Regiodivergent Construction of Medium-Sized Heterocycles from Vinylethylene Carbonates and Allylidenemalononitrils

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1. General Information

General Procedures

● All reactions were performed in oven-dried or flame-dried reaction vessels, modified Schlenk flasks, or round-bottom flasks. The flasks were fitted with Teflon screw caps and reactions were conducted under an atmosphere of argon if needed. Gas-tight syringes with stainless steel needles were used to transfer air- and moisture-sensitive liquids. All moisture and/or air sensitive solid compounds were manipulated inside normal desiccators. Flash column chromatography was performed using silica gel (40–63 µm, 230–400 mesh).

● Analytical thin layer chromatography (TLC) was performed on silica gel 60 F254 aluminum plates (Merck) containing a 254 nm fluorescent indicator. TLC plates were visualized by exposure to short wave ultraviolet light (254 nm) and I₂.

● Organic solutions were concentrated at 30-50 °C on rotary evaporators at ~10 torr followed by drying on vacuum pump at ~1 torr. Reaction temperatures are reported as the temperature of the bath surrounding the vessel unless otherwise stated.

Materials

● Commercial reagents and solvents were were purchased from Adamas-beta, Aldrich Chemical Co., Alfa Aesar, Macklin and Energy Chemical and used as received with the following exceptions: THF, Et₂O and toluene were purified by refluxing over Na-benzophenone under positive argon pressure followed by distillation.¹ The allylidene malononitriles 1², vinylethylene carbonates 2³, and oxazolidinone 9⁴ were prepared according to literature procedure.

Instrumentation

● Proton nuclear magnetic resonance (¹H NMR) spectra were recorded with JEOL-600M. Proton chemical shifts are reported in parts per million (δ scale), and are referenced using residual protium in the NMR solvent (CDCl₃: δ 7.26 (CHCl₃)). Data are reported as follows: chemical shift [multiplicity (s = singlet, d = doublet, t = triplet, q = quartet, m = multiplet, br s = broad singlet), coupling constant(s) (Hz), integration].

● Carbon-13 nuclear magnetic resonance (¹³C NMR) spectra were recorded with JEOL 150 MHz spectrometers. Carbon chemical shifts are reported in parts per million (δ scale), and are referenced using the carbon resonances of the solvent (δ 77.0 (CHCl₃)). Data are reported as follows: chemical shift [multiplicity (if not singlet), assignment (Cq = fully substituted carbon)].

● High resolution mass spectra (HRMS) were recorded on a Waters SYNAPT G2 using an electrospray (ESI) ionization source.

● Melting points were recorded on WRX-X-4A melting point apparatus.

● The reaction temperature of 20 °C and 10 °C were controlled with a DHJF-8002 Zhengzhou Changsheng cryogenic thermostatic reaction bath.
2. Further Optimization Studies

Table S1. Further screening of ligands and additives

![Chemical Structures]

<table>
<thead>
<tr>
<th>entry</th>
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<th>ligand</th>
<th>additive</th>
<th>yield (%)</th>
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<tbody>
<tr>
<td>1</td>
<td>Pd$_2$(dba)$_3$:CHCl$_3$</td>
<td>–</td>
<td>–</td>
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<td>/</td>
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<tr>
<td>2$^d$</td>
<td>Pd$_2$(dba)$_3$:CHCl$_3$</td>
<td>L8</td>
<td>–</td>
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<td>3$^d$</td>
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<td>L9</td>
<td>–</td>
<td>/</td>
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<td>–</td>
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<td>L11</td>
<td>–</td>
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<td>Pd$_2$(dba)$_3$:CHCl$_3$</td>
<td>L12</td>
<td>–</td>
<td>/</td>
<td>/</td>
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<td>–</td>
<td>&lt;5</td>
<td>/</td>
</tr>
<tr>
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<td>–</td>
<td>/</td>
<td>/</td>
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<td>9</td>
<td>Pd(PPh$_3$)$_4$</td>
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<td>Sc(OTf)$_3$</td>
<td>&lt;5</td>
<td>/</td>
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<td>TMSCl</td>
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<td>/</td>
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$^a$ Unless noted otherwise, the reactions were carried out with 1a (0.10 mmol), 2a (0.15 mmol), Pd catalyst (5 mol %) and additive (0.02 mmol) in solvent (1.0 mL) for 12 h. $^b$ Yield was determined by $^1$H-NMR analysis with CH$_2$Br$_2$ as the internal standard. $^c$ The ratio of 3a:4a was determined by $^1$H-NMR analysis of the crude reaction mixture. $^d$ The Pd/ligand complex was pre-prepared with Pd$_2$(dba)$_3$:CHCl$_3$ and ligand in THF at rt for 1 h. $^e$ The reactions were carried out with additive (0.12 mmol).
Table S2. Further screening of solvents and temperature "

<table>
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<tr>
<th>entry</th>
<th>solvent</th>
<th>T (°C)</th>
<th>t (h)</th>
<th>yield (%)(^b)</th>
<th>3a:4a(^c)</th>
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<tr>
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<td>ethyl acetate</td>
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<td>24</td>
<td>84</td>
<td>3.1:1</td>
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<td>24</td>
<td>&lt;5</td>
<td>/</td>
</tr>
<tr>
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<td>acetone</td>
<td>60</td>
<td>12</td>
<td>64</td>
<td>12.8:1</td>
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<tr>
<td>5</td>
<td>ethyl acetate</td>
<td>60</td>
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<td>77</td>
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<tr>
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<td>83</td>
<td>&gt;20:1</td>
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<td>60</td>
<td>12</td>
<td>65</td>
<td>2.9:1</td>
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</table>

\(^a\) Unless noted otherwise, the reactions were carried out with 1a (0.10 mmol), 2a (0.15 mmol), and Pd(PPh\(_3\))\(_4\) (5 mol %) in solvent (1.0 mL). \(^b\) Yield was determined by \(^1\)H-NMR analysis with CH\(_2\)Br\(_2\) as the internal standard. \(^c\) The ratio of 3a:4a was determined by \(^1\)H-NMR analysis of the crude reaction mixture.
3. Further Substrate Scope Investigation

Scheme S1. Further substrate scope investigation of allylideneamalononitriles

Scheme S2. Further substrate scope investigation of VECs
4. General Procedure for the Preparation of Nine-Membered Products 3

General procedure for the synthesis of nine-membered products 3

To an over-dried Schlenk tube was added Pd(PPh₃)₄ (5 mol %), after which the tube was evacuated and back-filled with argon three times. Subsequently, under the protection of argon, a solution of dried allylidene malononitriles 1 (0.10 mmol) and vinylethylene carbonates 2 (0.15 mmol) in dry MeCN (1.0 mL) was added via syringe and the reaction mixture was stirred at 20 °C for 24 hours. Then the mixture was concentrated and purified by column chromatography on silica gel (petroleum ether/ dichloromethane = 3/1 to 1/1, then petroleum ether/ethyl acetate = 10/1) to afford the corresponding 3 in 51–96% yields, which were dried under vacuum and further analyzed by ¹H NMR, ¹³C NMR, HRMS, etc.

Gram-scale synthesis of the nine-membered product 3a

To an over-dried 100 mL Schlenk flask, was added Pd(PPh₃)₄ (0.20 mmol, 0.23 g), after which the tube was evacuated and back-filled with argon three times. Subsequently, under the protection of argon, a solution of dried allylidene malononitrile 1a (4.00 mmol, 1.01 g) and vinylethylene carbonate 2a (6.00 mmol, 1.14 g) in dry MeCN (40 mL) was added via syringe and the reaction mixture was stirred at 20 °C for 24 hours. Then the mixture was concentrated and purified by column chromatography on silica gel (petroleum ether/ dichloromethane = 3/1 to 1/1, then petroleum ether/ethyl acetate = 10/1) to afford 3a (1.08 g) as white solid in 68% yields.

ethyl-(3E,7Z)-5,5-dicyano-4,8-diphenyl-2,5,6,9-tetrahydrooxonine-3-carboxylate 3a

Prepared according to the general procedure to afford 3a (35.8 mg, m. p. = 131 – 135 °C) in
90% yield as white solid. The regioisomeric ratio was determined to be >20:1 by crude $^1$H NMR analysis.

**NMR and HRMS data** for the product 3a:

$^1$H NMR (600 MHz, CDCl$_3$) δ (ppm): 7.55 (d, $J = 6.6$ Hz, 2H), 7.45 – 7.33 (m, 6H), 7.20 (d, $J = 8.4$ Hz, 2H), 6.25 (t, $J = 9.0$ Hz, 1H), 4.61 (s, 2H), 4.57 (s, 2H), 3.85 (q, $J = 7.2$ Hz, 2H), 3.63 (d, $J = 9.0$ Hz, 2H), 0.80 (t, $J = 7.2$ Hz, 3H).

$^{13}$C NMR (150 MHz, CDCl$_3$) δ (ppm): 167.6, 143.8, 139.4, 138.9, 137.4, 135.9, 128.7, 128.6, 128.1, 126.6, 122.2, 114.2, 66.6, 63.4, 61.5, 40.2, 39.0, 13.4.

HRMS (ESI-TOF) m/z: [M + Na]$^+$ calculated for C$_{25}$H$_{22}$N$_2$O$_3$Na$: 421.1523, found: 421.1530.

**ethyl-(3E,7Z)-4-(3-chlorophenyl)-5,5-dicyano-8-phenyl-2,5,6,9-tetrahydrooxonine-3-carboxylate 3b**

Prepared according to the general procedure to afford 3b (29.9 mg, m. p. = 142 – 145 °C) in 69% yield as pale yellow solid. The regioisomeric ratio was determined to be >20:1 by crude $^1$H NMR analysis.

**NMR and HRMS data** for the product 3b:

$^1$H NMR (600 MHz, CDCl$_3$) δ (ppm): 7.54 (d, $J = 7.8$ Hz, 2H), 7.41 – 7.36 (m, 4H), 7.33 (t, $J = 8.4$ Hz, 1H), 7.20 (s, 1H), 7.10 (d, $J = 7.2$ Hz, 1H), 6.24 (t, $J = 9.0$ Hz, 1H), 4.61 (s, 2H), 4.56 (d, $J = 4.8$ Hz, 2H), 3.91 (q, $J = 6.0$ Hz, 2H), 3.62 (d, $J = 11.4$ Hz, 2H), 0.87 (t, $J = 7.2$ Hz, 3H).

$^{13}$C NMR (150 MHz, CDCl$_3$) δ (ppm): 167.2, 143.9, 139.2, 138.8, 137.5, 136.8, 134.6, 130.0, 129.8, 128.74, 128.68, 128.3, 126.6, 126.4, 122.0, 114.0, 66.8, 63.4, 61.7, 39.9, 39.1, 13.8.

HRMS (ESI-TOF) m/z: [M + Na]$^+$ calculated for C$_{25}$H$_{21}^{35}$ClN$_2$O$_3$Na$: 455.1133, found: 455.1131; calculated for C$_{25}$H$_{21}^{37}$ClN$_2$O$_3$Na$: 457.1103, found: 457.1114.
ethyl-(3E,7Z)-4-(3-bromophenyl)-5,5-dicyano-8-phenyl-2,5,6,9-tetrahydrooxonine-3-carboxylate 3c

![Chemical structure of 3c](image)

Prepared according to the general procedure for 48 h to afford 3c (25.3 mg) in 53% yield as yellow semisolid. The regioisomeric ratio was determined to be >20:1 by crude $^1$H NMR analysis.

*NMR and HRMS data for the product 3c:*

$^1$H NMR (600 MHz, CDCl$_3$) $\delta$ (ppm): 7.59 – 7.51 (m, 3H), 7.44 – 7.36 (m, 3H), 7.36 – 7.32 (m, 1H), 7.28 (d, $J = 8.4$ Hz, 1H), 7.15 (d, $J = 7.8$ Hz, 1H), 6.23 (t, $J = 9.0$ Hz, 1H), 4.60 (s, 2H), 4.56 (d, $J = 4.2$ Hz, 2H), 3.91 (q, $J = 7.2$ Hz, 2H), 3.62 (dd, $J = 9.0$, $5.4$ Hz, 2H), 0.87 (t, $J = 7.2$ Hz, 3H).

$^{13}$C NMR (150 MHz, CDCl$_3$) $\delta$ (ppm): 167.2, 143.9, 139.2, 139.1, 137.7, 136.8, 132.7, 131.1, 130.1, 128.7, 128.8, 126.9, 126.5, 122.5, 122.0, 114.0, 66.8, 63.4, 61.7, 39.9, 39.1, 13.4.

HRMS (ESI-TOF) m/z: [M + Na]$^+$ calculated for C$_{25}$H$_{21}$BrN$_2$O$_3$Na$: 499.0628, found: 499.0629; calculated for C$_{25}$H$_{21}$BrN$_2$O$_3$Na$: 501.0607, found: 501.0607.

eethyl-(3E,7Z)-5,5-dicyano-8-phenyl-4-(m-tolyl)-2,5,6,9-tetrahydrooxonine-3-carboxylate 3d

![Chemical structure of 3d](image)

Prepared according to the general procedure to afford 3d (33.8 mg) in 82% yield as colorless semisolid. The regioisomeric ratio was determined to be >20:1 by crude $^1$H NMR analysis.

*NMR and HRMS data for the product 3d:*

$^1$H NMR (600 MHz, CDCl$_3$) $\delta$ (ppm): 7.56 (d, $J = 6.6$ Hz, 2H), 7.43 – 7.34 (m, 3H), 7.27 (t, $J = 7.2$ Hz, 1H), 7.21 (d, $J = 7.2$ Hz, 1H), 7.00 (d, $J = 5.4$ Hz, 2H), 6.27 (t, $J = 9.0$ Hz, 1H), 4.59
(s, 2H), 4.56 (d, J = 3.0 Hz, 2H), 3.87 (q, J = 7.2 Hz, 2H), 3.61 (d, J = 9.0 Hz, 2H), 2.34 (s, 3H), 0.81 (t, J = 7.2 Hz, 3H).

$^1$H NMR (150 MHz, CDCl$_3$) δ (ppm): 6.74, 143.5, 139.3, 138.4, 137.3, 135.5, 130.4, 128.7, 128.65, 128.5, 126.6, 125.1, 122.4, 114.2, 66.2, 63.1, 61.4, 40.2, 39.0, 21.3, 13.4.

HRMS (ESI-TOF) m/z: [M + Na]$^+$ calculated for C$_{25}$H$_{24}$N$_2$O$_3$Na$: 435.1679, found: 435.1677.

ethyl-(3$E$,7$Z$)-4-(4-chlorophenyl)-5,5-dicyano-8-phenyl-2,5,6,9-tetrahydrooxonine-3-carboxylate 3e

![Chemical structure of 3e](image)

Prepared according to the general procedure for 48 h to afford 3e (31.2 mg, m. p. = 86 – 89 °C) in 72% yield as pale yellow solid. The regioisomeric ratio was determined to be >20:1 by crude $^1$H NMR analysis.

$^1$H NMR and HRMS data for the product 3e:

$^1$H NMR (600 MHz, CDCl$_3$) δ (ppm): 7.54 (d, J = 6.6 Hz, 2H), 7.43 – 7.36 (m, 4H), 7.34 (t, J = 7.2 Hz, 1H), 7.20 (brs, 1H), 7.10 (d, J = 7.2 Hz, 1H), 6.24 (t, J = 9.0 Hz, 1H), 4.61 (s, 2H), 4.56 (d, J = 4.2 Hz, 2H), 3.91 (q, J = 7.2 Hz, 2H), 3.62 (d, J = 9.0 Hz, 2H), 0.87 (t, J = 7.2 Hz, 3H).

$^1$C NMR (150 MHz, CDCl$_3$) δ (ppm): 167.2, 143.9, 139.2, 138.8, 136.8, 134.6, 129.8, 128.74, 128.68, 128.3, 126.6, 126.4, 122.0, 114.0, 66.8, 63.4, 61.7, 39.9, 39.1, 13.5.

HRMS (ESI-TOF) m/z: [M + Na]$^+$ calculated for C$_{25}$H$_{21}$ClN$_2$O$_3$Na$: 455.1133, found: 455.1128; calculated for C$_{25}$H$_{21}$ClN$_2$O$_3$Na$: 457.1103, found: 457.1107.

ethyl-(3$E$,7$Z$)-4-(4-bromophenyl)-5,5-dicyano-8-phenyl-2,5,6,9-tetrahydrooxonine-3-carboxylate 3f
Prepared according to the general procedure to afford 3f (24.3 mg, m. p. = 121 – 125 °C) in 51% yield as pale yellow solid. The regioisomeric ratio was determined to be >20:1 by crude $^1$H NMR analysis.

**NMR and HRMS data for the product 3f:**

$^1$H NMR (600 MHz, CDCl$_3$) δ (ppm): 7.57 – 7.48 (m, 4H), 7.44 – 7.33 (m, 3H), 7.06 (d, $J$ = 8.4 Hz, 2H), 6.19 (t, $J$ = 9.0 Hz, 1H), 4.61 (s, 2H), 4.57 (s, 2H), 3.90 (q, $J$ = 7.2 Hz, 2H), 3.64 (d, $J$ = 9.0 Hz, 2H), 0.88 (t, $J$ = 7.2 Hz, 3H).

$^{13}$C NMR (150 MHz, CDCl$_3$) δ (ppm): 167.3, 144.3, 139.3, 137.7, 136.7, 136.2, 131.8, 129.9, 128.8, 128.7, 126.6, 124.1, 121.9, 114.1, 67.2, 63.8, 61.7, 39.9, 39.2, 13.5.

HRMS (ESI-TOF) m/z: [M + Na]$^+$ calculated for C$_{25}$H$_{21}$BrN$_2$O$_3$Na$: 499.0628, found: 499.0626; calculated for C$_{25}$H$_{21}$BrN$_2$O$_3$Na$: 501.0607, found: 501.0608.

**ethyl-(3E,7Z)-5,5-dicyano-8-phenyl-4-(p-tolyl)-2,5,6,9-tetrahydrooxonine-3-carboxylate 3g**

Prepared according to the general procedure to afford 3g (31.7 mg, m. p. = 129 – 132 °C) in 77% yield as white solid. The regioisomeric ratio was determined to be >20:1 by crude $^1$H NMR analysis.

**NMR and HRMS data for the product 3g:**

$^1$H NMR (600 MHz, CDCl$_3$) δ (ppm): 7.55 (d, $J$ = 7.8 Hz, 2H), 7.44 – 7.33 (m, 3H), 7.18 (d, $J$ = 7.2 Hz, 2H), 7.08 (d, $J$ = 7.8 Hz, 2H), 6.25 (t, $J$ = 9.0 Hz, 1H), 4.59 (s, 2H), 4.55 (s, 2H), 3.87 (q, $J$ = 7.2 Hz, 2H), 3.60 (d, $J$ = 9.0 Hz, 2H), 2.36 (s, 3H), 0.84 (t, $J$ = 7.2 Hz, 3H).

$^{13}$C NMR (150 MHz, CDCl$_3$) δ (ppm): 167.7, 143.6, 139.7, 139.4, 139.1, 135.6, 134.4, 129.2, 128.7, 128.6, 128.0, 126.6, 122.4, 114.3, 66.3, 63.3, 61.5, 40.3, 38.9, 21.4, 13.5.

HRMS (ESI-TOF) m/z: [M + Na]$^+$ calculated for C$_{26}$H$_{24}$N$_2$O$_3$Na$: 435.1679, found:
ethyl-(3\textit{E},7\textit{Z})-5,5-dicyano-4-(4-methoxyphenyl)-8-phenyl-2,5,6,9-tetrahydrooxonine-3-carboxylate 3h

The reaction was performed according to the general procedure by using 0.30 mmol of the corresponding vinylethylene carbonates 2 to afford 3h (37.7 mg) in 88% yield as pale yellow semisolid. The regioisomeric ratio was determined to be >20:1 by crude $^1$H NMR analysis.

