SUPPORTING INFORMATION

Protecting Group-Free and Catalysis-Based Total Synthesis of the Ecklonialactones

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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 (FC): Merck silica gel 60 (230–400 mesh). NMR: Spectra were recorded on Bruker DPX 300, AMX 300, AV 400, and AVIII 600 spectrometer in the solvents indicated; chemical shifts (δ) 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 $CDCl_3$: $\delta_H \equiv 7.26$ ppm; CD_2Cl_2: $\delta_C \equiv 53.8$ ppm; residual ^1H: $\delta_H \equiv 5.32$ ppm; [D_8]-toluene: $\delta_C \equiv 20.7$ ppm; residual $D_5C_6CD_2H$: $\delta_H \equiv 2.09$ 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.

Pinacol Boronate 12. 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 **12** as a colorless oil, which crystallized upon storage in the freezer (22.6 g, 89 %). ^1H NMR (400 MHz, $CDCl_3$): δ = 7.48-7.50 (m, 2 H), 7.40 (d, J = 18.4 Hz, 1 H), 7.27-7.36 (m, 3 H), 6.18 (d, J = 18.4 Hz, 1 H), 1.32 ppm (s, 12 H); ^{13}C NMR (100 MHz, $CDCl_3$): δ = 149.5, 137.4, 128.9, 128.5, 127.0, 83.3, 24.8 ppm; ^{11}B NMR (128 MHz, $CDCl_3$): δ = 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 13. Diene **21** (15 mg, 57 µmol)[1] 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 **12** (790 mg, 3.4 mmol) and 2[5*H*]-furnanone **11** (140 mg, 1.7 mmol) and a catalytic amount of SiO_2 were introduced. The mixture was stirred for 3d at ambient temperature before all volatile materials were evaporated. The residue was purified by flash chromatography (pentanes/Et_2O, 1:1) to give compound **13** 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, 43%) (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). ^1H NMR (400 MHz, $CDCl_3$): δ = 7.24-7.37 (m, 5 H), 6.53 (d, J = 15.9 Hz, 1 H), 6.11 (dd, J = 15.7, 8.1 Hz, 1 H), 4.51 (dd, J = 8.8, 7.8 Hz, 1 H), 4.10 (dd, J = 9.0, 8.2 Hz, 1 H), 3.35-3.46 (m, 1 H), 2.76 (dd, J = 17.4, 8.3 Hz, 1 H), 2.48 ppm (dd, J = 17.4, 9.1 Hz, 1 H); ^{13}C NMR (100 MHz, $CDCl_3$): δ = 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 $[M]^+$; found: 188.0838. The enantiomer of this compound has been prepared in the

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

literature by a different route, allowing the absolute configuration of **13** to be assigned as shown in Scheme 1 by comparison of the rotatory power [*ent*-**13**, ee = 91%, $[\alpha]_D^{23}$ = –33.9 (c = 1.0, $CHCl_3$)].[2]

Compound 14. *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 stirred at 0° C for 30 min. After cooling to –78° C, a solution of compound **13** (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 (3 x 5 mL), 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 **14** as a colorless oil (63 mg, 87%). $[\alpha]_D^{20}$ = + 56 (c = 0.05, CH_2Cl_2); ^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.38-7.25 (m, 5 H), 6.52 (d, *J* = 15.7 Hz, 1 H), 6.03 (dd, *J* = 15.9, 8.6 Hz, 1 H), 5.87-5.77 (m, 1 H), 5.19-5.12 (m, 2 H), 4.42 (dd, *J* = 9.1, 8.1 Hz, 1 H), 3.99 (dd, *J* = 9.9, 9.1 Hz, 1 H), 3.21-3.11 (m, 1 H), 2.58-2.47 ppm (m, 3 H); ^{13}C NMR (100 MHz, $CDCl_3$): δ = 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 16. 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 **14** (60 mg, 0.26 mmol) in CH_2Cl_2 (2 mL) was then 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 **15** thus obtained was immediately dissolved in CH_2Cl_2 (10 mL), indenylidene metathesis catalyst **22** (19 mg, 0.02 mmol, 8 mol%) was added, and the resulting mixture was 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 **16** as a yellow syrup (36 mg, 75 % for two steps). $[\alpha]_D^{20}$ = –169 (c = 0.7, CH_2Cl_2); ^{1}H NMR (400 MHz, $CDCl_3$): δ = 5.57-5.53 (m, 1 H), 5.57-5.54 (m, 1 H), 3.71 (s, 3 H), 3.69-3.65 (m, 1 H), 5.38-3.54 (m, 1 H), 3.28 (br t, *J* = 6.1 Hz, 2 H), 3.20 (s, 3 H), 2.74-2.66 (m, 1 H), 2.59-2.51 (m, 1 H), 2.02 ppm (br s, 1 H); ^{13}C NMR (100 MHz, $CDCl_3$): δ = 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 17. $NaHCO_3$ (908 mg, 10.81 mmol) and Dess-Martin periodinane (688 mg, 1.61 mmol) were successively added to a solution of compound **16** (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. $Na_2S_2O_3$, 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

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

(pentanes/Et_2O, 1:1) to give aldehyde **17** 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, $CDCl_3$): δ = 9.69 (s, 1 H), 5.84-5.81-5.84 (m, 1 H), 5.73-5.70 (m, 1 H), 4.01 (br s, 1 H), 3.81 (q, *J* = 7.3 Hz, 1 H), 3.72 (br s, 3 H), 3.20 (s, 3 H), 2.78-2.62 ppm (m, 2 H); ^{13}C NMR (100 MHz, $CDCl_3$): δ = 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 18. Compound **23** (227 mg, 1.18 mmol) and K_2CO_3 (217 mg, 1.57 mmol) were added to a solution of aldehyde **17** (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, $CDCl_3$): δ = 5.71-5.68 (m, 1 H), 5.64-5.61 (m, 1 H), 3.99-3.94 (m, 1 H), 3.74 (s, 3 H), 3.58 (br q, *J* = 7.4 Hz, 1 H), 3.22 (s, 3 H), 2.77 (ddq, *J* = 16.4, 9.5, 2.3 Hz, 1 H), 2.49 (ddq, *J* = 16.3, 7.4, 2.4 Hz, 1 H), 2.14 ppm (d, *J* = 2.5 Hz, 1 H); ^{13}C NMR (100 MHz, $CDCl_3$): δ = 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 **18** as a colorless oil (130 mg, 80 %). $[\alpha]_D^{20}$ = –307 (c = 0.4, CH_2Cl_2); ^{1}H NMR (400 MHz, $CDCl_3$): δ = 5.66-5.63 (m, 1 H), 5.60-5.57 (m, 1 H), 3.91-3.86 (m, 1 H), 3.73 (s, 3 H), 3.53-3.48 (m, 1 H), 2.21 (s, 3 H), 2.78-2.69 (m, 1 H), 2.49-2.43 (m, 1 H), 1.76 ppm (d, *J* = 2.5 Hz, 3 H); ^{13}C NMR (100 MHz, $CDCl_3$): δ = 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.

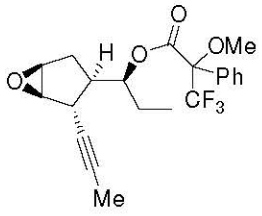
Ketone 19. EtMgBr (3 M in THF, 95 µL, 0.28 mmol) was added to a solution of Weinreb amide **18** (50 mg, 0.26 mmol) in THF (2 mL) at 0° C and the resulting mixture stirred at that temperature for 30 min before the reaction was quenched with aq. sat. NH_4Cl (2 mL). The aqueous layer was extracted with 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 **19** as a colorless oil (39 mg, 93 %). $[\alpha]_D^{20}$ = –394 (c = 0.25, CH_2Cl_2); ^{1}H NMR (300 MHz, $CDCl_3$): δ = 5.53-5.49 (m, 1 H); 5.43-5.39 (m, 1 H), 3.59-3.52 (m, 1 H), 3.13 (dt, *J* = 9.2, 7.6 Hz, 1 H), 2.57-2.33 (m, 4 H), 1.65 (d, *J* = 2.6 Hz, 3 H), 0.95 ppm (t, *J* = 7.3 Hz, 3 H); ^{13}C NMR (75 MHz, $CDCl_3$): δ = 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 20. L-Selectride (1 M in THF, 660 µL, 0.66 mmol) was added dropwise to a solution of ketone **19** (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 **20** as a colorless oil (68 mg, 69 %). $[\alpha]_D^{20}$ = –232 (c = 0.2, CH_2Cl_2); ^{1}H NMR (400 MHz, $CDCl_3$): δ = 5.71-5.68 (m, 1 H), 5.59-5.56 (m, 1 H), 3.58-3.53 (m, 1 H), 3.43-3.38 (m, 1 H), 2.51-2.44 (m, 1 H), 2.37 (dq, *J* = 8.3, 7.6 Hz, 1 H), 2.12-2.04 (m, 1 H), 1.79 (d, *J* = 2.3 Hz, 3 H), 1.67-1.57 (m, 1 H), 1.52-1.40 (m, 1 H), 0.99 ppm (t, *J* = 7.5 Hz, 3 H); ^{13}C NMR (100 MHz, $CDCl_3$): δ = 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.

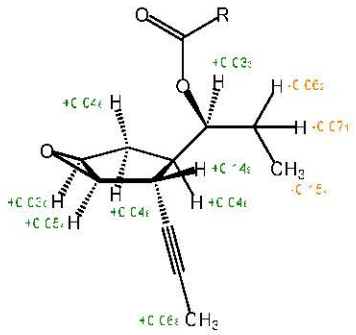
Compound 28. $VO(acac)_2$ (7.8 mg, 0.03 mmol) was added to a solution of alcohol **20** (85 mg, 0.52 mg) in CH_2Cl_2 (10 mL) prior to the slow addition of *t*BuOOH (5.5 M in decane, 133 µL, 0.73 mmol). After stirring for 2 h, additional $VO(acac)_2$ (7.8 mg, 0.03 mmol) was introduced and stirring continued 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 **28** as a colorless oil (90 mg, 94 %). $[\alpha]_D^{20}$ = –97 (c = 0.14, CH_2Cl_2); ^{1}H NMR (600 MHz, $CDCl_3$): δ = 3.57 (dd, *J* = 4.2 Hz, 1 H), 3.53 (d, *J* = 2.7 Hz, 1 H), 3.38 (d, *J* = 2.7 Hz, O*H*), 3.31 (ddt, *J* = 7.6, 5.5, 3.0 Hz, 1 H), 3.15 (dq, *J* = 4.7 Hz, 1 H), 2.39 (ddt, *J* = 10.7, 3.2, 1.7 Hz, 1 H), 2.31 (ddd, *J* = 14.9, 10.8, 1.6 Hz, 1 H), 1.96 (dd, *J* = 14.9, 1.7 Hz, 1 H), 1.77 (d, *J* = 2.6 Hz, 3 H), 1.46 (dqi., *J* = 13.7, 7.5 Hz, 1 H), 1.41 (ddq, *J* = 13.8, 7.4, 5.6 Hz, 1 H), 0.91 ppm (t, *J* = 7.4 Hz, 3 H); ^{13}C NMR (150 MHz, $CDCl_3$): δ = 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: ^{1}H NMR (600 MHz, $CDCl_3$): δ = 7.56 (m, 2 H), 7.40 (m, 3 H), 4.96 (ddd, *J* = 9.9, 6.2, 3.4 Hz, 1 H), 3.59 (q, *J* = 1.0 Hz, 3 H), 3.48 (m, 1 H), 3.43 (d, *J* = 2.5 Hz, 1 H), 2.66 (dq, *J* = 4.6 Hz, 1 H), 2.36 (tt, *J* = 9.9, 1.9 Hz, 1 H), 2.03 (ddd, *J* = 15.0, 9.9, 1.4 Hz, 1 H), 1.83 (dd, *J* = 15.0, 2.0 Hz, 1 H), 1.77 (ddq, *J* = 15.1, 3.4, 7.5 Hz, 1 H), 1.57 (ddq, *J* = 15.0, 6.3, 7.5 Hz, 1 H), 1.70 (d, *J* = 2.5 Hz, 3 H), 0.83 ppm (t, *J* = 7.5 Hz, 3 H); ^{13}C NMR (150 MHz, $CDCl_3$): δ = 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, 46.7, 33.8, 28.7, 24.5, 8.4, 3.5 ppm.

(*S*)-Mosher-Ester: ^{1}H NMR (600 MHz, $CDCl_3$): δ = 7.59 (m, 2 H), 7.39 (m, 3 H), 4.99 (ddd, *J* = 10.2, 6.4, 3.4, 1 H), 3.59 (q, *J* = 1.1 Hz, 3 H), 3.51 (m, 1 H), 3.49 (d, *J* = 2.5 Hz, 1 H), 2.81 (dq, *J* = 4.4 Hz, 1 H), 2.41 (tt, *J* = 9.9, 1.8 Hz, 1 H), 2.08 (ddd, *J* = 15.0, 9.9, 1.3, 1 H), 1.88 (dd, *J* = 15.0, 1.9 Hz, 1 H), 1.77 (d, *J* = 2.5 Hz, 3 H), 1.70 (ddq, *J* = 15.0, 3.4, 7.5 Hz, 1 H), 1.50 (ddq, *J* = 15.0, 6.7, 7.4 Hz, 1 H), 0.68 ppm (t, *J* = 7.4 Hz, 3 H); ^{13}C NMR (150 MHz, $CDCl_3$): δ = 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 S-1. Analysis of the Mosher Esters

9-Undecynoic acid chloride. 9-Undecynoic acid (350 mg, 1.92 mmol) was dissolved in $SOCl_2$ (8 mL) and the resulting solution stirred for 2 h at 85° C. After reaching ambient temperature, excess $SOCl_2$ was distilled off under vacuum and the residue purified by bulb-to-bulb distillation ($4\cdot10^{-3}$ mbar, 60-63 ° C) to give the title compound as a colorless liquid (348 mg, 90 %). ^{1}H NMR (400 MHz, C_6D_6): δ = 2.17-2.14 (m, 2 H), 2.08-2.03 (m, 2 H), 1.59 (t, *J* = 2.5 Hz, 3 H), 1.34 (m, 2 H), 1.20-1.12 (m, 4 H), 0.93-0.78 ppm (m, 4 H); ^{13}C NMR (100 MHz, C_6D_6): δ = 173.8, 79.9, 76.3, 47.5, 29.9, 29.3 (2 C), 28.9, 25.6, 19.7, 3.9 ppm; IR (film): $\tilde{\nu}$ = 2931 (s), 2858 (s), 1795 (s), 1463 (m), 1404 (m), 954 (s), 719 (s), 679 (s) cm^{-1}; MS (EI): *m/z* (%): 200 (1) $[M]^+$, 185 (1), 165 (26), 158 (4), 147 (6), 135 (4), 121 (13), 107 (15), 95 (49), 81 (63), 68 (86), 55 (100), 41 (90), 27 (39); HRMS (CI, *i*-butane): calcd. for $C_{11}H_{18}OCl$: 201.1046 $[M+H]^+$; found: 201.1044.

Compound 29. Carbodiimide *p*-toluenesulfonate **31** (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 stirred for 1.5 h before a solution of alcohol **28** (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 **29** as a colorless oil (23 mg, 61 %). $[\alpha]_D^{20}$ = –101 (c = 0.78, CH_2Cl_2); ^{1}H NMR (400 MHz, $CDCl_3$): δ = 4.77 (ddd, *J* = 9.2, 7.5, 3.6 Hz, 1 H), 3.49 (t, *J* = 1.9 Hz, 1 H), 3.48 (t, *J* = 2.9 Hz, 1 H), 2.83 (dt, *J* = 5.0, 2.5 Hz, 1 H), 2.39 (tt, *J* = 2.9, 2.5 Hz, 1 H), 2.32 (td, *J* = 7.5, 1.7 Hz, 2 H), 2.14-2.06 (m, 3 H), 1.87 (dd, *J* = 14.8, 2.7 Hz, 1 H), 1.79 (d, *J* = 2.6 Hz, 3 H), 1.78 (t, *J* = 2.6 Hz, 3 H), 1.72-1.61 (m, 3 H), 1.50-1.20 (m, 9 H), 0.83 ppm (t, *J* = 7.5 Hz, 3 H); ^{13}C NMR (100 MHz, $CDCl_3$): δ = 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 24. DMAP (27 mg, 0.23 mmol) and 9-undecynoic acid chloride (40 mg, 0.20 mmol) were successively added to a solution of alcohol **20** (20 mg, 0.12 mmol) in CH_2Cl_2 (5 mL) at 0° C before the mixture was warmed to ambient temperature. After stirring for 1 h, the reaction was quenched with aq. sat. $NaHCO_3$ (4 mL), the aqueous phase was extracted with CH_2Cl_2 (3 x 2 mL), the combined organic layers were dried (Na_2SO_4) and evaporated, and the residue was purified by flash chromatography (hexanes/EtOAc, 20:1) to give ester **24** as a colorless oil (27.5 mg, 70 %). $[\alpha]_D^{20}$ = –94 (c = 0.16, CH_2Cl_2); ^{1}H NMR (400 MHz, $CDCl_3$): δ = 5.68-5.64 (m, 1 H), 5.57-5.53 (m, 1 H), 4.99-4.94 (m, 1 H), 3.39-3.34 (m, 1 H), 2.56-2.44 (m, 2 H), 2.35-2.31 (m, 2 H), 2.14-2.08 (m, 2 H), 2.07-1.99 (m, 1 H), 1.77-1.70 (m, 6 H), 1.72-1.57 (m, 4 H), 1.50-1.43 (m, 2 H), 1.40-1.30 (m, 6 H), 0.93-0.89 ppm (m, 3 H); ^{13}C NMR (100 MHz, $CDCl_3$): δ = 173.8, 131.7, 129.7, 81.6, 79.3, 77.2, 76.0, 75.4, 49.7, 38.5, 35.3, 34.6, 29.1, 29.0, 28.8, 28.7, 26.1, 25.0, 18.7, 9.8, 3.6, 3.4 ppm; IR (film): $\tilde{\nu}$ = 2931 (s), 2856 (m), 1730 (s), 1460 (m) 1380 (m), 1246 (m), 1184 (m), 1124 (m), 1098 (m), 946 (w), 723 (m) cm^{-1}; MS (EI): *m/z* (%): 328 (2) $[M]^+$, 299 (1), 285 (1), 256 (1), 206 (5), 191 (5), 164 (4), 146 (91), 131 (38), 117 (100), 105 (24), 91 (16), 81 (11), 67 (9), 55 (13), 41 (1); HRMS (ESI): *m/z*: calcd. for $C_{22}H_{32}O_2Na$: 351.2295 $[M+Na]^+$; found: 351.2297.

Cycloalkyne 25. A solution of complex **32** (19 mg, 0.017 mmol) in toluene (2 mL) and CH_2Cl_2 (589 µL) was stirred for 15 min before a solution of diyne **24** (15 mg, 0.046 mmol) in toluene (2 mL) was introduced. After stirring at 80° C for 20 h, the solvents were evaporated at ambient temperature and the residue was purified by flash chromatography (hexanes/EtOAc, 30:1) to give cycloalkyne **25** as a colorless oil (8.6 mg, 71 %). $[\alpha]_D^{20}$ = –12 (c = 0.05; CH_2Cl_2); ^{1}H NMR (400 MHz, $CDCl_3$): δ = 5.66-5.63 (m, 1 H), 5.55-5.52 (m, 1 H), 4.87 (ddd, *J* = 10.6, 7.6, 3.1 Hz, 1 H), 3.35-3.30 (m, 1 H), 2.56-2.42 (m, 2 H), 2.39-2.29 (m, 2 H), 2.24-2.20 (m, 2 H), 2.05-1.97 (m, 1 H), 1.89-1.81 (m, 1 H), 1.72 (ddd, *J* = 14.1, 6.8, 2.9 Hz, 2 H), 1.52-141 (m, 9 H), 0.89 ppm (t, *J* = 7.4 Hz, 3 H); ^{13}C NMR (100 MHz, $CDCl_3$): δ = 174.2, 132.2, 129.2, 83.5, 80.4, 78.9, 50.1, 40.9, 35.8, 32.6, 26.4, 25.7, 25.6, 24.8, 23.8, 22.4, 17.8, 9.0 ppm; IR (film): $\tilde{\nu}$ = 2932 (s), 1730 (s), 1460 (w), 1246 (m), 1183 (m), 1098 (w), 723 (w) cm^{-1}; MS (EI): *m/z* (%): 274 (1) $[M]^+$, 259 (1), 245 (4), 231 (2), 209 (2), 187 (6), 173 (5), 159 (8), 146 (53), 131 (40), 117 (100), 105 (23), 91 (46), 79 (16), 67 (12), 55 (17), 41 (19); HRMS (ESI): *m/z*: calcd. for $C_{18}H_{26}O_2Na$: 297.1825 $[M+Na]^+$; found: 297.1827.

