SUPPORTING INFORMATION

Stereoselective Synthesis of Enamides by a Peterson Reaction Manifold

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General: All reactions were carried out under Ar. The solvents used were purified by distillation over the drying agents indicated and were transferred under Ar: THF, Et_2O (Mg-anthracene), CH_2Cl_2 (P_4O_{10}), MeCN, Et_3N (CaH_2), MeOH (Mg), DMF (Desmodur®, dibutyltin dilaurate), hexane, heptane, toluene (Na/K). Flash chromatography: Merck silica gel 60 (230-400 mesh). NMR: Spectra were recorded on a DPX 300 or AMX 400 spectrometer (Bruker) in the solvents indicated; chemical shifts (δ) are given in ppm relative to TMS, coupling constants (J) in Hz. IR: Nicolet FT-7199 spectrometer, wavenumbers in cm^{-1}. MS (EI): Finnigan MAT 8200 (70 eV), HRMS: Finnigan MAT 95. Melting points: Gallenkamp melting point apparatus (uncorrected). Elemental analyses: Kolbe, Mülheim/Ruhr. All commercially available compounds (Lancaster, Aldrich) were used as received.

Representative procedures:

(*Z*)-Styryl-trimethylsilane (*Z*-6b, R^1 = Ph). To a solution of of DIBAL-H (1 M in hexane, 10 mL, 10 mmol) and heptane (10 mL) was added 1-methylpyrrolidine (1.56 mL, 15.00 mmol). After stirring for 5 min at ambient temperature, 1-phenyl-2-(trimethylsilyl) acetylene (2.61 g, 15.00 mmol) was introduced and the resulting mixture was stirred at 60°C for 15 h and then at 100°C for another 18 h. The mixture was then cooled to 0°C before aq. HCl (2N, 100 mL) was carefully added. Extraction of the aqueous phase with hexane (4 x 50 mL), drying of the combined organic layers (Na_2SO_4) and evaporation of the solvent afforded *Z*-**6b** (R^1 = Ph) as a colorless liquid (2.00 g, 76%) which can be used without further purifications. The analytical data are in agreement with those previously reported in the literature.[14c]

***cis*-3-Phenyl-2-trimethylsilyloxirane (*cis*-7b, R^1 = Ph).** Na_2HPO_4 (3.38 g, 23.78 mmol) and *m*-chloroperbenzoic acid (70%, 5.47 g, 22.19 mmol) were added to a solution of (*Z*)-**6** (R^1 = Ph, 2.26 g, 12.84 mmol) in CH_2Cl_2 (75 mL) and the mixture was stirred for 18 h at room temperature. Ether (250 mL) and aq. sat. $NaHCO_3$ were added to the resulting suspension, the mixture was stirred for additional 30 min before the organic layer was washed with aq. sat. $NaHSO_3$, dried over Na_2SO_4 and concentrated. Flash chromatography of the residue (SiO_2, hexane/ethyl acetate, 30:1) provided the epoxide *cis*-**7b** (R^1 = Ph, 1.99 g, 81%) as a colorless liquid. The analytical data are in agreement with those previously reported in the literature.[1]

(1*R,2*R**)-2-Azido-1-phenyl-trimethylsilyl-ethanol (*anti*-8b, R^1 = Ph).** A suspension of *cis*-**7** (R^1 = Ph, 1.87 g, 9.74 mmol), NaN_3 (2.53 g, 38.96 mmol) and NH_4Cl (1.15 g, 21.43 mmol) in a mixture of MeOH (32 mL) and water (4 mL) was stirred for 48 h. For work-up, aq. sat. NH_4Cl (50 mL) was added, the MeOH was removed in vacuo, the resulting aqueous phase was repeatedly extracted with ether (3 x 50 mL), the combined organic layers were dried over Na_2SO_4 and concentrated, and the residue was purified by flash chromatography (SiO_2, hexane/ethyl acetate, 4:1) to afford the title compound *anti*-**8b** (R^1 = Ph, 2.03 g, 89%) as a colorless liquid. ^{1}H NMR (CH_2Cl_2, 300 MHz) 0.03 (s, 9H), 3.11 (d, *J* = 7.1 Hz, 1H), 4.80 (dd, *J* = 7.1, 4.0 Hz, 1H), 7.32 – 7.40 (m, 5H); ^{13}C NMR (CH_2Cl_2, 75.5 MHz) –2.9, 61.9,

[1] Burford, C.; Cooke, F.; Roy, G.; Magnus, P. *Tetrahedron* **1983**, *39*, 867-876.

