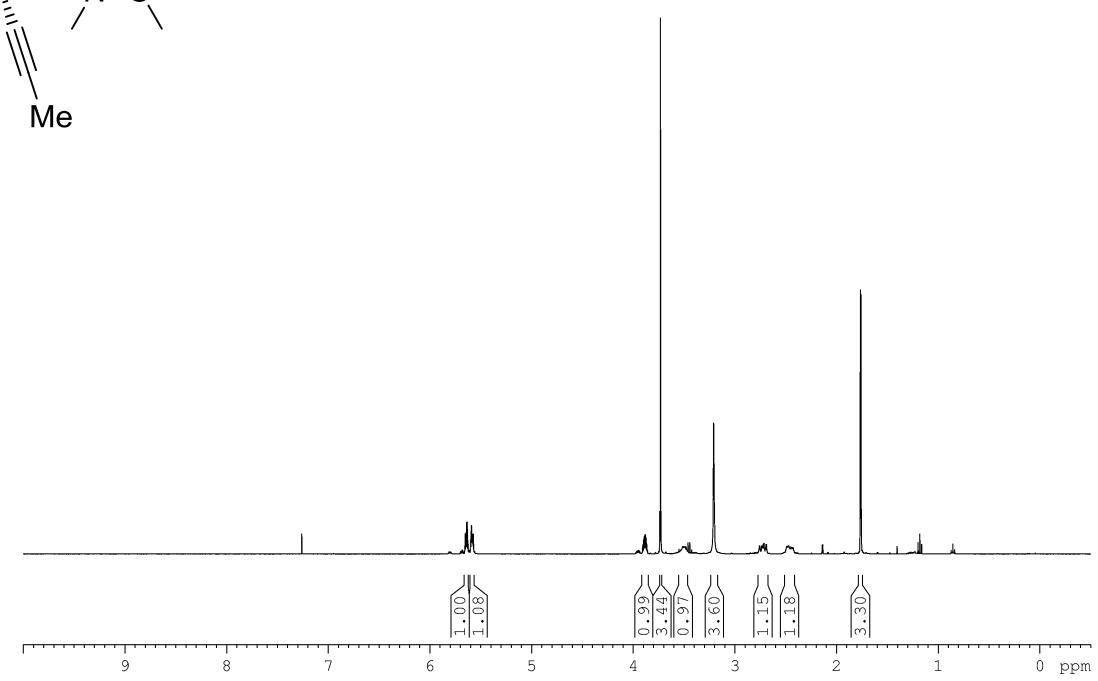

199.70
174.81
132.68
124.61
77.32
77.00
76.69
62.74
61.27
38.37
36.50
32.51
20.53
200
180
160
140
120
100
80
60
40
20
0
ppm

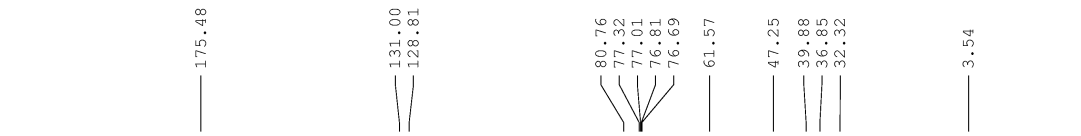

O
N
O
H

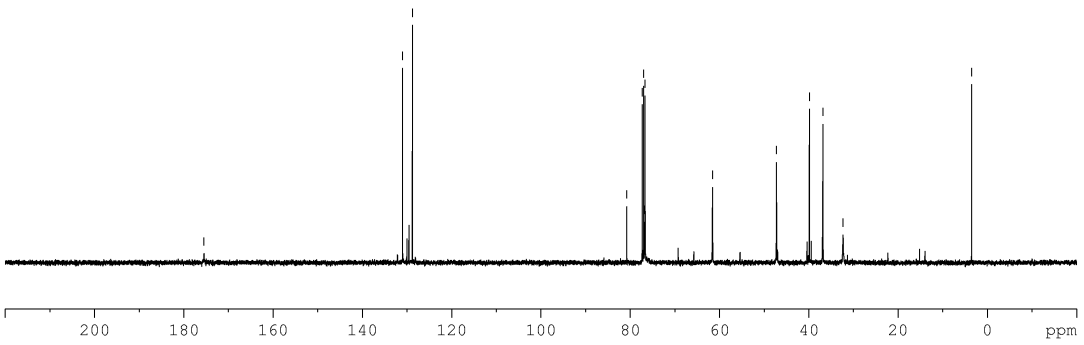

1.00
0.98
1.02
3.18
0.99
3.03
1.05
1.04
0.92
9
8
7
6
5
4
3
2
1
0
ppm

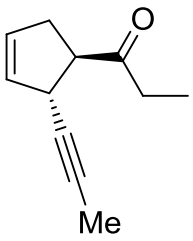

175.24
130.06
129.63
85.99
77.33
77.01
76.69
69.30
61.65
47.03
39.51
36.96
32.39
200
180
160
140
120
100
80
60
40
20
0
ppm

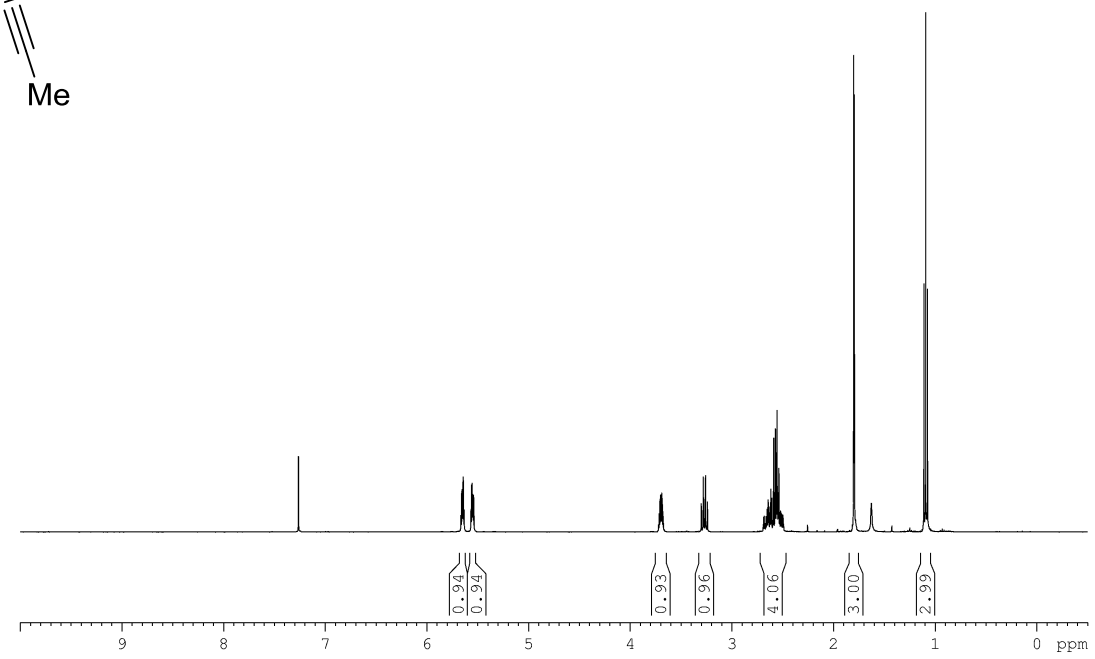

O
N−O
Me

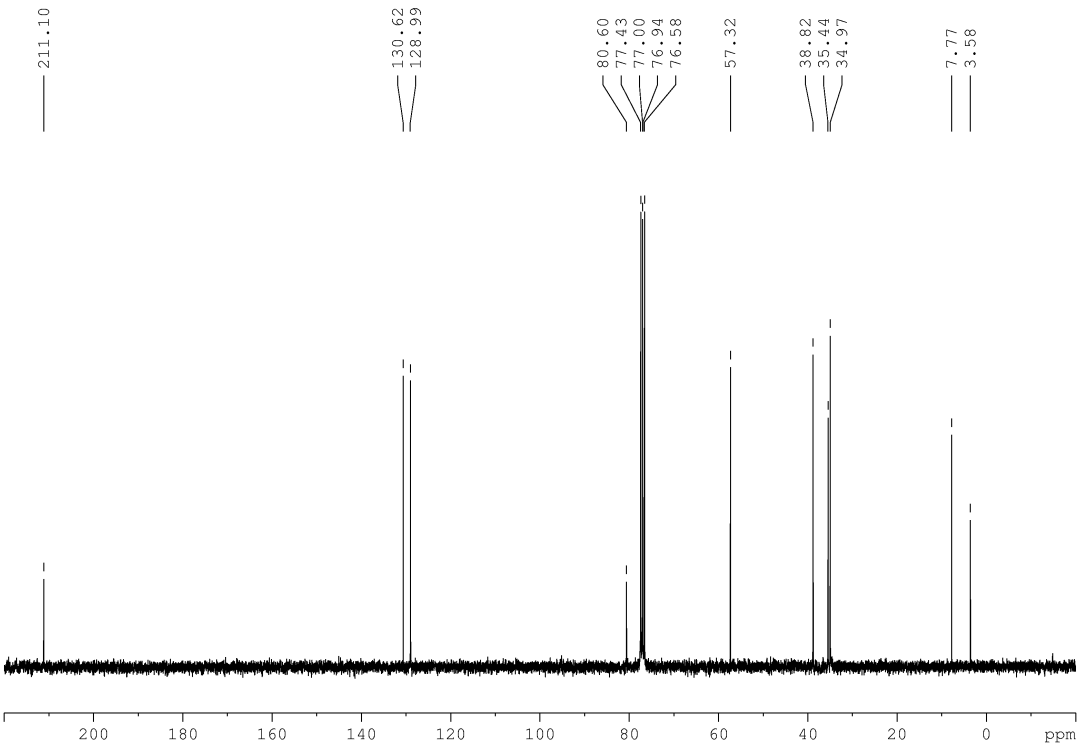

1.00
1.08
0.99
3.44
0.97
3.60
1.15
1.18
3.30
9
8
7
6
5
4
3
2
1
0
ppm

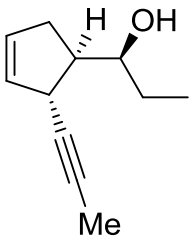

175.48
131.00
128.81
80.76
77.32
77.01
76.81
76.69
61.57
47.25
39.88
36.85
32.32
3.54

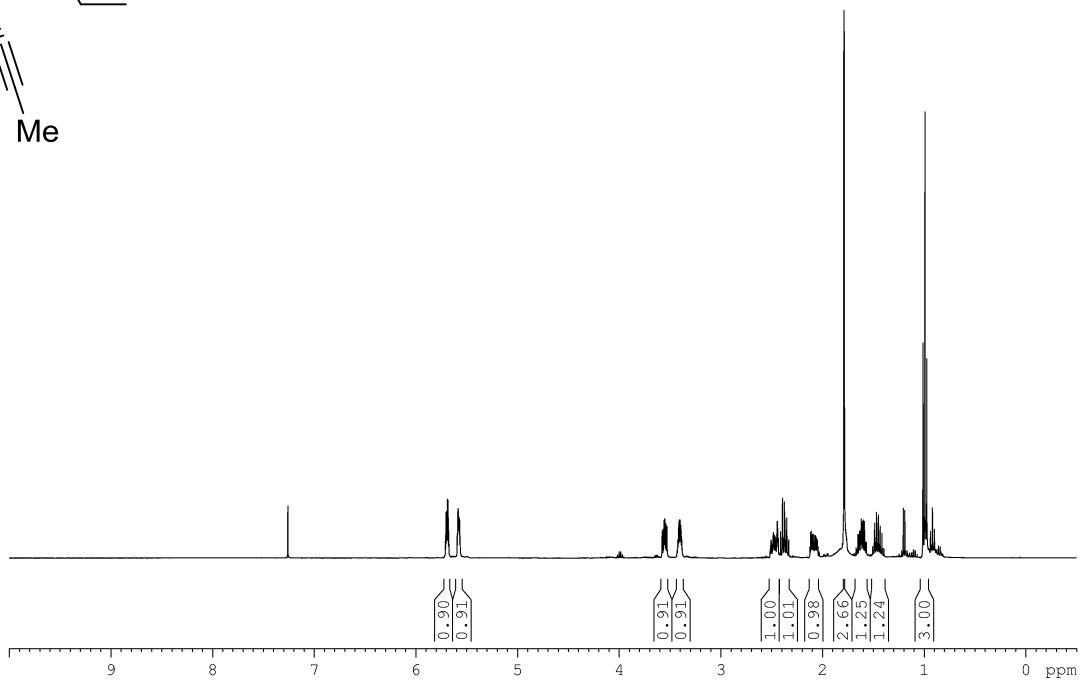

200
180
160
140
120
100
80
60
40
20
0
ppm

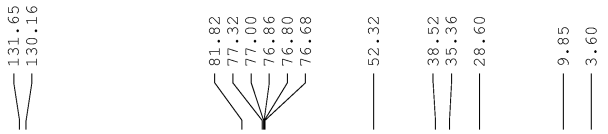

O
Me

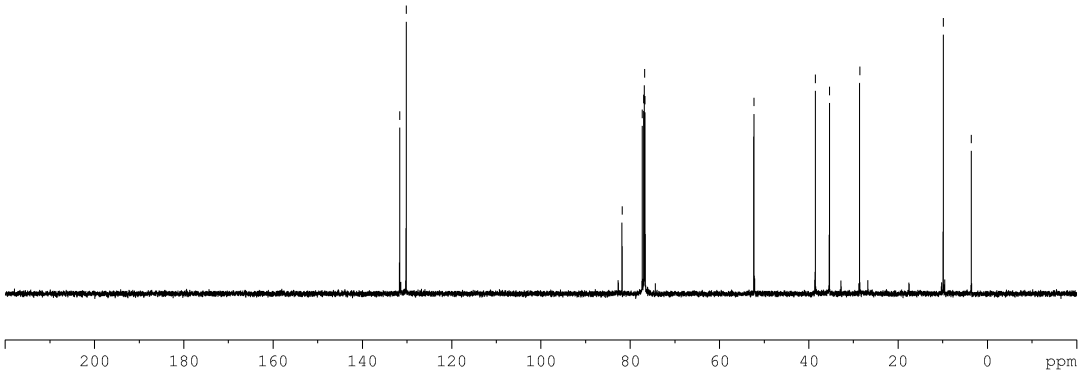

0.94
0.94
0.93
0.96
4.06
3.00
2.99
9
8
7
6
5
4
3
2
1
0
ppm

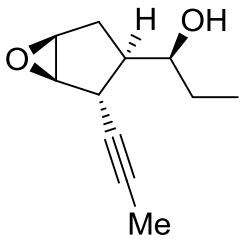

211.10
130.62
128.99
80.60
77.43
77.00
76.94
76.58
57.32
38.82
35.44
34.97
7.77
3.58
200
180
160
140
120
100
80
60
40
20
0
ppm

