N-Heterocyclic carbene-catalyzed enantioselective synthesis of functionalized cyclopentenes via α,β-unsaturated acyl azoliums


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1. General Information

Unless otherwise specified, all reactions were carried out under an atmosphere of argon in flame-dried reaction vessels with Teflon screw caps. Dry DME was purchased from commercial sources and stored under argon over 4 Å molecular sieves. The 2-bromoenals were synthesized from the corresponding \( \alpha,\beta \)-unsaturated aldehydes following the literature procedure.\(^1\) All the malonic ester derivatives were prepared following the literature procedure.\(^2\) The triazolium salt 4 was synthesized following the literature procedure.\(^3\) Na\(_2\)CO\(_3\) was dried by heating at 120 °C under vacuum and cooling under argon.

Analytical thin layer chromatography was performed on TLC Silica gel 60 F\(_{254}\). Visualization was accomplished with short wave UV light or KMnO\(_4\) staining solutions followed by heating. Flash chromatography was performed on silica gel (230-400 mesh) by standard techniques eluting with Pet. Ether-EtOAc solvent system.

All compounds were fully characterized. \(^1\)H and \(^1\)\(^3\)C NMR spectra were recorded on Bruker AV 400 in solvents as indicated. Chemical shifts (\(\delta\)) are given in ppm. The residual solvent signals were used as references and the chemical shifts converted to the TMS scale (CDCl\(_3\) : \(\delta\)H = 7.26 ppm, \(\delta\)C = 77.16 ppm). Infra-red spectra were recorded on a Bruker FT-IR (ATR mode) Infra-red Spectrophotometer. The wave numbers (\(n\)) of recorded IR-signals are quoted in cm\(^{-1}\). HRMS (ESI) data were recorded on a Thermo Scientific Q-Exactive, Accela 1250 pump. Optical rotation was measured with a JASCO P 2000 digital polarimeter at rt using 50 mm cell of 1 mL capacity. HPLC analysis was performed on Shimadzu Class-VP V6.12 SP5 with UV detector. X-ray intensity data were collected on a Bruker SMART APEX II CCD diffractometer with graphite-monochromatized (Mo Ka=0.71073 Å) radiation at ambient temperature.

2. General Procedure for the Optimization of Reaction Conditions

To a oven-dried Schlenk reaction vessel equipped with a magnetic stir bar was taken the (Z)-2-bromo-3-phenylacrylaldehyde 1a (0.080 g, 0.38 mmol), dimethyl 2-(2-oxo-2-phenylethyl)malonate 2a (0.062 g, 0.25 mmol) and base (1.00 mmol, 4.00 equiv) was added. The mixture was kept under argon atmosphere. To this mixture was added solvent (3.0 mL) under a positive pressure of argon, and the mixture was stirred at 32 °C. To this stirring solution was added the triazolium salt 4 (9.2 mg, 0.025 mmol, 10 mol %), and the resulting mixture was stirred at 32 °C for 24 h. Evaporation of the solvent followed by silica gel flash column chromatography afforded the cyclopentene derivative 3a. The enantiomeric excess was determined by HPLC analysis on a chiral column.

### Optimization Studies

<table>
<thead>
<tr>
<th>entry</th>
<th>variation of the standard conditions(^a)</th>
<th>yield 3a (%)(^b)</th>
<th>ee 3a (%)(^c)</th>
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<tr>
<td>1</td>
<td>none</td>
<td>52</td>
<td>99</td>
</tr>
<tr>
<td>2</td>
<td>reaction time 60 h instead of 24 h</td>
<td>65</td>
<td>99</td>
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<td>3</td>
<td>reaction run at 60 °C instead of 32 °C</td>
<td>&lt;5 n.d.</td>
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<tr>
<td>4</td>
<td>Cs(_2)CO(_3) instead of Na(_2)CO(_3)</td>
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<td>91</td>
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<td>5</td>
<td>KO(_\text{t-Bu}) instead of Na(_2)CO(_3)</td>
<td>&lt;5 n.d.</td>
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<td>DBU instead of Na(_2)CO(_3)</td>
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<td>9</td>
<td>1,4-dioxane instead of THF</td>
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<td>toluene instead of THF</td>
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<td>11</td>
<td>DME instead of THF</td>
<td>54</td>
<td>99</td>
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<tr>
<td>12</td>
<td>DME instead of THF, run for 72 h</td>
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\(^a\) Standard conditions: 1a (0.38 mmol), 2a (0.25 mmol), 4 (10 mol %), Na\(_2\)CO\(_3\) (4.0 equiv), THF (3.0 mL), 32 °C and 24 h. \(^b\) Isolated yield after column chromatography. \(^c\) Determined by HPLC analysis on a chiral column.
3. General Procedure for the Enantioselective Synthesis of Functionalized Cyclopentenes

To an oven-dried Schlenk reaction vessel with a teflon screw cap was taken the 2-bromoenal 1 (0.75 mmol), the malonic ester derivative 2 (0.50 mmol), and Na$_2$CO$_3$ (212 mg, 2.0 mmol, 4.0 equiv). The mixture was kept under argon atmosphere, and dry DME (6.0 mL) was then introduced into the vessel by syringe under a positive pressure of argon, and the mixture was stirred at 32 °C. To this stirring solution was added the triazolium salt 4 (18.4 mg, 0.05 mmol), and the resulting mixture was stirred at 32 °C for 72 h. Evaporation of the solvent followed by silica gel flash column chromatography afforded the cyclopentene derivatives 3 in moderate to good yields with excellent enantioselectivity. [The racemic cyclopentenes were synthesized by treating 1 and 2 with IMes.HCl in the presence of Cs$_2$CO$_3$ (1.5 equiv) and NaH (1.0 equiv) in THF for 12 h at 32 °C]
4. X-ray data of 3c and 11r

Single crystals of compound 3c, obtained from dichloromethane. X-ray intensity data were collected on a Bruker SMART APEX II CCD diffractometer with graphite-monochromatized (Mo Kα=0.71073 Å) radiation at ambient temperature. The X-ray generator was operated at 50 kV and 30 mA. Diffraction data were collected with a ω scan width of 0.5° and at different settings of φ and 2θ. The sample-to-detector distance was fixed at 5.00 cm. The X-ray data acquisition was monitored by APEX II program suite. All the data were corrected for Lorentz-polarization and absorption effects using SAINT and SADABS programs integrated in APEX II program package. The structures were solved by direct method and refined by full matrix least squares, based on $F^2$, using SHELX-97. All the H-atoms were placed in geometrically idealized position (C-H = 0.93 Å for the phenyl H-atom, C-H = 0.97 Å for the methylene H-atom, C-H = 0.98 Å for the methine H-atom and C-H = 0.96 Å for the methyl H-atom) and constrained to ride on their parent atoms [$U_{\text{iso}}(H) = 1.2U_{\text{eq}}(C)$ for the phenyl, methylene and methine group and $U_{\text{iso}}(H) = 1.5U_{\text{eq}}(C)$ for the methyl group]. ORTEP was generated using ORTEP-32 program.

Crystallographic data for 3c. (C$_{21}$H$_{19}$O$_4$Br): $M = 415.27$, Crystal dimensions 0.49 x 0.45 x 0.41 mm$^3$, trigonal, space group $P\overline{3}$_2, $a = 11.7082(7)$, $b = 11.7082(7)$, $c = 11.9217(8)$ Å, $\alpha = 90^\circ$, $\beta = 90^\circ$, $\gamma = 120^\circ$, $V = 1415.30(15)$ Å$^3$, $Z = 3$, $\rho_{\text{calc}} = 1.462$ gcm$^{-3}$, $\mu$ (Mo-Kα) = 2.201 mm$^{-1}$, $F(000) = 636$, $2\theta_{\text{max}} = 67.22^\circ$, $T = 296(2)$ K, 32442 reflections collected, 7324 unique ($R_{\text{int}}=0.0360$), 4525 observed ($I > 2\sigma(I)$) reflections, 238 refined parameters, $R$ value 0.0340, $wR2 = 0.0730$, (all data $R = 0.0759$, $wR2 = 0.0838$), $S = 0.995$, minimum and maximum transmission 0.412 and 0.466; maximum and minimum residual electron densities +0.44 and −0.43 e Å$^{-3}$. The absolute configuration was established by anomalous dispersion effect (Flack parameter of 0.0174(11)) in X-ray diffraction measurements which is caused by the presence of bromine atom in the molecule.

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Figure 1. ORTEP of 3c showing atom numbering scheme. Displacement ellipsoids are drawn at the 30% probability level and H atoms are shown as small spheres of arbitrary radii.

X-ray intensity data measurements of compound 11r was carried out on a Bruker SMART APEX II CCD diffractometer with graphite-monochromatized (MoKα = 0.71073Å) radiation at room temperature. The X-ray generator was operated at 50 kV and 30 mA. A preliminary set of cell constants and an orientation matrix were calculated from three sets of 36 frames. Data were collected with ω scan width of 0.5° at different settings of φ and 2θ with a frame time of 15 secs keeping the sample-to-detector distance fixed at 5.00 cm. The X-ray data collection was monitored by APEX2 program (Bruker, 2006). All the data were corrected for Lorentzian, polarization and absorption effects using SAINT and SADABS programs (Bruker, 2006). SHELX-97 was used for structure solution and full matrix least-squares refinement on $F^2$. All the hydrogen atoms were placed in geometrically idealized position and constrained to ride on their parent atoms. ORTEP III3 views of both compounds were drawn with 30% probability displacement ellipsoids and H atoms are shown as small spheres of arbitrary radii.
Crystal data of 11r C_{20}H_{22}O_{8}, M = 390.38, colorless block, 0.39 x 0.09 x 0.06 mm^3, monoclinic, space group C2, \(a = 20.4540(10)\) Å, \(b = 7.1698(3)\) Å, \(c = 15.6356(8)\) Å, \(\beta = 121.607(6)°\), \(V = 1952.84(16)\) Å^3, \(Z = 4\), \(T = 296(2)\) K, \(2\theta_{\text{max}} = 52.00°\), \(D_{\text{calc}}(\text{g cm}^{-3}) = 1.328\), \(F(000) = 824\), \(\mu(\text{mm}^{-1}) = 0.103\), 11890 reflections collected, 3508 unique reflections \(R_{\text{int}} = 0.0436\), 2708 observed \((I > 2\sigma(I))\) reflections, multi-scan absorption correction, \(T_{\text{min}} = 0.961\), \(T_{\text{max}} = 0.994\), 257 refined parameters, \(S = 1.095\), \(R_1 = 0.0515\), \(wR_2 = 0.0972\) (all data \(R = 0.0722\), \(wR_2 = 0.1054\)), maximum and minimum residual electron densities; \(\Delta \rho_{\text{max}} = 0.14\), \(\Delta \rho_{\text{min}} = -0.17\) (eÅ^{-3}).

