SUPPORTING INFORMATION

Selective Iron-Catalyzed Cross-Coupling Reactions of Grignard Reagents with Enol Triflates, Acid Chlorides, and Dichloroarenes

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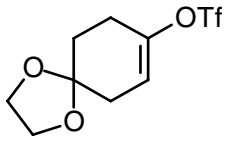
Contents

General. All reactions were carried out in flame dried glassware under an argon atmosphere. All solvents were purified by distillation over the drying agents indicated and were transferred under Ar: THF (Na/K alloy), Et_2O (Mg/benzophenone), CH_2Cl_2, $^iPr_2NH$, pyridine, DMPU, NMP (CaH_2). Merck silica gel 60 (230-400 mesh). Melting points are uncorrected. NMR: chemical shifts are given in ppm relative to TMS, coupling constants (*J*) in Hz. IR: wavenumbers ($\tilde{\nu}$) in cm^{-1}. All commercially available compounds were used as received.

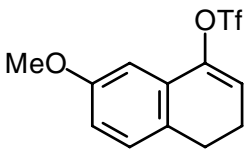
STARTING MATERIALS

General Procedure for the Preparation of Enol Triflates. A solution of the ketone (3.8 mmol) in THF (3 mL) was added to a freshly prepared solution of LDA (4.2 mmol) and DMPU (1.4 mL, 11.4 mmol) in THF (10 mL) at –78°C. The resulting solution was stirred for 2 h at that temperature before a solution of *N*-phenyltrifluoromethanesulfonimide (1.5 g, 4.2 mmol) in THF (5 mL) was added. The mixture was allowed to reach 0°C and was stirred at this temperature for 9 h. After removal of the solvent, the residue was purified by flash chromatography on silica to yield the corresponding enol triflate. The analytical and spectroscopic data of the products thus obtained are compiled below.

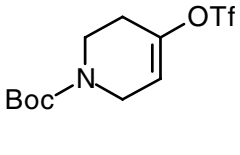
Trifluoromethanesulfonic acid 1,4-dioxa-spiro[4.5]dec-7-en-8-yl ester. Colorless oil (97%). ^{1}H-NMR (400 MHz, CD_2Cl_2): δ = 5.67 (m, 1H), 3.97 (m, 4H), 2.52 (m, 2H), 2.39 (m, 2H), 1.87 (t, J = 6.6 Hz, 2H). ^{13}C-NMR (100 MHz, CD_2Cl_2): δ = 148.7, 118.9 (q, J_{CF} = 320 Hz), 116.4, 106.4, 65.1, 34.5, 31.3, 26.8. IR (film): 2965, 2892, 1691, 1417, 1248, 1209, 1142, 1069, 983, 881, 609. MS (EI): *m/z* (rel. intensity) 225 (6), 155 (100), 127 (5), 111 (17), 92 (14), 83 (19), 73 (9), 55 (33), 39 (5). HR-MS *calcd.* for $C_9H_{11}F_3O_5S$: 289.035758 [$(M+H)^+$]; *found*: 289.036089 [$(M+H)^+$].



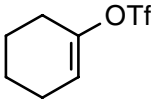
Trifluoromethanesulfonic acid 7-methoxy-3,4-dihydronaphthalen-1-yl ester. Colorless oil (97%). ^{1}H-NMR (400 MHz, $CDCl_3$): δ = 7.12 (d, J = 8.3 Hz, 1H), 6.88 (d, J = 2.6 Hz, 1H), 6.81 (dd, J = 2.6 Hz, J = 8.3 Hz, 1H), 6.05 (t, J = 4.8 Hz, 1H), 3.79 (s, 3H), 2.79 (t, J = 8.2 Hz, 2H), 2.49 (m, 2H). ^{13}C-NMR (100 MHz, $CDCl_3$): δ = 159.0, 146.6, 129.9, 129.1, 128.8, 119.2, 114.6, 107.5, 55.7, 26.3, 23.1. IR (film): 2945, 2898, 2838, 1653, 1608, 1574, 1495, 1419, 1250, 1212, 1142, 1013, 904, 811, 612. MS (EI): *m/z* (rel. intensity) 308 (100 [M^+]), 175 (41), 160 (18), 147 (44), 131 (11), 115 (26), 91 (18), 77 (8), 51 (5), 41 (2). HR-MS *calcd.* for $C_{12}H_{11}F_3O_4S$: 308.033018; *found*: 308.032876.



4-Trifluoromethanesulfonyloxy-3,6-dihydro-2*H*-pyridine-1-carboxylic acid *tert*-butyl ester.[1] Colorless oil (73%). ^{1}H-NMR (300 MHz, CD_2Cl_2): δ = 5.77 (m, 1H), 4.02 (m, 2H), 3.61 (m, 2H), 2.43 (m, 2H), 1.45 (s, 9H). ^{13}C-NMR (75 MHz, CD_2Cl_2): δ = 154.5, 121.0, 116.8, 80.5, 42.2, 28.4. IR (film): 2979, 1703, 1418, 1368, 1335, 1246, 1211, 1169, 1142, 1065, 875, 826, 612. MS (EI): *m/z* (rel. intensity) = 331 (0.3 [M^+]), 274 (11), 258 (11), 230 (3), 142 (11), 98 (5), 69 (5), 57 (100), 41 (14).



Trifluoromethanesulfonic acid cyclohex-1-enyl ester.[2] Colorless oil (72%). ^{1}H-NMR (400 MHz, CD_2Cl_2): δ/ppm = 5.76 (m, 1H), 2.32 (m, 2H), 2.18 (m, 2H), 1.80 (m, 2H), 1.58 (m, 2H). ^{13}C-NMR (100 MHz, CD_2Cl_2): δ = 149.9, 119.0 (q, J_{CF} = 320 Hz), 118.9, 27.9, 24.3, 23.1, 21.4. IR (film): 2945, 2894, 2868, 1690. MS (EI): *m/z* (rel. intensity) 230 (23 [M^+]), 151 (3), 138 (11), 125 (4), 97 (6), 85



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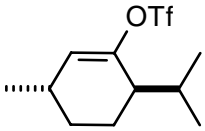
1 Wustrow, D. J.; Wise, L. D. *Synthesis* **1991**, 993.

2 Mc Murry J. E.; Scott, W. J. *Tetrahedron* **1983**, *24*, 979.

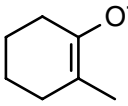
(3), 79 (40), 69 (75), 55 (43), 41 (100).

Trifluoromethanesulfonic acid (6*R*)-isopropyl-(3*S*)-methylcyclohex-1-enyl ester.[3]



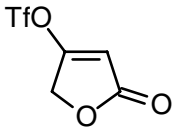
Colorless oil (97%). $[\alpha]_D^{20}$ = +56.3 (c = 1.9, CH_2Cl_2). ^{1}H-NMR (400 MHz, CD_2Cl_2): δ = 5.66 (m, 1H), 2.48 (m, 1H), 2.33 (m, 1H), 2.14 (m, 1H), 1.82 (m, 2H), 1.43 (m, 1H), 1.13 (m, 1H), 1.03 (d, J = 7.1 Hz, 3H), 0.95 (d, J = 7.0 Hz, 3H), 0.82 (d, J = 6.9 Hz, 3H). ^{13}C-NMR (100 MHz, CD_2Cl_2): δ = 152.3, 126.5, 119.0 (q, J_{CF} = 320 Hz), 43.5, 31.1, 30.3, 27.8, 22.9, 21.8, 19.9, 16.5. IR (film): 2964, 2935, 2876, 1675, 1418, 1372, 1247, 1208, 1144, 1082, 895, 608. MS (EI): *m/z* (rel. intensity) 286 (9 [M^+]), 244 (3), 216 (2), 153 (44), 136 (12), 111 (24), 93 (34), 79 (96), 69 (74), 55 (37), 43 (100).

Trifluoromethanesulfonic acid 2-methylcyclohex-1-enyl ester.[4] Colorless oil (55%). ^{1}H-



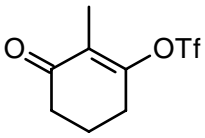
NMR (400 MHz, CD_2Cl_2): δ = 2.33-2.29 (m, 2H), 2.15-2.12 (m, 2H), 1.78-1.72 (m, 5H), 1.65-1.59 (m, 2H). ^{13}C-NMR (100 MHz, CD_2Cl_2): δ = 143.9, 127.0, 118.9 (q, J_{CF} = 319 Hz), 31.1, 18.0, 23.7, 22.2, 16.9. IR (film): 2944, 2867, 1707, 1413, 1208, 1143, 893, 607. MS (EI): *m/z* (rel. intensity) 244 (27 [M^+]), 111 (4), 95 (10), 83 (55), 79 (10), 69 (31), 55 (100), 41 (35).

Trifluoromethanesulfonic acid 5-oxo-2,5-dihydrofuran-3-yl ester.[5] Colorless oil (93%).



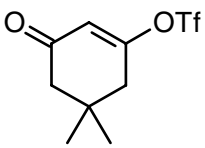
^{1}H-NMR (400 MHz, CH_2Cl_2): δ = 6.06 (t, J = 1.8 Hz, 1H), 4.89 (d, J = 1.8 Hz, 2H). ^{13}C-NMR (100 MHz, CH_2Cl_2): δ = 169.2, 167.3, 118.8 (q, J_{CF} = 322 Hz), 105.0, 68.0. IR (film): 3143, 2953, 1789, 1760, 1652, 1439, 1248, 1221, 815, 606. MS (EI): *m/z* (rel. intensity) 232 (1 [M^+]), 167 (2), 139 (49), 69 (100), 41 (31).

Trifluoromethanesulfonic acid 2-methyl-3-oxocyclohex-1-enyl ester.[6] Light yellow oil



(65%). ^{1}H-NMR (400 MHz, $CDCl_3$): δ = 2.77-2.73 (m, 2H), 2.51-2.47 (m, 2H), 2.12-2.08 (m, 2H), 1.86 (t, J = 2.1 Hz, 3H). ^{13}C-NMR (100 MHz, $CDCl_3$): δ = 197.6, 162.0, 128.0, 118.2 (q, J_{CF} = 323 Hz), 36.5, 28.7, 20.5, 9.0. IR (film): 2964, 1692, 1670, 1421, 1244, 1214, 1140, 1035, 915. MS (EI): *m/z* (rel. intensity) 258 (21 [M^+]), 230 (34), 166 (11), 138 (2), 125 (100), 109 (12), 108 (3), 100 (17), 97 (10), 81 (4), 80 (6), 79 (9), 77 (3), 72 (25), 69 (42), 55 (50), 54 (3), 53 (9), 52 (3), 51 (2), 43 (6), 42 (13), 39 (12), 27 (18), 26 (2).

Trifluoromethanesulfonic acid 5,5-dimethyl-3-oxocyclohex-1-enyl ester.[7] Colorless oil



(74%). ^{1}H-NMR (400 MHz, CD_2Cl_2): δ = 6.04 (t, J = 1.4 Hz, 1H), 2.55 (d, J = 1.4 Hz, 2H), 2.29 (s, 2H), 1.12 (s, 6H). ^{13}C-NMR (100 MHz, CD_2Cl_2): δ = 197.5, 166.5, 118.7 (q, J_{CF} = 320 Hz), 118.7, 50.9, 42.6, 33.6, 28.0. IR (film): 2966, 2878, 1690, 1650, 1429, 1354, 1216, 1139, 1055, 908, 821,

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3 Ritter, K. *Synthesis* **1993**, 735.

4 Crisp, G. T.; Scott, W. J.; Stille, J. K. *J. Am. Chem. Soc.* **1984**, *106*, 7500.

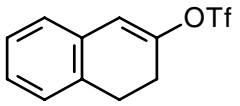
5 Grigg, R.; Kennewell, P.; Savic, V. *Tetrahedron* **1994**, *50*, 5489.

6 Yamano, Y.; Mimuro, M.; Ito, M. *J. Chem. Soc., Perkin Trans 1* **1997**, 2713.

7 Garcia Martinez, A.; Martinez Alvarez, R.; Madueno Casado, M., Subramanian, L. R.; Hanack, M. *Tetrahedron* **1987**, *43*, 275.

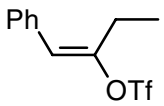
609. MS (EI): *m/z* (rel. intensity) 272 (31 [M^+]), 257 (3), 244 (10), 216 (100), 86 (13), 69 (22), 55 (6), 41 (7).

Trifluoromethanesulfonic acid 3,4-dihydronaphthalen-2-yl ester.[8] Colorless oil (96%).



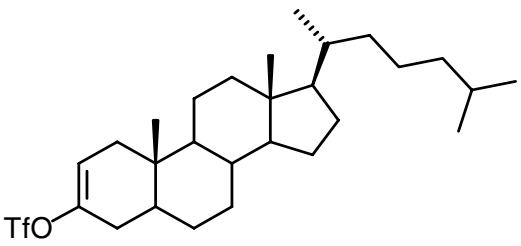
^{1}H-NMR (400 MHz, $CDCl_3$): δ = 7.20-7.02 (m, 4H), 6.46 (s, 1H), 3.03 (t, J = 8.3 Hz, 2H), 2.66 (dt, J = 1.2 Hz, J = 8.3 Hz, 2H). ^{13}C-NMR (100 MHz, $CDCl_3$): δ = 149.9, 132.9, 131.1, 128.4, 127.5, 127.3, 127.0, 118.6 (q, J_{CF} = 320 Hz), 118.5, 28.5, 26.5. IR (film): 3070, 3023, 2951, 2899, 2841, 1665, 1575, 1421, 1249, 1221, 1141, 1065, 828, 756, 617, 497. MS (EI): *m/z* (rel. intensity) = 278 (42 [M^+]), 145 (49), 117 (100), 91 (11), 69 (5), 51 (3), 39 (5).

