Supporting Information

Synthesis of ω -Hydroxy Ketones from ω -Benzyloxy Weinreb Amides by Using a Chemoselective Nucleophilic Addition/Birch Reduction Process

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General

TLC was performed on Merck 60F₂₅₄ silica gel plates and visualized either with a UV lamp (254 nm), or by using a solution of *p*-anisaldehyde/sulfuric acid/acetic acid in EtOH followed by heating.

Flash chromatography was performed with Merck Geduran Si60 silica gel (40-63 μ m).

Infrared (IR) spectra were recorded on a Perkin-Elmer 298, wave-numbers are indicated in cm^{-1} . ^1H NMR spectra were recorded on a Bruker AC 300 at 300 MHz and data are reported as follows: chemical shift in ppm from tetramethylsilane as an internal standard, multiplicity (s = singlet, d = doublet, t = triplet, q = quartet, m = multiplet or overlap of non equivalent resonances), integration. ^{13}C NMR spectra were recorded on a Bruker AC 300 at 75 MHz and data are reported as follows: chemical shift in ppm from tetramethylsilane with the solvent as an internal indicator (CDCl_3 δ 77.0 ppm), multiplicity with respect to proton (deduced from DEPT experiments, s = quaternary C, d = CH, t = CH_2 , q = CH_3). Mass spectra with electronic impact (MS-EI) were recorded from a Hewlett-Packard tandem 5890A GC (12 m capillary column) – 5971 MS (70 eV). Elemental analyses were performed by the Centre Régional de Microanalyses (Université Pierre et Marie Curie, Paris VI).

Spectral data of various compounds

5-Benzyloxy-*N*-methoxy-*N*-methylundecanamide (1): The Weinreb amide **1** was prepared from the commercially available undecanoic δ -lactone with an overall yield of 80%. Colorless oil, R_f 0.3 (CH_2Cl_2 /EtOAc: 80/20); IR (film): 1665, 1465, 1450, 1380, 1095, 740, 700 cm^{-1} ; 1H NMR ($CDCl_3$) δ 7.40-7.21 (m, 5H), 4.50 (s, 2H), 3.63 (s, 3H, N-OMe), 3.40 (apparent quintuplet, $J = 5.7$ Hz, 1H), 3.16 (s, 3H, N-Me), 2.43 (t, $J = 7.4$ Hz, 2H), 1.85-1.20 (m, 14H), 0.88 (t, $J = 6.6$ Hz, 3H); ^{13}C NMR ($CDCl_3$) δ 174.3 (br s, C=O), 138.9 (s), 128.1 (d, 2C), 127.6 (d, 2C), 127.2 (d), 78.7 (d), 70.6 (t), 61.0 (q, N-OMe), 33.6 (t), 33.4 (t), 32.0 (br q, N-Me), 31.8 (t), 31.7 (t), 29.4 (t), 25.1 (t), 22.5 (t), 20.4 (t), 14.0 (q); MS-EI m/z (%): 336 ($M+H^+$, 1), 275 (6), 183 (8), 169 (5), 152 (7), 92 (10), 91 (100), 61 (16).

5-Benzyloxy-*N*-methoxy-*N*-methylpentanamide (7): The Weinreb amide **7** was prepared from the commercially available δ -valerolactone with an overall yield of 75%. Colorless oil, R_f 0.55 (petroleum ether/EtOAc: 80/20); IR (film): 1660, 1450, 1415, 1385, 1105, 740, 700 cm^{-1} ; 1H NMR ($CDCl_3$) δ 7.35-7.22 (m, 5H), 4.49 (s, 2H), 3.63 (s, 3H, N-OMe), 3.50 (br t, $J = 6.1$ Hz, 2H), 3.16 (s, 3H, N-Me), 2.44 (br t, $J = 7.0$ Hz, 2H), 1.80-1.61 (m, 4H); ^{13}C NMR ($CDCl_3$) δ 174.3 (br s, C=O), 138.5 (s), 128.2 (d, 2C), 127.5 (d, 2C), 127.3 (d), 72.7 (t), 70.0 (t), 61.0 (q, N-OMe), 32.0 (br q, N-Me), 31.4 (t), 29.3 (t), 21.3 (t); MS-EI m/z (%): 252 ($M+H^+$, 1), 191 (9), 160 (4), 151 (3), 92 (9), 91 (100), 61 (11); Anal Calcd for $C_{14}H_{21}NO_3$: C, 66.91 ; H, 8.42 ; N, 5.57. Found: C, 66.72 ; H, 8.61 ; N, 5.50.