Figure 2. ORTEP of 11r showing atom numbering scheme. Displacement ellipsoids are drawn at the 30% probability level and H atoms are shown as small spheres of arbitrary radii.
5. Synthesis and Characterization of Functionalized Cyclopentenes

Dimethyl (S)-2,4-diphenylcyclopent-3-ene-1,1-dicarboxylate (3a)

Following the general procedure, treatment of \((Z)-2\)-bromo 3-phenylacrylaldehyde 1a (158.3 mg, 0.75 mmol) and dimethyl 2-(2-oxo-2-phenylethyl)malonate 2a (125.1 mg, 0.50 mmol) with triazolium salt 4 (18.4 mg, 0.05 mmol), Na₂CO₃ (212 mg, 2.0 mmol) in DME (6.0 mL) and stirring the reaction mixture at 32 °C for 72 h followed by flash column chromatography (EtOAc-Pet. ether 10:90) to afford dimethyl (S)-2,4-diphenylcyclopent-3-ene-1,1-dicarboxylate 3a as a light yellow solid (126.1 mg, 75%).

\[ R_f (\text{Pet. ether } / \text{EtOAc} = 80/20): 0.65; 99\% \text{ ee, } [\alpha]_D^{25} = -279.45 \text{ (c 0.4, CHCl}_3). \]

**HPLC** (Kromasil 5-AmyCoat, 90:10 Hexane / IPA, 0.7 mL/min.) Major: 10.0 min, Minor: 13.3 min. **¹H NMR** (400 MHz, CDCl₃) \( \delta \) 7.54 (d, \( J = 7.4 \text{ Hz} \), 2H, Hₐ), 7.39 (t, \( J = 7.7 \text{ Hz} \), 2H, Hₐ), 7.33-7.22 (m, 6H, Hₐ), 6.16 (s, 1H, Hₖ), 5.08 (s, 1H), 3.97-3.92 (m, 1H), 3.81 (s, 3H, CH₃), 3.21(d, \( J = 17.0 \text{ Hz} \), 1H), 3.18 (s, 3H, CH₃). **¹³C NMR** (100 MHz, CDCl₃) \( \delta \) 172.56, 169.86, 140.39, 139.22, 135.09, 129.19, 128.62, 128.17, 127.99, 127.50, 126.39, 125.95, 65.22, 57.35, 53.11, 52.06, 40.83. **HRMS (ESI)** calculated [M+Na]⁺ for C₂₁H₂₀O₄Na: 359.1254, found: 359.1247. **FTIR (cm⁻¹)** 3463, 3059, 3029, 2952, 2843, 2104, 1734, 1697, 1638, 1436, 1257, 1196, 1164, 1028, 964, 863, 697.

Dimethyl (S)-2-phenyl-4-(p-tolyl)cyclopent-3-ene-1,1-dicarboxylate (3b)

Following the general procedure, treatment of \((Z)-2\)-bromo 3-phenylacrylaldehyde 1a (158.2 mg, 0.75 mmol) and dimethyl 2-(2-oxo-2-(p-tolyl)ethyl)malonate 2b (132.0 mg, 0.50 mmol) with triazolium salt 4 (18.4 mg, 0.05 mmol), Na₂CO₃ (212 mg, 2.0 mmol) in DME (6.0 mL) and stirring the reaction mixture at 32 °C for 72 h followed by flash column chromatography (EtOAc-Pet. ether 10:90) to afford dimethyl (S)-2-phenyl-4-(p-tolyl)cyclopent-3-ene-1,1-dicarboxylate 3b as a white solid (96.4 mg, 55%).

\[ R_f (\text{Pet. ether } / \text{EtOAc} = 80/20): 0.67; 99\% \text{ ee, } [\alpha]_D^{25} = -250.61 \text{ (c 0.3, CHCl}_3). \]

**HPLC** (Kromasil 5-AmyCoat, 90:10 Hexane / IPA, 0.7 mL/min.) Major: 11.4 min, Minor: 20.0 min. **¹H NMR** (400 MHz, CDCl₃) \( \delta \) 7.45 (d, \( J = 8.1 \text{ Hz} \), 2H, Hₐ), 7.32-7.25 (m, 5H, Hₐ), 7.22 (d, \( J = 8.0 \), 2H, 2013, 2088.

\[ \text{S8} \]
H_{ar}) 6.12 (s, 1H, Holefinic), 5.09 (s, 1H), 3.97-3.93 (m, 1H), 3.82 (s, 3H, CH_{3}), 3.23-3.19 (m,4H), 2.41 (s, 3H, CH_{3}). \textbf{^{13}C NMR (100 MHz, CDCl}_3) \delta 172.57, 169.90, 140.25, 139.34, 137.84, 132.28, 129.28, 129.18, 128.13, 127.44, 125.86, 125.39, 65.21, 57.31, 53.08, 52.03, 40.83, 21.31. \textbf{HRMS (ESI)} calculated [M+Na]^+ for C_{22}H_{22}O_{4}Na: 373.1410, found: 373.1401. \textbf{FTIR (cm}^{-1}) 3427, 3028, 2951, 1734, 1634, 1514, 1492, 1435, 1262, 1222, 1196, 1164, 1058, 964, 903, 763, 668.

**Dimethyl (S)-4-(4-bromophenyl)-2-phenylcyclopent-3-ene-1,1-dicarboxylate (3c)**

Following the general procedure, treatment of (Z)-2-bromo 3-phenylacrylaldehyde 1a (158.2 mg, 0.75 mmol) and dimethyl 2-(2-(4-bromophenyl)-2-oxoethyl)malonate 2c (164.5 mg, 0.50 mmol) with triazolium salt 4 (18.4 mg, 0.05 mmol), Na_{2}CO_{3} (212 mg, 2.0 mmol) in DME (6.0 mL) and stirring the reaction mixture at 32 °C for 72 h followed by flash column chromatography (EtOAc-Pet. ether 10:90) to afford Dimethyl (S)-4-(4-bromophenyl)-2-phenylcyclopent-3-ene-1,1-dicarboxylate 3c as a white solid (176.0 mg, 85%).

\[ R_f \text{ (Pet. ether /EtOAc = 80/20): 0.64; 99% ee, } [\alpha]^D_{25} = -203.02 \text{ (c 0.25, CHCl}_3). \textbf{HPLC (Kromasil 5-AmyCoat, 90:10 Hexane / IPA, 0.7 mL/min.) Major: 13.8 min, Minor: 27.6 min.} \textbf{^1H NMR (400 MHz, CDCl}_3) \delta 7.52−7.49 (m, 2H, H_{ar}), 7.40−7.38 (m, 2H, H_{ar}), 7.31−7.21(m, 5H, H_{ar}), 6.16−6.14 (m, 1H, Holefinic), 5.07 (s, 1H), 3.93-3.88 (m, 1H), 3.81 (s, 3H, CH_{3}), 3.18 3.14 (m, 4H). \textbf{^{13}C NMR (100 MHz, CDCl}_3) \delta 172.43, 169.78, 139.41, 138.99, 134.02, 131.76, 129.16, 128.24, 127.61, 127.54, 127.24, 121.91, 65.22, 57.42, 53.19, 52.14, 40.83. \textbf{HRMS (ESI)} calculated [M+Na]^+ for C_{22}H_{21}O_{4}BrNa: 437.0359, found: 437.0349. \textbf{FTIR (cm}^{-1}) 3685, 3432, 3021, 2401, 2357, 1713, 1602, 1521, 1490, 1433, 1266, 1216, 1075, 929, 772, 670.

**Dimethyl (S)-4-(4-fluorophenyl)-2-phenylcyclopent-3-ene-1,1-dicarboxylate (3d)**

Following the general procedure, treatment of (Z)-2-bromo 3-phenylacrylaldehyde 1a (158.2 mg, 0.75 mmol) and dimethyl 2-(2-(4-fluorophenyl)-2-oxoethyl)malonate 2d (134.1 mg, 0.50 mmol) with triazolium salt 4 (18.4 mg, 0.05 mmol), Na_{2}CO_{3} (212 mg, 2.0 mmol)
in DME (6.0 mL) and stirring the reaction mixture at 32 °C for 72 h followed by flash column chromatography (EtOAc-Pet. ether 10:90) to afford dimethyl (S)-4-(4-fluorophenyl)-2-phenylcyclopent-3-ene-1,1-dicarboxylate 3d as a white solid (110.0 mg, 62%). 

\[ R_f \] (Pet. ether /EtOAc = 80/20): 0.62; >99% ee, \([\alpha]_{D}^{25} = -234.52 \) (c 0.5, CHCl3). HPLC (Kromasil 5-AmyCoat, 90:10 Hexane / IPA, 0.7 mL/min.) Major: 12.6 min, Minor: 20.9 min. 

\(^1\)H NMR (400 MHz, CDCl3) \(\delta \) 7.51-7.48 (m, 2H, H\text{ar}), 7.31-7.23 (m, 5H, H\text{ar}), 7.09-7.05 (m, 2H, H\text{ar}), 6.08 (s, 1H, Holefinic), 5.08 (s, 1H), 3.94-3.89 (m, 1H), 3.81 (s, 3H, CH3), 3.19-3.15 (m, 4H). 

\(^{13}\)C NMR (100 MHz, CDCl3) \(\delta \) 172.45, 169.80, 162.54 (d, \(J = 248.6 \) Hz), 139.22 (d, \(J = 18.7 \) Hz), 131.27 (d, \(J = 3.2 \) Hz), 129.12, 128.18, 127.62, 127.53, 126.07, 115.50 (d, \(J = 21.6 \) Hz), 65.20, 57.32, 53.13, 52.08, 40.97. HRMS (ESI) calculated [M+Na]+ for C\textsubscript{21}H\textsubscript{19}O\textsubscript{4}FNa: 377.1160, found: 377.1150. 

FTIR (cm\(^{-1}\)) 3466, 3027, 2953, 2845, 1732, 1638, 1603, 1511, 1436, 1224, 1099, 1059, 1023, 939, 834, 759.

Dimethyl (S)-4-(4-nitrophenyl)-2-phenylcyclopent-3-ene-1,1-dicarboxylate (3e) 

Following the general procedure, treatment of (Z)-2-bromo 3-phenylacryaldehyde 1a (158.2 mg, 0.75 mmol) and dimethyl 2-(2-(4-nitrophenyl)-2-oxoethyl)malonate 2e (147.6 mg, 0.50 mmol) with triazolium salt 4 (18.4 mg, 0.05 mmol), Na\textsubscript{2}CO\textsubscript{3} (212 mg, 2.0 mmol) in DME (6.0 mL) and stirring the reaction mixture at 32 °C for 120 h followed by flash column chromatography (EtOAc-Pet. ether 10:90) to afford Dimethyl (S)-4-(4-nitrophenyl)-2-phenylcyclopent-3-ene-1,1-dicarboxylate 3e as a yellow oil (134.0 mg, 70%). 

\[ R_f \] (Pet. ether /EtOAc = 80/20): 0.48; 99% ee, \([\alpha]_{D}^{25} = -217.42 \) (c 0.2, CHCl3). HPLC (Kromasil 5-AmyCoat, 80:20 Hexane / IPA, 0.7 mL/min.) Major: 19.6 min, Minor: 40.7 min. 

