Organic Letters

Supporting Information

Stereospecific Cyclopropanation of Highly Substituted C-C Double Bonds Promoted by CrCl₂. Stereoselective Synthesis of Cyclopropanecarboxamides and Cyclopropyl Ketones

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GENERAL

Reactions requiring an inert atmosphere were conducted under dry nitrogen, and the glassware was oven dried (120 °C). THF was distilled from sodium/benzophenone ketyl immediately prior to use. All reagents were purchased in the higher quality available and were used without further purification. Flash column chromatography was carried out on silica gel 230-400 mesh. Compounds were visualized on analytical thin layer chromatograms (TLC) by UV light (254 nm). ^1H NMR spectra were recorded at 200, 300 or 400 MHz. ^{13}C NMR spectra and DEPT experiments were determined at 50 or 75 MHz. Chemical shifts are given in ppm relative to tetramethylsilane (TMS), which is used as an internal standard, and coupling constants (J) are reported in Hz. The diastereoisomeric ratio were obtained using ^1H NMR analysis and GC-MS of crude products. GC-MS and HRMS were measured at 70 eV or using FAB conditions. When HRMS could not be measured on molecular ion the HRMS of a significant fragment is given. Only the most important IR absorptions (cm^{-1}) and the molecular ions and/or base peaks in MS are given.

General Procedures.

Synthesis of cyclopropanecarboxamides 2:

To a suspension of anhydrous CrCl_2 (1.6 mmol, 4.0 equiv.) in THF (4 mL) was added dropwise the corresponding α,β -unsaturated amide **1** (0.4 mmol, 1.0 equiv.) in THF (2 mL) and CH_2I_2 (1.5 mmol, 3.75 equiv.) at room temperature and under inert atmosphere. After stirring for 18 hours at reflux, the reaction mixture was quenched by the addition of 1.0 M aqueous HCl (5 mL) and extracted with diethyl ether (3 x 10 mL). The combined extracts were washed with NH_4Cl sat. and water, dried over Na_2SO_4 , concentrated under vacuum and filtered through a pad of celite[®]. Purification by column chromatography on silica gel (hexane/EtOAc 10:1) afforded the pure compounds **2**.

Compounds **2b**, **2e-f**, **2h**, **2j-l**, and **2s** were compared with the spectroscopical data of those previously described in reference 10a. Compound **2d** was compared with the same product reported in reference 10b.

Synthesis of cyclopropyl ketones 3:

The corresponding organolithium compound (1.2 mmol, 3.0 equiv.) was added dropwise to a solution of the amide **2g** (0.4 mmol, 1.0 equiv.) in anhydrous THF (2 mL) at -78°C under nitrogen atmosphere. The mixture was stirred at -78°C for 1h and was left to reach room temperature. Then, the reaction was quenched with an aqueous saturated solution of ammonium chloride (5 mL) and extracted with dichloromethane (3 x 10 mL). The organic layers were washed with water, dried over Na_2SO_4 and concentrated under vacuum to yield the crude cyclopropyl ketones **3** which were purified by column chromatography on silica gel (hexane/EtOAc 5/1).

***trans*-N,N-Diethyl-2-methylcyclopropanecarboxamide (2a):** Yellow oil. ^1H NMR (300 MHz, CDCl_3): δ 3.45-3.20 (m, 4 H), 1.30-1.24 (m, 1 H), 1.23 (ddd, $J = 8.5, 6.9, 2.8$ Hz, 1 H), 1.14 (t, $J = 7.2$ Hz, 3 H), 1.08 (dd, $J = 8.5, 3.8$ Hz, 1 H), 1.02 (d, $J = 5.8$ Hz, 3 H), 1.00 (t, $J = 7.5$ Hz, 3 H), 0.48-0.42 (m, 1 H); ^{13}C NMR (75 MHz, CDCl_3): δ 172.2 (C), 42.0 (CH_2), 40.7 (CH_2), 20.0 (CH), 18.0 (CH_3), 15.9 (CH), 15.7 (CH_2), 14.8 (CH_3), 13.2 (CH_3); MS (70 eV, EI) m/z (%) 155 [M^+] (14), 140 (52), 126 (17), 83 (100), 55 (53); IR (neat): 2942, 2360, 1628, 1450, 1382 cm^{-1} ; $R_f = 0.19$ (hexane/EtOAc 5:1); Anal. Calcd. for $\text{C}_9\text{H}_{17}\text{NO}$ C, 69.63; H, 11.04; N, 9.02. Found: C, 69.49; H, 11.10; N, 8.91.