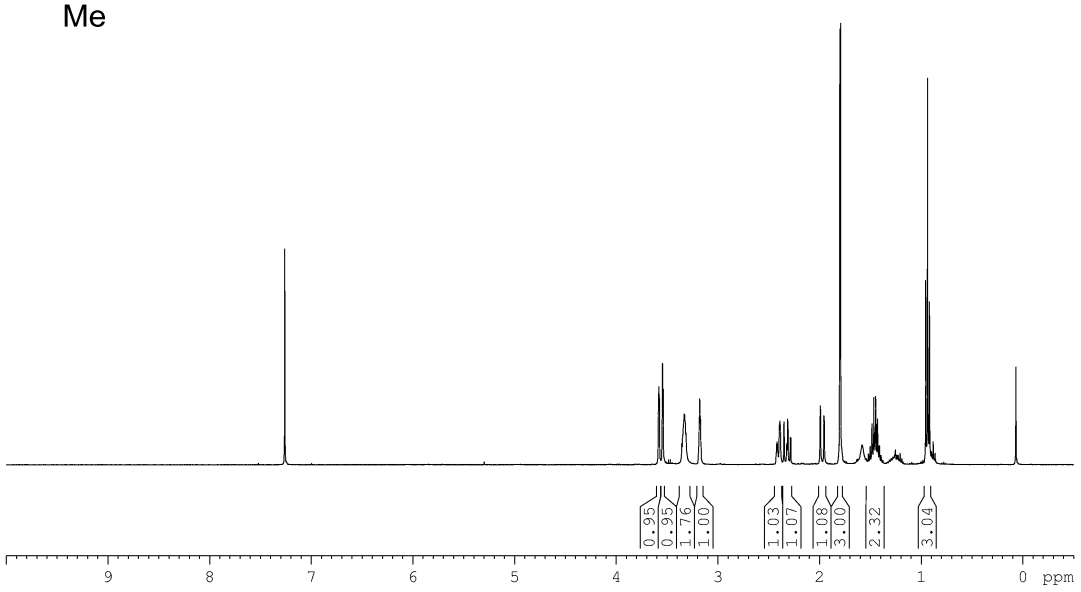

H
OH
Me

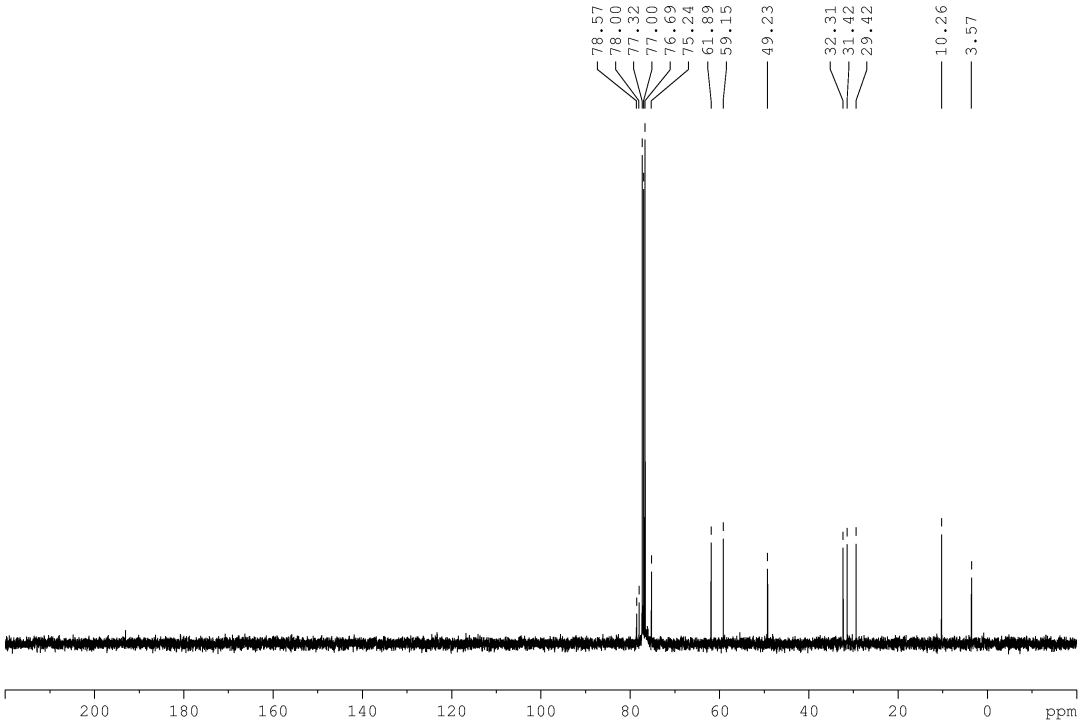

0.90
0.91
0.91
0.91
1.00
1.01
0.98
2.66
1.25
1.24
3.00
9 8 7 6 5 4 3 2 1 0 ppm

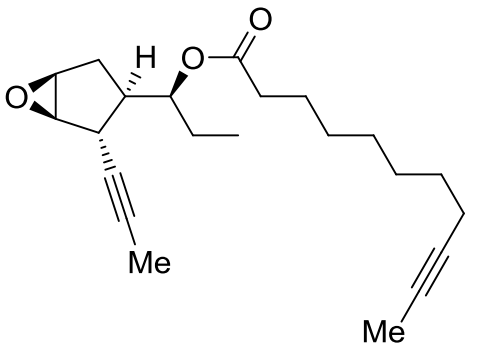

131.65
130.16
81.82
77.32
77.00
76.86
76.80
76.68
52.32
38.52
35.36
28.60
9.85
3.60


200 180 160 140 120 100 80 60 40 20 0 ppm

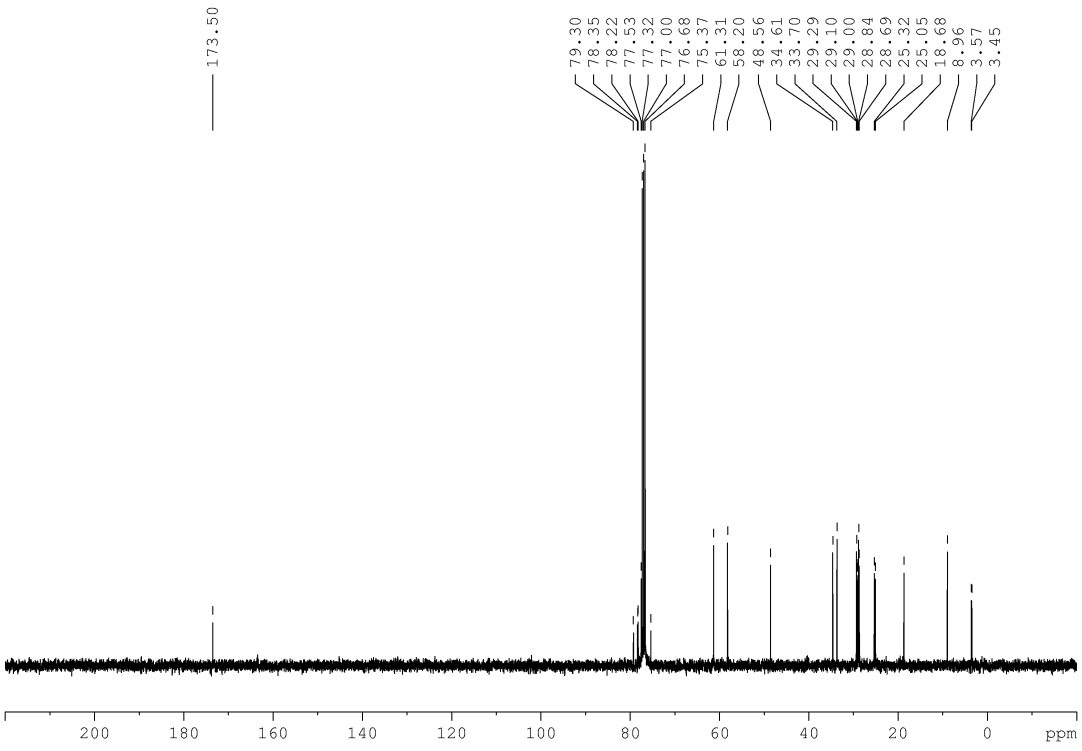

H
OH
O
Me

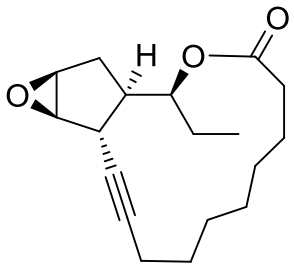

0.95
0.95
1.76
1.00
1.03
1.07
1.08
3.00
2.32
3.04
9
8
7
6
5
4
3
2
1
0
ppm


78.57
78.00
77.32
77.00
76.69
75.24
61.89
59.15
49.23
32.31
31.42
29.42
10.26
3.57
200
180
160
140
120
100
80
60
40
20
0
ppm

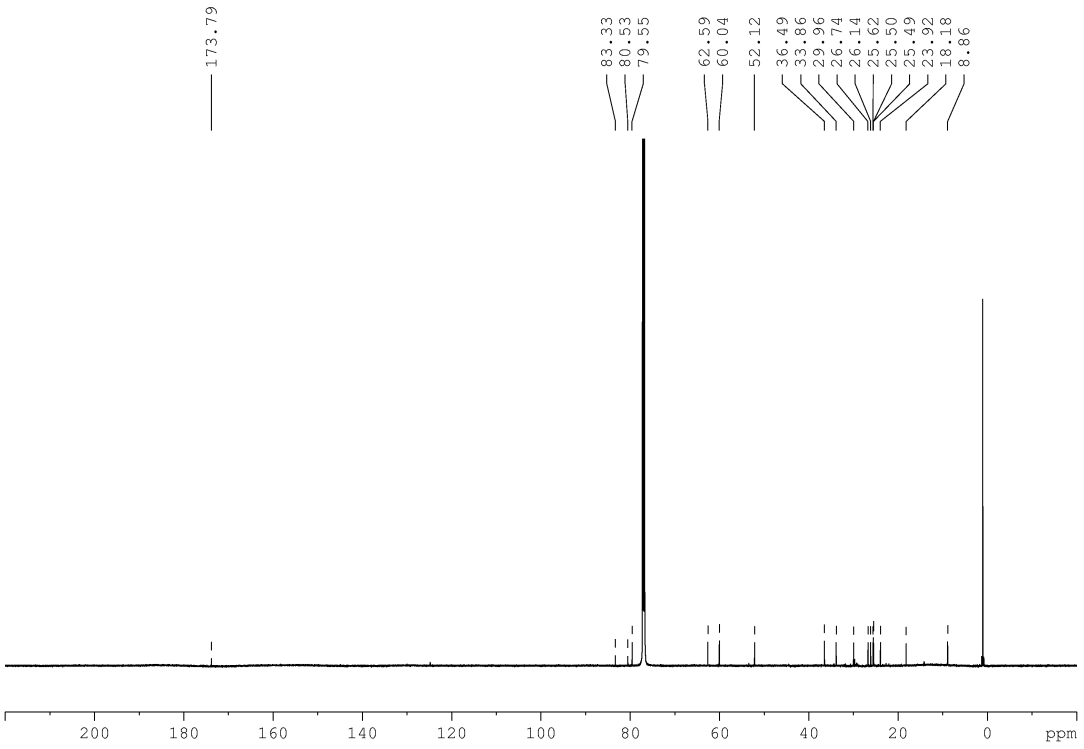

O
H
O
O
Me
Me

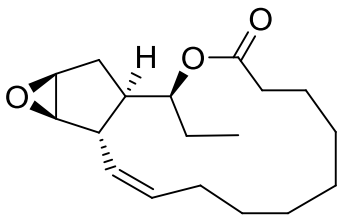

1.00
0.95
0.94
0.95
1.07
1.96
3.03
1.03
2.92
3.03
3.35
9.38
3.13
9
8
7
6
5
4
3
2
1
0 ppm

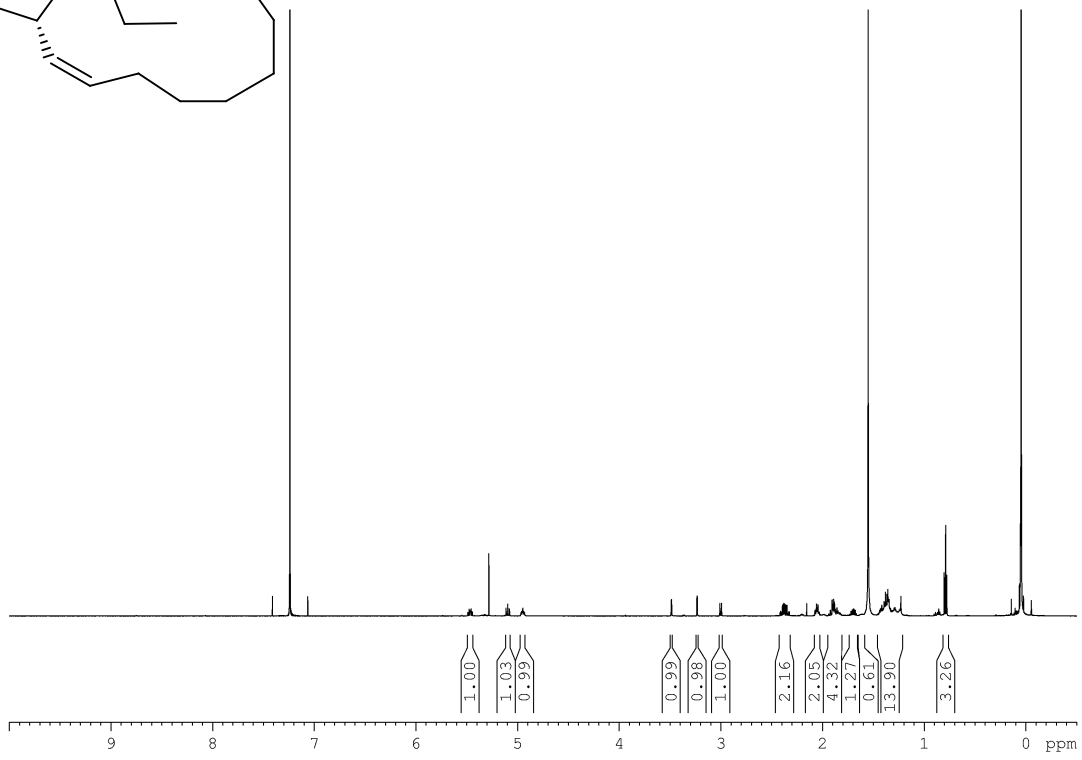

173.50
79.30
78.35
78.22
77.53
77.32
77.00
76.68
75.37
61.31
58.20
48.56
34.61
33.70
29.29
29.10
29.00
28.84
28.69
25.32
25.05
18.68
8.96
3.57
3.45
200
180
160
140
120
100
80
60
40
20
0
ppm

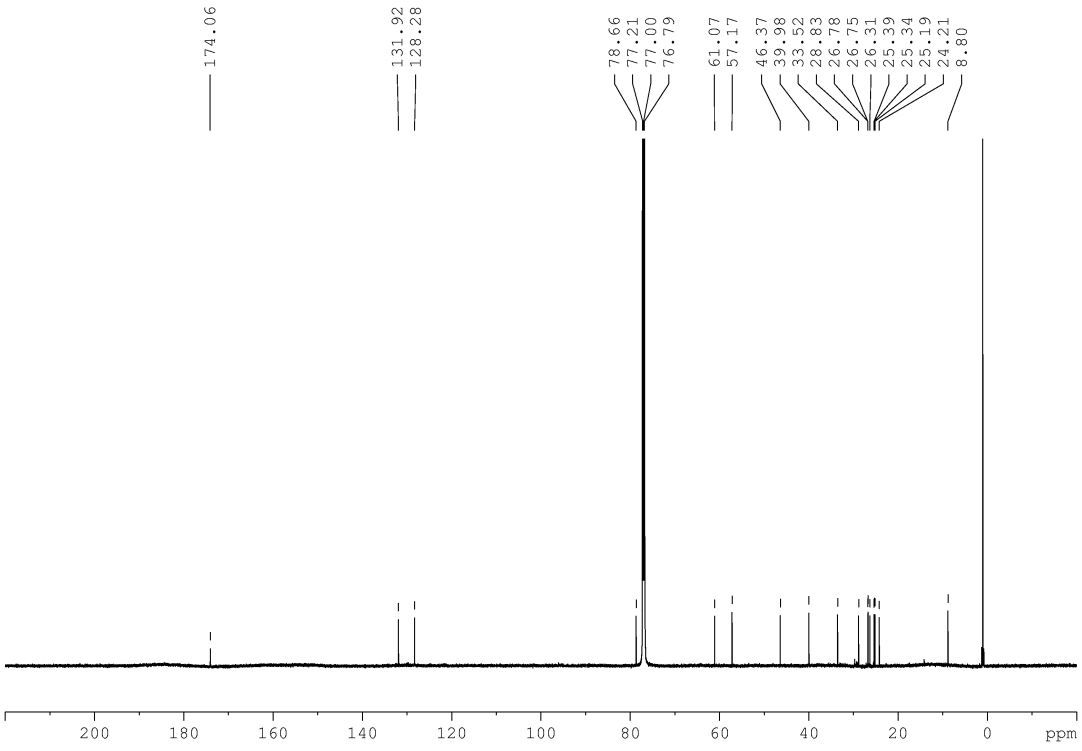

O
H
O
O

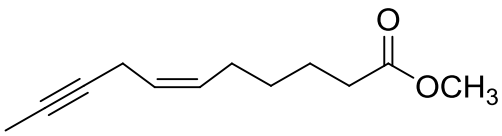

9
8
7
6
5
4
3
2
1
0
ppm

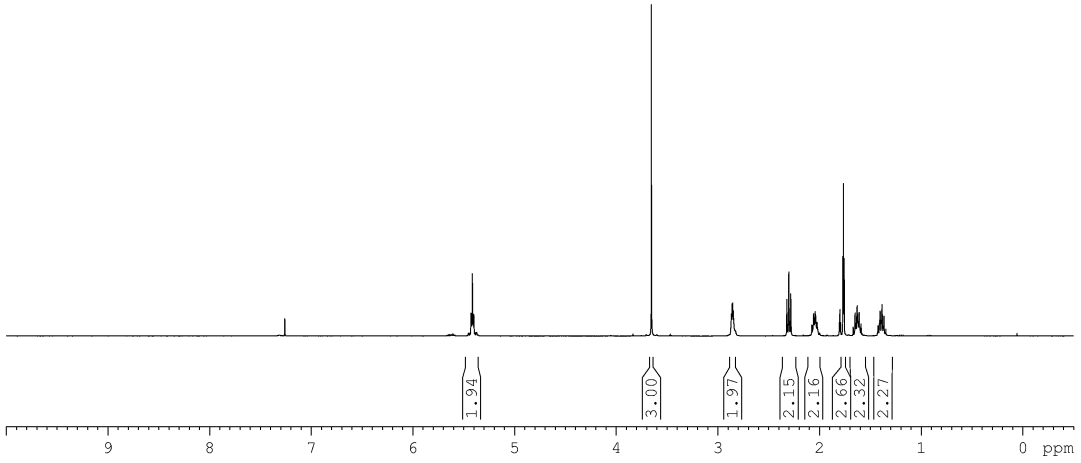

173.79
83.33
80.53
79.55
62.59
60.04
52.12
36.49
33.86
29.96
26.74
26.14
25.62
25.50
25.49
23.92
18.18
8.86
200
180
160
140
120
100
80
60
40
20
0
ppm

