Electronic Supplementary Information

Lewis Acids Catalyzed Asymmetric [4+2] Cycloaddition of Cyclobutenones to Synthesize α,β-Unsaturated δ-Lactones

Qian Yao, a Han Yu, a Hang Zhang, a Shunxi Dong, a Fenzhen Chang, a Lili Lin, a Xiaohua Liu, a and Xiaoming Feng a

a Key Laboratory of Green Chemistry & Technology, Ministry of Education, College of Chemistry, Sichuan University, Chengdu 610064, China.
E-mail: xmfeng@scu.edu.cn; Fax: + 86 28 85418249; Tel: + 86 28 85418249.

This journal is © The Royal Society of Chemistry 2018
## Contents

(A) General Information S3
(B) General procedure for the asymmetric $[4 + 2]$ cycloaddition S3
(C) Transformation of 3aa S4
(D) Control experiments S4
(E) X-ray structure for 3ia (CCDC 1560408) S6
(F) The analytical and spectral characterization data for the compounds S6
(G) Reference S34
(H) Copies of the NMR spectra S35
(A) General Information

$^1$H NMR spectra were recorded on commercial instruments (400 MHz). Chemical shifts are recorded in ppm relative to tetramethylsilane and with the solvent resonance as the internal standard. Data are reported as follows: chemical shift, multiplicity (s = singlet, d = doublet, t = triplet, m = multiplet, dd = doublet of doublets), coupling constants (Hz), integration.

$^{13}$C($^1$H) NMR data were collected on commercial instruments (101 MHz) with complete proton decoupling. Chemical shifts are reported in ppm from the tetramethylsilane with the solvent resonance as internal standard. The enantiomeric excesses were determined by HPLC analysis on chiral DAICEL CHIRALPAK IA or CHIRALPAK IB or CHIRALPAK IC or CHIRALPAK IE or CHIRALPAK ADH column at 254 nm. Optical rotations were measured on a commercial polarimeter and are reported as follows: $[\alpha]_D^\circ$ ($c = g/100$ mL, CH$_2$Cl$_2$).

HRMS was recorded on a commercial apparatus (ESI Source). Solvents were dried according to standard procedures. Racemic samples were prepared by using the racemic $N,N'$-dioxdes as the ligand. All reactions were performed in sealed oven-dried glass tubes under an atmosphere of nitrogen unless otherwise noted. The $N,N'$-dioxdes were prepared according to the previous reports. Starting materials of cyclobutenones, $\alpha$-ketoesters and $\alpha$-ketoamide were prepared according to the previous reports.

(B) General procedure for the asymmetric [4+2] cycloaddition

a) Preparing chiral catalyst: $N,N'$-dioxide L-PitBu (15.4 mg, 0.035 mmol), Yb(OTf)$_3$ (21.7 mg, 0.035 mmol), 5 Å molecular sieves (350 mg) and LiNTf$_2$ (30.1 mg, 0.105 mmol) were stirred in 3.5 mL CH$_2$Cl$_2$ at 30 °C for 3 hours. After the solvent was removed in vacuo, the solid of the chiral catalyst was obtained.
b) **Catalytic reaction**: A dry reaction tube was charged with the prepared chiral catalyst (119.2 mg, 0.01 mmol, 10 mol%), α-keto carbonyl compounds (1) (0.10 mmol) and cyclobutenones (2) (0.12 mmol) under an N₂ atmosphere. Then, CHCl₃ (1.0 mL) were added and the mixture was stirred at 50 ºC for 48 hours. The products were purified by silica gel column chromatographic (ethyl acetate/petroleum ether 1/20 to 1/6).

(C) **Transformation of 3aa**

a) The oxidant m-CPBA (0.2 mmol, 34.4 mg) was added to a solution of 3aa (0.10 mmol, 36.8 mg) in CH₂Cl₂ (1 mL) at 0 ºC. Then, the reaction mixture was stirred at 35 ºC for 18 hours. The product was purified by silica gel column chromatographic (ethyl acetate/petroleum ether 1/20 to 1/6).

![Chemical structure of 3aa and 4aa](image)

b) To a dry Schlenk tube was added 3aa (0.1 mmol, 36.8 mg), NaCl (1 mmol, 58.4 mg), H₂O (1 mmol, 18 mg) and DMSO (1.5 mL). The reaction was stirred at 120 ºC for 4 hours. The solution was then cooled to room temperature, diluted with water and extracted with ethyl acetate. The collected organic layer was dried over anhydrous Na₂SO₄, concentrated and the product was purified by silica gel column chromatographic (ethyl acetate/petroleum ether 1/20 to 1/6).

5aa: ¹H NMR (400 MHz, CDCl₃) δ = 7.70 – 7.55 (m, 12H), 7.55 – 7.48 (m, 5H), 7.46 – 7.30 (m, 3H), 6.73 (d, J = 16.0, 1H), 6.46 (dd, J = 24.0, 1.2, 2H).

¹³C{¹H} NMR (101 MHz, CDCl₃) δ = 162.6, 159.1, 155.6, 135.9, 135.6, 135.5, 130.8, 129.6, 129.3, 129.1, 127.6, 126.8, 119.1, 109.5, 105.3.

**3aa**: 95% ee, 17/1 dr

**5aa**: 70% yield.

(D) Control experiments

**a)** Cyclobutenones are known to undergo ring opening to form vinylketenes at high temperature ($\geq 80^\circ$C). Under our catalytic conditions, no product was detected when the reaction was carried out at 0°C. However, the reaction could occur at lower temperatures (50°C), which indicated in our system the thermal conditions might be not the only factor to cause such ring opening.

It showed that the thermal conditions were benefit for the reaction.

**General procedure for the reaction:** a dry reaction tube was charged with the prepared chiral catalyst (119.2 mg, 0.01 mmol, 10 mol%), $\alpha$-keto carbonyl compound 1a (0.10 mmol, 19.0 mg) and cyclobutenone 2a (0.12 mmol, 21.4 mg) under an N$_2$ atmosphere. Then, CHCl$_3$ (1.0 mL) were added and the mixture was stirred at 0°C for 48 hours.

**b)** In order to gain insight into the influence of our catalytic condition on the ring opening of cyclobutenones, we selected 2-naphthol 6a, which was weakly coordinated with Lewis acid, to trap the vinylketenes.
The results above suggested that the Lewis acid [Yb(OTf)$_3$] might participate in the activation of cyclobutanone to generate the active vinylketene intermediate assisted by LiNTf$_2$ and 5 Å molecular series under the thermal condition.

**General procedure for the reaction:** a dry reaction tube was charged with Yb(OTf)$_3$ (6.2 mg, 0.01 mmol), 5 Å molecular sieves (100 mg) and LiNTf$_2$ (8.6 mg, 0.03 mmol), cyclobutenone 2a (0.10 mmol, 17.8 mg) and 2-naphthol 6a (0.1 mmol, 14.4 mg) under an N$_2$ atmosphere. Then, CHCl$_3$ (1.0 mL) were added and the mixture was stirred at 50 ºC for 48 hours. The product was purified by silica gel column chromatographic (ethyl acetate/petroleum ether 1/20 to 1/9).

7aa: $^1$H NMR (400 MHz, CDCl$_3$) δ = 7.80 – 7.71 (m, 3H), 7.49 – 7.30 (m, 8H), 7.04 – 6.91 (m, 1H), 6.43 (d, J = 1.2, 1H), 3.70 (s, 2H).

$^{13}$C($^1$H) NMR (101 MHz, CDCl$_3$) δ = 168.9, 148.2, 136.6, 135.4, 133.7, 131.6, 129.5, 128.6, 128.5, 128.4, 127.9, 127.7, 126.7, 125.9, 120.8, 118.4, 118.4, 42.6.