\textit{NMR and HRMS data for the product 3h:}

$^1$H NMR (600 MHz, CDCl$_3$) $\delta$ (ppm): 7.55 (d, $J = 7.2$ Hz, 2H), 7.43 – 7.32 (m, 3H), 7.12 (d, $J = 9.0$ Hz, 2H), 6.88 (d, $J = 8.3$ Hz, 2H), 6.24 (t, $J = 8.4$ Hz, 1H), 4.59 (s, 2H), 4.55 (s, 2H), 3.89 (q, $J = 7.2$ Hz, 2H), 3.81 (s, 3H), 3.60 (d, $J = 9.0$ Hz, 2H), 0.87 (t, $J = 7.8$ Hz, 3H).

$^{13}$C NMR (150 MHz, CDCl$_3$) $\delta$ (ppm): 167.8, 160.4, 143.7, 139.4, 138.7, 135.9, 129.6, 129.5, 128.7, 128.6, 126.6, 122.3, 114.3, 113.9, 66.5, 63.4, 61.5, 55.3, 40.4, 39.0, 13.6.

HRMS (ESI-TOF) m/z: [M + Na]$^+$ calculated for C$_{26}$H$_{24}$N$_2$O$_4$Na$^+$: 451.1628, found: 451.1631.

ethyl-(3\textit{E},7\textit{Z})-5,5-dicyano-4-(naphthalen-2-yl)-8-phenyl-2,5,6,9-tetrahydrooxonine-3-carboxylate 3i

Prepared according to the general procedure to afford 3i (31.9 mg, m. p. = 165 – 168 °C) in 71% yield as pale yellow solid. The regioisomeric ratio was determined to be >20:1 by crude $^1$H NMR analysis.

\textit{NMR and HRMS data for the product 3i:}

$^1$H NMR (600 MHz, CDCl$_3$) $\delta$ (ppm): 7.87 (d, $J = 7.8$ Hz, 1H), 7.84 (d, $J = 7.8$ Hz, 1H), 7.74 (d, $J = 8.4$ Hz, 1H), 7.63 (s, 1H), 7.59 (d, $J = 6.6$ Hz, 2H), 7.56 – 7.48 (m, 2H), 7.46 – 7.37 (m,
ethyl-(3Z,7Z)-5,5-dicyano-8-phenyl-4-(thiophen-2-yl)-2,5,6,9-tetrahydrooxonine-3-carboxylate 3j

Prepared according to the general procedure to afford 3j (38.8 mg) in 96% yield as yellow semisolid. The regioisomeric ratio was determined to be >20:1 by crude $^1$H NMR analysis.

NMR and HRMS data for the product 3j:

$^1$H NMR (600 MHz, CDCl$_3$) $\delta$ (ppm): 7.54 (d, $J = 8.4$ Hz, 2H), 7.42 (dd, $J = 6.6$, 1.8 Hz, 1H), 7.41 – 7.33 (m, 3H), 7.06 – 7.01 (m, 2H), 6.23 (t, $J = 9.0$ Hz, 1H), 4.61 (s, 2H), 4.54 (s, 2H), 3.96 (q, $J = 7.2$ Hz, 2H), 3.58 (d, $J = 9.0$ Hz, 2H), 0.94 (t, $J = 7.2$ Hz, 3H).

$^{13}$C NMR (150 MHz, CDCl$_3$) $\delta$ (ppm): 167.2, 143.9, 139.3, 139.2, 136.3, 131.8, 129.4, 128.65, 128.55, 127.9, 127.0, 126.6, 122.2, 114.0, 67.1, 63.7, 61.7, 40.7, 38.8, 13.6.

HRMS (ESI-TOF) m/z: [M + Na]$^+$ calculated for C$_{29}$H$_{24}$N$_2$O$_3$Na$: 471.1679, found: 471.1680.

methyl-(3E,7Z)-5,5-dicyano-4,8-diphenyl-2,5,6,9-tetrahydrooxonine-3-carboxylate 3k

Prepared according to the general procedure to afford 3k (33.4 mg) in 87% yield as pale yellow semisolid. The regioisomeric ratio was determined to be >20:1 by crude $^1$H NMR analysis.
NMR and HRMS data for the product 3k:

$^1$H NMR (600 MHz, CDCl$_3$) $\delta$ (ppm): 7.56 (d, $J = 8.4$ Hz, 2H), 7.45 – 7.35 (m, 6H), 7.20 (d, $J = 7.8$ Hz, 2H), 6.29 (t, $J = 9.0$ Hz, 1H), 4.60 (s, 2H), 4.55 (s, 2H), 3.60 (d, $J = 9.0$ Hz, 2H), 3.38 (s, 3H).

$^{13}$C NMR (150 MHz, CDCl$_3$) $\delta$ (ppm): 168.0, 143.5, 139.5, 139.3, 137.3, 135.6, 129.7, 128.7, 128.6, 127.9, 126.6, 122.4, 114.1, 66.2, 63.0, 52.3, 40.2, 38.9.

HRMS (ESI-TOF) m/z: [M + Na]$^+$ calculated for C$_{29}$H$_{20}$N$_2$O$_3$Na$: 407.1366, found: 407.1362.

tert-butyl-$(3E,7Z)$-5,5-dicyano-4,8-diphenyl-2,5,6,9-tetrahydrooxonine-3-carboxylate 3l

The reaction was performed according to the general procedure by using 0.30 mmol of the corresponding vinylethylene carbonate 2 to afford 3l (35.0 mg, m. p. = 125 – 129 °C) in 82% yield as white solid. The regioisomeric ratio was determined to be >20:1 by crude $^1$H NMR analysis.

NMR and HRMS data for the product 3l:

$^1$H NMR (600 MHz, CDCl$_3$) $\delta$ (ppm): 7.56 (d, $J = 7.2$ Hz, 2H), 7.45 – 7.33 (m, 6H), 7.20 (d, $J = 7.2$ Hz, 2H), 6.23 (t, $J = 9.0$ Hz, 1H), 4.58 (s, 2H), 4.57 (s, 2H), 3.62 (d, $J = 9.0$ Hz, 2H), 1.07 (s, 9H).

$^{13}$C NMR (150 MHz, CDCl$_3$) $\delta$ (ppm): 166.7, 143.8, 139.5, 137.5, 137.3, 136.7, 129.5, 128.7, 128.6, 128.5, 126.6, 125.5, 122.2, 114.3, 82.7, 66.7, 63.7, 40.1, 39.0, 27.3.

HRMS (ESI-TOF) m/z: [M + Na]$^+$ calculated for C$_{27}$H$_{26}$N$_2$O$_3$Na$: 449.1836, found: 449.1836.

ethyl-$(3E,7Z)$-5,5-dicyano-8-(2-fluorophenyl)-4-phenyl-2,5,6,9-tetrahydrooxonine-3-carboxylate 3m
Prepared according to the general procedure to afford 3m (35.4 mg, m. p. = 109 – 111 °C) in 85% yield as white solid. The regioisomeric ratio was determined to be >20:1 by crude ¹H NMR analysis.

**NMR and HRMS data for the product 3m:**

¹H NMR (600 MHz, CDCl₃) δ (ppm): 7.50 – 7.37 (m, 4H), 7.36 – 7.30 (1H), 7.23 (d, J = 6.6 Hz, 2H), 7.17 (t, J = 7.2 Hz, 1H), 7.10 (dd, J = 10.2, 8.4 Hz, 1H), 6.16 (t, J = 9.0 Hz, 1H), 4.63 (s, 2H), 4.54 (s, 2H), 3.84 (q, J = 7.2 Hz, 2H), 3.67 (d, J = 9.0 Hz, 2H), 0.80 (t, J = 7.2 Hz, 3H).

¹³C NMR (150 MHz, CDCl₃) δ (ppm): 167.5, 159.6 (d, J_{C-F} = 247.1 Hz), 140.2, 138.6, 137.4, 135.9, 130.2 (d, J_{C-F} = 2.9 Hz), 130.1 (d, J_{C-F} = 8.7 Hz), 129.7, 128.6, 128.1, 127.4 (d, J_{C-F} = 12.9 Hz), 125.8, 124.5 (d, J_{C-F} = 3.0 Hz), 116.0 (d, J_{C-F} = 21.5 Hz), 114.2, 67.4, 64.1, 61.5, 40.1, 38.7, 13.4.

¹⁹F NMR (564 MHz, CDCl₃) δ (ppm): -115.0.

HRMS (ESI-TOF) m/z: [M + Na]⁺ calculated for C₂₅H₂₁F₂N₂O₃Na⁺ 439.1428, found: 439.1427.

**ethyl-(3E,7Z)-8-(3-chlorophenyl)-5,5-dicyano-4-phenyl-2,5,6,9-tetrahydrooxonine-3-carboxylate 3n**

Prepared according to the general procedure to afford 3n (37.7 mg, m. p. = 89 – 92 °C) in 87% yield as pale yellow solid. The regioisomeric ratio was determined to be >20:1 by crude ¹H NMR analysis.

**NMR and HRMS data for the product 3n:**
\(^1\)H NMR (600 MHz, CDCl\(_3\)) \(\delta\) (ppm): 7.55 (s, 1H), 7.47 – 7.36 (m, 4H), 7.36 – 7.30 (m, 2H), 7.19 (d, \(J = 8.4\) Hz, 2H), 6.27 (t, \(J = 9.0\) Hz, 1H), 4.60 (s, 2H), 4.52 (s, 2H), 3.86 (q, \(J = 7.2\) Hz, 2H), 3.62 (d, \(J = 9.0\) Hz, 2H), 0.80 (t, \(J = 7.2\) Hz, 3H).

\(^1\)C NMR (150 MHz, CDCl\(_3\)) \(\delta\) (ppm): 167.5, 142.6, 141.2, 138.8, 137.2, 135.8, 134.7, 130.0, 129.7, 128.6, 128.1, 126.8, 124.8, 123.5, 114.1, 66.4, 63.4, 61.6, 40.0, 38.9, 13.4.

HRMS (ESI-TOF) m/z: [M + Na]\(^+\) calculated for C\(_{25}\)H\(_{21}\)ClN\(_2\)O\(_3\)Na\(^+\): 455.1133, found: 455.1135; calculated for C\(_{25}\)H\(_{21}\)ClN\(_2\)O\(_3\)Na\(^+\): 457.1103, found: 457.1115.

**ethyl-(3E,7Z)-8-(3-bromophenyl)-5,5-dicyano-4-phenyl-2,5,6,9-tetrahydrooxonine-3-carboxylate 3o**

Prepared according to the general procedure to afford 3o (44.4 mg, m. p. = 104 – 106 °C) in 93% yield as white solid. The regioisomeric ratio was determined to be >20:1 by crude \(^1\)H NMR analysis.

**NMR and HRMS data for the product 3o:**

\(^1\)H NMR (600 MHz, CDCl\(_3\)) \(\delta\) (ppm): 7.70 (s, 1H), 7.53 – 7.46 (m, 2H), 7.45 – 7.35 (m, 3H), 7.27 (t, \(J = 8.4\) Hz, 1H), 7.19 (d, \(J = 7.2\) Hz, 2H), 6.26 (t, \(J = 9.0\) Hz, 1H), 4.61 (s, 2H), 4.52 (s, 2H), 3.86 (q, \(J = 7.2\) Hz, 2H), 3.62 (d, \(J = 9.0\) Hz, 2H), 0.80 (t, \(J = 7.2\) Hz, 3H).

\(^1\)C NMR (150 MHz, CDCl\(_3\)) \(\delta\) (ppm): 167.5, 142.5, 141.5, 138.8, 137.2, 135.8, 131.6, 130.2, 129.73, 129.69, 128.6, 128.1, 125.2, 123.5, 122.8, 114.1, 66.4, 63.5, 61.6, 40.0, 38.9, 13.4.

HRMS (ESI-TOF) m/z: [M + Na]\(^+\) calculated for C\(_{25}\)H\(_{21}\)^{79}BrN\(_2\)O\(_3\)Na\(^+\): 499.0628, found: 499.0628; calculated for C\(_{25}\)H\(_{21}\)^{81}BrN\(_2\)O\(_3\)Na\(^+\): 501.0607, found: 501.0599.

**ethyl-(3E,7Z)-5,5-dicyano-8-(3-nitrophenyl)-4-phenyl-2,5,6,9-tetrahydrooxonine-3-carboxylate 3p**
Prepared according to the general procedure to afford 3p (42.1 mg, m. p. = 145 – 148 °C) in 95% yield as pale yellow solid. The regioisomeric ratio was determined to be >20:1 by crude $^1$H NMR analysis.

**NMR and HRMS data for the product 3p:**

$^1$H NMR (600 MHz, CDCl$_3$) δ (ppm): 8.43 (s, 1H), 8.23 (d, $J$ = 8.4 Hz, 1H), 7.92 (d, $J$ = 8.4 Hz, 1H), 7.59 (t, $J$ = 8.4 Hz, 1H), 7.46 – 7.35 (m, 3H), 7.19 (d, $J$ = 6.0 Hz, 2H), 6.39 (t, $J$ = 9.0 Hz, 1H), 4.62 (s, 2H), 4.57 (s, 2H), 3.87 (q, $J$ = 7.2 Hz, 2H), 3.65 (d, $J$ = 8.4 Hz, 2H), 0.79 (t, $J$ = 7.2 Hz, 3H).

$^{13}$C NMR (150 MHz, CDCl$_3$) δ (ppm): 167.4, 148.5, 141.6, 141.1, 138.8, 137.0, 135.8, 132.6, 129.83, 129.81, 128.7, 128.0, 125.0, 123.3, 121.5, 113.9, 66.0, 63.4, 61.7, 39.9, 38.8, 13.4.

HRMS (ESI-TOF) m/z: [M + Na]$^+$ calculated for C$_{25}$H$_{21}$N$_3$O$_5$Na$: 466.1374, found: 466.1374.

ethyl-(3E,7Z)-5,5-dicyano-4-phenyl-8-(m-tolyl)-2,5,6,9-tetrahydrooxonine-3-carboxylate 3q

![Diagram of 3q]

The reaction was performed according to the general procedure by using 0.30 mmol of the corresponding vinylethylene carbonates 2 to afford 3q (37.5 mg) in 91% yield as colorless semisolid. The regioisomeric ratio was determined to be >20:1 by crude $^1$H NMR analysis.

**NMR and HRMS data for the product 3q:**

$^1$H NMR (600 MHz, CDCl$_3$) δ (ppm): 7.46 – 7.34 (m, 5H), 7.28 (t, $J$ = 8.4 Hz, 1H), 7.23 – 7.16 (m, 3H), 6.26 (t, $J$ = 8.4 Hz, 1H), 4.61 (s, 2H), 4.55 (s, 2H), 3.86 (q, $J$ = 7.2 Hz, 2H), 3.61 (q, $J$ = 9.0 Hz, 2H), 2.39 (s, 3H), 0.80 (t, $J$ = 7.2 Hz, 3H).

$^{13}$C NMR (150 MHz, CDCl$_3$) δ (ppm): 167.6, 143.7, 139.4, 139.0, 138.3, 137.4, 135.8, 129.6, 129.3, 128.6, 128.1, 127.3, 123.7, 122.1, 114.2, 66.4, 63.2, 61.5, 40.2, 39.0, 21.5, 13.4.

HRMS (ESI-TOF) m/z: [M + Na]$^+$ calculated for C$_{25}$H$_{24}$N$_3$O$_5$Na$: 435.1674, found: 435.1674.
ethyl-(3E,7Z)-5,5-dicyano-8-(3-methoxyphenyl)-4-phenyl-2,5,6,9-tetrahydrooxonine-3-carboxylate 3r

Prepared according to the general procedure to afford 3r (34.7 mg, m. p. = 101 – 106 °C) in 81% yield as white solid. The regioisomeric ratio was determined to be >20:1 by crude ¹H NMR analysis.

NMR and HRMS data for the product 3r:

¹H NMR (600 MHz, CDCl₃) δ (ppm): 7.44 – 7.35 (m, 3H), 7.31 (t, J = 8.4 Hz, 1H), 7.20 (d, J = 6.0 Hz, 2H), 7.13 (d, J = 8.4 Hz, 1H), 7.10 (s, 1H), 6.91 (d, J = 7.2 Hz, 1H), 6.24 (t, J = 9.0 Hz, 1H), 4.61 (s, 2H), 4.55 (s, 2H), 3.85 (q, J = 7.2 Hz, 2H), 3.84 (s, 3H), 3.62 (d, J = 9.0 Hz, 2H), 0.79 (t, J = 7.2 Hz, 3H).

¹³C NMR (150 MHz, CDCl₃) δ (ppm): 167.6, 159.8, 143.8, 140.9, 138.9, 137.4, 135.9, 129.7, 129.6, 128.6, 128.1, 122.4, 119.0, 114.2, 114.0, 112.4, 66.7, 63.5, 61.5, 55.3, 40.2, 39.0, 13.4.


ethyl-(3E,7Z)-5,5-dicyano-8-(4-fluorophenyl)-4-phenyl-2,5,6,9-tetrahydrooxonine-3-carboxylate 3s

Prepared according to the general procedure to afford 3s (35.8 mg, m. p. = 115 – 117 °C) in 86% yield as pale yellow solid. The regioisomeric ratio was determined to be >20:1 by crude ¹H NMR analysis.

NMR and HRMS data for the product 3s:

¹H NMR (600 MHz, CDCl₃) δ (ppm): 7.57 – 7.50 (m, 2H), 7.44 – 7.35 (m, 3H), 7.19 (d, J = 7.2 Hz, 2H), 7.08 (t, J = 7.8 Hz, 2H), 6.20 (t, J = 8.4 Hz, 1H), 4.60 (s, 2H), 4.53 (s, 2H), 3.85 (q, J = 7.8 Hz, 2H), 3.61 (d, J = 9.0 Hz, 2H), 0.80 (t, J = 7.2 Hz, 3H).
$^{13}$C NMR (150 MHz, CDCl$_3$) δ (ppm): 167.6, 163.0 (d, $J_{C-F} = 247.1$ Hz), 142.8, 138.9, 137.3, 135.8, 135.5 (d, $J_{C-F} = 2.9$ Hz), 129.7, 128.6, 128.4 (d, $J_{C-F} = 8.7$ Hz), 128.1, 122.3, 115.6 (d, $J_{C-F} = 21.6$ Hz), 114.1, 66.5, 63.4, 61.5, 40.2, 39.0, 13.4.

$^{19}$F NMR (564 MHz, CDCl$_3$) δ (ppm): -112.9.

HRMS (ESI-TOF) m/z: [M + Na]$^+$ calculated for C$_{25}$H$_{21}$F$_3$N$_2$O$_3$Na$: 439.1428, found: 439.1427.

**ethyl-(3E,7Z)-8-(4-chlorophenyl)-5,5-dicyano-4-phenyl-2,5,6,9-tetrahydrooxonine-3-carboxylate 3t**

![Structure of 3t](structure_image)

Prepared according to the general procedure to afford 3t (35.1 mg) in 81% yield as colorless semisolid. The regioisomeric ratio was determined to be >20:1 by crude $^1$H NMR analysis.

NMR and HRMS data for the product 3t:

$^1$H NMR (600 MHz, CDCl$_3$) δ (ppm): 7.49 (d, $J = 8.4$ Hz, 2H), 7.44 – 7.34 (m, 5H), 7.18 (d, $J = 7.2$ Hz, 2H), 6.24 (t, $J = 9.0$ Hz, 1H), 4.59 (s, 2H), 4.53 (s, 2H), 3.85 (q, $J = 7.2$ Hz, 2H), 3.61 (d, $J = 9.0$ Hz, 2H), 0.79 (t, $J = 7.2$ Hz, 3H).

$^{13}$C NMR (150 MHz, CDCl$_3$) δ (ppm): 167.6, 142.7, 138.9, 137.8, 137.3, 135.8, 134.6, 129.7, 128.9, 128.6, 128.1, 127.9, 122.8, 114.1, 66.4, 63.4, 61.6, 40.1, 39.0, 13.4.

HRMS (ESI-TOF) m/z: [M + Na]$^+$ calculated for C$_{25}$H$_{21}^{35}$ClN$_2$O$_3$Na$: 455.1133, found: 455.1135; calculated for C$_{25}$H$_{21}^{37}$ClN$_2$O$_3$Na$: 457.1103, found: 457.1112.