Trifluoromethanesulfonic acid 1-benzylidenepropyl ester.[9] Colorless oil (48%).



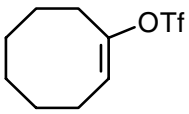
^{1}H-NMR (400 MHz, CD_2Cl_2): δ = 7.44-7.27 (m, 5H), 6.65 (m, 1H), 2.63 (q, J = 7.5 Hz, 2H), 1.23 (t, J = 7.5 Hz, 3H). ^{13}C-NMR (100 MHz, CD_2Cl_2): δ = 154.0, 133.1, 129.1, 129.1, 128.8, 128.7, 122.3, 119.1 (q, J_{CF} = 320 Hz), 24.7, 11.3. IR (film): 3086, 3061, 3030, 2984, 2944, 2885, 1671, 1602, 1578, 1496, 1417, 1211, 1144, 755, 697. MS (EI): *m/z* (rel. intensity) 280 (26 [M^+]), 147 (47), 119 (10), 91 (100), 69 (6), 51 (3), 41 (9).

Trifluoromethanesulfonic acid 17-(1,5-dimethyl-hexyl)-10,13-dimethyl-4,5,6,7,8,9,10,11, 12,13,14,15,16,17-tetradecahydro-1*H*-cyclopenta[α]phenanthren-3-yl ester.[10] White solid



(88%). $[\alpha]_D^{20}$ = +26.0 (c = 1.1, CH_2Cl_2). M.p. = 88.4-89.8 °C (hexanes). ^{1}H-NMR (400 MHz, CD_2Cl_2): δ = 5.67 (m, 1H), 2.15-1.12 (m, 44H). ^{13}C-NMR (75 MHz, CD_2Cl_2): δ = 117.7, 56.7, 53.7, 42.8, 42.6, 40.3, 39.9, 38.8, 36.5, 36.2, 35.8, 34.8, 32.4, 31.9, 28.6, 28.5, 28.4, 24.5, 24.2, 22.9, 22.7, 21.6, 18.8, 12.1, 11.7. IR (film): 2933, 2866, 1697, 1419, 1385, 1366, 1248, 1205, 1143, 1038, 901, 616, 579, 515. MS (EI): *m/z* (rel. intensity) 518 (89 [M^+]), 503 (15), 385 (29), 363 (100), 349 (20), 336 (5), 316 (19), 245 (9), 215 (9), 162 (20), 95 (27), 55 (28).

Trifluoromethanesulfonic acid cyclooct-1-enyl ester. A solution of cyclooctanone (1.0 g,



7.9 mmol) in THF (10 mL) was added to a cooled (–78°C) solution of KHMDS (21 ml, 0.5 M in THF, 10.5 mmol) under argon, followed by a solution of N-phenyl-trifluoromethanesulfonimide (3.7 g, 10.4 mmol) in THF (10 mL). The mixture was allowed to reach ambient temperature and was stirred overnight. A standard extractive work up followed by flash chromatography of the crude product afforded the title compound as a colorless liquid (1.58 g, 77%). ^{1}H-NMR (300 MHz, $CDCl_3$): δ 5.67 (t, 1H), 2.42-2.46 (m, 2H), 2.11-2.17 (m, 2H), 1.68-1.73 (br m, 2H), 1.49-1.60 (m, 6H). ^{13}C-NMR (75 MHz, $CDCl_3$): δ 151.3, 120.5, 118.5 (q, J_{CF} = 320 Hz), 29.4, 29.0, 27.0, 25.7, 25.4, 24.9. IR (film): 2934, 2859, 1682, 1415, 1244, 1208, 1144, 1032, 1010,

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8 Karnekawa, H.; Senboku, H.; Tokuda, M. *Tetrahedron Lett.* **1998**, *39*, 1591.

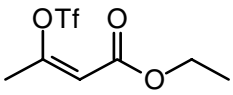
9 Brummond K. M.; Dilzer Gresenberg, K.; Kent, J. L.; Kerekes, A. D. *Tetrahedron Lett.* **1998**, *39*, 8613.

10 Cacchi, S.; Morera, E.; Ortar, G. *Tetrahedron Lett.* **1984**, *25*, 2271.

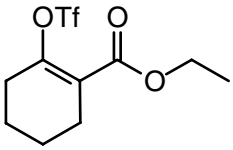
936, 860, 847, 611. MS (EI): *m/z* (rel. intensity) 258 (6, [M^+]), 230 (56), 108 (11), 93 (17), 81 (15), 80 (64), 79 (26), 69 (28), 68 (12), 67 (28), 55 (100). Anal. *calcd.* for $C_9H_{13}F_3SO_3$: C 41.85, H 5.07; *found*: C 41.96, H 5.10.

The following compounds have been prepared analogously:

(*Z*)-Trifluoromethanesulfonyloxy-but-2-enoic acid ethyl ester: ^{1}H-NMR (300 MHz, $CDCl_3$): δ 5.72 (s, 1H), 4.18 (q, 2H), 2.11 (s, 3H), 1.24 (t, 3H). ^{13}C-NMR (75 MHz, $CDCl_3$): δ 162.2, 155.0, 118.2 (q, J_{CF} = 319 Hz), 112.7, 61.0, 20.7, 13.8. IR (film): 2988, 1733, 1687, 1427, 1208, 928, 621. MS (EI): *m/z* (rel. intensity) 262 (51, [M^+]), 234 (39), 217 (96), 216 (56), 153 (19), 87 (85), 85 (24), 84 (57), 69 (100).



2-Trifluoromethanesulfonyloxy-cyclohexanecarboxylic acid ethyl ester: ^{1}H-NMR (300 MHz, $CDCl_3$): δ 4.23 (q, 2H), 2.41-2.47 (m, 2H), 2.33-2.39 (m, 2H), 1.71-1.78 (m, 2H), 1.59-1.67 (m, 2H), 1.28 (t, 3H). ^{13}C-NMR (75 MHz, $CDCl_3$): δ 164.7, 151.3, 123.2, 118.3 (q, J_{CF} = 319 Hz), 61.5, 28.4, 26.1, 22.3, 20.9, 13.9. IR (film): 2947, 2870, 1726, 1669, 1423, 1371, 1286, 1260, 1245, 1209, 1141, 1094, 1044, 915, 829, 766, 615. MS (EI): *m/z* (rel. intensity) 302 (7, [M^+]), 257 (32), 169 (34), 123 (100), 95 (20), 79 (15), 69 (15), 55 (26). Anal. *calcd.* for $C_{10}H_{13}F_3SO_5$: C 39.74, H 4.33; *found*: C 39.78, H 4.25.



CROSS COUPLING PRODUCTS DERIVED FROM ENOLTRFLATES

8-Phenyl-1,4-dioxaspiro[4.5]dec-7-ene. ^{1}H-NMR (400 MHz, CD_2Cl_2): δ = 7.41-7.38 (m 2H), 7.33-7.29 (m, 2H), 7.25-7.21 (m, 1H), 5.99 (t, *J* = 1.1 Hz, 1H), 3.99 (s, 4H), 2.64 (m, 2H), 2.43 (m, 2H), 1.90 (t, *J* = 6.5Hz, 2H). ^{13}C-NMR (100 MHz, CD_2Cl_2): δ = 142.0, 136.5, 128.6, 127.1, 125.4, 122.1, 107.9, 64.8, 36.5, 31.7, 27.1. IR (film): 3054, 2950, 2928, 1647, 1598, 1577, 1493, 1421, 1117, 1060, 945, 867, 745, 696. MS (EI): *m/z* (rel. intensity) = 216 (56 [M^+]), 201 (6), 186 (1), 155 (2), 143 (3), 129 (12), 115 (11), 99 (3), 86 (100), 77 (3), 71 (3), 42 (10). Anal *calcd.* for $C_{14}H_{16}O_2$: C 77.75, H 7.46; *found*: C 77.59, H 7.54.

4-Tetradecyl-3,6-dihydro-2*H*-pyridine-1-carboxylic acid *tert*-butyl ester. ^{1}H-NMR (300 MHz, $CDCl_3$): δ = 5.33 (m, 1H), 3.84 (m, 2H), 3.47 (t, *J* = 5.7 Hz, 2H), 2.04-1.95 (m, 4H), 1.47 (s, 9H), 1.44-1.21 (m, 24H), 0.88 (t, *J* = 6.7 Hz, 3H). ^{13}C-NMR (75 MHz, $CDCl_3$): δ = 155.0, 136.8, 117.5, 79.3, 43.2, 37.2, 31.9, 29.7, 29.6, 29.6, 29.6, 29.5, 29.3, 29.3, 28.5, 28.3, 27.3, 22.7, 14.2, 14.1. IR (film): 3006, 2924, 2853, 1702, 1365, 1175. MS (EI): *m/z* (rel. intensity) = 379 (0.3 [M^+]), 322 (100), 306 (7), 278 (7), 126 (93), 82 (44), 57 (56), 41 (12). HR-MS *calcd.* for $C_{24}H_{45}NO_2$: 380.352854 [$(M+H)^+$]; *found*: 380.352409 [$(M+H)^+$]. Anal *calcd.* for $C_{24}H_{45}NO_2$: C 75.93, H 11.95; *found*: C 76.08, H 11.83.

4-Phenyl-3,6-dihydro-2*H*-pyridine-1-carboxylic acid *tert*-butyl ester.[11] ^{1}H-NMR (300 MHz, $CDCl_3$): δ = 7.39-7.25 (m, 5H), 6.03 (m, 1H), 4.07 (m, 2H), 3.64 (t, *J* = 5.7 Hz, 2H),

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2.52 (m, 2H), 1.49 (s, 9H). ^{13}C-NMR (75 MHz, $CDCl_3$): δ = 140.7, 128.4, 127.2, 124.9, 79.6, 28.5, 27.4. IR (film): 2975, 2930, 2864, 1697, 1599, 1578, 1495, 1170, 748, 695. MS (EI): *m/z* (rel. intensity) = 259 (1 [M^+]), 202 (48), 158 (19), 129 (13), 115 (14), 91 (12), 57 (100), 41 (21). HR-MS *calcd.* for $C_{16}H_{21}NO_2$: 259.157229; *found*: 259.157265.

1-Butyl-cyclohexene.[12] ^{1}H-NMR (400 MHz, $CDCl_3$): ^{1}H-NMR (300 MHz, $CDCl_3$): δ = 5.38 (m, 1H), 1.95 (m, 6H), 1.58 (m, 4H), 1.32 (m, 4H), 0.89 (t, *J* = 7.2 Hz, 3H). ^{13}C-NMR (100 MHz, $CDCl_3$): δ = 138.1, 120.5, 37.8, 29.9, 28.3, 25.3, 23.1, 22.7, 22.5, 14.0. IR (film): 2924, 2854, 1668, 1378, 918, 800, 721. MS (EI): *m/z* (rel. intensity) = 138 (29 [M^+]), 109 (6), 96 (33), 81 (100), 67 (50), 55 (18), 41 (18).

1-Tetradecyl-cyclohexene. ^{1}H-NMR (400 MHz, C_6D_6): δ = 5.47 (m, 1H), 1.98 (m, 4H), 1.89 (m, 2H), 1.52 (m, 6H), 1.32 (m, 22H), 0.91 (t, *J* = 7.0 Hz, 3H). ^{13}C-NMR (100 MHz, C_6D_6): δ = 138.0, 121.0, 38.6, 32.3, 30.6, 30.2, 30.1, 30.1, 30.1, 29.9, 29.8, 28.7, 28.2, 25.7, 23.5, 23.1, 23.1, 14.3. IR (film): 2923, 2854, 1668, 1377, 800. MS (EI): *m/z* (rel. intensity) = 278 (21 [M^+]), 250 (3), 138 (3), 109 (10), 96 (100), 81 (57), 67 (26), 55 (15), 41(13). HR-MS *calcd.* for $C_{20}H_{38}$: 278.297350; *found*: 278.297281. Anal *calcd.* for $C_{20}H_{38}$: C 86.25, H 13.75; *found*: C 86.31, H 13.70.

Cyclohex-1-enylbenzene.[13] ^{1}H-NMR (300 MHz, CD_2Cl_2): δ = 7.42-7.19 (m, 5H), 6.15 (m, 1H), 2.43 (m, 2H), 2.24 (m, 2H), 1.82 (m, 2H), 1.69 (m, 2H). ^{13}C-NMR (75 MHz, CD_2Cl_2): δ = 143.2, 137.0, 128.5, 126.8, 125.3, 125.1, 27.8, 26.3, 23.5, 22.6. IR (film): 3028, 2928, 1643, 1599, 1576, 1493, 1445, 759, 741, 693. MS (EI): *m/z* (rel. intensity) = 158 (100 [M^+]), 143 (48), 129 (64), 115 (38), 104 (11), 91 (19), 77 (11), 67 (6), 51 (8), 39 (5), 27 (3).