2-Benzyloxy-*N*-methoxy-*N*-methylpropanamide (8): The Weinreb amide **8** was prepared from the commercially available ethyl lactate with an overall yield of 74%. Colorless oil, R_f 0.4 ($\text{CH}_2\text{Cl}_2/\text{EtOAc}$: 90/10); IR (film): 1675, 1450, 1160, 1110, 990, 745, 700 cm^{-1} ; ^1H NMR (CDCl_3) δ 7.41-7.23 (m, 5H), 4.67 (d, J = 11.8 Hz, 1H), 4.41 (d, J = 11.8 Hz, 1H), 4.40 (m, 1H), 3.57 (s, 3H, N-OMe), 3.20 (s, 3H, N-Me), 1.40 (d, J = 6.6 Hz, 3H); ^{13}C NMR (CDCl_3) δ 173.5 (br s, C=O), 137.7 (s), 128.2 (d, 2C), 127.8 (d, 2C), 127.6 (d), 71.3 (br q, N-OMe), 71.0 (t), 61.1 (d), 32.3 (br q, N-Me), 17.8 (q); MS-EI m/z (%): 224 ($\text{M}+\text{H}^+$, 1), 135 (7), 117 (31), 92 (9), 91 (100); Anal Calcd for $\text{C}_{12}\text{H}_{17}\text{NO}_3$: C, 64.55 ; H, 7.67 ; N, 6.27. Found: C, 64.54 ; H, 7.81 ; N, 6.16.

3-Benzyloxy-*N*-methoxy-*N*-methylbutanamide (9): The Weinreb amide **9** was prepared from the commercially available ethyl acetoacetate with an overall yield of 52%. Colorless oil, R_f 0.4 (petroleum ether/EtOAc: 70/30); IR (film): 1660, 1450, 1360, 1090, 740, 700 cm^{-1} ; ^1H NMR (CDCl_3) δ 7.36-7.20 (m, 5H), 4.58 (d, J = 11.4 Hz, 1H), 4.50 (d, J = 11.4 Hz, 1H), 4.10 (apparent sextuplet, J = 6.3 Hz, 1H), 3.63 (s, 3H, N-OMe), 3.17 (s, 3H, N-Me), 2.89 (dd, J = 15.4 and J = 6.8 Hz, 1H), 2.44 (dd, J = 15.4 and J = 5.9 Hz, 1H), 1.27 (d, J = 5.9 Hz, 3H); ^{13}C NMR (CDCl_3) δ 172.2 (br s, C=O), 138.7 (s), 128.1 (d, 2C), 127.5 (d, 2C), 127.3 (d), 72.1 (d), 70.9 (t), 61.1 (q, N-OMe), 39.2 (br t), 31.9 (br q, N-Me), 20.0 (q); MS-EI m/z (%): 238 ($\text{M}+\text{H}^+$, 1), 131 (23), 100 (15), 92 (10), 91 (100).

5-Benzyloxy-5-methyl-*N*-methoxy-*N*-methylhexanamide (10): The Weinreb amide **10** was prepared from the commercially available δ -valerolactone with an overall yield of 53%.

Colorless oil, R_f 0.5 (petroleum ether/EtOAc: 50/50); IR (film): 1665, 1455, 1385, 740 cm^{-1} ; ^1H NMR (CDCl_3) δ 7.38-7.18 (m, 5H), 4.42 (s, 2H), 3.64 (s, 3H, N-OMe), 3.17 (s, 3H, N-Me), 2.44 (br t, $J = 7.2$ Hz, 2H), 1.82–1.57 (m, 4H), 1.27 (s, 6H); ^{13}C NMR (CDCl_3) δ 174.3 (br s, C=O), 139.7 (s), 128.1 (d, 2C), 127.2 (d, 2C), 126.9 (d), 74.9 (s), 63.5 (t), 61.0 (q, N-OMe), 40.0 (t), 32.0 (br q, N-Me), 32.0 (br t), 25.4 (q, 2C), 19.0 (t); MS-EI m/z (%): 265 ($\text{M}^+ - \text{CH}_3$, 1), 219 (4), 201 (4), 91 (100), 61 (20).