75.4, 126.8, 128.3, 128.6, 141.9; IR (neat) 3409, 3064, 3031, 2899, 2097, 1600, 1541, 1494, 1454, 1409, 1251, 1053, 841, 764, 701.

(1*R,2*R**)-2-Amino-1-phenyl-2-trimethylsilyl-ethanol (*anti*-9b, R^1 = Ph).** To a suspension of $LiAlH_4$ (0.62 g, 16.42 mmol) in THF (50 mL) was added dropwise a solution of *anti*-**8** (R^1 = Ph, 1.93 g, 8.21 mmol) in THF (25 mL) and the resulting mixture was stirred for 5 h at room temperature. For work-up, water (0.7 mL) and aq. NaOH (2N, 1.2 mL) were added, the mixture was stirred for 15 h, the resulting white precipitate was filtered off and washed with ether (100 mL in several portions), the combined filtrates were dried over Na_2SO_4, and concentrated. The title compound (1.57 g, 91%) was obtained as a pale yellow solid which was used in the following step without further purification. Characteristic data: ^{1}H NMR (CD_2Cl_2, 300 MHz) δ −0.02 (s, 9H), 2.40 (d, J = 5.7 Hz, 1H), 4.63 (d, J = 5.4 Hz, 1H), 7.22 – 7.37 (m, 5H); ^{13}C NMR (d_8-THF, 75.5 MHz) δ −3.3, 48.8, 74.5, 126.5, 127.3, 128.2, 144.2; IR (KBr): 3359, 3095, 2952, 2879, 2850, 2922, 1577, 1453, 1360, 1327, 1246, 1241, 1199, 1065, 1038, 1003, 927, 844, 773, 743, 704, 687.

Representative Procedure for the synthesis of *E*- and *Z*-Enamides. Cyclohexane carboxylic acid (*Z*)-styryl amide (*Z*-10b, R^1 = Ph, R^2 = Cy): To a solution of *anti*-**9b** (R^1 = Ph, 400 mg, 1.91 mmol) in THF (30 mL) were added NEt_3 (0.27 mL, 1.91 mmol) and cyclohexane carboxylic acid chloride (0.26 mL, 1.91 mmol) at 0°C. After 2 h of stirring at 0°C and 15 h at room temperature, the reaction mixture was cooled to –35°C, a solution of KO^t-Bu (0.47 g, 4.20 mmol) in THF (20 mL) was added and the mixture was allowed to warm to ambient temperature. For work-up, the reaction was quenched with a phosphate puffer solution (pH 7, 30 mL), the aqueous phase was repeatedly extracted with ether (3 x 50 mL), the combined organic layers were washed with aqueous saturated $NaHCO_3$, dried over Na_2SO_4 and concentrated. Flash chromatography of the residue (alumina, hexane/ethyl acetate, 15:1) afforded the title compound as a colorless solid (370 mg, 85%). mp = 95 – 98°C; ^{1}H NMR (d_8-THF, 300 MHz) δ 1.18 – 1.92 (m, 10H), 2.25 (tt, J = 11.3, 3.3 Hz, 1H), 5.57 (d, J = 9.8 Hz, 1H), 6.90 (dd, J = 10.6, 9.7 Hz, 1H), 7.12 – 7.17 (m, 1H), 7.26 – 7.35 (m, 4H), 8.55 (d, 1H, J = 8.1 Hz); ^{13}C NMR (d_8-THF, 75.5 MHz) δ 26.9, 27.1, 30.6, 45.7, 109.7, 124.1, 127.2, 129.2, 129.6, 137.8, 174.4; IR (KBr): 3237, 3178, 2925, 2851, 1664, 1642,

1521, 1489, 1450, 1265, 1209, 1177, 775, 691; MS (EI): *m/z* (rel. intensity) 229 (25, [M^+]), 128 (2), 120 (11), 119 (100), 118 (9), 117 (4), 111 (2), 91 (6), 90 (2), 89 (2), 83 (30), 77 (2), 65 (2), 55 (20), 41 (11), 39 (2), 29 (2); HR-MS: *calcd* 229.1467, *found* 229.1468.

