Supporting Information

Recyclable Hypervalent-Iodine-Mediated Dehydrogenative Cyclopropanation Under Metal-Free Conditions

Ya-Nan Duan, Zhao Zhang, Chi Zhang*

State Key Laboratory of Elemento-Organic Chemistry, Collaborative Innovation Center of Chemical Science and Engineering (Tianjin), Nankai University, Tianjin 300071, China

zhangchi@nankai.edu.cn

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I. General Information

All the reactions were carried out under atmosphere without any special protection unless otherwise noted. The distilled CH$_3$CN and deionized water were used as solvents. The known compounds were synthesized by reported procedures and identified by the comparison of their NMR spectra with reported data in the literatures. The new compounds were characterized by NMR, IR, HRMS and melting point for solid samples. The $^1$H NMR spectra were recorded at 400 MHz and $^{13}$C NMR spectra were measured at 100 MHz using Bruker AV 400 as instrument; CDCl$_3$ was used as the solvent. $^1$H NMR spectra are reported as follows: chemical shift in ppm ($\delta$) relative to the chemical shift of CDCl$_3$ at 7.26 ppm, multiplicities, coupling constants (Hz) and integration. $^{13}$C NMR spectra are reported in ppm ($\delta$) relative to the central line of triplet of CDCl$_3$ at 77.00 ppm. IR spectra were recorded with a FT-IR Bruker EQUINOX55 spectrometer in KBr pellets. High-resolution mass spectroscopy (HRMS) was performed with a high-resolution ESI–FTICR mass spectrometer (Varian 7.0 T). The X-ray diffraction data were collected on Bruker SMART-1000 CCD diffractometer.

II. General Procedure for Substrate Synthesis:

\[ \text{HN} \quad \xrightarrow{\text{Boc$_2$O, DMAP, CH$_3$CN, 30 \degree C, 2.5 h}} \quad \text{Boc} \quad \xrightarrow{\text{indanone, NaH, THF, reflux, 2 h}} \quad \text{1a} \]

\text{N-Bocpyrrole:}^{1}$ (Boc)$_2$O, (7.8 g, 36 mmol) and DMAP, (0.5 g, 4.5 mmol) were added to pyrrole (2.0 g, 30 mmol) in acetonitrile (30 mL) under nitrogen at 30 °C. After the addition was completed, the mixture was stirred at room temperature for 2.5 h. The solvent was removed in vacuo and the residue was purified by column chromatography (Al$_2$O$_3$), giving 4.6 g of title compound as colorless liquid (92% yield). $^1$H NMR (CDCl$_3$, 300 MHz) $\delta$ 7.24 (t, $J = 2.4$ Hz, 2H), 6.22 (t, $J = 2.4$ Hz, 2H),

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1.60 (s, 9H).

**Tert-butyl 1-oxo-2,3-dihydro-1H-indene-2-carboxylate (1a):** A solution of indanone (660 mg, 5 mmol) in THF (5 mL) was added to the suspension of NaH (400 mg, 10 mmol) in THF (20 mL) at room temperature. After stirring for 20 min at this temperature, the solution of N-Bocpyrrole (1.67 g, 10 mmol) was added. The reaction mixture was then heated to reflux until complete consumption of indanone monitored by TLC. The resulting reaction mixture was cooled to room temperature, poured into ice water, acidified with diluted HCl and extracted with EtOAc. The combined organic layer was washed with brine and dried over anhydrous MgSO₄. The solvent was evaporated *in vacuo* and the residue was purified by column chromatography. The title compound was obtained in 66% yield (760 mg). Yellow solid, m.p. 49-51 °C; ¹H NMR (CDCl₃, 300 MHz) δ 7.76 (d, J = 7.8 Hz, 1H), 7.61 (t, J = 7.5 Hz, 1H), 7.49 (d, J = 7.5 Hz, 1H), 7.39 (t, J = 7.2 Hz, 1H), 3.62 (dd, J = 3.9 Hz, 8.1 Hz, 1H), 3.47–3.54 (m, 1H), 3.32 (dd, J = 8.1 Hz, 17.1 Hz, 1H), 1.49 (s, 9H).

All the rest β–keto esters were prepared according to the procedures reported in the literature unless otherwise noted.

![Tert-butyl 1-oxo-2,3-dihydro-1H-indene-2-carboxylate (1a)](image)

**Tert-butyl 4,6-dimethyl-1-oxo-2,3-dihydro-1H-indene-2-carboxylate (1d):**

Deep yellow solid (130 mg, 50%); m.p. 83-84 °C; ¹H NMR (CDCl₃, 400 MHz) δ 7.08 (s, 1H), 6.92 (s, 1H), 3.55–3.57 (m, 1H), 3.36–3.40 (m, 1H), 3.20 (dd, J₁ = 8 Hz, J₂ = 16 Hz, 1H), 2.56 (s, 3H), 2.37 (s, 3H), 1.49 (s, 9H); ¹³C NMR (CDCl₃, 100 MHz) δ 200.3, 168.9, 154.9, 145.8, 139.3, 124.2, 81.8, 54.9, 29.7, 28.1, 21.9, 18.3; IR(KBr) ν = 3393, 3011, 2982, 2952, 1697, 1606, 1479, 1457, 1417, 1370, 1318, 1306, 1251, 1227, 1201, 1170, 1153, 1142, 1004, 955, 883, 854, 839, 763 cm⁻¹; HRMS(ESI): calcd for C₁₆H₂₀NaO₃ [M+Na]^+ 283.1310, found 283.1305.

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Ethyl 1-oxo-2,3-dihydro-1H-cyclopenta[a]naphthalene-2-carboxylate (1f):
The mixture of tert-butyl 1-oxo-2,3-dihydro-1H-cyclopenta[a]naphthalene-2-carboxylate (425 mg, 1.5 mmol), ethanol (2.96 g, 66 mmol) and Bu₂SnO (38 mg, 10 mol%) was dissolved in toluene (15 mL) and the resulting solution was stirred at reflux for 24 h. After complete consumption of the starting material monitored by TLC, the mixture was concentrated under reduced pressure and purified by column chromatography to give the desired product in 88% yield (335 mg). Colorless solid, m.p. 82-83 °C; ¹H NMR (CDCl₃, 400MHz) δ 9.08 (d, J = 8.0 Hz, 1H), 8.08 (d, J = 8.0 Hz, 1H), 7.90 (d, J = 8.0 Hz, 1H), 7.68-7.70 (m, 1H), 7.54-7.59 (m, 2H), 4.26-4.29 (m, 2H), 3.84 (dd, J = 4.0 Hz, 8.0 Hz, 1H), 3.65 (dd, J = 4.0 Hz, 16.0 Hz, 1H), 3.45 (dd, J = 8.0 Hz, 16.0 Hz, 1H), 1.33 (t, J = 8.0 Hz, 3H); ¹³C NMR (CDCl₃, 100MHz) δ 199.9, 169.4, 157.3, 136.7, 129.6, 129.4, 129.3, 128.3, 126.9, 123.9, 123.7, 61.8, 53.9, 30.6, 14.3; IR(KBr) v = 3415, 2983, 2932, 2853, 1728, 1692, 1592, 1517, 1433, 1366, 1324, 1302, 1155, 1094, 1071, 826, 756 cm⁻¹; HRMS(ESI): calcd for C₁₆H₁₅O₃ [M+H]⁺ 255.1021, found 255.1019.

Ethyl 5-(allyloxy)-6-methoxy-1-oxo-2,3-dihydro-1H-indene-2-carboxylate (1g):
5-Hydroxy-6-methoxy-2,3-dihydro-1H-inden-1-one was prepared according to the reported procedure.²
To a solution of 5-hydroxy-6-methoxy-2,3-dihydro-1H-inden-1-one and K₂CO₃ (828 mg, 6 mmol) in DMF (20 mL), allyl bromide (545 mg, 4.5 mmol) was added slowly. The resulting mixture was stirred at room temperature until the starting material was consumed completely, which was indicated by TLC. The mixture was poured into 50 mL of water and the aqueous solution was extracted with EtOAc for three times. Then
the combined organic phase was successively washed with water and brine. After that, the organic phase was dried over anhydrous MgSO$_4$ and concentrated under vacuum to afford the crude product, which was used directly in the next step.