(6*R*)-Isopropyl-1,3(*S*)-dimethylcyclohexene. $[\alpha]_D^{20}$ = +5.2 (c = 2.33, $CHCl_3$). ^{1}H-NMR (400 MHz, $CDCl_3$): δ = 5.30-5.29 (m, 1H), 2.12-1.96 (m, 3H), 1.79-1.73 (m, 1H), 1.69-1-61 (m, 4H), 1.32-1.22 (m, 1H), 1.04-0.95 (m, 1H), 0.93 (d, *J* = 7.0 Hz, 3H), 0.92 (d, *J* = 7.0 Hz, 3H), 0.68 (d, *J* = 6.8 Hz, 3H). ^{13}C-NMR (100 MHz, $CDCl_3$): δ = 135.8, 131.2, 44.3, 31.8, 30.9, 27.7, 22.3, 21.9, 21.7, 20.7, 15.6. IR (film): 3025, 2958, 2926, 2868, 2851, 1454, 1385, 842. MS (EI): *m/z* (rel. intensity) 152 (27 [M^+]), 137 (12), 109 (100), 95 (15), 82 (31), 79 (8), 67 (51), 55 (13), 41 (14), 27 (4). HR-MS *calcd.* for $C_{11}H_{20}$: 152.156500; *found*: 152.156542. Anal *calcd.* for $C_{11}H_{20}$: C 86.76, H 13.24; *found* C 86,56, H. 13.27.

1-Butyl-2-methylcyclohexene.[14] ^{1}H-NMR (400 MHz, $CDCl_3$): δ = 1.99-1.91 (m, 6H), 1.59-1.55 (m, 7H), 1.36-1.24 (m, 4H), 0.90 (m, 3H). ^{13}C-NMR (100 MHz, $CDCl_3$): δ = 130.3, 125.6, 33.2, 31.9, 30.5, 29.6, 23.6, 23.5, 22.8, 19.0, 14.1. IR (film): 2956, 2924, 2857, 2831, 1457, 1377. MS (EI): *m/z* (rel. intensity) = 152 (59 [M^+]), 137 (2), 123 (6), 109 (67), 95 (100), 91 (8), 81 (61), 67 (74), 55 (27), 41 (24), 39 (11), 29 (8).

1-Methoxy-4-(2-methylcyclohex-1-enyl)-benzene.[15] ^{1}H-NMR (400 MHz, $CDCl_3$): δ = 7.08-7.04 (m, 2H), 6.87-6.83 (m, 2H), 3.80 (s, 3H), 2.22-2.20 (m, 2H), 2.06-2.05 (m, 2H), 1.72-

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1.65 (m, 4H), 1.55 (m, 3H). ^{13}C-NMR (100 MHz, $CDCl_3$): δ = 157.7, 136.9, 131.7, 129.4, 128.9, 113.3, 55.2, 32.0, 31.7, 23.6, 23.2, 20.8. IR (film): 2925, 2856, 2831, 1607, 1511, 1457, 1444, 1289, 1242, 1039, 826, 598. MS (EI): *m/z* (rel. intensity) 202 (100 [M^+]), 187 (39), 173 (37), 159 (43), 144 (11), 121 (20), 91 (8), 77 (7).

5,5-Dimethyl-3-tetradecylcyclohex-2-enone. ^{1}H-NMR (400 MHz, CD_2Cl_2): δ = 5.81 (m, 1H), 2.18 (m, 6H), 1.50 (m, 2H), 1.27 (m, 22H), 1.02 (s, 6H), 0.89 (t, J = 7.0 Hz, 3H). ^{13}C-NMR (100 MHz, CD_2Cl_2): δ = 199.8, 164.4, 124.9, 51.5, 44.2, 38.4, 33.8, 32.4, 30.1, 30.1, 30.1, 30.1, 30.0, 30.0, 29.8, 29.8, 29.7, 28.4, 27.4, 23.1, 14.3. IR (film): 2925, 2854, 1672, 1466, 902. MS (EI): *m/z* (rel. intensity) 320 (22 [M^+]), 305 (100), 151 (58), 138 (36), 125 (6), 109 (4), 95 (12), 82 (24), 67 (6), 55 (9), 43 (12). HR-MS *calcd.* for $C_{22}H_{40}O$: 320.307915; *found*: 320.308074. Anal *calcd.* for $C_{22}H_{40}O$: C 82.43, H 12.58; *found* C 82.61, H 12.40.

2,3-Dimethylcyclohex-2-enone.[16] ^{1}H-NMR (300 MHz, $CDCl_3$): δ = 2.41-2.33 (m, 4H), 1.98-1.91 (m, 5H), 1.77-1.76 (m, 3H). ^{13}C-NMR (75 MHz, $CDCl_3$): δ = 199.1, 155.4, 130.9, 37.4, 32.6, 22.1, 21.4, 10.6. IR (film): 2926, 2868, 2828, 1663, 1632, 1456, 1431, 1379,1303. MS (EI): *m/z* (rel. intensity) 124 (69 [M^+]), 123 (2), 96 (100), 79 (5), 77 (5), 68 (33), 67 (57), 66 (3), 52 (4), 51 (6), 50 (3), 43 (2), 41 (17), 40 (7), 39 (21), 29 (4), 27 (16).

3-Butyl-2-methylcyclohex-2-enone.[17] ^{1}H-NMR (300 MHz, $CDCl_3$): δ = 2.40-2.31 (m, 4H), 2.27-2.22 (m, 2H), 1.97-1.90 (m, 2H), 1.78-1.76 (m, 3H), 1.48-1.35 (m, 4H), 0.94 (t, J = 7.1 Hz, 3H). ^{13}C-NMR (75 MHz, $CDCl_3$): δ = 199.5, 159.3, 130.6, 37.7, 35.0, 30.8, 29.5, 22.8, 22.5, 13.8, 10.5. IR (film): 2956, 2930, 2871, 1665, 1627, 1457, 1429, 1379, 1355. MS (EI): *m/z* (rel. intensity) 166 (44 [M^+]), 137 (100), 124 (35), 96 (87), 95 (11), 87 (3), 79 (8), 77 (5), 68 (11), 67 (16), 55 (15), 52 (2), 51 (3), 43 (7), 41 (19), 39 (8), 29 (5).

2-Methyl-3-tetradecylcyclohex-2-enone. ^{1}H-NMR (300 MHz, $CDCl_3$): δ = 2.40-2.31 (m, 4H), 2.26-2.20 (m, 2H), 1.94-1.90 (m, 2H), 1.77-1.76 (m, 3H), 1.45-1.43 (m, 2H), 1.26 (m, 22H), 0.90-0.86 (m, 3H). ^{13}C-NMR (75 MHz, $CDCl_3$): δ = 199.6, 159.4, 130.7, 37.4, 35.3, 31.9, 30.9, 29.8, 29.7, 29.6, 29.6, 29.5, 29.5, 29.3, 27.4, 22.7, 22.5, 14.1, 10.6. IR (film): 2924, 2853, 1668, 1628, 1466, 1378, 721. MS (EI): *m/z* (rel. intensity) 306 (21 [M^+]), 137 (46), 124 (100), 111 (11), 109 (7), 96 (11), 79 (3), 68 (3), 67 (7), 55 (7), 43 (9), 41 (7). HR-MS *calcd.* for $C_{21}H_{38}O$: 329.28204 [$(M+Na)^+$]; *found*: 329.28192 [$(M+Na)^+$]. Anal *calcd.* for $C_{21}H_{38}O$: C 82.29, H 12.50; *found* C 82.38, H 12.38.

2-Tetradecyl-cyclohexen-1-carboxylic acid ethyl ester. ^{1}H-NMR (300 MHz, $CDCl_3$): δ = 4.14 (q, 2H), 2.26 (m, 4H), 2.08 (m, 2H), 1.56 (m, 4H), 1.39 (m, 2H), 1.23-1.28 (m, 25H), 0.85 (t, 3H). ^{13}C-NMR (75 MHz, $CDCl_3$): δ = 169.3, 148.8, 124.4, 59.8, 35.5, 31.9, 31.1, 29.9, 29.7, 29.64, 29.61, 29.5, 29.3, 28.7, 26.5, 22.6, 22.3, 22.0, 14.2, 14.0. IR (film): 2925, 2854, 1713, 1634, 1465, 1368, 1277, 1226, 1178, 1084, 1047, 766. MS (EI): *m/z* (rel. intensity) 350 (100, [M^+]), 306 (17), 305 (75), 181 (10), 169 (10), 168 (77), 153 (22), 150 (20), 139 (11), 136 (10), 135 (42), 122 (20), 121 (12), 107 (14), 95 (34), 94 (47), 93 (18), 81 (22), 79 (21), 67 (19), 55 (20), 43 (29), 41 (18), 29 (13). Anal. *calcd.* for $C_{23}H_{42}O_2$: C 77.36, H 12.33; *found*: C 77.18, H 11.22.

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2-Phenyl-cyclohexen-1-carboxylic acid ethyl ester. ^{1}H-NMR (300 MHz, $CDCl_3$): δ = 7.16-7.21 (m, 3H), 7.04-7.07 (m, 2H), 3.78 (q, 2H), 2.30-2.38 (br. m, 4H), 1.64-1.69 (br. m, 4H), 0.75 (t, 3H). ^{13}C-NMR (75 MHz, $CDCl_3$): δ = 169.9, 145.5, 143.5, 128.0, 127.9, 126.9, 126.8, 59.9, 32.5, 26.5, 22.4, 21.9, 13.4. IR (film): 3056, 3022, 2980, 2934, 2861, 1706, 1599, 1491, 1444, 1371, 1285, 1254, 1221, 1136, 1051, 757, 700. MS (EI): *m/z* (rel. intensity) 230 (52, [M^+]), 184 (100), 156 (33), 141 (14), 129 (36), 115 (24), 91 (40), 77 (10). Anal. *calcd.* for $C_{15}H_{18}O_2$: C 78.26, H 7.88; *found*: C 78.11, 7.74.

4-Methyl-5*H*-furan-2-one.[18] ^{1}H-NMR (400 MHz, $CDCl_3$): δ = 5.86-5.84 (m, 1H), 4.73 (m, 2H), 2.14 (m, 3H). ^{13}C-NMR (100 MHz, $CDCl_3$): δ = 174.1, 165.9, 116.3, 73.8, 14.0. IR (film): 3108, 2986, 2928, 2867, 1782, 1750, 1645, 1443, 1310, 1142, 1042. MS (EI): *m/z* (rel. intensity) 98 (12 [M^+]), 69 (94), 41 (100), 39 (83), 27 (12).

4-Hexyl-5*H*-furan-2-one.[19] ^{1}H-NMR (300 MHz, $CDCl_3$): δ = 5.83-5.81 (m, 1H), 4.75 (m, 2H), 2.45-2.40 (m, 2H), 1.62-1.55 (m, 2H), 1.40-1.28 (m, 6H), 0.90 (t, J = 6.7 Hz, 3H). ^{13}C-NMR (75 MHz, $CDCl_3$): δ = 174.0, 170.7, 114.9, 72.9, 31.2, 28.6, 28.3, 26.9, 22.2, 13.8. IR (film): 3104, 2955, 2930, 2859, 1781, 1749, 1639, 1455, 1169, 1140, 1032. MS (EI): *m/z* (rel. intensity) 168 (1 [M^+]), 139 (32), 126 (3), 108 (17), 99 (20), 81 (10), 69 (32), 55 (100), 43 (78), 39 (48), 29 (44).

4-Tetradecyl-5*H*-furan-2-one. ^{1}H-NMR (300 MHz, $CDCl_3$): δ = 5.83 (m, 1H), 4.74 (m, 2H), 2.41 (t, J = 7.5 Hz, 2H), 1.61-1.57 (m, 2H), 1.26 (m, 22H), 0.88 (t, J = 6.9 Hz, 3H). ^{13}C-NMR (75 MHz, $CDCl_3$): δ = 174.1, 170.7, 115.2, 73.0, 31.8, 29.6, 29.6, 29.5, 29.5, 29.4, 29.3, 29.1, 29.1, 28.5, 27.1, 22.6, 14.0. IR (film): 3108, 2920, 2849, 1783, 1746, 1733, 1639, 1469, 721. MS (EI): *m/z* (rel. intensity) 280 (11 [M^+]), 220 (32), 167 (5), 153 (4), 140 (4), 121 (8), 111 (63), 98 (100), 81 (8), 69 (6), 55 (10), 43 (10). HR-MS *calcd.* for $C_{18}H_{32}O_2$: 280.240230; *found*: 280.240081. Anal *calcd.* for $C_{18}H_{32}O_2$: C 77.09, H 11.50; *found* C 77.22, H 11.62.

4-Trimethylsilanylmethyl-5*H*-furan-2-one. M.p. = 37-38 °C ($CHCl_3$). ^{1}H-NMR (400 MHz, $CDCl_3$): δ = 5.64 (m, 1H), 4.66 (m, 2H), 1.97 (s, 3H), 0.11 (s, 9H). ^{13}C-NMR (100 MHz, $CDCl_3$): δ = 174.5, 169.6, 112.5, 73.8, 21.1, -1.7. IR (KBr): 3103, 2956, 2900, 1779, 1744, 1619, 1440, 1421, 1315, 1251, 1158, 1028, 885, 851. MS (EI): *m/z* (rel. intensity) 170 (31 [M^+]), 155 (3), 127 (2), 111 (3), 109 (3), 99 (3), 97 (3), 83 (2), 81 (3), 75 (7), 74 (8), 73 (100), 55 (2), 53 (4), 45 (11), 44 (2), 43 (7), 40 (2), 39 (3). HR-MS *calcd.* for $C_8H_{14}O_2Si$: 170.076309; *found.*: 170.076048. Anal *calcd.* for $C_8H_{14}O_2Si$: C 56.43, H 8.29; *found* C 56.65, H 8.34.

