Supporting Information

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An Intramolecular Organocatalytic Cyclopropanation Reaction

Nadine Bremeyer, Stephen C. Smith, Steven V. Ley, Matthew J. Gaunt*

Department of Chemistry
University of Cambridge
Lensfield Road
Cambridge
CB2 1EW, UK
General Information: $^1$H NMR Spectra were recorded on Bruker DPX 400, 500 and 600 spectrometers in deuterochloroform, unless stated otherwise, operating at 400, 500 and 600 MHz respectively. $^{13}$C NMR Spectra were recorded on a Bruker DPX 400, 500 and 600 spectrometer operating at 100, 125 and 150 MHz respectively. Chemical shifts are quoted relative to residual solvent (7.26 ppm for $^1$H and 77.0 ppm for $^{13}$C of CDCl$_3$) and coupling constants (J) are given in Hz. For convenience, the following abbreviations are used to indicate the multiplicity of the signals: s singlet; d doublet; t triplet; q quartet; dd doublet of doublets; dt doublet of triplet; m multiplet; br broad. The temperature of acquisition of the NMR spectra was 298 ± 3 K. DEPT135 and 2-dimensional experiments (COSY, HMBC, HMQC, NOESY) were used to support assignments where appropriate.

High resolution mass spectral (HRMS) analyses were measured on a Micromass Q-TOF spectrometer using EI (electron impact) or ESI (electrospray ionisation) techniques at the Department of Chemistry, University of Cambridge. Infrared spectra were recorded on a Perkin Elmer Spectrum 1FT-IR Spectrometer fitted with an ATR sampling accessory as neat films, either through direct application or deposited from CHCl$_3$.

All anhydrous solvents were dried by standard techniques and freshly distilled before use or purchased in anhydrous form from Fluka. All flash chromatography was carried out using dry-packed Merck 9385 Kieselgel 60 silica gel. Reactions were monitored by thin layer chromatography (TLC), carried out on Kieselgel 60 PF$_{254}$ (Merck) 0.2 mM plates.

All chemicals were purchased from The Aldrich Chemical Company, Fluka, Lancaster, Strem or Avocado and distilled or recrystallised before use, where necessary. All reactions were carried out in oven dried glassware and under an atmosphere of argon unless stated otherwise.

Na$_2$CO$_3$ was dried by grinding the pellets and heating the resulting powder to 120°C under vacuum for 48h. DABCO was azeotroped with benzene or sublimed.

Synthesis of $\alpha$-chlorecoketones substrates

The reaction substrates, 1, were formed by a simple two-step synthesis. Alkenyl a-chlorecoketone 4 was formed using a modification of Barluenga’s procedure,$^1$ where LiCH$_2$Cl reacts with Weinreb amide 3 to give the desired chloroketone 4 in excellent yield. Alkene cross-metathesis between the alkenyl $\alpha$-chlorecoketone 4 and an electron deficient alkenes, using 2.5mol% of Grubbs’ 2nd generation catalyst, formed the desired substrate 1 in good yield. Notably, the functional group sensitivity of alkenyl $\alpha$-chlorecoketones demonstrates the mild nature of the alkene cross-metathesis process (Scheme 2).$^2$

![Scheme 2](image_url)

### Alkene Cross metathesis using Grubbs’ 2nd Generation Catalyst

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Reagents and conditions: (a) 2 eq. ClCH$_2$I, 1.5 eq. MeLi, Et$_2$O, -78°C, 0.5 h; (b) Grubbs’ 2nd generation catalyst (2.5mol%), 1.5 eq. Alkene, CH$_2$Cl$_2$, 45°C.

**General procedure for formation of [−]-chloroketones:**

MeLi (48 mmol, 30ml of a 1.6 M solution in Et₂O) was added by syringe pump over 40 minutes to a solution of the Weinreb amide (5 g, 32 mmol) and iodochloromethane (4.64 ml, 64 mmol) in Et₂O or THF (150 ml) at 78°C over a period of 40 min. After addition the reaction mixture was stirred for 0.5 h at -78°C and then quenched with NH₄Cl (sat. solution, 150 ml). The aqueous layer was extracted with Et₂O (3 × 150 ml) and the combined organic layers were washed with water (300 ml), brine (300 ml) and dried over MgSO₄. The solution was then concentrated under reduced pressure and the crude product was purified by flash column chromatography on silica gel.