Compound 30. MS 5Å (powder, ca. 10 mg) was added to a solution of compound **29** (5.0 mg, 14.5 µmol) in toluene (1 mL) and the resulting mixture stirred for 20 min. In a second flask, complex **34** (17.6 mg, 16.2 µmol) was dissolved in toluene (1 mL) and 45 µL (0.72 µmol, 5 mol%) of this stock solution were added to the suspension containing diyne **29**. The reaction 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 **30** as a colorless oil (3.4 mg, 80%). $[\alpha]_D^{20}$ = –52 (c = 0.05, CH_2Cl_2); ^{1}H NMR (600 MHz, $CDCl_3$): δ = 4.66 (ddd, *J* = 10.9, 7.8, 3.0 Hz, 1 H), 3.51 (dd, *J* = 4.7 Hz, 1 H), 3.48 (d, *J* = 2.5 Hz, 1 H), 2.89 (tt, *J* = 4.6, 2.1 Hz, 1 H), 2.57 (tt, *J* = 10.8, 4.8 Hz, 1 H), 2.29 (t, *J* = 7.2 Hz, 2 H), 2.16 (m, 2 H), 2.09 (ddd, *J* = 14.9, 10.9, 2.2 Hz, 1 H), 1.75 (m, 1 H), 1.71 (dd, *J* = 14.8, 5.1 Hz, 1 H), 1.66 (ddq, *J* = 14.5, 7.4, 3.1 Hz, 1 H), 1.69-1.51 (m, 9 H), 1.41 (dqi., *J* = 14.5, 7.4 Hz, 1 H), 0.82 ppm (t, *J* = 7.4 Hz, 3 H); ^{13}C NMR (150 MHz, $CDCl_3$): δ = 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), 29.9 (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.

Compound 26. Dimethyldioxirane (DMDO, 0.8 M in acetone, 684 µL) was added at –78° C to a solution of compound **25** (10 mg, 0.037 mmol) in CH_2Cl_2 (1 mL). After 1 h as well as after 2 h, further aliquots of DMDO (456 µL, 0.037 mmol each) were introduced and stirring continued at –78° C or 14 h and then for another 14 h at ambient temperature. For work up, the reaction was quenched with aq. sat. $Na_2S_2O_3$ (1 mL), the aqueous phase was extracted with CH_2Cl_2 (3 x 2 mL), the combined organic layers were dried (Na_2SO_4) and evaporated, and the residue purified by flash chromatography (hexanes/EtOAc, 30:1 → 4:1) to give product **26** (6 mg, 56%) and a second fraction of compound **30** (2 mg, 19%) as colorless oils each. Analytical and spectral data of compound **26**: $[\alpha]_D^{20}$ = –73 (c = 0.11, CH_2Cl_2); ^{1}H NMR (600 MHz, $CDCl_3$): δ = 4.71 (ddd, *J* = 10.8, 7.7, 3.1 Hz, 1 H), 3.51 (dd, *J* = 2.5, 1.7 Hz, 1 H), 3.46 (m, 1 H), 2.64 (dq, *J* = 8.4, 1.7 Hz, 1 H), 2.36 (ddd, *J* = 15.5, 9.1, 6.3 Hz, 1 H), 2.30 (ddd, *J* = 15.5, 9.1, 6.4 Hz, 1 H), 2.28 (m, 2 H), 2.20 (dd, *J* = 14.0, 7.9 Hz, 1 H), 2.03 (ddt, *J* = 10.6, 9.5, 8.2 Hz, 1 H), 1.83 (m, 1 H), 1.72 (m, 1 H), 1.62 (ddq, *J* = 14.5, 7.4, 3.2 Hz, 1 H), 1.48-1.44 (m, 8 H), 1.41 (dqi., *J* = 14.6, 7.4 Hz, 1 H), 1.36 (ddd, *J* = 14.1, 9.4, 1.4 Hz, 1 H), 0.83 ppm (t, *J* = 7.4 Hz, 3 H); ^{13}C NMR (150 MHz, $CDCl_3$): δ = 174.4 (s), 81.4 (s), 79.4 (s), 78.1 (d, J_{CH} = 146 Hz), 60.5 (d, J_{CH} = 190 Hz), 56.5 (d, J_{CH} = 186 Hz), 43.3 (d, J_{CH} = 136 Hz), 36.6 (d, J_{CH} = 130 Hz), 31.71 (t, J_{CH} = 128 Hz), 31.68 (t, J_{CH} = 130 Hz), 26.0 (t, J_{CH} = 127 Hz), 25.4 (t, J_{CH} = 128 Hz), 25.2 (t), 24.3 (t, J_{CH} = 124 Hz), 23.1 (t, J_{CH} = 125 Hz), 21.7 (t, J_{CH} = 128 Hz), 17.6 (t, J_{CH} = 130 Hz), 8.8 (q, J_{CH} = 126 Hz) ppm; IR (film): $\tilde{\nu}$ = 2930 (m), 2857 (m), 1727 (s), 1459 (w), 1378 (w), 1260 (m), 1181 (m), 1084 (m), 1018 (m), 854 (m), 799 (s) 731 (w), 648 (w) cm^{-1}; HRMS (ESI): *m/z*: calcd. for $C_{18}H_{26}O_3Na$: 313.1774 $[M+Na]^+$; found: 313.1752.

12,13-*epi*-Ecklonialactone B (27). Prepared as a pale yellow oil (8 mg, 80 %) starting from compound **26** (10 mg, 0.034 mmol), following the procedure described below for ecklonialactone B. $[\alpha]_D^{20}$ = –127 (c = 0.11, CH_2Cl_2); ^{1}H NMR (600 MHz, $CDCl_3$): δ = 5.54 (tdd, *J* = 10.8, 4.5, 0.6 Hz, 1 H), 5.48 (ddd, *J* = 11.0, 9.0, 1.1 Hz, 1 H), 4.70 (ddd, *J* = 7.3, 6.4, 3.2 Hz, 1 H), 3.41 (d, *J* = 2.6 Hz, 1 H), 3.31 (dd, *J* = 4.1, 1 H), 3.10 (t, *J* = 9.3 Hz, 1 H), 2.46 (ddd, *J* = 15.0, 8.9, 4.2 Hz, 1 H), 2.40 (ddt, *J* = 14.0, 10.6, 7.9 Hz, 1 H), 2.27 (ddd, *J* = 15.0, 8.0, 4.0 Hz, 1 H), 2.11 (dd, *J* = 13.8, 7.4 Hz, 1 H), 1.92 (4d, *J* = 10.3, 9.3, 7.5, 3.2 Hz, 1 H), 1.89 (m, 1 H), 1.47 (ddd, *J* = 13.8, 10.3, 1.3 Hz, 1 H), 1.66-1.21 (m, 12 H), 0.81 ppm (t, *J* = 7.5, 3 H) ; ^{13}C NMR (150 MHz, $CDCl_3$): δ = 173.6 (s), 131.7 (d, J_{CH} = 154 Hz), 129.9 (d, J_{CH} = 156 Hz), 76.7 (d, J_{CH} = 146 Hz), 61.3 (d, J_{CH} = 186 Hz), 55.1 (d, J_{CH} = 185 Hz), 39.2 (d, J_{CH} = 126 Hz), 38.7 (d, J_{CH} = 130 Hz), 33.20 (t, J_{CH} = 129 Hz), 32.19 (t, J_{CH} = 130 Hz), 27.1 (t, J_{CH} = 122 Hz), 26.34 (t), 26.29 (t), 25.8 (t), 25.7 (t, J_{CH} = 128 Hz), 25.1 (t, J_{CH} = 120 Hz), 24.0 (t, J_{CH} = 128 Hz), 9.9 (q, J_{CH} = 126 Hz) ppm; IR (film): $\tilde{\nu}$ = 3012 (w), 2927 (m), 2857 (m), 1728 (s), 1457 (w), 1336 (w), 1258 (s), 1181 (m), 1105 (s), 1022 (s), 955 (w), 851 (s), 797 (s), 745 (m), 700 (w) cm^{-1}; HRMS (ESI): *m/z*: calcd. for $C_{18}H_{28}O_3Na$: 315.1931 $[M+Na]^+$; found: 315.1929.

Ecklonialactone B (2). A mixture containing compound **30** (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 **2** as a colorless oil (1.8 mg, 90 %). $[\alpha]_D^{20}$ = –19 (c = 0.07, CH_2Cl_2); ^{1}H NMR (600 MHz, $CDCl_3$): δ = 5.47 (4d, *J* = 10.6, 8.4, 7.0, 1.2 Hz, 1 H), 5.10 (ddt, *J* = 10.7, 9.6, 1.2 Hz, 1 H), 4.95 (3d, *J* = 10.3, 7.6, 3.0 Hz, 1 H), 3.49 (d, *J* = 2.6 Hz, 1 H), 3.23 (d, *J* = 2.6 Hz, 1 H), 3.00 (d, *J* = 9.7 Hz, 1 H), 2.40 (3d, *J* = 15.2, 6.9, 3.8 Hz, 1 H), 2.35 (3d, *J* = 15.2, 10.3, 3.2 Hz, 1 H), 2.05 (m, 2 H), 1.92 (m, 1 H), 1.90 (m, 1 H), 1.87 (m, 1 H), 1.85 (m, 1 H), 1.70 (ddq, *J*

= 14.6, 3.1, 7.4 Hz, 1 H), 1.55 (m, 1 H), 1.42 (m, 2 H), 1.38 (m, 2 H), 1.37 (m, 1 H), 1.35 (m, 3 H), 1.29 (m, 1 H), 0.78 ppm (t, J = 7.4 Hz, 3 H); ^{13}C NMR (150 MHz, $CDCl_3$): δ = 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 S-1. Comparison of the recorded ^{13}C NMR data of ecklonialactone B (**2**) with those reported in the literature.[3]

Position	δ_C (lit.)	multiplicity	δ_C (exp.)	multiplicity, $^1J_{CH}$	$\Delta\delta$
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

[3] (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.

Methyl 6-Oxohexanoate.[4] Ozone (ca. 40-50 g/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 %). ^{1}H NMR (400 MHz, $CDCl_3$): δ = 9.74 (t, *J* = 1.6 Hz, 1 H), 3.64 (s, 3 H), 2.46-2.41 (m, 2 H), 2.34-2.29 (m, 2 H), 1.68-1.59 ppm (m, 4 H); ^{13}C NMR (100 MHz, $CDCl_3$): δ = 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}; 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.

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, $CDCl_3$): δ = 3.19 (t, *J* = 7.3 Hz, 2 H), 2.71 (tq, *J* = 7.5, 2.5 Hz, 2 H), 1.77 ppm (t, *J* = 2.5 Hz, 3 Hz); ^{13}C NMR (100 MHz, $CDCl_3$): δ = 77.9, 77.8, 24.1, 3.5, 2.6 ppm.

But-2-ynyl-5-triphenylphosphonium iodide. 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): δ = 7.92-7.75 (m, 15 H), 3.84 (dt, *J* = 13.1, 7.2 Hz, 2 H), 3.33 (s, 3 H), 1.52 ppm (t, *J* = 2.3 Hz, 2 H); ^{13}C NMR (100 MHz, [D_6]-DMSO): δ = 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.

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

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

(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, $CDCl_3$): δ = 5.45-5.36 (m, 2 H), 3.63 (s, 3 H), 2.87-2.84 (m, 2 H), 2.31 (t, *J* = 7.5 Hz, 2 H), 2.07-2.02 (m, 2 H), 1.76 (t, *J* = 2.6 Hz, 3 H), 1.67-1.59 (m, 2 H), 1.42-1.35 ppm (m, 2 H); ^{13}C NMR (100 MHz, $CDCl_3$): δ = 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_20 (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 solvent 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, $CDCl_3$): δ = 1.45-1.38 (m, 2 H), 1.69-1.61 (m, 2 H), 1.77 (t, *J* = 2.5 Hz, 3 H), 2.09-2.04 (m, 2 H), 2.36 (t, *J* = 7.4 Hz, 2 H), 2.88-2.85 (m, 2 H), 5.47-5.38 ppm (m, 2 H); ^{13}C NMR (100 MHz, $CDCl_3$): δ = 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 36. Carbodiimide *p*-toluenesulfonate **31** (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 **28** (7.0 mg, 39 µmol) in CH_2Cl_2 (0.5 mL) followed by 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 **36** as a colorless oil (8.6 mg, 65 %). $[\alpha]_D^{20}$ = –86 (CH_2Cl_2, c = 0.43); ^{1}H NMR (400 MHz, $CDCl_3$): δ = 5.47-5.39 (m, 2 H), 4.76 (ddd, *J* = 9.2, 7.4, 3.5 Hz, 1 H), 3.50-3.47 (m, 2 H), 2.88 (dq, *J* = 4.9, 2.5 Hz, 2 H), 2.83 (dq, *J* = 2.4, 2.1 Hz, 1 H), 2.40-2.31 (m, 3 H), 2.40-2.11 (m, 3 H), 1.85 (dd, *J* = 14.9, 2.5 Hz, 1 H), 1.80 (d, *J* = 2.5 Hz, 3 H), 1.78 (t, *J* = 2.5 Hz, 3 H), 1.73-1.62 (m, 3 H), 1.49-1.38 (m, 3 H), 0.83 ppm (t, *J* = 7.4 Hz, 3 H); ^{13}C NMR (100 MHz, $CDCl_3$): δ = 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 37. Diyne **36** (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 **34** [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 **37** as a colorless liquid (3.5 mg, 90 %). $[\alpha]_D^{20}$ = –84 (CH_2Cl_2, c = 0.05); ^{1}H NMR (400 MHz, $CDCl_3$): δ = 5.56 (dt, *J* = 10.6, 7.0 Hz, 1 H), 5.51 (ddd, *J* = 10.6, 8.3, 6.8 Hz, 1 H), 4.75 (ddd, *J* = 10.7, 8.4, 2.9, 1 H), 3.50 (t, *J* = 2.5 Hz, 1 H), 3.46 (d, *J* = 2.5 Hz, 1 H), 2.92 (ddd, *J* = 17.2, 6.8, 2.0 Hz, 1 H), 2.83 (dt, *J* = 5.4, 2.0 Hz, 1 H), 2.75 (ddd, *J* = 17.1, 7.1, 2.6 Hz, 1 H), 2.54 (tt, *J* = 10.6, 5.8 Hz, 1 H), 2.41 (dt, *J* = 15.2, 7.2 Hz, 1 H), 2.27 (dt, *J* = 15.2, 7.4 Hz, 2 H), 2.21 (ddt, *J* = 12.9, 8.3, 7.7 Hz, 1 H), 2.07 (ddd, *J* = 14.8, 10.6, 2.4 Hz, 1 H), 1.99 (dq, *J* = 13.0, 6.8 Hz, 2 H), 1.71 (m, 1 H), 1.66 (dd, *J* = 14.8, 6.0, 1 H), 1.61 (ddq, *J* = 14.4, 7.4, 2.8 Hz, 1 H), 1.48 (qi., *J* = 7.4 Hz, 1 H), 1.37 (ddq, *J* = 14.4, 8.4, 7.4 Hz, 1 H), 0.82 ppm (t, *J* = 7.4 Hz, 3 H); ^{13}C NMR (100 MHz, $CDCl_3$): δ = 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 (1). $NaBH_4$ (9.6 mg, 0.25 mmol) and ethylenediamine (17 µL, 0.25 mmol) were successively added to a solution of $Ni(OAc)_2$ (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 **37** (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 (**1**) as a colorless solid (5.5 mg, 69 %). $[\alpha]_D^{20}$ = - 59 (CH_2Cl_2, c = 0.025); ^{1}H NMR (600 MHz, $CDCl_3$): δ = 5.49 (tdd, *J* = 10.5, 5.1, 1.2 Hz, 1 H), 5.48 (dtt, *J* = 10.6, 7.6, 1.5 Hz, 1 H), 5.41 (m, 1 H), 5.07 (4d, *J* = 10.6, 9.9, 2.3, 0.9 Hz, 1 H), 4.89 (4d, *J* = 8.9, 7.3, 3.1, 1.7 Hz, 1 H), 3.50 (d, *J* = 2.4 Hz, 1 H), 3.21 (d, *J* = 2.4 Hz, 1 H), 3.08 (ddd, *J* = 15.6 Hz, 1 H), 3.06 (d, *J* = 9.8 Hz, 1 H), 2.63 (ddd, *J* = 15.6 Hz, 1 H), 2.41 (ddd, *J* = 15.1, 7.3, 5.2 Hz, 1 H), 2.35 (ddd, *J* = 15.0, 8.9, 5.1 Hz, 1 H), 2.04-1.87 (m, 5 H), 1.74-1.69 (m, 3 H), 1.43 (m, 2 H), 1.39 (dqi, *J* = 14.6, 7.3 Hz, 1 H), 0.79 ppm (t, *J* = 7.4 Hz, 3 H); ^{1}H NMR (600 MHz, C_6D_6): δ = 5.42 (m, 1 H), 5.39 (m, 1 H), 5.37 (tdd, *J* = 10.5, 5.0, 1.3 Hz, 1 H), 5.27 (ddd, *J* = 10.9, 7.4, 3.2 Hz, 1 H), 4.87 (4d, *J* = 10.6, 10.0, 3.2, 1.0 Hz, 1 H), 3.19 (d, *J* = 9.9 Hz, 1 H), 3.05 (app. d, 1 H), 3.04 (ddt, *J* = 2.6, 0.5 Hz, 1 H), 2.96 (m, 1 H), 2.48 (m, 1 H), 2.21 (ddd, *J* = 14.9, 6.9, 5.5 Hz, 1 H), 2.17 (ddd, *J* = 14.9, 8.8, 5.1 Hz, 1 H), 1.90 (m, 1 H), 1.84 (m, 1 H), 1.80 (t, *J* = 10.0 Hz, 1 H), 1.68 (m, 1 H), 1.62 (ddq, *J* = 14.5, 3.2, 7.4, 1 H), 1.50 (ddt, *J* = 14.9, 1.2 Hz, 1 H), 1.41 (m, 1 H), 1.37 (ddd, *J* = 15.0, 9.4, 1.3 Hz, 1 H), 1.30 (m, 2 H), 1.24 (dqi., *J* = 14.5, 7.4 Hz, 1 H), 0.77 ppm (t, *J* = 7.4 Hz, 3 H); ^{13}C NMR (150 MHz, $CDCl_3$): δ = 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.