5-(4-Methoxybenzyloxy)-N-methoxy-N-methylundecanamide (11): The Weinreb amide **11** was prepared from the commercially available undecanoic δ -lactone with an overall yield of 53%. Colorless oil, R_f 0.5 ($\text{CH}_2\text{Cl}_2/\text{EtOAc}$: 80/20); IR (film): 1660, 1610, 1510, 1465, 1300, 1245, 1180, 1170, 1035 cm^{-1} ; ^1H NMR (CDCl_3) δ 7.32-7.20 (m, 2H), 6.91-6.82 (m, 2H), 4.43 (s, 2H), 3.79 (s, 3H), 3.65 (s, 3H, N-OMe), 3.38 (apparent quintuplet, $J = 5.9$ Hz, 1H), 3.17 (s, 3H, N-Me), 2.42 (t, $J = 7.3$ Hz, 2H), 1.83-1.18 (m, 14H), 0.88 (br t, $J = 6.8$ Hz, 3H); ^{13}C NMR (CDCl_3) δ 174.4 (br s, C=O), 158.9 (s), 131.1 (s), 129.2 (d, 2C), 113.6 (d, 2C), 78.4 (d), 70.3 (t), 61.0 (q, N-OMe), 55.1 (q), 33.7 (t), 33.5 (t), 32.1 (br q, N-Me), 31.8 (t), 31.7 (t), 29.4 (t), 25.1 (t), 22.5 (t), 20.5 (t), 14.0 (q); MS-EI m/z (%): 305 ($\text{M} - \text{N}(\text{OMe})\text{Me}$, 1), 228 (1), 169 (7), 137 (12), 122 (10), 121 (100), 61 (53); Anal Calcd for $\text{C}_{21}\text{H}_{35}\text{NO}_4$: C, 69.01 ; H, 9.65 ; N, 3.83. Found: C, 68.70 ; H, 9.50 ; N, 3.47.

5-Trityloxy-N-methoxy-N-methylpentanamide (12): The Weinreb amide **12** was prepared from the commercially available δ -valerolactone with an overall yield of 66%. Colorless oil,

R_f 0.5 ($\text{CH}_2\text{Cl}_2/\text{EtOAc}$: 90/10); IR (film): 1665, 1480, 1445, 1380, 1115, 1070, 765, 745, 710 cm^{-1} ; ^1H NMR (CDCl_3) δ 7.48-7.40 (m, 6H), 7.33-7.17 (m, 9H), 3.61 (s, 3H, N-OMe), 3.15 (s, 3H, N-Me), 3.08 (br t, J = 5.9 Hz, 2H), 2.41 (br t, J = 7.0 Hz, 2H), 1.81-1.61 (m, 4H); ^{13}C NMR (CDCl_3) δ 174.4 (br s, C=O), 144.3 (s, 3C), 128.6 (d, 6C), 127.6 (d, 6C), 126.7 (d, 3C), 86.2 (s), 63.1 (t), 61.1 (q, N-OMe), 32.1 (br q, N-Me), 31.6 (br t), 29.6 (t), 21.4 (t); MS-EI m/z (%): 259 (1), 244 (25), 243 (100), 165 (41), 160 (62), 144 (23), 105 (12); Anal Calcd for $\text{C}_{26}\text{H}_{29}\text{NO}_3$: C, 77.39 ; H, 7.24 ; N, 3.47. Found: C, 77.25 ; H, 7.36 ; N, 3.43.

