Supporting Information
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Stereoselective $\gamma$-Olefination of Substituted Cyclobutenediones by Organocatalysis

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Supporting Information

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Experimental Section

General: \(^1\)H NMR (400 MHz) and \(^{13}\)C NMR (100 MHz) spectra were recorded in CDCl\(_3\) and TMS was used as reference (\(\delta = 0\) ppm). Melting points are uncorrected. IR spectra were recorded on a JASCO FT-5300 instrument with polystyrene as reference. Mass spectral analysis was carried out on VG 7070H mass spectrometer using EI technique at 70 eV. Cyclobutenediones were synthesized by reported procedures.\(^1\) The aldehydes and alcohols used in the reactions were supplied by Merck. Chromatographic purification was conducted by column chromatography using 100-200 mesh silica gel obtained from Acme Synthetic Chemicals, India.

Preparation of (E)-3-phenyl-4-styrylcyclobut-3-ene-1,2-dione \(3a\).

To a mixture of 3-methyl-4-phenyl-cyclobutene-1,2-dione (0.086 g, 0.5 mmol) and benzaldehyde (0.15 mL, 1.5 mmol) in 2.5 mL of MeOH solvent catalytic amount of pyrrolidine (8.2 µL, 0.1 mmol) was added. The reaction mixture was stirred for 1 h at room temperature. It was treated with 5 mL of saturated ammonium chloride solution and extracted with ethyl acetate (3×10 mL). The combined organic layer was dried over anhydrous Na\(_2\)SO\(_4\) and concentrated under reduced pressure. The residue was subjected to column chromatography (silica gel, hexane-EtOAc). Ethyl acetate (3%) in hexane eluted the (E)-3-phenyl-4-styrylcyclobut-3-ene-1,2-dione \(3a\).

\(3a\): Yield: 88%, 0.114 g; mp 148-150 °C (Lit.\(^2\) mp 160 °C); IR (KBr): \(\nu_{\text{max}}\) 1759 cm\(^{-1}\); \(^1\)H NMR (400 MHz, CDCl\(_3\)): \(\delta\) 8.30 (d, \(J = 14.8\) Hz, 1H), 8.09-8.07 (m, 2H); 7.68-7.45 (m, 9H). \(^{13}\)C NMR (100 MHz, CDCl\(_3\)): \(\delta\) 196.7, 195.9, 184.2, 183.4, 146.1, 134.9, 133.2, 131.4, 129.4, 129.2, 129.0, 128.7, 128.4, 115.2. MS (EI): \(m/z\) 261 (M+1). Anal. Calcd. for C\(_{18}\)H\(_{12}\)O\(_2\) C 83.06%, H 4.65% Found C 83.25%, H 4.59%

\(3b\). Yield: 85%, 0.125 g; mp 171-173 °C (Lit.\(^2\) mp 185 °C); IR (KBr): \(\nu_{\text{max}}\) 1759 cm\(^{-1}\); \(^1\)H NMR (400 MHz, CDCl\(_3\)): \(\delta\) 8.25 (d, \(J = 15.6\) Hz, 1H), 8.09-8.06 (m, 2H), 7.62-7.56 (m, 5H), 7.48 (d, \(J = 15.6\) Hz, 1H), 7.43-7.41 (M, 2H). \(^{13}\)C NMR (100 MHz, CDCl\(_3\)): \(\delta\) 196.6, 195.8, 183.8, 183.7,
144.4, 137.4, 133.4, 129.8, 129.5, 128.9, 128.4, 115.7. **MS (EI): m/z 295 (M+1). Anal. Calcd. for C\textsubtext{18}H\textsubtext{11}ClO\textsubtext{2} C 73.35%, H 3.76% Found C 73.51%, H 3.71%**

**3c.** Yield: 82%, 0.138 g; mp 166-168 °C; IR (KBr): ν\textsubscript{max} 1747 cm\textsuperscript{-1}; \textsuperscript{1}H NMR (400 MHz, CDCl\textsubscript{3}): δ 8.26 (d, J = 15.6 Hz, 1H), 8.10-8.08 (m, 2H), 7.62- 7.54 (m, 7H), 7.51 (d, J = 15.6 Hz, 1H). \textsuperscript{13}C NMR (100 MHz, CDCl\textsubscript{3}): δ 196.5, 195.8, 183.85, 183.81, 144.5, 133.8, 133.3, 132.5, 129.9, 129.5, 128.9, 128.4, 125.8, 115.7. **MS (EI): m/z 339 (M+2). Anal. Calcd. for C\textsubtext{18}H\textsubtext{11}BrO\textsubtext{2} C 63.74%, H 3.27% Found C 63.85%, H 3.21%**