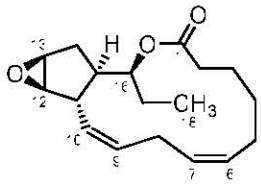
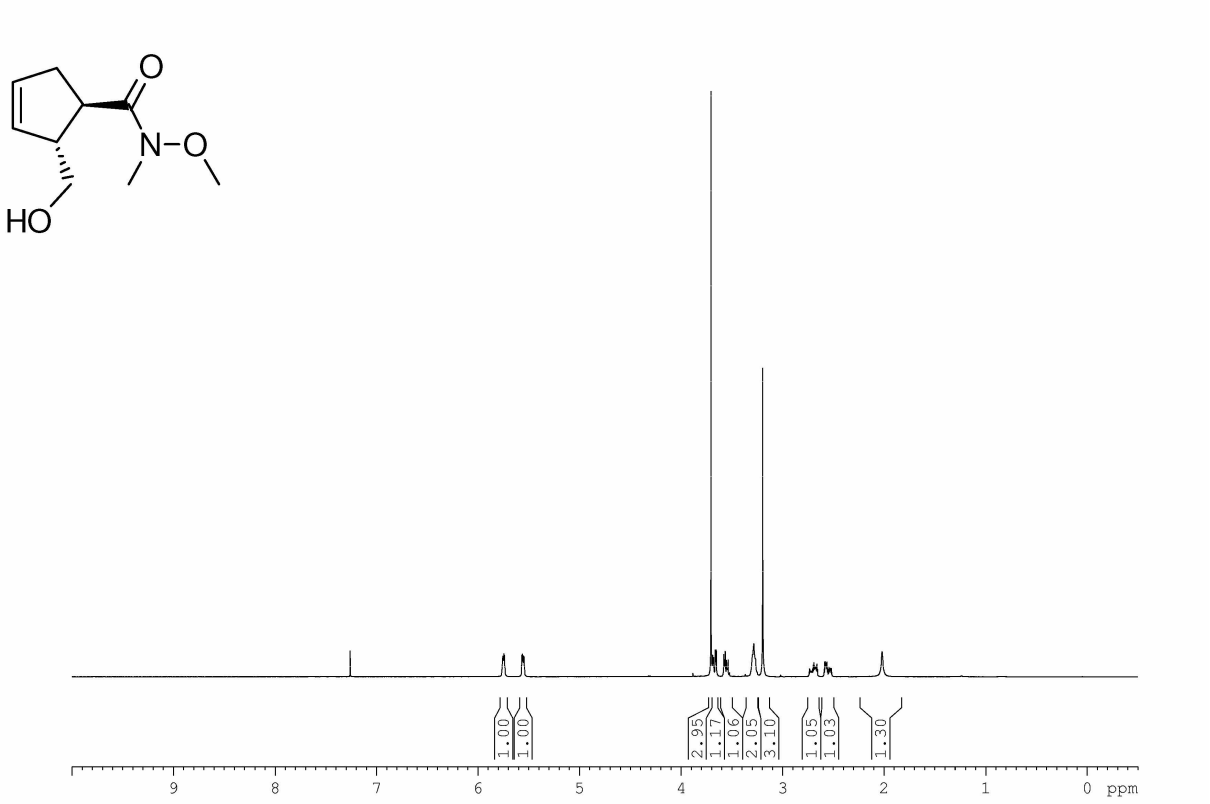


Table S-2. Comparison of the recorded ^{13}C NMR data ($CDCl_3$) of ecklonialactone A (**1**) with those reported in the literature.[3] Assignments marked * may be interchanged.

Position	δ_C (lit., 67.9 Hz), ppm	δ_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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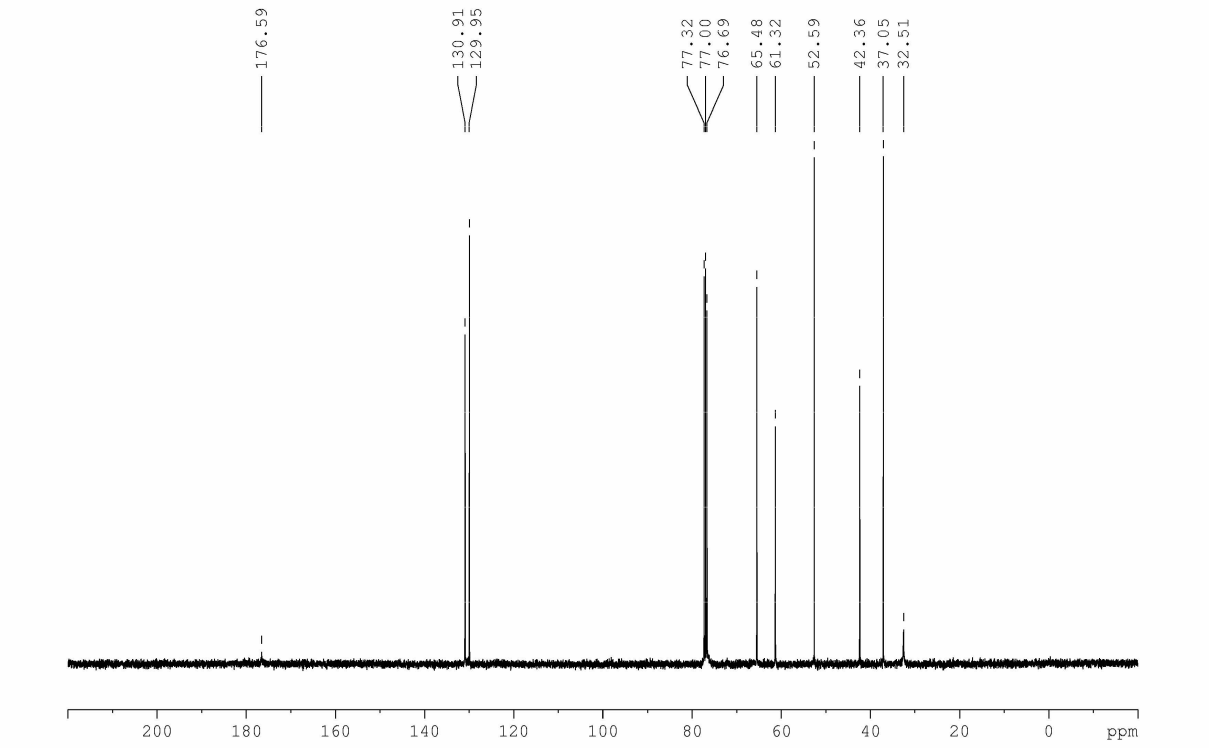
N–O
HO
1.00
1.00
2.95
1.17
1.06
2.05
3.10
1.05
1.03
1.30
9
8
7
6
5
4
3
2
1
0
ppm


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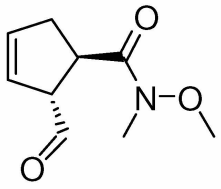
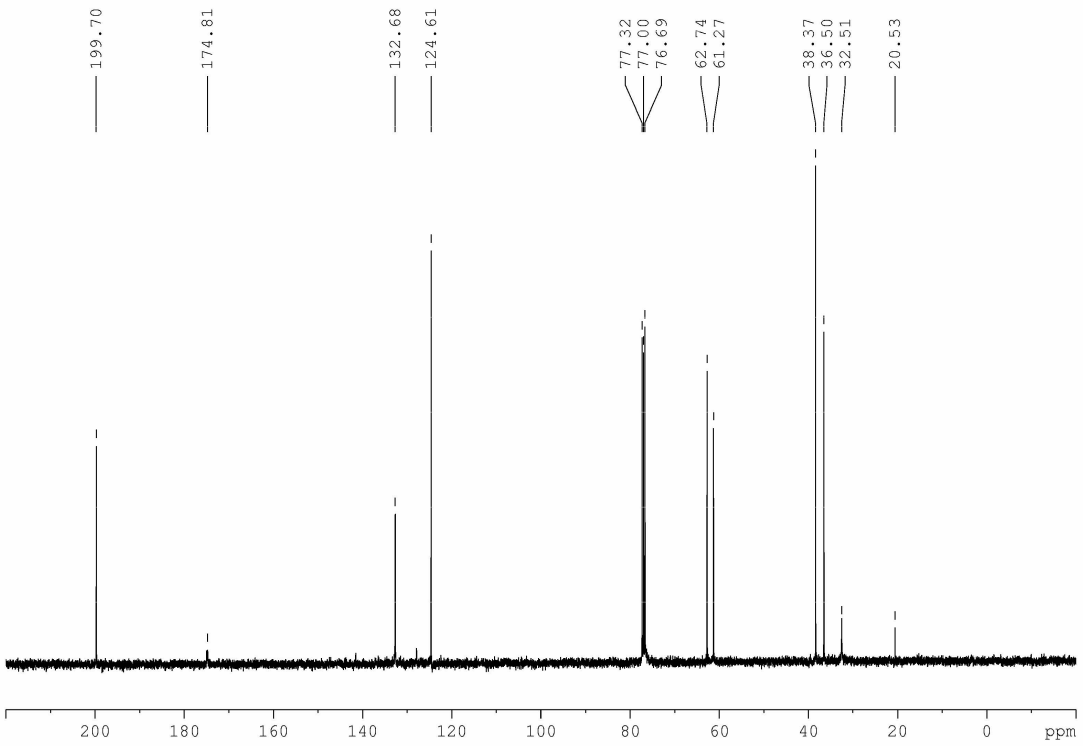
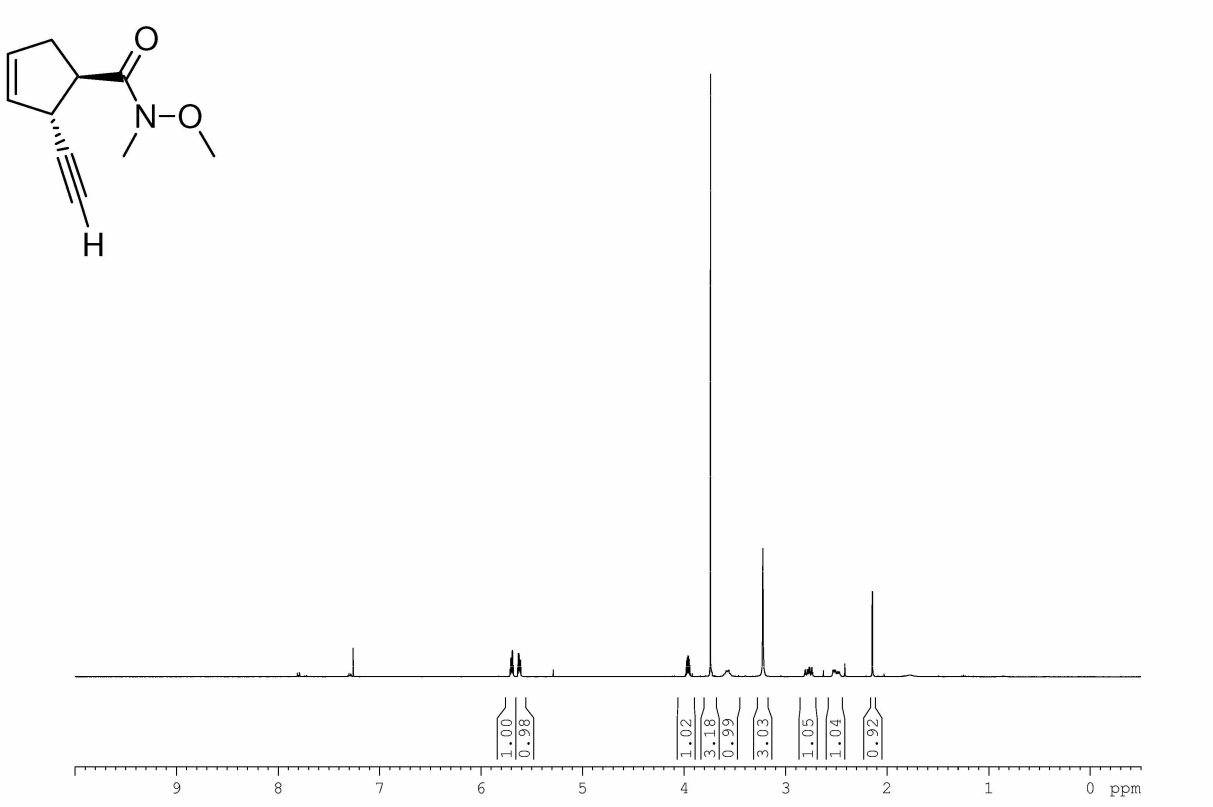
180
160
140
120
100
80
60
40
20
0
ppm


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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N–O
H
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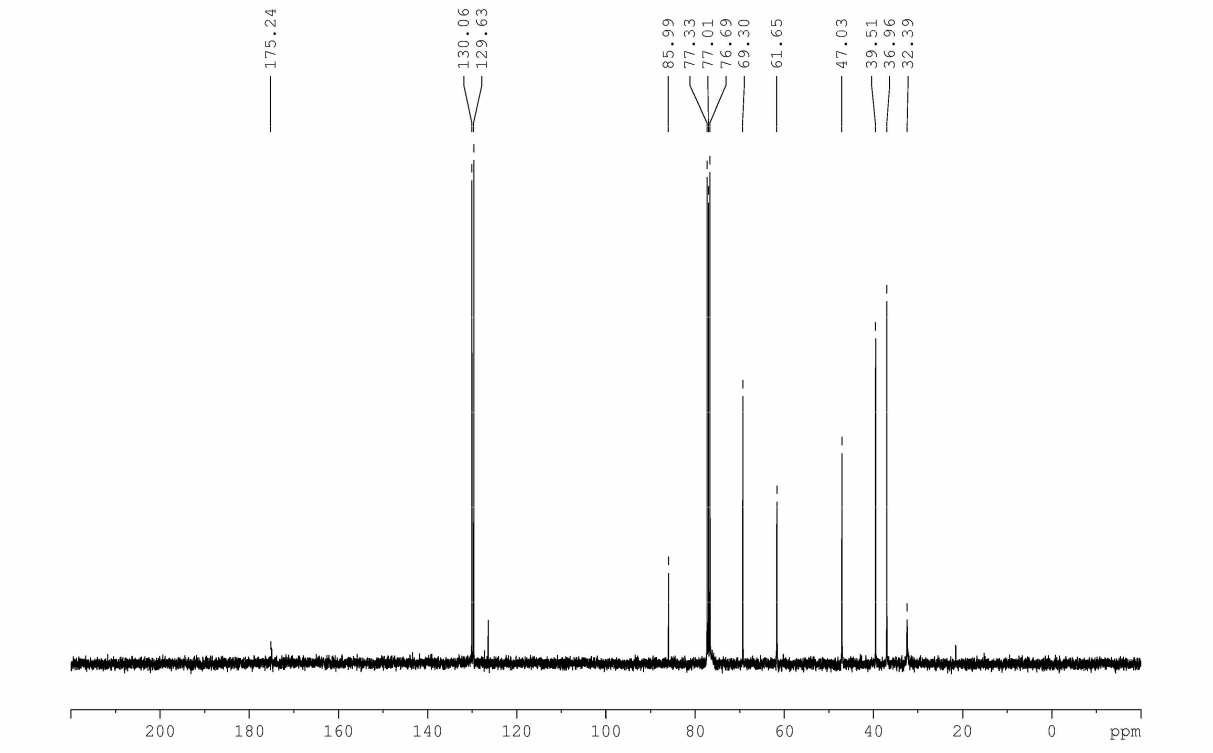
0.98
1.02
3.18
0.99
3.03
1.05
1.04
0.92
9
8
7
6
5
4
3
2
1
0
ppm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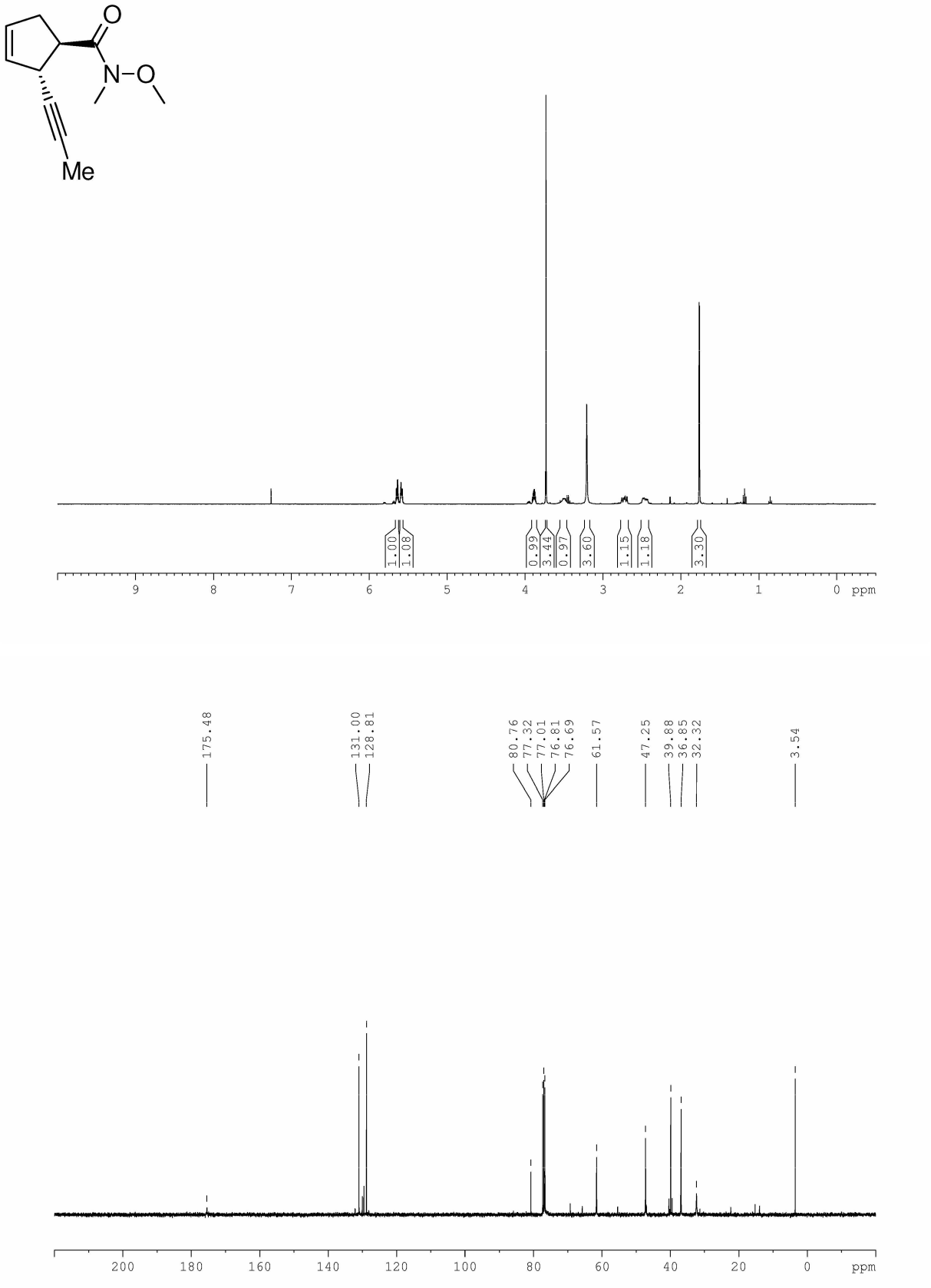
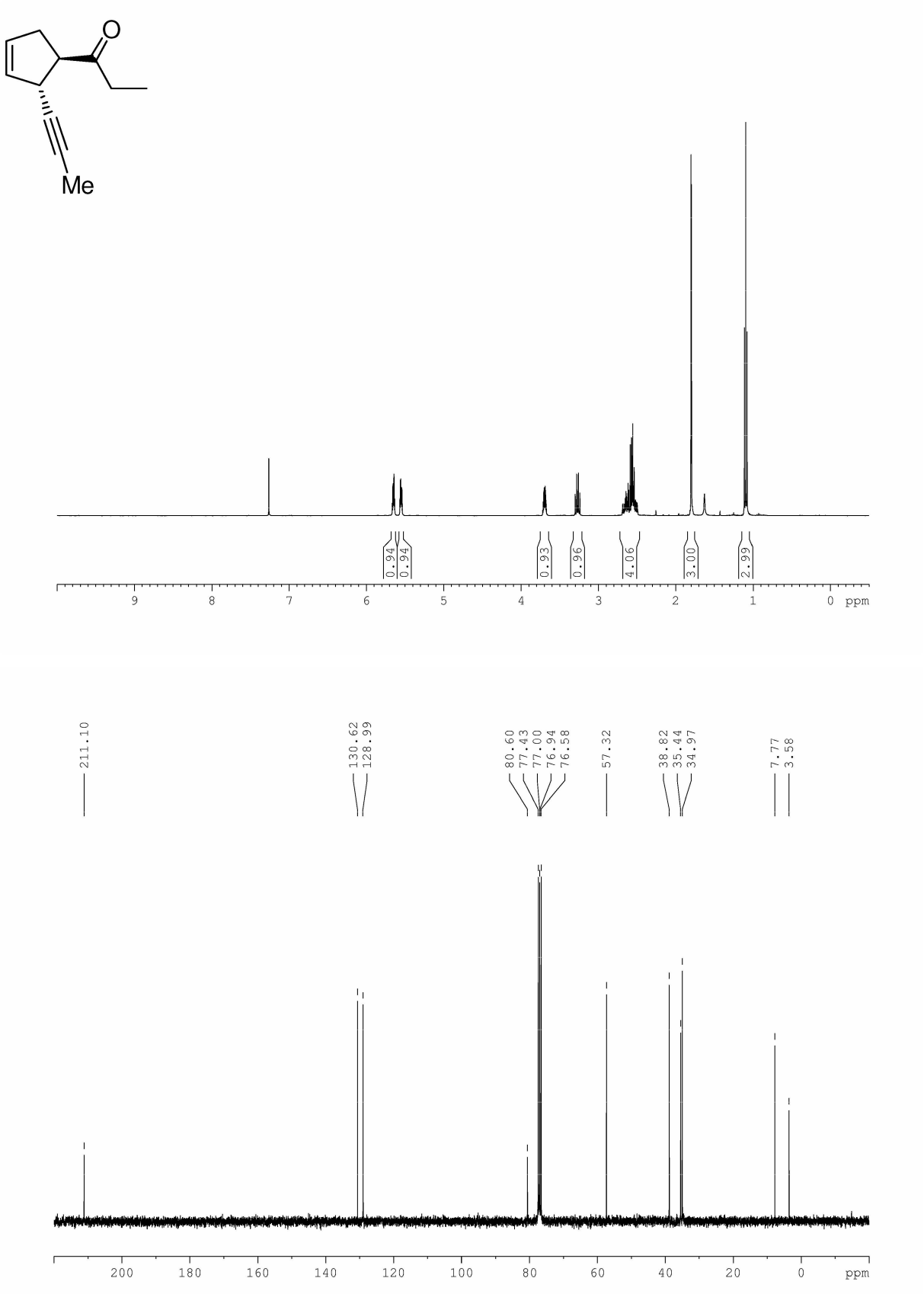
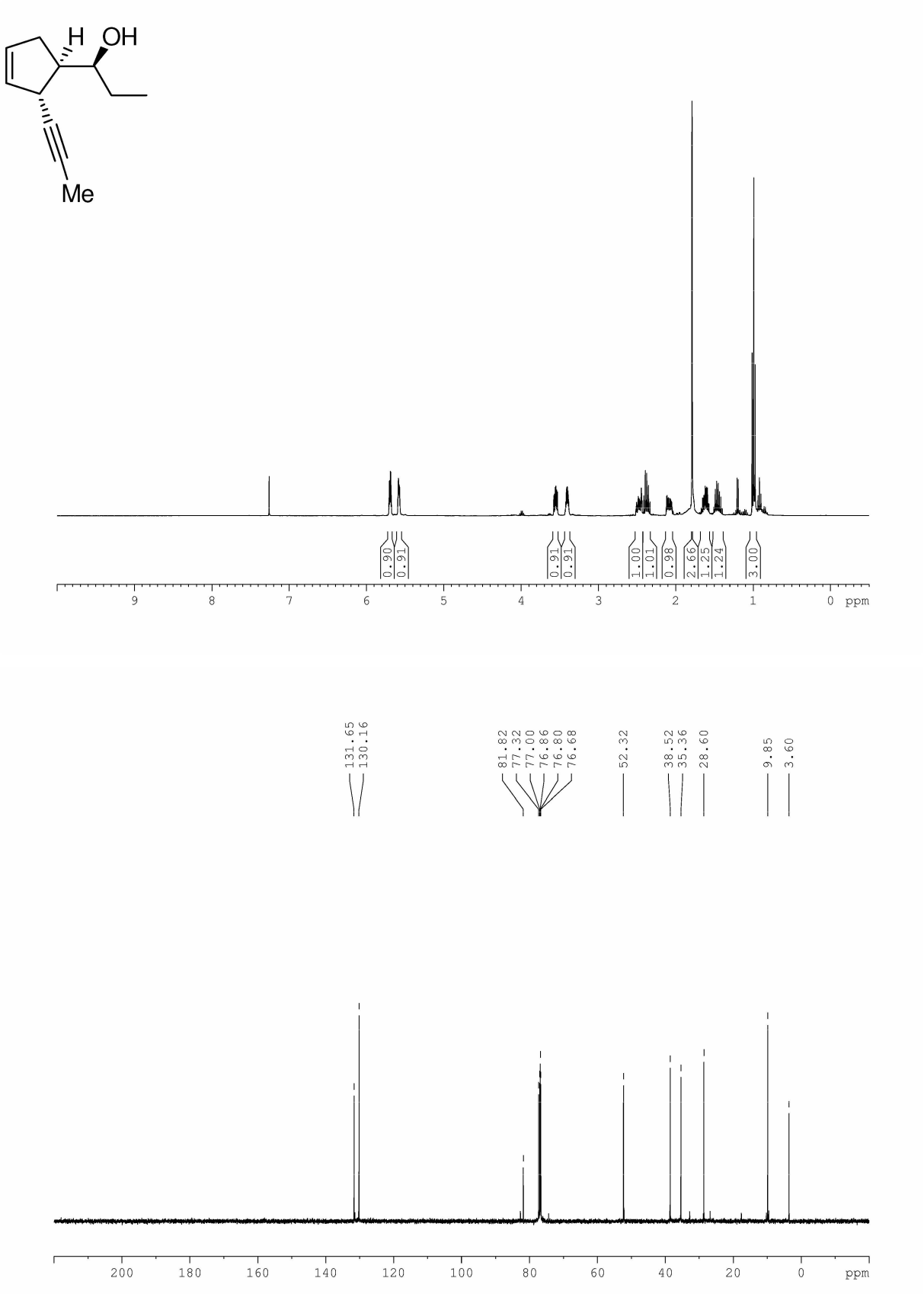
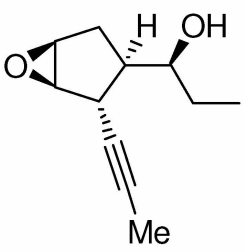
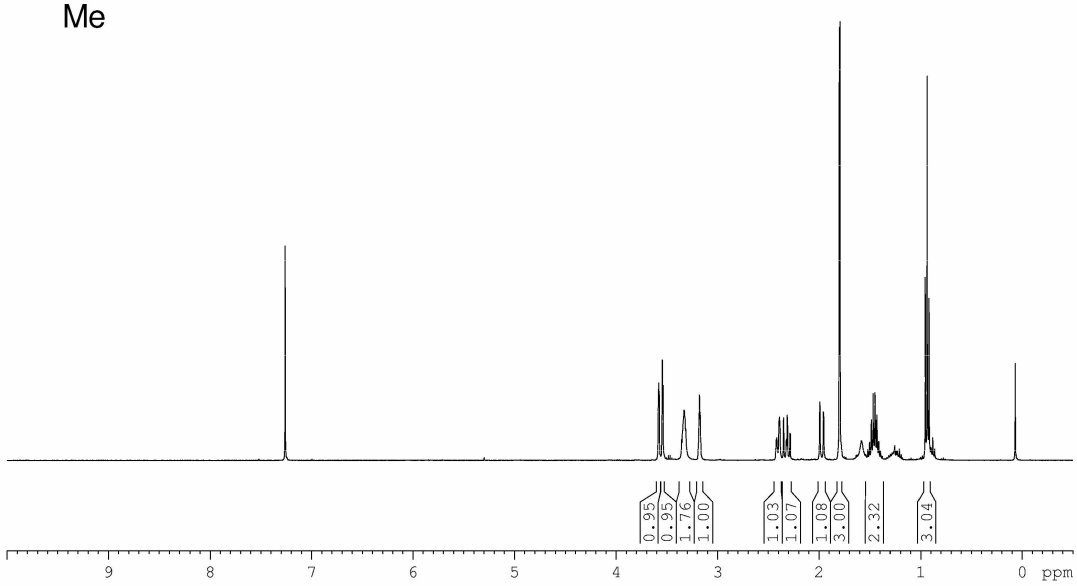
129.63
85.99
77.33
77.01
76.69
69.30
61.65
47.03
39.51
36.96
32.39
200
180
160
140
120
100
80
60
40
20
0
ppm