HRMS (ESI-FT): calcd for C$_{20}$H$_{16}$ClKO$_2$+ ([M + K]$^+$) 323.0839, found 323.0837, calcd for C$_{20}$H$_{16}$ClKO$_2$+ ([M + K]$^+$) 325.0809, found 325.0809.

(E) The X-ray structure for 3ia (CCDC 1560408)
The compound 3ia was recrystallized from CH₂Cl₂ and petroleum ether.
CCDC 1560408 contains the supplementary crystallographic data of the adduct 3ia for this paper. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data_request/cif.

(F) The analytical and spectral characterization data for the compounds

Methyl (E)-3-chloro-6-oxo-4-phenyl-2-styryl-3,6-dihydro-2H-pyran-2-carboxylate (3aa)

White solid, 92% yield (1.19 g). 17/1 dr determined by ¹H NMR, 95% ee determined by HPLC (chiral IA column), n-hexane/i-PrOH = 90/10, flow rate 1.0 mL/min, λ = 254 nm, retention time: 9.7 min, 10.6 min, 12.8 min, 13.6 min. [α]D²⁰ = −240.31 (c = 0.52).

¹H NMR (400 MHz, CDCl₃) δ = 7.65 – 7.60 (m, 2H), 7.54 – 7.44 (m, 5H), 7.40 – 7.30 (m, 3H), 7.17 (d, J = 16.0, 1H), 6.42 (s, 1H), 6.30 (d, J = 16.0, 1H), 5.53 (s, 1H), 3.77 (s, 3H).

¹³C{¹H} NMR (101 MHz, CDCl₃) δ = 169.4, 161.9, 153.3, 135.3, 134.7, 133.2, 131.6, 129.5, 129.0, 128.9, 127.2, 126.7, 121.7, 116.6, 85.5, 54.5, 54.2.


<table>
<thead>
<tr>
<th>Retention Time</th>
<th>Area</th>
<th>% Area</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>9.677</td>
<td>601262</td>
</tr>
<tr>
<td>2</td>
<td>10.556</td>
<td>604814</td>
</tr>
<tr>
<td>3</td>
<td>12.800</td>
<td>147979</td>
</tr>
</tbody>
</table>
Ethyl (E)-3-chloro-6-oxo-4-phenyl-2-styryl-3,6-dihydro-2H-pyran-2-carboxylate (3ba)

White solid, 87% yield (33.2 mg). 16/1 dr determined by $^1$H NMR,
94% ee determined by HPLC (chiral ADH column), n-hexane/i-PrOH
= 90/10, flow rate 1.0 mL/min, $\lambda = 254$ nm, retention time: 11.0 min,
12.5 min, 20.4 min. $[\alpha]_D^{20} = -259.89$ (c = 0.53).

$^1$H NMR (400 MHz, CDCl$_3$) $\delta = 7.65 - 7.60$ (m, 2H), 7.54 – 7.44 (m, 5H), 7.41 – 7.31 (m,
3H), 7.18 (d, $J = 16.0$, 1H), 6.42 (s, 1H), 6.31 (d, $J = 16.0$, 1H), 5.53 (s, 1H), 4.23 (dd, $J =
14.0$, 6.8, 2H), 1.20 (t, $J = 6.8$, 3H).

$^{13}$C($^1$H) NMR (101 MHz, CDCl$_3$) $\delta = 168.8$, 162.0, 153.2, 135.4, 134.7, 133.3, 131.6, 129.5,
128.9, 128.9, 127.2, 126.7, 121.7, 116.7, 85.4, 63.5, 54.6, 14.1.

HRMS (ESI-TOF): calcd for C$_{22}$H$_{19}$ClNaO$_4$ ($[M + Na]^+$) 405.0870, found 405.0864,
calcd for C$_{22}$H$_{19}$ClNaO$_4$ ($[M + Na]^+$) 407.0840, found 407.0850.
Retention Time | Area     | % Area
---|---------|--------
1   | 11.050  | 23819289 | 93.00
2   | 12.488  | 739739  | 2.89
3   | 20.421  | 1052883 | 4.11

Isopropyl (E)-3-chloro-6-oxo-4-phenyl-2-styryl-3,6-dihydro-2H-pyran-2-carboxylate (3ca)

White solid, 83% yield (32.7 mg). 16/1 dr determined by $^1$H NMR, 93% ee determined by HPLC (chiral ADH column), n-hexane/i-PrOH = 90/10, flow rate 1.0 mL/min, $\lambda$ = 254 nm, retention time: 8.4 min, 9.1 min, 19.7 min, 20.2 min. $[\alpha]_D^{20} = -200.19$ ($c = 0.54$).

$^1$H NMR (400 MHz, CDCl$_3$) δ = 7.64 – 7.60 (m, 2H), 7.53 – 7.45 (m, 5H), 7.41 – 7.31 (m, 3H), 7.17 (d, $J = 16.0$, 1H), 6.42 (s, 1H), 6.31 (d, $J = 16.0$, 1H), 5.51 (s, 1H), 5.12 – 4.96 (m, 1H), 1.21 (d, $J = 6.0$, 3H), 1.16 (d, $J = 6.0$, 3H).

$^{13}$C($^1$H) NMR (101 MHz, CDCl$_3$) δ = 168.2, 162.1, 153.1, 135.5, 134.6, 133.4, 131.6, 129.5, 128.9, 127.2, 126.6, 121.7, 116.8, 85.3, 71.8, 54.8, 21.6, 21.5.

HRMS (ESI-TOF): calcd for C$_{23}$H$_{21}$O$_{14}$Na$_4$ Cl ([M + Na]$^+$) 419.1026, found 419.1028, calcd for C$_{23}$H$_{21}$O$_{14}$Na$_4$ Cl ([M + Na]$^+$) 421.0997, found 421.1006.
Methyl (E)-3-chloro-6-oxo-2-styryl-4-(p-tolyl)-3,6-dihydro-2H-pyran-2-carboxylate (3ab)

White solid, 82% yield (31.5 mg). 17/1 dr determined by \(^1\)H NMR, 95% ee determined by HPLC (chiral IC column), n-hexane/i-PrOH = 90/10, flow rate 1.0 mL/min, \(\lambda = 254\) nm, retention time: 19.4 min, 22.6 min, 35.1 min, 36.6 min. \([\alpha]_{D}^{20} = -227.30\) (c = 0.63).

\(^1\)H NMR (400 MHz, CDCl\(_3\)) \(\delta = 7.55 – 7.46\) (m, 4H), 7.39 – 7.29 (m, 5H), 7.17 (d, \(J = 16.0, 1H\)), 6.40 (s, 1H), 6.30 (d, \(J = 16.0, 1H\)), 5.53 (s, 1H), 3.76 (s, 3H), 2.42 (s, 3H).

\(^{13}\)C\(^{1}\)H NMR (101 MHz, CDCl\(_3\)) \(\delta = 169.4, 162.1, 153.2, 142.4, 135.3, 134.6, 130.2, 128.9, 128.9, 127.2, 126.6, 121.8, 115.5, 85.4, 54.4, 54.2, 21.6.

HRMS (ESI-TOF): calcd for \(C_{22}H_{19}^{34,9658}ClNaO_{4}\)\(^+\) ([M + Na]\(^+\)) 405.0870, found 405.0869, calcd for \(C_{22}H_{19}^{36,9658}ClNaO_{4}\)\(^+\) ([M + Na]\(^+\)) 407.0840, found 407.0861.
Methyl (E)-3-chloro-4-(4-methoxyphenyl)-6-oxo-2-styryl-3,6-dihydro-2H-pyran-2-carboxylate (3ac)

White solid, 56% yield (22.5 mg). 15/1 dr determined by $^1$H NMR, 93% ee determined by HPLC (chiral ADH column), n-hexane/i-PrOH = 90/10, flow rate 1.0 mL/min, $\lambda = 254$ nm, retention time: 17.0 min, 19.4 min, 31.0 min, 33.9 min. $[\alpha]_{D}^{20} = -260.67$ (c = 0.45).