The following enamides were prepared analogously:

Cinnamic acid (*Z*)-styryl amide (lansiumamide A): Pale yellow solid, mp = 120 – 122°C; ^{1}H NMR (d_8-THF, 300 MHz): δ 5.68 (d, *J* = 9.8 Hz, 1H), 6.77 (d, *J* = 15.6 Hz, 1H), 7.07 (dd, *J* = 10.7, 9.9 Hz, 1H), 7.14 – 7.21 (m, 1H), 7.29 – 7.41 (m, 8H), 7.51 – 7.58 (m, 1H), 7.68 (d, *J* = 15.6 Hz, 1H), 8.95 (d, *J* = 10.5 Hz, 1H); ^{13}C NMR (d_8-THF, 75.5 MHz): δ 110.7, 121.9, 124.1, 127.4, 128.9, 129.4, 129.6, 129.9, 130.7, 136.7, 137.7, 142.6, 164.2; IR (KBr): 3245, 3051, 3023, 1662, 1644, 1626, 1578, 1513, 1488, 1451, 1443, 1338, 1257, 1202, 1190, 1081, 988, 979, 764, 695, 678; MS (EI): *m/z* (relative intensity) 249 (40, [M^+]), 131 (100), 120 (4), 119 (42), 118 (3), 117 (2), 103 (39), 102 (4), 91 (3), 77 (18), 51 (3); HR-MS *calcd* 249.1154 *found* 249.1153.

2,2-Dimethylpropionic acid (*Z*)-styryl amide: Colorless solid, mp = 49 – 51°C; ^{1}H NMR (d_8-THF, 400 MHz) δ 1.19 (s, 9H), 5.66 (d, *J* = 9.6 Hz, 1H), 6.92 (dd, *J* = 10.4, 9.8 Hz, 1H), 7.14 – 7.21 (m, 1H), 7.28 – 7.38 (m 4H), 8.17 (s, 1H); ^{13}C NMR (d_8-THF, 100 MHz) δ 27.7, 39.8, 110.3, 124.2, 127.5, 129.0, 129.9, 137.8, 175.9; IR (KBr): 3366, 3084, 2970, 2932, 2908, 1730, 1678, 1645, 1598, 1573, 1503, 1480, 1439, 1398, 1365, 1302, 1277, 1201, 1168, 1085, 1030, 950, 808, 779, 694, 627; MS (EI): *m/z* (rel. intensity) 204 (9, [M^++1]), 203 (53 [M^+]), 160 (2), 128 (3), 120 (6), 119 (45), 118 (15), 117 (6), 91 (8), 90 (4), 89 (3), 85 (5), 77 (4), 65 (3), 57 (100), 51 (2), 41 (17), 29 (12); HR-MS: *calcd* 203.1310, *found* 203.1311.

***m*-Nitrobenzoic acid (*Z*)-styryl amide:** Colorless solid, mp = 114 – 116°C; ^{1}H NMR (d_8-THF, 300 MHz) δ 5.88 (d, *J* = 9.7 Hz, 1H), 7.11 (t, *J* = 9.7 Hz, 1H), 7.18 – 7.24 (m, 1H), 7.34 – 7.39 (m, 2H), 7.45 – 7.48 (m, 2H), 7.72 (dd, *J* = 8.1, 8.0 Hz, 1H), 8.27 (dt, *J* = 8.0, 1.3 Hz, 1H), 8.38 (ddd, *J* = 8.1, 2.3, 1.0 Hz, 1H), 8.74 (t, *J* = 2.0 Hz, 1H), 9.56 (d, *J* = 9.6 Hz, 1H); ^{13}C NMR (d_8-THF, 75.5 MHz) δ 113.5, 123.6, 123.9, 127.1, 127.8, 129.5, 129.8, 130.8, 134.8, 137.0, 137.5, 149.6, 163.9; IR (KBr): 3265, 1665, 1648, 1523, 1490, 1475, 1350, 1304,