The crude product yielded above was dissolved in 20 mL diethyl carboxylate and then NaH (1.2 g, 30 mmol) was added to the above solution at room temperature. After that, the solution was heated to reflux for 40 min. After being cooled to room temperature, the mixture was poured into ice water. The resulting aqueous solution was acidified with diluted HCl and extracted with EtOAc for three times. Then the extracts were combined and dried over anhydrous MgSO$_4$. After that, the solvent was removed under vacuum and the resulting residue was subjected to column chromatography to afford the title compound in 83% yield (1.44 g). Colorless solid, m.p. 103-104 °C; $^1$H NMR (CDCl$_3$, 400 MHz) δ 7.16 (s, 1H), 6.88 (s, 1H), 6.03-6.12 (m, 1H), 5.43 (dd, $J = 1.2$ Hz, 18.4 Hz, 1H), 5.34 (dd, $J = 1.2$ Hz, 10.4 Hz, 1H), 4.79 (d, $J = 5.2$ Hz, 2H), 4.22 (q, $J = 7.2$ Hz, 2H), 3.88 (s, 3H), 3.68 (dd, $J = 3.6$ Hz, 7.6 Hz, 1H), 3.42 (dd, $J = 3.6$ Hz, 17.2 Hz, 1H), 3.24 (dd, $J = 8.0$ Hz, 16.8 Hz, 1H), 1.29 (t, $J = 7.2$ Hz, 3H); $^{13}$C NMR (CDCl$_3$, 100 MHz) δ 198.1, 169.5, 155.0, 150.0, 149.0, 132.0, 128.1, 118.9, 108.6, 105.1, 69.9, 61.7, 56.2, 53.6, 30.0, 14.2; IR(KBr) ν = 3082, 2988, 2959, 2929, 2840, 1718, 1696, 1606, 1590, 1505, 1470, 1460, 1431, 1312, 1269, 1250, 1209, 1196, 1156, 1119, 1025, 993, 931, 873, 861 cm$^{-1}$; HRMS(ESI): calcd for C$_{16}$H$_{19}$O$_5$ [M+H]$^+$ 291.1232, found 291.1228.

**Tert-butyl 7-bromo-1-oxo-2,3-dihydro-1H-indene-2-carboxylate (1k):**

Pink solid (93 mg, 30%); m.p. 90-91 °C; $^1$H NMR (CDCl$_3$, 400 MHz) δ 10.69 (brs, 0.16H), 7.35 (d, $J = 6.0$ Hz, 1H), 7.31 (d, $J = 8.4$ Hz, 0.36H), 7.24-7.26 (m, 2H), 7.20 (d, $J = 7.6$ Hz, 0.35H), 7.03-7.04 (m, 0.21H), 3.66 (dd, $J = 4.0$ Hz, 8.0 Hz, 1H), 3.47 (dd, $J = 4.0$ Hz, 11.6 Hz, 1H), 3.44 (s, 0.68H), 3.26 (dd, $J = 8.0$ Hz, 11.6 Hz, 1H), 1.41 (s, 2.1H), 1.34 (s, 9H) (keto/enol = 10/3); $^{13}$C NMR (CDCl$_3$, 100MHz) δ 197.0, 167.8, 156.2, 145.7, 135.5, 135.3, 131.6, 129.8, 125.4, 123.5, 120.1, 115.3, 107.8,
105.1, 82.2, 81.3, 54.9, 32.5, 29.2, 28.3, 27.9; IR(KBr) ν = 3414, 3080, 3007, 2978, 2934, 1712, 1593, 1455, 1317, 1149, 790 cm−1; HRMS(ESI): calcd. for C₁₄H₁₆BrO₃ [M+H]⁺ 311.0283, found 311.0271.

**Tert-butyl 4-bromo-1-oxo-2,3-dihydro-1H-indene-2-carboxylate (1l):**
Colorless solid (242 mg, 26%); m.p. 128-129 °C; ¹H NMR (CDCl₃, 400 MHz) δ 10.5 (brs, 0.32H), 7.79 (d, J = 8.0 Hz, 1H), 7.73 (d, J = 8.0 Hz, 1H), 7.53-7.59 (m, 0.8H), 7.26-7.33 (m, 1.7H), 3.68 (dd, J = 4.0 Hz, 8.0 Hz, 1H), 3.45 (dd, J = 4.0 Hz, 16.0 Hz, 1H), 3.43 (s, 0.6H), 3.30 (dd, J = 8.0 Hz, 16.0 Hz, 1H), 1.61 (s, 3H), 1.52 (s, 9H) (keto/enol = 3/1); ¹³C NMR (CDCl₃, 100MHz) δ 199.2, 167.8, 153.3, 138.0, 132.0, 129.5, 128.7, 123.4, 122.0, 119.6, 82.4, 81.4, 54.3, 34.3, 31.5, 28.5, 28.0; IR(KBr) ν = 2998, 2986, 1726, 1701, 1367, 1237, 1153, 1013, 839, 782 cm⁻¹; HRMS(ESI): calcd. for C₁₄H₁₅BrNaO₃ [M+Na]⁺ 333.0102, found 333.0101.

**Adamantan-1-ylmethyl 1-oxo-2,3-dihydro-1H-indene-2-carboxylate (1o):**
The mixture of methyl 1-oxo-2,3-dihydro-1H-indene-2-carboxylate (950 mg, 5 mmol), 1-adamantanemethanol (1.04 g, 6.5 mmol) and Bu₂SnO (126 mg, 10 mol%) was dissolved in toluene (50 mL) and the suspension was stirred at reflux for 24 h. After complete consumption of the starting material, the reaction mixture was then concentrated and purified by column chromatography to give the desired product in 70% yield (1.13 g). Colorless solid, m.p. 94-95 °C; ¹H NMR (CDCl₃, 400 MHz) δ 10.44 (s, 0.31H), 7.78 (d, J = 7.6 Hz, 1H), 7.61-7.66 (m, 1.24H), 7.51 (d, J = 7.6 Hz, 1H), 7.47-7.52 (m, 0.33H), 7.38-7.43 (m, 1.36H), 3.86 (d, J = 4.4 Hz, 1H), 3.83 (s, 0.67H), 3.74-3.76 (m, 1.66H), 3.70 (s, 0.4H), 3.54-3.59 (m, 1.57H), 3.38 (dd, J = 8.4 Hz, 1H), 1.98-2.01 (m, 4H), 1.76-1.78 (m, 2H), 1.73 (s, 3H), 1.70 (s, 3H), 1.61-1.63
(m, 2.56H), 1.60 (s, 1.75H), 1.54 (d, J = 2.0 Hz, 6H); 13C NMR (CDCl3, 100 MHz) δ 199.5, 153.6, 135.4, 135.3, 127.8, 126.8, 126.6, 124.6, 120.7, 75.1, 73.4, 53.5, 39.4, 39.1, 37.0, 36.9, 33.4, 30.4, 28.1, 28.0 (keto/enol = 3.3/1); IR(KBr) ν = 3422, 3056, 3038, 2941, 2930, 2903, 2891, 2843, 2671, 1660, 1633, 1597, 1575, 1461, 1417, 1353, 1346, 1266, 1258, 1212, 1188, 1128, 1089, 998, 989, 789, 761, 728, 717 cm⁻¹; HRMS(ESI): calcd for C21H25O3 [M+H]⁺ 325.1804, found 325.1794.

Benzyl 2-oxocyclopentane-1-carboxylate (1p):³

To the solution of ethyl 2-oxocyclopentane-1-carboxylate (30 mmol, 4.68 g) and benzyl alcohol (39 mmol, 4.20 g) in toluene was added I₂ (10 mol%, 762 mg). The reaction mixture was stirred at reflux and detected by TLC. After 12 h, the mixture was cooled to room temperature and concentrated under reduced pressure. The resulting residue was purified by column chromatography to afford the desired compound in 25% yield (1.63 g) as colorless viscous oil. The data are identical to those reported in the literature.