4a: \( \delta_{\text{max}} \) (film)/ cm⁻¹ 3080, 2981, 2938, 1719, 1642, 1401, 1068, 998, 915, 773; \( \delta \) (400 MHz, CDCl₃) 5.95-5.70 (m, 1H), 5.04-4.98 (m, 2H) 4.06 (s, 2H), 2.61-2.57 (t, \( J = 7.2, 2H \)), 2.11-2.06 (dt, \( J = 7.2, 2H \)), 1.89-1.69 (tt, \( J = 7.2, 2H \)), \( \delta \) (100 MHz, CDCl₃) 202.5, 137.5, 115.6, 48.2, 38.7, 32.8, 22.5; HRMS found EI [M⁺] 146.0498, C₃H₇ClO requires 146.0498.

4b: \( \delta_{\text{max}} \) (film)/ cm⁻¹ 3080, 2981, 2938, 1719, 1642, 1401, 1068, 998, 915, 773; \( \delta \) (400 MHz, CDCl₃) 5.95-5.88 (m, 1H), 5.19-5.10 (m, \( J = 17.2, 10.2, 2H \)), 4.17 (s, 2H), 2.83-2.79 (dt, \( J = 7.3, 2H \)), 2.51-2.45 (m, 2H), \( \delta \) (100 MHz, CDCl₃) 202.0, 136.4, 115.9, 48.2, 38.9, 27.6; HRMS found EI [M⁺] 132.0344, C₆H₉ClO requires 132.0342.

**General Procedure for the cross-metathesis reaction:** Grubbs’ catalyst (tricyclohexylphosphine [1,3-bis(2,4,6-trimethylphenyl)-4,5-dihydroimidazol-2-ylidene][benzylidene]ruthenium(IV)dichloride), 2.5 mol%) was added to a solution of the alkenyl chloroketone (1mmol) and an electron deficient alkene (1.5 mmol) in DCM (5 ml). The reaction mixture was stirred at 40°C for the time stated and after completion the reaction mixture was filtered through a plug of silica eluting with Et₂O. The filtrate was concentrated under reduced pressure and the crude product was purified by flash column chromatography on silica gel.

1a: \( \delta_{\text{max}} \) (film)/ cm⁻¹ 2935, 1733, 1667, 1617, 1447, 1345, 1285, 1225, 975, 770, 693; \( \delta \) (400 MHz, CDCl₃) 7.92-7.90 (m, 2H), 7.57-7.53 (m, 1H), 7.53-7.44 (m, 2H), 7.02-6.96 (dt, \( J = 15.4, 6.6, 1H \)), 6.91-6.87 (dt, \( J = 15.4, 1.2, 1H \)), 4.06 (s, 2H), 2.66 (t, \( J = 7.2, 2H \)), 2.38-2.32 (dd, \( J = 7.2, 6.6, 1.2, 2H \)) 1.90-1.83 (tt, \( J = 7.2, 7.2, 2H \)); \( \delta \) (100 MHz, CDCl₃) 202.1, 190.5, 147.9, 137.8, 132.7, 128.5 (2C), 126.7, 48.1, 38.6, 31.7, 21.9; HRMS found ESI [M+Na⁺] 273.0659, C₁₂H₁₅ClO₂Na requires 273.0659.
**1b:** $\lambda_{\text{max}}$ (film)/cm$^{-1}$ 2935, 1734, 1694, 1668, 1627, 1496, 1454, 1404, 1366, 1292, 1185, 1092, 977, 750, 699; $\delta$ (400 MHz, CDCl$_3$) 7.30-7.26 (m, 2H), 7.21-7.17 (m, 3H), 6.79-6.72 (dt, $J = 15.9, 6.9$ Hz, 1 H), 6.13-6.09 (dt, $J = 15.9, 1.5$ Hz, 1H), 4.03 (s, 2H), 2.94-2.84 (m, 4H), 2.62 (t, $J = 7.2$ Hz, 2H), 2.27-2.13 (tdd, $J = 7.2, 6.9, 1.5, 2$ H), 1.83-1.76 (tt, $J = 7.2, 7.2, 2$ H); $\delta$ (100 MHz, CDCl$_3$) 202.0, 199.2, 145.7, 141.2, 130.9, 128.4, 128.3, 126.1, 48.0, 41.8, 38.6, 38.6, 31.4, 21.7; HRMS found ESI [M+Na]$^+$ 301.0980, C$_{16}$H$_{15}$ClO$_2$Na requires 301.0972.

