Supporting information for

Construction of cis-fused hydrindane skeleton with a lactone tether utilizing intramolecular Diels-Alder reaction

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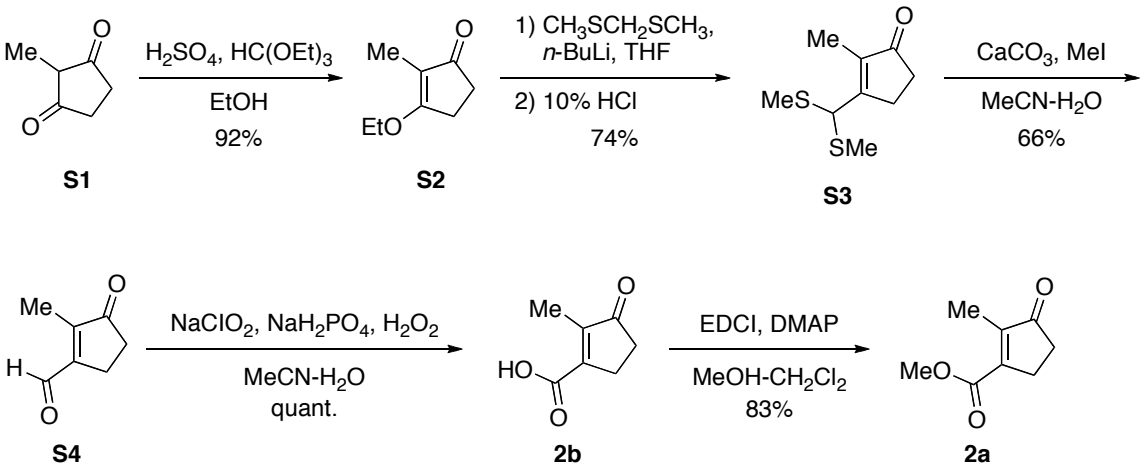

3-Ethoxy-2-methyl-2-cyclopenten-1-one (S2).[1] To a stirred solution of 2-methylcyclopentane-1,3-dione **S1**[2] (4.93 g, 44 mmol) in ethanol (88 mL) were added ethyl orthoformate (32.1 mL, 176.2 mmol) and concentrated H_2SO_4 (2.45 mL, 44 mmol) at room temperature. The reaction mixture was allowed to stir overnight, which was neutralized with saturated aqueous Na_2CO_3. Then the aqueous phase was extracted with CH_2Cl_2 (3 x 70 mL), and the combined organic extracts were washed with brine, dried over Na_2SO_4, filtered, and concentrated in *vacuo* to ethyl enol ether **S2** (5.7 g, 92%) as a pale yellow oil. ^{1}H NMR spectrum of this enone was identical with that reported.[1]

^{1}H NMR (300 MHz, $CDCl_3$) δ 4.22 (2H, q, J = 6.9 Hz), 2.65–2.61 (2H, m), 2.44–2.41 (2H, m), 1.63 (3H, s), 1.40 (3H, t, J = 6.9 Hz).

3-[bis(methylthio)methyl]-2-methyl-2-cyclopenten-1-one (S3). To a stirred solution of bis(methylthio)methane (4.4 mL, 42.9 mmol) in THF (42.9 mL) at 0 °C was added *n*-BuLi (1.6 M in hexane, 26.8 mL, 42.9 mmol), maintained at this temperature for 30 minutes. Then the ethyl enol ether **S2** (5.0 g, 35.7 mmol, neat) was cannulated to the above solution of

bis(methylthio)methyllithium (1 M in THF). After stirring at 0 °C for 4 h, the reaction mixture was added 10% aqueous HCl (20 mL) and extracted with EtOAc (50 mL) twice. The combined organic extracts were washed with brine, dried over Na_2SO_4, filtered, and concentrated in *vacuo*. The residue was purified by flash chromatography on silica gel (eluent: hexane/AcOEt = 5:1) to yield the dithioacetal **S3** (5.34 g, 74%) as a yellow oil. ^{1}H NMR (400 MHz, $CDCl_3$) δ 4.74 (1H, s), 2.69–2.66 (2H, m), 2.42–2.39 (2H, m), 2.15 (6H, s), 1.73 (3H, t, *J* = 2.4 Hz); ^{13}C NMR (100 MHz, $CDCl_3$) δ 209.5, 167.2, 136.6, 51.8, 33.9, 25.4, 15.5, 8.5; IR (neat) 2919, 1700, 737 cm^{-1}; MS (EI) *m/z* 202 (M^+); HRMS (EI) calcd for $C_9H_{14}OS_2$ (M^+) 202.0486, found 202.0490.