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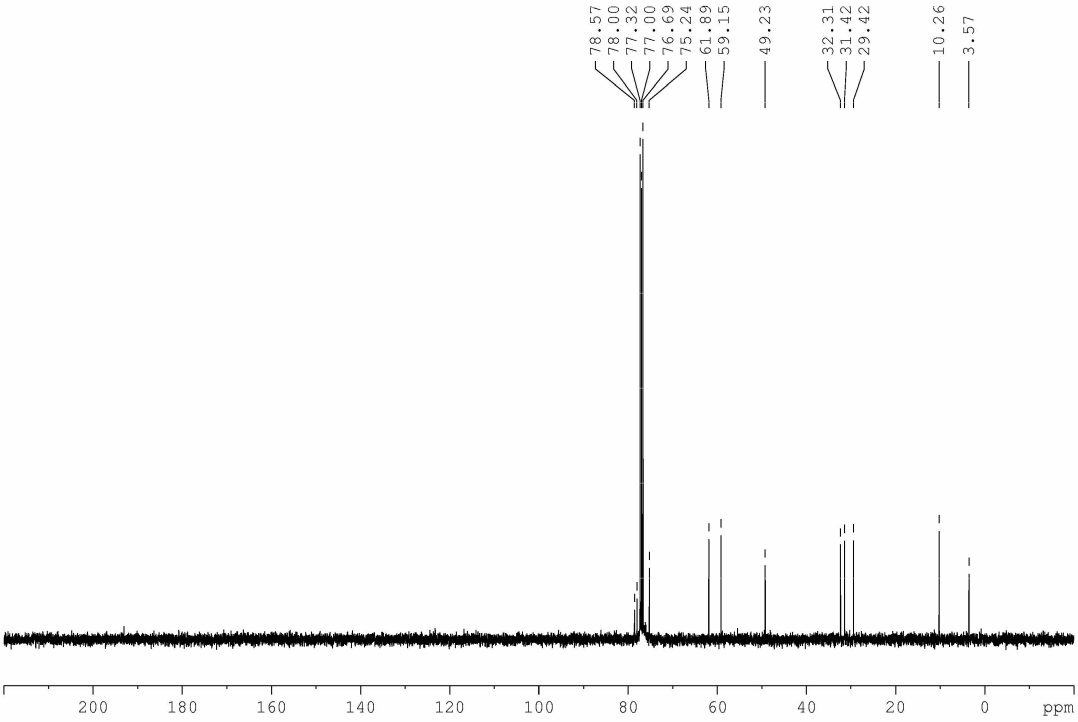
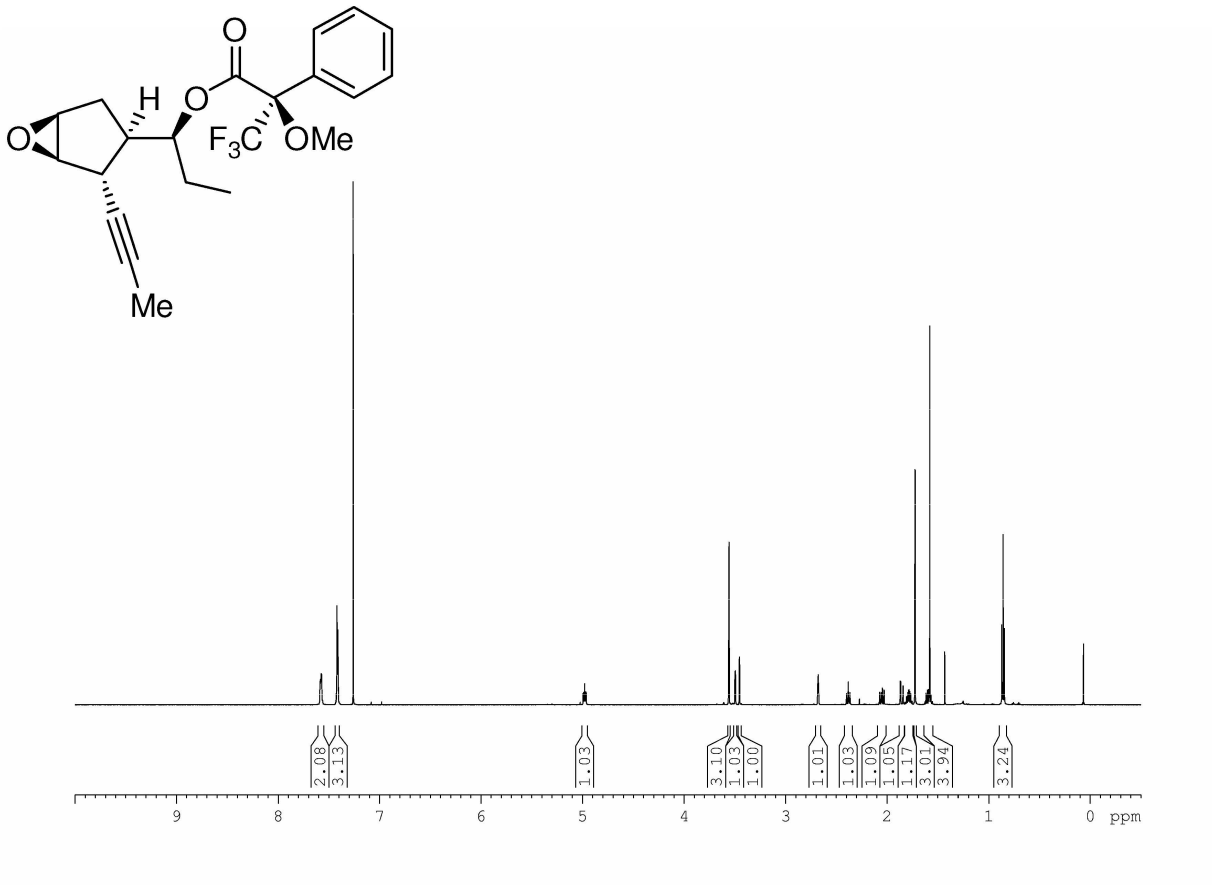
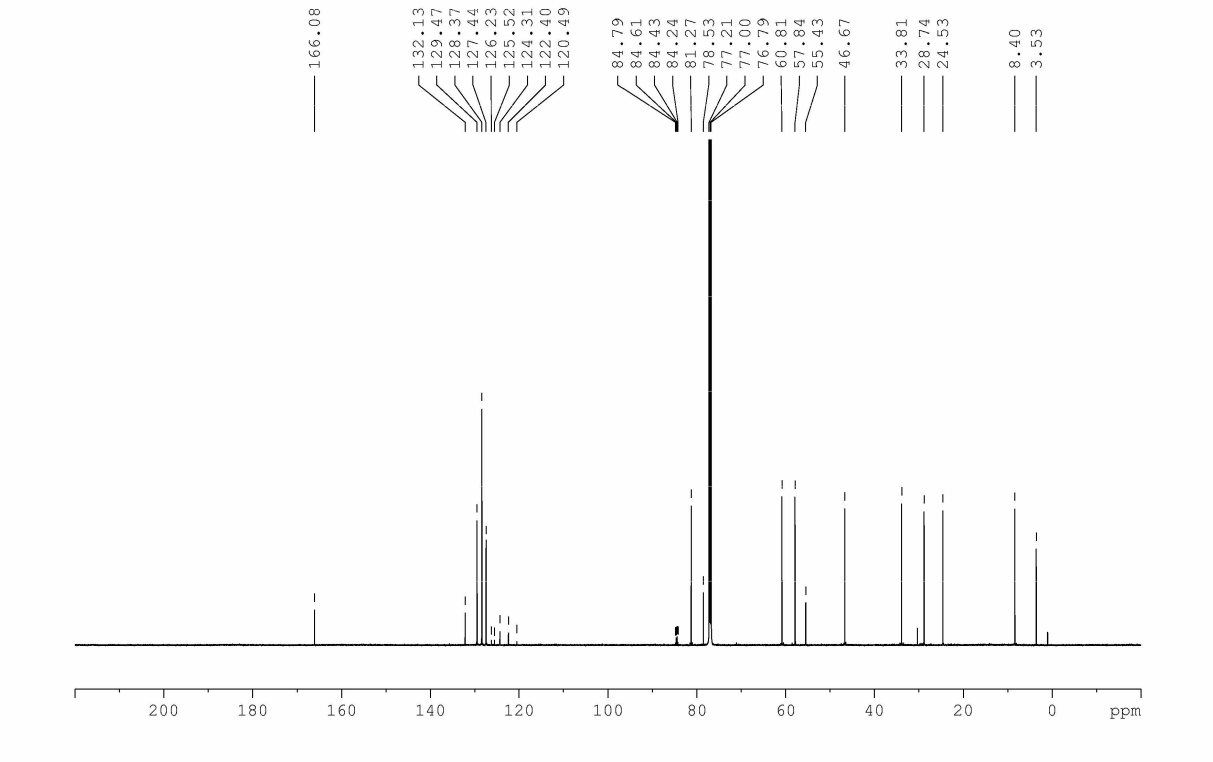
0.95
1.76
1.00
1.03
1.07
1.08
3.00
2.32
3.04
9
8
7
6
5
4
3
2
1
0
ppm


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
F3C
OMe
Me
2.08
3.13
1.03
3.10
1.03
1.00
1.01
1.03
1.09
1.05
1.17
3.01
3.94
3.24
9
8
7
6
5
4
3
2
1
0
ppm


166.08
132.13
129.47
128.37
127.44
126.23
125.52
124.31
122.40
120.49
84.79
84.61
84.43
84.24
81.27
78.53
77.21
77.00
76.79
60.81
57.84
55.43
46.67
33.81
28.74
24.53
8.40
3.53
200
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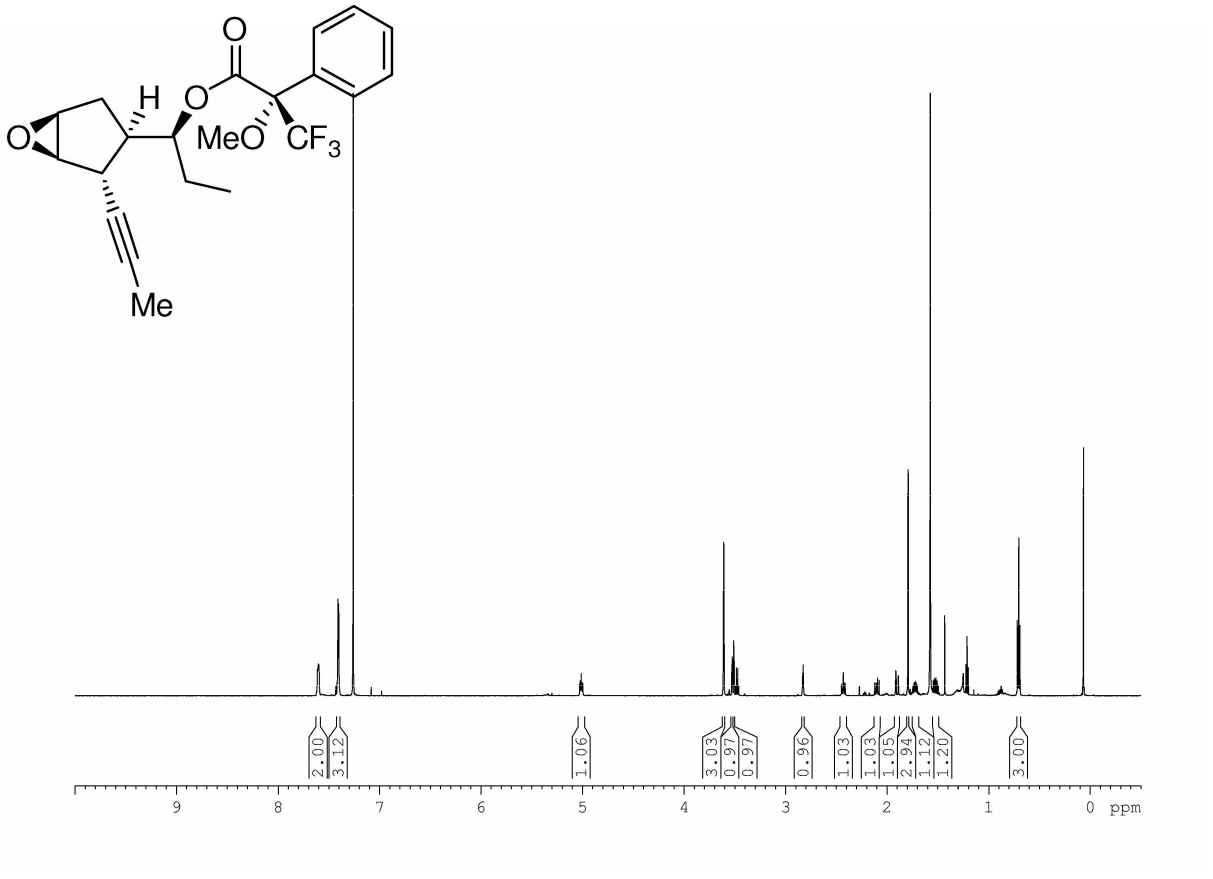
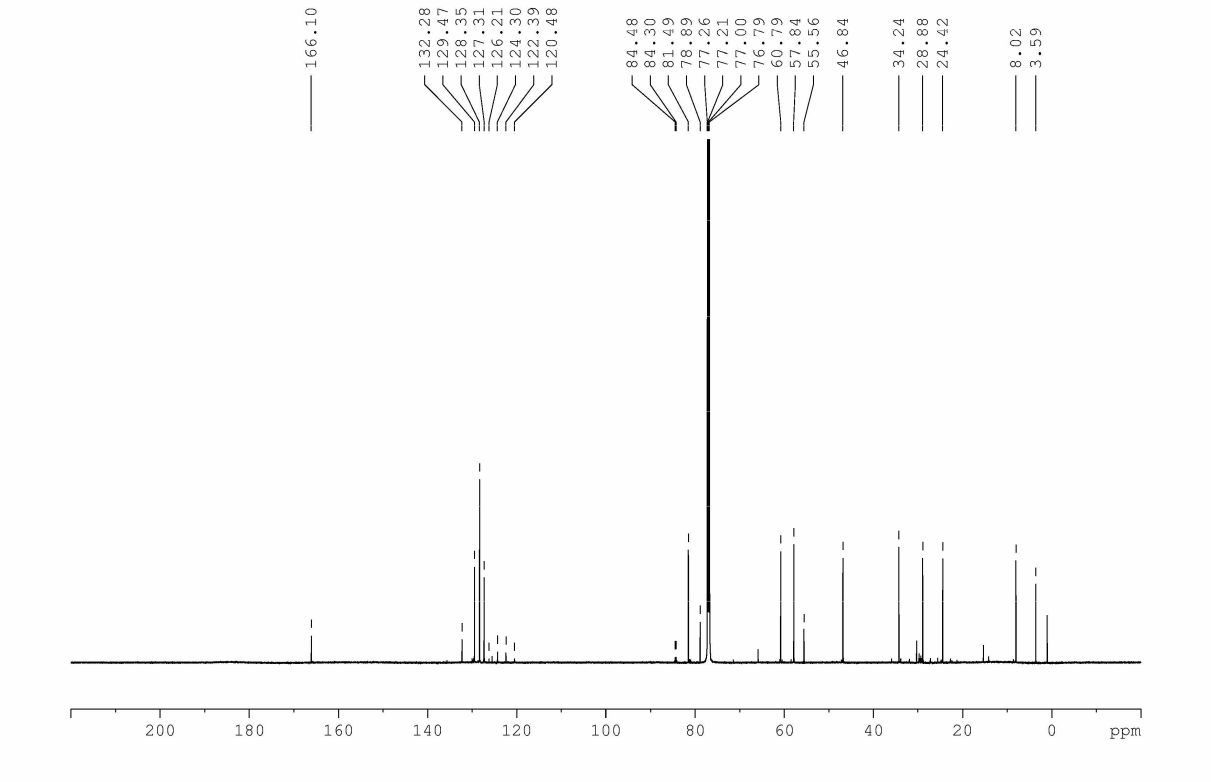
140
120
100
80
60
40
20
0
ppm


