Supporting Information

A One-Pot Reformatsky/Cyclopropanation Sequence Induced by Diethylzinc

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General Experimental Methods:

Infrared (IR) spectra were recorded on a Perkin-Elmer 298, wavenumbers are indicated in cm^{-1}. ^{1}H NMR spectra were recorded on a Bruker AC 300 at 300 MHz in $CDCl_3$ 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 massif), integration. ^{13}C NMR spectra were recorded on a Bruker AC 300 at 75 MHz in $CDCl_3$ 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 (EI-MS) were recorded using 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). 1,2-Dichloroethane was distilled from CaH_2. Other reagents were obtained from commercial suppliers and used as received. TLC was performed on Merck $60F_{254}$ silica gel plates and flash chromatography was performed with SDS 60 silica gel (230-400 mesh).

General Procedure:

To a stirred solution of Wilkinson's catalyst (92.5 mg, 0.1 mmol, 0.05 equiv) in dry dichloroethane (14 mL) at 0 °C were successively added the ω-unsaturated carbonyl compound (2 mmol), methyl bromoacetate (190 μL, 2 mmol, 1 equiv) and slowly, a 1 M solution of diethylzinc in hexane (10 mL, 10 mmol, 5 equiv). After 30 min at 0 °C, the reaction mixture was cooled to – 30 °C and chloroiodomethane (874 μL, 12 mmol, 6 equiv) was then added dropwise. After 9 h at –15 °C, the temperature was raised to 0 °C and after 3 h, the temperature was raised up to rt. After 16 h, the mixture was carefully diluted with saturated aqueous NH_4Cl (25 mL) and vigorously stirred. After extraction with EtOAc (3 x 50 mL), the combined organic extracts were dried over $MgSO_4$, filtered and concentrated under reduced pressure. The crude material was purified by flash chromatography on silica gel to give the desired ω-cyclopropyl alcohol (**3**, **9-13**, **19-23**), sometimes accompanied by the intermediate Reformatsky compound (**2**, **11'**, **12'**, **20'**, **21'**, **23'**).

Product 2. Yield = 10%; R_f = 0.58 (Pet ether/EtOAc: 8/2); IR (film) 3490 (broad), 1725, 1640, 1440, 1200, 1010, 915, 740 cm^{-1}; ^1H NMR δ 5.82 (ddt, J = 17.4, J = 10.3 and J = 6.3 Hz, 1H), 5.08-4.92 (m, 2H), 3.72 (s, 3H), 3.48 (broad s, 1H, OH), 2.54 (d syst. AB, J = 15.8 Hz, 1H), 2.46 (d syst. AB, J = 15.8 Hz, 1H), 2.14 (m, 2H), 1.61 (m, 2H), 1.25 (s, 3H); ^{13}C NMR δ 173.2 (s), 138.4 (d), 114.4 (t), 70.6 (s), 51.5 (q), 44.6 (t), 40.8 (t), 28.1 (t), 26.5 (q); EI-MS (relative intensity) *m/z* 157 (M-15, 10), 117 (100), 99 (15), 95 (14), 94 (8), 85 (60), 83 (19), 81 (10), 79 (9), 75 (10), 55 (15); Anal Calcd for $C_9H_{16}O_3$: C, 62.77; H, 9.36. Found: C, 62.55; H, 9.40.

Product 3. Yield = 79%; R_f = 0.54 (Pet ether/EtOAc: 8/2); IR (film) 3480 (broad), 1725, 1440, 1205, 1015 cm^{-1}; ^1H NMR δ 3.71 (s, 3H), 3.42 (s, 1H, OH), 2.50 (d syst. AB, J = 15.5 Hz, 1H), 2.42 (d syst. AB, J = 15.5 Hz, 1H), 1.63 (m, 2H), 1.25 (m, 2H), 1.21 (s, 3H), 0.64 (m, 1H), 0.40 (m, 2H), 0.01 (m, 2H); ^{13}C NMR δ 173.4 (s), 70.7 (s), 51.6 (q), 44.8 (t), 41.8 (t), 29.1 (t), 26.6 (q), 11.1 (d), 4.5 (t, 2C); EI-MS (relative intensity) *m/z* 171 (M-15, 11), 125 (14), 117 (100), 113 (22), 112 (31), 108 (21), 97 (26), 95 (40), 94 (31), 93 (14), 85 (79), 79 (13), 69 (17), 55 (31); Anal Calcd for $C_{10}H_{18}O_3$: C, 64.49; H, 9.74. Found: C, 64.15; H, 9.79.