**ethyl-(3E,7Z)-8-(4-bromophenyl)-5,5-dicyano-4-phenyl-2,5,6,9-tetrahydrooxonine-3-carboxylate 3u**

![Structure of 3u](structure_image)

Prepared according to the general procedure to afford 3u (36.7 mg, m. p. = 149 – 152 °C) in 77% yield as white solid. The regioisomeric ratio was determined to be >20:1 by crude $^1$H
NMR analysis.

**NMR and HRMS data for the product 3u:**

$^1$H NMR (600 MHz, CDCl$_3$) δ (ppm): 7.52 (d, $J = 9.0$ Hz, 2H), 7.46 – 7.36 (m, 5H), 7.18 (d, $J = 7.2$ Hz, 2H), 6.24 (t, $J = 9.0$ Hz, 1H), 4.59 (s, 2H), 4.52 (s, 2H), 3.85 (q, $J = 7.2$ Hz, 2H), 3.61 (d, $J = 9.0$ Hz, 2H), 0.79 (t, $J = 7.2$ Hz, 3H).

$^{13}$C NMR (150 MHz, CDCl$_3$) δ (ppm): 167.6, 142.7, 138.9, 138.3, 137.2, 135.8, 131.8, 129.7, 128.6, 128.2, 128.1, 122.84, 122.81, 114.1, 66.3, 63.4, 61.6, 40.0, 39.0, 13.4.

HRMS (ESI-TOF) m/z: [M + Na]$^+$ calculated for C$_{25}$H$_{21}$BrN$_2$O$_3$Na$^+$: 499.0628, found: 499.0632; calculated for C$_{25}$H$_{21}$81BrN$_2$O$_3$Na$^+$: 501.0607, found: 501.0609.

**ethyl-(3E,7Z)-5,5-dicyano-4-phenyl-8-(p-tolyl)-2,5,6,9-tetrahydrooxonine-3-carboxylate 3v**

![Structure of 3v](image)

Prepared according to the general procedure to afford 3v (33.8 mg, m. p. = 110 – 115 °C) in 82% yield as pale yellow solid. The regioisomeric ratio was determined to be >20:1 by crude $^1$H NMR analysis.

**NMR and HRMS data for the product 3v:**

$^1$H NMR (600 MHz, CDCl$_3$) δ (ppm): 7.45 (d, $J = 8.4$ Hz, 2H), 7.43 – 7.36 (m, 3H), 7.23 – 7.18 (m, 4H), 6.24 (t, $J = 9.0$ Hz, 1H), 4.59 (s, 2H), 4.54 (s, 2H), 3.85 (q, $J = 7.8$ Hz, 2H), 3.60 (d, $J = 9.0$ Hz, 2H), 2.38 (s, 3H), 0.80 (t, $J = 7.2$ Hz, 3H).

$^{13}$C NMR (150 MHz, CDCl$_3$) δ (ppm): 167.6, 143.4, 139.0, 138.6, 137.4, 136.4, 135.8, 129.6, 129.4, 128.6, 128.1, 126.5, 121.5, 114.2, 66.3, 63.2, 61.5, 40.2, 39.0, 21.2, 13.4.

HRMS (ESI-TOF) m/z: [M + Na]$^+$ calculated for C$_{26}$H$_{24}$N$_2$O$_3$Na$^+$: 435.1679, found: 435.1682.

**ethyl-(3E,7Z)-5,5-dicyano-8-(4-ethylphenyl)-4-phenyl-2,5,6,9-tetrahydrooxonine-3-carboxylate 3w**
Prepared according to the general procedure to afford 3w (38.9 mg, m. p. = 94 – 97 °C) in 91% yield as white solid. The regioisomeric ratio was determined to be >20:1 by crude \(^1\)H NMR analysis.

**NMR and HRMS data for the product 3w:**

\(^1\)H NMR (600 MHz, CDCl\(_3\)) \(\delta\) (ppm): 7.48 (d, \(J = 7.8\) Hz, 2H), 7.44 – 7.35 (m, 3H), 7.25 – 7.19 (m, 4H), 6.25 (t, \(J = 9.0\) Hz, 1H), 4.60 (s, 2H), 4.55 (s, 2H), 3.85 (q, \(J = 7.2\) Hz, 2H), 3.60 (d, \(J = 8.4\) Hz, 2H), 2.67 (q, \(J = 7.8\) Hz, 2H), 1.26 (t, \(J = 7.8\) Hz, 3H), 0.80 (t, \(J = 7.2\) Hz, 3H).

\(^{13}\)C NMR (150 MHz, CDCl\(_3\)) \(\delta\) (ppm): 167.6, 144.9, 143.4, 139.0, 137.4, 136.7, 135.8, 129.6, 128.6, 128.2, 128.1, 126.6, 121.5, 114.2 66.3, 63.2, 61.5, 40.3, 39.0, 28.5, 15.4, 13.4.

**HRMS (ESI-TOF) m/z:** [M + Na]\(^+\) calculated for C\(_{27}\)H\(_{28}\)N\(_2\)O\(_3\)Na\(^+\): 449.1836, found: 449.1836.

**ethyl-(3E,7Z)-5,5-dicyano-8-(4-methoxyphenyl)-4-phenyl-2,5,6,9-tetrahydrooxonine-3-carboxylate 3x**

Prepared according to the general procedure to afford 3x (34.7 mg) in 81% yield as pale yellow semisolid. The regioisomeric ratio was determined to be >20:1 by crude \(^1\)H NMR analysis.

**NMR and HRMS data for the product 3x:**

\(^1\)H NMR (600 MHz, CDCl\(_3\)) \(\delta\) (ppm): 7.51 (d, \(J = 9.0\) Hz, 2H), 7.44 – 7.35 (m, 3H), 7.20 (d, \(J = 6.6\) Hz, 2H), 6.92 (d, \(J = 9.0\) Hz, 2H), 6.21 (t, \(J = 9.0\) Hz, 1H), 4.59 (s, 2H), 4.53 (s, 2H), 3.85 (q, \(J = 7.2\) Hz, 2H), 3.84 (s, 3H), 3.59 (d, \(J = 9.0\) Hz, 2H), 0.80 (t, \(J = 6.6\) Hz, 3H).

\(^{13}\)C NMR (150 MHz, CDCl\(_3\)) \(\delta\) (ppm): 167.7, 159.9, 142.8, 139.0, 137.4, 135.8, 131.7, 129.6, 128.6, 128.1, 127.9, 120.7, 114.2, 114.0, 66.2, 63.1, 61.5, 55.3, 40.3, 39.1, 13.4.

**HRMS (ESI-TOF) m/z:** [M + Na]\(^+\) calculated for C\(_{28}\)H\(_{24}\)N\(_2\)O\(_4\)Na\(^+\): 451.1628, found: 451.1629.
ethyl-(3E,7Z)-5,5-dicyano-8-(3,4-dichlorophenyl)-4-phenyl-2,5,6,9-tetrahydrooxonine-3-carboxylate 3y

Prepared according to the general procedure to afford 3y (36.4 mg, m. p. = 118 – 121 °C) in 78% yield as white solid. The regioisomeric ratio was determined to be >20:1 by crude \(^1\)H NMR analysis.

NMR and HRMS data for the product 3y:

\(^1\)H NMR (600 MHz, CDCl\(_3\)) \(\delta\) (ppm): 7.66 (d, \(J = 2.4\) Hz, 1H), 7.46 (d, \(J = 8.4\) Hz, 1H), 7.44 – 7.36 (m, 4H), 7.18 (d, \(J = 6.6\) Hz, 2H), 6.27 (t, \(J = 9.0\) Hz, 1H), 4.59 (s, 2H), 4.50 (s, 2H), 3.86 (q, \(J = 7.2\) Hz, 2H), 3.61 (d, \(J = 9.6\) Hz, 2H), 0.80 (t, \(J = 7.2\) Hz, 3H).

\(^{13}\)C NMR (150 MHz, CDCl\(_3\)) \(\delta\) (ppm): 167.5, 141.6, 139.4, 138.8, 137.1, 135.8, 132.9, 132.8, 130.6, 129.8, 128.65, 128.59, 128.1, 125.9, 123.8, 114.0, 66.1, 63.4, 61.6, 40.0, 38.9, 13.4.

HRMS (ESI-TOF) m/z: [M + Na]\(^+\) calculated for C\(_{25}\)H\(_{20}\)Cl\(_2\)N\(_2\)O\(_3\)Na\(^+\): 489.0743, found: 489.0740; calculated for C\(_{25}\)H\(_{20}\)Cl\(_3\)O\(_3\)Na\(^+\): 491.0714, found: 491.0717; calculated for C\(_{25}\)H\(_{20}\)Cl\(_3\)N\(_2\)O\(_3\)Na\(^+\): 493.0684, found: 493.0689.

ethyl-(3E,7Z)-5,5-dicyano-8-(naphthalen-2-yl)-4-phenyl-2,5,6,9-tetrahydrooxonine-3-carboxylate 3z

Prepared according to the general procedure to afford 3z (40.9 mg, m. p. = 116 – 118 °C) in 91% yield as white solid. The regioisomeric ratio was determined to be >20:1 by crude \(^1\)H NMR analysis.

NMR and HRMS data for the product 3z:

\(^1\)H NMR (600 MHz, CDCl\(_3\)) \(\delta\) (ppm): 8.04 (s, 1H), 7.92 – 7.82 (m, 3H), 7.68 (d, \(J = 10.2\) Hz, 1H), 7.56 – 7.47 (m, 2H), 7.44 – 7.35 (m, 3H), 7.21 (d, \(J = 6.0\) Hz, 2H), 6.41 (t, \(J = 9.0\) Hz,
1H), 4.68 (s, 2H), 4.66 (s, 2H), 3.86 (q, J = 7.8 Hz, 2H), 3.68 (d, J = 8.4 Hz, 2H), 0.79 (t, J = 7.2 Hz, 3H).

\[^{13}\text{C NMR (150 MHz, CDCl}_3\text{) }\delta\text{ (ppm):}\]

167.6, 143.4, 138.9, 137.4, 136.5, 135.9, 133.3, 133.1, 129.7, 128.8, 128.6, 128.4, 128.1, 127.6, 126.6, 126.5, 126.0, 124.2, 122.7, 114.2, 66.4, 63.4, 61.5, 40.2, 39.2, 13.4.

**HRMS (ESI-TOF) m/z: [M + Na]^+ calculated for C\textsubscript{23}H\textsubscript{20}N\textsubscript{2}O\textsubscript{3}Na\textsuperscript{+}: 427.1087, found: 427.1089.**
5. General Procedure for the Preparation of Seven-Membered Products 4

**General procedure for the synthesis of seven-membered products 4**

To an over-dried Schlenk tube was added Pd(PPh₃)₄ (5 mol %), after which the tube was evacuated and back-filled with argon three times. Subsequently, under the protection of argon, a solution of dried allylidemalononitriles 1 (0.10 mmol) and vinylethylene carbonates 2 (0.15 mmol) in dry THF (1.0 mL) was added via syringe and the reaction mixture was stirred at 60 °C for 12 hours. Then the mixture was concentrated and purified by column chromatography on silica gel (petroleum ether/ dichloromethane = 3/1 to 1/1, then petroleum ether/ethyl acetate = 10/1) to afford the corresponding 4 in 71–94% yields, which were dried under vacuum and further analyzed by ^1H NMR, ^13C NMR, HRMS, etc.

**Gram-scale synthesis of the seven-membered product 4a**

To an over-dried 100 mL Schlenk flask, was added Pd(PPh₃)₄ (0.20 mmol, 231 mg), after which the tube was evacuated and back-filled with argon three times. Subsequently, under the protection of argon, a solution of dried allylidemalononitrile 1a (4.00 mmol, 1.01 g) and vinylethylene carbonate 2a (6.00 mmol, 1.14 g) in dry THF (40 mL) was added via syringe and the reaction mixture was stirred at 60 °C for 12 hours. Then the mixture was concentrated and purified by column chromatography on silica gel (petroleum ether/ dichloromethane = 3/1 to 1/1, then petroleum ether/ethyl acetate = 10/1) to afford 4a (1.16 g) as pale yellow solid in 73% yields.

**ethyl-3-(2,2-dicyano-1-phenylvinyl)-6-phenyl-2,3,4,7-tetrahydrooxepine-3-carboxylate 4a**

Prepared according to the general procedure to afford 4a (33.4 mg, m. p. = 104 – 108 °C) in
84% yield as pale yellow solid. The regioisomeric ratio was determined to be >20:1 by crude 

\(^1\)H NMR analysis.

**NMR and HRMS data for the product 4a:**

\(^1\)H NMR (600 MHz, CDCl\(_3\)) \(\delta\) (ppm): 7.55 – 7.44 (m, 3H), 7.34 – 7.20 (m, 5H), 7.09 (d, \(J = 6.6\) Hz, 2H), 5.50 (t, \(J = 6.6\) Hz, 1H), 4.69 (d, \(J = 16.2\) Hz, 1H), 4.64 (d, \(J = 16.2\) Hz, 1H), 4.55 (d, \(J = 13.2\) Hz, 1H), 4.39 – 4.25 (m, 2H), 4.18 (d, \(J = 12.0\) Hz, 1H), 3.01 (dd, \(J = 14.4, 6.0\) Hz, 1H), 2.94 (dd, \(J = 15.0, 6.6\) Hz, 1H), 1.35 (t, \(J = 6.6\) Hz, 3H).

\(^13\)C NMR (150 MHz, CDCl\(_3\)) \(\delta\) (ppm): 180.7, 170.5, 141.4, 139.1, 135.5, 130.4, 128.8, 128.5, 127.7, 126.7, 125.6, 122.2, 111.8, 111.3, 90.2, 75.0, 74.3, 62.7, 60.9, 32.5, 14.1.

**HRMS (ESI-TOF)** m/z: [M + Na]\(^+\) calculated for C\(_{25}\)H\(_{22}\)N\(_2\)O\(_3\)Na\(^+\): 421.1523, found: 421.1521.

**ethyl-3-(1-(3-chlorophenyl)-2,2-dicyanovinyl)-6-phenyl-2,3,4,7-tetrahydrooxepine-3-carboxylate 4b**

![Chemical structure image]

Prepared according to the general procedure to afford 4b (35.5 mg) in 82% yield as pale yellow semisolid. The regioisomeric ratio was determined to be >20:1 by crude \(^1\)H NMR analysis.

**NMR and HRMS data for the product 4b:**

\(^1\)H NMR (600 MHz, CDCl\(_3\)) \(\delta\) (ppm): 7.40 (d, \(J = 7.8\) Hz, 2H), 7.30 – 7.19 (m, 3H), 7.13 (d, \(J = 8.4\) Hz, 2H), 7.06 (d, \(J = 8.4\) Hz, 2H), 5.53 (t, \(J = 6.6\) Hz, 1H), 4.62 (d, \(J = 15.6\) Hz, 1H), 4.58 (d, \(J = 15.6\) Hz, 1H), 4.40 (d, \(J = 13.2\) Hz, 1H), 4.34 – 4.22 (m, 2H), 4.17 (d, \(J = 13.2\) Hz, 1H), 2.98 (dd, \(J = 14.4, 6.6\) Hz, 1H), 2.88 (dd, \(J = 14.4, 6.0\) Hz, 1H), 1.30 (t, \(J = 6.6\) Hz, 3H).

\(^13\)C NMR (150 MHz, CDCl\(_3\)) \(\delta\) (ppm): 179.7, 170.2, 142.0, 139.1, 136.8, 133.9, 129.2, 128.7, 128.6, 128.3, 127.9, 126.6, 125.6, 122.2, 111.6, 111.1, 90.7, 74.9, 74.7, 62.7, 60.5, 32.7, 14.1.

**HRMS (ESI-TOF)** m/z: [M + Na]\(^+\) calculated for C\(_{25}\)H\(_{21}\)\(^{35}\)Cl\(_2\)O\(_3\)Na\(^+\): 455.1133, found: 455.1131; calculated for C\(_{25}\)H\(_{21}\)\(^{37}\)Cl\(_2\)O\(_3\)Na\(^+\): 457.1103, found: 457.1108.
ethyl-3-(1-(3-bromophenyl)-2,2-dicyanovinyl)-6-phenyl-2,3,4,7-tetrahydrooxepine-3-carboxylate 4c

Prepared according to the general procedure to afford 4c (33.9 mg, m. p. = 106 – 111 °C) in 71% yield as pale yellow solid. The regioisomeric ratio was determined to be >20:1 by crude \(^1\)H NMR analysis.

\textit{NMR and HRMS data for the product 4c:}

\(^1\)H NMR (600 MHz, CDCl\(_3\)) \(\delta\) (ppm): 7.64 (d, \(J = 8.4\) Hz, 1H), 7.41 – 7.27 (m, 5H), 7.18 (d, \(J = 6.6\) Hz, 1H), 7.12 (d, \(J = 6.6\) Hz, 2H), 5.52 (brs, 1H), 5.46 (brs, 2H), 4.49 (d, \(J = 12.6\) Hz, 1H), 4.93 – 4.27 (m, 2H), 4.22 (d, \(J = 13.2\) Hz, 1H), 3.01 (dd, \(J = 14.4, 6.6\) Hz, 1H), 2.95 (dd, \(J = 14.4, 6.6\) Hz, 1H), 1.37 (t, \(J = 7.2\) Hz, 3H).

\(^{13}\)C NMR (150 MHz, CDCl\(_3\)) \(\delta\) (ppm): 179.0, 170.2, 142.1, 139.0, 137.3, 133.4, 130.3, 129.6, 128.6, 127.9, 125.7, 125.5, 122.8, 122.1, 111.4, 111.0, 91.0, 74.9, 74.7, 62.9, 60.4, 32.7, 14.1.

HRMS (ESI-TOF) \(m/z\): [M + Na]\(^+\) calculated for C\(_{25}\)H\(_{21}\)BrN\(_2\)O\(_3\)Na\(^+\): 499.0628, found: 499.0633; calculated for C\(_{25}\)H\(_{21}\)\(^{79}\)BrN\(_2\)O\(_3\)Na\(^+\): 501.0607, found: 501.0607.

ethyl-3-(2,2-dicyano-1-(m-tolyl)vinyl)-6-phenyl-2,3,4,7-tetrahydrooxepine-3-carboxylate 4d

The reaction was performed according to the general procedure at 80 °C to afford 4d (26.0 mg) in 63% yield as pale yellow semisolid. The regioisomeric ratio was determined to be >20:1 by crude \(^1\)H NMR analysis.

\textit{NMR and HRMS data for the product 4d:}
$^1$H NMR (600 MHz, CDCl$_3$) δ (ppm): 7.37 (t, $J = 7.8$ Hz, 1H), 7.33 – 7.26 (m, 4H), 7.08 (d, $J = 7.2$ Hz, 2H), 7.05 – 6.94 (m, 2H), 5.46 (brs, 1H), 4.71 (d, $J = 15.6$ Hz, 1H), 4.63 (d, $J = 16.8$ Hz, 1H), 4.58 (d, $J = 12.6$ Hz, 1H), 4.37 – 4.27 (m, 2H), 4.15 (d, $J = 12.0$ Hz, 1H), 3.04 – 2.89 (m, 2H), 2.37 (s, 3H), 1.35 (t, $J = 7.2$ Hz, 3H).

$^{13}$C NMR (150 MHz, CDCl$_3$) δ (ppm): 181.0, 170.6, 141.2, 139.1, 138.7, 135.5, 131.1, 128.7, 128.5, 127.7, 127.2, 125.6, 123.7, 122.3, 111.8, 111.4, 89.9, 75.0, 74.2, 62.7, 61.0, 32.4, 21.4, 14.1.

HRMS (ESI-TOF) m/z: [M + Na]$^+$ calculated for C$_{26}$H$_{24}$N$_2$O$_3$Na$: 435.1679, found: 435.1677.

**ethyl-3-(1-(4-chlorophenyl)-2,2-dicyanovinyl)-6-phenyl-2,3,4,7-tetrahydrooxepine-3-carboxylate 4e**

![Chemical Structure](image)

The reaction was performed according to the general procedure at 80 °C to afford 4e (23.4 mg) in 54% yield as yellow semisolid. The regioisomeric ratio was determined to be >20:1 by crude $^1$H NMR analysis.