4-Phenyl-5*H*-furan-2-one.[20] M.p.: 87-88°C. ^{1}H-NMR (300 MHz, $CDCl_3$): δ = 7.55-7.26 (m, 5H), 6.39 (t, J = 1.8 Hz, 1H), 5.23 (d, J = 1.8 Hz, 2H). ^{13}C-NMR (75 MHz, $CDCl_3$): δ = 173.8, 163.9, 131.8, 129.7, 129.3, 126.4, 113.1, 71.0. IR (film): 3112, 3060, 2956, 2931, 2870, 1790, 1744, 1733, 1622, 1496, 1451, 770, 686. MS (EI): *m/z* (rel. intensity) = 160 (70 [M^+]), 131 (100), 103 (40), 77 (12), 63 (39), 51 (7).

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4-(2-[1,3]Dioxan-2-ylethyl)-5*H*-furan-2-one. M.p. = 53-54 °C (EtOAc). ^{1}H-NMR (400 MHz, $CDCl_3$): δ = 5.86 (pent, J = 1.7 Hz, 1H), 4.75 (m, 2H), 4.60 (t, J = 4.7 Hz, 1H), 4.13-4.08 (m, 2H), 3.79-3.73 (m, 2H), 2.56-2.52 (m, 2H), 2.12-2.00 (m, 1H), 1.91-1.86 (m, 2H), 1.39-1.33 (m, 1H). ^{13}C-NMR (100 MHz, $CDCl_3$): δ = 174.0, 170.0, 115.4, 100.4, 73.1, 66.9, 32.4, 25.6, 22.8. IR (film): 2979, 2967, 2938, 2855, 2736, 2655, 1783, 1743, 1631, 1441, 1410, 1150, 1128, 1004. MS (EI): *m/z* (rel. intensity) 198 (4 [M^+]), 197 (6), 141 (2), 140 (2), 139 (6), 122 (3), 113 (7), 112 (5), 111 (10), 100 (10), 96 (6), 95 (2), 87 (100), 83 (5), 68 (5), 67 (6), 59 (14), 55 (9), 41 (10), 39 (7), 31 (15), 29 (8), 27 (6). HR-MS *calcd.* for $C_{10}H_{14}O_4$: 221.07897 [$(M+Na)^+$]; *found*: 221.07861 [$(M+Na)^+$]. Anal *calcd.* for $C_{10}H_{14}O_4$: C 60.59, H 7.12; *found* C 60.72, H 7.07.

4-[2-(4-Methoxyphenyl)-ethyl]-5*H*-furan-2-one. M.p. = 61-62 °C (EtOAc). ^{1}H-NMR (300 MHz, $CDCl_3$): δ = 7.11-7.08 (m, 2H), 6.86-6.83 (m, 2H), 5.84 (pent, J = 1.7 Hz, 1H), 4.65 (m, 2H), 3.80 (s, 3H), 2.89-2.84 (m, 2H), 2.73-2.71 (m, 2H). ^{13}C-NMR (75 MHz, $CDCl_3$): δ = 173.9, 169.5, 158.3, 131.6, 129.1, 116.0, 114.1, 73.1, 55.3, 32.6, 30.3. IR (film): 3105, 3001, 2933, 1780, 1748, 1637, 1513, 1247, 1177, 1034, 888, 847. MS (EI): *m/z* (rel. intensity) 218 (7 [M^+]), 121 (100), 91 (3), 78 (4), 77 (4), 65 (2), 39 (2). HR-MS *calcd.* for $C_{13}H_{14}O_3$: 241.08406 [$(M+Na)^+$]; *found*: 241.08374 [$(M+Na)^+$]. Anal *calcd.* for $C_{13}H_{14}O_3$: C 71.54, H 6.47; *found* C 71.68, H 6.61.

1-Tetradecyl-cycloocten. ^{1}H-NMR (300 MHz, $CDCl_3$): δ = 5.18 (t, 1H), 1.99-1.97 (br., 3H), 1.82 (br, 2H), 1.32 (br. m, 6H), 1.22 (br. s, 26H), 0.74 (br. s, 4H). ^{13}C-NMR (75 MHz, $CDCl_3$): δ = 141.5, 123.7, 38.0, 32.3, 30.4, 30.1, 30.04, 30.00, 29.7, 29.3, 29.2, 28.5, 26.9, 26.7, 26.6, 23.0, 14.4. IR (film): 3037, 2954, 2923, 2853, 1663, 1467, 1378, 900, 834, 721. MS (EI): *m/z* (rel. intensity) 306 (18, [M^+]), 279 (12), 278 (53), 124 (10), 110 (21), 109 (30), 97 (24), 96 (100), 95 (23), 83 (15), 82 (35), 81 (44), 69 (21), 68 (16), 67 (29), 57 (14), 55 (25), 43 (16), 41 (17). Anal *calcd.* for $C_{22}H_{42}$: C 86.18, H 13.80; *found*: C 85.89, H 13.73.

1-Phenyl-cyclooctene. ^{1}H-NMR (300 MHz, $CDCl_3$): δ = 7.13-7.16 (m, 2H), 7.00-7.06 (m, 2H), 6.91-6.96 (m, 1H), 5.74 (t, 1H), 2.34-2.38 (m, 2H), 1.99-2.04 (m, 2H), 1.24-1.39 (m, 8H). ^{13}C-NMR (75 MHz, $CDCl_3$): δ = 143.1, 140.2, 128.7, 128.1, 127.9, 127.2, 126.3, 125.7, 29.9, 29.4, 28.4, 27.5, 27.3, 26.1. IR (film): 3079, 3056, 3022, 2923, 2849, 1598, 1573, 1494, 1469, 1448, 1355, 1075, 901, 848, 759, 738, 696. MS (EI): *m/z* (rel. intensity) 186 (50, [M^+]), 158 (66), 154 (100), 144 (24), 129 (46), 118 (68), 104 (15), 91 (20), 77 (17). Anal *calcd.* for $C_{14}H_{18}$: C 90.25, H 9.75; *found*: C 90.21, H 9.65.

1-(4-Chlorophenyl)-cyclooctene. ^{1}H-NMR (300 MHz, $CDCl_3$): δ = 7.22-7.34 (m, 4H), 5.99 (t, 1H), 2.57-2.61 (m, 2H), 2.24-2.31 (m, 2H), 1.50-1.61 (br., 8H). ^{13}C-NMR (75 MHz, $CDCl_3$): δ = 141.5, 139.1, 132.1, 128.5, 128.2, 127.0, 29.8, 29.2, 28.3, 27.4, 26.8, 26.0. IR (film): 3031, 2926, 2854, 1726, 1688, 1640, 1492, 1470, 1448, 1398, 1285, 1176, 1093, 1012, 934, 818, 744. MS (EI): *m/z* (rel. intensity) 220 (50, [M^+]), 192 (96), 185 (31), 177 (19), 165 (35), 152 (100), 143 (30), 129 (58), 115 (36), 101 (10), 91 (10), 77 (10), 41 (17). Anal *calcd.* for $C_{14}H_{17}Cl$: C 76.19, H 7.76; *found*: C 76.04, H 7.54.

6-Methoxy-4-tetradecyl-1,2-dihydronaphthalene. ^{1}H-NMR (400 MHz, $CDCl_3$): δ = 7.05 (d, J = 8.2 Hz, 1H), 6.83 (d, J = 2.6 Hz, 1H), 6.68 (dd, J = 2.6 Hz, J = 6.3 Hz, 1H), 5.86 (t, J = 4.5 Hz, 1H), 3.80 (s, 3H), 2.66 (t, J = 7.9 Hz, 2H), 2.39 (m, 2H), 2.22 (m, 2H), 1.52 (m,

2H), 1.25 (m, 22H), 0.88 (t, J = 7.0 Hz, 3H). ^{13}C-NMR (100 MHz, $CDCl_3$): δ = 136.5, 129.0, 128.0, 125.3, 110.6, 109.7, 55.3, 32.8, 31.9, 29.7, 29.7, 29.6, 29.5, 29.4, 28.5, 27.6, 23.5, 22.7, 14.1. IR (film): 3018, 2956, 2916, 2851, 2812, 1612, 1572, 1489, 1471, 1458, 1428, 1043, 868, 802, 718. MS (EI): *m/z* (rel. intensity) 356 (24 [M^+]), 174 (100), 159 (15), 128 (2), 43 (4). HR-MS *calcd.* for $C_{25}H_{40}O$: 356.307915; *found*: 356.308297. Anal *calcd.* for $C_{25}H_{40}O$: C 84.21, H 11.31; *found*: C 84.20, H 11.32.

3-Methyl-1,2-dihydronaphthalene.[21] ^{1}H-NMR (400 MHz, $CDCl_3$): δ = 7.18-7.03 (m, 3H), 6.94-6.92 (m, 1H), 6.19 (m, 1H), 2.79 (t, J = 8.2 Hz, 2H), 2.24-2.19 (m, 2H), 1.89 (m, 3H). ^{13}C-NMR (100 MHz, $CDCl_3$): δ = 138.1, 135.0, 134.0, 127.1, 126.3, 125.9, 125.1, 122.7, 28.9, 28.1, 23.4. IR (film): 3062, 3014, 2965, 2925, 2881, 2828, 1653, 1601, 1573, 1485, 1437, 1377, 753. MS (EI): *m/z* (rel. intensity) 144 (54 [M^+]), 129 (100), 115 (13).

3-Butyl-1,2-dihydronaphthalene.[22] ^{1}H-NMR (400 MHz, $CDCl_3$): δ = 7.12-7.02 (m, 3H), 6.96-6.94 (m, 1H), 6.19 (m, 1H), 2.78 (t, J = 7.8 Hz, 2H), 2.76-2.16 (m, 4H), 1.52-1.44 (m, 2H), 1.39-1.62 (m, 2H), 0.93 (t, J = 7.1 Hz, 3H). ^{13}C-NMR (100 MHz, $CDCl_3$): δ = 142.4, 135.1, 134.4, 127.1, 126.3, 125.9, 125.3, 122.1, 37.1, 29.8, 28.2, 27.3, 22.4, 14.0. IR (film): 3062, 3015, 2956, 2928, 2872, 2858, 2829, 1648, 1601, 1486, 1453, 754, 747. MS (EI): *m/z* (rel. intensity) 186 (50 [M^+]), 143 (100), 129 (55), 115 (13).

3-Phenyl-1,2-dihydronaphthalene.[23] M.p. = 56-57 °C (CH_2Cl_2). ^{1}H-NMR (400 MHz, $CDCl_3$): δ = 7.55-7.52 (m, 2H), 7.38-7.34 (m, 2H), 7.29-7.11 (m, 5H), 6.84 (m, 1H), 2.97-2.93 (m, 2H), 2.77-2.73 (m, 2H). ^{13}C-NMR (100 MHz, $CDCl_3$): δ = 141.1, 138.7, 134.8, 134.7, 128.4, 127.3, 127.2, 127.0, 126.6, 125.1, 124.4, 28.2, 26.4. IR (KBr): 3053, 3027, 2926, 2890, 2831, 1596, 1495, 1450, 751, 690. MS (EI): *m/z* (rel. intensity) 206 (100 [M^+]), 191 (14), 178 (6), 165 (5), 128 (20), 115 (9), 101 (9), 91 (54).

Ethyl 3-methyl-(2*Z*)-heptadecenoate. ^{1}H-NMR (300 MHz, $CDCl_3$): δ = 5.61 (s, 1H), 4.10 (q, 2H), 2.58 (m, 2H), 1.84 (s, 3H), 1.45-1.21 (m, 27H), 0.85 (m, 3H). ^{13}C-NMR (75 MHz, $CDCl_3$): δ = 166.3, 160.7, 115.9, 59.3, 33.3, 31.9, 29.7, 29.6, 29.59, 29.51, 29.4, 29.3, 29.1, 28.2, 27.3, 25.1, 22.6, 14.3, 14.0. IR (film): 2955, 2925, 2854, 1720, 1648, 1465, 1377, 1221, 1148, 1045, 858. MS (EI): *m/z* (rel. intensity) 311 (20), 310 (89, [M^+]), 265 (40), 222 (33), 199 (16), 141 (83), 129 (15), 128 (100), 115 (14), 113 (54), 109 (10), 100 (16), 97 (12), 96 (11), 95 (38), 88 (13), 87 (10), 83 (19), 82 (24), 81 (18), 69 (26), 68 (12), 67 (16), 55 (33), 43 (48), 29 (23). Anal *calcd.* for $C_{20}H_{38}O_2$: C 77.36, H 12.33; *found* C 77.26, H 12.35.

Ethyl 3-methyl-(2*Z*)-hepten-6-ynoate. ^{1}H-NMR (300 MHz, $CDCl_3$): δ = 5.65 (s, 1H), 4.10 (q, 2H), 2.75 (t, 2H), 2.29 (m, 2H), 1.89 (s, 3H), 1.73 (m, 3H), 1.22 (t, 3H). ^{13}C-NMR (75 MHz, $CDCl_3$): δ = 166.0, 158.5, 116.9, 78.3, 76.5, 59.4, 32.6, 25.5, 17.6, 14.2, 3.3. IR (film): 2979, 2920, 2255, 1715, 1648, 1444, 1377, 1235, 1176, 1141, 1063, 859, 604. MS (EI): *m/z* (rel. intensity) 180 (16, [M^+]), 152 (20), 151 (27), 135 (29), 107 (100), 106 (23), 105 (21), 91

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(63), 79 (31), 77 (11), 53 (21), 43 (17), 41 (11), 39 (16), 29 (21), 27 (17). Anal *calcd.* for $C_{11}H_{16}O_2$: C 73.30, H 8.95; *found* C 73.21, H 9.03.