\(^1\)H NMR (400 MHz, CDCl3) \(\delta \) 8.23 (d, \(J = 8.5 \) Hz, 2H, H\text{ar}), 7.64 (d, \(J = 8.8 \) Hz, 2H, H\text{ar}), 7.29-7.20 (m, 5H, H\text{ar}), 6.36 (s, 1H, Holefinic), 5.12 (s, 1H), 3.98-3.92 (m, 1H), 3.82 (s, 3H, CH3), 3.21 (d, \(J = 16.7 \) Hz), 3.16 (s, 3H, CH3). 

\(^{13}\)C NMR (100 MHz, CDCl3) \(\delta \) 172.15, 169.53, 147.15, 141.26, 138.18, 138.36, 131.33, 129.07, 28.31, 127.77, 126.54, 123.98, 65.10, 57.51, 53.25, 52.20, 40.80. HRMS (ESI) calculated [M+Na]+ for C\textsubscript{21}H\textsubscript{19}O\textsubscript{6}NNa: 404.1105, found: 404.1097. FTIR (cm\(^{-1}\)) 3444, 3021, 2401, 2357, 1731, 1635, 1520, 1434, 1345, 1268, 1216, 1107, 929, 848, 771, 670.
Dimethyl (S)-4-(2-methoxyphenyl)-2-phenylcyclopent-3-ene-1,1-dicarboxylate (3f)

Following the general procedure, treatment of (Z)-2-bromo 3-phenylacryaldehyde 1a (158.2 mg, 0.75 mmol) and dimethyl 2-(2-(2-methoxyphenyl)-2-oxoethyl)malonate 2f (104.1 mg, 0.50 mmol) with triazolium salt 4 (18.4 mg, 0.05 mmol), Na₂CO₃ (212 mg, 2.0 mmol) in DME (6.0 mL) and stirring the reaction mixture at 32 °C for 72 h followed by flash column chromatography (DCM-Pet. ether 40:60) to afford dimethyl (S)-4-(2-methoxyphenyl)-2-phenylcyclopent-3-ene-1,1-dicarboxylate 3f as a white solid (124.5 mg, 68%).

R f (Pet. ether/EtOAc = 80/20): 0.57; >99% ee, [α]D²⁵ = -218.22 (c 0.25, CHCl₃). HPLC (Chiralcel OJ-H, 90:10 Hexane / IPA, 0.7 mL/min.) Major: 17.3 min. ¹H NMR (400 MHz, CDCl₃) δ 7.39 (dd, J₁ = 1.56 Hz, J₂ = 7.56 Hz, 1H, Har), 7.29-7.20 (m, 6H, Har), 7.00-6.93 (m, 2H, Har), 6.40-6.39 (m, 1H, H olefinic), 5.06 (s, 1H), 4.00-3.96 (m, 1H), 3.87 (s, 3H, CH₃), 3.79 (s, 3H, CH₃), 3.23 (d, J = 17.1 Hz, 1H), 3.17 (s, 3H, CH₃). ¹³C NMR (100 MHz, CDCl₃) δ 172.14, 170.12, 157.97, 139.51, 137.32, 130.62, 129.26, 128.94, 128.75, 128.13, 127.36, 124.55, 120.55, 111.08, 64.65, 57.60, 55.38, 53.05, 52.03, 42.51. HRMS (ESI) calculated [M+Na]⁺ for C₂₂H₂₂O₅Na: 389.1359, found: 389.1348. FTIR (cm⁻¹) 3433, 3022, 2953, 2839, 2402, 2108, 1730, 1629, 1601, 1458, 1437, 1218, 1166, 1057, 968, 870, 702.

Dimethyl (S)-4-(2-bromophenyl)-2-phenylcyclopent-3-ene-1,1-dicarboxylate (3g)

Following the general procedure, treatment of (Z)-2-bromo 3-phenylacryaldehyde 1a (158.2 mg, 0.75 mmol) and dimethyl 2-(2-(2-bromophenyl)-2-oxoethyl)malonate 2g (164.5 mg, 0.50 mmol) with triazolium salt 4 (18.4 mg, 0.05 mmol), Na₂CO₃ (212 mg, 2.0 mmol) in DME (6.0 mL) and stirring the reaction mixture at 32 °C for 72 h followed by flash column chromatography (DCM-Pet. ether 40:90) to afford dimethyl (S)-4-(2-bromophenyl)-2-phenylcyclopent-3-ene-1,1-dicarboxylate 3g as a colourless oil (135.0 mg, 65%).

R f (Pet. ether/EtOAc = 80/20): 0.62; >99% ee, [α]D²⁵ = -202.26 (c 0.2, CHCl₃). HPLC (Kromasil 5-AmyCoat, 80:20 Hexane / IPA, 0.7 mL/min.) Major: 6.5 min, Minor: 8.0 min. ¹H NMR (400 MHz, CDCl₃) δ 7.63 (d, J = 7.9 Hz, 1H, Har), 7.39-7.26 (m, 7H, Har), 7.18 (t, J = 7.4 Hz, 1H, Har), 5.96 (s, 1H, H olefinic), 5.07 (s, 1H), 3.96 (d, J = 17.1 Hz, 1H), 3.83 (s, 3H, CH₃), 3.25-3.19 (m, 4H). ¹³C NMR (100 MHz, CDCl₃) δ 172.44, 169.76, 141.32, 138.82, 137.82,

**FTIR (cm⁻¹)** 3685, 3619, 3435, 3021, 2975, 2401, 2357, 1731, 1603, 1521, 1432, 1216, 1051, 929, 774, 670.

**Dimethyl (S)-4-(3-methoxyphenyl)-2-phenylcyclopent-3-ene-1,1-dicarboxylate (3h)**

Following the general procedure, treatment of (Z)-2-bromo 3-phenylacrylaldehyde 1a (158.2 mg, 0.75 mmol) and dimethyl 2-(2-(3-methoxyphenyl)-2-oxoethyl)malonate 2h (140.1 mg, 0.50 mmol) with triazolium salt 4 (18.4 mg, 0.05 mmol), Na₂CO₃ (212 mg, 2.0 mmol) in DME (6.0 mL) and stirring the reaction mixture at 32 °C for 72 h followed by flash column chromatography (EtOAc-Pet. ether 10:90) to afford dimethyl (S)-4-(3-methoxyphenyl)-2-phenylcyclopent-3-ene-1,1-dicarboxylate 3h as a light yellow oil (97 mg, 53%).

Rᶠₜ (Pet. ether /EtOAc = 80/20): 0.64; 99% ee, [α]D[^25] = -195.5 (c 0.1, CHCl₃). **HPLC** (Kromasil 5-AmyCoat, 80:20 Hexane / IPA, 0.7 mL/min.) Major: 8.2 min, Minor: 10.3 min. **¹H NMR (400 MHz, CDCl₃)** δ 7.33 (m, 6H, Har), 7.14 (d, J = 7.7 Hz, 1H, Har), 7.06 (s, 1H, Har), 6.89-6.87 (m, 1H, Har), 6.16 (s, 1H, Holefinic), 5.07 (s, 1H), 3.93 (d, J = 16.9 Hz, 1H), 3.86 (s, 3H, CH₃), 3.81 (s, 3H, CH₃), 3.21-3.18 (m, 4H). **¹³C NMR (100 MHz, CDCl₃)** δ 172.55, 169.88, 159.87, 140.33, 139.14, 136.52, 129.62, 129.20, 128.21, 127.55, 126.83, 118.57, 113.63, 111.54, 65.19, 57.31, 55.41, 53.17, 52.12, 40.88. **HRMS (ESI)** calculated [M+Na]⁺ for C₂₂H₂₂O₅Na: 389.1359, found: 389.1353. **FTIR (cm⁻¹)** 3021, 1731, 1599, 1433, 1264, 1170, 1052, 742, 668.

**Dimethyl (S)-4-(2,4-dichlorophenyl)-2-phenylcyclopent-3-ene-1,1-dicarboxylate (3i)**

Following the general procedure, treatment of (Z)-2-bromo 3-phenylacrylaldehyde 1a (158.2 mg, 0.75 mmol) and dimethyl 2-(2-(2,4-dichlorophenyl)-2-oxoethyl)malonate 2i (158.2 mg, 0.50 mmol) with triazolium salt 4 (18.4 mg, 0.05 mmol), Na₂CO₃ (212 mg, 2.0 mmol) in DME (6.0 mL) and stirring the reaction mixture at 32 °C for 72 h followed by flash column chromatography (dcm-Pet. ether 40:60) to afford dimethyl (S)-4-(2,4-dichlorophenyl)-2-phenylcyclopent-3-ene-1,1-dicarboxylate 3i as a colourless oil (117.0 mg, 58%).
**Rf** (Pet. ether /EtOAc = 80/20): 0.78; >99% ee, [α]D$^{25}$ = -191.90 (c 0.3, CHCl₃). **HPLC** (Kromasil 5-AmyCoat, 90:10 Hexane / IPA, 0.7 mL/min.) Major: 8.5 min, Minor: 9.9 min. **¹H NMR (400 MHz, CDCl₃)** δ 7.43 (d, J = 2.1 Hz, 1H, H_ar), 7.33-7.24 (m, 7H, H_ar), 6.09-6.07 (m, 1H, H_olefinic), 5.07 (s, 1H), 3.95-3.90 (m, 1H), 3.81 (s, 3H, CH₃), 3.20-3.16 (m, 4H). **¹³C NMR (100 MHz, CDCl₃)** δ 172.29, 169.64, 138.59, 138.42, 133.85, 133.45, 132.58, 130.81, 130.12, 129.12, 128.26, 127.62, 127.14, 65.28, 57.26, 53.13, 52.11, 42.96. **HRMS (ESI)** calculated [M+Na]$^+$ for C₂₁H₁₈O₄Cl₂Na: 427.0474, found: 427.0465. **FTIR (cm⁻¹)** 3428, 3021, 2401, 2313, 1731, 1635, 1437, 1217, 1057, 769, 670.