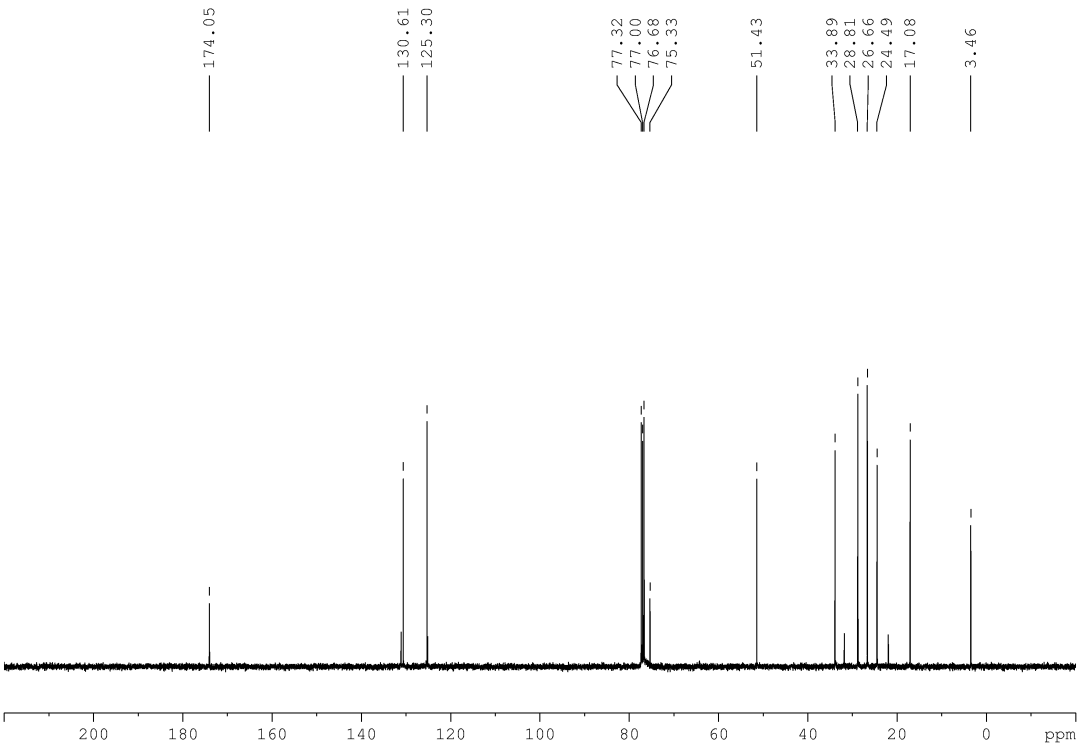

O
H
O
O

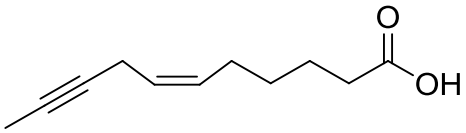

1.00
1.03
0.99
0.99
0.98
1.00
2.16
2.05
4.32
1.27
0.61
13.90
3.26
9
8
7
6
5
4
3
2
1
0
ppm

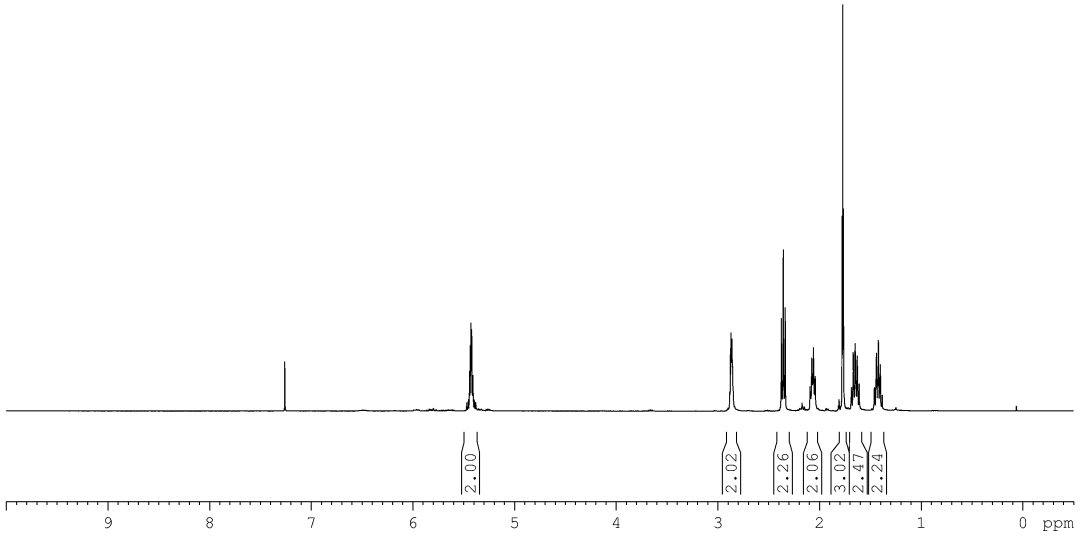

174.06
131.92
128.28
78.66
77.21
77.00
76.79
61.07
57.17
46.37
39.98
33.52
28.83
26.78
26.75
26.31
25.39
25.34
25.19
24.21
8.80
200
180
160
140
120
100
80
60
40
20
0
ppm

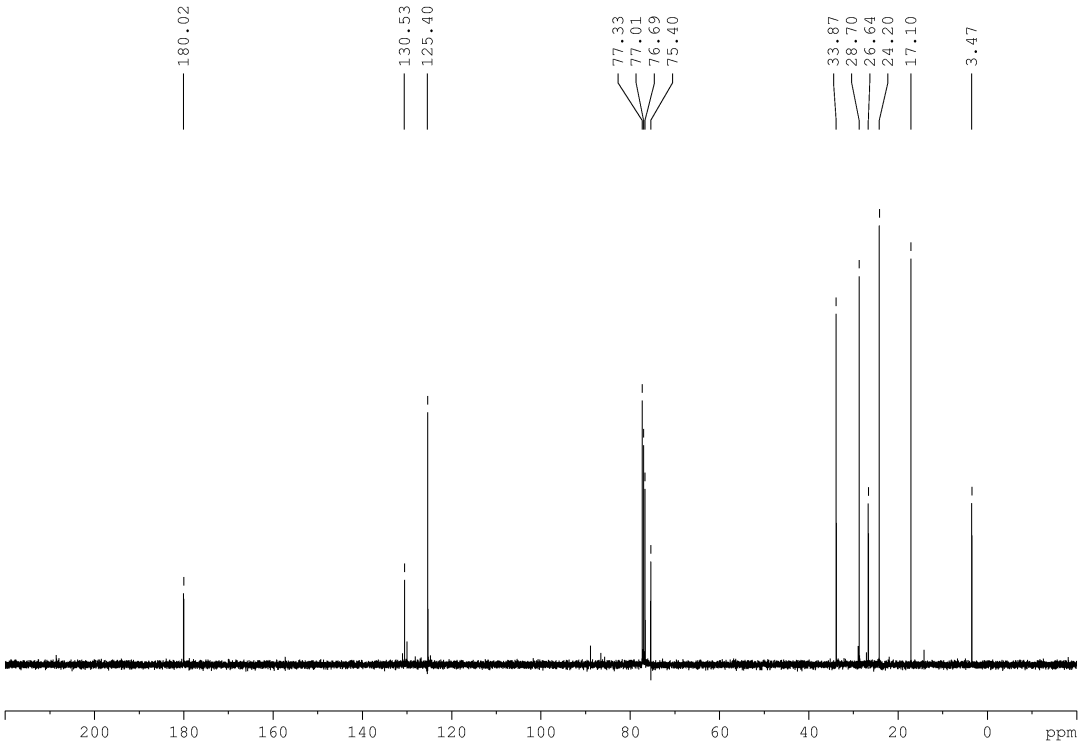

O
OCH3

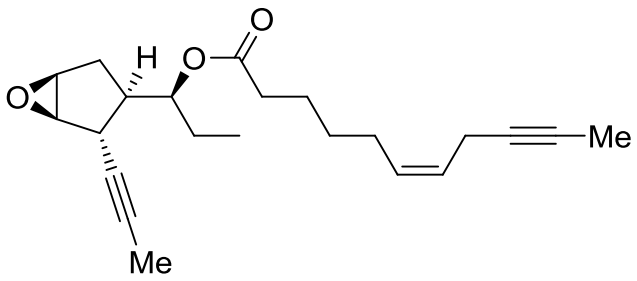

1.94
3.00
1.97
2.15
2.16
2.66
2.32
2.27
9
8
7
6
5
4
3
2
1
0
ppm

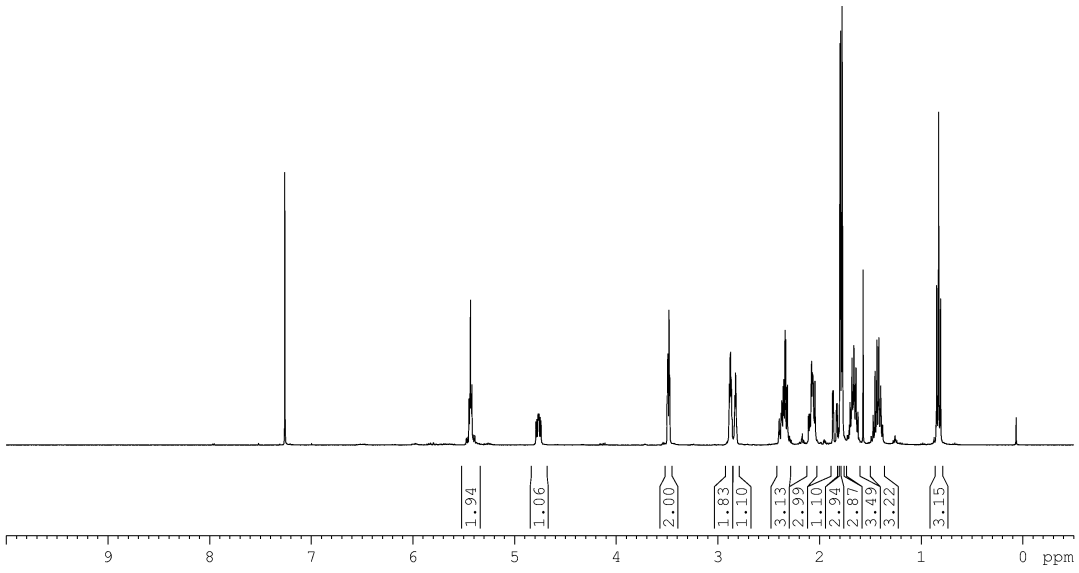

174.05
130.61
125.30
77.32
77.00
76.68
75.33
51.43
33.89
28.81
26.66
24.49
17.08
3.46
200
180
160
140
120
100
80
60
40
20
0
ppm