(1R,2S,5R)-5-Methyl-2-(2-phenylpropan-2-yl)cyclohexyl-1-oxo-2,3-dihydro-1H-indene-2-carboxylate (1s):⁴

To a solution of DMAP (32.2 mg, 0.1 eq.) in toluene (0.4 M) was added methyl 1-oxo-2,3-dihydro-1H-indene-2-carboxylate (0.499 g, 2.63 mmol) and 8-phenylmenthol (0.60 g, 1.0 eq.) at room temperature. After refluxing for 2 days using a Dean-Stark apparatus, the mixture was concentrated in vacuo. The residue

was directly purified by chromatography on silica gel (elution with hexane/EtOAc, 1:1) to give the title β-ketoester (575.3 mg, 56%) as colorless oil. The data are identical to those reported in the literature.

Tert-butyl 1-oxo-3-phenyl-2,3-dihydro-1H-indene-2-carboxylate (1t):
Substrate 1t was prepared according to the reported procedure. The data about substrate 1t are identical to those in the literature.

Methyl 1-oxo-4-tosyl-1, 2, 3, 4-tetrahydrocyclopenta[b]indole-2-carboxylate (1u):
To a solution of NC001-8 (217 mg, 1.38 mmol) in the mixed solvent of CH₂Cl₂ and EtOAc (v/v = 2/3, 10 mL) was added NaOH (172 mg, 4.31 mmol) in portions at 0 °C, after that a catalytic amount of Bu₄HSO₄ (2.4 mol%, 11.2 mg) was added in one portion to the above solution. Then a solution of TsCl (328 mg, 1.73 mmol) in the mixed solvent of CH₂Cl₂ and EtOAc was added dropwise to the mixture under stirring. After the reaction was complete determined by TLC, the reaction was quenched using 10 mL H₂O and the resulting aqueous solution was extracted with EtOAc for three times. The combined organic phase was successively washed by water, saturated NaHCO₃ solution and brine. Then the organic phase was dried over anhydrous MgSO₄ and evaporated under reduced pressure to afford the crude product, which was used directly in the next step.
To the solution of the crude product above (432 mg, 1.33 mmol) in 10 mL dry THF

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was added the THF solution of LiHMDS (2.6 mmol, 2.66 mL) slowly at -78 °C under nitrogen gas atmosphere. After stirring for 1 h, ClCO₂Me in dry THF was added slowly to the above mixture. After complete consumption of the starting material, the reaction was quenched using 10 mL saturated NH₄Cl solution. Then the resulting aqueous solution was extracted with EtOAc for three times and the extracts were combined and dried over anhydrous MgSO₄. After that, the organic solvent was evaporated under reduced pressure to afford the residue which was purified using column chromatography. The desired product was offered in 90% yield (476 mg) as yellowish oil. ¹H NMR (CDCl₃, 400 MHz) δ 7.97 (d, J = 8.0 Hz, 1H), 7.86-7.88 (m, 2H), 7.81 (d, J = 8.0 Hz, 1H), 4.04 (dd, J = 2.8 Hz, 7.2 Hz, 1H), 3.83 (dd, J = 2.8 Hz, 18.4 Hz, 1H), 3.82 (s, 3H), 3.65 (dd, J = 7.2 Hz, 18.8 Hz, 1H), 2.39 (s, 3H); ¹³C NMR (CDCl₃, 100 MHz) δ 188.6, 169.2, 166.1, 146.4, 140.6, 134.5, 130.5, 127.1, 126.0, 125.0, 123.8, 122.2, 112.1, 114.0, 57.3, 52.9, 28.3, 21.7; IR (KBr) ν = 3432, 3070, 2949, 1960, 1921, 1733, 1706, 1611, 1594, 1559, 1481, 1448, 1410, 1369, 1313, 1216, 1180, 1142, 1117, 1039, 944, 789, 760, 670, 578, 540; HRMS(ESI): calcd for C₂₀H₁₈NO₅S [M+H]+ 384.0906, found 384.0900.

III. General Procedure for AIBX-Mediated Dehydrogenative Cyclopropanation Using Malononitrile as a Nucleophile

To a solution of 1a (46.4 mg, 0.2 mmol) and malononitrile (26.4 mg, 0.4 mmol) in 1:3 (v/v) CH₃CN/water (5.2 mL) were added AcOH (11.4 μL, 0.2 mmol) and AIBX (170 mg, 0.5 mmol) successively. The reaction mixture was heated to 40 °C with stirring and monitored by TLC. After 1a was consumed, the reaction mixture was allowed to cool to room temperature and extracted with EtOAc (3 × 50 mL). The combined organic layers were washed with brine and dried over anhydrous MgSO₄. The solvent was evaporated, and the residue was purified by column chromatography to afford 2a in 98% yield (58 mg); colorless solid, m.p. 160-162 °C; ¹H NMR (CDCl₃, 400MHz) δ 7.80 (d, J = 7.6 Hz, 1H), 7.71-7.58 (m, 2H), 7.51-7.53 (m, 1H), 4.36 (q, J = 7.2 Hz, 2H), 4.13 (s, 1H), 1.50 (s, 9H), 1.39 (t, J = 7.2 Hz, 3H); ¹³C NMR (CDCl₃, 100MHz) δ
190.9, 162.0, 161.3, 145.1, 135.9, 133.3, 130.0, 126.5, 125.7, 113.2, 84.2, 63.9, 49.8, 43.3, 37.5, 27.8, 13.9; IR(KBr) ν = 3417, 3097, 3077, 3006, 2979, 2934, 2250, 1745, 1714, 1608, 1597, 1467, 1374, 1328, 1298, 1254, 1226, 1149, 1094, 1012, 918, 833, 805, 773 cm⁻¹; HRMS(ESI): calcd for C_{17}H_{18}N_{3}O_{3} [M+NH_{4}]⁺ 312.1348, found 312.1341. The aqueous phase was evaporated under vacuum to afford the white solid which was reoxidized by freshly prepared dimethyldioxirane to regenerate AIBX in 91% yield.
IV. Optimization

Table 1. Optimization of cyclopropanation conditions$^a$

<table>
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<tr>
<th>entry</th>
<th>malononitrile (equiv)</th>
<th>organic solvent/H$_2$O (v/v)</th>
<th>time (h)</th>
<th>yield (%)$^b$</th>
</tr>
</thead>
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<td>CH$_3$CN/H$_2$O (3/1)</td>
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<td>65</td>
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<tr>
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<td>CH$_3$CN/H$_2$O (3/1)</td>
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<td>CH$_3$CN/H$_2$O (1/2)</td>
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</tr>
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<td>CH$_3$CN/H$_2$O (1/3)</td>
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<tr>
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<td>THF/H$_2$O (1/3)</td>
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<td>9</td>
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<td>14</td>
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<td>CHCl$_3$/H$_2$O (1/3)</td>
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<td>12 (16)$^d$</td>
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<td>15</td>
<td>2.0</td>
<td>EtOAc/H$_2$O (1/3)</td>
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<td>52 (78)$^d$</td>
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<td>HFIP/H$_2$O (1/3)</td>
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<td>t-BuOH/H$_2$O (1/3)</td>
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<td>45 (85)$^d$</td>
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<td>20</td>
<td>1.5</td>
<td>CH$_3$CN/H$_2$O (1/3)</td>
<td>4</td>
<td>83</td>
</tr>
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</table>

$^a$Reactions were carried out with 0.2 mmol of 1a in 5.2 mL of solvent at 40 °C. $^b$Isolated yields.