O
H
O
MeO
CF3
O
Me
2.00
3.12
1.06
3.03
0.97
0.97
0.96
1.03
1.03
1.05
2.94
1.12
1.20
3.00
9
8
7
6
5
4
3
2
1
0 ppm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132.28
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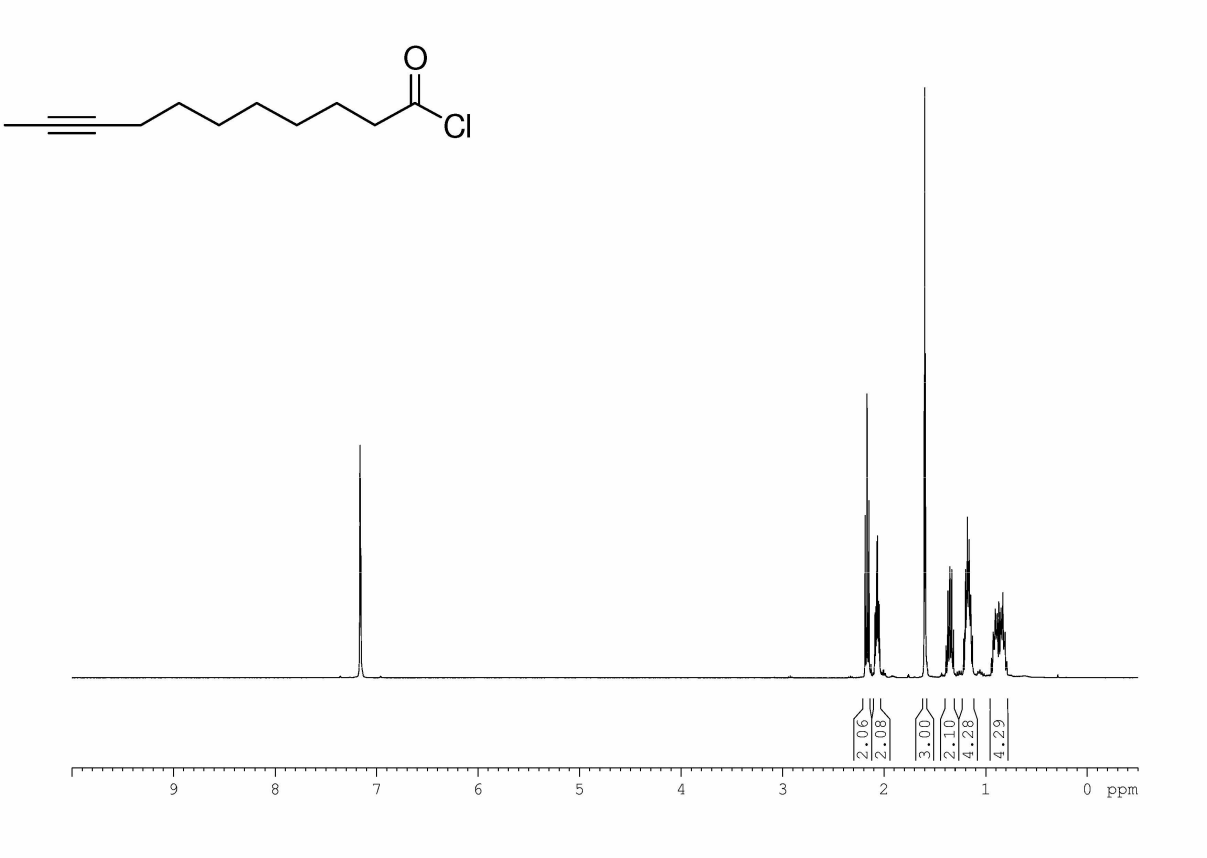
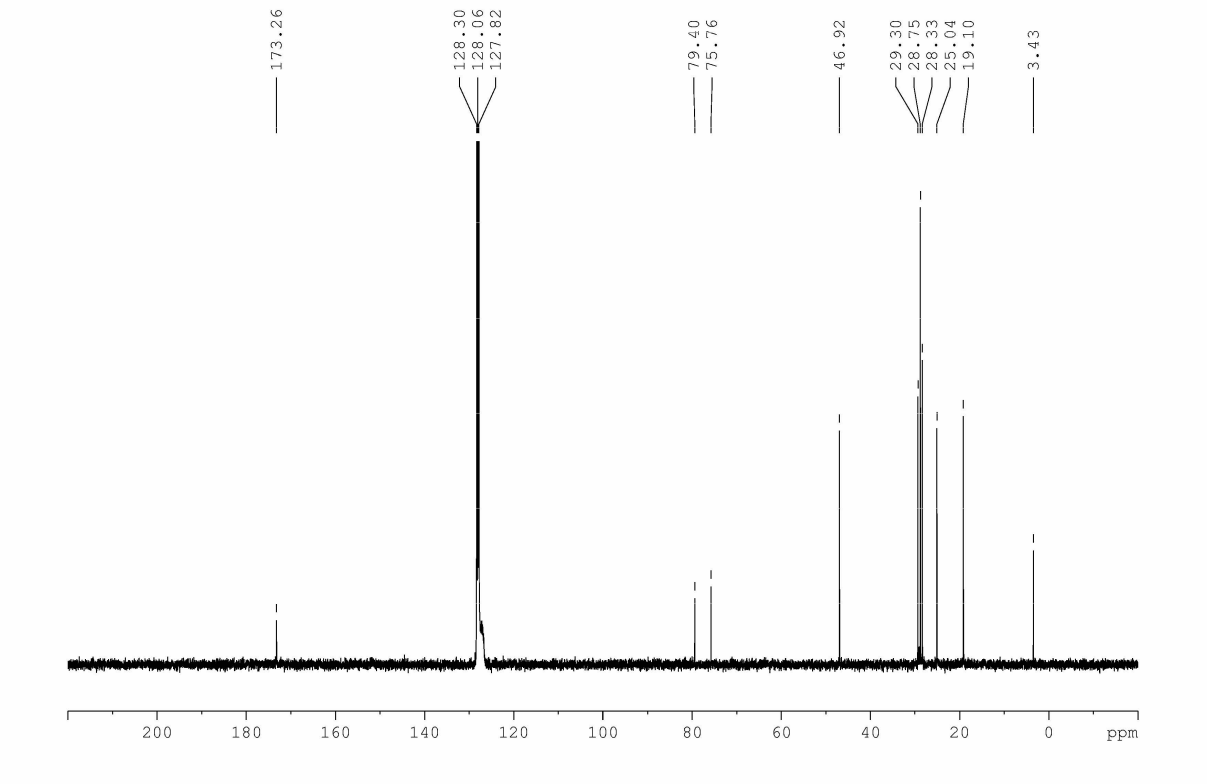
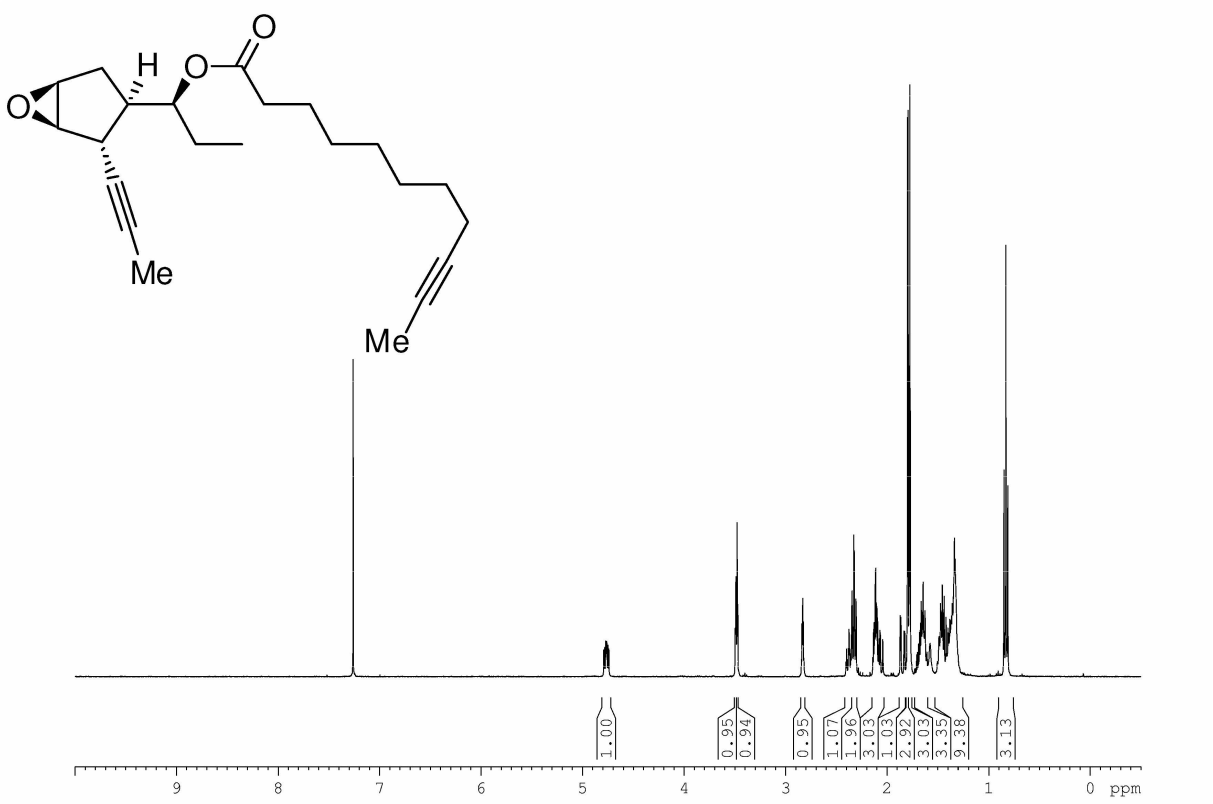
127.31
126.21
124.30
122.39
120.48
84.48
84.30
81.49
78.89
77.26
77.21
77.00
76.79
60.79
57.84
55.56
46.84
34.24
28.88
24.42
8.02
3.59
200
180
160
140
120
100
80
60
40
20
0
ppm


O
Cl
2.06
2.08
3.00
2.10
4.28
4.29
9
8
7
6
5
4
3
2
1
0 ppm


173.26
128.30
128.06
127.82
79.40
75.76
46.92
29.30
28.75
28.33
25.04
19.10
3.43
200
180
160
140
120
100
80
60
40
20
0
ppm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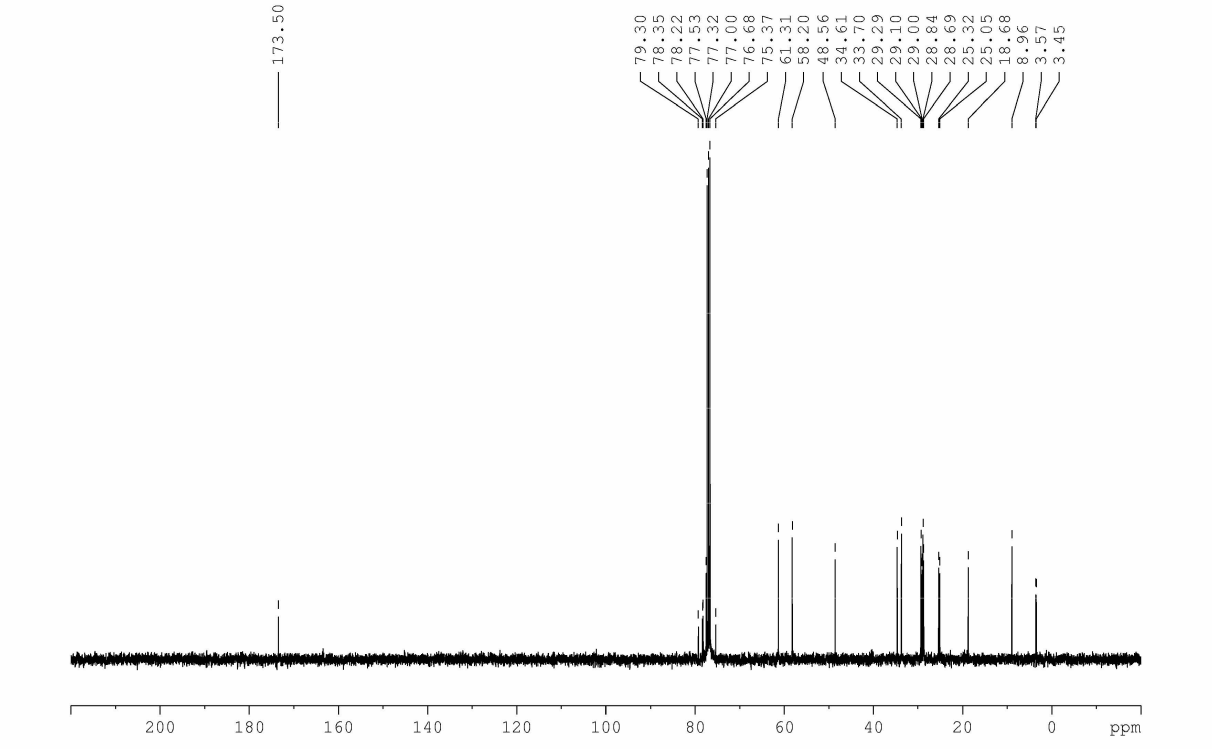
H
O
O
Me
Me
1.00
0.95
0.94
0.95
1.07
1.96
3.03
1.03
2.92
3.03
3.35
9.38
3.13
9
8
7
6
5
4
3
2
1
0
ppm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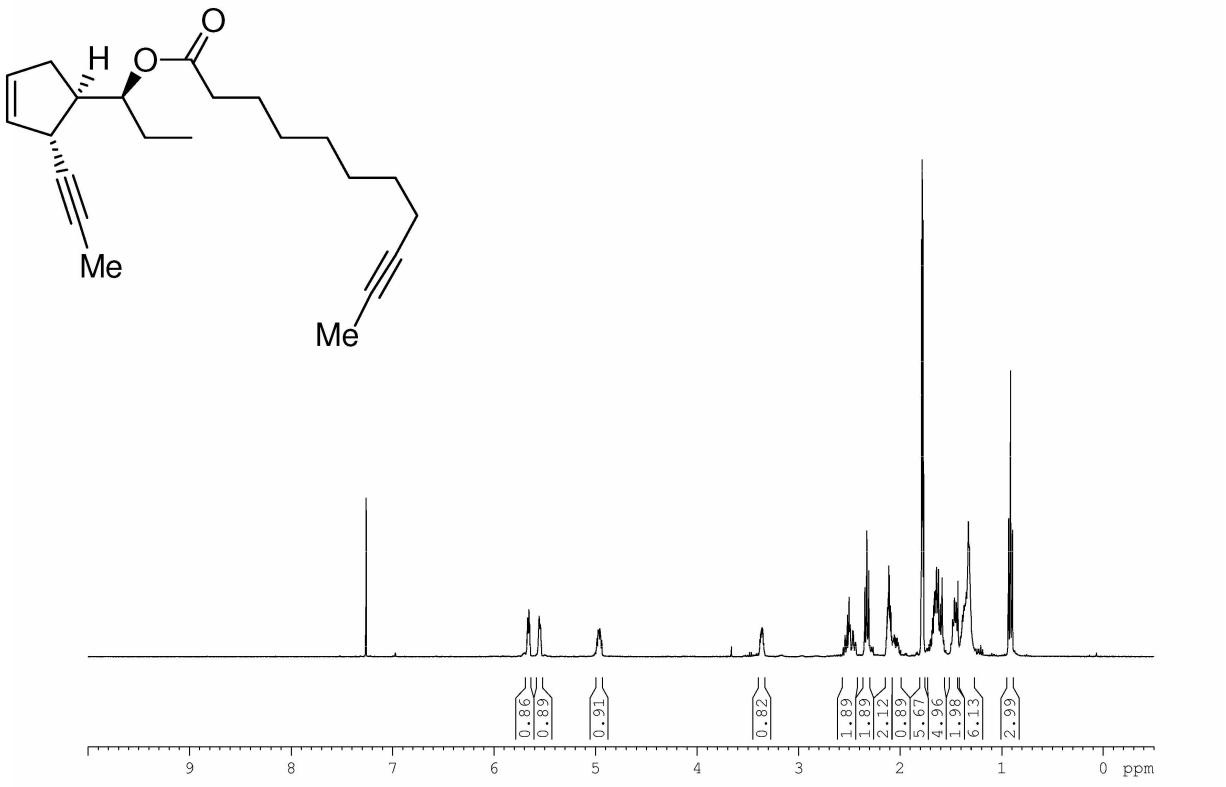
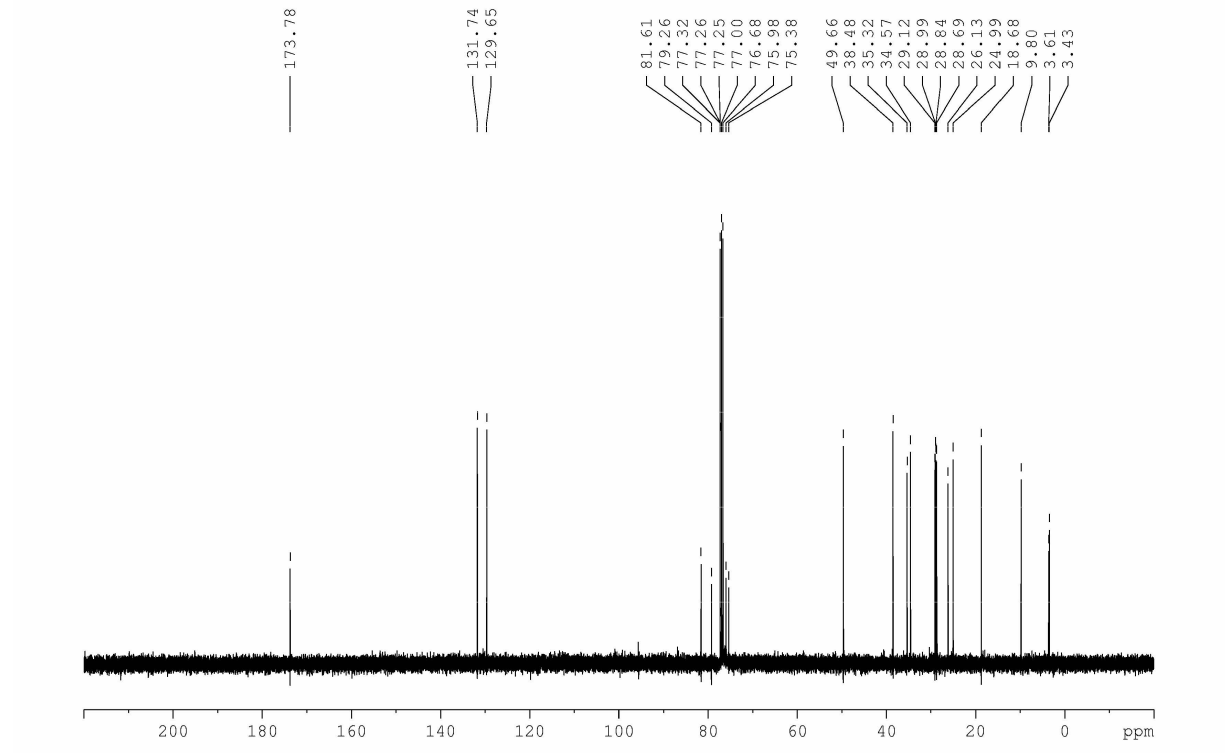
78.35
78.22
77.53
77.32
77.00
76.68
75.37
61.31
58.20
48.56
34.61
33.70
29.29
29.10
29.00
28.84
28.69
25.32
25.05
18.68
8.96
3.57
3.45
200
180
160
140
120
100
80
60
40
20
0
ppm