**Dimethyl (S)-4-(2,4-difluorophenyl)-2-phenylcyclopent-3-ene-1,1-dicarboxylate (3j)**

Following the general procedure, treatment of (Z)-2-bromo 3-phenylacrylaldehyde 1a (158.2 mg, 0.75 mmol) and dimethyl 2-(2-(2,4-difluorophenyl)-2-oxoethyl)malonate 2j (143.0 mg, 0.50 mmol) with triazolium salt 4 (18.4 mg, 0.05 mmol), Na₂CO₃ (212 mg, 2.0 mmol) in DME (6.0 mL) and stirring the reaction mixture at 32 °C for 72 h followed by flash column chromatography (EtOAc-Pet. ether 10:90) to afford dimethyl (S)-4-(2,4-difluorophenyl)-2-phenylcyclopent-3-ene-1,1-dicarboxylate 3j as a white solid (143.0 mg, 77%). **Rf** (Pet. ether /EtOAc = 80/20): 0.62; 99% ee, [α]D$^{25}$ = -249.26 (c 0.35, CHCl₃). **HPLC** (Kromasil 5-AmyCoat, 99.3:0.7:0.1 Hexane / IPA/TFA, 0.5 mL/min.) Major: 20.2 min, Minor: 22.6 min. **¹H NMR (400 MHz, CDCl₃)** δ 7.41−7.35 (m, 1H, H_ar), 7.30−7.22 (m, 5H, H_ar), 6.92−6.83 (m, 2H, H_ar), 6.25 (s, 1H, H_olefinic), 5.09 (s, 1H), 3.92 (d, J = 16.7 Hz, 1H), 3.80 (s, 3H, CH₃), 3.21-3.15 (m, 4H). **¹³C NMR (100 MHz, CDCl₃)** δ 172.42, 169.83, 161.58 (dd, J₁ = 12.2 Hz, J₂ = 250.1 Hz), 161.58 (dd, J₁ = 11.7 Hz, J₂ = 254.5 Hz), 138.93, 134.08, 130.94 (d, J = 10.2 Hz), 129.66-129.51 (m, 129.15, 128.22, 127.57, 119.70 (dd, J₁ = 3.8 Hz, J₂ = 12.6 Hz), 111.33 (dd, J₁ = 3.4 Hz, J₂ = 21.2 Hz), 104.61 (t, J = 25.8 Hz), 64.57, 57.55, 53.17, 52.13, 42.08. **HRMS (ESI)** calculated [M+Na]$^+$ for C₂₁H₁₈O₄F₂Na: 395.1065, found: 395.1058. **FTIR (cm⁻¹)** 3430, 3023, 2954, 1731, 1619, 1502, 1271, 1217, 1162, 1141, 1105, 965, 854, 761, 702.
Diethyl (S) 2, 4-diphenylcyclopent-3-ene-1, 1-dicarboxylate (3k)

Following the general procedure, treatment of (Z)-2-bromo 3-phenylacrylaldehyde 1a (158.2 mg, 0.75 mmol) and diethyl 2-(2-oxo-2-phenylethyl)malonate 2k (208.7 mg, 0.50 mmol) with triazolium salt 4 (18.4 mg, 0.05 mmol), Na₂CO₃ (212 mg, 2.0 mmol) in DME (6.0 mL) and stirring the reaction mixture at 32 °C for 72 h followed by flash column chromatography (EtOAc-Pet. ether 10:90) to afford diethyl (S)-2,4-diphenylcyclopent-3-ene-1,1-dicarboxylate 3k as a colourless oil (110 mg, 61%).

Rf (Pet. ether /EtOAc = 80/20): 0.69; >99% ee, [α]D²⁵ = -265.10 (c 0.45, CHCl₃). HPLC (Kromasil 5-AmyCoat, 90:10 Hexane / IPA, 0.7 mL/min.) Major: 10.5 min, Minor: 12.0 min. ¹H NMR (400 MHz, CDCl₃) δ 7.55 (d, J = 7.4 Hz, 2H, Har), 7.40 (t, J = 7.4 Hz, 2H, Har), 7.33 (d, J = 7.4 Hz, 1H, Har), 7.31-7.22 (m, 5H, Har), 6.17 (s, 1H, Holefinic), 5.09 (s, 1H), 4.38-4.30 (m, 1H), 4.27-4.19 (m, 1H), 3.81-3.73 (m, 1H), 3.55-3.47 (m, 1H), 3.21(d, J = 16.9 Hz, 1H), 1.31 (t, J = 7.1 Hz, 3H, CH₃), 0.89 (t, J = 7.1 Hz, 3H, CH₃) ¹³C NMR (100 MHz, CDCl₃) δ 172.09, 169.53, 140.18, 139.44, 135.19, 129.34, 128.59, 128.13, 127.91, 127.43, 126.72, 125.95, 65.01, 61.85, 61.25, 57.18, 40.94, 14.14, 13.61. HRMS (ESI) calculated [M+Na]+ for C₂₃H₂₄O₄Na: 387.1567, found: 387.1555. FTIR (cm⁻¹) 3430, 3021, 2401, 1726, 1636, 1449, 1261, 1216, 1097, 928, 760, 669

(R)-1,1'-(2,4-Diphenylcyclopent-3-ene-1,1-diyl)bis(ethan-1-one) (3l)

Following the general procedure, treatment of (Z)-2-bromo 3-phenylacrylaldehyde 1a (158.2 mg, 0.75 mmol) and 3-acetyl-1-phenylpentane-1,4-dione 2l (109.0 mg, 0.50 mmol) with triazolium salt 4 (18.4 mg, 0.05 mmol), Na₂CO₃ (212 mg, 2.0 mmol) in DME (6.0 mL) and stirring the reaction mixture at 32 °C for 72 h followed by flash column chromatography (EtOAc-Pet. ether 10:90) to afford (S)-1,1'- (2,4-diphenylcyclopent-3-ene-1,1-diyl)bis(ethan-1-one) 3l as a white solid (76 mg, 50%).

Rf (Pet. ether /EtOAc = 80/20): 0.53; >99% ee, [α]D²⁵ = -406.95 (c 0.4, CHCl₃). HPLC (Kromasil 5-AmyCoat, 90:10 Hexane / IPA, 0.7 mL/min.) Major: 11.1 min, Minor: 12.3 min. ¹H NMR (400 MHz, CDCl₃) δ 7.52-7.50 (m, 2H, Har), 7.37 (t, J = 7.1 Hz, 2H, Har), 7.32-7.18 (m, 6H, Har), 6.13 (s, 1H, Holefinic), 5.06 (s, 1H), 4.06-4.00 (m, 1H), 2.94 (d, J = 17.0 Hz, 1H), 2.25 (s,
$^3$H, CH$_3$), 1.63 (s, 3H, CH$_3$). $^{13}$C NMR (100 MHz, CDCl$_3$) $\delta$ 204.43, 204.18, 139.68, 138.97, 135.10, 129.36, 128.74, 128.67, 128.06, 127.85, 127.62, 125.89, 79.24, 55.11, 38.22, 28.54, 26.81. HRMS (ESI) calculated [M+Na]$^+$ for C$_{21}$H$_{20}$O$_2$Na: 327.1356, found: 327.1346. FTIR (cm$^{-1}$) 3411, 3021, 2928, 2401, 1697, 1492, 1216, 1144, 1029, 760, 669, 622.

**Dimethyl (S)-4-phenyl-2-(p-tolyl)cyclopent-3-ene-1,1-dicarboxylate (3m)**

Following the general procedure, treatment of (Z)-2-bromo-3-(p-tolyl)acrylaldehyde 1m (168.8 mg, 0.75 mmol) and dimethyl 2-(2-oxo-2-phenylethyl)malonate 2a (125.1 mg, 0.50 mmol) with triazolium salt 4 (18.4 mg, 0.05 mmol), Na$_2$CO$_3$ (212 mg, 2.0 mmol) in DME (6.0 mL) and stirring the reaction mixture at 32 °C for 72 h followed by flash column chromatography (EtOAc-Pet. ether 10:90) to afford dimethyl (S)-4-phenyl-2-(p-tolyl)cyclopent-3-ene-1,1-dicarboxylate 3m as a colourless oil (105.0 mg, 60%).

$R_f$ (Pet. ether /EtOAc = 80/20): 0.64; >99% ee, $\left[\alpha\right]_{D}^{25} = -235.55$ (c 0.25, CHCl$_3$). HPLC (Kromasil 5-AmyCoat, 90:10 Hexane / IPA, 0.7 mL/min.) Major: 12.5 min, Minor: 24.4 min. $^1$H NMR (400 MHz, CDCl$_3$) $\delta$ 7.52 (d, $J$ = 7.4 Hz, 2H, Har), 7.37 (t, $J$ = 7.2 Hz, 2H, H$_{ar}$), 7.30 (t, $J$ = 7.3 Hz, 1H, H$_{ar}$), 7.12-7.06 (m, 4H, H$_{ar}$), 6.13 (s, 1H, Holefinic), 5.02 (s, 1H), 3.94-3.89 (m, 1H), 3.79 (s, 3H, CH$_3$), 3.20-3.16 (m, 4H), 2.31 (s, 3H, CH$_3$). $^{13}$C NMR (100 MHz, CDCl$_3$) $\delta$ 172.63, 169.95, 140.14, 137.12, 135.94, 135.15, 129.06, 128.89, 128.62, 127.95, 126.65, 125.95, 65.16, 53.12, 52.12, 40.69, 21.19. HRMS (ESI) calculated [M+Na]$^+$ for C$_{22}$H$_{22}$O$_4$Na: 373.1410, found: 373.1400. FTIR (cm$^{-1}$) 3427, 3021, 2954, 1731, 1635, 1439, 1267, 1144, 1029, 760, 669, 622.

**Dimethyl (S)-2-(4-methoxyphenyl)-4-phenylcyclopent-3-ene-1,1-dicarboxylate (3n)**

Following the general procedure, treatment of (Z)-2-bromo-3-(4-methoxyphenyl)acrylaldehyde 1n (180.8 mg, 0.75 mmol) and dimethyl 2-(2-oxo-2-phenylethyl)malonate 2a (125.1 mg, 0.50 mmol) with triazolium salt 4 (18.4 mg, 0.05 mmol), Na$_2$CO$_3$ (212 mg, 2.0 mmol) in DME (6.0 mL) and stirring the reaction mixture at 32 °C for 72 h followed by flash column chromatography (EtOAc-Pet. ether 10:90) to afford dimethyl (S)-2-(4-methoxyphenyl)-4-phenylcyclopent-3-ene-1,1-dicarboxylate 3n as a light yellow oil (110 mg, 60%).
\(R_f (\text{Pet. ether /EtOAc} = 80/20): 0.63; 95\% \text{ ee, } [\alpha]_D^{25} = -217.4 \text{ (c 0.25, CHCl}_3).\) **HPLC** (Kromasil 5-AmyCoat, 90:10 Hexane / IPA, 0.7 mL/min.) Major: 14.9 min, Minor: 28.8 min. \[^1\text{H NMR}\] (400 MHz, CDCl\(_3\)) \(\delta\) 7.51 (d, \(J = 7.3 \text{ Hz, } 2\text{H, } \text{H}_a\)), 7.37 (t, \(J = 7.1 \text{ Hz, } 2\text{H, } \text{H}_a\)), 7.30 (d, \(J = 7.2 \text{ Hz, } 1\text{H, } \text{H}_a\)), 7.13 (d, \(J = 8.7 \text{ Hz, } 2\text{H, } \text{H}_a\)), 6.80 (d, \(J = 8.7 \text{ Hz, } 2\text{H, } \text{H}_a\)), 6.11 (s, 1H, H\text{olefinic}), 5.00 (s, 1H), 3.92-3.87 (m, 1H), 3.78-3.77 (m, 6H, 2CH\(_3\)), 3.21 (s, 3H, CH\(_3\)), 3.16 (d, \(J = 16.9 \text{ Hz, } 1\text{H}).\) \[^{13}\text{C NMR}\] (100 MHz, CDCl\(_3\)) \(\delta\) 172.66, 170.00, 159.03, 140.03, 135.15, 131.00, 130.25, 128.64, 127.97, 126.69, 125.95, 113.57, 65.11, 56.60, 55.35, 53.13, 52.21, 40.64. **HRMS** (ESI) calculated [M+Na]\(^+\) for C\(_{22}\)H\(_{22}\)O\(_5\)Na: 389.1359, found: 389.1346. **FTIR** (cm\(^{-1}\)) 3021, 1733, 1215, 908, 742, 669.