**1c:** $\lambda_{\text{max}}$ (film)/cm$^{-1}$ 2937, 1733, 1695, 1669, 1625, 1403, 1361, 1255, 977, 766; $\delta$ (400 MHz, CDCl$_3$) 6.76-6.68 (dt, $J = 16.0, 6.9, 1$ H), 6.08-6.03 (dt, $J = 16.0, 1.5, 1$ H), 4.04 (s, 2H), 2.62 (t, $J = 7.2, 2$ H), 2.27-2.21 (tdd, $J = 7.2, 6.9, 1.5, 2$ H), 2.21 (s, 3H), 1.83-1.76 (tt, $J = 7.2, 7.2, 2$ H); $\delta$ (100 MHz, CDCl$_3$) 201.9, 198.3, 146.5, 131.9, 48.1, 38.6, 31.4, 26.9, 21.7; HRMS found EI [M]$^+$ 188.0601, C$_9$H$_{12}$ClO$_2$ requires 188.0604.

**1d:** $\lambda_{\text{max}}$ (film)/cm$^{-1}$ 2938, 1712, 1683, 1637, 1409, 1367, 1160, 1127, 975, 767; $\delta$ (400 MHz, CDCl$_3$) 9.50 (d, $J = 7.9, 1$ H), 6.83-6.76 (dt, $J = 15.7, 6.8, 1$ H), 6.15-6.09 (ddt, $J = 15.7, 7.9, 1.5, 1$ H), 4.04 (s, 2H), 2.67 (t, $J = 7.2, 2$ H), 2.40-2.34 (tdd, $J = 7.2, 6.8, 1.5, 2$ H), 1.89-1.82 (tt, $J = 7.2, 7.2, 2$ H); $\delta$ (100 MHz, CDCl$_3$) 202.3, 194.1, 157.2, 133.9, 48.4, 38.9, 32.1, 21.9; HRMS found EI [M]$^+$ 174.0448, C$_9$H$_{11}$ClO$_2$ requires 174.0448.

**1e:** $\lambda_{\text{max}}$ (film)/cm$^{-1}$ 2935, 1733, 1667, 1617, 1447, 1345, 1285, 1225, 975, 770, 693; $\delta$ (400 MHz, CDCl$_3$) 6.83-6.76 (dt, $J = 15.6, 6.9, 1$ H), 5.76 (d, $J = 15.6, 1$ H), 4.05 (s, 2H), 2.62 (t, $J = 7.3, 2$ H), 2.24-2.18 (td, $J = 7.3, 6.9, 2$ H), 1.83-1.76 (tt, $J = 7.3, 7.3, 2$ H) 1.48 (s, 9H); $\delta$ (100 MHz, CDCl$_3$) 202.5, 166.2, 146.6, 124.4, 80.7, 48.5, 39.1, 31.4, 28.5, 22.2; HRMS found ESI [M+Na]$^+$ 269.0931, C$_{12}$H$_{16}$ClO$_2$Na requires 269.0921.

**1f:** $\lambda_{\text{max}}$ (film)/cm$^{-1}$ 2871, 1733, 1447, 1306, 1145, 1086, 753, 688; $\delta$ (400 MHz, CDCl$_3$) 7.89-7.86 (m, 2H), 7.62-7.56 (m, 1H), 7.55-7.52 (m, 2H), 6.96-6.92 (dt, $J = 15.1, 6.8, 1$ H), 6.37-6.32 (dt, $J = 15.1, 1.6, 1$ H), 4.01 (s, 2H), 2.62 (t, $J = 7.1, 2$ H), 2.31-2.25 (tdd, $J = 7.1, 6.8, 1.6, 2$ H), 1.84-1.77 (tt, $J = 7.1, 7.1, 2$ H); $\delta$ (100 MHz, CDCl$_3$) 202.2, 145.8, 140.9, 133.8, 131.8, 129.7, 128.0, 48.4, 38.7, 30.8, 21.6; HRMS found ESI [M+Na]$^+$ 309.0319, C$_{13}$H$_{15}$ClO$_3$Na requires 309.0328.