***trans*-N,N-Diethyl-2-heptylcyclopropanecarboxamide (2c):** Yellow oil. ^1H NMR (300 MHz, CDCl_3): δ = 3.38-3.19 (m, 4 H), 1.35-0.97 (m, 18 H), 0.98 (t, J = 7.1 Hz, 3 H), 0.75 (t, J = 7.0 Hz, 3 H), 0.48-0.42 (m, 1 H); ^{13}C NMR (75 MHz, CDCl_3): δ 172.3 (C), 41.9 (CH_2), 40.7 (CH_2), 33.3 (CH_2), 31.7 (CH_2); 29.2 (2 x CH_2), 29.1 (2 x CH_2), 22.5 (CH_2), 21.8 (CH), 18.7 (CH), 14.7 (CH_3), 14.0 (CH_3), 13.1 (CH_3); MS (70 eV, EI) m/z (%) 239 [M^+] (17), 224 (13), 182 (55), 140 (57), 55 (100); IR (neat): 2925, 2360, 1632, 1462 cm^{-1} ; R_f = 0.39 (hexane/EtOAc 3:1); Anal. Calcd. for $\text{C}_{15}\text{H}_{29}\text{NO}$ C, 75.26; H, 12.21; N, 5.85. Found: C, 75.43; H, 12.15; N, 5.52.

***trans*-4-[(3-Phenylcyclopropyl)carbonyl]morpholine (2g)**: Colourless oil. ^1H NMR (300 MHz, CDCl_3): δ 7.25-7.00 (m, 5 H), 3.63-3.45 (m, 8 H), 2.40 (ddd, $J = 10.2, 6.2, 4.5$ Hz, 1 H), 1.83 (dt, $J = 9.6, 5.1$ Hz, 1 H), 1.58 (dt, $J = 9.6, 4.5$ Hz, 1 H), 1.21 (m, 1 H); ^{13}C NMR (75 MHz, CDCl_3): δ 170.7 (C), 140.7 (C), 128.4 (2 x CH), 126.2 (CH), 126.0 (2 x CH), 66.5 (2 x CH_2), 45.9 (CH_2), 42.5 (CH_2), 25.5 (CH), 22.9 (CH), 16.1 (CH_2); MS (70 eV, EI) m/z (%) 231 [M^+] (100), 216 (5), 144 (81), 115 (82), 91 (50); IR (neat): 2923, 2360, 1632, 1462, 1443, 1235 cm^{-1} ; HRMS (70 eV) calcd. for $\text{C}_{14}\text{H}_{17}\text{NO}_2$ 231.1959. Found 231.1245; $R_f = 0.32$ (hexane/EtOAc 1:1); Anal. Calcd. for $\text{C}_{14}\text{H}_{17}\text{NO}_2$ C, 72.70; H, 7.41; N, 6.06. Found: C, 72.60; H, 7.52; N, 6.11.