Product 9. Yield = 71%; R_f = 0.31 (Pet ether/EtOAc: 9/1); mp = 34 °C; IR (film) 3500 (broad), 1715, 1440, 1345, 1210, 1175, 775, 760, 705 cm^{-1}; ^1H NMR δ 7.47-7.20 (m, 5H), 4.34 (s, 1H, OH), 3.58 (s, 3H), 3.11 (d syst AB, J = 16.0 Hz, 1H), 2.98 (d syst AB, J = 16.0 Hz, 1H), 1.80 (dd syst. ABX, J = 14.2 and J = 6.4 Hz, 1H), 1.61 (dd syst ABX, J = 14.2 and J = 7.2 Hz, 1H), 0.66 (m, 1H), 0.47-0.28 (m, 2H), 0.01 (m, 1H), -0.10 (m, 1H); ^{13}C NMR δ 173.3 (s), 145.9 (s), 127.9 (d, 2C), 126.7 (d), 124.9 (d, 2C), 75.5 (s), 51.6 (q), 48.2 (t), 43.8 (t), 5.8 (d), 4.6 (t), 3.9 (t); EI-MS (relative intensity) *m/z* 217 (M-17, 1), 180 (10), 179 (84), 161 (3), 147 (18), 143 (3), 106 (9), 105 (100), 91 (4), 78 (4), 77 (20); Anal Calcd for $C_{14}H_{18}O_3$: C, 71.77; H, 7.74. Found: C, 71.50; H, 7.74.

Product 10. Yield = 43%; R_f = 0.56 (Pet ether/EtOAc: 8/2); IR (film) 3500 (broad), 1725, 1455, 1440, 1365, 1345, 1205, 1100, 740, 705 cm^{-1}; ^1H NMR δ 7.38-7.25 (m, 5H), 4.51 (s, 2H), 3.70 (s, 3H), 3.52 (t, J = 6.8 Hz, 2H), 3.27 (broad s, 1H, OH), 2.55 (d syst. AB, J = 15.0 Hz, 1H), 2.49 (d syst. AB, J = 15.0 Hz, 1H), 1.64 (m, 1H), 1.43 (m, 1H), 1.21 (s, 3H), 0.87 (m, 1H), 0.70-0.58 (m, 2H), 0.21 (m, 1H); ^{13}C NMR δ 173.3 (s), 138.6 (s), 128.4 (d, 2C), 127.7 (d, 2C), 127.6 (d), 73.0 (t), 70.4 (t), 69.1 (s), 51.7 (q), 45.9 (t), 33.8 (t), 28.4 (d), 27.1 (q), 11.1 (d), 7.8 (t); EI-MS (relative intensity) *m/z* 277 (M-15, 1), 160 (5), 159 (16), 117 (7), 109 (4), 98 (4), 93 (5), 92 (10), 91 (100), 85 (6), 79 (4), 69 (4), 65 (9); Anal Calcd for $C_{17}H_{24}O_4$: C, 69.84; H, 8.27. Found: C, 69.91; H, 8.30.