**NMR and HRMS data for the product 4e:**

$^1$H NMR (600 MHz, CDCl$_3$) δ (ppm): 7.46 (d, $J = 8.4$ Hz, 2H), 7.34 – 7.27 (m, 3H), 7.18 (d, $J = 8.4$ Hz, 2H), 7.11 (d, $J = 6.6$ Hz, 2H), 5.59 (t, $J = 6.0$ Hz, 1H), 4.67 (d, $J = 16.2$ Hz, 1H), 4.64 (d, $J = 16.8$ Hz, 1H), 4.46 (d, $J = 13.2$ Hz, 1H), 4.38 – 4.27 (m, 2H), 4.22 (d, $J = 12.6$ Hz, 1H), 3.03 (dd, $J = 13.8$, 6.6 Hz, 1H), 2.93 (dd, $J = 14.4$, 7.2 Hz, 1H), 1.35 (t, $J = 7.2$ Hz, 3H).

$^{13}$C NMR (150 MHz, CDCl$_3$) δ (ppm): 179.7, 170.2, 141.9, 139.0, 136.8, 133.9, 129.2, 128.6, 128.3, 127.9, 125.6, 122.2, 111.6, 111.1, 90.7, 74.9, 74.7, 62.9, 60.5, 32.7, 14.1.

HRMS (ESI-TOF) m/z: [M + Na]$^+$ calculated for C$_{26}$H$_{24}$Cl$_2$O$_3$Na$: 455.1133, found: 455.1130; calculated for C$_{26}$H$_{24}$Cl$_2$O$_3$Na$: 457.1103, found: 457.1107.
ethyl-3-(1-(4-bromophenyl)-2,2-dicyanovinyl)-6-phenyl-2,3,4,7-tetrahydrooxepine-3-carboxylate 4f

The reaction was performed according to the general procedure at 100 °C to afford 4f (20.0 mg) in 42% yield as pale yellow semisolid. The regioisomeric ratio was determined to be >20:1 by crude $^1$H NMR analysis.

$NMR$ and $HRMS$ data for the product 4f:

$^1$H NMR (600 MHz, CDCl₃) δ (ppm): 7.62 (d, $J = 8.4$ Hz, 2H), 7.34 – 7.27 (m, 3H), 7.16 – 7.06 (m, 4H), 5.59 (t, $J = 6.6$ Hz, 1H), 4.67 (d, $J = 16.8$ Hz, 1H), 4.64 (d, $J = 16.8$ Hz, 1H), 4.45 (d, $J = 12.0$ Hz, 1H), 4.37 – 4.27 (m, 2H), 4.22 (d, $J = 12.6$ Hz, 1H), 3.03 (dd, $J = 14.4$, 6.0 Hz, 1H), 2.93 (dd, $J = 14.4$, 6.0 Hz, 1H), 1.35 (t, $J = 7.2$ Hz, 3H).

$^{13}$C NMR (150 MHz, CDCl₃) δ (ppm): 179.7, 170.2, 142.0, 139.0, 134.4, 132.1, 128.6, 128.4, 127.9, 125.6, 125.0, 122.2, 111.6, 111.1, 90.7, 74.9, 74.7, 62.9, 60.5, 32.7, 14.1.

HRMS (ESI-TOF) m/z: [M + Na]$^+$ calculated for C$_{25}$H$_{21}$^{79}BrN$_2$O$_3$Na$: 499.0628, found: 499.0622; calculated for C$_{25}$H$_{21}$^{81}BrN$_2$O$_3$Na$: 501.0607, found: 501.0607.

ethyl-3-(2,2-dicyano-1-(p-tolyl)vinyl)-6-phenyl-2,3,4,7-tetrahydrooxepine-3-carboxylate 4g

Prepared according to the general procedure to afford 4g (30.1 mg, m. p. = 104 – 107 °C) in 73% yield as pale yellow solid. The regioisomeric ratio was determined to be >20:1 by crude $^1$H NMR analysis.

$NMR$ and $HRMS$ data for the product 4g:
$^1$H NMR (600 MHz, CDCl$_3$) δ (ppm): 7.35 – 7.26 (m, 5H), 7.12 (d, $J = 8.4$ Hz, 2H), 7.09 (d, $J = 6.6$ Hz, 2H), 5.55 (t, $J = 7.2$ Hz, 1H), 4.69 (d, $J = 16.2$ Hz, 1H), 4.64 (d, $J = 16.2$ Hz, 1H), 4.53 (d, $J = 12.6$ Hz, 1H), 4.37 – 4.24 (m, 2H), 4.16 (d, $J = 12.6$ Hz, 1H), 3.03 (dd, $J = 14.4$, 6.0 Hz, 1H), 2.93 (dd, $J = 15.0$, 6.6 Hz, 1H), 2.42 (s, 3H), 1.34 (t, $J = 7.2$ Hz, 3H).

$^{13}$C NMR (150 MHz, CDCl$_3$) δ (ppm): 181.0, 170.6, 141.3, 140.7, 139.1, 132.6, 129.5, 128.5, 127.7, 126.7, 125.6, 122.3, 112.0, 111.4, 89.8, 75.0, 74.2, 62.7, 61.0, 32.4, 21.4, 14.0.

HRMS (ESI-TOF) m/z: $[M + Na]^+$ calculated for C$_{26}$H$_{24}$N$_2$O$_3$Na$: 435.1679, found: 435.1677.

**ethyl-3-(2,2-dicyano-1-(4-methoxyphenyl)vinyl)-6-phenyl-2,3,4,7-tetrahydrooxepine-3-carboxylate 4h**

Prepared according to the general procedure to afford 4h (38.9 mg) in 91% yield as yellow semisolid. The regioisomeric ratio was determined to be >20:1 by crude $^1$H NMR analysis.

*NMR and HRMS data for the product 4h:*

$^1$H NMR (600 MHz, CDCl$_3$) δ (ppm): 7.33 – 7.27 (m, 3H), 7.18 (d, $J = 9.0$ Hz, 2H), 7.11 (d, $J = 8.4$ Hz, 2H), 6.98 (d, $J = 9.0$ Hz, 2H), 5.56 (t, $J = 7.2$ Hz, 1H), 4.69 (d, $J = 17.4$ Hz, 1H), 4.65 (d, $J = 15.6$ Hz, 1H), 4.53 (d, $J = 12.6$ Hz, 1H), 4.37 – 4.24 (m, 2H), 4.18 (d, $J = 12.0$ Hz, 1H), 3.85 (s, 3H), 3.05 (dd, $J = 14.4$, 6.0 Hz, 1H), 2.93 (dd, $J = 15.0$, 6.6 Hz, 1H), 1.33 (t, $J = 7.2$ Hz, 3H).

$^{13}$C NMR (150 MHz, CDCl$_3$) δ (ppm): 180.8, 170.6, 161.1, 141.3, 139.1, 128.6, 128.5, 127.7, 127.6, 125.6, 122.4, 114.2, 112.2, 111.6, 89.7, 75.0, 74.3, 62.7, 61.2, 55.4, 32.4, 14.0.

HRMS (ESI-TOF) m/z: $[M + Na]^+$ calculated for C$_{26}$H$_{24}$N$_2$O$_3$Na$: 451.1628, found: 451.1624.

**ethyl-3-(2,2-dicyano-1-(naphthalen-2-yl)vinyl)-6-phenyl-2,3,4,7-tetrahydrooxepine-3-carboxylate 4i**
The reaction was performed according to the general procedure at 80 °C to afford 4i (31.0 mg) in 69% yield as yellow semisolid. The regioisomeric ratio was determined to be >20:1 by crude $^1$H NMR analysis.

NMR and HRMS data for the product 4i:

$^1$H NMR (600 MHz, CDCl$_3$) $\delta$ (ppm): 7.96 (d, $J = 9.0$ Hz, 1H), 7.91 (d, $J = 7.8$ Hz, 1H), 7.86 (d, $J = 8.4$ Hz, 1H), 7.72 (s, 1H), 7.65 – 7.55 (m, 2H), 7.34 (d, $J = 7.8$ Hz, 1H), 7.24 (brs, 3H), 7.00 (brs, 2H), 5.46 (brs, 1H), 4.70 (d, $J = 15.6$ Hz, 1H), 4.64 (d, $J = 16.8$ Hz, 1H), 4.61 (d, $J = 13.2$ Hz, 1H), 4.42 – 4.30 (m, 2H), 4.26 (d, $J = 12.6$ Hz, 1H), 3.07 (brs, 1H), 2.99 (dd, $J = 6.8$ Hz, 1H), 1.38 (t, $J = 7.2$ Hz, 3H).

$^{13}$C NMR (150 MHz, CDCl$_3$) $\delta$ (ppm): 180.8, 170.6, 141.4, 139.0, 133.6, 132.9, 132.4, 128.8, 128.5, 128.4, 128.0, 127.8, 127.7, 127.3, 126.9, 125.5, 123.4, 122.2, 111.9, 111.4, 90.3, 75.0, 74.4, 62.8, 61.1, 32.5, 14.1.

HRMS (ESI-TOF) m/z: [M + Na]$^+$ calculated for C$_{29}$H$_{24}$N$_2$O$_3$Na$: 471.1679, found: 471.1679.

ethyl-3-(2,2-dicyano-1-(thiophen-2-yl)vinyl)-6-phenyl-2,3,4,7-tetrahydrooxepine-3-carboxylate 4j

Prepared according to the general procedure to afford 4j (35.1 mg) in 87% yield as dark yellow semisolid. The regioisomeric ratio was determined to be >20:1 by crude $^1$H NMR analysis.

NMR and HRMS data for the product 4j:

$^1$H NMR (600 MHz, CDCl$_3$) $\delta$ (ppm): 7.62 (d, $J = 3.6$ Hz, 1H), 7.36 – 7.26 (m, 3H), 7.19 (dd, $J = 3.6$, 1.2 Hz, 1H), 7.17 – 7.12 (m, 3H), 5.68 (t, $J = 6.6$ Hz, 1H), 4.69 (s, 2H), 4.48 (d, $J =$
12.0 Hz, 1H), 4.37 – 4.26 (m, 2H), 4.24 (d, J = 13.8 Hz, 1H), 3.16 (dd, J = 15.6, 7.2 Hz, 1H), 3.00 (dd, J = 14.4, 6.0 Hz, 1H), 1.34 (t, J = 7.2 Hz, 3H).

$^{13}$C NMR (150 MHz, CDCl$_3$) δ (ppm): 172.8, 170.3, 141.7, 139.2, 134.2, 130.4, 130.1, 128.5, 127.8, 127.7, 125.7, 122.2, 112.1, 111.3, 90.9, 75.0, 74.2, 62.8, 61.5, 32.5, 14.0.

HRMS (ESI-TOF) m/z: [M + Na]$^+$ calculated for C$_{23}$H$_{20}$N$_2$O$_3$SNa$: 427.1087, found: 427.1084.

**methyl-3-(2,2-dicyano-1-phenylvinyl)-6-phenyl-2,3,4,7-tetrahydrooxepine-3-carboxylate 4k**

![Structure](image)

Prepared according to the general procedure to afford 4k (30.0 mg, m. p. = 83 – 87 °C) in 78% yield as yellow solid. The regioisomeric ratio was determined to be >20:1 by crude $^1$H NMR analysis.

**NMR and HRMS data for the product 4k:**

$^1$H NMR (600 MHz, CDCl$_3$) δ (ppm): 7.54 – 7.45 (m, 3H), 7.33 – 7.20 (m, 5H), 7.07 (d, J = 8.4 Hz, 2H), 5.47 (t, J = 6.6 Hz, 1H), 4.70 (d, J = 18.0 Hz, 1H), 4.64 (d, J = 15.0 Hz, 1H), 4.56 (d, J = 12.0 Hz, 1H), 4.16 (d, J = 12.6 Hz, 1H), 3.86 (s, 3H), 2.99 (dd, J = 15.0, 6.6 Hz, 1H), 2.94 (q, J = 15.6, 7.2 Hz, 1H).

$^{13}$C NMR (150 MHz, CDCl$_3$) δ (ppm): 180.4, 171.2, 141.4, 139.0, 135.4, 130.4, 128.8, 128.5, 127.8, 126.7, 125.6, 122.0, 111.7, 111.2, 90.3, 75.1, 74.1, 61.0, 53.5, 32.4.

HRMS (ESI-TOF) m/z: [M + Na]$^+$ calculated for C$_{24}$H$_{22}$N$_2$O$_3$Na$: 407.1366, found: 407.1363.

**tert-butyl-3-(2,2-dicyano-1-phenylvinyl)-6-phenyl-2,3,4,7-tetrahydrooxepine-3-carboxylate 4l**
Prepared according to the general procedure to afford 4l (40.1 mg, m. p. = 87 – 90 °C) in 94% yield as pale yellow solid. The regioisomeric ratio was determined to be >20:1 by crude $^1$H NMR analysis.

*NMR and HRMS data for the product 4l:*

$^1$H NMR (600 MHz, CDCl$_3$) δ (ppm): 7.54 – 7.43 (m, 3H), 7.33 – 7.26 (m, 3H), 7.22 (d, $J$ = 6.6 Hz, 2H), 7.10 (d, $J$ = 7.2 Hz, 2H), 5.51 (t, $J$ = 6.6 Hz, 1H), 4.68 (d, $J$ = 16.2 Hz, 1H), 4.64 (d, $J$ = 15.6 Hz, 1H), 4.52 (d, $J$ = 12.0 Hz, 1H), 4.19 (d, $J$ = 12.0 Hz, 1H), 3.01 (dd, $J$ = 15.6, 7.2 Hz, 1H), 2.90 (q, $J$ = 15.0, 7.8 Hz, 1H), 1.53 (s, 9H).

$^{13}$C NMR (150 MHz, CDCl$_3$) δ (ppm): 181.6, 169.1, 141.4, 139.2, 135.9, 130.3, 128.7, 128.5, 127.7, 126.7, 125.5, 122.5, 111.9, 111.6, 89.8, 84.0, 74.9, 74.8, 61.4, 32.7, 27.8.

HRMS (ESI-TOF) m/z: [M + Na]$^+$ calculated for C$_{27}$H$_{26}$N$_{2}$O$_3$Na$: 449.1836, found: 449.1832.

*ethyl-3-(2,2-dicyano-1-phenylvinyl)-6-(2-fluorophenyl)-2,3,4,7-tetrahydrooxepine-3-carboxylate 4m*

The reaction was performed according to the general procedure at 100 °C to afford 4m (23.3 mg) in 56% yield as pale yellow semisolid. The regioisomeric ratio was determined to be >20:1 by crude $^1$H NMR analysis.

*NMR and HRMS data for the product 4m:*

$^1$H NMR (600 MHz, CDCl$_3$) δ (ppm): 7.52 – 7.43 (m, 3H), 7.31 – 7.21 (m, 3H), 7.06 (t, $J$ = 7.2 Hz, 1H), 7.04 – 6.97 (m, 2H), 5.41 (t, $J$ = 6.0 Hz, 1H), 4.56 (brs, 2H), 4.52 (d, $J$ = 13.2 Hz, 1H), 4.38 – 4.29 (m, 2H), 4.27 (d, $J$ = 12.6 Hz, 1H), 3.02 (dd, $J$ = 14.4, 6.0 Hz, 1H), 2.92 (dd, $J$ = 15.6, 7.2 Hz, 1H), 1.36 (t, $J$ = 7.2 Hz, 3H).
$^1$H NMR (600 MHz, CDCl$_3$) δ (ppm): 7.56 – 7.47 (m, 3H), 7.25 – 7.17 (m, 4H), 7.03 (s, 1H), 6.95 (d, $J = 7.2$ Hz, 1H), 5.47 (t, $J = 7.2$ Hz, 1H), 4.66 (d, $J = 16.2$ Hz, 1H), 4.62 – 4.52 (m, 2H), 4.37 – 4.26 (m, 2H), 4.17 (d, $J = 12.6$ Hz, 1H), 2.99 (dd, $J = 15.0, 6.6$ Hz, 1H), 2.93 (dd, $J = 14.4, 6.0$ Hz, 1H), 1.35 (t, $J = 7.2$ Hz, 3H).

$^{13}$C NMR (150 MHz, CDCl$_3$) δ (ppm): 180.4, 170.4, 140.9, 140.2, 135.5, 134.4, 130.5, 129.7, 128.9, 127.8, 126.7, 125.9, 123.7, 123.5, 111.7, 111.3, 90.2, 74.8, 74.3, 62.8, 60.9, 32.4, 14.0.

HRMS (ESI-TOF) m/z: [M + Na]$^+$ calculated for C$_{25}$H$_{21}$BrClN$_2$O$_3$Na$: 455.1133, found: 455.1135; calculated for C$_{25}$H$_{21}$ClN$_2$O$_3$Na$: 457.1103, found: 457.1112.

ethyl-6-(3-chlorophenyl)-3-(2,2-dicyano-1-phenylvinyl)-2,3,4,7-tetrahydrooxepine-3-carboxylate 4n

Prepared according to the general procedure to afford 4n (35.1 mg, m. p. = 96 – 101 °C) in 81% yield as yellow solid. The regioisomeric ratio was determined to be >20:1 by crude $^1$H NMR analysis.

NMR and HRMS data for the product 4n:

$^1$H NMR (600 MHz, CDCl$_3$) δ (ppm): 7.56 – 7.47 (m, 3H), 7.25 – 7.17 (m, 4H), 7.03 (s, 1H), 6.95 (d, $J = 7.2$ Hz, 1H), 5.47 (t, $J = 7.2$ Hz, 1H), 4.66 (d, $J = 16.2$ Hz, 1H), 4.62 – 4.52 (m, 2H), 4.37 – 4.26 (m, 2H), 4.17 (d, $J = 12.6$ Hz, 1H), 2.99 (dd, $J = 15.0, 6.6$ Hz, 1H), 2.93 (dd, $J = 14.4, 6.0$ Hz, 1H), 1.35 (t, $J = 7.2$ Hz, 3H).

$^{13}$C NMR (150 MHz, CDCl$_3$) δ (ppm): 180.4, 170.4, 140.9, 140.2, 135.5, 134.4, 130.5, 129.7, 128.9, 127.8, 126.7, 125.9, 123.7, 123.5, 111.7, 111.3, 90.2, 74.8, 74.3, 62.8, 60.9, 32.4, 14.0.

HRMS (ESI-TOF) m/z: [M + Na]$^+$ calculated for C$_{25}$H$_{21}$ClN$_2$O$_3$Na$: 455.1133, found: 455.1135; calculated for C$_{25}$H$_{21}$BrClN$_2$O$_3$Na$: 457.1103, found: 457.1112.

ethyl-6-(3-bromophenyl)-3-(2,2-dicyano-1-phenylvinyl)-2,3,4,7-tetrahydrooxepine-3-carboxylate 4o
Prepared according to the general procedure to afford 4o (41.0 mg, m. p. = 130 – 132 °C) in 86% yield as pale yellow solid. The regioisomeric ratio was determined to be >20:1 by crude \(^1\)H NMR analysis.

**NMR and HRMS data for the product 4o:**

\(^1\)H NMR (600 MHz, CDCl\(_3\)) \(\delta\) (ppm): 7.57 – 7.47 (m, 3H), 7.38 (d, \(J = 7.2\) Hz, 1H), 7.23 (d, \(J = 6.6\) Hz, 2H), 7.18 (s, 1H), 7.15 (t, \(J = 8.4\) Hz, 1H), 6.99 (d, \(J = 7.8\) Hz, 1H), 5.45 (t, \(J = 6.6\) Hz, 1H), 4.65 (d, \(J = 16.2\) Hz, 1H), 4.57 (d, \(J = 17.4\) Hz, 1H), 4.56 (d, \(J = 12.0\) Hz, 1H), 4.37 – 4.26 (m, 2H), 4.17 (d, \(J = 12.0\) Hz, 1H), 2.99 (dd, \(J = 15.6, 6.6\) Hz, 1H), 2.93 (dd, \(J = 14.4, 6.6\) Hz, 1H), 1.35 (t, \(J = 7.2\) Hz, 3H).