(1*S,2*S**)-*N,N*-Diethyl-2-*iso*-butyl-1-methylcyclopropanecarboxamide (2i):** Yellow oil. ^1H NMR (300 MHz, CDCl_3): δ 3.49-3.10 (m, 4 H), 1.69-1.56 (m, 1 H), 1.48-1.39 (m, 1 H), 1.17-0.89 (m, 9 H), 1.13 (s, 3 H), 0.85 (d, $J = 6.5$ Hz, 3 H), 0.84 (d, $J = 6.5$ Hz, 3 H), 0.10 (apparent t, $J = 5.0$ Hz, 1 H); ^{13}C NMR (75 MHz, CDCl_3): δ 174.6 (C), 40.8 (CH_2), 39.1 (CH_2), 37.4 (CH_2), 28.5 (CH), 23.9 (C), 22.6 (CH_3), 22.5 (CH), 20.7 (CH_3), 18.9 (CH_3), 16.5 (CH_2), 14.1 (CH_3), 12.3 (CH_3); MS (70 eV, EI) m/z (%) 211 [M^+] (47), 196 (36), 155 (38), 100 (98), 69 (100), 55 (61); IR (neat): 2959, 2926, 2360, 1620, 1462 cm^{-1} ; HRMS (70 eV) calcd. for $\text{C}_{13}\text{H}_{25}\text{NO}$ 211.1936. Found 211.1921; $R_f = 0.25$ (hexane/EtOAc 3:1); Anal. Calcd. for $\text{C}_{13}\text{H}_{25}\text{NO}$ C, 73.88; H, 11.92; N, 6.63. Found: C, 73.60; H, 11.99; N, 6.52.

(1*S,2*R**)-*N,N*-Diisopropyl-1-methyl-2-phenylcyclopropanecarboxamide (2m)**: Orange oil. ^1H NMR (300 MHz, CDCl_3): δ 7.35-7.07 (m, 5 H), 4.35-4.15 (m, 1 H), 3.56 (apparent d, $J = 9.0$ Hz, 1 H), 3.30 3.17 (m, 1 H), 2.58 (apparent d, $J = 7.9$ Hz, 1 H), 1.38-1.08 (m, 13 H), 1.07 (s, 3 H); ^{13}C NMR (75 MHz, CDCl_3): δ 173.1 (C), 137.4 (C), 128.3 (2 x CH), 128.0 (2 x CH), 126.0 (CH), 48.1 (CH), 45.5 (CH), 29.2 (C), 27.3 (CH), 20.5 (CH_3), 20.3 (2 x CH_3), 16.3 (CH_2), 16.0 (2 x CH_3); MS (70 eV, EI) m/z (%) 259 [M^+] (39), 216 (69), 131 (83), 91 (89), 43 (100); IR (neat): 3053, 2970, 2242, 1622, 1440, 1370, 1334, 1265 cm^{-1} ; $R_f = 0.50$ (hexane/EtOAc 3:1); Anal. Calcd. for $\text{C}_{17}\text{H}_{25}\text{NO}$ C, 78.72; H, 9.71; N, 5.40. Found: C, 78.60; H, 9.83; N, 5.52.

4-[(1*S,2*R**)-(1-Methyl-2-phenylcyclopropyl)carbonyl]morpholine (**2n**):** Yellow oil. ^1H NMR (400 MHz, CDCl_3): δ 7.39-7.27 (m, 3 H), 7.16 (d; $J = 7.4$ Hz, 2 H), 3.73 (m, 8 H), 2.36 (dd, $J = 9.0, 6.6$ Hz, 1 H), 1.51 (dd, $J = 9.0, 5.6$ Hz, 1 H), 1.20 (apparent t, $J = 6.1$ Hz, 1 H), 1.06 (s, 3 H); ^{13}C NMR (100 MHz, CDCl_3): δ 172.9 (C), 136.0 (C), 128.1 (2 x CH), 128.0 (2 x CH), 126.2 (CH), 66.5 (CH_2), 66.3 (CH_2), 45.9 (CH_2), 41.7 (CH_2), 27.5 (CH), 27.1 (C), 15.5 (CH_2), 15.3 (CH_3); MS (70 eV, EI) m/z (%) 245 [M^+] (100), 176 (27), 158 (82), 131 (52), 114 (30), 91 (37); IR (neat): 2861, 1639, 1429, 1282, 1193 cm^{-1} ; HRMS (70 eV) calcd. for $\text{C}_{15}\text{H}_{19}\text{NO}_2$ 245.1416. Found 245.1411; $R_f = 0.28$ (hexane/EtOAc 1:1).