**3d.** Yield: 83%, 0.114g; mp 156-158 °C (Lit.\textsuperscript{2} mp 163 °C); IR (KBr): ν\textsubscript{max} 1751, 1736 cm\textsuperscript{-1}; \textsuperscript{1}H NMR (400 MHz, CDCl\textsubscript{3}): δ 8.33 (d, J = 15.6 Hz, 1H), 8.12-8.10 (m, 2H), 7.61- 7.60 (m, 5H), 7.50 (d, J = 15.6 Hz, 1H), 7.29- 7.27 (m, 2H), 2.44 (s, 3H). \textsuperscript{13}C NMR (100 MHz, CDCl\textsubscript{3}): δ 196.8, 195.8, 184.4, 182.8, 146.3, 142.2, 133.0, 132.2, 129.9, 129.4, 129.1, 128.8, 128.3, 114.2, 21.6. **MS (EI): m/z 275 (M+1). Anal. Calcd. for C\textsubtext{19}H\textsubtext{14}O\textsubtext{2} C 83.19%, H 5.14% Found C 83.31%, H 5.08%**

**3e.** Yield: 85%, 0.122g; mp 118-120 °C; IR (KBr): ν\textsubscript{max} 1751 cm\textsuperscript{-1}; \textsuperscript{1}H NMR (400 MHz, CDCl\textsubscript{3}): δ 8.32 (d, J = 15.6 Hz, 1H), 8.10-8.08 (m, 2H); 7.63- 7.57 (m, 5H), 7.48 (d, J = 15.6 Hz, 1H), 7.30-7.28 (m, 2H), 2.70 (q, J = 7.6 Hz, 2H), 1.27 (t, J = 7.6 Hz, 3H). \textsuperscript{13}C NMR (100 MHz, CDCl\textsubscript{3}): δ 196.8, 195.8, 184.4, 182.8, 146.4, 133.0, 132.5, 129.4, 129.1, 128.9, 128.7, 128.3, 114.3, 28.9, 15.1. **MS (EI): m/z 289 (M+1). Anal. Calcd. for C\textsubtext{20}H\textsubtext{16}O\textsubtext{2} C 83.31%, H 5.59% Found C 83.45%, H 5.51%**

**3f.** Yield: 78%, 0.118g; mp 126-128 °C; IR (KBr): ν\textsubscript{max} 1766 cm\textsuperscript{-1}; \textsuperscript{1}H NMR (400 MHz, CDCl\textsubscript{3}): δ 8.32 (d, J= 15.6 Hz, 1H), 8.10- 8.08 (m, 2H), 7.63- 7.57 (m, 5H), 7.48 (d, J = 15.6 Hz, 1H), 7.33- 7.31 (m, 2H), 3.01- 2.91 (m, 1H), 1.28 (d, J = 6.8 Hz, 6H). \textsuperscript{13}C NMR (100 MHz, CDCl\textsubscript{3}): δ 196.8, 195.8, 184.4, 182.9, 153.1, 146.4, 133.0, 132.6, 129.4, 129.2, 128.9, 128.3, 127.3, 114.4, 34.2, 23.6. **MS (EI): m/z 303 (M+1). Anal. Calcd. for C\textsubtext{21}H\textsubtext{18}O\textsubtext{2} C 83.42%, H 6.00% Found C 83.35%, H 6.12%**
3g. Yield: 82%, 0.119g; mp 140-142 °C (Lit.2 mp 156 °C); IR (KBr): $\nu_{\max}$ 1763, 1751 cm$^{-1}$; $^1$H NMR (400 MHz, CDCl$_3$): $\delta$ 8.31 (d, $J$ = 15.6 Hz, 1 H), 8.09-8.08 (m, 2H), 7.67- 7.57 (m, 5H), 7.39 (d, $J$ = 15.6 Hz, 1H), 6.97 (d, $J$ = 8.4 Hz, 2H), 3.87 (s, 3H). $^{13}$C NMR (100 MHz, CDCl$_3$): $\delta$ 197.1, 195.7, 184.5, 182.1, 162.5, 146.2, 132.8, 130.8, 129.4, 129.3, 128.2, 127.7, 114.7, 113.0, 55.5. MS (El): $m/z$ 291 (M+1). Anal. Calcd. for C$_{19}$H$_{14}$O$_3$ C 78.61%, H 4.86% Found C 78.45%, H 4.92%