\(^{13}\)C NMR (150 MHz, CDCl\(_3\)) \(\delta\) (ppm): 180.4, 170.4, 141.1, 140.1, 135.5, 130.7, 130.5, 130.0, 128.9, 128.8, 126.7, 124.1, 123.6, 122.6, 111.7, 111.3, 90.2, 74.7, 74.3, 62.8, 60.9, 32.4, 14.0.

**HRMS (ESI-TOF) m/z:** [M + Na\(^+\)] calculated for C\(_{25}\)H\(_{21}\)BrN\(_2\)O\(_3\)Na\(^+\): 499.0628, found: 499.0622; calculated for C\(_{25}\)H\(_{21}\)BrN\(_2\)O\(_3\)Na\(^+\): 501.0607, found: 501.0607.

**ethyl-3-(2,2-dicyano-1-phenylvinyl)-6-(3-nitrophenyl)-2,3,4,7-tetrahydrooxepine-3-carboxylate 4p**

The reaction was performed according to the general procedure at 80 °C to afford 4p (40.3 mg) in 91% yield as yellow semisolid. The regioisomeric ratio was determined to be >20:1 by crude \(^1\)H NMR analysis.

**NMR and HRMS data for the product 4p:**

\(^1\)H NMR (600 MHz, CDCl\(_3\)) \(\delta\) (ppm): 8.11 (d, \(J = 8.4\) Hz, 1H), 7.89 (s, 1H), 7.60 – 7.50 (m, 3H), 7.47 (t, \(J = 8.4\) Hz, 1H), 7.39 (d, \(J = 8.4\) Hz, 1H), 7.25 (d, \(J = 7.2\) Hz, 2H), 5.55 (t, \(J = 6.6\) Hz, 1H), 4.73 (d, \(J = 16.2\) Hz, 1H), 4.63 (d, \(J = 16.2\) Hz, 1H), 4.60 (d, \(J = 12.6\) Hz, 1H), 4.37 –
4.28 (m, 2H), 4.21 (d, \(J = 12.6\) Hz, 1H), 3.02 (dd, \(J = 14.4, 7.2\) Hz, 1H), 2.97 (dd, \(J = 14.4, 6.0\) Hz, 1H), 1.36 (t, \(J = 7.2\) Hz, 3H).

\(^{13}\)C NMR (150 MHz, CDCl\(_3\)) \(\delta\) (ppm): 180.0, 170.3, 148.3, 140.7, 139.4, 135.4, 131.4, 130.7, 129.5, 129.0, 126.7, 125.2, 122.5, 120.6, 111.6, 111.2, 90.3, 74.6, 74.5, 62.9, 60.9, 32.5, 14.0.

HRMS (ESI-TOF) m/z: \([M + Na]^+\) calculated for \(\text{C}_{25}\text{H}_{21}\text{N}_{3}\text{O}_{3}\text{Na}^+\): 466.1373, found: 466.1363.

**ethyl-3-(2,2-dicyano-1-phenylvinyl)-6-(m-tolyl)-2,3,4,7-tetrahydrooxepine-3-carboxylate 4q**

Prepared according to the general procedure to afford 4q (36.7 mg, m. p. = 126 – 129 °C) in 89% yield as pale yellow solid. The regioisomeric ratio was determined to be >20:1 by crude \(^1\)H NMR analysis.

**NMR and HRMS data for the product 4q:**

\(^1\)H NMR (600 MHz, CDCl\(_3\)) \(\delta\) (ppm): 7.56 – 7.46 (m, 3H), 7.24 (d, \(J = 6.6\) Hz, 2H), 7.18 (t, \(J = 7.8\) Hz, 1H), 7.08 (d, \(J = 7.2\) Hz, 1H), 6.88 (d, \(J = 6.0\) Hz, 2H), 5.48 (t, \(J = 6.0\) Hz, 1H), 4.69 (d, \(J = 16.8\) Hz, 1H), 4.62 (d, \(J = 15.0\) Hz, 1H), 4.56 (d, \(J = 12.6\) Hz, 1H), 4.38 – 4.26 (m, 2H), 4.17 (d, \(J = 12.0\) Hz, 1H), 3.00 (dd, \(J = 14.4, 7.2\) Hz, 1H), 2.95 (dd, \(J = 14.4, 6.6\) Hz, 1H), 2.33 (s, 3H), 1.36 (t, \(J = 7.2\) Hz, 3H).

\(^{13}\)C NMR (150 MHz, CDCl\(_3\)) \(\delta\) (ppm): 180.7, 170.5, 141.5, 139.1, 138.0, 135.6, 130.3, 128.8, 128.4, 128.3, 126.7, 126.4, 122.6, 121.9, 111.8, 111.3, 90.1, 75.0, 74.2, 62.7, 60.9, 32.4, 21.4, 14.0.

HRMS (ESI-TOF) m/z: \([M + Na]^+\) calculated for \(\text{C}_{26}\text{H}_{23}\text{N}_{3}\text{O}_{3}\text{Na}^+\): 435.1679, found: 435.1677.

**ethyl-3-(2,2-dicyano-1-phenylvinyl)-6-(3-methoxyphenyl)-2,3,4,7-tetrahydrooxepine-3-carboxylate 4r**
Prepared according to the general procedure to afford 4r (34.7 mg, m. p. = 149 – 152 °C) in 81% yield as yellow solid. The regioisomeric ratio was determined to be >20:1 by crude $^1$H NMR analysis.

NMR and HRMS data for the product 4r:

$^1$H NMR (600 MHz, CDCl$_3$) δ (ppm): 7.54 – 7.45 (m, 3H), 7.25 – 7.17 (m, 3H), 6.81 (d, $J = 8.4$ Hz, 1H), 6.67 (d, $J = 7.8$ Hz, 1H), 6.60 (s, 1H), 5.50 (t, $J = 6.0$ Hz, 1H), 4.67 (d, $J = 16.8$ Hz, 1H), 4.62 (d, $J = 15.6$ Hz, 1H), 4.55 (d, $J = 13.2$ Hz, 1H), 4.38 – 4.26 (m, 2H), 4.18 (d, $J = 15.6$ Hz, 1H), 1.35 (t, $J = 6.6$ Hz, 3H).

$^{13}$C NMR (150 MHz, CDCl$_3$) δ (ppm): 180.7, 170.5, 159.6, 141.3, 140.6, 135.5, 130.4, 129.5, 128.8, 126.7, 122.3, 118.0, 112.8, 111.8, 111.7, 111.3, 90.2, 75.0, 74.3, 62.7, 60.9, 55.2, 32.5, 14.1.

HRMS (ESI-TOF) m/z: [M + Na]$^+$ calculated for C$_{26}$H$_{24}$N$_2$O$_4$Na$^+$: 451.1628, found: 451.1628.

**ethyl-3-(2,2-dicyano-1-phenylvinyl)-6-(4-fluorophenyl)-2,3,4,7-tetrahydrooxepine-3-carboxylate 4s**

The reaction was performed according to the general procedure at 80 °C to afford 4s (29.5 mg, m. p. = 107 – 112 °C) in 71% yield as pale yellow solid. The regioisomeric ratio was determined to be >20:1 by crude $^1$H NMR analysis.

NMR and HRMS data for the product 4s:

$^1$H NMR (600 MHz, CDCl$_3$) δ (ppm): 7.53 – 7.41 (m, 3H), 7.21 (d, $J = 6.6$ Hz, 2H), 7.07 – 7.01 (m, 2H), 6.96 (t, $J = 9.0$ Hz, 2H), 5.44 (t, $J = 6.6$ Hz, 1H), 4.63 (d, $J = 16.8$ Hz, 1H), 4.59
(d, J = 17.4 Hz, 1H), 4.53 (d, J = 12.6 Hz, 1H), 4.35 – 4.25 (m, 2H), 4.17 (d, J = 13.2 Hz, 1H),
2.99 (dd, J = 14.4, 6.6 Hz, 1H), 2.89 (dd, J = 15.0, 6.6 Hz, 1H), 1.33 (t, J = 7.2 Hz, 3H).

$^{13}$C NMR (150 MHz, CDCl$_3$) δ (ppm): 180.6, 170.4, 162.3 (d, $J_{C,F} = 245.6$ Hz), 140.6, 135.5,
135.2 (d, $J_{C,F} = 2.9$ Hz), 130.4, 128.8, 127.3 (d, $J_{C,F} = 7.2$ Hz), 126.7, 122.3, 115.4 (d, $J_{C,F} = 21.5$ Hz), 111.7, 111.3, 90.2, 75.0, 74.4, 62.8, 60.9, 32.4, 14.1.

$^{19}$F NMR (564 MHz, CDCl$_3$) δ (ppm): -114.1.

HRMS (ESI-TOF) m/z: [M + Na]$^+$ calculated for C$_{25}$H$_{21}$FN$_2$O$_3$Na$: 439.1428, found:
439.1434.

**ethyl-6-(4-chlorophenyl)-3-(2,2-dicyano-1-phenylvinyl)-2,3,4,7-tetrahydrooxepine-3-carboxylate 4t**

[Diagram of the compound]

Prepared according to the general procedure to afford 4t (37.7 mg, m. p. = 103 – 107 °C) in
87% yield as yellow solid. The regioisomeric ratio was determined to be >20:1 by crude $^1$H
NMR analysis.

**NMR and HRMS data for the product 4t:**

$^1$H NMR (600 MHz, CDCl$_3$) δ (ppm): 7.53 – 7.44 (m, 3H), 7.25 (d, J = 7.8 Hz, 2H), 7.22 (d, J =
6.6 Hz, 2H), 7.01 (d, J = 8.4 Hz, 2H), 5.49 (t, J = 6.6 Hz, 1H), 4.64 (d, J = 15.6 Hz, 1H), 4.60
(d, J = 16.2 Hz, 1H), 4.54 (d, J = 12.6 Hz, 1H), 4.35 – 4.25 (m, 2H), 4.19 (d, J = 13.2 Hz, 1H),
3.00 (dd, J = 14.4, 6.6 Hz, 1H), 2.91 (dd, J = 14.4, 6.0 Hz, 1H), 1.34 (t, J = 7.2 Hz, 3H).

$^{13}$C NMR (150 MHz, CDCl$_3$) δ (ppm): 180.5, 170.4, 140.4, 137.5, 135.5, 133.6, 130.4, 128.8,
128.6, 126.9, 126.7, 122.9, 111.7, 111.3, 90.2, 74.8, 74.4, 62.8, 60.8, 32.5, 14.0.

HRMS (ESI-TOF) m/z: [M + Na]$^+$ calculated for C$_{25}$H$_{21}^{35}$ClN$_2$O$_3$Na$: 455.1133, found:
455.1124; calculated for C$_{25}$H$_{21}^{37}$ClN$_2$O$_3$Na$: 457.1103, found: 457.1106.

**ethyl-6-(4-bromophenyl)-3-(2,2-dicyano-1-phenylvinyl)-2,3,4,7-tetrahydrooxepine-3-carboxylate 4u**
Prepared according to the general procedure to afford 4u (42.0 mg, m. p. = 128 – 132 °C) in 88% yield as pale yellow solid. The regioisomeric ratio was determined to be >20:1 by crude \(^1\)H NMR analysis.

**NMR and HRMS data for the product 4u:**

\(^1\)H NMR (600 MHz, CDCl\(_3\)) \(\delta\) (ppm): 7.55 – 7.44 (m, 3H), 7.41 (d, \(J = 8.4\) Hz, 2H), 7.22 (d, \(J = 6.6\) Hz, 2H), 6.95 (d, \(J = 8.4\) Hz, 2H), 5.49 (t, \(J = 6.0\) Hz, 1H), 4.64 (d, \(J = 15.6\) Hz, 1H), 4.59 (d, \(J = 17.4\) Hz, 1H), 4.54 (d, \(J = 13.2\) Hz, 1H), 4.36 – 4.25 (m, 2H), 4.19 (d, \(J = 13.2\) Hz, 1H), 3.00 (dd, \(J = 15.0, 6.6\) Hz, 1H), 2.91 (dd, \(J = 14.4, 6.0\) Hz, 1H), 1.34 (t, \(J = 7.2\) Hz, 3H).

\(^{13}\)C NMR (150 MHz, CDCl\(_3\)) \(\delta\) (ppm): 180.5, 170.4, 140.5, 137.9, 135.5, 131.6, 130.4, 128.8, 127.2, 126.7, 122.9, 121.7, 111.7, 111.3, 90.2, 74.7, 74.4, 62.8, 60.8, 32.5, 14.0.

HRMS (ESI-TOF) m/z: \([M + Na]^+\) calculated for C\(_{25}\)H\(_{21}\)BrN\(_2\)O\(_3\)Na\(^+\): 499.0628, found: 499.0619; calculated for C\(_{25}\)H\(_{21}\)BrN\(_2\)O\(_3\)Na\(^+\): 501.0607, found: 501.0603.

**ethyl-3-(2,2-dicyano-1-phenylvinyl)-6-(p-tolyl)-2,3,4,7-tetrahydrooxepine-3-carboxylate 4v**

Prepared according to the general procedure to afford 4v (34.2 mg, m. p. = 78 – 83 °C) in 83% yield as yellow solid. The regioisomeric ratio was determined to be >20:1 by crude \(^1\)H NMR analysis.

**NMR and HRMS data for the product 4v:**

\(^1\)H NMR (600 MHz, CDCl\(_3\)) \(\delta\) (ppm): 7.55 – 7.44 (m, 3H), 7.23 (d, \(J = 6.6\) Hz, 2H), 7.10 (d, \(J = 8.4\) Hz, 2H), 6.98 (d, \(J = 8.4\) Hz, 2H), 5.47 (t, \(J = 6.6\) Hz, 1H), 4.67 (d, \(J = 15.6\) Hz, 1H), 4.62 (d, \(J = 16.2\) Hz, 1H), 4.55 (d, \(J = 12.6\) Hz, 1H), 4.37 – 4.25 (m, 2H), 4.16 (d, \(J = 12.6\) Hz, 1H),
2.99 (dd, J = 15.6, 7.2 Hz, 1H), 2.93 (dd, J = 14.4, 6.0 Hz, 1H), 2.33 (s, 3H), 1.35 (t, J = 7.2 Hz, 3H).

\(^{13}\)C NMR (150 MHz, CDCl\(_3\)) δ (ppm): 180.8, 170.5, 141.2, 137.6, 136.2, 135.6, 130.4, 129.1, 128.8, 126.7, 125.4, 121.4, 111.8, 111.3, 90.1, 75.0, 74.3, 62.7, 61.0, 32.4, 21.1, 14.1.

HRMS (ESI-TOF) m/z: [M + Na\(^+\)] calculated for C\(_{26}\)H\(_{24}\)N\(_2\)O\(_3\)Na\(^+\): 435.1679, found: 435.1682.

ethyl-3-(2,2-dicyano-1-phenylvinyl)-6-(4-ethylphenyl)-2,3,4,7-tetrahydrooxepine-3-carboxylate 4w

[Chemical structure image]

Prepared according to the general procedure to afford 4w (31.6 mg) in 74% yield as yellow semisolid. The regioisomeric ratio was determined to be >20:1 by crude \(^1\)H NMR analysis.

NMR and HRMS data for the product 4w:

\(^1\)H NMR (600 MHz, CDCl\(_3\)) δ (ppm): 7.55 – 7.44 (m, 3H), 7.23 (d, J = 6.0 Hz, 2H), 7.13 (d, J = 8.4 Hz, 2H), 7.01 (d, J = 8.4 Hz, 2H), 5.48 (t, J = 6.6 Hz, 1H), 4.68 (d, J = 17.4 Hz, 1H), 4.63 (d, J = 15.0 Hz, 1H), 4.55 (d, J = 12.6 Hz, 1H), 4.37 – 4.26 (m, 2H), 4.16 (d, J = 12.0 Hz, 1H), 3.00 (dd, J = 15.0, 6.6 Hz, 1H), 2.94 (dd, J = 14.4, 6.0 Hz, 1H), 2.62 (q, J = 7.2 Hz, 2H), 1.35 (t, J = 7.2 Hz, 3H), 1.22 (t, J = 7.2 Hz, 3H).

\(^{13}\)C NMR (150 MHz, CDCl\(_3\)) δ (ppm): 180.8, 170.5, 143.9, 141.2, 136.4, 135.6, 130.4, 128.8, 127.9, 126.7, 125.5, 121.4, 111.8, 111.3, 90.1, 75.0, 74.2, 62.7, 61.0, 32.4, 28.4, 15.5, 14.0.

HRMS (ESI-TOF) m/z: [M + Na\(^+\)] calculated for C\(_{27}\)H\(_{26}\)N\(_2\)O\(_3\)Na\(^+\): 449.1836, found: 449.1839.

ethyl-3-(2,2-dicyano-1-phenylvinyl)-6-(4-methoxyphenyl)-2,3,4,7-tetrahydrooxepine-3-carboxylate 4x
Prepared according to the general procedure to afford \(4x\) (32.5 mg) in 76% yield as yellow semisolid. The regioisomeric ratio was determined to be >20:1 by crude \(^1\)H NMR analysis.

**NMR and HRMS data for the product 4x:**

\(^1\)H NMR (600 MHz, CDCl\(_3\)) \(\delta\) (ppm): 7.55 – 7.44 (m, 3H), 7.22 (d, \(J = 6.6\) Hz, 2H), 7.02 (d, \(J = 9.0\) Hz, 2H), 6.82 (d, \(J = 8.4\) Hz, 2H), 5.42 (t, \(J = 6.6\) Hz, 1H), 4.66 (d, \(J = 16.2\) Hz, 1H), 4.61 (d, \(J = 16.2\) Hz, 1H), 4.55 (d, \(J = 12.6\) Hz, 1H), 4.37 – 4.25 (m, 2H), 4.15 (d, \(J = 13.2\) Hz, 1H), 3.79 (s, 3H), 2.99 (dd, \(J = 15.0, 7.2\) Hz, 1H), 2.92 (dd, \(J = 14.4, 6.6\) Hz, 1H), 1.35 (t, \(J = 7.2\) Hz, 3H).

\(^13\)C NMR (150 MHz, CDCl\(_3\)) \(\delta\) (ppm): 180.8, 170.5, 159.2, 140.8, 135.6, 131.5, 130.3, 128.8, 126.7, 120.6, 113.8, 111.8, 111.3, 90.1, 75.0, 74.2, 62.7, 61.0, 55.3, 32.4, 14.1.

**HRMS (ESI-TOF) m/z:** [M + Na\(^+\)] calculated for C\(_{26}\)H\(_{24}\)N\(_2\)O\(_4\)Na\(^+\): 451.1628, found: 451.1628.

**ethyl-6-(3,4-dichlorophenyl)-3-(2,2-dicyano-1-phenylvinyl)-2,3,4,7-tetrahydrooxepine-3-carboxylate 4y**

The reaction was performed according to the general procedure at 80 °C to afford \(4y\) (36.9 mg, m. p. = 125 – 129 °C) in 79% yield as pale yellow solid. The regioisomeric ratio was determined to be >20:1 by crude \(^1\)H NMR analysis.

**NMR and HRMS data for the product 4y:**

\(^1\)H NMR (600 MHz, CDCl\(_3\)) \(\delta\) (ppm): 7.56 – 7.47 (m, 3H), 7.35 (d, \(J = 7.8\) Hz, 1H), 7.22 (d, \(J = 7.2\) Hz, 2H), 7.13 (s, 1H), 6.90 (d, \(J = 8.4\) Hz, 1H), 5.48 (t, \(J = 6.6\) Hz, 1H), 4.63 (d, \(J = 16.2\) Hz, 1H), 4.56 (d, \(J = 15.6\) Hz, 1H), 4.55 (d, \(J = 12.0\) Hz, 1H), 4.37 – 4.25 (m, 2H), 4.18 (d, \(J = 13.2\) Hz, 2H).
13.2 Hz, 1H), 2.99 (dd, J = 14.4, 6.0 Hz, 1H), 2.92 (dd, J = 15.6, 7.2 Hz, 1H), 1.34 (t, J = 7.2 Hz, 3H).