(1*R,2*R**)-2-(*p*-Chlorophenyl)-*N,N*-diisopropyl-1-methylcyclopropanecarboxamide (2o):** Yellow oil.

^1H NMR (300 MHz, CDCl_3): δ 7.16 (d, $J = 8.4$ Hz, 2 H), 6.98 (d, $J = 8.4$ Hz, 2 H), 4.01 (m, $J = 6.5$ Hz, 1 H), 3.07 (m, $J = 6.8$ Hz, 1 H), 2.02 (dd, $J = 8.5, 6.4$ Hz, 1 H), 1.64 (apparent t, $J = 5.6$ Hz, 1 H), 1.40 (s, 3 H), 1.34 (d, $J = 6.8$ Hz, 3 H), 1.19 (d, $J = 6.8$ Hz, 3 H), 1.10 (d, $J = 6.8$ Hz, 3 H), 1.06 (dd, $J = 8.5, 5.6$ Hz, 1 H), 0.16 (d, $J = 6.6$ Hz, 3 H); ^{13}C NMR (75 MHz, CDCl_3): δ 169.8 (C), 138.3 (C), 131.5 (C), 128.1 (2 x CH), 127.8 (2 x CH), 48.4 (CH), 45.8 (CH), 33.4 (C), 31.6 (CH), 23.5 (CH_3), 21.4 (CH_2), 21.1 (CH_3), 20.2 (2 x CH_3), 20.1 (CH_3); MS (70 eV, EI) m/z (%) 293 [M^+] (25), 250 (30), 236 (27), 125 (34), 86 (50), 43 (100); IR (neat): 2967, 2932, 2360, 1625, 1497, 1462, 1369 cm^{-1} ; $R_f = 0.37$ (hexane/EtOAc 3:1); Anal. Calcd. for $\text{C}_{17}\text{H}_{24}\text{ClNO}$ C, 69.49; H, 8.23; N, 4.77. Found: C, 69.64; H, 8.15; N, 4.61.

***N,N*,2,2-Tetraethyl-1-methylcyclopropanecarboxamide (2p):** Yellow oil. ^1H NMR (300 MHz, CDCl_3): δ 3.53-3.37 (m, 2 H), 3.14-3.07 (m, 2 H), 1.41-1.08 (m, 4 H), 1.16 (t, $J = 7.2$ Hz, 3 H), 1.11 (t, $J = 7.1$ Hz, 3 H), 0.98 (s, 3 H), 0.97 (t, $J = 6.9$ Hz, 3 H), 0.82 (app. dd, $J = 6.9$ Hz, 2 H), 0.73 (t, $J = 7.1$ Hz, 3 H); ^{13}C NMR (75 MHz, CDCl_3): δ 173.9 (C), 41.0 (CH_2), 38.4 (CH_2), 36.3 (CH_2), 30.0 (C), 25.6 (C), 24.3 (CH_2), 19.9 (CH_2), 16.7 (CH_3), 15.0 (CH_3), 14.0 (2 x CH_3), 12.1 (CH_3); MS (70 eV, EI) m/z (%) 211 [M^+] (38), 196 (17), 182 (44), 140 (70), 100 (84), 69 (89), 41 (100); IR (neat): 2928, 2360, 2336, 1641, 1462 cm^{-1} ; HRMS (70 eV) calcd. for $\text{C}_{13}\text{H}_{25}\text{NO}$ 211.1936. Found 211.1930; $R_f = 0.33$ (hexane/EtOAc 3:1).