8-Benzyloxy-N-methoxy-N-methyloct-4-ynamide (18): The Weinreb amide **18** was prepared from the commercially available 4-pentyn-1-ol with an overall yield of 43%. Colorless oil, R_f 0.65 (petroleum ether/EtOAc: 50/50); IR (film): 1665, 1430, 1385, 1100, 740, 700 cm^{-1} ; ^1H NMR (CDCl_3) δ 7.35-7.23 (m, 5H), 4.50 (s, 2H), 3.68 (s, 3H, N-OMe), 3.55 (t, J = 6.3 Hz, 2H), 3.17 (s, 3H, N-Me), 2.62 (m, 2H), 2.47 (m, 2H), 2.26 (m, 2H), 1.78 (apparent quintuplet, J = 6.3 Hz, 2H); ^{13}C NMR (CDCl_3) δ 172.6 (br s, C=O), 138.4 (s), 128.1 (d, 2C), 127.4 (d, 2C), 127.3 (d), 79.7 (s), 79.1 (s), 72.7 (t), 68.7 (t), 61.1 (q, N-OMe), 32.0 (br q, N-Me), 31.5 (t), 28.9 (t), 15.4 (t), 14.1 (t); MS-EI m/z (%): 288 (M-H, 1), 258 (4), 198 (11), 187 (10), 155 (9), 91 (100), 61 (9).

5-Hydroxy-N-methylundecanamide (6): A solution of Weinreb amide (0.3 mmol, 1 equiv) in dry THF (3 mL) was added dropwise to a solution of lithium (20 mmol, 66 equiv) in ammoniac (*ca* 20 mL) at -78 °C. After 5 min at -78 °C, solid NH_4Cl was added portionwise until complete disparition of the dark blue coloration. The reaction mixture was then diluted with ether (10mL) and ammoniac was evaporated. Water (10 mL) was further added and the aqueous layer was extracted with diethyl ether (3×15 mL). The combined organic extracts

were dried over MgSO_4 , filtered and concentrated *in vacuo*. Purification by flash chromatography on silica gel (EtOAc) afforded 61 mg of amide **6** as a whitish oil; R_f 0.2 (EtOAc); IR (film): 3310, 1645, 1555, 1465, 1455, 1410, 1135 cm^{-1} ; ^1H NMR (CDCl_3) δ 6.22 (br s, 1H, NH), 3.57 (m, 1H), 2.85 (br s, 1H, OH), 2.78 (d, $J = 4.8$ Hz, 3H), 2.22 (m, 2H), 1.89-1.10 (m, 14H), 0.88 (t, $J = 6.6$ Hz, 3H); ^{13}C NMR (CDCl_3) δ 174.0 (s), 71.0 (d), 37.4 (t), 36.5 (t), 36.0 (t), 31.7 (t), 29.2 (t), 26.1 (q), 25.5 (t), 22.5 (t), 21.6 (t), 13.9 (q); MS-EI m/z (%): 216 ($\text{M}+\text{H}^+$, 1), 197 ($\text{M}-\text{H}_2\text{O}$, 6), 130 (53), 101 (14), 100 (16), 99 (15), 86 (11), 73 (100), 58 (22), 55 (17).

General procedure for consecutive addition of nucleophiles/Birch reduction process:

To a solution of Weinreb amide (0.3 mmol, 1 equiv) in dry THF (3 mL) at -78 $^\circ\text{C}$ was added a solution of organometallic reagent (5 equiv). After 10 min at -78 $^\circ\text{C}$ (conversion of starting amide was monitored by TLC after aqueous work-up of an aliquot), the reaction mixture was added dropwise to a solution of lithium (20 mmol, 66 equiv) in ammoniac (*ca* 20 mL) at -78 $^\circ\text{C}$, which contains a mixture of *t*-BuOH (0.1 mL) and THF (0.4 mL). After 5 min at -78 $^\circ\text{C}$, solid NH_4Cl was added portionwise until complete disparition of the dark blue coloration. The reaction mixture was then diluted with ether (10mL) and ammoniac was evaporated. Water (10 mL) was further added and the aqueous layer was extracted with diethyl ether (3 $\times$ 15 mL). The combined organic extracts were dried over MgSO_4 , filtered and concentrated *in vacuo*. Purification of the crude by flash chromatography on silica gel afforded the corresponding hydroxy ketones.