**Dimethyl (S)-2-(4-bromophenyl)-4-phenylcyclopent-3-ene-1,1-dicarboxylate (3o)**

Following the general procedure, treatment of (Z)-2-bromo-3-(4-bromophenyl)acrylaldehyde 1o (108.7 mg, 0.38 mmol) and dimethyl 2-(2-oxo-2-phenylethyl)malonate 2a (62.5 mg, 0.25 mmol) with triazolium salt 4 (9.2 mg, 0.025 mmol), Na\(_2\)CO\(_3\) (106 mg, 1.0 mmol) in DME (3.0 mL) and stirring the reaction mixture at 32 °C for 72 h followed by flash column chromatography (EtOAc-Pet. ether 10:90) to afford dimethyl (S)-2-(4-bromophenyl)-4-phenylcyclopent-3-ene-1,1-dicarboxylate 3o as a light yellow oil (65.4 mg, 63%).

\(R_f (\text{Pet. ether /EtOAc} = 80/20): 0.64; >99\% \text{ ee, } [\alpha]_D^{25} = -200.97 \text{ (c 0.45, CHCl}_3).\) **HPLC** (Kromasil 5-AmyCoat, 80:20 Hexane / IPA, 0.7 mL/min.) Major: 10.5 min, Minor: 16.3 min. \[^1\text{H NMR}\] (400 MHz, CDCl\(_3\)) \(\delta\) 7.51 (d, \(J = 7.3 \text{ Hz, } 2\text{H, } \text{H}_a\)), 7.41-7.36 (m, 4H, \text{H}_a), 7.33-7.29 (m, 1H, \text{H}_a), 7.11 (d, \(J = 8.4 \text{ Hz, } 2\text{H, } \text{H}_a\)), 6.08 (d, \(J = 1.5 \text{ Hz, } 1\text{H, } \text{H}_a\)), 5.03 (s, 1H), 3.92-3.88 (m, 1H), 3.79 (s, 3H, \text{CH}_3), 3.22-3.17 (m, 4H). **HRMS** (ESI) calculated [M+Na]\(^+\) for C\(_{22}\)H\(_{22}\)O\(_5\)Na: 437.0359, found: 437.0355. **FTIR** (cm\(^{-1}\)) 3436, 3022, 2954, 2401, 1732, 1636, 1437, 1267, 1216, 1167, 1073, 932, 758.

**Dimethyl (S)-2-(4-chlorophenyl)-4-phenylcyclopent-3-ene-1,1-dicarboxylate (3p)**

Following the general procedure, treatment of (Z)-2-bromo-3-(4-chlorophenyl)acrylaldehyde 1p (92.0 mg, 0.38 mmol) and dimethyl 2-(
oxo-2-phenylethyl)malonate 2a (62.5 mg, 0.25 mmol) with triazolium salt 4 (9.2 mg, 0.025 mmol), Na₂CO₃ (106.0 mg, 1.0 mmol) in THF (3.0 mL) and stirring the reaction mixture at 32 °C for 72 h followed by flash column chromatography (EtOAc-Pet. ether 10:90) to afford dimethyl (S)-2-(4-chlorophenyl)-4-phenylcyclopent-3-ene-1,1-dicarboxylate 3p as a light yellow oil (37.0 mg, 40%).

\[ R_f (\text{Pet. ether /EtOAc} = 80/20): 0.65; 99\% \text{ ee, } [\alpha]_D^{25} = -334.60 (c 0.1, CHCl₃). \text{ HPLC (Kromasil 5-AmyCoat, 80:20 Hexane / IPA, 0.7 mL/min.) Major: 10.1 min, Minor: 14.8 min. } \]

\[ ^1H \text{ NMR (400 MHz, CDCl₃)} \delta 7.53 (d, J = 7.2 Hz, 2H, H_{ar}), 7.40 (t, J = 7.1 Hz, 2H, H_{ar}), 7.33 (t, J = 7.2 Hz, 1H, H_{ar}), 7.26 (d, J = 8.5 Hz, 2H, H_{ar}), 7.18 (d, J = 8.5 Hz, 2H, H_{ar}) 6.11 (s, 1H, H_{olefinic}), 5.06 (s, 1H), 3.94-3.89 (m, 1H), 3.81 (s, 3H, CH₃), 3.24 (s, 3H, CH₃), 3.21 (d, J = 17.3 Hz, 1H). \]

\[ ^{13}C \text{ NMR (100 MHz, CDCl₃)} \delta 172.37, 169.75, 140.90, 137.79, 134.86, 133.36, 130.55, 128.68, 128.34, 128.19, 125.99, 125.79, 65.09, 56.63, 53.23, 52.26, 40.79. \text{ HRMS (ESI) calculated } [\text{M+Na}^+] \text{ for C}_{21}H_{19}O_{4}ClNa: 393.0864, \text{ found: 393.0859. } \text{ FTIR (cm}^{-1}\text{)} 3435, 3021, 2955, 2401, 1732, 1635, 1489, 1437, 1267, 1216, 1169, 1091, 1017, 930, 770, 672. \]

Dimethyl (S)-2-(4-fluorophenyl)-4-phenylcyclopent-3-ene-1,1-dicarboxylate (3q)

Following the general procedure, treatment of (Z)-2-bromo-3-(4-fluorophenyl)acrylaldehyde 1q (171.7 mg, 0.75 mmol) and dimethyl 2-(2-oxo-2-phenylethyl)malonate 2a (125.1 mg, 0.50 mmol) with triazolium salt 4 (18.4 mg, 0.05 mmol), Na₂CO₃ (212 mg, 2.0 mmol) in DME (6.0 mL) and stirring the reaction mixture at 32 °C for 72 h followed by flash column chromatography (EtOAc-Pet. ether 10:90) to afford dimethyl (S)-2-(4-fluorophenyl)-4-phenylcyclopent-3-ene-1,1-dicarboxylate 3q as a light yellow oil (133.0 mg, 75%).

\[ R_f (\text{Pet. ether /EtOAc} = 80/20): 0.60; 99\% \text{ ee, } [\alpha]_D^{25} = -232.72 (c 0.15, CHCl₃). \text{ HPLC (Kromasil 5-AmyCoat, 90:10 Hexane / IPA, 0.7 mL/min.) Major: 11.4 min, Minor: 17.4 min. } \]

\[ ^1H \text{ NMR (400 MHz, CDCl₃)} \delta 7.52 (d, J = 8.5 Hz, 2H, H_{ar}), 7.38 (t, J = 7.1 Hz, 2H, H_{ar}), 7.31 (t, J = 7.3 Hz, 1H, H_{ar}), 7.22-7.18 (m, 2H, H_{ar}), 6.98-6.94 (m, 2H, H_{ar}), 6.11 (s, 1H, H_{olefinic}), 5.06 (s, 1H), 3.93-3.88 (m, 1H), 3.79 (s, 3H, CH₃), 3.21-3.17 (m, 4H). \]

\[ ^{13}C \text{ NMR (100 MHz, CDCl₃)} \delta 172.41, 169.80, 162.27 (d, J = 246.1 Hz), 140.61, 134.92, 130.74 (d, J = 8.0 Hz), 128.65, 128.11, 126.07, 125.96, 114.99 (d, J = 21.3 Hz), 65.09, 56.52, 53.15, 52.16, 40.74. \text{ HRMS (ESI) } \]
calculated $[\text{M+Na}]^+$ for $\text{C}_{21}\text{H}_{19}\text{O}_4\text{FNa}$: 377.1160, found: 377.1154. **FTIR (cm}$^{-1}$\)** 3441, 3028, 2053, 1734, 1636, 1604, 1507, 1438, 1265, 1224, 1098, 1018, 901, 841, 759.

**Dimethyl (S)-2-(4-(methoxycarbonyl)phenyl)-4-phenylcyclopent-3-ene-1,1-dicarboxylate (3r)**

Following the general procedure, treatment of methyl (Z)-4-(2-bromo-3-oxoprop-1-en-1-yl)benzoate 1r (201.8 mg, 0.75 mmol) and dimethyl 2-(2-oxo-2-phenylethyl)malonate 2a (125.1 mg, 0.50 mmol) with triazolium salt 4 (18.4 mg, 0.05 mmol), Na$_2$CO$_3$ (212 mg, 2.0 mmol) in DME (6.0 mL) and stirring the reaction mixture at 32 °C for 72 h followed by flash column chromatography (EtOAc-Pet. ether 10:90) to afford dimethyl (S)-2-(4-(methoxycarbonyl)phenyl)-4-phenylcyclopent-3-ene-1,1-dicarboxylate 3r as a light yellow solid (110.4 mg, 56%).

$R_f$ (Pet. ether /EtOAc = 80/20): 0.44; $\geq$99% ee, $[\alpha]_D^{25} = -224.45$ (c 0.55, CHCl$_3$). **HPLC** (Kromasil 5-AmyCoat, 90:10 Hexane / IPA, 0.7 mL/min.) Major: 27.3 min. **$^1$H NMR (400 MHz, CDCl$_3$)** $\delta$ 7.94 (d, $J = 8.2$ Hz, 2H, H$_{ar}$), 7.50 (d, $J = 7.4$ Hz, 2H, H$_{ar}$), 7.37 (t, $J = 7.3$ Hz, 2H, H$_{ar}$), 7.31 (t, $J = 6.9$ Hz, 3H, H$_{ar}$), 6.10 (d, $J = 1.5$ Hz, 1H, H$_{olefinic}$), 5.11 (s, 1H), 3.94-3.89 (m, 4H), 3.79 (s, 3H, CH$_3$), 3.21(d, $J = 16.9$ Hz, 1H), 3.15 (s, 3H, CH$_3$). **$^{13}$C NMR (100 MHz, CDCl$_3$)** $\delta$ 172.28, 169.63, 167.03, 144.79, 141.17, 134.80, 129.47, 129.34, 129.24, 128.68, 128.22, 126.00, 125.53, 65.21, 57.12, 53.27, 52.24, 52.19, 40.91. **HRMS (ESI)** calculated [M+Na]$^+$ for $\text{C}_{23}\text{H}_{22}\text{O}_6\text{Na}$: 417.1309, found: 417.1300. **FTIR (cm}$^{-1}$\)** 3426, 3021, 2401, 1729, 1617, 1439, 1281, 1217, 1113, 969, 766, 670.