(1S*,2S*)-N,N-Diethyl-1,2-dimethyl-2-propylcyclopropanecarboxamide (2q): Orange oil. ^1H NMR (300 MHz, CDCl_3): δ 3.57-3.26 (m, 2 H), 3.10-2.98 (m, 2 H), 1.45-1.19 (m, 2 H), 1.15 (s, 3 H), 1.15 (t, $J = 7.3$ Hz, 2 H), 1.10 (t, $J = 7.3$ Hz, 3 H), 0.98 (s, 3H), 0.95 (t, $J = 6.8$ Hz, 3 H), 0.81 (app. dd, $J = 7.3$ Hz, 2 H), 0.72 (t, $J = 7.3$ Hz, 3 H); ^{13}C NMR (75 MHz, CDCl_3): δ 173.7 (C), 41.0 (CH_2), 38.4 (2 x CH_2), 30.1 (C), 25.6 (C), 24.5 (CH_2), 20.0 (CH_2), 18.4 (CH_3), 16.8 (CH_3), 14.1 (2 x CH_3), 12.1 (CH_3); MS (70 eV, EI) m/z (%) 211 $[\text{M}^+]$ (53), 196 (25), 140 (98), 100 (100), 55 (50); IR (neat): 2927, 2361, 1641, 1426 cm^{-1} ; HRMS (70 eV) calcd. for $\text{C}_{13}\text{H}_{25}\text{NO}$ 211.2936. Found 211.1982; $R_f = 0.30$ (hexane/EtOAc 3:1); Anal. Calcd. for $\text{C}_{13}\text{H}_{25}\text{NO}$ C, 73.88; H, 11.92; N, 6.63. Found: C, 73.75; H, 11.99; N, 6.59.

(1*S,2*S**)-*N,N*-Diethyl-1,2-dimethyl-2-pentylcyclopropanecarboxamide (2r):** Yellow oil. ^1H NMR (300 MHz, CDCl_3): δ 3.45-3.35 (m, $J = 7.1$ Hz, 2 H), 3.11-3.00 (m, $J = 6.8, 3.4$ Hz, 2 H), 1.44-1.00 (m, 8 H), 1.15 (s, 3 H), 1.10 (t, $J = 7.1$ Hz, 3 H), 0.97 (s, 3 H), 0.95 (t, $J = 7.1$ Hz, 3 H), 0.84 (dd, $J = 6.6, 3.5$ Hz, 2 H), 0.73 (t, $J = 6.8$ Hz, 3 H); ^{13}C NMR (75 MHz, CDCl_3): δ 174.5 (C), 40.9 (CH_2), 38.5 (CH_2), 36.1 (CH_2), 30.0 (C), 26.5 (CH_2), 25.4 (C), 22.6 (2 x CH_2), 22.5 (CH_2), 18.4 (CH_3), 16.9 (CH_3), 14.1 (CH_3), 13.9 (CH_3), 12.2 (CH_3); MS (70 eV, EI) m/z (%) 239 [M^+] (27), 224 (16), 140 (56), 129 (69), 100 (100), 72 (70), 41 (86); IR (neat): 2958, 2992, 2360, 1632, 1462, 1382 cm^{-1} ; HRMS (70 eV) calcd. for $\text{C}_{15}\text{H}_{29}\text{NO}$ 239.2249. Found 239.2259; $R_f = 0.32$ (hexane/EtOAc 3:1)