$^1$H NMR (400 MHz, CDCl$_3$) $\delta = 7.62 - 7.58$ (m, 2H), 7.50 – 7.45 (m, 2H), 7.39 – 7.30 (m, 3H), 7.16 (d, $J = 16.0$, 1H), 7.02 – 6.98 (m, 2H), 6.35 (s, 1H), 6.30 (d, $J = 15.6$, 1H), 5.52 (s, 1H), 3.87 (s, 3H), 3.76 (s, 3H).

$^{13}$C($^1$H) NMR (101 MHz, CDCl$_3$) $\delta = 169.5$, 162.5, 162.3, 152.6, 135.4, 134.6, 128.9, 128.9, 128.4, 127.2, 125.2, 121.9, 115.0, 114.0, 85.3, 55.7, 54.3, 54.1.

HRMS (ESI-TOF): calcd for C$_{22}$H$_{19}^{34,9658}$ClNaO$_5$+ ([M + Na]$^+$) 421.0819, found 421.0815, calcd for C$_{22}$H$_{19}^{36,9658}$ClNaO$_5$+ ([M + Na]$^+$) 423.0789, found 423.0801.
Methyl (E)-3-chloro-6-oxo-2-styryl-4-(m-tolyl)-3,6-dihydro-2H-pyran-2-carboxylate (3ad)

White solid, 78% yield (30.0 mg). >19/1 dr determined by $^1$H NMR, 95% ee determined by HPLC (chiral IA column), $n$-hexane/i-PrOH = 90/10, flow rate 1.0 mL/min, $\lambda$ = 254 nm, retention time: 7.4 min, 8.7 min, 9.7 min, 10.1 min. $\left[\alpha\right]_D^{20} = -279.83$ (c = 0.60).

$^1$H NMR (400 MHz, CDCl$_3$) $\delta$ = 7.50 – 7.46 (m, 2H), 7.44 – 7.31 (m, 7H), 7.17 (d, $J$ = 16.0, 1H), 6.41 (s, 1H), 6.31 (d, $J$ = 16.0, 1H), 5.53 (s, 1H), 3.77 (s, 3H), 2.43 (s, 3H).

$^{13}$C($^1$H) NMR (101 MHz, CDCl$_3$) $\delta$ = 169.5, 162.0, 153.5, 139.3, 135.3, 134.7, 133.2, 132.5, 129.4, 129.0, 128.9, 127.3, 127.2, 123.9, 121.8, 116.4, 85.5, 54.5, 54.2, 21.6.

HRMS (ESI-TOF): calcd for C$_{22}$H$_{19}$O$_{34.9659}$ClNaO$_4^+$ ([M + Na$^+$]) 405.0870, found 405.0873, calcd for C$_{22}$H$_{19}$O$_{36.9659}$ClNaO$_4^+$ ([M + Na$^+$]) 407.0850, found 407.0853.
Methyl (E)-3-chloro-4-(3-chlorophenyl)-6-oxo-2-styryl-3,6-dihydro-2H-pyran-2-carboxylate (3ae)

White solid, 53% yield (10.7 mg). 16/1 dr determined by \(^1\)H NMR, 93% ee determined by HPLC (chiral IA column), n-hexane/i-PrOH = 90/10, flow rate 1.0 mL/min, \(\lambda\) = 254 nm, retention time: 7.9 min, 9.3 min, 10.0 min, 11.2 min. \([\alpha\]_D\(^{20}\) = −316.36 (c = 0.21).

\(^1\)H NMR (400 MHz, CDCl\(_3\)) \(\delta\) = 7.59 (t, \(J = 2.0, 1\)H), 7.53 – 7.43 (m, 5H), 7.41 – 7.32 (m, 3H), 7.16 (d, \(J = 16.0, 1\)H), 6.41 (s, 1H), 6.28 (d, \(J = 16.0, 1\)H), 5.45 (s, 1H), 3.79 (s, 3H).

\(^{13}\)C\(^{(1)}\)H NMR (101 MHz, CDCl\(_3\)) \(\delta\) = 169.3, 161.4, 152.1, 135.7, 135.2, 135.2, 134.9, 131.6, 130.8, 129.1, 128.9, 127.2, 126.8, 124.9, 121.4, 117.7, 85.5, 54.4, 54.3.

HRMS (ESI-FT): calcd for C\(_{21}\)H\(_{16}\)Cl\(_2\)NaO\(_4\)\(^+\) ([M + Na]\(^+\)) 425.0323, found 425.0321, calcd for C\(_{21}\)H\(_{16}\)Cl\(_2\)NaO\(_4\)\(^+\) ([M + Na]\(^+\)) 427.0294, found 427.0294.
<table>
<thead>
<tr>
<th>Retention Time</th>
<th>Area</th>
<th>% Area</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>7.929</td>
<td>6666177</td>
</tr>
<tr>
<td>2</td>
<td>9.260</td>
<td>245460</td>
</tr>
<tr>
<td>3</td>
<td>9.956</td>
<td>31839</td>
</tr>
<tr>
<td>4</td>
<td>11.170</td>
<td>297515</td>
</tr>
</tbody>
</table>

Methyl (E)-3-chloro-2-(4-fluorostyryl)-6-oxo-4-phenyl-3,6-dihydro-2H-pyran-2-carboxylate (3da)

White solid, 86% yield (33.1 mg). 19/1 dr determined by $^1$H NMR, 95% ee determined by HPLC (chiral IA column), n-hexane/i-PrOH = 90/10, flow rate 1.0 mL/min, $\lambda$ = 254 nm, retention time: 11.6 min, 13.7 min, 14.7 min, 16.5 min. $[\alpha]_{D}^{20} = -254.98$ (c = 0.66).

$^1$H NMR (400 MHz, CDCl$_3$) $\delta$ = 7.64 – 7.59 (m, 2H), 7.53 – 7.43 (m, 5H), 7.13 (d, $J$ = 15.6, 1H), 7.09 – 7.02 (m, 2H), 6.42 (s, 1H), 6.21 (d, $J$ = 16.0, 1H), 5.52 (s, 1H), 3.77 (s, 3H).

$^{13}$C($^1$H) NMR (101 MHz, CDCl$_3$) $\delta$ = 167.9 (d, $J$ = 502.0), 161.9 (d, $J$ = 90.9), 153.3, 133.6, 133.2, 131.7, 131.5 (d, $J$ = 3.0), 129.5, 128.9 (d, $J$ = 8.1), 126.7, 121.4, 116.6, 116.0, 115.8, 85.4, 54.5, 54.2.

HRMS (ESI-TOF): calcd for C$_{21}$H$_{17}$ClFO$_4^+$ ([M + H]$^+$) 387.0799, found 387.0792, calcd for C$_{21}$H$_{17}$ClFO$_4^+$ ([M + H]$^+$) 389.0770, found 389.0771.
Methyl (E)-3-chloro-2-(4-chlorostyryl)-6-oxo-4-phenyl-3,6-dihydro-2H-pyrano-2-carboxylate (3ea)

White solid, 90% yield (36.0 mg). >19/1 dr determined by $^1$H NMR, 93% ee determined by HPLC (chiral IA-IB column), n-hexane/i-PrOH = 90/10, flow rate 1.0 mL/min, $\lambda$ = 254 nm, retention time:

26.3 min, 30.4 min, 32.1 min, 33.8 min. $[\alpha]_D^{20} = -181.39$ (c = 0.72).