$^{13}$C NMR (150 MHz, CDCl$_3$) $\delta$ (ppm): 180.2, 170.3, 139.4, 139.0, 135.4, 132.6, 131.8, 130.5, 130.4, 128.9, 127.6, 126.7, 124.8, 124.1, 111.7, 111.2, 90.3, 74.6, 74.4, 62.9, 60.9, 32.5, 14.0.

HRMS (ESI-TOF) m/z: [M + Na]$^+$ calculated for C$_{25}$H$_{20}$Cl$_2$N$_2$O$_3$Na$: 489.0743, found: 489.0734; calculated for C$_{25}$H$_{20}$Cl$_3$ClN$_2$O$_3$Na$: 491.0714, found: 491.0714; calculated for C$_{25}$H$_{20}$Cl$_2$N$_2$O$_3$Na$: 493.0684, found: 493.0681.

**ethyl-3-(2,2-dicyano-1-phenylvinyl)-6-(naphthalen-2-yl)-2,3,4,7-tetrahydrooxepine-3-carboxylate 4z**

![Structure of 4z](image)

Prepared according to the general procedure to afford 4z (36.8 mg, m. p. = 131 – 133 °C) in 82% yield as yellow solid. The regioisomeric ratio was determined to be >20:1 by crude $^1$H NMR analysis.

**NMR and HRMS data for the product 4z:**

$^1$H NMR (600 MHz, CDCl$_3$) $\delta$ (ppm): 7.83 – 7.74 (m, 3H), 7.57 – 7.43 (m, 6H), 7.30 – 7.19 (m, 3H), 5.63 (t, J = 6.6 Hz, 1H), 4.81 (d, J = 17.4 Hz, 1H), 4.76 (d, J = 15.0 Hz, 1H), 4.61 (d, J = 12.0 Hz, 1H), 4.39 – 4.28 (m, 2H), 4.22 (d, J = 13.2 Hz, 1H), 3.06 (dd, J = 14.4, 7.2 Hz, 1H), 3.01 (dd, J = 14.4, 6.0 Hz, 1H), 1.36 (t, J = 7.2 Hz, 3H).

$^{13}$C NMR (150 MHz, CDCl$_3$) $\delta$ (ppm): 180.7, 170.5, 141.2, 136.3, 135.6, 133.1, 132.7, 130.4, 128.8, 128.1, 128.0, 127.6, 126.8, 126.4, 126.2, 124.2, 123.8, 122.8, 111.8, 111.3, 90.2, 75.0, 74.4, 62.8, 61.0, 32.6, 14.1.

HRMS (ESI-TOF) m/z: [M + Na]$^+$ calculated for C$_{25}$H$_{24}$N$_2$O$_3$Na$: 471.1679, found: 471.1680.

**ethyl-3-(2,2-dicyano-1-phenylvinyl)-6-(thiophen-2-yl)-2,3,4,7-tetrahydrooxepine-3-carboxylate 4aa**
Prepared according to the general procedure to afford 4aa (36.0 mg) in 89% yield as dark yellow semisolid. The regioisomeric ratio was determined to be >20:1 by crude $^1$H NMR analysis.

**NMR and HRMS data for the product 4aa:**

$^1$H NMR (600 MHz, CDCl$_3$) δ (ppm): 7.54 – 7.45 (m, 3H), 7.22 (brs, 2H), 7.14 (d, $J$ = 5.4 Hz, 1H), 6.94 (dd, $J$ = 5.4, 4.2 Hz, 1H), 6.77 (d, $J$ = 3.6 Hz, 1H), 5.55 (t, $J$ = 6.0 Hz, 1H), 4.70 (d, $J$ = 18.0 Hz, 1H), 4.66 (d, $J$ = 18.0 Hz, 1H), 4.61 (d, $J$ = 12.0 Hz, 1H), 4.37 – 4.26 (m, 2H), 4.10 (d, $J$ = 12.6 Hz, 1H), 2.94 (dd, $J$ = 14.4, 7.2 Hz, 1H), 2.89 (dd, $J$ = 15.6, 7.2 Hz, 1H), 1.35 (t, $J$ = 7.2 Hz, 3H).

$^{13}$C NMR (150 MHz, CDCl$_3$) δ (ppm): 180.6, 170.5, 141.6, 135.4, 134.6, 130.4, 128.9, 127.5, 126.7, 124.3, 122.6, 120.7, 111.7, 111.3, 90.2, 74.5, 74.0, 62.8, 61.4, 32.1, 14.0.

HRMS (ESI-TOF) m/z: [M + Na]$^+$ calculated for C$_{23}$H$_{20}$N$_2$O$_3$SNa$: 427.1087, found: 427.1096.
6. Synthetic Transformation of 3a and 4a

6.1 Procedure for the hydrolysis of cyano group on 3a

![Chemical structure](image)

A mixture of nine-membered product 3a (39.8 mg, 0.10 mmol) and Pd(OAc)$_2$ (1.1 mg, 0.005 mmol) in HCOOH (1.0 mL) was stirred at room temperature for 10 min and then diluted with water. The mixture was saturated with sodium carbonate until the pH = 7 – 8, followed by extraction with ethyl acetate (3 × 5 mL). The combined organic phase was washed with saturated brine (3 × 5 mL), dried over Na$_2$SO$_4$, filtered, and concentrated in vacuo. The crude product was purified by column chromatography on silica gel (petroleum ether/ethyl acetate = 6/1 to 2/1) to afford 5 (33.7 mg) as colorless semisolid in 81% yields, which was dried under vacuum and further analyzed by $^1$H NMR, $^{13}$C NMR, HRMS, etc.

**ethyl-(3E,7Z)-5-carbamoyl-5-cyano-4,8-diphenyl-2,5,6,9-tetrahydrooxonine-3-carboxylate**

![Chemical structure](image)

Purification of the crude product via column chromatography delivered 5 (33.7 mg) in 81% yield as colorless semisolid.

NMR and HRMS data for the product 5:

$^1$H NMR (600 MHz, CDCl$_3$) δ (ppm): 7.52 (d, $J$ = 7.8 Hz, 2H), 7.39 – 7.26 (m, 6H), 7.10 (brs, 2H), 6.21 (dd, $J$ = 12.0, 7.2 Hz, 1H), 6.00 (d, $J$ = 127.2 Hz, 2H), 4.77 (d, $J$ = 13.8 Hz, 1H), 4.62 (d, $J$ = 13.8 Hz, 1H), 4.61 (d, $J$ = 13.8 Hz, 1H), 4.55 (d, $J$ = 13.2 Hz, 1H), 4.00 (dd, $J$ = 14.4, 12.0 Hz, 1H), 3.79 – 3.63 (m, 2H), 3.27 (dd, $J$ = 14.4, 6.6 Hz, 1H), 0.69 (t, $J$ = 7.2 Hz, 3H).

$^{13}$C NMR (150 MHz, CDCl$_3$) δ (ppm): 168.9, 166.6, 142.2, 141.5, 138.7, 137.7, 137.0, 129.4, 128.8, 128.3, 128.0, 127.6, 126.3, 126.1, 119.7, 68.5, 66.1, 61.0, 54.7, 36.6, 13.3.

HRMS (ESI-TOF) m/z: [M + Na]$^+$ calculated for C$_{25}$H$_{24}$N$_2$O$_4$Na$: 439.1628, found: 439.1634.
6.2 Procedure for the reductive ring-opening reaction of 3a

Nine-membered product 3a (39.8 mg, 0.10 mmol) was dissolved in THF (1.0 mL) and stirred at room temperature. To this solution was slowly added L-Selectride (0.15 mL, 1.0 M in THF). The reaction mixture was stirred for 5 min at the same temperature, diluted with brine (5 mL) and extracted with ethyl acetate (3 × 5 mL). The combined organic phase was dried over Na₂SO₄, filtered and concentrated in vacuo. The crude product was purified by column chromatography on silica gel (petroleum ether/ethyl acetate = 10/1 to 3/1) to afford 6 (17.6 mg) as pale yellow oil in 47% yields, which was dried under vacuum and further analyzed by ¹H NMR, ¹³C NMR, HRMS, etc.

**ethyl-(3Z,6Z)-4-cyano-8-hydroxy-2-methyl-3,7-diphenylocta-3,6-dienoate 6**

Purification of the crude product via column chromatography delivered 6 (17.6 mg) in 47% yield as pale yellow oil.

**NMR and HRMS data for the product 6:**

¹H NMR (600 MHz, CDCl₃) δ (ppm): 7.49 (d, J = 6.6 Hz, 2H), 7.41 – 7.34 (m, 5H), 7.30 (t, J = 6.6 Hz, 1H), 7.23 – 7.19 (m, 2H), 5.92 (t, J = 7.2 Hz, 1H), 4.66 (s, 2H), 4.21 – 4.09 (m, 2H), 3.94 (q, J = 7.2 Hz, 1H), 3.46 (t, J = 7.8 Hz, 2H), 1.88 (brs, 1H), 1.26 (d, J = 6.6 Hz, 3H), 1.22 (t, J = 7.2 Hz, 3H).

¹³C NMR (150 MHz, CDCl₃) δ (ppm): 171.7, 156.7, 142.5, 140.3, 137.6, 129.0, 128.6, 128.5, 128.0, 127.7, 126.5, 124.9, 118.8, 113.5, 61.6, 59.9, 43.0, 29.7, 15.3, 14.0.

HRMS (ESI-TOF) m/z: [M + Na]⁺ calculated for C₂₄H₂₅NO₃Na⁺: 398.1727, found: 398.1731.
6.3 Procedure for the retro-Knoevenagel reaction of seven-membered product 4a

A glass tube was charged with seven-membered product 4a (39.8 mg, 0.1 mmol), triethylamine (50 μL) in H2O (1.0 mL). The mixture was stirred at 70 °C for 12 hour. Then the mixture was added with water (5 mL) and extracted with ethyl acetate (5 mL × 3). The organic layer was dried over Na2SO4, filtered and concentrated in vacuo. The crude product was purified by column chromatography on silica gel (petroleum ether/dichloromethane = 3/1 to 1/1) to afford 7 (18.2 mg) as pale yellow oil in 52% yields, which was dried under vacuum and further analyzed by 1H NMR, 13C NMR, HRMS, etc.

ethyl-3-benzoyl-6-phenyl-2,3,4,7-tetrahydrooxepine-3-carboxylate 7

Purification of the crude product via column chromatography delivered 7 (18.2 mg) in 52% yield as pale yellow oil.

NMR and HRMS data for the product 7:

1H NMR (600 MHz, CDCl3) δ (ppm): 7.80 (d, J = 7.8 Hz, 2H), 7.54 (t, J = 7.8 Hz, 1H), 7.43 (t, J = 8.4 Hz, 2H), 7.32 – 7.22 (m, 3H), 7.19 (d, J = 8.4 Hz, 2H), 5.88 (t, J = 6.6 Hz, 1H), 4.76 (d, J = 16.2 Hz, 1H), 4.69 (d, J = 18.0 Hz, 1H), 4.51 (d, J = 12.6 Hz, 1H), 4.34 (d, J = 12.0 Hz, 1H), 4.22 – 4.10 (m, 2H), 3.14 (d, J = 6.6 Hz, 2H), 1.10 (t, J = 7.2 Hz, 3H).

13C NMR (150 MHz, CDCl3) δ (ppm): 195.3, 172.1, 140.6, 139.5, 135.6, 133.0, 128.6, 128.5, 128.3, 127.4, 125.9, 122.9, 74.9, 72.3, 65.8, 61.8, 29.7, 13.9.

HRMS (ESI-TOF) m/z: [M + Na]+ calculated for C22H22O4Na+: 373.1410, found: 373.1411.
6.4 Procedure for the removal of benzylidene malononitrile of 4a

A glass tube was charged with seven-membered product 4a (39.8 mg, 0.1 mmol), triethylamine (100 μL) in i-PrOH/H₂O (2 mL, 3:1 (v/v)). The mixture was stirred at 80 °C for 24 hours. Then the mixture was added with water (5 mL) and extracted with ethyl acetate (5 mL × 3). The organic layer was dried over Na₂SO₄, filtered and concentrated in vacuo. The crude product was purified by column chromatography on silica gel (petroleum ether/dichloromethane = 3/1 to 1/1) to afford 8 (22.9 mg) as pale yellow oil in 93% yields, which was dried under vacuum and further analyzed by ¹H NMR, ¹³C NMR, HRMS, etc.

ethyl-6-phenyl-2,3,4,7-tetrahydrooxepine-3-carboxylate 8

Prepared according to the general procedure to afford 8 (22.9 mg) in 93% yield as pale yellow oil.

NMR and HRMS data for the product 8:

¹H NMR (600 MHz, CDCl₃) δ (ppm): 7.33 – 7.28 (m, 2H), 7.27 – 7.22 (m, 3H), 6.05 (t, J = 6.0 Hz, 1H), 4.61 (t, J = 14.4 Hz, 1H), 4.59 – 4.55 (m, 1H), 4.21 – 4.07 (m, 4H), 3.05 – 2.98 (m, 1H), 2.82 – 2.74 (m, 1H), 2.72 – 2.66 (m, 1H), 1.26 (t, J = 7.2 Hz, 3H).

¹³C NMR (150 MHz, CDCl₃) δ (ppm): 173.1, 142.3, 140.8, 128.3, 127.2, 127.0, 125.9, 72.8, 72.5, 60.7, 45.3, 27.9, 14.2.

7. Procedure for the Synthesis of Medium-Sized Azacycles

7.1 Procedure for the synthesis of nine-membered product 10

To an over-dried Schlenk tube was added Pd(PPh₃)₄ (5 mol %), after which the tube was evacuated and back-filled with argon three times. Subsequently, under the protection of argon, a solution of allylidemalononitrile 1a (0.10 mmol) and oxazolidinone 9 (0.15 mmol) in dry MeCN (1.0 mL) was added via syringe and the reaction mixture was stirred at 10 °C for 48 hours. Then the mixture was concentrated and purified by column chromatography on silica gel (petroleum ether/ethyl acetate = 20/1 to 6/1) to afford the corresponding 10 (33.7 mg) as white solid in 61% yield, which were dried under vacuum and further analyzed by ¹H NMR, ¹³C NMR, HRMS, etc.

ethyl-(3E,7Z)-5,5-dicyano-4,8-diphenyl-1-tosyl-2,5,6,9-tetrahydro-1H-azonine-3-carboxylate 10

Prepared according to the general procedure to afford 10 (33.7 mg, m. p. = 152 – 154 °C) in 61% yield as white solid. The regioisomeric ratio was determined to be >20:1 by crude ¹H NMR analysis.

NMR and HRMS data for the product 10:

¹H NMR (600 MHz, CDCl₃, 55 °C) δ (ppm): 7.43 – 7.34 (m, 7H), 7.34 – 7.27 (m, 3H), 7.18 (d, J = 5.4 Hz, 2H), 7.12 (d, J = 8.4 Hz, 2H), 6.05 (t, J = 9.0 Hz, 1H), 4.32 (brs, 4H), 3.84 (q, J = 7.8 Hz, 2H), 3.57 (brs, 2H), 2.38 (s, 3H), 0.85 (t, J = 7.2 Hz, 3H).

¹³C NMR (150 MHz, CDCl₃, 55 °C) δ (ppm): 166.4, 143.6, 143.3, 140.0, 137.1, 136.7, 135.8, 135.6, 129.73, 129.70, 128.7, 128.6, 128.4, 128.2, 127.2, 126.8, 123.7, 114.1, 61.7, 46.8, 45.2, 40.1, 38.8, 21.4, 13.4.
HRMS (ESI-TOF) m/z: [M + Na]⁺ calculated for C₃₂H₂₉N₃O₄SNa⁺: 574.1771, found: 574.1769.

7.2 Procedure for the synthesis of seven-membered product 11

To an over-dried Schlenk tube was added Pd(PPh₃)₄ (5 mol %), after which the tube was evacuated and back-filled with argon three times. Subsequently, under the protection of argon, a solution of allylidemalononitrile 1a (0.10 mmol) and oxazolidinone 9 (0.15 mmol) in dry THF (1.0 mL) was added via syringe and the reaction mixture was stirred at 60 °C for 12 hours. Then the mixture was concentrated and purified by column chromatography on silica gel (petroleum ether/ dichloromethane = 3/1 to 1/1, then petroleum ether/ethyl acetate = 10/1 to 6/1) to afford the corresponding 11 (46.9 mg) as white solid in 85% yield, which were dried under vacuum and further analyzed by ¹H NMR, ¹³C NMR, HRMS, etc.

**ethyl-3-(2,2-dicyano-1-phenylvinyl)-6-phenyl-1-tosyl-2,3,4,7-tetrahydro-1H-azepine-3-carboxylate 11**

Prepared according to the general procedure to afford 11 (46.9 mg, m. p. = 101 – 105 °C) in 85% yield as white solid. The regioisomeric ratio was determined to be >20:1 by crude ¹H NMR analysis.

*NMR and HRMS data for the product 11:*

¹H NMR (600 MHz, CDCl₃) δ (ppm): 7.78 (d, J = 8.4 Hz, 2H), 7.63 – 7.47 (m, 4H), 7.41 (d, J = 7.8 Hz, 2H), 7.34 – 7.28 (m, 4H), 7.17 (d, J = 8.4 Hz, 2H), 5.52 (t, J = 7.8 Hz, 1H), 4.64 (d, J = 16.2 Hz, 1H), 4.45 – 4.33 (m, 3H), 4.23 (d, J = 15.0 Hz, 1H), 3.88 (d, J = 16.8 Hz, 1H), 3.07 (dd, J = 14.4, 6.0 Hz, 1H), 2.50 (s, 3H), 2.45 (dd, J = 14.4, 8.4 Hz, 1H), 1.41 (t, J = 7.2 Hz, 3H).
$^1$H).

$^{13}$C NMR (150 MHz, CDCl$_3$) $\delta$ (ppm): 181.3, 170.1, 144.2, 140.0, 139.9, 135.2, 134.8, 130.3, 130.1, 128.9, 128.5, 127.9, 127.1, 126.8, 125.9, 122.2, 111.7, 111.4, 90.4, 63.1, 58.2, 54.3, 53.6, 33.6, 21.5, 14.1.

HRMS (ESI-TOF) m/z: [M + Na]$^+$ calculated for C$_{32}$H$_{29}$N$_3$O$_4$SNa$: 574.1771, found: 574.1772.
8. General Procedure and Mechanism Studies for the [2+2] Cycloaddition

8.1 General procedure for the transannular [2+2] cycloaddition

To an over-dried Schlenk tube was added the nine-membered products 3 (0.10 mmol), after which the tube was evacuated and back-filled with argon three times. Subsequently, under the protection of argon, dry toluene (1.0 mL) was added via syringe and the reaction mixture was stirred at 150 °C for 5 hours. Then the mixture was cooled to room temperature and purified by column chromatography on silica gel (petroleum ether/ethyl acetate = 20/1 to 10/1 to afford the corresponding 12 in 64–86% yields.

**ethyl-9,9-dicyano-1,6-diphenyl-4-oxatricyclo[4.3.0.0²⁷]nonane-2-carboxylate 12a**

Prepared according to the general procedure to afford 12a (30.2 mg, m. p. = 158 – 160 °C) in 76% yield as white solid. The diastereomeric ratio was determined to be >20:1 by crude ¹H NMR analysis.

**NMR and HRMS data for the product 12a:**

**¹H NMR (600 MHz, CDCl₃) δ (ppm):** 8.15 (d, J = 7.2 Hz, 2H), 7.61 – 7.47 (m, 4H), 7.46 – 7.33 (m, 3H), 7.10 (brs, 1H), 4.48 (d, J = 12.0 Hz, 1H), 4.33 – 4.26 (m, 1H), 4.24 – 4.20 (m, 1H), 4.18 (d, J = 12.0 Hz, 1H), 4.14 (d, J = 11.4 Hz, 1H), 3.86 (d, J = 11.4 Hz, 1H), 3.28 (s, 1H), 1.30 (t, J = 7.2 Hz, 3H).