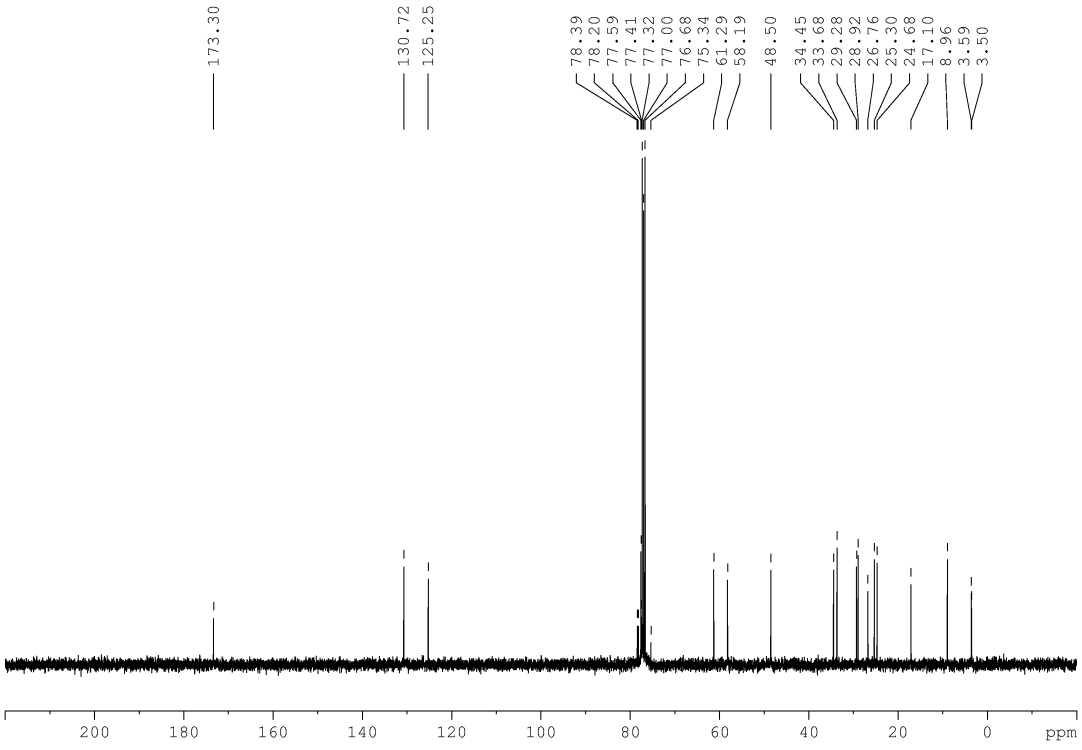

O
OH

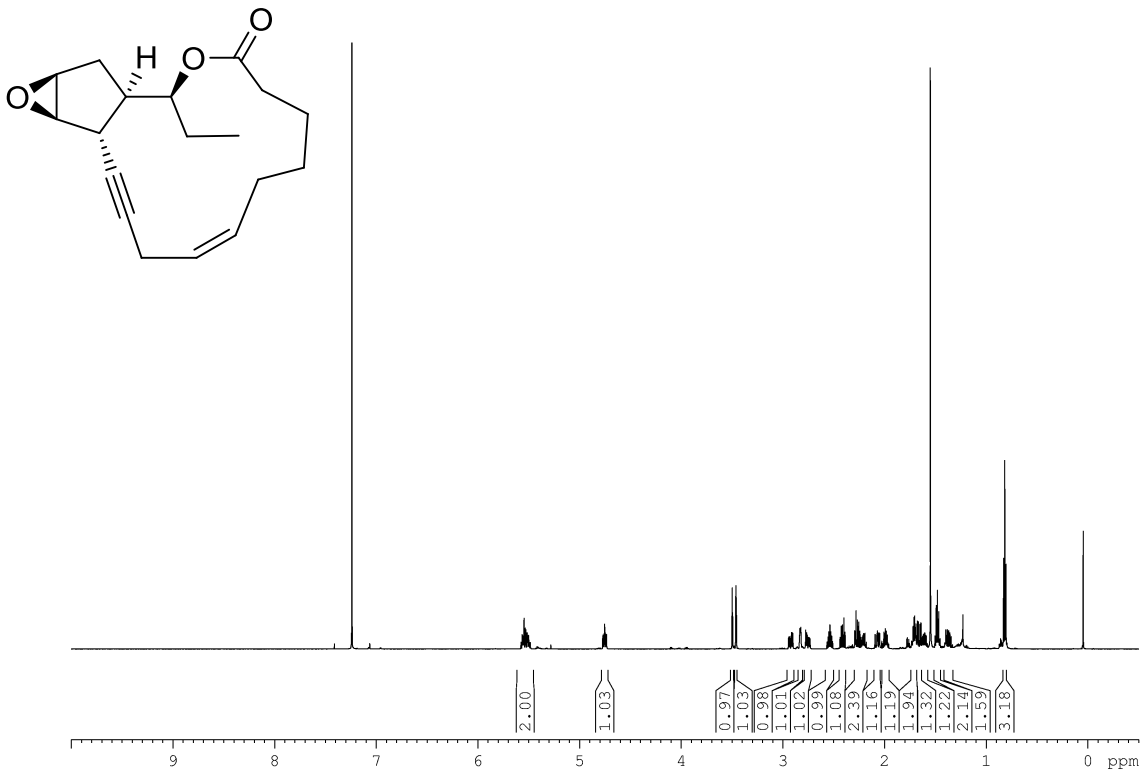

2.00
2.02
2.26
2.06
3.02
2.47
2.24
9
8
7
6
5
4
3
2
1
0
ppm

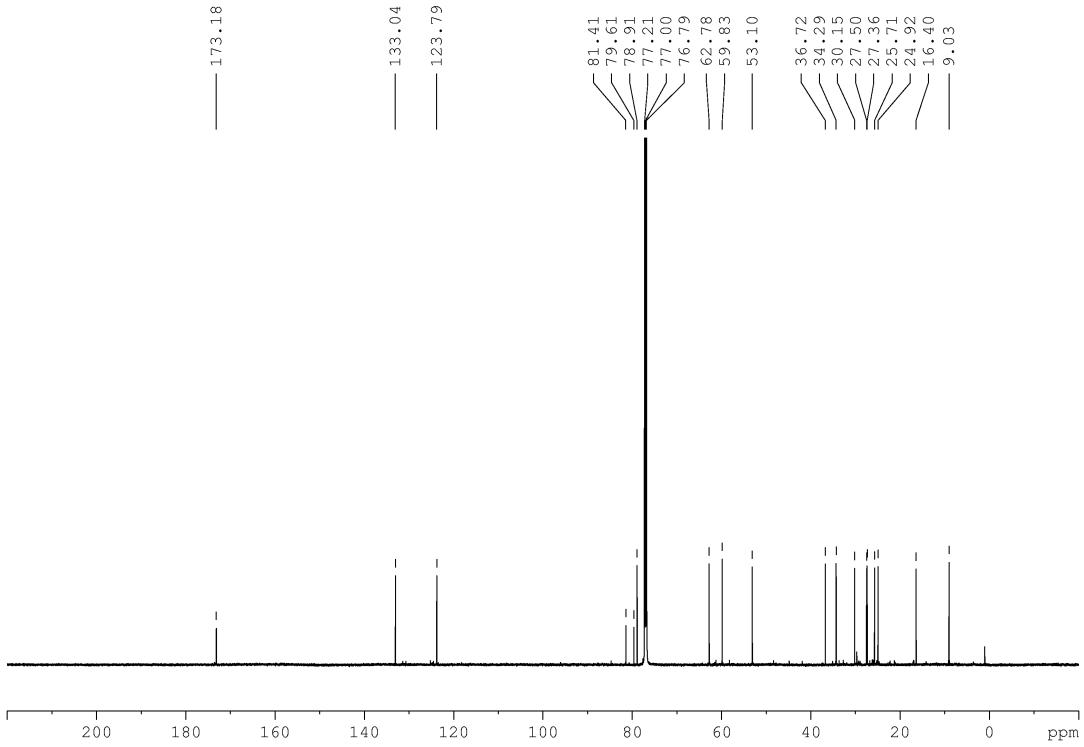

180.02
130.53
125.40
77.33
77.01
76.69
75.40
33.87
28.70
26.64
24.20
17.10
3.47
200
180
160
140
120
100
80
60
40
20
0
ppm

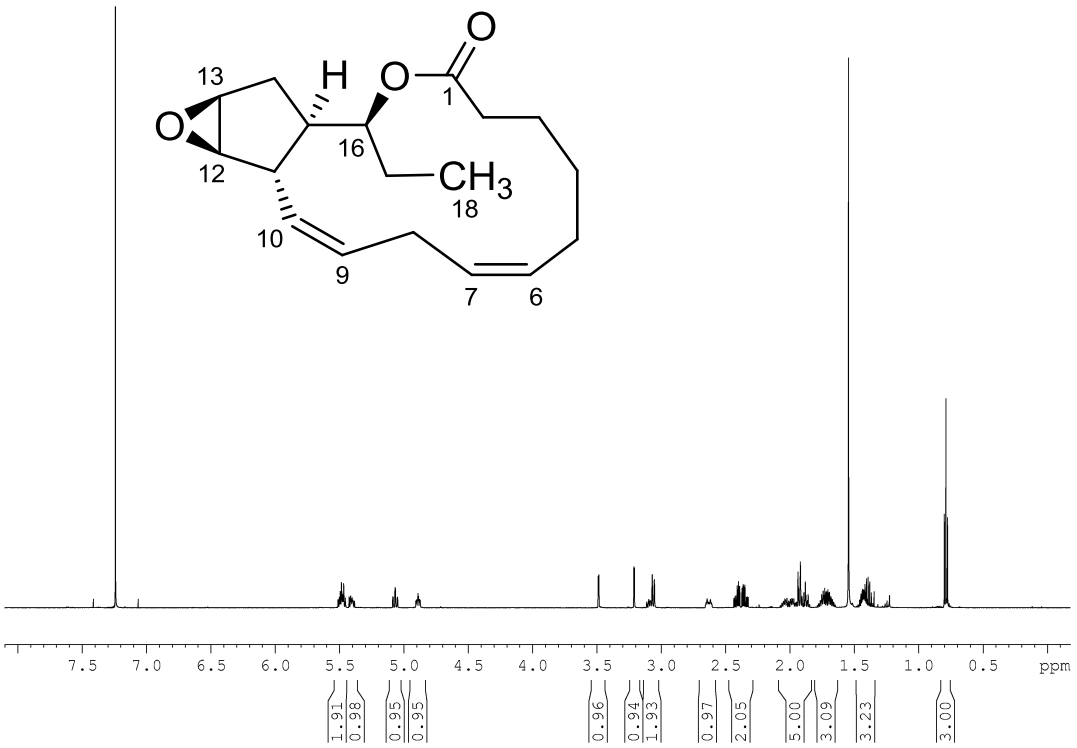

O
H
O
O
Me
Me

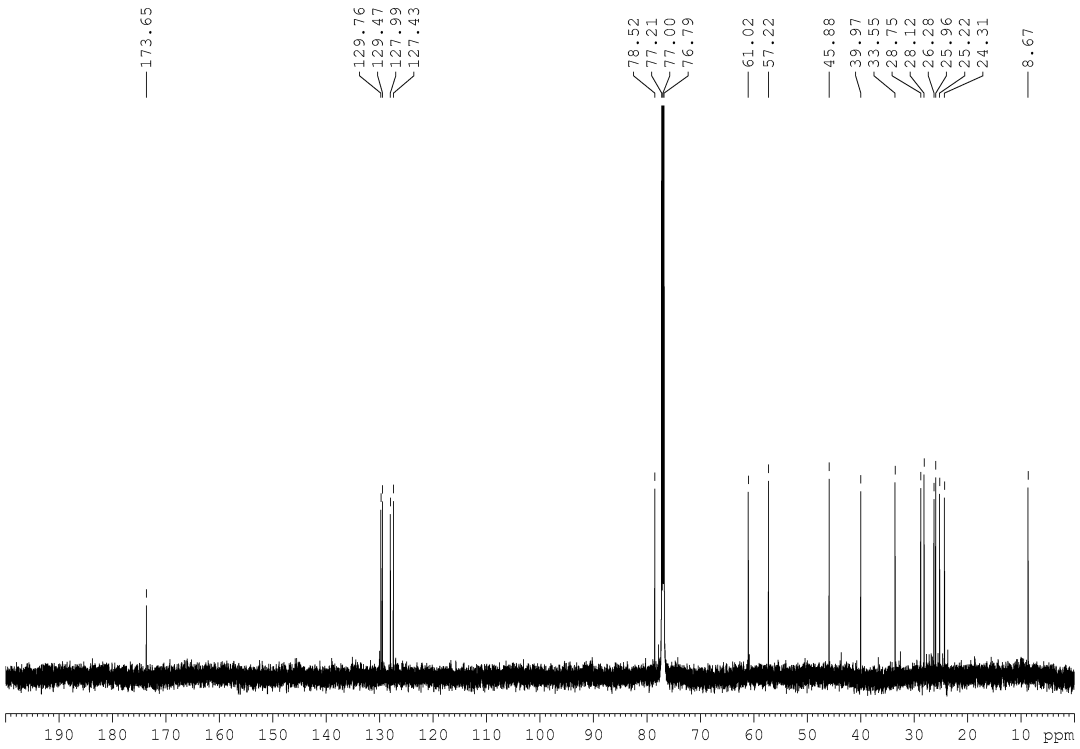

1.94
1.06
2.00
1.83
1.10
3.13
2.99
1.10
2.94
2.87
3.49
3.22
3.15
9
8
7
6
5
4
3
2
1
0
ppm

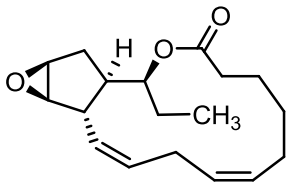

173.30
130.72
125.25
78.39
78.20
77.59
77.41
77.32
77.00
76.68
75.34
61.29
58.19
48.50
34.45
33.68
29.28
28.92
26.76
25.30
24.68
17.10
8.96
3.59
3.50
200
180
160
140
120
100
80
60
40
20
0
ppm


O
H
O
O
2.00
1.03
0.97
1.03
0.98
1.01
1.02
0.99
1.08
2.39
1.16
1.19
1.94
1.32
1.22
2.14
1.59
3.18
9
8
7
6
5
4
3
2
1
0
ppm

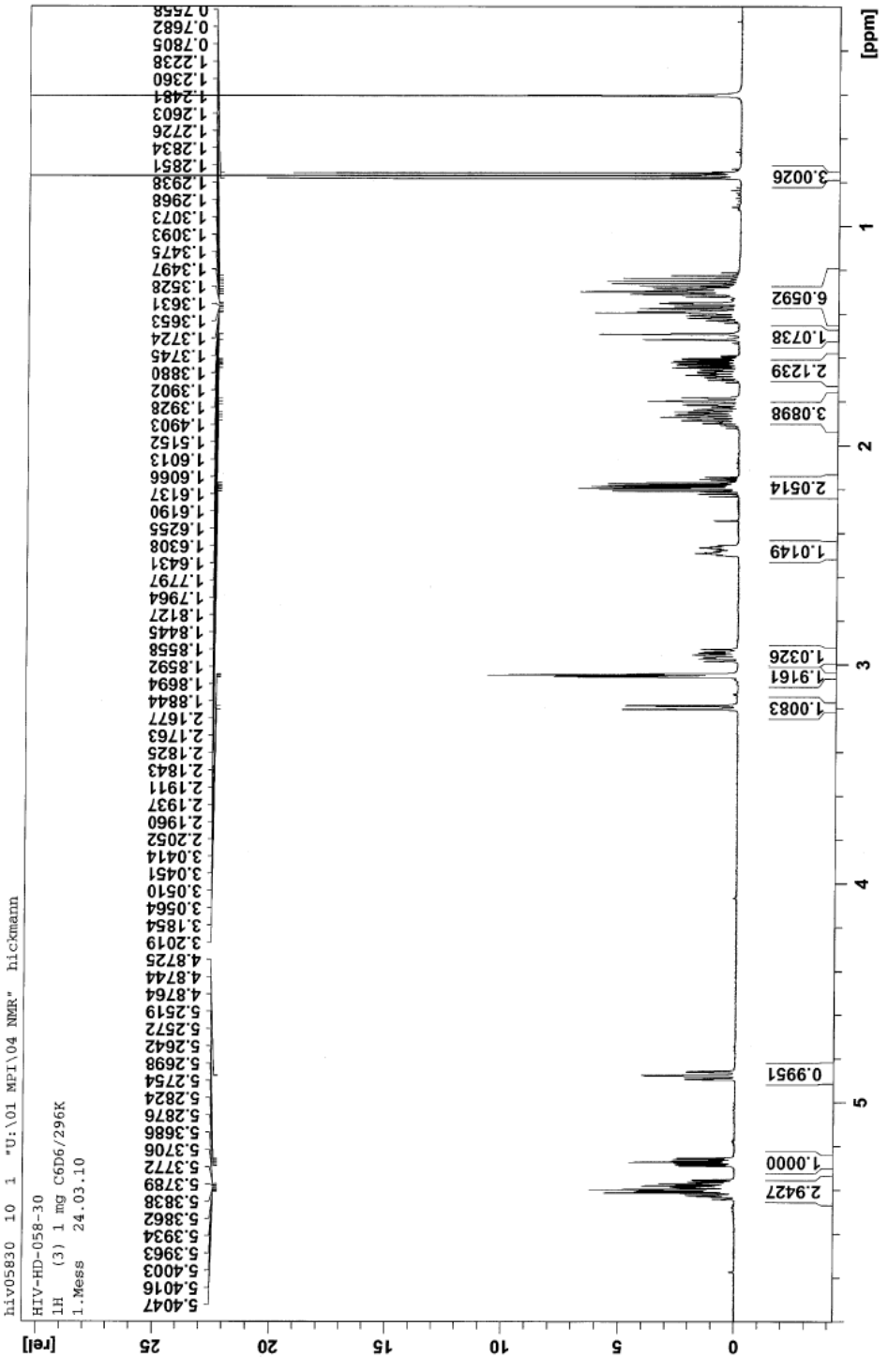

173.18
133.04
123.79
81.41
79.61
78.91
77.21
77.00
76.79
62.78
59.83
53.10
36.72
34.29
30.15
27.50
27.36
25.71
24.92
16.40
9.03
200
180
160
140
120
100
80
60
40
20
0
ppm

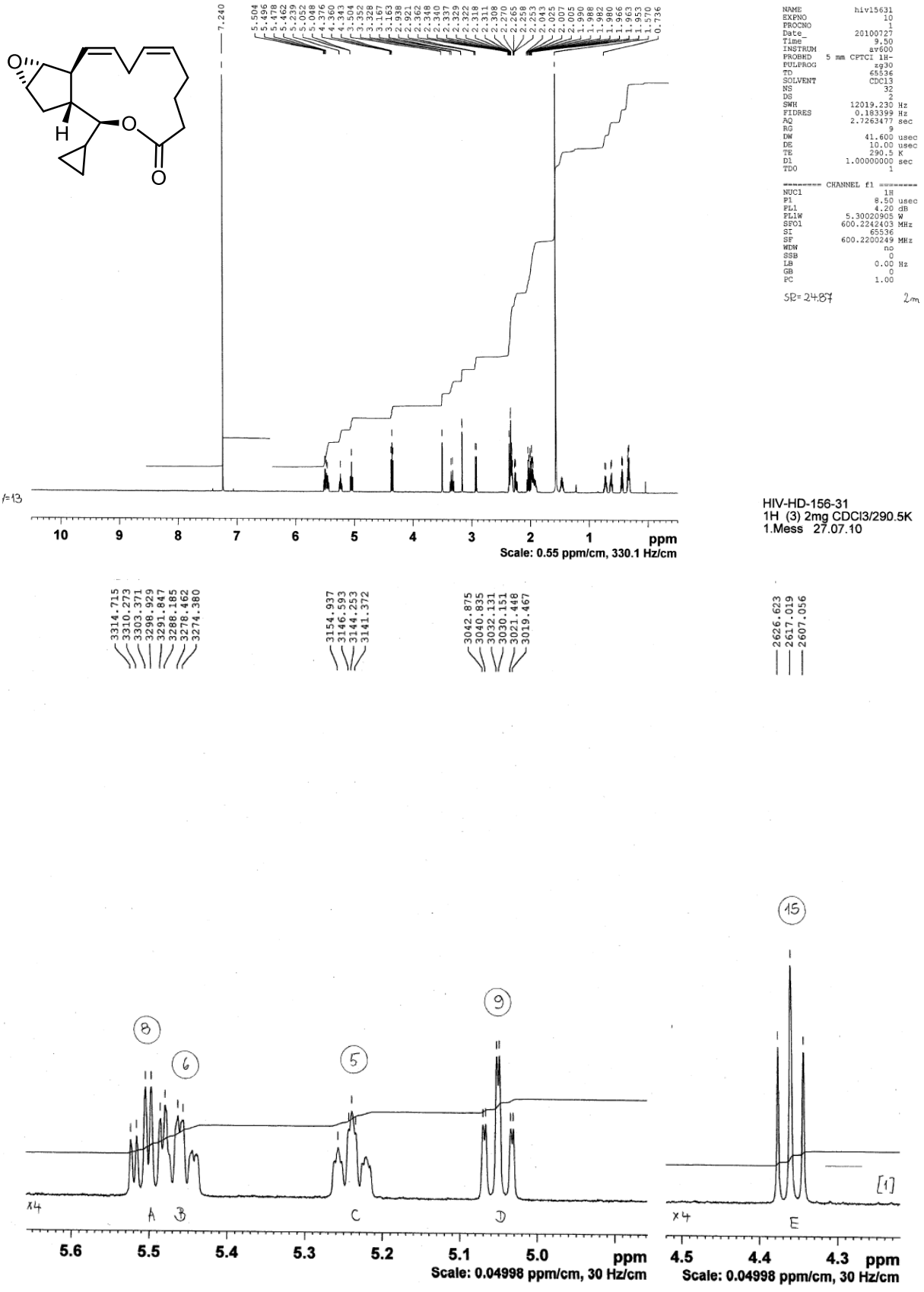

O
13
H
O
1
O
16
12
CH3
18
10
9
7
6
7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 ppm
1.91 0.98 0.95 0.95 0.96 0.94 1.93 0.97 2.05 5.00 3.09 3.23 3.00