(1*S,2*R**)-*N,N*-Diethyl-1,2-dimethyl-2-phenylcyclopropanecarboxamide (2s):** Yellow oil. ^1H NMR (300 MHz, CDCl_3): δ 7.26-6.91 (m, 5 H), 3.35-3.15 (m, 2 H), 2.67-2.40 (m, 2 H), 2.12 (d, $J = 6.6$ Hz, 1 H), 1.50 (s, 3 H), 1.34 (s, 3 H), 0.85 (t, $J = 6.8$ Hz, 3 H), 0.57 (d, $J = 6.6$ Hz, 1 H), 0.35 (t, $J = 6.8$ Hz, 3 H); ^{13}C NMR (75 MHz, CDCl_3): δ 171.7 (C), 141.7 (C), 127.6 (2 x CH), 126.2 (2 x CH), 125.6 (CH), 40.7 (CH_2), 37.9 (CH_2), 34.2 (C), 28.7 (C), 25.4 (CH_2), 20.1 (CH_3), 18.9 (CH_3), 13.4 (CH_3), 11.1 (CH_3); MS (70 eV, EI) m/z (%) 245 [M^+] (95), 172 (39), 145 (100), 91 (41), 77 (34); IR (neat): 2969, 2933, 2360, 1631, 1452, 1381 cm^{-1} ; HRMS (70 eV) calcd. for $\text{C}_{16}\text{H}_{23}\text{NO}$ 245.1780. Found 245.1770; $R_f = 0.38$ (hexane/EtOAc 3:1)

2s

(1*S,2*S**)-Methyl(2-phenylcycloprop-1-yl)ketone (3a):** Yellow oil. ^1H NMR (300 MHz, CDCl_3): δ 7.25-6.95 (m, 5 H), 2.44 (ddd, $J = 8.0, 4.2, 4.1$ Hz, 1 H), 2.21 (s, 3 H), 2.14 (ddd, $J = 8.9, 6.8, 4.2$ Hz, 1 H), 1.59 (ddd, $J = 8.9, 4.3, 4.1$ Hz, 1 H), 1.29 (ddd, $J = 8.0, 6.8, 4.3$ Hz, 1 H); ^{13}C NMR (75 MHz, CDCl_3): δ 206.8 (C), 140.2 (C), 128.4 (2 x CH), 126.4 (CH), 125.9 (2 x CH), 32.8 (CH), 30.8 (CH_3), 28.9 (CH), 19.1 (CH_2); MS (70 eV, EI) m/z (%) 160 [M^+] (19), 117 (100), 115 (59), 91 (26), 43 (58); IR (neat): $\tilde{\nu} = 3054, 1694, 1265, 909\text{ cm}^{-1}$; HRMS (70 eV) calcd. for $\text{C}_{11}\text{H}_{12}\text{O}$ 160.0888. Found 160.0875; $R_f = 0.58$ (hexane/EtOAc 3:1); Anal. Calcd. for $\text{C}_{11}\text{H}_{12}\text{O}$ C, 82.46; H, 7.55. Found: C, 82.93; H, 7.19

(1*S,2*S**)-Butyl(2-phenylcycloprop-1-yl)ketone (3b):** Yellow oil. ^1H NMR (300 MHz, CDCl_3): δ 7.29-6.95 (m, 5 H), 2.50 (t, $J = 7.4$ Hz, 2 H), 2.41 (ddd, $J = 8.8, 6.2, 4.1$ Hz, 1 H), 2.11 (ddd, $J = 8.3, 4.3, 4.1$ Hz, 1 H), 1.62-1.41 (m, 3 H), 1.38-1.08 (m, 3 H), 0.82 (t, $J = 7.4$ Hz, 3 H); ^{13}C NMR (75 MHz, CDCl_3): δ 209.1 (C), 140.4 (C), 128.4 (2 x CH), 126.3 (CH), 125.9 (2 x CH), 43.6 (CH_2), 32.1 (CH), 28.7 (CH), 25.9 (CH_2), 22.2 (CH_2), 18.7 (CH_2), 13.7 (CH_3); MS (70 eV, EI) m/z (%) 202 [M^+] (14), 160 (97), 145 (61), 127 (55), 117 (91), 115 (84), 91 (75), 85 (70), 57 (100), 41 (61); IR (neat): $\tilde{\nu} = 1698, 1400, 1067, 697\text{ cm}^{-1}$; HRMS (70 eV) calcd. for $\text{C}_{14}\text{H}_{18}\text{O}$ 202.1358. Found 202.1360; $R_f = 0.62$ (hexane/EtOAc 3:1); Anal. Calcd. for $\text{C}_{14}\text{H}_{18}\text{O}$ C, 83.12; H, 8.97. Found: C, 83.60; H, 8.51.