Ethyl 3-phenyl-(2*Z*)-butenoate. ^{1}H-NMR (300 MHz, $CDCl_3$): δ = 7.47-7.44 (m, 2H), 7.37-7.33 (m, 3H), 6.11 (m, 1H), 4.20 (q, 2H), 2.57 (s, 3H), 1.30 (t, 3H). ^{13}C-NMR (75 MHz, $CDCl_3$): δ = 166.8, 155.4, 142.2, 128.9, 128.4, 126.2, 117.1, 59.7, 17.8, 14.3. IR (film): 3058, 3022, 2980, 2937, 1713, 1629, 1577, 1446, 1377, 1366, 1344, 1273, 1172, 1044, 873, 767, 695. MS (EI): *m/z* (rel. intensity) 190 (89, [M^+]), 189 (15), 161 (37), 145 (100), 144 (44), 117 (38), 115 (53), 91 (19). Anal *calcd.* for $C_{12}H_{14}O_2$: C 75.77, H 7.41; *found* C 75.92, H 7.34.

Ethyl 3-(4-methoxyphenyl)-(2*Z*)-butenoate. ^{1}H-NMR (300 MHz, $CDCl_3$): δ = 7.43 (d, J = 8.8 Hz, 2H), 6.86 (d, J = 8.8 Hz, 2H), 6.08 (s, 1H), 4.18 (q, 2H), 3.80 (s, 3H), 2.50 (s, 3H), 1.29 (t, 3H). ^{13}C-NMR (75 MHz, $CDCl_3$): δ = 167.0, 160.3, 154.8, 134.2, 127.6, 115.2, 113.7, 59.6, 55.2, 17.5, 14.3. IR (film): 2980, 2957, 2905, 2838, 1711, 1626, 1604, 1575, 1513, 1463, 1344, 1253, 1162, 1035, 873, 831, 562. MS (EI): *m/z* (rel. intensity) 220 (100, [M^+]), 175 (95), 174 (41), 148 (62), 147 (15), 146 (15), 115 (13), 108 (11), 103 (10), 91 (13). Anal *calcd.* for $C_{13}H_{16}O_3$: C 70.90, H 7.32; *found*: C 70.69, H 7.32.

(2-Methyl-but-1-enyl)-benzene.[24] ^{1}H-NMR (300 MHz, $CDCl_3$): δ = 7.32-7.14 (m, 5H), 6.25 (m, 1H), 2.24 (t, J = 7.5 Hz, 2H), 1.87 (s, J = 1.5 Hz, 3H), 1.09 (t, J = 7.5 Hz, 3H). ^{13}C-NMR (75 MHz, $CDCl_3$): δ = 141.0, 138.6, 128.5, 128.0, 125.8, 124.8, 25.5, 23.5, 12.8. IR (film): 3079, 3056, 3022, 2967, 2935, 2913, 2875, 1650, 1599, 1493, 1441, 733, 698. MS (EI): *m/z* (rel. intensity) 146 (60 [M^+]), 131 (100), 115 (22), 91 (45).

(2-Ethyl-hex-1(*E*)-enyl)-benzene.[25] ^{1}H-NMR (400 MHz, $CDCl_3$): δ = 7.30-7.13 (m, 5H), 6.24 (m, 1H), 2.28-2.22 (m, 2H), 2.19-2.14 (m, 2H), 1.51-1.45 (m, 2H), 1.43-1.34 (m, 2H), 1.06 (t, J = 7.5 Hz, 3H), 0.94 (t, J = 7.3 Hz, 3H). ^{13}C-NMR (100 MHz, $CDCl_3$): δ = 145.1, 138.7, 128.7, 128.6, 128.0, 125.8, 124.3, 36.5, 30.4, 23.6, 22.6, 14.0, 13.0. IR (film): 3080, 3056, 3023, 2961, 2930, 2873, 2859, 1647, 1599, 1493, 1466, 1377, 744, 698. MS (EI): *m/z* (rel. intensity) 188 (86 [M^+]), 159 (19), 145 (86), 131 (55), 117 (100), 105 (12), 97 (15), 91 (49), 77 (7), 65 (7), 55 (19), 41 (89), 29 (6).

1-(1-Benzylidenepropyl)-4-methoxybenzene.[26] M.p. = 56-57 °C (hexanes). ^{1}H-NMR (400 MHz, $CDCl_3$): δ = 7.43-7.21 (m, 7H), 6.94-6.90 (m, 2H), 6.64 (m, 1H), 3.84 (s, 3H), 2.71 (q, J = 7.5 Hz, 2H), 1.07 (t, J = 7.5 Hz, 3H). ^{13}C-NMR (100 MHz, $CDCl_3$): δ = 158.9, 143.8, 138.5, 135.0, 128.7, 128.2, 127.7, 126.3, 126.3, 113.7, 55.3, 23.2, 13.6. IR (film): 3078, 3054, 3021, 2998, 2962, 2933, 2873, 2834, 1606, 1511, 1465, 1442, 1249, 824, 754, 706. MS (EI): *m/z* (rel. intensity) 238 (100 [M^+]), 223 (16), 209 (17), 194 (6), 178 (8), 165 (13), 147 (16), 129 (8), 115 (20), 91 (11).

17-(1,5-Dimethylhexyl)-3,10,13-trimethyl-4,5,6,7,8,9,10,11,12,13,14,15,16,17-tetradeca-hydro-1*H*-cyclopenta[α]phenanthrene.[27] $[\alpha]_D^{20}$ = +71.2 (c = 2, $CHCl_3$). M.p. = 77-77.5°C ($CHCl_3$). ^{1}H-NMR (400 MHz, $CDCl_3$): δ = 5.27-5.26 (m, 1H), 1.99-0.63 (m, 47H). ^{13}C-NMR

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(100 MHz, $CDCl_3$): δ = 132.6, 120.0, 56.5, 56.4, 54.1, 42.5, 41.9, 40.1, 40.1, 39.6, 36.2, 35.8, 35.7, 35.3, 34.3, 31.9, 28.8, 28.2, 28.0, 24.3, 23.9, 22.2, 22.8, 22.6, 21.1, 18.7, 12.0, 11.7. IR (film): 2959, 2931, 2906, 2868, 1674, 1605, 1506, 1467, 1442, 1381, 1374, 733. MS (EI): *m/z* (rel. intensity) 384 (100 [M^+]), 369 (26), 316 (73), 301 (13), 271 (12), 229 (30), 215 (6), 203 (33), 176 (16), 161 (37), 120 (27), 81 (22), 55 (16), 43 (15).

17-(1,5-Dimethylhexyl)-10,13-dimethyl-3-tetradecyl-4,5,6,7,8,9,10,11,12,13,14,15,16,17-tetradecahydro-1*H*-cyclopenta[α]phenanthrene.[28] $[\alpha]_D^{20}$ = +24.4 (c = 1.1, CH_2Cl_2). M.p. = 28-30 °C (hexanes). ^{1}H-NMR (300 MHz, CD_2Cl_2): δ = 5.27 (m, 1H), 2.00-1.15 (m, 73H). ^{13}C-NMR (75 MHz, CD_2Cl_2): δ = 137.0, 119.8, 56.9, 56.7, 54.5, 42.9, 42.2, 40.5, 40.5, 39.9, 37.9, 36.6, 36.2, 36.1, 34.8, 33.6, 32.3, 32.3, 30.1, 29.9, 29.8, 29.7, 29.3, 28.6, 28.4, 28.1, 24.6, 24.2, 23.1, 22.9, 22.7, 21.4, 18.9, 14.3, 12.1, 11.8. IR (KBr): 3015, 2916, 2851, 1672, 1472, 1444, 802. MS (EI): *m/z* (rel. intensity) 566 (100 [M^+]), 551 (24), 453 (9), 411 (13), 384 (42), 316 (55), 230 (14), 203 (22), 161 (20), 81 (28), 57 (19).

17-(1,5-Dimethylhexyl)-3-(9-methoxymethoxyoctyl)-10,13-dimethyl-4,5,6,7,8,9,10,11,12,13,14,15,16,17-tetradecahydro-1*H*-cyclopenta[α]phenanthrene. $[\alpha]_D^{20}$ = +60.8 (c = 0.7, CH_2Cl_2). ^{1}H-NMR (400 MHz, CD_2Cl_2): δ = 5.27 (m, 1H), 4.57 (s, 2H), 3.48 (t, *J* = 6.7 Hz, 2H), 3.32 (s, 3H), 2.00-0.97 (m, 42H), 0.93-0.86 (m, 10H), 0.73-0.67 (m, 6H). ^{13}C-NMR (100 MHz, CD_2Cl_2): δ = 136.9, 119.9, 96.8, 68.2, 56.9, 56.8, 55.2, 54.5, 42.9, 42.3, 40.6, 40.5, 39.9, 37.9, 36.6, 36.2, 36.1, 34.9, 33.7, 32.3, 30.2, 29.9, 29.8, 29.7, 29.3, 28.6, 28.4, 28.2, 26.6, 24.6, 24.2, 22.9, 22.7, 21.5, 18.9, 12.2, 11.9. IR (film): 2927, 2869, 2852, 1466, 1444, 1383, 1212, 1148, 1112, 1047, 920. MS (EI): *m/z* (rel. intensity) 510 (100), 497 (89), 382 (8), 301 (10), 248 (17), 209 (7), 161 (14), 119 (16), 95 (26), 81 (25), 45 (20). HR-MS *calcd.* for $C_{37}H_{66}O_2$: 543.514105 [$(M+H)^+$]; *found*: 543.513581 [$(M+H)^+$]. Anal *calcd.* for $C_{37}H_{66}O_2$: C 81.85, H 12.25; *found*: C 81.92, H 12.29.

17-(1,5-Dimethylhexyl)-10,13-dimethyl-3-phenyl-4,5,6,7,8,9,10,11,12,13,14,15,16,17-tetradecahydro-1*H*-cyclopenta[α]phenanthrene.[29] $[\alpha]_D^{20}$ = +74.5 (c = 1.1, CH_2Cl_2). M.p. = 150.5-152.8°C (pentane). ^{1}H-NMR (300 MHz, CD_2Cl_2): δ = 7.4-7.16 (m, 5H), 6.07 (m, 1H), 2.30-1.15 (m, 44H). ^{13}C-NMR (75 MHz, CD_2Cl_2): δ = 142.4, 135.3, 128.5, 126.8, 125.1, 123.8, 56.9, 56.7, 54.3, 42.9, 42.3, 41.0, 40.5, 39.9, 36.6, 36.2, 36.1, 34.7, 32.7, 32.6, 32.2, 29.3, 28.6, 28.4, 24.6, 24.2, 22.9, 22.7, 21.5, 18.9, 12.1. IR (KBr): 3053, 3028, 2960, 2929, 2908, 2866, 2846, 1647, 1597, 1494, 1467, 1444, 751, 693. MS (EI): *m/z* (rel. intensity) 446 (100 [M^+]), 431 (12), 333 (10), 316 (28), 301 (8), 203 (22), 161 (16), 130 (14), 95 (14), 81 (13), 43 (11).

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CROSS COUPLING PRODUCTS DERIVED FROM ACID CHLORIDES

1-(4-Bromophenyl)ethanone.[30] White solid. mp = 46-47°C. ^{1}H-NMR (400 MHz, $CDCl_3$): δ = 7.81 (m, 2H), 7.60 (m, 2H), 2.58 (s, 3H). ^{13}C-NMR (100 MHz, $CDCl_3$): δ = 197.1, 136.0, 132.5, 132.0, 130.9, 130.0, 128.4, 26.7. IR (film): 3336, 3087, 3060, 2962, 2920, 1677, 1639, 1614, 1588, 1482, 1418, 1396, 1363, 824. MS (EI): *m/z* (rel. intensity) 200 (35), 198 ([M^+], 36), 185 (98), 183 (100), 157 (38), 155 (39), 76 (24), 75 (25), 74 (13), 50 (24), 43 (25). HR-MS *calcd.* for C_8H_7BrO: 197.968040; *found*: 197.968223. Anal. *calcd.* for C_8H_7BrO: C 48.27, H 3.54; *found*: C 48.45, H 3.66.

1-(4-Bromophenyl)propan-1-one. White solid. mp = 47-48°C. ^{1}H-NMR (400 MHz, $CDCl_3$): δ = 7.82 (m, 2H), 7.59 (m, 2H), 2.97 (q, *J* = 7.2 Hz, 3H), 1.22 (t, *J* = 7.2 Hz, 2H). ^{13}C-NMR (100 MHz, $CDCl_3$): δ = 199.9, 135.8, 132.0, 129.7, 128.1, 31.9, 8.3. IR (film): 3349, 3083, 3068, 3034, 2977, 2924, 2933, 2873, 1685, 1588, 1567, 1481, 1461, 1449, 1418, 790. MS (EI): *m/z* (rel. intensity) 214 (17), 212 ([M^+], 17), 185 (98), 183 (100), 157 (27), 155 (28), 76 (18), 75 (17), 50 (12). HR-MS *calcd.* for C_9H_9BrO: 211.983690; *found*: 211.983827. Anal. *calcd.* for C_9H_9BrO: C 50.73, H 4.26; *found*: C 50.92, H 4.32.