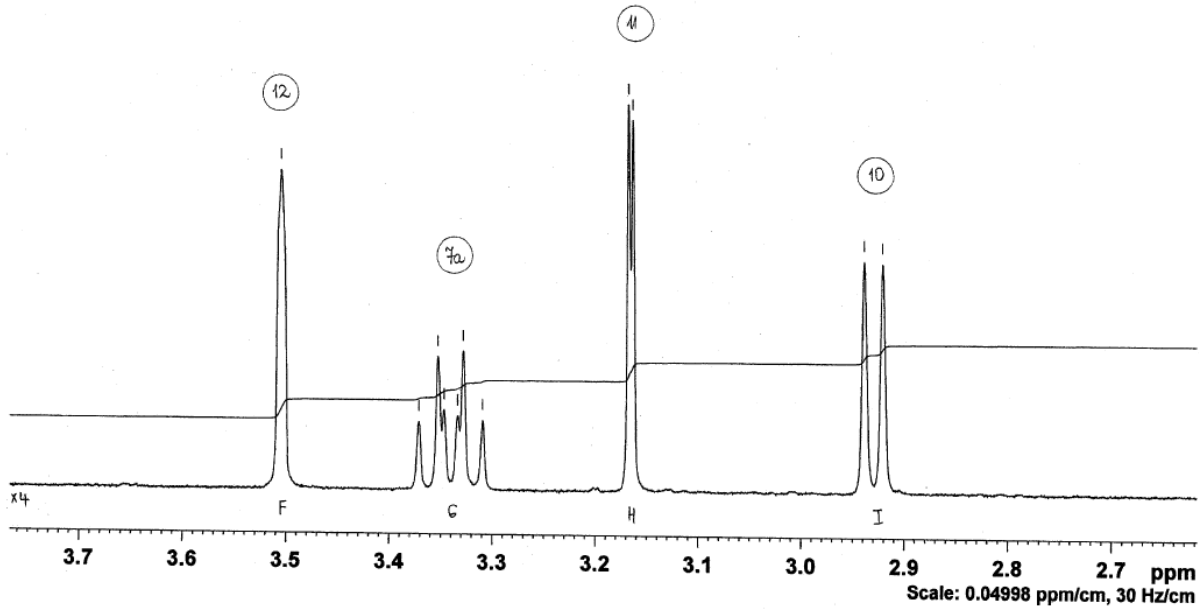

173.65
129.76
129.47
127.99
127.43
78.52
77.21
77.00
76.79
61.02
57.22
45.88
39.97
33.55
28.75
28.12
26.28
25.96
25.22
24.31
8.67
190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 ppm

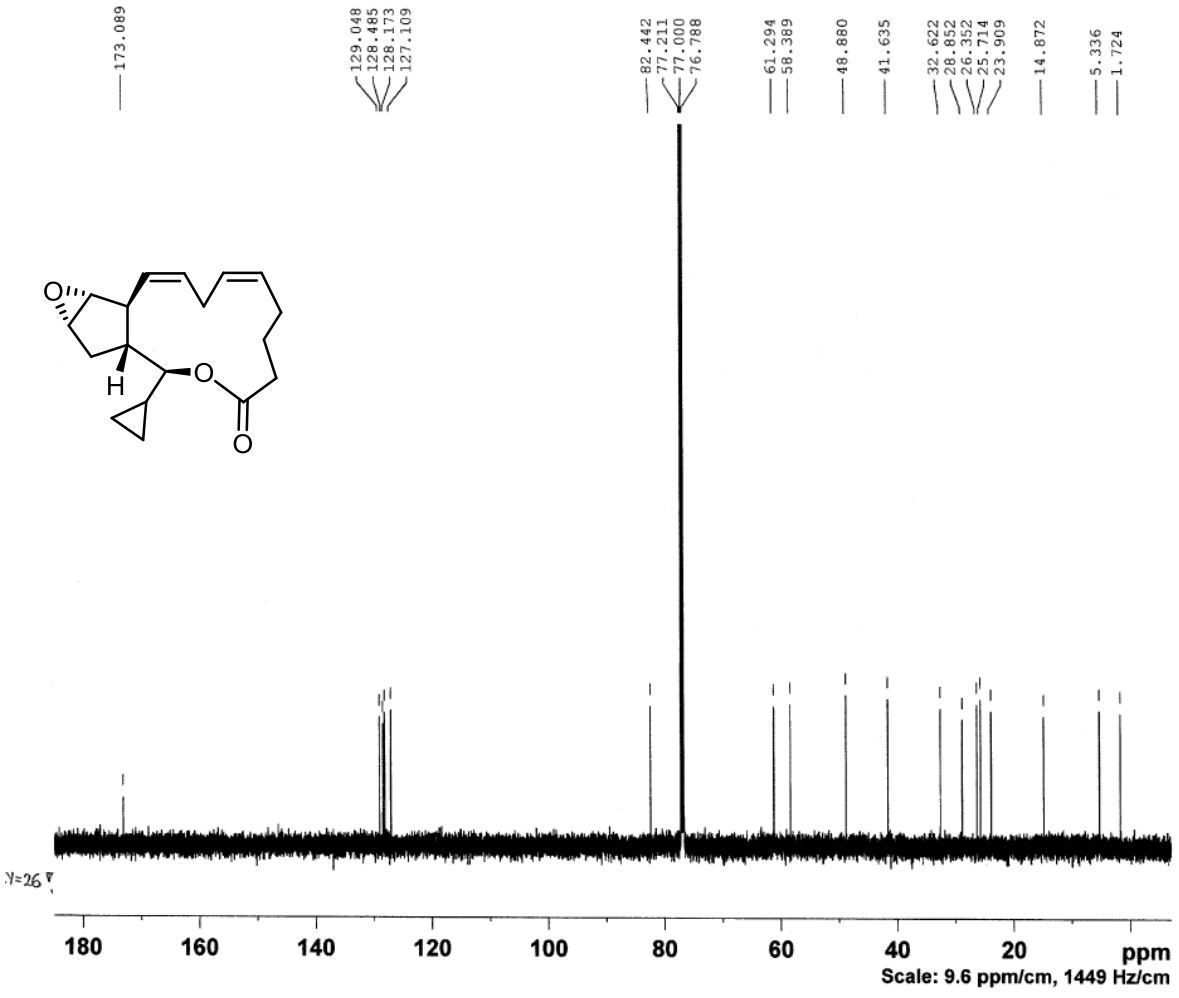

H
O
O
O
CH3

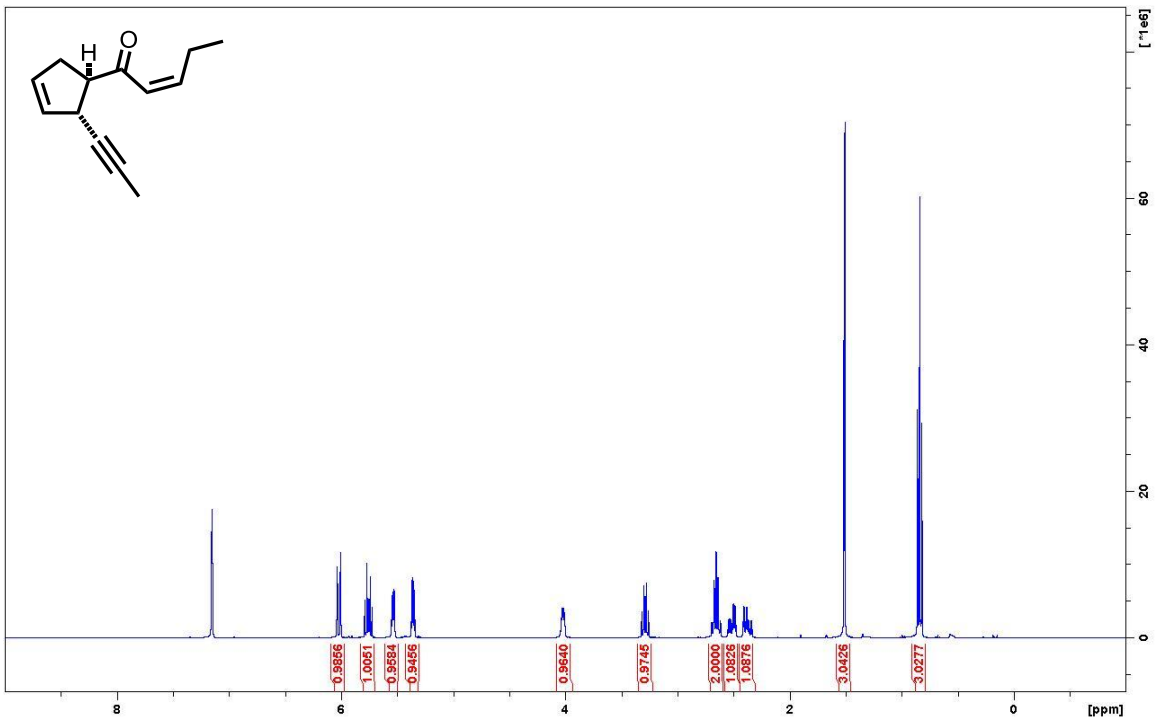
in $C_6D_6$

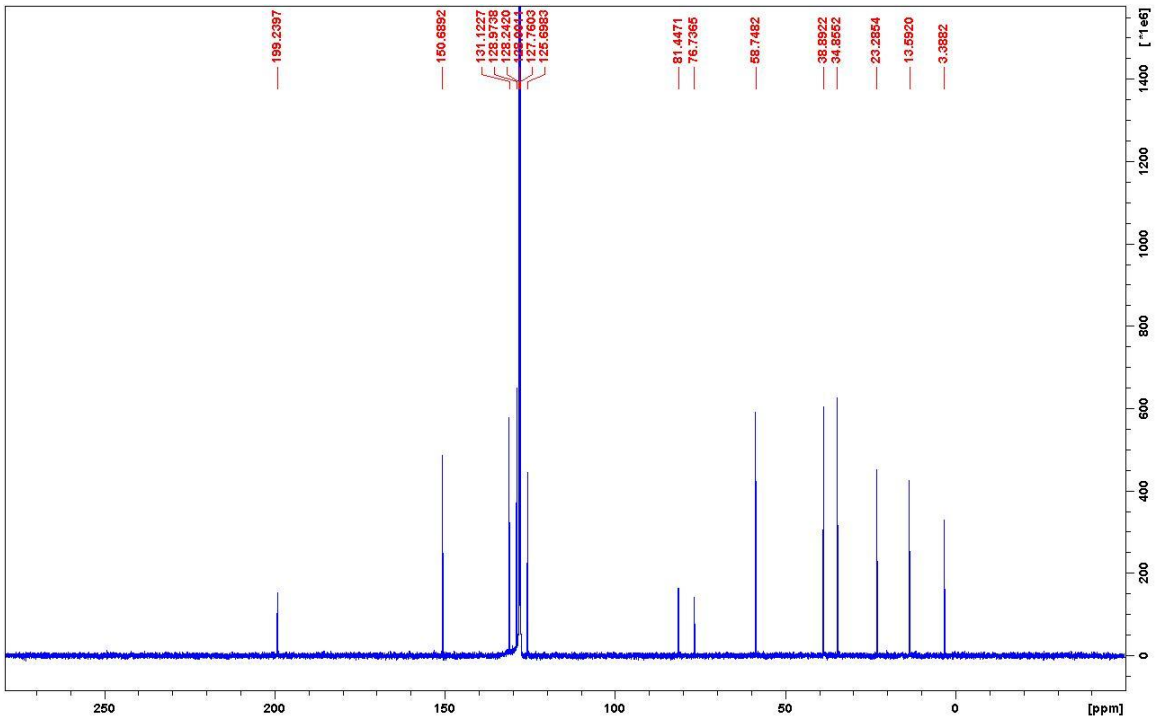

hiv05830 10 1 "U:\01 MPI\04 NMR" hickmann
HIV-HD-058-30
1H (3) 1 mg C6D6/296K
1.Mess 24.03.10
[rel]
[ppm]
3.0026
6.0592
1.0738
2.1239
3.0898
2.0514
1.0149
1.0326
1.9161
1.0083
0.9951
1.0000
2.9427

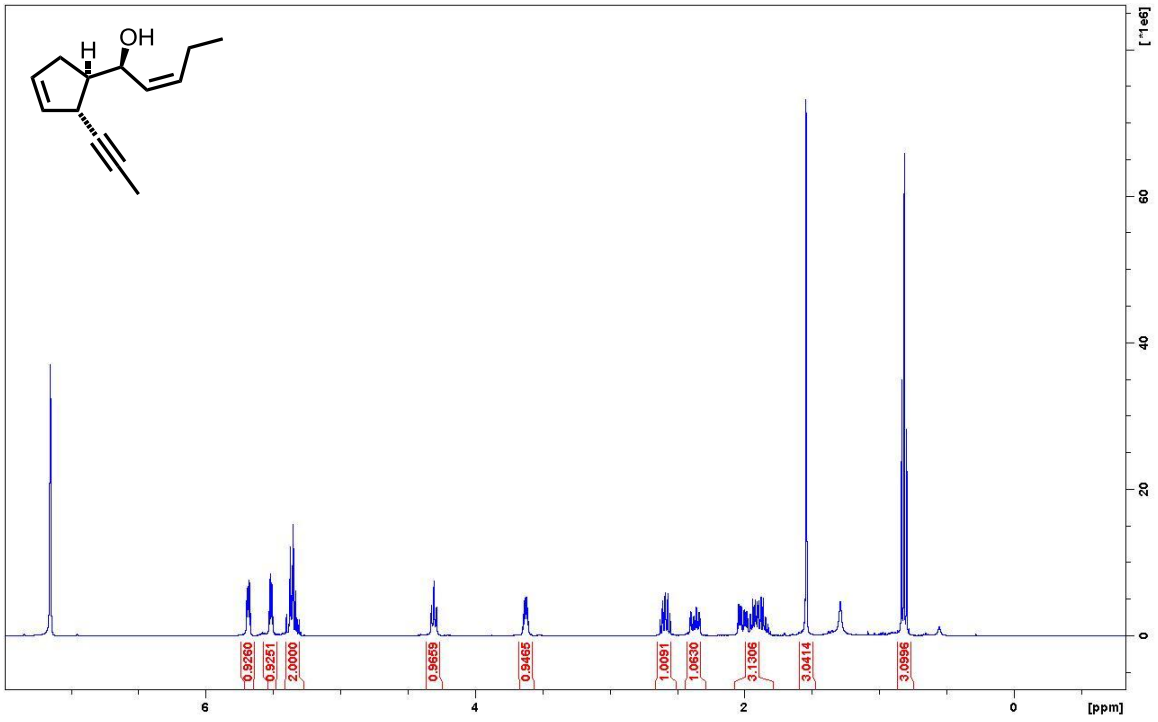

NAME hiv15631
EXPNO 10
PROCNO 1
Date_ 20100727
Time 9.50
INSTRUM av600
PROBHD 5 mm CPTCI 1H-
PULPROG zg30
TD 65536
SOLVENT CDCl3
NS 32
DS 2
SWH 12019.230 Hz
FIDRES 0.183399 Hz
AQ 2.7263477 sec
RG 9
DW 41.600 usec
DE 10.00 usec
TE 290.5 K
D1 1.00000000 sec
TD0 1
CHANNEL f1
NUC1 1H
P1 8.50 usec
PL1 4.20 dB
PL1W 5.30020905 W
SFO1 600.2242403 MHz
SI 65536
SF 600.2200249 MHz
WDW no
SSB 0
LB 0.00 Hz
GB 0
PC 1.00
SP= 24.87
2m
HIV-HD-156-31
1H (3) 2mg CDCl3/290.5K
1.Mess 27.07.10
Scale: 0.55 ppm/cm, 330.1 Hz/cm
Scale: 0.04998 ppm/cm, 30 Hz/cm
Scale: 0.04998 ppm/cm, 30 Hz/cm

