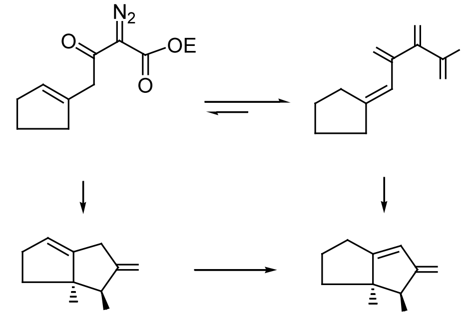
N2
O
OE
O

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6. General procedure for the condensation of cyclic ketones with α-diazo-β-ketoesters or ketones. To a solution of ethyl 2-diazoacetoacetate (624 mg, 4 mmol) in anhydrous CH_2Cl_2 (40 mL) at −23°C with dry ice/CCl_4 under N_2 was added dropwise $TiCl_4$ (836 mg, 4.4 mmol) and Et_3N (444 mg, 4.4 mmol). After the resulting red-dark solution was stirred at −23°C for 1 h, a solution of cyclohexanone (392 mg, 4 mmol) and $Ti(O^iPr)_4$ (1136 mg, 4 mmol) in anhydrous CH_2Cl_2 (4 mL) was added dropwise. The reaction mixture was stirred at −23°C for 9.5 h and was then quenched with saturated aqueous NH_4Cl (10 mL). The organic layer was separated and the aqueous layer was extracted with CH_2Cl_2 (2×20 mL). The combined organic layers were washed with saturated aqueous $NaHCO_3$ (2×20 mL), and then dried over Na_2SO_4. The product was purified by flash chromatography to yield **3b** as a yellow oil (863 mg, 85%). IR (CCl_4) 3514, 2135, 1721, 1638 cm^{-1}; ^1H NMR (200 MHz, $CDCl_3$) δ 1.34 (t, $J=7.2$ Hz, 3H), 1.44–1.53 (m, 6H), 1.60–1.70 (m, 4H), 3.05 (s, 2H), 3.62 (s, 1H), 4.31 (q, $J=7.2$ Hz, 2H); ^{13}C (50 MHz, $CDCl_3$) δ 14.1, 21.8, 25.5, 37.6, 49.0, 61.5, 71.3, 161.4, 193.0; MS (FAB) m/z 261 [$(M+Li)^+$, 25], 241 (63), 233 (13), 187 (19), 143 (100), 121 (42), 97 (29).
7. General procedure for the dehydration of the alcohols **3a**–**g**. Under N_2, **3b** (254 mg, 1 mmol) was dissolved in anhydrous CH_2Cl_2 (10 mL) and the solution was cooled to −78°C. While stirring, $(CF_3CO)_2O$ (420 mg, 2 mmol) and Et_3N (202 mg, 2 mmol) were added and the reaction temperature was allowed to rise to rt within 2 h. Another 5 mL Et_3N was added and the reaction mixture was stirred at rt for 23 h. Volatile fractions were removed by rotovap to leave a crude residue, which was purified by silica gel column chromatography to give **4b** (198 mg, 84%). IR (CCl_4) 2134, 1717, 1645, 1444, 1362 cm^{-1}; ^1H NMR (200 MHz, $CDCl_3$) δ 1.33 (t, $J=7.2$ Hz, 3H), 1.62–1.72 (m, 6H), 2.23–2.39 (m, 2H), 2.81–2.87 (m, 2H), 4.29 (q, $J=7.2$ Hz, 2H), 6.81 (s, 1H); ^{13}C NMR (50 MHz, $CDCl_3$) δ 14.3, 26.2, 27.9, 28.8, 30.7, 38.4, 61.2, 117.8, 161.5, 163.9, 182.6; MS (FAB) m/z 237 [$(M+H)^+$, 22], 163 (9), 135 (10), 123 (19), 95 (41), 69 (64), 43 (100).
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9. The *cis* configuration of the product was assigned by comparison with the ^1H NMR data of the *trans* isomer reported in Ref. 1c.
10. Typical procedure for the $Rh_2(NHCOCH_3)_4$-catalyzed reaction of diazo compounds **4a**–**g** and **5a**–**g**. To a solution of **4b** (118 mg, 0.5 mmol) in anhydrous CH_2Cl_2 (10 mL) was added $Rh_2(NHCOCH_3)_4$ (0.5 mg, 0.025 mmol). The solution was stirred under N_2 for 48 h. The solvent was removed under reduced pressure to give a crude residue, which was purified by column chromatography to yield **6b** (79 mg, 76%) as an oil. IR (CCl_4) 1719, 1636, 1552, 1253 cm^{-1}; ^1H NMR (200 MHz, $CDCl_3$) δ 1.18 (dq, $J=13$, 3.2 Hz, 1H), 1.31 (t, $J=7.1$ Hz, 3H), 1.40 (tq, $J=13$, 3.8 Hz, 1H), 1.54 (tq, $J=13$, 3.2 Hz, 1H), 1.88 (d, $J=13$ Hz, 1H), 2.02–2.07 (m, 1H), 2.25–2.29 (m, 1H), 2.33 (dt, $J=13$, 5 Hz, 1H), 2.86 (d, $J=13.9$ Hz, 1H), 3.02 (s, 1H), 3.05 (d, $J=3.8$ Hz, 1H), 4.22 (q, $J=7.1$ Hz, 2H), 5.82 (s, 1H); ^{13}C NMR (50 MHz, $CDCl_3$) δ 14.1, 25.0, 26.5, 30.8, 33.9, 45.8, 59.3, 61.4, 124.9, 169.2, 184.1, 201.3; MS (EI) m/z 208 (M^+, 28), 162 (32), 134 (100), 107 (15), 106 (20), 79 (22), 53 (8), 39 (22).