1271, 1080, 771, 714, 683; MS (EI): *m/z* (rel. intensity) 269 (13, [M^++1]), 268 (70 [M^+]), 150 (100), 134 (3), 122 (2), 117 (5), 104 (30), 92 (3), 91 (10), 76 (21), 75 (4), 65 (4), 50 (3); HR-MS: *calcd* 268.0848, *found* 268.0848.

Cyclohexane-carboxylic acid (*E*)-styryl amide: Colorless solid, mp = 148 – 150°C; ^{1}H NMR (d_8-THF, 300 MHz) δ 1.17 – 1.90 (m, 10H), 2.14 (tt, *J* = 11.4, 3.2 Hz, 1H), 6.03 (d, *J* = 14.8 Hz, 1H), 7.01 – 7.10 (m, 1H), 7.14 – 7.32 (m, 4H), 7.55 (dd, *J* = 14.8, 10.5 Hz, 1H), 8.99 (d, 1H, *J* = 9.5 Hz); ^{13}C NMR (d_8-THF, 75.5 MHz) δ 26.9, 27.8, 30.6, 45.2, 111.7, 125.4, 126.2, 126.8, 129.5, 138.6, 173.7; IR (KBr): 3269, 3073, 2933, 2852, 1666, 1641, 1536, 1496, 1486, 1446, 1254, 1230, 1197, 958, 750, 721, 690; MS (EI): *m/z* (rel. intensity) 229 (31, [M^+]), 120 (11), 119 (100), 118 (10), 117 (4), 111 (2), 91 (6), 90 (2), 89 (2), 83 (32), 81 (2), 77 (2), 65 (2), 55 (23), 41 (12), 39 (3), 29 (2); HR-MS: *calcd* 229.1467, *found* 229.1466.

***m*-Nitrobenzoic acid (*E*)-styryl amide:** Yellow solid, mp = 178 – 179°C; ^{1}H NMR (d_8-THF, 400 MHz) δ 6.37 (d, *J* = 14.7 Hz, 1H), 7.13 (t, *J* = 7.3 Hz, 1H), 7.25 (t, *J* = 7.7 Hz, 2H), 7.36 (d, *J* = 7.7 Hz, 2H), 7.68 – 7.82 (m, 2H), 8.34 (dt, *J* = 7.8, 1.3 Hz, 1H), 8.39 (ddd, *J* = 8.2, 2.2, 1.0 Hz, 1H), 8.79 (t, *J* = 1.9 Hz, 1H), 9.99 (d, *J* = 9.3 Hz, 1H); ^{13}C NMR (d_8-THF, 100 MHz) δ 114.7, 123.1, 125.1, 126.6, 127.1, 127.5, 129.6, 130.9, 134.9, 136.9, 138.0, 149.7, 163.0; IR (KBr): 3303, 3075, 1643, 1616, 1526, 1489, 1447, 1350, 1337, 1177, 947, 751, 715, 693; MS (EI): *m/z* (rel. intensity) 269 (13, [M^++1]), 268 (72 [M^+]), 150 (100), 134 (3), 122 (2), 117 (5), 104 (33), 92 (4), 91 (11), 76 (22), 75 (5), 65 (4), 63 (2), 50 (3); HR-MS: *calcd* 268.0848, *found* 268.0848.