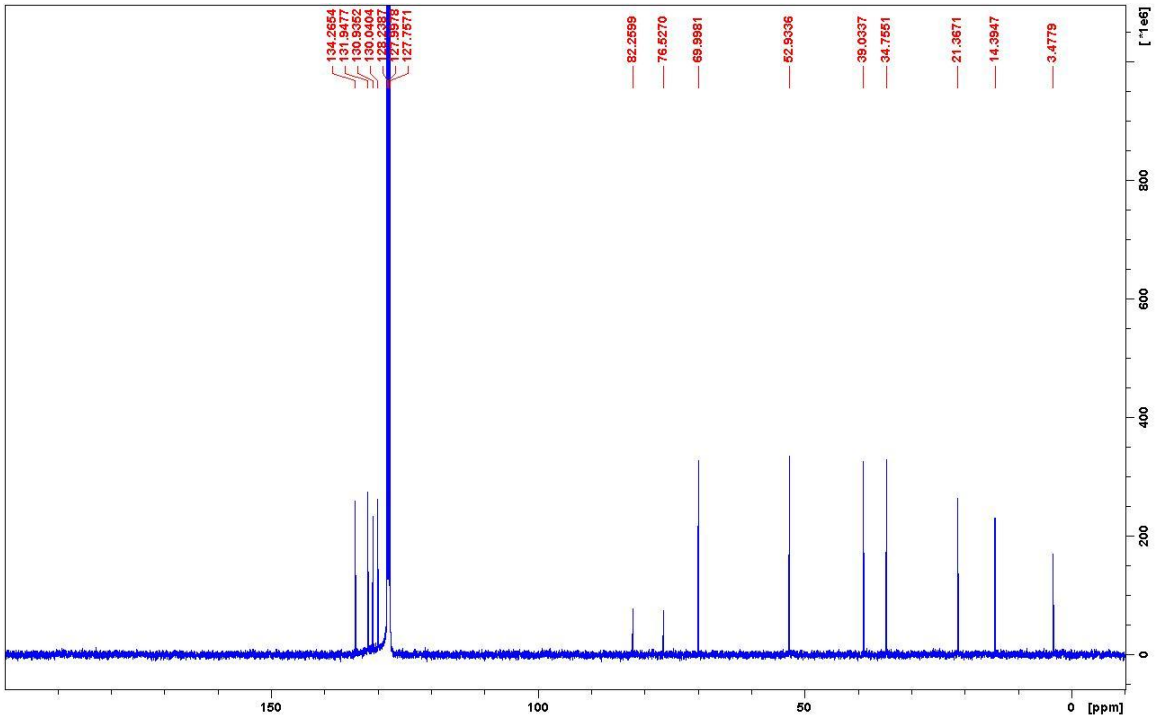

12
11
7a
10
x4
F
G
H
I
3.7
3.6
3.5
3.4
3.3
3.2
3.1
3.0
2.9
2.8
2.7
ppm
Scale: 0.04998 ppm/cm, 30 Hz/cm

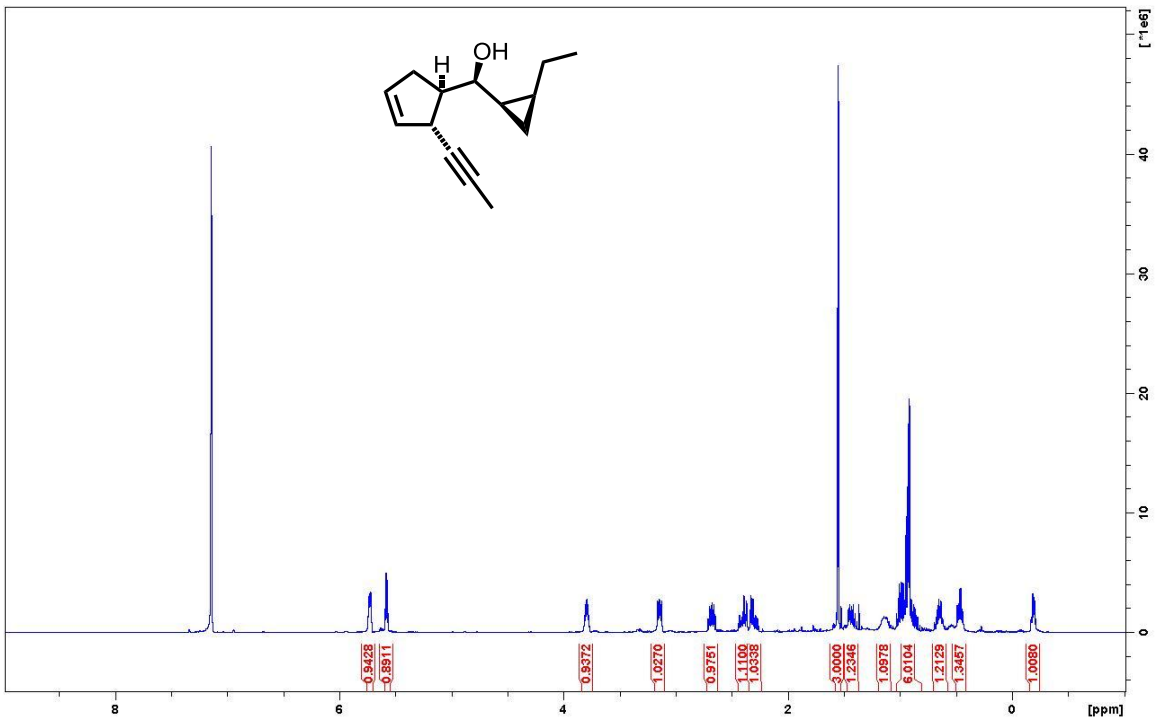

173.089
129.048
128.485
128.173
127.109
82.442
77.211
77.000
76.788
61.294
58.389
48.880
41.635
32.622
28.852
26.352
25.714
23.909
14.872
5.336
1.724
O
H
O
O
180
160
140
120
100
80
60
40
20
ppm
Scale: 9.6 ppm/cm, 1449 Hz/cm

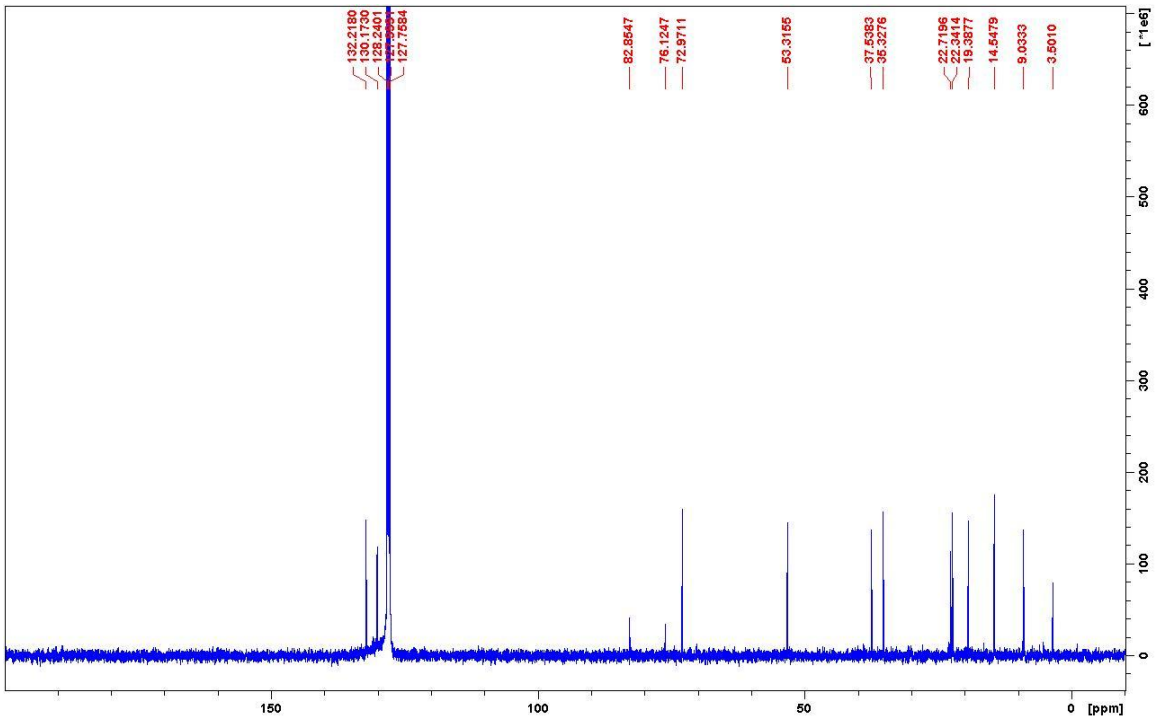

H
O
0.9856
1.0051
0.9584
0.9456
0.9640
0.9745
2.0000
1.0826
1.0876
3.0426
3.0277
8
6
4
2
0
[ppm]
[*1e6]

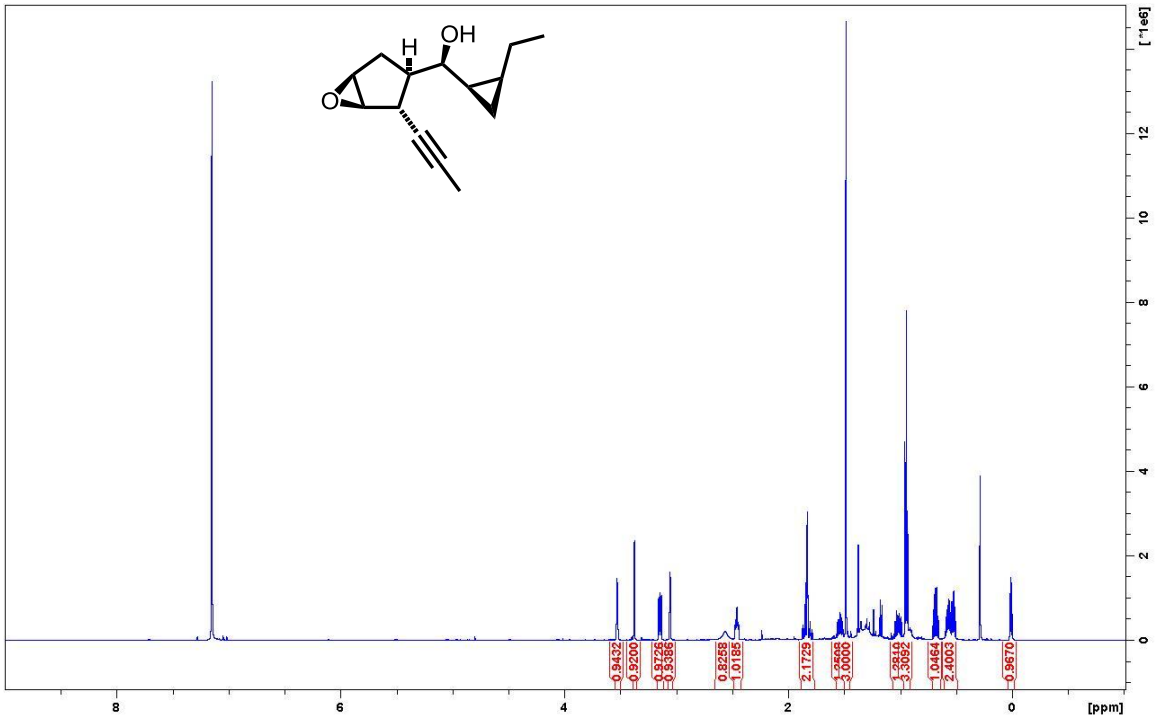

199.2397
150.6892
131.1227
128.9738
128.2420
127.7603
125.6583
81.4471
76.7365
58.7482
38.8922
34.8552
23.2854
13.5920
3.3882
250
200
150
100
50
0
[ppm]
[*1e6]

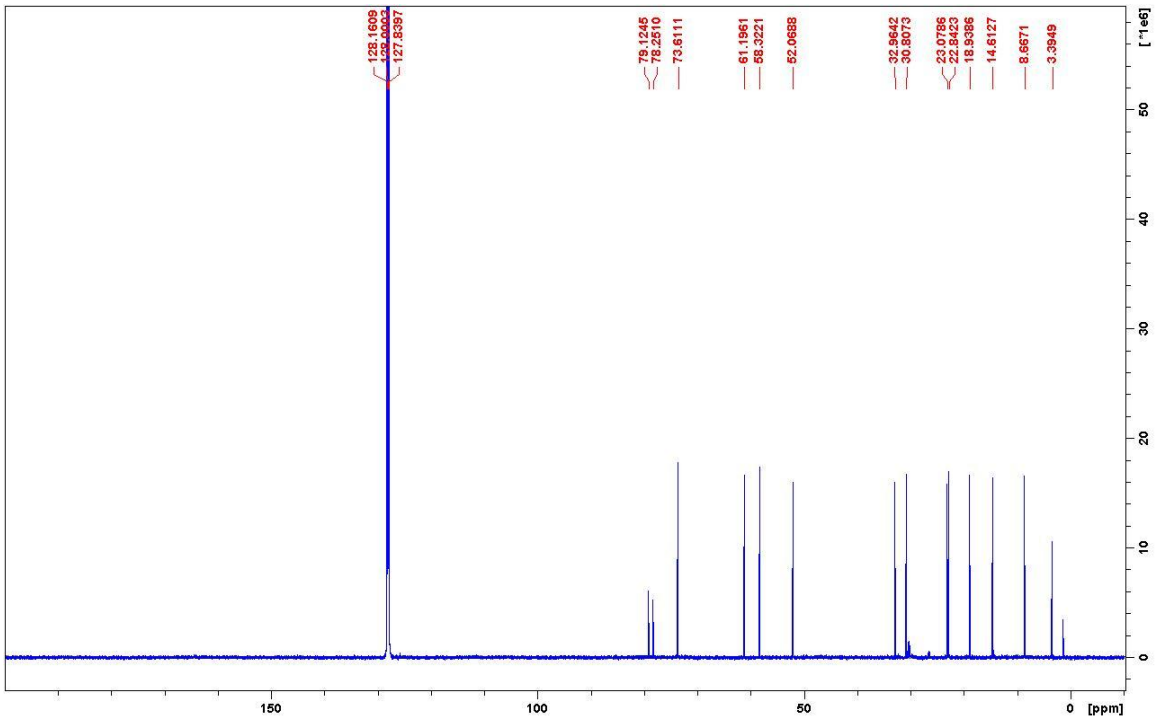

H
OH
0.9260
0.9251
2.0000
0.9659
0.9465
1.0091
1.0630
3.1306
3.0414
3.0956
6
4
2
0
[ppm]
[*1e6]

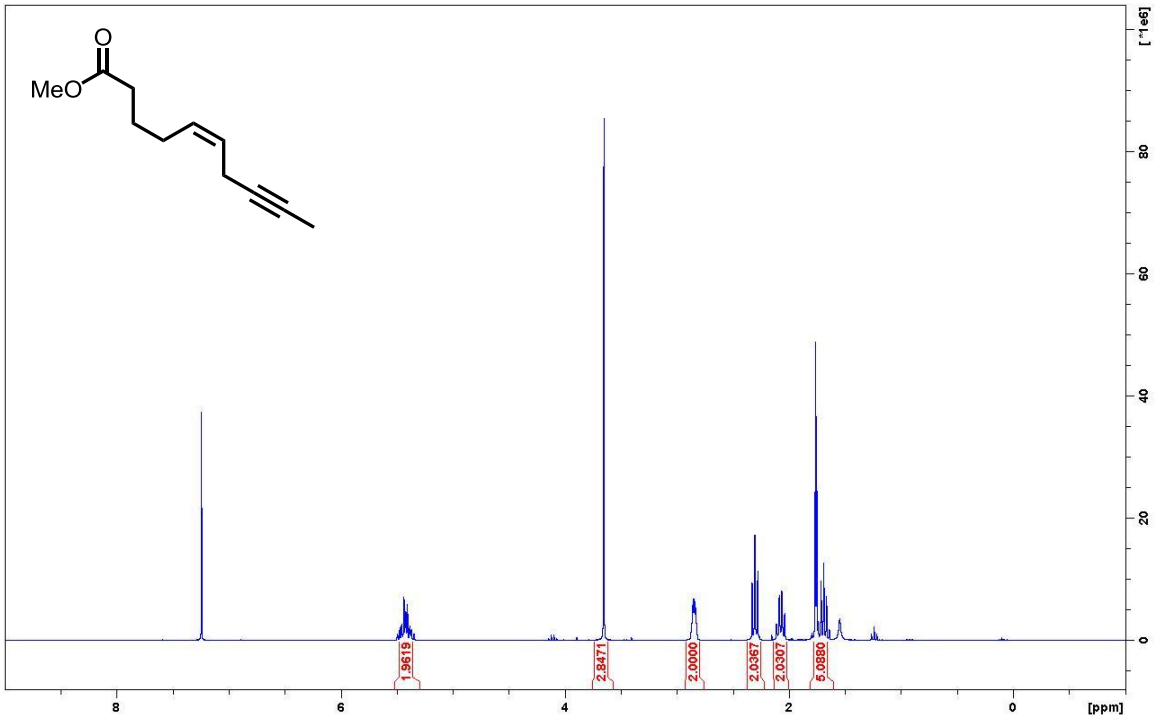

134.2654
131.9477
130.9362
130.0404
128.2387
127.9978
127.7671
82.2599
76.5270
69.9981
52.9336
39.0337
34.7551
21.3671
14.3947
3.4779
150
100
50
0
[ppm]
[*1e6]