**1g:** $\lambda_{\text{max}}$ (film)/cm$^{-1}$ 1726, 1655, 1626, 1598, 1584, 1572, 1363, 1267, 1011, 762, 698; $\delta$ (400 MHz, CDCl$_3$) $\delta$ 7.93 (d, $J = 7.2, 2$ H), 7.55 (t, $J = 7.2, 1$ H), 7.49 (t, $J = 7.2, 2$ H), 7.42-7.35 (dd, $J = 15.1, 10.9, 1$ H), 6.91 (d, $J = 15.1, 1$ H), 6.37-6.31 (dd, $J = 15.1, 10.9, 1$ H), 6.23-6.16 (dt, $J = 15.1, 7.2, 1$ H), 4.06 (s, 2H), 2.64 (t, $J = 7.2, 2$ H), 2.29-2.24 (dt, $J = 7.2, 7.2, 2$ H), 1.85-1.78 (tt, $J = 7.2, 7.2, 2$ H); $\delta$ (100 MHz, CDCl$_3$) 202.2, 190.8, 144.7, 144.2, 138.2, 132.6,
103.1, 128.5, 128.3, 124.3, 48.1, 38.6, 32.2, 22.4; HRMS found ESI [M+Na]^+ 299.0815, C_{16}H_{17}ClO_{2}Na requires 299.0815.

![Structural formula](image)

1h: \( \delta_{\text{max}} \) (film)/ cm\(^{-1}\) 2979, 2935, 1706, 1654, 1393, 1367, 1293, 1254, 1153, 1153, 977, 848; \( \delta_{t} \) (400 MHz, CDCl\(_3\)) 6.84-6.77 (dt, J = 15.6, 6.8, 1H), 5.80-5.75 (dt, J = 15.6, 1.6, 1H), 4.07 (s, 2H), 2.78 (t, J = 7.1, 2H), 2.52-2.47 (tdd, J = 7.1, 6.8, 1.6, 2H), 1.48 (s, 9H); \( \delta_{t} \) (100 MHz, CDCl\(_3\)) 201.6, 166.0, 145.2, 124.7, 80.8, 48.4, 38.2, 28.5, 25.9; HRMS found ESI [M+Na]^+ 255.0777, C_{11}H_{17}ClO_{3}Na requires 255.0764.

![Structural formula](image)

1i: \( \delta_{\text{max}} \) (film)/ cm\(^{-1}\) 2983, 1709, 1654, 1400, 1368, 1268, 1207, 1178, 1093, 1039, 974, 854, 773, 710; \( \delta_{t} \) (400 MHz, CDCl\(_3\)) 6.95-6.88 (dt, J = 15.7, 6.8, 1H), 5.87-5.83 (dt, J = 15.7, 1.5, 1H), 4.27-4.17 (q, J = 7.2, 2H), 4.07 (s, 2H), 2.80 (t, J = 7.2, 2H), 2.55-2.50 (tdd, J = 7.0, 7.0, 1.5, 2H), 1.28 (t, J = 7.2, 3H); \( \delta_{t} \) (100 MHz, CDCl\(_3\)) 201.1, 166.2, 146.1, 122.6, 60.3, 47.9, 37.7, 25.7, 14.2; HRMS found ESI [M+Na]^+ 227.0454, C_{9}H_{15}ClO_{3}Na requires 227.0451.

![Structural formula](image)

1j: \( \delta_{\text{max}} \) (film)/ cm\(^{-1}\) 3775, 3312, 2937, 2482, 1658, 1452, 1202, 796, 736, 700; \( \delta_{t} \) (500 MHz, DMSO, 98°C) 7.36-7.33 (m, 2H), 7.28-7.25 (m, 3H), 6.80-6.67 (m, 1H), 6.08 (d, J = 16.1, 1H), 4.58 (s, 1H), 4.34 (s, 1H), 3.44 (t, J = 7.2, 2H), 2.52-2.43 (m, 4H), 0.90 (t, J = 7.2, 3H); \( \delta_{t} \) (100 MHz, DMSO) a mixture of rotamers \( \delta_{t} \), 200.2, 166.4, 166.3, 143.7, 143.0, 137.5, 136.9, 131.8, 131.2, 128.8, 128.5, 127.5, 127.2, 50.5, 47.9, 45.6, 44.3, 42.2, 42.1, 32.5, 32.2, 31.0, 29.9, 8.0; HRMS found EI [M]^+ 293.1775, C_{16}H_{15}NO_{2} requires 293.1183.