2-Methyl-3-oxo-1-cyclopentene-1-carboxaldehyde (S4). Iodomethane (21 mL, 337 mmol) and calcium carbonate (33.7 g, 337 mmol) were added to a solution of **S3** (3.4 g, 16.8 mmol) in a mixed solvent of acetonitrile (75 mL) and water (25 mL). After stirred at room temperature for 1 week, the reaction mixture was filtered and extracted with CH_2Cl_2 (3 x 50 mL). The combined organic extracts were washed with brine, dried over Na_2SO_4, filtered, and concentrated in *vacuo*. The residue was purified by flash chromatography on silica gel (eluent: hexane/AcOEt = 3:1) to yield the aldehyde **S4** (1.37 g, 66%) as a brown solid. ^{1}H NMR (300 MHz, $CDCl_3$) δ 10.4 (1H, s), 2.72–2.68 (2H, m), 2.52–2.48 (2H, m), 2.12 (3H, s); ^{13}C NMR (75 MHz, $CDCl_3$) δ 210.7, 190.2, 158.4, 149.7, 34.0, 23.7, 8.4; IR (neat) 1709, 1679 cm^{-1}; MS (EI) *m/z* 124 (M^+); HRMS (EI) calcd for $C_7H_8O_2$ (M^+) 124.0524, found 124.0517.

2-Methyl-3-oxo-1-cyclopentene-1-carboxylic acid (2b). Aldehyde **14** (1.3 g, 10.5 mmol) was dissolved in a mixture of acetonitrile (50 mL) and 30% hydrogen peroxide (5.9 g) and stirred at room temperature. A solution of sodium chlorite (6.77 g, 52.4 mmol) and sodium dihydrogen phosphate (8.18 g, 52.4 mmol) in water (30 mL) was added dropwise over a period of 10 minutes. The reaction was stirred at room temperature for 2 h, acidified to pH 3 with 10% aqueous HCl and extracted with CH_2Cl_2 (8 x 30 mL). The combined organic extracts were dried over Na_2SO_4, and the solvent was evaporated to give the carboxylic acid **2b** (1.48 g, 100%) as a white solid. ^{1}H NMR (300 MHz, $CDCl_3$) δ 2.81–2.79 (2H, m), 2.54–2.50 (2H, m), 2.10 (3H, s); ^{13}C NMR (75 MHz, $CDCl_3$) δ 209.7 170.4, 153.3, 34.2, 26.5, 10.3; IR (neat) 1719 cm^{-1}; MS (EI) *m/z* 140 (M^+); HRMS (EI) calcd for $C_7H_8O_3$ (M^+) 140.0473, found 140.0446.

Methyl 2-methyl-3-oxo-1-cyclopentene-1-carboxylate (2a). To a solution of the carboxylic acid **2** (725 mg, 5.18 mmol) in a mixed solution of methanol (10 mL) and CH_2Cl_2 (10 mL), DMAP (316 mg, 2.59 mmol), EDCI (1.5 g, 7.77 mmol) were added. The reaction mixture was allowed to stir overnight and concentrated in *vacuo*. The residue was purified by flash chromatography on silica gel (eluent: hexane/AcOEt = 5:1) to give the ester **2a** (662 mg, 83%) as a colorless oil. The ^{1}H and

^{13}C NMR spectrum of this carboxylate was identical with that reported.[3] ^{1}H NMR (300 MHz, $CDCl_3$) δ 3.86 (3H, s), 2.77–2.73 (2H, m), 2.48–2.45 (2H, m), 2.04 (3H, t, *J* = 2.4 Hz); ^{13}C NMR (75 MHz, $CDCl_3$) δ 208.9, 165.3, 153.6, 146.8, 51.7, 33.5, 26.1, 9.5.

References

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3) D. C. Ebner, J. T. Bagdanoff, E. M. Ferreira, R. M. McFadden, D. D. Caspi, R. M. Trend and B. M. Stoltz, *Chem. Eur. J.*, **2009**, *15*, 12978.