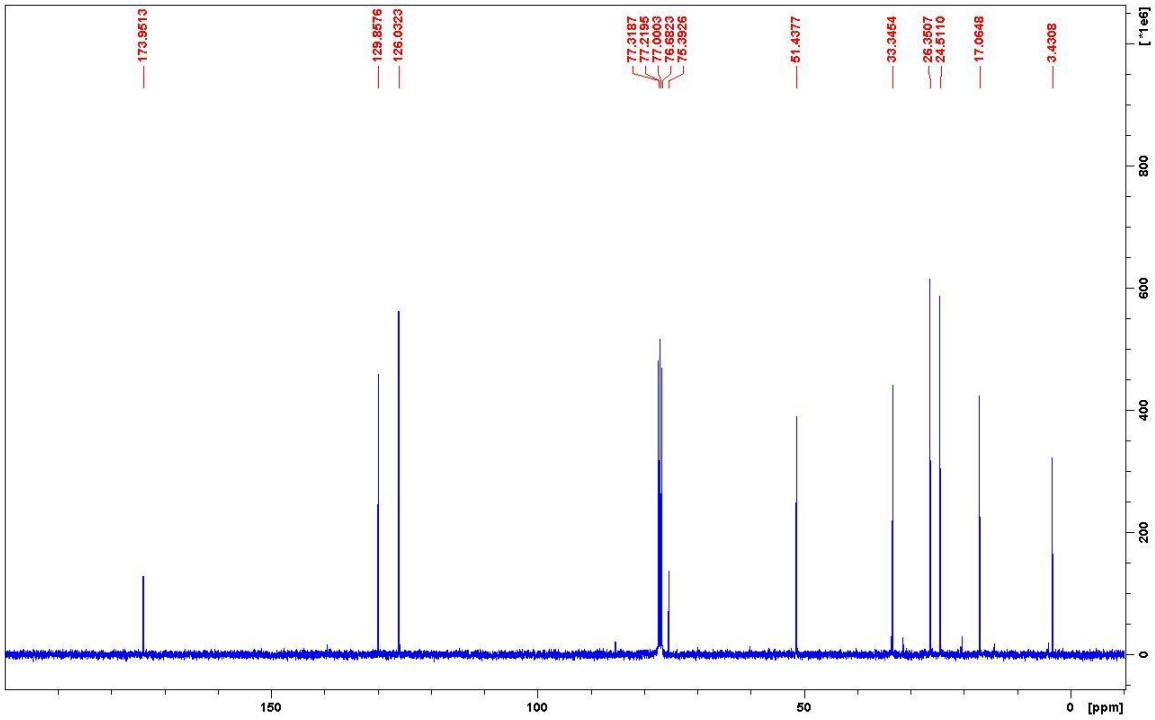

H
OH
0.9428
0.8911
0.9372
1.0270
0.9751
1.1100
1.0338
3.0000
1.2346
1.0978
6.0104
1.2129
1.3457
1.0060
8
6
4
2
0
[ppm]
[*1e6]

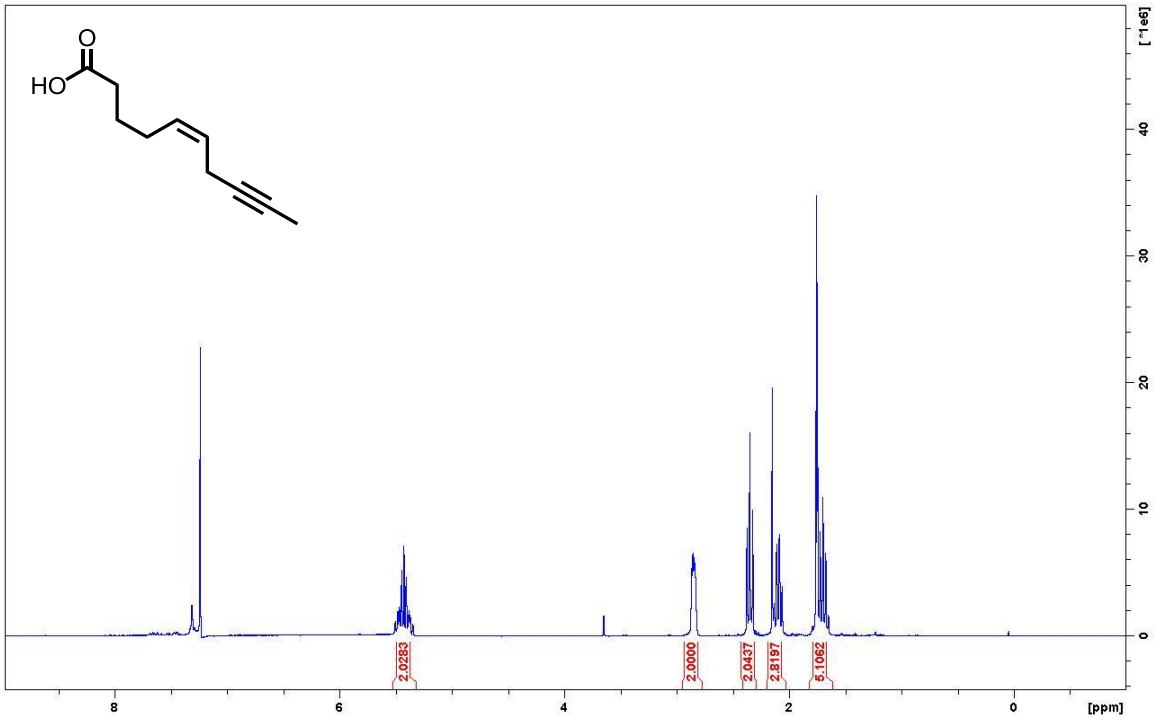

132.2180
130.1730
128.2401
127.7584
82.8547
76.1247
72.9711
53.3165
37.5383
36.3276
22.7196
22.3414
19.3877
14.5479
9.0333
3.5010
150
100
50
0
[ppm]
[*1e6]

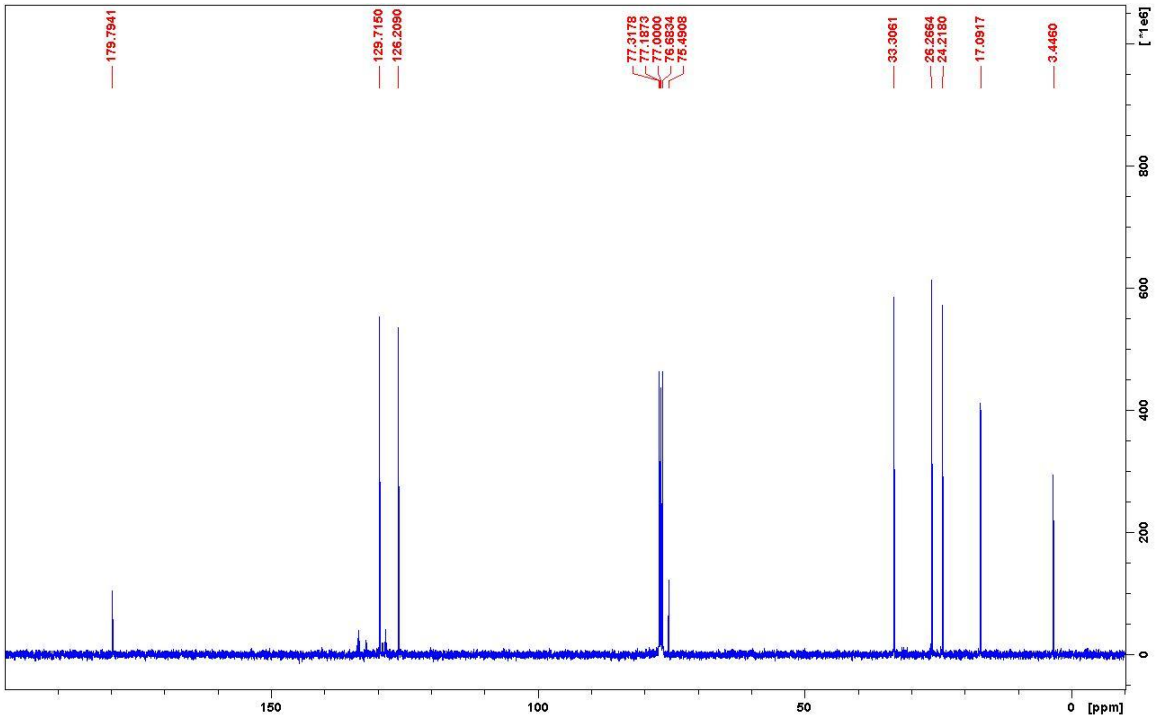

H
OH
O
0.9432
0.9200
0.9726
0.9388
0.8258
1.0185
2.1729
3.0000
3.3852
3.3982
1.0464
2.4003
0.9670
8
6
4
2
0
[ppm]
[*1e6]

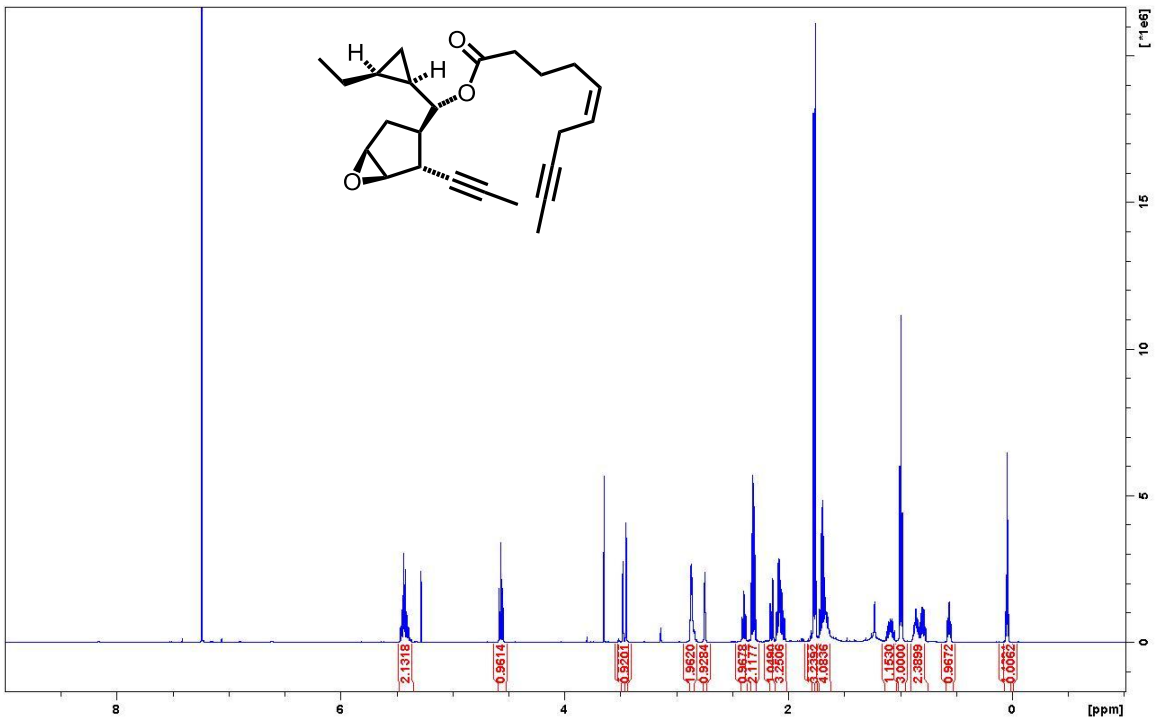

128.1609
128.0003
127.8397
79.1245
78.2510
73.6111
61.1961
58.3221
52.0688
32.9642
30.8073
23.0786
22.8423
18.9386
14.6127
8.6671
3.3949
150
100
50
0
[ppm]
[*1e6]

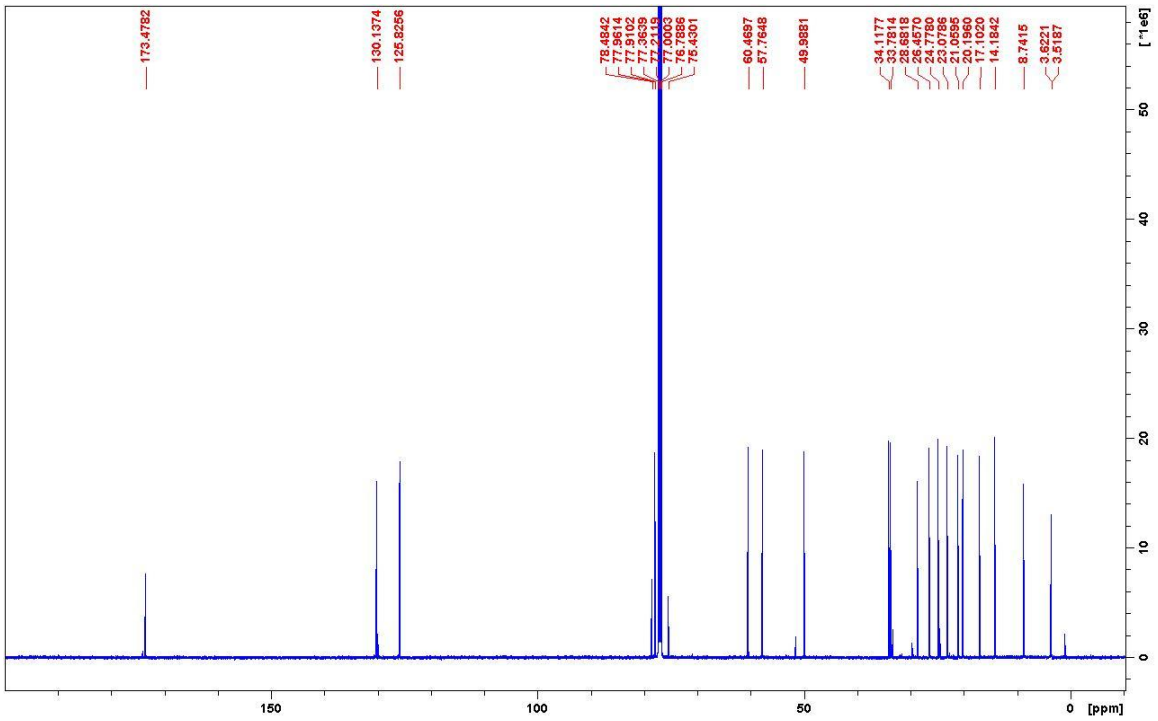

MeO
O
1.9619
2.8471
2.0000
2.0367
2.0307
5.0880
8
6
4
2
0
[ppm]
[*1e6]

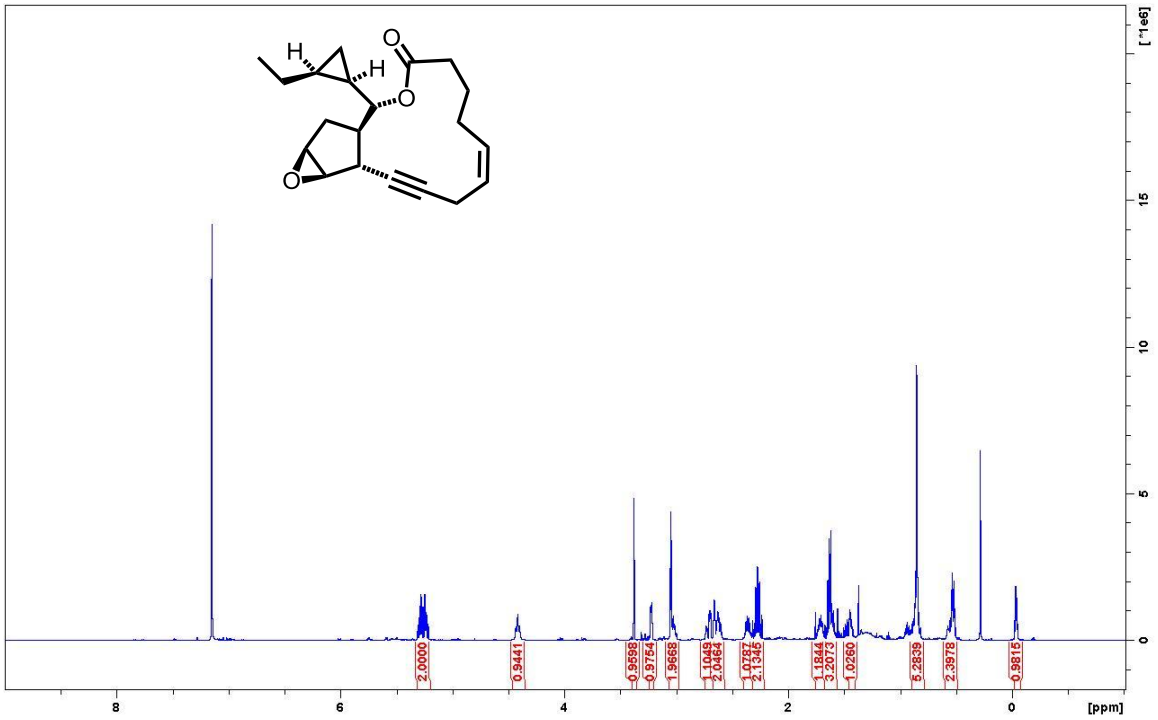

173.9613
129.8576
126.0323
77.3187
77.2195
77.0003
76.6823
76.3926
51.4377
33.3454
26.3507
24.5110
17.0648
3.4308
150
100
50
0
[ppm]
[*1e6]