**General procedure for the diastereoselective cyclopropanation Reaction:** DABCO (11.2 mg, 0.1 mmol, in 2.5 ml MeCN) and Na\(_2\)CO\(_3\) (0.65 mmol, 69 mg) were added to a solution of chloroketone (0.5 mmol) in MeCN (2.5 ml) and the reaction mixture was stirred at 80°C for the time stated. After completion, the reaction mixture was diluted with Et\(_2\)O (10 ml) and an aqueous solution of ammonium chloride was added (15 ml). The aqueous layer was extracted with Et\(_2\)O (3 • 10 ml). The combined organic layers were washed with water (30 ml), brine (30 ml) and dried over MgSO\(_4\). The solvent was removed under reduced pressure and the crude product was purified by column chromatography on silica gel.

![Structural formula](image)

2a: \( \delta_{\text{max}} \) (film)/ cm\(^{-1}\) 2940, 1695, 1497, 1416, 1295, 1236, 1172, 1103, 1064, 1031, 880, 749 701; \( \delta_{t} \) (600 MHz, CDCl\(_3\)) 7.30-7.26 (m, 2H), 7.21-7.17 (m, 3H), 2.91 (s, 4H), 2.48-2.47 (dd, J = 4.1, 4.1, 1H), 2.31-2.29 (dd, J = 8.2, 4.1, 1H), 2.28 (dd, J = 4.4, 4.4 1H), 2.12-2.09 (m, 1H), 2.12-2.05 (m, 1H), 1.94-1.90 (m, 2H), 1.79-1.72 (m, 1H), 1.58-1.50 (m, 1H); \( \delta_{t} \) (125 MHz, CDCl\(_3\)) 205.1, 205.2, 140.7, 128.5, 128.3, 126.2, 45.5, 37.1, 35.7, 30.3, 29.9, 26.6, 20.6, 18.2; HRMS found EI [M]^+ 242.1317, C_{15}H_{15}O requires 242.1307.
2b: $\delta_{\text{max}}$ (film)/ cm$^{-1}$ 2941, 1694, 1668, 1449, 1292, 1222, 1038, 897, 697; $\nu_\text{t}$ (600 MHz, CDCl$_3$) 7.96-7.94 (m, 2H), 7.60-7.58 (m, 1H), 7.50-7.47 (m, 2H), 3.27 (t, $J = 4.0$, 1H), 2.54-2.52 (dd, $J = 8.0$, 4.0, 1H), 2.44-2.34 (dt, $J = 18$, 4.5, 1H), 2.37-2.34 (m, 1H), 2.22-2.16 (ddd, $J = 18.0$, 11.8, 6.2, 1H), 2.13 (m, 1H), 2.07-2.01 (m, 1H), 1.91-1.85 (m, 1H), 1.78-1.70 (m, 1H); $\delta_\text{C}$ (125 MHz, CDCl$_3$) 205.2, 195.9, 137.3, 133.3, 128.7, 128.1, 37.3, 36.0, 27.3, 27.3, 20.8, 18.5; HRMS found ESI [M+Na]$^+$ 237.0866, C$_{12}$H$_{14}$O$_2$Na requires 237.0892.

2c: $\delta_{\text{max}}$ (film)/ cm$^{-1}$ 2943, 1692, 1415, 1358, 1290, 1237, 1180, 976, 881; $\nu_\text{t}$ (400 MHz, CDCl$_3$) 2.55-2.53 (dd, $J = 4.2$, 4.2, 1H), 2.31-2.21 (m, 2H), 2.25 (s, 3H), 2.15-2.02 (m, 2H), 2.01-1.88 (m, 2H), 1.80-1.72 (m, 1H), 1.65-1.54 (m, 1H); $\delta_\text{C}$ (100 MHz, CDCl$_3$) 205.5, 204.2, 37.5, 36.1, 31.2, 31.1, 27.0, 21.0, 18.7; HRMS found ESI [M]$^+$ 152.0837, C$_9$H$_{12}$O$_2$ requires 152.0837.