9-Hydroxypentadecan-5-one (2): White solid, R_f 0.2 (CH_2Cl_2); decomposition at $t < 50^\circ\text{C}$; IR (film): 3440 (br, OH), 1710, 1465, 1140 cm^{-1} ; ^1H NMR (CDCl_3) δ 3.55 (m, 1H), 2.44 (t, $J = 7.2$ Hz, 2H), 2.40 (t, $J = 7.4$ Hz, 2H), 1.80-1.10 (m, 19H), 0.94-0.84 (m, 6H); ^{13}C NMR (CDCl_3) δ 211.5 (s), 71.3 (d), 42.4 (2t, 2C), 37.3 (t), 36.7 (t), 31.7 (t), 29.2 (t), 25.8 (t), 25.5 (t), 22.5 (t), 22.2 (t), 19.5 (t), 13.9 (q), 13.7 (q); MS-EI m/z (%): 242 (M^+ , 1), 224 (26), 195 (12), 182 (15), 167 (35), 154 (25), 139 (40), 124 (29), 113 (84), 97 (70), 96 (45), 95 (31), 85 (100), 83 (51), 71 (42), 69 (57), 58 (48), 57 (75), 55 (81); Anal Calcd for $\text{C}_{15}\text{H}_{30}\text{O}_2$: C, 74.32 ; H, 12.47. Found: C, 74.30 ; H, 12.39.

7-Hydroxytridecan-3-one (3): Colorless oil, R_f 0.45 (CH_2Cl_2); IR (film): 3400 (br, OH), 1710, 1465 cm^{-1} ; ^1H NMR (CDCl_3) δ 3.56 (m, 1H), 2.45 (t, $J = 7.2$ Hz, 2H), 2.43 (q, $J = 7.4$ Hz, 2H), 1.87-1.00 (m, 15H), 1.06 (t, $J = 7.4$ Hz, 3H), 0.88 (m, 3H); ^{13}C NMR (CDCl_3) δ 211.7 (s), 71.3 (d), 42.0 (t), 37.3 (t), 36.7 (t), 35.7 (t), 31.7 (t), 29.2 (t), 25.5 (t), 22.5 (t), 19.6 (t), 13.9 (q), 7.7 (q); MS-EI m/z (%): 214 (M^+ , 1), 196 (41), 167 (16), 153 (13), 149 (14), 139 (31), 126 (42), 111 (44), 97 (31), 85 (100), 83 (61), 72 (40), 69 (44), 57 (86), 55 (67).

8-Hydroxytetradec-1-en-4-one 4a and 2-allyl-6-hexyltetrahydropyran-2-ol 4b (4): Colorless oil, R_f 0.3 (CH_2Cl_2); IR (film): 3420 (br, OH), 1665, 1630, 1470, 1455, 1445, 1380, 950 cm^{-1} ; ^1H NMR (CDCl_3) δ isomer **4a**: 5.93 (m, 1H), 5.23-5.09 (m, 2H), 3.56 (m, 1H), 3.18 (dt, $J = 7.0$ et $J = 1.3$ Hz, 2H), 2.49 (t, $J = 7.2$ Hz, 2H), 1.93-1.05 (m, 15H), 0.88 (m, 3H); isomer **4b**: 5.93 (m, 1H), 5.23-5.09 (m, 2H), 3.81 (m, 1H), 2.44 (m, 1H), 2.31-2.16 (m, 2H),

1.93-1.05 (m, 16H), 0.88 (m, 3H); ^{13}C NMR (CDCl_3) δ (Mixture of isomers **4a/4b** 1/1): 208.8 (s, Cq **4a**), 132.8 and 130.5 (d), 119.4 and 118.7 (t), 95.5 (s, Cq **4b**), 71.3 and 69.9 (d), 47.6 (t), 47.5 (t), 42.0 (t), 37.3 (t), 36.6 (t), 36.1 (t), 33.4 (t), 31.7 (t), 31.6 (t), 30.9 (t), 29.2 (t), 25.4 (t), 25.3 (t), 22.5 (t), 22.4 (t), 19.4(t), 19.1 (t), 14.0 and 13.9 (q); MS-EI m/z (%): 208 (M-H₂O, 28), 185 (16), 167 (18), 165 (11), 151 (13), 149 (29), 141 (13), 123 (16), 113 (11), 111 (13), 109 (12), 99 (19), 97 (74), 95 (31), 84 (36), 83 (54), 81 (35), 69 (78), 55 (100).