(1*S,2*S**)-Phenyl(2-phenylcycloprop-1-yl)ketone (3c):** Yellow oil. ^1H NMR (300 MHz, CDCl_3): δ 7.92 (d, $J = 7.7$ Hz, 2 H), 7.48-7.35 (m, 3 H), 7.26-7.09 (m, 5 H), 2.83 (ddd, $J = 8.0, 4.2, 4.0$ Hz, 1 H), 2.63 (m, $J = 6.9$ Hz, 1 H), 1.84 (ddd, $J = 9.0, 4.2, 4.1$ Hz, 1 H), 1.48 (ddd, $J = 8.0, 6.9, 4.1$ Hz, 1 H); ^{13}C NMR (75 MHz, CDCl_3): δ 198.5 (C), 140.4 (C), 137.6 (C), 132.8 (CH), 128.5 (4 x CH), 128.0 (2 x CH), 126.5 (CH), 126.1 (2 x CH), 29.9 (CH), 29.2 (CH), 19.2 (CH_2); MS (70 eV, EI) m/z (%) 222 [M^+] (42), 115 (47), 105 (100), 77 (84), 51 (33); IR (neat): $\tilde{\nu} = 3055, 1666, 1265, 1224, 909\text{ cm}^{-1}$; HRMS (70 eV) calcd. for $\text{C}_{16}\text{H}_{14}\text{O}$ 222.1045. Found 222.1024; $R_f = 0.58$ (hexane/EtOAc 3:1); Anal. Calcd. for $\text{C}_{16}\text{H}_{14}\text{O}$ C, 86.45; H, 6.35. Found: C, 86.81; H, 6.12.

3c

(1*S,2*R**)-Methyl(1-methyl-2-phenylcycloprop-1-yl)ketone 3d:** Yellow oil. ^1H NMR (300 MHz, CDCl_3): δ 7.35-7.20 (m, 5 H), 2.77 (dd, $J = 9.1, 7.1$ Hz, 1 H), 2.23 (s, 3 H), 1.74 (dd, $J = 9.1, 4.6$ Hz, 1 H), 1.21 (dd, $J = 7.1, 4.6$ Hz, 1 H), 1.06 (s, 3 H); ^{13}C NMR (75 MHz, CDCl_3): δ 209.5 (C), 136.9 (C), 129.2 (2 x CH), 128.2 (2 x CH), 126.7 (CH), 33.6 (CH), 33.2 (C), 26.8 (CH_3), 21.2 (CH_2), 15.2 (CH_3); MS (70 eV, EI) m/z (%) 174 [M^+] (72), 159 (38), 131 (100), 129 (15), 91 (21); IR (neat): $\tilde{\nu} = 3021, 1691, 1273, 945\text{ cm}^{-1}$; HRMS (70 eV) calcd. for $\text{C}_{12}\text{H}_{14}\text{O}$ 174.1045. Found 174.1039; $R_f = 0.53$ (hexane/EtOAc 3:1)