2d: $\delta_{\text{max}}$ (film)/ cm$^{-1}$ 3500, 2946, 1692, 1343, 1238, 1111, 1087, 999, 891, 878, 751, 687; $\nu_\text{t}$ (600 MHz, CDCl$_3$) 9.20 (d, $J = 4.3$, 1H), 2.54-2.52 (dd, $J = 4.2$, 4.2 1H), 2.38-2.35 (m, 1H), 2.33 (dd, $J = 4.4$, 1H), 2.23-2.20 (m, 1H), 2.15-2.09 (ddd, $J = 18.2$, 11.9, 6.3, 1H), 2.07-2.03 (m, 1H), 2.02-1.96 (m, 1H), 1.83-1.76 (m, 1H), 1.64-1.56 (m, 1H); $\delta_\text{C}$ (125 MHz, CDCl$_3$) 203.9, 196.8, 37.1, 32.8, 31.9, 24.3, 20.3, 18.0; HRMS found EI [M]$^+$ 138.0687, C$_9$H$_{10}$O$_2$ requires 138.0681.

2e: $\delta_{\text{max}}$ (film)/ cm$^{-1}$ 2978, 1721, 1369, 1251, 1149; $\nu_\text{t}$ (600 MHz, CDCl$_3$) 2.32-2.26 (dt, $J = 18.1$, 4.6, 1H), 2.24-2.19 (m, 2H), 2.13-2.00 (m, 3H), 1.97-1.88 (m, 1H), 1.79-1.70 (m, 1H), 1.64-1.52 (m, 1H), 1.43 (s, 9H); $\delta_\text{C}$ (125 MHz, CDCl$_3$) 205.7, 170.2, 81.4, 37.0, 33.5, 28.0, 24.88, 24.5, 20.5, 18.3; HRMS found ESI [M+Na]$^+$ 233.1149, C$_{12}$H$_{13}$O$_2$Na requires 233.1154.

2f: $\delta_{\text{max}}$ (film)/ cm$^{-1}$ 2947, 1701, 1447, 1306, 1147, 1086, 689; $\nu_\text{t}$ (600 MHz, CDCl$_3$) 7.86-7.78 (m, 2H), 7.63-7.60 (m, 1H), 7.54-7.49 (m, 2H), 2.90 (dd, $J = 4.4$, 4.4 1H), 2.50-2.47 (m, 1H), 2.41-2.38 (dd, $J = 8.7$, 4.2 1H), 2.23-2.17 (m, 1H), 2.06-1.88 (m, 3H), 1.74-1.67 (m, 1H), 1.47-1.36 (m, 1H); $\delta_\text{C}$ (125 MHz, CDCl$_3$) 202.9, 140.2, 134.3, 129.9, 128.1, 41.1, 37.6, 31.4, 22.1, 20.2, 18.3; HRMS found ESI [M]$^+$ 250.0665, C$_{13}$H$_{14}$O$_3$S requires 250.0664.
2g: $\delta_{\text{max}}$ (film)/ cm$^{-1}$ 2939, 2869, 1688, 1665, 1607, 1447, 1338, 1242, 1179, 1128, 992, 893, 697; $\delta$ (600 MHz, CDCl$_3$) 7.94-7.91 (m, 2H), 7.58-7.55 (m, 1H), 7.48-7.46 (m, 2H), 7.04 (d, J = 15.1, 1H), 6.55-6.51 (dd, J = 15.1, 9.8, 1H), 2.42-2.42 (m, 1H), 2.36 (dt, J = 18.2, 4.6, 1H), 2.17-2.07 (m, 3H), 2.04-1.97 (m, 2H), 1.85-1.65 (m, 2H); $\delta$ (125 MHz, CDCl$_3$) 205.2, 189.5, 148.6, 137.7, 132.8, 128.6, 128.4, 124.9, 37.0, 35.0, 26.8, 26.4, 20.9, 18.4; HRMS found EI [M]$^+$ 240.1149, C$_{10}$H$_{16}$O$_2$ requires 240.1150.