Product 11. Yield = 52%; R_f = 0.23 (Pet ether/EtOAc : 9/1); mp = 68-69 °C; IR (film) 3480 (broad), 1715, 1450, 1440, 1345, 1210, 760, 700 cm^{-1}; ^1H NMR δ 7.52-6.90 (m, 10H), 4.35 (broad s, 1H, OH), 3.66 (s, 3H), 3.13 (d syst AB, J = 15.6 Hz, 1H), 2.94 (d syst AB, J = 15.6 Hz, 1H), 2.03 (dt, J = 8.5 and J = 5.1 Hz, 1H), 1.50 (dt, J = 8.5 and J = 5.1 Hz, 1H), 1.22 (m, 1H), 0.95 (m, 1H); ^{13}C NMR δ 173.1 (s), 145.3 (s), 142.4 (s), 128.1 (d, 2C), 128.0 (d, 2C), 126.2 (d, 2C), 125.0 (d, 2C), 127.0 (d), 125.3 (d), 72.8 (s), 51.8 (q), 45.4 (t), 32.8 (d), 18.4 (d), 11.4 (t); EI-MS (relative intensity) *m/z* 278 (M-18, 1), 222 (22), 221 (18), 192 (45), 118 (42), 117 (17), 116 (12), 115 (26), 105 (100), 91 (16), 77 (45), 51 (10); Anal Calcd for $C_{19}H_{20}O_3$: C, 77.00; H, 6.80. Found: C, 76.67; H, 6.70.

Product 11'. Yield = 10%; Previously described: Kohler, E. P.; Butler, F. R. *J. Am. Chem. Soc.* **1926**, *48*, 1036.

Product 12. Yield = 68%; R_f = 0.35 (Pet ether/EtOAc: 8/2); IR (film) 3470 (broad), 1725, 1435, 1200, 1170, 1065, 1015 cm^{-1}; ^{1}H NMR δ 3.74 (s, 3H), 3.33 (broad s, 1H, OH), 2.74 (d syst AB, J = 15.3 Hz, 1H), 2.67 (d syst AB, J = 15.3 Hz, 1H), 1.82-1.59 (m, 2H), 1.47-1.18 (m, 4H), 1.18-0.98 (m, 2H), 0.58 (m, 1H), 0.48 (m, 1H); ^{13}C NMR δ 173.1 (s), 68.6 (s), 51.5 (q), 46.7 (t), 35.0 (t), 22.5 (t), 20.9 (d), 17.2 (t), 12.0 (d), 7.0 (t, C_9); EI-MS (relative intensity) *m/z* 184 (M, 9), 129 (59), 116 (74), 111 (74), 110 (72), 106 (31), 101 (36), 97 (46), 93 (71), 91 (44), 82 (100), 81 (39), 79 (31), 74 (50), 68 (38), 67 (47), 55 (96), 54 (37); Anal Calcd for $C_{10}H_{16}O_3$: C, 65.19; H, 8.75. Found: C, 65.45; H, 8.79.

Product 12'. Yield = 5%; Previously described: Denmark, S. E.; Fan, Y. *J. Am. Chem. Soc.* **2002**, *124*, 4233.

Product 13. Yield = 31%; R_f = 0.25 (8/2 Pet ether/EtOAc); IR (film) 3450 (broad), 1725, 1440, 1340, 1200 cm^{-1}; ^{1}H NMR δ 3.74 (s, 3H), 3.59 (broad s, 1H, OH), 2.67 (d syst AB, J = 15.8 Hz, 1H), 2.61 (d syst AB, J = 15.8 Hz, 1H), 1.90-1.15 (m, 5H), 0.91 (m, 1H), 0.63 (m, 1H), 0.46 (m, 1H); ^{13}C NMR δ 173.3 (s), 79.2 (s), 51.7 (q), 44.2 (t), 32.9 (t), 25.5 (d), 25.3 (t), 16.2 (d), 5.3 (t); EI-MS (relative intensity) *m/z* 170 (M, 9), 138 (13), 129 (27), 116 (15), 97 (100), 96 (65), 93 (17), 92 (16), 91 (17), 79 (27), 77 (17), 74 (29), 69 (16), 68 (50), 67 (23), 55 (71), 53 (13); Anal Calcd for $C_9H_{14}O_3$: C, 63.51; H, 8.29. Found: C, 63.66; H, 8.57.