3h. Yield: 80%, 0.122g; mp 136-138 °C IR (KBr): $\nu_{\max}$ 1763, 1743 cm$^{-1}$; $^1$H NMR (400 MHz, CDCl$_3$): $\delta$ 8.28 (d, $J$ = 15.6 Hz, 1H), 8.08-8.06 (m, 2H), 7.64-7.55 (m, 5H), 7.36 (d, $J$ = 15.6 Hz, 1H), 6.94 (d, $J$ = 8.4 Hz, 2H), 4.08 (q, $J$ = 7 Hz, 2H), 1.44 (t, $J$ = 7 Hz, 3H). $^{13}$C NMR (100 MHz, CDCl$_3$): $\delta$ 197.1, 195.7, 184.5, 182.0, 161.9, 146.3, 132.8, 130.8, 129.4, 129.3, 128.2, 127.5, 115.2, 112.8, 63.85, 14.7. MS (El): $m/z$ 303 (M-1). Anal. Calcd. for C$_{20}$H$_{16}$O$_3$ C 78.93%, H 5.30% Found C 78.81%, H 5.41%

3i. Yield: 90%, 0.136g; mp 215-217 °C (Lit.2 mp 227 °C); IR (KBr): $\nu_{\max}$ 1755, 1728cm $^{-1}$; $^1$H NMR (400 MHz, CDCl$_3$): $\delta$ 8.28 (d, $J$ = 15.6 Hz, 1H), 8.08- 8.06 (m, 2H); 7.58-7.54 (m, 5H), 7.22 (d, $J$ = 15.6 Hz, 1H), 6.67(d, $J$ = 9.2 Hz, 2H), 3.06 (s, 6H). $^{13}$C NMR (100 MHz, CDCl$_3$): $\delta$ 197.7, 195.3, 184.5, 179.5, 152.6, 147.5, 132.2, 131.2, 129.8, 129.2, 127.9, 122.7, 111.9, 109.8, 40.0. MS (El): $m/z$ 304 (M+1). Anal. Calcd. for C$_{20}$H$_{17}$NO$_2$ C 79.19%, H 5.65% Found C 79.10%, H 5.61%

3j. Yield: 91%, 0.149g; mp 140-142 °C; IR (KBr): $\nu_{\max}$ 1768, 1747 cm$^{-1}$; $^1$H NMR (400 MHz, CDCl$_3$): $\delta$ 8.30 (d, $J$ = 15.6 Hz, 1 H), 8.09 (d, $J$ = 8 Hz, 2H), 7.79 (d, $J$ = 8 Hz, 2H), 7.70 (d, $J$ = 8 Hz, 2H), 7.62-7.58 (m, 4H). $^{13}$C NMR (100 MHz, CDCl$_3$): $\delta$ 196.3, 195.8, 184.6, 183.4, 143.6, 138.2, 133.6, 132.3 (q, $J$ = 32 Hz), 129.6, 128.8, 128.7, 128.6, 126.1 (q, $J$ = 4 Hz), 123.7 (q, $J$ = 271 Hz), 117.4. MS (El): $m/z$ 329 (M+1). Anal. Calcd. for C$_{19}$H$_{11}$F$_3$O$_2$ C 69.51%, H 3.38% Found C 69.38%, H 3.45%

3k. Yield: 85 %, 0.117 g; mp 96-98 °C; IR (KBr): $\nu_{\max}$ 2968, 1765 cm$^{-1}$; $^1$H NMR (400 MHz, CDCl$_3$): $\delta$ 8.02 (s, 1H), 7.89-7.86 (m, 2H), 7.56-7.36 (m, 8H), 2.31 (s, 3H). $^{13}$C NMR (100 MHz, CDCl$_3$): $\delta$ 196.1, 195.7, 190.2, 186.2, 141.6, 135.3, 132.3, 130.3, 129.3, 128.9, 128.8,
128.6, 128.0, 127.1, 16.9. MS (EI): m/z 275 (M+1). Anal. Calcd. for C_{19}H_{14}O_{2} C 83.19%, H 5.14% Found C 83.31%, H 5.08%