1-(4-Bromophenyl)heptan-1-one. White solid. mp = 72-73°C. ^{1}H-NMR (400 MHz, $CDCl_3$): δ = 7.82 (m, 2H), 7.60 (m, 2H), 2.92 (t, *J* = 7.4 Hz, 2H), 1.72 (quint, *J* = 7.4 Hz, 2H), 1.35 (m, 6H), 0.89 (t, *J* = 7.0 Hz, 3H). ^{13}C-NMR (100 MHz, $CDCl_3$): δ = 199.6, 135.9, 132.0, 129.7, 128.1, 38.7, 31.8, 29.1, 24.4, 22.7, 14.2. IR (film): 3086, 3057, 2953, 2929, 2914, 2854, 1931, 1675, 1638, 1586, 1568, 1485, 1466, 1455, 1404, 833. MS (EI): *m/z* (rel. intensity) 270 (4), 268 ([M^+], 4), 200 (99), 198 (100), 185 (90), 183 (92), 157 (25), 155 (26), 132 (10), 76 (16), 75 (12). HR-MS *calcd.* for $C_{13}H_{17}BrO$: 268.046290; *found*: 268.046195. Anal. *calcd.* for $C_{13}H_{17}BrO$: C 58.01, H 6.37; *found*: C 57.99, H 6.31.

1-(4-Bromophenyl)-3-(1,3-dioxan-2-yl)propan-1-one. White solid. mp = 72-73°C. ^{1}H-NMR (400 MHz, $CDCl_3$): δ = 7.84 (m, 2H), 7.59 (m, 2H), 4.66 (t, *J* = 4.8 Hz, 2H), 4.08 (ddm, *J* = 10.6 Hz, *J* = 5.0 Hz, 2H), 3.75 (tm, *J* = 11.0 Hz, 2H), 3.07 (t, *J* = 7.3 Hz, 2H), 2.06 (m, 3H), 1.33 (dm, *J* = 13.5 Hz, 1H). ^{13}C-NMR (100 MHz, $CDCl_3$): δ = 198.8, 135.8, 132.0, 129.8, 128.2, 101.0, 67.0, 32.7, 29.4, 25.9. IR (film): 3090, 3062, 2963, 2851, 2732, 2658, 1687, 1585, 1568, 1483, 1469, 1430, 1400, 1215, 1204, 1177, 1147, 1134, 1084, 1070, 1045, 1008, 891, 826. MS (EI): *m/z* (rel. intensity) 300 (3), 299 ([M^+], 3), 185 (18), 183 (18), 100 (100), 87 (59), 59 (10). HR-MS *calcd.* for $C_{13}H_{15}BrO_3$: 321.010239 (M+Na); *found*: 321.010370 (M+Na). Anal. *calcd.* for $C_{13}H_{15}BrO_3$: C 52.19, H 5.05; *found*: C 52.10, H 4.97.

1-(4-Bromophenyl)-3-(4-methoxyphenyl)propan-1-one. White solid. mp = 80-81°C. ^{1}H-NMR (400 MHz, $CDCl_3$): δ = 7.81 (m, 2H), 7.59 (m, 2H), 7.16 (m, 2H), 6.84 (m, 2H), 3.79 (s, 3H), 3.23 (t, *J* = 7.6 Hz, 2H), 3.00 (t, *J* = 7.6 Hz, 2H). ^{13}C-NMR (100 MHz, $CDCl_3$): δ = 198.5, 158.2, 135.8, 133.2, 132.0, 129.7, 129.5, 128.3, 114.1, 55.4, 40.8, 29.3. IR (film): 3094, 3032, 3001, 2962, 2935, 2836, 1675, 1610, 1584, 1567, 1513, 1462, 1444, 1412, 1397, 1245, 1027, 818. MS (EI): *m/z* (rel. intensity) 320 (22), 318 ([M^+], 22), 185 (12), 183 (12),

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30 Suzuki, Y., Takemura; Y.; Iwamoto, K.; Higashino, T.; Miyashita, A. *Chem. Pharm. Bull.* **1998**, *46*, 199.

121 (100), 108 (16). HR-MS *calcd.* for $C_{16}H_{15}BrO_2$: 318.025555; *found*: 318.025014. Anal. *calcd*. for $C_{16}H_{15}BrO_2$: C 60.21, H 4.74; *found*: C 60.08, H 4.68.

1-(2-Bromophenyl)ethanone.[31] Yellow oil. ^{1}H-NMR (400 MHz, $CDCl_3$): δ = 7.60 (m, 1H), 7.45 (m, 1H), 7.35 (m, 1H), 7.28 (m, 1H), 2.62 (s, 3H). ^{13}C-NMR (100 MHz, $CDCl_3$): δ = 201.5, 141.6, 133.9, 132.1, 131.9, 131.6, 129.4, 129.0, 127.6, 125.8, 119.0, 30.4. IR (film): 3064, 3003, 2923, 1701, 1587, 1564, 1465, 1427, 1356, 758. MS (EI): *m/z* (rel. intensity) 200 (30), 198 ([M^+], 30), 185 (98), 183 (100), 157 (29), 155 (30), 76 (16), 75 (15), 50 (14), 43 (22). HR-MS *calcd.* for C_8H_7BrO: 197.968040; *found*: 197.968141.

1-(4-Chlorophenyl)ethanone.[32] Yellow oil. ^{1}H-NMR (400 MHz, $CDCl_3$): δ = 7.89 (m, 2H), 7.43 (m, 2H), 2.58 (s, 3H). ^{13}C-NMR (100 MHz, $CDCl_3$): δ = 197.0, 139.7, 135.6, 129.9, 129.0, 128.8, 26.7. IR (film): 3352, 3091, 3062, 3004, 2965, 2923, 1686, 1589, 1572, 1487, 1428, 1396, 829. MS (EI): *m/z* (rel. intensity) 154 (12), 154 ([M^+], 37), 141 (33), 139 (100), 113 (15), 111 (46), 75 (22), 50 (12), 43 (16). HR-MS *calcd.* for C_8H_7ClO: 154.018543; *found*: 154.018428. Anal. *calcd.* for C_8H_7ClO: C 62.15, H 4.56; *found*: C 61.97, H 4.47.

1-(4-Chlorophenyl)propan-1-one.[33] White solid. mp = 36-37°C. ^{1}H-NMR (400 MHz, $CDCl_3$): δ = 7.90 (m, 2H), 7.43 (m, 2H), 2.97 (q, *J* = 7.2 Hz, 2H), 1.22 (t, *J* = 7.2 Hz, 3H). ^{13}C-NMR (100 MHz, $CDCl_3$): δ = 199.7, 139.4, 135.4, 129.5, 129.0, 31.9, 8.3. IR (film): 3069, 3038, 2976, 2938, 2876, 1672, 1591, 1570, 1487, 1458, 1446, 1402, 790. MS (EI): *m/z* (rel. intensity) 170 (5), 168 ([M^+], 16), 141 (32), 139 (100), 111 (29), 75 (14). HR-MS *calcd.* for C_9H_9ClO: 168.034193; *found*: 168.034357. Anal. *calcd.* for C_9H_9ClO: C 64.11, H 5.38; *found*: C 64.03, H 5.28.

1-(4-Chlorophenyl)heptan-1-one. White solid. mp = 64-65°C. ^{1}H-NMR (400 MHz, $CDCl_3$): δ = 7.89 (m, 2H), 7.43 (m, 2H), 2.93 (t, *J* = 7.4 Hz, 2H), 1.73 (quint, *J* = 7.4 Hz, 2H), 1.35 (m, 6H), 0.89 (t, *J* = 6.9 Hz, 3H). ^{13}C-NMR (100 MHz, $CDCl_3$): δ = 199.5, 139.4, 135.6, 129.6, 129.0, 38.8, 31.8, 29.1, 24.4, 22.7, 14.2. IR (film): 3091, 3059, 2955, 2931, 2914, 2854, 1931, 1673, 1639, 1589, 1571, 1489, 1467, 1456, 1404, 1373, 836. MS (EI): *m/z* (rel. intensity) 224 ([M^+], 4), 167 (10), 156 (31), 154 (96), 141 (33), 139 (100), 113 (10), 111 (30), 75 (11). HR-MS *calcd.* for $C_{13}H_{17}ClO$: 224.096793; *found*: 224.096478. Anal. *calcd.* for $C_{13}H_{17}ClO$: C 69.48, H 7.62; *found*: C 69.54, H 7.68.

1-(4-Chlorophenyl)-3-(1,3-dioxan-2-yl)propan-1-one. White solid. mp = 80-81°C. ^{1}H-NMR (400 MHz, $CDCl_3$): δ/ppm = 7.91 (m, 2H), 7.42 (m, 2H), 4.66 (t, *J* = 4.8 Hz, 2H), 4.09 (ddm, *J* = 10.6Hz, *J* = 5.0 Hz, 2H), 3.76 (tm, *J* = 11.9 Hz, 2H), 3.08 (t, *J* = 7.3 Hz, 2H), 2.05 (m, 3H), 1.33 (dm, *J* = 13.4 Hz, 1H). ^{13}C-NMR (100 MHz, $CDCl_3$): δ = 198.6, 139.5, 135.5, 129.7, 129.0, 101.0, 67.0, 32.7, 29.4, 25.9. IR (film): 3089, 3063, 2964, 2852, 2731, 2658, 1687, 1589, 1571, 1488, 1469, 1430, 1400, 1376, 1288, 1241, 1205, 1147, 1134, 1092, 1045, 1010, 891, 831. MS (EI): *m/z* (rel. intensity) 256 (2), 254 ([M^+], 6), 253 (5), 141 (13), 139 (40), 111 (20), 100 (100), 87 (67), 59 (11), 31 (11). HR-MS *calcd.* for $C_{13}H_{15}ClNaO_3$:

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[31] Nishiyama, T.; Ono, Y.; Kurokawa, S.; Kimura, S. *Chem. Pharm. Bull.* **2000**, *48*, 1999.

[32] Hong, J. E; Shin, W.-S.; Jang, W. B.; Oh, D. Y *J. Org. Chem.* **1996**, *61*, 2199.

[33] Gompper, R.; Vogt, H.-H. *Chem. Ber.* **1981**, *114*, 2866.

277.060742 (M+Na); *found*: 277.060820 (M+Na). Anal. *calcd.* for $C_{13}H_{15}ClO_3$: C 61.30, H 5.94; *found*: C 61.43, H 5.87.

1-(4-Chlorophenyl)-3-(4-methoxyphenyl)propan-1-one. White solid. mp = 64-65°C. ^{1}H-NMR (400 MHz, $CDCl_3$): δ = 7.88 (m, 2H), 7.42 (m, 2H), 7.16 (m, 2H), 6.84 (m, 2H), 3.79 (s, 3H), 3.23 (t, *J* = 7.6 Hz, 2H), 3.00 (t, *J* = 7.6 Hz, 2H). ^{13}C-NMR (100 MHz, $CDCl_3$): δ = 198.3, 158.2, 139.6, 135.4, 133.2, 129.6, 129.5, 129.0, 114.1, 55.4, 40.8, 29.3. IR (film): 3096, 3033, 3002, 2961, 2936, 2856, 2837, 1676, 1610, 1587, 1570, 1513, 1488, 1462, 1443, 1410, 1400, 1247, 1028, 819, 799. MS (EI): *m/z* (rel. intensity) 276 (10), 274 ([M^+], 30), 139 (21), 121 (100), 111 (11), 108 (15). HR-MS *calcd.* for $C_{16}H_{15}ClNaO_2$: 297.065827 (M+Na); *found*: 297.065970 (M+Na). Anal. *calcd.* for $C_{16}H_{15}ClO_2$: C 69.95, H 5.50; *found*: C 70.06, H 5.64.

1-(4-Methoxyphenyl)heptane-1-one. White solid. mp = 44-45°C. ^{1}H-NMR (400 MHz, $CDCl_3$): δ = 7.94 (m, 2H), 6.93 (m, 2H), 3.9 (s, 3H), 2.90 (t, *J* = 7.5 Hz, 2H), 1.72 (quint, *J* = 7.4 Hz, 4H), 1.36 (m, 4H), 0.89 (t, *J* = 6.9 Hz, 3H). ^{13}C-NMR (100 MHz, $CDCl_3$): δ = 199.4, 163.4, 130.5, 113.5, 55.6, 38.5, 31.9, 29.3, 24.8, 22.7, 14.2. IR (film): 3202, 3103, 3067, 3004, 2958, 2932, 2859, 2063, 1925, 1673, 1604, 1579, 1510, 1468, 1450, 1258, 838. MS (EI): *m/z* (rel. intensity) 220 ([M^+], 8), 163 (8), 150 (78), 135 (100), 77 (11). HR-MS *calcd*. for $C_{14}H_{20}O_2$: 220.146330; found: 220.146362. Anal. *calcd*. for $C_{14}H_{20}O_2$: C 76.33, H 9.15; found: C 76.22, H 9.11.

2-Methyldec-2-en-4-one.[34] Yellow oil. ^{1}H-NMR (400 MHz, $CDCl_3$): δ = 6.03 (m, 1H), 2.35 (t, *J* = 7.4 Hz, 2H), 2.10 (d, *J* = 1.0 Hz, 3H), 1.84 (d, *J* = 1.1 Hz, 3H), 1.54 (quint, J = 7.2 Hz, 2H), 1.27 (m, 6H), 0.84 (t, *J* = 6.8 Hz, 3H). ^{13}C-NMR (100 MHz, $CDCl_3$): δ = 201.4, 154.7, 123.9, 44.4, 31.8, 29.1, 27.7, 24.3, 22.6, 20.7, 14.1. IR (film): 2956, 2930, 2858, 1690, 1622, 1447, 1410, 1379, 832. MS (EI): *m/z* (rel. intensity) 168 ([M^+], 5), 98 (25), 83 (100), 55 (18). HR-MS *calcd*. for $C_{11}H_{20}O$: 168.151415; *found*: 168.151665. Anal. *calcd*. for $C_{11}H_{20}O$: C 78.51, H 11.98; *found*: C 78.36, H 11.87.