Product 19. Yield = 21%; R_f = 0.18 (Pet ether/EtOAc: 8/2); IR (film) 3420 (broad), 1730, 1440, 1175, 1040, 760, 705 cm^{-1}; ^{1}H NMR δ 7.31-7.04 (m, 5H), 3.71 (s, 3H), 3.65 (m, 1H), 2.91 (broad d, J = 2.9 Hz, 1H, OH), 2.72 (dd syst ABX, J = 16.2 and J = 4.2 Hz, 1H), 2.65 (dd syst ABX, J = 16.2 and J = 8.5 Hz, 1H), 1.88 (m, 1H), 1.30 (m, 1H), 1.12 (dt, J = 8.8 and J = 5.2 Hz, 1H), 1.01 (dt, J = 8.5 and J = 5.2 Hz, 1H); ^{13}C NMR δ 172.9 (s), 141.9 (s), 128.2 (d, 2C), 125.7 (d, 2C), 125.6 (d), 71.2 (d), 51.7 (q), 41.1 (t), 28.1 (d), 20.5 (d), 13.6 (t); EI-MS (relative intensity) *m/z* 220 (M, 9), 145 (17), 143 (20), 129 (73), 128 (100), 118 (35), 117 (91), 116 (32), 115 (68), 114 (42), 107 (43), 104 (69), 103 (41), 91 (58), 77 (17), 71 (33); Previously described: Sugimura, T.; Nagakawa, S.; Tai, A. *Bull. Chem. Soc. Jpn.* **2002**, *75*, 355.

Product 20. Yield = 48%; R_f = 0.48 (Pet ether/EtOAc: 6/4); IR (film) 3420 (broad), 1725, 1445, 895 cm^{-1}; ^1H NMR δ 3.71 (s, 3H), 3.37 (m, 1H), 2.65 (m,1H, OH), 2.66-2.59 (m, 2H), 1.03 (d, J = 5.3 Hz, 3H), 0.70-0.60 (m, 2H), 0.56 (m, 1H), 0.32 (m, 1H); ^{13}C NMR δ 172.9 (s), 72.1 (d), 51.6 (q), 41.4 (t), 25.4 (d), 18.1 (q), 11.4 (t), 10.4 (d); EI-MS (relative intensity) *m/z* 157 (M-1, 1), 129 (53), 116 (57), 103 (100), 98 (40), 85 (98), 84 (89), 83 (43), 81 (65), 74 (80), 71 (100), 67 (43), 59 (45), 57 (69), 56 (75), 55 (95); Previously described: Sugimura, T.; Nagakawa, S.; Tai, A. *Bull. Chem. Soc. Jpn.* **2002**, *75*, 355.

Product 20'. Yield = 3%; Previously described: Chamberlin, A. R.; Dezube, M.; Dussault, P.; McMills, M. C. *J. Am. Chem. Soc.* **1983**, *105*, 5819.

Product 21. Yield = 74%; R_f = 0.45 (Pet ether/EtOAc: 8/2); IR (film) 3420 (broad), 1730, 1440, 1170, 1015 cm^{-1}; ^1H NMR δ 4.01 (m, 1H), 3.72 (s, 3H), 2.90 (broad d, J = 3.8 Hz, 1H, OH), 2.53 (dd syst. ABX, J = 16.4 and J = 3.2 Hz, 1H), 2.41 (dd syst. ABX, J = 16.4 and J = 8.8 Hz, 1H), 1.65-1.37 (m, 4H), 1.22 (m, 2H), 0.65 (m, 1H), 0.43-0.37 (m, 2H), 0.03--0.03 (m, 2H); ^{13}C NMR δ 173.5 (s), 68.1 (d), 51.7 (q), 41.1 (t), 36.3 (t), 34.6 (t), 25.5 (t), 10.7 (d), 4.4 (t, 2C); EI-MS (relative intensity) *m/z* 185 (M-1, 1), 116 (40), 103 (74), 95 (66), 94 (92), 80 (45), 79 (55), 74 (52), 71 (100), 68 (69), 67 (74), 55 (73); Anal Calcd for $C_{10}H_{18}O_3$: C, 64.49; H, 9.74. Found: C, 64.23; H, 9.78.