3l. Yield: 80 %, 0.121g ;( semi solid); IR (KBr): \nu_{\text{max}} 2962, 2934, 1786, 1768 cm^{-1}; \textsuperscript{1}H NMR (400 MHz, CDCl\textsubscript{3}): \delta 7.96-7.93 (m, 2H), 7.76 (s, 1H), 7.58-7.38 (m, 8H), 2.81 (t, J =7.6 Hz, 2H), 1.47-1.37 (m, 2H), 0.81 (t, J =7.2 Hz, 3H). \textsuperscript{13}C NMR (100 MHz, CDCl\textsubscript{3}): \delta 196.5, 196.0, 191.5, 186.9, 139.2, 135.1, 133.0, 132.6, 129.7, 129.0, 128.7, 128.4, 128.3, 30.4, 22.1, 13.6. MS (EI): m/z 303 (M+1). Anal. Calcd. for C_{21}H_{18}O_{2} C 83.42%, H 6.00% Found C 83.31%, H 5.92%

Preparation of 3,4-bis((E)-1-phenylprop-1-en-2-yl)cyclobutene-1,2-dione 4a

To a mixture of 3,4-diethylcyclobutenedione (0.069 g, 0.5 mmol) and benzaldehyde (0.2 mL, 2 mmol) in 3 mL of MeOH solvent catalytic amount of pyrrolidine (8.2 \mu L, 0.1 mmol) was added. And the reaction mixture was stirred for 1.5 h at roomtemperature. The reaction mixture was treated with 5 mL of saturated ammonium chloride solution and extracted with ethyl acetate (3x10 mL). The combined organic layer was dried over anhydrous Na\textsubscript{2}SO\textsubscript{4} and concentrated under reduced pressure. The residue was subjected to column chromatography (silica gel, hexane-EtOAc). Ethyl acetate (3%) in hexane eluted the 3,4-bis((E)-1-phenylprop-1-en-2-yl)cyclobutene-1,2-dione 4a

4a. Yield: 85 %, 0.133g; mp 118- 120 °C; IR (KBr): \nu_{\text{max}} 1743 cm^{-1}; \textsuperscript{1}H NMR (400 MHz, CDCl\textsubscript{3}): \delta 7.74 (s 2H), 7.54-7.39 (m, 10H), 2.37 (s, 6H). \textsuperscript{13}C NMR (100 MHz, CDCl\textsubscript{3}): \delta 196.1, 189.7, 140.7, 135.6, 130.3, 129.2, 128.7, 127.2, 17.4. MS (EI): m/z 315 (M+1). Anal. Calcd. for C_{22}H_{18}O_{2} C 84.05%, H 5.77% Found C 84.18%, H 5.71%

4b. Yield: 82 %, 0.140 g; mp 156- 158 °C; IR (KBr): \nu_{\text{max}} 2922, 1745 cm^{-1}; \textsuperscript{1}H NMR (400 MHz, CDCl\textsubscript{3}): \delta 7.74 (s 2H), 7.46 (d, J = 8 Hz, 4H), 7.27 (d, J= 8 Hz, 4H), 2.42 (s, 6H), 2.38 (s, 6H). \textsuperscript{13}C NMR (100 MHz, CDCl\textsubscript{3}): \delta 196.2, 189.3, 140.8, 139.6, 132.8, 130.4, 129.4, 126.3, 21.5, 17.6. MS (EI): m/z 343 (M+1). Anal. Calcd. for C_{24}H_{22}O_{2} C 84.18%, H 6.48% Found C 84.05%, H 6.55 %
4c. Yield: 75%, 0.140 g; mp 164–166 °C; IR (KBr): νmax 2961, 1739 cm⁻¹; ¹H NMR (400 MHz, CDCl₃): δ 7.72 (s, 2H), 7.52 (d, J = 8.8 Hz, 4H), 6.96 (d, J = 8.8 Hz, 4H), 3.86 (s, 6H), 2.38 (s, 6H). ¹³C NMR (100 MHz, CDCl₃): δ 196.2, 188.9, 160.4, 140.5, 132.3, 128.5, 125.0, 114.2, 55.4, 17.8. MS (EI): m/z 373 (M⁻1). Anal. Calcd. for C₂₄H₂₂O₄: C 76.99%, H 5.92% Found C 76.88%, H 5.97%