$^1$H NMR (400 MHz, CDCl$_3$) $\delta$ = 7.62 (d, $J$ = 8.0, 2H), 7.55 – 7.47 (m, 3H), 7.37 (dd, $J$ = 26.0, 8.0, 4H), 7.12 (d, $J$ = 16.0, 1H), 6.42 (s, 1H), 6.27 (d, $J$ = 15.6, 1H), 5.51 (s, 1H), 3.78 (s, 3H).

$^{13}$C($^1$H) NMR (101 MHz, CDCl$_3$) $\delta$ = 169.3, 161.8, 153.3, 134.8, 133.8, 133.5, 133.2, 131.7, 129.5, 129.1, 128.4, 126.7, 122.3, 116.6, 85.4, 54.4, 54.3.

Methyl (E)-2-(4-bromostyryl)-3-chloro-6-oxo-4-phenyl-3,6-dihydro-2H-pyran-2-carboxylate (3fa)

White solid, 85% yield (38.0 mg). >19/1 dr determined by $^1$H NMR, 95% ee determined by HPLC (chiral IA column), n-hexane/i-PrOH = 90/10, flow rate 1.0 mL/min, $\lambda = 254$ nm, retention time: 13.5 min, 16.3 min, 17.1 min, 18.8 min. $[^\alpha]_D^{20} = -207.76$ (c = 0.76).

$^1$H NMR (400 MHz, CDCl$_3$) $\delta = 7.65 – 7.59$ (m, 2H), 7.56 – 7.44 (m, 5H), 7.34 (d, $J = 8.8$, 2H), 7.11 (d, $J = 16.0$, 1H), 6.42 (s, 1H), 6.29 (d, $J = 16.0$, 1H), 5.51 (s, 1H), 3.78 (s, 3H).

$^{13}$C($^1$H) NMR (101 MHz, CDCl$_3$) $\delta = 169.2, 161.7, 153.2, 134.2, 133.6, 133.2, 132.1, 131.7, 129.5, 128.7, 126.7, 123.0, 122.4, 116.6, 85.4, 54.4, 54.3.$

HRMS (ESI-TOF): calcd for C$_{21}$H$_{17}$Br$_4$ClO$_4$* ([M + H]*) 446.9999, found 446.9994, calcd for C$_{22}$H$_{17}$Br$_4$ClO$_4$* ([M + H]*) 448.9978, found 448.9975.
Retention Time | Area | % Area
---|---|---
1 | 13.516 | 17524641 | 96.89
2 | 16.297 | 21643 | 0.12
3 | 17.086 | 466305 | 2.58
4 | 18.761 | 74887 | 0.41

Methyl (E)-3-chloro-2-(2-fluorostyryl)-6-oxo-4-phenyl-3,6-dihydro-2H-pyran-2-carboxylate (3ga)

White solid, 80% yield (30.9 mg). 11/1 dr determined by $^1$H NMR, 86% ee determined by HPLC (chiral ADH column), n-hexane/i-PrOH = 90/10, flow rate 1.0 mL/min, $\lambda$ = 254 nm, retention time: 10.9 min, 12.2 min, 19.4 min, 21.2 min. $[\alpha]_D^{20} = -250.81$ (c = 0.62).

$^1$H NMR (400 MHz, CDCl$_3$) $\delta$ = 7.64 – 7.60 (m, 2H), 7.55 – 7.47 (m, 4H), 7.32 – 7.22 (m, 2H), 7.18 – 7.12 (m, 1H), 7.11 – 7.05 (m, 1H), 6.49 – 6.42 (m, 2H), 5.54 (s, 1H), 3.78 (s, 3H).

$^{13}$C($^1$H) NMR (101 MHz, CDCl$_3$) $\delta$ = 169.3, 162.0 (d, $J = 35.4$), 159.7, 153.3, 133.2, 131.7, 130.3 (d, $J = 8.1$), 129.5, 128.9 (d, $J = 3.0$), 128.0 (d, $J = 3.0$), 126.7, 124.6 (d, $J = 7.1$), 124.4 (d, $J = 4.0$), 123.2 (d, $J = 11.1$), 116.6, 116.1 (d, $J = 22.2$), 85.5, 54.4, 54.2.

HRMS (ESI-TOF): calcd for C$_{21}$H$_{17}^{34,9689}$ClFO$_4^+$ ([M + H]$^+$) 387.0799, found 387.0800, calcd for C$_{21}$H$_{17}^{36,9659}$ClFO$_4^+$ ([M + H]$^+$) 389.0770, found 389.0772.
Methyl (E)-3-chloro-2-(2-chlorostyryl)-6-oxo-4-phenyl-3,6-dihydro-2H-pyran-2-carboxylate (3ha)

White solid, 85% yield (34.4 mg). 8/1 dr determined by $^1$H NMR, 86% ee determined by HPLC (chiral ADH column), n-hexane/i-PrOH = 90/10, flow rate 1.0 mL/min, $\lambda$ = 254 nm, retention time: 10.3 min, 11.4 min, 16.0 min, 17.5 min. $[\alpha]_{D}^{20} = -209.16$ (c = 0.69).

$^1$H NMR (400 MHz, CDCl$_3$) $\delta$ = 7.64 – 7.61 (m, 2H), 7.59 – 7.56 (m, 1H), 7.54 – 7.48 (m, 4H), 7.42 – 7.37 (m, 1H), 7.28 – 7.24 (m, 2H), 6.43 (s, 1H), 6.32 (d, $J$ = 16.0, 1H), 5.53 (s, 1H), 3.79 (s, 3H).

$^{13}$C($^1$H) NMR (101 MHz, CDCl$_3$) $\delta$ = 169.2, 161.8, 153.2, 134.0, 133.7, 133.2, 131.7, 131.2, 130.1, 129.9, 129.5, 127.4, 127.1, 126.7, 124.9, 116.7, 85.5, 54.5, 54.3.

HRMS (ESI-TOF): calcd for C$_{22}$H$_{16}$O$_3$Cl$_2$NaO$_4$ $^+$ ([M + Na$^+$]) 425.0323, found 425.0320, calcd for C$_{22}$H$_{16}$O$_3$Cl$_2$NaO$_4$ $^+$ ([M + Na$^+$]) 427.0294, found 427.0289.
<table>
<thead>
<tr>
<th>Retention Time</th>
<th>Area</th>
<th>% Area</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>10.259</td>
<td>84.01</td>
</tr>
<tr>
<td>2</td>
<td>11.437</td>
<td>6.17</td>
</tr>
<tr>
<td>3</td>
<td>15.975</td>
<td>1.92</td>
</tr>
<tr>
<td>4</td>
<td>17.543</td>
<td>7.90</td>
</tr>
</tbody>
</table>

**Methyl (E)-3-chloro-2-(4-methylstyryl)-6-oxo-4-phenyl-3,6-dihydro-2H-pyran-2-carboxylate (3ia)**

White solid, 91% yield (34.8 mg). >19/1 dr determined by $^1$H NMR,
97% ee determined by HPLC (chiral IA column), n-hexane/i-PrOH = 90/10, flow rate 1.0 mL/min, $\lambda = 254$ nm, retention time: 9.1 min, 11.0 min, 12.5 min, 13.5 min. $\left[\alpha\right]_{D}^{20} = -293.65$ (c = 0.63).

$^1$H NMR (400 MHz, CDCl$_3$) $\delta = 7.65 – 7.60$ (m, 2H), 7.54 – 7.46 (m, 3H), 7.41 – 7.32 (m, 2H), 7.20 – 7.09 (m, 3H), 6.42 (s, 1H), 6.25 (d, $J = 16.0$, 1H), 5.52 (s, 1H), 3.77 (s, 3H), 2.36 (s, 3H).

$^{13}$C($^1$H) NMR (101 MHz, CDCl$_3$) $\delta = 169.5$, 162.0, 153.4, 139.0, 134.6, 133.3, 132.5, 131.6, 129.6, 129.5, 127.1, 126.7, 120.6, 116.6, 85.5, 54.6, 54.1, 27.0, 21.4.