$^c$Reaction was conducted without AcOH. $^d$Numbers in parentheses indicate conversion of 1a.
Table 2. Optimization of additives and oxidants

<table>
<thead>
<tr>
<th>entry</th>
<th>malononitrile (equiv)</th>
<th>additive</th>
<th>oxidant</th>
<th>time (h)</th>
<th>yield (%)</th>
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</thead>
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<td>1</td>
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<td>Cl₂CHCO₂H</td>
<td>AIBX</td>
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<td>88</td>
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*a*The reaction was carried out on 0.2 mmol of 1a in 5.2 mL of solvent at 40 °C. *b*Isolated yields. *c*Not detected. *d*IBX was referred as 2-iodoxybenzoic acid. *e*Dess-Martin reagent was used as oxidant. *f*(Diacetoxyiodo)benzene was used as oxidant. *g*[bis(trifluoroacetoxy)iodo]benzene was used as oxidant. *h*Ceric ammonium nitrate was used as oxidant. *i*2,3-Dicyano-5,6-dichlorobenzoquinone was used as oxidant.
V. Procedure for AIBX-Mediated Dehydrogenative Cyclopropanation Using Methyl Cyanoacetate as a Nucleophile

To a solution of 1a (46.4 mg, 0.2 mmol) and methyl cyanoacetate (39.6 mg, 0.4 mmol) in 2:3 (v/v) CH$_3$CN/water (5.2 mL) were added AcOH (11.4 μL, 0.2 mmol) and AIBX (170 mg, 0.5 mmol) successively. The reaction mixture was heated to 40 °C with stirring and monitored by TLC. After 1a was consumed, the reaction mixture was allowed to cool to room temperature and extracted with EtOAc (3 × 50 mL). The combined organic layer was washed with brine and dried over anhydrous MgSO$_4$. The solvent was evaporated, and the residue was purified by column chromatography to afford 2r in 76% yield (50 mg); yellowish solid, m.p. 103-104 °C; $^1$H NMR (CDCl$_3$, 400 MHz) δ 7.79 (d, $J = 8.0$ Hz, 1H), 7.66-7.70 (m, 1H), 7.61 (d, $J = 8.0$ Hz, 1H), 7.50-7.53 (m, 1H), 4.51 (s, 1H), 3.89 (s, 3H), 1.51 (s, 9H); $^{13}$C NMR (CDCl$_3$, 100 MHz) δ 191.0, 162.6, 161.4, 145.1, 130.1, 126.6, 125.8, 113.2, 84.4, 54.2, 49.8, 37.7, 27.9; IR(KBr) ν = 3420, 3101, 3008, 2984, 2963, 2934, 2852, 2247, 1744, 1731, 1605, 1590, 1471, 1454, 1435, 1394, 1369, 1292, 1257, 1203, 1158, 1145, 1087, 973, 937, 858, 808, 772, 765, 719, 709 cm$^{-1}$; HRMS(ESI): calcd for C$_{18}$H$_{21}$N$_2$O$_5$ [M+NH$_4$]$^+$ 345.1450, found 345.1449.
VI. Single Crystallographic Data of Cyclopropane 2a and 2r

Single crystallographic structure of cyclopropane 2a

Single crystallographic structure of cyclopropane 2r
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### VII. Optimization for Cyclopropanation of Fully Saturated Substrate

![Cyclopropanation Reaction Scheme]

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<sup>a</sup>Isolated yield. <sup>b</sup>TSA = p-toluenesulfonic acid. <sup>c</sup>CSA = Camphorsulfonic acid. <sup>d</sup>not detected.
VIII. Characterization of Cyclopropane Products

*Tert*-butyl

1,1-dicyano-3-methoxy-6-oxo-1a,6-dihydrocyclopropa[a]indene-6a(1H)-Carboxylate (2b):

Colorless solid (60 mg, 92%); m.p. 148-149 °C; $^1$H NMR (CDCl$_3$, 400MHz) $\delta$ 7.74 (d, $J = 8.8$ Hz, 1H), 7.14 (s, 1H), 7.04 (d, $J = 8.8$ Hz, 1H), 4.00 (s, 1H), 3.95 (s, 3H), 1.58 (s, 9H); $^{13}$C NMR (CDCl$_3$, 100MHz) $\delta$ 185.7, 166.4, 160.2, 145.4, 128.0, 126.0, 117.4, 111.9, 110.3, 110.1, 86.1, 56.1, 45.6, 37.9, 27.8, 26.9; IR(KBr) $\nu = 3396$, 3064, 2982, 2937, 2248, 1742, 1701, 1613, 1587, 1486, 1455, 1443, 1370, 1355, 1340, 1305, 1278, 1153, 1119, 1096, 1023, 1013, 885, 838, 800, 652 cm$^{-1}$; HRMS(ESI): calcd for C$_{18}$H$_{20}$N$_3$O$_4$[M+NH$_4$]$^+$ 342.1454, found 342.1443.

*Tert*-butyl

1,1-dicyano-4-methyl-6-oxo-1a,6-dihydrocyclopropa[a]indene-6a(1H)-Carboxylate (2c):

Colorless solid (60 mg, 97%); m.p. 154-155 °C; $^1$H NMR (CDCl$_3$, 400 MHz) $\delta$ 7.61 (s, 1H), 7.58 (d, $J = 7.6$ Hz, 1H), 7.53 (d, $J = 7.6$ Hz, 1H), 4.07 (s, 1H), 2.44 (s, 3H), 1.59 (s, 9H); $^{13}$C NMR (CDCl$_3$, 100MHz) $\delta$ 187.7, 160.2, 141.9, 137.4, 133.6, 126.3, 110.3, 110.2, 86.2, 45.4, 38.3, 27.9, 27.4, 21.4; IR(KBr) $\nu = 3443$, 3069, 2990, 2981, 2930, 2247, 1927, 1880, 1744, 1616, 1589, 1491, 1374, 1367, 1326, 1269, 1236, 1161, 846, 828, 765, 739, 680, 611, 502; HRMS (ESI): calcd for C$_{18}$H$_{17}$N$_2$O$_3$ [M+H]$^+$ 309.1234, found 309.1234.
**Tert-butyl 1,1-dicyano-2-methyl-6-oxo-1a,6-dihydrocyclopropa[a]indene-6a(1H)-carboxylate (2d):**

Colorless solid (57 mg, 93%); m.p. 163-164 °C; $^1$H NMR (CDCl$_3$, 400MHz) δ 7.65 (d, $J = 7.6$ Hz, 1H), 7.54 (d, $J = 7.6$ Hz, 1H), 7.47-7.49 (m, 1H), 4.07 (s, 1H), 2.57 (s, 3H), 1.60 (s, 9H); $^{13}$C NMR (CDCl$_3$, 100 MHz) δ 187.8, 160.1, 141.4, 136.8, 133.5, 131.1, 131.1, 123.6, 110.3, 110.0, 86.2, 45.2, 37.1, 27.8, 26.9, 17.8; IR (KBr) ν = 3419, 3051, 2985, 2935, 2248, 1743, 1732, 1718, 1594, 1485, 1458, 1373, 1364, 1333, 1281, 1244, 1154, 1106, 955, 816, 779, 735 cm$^{-1}$; HRMS(ESI): calcd for C$_{18}$H$_{14}$N$_3$O$_3$ [M+NH$_4$]$^+$ 326.1505, found 326.1498.

**Tert-butyl 1,1-dicyano-2,4-dimethyl-6-oxo-1a,6-dihydrocyclopropa[a]indene-6a(1H)-carboxylate (2e):**

Colorless solid (48 mg, 75%); m.p. 167-168 °C; $^1$H NMR (CDCl$_3$, 400MHz) δ 7.30 (s, 1H), 7.13 (s, 1H), 4.00 (s, 1H), 2.57 (s, 3H), 2.45 (s, 3H), 1.59 (s, 9H); $^{13}$C NMR (CDCl$_3$, 100MHz) δ 187.8, 160.3, 147.5, 141.5, 134.2, 128.2, 125.1, 110.5, 110.2, 85.9, 45.7, 38.0, 27.8, 26.4, 22.0, 18.1; IR(KBr) ν = 3071, 2976, 2928, 2248, 1741, 1702, 1609, 1373, 1274, 1252, 1156, 1098, 911 cm$^{-1}$; HRMS(ESI): calcd for C$_{19}$H$_{18}$N$_2$NaO$_3$[M+Na]$^+$ 345.1215, found 345.1206.