H
O
O
Me
Me
0.86
0.89
0.91
0.82
1.89
1.89
2.12
0.89
5.67
4.96
1.98
6.13
2.99
9
8
7
6
5
4
3
2
1
0
ppm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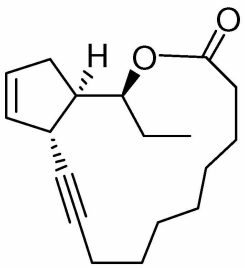
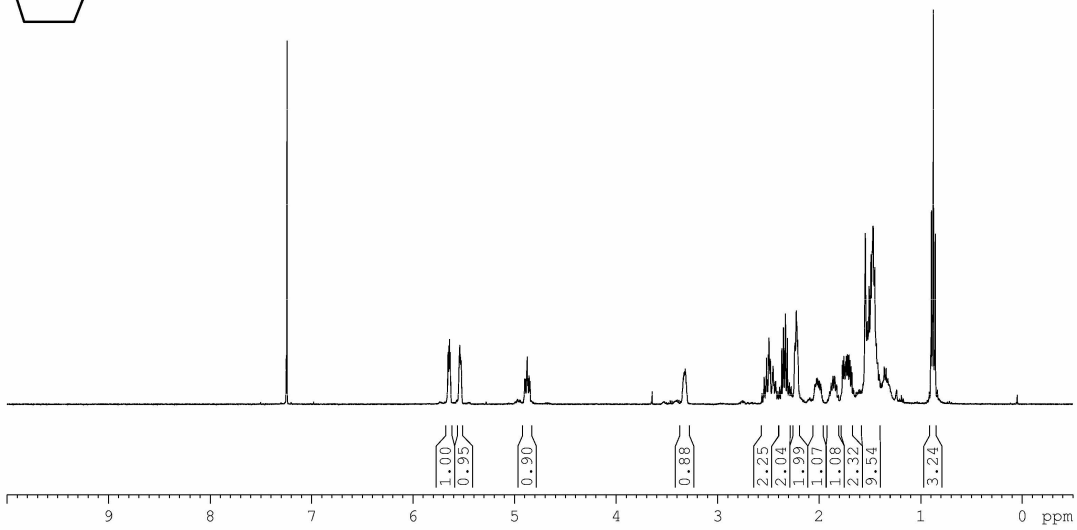
129.65
81.61
79.26
77.32
77.26
77.25
77.00
76.68
75.98
75.38
49.66
38.48
35.32
34.57
29.12
28.99
28.84
28.69
26.13
24.99
18.68
9.80
3.61
3.43
200
180
160
140
120
100
80
60
40
20
0
ppm


H
O
O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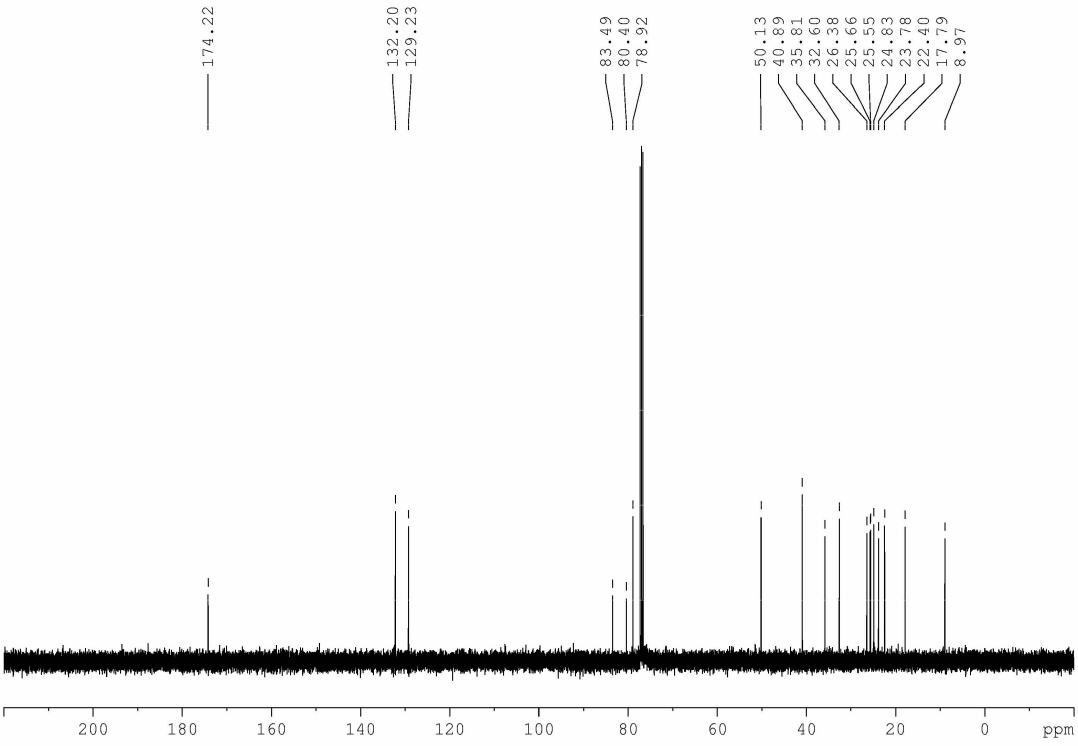
0.95
0.90
0.88
2.25
2.04
1.99
1.07
1.08
2.32
9.54
3.24
9
8
7
6
5
4
3
2
1
0
ppm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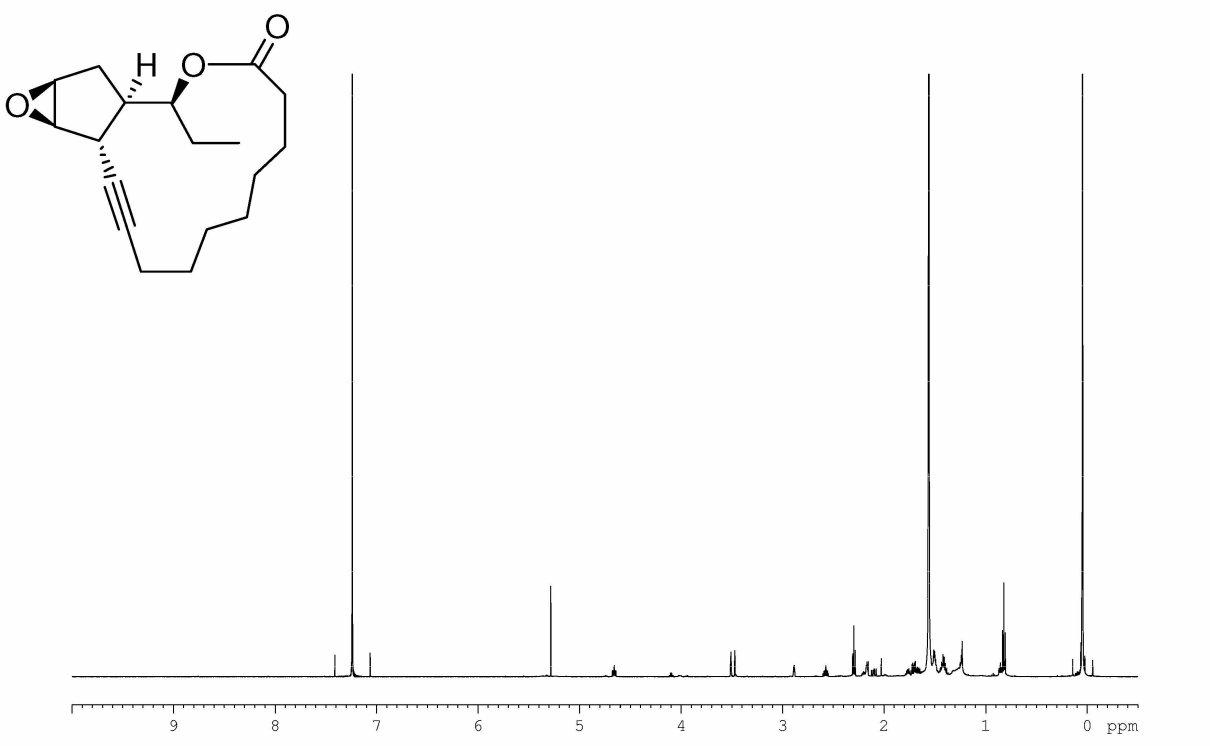
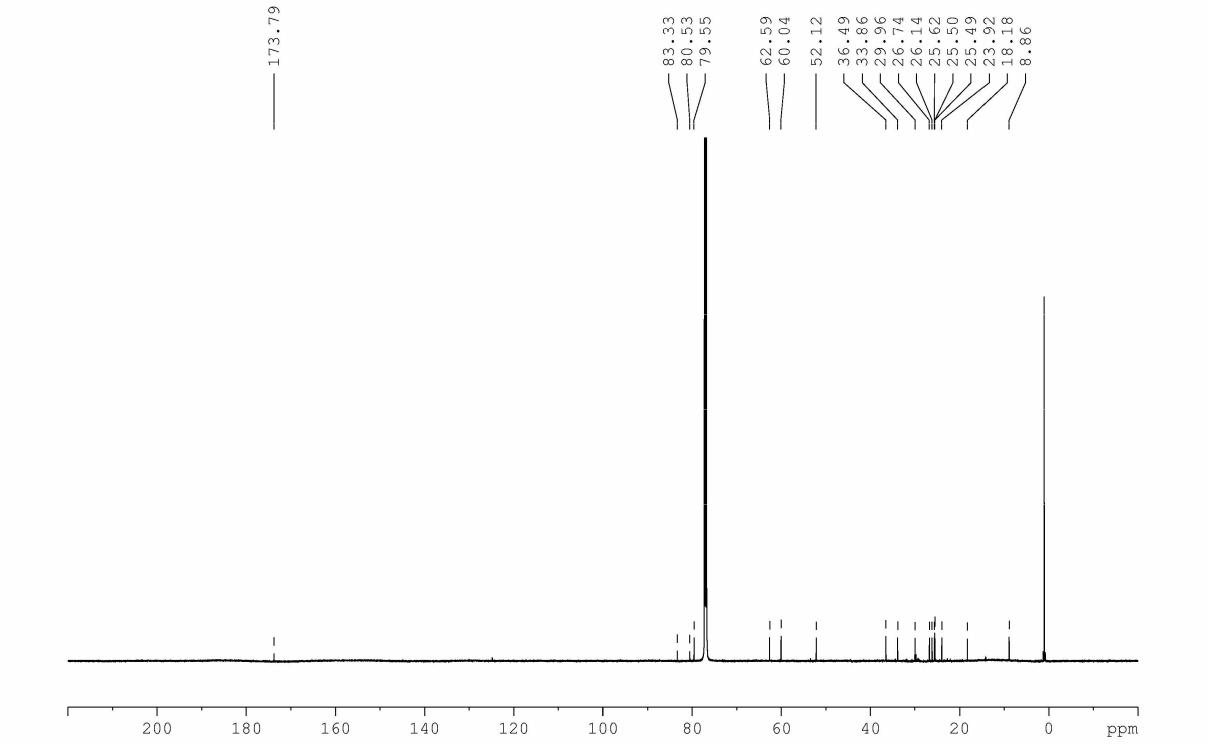
132.20
129.23
83.49
80.40
78.92
50.13
40.89
35.81
32.60
26.38
25.66
25.55
24.83
23.78
22.40
17.79
8.97
200
180
160
140
120
100
80
60
40
20
0
ppm


O
H
O
O
9
8
7
6
5
4
3
2
1
0
ppm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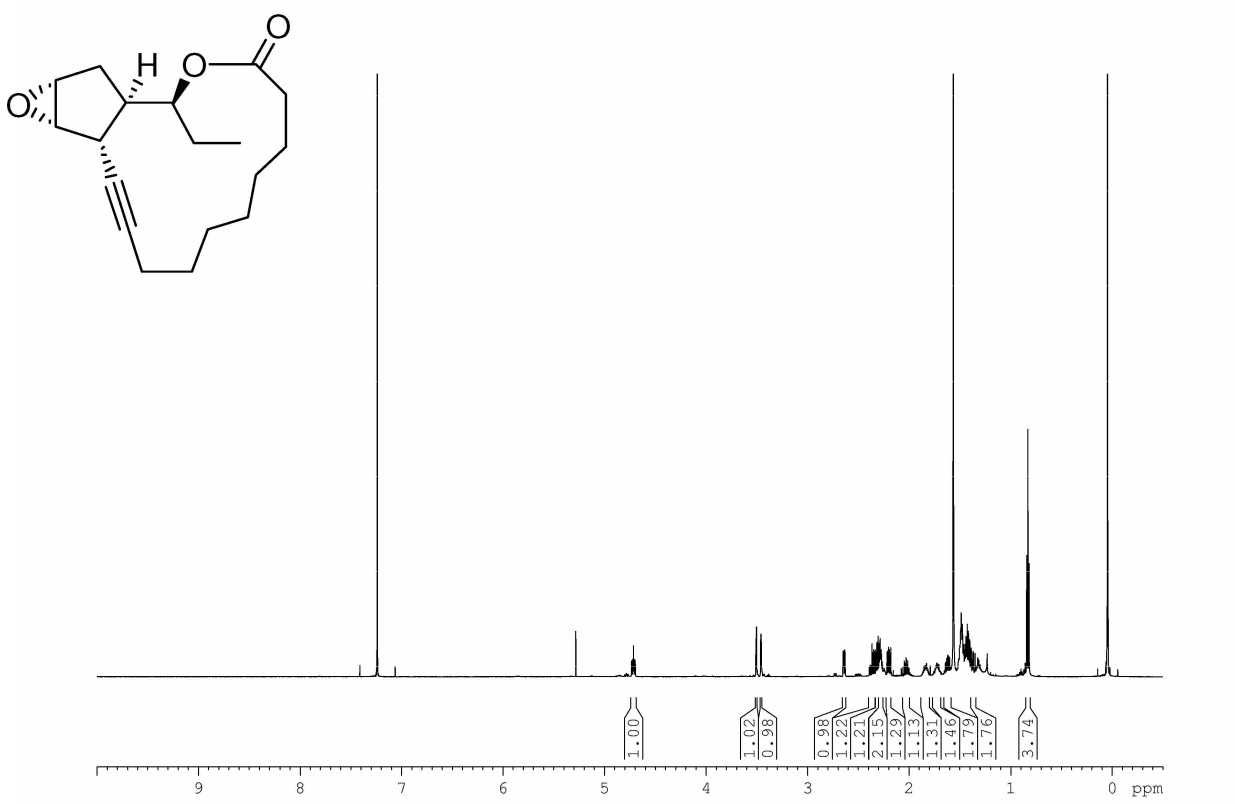
83.33
80.53
79.55
62.59
60.04
52.12
36.49
33.86
29.96
26.74
26.14
25.62
25.50
25.49
23.92
18.18
8.86
200
180
160
140
120
100
80
60
40
20
0
ppm