HRMS (ESI-TOF): calcd for C$_{22}$H$_{19}$ClNaO$_4$+ ([M + Na]$^+$) 405.0870, found 405.0872, calcd for C$_{22}$H$_{19}$ClNaO$_4$+ ([M + Na]$^+$) 407.0840, found 407.0828.
Methyl (E)-3-chloro-2-(4-methoxystyryl)-6-oxo-4-phenyl-3,6-dihydro-2H-pyran-2-carboxylate (3ja)

White solid, 80% yield (31.9 mg). >19/1 dr determined by $^1$H NMR, 98% ee determined by HPLC (chiral IA column), $n$-hexane/$i$-PrOH = 90/10, flow rate 1.0 mL/min, $\lambda$ = 254 nm, retention time: 14.0 min, 17.3 min, 18.7 min, 20.8 min. $[\alpha]_D^{20} = -264.89$ ($c = 0.64$).

$^1$H NMR (400 MHz, CDCl$_3$) $\delta$ = 7.65 – 7.59 (m, 2H), 7.53 – 7.46 (m, 3H), 7.45 – 7.38 (m, 2H), 7.10 (d, $J$ = 16.0, 1H), 6.90 (dd, $J$ = 8.8, 2.8, 2H), 6.41 (s, 1H), 6.16 (d, $J$ = 16.0, 1H), 5.51 (s, 1H), 3.82 (s, 3H), 3.76 (s, 3H).

$^{13}$C($^1$H) NMR (101 MHz, CDCl$_3$) $\delta$ = 169.6, 162.0, 160.3, 153.4, 134.1, 133.3, 131.6, 129.5, 128.5, 128.0, 126.7, 119.3, 116.6, 114.3, 85.5, 55.5, 54.6, 54.1.

HRMS (ESI-TOF): calcd for C$_{22}$H$_{19}$ClNaO$_5$* ([M + Na]*) 421.0819, found 421.0819, calcd for C$_{22}$H$_{19}$ClNaO$_5$* ([M + Na]*) 423.0789, found 423.0799.
Methyl (E)-2-(2-([1,1′-biphenyl]-4-yl)vinyl)-3-chloro-oxo-4-phenyl-3,6-dihydro-2H-pyran-2-carboxylate (3ka)

White solid, 79% yield (34.9 mg). 17/1 dr determined by $^1$H NMR, 95% ee determined by HPLC (chiral IB column), n-hexane/i-PrOH = 90/10, flow rate 1.0 mL/min, $\lambda$ = 254 nm, retention time: 20.4 min, 22.6 min, 26.4 min, 37.1 min. [$\alpha$]$_{D}^{20} = -223.50$ ($c = 0.70$).

$^1$H NMR (400 MHz, CDCl$_3$) $\delta$ = 7.66 – 7.60 (m, 6H), 7.58 – 7.45 (m, 7H), 7.39 – 7.35 (m, 1H), 7.22 (d, $J = 16.0$, 1H), 6.44 (s, 1H), 6.35 (d, $J = 16.0$, 1H), 5.55 (s, 1H), 3.79 (s, 3H).

$^{13}$C($^1$H) NMR (101 MHz, CDCl$_3$) $\delta$ = 169.4, 161.9, 153.4, 141.8, 140.5, 134.3, 134.3, 133.3, 131.6, 129.5, 129.0, 127.7, 127.7, 127.6, 127.1, 126.7, 121.7, 116.6, 85.5, 54.5, 54.2.

HRMS (ESI-TOF): calcd for C$_{27}$H$_{21}$^{36,9659}ClNaO$_4$+ ([M + Na]$^+$) 467.1026, found 467.1026, calcd for C$_{27}$H$_{21}$^{36,9659}ClNaO$_4$+ ([M + Na]$^+$) 469.0997, found 469.1119.
Methyl (E)-3-chloro-2-(3-methoxystyryl)-6-oxo-4-phenyl-3,6-dihydro-2H-pyran-2-carboxylate (3la)

White solid, 85% yield (33.7 mg). 17/1 dr determined by 1H NMR, 95% ee determined by HPLC (chiral IA column), n-hexane/i-PrOH = 90/10, flow rate 1.0 mL/min, λ = 254 nm, retention time: 12.2 min, 14.0 min, 17.9 min. [α]D20 = −247.92 (c = 0.67).

1H NMR (400 MHz, CDCl3) δ = 7.65 – 7.60 (m, 2H), 7.54 – 7.47 (m, 3H), 7.29 (t, J = 8.0, 1H), 7.14 (d, J = 16.0, 1H), 7.08 (d, J = 7.6, 1H), 7.00 (s, 1H), 6.88 (dd, J = 8.4, 2.4, 1H), 6.42 (s, 1H), 6.29 (d, J = 16.0, 1H), 5.53 (s, 1H), 3.84 (s, 3H), 3.77 (s, 3H).

13C{[1H]} NMR (101 MHz, CDCl3) δ = 169.4, 161.9, 160.0, 153.3, 136.7, 134.6, 133.2, 131.7, 129.9, 129.5, 126.7, 122.0, 119.8, 116.6, 114.8, 112.4, 85.4, 55.4, 54.4, 54.2.

HRMS (ESI-TOF): calcd for C_{22}H_{19}^{34}\text{ClNaO}_5^{+} ([M + Na]^+) 421.0819, found 421.0812, calcd for C_{22}H_{19}^{36}\text{ClNaO}_5^{+} ([M + Na]^+) 423.0789, found 423.0799.
<table>
<thead>
<tr>
<th>Retention Time</th>
<th>Area</th>
<th>% Area</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>12.241</td>
<td>4050086</td>
</tr>
<tr>
<td>2</td>
<td>14.013</td>
<td>99674</td>
</tr>
<tr>
<td>3</td>
<td>17.889</td>
<td>123045</td>
</tr>
</tbody>
</table>

**Methyl (E)-3-chloro-2-(2-methoxystyryl)-6-oxo-4-phenyl-3,6-dihydro-2H-pyran-2-carboxylate (3ma)**

White solid, 77% yield (30.6 mg). 14/1 dr determined by $^1$H NMR, 94% ee determined by HPLC (chiral IA column), n-hexane/i-PrOH = 90/10, flow rate 1.0 mL/min, $\lambda = 254$ nm, retention time: 11.2 min, 12.1 min, 14.8 min, 17.4 min. [$\alpha$]$_{D}^{20}$ = −261.76 ($c = 0.61$).

$^1$H NMR (400 MHz, CDCl$_3$) $\delta$ = 7.66 – 7.61 (m, 2H), 7.53 – 7.45 (m, 4H), 7.41 (d, $J = 16.0$, 1H), 7.32 – 7.27 (m, 1H), 7.01 – 6.88 (m, 2H), 6.47 – 6.36 (m, 2H), 5.54 (s, 1H), 3.88 (s, 3H).

$^{13}$C{$^1$H} NMR (101 MHz, CDCl$_3$) $\delta$ = 169.6, 162.1, 157.6, 153.5, 133.3, 131.6, 130.1, 130.0, 129.5, 128.2, 126.7, 124.2, 122.4, 120.7, 116.6, 111.2, 85.8, 55.5, 54.7, 54.1.

**HRMS (ESI-TOF):** calcd for C$_{22}$H$_{19}$34.9669ClNaO$_5$* ([M + Na]$^+$) 421.0819, found 421.0823, calcd for C$_{22}$H$_{19}$36.9695ClNaO$_5$* ([M + Na]$^+$) 423.0789, found 423.0760.