**Ethyl 7,7-dicyano-8-oxo-6b,8-dihydrocyclopropa[3,4]cyclopenta[1,2-a]naphthalene**
-7a(7H)-carboxylate (2f):
Colorless solid (57 mg, 91%); m.p. 218-219 °C; $^1$H NMR (CDCl$_3$, 400MHz) δ 8.97 (d, $J = 8.4$ Hz, 1H), 8.24 (d, $J = 8.4$ Hz, 1H), 7.96 (d, $J = 8.0$ Hz, 1H), 7.74-7.77 (m, 2H), 7.63-7.68 (m, 1H), 4.42-4.53 (m, 2H), 4.25 (s, 1H), 1.44 (t, $J = 6.8$ Hz, 3H); $^{13}$C NMR (CDCl$_3$, 100MHz) δ 187.8, 161.7, 145.4, 138.3, 134.5, 130.8, 129.4, 128.8, 128.5, 124.2, 122.6, 110.1, 110.0 64.0, 44.9, 38.2, 29.2, 14.0; IR(KBr) ν = 3421, 3060, 2248, 1736, 1721, 1587, 1569, 1374, 1289, 1165, 1062, 1032, 1009, 840, 753 cm$^{-1}$; HRMS(ESI): calcd for C$_{19}$H$_{13}$N$_2$O$_3$[M+H]$^+$ 317.0926, found 317.0916.

![Ethyl-3-(allyloxy)-1,1-dicyano-4-methoxy-6-oxo-1a,6-dihydrocyclopenta[a]inden e-6a(1H)-carboxylate (2g):](image)

Ethyl-3-(allyloxy)-1,1-dicyano-4-methoxy-6-oxo-1a,6-dihydrocyclopenta[a]inden e-6a(1H)-carboxylate (2g):
Colorless solid (66 mg, 94%); m.p. 214-215 °C; $^1$H NMR (CDCl$_3$, 400 MHz) δ 7.20 (s, 1H), 7.09 (s, 1H), 6.04-6.10 (m, 1H), 5.44 (dd, $J = 12$ Hz, 28 Hz, 2H), 4.76 (q, $J = 8.0$ Hz, 2H), 4.41-4.44 (m, 2H), 4.03 (s, 1H), 3.91 (s, 3H), 1.39 (t, $J = 8.0$ Hz, 3H); $^{13}$C NMR (CDCl$_3$, 100MHz) δ 186.0, 161.8, 155.5, 152.1, 137.7, 126.1, 119.6, 110.1, 109.5, 106.6, 63.9, 56.4, 45.0, 38.1, 28.4, 14.0; IR(KBr) ν = 3410, 3069, 2982, 2929, 2243, 1753, 1711, 1589, 1508, 1469, 1354, 1311, 1264, 1231, 1125, 1231, 1125, 1081, 1081, 998, 772 cm$^{-1}$; HRMS(ESI): calcd for C$_{19}$H$_{17}$N$_2$O$_5$ [M+H]$^+$ 353.1137, found 353.1134.

![Tert-butyl 1,1-dicyano-4-fluoro-6-oxo-1a,6-dihydrocyclopenta[a]indene-6a(1H)-carboxylate (2h):](image)

Tert-butyl 1,1-dicyano-4-fluoro-6-oxo-1a,6-dihydrocyclopenta[a]indene-6a(1H)-carboxylate (2h):
Colorless solid (57 mg, 91%), m.p. 170-171 °C; $^1$H NMR (CDCl$_3$, 400MHz) δ 7.70 (dd, $J = 4.0$ Hz, 8.0 Hz, 1H), 7.42-7.49 (m, 2H), 4.11 (s, 1H), 1.59 (s, 9H); $^{13}$C NMR
(CDCl$_3$, 100MHz) $\delta$ 186.5, 165.4, 162.9, 159.6, 138.2, 138.1, 135.8, 135.7, 128.6, 123.7, 112.8, 112.6, 110.0, 109.9, 86.5, 45.9, 37.7, 27.8, 27.4; IR(KBr) $\nu$ = 3455, 3070, 2938, 2249, 1740, 1728, 1614, 1489, 1372, 1330, 1273, 1242, 1218, 1158, 1147, 1107, 1088, 1021, 914, 839, 775 cm$^{-1}$; HRMS(ESI): calcd for C$_{17}$H$_{13}$FN$_2$NaO$_3$$^{[M+Na]^+}$ 335.0808, found 335.0798.

\[ \text{Tert-butyl4-chloro-1,1-dicyano-6-oxo-1a,6-dihydrocyclopropa[a]indene-6a(1H)-Carboxylate (2i):} \]

Colorless solid (57 mg, 87%); m.p. 170-171 °C; $^1$H NMR (CDCl$_3$, 400 MHz) $\delta$ 7.78 (d, $J$ = 4.0 Hz, 1H), 7.70 (dd, $J$ = 4.0 Hz, 8.0 Hz, 1H), 7.66 (d, $J$ = 8.0 Hz, 1H), 4.11 (s, 1H), 1.58 (s, 9H); $^{13}$C NMR (CDCl$_3$, 100MHz) $\delta$ 186.3, 159.6, 140.7, 136.4, 135.0, 128.1, 126.1, 110.0, 109.8, 86.7, 45.6, 37.9, 27.8, 27.2; IR(KBr) $\nu$ = 3460, 3092, 3040, 2984, 2936, 2248, 1743, 1730, 1473, 1423, 1393, 1370, 1322, 1252, 1238, 1176, 1157, 1111, 1071, 1019, 913, 841, 833, 738, 719, 609, 508 cm$^{-1}$; HRMS(ESI): calcd for C$_{17}$H$_{17}$ClN$_3$O$_3$$^{[M+NH_4]^+}$ 346.0958, found 346.0954.

\[ \text{Tert-butyl 3-bromo-1,1-dicyano-6-oxo-1a,6-dihydrocyclopropa[a]indene-6a(1H)-Carboxylate (2j):} \]

Colorless solid (71 mg, 95%), m.p. 177-179 °C; $^1$H NMR (CDCl$_3$, 400 MHz) $\delta$ 7.88 (s, 1H), 7.73 (d, $J$ = 8.0 Hz, 1H), 7.67 (d, $J$ = 8.0 Hz, 1H), 4.09 (s, 1H), 1.59 (s, 9H); $^{13}$C NMR (CDCl$_3$, 100MHz) $\delta$ 186.3, 159.6, 144.0, 134.8, 131.9, 130.4, 127.1, 109.9, 109.7, 86.6, 45.3, 37.6, 27.8, 27.0; IR(KBr) $\nu$ = 3421, 3097, 3066, 2986, 2248, 1752, 1000, 1578, 1372, 1351, 1313, 1290, 1252, 1146, 1100, 1054, 1015, 927, 837, 801 cm$^{-1}$, HRMS(ESI): calcd for C$_{17}$H$_{17}$BrN$_3$O$_3$$^{[M+NH_4]^+}$ 390.0453, found 390.0442.
**Tert-butyl 5-bromo-1,1-dicyano-6-oxo-1a,6-dihydrocyclopropa[a]indene-6a(1H)-carboxylate (2k):**

Colorless solid (52 mg, 70%); m.p. 151-152 °C; \(^1\)H NMR (CDCl\(_3\), 400 MHz) \(\delta\) 7.75 (d, \(J = 8.0\) Hz, 1H), 7.67 (d, \(J = 7.2\) Hz, 1H), 7.57-7.59 (m, 1H), 4.08 (s, 1H), 1.60 (s, 9H); \(^{13}\)C NMR (CDCl\(_3\), 100 MHz) \(\delta\) 184.9, 159.6, 145.1, 136.6, 136.4, 130.9, 126.0, 122.2, 110.1, 109.7, 86.6, 46.0, 37.1, 27.8, 26.4; IR(KBr) \(\nu = 3409\), 3074, 2997, 2985, 2929, 2248, 1749, 1715, 1592, 1375, 1155, 788 cm\(^{-1}\); HRMS(ESI): calcd for C\(_{17}\)H\(_{17}\)BrN\(_3\)O\(_3\) \([M+NH_4]^+\) 390.0453, found 390.0453.