**Dimethyl (R)-2-(2-fluorophenyl)-4-phenylcyclopent-3-ene-1,1-dicarboxylate (3s)**

Following the general procedure, treatment of (Z)-2-bromo-3-(2-fluorophenyl)acrylaldehyde 1s (171.7 mg, 0.75 mmol) and dimethyl 2-(2-oxo-2-phenylethyl)malonate 2a (125.1 mg, 0.50 mmol) with triazolium salt 4 (18.4 mg, 0.05 mmol), Na$_2$CO$_3$ (212 mg, 2.0 mmol) in DME (6.0 mL) and stirring the reaction mixture at 32 °C for 72 h followed by flash column chromatography (EtOAc-Pet. ether 10:90) to afford dimethyl (R)-2-(2-fluorophenyl)-4-phenylcyclopent-3-ene-1,1-dicarboxylate 3s as a colourless solid (90.3 mg, 51%).
**Rf** (Pet. ether/EtOAc = 80/20): 0.59; 94% ee, [α]D25 = -167.96 (c 0.1, CHCl3). **HPLC** (Kromasil 5-AmyCoat, 90:10 Hexane / IPA, 0.7 mL/min.) Major: 10.5 min, Minor: 12.9 min. **1H NMR** (400 MHz, CDCl3) δ 7.51 (d, J = 7.3 Hz, 2H, H_ar), 7.37 (t, J = 7.1 Hz, 2H, H_ar), 7.32-7.28 (m, 1H, H_ar), 7.22-7.17 (m, 1H, H_ar), 7.10 (t, J = 6.2 Hz, 1H, H_ar), 7.02 (t, J = 8.6 Hz, 2H, H_ar), 6.05 (s, 1H, H_olefinic), 5.46 (s, 1H), 4.02-3.97 (m, 1H), 3.79 (s, 3H, CH3), 3.22 (s, 3H, CH3) 3.18 (d, J = 17.2 Hz, 1H). **13C NMR** (100 MHz, CDCl3) δ 172.18, 169.90, 160.87 (d, J = 248.7 Hz), 140.86, 134.92, 124.39 (d, J = 3.4 Hz), 129.19 (d, J = 8.2 Hz), 126.87, 128.13, 126.52, 126.37, 126.00, 125.43, 123.96 (d, J = 8.2 Hz), 115.29 (d, J = 22.4 Hz), 64.54, 53.26, 52.24, 49.19 (d, J = 3.3 Hz), 41.01. **HRMS** (ESI) calculated [M+Na]+ for C_{21}H_{19}O_{4}FNa: 377.1160, found: 377.1152. **FTIR** (cm⁻¹) 3685, 3619, 3434, 3021, 2401, 2358, 1733, 1605, 1521, 1491, 1435, 1216, 1049, 929,773, 670.

**Dimethyl (S)-2-(naphthalen-2-yl)-4-phenylcyclopent-3-ene-1,1-dicarboxylate (3t)**

Following the general procedure, treatment of (Z)-2-bromo-3-(naphthalen-2-yl)acrylaldehyde 1t (98.0 mg, 0.38 mmol) and dimethyl 2-(2-oxo-2-phenylethyl)malonate 2a (62.5 mg, 0.25 mmol) with triazolium salt 4 (9.2 mg, 0.025 mmol), Na2CO3 (106 mg, 1.0 mmol) in DME (3.0 mL) and stirring the reaction mixture at 32 °C for 72 h followed by flash column chromatography (EtOAc-Pet. ether 10:90) to afford dimethyl (S)-2-(naphthalen-2-yl)-4-phenylcyclopent-3-ene-1,1-dicarboxylate 3t as a light yellow oil (55.0 mg, 57%).

**Rf** (Pet. ether/EtOAc = 80/20): 0.64; 99% ee, [α]D25 = -200.97 (c 0.45, CHCl3). **HPLC** (Kromasil 5-AmyCoat, 80:20 Hexane / IPA, 0.7 mL/min.) Major: 14.6 min, Minor: 20.0 min. **1H NMR** (400 MHz, CDCl3) δ 7.78-7.73 (m, 3H, H_ar), 7.68 (s, 1H, H_ar), 7.56 (d, J = 7.3 Hz, 2H, H_ar), 7.45-7.30 (m, 6H, H_ar), 6.21 (s, 1H, H_olefinic), 5.24 (s, 1H), 4.00 (d, J = 16.9 Hz, 1H), 3.81 (s, 3H, CH3), 3.25 (d, J = 16.9 Hz, 1H), 3.03 (s, 3H, CH3). **13C NMR** (100 MHz, CDCl3) δ 172.62, 169.90, 140.57, 136.80, 135.11, 133.35, 132.89, 128.69, 128.09, 128.00, 127.93, 127.68, 127.42, 126.40, 126.10, 125.92, 125.31, 65.31, 57.44, 53.22, 52.14, 40.96. **HRMS** (ESI) calculated [M+Na]+ for C_{25}H_{22}O_{4}FNa: 409.1410, found: 409.1399. **FTIR** (cm⁻¹) 3685, 3430, 3021, 2956, 2401, 2355, 1731, 1603, 1517, 1436, 1216, 1053, 928, 767.
Dimethyl (R) 2-methyl-4-(p-toly)cyclopent-3-ene-1,1-dicarboxylate (3u)

Following the general procedure, treatment of (Z)-2-bromobut-2-enal 1u (28.0 mg, 0.188 mmol) and dimethyl 2-(2-oxo-2-(p-toly)ethyl)malonate 2b (33.0 mg, 0.125 mmol) with triazolium salt 4 (4.6 mg, 0.0125 mmol), Na\(_2\)CO\(_3\) (53.0 mg, 0.5 mmol) in DME (2.0 mL) and stirring the reaction mixture at 32 °C for 72 h followed by flash column chromatography (EtOAc-Pet. ether 10:90) to afford dimethyl (R) 2-methyl-4-(p-toly)cyclopent-3-ene-1,1-dicarboxylate 3u as a light yellow oil (15.0 mg, 42%).

\[ R_f (\text{Pet. ether /EtOAc = 80/20}): 0.70; 90\% \text{ ee, } [\alpha]_D^{25} = -60.5 \text{ (c 0.1, CHCl}_3) \].

**HPLC** (Kromasil 5-AmyCoat, 95:05 Petroleum ether / IPA, 0.5 mL/min.) Major: 12.8 min, Minor: 14.5 min.

**1H NMR** (500 MHz, CDCl\(_3\)) \(\delta\) 7.30 (d, \(J = 8.2\) Hz, 2H, H\(_{\text{ar}}\)), 7.12 (d, \(J = 8.0\) Hz, 2H, H\(_{\text{ar}}\)), 5.93 (s, 1H), 3.79-3.76 (m, 1H), 3.75 (s, 3H, CH\(_3\)), 3.73 (s, 3H, CH\(_3\)), 3.70-3.66 (m, 1H), 3.09 (d, \(J = 16.5\) Hz, 1H), 2.33 (s, 3H), 1.02 (d, \(J = 7.2\) Hz, 3H).

**13C NMR** (125 MHz, CDCl\(_3\)) \(\delta\) 172.78, 171.00, 137.90, 137.49, 132.61, 129.20, 127.84, 125.64, 63.47, 52.97, 52.51, 45.62, 40.12, 21.32, 16.09.

**HRMS (ESI)** calculated [M+Na]\(^+\) for C\(_{17}\)H\(_{20}\)O\(_4\)Na: 311.1254, found: 311.1251.

**FTIR** (cm\(^{-1}\)) 3917, 3750, 3507, 3015, 2947, 2829, 2387, 2351, 1823, 1727, 1673, 1566, 1438, 1213, 1095, 1049, 949.

Ethyl (2S)-1-acetyl-2,4-diphenylcyclopent-3-ene-1-carboxylate (3v)

Following the general procedure, treatment of (Z)-2-bromo 3-phenylacrylaldehyde 1a (158.2 mg, 0.75 mmol) and ethyl 2-acetyl-4-oxo-4-phenylbutanoate 2v (124 mg, 0.50 mmol) with triazolium salt 4 (18.4 mg, 0.05 mmol), Na\(_2\)CO\(_3\) (212 mg, 2.0 mmol) in DME (6.0 mL) and stirring the reaction mixture at 32 °C for 72 h followed by flash column chromatography (EtOAc-Pet. ether 10:90) to afford 3:1 diastereomeric mixture of ethyl (2S)-1-acetyl-2,4-diphenylcyclopent-3-ene-1-carboxylate 3v as a white solid (Major isomer 67 mg yield 38% and minor isomer 23 mg yield 16%, diastereomeric ratio was determined by \(^1\)H-NMR analysis of crude reaction mixture).

**Major Isomer** \(R_f\) (Pet. ether /EtOAc = 80/20): 0.61; >99% ee, \([\alpha]_D^{25} = -359.98\) (c 0.35, CHCl\(_3\)).

**HPLC** (Kromasil 5-AmyCoat, 90:10 Hexane / IPA, 0.7 mL/min.) Major: 10.5 min, Minor: 16.2 min.

**\(^1\)H NMR** (400 MHz, CDCl\(_3\)) \(\delta\) 7.54-7.52 (m, 2H, H\(_{\text{ar}}\)), 7.39 (t, \(J = 7.8\) Hz, 2H, H\(_{\text{ar}}\)), 7.33-
7.22 (m, 6H, H_{ar}), 6.15 (s, 1H, Holefinic), 5.06 (s, 1H), 4.01-3.96 (m, 1H), 3.81-3.75 (m, 1H), 3.54-3.48 (m, 1H), 2.98 (d, J = 16.6 Hz, 1H), 2.29 (s, 3H, CH$_3$), 0.88 (t, J = 7.1 Hz, 3H, CH$_3$).

**13C NMR (100 MHz, CDCl$_3$)** δ 201.74, 170.24, 139.83, 139.01, 135.08, 129.35, 128.57, 128.11, 127.90, 127.43, 127.30, 125.84, 71.31, 61.40, 55.25, 39.53, 26.36, 13.53. **HRMS (ESI)** calculated [M+Na]$^+$ for **C$_{22}$H$_{22}$O$_3$Na**: 357.1461, found: 357.1456. **FTIR (cm$^{-1}$)** 3429, 3022, 2401, 2311, 1711, 1636, 1491, 1358, 1217, 1090, 768, 670.

**Minor Isomer** $R_f$ (Pet. ether /EtOAc = 80/20): 0.64; >99% ee, [α]$_D^{25}$ = -326.84 (c 0.25, CHCl$_3$).

**HPLC** (Kromasil 5-AmyCoat, 90:10 Hexane / IPA, 0.7 mL/min.) Major: 10.4 min, Minor: 11.6 min. **1H NMR (400 MHz, CDCl$_3$)** δ 7.53-7.51 (m, 2H, H$_{ar}$), 7.38-7.35 (m, 2H, H$_{ar}$), 7.31-7.20 (m, 6H, H$_{ar}$), 6.09-6.08 (m, 1H, Holefinic), 5.08 (s, 1H), 4.32-4.22 (m, 2H), 4.01-3.96 (m, 1H), 3.05 (d, J = 17.0 Hz, 1H), 1.63 (s, 3H, CH$_3$), 1.30 (t, J = 7.1 Hz, 3H, CH$_3$). **13C NMR (100 MHz, CDCl$_3$)** δ 202.00, 173.09, 140.11, 139.24, 135.21, 129.47, 128.67, 128.61, 127.96, 127.72, 126.73, 125.99, 71.38, 62.13, 57.10, 39.63, 27.93, 14.16. **HRMS (ESI)** calculated [M+Na]$^+$ for **C$_{22}$H$_{22}$O$_3$Na**: 357.1461, found: 357.1455. **FTIR (cm$^{-1}$)** 3437, 3057, 3029, 2981, 1953, 1711, 1600, 1492, 1354, 1233, 1158, 1058, 840, 755.