<table>
<thead>
<tr>
<th>Retention Time</th>
<th>Area</th>
<th>% Area</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>11.257</td>
<td>1840441</td>
</tr>
<tr>
<td>2</td>
<td>12.086</td>
<td>1845689</td>
</tr>
<tr>
<td>3</td>
<td>14.849</td>
<td>126916</td>
</tr>
<tr>
<td>4</td>
<td>17.454</td>
<td>127478</td>
</tr>
</tbody>
</table>
Methyl (E)-3-chloro-2-(3-methylstyril)-6-oxo-4-phenyl-3,6-dihydro-2H-pyran-2-carboxylate (3na)

White solid, 83% yield (31.7 mg). 17/1 dr determined by $^1$H NMR, 95% ee determined by HPLC (chiral IC column), n-hexane/i-PrOH = 90/10, flow rate 1.0 mL/min, $\lambda$ = 254 nm, retention time: 17.2 min, 18.8 min, 28.1 min, 31.4 min. $[\alpha]_D^{20} = -26.703$ (c = 0.63).

$^1$H NMR (400 MHz, CDCl$_3$) $\delta$ = 7.62 (dd, $J$ = 7.2, 1.6, 2H), 7.54 – 7.47 (m, 3H), 7.32 – 7.25 (m, 3H), 7.13 (dd, $J$ = 10.4, 4.4, 2H), 6.42 (s, 1H), 6.28 (d, $J$ = 16.0, 1H), 5.52 (s, 1H), 3.77 (s, 3H), 2.37 (s, 3H).

$^{13}$C{$^1$H} NMR (101 MHz, CDCl$_3$) $\delta$ = 169.5, 161.9, 153.3, 138.5, 135.2, 134.8, 133.3, 131.6, 129.8, 129.5, 128.8, 127.8, 126.7, 124.4, 121.5, 116.6, 85.5, 54.5, 54.2, 21.5.

HRMS (ESI-TOF): calcd for C$_{22}$H$_{19}$ClNaO$_4$ ([M + Na]$^+$) 405.0870, found 405.0873, calcd for C$_{22}$H$_{19}$ClNaO$_4$ ([M + Na]$^+$) 407.0840, found 407.0853.
Methyl (E)-3-chloro-2-(3,4-dichlorostyryl)-6-oxo-4-phenyl-3,6-dihydro-2H-pyran-2-carboxylate (3oa)

White solid, 73% yield (31.7 mg). >19/1 dr determined by $^1$H NMR, 90% ee determined by HPLC (chiral IA column), n-hexane/i-PrOH = 95/5, flow rate 1.0 mL/min, $\lambda$ = 254 nm, retention time: 17.2 min, 18.5 min, 21.4 min, 22.6 min. [α]D$^20$ = −216.72 (c = 0.63).

$^1$H NMR (400 MHz, CDCl$_3$) δ = 7.64 – 7.59 (m, 2H), 7.56 (d, $J$ = 1.6, 1H), 7.54 – 7.46 (m, 3H), 7.44 (d, $J$ = 8.0, 1H), 7.28 (dd, $J$ = 8.0, 1.6, 1H), 7.09 (d, $J$ = 16.0, 1H), 6.42 (s, 1H), 6.29 (d, $J$ = 16.0, 1H), 5.51 (s, 1H), 3.78 (s, 3H).

$^{13}$C{¹H} NMR (101 MHz, CDCl$_3$) δ = 169.1, 161.6, 153.1, 135.4, 133.1, 132.8, 132.5, 131.7, 130.9, 129.5, 128.7, 126.7, 126.6, 123.7, 116.6, 85.3, 54.3, 54.3.

HRMS (ESI-TOF): calcd for C$_{21}$H$_{15}$Cl$_3$NaO$_4$ (M + Na$^+$) 458.9934, found 458.9932, calcd for C$_{21}$H$_{15}$Cl$_3$NaO$_4$ (M + Na$^+$) 460.9904, found 461.0035.
Methyl (E)-3-chloro-2-(2,6-dimethylstyryl)-6-oxo-4-phenyl-3,6-dihydro-2H-pyran-2-carboxylate (3pa)

White solid, 82% yield (32.6 mg). >19/1 dr determined by $^1$H NMR, 95% ee determined by HPLC (chiral IA column), n-hexane/i-PrOH = 90/10, flow rate 1.0 mL/min, $\lambda$ = 254 nm, retention time: 6.4 min, 6.9 min, 7.7 min, 8.5 min. $[\alpha]_D^{20} = -227.45$ (c = 0.65).

$^1$H NMR (400 MHz, CDCl$_3$) $\delta$ = 7.67 – 7.61 (m, 2H), 7.55 – 7.47 (m, 3H), 7.19 (d, $J$ = 16.4, 1H), 7.14 – 7.04 (m, 3H), 6.44 (s, 1H), 5.85 (d, $J$ = 16.0, 1H), 5.52 (s, 1H), 3.79 (s, 3H), 2.33 (s, 6H).

$^{13}$C($^1$H) NMR (101 MHz, CDCl$_3$) $\delta$ = 169.4, 162.0, 153.2, 136.2, 135.3, 133.4, 133.2, 131.6, 129.5, 128.0, 127.5, 127.2, 126.7, 116.7, 85.5, 54.3, 54.1, 20.9.

HRMS (ESI-TOF): calcd for C$_{23}$H$_{22}$ClO$_4^+$ ([M + H]$^+$) 397.1207, found 397.1201, calcd for C$_{23}$H$_{22}$ClO$_4^+$ ([M + H]$^+$) 399.1177, found 399.1152.

<table>
<thead>
<tr>
<th>Retention Time</th>
<th>Area</th>
<th>% Area</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>6.442</td>
<td>42.33</td>
</tr>
<tr>
<td>2</td>
<td>6.920</td>
<td>42.39</td>
</tr>
<tr>
<td>3</td>
<td>7.671</td>
<td>7.79</td>
</tr>
<tr>
<td>4</td>
<td>8.476</td>
<td>7.49</td>
</tr>
</tbody>
</table>
Methyl (E)-3-chloro-2-(2-(naphthalen-2-yl)vinyl)-6-oxo-4-phenyl-3,6-dihydro-2H-pyran-2-carboxylate (3qa)

White solid, 80% yield (33.4 mg). 17/1 dr determined by $^1$H NMR, 96% ee determined by HPLC (chiral IA column), n-hexane/i-PrOH = 90/10, flow rate 1.0 mL/min, $\lambda = 254$ nm, retention time: 12.7 min, 13.9 min, 16.2 min, 16.8 min. $[\alpha]_D^{20} = -221.41$ (c = 0.67).

$^1$H NMR (400 MHz, CDCl$_3$) $\delta = 7.87 – 7.80$ (m, 4H), 7.67 – 7.61 (m, 3H), 7.53 – 7.46 (m, 5H), 7.33 (d, $J = 16.0$, 1H), 6.46 – 6.38 (m, 2H), 5.57 (s, 1H), 3.78 (s, 3H).

$^{13}$C($^1$H) NMR (101 MHz, CDCl$_3$) $\delta = 169.4, 161.9, 153.4, 134.8, 133.8, 133.6, 133.3, 132.7, 131.6, 129.5, 128.6, 128.4, 128.1, 127.8, 126.7, 126.7, 123.5, 122.0, 116.6, 85.6, 54.6, 54.2.

HRMS (ESI-TOF): calcd for C$_{25}$H$_{19}$ClNaO$_4$ ([M + Na]$^+$) 441.0870, found 441.0873, calcd for C$_{25}$H$_{19}$ClNaO$_4$ ([M + Na]$^+$) 443.0840, found 443.0854.