**Tert-butyl 2-bromo-1,1-dicyano-6-oxo-1a,6-dihydrocyclopropa[a]indene-6a(1H)-carboxylate (2l):**

Colorless solid (68 mg, 91%); m.p. 128-129 °C; \(^1\)H NMR (CDCl\(_3\), 400 MHz) \(\delta\) 7.88 (d, \(J = 8.0\) Hz, 1H), 7.77 (d, \(J = 8.0\) Hz, 1H), 7.44-7.48 (m, 1H), 4.20 (s, 1H), 1.60 (s, 9H); \(^{13}\)C NMR (CDCl\(_3\), 100 MHz) \(\delta\) 186.7, 159.5, 142.9, 139.3, 135.4, 132.7, 124.8, 121.7, 109.8, 109.6, 86.7, 45.3, 38.5, 27.8, 26.7; IR(KBr) \(\nu = 3461\), 3435, 3047, 2985, 2973, 2933, 2248, 1983, 1849, 1743, 1725, 1596, 1575, 1479, 1458, 1394, 1371, 1361, 1331, 1275, 1242, 1171, 1154, 1128, 1103, 1021, 977, 922, 836, 824, 786, 754, 724, 622, 598 cm\(^{-1}\); HRMS(ESI): calcd for C\(_{17}\)H\(_{17}\)BrN\(_3\)O\(_3\) \([M+NH_4]^+\) 390.0453, found 390.0447.

**Ethyl 1,1-dicyano-6-oxo-4-(trifluoromethyl)-1a,6-dihydrocyclopropa[a]indene-6a(1H)-carboxylate (2m):**
Colorless solid (44 mg, 65%), m.p. 124-125 °C; $^1$H NMR (CDCl$_3$, 400 MHz) δ 8.10 (s, 1H), 8.02 (d, $J = 8.0$ Hz, 1H), 7.89 (d, $J = 8.0$ Hz, 1H), 4.41-4.49 (m, 2H), 4.28 (s, 1H), 1.41 (t, $J = 7.2$ Hz, 3H); $^{13}$C NMR (CDCl$_3$, 100MHz) δ 185.8, 160.8, 145.4, 134.1, 134.0, 133.8, 133.2, 133.2, 127.8, 124.2, 123.3, 121.4, 109.6, 109.3, 64.3, 45.2, 38.0, 27.1, 13.9; IR(KBr) ν = 3440, 3075, 3000, 2248, 1772, 1760, 1652, 1336, 1327, 1282, 1246, 1218, 1167, 1133, 1109, 1057, 1014, 922, 854, 689, 629 cm$^{-1}$; HRMS(ESI): calcd for C$_{16}$H$_{10}$F$_3$N$_2$O$_3$[M +H]$^+$ 335.0644, found 335.0642.

Benzyl 1,1-dicyano-6-oxo-1a,6-dihydrocyclopropa[a]indene-6a(1H)-carboxylate (2n):

Colorless solid (52 mg, 80%), m.p. 135-136°C; $^1$H NMR (CDCl$_3$, 400 MHz) δ 7.84 (d, $J = 4$ Hz, 1H), 7.69-7.77 (m, 2H), 7.60 (t, $J = 8$ Hz, 1H), 7.36-7.46 (m, 5H), 5.35-5.42 (m, 2H), 4.19 (s, 1H); $^{13}$C NMR (CDCl$_3$, 100MHz) δ 186.9, 161.5, 142.4, 133.2, 128.8, 126.3, 110.0, 109.7, 69.4, 61.7, 44.7, 42.4, 38.5, 27.5, 17.7; IR(KBr) ν = 3446, 3050, 2250, 1747, 1730, 1607, 1463, 1392, 1301, 1253, 1229, 1181, 1096, 975, 953, 767, 738, 697, 623 cm$^{-1}$; HRMS(ESI): calcd for C$_{20}$H$_{16}$N$_3$O$_3$ [M+NH$_4$]$^+$ 346.1192, found 346.1182.

(Adamantan-1-yl)methyl-1,1-dicyano-6-oxo-1a,6-dihydrocyclopropa[a]indene-6a (1H)-carboxylate (2o):

Colorless solid (67 mg, 87%); m.p. 185-186 °C. $^1$H NMR (CDCl$_3$, 400MHz) δ 7.85 (d, $J = 7.6$ Hz, 1H), 7.72-7.79 (m, 2H), 7.59-7.63 (m, 1H), 4.18 (s, 1H), 3.92-4.01 (m, 2H), 2.02 (brs, 3H), 1.70 (m, 6H), 1.61 (s, 6H); $^{13}$C NMR (CDCl$_3$, 100MHz) δ 187.1, 161.8, 142.5, 131.3, 127.1, 126.3, 110.2, 109.9, 45.1, 39.0, 38.5, 36.8, 33.5, 27.9, 27.4;
IR(KBr) ν = 3448, 3068, 2910, 2848, 2674, 2653, 2247, 1733, 1604, 1594, 1466, 1454, 1385, 1365, 1329, 1297, 1257, 1250, 1219, 1185, 1158, 1095, 981, 955, 804, 768, 683, 625, 598 cm⁻¹; HRMS(ESI): calcd for C_{24}H_{26}N_{3}O_{3}[M+NH_{4}]⁺ 404.1974, found 404.1976.

**Benzyl-6,6-dicyano-2-oxobicyclo[3.1.0]hexane-1-carboxylate (2p):**

Red oil (40 mg, 65%); ¹H NMR (CDCl₃, 400MHz) δ 7.37-7.41 (m, 5H), 5.23 (m, 2H), 3.27 (d, J = 5.6 Hz, 1H), 2.48-2.65 (m, 3H), 2.31-2.36 (m, 1H); ¹³C NMR (CDCl₃, 100MHz) δ 199.5, 161.4, 134.0, 129.0, 128.9, 128.8, 110.3, 110.2, 69.3, 49.5, 40.7, 35.1, 19.6, 15.3; IR(KBr) ν = 3066, 2955, 2249, 1758, 1740, 1498, 1404, 1388, 1294, 1214, 1024, 990, 747, 698 cm⁻¹; HRMS(ESI): calcd for C_{16}H_{12}N_{2}NaO_{3} [M+Na]⁺ 303.0746, found 303.0742.

**Methyl 6,6-dicyano-2-oxobicyclo[3.1.0]hexane-1-carboxylate (2q):**

Red oil (32 mg, 77%); ¹H NMR (CDCl₃, 400 MHz) δ 3.92 (s, 3H), 3.37 (s, 1H), 2.49-2.71 (m, 3H), 2.32-2.39 (m, 1H); ¹³C NMR (CDCl₃, 100MHz) δ 199.4, 161.9, 110.2, 110.1, 54.2, 49.6, 40.7, 35.1, 19.6, 15.2; IR(KBr) ν = 3646, 3444, 3353, 3069, 2958, 2924, 2853, 2250, 2222, 1732, 1715, 1651, 1462, 1407, 1377, 1260, 1075, 1023, 867, 800 cm⁻¹; HRMS(ESI): calcd for C_{16}H_{12}N_{2}O_{3}[M+H]⁺ 205.0613, found 205.0602.

**6a-(Tert-butyl)1-methyl1-cyano-6-oxo-1a,6-dihydrocyclopropa[a]indene-1,6a(1H)-Dicarboxylate (2r):**

23
Yellow solid (50 mg, 76%), m.p. 103-104 °C; \(^1\)H NMR (CDCl\(_3\), 400 MHz) \(\delta\) 7.79 (d, \(J = 8.0\) Hz, 1H), 7.66-7.70 (m, 1H), 7.61 (d, \(J = 8.0\) Hz, 1H), 7.50-7.53 (m, 1H), 4.51 (s, 1H), 3.89 (s, 3H), 1.51 (s, 9H); \(^{13}\)C NMR (CDCl\(_3\), 100MHz) \(\delta\) 191.0, 162.6, 161.4, 145.1, 130.1, 126.6, 125.8, 113.2, 84.4, 54.2, 49.8, 37.7, 27.9; IR(KBr) \(\nu = \) 3420, 3101, 3008, 2984, 2963, 2934, 2852, 2247, 1744, 1731, 1605, 1590, 1471, 1454, 1435, 1394, 1369, 1292, 1257, 1203, 1158, 1145, 1087, 973, 937, 858, 808, 772, 765, 719, 709 cm\(^{-1}\); HRMS(ESI): calcd for C\(_{18}\)H\(_{21}\)N\(_2\)O\(_5\) [M+NH\(_4\)]\(^+\) 345.1450, found 345.1449.