Cyclohexanecarboxylic acid (*Z*)-1-heptenylamide: Colorless solid, mp = 74 – 77°C; ^{1}H NMR (d_8-THF, 300 MHz) δ 0.89 (t, *J* = 6.8 Hz, 3H,), 1.18 – 1.83 (m, 16H), 1.95- 2.10 (m, 2H), 2.12 – 2.23 (m, 1H), 4.52 (dt, *J* = 9.0, 7.5 Hz, 1H), 6.65 (ddt, *J* = 9.1, 9.0, 1.6 Hz, 1H), 8.20 (d, *J* = 9.0 Hz, 1H); ^{13}C NMR (d_8-THF, 75.5 MHz) δ 14.7, 23.8, 26.7, 27.0, 27.1, 30.6, 30.8, 32.8, 45.8, 110.2, 123.0, 173.8; IR (KBr): 3293, 3192, 2931, 2854, 1684, 1674, 1525, 1467, 1449, 1396, 1334, 1255, 1208, 1157, 959, 758, 708; MS (EI): *m/z* (rel. intensity) 223 (16, [M^+]), 208 (2), 168 (8), 166 (6), 128 (90), 113 (43), 83 (100), 70 (29), 67 (7), 56 (93), 55 (56), 41 (30), 29 (11); HR-MS: *calcd* 223.1936, *found* 223.1937.

(2*E*,4*E*)-Hexa-2,4-dienoic acid (*Z*)-1-heptenylamide: Colorless solid, mp = 78 – 79°C; ^{1}H NMR (d_8-THF, 400 MHz) δ 0.89 (t, J = 7.2 Hz, 3H,), 1.25 – 1.44 (m, 6H), 1.80 (d, J = 6.4 Hz, 1H), 2.02- 2.11 (m, 2H), 4.57 (dt, J = 9.2, 7.2 Hz, 1H), 5.92 (d, J = 14.8 Hz, 1H), 6.01 – 6.23 (m, 2H), 6.76 (ddt, J = 10.8, 9.2, 1.6 Hz, 1H), 7.19 (dd, J = 14.9, 10.3 Hz, 1H), 8.39 (d, J = 9.6 Hz, 1H); ^{13}C NMR (d_8-THF, 100 MHz) δ 14.7, 18.9, 23.8, 26.8, 30.6, 32.8, 110.9, 111.1, 123.1, 123.2, 137.8, 142.3, 163.7; IR (KBr): 3268, 3174, 3018, 2950, 2927, 2857, 1677, 1654, 1628, 1615, 1517, 1339, 1254, 1228, 1201, 1157, 1000, 689; MS (EI): *m/z* (rel. intensity) 207 (8, [M^+]), 192 (2), 150 (3), 136 (3), 112 (19), 95 (100), 67 (28), 65 (5), 56 (10), 41 (18), 29 (3); HR-MS: *calcd* 207.1623, *found* 207.1624.

2,2-Dimethylpropionic acid (*Z*)-1-heptenyl amide: Colorless solid, mp = 41 – 42°C; ^{1}H NMR (d_8-THF, 300 MHz) δ 0.90 (t, J = 6.7 Hz, 3H), 1.18 (s, 9H), 1.25 – 1.49 (m, 6H), 2.00 – 2.10 (m, 2H), 4.61 (dt, J = 9.0, 7.5 Hz, 1H), 6.66 (dt, J = 9.0, 1.6 Hz, 1H), 7.52 (s, 1H); ^{13}C NMR (d_8-THF, 75.5 MHz) δ 14.7, 23.7, 26.6, 27.9, 30.5, 32.7, 39.7, 111.0, 123.2, 175.5; IR (KBr): 3226, 3180, 2960, 2922, 2856, 1676, 1644, 1505, 1481, 1465, 1401, 1396, 1281, 1262, 1193, 1077, 945, 735, 658; MS (EI): *m/z* (rel. intensity) 197 (12, [M^+]), 154 (3), 140 (18), 102 (49), 97 (13), 85 (16), 57 (100), 56 (35), 41 (17), 29 (12); HR-MS: *calcd* 197.178, *found* 197.1781.