<table>
<thead>
<tr>
<th>Retention Time</th>
<th>Area</th>
<th>% Area</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>12.702</td>
<td>46.75</td>
</tr>
<tr>
<td>2</td>
<td>13.888</td>
<td>46.94</td>
</tr>
<tr>
<td>3</td>
<td>16.242</td>
<td>3.14</td>
</tr>
<tr>
<td>4</td>
<td>16.750</td>
<td>3.17</td>
</tr>
</tbody>
</table>

<table>
<thead>
<tr>
<th>Retention Time</th>
<th>Area</th>
<th>% Area</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>12.644</td>
<td>94.94</td>
</tr>
</tbody>
</table>
**Methyl (E)-3-chloro-6-oxo-4-phenyl-2-(2-(thiophen-3-yl)vinyl)-3,6-dihydro-2H-pyran-2-carboxylate (3ra)**

White solid, 91% yield (33.9 mg). 19/1 dr determined by $^1$H NMR, 96% ee determined by HPLC (chiral IA column), n-hexane/i-PrOH = 90/10, flow rate 1.0 mL/min, $\lambda$ = 254 nm, retention time: 11.6 min, 14.2 min, 17.7 min, 19.6 min. $[\alpha]_{D}^{20} = -248.23$ (c = 0.68).

$^1$H NMR (400 MHz, CDCl$_3$) $\delta$ = 7.64 – 7.59 (m, 2H), 7.56 – 7.47 (m, 3H), 7.35 – 7.26 (m, 3H), 7.16 (d, $J$ = 15.6, 1H), 6.41 (s, 1H), 6.15 (d, $J$ = 15.6, 1H), 5.50 (s, 1H), 3.76 (s, 3H).

$^{13}$C($^1$H) NMR (101 MHz, CDCl$_3$) $\delta$ = 169.4, 161.9, 153.4, 138.0, 133.2, 131.6, 129.5, 128.8, 126.7, 126.7, 125.1, 124.9, 121.4, 116.6, 85.3, 54.5, 54.2.

HRMS (ESI-TOF): calcd for C$_{19}$H$_{15}$ClNaO$_{4}$S $([M + Na]^+)$ 397.0277, found 397.0282, calcd for C$_{19}$H$_{16}$ClNaO$_{4}$S $([M + Na]^+)$ 399.0248, found 399.0238.

<table>
<thead>
<tr>
<th>Retention Time</th>
<th>Area</th>
<th>% Area</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>11.646</td>
<td>47.28</td>
</tr>
<tr>
<td>2</td>
<td>14.182</td>
<td>47.26</td>
</tr>
<tr>
<td>3</td>
<td>17.738</td>
<td>2.76</td>
</tr>
<tr>
<td>4</td>
<td>19.605</td>
<td>2.70</td>
</tr>
</tbody>
</table>

<table>
<thead>
<tr>
<th>Retention Time</th>
<th>Area</th>
<th>% Area</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>11.667</td>
<td>95.53</td>
</tr>
<tr>
<td>2</td>
<td>14.232</td>
<td>1.91</td>
</tr>
</tbody>
</table>
Methyl (E)-3-chloro-2-(2-cyclohexylvinyl)-6-oxo-4-phenyl-3,6-dihydro-2H-pyran-2-carboxylate (3sa)

Colorless oil, 64% yield (24.1 mg). 9/1 dr determined by $^1$H NMR, 93% ee determined by HPLC (chiral ADH column), n-hexane/i-PrOH = 90/10, flow rate 1.0 mL/min, $\lambda = 254$ nm, retention time: 6.7 min, 7.4 min, 9.8 min, 10.3 min. $[\alpha]_{D20}^{20} = -286.31$ (c = 0.48).

$^1$H NMR (400 MHz, CDCl$_3$) $\delta$ = 7.59 (dd, $J = 7.2, 1.2$, 2H), 7.49 (t, $J = 4.2$, 3H), 6.36 (s, 1H), 6.21 (dd, $J = 15.6, 6.4$, 1H), 5.57 (dd, $J = 16.0, 1.2$, 1H), 5.38 (s, 1H), 3.73 (s, 3H), 2.14 – 2.06 (m, 1H), 1.81 – 1.71 (m, 4H), 1.34 – 1.09 (m, 6H).

$^{13}$C($^1$H) NMR (101 MHz, CDCl$_3$) $\delta$ = 169.8, 162.2, 153.5, 142.5, 133.4, 131.5, 129.4, 126.7, 120.6, 116.5, 85.2, 54.5, 54.0, 40.6, 32.4, 26.1, 25.9.

HRMS (ESI-TOF): calcd for C$_{21}$H$_{23}$ClNaO$_4^+$ ([M + Na]$^+$) 397.1183, found 397.1186, calcd for C$_{21}$H$_{23}$ClNaO$_4^+$ ([M + Na]$^+$) 399.1153, found 399.1161.
Methyl 3-chloro-6-oxo-4-phenyl-2-((1E,3E)-4-phenylbuta-1,3-dien-1-yl)-3,6-dihydro-2H-pyran-2-carboxylate (3ta)

White solid, 77% yield (30.2 mg). 14/1 dr determined by $^1$H NMR, 96% ee determined by HPLC (chiral IB column), n-hexane/i-PrOH = 90/10, flow rate 1.0 mL/min, $\lambda = 254$ nm, retention time: 17.4 min, 19.5 min, 20.3 min, 24.3 min. $[\alpha]_{D}^{20} = -256.29$ (c = 0.60).

$^1$H NMR (400 MHz, CDCl$_3$) $\delta$ = 7.63 – 7.58 (m, 2H), 7.52 – 7.47 (m, 3H), 7.46 – 7.40 (m, 2H), 7.34 (t, $J = 7.2$, 2H), 7.29 – 7.24 (m, 1H), 6.95 (dd, $J = 14.8$, 10.0, 1H), 6.84 (dd, $J = 15.6$, 10.4, 1H), 6.74 (d, $J = 15.2$, 1H), 6.40 (s, 1H), 5.89 (d, $J = 14.8$, 1H), 5.46 (s, 1H), 3.76 (s, 3H).

$^{13}$C($^1$H) NMR (101 MHz, CDCl$_3$) $\delta$ = 169.4, 161.9, 153.3, 136.6, 136.5, 135.1, 133.3, 131.6, 129.5, 128.4, 126.4, 126.9, 126.7, 126.7, 124.8, 116.6, 85.4, 54.5, 54.2.

HRMS (ESI-TOF): calcd for C$_{23}$H$_{20}$O$_3$ClO$_4$ $^+$ ([M + H]$^+$) 395.1050, found 395.1052, calcd for C$_{23}$H$_{20}$O$_3$ClO$_4$ $^+$ ([M + H]$^+$) 397.1021, found 397.1019.

<table>
<thead>
<tr>
<th>Retention Time</th>
<th>Area</th>
<th>% Area</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>17.436</td>
<td>47.14</td>
</tr>
<tr>
<td>2</td>
<td>19.526</td>
<td>2.81</td>
</tr>
<tr>
<td>3</td>
<td>20.328</td>
<td>2.88</td>
</tr>
<tr>
<td>4</td>
<td>24.250</td>
<td>47.16</td>
</tr>
</tbody>
</table>

<table>
<thead>
<tr>
<th>Retention Time</th>
<th>Area</th>
<th>% Area</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>17.587</td>
<td>1.93</td>
</tr>
<tr>
<td>2</td>
<td>19.418</td>
<td>4.54</td>
</tr>
<tr>
<td>3</td>
<td>23.896</td>
<td>93.53</td>
</tr>
</tbody>
</table>
carboxamide (3ua)

White solid, 59% yield (24.1 mg). 11/1 dr determined by $^1$H NMR, 94% ee determined by HPLC (chiral ADH column), $n$-hexane/i-PrOH = 90/10, flow rate 1.0 mL/min, $\lambda = 254$ nm, retention time: 6.0 min, 6.6 min, 7.8 min, 8.4 min. $[\alpha]_D^{20} = -292.53$ ($c = 0.48$).