5-Methyl-2-(2-phenylpropan-2-yl)cyclohexyl(1aS,6aR)-1,1-dicyano-6-oxo-1a,6-di hydrocycloprop[a]indene-6a(1H)-carboxylate (2s):

Bubble-shaped solid (84 mg, 93%), m.p. 80-81°C; Only one diastereomer was observed from its crude NMR spectra (> 90% \(de\) value). \(^1\)H NMR (CDCl\(_3\), 400 MHz) \(\delta\) 7.80 (d, \(J = 8.0\) Hz, 1H), 7.74 (m, 1H), 7.59 (d, \(J = 8.0\) Hz, 1H), 7.54 (d, \(J = 8.0\) Hz, 1H), 7.26 (d, \(J = 8.0\) Hz, 2H), 7.05 (m, 2H), 6.72 (m, 1H), 5.11 (td, \(J = 4.0\) Hz, 6.0 Hz, 1H), 2.79 (s, 1H), 2.28 (m, 1H), 2.05 (m, 1H), 1.99 (m, 2H), 1.74 (m, 2H), 1.60 (m, 2H), 1.26 (s, 3H), 1.12 (s, 3H), 0.92 (d, \(J = 4.0\) Hz, 3H); \(^{13}\)C NMR (CDCl\(_3\), 100MHZ) \(\delta\) 186.6, 159.3, 152.5, 142.6, 133.3, 130.9, 128.0, 127.0, 125.9, 125.4, 125.2, 110.0, 109.9, 78.3, 49.3, 42.2, 41.4, 39.3, 37.0, 34.3, 31.5, 27.5, 26.2, 21.7, 21.1; IR(KBr) \(\nu = \) 3425, 3062, 2957, 2927, 2869, 2247, 1754, 1605, 1496, 1469, 1388, 1371, 1324, 1299, 1243, 1174, 1156, 1092, 1047, 1031, 975, 950, 926, 776, 764, 701, 681, 622, 604, 563 cm\(^{-1}\); HRMS(ESI): calcd for C\(_{29}\)H\(_{32}\)N\(_3\)O\(_3\)[M+NH\(_4\)]\(^+\) 470.2444, found 470.2439.
**Tert-butyl 1-oxo-3-phenyl-1H-indene-2-carboxylate (3t):**

Yellow oil (32 mg, 52%); \(^1\)H NMR (CDCl\(_3\), 400MHz) \(\delta 7.58-7.60\) (m, 1H), 7.50 (s, 5H), 7.37-7.40 (m, 2H), 7.15-7.17 (m, 1H), 1.34 (s, 9H); \(^{13}\)C NMR (CDCl\(_3\), 100MHz) \(\delta 192.3, 163.6, 162.1, 143.3, 133.4, 132.0, 130.1, 128.4, 127.9, 125.7, 123.3, 123.1, 81.9, 27.8\); IR(KBr) \(\nu = 3469, 3081, 3004, 2980, 2927, 1817, 1739, 1601, 1563, 1473, 1461, 1395, 1369, 1332, 1290, 1240, 1169, 1154, 1089, 907, 851, 773, 725, 694, 531\) cm\(^{-1}\); HRMS(ESI): calcd for C\(_{20}\)H\(_{19}\)O\(_3\) \([M+H]^+\) 307.1334, found 307.1337.

![Chemical Structure of 3t](image)

**Methyl 1,1-dicyano-7-oxo-2-tosyl-1,1a,2,7-tetrahydro-7aH-cyclopropa[4,5]cyclopenta[1,2-b]indole-7a-carboxylate (2u):**

Colorless solid (76 mg, 85%), m.p. 177-178 °C; \(^1\)H NMR (CDCl\(_3\), 400 MHz) \(\delta 8.09\) (d, \(J = 8.4\) Hz, 1H), 7.95 (d, \(J = 8.0\) Hz, 2H), 7.84 (d, \(J = 7.6\) Hz, 1H), 7.50-7.54 (m, 2H), 7.44 (d, \(J = 8.4\) Hz, 2H), 4.58 (s, 1H), 4.03 (s, 3H), 2.46 (s, 3H); \(^{13}\)C NMR (CDCl\(_3\), 100MHz) \(\delta 177.5, 161.7, 154.3, 147.7, 140.9, 133.8, 131.0, 127.8, 127.2, 126.1, 122.9, 122.1, 121.0, 114.3, 109.3, 100.0, 54.4, 47.3, 33.7, 30.3, 21.8\); IR(KBr) \(\nu = 3436, 3071, 2956, 2850, 2252, 1726, 1425, 1391, 1192, 1179, 1086, 667, 571, 539\) cm\(^{-1}\); HRMS(ESI): calcd for C\(_{23}\)H\(_{15}\)N\(_3\)O\(_5\)S \([M+H]^+\) 446.0811, found 446.0801.

**IX. Procedure for Ring-cleavage of Cyclopropane Product:**

![Chemical Structure of 2u](image)

Methyl 2-(2,2-dicyano-3-(methoxycarbonyl)cyclopropyl)-1-tosyl-1H-indole-3-carboxylate (8u): To a solution of cyclopropane 2u (22 mg, 0.05 mmol) in methanol (2 mL), Bu\(_2\)SnO (2.2 mg, 10 mol%) was added in one portion. The resulting suspension was
heated to reflux until the starting material was consumed completely. Then the mixture was diluted with EtOAc and washed with water. The aqueous solution was extracted with EtOAc for three times and the extracts were combined and dried over anhydrous MgSO₄. After that, the solvent was evaporated under reduced pressure to afford the residue which was subjected to column chromatography to offer the ring-cleavage product 8u in 91% yield (22 mg). ¹H NMR (CDCl₃, 400MHz) δ 8.19 (d, J = 8.4 Hz, 1H), 8.11 (d, J = 6.8 Hz, 1H), 7.55 (brs, 2H), 7.43-7.47 (m, 1H), 7.35-7.39 (m, 1H), 4.03 (s, 3H), 4.00 (s, 3H), 3.79 (d, J = 8.4 Hz, 1H), 3.28 (s, 1H), 2.34 (s, 3H); ¹³C NMR (CDCl₃, 100 MHz) δ 165.6, 163.4, 146.4, 134.5, 130.3, 127.2, 126.6, 125.6, 122.7, 115.4, 112.0, 111.7, 63.9, 62.7, 38.7, 31.1, 21.7, 16.6; IR(KBr) ν =3465, 3386, 3075, 3006, 2947, 2852, 2255, 1744, 1701, 1383, 1265, 1179, 1105, 572 cm⁻¹; HRMS(ESI): calcd for C₂₄H₂₃N₄O₆S [M+NH₄]⁺ 495.1338, found 495.1329.