Benzoic acid (*Z*)-1-heptenyl amide: Colorless syrup. ^{1}H NMR (d_8-THF, 300 MHz) δ 0.91 (t, J = 7.0 Hz, 3H), 1.27 – 1.50 (m, 6H), 2.14 – 2.24 (m, 2H), 4.73 (dt, J = 9.0, 7.5 Hz, 1H), 6.88 (ddt, J = 10.4, 9.0, 1.6 Hz, 1H), 7.40 – 7.49 (m, 3H), 7.83 – 7.87 (m, 2H), 8.65 (d, J = 7.9 Hz, 1H); ^{13}C NMR (d_8-THF, 75.5 MHz) δ 14.7, 23.8, 26.8, 30.6, 32.8, 112.5, 123.1, 128.6, 129.2, 132.3, 136.0, 165.3; IR (neat): 3301, 3057, 2956, 2926, 2870, 2857, 1645, 1603, 1580, 1512, 1484, 1379, 1278, 1152, 1075, 1028, 888, 798, 706, 693, 675; MS (EI): *m/z* (rel. intensity) 217 (5, [M^+]), 160 (9), 146 (2), 122 (32), 105 (100), 96 (2), 77 (35), 51 (5), 41 (2), 29 (2); HR-MS: *calcd* 217.1467, *found* 217.1468.

***m*-Nitrobenzoic acid (*Z*)-1-heptenyl amide:** Colorless syrup. ^{1}H NMR (d_8-THF, 300 MHz) δ 0.91 (t, J = 7.0 Hz, 3H), 1.26 – 1.50 (m, 6H), 2.15 - 2.26 (m, 2H), 4.82 (dt, J = 8.9, 7.5 Hz, 1H), 6.86 (ddt, J = 10.1, 9.1, 1.6 Hz, 1H), 7.70 (t, J = 8.0 Hz, 1H), 8.27 (dt, J = 8.6, 1.2 Hz, 1H), 8.36 (ddd, J = 8.1, 2.3, 1.0 Hz, 1H), 8.72 (t, J = 1.9 Hz, 1H), 9.10 (br s, 1H); ^{13}C NMR

(d_8-THF, 75.5 MHz) δ 14.7, 23.8, 26.9, 30.6, 32.8, 114.2, 122.8, 123.5, 126.9, 130.8, 134.9, 137.6, 149.5, 163.6; IR (neat): 3300, 3088, 2956, 2927, 2857, 1648, 1617, 1579, 1533, 1515, 1473, 1433, 1378, 1350, 1296, 1270, 1159, 1096, 1079, 715; MS (EI): *m/z* (rel. intensity) 262 (5, [M^+]), 219 (3), 205 (23), 179 (3), 167 (29), 150 (100), 134 (4), 122 (2), 119 (2), 112 (2), 104 (28), 96 (16), 92 (4), 81 (4), 76 (20), 75 (4); HR-MS: *calcd* 262.1317, *found* 262.1316.

***p*-Methoxybenzoic acid (*Z*)-1-heptenyl amide**. Yellow syrup. ^{1}H NMR (d_8-THF, 300 MHz) δ 0.90 (t, 3H, J = 6.9 Hz), 1.22 – 1.50 (m, 6H), 2.12 – 2.24 (m, 2H), 3.81 (s, 3H), 4.69 (dt, 1H, J = 9.0, 7.5 Hz), 6.82 – 6.96 (m, 3H), 7.84 (d, 2H, J = 8.7 Hz), 8.54 (d, 1H, J = 9.0 Hz); ^{13}C NMR (d_8-THF, 75.5 MHz) δ 14.7, 23.8, 26.8, 30.8, 32.8, 55.9, 111.9, 114.4, 123.3, 128.0, 130.4, 163.7, 165.4; IR (neat): 3311, 2956, 2928, 2857, 1642, 1607, 1577, 1523, 1491, 1309, 1256, 1177, 1110, 1032, 891, 843, 765, 694, 622; MS: *m/z* (rel. intensity) 247 (11, [M^+]), 152 (11), 135 (100), 107 (4), 92 (6), 77 (8), 64 (2), 41 (1), 29 (1); HR-MS: *calcd* 247.1572, *found* 247.1574.