$^1$H NMR (400 MHz, CDCl$_3$) $\delta = 7.68 – 7.63$ (m, 2H), 7.52 – 7.44 (m, 5H), 7.40 – 7.31 (m, 3H), 7.05 (d, $J = 16.0$, 1H), 6.35 (d, $J = 15.6$, 1H), 6.33 (s, 1H), 6.14 (s, 1H), 5.78 (s, 1H), 1.28 (s, 9H).

$^{13}$C($^1$H) NMR (101 MHz, CDCl$_3$) $\delta = 167.9$, 162.4, 156.5, 135.6, 133.8, 133.0, 131.5, 129.4, 128.9, 128.8, 127.1, 127.0, 123.5, 114.8, 86.8, 54.9, 52.4, 28.5.

HRMS (ESI-TOF): calcd for C$_{24}$H$_{24}$ClNNaO$_3$ ([M + Na]$^+$) 432.1342, found 432.1347, calcd for C$_{24}$H$_{24}$ClNNaO$_3$ ([M + Na]$^+$) 434.1313, found 434.1319.

<table>
<thead>
<tr>
<th>Retention Time</th>
<th>Area</th>
<th>% Area</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>5.993</td>
<td>6222598</td>
</tr>
<tr>
<td>2</td>
<td>6.616</td>
<td>6224287</td>
</tr>
<tr>
<td>3</td>
<td>7.837</td>
<td>492315</td>
</tr>
<tr>
<td>4</td>
<td>8.382</td>
<td>527360</td>
</tr>
</tbody>
</table>

Methyl 3-chloro-6-oxo-2,4-diphenyl-3,6-dihydro-2H-pyran-2-carboxylate (3va)
White solid, 63% yield (21.6 mg). >19/1 dr determined by $^1$H NMR, 96% ee determined by HPLC (chiral IB column), $n$-hexane/i-PrOH = 90/10, flow rate 1.0 mL/min, $\lambda = 254$ nm, retention time: 8.7 min, 9.6 min. [$\alpha$]$_{D}^{20} = -321.43$ ($c = 0.42$).

$^1$H NMR (400 MHz, CDCl$_3$) $\delta = 7.84 – 7.75$ (m, 2H), 7.71 – 7.64 (m, 2H), 7.55 – 7.40 (m, 6H), 6.43 (s, 1H), 5.79 (s, 1H), 3.71 (s, 3H).

$^{13}$C{$^1$H} NMR (101 MHz, CDCl$_3$) $\delta = 169.9, 161.8, 154.7, 134.0, 133.5, 131.7, 129.5, 129.5, 128.9, 126.8, 126.6, 116.4, 86.4, 55.3, 54.2.$


<table>
<thead>
<tr>
<th>Retention Time</th>
<th>Area</th>
<th>% Area</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>8.764</td>
<td>49.65</td>
</tr>
<tr>
<td>2</td>
<td>9.583</td>
<td>50.35</td>
</tr>
</tbody>
</table>

Methyl 3-chloro-6-oxo-4-phenyl-2-(phenylethynyl)-3,6-dihydro-2H-pyran-2-carboxylate (3wa)

White solid, 38% yield (13.8 mg). >19/1 dr determined by $^1$H NMR, 64% ee determined by HPLC (chiral IE column), $n$-hexane/i-PrOH = 90/10, flow rate 1.0 mL/min, $\lambda = 254$ nm, retention time: 29.5 min, 31.8 min, 44.6 min. [$\alpha$]$_{D}^{20} = -101.34$ ($c = 0.22$).

$^1$H NMR (400 MHz, CDCl$_3$) $\delta = 7.61$ (d, $J = 8.0$, 2H), 7.58 – 7.46 (m, 5H), 7.45 – 7.31 (m,
3H), 6.38 (s, 1H), 5.59 (s, 1H), 3.86 (s, 3H).

$^{13}$C{$^{1}$H} NMR (101 MHz, CDCl$_3$) $\delta$ = 166.8, 161.0, 152.9, 133.1, 132.4, 131.8, 129.9, 129.6, 128.6, 126.7, 120.7, 116.2, 89.7, 80.5, 80.4, 54.8, 54.4.


### Table 1: Retention Time, Area, and % Area

<table>
<thead>
<tr>
<th>Retention Time</th>
<th>Area</th>
<th>% Area</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>29.248</td>
<td>49.15</td>
</tr>
<tr>
<td>2</td>
<td>31.363</td>
<td>49.15</td>
</tr>
<tr>
<td>3</td>
<td>43.861</td>
<td>1.69</td>
</tr>
</tbody>
</table>

### Table 2: Retention Time, Area, and % Area

<table>
<thead>
<tr>
<th>Retention Time</th>
<th>Area</th>
<th>% Area</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>29.488</td>
<td>17.93</td>
</tr>
<tr>
<td>2</td>
<td>31.802</td>
<td>80.11</td>
</tr>
<tr>
<td>3</td>
<td>44.583</td>
<td>1.96</td>
</tr>
</tbody>
</table>

Methyl 3-chloro-6-oxo-4-phenyl-2-(3-phenyloxiran-2-yl)-3,6-dihydro-2H-pyran-2-carboxylate (4aa)

White solid, 68% yield (26.1 mg). >19/1 dr determined by $^1$H NMR, 95% ee determined by HPLC (chiral IE column), n-hexane/i-PrOH = 80/20, flow rate 1.0 mL/min, $\lambda$ = 254 nm, retention time: 21.3 min, 26.4 min, 36.5 min. [$\alpha$]$^2_{D20} =$ −736.78 (c = 0.52, $\lambda$ = 405 nm).

$^1$H NMR (400 MHz, CDCl$_3$) $\delta$ = 7.63 – 7.55 (m, 2H), 7.54 – 7.45 (m, 3H), 7.44 – 7.27 (m, 5H), 6.44 (s, 1H), 5.53 (s, 1H), 4.40 (s, 1H), 3.85 (s, 3H), 3.61 (d, J = 1.2, 1H).

$^{13}$C{$^{1}$H} NMR (101 MHz, CDCl$_3$) $\delta$ = 168.2, 161.0, 152.0, 135.4, 132.7, 131.8, 129.6, 128.9, 128.8, 126.7, 126.0, 117.0, 83.2, 63.0, 56.5, 54.5, 52.6.
HRMS (ESI-FT): calcd for C_{21}H_{17}^{34.9689}ClNaO_{5}^+ ([M + Na]^+) 407.0662, found 407.0661, calcd for C_{21}H_{17}^{36.9659}ClNaO_{5}^+ ([M + Na]^+) 409.0633, found 409.0630.

<table>
<thead>
<tr>
<th>Retention Time</th>
<th>Area</th>
<th>% Area</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>21.126</td>
<td>6.04</td>
</tr>
<tr>
<td>2</td>
<td>26.114</td>
<td>46.98</td>
</tr>
<tr>
<td>3</td>
<td>35.617</td>
<td>46.98</td>
</tr>
</tbody>
</table>

<table>
<thead>
<tr>
<th>Retention Time</th>
<th>Area</th>
<th>% Area</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>21.292</td>
<td>0.70</td>
</tr>
<tr>
<td>2</td>
<td>26.381</td>
<td>96.57</td>
</tr>
<tr>
<td>3</td>
<td>36.508</td>
<td>2.72</td>
</tr>
</tbody>
</table>

(G) Reference

3678.


(H) Copies of the NMR spectra

Compound 3aa
Compound 3ba
Compound 3ca
Compound 3ab
Compound 3ac
Compound 3ae
Compound 3da
Compound 3ea
Compound 3fa
Compound 3ga
Compound 3ia
Compound 3ja
Compound 3ka
Compound 3ma
Compound 3pa
Compound 3qa
Compound 3ra
Compound 3sa
Compound 3ta
Compound 3ua
Compound 3va
Compound 7aa