(1*S,2*R**)-Butyl(1-methyl-2-phenylcycloprop-1-yl)ketone 3e:** Yellow oil. ^1H NMR (300 MHz, CDCl_3): δ 7.26-7.16 (m, 5 H), 2.75 (dd, $J = 9.0, 7.1$ Hz, 1 H), 2.56 (t, $J = 7.3$ Hz, 2 H), 1.75 (dd, $J = 9.0, 4.4$ Hz, 1 H), 1.65-1.57 (m, 2 H), 1.41-1.33 (m, 2 H), 1.19 (dd, $J = 7.1, 4.4$ Hz, 1 H), 1.09 (s, 3 H), 0.96 (t, $J = 7.3$ Hz, 3 H); ^{13}C NMR (75 MHz, CDCl_3): δ 211.4 (C), 137.1 (C), 129.2 (2 x CH), 128.1 (2 x CH), 126.6 (CH), 38.6 (CH_2), 33.5 (CH), 32.7 (C), 26.1 (CH_2), 22.3 (CH_2), 21.1 (CH_2), 15.0 (CH_3), 13.9 (CH_3); MS (70 eV, EI) m/z (%) 216 [M^+] (40), 174 (21), 159 (55), 131 (100), 91 (88), 57 (47); IR (neat): $\tilde{\nu} = 2958, 1687, 1379, 1125, 699\text{ cm}^{-1}$; HRMS (70 eV) calcd. for $\text{C}_{15}\text{H}_{20}\text{O}$ 216.1514. Found 216.1510; $R_f = 0.75$ (hexane/EtOAc 3:1)

(1*S,2*R**)-Trimethylsilylmethyl(1-methyl-2-phenylcycloprop-1-yl)ketone 3f:** Orange oil. ^1H NMR (300 MHz, CDCl_3): δ 7.32-7.17 (m, 5 H), 2.82 (dd, $J = 8.9, 7.2$ Hz, 1 H), 2.38 (d, $J = 3.8$ Hz, 2 H), 1.68 (dd, $J = 8.9, 4.2$ Hz, 1 H), 1.18 (dd, $J = 7.2, 4.2$ Hz, 1 H), 1.07 (s, 3 H), 0.18 (s, 9 H); ^{13}C NMR (75 MHz, CDCl_3): δ 210.2 (C), 137.2.2 (C), 129.1 (2 x CH), 128.1 (2 x CH), 126.5 (CH), 33.2 (CH_2), 33.1 (CH), 32.9 (C), 21.5 (CH_2), 15.8 (CH_3), -0.8 (3 x CH_3); MS (70 eV, EI) m/z (%) 246 [M^+] (45), 155 (33), 141 (100), 131 (26), 115 (30), 73 (84); IR (neat): $\tilde{\nu} = 3053, 2958, 1655, 1251, 854\text{ cm}^{-1}$; HRMS (70 eV) calcd. for $\text{C}_{15}\text{H}_{22}\text{OSi}$ 246.1440. Found 246.1433; $R_f = 0.70$ (hexane/EtOAc 3:1)

(1*S,2*R**)-Allyl(1-methyl-2-phenylcycloprop-1-yl)ketone 3g:** Yellow oil. ^1H NMR (300 MHz, CDCl_3): δ 7.43-7.17 (m, 5 H), 6.02 (ddt, $J = 16.8, 10.2, 6.5$ Hz, 1 H), 5.25-5.13 (m, 2 H), 3.38 (dd, $J = 6.6, 1.3$ Hz, 2 H), 2.80 (apparent t, $J = 8.1$ Hz, 1 H), 1.79 (dd, $J = 9.0, 4.5$ Hz, 1 H), 1.22 (dd, $J = 7.1, 4.5$ Hz, 1 H), 1.11 (s, 3 H); ^{13}C NMR (75 MHz, CDCl_3): δ 209.1 (C), 136.8 (C), 131.2 (CH), 129.2 (2 x CH), 128.2 (2 x CH), 126.7 (CH), 118.2 (CH_2), 43.7 (CH_2), 33.9 (CH), 32.7 (C), 21.4 (CH_2), 14.9 (CH_3); MS (70 eV, EI) m/z (%) 200 [M^+] (27), 159 (40), 131 (75), 91 (100), 84 (54), 49 (63); IR (neat): $\tilde{\nu} = 3056, 2984, 1685, 1273, 923\text{ cm}^{-1}$; HRMS (70 eV) calcd. for $\text{C}_{14}\text{H}_{16}\text{O}$ 200.1201. Found 200.1196; $R_f = 0.60$ (hexane/EtOAc 5:1)

3g