**Tert-butyl 2-(2-(tert-butoxycarbonyl)-3,3-dicyanoallyl)benzoate (4a):**

To a stirring solution of 2a (29.4 mg, 0.1 mmol) in toluene (3 mL) at 0 °C, tBuOK (33.6 mg, 0.3 mmol) was added slowly in portions. Then the mixture was allowed to be stirred at room temperature until the starting material 2a was consumed completely. After that, the toluene was evaporated under reduced pressure and the residue was diluted with EtOAc and the resulting organic solution was washed with water. Then the aqueous phase was extracted with EtOAc for three times and the combined extracts were dried over anhydrous MgSO₄. After evaporating the solvent, the residue was subjected to the column chromatography to offer tetra-substituted alkene 4a (26 mg). Yield: 70%; yellow oil; ¹H NMR (CDCl₃, 400 MHz) δ 7.85 (d, J = 8.0 Hz, 1H), 7.37-7.41 (m, 1H), 7.28-7.32 (m, 1H), 7.13 (d, J = 8.0 Hz, 1H), 4.41 (s, 2H), 1.52 (s, 9H), 1.24 (s, 9H); ¹³C NMR (CDCl₃, 100MHz) δ 167.4, 165.9, 161.5, 134.8, 132.1, 131.9, 131.5, 131.2, 128.2, 111.1, 111.0, 90.2, 86.0, 82.0, 38.4, 28.2, 27.5; IR(KBr) ν
= 3346, 3070, 2978, 2927, 2854, 2236, 2217, 1715, 1370, 1302, 1258, 1153, 1081 cm\(^{-1}\); HRMS(ESI): calcd for C\(_{21}\)H\(_{28}\)N\(_{3}\)O\(_{4}\) [M+NH\(_{4}\)]\(^{+}\) 386.2080, found 386.2076.
X. $^1$H NMR and $^{13}$C NMR Spectra of Substrates

*Tert*-butyl 4,6-dimethyl-1-oxo-2,3-dihydro-1H-indene-2-carboxylate (1e):

![$^1$H NMR CDCl₃ 400M](image1)

![$^{13}$C NMR, CDCl₃ 100M](image2)

Ethyl 1-oxo-2,3-dihydro-1H-cyclopenta[a]naphthalene-2-carboxylate (1f):

![$^1$H NMR CDCl₃ 400M](image3)

![$^{13}$C NMR, CDCl₃ 100M](image4)
Ethyl 5-(allyloxy)-6-methoxy-1-oxo-2,3-dihydro-1H-indene-2-carboxylate (1g):
**Tert-butyl 4-bromo-1-oxo-2,3-dihydro-1H-indene-2-carboxylate (II):**

\[
\begin{array}{cccccccccccccc}
9.07 & 3.29 & 1.10 & 1.38 & 0.35 & 1.01 & 0.55 & 1.19 & 0.81 & 1.00 & 1.00 & 0.32 & 1.52 & 1.61 & 3.27 & 3.29 & 3.31 & 3.33 & 3.42 & 3.43 & 3.43 & 3.46 & 3.47 & 3.66 & 3.67 & 3.68 & 3.69
\end{array}
\]

\[
\begin{array}{cccccccccccccc}
28.01 & 28.48 & 31.45 & 34.34 & 54.31 & 76.76 & 77.08 & 77.39 & 81.44 & 82.40 & 119.60 & 122.01 & 123.38 & 128.65 & 137.41 & 137.98 & 142.85 & 153.33 & 167.76 & 199.20
\end{array}
\]
**Tert-butyl 7-bromo-1-oxo-2,3-dihydro-1H-indene-2-carboxylate (1k):**

![Chemical structure of tert-butyl 7-bromo-1-oxo-2,3-dihydro-1H-indene-2-carboxylate](image1)

**Adamantan-1-ylmethyl 1-oxo-2,3-dihydro-1H-indene-2-carboxylate (1o):**

![Chemical structure of Adamantan-1-ylmethyl 1-oxo-2,3-dihydro-1H-indene-2-carboxylate](image2)
Methyl 1-oxo-4-tosyl-1,2,3,4-tetrahydrocyclopenta[b]indole-2-carboxylate (1u):
XI. $^1$H NMR and $^{13}$C NMR Spectra of Cyclopropane Products

Tert-butyl 1,1-dicyano-6-oxo-1a,6-dihydrocycloprop[a]indene-6a(1H)-carboxylate (2a):
Tert-butyl 1,1-dicyano-3-methoxy-6-oxo-1a,6-dihydrocycloprop[a]indene-6a(1H)-carboxylate (2b):

**H NMR, CDCl₃, 400 MHz**

**C NMR, CDCl₃, 100 MHz**

Tert-butyl 1,1-dicyano-4-methyl-6-oxo-1a,6-dihydrocycloprop[a]indene-6a(1H)-carboxylate
(2c): 

\[
\text{CDCl}_3, ^1\text{H NMR, 400M}
\]

\[
\begin{array}{cccccccccccccccc}
0.0 & 21.4 & 27.4 & 27.9 & 38.3 & 45.4 & 76.7 & 77.0 & 77.4 & 86.2 & 110.2 & 110.3 & 126.3 & 126.6 & 133.6 & 137.4 & 140.0 & 141.9 & 160.2 & 187.7
\end{array}
\]

\[
Tert\text{-butyl 1,1-dicyano-2-methyl-6-oxo-1a,6-dihydrocyclopropa[a]indene-6a(1H)-carboxylate (2d):}
\]

\[
\text{CDCl}_3, ^1\text{H NMR, 100M}
\]
Tert-butyl 1,1-dicyano-2,4-dimethyl-6-oxo-1a,6-dihydrocycloprop[a]indene-6a(1H)-carboxylate (2e):
Ethyl 7,7-dicyano-8-oxo-6b,8-dihydrocyclopropa[3,4]cyclopenta[1,2-a]naphthalene-7a(7H)-carboxylate
(2f):

Ethyl-3-(allyloxy)-1,1-dicyano-4-methoxy-6-oxo-1a,6-dihydrocyclopropa[a]indene-6a(1H)-carboxylate (2g):
Tert-butyl 1,1-dicyano-4-fluoro-6-oxo-1a,6-dihydrocyclopropa[a]indene-6a(1H)-carboxylate (2h):
Tert-butyl-4-chloro-1,1-dicyano-6-oxo-1a,6-dihydrocycloprop[a]indene-6a(1H)-Carboxylate (2i):
Tert-butyl 3-bromo-1,1-dicyano-6-oxo-1a,6-dihydrocyclopropa[a]indene-6a(1H)-Carboxylate (2j):
Tert-butyl 5-bromo-1,1-dicyano-6-oxo-1a,6-dihydrocyclopropa[a]indene-6a(1H)-carboxylate (2k):
Tert-butyl 2-bromo-1,1-dicyano-6-oxo-1a,6-dihydrocyclopropa[a]indene-6a(1H)-Carboxylate (2l):

**CDCl₃, 400 M**

**CDCl₃, 100M**
Ethyl 1,1-dicyano-6-oxo-4-(trifluoromethyl)-1a,6-dihydrocyclopropa[a]indene-6a(1H)-carboxylate (2m):
Benzyl 1,1-dicyano-6-oxo-1a,6-dihydrocyclopropa[a]indene-6a(1H)-carboxylate (2n):
(Adamantan-1-yl)methyl-1,1-dicyano-6-oxo-1a,6-dihydrocycloprop[a]indene-6a(1H)-carboxylate (2o):
Benzyl-6,6-dicyano-2-oxobicyclo[3.1.0]hexane-1-carboxylate (2p):
Methyl 6,6-dicyano-2-oxobicyclo[3.1.0]hexane-1-carboxylate (2q):
6α-(Tert-butyl)1-methyl1-cyano-6-oxo-1a,6-dihydrocyclopropa[a]indene-1,6a(1H)-Dicarboxylate (2r):
5-Methyl-2-(2-phenylpropan-2-yl)cyclohexyl-1,1-dicyano-6-oxo-1a,6-dihydrocyclopropa[a]inden-6a(1H)-carboxylate (2s):
Tert-butyl 1-oxo-3-phenyl-1H-indene-2-carboxylate (3t):
Methyl

1,1-dicyano-7-oxo-2-tosyl-1,1a,2,7-tetrahydro-7aH-cyclopropa[4,5]cyclo-penta[1,2-b]indole-7a-c
arboxylate (2u):
Tert-butyl 2-(2-(tert-butoxycarbonyl)-3,3-dicyanoallyl)benzoate (4a):

$^{1}H$ NMR, CDCl$_3$, 400M

$^{13}C$ NMR, CDCl$_3$, 100M
Methyl 2-(2,2-dicyano-3-(methoxycarbonyl)cyclopropyl)-1-tosyl-1H-indole-3-carboxylate (8u):