**Ethyl (2S)-1-cyano-2,4-diphenylcyclopent-3-ene-1-carboxylate (3w)**

Following the general procedure, treatment of (Z)-2-bromo 3-phenylacrylaldehyde **1a** (158.2 mg, 0.75 mmol) and ethyl 2-cyano-4-oxo-4-phenylbutanoate **2w** (115.6 mg, 0.50 mmol) with triazolium salt **4** (18.4 mg, 0.05 mmol), Na$_2$CO$_3$ (212 mg, 2.0 mmol) in DME (6.0 mL) and stirring the reaction mixture at 32 °C for 72 h followed by flash column chromatography (EtOAc-Pet. ether 10:90) to afford 3:1 diastereomeric mixture of ethyl (2S)-1-cyano-2,4-diphenylcyclopent-3-ene-1-carboxylate **3w** as a colourless oil (Major isomer 48 mg yield 30% and minor isomer 18 mg yield 12%, diastereomeric ratio was determined by $^1$H-NMR analysis of crude reaction mixture).

**Major Isomer** $R_f$ (Pet. ether /EtOAc = 80/20): 0.55; 85% ee, [α]$_D^{25}$ = -43.86 (c 0.15, CHCl$_3$).

**HPLC** (Chiralcel OD-H, 95:05 Hexane / IPA, 0.7 mL/min.) Major: 22.9 min, Minor: 18.6 min. **1H NMR (400 MHz, CDCl$_3$)** δ 7.50 (d, J = 7.1 Hz, 2H, H$_{ar}$), 7.43-7.34 (m, 8H, H$_{ar}$), 6.20 (s, 1H, Holefinic), 4.81 (s, 1H), 4.39-4.36 (m, 2H), 3.66 (d, J = 16.1 Hz, 1H), 3.54 (d, J = 16.1 Hz, 1H),
1.38 (t, J = 7.1 Hz, 3H, CH₃). \(^{13}\)C NMR (100 MHz, CDCl₃) \(\delta\) 168.83, 140.81, 137.99, 134.16, 128.83, 128.80, 128.70, 128.57, 128.55, 125.95, 125.31, 118.53, 63.39, 59.32, 55.02, 44.07, 14.15. HRMS (ESI) calculated [M+Na]^+ for C₂₁H₁₉O₂NNa: 340.1308, found: 340.1304. FTIR (cm\(^{-1}\)) 3440, 3021, 1740, 1635, 1493, 1499, 1216, 1074, 757, 897, 669.

Minor Isomer \(R_f\) (Pet. ether /EtOAc = 80/20): 0.64; 95% ee, \([\alpha]_D^{25} = -95.71\) (c 0.6, CHCl₃). HPLC (Kromasil 5-AmyCoat, 90:10 Hexane / IPA, 0.7 mL/min.) Major: 14.1 min, Minor: 10.9 min. \(^1\)H NMR (400 MHz, CDCl₃) \(\delta\) 7.52 (d, J = 7.3 Hz, 2H, H\(_{ar}\)), 7.41 (t, J = 7.7 Hz, 2H, H\(_{ar}\)), 7.36-7.29 (m, 4H, H\(_{ar}\)), 7.23-7.21 (m, 2H, H\(_{ar}\)), 6.15 (d, J = 2.0 Hz, 1H, H\(_{olefinic}\)), 4.82 (s, 1H), 3.88-3.84 (m, 1H), 3.82-3.79 (m, 1H), 3.64-3.61 (m, 1H), 3.35 (d, J = 16.4 Hz, 1H), 0.93 (t, J = 7.2 Hz, 3H, CH₃). \(^{13}\)C NMR (100 MHz, CDCl₃) \(\delta\) 166.37, 141.68, 136.81, 134.25, 129.05, 128.83, 128.65, 128.57, 126.13, 124.26, 121.68, 62.78, 62.52, 52.12, 41.99, 13.60. HRMS (ESI) calculated [M+Na]^+ for C₂₁H₁₉O₂NNa: 340.1308, found: 340.1303. FTIR (cm\(^{-1}\)) 3682, 3464, 3021, 2984, 2931, 2401, 1743, 1246, 1072, 774, 669.

Diastereoselective Hydrogenation of 3a

Dimethyl (2S)-2,4-diphenylcyclopentane-1,1-dicarboxylate (8a)

An oven dried round bottomed flask was charged with dimethyl (S)-2,4-diphenylcyclopent-3-ene-1,1-dicarboxylate 3a (84.1 mg, 0.25 mmol, 1 equiv) and Pd 10% on activated carbon (10 mg, 0.03 equiv) in methanol (10 mL). The reaction mixture was kept stirring at 32 °C for 12 h under H₂ atmosphere (balloon pressure). Upon consumption of the starting material 3a (TLC), the crude reaction mixture was passed through celite and concentrated under reduced pressure to get a sufficiently pure dimethyl (2S)-2,4-diphenylcyclopentane-1,1-dicarboxylate 8a in 98% yield (82 mg, dr 20:1).

\(R_f\) (Pet. ether /EtOAc = 80/20): 0.65; \([\alpha]_D^{25} = -38.88\) (c 0.2, CHCl₃). HPLC (Kromasil 5-AmyCoat, 99:1 Hexane / IPA, 0.5 mL/min.) Major diastereomer (Major: 19.2 min, Minor: 20.7 min). Minor diastereomer (Major: 22.6 min, Minor: 25.5 min). \(^1\)H NMR (400 MHz, CDCl₃) \(\delta\) 7.46-7.39 (m, 6H, H\(_{ar}\)), 7.34-7.25 (m, 4H, H\(_{ar}\)), 4.37-4.33 (m, 1H), 3.82 (s, 3H, CH₃), 3.24-3.16 (m, 1H), 2.64-2.59 (m, 1H), 2.46-2.32 (m, 2H). \(^{13}\)C NMR (100 MHz,
Decarboxylation of 3a

Methyl (2R)-2,4-diphenylcyclopent-3-ene-1-carboxylate (9a)

To a microwave reaction tube was charged with 3a (0.084 gm, 0.25 mmol) and LiCl (0.083 gm, 1.95 mmol, 7.8 equiv). Then the mixture was dissolved in DMSO (2.0 mL) : H2O (1.5 mL). The reaction mixture was placed in a microwave reactor (Anton Paar, Monowave 300), and heated to 185 °C for 30 min. The resultant reaction mixture was quenched with saturated aq. solution of NaHCO3 and extracted with Et2O (3x10 mL). Then the organic layer was washed with brine, dried over Na2SO4, concentrated and the crude reaction mixture was purified by flash column chromatography to afford the diastereomeric mixture of methyl (2R)-2,4-diphenylcyclopent-3-ene-1-carboxylate 9a in 51% yield (35 mg, dr 1:1).

Rf (Pet. ether/EtOAc = 80/20): 0.72; [α]D25 = +104.5 (c 0.2, CHCl3). 1H NMR (400 MHz, CDCl3) δ 7.56 (d, J = 7.2 Hz, 2H, H ar), 7.51 (d, J = 7.2 Hz, 2H, H ar), 7.41-7.22 (m, 14H, H ar), 7.20-7.17 (m, 2H, H ar), 6.16 (s, 2H, olefinic), 4.45-4.42 (m, 2H), 3.80-3.73 (m, 4H), 3.49-3.41 (m, 1H), 3.26-3.14 (m, 6H), 2.96-2.89 (m, 1H). 13C NMR (100 MHz, CDCl3) δ 175.61, 173.36, 144.49, 142.67, 141.43, 140.24, 135.56, 128.75, 128.62, 128.20, 128.20, 127.81, 127.65, 127.18, 126.93, 126.77, 126.00, 125.90, 55.27, 54.66, 52.27, 52.08, 51.25, 48.75, 37.14, 34.62. HRMS (ESI) calculated [M+Na]+ for C19H18O2Na: 301.1199, found: 301.1196. FTIR (cm⁻¹) 3021, 1745, 1379, 1214, 742, 669.

Dimethyl (1R,2S,5S) 5-ethyl-7-oxo-2-phenyl-6-oxabicyclo[3.2.0]heptane-3,3-dicarboxylate (11a)

To an oven-dried Schlenk reaction vessel with a teflon screw cap was taken the (Z)-2-bromo 3-phenylacrylaldehyde 1a (79.1 mg, 0.38 mmol), the dimethyl 2-(2-oxobutyl)malonate 10 (50.0 mg, 0.25 mmol) and Na2CO3
(106 mg, 1.0 mmol, 4.0 equiv). The mixture was kept under argon atmosphere, and dry DME (3.0 mL) was then introduced into the vessel by syringe under a positive pressure of argon, and the mixture was stirred at 32 °C. To this stirring solution was added the triazolium salt 4 (9.2 mg, 0.025 mmol), and the resulting mixture was stirred at 32 °C for 72 h followed by flash column chromatography (EtOAc-Pet. ether 10:90) to afford dimethyl (IR,2S,5S)-5-ethyl-7-oxo-2-phenyl-6-oxabicyclo[3.2.0]heptane-3,3-dicarboxylate 11a as a white solid (38.0 mg, 46%).

\[ R_f \text{ (Pet. ether /EtOAc = 80/20): 0.4, 99% ee, } [\alpha]_D^{25} = -188.7 \text{ (c 0.1, CHCl}_3) \].

**HPLC (Chiralpak IA, 97:03 Petroleum ether / IPA, 0.5 mL/min, } \lambda = 210 \text{ nm)} Major: 18.7 min, Minor: 21.9 min.**

**1H NMR (400 MHz, CDCl}_3 \delta 7.31-7.27 \text{ (m, 3H, } H_{ar}), 6.99-6.97 \text{ (m, 2H, } H_{ar}), 4.65 \text{ (s, 1H), 3.81 (s, 3H, CH}_3), 3.70 \text{ (s, 1H), 3.31 (s, 3H, CH}_3), 2.95-2.85 \text{ (m, 2H), 2.28-2.12 (m, 2H), 1.18 (s, } J = 7.3 \text{ Hz, 3H, CH}_3) \].

**13C NMR (100 MHz, CDCl}_3 \delta 170.89, 168.36, 167.95, 138.52, 128.85, 128.10, 128.06, 90.77, 63.74, 53.65, 52.71, 50.68, 40.59, 28.57, 8.88.**

**HRMS (ESI) calculated [M+Na]^+ for C_{18}H_{20}O_6Na: 355.1152, found: 355.1150. FTIR (cm^{-1}) 3118, 3022, 2430, 1827, 1734, 1780, 1556, 1445, 1035, 924.**

**Dimethyl (IR,2S,5S)-5-ethyl-2-(4-(methoxycarbonyl)phenyl)-7-oxo-6-oxabicyclo[3.2.0]heptane-3,3 dicarboxylate (11r)**

To an oven-dried Schlenk reaction vessel with a teflon screw cap was taken the (Z)-4-(2-bromo-3-oxoprop-1-en-1-yl)benzoate 1r (101.0 mg, 0.38 mmol), the dimethyl 2-(2-oxobutyl)malonate 10 (50.0 mg, 0.25 mmol) and Na$_2$CO$_3$ (106 mg, 1.0 mmol, 4.0 equiv). The mixture was kept under argon atmosphere, and dry DME (3.0 mL) was then introduced into the vessel by syringe under a positive pressure of argon, and the mixture was stirred at 32 °C. To this stirring solution was added the triazolium salt 4 (9.2 mg, 0.025 mmol), and the resulting mixture was stirred at 32 °C for 72 h followed by flash column chromatography (EtOAc-Pet. ether 10:90) to afford dimethyl (IR,2S,5S)-5-ethyl-2-(4-(methoxycarbonyl)phenyl)-7-oxo-6-oxabicyclo[3.2.0]heptane-3,3 dicarboxylate 11r as a white solid (70.0 mg, 72%).

\[ R_f \text{ (Pet. ether /EtOAc = 80/20): 0.23, 99% ee, } [\alpha]_D^{25} = -74.1 \text{ (c 0.1, CHCl}_3) \].