Product 21'. Yield = 7%; Previously described: Beuerle, T.; Engelhard, S.; Bicchi, C.; Schwab, W. *J. Nat. Prod.* **1999**, *62*, 35.

Product 22. Yield = 88%; R_f = 0.11 (Pet ether/EtOAc: 9/1); IR (film) 3430 (broad), 1735, 1440, 1170, 1015 cm^{-1}; ^1H NMR δ 4.01 (m, 1H), 3.73 (s, 3H), 2.95 (broad s, 1H, OH), 2.53 (dd syst. ABX, J = 16.2 and J = 3.4 Hz, 1H), 2.42 (dd syst. ABX, J = 16.4 and J = 9.1 Hz, 1H), 1.60-1.24 (m, 12H), 1.18 (q, J = 6.9 Hz, 2H), 0.65 (m, 1H), 0.43-0.35 (m, 2H), 0.03--0.04 (m, 2H); ^{13}C NMR δ 173.5 (s), 68.0 (d), 51.7 (q), 41.1 (t), 36.5, 34.2, 29.6, 29.5, 29.4 and 25.5 (7 t, 7C), 10.9 (d), 4.3 (t, 2C); EI-MS (relative intensity) *m/z* 224 (M-18, 1), 103 (100), 95 (34), 81 (44), 74 (35), 71 (53), 67 (41), 55 (64); Anal Calcd for $C_{14}H_{26}O_3$: C, 69.38; H, 10.81. Found: C, 69.27; H, 11.14.

Product 23. Yield = 71%; R_f = 0.34 (Pet ether/EtOAc: 8/2); IR (film) 3520 (broad), 1730, 1500, 1440, 1170, 760, 750, 705 cm^{-1}; ^1H NMR δ 7.38-7.00 (m, 5H), 3.87 (m, 1H), 3.71 (s, 3H), 2.90 (m,1H, OH), 2.53 (m, 1H), 2.38 (dd syst. ABX, J = 16.4 and J = 10.5 Hz, 1H), 1.70-1.17 (m, 4H), 0.95 (s, 6H), 0.95 (m, 1H), 0.78 (m, 1H); ^{13}C NMR δ 174.3 (s), 143.2 (s), 128.3 (d, 2C), 125.5 (d, 2C), 125.3 (d), 74.1 (d), 51.8 (q), 43.3 (t), 38.0 (s), 36.2 (t), 23.7 (d), 22.7 (q, 2C), 19.5 (d), 16.2 (t); EI-MS (relative intensity) *m/z* 276 (M, 1), 202 (31), 144 (95), 131 (46), 130 (100), 129 (65), 117 (71), 115 (56), 104 (100), 103 (31), 91 (100), 71 (35); Anal Calcd for $C_{17}H_{24}O_3$: C, 73.88; H, 8.75. Found: C, 73.51; H, 8.66.

Product 23'. Yield = 13%; R_f = 0.40 (Pet ether/EtOAc: 8/2); IR (film) 3520 (broad), 1730, 1600, 1580, 1500, 1440, 1370, 970, 750, 700 cm^{-1}; ^{1}H NMR δ 7.40-7.15 (m, 5H), 6.42 (d, J = 15 Hz, 1H), 6.26 (m, 1H), 3.82 (m, 1H), 3.71 (s, 3H), 2.94 (d, J = 6 Hz,1H, OH), 2.60-2.07 (m, 4H), 0.95 (s, 3H), 0.92 (s, 3H); ^{13}C NMR δ 174.2 (s), 137.7 (s), 132.7 (d), 128.5 (d, 2C), 127.0 (d), 126.8 (d), 126.1 (d, 2C), 74.0 (d), 51.8 (q), 42.5 (t), 37.9 (s), 36.2 (t), 23.3 (q), 22.4 (q); EI-MS (relative intensity) *m/z* 262 (M, 8), 244 (34), 229 (10), 171 (30), 153 (16), 143 (14), 129 (15), 117 (100), 104 (29), 91 (40), 71 (58); Anal Calcd for $C_{16}H_{22}O_3$: C, 73.25; H, 8.45. Found: C, 73.04; H, 8.47.