6-Hexyltetrahydropyran-2-ol (5) (two diastereomers 2/1): Colorless oil, R_f 0.2 (CH_2Cl_2); IR (film): 3390 (br, OH), 1465, 1455, 1445, 1195, 1120, 1105, 1070, 1030, 970 cm^{-1} ; ^1H NMR (CDCl_3) δ minor diastereomer: 5.30 (br s, 1H), 3.92 (m, 1H), 3.03 (m, 1H, OH), 1.95-1.05 (m, 16H), 0.87 (m, 3H); major diastereomer: 4.69 (ddd, $J = 9.6$ and $J = 6.6$ and $J = 1.8$ Hz, 1H), 3.67 (d, $J = 6.6$ Hz, 1H, OH), 3.40 (m, 1H), 1.95-1.05 (m, 16H), 0.87 (m, 3H); ^{13}C NMR (CDCl_3) δ minor diastereomer: 91.7 (d), 68.7 (d), 36.0 (t), 31.7 (t), 31.0 (t), 29.7 (t), 29.2 (t), 25.2 (t), 22.5 (t), 17.3 (t), 13.9 (q); major diastereomer: 96.3 (d), 76.4 (d), 35.9 (t), 32.7 (t), 31.7 (t), 30.2 (t), 29.2 (t), 25.3 (t), 22.5 (t), 22.0 (t), 13.9 (q); MS-EI m/z (%): 186 (M^+ , 1), 168 (21), 140 (11), 116(12), 115 (21), 114(27), 113 (26), 112 (22), 111 (30), 101 (55), 98 (58), 97 (65), 84 (26), 83 (70), 70 (44), 69 (41), 57 (62), 55 (100).

1-Hydroxynonan-5-one (13): Colorless oil, R_f 0.2 ($\text{CH}_2\text{Cl}_2/\text{Et}_2\text{O}$: 90/10); IR (film): 3420 (br, OH), 1710, 1465 cm^{-1} ; ^1H NMR (CDCl_3) δ 3.63 (m, 3H), 2.46 (t, $J = 7.0$ Hz, 2H), 2.41 (t, $J = 7.5$ Hz, 2H), 1.75-1.15 (m, 11H); ^{13}C NMR (CDCl_3) δ 211.7 (s), 62.0 (t), 42.4 (t), 42.1 (t), 31.9 (t), 25.8 (t), 22.2 (t), 19.6 (t), 13.7 (q); MS-EI m/z (%): 140 (M-H₂O, 19), 116 (28), 111 (15), 101 (28), 98 (79), 85 (100), 83 (65), 71 (10), 70 (11), 59 (12), 58 (18), 57 (94), 56 (13), 55 (86).

2-Hydroxyheptan-3-one (14): Colorless oil, R_f 0.3 (CH_2Cl_2); IR (film): 3430 (br, OH), 1710, 1465, 1120, 740 cm^{-1} ; ^1H NMR (CDCl_3) δ 4.24 (q, $J = 7.2$ Hz, 1H), 2.53 (dt, $J = 16.9$ and $J = 7.5$ Hz, 1H), 2.43 (dt, $J = 16.9$ and $J = 7.3$ Hz, 1H), 1.68-1.51 (m, 3H), 1.46-0.85 (m, 8H); ^{13}C NMR (CDCl_3) δ 212.6 (s), 72.4 (d), 37.1 (t), 25.5 (t), 22.2 (t), 19.7 (q), 13.6 (q); MS-EI m/z (%): 130 (M^+ , 4), 112 ($\text{M}-\text{H}_2\text{O}$, 1), 88 (13), 87 (21), 86 (13), 85 (98), 69 (37), 57 (100).

2-Hydroxy-octan-4-one (15): Colorless oil, R_f 0.3 (CH_2Cl_2); IR (film): 3410 (br, OH), 1710, 1470, 1410, 1375, 1125 cm^{-1} ; ^1H NMR (CDCl_3) δ 4.21 (m, 1H), 3.20 (br s, 1H, OH), 2.59 (dd, $J = 17.7$ and $J = 3.3$ Hz, 1H), 2.49 (dd, $J = 17.7$ and $J = 8.5$ Hz, 1H), 2.41 (t, $J = 7.5$ Hz, 2H), 1.55 (m, 2H), 1.29 (m, 2H), 1.17 (d, $J = 6.3$ Hz, 3H), 0.89 (t, $J = 7.3$ Hz, 3H); ^{13}C NMR (CDCl_3) δ 212.3 (s), 63.7 (d), 50.3 (t), 43.1 (t), 25.5 (t), 22.2 (t), 22.1 (q), 13.6 (q); MS-EI m/z (%): 129 ($\text{M}-\text{CH}_3^+$, 2), 111 (10), 103 (21), 100 (16), 87 (33), 85 (45), 84 (29), 71 (13), 69 (80), 58 (100), 57 (60), 55 (12).