2h: $\delta_{\text{max}}$ (film)/ cm$^{-1}$ 2978, 1721, 1369, 1251, 1149; $\delta$ (400 MHz, CDCl$_3$) 2.43-2.41 (dd, J = 8.8, 1H), 2.25-2.17 (m, 2H), 2.13-1.96 (m, 3H), 1.90 (dd, J = 3.0, 1H), 1.42 (s, 9H); $\delta$ (100 MHz, CDCl$_3$) 212.1, 169.4, 81.6, 35.7, 32.0, 28.9, 28.0, 27.6, 22.4; HRMS found ESI [M+Na]$^-$ 219.1000, C$_{11}$H$_{16}$O$_3$Na requires 219.097

2i: $\delta_{\text{max}}$ (film)/ cm$^{-1}$ 2984, 1710, 1654, 1268, 1179, 1039; $\delta$ (600 MHz, CDCl$_3$) 4.16 (q, J = 7.3, 2H), 2.53-2.49 (m, 1H), 2.29-2.20 (m, 2H), 2.17-2.03 (m, 3H), 2.01-1.99 (dd, J = 3.3, 2.7, 1H) 1.27 (t, J = 7.3, 3H); $\delta$ (125 MHz, CDCl$_3$) 211.7, 170.4, 61.2, 35.8, 31.9, 29.2, 26.5, 22.5, 14.2; HRMS found EI [M]$^+$ 168.0789, C$_9$H$_{12}$O$_3$ requires 168.0786.

2j: $\delta_{\text{max}}$ (film)/ cm$^{-1}$ 3057, 2939, 2856, 2865, 1691, 1630, 1499, 1454, 1359, 1314, 1243, 1217, 1180, 1126, 1087, 1072, 1030, 986, 876, 760, 732; $\delta$ (400 MHz, CDCl$_3$) 7.35-7.26 (m, 3H), 7.23-7.21 (m, 2H), 4.69 (d, J = 14.8, 1H), 4.44 (d, J = 14.8, 1H), 3.13-2.99 (m, 2H), 2.65-2.59 (m, 2H), 2.57-2.55 (dd, J = 4.1, 1.7, 1H), 2.40-2.37 (dd, J = 8.3, 3.5, 1H), 2.15-2.12 (m, 1H), 2.00-1.95 (m, 2H), 1.08 (t, J = 7.25, 3H); $\delta$ (100 MHz, CDCl$_3$) 206.7, 167.8, 136.9, 128.7, 127.9, 127.5, 50.2, 41.9, 37.0, 28.1, 27.6, 24.6, 20.0, 7.6; HRMS found EI [M]$^+$ 257.1423, C$_{19}$H$_{19}$NO$_2$ requires 257.1416.

**Enantioselective Organocatalytic Cyclopropanation Reaction:** Quinine derivate 5 (0.1 mmol, 33.8 mg, in 2.5 ml MeCN) Na$_2$CO$_3$ (0.6 mmol, 50 mg) and NaBr (0.125 mmol, 12.8 mg) were added to a solution of chloroketone (0.5 mmol) in MeCN (2.5 ml) and the reaction mixture was stirred at 80°C for 24 hours. After completion, the reaction mixture was diluted with Et$_2$O (10 ml) and an aqueous solution of ammonium chloride was added (15 ml). The aqueous layer was extracted with Et$_2$O (3 x 10 ml). The combined organic layers were washed with water (30 ml), brine (30 ml) and dried over MgSO$_4$. The solvent was removed under reduced pressure and the crude product was purified by column chromatography on silica gel.
\([\delta]_D^{25} = +66.1 \quad \delta = +0.390 \quad c = 0.59 \text{ chloroform (for 94\% ee)}\)

\([\delta]_D^{25} = +50.3 \quad \delta = +0.318 \quad c = 0.63 \text{ chloroform (for 70\% ee)}\)

\([\delta]_D^{25} = -66.2 \quad \delta = +0.255 \quad c = 0.385 \text{ chloroform (for 93\% ee)}\)

HPLC:
OD column, 85:15 hexane/IPA, flow 1ml/min
Retention time
(+)-enantiomer 12.075 min, (-)-enantiomer 13.298 min

Note: Absolute stereochemistry has not yet been determined.