**¹³C NMR (150 MHz, CDCl₃) δ (ppm):** 169.1, 135.1, 131.9, 130.0, 129.1, 128.9, 128.8, 128.7, 127.4, 115.5, 114.9, 71.1, 70.8, 66.5, 62.4, 58.2, 57.8, 46.3, 38.3, 37.8, 13.6.

**HRMS (ESI-TOF) m/z: [M + Na]⁺ calculated for C₂₅H₂₂N₂O₃Na⁺: 421.1523, found: 420.1524.**

**ethyl-1-(3-chlorophenyl)-9,9-dicyano-6-phenyl-4-oxatricyclo[4.3.0.0²⁷]nonane-2-carboxylate**
Prepared according to the general procedure to afford 12b (33.3 mg, m. p. = 187 – 192 °C) in 77% yield as white solid. The diastereomeric ratio was determined to be >20:1 by crude ¹H NMR analysis.

**NMR and HRMS data for the product 12b:**

¹H NMR (600 MHz, CDCl₃) δ (ppm): 8.22 (s, 1H), 8.09 – 7.99 (m, 1H), 7.65 – 7.46 (m, 3H), 7.44 – 7.37 (m, 3H), 7.10 (brs, 1H), 4.45 (d, J = 11.4 Hz, 1H), 4.34 – 4.21 (m, 2H), 4.13 (t, J = 10.8 Hz, 2H), 3.86 (d, J = 11.4 Hz, 1H), 3.30 (d, J = 12.6 Hz, 1H), 3.27 (s, 1H), 3.02 (d, J = 12.0 Hz, 1H), 1.35 (t, J = 7.2 Hz, 3H).

¹³C NMR (150 MHz, CDCl₃) δ (ppm): 168.9, 135.0, 134.7, 134.1, 130.1, 129.4, 129.2, 129.0, 128.9, 127.5, 126.6, 115.1, 114.6, 70.8, 70.5, 66.5, 62.7, 58.3, 58.1, 46.6, 38.3, 37.8, 13.6.

HRMS (ESI-TOF) m/z: [M + Na]⁺ calculated for C₂₅H₂₁³⁵ClN₂O₅Na⁺: 455.1133, found: 455.1129; calculated for C₂₅H₂₁³⁷ClN₂O₅Na⁺: 457.1103, found: 457.1110.

**ethyl-9,9-dicyano-6-phenyl-1-(p-tolyl)-4-oxatricyclo[4.3.0.0²⁷]nonane-2-carboxylate 12c**

Prepared according to the general procedure to afford 12c (30.1 mg, m. p. = 161 – 165 °C) in 73% yield as white solid. The diastereomeric ratio was determined to be >20:1 by crude ¹H NMR analysis.

**NMR and HRMS data for the product 12c:**

¹H NMR (600 MHz, CDCl₃) δ (ppm): 8.02 (d, J = 8.4 Hz, 2H), 7.52 (brs, 1H), 7.44 – 7.30 (m, 5H), 7.08 (brs, 1H), 4.47 (d, J = 10.8 Hz, 1H), 4.33 – 4.26 (m, 1H), 4.24 – 4.15 (m, 1H), 4.18 (d, J = 12.0 Hz, 1H), 4.13 (d, J = 11.4 Hz, 1H), 3.84 (d, J = 11.4 Hz, 1H), 3.30 (d, J = 13.2 Hz, 1H), 3.26 (s, 1H), 3.00 (d, J = 12.6 Hz, 1H), 2.44 (s, 3H), 1.30 (t, J = 7.2 Hz, 3H).
$^{13}$C NMR (150 MHz, CDCl$_3$) $\delta$ (ppm): 169.2, 139.0, 135.2, 129.6, 128.9, 128.8, 128.7, 128.6, 127.4, 115.6, 115.0, 71.1, 70.8, 66.5, 62.3, 58.1, 57.7, 46.2, 38.3, 37.7, 21.2, 13.6.

HRMS (ESI-TOF) m/z: [M + Na]$^+$ calculated for C$_{26}$H$_{24}$N$_2$O$_3$Na$: 435.1679, found: 435.1685.

**ethyl-9,9-dicyano-1-(naphthalen-2-yl)-6-phenyl-4-oxatricyclo[4.3.0.0$^{2,7}$]nonane-2-carboxylate 12d**

[Diagram of 12d]

Prepared according to the general procedure to afford 12d (36.8 mg, m. p. = 205 – 206 °C) in 82% yield as white solid. The diastereomeric ratio was determined to be >20:1 by crude $^1$H NMR analysis.

**NMR and HRMS data for the product 12d:**

$^1$H NMR (600 MHz, CDCl$_3$) $\delta$ (ppm): 8.68 (s, 1H), 8.24 (d, $J = 11.4$ Hz, 1H), 8.03 (d, $J = 9.0$ Hz, 1H), 7.98 – 7.91 (m, 2H), 7.67 – 7.51 (m, 3H), 7.48 – 7.33 (m, 3H), 7.14 (brs, 1H), 4.57 (d, $J = 11.4$ Hz, 1H), 4.37 – 4.29 (m, 1H), 4.28 – 4.21 (m, 1H), 4.24 (d, $J = 11.4$ Hz, 1H), 4.19 (d, $J = 12.0$ Hz, 1H), 3.90 (d, $J = 11.4$ Hz, 1H), 3.36 (d, $J = 13.2$ Hz, 1H), 3.33 (s, 1H), 3.07 (d, $J = 12.0$ Hz, 1H), 1.33 (t, $J = 7.2$ Hz, 3H).

$^{13}$C NMR (150 MHz, CDCl$_3$) $\delta$ (ppm): 169.2, 135.1, 133.11, 133.08, 130.1, 129.4, 129.1, 129.0, 128.8, 128.7, 128.6, 127.6, 127.2, 126.7, 125.4, 115.6, 115.0, 71.3, 70.9, 66.6, 62.5, 58.4, 58.0, 46.4, 38.4, 37.9, 13.7.

HRMS (ESI-TOF) m/z: [M + Na]$^+$ calculated for C$_{26}$H$_{24}$N$_2$O$_3$Na$: 471.1679, found: 471.1684.

**ethyl-9,9-dicyano-6-phenyl-1-(thiophen-2-yl)-4-oxatricyclo[4.3.0.0$^{2,7}$]nonane-2-carboxylate 12e**

[Diagram of 12e]
Prepared according to the general procedure to afford 12e (29.9 mg, m. p. = 171 – 175 °C) in 74% yield as colorless semisolid. The diastereomeric ratio was determined to be >20:1 by crude 1H NMR analysis.

**NMR and HRMS data for the product 12e:**

1H NMR (600 MHz, CDCl3) δ (ppm): 7.80 (d, J = 4.8 Hz, 1H), 7.56 (d, J = 4.8 Hz, 1H), 7.39 (t, J = 7.8 Hz, 1H), 7.34 (t, J = 7.2 Hz, 1H), 7.32 – 7.26 (m, 2H), 7.23 (dd, J = 4.8, 3.0 Hz, 1H), 7.04 (d, J = 7.2 Hz, 1H), 4.57 (d, J = 10.8 Hz, 1H), 4.35 (d, J = 11.4 Hz, 1H), 4.27 – 4.20 (m, 1H), 4.16 – 4.08 (m, 1H), 4.13 (d, J = 12.0 Hz, 1H), 3.84 (d, J = 12.6 Hz, 1H), 3.37 (s, 1H), 3.32 (d, J = 13.2 Hz, 1H), 3.02 (d, J = 13.2 Hz, 1H), 1.21 (t, J = 7.2 Hz, 3H).

13C NMR (150 MHz, CDCl3) δ (ppm): 168.7, 134.5, 132.7, 129.4, 128.91, 128.86, 127.6, 127.3, 126.8, 115.4, 114.5, 70.0, 68.0, 65.7, 62.2, 58.6, 58.0, 45.2, 38.6, 37.3, 13.5.

**HRMS (ESI-TOF) m/z: [M + Na]+ calculated for C23H26N2O3SNa+: 427.1087, found: 427.1092.**

**tert-butyl-9,9-dicyano-1,6-diphenyl-4-oxatricyclo[4.3.0.0^2.7]nonane-2-carboxylate 12f**

![Diagram of 12f](Image)

Prepared according to the general procedure to afford 12f (29.9 mg) in 70% yield as colorless semisolid. The diastereomeric ratio was determined to be >20:1 by crude 1H NMR analysis.

**NMR and HRMS data for the product 12f:**

1H NMR (600 MHz, CDCl3) δ (ppm): 8.17 (d, J = 7.8 Hz, 2H), 7.63 (brs, 1H), 7.55 (t, J = 7.2 Hz, 2H), 7.48 (t, J = 9.6 Hz, 1H), 7.45 – 7.35 (m, 3H), 7.11 (brs, 1H), 4.40 (d, J = 11.4 Hz, 1H), 4.14 (d, J = 12.0 Hz, 1H), 4.08 (d, J = 10.8 Hz, 1H), 3.80 (d, J = 12.6 Hz, 1H), 3.24 (d, J = 13.8 Hz, 2H), 3.04 (d, J = 13.2 Hz, 1H), 1.54 (s, 9H).

13C NMR (150 MHz, CDCl3) δ (ppm): 168.2, 135.4, 132.1, 130.1, 129.0, 128.9, 128.79, 128.76, 127.6, 115.6, 115.1, 84.3, 71.2, 70.8, 67.0, 58.8, 57.7, 46.0, 38.6, 37.9, 27.9.

**HRMS (ESI-TOF) m/z: [M + Na]+ calculated for C23H26N2O3SNa+: 449.1836, found: 449.1838.**
ethyl-6-(3-bromophenyl)-9,9-dicyano-1-phenyl-4-oxatricyclo[4.3.0.0^2.7]nonane-2-carboxylate 12g

Prepared according to the general procedure to afford 12g (41.0 mg, m. p. = 160 – 162 °C) in 86% yield as colorless semisolid. The diastereomeric ratio was determined to be >20:1 by crude 'H NMR analysis.

NMR and HRMS data for the product 12g:

^1H NMR (600 MHz, CDCl₃) δ (ppm): 8.11 (d, J = 7.8 Hz, 2H), 7.56 (t, J = 6.6 Hz, 2H), 7.53 – 7.41 (m, 3H), 7.26 (brs, 2H), 4.55 – 4.40 (m, 1H), 4.34 – 4.27 (m, 1H), 4.24 – 4.17 (m, 1H), 4.17 – 4.11 (m, 2H), 3.84 (d, J = 11.4 Hz, 1H), 3.33 (d, J = 13.2 Hz, 1H), 3.26 (s, 1H), 2.96 (d, J = 13.2 Hz, 1H), 1.30 (t, J = 7.2 Hz, 3H).

^13C NMR (150 MHz, CDCl₃) δ (ppm): 168.9, 137.5, 131.9, 131.5, 130.4, 129.3, 129.2, 129.0, 128.6, 125.6, 122.9, 115.3, 114.9, 71.2, 70.6, 66.4, 62.5, 58.1, 57.6, 46.3, 38.2, 37.7, 13.6.


ethyl-9,9-dicyano-6-(4-ethylphenyl)-1-phenyl-4-oxatricyclo[4.3.0.0^2.7]nonane-2-carboxylate 12h

Prepared according to the general procedure to afford 12h (31.6 mg, m. p. = 168 – 169 °C) in 74% yield as colorless semisolid. The diastereomeric ratio was determined to be >20:1 by crude 'H NMR analysis.

NMR and HRMS data for the product 12h:

^1H NMR (600 MHz, CDCl₃) δ (ppm): 8.15 (d, J = 7.8 Hz, 2H), 7.55 (t, J = 7.8 Hz, 2H), 7.49 (t, J = 7.8 Hz, 1H), 7.43 (brs, 1H), 7.21 (d, J = 8.4 Hz, 2H), 7.01 (brs, 1H), 4.45 (d, J = 11.4 Hz, 1H), 4.34 – 4.27 (m, 1H), 4.25 – 4.18 (m, 1H), 4.15 (d, J = 11.4 Hz, 1H), 4.12 (d, J = 11.4 Hz,
1H), 3.83 (d, J = 11.4 Hz, 1H), 3.28 (d, J = 13.2 Hz, 1H), 3.25 (s, 1H), 3.02 (d, J = 12.0 Hz, 1H), 2.65 (q, J = 7.2 Hz, 2H), 1.31 (t, J = 7.2 Hz, 3H), 1.23 (t, J = 7.2 Hz, 3H).

$^{13}$C NMR (150 MHz, CDCl$_3$) δ (ppm): 169.2, 144.9, 132.11, 132.06, 130.0, 129.0, 128.8, 128.7, 128.3, 115.6, 114.9, 71.2, 70.9, 66.5, 62.3, 58.2, 57.7, 46.4, 38.3, 37.8, 28.4, 13.6.

HRMS (ESI-TOF) m/z: [M + Na]$^+$ calculated for C$_{27}$H$_{26}$N$_2$O$_3$Na$: 449.1836, found: 449.1839.

**ethyl-9,9-dicyano-6-(3,4-dichlorophenyl)-1-phenyl-4-oxatricyclo[4.3.0.0$^{2,7}$]nonane-2-carboxylate 12i**

Prepared according to the general procedure to afford 12i (39.2 mg, m. p. = 189 – 193 ºC) in 84% yield as colorless semisolid. The diastereomeric ratio was determined to be >20:1 by crude $^1$H NMR analysis.

**NMR and HRMS data for the product 12i:**

$^1$H NMR (600 MHz, CDCl$_3$) δ (ppm): 8.09 (d, J = 8.4 Hz, 2H), 7.74 – 7.29 (m, 5H), 7.20 – 6.89 (m, 1H), 4.45 (d, J = 12.0 Hz, 1H), 4.34 – 4.27 (m, 1H), 4.25 – 4.17 (m, 1H), 4.12 (d, J = 11.4 Hz, 2H), 3.82 (d, J = 11.4 Hz, 1H), 3.35 (d, J = 12.6 Hz, 1H), 3.25 (s, 1H), 2.92 (d, J = 12.6 Hz, 1H), 1.30 (t, J = 7.2 Hz, 3H).

$^{13}$C NMR (150 MHz, CDCl$_3$) δ (ppm): 168.8, 135.4, 133.2, 131.4, 131.0, 129.4, 129.3, 129.2, 129.1, 128.5, 126.7, 115.1, 115.0, 71.2, 70.5, 66.4, 62.6, 58.2, 57.3, 46.3, 38.2, 37.7, 13.6.

HRMS (ESI-TOF) m/z: [M + Na]$^+$ calculated for C$_{27}$H$_{20}^{35}$Cl$_2$N$_2$O$_3$Na$: 489.0743, found: 489.0750; calculated for C$_{27}$H$_{20}^{37}$Cl$_2$N$_2$O$_3$Na$: 491.0714, found: 491.0726; calculated for C$_{27}$H$_{20}^{37}$Cl$_2$N$_2$O$_3$Na$: 493.0684, found: 493.0688.

**ethyl-9,9-dicyano-1-phenyl-6-(thiophen-2-yl)-4-oxatricyclo[4.3.0.0$^{2,7}$]nonane-2-carboxylate 12j**
Prepared according to the general procedure to afford 12j (25.9 mg, m. p. = 198 – 199 °C) in 64% yield as colorless semisolid. The diastereomeric ratio was determined to be >20:1 by crude ¹H NMR analysis.

**NMR and HRMS data for the product 12j:**

**¹H NMR (600 MHz, CDCl₃) δ (ppm):** 8.17 (d, J = 7.2 Hz, 2H), 7.55 (t, J = 6.6 Hz, 2H), 7.49 (t, J = 7.8 Hz, 1H), 7.45 (d, J = 4.8 Hz, 1H), 7.10 (d, J = 2.4 Hz, 1H), 7.07 (dd, J = 4.8, 3.6 Hz, 1H), 4.45 – 4.33 (m, 1H), 4.36 (d, J = 10.8 Hz, 1H), 4.33 – 4.25 (m, 1H), 4.15 (d, J = 11.4 Hz, 1H), 4.05 (d, J = 12.0 Hz, 1H), 3.81 (d, J = 11.4 Hz, 1H), 3.37 (s, 2H), 3.28 (s, 1H), 1.40 (t, J = 7.2 Hz, 3H).

**¹³C NMR (150 MHz, CDCl₃) δ (ppm):** 169.1, 137.8, 131.3, 129.3, 129.0, 128.9, 128.1, 127.2, 127.0, 114.9, 114.2, 73.0, 70.7, 66.1, 62.7, 58.3, 54.9, 46.8, 39.1, 38.1, 13.8.

**HRMS (ESI-TOF) m/z: [M + Na]+ calculated for Cₒ₃H₂₀N₂O₃SNa+:** 427.1087, found: 427.1087.

### 8.2 Mechanism studies for the transannular [2+2] cycloaddition

To an over-dried NMR tube was added the nine-membered products 3 (20 mg). Subsequently, dry d⁶-DMSO (0.6 mL) was added via syringe and the reaction mixture was probed by ¹H NMR at 150 °C for 75 min and ¹H NMR spectra results were collected every 15 minutes.

From the ¹H NMR spectra results, it is clear that the peaks of the product are increasing and the peaks of the substrate material are decreasing. When zooming in on the spectrum at 6.29 ppm, we could still observe a new small triplet peak overlapping in the substrate’s triplet peak, which might support an isomerization of the styryl moiety (E to Z).
9. Preliminary Evaluation of Biological Activity for Compounds 12

9.1 Cell culture and cellular proliferation assay

The A549, PC12, SH-SY5Y, A375 and MDA-MB231 cell line were obtained from the Type Culture Collection of the Chinese Academy of Sciences, Shanghai, China. A549 and PC12 cells were grown in RPMI 1640 (Hyclone, USA) supplemented with 10% fetal bovine serum (FBS, Gibco, USA), while SH-SY5Y, A375 and MDA-MB231 cells were grown in DMEM (Hyclone, USA) supplemented with 10% fetal bovine serum (FBS, Gibco, USA). All the cells were maintained at 37 °C in a humidified incubator containing 5% CO₂. A 20 μM chemical stock solution was prepared by dissolving in DMSO before cell viability assays. Cell viability was determined by MTT (Sigma-Aldrich) assays. All the five cell lines were seeded in 96-well plates 24 h earlier before treated by the chemicals for 24 h. Chemical treatment concentration set to 20 μM and paclitaxel was prepared as a positive control (5 μM, 24 h). After the treatment, 200 μL fresh medium containing 20 μL MTT (5 mg/mL) was added to each pore to replace the chemical containing medium and incubated for 4 h. Then discarded the medium and added 150 μL DMSO to dissolve purple crystals. The absorbance value at 570 nm was determined. The mean percentage of cell survival rates was determined from data of three individual experiments.

9.2 The Mean Inhibitory Ratio of Compounds 12 against A Panel of Cancer Cell Lines

MTT assay was applied to determine the cell viability after 24 h treatment of tested compounds. All the typical cancer cell lines were obtained from American Type Culture Collection (ATCC, USA). PTX is FDA approved to be used for AIDS-related Kaposi sarcoma, breast cancer, non-small cell lung cancer, and ovarian cancer. Results exerted that PTX showed a significant inhibitory effect on most type of cancer, except triple negative breast cancer (TNBC) MDA-MB-231 at the concentration of 5 μM. Interestingly, compound 12a had a more critical effect on MDA-MB-231 than other compounds at the concentration of 20 μM, suggesting a promising application for TNBC therapy after further exploration. However, its effect on lung cancer A-549 was least effective compare to other compounds. Compounds 12c, 12j and 12i could suppress A-549 proliferation significantly, while compounds 12e and 12f displayed a moderate inhibitory effect. PC12 is a rat pheochromocytoma cell line. Compounds 12c and 12h could block the growth of PC12 slightly, while compounds 12i and 12j manifested
a dramatic inhibitory effect. SH-SY-5Y is a neuroblastoma cell line. Most of synthesized compounds could interfere with the proliferative ability of SH-SY-5Y, except compound 12j. A375 cells are human melanoma cancer cells containing the endogenous B-Raf mutation V600E. The ratio of inhibited A375 cells for all the tested compounds were above 50%.