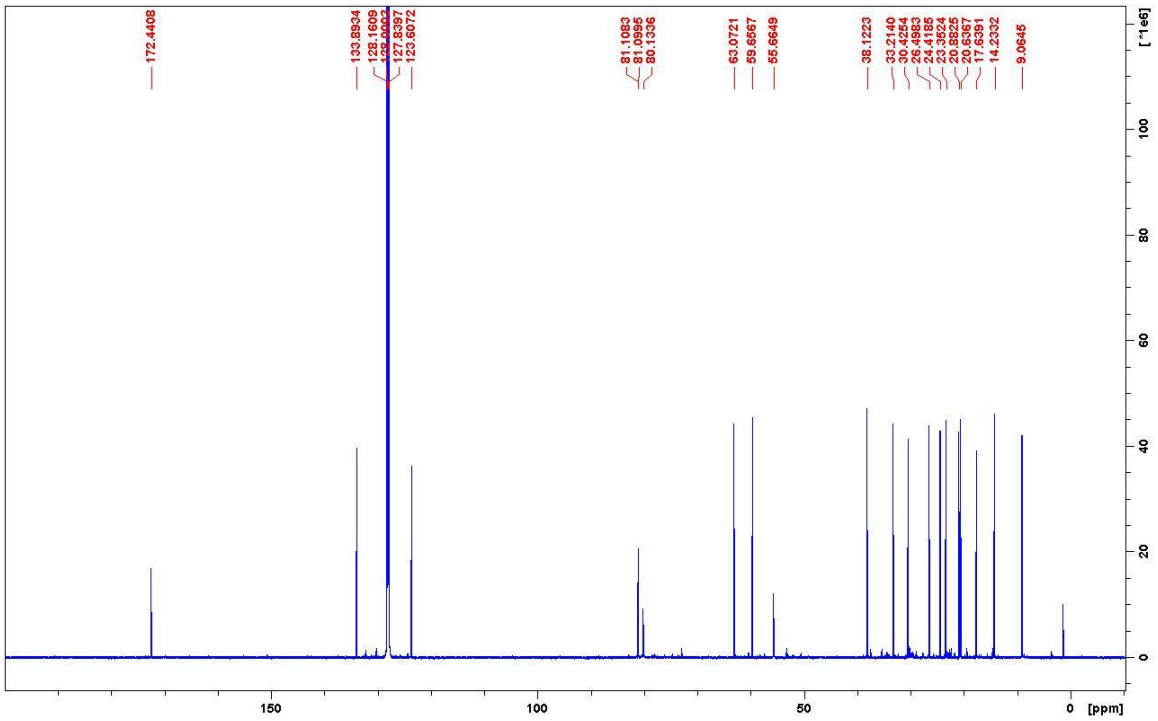

HO
O
2.0263
2.0000
2.0437
2.8197
5.1062
8
6
4
2
0
[ppm]
[*1e6]
40
30
20
10
0

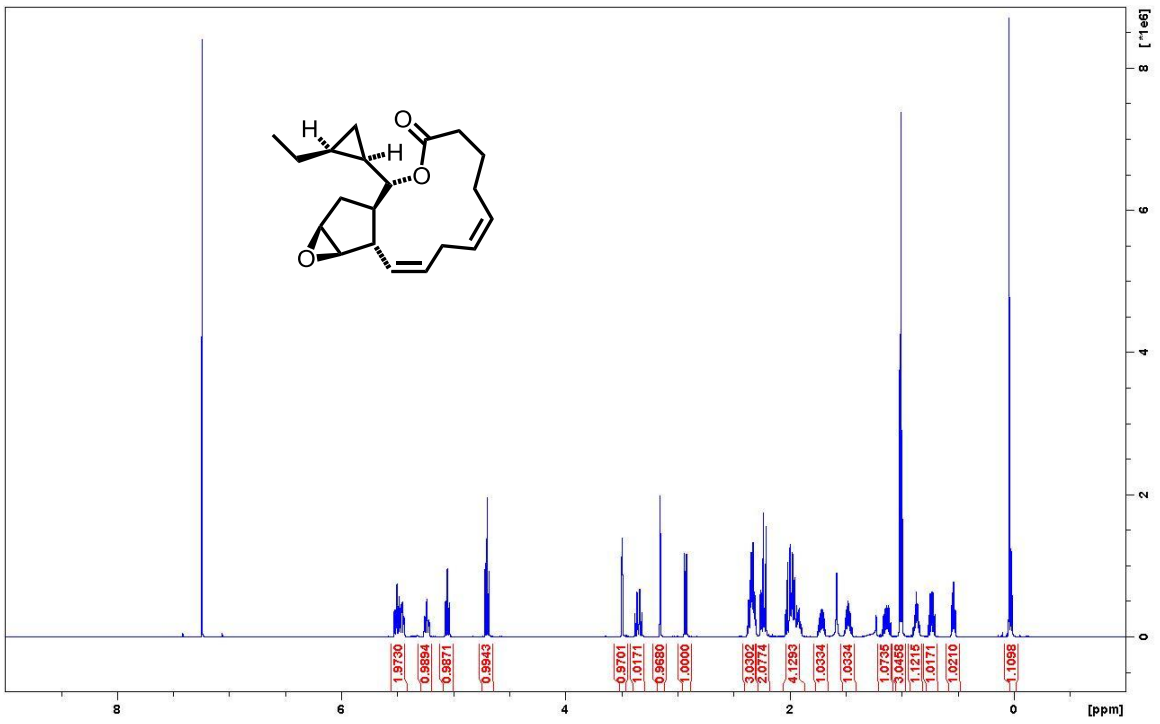

179.7941
129.7180
126.2090
77.3178
77.1873
77.0000
76.6834
76.4508
33.3061
26.2664
24.2180
17.0917
3.4460
150
100
50
0
[ppm]
[*1e6]
800
600
400
200
0

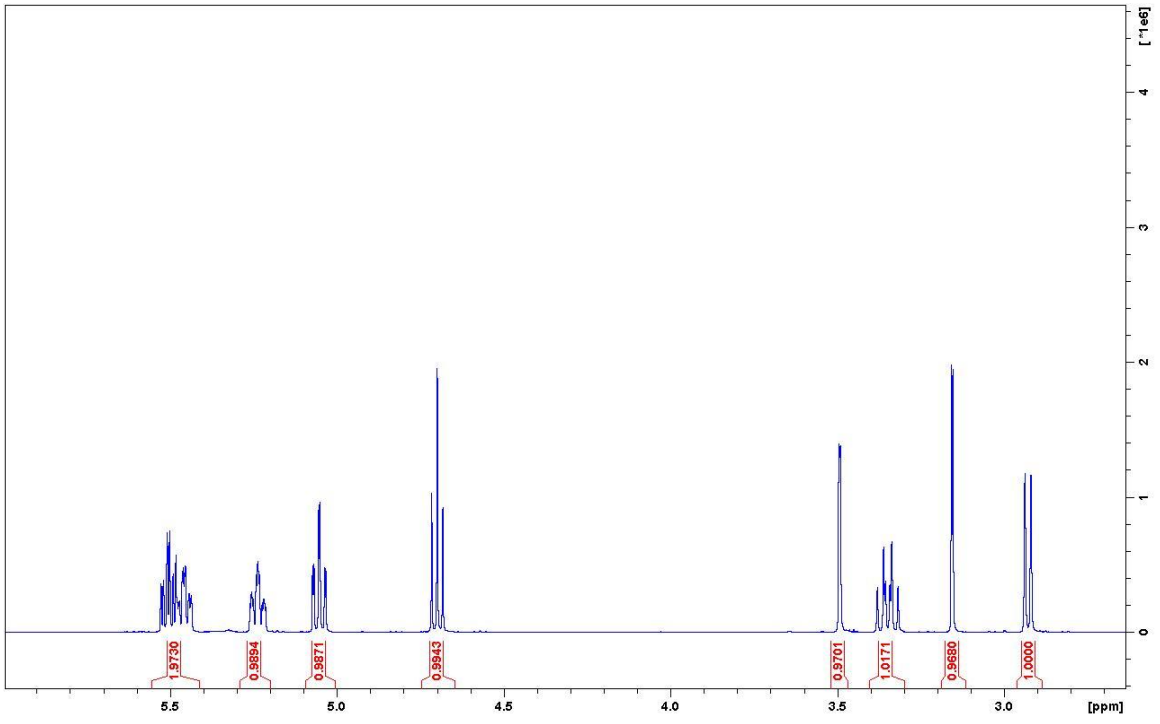

H
H
O
O
O
2.1318
0.9614
0.9201
1.9620
0.9284
0.9678
2.1177
1.0466
3.2606
3.2382
4.0836
1.1530
3.0000
2.3899
0.9672
0.0062
8
6
4
2
0
[ppm]
[*1e6]

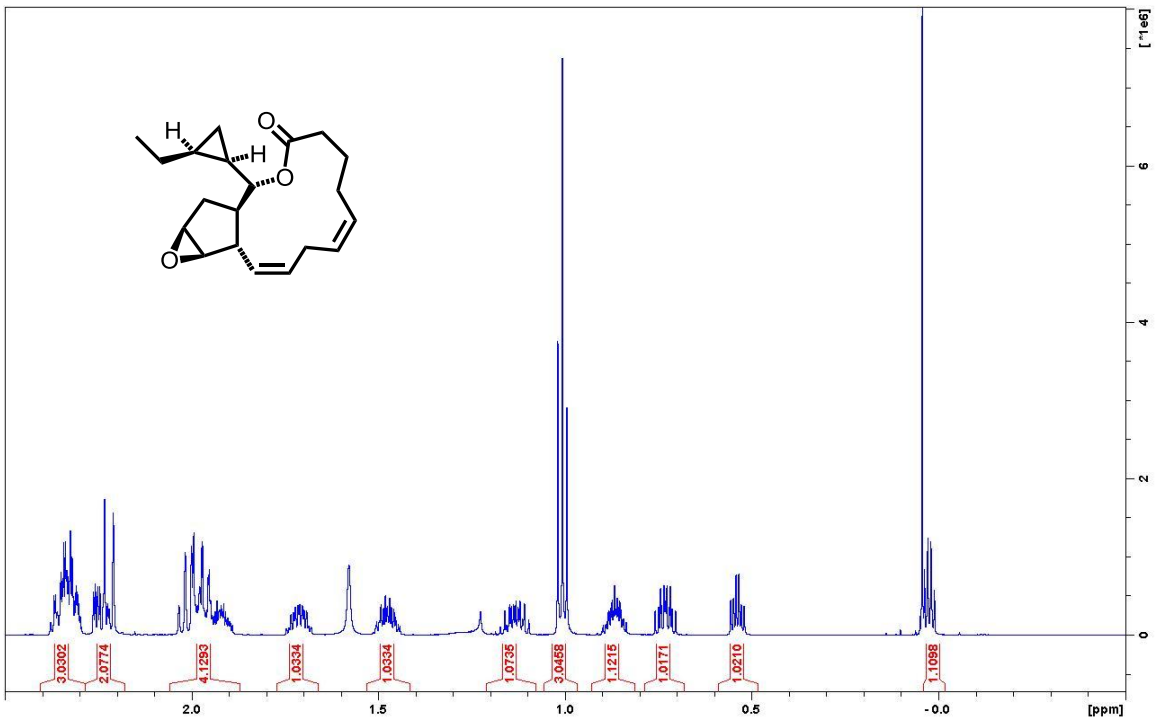

173.4782
130.1374
125.8256
78.4842
77.9614
77.9102
77.3639
77.2114
77.0003
76.7886
76.4301
60.4697
57.7648
49.9881
34.1177
33.7814
28.6818
26.4570
24.7780
23.0786
21.0595
20.1960
17.1020
14.1842
8.7415
3.6221
3.5187
150
100
50
0
[ppm]
[*1e6]

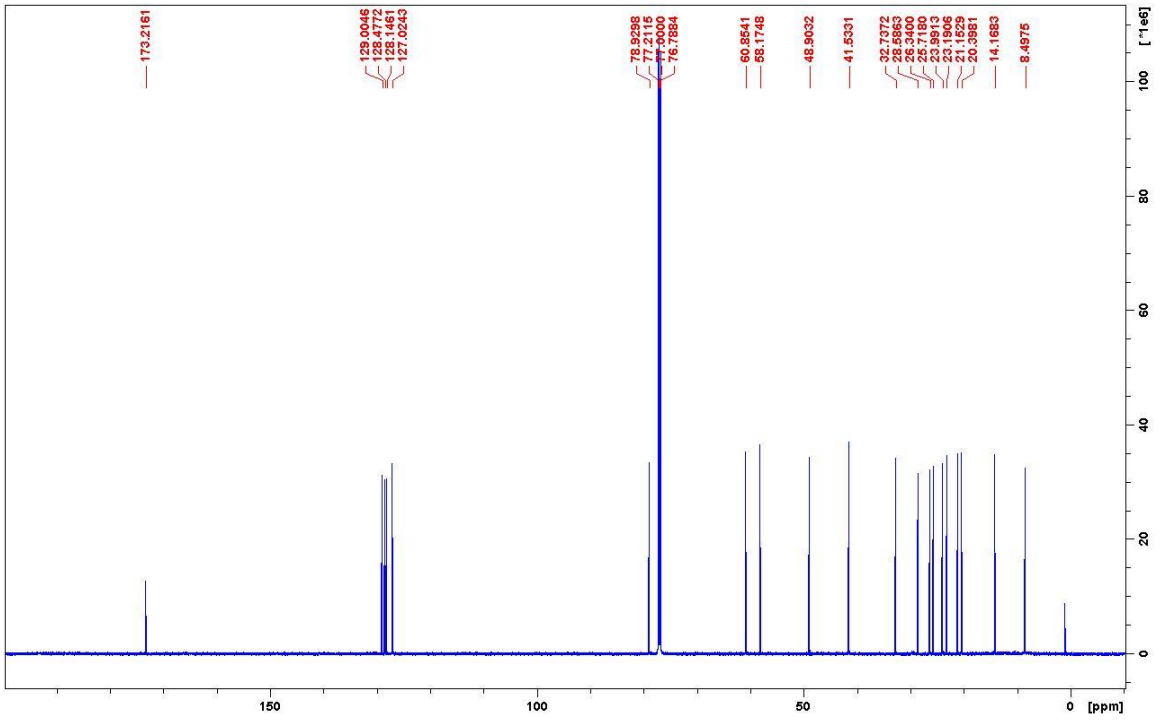

H
H
O
O
O
2.0000
0.9441
0.9598
0.9754
1.9668
1.1049
2.0464
1.0787
2.1345
1.1844
3.2073
1.0260
5.2839
2.3978
0.9815
8
6
4
2
0
[ppm]
[*1e6]


172.4408
133.8934
128.1609
128.0003
127.8397
123.8072
81.1083
81.0995
80.1336
63.0721
59.6667
55.6649
38.1223
33.2140
30.4254
26.4983
24.4185
23.3524
20.8825
20.6367
17.6391
14.2332
9.0645
150
100
50
0
[ppm]
[*1e6]


H
H
O
O
O
1.9730
0.9894
0.9871
0.9943
0.9701
1.0171
0.9680
1.0000
3.0302
2.0774
4.1293
1.0334
1.0334
1.0735
3.0468
1.1215
1.0171
1.0210
1.1098
8
6
4
2
0
[ppm]
[*1e6]


1.9730
0.9894
0.9871
0.9943
0.9701
1.0171
0.9680
1.0000
5.5
5.0
4.5
4.0
3.5
3.0
[ppm]
[*1e6]


H
H
O
O
O
3.0302
2.0774
4.1293
1.0334
1.0334
1.0735
3.0458
1.1215
1.0171
1.0210
1.1098
2.0
1.5
1.0
0.5
-0.0
[ppm]
[*1e6]


173.2161
129.0046
128.4772
128.1461
127.0243
78.9298
77.2115
77.0000
76.7884
60.8541
58.1748
48.9032
41.5331
32.7372
28.5863
26.3400
25.7180
23.9913
23.1906
21.1529
20.3981
14.1683
8.4975
150
100
50
0
[ppm]
[*1e6]