Cyclohexanecarboxylic acid (*E*)-1-heptenyl amide: Colorless solid, mp = 90 – 94°C; ^{1}H NMR (CD_2Cl_2, 300 MHz) δ 0.88 (t, J = 6.7 Hz, 3H,), 1.22 – 1.49 (m, 10H), 1.57- 1.88 (m, 6H), 1.97 – 2.13 (m, 3H), 5.15 (dt, J = 14.2, 7.1 Hz, 1H), 6.65 (ddt, J = 14.3, 10.5, 1.5 Hz, 1H), 7.08 (br s, 1H); ^{13}C NMR (CD_2Cl_2, 75.5 MHz) δ 13.9, 22.6, 25.7, 25.8, 29.6, 29.7, 29.8, 31.4, 45.4, 112.7, 122.6, 172.9; IR (KBr): 3283, 3204, 3078, 2926, 2854, 1681, 1641, 1532, 1466, 1446, 1389, 1334, 1258, 1251, 1215, 949, 719; MS (EI): *m/z* (rel. intensity) 223 (9, [M^+]), 168 (4), 166 (4), 140 (2), 128 (60), 113 (34), 111 (8), 96 (4), 84 (11), 83 (93), 70 (30), 67 (6), 56 (100), 55 (59), 41 (35), 29 (14); HR-MS: *calcd* 223.1936, *found* 223.1937.

(2*E*,4*E*)-Hexa-2,4-dienoic acid (*E*)-1-heptenyl amide: Colorless solid, mp = 112 – 115°C; ^{1}H NMR (CD_2Cl_2, 300 MHz) δ 0.88 (t, J = 6.8 Hz, 3H,), 1.20 – 1.44 (m, 6H), 1.83 (d, J = 5.8 Hz, 3H), 1.97- 2.09 (m, 2H), 4.52 (dt, J = 14.3, 7.1 Hz, 1H), 5.77 (d, J = 15.0 Hz, 1H), 6.03 – 6.26 (m, 2H), 6.80 (ddt, J = 14.3, 10.6, 1.4 Hz, 1H), 7.20 (dd, J = 15.0, 10.0 Hz, 1H), 7.35 (d, J = 9.3 Hz, 1H); ^{13}C NMR (CD_2Cl_2, 75.5 MHz) δ 13.9, 18.4, 22.6, 29.7, 29.9, 31.4, 113.6, 121.1, 122.7, 129.7, 138.5, 142.0, 163.0; IR (KBr): 3275, 3202, 3024, 2954, 2922, 2852, 1678, 1655, 1629, 1615, 1533, 1349, 1250, 1209, 996, 954; MS (EI): *m/z* (rel. intensity) 207

(8, [M^+]), 192 (2), 150 (3), 136 (2), 95 (100), 67 (28), 65 (6), 56 (10), 41 (23), 29 (5); HR-MS: *calcd* 207.1623, *found* 207.1623.

2,2-Dimethylpropionic acid (*E*)-1-heptenyl amide: Colorless solid, mp = 78 – 80°C; ^{1}H NMR (C_6D_6, 300 MHz) δ 0.98 (t, *J* = 6.8 Hz, 3H), 1.16 (s, 9H), 1.26 – 1.47 (m, 6H), 1.98 – 2.08 (m, 2H), 5.15 (dt, *J* = 13.8, 7.0 Hz, 1H), 7.20 – 7.42 (m, 2H); ^{13}C NMR (C_6D_6, 75.5 MHz) δ 14.2, 22.9, 27.4, 30.1, 30.2, 31.6, 38.5, 112.2, 124.0, 174.8; IR (KBr): 3286, 3200, 2958, 2926, 2871, 1681, 1637, 1524, 1480, 1228, 1214, 960, 718; MS (EI): *m/z* (rel. intensity) 197 (11, [M^+]), 182 (2), 154 (3), 140 (16), 102 (41), 97 (11), 85 (14), 57 (100), 56 (34), 41 (19), 29 (12); HR-MS: *calcd* 197.178, *found* 197.1779.