Table S3. The mean inhibitory ratio.

<table>
<thead>
<tr>
<th>Compounds</th>
<th>A549</th>
<th>PC12</th>
<th>SH-SY5Y</th>
<th>A375</th>
<th>MDA-MB231</th>
</tr>
</thead>
<tbody>
<tr>
<td>12a</td>
<td>6.82</td>
<td>25.41</td>
<td>68.31</td>
<td>64.36</td>
<td>46.33</td>
</tr>
<tr>
<td>12b</td>
<td>27.72</td>
<td>4.41</td>
<td>31.10</td>
<td>54.72</td>
<td>40.32</td>
</tr>
<tr>
<td>12c</td>
<td>74.76</td>
<td>43.18</td>
<td>22.39</td>
<td>38.23</td>
<td>9.53</td>
</tr>
<tr>
<td>12d</td>
<td>9.07</td>
<td>14.14</td>
<td>64.31</td>
<td>79.73</td>
<td>41.57</td>
</tr>
<tr>
<td>12e</td>
<td>59.50</td>
<td>16.88</td>
<td>67.40</td>
<td>70.63</td>
<td>35.63</td>
</tr>
<tr>
<td>12f</td>
<td>51.40</td>
<td>22.66</td>
<td>29.92</td>
<td>42.25</td>
<td>17.58</td>
</tr>
<tr>
<td>12g</td>
<td>30.57</td>
<td>19.77</td>
<td>56.87</td>
<td>40.53</td>
<td>30.00</td>
</tr>
<tr>
<td>12h</td>
<td>38.93</td>
<td>45.39</td>
<td>46.35</td>
<td>66.19</td>
<td>37.04</td>
</tr>
<tr>
<td>12i</td>
<td>73.76</td>
<td>61.87</td>
<td>39.36</td>
<td>36.22</td>
<td>22.27</td>
</tr>
<tr>
<td>12j</td>
<td>74.89</td>
<td>72.66</td>
<td>10.87</td>
<td>35.98</td>
<td>1.48</td>
</tr>
<tr>
<td>PTX</td>
<td>66.14</td>
<td>67.63</td>
<td>57.47</td>
<td>77.23</td>
<td>38.75</td>
</tr>
</tbody>
</table>

a Each compound was tested in triplicate; the data are presented as the mean values.
10. Experiments for Mechanism Studies

10.1 The tracking experiments

I. The tracking experiments of the [5+4] cyclization

Five reactions were parallelly carried out following the same operational procedure:

To over-dried Schlenk tubes was added Pd(PPh₃)₄ (5 mol %), after which the tube was evacuated and back-filled with argon three times. Subsequently, under the protection of argon, a solution of allylidene malononitrile 1a (0.10 mmol) and vinylethylene carbonate 2a (0.15 mmol) in dry MeCN (1.0 mL) was added.

Then, the five reactions were stirred at 20 °C for 3 hours, 6 hours, 12 hours, 18 hours and 24 hours, respectively. After the corresponding time, the reaction mixture was filtered through a plug of silica (eluting with ethyl acetate) and concentrated, which were dried under vacuum and further analyzed by ¹H NMR with CH₂Br₂ as the internal standard. The results were listed as follow:

Table S4. The results of the tracking experiments I.

<table>
<thead>
<tr>
<th>reaction time (h)</th>
<th>3</th>
<th>6</th>
<th>12</th>
<th>18</th>
<th>24</th>
</tr>
</thead>
<tbody>
<tr>
<td>NMR yield of 3a (%)</td>
<td>22</td>
<td>57</td>
<td>71</td>
<td>85</td>
<td>96</td>
</tr>
<tr>
<td>NMR yield of 4a (%)</td>
<td>&lt;1</td>
<td>&lt;1</td>
<td>&lt;1</td>
<td>&lt;1</td>
<td>&lt;1</td>
</tr>
</tbody>
</table>

II. The tracking experiments of the [5+2] cyclization

Six reactions were parallelly carried out following the same operational procedure:

To over-dried Schlenk tubes was added Pd(PPh₃)₄ (5 mol %), after which the tube was evacuated and back-filled with argon three times. Subsequently, under the protection of argon, a solution of allylidene malononitrile 1a (0.10 mmol) and vinylethylene carbonate 2a (0.15 mmol) in dry THF (1.0 mL) was added.
Then, the six reactions were stirred at 60 °C for 45 min, 1.5 hours, 3 hours, 6 hours, 9 hours and 12 hours, respectively. After the corresponding time, the reaction mixture was cooled to room temperature, filtered through a plug of silica (eluting with ethyl acetate) and concentrated, which were dried under vacuum and further analyzed by \(^1\)H NMR with CH\(_2\)Br\(_2\) as the internal standard. The results were listed as follow:

<table>
<thead>
<tr>
<th>reaction time (h)</th>
<th>0.75</th>
<th>1.5</th>
<th>3</th>
<th>6</th>
<th>9</th>
<th>12</th>
</tr>
</thead>
<tbody>
<tr>
<td>NMR yield of 3a (%)</td>
<td>87</td>
<td>85</td>
<td>71</td>
<td>60</td>
<td>36</td>
<td>&lt;1</td>
</tr>
<tr>
<td>NMR yield of 4a (%)</td>
<td>6</td>
<td>8</td>
<td>21</td>
<td>32</td>
<td>55</td>
<td>91</td>
</tr>
</tbody>
</table>

10.2 The transformation from 3a to 4a

To an over-dried Schlenk tube was added Pd(PPh\(_3\))\(_4\) (5 mol %), after which the tube was evacuated and back-filled with argon three times. Subsequently, under the protection of argon, a solution of nine-membered product 3a (39.8 mg, 0.10 mmol) in dry THF (1.0 mL) was added via syringe and the reaction mixture was stirred at 60 °C for 12 hours. Then the mixture was concentrated and purified by column chromatography on silica gel (petroleum ether/ethyl acetate = 10/1) to afford 4a (38.2 mg) as pale yellow solid in 96% yields.

10.3 The effect of the loading of VEC on the regioisomeric ratio

Four reactions were parallely carried out under the similar operational procedure:
To over-dried Schlenk tubes was added Pd(PPh₃)₄ (5 mol %), after which the tube was evacuated and back-filled with argon three times. Subsequently, under the protection of argon, a solution of allylidenedimalononitrile 1a (0.10 mmol) and vinylethylene carbonate 2a in dry THF (1.0 mL) was added.

The amounts of 2a in the four reactions respectively refer to 0.15 mmol, 0.25 mmol, 0.35 mmol and 0.45 mmol. Then, the four reactions were stirred at 60 °C for 12 hours, respectively. After then, the reaction mixture was cooled to room temperature, filtered through a plug of silica (eluting with ethyl acetate) and concentrated, which were dried under vacuum and further analyzed by ¹H NMR with CH₂Br₂ as the internal standard. The results were listed as follow:

**Table S6.** The results of the control experiments.

<table>
<thead>
<tr>
<th>The ratio of 1a:2a</th>
<th>1:1.5</th>
<th>1:2.5</th>
<th>1:3.5</th>
<th>1:4.5</th>
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</thead>
<tbody>
<tr>
<td>NMR yield of 3a (%)</td>
<td>&lt;1</td>
<td>72</td>
<td>85</td>
<td>92</td>
</tr>
<tr>
<td>NMR yield of 4a (%)</td>
<td>91</td>
<td>21</td>
<td>6</td>
<td>&lt;1</td>
</tr>
</tbody>
</table>

10.4 The effect of the loading of ligand on the regioisomeric ratio

I. Condition: THF, 20 °C

Five reactions were parallely carried out under the similar operational procedure:

To over-dried Schlenk tubes was added Pd₂(dba)₃·CHCl₃ (2.5 mol %) and PPh₃, after which the tube was evacuated and back-filled with argon three times. Then under the protection of argon, dry THF (0.5 mL) was added and stirred at 20 °C for 1 hour. The amounts of PPh₃ in the five reactions respectively refer to 5 mol %, 10 mol %, 20 mol %, 40 mol %, and 80 mol %.

Subsequently, under the protection of argon, a solution of allylidenedimalononitrile 1a (0.10 mmol) and vinylethylene carbonate 2a in dry THF (0.5 mL) was added respectively. Then, the five reactions were stirred at 20 °C for 12 hours. After then, the reaction mixture was filtered through a plug of silica (eluting with ethyl acetate) and concentrated, which were dried under
vacuum and further analyzed by $^1$H NMR with CH$_2$Br$_2$ as the internal standard.

**II. Condition: THF, 60 °C**

Four reactions were parallelly carried out under the similar operational procedure:

To over-dried Schlenk tubes was added Pd$_2$(dba)$_3$·CHCl$_3$ (2.5 mol %) and PPh$_3$, after which the tube was evacuated and back-filled with argon three times. Then under the protection of argon, dry THF (0.5 mL) was added and stirred at 20 °C for 1 hour. The amounts of PPh$_3$ in the four reactions respectively refer to 5 mol %, 10 mol %, 20 mol % and 40 mol %.

Subsequently, under the protection of argon, a solution of allylidenemalononitrile 1a (0.10 mmol) and vinylethylene carbonate 2a in dry THF (0.5 mL) was added respectively. Then, the four reactions were stirred at 60 °C for 12 hours. After then, the reaction mixture was cooled to room temperature, filtered through a plug of silica (eluting with ethyl acetate) and concentrated, which were dried under vacuum and further analyzed by $^1$H NMR with CH$_2$Br$_2$ as the internal standard.

**III. Condition: MeCN, 60 °C**

Four reactions were parallelly carried out under the similar operational procedure:

To over-dried Schlenk tubes was added Pd$_2$(dba)$_3$·CHCl$_3$ (2.5 mol %) and PPh$_3$, after which the tube was evacuated and back-filled with argon three times. Then under the protection of argon, dry MeCN (0.5 mL) was added and stirred at 20 °C for 1 hour. The amounts of PPh$_3$ in the four reactions respectively refer to 5 mol %, 10 mol %, 20 mol % and 40 mol %.

Subsequently, under the protection of argon, a solution of allylidenemalononitrile 1a (0.10 mmol) and vinylethylene carbonate 2a in dry MeCN (0.5 mL) was added respectively. Then, the four reactions were stirred at 60 °C for 12 hours. After then, the reaction mixture was cooled to room temperature, filtered through a plug of silica (eluting with ethyl acetate) and concentrated, which were dried under vacuum and further analyzed by $^1$H NMR with CH$_2$Br$_2$ as the internal standard.

The results were listed as follow:
Table S7. The results of effect of the loading of ligand.a

<table>
<thead>
<tr>
<th>entry</th>
<th>PPh₃ (x mol%)</th>
<th>solvent</th>
<th>T (°C)</th>
<th>yield (%)b</th>
<th>3a:4ac</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>5</td>
<td>THF</td>
<td>20</td>
<td>18</td>
<td>&gt;20:1</td>
</tr>
<tr>
<td>2</td>
<td>10</td>
<td>THF</td>
<td>20</td>
<td>66</td>
<td>&gt;20:1</td>
</tr>
<tr>
<td>3</td>
<td>20</td>
<td>THF</td>
<td>20</td>
<td>82</td>
<td>10.5:1</td>
</tr>
<tr>
<td>4</td>
<td>40</td>
<td>THF</td>
<td>20</td>
<td>79</td>
<td>5.7:1</td>
</tr>
<tr>
<td>5</td>
<td>80</td>
<td>THF</td>
<td>20</td>
<td>54</td>
<td>1:1.7</td>
</tr>
<tr>
<td>6</td>
<td>5</td>
<td>THF</td>
<td>60</td>
<td>39</td>
<td>&gt;20:1</td>
</tr>
<tr>
<td>7</td>
<td>10</td>
<td>THF</td>
<td>60</td>
<td>96</td>
<td>1.9:1</td>
</tr>
<tr>
<td>8</td>
<td>20</td>
<td>THF</td>
<td>60</td>
<td>89</td>
<td>2.2:1</td>
</tr>
<tr>
<td>9</td>
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<td>THF</td>
<td>60</td>
<td>96</td>
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<td>69</td>
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<td>90</td>
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<td>20</td>
<td>MeCN</td>
<td>60</td>
<td>57</td>
<td>8.2:1</td>
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<tr>
<td>13</td>
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<td>MeCN</td>
<td>60</td>
<td>45</td>
<td>2.3:1</td>
</tr>
</tbody>
</table>

a Unless noted otherwise, the reactions were carried out with 1a (0.10 mmol), 2a (0.15 mmol), and Pd catalyst (5 mol %) in solvent (1.0 mL) for 12 h. And the Pd/ligand complex was pre-prepared with Pd₂dba₂·CHCl₃ and PPh₃ in solvent at rt for 1 h. b Yield was determined by ¹H-NMR analysis with CH₂Br₂ as the internal standard. c The ratio of 3a:4a was determined by ¹H-NMR analysis of the crude reaction mixture. d
### Crystal Data and Structure Refinement

<table>
<thead>
<tr>
<th><strong>Identification code</strong></th>
<th>3a</th>
</tr>
</thead>
<tbody>
<tr>
<td><strong>Empirical formula</strong></td>
<td>C_{25}H_{22}N_{2}O_{3}</td>
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<tr>
<td><strong>Formula weight</strong></td>
<td>398.44</td>
</tr>
<tr>
<td><strong>Temperature/K</strong></td>
<td>296.6(3)</td>
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<tr>
<td><strong>Crystal system</strong></td>
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<td><strong>Space group</strong></td>
<td>P2\textsubscript{1}</td>
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<td><strong>a/Å</strong></td>
<td>9.0919(5)</td>
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<td><strong>b/Å</strong></td>
<td>9.9836(5)</td>
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<tr>
<td><strong>c/Å</strong></td>
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<td><strong>ρ\textsubscript{calc} g/cm\textsuperscript{3}</strong></td>
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<td><strong>F(000)</strong></td>
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<td><strong>Crystal size/mm\textsuperscript{3}</strong></td>
<td>0.6 \times 0.4 \times 0.2</td>
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<td><strong>Radiation</strong></td>
<td>CuKα (λ = 1.54184)</td>
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<tr>
<td><strong>2Θ range for data collection/°</strong></td>
<td>7.548 to 145.832</td>
</tr>
<tr>
<td><strong>Index ranges</strong></td>
<td>-9 ≤ h ≤ 11, -7 ≤ k ≤ 12, -14 ≤ l ≤ 14</td>
</tr>
<tr>
<td><strong>Reflections collected</strong></td>
<td>6415</td>
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<tr>
<td><strong>Independent reflections</strong></td>
<td>3358 [R\textsubscript{int} = 0.0288, R\textsubscript{sigma} = 0.0365]</td>
</tr>
<tr>
<td><strong>Data/restraints/parameters</strong></td>
<td>3358/1/272</td>
</tr>
<tr>
<td><strong>Goodness-of-fit on F\textsuperscript{2}</strong></td>
<td>1.042</td>
</tr>
<tr>
<td><strong>Final R indexes [I&gt;=2σ (I)]</strong></td>
<td>R\textsubscript{1} = 0.0549, wR\textsubscript{2} = 0.1433</td>
</tr>
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<td><strong>Final R indexes [all data]</strong></td>
<td>R\textsubscript{1} = 0.0573, wR\textsubscript{2} = 0.1472</td>
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<tr>
<td><strong>Largest diff. peak/hole / e Å\textsuperscript{-3}</strong></td>
<td>0.24/-0.29</td>
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<td>Property</td>
<td>Value</td>
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<tr>
<td>--------------------------------</td>
<td>--------------------------------------------</td>
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<td>Formula weight</td>
<td>398.44</td>
</tr>
<tr>
<td>Temperature/K</td>
<td>295.4(4)</td>
</tr>
<tr>
<td>Crystal system</td>
<td>monoclinic</td>
</tr>
<tr>
<td>Space group</td>
<td>P2_{1}/n</td>
</tr>
<tr>
<td>a/Å</td>
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</tr>
<tr>
<td>b/Å</td>
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</tr>
<tr>
<td>c/Å</td>
<td>17.3578(10)</td>
</tr>
<tr>
<td>α/°</td>
<td>90</td>
</tr>
<tr>
<td>β/°</td>
<td>99.745(5)</td>
</tr>
<tr>
<td>γ/°</td>
<td>90</td>
</tr>
<tr>
<td>Volume/Å³</td>
<td>2194.0(2)</td>
</tr>
<tr>
<td>Z</td>
<td>4</td>
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<tr>
<td>ρ_{calc}/g/cm³</td>
<td>1.206</td>
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<tr>
<td>μ/mm⁻¹</td>
<td>0.642</td>
</tr>
<tr>
<td>F(000)</td>
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</tr>
<tr>
<td>Crystal size/mm³</td>
<td>0.6 × 0.4 × 0.3</td>
</tr>
<tr>
<td>Radiation</td>
<td>CuKα (λ = 1.54184)</td>
</tr>
<tr>
<td>2Θ range for data collection/°</td>
<td>8.43 to 146.126</td>
</tr>
<tr>
<td>Index ranges</td>
<td>-11 ≤ h ≤ 11, -16 ≤ k ≤ 16, -21 ≤ l ≤ 21</td>
</tr>
<tr>
<td>Reflections collected</td>
<td>12330</td>
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<tr>
<td>Independent reflections</td>
<td>4284 [R_{int} = 0.0225, R_{sigma} = 0.0183]</td>
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<td>Data/restraints/parameters</td>
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<tr>
<td>Goodness-of-fit on F²</td>
<td>1.044</td>
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<tr>
<td>Final R indexes [I&gt;=2σ(I)]</td>
<td>R_1 = 0.0608, wR_2 = 0.1748</td>
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<tr>
<td>Final R indexes [all data]</td>
<td>R_1 = 0.0752, wR_2 = 0.1940</td>
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<td>Largest diff. peak/hole / e Å⁻³</td>
<td>0.18/-0.22</td>
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<tr>
<td>Identification code</td>
<td>12a</td>
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<tr>
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<tr>
<td>Empirical formula</td>
<td>C_{25}H_{22}N_{2}O_{3}</td>
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<td>Formula weight</td>
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</tr>
<tr>
<td>Temperature/K</td>
<td>225(100)</td>
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<td>Crystal system</td>
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<tr>
<td>b/Å</td>
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<td>c/Å</td>
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<tr>
<td>α/°</td>
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<tr>
<td>β/°</td>
<td>85.531(8)</td>
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<td>γ/°</td>
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<td>Volume/Å³</td>
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<td>Z</td>
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<td>ρ_{calc}/g/cm³</td>
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<tr>
<td>μ/μm⁻¹</td>
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<td>F(000)</td>
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<td>Crystal size/mm³</td>
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<tr>
<td>Radiation</td>
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<td>2Θ range for data collection/°</td>
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<tr>
<td>Index ranges</td>
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<td>Reflections collected</td>
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<tr>
<td>Independent reflections</td>
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<td>Data/restraints/parameters</td>
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<td>Goodness-of-fit on F²</td>
<td>1.040</td>
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<tr>
<td>Final R indexes [I≥2σ (I)]</td>
<td>R₁ = 0.0793, wR₂ = 0.2132</td>
</tr>
<tr>
<td>Final R indexes [all data]</td>
<td>R₁ = 0.0877, wR₂ = 0.2314</td>
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<tr>
<td>Largest diff. peak/hole / e Å⁻³</td>
<td>0.71/-0.47</td>
</tr>
</tbody>
</table>
12. References and Notes


13. **NMR Spectra**

![NMR Spectra Image]
S117
S122
$\text{S125}$
HMOC of 3a
($\sigma^6$-DMSO, 25 °C)
12a
(d<sup>6</sup>-DMSO, 150 °C)

75 min
(d<sup>6</sup>-DMSO, 150 °C)

60 min
(d<sup>6</sup>-DMSO, 150 °C)

45 min
(d<sup>6</sup>-DMSO, 150 °C)

30 min
(d<sup>6</sup>-DMSO, 150 °C)

15 min
(d<sup>6</sup>-DMSO, 150 °C)

3a
(d<sup>6</sup>-DMSO, 150 °C)