H
O
O
O
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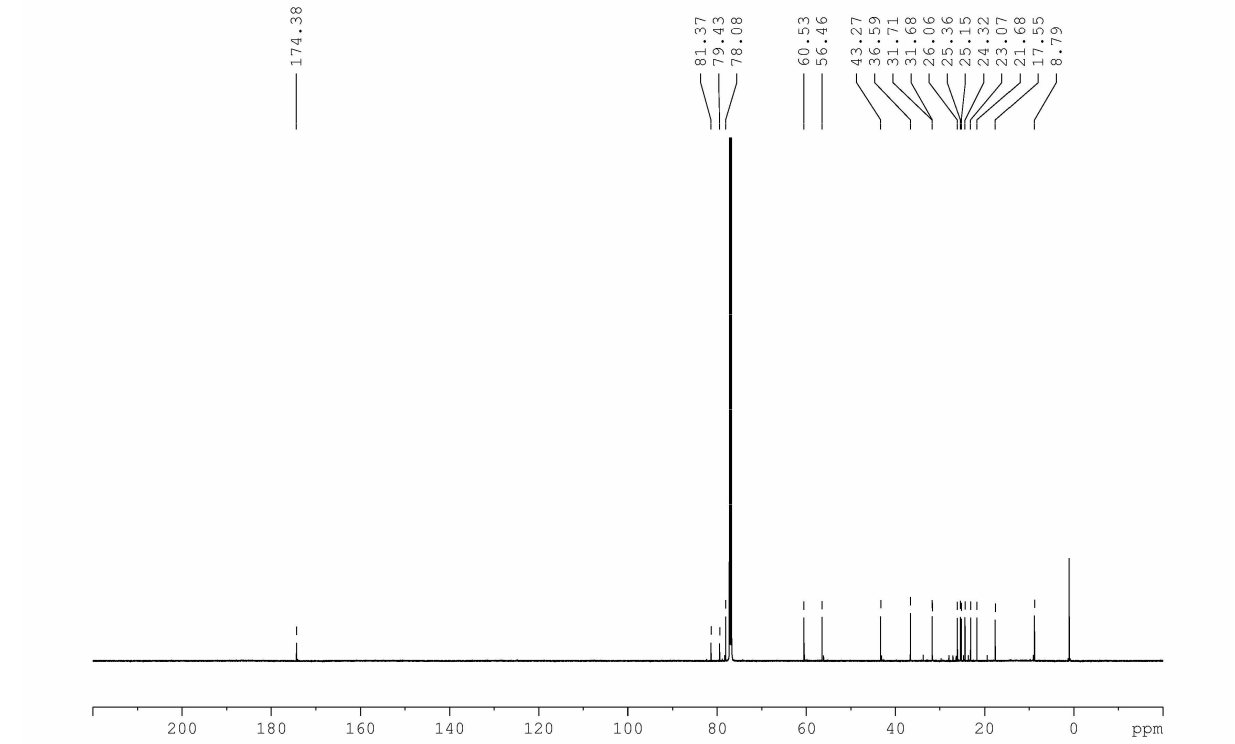
1.02
0.98
0.98
1.22
1.21
2.15
1.29
1.13
1.31
1.46
1.79
1.76
3.74
9
8
7
6
5
4
3
2
1
0
ppm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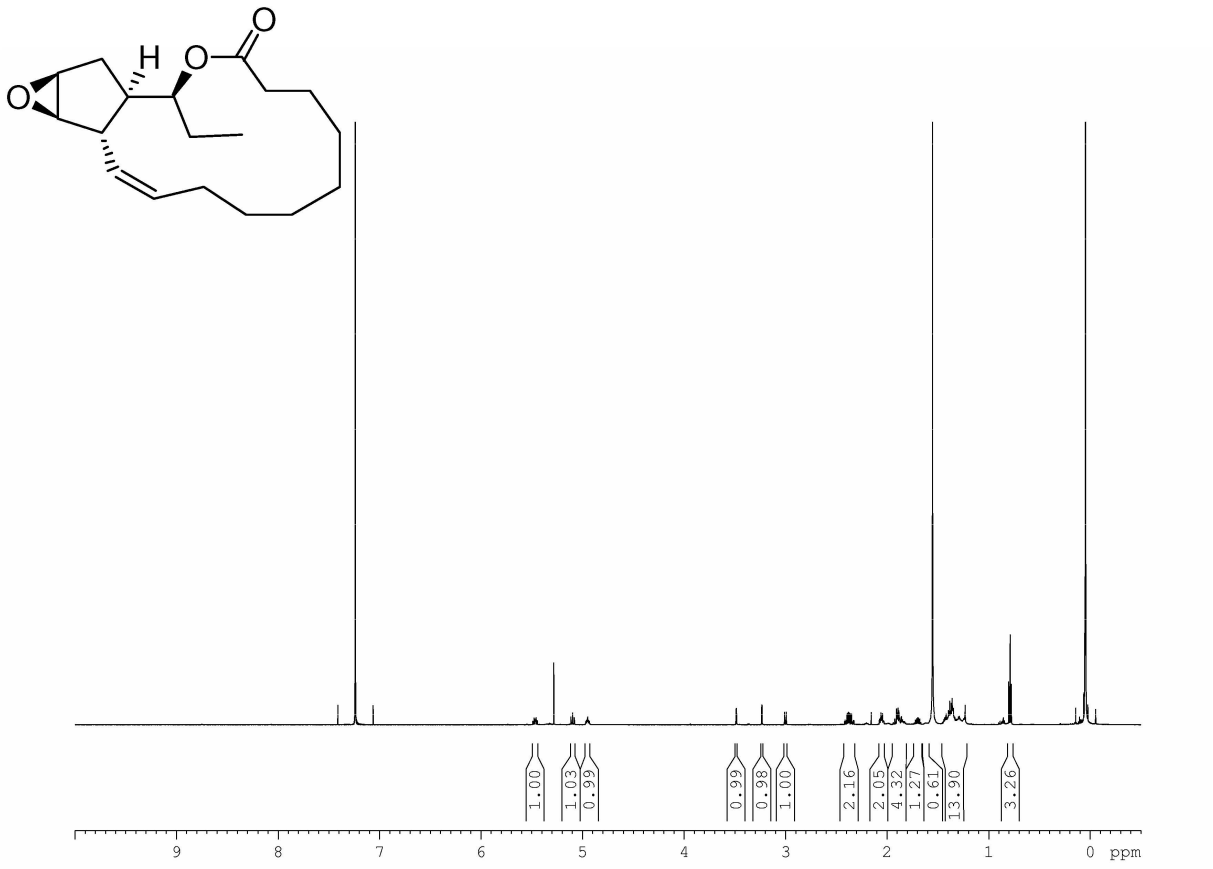
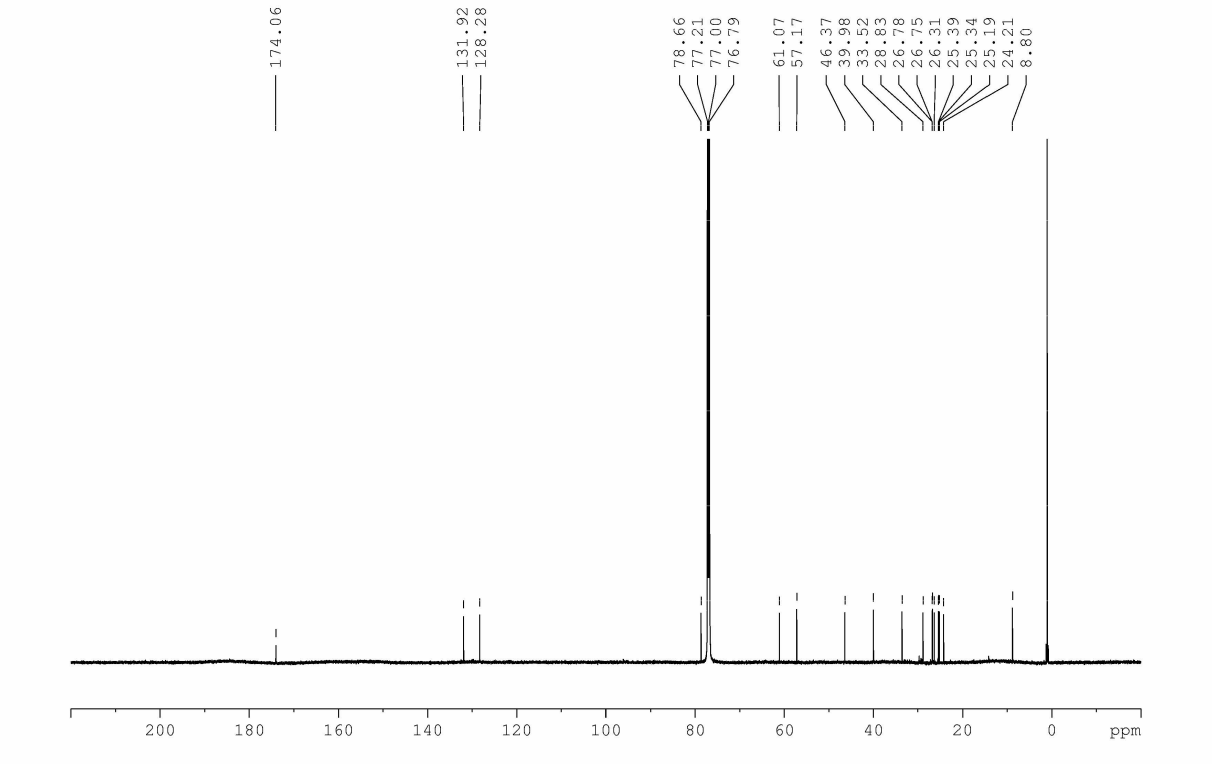
56.46
43.27
36.59
31.71
31.68
26.06
25.36
25.15
24.32
23.07
21.68
17.55
8.79
200
180
160
140
120
100
80
60
40
20
0
ppm


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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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
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120
100
80
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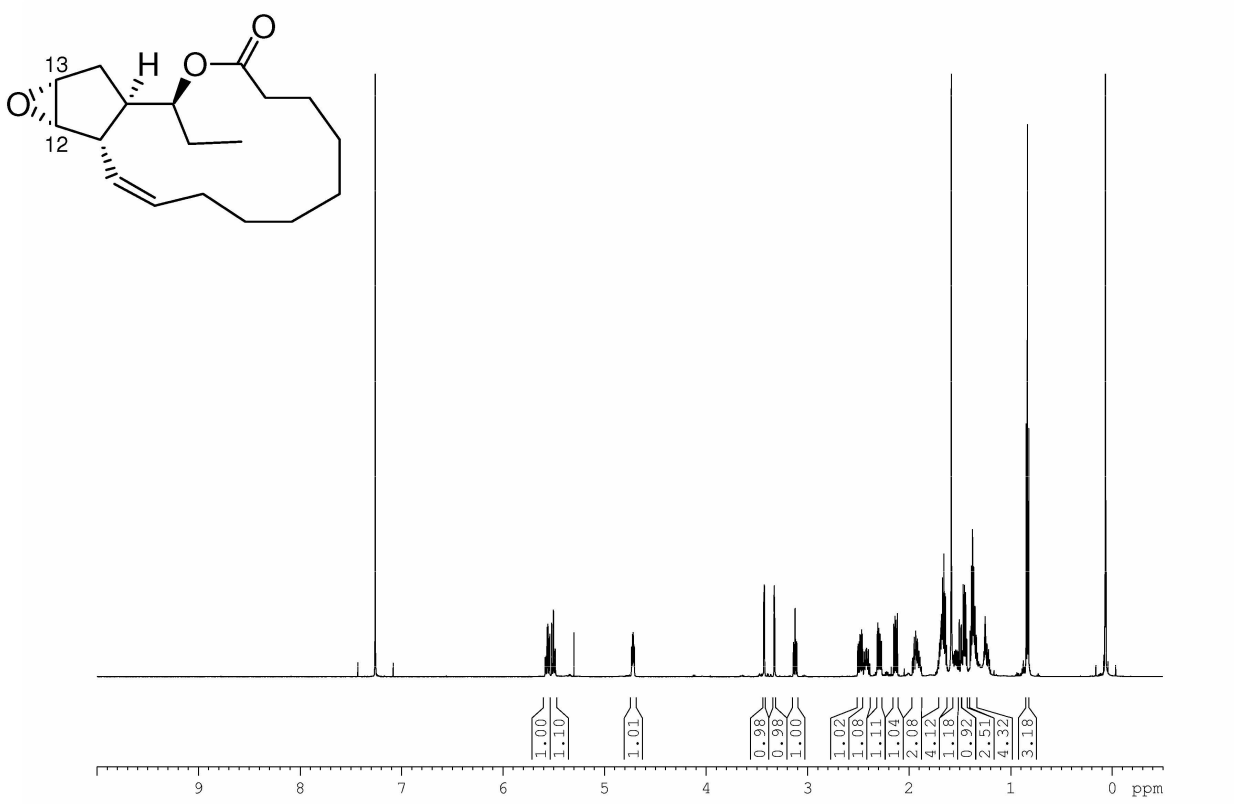
40
20
0
ppm


13
H
O
O
O
12
1.00
1.10
1.01
0.98
0.98
1.00
1.02
1.08
1.11
1.04
2.08
4.12
1.18
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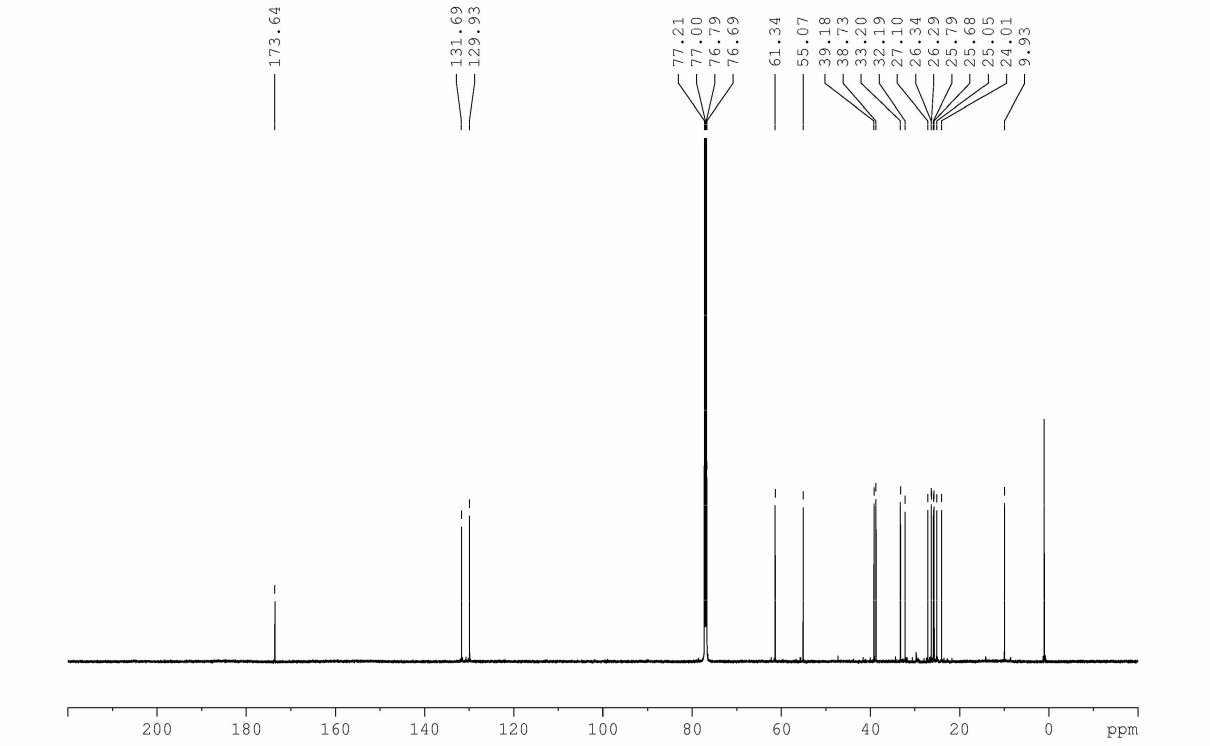
2.51
4.32
3.18
9
8
7
6
5
4
3
2
1
0
ppm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76.69
61.34
55.07
39.18
38.73
33.20
32.19
27.10
26.34
26.29
25.79
25.68
25.05
24.01
9.93
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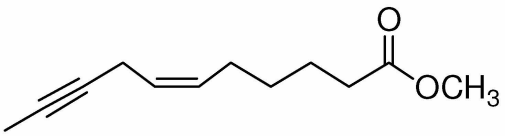
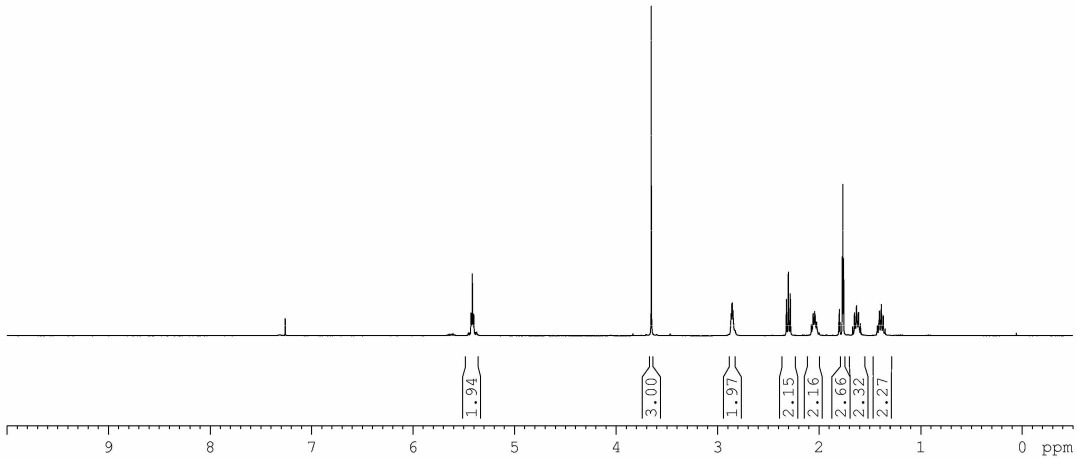
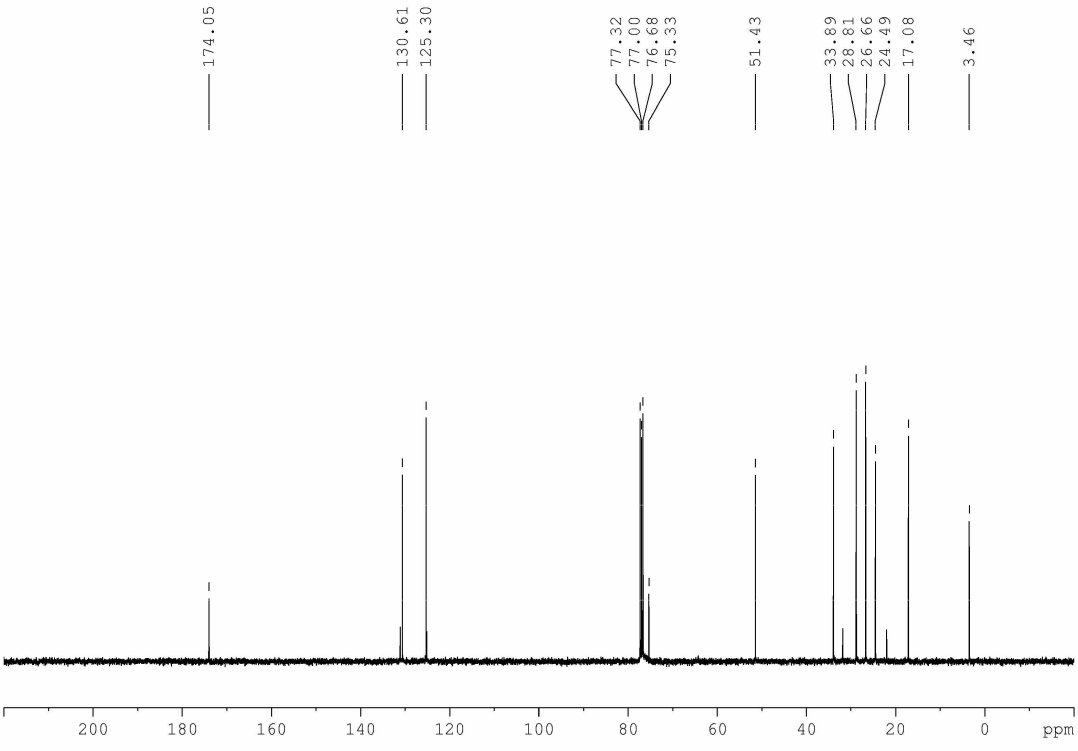
160
140
120
100
80
60
40
20
0
ppm