Benzoic acid (*E*)-1-heptenyl amide: Colorless solid, mp = 80 – 83°C; ^{1}H NMR (d_8-THF, 400 MHz) δ 0.90 (t, *J* = 6.9 Hz, 3H), 1.26 – 1.46 (m, 6H), 2.01 – 2.11 (m, 2H), 5.32 (dt, *J* = 14.3, 7.2 Hz, 1H), 6.97 (ddt, *J* = 14.3, 10.0, 1.3 Hz, 1H), 7.34 – 7.48 (m, 3H), 7.83 – 7.88 (m, 2H), 9.19 (d, *J* = 8.5 Hz, 1H). ^{13}C NMR (C_6D_6, 75.5 MHz) δ 14.3, 22.9, 30.1, 30.3, 31.6, 114.3, 123.9, 131.5, 134.5, 164.4; IR (KBr): 3269, 3199, 3066, 2959, 2927, 2855, 1673, 1628, 1601, 1577, 1530, 1490, 1458, 1431, 1337, 1318, 1192, 961, 708; MS (EI): *m/z* (rel. intensity) 217 (5, [M^+]), 160 (8), 146 (2), 122 (34), 105 (100), 96 (2), 77 (32), 51 (6), 41 (2), 29 (2); HR-MS: *calcd* 217.1467, *found* 217.1465.

***m*-Nitrobenzoic acid (*E*)-1-heptenyl amide:** Colorless solid, mp = 128 – 129°C; ^{1}H NMR (d_8-THF, 300 MHz) δ 0.91 (t, *J* = 6.7 Hz, 3H), 1.25 – 1.48 (m, 6H), 2.03 - 2.13 (m, 2H), 5.40 (dt, *J* = 14.3, 7.1 Hz, 1H), 6.88 (dd, *J* = 14.3, 9.8 Hz, 1H), 7.70 (t, *J* = 8.0 Hz, 1H), 8.29 (dt, *J* = 7.8, 1.2 Hz, 1H), 8.35 (ddd, *J* = 8.2, 2.2, 1.0 Hz, 1H), 8.73 (t, *J* = 1.8 Hz, 1H), 9.60 (d, *J* = 8.7 Hz, 1H); ^{13}C NMR (d_8-THF, 75.5 MHz) δ 14.7, 23.7, 31.1, 31.2, 32.6, 114.8, 123.0, 125.1, 126.9, 130.8, 134.8, 137.3, 149.6, 162.5; IR (KBr): 3309, 2948, 2925, 2868, 1638, 1616, 1541, 1528, 1347, 1331, 950, 911, 846, 717; MS (EI): *m/z* (rel. intensity) 262 (7, [M^+]), 219 (3), 205 (24), 179 (2), 167 (28), 150 (100), 134 (3), 122 (2), 112 (1), 104 (25), 96 (17), 92 (3), 81 (4), 76 (16), 75 (4), 67 (3); HR-MS: *calcd* 262.1317, *found* 262.1317.

***p*-Methoxybenzoic acid (*E*)-1-heptenyl amide:** Colorless solid, mp = 80 – 83°C; ^{1}H NMR (d_8-THF, 300 MHz) δ 0.90 (t, *J* = 6.8 Hz, 3H), 1.26 – 1.47 (m, 6H), 2.00 – 2.11 (m, 2H), 3.81 (s, 3H), 5.26 (dt, *J* = 14.3, 7.2 Hz, 1H), 6.88 – 7.03 (m, 3H), 7.82 (d, *J* = 8.9 Hz, 2H), 9.04 (d,

J = 9.7 Hz, 1H). ^{13}C NMR (d_8-THF, 75.5 MHz) δ 14.7, 23.7, 31.2, 31.3, 32.6, 55.8, 112.4, 114.4, 125.7, 128.0, 130.2, 163.5, 164.0; IR (KBr): 3285, 2953, 2924, 2858, 1676, 1635, 1607, 1577, 1526, 1503, 1325, 1304, 1255, 1175, 1109, 1023, 954, 842, 610; MS (EI): *m/z* (rel. intensity) 247 (8, [M^+]), 152 (10), 151 (3), 135 (100), 107 (5), 92 (7), 77 (8), 64 (2), 41 (2), 29 (2); HR-MS: *calcd* 247.1572, *found* 247.1573.