**HPLC (Chiralpak IA, 97:03 Petroleum ether / IPA, 1.0 mL/min, } \lambda = 210 \text{ nm)}. Major: 15.8 min, Minor: 16.8 min.**

**1H NMR (400 MHz, CDCl}_3 \delta 7.97 \text{ (d, } J = 8.4 \text{ Hz, 2H, } H_{ar}), 7.06 \text{ (d, } J = 8.2 \text{ Hz, 2H, } H_{ar}), 4.71 \text{ (s, 1H), 3.90 (d, 3H, CH}_3), 3.81 \text{ (s, 3H, CH}_3), 3.69 \text{ (s, 1H), 3.31 (s, 3H, CH}_3), 2.97-2.85 \text{ (m, 2H),} \]
2.26-2.14 (m, 2H), 1.19 (t, J = 7.5 Hz, 3H, CH₃). ¹³C NMR (100 MHz, CDCl₃) δ 170.57, 167.85, 167.68, 166.50, 130.11, 128.16, 90.68, 66.62, 63.53, 53.77, 52.86, 52.38, 50.52, 40.65, 28.60, 8.88. HRMS (ESI) calculated [M+Na]⁺ for C₂₀H₂₂O₈Na: 413.1207, found: 413.1203. FTIR (cm⁻¹) 2973, 2954, 1828, 1723, 1612, 1531, 1435, 1418, 1375, 1280, 1227, 1153, 1112, 1018, 900, 864, 810, 763, 707, 665.
6. $^1$H and $^{13}$C NMR Spectra of Functionalized Cyclopentenes

Dimethyl (S)-2,4-diphenylcyclopent-3-ene-1,1-dicarboxylate (3a)
Dimethyl (S)-2-phenyl-4-(p-tolyl)cyclopent-3-ene-1,1-dicarboxylate (3b)
Dimethyl (S)-4-(4-bromophenyl)-2-phenylcyclopent-3-ene-1,1-dicarboxylate (3c)
Dimethyl (S)-4-(4-fluorophenyl)-2-phenylcyclopent-3-ene-1,1-dicarboxylate (3d)
Dimethyl (S)-4-(4-nitrophenyl)-2-phenylcyclopent-3-ene-1,1-dicarboxylate (3e)
Dimethyl (5)-4-(2-methoxyphenyl)-2-phenylcyclopent-3-ene-1,1-dicarboxylate (3f)
Dimethyl (S)-4-(2-bromophenyl)-2-phenylcyclopent-3-ene-1,1-dicarboxylate (3g)
Dimethyl (S)-4-(3-methoxyphenyl)-2-phenylcyclopent-3-ene-1,1-dicarboxylate (3h)
Dimethyl (S)-4-(2,4-dichlorophenyl)-2-phenylcyclopent-3-ene-1,1-dicarboxylate (3i)
Dimethyl (S)-4-(2,4-difluorophenyl)-2-phenylcyclopent-3-ene-1,1-dicarboxylate (3j)
Diethyl 2,4-diphenylcyclopent-3-ene-1,1-dicarboxylate (3k)
(S)-1,1'-(2,4-Diphenylcyclopent-3-ene-1,1-diyl)bis(ethan-1-one) (3I)
Dimethyl (S)-4-phenyl-2-((p-tolyl)cyclopent-3-ene-1,1-dicarboxylate (3m)
Dimethyl (S)-2-(4-methoxyphenyl)-4-phenylcyclopent-3-ene-1,1-dicarboxylate (3n)
Dimethyl (S)-2-(4-bromophenyl)-4-phenylcyclopent-3-ene-1,1-dicarboxylate (3o)
Dimethyl (S)-2-(4-chlorophenyl)-4-phenylcyclopent-3-ene-1,1-dicarboxylate (3p)
Dimethyl (S)-2-(4-fluorophenyl)-4-phenylcyclopent-3-enec-1,1-dicarboxylate (3q)
Dimethyl (S)-2-(4-(methoxycarbonyl)phenyl)-4-phenylcyclopent-3-ene-1,1-dicarboxylate (3r)
Dimethyl (R)-2-(2-fluorophenyl)-4-phenylcyclopent-3-ene-1,1-dicarboxylate (3s)
Dimethyl (S)-2-(naphthalen-2-yl)-4-phenylcyclopent-3-ene-1,1-dicarboxylate (3t)
Dimethyl (R) 2-methyl-4-(p-tolyl)cyclopent-3-ene-1,1-dicarboxylate (4u)
Ethyl (2S)-1-acetyl-2,4-diphenylcyclopent-3-ene-1-carboxylate (3v major)
Ethyl (2S)-1-acetyl-2,4-diphenylcyclopent-3-ene-1-carboxylate (3v minor)
Ethyl (2S)-1-cyano-2,4-diphenylcyclopent-3-ene-1-carboxylate (3w major)
Ethyl (2S)-1-cyano-2,4-diphenylcyclopent-3-ene-1-carboxylate (3w minor)
Dimethyl (2S)-2,4-diphenylcyclopentane-1,1-dicarboxylate (8a)
Methyl (2R)-2,4-diphenylcyclopent-3-ene-1-carboxylate (9a)
Dimethyl (1R2S5S) 5-ethyl-7-oxo-2-phenyl-6-oxabicyclo[3.2.0]heptane-3,3-dicarboxylate (11a)
Dimethyl (1R2S5S) 5-ethyl-2-(4-(methoxycarbonyl)phenyl)-7-oxo-6-oxabicyclo[3.2.0]heptane-3,3-dicarboxylate (11r)
7. HPLC Scans of Functionalized Cyclopentenes

Dimethyl (S)-2,4-diphenylcyclopent-3-ene-1,1-dicarboxylate (3a)
Dimethyl (S)-2-phenyl-4-(p-tolyl)cyclopent-3-ene-1,1-dicarboxylate (3b)
Dimethyl (S)-4-(4-bromophenyl)-2-phenylcyclopent-3-ene-1,1-dicarboxylate (3c)
Dimethyl (S)-4-(4-fluorophenyl)-2-phenylcyclopent-3-ene-1,1-dicarboxylate (3d)
Dimethyl (S)-4-(4-nitrophenyl)-2-phenylcyclopent-3-ene-1,1-dicarboxylate (3e)
Dimethyl (S)-4-(2-methoxyphenyl)-2-phenylcyclopent-3-ene-1,1-dicarboxylate (3f)
Dimethyl (S)-4-(2-bromophenyl)-2-phenylcyclopent-3-ene-1,1-dicarboxylate (3g)
Dimethyl (S)-4-(3-methoxyphenyl)-2-phenylcyclopent-3-ene-1,1-dicarboxylate (3h)

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Detector A - 1 (254nm)

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Totals  | 10711804     | 100.000 |

Project Leader: Dr. A. T. Biju
Column: Kromasil 5- AmlyCoat (250mm x 4.6mm)
Mobile Phase: IPA:n-Hexane (20:80)
Wavelength: 254 nm
Flow Rate: 0.7 ml/min
Conc.: 1mg/1ml
Inj vol.: 5ul
Dimethyl (S)-4-(2,4-dichlorophenyl)-2-phenylcyclopent-3-ene-1,1-dicarboxylate (3i)
Dimethyl (S)-4-(2,4-difluorophenyl)-2-phenylcyclopent-3-ene-1,1-dicarboxylate (3j)
Diethyl (S)-2,4-diphenylcyclopent-3-ene-1,1-dicarboxylate (3k)
(S)-1,1'-(2,4-Diphenylcyclopent-3-ene-1,1-diyl)bis(ethan-1-one) (3l)
Dimethyl (S)-4-phenyl-2-\((p\text{-tolyl})\)cyclopent-3-ene-1,1-dicarboxylate (3m)

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**Detector A - 1 (254nm)**

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**Project Leader:** Dr. A. T. Biju
**Column:** Kromasil 5-Amy C18
**Mobile Phase:** IPA:Hexane (10:90)
**Wavelength:** 254 nm
**Flow Rate:** 0.7 ml/min
**Conc:** 10 µg/1 ml
**Inj vol:** 5 µl
Dimethyl (S)-2-(4-methoxyphenyl)-4-phenylcyclopent-3-ene-1,1-dicarboxylate (3n)
Dimethyl (S)-2-(4-bromophenyl)-4-phenylcyclopent-3-ene-1,1-dicarboxylate (3o)
Dimethyl (S)-2-(4-chlorophenyl)-4-phenylcyclopent-3-ene-1,1-dicarboxylate (3p)
Dimethyl (S)-2-(4-fluorophenyl)-4-phenylcyclopent-3-ene-1,1-dicarboxylate (3q)
Dimethyl \((S)-2-(4-(methoxycarbonyl)phenyl)-4-phenylcyclopent-3-ene-1,1-dicarboxylate\) (3r)
Dimethyl (R)-2-(2-fluorophenyl)-4-phenylcyclopent-3-ene-1,1-dicarboxylate (3s)
Dimethyl (S)-2-(naphthalen-2-yl)-4-phenylcyclopent-3-ene-1,1-dicarboxylate (3t)
Dimethyl (R) 2-methyl-4-(p-tolyl)cyclopent-3-ene-1,1-dicarboxylate (4u)
Ethyl (2S)-1-acetyl-2,4-diphenylcyclopent-3-ene-1-carboxylate (3v major)
Ethyl (2S)-1-acetyl-2,4-diphenylcyclopent-3-ene-1-carboxylate (3v minor)
Ethyl (2S)-1-cyano-2,4-diphenylcyclopent-3-ene-1-carboxylate (3w major)
Ethyl (2S)-1-cyano-2,4-diphenylcyclopent-3-ene-1-carboxylate (3w minor)
Dimethyl (2S)-2,4-diphenylcyclopentane-1,1-dicarboxylate (8a)

Detector A - 1 (254nm)

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Totals | 196848 | 100.000

Detector A - 1 (254nm)

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Totals | 189892 | 100.000

ee of major diastereomer = 99%

ee of minor diastereomer = 99%
Dimethyl (1R2S5S) 5-ethyl-7-oxo-2-phenyl-6-oxabicyclo[3.2.0]heptane-3,3-dicarboxylate (11a)
Dimethyl (1R,2S,5S) 5-ethyl-2-(4-(methoxycarbonyl)phenyl)-7-oxo-6-oxabicyclo[3.2.0]heptane-3,3-dicarboxylate (11r)