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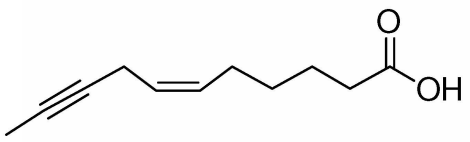
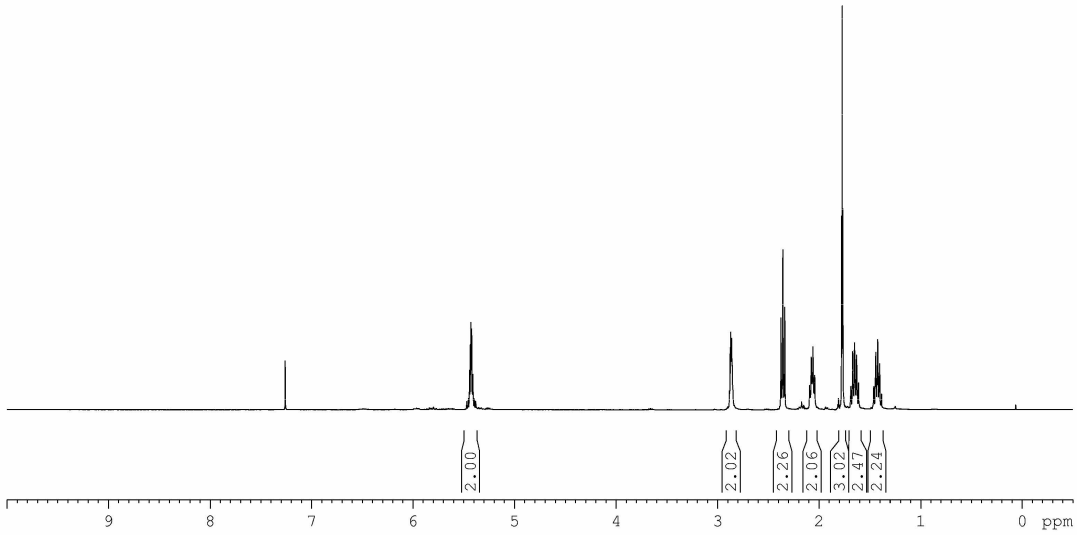
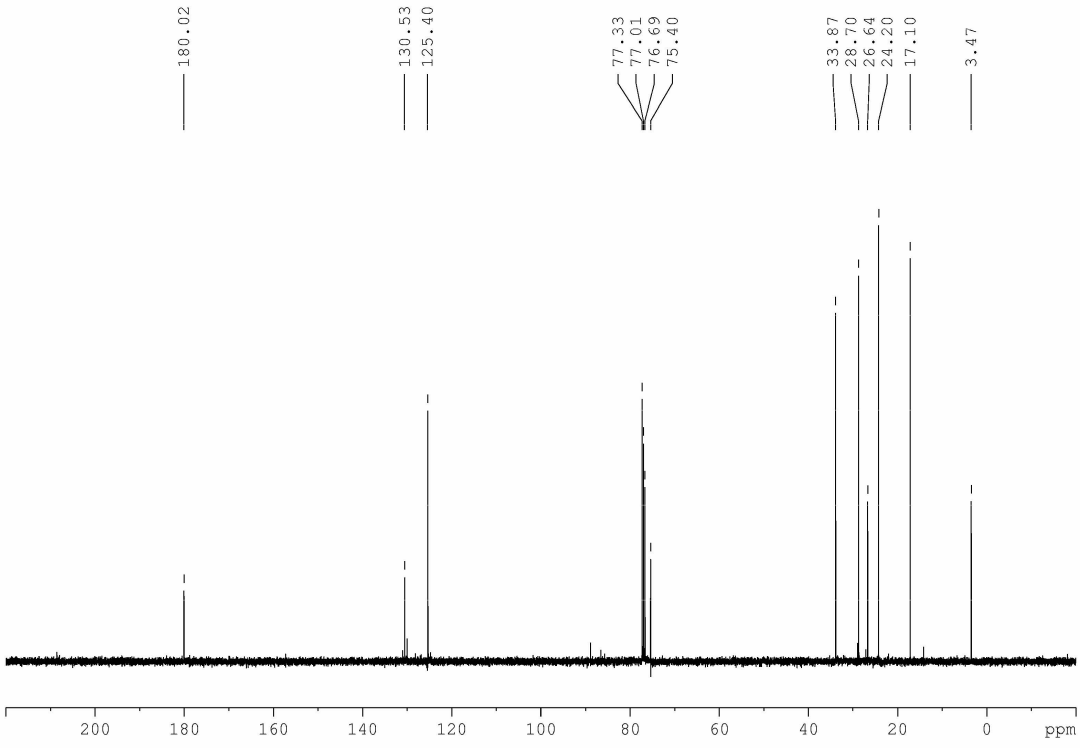
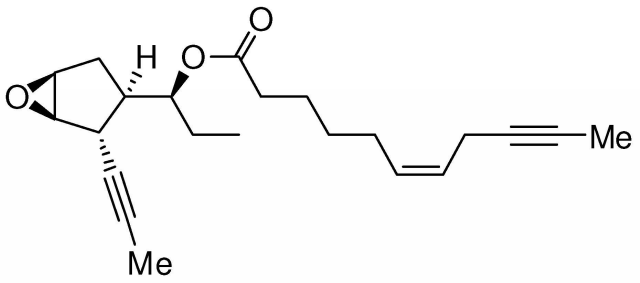
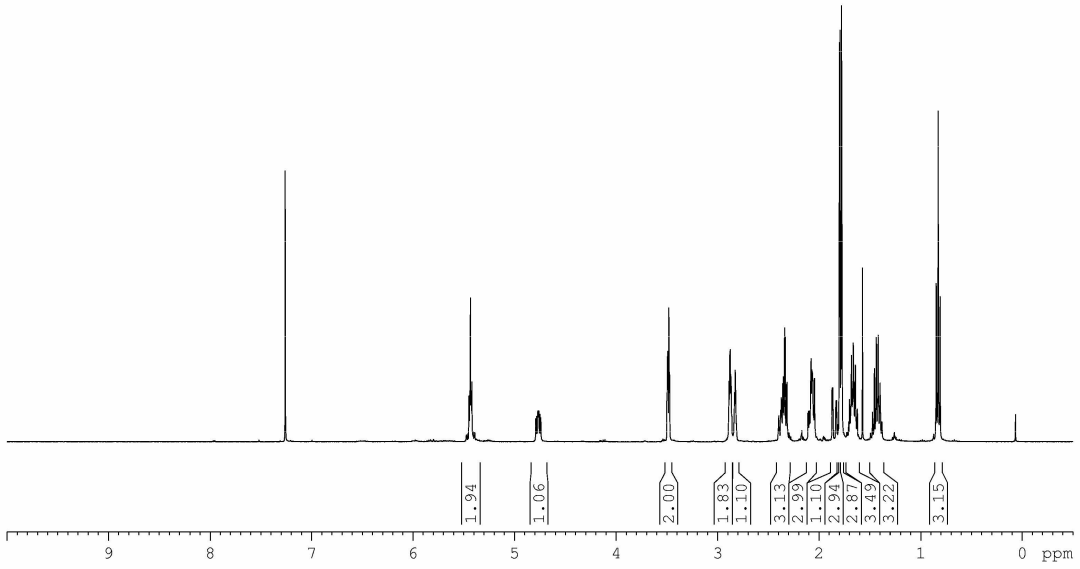
130.61
125.30
77.32
77.00
76.68
75.33
51.43
33.89
28.81
26.66
24.49
17.08
3.46
200
180
160
140
120
100
80
60
40
20
0 ppm

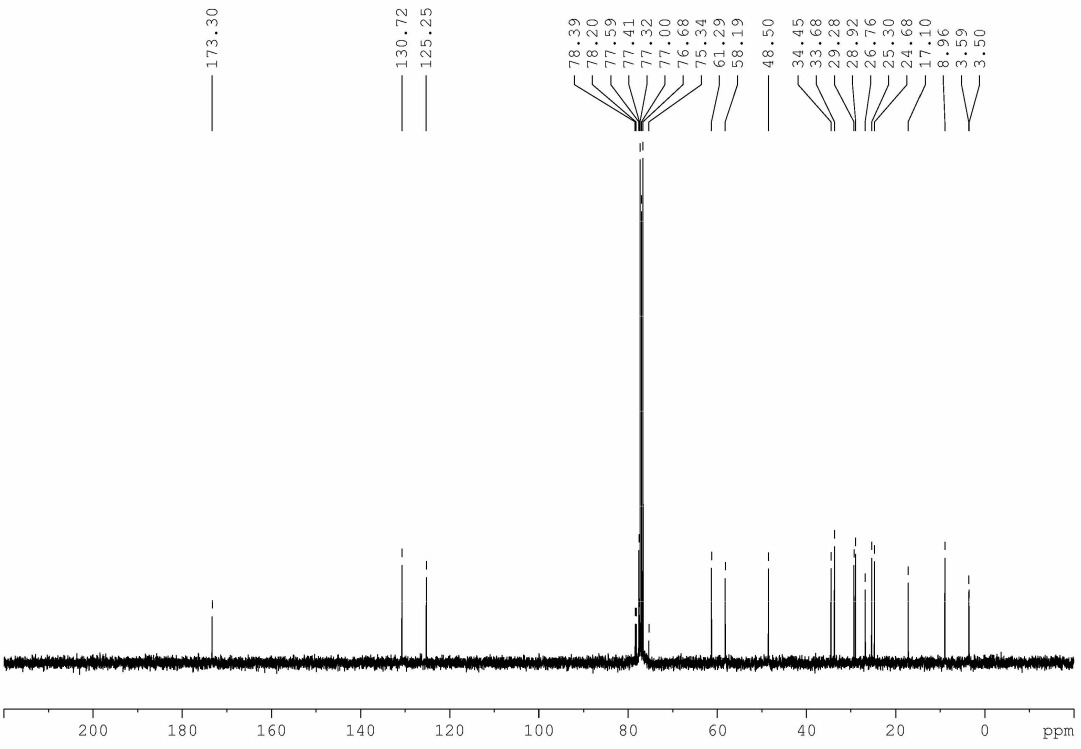

O
OH


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
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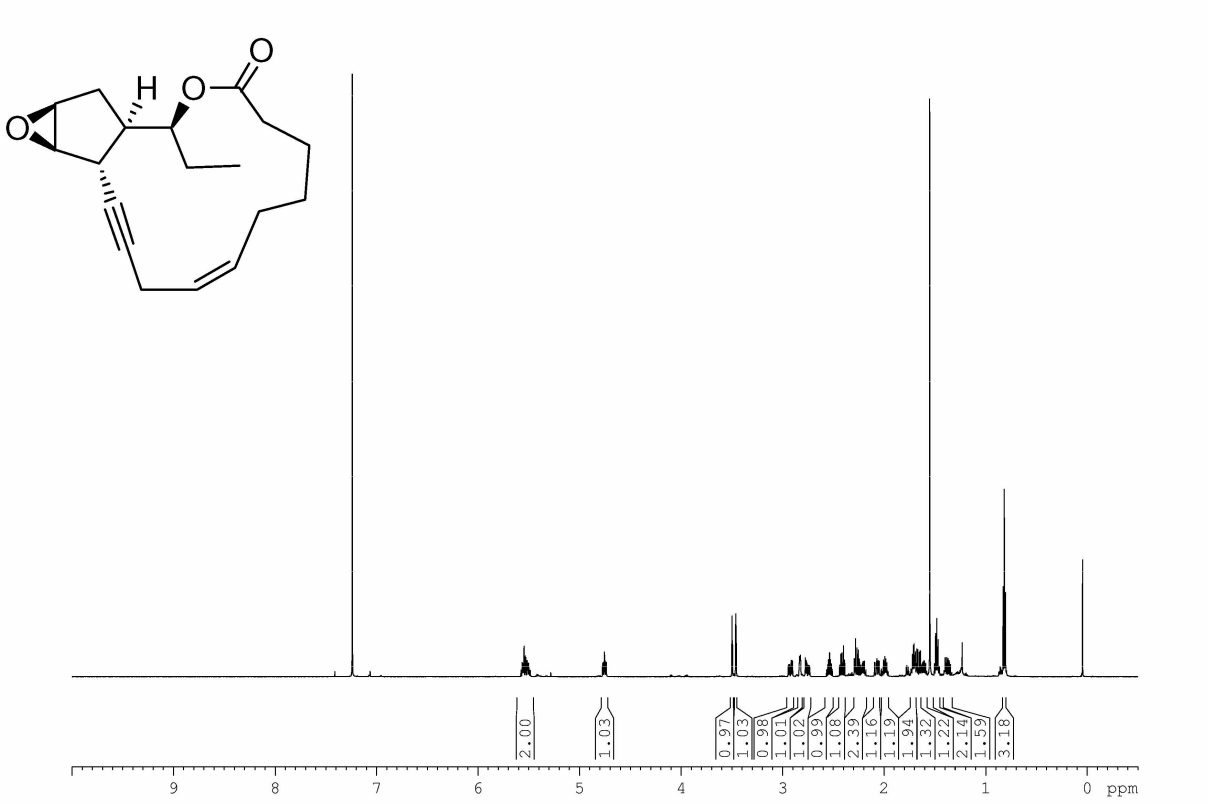
78.39
78.20
77.59
77.41
77.32
77.00
76.68
75.34
61.29
58.19
48.50
34.45
33.68
29.28
28.92
26.76
25.30
24.68
17.10
8.96
3.59
3.50
200
180
160
140
120
100
80
60
40
20
0
ppm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O
O
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1.03
0.97
1.03
0.98
1.01
1.02
0.99
1.08
2.39
1.16
1.19
1.94
1.32
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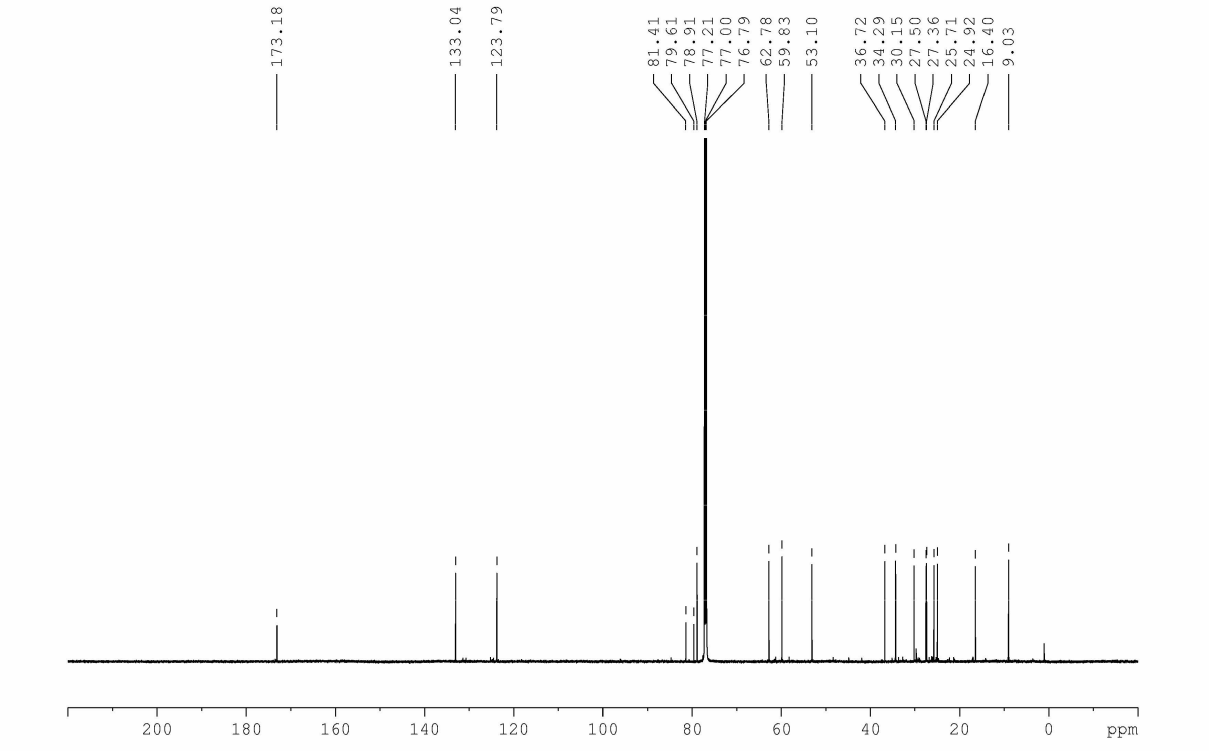
2.14
1.59
3.18
9
8
7
6
5
4
3
2
1
0
ppm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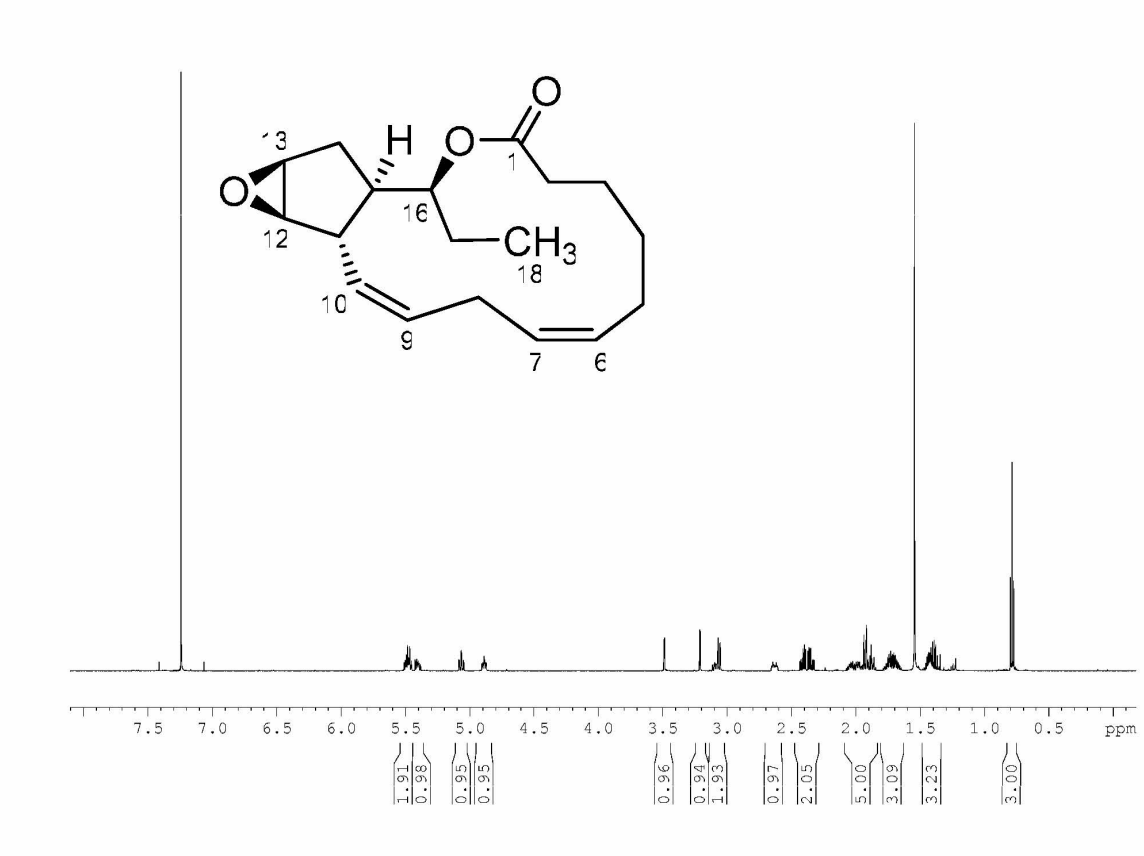
133.04
123.79
81.41
79.61
78.91
77.21
77.00
76.79
62.78
59.83
53.10
36.72
34.29
30.15
27.50
27.36
25.71
24.92
16.40
9.03
200
180
160
140
120
100
80
60
40
20
0
ppm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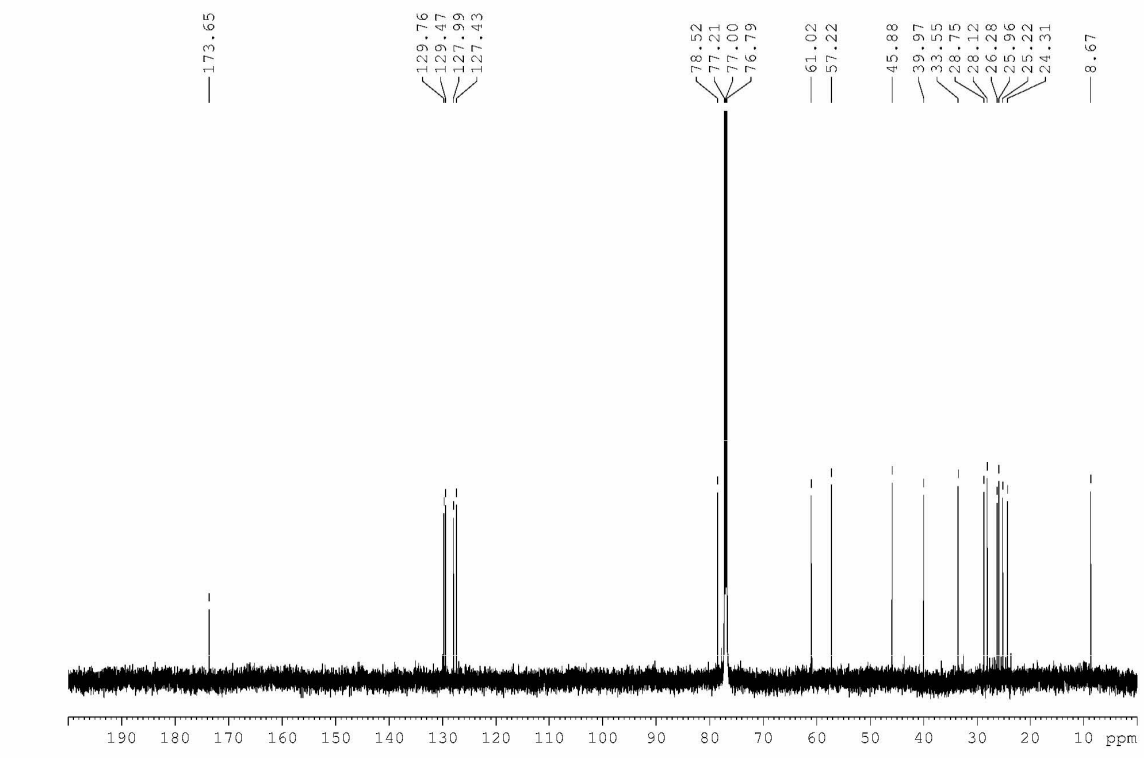
H
O
1
13
O
16
12
CH3
18
10
9
7
6
7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 ppm
1.91 0.98 0.95 0.95 0.96 0.94 1.93 0.97 2.05 5.00 3.09 3.23 3.00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129.47
127.99
127.43
78.52
77.21
77.00
76.79
61.02
57.22
45.88
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33.55
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