1-(1,3-Dioxan-2-yl)-5-methylhex-4-en-3-one. Yellow oil. ^{1}H-NMR (400 MHz, $CDCl_3$): δ = 6.04 (sept, *J* = 1.3 Hz, 1H), 4.56 (t, *J* = 5.1 Hz, 1H), 4.06 (ddm, *J* = 11.8 Hz, *J* = 5.0 Hz, 2H), 3.72 (tm, *J* = 10.9 Hz, 2H), 2.52 (t, *J* = 7.4 Hz, 2H), 2.11 (d, *J* = 1.2 Hz, 3H), 2.03 (m, 1H), 1.86 (m, 2H), 1.85 (d, *J* = 1.5 Hz, 3H), 1.30 (dsept, *J* = 13.4 Hz, *J* = 1.3 Hz, 1H). ^{13}C-NMR (100 MHz, $CDCl_3$): δ = 200.2, 154.9, 123.8, 101.3, 67.0, 38.2, 29.4, 27.7, 25.9, 20.8. IR (film): 2966, 2936, 2851, 2780, 2731,2658, 1689, 1621, 1241, 1146, 1110, 1082, 1025, 1004, 889. MS (EI): *m/z* (rel. intensity) 198 ([M^+], 15), 139 (10), 100 (47), 87 (34), 83 (100), 55 (29), 31 (10), 29 (17). HR-MS *calcd*. for $C_{11}H_{18}NaO_3$: 221.115364 (M+Na); *found*: 221.115400 (M+Na). Anal. *calcd.* for $C_{11}H_{18}O_3$: C 66.64, H 9.15; *found*: 66.61, H 9.22.

Methyl 5-oxoundecanoate. Yellow oil. ^{1}H-NMR (400 MHz, $CDCl_3$): δ = 3.63 (s, 3H), 2.44 (t, *J* = 7.2 Hz, 2H), 2.35 (t, *J* = 7.5 Hz, 2H), 2.30 (t, *J* = 7.2 Hz, 2H), 1.86 (quint, *J* = 7.2 Hz, 2H), 1.52 (quint, *J* = 7.3 Hz, 2H), 1.26 (m, 6H), 0.88 (t, *J* = 6.8 Hz, 3H). ^{13}C-NMR (100 MHz, $CDCl_3$): δ = 210.5, 173.7, 51.6, 43.0, 41.5, 33.2, 31.7, 29.0, 23.9, 22.6, 19.0, 14.1. IR (film): 2954, 2932, 2872, 2858, 1740, 1714, 1619, 1437, 1414, 1376, 1315, 1199, 1174. MS (EI): *m/z*

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[34] Zweifel, G.; Shoup, T. M. *Synthesis* **1988**, *2*, 130.

(rel. intensity) 214 ([M^+], 3), 183 (23), 155 (12), 144 (60), 129 (40), 113 (44), 112 (89), 101 (47), 97 (11), 85 (28), 84 (29), 59 (44), 55 (42), 43 (100), 42 (18), 41 (32). HR-MS *calcd*. for $C_{12}H_{22}O_3$: 214.156895; *found*: 214.157198. Anal. *calcd*. for $C_{12}H_{22}O_3$: C 67.26, H 10.35; found: C 67.18, H 10.28.

Methyl 11-(benzyloxy)-5-oxoundecanoate. Yellow oil. ^{1}H-NMR (400 MHz, $CDCl_3$): δ = 7.23 (m, 5H), 4.43 (s, 2H), 3.59 (s, 3H), 3.39 (t, *J* = 6.5Hz, 2H), 2.39 (t, *J* = 7.2Hz, 2H), 2.31 (t, *J* = 7.4Hz, 2H), 2.26 (t, *J* = 7.3Hz, 2H), 1.82 (quint, *J* = 7.2 Hz, 2H), 1.52 (sept., *J* = 7.5Hz, 4H), 1.27 (m, 4H). ^{13}C-NMR (100 MHz, $CDCl_3$): δ = 210.2, 173.6, 138.7, 128.3, 127.6, 127.5, 72.9, 70.3, 51.5, 42.7, 41.5, 33.1, 29.6, 29.0, 26.0, 23.7, 18.9. IR (film): 3087, 3063, 3029, 2936, 2857, 2794, 1738, 1713, 1604, 1586, 1496, 1454, 1437, 1413, 1365, 1202, 1171, 1102, 738, 699. MS (EI): *m/z* (rel. intensity) 320 ([M^+], 5), 157 (10), 144 (21), 125 (14), 112 (13), 92 (12), 91 (100). HR-MS *calcd*. for $C_{19}H_{28}NaO_4$: 343.188529 (M+Na); *found*: 343.188860 (M+Na). Anal. *calcd.* for $C_{19}H_{28}O_4$: C 71.22, H 8.81; *found*: C 71.28, H 8.73.

Methyl 7-(1,3-dioxan-2-yl)-5-oxoheptanoate.[35] Yellow oil. ^{1}H-NMR (400 MHz, $CDCl_3$): δ = 4.47 (t, *J* = 4.9 Hz, 1H), 3.97 (dd, *J* = 10.9 Hz, *J* = 5.0 Hz, 2H), 3.64 (tm, *J* = 12.3 Hz, 2H), 3.57 (s, 3H), 2.46 (t, *J* = 7.1 Hz, 2H), 2.39 (t, *J* = 6.6 Hz, 2H), 2.24 (t, *J* = 7.3 Hz, 2H), 1.94 (m, 1H), 1.79 (m, 4H), 1.24 (dm, *J* = 13.4 Hz, 1H). ^{13}C-NMR (100 MHz, $CDCl_3$): δ = 209.4, 173.6, 100.8, 66.7, 51.4, 41.44, 36.6, 33.0, 28.9, 25.7, 18.9. IR (film): 2955, 2854, 2733, 2660, 1737, 1714, 1146, 1103, 1085, 1008, 893. MS (EI): *m/z* (rel. intensity) 244 ([M^+], 5), 143 (41), 137 (23), 126 (10), 100 (100), 87 (73), 85 (42), 59 (22), 55 (15), 41 (10), 29 (11). HR-MS *calcd*. for $C_{12}H_{20}NaO_5$: 267.120844 (M+Na); found: 267.121090 (M+Na). Anal. *calcd*. for $C_{12}H_{20}O_5$: C 59.00, H 8.25; found: C 59.11, H 8.18.

Methyl 7-(4-methoxyphenyl)-5-oxoheptanoate. Yellow oil. ^{1}H-NMR (400 MHz, $CDCl_3$): δ = 7.08 (m, 2H), 6.81 (m, 2H), 3.77 (s, 3H), 3.65 (s, 3H), 2.83 (t, *J* = 7.5 Hz, 2H), 2.68 (t, *J* = 7.5 Hz, 2H), 2.44 (t, *J* = 7.2 Hz, 2H), 2.30 (t, *J* = 7.2 Hz, 2H), 1.87 (t, *J* = 7.2 Hz, 2H), 1.87 (quint, *J* = 7.2 Hz, 2H). ^{13}C-NMR (100 MHz, $CDCl_3$): δ = 209.4, 173.7, 158.1, 133.1, 129.3, 114.0, 55.3, 51.6, 44.6, 41.9, 33.1, 29.0, 18.9. IR (film): 2997, 2952, 2837, 1736, 1713, 1612, 1584, 1513, 1439, 1247, 1177, 829. MS (EI): *m/z* (rel. intensity) 264 ([M^+], 34), 163 (29), 121 (100),. HR-MS *calcd.* for $C_{15}H_{20}NaO_4$: 287.125929 (M+Na); *found*: 287.125960. Anal. *calcd.* for $C_{15}H_{20}O_4$: C 68.16, H 7.63; *found*: C 68.25, H 7.54.

Octadecane-7,12-dione. White solid. mp = 80-81°C. ^{1}H-NMR (400 MHz, $CDCl_3$): δ = 2.38 (m, 8H), 1.53 (m, 8H), 1.27 (m, 12H), 0.87 (t, *J* = 6.9 Hz, 6H). ^{13}C-NMR (100 MHz, $CDCl_3$): δ = 211.3, 43.0, 42.6, 31.7, 29.1, 24.0, 23.5, 22.6, 14.2. IR (film): 2954, 2931, 2919, 2849, 1702, 1697, 720. MS (EI): *m/z* (rel. intensity) 282 ([M^+], 7), 212 (26), 179 (11), 154 (65), 151 (16), 142 (22), 128 (23), 113 (100), 95 (26), 85 (24), 84 (70), 69 (12), 55 (15), 43 (66), 41 (13). HR-MS *calcd*. for $C_{18}H_{34}O_2$: 282.255880; found: 282.255923. Anal. *calcd*. for $C_{18}H_{34}O_2$: C 76.54, H 12.13; *found*: C 76.54, H 12.17.

1-Cyclopropylheptan-1-one. Yellow oil. ^{1}H-NMR (400 MHz, $CDCl_3$): δ = 2.5 (t, *J* = 7.4 Hz, 2H), 1.89 (m, 1H), 1.57 (quint, *J* = 7.2 Hz, 2H), 1.26 (m, 6H), 0.96 (m, 2H), 0.82 (m, 5H). ^{13}C-NMR (100 MHz, $CDCl_3$): δ = 211.3, 43.6, 31.7, 29.0, 24.1, 22.6, 20.3, 14.1, 10.6. IR

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[35] Babudri, F.; Fiandanese, V.; Marchese, G.; Punzi, A. *Tetrahedron* **1996**, *52*, 13513.

(film): 3094, 3009, 2956, 2930, 2858, 1700, 1467, 1457, 1387, 1074, 725. MS (EI): *m/z* (rel. intensity) 154 ([M^+], 9), 84 (85), 69 (100), 43 (16), 41 (40), 39 (11). HR-MS *calcd*. for $C_{10}H_{18}O$: 154.135765; *found*: 154.135996. Anal. *calcd.* for $C_{10}H_{18}O$: C 77.87, H 11.76; *found:* C 77.75, H 11.80.

1-Cyclopropyl-3-(1,3-dioxan-2-yl)propan-1-one. Yellow oil. ^{1}H-NMR (400 MHz, $CDCl_3$): δ = 4.51 (t, *J* = 5.0 Hz, 1H), 4.02 (ddm, *J* = 10.6 Hz, *J* = 5.0 Hz, 2H), 3.68 (tm, J = 11.0 Hz, 2H), 2.61 (t, *J* = 7.4 Hz, 2H), 1.99 (m, 1H), 1.84 (m, 3H), 1.27 (dm, J = 13.4 Hz, 1H), 0.95 (m, 2H), 0.79 (m, 2H). ^{13}C-NMR (100 MHz, $CDCl_3$): δ = 210.2, 101.0, 66.8, 37.2, 29.1, 25.8, 20.5, 10.5. IR (film): 3094, 3008, 2965, 2852, 1699, 1241, 1146, 1087, 1020, 896. MS (EI): *m/z* (rel. intensity) 184 ([M^+], 6), 169 (21), 127 (11), 113 (18), 100 (53), 87 (100), 85 (16), 69 (52), 59 (14), 41 (36), 39 (12), 31 (19), 29 (18). HR-MS *calcd.* for $C_{10}H_{16}O_3$: 184.109945; *found*: 184.110052. Anal. *calcd*. for $C_{10}H_{16}O_3$: C 65.19, H 8.75; *found*: C 65.26, H 8.71.

Heptadec-16-en-7-one.[36] White solid. mp = 33-34°C. ^{1}H-NMR (400 MHz, $CDCl_3$): δ = 5.80 (m, 1H), 4.98 (d, *J* = 17.1 Hz, 1H), 4.92 (d, *J* = 10.2 Hz, 1H), 2.38 (t, *J* = 7.5 Hz, 4H), 2.03 (q, *J* = 7.1 Hz, 2H), 1.56 (m, 4H), 1.35 (m, 2H), 1.27 (s, 14H), 0.87 (t, *J* = 6.8 Hz, 3H). ^{13}C-NMR (100 MHz, $CDCl_3$): δ = 211.8, 139.3, 114.3, 43.0 (*2), 33.9, 31.8, 29.5 (*2), 29.4, 29.2, 29.1, 29.0, 24.0, 22.6, 14.2. IR (film): 3393, 3079, 3000, 2979, 2954, 2918, 2848, 1699, 1643, 993, 974, 914, 720. MS (EI): *m/z* (rel. intensity) 252 ([M^+], 13), 195 (23), 167 (41), 149 (29), 141 (25), 139 (19), 129 (24), 128 (25), 124 (22), 122 (15), 113 (99), 107 (12), 98 (12), 86 (12), 85 (44), 83 (35), 82 (21), 81 (29), 71 (50), 68 (18), 67 (31), 59 (19), 58 (61), 55 (72), 43 (100), 42 (14), 41 (60), 39 (10). HR-MS *calcd*. for $C_{17}H_{32}O$: 252.245315; *found*: 252.245026. Anal. *calcd*. for $C_{17}H_{32}O$: C 80.88, H 12.78; *found*: C 80.73, H 12.70.