4d. Yield: 70%, 0.140 g; mp 156–158 °C; IR (KBr): νmax 2922, 1743 cm⁻¹; ¹H NMR (400 MHz, CDCl₃): δ 7.74 (s, 2H), 7.51 (d, J = 8 Hz, 4H), 6.72 (d, J = 8 Hz, 4H), 3.05 (s, 12H), 2.37 (s, 6H). ¹³C NMR (100 MHz, CDCl₃): δ 196.4, 187.5, 150.7, 141.3, 132.6, 124.0, 122.7, 111.7, 40.1, 18.2. MS (EI): m/z 401 (M+1). Anal. Calcd. for C₂₆H₂₈N₂O₂: C 77.97%, H 7.05%, N 6.99% Found C 77.91%, H 7.15%, N 6.85%

X-ray Crystallography:

Crystal Data: For compound 3a: Molecular formula: C₁₈H₁₂O₂, MW = 260.28, Orthorhombic, space group: Pbca, a = 14.163(3) Å, b = 8.1161(17) Å, c = 23.806(5) Å, α = 90.000, β = 90.000, γ = 90.000, V = 2736.6(10) Å³, Z = 8, ρ = 1.263 Mg M⁻³, μ = 0.082 mm⁻¹, T = 298(2) K. Of the 14223 reflections collected, 2660 were unique (Rint = 0.0507). Refinement on all data converged at Rf = 0.0531, wr2 = 0.1023.

Crystal Data: For compound 3k: Molecular formula: C₁₉H₁₄O₂, MW = 274.30, monoclinic, space group: P2₁, a = 12.878(2) Å, b = 14.943(3) Å, c = 7.2161(12) Å, α = 90.000, β = 93.491(3), γ = 90.000, V = 1386.0(4) Å³, Z = 4, ρ = 1.315 Mg M⁻³, μ = 0.084 mm⁻¹, T = 100(2) K. Of the 12898 reflections collected, 2448 were unique (Rint = 0.0726). Refinement on all data converged at Rf = 0.0785, wr2 = 0.1635.

Crystal Data: For compound 4a: Molecular formula: C₂₂H₁₈O₂, MW = 314.36, Orthorhombic, space group: Pbca, a = 12.851(4) Å, b = 13.648(5) Å, c = 18.969(6) Å, α = 90.000, β = 90.000, γ = 90.000, V = 3327.0(19) Å³, Z = 8, ρ = 1.255 Mg M⁻³, μ = 0.079 mm⁻¹, T = 100(2) K. Of the 32135 reflections collected, 3251 were unique (Rint = 0.0610). Refinement on all data converged at Rf = 0.0614, wr2 = 0.1391.

\( ^1 \text{HNMR Spectrum of the compound 3a} \)
$^{13}$C NMR spectrum of the compound 3a
$^1$HNMR spectrum of the compound 3b
$^{13}$C NMR spectrum of the compound 3b
$^1$HNMR spectrum of the compound 3c
$^{13}\text{C} \text{ NMR spectrum of the compound 3c}$
$^1$HNMR spectrum of the compound 3d
$^{13}$CNMR spectrum of the compound 3d
$^1$HNMR spectrum of the compound 3e
$^{13}$C NMR spectrum of the compound 3e
1HNMR spectrum of the compound 3f
$^{13}$CNMR spectrum of the compound 3f
$^1$H NMR spectrum of the compound 3g
$^{13}$CNMR spectrum of the compound 3g
\(^1\)HNMR spectrum of the compound 3h
$^{13}$CNMR spectrum of the compound 3h
$^1$H NMR spectrum of the compound 3i
$^{13}$CNMR spectrum of the compound 3i
$^1$H NMR spectrum of the compound 3j
$^{13}$CNMR spectrum of the compound 3j
$^1$H NMR spectrum of the compound 3k
$^{13}$CNMR spectrum of the compound 3k
$^1$HNMR spectrum of the compound 3l
$^{13}$CNMR spectrum of the compound 3l
$^1$HNMR spectrum of the compound 4a
$^{13}$CNMR spectrum of the compound 4a
$^1$HNMR spectrum of the compound 4b
$^{13}$CNMR spectrum of the compound 4b
$^1$H NMR spectrum of the compound 4c
$^{13}$CNMR spectrum of the compound 4c
$^1\text{H} \text{ NMR spectrum of the compound 4d}$
$^{13}$CNMR spectrum of the compound 4d