9-Hydroxy-9-methyldecan-5-one (16): Colorless oil, R_f 0.35 (petroleum ether/EtOAc: 70/30); IR (film): 3410 (br, OH), 1710, 1465, 1375 cm^{-1} ; ^1H NMR (CDCl_3) δ 2.40 (t, $J = 7.2$ Hz, 2H), 2.37 (t, $J = 7.5$ Hz, 2H), 1.80 (br s, 1H, OH), 1.70-1.10 (m, 8H), 1.19 (s, 6H), 0.87 (t, $J = 7.3$ Hz, 3H); ^{13}C NMR (CDCl_3) δ 211.3 (s), 70.6 (s), 43.0 (t), 42.7 (t), 42.4 (t), 29.0 (q, 2C), 25.8 (t), 22.2 (t), 18.4 (t), 13.7 (q); MS-EI m/z (%): 171 ($\text{M}-\text{CH}_3^+$, 13), 168 ($\text{M}-\text{H}_2\text{O}$, 23), 153 (26), 144 (11), 127 (13), 126 (31), 116 (19), 113 (74), 111 (76), 98 (22), 93 (20), 86 (21), 85 (78), 83 (68), 71 (67), 69 (82), 59 (84), 58 (100), 57 (67), 56 (36), 55 (52).

2-Methyldecan-2,6-diol (17): Colorless oil, R_f 0.15 (petroleum ether/EtOAc: 70/30); IR (film): 3360 (br, OH), 1465, 1375, 1150 cm^{-1} ; ^1H NMR (CDCl_3) δ 3.60 (m, 1H), 1.87 (br s, 2H, OH), 1.60-1.10 (m, 12H), 1.25 (s, 6H), 0.92 (t, $J = 7.3$ Hz, 3H); ^{13}C NMR (CDCl_3) δ 71.5 (d), 70.8 (s), 43.5 (t), 37.6 (t), 37.1 (t), 29.2 (q), 29.0 (q), 27.7 (t), 22.6 (t), 20.2 (t), 13.9 (q); MS-EI m/z (%): 170 (M- H_2O , 1), 155 (14), 113 (19), 95 (70), 85 (14), 84 (17), 83 (11), 71 (10), 69 (43), 59 (100), 57 (23), 56 (37), 55 (19).

12-Hydroxydodec-8-yn-5-one (19): Colorless oil, R_f 0.25 (petroleum ether/EtOAc: 80/20); IR (film): 3390 (br, OH), 1710, 1465, 1430, 1405, 1370, 1055 cm^{-1} ; ^1H NMR (CDCl_3) δ 3.68 (t, $J = 6.3$ Hz, 2H), 2.57 (br t, $J = 7.3$ Hz, 2H), 2.39 (br t, $J = 7.3$ Hz, 2H), 2.37 (m, 2H), 2.21 (tt, $J = 6.8$ and $J = 2.4$ Hz, 2H), 2.15 (br s, 1H, OH), 1.68 (br quintuplet, $J = 6.6$ Hz, 2H), 1.53 (m, 2H), 1.27 (m, 2H), 0.87 (t, $J = 7.4$ Hz, 3H); ^{13}C NMR (CDCl_3) δ 209.3 (s), 79.8 (s), 79.1 (s), 61.5 (t), 42.4 (t), 41.7 (t), 31.4 (t), 25.7 (t), 22.1 (t), 15.1 (t), 13.6 (q), 13.2 (t); MS-EI m/z (%): 196 (M^+ , 7), 151 (15), 139 (21), 137 (14), 121 (11), 111 (53), 110 (10), 109 (15), 97 (100), 85 (35), 84 (22), 77 (25), 57 (63), 55 (40).