Heneicos-19-yn-7-one. White solid. mp = 51-52°C. ^{1}H-NMR (400 MHz, $CDCl_3$): δ = 2.38 (t, *J* = 7.5 Hz, 4H), 2.11 (m, 2H), 1.78 (t, *J* = 2.5 Hz, 3H), 1.55 (m, 4H), 1.46 (quint, *J* = 7.2 Hz, 2H), 1.31 (m, 20H), 0.88 (t, *J* = 6.8 Hz, 3H). ^{13}C-NMR (100 MHz, $CDCl_3$): δ = 211.9, 79.6, 75.4, 43.0, 31.8, 29.7 (*2), 29.6 (*2), 29.4, 29.3, 29.2, 29.1 (*2), 24.1, 24.0, 22.7, 18.8, 14.2, 3.6. IR (film): 2953, 2927, 2914, 2849, 2254, 1701, 1471, 1420, 909, 734. MS (EI): *m/z* (rel. intensity) 306 ([M^+], 18), 239 (26), 221 (24), 141 (11), 129 (12), 113 (79), 97 (13), 95 (46), 85 (28), 79 (11), 68 (57), 67 (32), 58 (31), 55 (53), 43 (100), 41 (44). HR-MS *calcd*. for $C_{21}H_{38}O$: 306.292265; *found*: 306.292584. Anal. *calcd.* for $C_{21}H_{38}O$: C 82.28, H 12.50; *found*: C 82.15, H 12.59.

(*R*)-2-Oxo-1-phenyloctylacetate.[37] Pale brown oil. $[\alpha]_D^{20} = -350.6°$ (*c* 1.75, $CHCl_3$); ee > 99% (HPLC). ^{1}H-NMR (400 MHz, $CDCl_3$): δ = 7.39 (m, 5H), 6.0 (s, 1H), 2.45 (ddd, J = 6.3 Hz, J = 8.2 Hz, J = 17.1 Hz, 1H), 2.31 (ddd, J = 6.8 Hz, J = 8.1 Hz, J = 17.1 Hz, 1H), 2.16 (s, 3H), 1.50 (m, 2H), 1.18 (m, 6H), 0.81 (t, *J* = 7.0 Hz, 3H). ^{13}C-NMR (100 MHz, $CDCl_3$): δ = 204.2, 170.4, 133.4, 129.4, 129.1, 128.8, 128.5, 128.3, 80.8, 38.7, 31.5, 28.7, 24.0, 23.3, 22.5, 20.8, 14.0. MS (EI): *m/z* (rel. intensity) 262 ([M^+], 2), 149 (70), 113 (59), 107 (100), 85 (19), 79 (10), 43 (94). HR-MS *calcd*. for $C_{16}H_{22}NaO_3$: 285.146664 (M+Na); *found*: 285.146540 (M+Na).

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(*R*)-4-(1,3-dioxan-2-yl)-2-oxo-1-phenylbutyl acetate.[38] Yellow oil. $[\alpha]_D^{20} = -346.1°$ (*c* 2.08, $CHCl_3$); ee > 99% (HPLC). ^{1}H-NMR (400 MHz, $CDCl_3$): δ = 7.39 (m, 5H), 5.98 (s, 1H), 4.43 (t, *J* = 5.0 Hz, 1H), 3.98 (m, 2H), 3.63 (m, 2H), 2.61 (dt, *J* = 16.05 Hz, *J* = 7.14 Hz, 1H), 2.44 (dt, *J* = 16.04 Hz, *J* = 7.10 Hz, 1H), 2.17 (s, 3H), 1.97 (m, 1H), 1.81 (m, 2H), 1.25 (dm, J = 13.5, 1H). ^{13}C-NMR (100 MHz, $CDCl_3$): δ = 203.7, 170.3, 133.5, 129.4, 129.1, 128.3, 100.6, 80.8, 67.0, 66.9, 66.8, 32.9, 28.6, 27.1, 25.8, 20.9. MS (EI): *m/z* (rel. intensity) 291 ([M^+ – 1], 2), 143 (100), 107 (14), 85 (58), 43 (21). HR-MS *calcd*. for $C_{16}H_{20}NaO_5$: 315.120844 (M+Na); *found*: 315.120900 (M+Na).

(*R*)-5-(3-(1,3-dioxan-2-yl)propanoyl)-dihydrofuran-2(3H)-one. White solid. mp = 62-63°C. $[\alpha]_D^{20} = +3.4°$ (*c* 1.0, $CHCl_3$); ee = 94% (GC). ^{1}H-NMR (400 MHz, $CDCl_3$): δ = 4.83 (t, *J* = 7.2 Hz, 1H), 4.56 (t, *J* = 4.7 Hz, 1H), 4.03 (dd, *J* = 11.2 Hz, *J* = 4.6 Hz, 2H), 3.71 (tm, *J* = 11.6 Hz, 2H), 2.69 (t, *J* = 7.1Hz, 2H), 2.47 (m, 3H), 2.24 (m, 1H), 1.97 (m, 3H), 1.30 (d, *J* = 13.4 Hz, 1H). ^{13}C-NMR (100 MHz, $CDCl_3$): δ = 207.0, 176.1, 100.6, 81.9, 66.9, 33.0, 28.5, 27.4, 27.1, 25.8, 24.7. MS (EI): *m/z* (rel. intensity) 227 ([M^+ + 1], 6), 143 (88), 100 (16), 87 (33), 85 (100), 57 (12), 31 (10), 29 (25). HR-MS *calcd.* for $C_{11}H_{16}NaO_5$: 251.089544 (M+Na); *found*: 251.089460 (M+Na). Anal. *calcd.* for $C_{11}H_{16}O_5$: C 57.89, H 7.07; *found* C 57.94, H 7.12.

(–)-4-Acetyl-3-(4-methoxybenzyl)-thiazolidinon-2-one.[39] White solid. $[\alpha]_D^{20} = -62.2°$ (c = 0.97, EtOH); ^{1}H-NMR (400MHz, $CDCl_3$) δ 7.08 (d, *J* = 8.6 Hz, 2H), 6.82 (d, *J* = 8.7 Hz, 2H), 4.96 (d, *J* = 14.7 Hz, 1H), 4.07 (dd, *J* = 3.9, 9.3 Hz, 1H), 3.86 (d, *J* = 14.7 Hz, 1H), 3.75 (s, 3 H), 3.47 (dd, *J* = 9.3, 11.5 Hz, 1H), 3.08 (dd, *J* = 3.9, 11.5 Hz, 1H), 2.10 (s, 3H); ^{13}C-NMR (100 MHz, $CDCl_3$) δ 204.4, 171.5, 159.4, 129.8, 127.1, 114.2, 65.4, 55.2, 47.3, 27.6, 26.1; MS *m/z* (rel. intensity) 265, 222 (8), 121 (60) (215).

SELECTIVE MONO-ALKYLATION OF DICHLOROBENZENE DERIVATIVES AND DICHLOROHETEROARENES

1-Chloro-4-octylbenzene. For the preparation, see Experimental Part. ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.21 (d, *J* = 8.5, 2 H), 7.07 (d, 2 H). 2.55 (t, *J* = 7.6, 2 H), 1.57 (m, 2 H), 1.38 – 1.20 (m, 10 H), 0.88 (t, *J* = 6.9, 3 H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 141.3, 131.2, 129.7, 128.3, 35.3, 31.9, 31.4, 29.5, 29.4, 29.3, 29.2, 14.1; MS: *m/z* (rel. intensity): 224 ([M^+], 51), 189 (3), 167 (2), 138 (5), 125 (100), 103 (6), 91 (24), 71 (5), 57 (31), 43 (16), 41 (14), 29 (8). Anal. *calcd*. for $C_{14}H_{21}Cl$: C 74.81, H 9.42; *found* C 74.75, H 9.30.

1-Chloro-3-octylbenzene. A solution of octylmagnesium bromide (0.63 M in THF, 106 mL) was added over 30 min to a solution of 1,3-dichlorobenzene (5.46 g, 37.1 mmol) and $Fe(acac)_3$ (1.35 g, 3.82 mmol) in THF (150 mL) and NMP (20 mL), causing an immediate color change from red to dark brown/black and a slight increase in temperature (ca. 40°C). After stirring for 30 min, the reaction was quenched with dilute HCl, the aqueous phase was repeatedly extracted with *tert*-butyl methyl ether, the combined organic layers were dried

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(Na_2SO_4) and evaporated, and the residue was purified by distillation (b.p. 68°C, 10^{-4} torr) to give 1-chloro-3-octyl-benzene as a colorless oil (6.79 g, 77%, GC purity ≈ 95%, remainder is hexadecane). ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.21 – 7.13 (m, 3 H), 7.04 (m, 1 H), 2.57 (t, *J* = 7.7, 2 H), 1.59 (m, 2 H), 1.37 – 1.20 (m, 10 H), 0.88 (t, *J* = 6.8, 3 H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 145.0, 133.9, 129.4, 128.5, 126.6, 125.7, 35.6, 31.9, 31.2, 29.4, 29.2 (2C), 22.7, 14.1. MS: *m/z* (rel. intensity): 224 ([M^+], 38), 189 (5), 167 (8), 139 (7), 126 (100), 103 (7), 91 (49), 71 (9), 57 (28), 43 (20), 41 (16), 29 (9). Anal. *calcd*. for $C_{14}H_{21}Cl$: C 74.81, H 9.42; *found* C 74.71, H 9.35.

2-Chloro-4-(1,3-dioxane-2-yl-ethyl)-pyrimidine. A solution of (1,3-dioxane-2-ylethyl)-magnesium bromide (0.5 M in THF, 7.3 mL, 3.64 mmol) was added at –78°C to a solution of 2,4-dichloropyrimidine (258 mg, 1.73 mmol) and $Fe(acac)_3$ (31 mg, 0.086 mmol) in THF (10 mL), causing an immediate color change from orange-red to brown/black. After stirring for 3 h at that temperature, a standard extractive work up followed by flash chromatography (hexanes/ethyl acetate, 4:1) of the crude product provided the title compound as a colorless solid (278 mg, 70%). ^{1}H NMR (300 MHz, $CDCl_3$): δ 8.43 (d, *J* = 5.2 Hz, 1H), 7.09 (d, *J* = 5.32 Hz, 1H), 4.53 (t, 1H), 4.04 (m, 2H), 3.70 (m, 2H), 2.84 (m, 2H), 1.99 (m, 3H), 1.30 (m, 1H). ^{13}C NMR (75 MHz, $CDCl_3$): δ 174.5, 161.2, 158.9, 118.8, 100.7, 66.7, 33.2, 31.7, 25.6. IR: 2968, 2858, 1577, 1540, 1437, 1385, 1347, 1210, 1187, 1155, 1132, 1074, 968, 887, 733 cm^{-1}. MS *m/z* (rel. intensity): 229 ([M^+], 2), 169 (9), 142 (14), 141 (24), 128 (13), 101 (45), 87 (100), 78 (7), 59 (14), 31 (17). Anal. *calcd*. for $C_{10}H_{13}ClN_2O_2$: C 52.52, H 5.73, N 12.25; *found* C 52.34, H 5.66, N 12.11.

2-Chloro-4-methyl-pyrimidine.[40] ^{1}H NMR (300 MHz, $CDCl_3$): δ 8.43 (d, *J* = 5.0 Hz, 1H), 7.09 (d, *J* = 5.3 Hz, 1H), 2.51 (s, 3H). ^{13}C NMR (75 MHz, $CDCl_3$): δ 170.7, 161.1, 158.9, 119.3, 23.9. MS *m/z* (rel. intensity): 128 ([M^+], 100), 92 (64), 87 (16), 66 (37), 52 (17).

2-Chloro-4-hexyl-pyrimidine.[41] ^{1}H NMR (300 MHz, $CDCl_3$): δ 8.43 (d, *J* = 5.0 Hz, 1H), 7.06 (d, *J* = 5.1 Hz, 1H), 2.70 (m, 2H), 1.68 (m, 2H), 1.31 (m, 2H), 1.26 (m, 4H), 0.90 (t, 3H). ^{13}C NMR (75 MHz, $CDCl_3$): δ 174.8, 161.2, 158.9, 118.6, 40.9, 31.4, 28.8, 28.6, 22.4, 13.9. MS *m/z* (rel. intensity): 199 (0.1), 155 (17), 141 (29), 130 (32), 128 (100), 41 (15), 39 (12).

2-Chloro-4-(2-(4-methoxyphenyl)-ethyl)-pyrimidine. ^{1}H NMR (300 MHz, $CDCl_3$): δ 8.40 (d, *J* = 5.0 Hz, 1H), 7.04 (d, *J* = 8.6 Hz, 2H), 6.95 (d, *J* = 5.0 Hz, 1H), 6.78 (d, *J* = 8.7 Hz, 2H), 3.75 (s, 3H), 2.99 (m, 4H). ^{13}C NMR (75 MHz, $CDCl_3$): δ 173.4, 161.2, 158.9, 158.0, 132.0, 129.2, 119.0, 113.8, 55.1, 39.4, 33.6. MS *m/z* (rel. intensity): 248 ([M^+], 17), 121 (100). Anal. *calcd*. for $C_{13}H_{13}ClN_2O$: C 62.78, H 5.27, N 11.26; *found* C 62.82, H 5.09, N 11.12.

2-Chloro-6-hexyl-pyrazine. ^{1}H NMR (300 MHz, $CDCl_3$): δ 8.36 (s, 1H), 8.30 (s, 1H), 2.74 (m, 2H), 1.68 (m, 2H), 1.27 (m, 6H), 0.85 (m, 3H). ^{13}C NMR (75 MHz, $CDCl_3$): 158.1, 148.6, 141.8, 141.6, 35.0, 31.4, 29.1, 28.8, 22.4, 13.9. MS *m/z* (rel. intensity): 198 ([M^+], 5), 141 (13), 130 (31), 128 (100). Anal. *calcd*. for $C_{10}H_{15}ClN_2$: C 60.45, H 7.61, N 14.10; *found* C 60.37, H 7.53, N 14.06.

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